Electronic Supplementary Material (ESI) for RSC Advances.
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Stereoselective polymerization of methyl methacrylate and *rac*-lactide mediated by iminomethylpyridine based Cu(II) complexes

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Electronic Supporting Information

FIGURE S1. FT-IR spectra of **[L_ACuCl$_2$]**. **03**

FIGURE S2. FT-IR spectra of **[L_BCu(μ-Cl)Cl]$_2$**. **04**

FIGURE S3. FT-IR spectra of **[L_CCuCl$_2$]**. **05**

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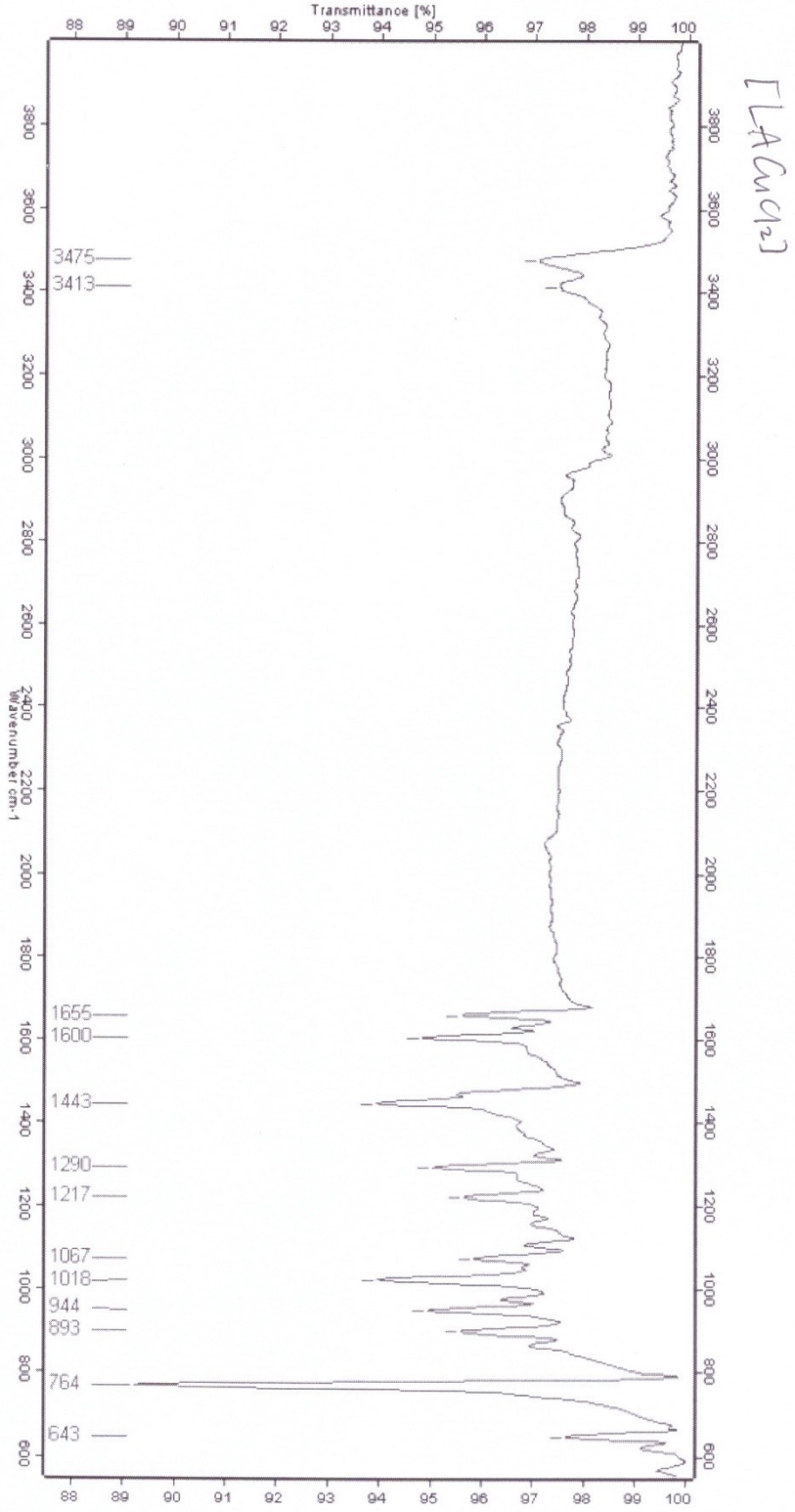
Scheme S1. Proposed mechanism for ROP of *rac*-LA catalyzed by **[L_nCuMe$_2$]** ($L_n = L_A$ – L_F). **22**

FIGURE S1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[LA Cu Cl2]
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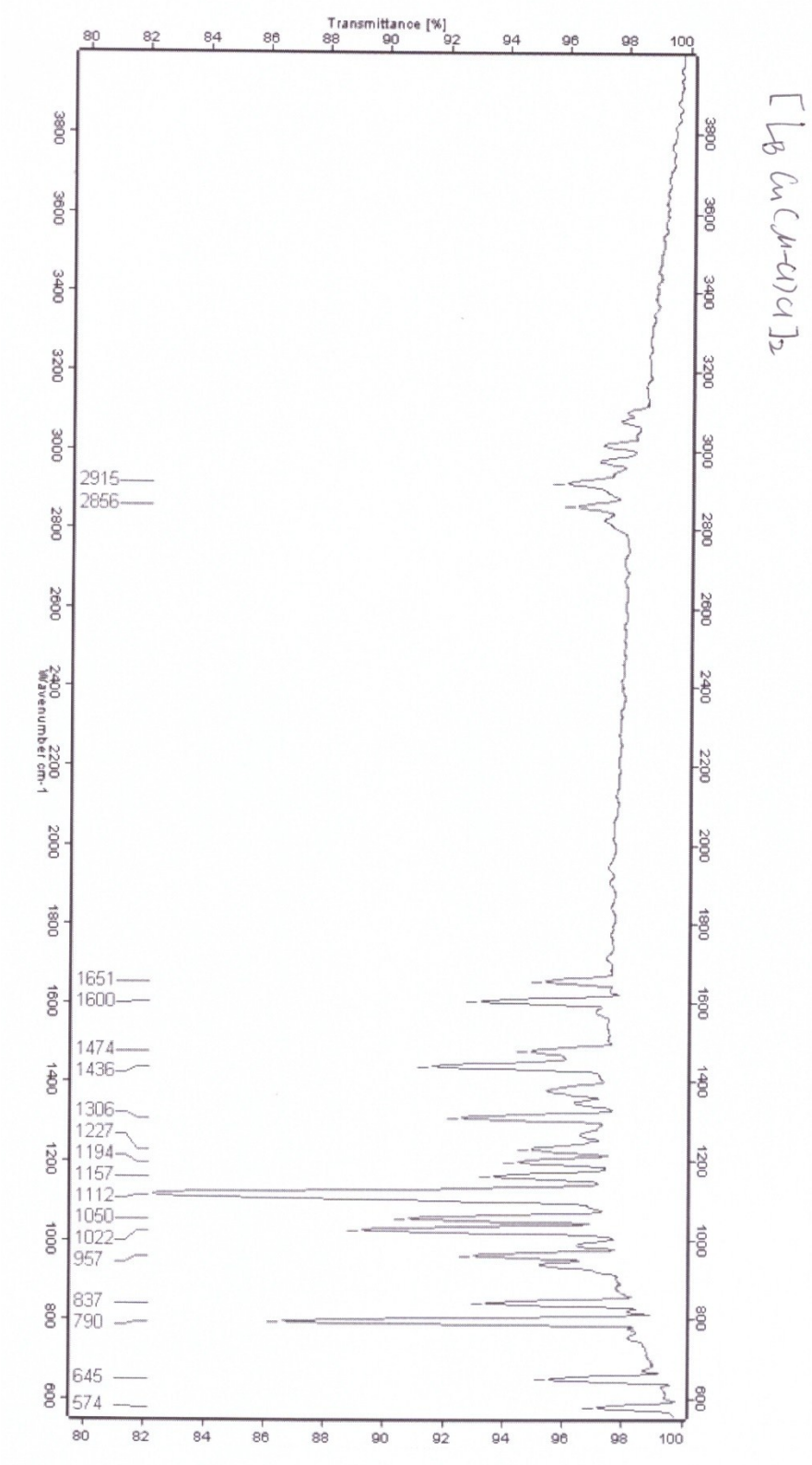
944
893
764
643

FIGURE **S2**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1022
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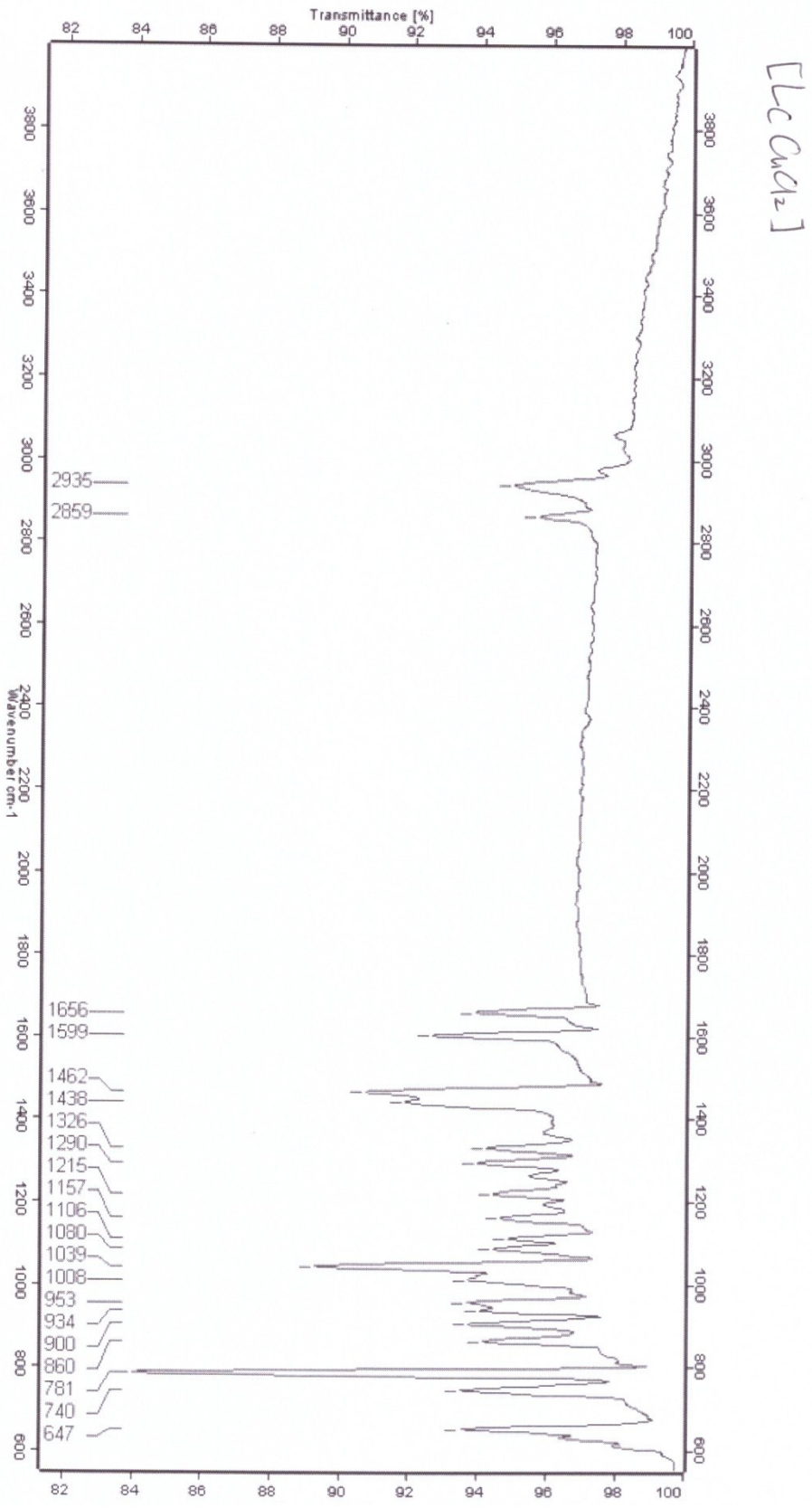
837
790
645
574

FIGURE S3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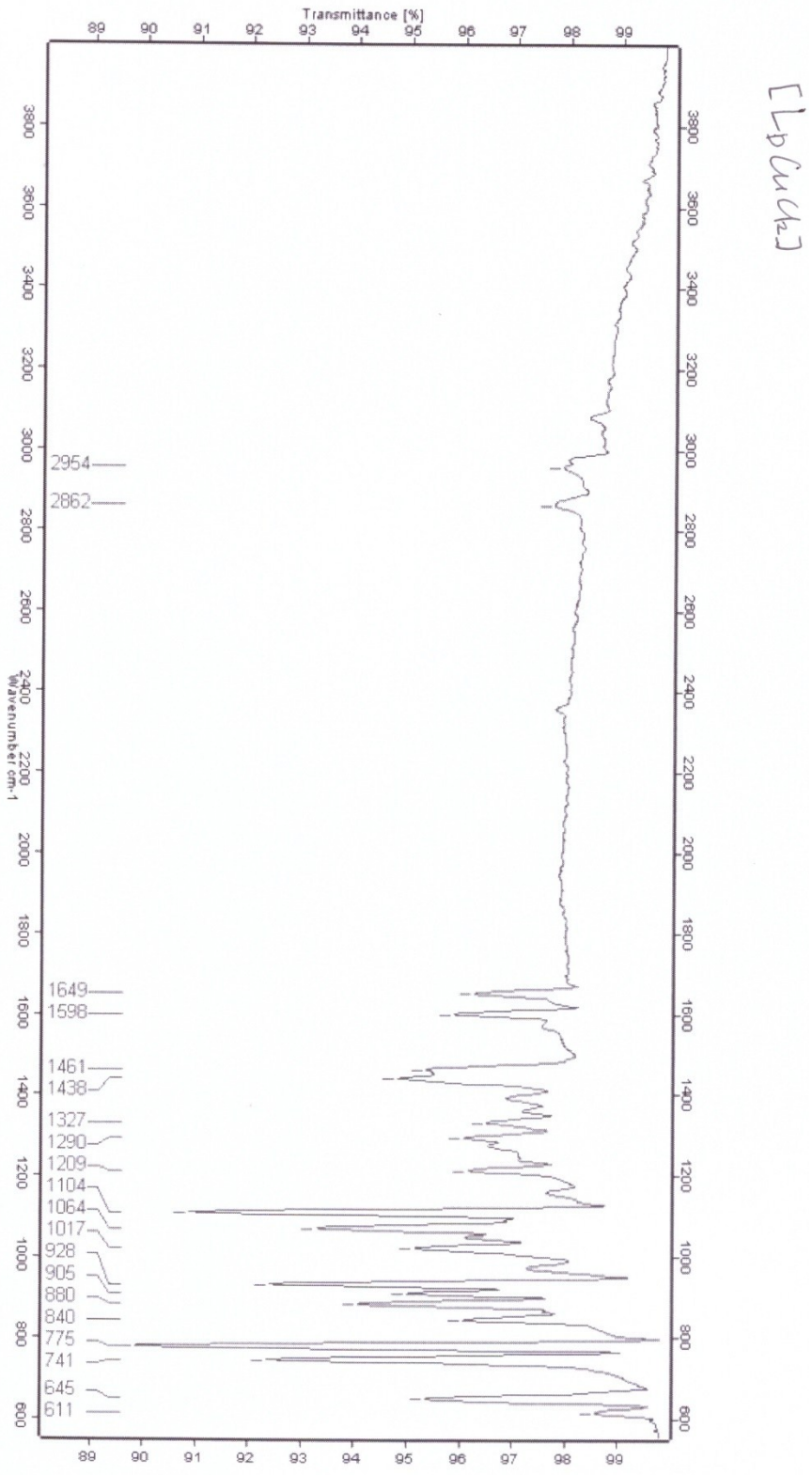
934
900
860
781
740
647

FIGURE **S4**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1017
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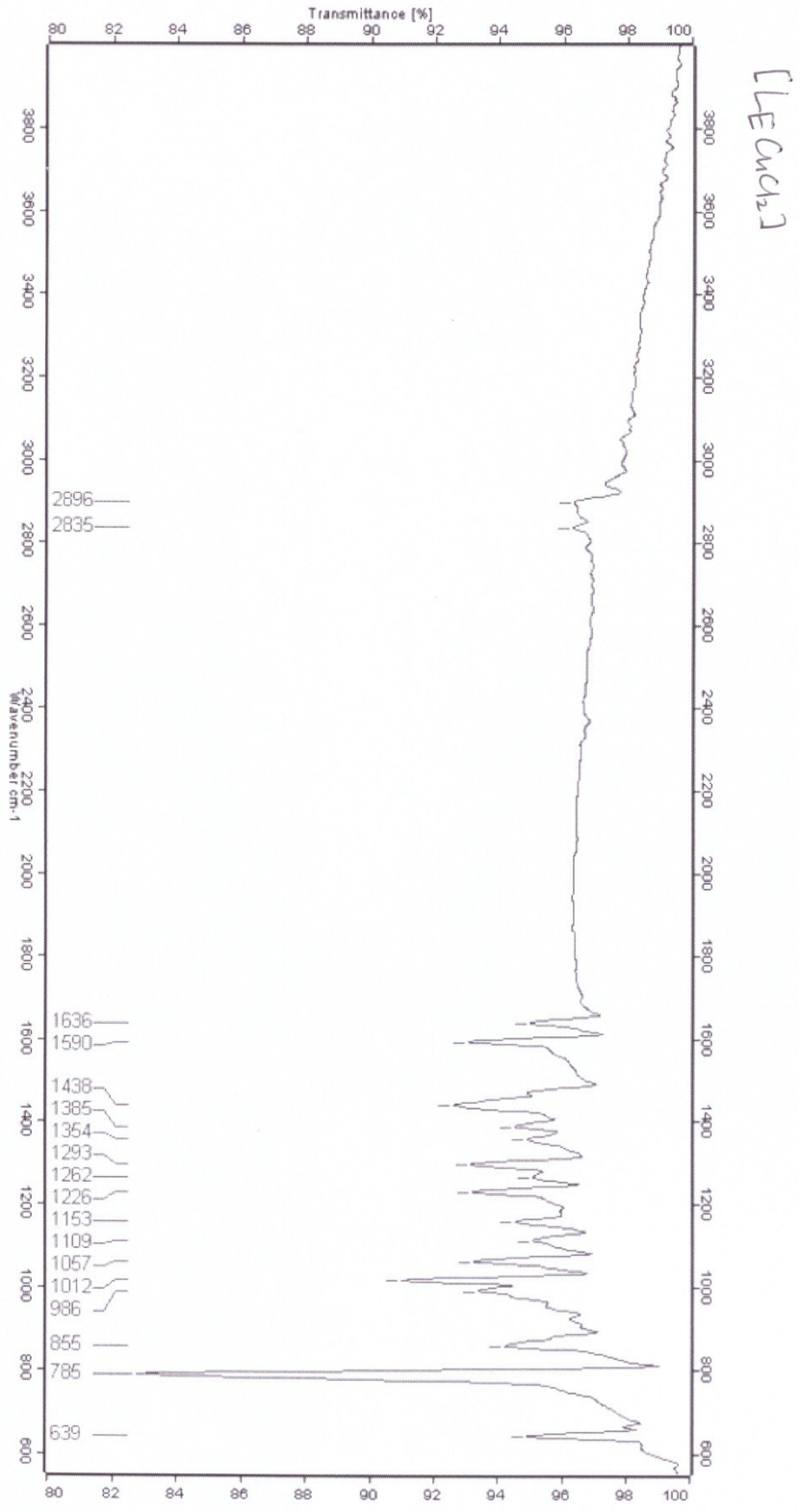
905
880
840
775
741
645
611

FIGURE S5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Wavenumber cm-1
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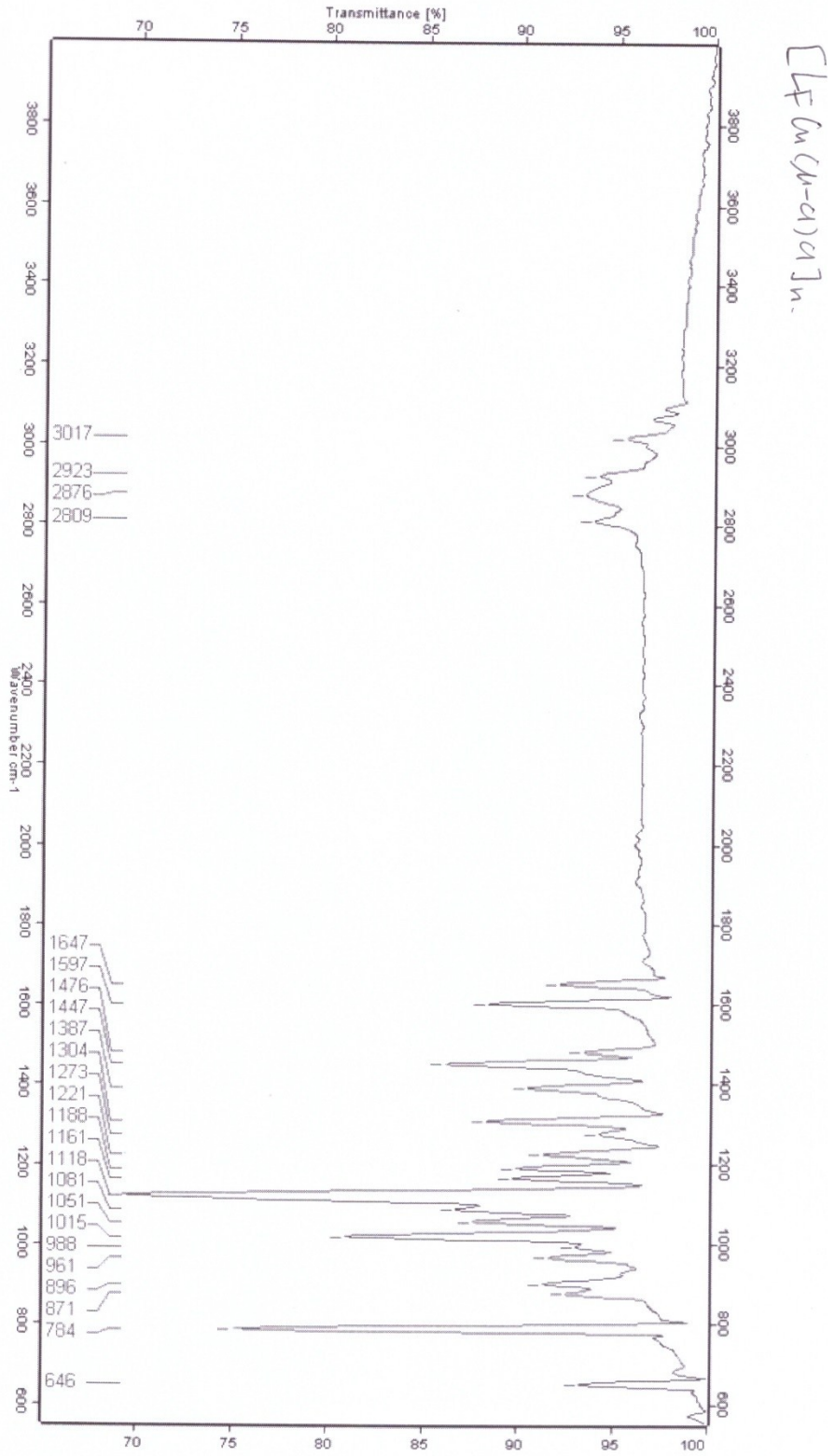
2835
1636
1590
1438
1385
1354
1293
1262
1226
1153
1109
1057
1012
986
855
785
639
[LE Cu(CH2)]

FIGURE S6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2000
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3017
2923
2876
2809
1647
1597
1476
1447
1387
1304
1273
1221
1188
1161
1118
1081
1051
1015
988
961
896
871
784
646

FIGURE S7

Eager Xperience Summarize Results

Date : 2018-02-28 at 08:44:38
Method Name : NCHS
Method Filename : EA-C_20180226.mth

Group No : 1	Element %			
Sample Name	Nitrogen	Carbon	Hydrogen	Sulphur
LA_CuCl	13.46959114	38.71767426	4.882183075	0
LA_CuCl	13.25759125	38.61170578	4.871536732	0

2 Sample(s) in Group No : 1	
Component Name	Average
Nitrogen	13.3635919
Carbon	38.6646902
Hydrogen	4.876859903
Sulphur	0

Group No : 2	Element %			
Sample Name	Nitrogen	Carbon	Hydrogen	Sulphur
LB_CuCl	9.192878723	35.97859192	4.020053864	0
LB_CuCl	9.114869118	36.03707123	4.01180172	0

2 Sample(s) in Group No : 2	
Component Name	Average
Nitrogen	9.15387392
Carbon	36.00783157
Hydrogen	4.015927792
Sulphur	0

Group No : 3	Element %			
Sample Name	Nitrogen	Carbon	Hydrogen	Sulphur
LD_CuCl	11.93679333	44.59290695	5.482099533	0
LD_CuCl	12.08079624	44.6649329	5.466984272	0

2 Sample(s) in Group No : 3	
Component Name	Average
Nitrogen	12.00879478
Carbon	44.62895012
Hydrogen	5.474541903
Sulphur	0

Eager Xperience Summarize Results

Date : 2018-02-28 at 08:44:49
Method Name : NCHS
Method Filename : EA-C_20180226.mth

Group No : 1	Element %			
Sample Name	Nitrogen	Carbon	Hydrogen	Sulphur
LE_CuCl	11.99687576	41.15446854	4.890295506	0
LE_CuCl	11.90109921	41.09791183	4.887745857	0

2 Sample(s) in Group No : 1	
Component Name	Average
Nitrogen	11.9489748
Carbon	41.12619019
Hydrogen	4.889020681
Sulphur	0

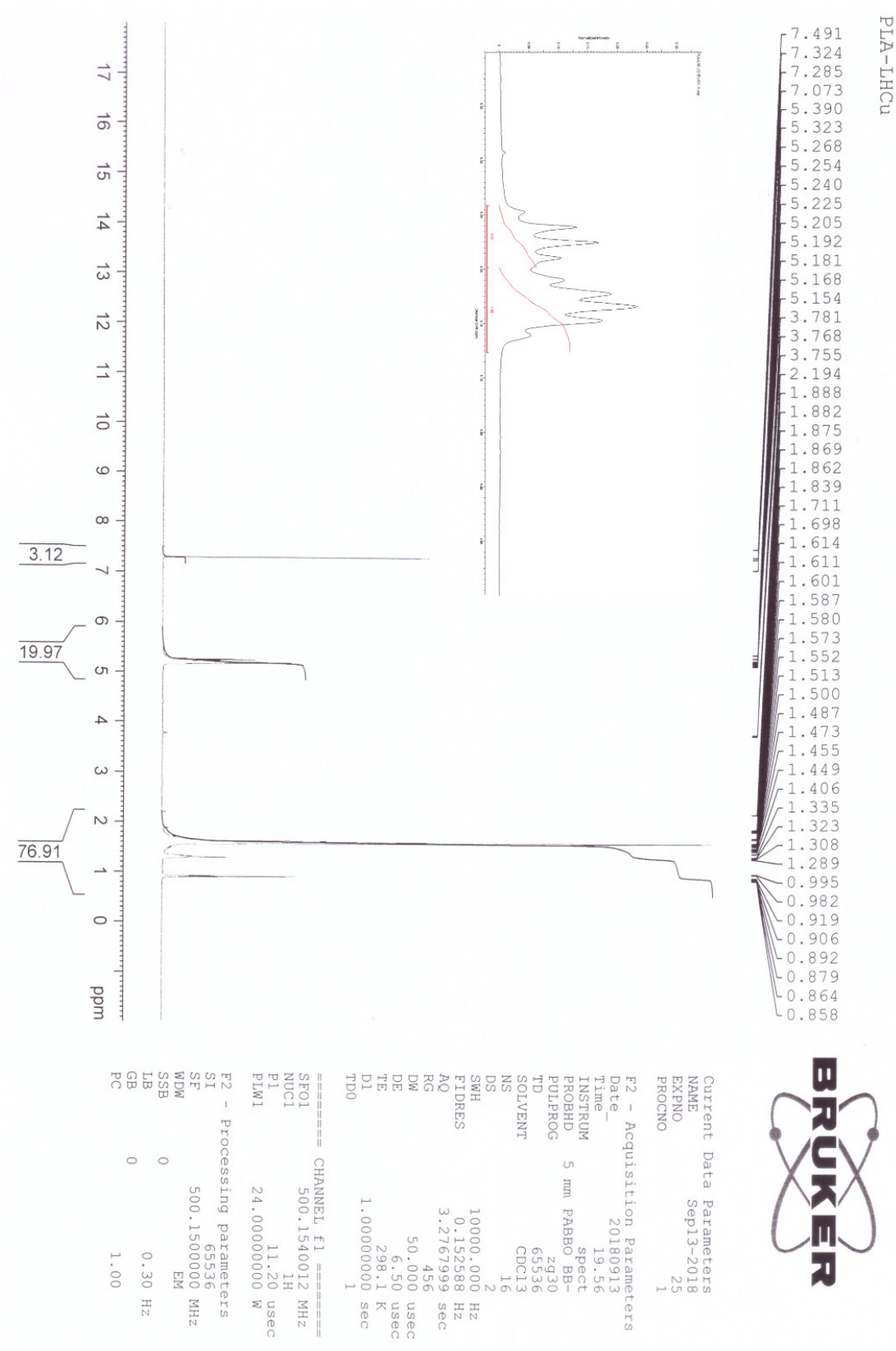
Group No : 2	Element %			
Sample Name	Nitrogen	Carbon	Hydrogen	Sulphur
LG_CuCl	13.12195015	40.93544006	5.30657959	0
LG_CuCl	12.86294174	40.7428894	5.235087395	0

2 Sample(s) in Group No : 2	
Component Name	Average
Nitrogen	12.99244595
Carbon	40.83916473
Hydrogen	5.270833492
Sulphur	0

Group No : 1	Element %			
Sample Name	Nitrogen%	Carbon%	Hydrogen%	Sulphur%
[LH$CuCl2]	8.981668472	38.65621185	4.508579254	0
[LH$CuCl2]	9.010733604	38.71915817	4.492286682	0

2 Sample(s) in Group No : 1	
Component Name	Average
Nitrogen%	8.996201038
Carbon%	38.68768501
Hydrogen%	4.500432968
Sulphur%	0

FIGURE S8


PLA-LHCu
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7.324
7.285
7.073
5.390
5.323
5.268
5.254
5.240
5.225
5.205
5.192
5.181
5.168
5.154
3.781
3.768
3.755
2.194
1.888
1.882
1.875
1.869
1.862
1.839
1.711
1.698
1.614
1.611
1.601
1.587
1.580
1.573
1.552
1.513
1.500
1.487
1.473
1.455
1.449
1.406
1.335
1.323
1.308
1.289
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0.906
0.892
0.879
0.864
0.858
3.12
19.97
76.91
ppm
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NAME Sep13-2018
EXPNO 25
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180913
Time 19.56
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PULPROG zg30
TD 65536
SOLVENT CDCl3
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DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 456
DW 50.000 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
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NUC1 1H
P1 11.20 usec
PLW1 24.00000000 W
F2 - Processing parameters
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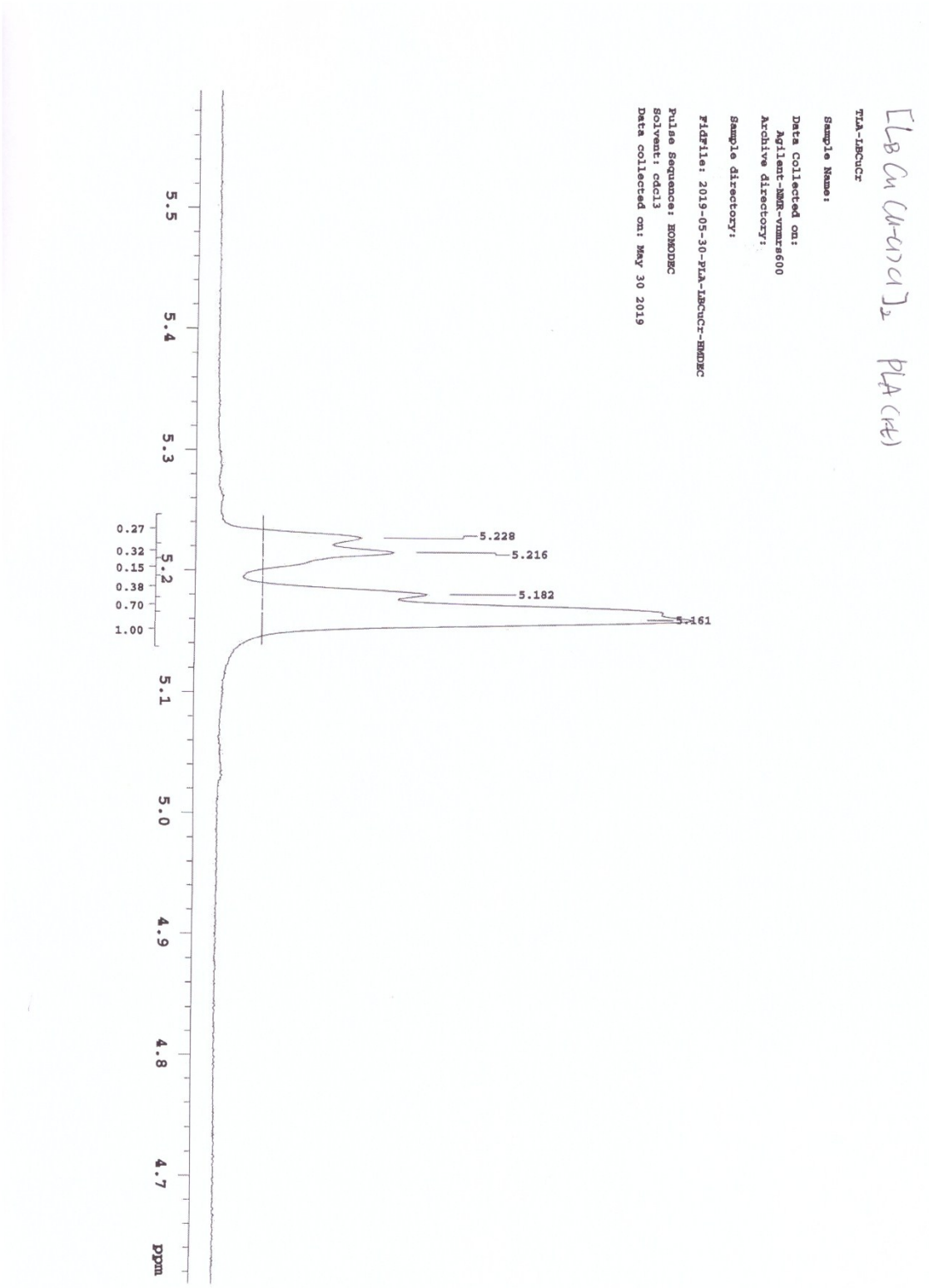
SF 500.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

FIGURE S9



[LBCu(Cu-Cl)Cl]2 PLA (H)
TLA-LBCuCr
Sample Name:
Data Collected on:
Agilent-NMR-vnmrs600
Archive directory:
Sample directory:
FidFile: 2019-05-30-PLA-LBCuCr-HMDEC
Pulse Sequence: HOMODEC
Solvent: cdcl3
Data collected on: May 30 2019
5.228
5.216
5.182
5.161
0.27
0.32
0.15
0.38
0.70
1.00
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
ppm

FIGURE S9-1

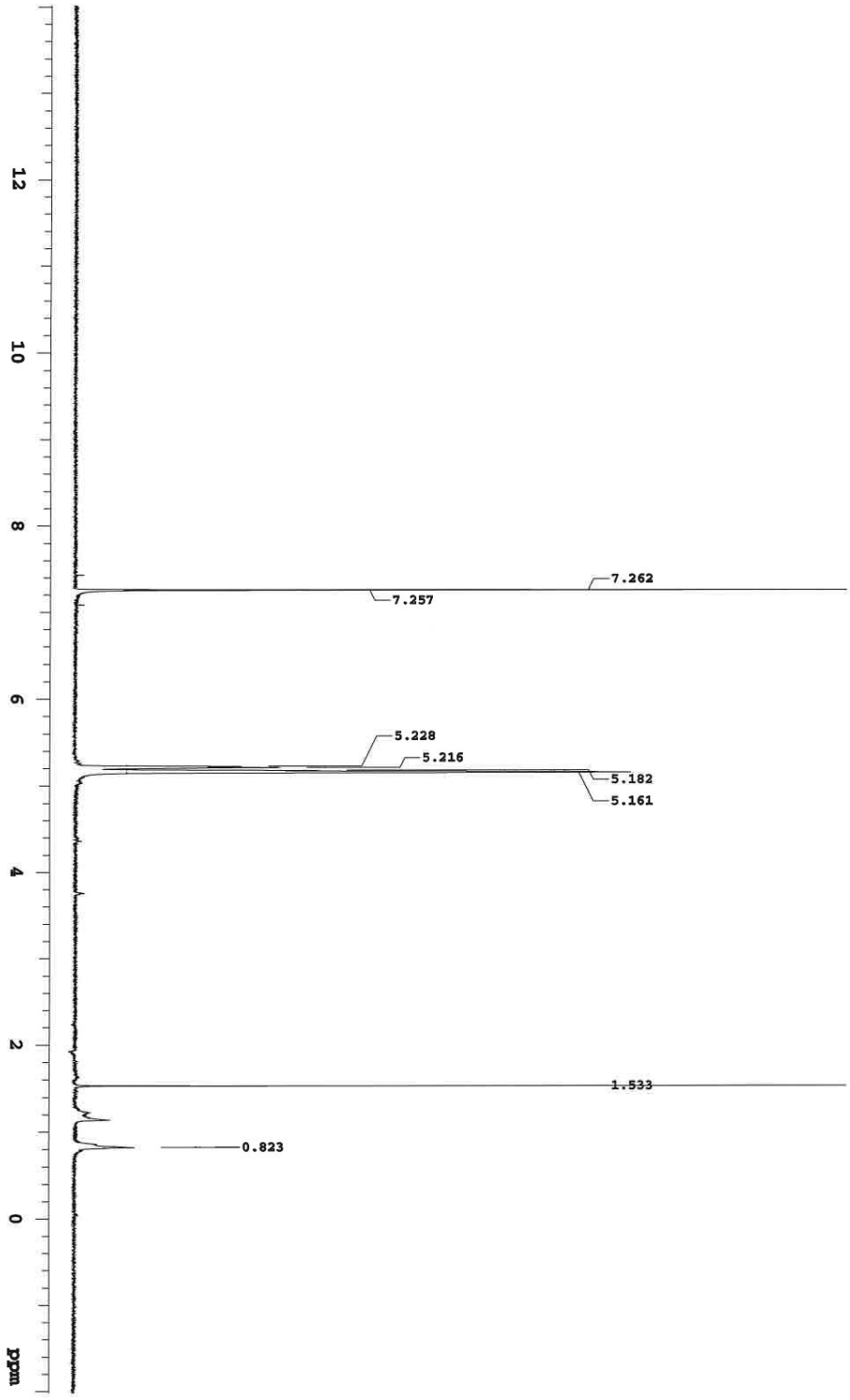


FIGURE S9-2

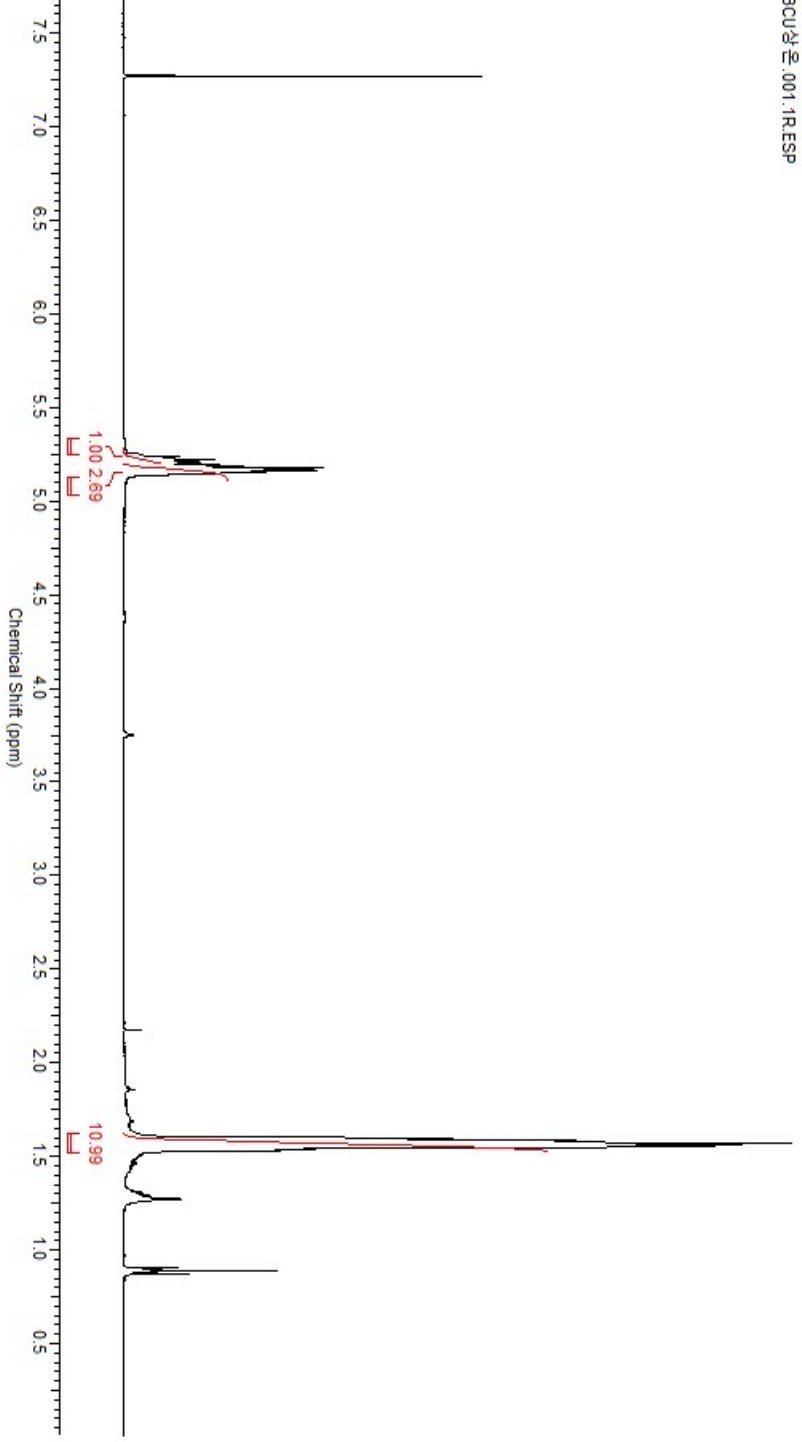
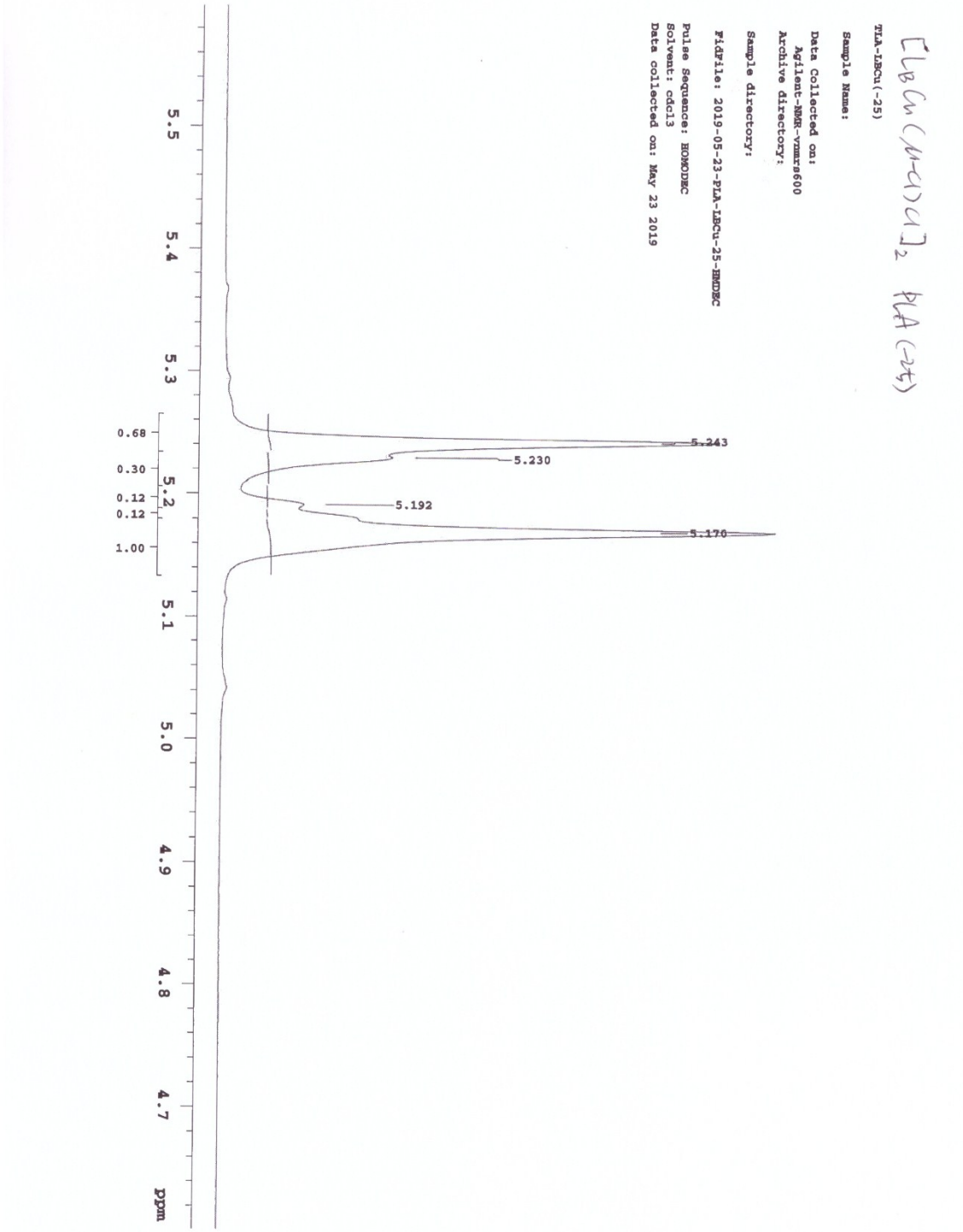


FIGURE S10


[LB Cu (μ-Cl) Cl]2 PLA (-25)
FLA-LBCu(-25)
Sample Name:
Data Collected on:
Agilent-NMR-vnmrs600
Archive directory:
Sample directory:
FidFile: 2019-05-23-PLA-LBCu-25-HMDBC
Pulse Sequence: HOMODEC
Solvent: cdcl3
Data collected on: May 23 2019
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5.230
5.192
5.170
0.68
0.30
0.12
0.12
1.00
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5.3
5.2
5.1
5.0
4.9
4.8
4.7
ppm

FIGURE S10-1

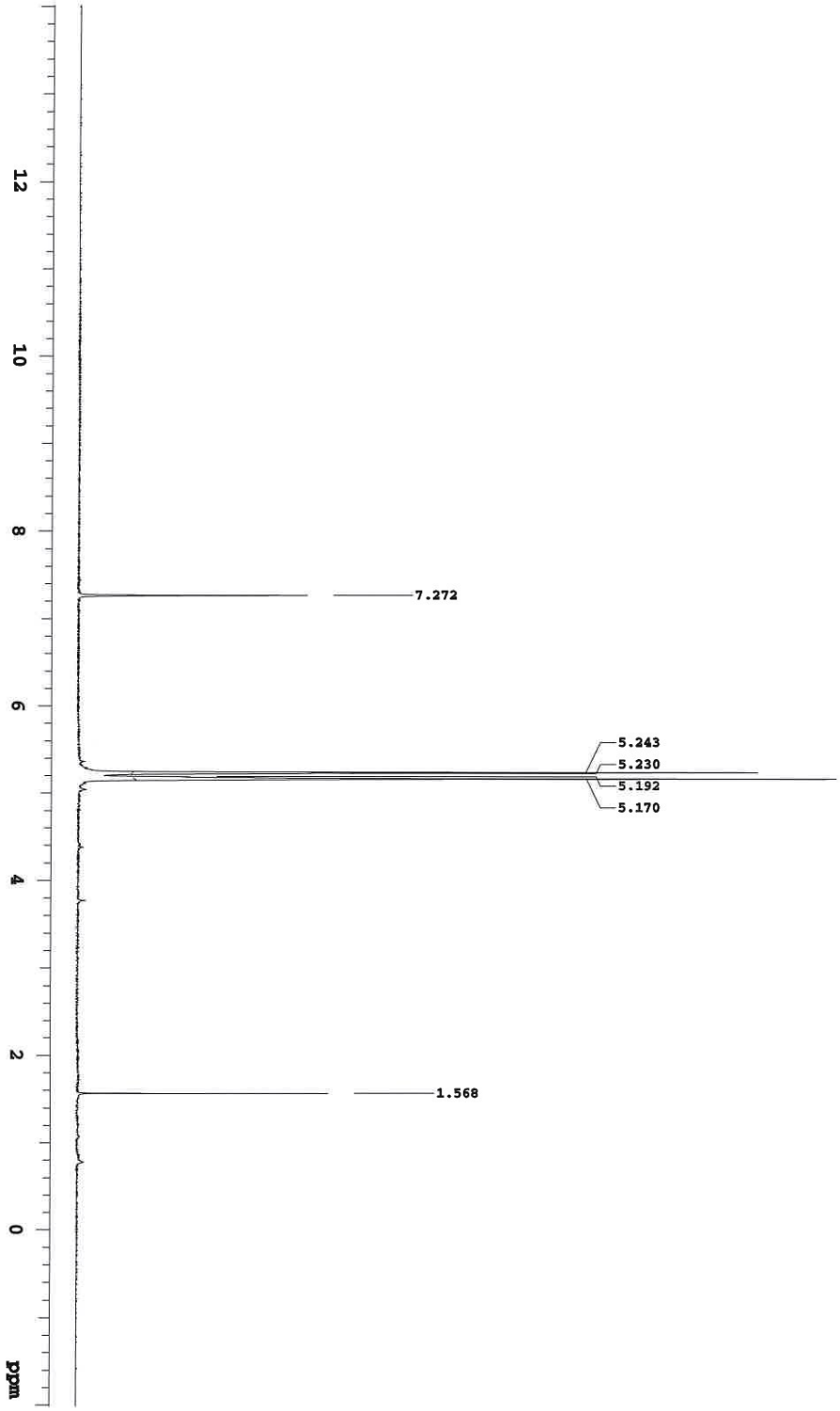


FIGURE S10-2

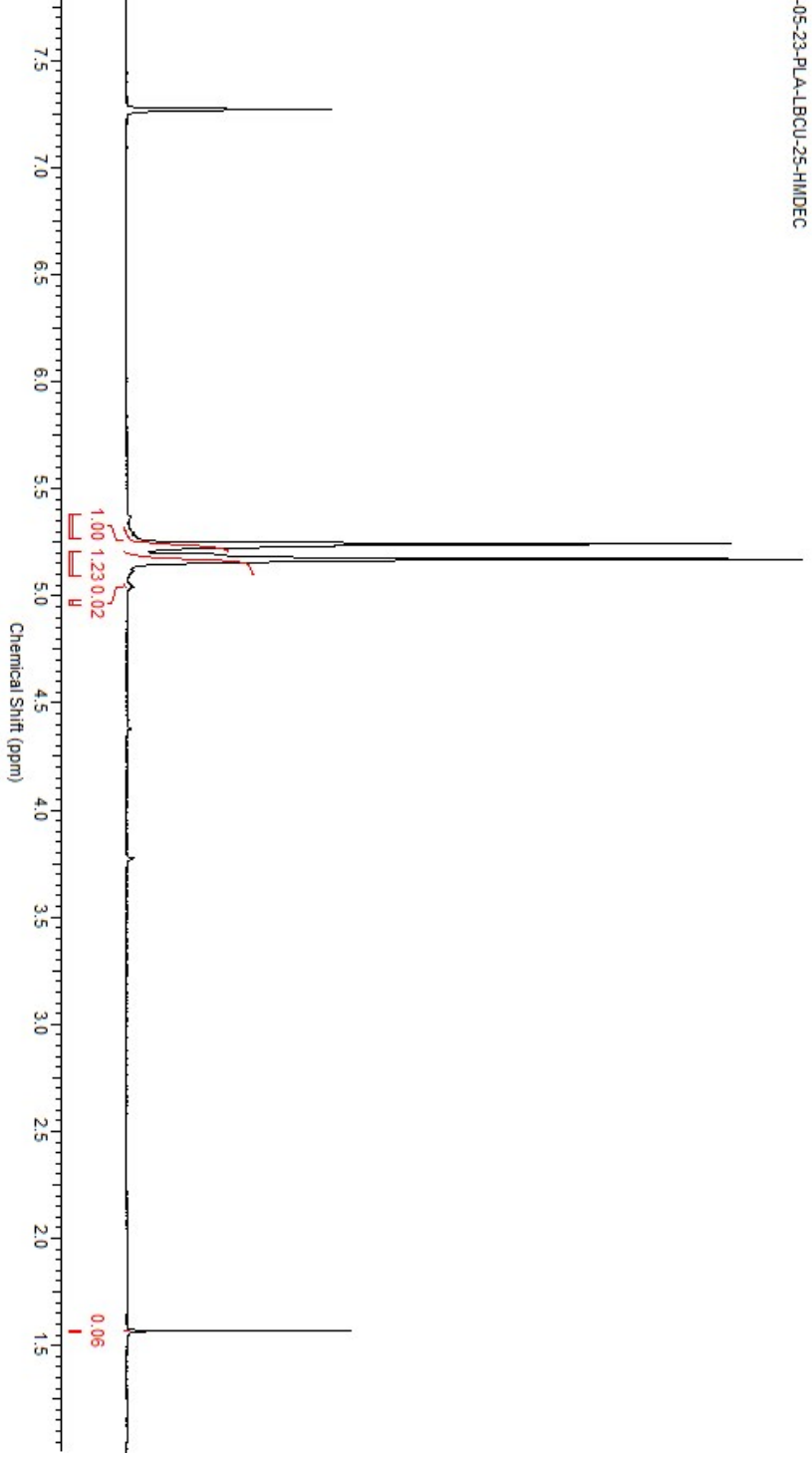
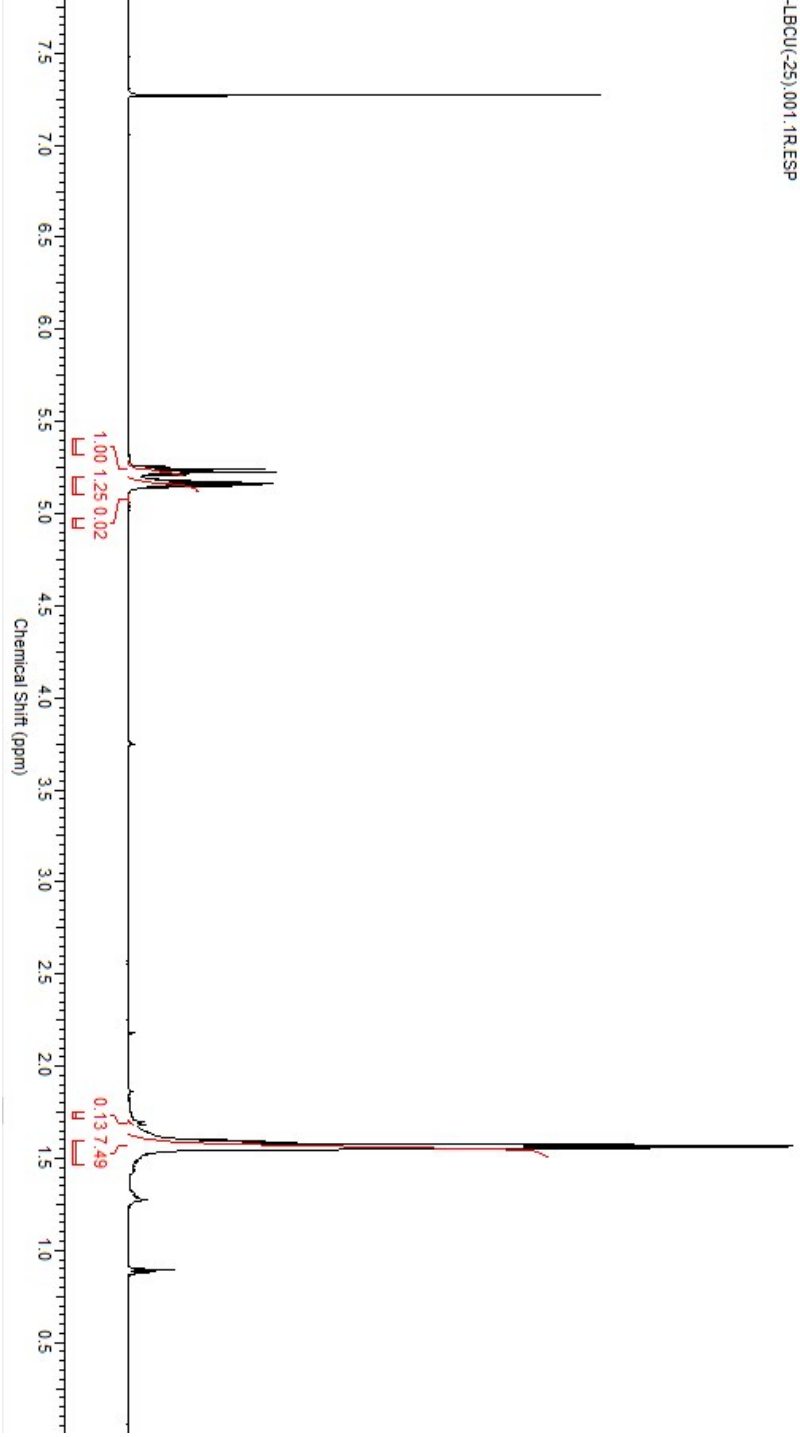


FIGURE S10-3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0.13 7.49
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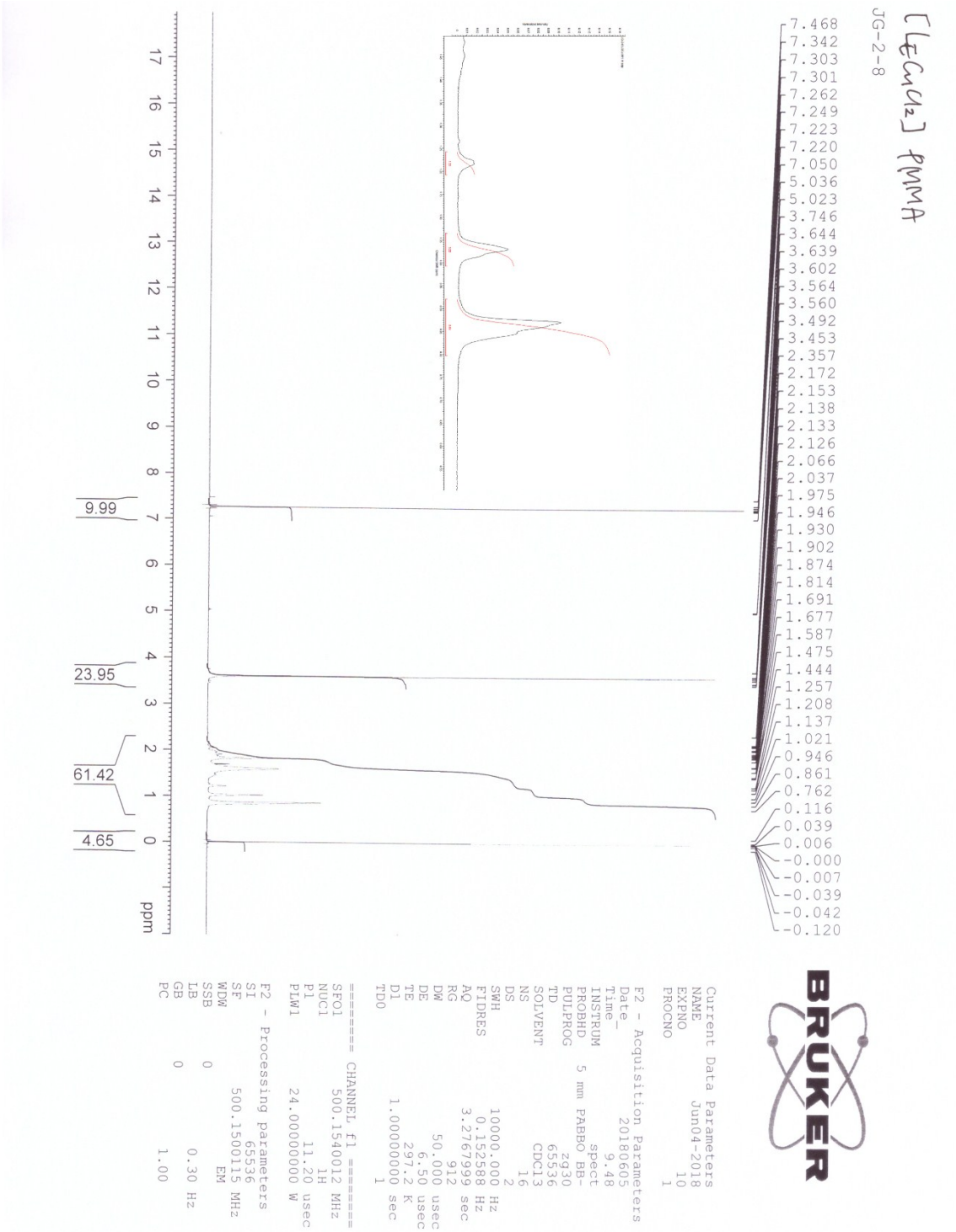
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

FIGURE S11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ppm
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PROCNO 1
F2 - Acquisition Parameters
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TD 65536
SOLVENT CDCl3
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RG 912
DW 50.000 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
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NUC1 1H
P1 11.20 usec
PLW1 24.00000000 W
F2 - Processing parameters
SI 65536
SF 500.1500115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Table S1

	$[L_BCu(\mu–Cl)Cl]_2$	$[L_CCuCl_2]$	$[L_ECuCl_2]$	$[L_FCuCl_2]$
Empirical formula	$C_{18}H_{24}Cl_4Cu_2N_4O_2$	$C_{13}H_{19}Cl_2CuN_3$	$C_{11}H_{17}Cl_2CuN_3$	$C_{10}H_{14}Cl_2CuN_2O$
Formula weight	597.29	351.75	325.71	312.67
Temperature (K)	100(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.630	0.71073	0.610	0.610
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	P-1	$P2_1/c$
a (Å)	8.8760(2)	11.3629(2)	7.2770(2)	19.137(4)
b (Å)	6.9330(1)	6.8532(1)	8.9970(2)	8.7180(2)
c (Å)	18.664(4)	19.328(3)	11.587(2)	7.4750(2)
α (°)	90	90	96.81(3)	90
β (°)	93.56(3)	104.988(4)	102.67(3)	93.40(3)
γ (°)	90	90	112.98(3)	90
Volume ($Å^3$), Z	1146.3(4), 2	1453.9(4), 4	663.5(3), 2	1244.9(4), 4
Density (calculated) (Mg m^{-3})	1.730	1.607	1.630	1.668
Absorption coefficient (mm^{-1})	1.677	1.859	1.332	1.419
F(000)	604	724	334	636
Crystal size (mm^3)	0.16 × 0.13 × 0.10	0.28 × 0.14 × 0.10	0.07 × 0.07 × 0.055	0.07 × 0.06 × 0.035
Theta range for data collection (°)	2.779 to 25.996	2.18 to 28.35	1.588 to 26.996	2.204 to 26.997
Index ranges	$-12 \le h \le 12$	$-15 \le h \le 14$	$-10 \le h \le 10$	$-27 \le h \le 28$

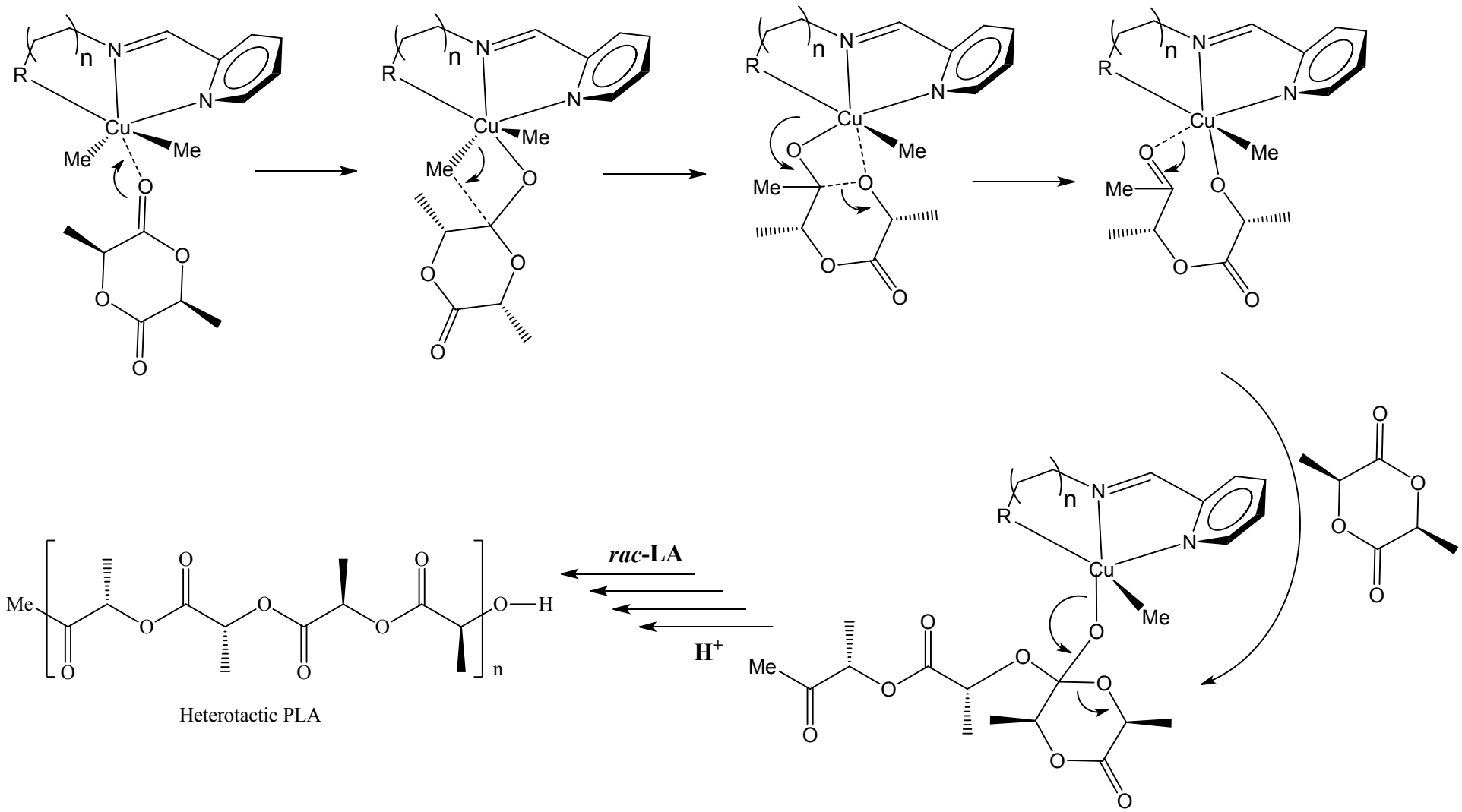
	$-9 \le k \le 9$	$-9 \le k \le 8$	$-13 \le k \le 13$	$-12 \le k \le 12$
	$-25 \le l \le 25$	$-25 \le l \le 23$	$-17 \le l \le 17$	$-11 \le l \le 11$
Reflections collected	9052	10348	7894	14302
Independent reflections	3086 [R(int) = 0.1035]	3615 [R(int) = 0.0675]	4278 [R(int) = 0.0234]	4258 [R(int) = 0.0763]
Completeness to theta	92.5 % (22.210°)	99.5 % (28.35°)	95.5 % (21.469°)	99.6 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3086 / 6 / 107	3615 / 0 / 172	4278 / 0 / 156	4258 / 0 / 147
Goodness-of-fit on F^2	1.077	1.110	1.093	1.083
Final R indices [I>2sigma(I)]	$R_1 = 0.0564$	$R_1 = 0.0512$	$R_1 = 0.0302$	$R_1 = 0.0360$
	$wR_2 = 0.1579$	$wR_2 = 0.0918$	$wR_2 = 0.0874$	$wR_2 = 0.1027$
R indices (all data)	$R_1 = 0.0573$	$R_1 = 0.1169$	$R_1 = 0.0305$	$R_1 = 0.0372$
	$wR_2 = 0.1587$	$wR_2 = 0.1519$	$wR_2 = 0.0878$	$wR_2 = 0.1038$
Largest diff. peak and hole (e.Å^{-3})	1.625 and -1.622	1.094 and -1.740	0.585 and -0.962	0.941 and -1.058

2

Table S2

$[L_BCu(\mu–Cl)Cl]_2$		$[L_CCuCl_2]$		$[L_ECuCl_2]$		$[L_FCuCl_2]$	
Bond lengths (Å)							
Cu(1)-N(1)	2.032(2)	Cu(1)-N(3)	2.041(5)	Cu(1)-N(1)	2.0652(1)	Cu(1)-N(1)	2.0332(1)
Cu(1)-N(2)	2.039(2)	Cu(1)-N(2)	1.967(5)	Cu(1)-N(2)	2.0341(1)	Cu(1)-N(2)	2.0449(1)
Cu(1)-Cl(2)	2.2625(8)	Cu(1)-N(1)	2.088(5)	Cu(1)-N(3)	2.1163(1)	Cu(1)-Cl(2)	2.2605(5)
Cu(1)-Cl(1)	2.2724(9)	Cu(1)-Cl(2)	2.2379(2)	Cu(1)-Cl(2)	2.2860(7)	Cu(1)-Cl(1)	2.2609(6)
N(2)-C(7)	1.465(3)	Cu(1)-Cl(1)	2.5855(2)	Cu(1)-Cl(1)	2.4659(1)	N(2)-C(7)	1.4700(2)
N(1)-C(1)	1.336(3)	C(13)-N(3)	1.330(7)	N(1)-C(1)	1.3364(2)	N(1)-C(1)	1.3366(2)
N(1)-C(5)	1.357(3)	C(9)-N(3)	1.363(7)	N(1)-C(5)	1.3547(2)	N(1)-C(5)	1.3503(2)
N(2)-C(6)	1.278(3)	N(2)-C(8)	1.269(7)	N(2)-C(6)	1.2751(2)	N(2)-C(6)	1.2703(2)
Bond angles (°)							
N(1)-Cu(1)-N(2)	80.16(9)	N(2)-Cu(1)-N(3)	79.06(2)	N(2)-Cu(1)-N(1)	78.89(5)	N(1)-Cu(1)-N(2)	79.98(5)
N(1)-Cu(1)-Cl(2)	170.10(6)	N(3)-Cu(1)-Cl(2)	96.93(1)	N(1)-Cu(1)-Cl(2)	89.61(4)	N(1)-Cu(1)-Cl(2)	170.23(3)
N(2)-Cu(1)-Cl(2)	94.05(7)	N(2)-Cu(1)-Cl(2)	156.81(2)	N(2)-Cu(1)-Cl(2)	156.49(4)	N(2)-Cu(1)-Cl(2)	94.69(4)
N(1)-Cu(1)-Cl(1)	92.36(6)	N(3)-Cu(1)-Cl(1)	94.49(1)	N(1)-Cu(1)-Cl(1)	101.86(4)	N(1)-Cu(1)-Cl(1)	92.69(4)
N(2)-Cu(1)-Cl(1)	172.43(7)	N(2)-Cu(1)-Cl(1)	100.44(2)	N(2)-Cu(1)-Cl(1)	96.93(4)	N(2)-Cu(1)-Cl(1)	167.84(3)
Cl(2)-Cu(1)-Cl(1)	93.52(3)	Cl(2)-Cu(1)-Cl(1)	102.65(6)	Cl(2)-Cu(1)-Cl(1)	105.53(3)	Cl(2)-Cu(1)-Cl(1)	93.88(3)
C(1)-N(1)-C(5)	118.5(2)	N(3)-Cu(1)-N(1)	159.69(2)	N(1)-Cu(1)-N(3)	160.41(4)	C(1)-N(1)-C(5)	118.10(1)
C(1)-N(1)-Cu(1)	127.88(2)	N(2)-Cu(1)-N(1)	82.08(2)	N(2)-Cu(1)-N(3)	92.36(5)	C(1)-N(1)-Cu(1)	128.06(1)
C(5)-N(1)-Cu(1)	113.50(2)	N(1)-Cu(1)-Cl(2)	97.43(1)	N(3)-Cu(1)-Cl(2)	91.92(4)	C(5)-N(1)-Cu(1)	113.76(9)
C(6)-N(2)-C(7)	119.0(2)	N(1)-Cu(1)-Cl(1)	96.30(2)	N(3)-Cu(1)-Cl(1)	96.55(4)	C(6)-N(2)-C(7)	118.89(1)

Scheme S1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