

A Formal *anti*-Markovnikov Hydroamination of Allylic Alcohols via Tandem Oxidation/1,4-Conjugate Addition/1,2-Reduction with Ru Catalyst

Yushi Nakamura, Yohei Oe, and Tetsuo Ohta

Department of Biomedical Information, Faculty of Life and Medical Sciences, Doshisha University, Kyotanabe, Kyoto, 610-0321

Supporting Information

Table of Contents

1. General information	S2
2. Screening of Ru catalysts for hydroamination	S2
3. Optimization of reaction conditions	S5
4. Synthesis of materials	S7
5. Hydroamination methods	S8
6. Characterization of products	S9
7. Analysis Charts	S16
8. References	S62

1. General information

NMR spectra were recorded with Varian Mercury Plus 300-4N spectrometers by using TMS ($\delta = 0$ ppm) as an internal standard for ^1H NMR and CDCl_3 ($\delta = 77$ ppm) for ^{13}C NMR spectroscopy. Mass spectra (GC-MS) were recorded with a Shimadzu QP5000 instrument. High-resolution mass spectra (FAB) were recorded by using a JEOL JMS-700 instrument with *meta*-nitrobenzyl alcohol as the matrix and PEG-200 as the calibration standard. Elemental analysis was depended on A Rabbit Science. All catalytic reactions were carried out under argon in sealed tube. Unless noted otherwise, all reagents and solvents were purchased from commercial suppliers. Reagents obtained from commercial sources were used without purification. Ru complexes ($[\text{RuCl}_2(p\text{-cymene})]_2$,¹ $\text{RuCl}_2(\text{DMSO})_4$,¹ $\text{RuCl}_2(\text{PPh}_3)_3$,¹ $\text{RuClH}(\text{CO})(\text{PPh}_3)_3$,¹ $\text{RuCl}_2(\text{PPh}_3)_2(\text{en})$,² $\text{RuCl}_2(\text{dppe})(\text{en})$,³ $\text{RuCl}_2(\text{dppf})(\text{en})$,³ $\text{RuCl}_2(\text{dppbenzene})(\text{en})$)³ and a part of Ligands (**L1**,⁴ **L2**,⁵ **L3**,⁴ **L5**)⁶ were synthesized according to literature protocols. A part of allylic alcohols (**1b**,⁷ **1c**,⁸ **1d**,⁹ **1e**,⁷ **1f**,¹⁰ **1g**)¹¹ were also synthesized according to literature protocols. 2,6-Bis(*n*-butyliminomethyl)pyridine (**L4**) was synthesized by reference to literature protocol.¹²

2. Screening of Ru catalysts for hydroamination

2.1. Screening of Ru Precursors or Solvents for Hydroamination

To an argon-purged reaction tube equipped with J-Young stop valve was added Ru pre. (2 mol% Ru), Dppe (0.044 mmol), and anhydrous CH_2Cl_2 (1 mL). The mixture was degassed by using freeze-pump-thaw cycles (FPT cycles) and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then the solvent was removed under reduced pressure. To the residue was added 3-buten-2-ol (**1a**) (6 mmol), morpholine (**2a**) (2 mmol), and anhydrous solvent (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 95°C for 5 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ^1H NMR.

Table S1. Screening of Ru Precursors or Solvents for Hydroamination

Entry	Ru pre.	Solvent (mL)	NMR Yield (3aa/4aa) (%)	
1	$[\text{RuCl}_2(p\text{-cymene})]_2$	Toluene/ H_2O (0.4/0.1)	0/60	
2	$[\text{RuCl}_2(p\text{-cymene})]_2$	1,4-Dioxane (0.5)	0/32	
3	$[\text{RuCl}_2(p\text{-cymene})]_2$	IPA (0.5)	0/62	
4	$\text{RuCl}_2(\text{DMSO})_4$	IPA (0.5)	0/13	
5	$\text{RuCl}_2(\text{PPh}_3)_3$	IPA (0.5)	0/18	
6	$\text{RuClH}(\text{CO})(\text{PPh}_3)_3$	IPA (0.5)	0/trace	

2.2. Screening of Ligands for Hydroamination

Method A: To an argon-purged reaction tube equipped with J-Young stop valve was added $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.02 mmol), Ligand (0.044 mmol), and anhydrous CH_2Cl_2 (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then the solvent was removed under reduced pressure. To the residue was added 3-buten-2-ol (**1a**) (6 mmol), morpholine (**2a**) (2 mmol), and anhydrous IPA (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 95°C for 5 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ^1H NMR.

Method B: To an argon-purged reaction tube equipped with J-Young stop valve was added $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.02 mmol), Ligand (0.044 mmol), and anhydrous CH_2Cl_2 (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then the solvent was removed under reduced pressure. To the residue was added 3-buten-2-ol (**1a**) (2.2 mmol), morpholine (**2a**) (2 mmol), and anhydrous IPA (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 95°C for 22 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ^1H NMR.

Fig. S1 Structure of Screening Ligands

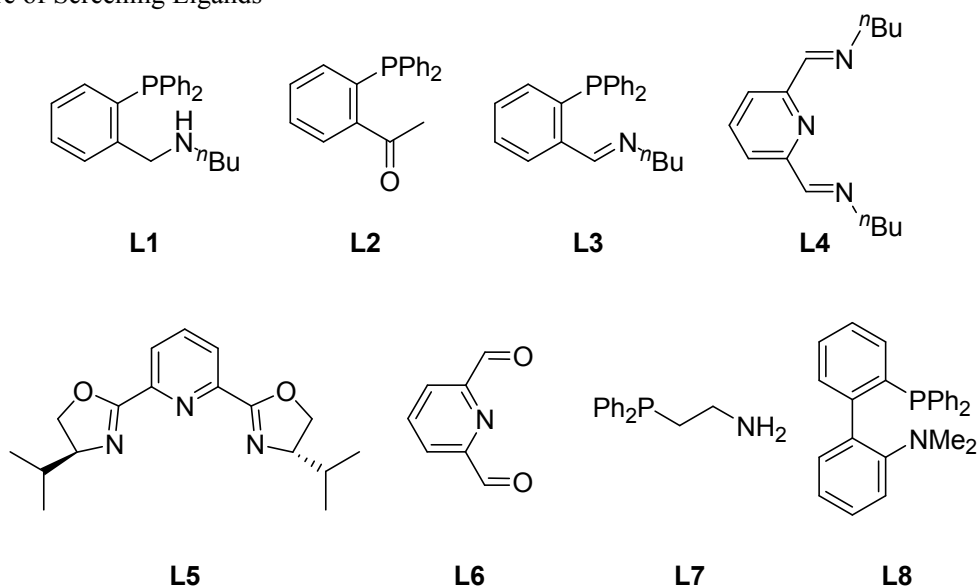


Table S2. Screening of Ligands for Hydroamination

Entry	Ligand	Method	NMR Yield (3aa/4aa) (%)
1	Dppe	Method A	0/63
2	PPh ₃	Method A	0/trace
3	(<i>R</i>)-BINAP	Method A	0/13
4	(<i>S</i>)-SEGPHOS	Method A	0/7
5	S-Phos	Method A	0/4
6	Xantphos	Method A	0/22
7	Dppf	Method A	0/trace
8	Dppbenzene	Method A	0/65
9	Ethylenediamine	Method A	0/0
10	1,10-Phenanthroline	Method A	0/trace
11	2,2'-Bis(2-oxazoline)	Method A	0/5
12	L7	Method A	0/0
13	L8	Method A	0/5
14	L1	Method A	0/15
15 ^a	L1	Method A	0/20
16 ^c	RuCl ₂ (PPh ₃) ₂ (en ^b)	Method B	0/6
17 ^c	RuCl ₂ (dppe)(en)	Method B	0/0
18 ^{a,c}	RuCl ₂ (dppe)(en)	Method B	0/7
19 ^c	RuCl ₂ (dppf)(en)	Method B	0/3
20 ^c	RuCl ₂ (dppbenzene)(en)	Method B	0/4
21	L2	Method B	0/4
22	L3	Method B	0/5
23	L4	Method B	0/5
24 ^d	L4	Method B	trace/7
25 ^{d,e}	L4	Method B	26/0
26 ^{d,e}	L5	Method B	0/12
27 ^{d,e}	L6	Method B	trace/0

^aKOH (5 mol%) was added. ^ben = ethylenediamine. ^cPrepared Ru complex (2 mol% Ru) was used. ^dRuClH(CO)(PPh₃)₃ (2 mol% Ru) was used as a catalyst precursor. ^eKOBu^t (5 mol%) was added.

3. Optimization of reaction conditions

3.1. Optimization of Reaction Conditions for Hydroamination with 3-Buten-2-ol (**1a**) and Morpholine (**2a**)

To an argon-purged reaction tube equipped with J-Young stop valve was added RuClH(CO)(PPh₃)₃ (0.04 mmol), 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**) (0.044 mmol) prepared from pyridine-2,6-carbaldehyde and *n*-butylamine, and anhydrous CH₂Cl₂ (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then the solvent was removed under reduced pressure. To the residue was added KOBu^t, 3-buten-2-ol (**1a**), morpholine (**2a**) (2 mmol), and anhydrous IPA (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at the respective temperature for 22 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ¹H NMR.

Table S3. Optimization of Reaction Conditions for Hydroamination with 3-Buten-2-ol (**1a**) and Morpholine (**2a**)

Entry	1a (mmol)	KOBu ^t (mol%)	Temp. (°C)	NMR Yield (%)
1	2.2	5	95	26
2	2.2	5	70	56
3	2.2	7.5	70	38
4	2.2	3	70	70
5	2.6	3	70	>99
6 ^a	2.6	3	70	72
7 ^b	2.6	3	70	0

^aRuCl₂(PPh₃)₃ was used. ^b[Ru(CO)₃Cl₂]₂ was used.

3.2. Optimization of Reaction Conditions for Hydroamination with Allyl Alcohol (**1a**) and Morpholine (**2a**)

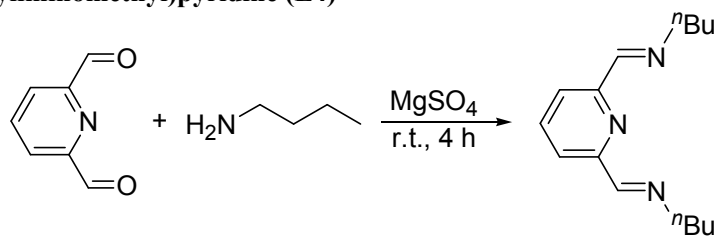
To an argon-purged reaction tube equipped with J-Young stop valve was added RuClH(CO)(PPh₃)₃ (0.04 mmol), 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**) prepared from pyridine-2,6-carbaldehyde and *n*-butylamine (0.044 mmol), and anhydrous CH₂Cl₂ (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then the solvent was removed under reduced pressure. To the residue was added KOBu^t (0.06 mmol), allyl alcohol (**1a**) (2.6 mmol), morpholine (**2a**) (2 mmol), and anhydrous solvent (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at the respective temperature for 22 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ¹H NMR.

Table S4. Optimization of Reaction Conditions for Hydroamination with Allyl Alcohol (**1h**) and Morpholine (**2a**)

<chem>HOCH2CH=CH2</chem> 1h <chem>C1CCNCCO1</chem> 2a + $\text{RuClH(CO)(PPh}_3)_3$ (2 mol% Ru) L4 (2.2 mol%) KOBu^t (3 mol%) Solvent, Temp., 22 h <chem>HOCH2CH2CH2N1CCOCC1</chem> 3ha			
Entry	Solvent (mL)	Temp.	NMR Yield (%)
1	IPA (0.5)	70	55
2	IPA (0.5)	80	82
3	IPA (0.5)	85	90
4	IPA (0.5)	90	50
5	IPA/Toluene (0.5/0.5)	85	99

4. Synthesis of materials

Synthesis of 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**)

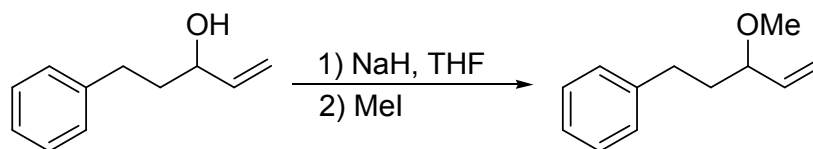


Scheme S1. Synthesis of 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**)

Under argon atmosphere, to a 80 mL Schlenk flask was added MgSO_4 (0.6 g), pyridine-2,6-carbaldehyde (0.1 mmol), *n*-butylamine (0.05 mL), and CHCl_3 (1.6 mL). The reaction mixture was stirred at r.t. for 4 h, then filtrated, and the filtrate was concentrated. The residue was dried under reduced pressure to give the product as a colorless oil quantitatively. The 0.05M solution of **L4** in CH_2Cl_2 was prepared by adding CH_2Cl_2 (2 mL) to the residue, and used for catalytic reactions.

^1H NMR: δ = 0.95 (t, J = 7.2 Hz, 6H, - CH_3), 1.41 (sex, J = 7.5 Hz, 4H, - CH_2CH_3), 1.72 (quin, J = 7.2 Hz, 4H, - $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.69 (t, J = 7.2 Hz, 4H, - CH_2N -), 7.80 (t, J = 7.8 Hz, 1H, Ar- H), 8.00 (d, J = 7.8 Hz, 2H, Ar- H), 8.41 (s, 2H, - NCH -) ppm. ^{13}C NMR: δ = 13.8, 20.4, 32.7, 61.3, 122.1, 137.0, 154.4, 161.4 ppm. GC-MS: m/z = 245. HRMS (FAB, *m*-NBA): Calcd. for $\text{C}_{15}\text{H}_{24}\text{N}_3$ ($[\text{M}+\text{H}]^+$) 246.1970; found 246.1964. CAS Registry Number: 1469980-53-7.

Synthesis of (3-methoxy-4-penten-1-yl)benzene (**1c'**)



Scheme S2. Synthesis of (3-methoxy-4-penten-1-yl)benzene (**1c'**)

Under argon, to a 200 mL reaction container was added **1c** (11.7 mmol), and THF (20 mL). To the mixture was slowly added NaH, in oil (14 mmol) at 0°C , and the mixture was stirred at r.t. for 1 h. Then, methyl iodide (17.6 mmol) was added at 0°C , and the reaction mixture was stirred at r.t. for 17 h. After the reaction was quenched with the distilled water and sat. NH_4Cl aq., the solution extracted with Et_2O from the resulting mixture was washed with Brine, dehydrated with Na_2SO_4 , and then filtrated. The filtrate was concentrated, and the residue was dried under reduced pressure. The residue was purified by vacuum distillation to give the product as a colorless oil (82 % yield).

^1H NMR: δ = 1.71-1.98 (m, 2H, - CHCH_2 -), 2.60-2.80 (m, 2H, - CH_2Ar), 3.27 (s, 3H, - OCH_3), 3.50 (quart, J = 7.2 Hz, 1H, - CHOCH_3), 5.16-5.24 (m, 2H, - $\text{CH}=\text{CH}_2$), 5.62-5.74 (m, 1H, - $\text{CH}=\text{CH}_2$), 7.15-7.30 (m, 5H, Ar- H) ppm. ^{13}C NMR: δ = 31.5, 37.0, 56.2, 82.0, 117.3, 125.8, 128.3, 128.5, 138.6, 142.1 ppm. GC-MS: m/z = 176. HRMS (FAB, *m*-NBA): Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}$ (M^+) 176.1201; found 176.1201. CAS Registry Number: 37904-38-4.

5. Hydroamination methods

Method A: Hydroamination of 3-buten-2-ol (**1a**)

To an argon-purged reaction tube equipped with J-Young stop valve was added RuClH(CO)(PPh₃)₃ (0.04 mmol), 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**) (0.044 mmol) prepared from pyridine-2,6-carbaldehyde and *n*-butylamine, and anhydrous CH₂Cl₂ (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then the solvent was removed under reduced pressure. To the residue was added KOBu^t (0.06 mmol), 3-buten-2-ol (**1a**) (2.6 mmol), amine (2 mmol), and anhydrous IPA (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred for at 70°C 22 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ¹H NMR.

Method B: Hydroamination of allylic alcohols

To an argon-purged reaction tube equipped with J-Young stop valve was added RuClH(CO)(PPh₃)₃ (0.04 mmol), 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**) (0.044 mmol) prepared from pyridine-2,6-carbaldehyde and *n*-butylamine, and anhydrous CH₂Cl₂ (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then vacuum distilled. To the residue was added KOBu^t (0.06 mmol), allylic alcohols (2.6 mmol), morpholine (**2a**) (2 mmol), and corresponding anhydrous solvent (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at the corresponding temperature for 22 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ¹H NMR.

Method C: Hydroamination of allyl alcohol (**1h**)

To an argon-purged reaction tube equipped with J-Young stop valve was added RuClH(CO)(PPh₃)₃ (0.04 mmol), 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**) (0.044 mmol) prepared from pyridine-2,6-carbaldehyde and *n*-butylamine, and anhydrous CH₂Cl₂ (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then vacuum distilled. To the residue was added KOBu^t (0.06 mmol), allyl alcohol (**1h**) (2.6 mmol), amine (2 mmol), anhydrous IPA (0.5 mL), and Toluene (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 85°C for 22 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ¹H NMR.

Method D: Hydroamination of (3-methoxy-4-penten-1-yl)benzene (**1c'**)

To an argon-purged reaction tube equipped with J-Young stop valve was added RuClH(CO)(PPh₃)₃ (0.04 mmol), 2,6-bis(*n*-butyliminomethyl)pyridine (**L4**) (0.044 mmol) prepared from pyridine-2,6-carbaldehyde and *n*-butylamine, and anhydrous CH₂Cl₂ (1 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 40°C for 1 h, then vacuum distilled. To the residue was added KOBu^t (0.06 mmol), (3-methoxy-4-penten-1-yl)benzene (**1c'**) (2.6 mmol), morpholine (**2a**) (2 mmol), and IPA (0.5 mL). The mixture was degassed by using FPT cycles and then purged with argon again. The reaction mixture was stirred at 70°C for 22 h, then to the mixture was added triphenylmethane (0.2 mmol) as an internal standard for NMR yield. A part of the solution was picked up and evaporated, and then the yield was measured by ¹H NMR.

6. Characterization of products

4-(Morpholin-1-yl)butan-2-ol (**3aa**)

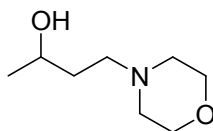


Fig S2. Chemical Structure of **3aa**

The reaction was conducted according to Method A with amine **2a** (>99% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.18 (d, J = 6.0 Hz, 3H, $-\text{CH}_3$), 1.45-1.53 (m, 1H, $-\text{CHCHH}-$), 1.58-1.72 (m, 1H, $-\text{CHCHH}-$), 2.40 (br-s, 2H, $-\text{CHCH}_2\text{CH}_2-$), 2.53-2.70 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{O}-$), 3.71 (br-s, 4H, $-\text{NCH}_2\text{CH}_2\text{O}-$), 3.91-4.01 (m, 1H, $-\text{CHOH}$) ppm. ^{13}C NMR: δ = 23.2, 32.8, 53.5, 58.1, 66.8, 69.6 ppm. GC-MS: m/z = 159. HRMS (FAB, m -NBA): Calcd. for $\text{C}_8\text{H}_{18}\text{NO}_2$ ($[\text{M}+\text{H}]^+$) 160.1338; found 160.1342. CAS Registry Number: 858440-45-6.

4-(Piperizin-1-yl)butan-2-ol (**3ab**)

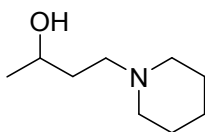


Fig S3. Chemical Structure of **3ab**

The reaction was conducted according to Method A with amine **2b** (86% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR (CDCl_3): δ = 1.16 (d, J = 6.0 Hz, 3H, $-\text{CH}_3$), 1.31-1.70 (m, 8H, $-\text{CHCH}_2-$, $-\text{NCH}_2(\text{CH}_2)_3-$), 2.30 (br-s, 2H, $-\text{CHCH}_2\text{CH}_2-$), 2.44-2.63 (m, 4H, $-\text{NCH}_2(\text{CH}_2)_2-$), 3.89-4.00 (m, 1H, $-\text{CHOH}$) ppm. ^{13}C NMR: δ = 23.4, 24.1, 25.9, 33.2, 54.5, 58.4, 69.8 ppm. GC-MS: m/z = 157. HRMS (FAB, m -NBA): Calcd. for $\text{C}_9\text{H}_{20}\text{NO}$ ($[\text{M}+\text{H}]^+$) 158.1545; found 158.1546. CAS Registry Number: 71648-40-3.

4-(4-Phenylpiperazin-1-yl)butan-2-ol (**3ac**)

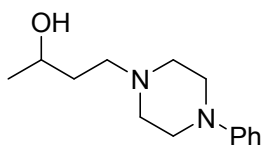


Fig S4. Chemical Structure of **3ac**

The reaction was conducted according to Method A with amine **2c** (>99% yield). The product was purified by column chromatography (CHCl_3 :Hexane = 1:1). The product was obtained as a white solid.

^1H NMR: δ = 1.19 (d, J = 6.0 Hz, 3H, $-\text{CH}_3$), 1.48-1.57 (m, 1H, $-\text{CHCHH}-$), 1.62-1.75 (m, 1H, $-\text{CHCHH}-$), 2.51-2.86 (m, 6H, $-\text{CHCH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{NAr}$), 3.15-3.25 (m, 4H, $-\text{CH}_2\text{CH}_2\text{NAr}$), 3.94-4.02 (m, 1H, $-\text{CHOH}$), 5.91 (br-s, 1H, $-\text{OH}$), 6.84-6.93 (m, 3H, Ar- H), 7.24-7.29 (m, 2H, Ar- H) ppm. ^{13}C NMR: δ = 23.3, 33.2, 49.1, 53.2, 57.7, 69.7, 116.1, 119.8, 129.0, 151.0 ppm. GC-MS: m/z = 234. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{14}\text{H}_{23}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$) 235.1810; found 235.1812. CAS Registry Number: 1034267-00-9.

4-(1,2,3,4-Tetrahydroisoquinolin-2-yl)butan-2-ol (**3ad**)

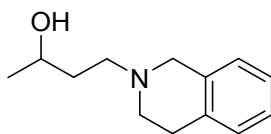


Fig S5. Chemical Structure of **3ad**

The reaction was conducted according to Method A with amine **2d** (90% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.18 (d, J = 6.3 Hz, 3H, $-\text{CH}_3$), 1.54-1.61 (m, 1H, $-\text{CHCHH}-$), 1.68-1.81 (m, 1H, $-\text{CHCHH}-$), 2.58-3.01 (m, 6H, $-\text{CHCH}_2\text{CH}_2-$, $-\text{N}(\text{CH}_2)_2\text{Ar}$), 3.61-3.66 (d, 1H, J = 14.7 Hz $-\text{NCHHAr}$), 3.73-3.78 (d, J = 14.7 Hz, 1H, $-\text{NCHHAr}$), 3.96-4.03 (m, 1H, $-\text{CHOH}$), 7.01-7.15 (m, 4H, Ar- H) ppm. ^{13}C NMR: δ = 23.4, 28.8, 33.6, 50.5, 56.3, 57.5, 69.7, 125.7, 126.2, 126.5, 128.5, 133.9, 134.0 ppm. GC-MS: m/z = 205. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{13}\text{H}_{20}\text{NO}$ ($[\text{M}+\text{H}]^+$) 206.1545; found 206.1548. CAS Registry Number: 1247753-69-0.

4-(1,4-Dioxo-8-azaspiro[4.5]decan-8-yl)butan-2-ol (**3ae**)

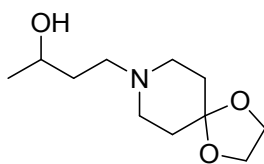


Fig S6. Chemical Structure of **3ae**

The reaction was conducted according to Method A with amine **2e** (75% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.17 (d, J = 6.3 Hz, 3H, $-\text{CH}_3$), 1.43-1.52 (m, 1H, $-\text{CHCHH}-$), 1.56-1.80 (m, 5H, $-\text{CHCHH}-$, $-\text{CCH}_2-$), 2.46 (br-s, 2H, $-\text{CHCH}_2\text{CH}_2-$), 2.54-2.80 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{C}-$), 3.90-4.00 (m, 5H, $-\text{CHOH}$, $-\text{CH}_2\text{O}-$), 6.23 (br-s, 1H, $-\text{OH}$) ppm. ^{13}C NMR: δ = 23.3, 33.6, 34.7, 51.4, 57.4, 64.2, 69.7, 106.8 ppm. GC-MS: m/z = 215. Anal. Calcd. for $\text{C}_{11}\text{H}_{21}\text{NO}_3$: C, 61.37; H, 9.83; N, 6.51. Found: C, 61.43; H, 9.76; N, 6.55.

4-(Indolin-1-yl)butan-2-ol (**3af**)

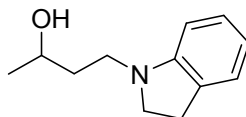


Fig S7. Chemical Structure of **3af**

The reaction was conducted according to Method A with amine **2f** (86% yield). The product was purified by column chromatography (EtOAc:Hexane = 1:3) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.24 (d, J = 6.0 Hz, 3H, $-\text{CH}_3$), 1.70-1.83 (m, 2H, $-\text{CHCH}_2-$), 2.95 (t, J = 8.1 Hz, 2H, $-\text{NCH}_2\text{CH}_2\text{Ar}$), 3.10-3.51 (m, 5H, $-\text{CHCH}_2\text{CH}_2-$, $-\text{NCH}_2\text{CH}_2\text{Ar}$, $-\text{OH}$), 3.96-4.07 (m, 1H, $-\text{CHOH}$), 6.61 (d, J = 7.8 Hz, 1H, Ar- H), 6.72 (t, J = 7.2 Hz, 1H, Ar- H), 7.09 (t, J = 7.2 Hz, 2H, Ar- H) ppm. ^{13}C NMR: δ = 23.6, 28.5, 35.7, 48.5, 53.9, 67.9, 108.0, 118.6, 124.4, 127.2, 130.4, 152.4 ppm. GC-MS: m/z = 191. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}$ (M^+) 191.1310; found 191.1309. CAS Registry Number: 56771-63-2.

4-(*N,N*-dibenzylamino)butan-2-ol (**3ag**)

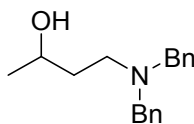


Fig S8. Chemical Structure of **3ag**

The reaction was conducted according to Method A with amine **2g** (74% yield). The product was purified by column chromatography (EtOAc:Hexane = 1:5) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.08 (d, J = 6.3 Hz, 3H, $-\text{CH}_3$), 1.45-1.54 (m, 1H, $-\text{CHCHH}-$), 1.67-1.80 (m, 1H, $-\text{CHCHH}-$), 2.51-2.58 (m, 1H, $-\text{CHCH}_2\text{CHH}-$), 2.71-2.81 (m, 1H, $-\text{CHCH}_2\text{CHH}-$), 3.24 (d, J = 13.2 Hz, 2H, $-\text{CHHAr}$), 3.68-3.78 (m, 1H, $-\text{CHOH}$), 3.89 (d, J = 13.2 Hz, 2H, $-\text{CHHAr}$), 7.23-7.36 (m, 10H, Ar- H) ppm. ^{13}C NMR: δ = 23.1, 34.0, 52.6, 58.5, 69.2, 127.3, 128.4, 129.2, 138.0 ppm. GC-MS: m/z = 269. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{18}\text{H}_{24}\text{NO}$ ($[\text{M}+\text{H}]^+$) 270.1858; found 270.1857. CAS Registry Number: 177550-45-7.

4-(benzylamino)butan-2-ol (**3ah**)

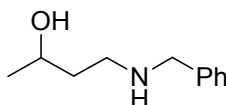


Fig S9. Chemical Structure of **3ah**

The reaction was conducted according to Method A with amine **2h** (44% yield). The product was purified by column chromatography (EtOAc:Hexane = 6:5, + Et_3N (7%)) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.17 (d, J = 6.0 Hz, 3H, $-\text{CH}_3$), 1.42-1.65 (m, 2H, $-\text{CHCH}_2-$), 2.74-2.83 (m, 1H, $-\text{CHCH}_2\text{CHH}-$), 2.98-3.05 (m, 1H, $-\text{CHCHH}-$), 3.73 (d, J = 12.9 Hz, 1H, $-\text{CHHAr}$), 3.82 (d, J = 13.2 Hz, 2H, $-\text{CHHAr}$), 3.94-4.02 (m, 1H, $-\text{CHOH}$), 7.22-7.35 (m, 5H, Ar- H) ppm. ^{13}C NMR: δ = 23.5, 36.7, 48.2, 53.7, 69.6, 127.1, 128.1, 128.4, 139.3 ppm. GC-MS: m/z = 179. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{11}\text{H}_{18}\text{NO}$ ($[\text{M}+\text{H}]^+$) 180.1388; found 180.1391. CAS Registry Number: 93293-37-9.

1-(Morpholin-1-yl)heptan-3-ol (**3ba**)

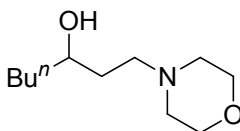


Fig S10. Chemical Structure of **3ba**

The reaction was conducted according to Method B with allylic alcohols **1b** at 70°C in IPA (0.5 mL) (>99% yield). The product was purified by column chromatography (EtOAc only) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 0.91 (t, J = 7.2 Hz, 3H, $-\text{CH}_3$), 1.21-1.70 (m, 8H, $-(\text{CH}_2)_3\text{CH}_3$, $-\text{CHCH}_2\text{CH}_2\text{N}-$), 2.43 (br-s, 2H, $-\text{CHCH}_2\text{CH}_2\text{N}-$), 2.51-2.69 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{O}-$), 3.56-3.81 (m, 5H, $-\text{NCH}_2\text{CH}_2\text{O}-$, $-\text{CHOH}$) ppm. ^{13}C NMR: δ = 14.0, 22.7, 27.7, 31.2, 37.4, 53.6, 58.3, 66.9, 73.7 ppm. GC-MS: m/z = 201. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{11}\text{H}_{24}\text{NO}_2$ ($[\text{M}+\text{H}]^+$) 202.1807; found 202.1801.

5-Phenyl-1-(morpholin-1-yl)pentan-3-ol (**3ca**)

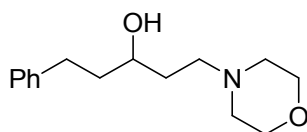


Fig S11. Chemical Structure of **3ca**

The reaction was conducted according to Method B with allylic alcohols **1c** at 70°C in IPA (0.5 mL) (90% yield). The product was purified by column chromatography (EtOAc:Hexane = 1:1) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.41-1.54 (m, 1H, -CHCHHCH₂N-), 1.60-1.87 (m, 3H, -CHCHHCH₂N-, -CH₂CH₂Ar), 2.41 (br-s, 2H, -CHCH₂CH₂N-), 2.55-2.87 (m, 6H, -CH₂Ar, -NCH₂CH₂O-), 3.62-3.85 (m, 5H, -NCH₂CH₂O-, -CHOH), 6.09 (br-s, 1H, -CHOH), 7.15-7.31 (m, 5H, Ar-H) ppm. ^{13}C NMR: δ = 31.2, 31.9, 39.4, 53.6, 58.3, 66.9, 73.0, 125.6, 128.3, 128.4, 142.4 ppm. GC-MS: m/z = 249. HRMS (FAB, *m*-NBA): Calcd. for C₁₅H₂₄NO₂ ([M+H]⁺) 250.1807; found 250.1803.

4-(Morpholin-1-yl)-1-phenylbutan-2-ol (**3da**)

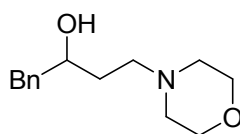


Fig S12. Chemical Structure of **3da**

The reaction was conducted according to Method B with allylic alcohols **1d** at 100°C in IPA (0.5 mL) and Toluene (0.5 mL) (91% yield). The product was purified by column chromatography (EtOAc:Hexane = 1:1) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.46-1.55 (m, 1H, -CHCHHCH₂-), 1.61-1.74 (m, 1H, -CHCHHCH₂-), 2.39 (br-s, 2H, -CHCH₂CH₂-), 2.54-2.70 (m, 5H, -CHHAr, -NCH₂CH₂O-), 2.85 (dd, J = 13.5 Hz, J = 6.9 Hz, 1H, -CHHAr), 3.61-3.78 (m, 4H, -NCH₂CH₂O-), 3.99-4.07 (m, 1H, -CHOH), 7.17-7.32 (m, 5H, Ar-H) ppm. ^{13}C NMR: δ = 30.4, 44.1, 53.6, 58.2, 66.8, 74.8, 126.1, 128.2, 129.2, 138.8 ppm. GC-MS: m/z = 235. HRMS (FAB, *m*-NBA): Calcd. for C₁₄H₂₂NO₂ ([M+H]⁺) 236.1651; found 236.1651.

3-(Morpholin-1-yl)-1-phenylpropan-1-ol (**3ea**)¹³

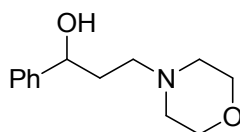


Fig S13. Chemical Structure of **3ea**

The reaction was conducted according to Method B with allylic alcohols **1e** at 80°C in IPA (0.5 mL) and Toluene (0.5 mL) (>99% yield). The product was purified by column chromatography (EtOAc only) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR (CDCl₃): δ = 1.84-1.91 (m, 2H, -CHCH₂-), 2.40-2.74 (m, 6H, -CHCH₂CH₂-, -NCH₂CH₂O-), 3.76 (t, J = 4.8 Hz, 4H, -NCH₂CH₂O-), 4.95 (t, J = 5.4 Hz, 1H, -CHOH), 6.47 (br-s, 1H, -OH), 7.20-7.39 (m, 5H, Ar-H) ppm. ^{13}C NMR: δ = 33.4, 53.7, 57.6, 66.9, 75.5, 125.5, 127.0, 128.3, 144.7 ppm. GC-MS: m/z = 221. CAS Registry Number: 4441-34-3.

3-(Morpholin-1-yl)-1-(4-methoxyphenyl)propan-1-ol (**3fa**)¹³

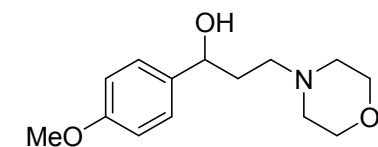


Fig S14. Chemical Structure of **3fa**

The reaction was conducted according to Method B with allylic alcohols **1f** at 65°C in IPA (0.5 mL) and Toluene (0.5 mL) (70% yield). The product was purified by column chromatography (EtOAc only) and vacuum distillation. The product was obtained as a colorless oil.

¹H NMR: δ = 1.76-1.93 (m, 2H, -CHCH₂-), 2.49 (br-s, 2H, -CHCH₂CH₂-), 2.54-2.73 (m, 4H, -NCH₂CH₂O-), 3.75 (t, J = 4.5 Hz, 4H, -NCH₂CH₂O-), 3.80 (s, 3H, Ar-OCH₃), 4.89 (dd, J = 7.8 Hz, J = 3.6 Hz, 1H, -CHOH), 6.86-6.89 (m, 2H, Ar-H), 7.26-7.30 (m, 2H, Ar-H) ppm. ¹³C NMR: δ = 33.5, 53.7, 55.3, 57.6, 66.9, 75.2, 113.6, 126.6, 136.9, 158.6 ppm. GC-MS: m/z = 251. CAS Registry Number: 109562-49-4.

4-(Morpholin-1-yl)-1-phenoxybutan-2-ol (**3ga**)

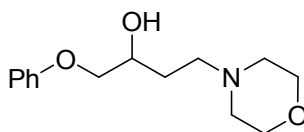


Fig S15. Chemical Structure of **3ga**

The reaction was conducted according to Method B with allylic alcohols **1g** at 90°C in IPA (0.5 mL) and Toluene (0.5 mL) (92% yield). The product was purified by column chromatography (EtOAc only) and vacuum distillation. The product was obtained as a colorless oil.

¹H NMR: δ = 1.68-1.89 (m, 2H, -CHCH₂CH₂-), 2.47 (br-s, 2H, -CHCH₂CH₂-), 2.57-2.77 (m, 4H, -NCH₂CH₂O-), 3.72 (t, J = 4.5 Hz, 4H, -NCH₂CH₂O-), 3.87 (dd, J = 9.3 Hz, J = 5.7 Hz, 1H, -OCHHCH-), 3.97 (dd, J = 9.3 Hz, J = 5.7 Hz, 1H, -OCHHCH-), 4.15-4.23 (m, 1H, -CHOH), 6.89-6.97 (m, 3H, Ar-H), 7.24-7.31 (m, 2H, Ar-H) ppm. ¹³C NMR: δ = 28.0, 53.7, 57.6, 66.9, 71.4, 71.7, 114.5, 120.8, 129.4, 158.8 ppm. FAB-MS: m/z = 252 ([M + H]⁺). HRMS (FAB, *m*-NBA): Calcd. for C₁₄H₂₂NO₃ ([M+H]⁺) 252.1600; found 252.1595. CAS Registry Number: 873390-19-3.

3-(Morpholin-1-yl)propan-1-ol (**3ha**)¹⁴

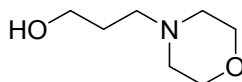


Fig S16. Chemical Structure of **3ha**

The reaction was conducted according to Method C with amine **2a** (99% yield). The product was purified by column chromatography (EtOAc:MrOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

¹H NMR: δ = 1.73 (quin, J = 5.4 Hz, 2H, -CH₂CH₂OH), 2.53 (br-s, 2H, -CH₂CH₂CH₂OH), 2.59 (t, J = 5.7 Hz, 4H, -NCH₂CH₂O-), 3.71 (t, J = 4.5 Hz, 4H, -NCH₂CH₂O-), 3.81 (t, J = 5.4 Hz, 2H, -CH₂OH), 4.44 (br-s, 1H, -OH) ppm. ¹³C NMR: δ = 26.8, 53.7, 59.0, 64.3, 66.8 ppm. GC-MS: m/z = 145. CAS Registry Number: 4441-30-9.

3-(Piperizin-1-yl)propan-1-ol (**3hb**)¹⁴

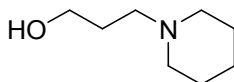


Fig S17. Chemical Structure of **3hb**

The reaction was conducted according to Method C with amine **2b** (94% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

¹H NMR: δ = 1.37-1.49 (m, 2H, -CH₂CH₂CH₂CH₂N-), 1.57 (quin, J = 5.4 Hz, 4H, -CH₂CH₂CH₂N-), 1.68 (quin, J = 5.4 Hz, 2H, -CH₂CH₂OH), 2.45 (br-s, 2H, -CH₂CH₂CH₂OH), 2.56 (t, J = 5.7 Hz, 4H, -CH₂CH₂CH₂CH₂N-), 3.80 (t, J = 5.4 Hz, 2H, -CH₂OH) ppm. ¹³C NMR: δ = 24.2, 26.0, 27.0, 54.7, 59.7, 64.8 ppm. GC-MS: m/z = 143. CAS Registry Number: 104-58-5.

3-(4-Phenylpiperazin-1-yl)propan-1-ol (**3hc**)

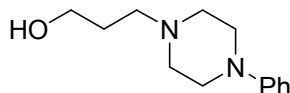


Fig S18. Chemical Structure of **3hc**

The reaction was conducted according to Method C with amine **2c** at 90°C (98% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

¹H NMR: δ = 1.76 (quart, J = 5.4 Hz, 2H, -CH₂CH₂OH), 2.65-2.71 (m, 6H, -CH₂CH₂CH₂OH, -CH₂CH₂NAr), 3.20 (t, J = 5.1 Hz, 4H, -CH₂NAr), 3.82 (t, J = 5.1 Hz, 2H, -CH₂OH), 5.13 (br-s, 1H, -OH), 6.84-6.94 (m, 3H, Ar-*H*), 7.23-7.29 (m, 2H, Ar-*H*) ppm. ¹³C NMR: δ = 27.1, 49.2, 53.3, 58.7, 64.5, 116.1, 119.9, 129.1, 151.1 ppm. GC-MS: m/z = 220. HRMS (FAB, *m*-NBA): Calcd. for C₁₃H₂₁N₂O ([M+H]⁺) 221.1654; found 221.1652. CAS Registry Number: 67514-07-2.

3-(1,2,3,4-Tetrahydroisoquinolin-2-yl)propan-1-ol (**3hd**)¹⁵

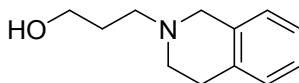


Fig S19. Chemical Structure of **3hd**

The reaction was conducted according to Method C with amine **2d** (95% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

¹H NMR: δ = 1.82 (quin, 2H, J = 5.7 Hz, -CH₂CH₂OH), 2.76-2.81 (m, 4H, -CH₂CH₂CH₂OH, -CH₂CH₂Ar), 2.91 (t, J = 5.7 Hz, 2H, -CH₂CH₂Ar), 3.70 (s, 2H, -NCH₂Ar), 3.84 (t, 2H, J = 5.4 Hz, -CH₂OH) 7.00-7.15 (m, 4H, Ar-*H*) ppm. ¹³C NMR: δ = 27.5, 29.0, 50.8, 56.5, 58.7, 64.6, 125.7, 126.3, 126.5, 128.6, 134.1, 134.2 ppm. GC-MS: m/z = 191. CAS Registry Number: 86368-07-2.

3-(1,4-Dioxo-8-azaspiro[4.5]decan-8-yl)propan-1-ol (**3he**)

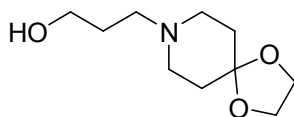


Fig S20. Chemical Structure of **3he**

The reaction was conducted according to Method C with amine **2e** (80% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.68-1.76 (m, 6H, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{C}-$), 2.51-2.65 (m, 6H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, $-\text{NCH}_2\text{CH}_2\text{C}-$), 3.81 (t, J = 5.1 Hz, 2H, $-\text{CH}_2\text{OH}$), 3.95 (s, 4H, $-\text{CH}_2\text{O}-$), 5.44 (br-s, 1H, $-\text{OH}$) ppm. ^{13}C NMR: δ = 27.4, 34.8, 51.6, 58.6, 64.2, 64.7, 106.9 ppm. GC-MS: m/z = 201. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{10}\text{H}_{20}\text{NO}_3$ ($[\text{M}+\text{H}]^+$) 202.1443; found 202.1446. CAS Registry Number: 91017-21-9.

3-(Indolin-1-yl)propan-1-ol (**3hf**)

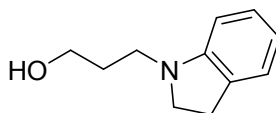


Fig S21. Chemical Structure of **3hf**

The reaction was conducted according to Method C with amine **2f** (92% yield). The product was purified by column chromatography (EtOAc:Hexane = 1:2) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 1.89 (quin, J = 6.6 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 2.40 (br-s, 1H, $-\text{OH}$), 2.96 (t, J = 8.1 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.22 (t, J = 6.3 Hz, 2H, $-\text{CH}_2\text{Ar}$), 3.36 (t, J = 8.1 Hz, 2H, $-\text{NCH}_2\text{CH}_2\text{Ar}$), 3.79-3.84 (m, 2H, $-\text{CH}_2\text{OH}$), 6.59 (d, J = 7.8 Hz, 1H, Ar- H), 6.70 (t, J = 7.5 Hz, 1H, Ar- H), 7.10-7.12 (m, 2H, Ar- H) ppm. ^{13}C NMR: δ = 28.6, 29.9, 48.1, 53.8, 62.1, 107.7, 118.3, 124.5, 127.3, 130.2, 152.5 ppm. GC-MS: m/z = 177. HRMS (FAB, m -NBA): Calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}$ (M^+) 177.1154; found 177.1158. CAS Registry Number: 105150-22-9.

3-(*N,N*-dipropylamino)propan-1-ol (**3hi**)

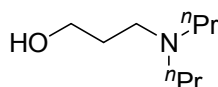


Fig S22. Chemical Structure of **3hi**

The reaction was conducted according to Method C with amine **2i** (87% yield). The product was purified by column chromatography (EtOAc:MeOH = 20:3) and vacuum distillation. The product was obtained as a colorless oil.

^1H NMR: δ = 0.89 (t, J = 7.5, 6H, $-\text{CH}_3$), 1.44-1.57 (m, 4H, $-\text{CH}_2\text{CH}_3$), 1.68 (quin, J = 5.4 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 2.34-2.41 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{CH}_3$), 2.65 (t, J = 5.4 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.81 (t, J = 5.1 Hz, 2H, $-\text{CH}_2\text{OH}$) ppm. ^{13}C NMR: δ = 11.8, 20.0, 27.8, 55.4, 56.1, 64.8 ppm. GC-MS: m/z = 159. HRMS (FAB, m -NBA): Calcd. for $\text{C}_9\text{H}_{22}\text{NO}$ ($[\text{M}+\text{H}]^+$) 160.1701; found 160.1705. CAS Registry Number: 34003-67-3.

7. Analysis Charts

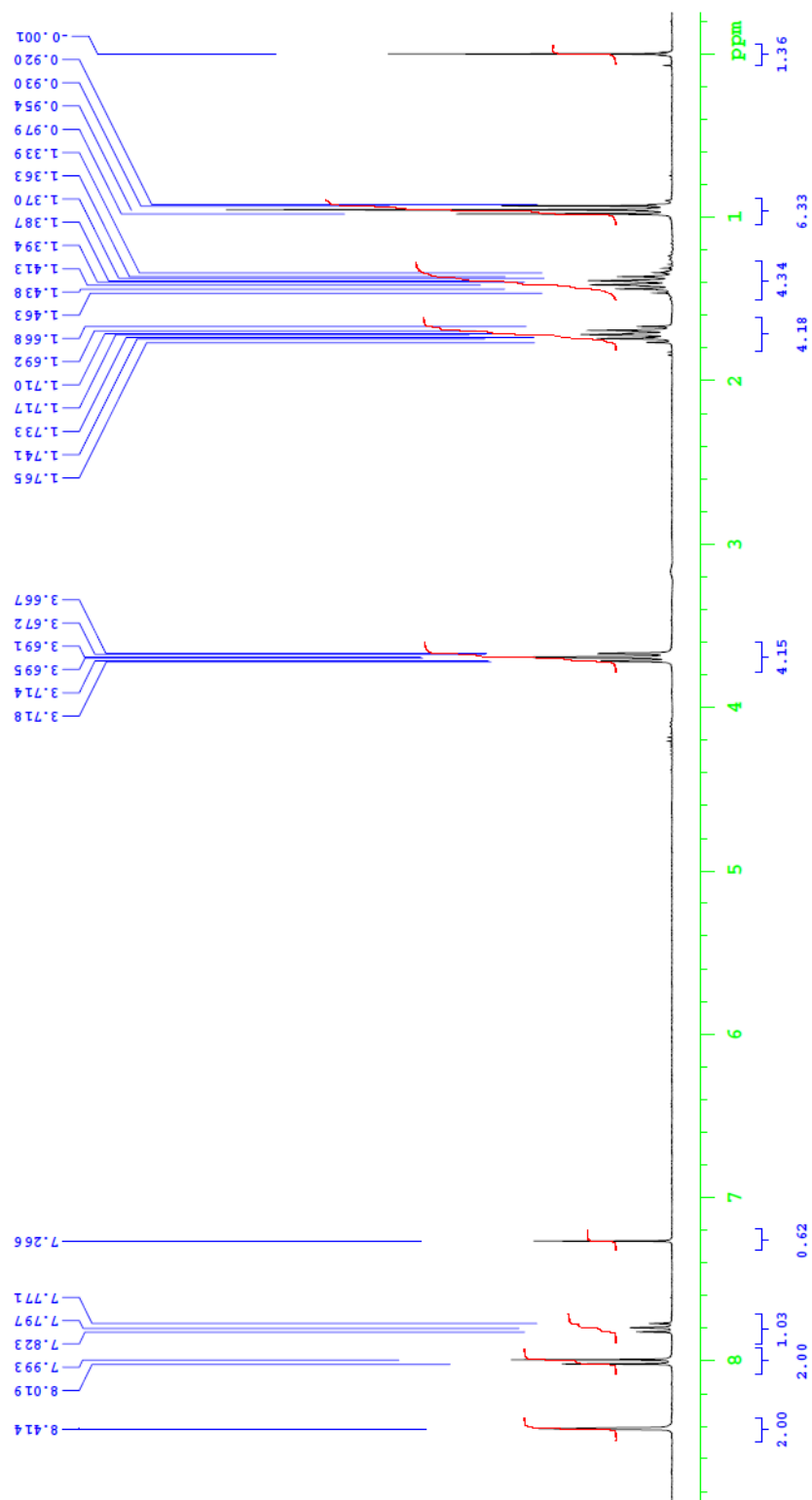


Fig S23. ¹H NMR spectrum of L4

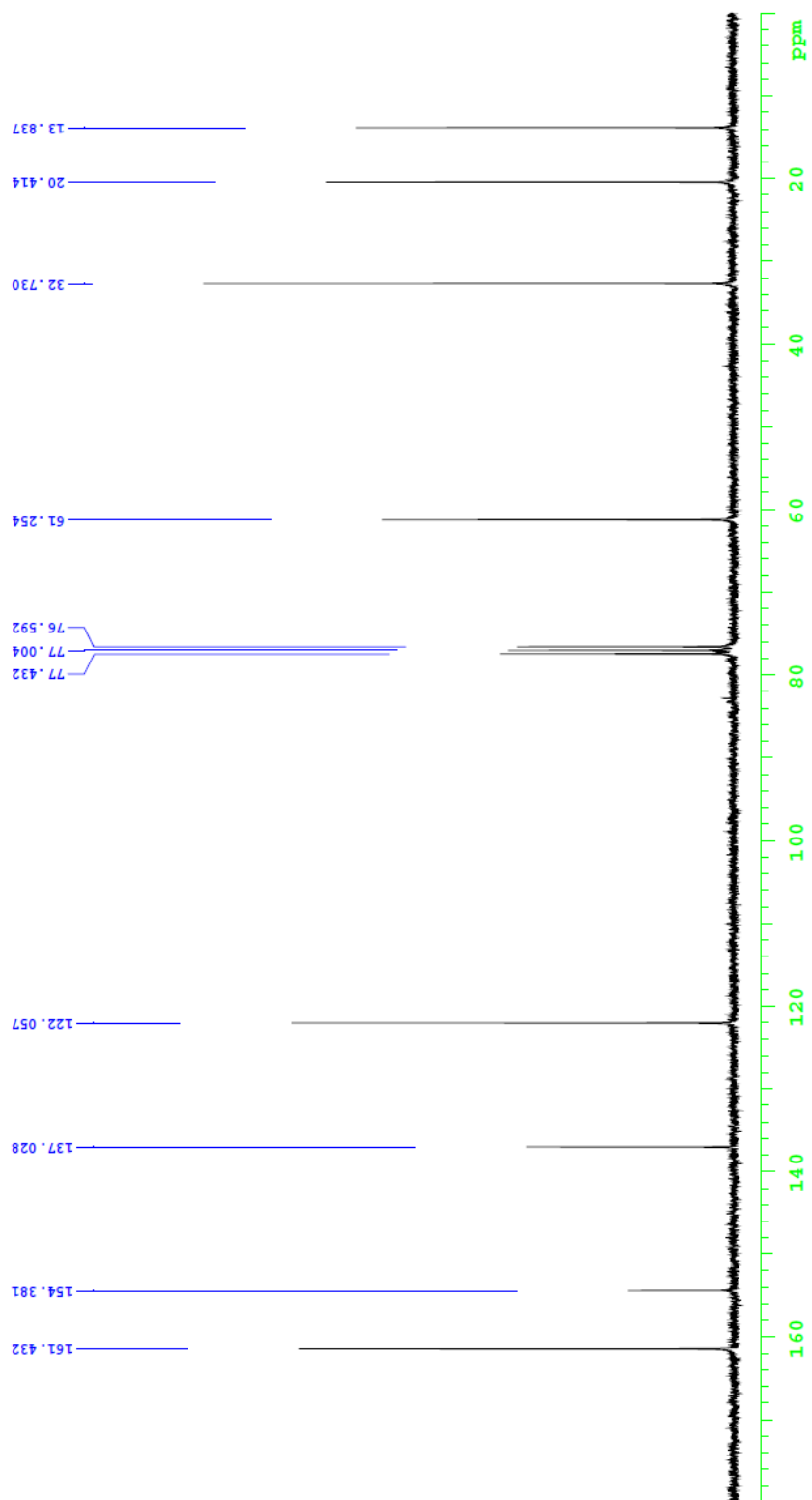


Fig S24. ^{13}C NMR spectrum of L4

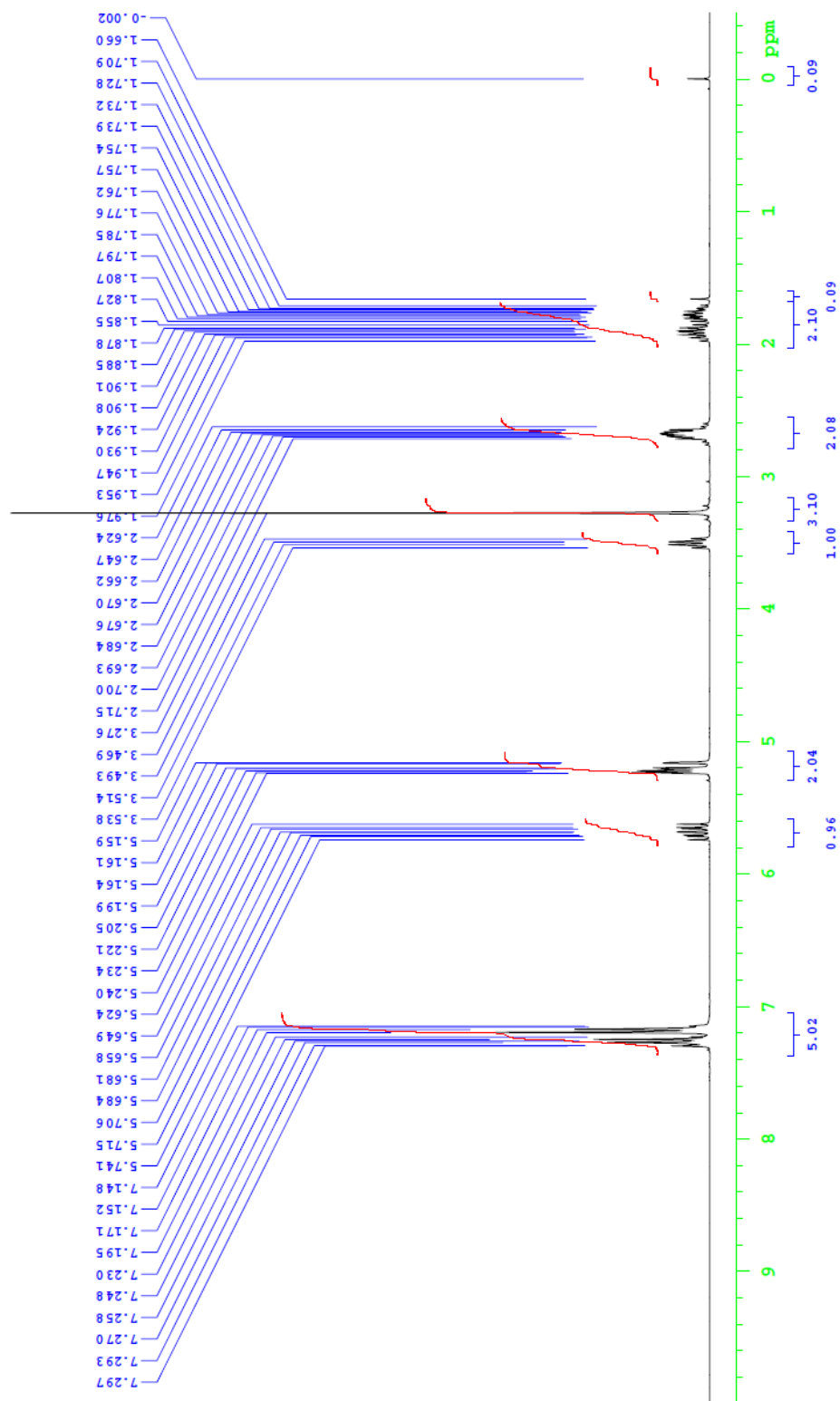


Fig S25. ^1H NMR spectrum of **1c'**

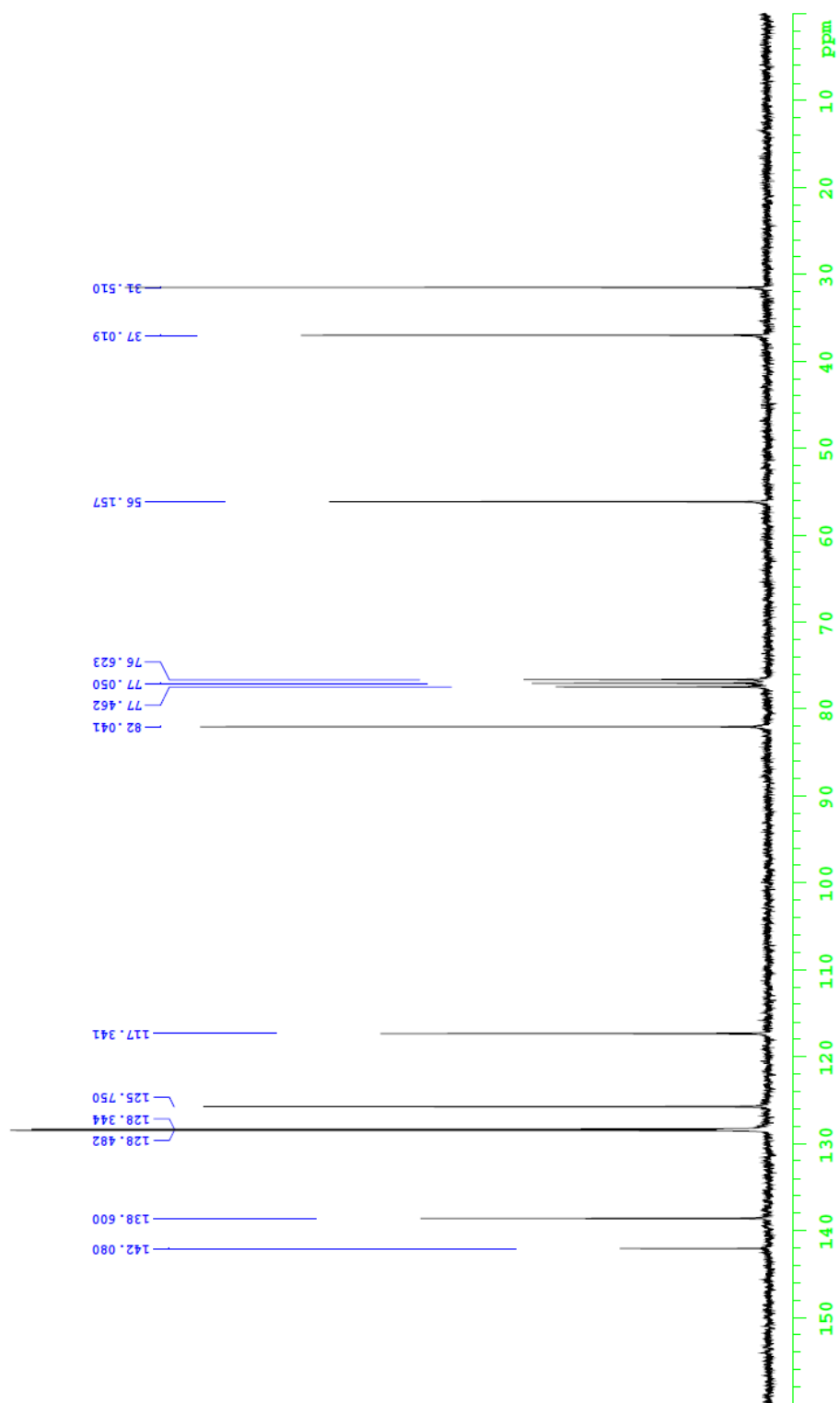


Fig S26. ^{13}C NMR spectrum of **1c'**

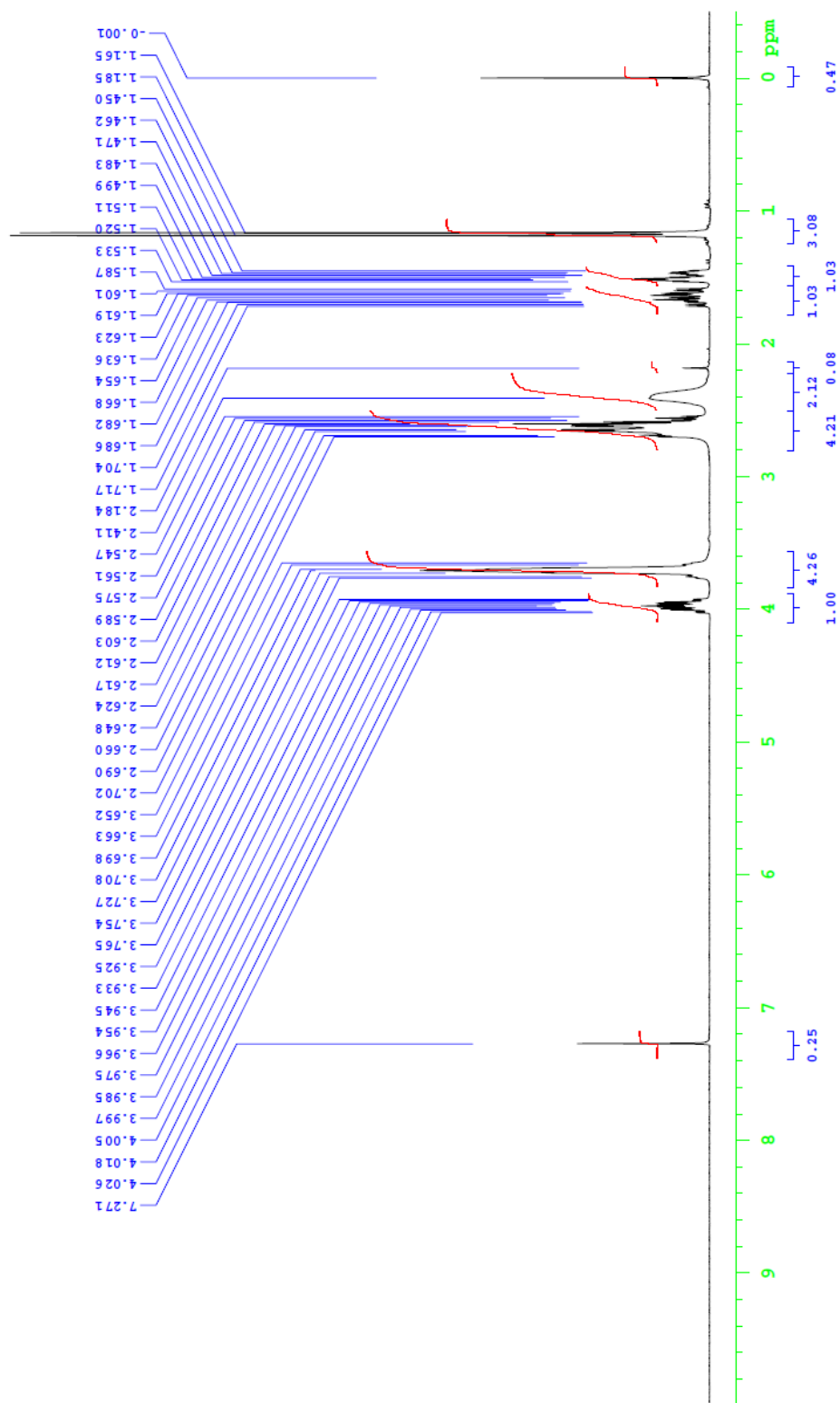


Fig S27. ¹H NMR spectrum of **3aa**

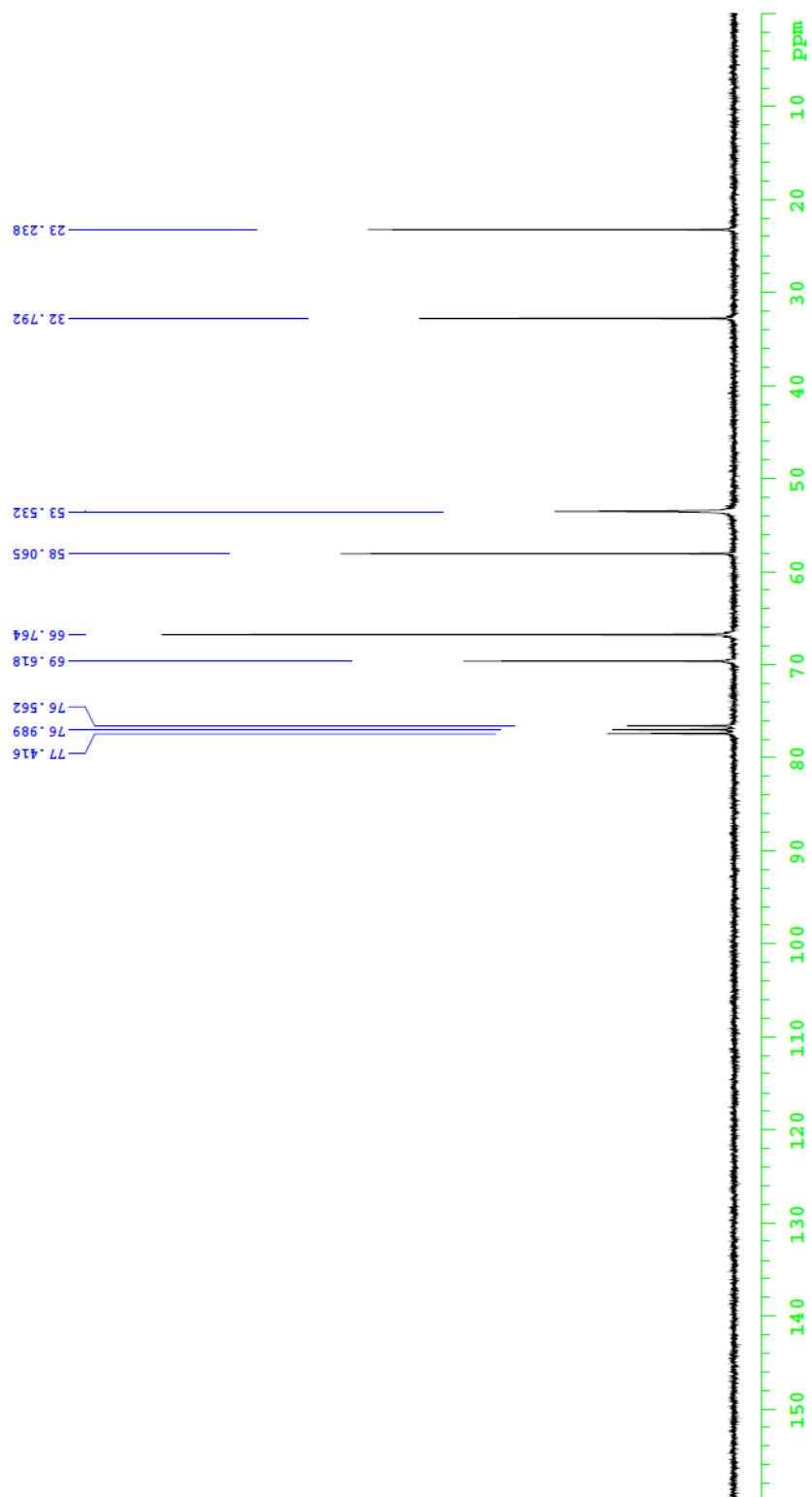


Fig S28. ^{13}C NMR spectrum of **3aa**

S22

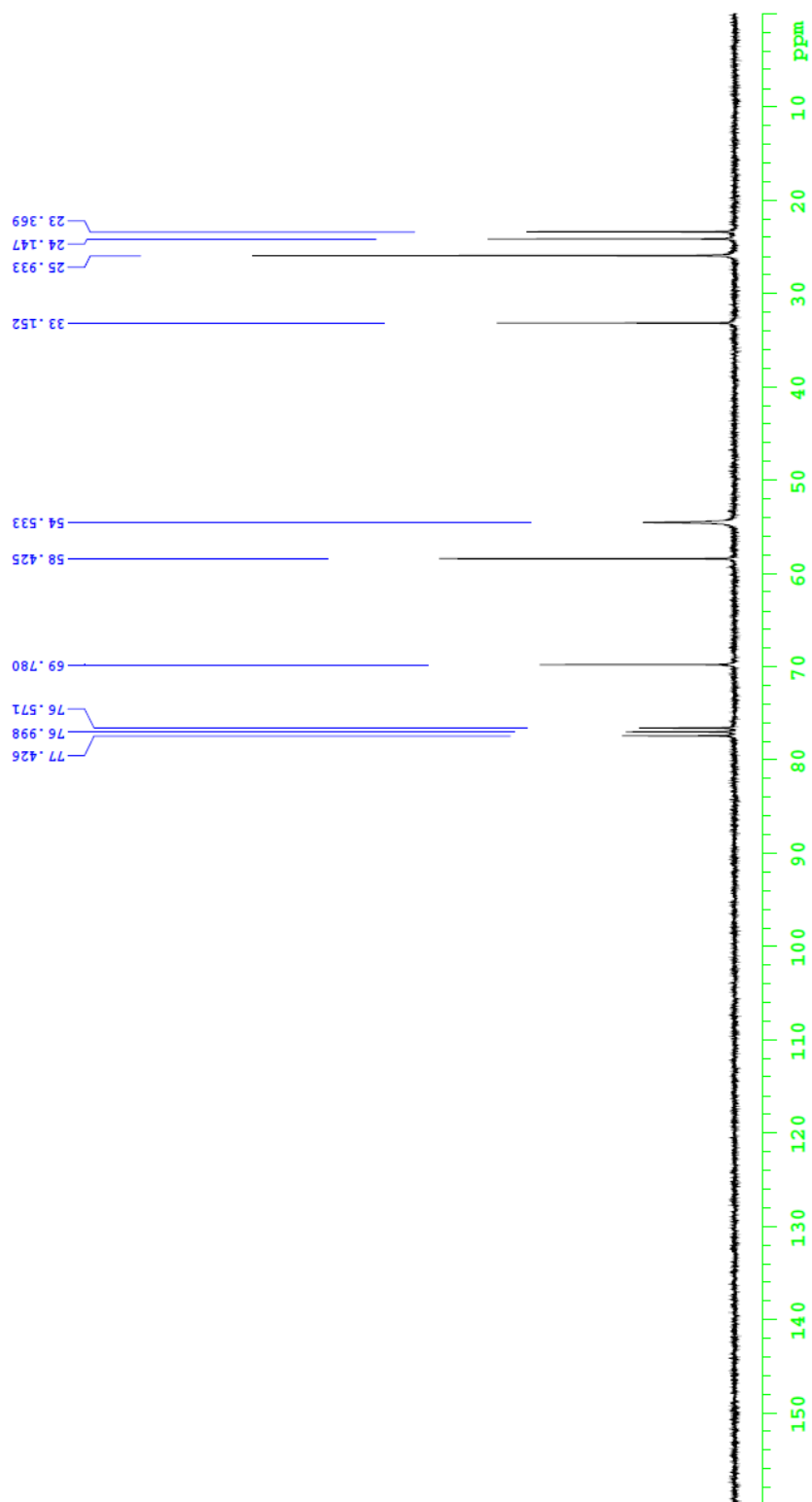


Fig S30. ^{13}C NMR spectrum of **3ab**

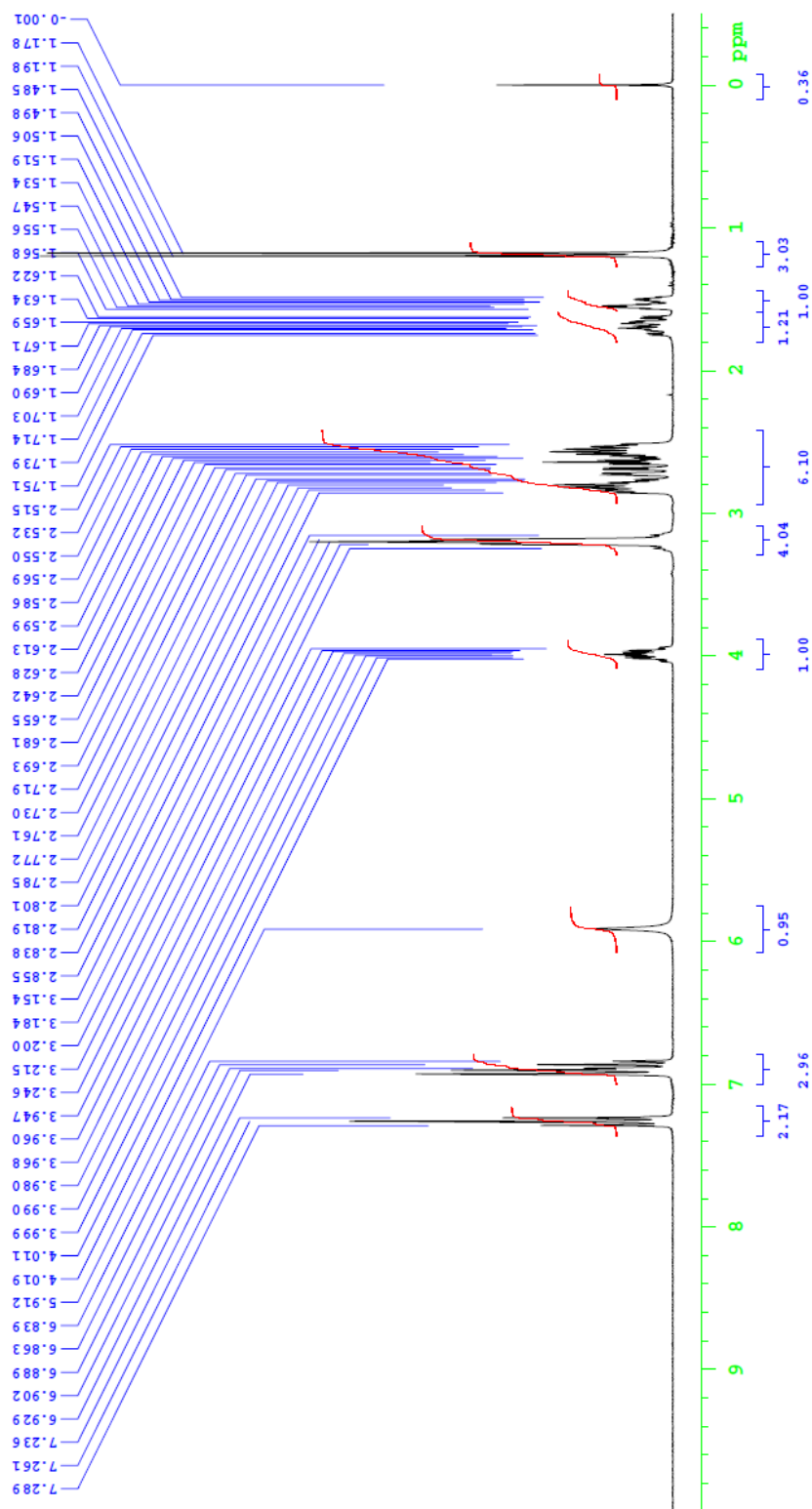


Fig S31. ¹H NMR spectrum of **3ac**

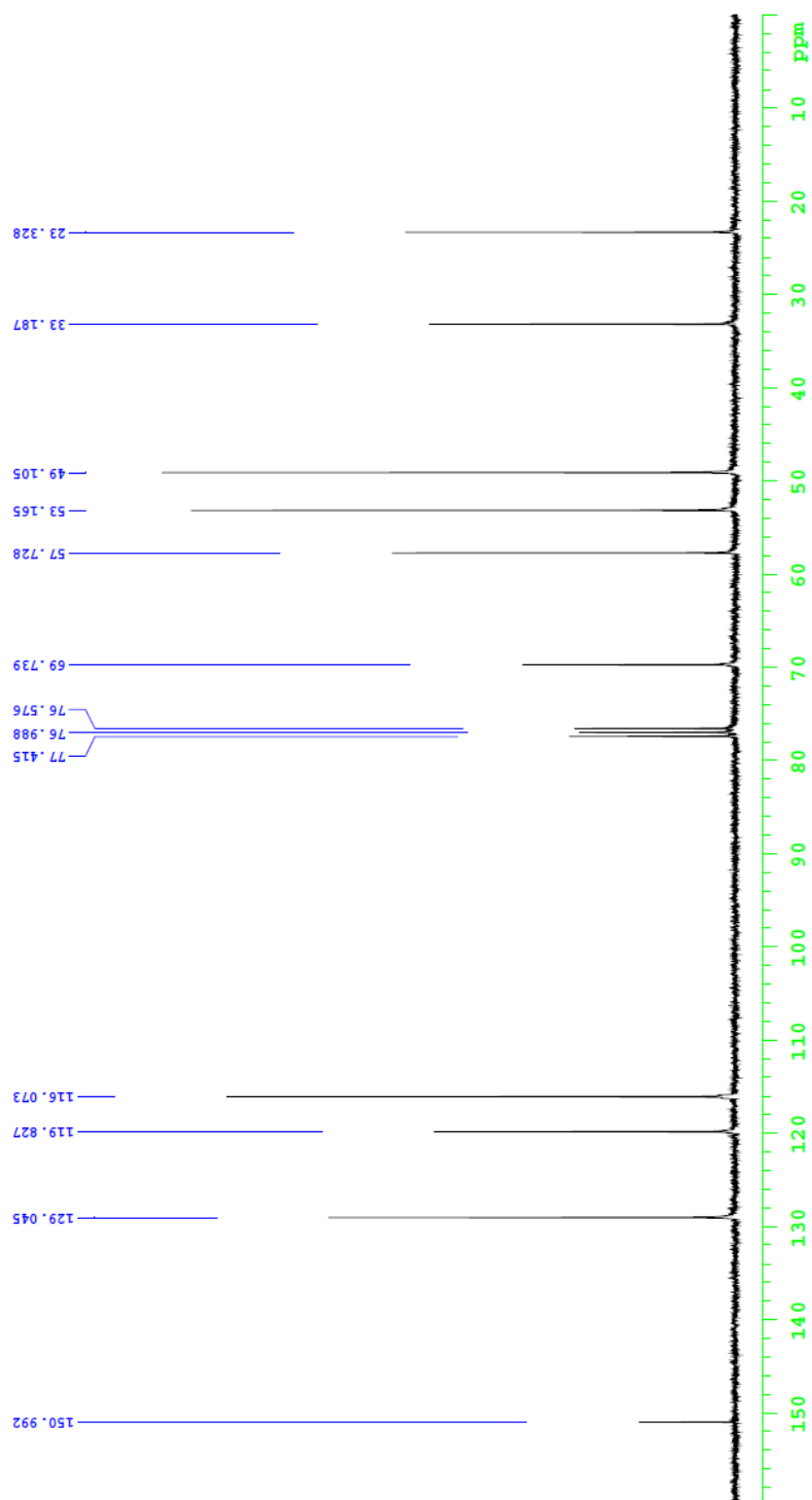


Fig S32. ¹³C NMR spectrum of **3ac**

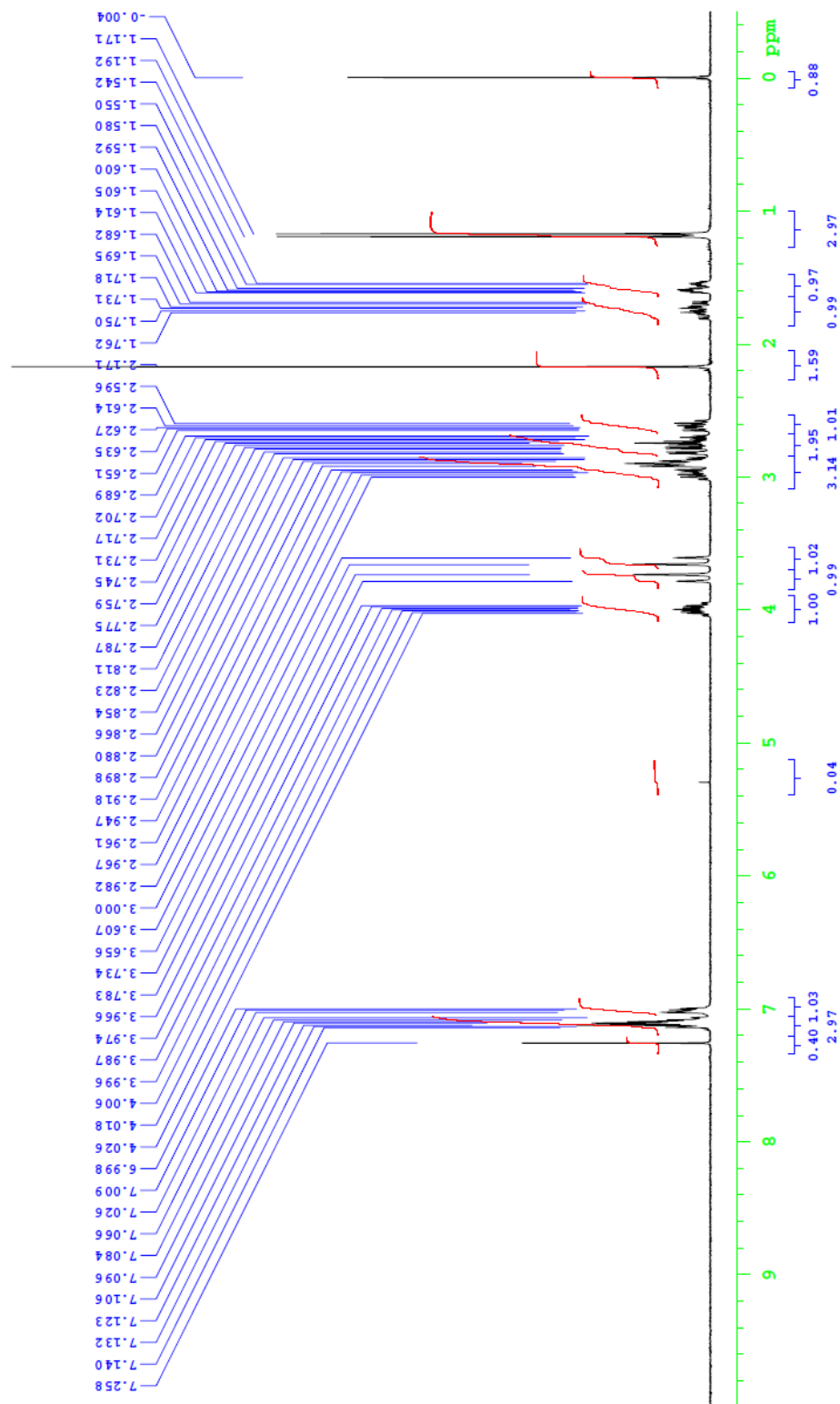


Fig S33. ¹H NMR spectrum of 3ad

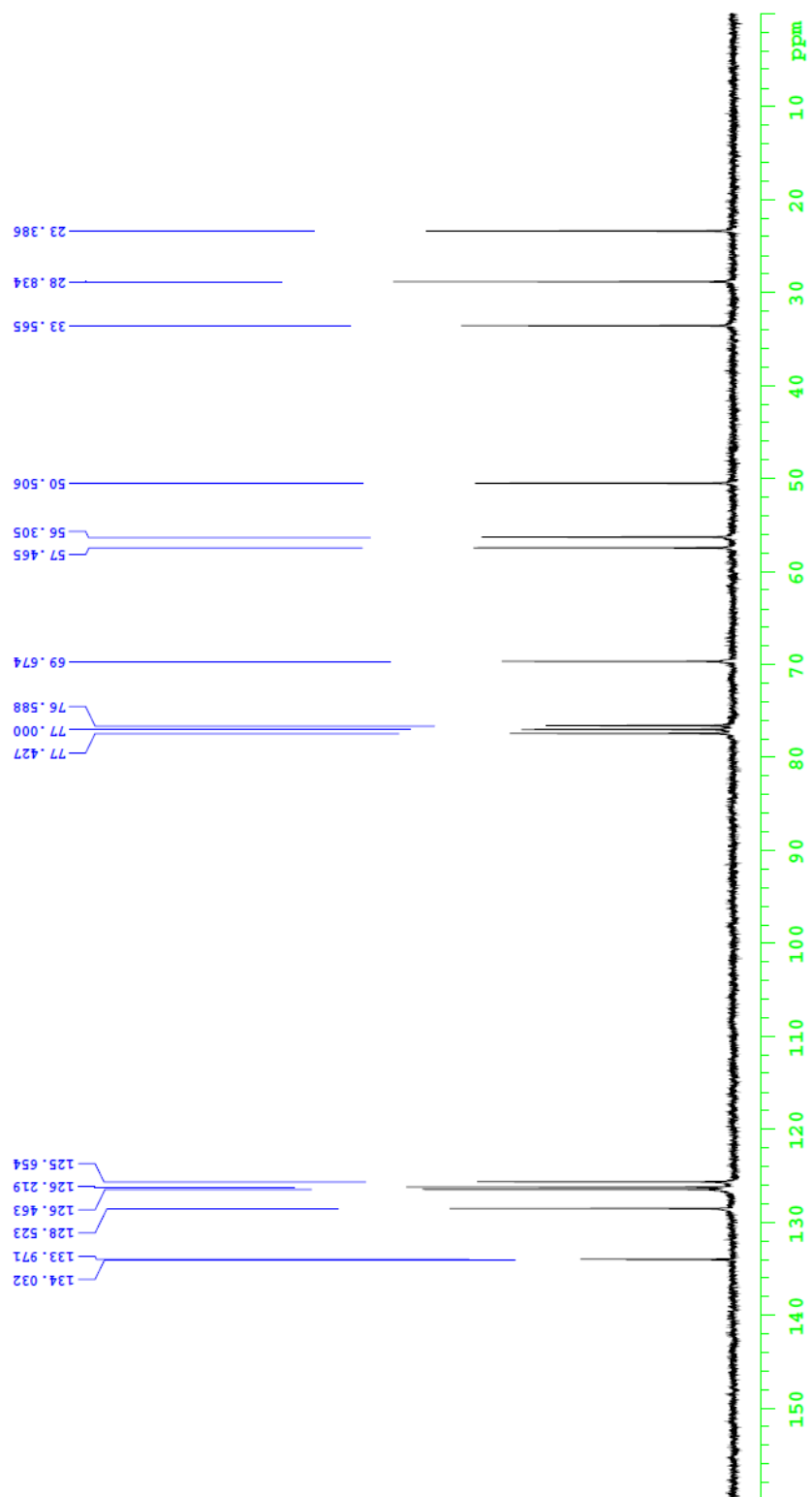


Fig S34. ^{13}C NMR spectrum of **3ad**

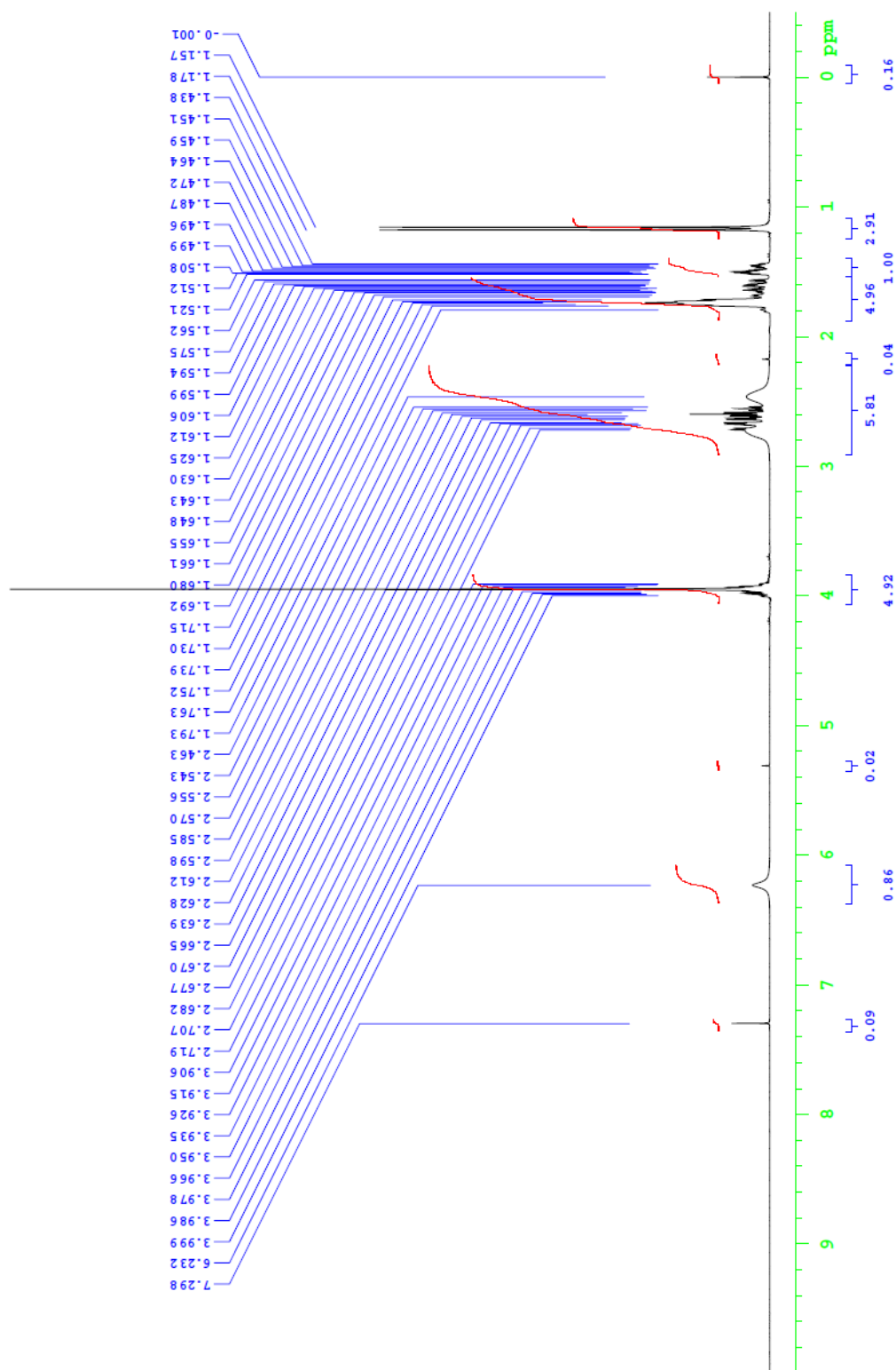


Fig S35. ^1H NMR spectrum of **3ae**

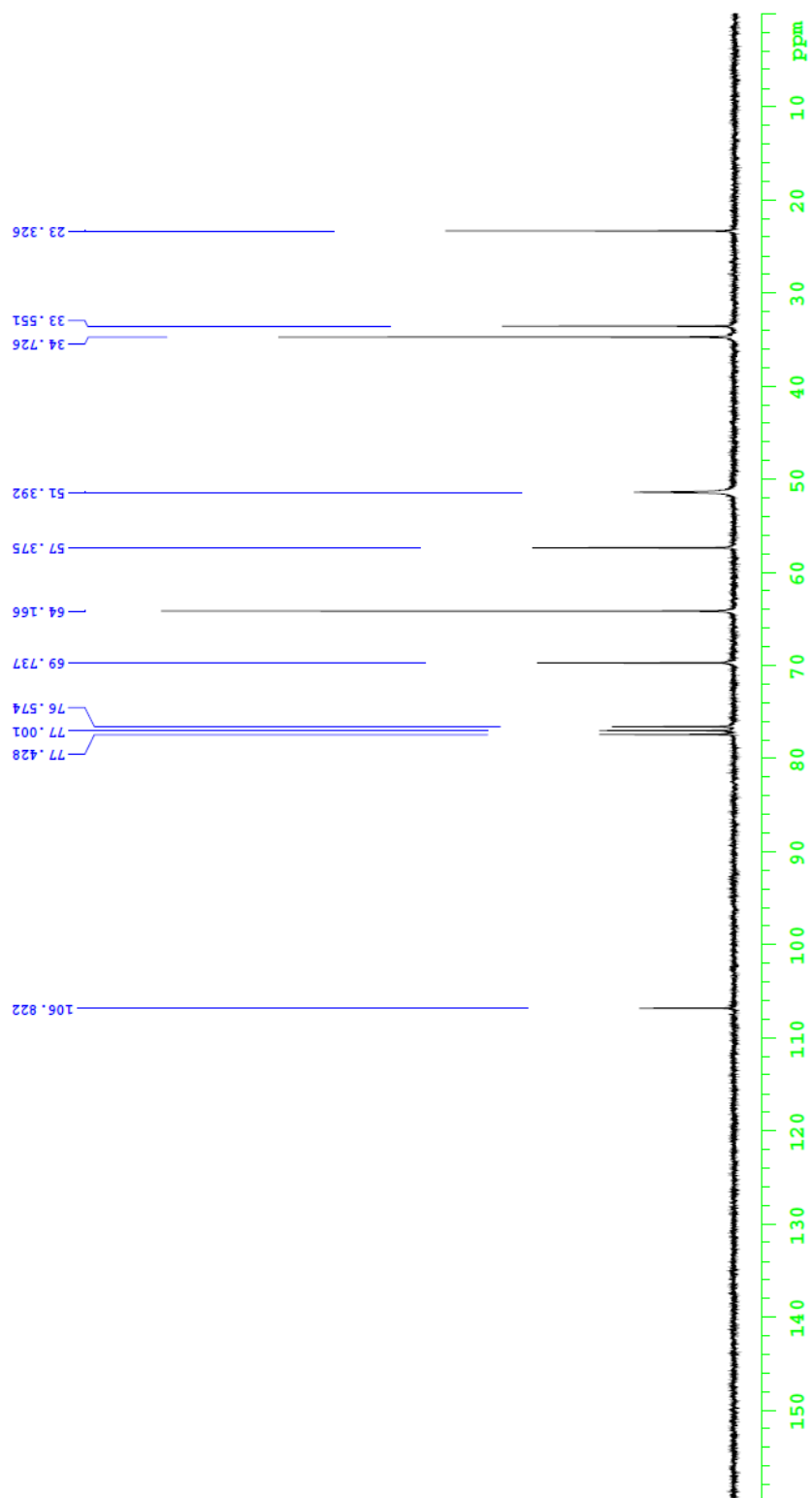


Fig S36. ^{13}C NMR spectrum of **3ae**

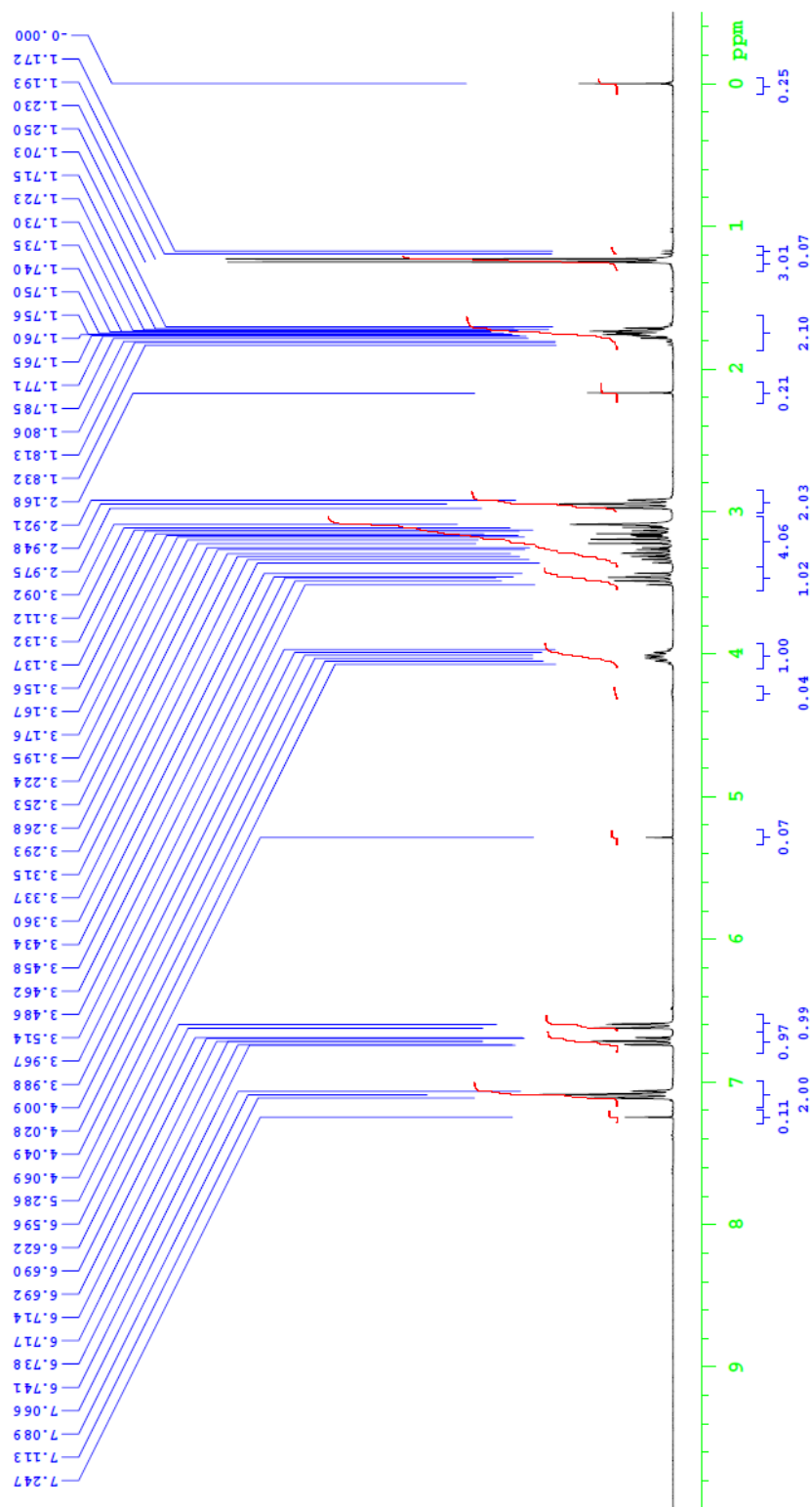


Fig S37. ^1H NMR spectrum of **3af**

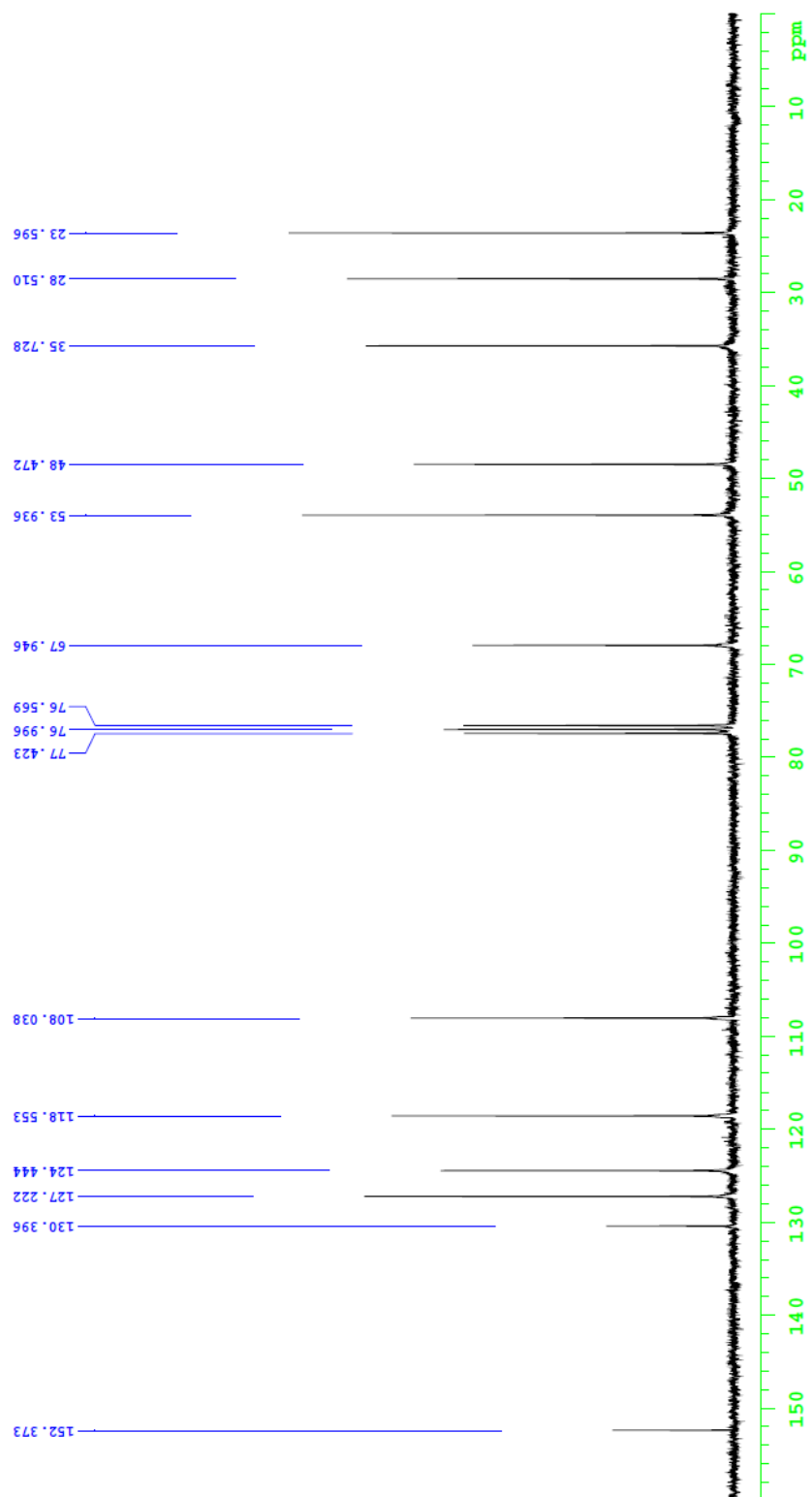


Fig S38. ¹³C NMR spectrum of 3af

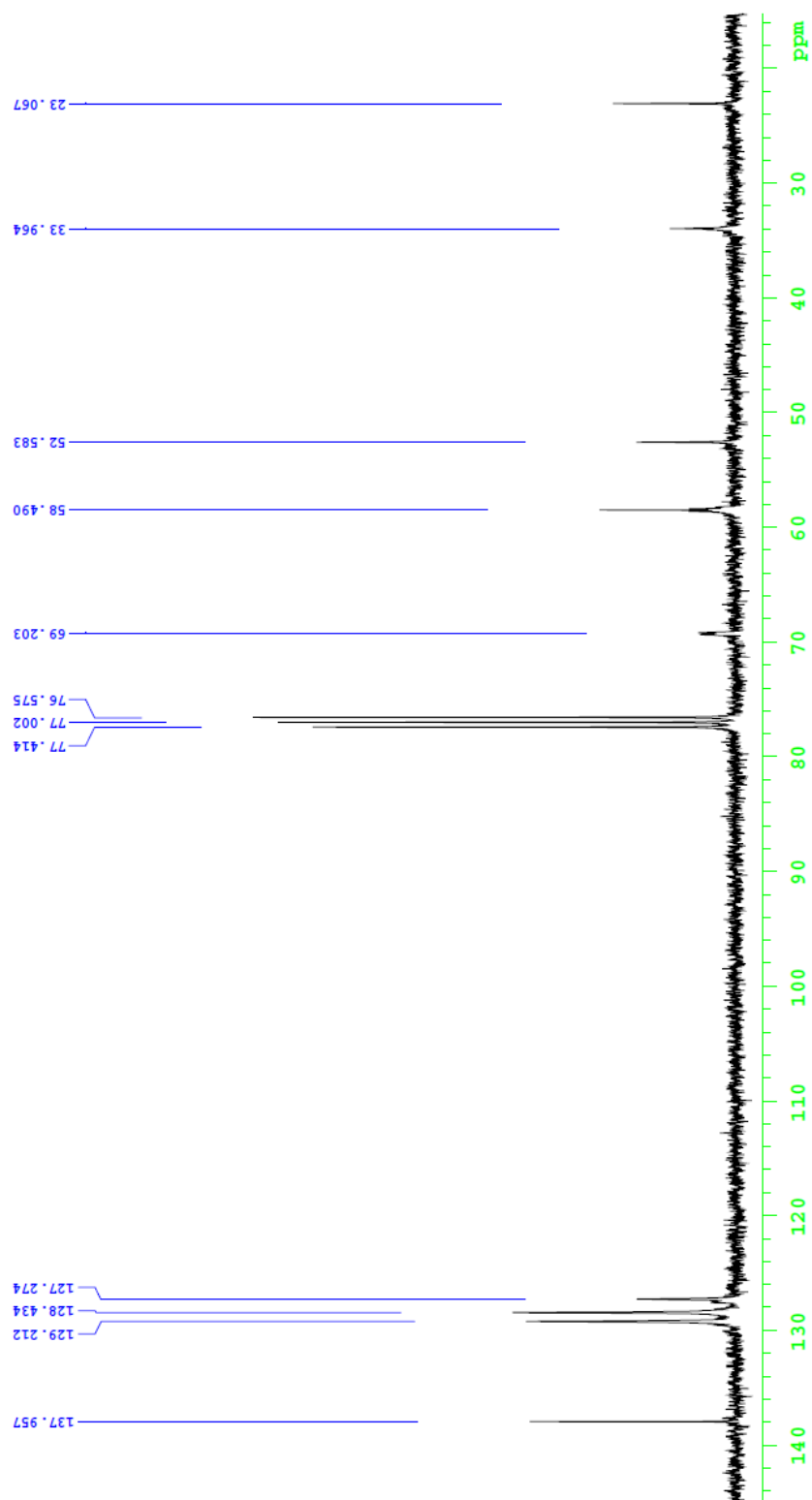


Fig S40. ¹³C NMR spectrum of **3ag**

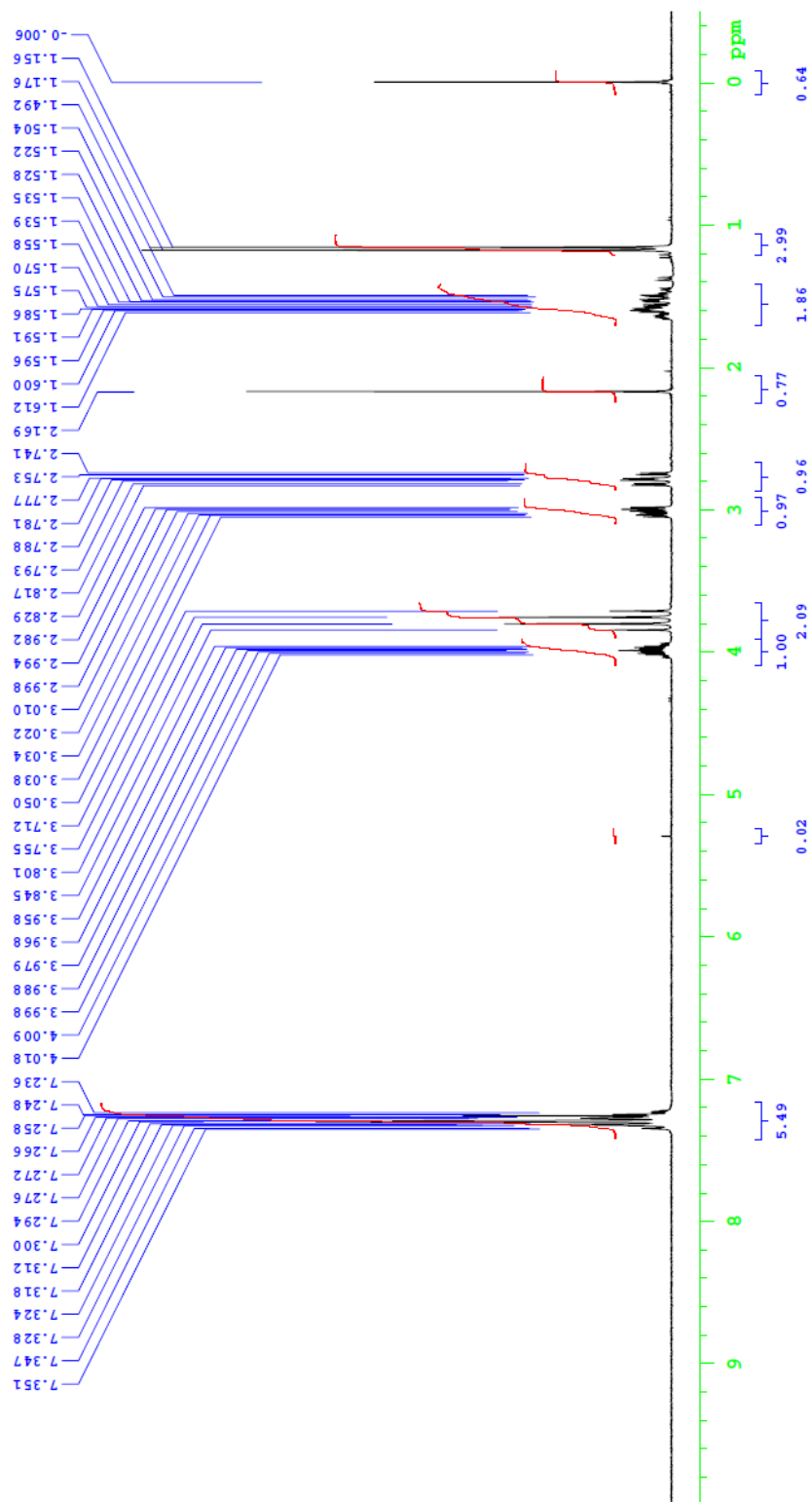


Fig S41. ^1H NMR spectrum of 3ah

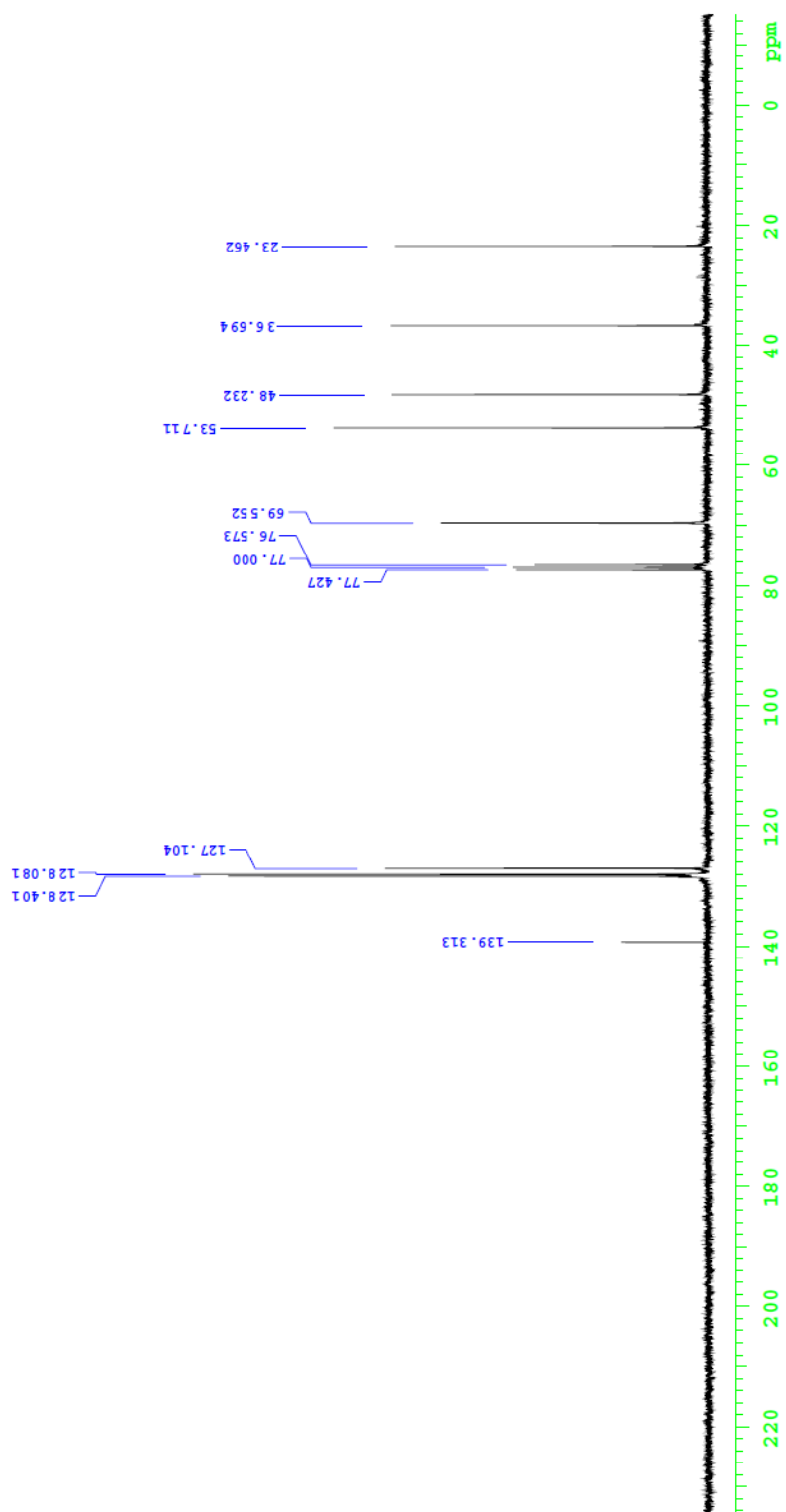


Fig S42. ¹³C NMR spectrum of **3ah**

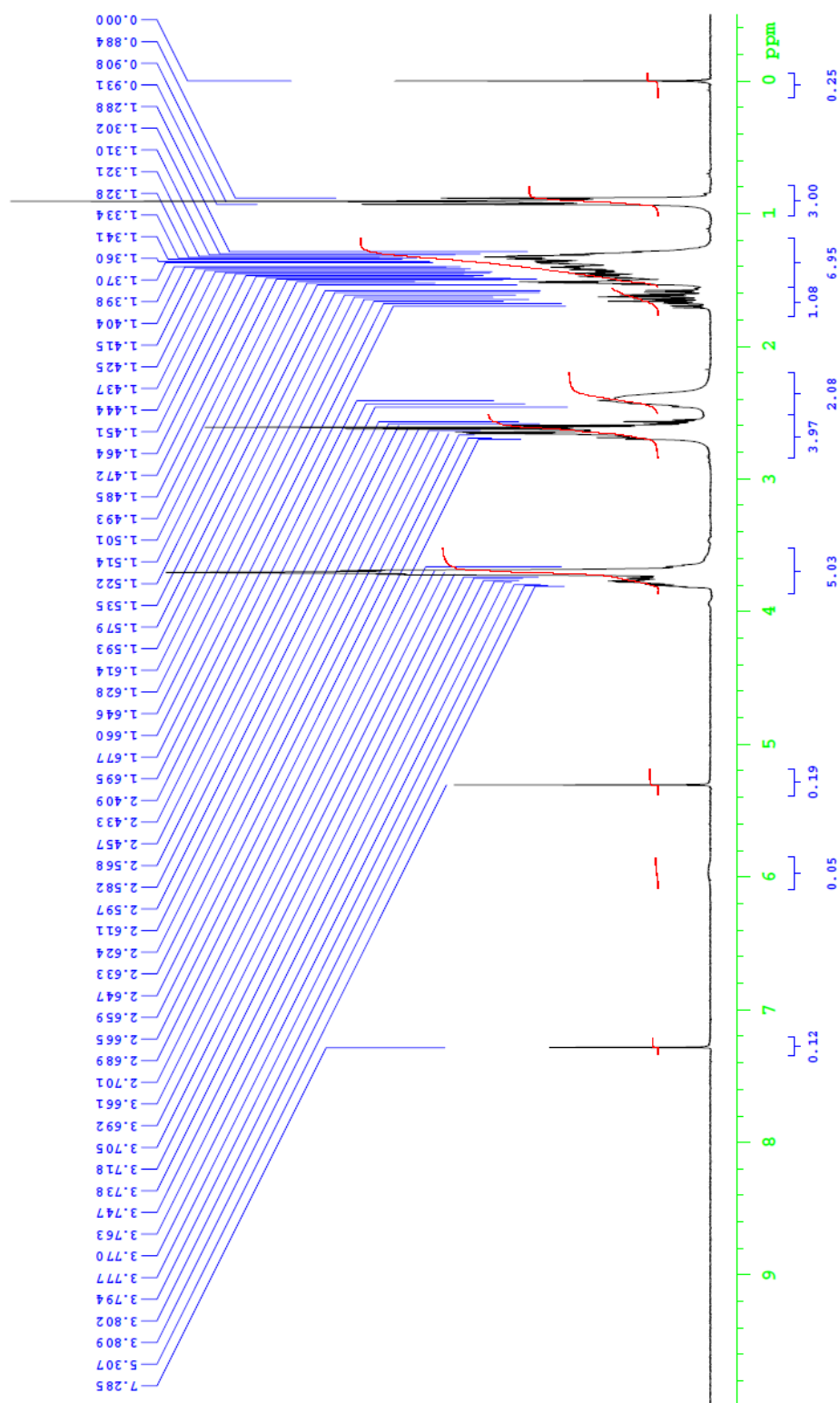


Fig S43. ^1H NMR spectrum of **3ba**

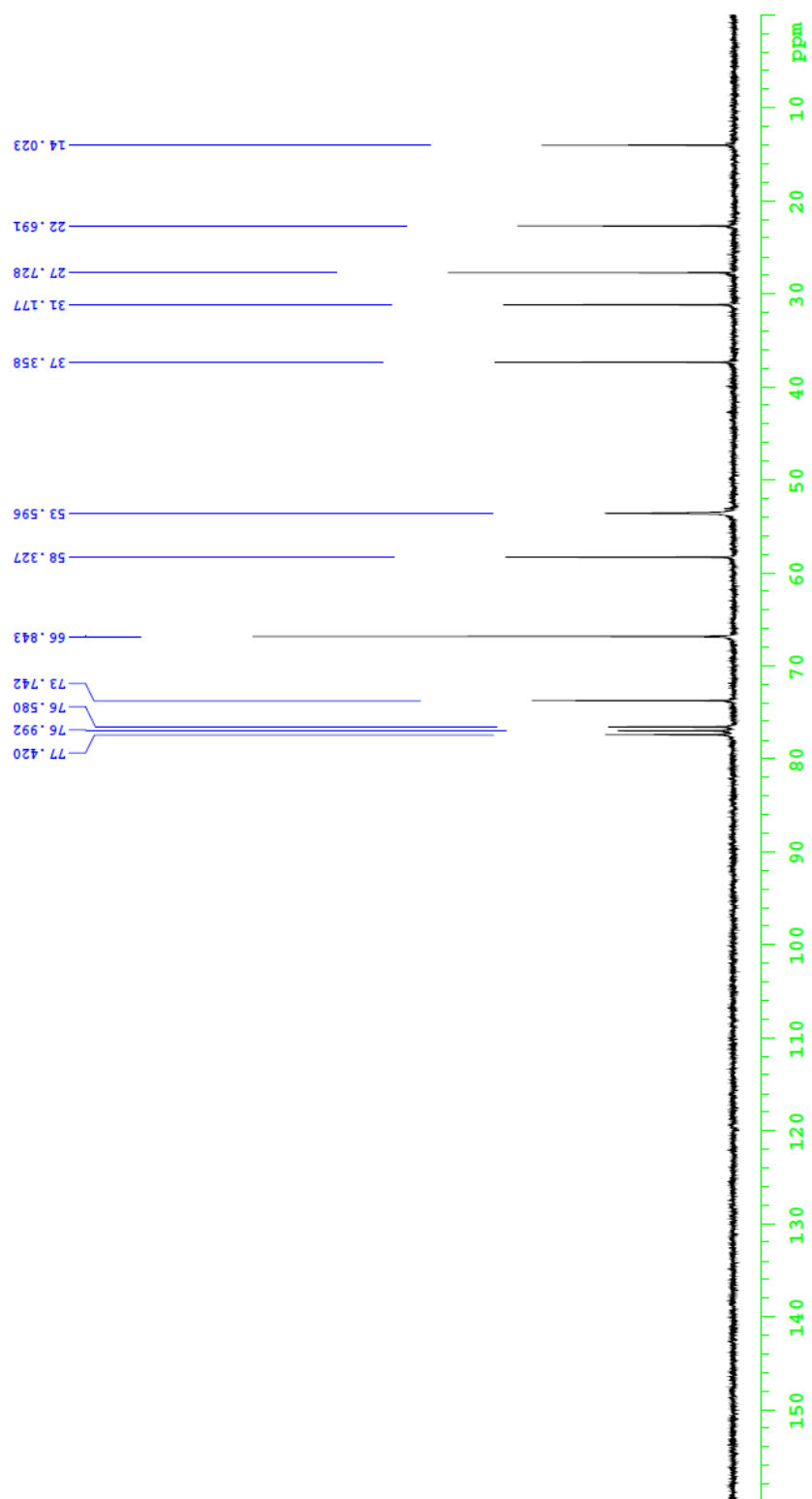


Fig S44. ^{13}C NMR spectrum of **3ba**

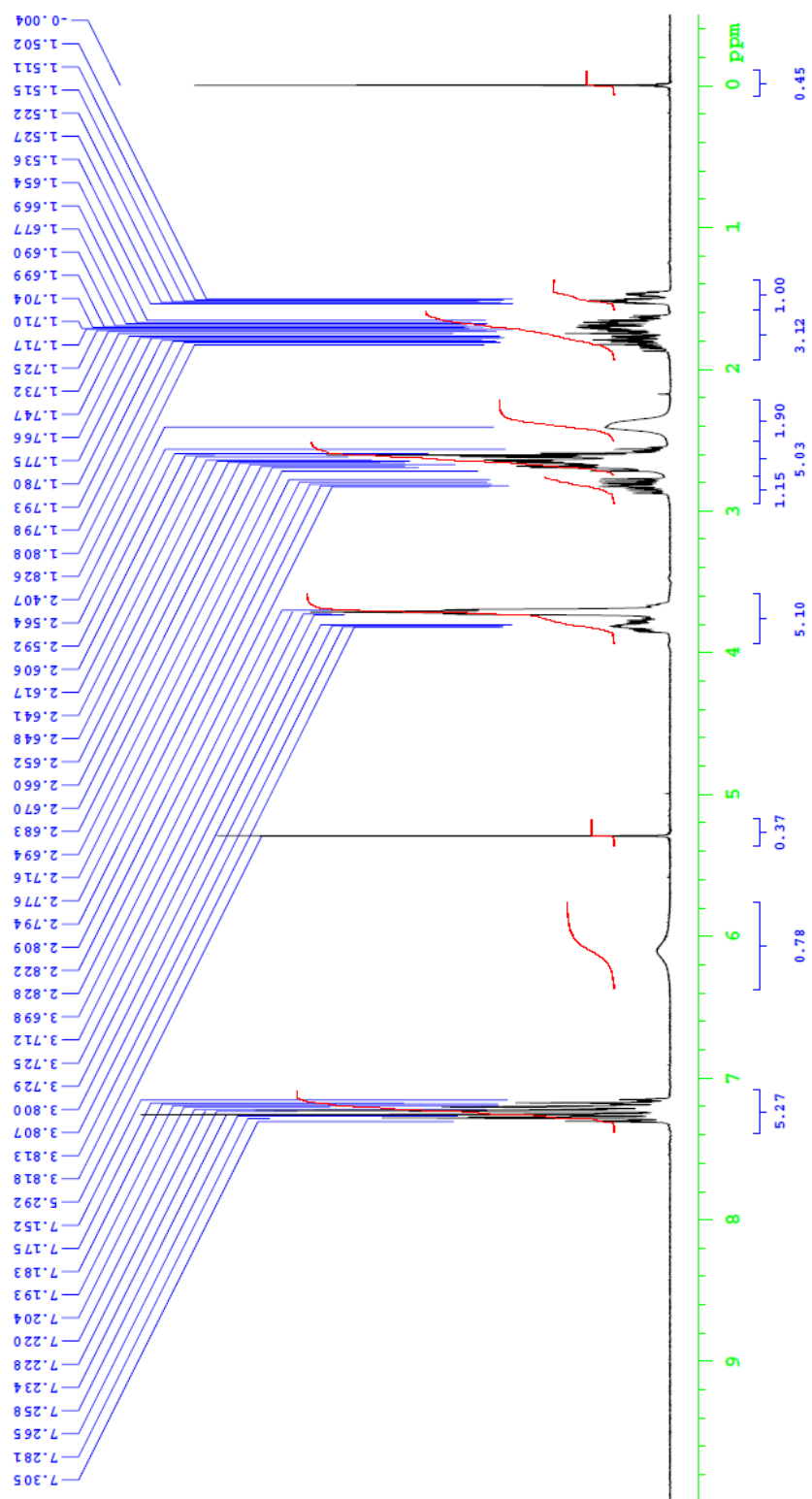


Fig S45. ^1H NMR spectrum of **3ca**

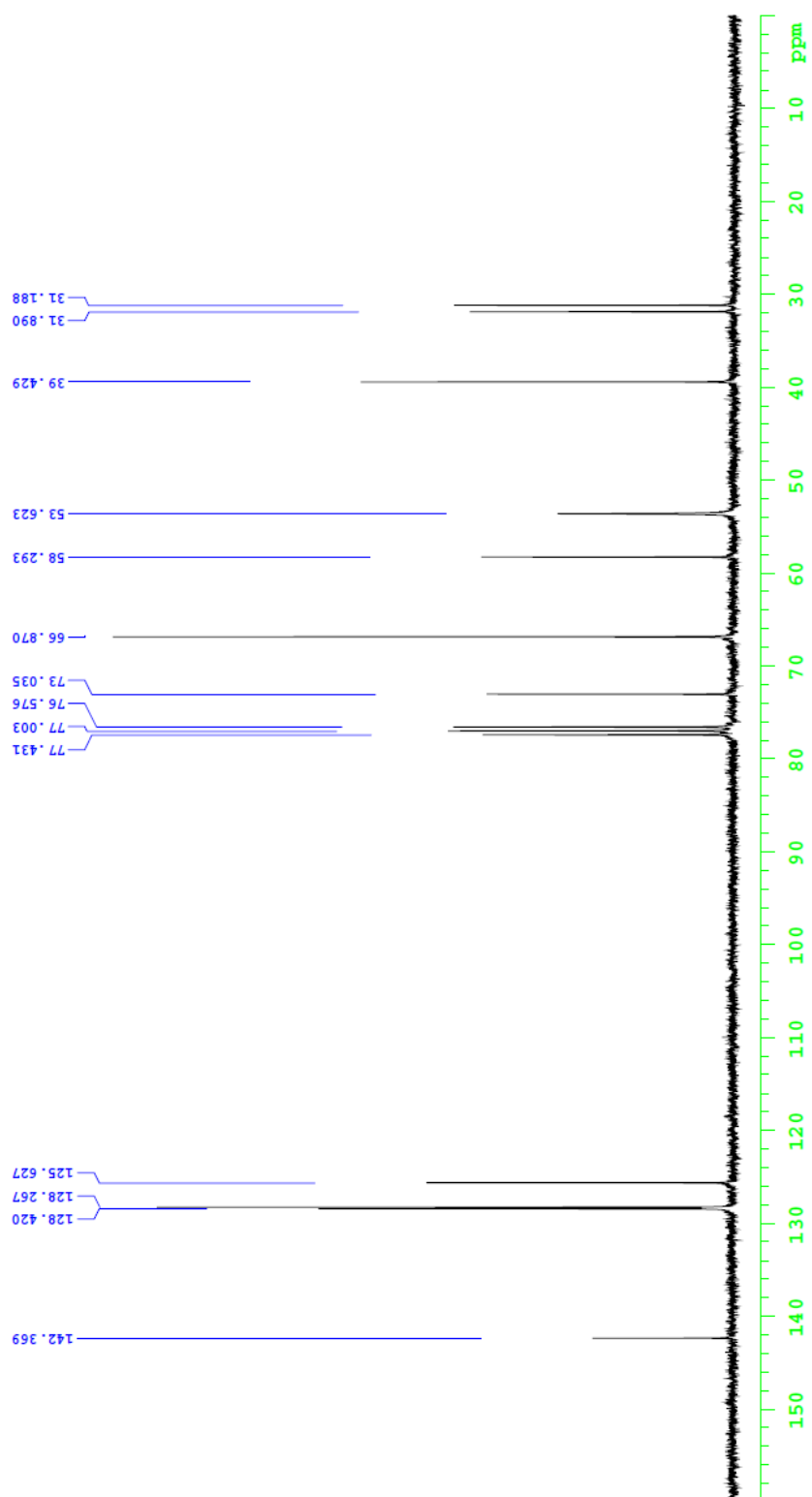


Fig S46. ¹³C NMR spectrum of 3ca

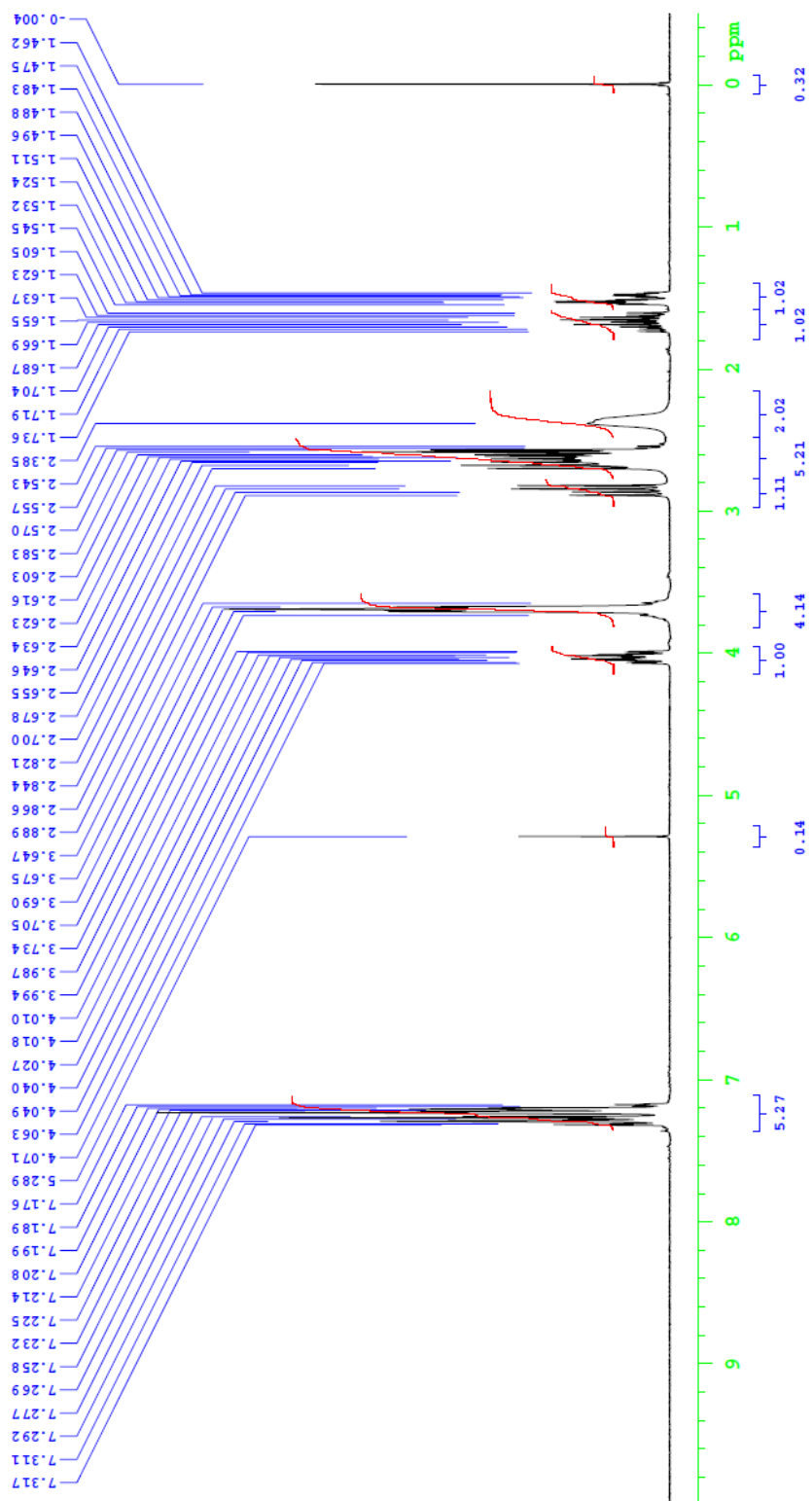


Fig S47. ^1H NMR spectrum of 3da

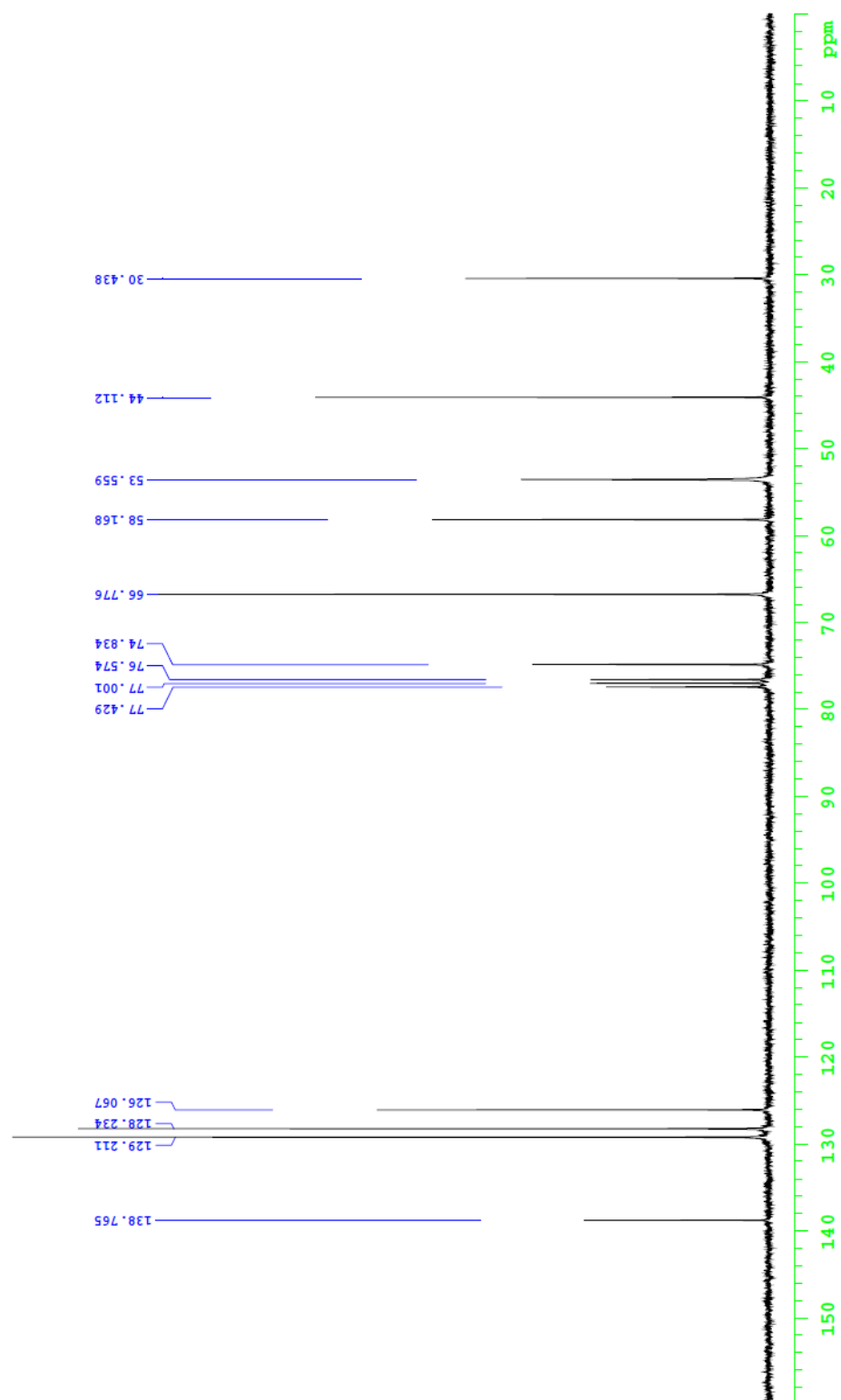


Fig S48. ^{13}C NMR spectrum of **3da**

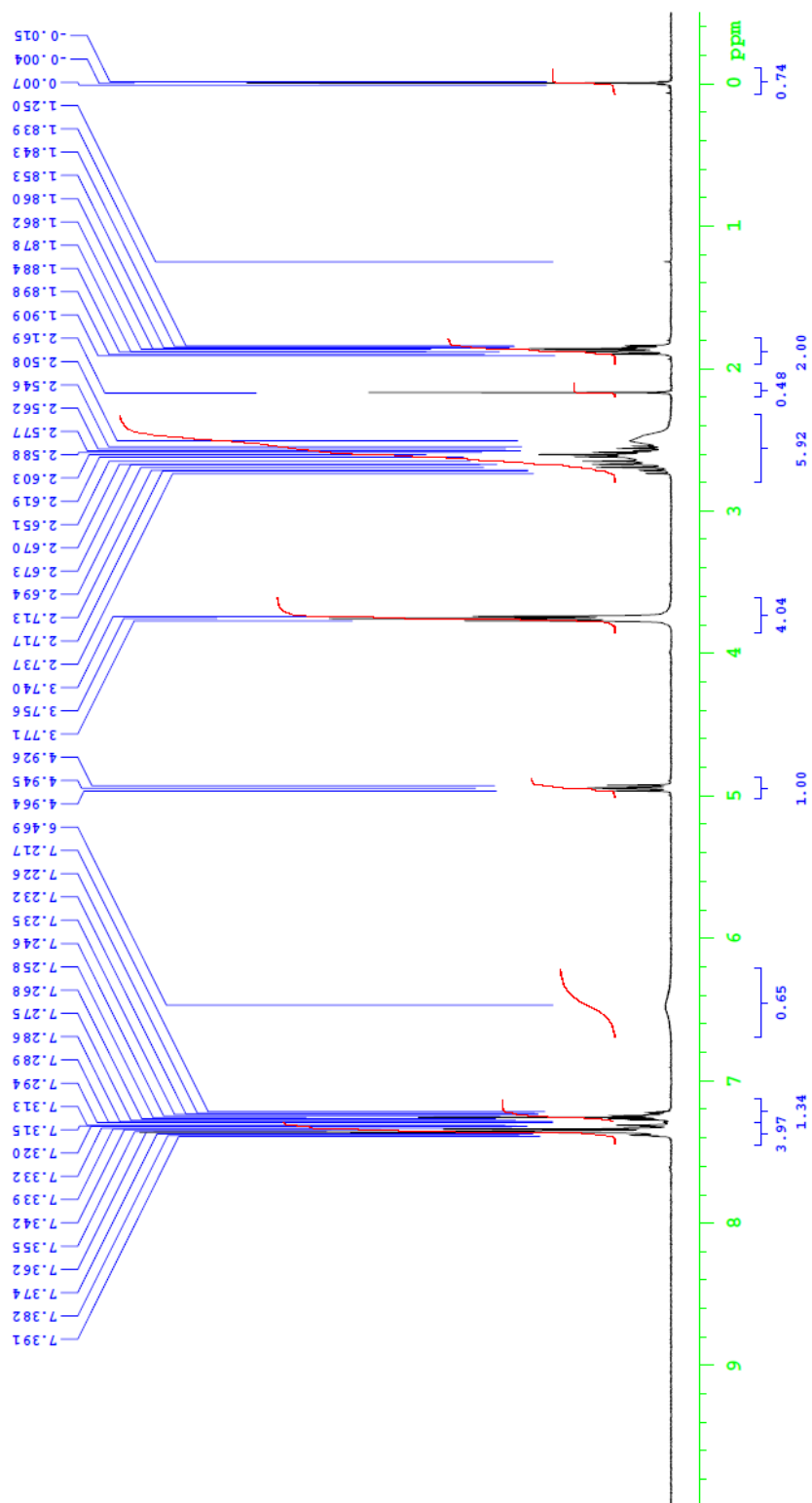


Fig S49. ^1H NMR spectrum of **3ea**

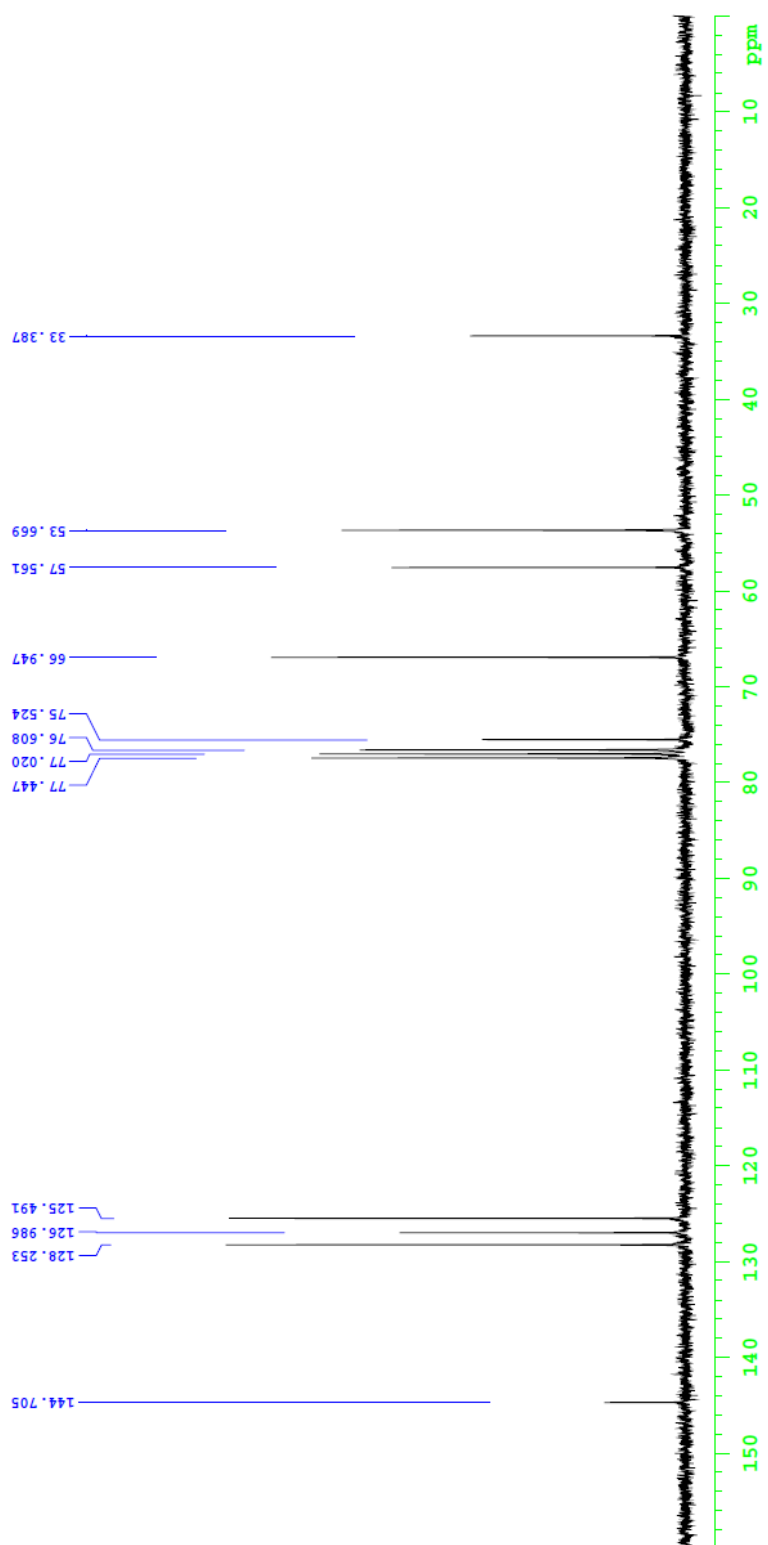


Fig S50. ¹³C NMR spectrum of 3ea

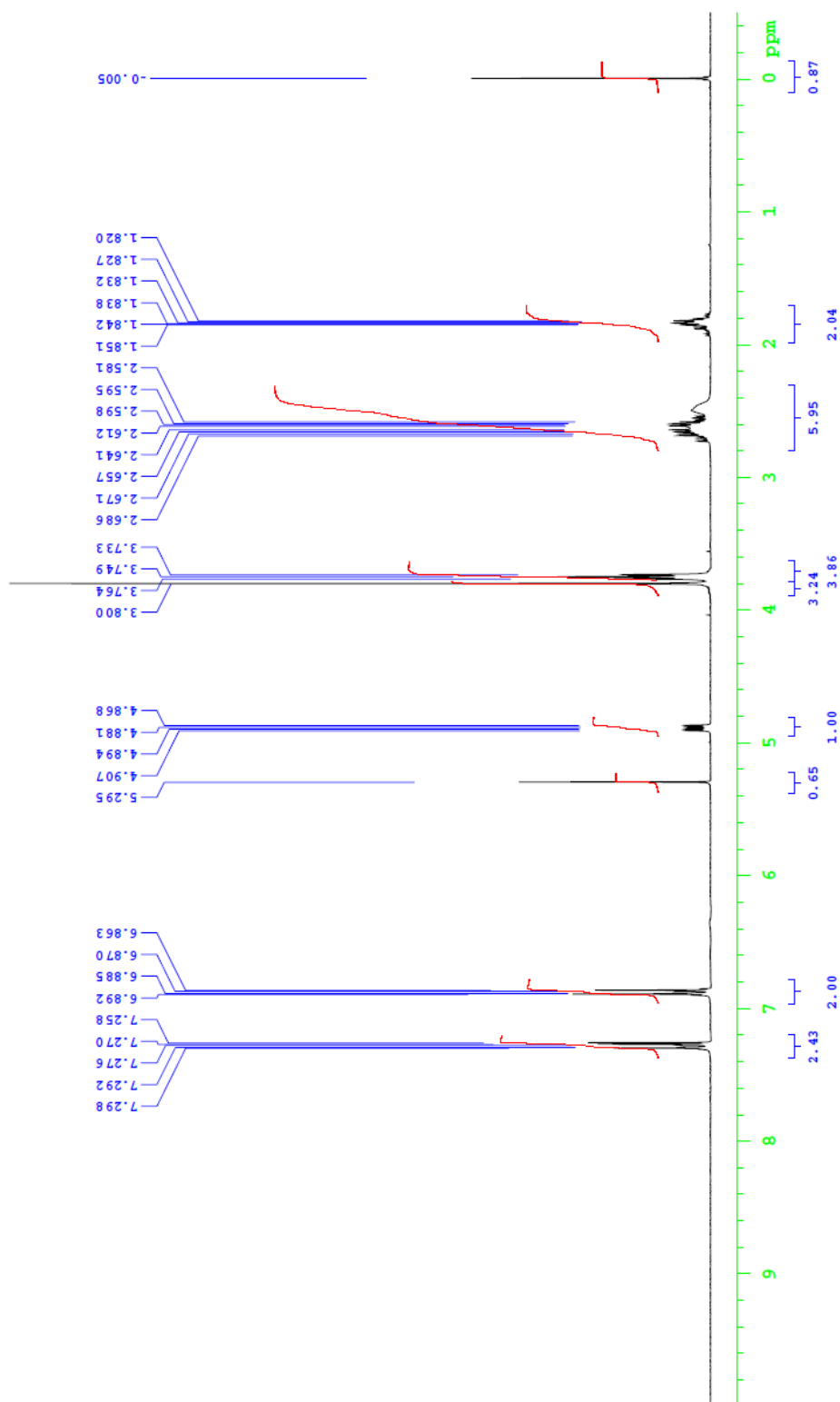


Fig S51. ^1H NMR spectrum of **3fa**

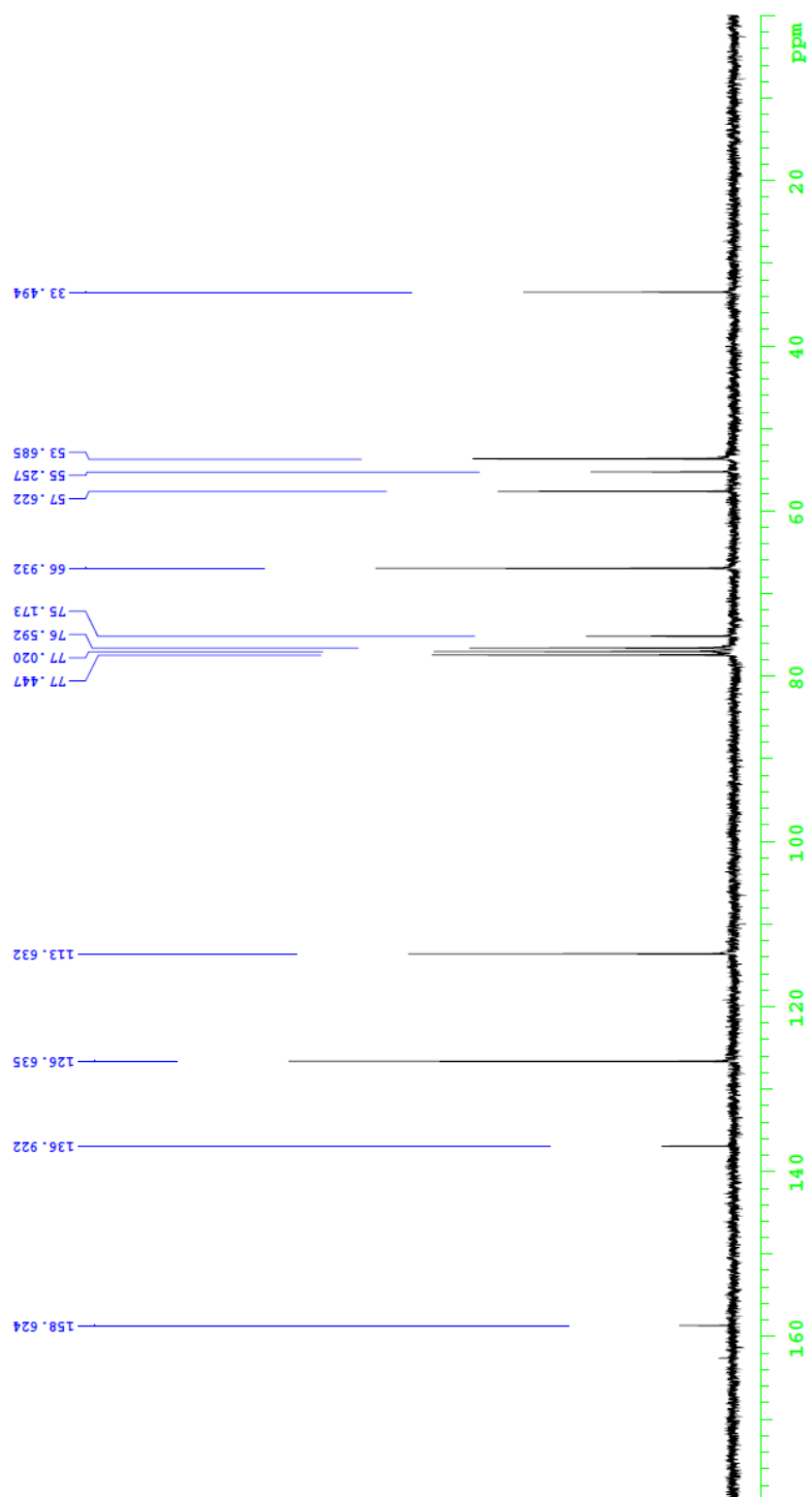


Fig S52. ^{13}C NMR spectrum of 3fa

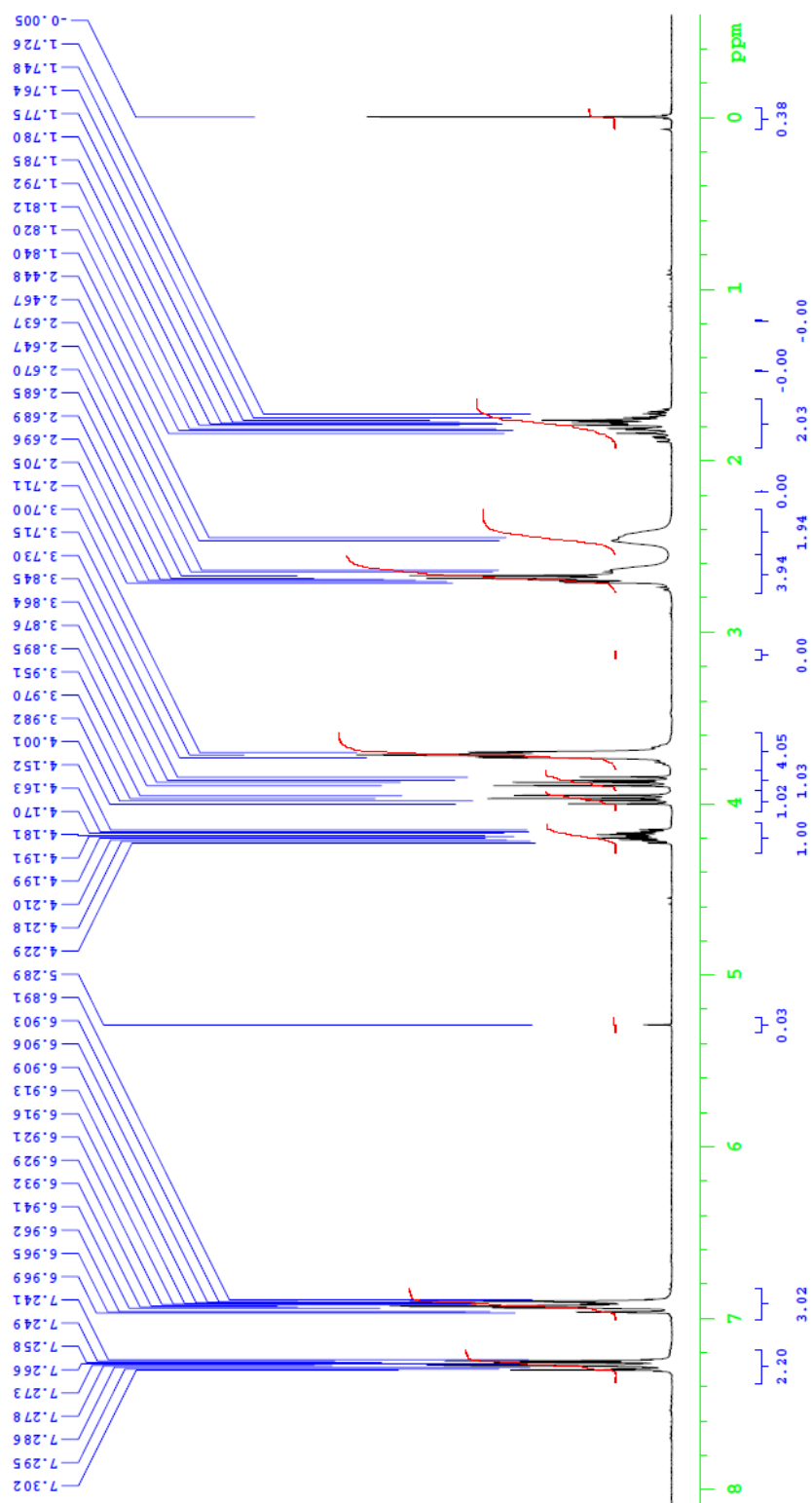


Fig S53. ¹H NMR spectrum of 3ga

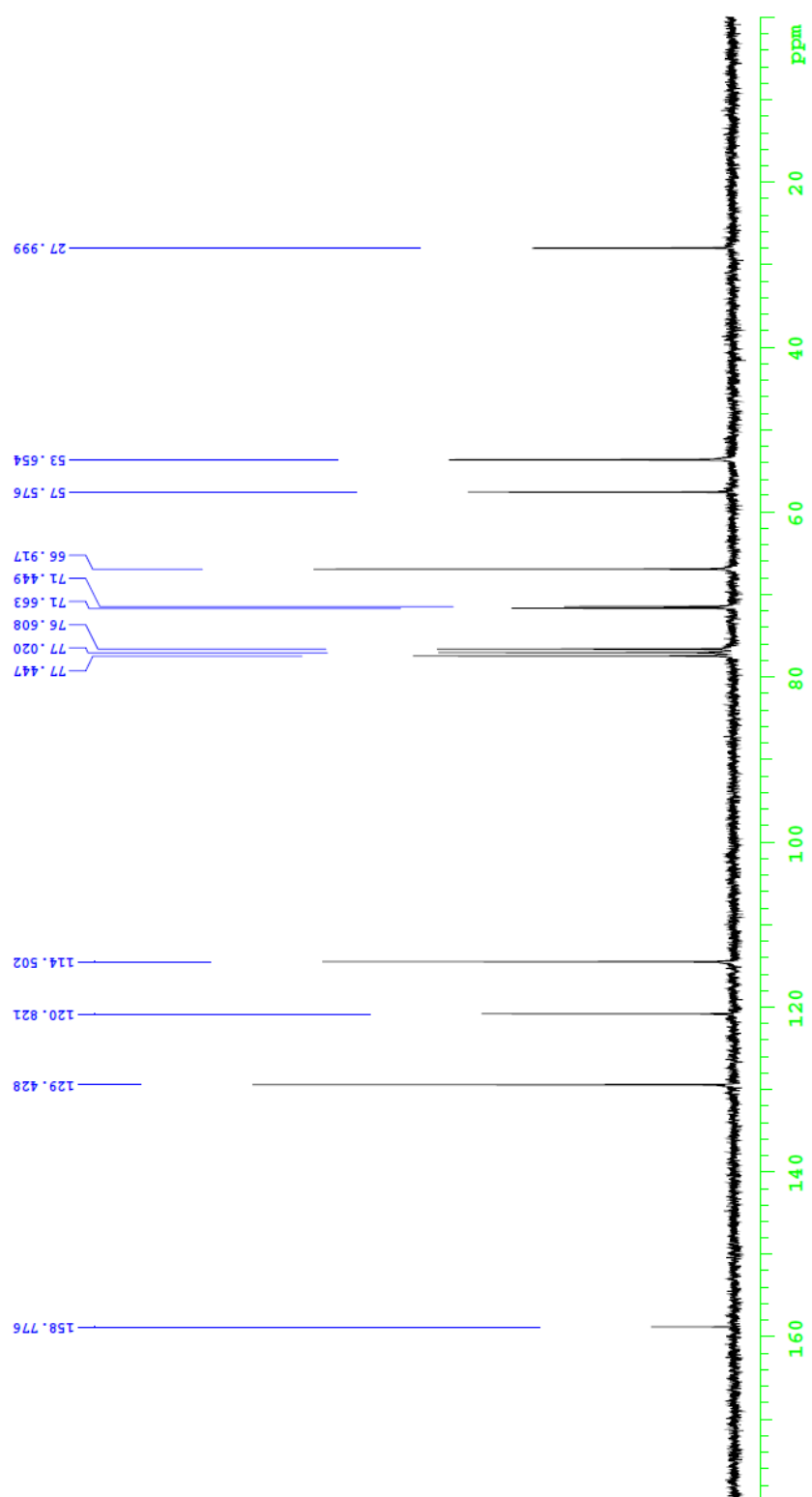


Fig S54. ^{13}C NMR spectrum of **3ga**

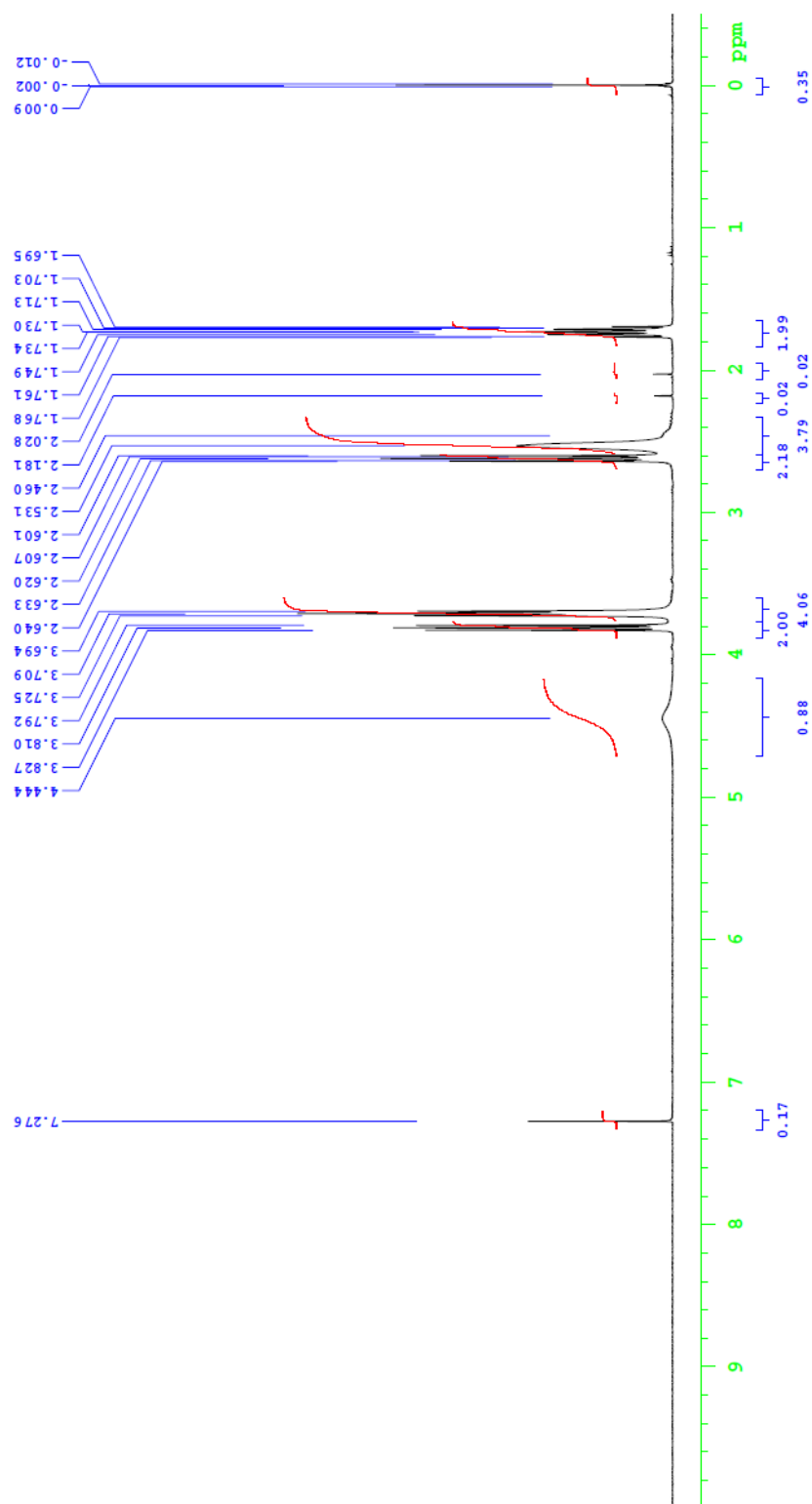


Fig S55. ^1H NMR spectrum of **3ha**

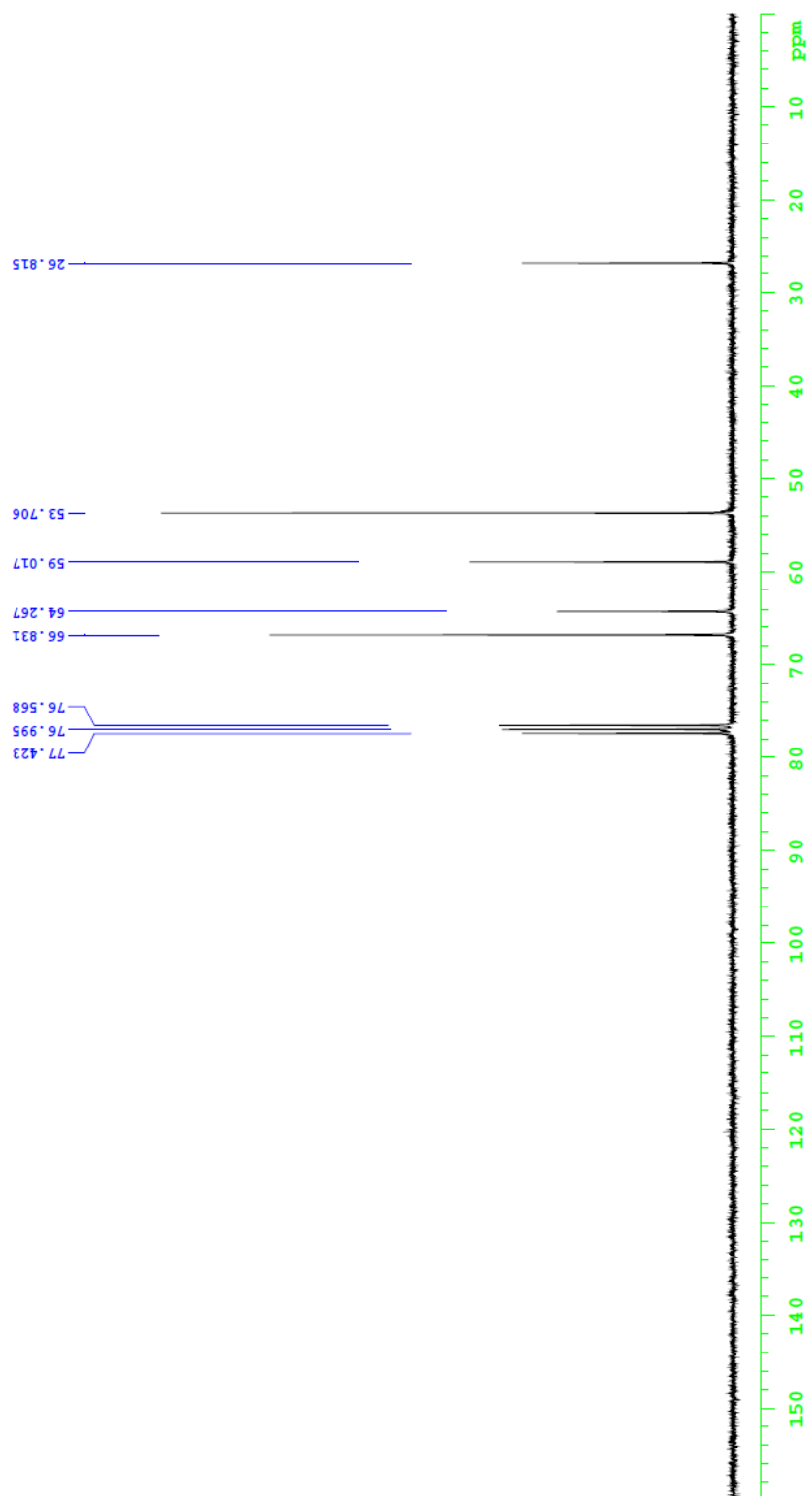


Fig S56. ^{13}C NMR spectrum of **3ha**

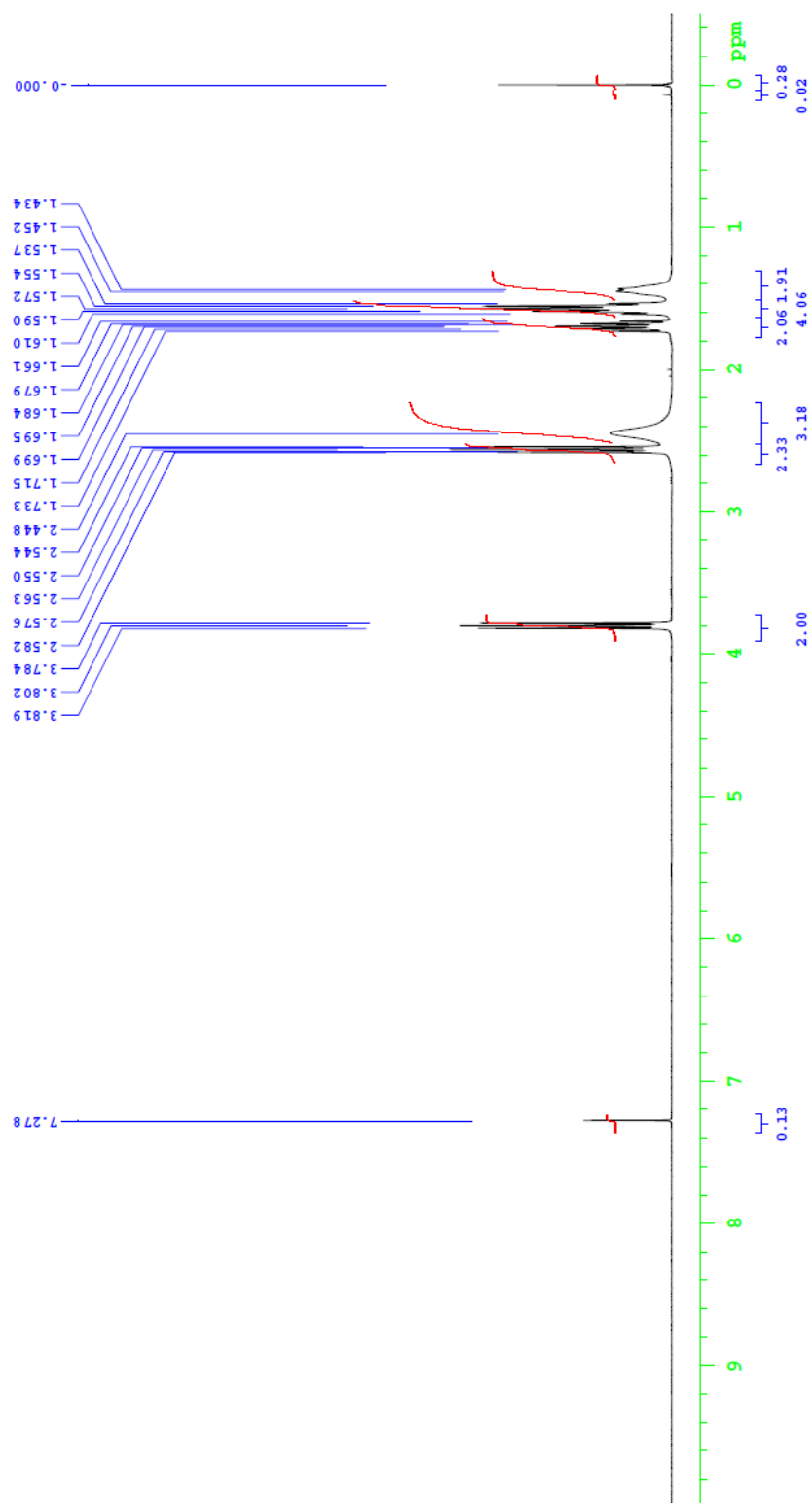


Fig S57. ^1H NMR spectrum of **3hb**

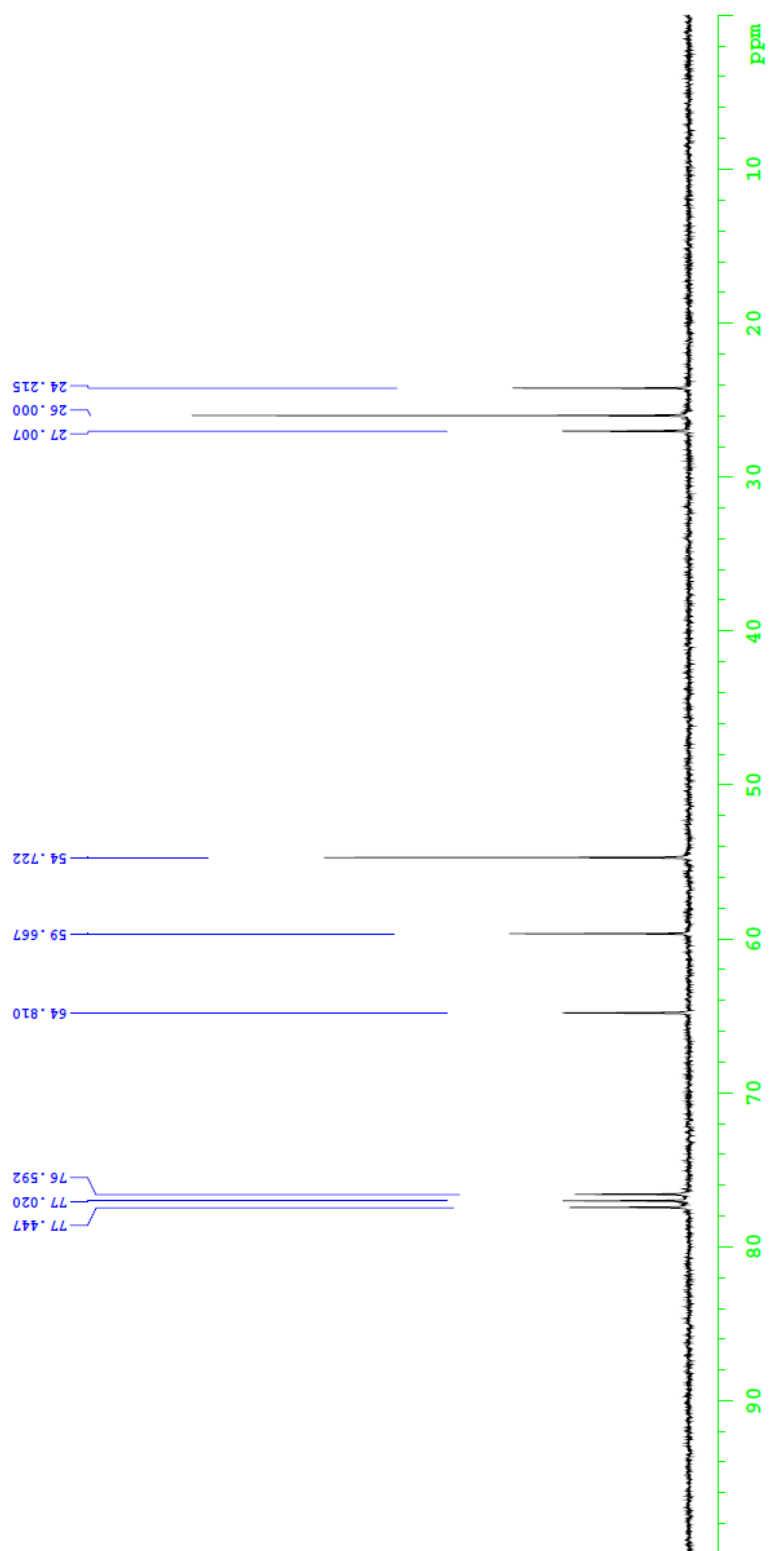


Fig S58. ¹³C NMR spectrum of **3hb**

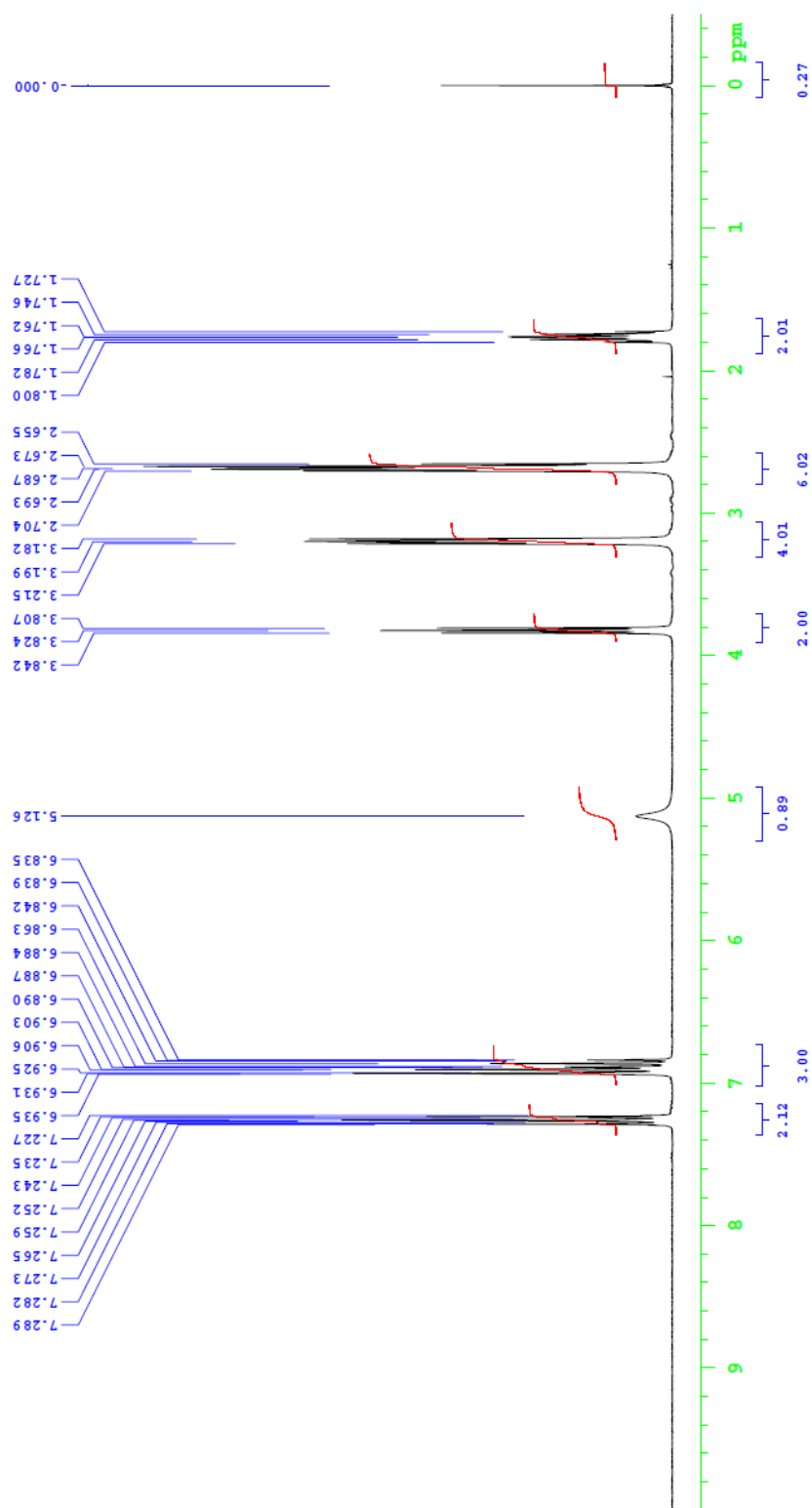


Fig S59. ¹H NMR spectrum of **3hc**

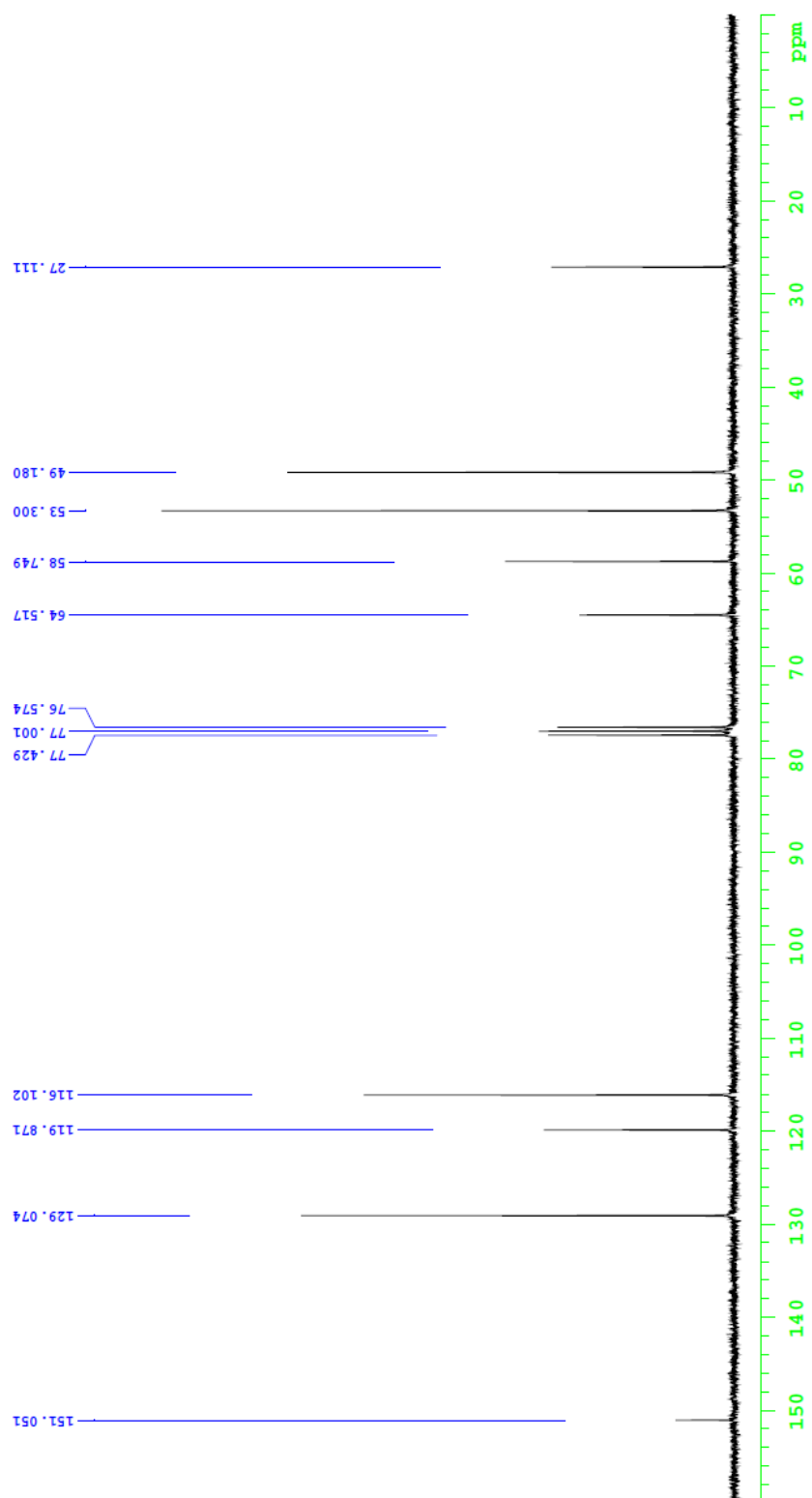


Fig S60. ^{13}C NMR spectrum of **3hc**

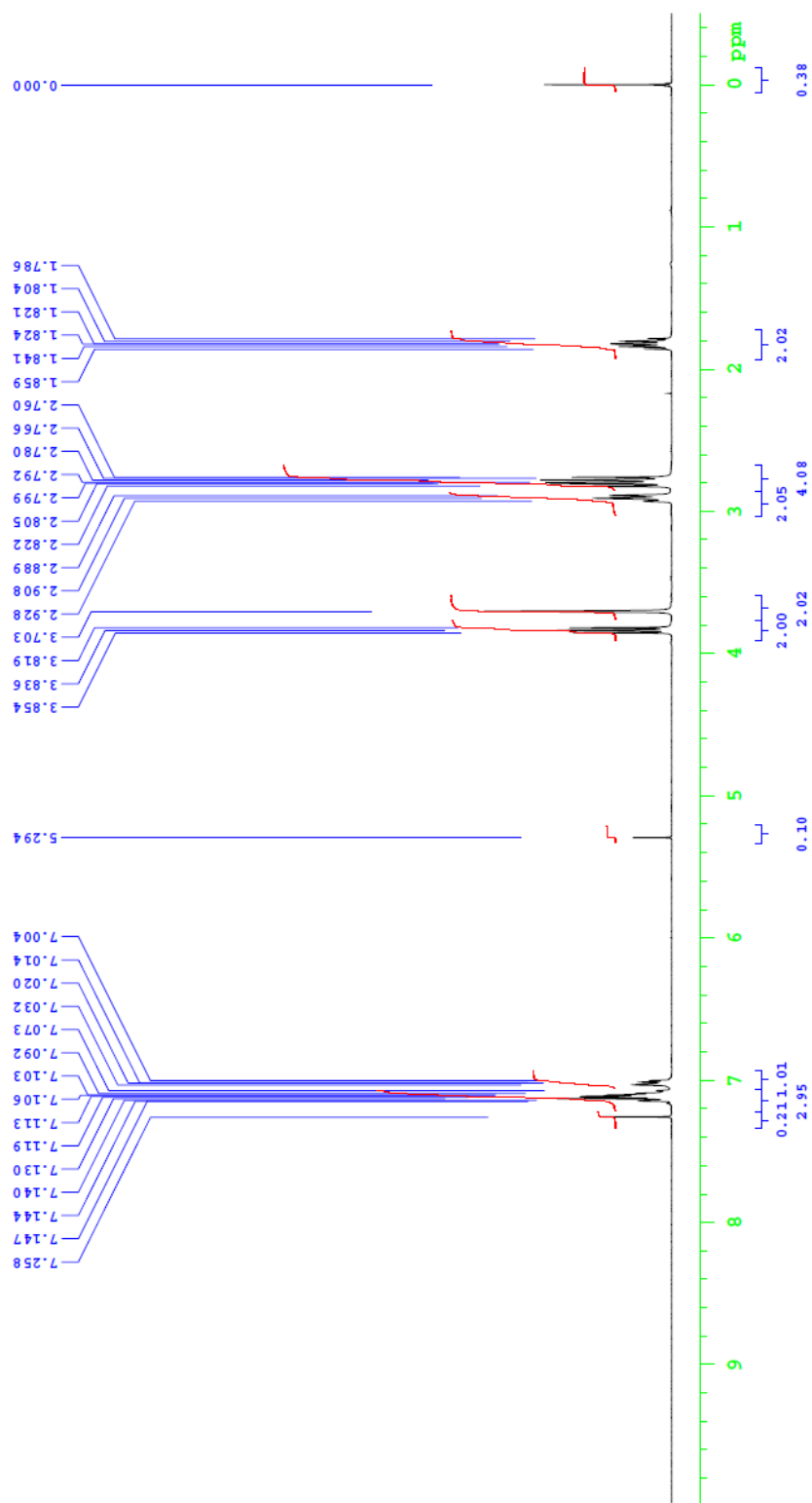


Fig S61. ^1H NMR spectrum of **3hd**

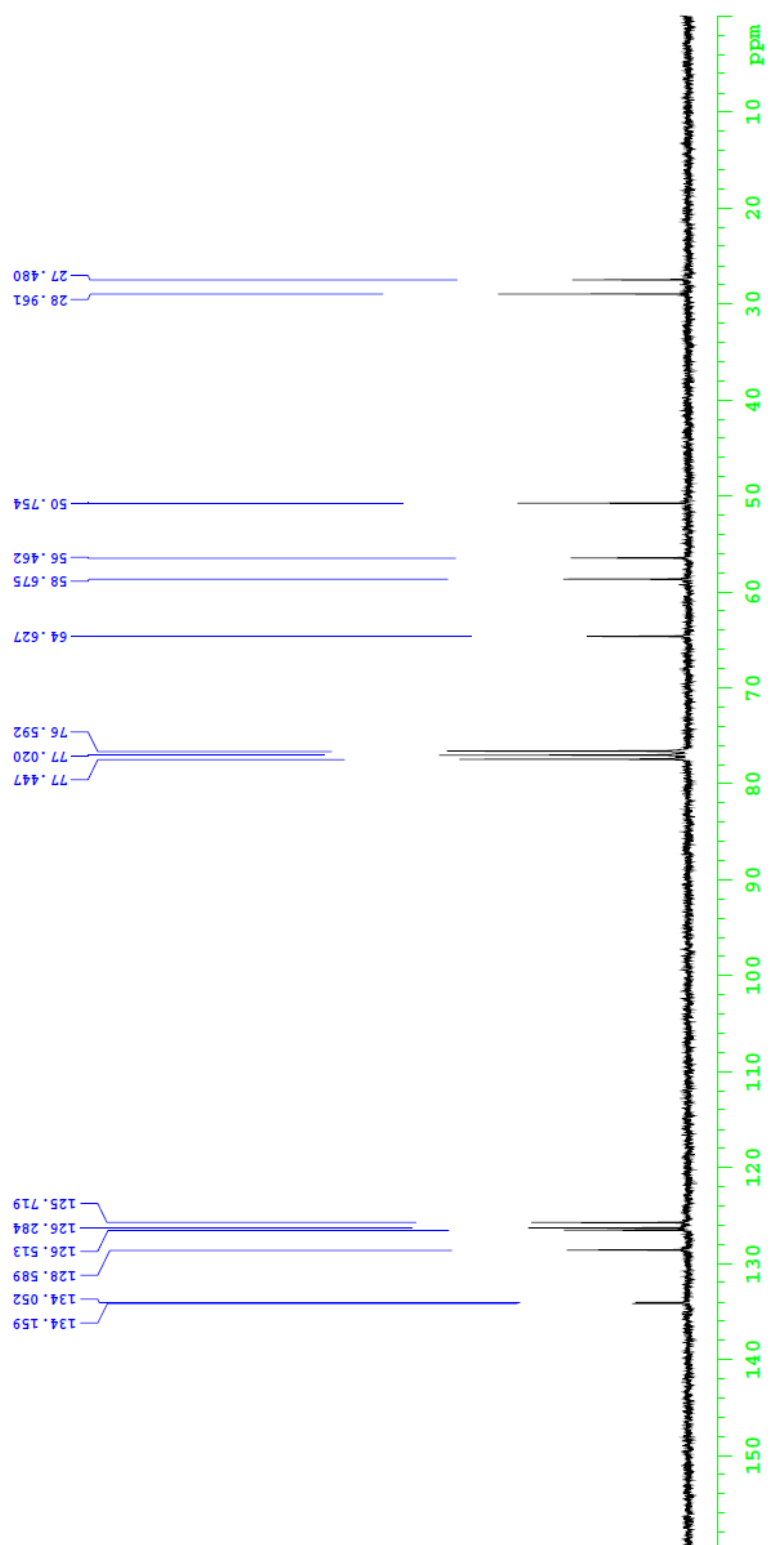


Fig S62. ^{13}C NMR spectrum of **3hd**

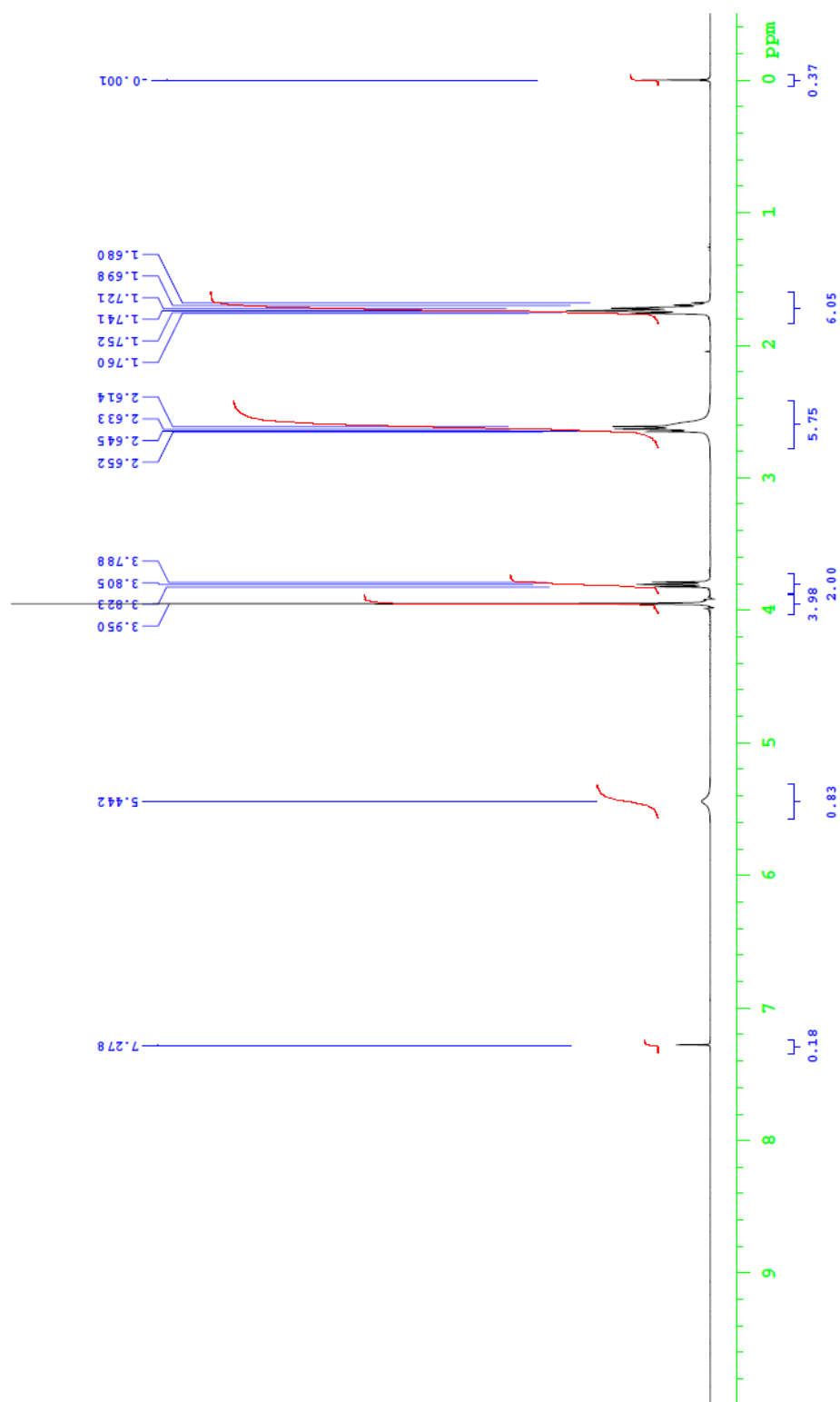


Fig S63. ¹H NMR spectrum of **3he**

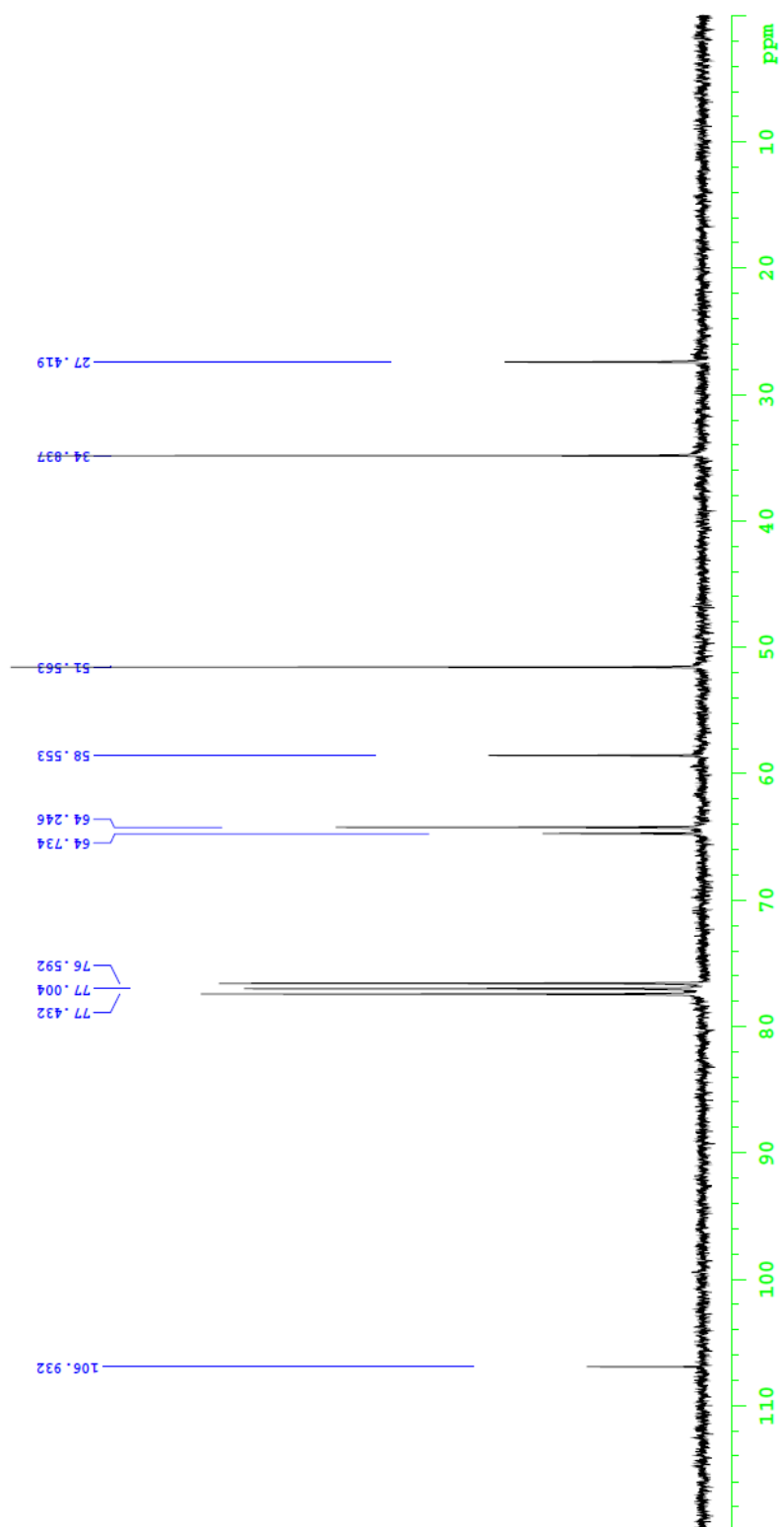


Fig S64. ^{13}C NMR spectrum of **3he**

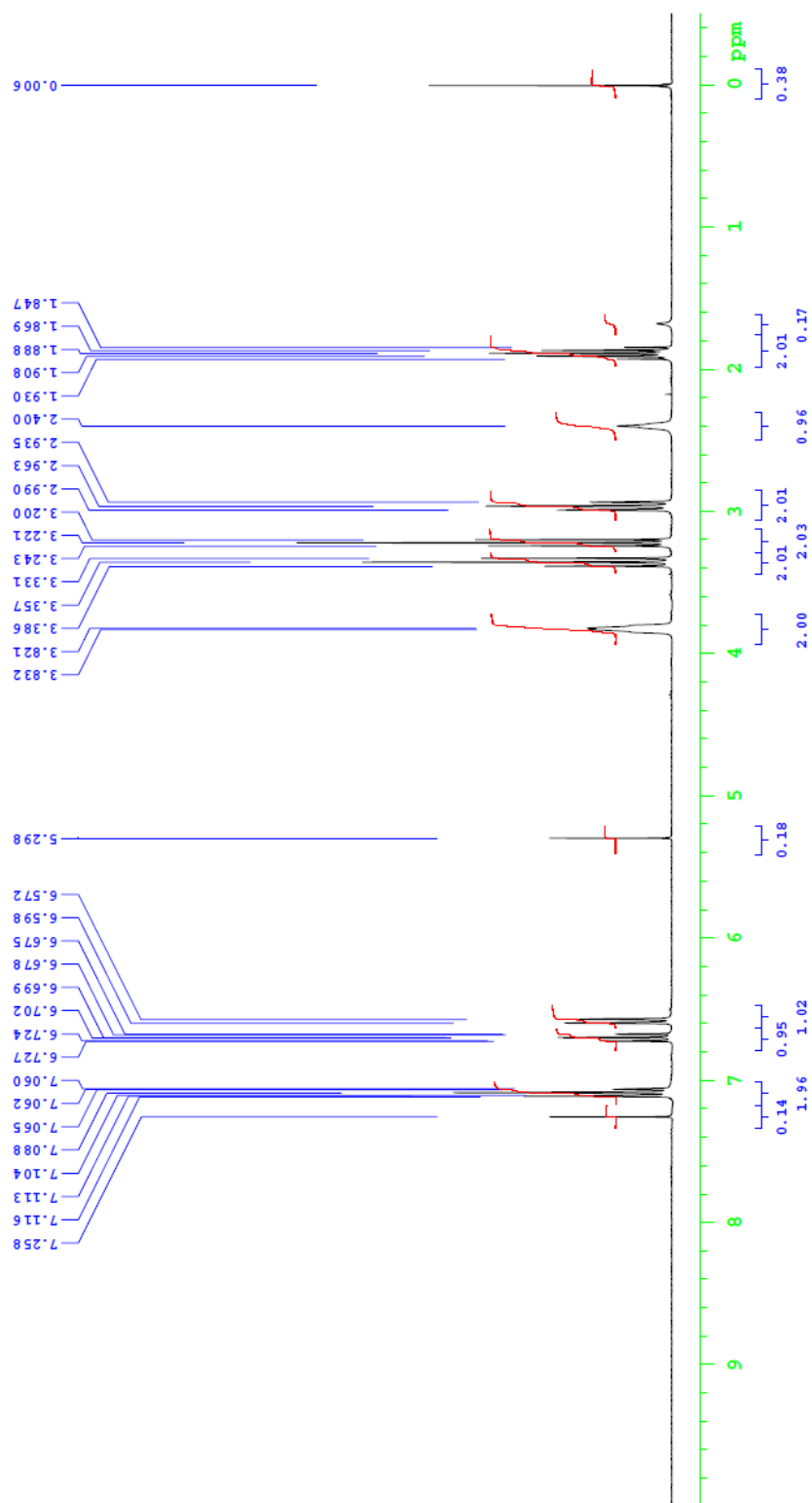


Fig S65. ¹H NMR spectrum of **3hf**

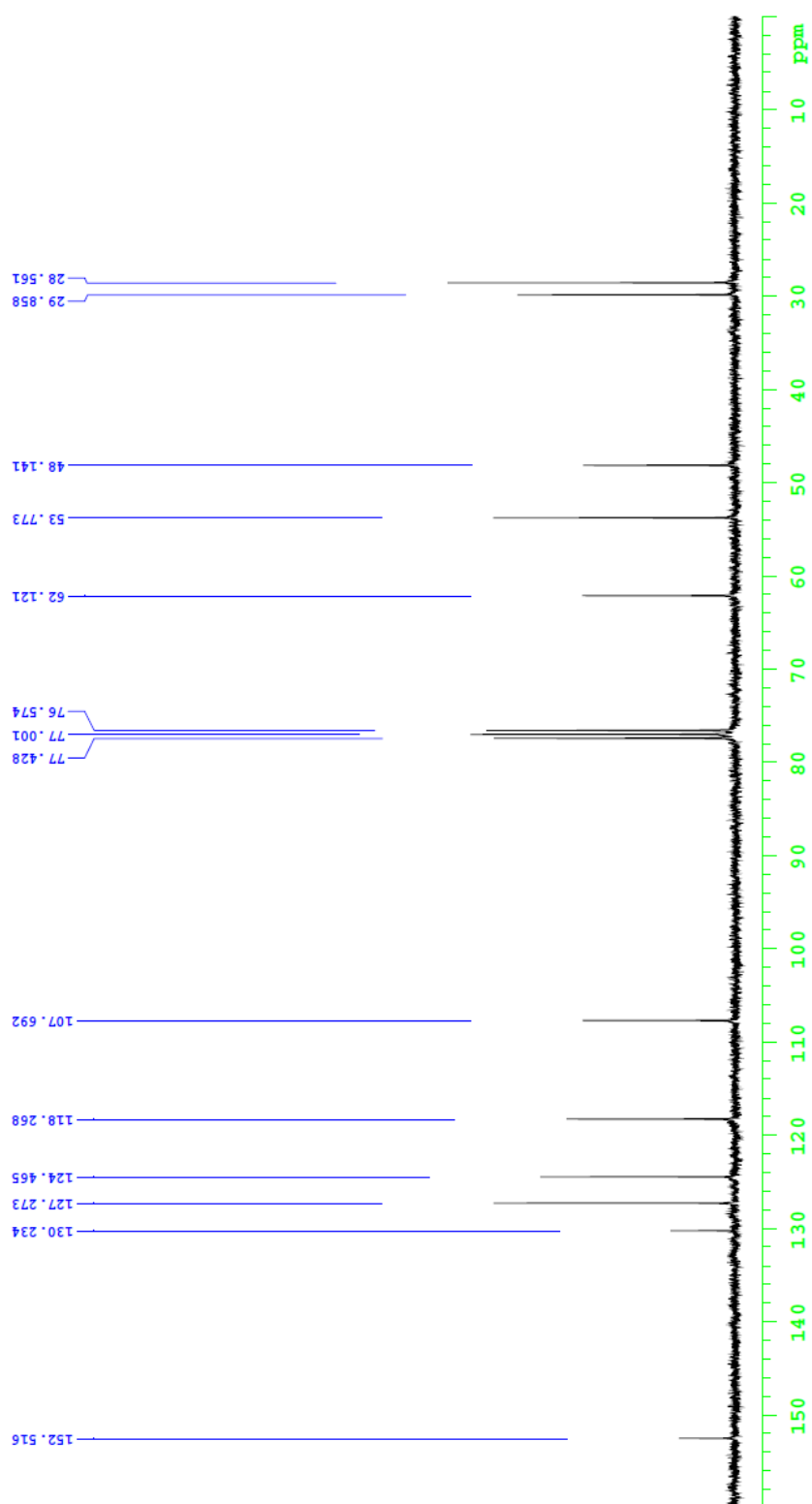


Fig S66. ¹³C NMR spectrum of **3hf**

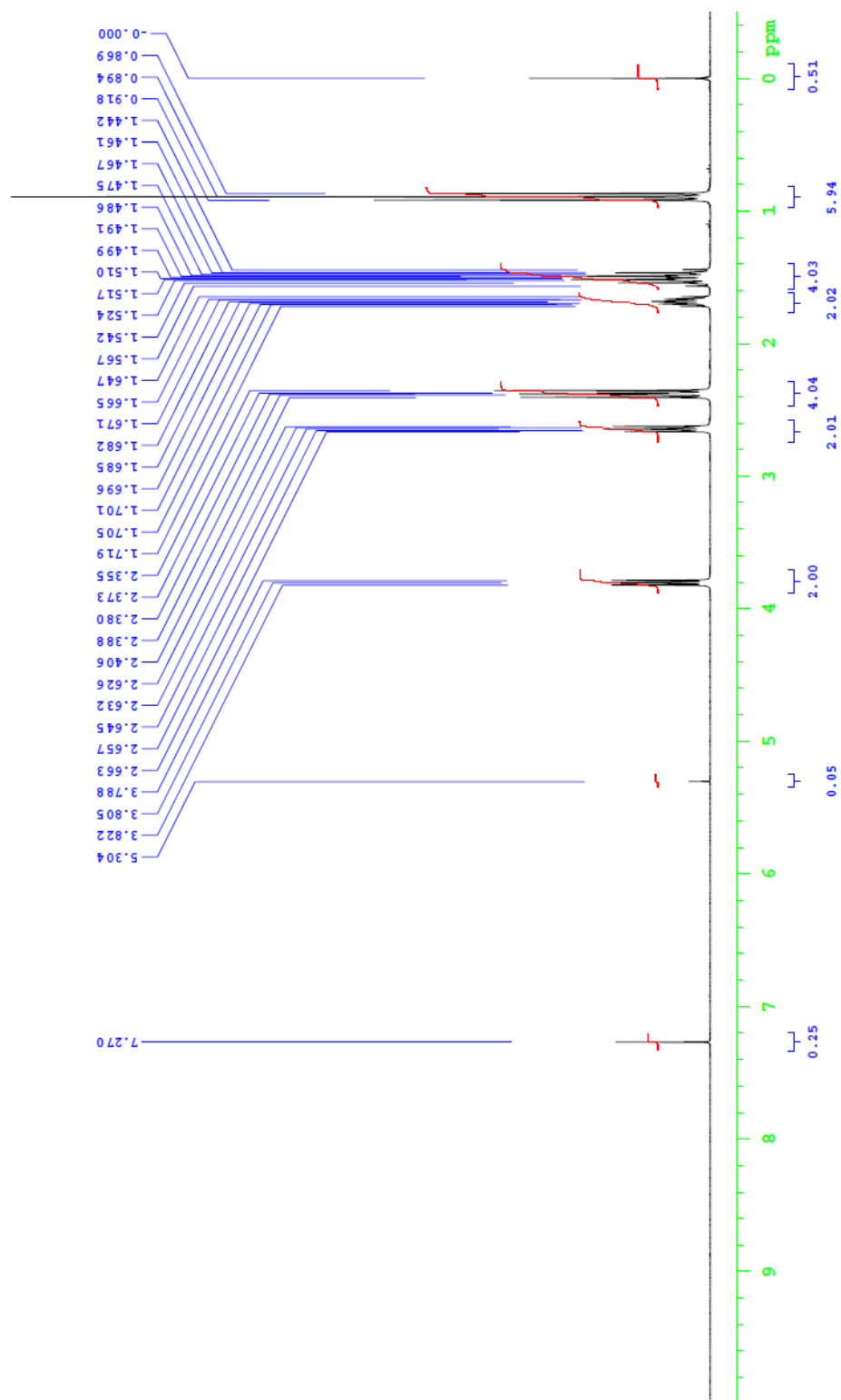


Fig S67. ^1H NMR spectrum of **3hi**

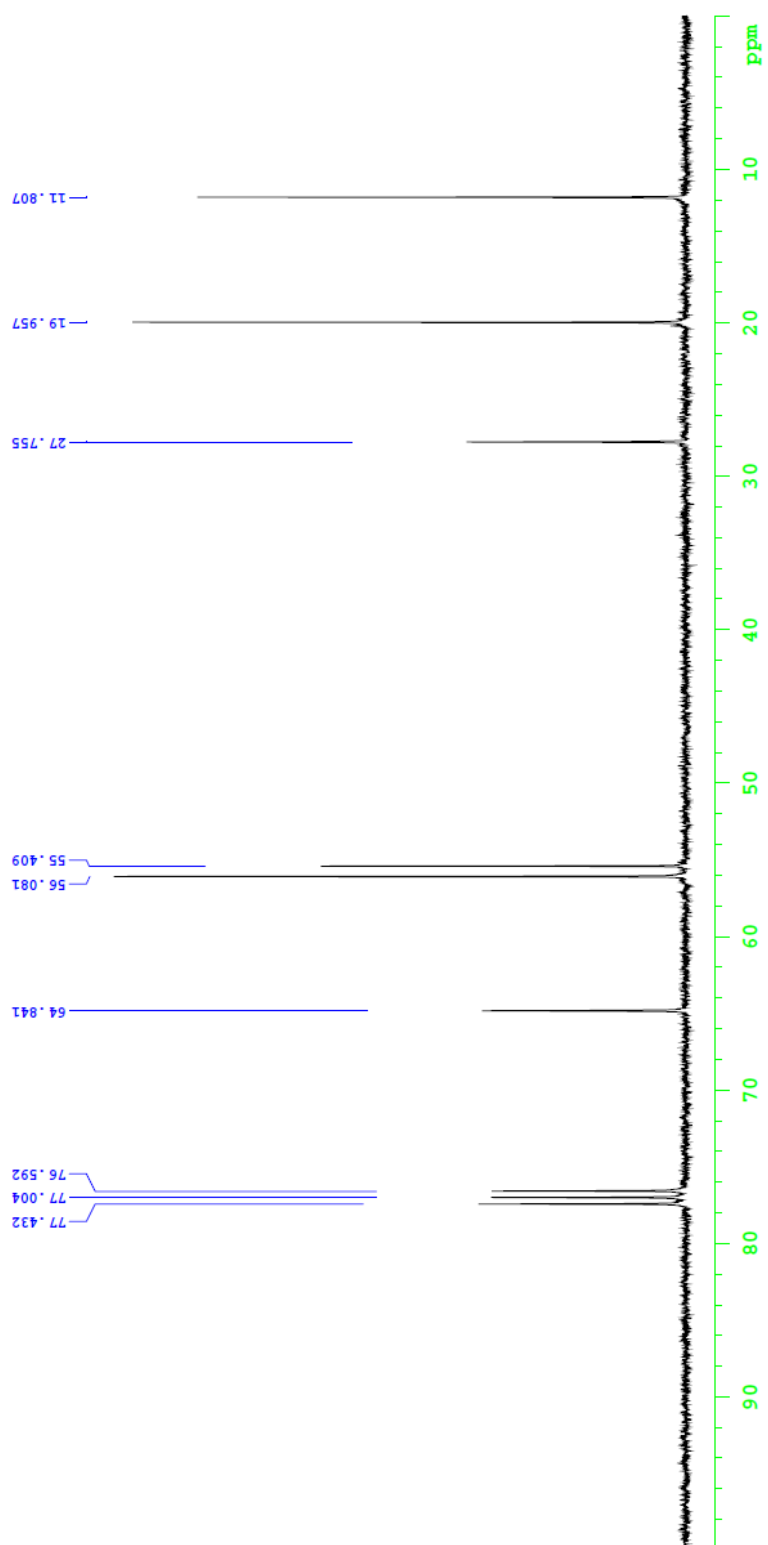


Fig S68. ¹³C NMR spectrum of **3hi**

8. References

- 1) Nihonkagakukai ed., Jikken Kagaku-Kouza [Course of Experimental Chemistry] (in Japanese), vol. 18, 4th Edition, Maruzen, Kyoto (**1991**).
- 2) P. D. de Koning, M. Jackson, I. C. Lennon, *Org. Process. Res. Dev.*, **2006**, *10*, 1054-1058.
- 3) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya, R. Noyori, *Angew. Chem., Int. Ed.* **1998**, *37*, 1703-1707.
- 4) R. García-Alvarez, J. Diez, P. Crochet, V. Cadierno, *Organometallics*, **2010**, *29*, 3955-3965.
- 5) S. J. Coote, G. J. Dawson, C. G. Frost, J. M. J. Williams, *Synlett*, **1993**, *7*, 509-510.
- 6) A. Habtemariam, B. Watchman, B. S. Potter, R. Palmer, S. Parsons, A. Parkin, P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, **2001**, 1306-1318.
- 7) K. Hayashi, H. Tanimoto, H. Zhang, T. Morimoto, Y. Nishiyama, K. Kakiuchi, *Org. Lett.*, **2012**, *14*, 5728-5731.
- 8) Y. Lu, G. Zou, G. Zhao, *ACS Catal.*, **2013**, *3*, 1356-1359.
- 9) H. Lin, Y. Liu, Z. Wu, *Chem. Commun.*, **2011**, *47*, 2610-2612.
- 10) H. Le, R. E. Kyne, L. A. Brozek, J. P. Morken, *Org. Lett.*, **2013**, *15*, 1432-1435.
- 11) Y. Hon, Y. Wong, K. Wu, *J. Chin. Chem. Soc.*, **2008**, *55*, 896-914.
- 12) V. Saggiomo, U. Lüning, *Eur. J. Org. Chem.*, **2008**, 4329-4333.
- 13) S. Ueno, K. Usui, R. Kuwano, *Synlett*, **2011**, *9*, 1303-1307.
- 14) C. L. Sann, J. Huddleston, J. Mann, *Tetrahedron*, **2007**, *63*, 12903-12911.
- 15) M. Ferles, A. Šilhánková, S. Kafka, P. Taufmann, T. Motáček, *Collect. Czech. Chem. Commun.*, **1983**, *48*, 1759-1764.