Supplementary Information

Visible-light-promoted C(sp^3)-H thiolation of aliphatic ethers with thiosulfonates

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1. General information of reagents and instruments

All reagents and solvents were purchased from commercial suppliers without further purification. All reactions were carried out in borosilicate glass vessels in a photo reactor manufactured by Beijing Roger Technology Co., Ltd. And, all reactions were performed under the irradiation of 5 W blue LED light without using filters (Figure S1, left). The blue light's energy peak wavelength is 452.6 nm, peak width at half-height is 21.6 nm and the irradiance@5W is 146.2 mW/cm^2 (Figure S1, right). LED irradiate through a high-reflection channel (path length is 2 cm) to the test tube. The progress of the reactions were monitored by TLC (thin-layer chromatography) under 254 nm UV light. Products were purified by chromatography on 200-300 mesh silica gels. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 2 °C) with Bruker Avance 400 MHz spectrometer operating at 400 MHz and 100 MHz, respectively. Chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained on Agilent Technologies 6530 Accurate mass Q-TOF LC/MS with ESI as ion source and Agilent Technologies 7250 Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) GC/MS with EI as ion source. GC-MS analysis of the products were performed on Thermo Fisher DSQ II with EI ion source. Injection port was set at 220 °C, ion source temperature and AUX temperature zone were set at 250 °C, and injection volume was 1.0 μL. Fluorescence quenching experiments were performed by Hitachi F7000 fluorescence spectrometer.

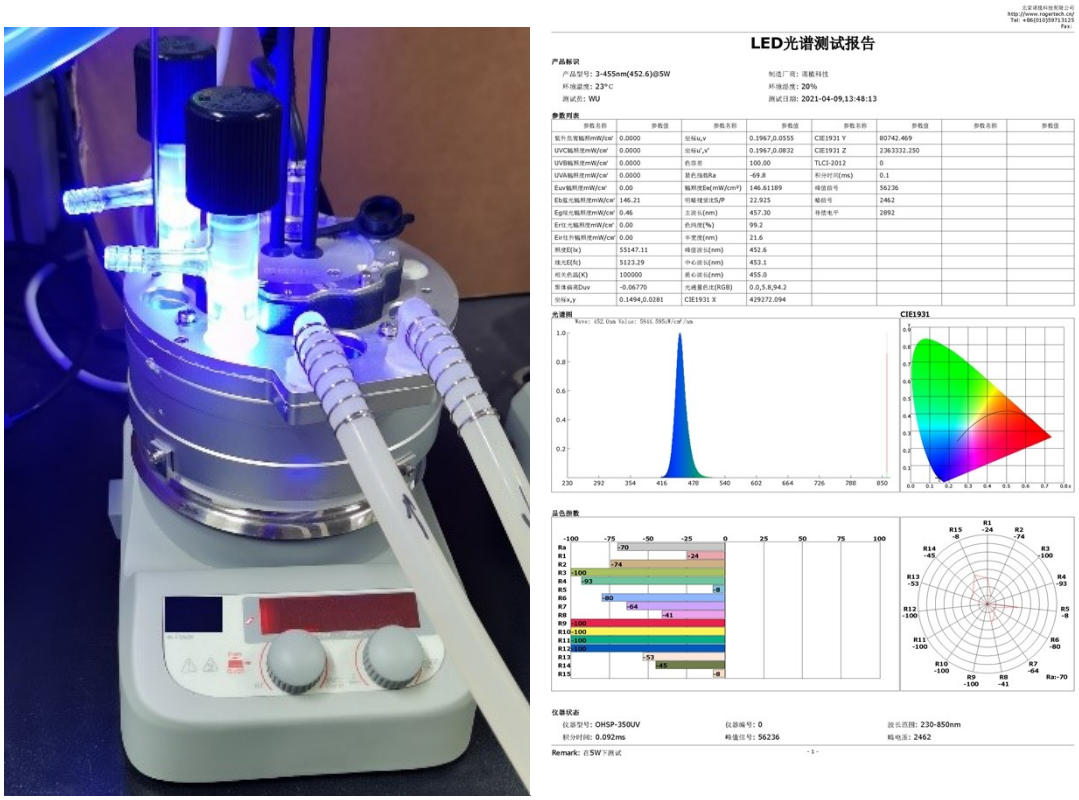
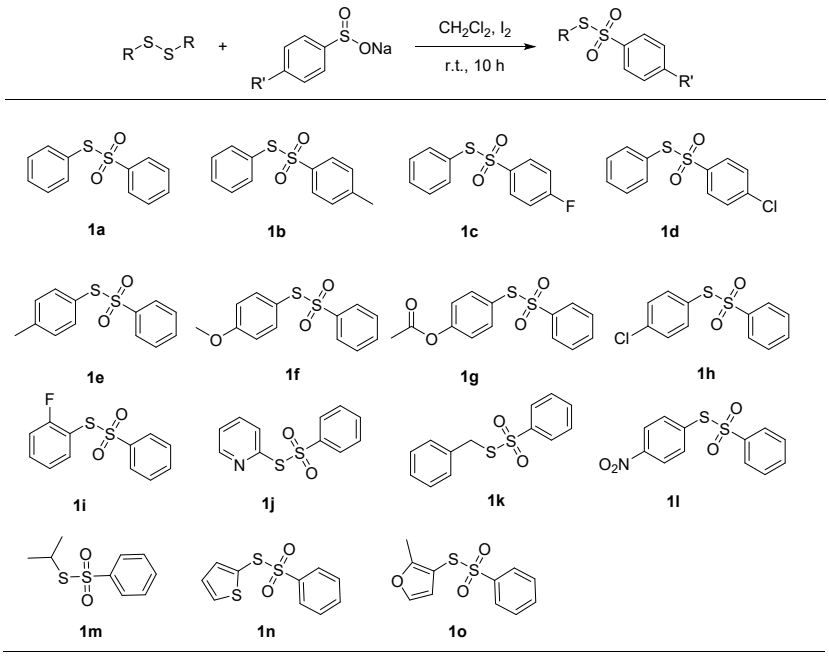


Figure S1 The photo reactor (left) and the blue LED light source test report (right).

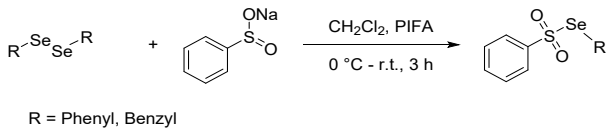
2. General synthetic procedure for thiosulfonates and selenosulfonates

2.1 Synthesis of thiosulfonates. Thiosulfonates were synthesized according to literature (*Org. Lett.*, 2020, **22**, 4908) with minor modifications using disulfides, sodium benzenesulfonates and iodine in CH_2Cl_2. After completion of the reaction, sodium thiosulfate was added to remove the excess iodine. Then, the mixture was washed by brine; the organic phase were combined and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) to give the corresponding desired products (Scheme S1).



Scheme S1 Structure of the synthesized thiosulfonates **1a-o**

2.2 Synthesis of selenosulfonates. *Se*-phenyl benzenesulfonoselenoate and *Se*-benzyl benzenesulfonoselenoate were synthesized according to literature (*J. Org. Chem.,* 2019, **84**, 8100.) by the use of 1,2-diphenyldiselane or 1,2-dibenzyldiselane and sodium benzenesulfonate with [bis(trifluoroacetoxy)iodo]benzene (PIFA) in dichloromethane at 0 °C to room temperature for 3 h. The desired product was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 10 : 1, v/v).

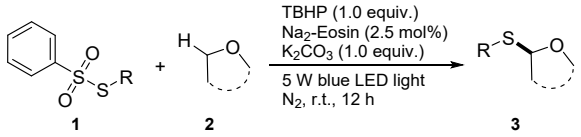


Scheme S2 Synthesis of selenosulfonates

3. General synthetic procedure for products 3

Thiosulfonates (**1**, 0.4 mmol), TBHP (0.4 mmol, 70% aqueous solution), Na_2-eosin Y (2.5 mol%) and K_2CO_3 (1.0 equiv.) were dissolved in corresponding ethers (**2**, 2.0 mL) in a 25 mL reaction tube, and then the mixture was stirred with the irradiation of 5 W blue LED light under N_2 at room temperature for 12 h. After reaction, the mixture was diluted with brine and extracted with CH_2Cl_2 (15 mL × 3). The organic layers were combined and dried over anhydrous Na_2SO_4. The residue was

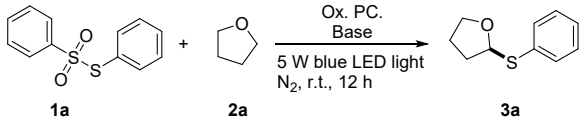
purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10~20/1, v/v) to afford the desired products **3**.



Scheme S3 Synthesis of products **3**

4. Investigations of photocatalyst, oxidant and base on the model reaction

Table S1 Optimization of reaction conditions.[a]



Entry	**1**	Ox.	PC.	Base	Yield (%)[b]
1	**1a**	TBHP	RhB	K_2CO_3	63
2	**1a**	TBHP	EB	K_2CO_3	77
3	**1a**	TBHP	MB	K_2CO_3	73
4	**1a**	TBHP	RB	K_2CO_3	62
5	**1a**	TBHP	FL	K_2CO_3	61
6	**1a**	TBHP	EYH_2	K_2CO_3	67
7	**1a**	TBHP	Na_2-EY	K_2CO_3	83
8	**1a**	TBHP	$Ru(bpy)_3Cl_2$	K_2CO_3	43
9	**1a**	DTBP	Na_2-EY	K_2CO_3	25
10	**1a**	$K_2S_2O_8$	Na_2-EY	K_2CO_3	17
11	**1a**	TBPB	Na_2-EY	K_2CO_3	trace
12	**1a**	BPO	Na_2-EY	K_2CO_3	trace
13	**1a**	H_2O_2	Na_2-EY	K_2CO_3	33
14	**1a**	*m*-CPBA	Na_2-EY	K_2CO_3	trace
15	**1a**	TBHP	Na_2-EY	KOH	44
16	**1a**	TBHP	Na_2-EY	NEt_3	38
17	**1a**	TBHP	Na_2-EY	$NaHCO_3$	21
18	**1a**	-	Na_2-EY	K_2CO_3	n.r.
19	**1a**	TBHP	Na_2-EY-	-	n.r.

[a] Reaction conditions: **1a** (0.4 mmol), oxidant (1.0 equiv.), photocatalyst (2.5 mol%) and base (1.0 equiv.) were mixed in THF (**2a**, 2.0 mL) with the irradiation of 5 W blue LED light under N_2 atmosphere at room temperature for 12 h. [b] Isolated yield based on **1** were provided. RhB = rhodamine B, EB = eosin B, MB = methylene blue, RB = rose bengal, FL = fluorescein, EYH_2 = eosin Y, Na_2-EY = Na_2-eosin Y, TBHP = *tert*-butyl hydroperoxide (70% aqueous solution), DTBP = di-*tert*-butyl peroxide, TBPB = *tert*-butyl peroxybenzoate, BPO = benzoyl peroxide, H_2O_2 was 30% aqueous solution, *m*-CPBA = *m*-chloroperoxybenzoic acid. n.r. = no reaction.

5. Mechanism Study

5.1 Experiment interfered with radical scavenger

In a 25 mL reaction tube, *S*-phenyl benzenethiosulfonate (**1a**, 0.4 mmol), TBHP (0.4 mmol, 70% aqueous solution), Na_2-eosin Y (2.5 mol%), K_2CO_3 (1.0 equiv.) and 2.0 equiv. of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) or 1,1-diphenylethylene (ASYM) were dissolved in THF (2.0 mL), respectively. The mixtures were stirred under standard reaction conditions for 12 h and then detected by HRMS.

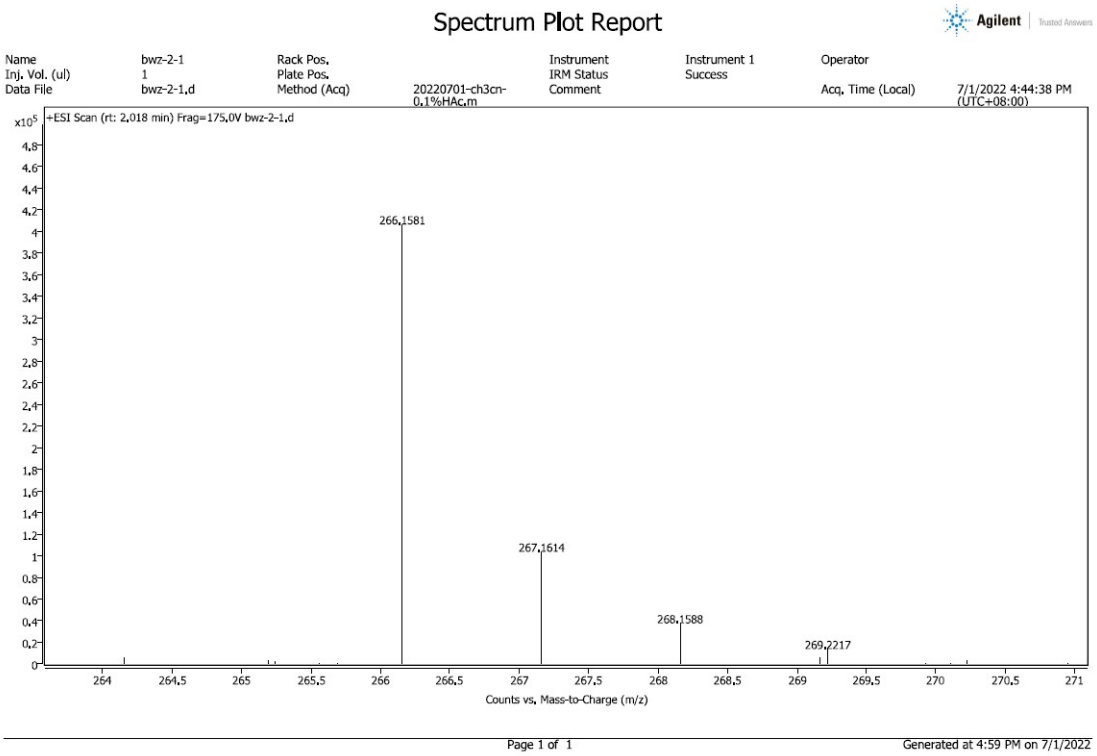


Figure S2 HRMS spectrum of the benzenesulfenyl radical/TEMPO adduct **5**

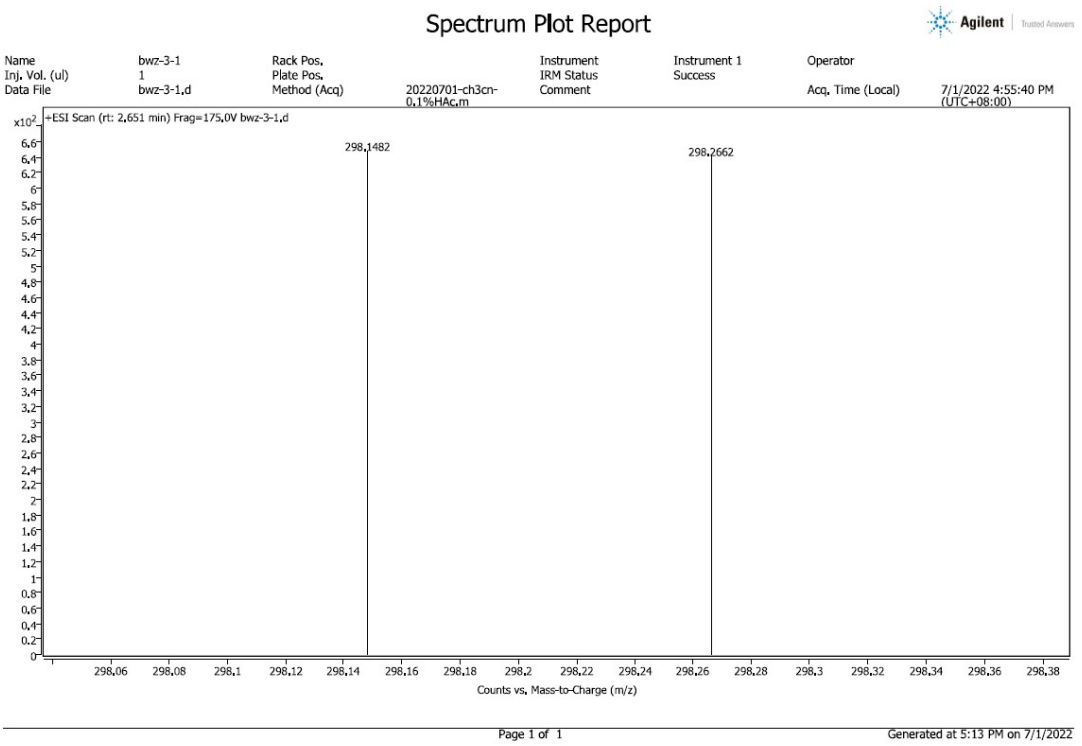


Figure S3 HRMS spectrum of the benzenesulfonyl radical/TEMPO adduct **6**

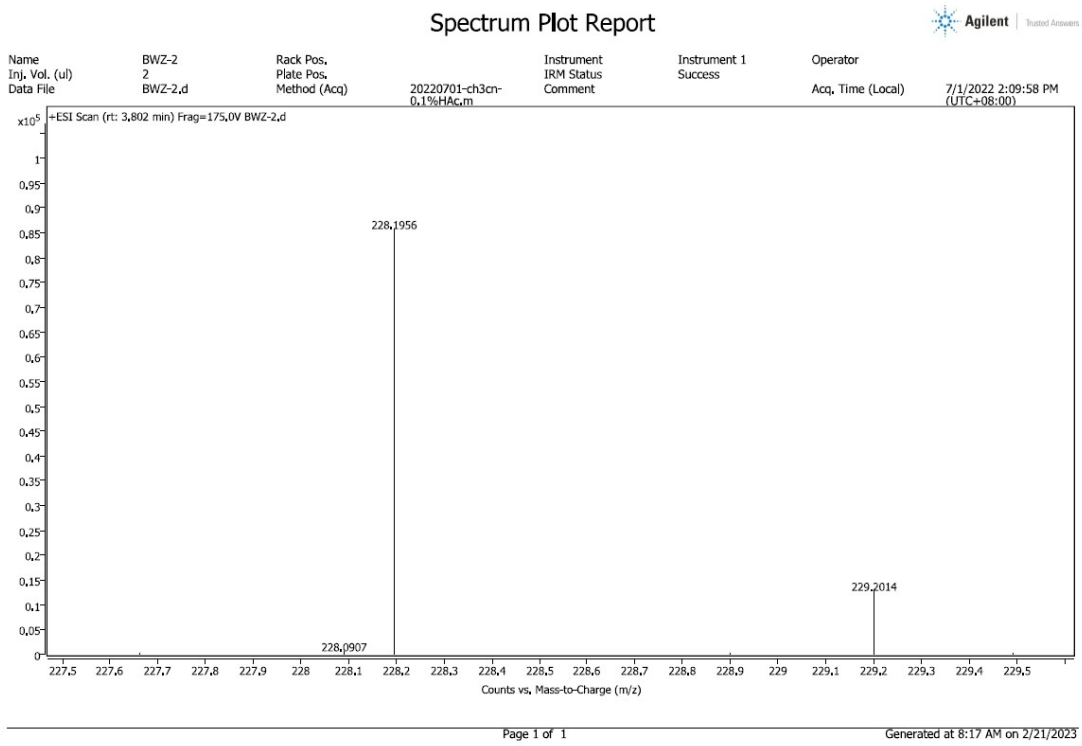


Figure S4 HRMS spectrum of the α-alkoxyalkyl radical /TEMPO adduct **7**

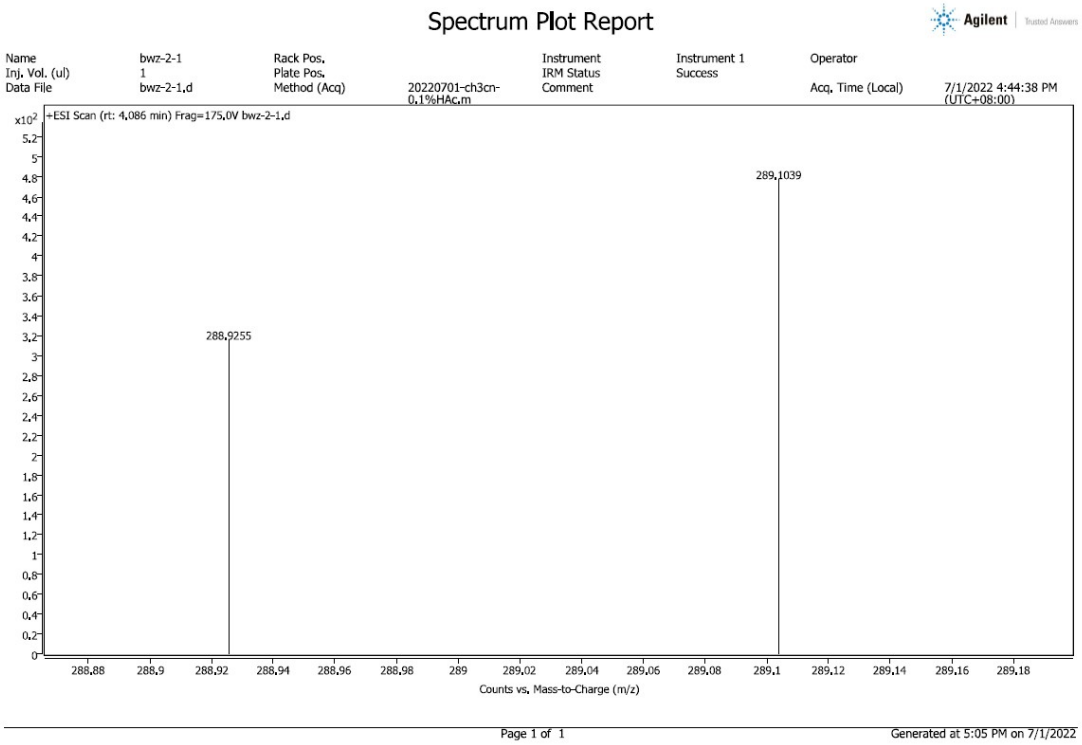


Figure S5 HRMS Spectrum of the benzenesulfenyl radical /ASYM adduct **8**

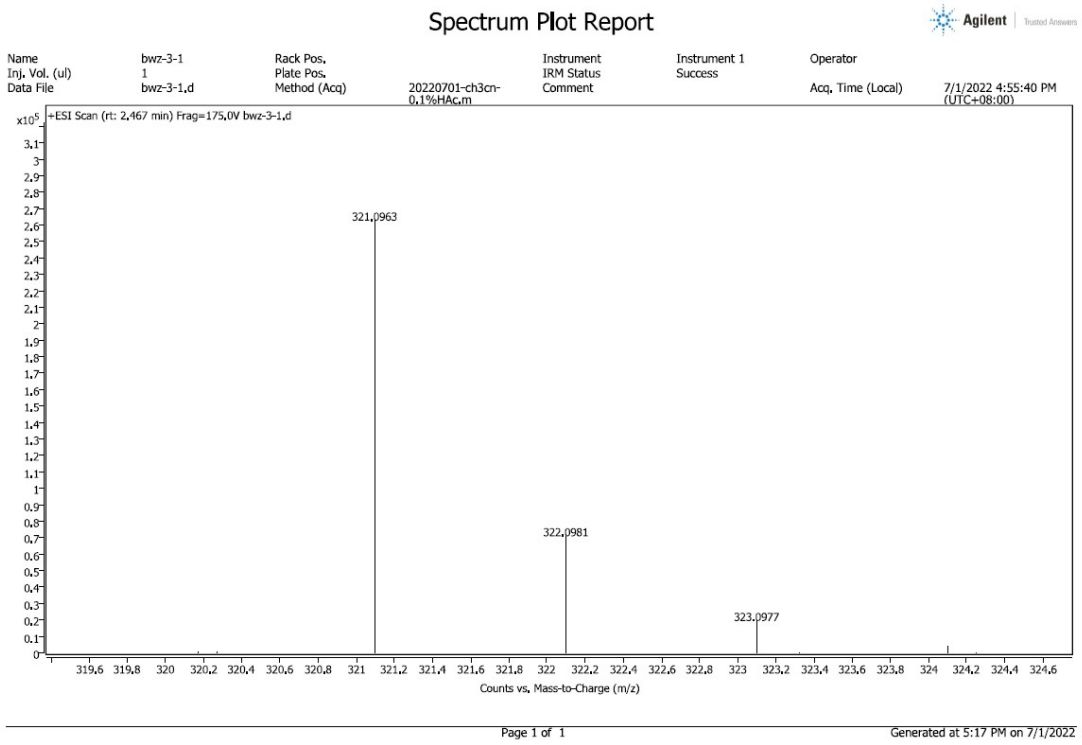


Figure S6 HRMS spectrum of the benzenesulfonyl radical / ASYM adduct **9**

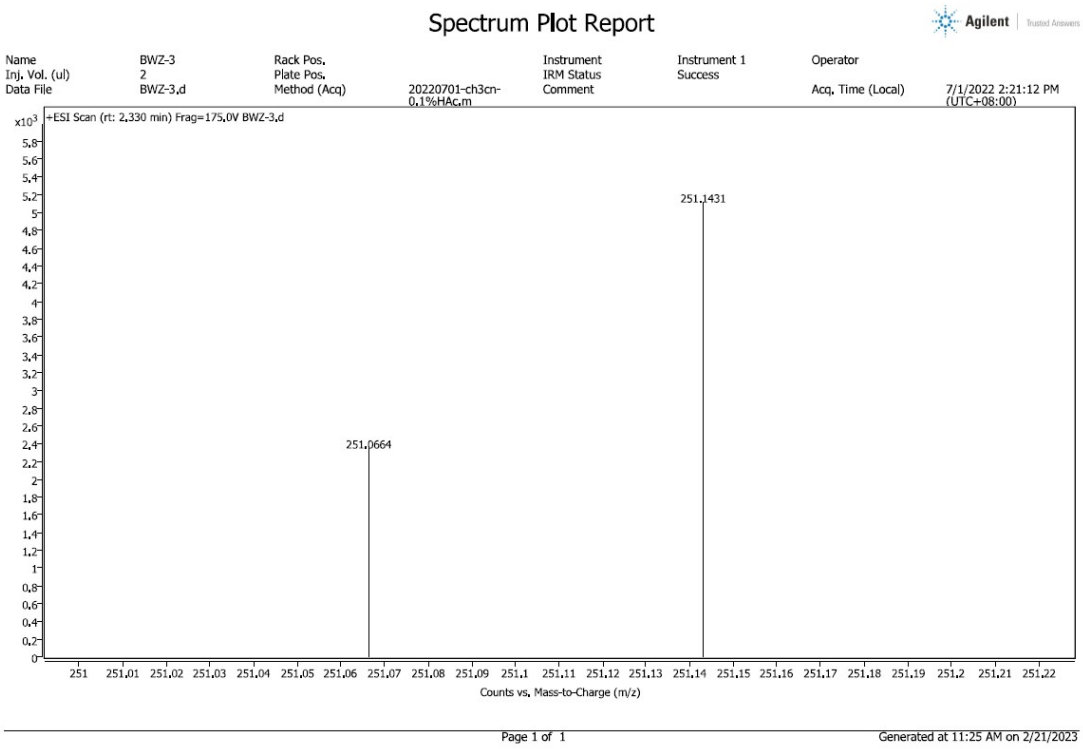


Figure S7 HRMS spectrum of the α-alkoxyalkyl radical / ASYM adduct **10**

5.2 Fluorescence quenching experiments

A stock solution of Na_2-eosin Y (5 mM in THF) was prepared for the quenching experiment. 200 μL Na_2-eosin Y stock solution was diluted to 2.0 mL with THF in a quartz cuvette (1 cm × 1 cm). The fluorescence excitation and emission spectra were firstly recorded as shown below. The maximum excitation/emission wavelength were detected as 461/559 nm. Then, quenching experiments were performed with addition of TBHP (70% aqueous solution) or **1a**, respectively.

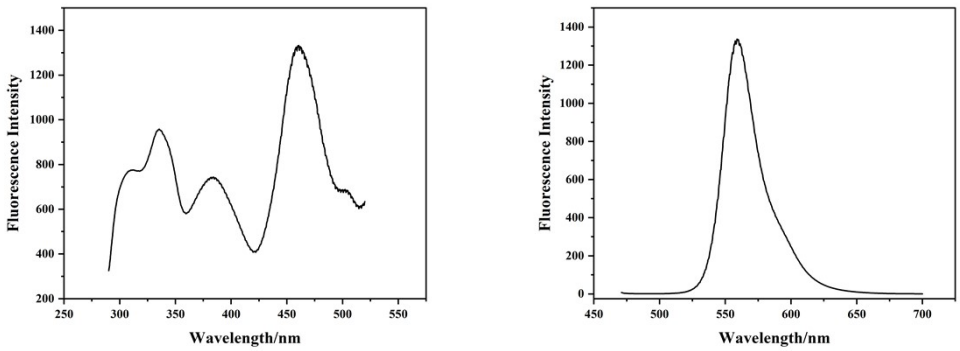


Figure S8 Fluorescence excitation (left) and emission (right) spectra of Na_2-eosin Y (5×10^{-4} M) in THF

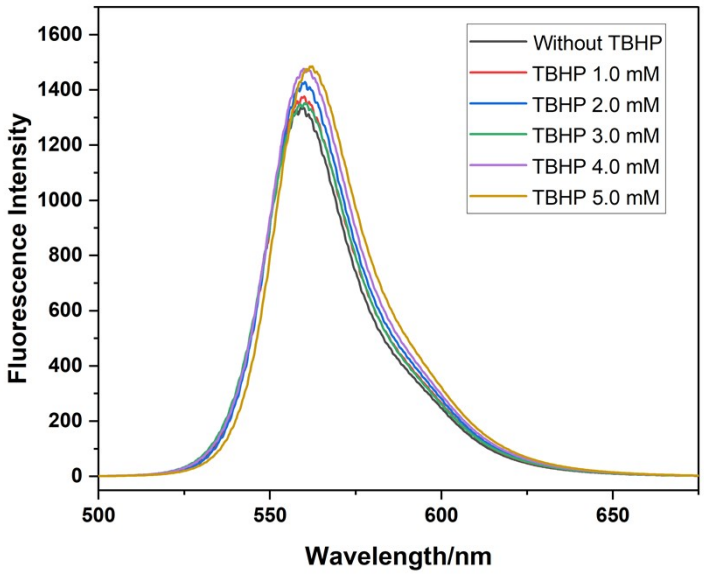


Figure S9 Fluorescence emission spectra of Na_2-eosin Y (5×10^{-4} M) in THF with TBHP (1.0 - 5.0 mM)

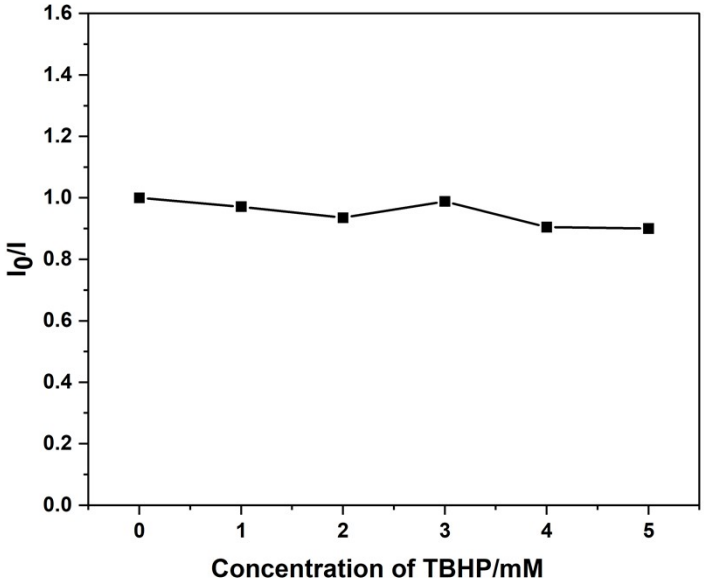


Figure S10 The linear relationship between I_0/I (I_0 and I are the fluorescence intensities before and after the addition of **TBHP**) and the concentration of **TBHP**

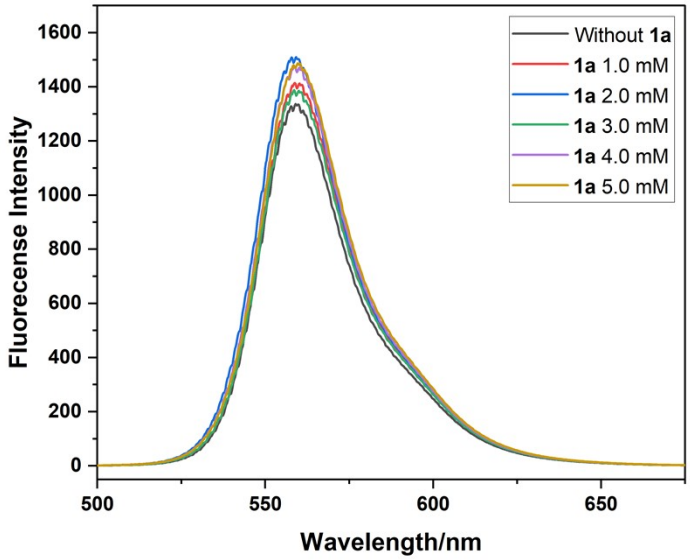


Figure S11 Fluorescence emission spectra of Na_2-eosin Y (5×10^{-4} M) in THF with **1a** (1.0 - 5.0 mM)

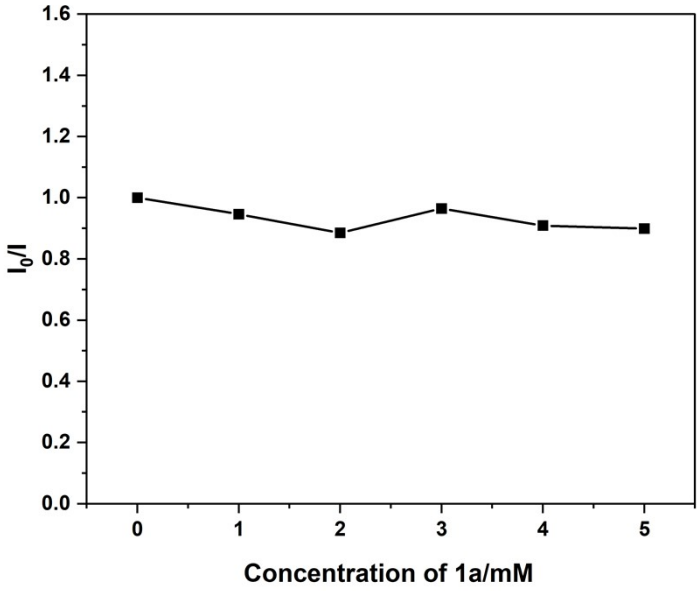
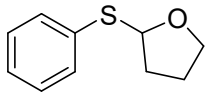


Figure S12 The linear relationship between I_0/I (I_0 and I are the fluorescence intensities before and after the addition of **1a**) and the concentration of **1a**

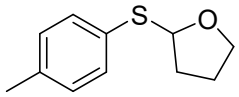
6. Characterization data of compounds 3a-aa and 4a-c

2-(phenylthio)tetrahydrofuran (3a)



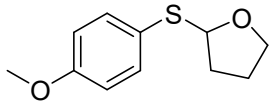
Pale oil, yield: 83%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.51 (m, 2H), 7.29 (m, 2H), 7.22 (m, 1H), 5.65 (m, 1H), 4.06-3.94 (m, 2H), 2.39-2.34 (m, 1H), 2.04-1.90 (m, 2H), 1.90-1.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.7, 131.1, 128.8, 126.8, 87.2, 67.3, 32.7, 24.8. GC-HRMS (EI) for $C_{10}H_{12}OS$ (m/z): calcd. 180.0609, found 180.0583.

2-(*p*-tolylthio)tetrahydrofuran (3b)



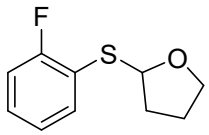
Pale oil, yield: 69%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.40 (m, 2H), 7.11 (m, 2H), 5.57 (m, 1H), 4.03-3.93 (m, 2H), 2.36-2.30 (m, 4H), 2.03-1.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.0, 131.9, 131.7, 129.6, 87.6, 67.2, 32.6, 24.8, 21.1. GC-MS (EI) for $C_{11}H_{14}OS$ (m/z): calcd. 194.08, found 194.10.

2-((4-methoxyphenyl)thio)tetrahydrofuran (3c)



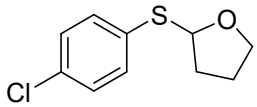
Pale oil, yield: 73%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.46 (m, 2H), 6.85 (m, 2H), 5.47 (m, 1H), 4.02-3.90 (m, 2H), 3.79 (s, 3H), 2.34-2.27 (m, 1H), 2.00-1.83 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.4, 134.6, 125.6, 114.4, 88.2, 67.2, 55.3, 32.5, 24.8. GC-MS (EI) for $C_{11}H_{14}O_2S$ (m/z): calcd. 210.07, found 210.08.

2-((2-fluorophenyl)thio)tetrahydrofuran (3d)



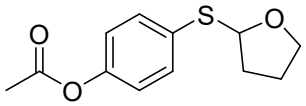
Pale oil, yield: 81%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.60 (m, 1H), 7.25 (m, 1H), 7.12-7.04 (m, 2H), 5.70 (m, 1H), 4.07-3.93 (m, 2H), 2.40-2.33 (m, 1H), 2.08-2.00 (m, 2H), 1.92-1.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 162.7 and 160.3, 133.9, 129.0 and 128.9, 124.52 and 124.48, 122.4 and 122.2, 115.7 and 115.4, 86.44 and 86.43, 67.4, 32.7, 24.6. GC-MS (EI) for $C_{10}H_{11}FOS$ (m/z): calcd. 198.05, found 198.04.

2-((4-chlorophenyl)thio)tetrahydrofuran (3e)



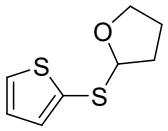
Pale oil, yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.43 (m, 2H), 7.26 (m, 2H), 5.60 (m, 1H), 4.04-3.93 (m, 2H), 2.39-2.34 (m, 1H), 2.04-1.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.2, 133.0, 132.4, 128.9, 87.3, 67.3, 32.6, 24.8. GC-MS (EI) for $C_{10}H_{11}ClOS$ (m/z): calcd. 214.02, found 214.03.

2-((tetrahydrofuran-2-yl)thio)phenyl acetate (3f)



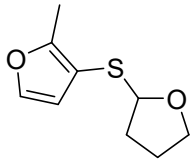
Pale oil, yield: 77%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.52 (m, 2H), 7.02 (m, 2H), 5.60 (m, 1H), 4.03-3.93 (m, 2H), 2.38-2.33 (m, 1H), 2.28 (s, 3H), 2.03-1.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.3, 149.8, 132.5, 122.0, 87.5, 67.2, 32.6, 24.8, 21.1. GC-MS (EI) for $C_{12}H_{14}O_3S$ (m/z): calcd. 238.07, found 238.08.

2-(thiophen-2-ylthio)tetrahydrofuran (3g)



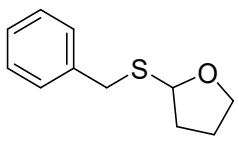
Pale oil, yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.36 (m, 1H), 7.17 (m, 1H), 7.00 (m, 1H), 5.43 (m, 1H), 4.06-4.00 (m, 1H), 3.98-3.93 (m, 1H), 2.32-2.26 (m, 1H), 2.01-1.97 (m, 2H), 1.95-1.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.3, 132.4, 129.9, 127.5, 89.5, 67.5, 32.1, 24.6. GC-MS (EI) for $C_8H_{10}OS_2$ (m/z): calcd. 186.02, found 186.10.

2-methyl-3-((tetrahydrofuran-2-yl)thio)furan (3h)



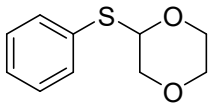
Pale oil, yield: 69%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.27 (m, 1H), 6.41 (m, 1H), 5.32 (m, 1H), 4.02-3.93 (m, 1H), 3.92-3.88 (m, 1H), 2.35 (s, 3H), 2.28-2.22 (m, 1H), 2.01-1.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.4, 140.4, 115.5, 109.3, 87.7, 67.2, 32.3, 24.8, 11.9. GC-MS (EI) for $C_9H_{12}O_2S$ (m/z): calcd. 184.06, found 184.05.

2-(benzylthio)tetrahydrofuran (3i)



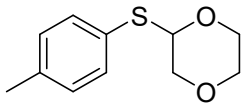
Pale oil, yield: 78%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.36-7.29 (m, 4H), 7.23 (m, 1H), 5.23 (m, 1H), 3.98-3.88 (m, 2H), 3.77-3.73 (m, 2H), 2.22-2.18 (m, 1H), 2.02-1.97 (m, 1H), 1.97-1.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.6, 129.0, 128.4, 126.8, 83.0, 66.8, 32.0, 32.1, 24.8. GC-MS (EI) for $C_{11}H_{14}OS$ (m/z): calcd. 194.08, found 194.10.

2-(phenylthio)-1,4-dioxane (3l)



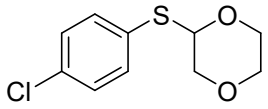
Pale oil, yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.50 (m, 2H), 7.32-7.26 (m, 3H), 5.12 (m, 1H), 4.25-4.20 (m, 1H), 4.00-3.96 (m, 1H), 3.74-3.65 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.0, 131.6, 129.0, 127.4, 83.3, 70.0, 66.5, 63.8. GC-MS (EI) for $C_{10}H_{12}O_2S$ (m/z): calcd. 196.06, found 196.07.

2-(*p*-tolylthio)-1,4-dioxane (3m)



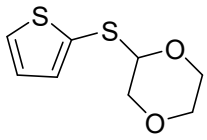
Pale oil, yield: 76%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.41 (m, 2H), 7.11 (m, 2H), 5.02 (m, 1H), 4.22-4.18 (m, 1H), 3.98-3.94 (m, 1H), 3.72-3.65 (m, 4H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.7, 136.5, 132.4, 129.7, 83.5, 69.9, 66.4, 64.0, 21.1. GC-MS (EI) for $C_{11}H_{14}O_2S$ (m/z): calcd. 210.07, found 210.07.

2-((4-chlorophenyl)thio)-1,4-dioxane (3n)



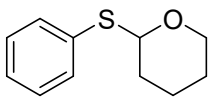
Pale oil, yield: 83%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.43 (m, 2H), 7.27 (m, 2H), 5.08 (m, 1H), 4.26-4.21 (m, 1H), 3.99-3.95 (m, 1H), 3.74-3.64 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 133.6, 132.9, 132.5, 129.1, 83.3, 69.8, 66.5, 63.6. GC-MS (EI) for $C_{10}H_{11}ClO_2S$ (m/z): calcd. 230.02, found 230.02.

2-(thiophen-2-ylthio)-1,4-dioxane (3o)



Pale oil, yield: 67%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.39 (m, 1H), 7.19 (m, 1H), 7.00 (m, 1H), 4.91 (m, 1H), 4.28-4.23 (m, 1H), 3.96-3.93 (m, 1H), 3.72-3.66 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.0, 130.4, 130.3, 127.5, 84.5, 69.4, 66.5, 63.7. GC-MS (EI) for $C_8H_{10}O_2S_2$ (m/z): calcd. 202.01, found 202.01.

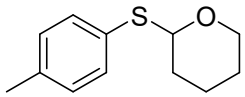
2-(phenylthio)tetrahydro-*2H*-pyran (3p)



Pale oil, yield: 71%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.48 (m, 2H), 7.29 (m, 2H), 7.26-7.19 (m, 1H), 5.21 (m, 1H), 4.20-4.15 (m, 1H), 3.61-3.56 (m, 1H), 2.04-1.99 (m, 1H), 1.86-1.81 (m, 2H), 1.67-1.61 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.4, 130.9, 128.8, 126.7, 85.3, 64.5, 31.6, 25.5,

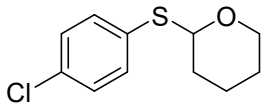
21.7. GC-MS (EI) for $C_{11}H_{14}OS$ (m/z): calcd. 194.08, found 194.08.

2-(p-tolylthio)tetrahydro-*2H*-pyran (3q)



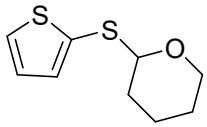
Pale oil, yield: 67%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.38 (m, 2H), 7.10 (m, 2H), 5.12 (m, 1H), 4.20-4.14 (m, 1H), 3.59-3.53 (m, 1H), 2.32 (s, 3H), 2.04-1.98 (m, 1H), 187-1.78 (m, 2H), 1.78-1.60 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.9, 131.7, 131.4, 129.6, 85.7, 64.6, 31.6, 25.5, 21.7, 21.1.

2-((4-chlorophenyl)thio)tetrahydro-*2H*-pyran (3r)



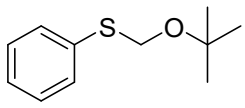
Pale oil, yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.40 (m, 2H), 7.25 (m, 2H), 5.17 (m, 1H), 4.18-4.12 (m, 1H), 3.61-3.55 (m, 1H), 2.03-2.00 (m, 1H), 1.85-1.81 (m, 2H), 1.66-1.61 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 133.9, 132.8, 132.2, 128.9, 85.4, 64.4, 31.5, 25.5, 21.5. GC-MS (EI) for $C_{11}H_{13}ClOS$ (m/z): calcd. 228.04, found 228.04.

2-(thiophen-2-ylthio)tetrahydro-*2H*-pyran (3s)



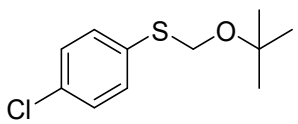
Pale oil, yield: 63%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.36 (m, 1H), 7.15 (m, 1H), 6.99 (m, 1H), 5.00 (m, 1H), 4.22-4.16 (m, 1H), 3.61-3.56 (m, 1H), 2.02-1.95 (m, 1H), 1.86-1.77 (m, 2H), 1.64-1.60 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.1, 132.0, 129.6, 127.4, 87.3, 64.4, 30.9, 25.5, 21.3. GC-MS (EI) for $C_9H_{12}OS_2$ (m/z): calcd. 200.03, found 200.04.

(*tert*-butoxymethyl)(phenyl)sulfane (3t)



Pale oil, yield: 57%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.49 (m, 2H), 7.29-7.26 (m, 2H), 7.20 (m, 1H), 4.90 (s, 2H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.6, 130.0, 128.8, 126.4, 75.3, 68.2, 27.8. GC-MS (EI) for $C_{11}H_{16}OS$ (m/z): calcd. 196.09, found 196.09.

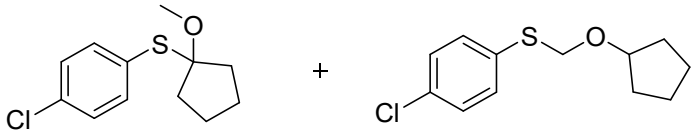
(*tert*-butoxymethyl)(4-chlorophenyl)sulfane (3u)



Pale oil, yield: 62%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.42 (m, 2H), 7.25 (m, 2H), 4.87 (s, 2H), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.1, 132.6, 131.4, 128.9, 75.5, 68.3, 27.8. GC-MS (EI)

for $C_{10}H_{13}ClO_2S$ (m/z): calcd. 230.05, found 230.05.

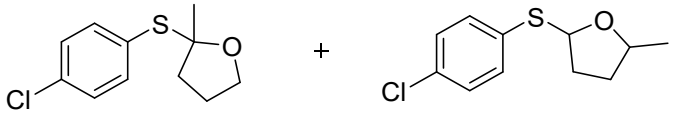
(4-chlorophenyl)(1-methoxycyclopentyl)sulfane (3x-i) and (4-chlorophenyl)((cyclopentyloxy)-methyl)sulfane (3x-ii) (3x)



3x-i **3x-ii**

Pale oil, yield: 75% (**3x-i** : **3x-ii** = 2.5 : 1.0). ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.40 (m, 3H), 7.25 (m, 3H), 4.93-4.33 (m, 1H), 3.46 (s, 3H), 1.87-1.68 (m, 11H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.8 and 134.7, 133.6 and 132.9, 132.6 and 131.4, 129.0 and 128.7, 100.4, 79.1 and 73.9, 51.4, 38.0, 32.0, 23.5 and 23.2. GC-MS (EI) for $C_{12}H_{15}ClOS$ (m/z): calcd. 242.05, found 242.04.

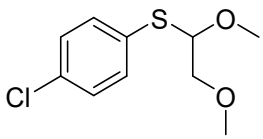
2-((4-chlorophenyl)thio)-2-methyltetrahydrofuran (3y-i) and 2-((4-chlorophenyl)thio)-5-methyltetrahydrofuran (3y-ii) (3y)



3y-i **3y-ii**

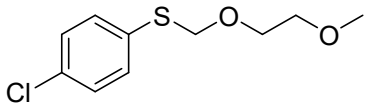
Pale oil, yield: 81% (**3y-i** : **3y-ii** = 3.0 : 1.0). ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.36 (m, 2H), 7.86 (m, 2H), 1.58 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 152.9, 149.8, 126.3, 124.2, 84.3, 29.9. GC-MS (EI) for $C_{11}H_{13}ClOS$ (m/z): calcd. 228.04, found 228.02.

(4-chlorophenyl)(1,2-dimethoxyethyl)sulfane (3z-i)



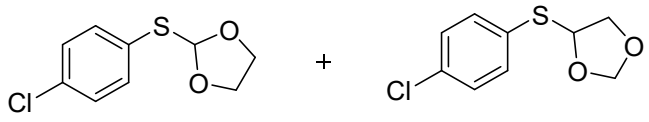
Pale oil, yield: 46%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.42 (m, 2H), 7.27 (m, 2H), 4.72 (m, 1H), 3.56-3.49 (m, 5H), 3.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.2, 134.2, 130.6, 129.0, 88.8, 74.5, 59.1, 56.3. GC-MS (EI) for $C_{10}H_{13}ClO_2S$ (m/z): calcd. 232.03, found 232.06.

(4-chlorophenyl)((2-methoxyethoxy)methyl)sulfane (3z-ii)



Pale oil, yield: 31%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.41 (m, 2H), 7.25 (m, 2H), 5.03 (s, 2H), 3.79-3.76 (m, 2H), 3.59-3.55 (m, 2H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.4, 132.8, 131.5, 129.0, 76.5, 71.5, 67.5, 59.0. GC-MS (EI) for $C_{10}H_{13}ClO_2S$ (m/z): calcd. 232.03, found 232.06.

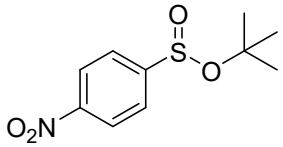
2-((4-chlorophenyl)thio)-1,3-dioxolane (3aa-i) and 4-((4-chlorophenyl)thio)-1,3-dioxolane (3aa-ii) (3aa)



3aa-i **3aa-ii**

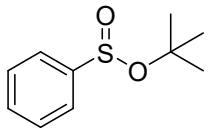
Pale oil, yield: 68% (**3aa-i** : **3aa-ii** = 2.7 : 1.0). ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.69-7.67 (m, 2H), 7.52-7.50 (m, 3H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.6, 131.5, 128.9, 124.9, 82.8, 29.9. GC-MS (EI) for $C_9H_9ClO_2S$ (m/z): calcd. 216.00, found 216.00.

***tert*-butyl 4-nitrobenzenesulfinate (4a)**



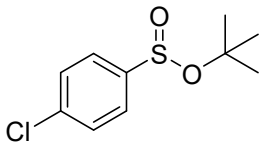
Yellow solid, yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.36 (m, 2H), 7.86 (m, 2H), 1.58 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 152.9, 149.8, 126.3, 124.2, 84.3, 29.9.

***tert*-butyl benzenesulfinate (4b)**



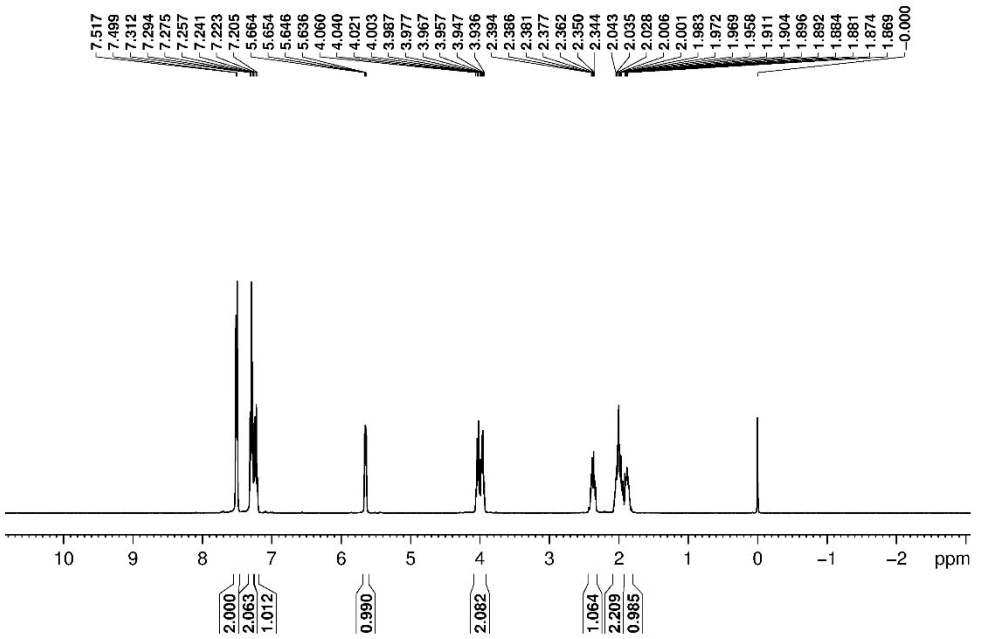
White oil, yield: 78%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.69-7.67 (m, 2H), 7.52-7.50 (m, 3H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.6, 131.5, 128.9, 124.9, 82.8, 29.9.

***tert*-butyl 4-chlorobenzenesulfinate (4c)**

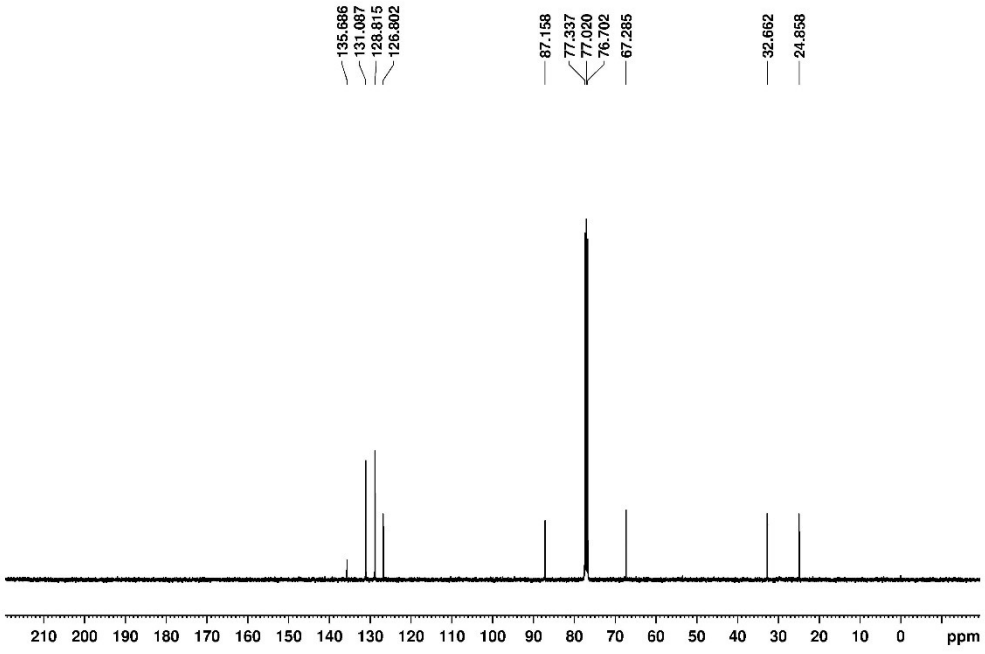


White oil, yield: 81%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.62-7.60 (m, 2H), 7.50-7.48 (m, 2H), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 145.2, 137.9, 129.2, 126.4, 83.3, 29.9.

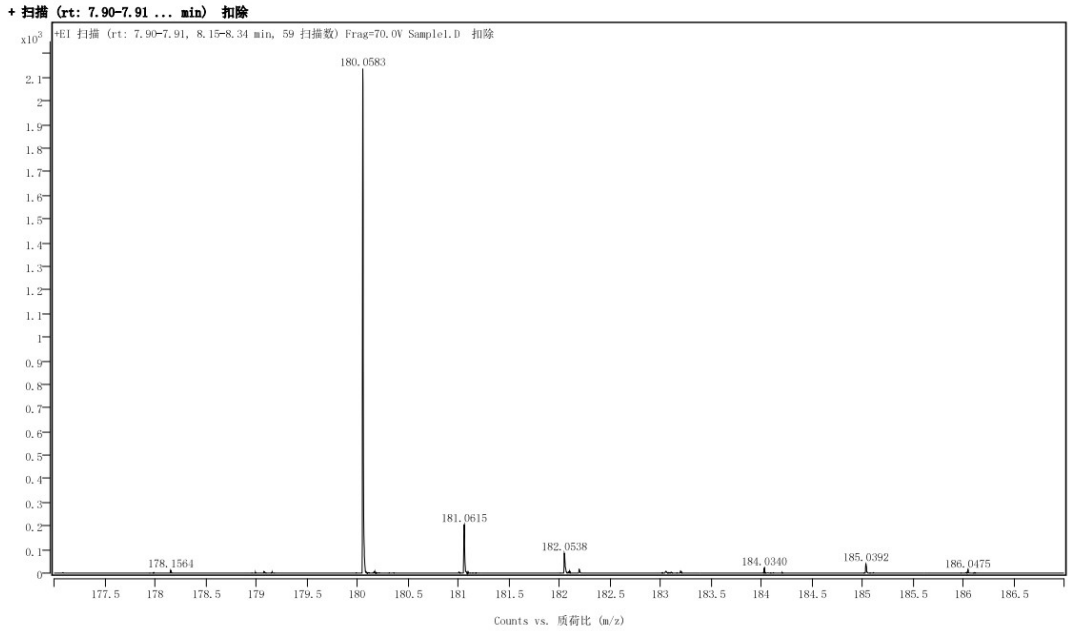
7. ^{1}H NMR, ^{13}C NMR and HRMS/MS copies of compounds 3a-aa and 4a-c



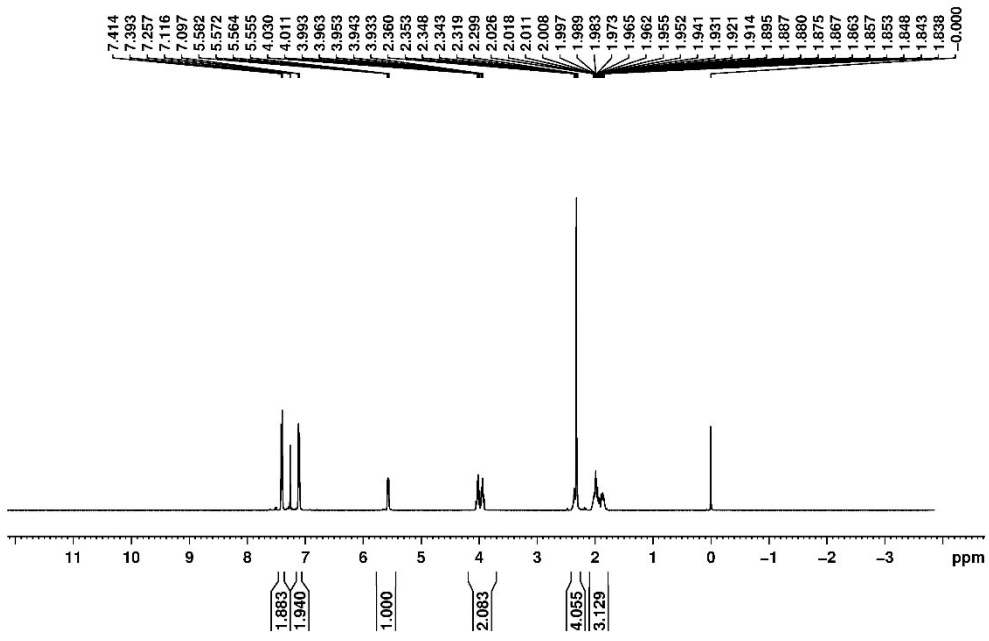
^{1}H NMR spectrum of compound **3a**



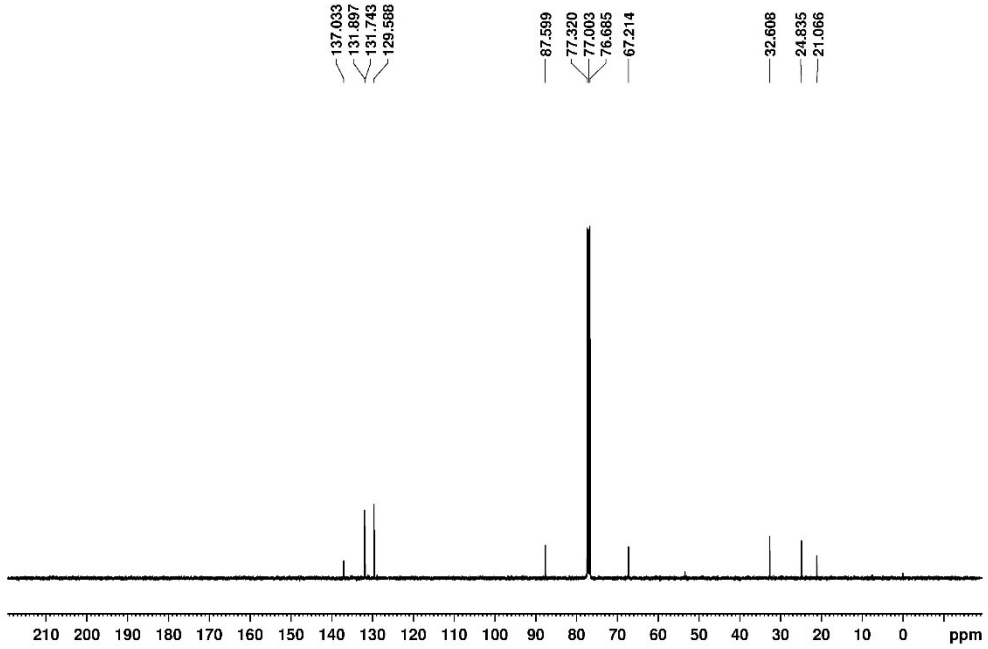
^{13}C NMR spectrum of compound **3a**



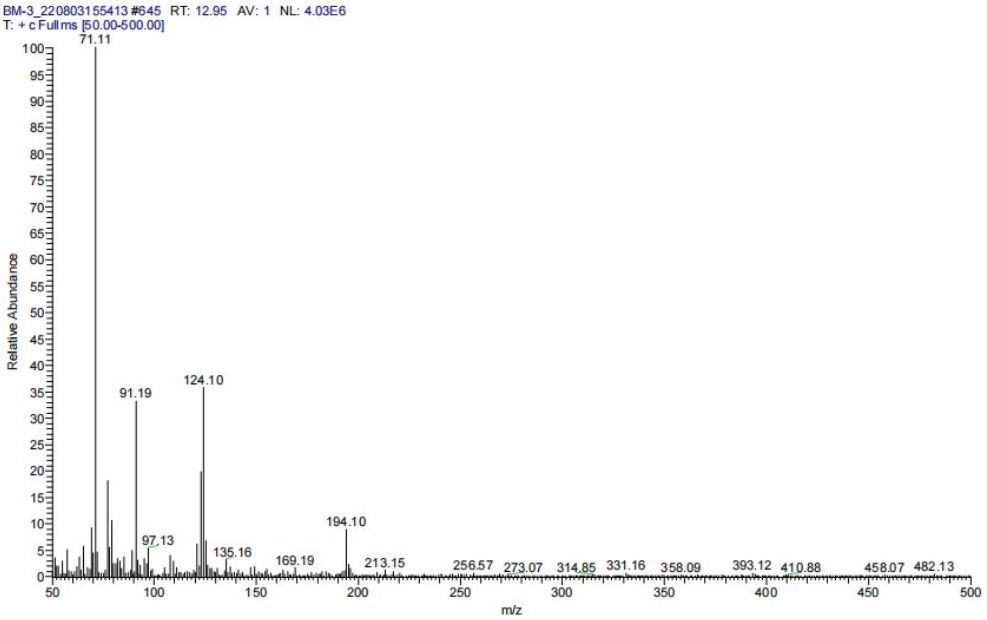
HRMS spectrum of compound **3a**



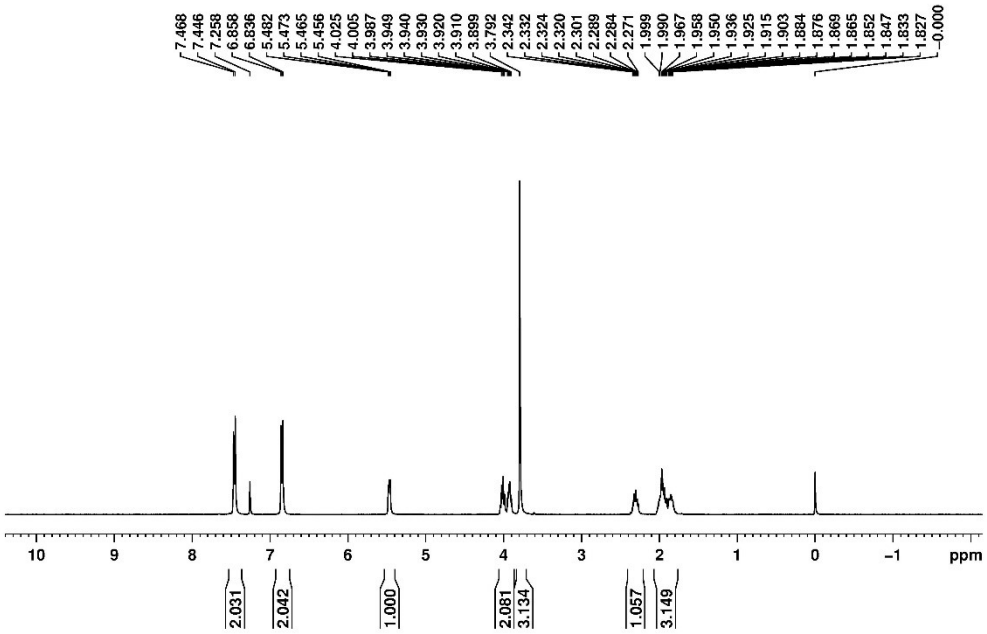
^{1}H NMR spectrum of compound **3b**



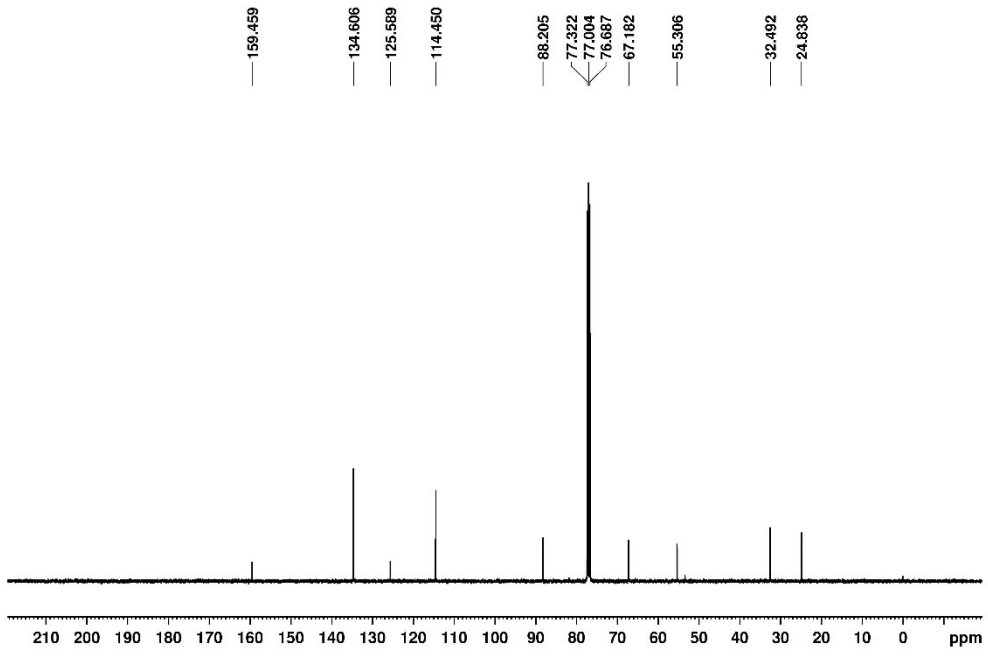
^{13}C NMR spectrum of compound **3b**



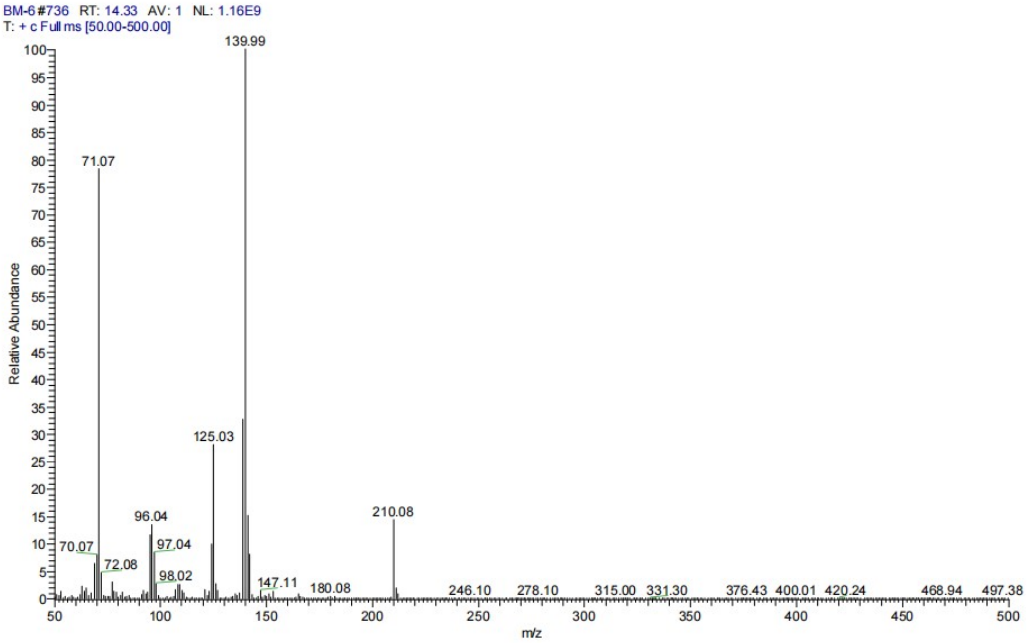
MS spectrum of compound **3b**



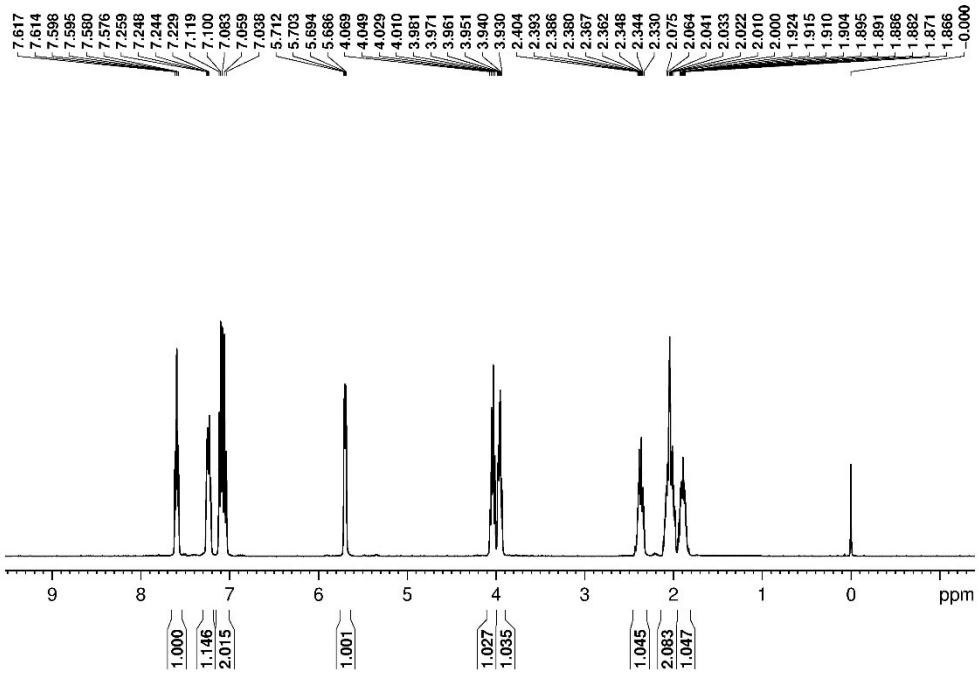
^{1}H NMR spectrum of compound **3c**



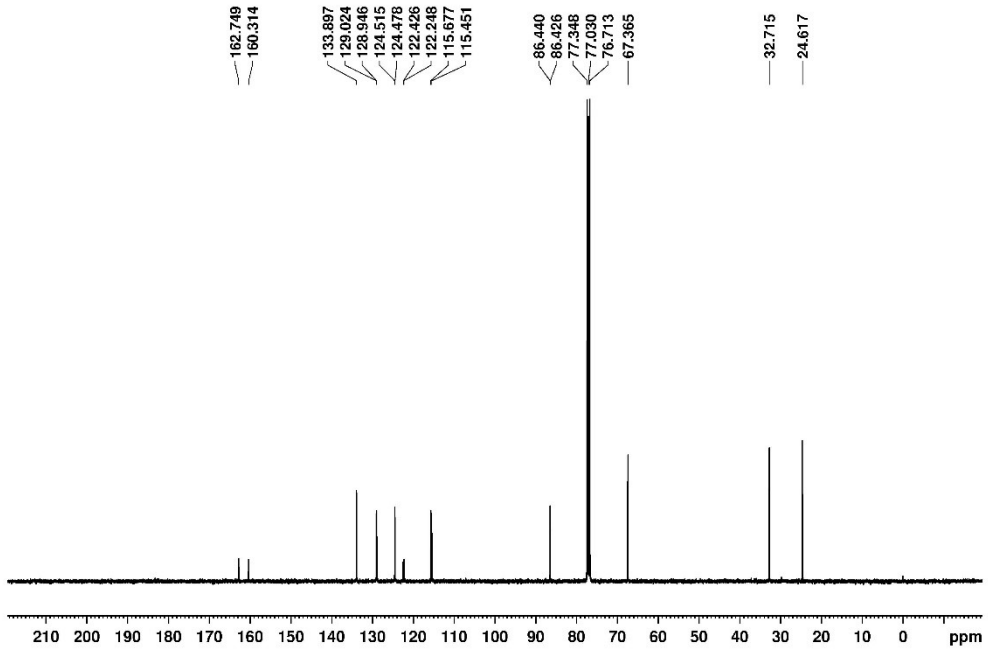
^{13}C NMR spectrum of compound **3c**



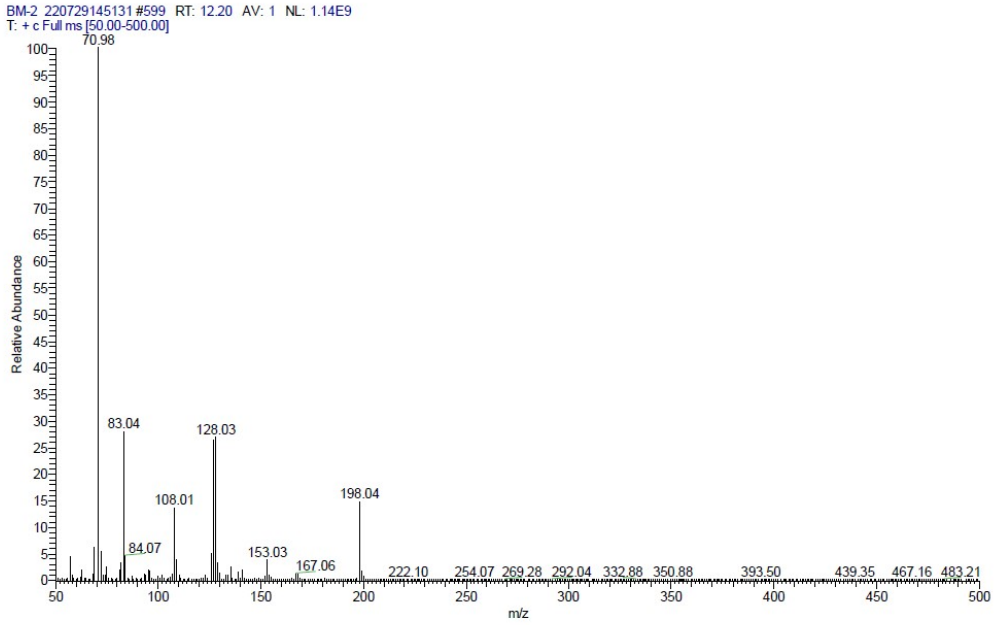
MS spectrum of compound **3c**



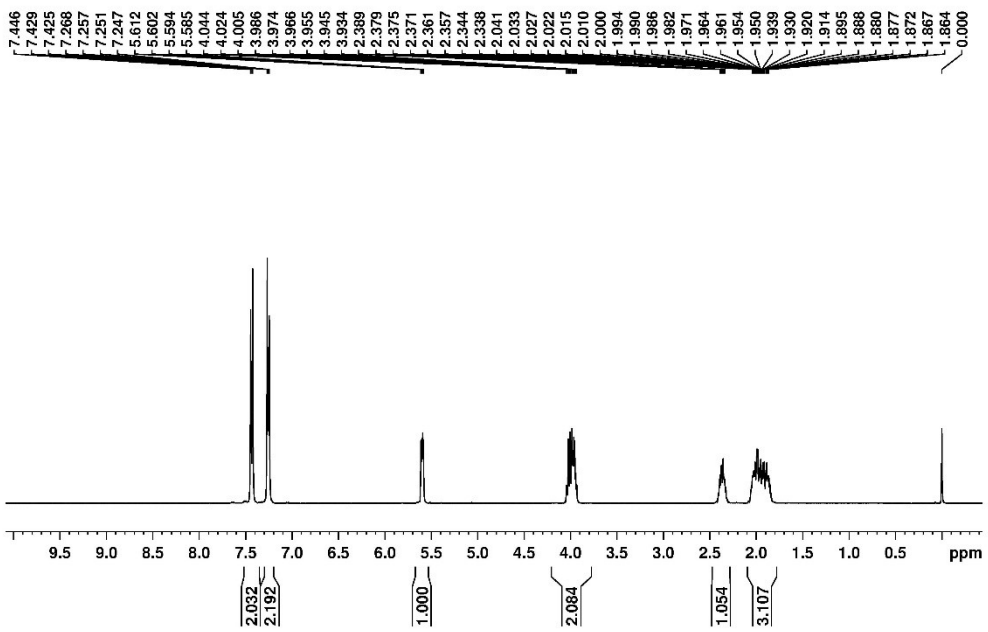
^{1}H NMR spectrum of compound **3d**



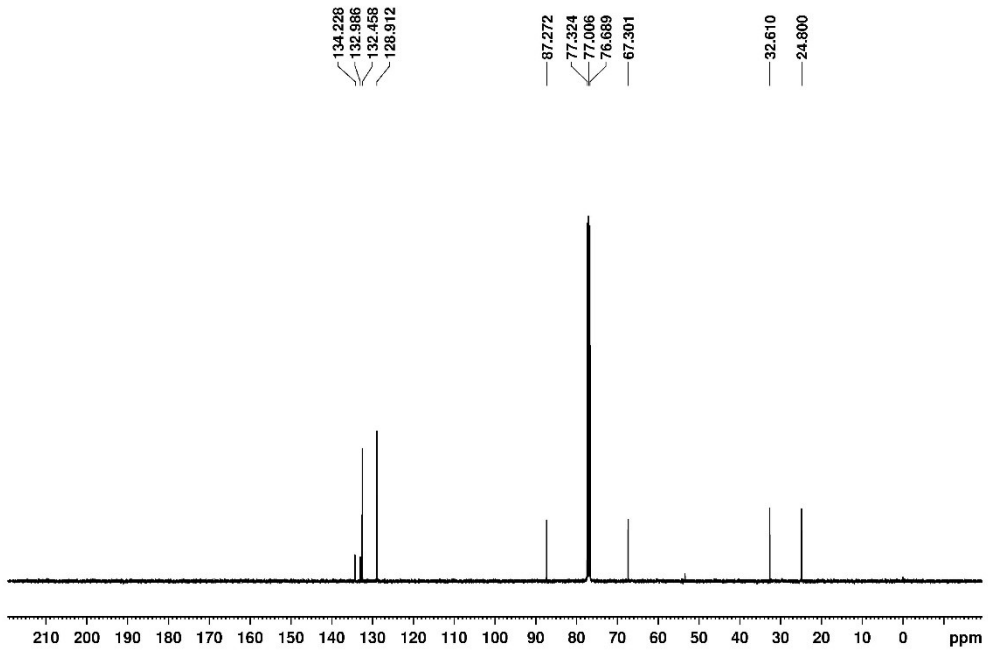
^{13}C NMR spectrum of compound **3d**



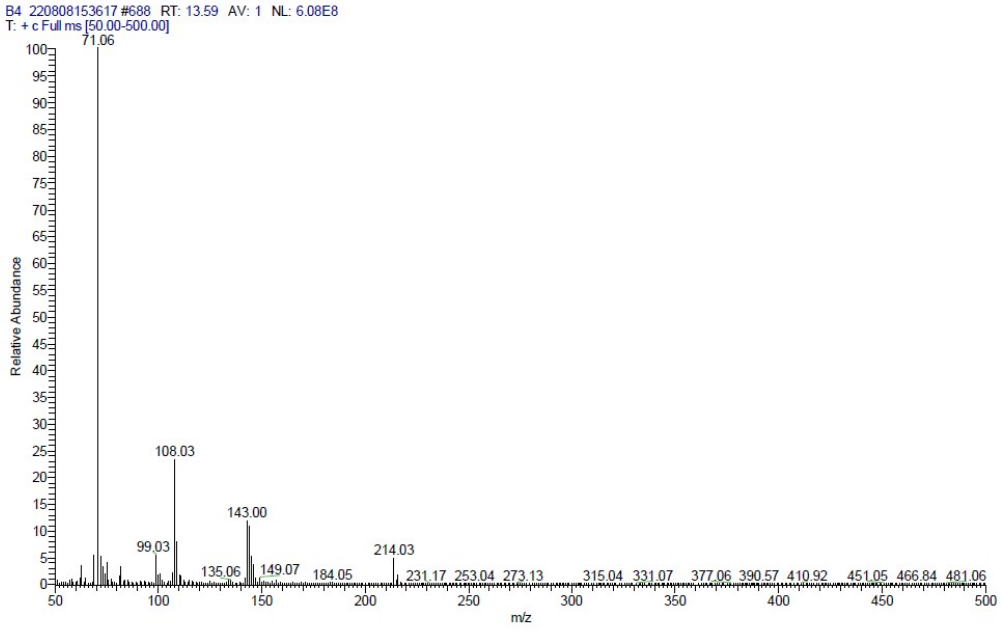
MS spectrum of compound **3d**



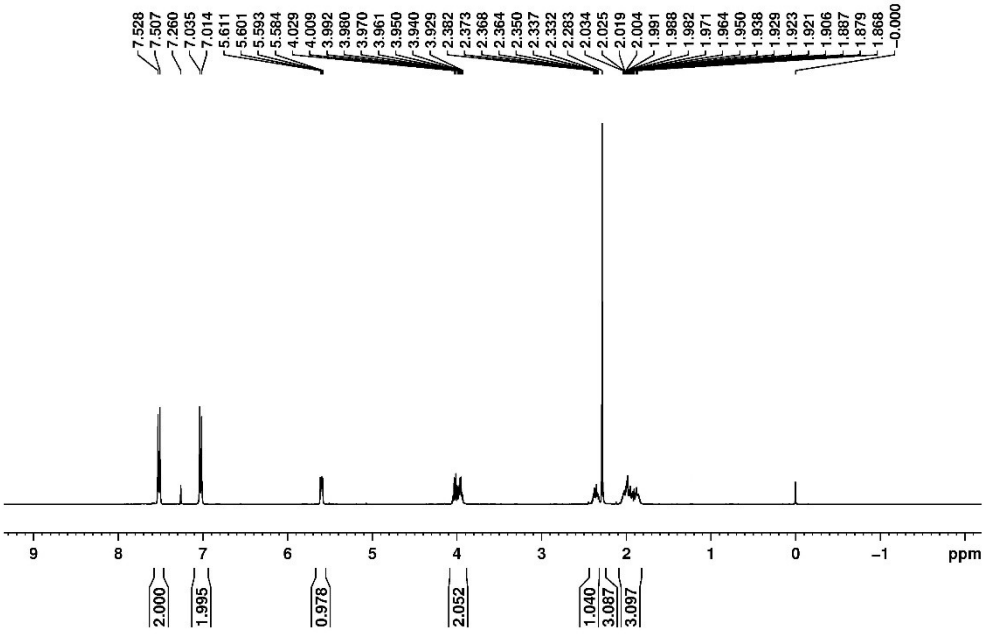
H NMR spectrum of compound **3e**



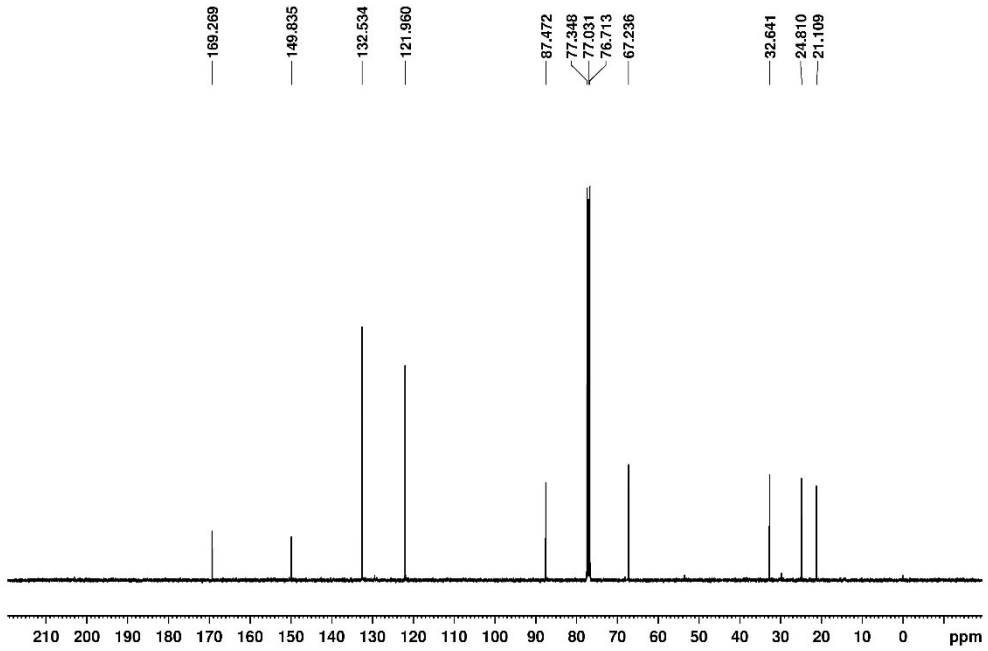
^{13}C NMR spectrum of compound **3e**



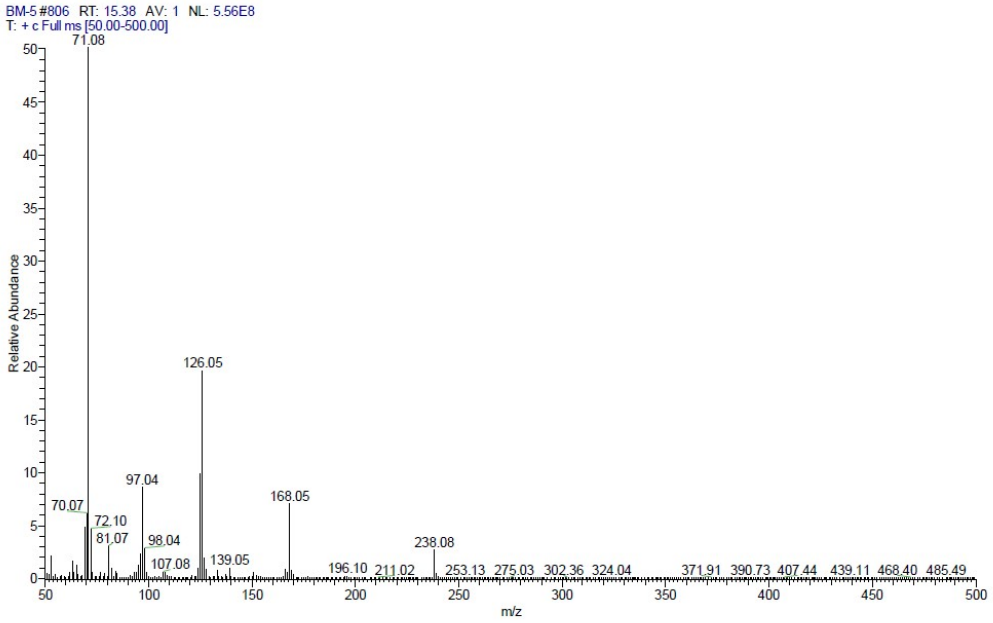
MS spectrum of compound **3e**



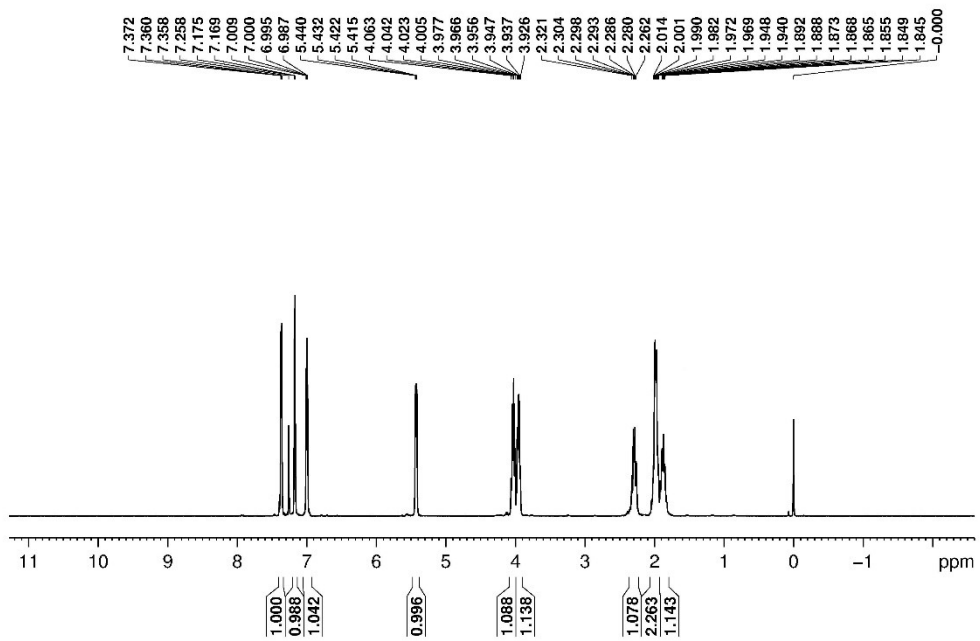
^{1}H NMR spectrum of compound **3f**



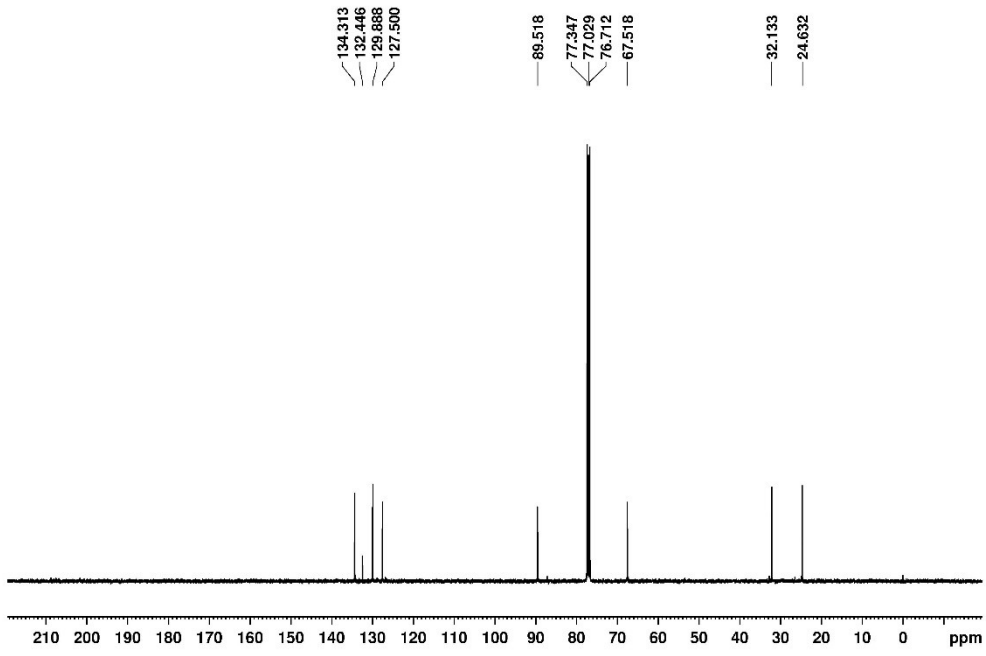
^{13}C NMR spectrum of compound **3f**



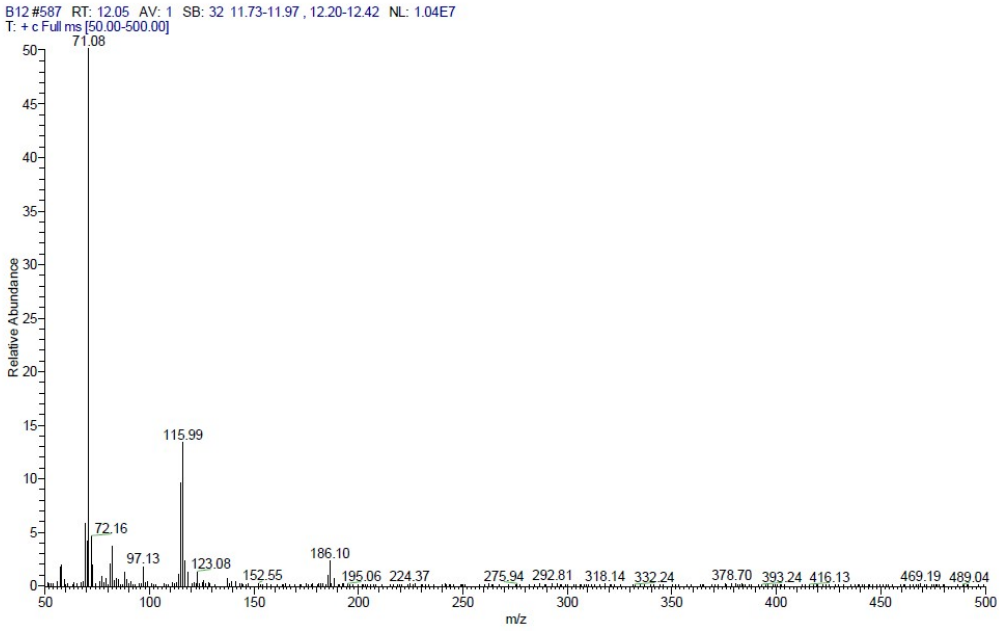
MS spectrum of compound **3f**



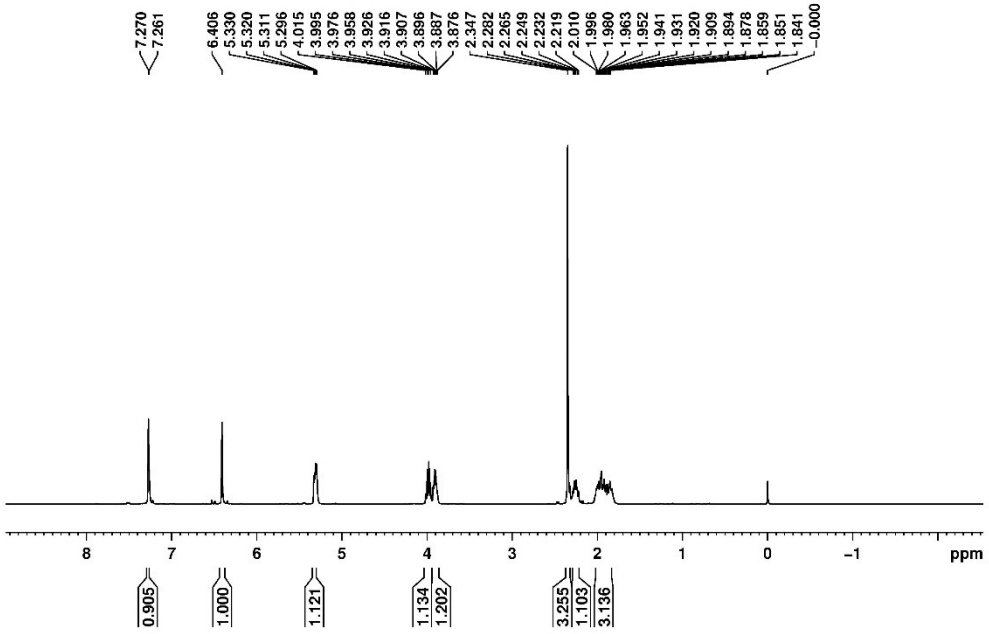
^{1}H NMR spectrum of compound **3g**



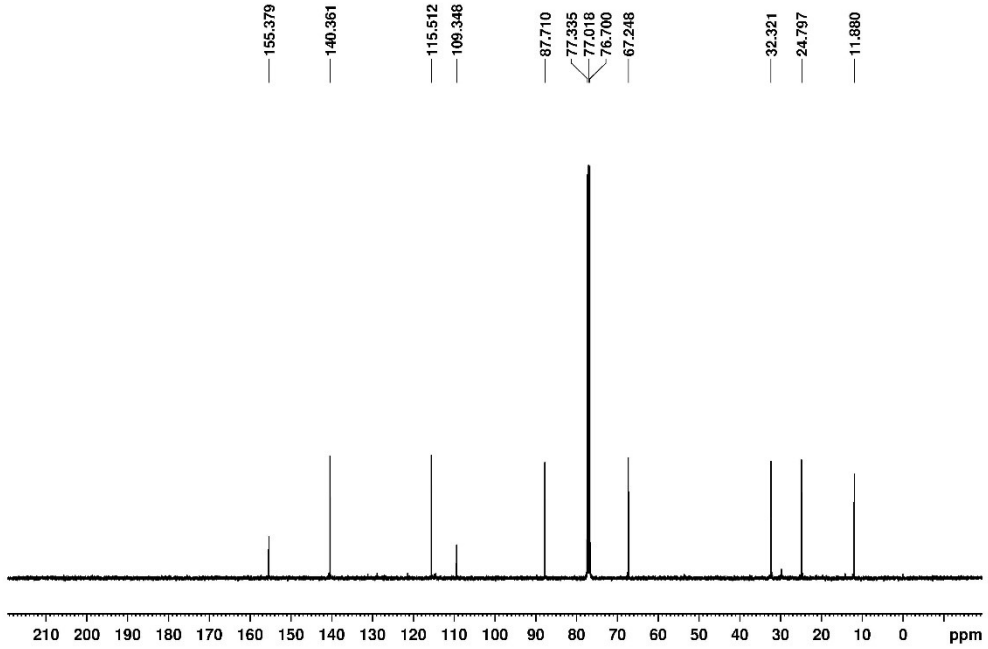
^{13}C NMR spectrum of compound **3g**



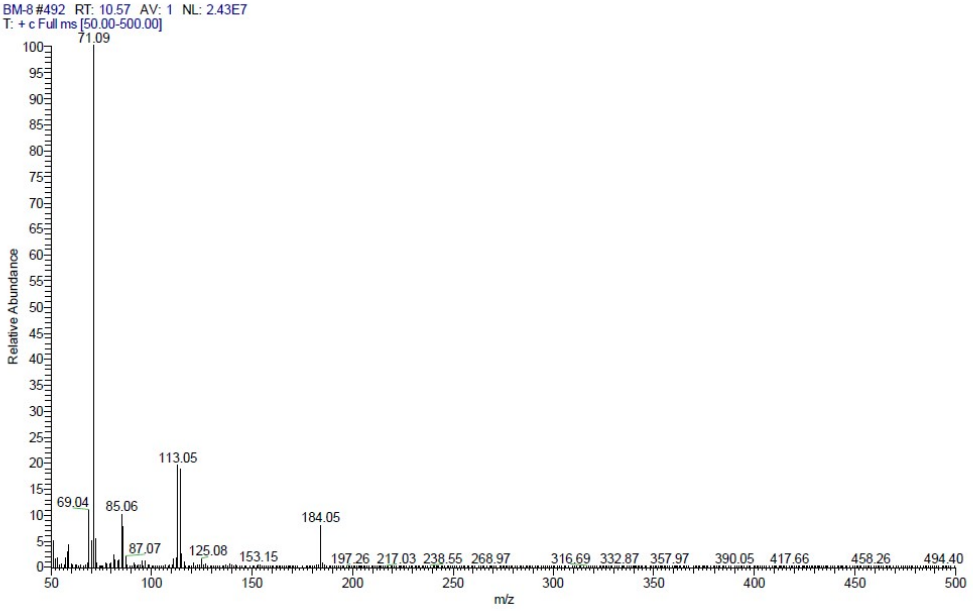
MS spectrum of compound **3g**



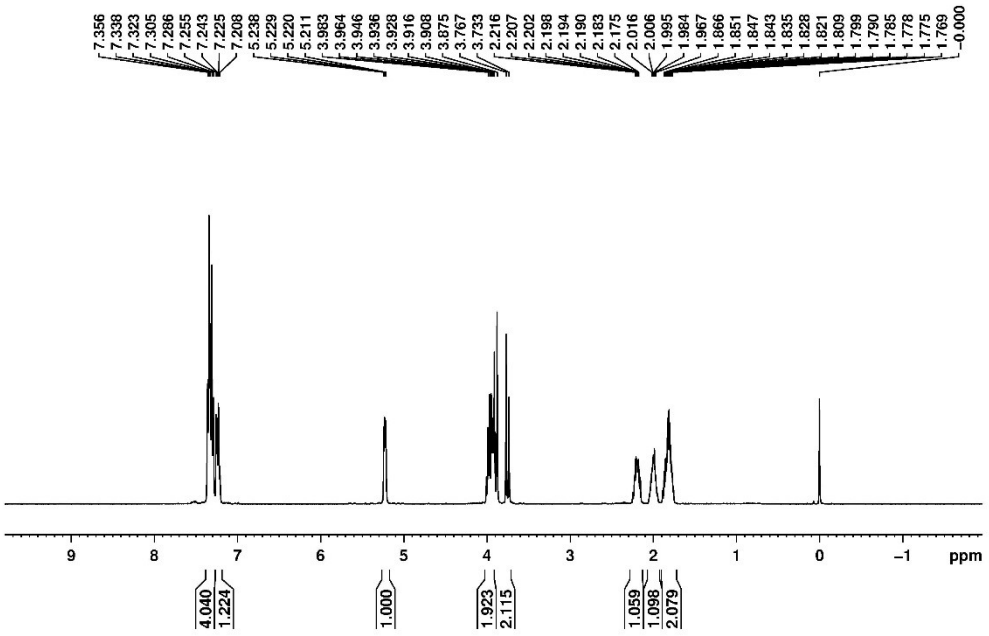
^{1}H NMR spectrum of compound **3h**



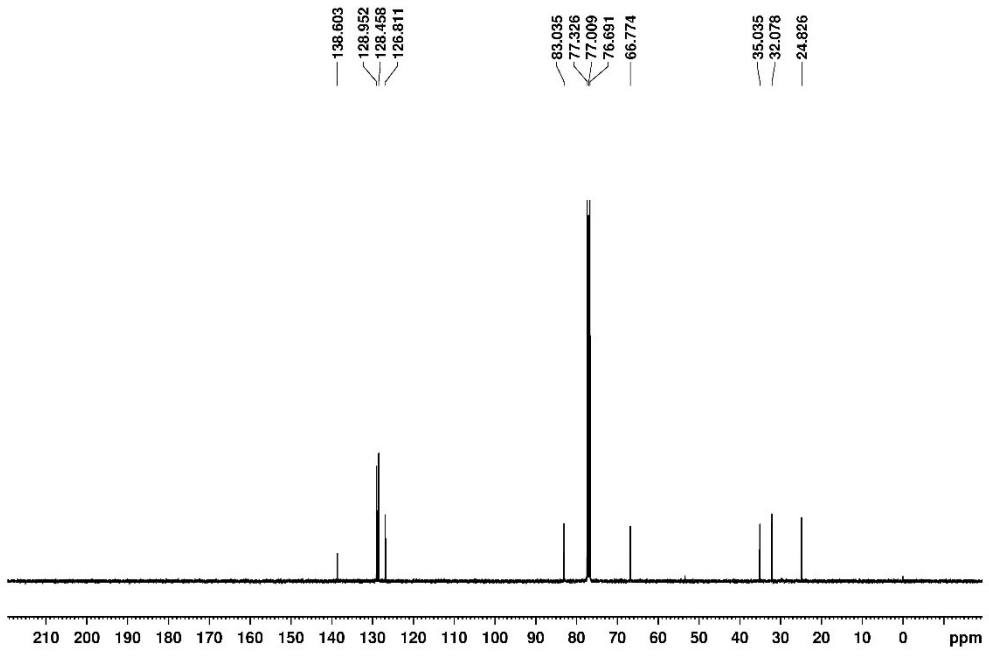
^{13}C NMR spectrum of compound **3h**



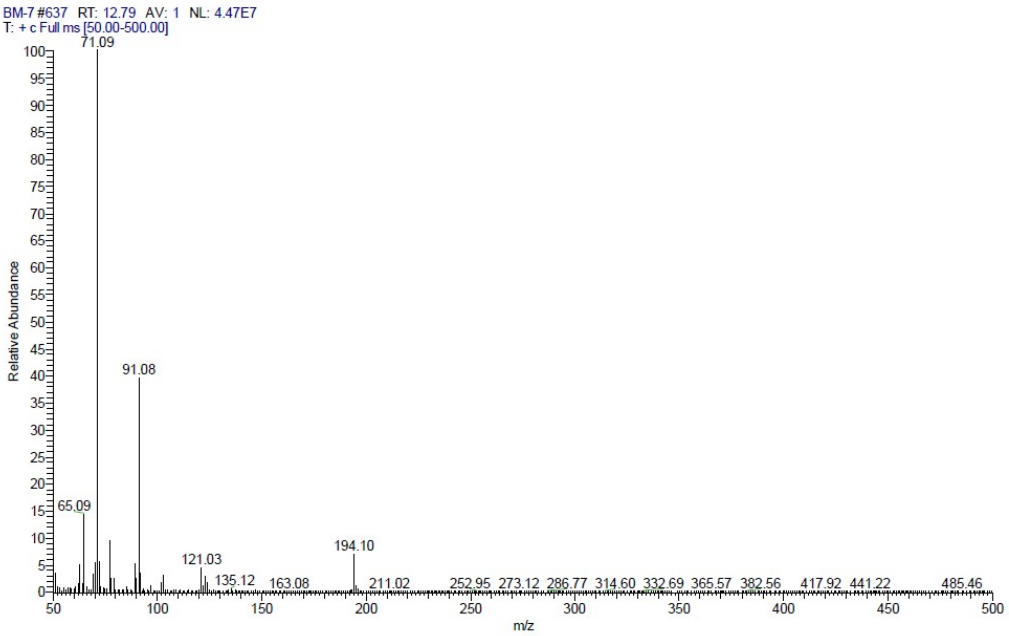
MS spectrum of compound **3h**



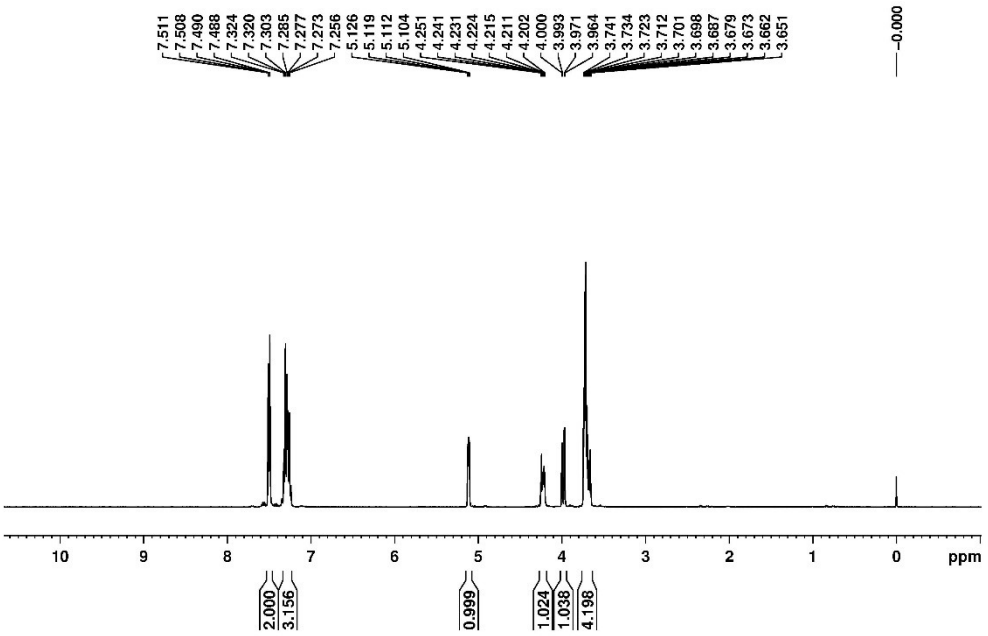
^{1}H NMR spectrum of compound **3i**



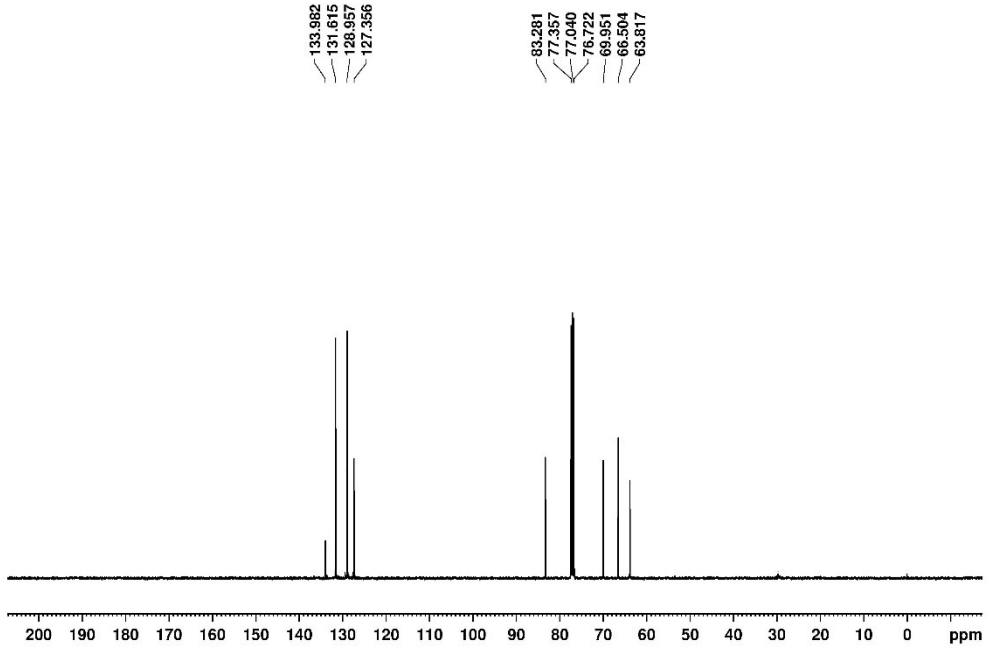
^{13}C NMR spectrum of compound **3i**



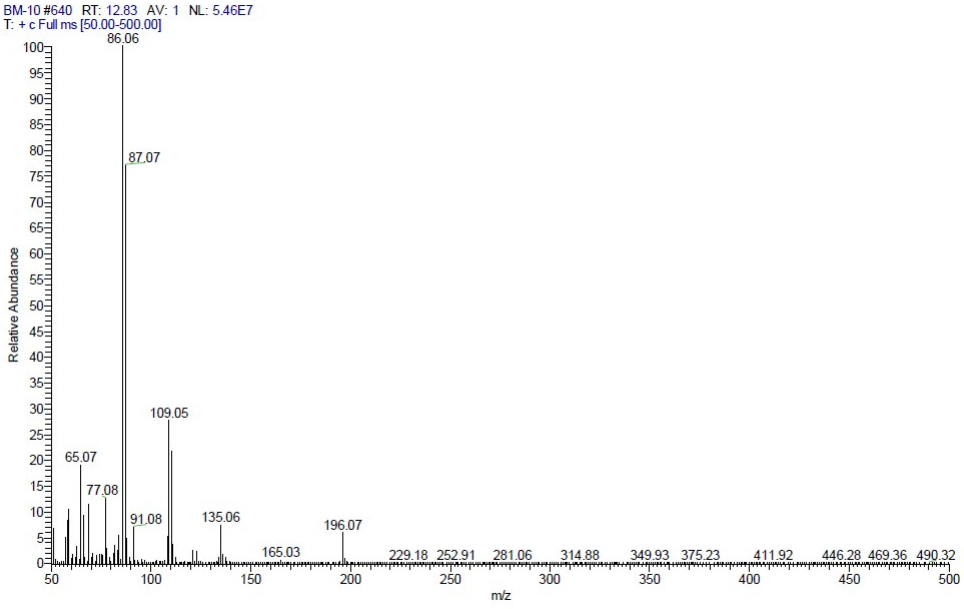
MS spectrum of compound **3i**



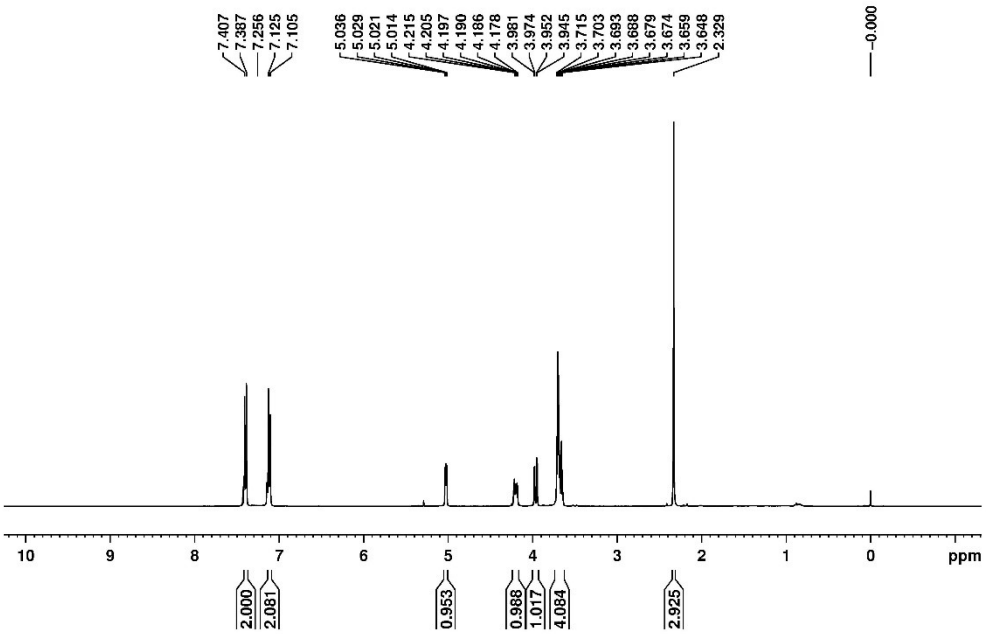
^{1}H NMR spectrum of compound **3l**



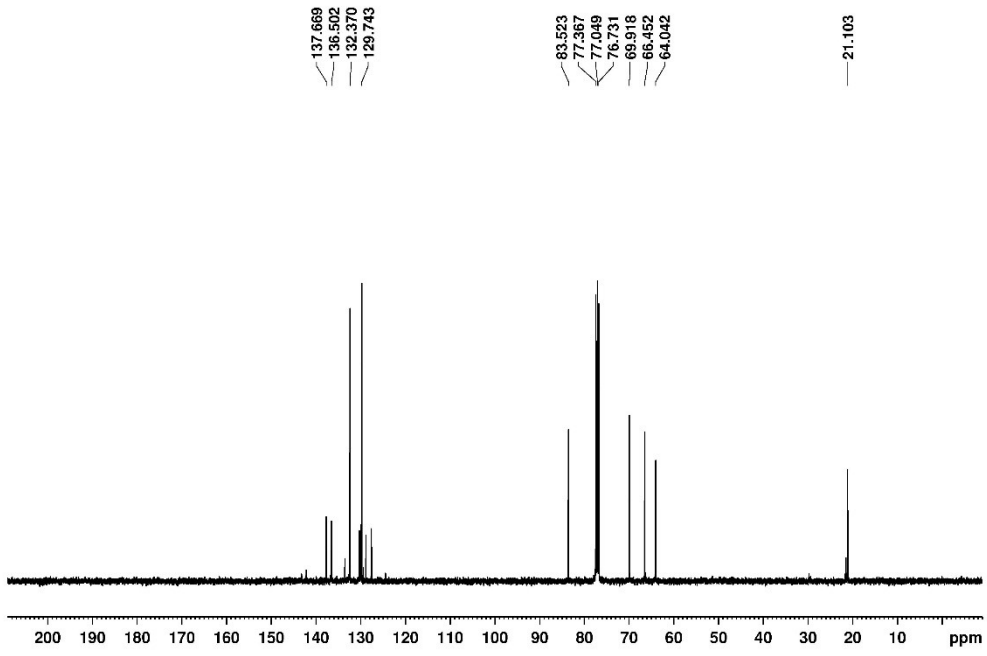
^{13}C NMR spectrum of compound **3l**



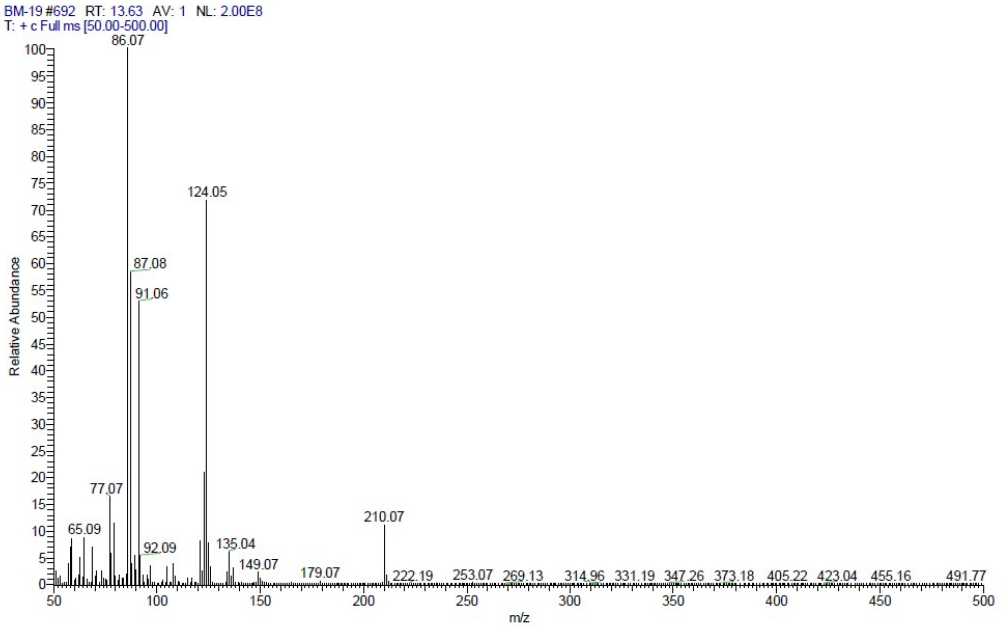
MS spectrum of compound **3l**



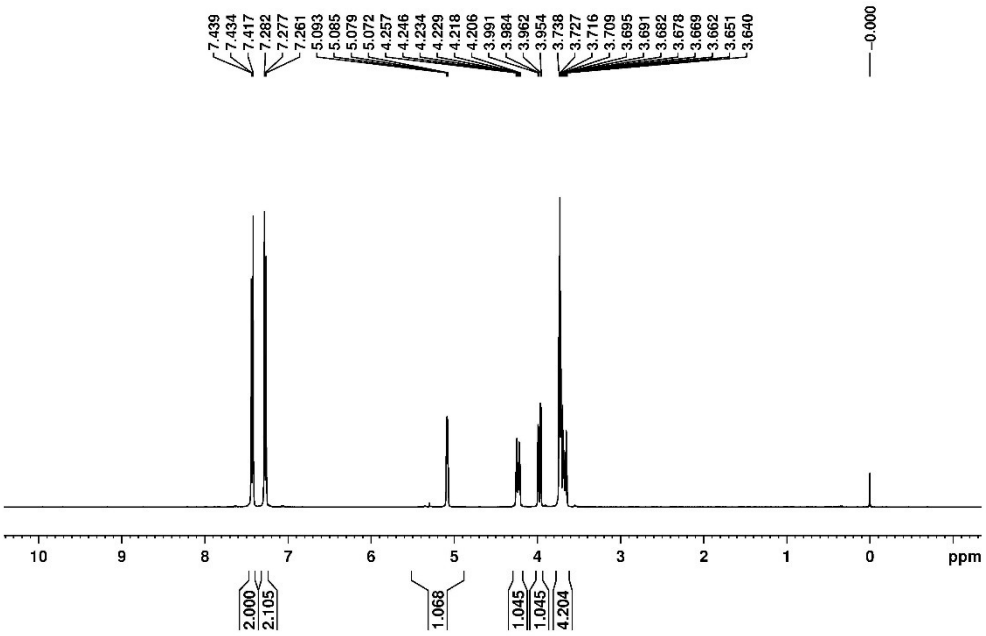
^{1}H NMR spectrum of compound **3m**



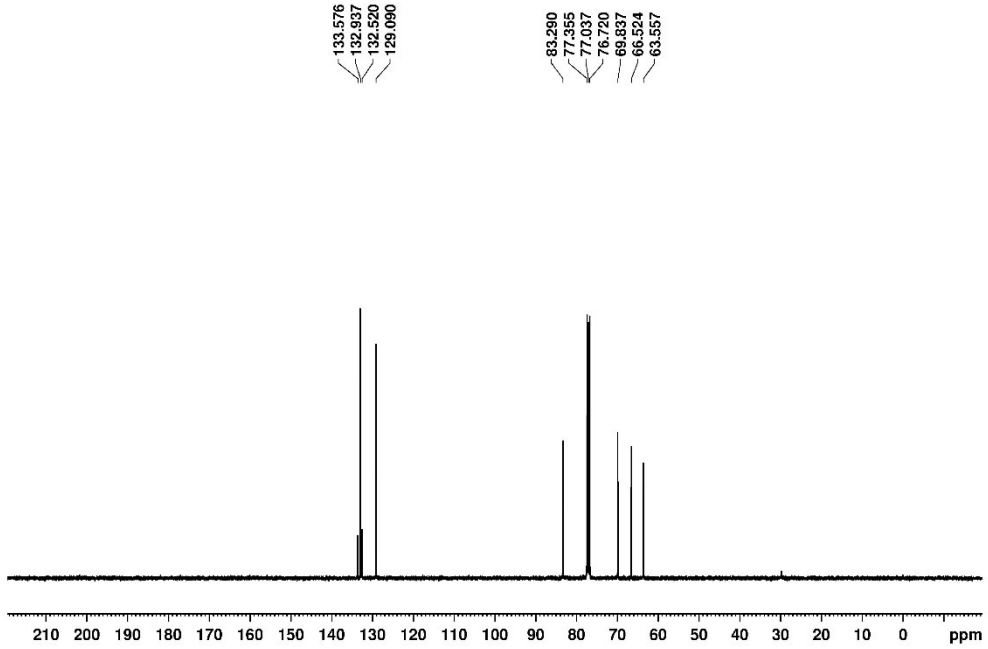
^{13}C NMR spectrum of compound **3m**



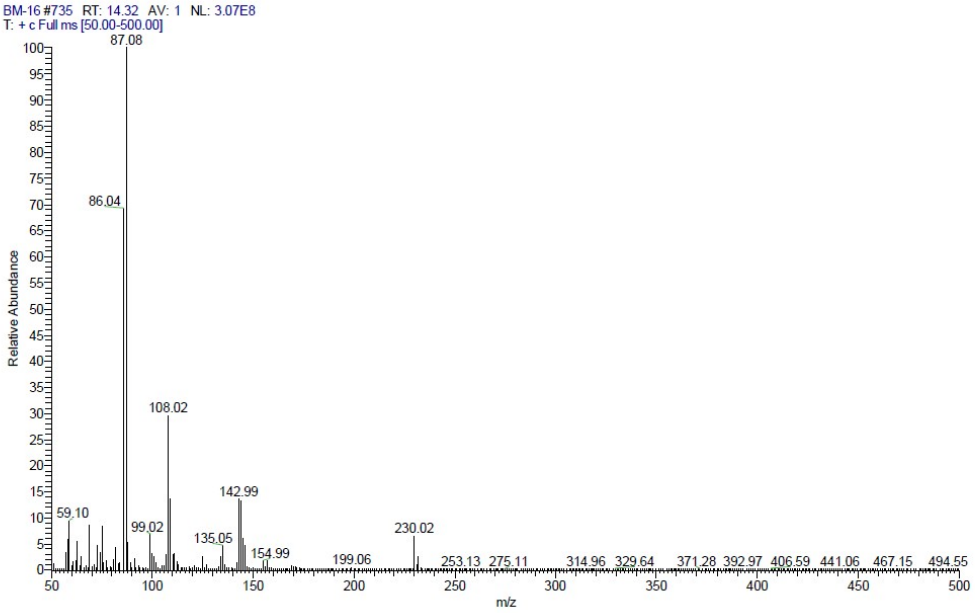
MS spectrum of compound **3m**



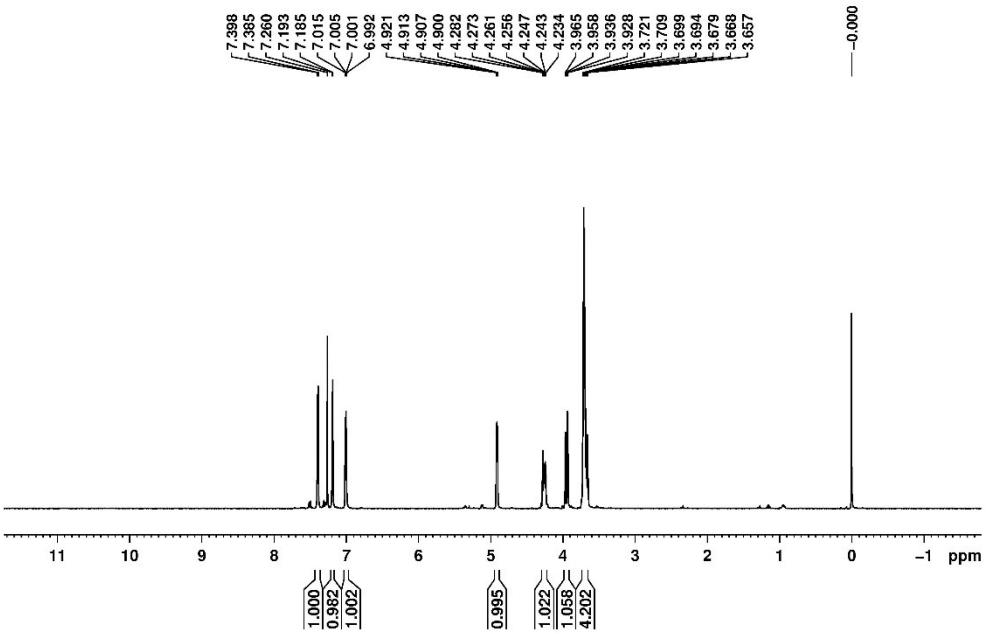
^{1}H NMR spectrum of compound **3n**



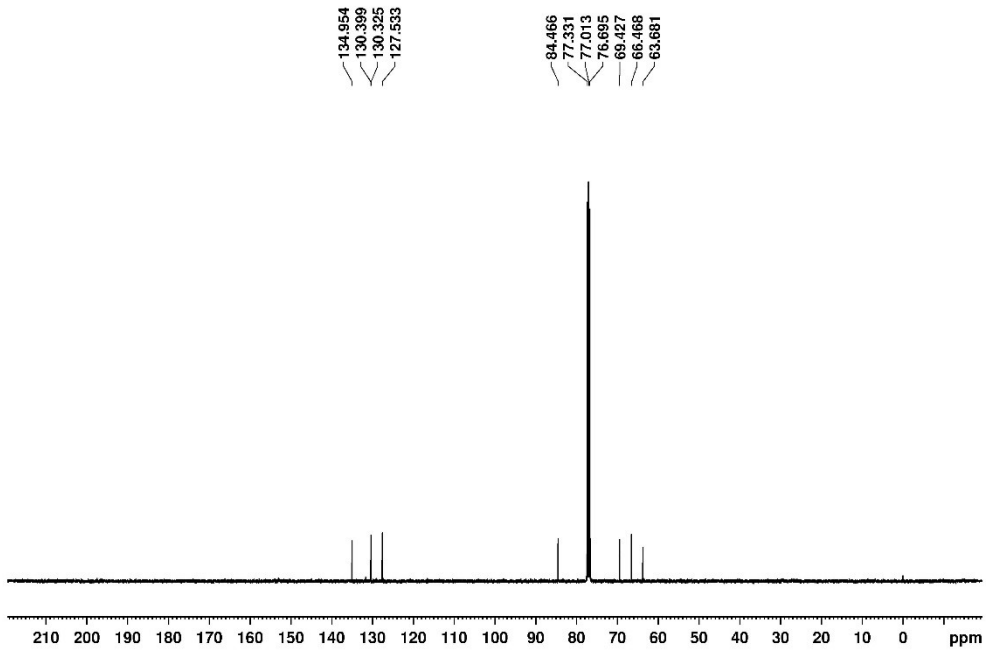
^{13}C NMR spectrum of compound **3n**



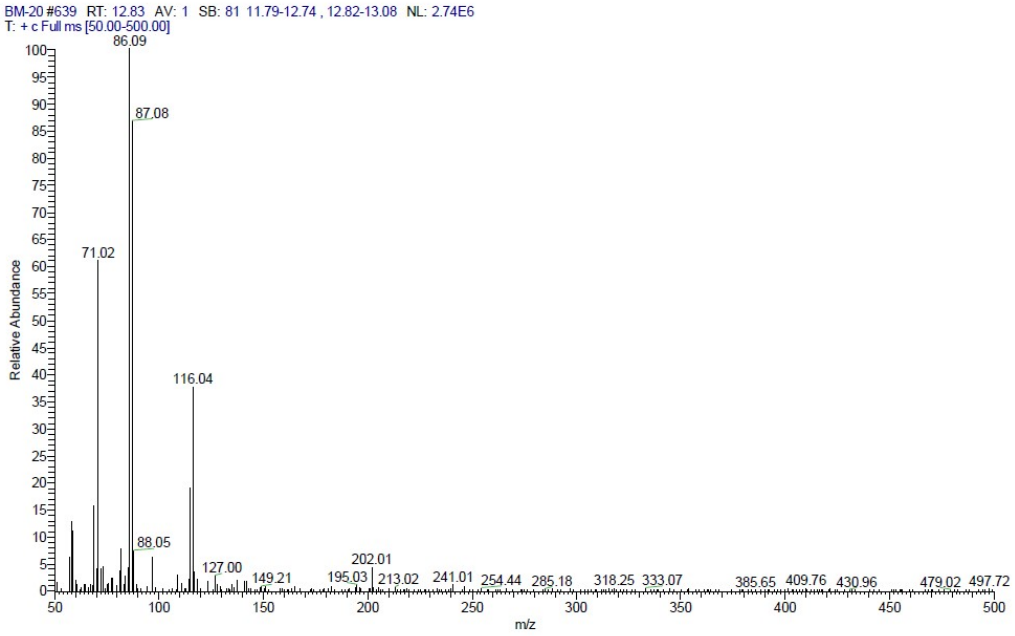
MS spectrum of compound **3n**



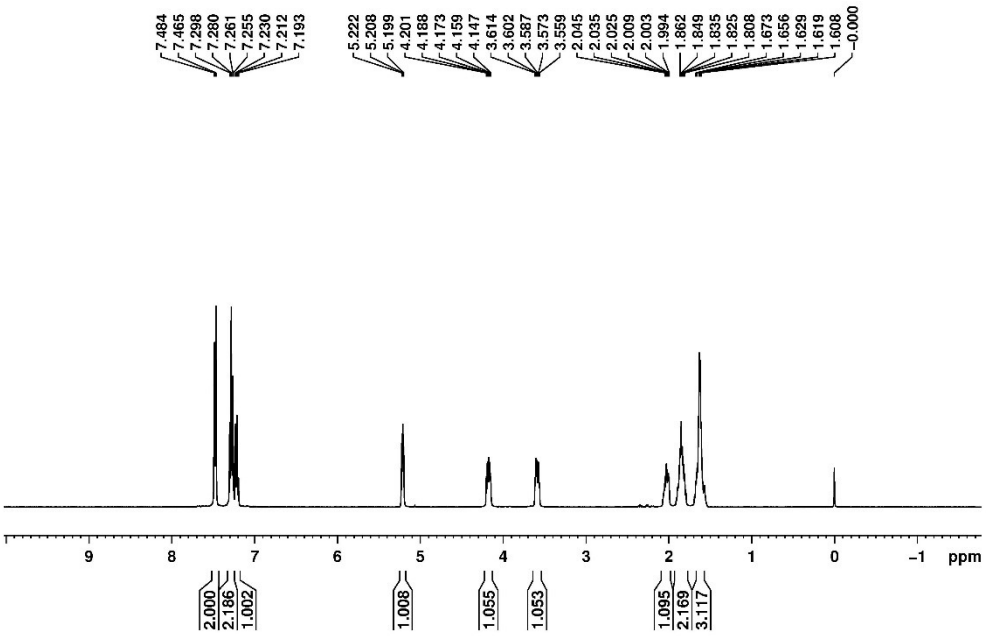
^{1}H NMR spectrum of compound **3o**



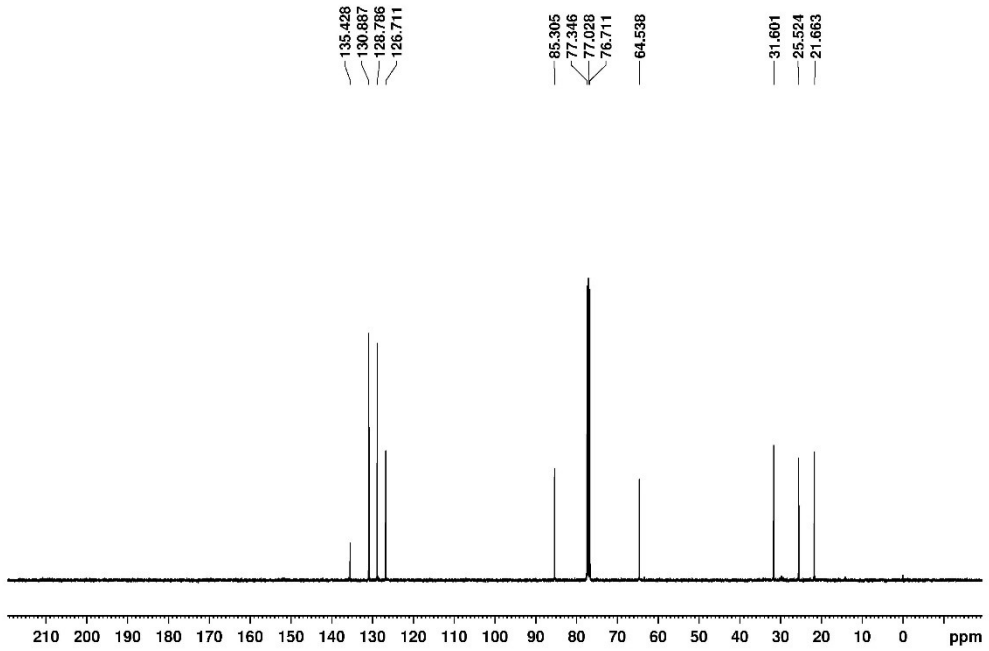
^{13}C NMR spectrum of compound **3o**



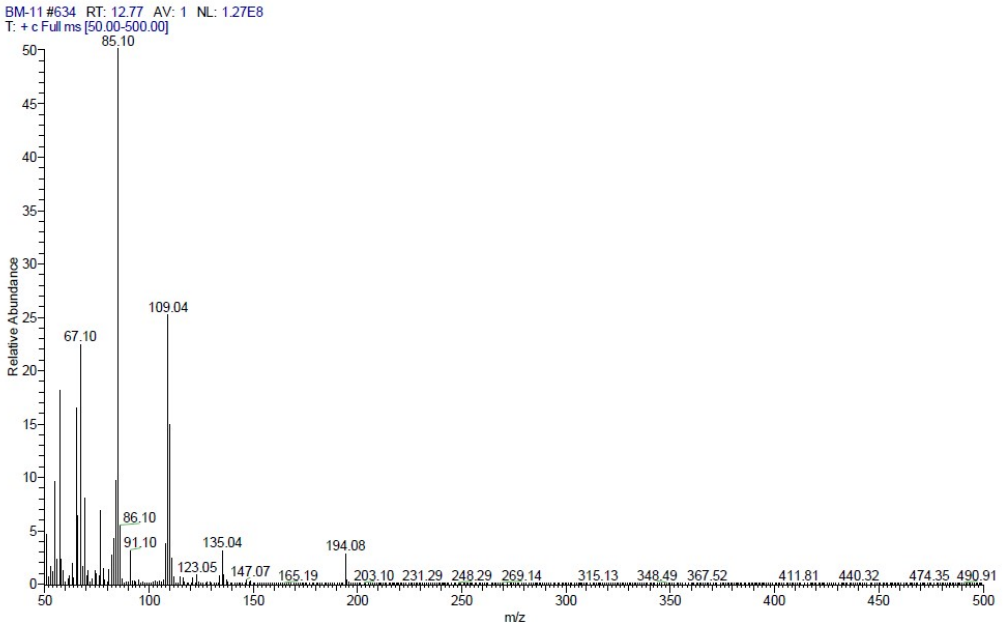
MS spectrum of compound **3o**



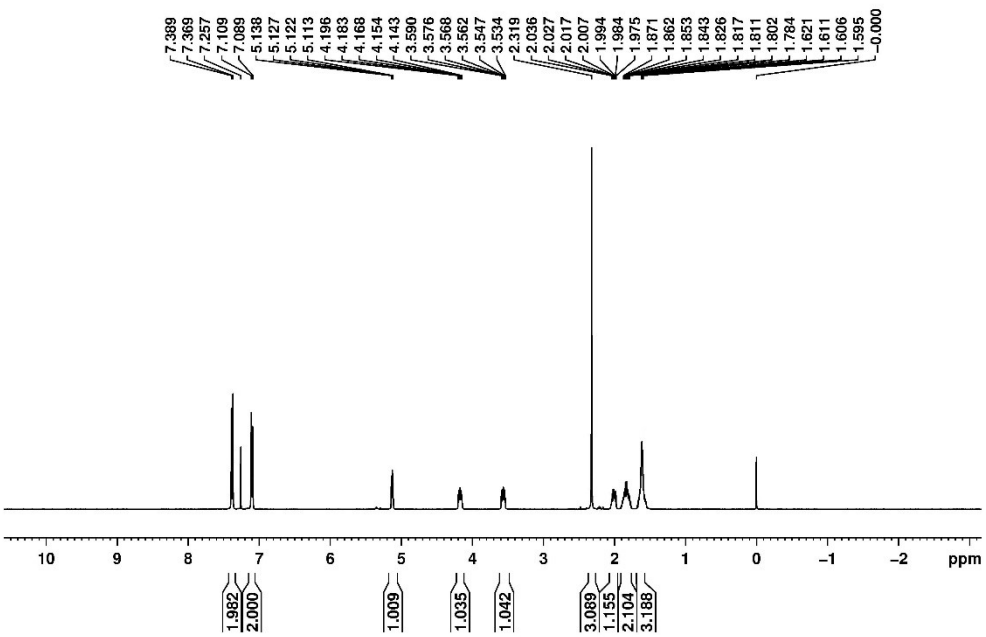
^{1}H NMR spectrum of compound **3p**



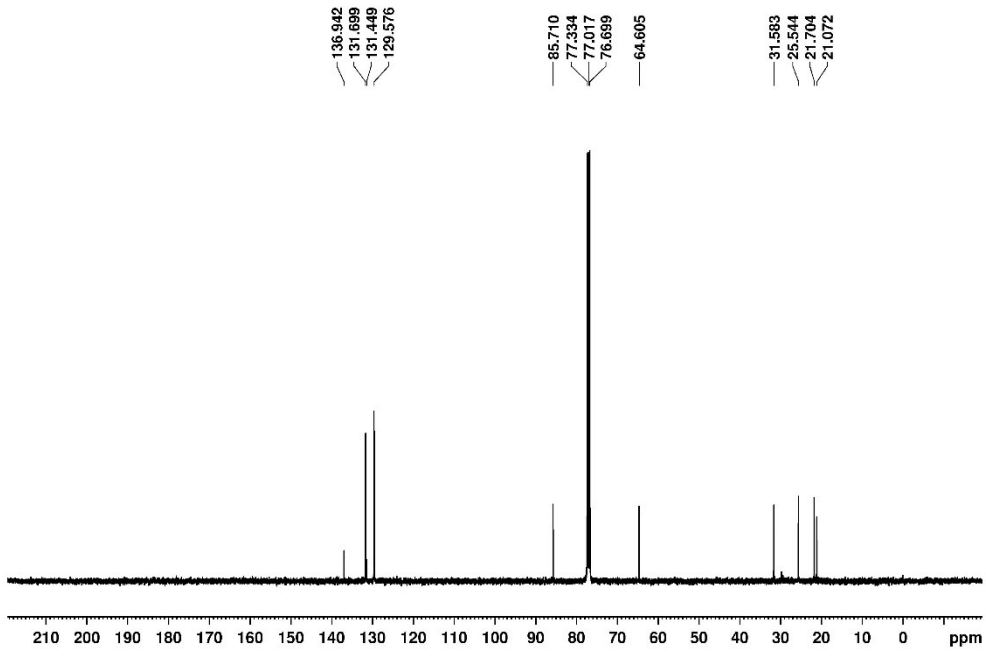
^{13}C NMR spectrum of compound **3p**



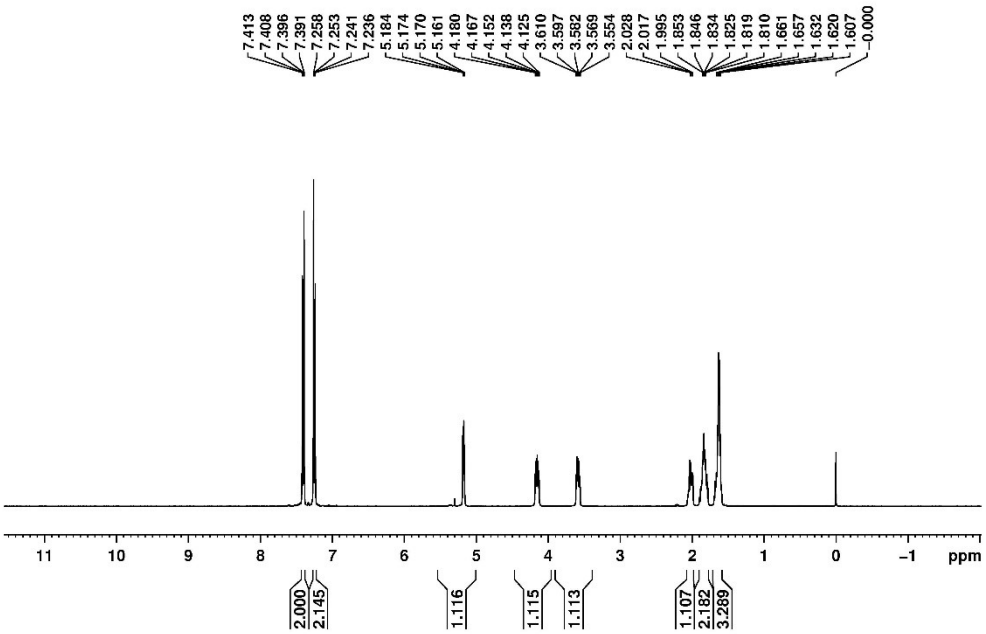
MS spectrum of compound **3p**



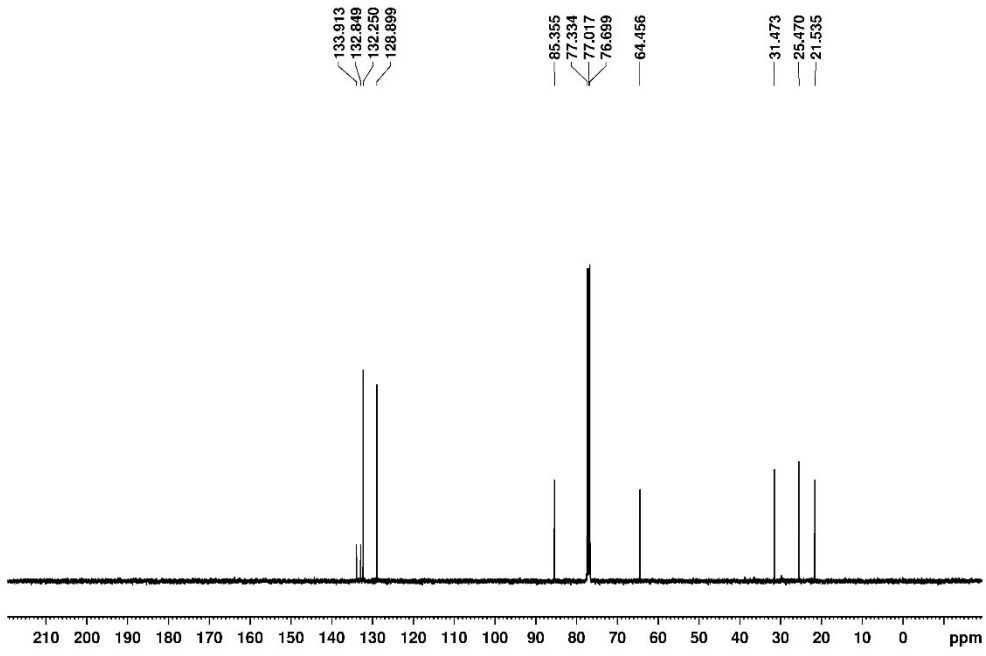
^{1}H NMR spectrum of compound **3q**



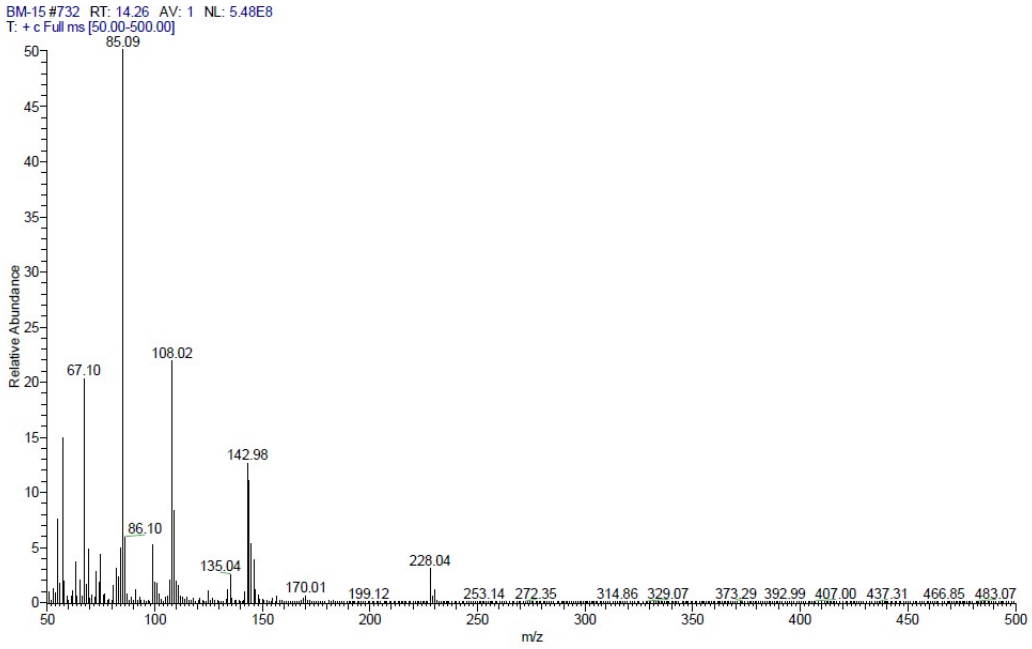
^{13}C NMR spectrum of compound **3q**



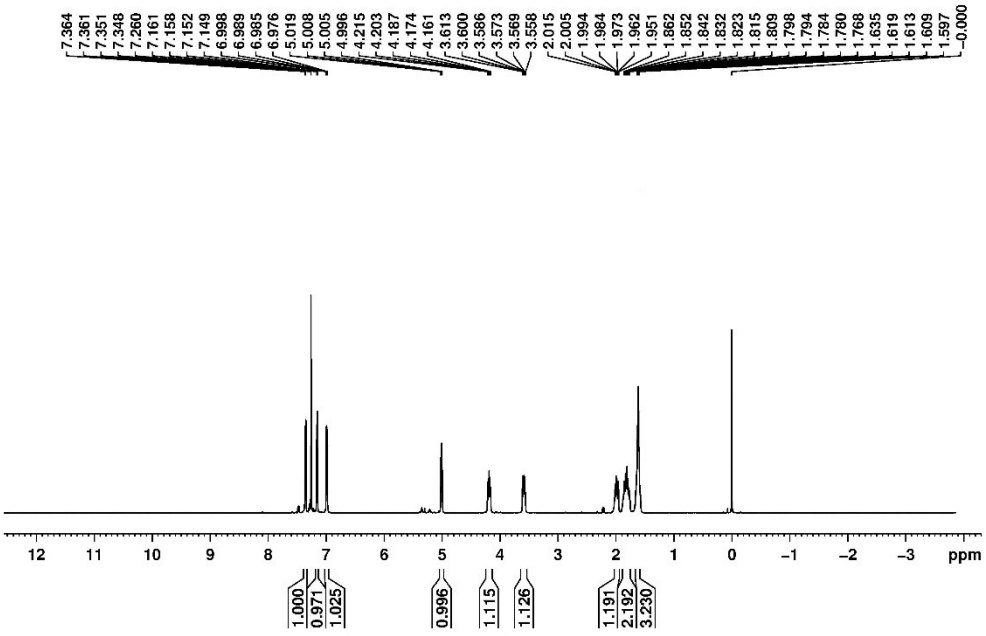
^{1}H NMR spectrum of compound **3r**



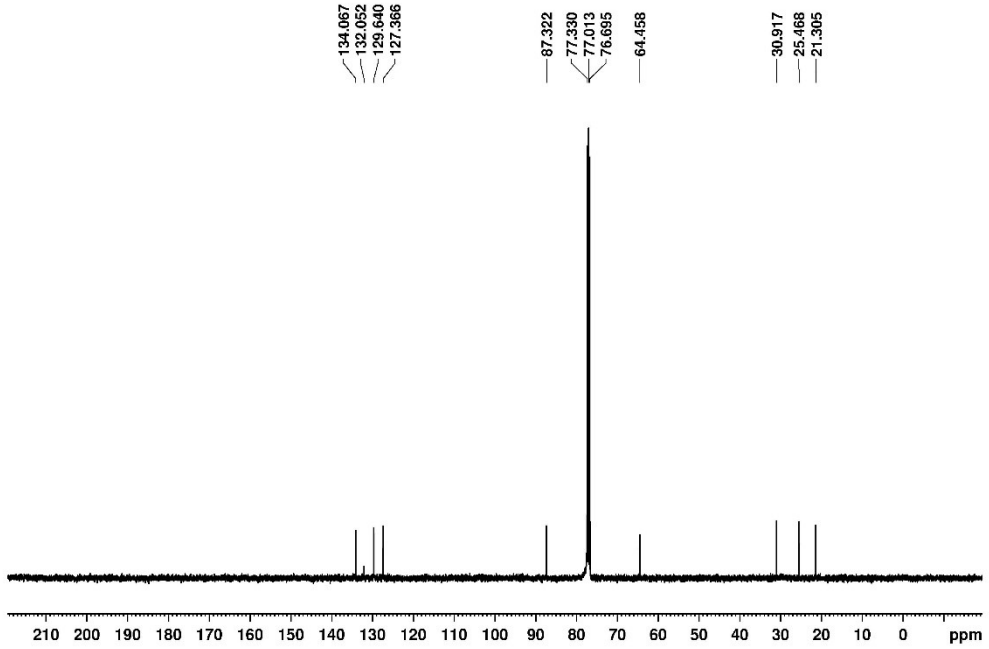
^{13}C NMR spectrum of compound **3r**



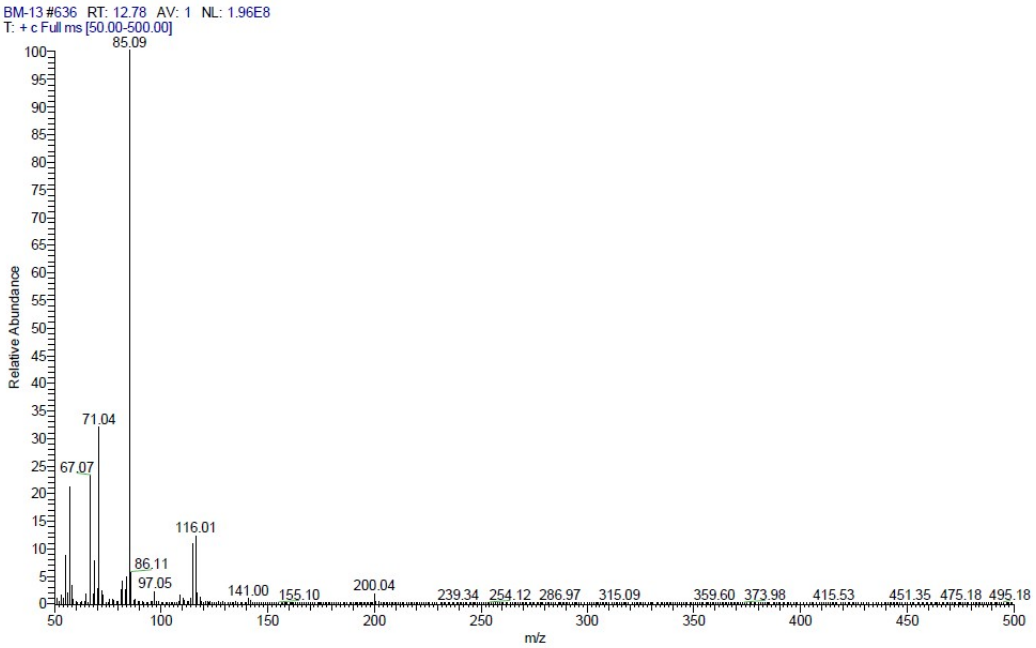
MS spectrum of compound **3r**



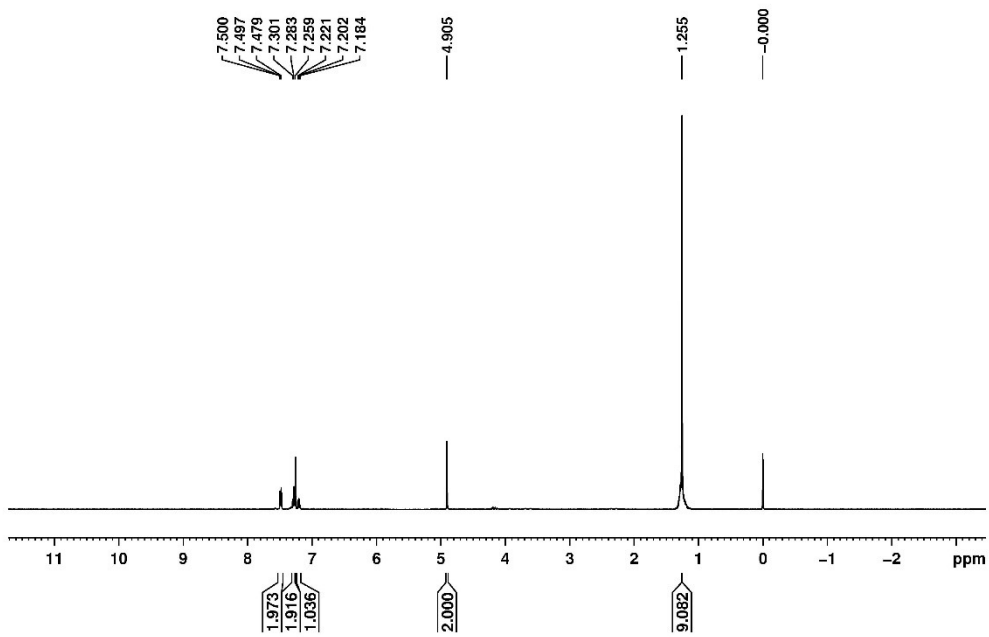
^{1}H NMR spectrum of compound **3s**



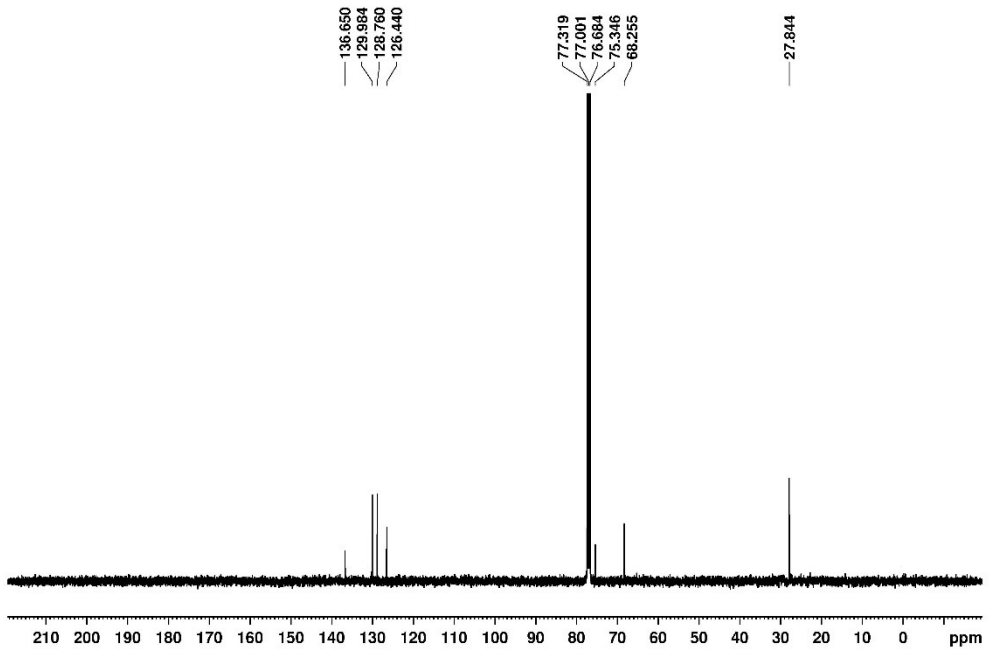
^{13}C NMR spectrum of compound **3s**



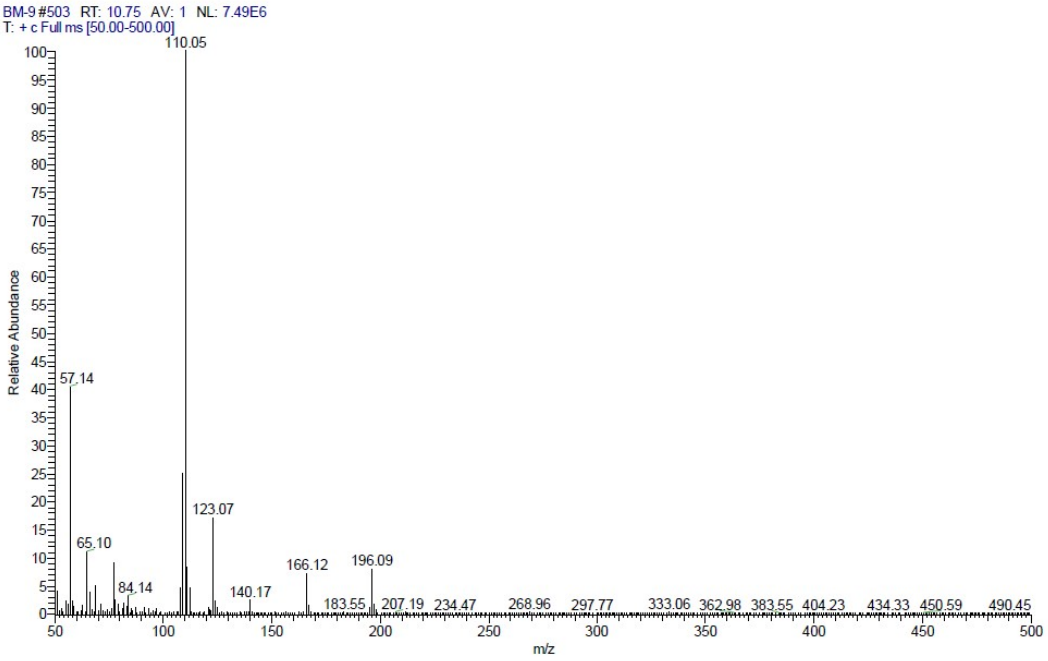
MS spectrum of compound **3s**



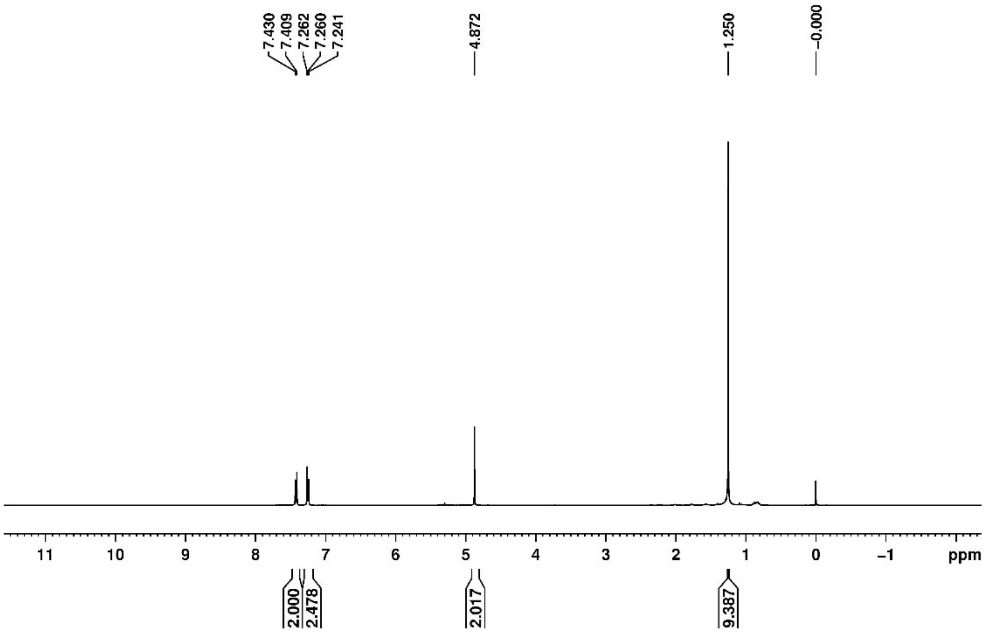
^{1}H NMR spectrum of compound **3t**



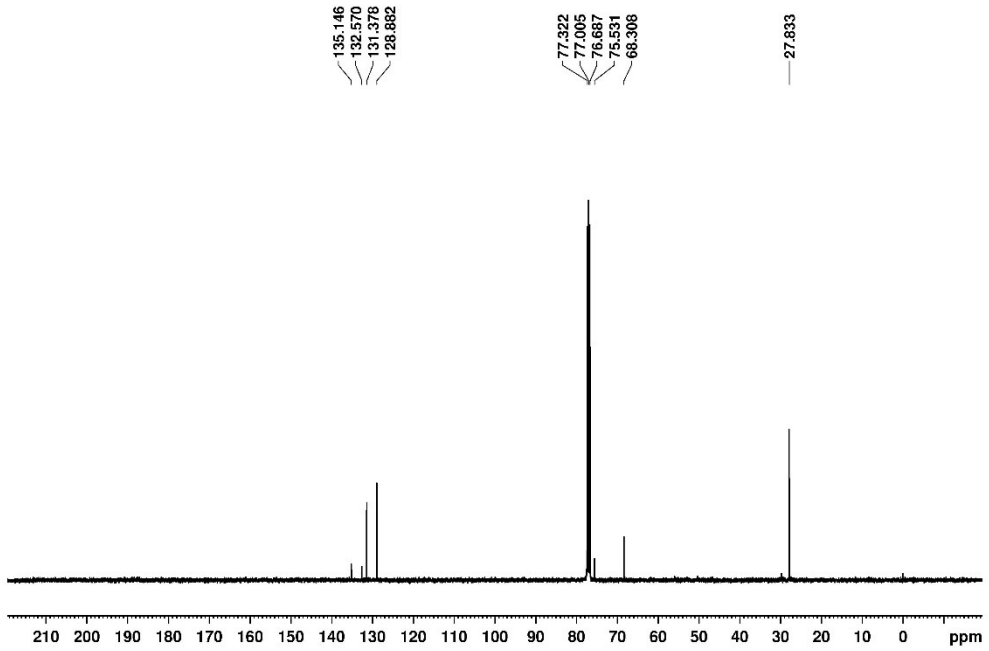
^{13}C NMR spectrum of compound **3t**



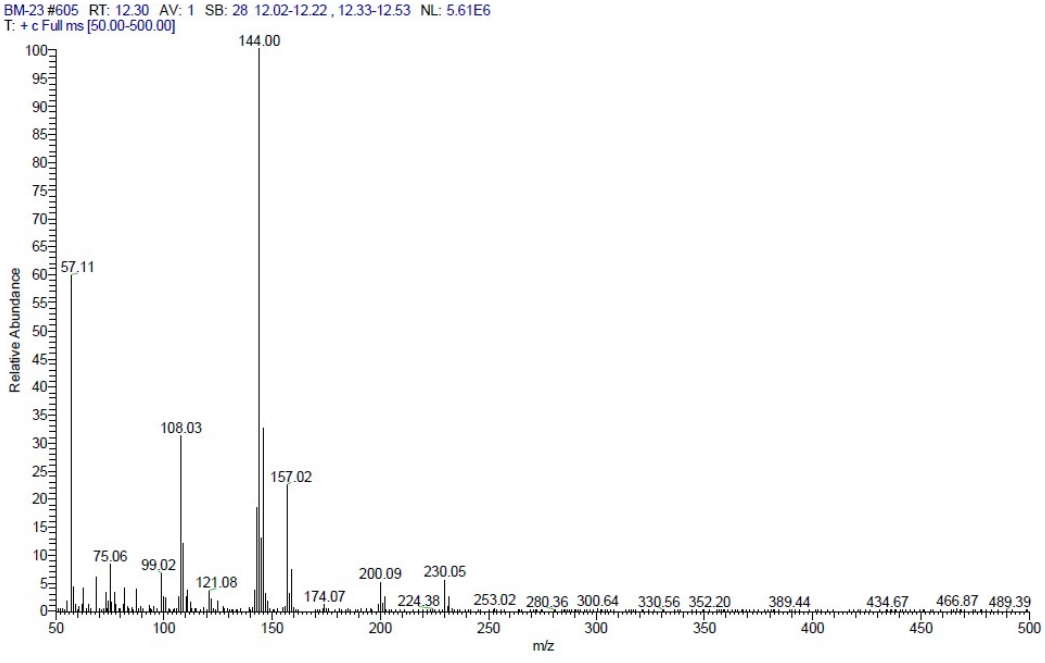
MS spectrum of compound **3t**



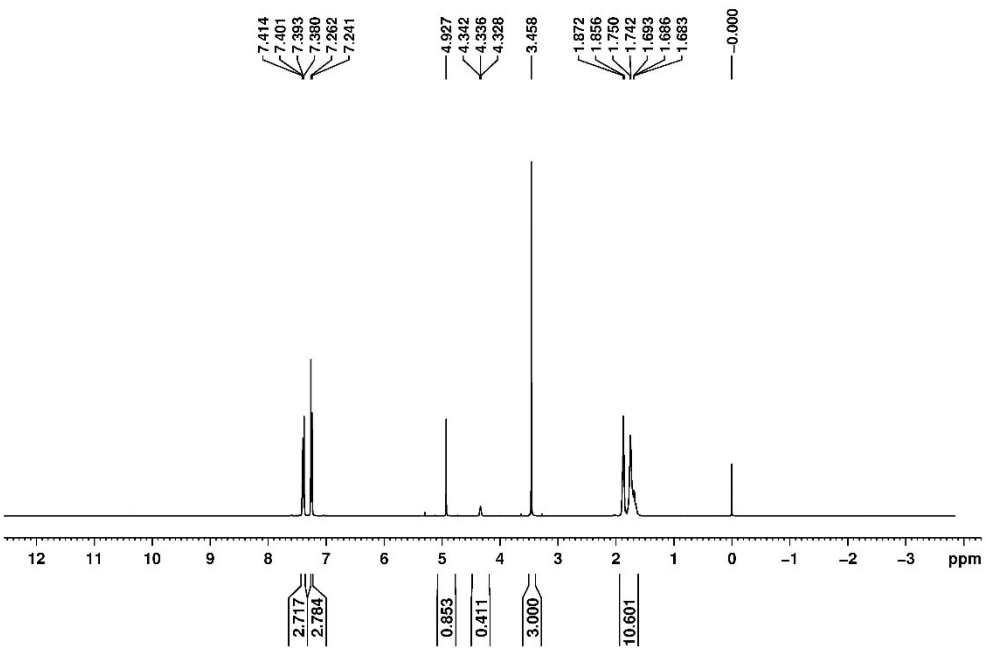
^{1}H NMR spectrum of compound **3u**



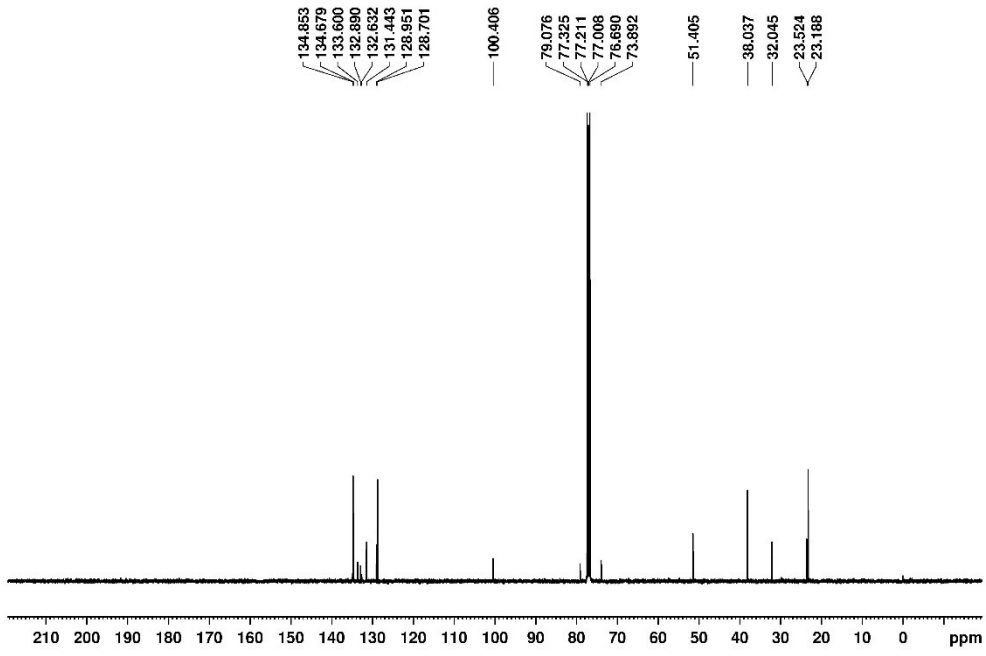
^{13}C NMR spectrum of compound **3u**



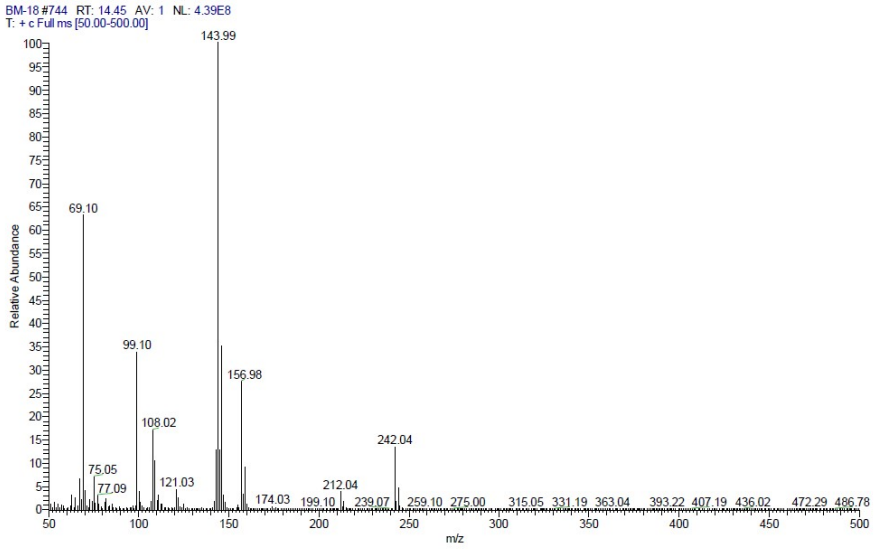
MS spectrum of compound **3u**



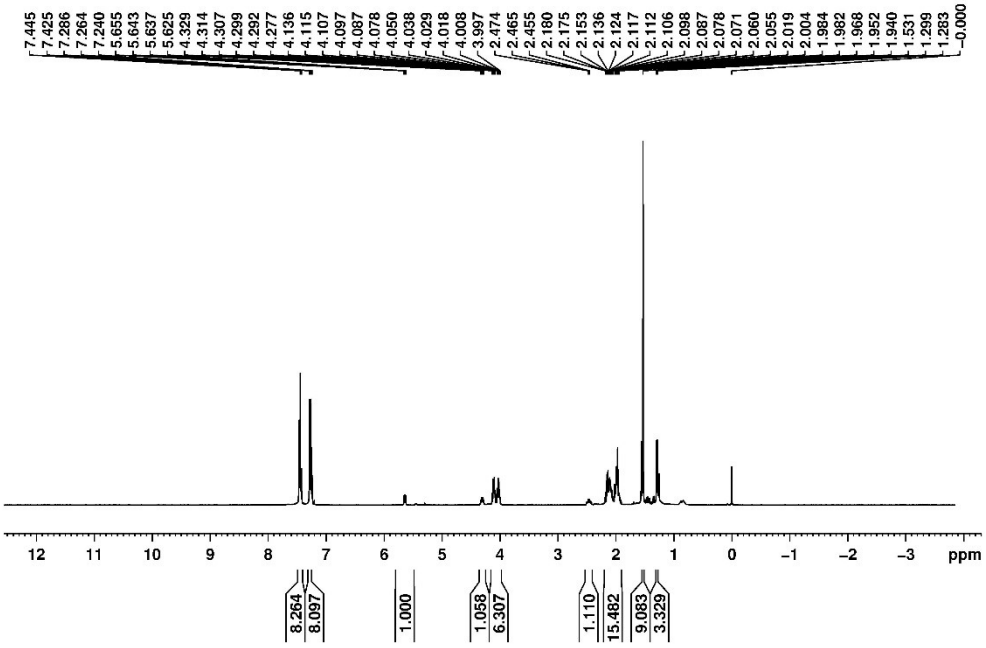
^{1}H NMR spectrum of compound **3x**



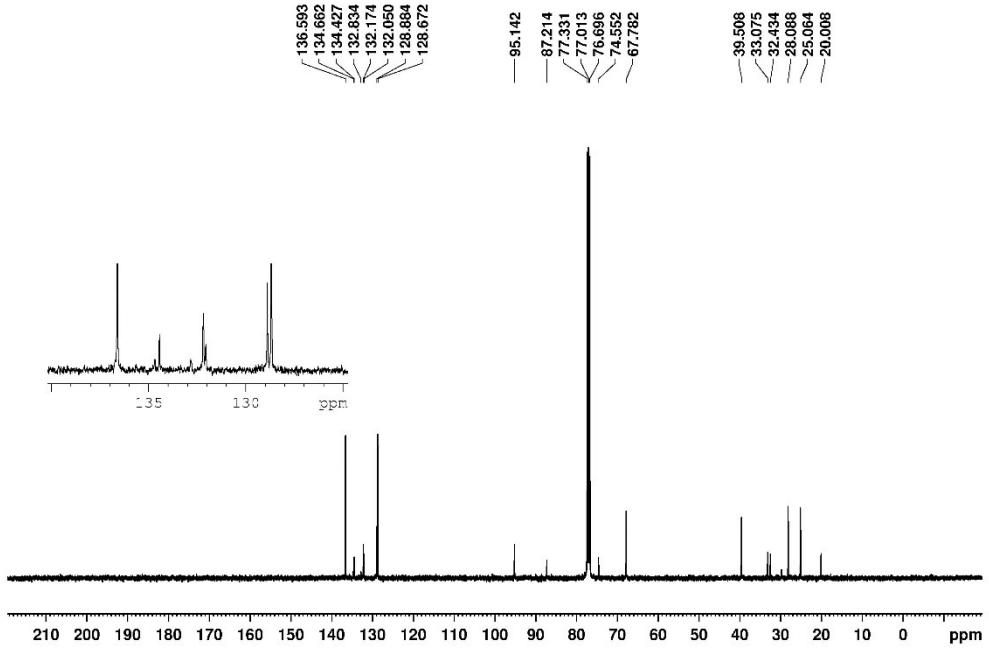
^{13}C NMR spectrum of compound **3x**



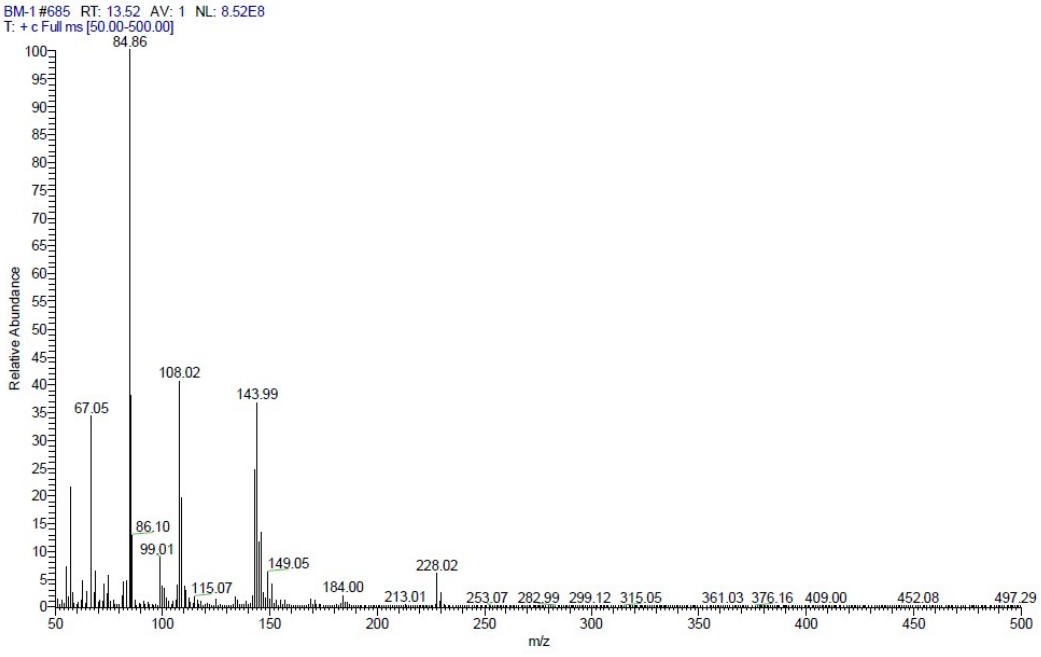
MS spectrum of compound **3x**



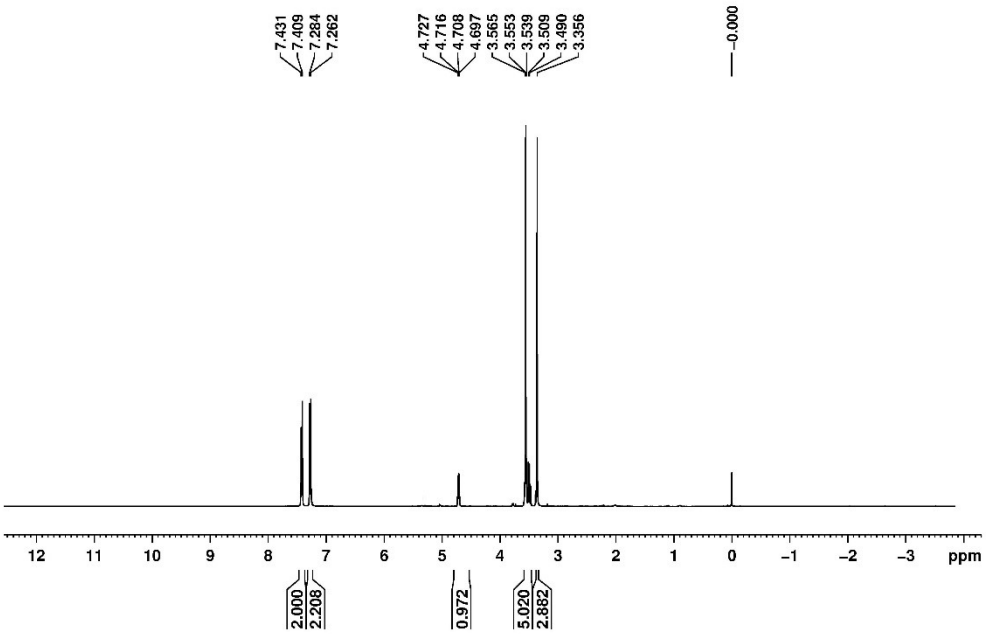
^{1}H NMR spectrum of compound **3y**



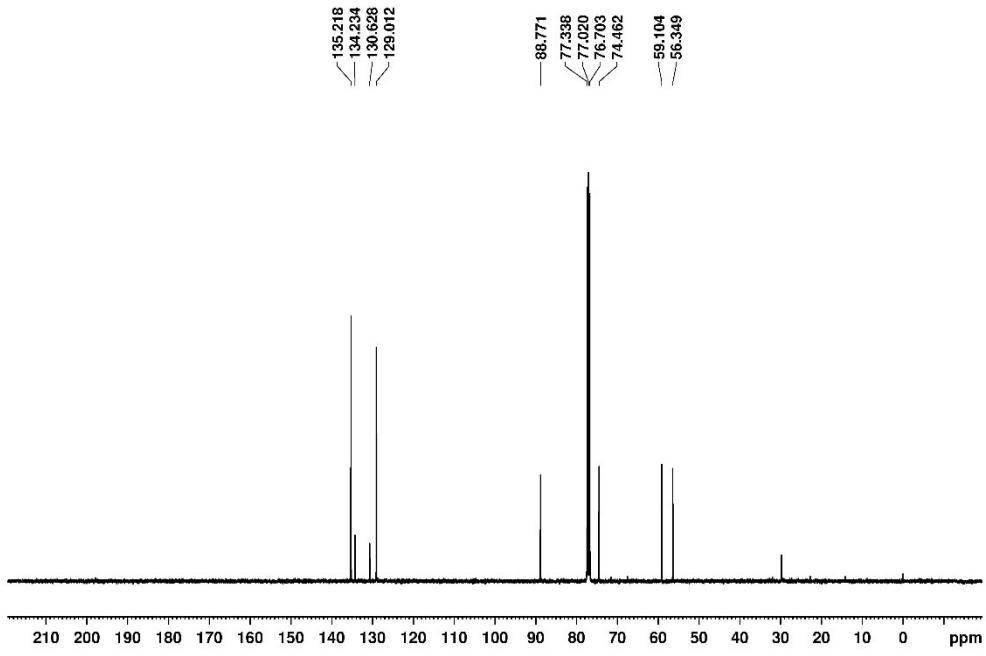
^{13}C NMR spectrum of compound **3y**



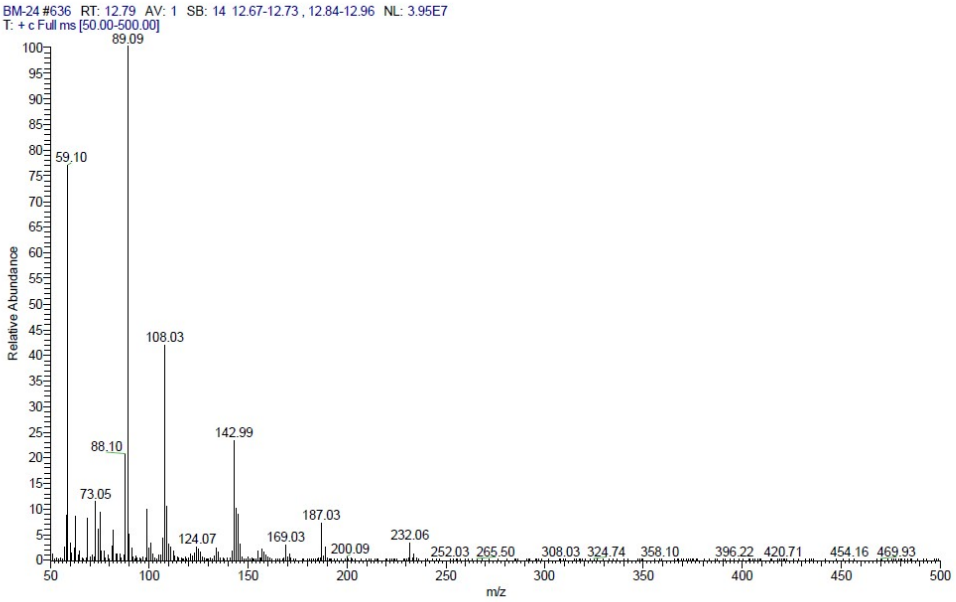
MS spectrum of compound **3y**



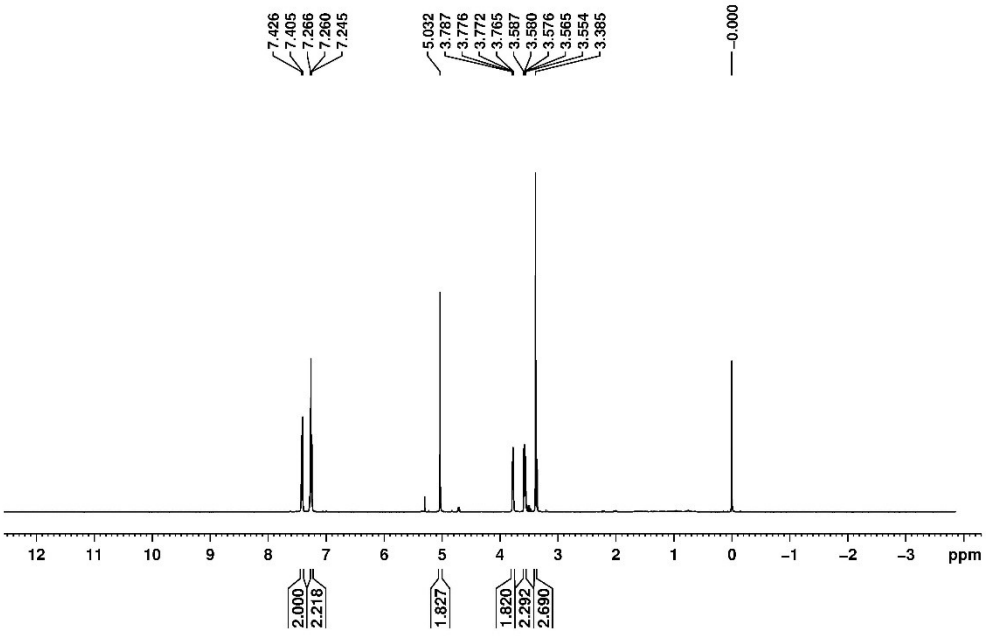
^{1}H NMR spectrum of compound **3z-i**



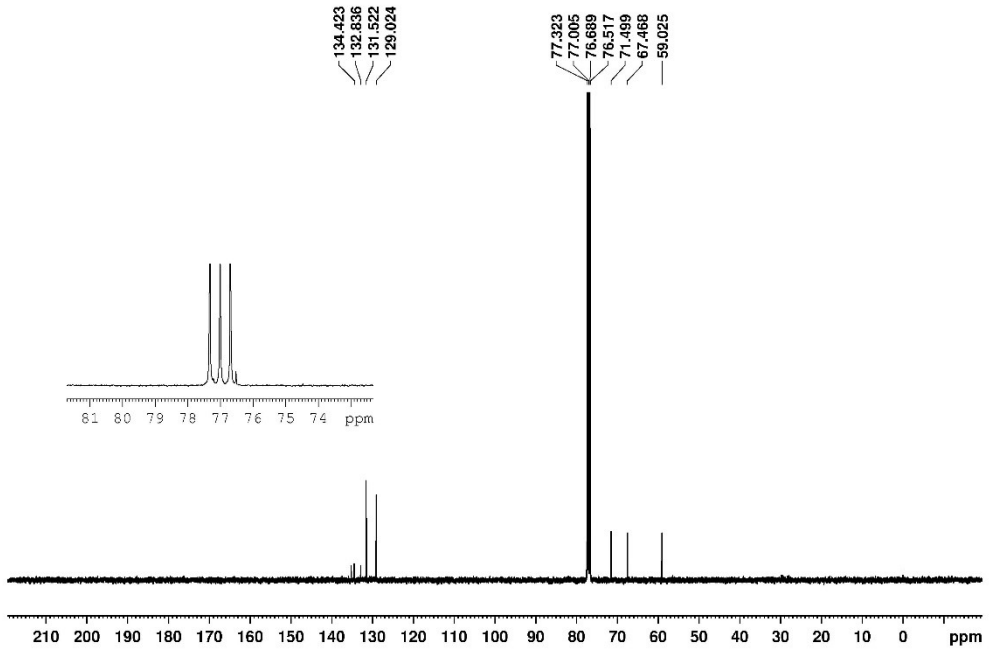
^{13}C NMR spectrum of compound **3z-i**



MS spectrum of compound **3z-i**

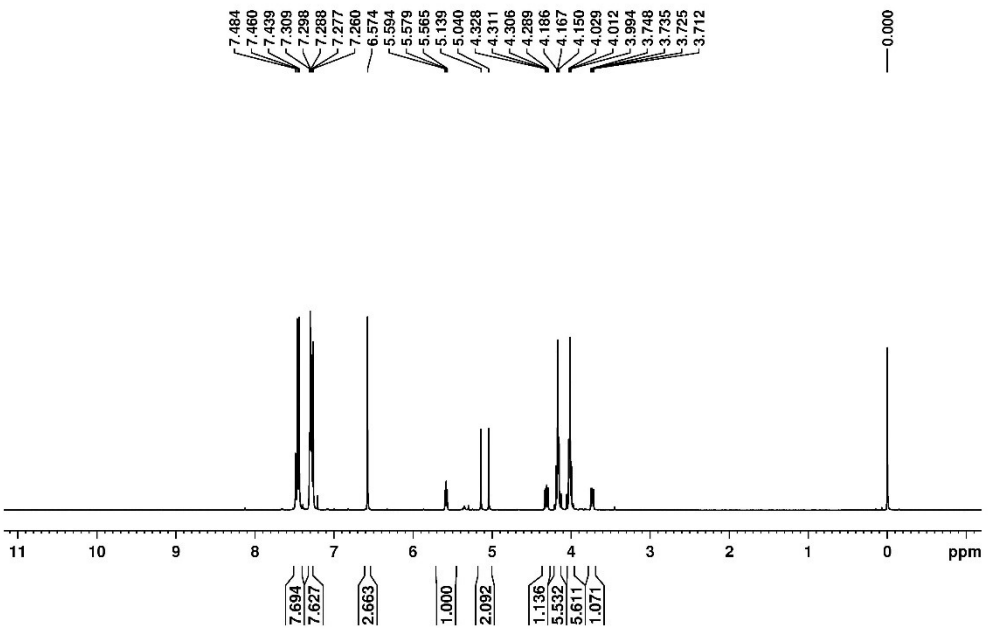


^{1}H NMR spectrum of compound **3z-ii**

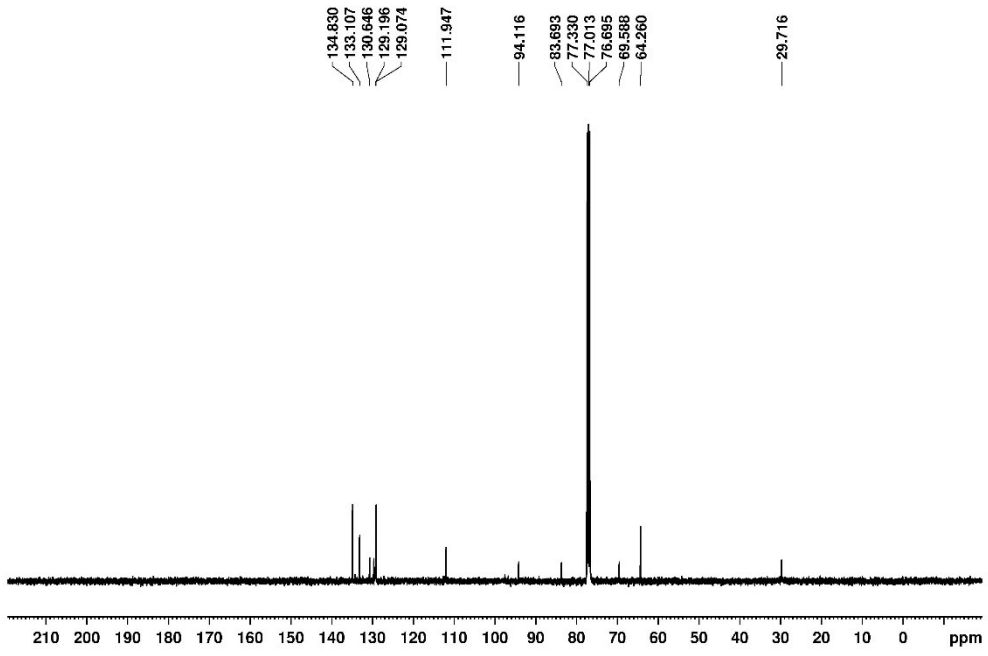


^{13}C NMR spectrum of compound **3z-ii**

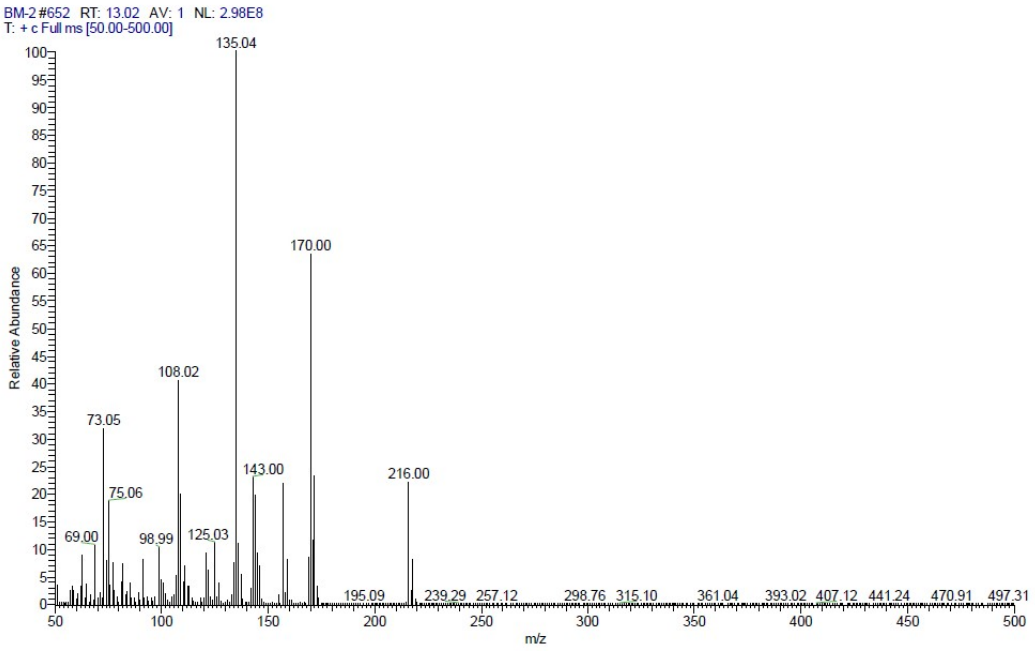
MS spectrum of compound **3z-ii**



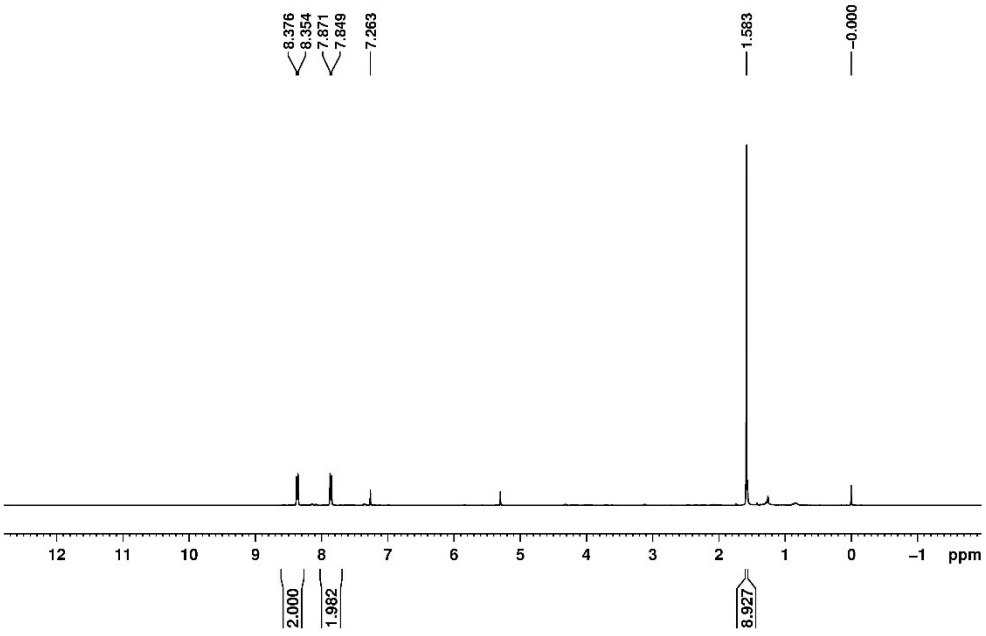
^{1}H NMR spectrum of compound **3aa**



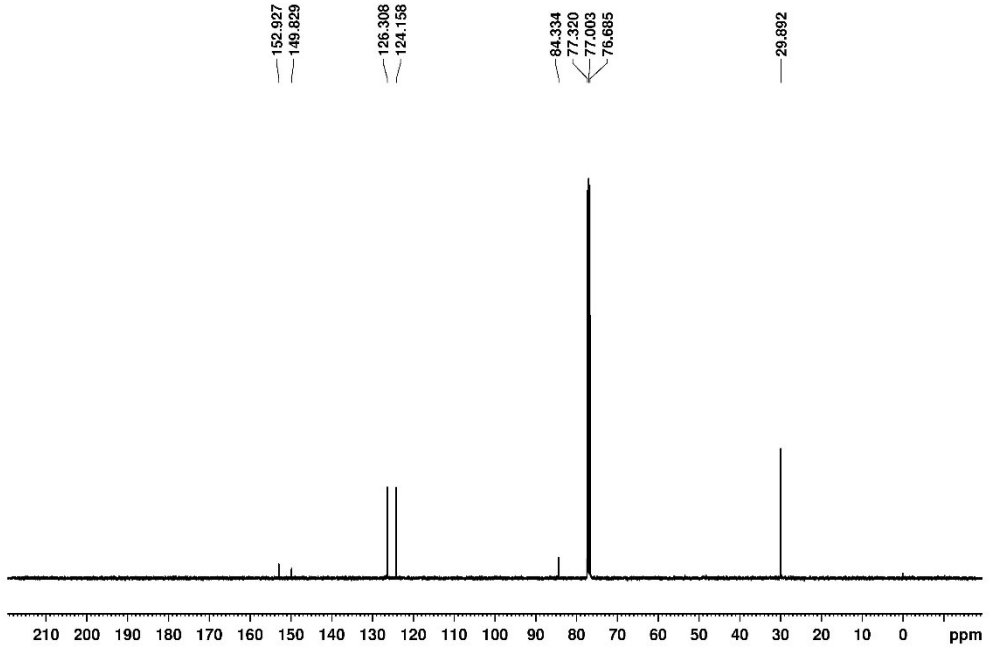
^{13}C NMR spectrum of compound **3aa**



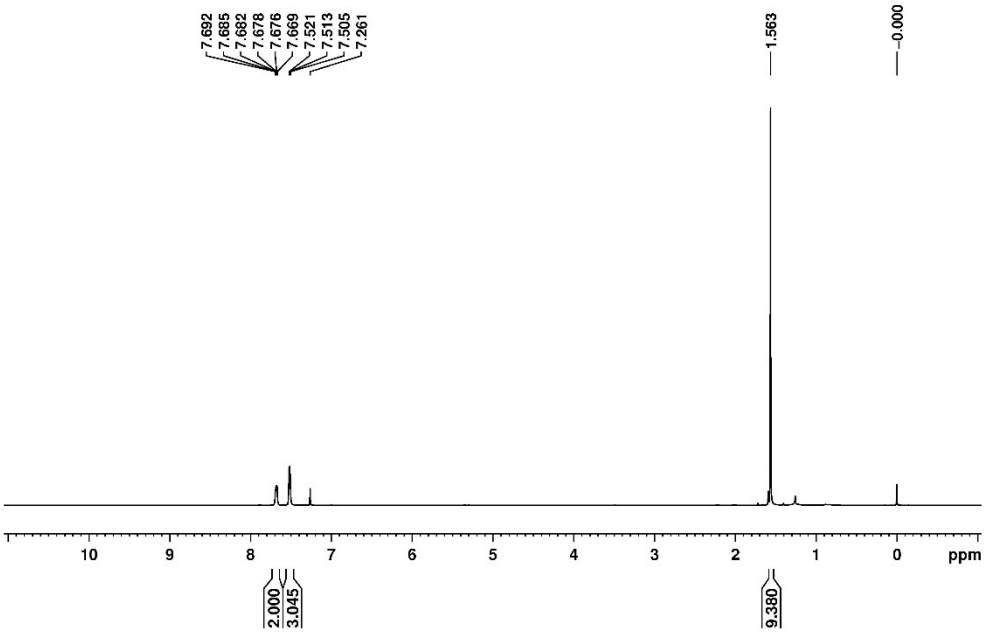
MS spectrum of compound **3aa**



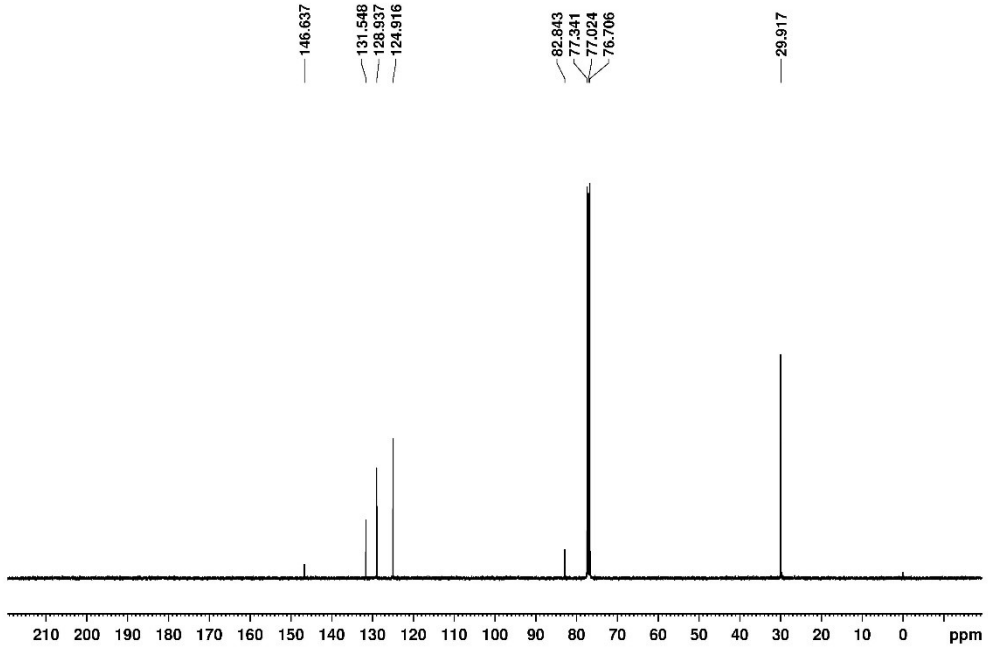
^{1}H NMR spectrum of compound **4a**



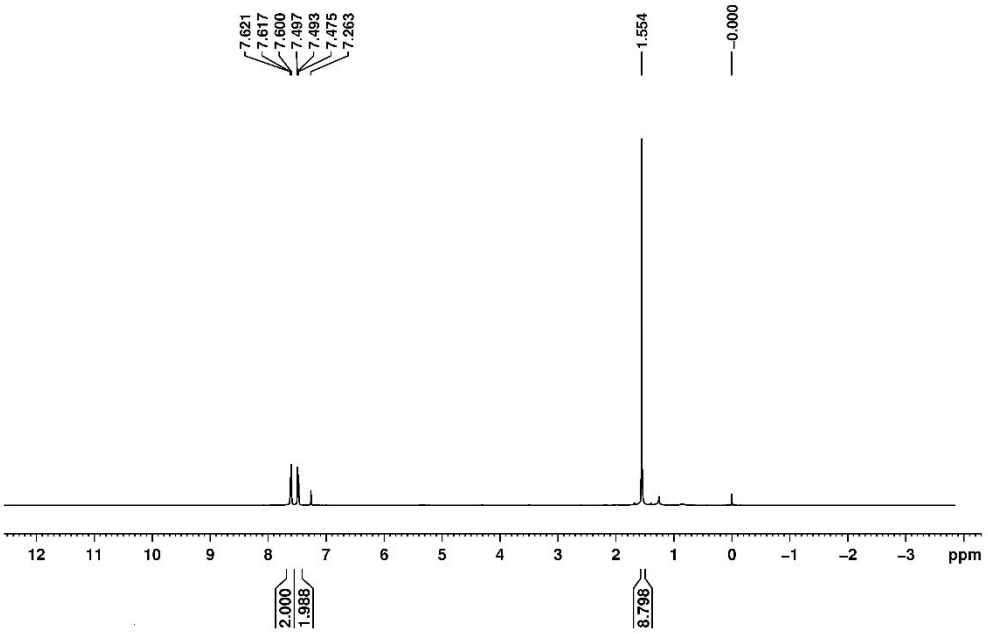
^{13}C NMR spectrum of compound **4a**



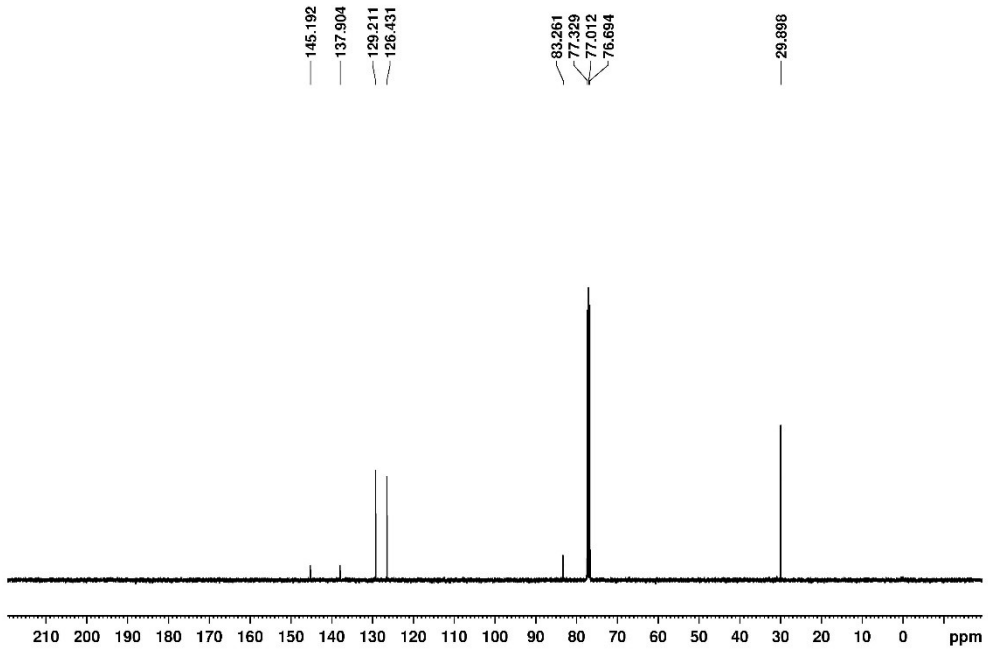
^{1}H NMR spectrum of compound **4b**



^{13}C NMR spectrum of compound **4b**



^{1}H NMR spectrum of compound **4c**



^{13}C NMR spectrum of compound **4c**