

Supplementary Information

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Dinuclear cobalt complexes supported by biphenol and binaphthol-derived bis (salicylaldimine) ligands: Synthesis, characterization and catalytic application in β -enaminones synthesis from 1, 3-dicarbonyl compounds and Aliphatic amines

Dr. Adelew Estifanos Filkale^{a,*} Dr. Chandni Pathak^b

^aDepartment of Chemistry, College of Computational & Natural Sciences, Hawassa University, P.O. Box,05, Ethiopia

^bDepartment of Applied Chemistry, Jabalpur Engineering College, Jabalpur, M.P.,

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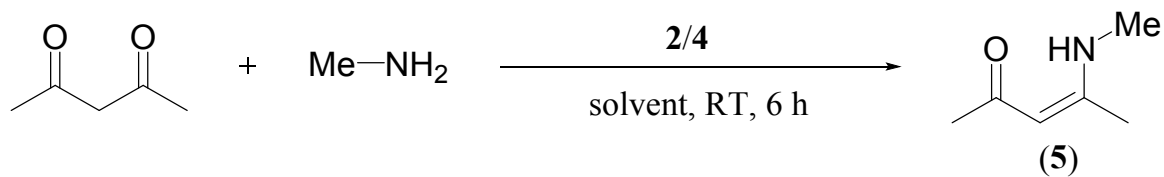
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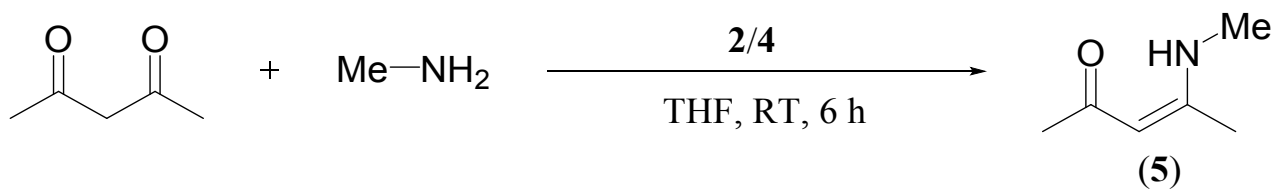
Table 1S. Solvent variation study for the β -enaminone reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes



S.No	Solvent	Yield ^b	
		(2)	(4)
1	CHCl ₃	89	76
2	CH ₂ Cl ₂	75	71
3	THF	93	89
4	DMSO	86	77
5	DMF	63	65

(a). Reaction conditions: 1.00 mmol of ketone, 4.0 mmol of amine, 1 mol % of catalyst (2/4), 2.5 mL of solvent at room temperature, stir for 6 h. (b) Isolated yields (%).

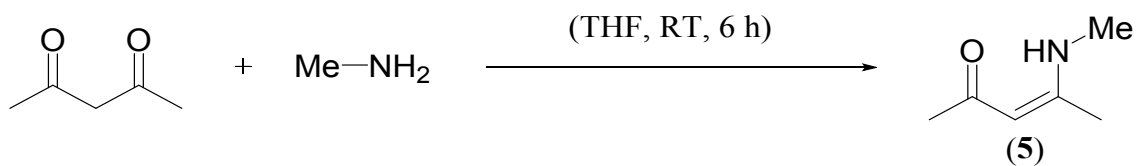
Table 2S. Time variation study for the β -enaminone reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.



S.No	Time (h)	Yield ^b	
		(2)	(4)
1	0.5	63	59
2	2	78	63
3	4	83	78
4	6	93	89
5	12	90	85

(a). Reaction conditions: 1.00 mmol of ketone, 4.0 mmol of amine, 1 mol % of catalyst (2/4), 2.5 mL of THF at room temperature, stir for the given time. (b). Isolated yields (%).

Table 3S. Selected results of blank, control and mercury drop experiments for the β -enaminone reaction of acetyl acetone and methylamine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.



S.No	Catalyst	Yield ^b	Hg/Yield ^b
1	(2) ^a	93	90
2	(4) ^a	89	87
3	-	40	
4	Co(OAc) ₂ •4H ₂ O	42	
5	H ₂ L ¹ (1)	64	
6	H ₂ L ² (3)	67	

(a). Reaction conditions: 1.00 mmol of ketone, 4.0 mmol of amine, 1 mol % of catalyst (2/4) or 2 mol % of Co(OAc)₂•4H₂O/H₂L¹/H₂L², 2.5 mL of THF at room temperature, stir for 6 h.

(b). Isolated yields (%).

PG-CP-14-46-1-1H

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PROCNO 1

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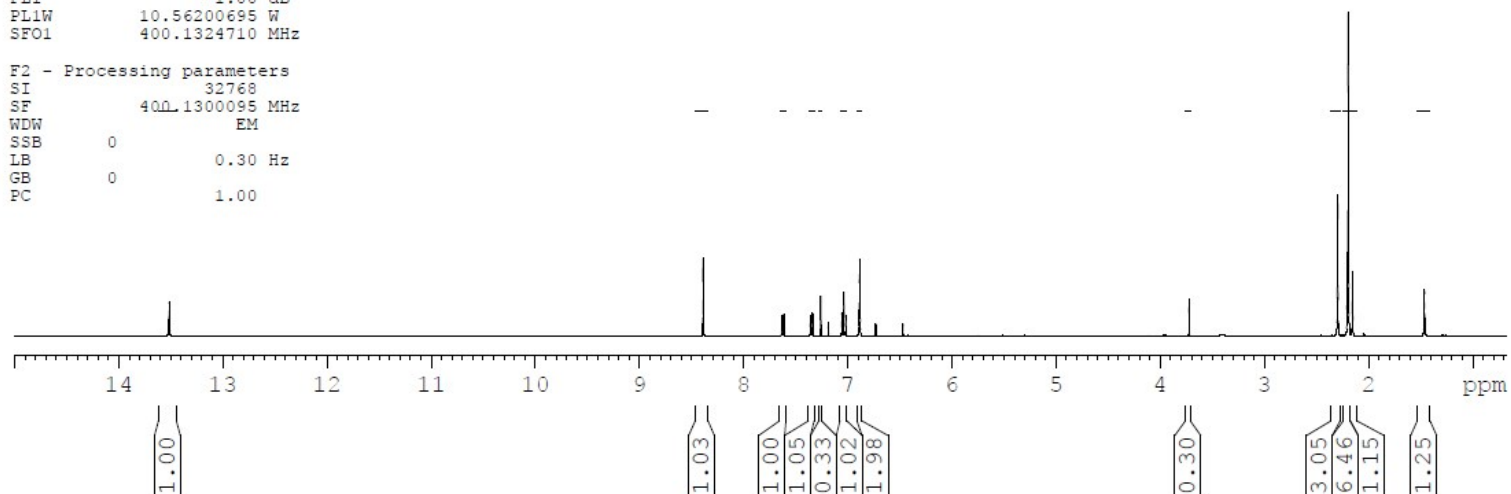
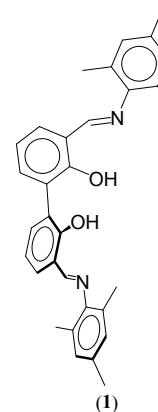


Fig. S1 ¹H NMR spectrum of **1** in CDCl₃.

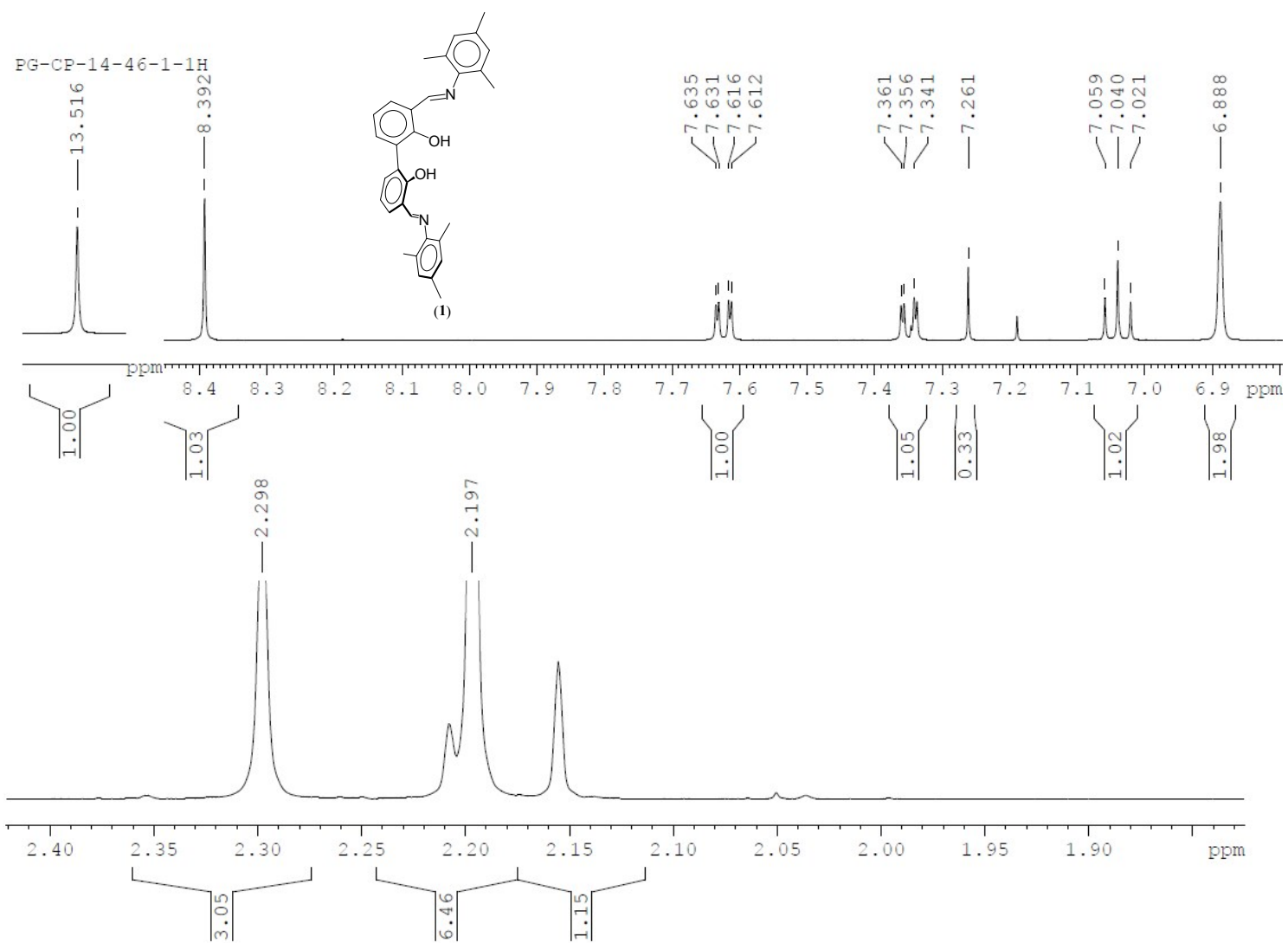


Fig. S2 Expanded ^1H NMR spectrum of **1** in CDCl_3 .

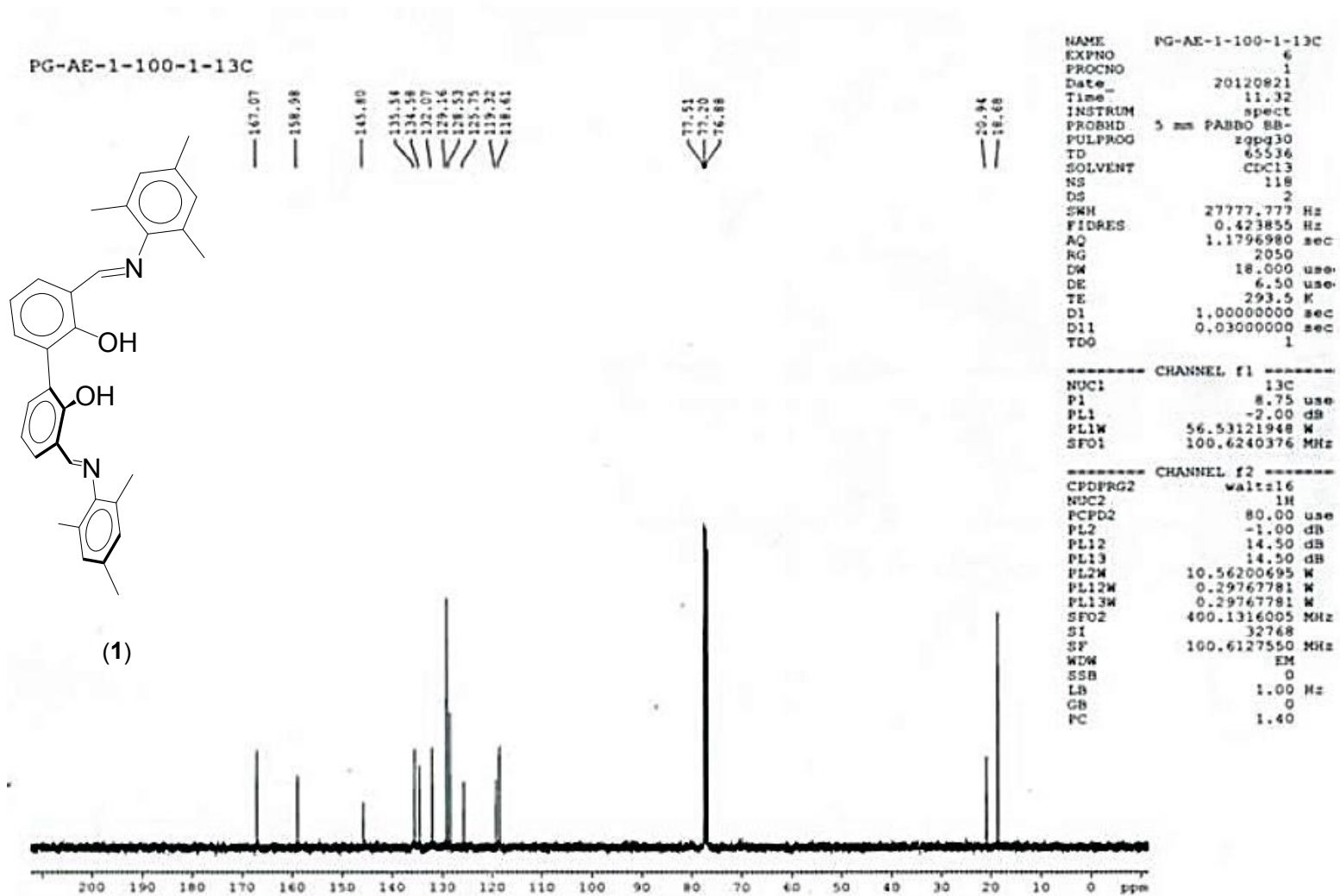


Fig. S3 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 .

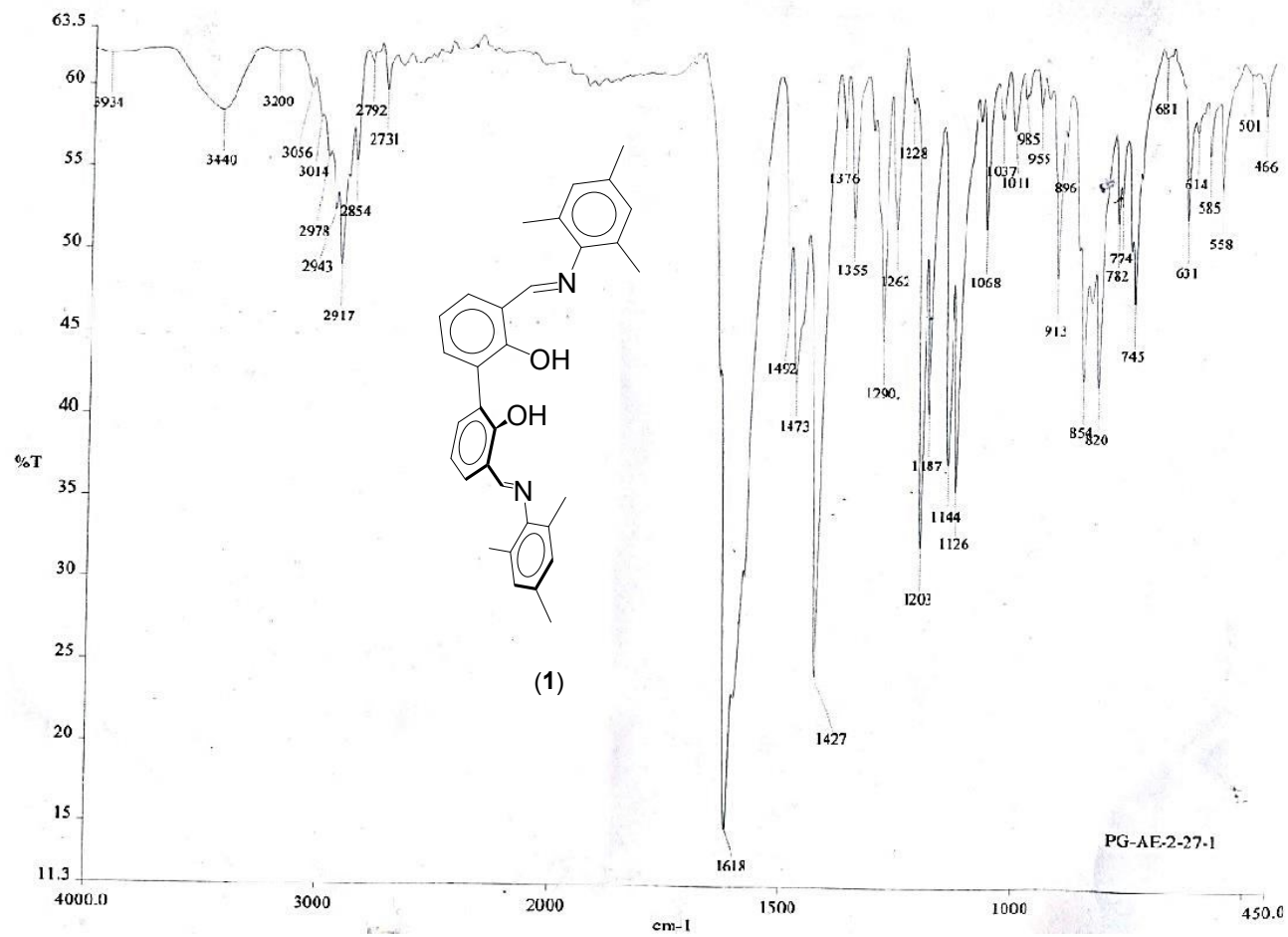


Fig. S4 Infrared spectrum of **1** in KBr.

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Analysis Info

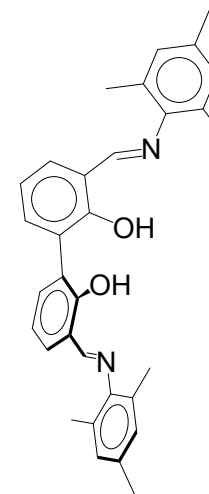
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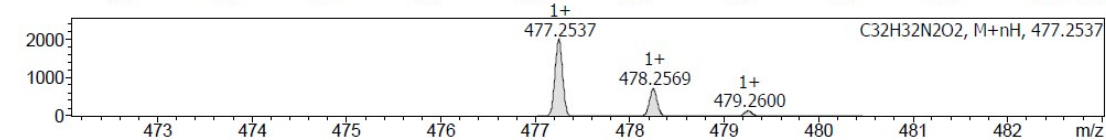
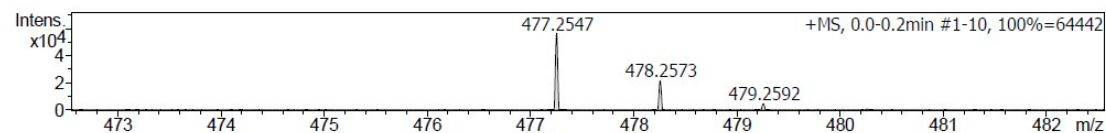
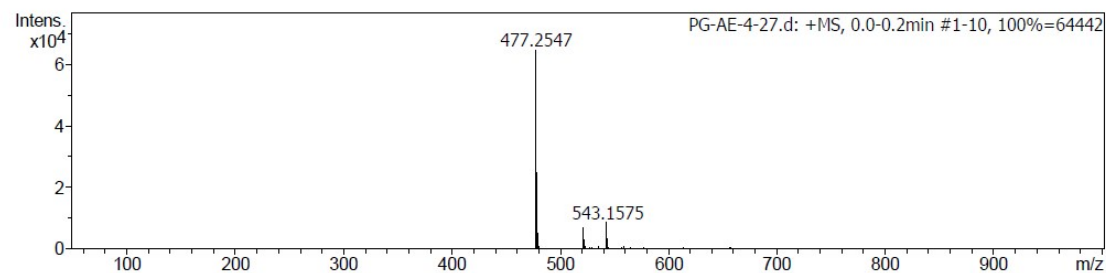
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 Scan End 1000 m/z Set Collision Cell RF 1200.0 Vpp Set Divert Valve Source



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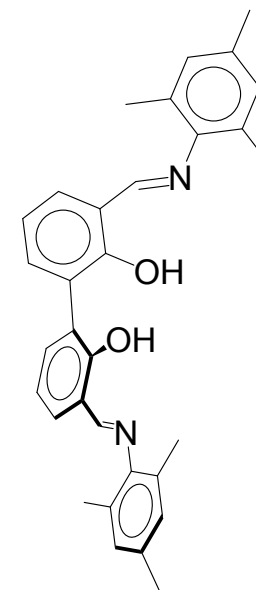
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Fig. S5 High Resolution Mass Spectrometry (HRMS) data of 1.

Eager 300 Report

Page: 1 Sample: PG-AE-2-27-1 (PG-AE-2-27-1)

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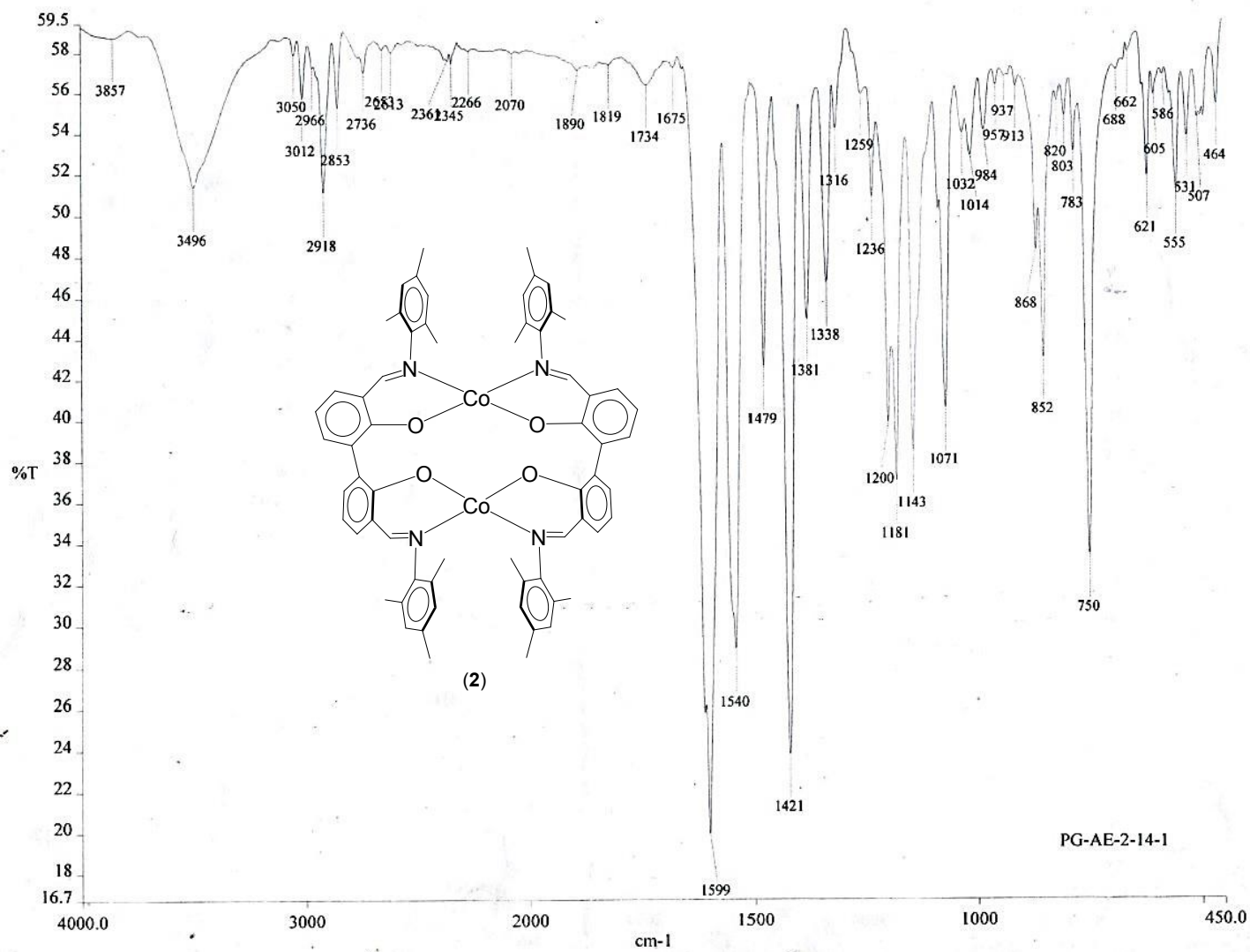
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!!! Warning missing one or more peaks.

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2	0.0000	6	99279	FU		0.0000
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Carbon	80.8003	65	1604465	RS	1.000000	.264014E+07
Hydrogen	5.9919	178	336173	RS	4.772736	.705507E+07
Totals	92.7099		2119363			

(1)

Fig. S6 Elemental analysis data of 1.



PG-AE-2-14-1

Fig. S7 Infrared spectrum of **2** in KBr.

Table 4S. Important IR bands of 1(H_2L^1) and 3 (H_2L^2) dinuclear complexes **2** and **4**

Compound	$\nu_{(\text{O-H})/\text{H}_2\text{O}}$ (cm^{-1})	$\nu_{(\text{C=N})}$ (cm^{-1})	$\nu_{(\text{C-O})}$ (cm^{-1})	$\nu_{(\text{C=C})}$ (cm^{-1})
H_2L^1(1)	3440	1618	1203	1427
2	3446	1599	1143	1421
H_2L^2(3)	3386	1623	1255	1449
4	3451	1620	1254	1457

Table 5S. UV–Visible spectra of **1**, **2**, **3** and **4**

Compound	λ_{max} , nm	absorbance	ϵ , $\text{M}^{-1}\text{cm}^{-1}$	transition
H₂L¹ (1)	236	3.5	52000	$\pi \rightarrow \pi^*$
	341	1.7	25000	$n \rightarrow \pi^*$
2	230	1.22	18000	$\pi \rightarrow \pi^*$
	280	0.54	8000	$n \rightarrow \pi^*$
	393	0.26	4000	$d \rightarrow \pi^*$
H₂L² (3)	244	0.23	3400	$\pi \rightarrow \pi^*$
	342	0.11	1600	$n \rightarrow \pi^*$
4	260	0.97	14000	$\pi \rightarrow \pi^*$
	306	0.33	4900	$n \rightarrow \pi^*$
	350	0.21	3100	$d \rightarrow \pi^*$

Indian Institute of Technology (B)

Analysis Info

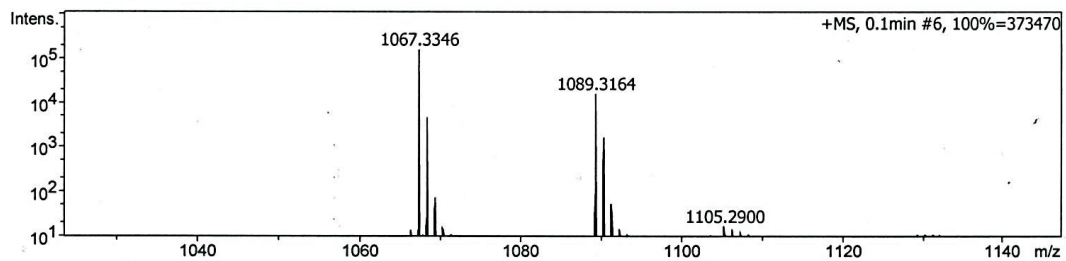
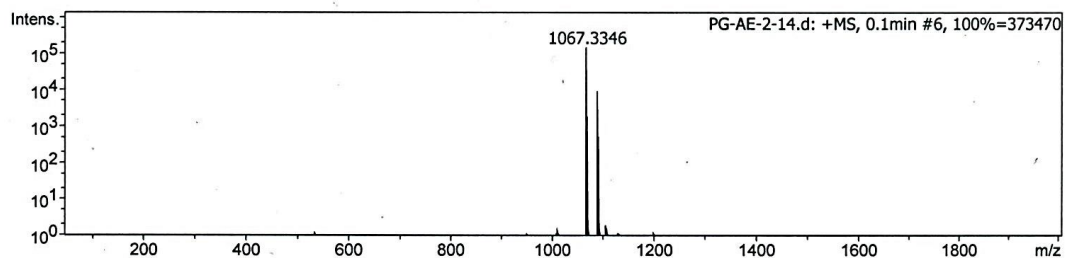
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Acquisition Date 8/27/2013 12:44:25 PM

Operator MSB IN
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	2100.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
1067.3346	1	C64H61Co2N4O4	1067.3351	-0.5	45.9	1	100.00	36.5	even	ok
1089.3164	1	C64H60Co2N4NaO4	1089.3171	-0.6	20.3	1	100.00	36.5	even	ok

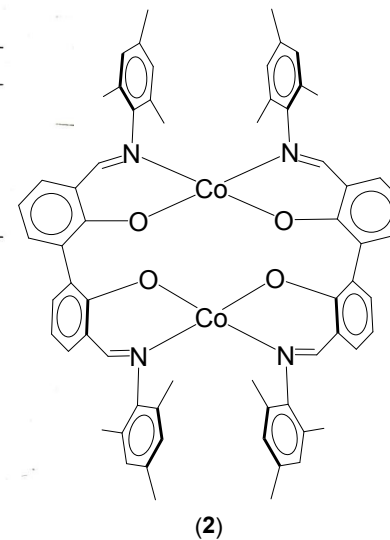
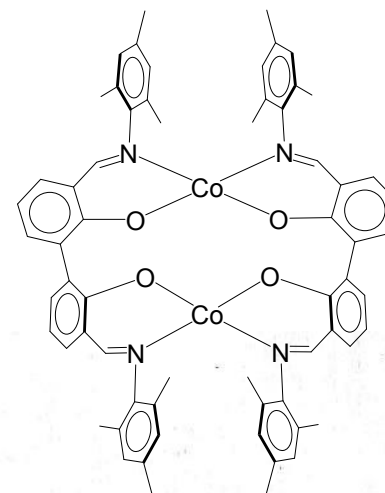


Fig. S8 High Resolution Mass Spectrometry (HRMS) data of **2**.

Eager 300 Report

Page: 1 Sample: PG-AE-2-31-1 (PG-AE-2-31-1)

Method Name : SRM23092014	Company Name : C.E. Instruments
Method File : D:\CHNS2012-13\SRM23092014.mth	Printed : 9/23/2014 19:31
Chromatogram : PG-AE-2-31-1	Instrument N. : Instrument #1
Operator ID : SONALI	Sample weight : .926
Analysed : 09/23/2014 15:14	
Sample ID : PG-AE-2-31-1 (# 18)	
Analysis Type : UnkNown (Area)	



Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	5.3271	43	73812	FU	24.869010	.149634E+07
Carbon	72.1021	66	1835641	FU	1.000000	.274934E+07
Hydrogen	5.5911	181	374665	RS	4.899418	.697271E+07
Totals	83.0203		2284118			

Fig. S9 Elemental analysis data of 2.

PG-CP-14-49-1-1H

Current Data Parameters
NAME PG-CP-14-49-1-1H
EXPNO 15
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170811
Time 16.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
SFO1 500.1330885 MHz
NUC1 1H
P1 13.50 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

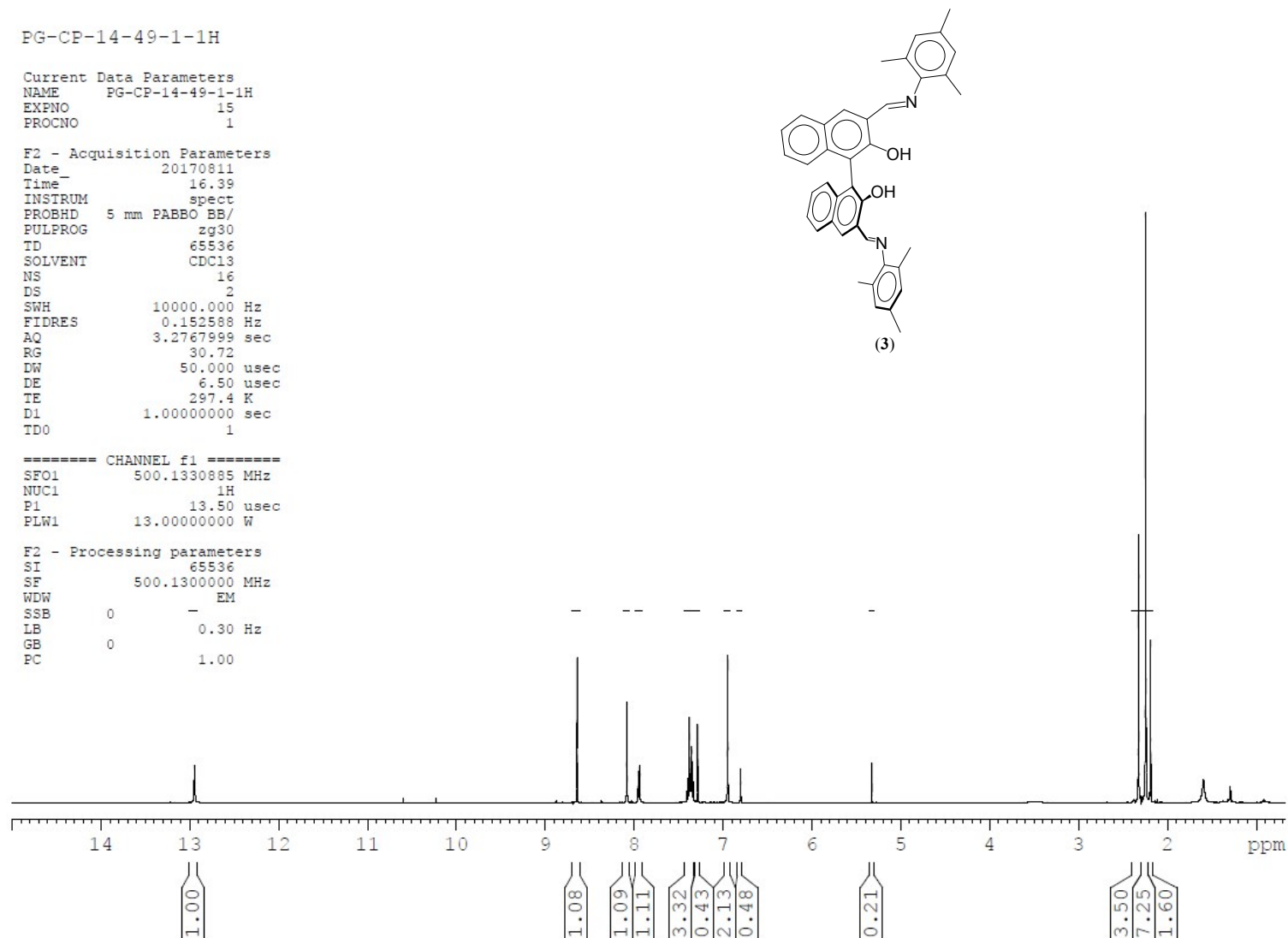


Fig. S10 ¹H NMR spectrum of **3** in CDCl₃.

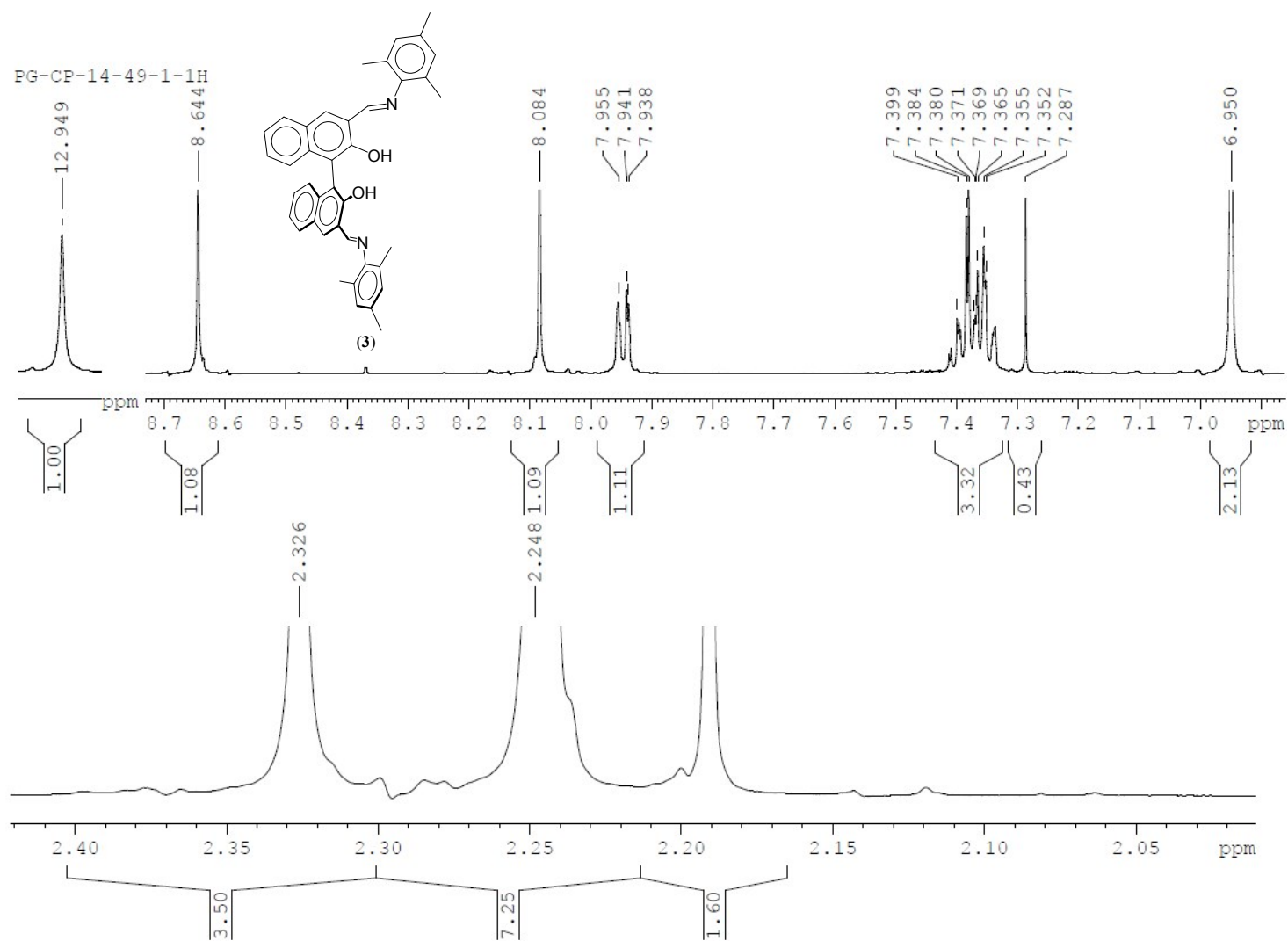


Fig S11 Expanded ^1H NMR spectrum of **3** in CDCl_3 .

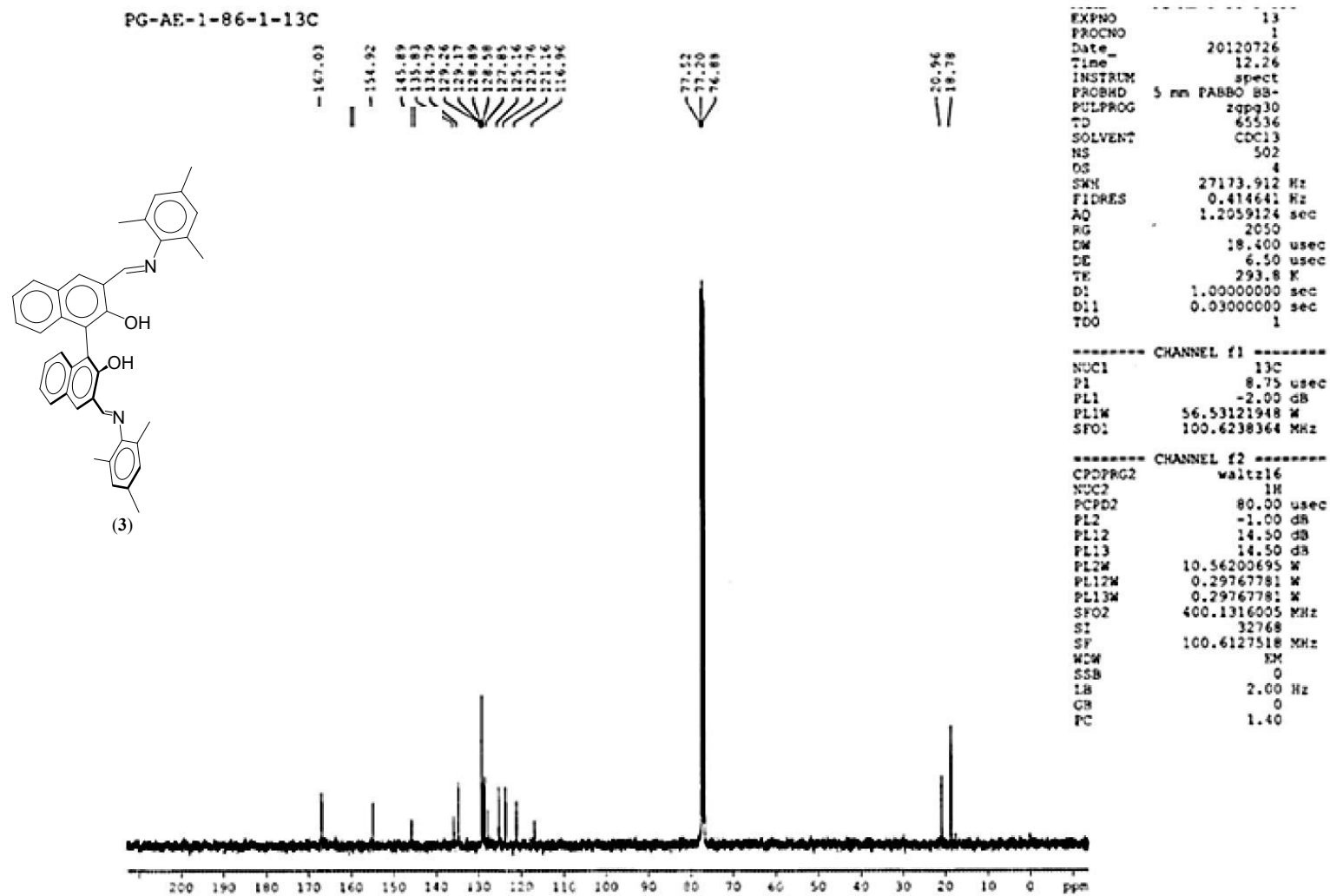


Fig. S12 ¹³C{¹H} NMR spectrum of **3** in CDCl₃.

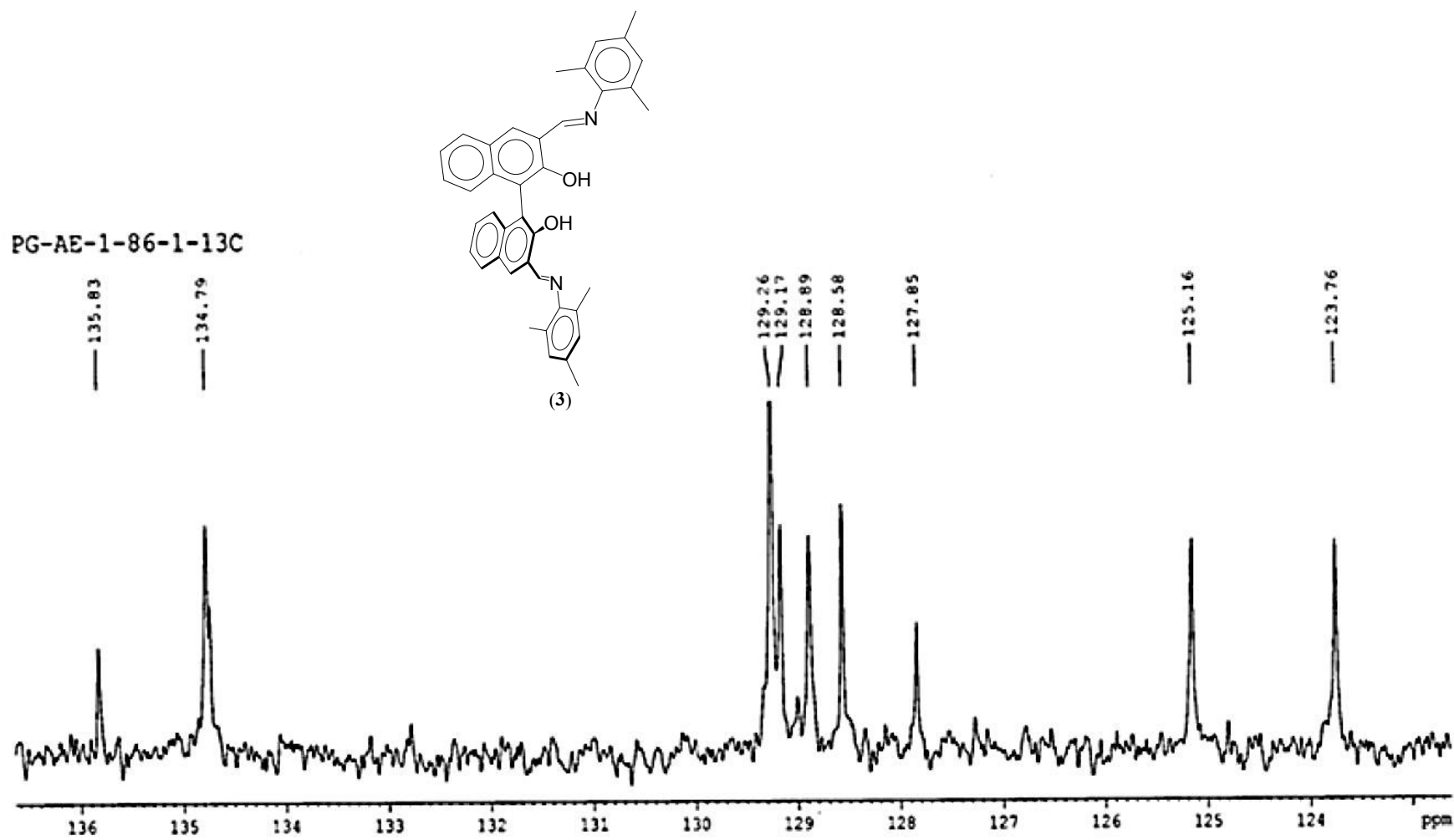


Fig S13 Expanded $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 .

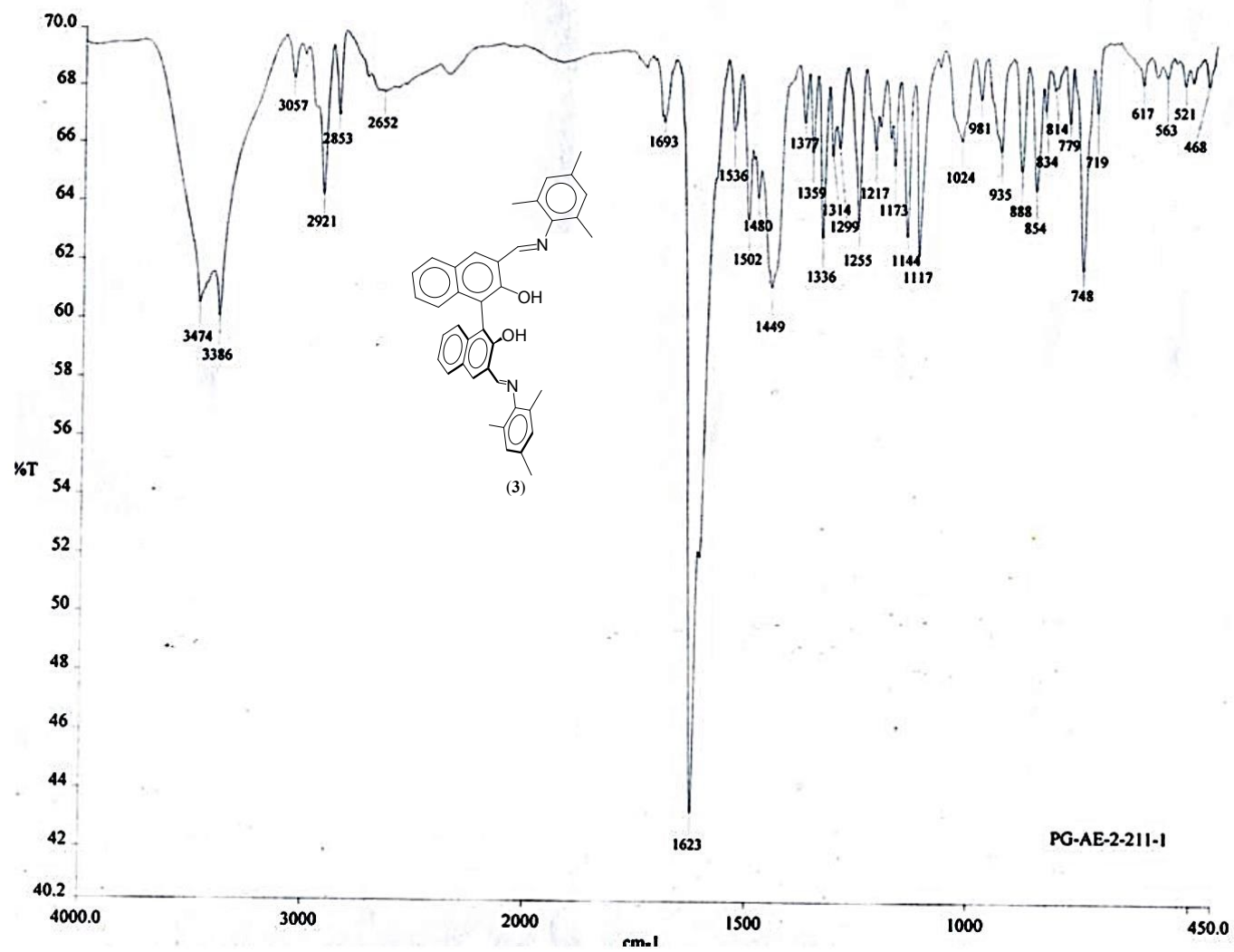


Fig.S14 Infrared spectrum of 3 in KBr.

Elemental Composition Report

Single Mass Analysis (displaying only valid results)

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 200.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

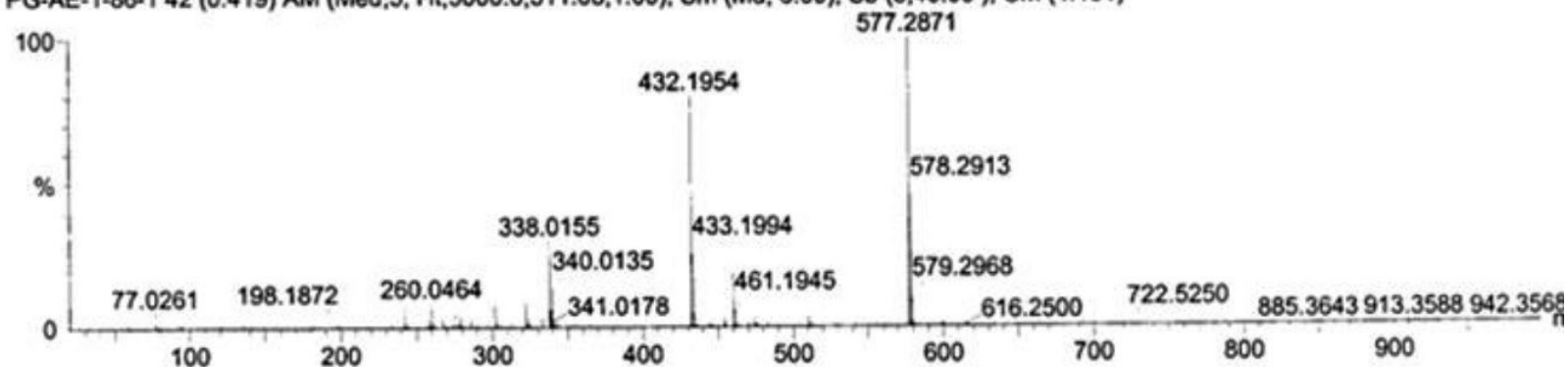
30 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105)

Dept. Of Chemistry I.I.T.(B)

C₄₀H₃₆N₂O₂

PG-AE-1-86-1 42 (0.419) AM (Med,5, Ht,5000.0,311.08,1.00); Sm (Md, 6.00); Sb (5,40.00); Cm (4:101)



Minimum: -1.5
Maximum: 200.0 40.0 200.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
577.2871	577.2855	1.6	2.8	23.5	1	C ₄₀ H ₃₇ N ₂ O ₂

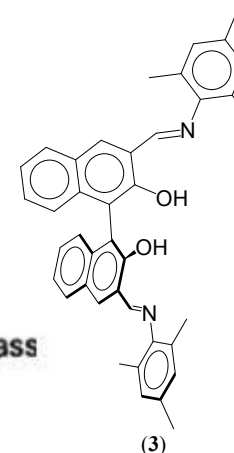
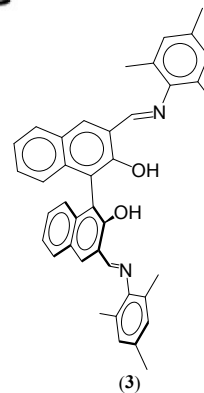


Fig. S15 High Resolution Mass Spectrometry (HRMS) data of 3.

Eager 300 Report

Page: 1 Sample: PG-AE-1-86-2 (PG-AE-1-86-2)

Method Name : SP-230712
Method File : D:\CHNS2012\SP-230712.mth
Chromatogram : PG-AE-1-86-2
Operator ID : MNRAO
Analysed : 07/23/2012 15:16
Sample ID : PG-AE-1-86-2 (# 9)
Analysis Type : UnkNown (Area)



Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	4.5275	43	45902 RS	32.170660	905300.9000
Carbon	80.6678	67	1476682 RS	1.000000	.242139E+07
Hydrogen	6.6426	175	290366 RS	5.085596	.578213E+07
Totals	91.8379		1812949		

Fig. S16 Elemental analysis data of 3.

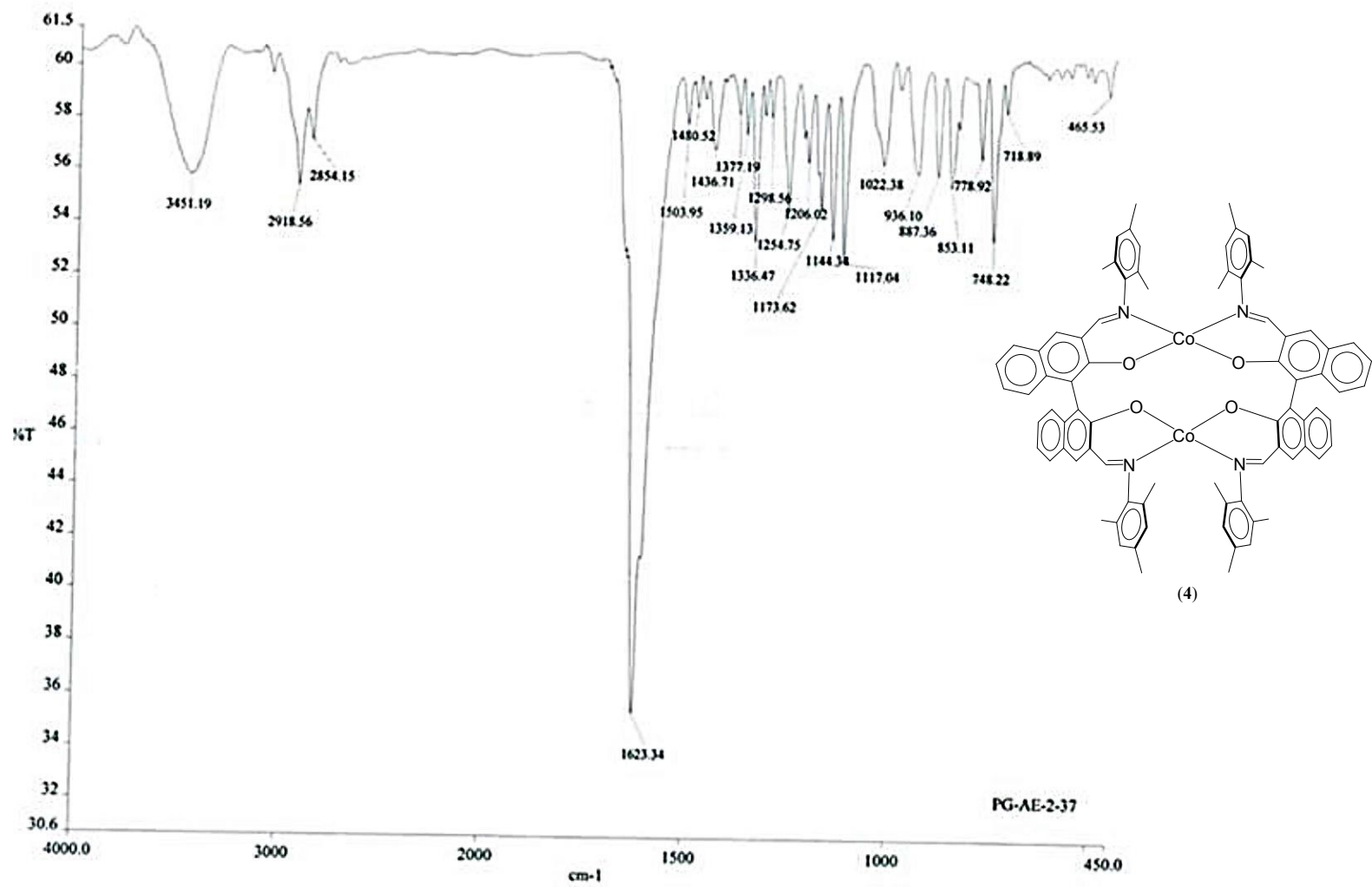


Fig. S17 Infrared spectrum of 4 in KBr.

Indian Institute of Technology (B)

Analysis Info

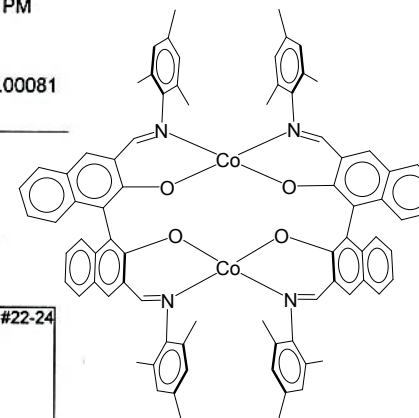
Analysis Name D:\Data\JAN-13\PG-AE-1-125.d
 Method Tune_pos_Standard_NAI-1500.m
 Sample Name PG-AE-1-125
 Comment C80H68Co2N2O4

Acquisition Date 1/27/2013 12:40:01 PM

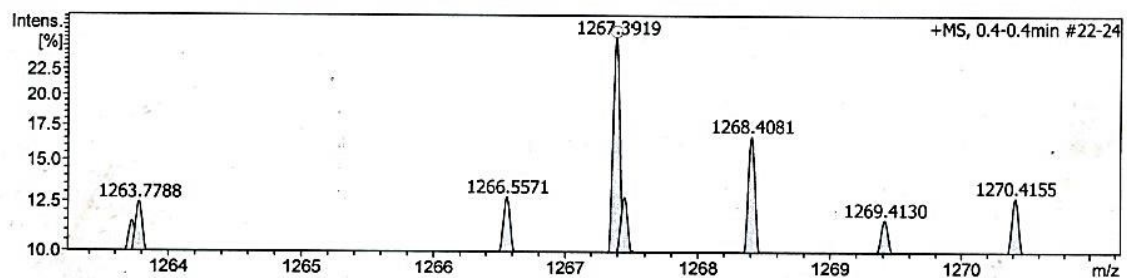
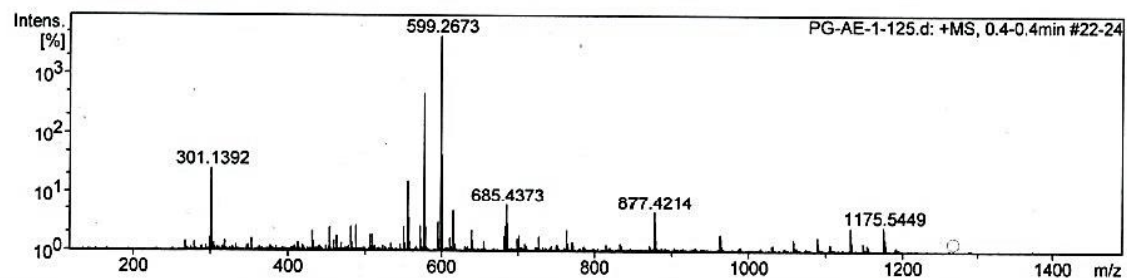
Operator IIT-B
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.1 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Divert Valve	Waste

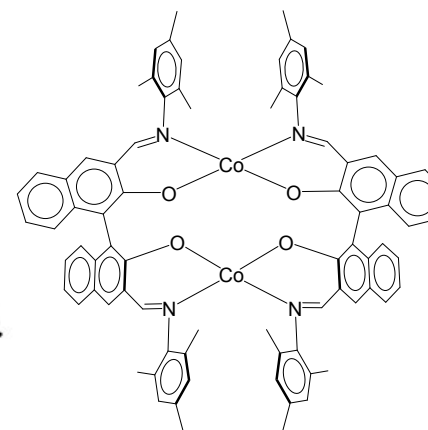


(4)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
1267.3919	1	C80H69Co2N4O4	1267.3977	4.6	401.1	1	100.00	48.5	even ok

Fig. S18 High Resolution Mass Spectrometry (HRMS) data of **4**.



(4)

Eager 300 Report

Page: 1 Sample: PG-CP-14-60-1 (PG-CP-14-60-1)

Method Name : PGCP28082017
 Method File : D:\chns2016 -1\PGCP28082017.mth
 Chromatogram : PG-CP-14-60-1
 Operator ID : CHANDNI
 Analysed : 08/28/2017 17:47
 Sample ID : PG-CP-14-60-1 (# 7)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 8/28/2017 19:13
 Instrument N. : Instrument #1
 Sample weight : .856

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	4.8811	42	45575	RS	37.650750	.109078E+07
Carbon	76.5413	65	1715933	RS	1.000000	.261897E+07
Hydrogen	5.9255	181	326290	RS	5.258920	.643284E+07
Totals	87.3479		2087798			

Fig.S19 Elemental analysis data of 4.

Current Data Parameters
NAME PG-CP-14-158-1-1H
EXPNO 1
PROCNO 1

PG-CP-14-158-1-1H

F2 - Acquisition Parameters
Date_ 20171202
Time 7.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 9
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 203
DN 60.800 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

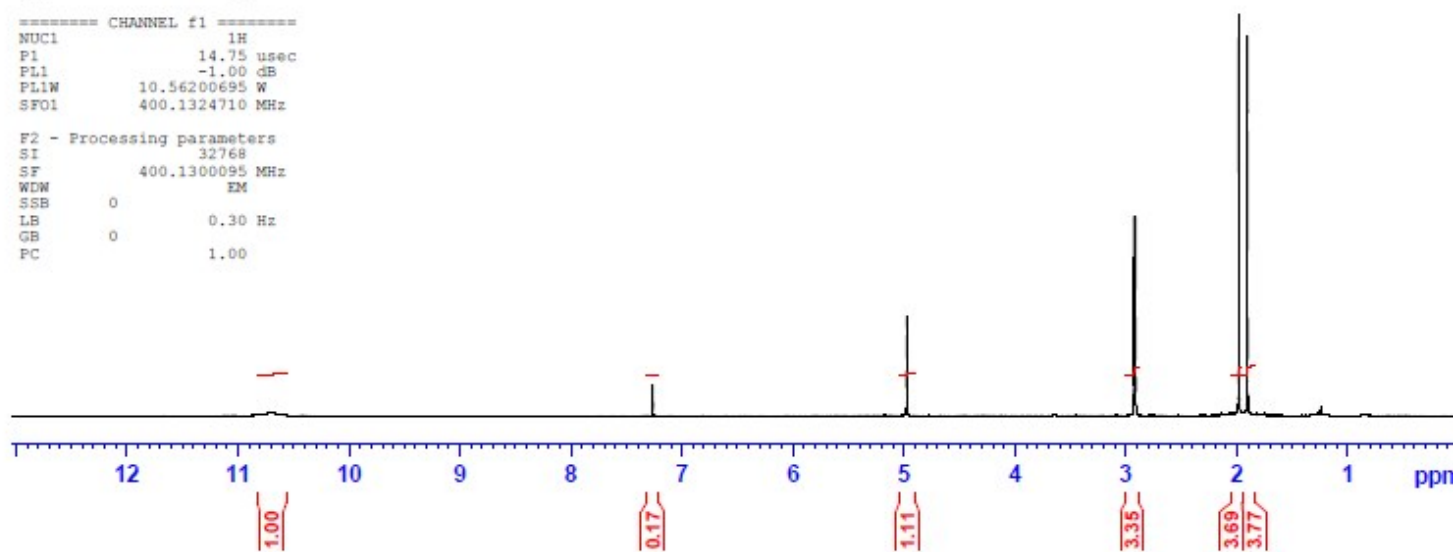


Fig. S20 ¹H NMR spectrum of **5** in CDCl₃ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

PG-CP-14-158-1-1H

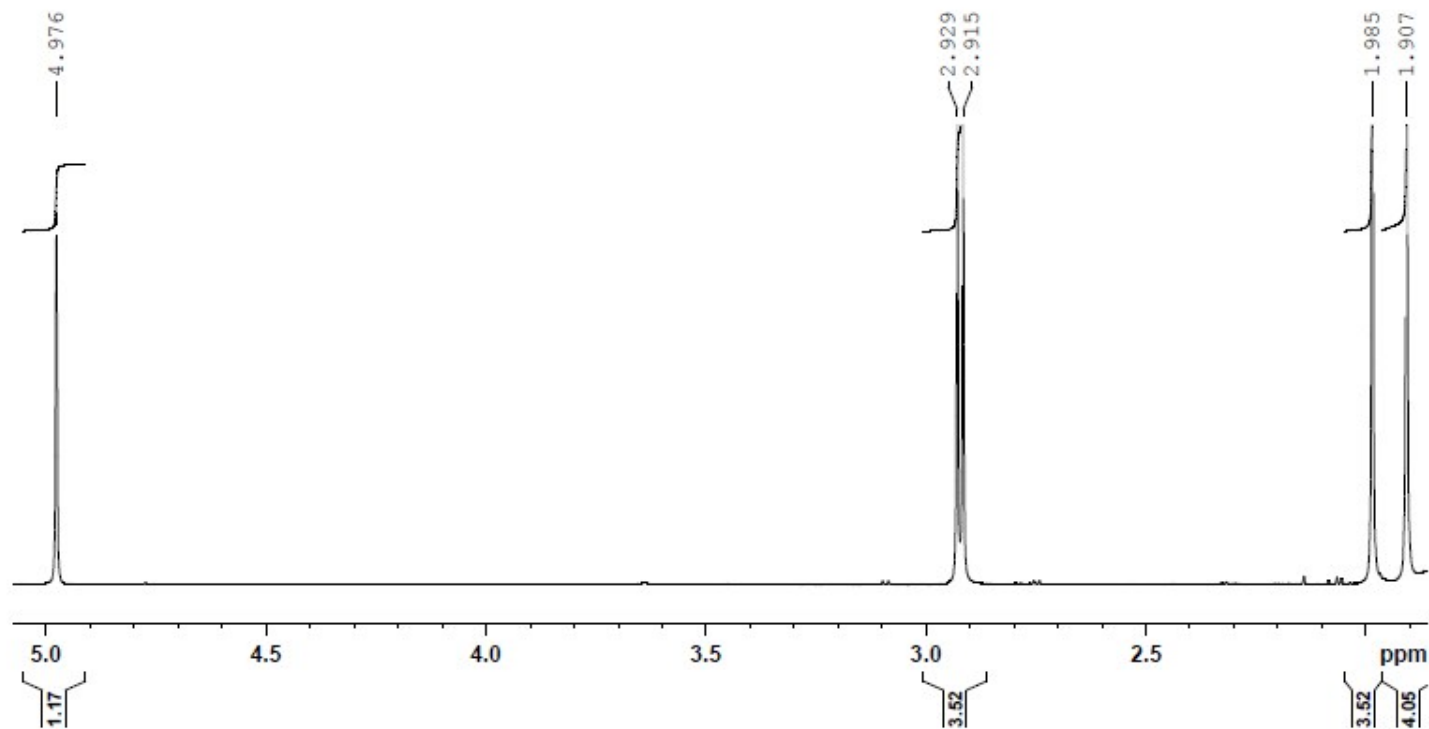
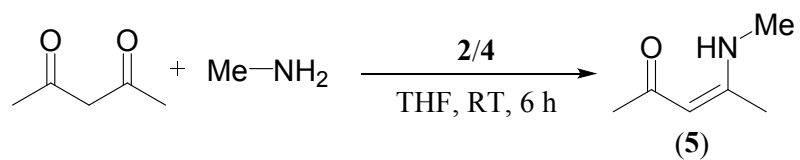


Fig. S21 Expanded ¹H NMR spectrum of **5** in CDCl₃ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

PG-CP-14-159-1-13C

Current Data Parameters
NAME PG-CP-14-159-1-13C
EXPNO 16
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171207
Time 17.50
INSTRUM spect
PROBHD 5 mm FANNO BH/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 92
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 298.7 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

----- CHANNEL F1 -----
SFO1 125.7703637 MHz
NUC1 13C
P1 8.90 usec
P1M1 103.0000000 W

----- CHANNEL F2 -----
SFO2 500.1320005 MHz
NUC2 1H
CPOPRG12 waltz16
PCPD2 80.00 usec
P1M2 16.00000000 W
P1M12 0.44556001 W
P1M13 0.22411001 W

F2 - Processing parameters
SI 32768
SF 125.7577592 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

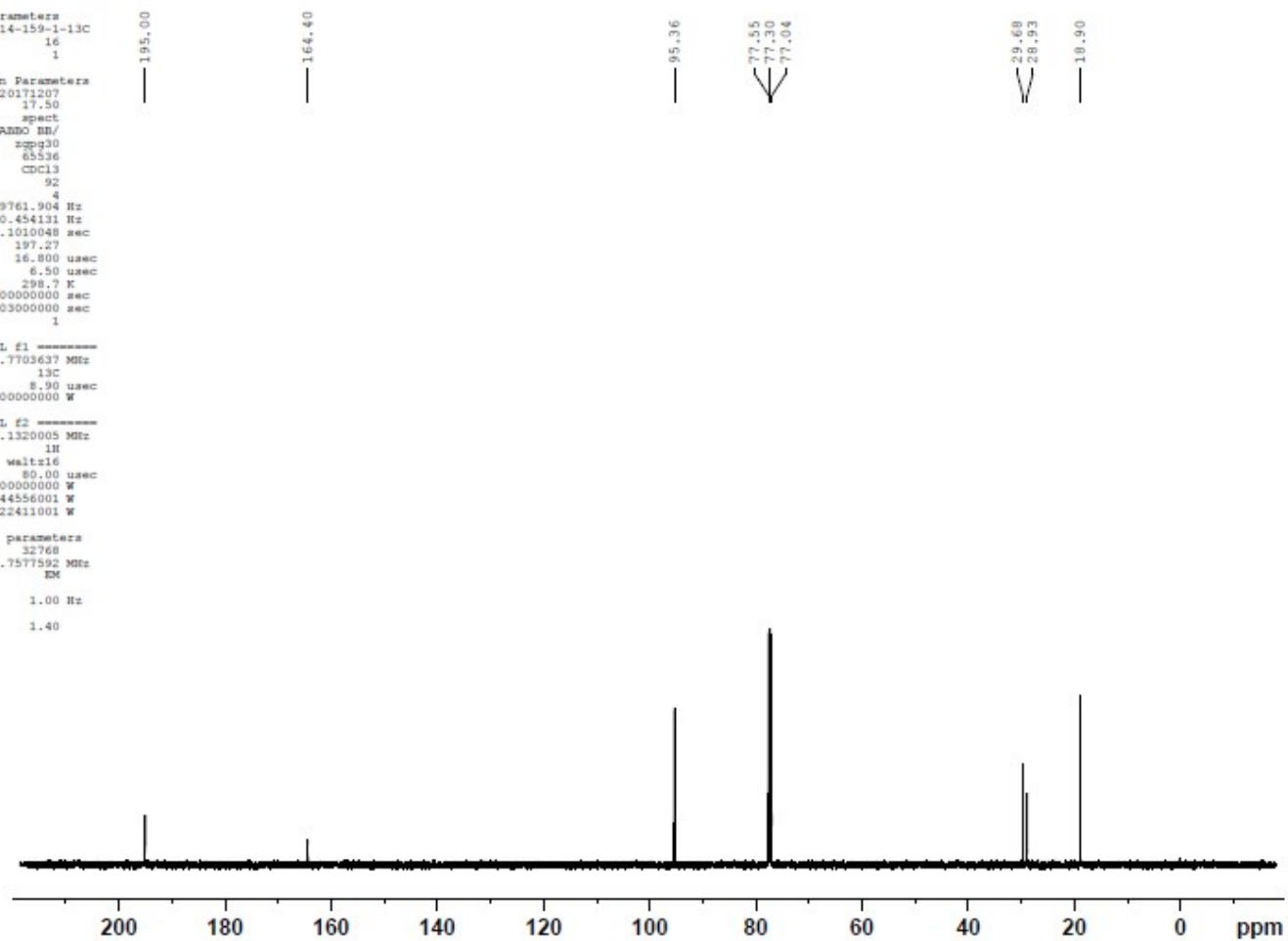


Fig. S22 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in CDCl_3 formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

File : F:\GCMSDATA2017\November2017\PG-CP-14-159-2.D
Operator : CP
Acquired : 30 Nov 2017 20:09 using AcqMethod COMMON METHOD-2017.M
Instrument : GCMS
Sample Name: PG-CP-14-159-2
Misc Info :
Vial Number: 1

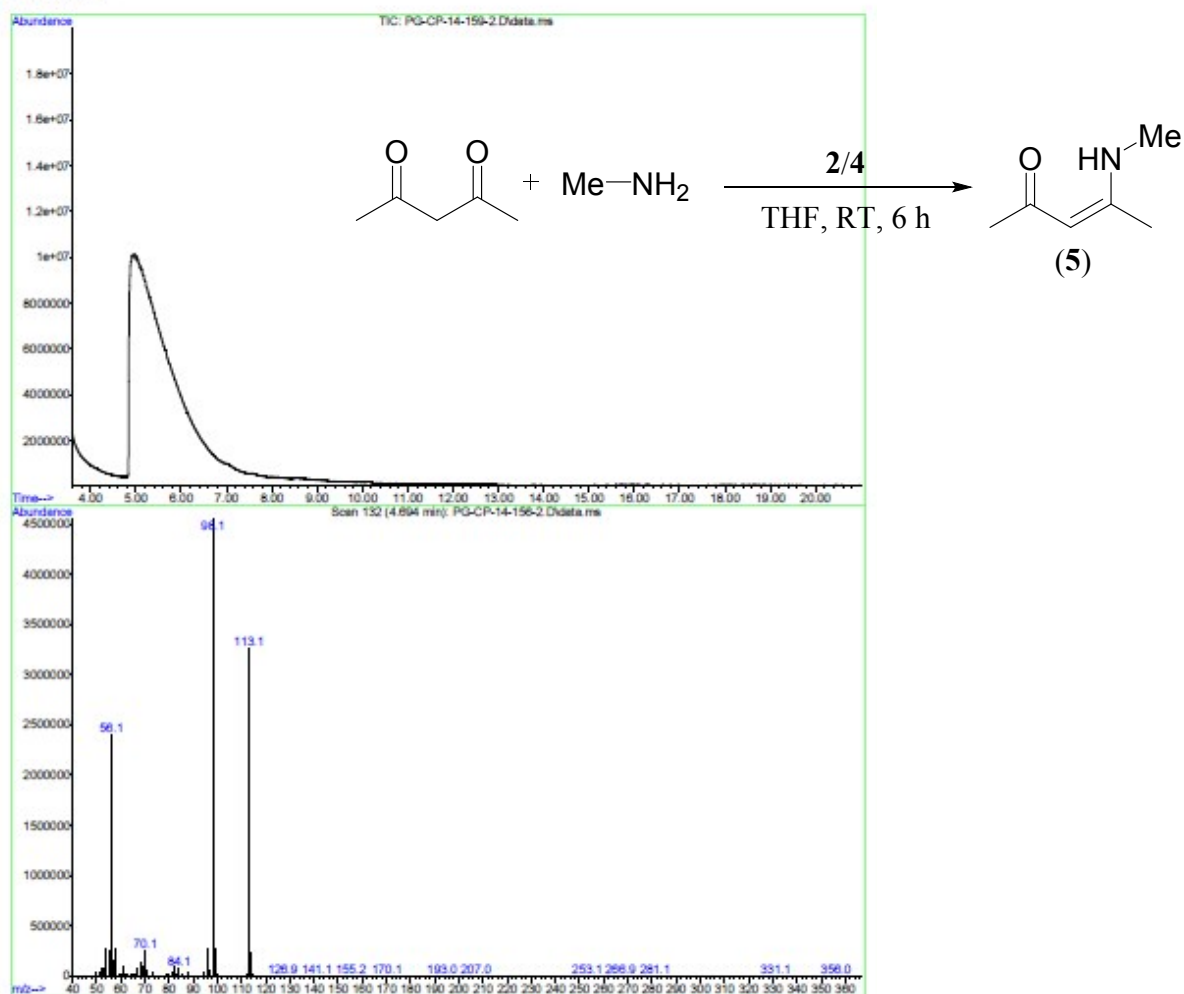


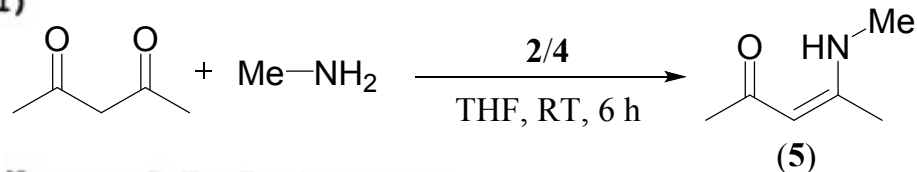
Fig. S23 GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by the the dinuclear [CoL¹]₂ (2) and [CoL²]₂ (4) complexes.

Eager 300 Report

Page: 1 Sample: PG-CP-14-197-1 (PG-CP-14-197-1)

Method Name : PGCP30122017
 Method File : D:\CHNS-2017\PGCP30122017.mth
 Chromatogram : PG-CP-14-197-1
 Operator ID : CHANDNI
 Analysed : 12/30/2017 17:34
 Sample ID : PG-CP-14-197-1 (# 6)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 12/31/2017 22:02
 Instrument N. : Instrument #1
 Sample weight : 1.271



Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	2	139533	RS		0.0000
Nitrogen	12.3527	41	170136	RS	12.354090	.108364E+07
Carbon	63.6455	63	2101869	RS	1.000000	.259525E+07
Hydrogen	9.1709	190	775439	RS	2.710554	.665260E+07
Totals	85.1691		3186977			

Fig.S24 Elemental analysis data of **5** formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

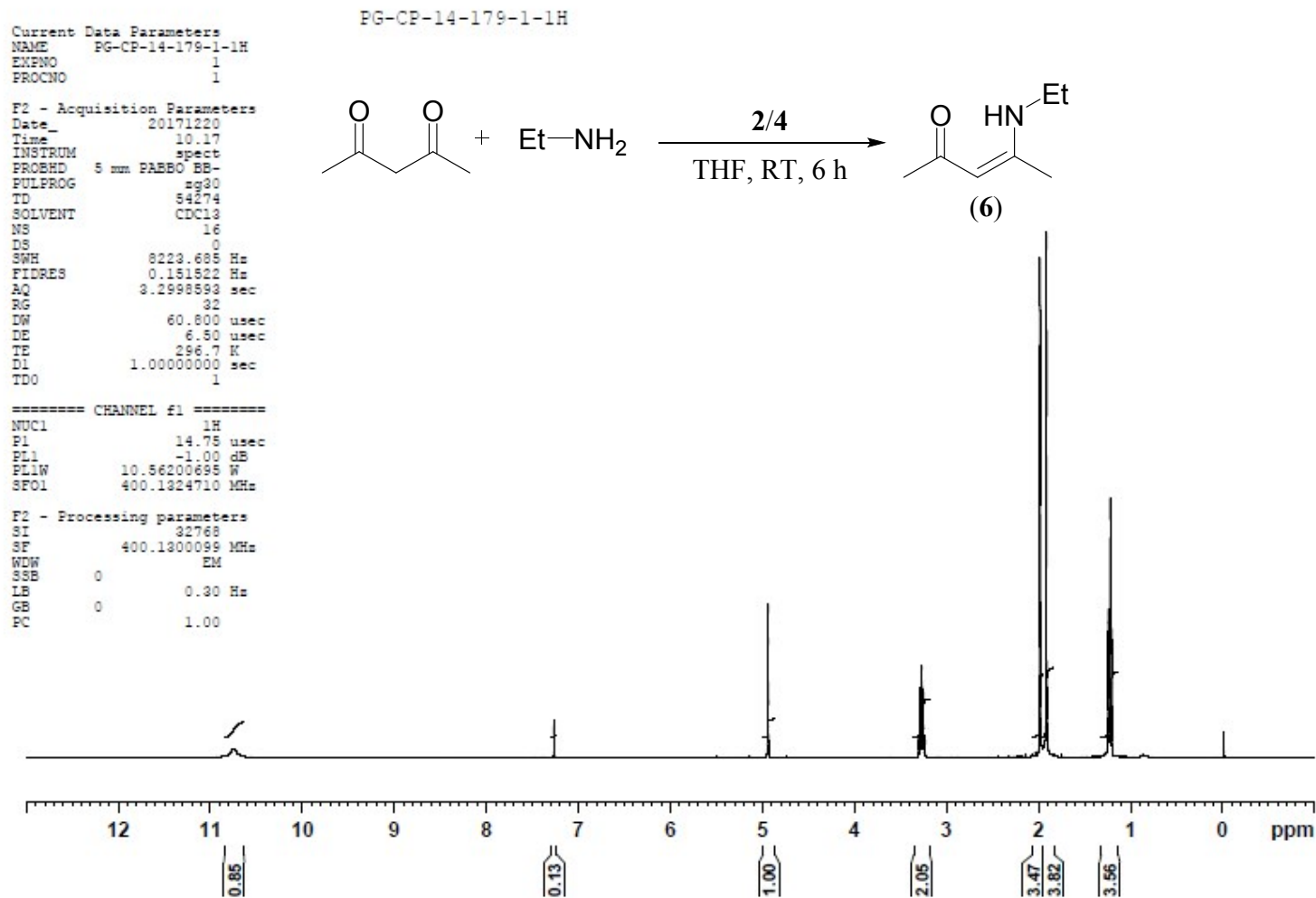


Fig. S25 ^1H NMR spectrum of **6** in CDCl_3 formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

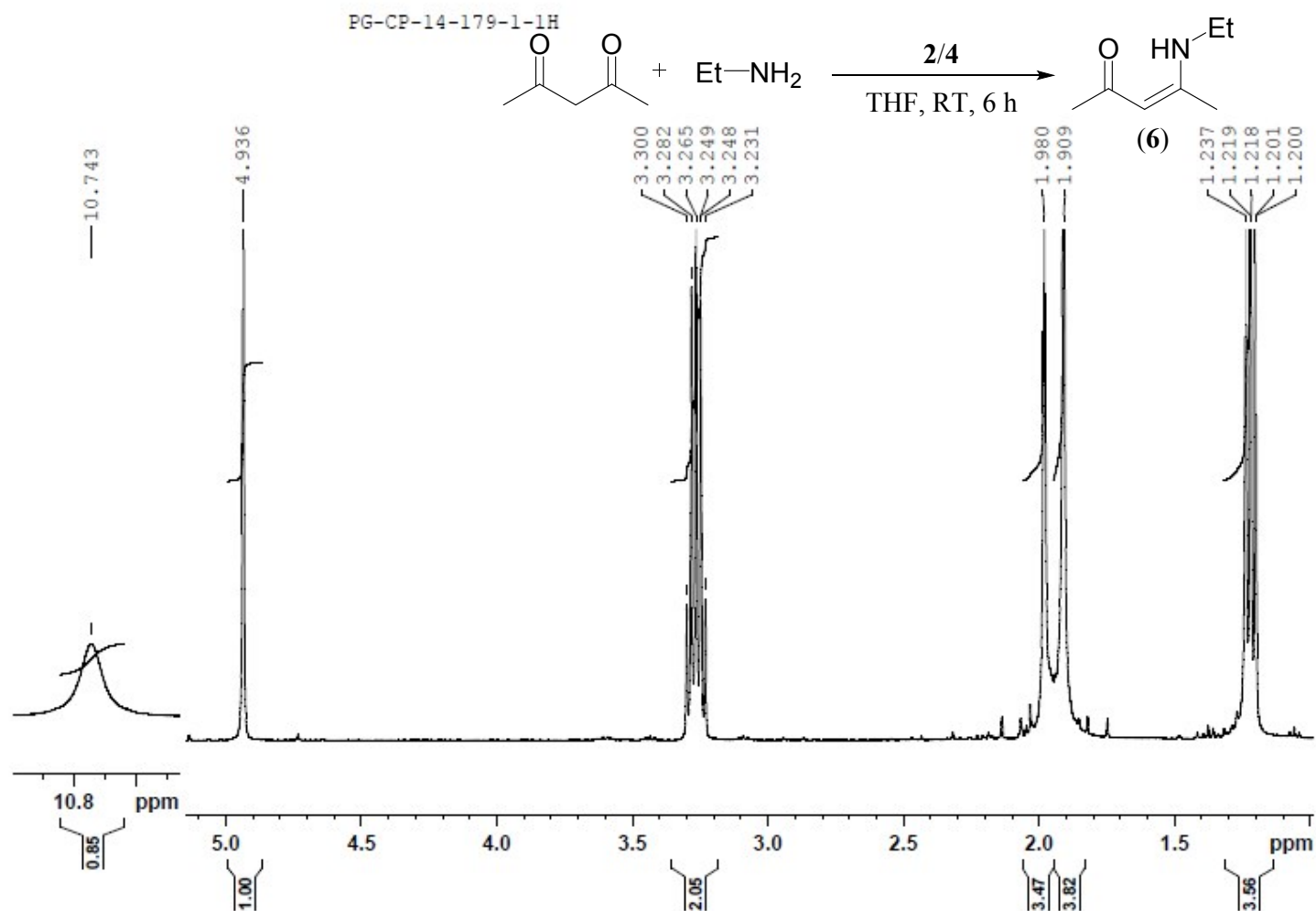


Fig. S26 Expanded ¹H NMR spectrum of **6** in CDCl₃ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

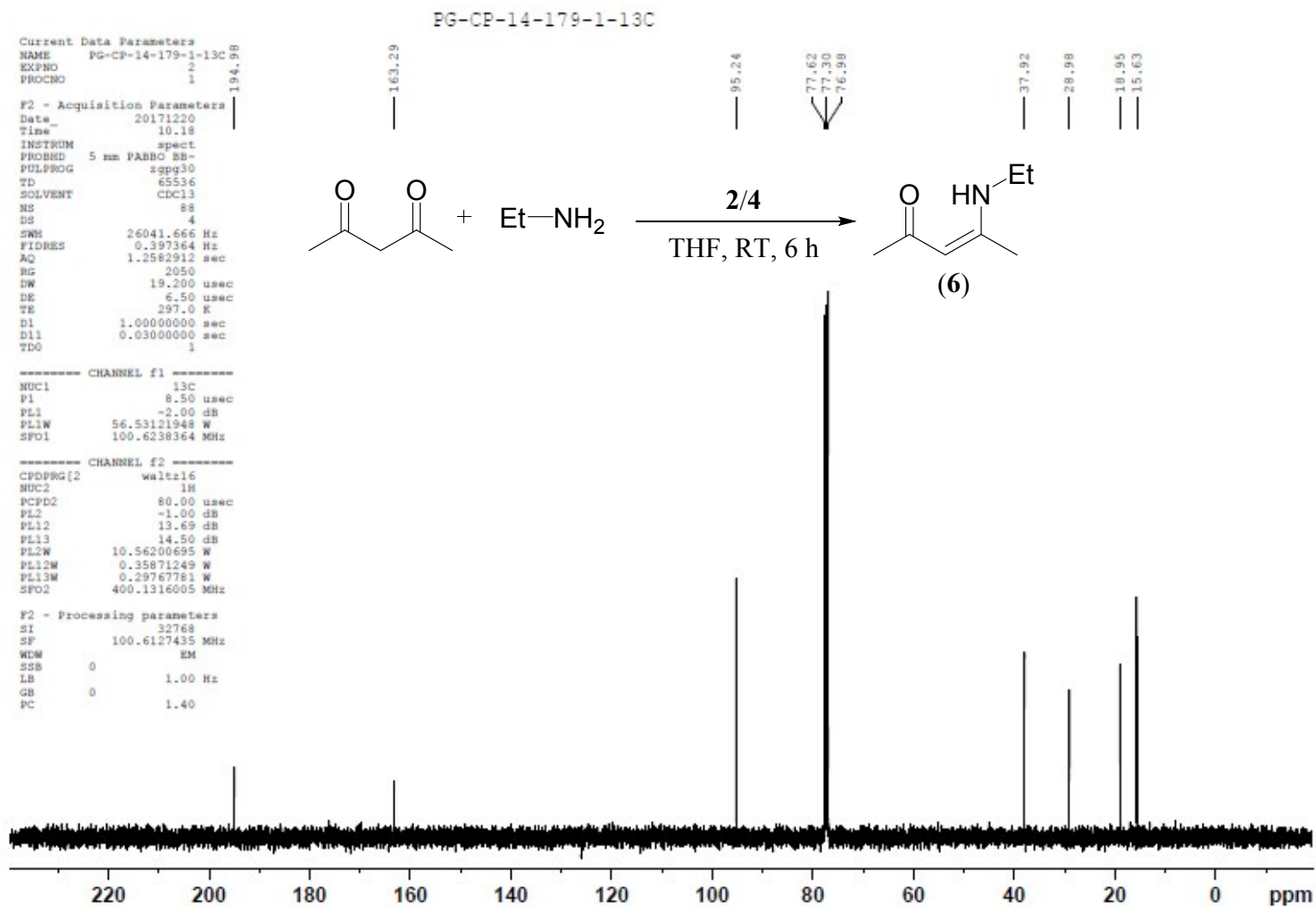


Fig. S27 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in CDCl_3 formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

File : F:\GCMSDATA2017\DECEMBER-2017\PG-CP-14-179-1.D
Operator : CP
Acquired : 18 Dec 2017 15:29 using AcqMethod COMMON METHOD-2017.M
Instrument : GCMS
Sample Name : PG-CP-14-179-1
Misc Info :
Vial Number: 1

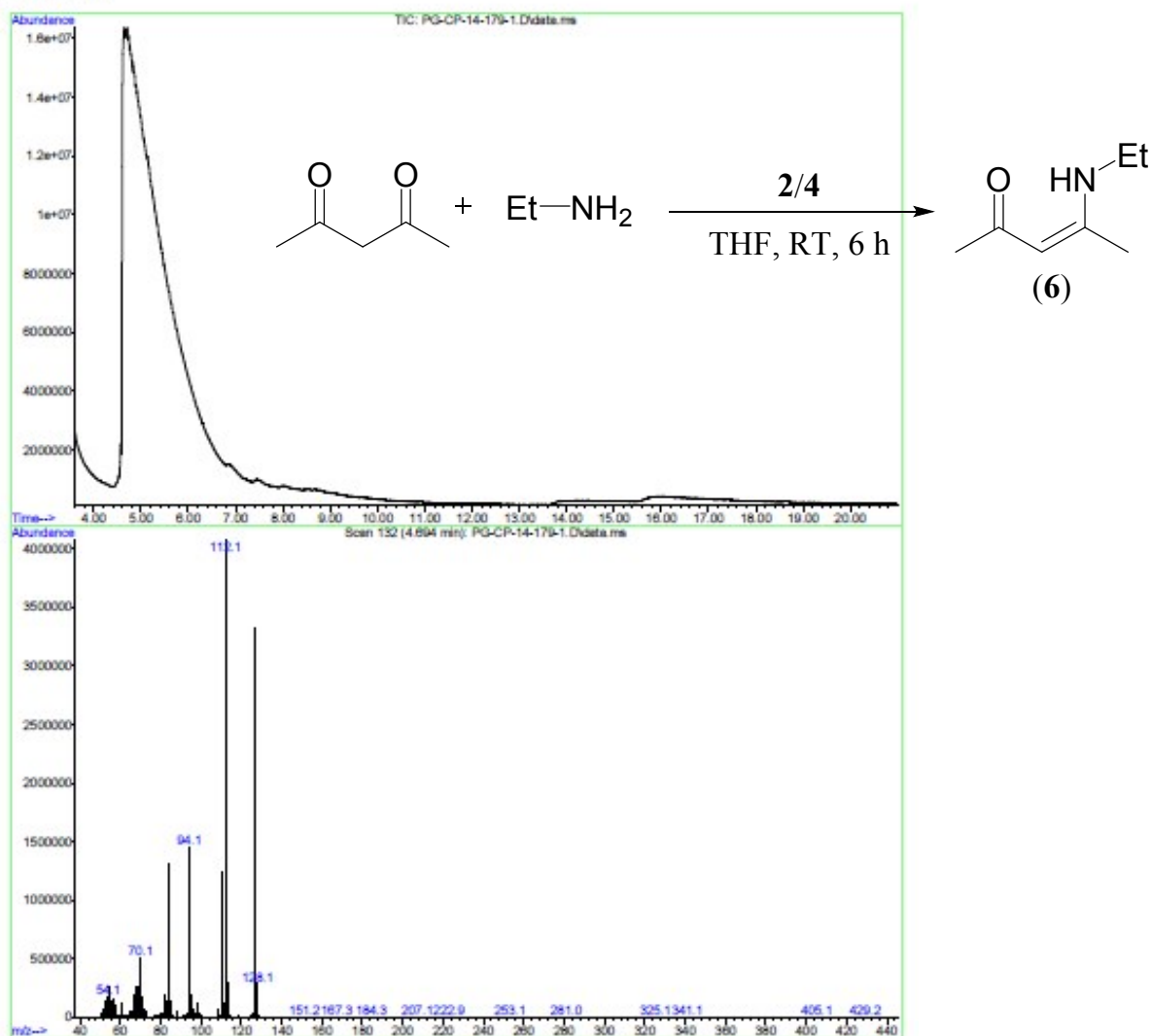


Fig. S28 GCMS trace of **6** (m/z 127) in EtOAc formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

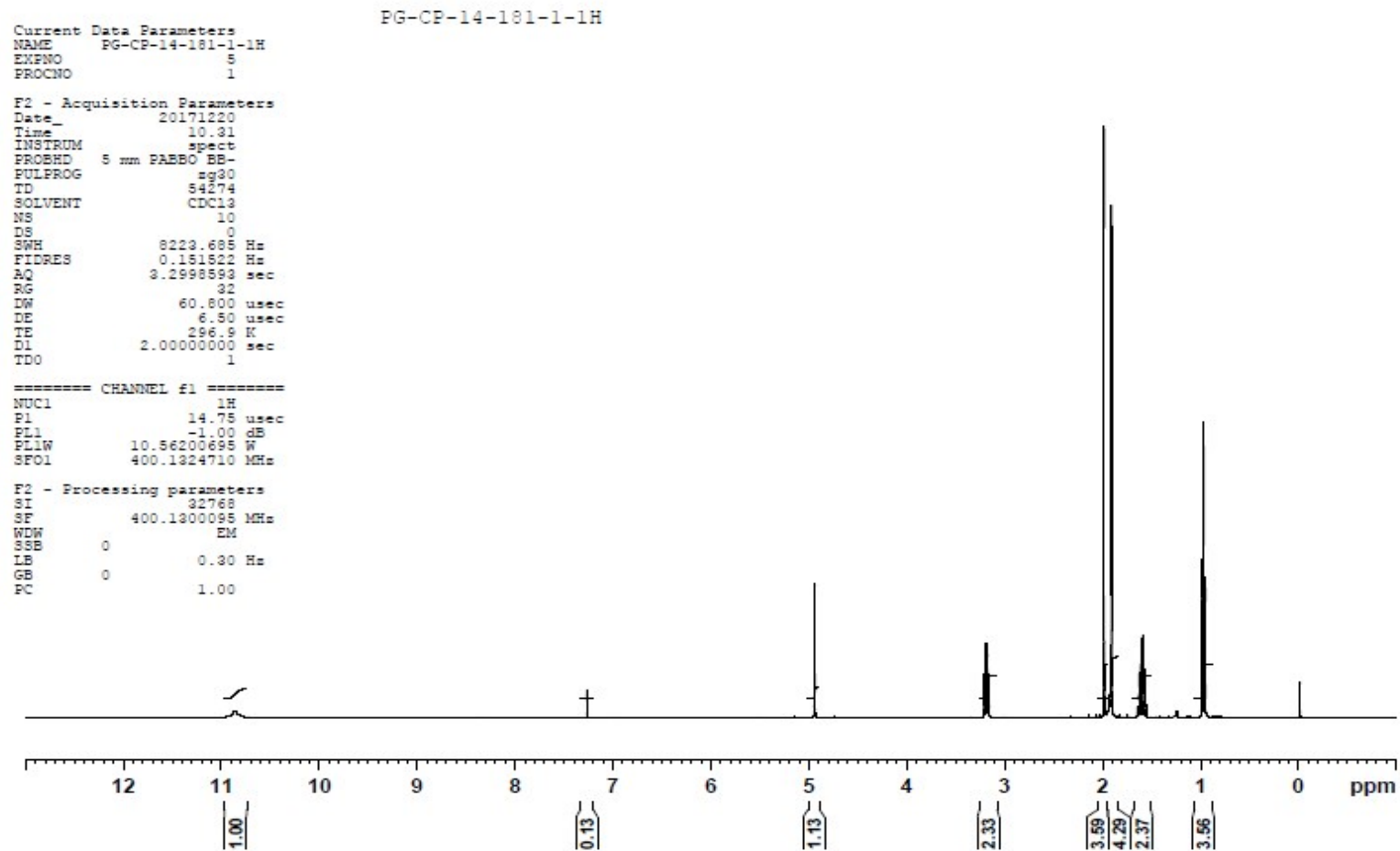


Fig. S29 ^1H NMR spectrum of **7** in CDCl_3 formed in the reaction of acetyl acetone and *n*-propyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

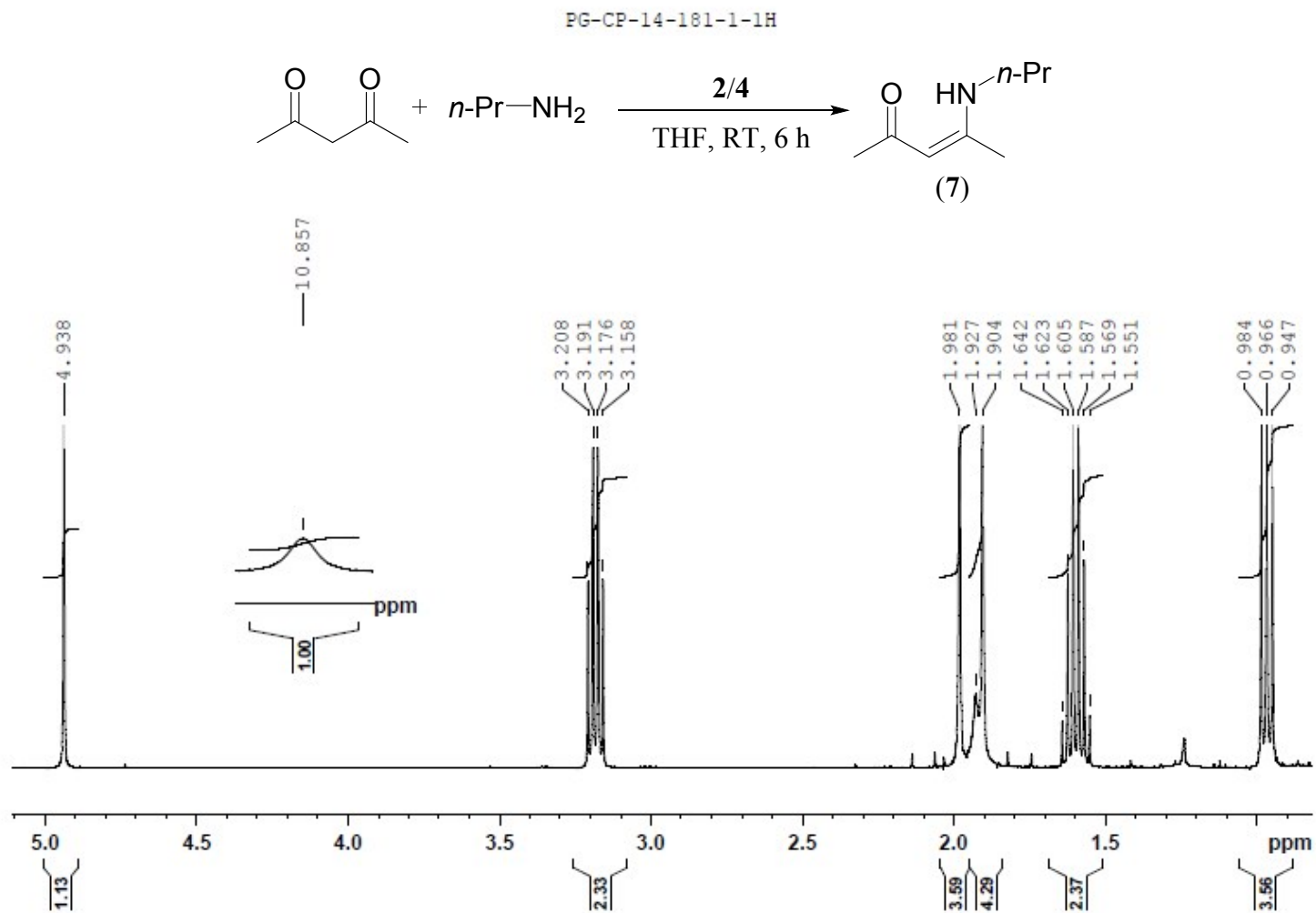


Fig. S30 Expanded ^1H NMR spectrum of 7 in CDCl_3 formed in the reaction of acetyl acetone and *n*-propyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (2) and $[\text{CoL}^2]_2$ (4) complexes.

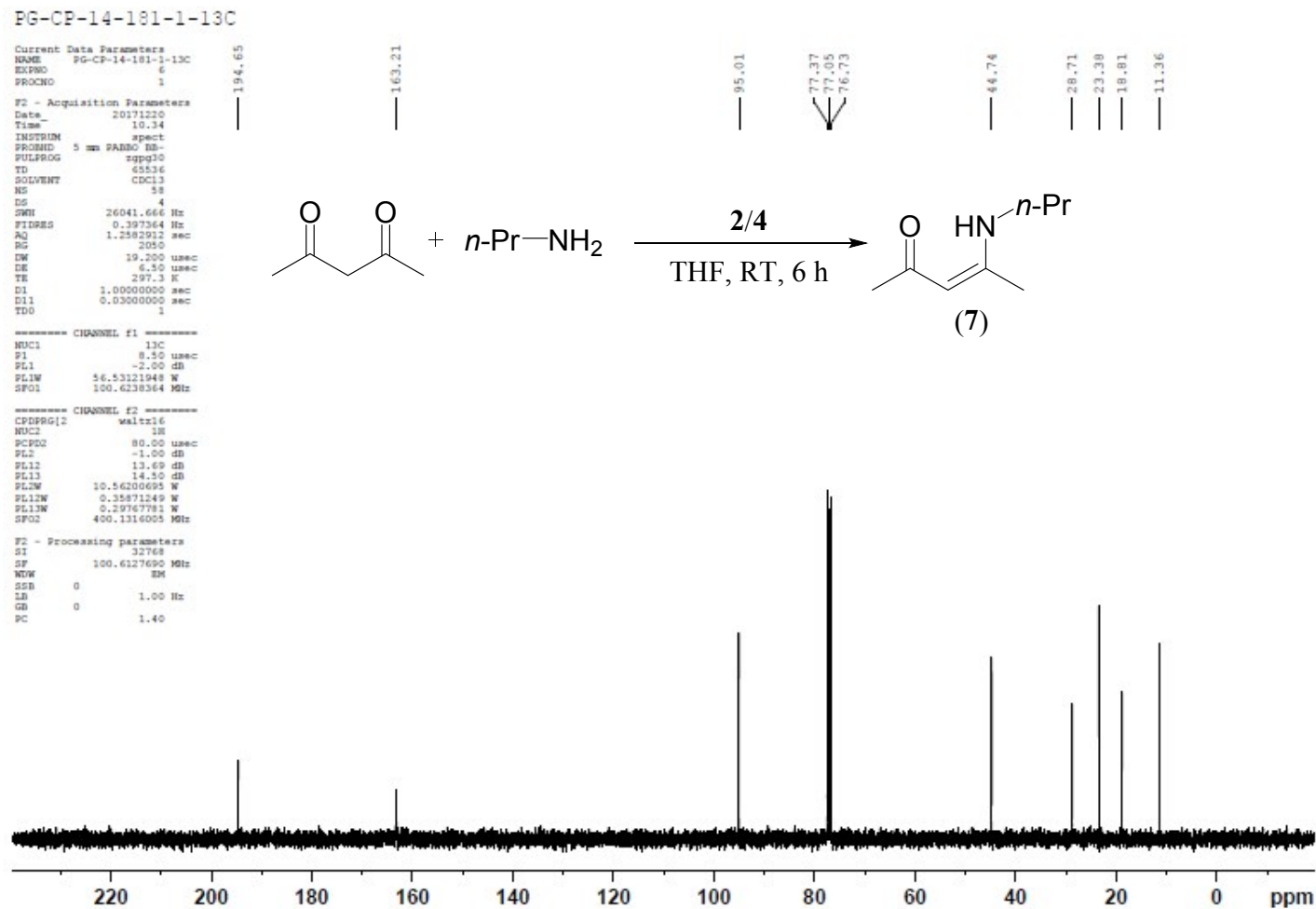


Fig.S31 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in CDCl_3 formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

File :F:\GCMSDATA2017\DECEMBER-2017\PG-CP-14-181-1.D
 Operator : CP
 Acquired : 18 Dec 2017 16:20 using AcqMethod COMMON METHOD-2017.M
 Instrument : GCMS
 Sample Name: PG-CP-14-181-1
 disc Info :
 Prial Number: 3

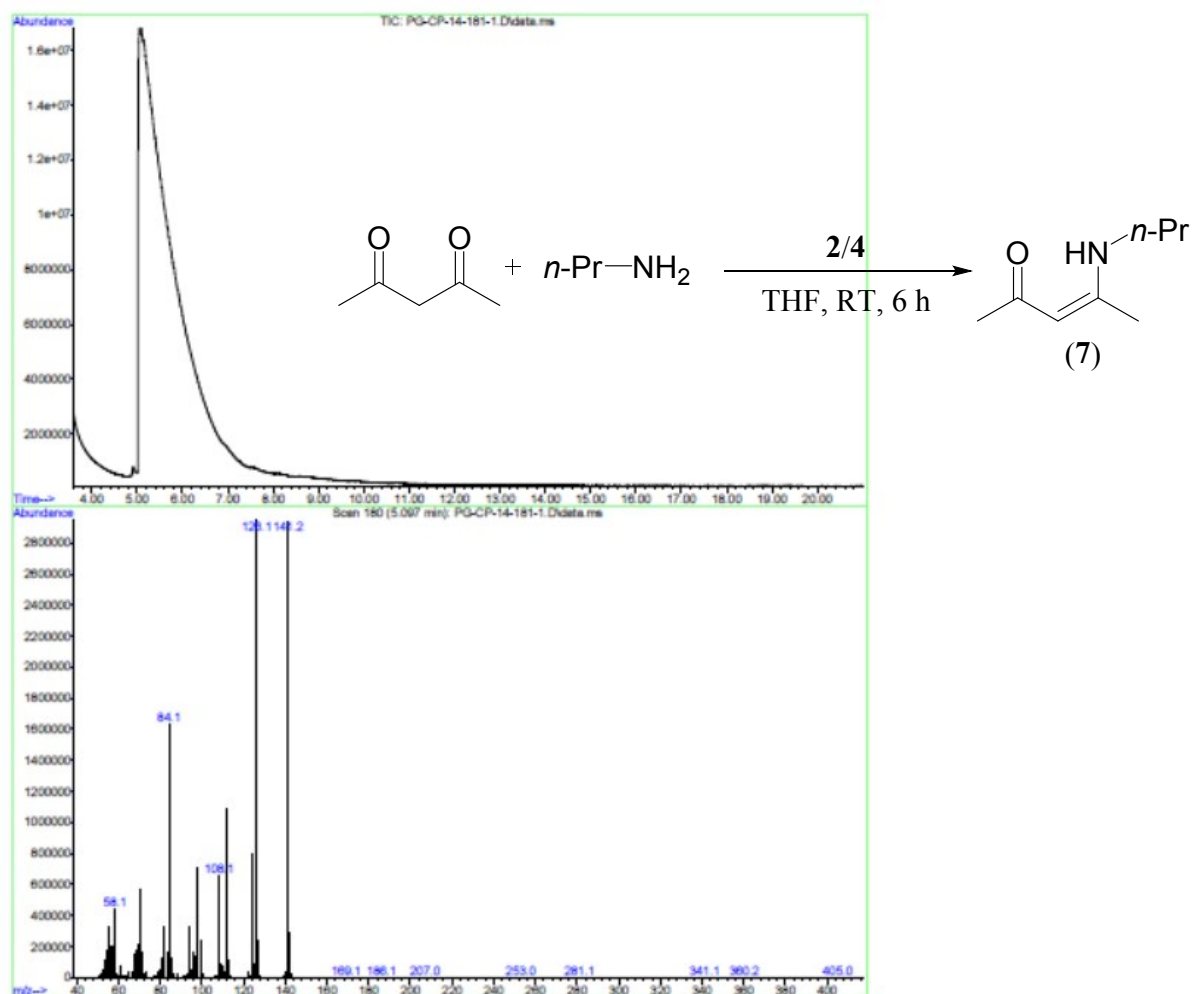


Fig. S32 GCMS trace of 7 (m/z 141) in EtOAc formed in the reaction of acetyl acetone and *n*-propyl amine as catalyzed by the the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

```

Current Data Parameters
NAME PG-CP-14-184-1-1H
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171222
Time_ 8.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 64274
SOLVENT CDCl3
NS 9
DS 0
SWH 8223.605 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 296.1 K
DL 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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PG-CP-14-184-1-1H

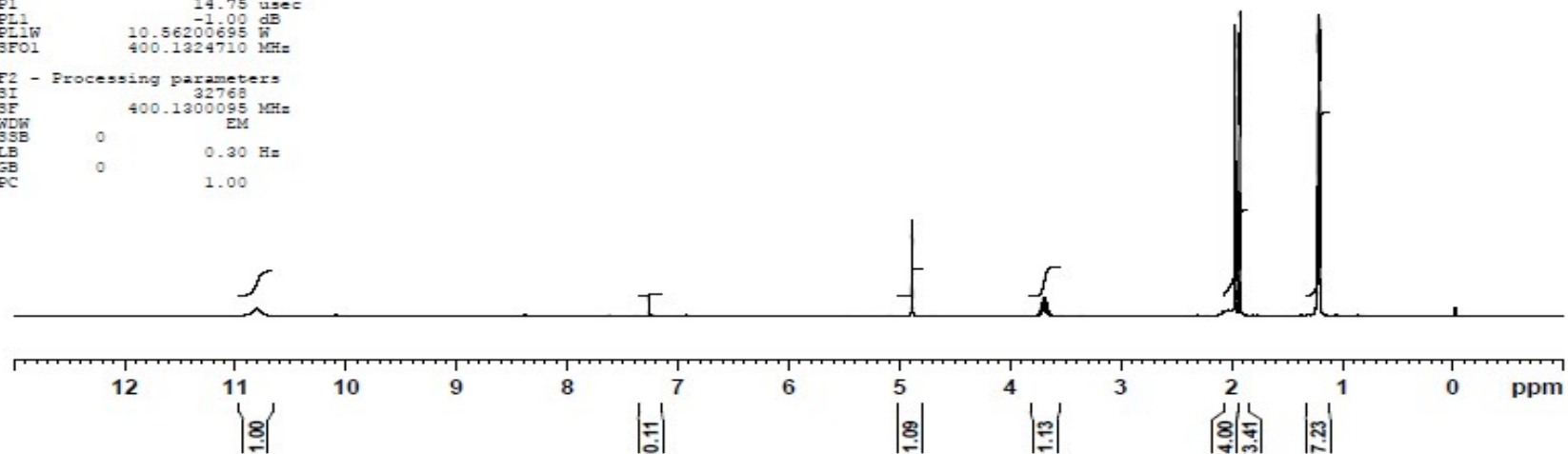
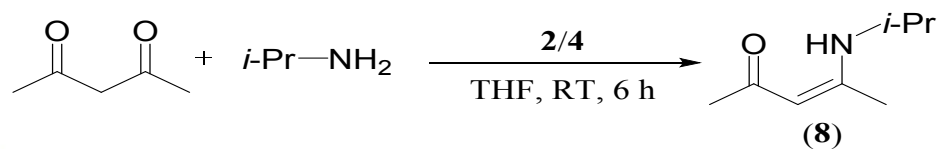


Fig.S33 ¹H NMR spectrum of **8** in CDCl₃ formed in the reaction of acetyl acetone and *i*-propyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

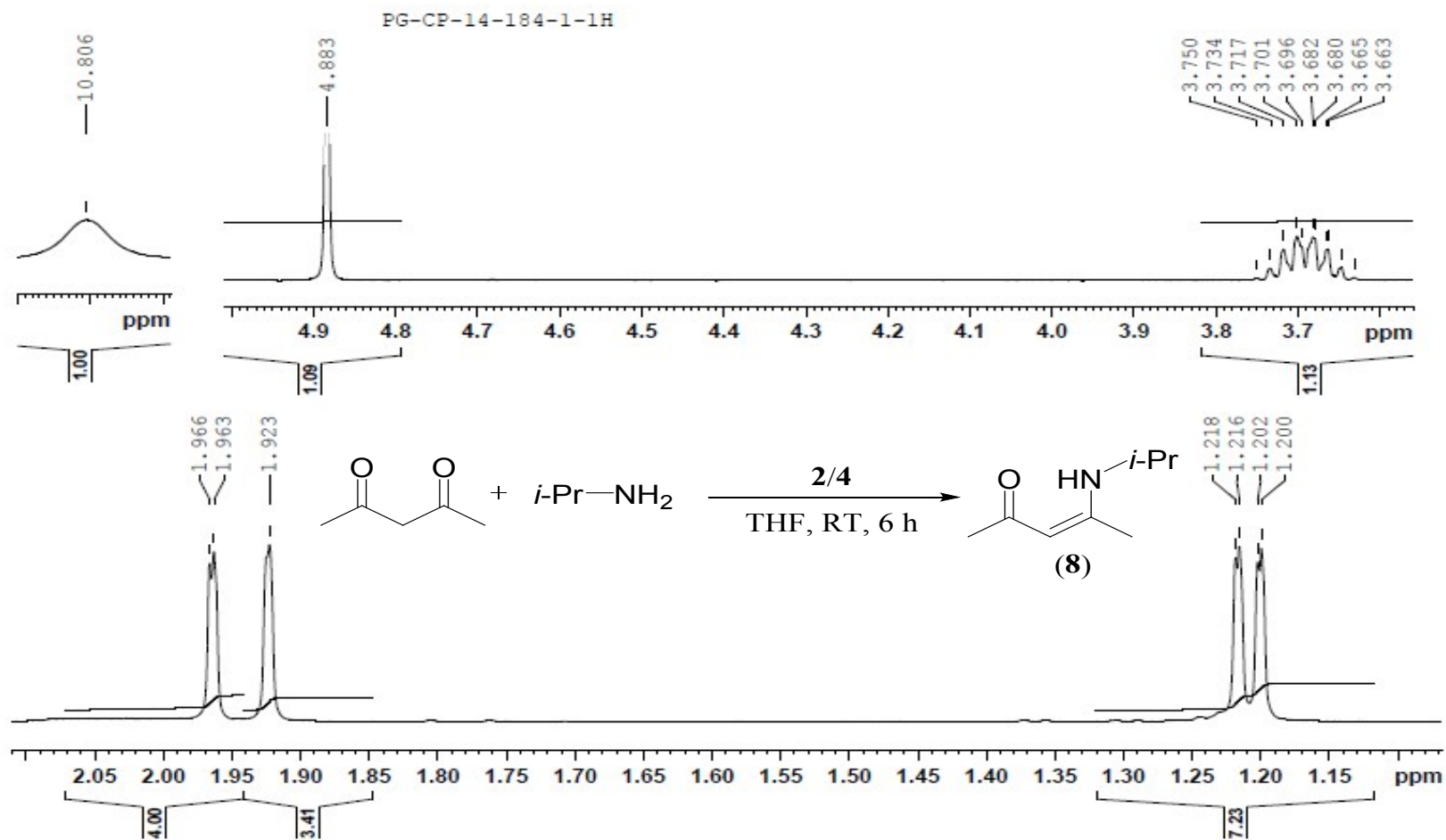


Fig. S34 Expanded ^1H NMR spectrum of **8** in CDCl_3 formed in the reaction of acetyl acetone and *i*-propyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

PG-CP-14-184-1-13C

```

Current Data Parameters
NAME      PG-CP-14-184-1-13C
EXPNO     4
PROCNO    1
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F2 - Acquisition Parameters
Date_     20171222
Time      8.18
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         66
DS         4
SWH        26041.666 Hz
FIDRES     0.397364 Hz
AQ         1.2582912 sec
RG         2050
DM         19.200 usec
DE         6.50 usec
TE         298.5 K
D1         1.0000000 sec
D11        0.0300000 sec
TD0        1
-----
CHANNEL f1
NUC1       13C
P1         8.50 usec
PL1        -2.00 dB
PL1W       56.53121948 W
SFO1       100.6238364 MHz
-----
CHANNEL f2
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        -1.00 dB
PL12       13.69 dB
PL13       14.50 dB
PL2W      10.56200695 W
PL12W     0.35871249 W
PL13W     0.29767781 W
SFO2       400.1316005 MHz
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F2 - Processing parameters
SI         32768
SF         100.6127453 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
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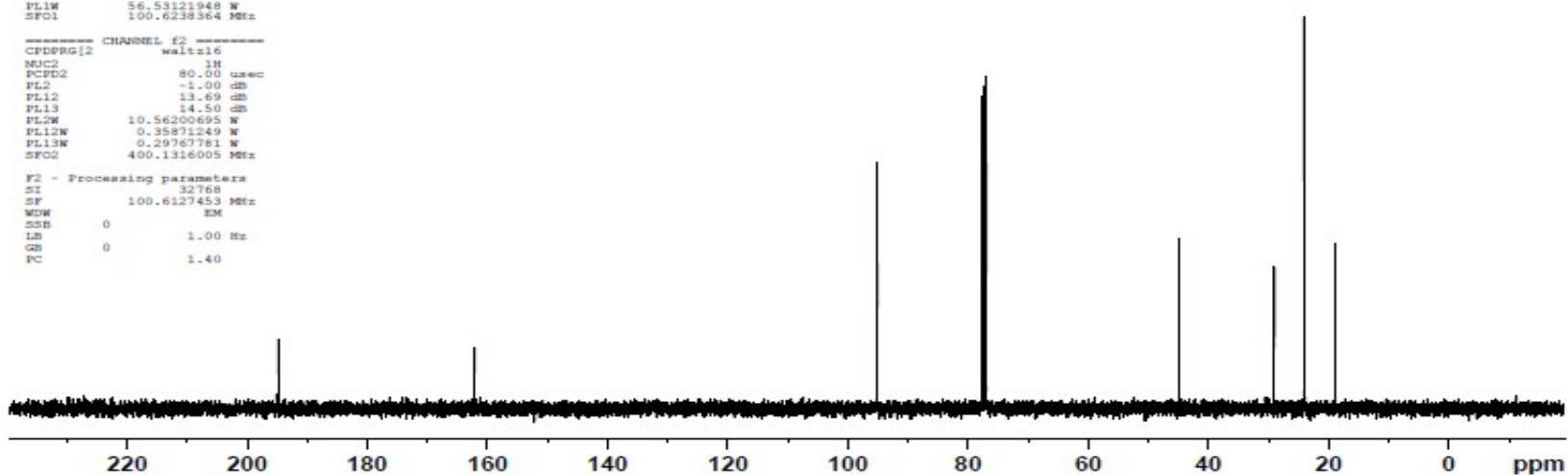
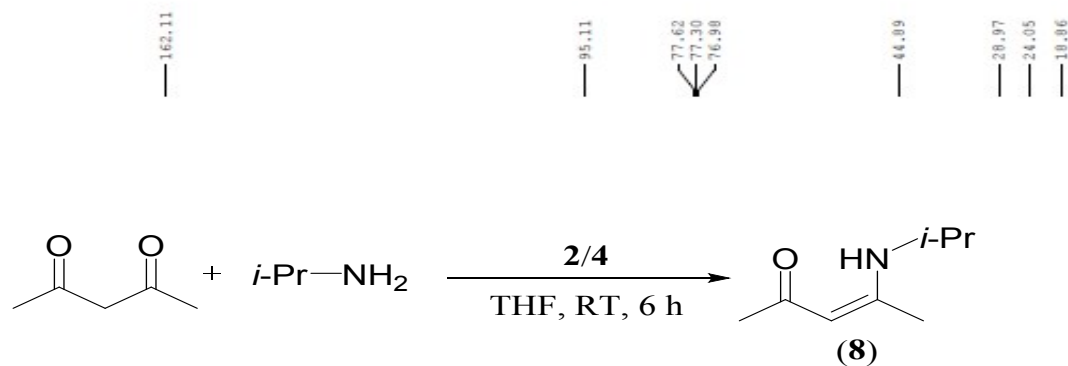


Fig. S35 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3 formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear $[\text{CoL1}]_2$ (**2**) and $[\text{CoL2}]_2$ (**4**) complexes.

File : F:\GCMSDATA2017\DECEMBER-2017\PG-CP-14-184-1.D
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Instrument : GCMS
Sample Name: PG-CP-14-184-1
Misc Info :
Vial Number: 2

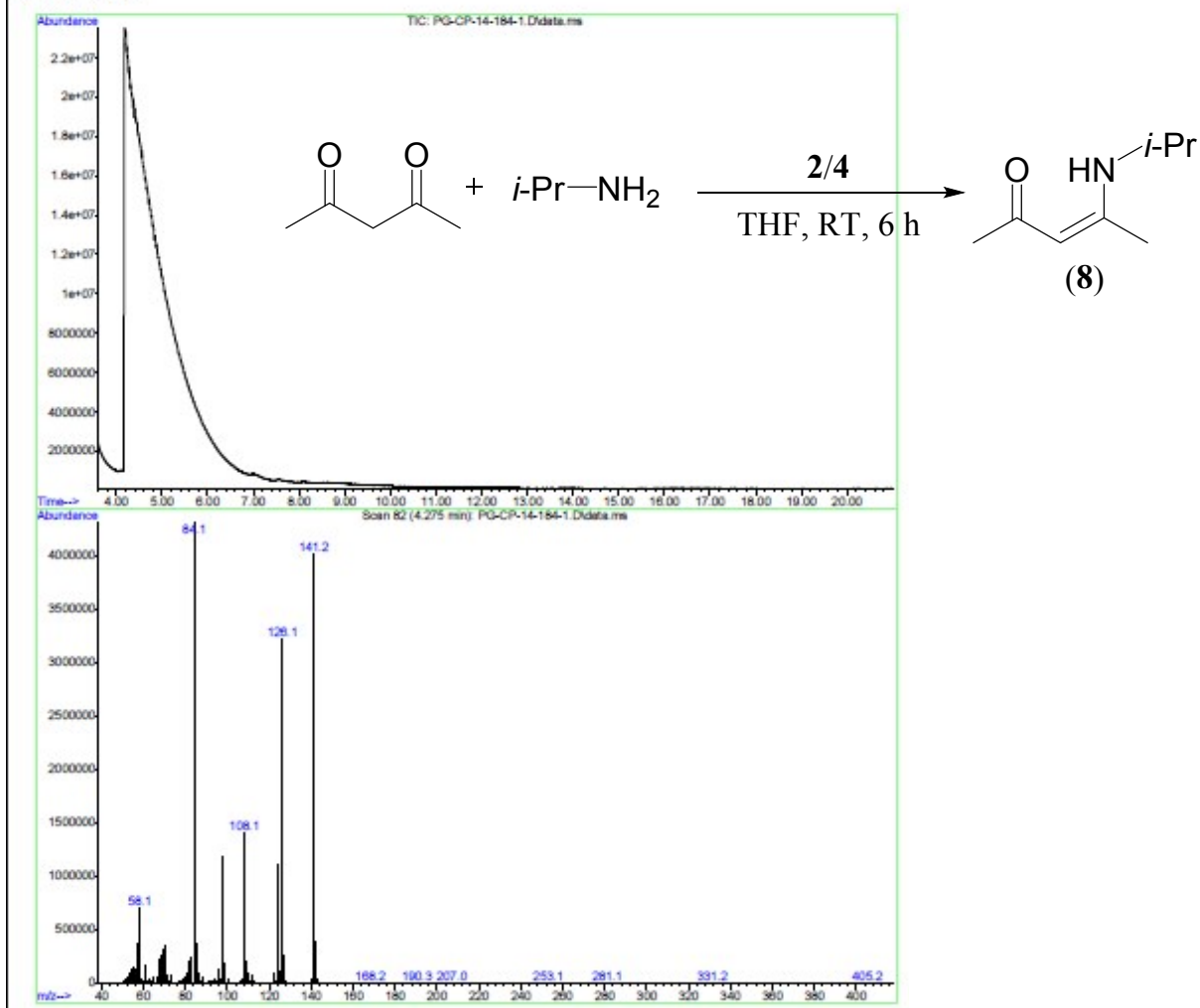


Fig. S36 GCMS trace of **8** (m/z 141) in EtOAc formed in the reaction of acetyl acetone and *i*-propyl amine as catalyzed by the the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

```

Current Data Parameters
NAME PG-CP-14-182-1-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 8.09
INSTRUM spect
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PULPROG zg30
TD 84274
SOLVENT CDCl3
NS 11
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 32
LW 60.800 usec
DE 6.80 usec
TE 296.0 K
DL 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
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P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 0.30 Hz
GB 0
FC 1.00

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PG-CP-14-182-1-1H

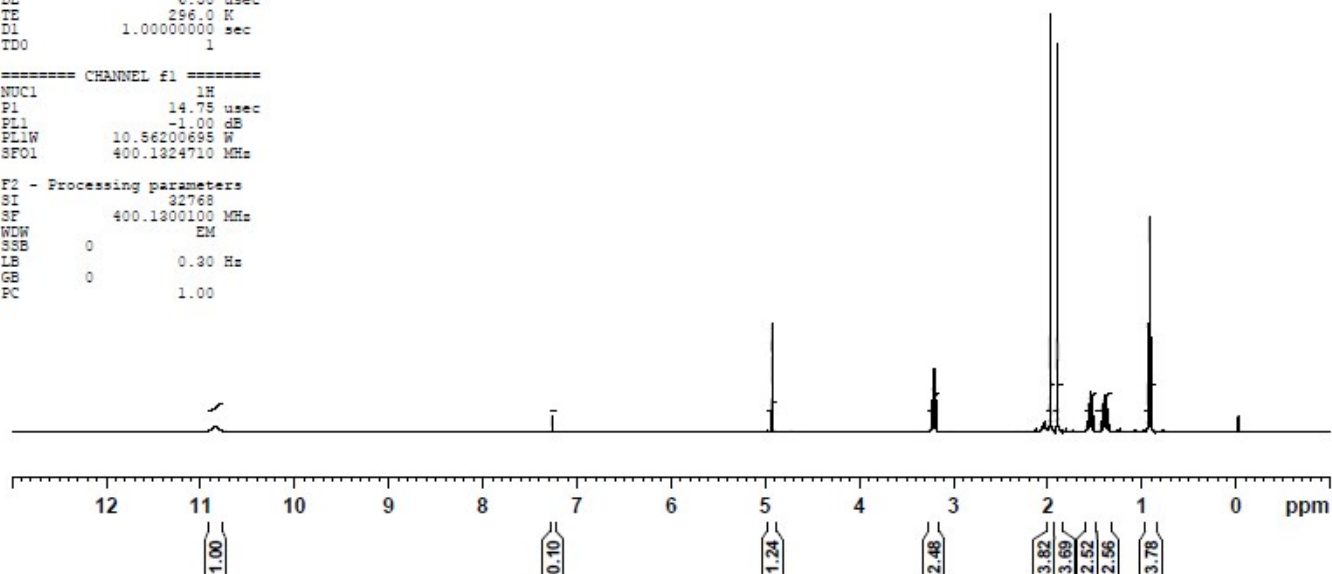
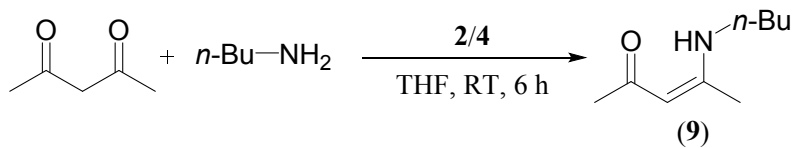


Fig. S37 ^1H NMR spectrum of **9** in CDCl_3 formed in the reaction of acetyl acetone and n -butyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

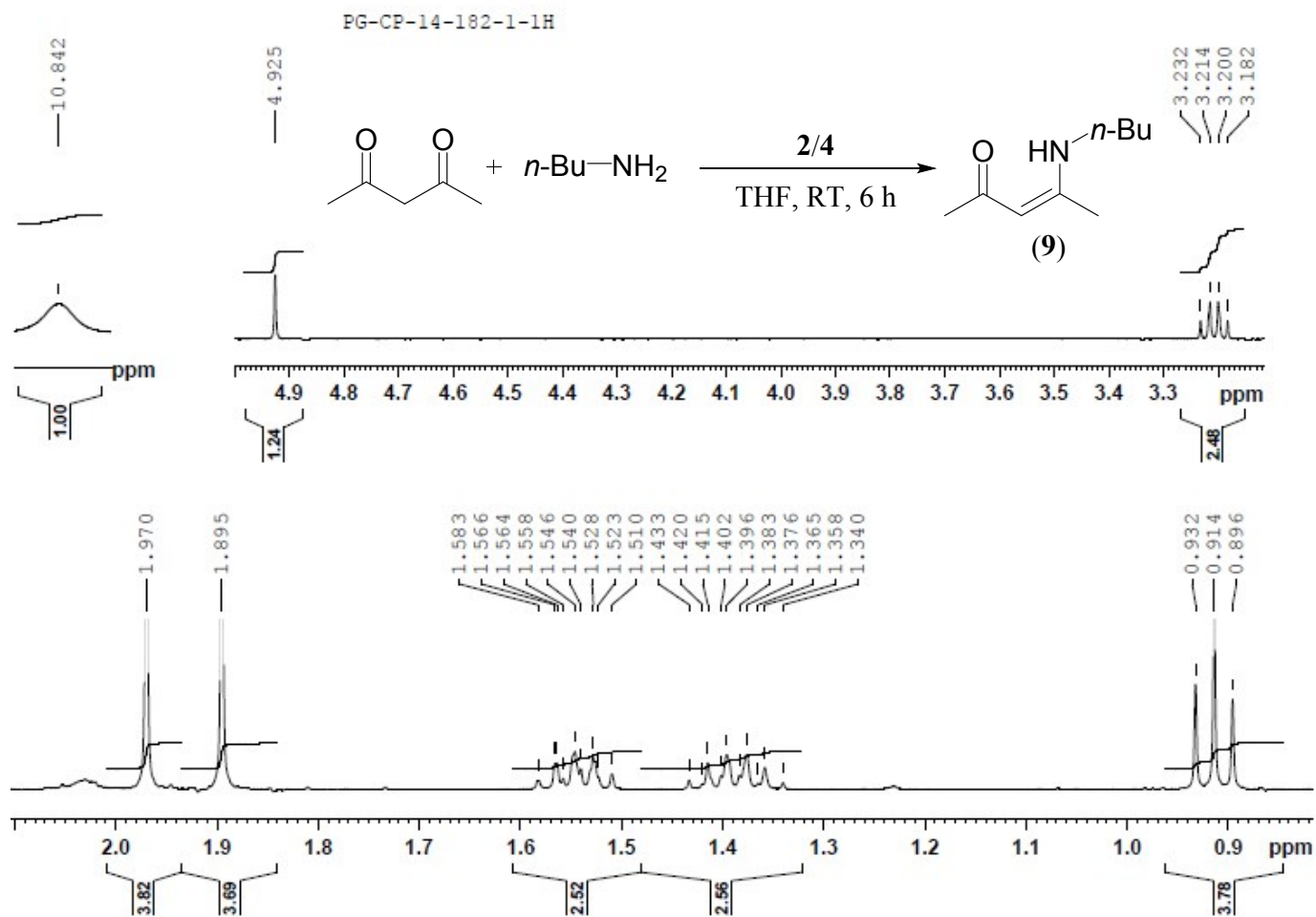


Fig. S38 Expanded ^1H NMR spectrum of **9** in CDCl_3 formed in the reaction of acetyl acetone and n -butyl amine as catalyzed by the dinuclear $[\text{CoL1}]_2$ (**2**) and $[\text{CoL2}]_2$ (**4**) complexes.

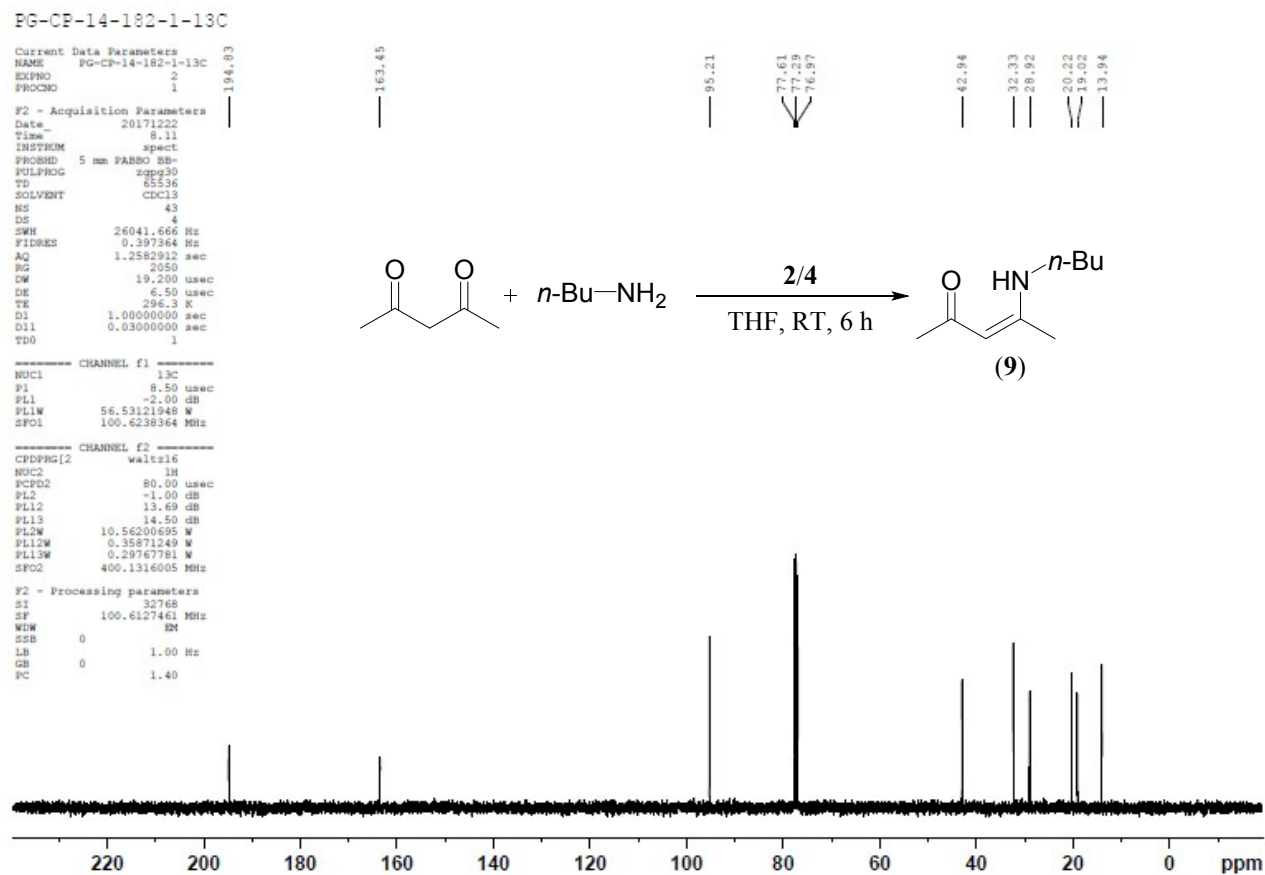


Fig. S39 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3 formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

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Instrument : GCMS
Sample Name: PG-CP-14-182-1
Misc Info :
Vial Number: 1

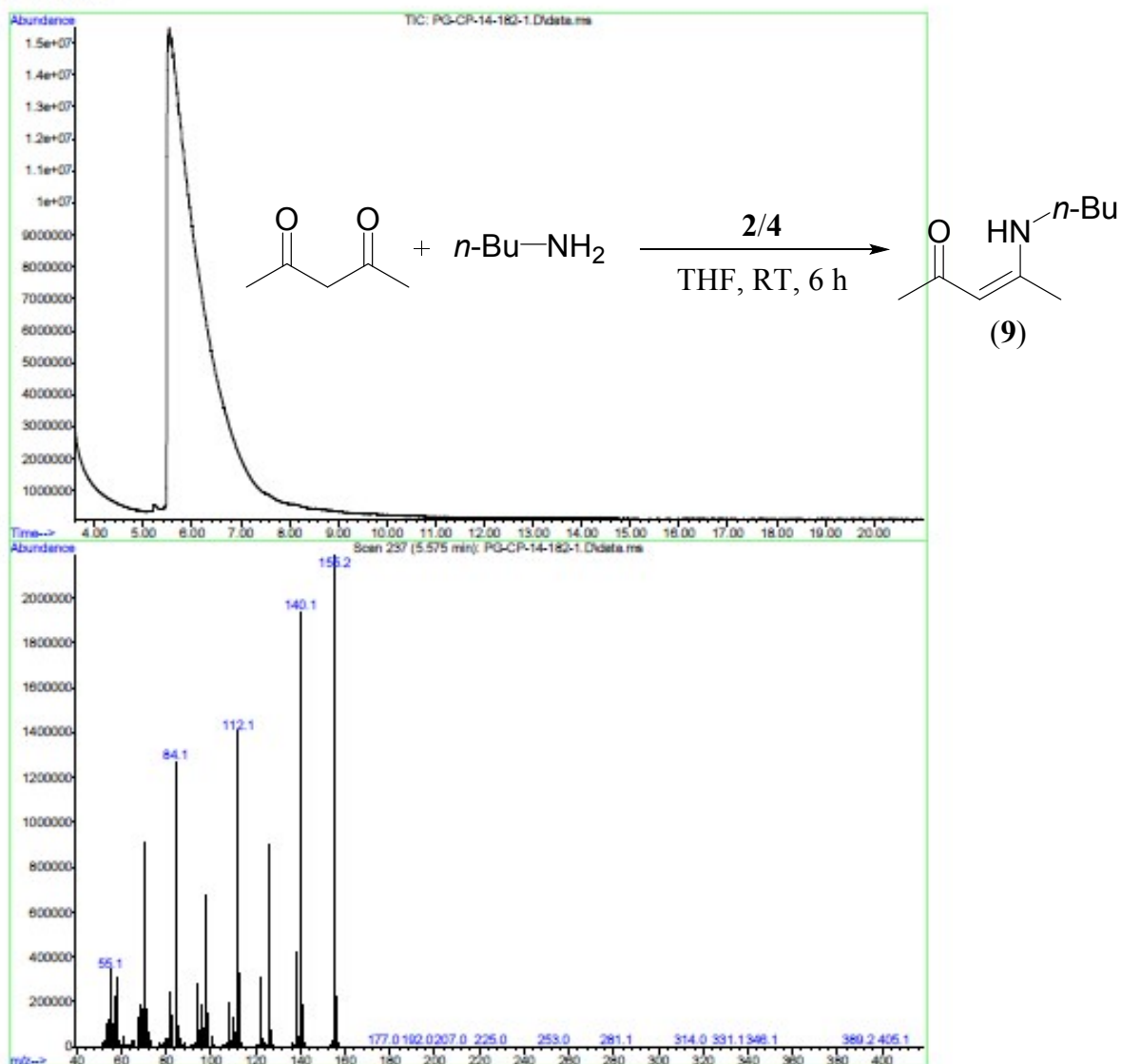


Fig. S40 GCMS trace of **9** (m/z 155) in EtOAc formed in the reaction of acetyl acetone and *n*-butyl amine as catalyzed by the the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

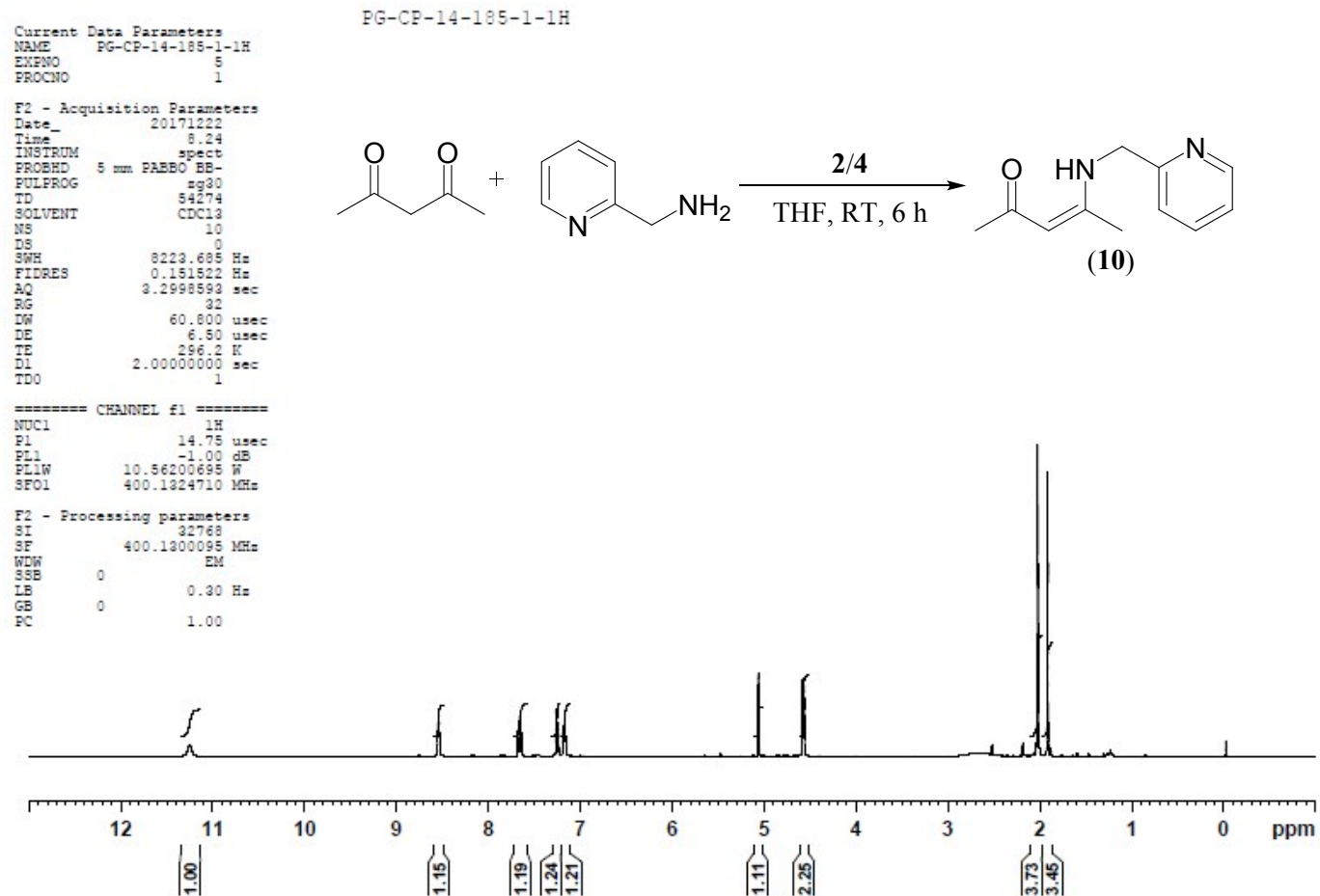


Fig. S41 ^1H NMR spectrum of **10** in CDCl_3 formed in the reaction of acetyl acetone and 2-picolyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

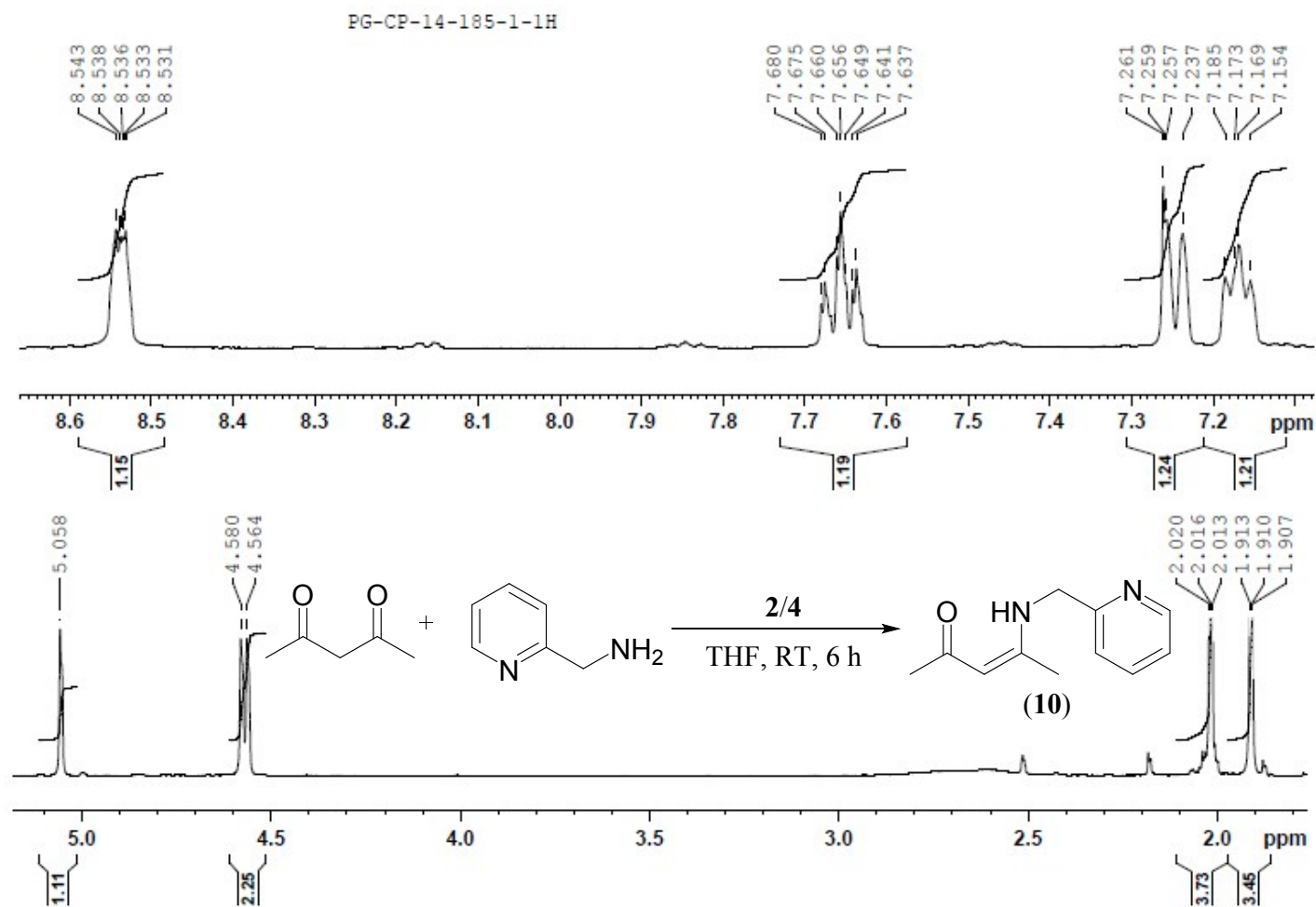


Fig. S42 Expanded ^1H NMR spectrum of **10** in CDCl_3 formed in the reaction of acetyl acetone and 2-picolyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

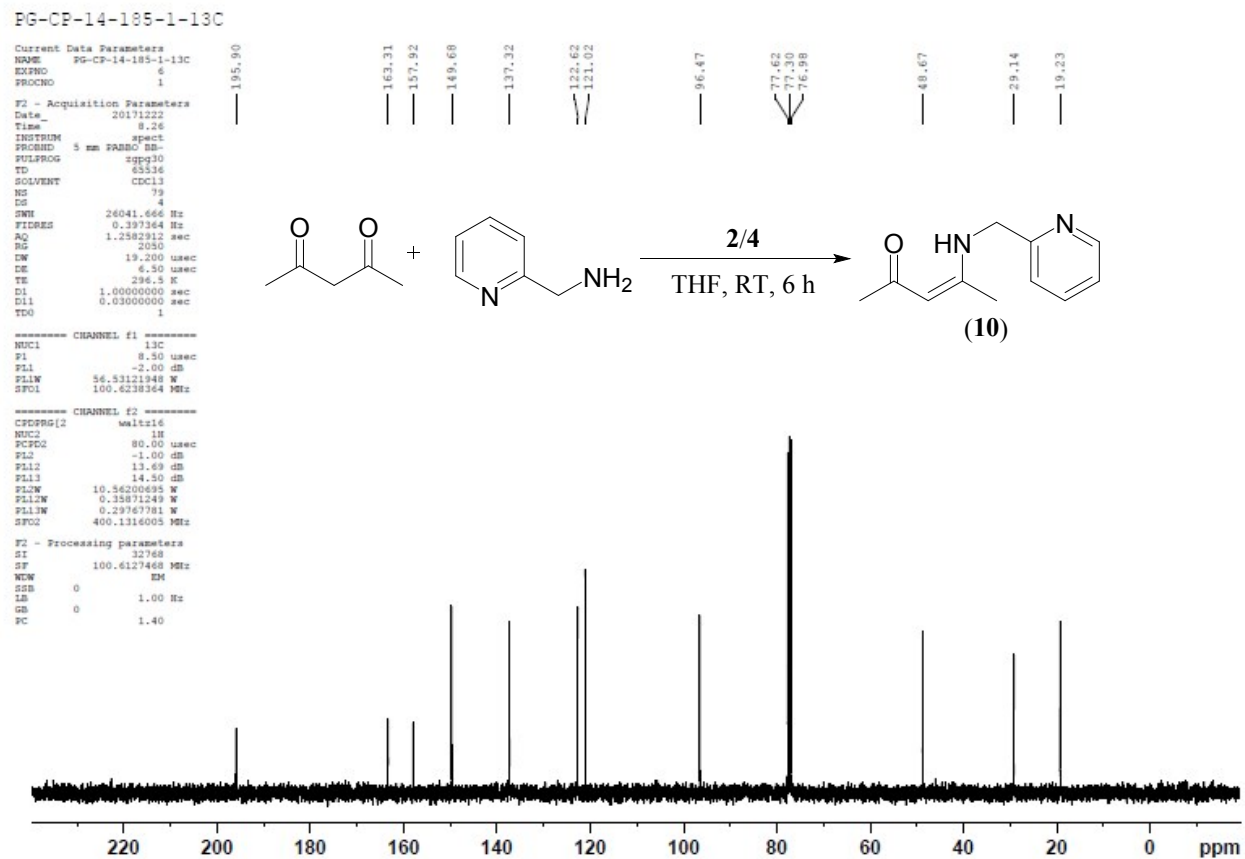


Fig. S43 ¹³C{¹H} NMR spectrum of **10** in CDCl₃ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

File : F:\GCMSDATA2017\DECEMBER-2017\PG-CP-14-185-1.D
Operator :
Acquired : 19 Dec 2017 23:25 using AcqMethod COMMON METHOD-2017.M
Instrument : GCMS
Sample Name : PG-CP-14-185-1
Disc Info :
Vial Number : 3

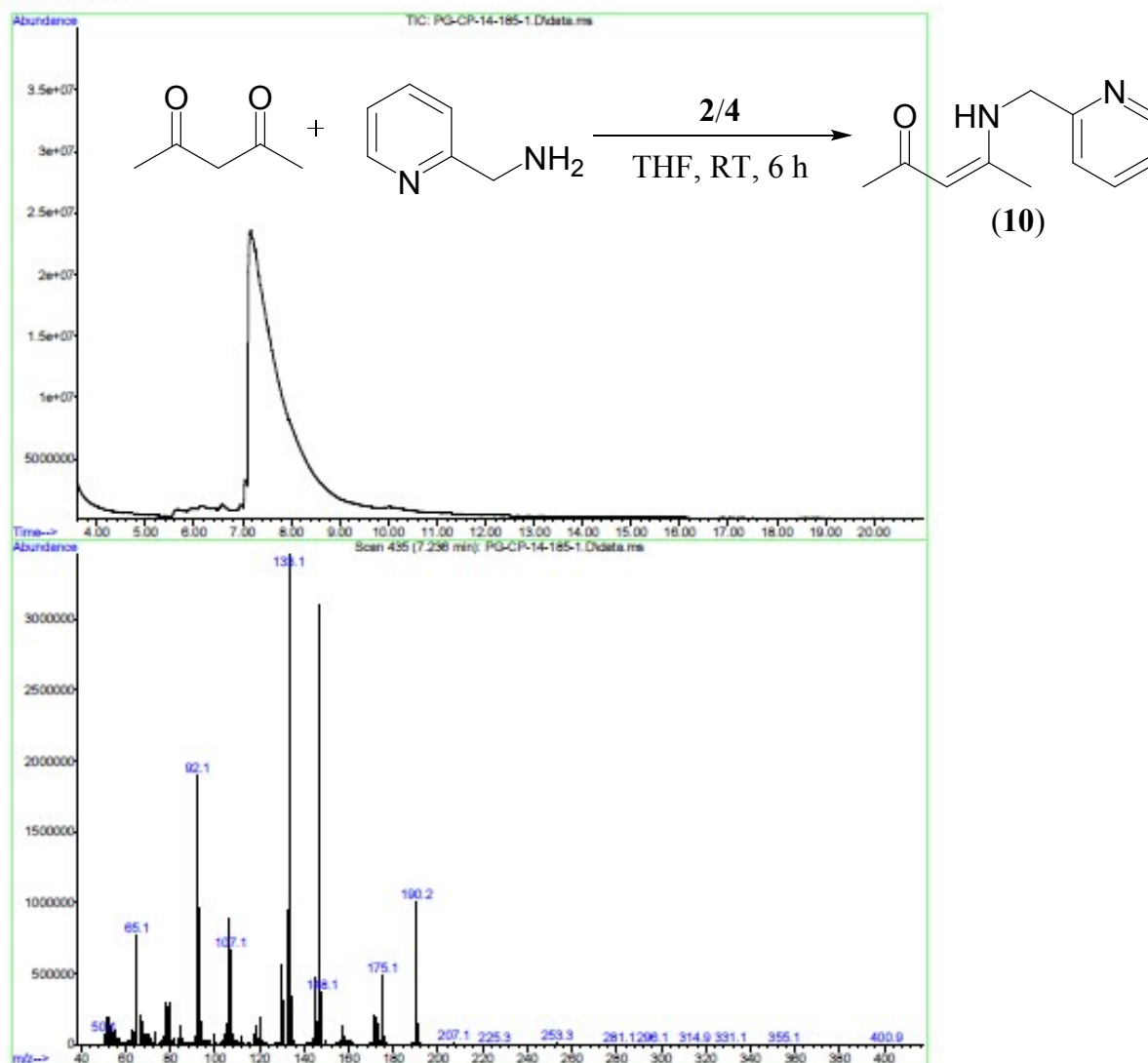


Fig.S44 GCMS trace of **10** (m/z 190) in EtOAc formed in the reaction of acetyl acetone and 2-picolyl amine as catalyzed by the the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

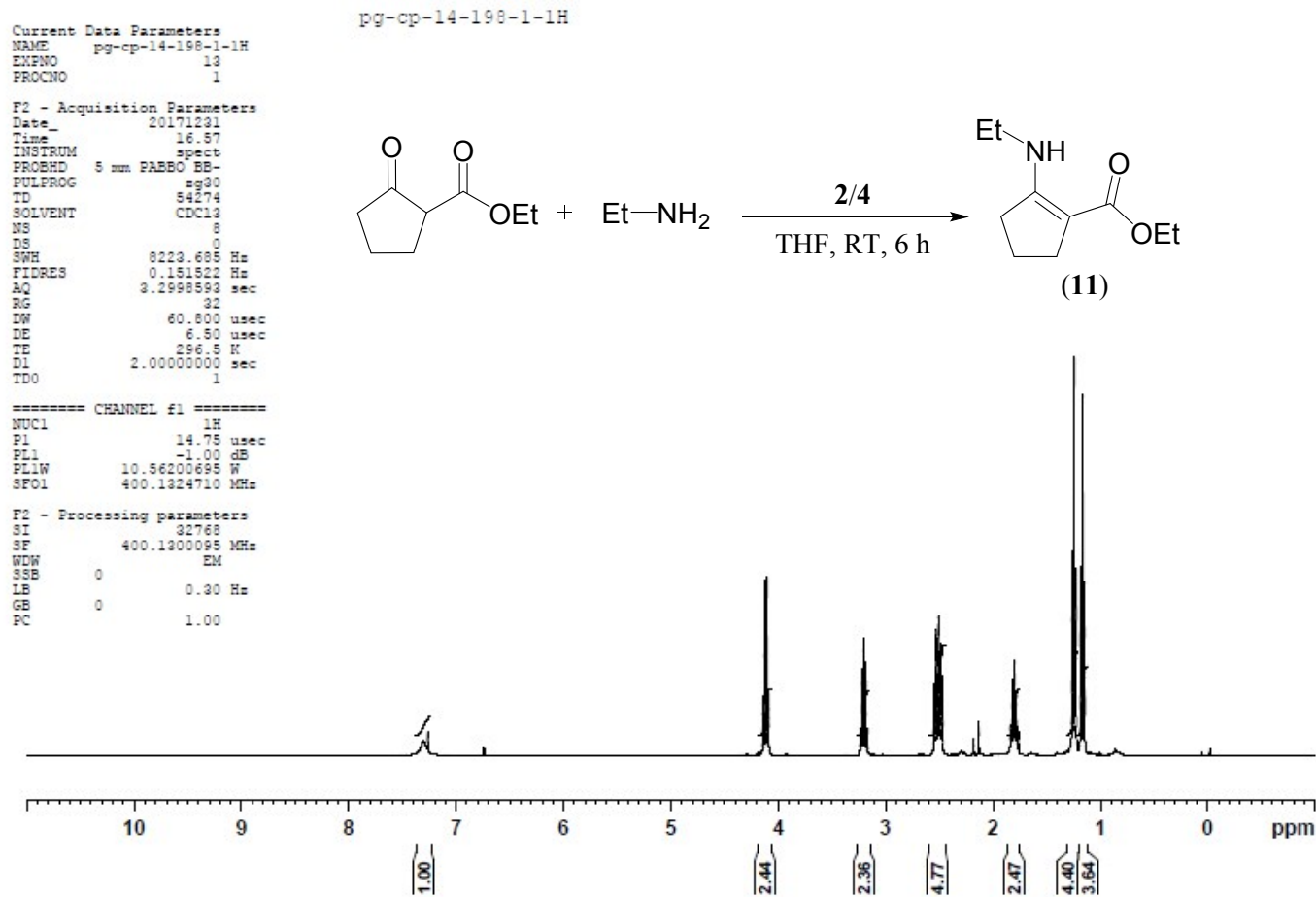


Fig. S45 ^1H NMR spectrum of **11** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

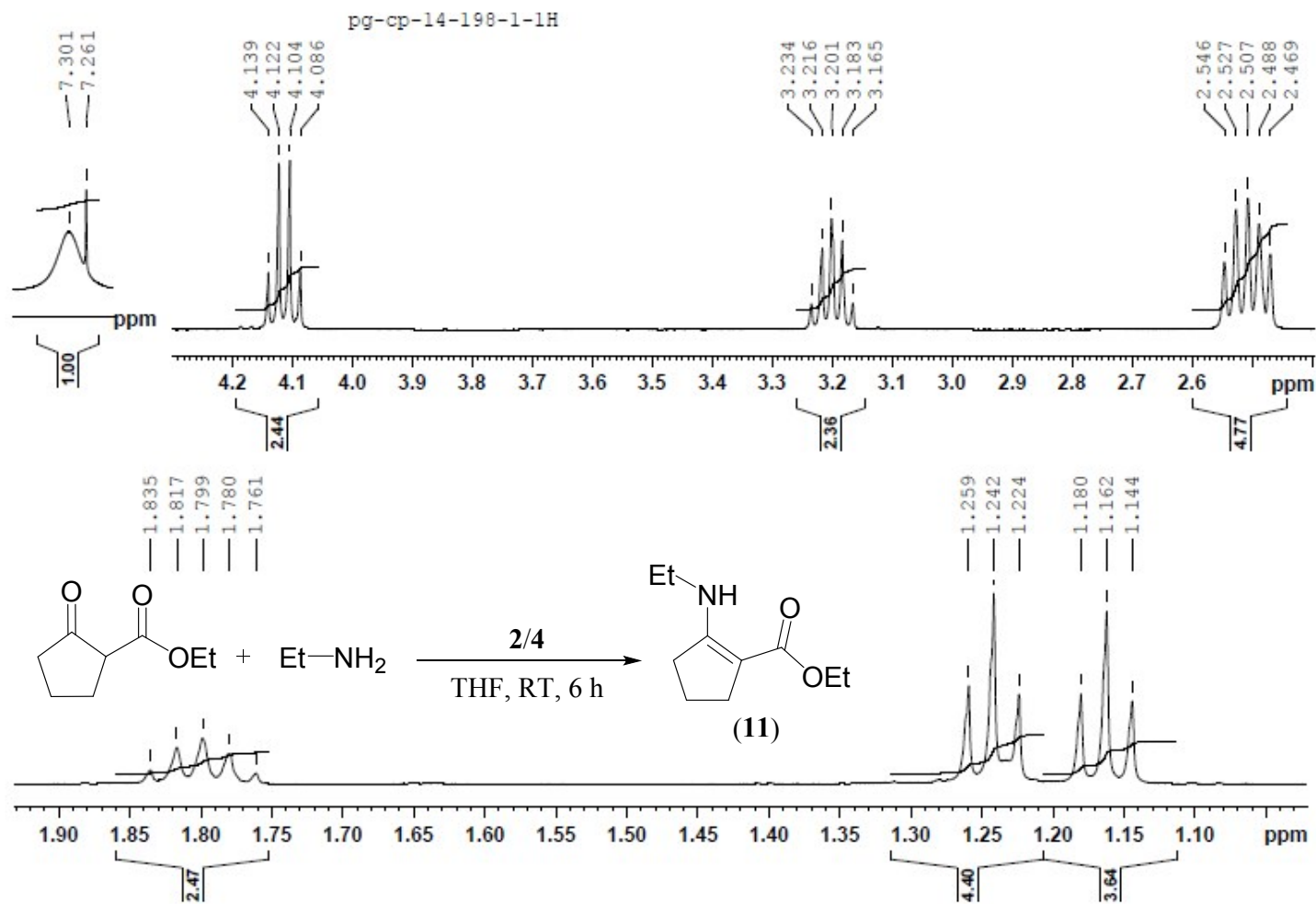


Fig. S46 Expanded ^1H NMR spectrum of **11** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

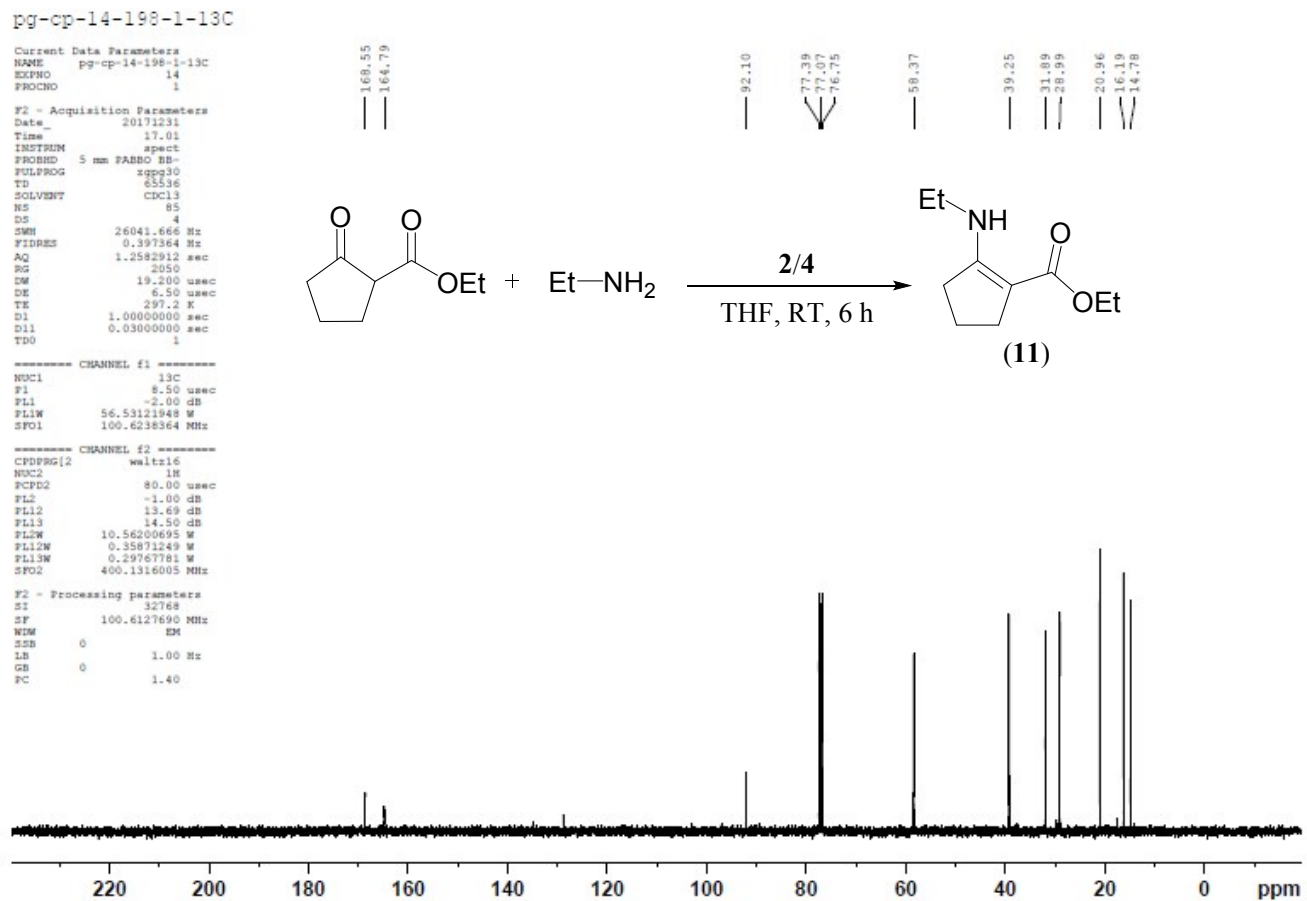


Fig. S47 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **11** in CDCl_3 formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

File : F:\GCMSDATA2017\DECEMBER-2017\PG-CP-14-198-2.D
 Operator : MSB
 Acquired : 30 Dec 2017 12:12 using AcqMethod COMMON METHOD-2017.M
 Instrument : GCMS
 Sample Name : PG-CP-14-198-2
 Misc Info :
 Vial Number : 4

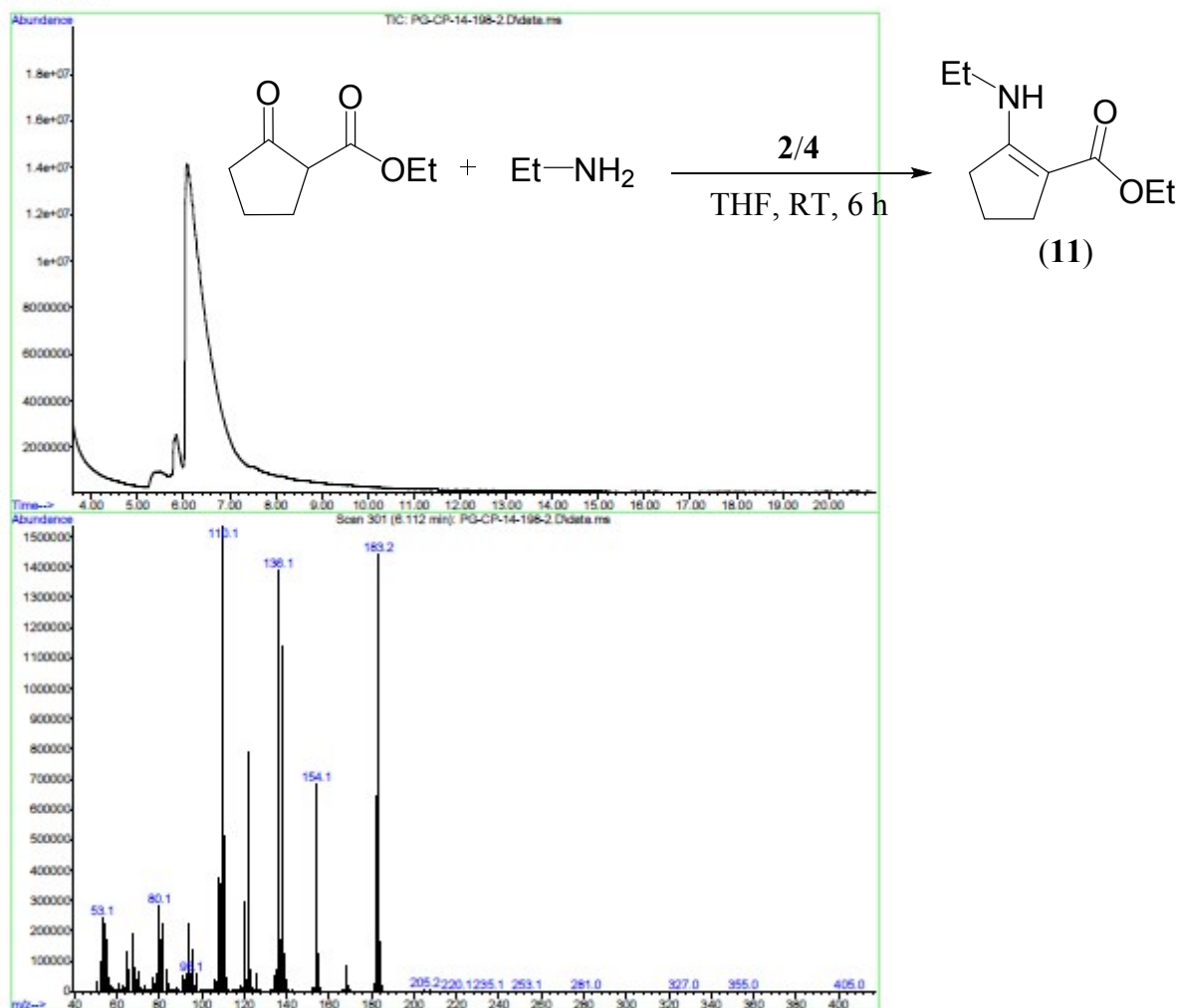


Fig. S48 GCMS trace of **11** (m/z 183) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

Eager 300 Report

Page: 1 Sample: PG-CP-14-198-1 (PG-CP-14-198-1)

Method Name : PGCP30122017

Method File : D:\CHNS-2017\PGCP30122017.mth

Chromatogram : PG-CP-14-198-1

Operator ID : CHANDNI

Analysed : 12/30/2017 19:02

Sample ID : PG-CP-14-198-1 (# 14)

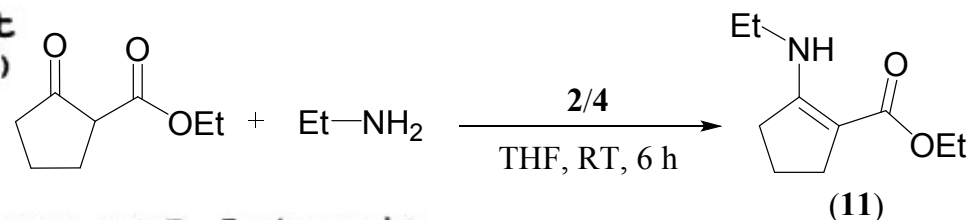
Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments

Printed : 12/31/2017 22:03

Instrument N. : Instrument #1

Sample weight : 1.068



Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	2	135514	RS		0.0000
Nitrogen	7.0577	41	81682	RS	22.042400	.108364E+07
Carbon	64.8684	63	1800456	RS	1.000000	.259525E+07
Hydrogen	9.1551	184	650466	RS	2.767948	.665260E+07
Totals	81.0812		2668118			

Fig.S49 Elemental analysis data of **11** formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

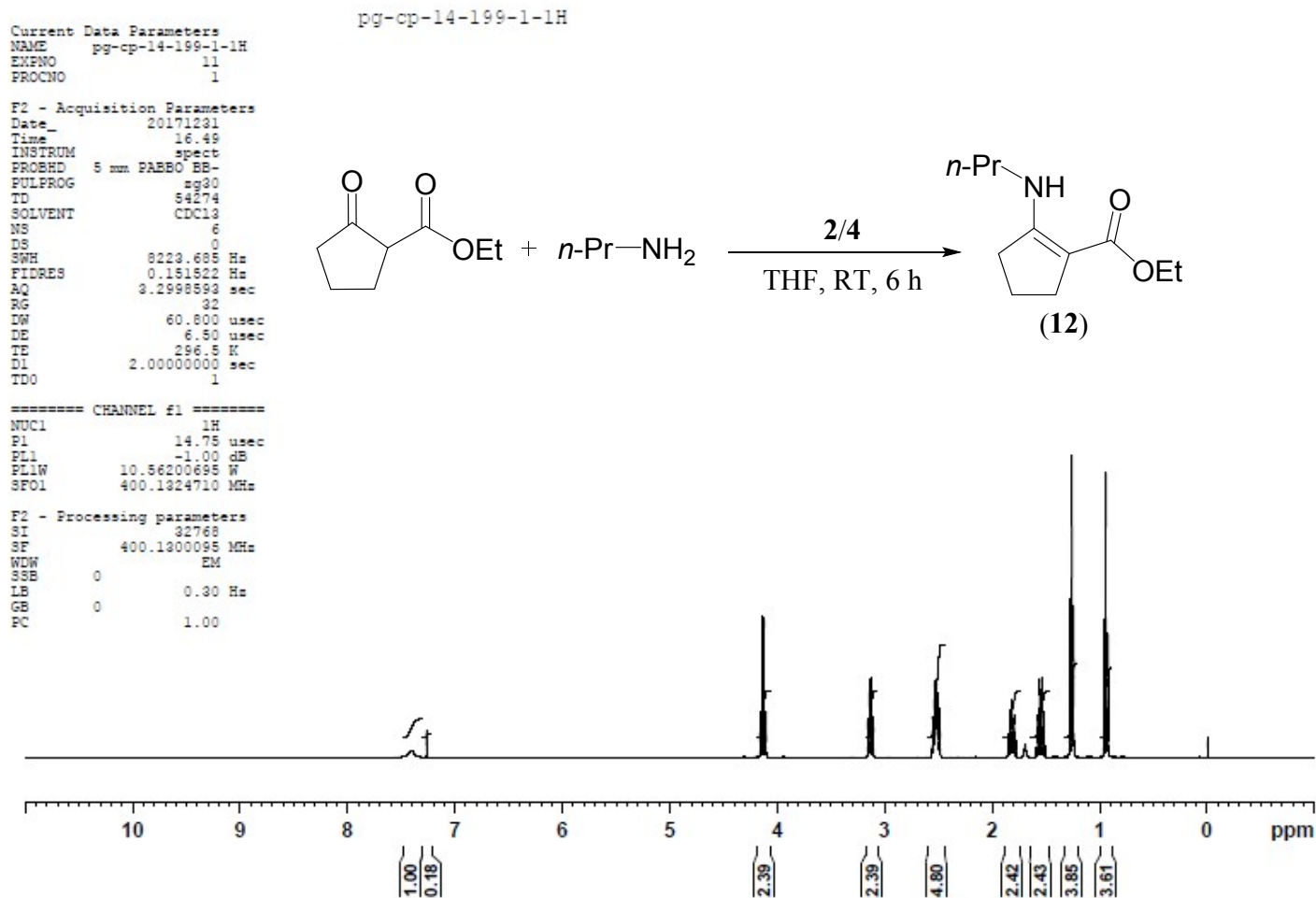


Fig.S50 ^1H NMR spectrum of **12** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-propyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

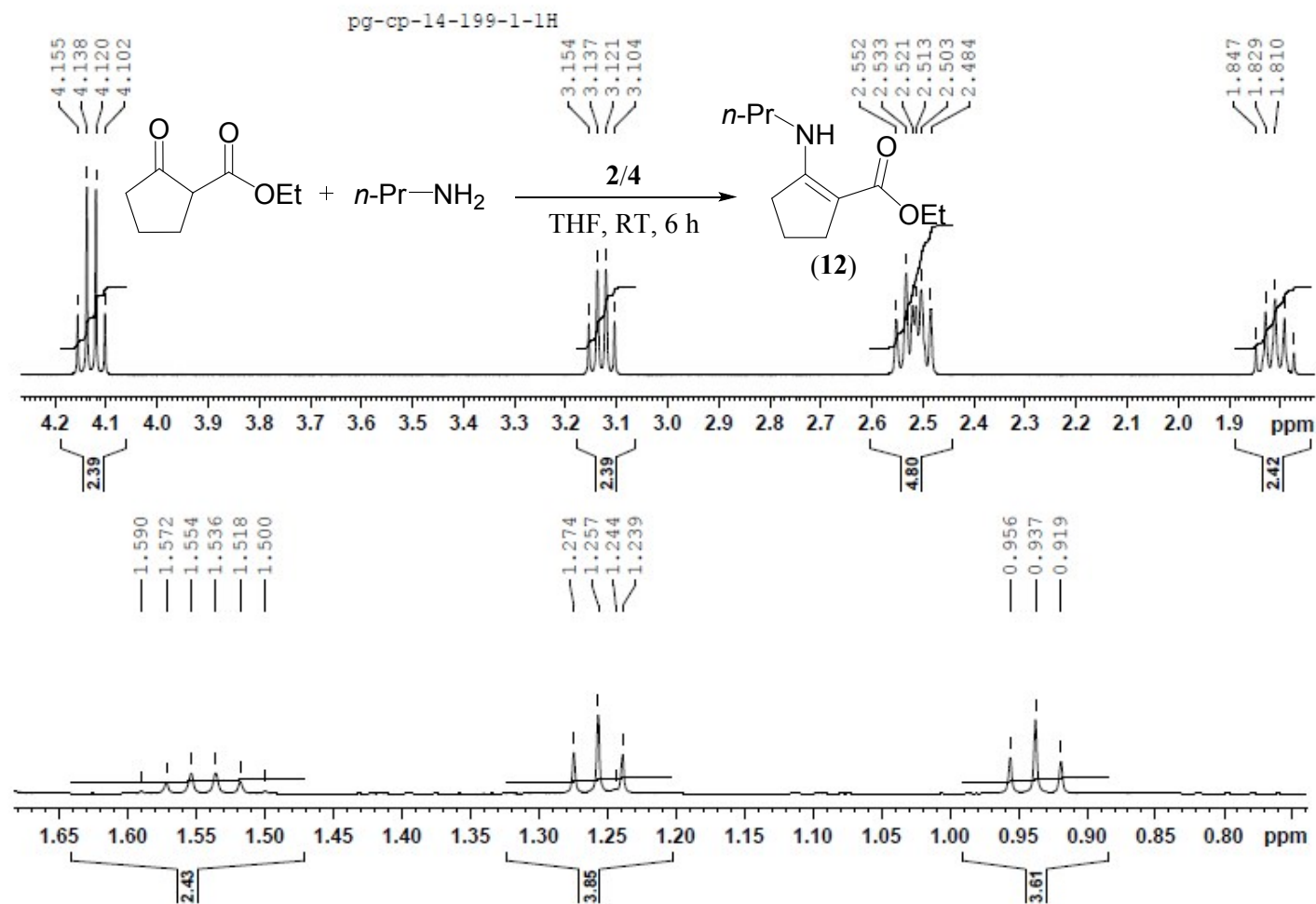


Fig. S51 Expanded ¹H NMR spectrum of **12** in CDCl₃ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-propyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

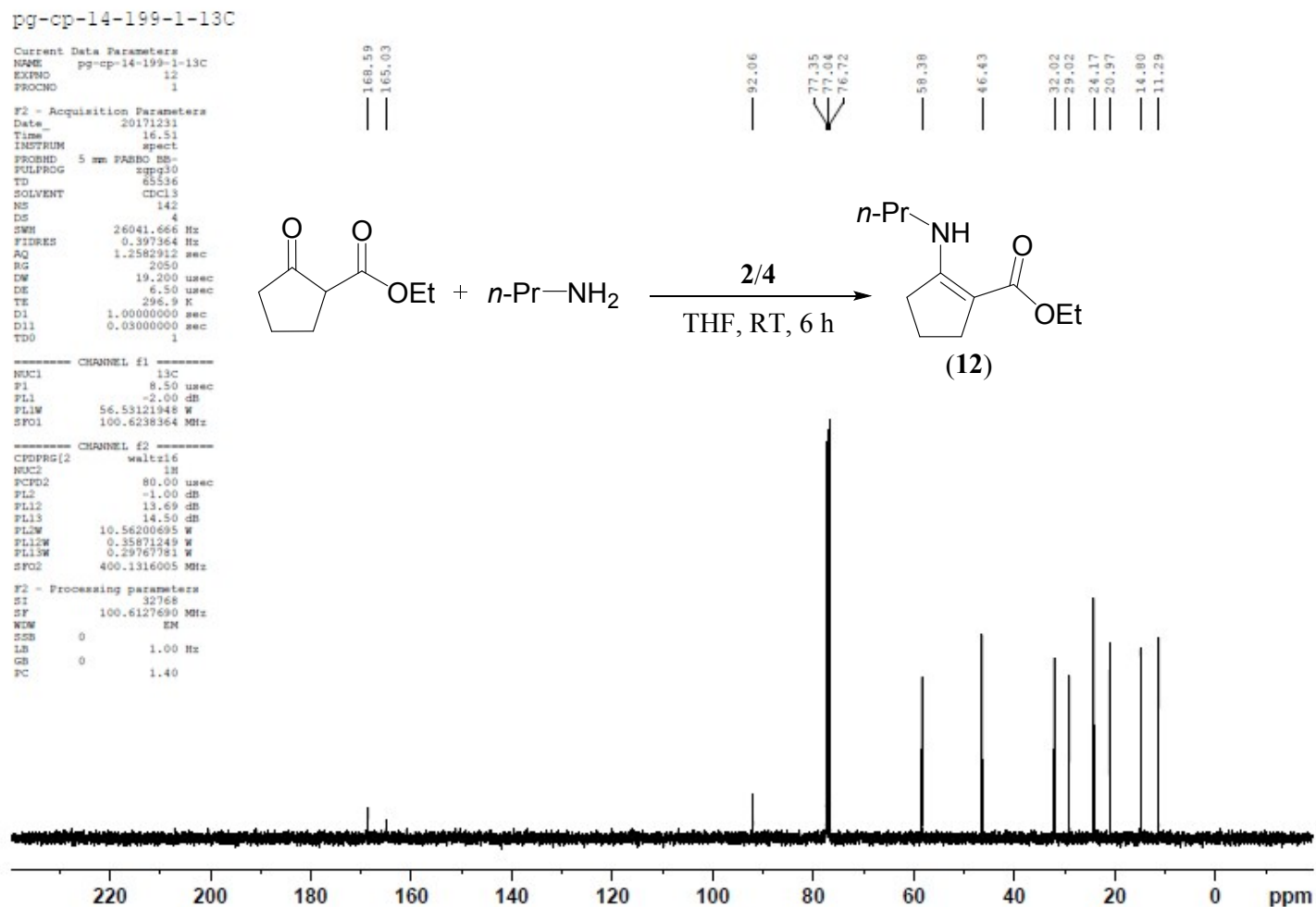


Fig. S52 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **12** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-propyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

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 Instrument : GCMS
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 Misc Info :
 Vial Number: 2

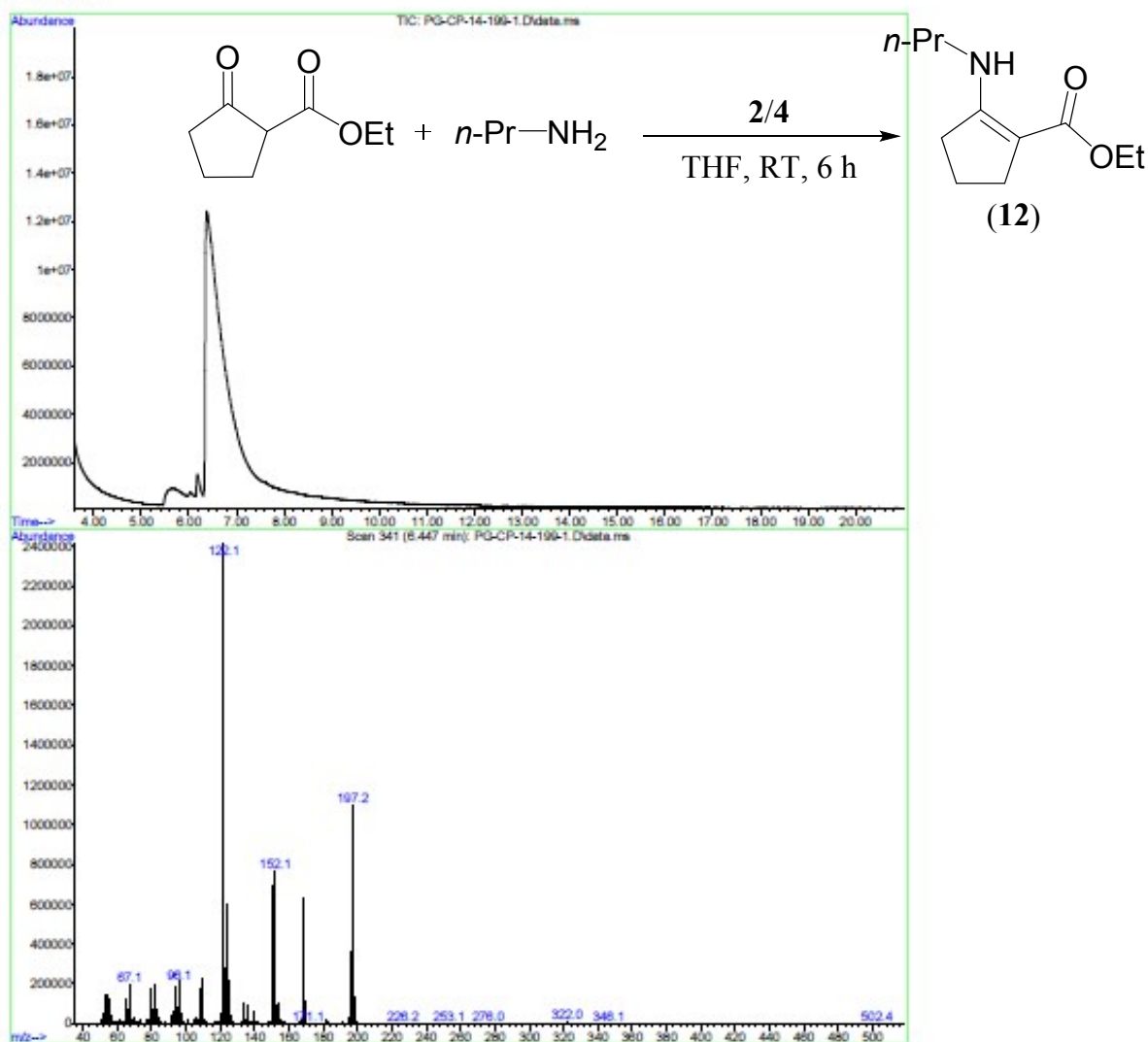


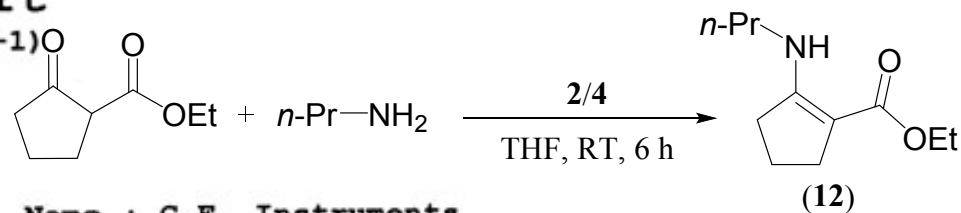
Fig. S53 GCMS trace of **12** (*m/z* 197) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-propyl amine as catalyzed by the the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

Eager 300 Report

Page: 1 Sample: PG-CP-14-199-1 (PG-CP-14-199-1)

Method Name : PGCP30122017
 Method File : D:\CHNS-2017\PGCP30122017.mth
 Chromatogram : PG-CP-14-199-1
 Operator ID : CHANDNI
 Analysed : 12/30/2017 18:42
 Sample ID : PG-CP-14-199-1 (# 12)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 12/31/2017 22:04
 Instrument N. : Instrument #1
 Sample weight : 2.013



Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	2	135395	RS		0.0000
Nitrogen	6.9002	42	150520	RS	23.062270	.108364E+07
Carbon	66.3992	62	3471333	RS	1.000000	.259525E+07
Hydrogen	10.0655	211	1347941	RS	2.575286	.665260E+07
Totals	83.3650		5105189			

Fig. S54 Elemental analysis data of **12** formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-propyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

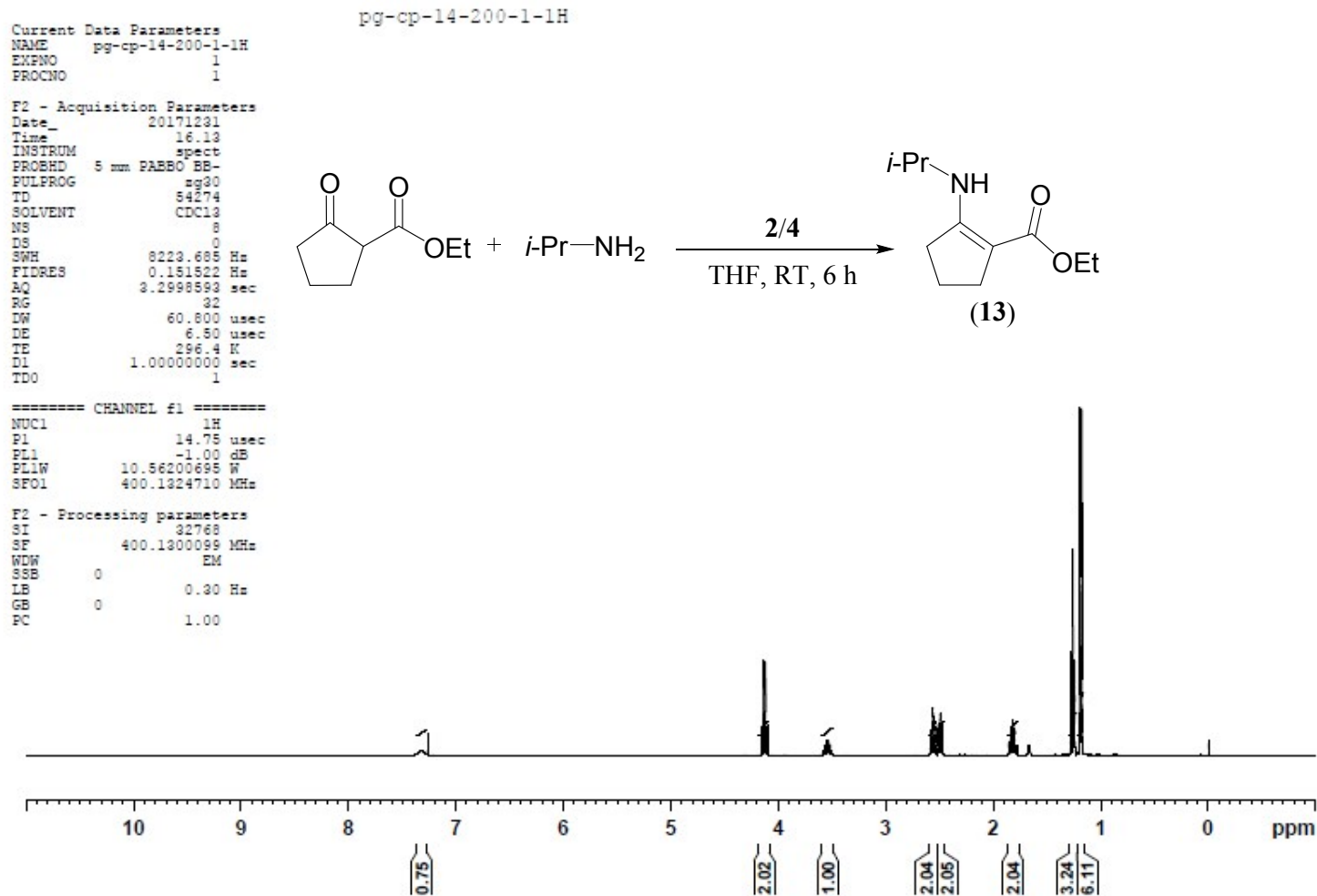


Fig. S55 ^1H NMR spectrum of **13** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *i*-propyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

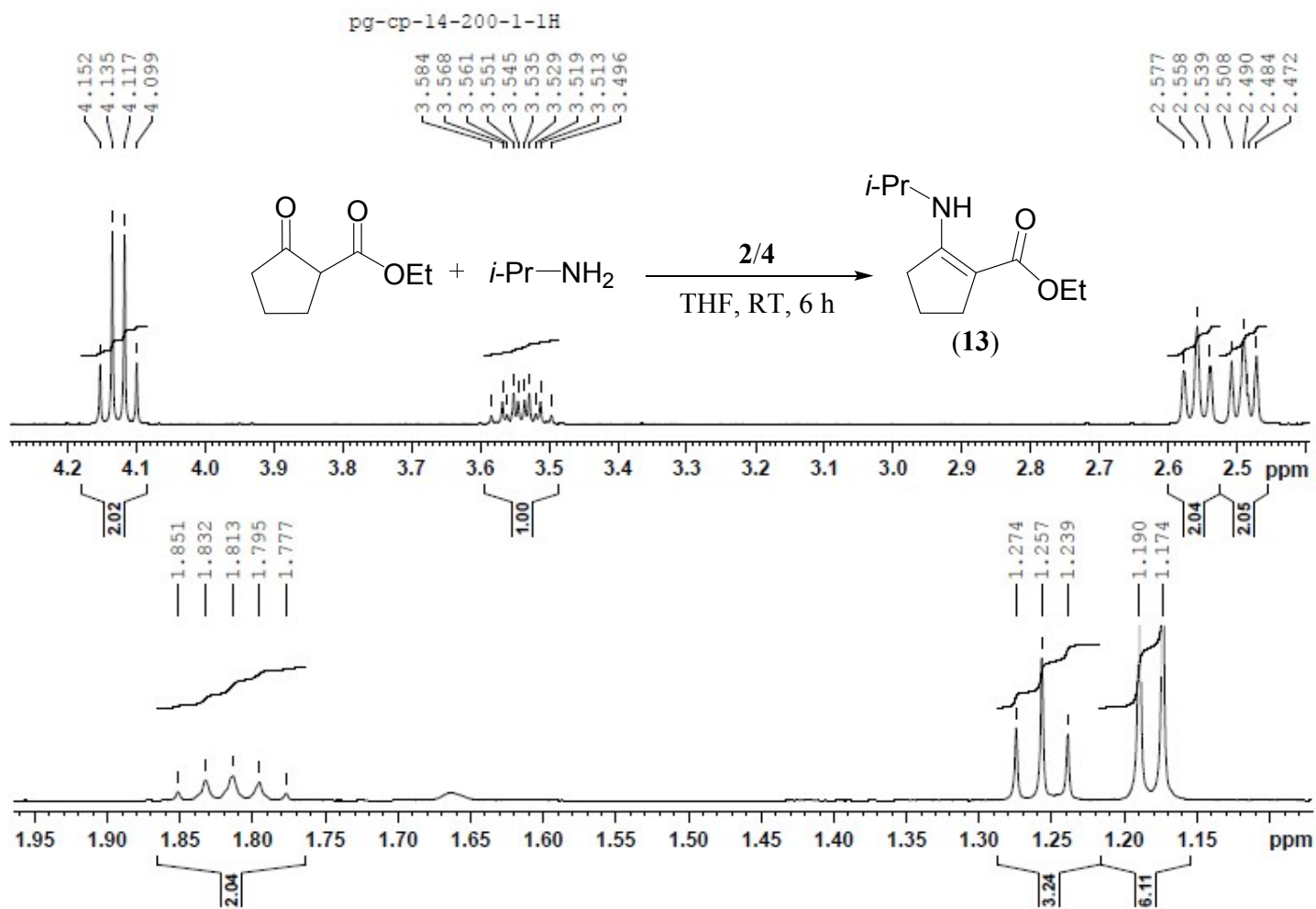


Fig. S56 Expanded ^1H NMR spectrum of **13** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *i*-propyl amine as catalyzed by the dinuclear $[\text{CoL1}]_2$ (**2**) and $[\text{CoL2}]_2$ (**4**) complexes.

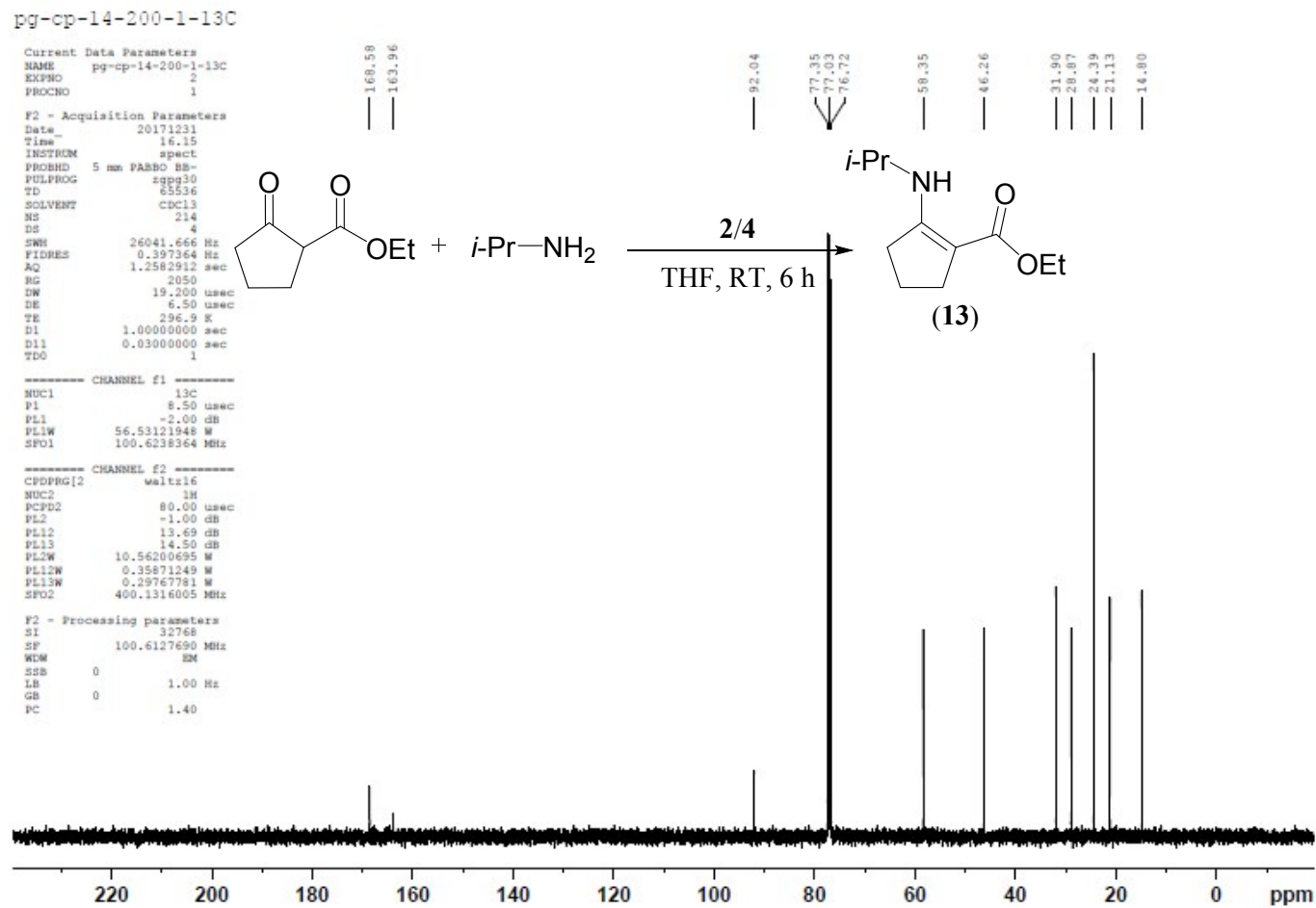


Fig. S57 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **13** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *i*-propyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

File : F:\GCMSDATA2017\DECEMBER-2017\PG-CP-14-200-1.D
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 Sample Name : PG-CP-14-200-1
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 Vial Number : 3

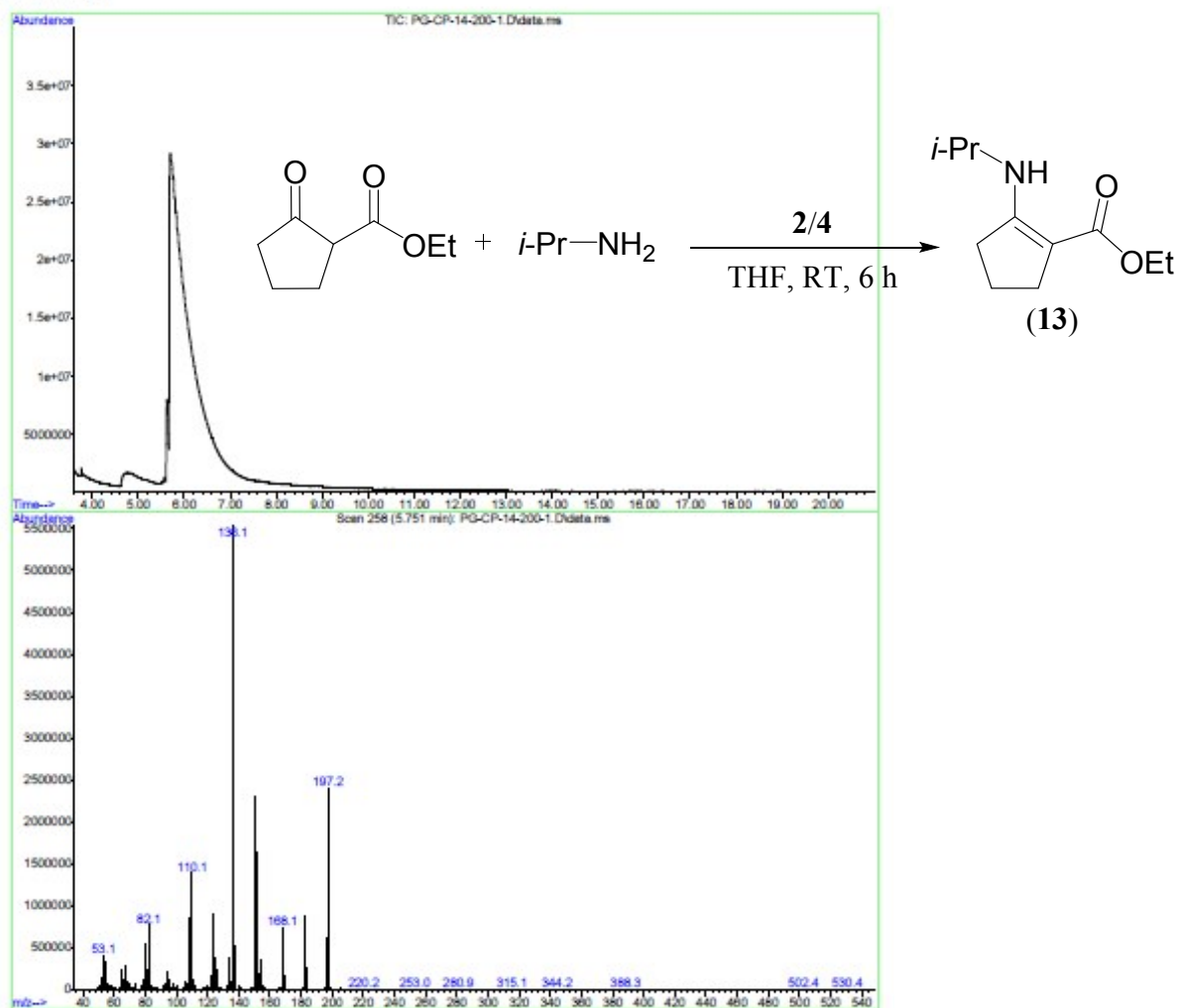


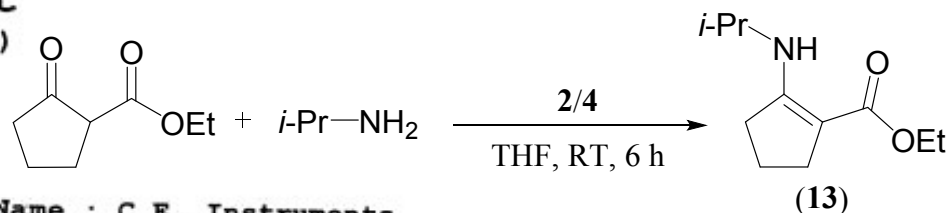
Fig. S58 GCMS trace of **13** (m/z 197) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *i*-propyl amine as catalyzed by the the dinuclear [CoL1]**2** (**2**) and [CoL2]**2** (**4**) complexes.

Eager 300 Report

Page: 1 Sample: PG-CP-14-200-2 (PG-CP-14-200-2)

Method Name : PGCP30122017
 Method File : D:\CHNS-2017\PGCP30122017.mth
 Chromatogram : PG-CP-14-200-2
 Operator ID : CHANDNI
 Analysed : 12/30/2017 18:52
 Sample ID : PG-CP-14-200-2 (# 13)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 12/31/2017 22:05
 Instrument N. : Instrument #1
 Sample weight : 1.767



Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret. Time	Area	BC	Area ratio	K factor
Nitrogen	6.8667	41	131484	RS	23.114010	.108364E+07
Carbon	66.2180	62	3039112	RS	1.000000	.259525E+07
Hydrogen	10.1263	202	1190365	RS	2.553092	.665260E+07
Totals	83.2111		4360960			

Fig. S59 Elemental analysis data of **13** formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and i-propyl amine as catalyzed by the dinuclear [CoL1]₂ (**2**) and [CoL2]₂ (**4**) complexes.

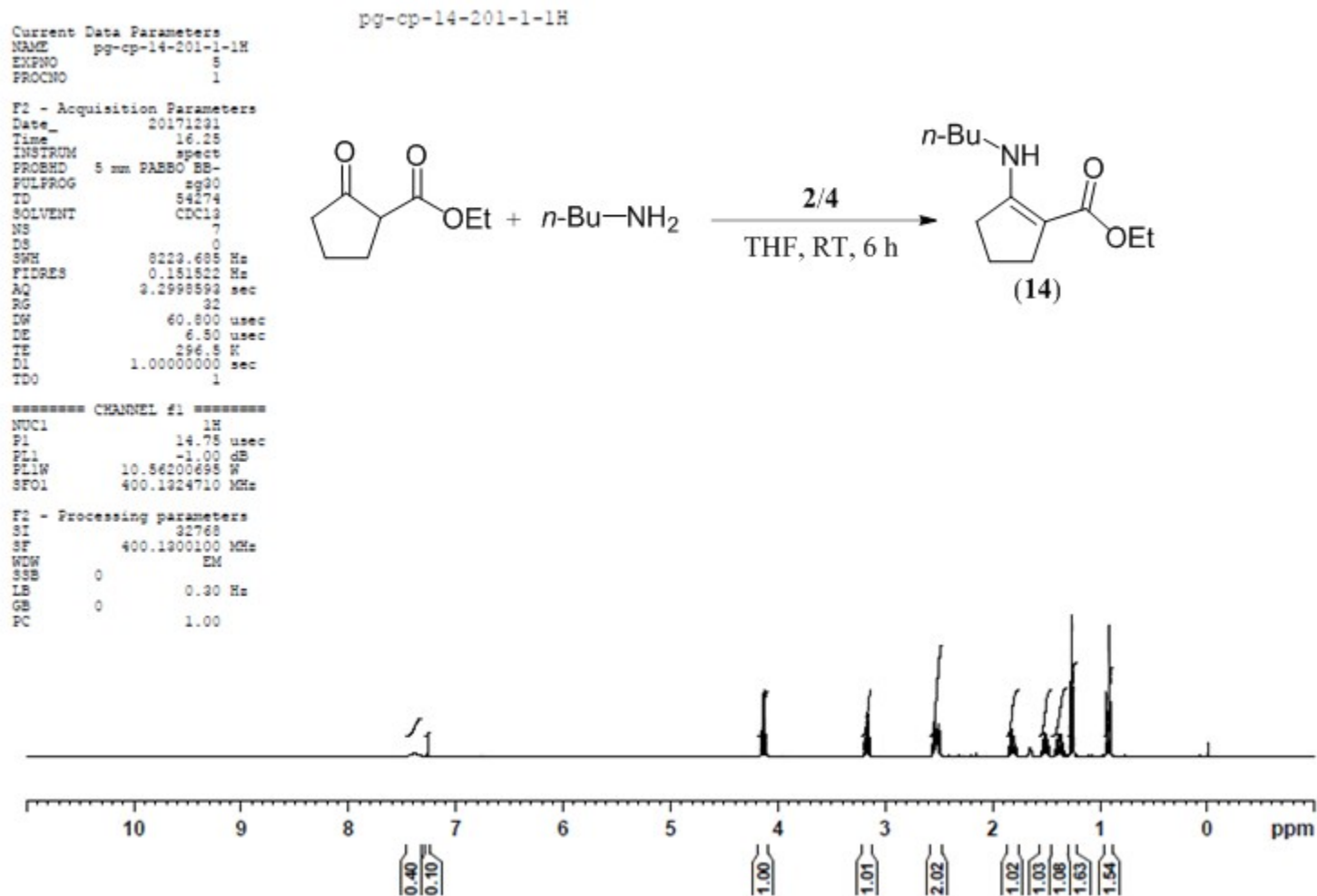


Fig. S60 ^1H NMR spectrum of **14** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-butyl amine as catalyzed by the dinuclear $[\text{CoL1}]_2$ (**2**) and $[\text{CoL2}]_2$ (**4**) complexes.

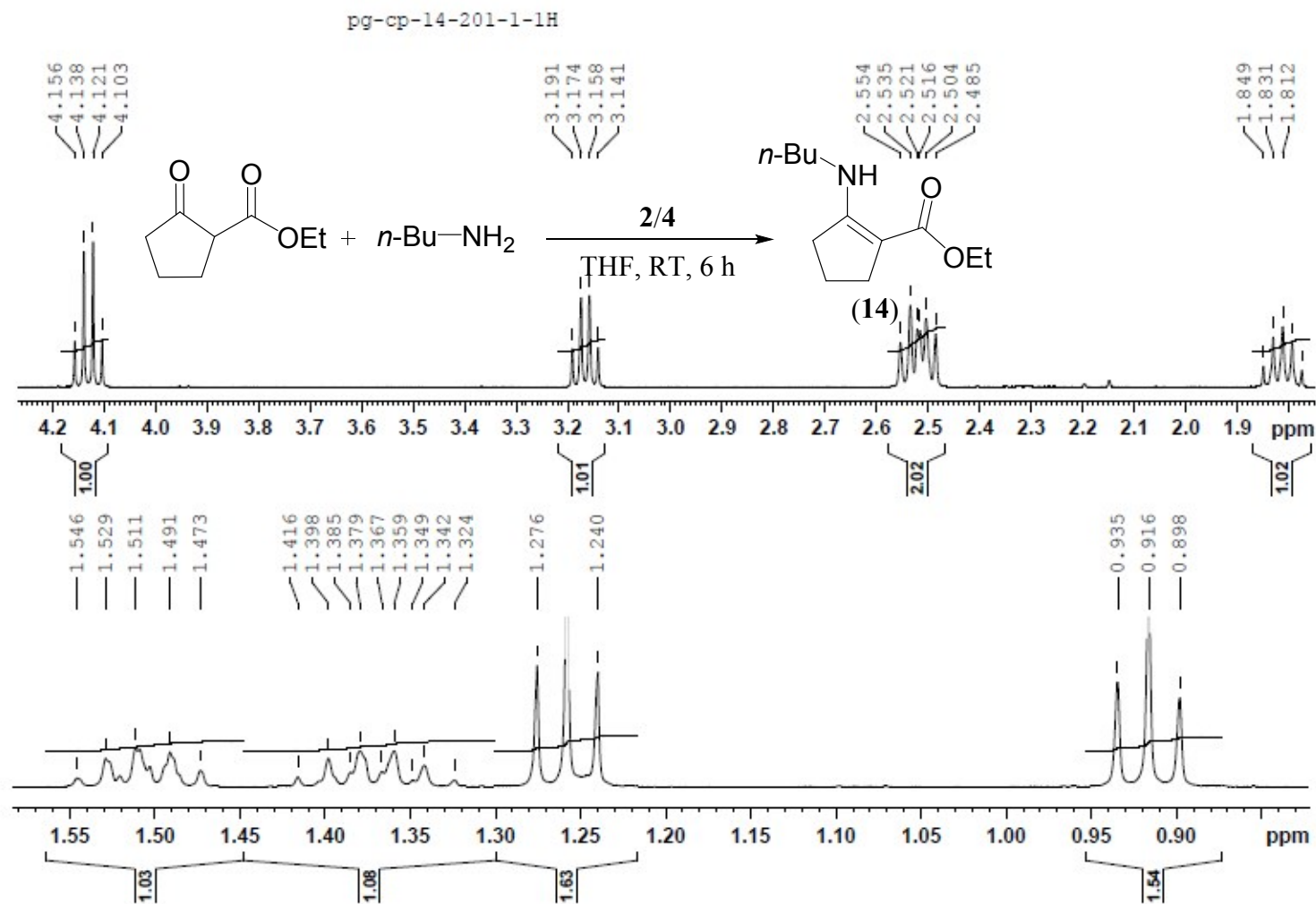


Fig. S61 Expanded ^1H NMR spectrum of **14** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-butyl amine as catalyzed by the dinuclear $[\text{CoL1}]_2$ (**2**) and $[\text{CoL2}]_2$ (**4**) complexes.

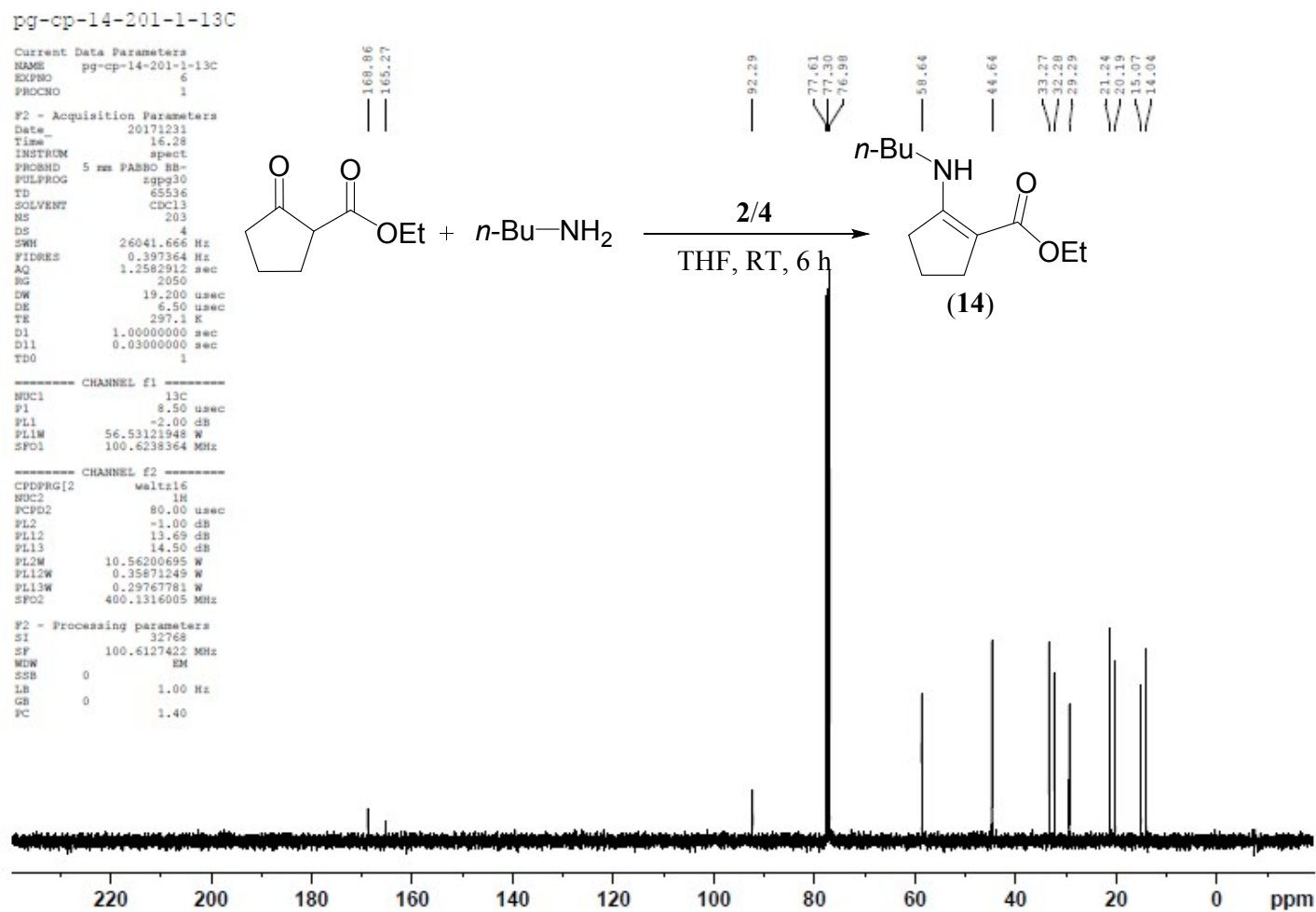


Fig. S62 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **14** in CDCl_3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-butyl amine as catalyzed by the dinuclear $[\text{CoL}^1]_2$ (**2**) and $[\text{CoL}^2]_2$ (**4**) complexes.

File : F:\GCMSDATA\2017\DECEMBER-2017\PG-CP-14-201-1.D
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 Acquired : 30 Dec 2017 00:43 using AcqMethod COMMON METHOD-2017.M
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 disc Info :
 Vial Number: 5

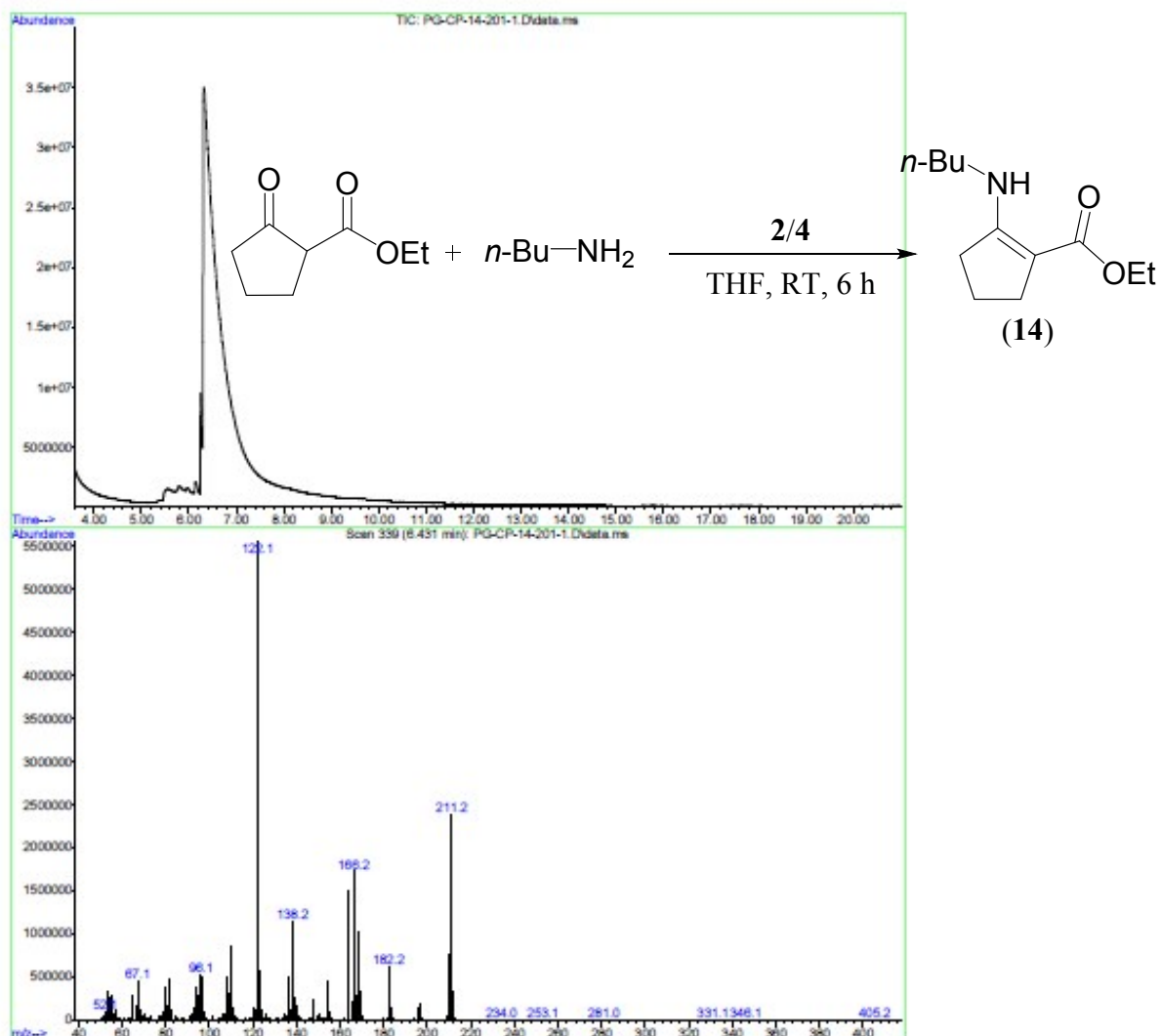


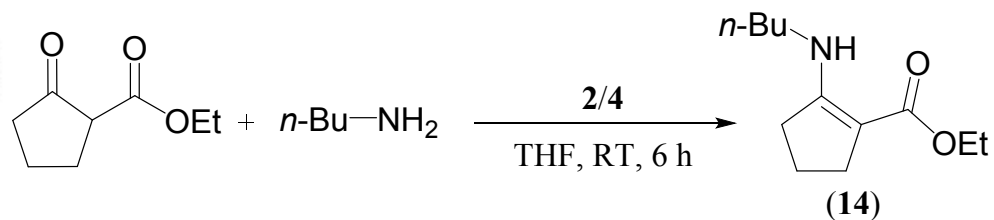
Fig. S63 GCMS trace of **14** (m/z 211) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and n-butyl amine as catalyzed by the the dinuclear [CoL1]**2** (**2**) and [CoL2]**2** (**4**) complexes.

Eager 300 Report

Page: 1 Sample: PG-CP-14-201-1 (PG-CP-14-201-1)

Method Name : PGCP30122017
 Method File : D:\CHNS-2017\PGCP30122017.mth
 Chromatogram : PG-CP-14-201-1
 Operator ID : CHANDNI
 Analysed : 12/30/2017 19:22
 Sample ID : PG-CP-14-201-1 (# 16)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 12/31/2017 22:05
 Instrument N. : Instrument #1
 Sample weight : 1.565



Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	2	131749	RS		0.0000
Nitrogen	6.5050	41	110319	RS	24.843690	.108364E+07
Carbon	67.4186	62	2740732	RS	1.000000	.259525E+07
Hydrogen	10.2791	199	1070187	RS	2.560984	.665260E+07
Totals	84.2027		4052987			

Fig. S64 Elemental analysis data of **14** formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and *n*-butyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes.

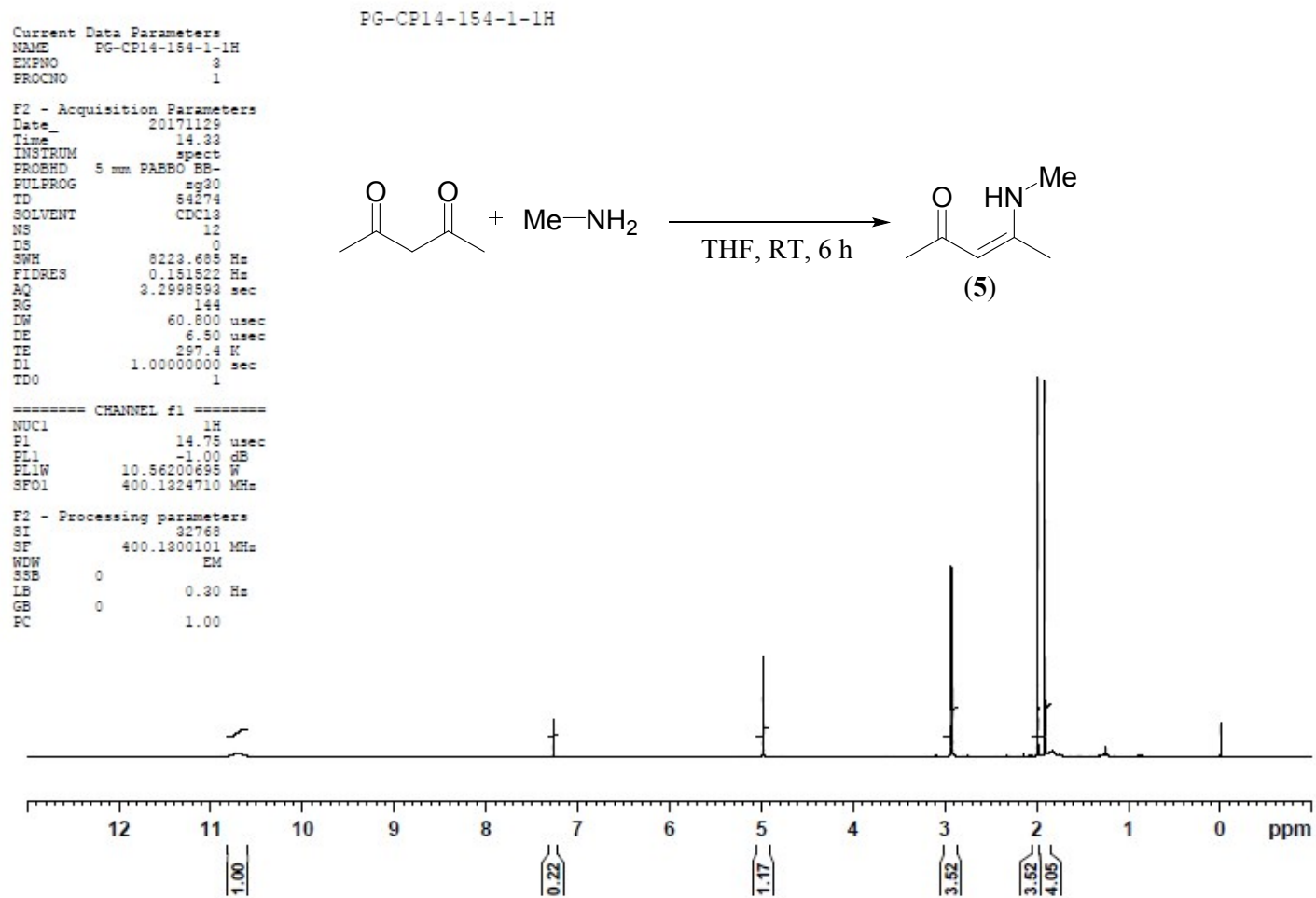


Fig. S65 ^1H NMR spectrum of **5** in CDCl_3 formed in the reaction of acetyl acetone and methyl amine.

File : F:\GCMSDATA2017\November2017\PG-CP-14-154-1.D
Operator : CP
Acquired : 29 Nov 2017 15:22 using AcqMethod COMMON METHOD-2017.M
Instrument : GCMS
Sample Name : PG-CP-14-154-1
Misc Info :
Vial Number : 1

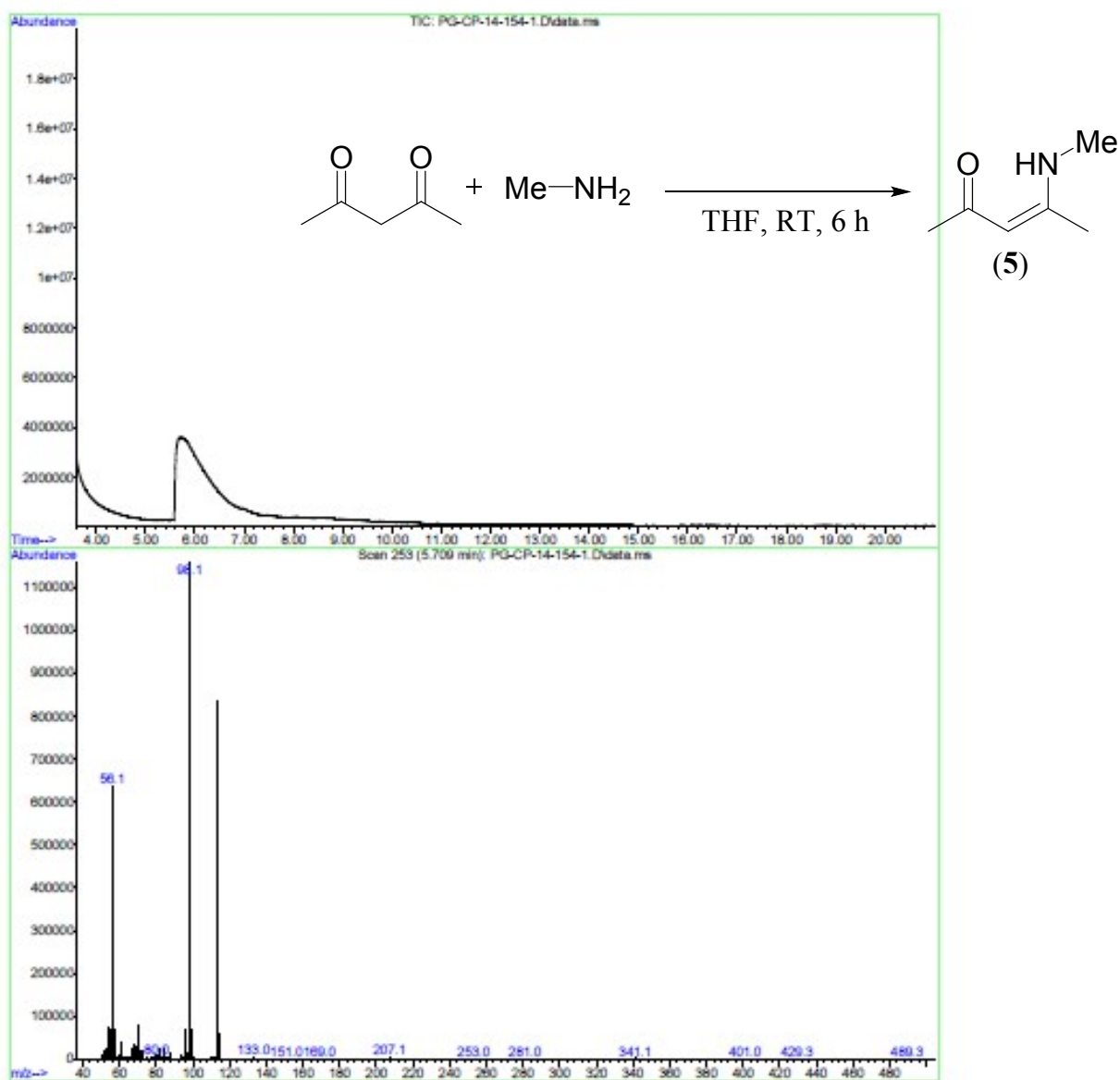


Fig. S66 GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine.

Current Data Parameters
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EXPNO 4
PROCNO 1

PG-CP-14-155-1-1H

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Time_ 14.40
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PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 12
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SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 144
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DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TDO 1

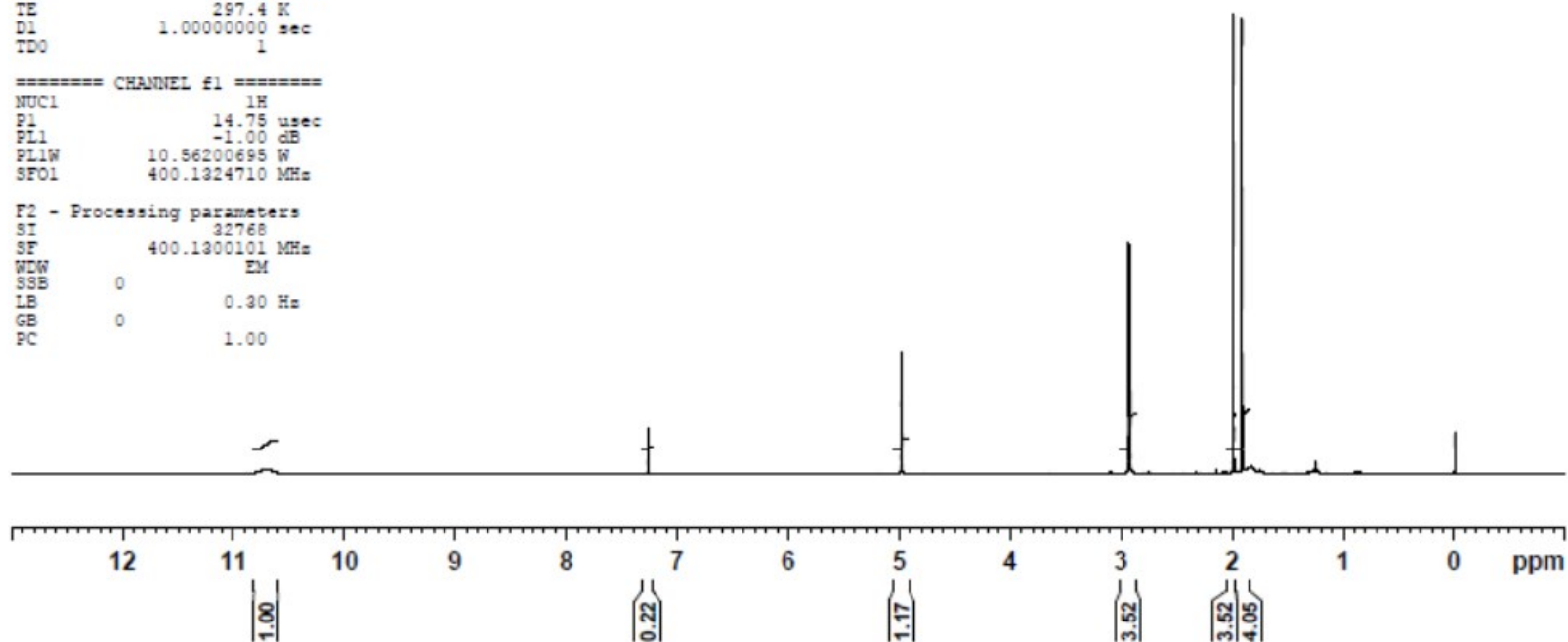
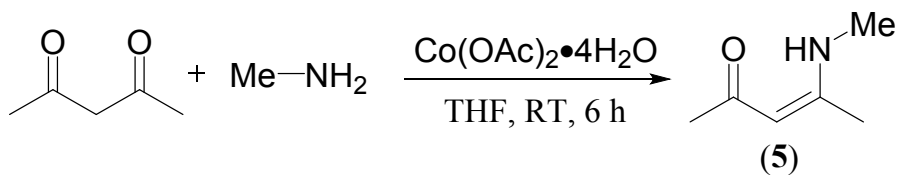


Fig. S67 ¹H NMR spectrum of **5** in CDCl₃ formed in the reaction of acetyl acetone and methyl amine as catalyzed by Co(OAc)₂•4H₂O.

File : F:\GCMSDATA2017\November2017\PG-CP-14-155-1.D
Operator : CP
Acquired : 29 Nov 2017 15:47 using AcqMethod COMMON METHOD-2017.M
Instrument : GCMS
Sample Name: PG-CP-14-155-1
disc Info :
Vial Number: 2

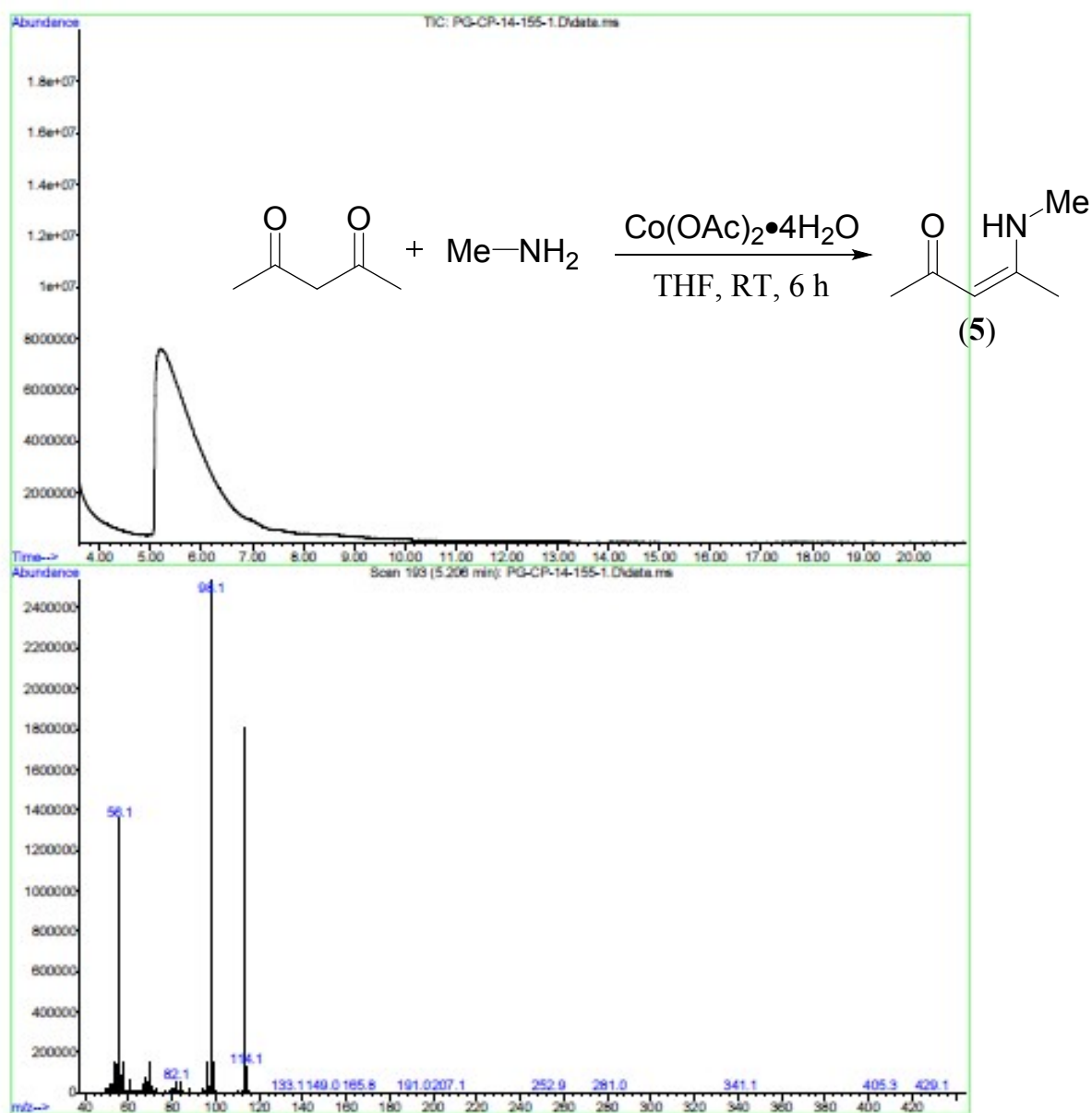


Fig. S68 GCMS trace of **5** (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by Co(OAc)₂•4H₂O.

Current Data Parameters
NAME PG-CP-14-167-1-1H
EXPNO 5
PROCNO 1

PG-CP-14-167-1-1H

F2 - Acquisition Parameters
Date_ 20171207
Time 17.23
INSTRUM spect
PROBHD 5 mm PAHBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 7
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TDD 1

----- CHANNEL f1 -----
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

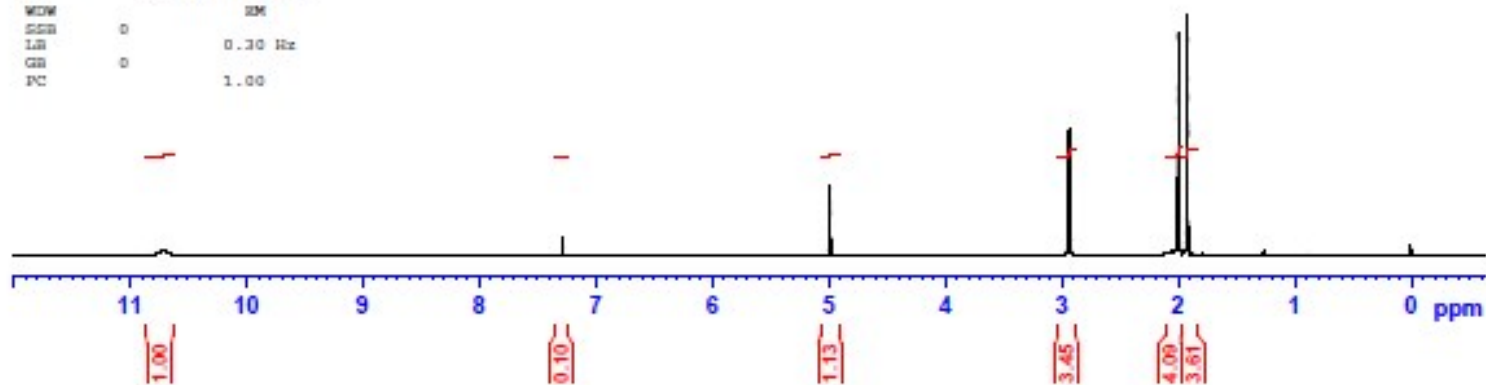
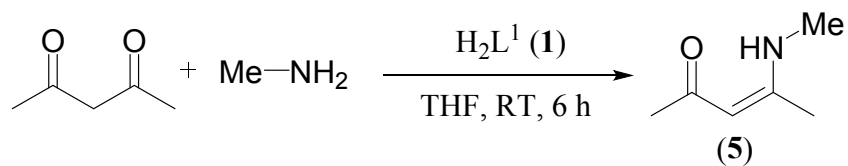


Fig. S69 ¹H NMR spectrum of 5 in CDCl₃ formed in the reaction of acetyl acetone and methyl amine as catalyzed by H₂L¹ (1).

File : F:\GCMSDATA2017\DECEMBER-2017\pg-cp-14-167-3.D
Operator :
Acquired : 6 Dec 2017 20:48 using AcqMethod COMMON METHOD-2017.M
Instrument : GCMS
Sample Name: pg-cp-14-167-3
Disc Info :
Vial Number: 1

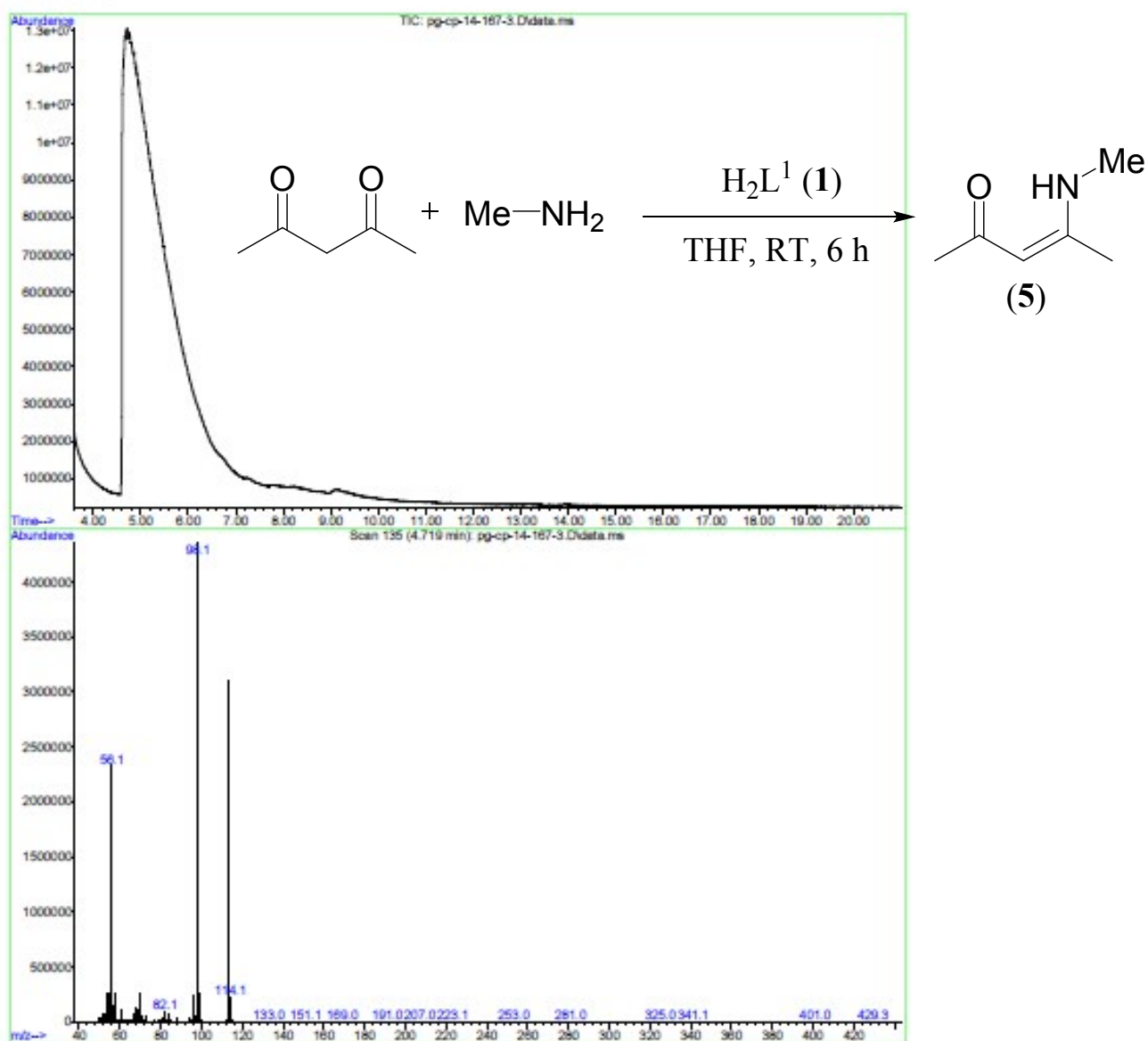


Fig. S70 GCMS trace of **5** (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by H₂L¹ (**1**).

Current Data Parameters
NAME PG-CP-14-194-1-1H
EXPNO 1
PROCNO 1

PG-CP-14-194-1-1H

F2 - Acquisition Parameters
Date_ 20171226
Time 17.16
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13
DS 2
SWH 10000.000 Hz
FIDRES 0.162888 Hz
AQ 3.2767889 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
WC 1.00

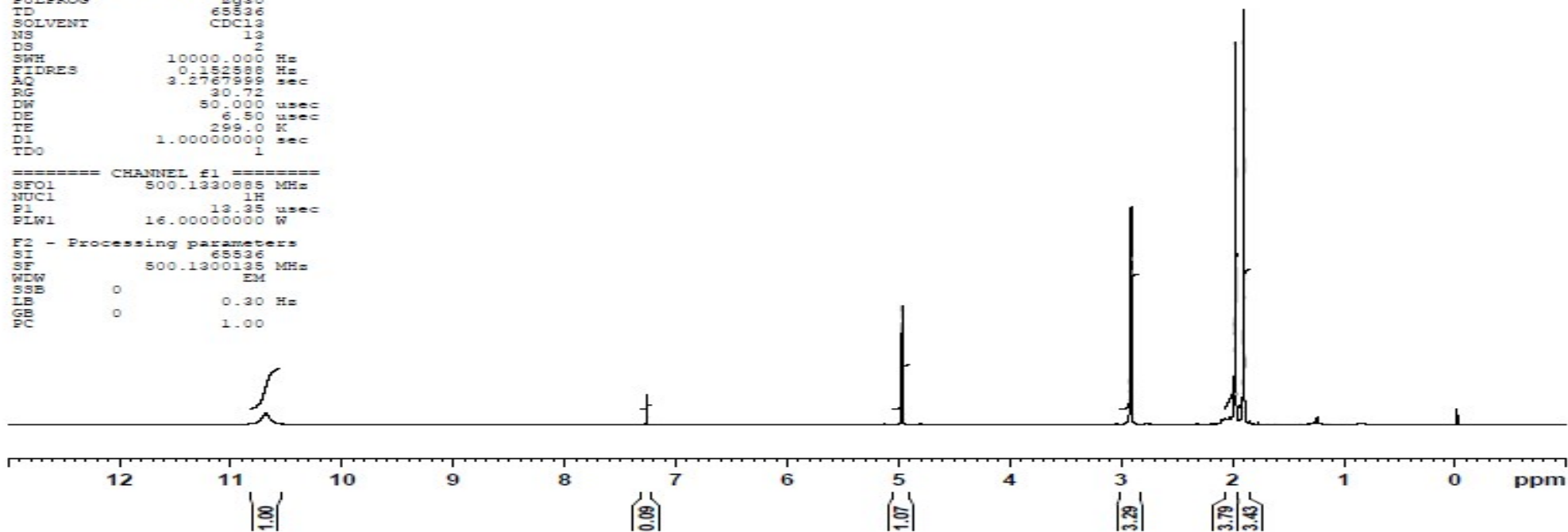


Fig. S71 ^1H NMR spectrum of 5 in CDCl_3 formed in the reaction of acetyl acetone and methyl amine as catalyzed by H_2L^2 (3).

```

Current Data Parameters
NAME      PG-CP-14-156-1-1H
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20171202
Time      8.07
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         54274
SOLVENT   CDCl3
NS         6
DS         0
SWH        8223.685 Hz
FIDRES     0.151522 Hz
AQ         3.2998593 sec
RG         144
DM         60.800 usec
DE         6.50 usec
TE         297.1 K
D1         1.00000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       10.56200695 W
SF01       400.1324710 MHz

F2 - Processing parameters
SI         32768
SF         400.1300101 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

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PG-CP-14-156-1-1H

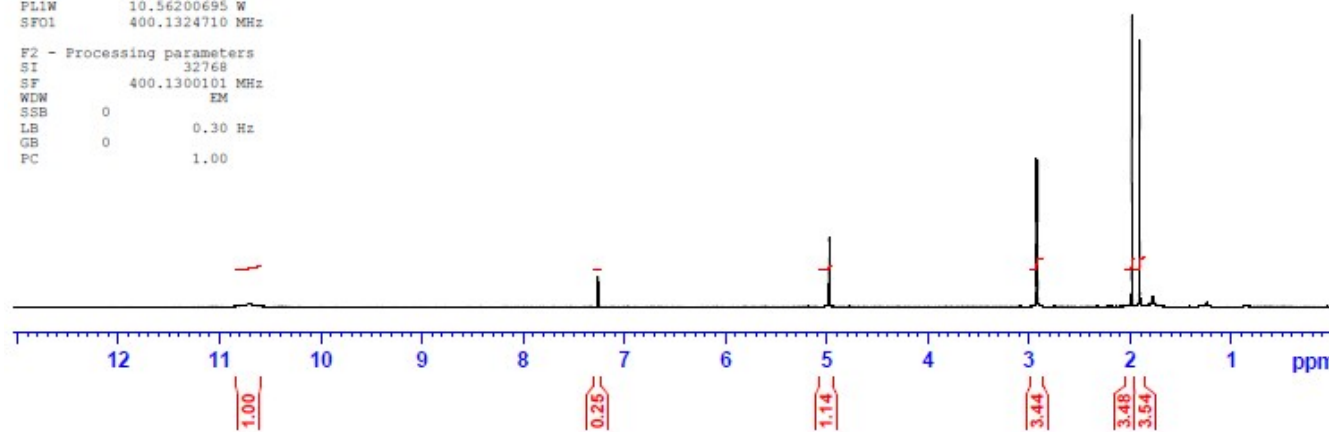
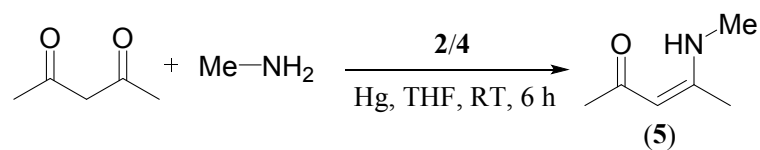


Fig. S72 ¹H NMR spectrum of **5** in CDCl₃ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL1]**2** (**2**) and [CoL2]**2** (**4**) complexes in the presence of Hg.

File : F:\GCMSDATA2017\November2017\PG-CP-14-156-2.D
 Operator : CP
 Acquired : 30 Nov 2017 21:25 using AcqMethod COMMON METHOD-2017.M
 Instrument : GCMS
 Sample Name : PG-CP-14-156-2
 Disc Info :
 Vial Number : 4

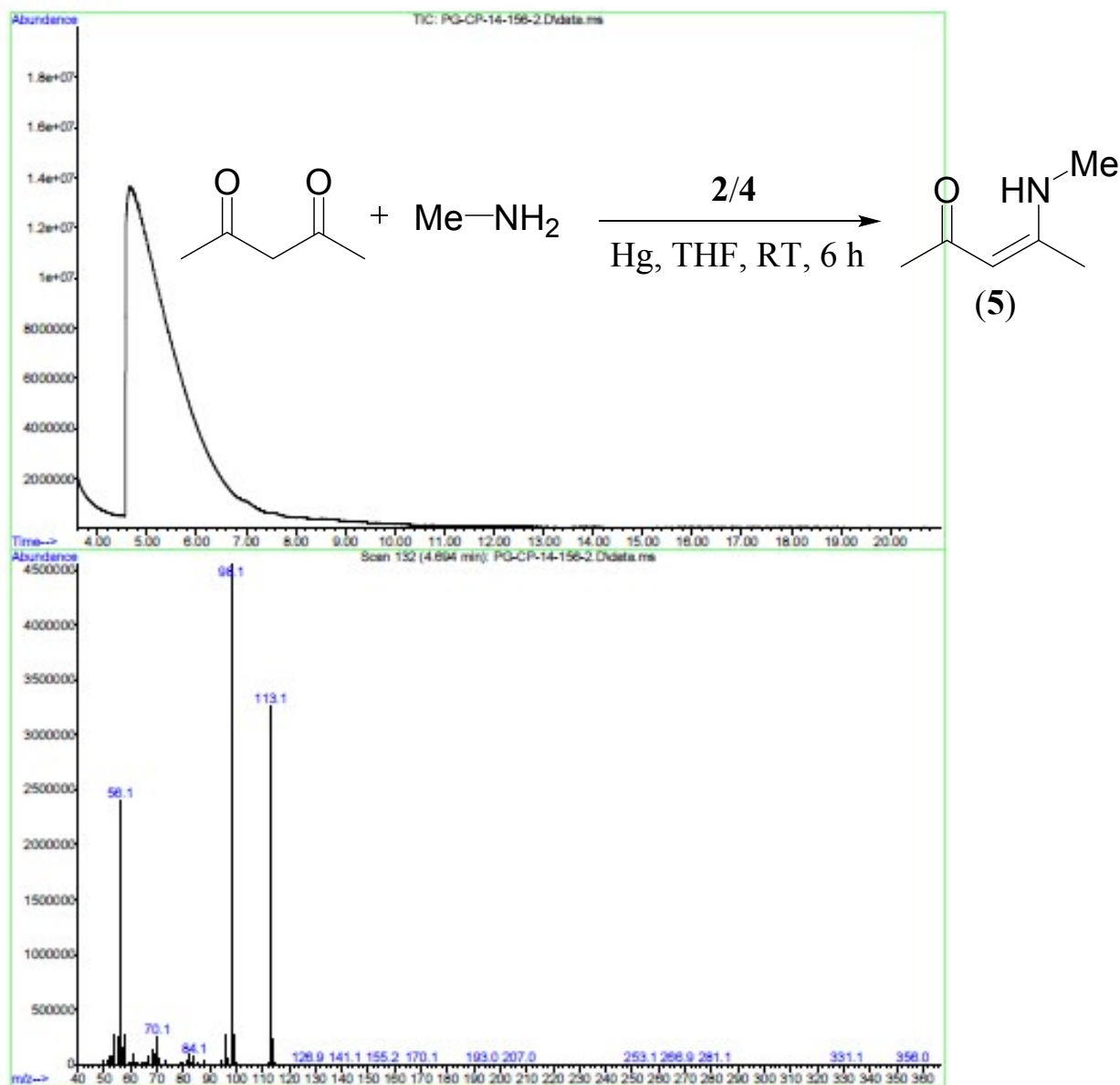


Fig. S73 GCMS trace of **5** (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL¹]₂ (**2**) and [CoL²]₂ (**4**) complexes in the presence of Hg.