Supporting Information

In Situ Generation of Novel Acyclic Diaminocarbene-Copper Complex

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CONTENTS

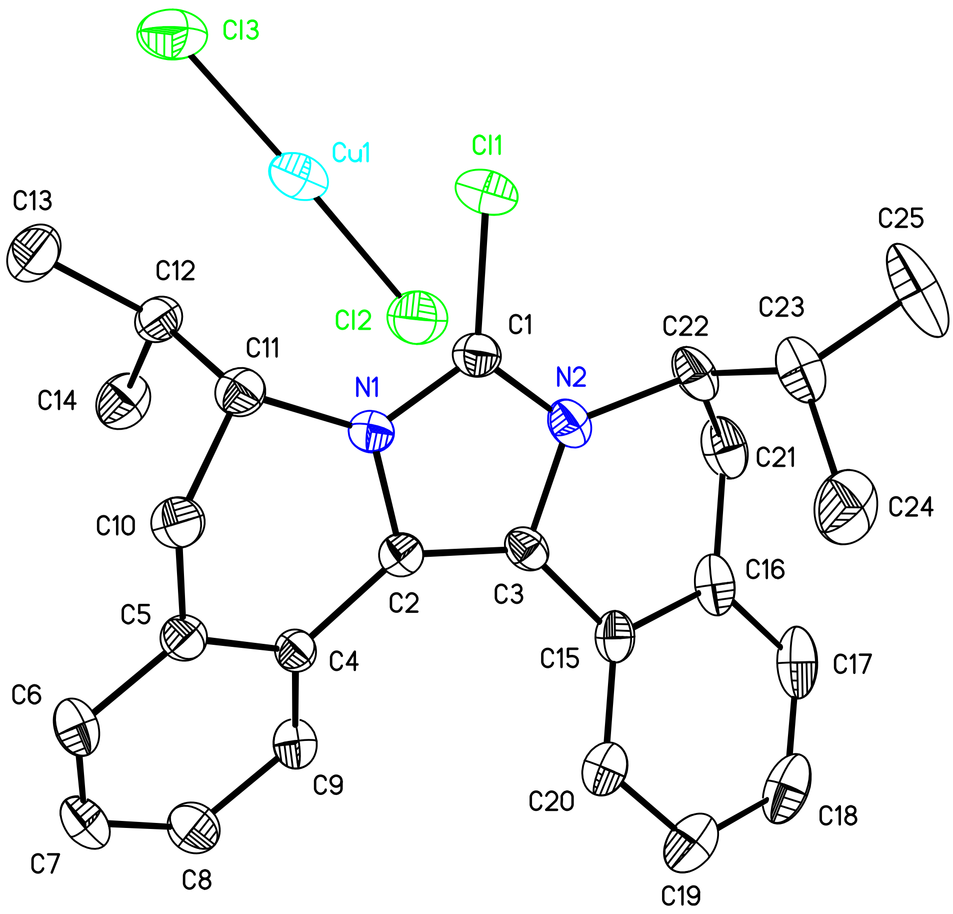
1. General Remarks

All reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon. THF, CH_2Cl_2, and Et_2O were passed through two packed columns of neutral alumina under positive pressure of dry nitrogen prior to use. Toluene was passed through an alumina column and a copper (II) oxide column under positive pressure of dry nitrogen prior to use. All the chemicals used were commercially available and were used as received without further purification. NMR spectra were recorded using a FT-NMR machine, operating at 300 MHz for ^1H NMR and at 75.4 MHz for ^{13}C NMR. All chemical shifts for ^1H and ^{13}C NMR spectroscopy were referenced to residual signals from $CDCl_3$ (^1H) 7.27 ppm and (^{13}C) 77.23 ppm. High resolution mass spectra were recorded on a GC/MS spectrometer or a TOF-LC/MS spectrometer. Enantiomer ratios were determined by chiral HPLC analysis using Chiralcel OJ-H, Chiralpak IA, and Whelk-O1 column. Compounds **1**, **7**, **8′•Cl⁻**, **12** and 1-tosylpiperidin-4-one are prepared according to the literature.[1,2,3,4]

2. X-Ray Analysis for Compound 3

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK$_\alpha$ radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 280 parameters were refined in the final cycle of refinement using 4548 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.45% and 7.82%, respectively. Refinement was done using F^2.



X-Ray Experimental: X-Ray structure of chloroimidazolium-CuCl$_2$ salt **3**. Thermal ellipsoids are drawn at the 50% probability level. C25H28Cl3CuN2, Mr = 526.38, Orthorhombic, P212121, a = 7.1072(5) Å, b = 17.443011) Å, c = 19.5633(13) Å, V = 2425.3(3) Å3, Z = 4, 9852 reflections measured (5109 independent; Rint. = 3.4%), T = 173 K, R1 = 3.45, wR2 = 7.82, Flack x = 0.02(11).

Table 1. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	C25 H28 Cl3 Cu N2	
Formula weight	526.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.1072(5) Å	α= 90°.
	b = 17.4430(11) Å	β= 90°.
	c = 19.5633(13) Å	γ = 90°.
Volume	2425.3(3) Å^3	
Z	4	
Density (calculated)	1.442 Mg/m^3	
Absorption coefficient	1.247 mm^{-1}	
F(000)	1088	
Crystal size	0.26 x 0.09 x 0.09 mm^3	
Theta range for data collection	1.56 to 28.03°.	
Index ranges	$-8 \leq h \leq 9$, $-18 \leq k \leq 22$, $-25 \leq l \leq 9$	
Reflections collected	9852	
Independent reflections	5109 [R(int) = 0.0340]	
Completeness to theta = 28.03°	92.7 %	
Absorption correction	Integration	
Max. and min. transmission	0.8961 and 0.7376	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5109 / 0 / 280	
Goodness-of-fit on F^2	1.014	

Final R indices [I>2sigma(I)]	R1 = 0.0345, wR2 = 0.0782 [4548]
R indices (all data)	R1 = 0.0408, wR2 = 0.0807
Absolute structure parameter	0.020(11)
Largest diff. peak and hole	0.314 and -0.275 e.Å^{-3}

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu1	5490(1)	4070(1)	8556(1)	36(1)
Cl1	172(1)	4544(1)	7976(1)	37(1)
Cl2	5352(1)	5260(1)	8735(1)	45(1)
Cl3	5702(1)	2883(1)	8408(1)	51(1)
N1	143(3)	4940(1)	9296(1)	22(1)
N2	618(3)	5890(1)	8606(1)	23(1)
C1	311(3)	5145(1)	8645(1)	24(1)
C2	380(3)	5593(1)	9702(1)	20(1)
C3	650(3)	6202(1)	9265(1)	21(1)
C4	391(3)	5483(1)	10445(1)	20(1)
C5	-479(4)	4817(1)	10701(1)	23(1)
C6	-459(4)	4679(2)	11400(1)	34(1)

C7	398(5)	5185(2)	11843(1)	37(1)
C8	1280(4)	5830(2)	11592(1)	33(1)
C9	1298(3)	5977(2)	10894(1)	26(1)
C10	-1386(3)	4264(2)	10211(1)	26(1)
C11	-264(3)	4160(1)	9552(1)	24(1)
C12	1532(4)	3673(2)	9581(1)	25(1)
C13	1015(4)	2839(2)	9704(1)	35(1)
C14	3021(4)	3946(2)	10092(1)	33(1)
C15	833(3)	7029(2)	9333(1)	23(1)
C16	1611(3)	7436(2)	8776(1)	28(1)
C17	1733(4)	8229(2)	8814(2)	36(1)
C18	1131(4)	8628(2)	9388(2)	38(1)
C19	364(4)	8223(2)	9933(2)	34(1)
C20	199(3)	7436(2)	9905(1)	26(1)
C21	2259(4)	6992(2)	8160(1)	33(1)
C22	950(4)	6336(2)	7969(1)	30(1)
C23	-928(4)	6540(2)	7618(1)	34(1)
C24	-2161(4)	7096(2)	8011(2)	47(1)
C25	-541(5)	6832(2)	6898(1)	63(1)

Table 3. Bond lengths [Å] and angles [°] for **3**.

Cu1-Cl3	2.0963(9)
Cu1-Cl2	2.1069(8)
Cl1-C1	1.680(2)
N1-C1	1.328(3)
N1-C2	1.398(3)

N1-C11	1.478(3)
N2-C1	1.321(3)
N2-C3	1.399(3)
N2-C22	1.487(3)
C2-C3	1.377(3)
C2-C4	1.467(3)
C3-C15	1.456(4)
C4-C9	1.389(3)
C4-C5	1.408(3)
C5-C6	1.389(3)
C5-C10	1.503(3)
C6-C7	1.378(4)
C7-C8	1.379(4)
C8-C9	1.390(3)
C10-C11	1.527(3)
C11-C12	1.535(4)
C12-C13	1.520(4)
C12-C14	1.532(3)
C15-C20	1.399(3)
C15-C16	1.412(3)
C16-C17	1.387(4)
C16-C21	1.504(4)
C17-C18	1.388(4)
C18-C19	1.391(4)
C19-C20	1.379(4)
C21-C22	1.522(4)
C22-C23	1.542(4)

C23-C24	1.516(4)
C23-C25	1.524(4)

Cl3-Cu1-Cl2	177.88(3)
C1-N1-C2	108.36(19)
C1-N1-C11	126.1(2)
C2-N1-C11	125.49(17)
C1-N2-C3	109.34(18)
C1-N2-C22	126.12(19)
C3-N2-C22	124.5(2)
N2-C1-N1	109.6(2)
N2-C1-Cl1	125.35(17)
N1-C1-Cl1	125.1(2)
C3-C2-N1	106.97(18)
C3-C2-C4	135.8(2)
N1-C2-C4	117.2(2)
C2-C3-N2	105.7(2)
C2-C3-C15	136.1(2)
N2-C3-C15	118.04(19)
C9-C4-C5	119.52(19)
C9-C4-C2	123.1(2)
C5-C4-C2	117.2(2)
C6-C5-C4	119.2(2)
C6-C5-C10	121.4(2)
C4-C5-C10	119.44(19)
C7-C6-C5	120.8(2)
C6-C7-C8	120.0(2)

C7-C8-C9	120.3(3)
C4-C9-C8	120.1(2)
C5-C10-C11	113.0(2)
N1-C11-C10	106.20(19)
N1-C11-C12	111.05(19)
C10-C11-C12	118.00(19)
C13-C12-C14	111.1(2)
C13-C12-C11	109.6(2)
C14-C12-C11	115.3(2)
C20-C15-C16	119.2(2)
C20-C15-C3	123.1(2)
C16-C15-C3	117.6(2)
C17-C16-C15	118.9(2)
C17-C16-C21	122.5(2)
C15-C16-C21	118.6(2)
C16-C17-C18	121.6(3)
C17-C18-C19	119.1(3)
C20-C19-C18	120.5(3)
C19-C20-C15	120.6(2)
C16-C21-C22	113.3(2)
N2-C22-C21	106.55(19)
N2-C22-C23	110.88(19)
C21-C22-C23	117.7(2)
C24-C23-C25	111.1(3)
C24-C23-C22	115.0(2)
C25-C23-C22	109.4(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

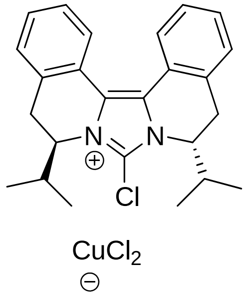
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu1	32(1)	50(1)	28(1)	-7(1)	-1(1)	4(1)
Cl1	48(1)	40(1)	23(1)	-9(1)	1(1)	2(1)
Cl2	47(1)	47(1)	41(1)	-6(1)	-1(1)	4(1)
Cl3	55(1)	53(1)	44(1)	-15(1)	4(1)	7(1)
N1	23(1)	22(1)	19(1)	-1(1)	2(1)	2(1)
N2	21(1)	29(1)	19(1)	4(1)	1(1)	1(1)
C1	26(1)	26(2)	22(1)	-2(1)	1(1)	3(1)
C2	17(1)	21(1)	22(1)	0(1)	2(1)	-1(1)
C3	18(1)	26(2)	18(1)	1(1)	1(1)	0(1)
C4	20(1)	22(1)	19(1)	2(1)	1(1)	4(1)
C5	24(1)	22(1)	24(1)	1(1)	4(1)	0(1)
C6	43(1)	32(2)	27(1)	9(1)	9(1)	-2(1)
C7	54(2)	39(2)	19(1)	4(1)	3(1)	2(2)
C8	39(1)	35(2)	25(1)	-3(1)	-6(1)	1(1)
C9	26(1)	25(2)	26(1)	3(1)	-1(1)	-1(1)
C10	26(1)	24(2)	29(1)	0(1)	7(1)	-5(1)
C11	25(1)	23(2)	25(1)	-2(1)	-1(1)	-4(1)
C12	27(1)	21(2)	27(1)	-1(1)	4(1)	1(1)
C13	43(2)	24(2)	40(1)	0(1)	-2(1)	2(1)
C14	28(1)	31(2)	41(2)	-1(1)	-5(1)	3(1)

C15	19(1)	24(2)	26(1)	6(1)	-3(1)	-1(1)
C16	21(1)	32(2)	31(1)	12(1)	-6(1)	-7(1)
C17	25(1)	36(2)	46(2)	20(1)	-11(1)	-9(1)
C18	28(1)	23(2)	63(2)	8(1)	-14(1)	-5(1)
C19	26(1)	26(2)	51(2)	-2(1)	-8(1)	0(1)
C20	23(1)	23(2)	34(1)	3(1)	-3(1)	-1(1)
C21	24(1)	44(2)	31(1)	13(1)	2(1)	-5(1)
C22	30(1)	39(2)	19(1)	8(1)	4(1)	-2(1)
C23	33(1)	42(2)	27(1)	10(1)	-5(1)	-7(1)
C24	33(2)	52(2)	55(2)	1(2)	-16(1)	7(2)
C25	54(2)	101(3)	32(2)	31(2)	-10(2)	-15(2)

3. Experimental Details

2.1. Synthesis of compounds 3, 4, 10, 16, 21′ and 22′•PF$_6^-$

[6(*R*),8(*R*)-Diisopropyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[c,g]fluoreniumchloride] copper (II) chloride (3).



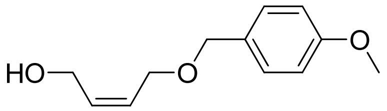
A flame dried Schlenk flask was charged with 0.100 g (0.254 mmol) of [6(R),8(R)-Diisopropyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[c,g]fluorenium] chloride (**1**), 0.036 g (0.153 mmol) of Ag_2O and 10 mL of CH_2Cl_2. After stirring for 12 h, the reaction mixture was filtered through a pad of celite. The solvent of the filtrate was removed under reduced pressure. To another flame-dried Schlenk flask was added the filtered silver complex and 0.038 g (0.279 mmol) of $CuCl_2$.

The reaction mixture was stirred for 5 h at room temperature. The reaction solution was filtered through a pad of celite and evaporated to dryness. The residue was purified by recrystallization using a mixture of CH_2Cl_2:hexane to yield 0.090 g (0.182 mmol, 71.6 %) of **3**.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.97 (d, *J*=7.6 Hz, 1 H), 7.30 - 7.56 (m, 3 H), 4.56 - 4.75 (m, 1 H), 3.68 (dd, *J*=15.9, 5.4 Hz, 1 H), 3.27 (d, *J*=16.1 Hz, 1 H), 1.74 - 2.00 (m, 1 H), 1.03 (d, *J*=6.8 Hz, 3 H), 0.87 (d, *J*=6.8 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 132.8, 131.4, 129.7, 128.1, 126.1, 124.9, 123.3, 61.2, 31.7, 30.6, 20.6, 19.2.

(*Z*)-4-(4-methoxybenzyloxy)but-2-en-1-ol.



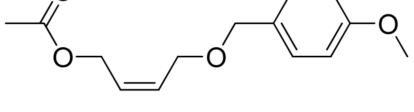
To a flame-dried Schlenk flask were added 1.25 g (14.16 mmol) of (*Z*)-2-buten-1,4-diol and 5 mL (0.06 mmol) of a solution of TfOH in Et_2O (10 µL in 10 mL of Et_2O). The reaction mixture was cooled to 0 °C and a solution of 4-methoxybenzyl-2,2,2-trichloroacetimidate (0.67 g, 2.36 mmol) in DCM (1.2 mL) was added dropwise. After stirring over 2 hours at 0 °C, it was quenched with 4 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with Et_2O (3 x 5mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, from 2.3:1 to 1:1 Hexanes/EtOAc) to yield 0.40 g (1.90 mmol, 80%) of (*Z*)-4-(4-methoxybenzyloxy)but-2-en-1-ol.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.26 (d, *J*=8.21 Hz, 2 H), 6.88 (d, *J*=8.78 Hz, 2 H), 5.65 - 5.85 (m, 2 H), 4.45 (s, 2 H), 4.14 (d, *J*=5.95 Hz, 2 H), 4.05 (d, *J*=5.66 Hz, 2 H), 3.79 (s, 3 H), 2.32 (br. s, 1 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.5, 132.6, 130.1, 129.7, 128.4, 114.1, 72.4, 65.6, 58.8, 55.5

HRMS Calcd. for $C_{12}H_{16}O_3$ $[M+Na]^+$: 231.0992, Found: 231.0991.

(*Z*)-4-(4-methoxybenzyloxy)but-2-enyl acetate (4).



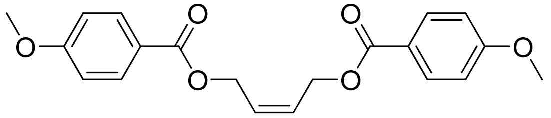
To a flame-dried Schlenk flask were added 356 mg (1.71 mmol) of (*Z*)-4-(4-methoxybenzyloxy)but-2-en-1-ol, 755 µL (5.42 mmol) of Et_3N, 44 mg (0.36 mmol) of DMAP, 205 µL (2.17 mmol) of Ac_2O, and 18 mL of DCM. The reaction mixture was stirred at room temperature over 12 hours. It was quenched with 10 mL of H_2O and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:1 Hexanes/EtOAc) to yield 400 mg (1.60 mmol, 93%) of (*Z*)-4-(4-methoxybenzyloxy)but-2-enyl acetate.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.27 (d, *J*=8.80 Hz, 2 H), 6.88 (d, *J*=8.80 Hz, 2 H), 5.76 - 5.86 (m, 1 H), 5.64 - 5.75 (m, 1 H), 4.62 (dd, *J*=6.45, 0.88 Hz, 2 H), 4.45 (s, 2 H), 4.09 (dd, *J*=6.16, 1.17 Hz, 2 H), 3.80 (s, 3 H), 2.06 (s, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 170.8, 159.3, 130.9, 130.1, 129.4, 126.6, 113.8, 72.1, 65.3, 60.3, 55.2, 20.9

HRMS Calcd. for $C_{14}H_{18}O_4$ $[M+Na]^+$: 273.1097, Found: 273.1104.

(*Z*)-but-2-ene-1,4-diyl bis(4-methoxybenzoate) (10).



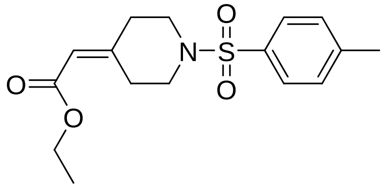
To a flame-dried Schlenk flask were added 54 mg (0.61 mmol) of (*Z*)-2-buten-1,4-diol, 212 µL (1.52 mmol) of Et_3N, 15 mg (0.12 mmol) of DMAP, 10 mL of DCM, and dropwise 206 µL (1.52 mmol) of 4-methoxybenzoylchloride. The reaction mixture was stirred at room temperature over 17 hours. It was quenched with 6 mL of 30% NaOH solution and extracted with DCM (3 x 8 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:1 Hexanes/EtOAc) to yield 217 mg (0.61 mmol, quantitative yield) of (*Z*)-but-2-ene-1,4-diyl bis(4-methoxybenzoate).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.00 (d, *J*=8.91 Hz, 4 H), 6.91 (d, *J*=8.91 Hz, 4 H), 5.93 (ddd, *J*=5.22, 3.98, 1.17 Hz, 2 H), 4.97 (d, *J*=5.26 Hz, 4 H), 3.86 (s, 6 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 166.2, 163.6, 131.8, 128.5, 122.5, 113.8, 60.5, 55.6

HRMS Calcd. for $C_{20}H_{20}O_4$ $[M+Na]^+$: 379.1152, Found: 379.1185.

Ethyl 2-(1-tosylpiperidin-4-ylidene)acetate.



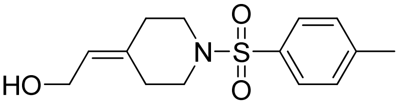
To a flame-dried Schlenk flask was added 177 mg of NaH (60% in mineral oil, 4.42 mmol) in 12 mL of toluene. To this suspensions at 0 °C was added dropwise 790 µL (3.95 mmol) of triethyl phosphonoacetate. The reaction mixture was stirred 30 min at room temperature then 1.00 g (3.95 mmol) of 1-tosylpiperidin-4-one was added portionwise. It was stirred at 60 °C over a day. The reaction mixture was quenched by 10 mL of H_2O and extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, from 1:0 to 4:1 Hexanes/EtOAc) to give 940 mg (2.9 mmol, 74%) of ethyl 2-(1-tosylpiperidin-4-ylidene)acetate.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.64 (d, *J*=8.20 Hz, 2 H), 7.31 (d, *J*=8.65 Hz, 2 H), 5.64 (s, 1 H), 4.11 (q, *J*=7.16 Hz, 2 H), 2.99 - 3.18 (m, 6 H), 2.42 (s, 2 H), 2.38 (t, *J*=6.34 Hz, 3 H), 1.24 (t, *J*=7.09 Hz, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 166.0, 153.4, 143.7, 133.1, 129.7, 127.6, 115.9, 59.9, 47.3, 46.8, 35.8, 28.5, 21.5, 14.2

HRMS Calcd. for $C_{16}H_{21}NO_4S$ $[M+Na]^+$: 346.1084, Found: 346.1086.

2-(1-tosylpiperidin-4-ylidene)ethanol.



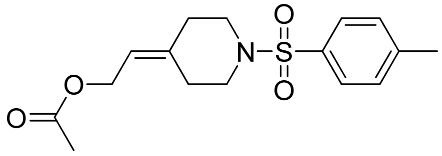
To a flame-dried Schlenk flask were added 1.14 g (3.52 mmol) of ethyl 2-(1-tosylpiperidin-4-ylidene)acetate and 38 mL of DCM. The reaction mixture was cooled at -78 °C and 10.6 mL (10.55 mmol) of DIBAL (1M in toluene) was added dropwise. It was stirred at -78 °C for 2 hours. It was quenched with 20 mL of a saturated solution of NH_4Cl and extracted with DCM (3 x 30 mL). The combined organic extracts were filtered on a celite pad, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, from 1:1.5 to 1:2.3 Hexanes/EtOAc) to yield 0.89 mg (3.17 mmol, 90%) of 2-(1-tosylpiperidin-4-ylidene)ethanol.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.62 (d, J=8.21 Hz, 2 H), 7.31 (d, J=8.49 Hz, 2 H), 5.42 (t, J=6.94 Hz, 1 H), 4.09 (d, J=6.79 Hz, 2 H), 2.98 - 3.09 (m, 4 H), 2.42 (s, 3 H), 2.37 (t, J=5.80 Hz, 2 H), 2.29 (t, J=5.80 Hz, 2 H), 1.36 (br. s., 1 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 143.55, 137.41, 133.08, 129.61, 127.58, 123.52, 58.08, 47.64, 47.08, 35.05, 27.76, 21.47

HRMS Calcd. for $C_{14}H_{19}NO_3S$ $[M+Na]^+$: 304.0978, Found: 304.0984.

2-(1-tosylpiperidin-4-ylidene)ethyl acetate (16).



To a flame-dried Schlenk flask were added 489 mg (1.74 mmol) of 2-(1-tosylpiperidin-4-ylidene)ethanol, 740 μL (5.31 mmol) of Et_3N, 43 mg (0.36 mmol) of DMAP, 201 μL (2.13 mmol) of Ac_2O, and 18 mL of DCM. The reaction mixture was stirred at room temperature over 17 hours. It was quenched with 10 mL of H_2O and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:1 Hexanes/EtOAc) to yield 548 mg (1.69 mmol, 97%) of 2-(1-tosylpiperidin-4-ylidene)ethyl acetate.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.64 (d, *J*=8.21 Hz, 2 H), 7.31 (d, *J*=8.78 Hz, 2 H), 5.36 (t, *J*=6.94 Hz, 1 H), 4.51 (d, *J*=7.36 Hz, 2 H), 3.06 (q, *J*=6.23 Hz, 4 H), 2.37 - 2.49 (m, 5 H), 2.31 (t, *J*=5.52 Hz, 2 H), 2.01 (s, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 171.1, 143.8, 140.1, 133.5, 129.9, 127.8, 118.9, 60.2, 47.7, 47.1, 35.3, 28.2, 21.7, 21.2

HRMS Calcd. for $C_{16}H_{21}NO_4S$ $[M+Na]^+$: 346.1084, Found: 346.1080.

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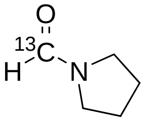
pyrrolidine-1-carbaldehyde-^{13}C (21′)



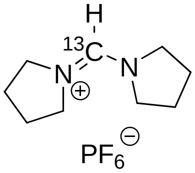
To a flame-dried pressurized vessel were added 1.42 mL (17.29 mmol) of pyrrolidine and 1000 mg (16.38 mmol) of methyl formate-^{13}C. The reaction mixture was stirred at 80 °C for 12 hours. It was warmed to room temperature and concentrated under reduced pressure to yield 1640 mg (16.38 mmol, 99%) of pyrrolidine-1-carbaldehyde-^{13}C

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.2 (d, *J*=188.8 Hz, 1 H), 3.4 (m, 4 H), 1.9 (m, 4 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 160.7, 45.9, 43.0, 24.8, 24.1

HRMS Calcd. for $C_4{}^{13}CH_9NO$ $[M+H]^+$: 101.0790, Found: 101.0793.

Piperidin-1-ylmethylidenepiperidinium hexafluorophosphate-^{13}C ($22'\bullet PF_6^-$)



To a flame-dried Schlenk flask were added 467 µL (5.01 mmol) of phosphorus oxychloride and 5 mL of DCM. To the reaction mixture at -78 °C in a dry ice-acetone bath was added a solution of 502 mg (5.01 mmol) of pyrrolidine-1-carbaldehyde-^{13}C in 2 mL of DCM. It was warmed up to room temperature and stirred for 2 hours. Then it was cooled at 0 °C and a solution of 693 µL (5.01 mmol) of triethyl amine and 412 µL (5.01 mmol) of pyrrolidine in 2.5 mL of DCM was added dropwise. It was stirred at room temperature for 2 hours. The reaction mixture was extracted with cold H_2O (3 x 2.5 mL), the combined aqueous layer was added to a cold solution of 1600 mg (10.02 mmol) of ammonium hexafluorophosphate in 5 mL of H_2O. The precipitate was filtered and washed with H_2O (2 x 3 mL) and Et_2O (2 x 5 mL). The yellowish solid was dried under reduced pressure to yield 1000 mg (3.34 mmol, 67% yield) of piperidin-1-ylmethylidenepiperidinium hexafluorophosphate-^{13}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.81 (d, *J*=190.0 Hz, 1 H), 3.81 (dt, *J*=14.0, 7.0 Hz, 4 H), 2.01 (dt, *J*=13.2, 7.0 Hz, 4 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 151.0, 54.2, 48.2, 25.8, 23.8

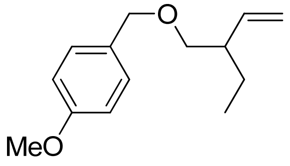
HRMS Calcd. for $C_8{}^{13}CH_{17}F_6N_2P$ $[M+H]^+$: 154.1420, Found: 154.1432.

2.2. Synthesis and analysis of 5, 11, 13, 15, and 17

Typical procedure for allylic alkylation:

A flame-dried Schlenk flask was charged with a copper source (5 mol %), 1-(chloro(pyrrolidin-1-yl)methylene)pyrrolidinium tetrafluoroborate (5 mol%) and 1 mL of a solvent. To this solution was added a Grignard reagent (0.22 mmol in Et_2O) at 0 °C. The mixture reaction was stirred for 5 min at 0 °C. Then a solution of substrate (0.15 mmol) in 1 mL of Et_2O was added over a 15 min period. After 1 hr, the reaction was quenched by a saturated aqueous NH_4Cl solution and extracted with Et_2O (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give a pure product.

1-((2-ethylbut-3-enyloxy)methyl)-4-methoxybenzene (5).

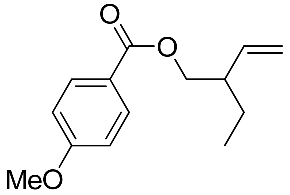


^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.20 - 7.37 (m, 2 H), 6.87 (d, *J*=8.4 Hz, 2 H), 5.54 - 5.79 (m, 1 H), 4.98 - 5.23 (m, 2 H), 4.44 (s, 2 H), 3.80 (s, 3 H), 3.36 (d, *J*=6.4 Hz, 2 H), 2.12 - 2.42 (m, 1 H), 1.45 - 1.71 (m, 1 H), 1.13 - 1.37 (m, 1 H), 0.86 (t, *J*=7.4 Hz, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.1, 140.0, 130.7, 129.1, 115.5, 113.7, 73.2, 72.6, 55.2, 45.7, 24.0, 11.4

HRMS Calcd. for $C_{14}H_{20}O_2$ $[M]^+$: 220.1463, Found: 220.1477.

2-ethylbut-3-enyl 4-methoxybenzoate (11).

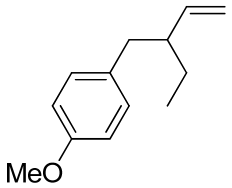


^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.91 (d, *J*=8.78 Hz, 2 H), 6.83 (d, *J*=9.06 Hz, 2 H), 5.62 (ddd, *J*=17.06, 10.40, 8.21 Hz, 1 H), 5.00 - 5.09 (m, 2 H), 4.15 (dd, *J*=6.51, 1.98 Hz, 2 H), 3.77 (s, 3 H), 2.25 - 2.41 (m, 1 H), 1.44 - 1.60 (m, 1 H), 1.23 - 1.39 (m, 1 H), 0.86 (t, *J*=7.36 Hz, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 166.52, 163.50, 139.18, 131.76, 123.07, 116.68, 113.79, 67.37, 55.61, 45.13, 24.23, 11.61

HRMS Calcd. for $C_{14}H_{18}O_3$ $[M+Na]^+$: 257.1148, Found: 257.1142.

1-(2-ethylbut-3-enyl)-4-methoxybenzene (13).

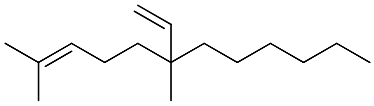


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J*=9 Hz, 2 H), 6.81 (d, *J*=9 Hz, 2 H), 5.47 - 5.72 (m, 1 H), 4.73 - 5.04 (m, 2 H), 3.79 (s, 3 H), 2.43 - 2.70 (m, 2 H), 2.05 - 2.27 (m, 1 H), 1.36 - 1.52 (m, 1 H), 1.17 - 1.36 (m, 1 H), 0.87 (t, *J*=8 Hz, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 142.6, 133.0, 130.3, 114.8, 113.7, 55.4, 47.7, 40.8, 27.0, 11.9

HRMS Calcd. for $C_{13}H_{18}O$ $[M+H]^+$: 191.1430, Found: 191.1436.

2,6-dimethyl-6-vinyldodec-2-ene (15).

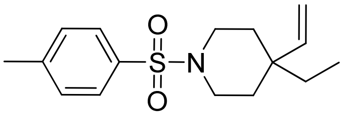


^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 5.71 (dd, *J*=17.6, 10.9 Hz, 1 H), 5.05 - 5.15 (m, 1 H), 4.84 - 5.02 (m, *J*=15.9, 11.0, 1.6 Hz, 2 H), 1.82 - 1.94 (m, 2 H), 1.69 (s, 3 H), 1.60 (s, 3 H), 1.21 - 1.34 (m, 12 H), 0.96 (s, 3 H), 0.86 - 0.92 (m, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 147.5, 130.9, 125.2, 111.3, 40.9, 40.8, 39.5, 32.0, 30.2, 25.7, 24.0, 22.9, 22.7, 22.6, 17.6, 14.1

HRMS Calcd. for $C_{16}H_{30}$ $[M]^+$: 222.2348, Found: 223.2342.

4-ethyl-1-tosyl-4-vinylpiperidine (17).



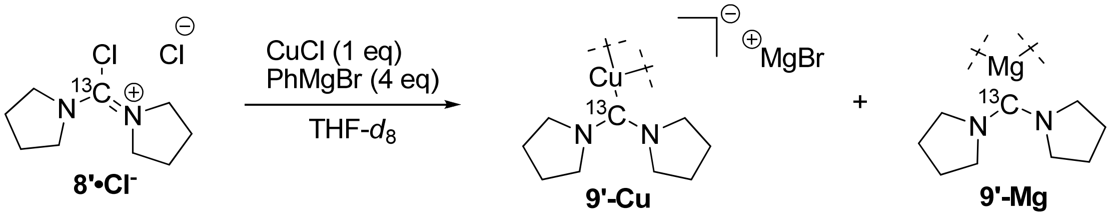
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (m, *J*=8 Hz, 2 H) 7.26 (m, *J*=8 Hz, 2 H), 5.36 (dd, *J*=18, 11 Hz, 1 H), 5.04 (d, *J*=11 Hz, 1 H), 4.77 (d, *J*=18 Hz, 1 H), 3.17 - 3.35 (m, 2 H), 2.55 - 2.71 (m, 2 H), 2.38 (s, 3 H), 1.59 - 1.76 (m, 2 H), 1.41 - 1.59 (m, 2 H), 1.22 (q, *J*=7 Hz, 2 H), 0.68 (t, *J*=7 Hz, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 133.8, 129.8, 127.8, 115.1, 42.9, 38.1, 34.1, 33.6, 21.8, 7.7

HRMS Calcd. for $C_{16}H_{23}NO_2S$ $[M+H]^+$: 294.1522, Found: 294.1499.

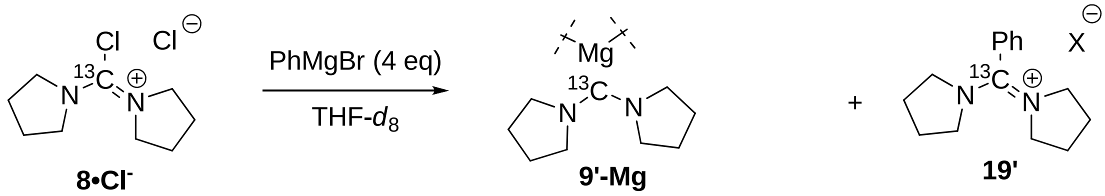
2.3. NMR experiments

Experiment 1:



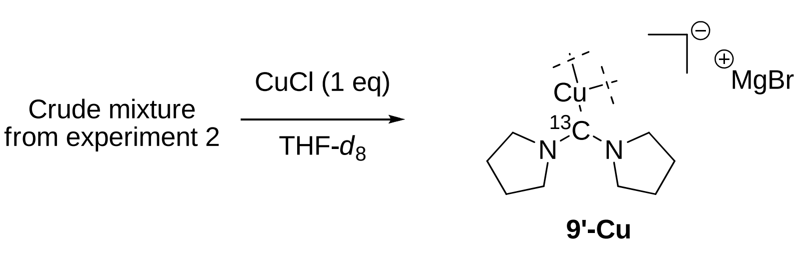
To a flame-dried Schlenk flask was added 20 mg (0.089 mmol) of 1-(chloro-1-pyrrolidinylmethylene)-pyrrolidinium chloride, 8.9 mg (0.089 mmol) of copper (I) chloride and 750 μL of THF-d_8. The reaction mixture was cooled to 0 °C and phenylmagnesium bromide (0.36 mmol in THF) was added. It was stirred at 0 °C for 5 min then it was transferred to a flame-dried NMR tube under argon via syringe. The NMR tube was cooled to -78 °C in a dry ice-acetone bath before being analyzed in the NMR instrument at -60 °C.

Experiment 2:



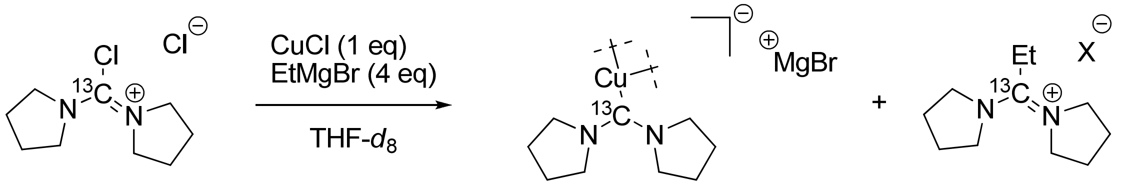
To a flame-dried Schlenk flask was added 10 mg (0.045 mmol) of 1-(chloro-1-pyrrolidinylmethylene)-pyrrolidinium chloride and 750 μL of THF-d_8. The reaction mixture was cooled to 0 °C and phenylmagnesium bromide (0.18 mmol in THF) was added. It was stirred at 0 °C for 5 min, and then it was transferred to a flame-dried NMR tube under argon via syringe. The NMR tube was cooled to -78 °C in a dry ice-acetone bath before being analyzed in the NMR instrument at -60 °C.

Experiment 3:



To the NMR tube from experiment 2 was added 4.5 mg (0.045 mmol) of copper (I) chloride at 0 °C. Then it was stirred at 0 °C for 5 min and cooled at -78 °C in a dry ice-acetone bath before being analyzed in the NMR instrument at -60 °C.

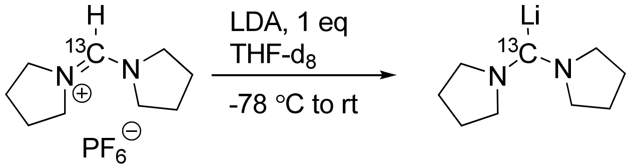
Experiment 4:



8'•Cl$^-$ **9'-Cu** **20**

To a flame-dried Schlenk flask was added 10 mg (0.045 mmol) of 1-(chloro-1-pyrrolidinylmethylene)-pyrrolidinium chloride, 4.4 mg (0.045 mmol) of copper (I) chloride and 750 µL of THF-d_8. The reaction mixture was cooled to 0 °C, and ethylmagnesium bromide (0.18 mmol in THF) was added. It was stirred at 0 °C for 5 min, and then it was transferred to a flame-dried NMR tube under argon via syringe. The NMR tube was cooled to -78 °C in a dry ice-acetone bath before being analyzed in the NMR instrument at -60 °C.

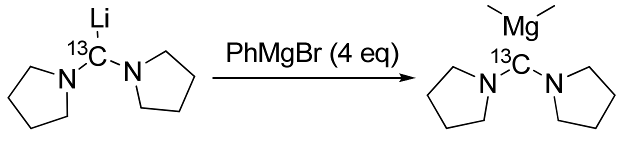
Experiment 5:



22′•PF$_6^-$ **9′•Li**

To a flame-dried NMR tube was added 41.4 mg (0.138 mmol) of piperidin-1-ylmethylidenepiperidinium hexafluorophosphate-^{13}C. Then it was cooled at -78 °C in a dry ice-acetone bath and 147 µL (0.94 M) of LDA followed by 750 µL of THF-d_8. It was stirred at room temperature for 5 min until dissolution of the suspension before being analyzed in the NMR experiment at room temperature.

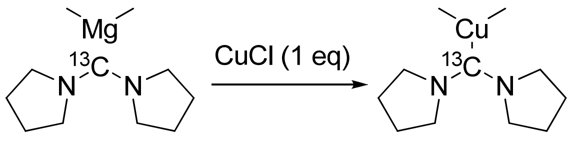
Experiment 6:



22′•Li **9′•Mg**

To the NMR tube from experiment 5 at -78 °C in a dry ice-acetone bath was added 548 µL (1 M in THF) of phenyl magnesiumbromide and the reaction mixture was stirred for 5 min at room temperature before being analyzed in the NMR experiment at room temperature.

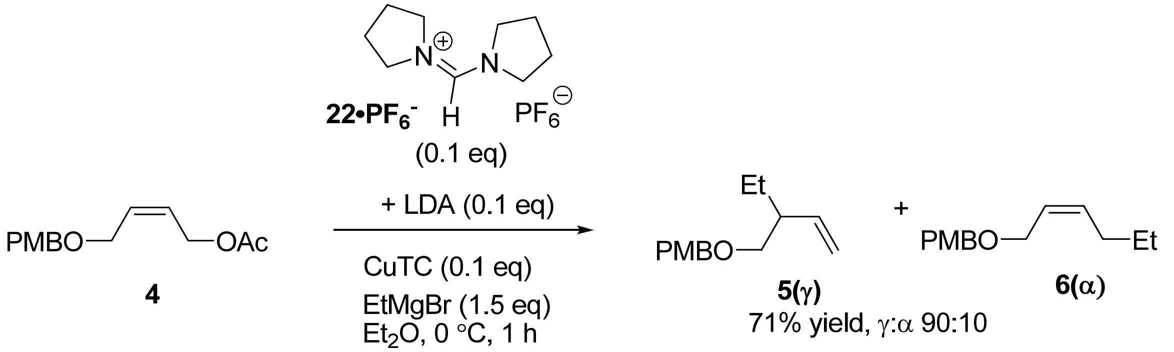
Experiment 7:



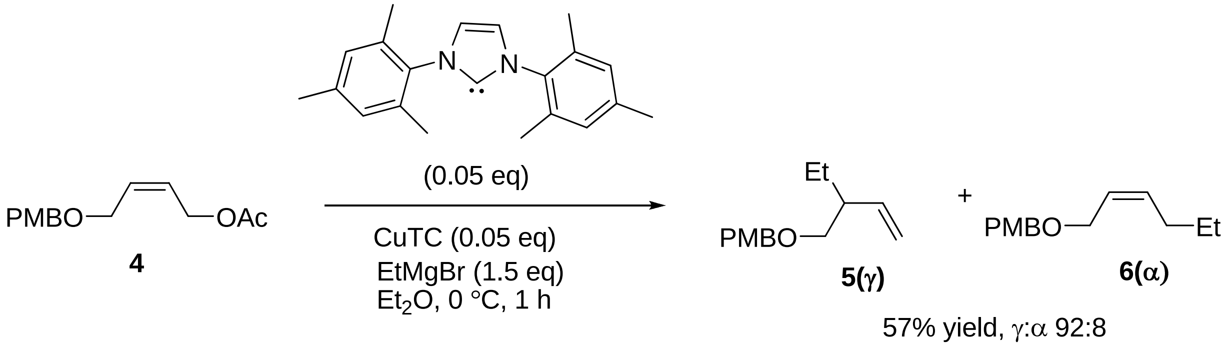
9′•Mg **9′•Cu**

To the NMR tube from experiment 6 at -78 °C in a dry ice-acetone bath was added 14 mg (0.138 mmol) of copper chloride and the reaction mixture was stirred for 5 min at room temperature before being analyzed in the NMR experiment at room temperature.

2.4. Controlled experiments Table 1 Entries 4 and 5



To a flame-dried Schlenk flask were added 201 mg (0.674 mmol) of piperidin-1-ylmethylidenepiperidinium hexafluorophosphate to a solution of 0.674 mmol (3 M in THF) of LDA. The reaction mixture was stirred at -20 °C for 30 min. 65 μL (0.022 mmol) of this carbene solution generated in situ was added to a flame-dried Schlenk flask at 0 °C containing 110 μL (3 M in Et_2O) of ethyl magnesiumbromide, 4.2 mg (0.022 mmol) of copper thiophene-2-carboxylate and 1 mL of Et_2O. The reaction mixture was stirred for 5 min then a solution of 55 mg (0.221 mmol) of (*Z*)-4-(4-methoxybenzyloxy)but-2-enyl acetate in 1 mL of Et_2O was added dropwise. After 1 hr, the reaction was quenched by a saturated aqueous NH_4Cl solution and extracted with Et_2O (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0.05 Hexanes/EtOAc) to yield 33.9 mg (0.154 mmol, 71%, γ:α 90:10) of 1-((2-ethylbut-3-enyloxy)methyl)-4-methoxybenzene.



To a flame-dried Schlenk flask were added 3.5 mg (0.011 mmol) of 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, 2.1 mg (0.011 mmol) of copper thiophene-2-carboxylate, 116 μL (3 M in Et_2O) of ethyl magnesiumbromide and 1 mL of Et_2O. The The reaction mixture was stirred for 5 min at 0 °C then a solution of 58 mg (0.231 mmol) of (*Z*)-4-(4-methoxybenzyloxy)but-2-enyl acetate in 1 mL of Et_2O was added dropwise. After 1 hr, the reaction was quenched by a saturated aqueous NH_4Cl solution and extracted with Et_2O (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0.05 Hexanes/EtOAc) to yield 29 mg (0.131 mmol, 60%, γ:α 92:8) of 1-((2-ethylbut-3-enyloxy)methyl)-4-methoxybenzene.

4. References

[1] For the preparation of **1** and **7**: H. Seo, D. Hirsch-Weil, K. A. Abboud and S. Hong, *J. Org. Chem.*, 2008, **73**, 1983

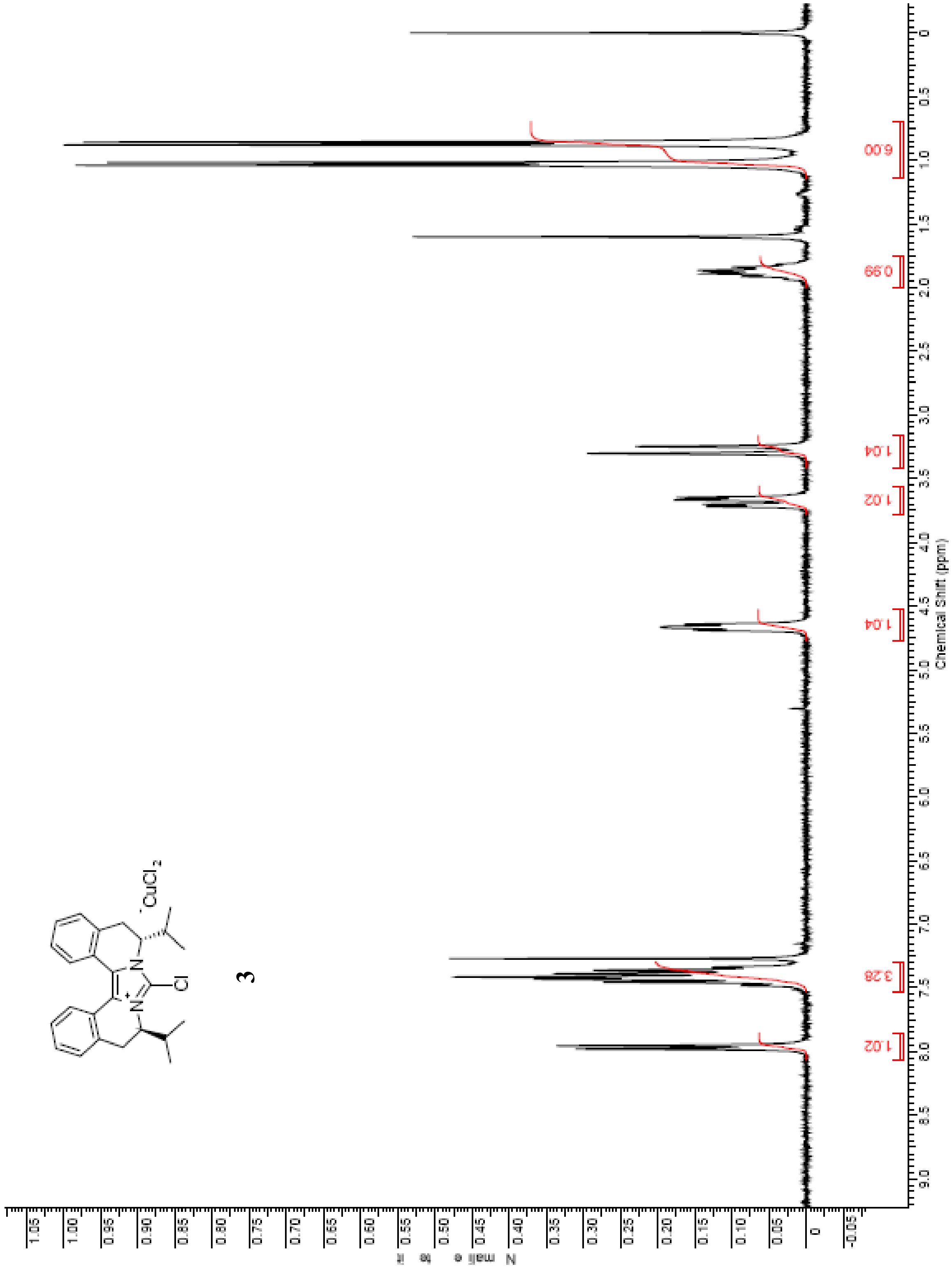
[2] For the preparation of **8′•Cl$^-$**: D. Kremzow, G. Seidel, C. W. Lehmann and A. Fürstner, *Chem. Eur. J.*, 2005, **11**, 1833.

[3] For the preparation of **12**: J. Dowden and J. Savović, *Chem. Commun.*, 2001, 37

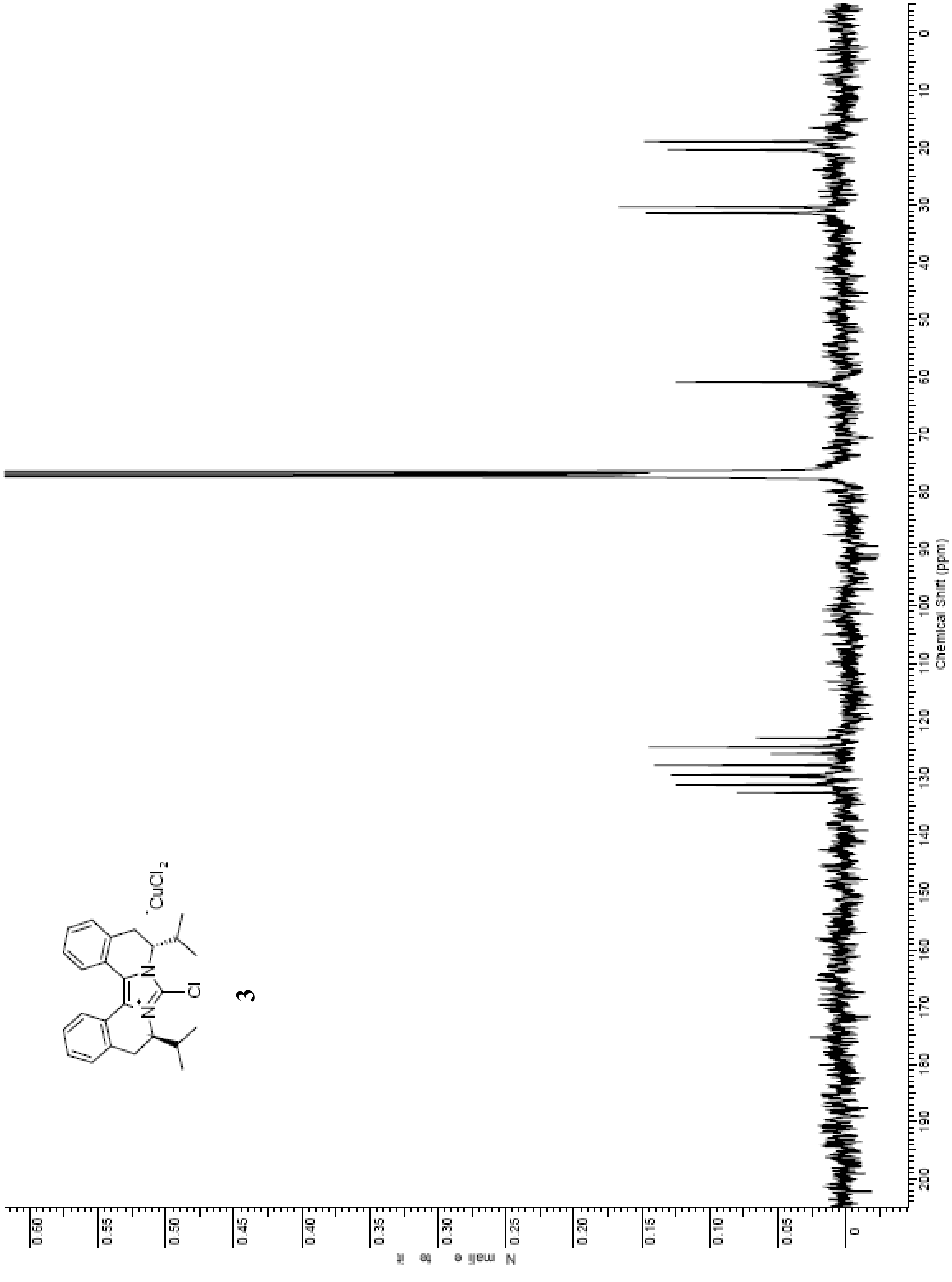
[4] For the preparation of 1-tosylpiperidin-4-one: R. Šebesta, M. G. Pizzuti, A. J. Boersma, A. J. Minnaard and B. L. Feringa, *Chem. Commun.*, 2005, 1711

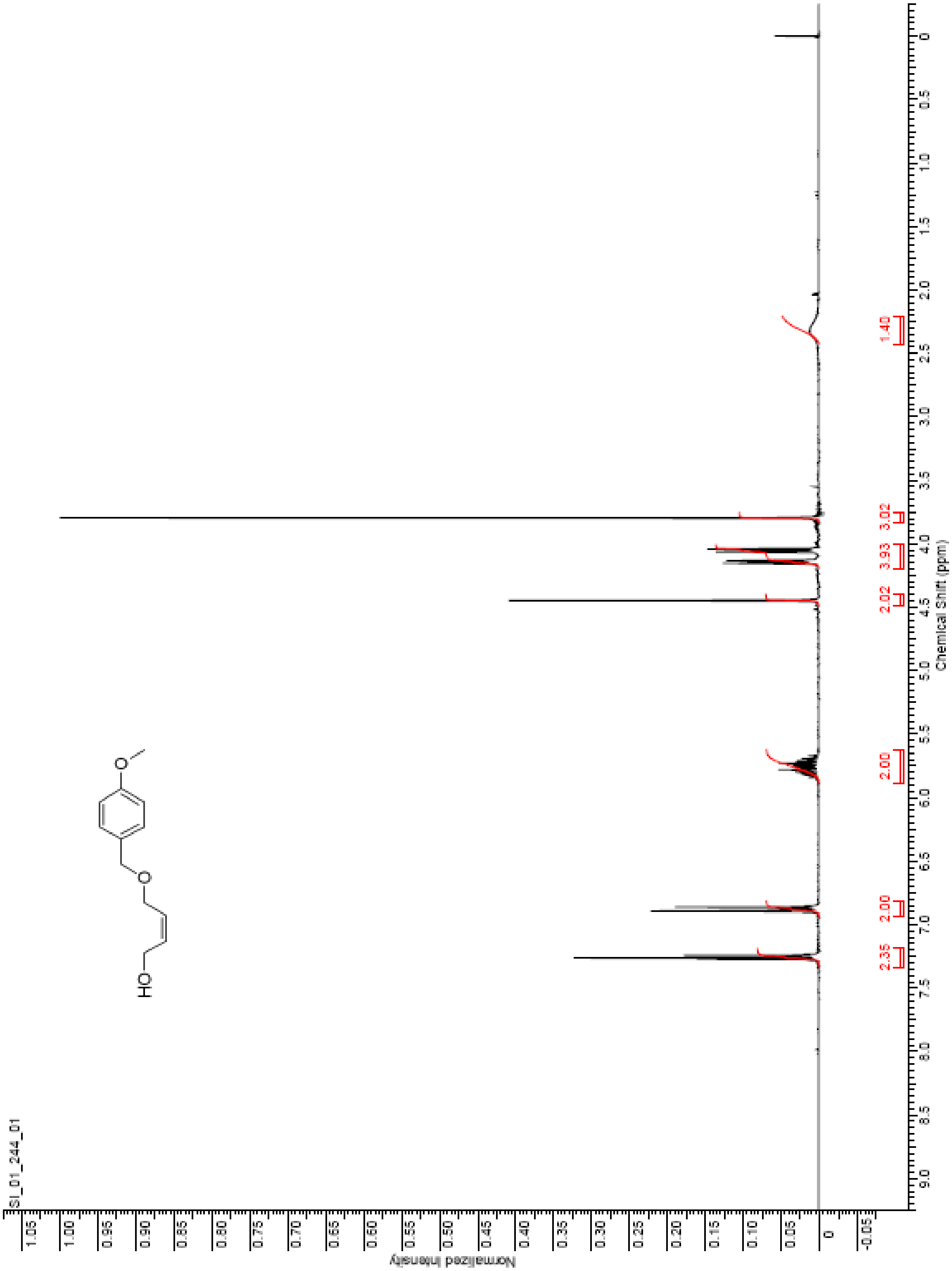
5. NMR Spectra for New Compounds

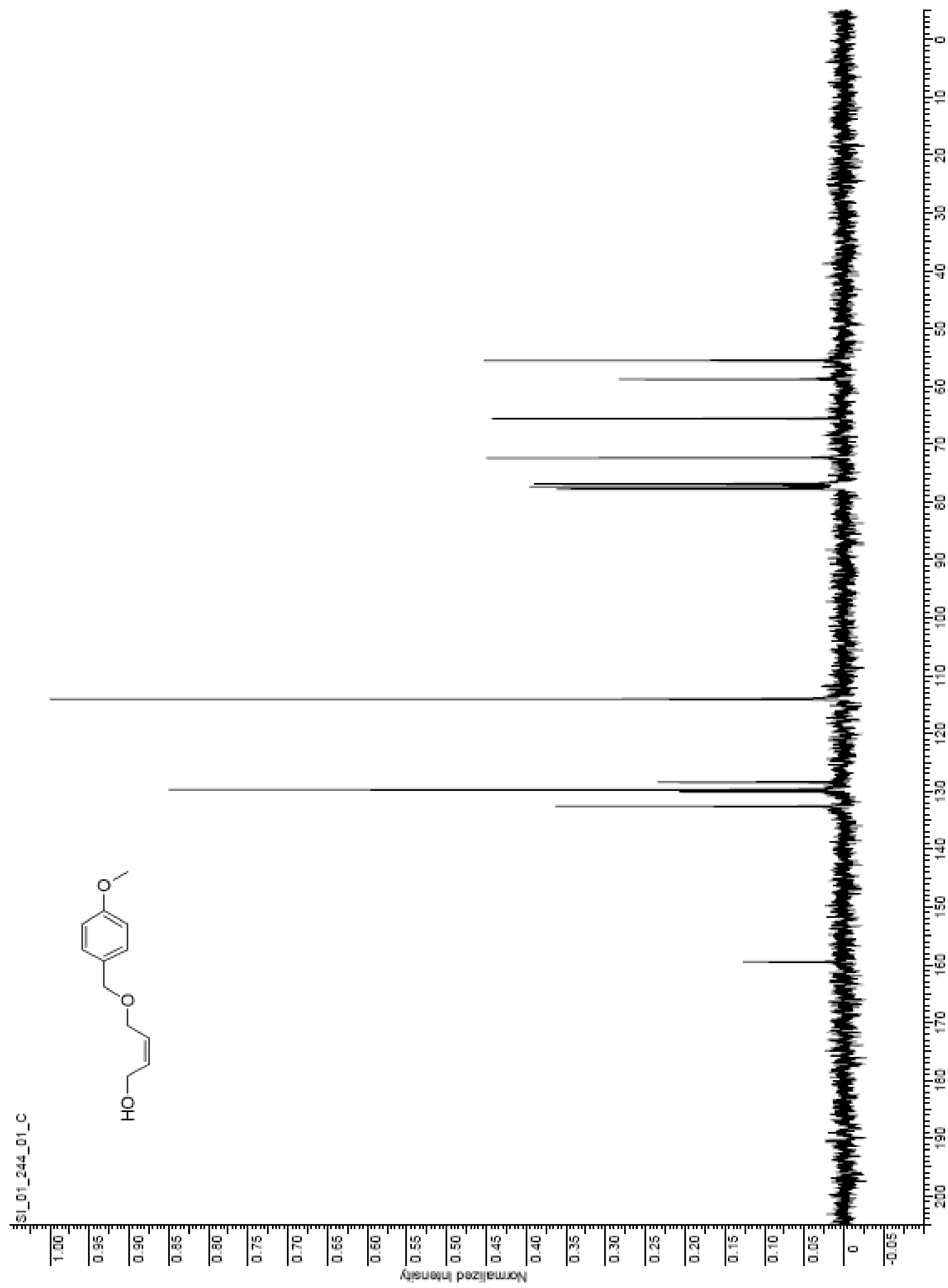
4.1. NMR Spectra for 3, 4, 10, 16, 21′ and 22′•PF_6^-

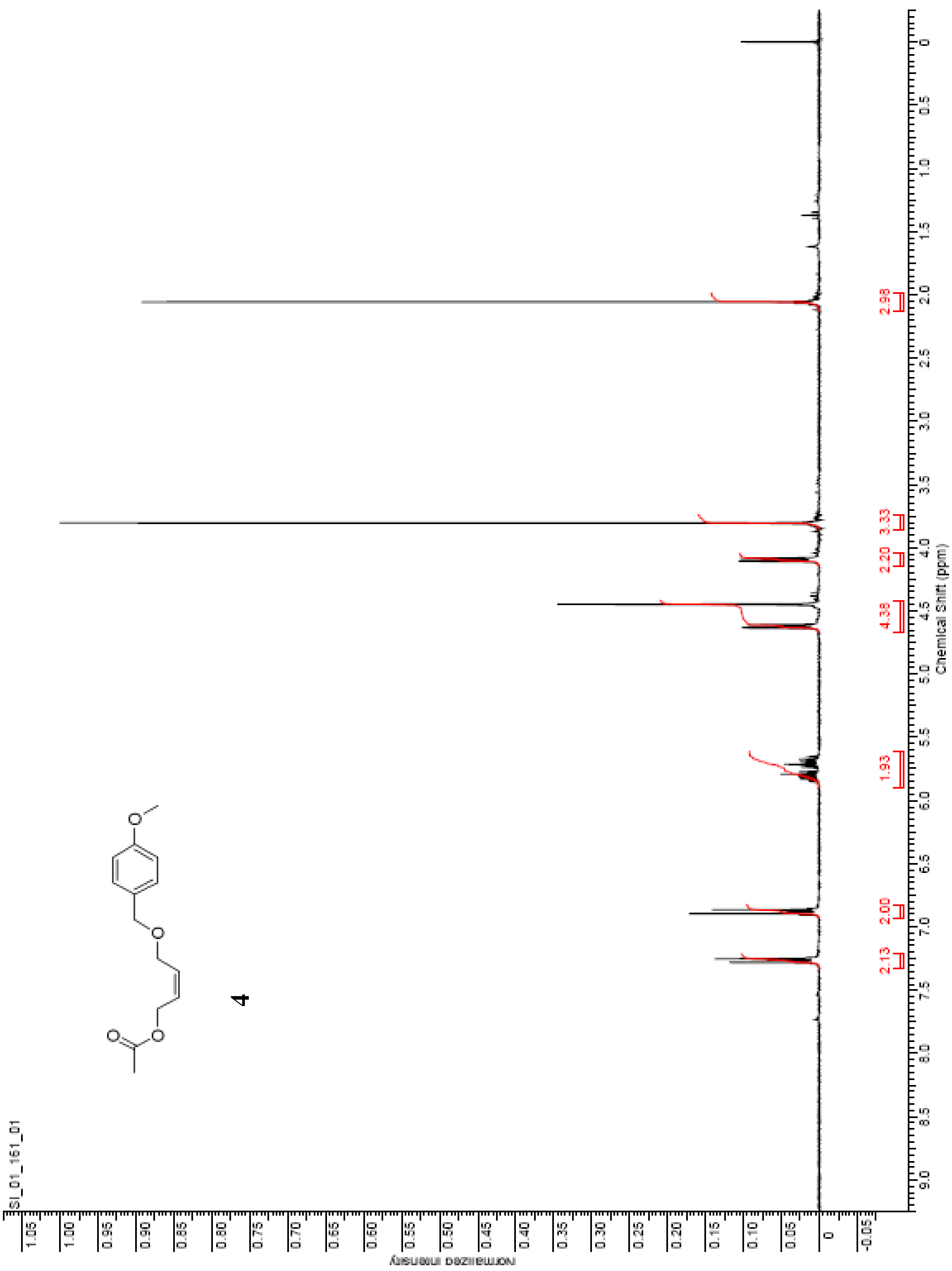


3

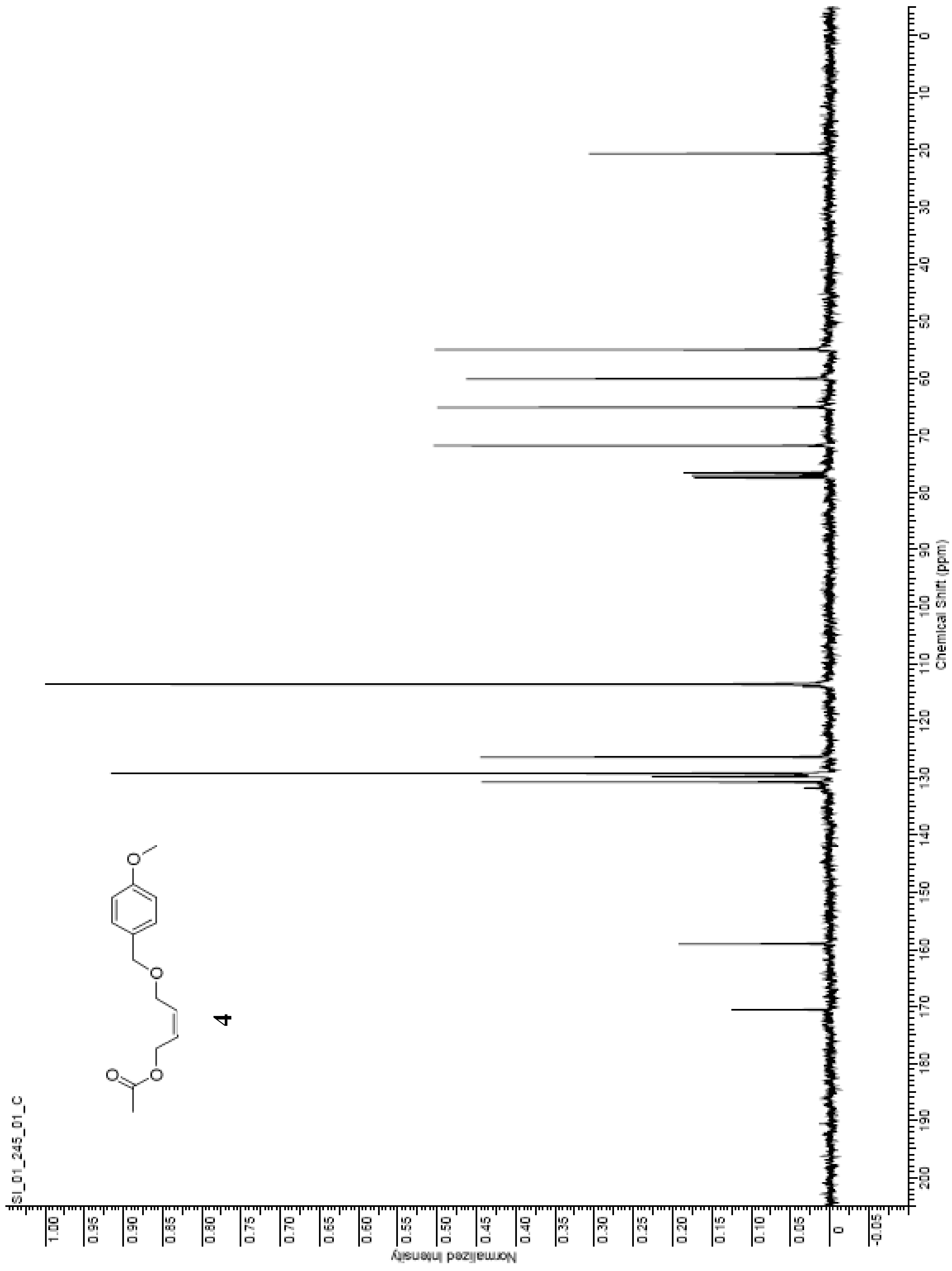

N
N+
Cl
·CuCl2
3
Chemical Shift (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60

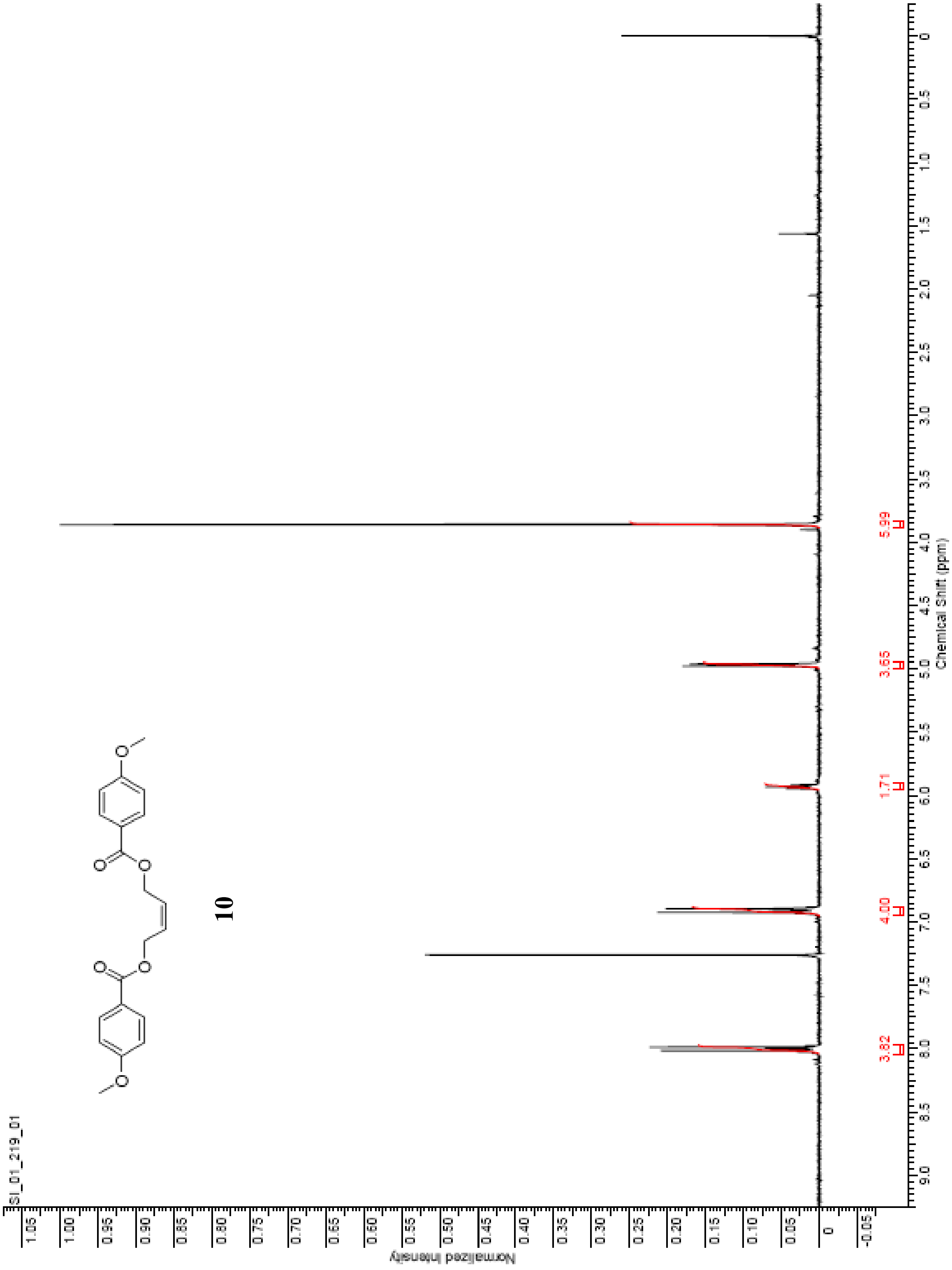

SI_01_244_01
HO
O
O
1.40
3.02
3.93
2.02
2.00
2.00
2.35
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Chemical Shift (ppm)
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
Normalized Intensity

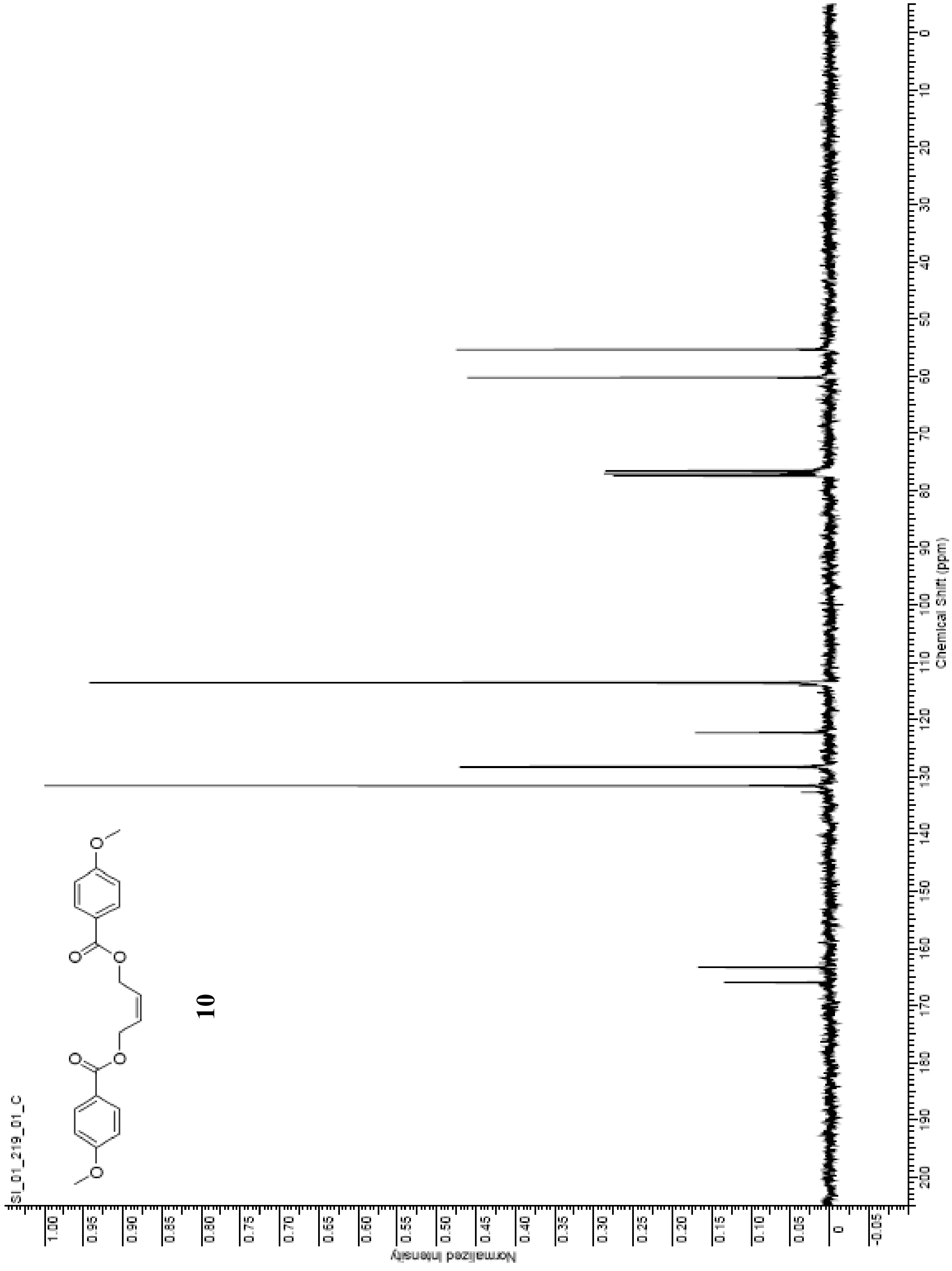

SI_01_244_01_C
HO
O
O
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05


4

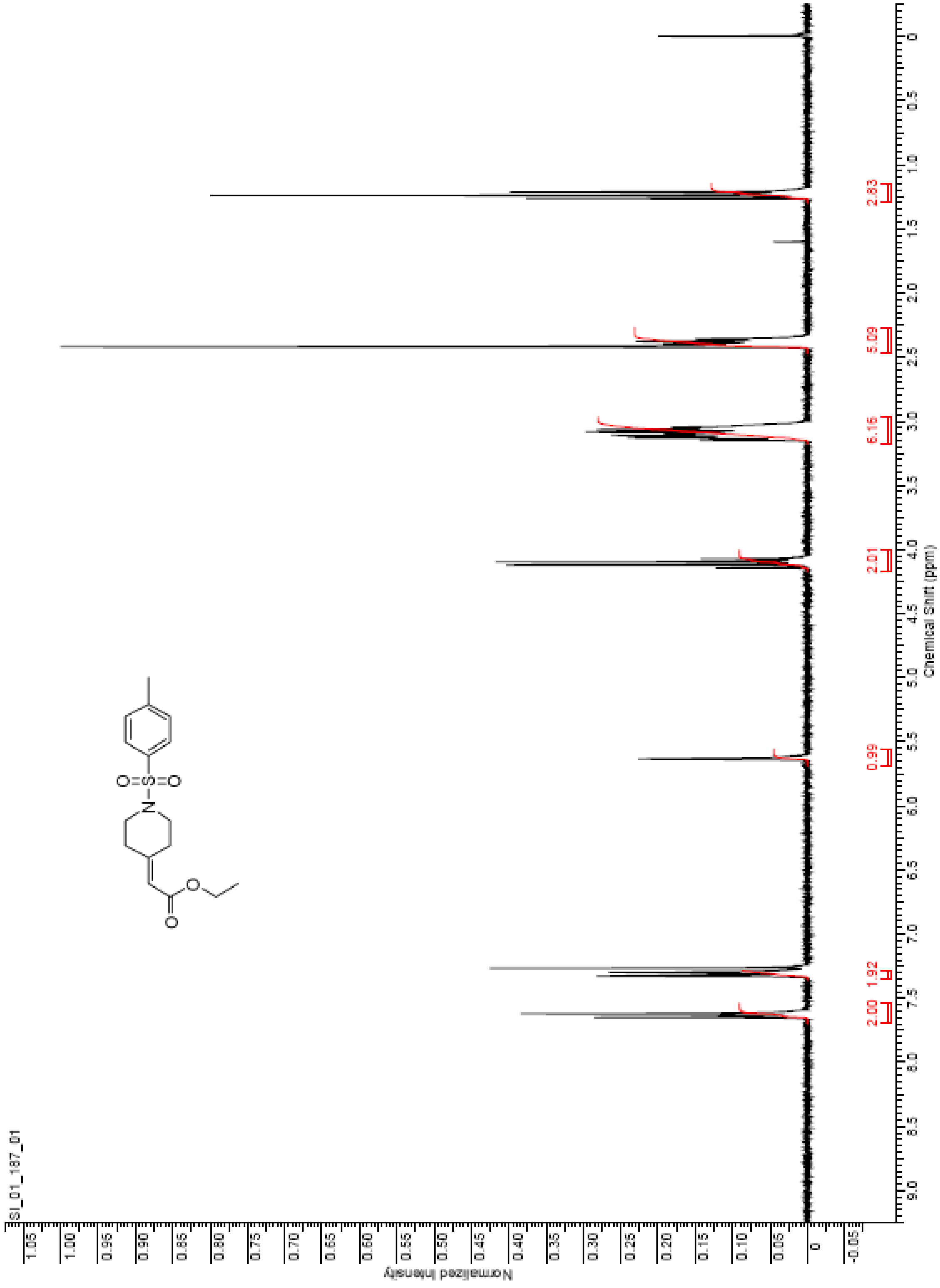
SI_01_161_01
2.98
3.33
2.20
4.38
1.93
2.00
2.13
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Chemical Shift (ppm)
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
normalized intensity

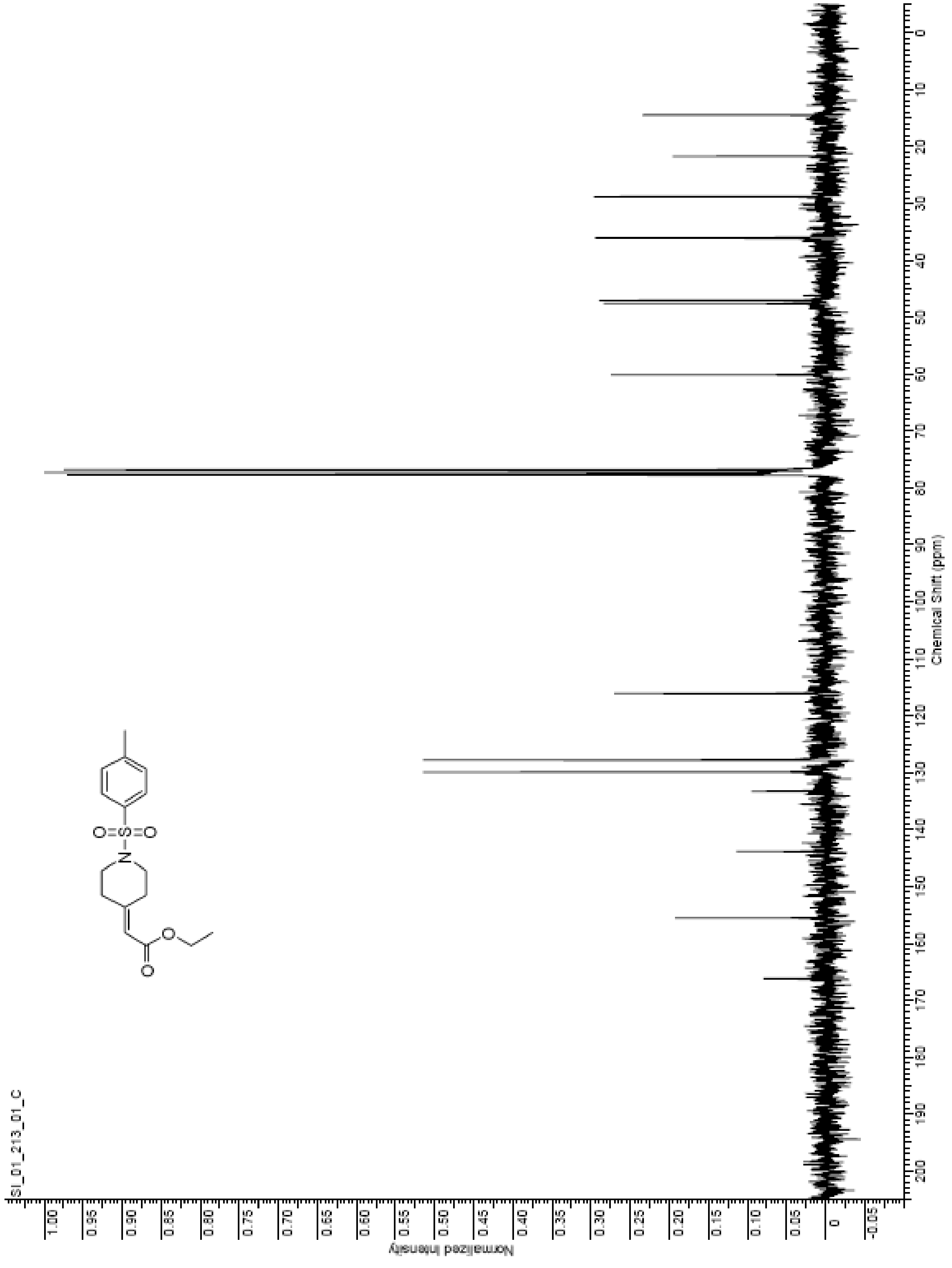

SI_01_245_01_C
4
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

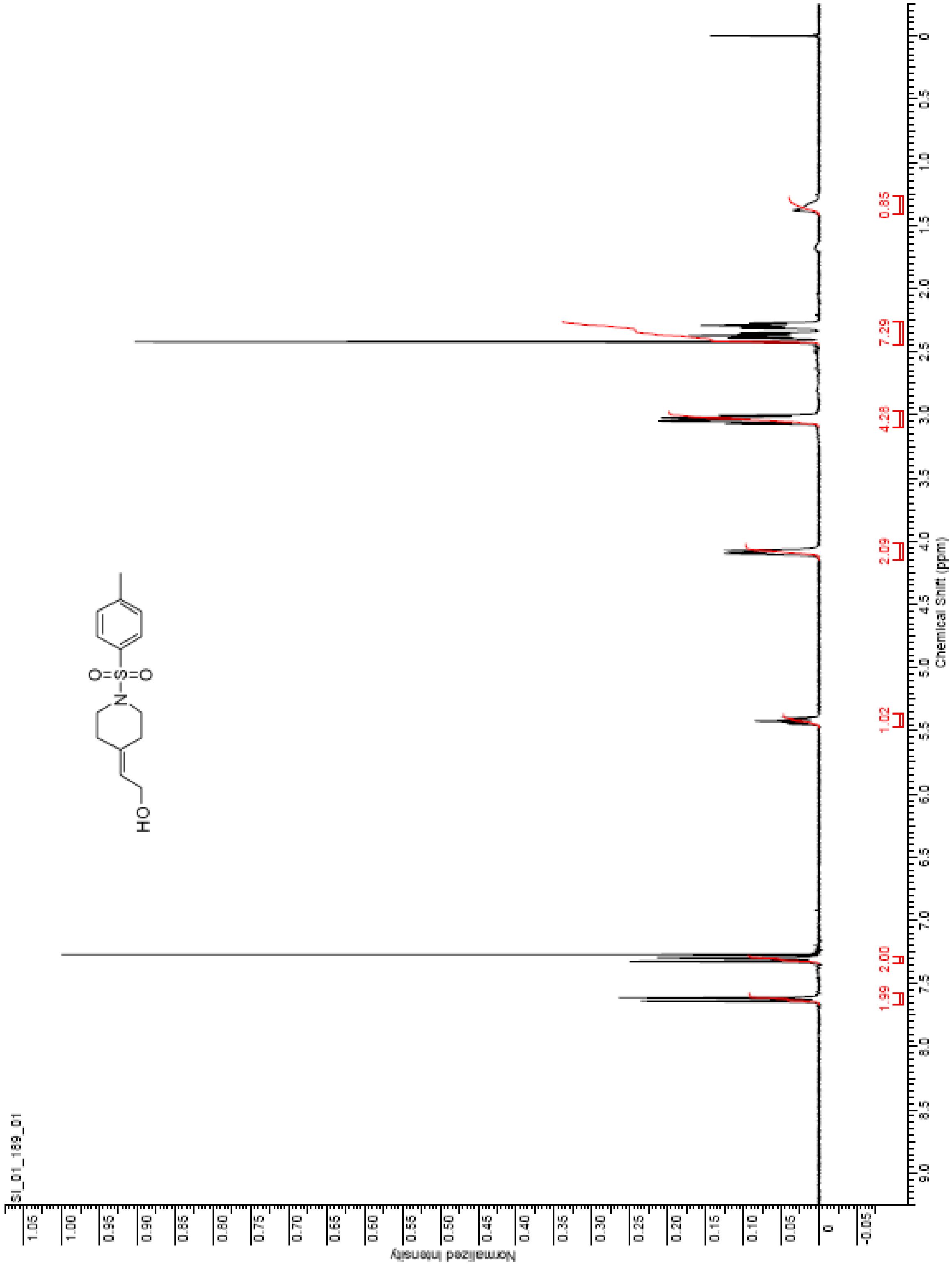

SI_01_219_01
10
Normalized Intensity
Chemical Shift (ppm)
3.82
4.00
1.71
3.65
5.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

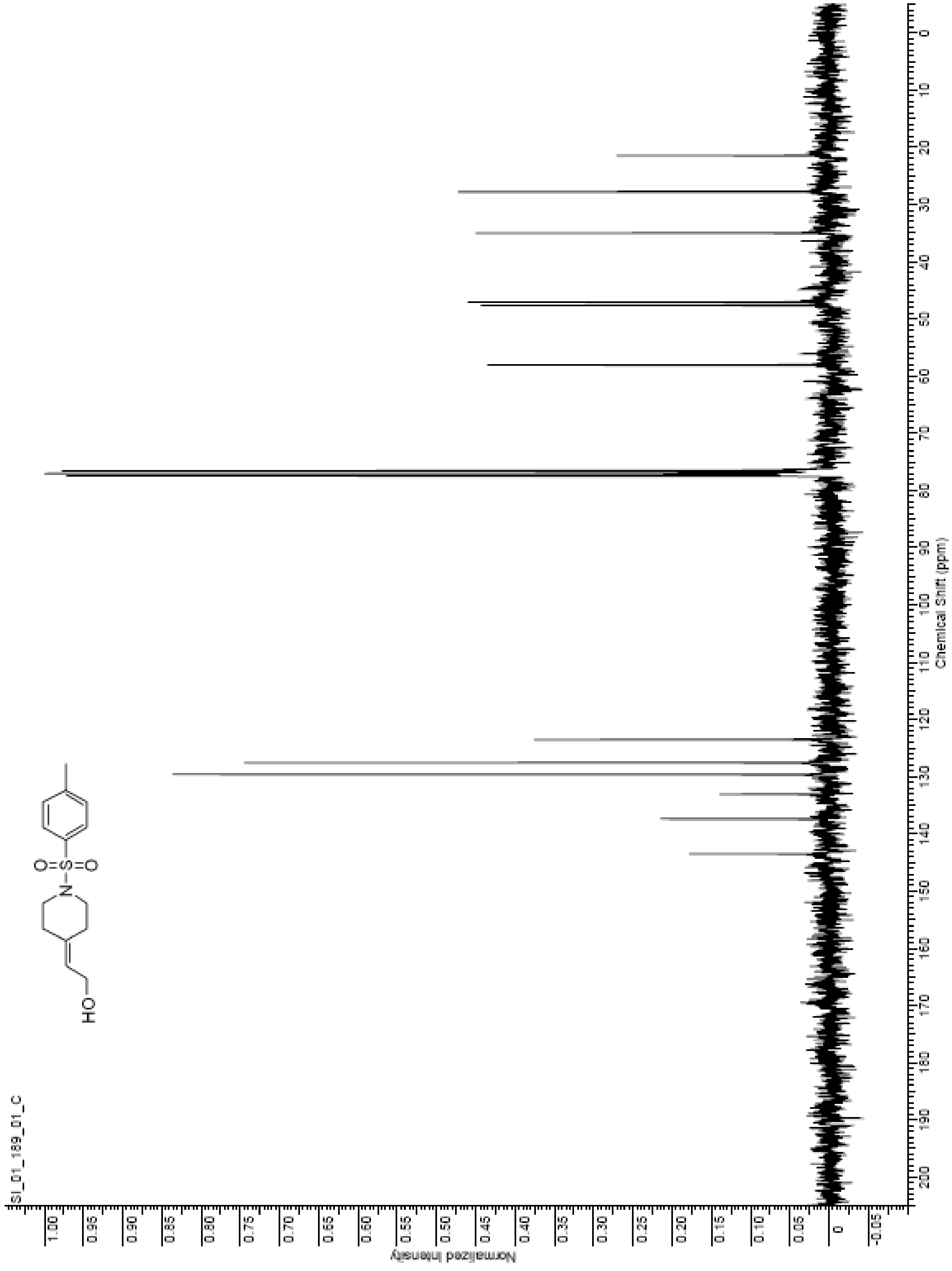

SI_01_219_01_C
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
O
O
O

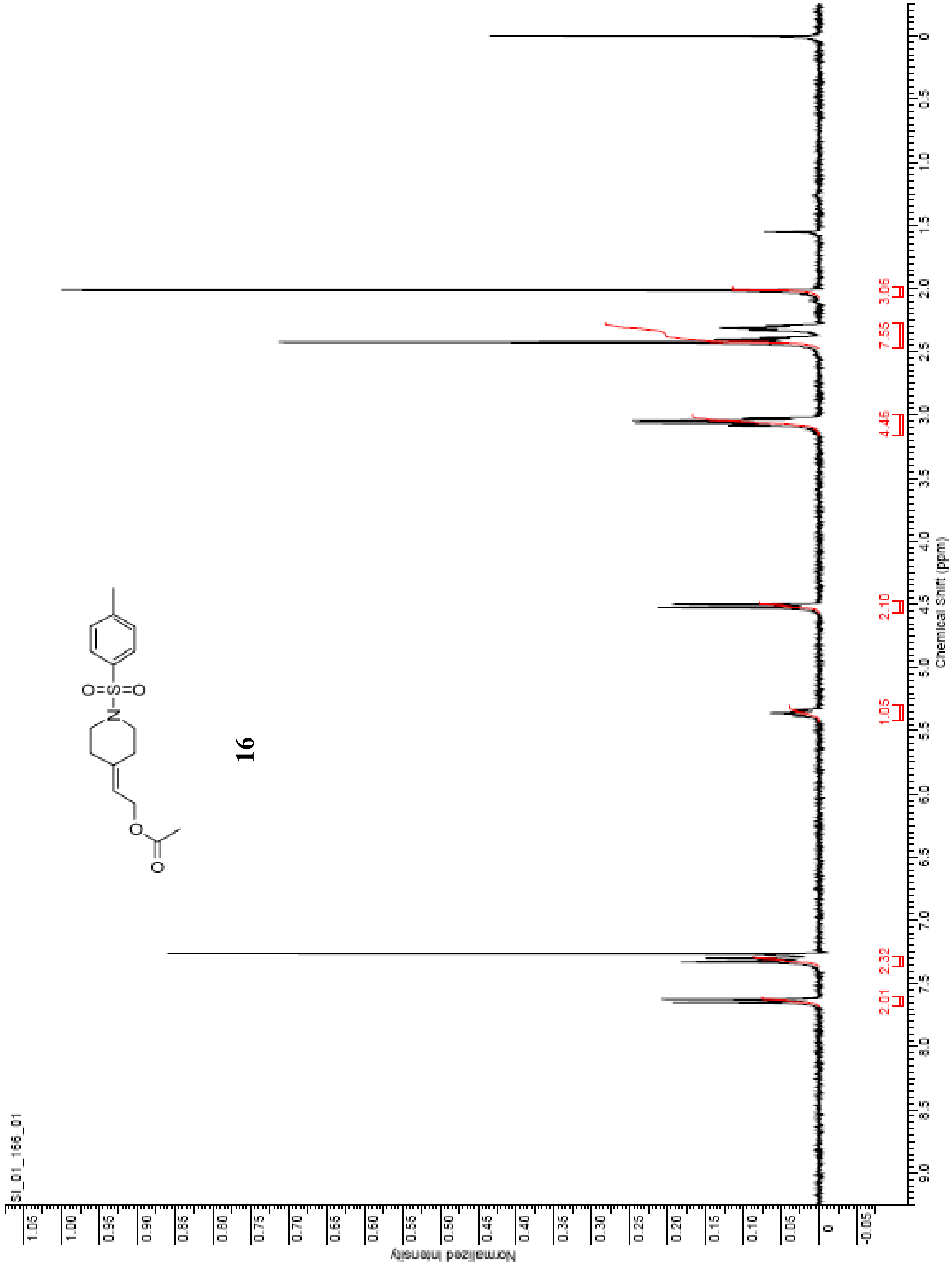
10


SI_D1_187_D1
Normalized Intensity
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
Chemical Shift (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
2.00
1.92
0.99
2.01
6.16
5.09
2.83
O
O
O
S
N
O

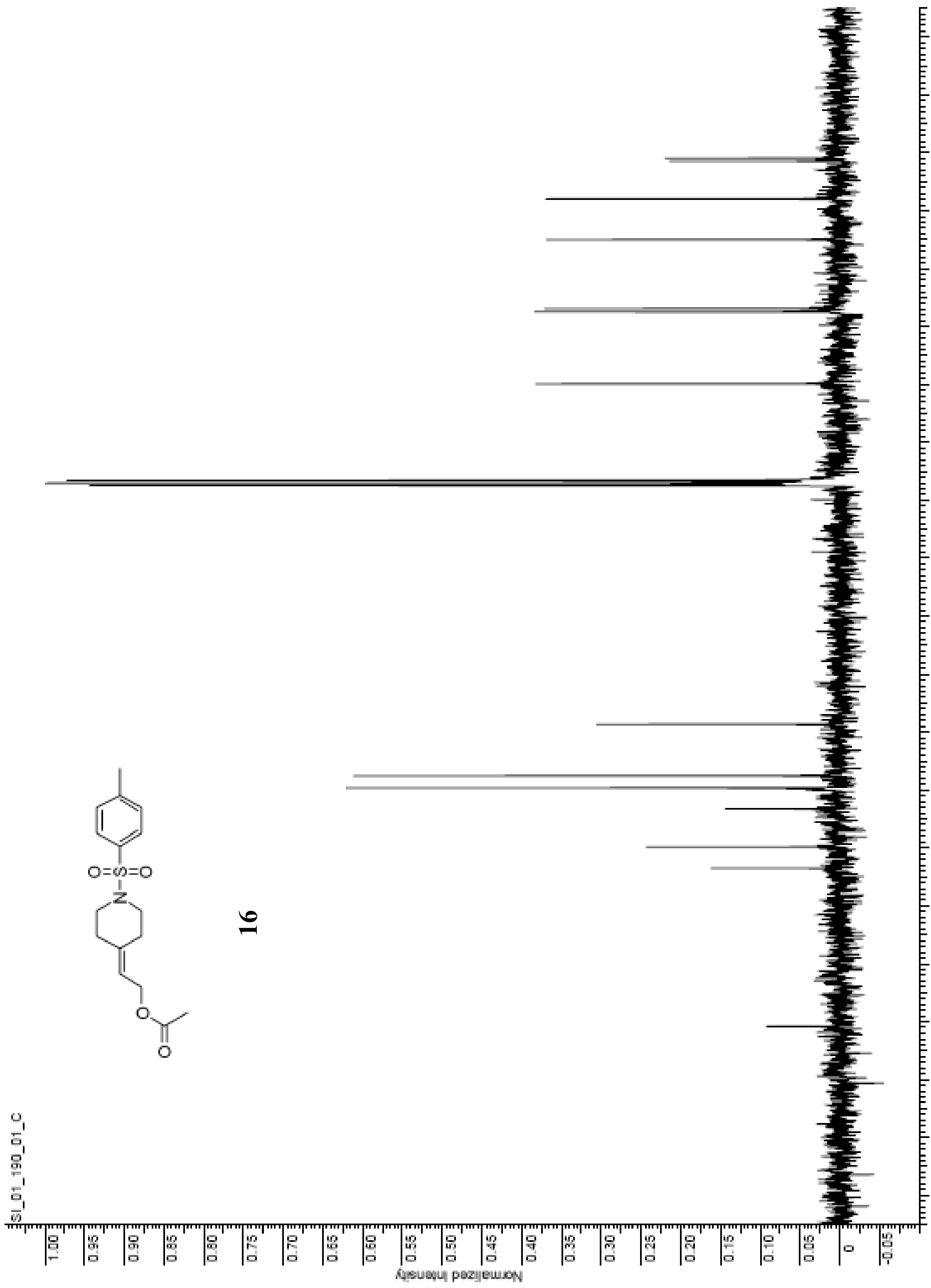

SI_01_213_01_C
O
O
O=S=O
N
Chemical Shift (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05


SI_01_189_01
HO
N
O=S=O
Normalized Intensity
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
Chemical Shift (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
1.99
2.00
1.02
2.09
4.28
7.29
0.85

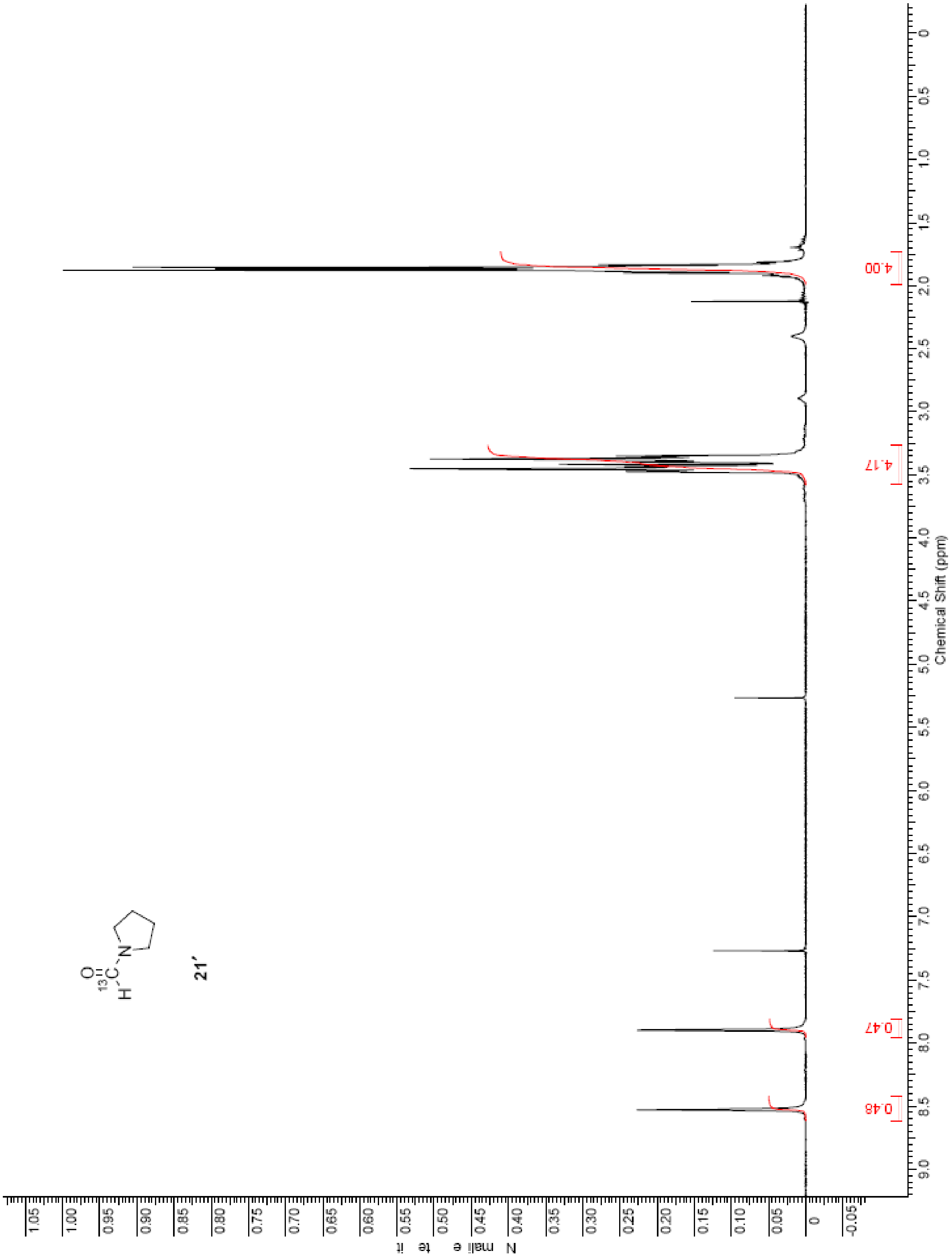

SI_01_189_01_C
HO
N
S
O
O
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05


SI_01_166_01
Normalized Intensity
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
Chemical Shift (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
2.01
2.32
1.05
2.10
4.46
7.55
3.06
O
O
N
S
O
O

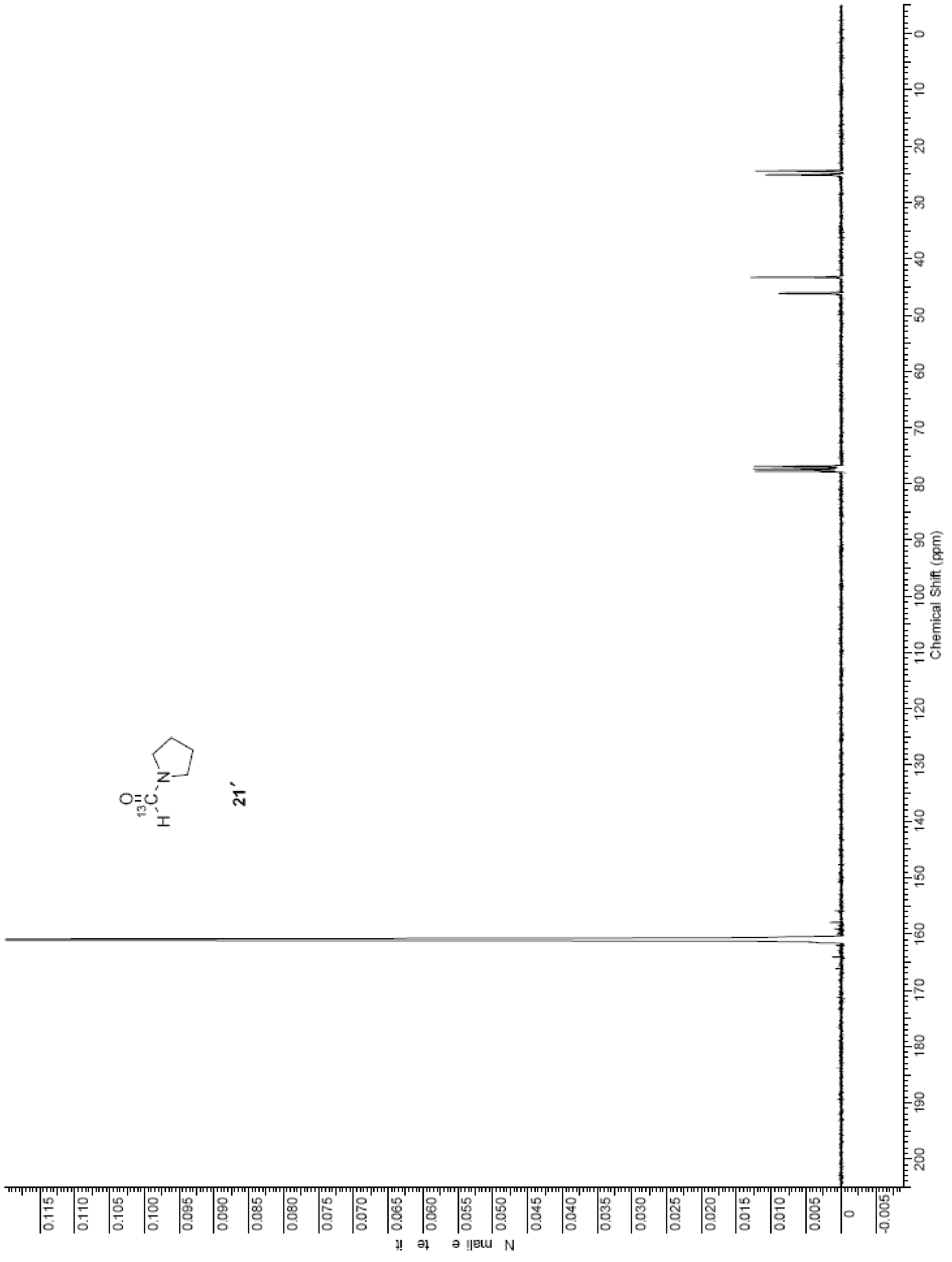
16


SI_01_190_01_C
O
O
S
O
O
N
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

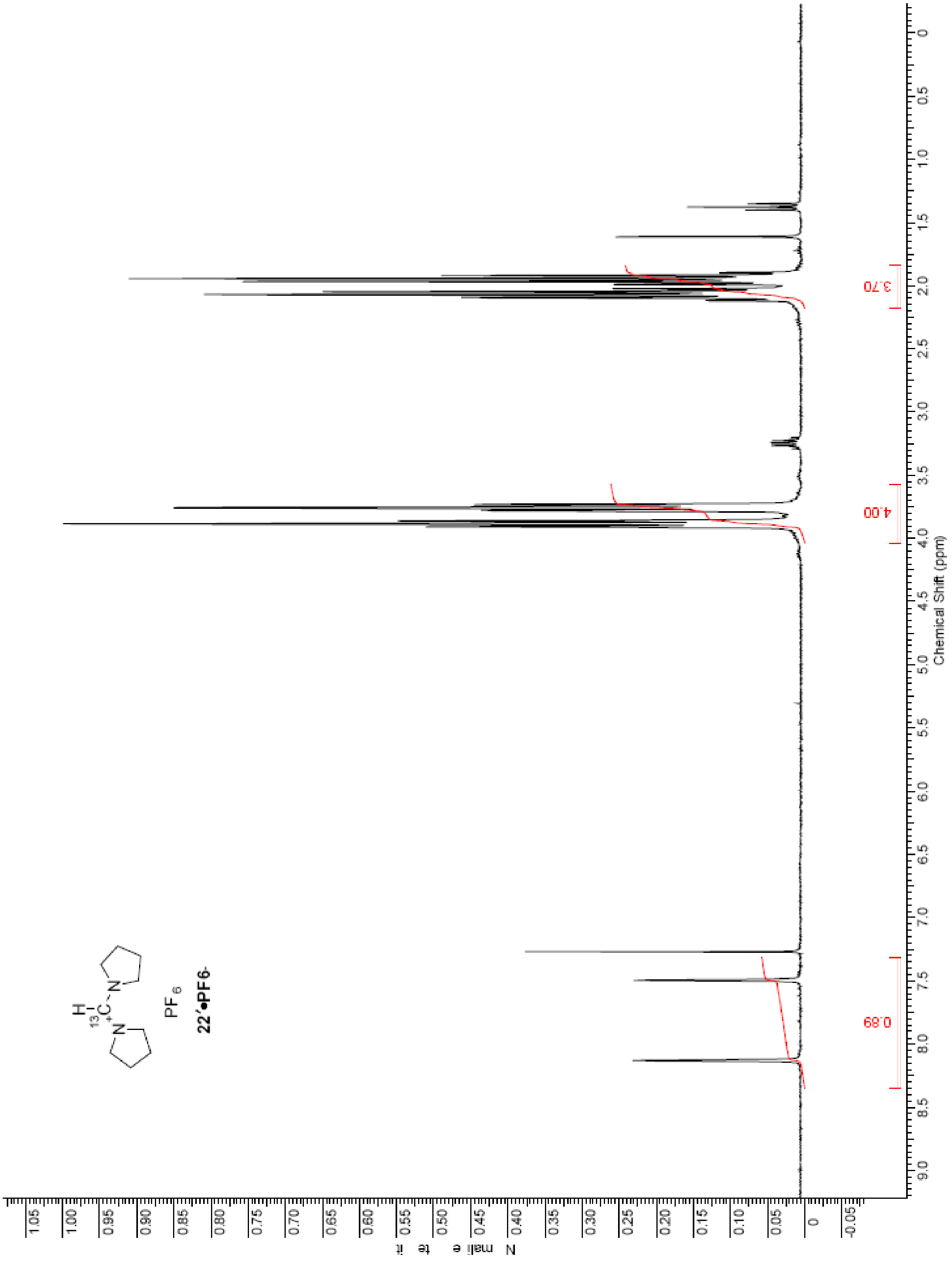
16

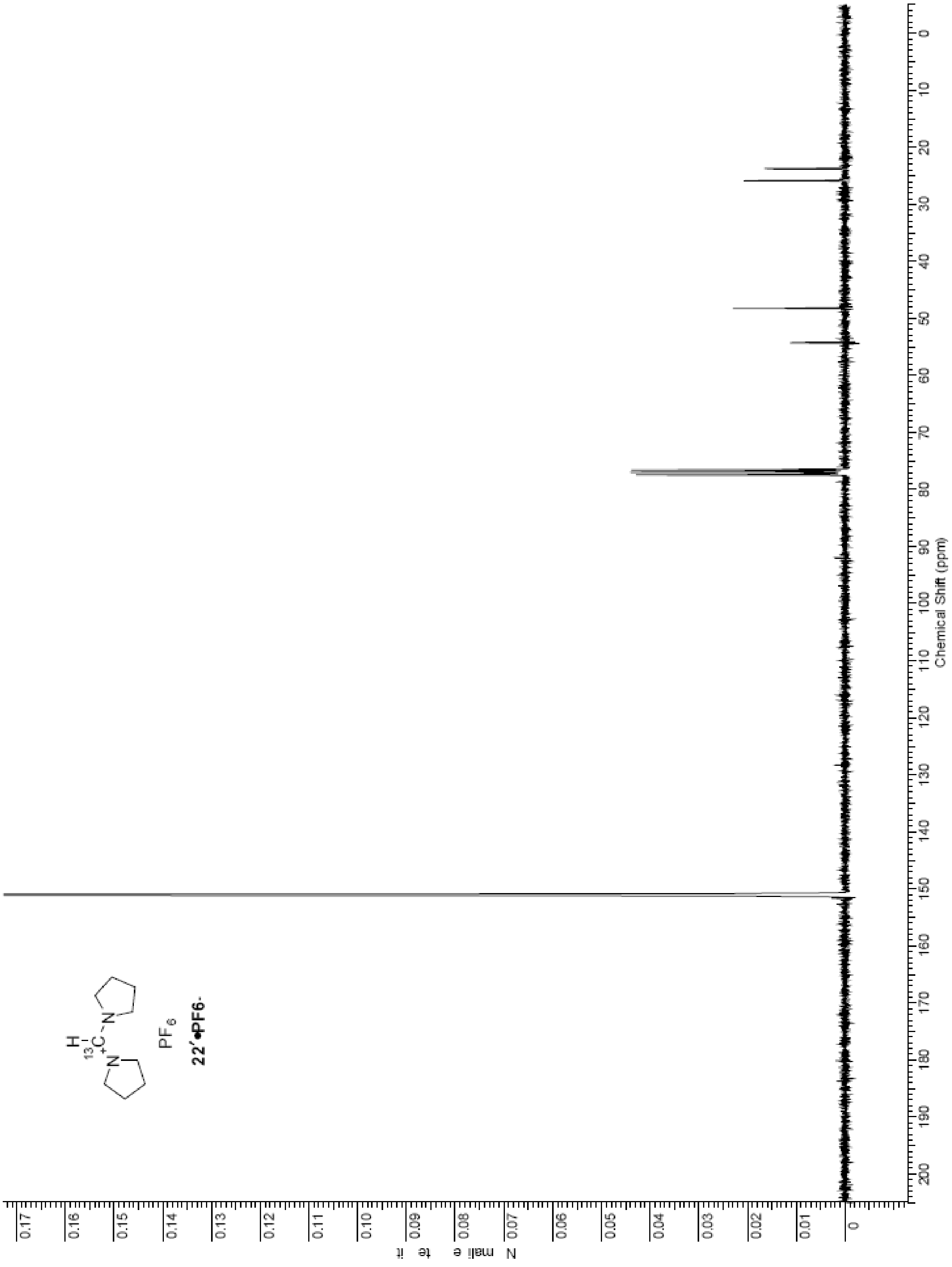

O
H
^{13}C
N
4.00
4.17
0.47
0.48
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Chemical Shift (ppm)
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

21'

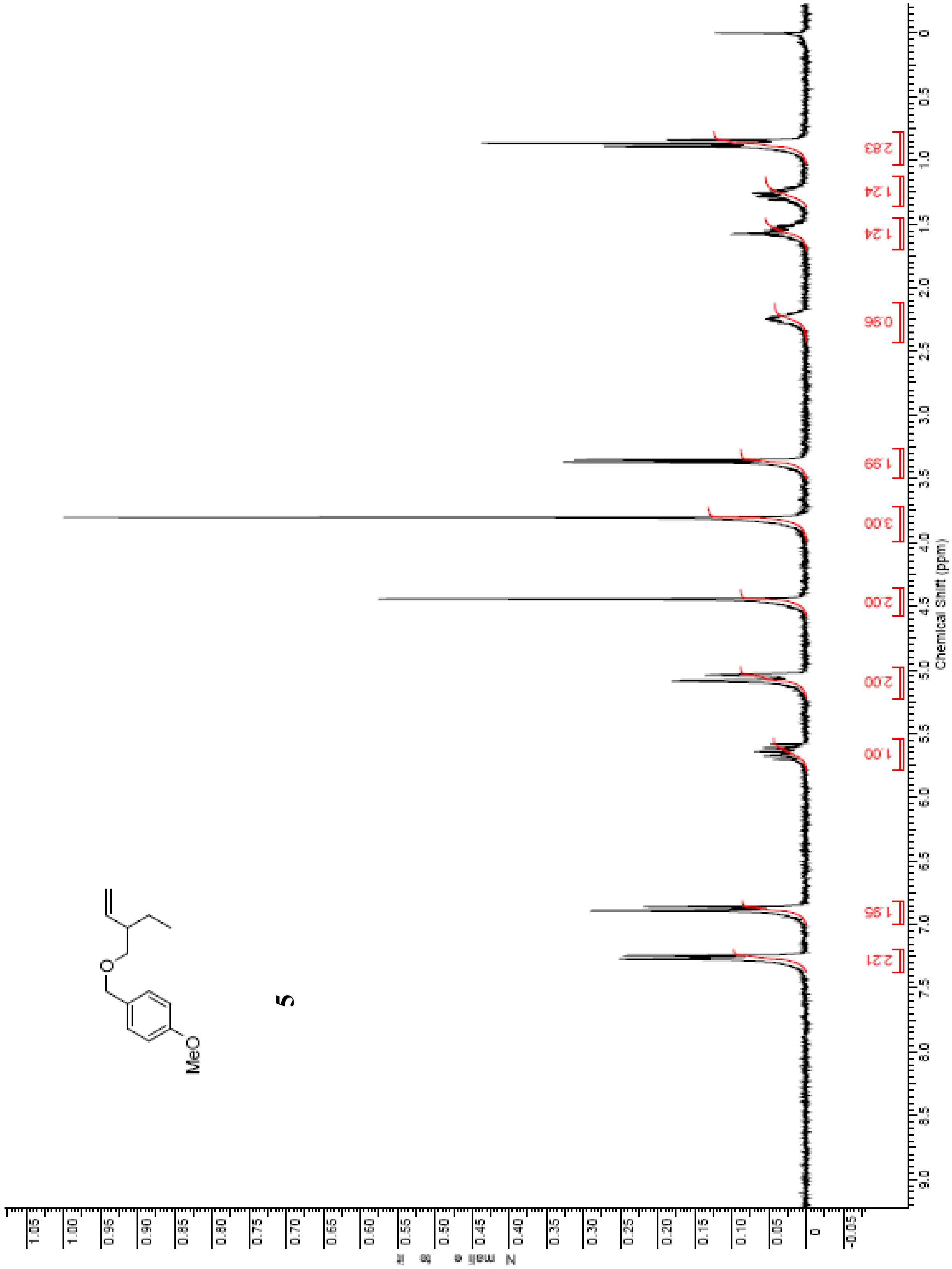

H
13C
O
N
Chemical Shift (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
0.115
0.110
0.105
0.100
0.095
0.090
0.085
0.080
0.075
0.070
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
-0.005
N mali e te it

21´

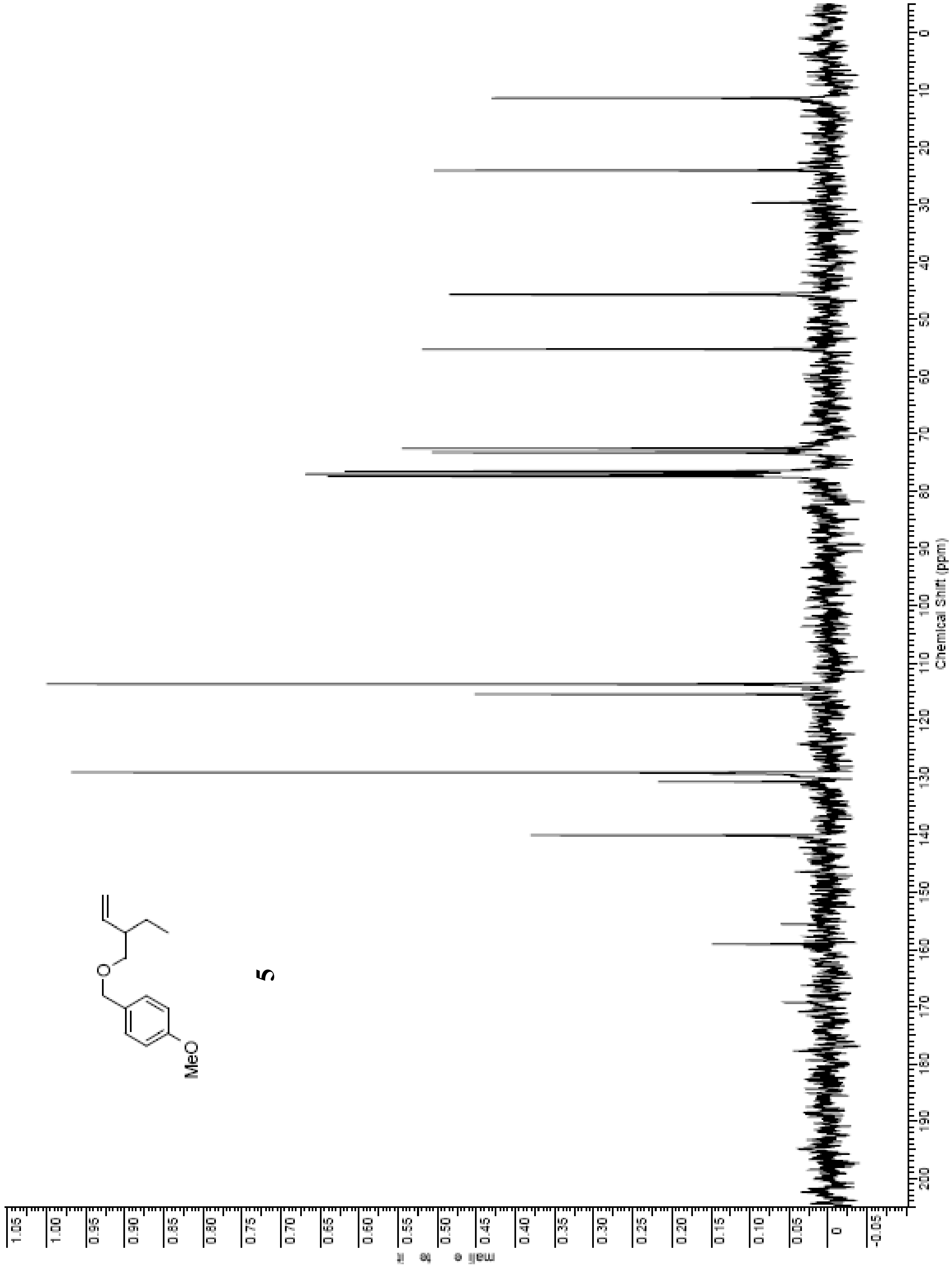

H
13C
N+
N
PF6
22'•PF6-
0.89
4.00
3.70
Chemical Shift (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05


H
13
C
N
+
N
PF6
22'•PF6-
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Chemical Shift (ppm)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.12
0.13
0.14
0.15
0.16
0.17
N mali e te it

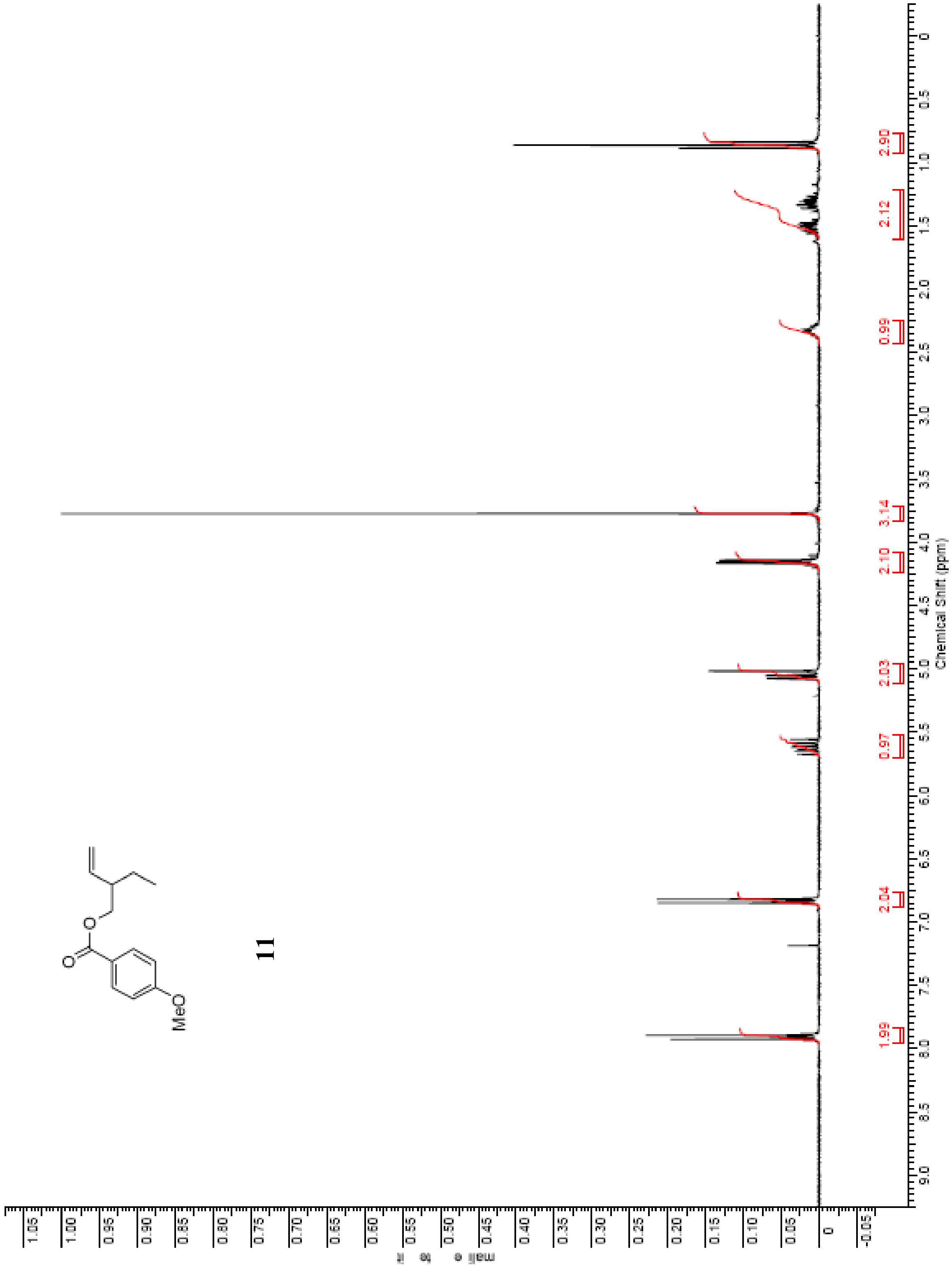
4.2. NMR Spectra for 5, 11, 13, 15, and 17

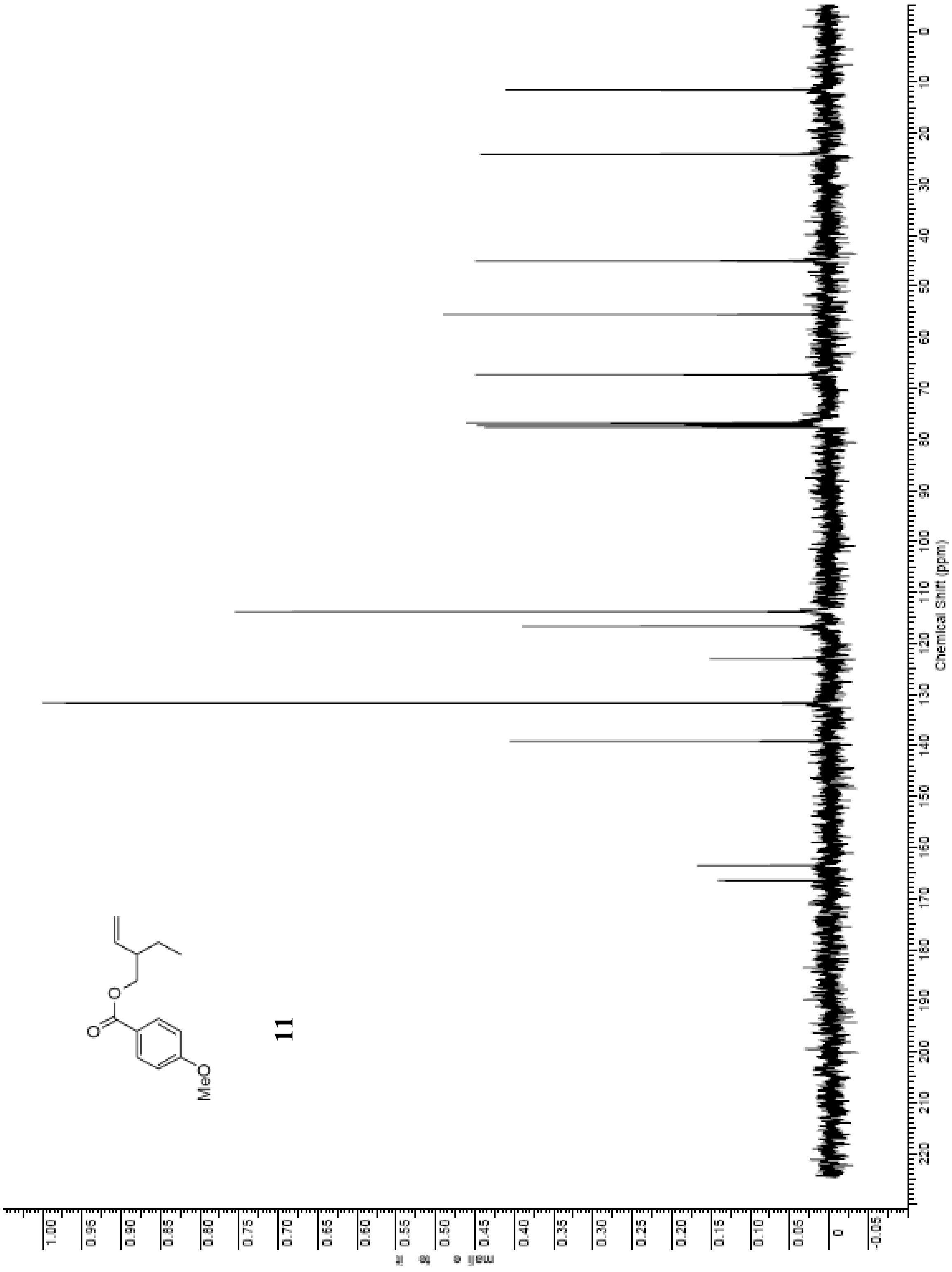


5

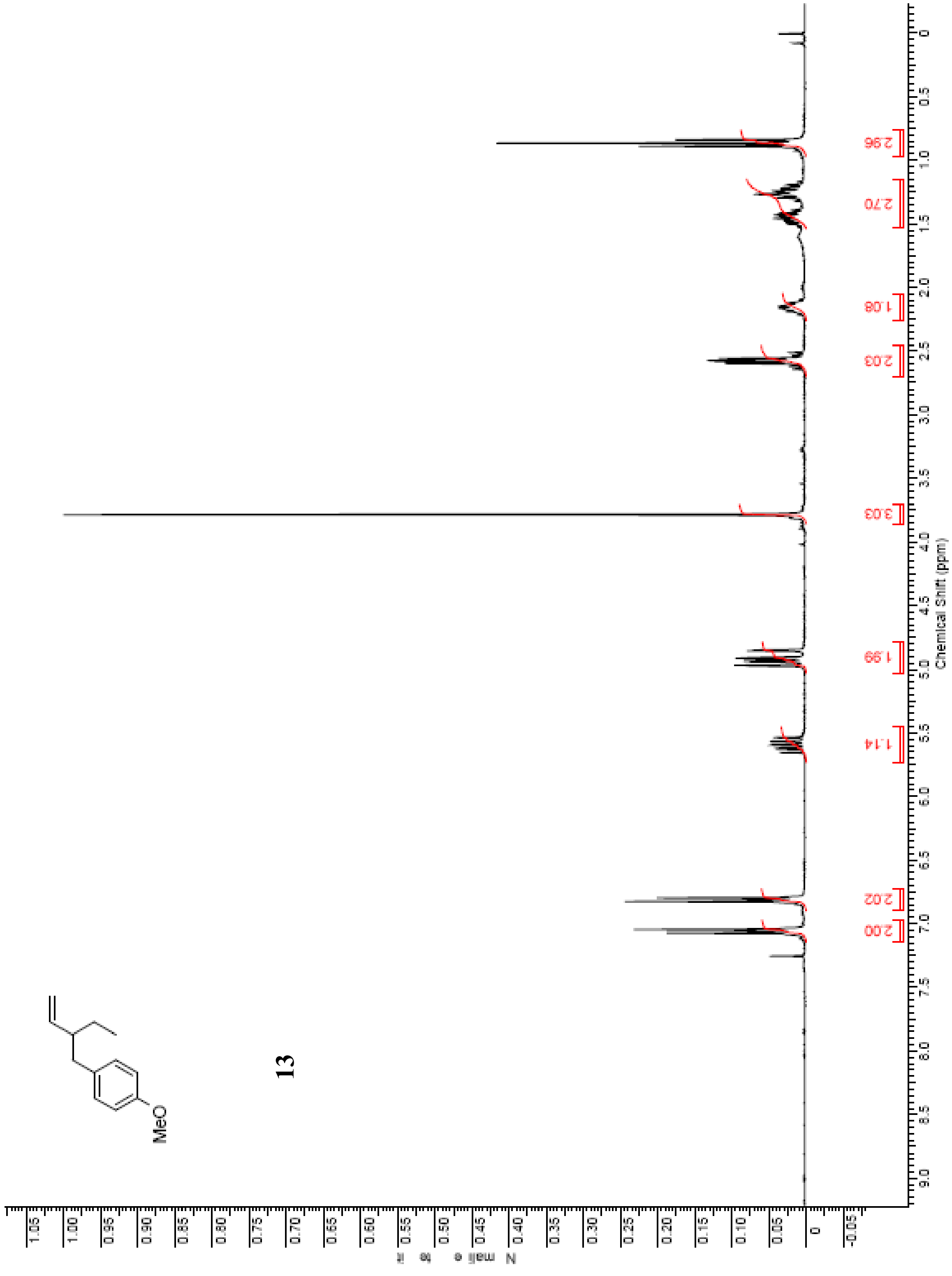

MeO
O
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

5

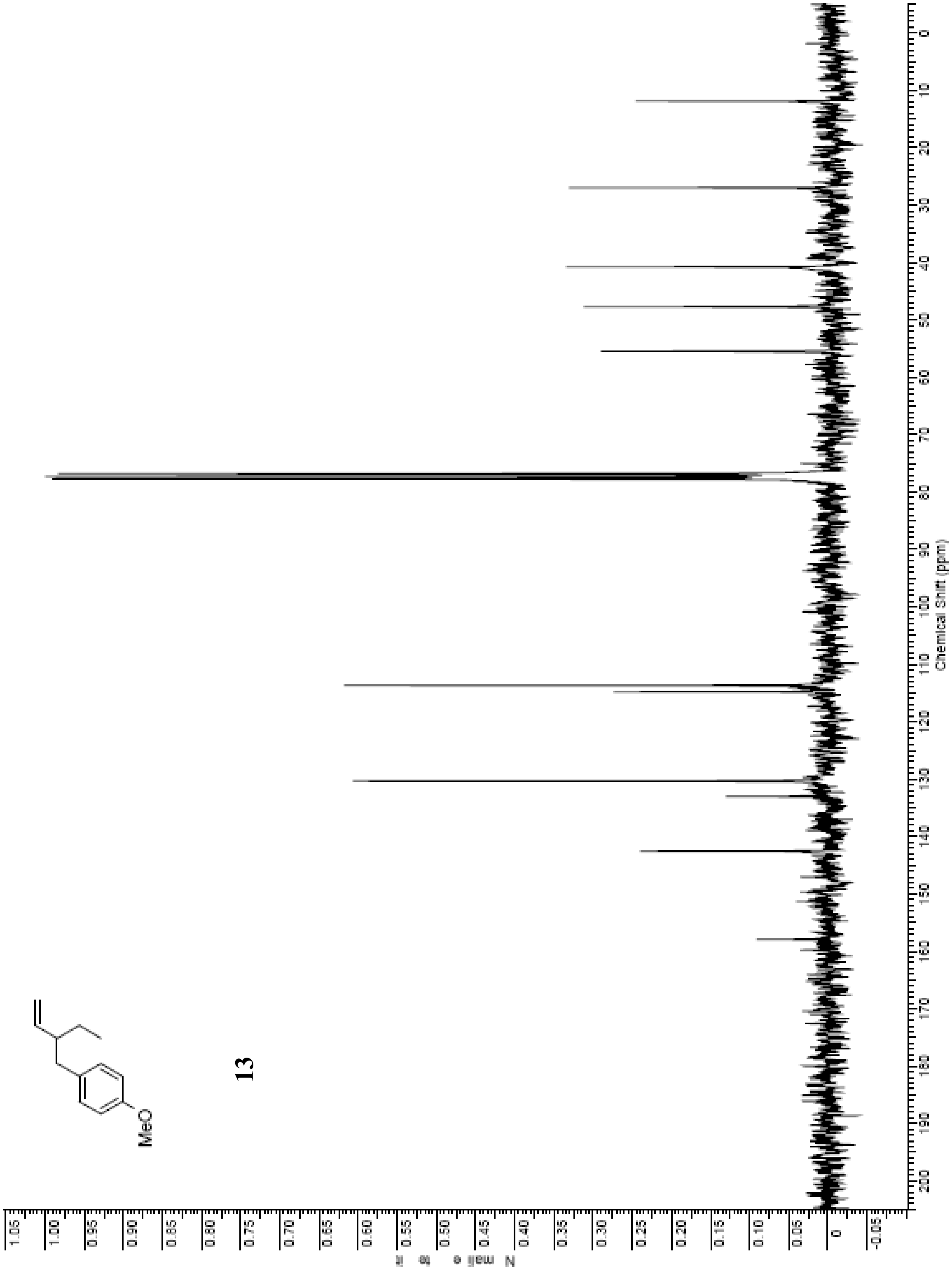

11
MeO
O
O
2.90
2.12
0.99
3.14
2.10
2.03
0.97
2.04
1.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05


MeO
O
O
Chemical Shift (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

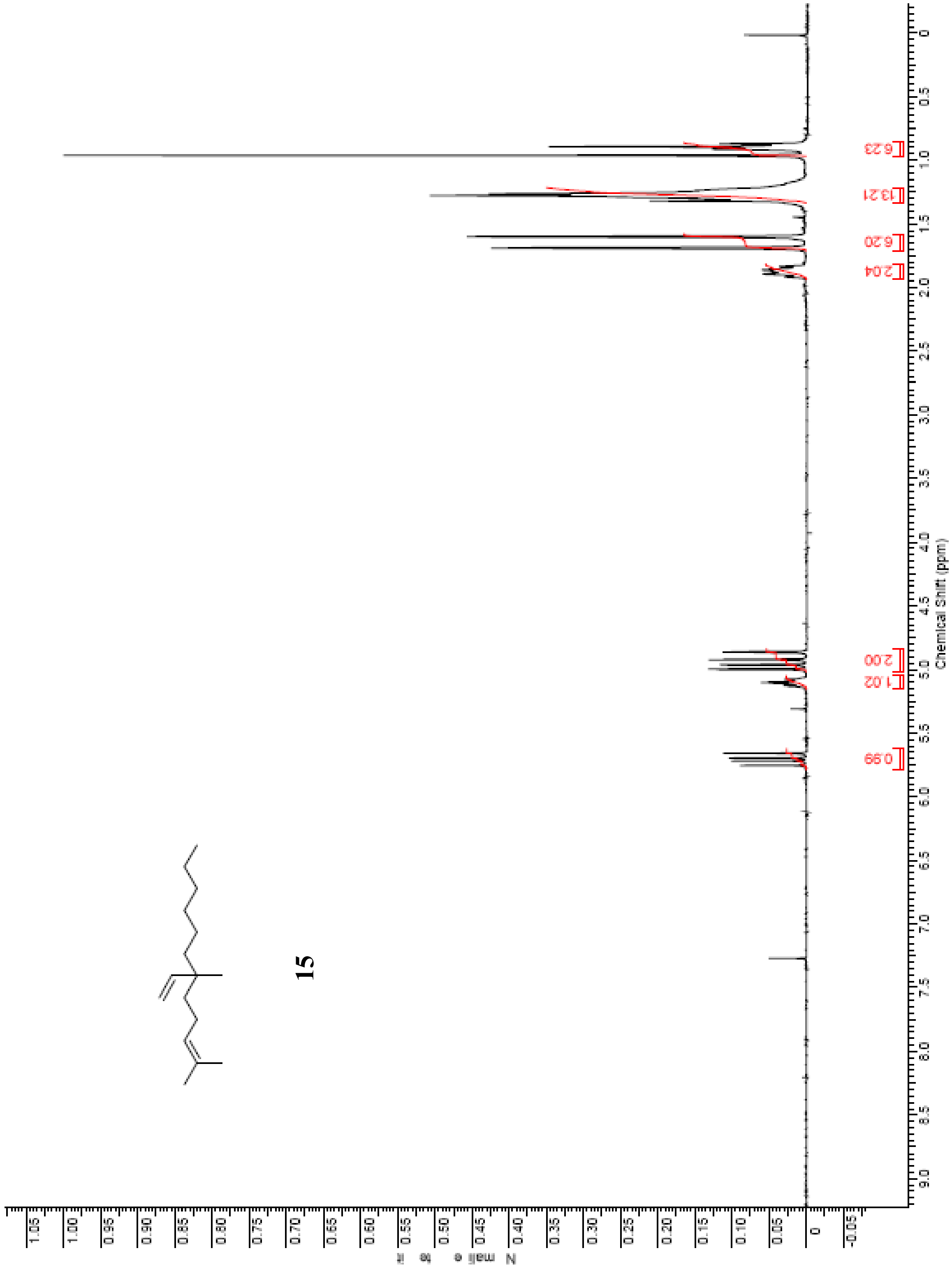
11


MeO
2.96
2.70
1.08
2.03
3.03
1.99
1.14
2.02
2.00
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Chemical Shift (ppm)
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

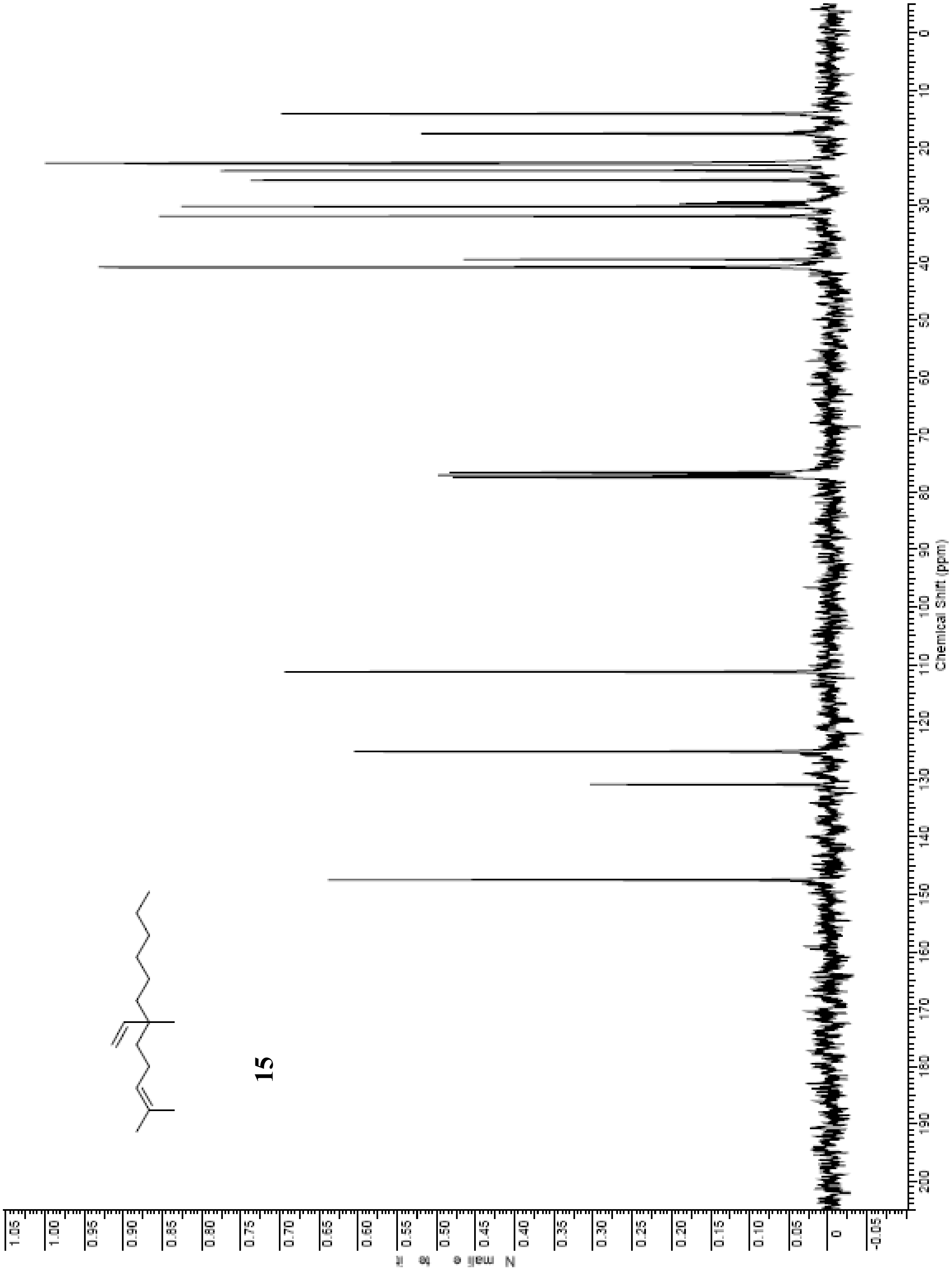
13


MeO
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Chemical Shift (ppm)
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

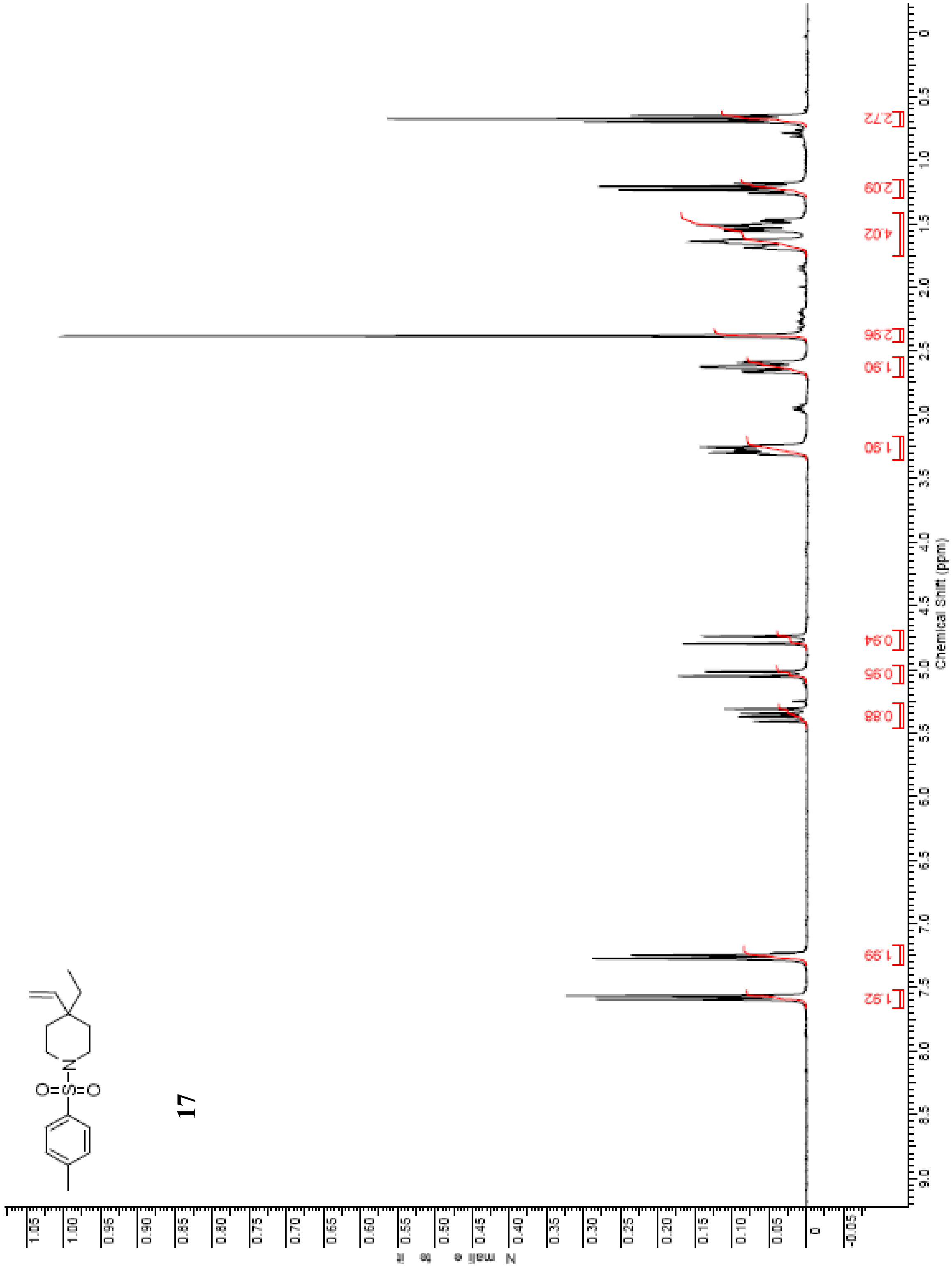
13


6.23
13.21
6.20
2.04
2.00
1.02
0.99
Chemical Shift (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

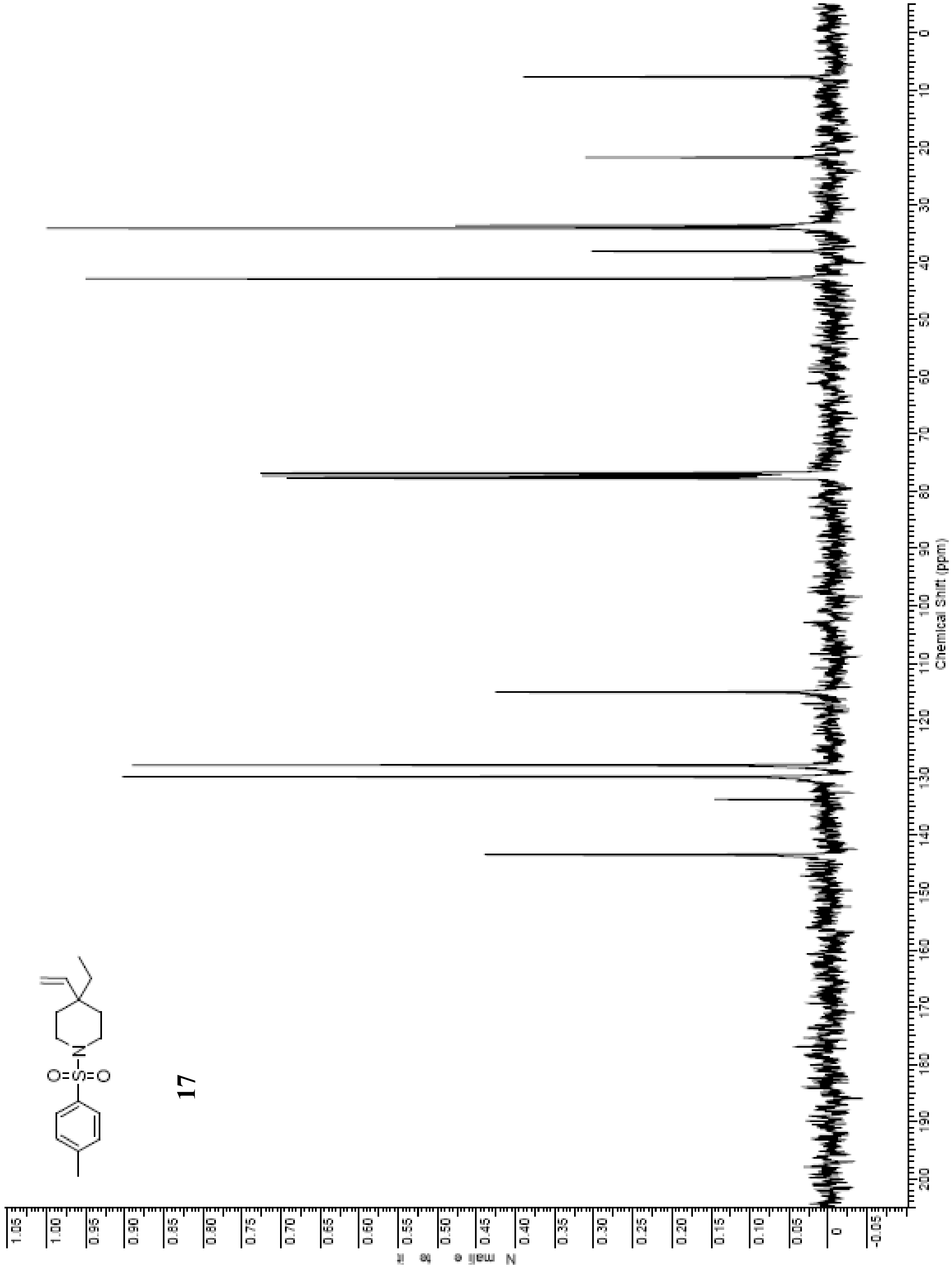
15


Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

15

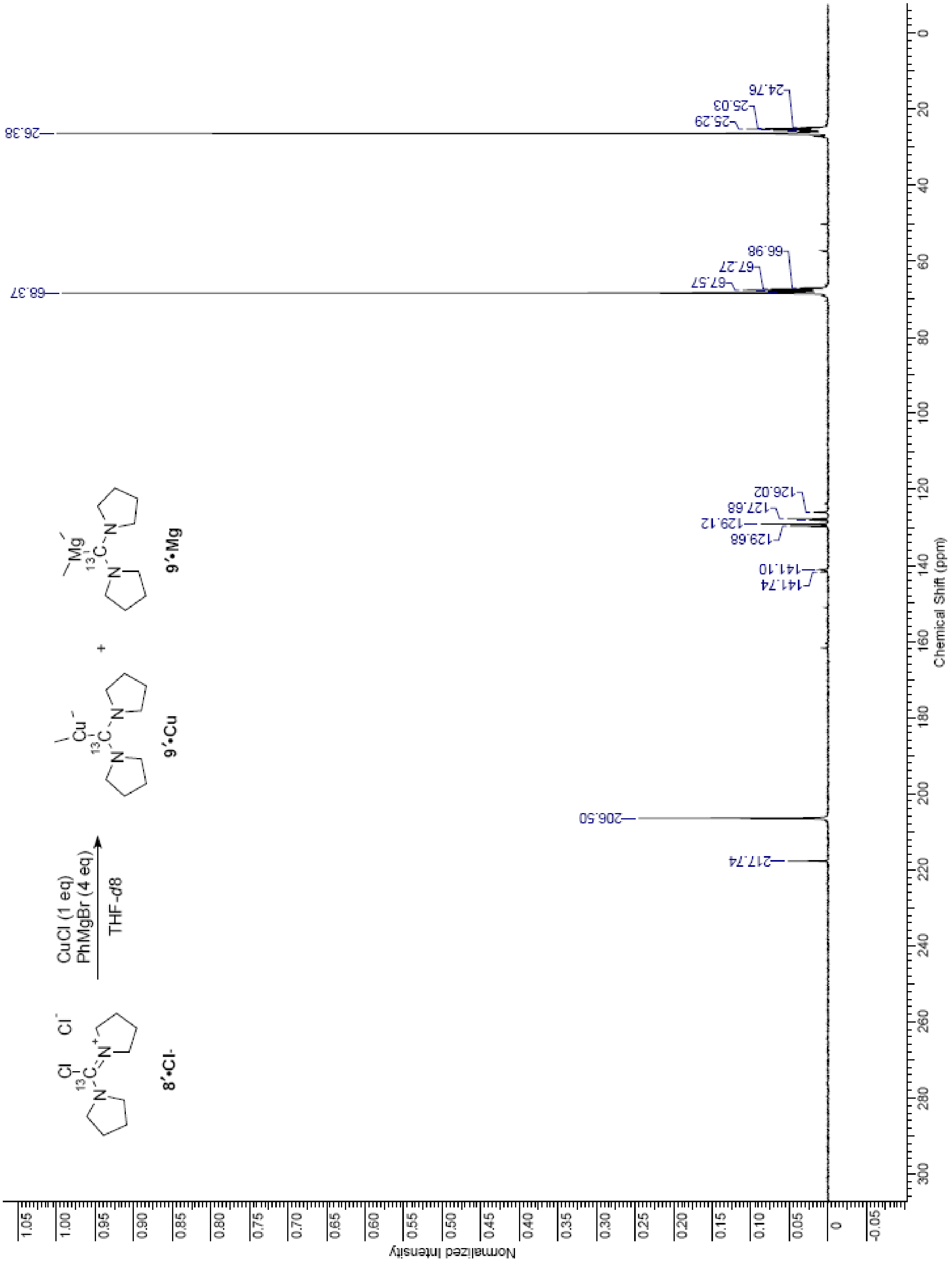

O=S=O
N
Chemical Shift (ppm)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
2.72
2.09
4.02
2.96
1.90
1.90
0.94
0.95
0.88
1.99
1.92
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

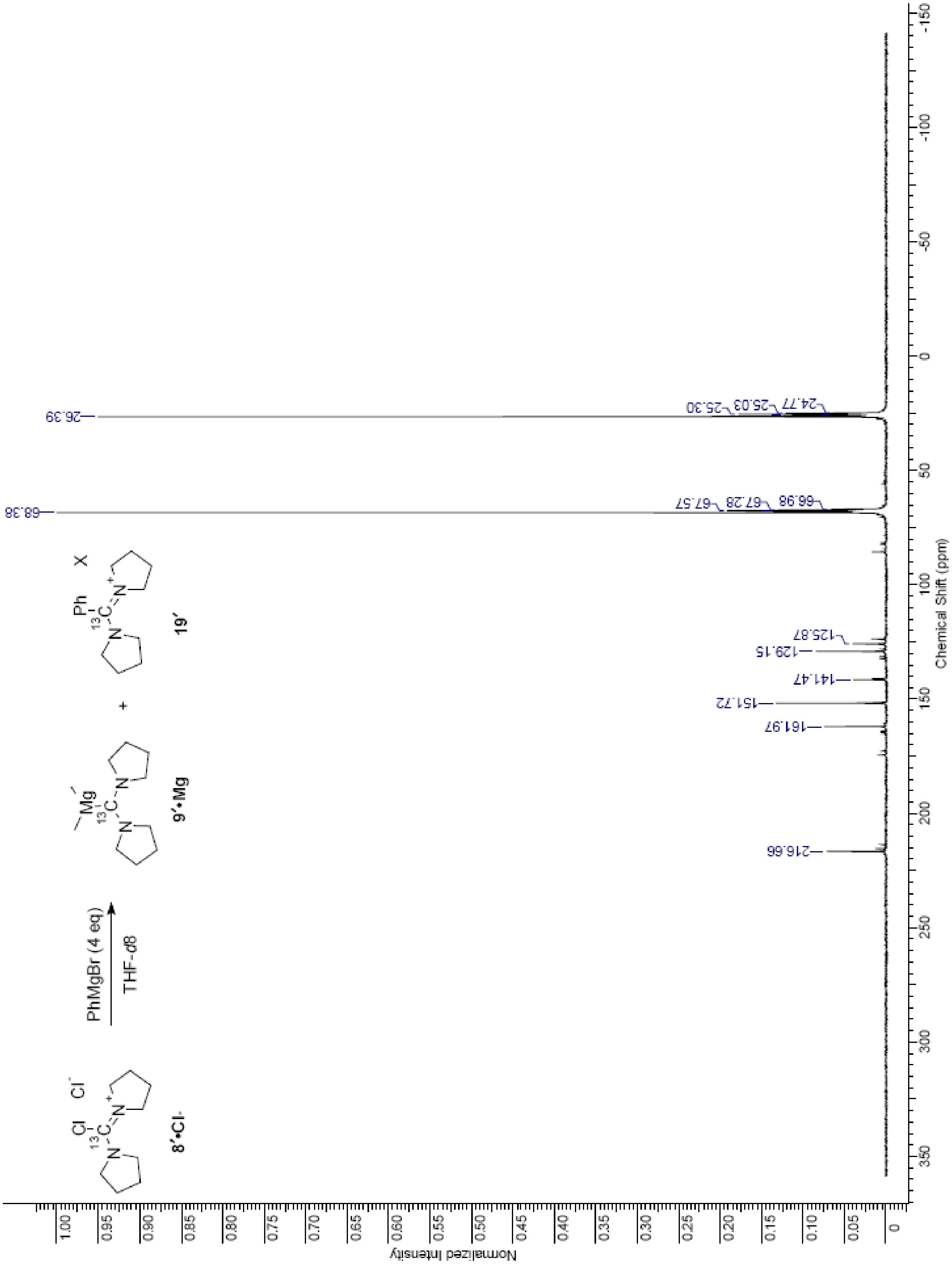
17

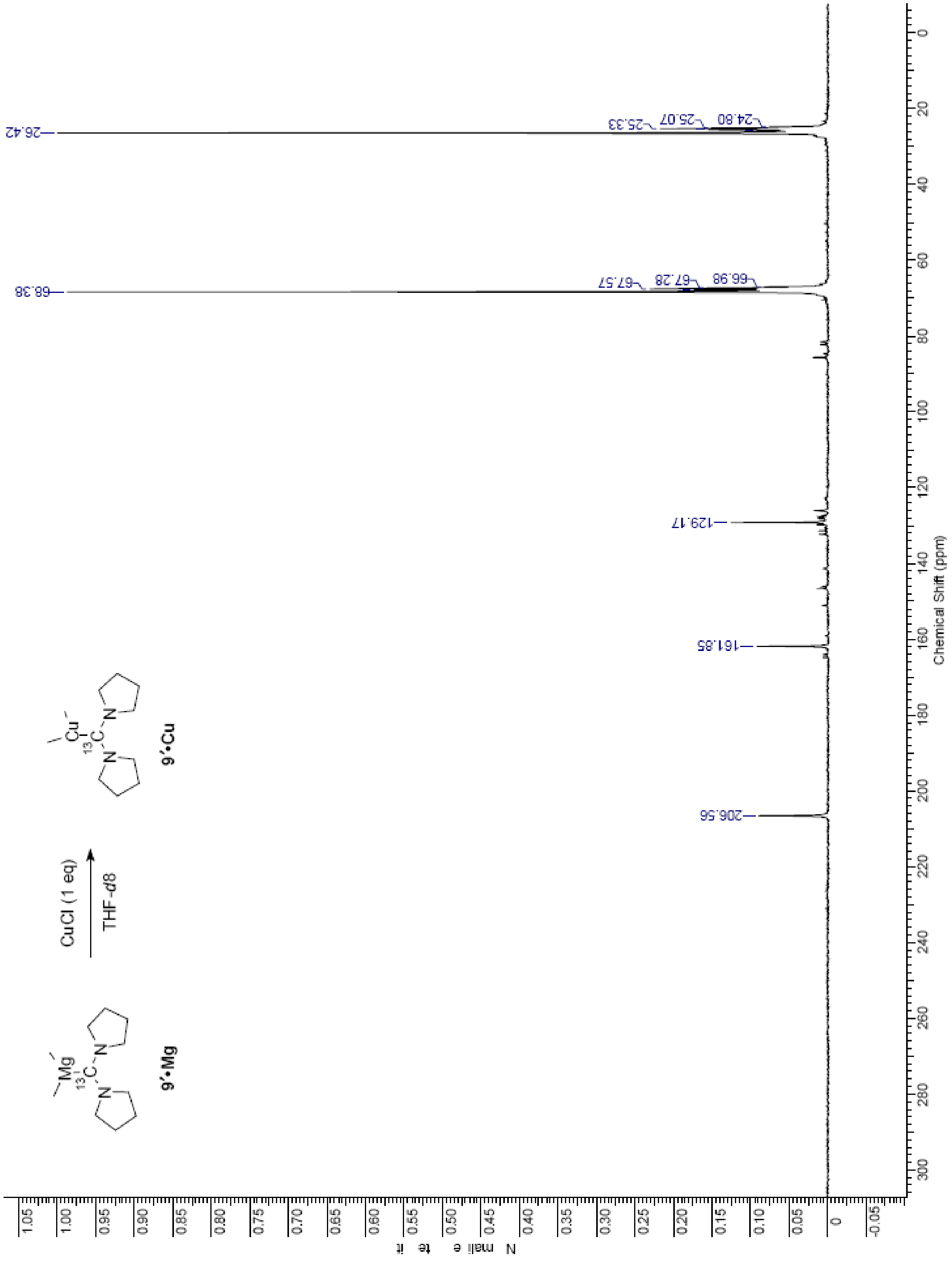

Chemical Shift (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

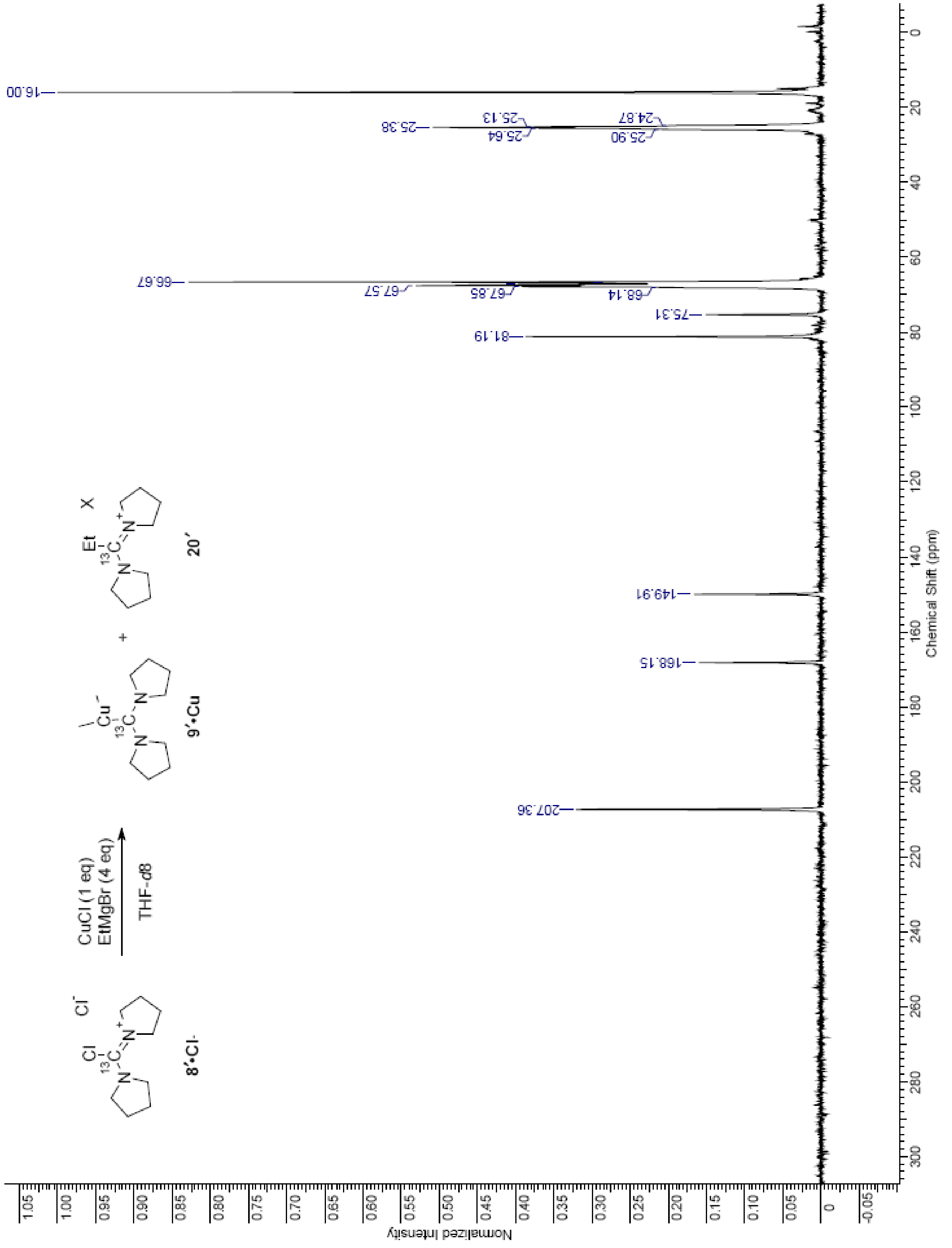
17

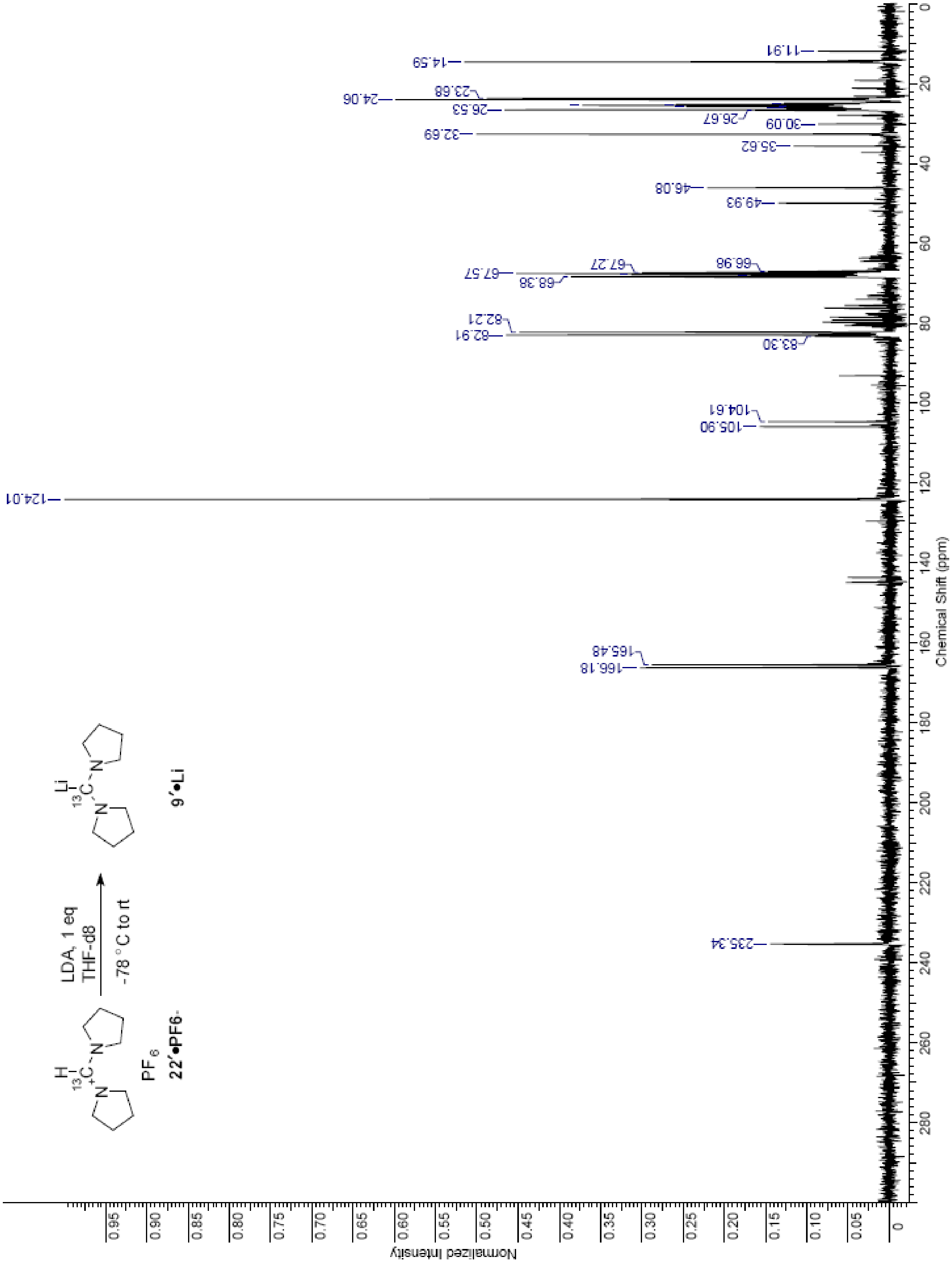
6. NMR spectra for NMR experiments

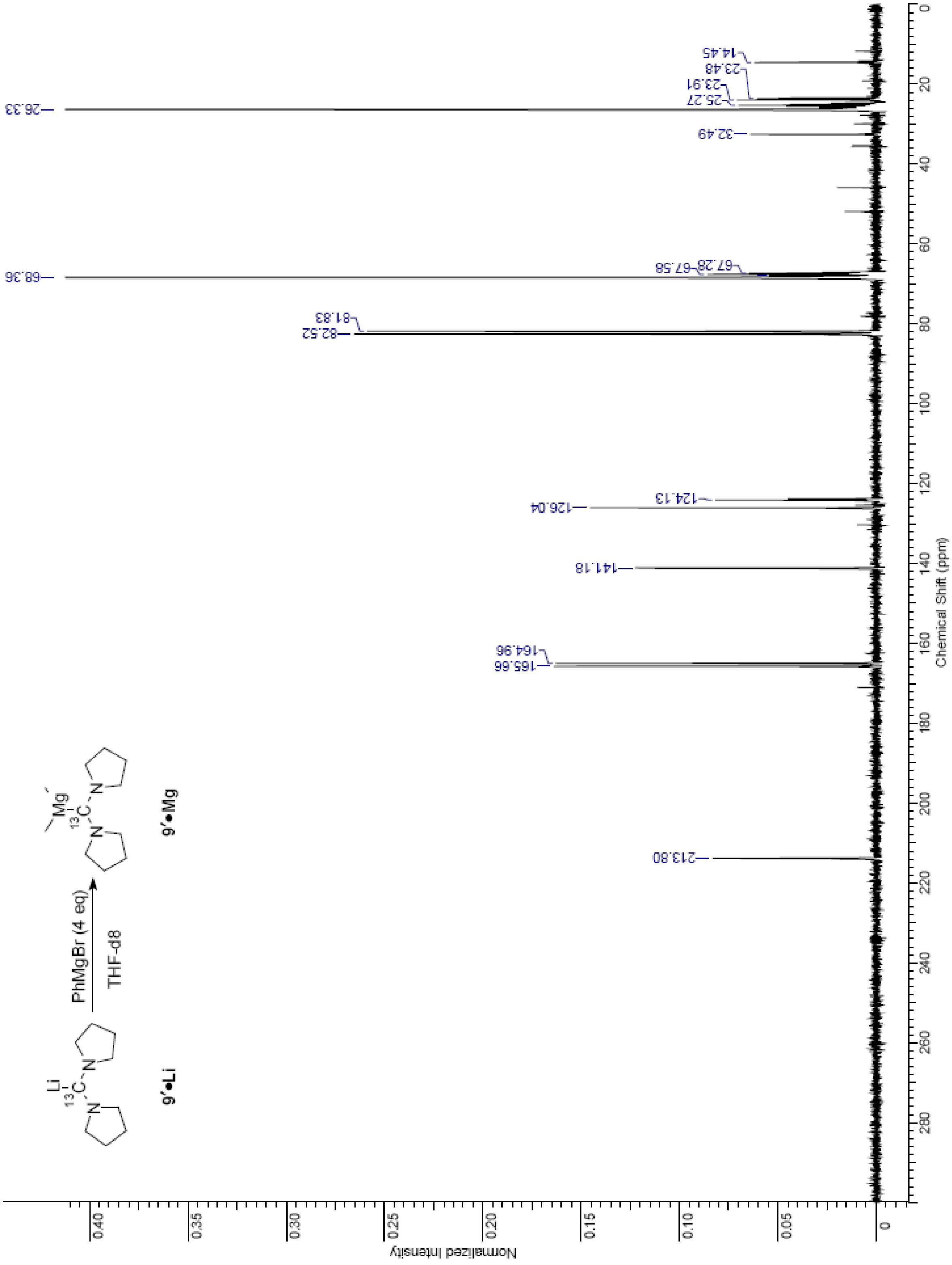


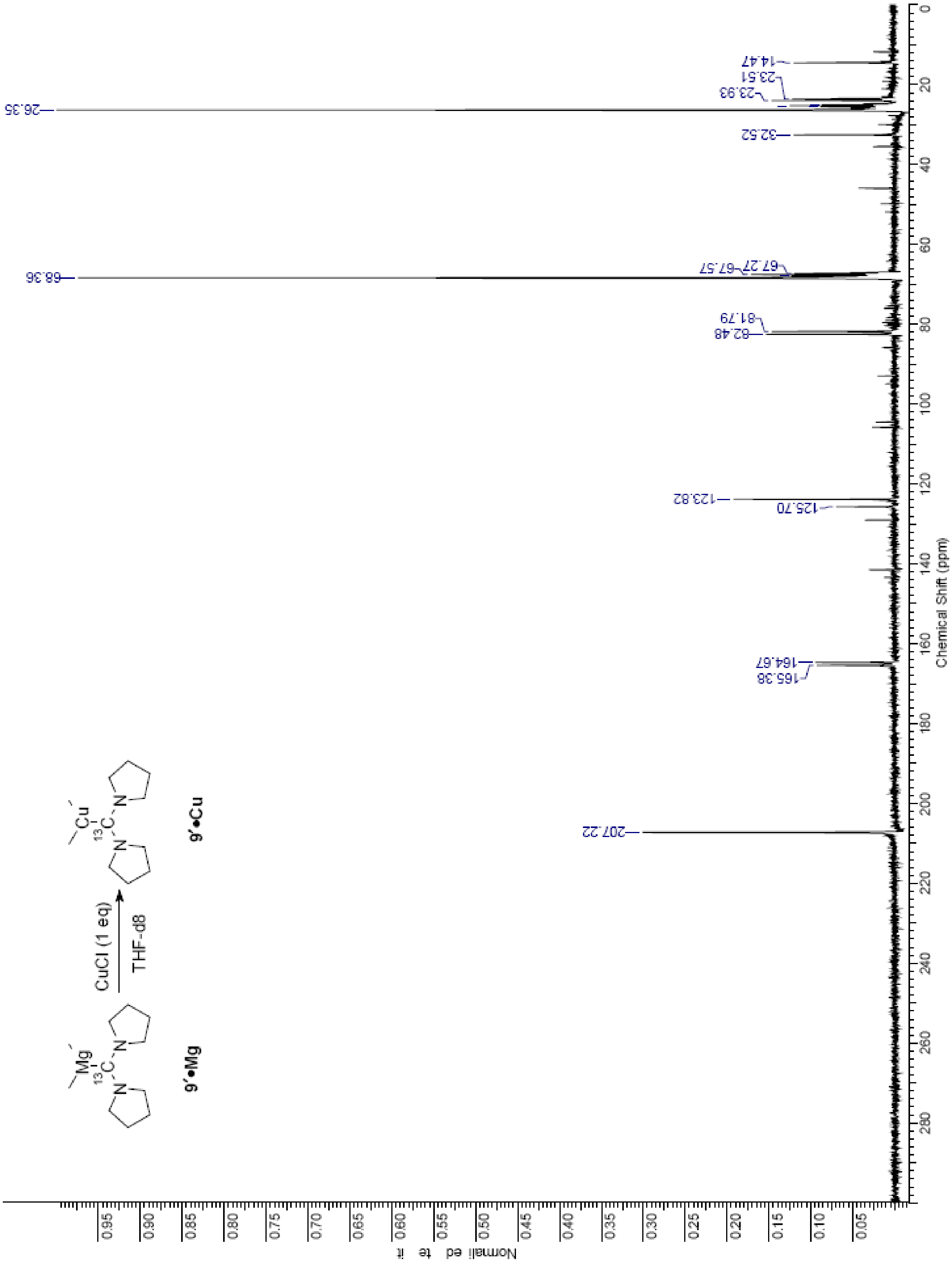

8'•Cl-
PhMgBr (4 eq)
THF-d8
9'•Mg
+
19'
Ph
X
Cl
Cl-
Mg
13C
N+
N
26.39
68.38
24.77
25.03
25.30
66.98
67.28
67.57
125.87
129.15
141.47
151.72
161.97
216.66
Chemical Shift (ppm)
350
300
250
200
150
100
50
0
-50
-100
-150
Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00


9'•Mg
Mg
13C
N
CuCl (1 eq)
THF-d8
9'•Cu
Cu
206.56
161.85
129.17
68.38
67.57
67.28
66.98
26.42
25.33
25.07
24.80
Chemical Shift (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05

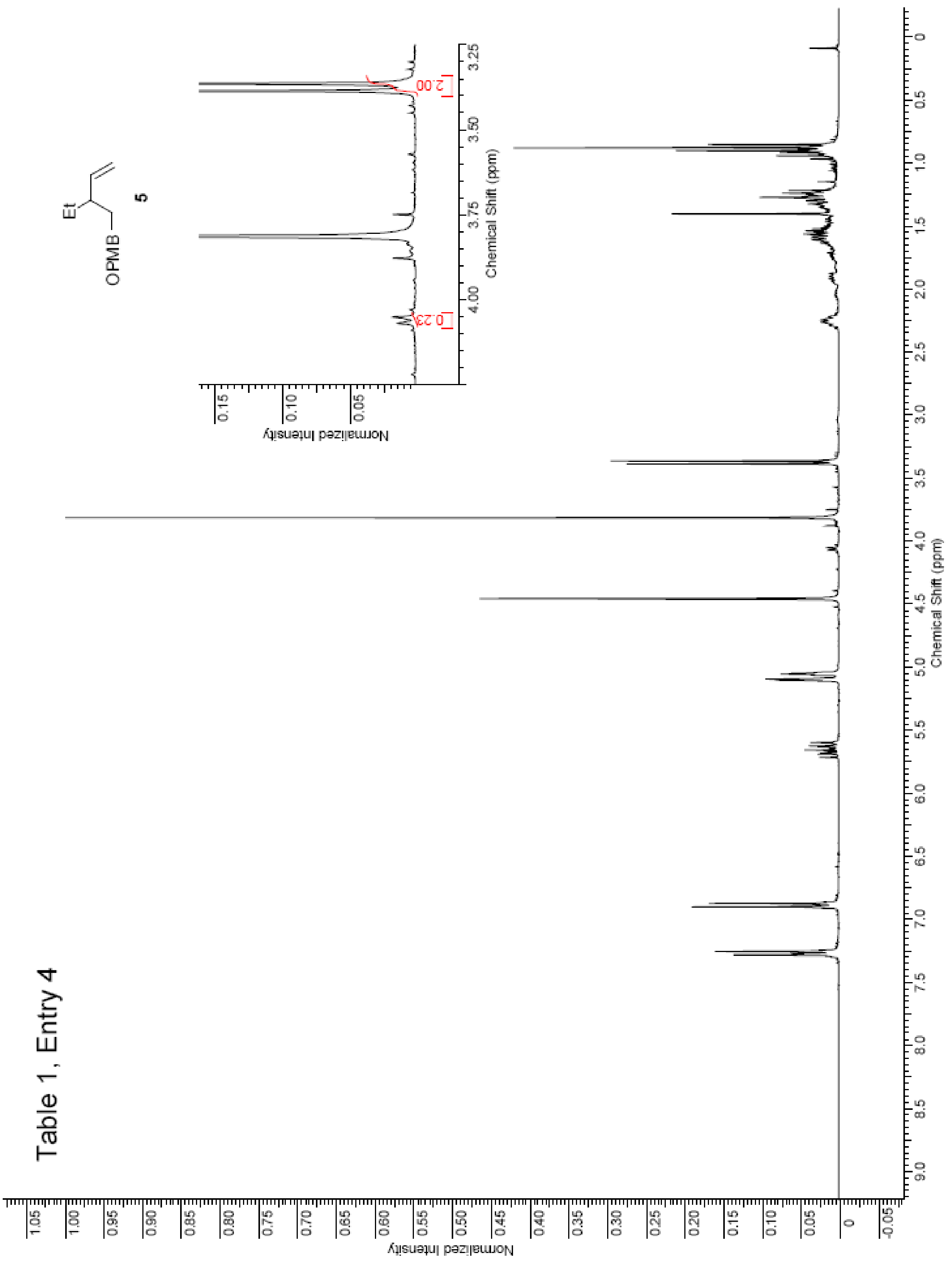

CuCl (1 eq)
EtMgBr (4 eq)
THF-d8
8'•Cl-
9'•Cu
20'
+
Cl
Cl⁻
Cu⁻
Et
X
^{13}C
16.00
25.38
25.13
25.64
24.87
25.90
66.67
67.57
67.85
68.14
75.31
81.19
149.91
168.15
207.36
Chemical Shift (ppm)
Normalized Intensity
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05


LDA, 1 eq
THF-d8
-78 °C to rt
PF6
22'•PF6-
9'•Li
11.91
14.59
23.68
24.06
26.53
26.67
30.09
32.69
35.62
46.08
49.93
66.98
67.27
67.57
68.38
82.21
82.91
83.30
104.61
105.90
124.01
165.48
166.18
235.34
Chemical Shift (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95


Li
13C
N
N
9'•Li
PhMgBr (4 eq)
THF-d8
Mg
13C
N
N
9'•Mg
26.33
14.45
23.48
23.91
25.27
32.49
68.36
67.28
67.58
81.83
82.52
126.04
124.13
141.18
164.96
165.66
213.80
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
Chemical Shift (ppm)
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
Normalized Intensity


CuCl (1 eq)
THF-d8
9'•Mg
9'•Cu
Mg
Cu
13C
N
26.35
68.36
14.47
23.51
23.93
32.52
67.27
67.57
81.79
82.48
123.82
125.70
164.67
165.38
207.22
Chemical Shift (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
Normalized Intensity
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95

7. NMR for controlled experiments Table 1 entries 4 and 5



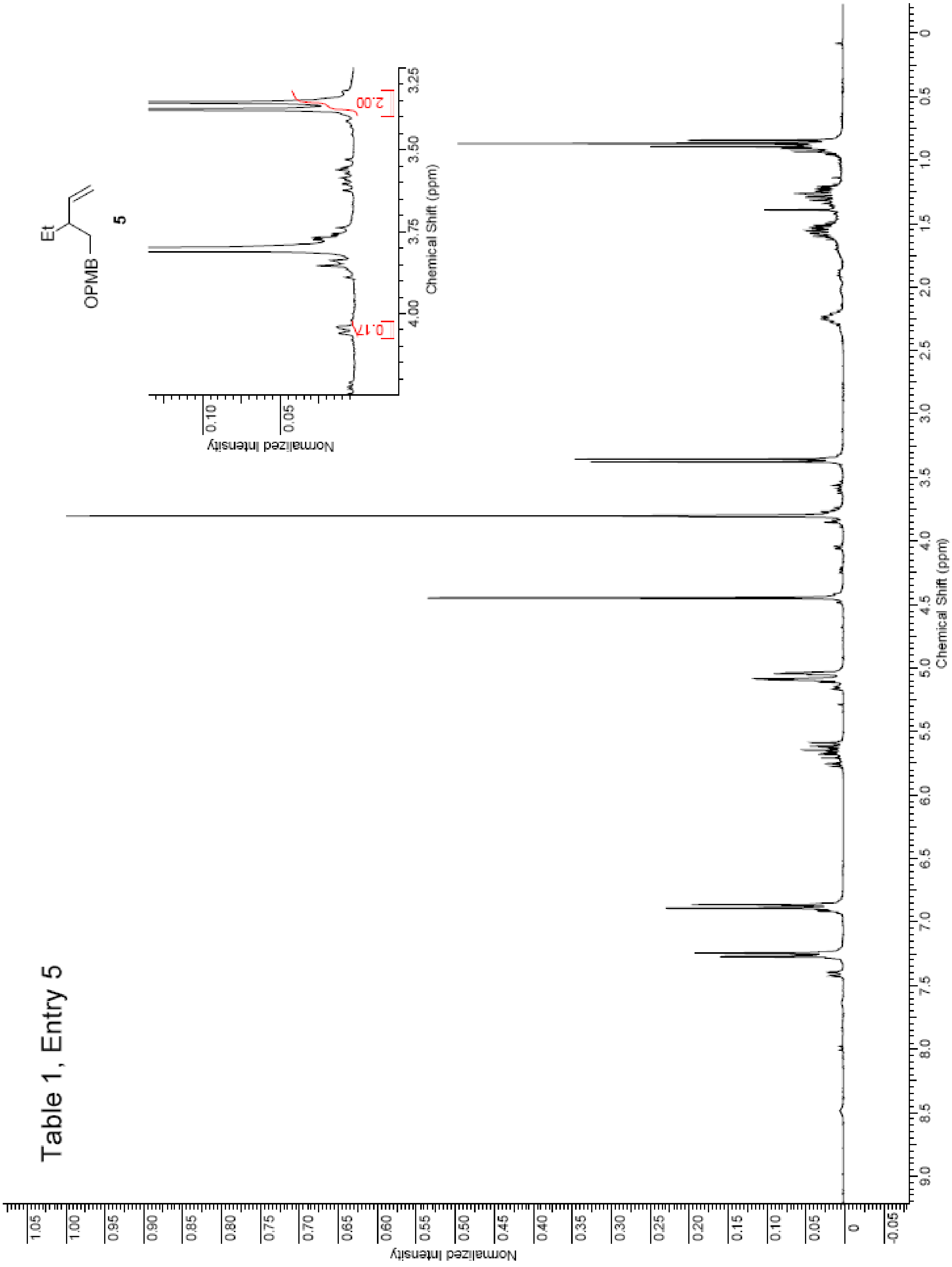
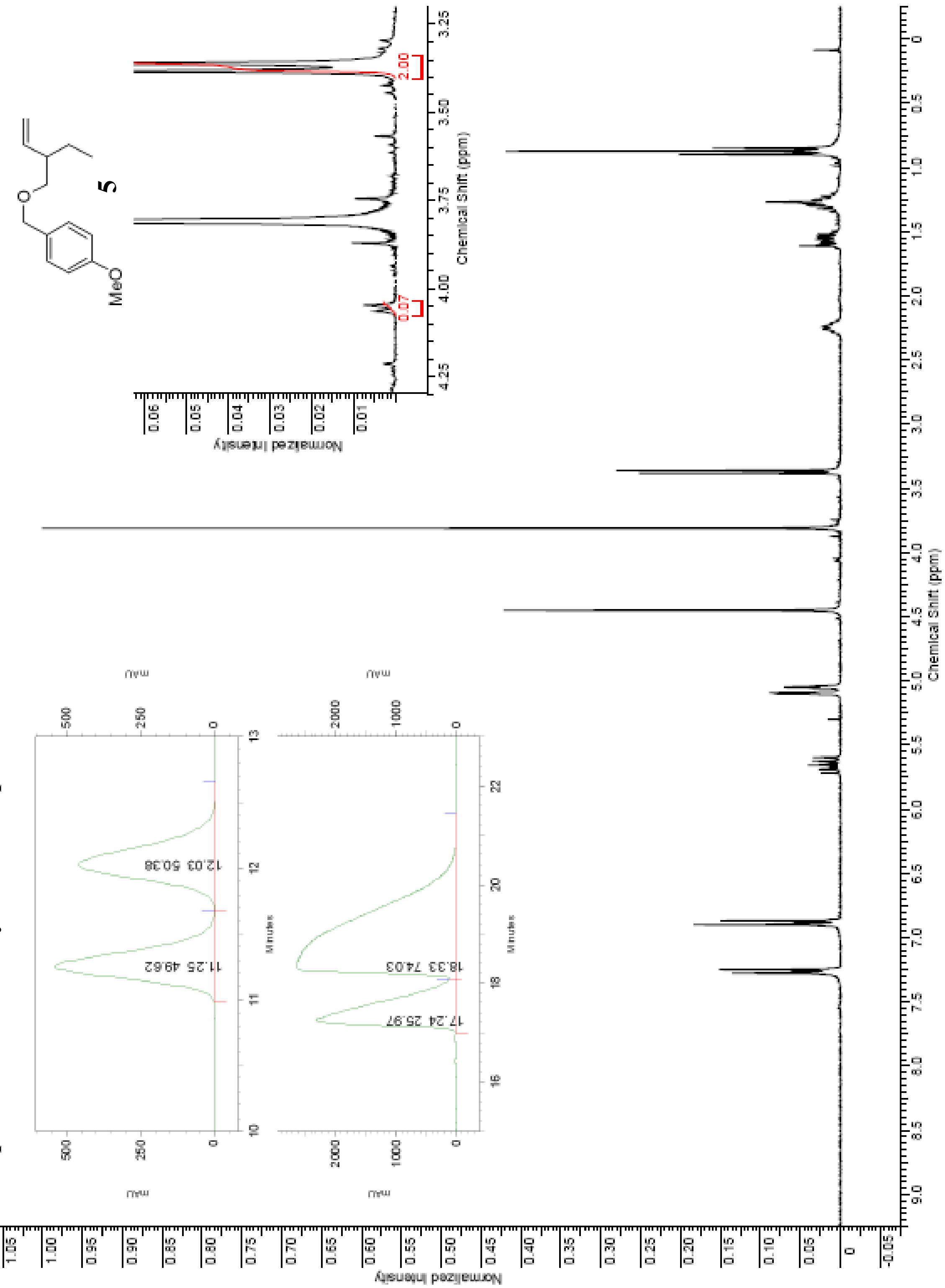


Table 1, Entry 5

5

8. HPLC Analysis Data and Regioselectivity Determination Data for Equation 1 and Table 1

Equation 1 with catalyst 3, Chiralpak IB, UV 215 nm, 100% hexane, 0.5mL/min



Equation 1 with catalyst 7: Chiralpak IB, UV 215 nm, 100% hexane, 0.5mL/min

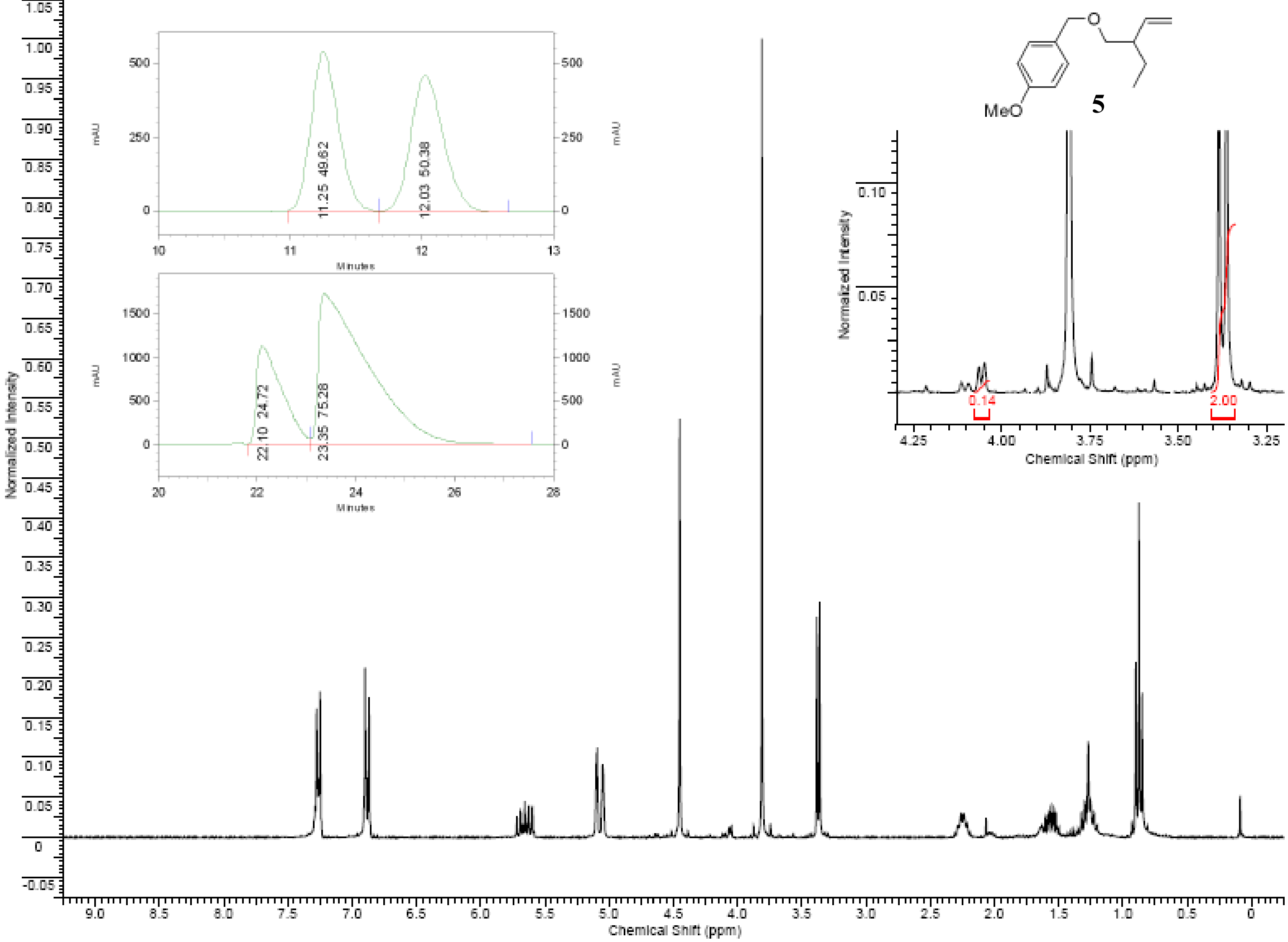
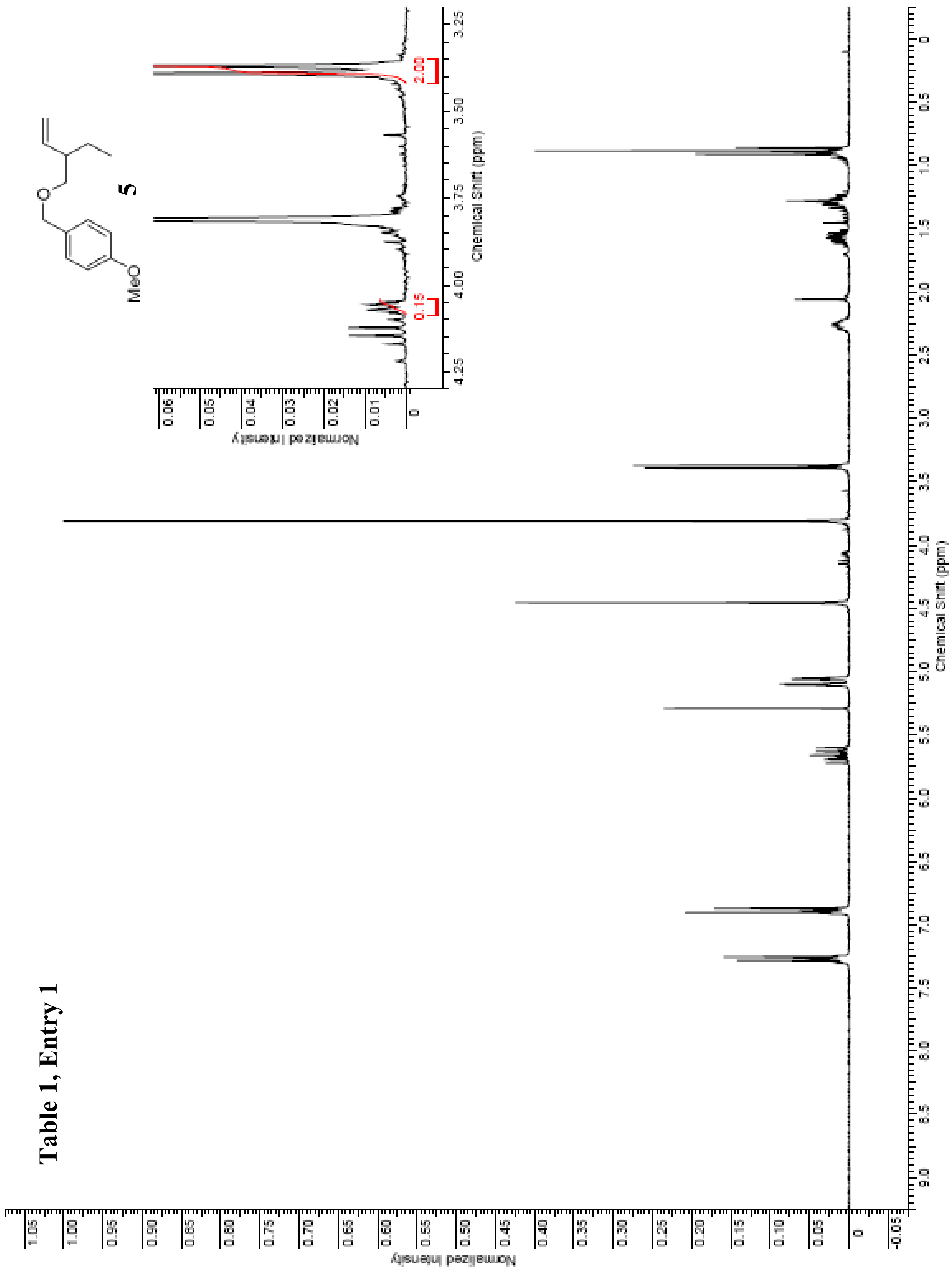


Table 1, Entry 1



5

Table 1, Entry 2

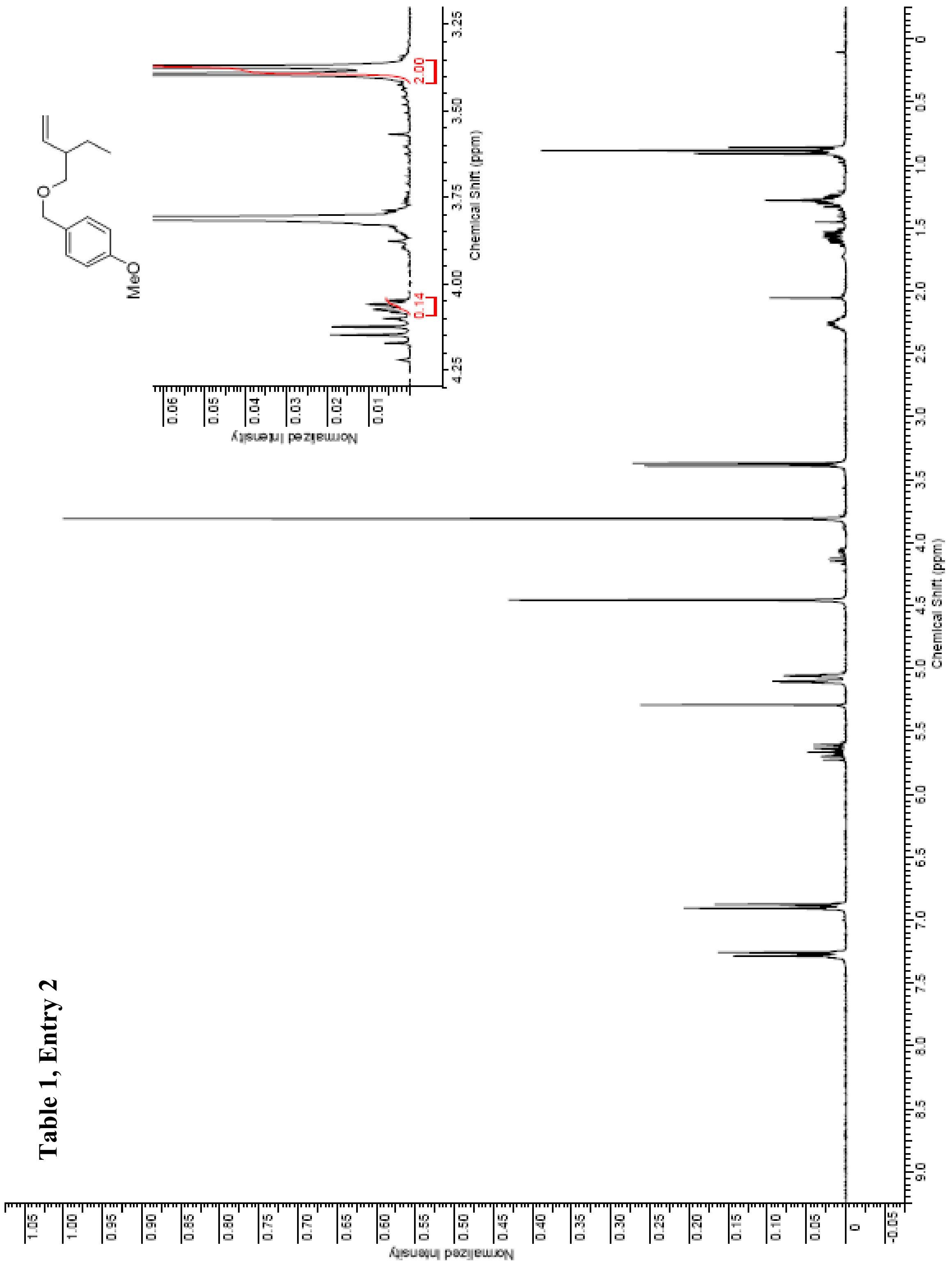


Table 1, Entry 3

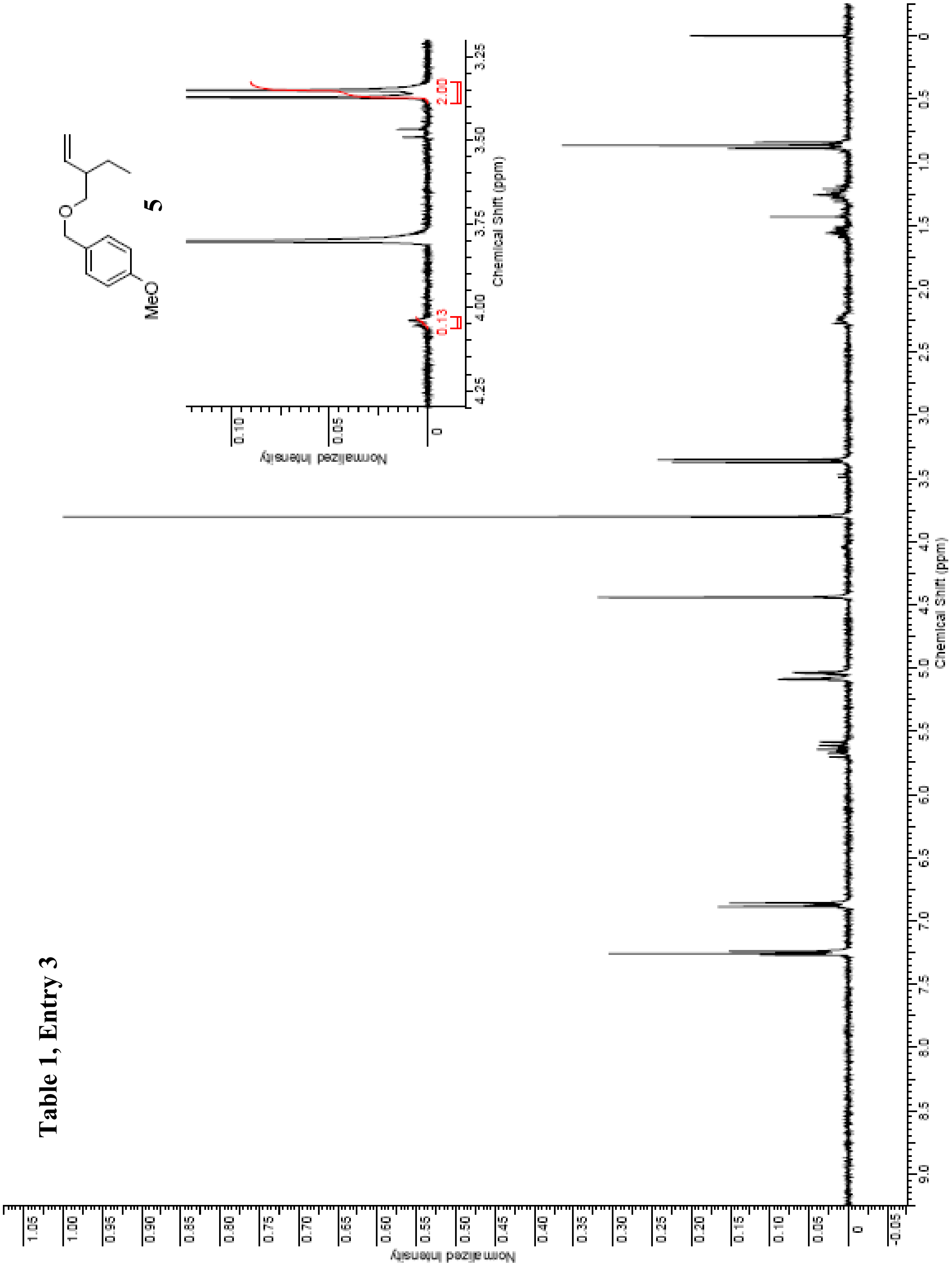
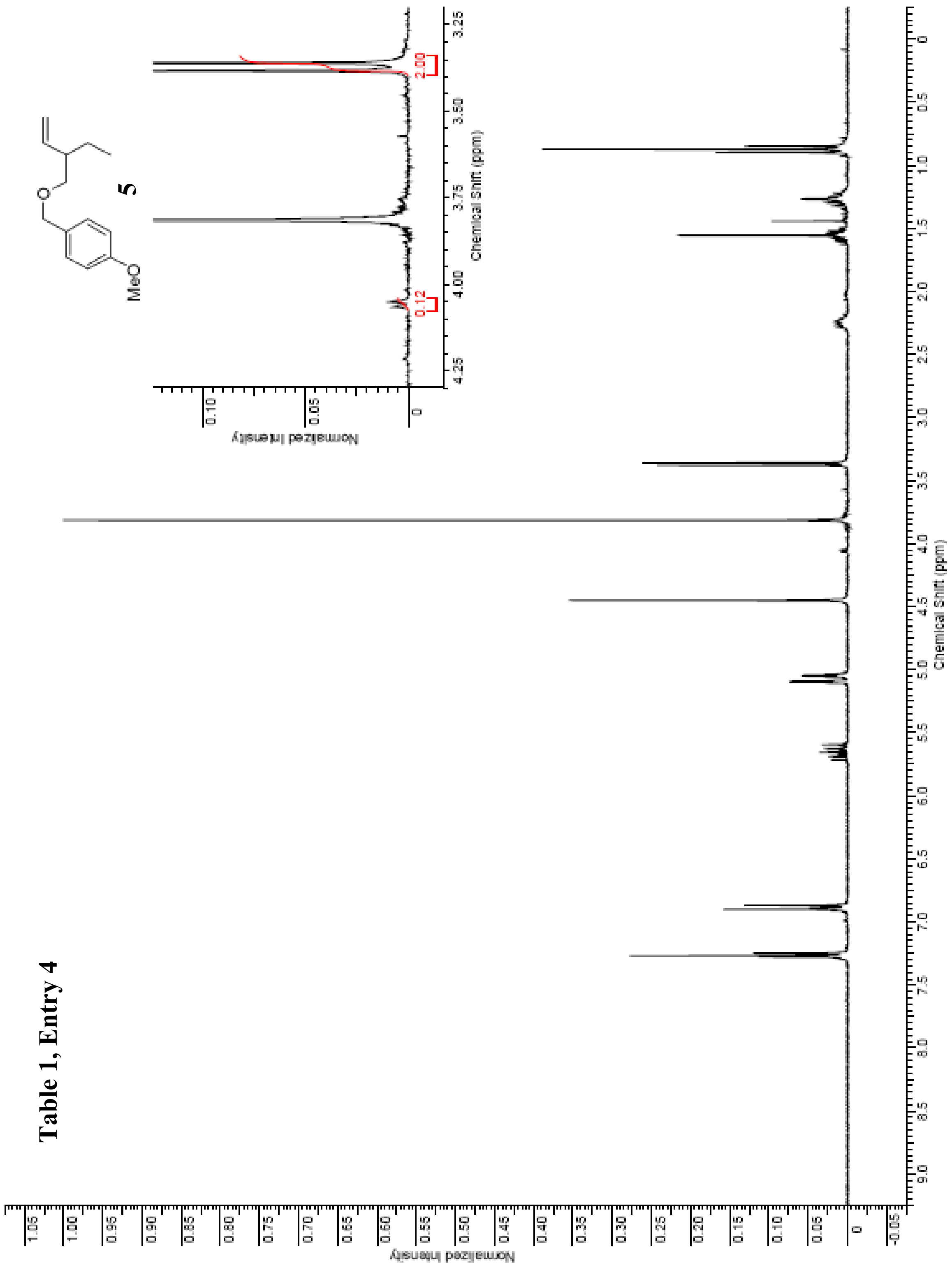


Table 1, Entry 4



5

Table 1, Entry 5