

Electronic Supporting Information

Access to 3-*O*-functionalized *N*-acetylneuraminic acid scaffolds

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Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3-bromo-3,5-dideoxy-β-D-erythro-L-manno-non-2-ulopyranosonate (3)

Table S1. Optimization of reaction conditions for hydrolysis of the C2 bromide of **4** to form *trans*-2,3-diaxial bromohydrin **3**.

Entry	Promoter/Scavenger	4 (mmol)	Solvent	Temperature	Time (h)	3 (Yield %) ^b
1	Ag ₂ CO ₃ (3 equiv.) ^{S1}	0.16	Acetone	rt	16	NR ^c
2	Ag ₂ CO ₃ (3 equiv.) ^{S1}	0.16	CH ₃ CN	rt	16	NR ^c
3	Ag ₂ O (1.5 equiv.) ^{S2}	0.16	DMSO	rt	16	NR ^c
4	NaI (0.3 equiv.) ^{S3}	0.16	CH ₃ CN	rt	2	— ^d
5	NaI (0.3 equiv.) ^{S3}	0.16	Acetone	rt	16	— ^e
6	AgOTf (1.4 equiv.) Na ₂ HPO ₄ (3.9 equiv.) ^{S4}	0.16	Toluene	0°C-rt	1	81
7	AgOTf (1.4 equiv.) Na ₂ HPO ₄ (3.9 equiv.)	0.79	Toluene- CH ₂ Cl ₂	0°C-rt	1	87
8	AgOTf (1.4 equiv.) Na ₂ HPO ₄ (3.9 equiv.)	8.07	Toluene- CH ₂ Cl ₂	0°C-rt	2	87
9	Ag ₂ CO ₃ (1.5 equiv.) Na ₂ HPO ₄ (3.9 equiv.)	0.16	Toluene- CH ₂ Cl ₂	0°C-rt	3	NR ^c
10	AgClO ₄ (4 equiv.) Ag ₂ CO ₃ (1.5 equiv.) ^{S5}	1.74	CH ₂ Cl ₂	0°C-rt	0.5	91
11	AgClO ₄ (1.5 equiv.) Ag ₂ CO ₃ (1.5 equiv.) ^{S5}	1.74	CH ₂ Cl ₂	0°C-rt	0.5	94
12	AgClO ₄ (4 equiv.)	0.79	CH ₂ Cl ₂	0°C-rt	3	40 ^f

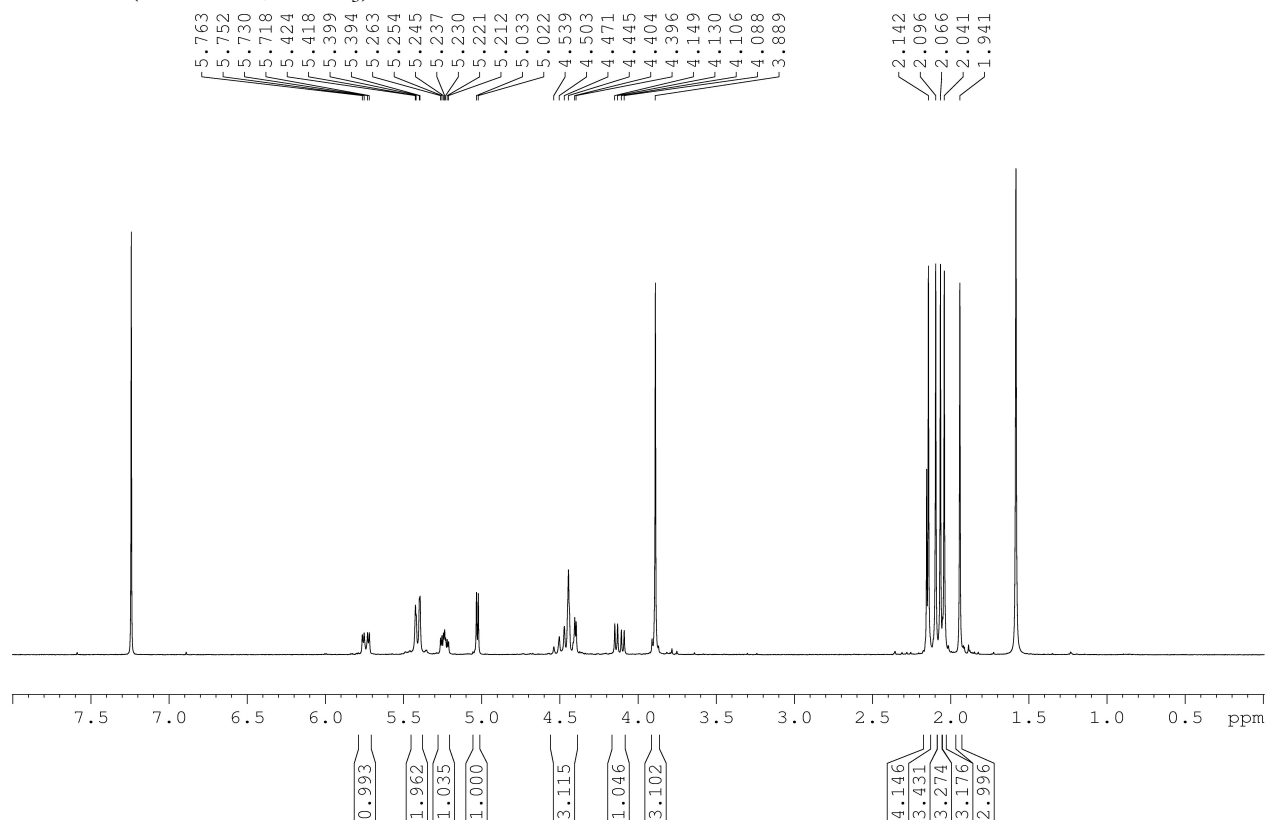
^aAll reactions were performed using H₂O (1.2 equiv.) as glycosyl acceptor. ^b Isolated yield. ^c NR = no reaction.

^d 82% **1** isolated as by-product. ^e 36% **1** isolated as by-product along with 61% starting material. ^f 43% starting material recovered.

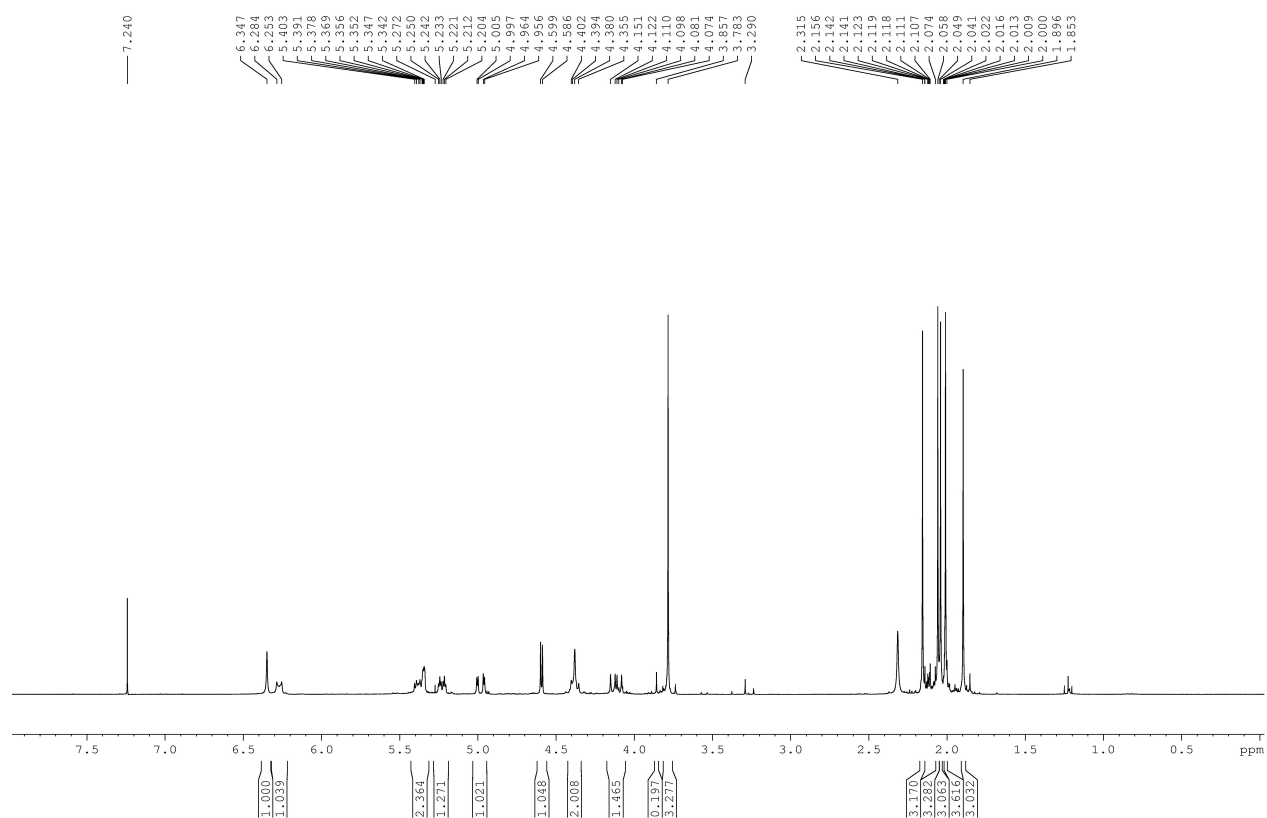
References

- S1)** Zhang, Z.; Yu, B.; *J. Org. Chem.* **2003**, 68, 6309.
- S2)** Somsák, L.; Kovács, L.; Tóth, M.; Ösz, E.; Szilágyi, L.; Györgydeák, Z.; Dinya, Z.; Docsa, T.; Tóth, B.; Gergely, P. *J. Med. Chem.* **2001**, 44, 2843.
- S3)** Mühlhausen, U.; Schirmmacher, R.; Piel, M.; Lecher, B.; Briegert, M.; Piee-Staffa, A.; Kaina, B.; Rösch, F. *J. Med. Chem.* **2006**, 49, 263.
- S4)** Okamoto, K.; Kondo, T.; Goto, T. *Chem. Lett.* **1986**, 1449.
- S5)** See for example: (a) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 155. (b) Banoub, J.; Boullanger, P.; Lafont, D. *J. Chem. Rev.* **1992**, 92, 1167.

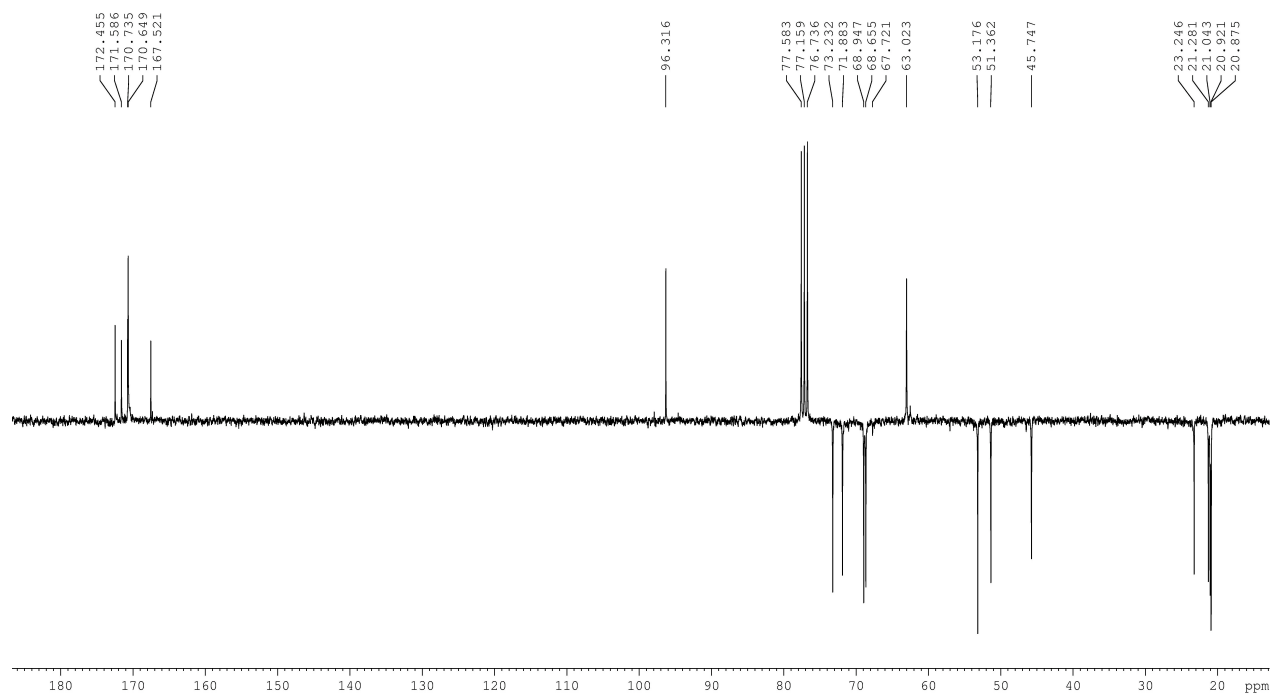
¹H NMR (300 MHz, CDCl₃) of **4**



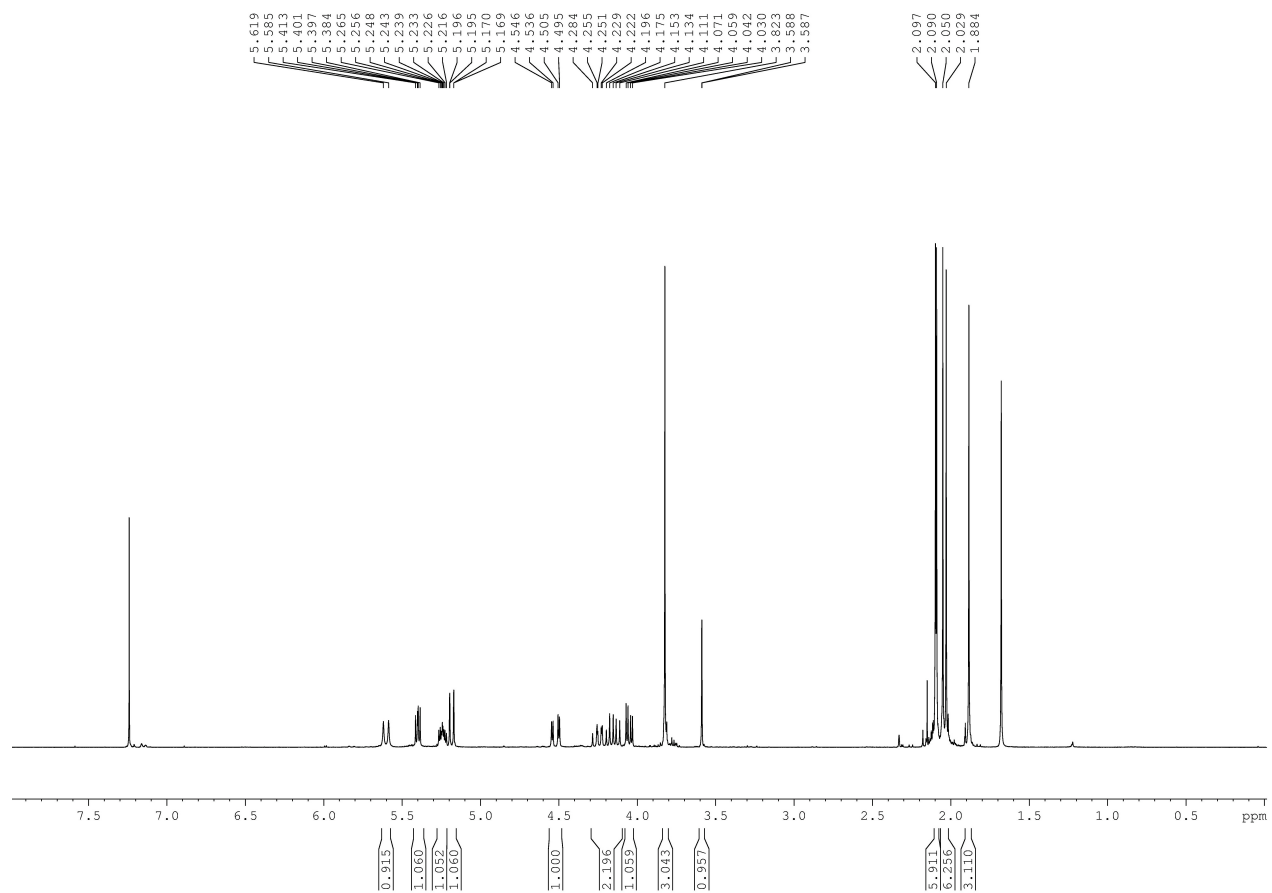
¹H NMR (300 MHz, CDCl₃) of **3**



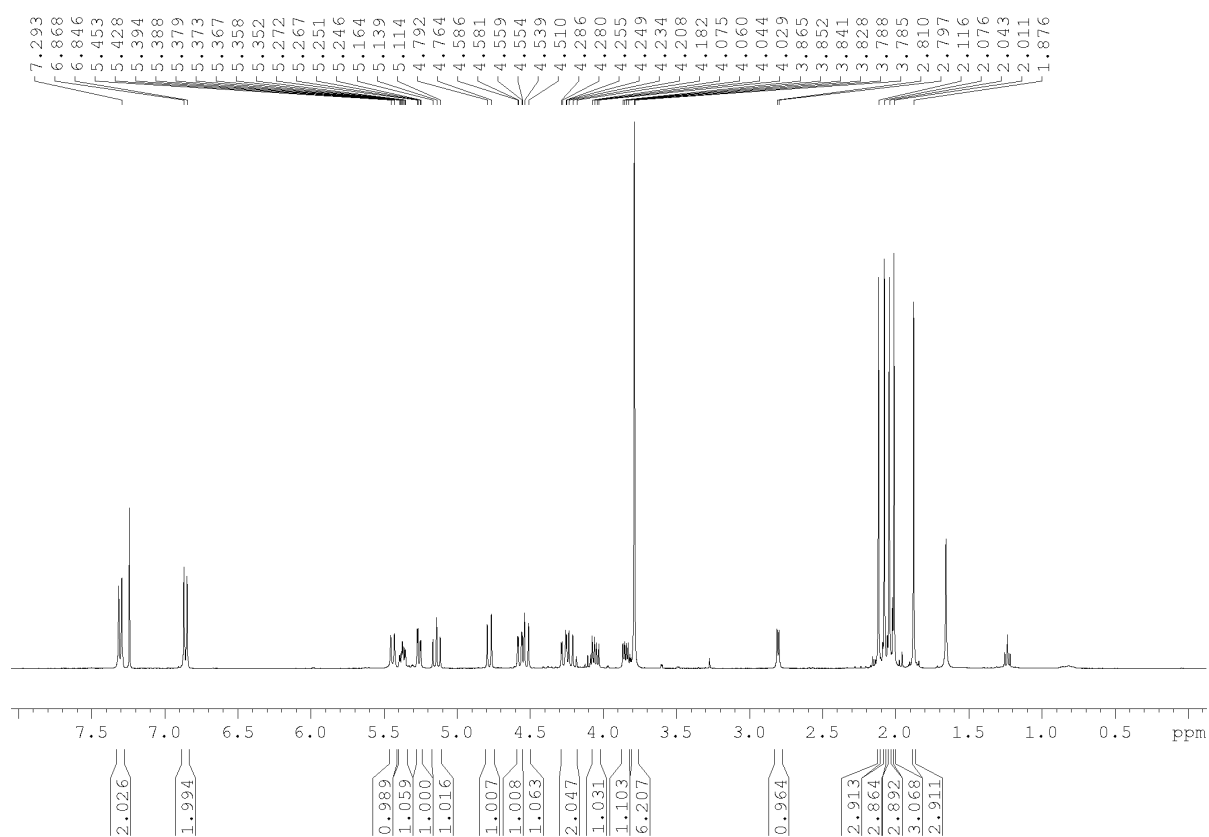
^{13}C NMR (75.5 MHz, CDCl_3) of **3**



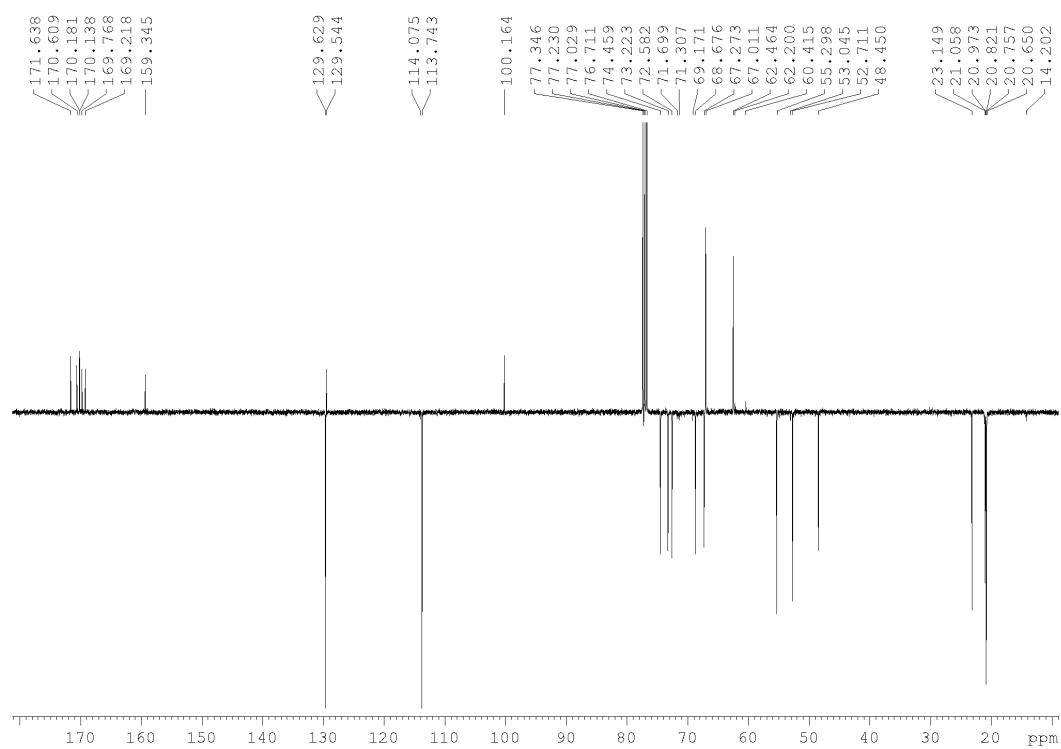
^1H NMR (300 MHz, CDCl_3) of **5**



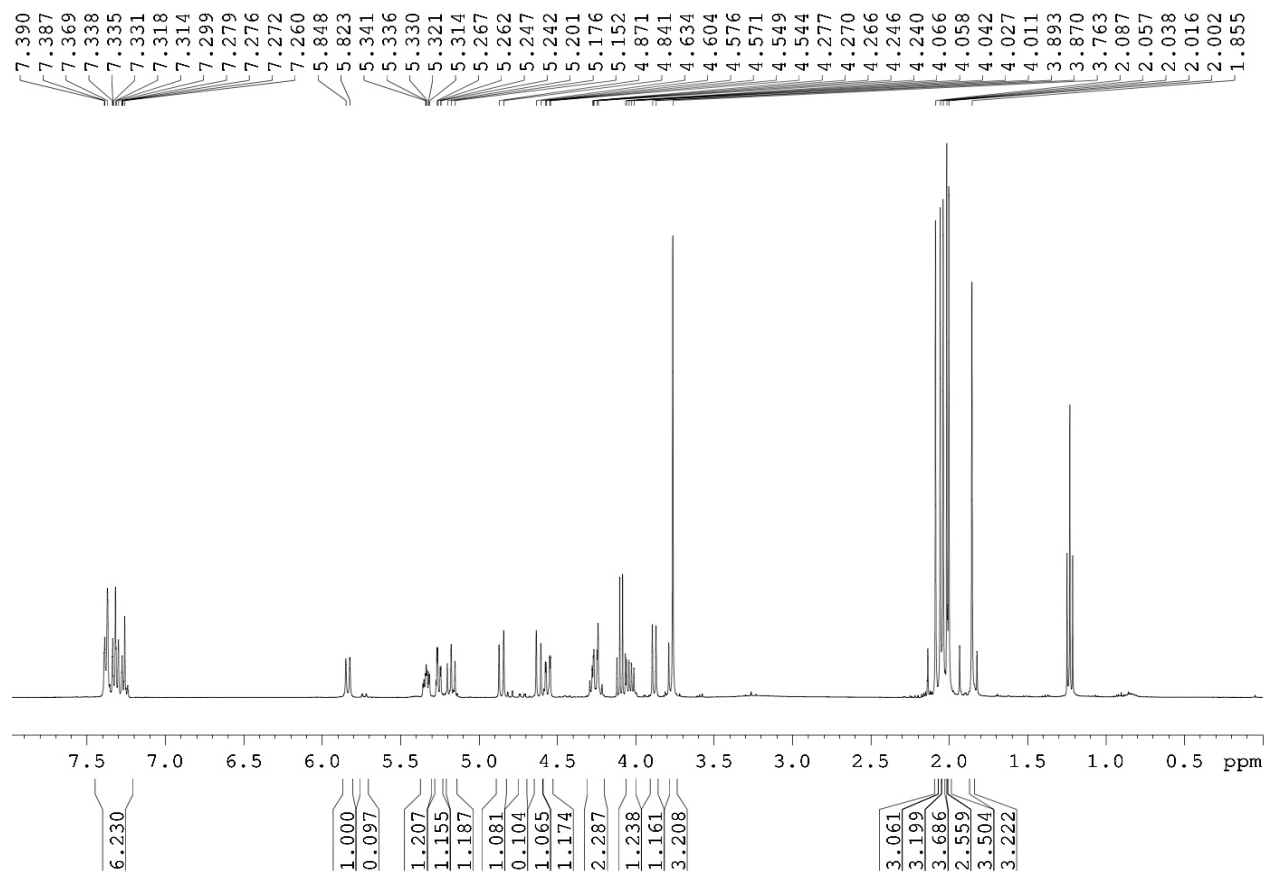
^1H NMR (400 MHz, CDCl_3) of **6a**



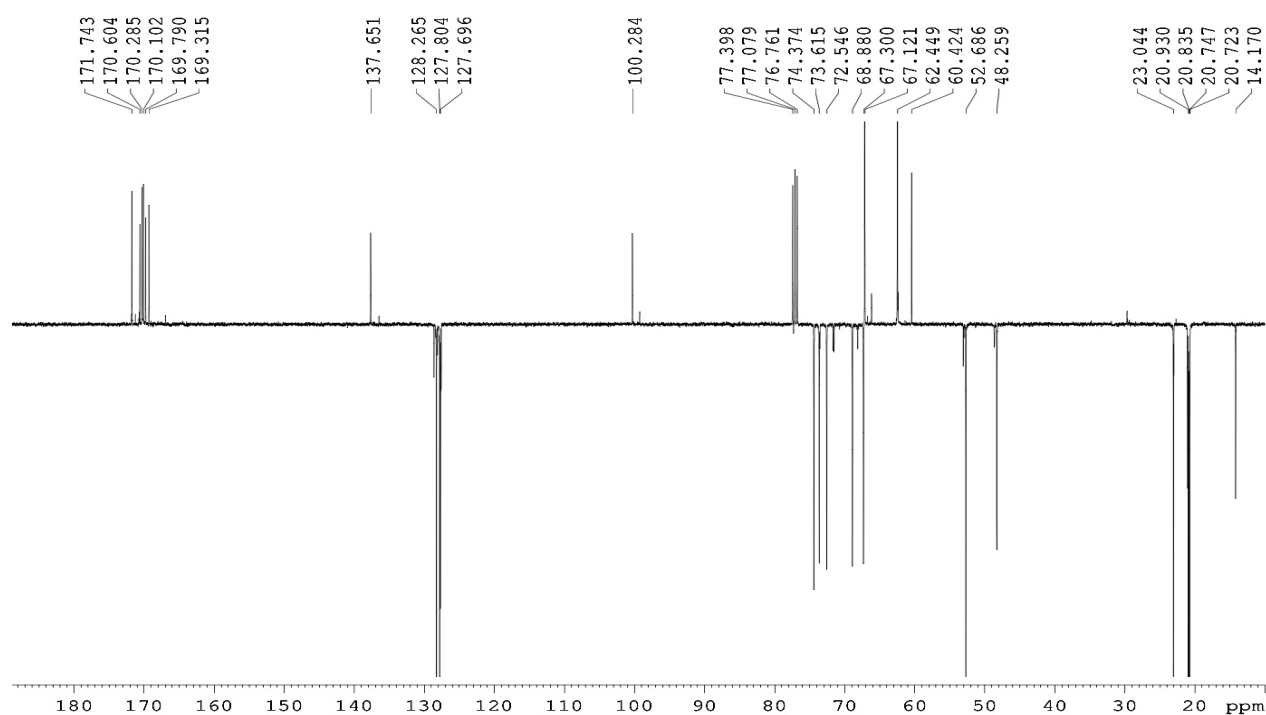
^{13}C NMR (100.6 MHz, CDCl_3) of **6a**



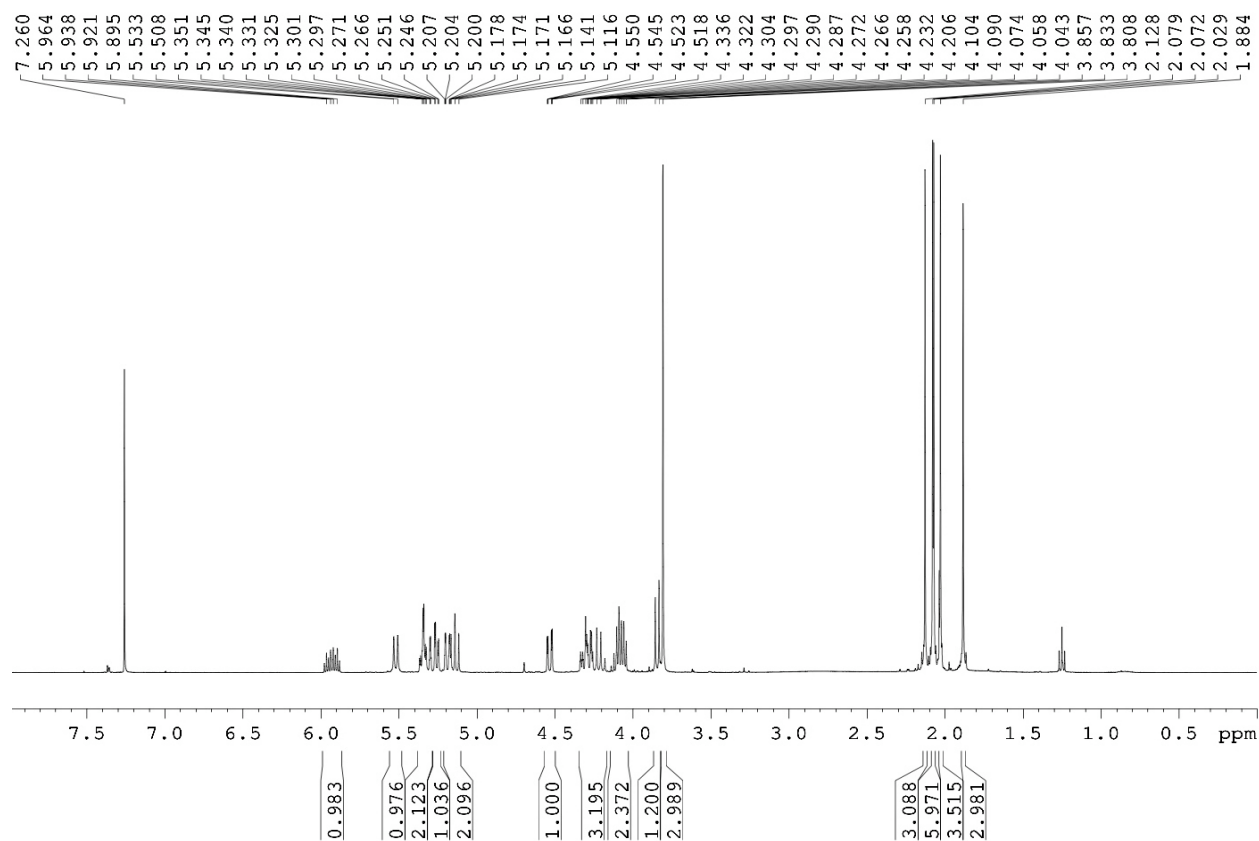
^1H NMR (400 MHz, CDCl_3) of **6b**



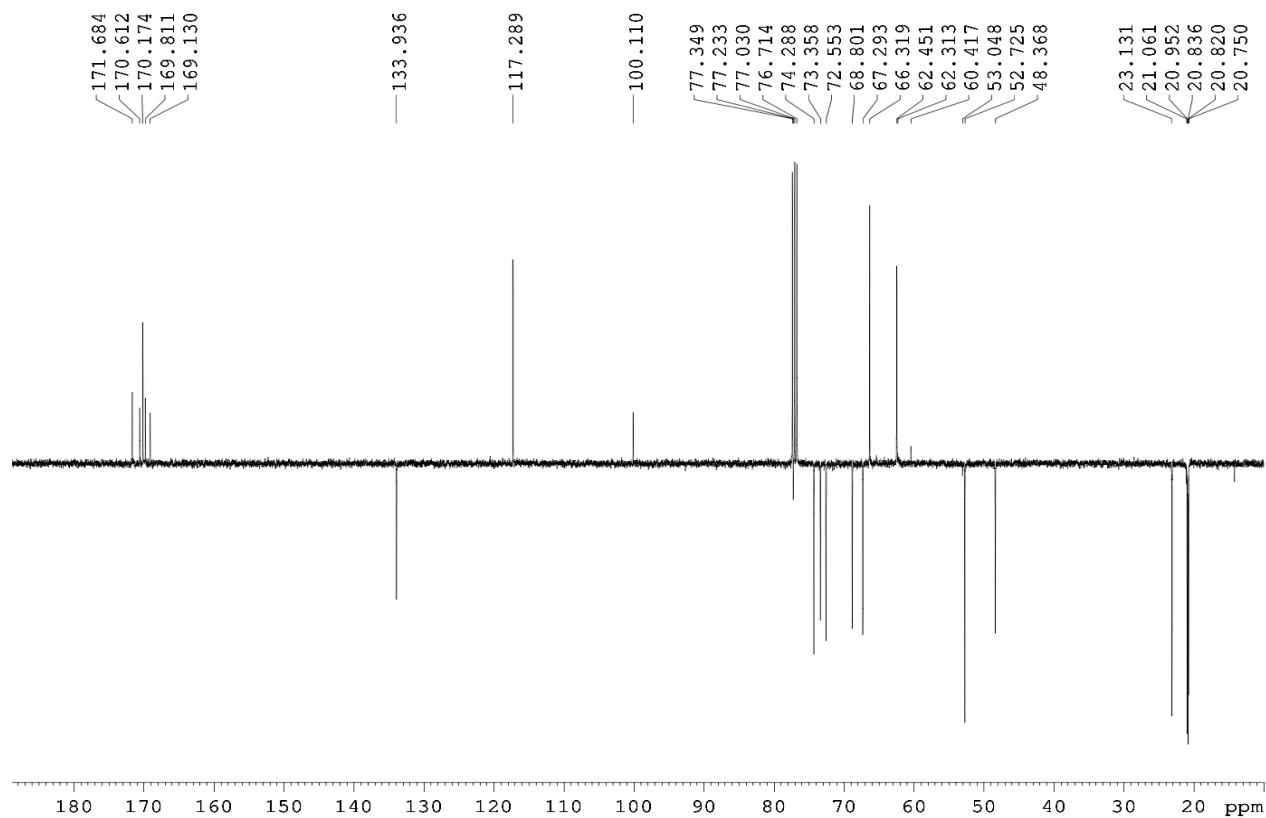
^{13}C NMR (100.6 MHz, CDCl_3) of **6b**



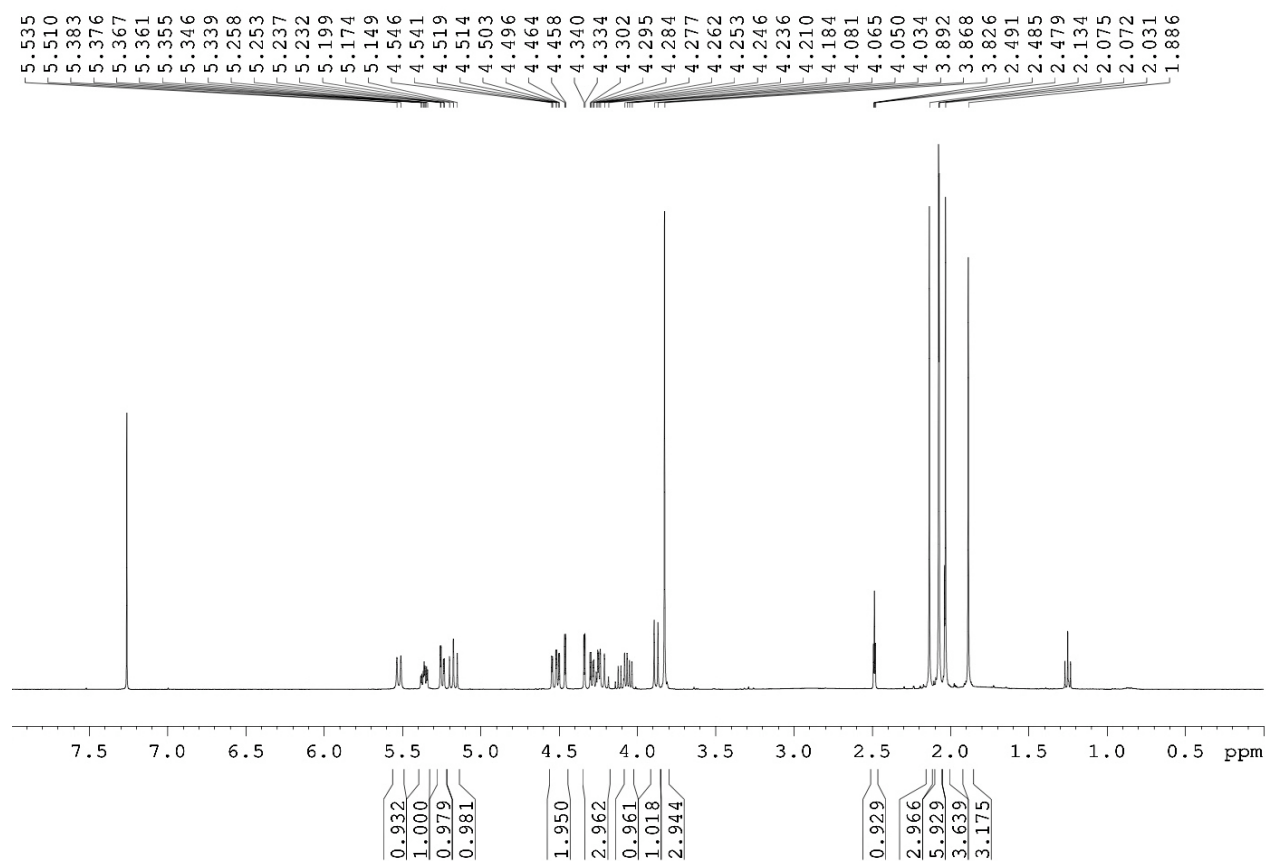
^1H NMR (400 MHz, CDCl_3) of **6c**



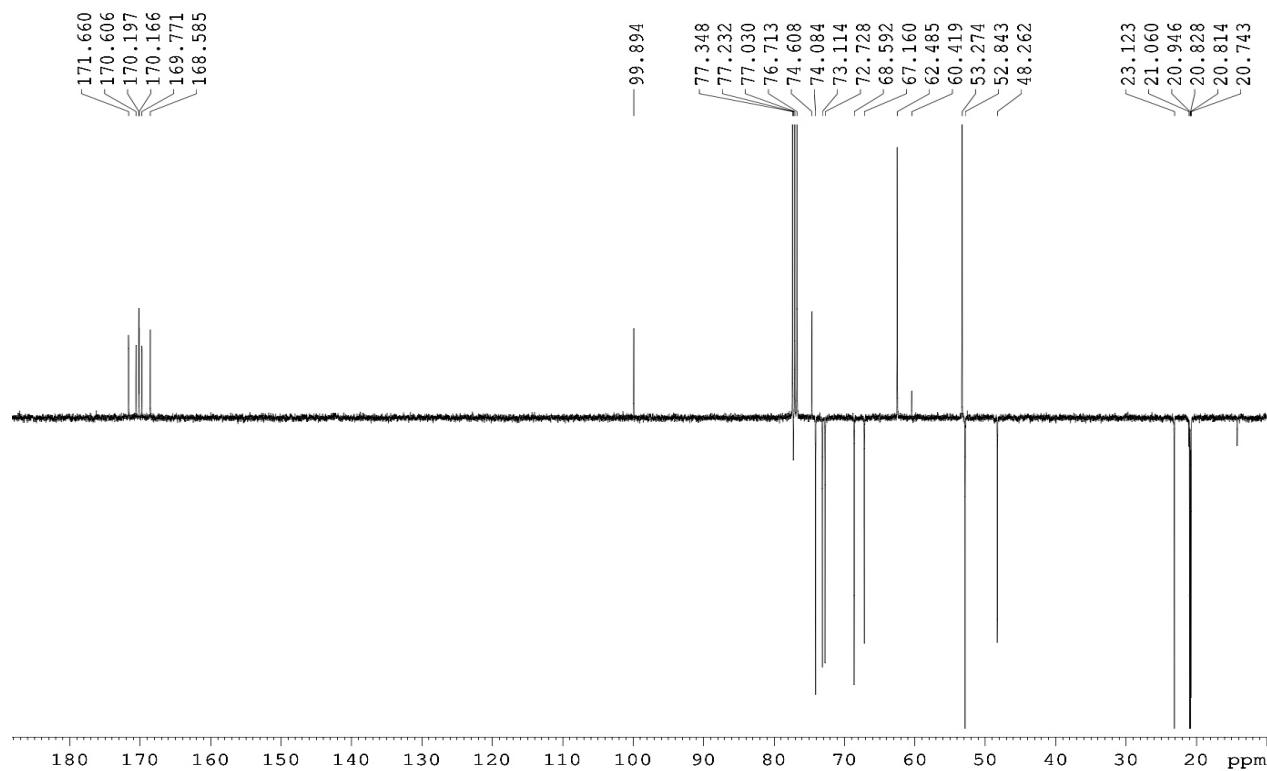
^{13}C NMR (100.6 MHz, CDCl_3) of **6c**



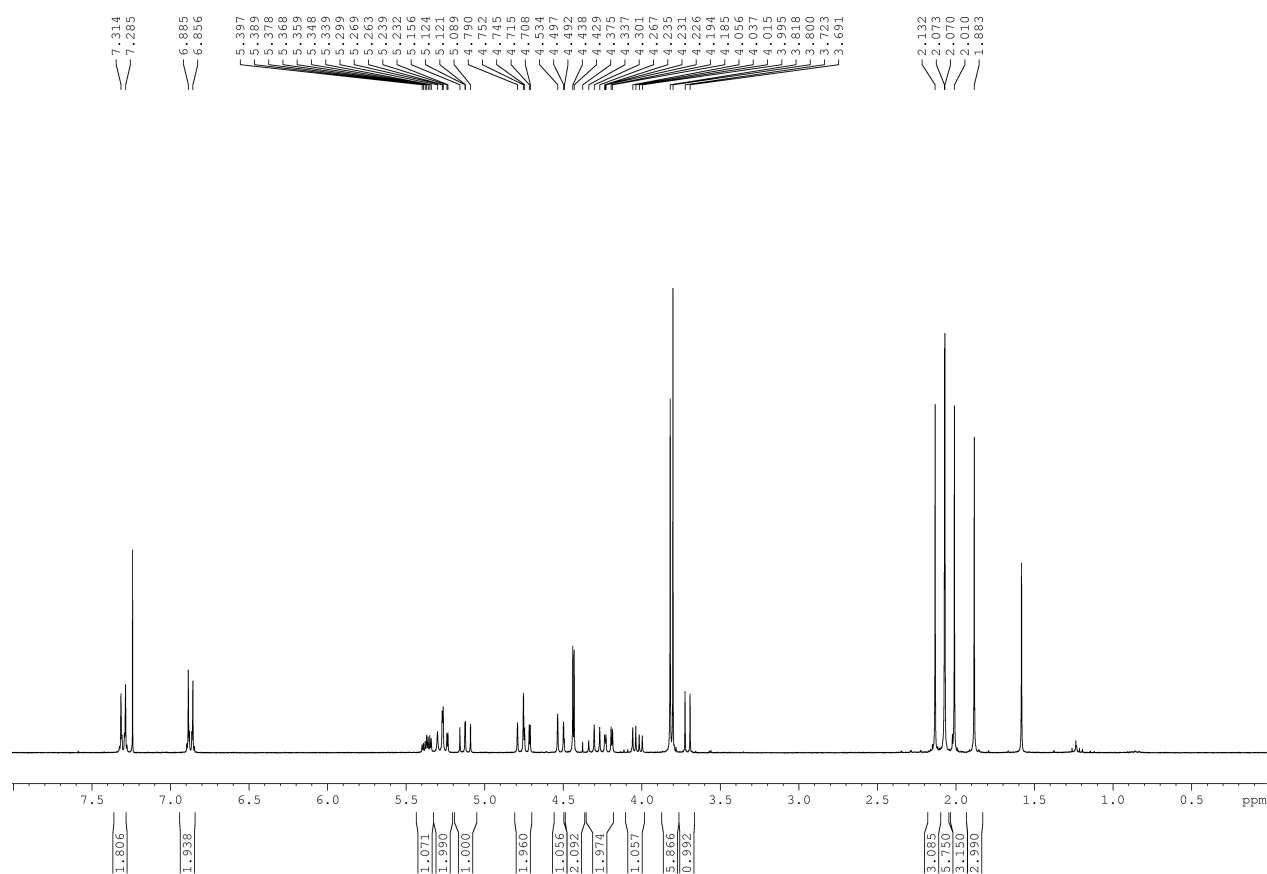
¹H NMR (400 MHz, CDCl₃) of **6d**



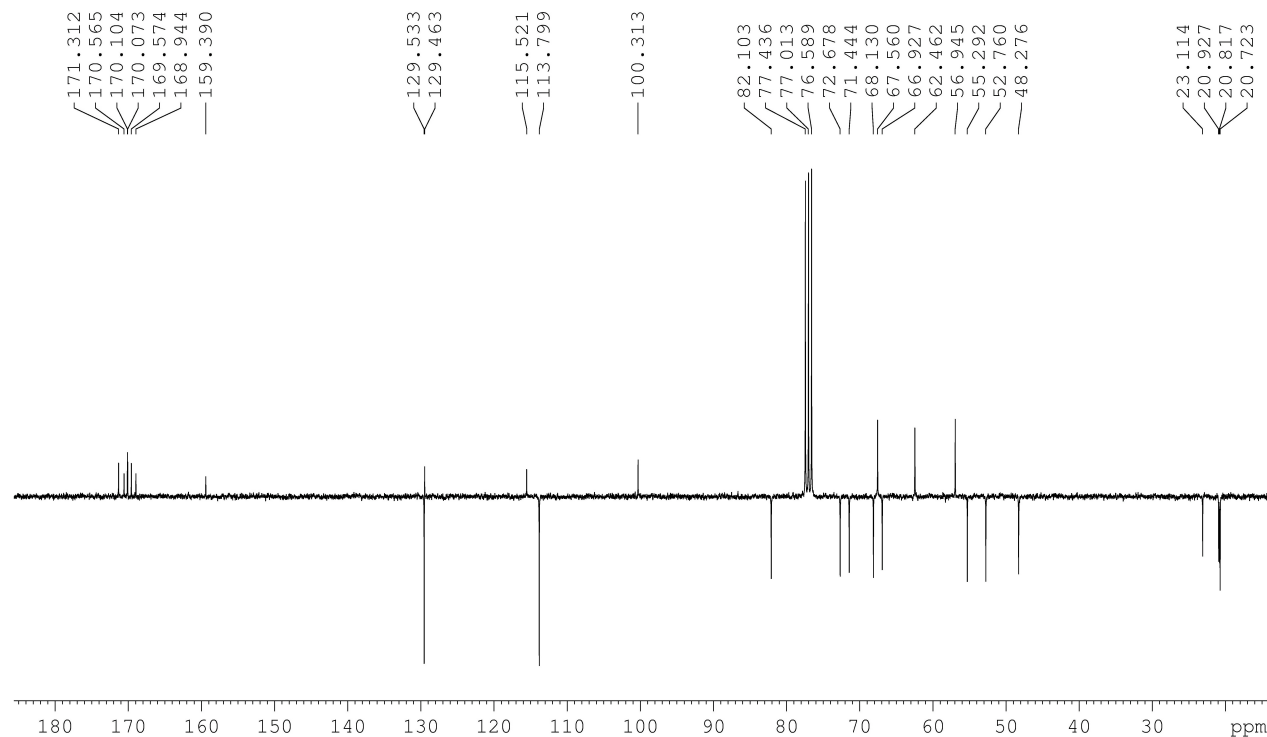
¹³C NMR (100.6 MHz, CDCl₃) of **6d**



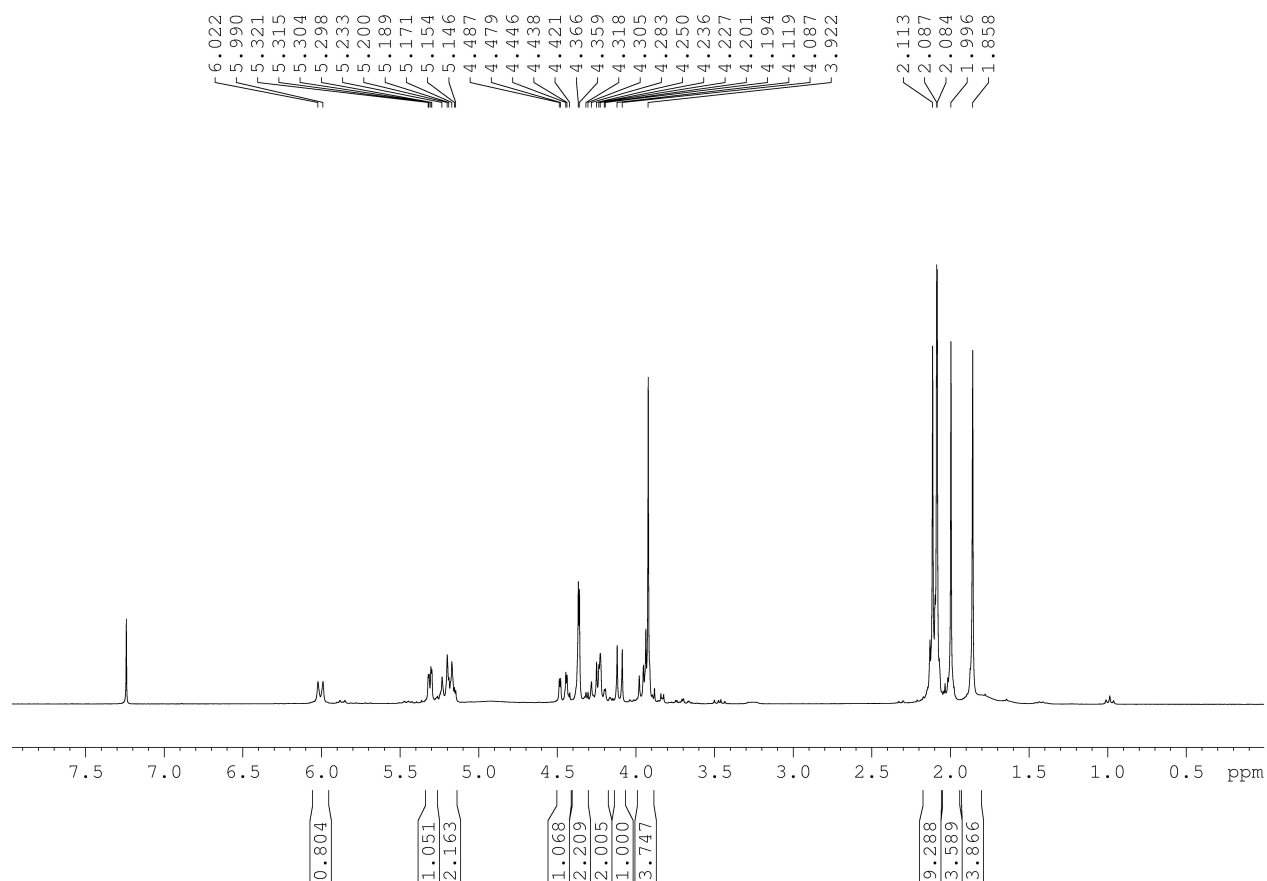
^1H NMR (300 MHz, CDCl_3) of **7**



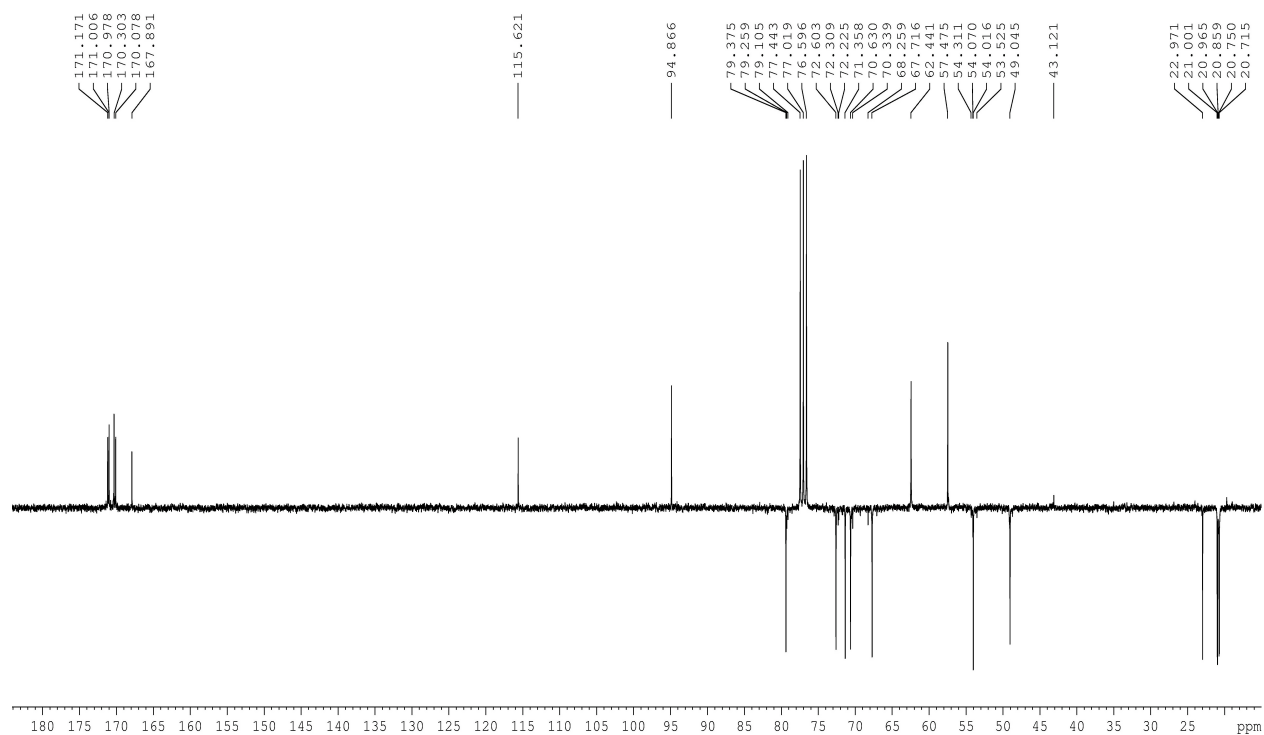
^{13}C NMR (75.5 MHz, CDCl_3) of **7**



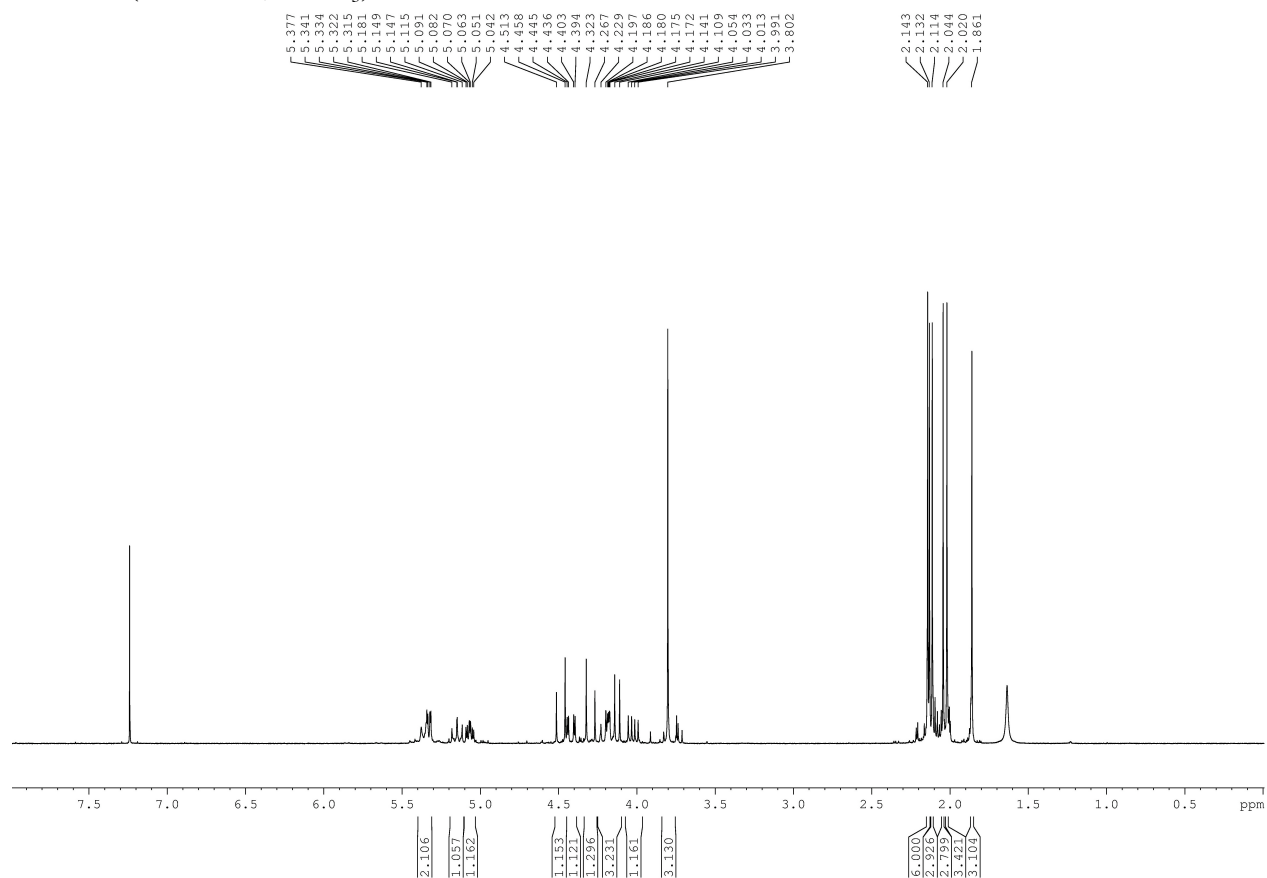
^1H NMR (300 MHz, CDCl_3) of **8**



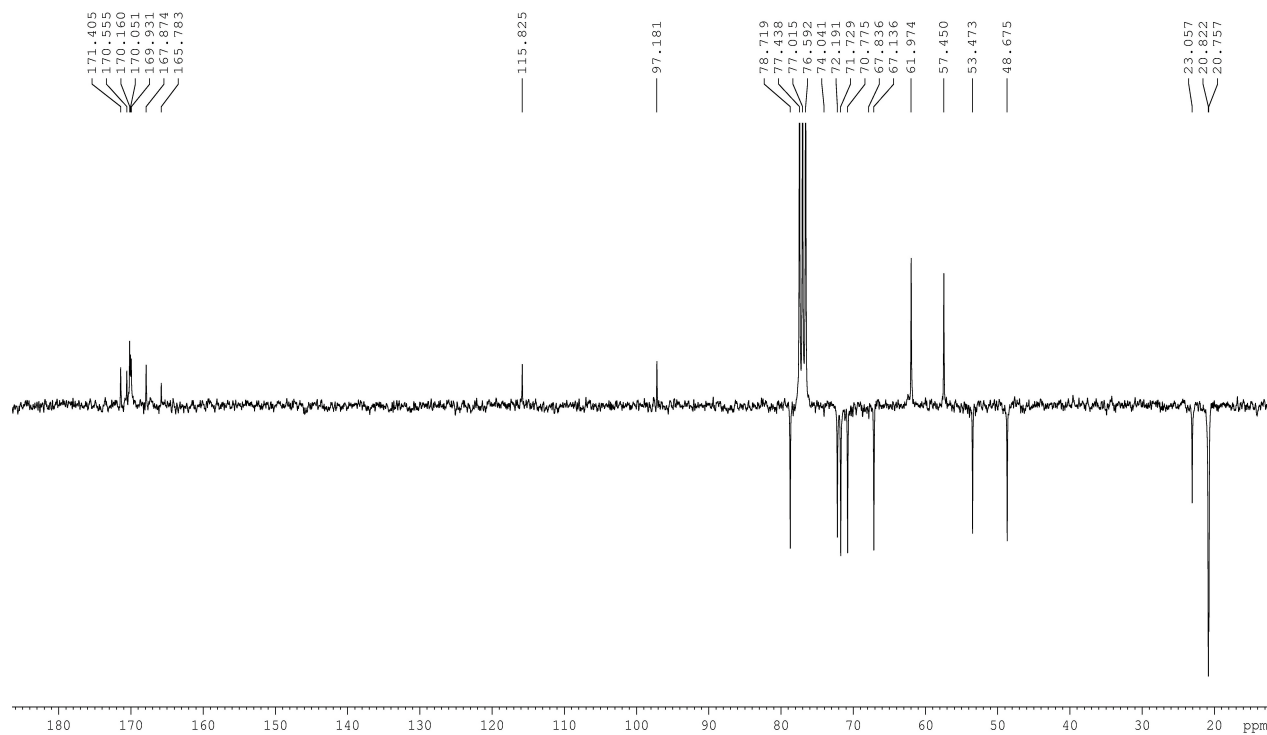
^{13}C NMR (75.5 MHz, CDCl_3) of **8**



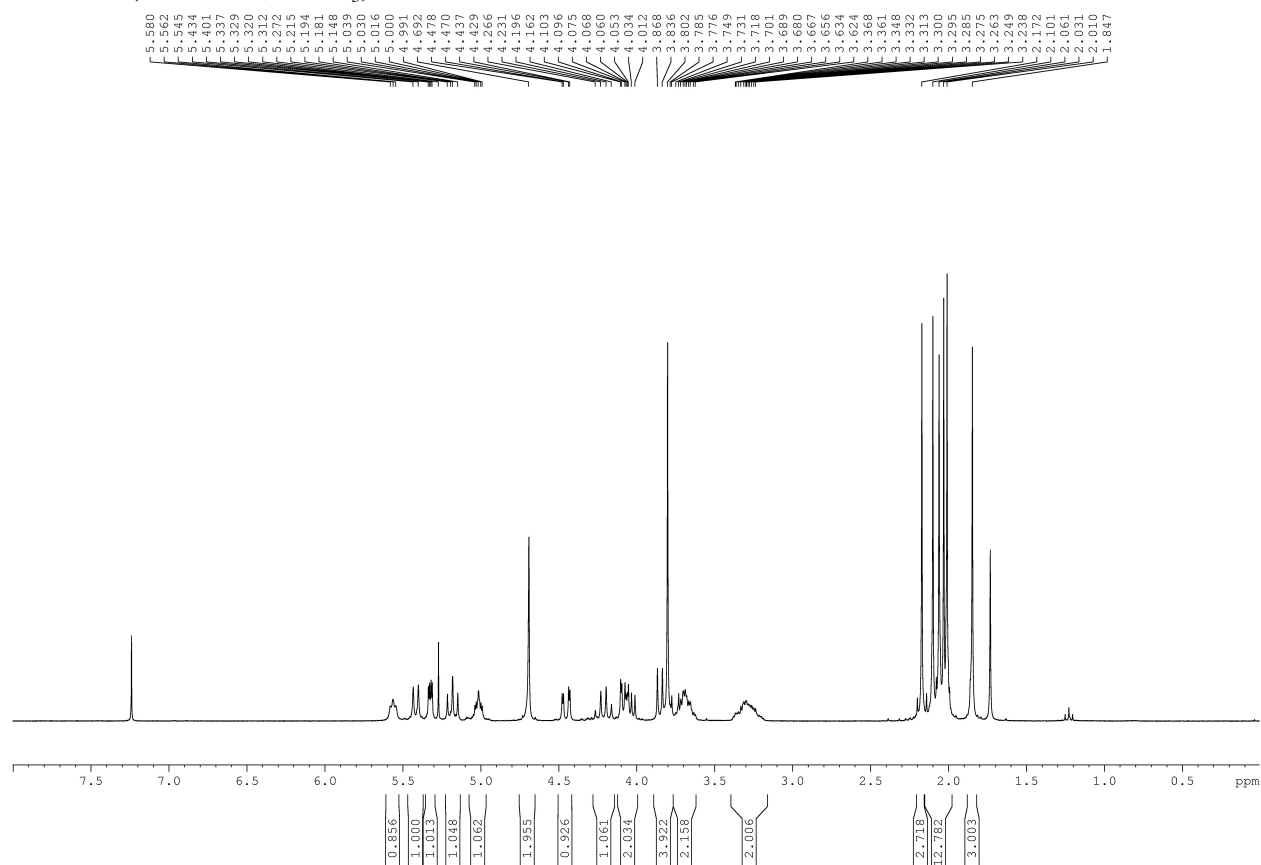
^1H NMR (300 MHz, CDCl_3) of **9**



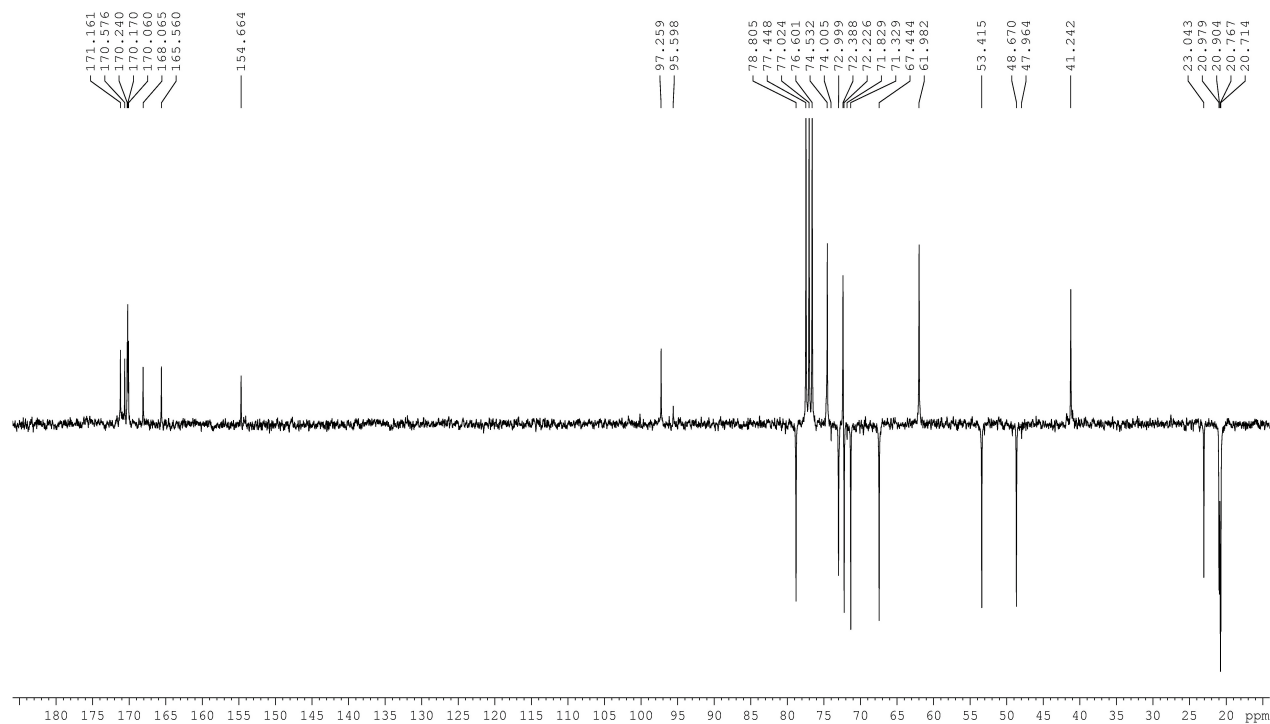
^{13}C NMR (75.5 MHz, CDCl_3) of **9**



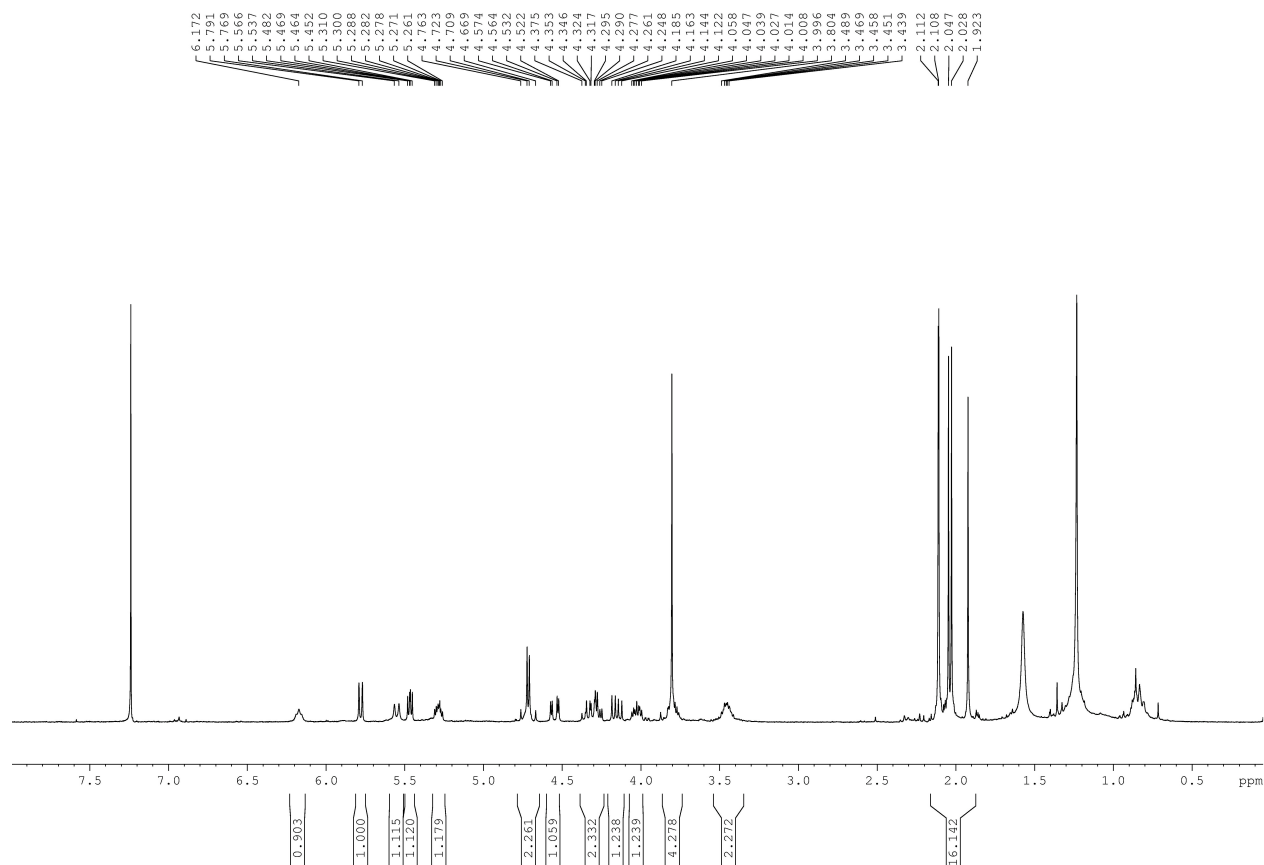
^1H NMR (300 MHz, CDCl_3) of **11**



^{13}C NMR (75.5 MHz, CDCl_3) of **11**



^1H NMR (300 MHz, CDCl_3) of **12**



^{13}C NMR (151 MHz, CDCl_3) of **12**

