Supporting Information

for

Stoichiometric Sensitivity and Structural Diversity in Click-Active Copper(I) N,S-Heterocyclic Carbene Complexes

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Table S1. Selected bond lengths (Å) for **1-7**

	1		**2a**		**2b**		**3**
Cu(1)…Cu(1A)	3.400	Cu(1)…Cu(2)	3.320	Cu(1)…Cu(2)	3.248	Cu(1)…Cu(2)	2.5626(7)
Cu(1)-C(1)	1.887(4)	Cu(1)-C(1)	1.900(2)	Cu(1)-C(1)	1.901(4)	Cu(1)-C(1)	1.926(4)
Cu(1)-Br(1)	2.3037(8)	Cu(2)-C(2)	1.910(3)	Cu(2)-C(2)	1.913(5)	Cu(2)-C(2)	1.932(4)
Cu(1)-Br(1A)	2.772(1)	Cu(1)-Br(1)	2.4030(5)	Cu(1)-Br(1)	2.4396(7)	Cu(1)-I(1)	2.6329(6)
–	–	Cu(1)-Br(2)	2.4482(5)	Cu(1)-Br(2)	2.4155(8)	Cu(1)-I(2)	2.6506(6)
–	–	Cu(2)-Br(1)	2.4608(5)	Cu(2)-Br(1)	2.4263(8)	Cu(2)-I(1)	2.6350(5)
–	–	Cu(2)-Br(2)	2.6867(5)	Cu(2)-Br(2)	2.6435(8)	Cu(2)-I(2)	2.8649(5)
–	–	Cu(2)-Br(2A)	2.5828(5)	Cu(2)-Br(2A)	2.7138(9)	Cu(1)-I(2A)	3.0456(6)
	4		**5a**		**5b**	Cu(2)-I(2A)	2.7835(6)
Cu(1)…Cu(2)	2.9964(8)	Cu(1)…Cu(2)	2.6338(6)	Cu(1)…Cu(2)	2.9099(7)		**6**
Cu(1)-C(1)	1.869(5)	Cu(1)-C(1)	1.899(3)	Cu(1)-C(1)	1.917(4)	Cu(1)-C(1)	1.904(3)
Cu(2)-C(2)	1.852(5)	Cu(2)-C(2)	1.914(3)	Cu(2)-C(2)	1.917(4)	Cu(2)-C(2)	1.924(3)
Cu(1)-Br(1)	2.7460(9)	Cu(2)-C(3)	1.931(3)	Cu(2)-C(3)	1.925(4)	Cu(1)-Br(1)	2.5146(5)
Cu(1)-O(1)	1.874(3)	Cu(1)-Br(1)	2.4343(5)	Cu(1)-Br(1)	2.4749(6)		**7**
Cu(2)-Br(1)	2.600(1)	Cu(1)-Br(2)	2.4538(5)	Cu(1)-Br(2)	2.3727(6)	Cu(1)…Cu(1A)	3.4725(7)
Cu(2)-O(1)	1.907(3)	Cu(2)-Br(1)	2.5794(5)	Cu(2)-Br(1)	2.7085(6)	Cu(1)-C(1)	1.925(3)
C(1)-Cu(1)-Br(1)	109.6(2)	Cu(2)-Br(2)	2.7097(5)	Cu(2)-Br(2)	2.6947(6)	Cu(1)-C(2)	1.923(3)
C(1)-Cu(1)-O(1)	161.5(2)	Br(1)-Cu(1)-Br(2)	101.60(2)	Br(1)-Cu(1)-Br(2)	110.43(2)	Cu(1)-I(1)	2.8594(5)
O(1)-Cu(1)-Br(1)	88.4(1)	–	–	–	–	Cu(1)-I(1A)	2.8331(5)
O(1)-Cu(2)-C(2)	154.6(2)	Br(1)-Cu(2)-Br(2)	91.45(2)	Br(1)-Cu(2)-Br(2)	94.94(2)	–	–
Br(1)-Cu(2)-C(2)	112.9(2)	Cu(1)-Br(1)-Cu(2)	63.30(2)	Cu(1)-Br(1)-Cu(2)	68.13(2)	–	–

Table S2. Selected crystal data, data collection and refinement parameters of compounds **1-7**

compound	**1**	**2a**	**2b**
Formula	$C_{20}H_{18}Br_2Cu_2N_2S_2$	$C_{40}H_{44}Br_4Cu_4N_4S_4$	$C_{44}H_{44}Br_4Cu_4N_4S_4$
formula weight	637.38	1282.83	1330.87
Crystal size/mm	0.30 × 0.10 × 0.04	0.70 × 0.34 × 0.14	0.40 × 0.36 × 0.10
temperature/K	293(2)	295(2)	223(2)
Crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	P2(1)/n
a/Å	7.8242(10)	9.5728(7)	11.1913(8)
b/Å	8.0124(11)	10.8961(8)	15.8654(11)
c/Å	9.5144(12)	11.5350(8)	13.3763(9)
α/°	94.764(3)	75.9430(10)	90
β/°	95.869(3)	89.9310(10)	93.003(2)
γ/°	110.659(2)	74.7520(10)	90

V/Å^3	550.62(12)	1123.53(14)	2371.8(3)
Z	1	1	2
D_c/g cm^{-3}	1.922	1.896	1.864
radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ/mm^{-1}	5.758	5.644	5.351
θ range/º	2.17 to 27.49	1.82 to 27.50	1.99 to 27.49
No. of unique reflections Measured	2512	5150	5430
max., min. transmission	0.8024 and 0.2770	0.5054 and 0.1100	0.6167 and 0.2234
final R indices [I >2σ(I)] [a, b]	R_1 = 0.0409, wR_2 = 0.1122	R_1 = 0.0325, wR_2 = 0.0875	R_1 = 0.0466, wR_2 = 0.1071
R indices (all data)	R_1 = 0.0571, wR_2 = 0.1375	R_1 = 0.0410, wR_2 = 0.0911	R_1 = 0.0775, wR_2 = 0.1196
Goodness-of-fit on F^2 [c]	1.075	1.057	0.966
large diff peak and hole, e Å^{-3}	0.701 and -0.464	0.403 and -0.702	1.027 and -0.375

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] GoF = $[(\Sigma\omega(|F_o| - |F_c|)^2/(N_{obs}-N_{param})]^{1/2}$

Table S2. (continued)

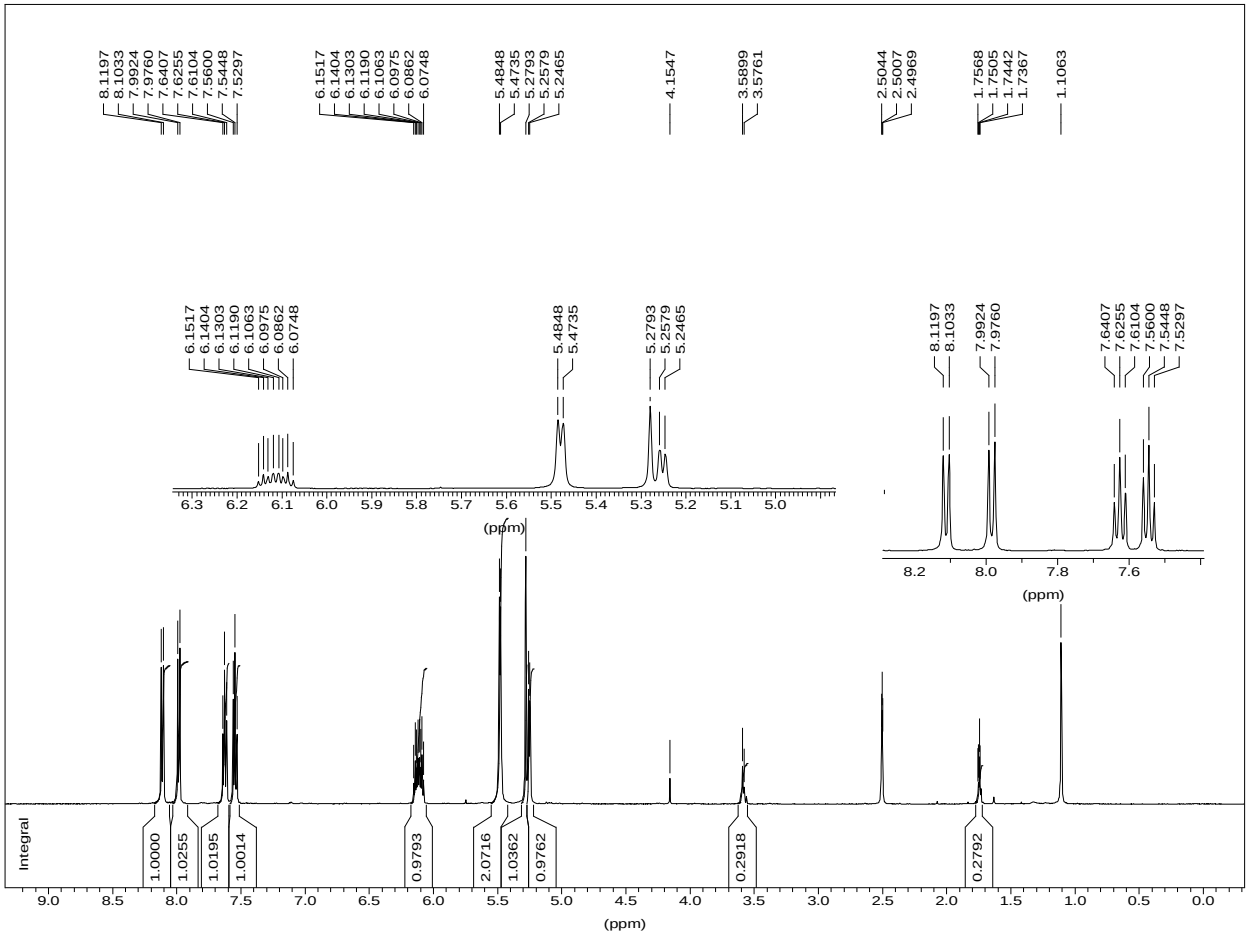
compound	**3**	**4**	**5a**
Formula	$C_{16}H_{14}Cu_2I_2N_2S_2$	$C_{26}H_{31}BrCu_2N_2OS_2$	$C_{30}H_{27}Br_2Cu_2N_3S_3$
formula weight	679.29	658.64	812.63
Crystal size/mm	0.32 × 0.26 × 0.12	0.30 × 0.10 × 0.06	0.50 × 0.16 × 0.06
temperature/K	100(2)	295(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
space group	P2(1)/c	P2(1)/c	P-1
a/Å	8.5427(5)	9.3023(6)	8.9738(3)
b/Å	16.1539(9)	21.4109(15)	18.1681(7)
c/Å	14.0458(8)	14.8244(9)	18.9695(7)
α/º	90	90	95.1390(10)
β/º	96.0100(10)	96.819(2)	92.8190(10)
γ/º	90	90	98.3760(10)
V/Å^3	1927.64(19)	2931.7(3)	3041.36(19)
Z	4	4	4
D_c/g cm^{-3}	2.341	1.492	1.775
radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ/mm^{-1}	5.627	2.976	4.258
θ range/º	1.93 to 27.44	1.68 to 27.50	1.08 to 27.49
No. of unique reflections Measured	4404	6713	13959
max., min. transmission	0.5516 and 0.2661	0.8416 and 0.4688	0.7842 and 0.2246
final R indices [I >2σ(I)] [a, b]	R_1 = 0.0293, wR_2 = 0.0676	R_1 = 0.0577, wR_2 = 0.1549	R_1 = 0.0362, wR_2 = 0.0826
R indices (all data)	R_1 = 0.0322, wR_2 = 0.0691	R_1 = 0.1113, wR_2 = 0.1776	R_1 = 0.0503, wR_2 = 0.0882
Goodness-of-fit on F^2 [c]	1.099	1.001	1.016
large diff peak and hole, e Å^{-3}	1.359 and -0.755	0.675 and -0.392	0.808 and -0.412

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] GoF = $[(\Sigma\omega(|F_o| - |F_c|)^2/(N_{obs}-N_{param})]^{1/2}$

^{1}H and ^{13}C NMR Spectra of **1**

1H AMX500

0318-Ally-Cu-DMSO



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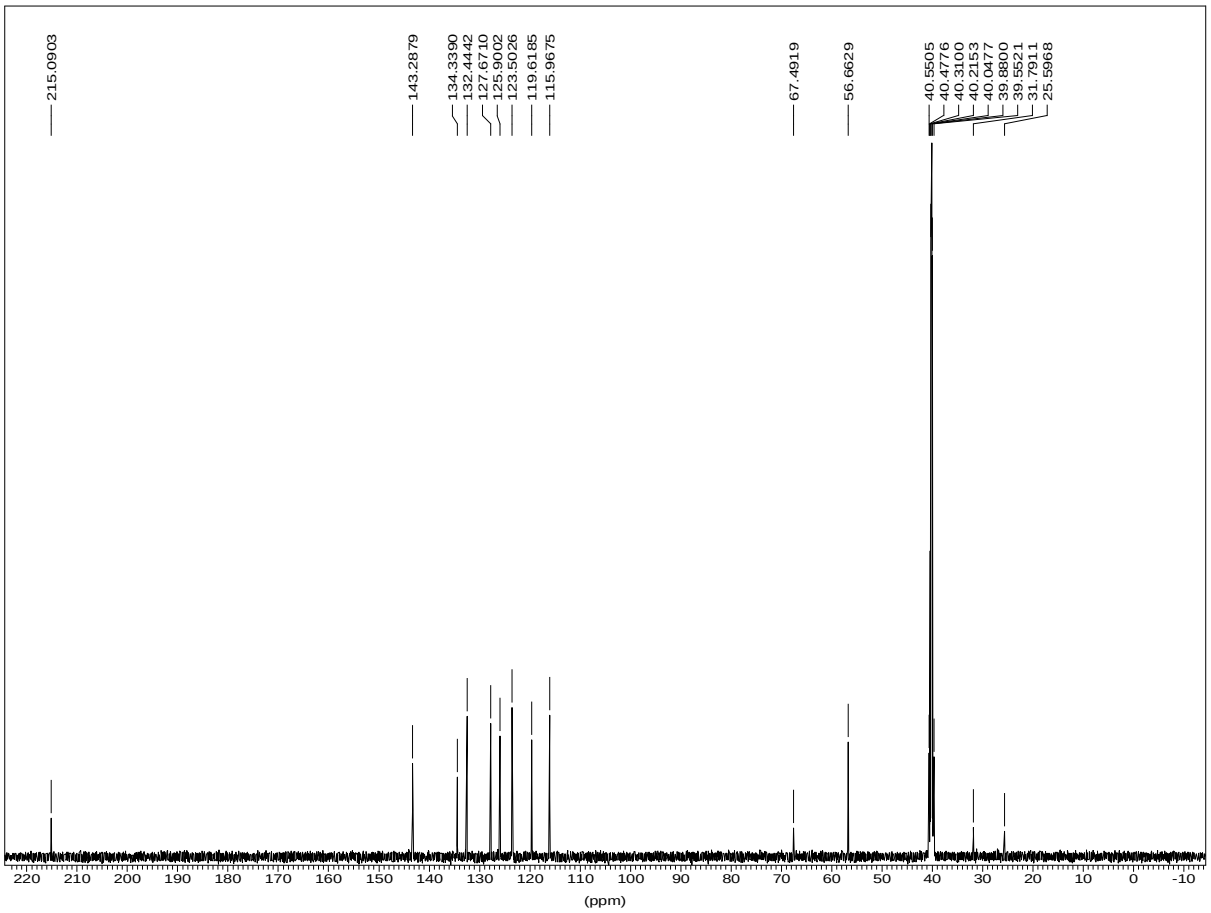

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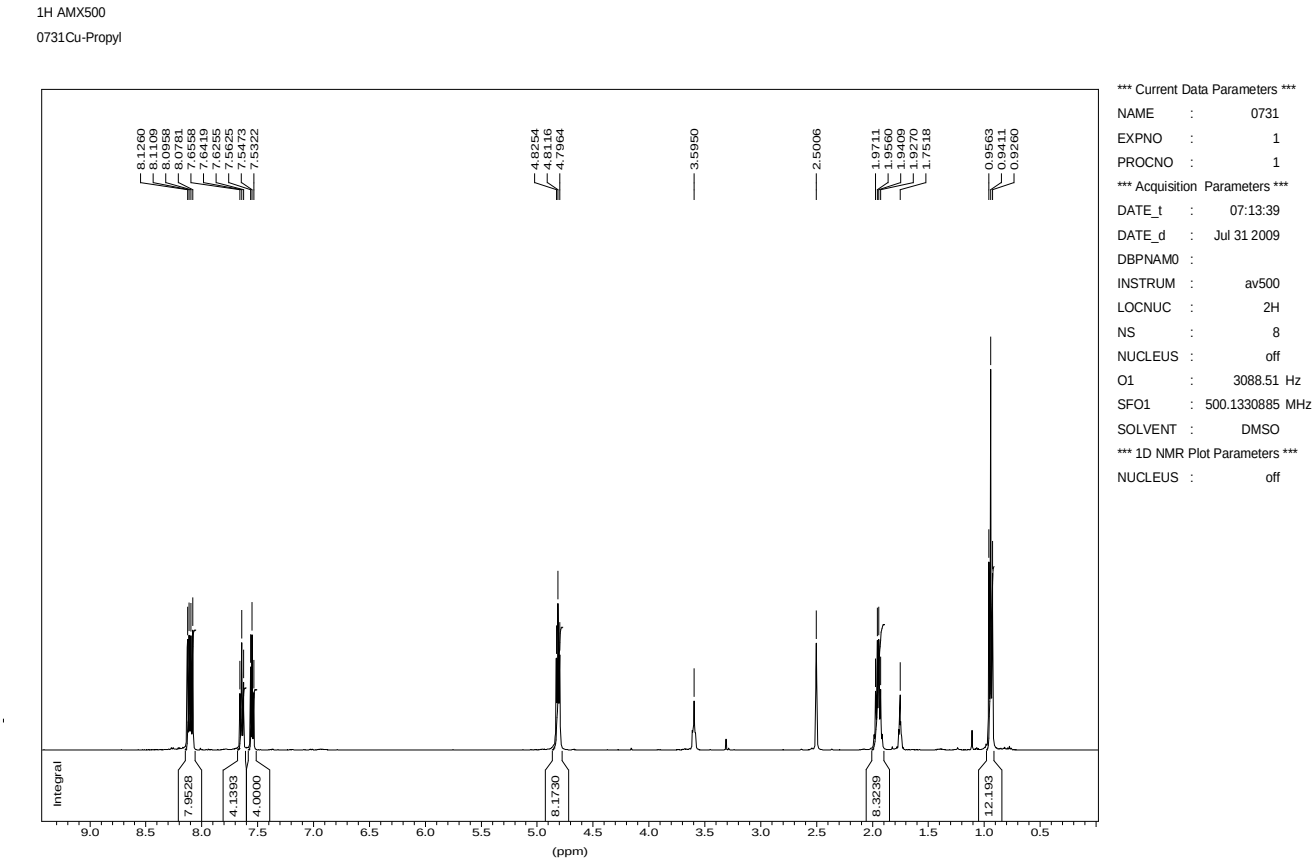
^{1}H and ^{13}C NMR Spectra of **2a**



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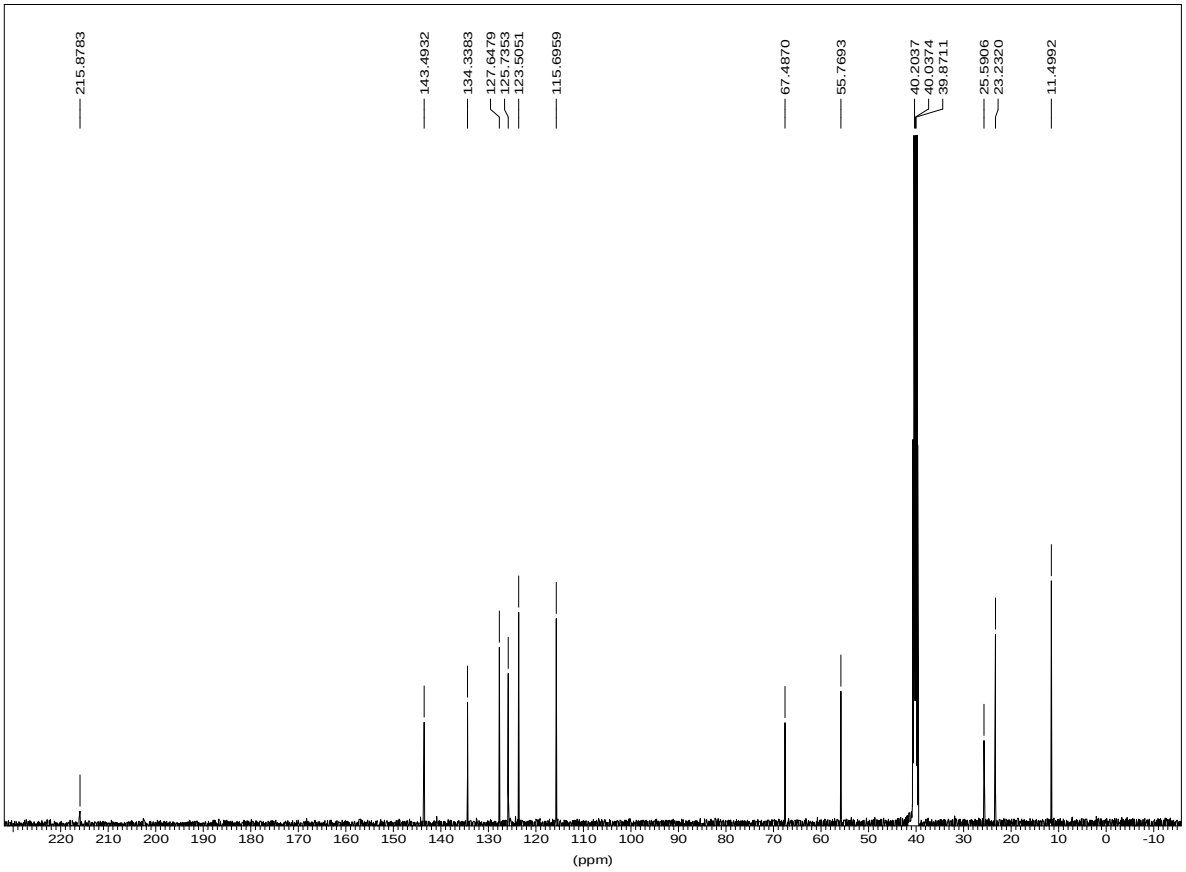

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^{1}H and ^{13}C NMR Spectra of **2b**

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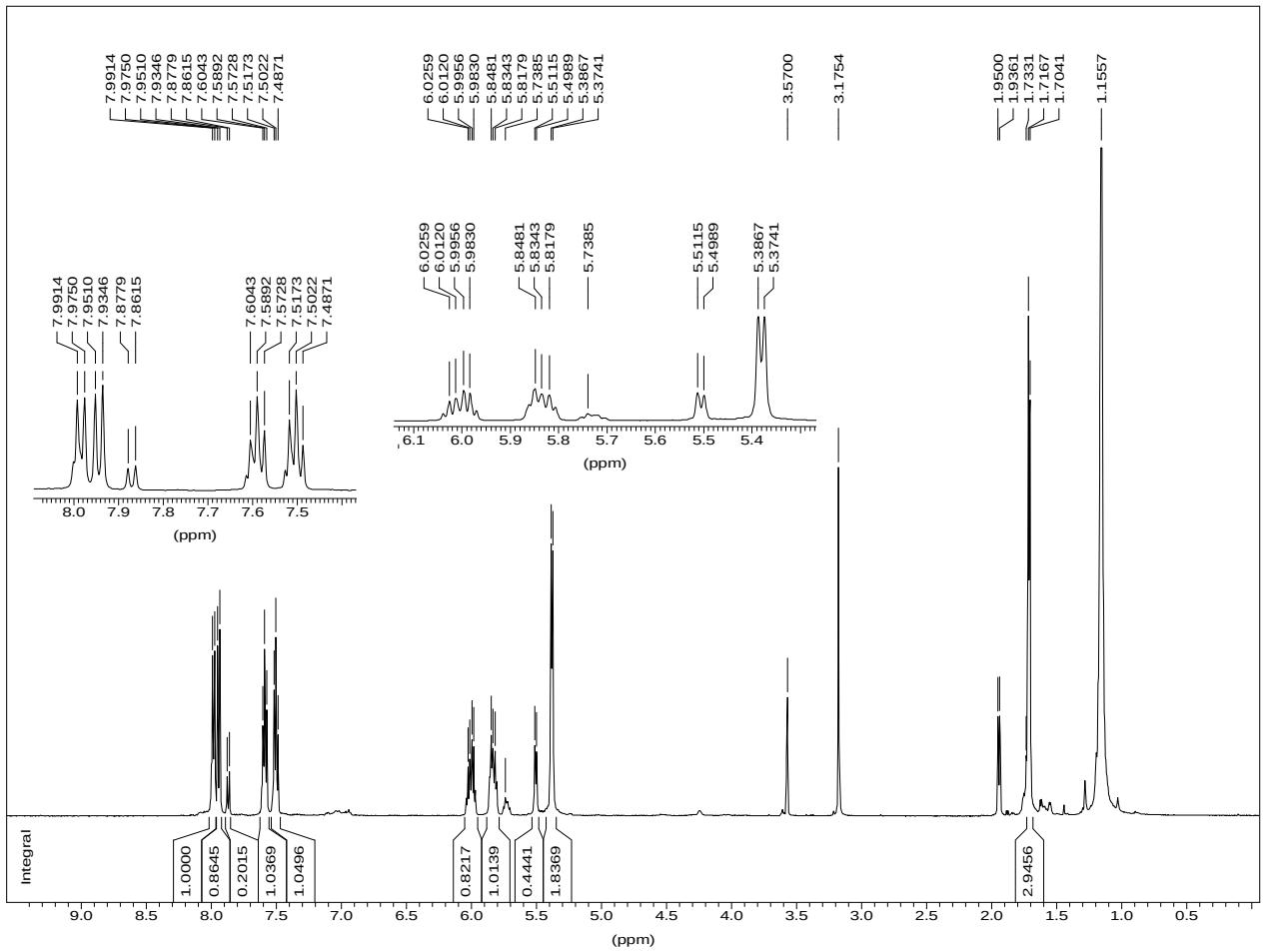

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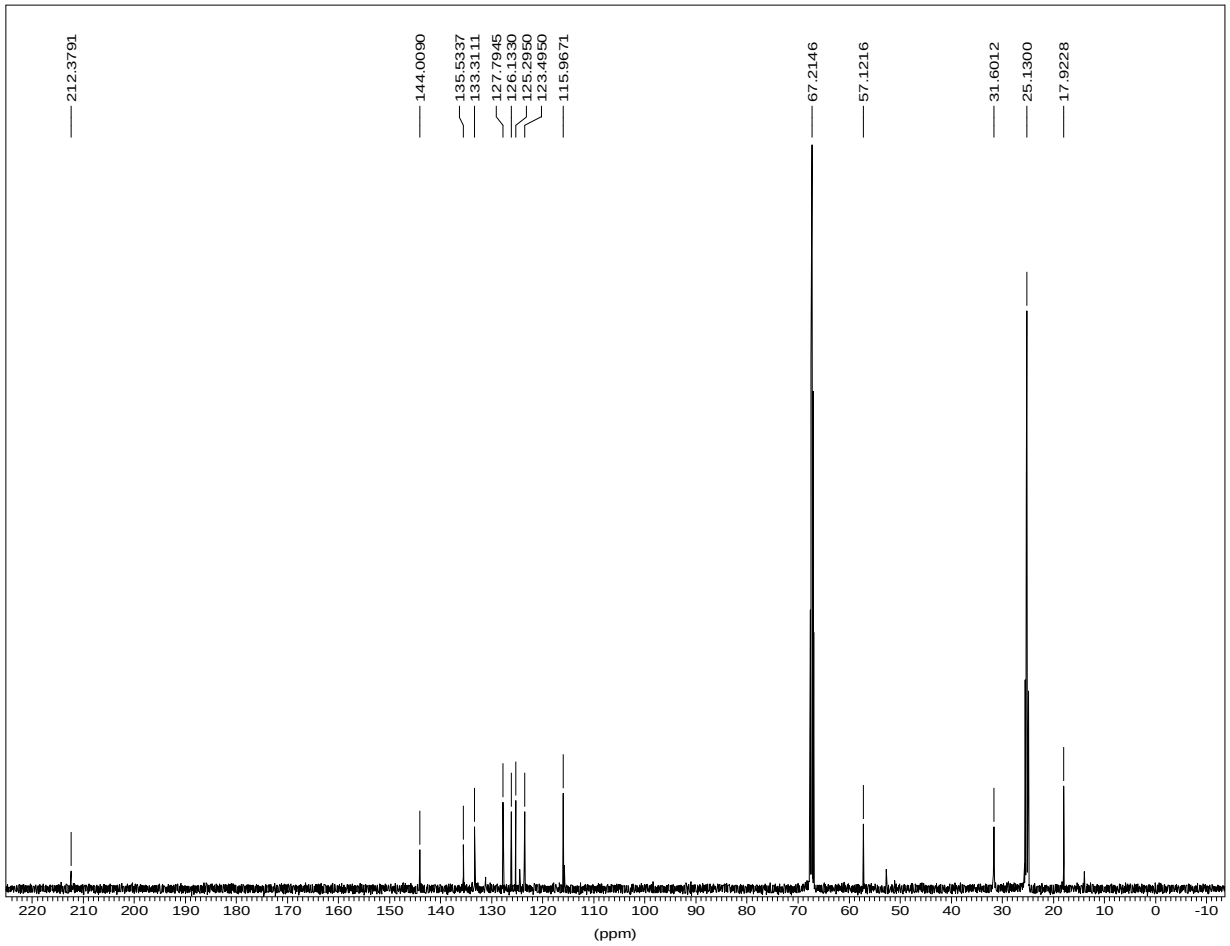

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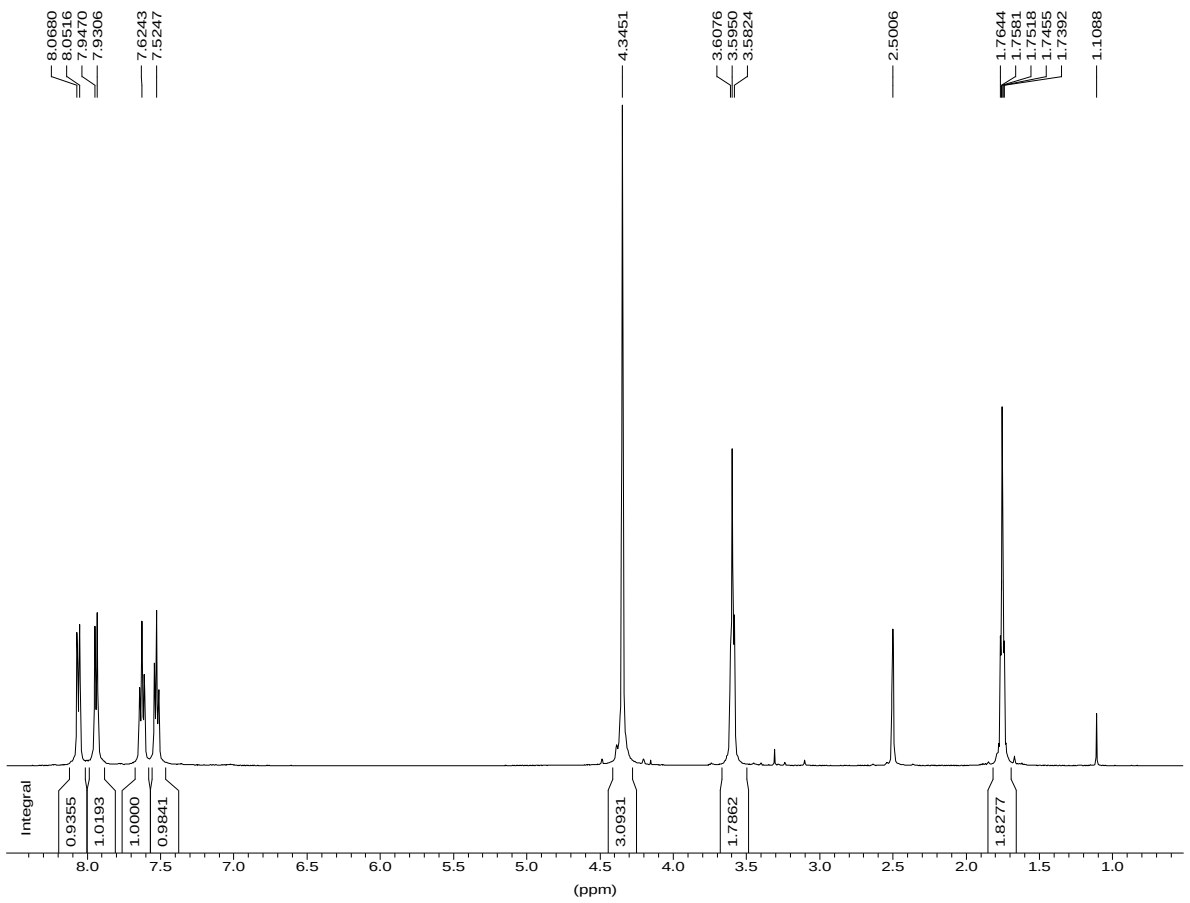
^{1}H and ^{13}C NMR Spectra of **3**

1H AMX500

05052-Cu-MeI-DMSO



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SOLVENT :

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TE :

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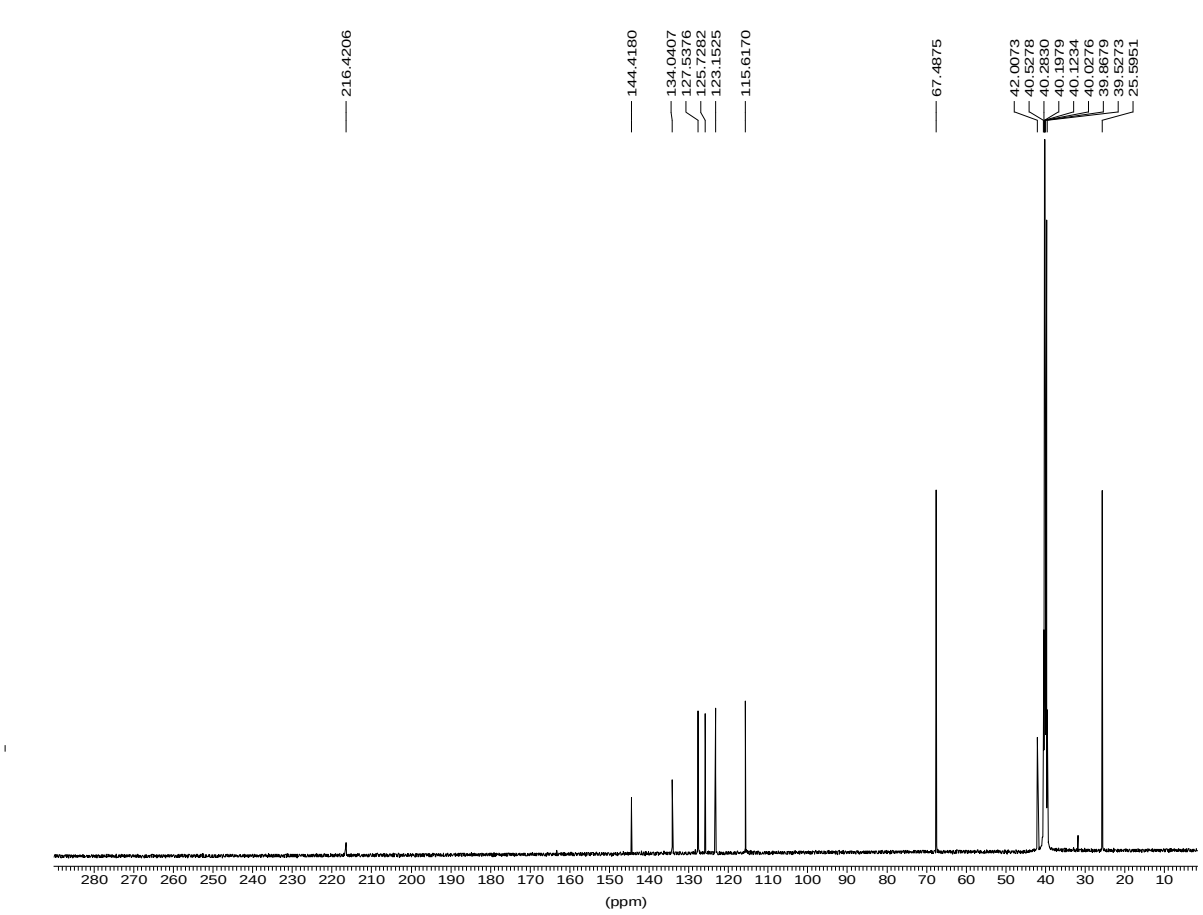
13C AMX500

05052-Cu-Mel-DMSO



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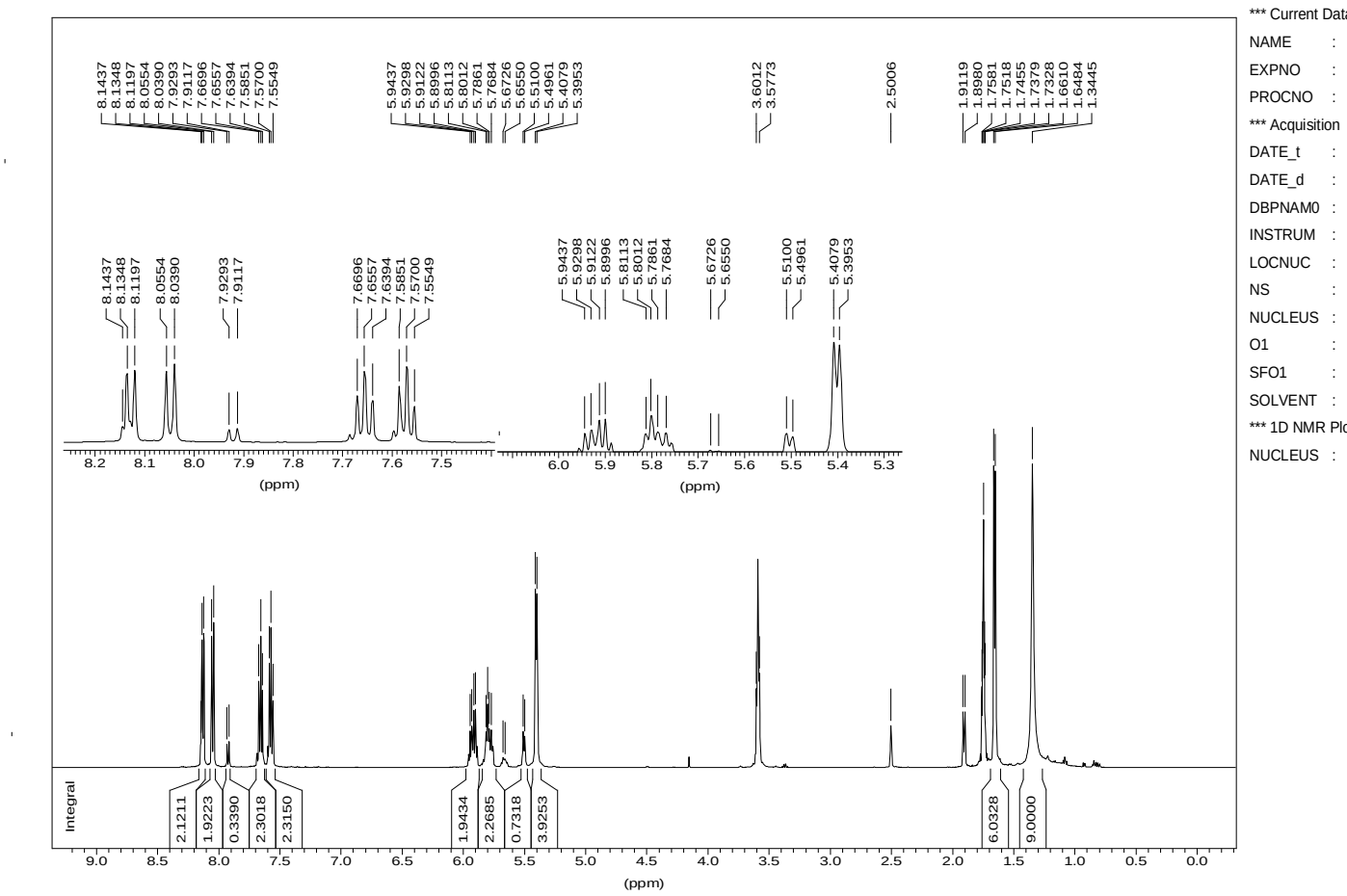
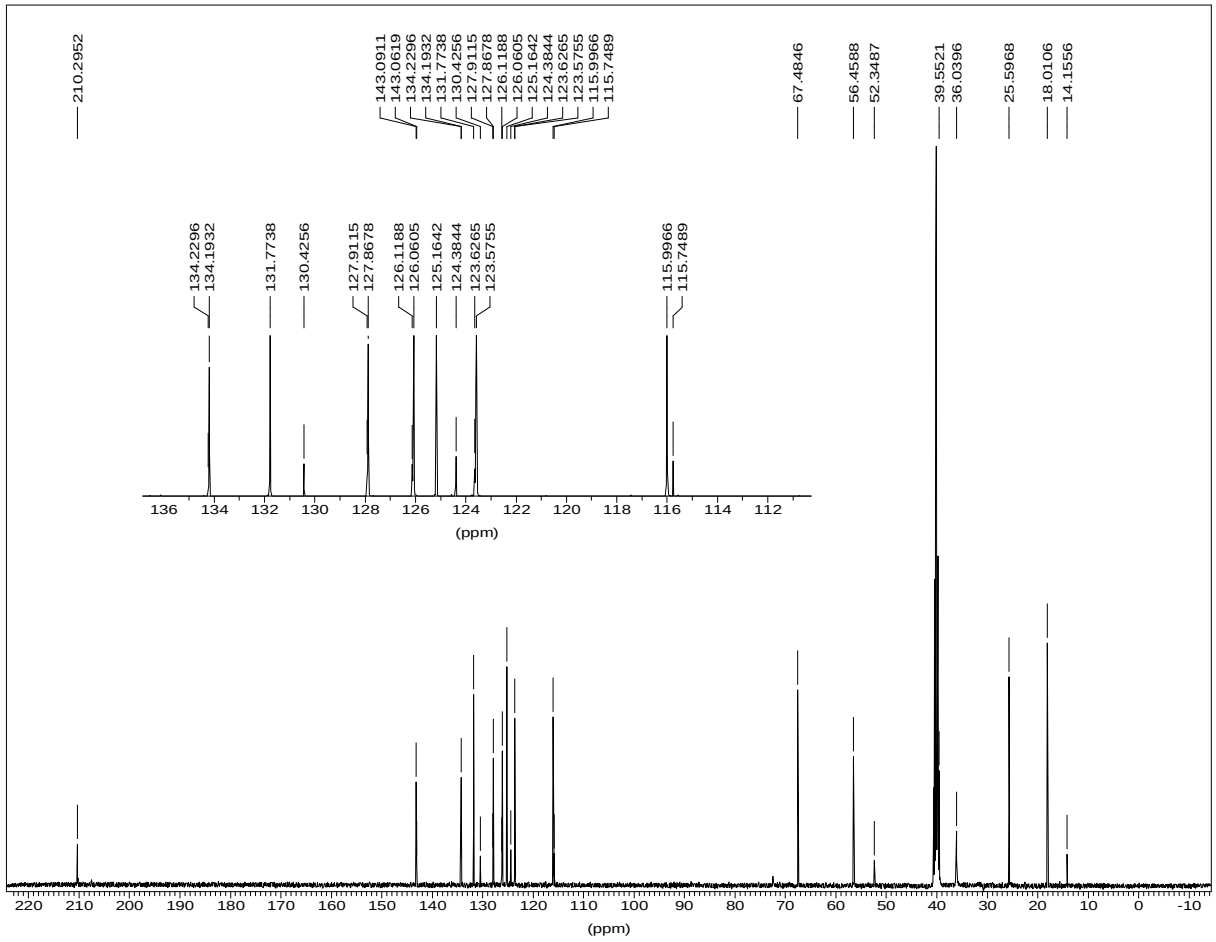
^{1}H and ^{13}C NMR Spectra of **4**



13C AMX500

0705-crotyl-OtBu



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O1 :

SFO1 : 12

SOLVENT :

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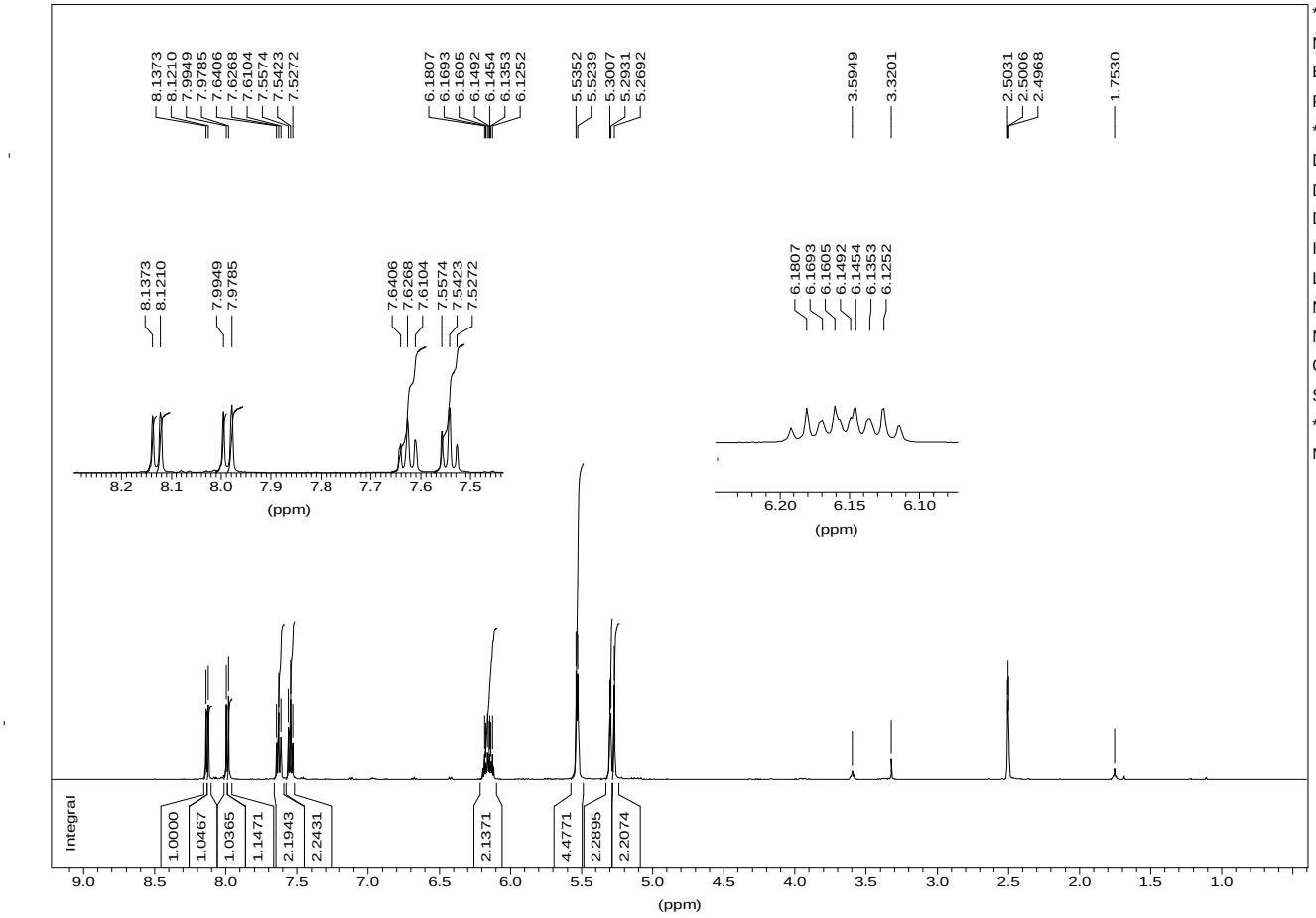
NUCLEUS :

^{1}H and ^{13}C NMR Spectra of **5a**

1H AMX500

090711-AllylBr-Cu=1:1- yellow reside



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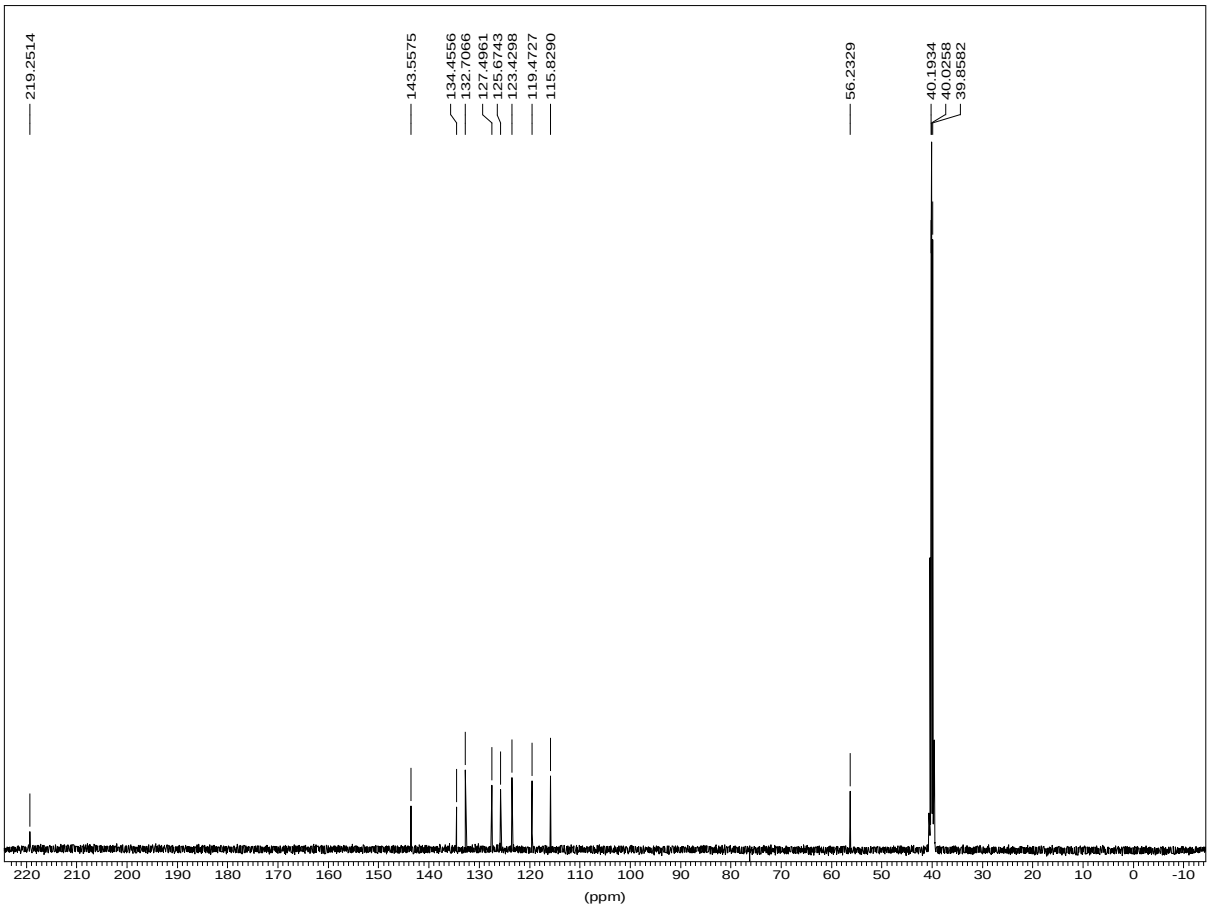

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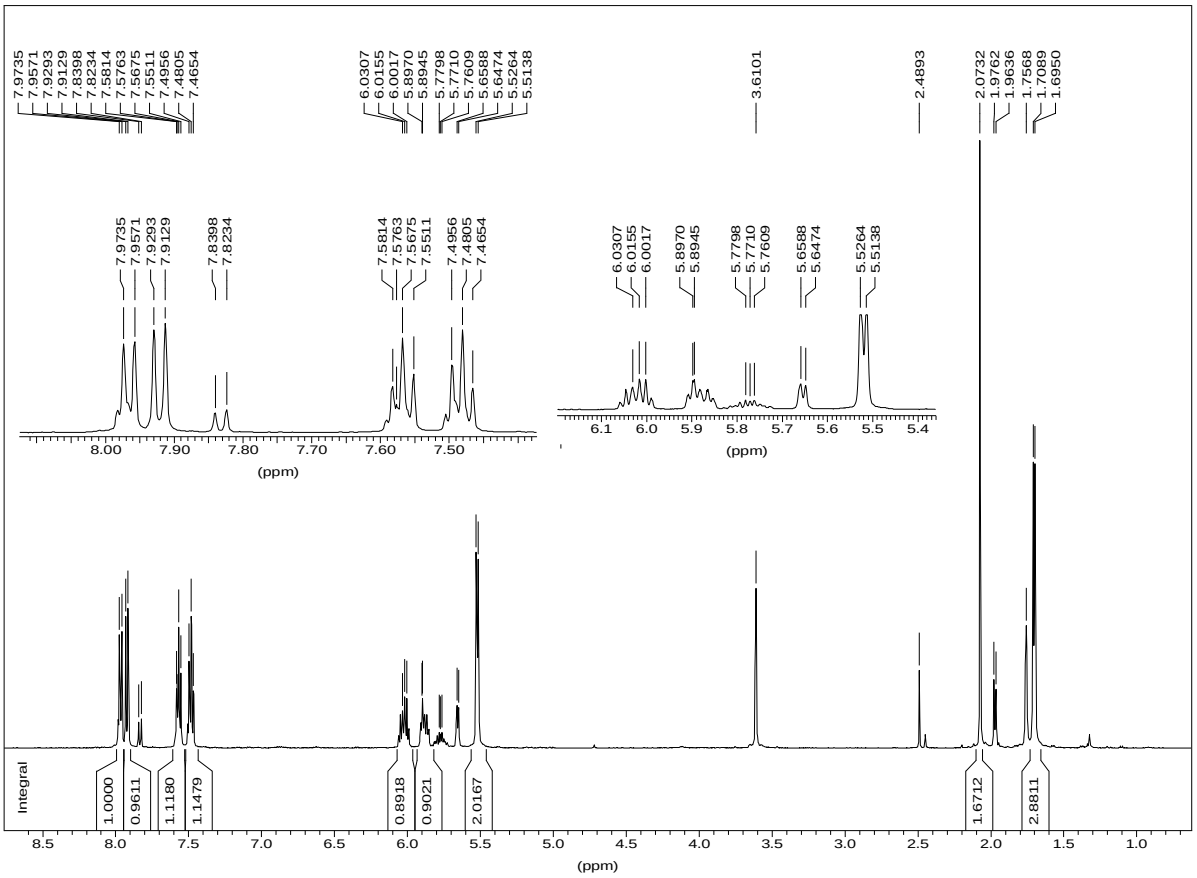
NUCLEUS :

^{1}H and ^{13}C NMR Spectra of **5b**

1H AMX500

0705-crotyl3-Cu2



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13C AMX500

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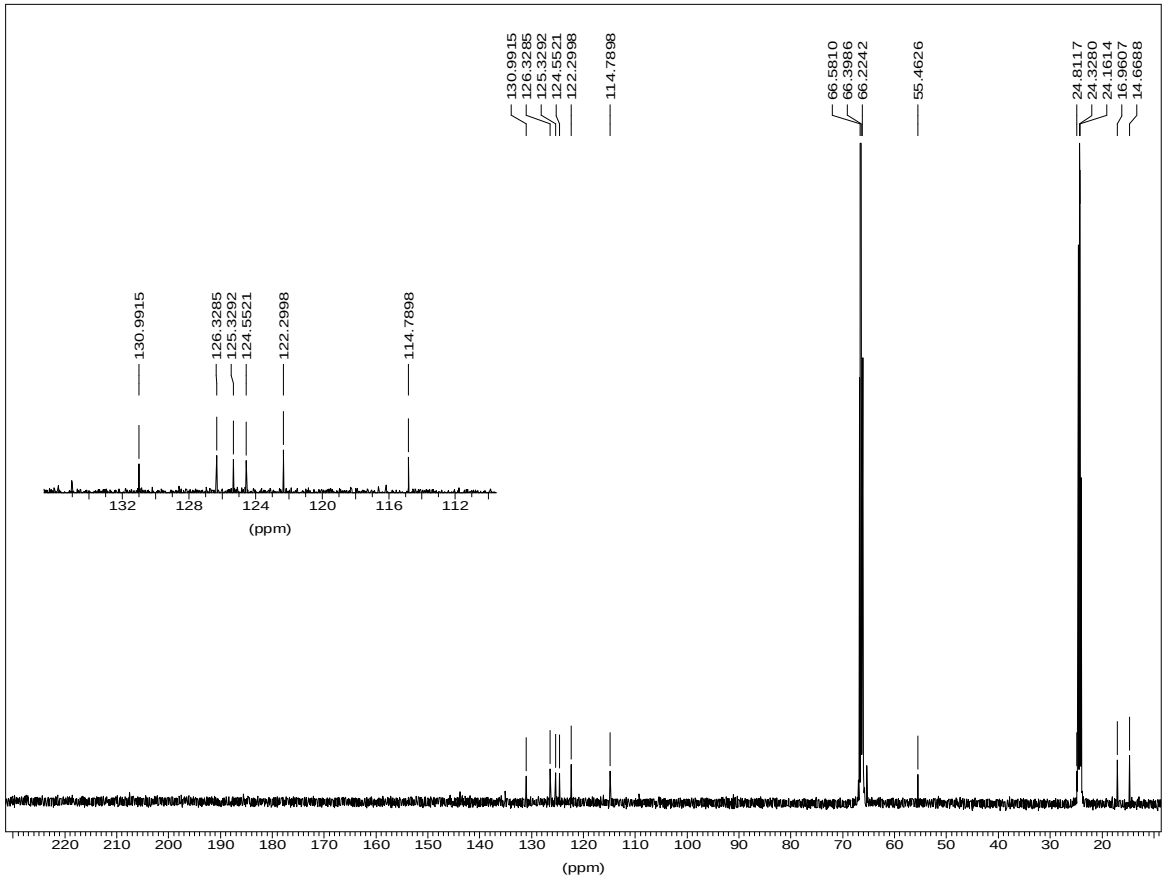

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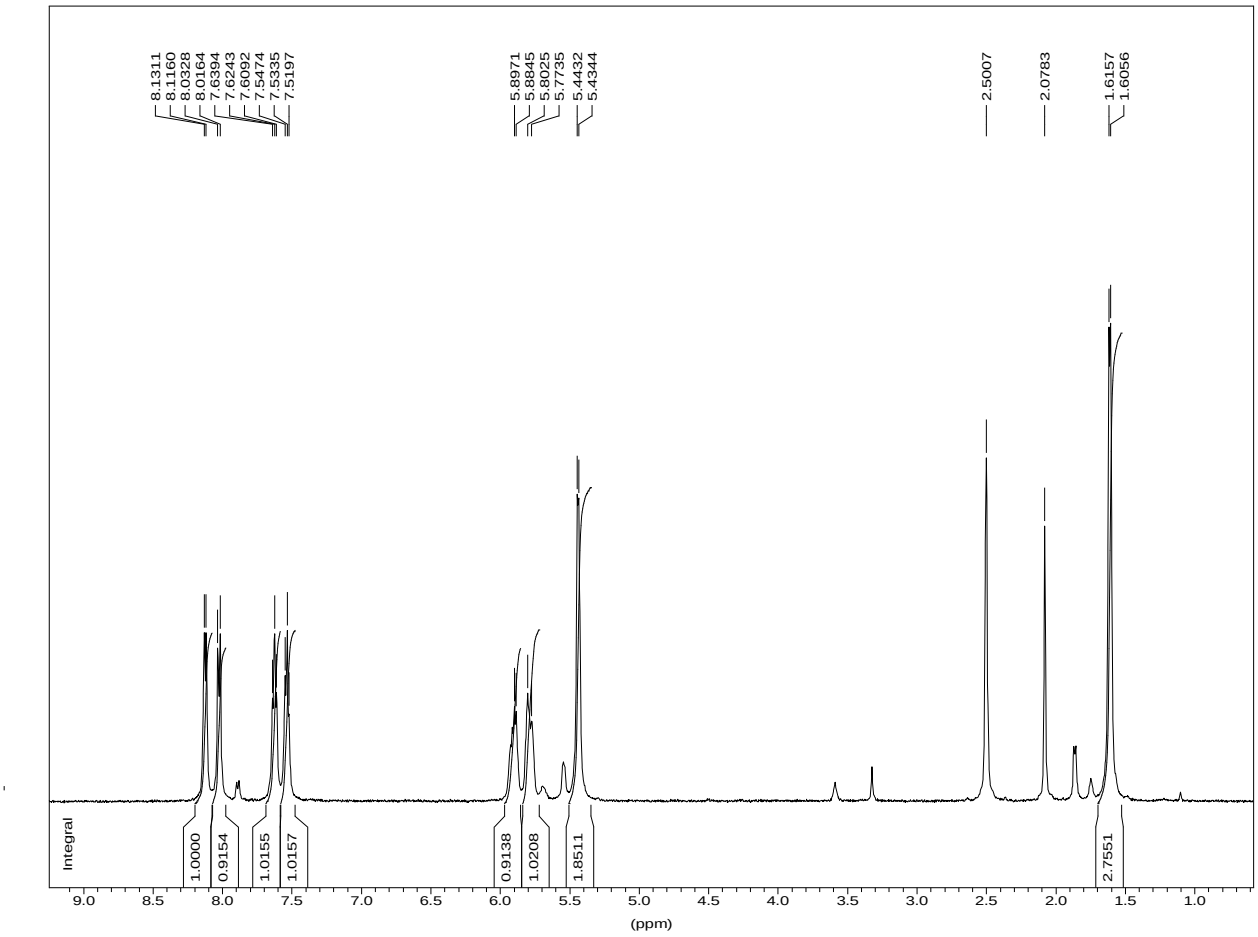
NUCLEUS :

^{1}H and ^{13}C NMR Spectra of **6**

1H AMX500

0713-CuOtBu-NatOBu-crotyl



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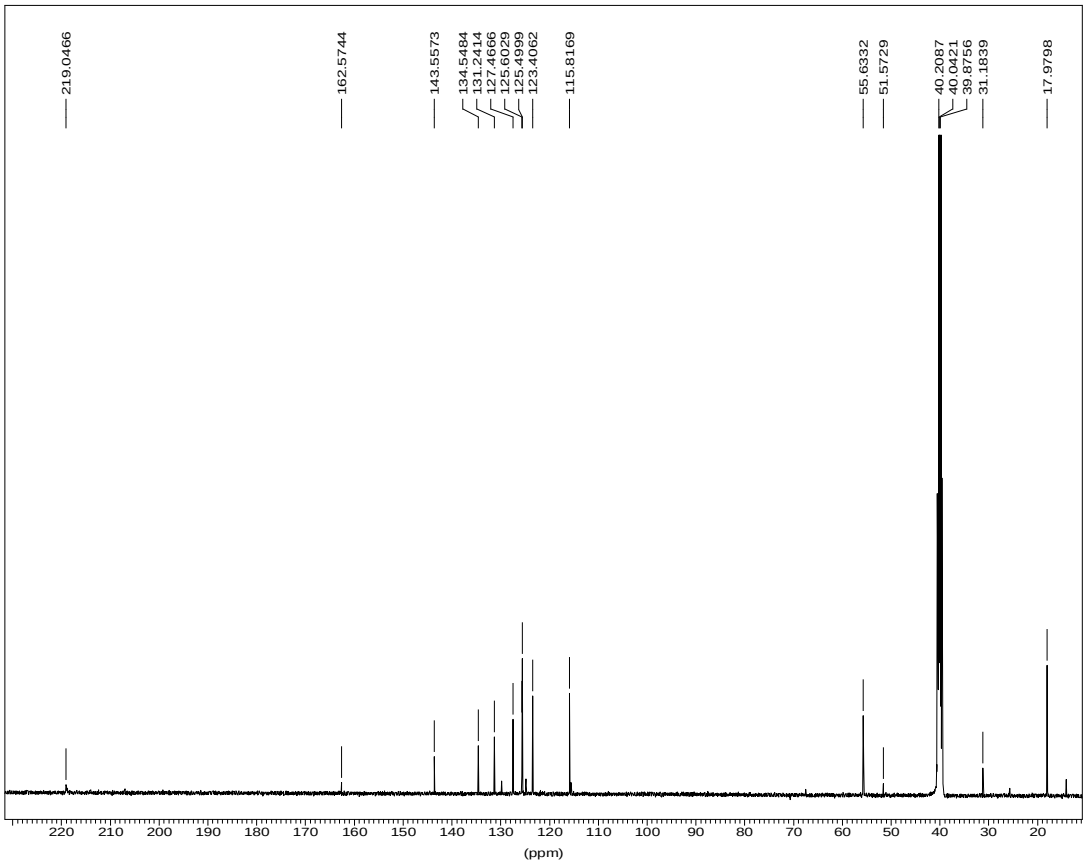
0713-CuOtBu-NatOBu-crotyl



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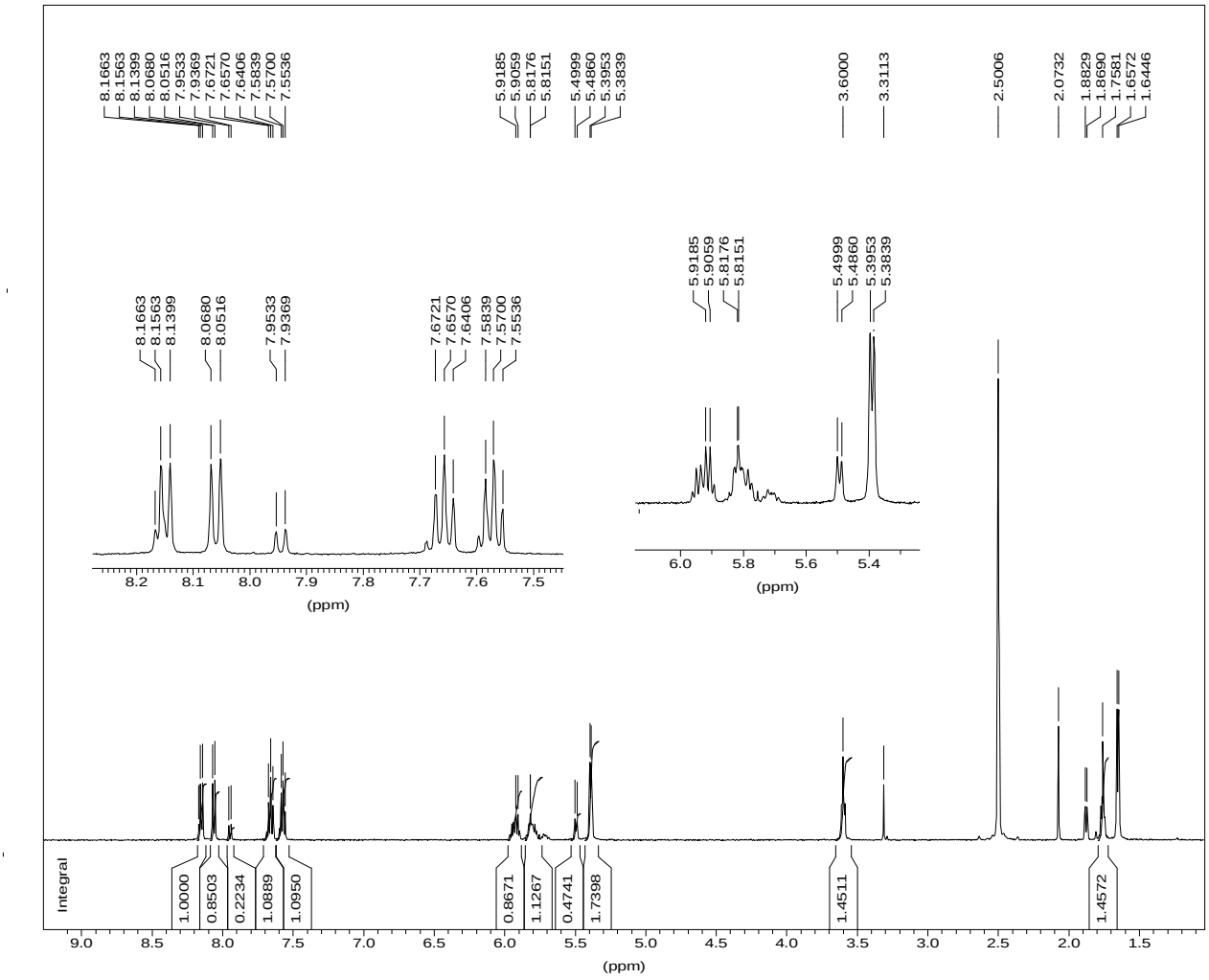
^{1}H and ^{13}C NMR Spectra of **7**

090711-allyl4-I-Cu2



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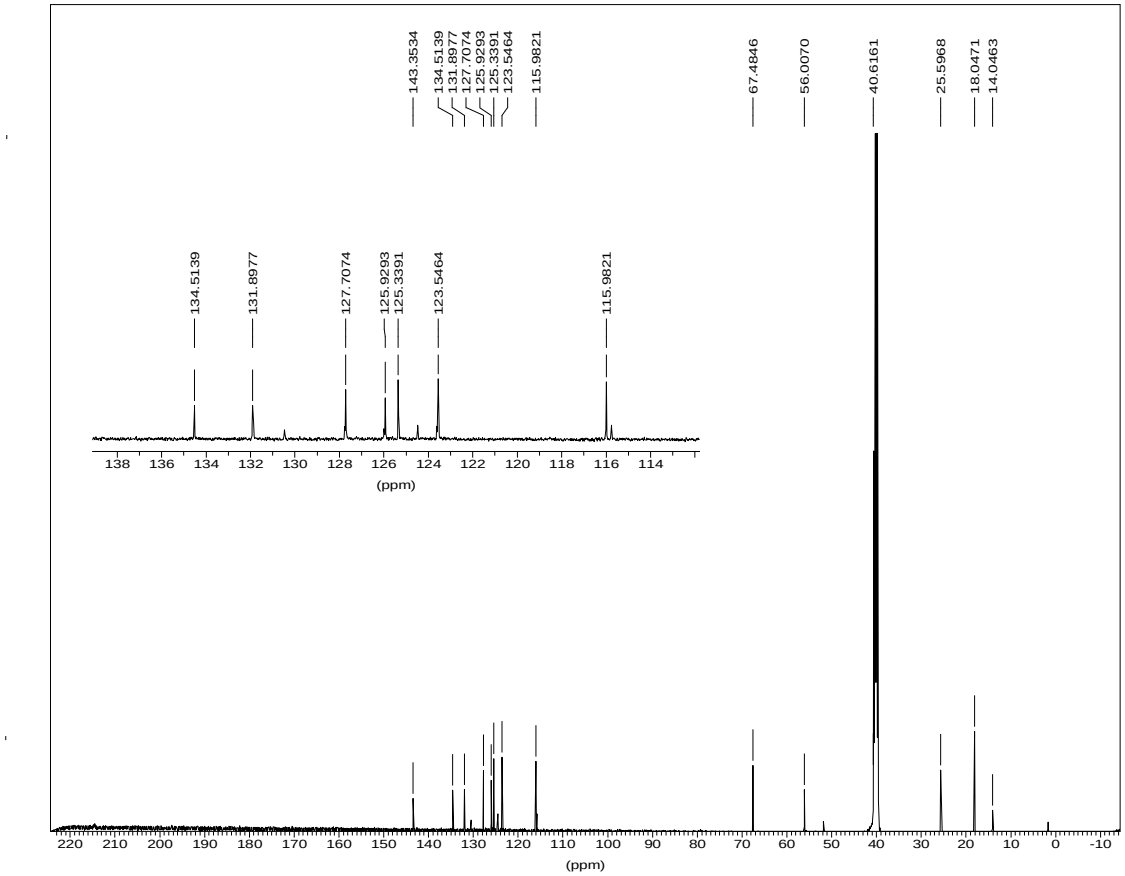
SFO1 :
*** 1D NMR Plo
NUCLEUS :



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*** 1D NMR Plot Parameters ***		
NUCLEUS	:	off

Electronic Supplementary Material (ESI) for Dalton Transactions

Table S2. (continued)

compound	**5b**	**6**	**7**
Formula	$C_{36}H_{39}Br_2Cu_2N_3OS_3$	$C_{22}H_{22}BrCuN_2S_2$	$C_{46}H_{48}Cu_2I_2N_4O_2S_4$
formula weight	912.78	521.99	1198.00
Crystal size/mm	0.20 × 0.08 × 0.06	0.40 × 0.06 × 0.06	0.36 × 0.21 × 0.06
temperature/K	223 (2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
space group	P2(1)/n	P2(1)/c	P-1
a/Å	8.9571(4)	12.0408(19)	8.8912(8)
b/Å	25.9573(11)	20.945(3)	9.9787(9)
c/Å	17.0010(8)	8.6404(14)	14.6609(13)
α/º	90	90	79.561(2)
β/º	100.6650(10)	99.034(3)	73.790(2)
γ/º	90	90	75.256(2)
V/Å^3	3884.5(3)	2152.0(6)	1199.39(19)
Z	4	4	1
D_c/g cm^{-3}	1.561	1.611	1.659
radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ/mm^{-1}	3.345	3.076	2.389
θ range/º	1.57 to 27.50	1.71 to 27.49	1.46 to 27.50
No. of unique reflections Measured	8913	4939	5463
max., min. transmission	0.8245 and 0.5543	0.8369 and 0.3725	0.8699 and 0.4801
final *R* indices [$I > 2\sigma(I)$] [a, b]	R_1 = 0.0462, wR_2 = 0.0972	R_1 = 0.0346, wR_2 = 0.0854	R_1 = 0.0357, wR_2 = 0.0952
R indices (all data)	R_1 = 0.0777, wR_2 = 0.1082	R_1 = 0.0433, wR_2 = 0.0954	R_1 = 0.0416, wR_2 = 0.1034
Goodness-of-fit on F^2 [c]	0.969	1.096	1.086
large diff peak and hole, e Å^{-3}	0.790 and -0.357	0.802 and -0.472	1.844 and -0.860

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] GoF $= [(\Sigma\omega(|F_o| - |F_c|)^2/(N_{obs}-N_{param})]^{1/2}$