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Supporting Information for

Methyl Glycosides Are Identified as Glycosyl Donors for the Synthesis of Glycosides, Disaccharides and Oligosaccharides

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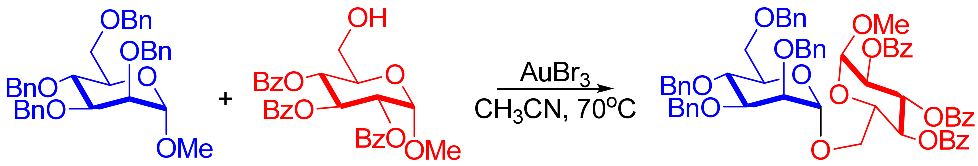
Abstract



Stable methyl glycosides are identified as glycosyl donors in the presence of $AuBr_3$ in acetonitrile. A panel of aglycones comprising aliphatic, alicyclic, steroidal and sugar alcohols are examined successfully for the glycosylation reaction. Methyl glycosides of di- and tri- saccharides are converted to corresponding tri- and tetra- saccharides exploiting salient features of our novel activation protocol.

General Experimental Techniques and Apparatus

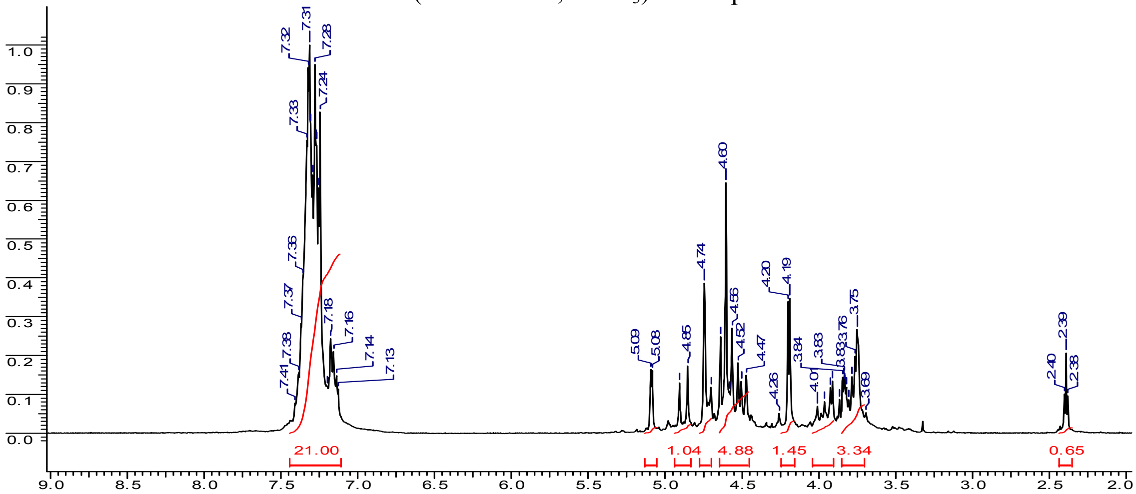
Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under argon atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. $AuCl_3$ was purchased from Aldrich. Analytical thin-layer chromatography was performed on pre-coated silica plates (F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. ^{1}H, ^{13}C NMR spectra were recorded on 200 MHz for ^{1}H and 50 MHz for ^{13}C NMR or 300 MHz for ^{1}H and 75 MHz for ^{13}C NMR or 500 MHz for ^{1}H and 125 MHz for ^{13}C NMR spectrometers. LC-MS data was recorded on UPLC coupled Mass Spectrometer (Waters). Chemical shifts (δ_H) are quoted in ppm and are referenced to tetramethylsilane (internal).

General Procedure for $AuBr_3$ mediated Glycosylation

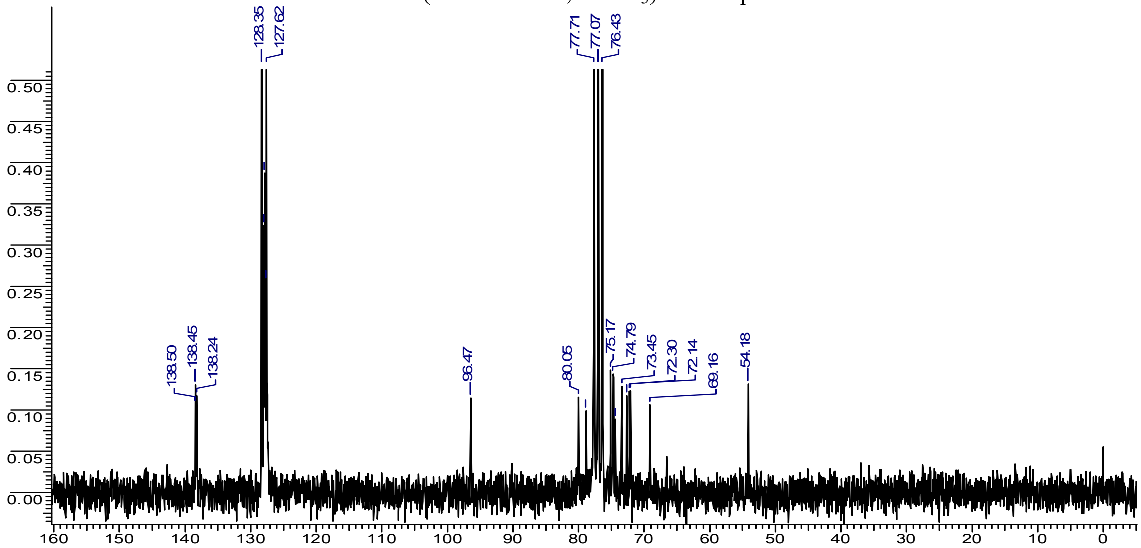
To a solution of glycosyl donor (0.1 mmol) and aglycone (0.12 mmol) in anhydrous acetonitrile (4 ml) was added 10 mol% of $AuBr_3$ under argon atmosphere at room temperature. The resulting mixture was heated to 70^{o}C and stirred till the completion of the reaction as judged by TLC analysis (Table 1 of manuscript). The reaction mixture was concentrated *in vacuo* to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase.

Spectral Charts

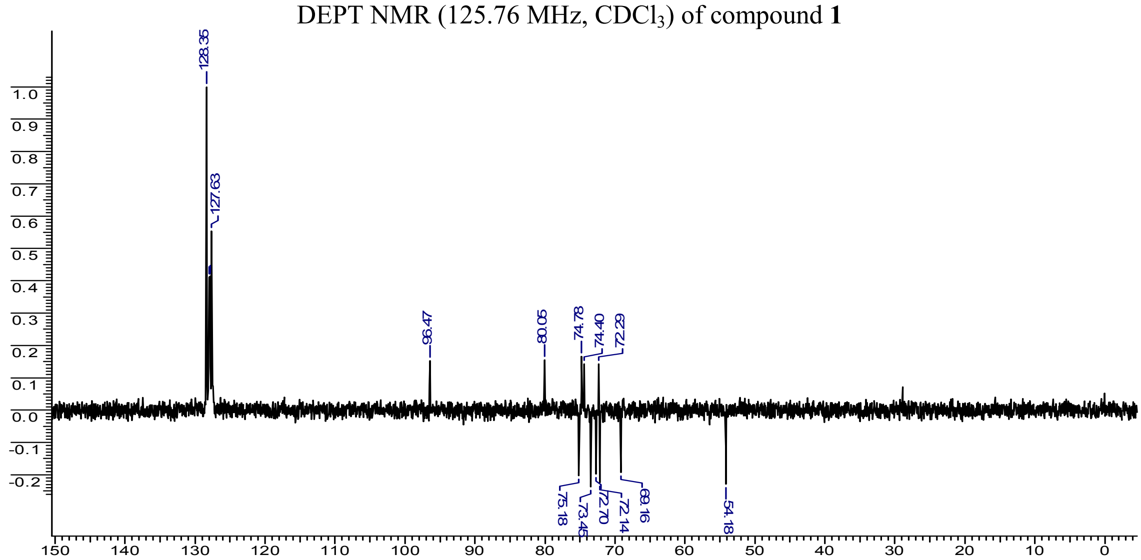
[1]H NMR (200.13 MHz, $CDCl_3$) of compound **1**



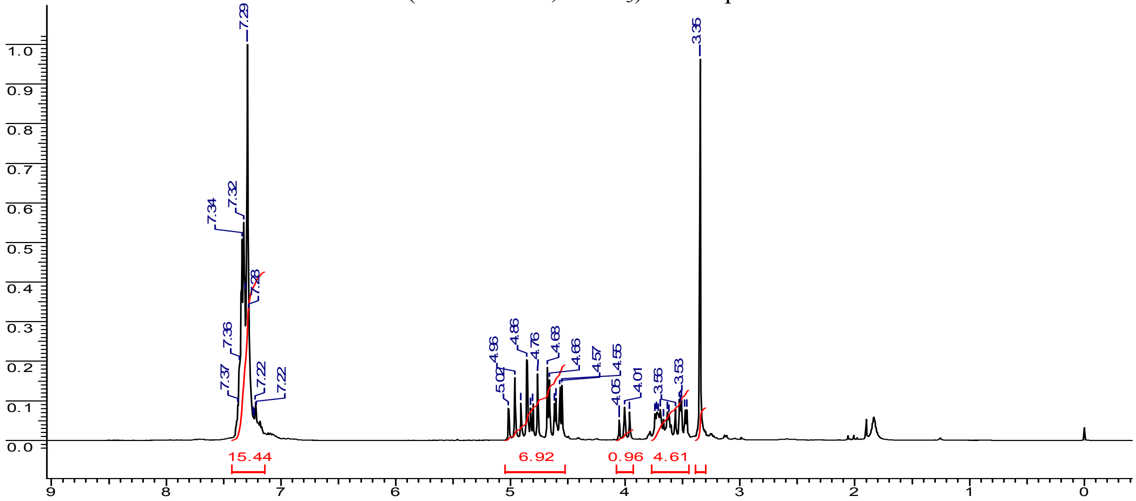
[13]C NMR (125.76 MHz, $CDCl_3$) of compound **1**



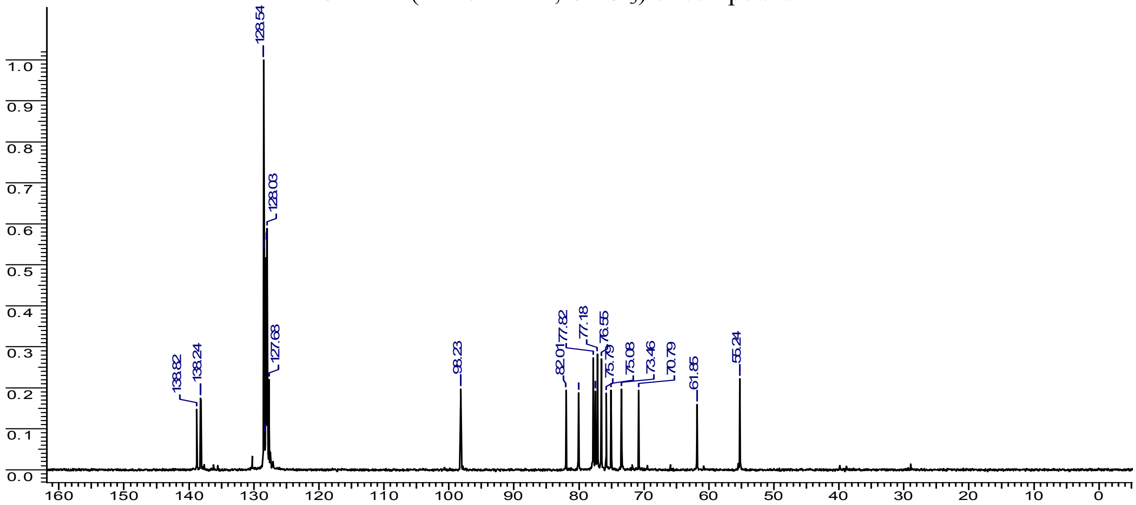
DEPT NMR (125.76 MHz, $CDCl_3$) of compound **1**



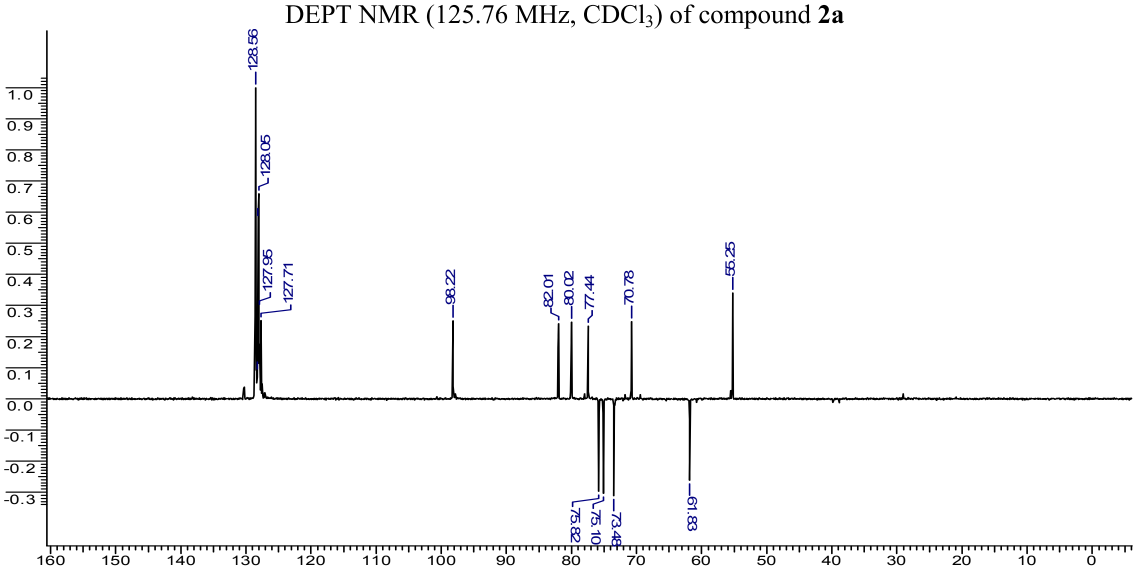
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **2a**



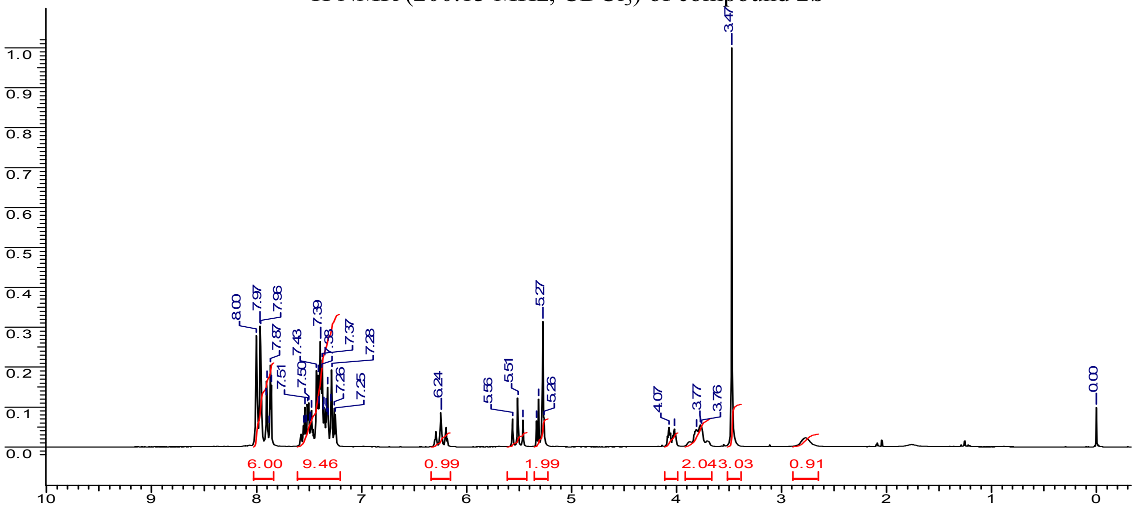
^{13}C NMR (125.76 MHz, $CDCl_3$) of compound **2a**



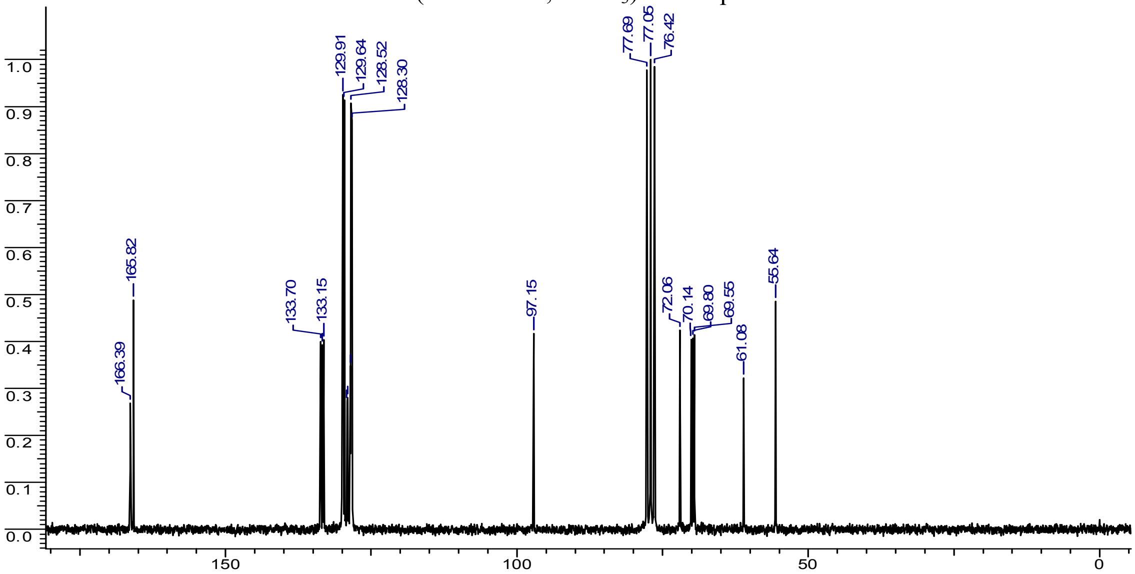
DEPT NMR (125.76 MHz, $CDCl_3$) of compound **2a**



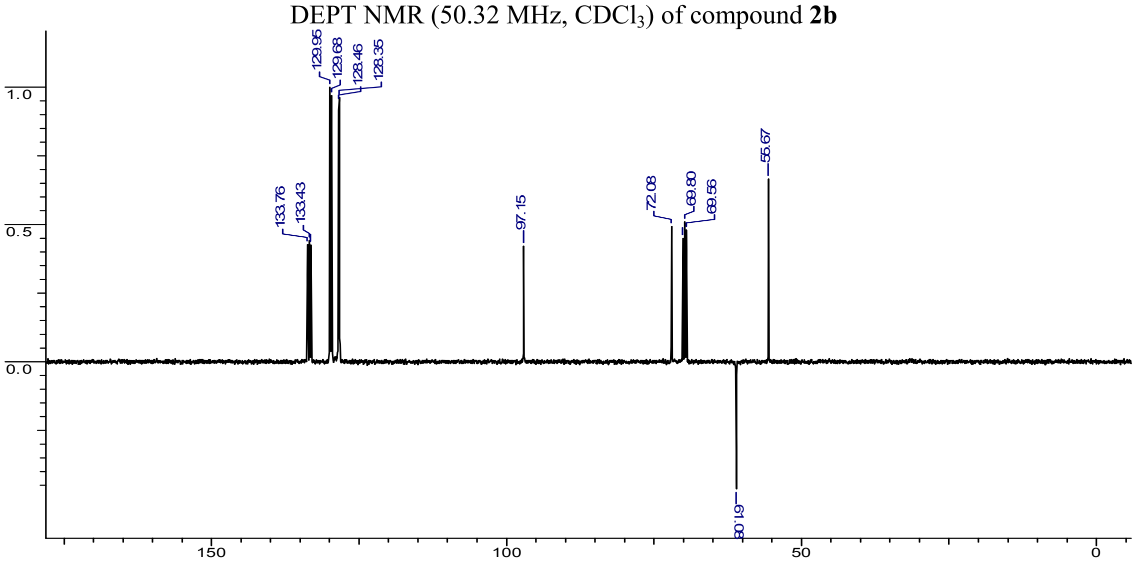
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **2b**



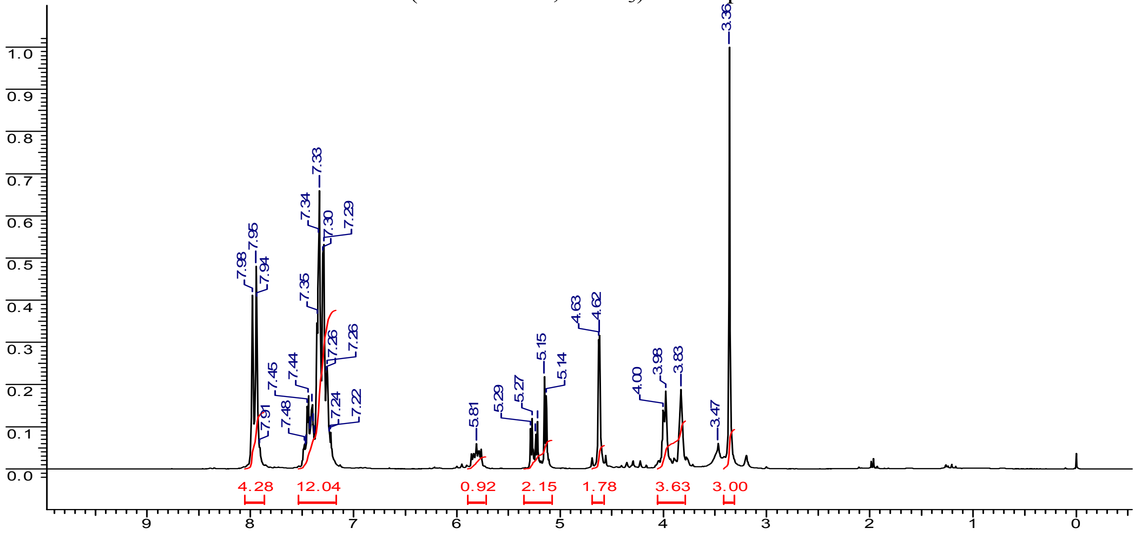
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **2b**



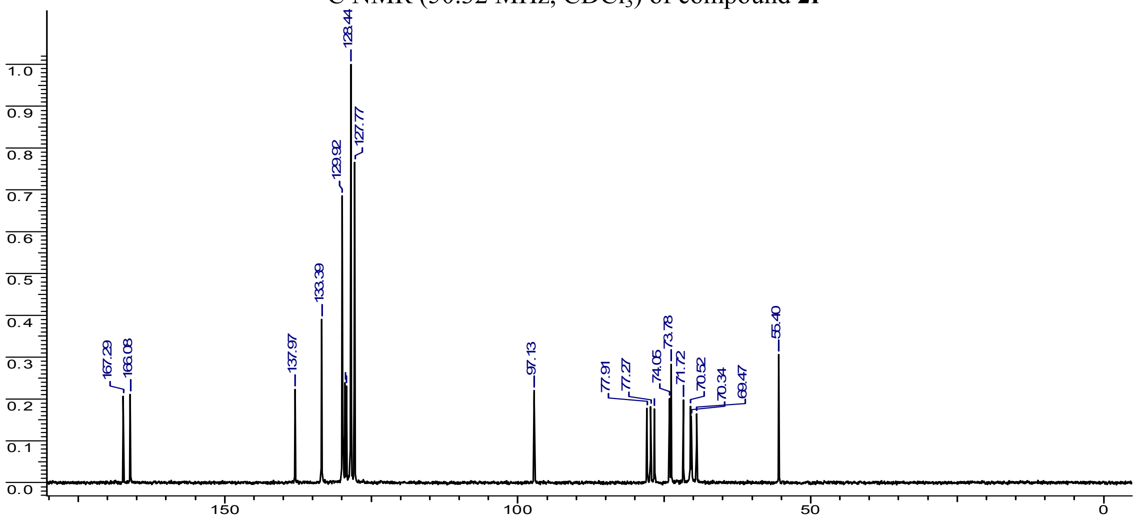
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **2b**



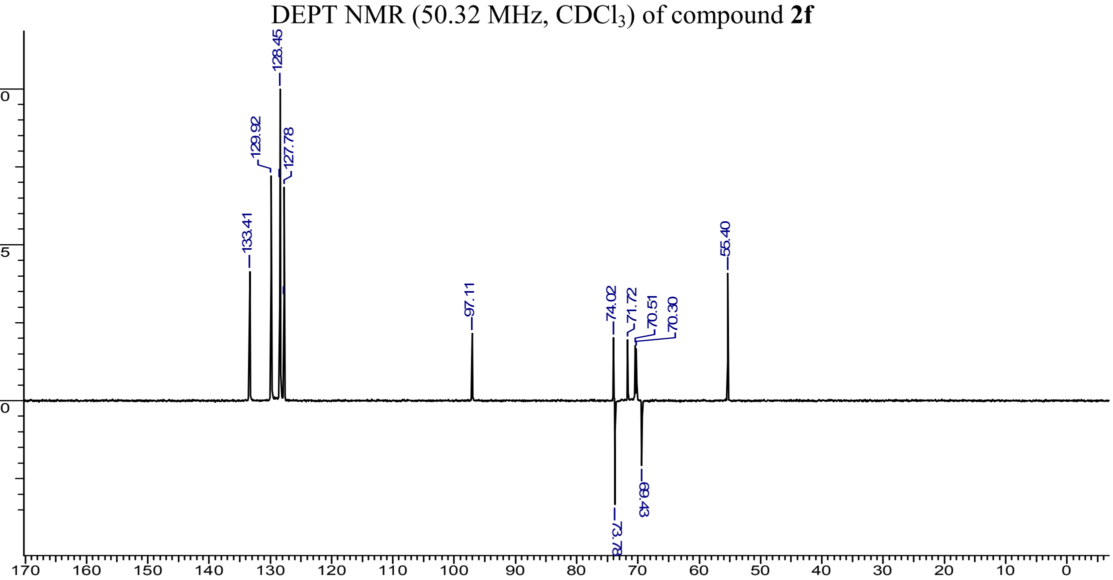
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **2f**



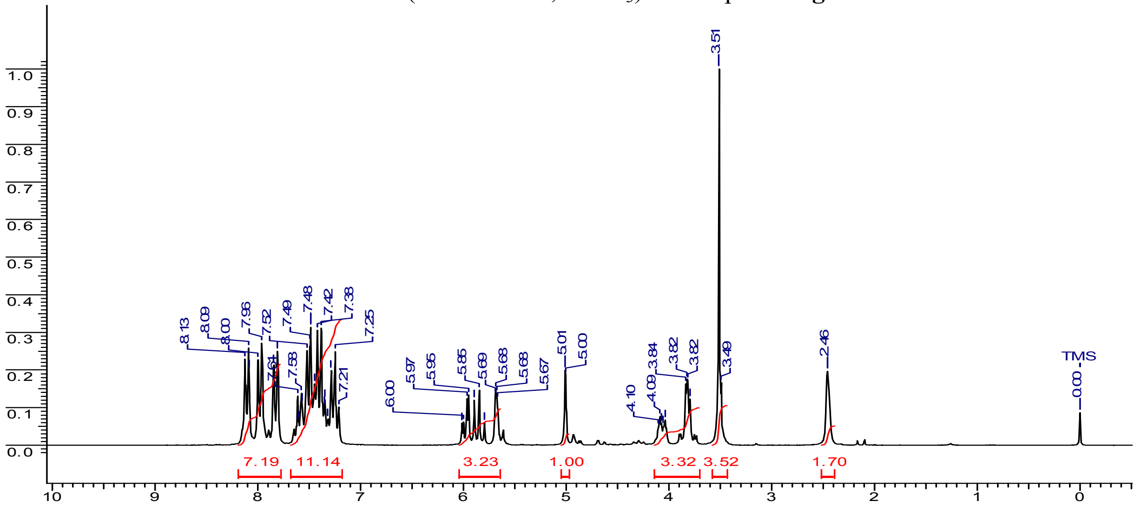
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **2f**



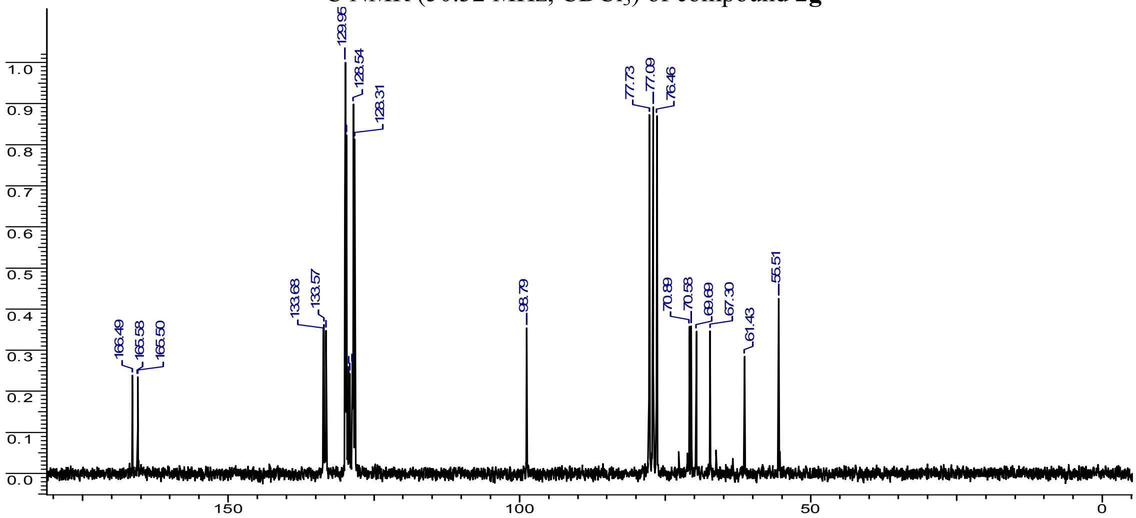
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **2f**



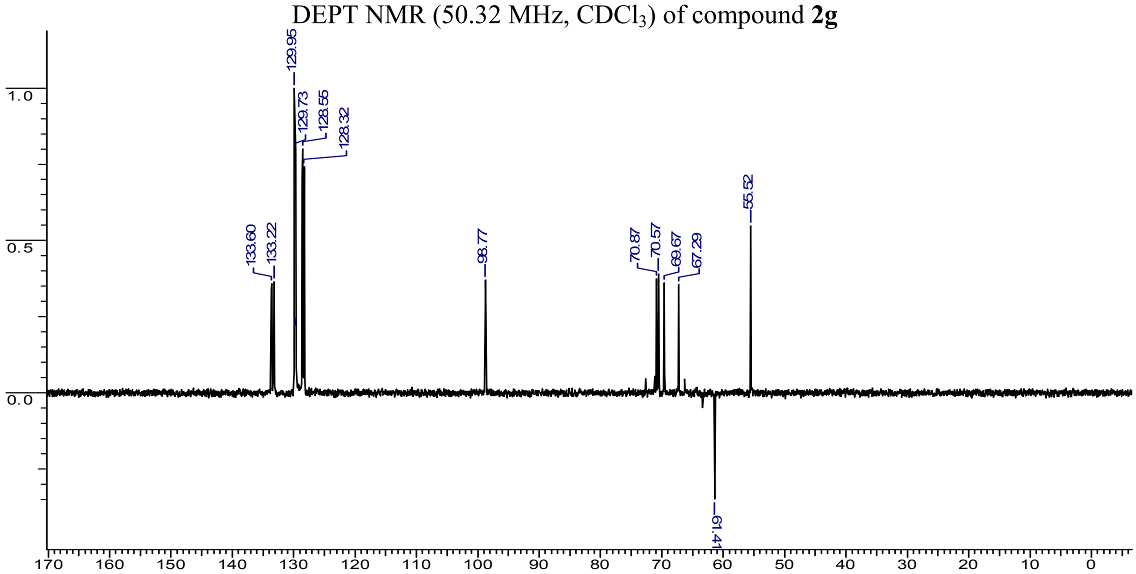
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **2g**



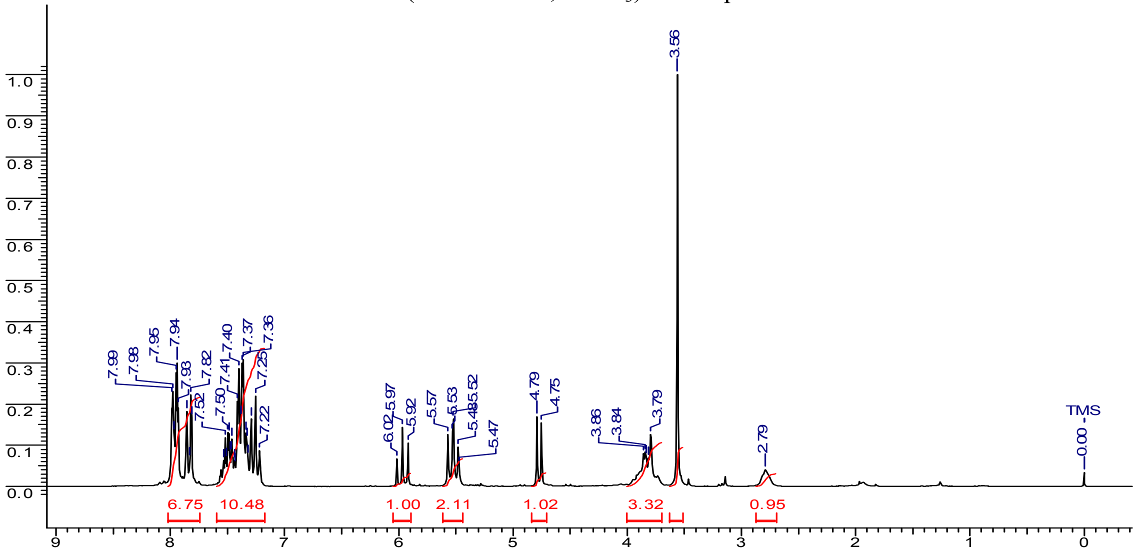
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **2g**



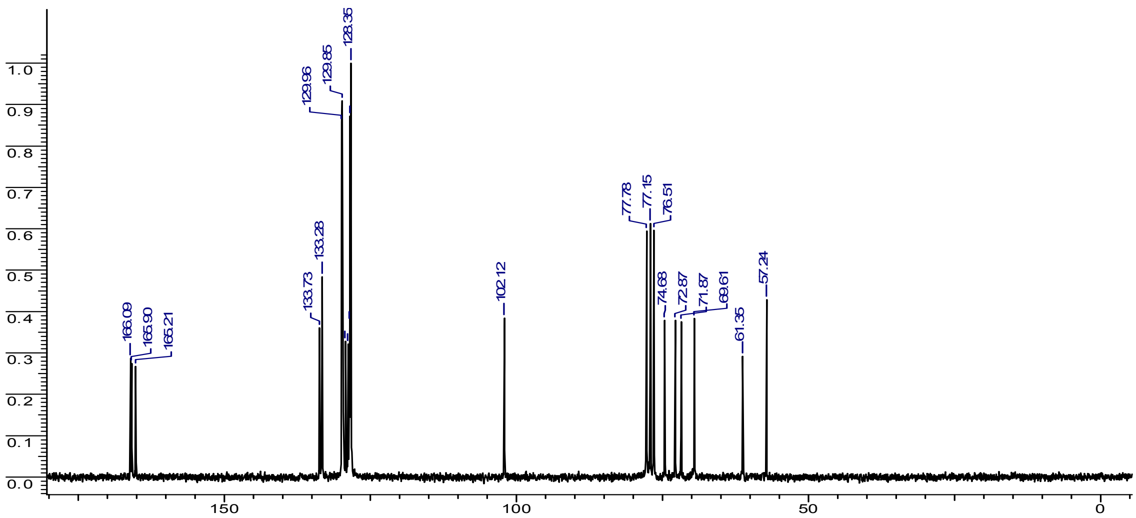
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **2g**



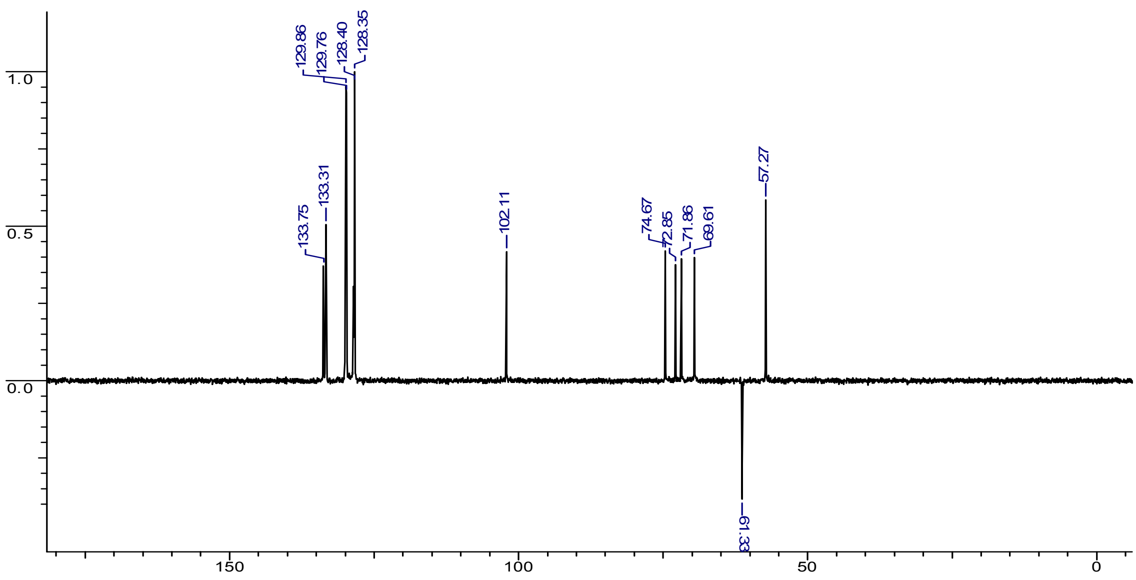
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **2h**



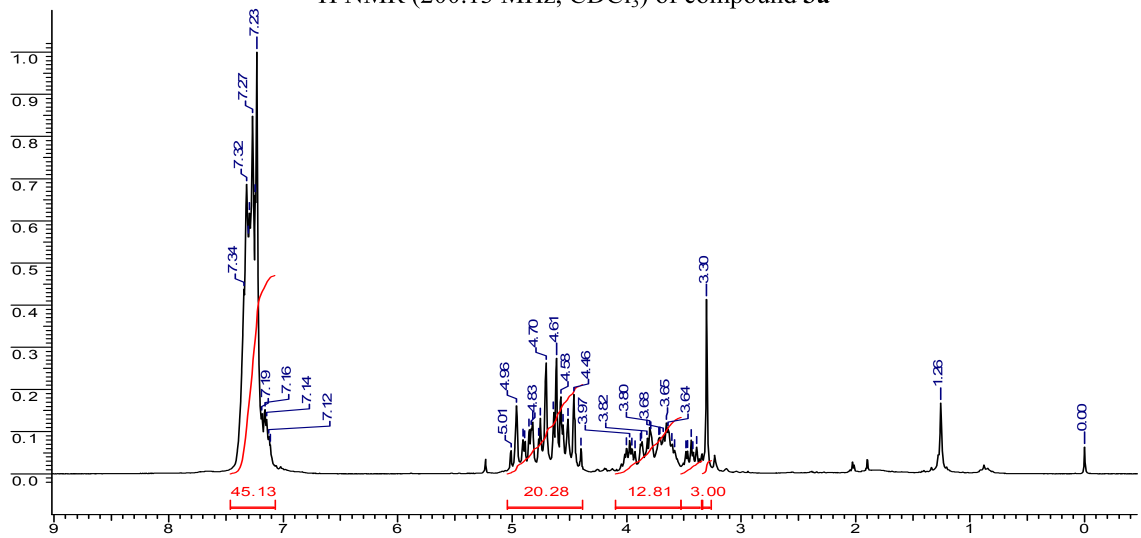
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **2h**



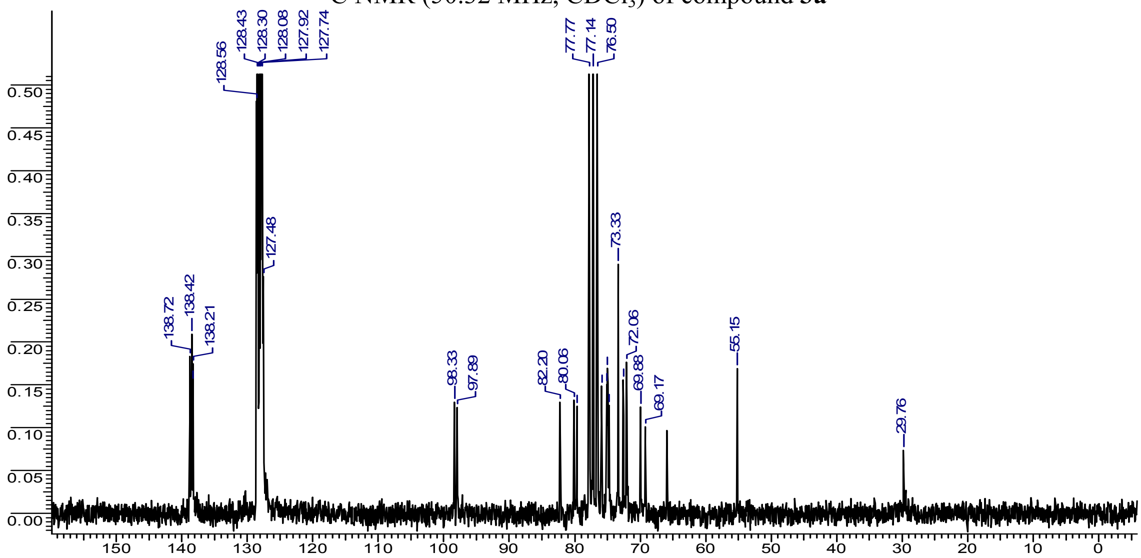
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **2h**



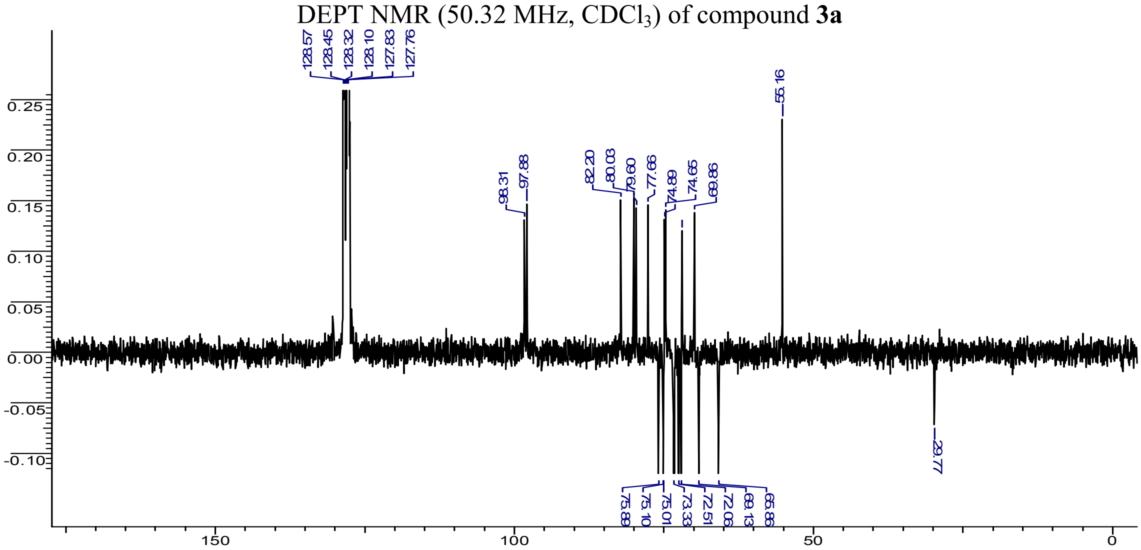
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **3a**



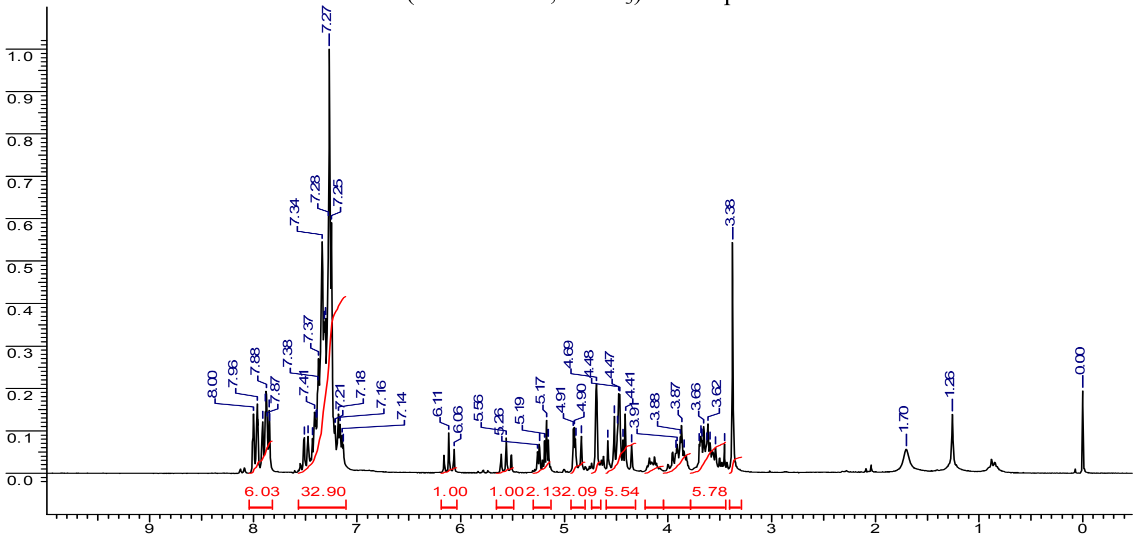
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **3a**



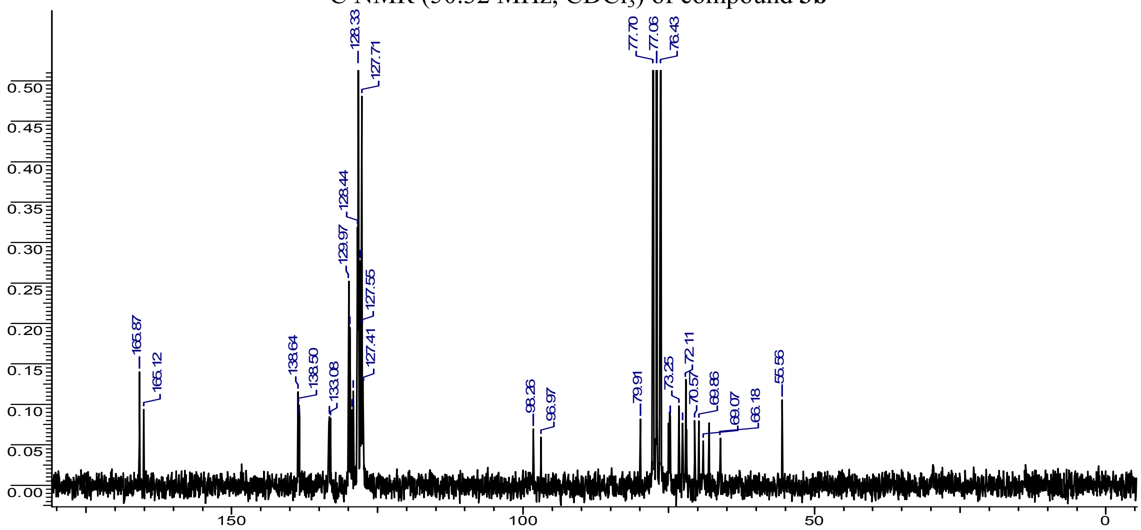
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **3a**



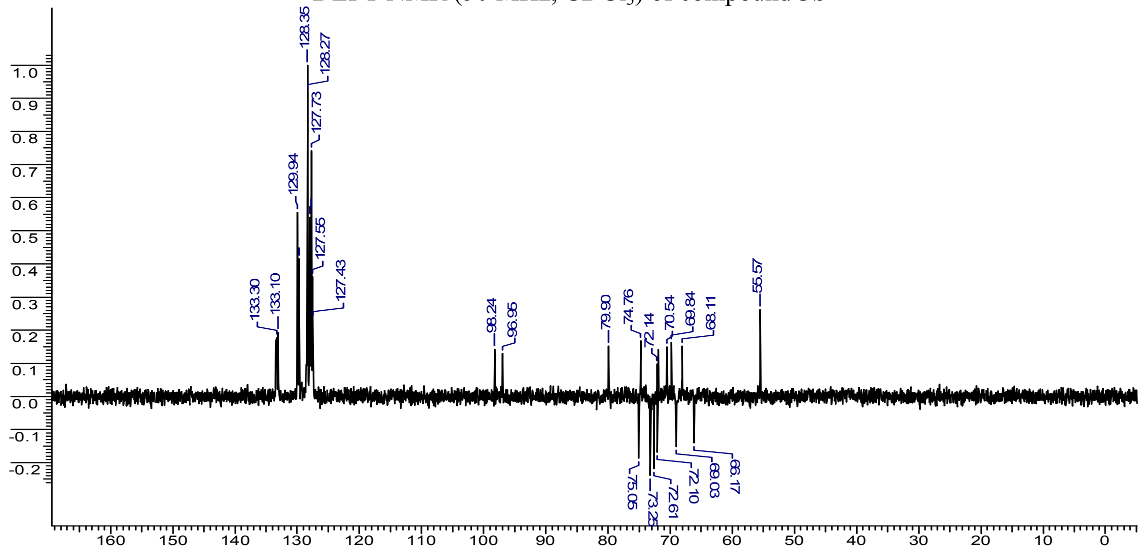
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **3b**



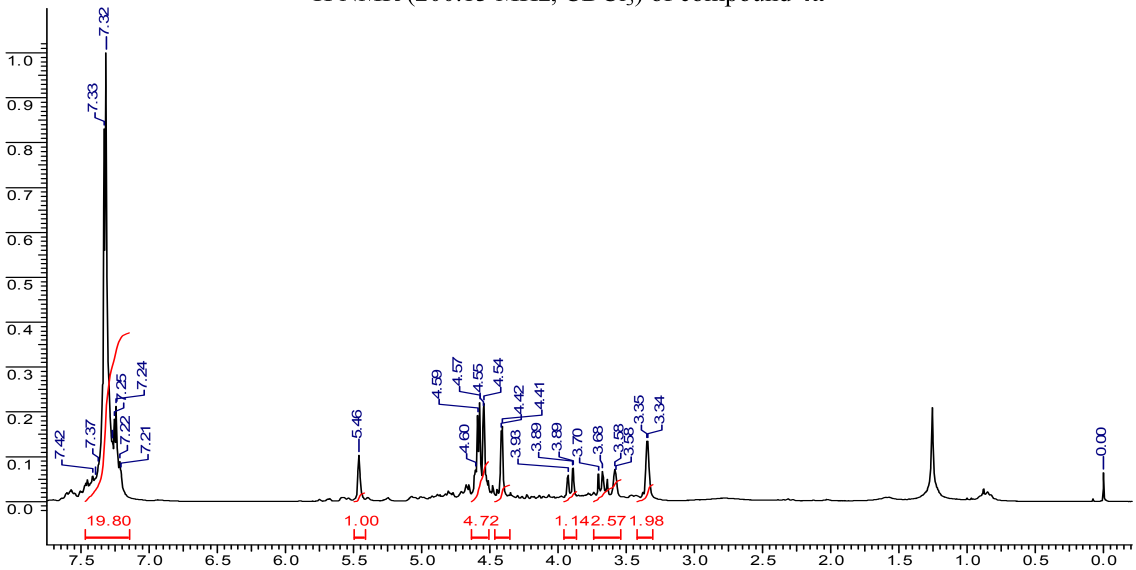
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **3b**



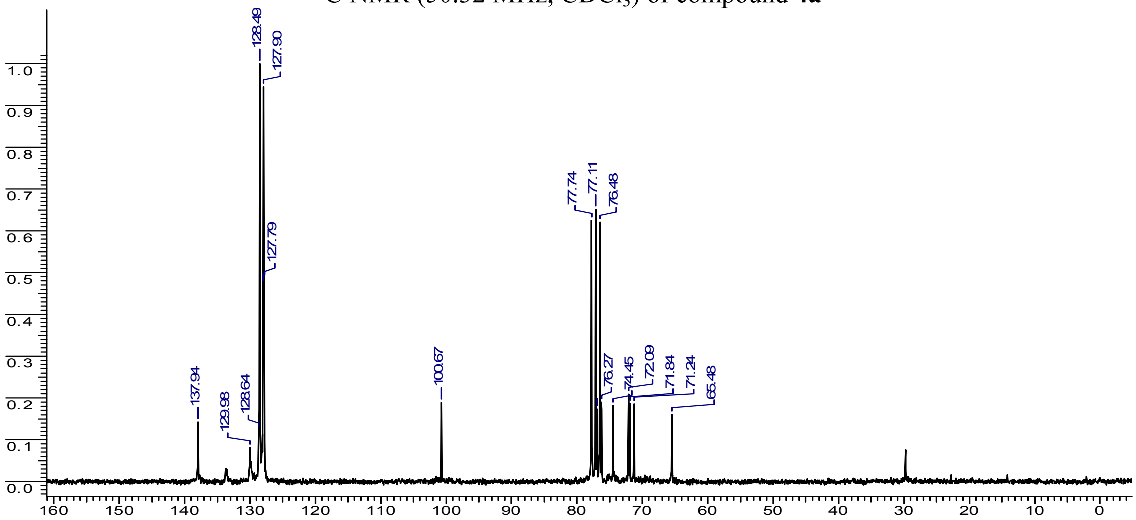
DEPT NMR (50 MHz, $CDCl_3$) of compound **3b**



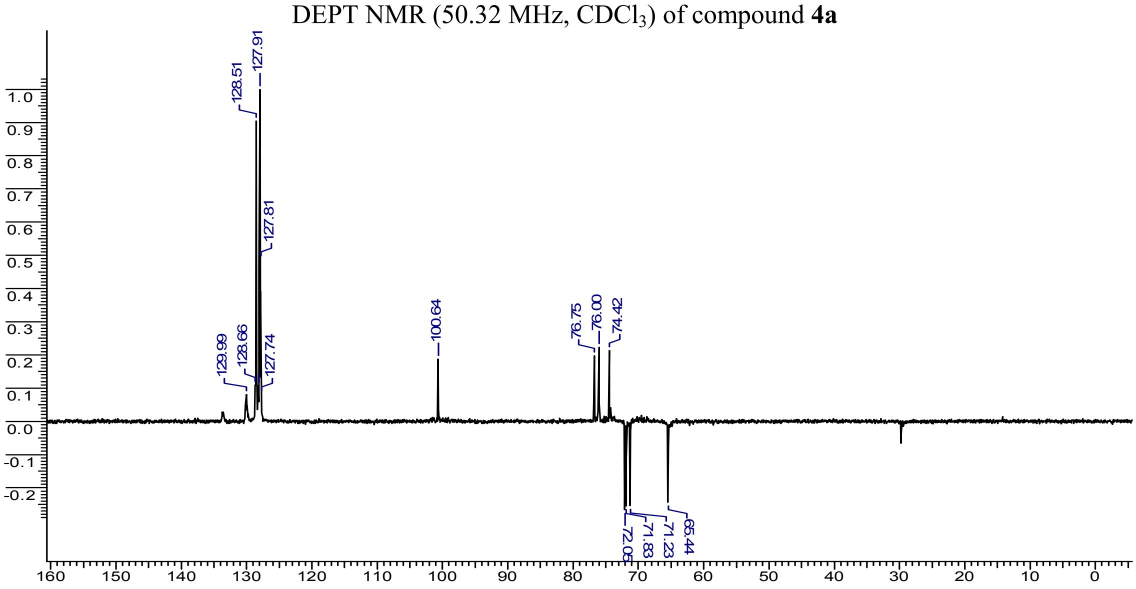
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **4a**



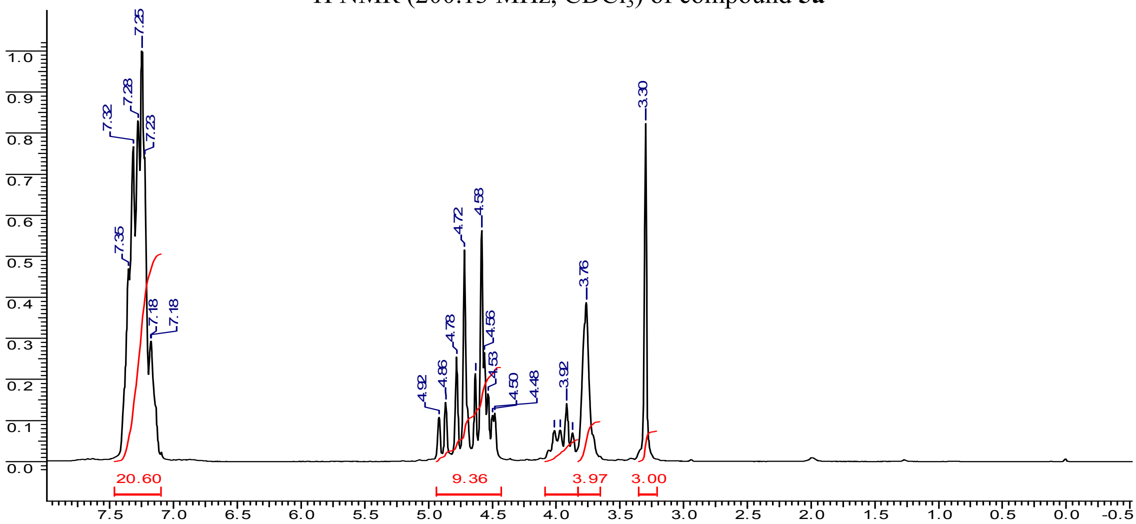
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **4a**



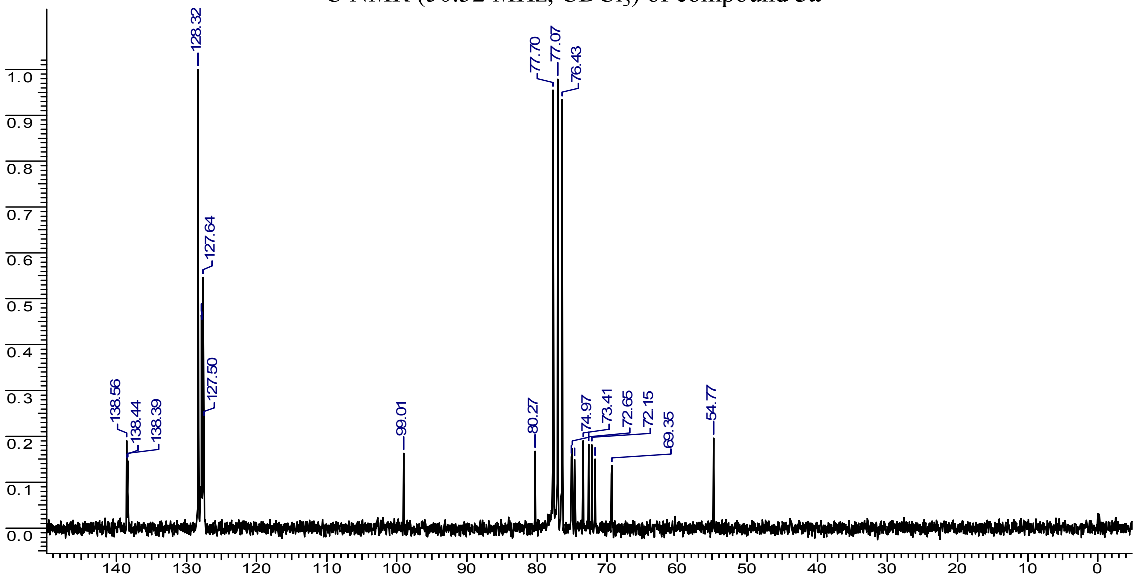
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **4a**



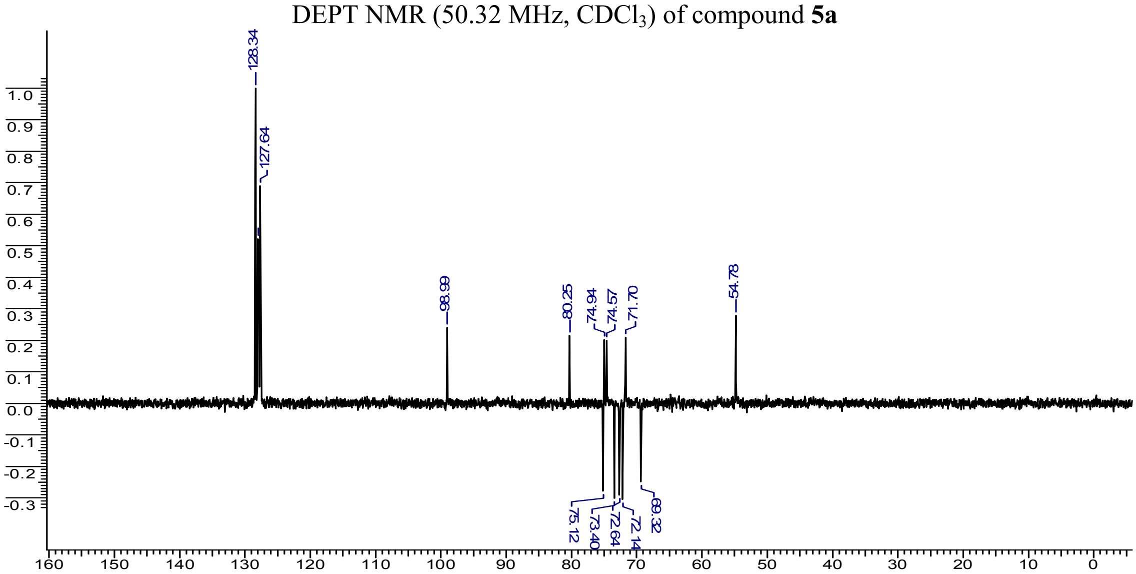
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5a**



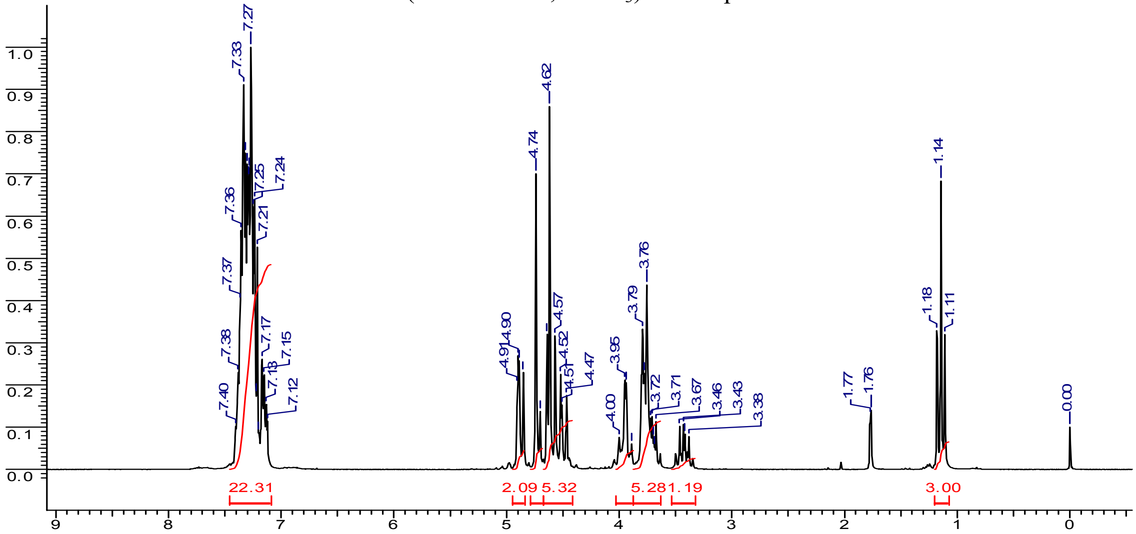
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5a**



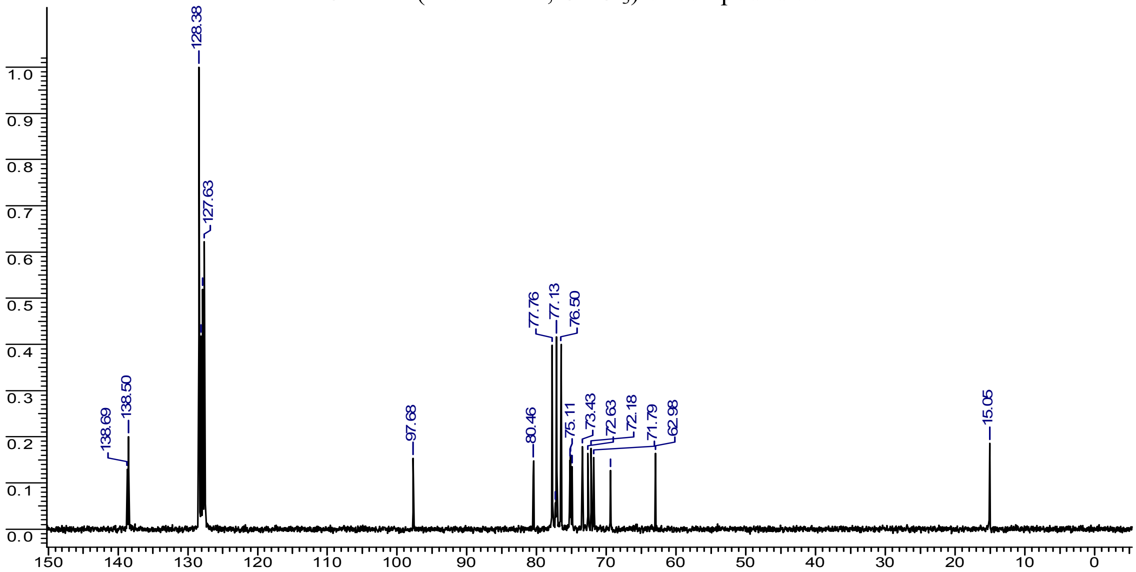
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5a**



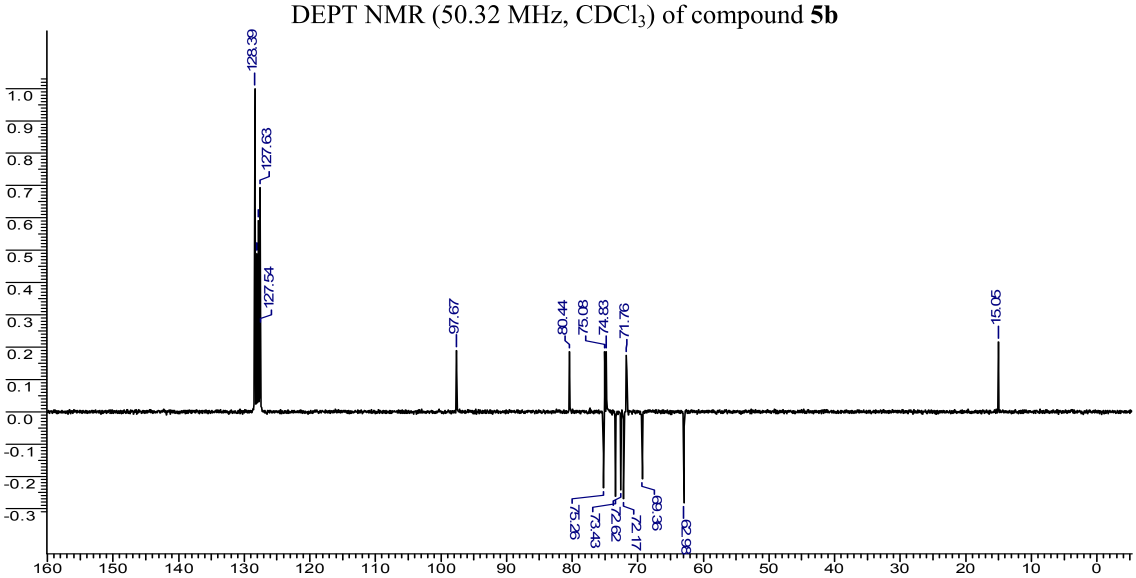
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5b**



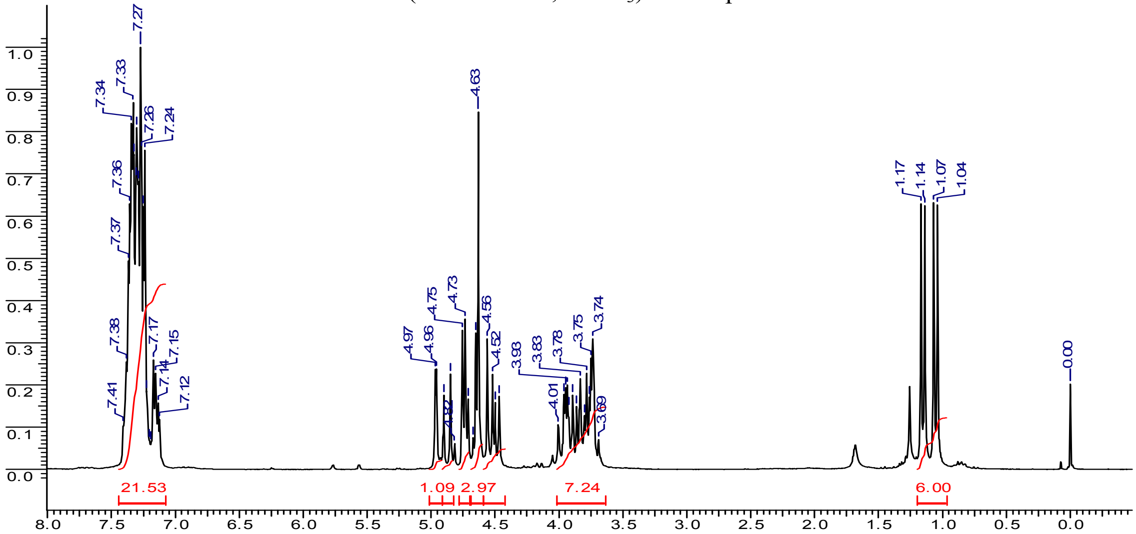
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5b**



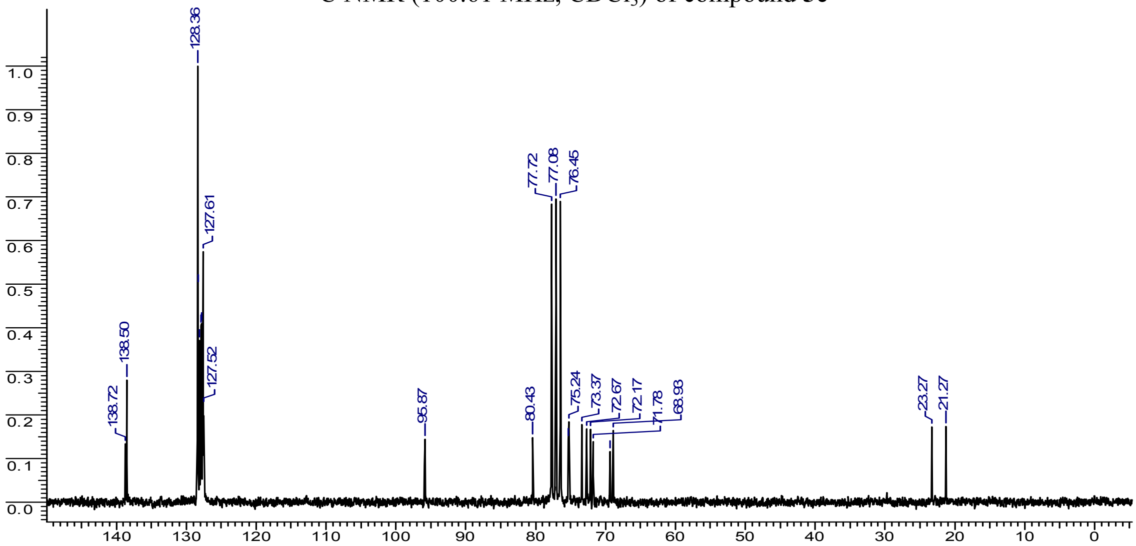
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5b**



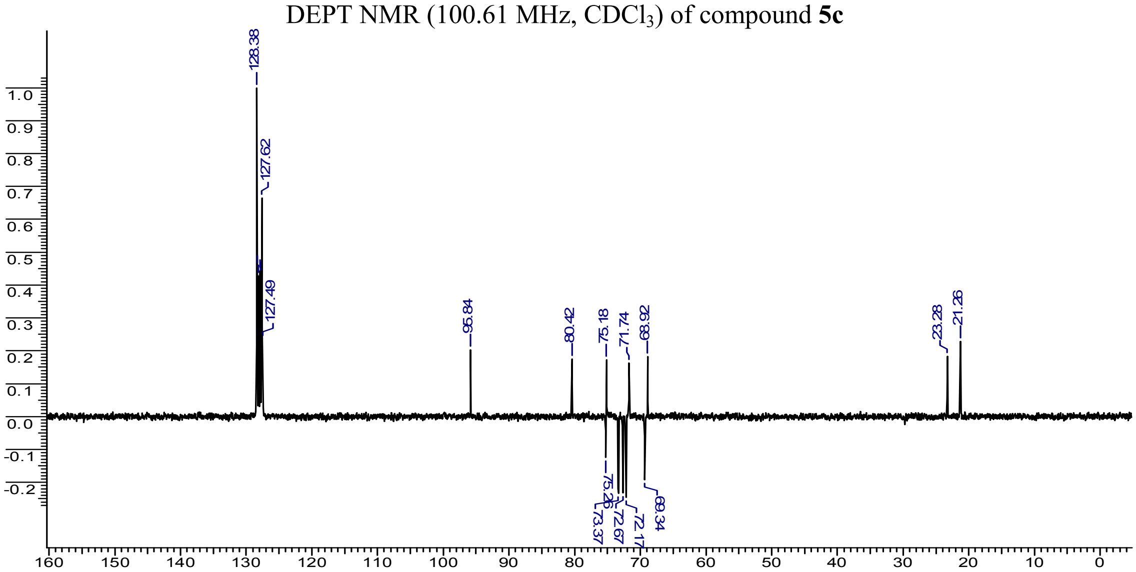
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5c**



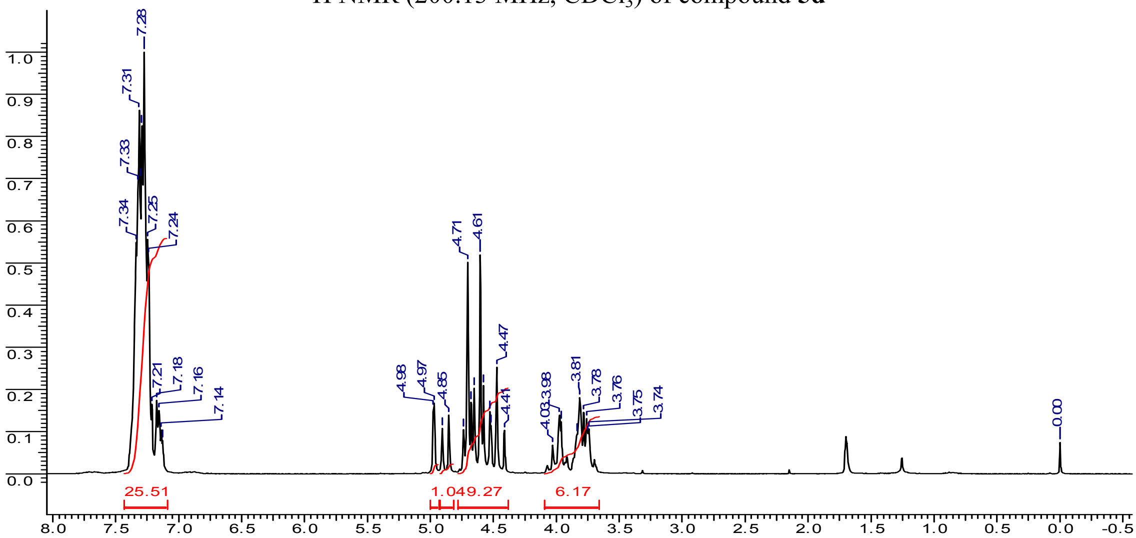
^{13}C NMR (100.61 MHz, $CDCl_3$) of compound **5c**



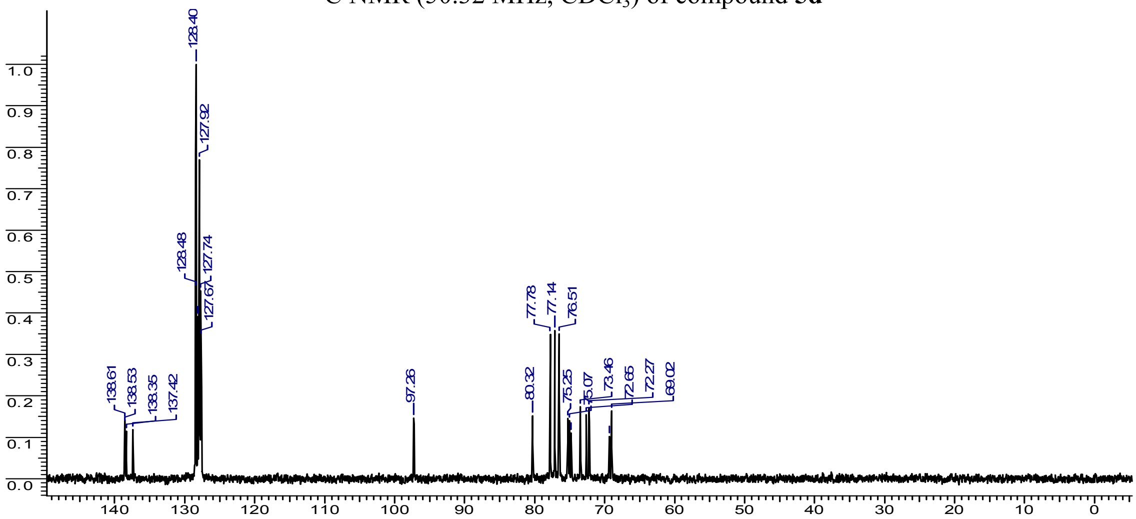
DEPT NMR (100.61 MHz, $CDCl_3$) of compound **5c**



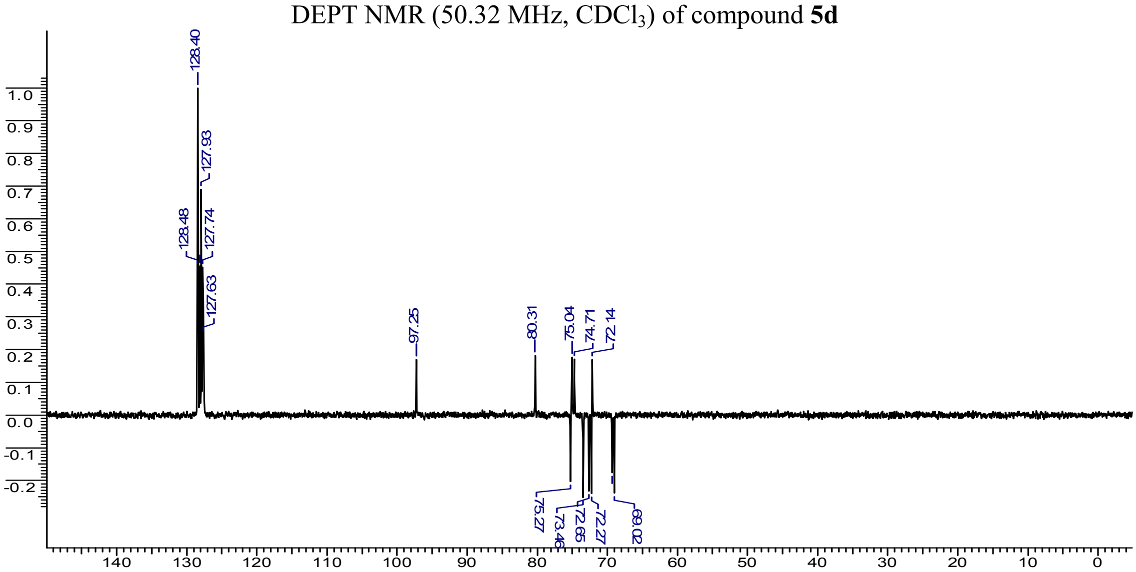
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5d**



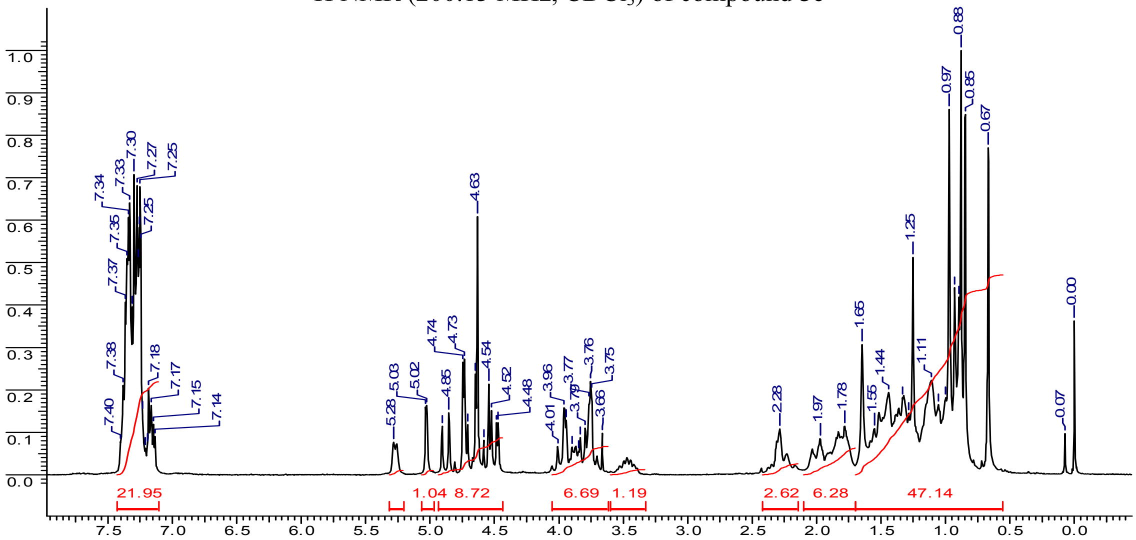
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5d**



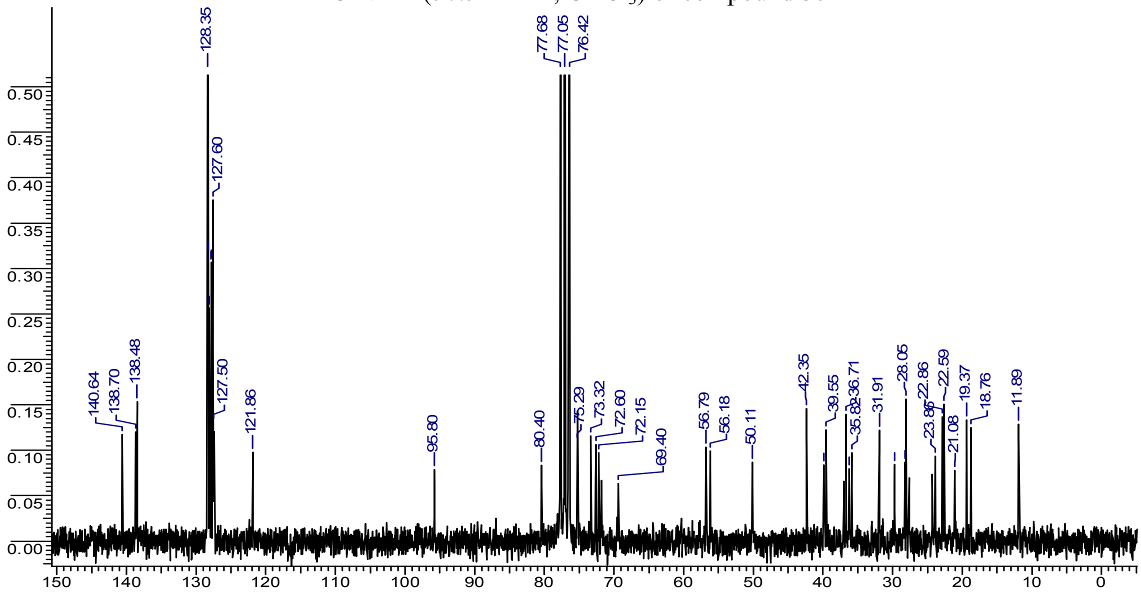
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5d**



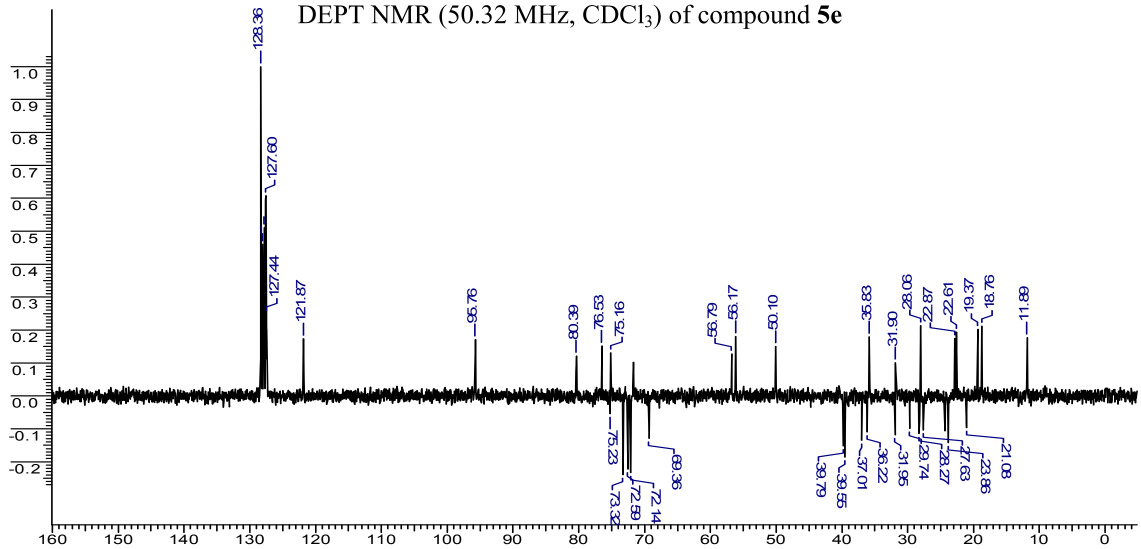
[1]H NMR (200.13 MHz, $CDCl_3$) of compound **5e**



[13]C NMR (50.32 MHz, $CDCl_3$) of compound **5e**



DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5e**



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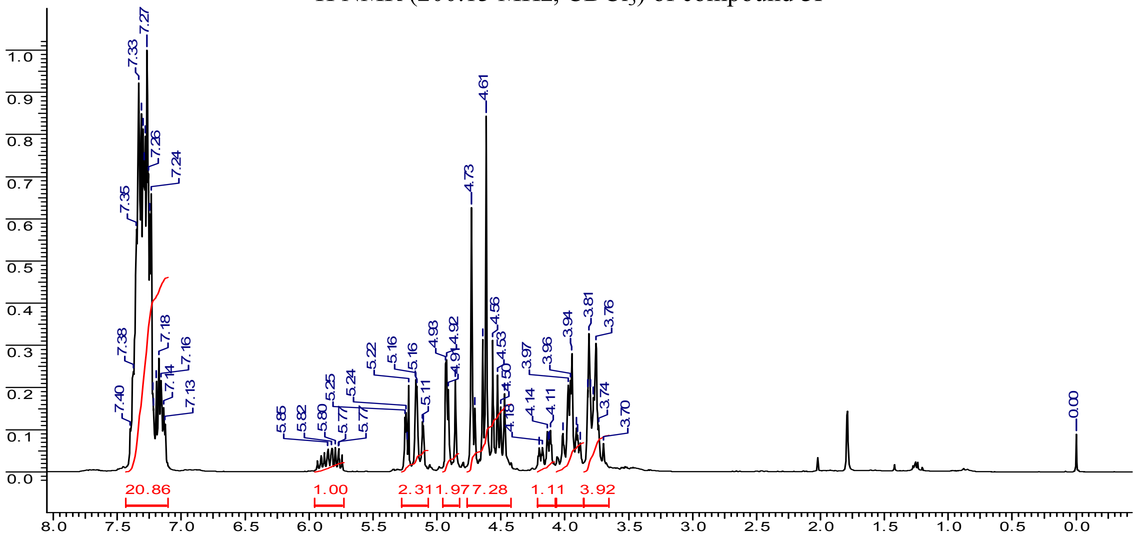
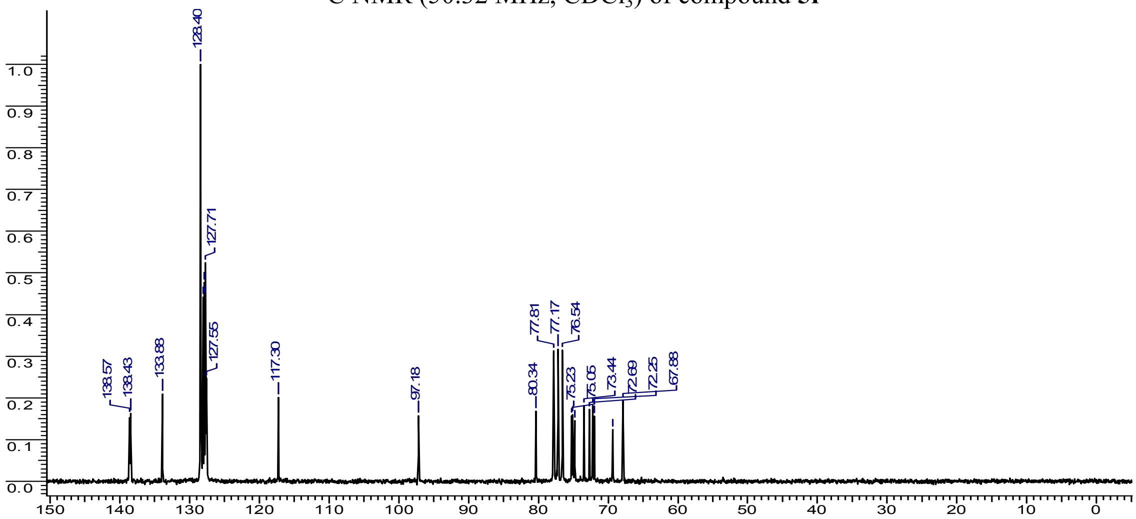
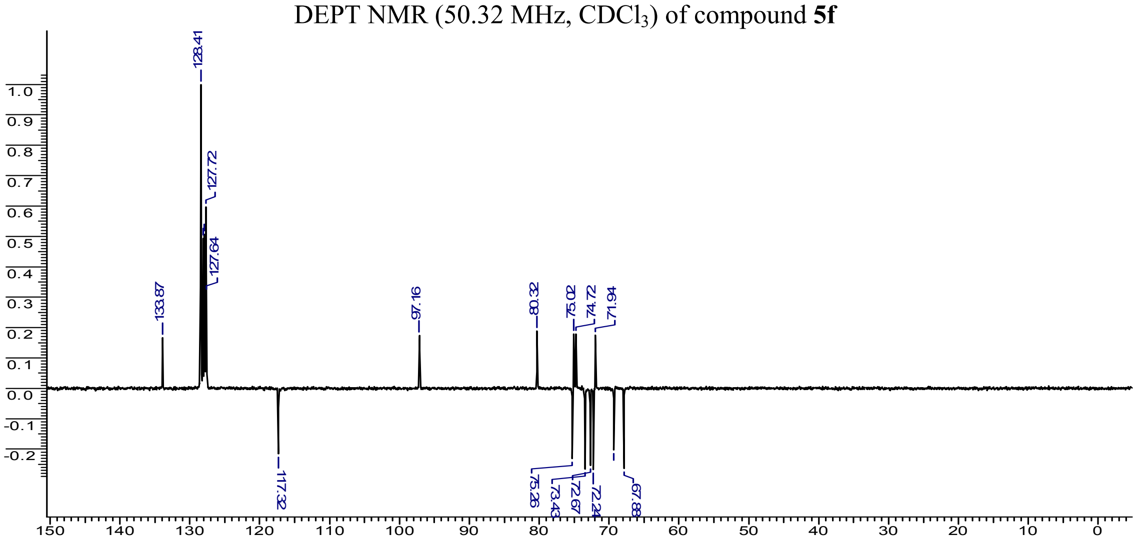


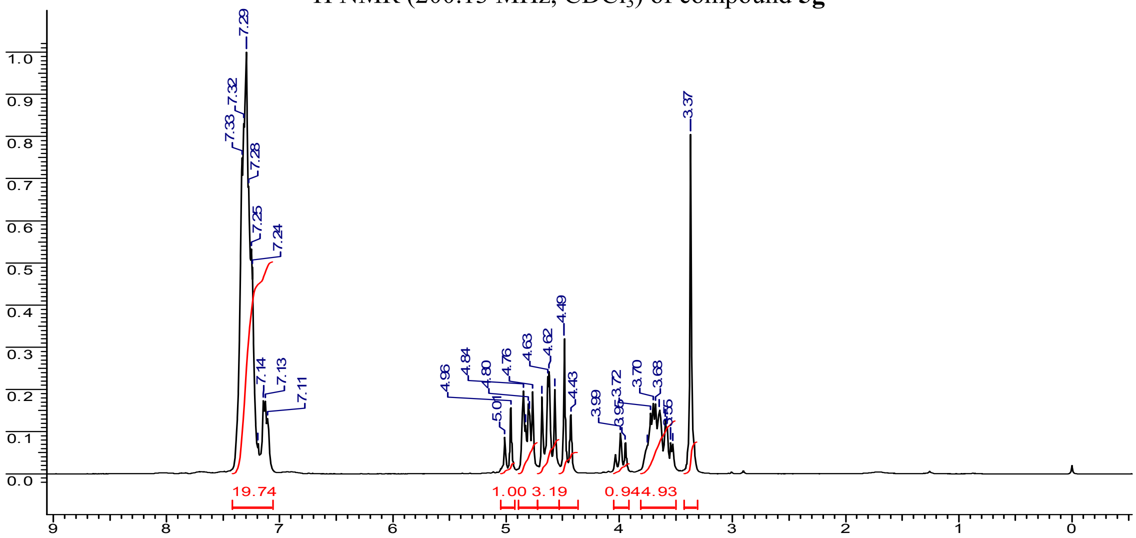
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5f**



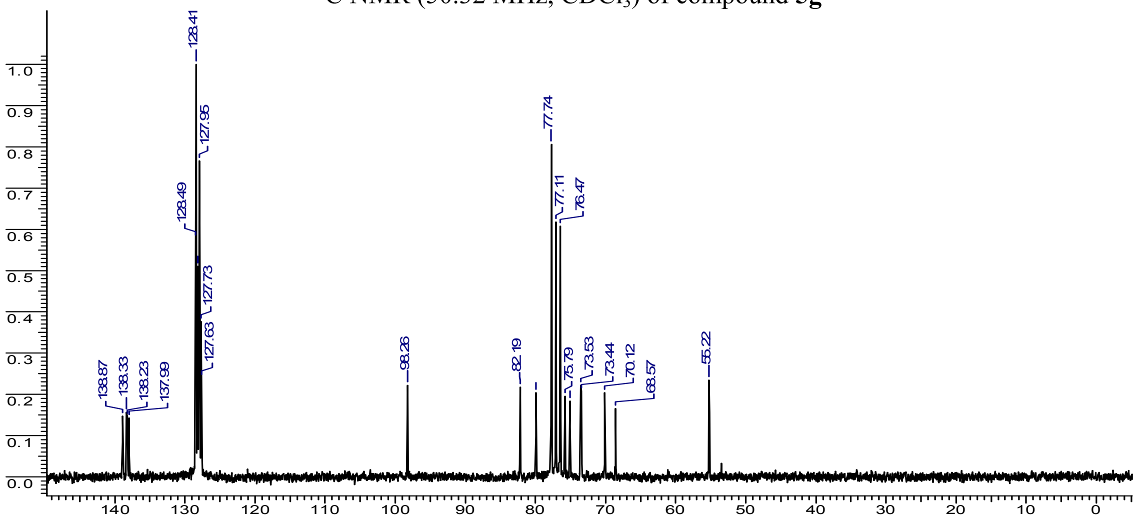
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5f**



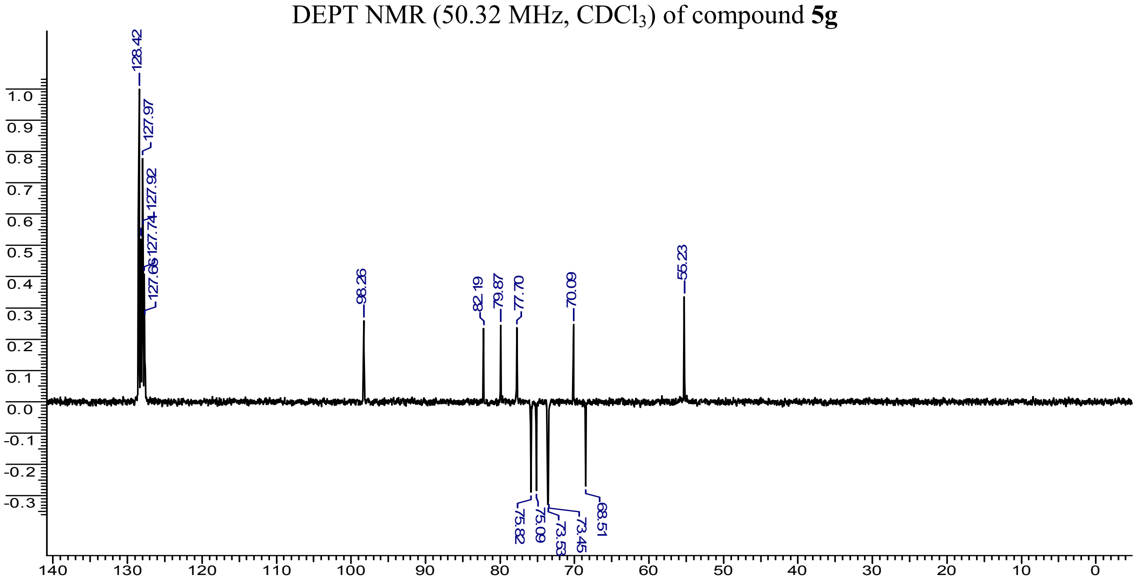
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5g**



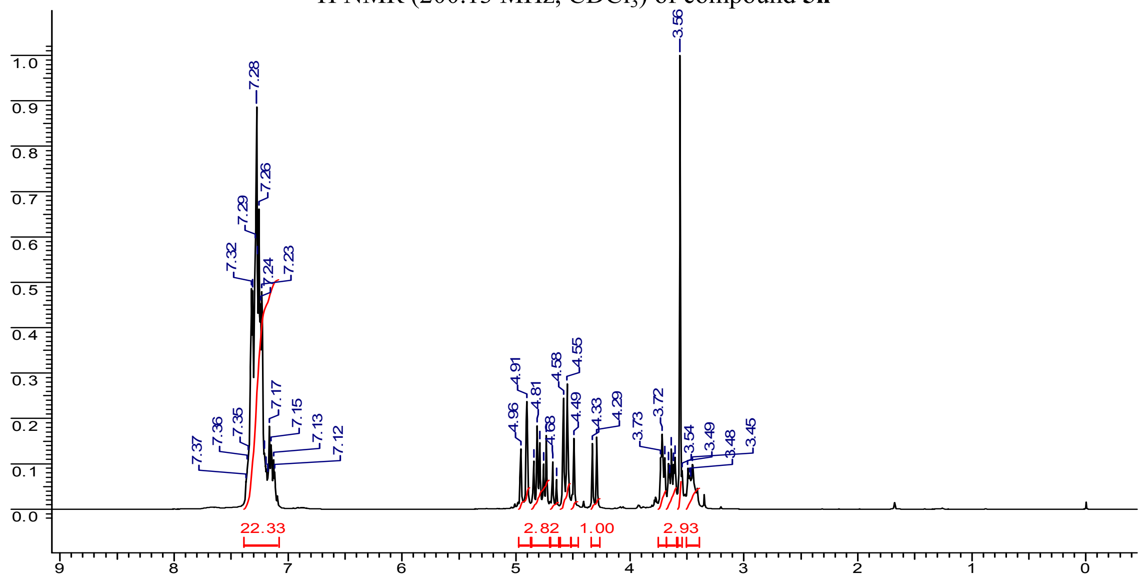
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5g**



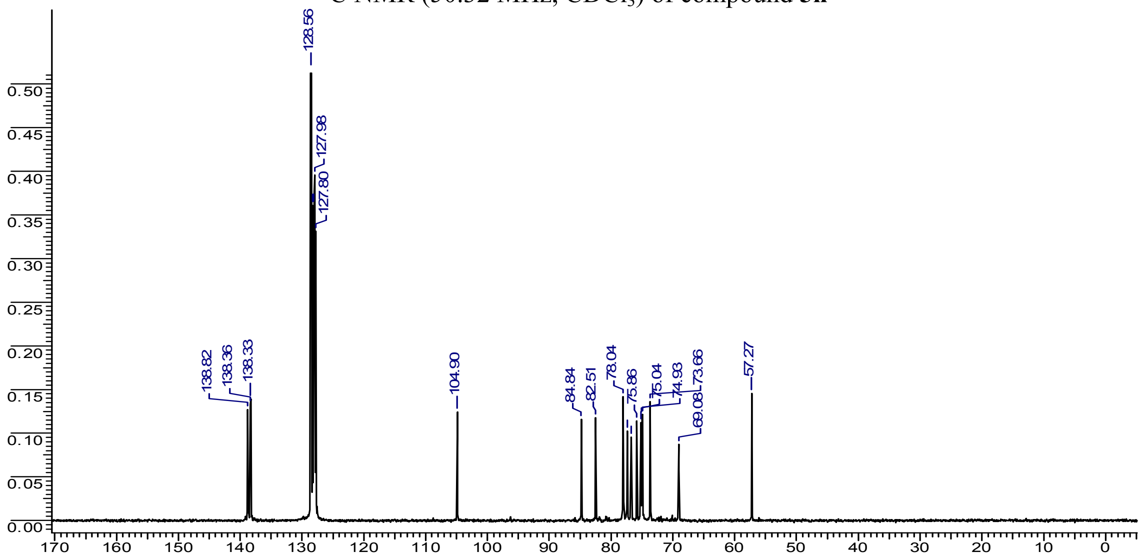
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5g**



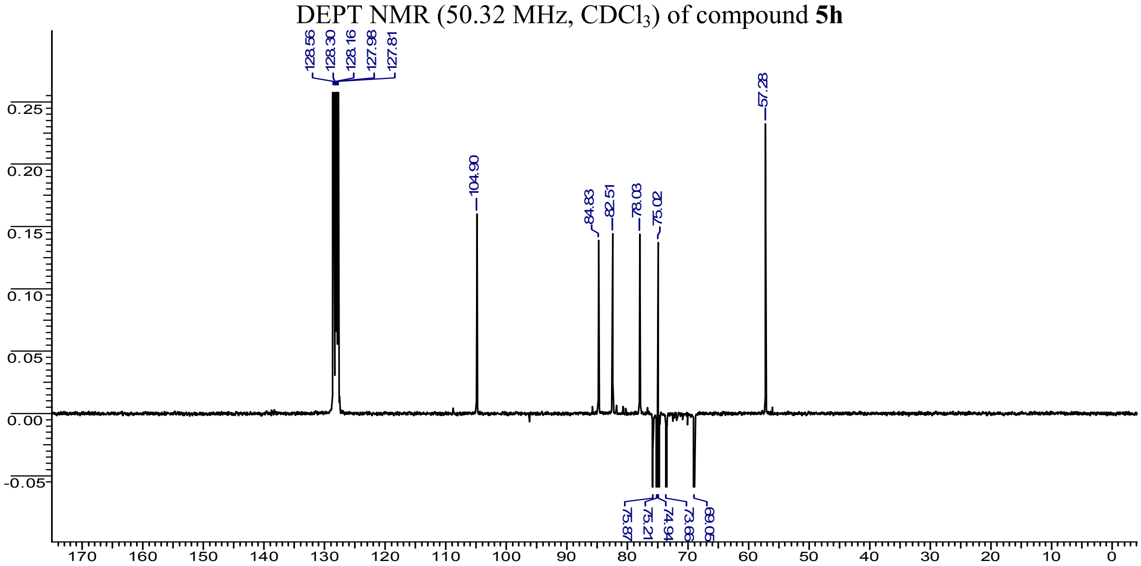
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5h**



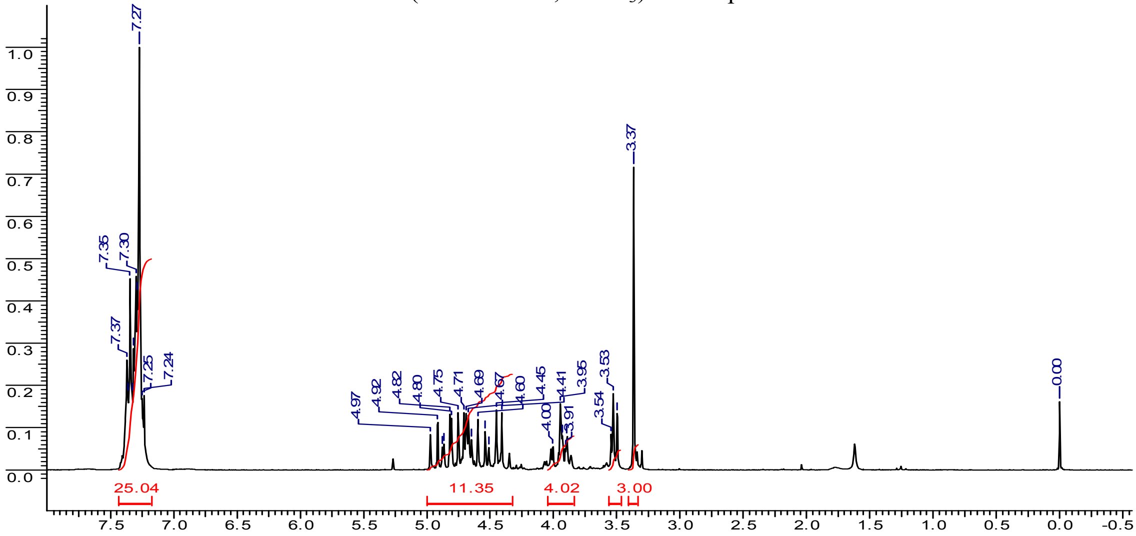
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5h**



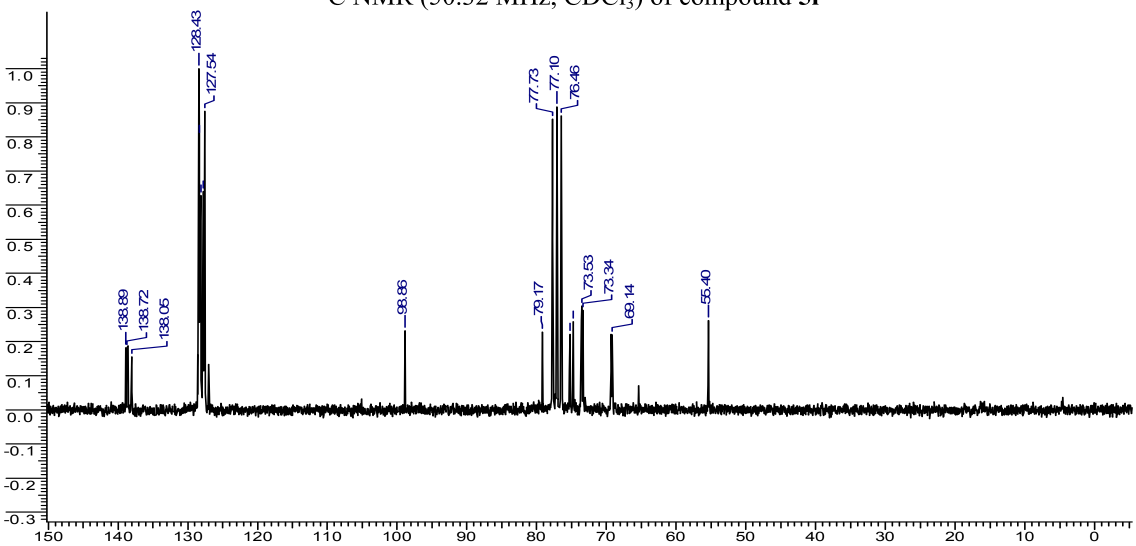
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5h**



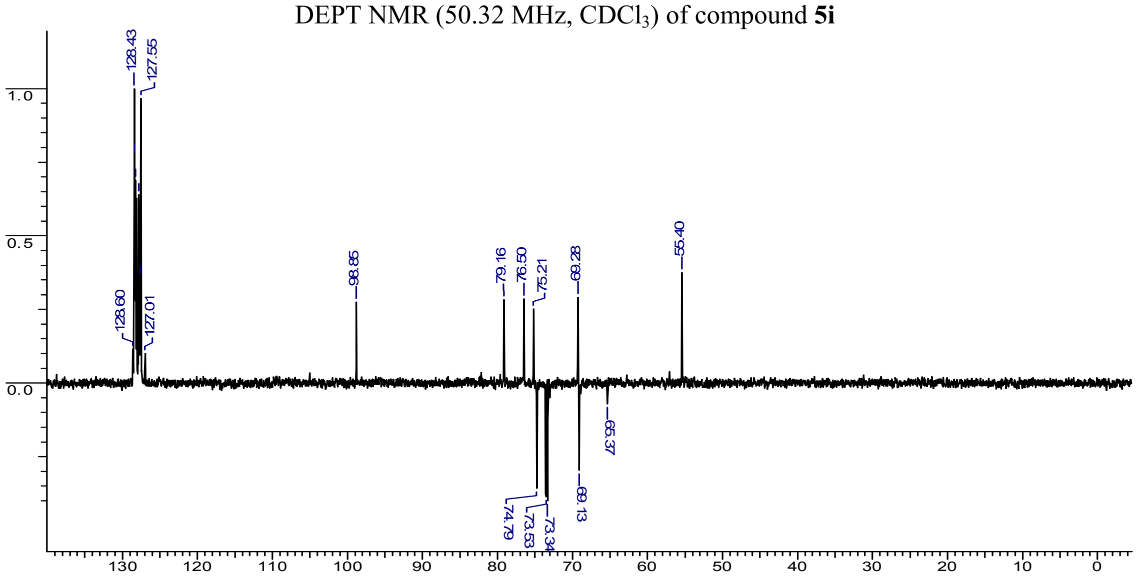
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5i**



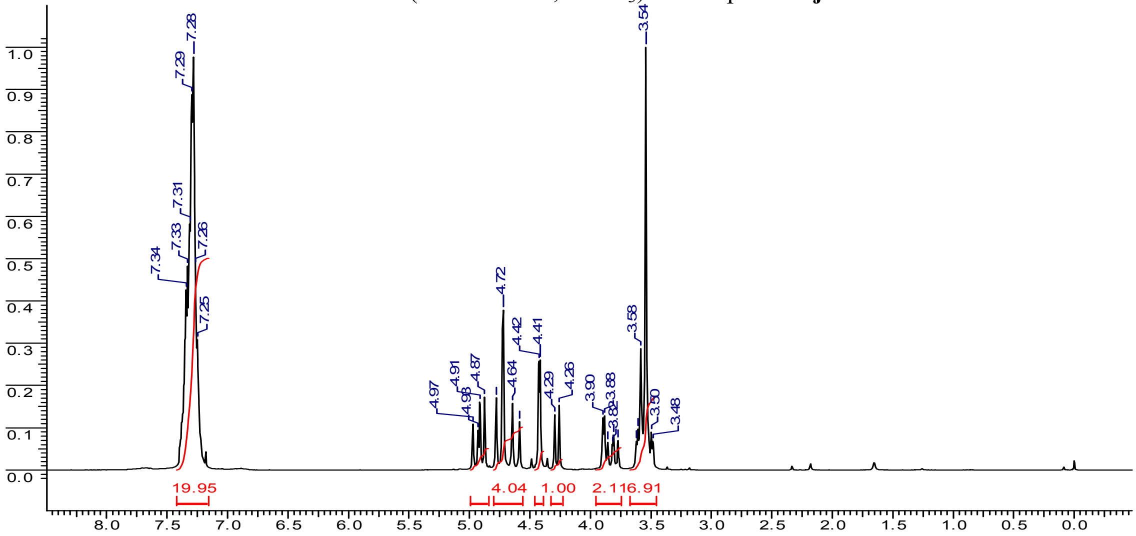
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5i**



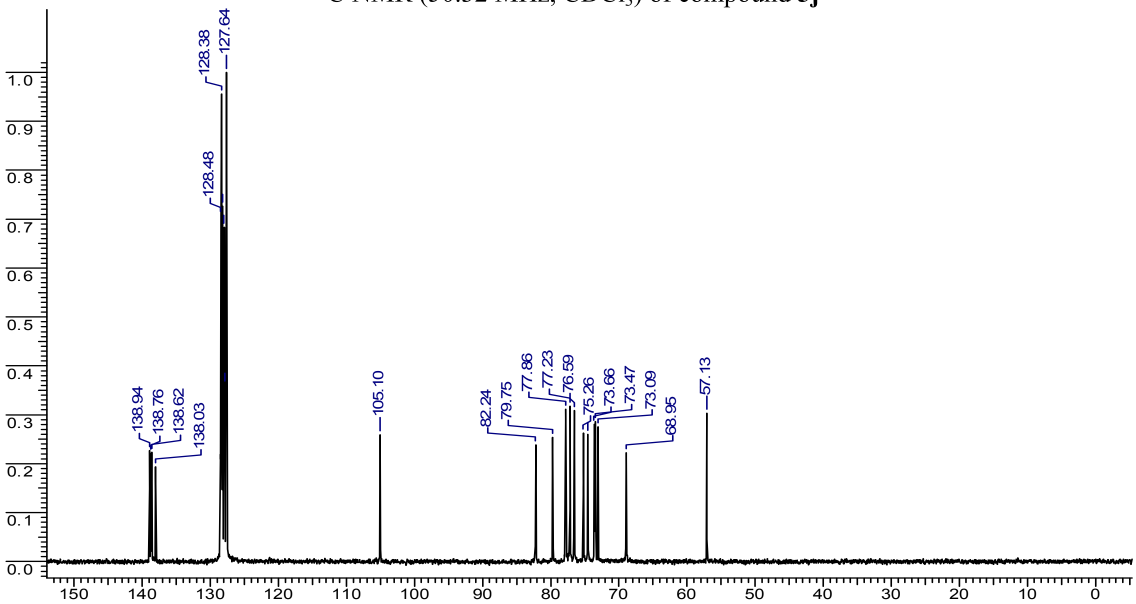
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5i**



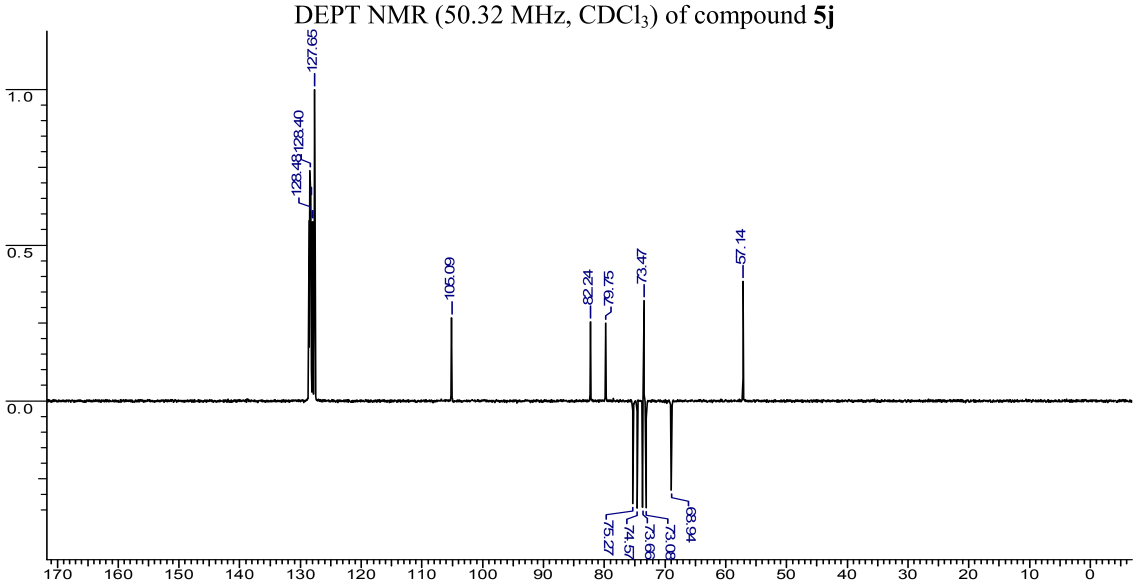
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **5j**



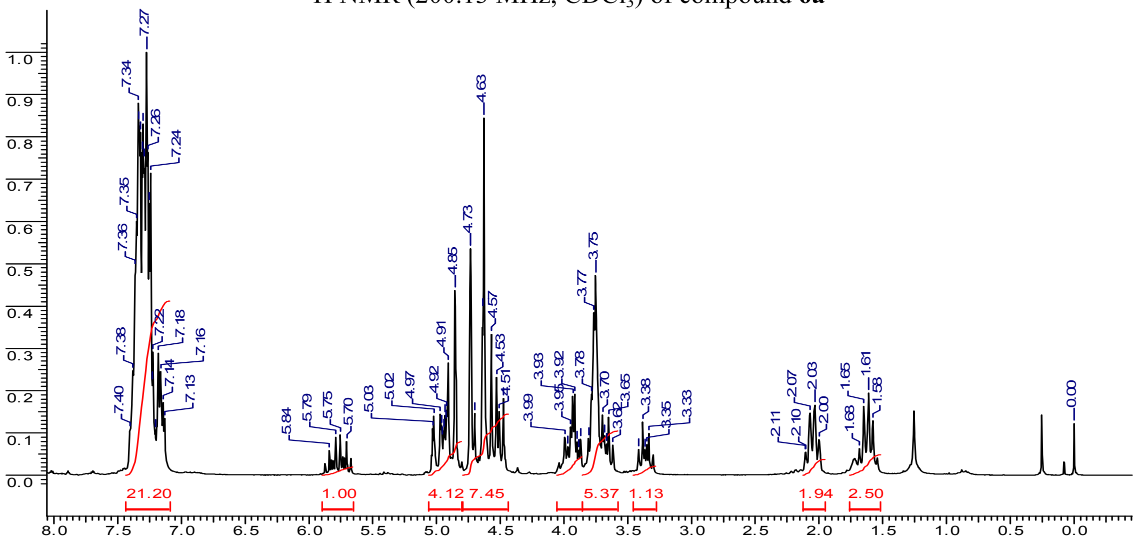
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **5j**



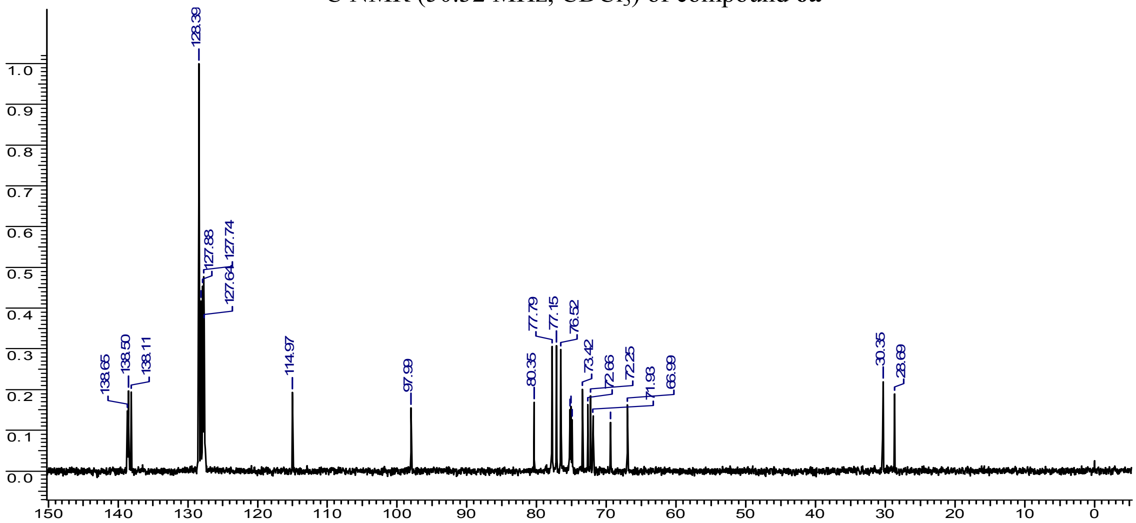
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **5j**



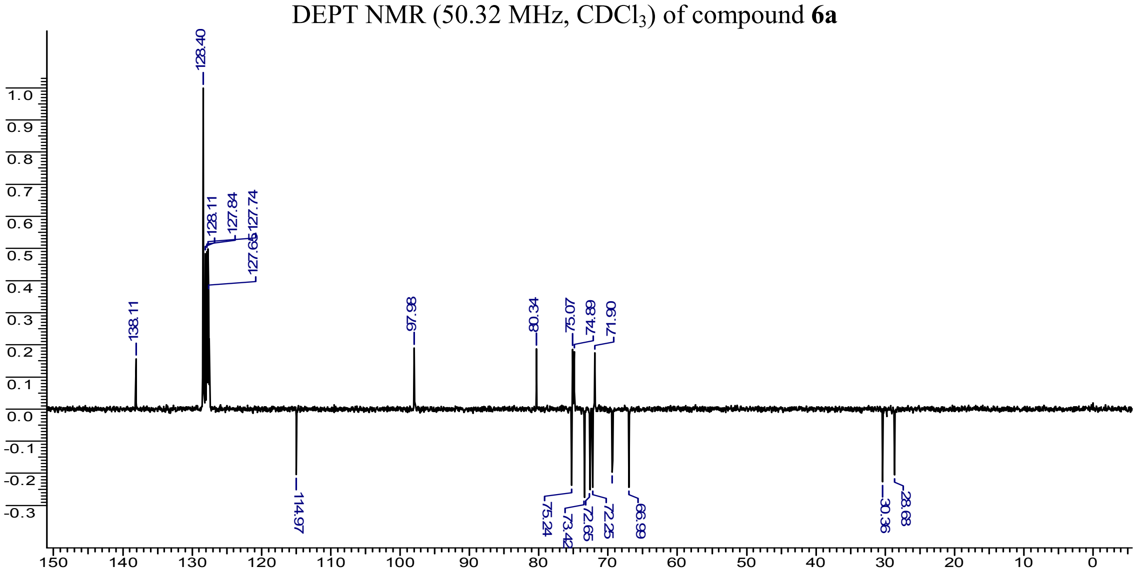
[1]H NMR (200.13 MHz, $CDCl_3$) of compound **6a**



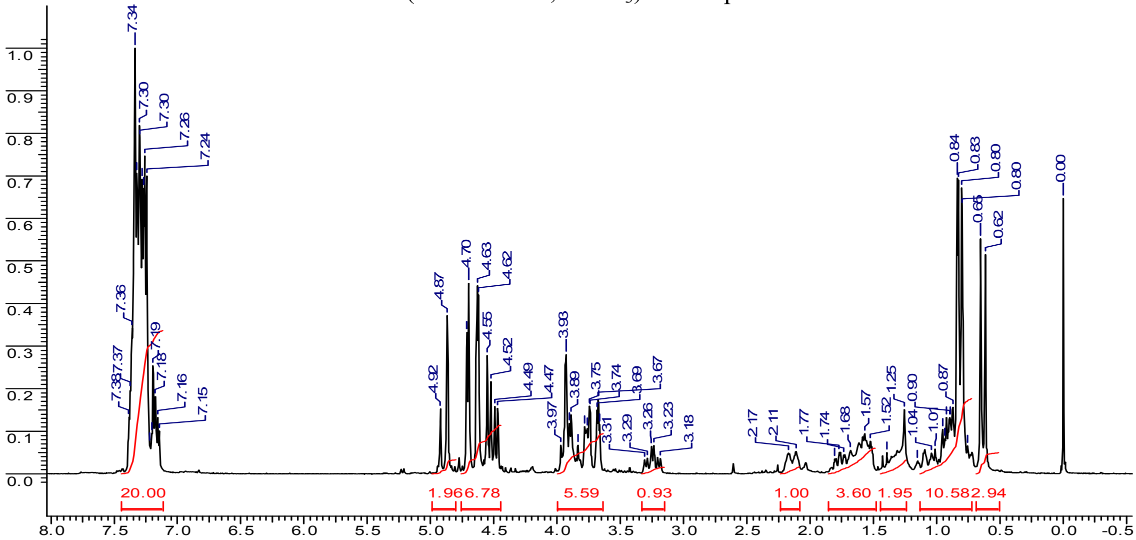
[13]C NMR (50.32 MHz, $CDCl_3$) of compound **6a**



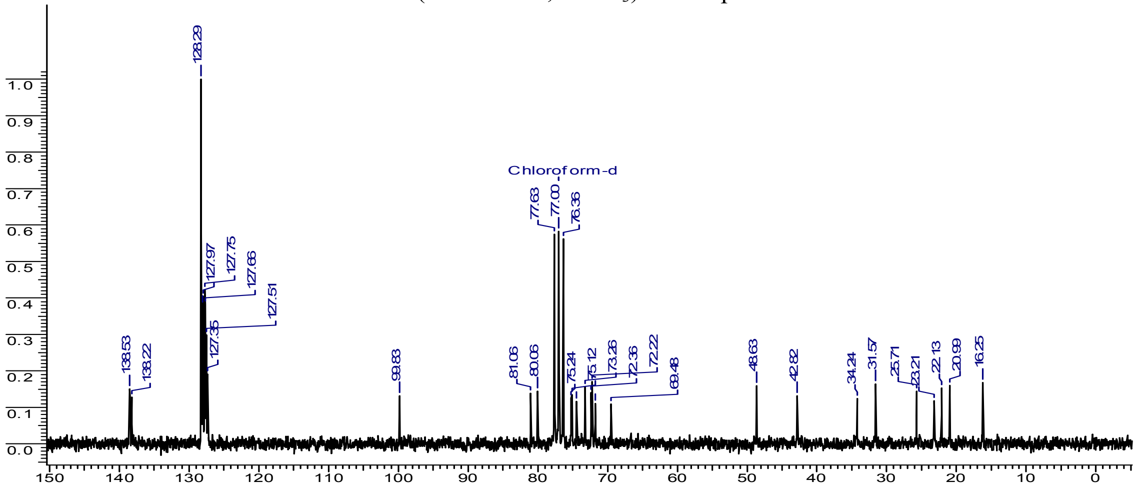
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **6a**



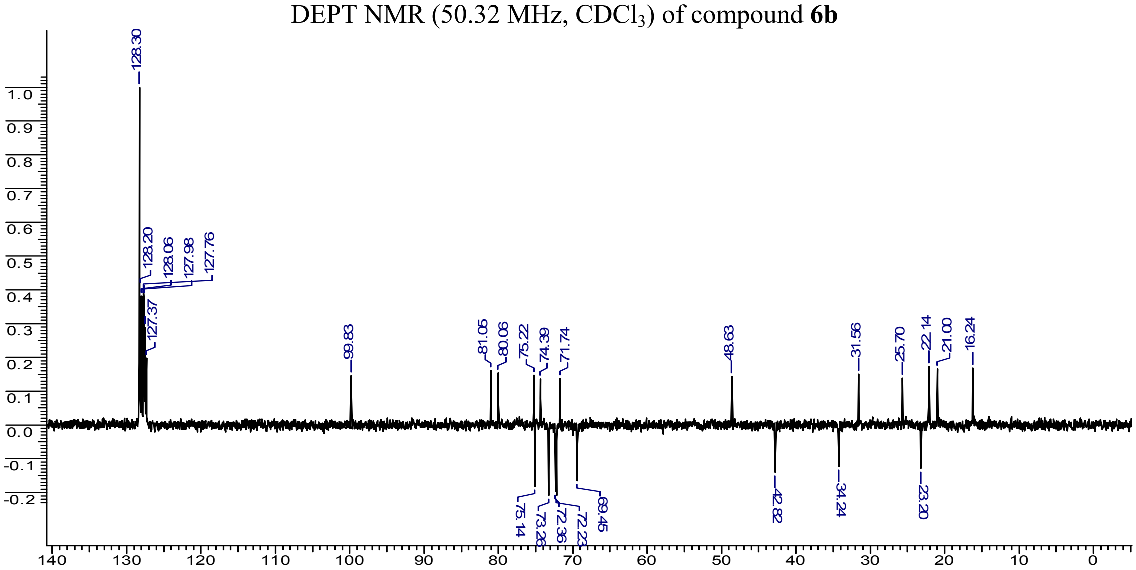
[1]H NMR (200.13 MHz, $CDCl_3$) of compound **6b**



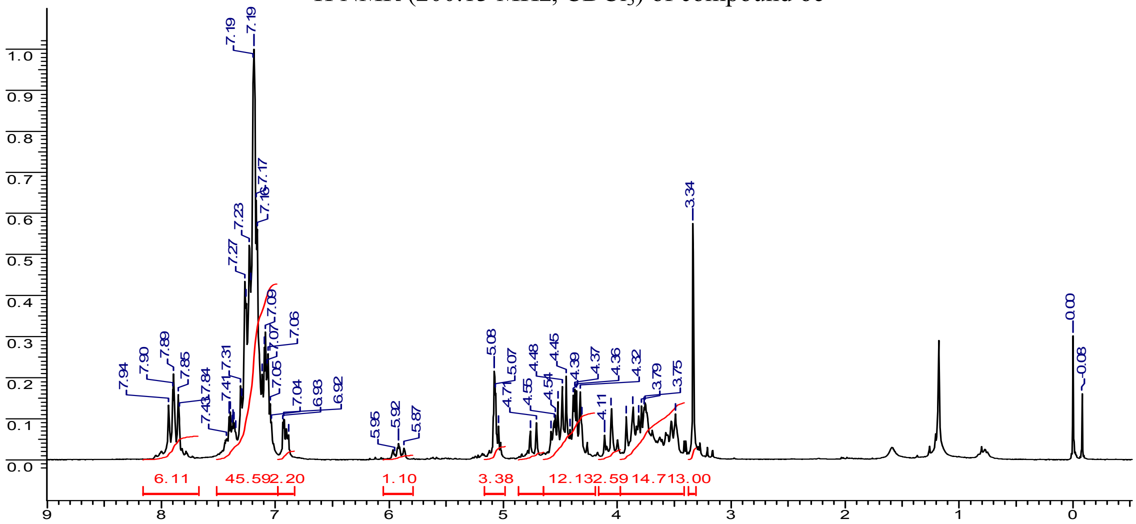
[13]C NMR (50.32 MHz, $CDCl_3$) of compound **6b**



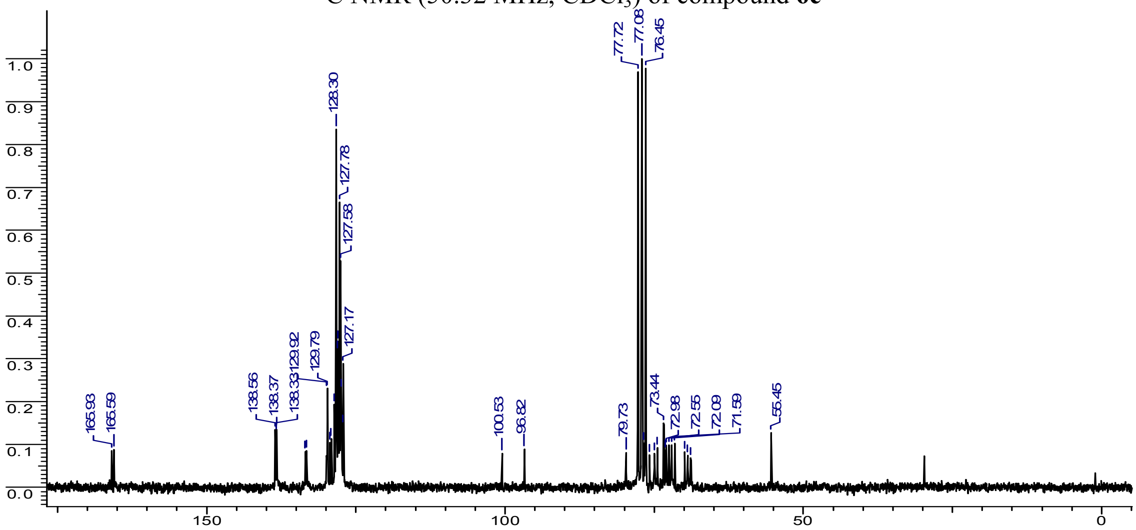
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **6b**



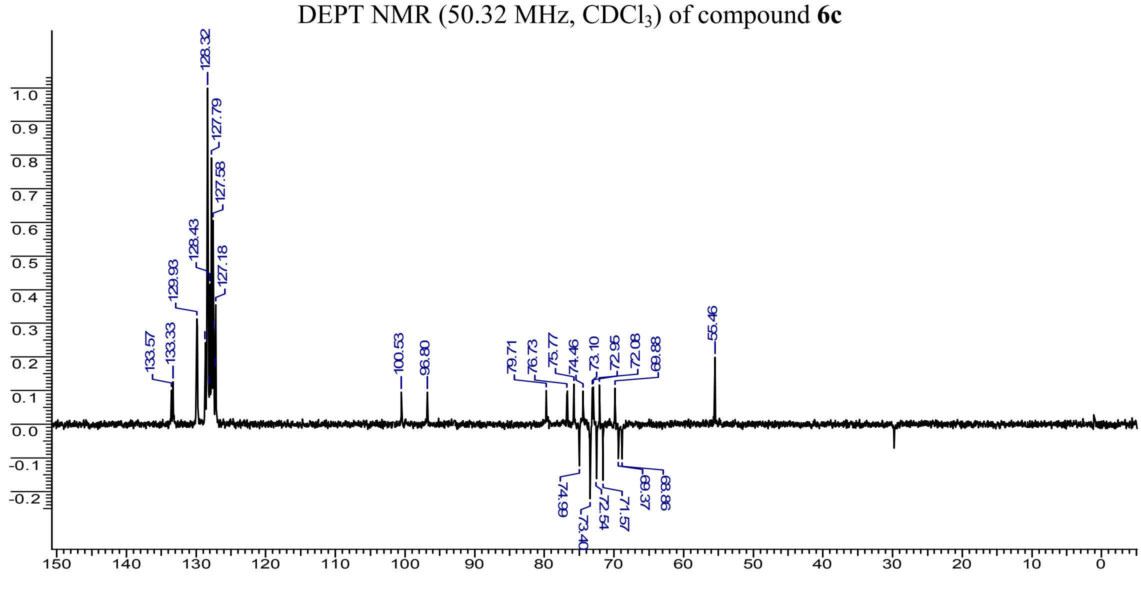
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **6c**



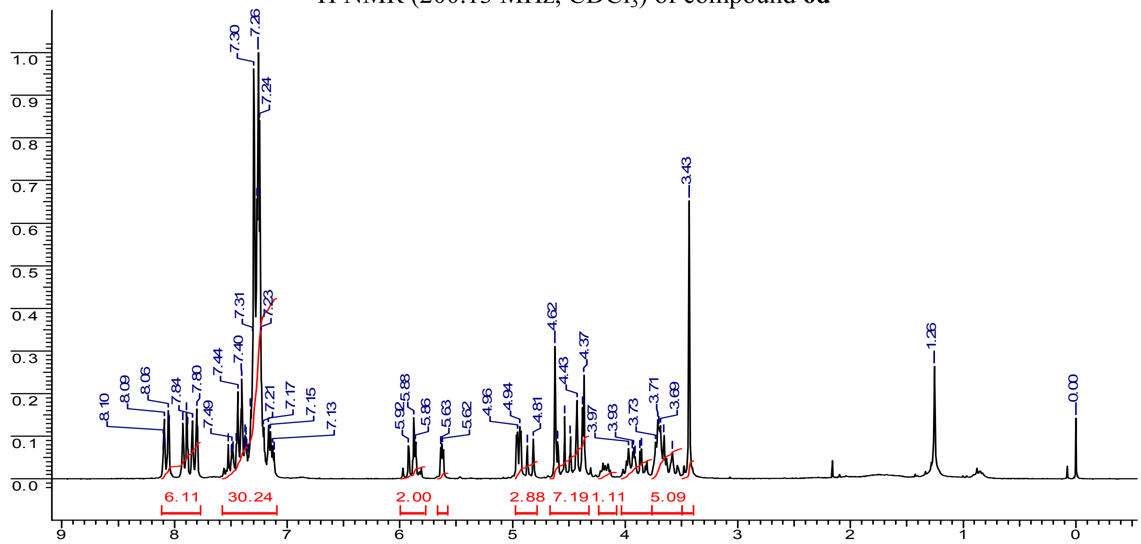
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **6c**



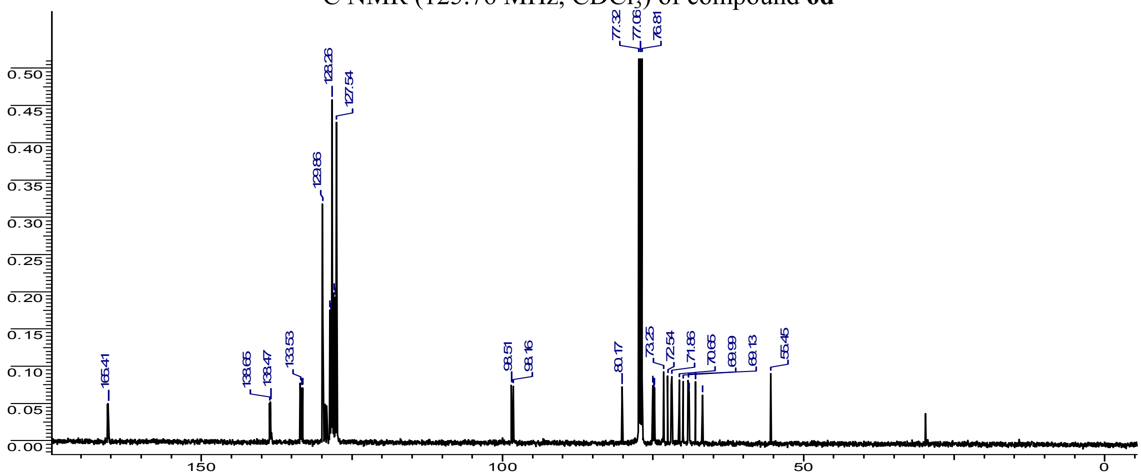
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **6c**



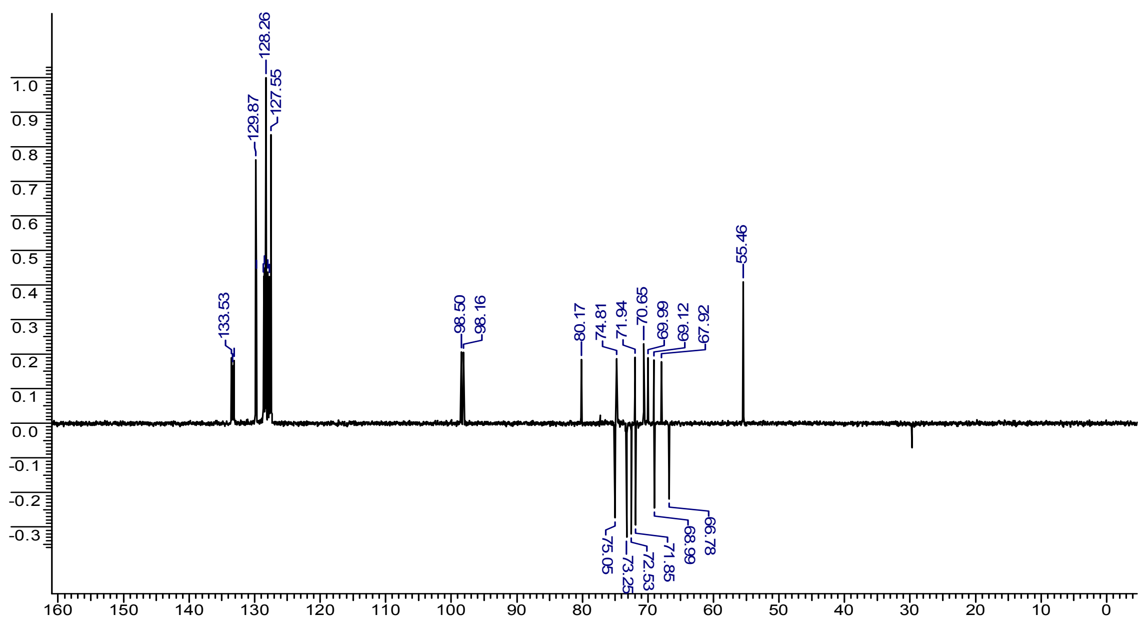
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **6d**



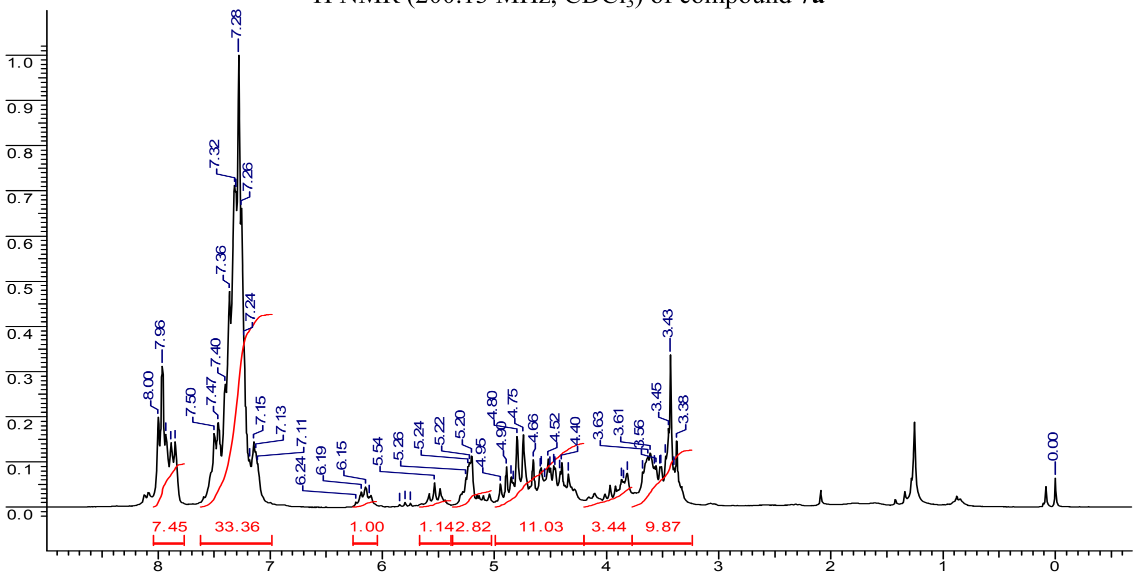
^{13}C NMR (125.76 MHz, $CDCl_3$) of compound **6d**



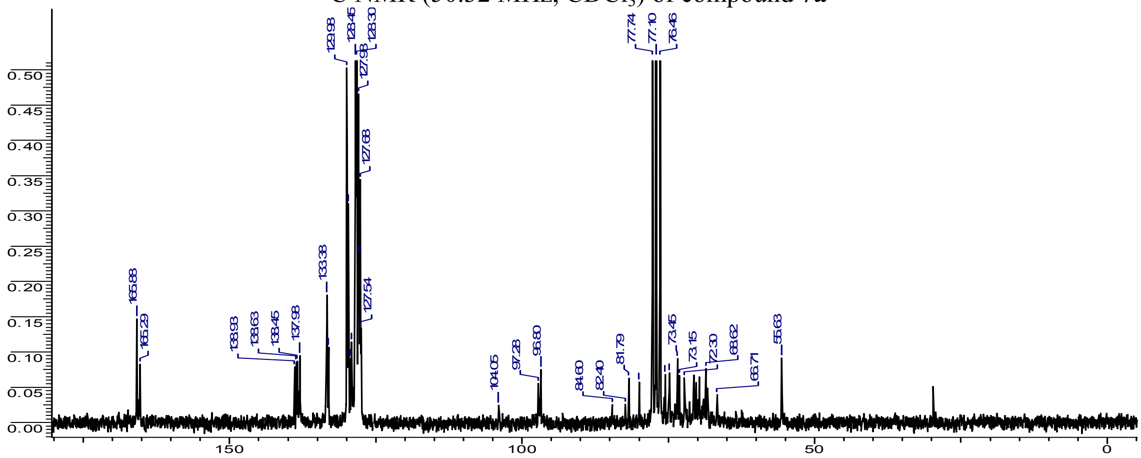
DEPT NMR (125.76 MHz, $CDCl_3$) of compound **6d**



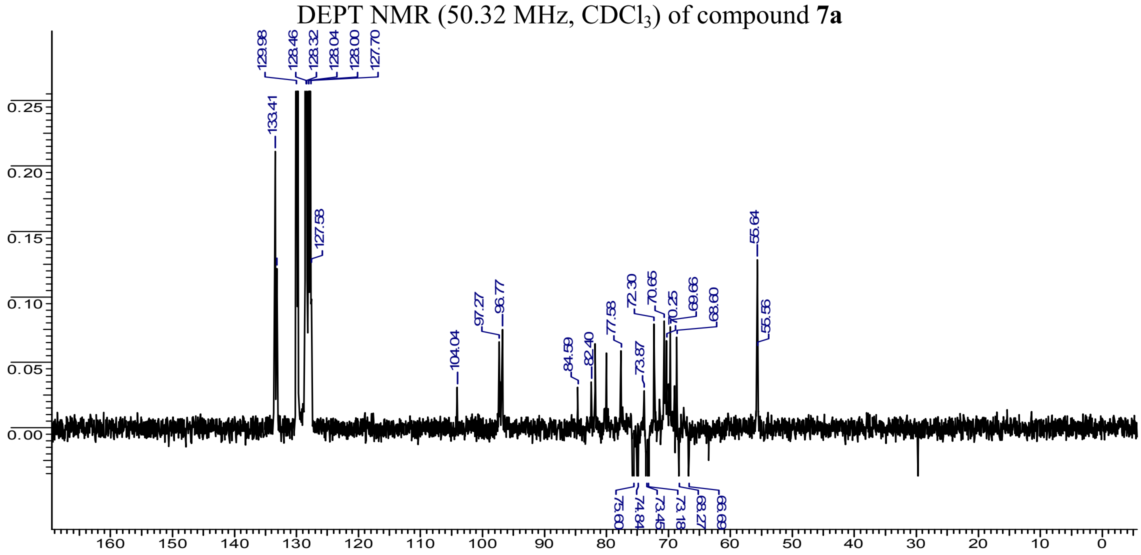
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **7a**



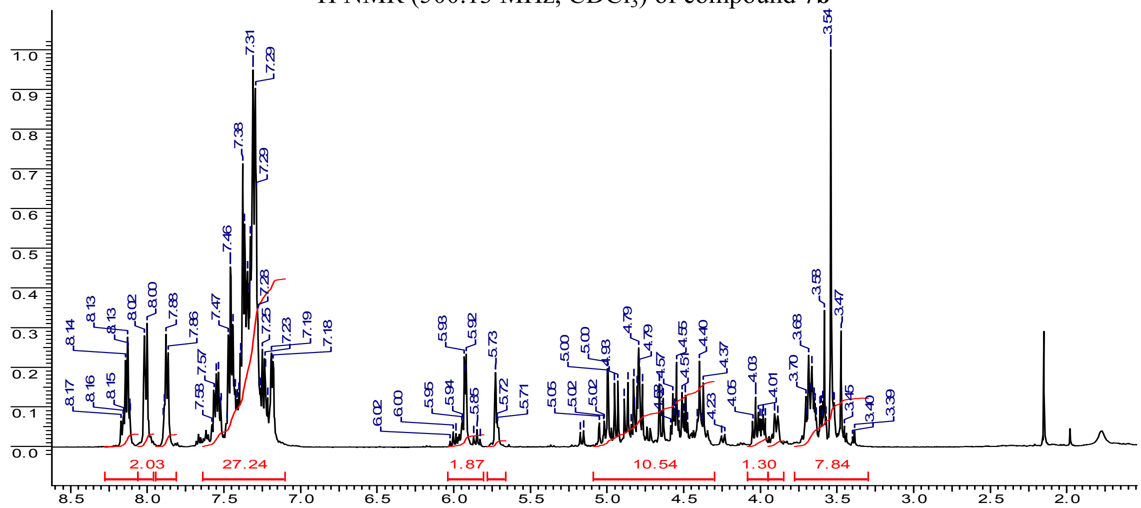
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **7a**



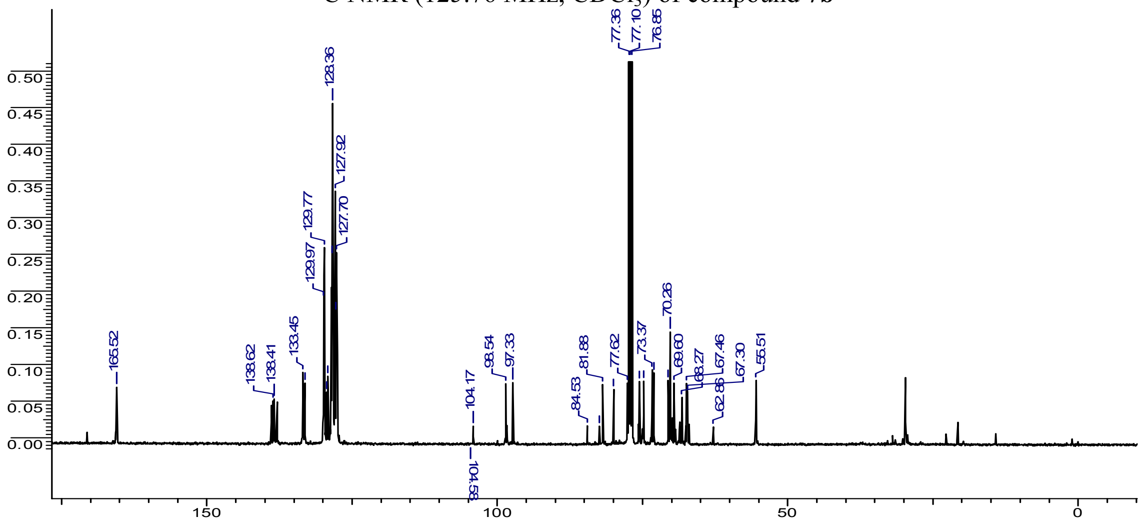
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **7a**



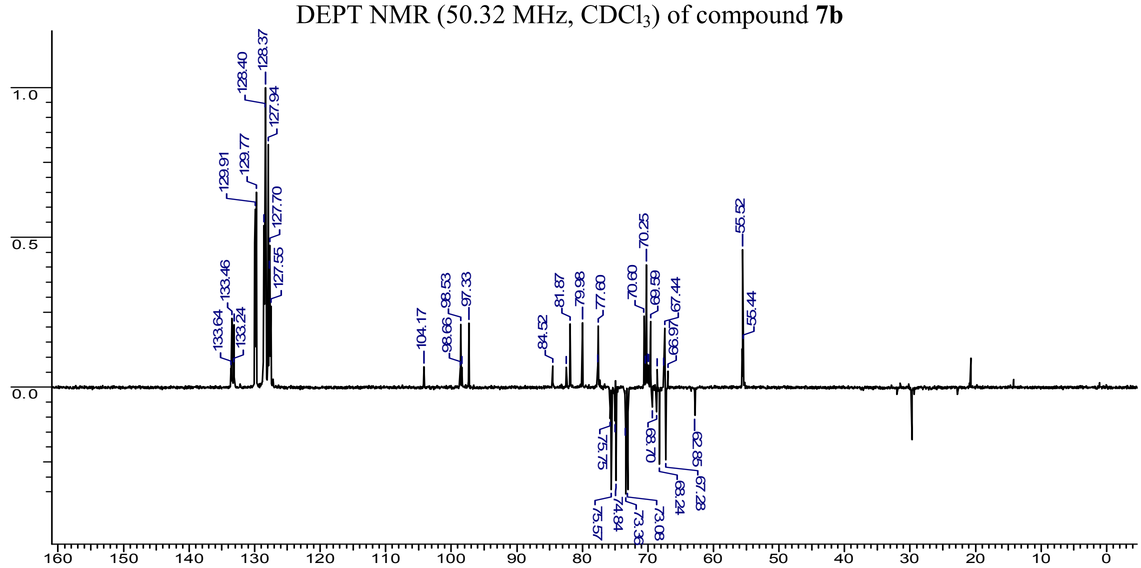
^{1}H NMR (500.13 MHz, $CDCl_3$) of compound **7b**



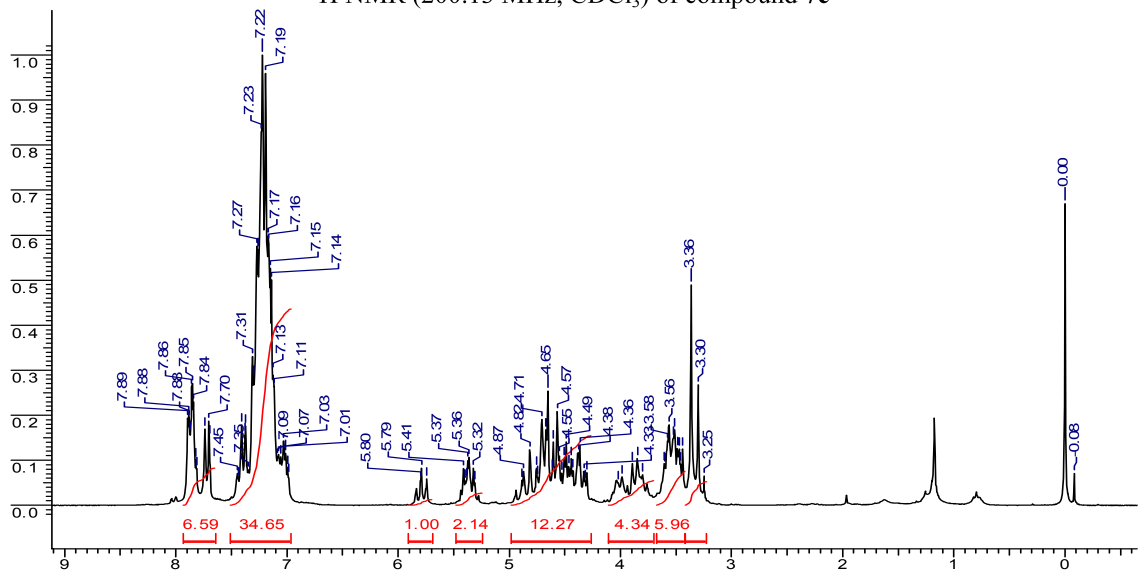
^{13}C NMR (125.76 MHz, $CDCl_3$) of compound **7b**



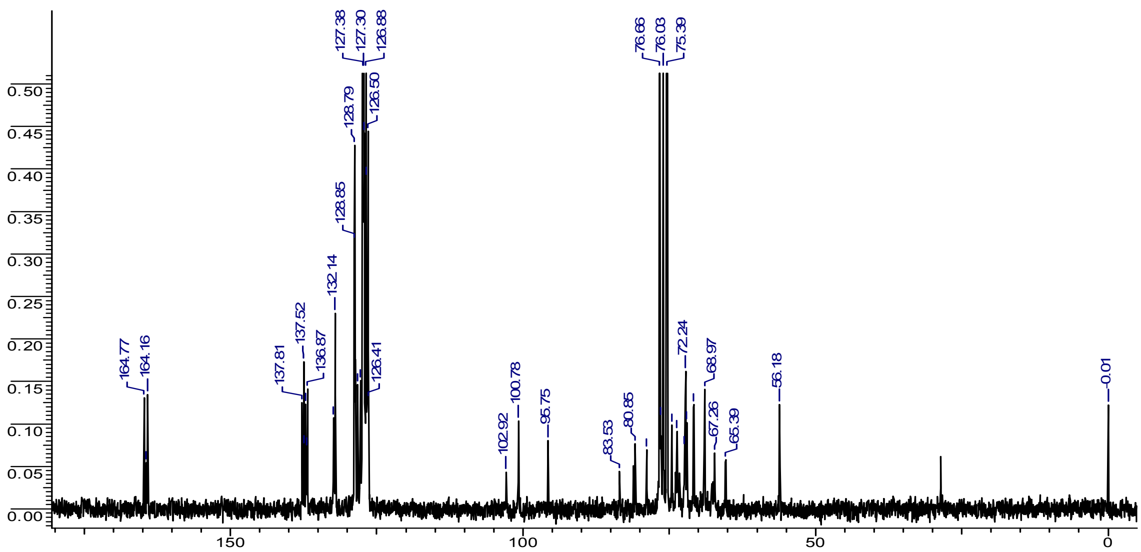
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **7b**



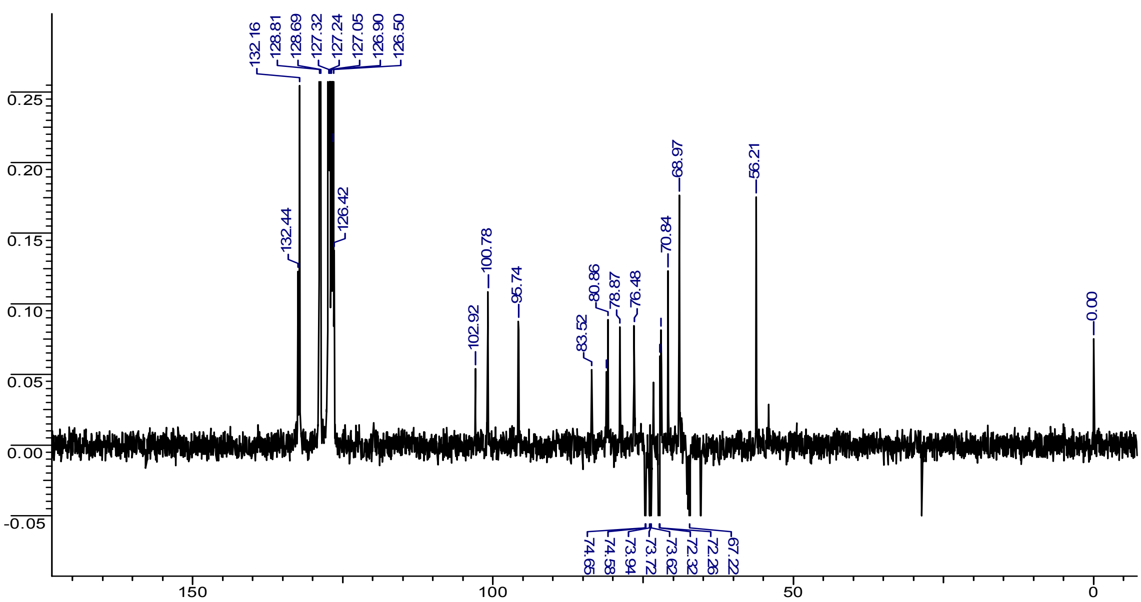
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **7c**



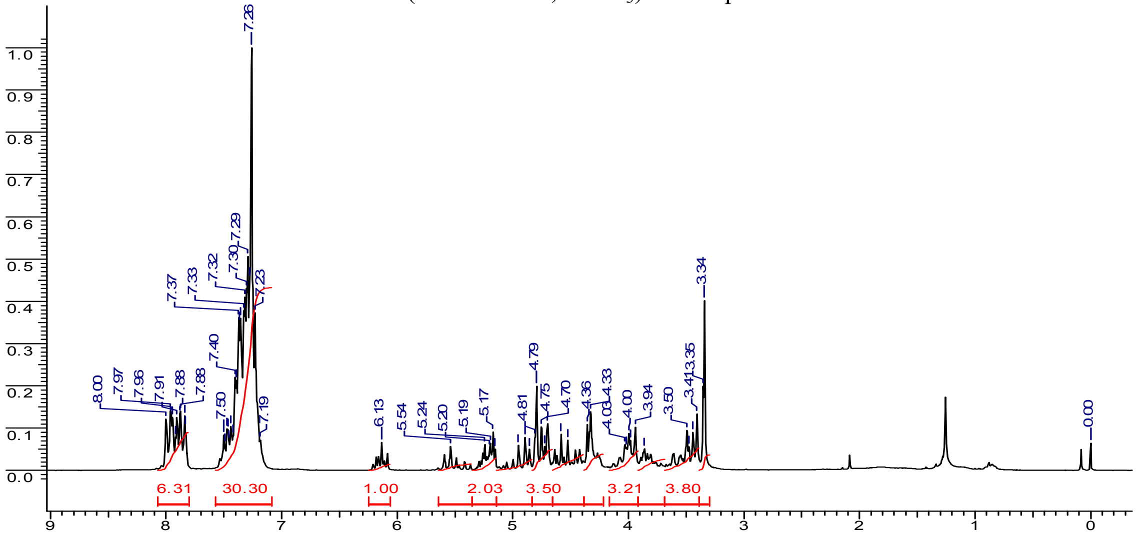
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **7c**



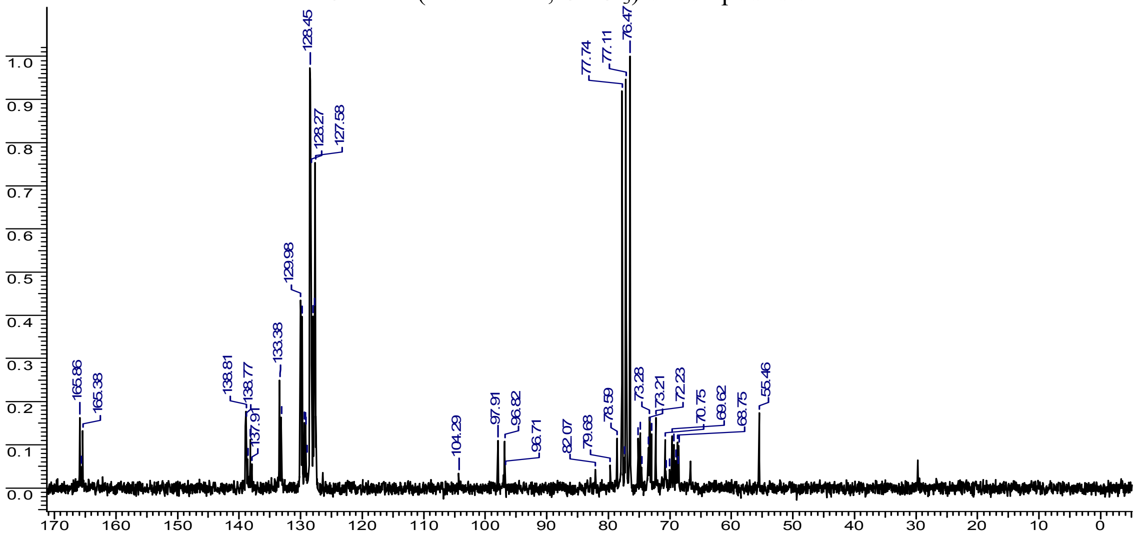
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **7c**



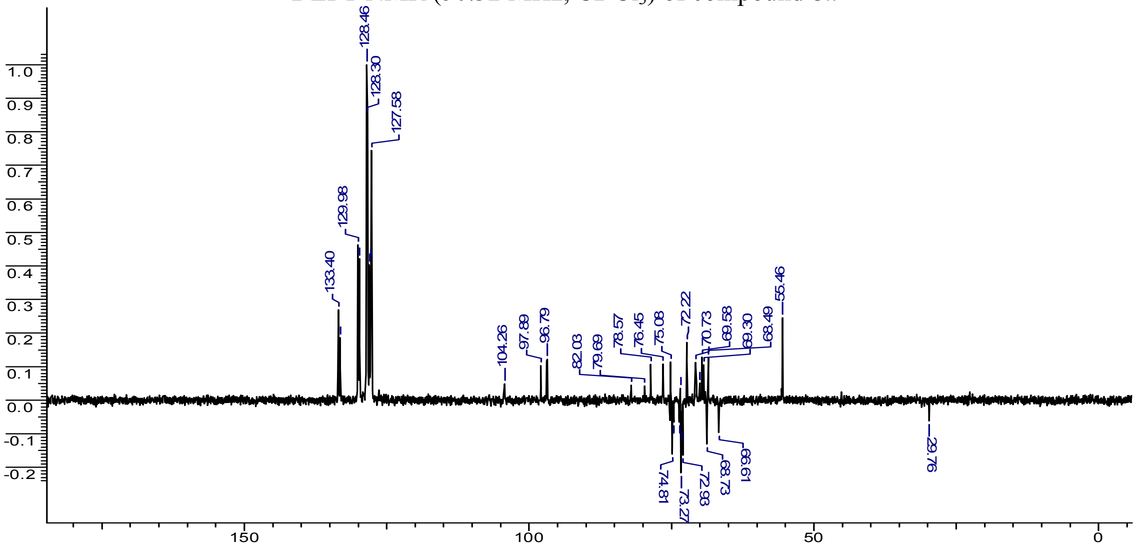
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **8a**



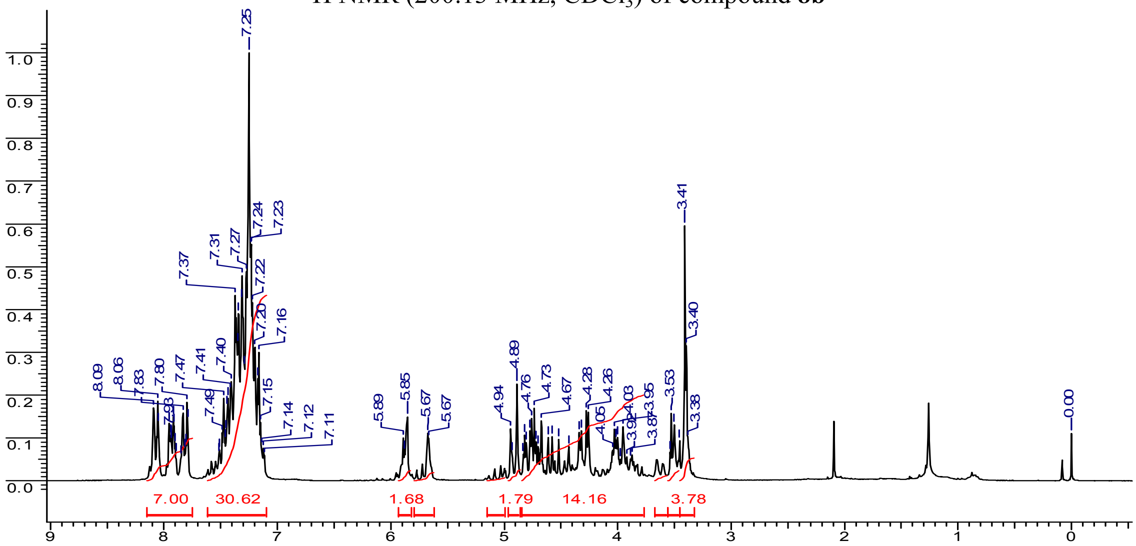
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **8a**



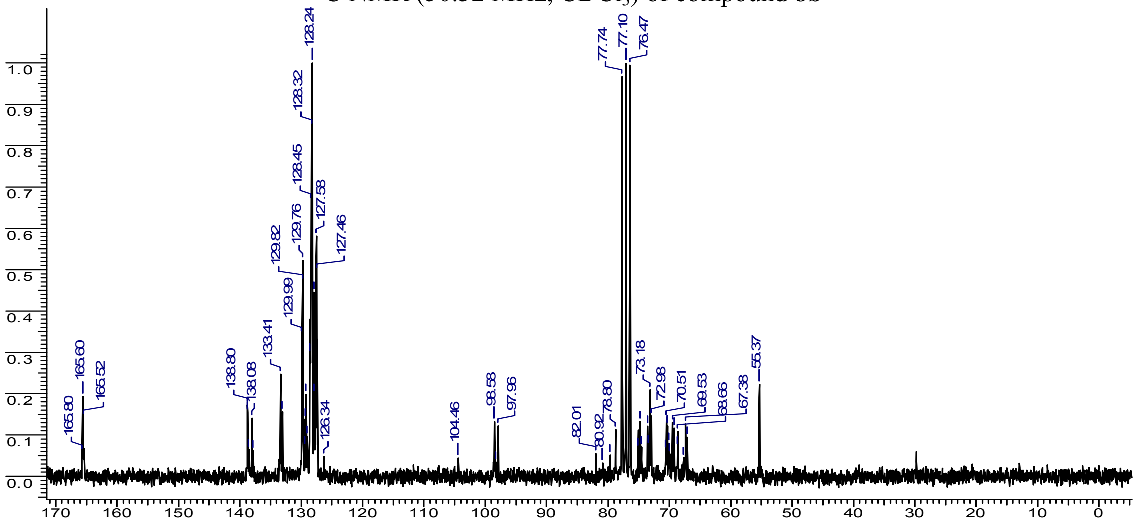
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **8a**



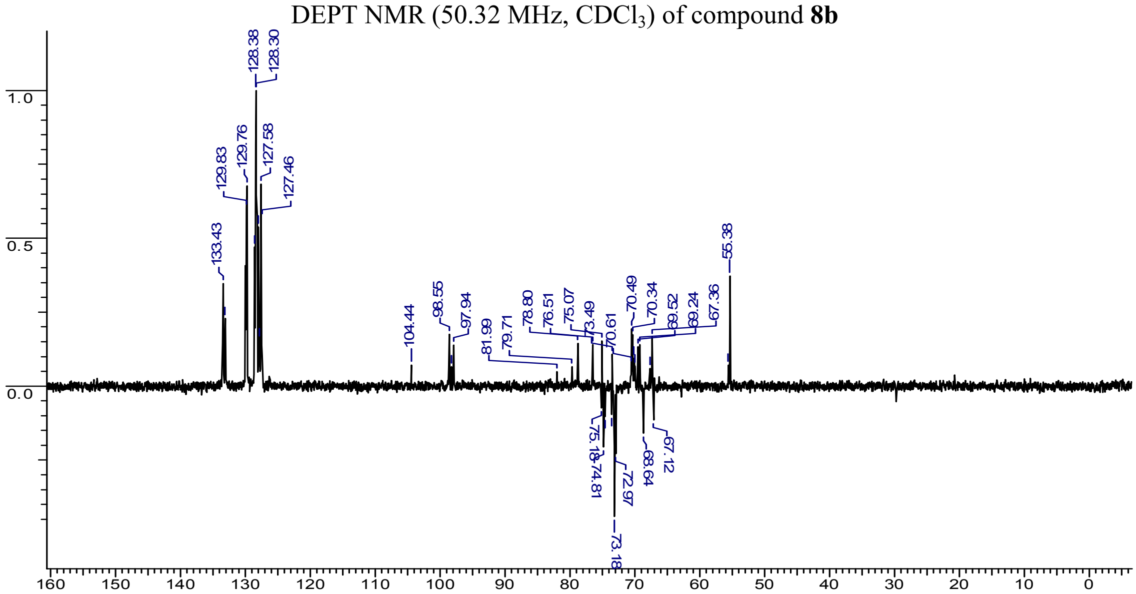
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **8b**



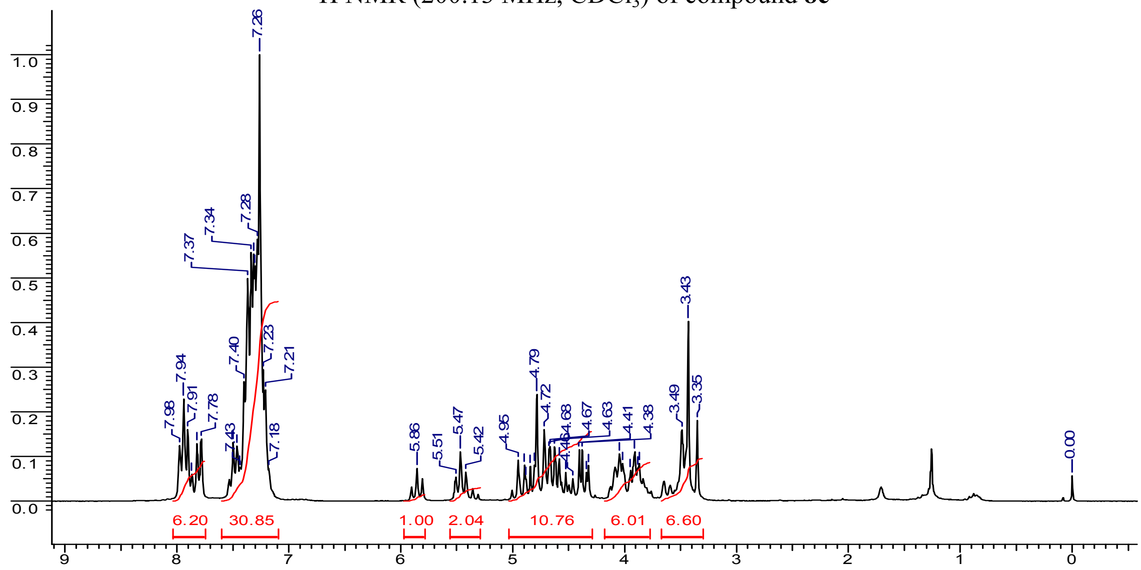
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **8b**



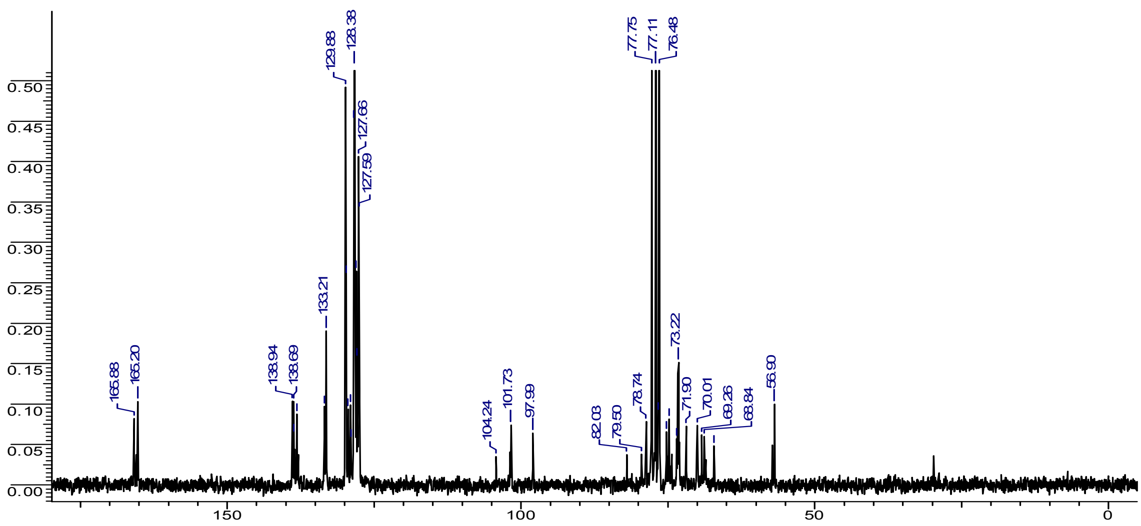
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **8b**



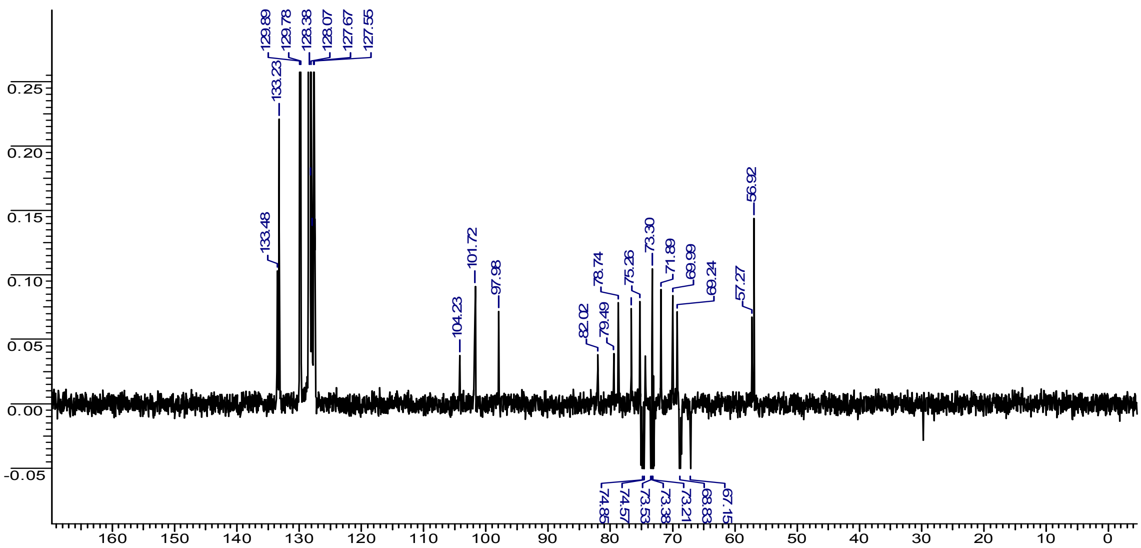
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **8c**



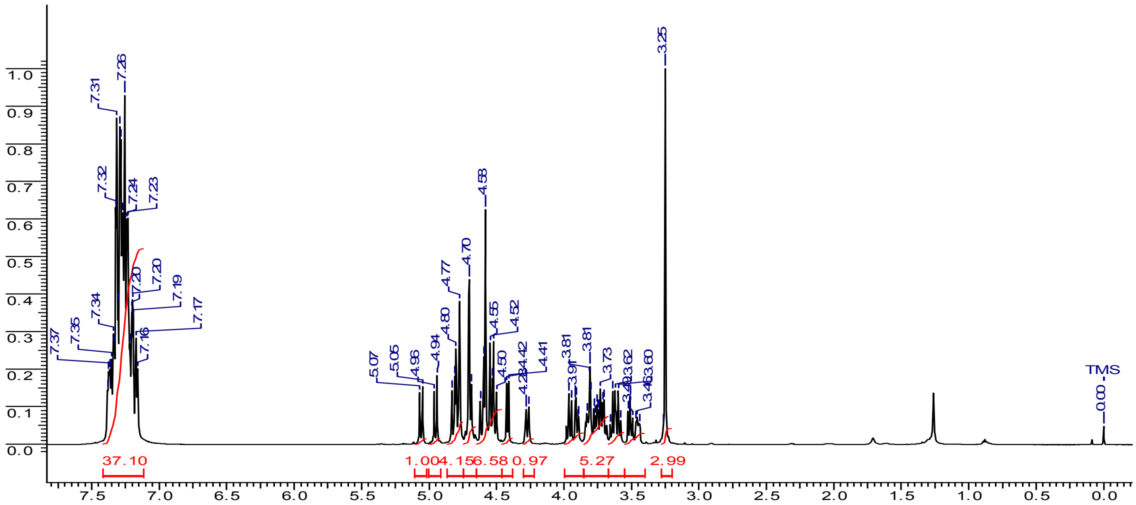
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **8c**



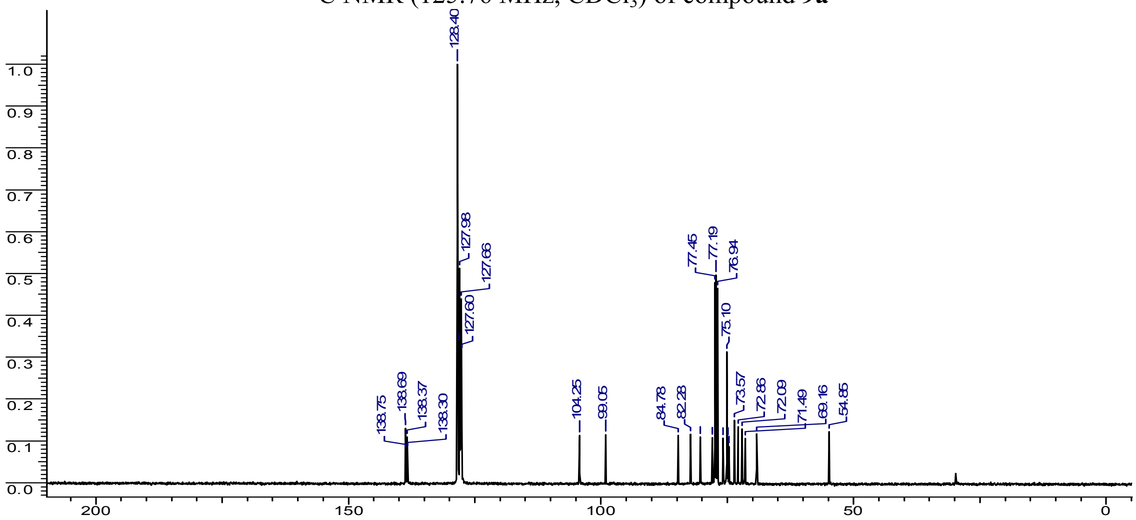
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **8c**



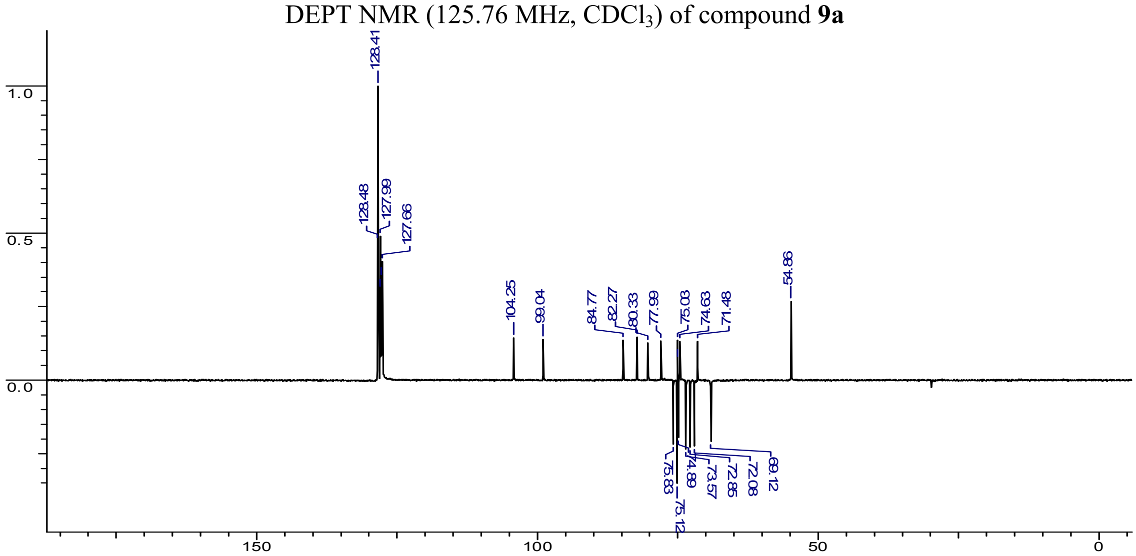
^{1}H NMR (500.13 MHz, $CDCl_3$) of compound **9a**



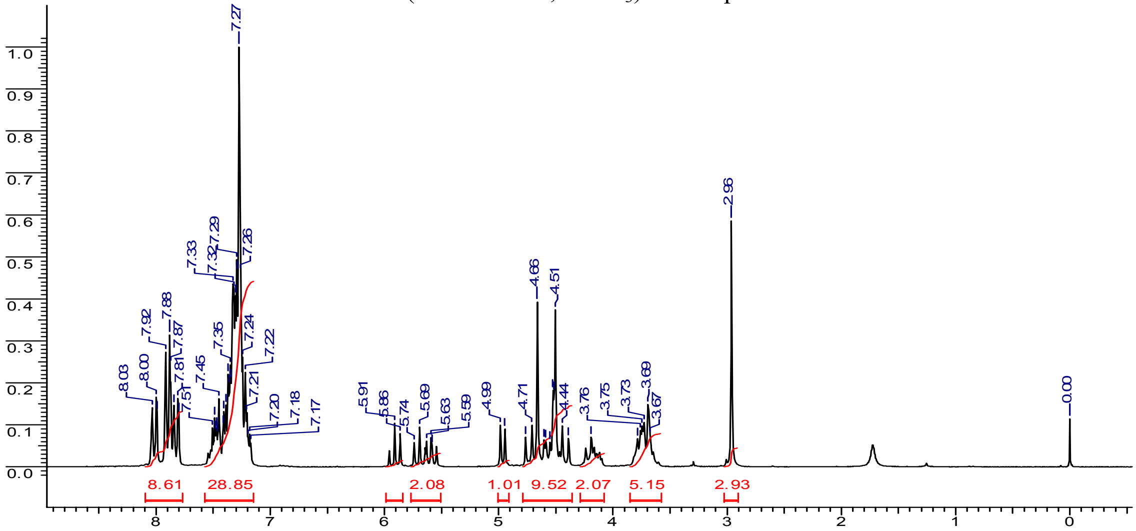
^{13}C NMR (125.76 MHz, $CDCl_3$) of compound **9a**



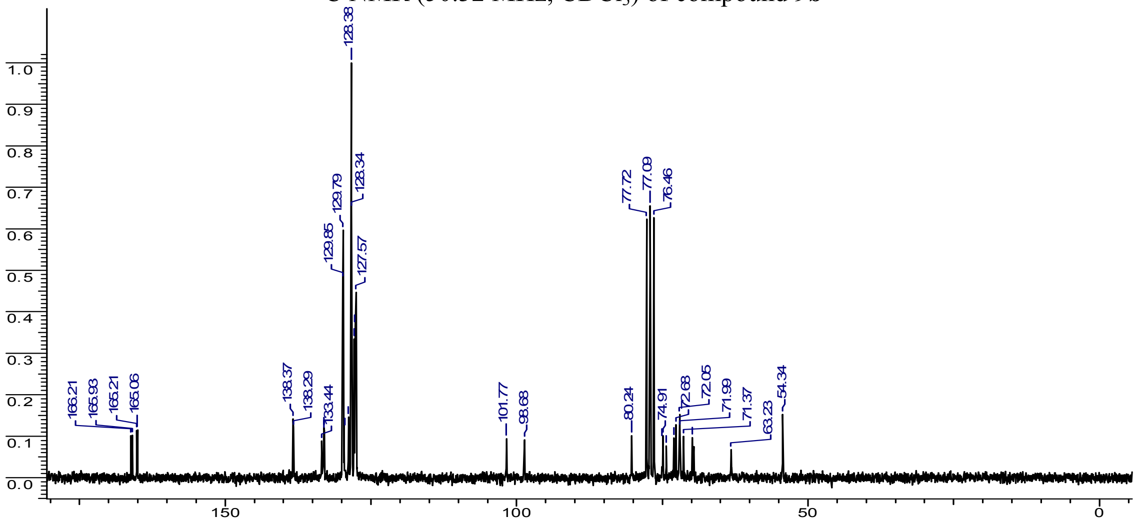
DEPT NMR (125.76 MHz, $CDCl_3$) of compound **9a**



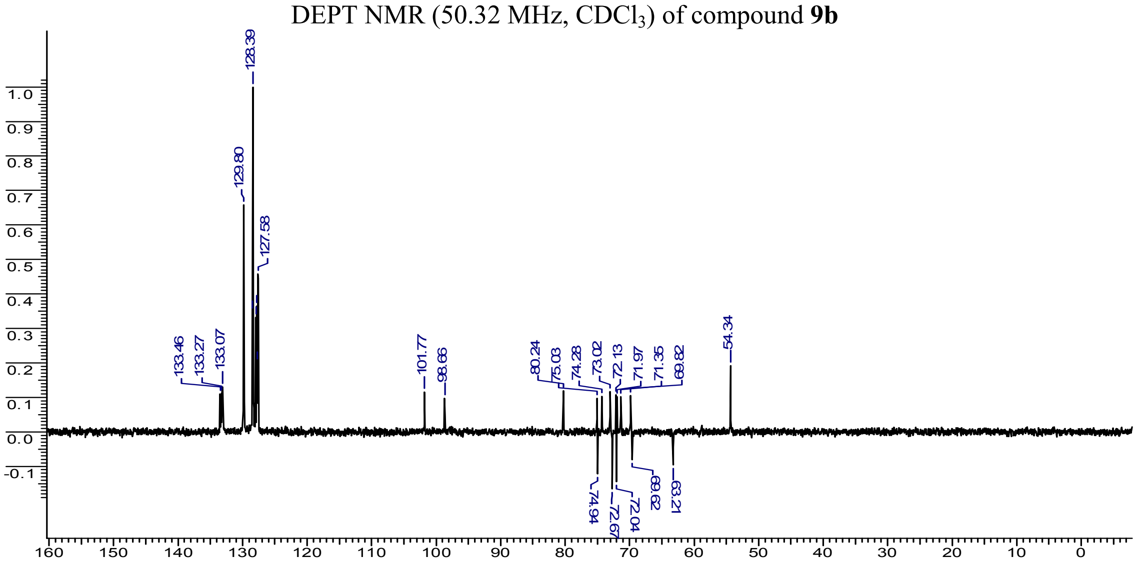
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **9b**



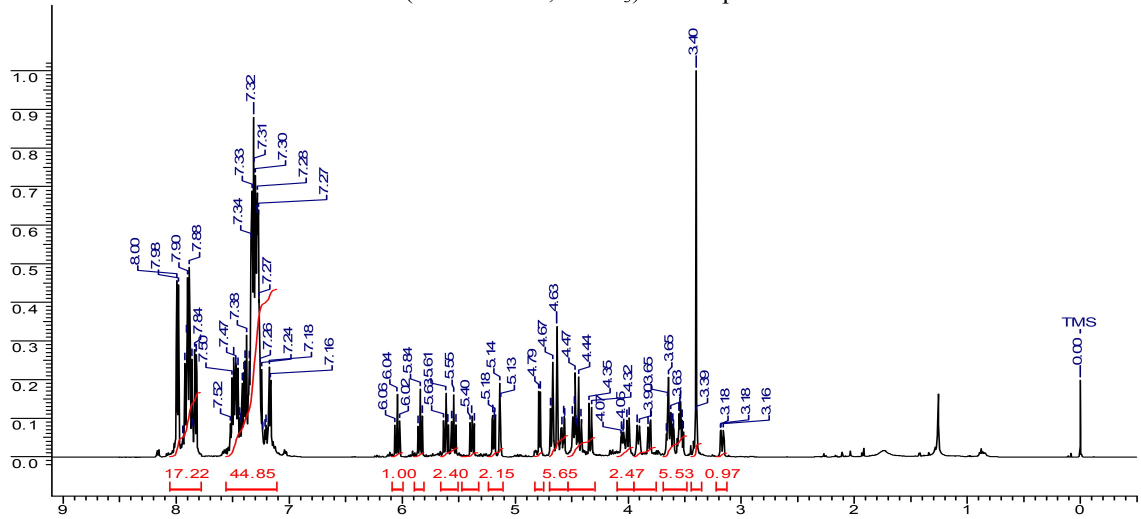
^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **9b**



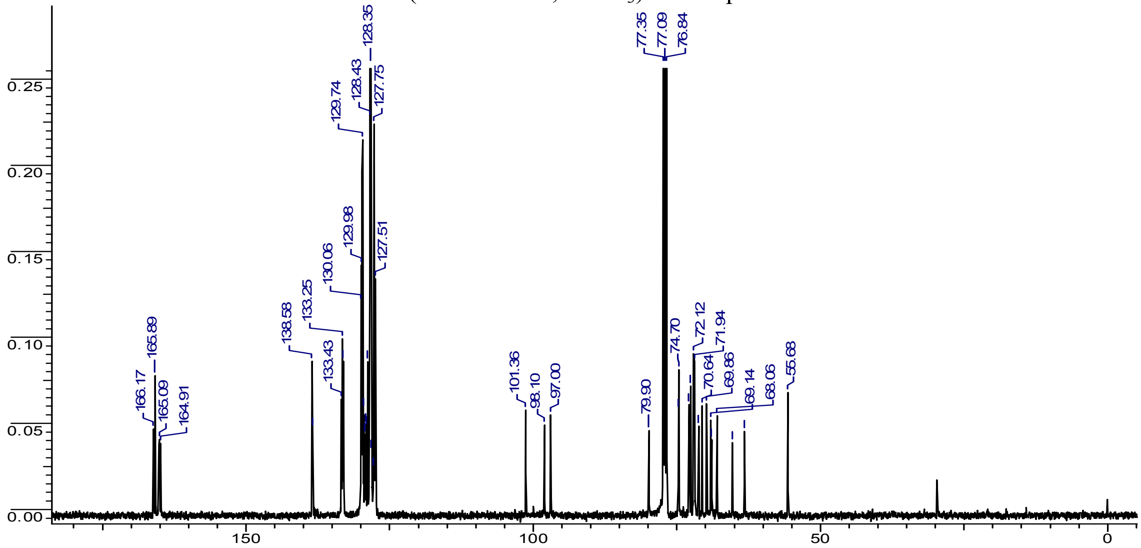
DEPT NMR (50.32 MHz, $CDCl_3$) of compound **9b**



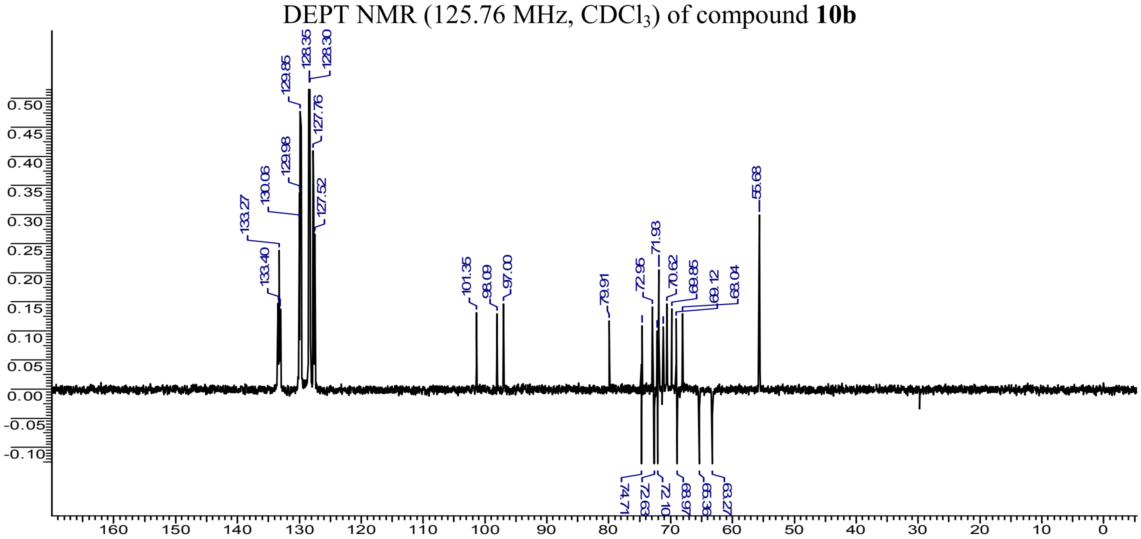
^{1}H NMR (500.13 MHz, $CDCl_3$) of compound **10b**



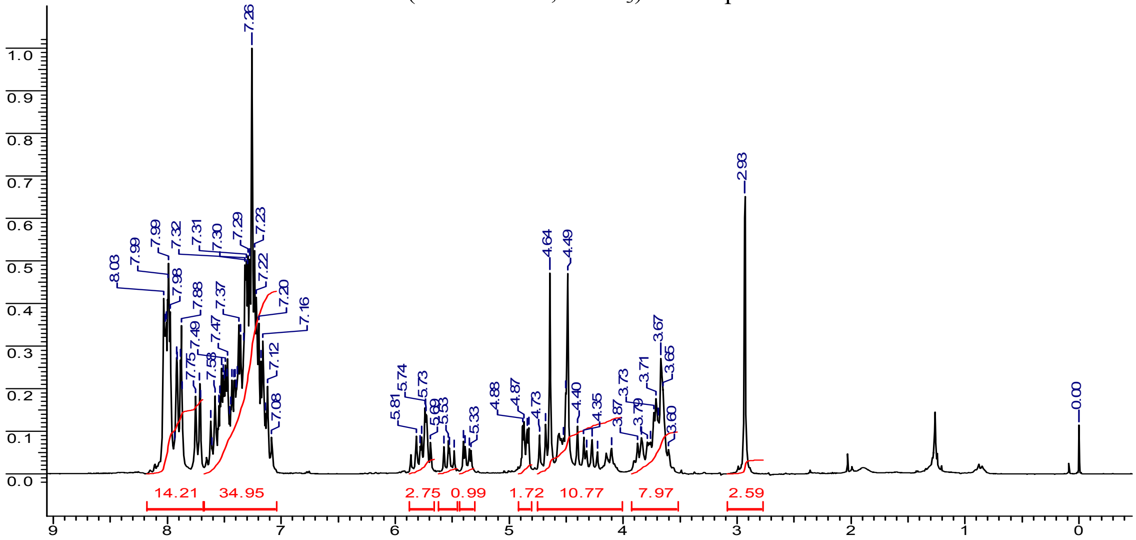
^{13}C NMR (125.76 MHz, $CDCl_3$) of compound **10b**



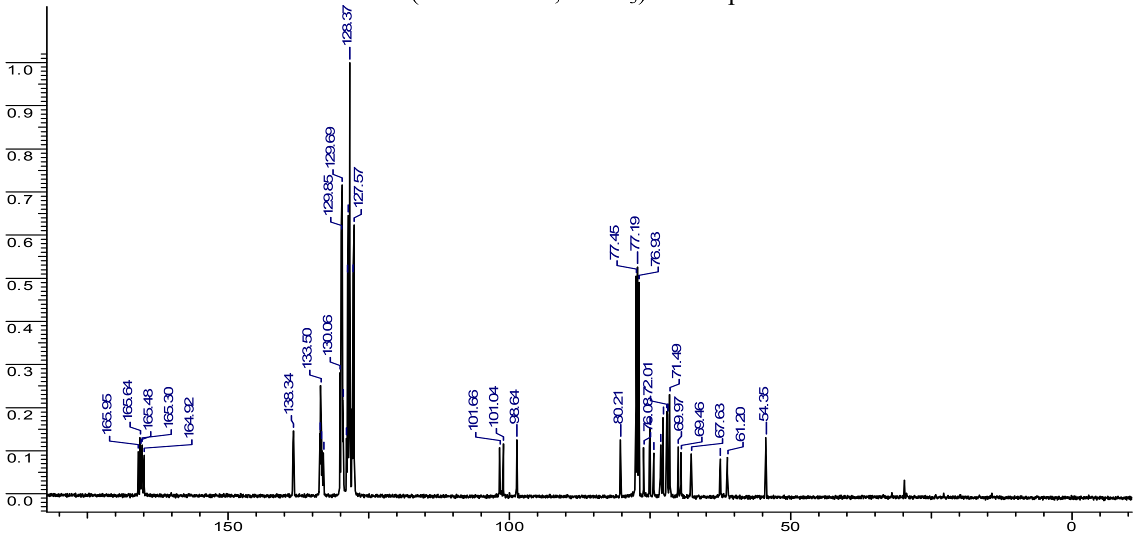
DEPT NMR (125.76 MHz, $CDCl_3$) of compound **10b**



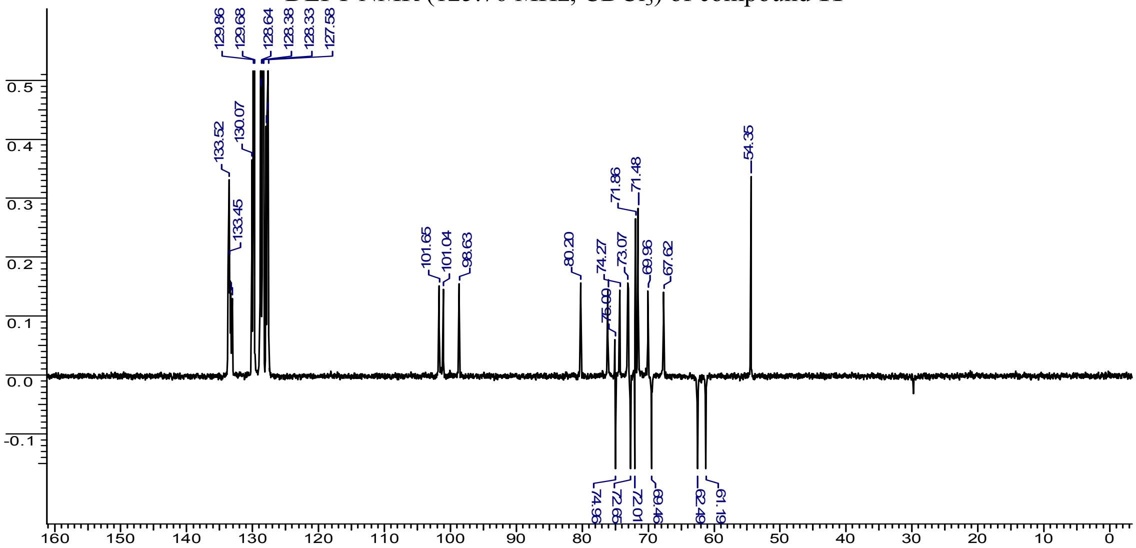
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **11**



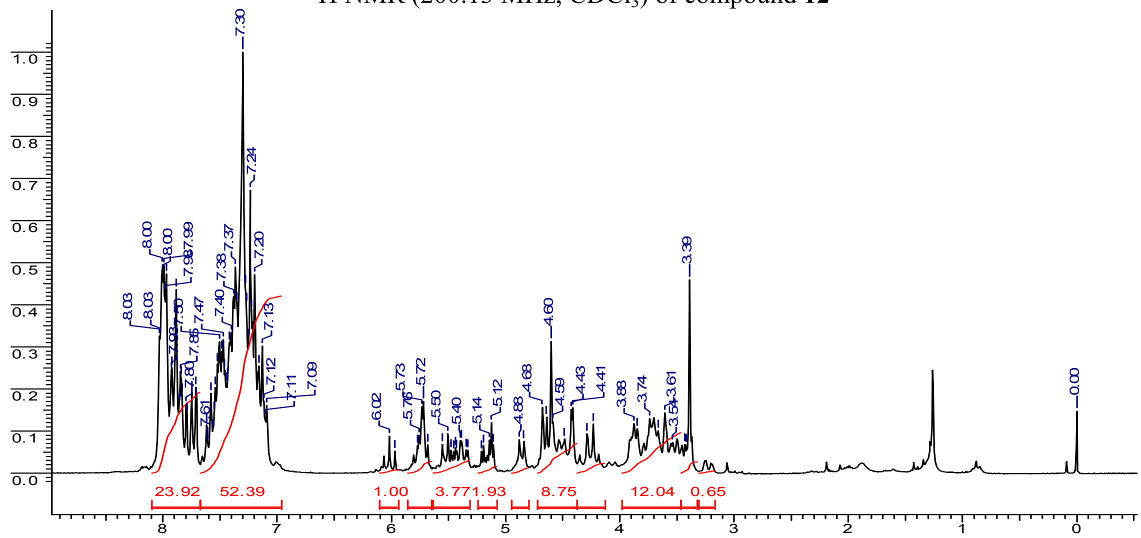
^{13}C NMR (125.76 MHz, $CDCl_3$) of compound **11**



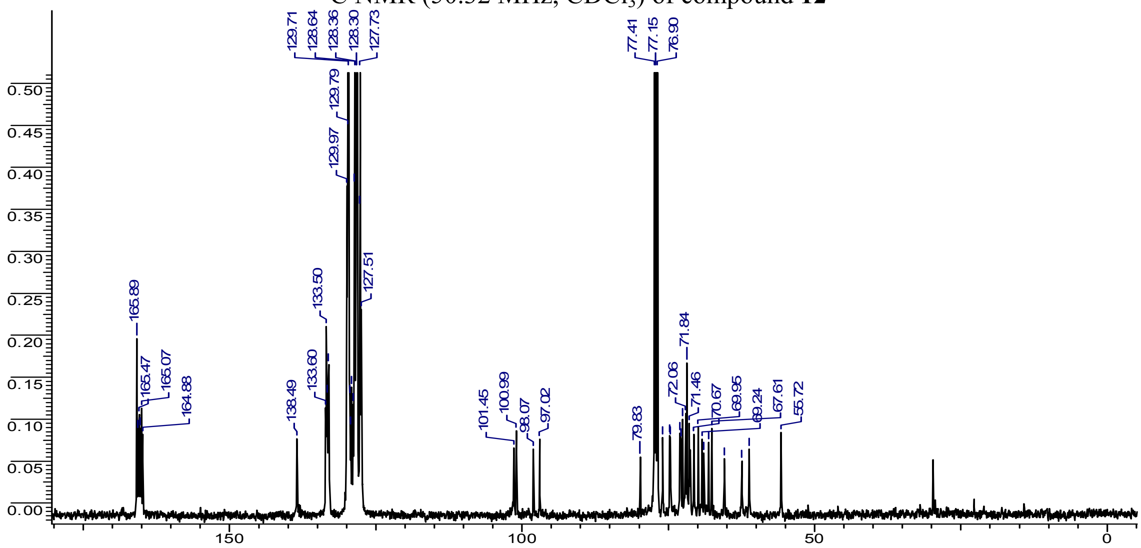
DEPT NMR (125.76 MHz, $CDCl_3$) of compound **11**



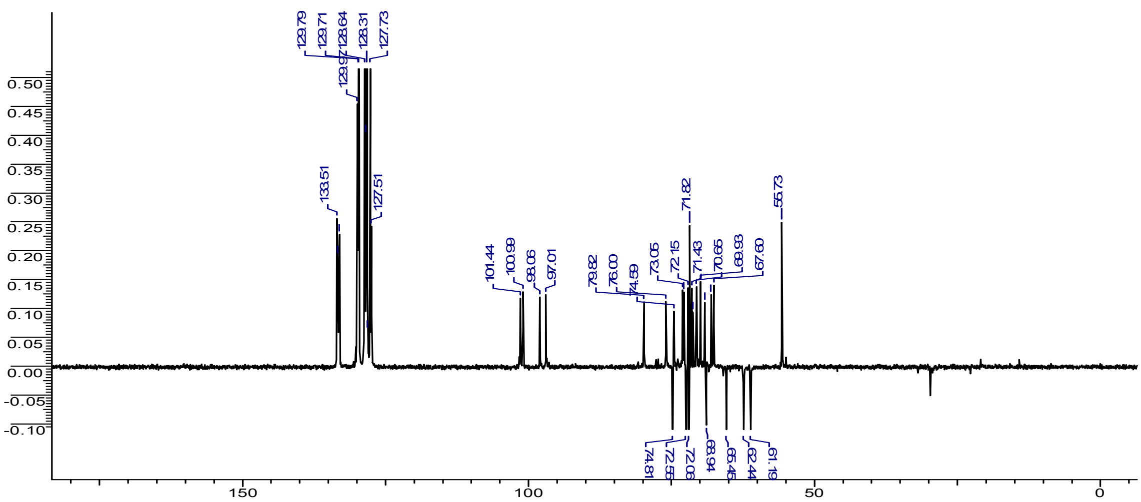
^{1}H NMR (200.13 MHz, $CDCl_3$) of compound **12**



^{13}C NMR (50.32 MHz, $CDCl_3$) of compound **12**



DEPT NMR (50.32 MHz, $CDCl_3$) of compound **12**

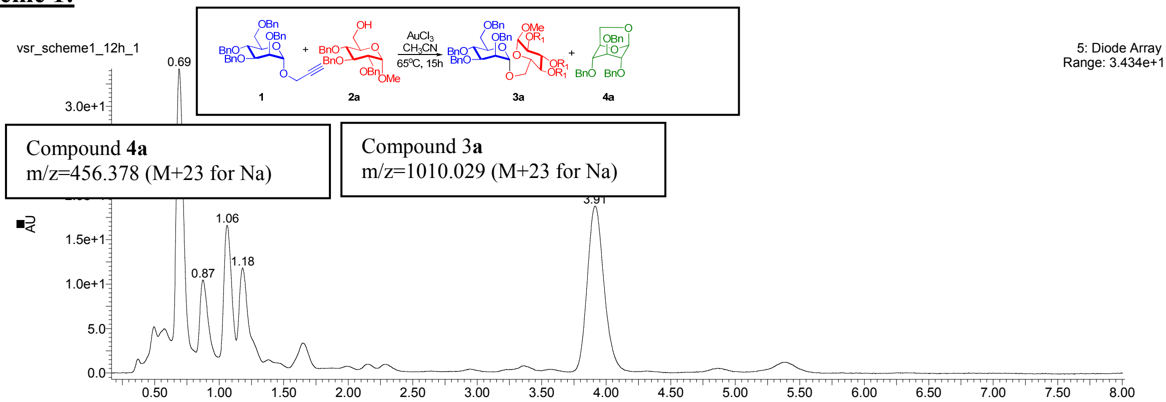


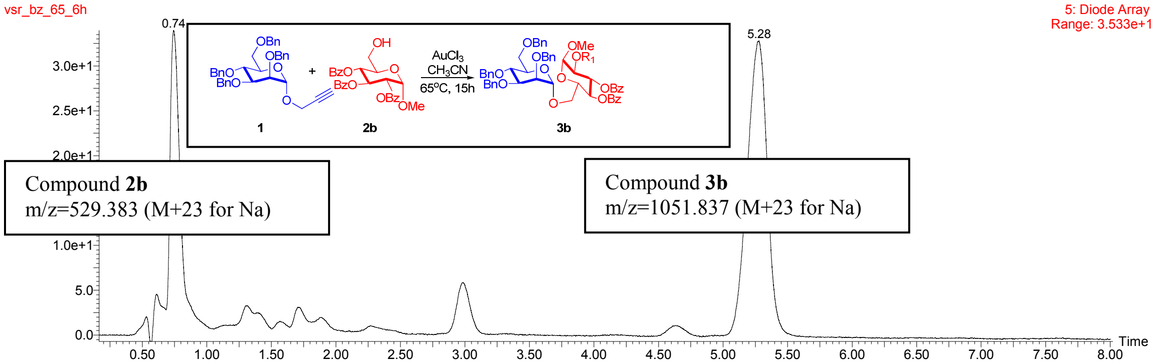
Mass Spectral Characterization Data

Sl. No.	Compound Number	Calculated Mol. Wt.	Observed Mol. Wt. (M^++23 for Na)
1.	**1**	578.694	601.475
2.	**2a**	464.55	488.215
3.	**2b**	506.501	529.383
4.	**2f**	492.517	515.357
5.	**2g**	506.501	529.383
6.	**2h**	506.501	529.380
7.	**3a**	987.181	1010.029
8.	**3b**	1029.131	1051.837
9.	**4a**	432.508	456.378
10.	**5a**	554.673	577.400
11.	**5b**	568.699	591.499
12.	**5c**	582.726	605.583
13.	**5d**	630.769	653.555
14.	**5e**	909.291	931.13
15.	**5f**	580.710	603.529
16.	**5g**	554.673	577.400
17.	**5h**	554.673	577.400
18.	**5i**	554.673	577.400
19.	**5j**	554.673	577401
20.	**6a**	608.763	631.403
21.	**6b**	678.90	701.02
22.	**6c**	1015.148	1037.901
23.	**6d**	1029.131	1051.911
24.	**7a**	1029.131	1051.911
25.	**7b**	1029.131	1051.911
26.	**7c**	1029.131	1051.911
27.	**8a**	1029.131	1051.837
28.	**8b**	1029.131	1051.911
29.	**8c**	1029.131	1051.910
30.	**9a**	987.181	1009.882
31.	**9b**	1043.115	1065.774
32.	**10b**	1517.554	1541.203
33.	**11**	1517.554	1540.074
34.	**12**	1992.032	2015.441

UPLC Chromatograms of Crude Reaction Mixtures

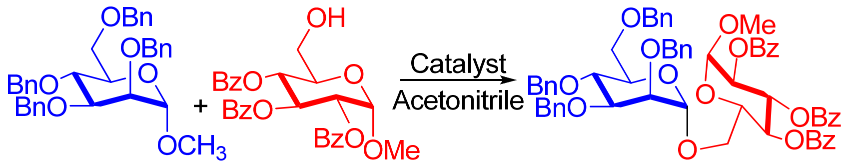
For Scheme 1:



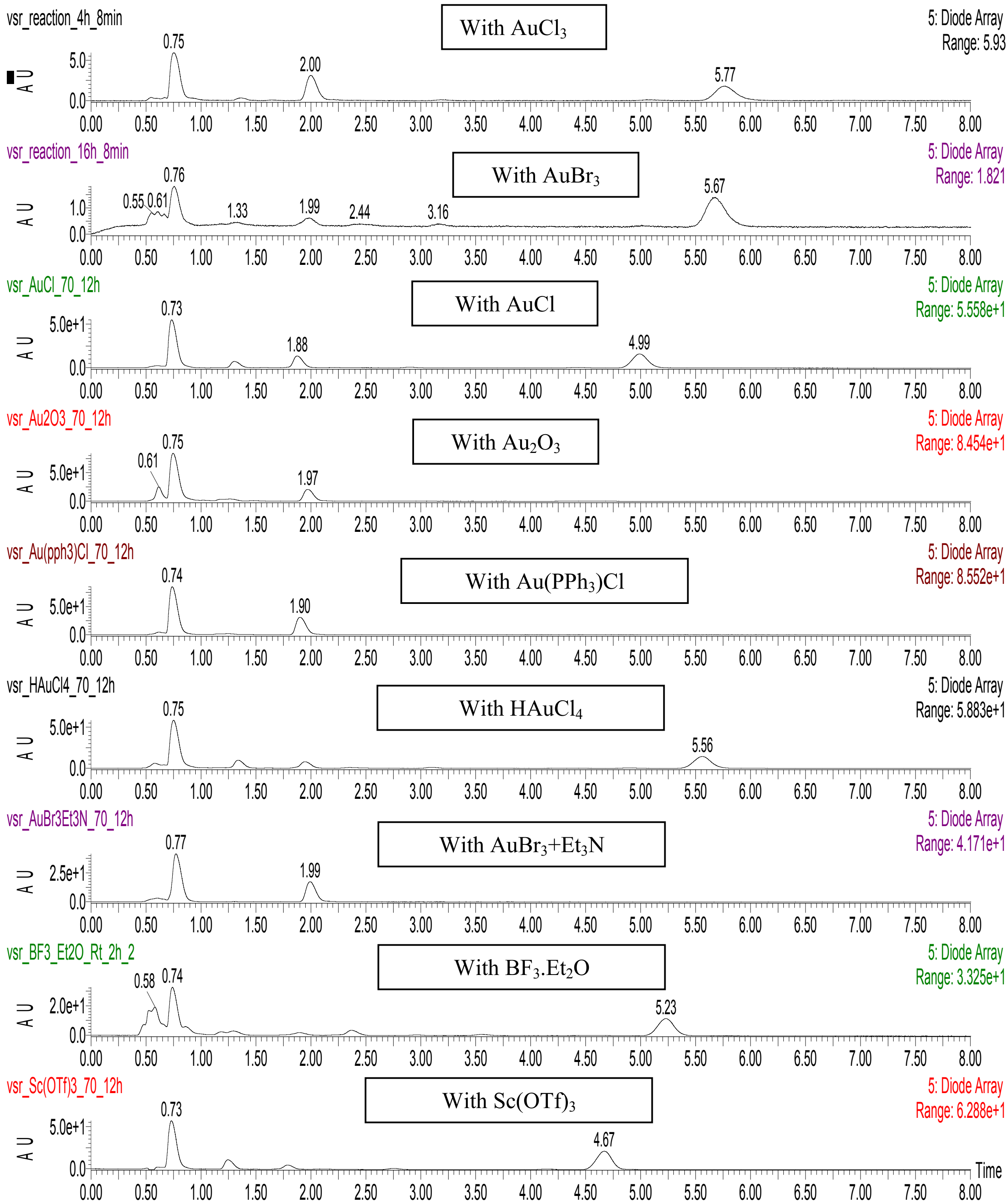


Studies on Catalyst optimization

UPLC Chromatograms of Crude Reaction Mixtures

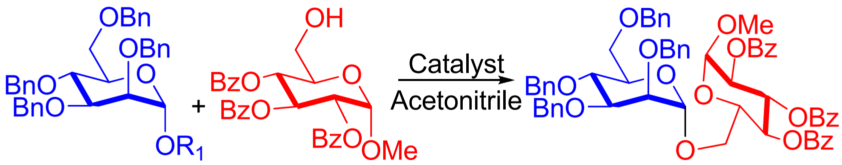


5a **2b** **3b**

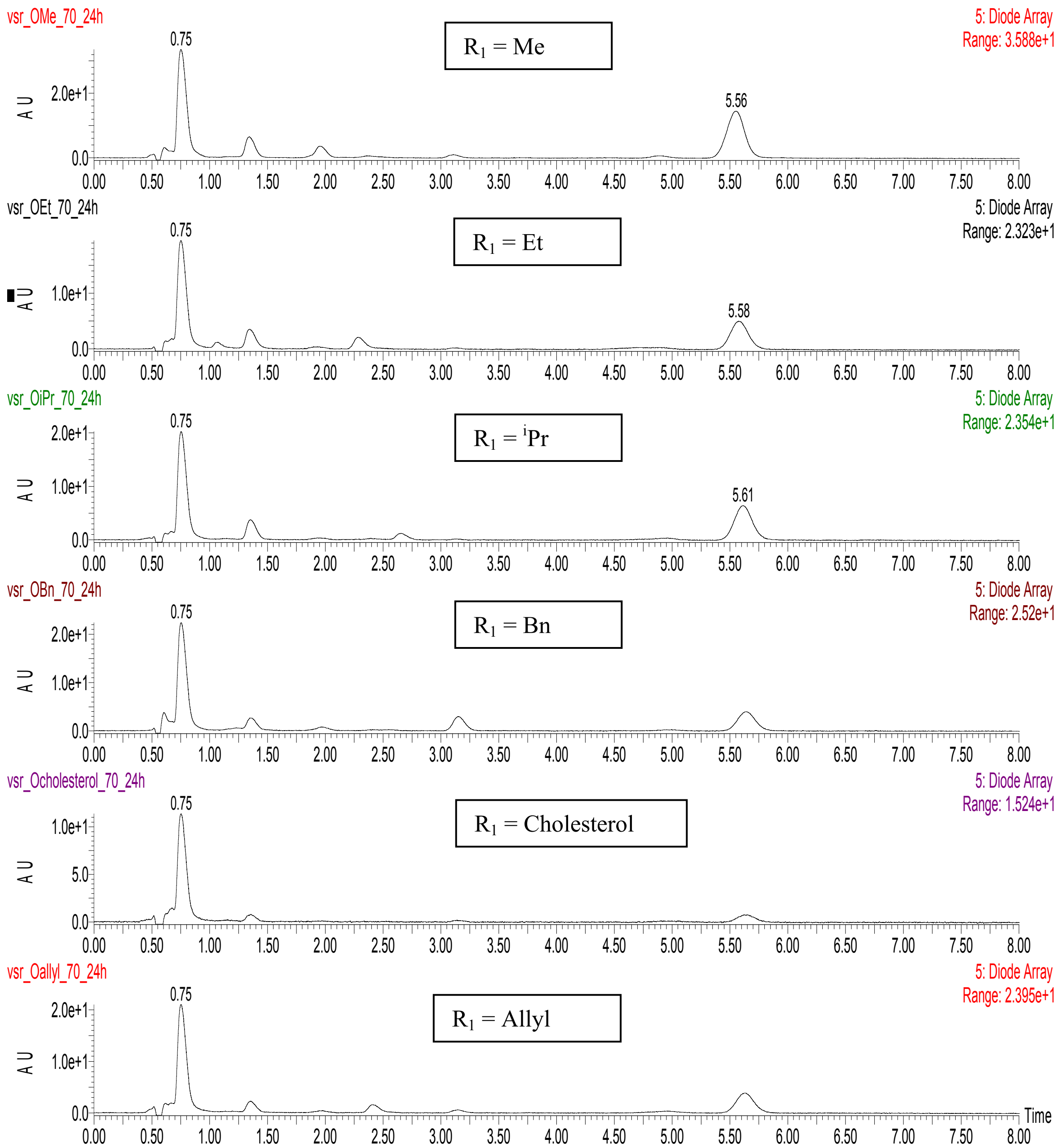


Gold Activation for Alkyl Glycosides

UPLC Chromatograms of Crude Reaction Mixtures

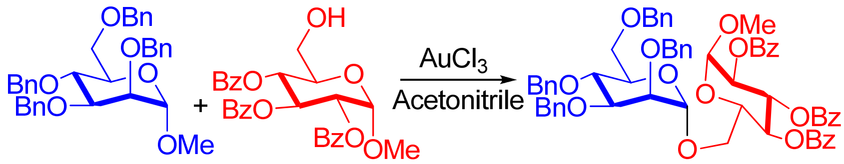


5a-5f 2b 3b

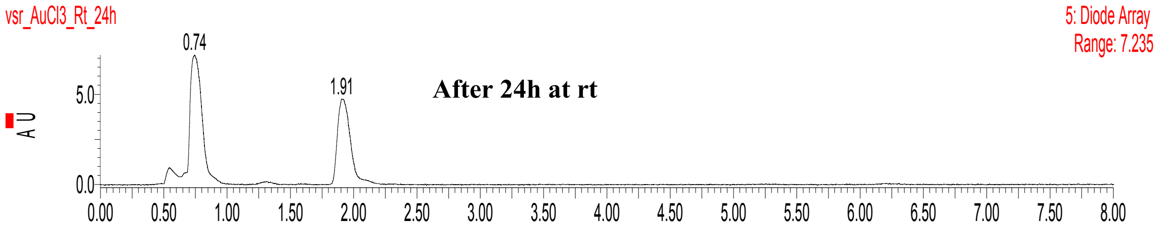


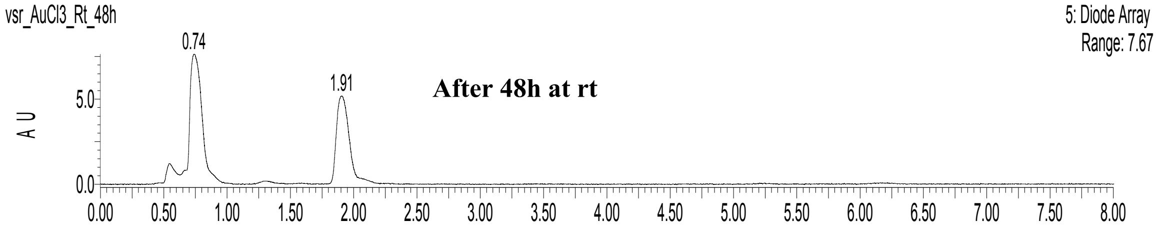
Time and Temperature Optimization Studies using $AuCl_3$

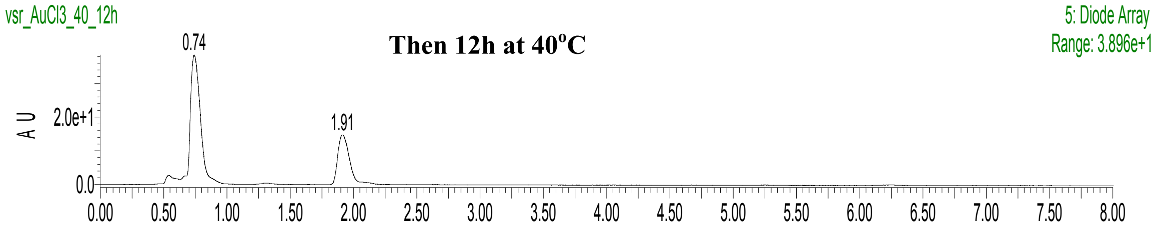
UPLC Chromatograms of Crude Reaction Mixtures

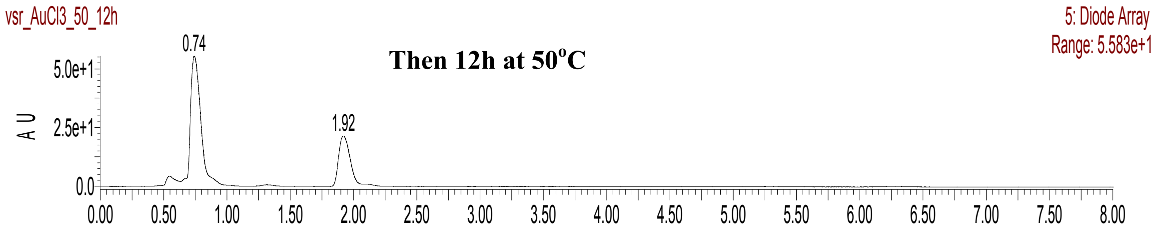


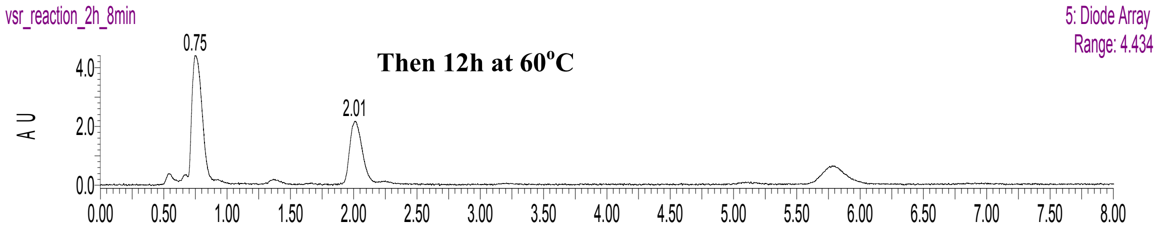
5a **2b** **3b**

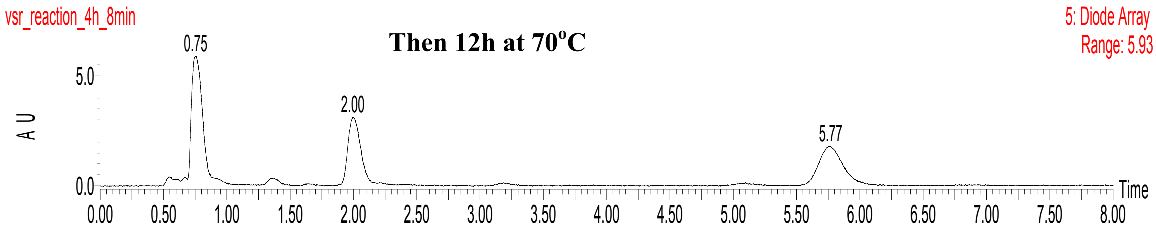






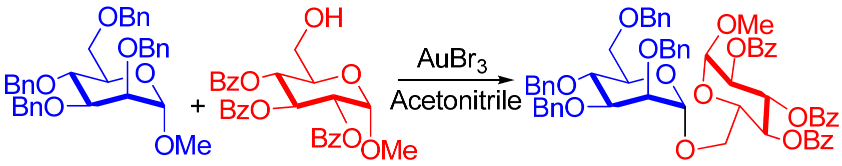


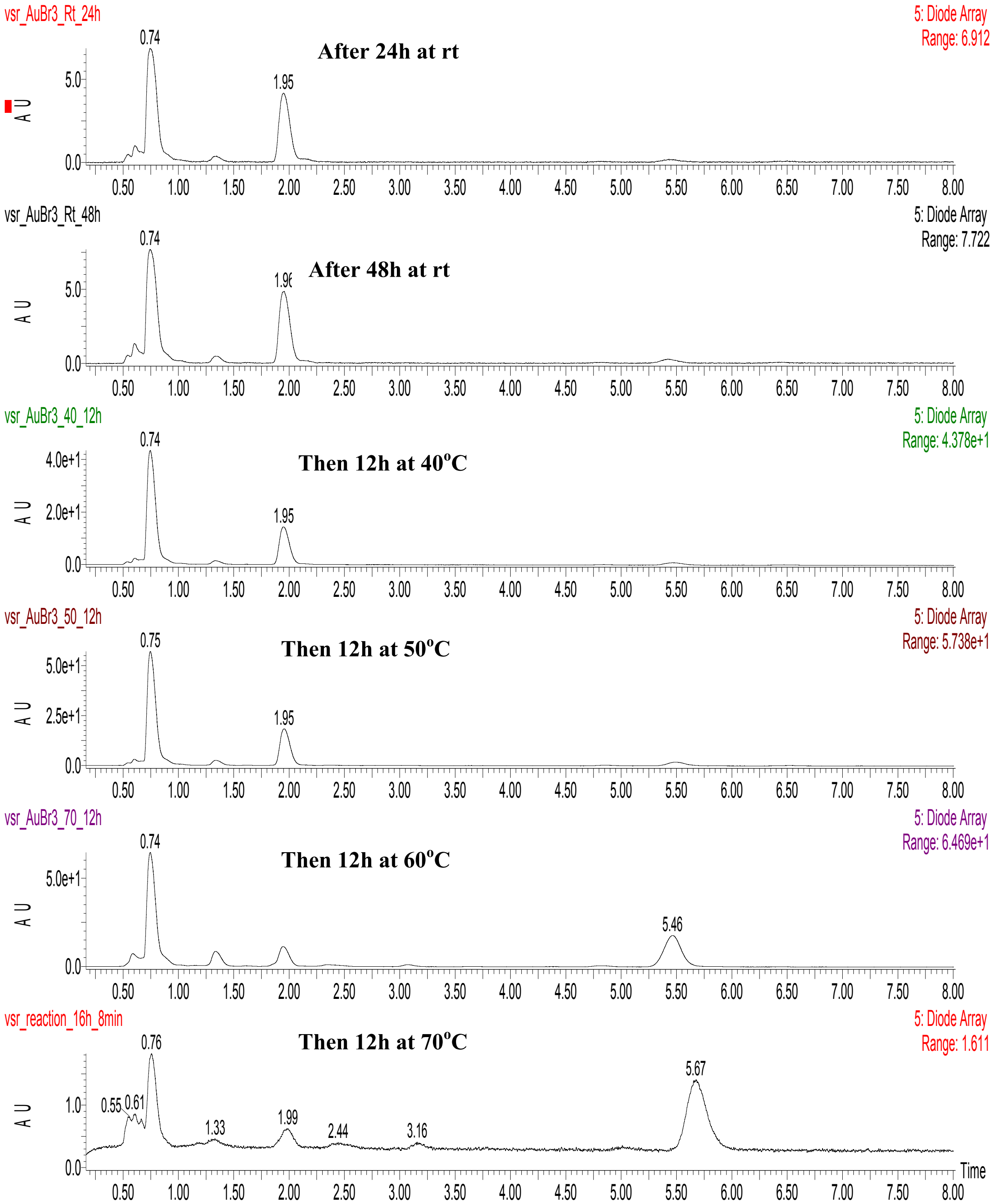




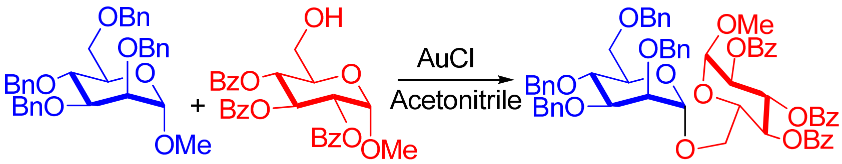
Time and Temperature Optimization Studies using $AuBr_3$

UPLC Chromatograms of Crude Reaction Mixtures

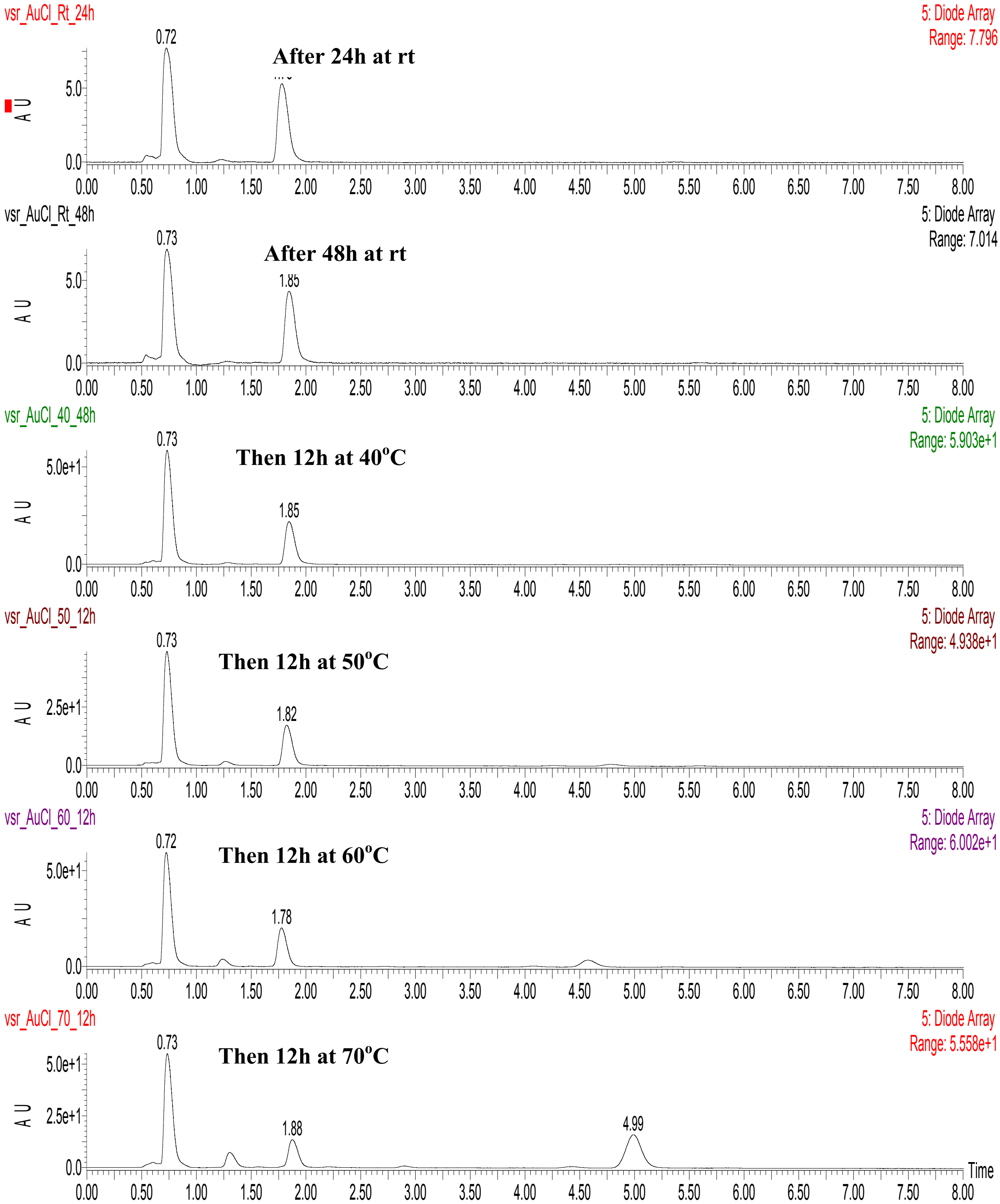




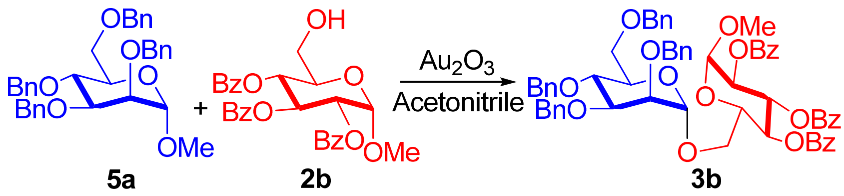
Time and Temperature Optimization Studies using AuCl
UPLC Chromatograms of Crude Reaction Mixtures

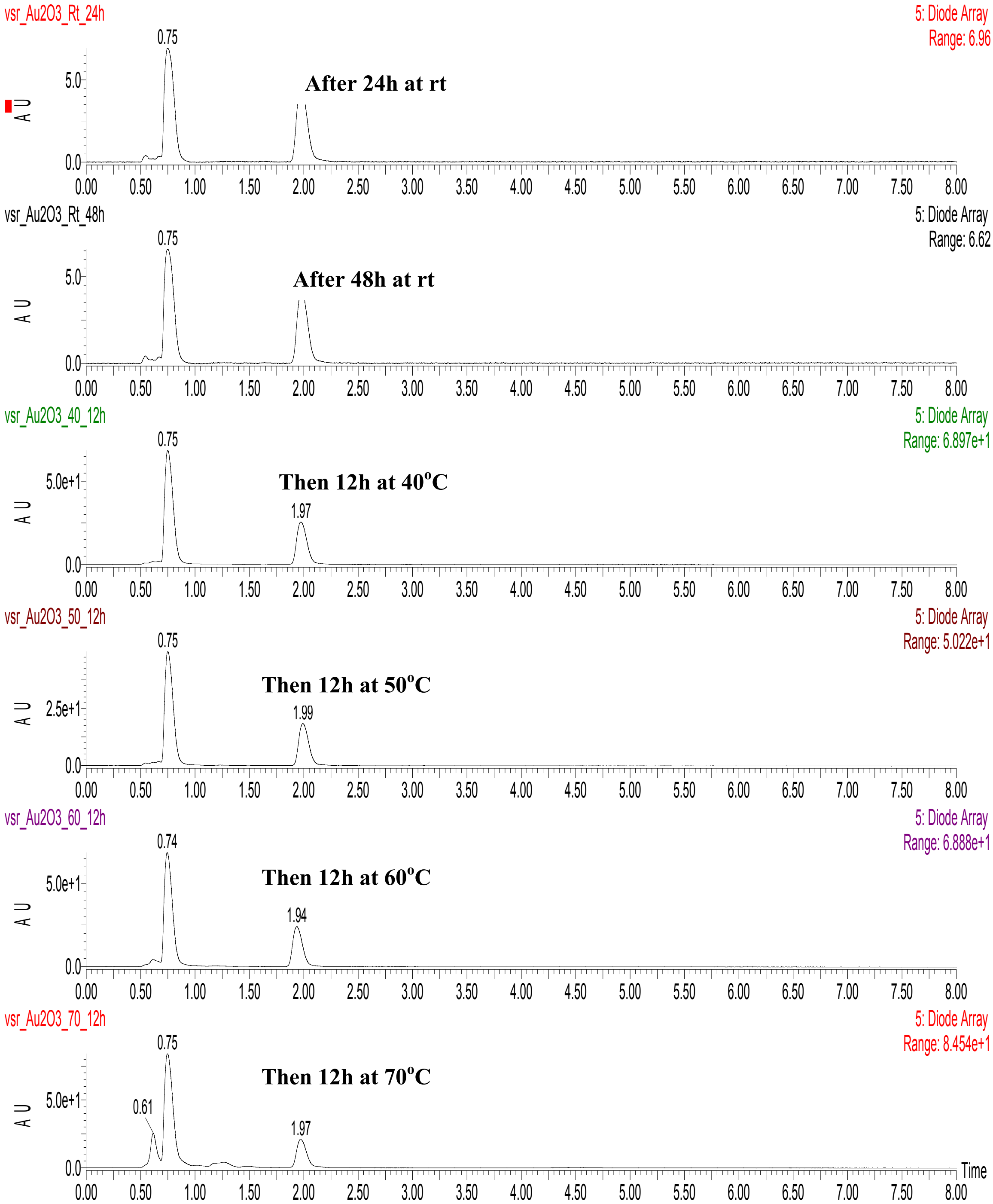


5a **2b** **3b**

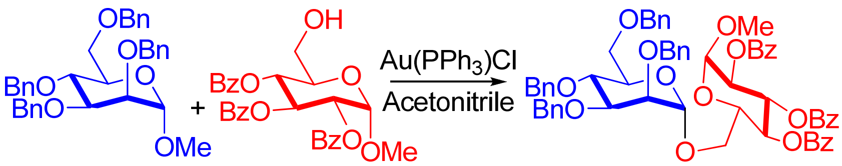


Time and Temperature Optimization Studies using Au_2O_3
UPLC Chromatograms of Crude Reaction Mixtures

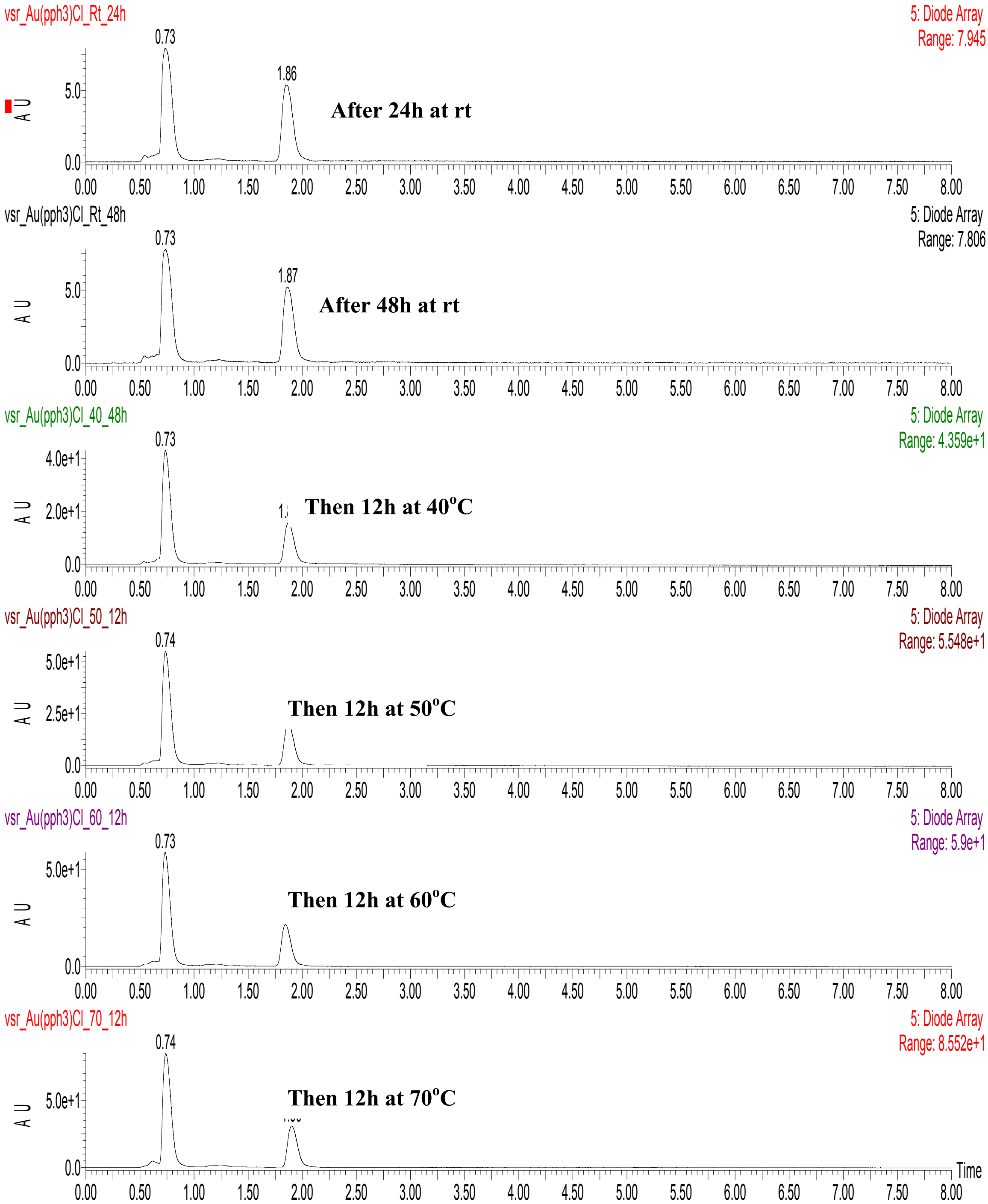




Time and Temperature Optimization Studies using Au(PPh$_3$)Cl
UPLC Chromatograms of Crude Reaction Mixtures

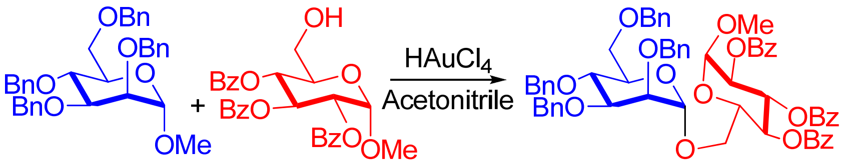


5a 2b 3b

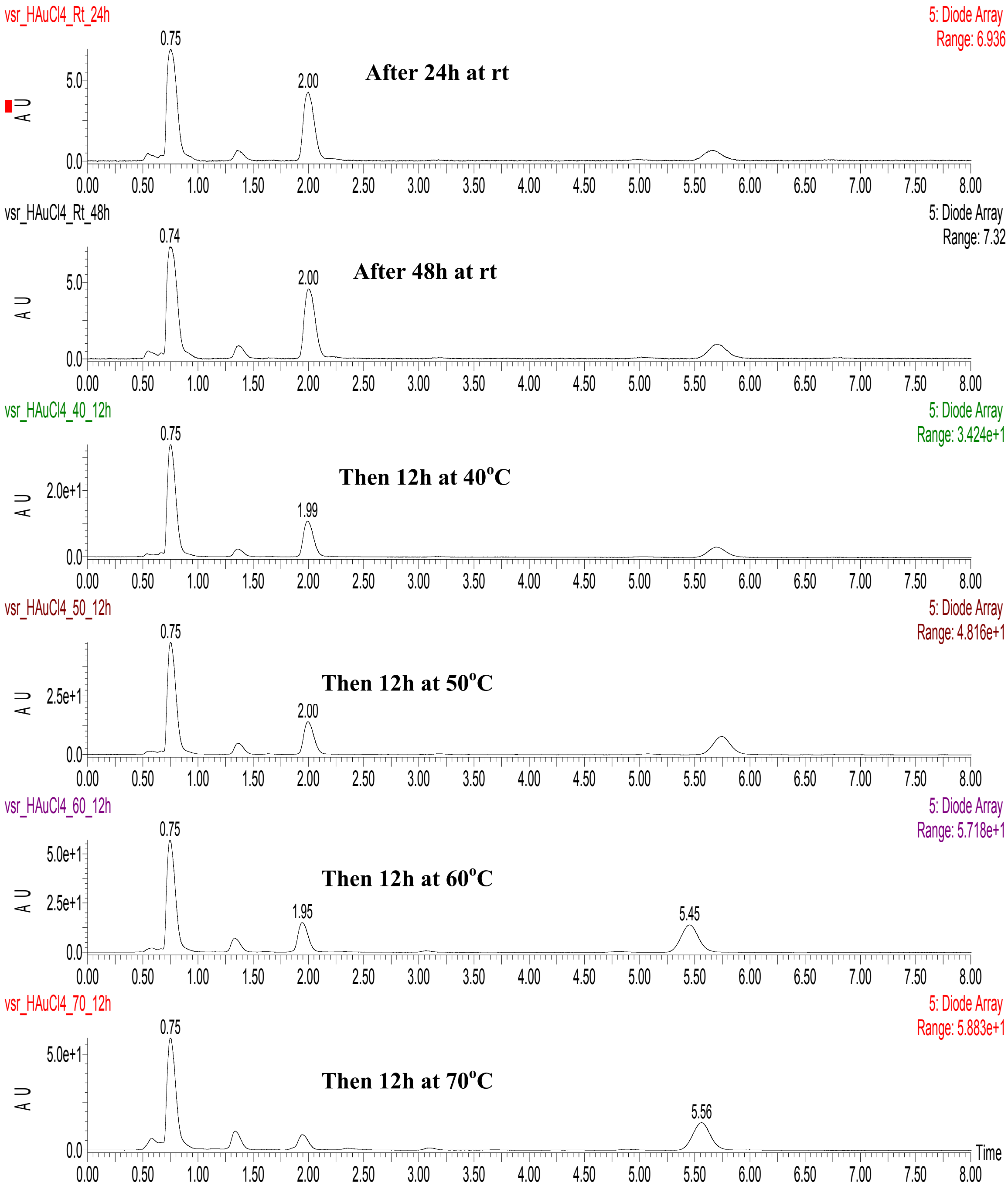


Time and Temperature Optimization Studies using $HAuCl_4$

UPLC Chromatograms of Crude Reaction Mixtures

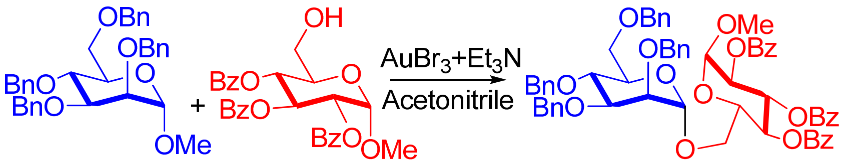


5a 2b 3b

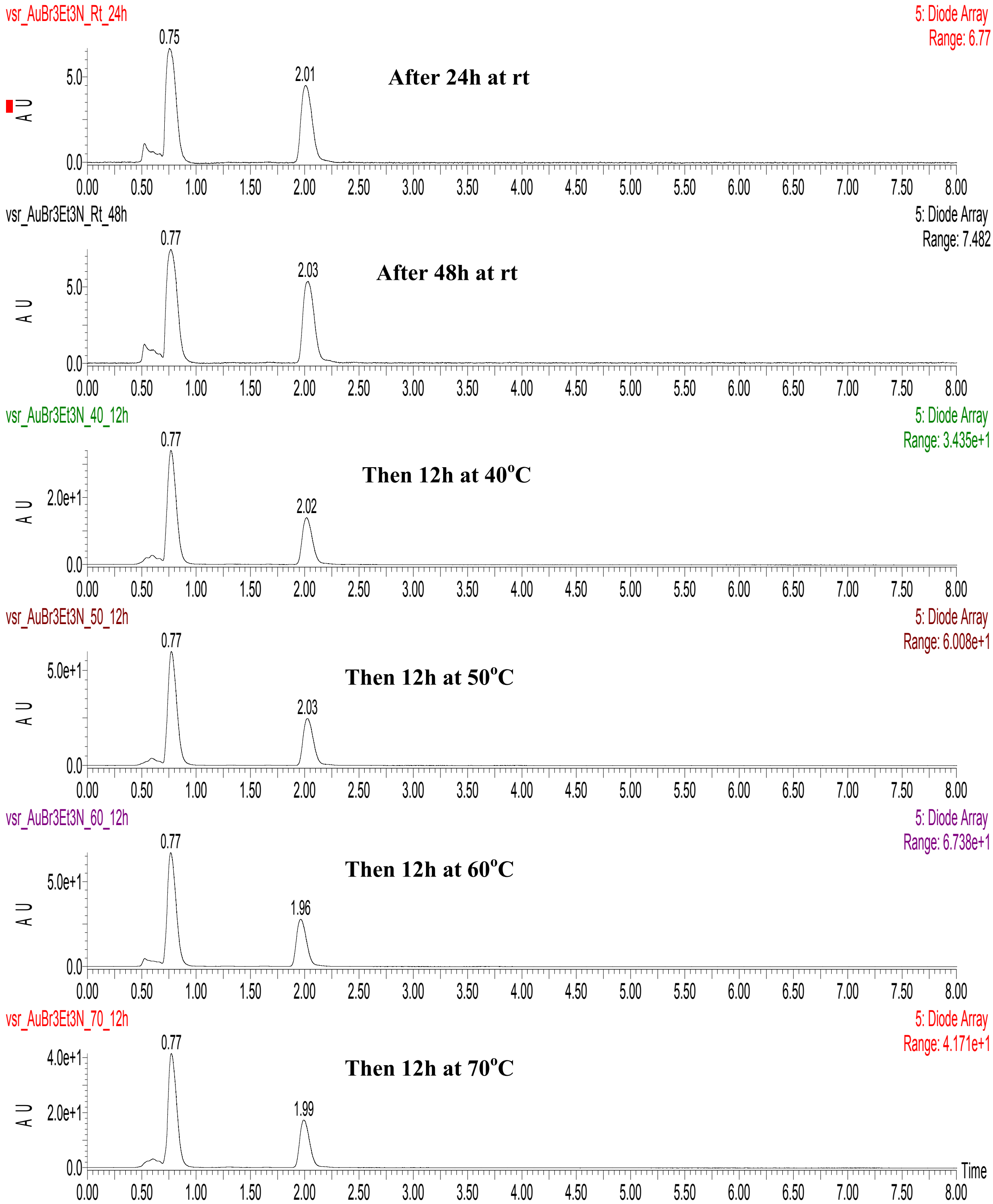


Time and Temperature Optimization Studies using $AuBr_3$+Et_3N

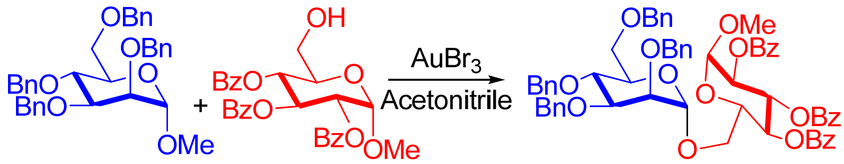
UPLC Chromatograms of Crude Reaction Mixtures

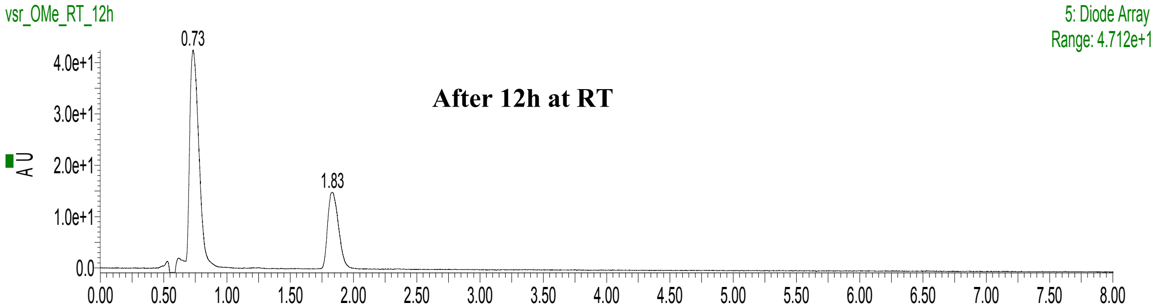


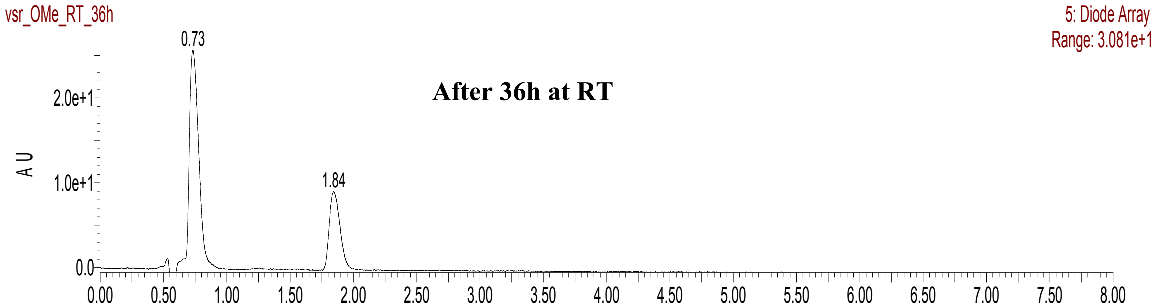
5a **2b** **3b**

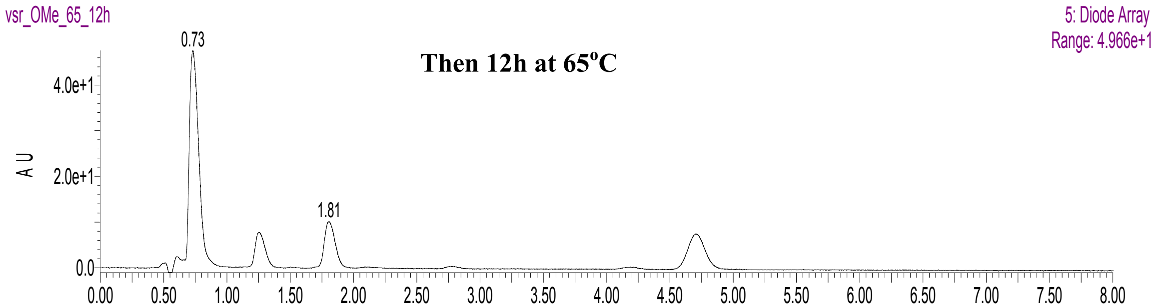


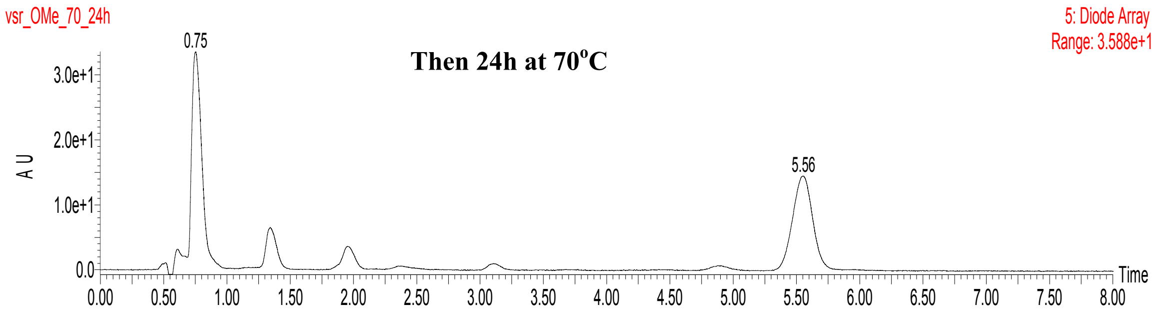
Time and Temperature Optimization Studies using $AuBr_3$ using Methyl Mannoside
UPLC Chromatograms of Crude Reaction Mixtures





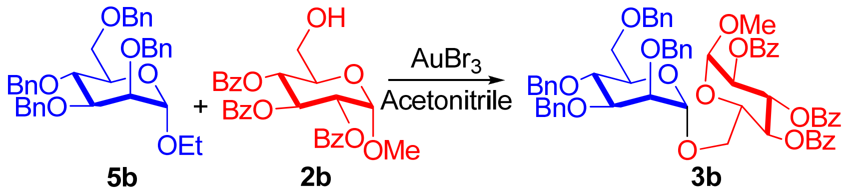


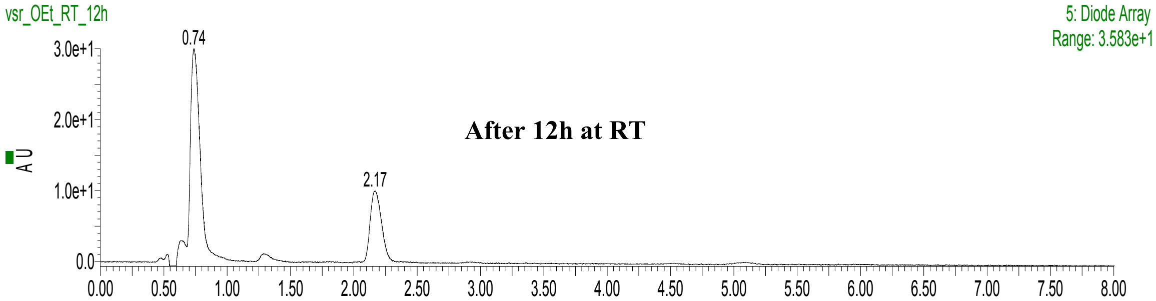


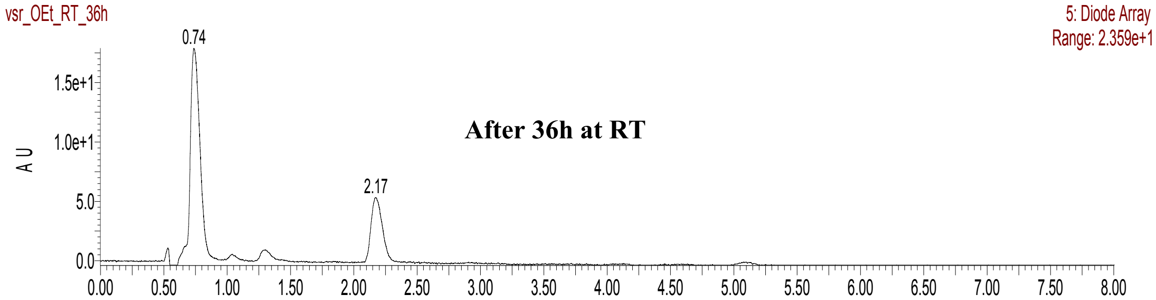


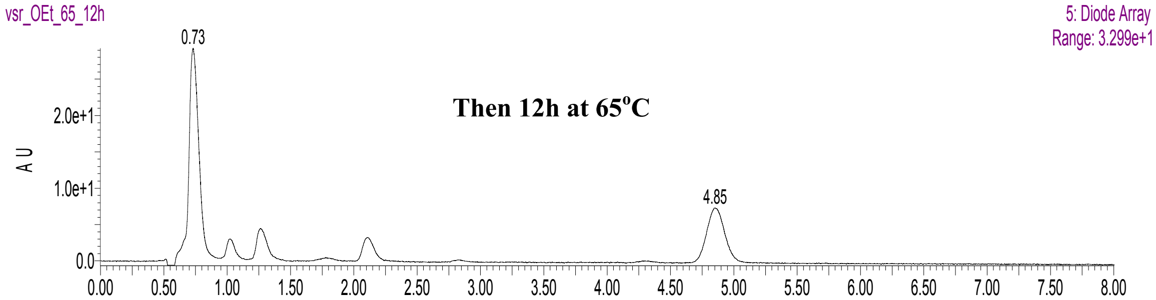
Time and Temperature Optimization Studies using $AuBr_3$ using Ethyl Mannoside

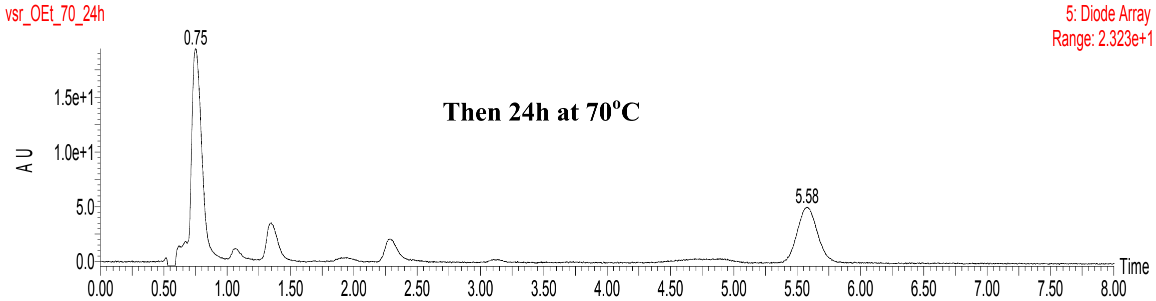
UPLC Chromatograms of Crude Reaction Mixtures





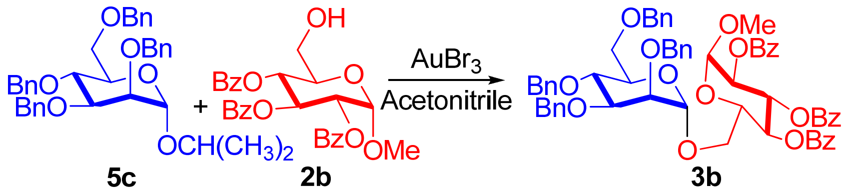


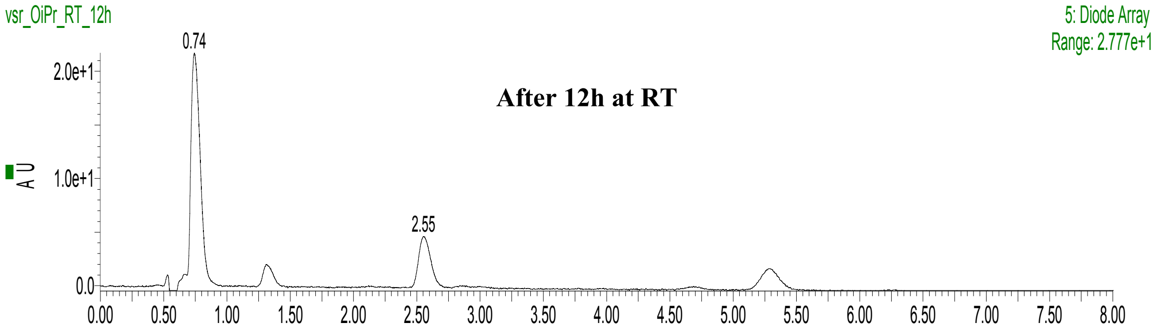


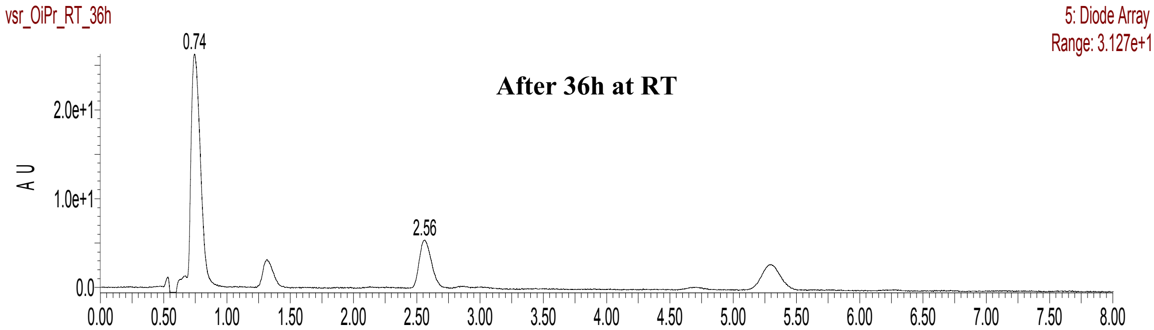


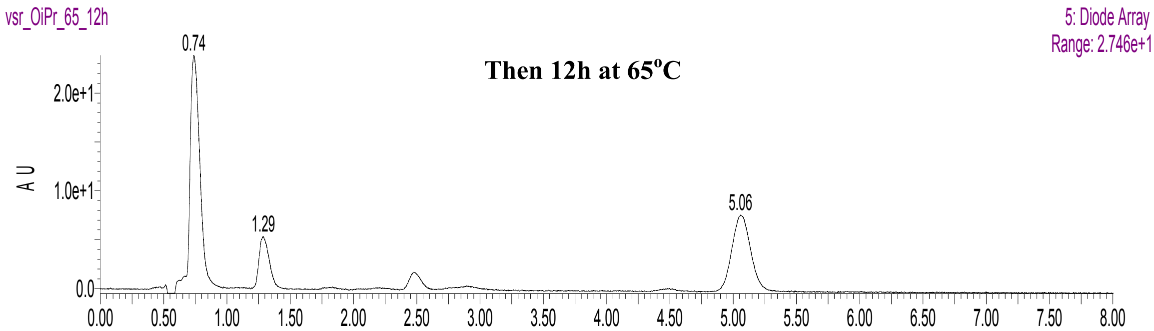
Time and Temperature Optimization Studies using $AuBr_3$ using Isopropyl Mannoside

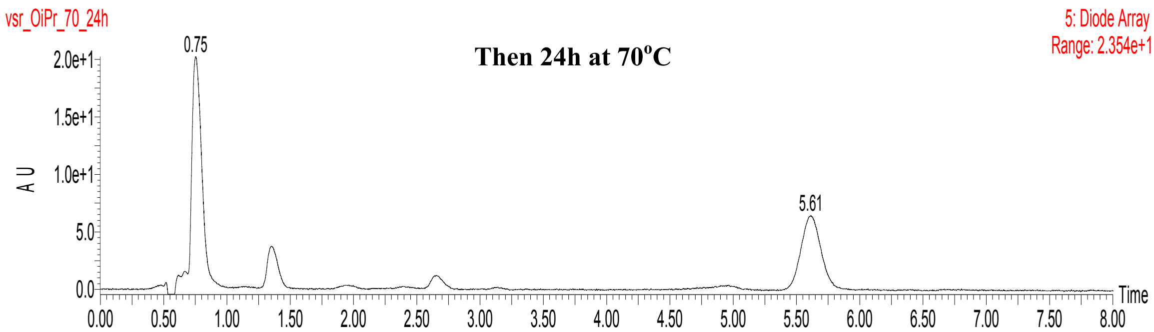
UPLC Chromatograms of Crude Reaction Mixtures





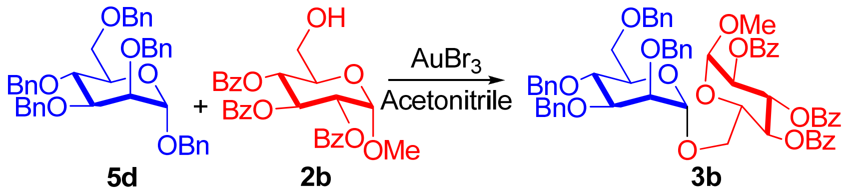


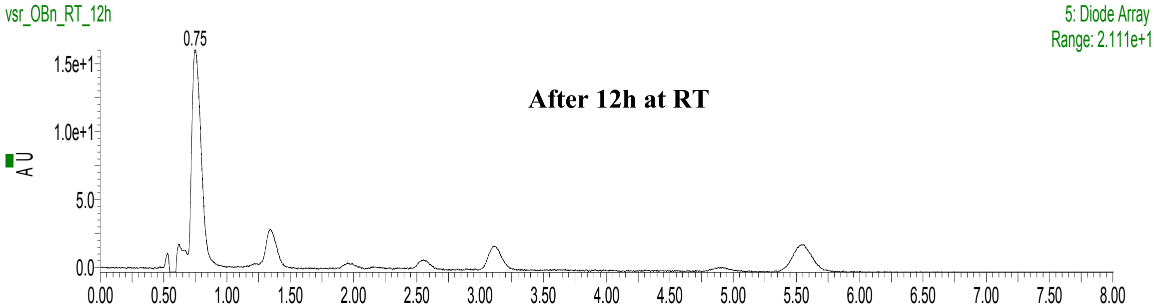


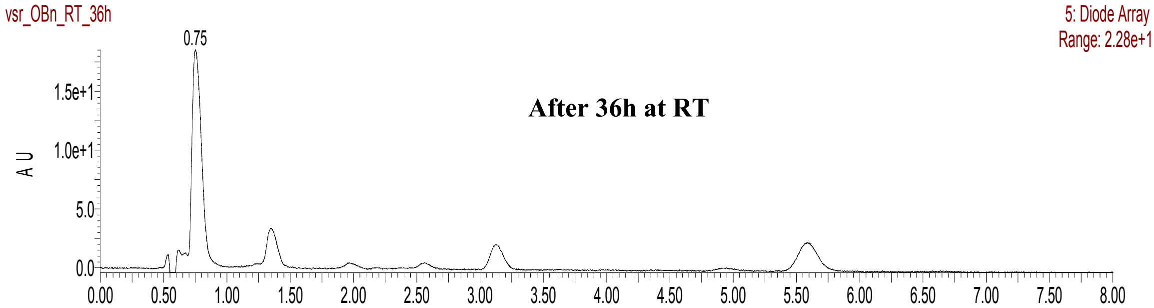


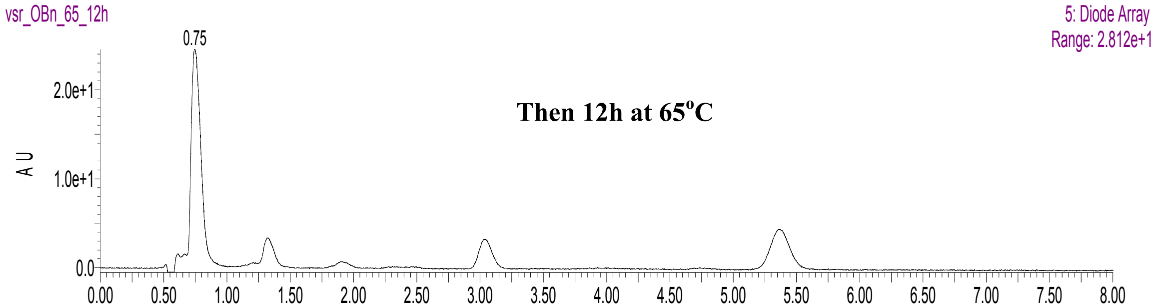
Time and Temperature Optimization Studies using $AuBr_3$ using Benzyl Mannoside

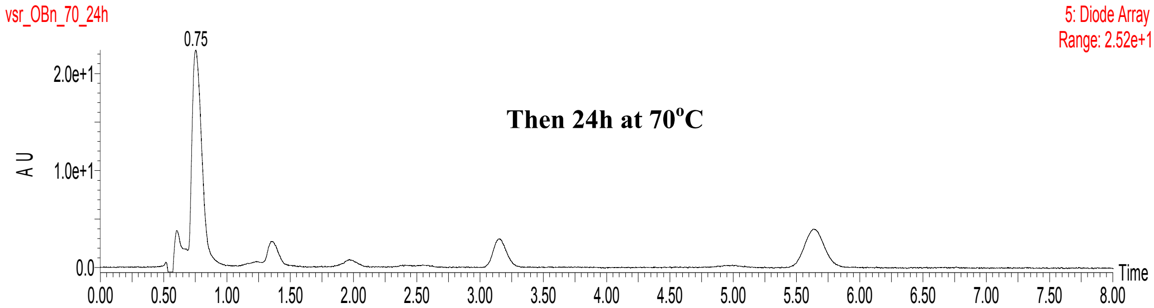
UPLC Chromatograms of Crude Reaction Mixtures



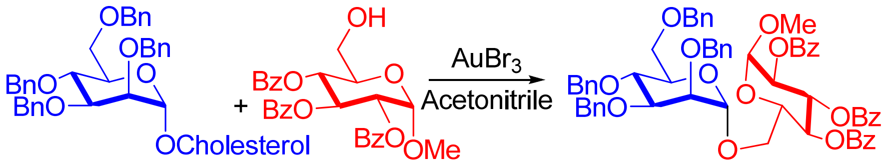




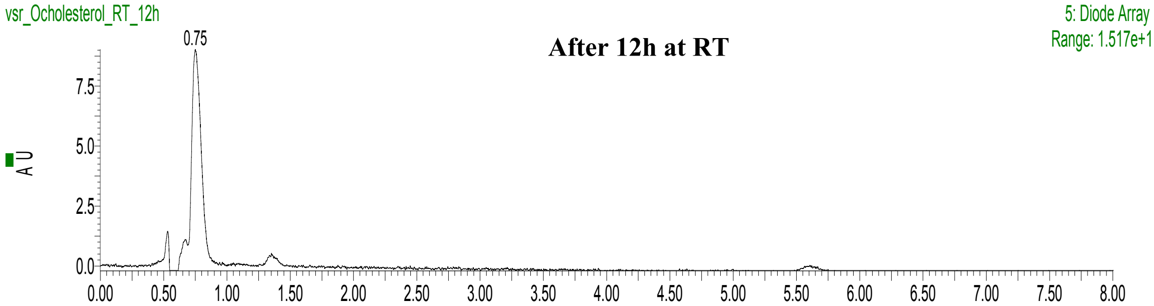


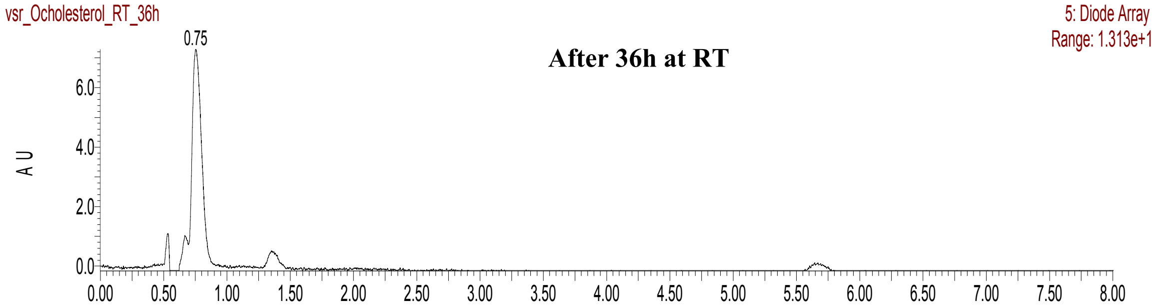


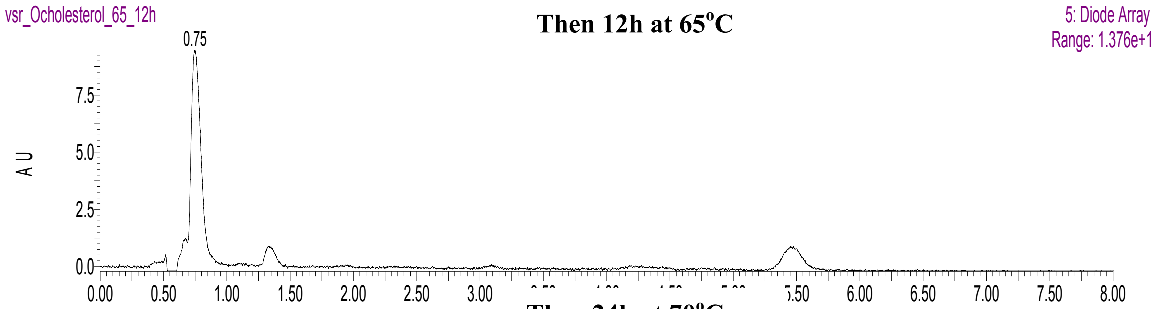
Time and Temperature Optimization Studies using $AuBr_3$ using Cholesteryl Mannoside
UPLC Chromatograms of Crude Reaction Mixtures

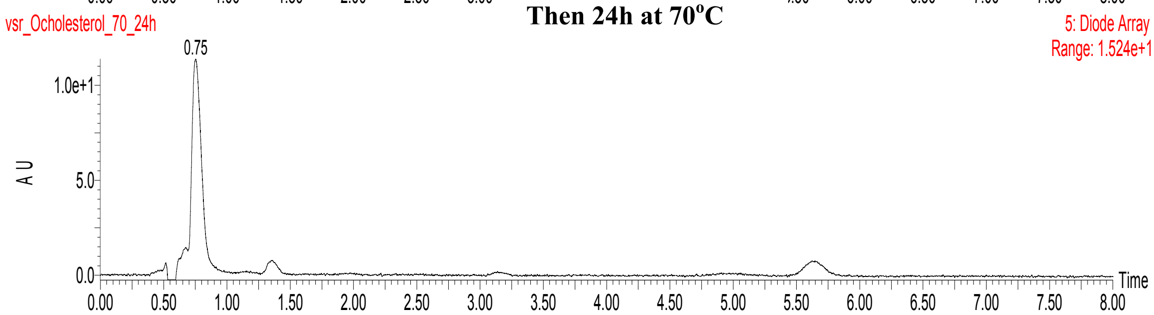


5e 2b 3b

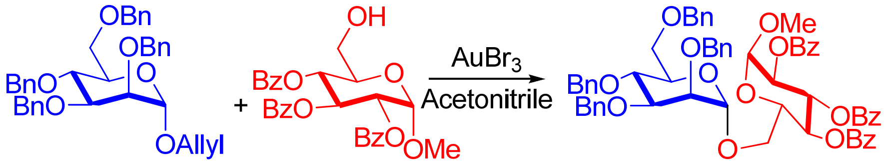








Time and Temperature Optimization Studies using $AuBr_3$ using Allyl Mannoside
UPLC Chromatograms of Crude Reaction Mixtures



5e 2b 3b