Supplementary Information

Photoexcited sulfenylation of C(sp^3)-H bonds in amides using thiosulfonates

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1. General information

All reagents and solvents were purchased from commercial suppliers without further purification. All reactions were carried out in borosilicate glass vessels under the irradiation of 5 W blue LED light from a photo reactor manufactured by Beijing Roger Technology Co., Ltd. without using filters. This blue light 5W LED's energy peak wavelength is 452.0 nm, peak width at half-height is 20.5 nm, Iirradiance@5W is 117 mW/cm^2. LED irradiate through a high-reflection channel (path length is 2 cm) to the test tube. The progress of the reactions were monitored by thin-layer chromatography under 254 nm UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded at Bruker Avance 400 MHz spectrometer operating at 400 MHz and 100 MHz, respectively. NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 2 °C). High-resolution mass spectra (HRMS) of the products were obtained on Agilent Technologies 6530 Accuratemass Q-TOF LC/MS with ESI as ion source. Fluorescence quenching experiments were performed by Hitachi F7000 fluorescence spectrometer.

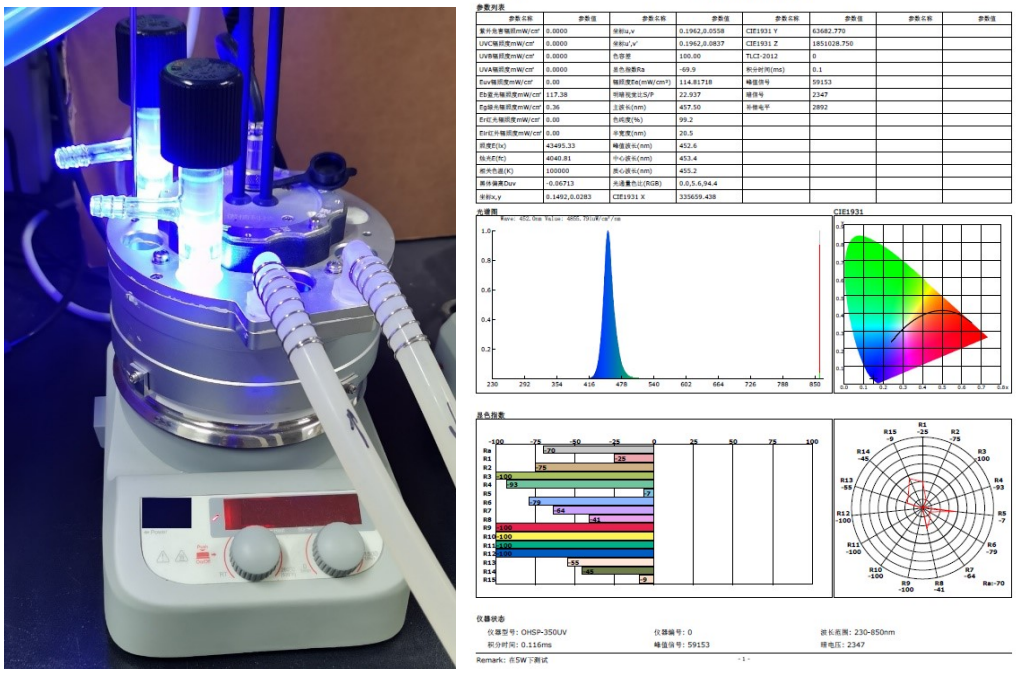
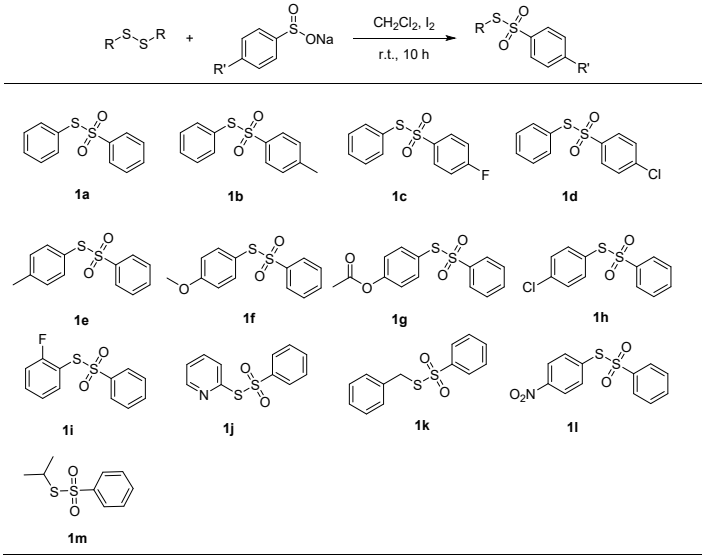


Figure S1 The photo reactor and blue LED light source test.

2. General procedure for the synthesis of thiosulfonates and selenosulfonate

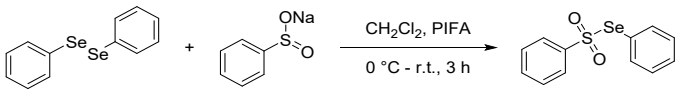
2.1 Synthesis of thiosulfonates. Thiosulfonates were synthesized according to literature (*Org. Lett.*, 2020, **22**, 4908) with minor modifications. Disulfides (0.5 mmol, 1.0 equiv.), sodium

benzenesulfonates (12 mmol, 2.4 equiv.), iodine (7.5 mmol, 1.5 equiv.) were mixed in CH_2Cl_2 (20 mL) in a 250 mL round bottom flask. The mixture was stirred at room temperature for 10 h. After completion of the reaction, sodium thiosulfate was added to remove the excess iodine. Then, the mixture was washed by brine (20 mL × 3). The organic phase were combined and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated and the crude product was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 10 : 1, v/v) to give the desired products.



Scheme S1 Synthesis of thiosulfonates

2.2 Synthesis of selenosulfonate. *Se*-phenyl benzenesulfonoselenoate was synthesized according to literature (*J. Org. Chem.,* 2019, **84**, 8100.) by the use of 1,2-diphenyldiselane 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).

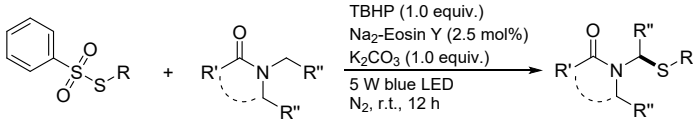


Scheme S2 Synthesis of selenosulfonate

3. General procedure for the synthesis of products 3

Thiosulfonates (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 *N,N*-disubstituted amides (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 to afford the desired products **3**.



Scheme S3 Synthesis of products **3**

4. Confirmation of compound 4

Yellow solid, yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.39 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 1.61 (s, 9H). HRMS (ESI) for $C_{10}H_{13}NNaO_4S$ $(M+Na)^+$: calcd. 266.0457, found 266.0456.

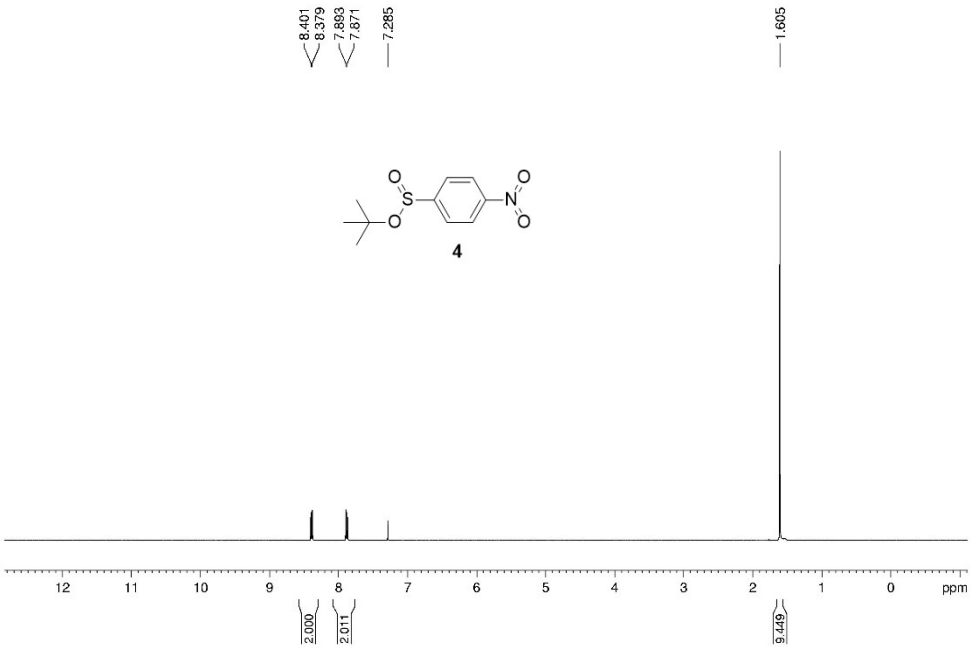


Figure S2 ^{1}H NMR of compound **4**

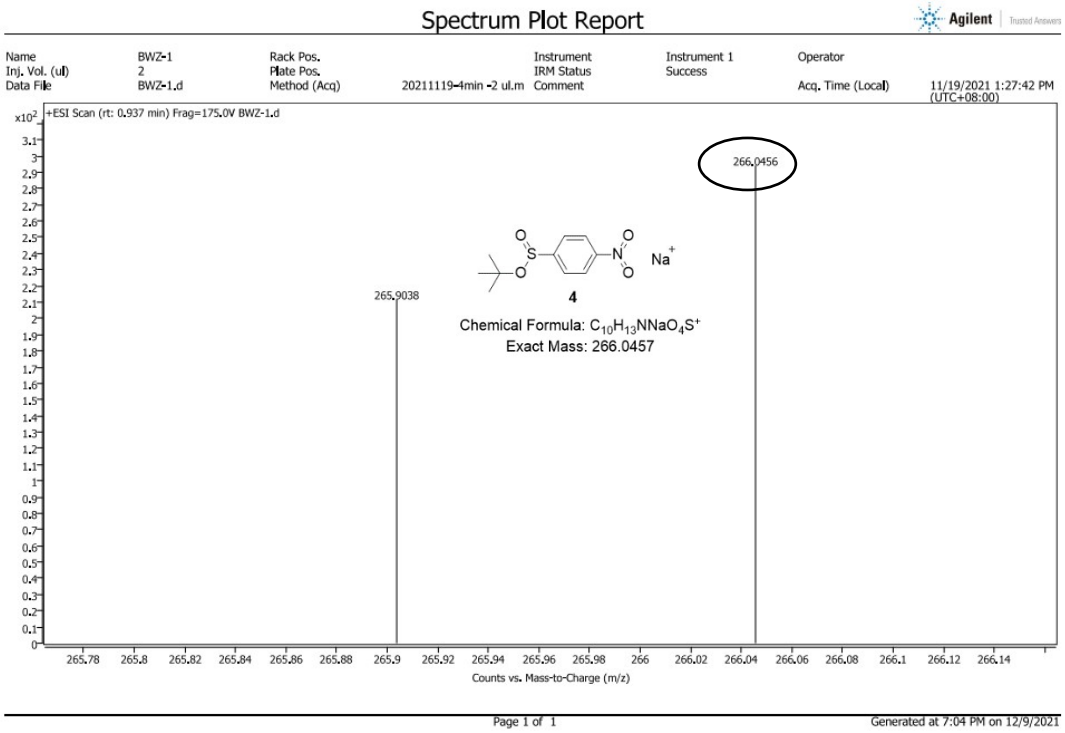


Figure S3 HRMS of compound **4**

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), 1,1-diphenylethylene (ASYM) or 2,6-di-tert-butyl-4-methylphenol (BHT) were dissolved in DMA (2.0 mL), respectively. The mixtures were stirred under standard reaction conditions for 12 h and then detected by HRMS.

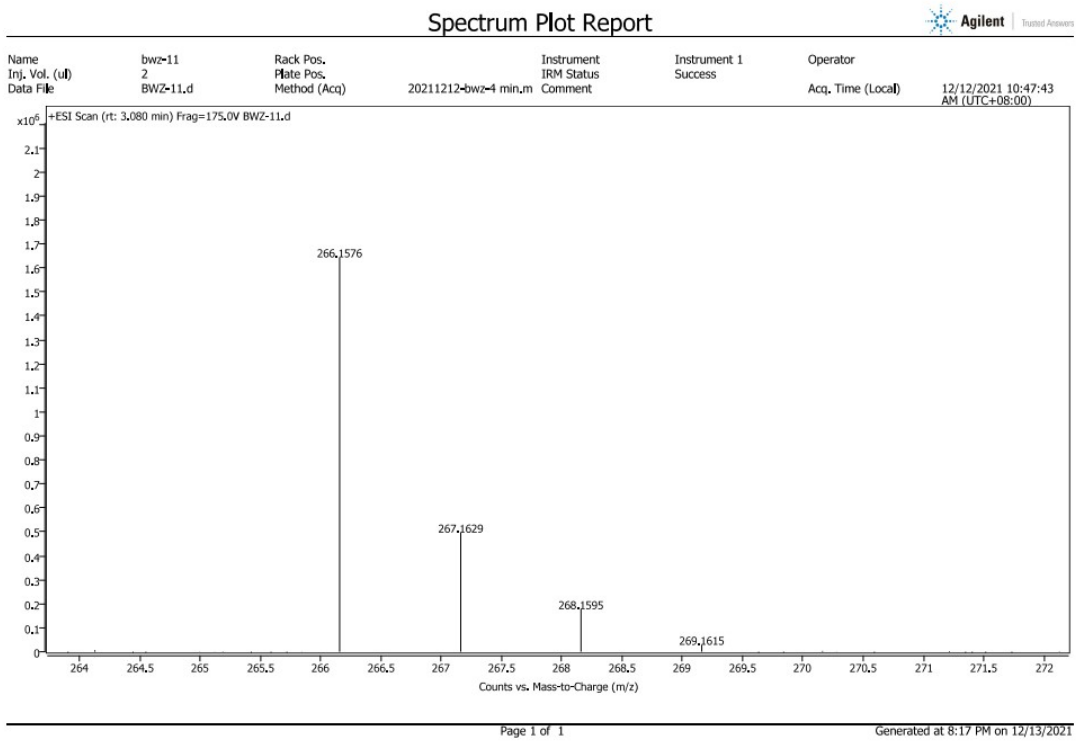


Figure S4 HRMS spectrum of the benzenesulfenyl radical/TEMPO adduct **6**

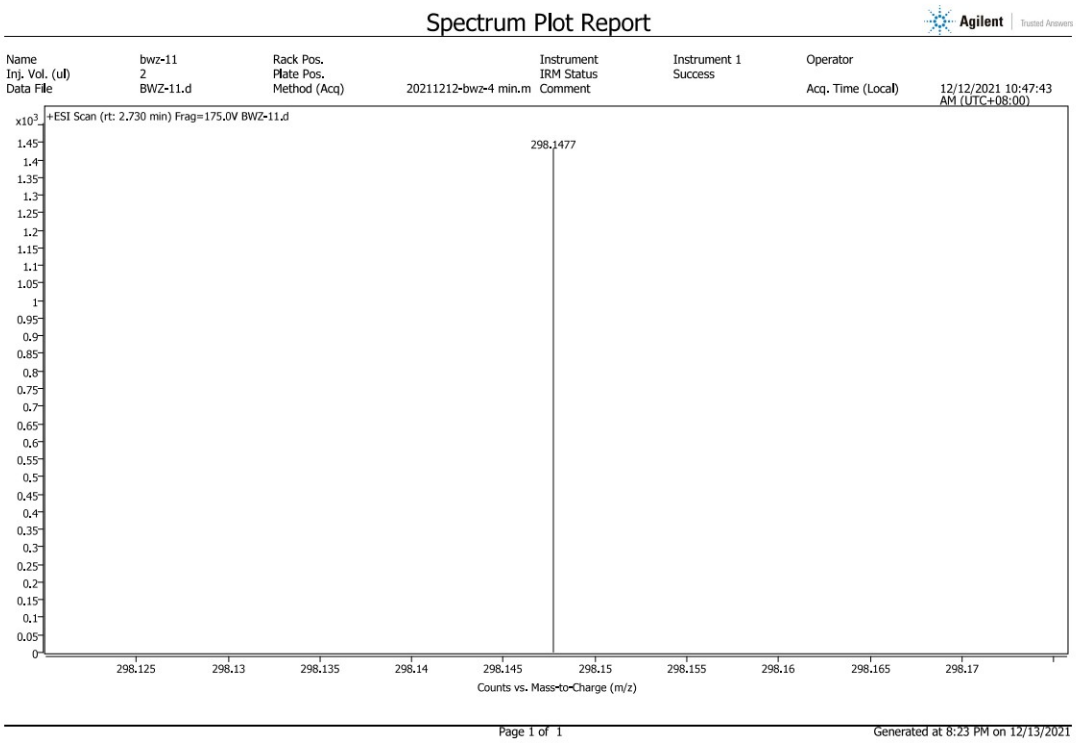


Figure S5 HRMS spectrum of the benzenesulfonyl radical/TEMPO adduct **7**

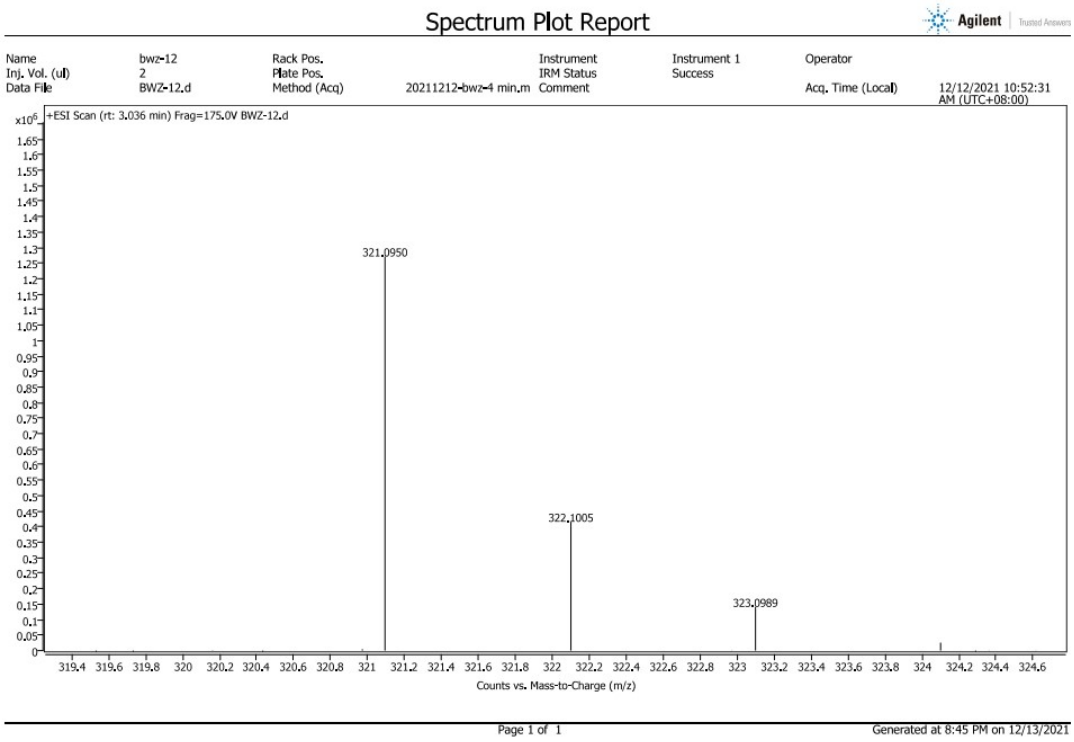


Figure S6 HRMS Spectrum of the benzenesulfonyl radical/ASYM adduct **8**

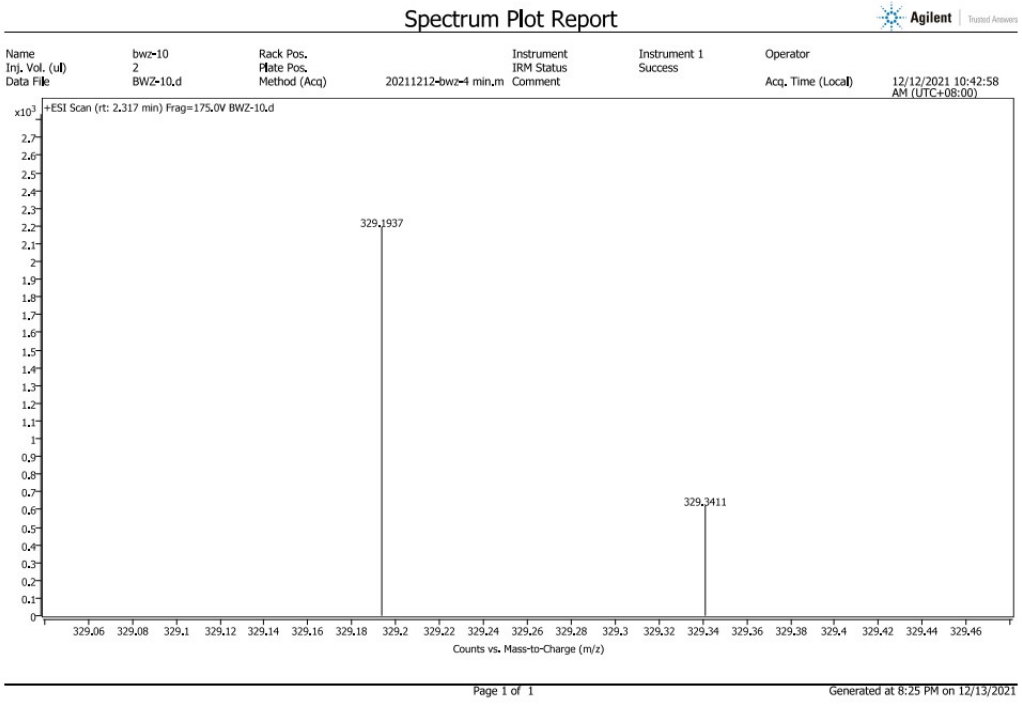


Figure S7 HRMS spectrum of the benzenesulfenyl radical/BHT adduct **9**

5.2 Fluorescence quenching experiments

A stock solution of Na_2-eosin Y (0.1 mM in dry DMA) was prepared for the quenching experiment. 20 μL Na_2-eosin Y stock solution was added in 2.0 mL of DMA 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 530/549 nm. Then, quenching experiments were performed with addition of TBHP (70% aqueous solution) or **1a** (0, 1, 2, 3, 4, 5 mM), respectively.

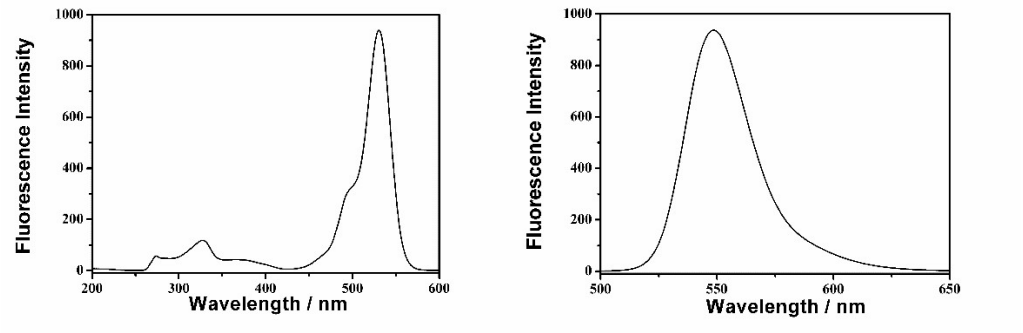


Figure S8 Fluorescence excitation (left) and emission (right) spectra of Na_2-eosin Y (10^{-6} M) in DMA

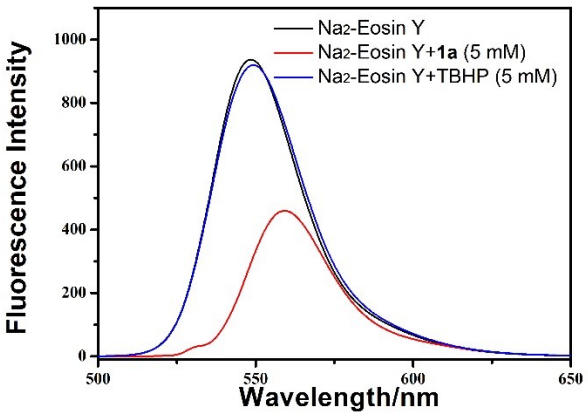


Figure S9 Fluorescence emission spectra of Na_2-eosin Y (10^{-6} M) in DMA with TBHP or **1a** (5 mM)

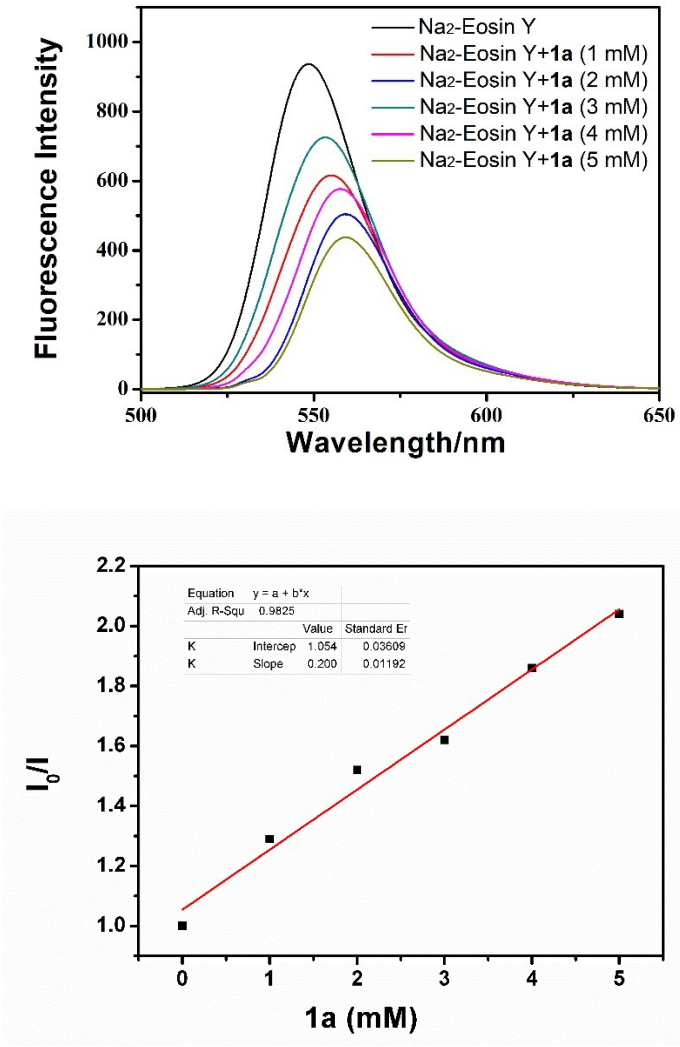
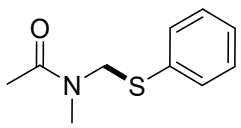


Figure S10 Fluorescence emission spectra of Na_2-eosin Y (10^{-6} M) in DMA with TBHP and **1a** (up) and the linear relationship between I_0/I and the concentration of **1a** (down)

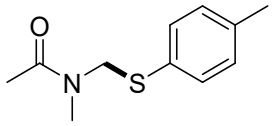
6. Characterization data of compounds 3a-h, 3k-u and 3w-y.

_N_-methyl-_N_-((phenylthio)methyl)acetamide (3a)



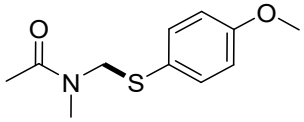
Light-yellow oil, yield: 87%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.52-7.47 (m, 2H), 7.38-7.25 (m, 3H), 4.91 and 4.67 (2×s, 2H), 3.01 and 2.99 (2×s, 3H), 2.04 and 1.67 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.7 and 170.6, 135.0 and 134.0, 132.4 and 131.5, 129.1 and 129.0, 127.2, 57.8 and 51.7, 35.2 and 32.8, 21.8 and 20.7. HRMS (ESI) for $C_{10}H_{14}NOS$ $(M+H)^+$: calcd. 196.0791, found 196.0799.

_N_-methyl-_N_-((p-tolylthio)methyl)acetamide (3b)



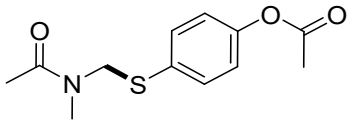
Light-yellow oil, yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.38-7.35 (m, 2H), 7.15-7.09 (m, 2H), 4.84 and 4.60 (2×s, 2H), 2.98 and 2.97 (2×s, 3H), 2.34 and 2.32 (2×s, 3H), 2.01 and 1.63(2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.6, 139.3 and 137.5, 135.2 and 132.2, 130.3 and 130.2, 129.8 and 128.7, 58.0 and 52.3, 35.2 and 32.8, 21.8 and 21.2, 21.0 and 20.7. HRMS (ESI) for $C_{11}H_{16}NOS(M+H)^+$: calcd. 210.0947, found 210.0943.

_N_-(((4-methoxyphenyl)thio)methyl)-_N_-methylacetamide (3c)



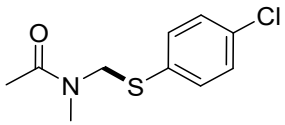
Light-yellow oil, yield: 81%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.43-7.40 (m, 2H), 6.87-6.82 (m, 2H), 4.77 and 4.56 (2×s, 2H), 3.80 and 3.79 (2×s, 3H), 2.982 and 2.975 (2×s, 3H), 2.00 and 1.61 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.59 and 170.55, 160.6 and 159.6, 137.1 and 134.9, 130.9 and 128.8, 124.2 and 122.7, 114.9 and 114.6, 58.2 and 55.4, 55.3 and 53.2, 35.3 and 32.7, 21.8 and 20.6. HRMS (ESI) for $C_{11}H_{15}NNaO_2S(M+Na)^+$: calcd. 248.0716, found 248.0723.

4-(((_N_-methylacetamido)methyl)thio)phenyl acetate (3d)



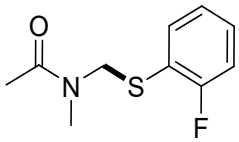
Light-yellow oil, yield: 71%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.51-7.46 (m, 2H), 7.10-7.02 (m, 2H), 4.88 and 4.64 (2×s, 2H), 3.00 and 2.98 (2×s, 3H), 2.30 and 2.29 (2×s, 3H), 2.03 and 1.69 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.8, 169.2 and 169.0, 151.4 and 150.0, 136.2 and 132.7, 131.2 and 130.9, 129.6 and 128.8, 122.7 and 122.2, 58.0 and 51.9, 35.2 and 32.9, 21.8 and 21.1, 20.7 and 19.2. HRMS (ESI) for $C_{12}H_{16}NO_3S(M+H)^+$: calcd. 254.0845, found 254.0842.

_N_-(((4-chlorophenyl)thio)methyl)-_N_-methylacetamid (3e)



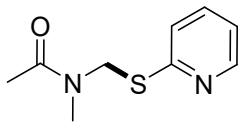
Light-yellow oil, yield: 62%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.43-7.38 (m, 2H), 7.33-7.25 (m, 2H), 4.88 and 4.64 (2×s, 2H), 3.01 and 2.97 (2×s, 3H), 2.03 and 1.72 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.8 and 170.5, 136.2 and 135.5, 133.4 and 132.8, 132.4 and 130.9, 129.6 and 129.1, 57.8 and 51.7, 35.1 and 33.0, 21.8 and 20.8. HRMS (ESI) for $C_{10}H_{13}ClNOS$ $(M+H)^+$: calcd. 230.0401, found 230.0400.

_N_-(((2-fluorophenyl)thio)methyl)-_N_-methylacetamide (3f)



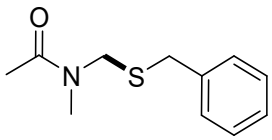
Light-yellow oil, yield: 53%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.55-7.27 (m, 2H), 7.26-7.04 (m, 2H), 4.85 and 4.69 (2×s, 2H), 3.02 and 2.97 (2×s, 3H), 2.01 and 1.80 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.8 and 170.5, 164.4 and 163.6, 161.9 and 161.2, 137.3 and 135.1, 131.6 and 131.5, 130.1 and 130.0, 125.0 and 124.9, 124.6 and 124.5, 120.8 and 120.6, 119.2 and 119.0, 116.3 and 116.0, 115.9 and 115.6, 56.4 and 51.6, 35.2 and 33.0, 21.8 and 20.6. HRMS (ESI) for $C_{10}H_{12}FKNOS(M+K)^+$: calcd. 252.0255, found 252.0256.

_N_-methyl-_N_-((pyridin-2-ylthio)methyl)acetamide (3g)



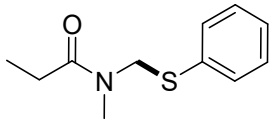
Light-yellow oil, yield: 77%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.45-8.42 (m, 1H), 7.63-7.48 (m, 1H), 7.25-7.20 (m, 1H), 7.07-7.00 (m, 1H), 5.29 and 5.26 (2×s, 2H), 3.10 and 2.97 (2×s, 3H), 2.24 and 2.09 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 171.4 and 171.0, 157.8 and 156.3, 149.4 and 149.2, 136.5 and 136.3, 123.4 and 122.7, 120.5 and 120.0, 51.5 and 47.2, 35.8 and 33.1, 21.8 and 21.6. HRMS (ESI) for $C_9H_{12}N_2NaOS(M+Na)^+$: calcd. 219.0563, found 219.0572.

_N_-((benzylthio)methyl)-_N_-methylacetamide (3h)



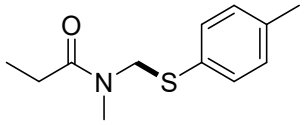
Light-yellow oil, yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.38-7.28 (m, 4H), 7.24-7.22 (m, 1H), 4.58 and 4.34 (2×s, 2H), 3.78 and 3.77 (2×s, 2H), 2.93 and 2.91 (2×s, 3H), 1.99 and 1.98 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 171.1 and 170.6, 138.8 and 137.2, 128.80 and 128.76, 128.7 and 128.4, 127.5 and 126.9, 52.3 and 49.2, 35.8 and 35.1, 34.7 and 33.0, 21.9 and 21.2. HRMS (ESI) for $C_{11}H_{15}NNaOS(M+Na)^+$: calcd. 232.0767, found 232.0767.

_N_-methyl-_N_-((phenylthio)methyl)propionamide (3k)



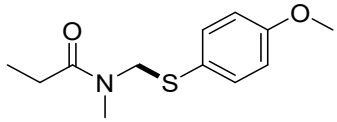
Light-yellow oil, yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.49-7.46 (m, 2H), 7.34-7.23 (m, 3H), 4.91 and 4.67 (2×s, 2H), 2.98 (2×s, 3H), 2.26 and 1.91 (2×q, 2H), 1.05 and 0.92 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 173.9 and 173.9, 134.8 and 134.0, 132.6 and 131.6, 129.3 and 129.0, 128.8 and 127.2, 56.8 and 52.0, 34.3 and 33.2, 26.9 and 25.7, 9.2 and 9.1. HRMS (ESI) for $C_{11}H_{16}NOS(M+H)^+$: calcd. 210.0947, found 210.0944.

***N*-methyl-*N*-((p-tolylthio)methyl)propionamide (3l)**



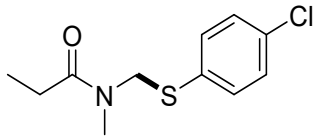
Light-yellow oil, yield: 83%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.37-7.35 (m, 2H), 7.14-7.08 (m, 2H), 4.85 and 4.62 (2×s, 2H), 2.97 (2×s, 3H), 2.34 and 2.31 (2×s, 3H), 2.25 and 1.89 (2×q, 2H), 1.05 and 0.91 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 173.9 and 173.8, 139.1 and 137.4, 135.0 and 132.3, 130.3 and 130.1, 129.7 and 128.9, 56.9 and 52.6, 34.4 and 33.1, 26.8 and 25.6, 21.2 and 21.1, 9.13 and 9.06. HRMS (ESI) for $C_{12}H_{18}NOS(M+H)^+$: calcd. 224.1104, found 224.1103.

***N*-(((4-methoxyphenyl)thio)methyl)-*N*-methylpropionamide (3m)**



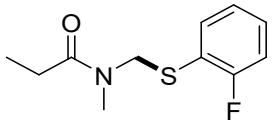
Light-yellow oil, yield: 81%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.43-7.39 (m, 2H), 6.88-6.82 (m, 2H), 4.79 and 4.57 (2×s, 2H), 3.80 and 3.79 (2×s, 3H), 2.97 and 2.96 (2×s, 3H), 2.24 and 1.86 (2×q, 2H), 1.04 and 0.90 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 173.9 and 173.8, 160.5 and 159.6, 138.4 and 137.0, 135.0 and 129.9, 124.2 and 122.8, 114.9 and 114.5, 113.8, 57.2 and 55.4, 55.3 and 53.4, 34.5 and 33.1, 26.8 and 25.6, 9.2 and 9.1. HRMS (ESI) for $C_{12}H_{18}NO_2S$ $(M+H)^+$: calcd. 240.1053, found 240.1059.

***N*-(((4-chlorophenyl)thio)methyl)-*N*-methylpropionamide (3n)**



Light-yellow oil, yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.42-7.38 (m, 2H), 7.32-7.24 (m, 2H), 4.89 and 4.66 (2×s, 2H), 2.99 and 2.97 (2×s, 3H), 2.27 and 1.97 (2×q, 2H), 1.06 and 0.96 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 174.0 and 173.8, 135.9 and 135.3, 133.3 and 132.9, 132.4 and 131.1, 129.5 and 129.1, 56.8 and 51.9, 34.3 and 33.3, 26.9 and 25.8, 9.15 and 9.07. HRMS (ESI) for $C_{11}H_{15}ClNOS(M+H)^+$: calcd. 244.0557, found 244.0563.

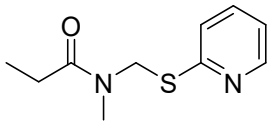
***N*-(((2-fluorophenyl)thio)methyl)-*N*-methylpropionamide (3o)**



Light-yellow oil, yield: 78%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.55-7.28 (m, 2H), 7.25-7.04 (m, 2H), 4.87 and 4.71 (2×s, 2H), 3.01 and 2.97 (2×s, 3H), 2.25 and 2.08 (2×q, 2H), 1.03 and 0.97 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 174.0 and 173.8, 164.2 and 163.6, 161.8 and 161.2, 137.1 and 135.2, 131.4 and 131.3, 130.03 and 129.95, 124.9 and 124.8, 124.53 and 124.49, 120.8 and 120.6, 119.4 and 119.2, 116.2 and 116.0, 115.9 and 115.6, 55.41 and 55.39, 51.86 and 51.84, 34.4 and

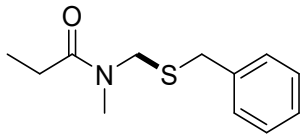
33.3, 26.8 and 25.6, 9.2 and 9.0. HRMS (ESI) for $C_{11}H_{15}FNOS(M+H)^+$: calcd. 228.0853, found 228.0851.

***N*-methyl-*N*-((pyridin-2-ylthio)methyl)propionamide (3p)**



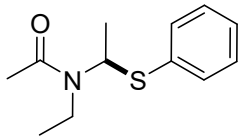
Light-yellow oil, yield: 77%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.44-8.41 (m, 1H), 7.52-7.47 (m, 1H), 7.25-7.19 (m, 1H), 7.06-6.99 (m, 1H), 5.30 and 5.27 (2×s, 2H), 3.08 and 2.97 (2×s, 3H), 2.52 and 2.33 (2×q, 2H), 1.16 and 1.13 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 174.5 and 174.2, 158.0 and 156.6, 149.4 and 149.2, 136.5 and 136.3, 123.4 and 122.7, 120.4 and 119.9, 50.6 and 47.5, 35.0 and 33.4, 26.8 and 26.4, 9.4 and 9.0. HRMS (ESI) for $C_{10}H_{15}N_2OS$ $(M+H)^+$: calcd. 211.0900, found 211.0904.

***N*-((benzylthio)methyl)-*N*-methylpropionamide (3q)**



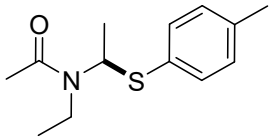
Light-yellow oil, yield: 81%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.38-7.22 (m, 5H), 4.60 and 4.35 (2×s, 2H), 3.78 and 3.76 (2×s, 2H), 2.94 and 2.90 (2×s, 3H), 2.20 (2×q, 2H), 1.10 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 174.3 and 173.8, 138.9 and 137.3, 128.8 and 128.7, 128.6 and 128.4, 127.4 and 126.9, 51.4 and 49.5, 35.8 and 35.2, 33.9 and 33.3, 26.9 and 26.1, 9.3 and 9.1. HRMS (ESI) for $C_{12}H_{18}NOS$ $(M+H)^+$: calcd. 224.1104, found 224.1114.

***N*-ethyl-*N*-(1-(phenylthio)ethyl)acetamide (3r)**



Light-yellow oil, yield: 63%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.45-7.43 (m, 1H), 7.38-7.32 (m, 3H), 7.24-7.23 (m, 1H), 6.47 and 5.23 (2×q, 1H), 3.71-3.57 and 3.33-3.20 (2×q, 2H), 1.94 and 1.51 (2×s, 3H), 1.59 and 1.48 (2×d, 3H), 1.20 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.8 and 169.8, 135.5 and 133.7, 132.5 and 131.7, 129.3 and 129.2, 128.8 and 127.2, 64.9 and 57.0, 37.8 and 36.3, 21.6 and 21.2, 21.1 and 20.1, 16.3 and 14.7. HRMS (ESI) for $C_{12}H_{18}NOS(M+H)^+$: calcd. 224.1104, found 224.1100.

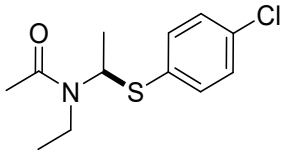
***N*-ethyl-*N*-(1-(p-tolylthio)ethyl)acetamide (3s)**



Light-yellow oil, yield: 61%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.32-7.28 (m, 2H), 7.13-7.06 (m, 2H),

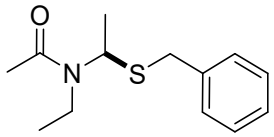
6.40 and 5.19 (2×q, 1H), 3.71-3.58 and 3.38-3.20 (2×q, 2H), 2.34 and 2.30 (2×s, 3H), 1.93 and 1.51 (2×s, 3H), 1.58 and 1.46 (2×d, 3H), 1.20 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.7 and 169.9, 139.4 and 137.5, 135.6 and 132.4, 130.0 and 129.9, 129.6 and 128.9, 64.9 and 57.4, 37.7 and 36.2, 21.6 and 21.3, 21.2 and 21.1, 21.0 and 20.1, 16.3 and 14.8. HRMS (ESI) for $C_{13}H_{20}NOS(M+H)^+$: calcd. 238.1260, found 238.1264.

_N_-(1-((4-chlorophenyl)thio)ethyl)-_N_-ethylacetamide (3t)



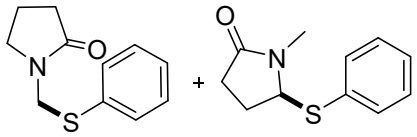
Light-yellow oil, yield: 67%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ:7.35-7.28 (m, 3H), 7.24-7.22 (m, 1H), 6.46 and 5.22 (2×q, 1H), 3.70-3.54 and 3.37-3.20 (2×q, 2H), 1.97 and 1.58 (2×s, 3H), 1.57 and 1.48 (2×d, 3H), 1.21 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.8 and 169.7, 136.7 and 135.6, 133.3 and 132.9, 132.3 and 131.0, 129.5 and 129.2, 129.0 and 126.4, 64.9 and 57.0, 37.7 and 36.3, 21.6 and 21.4, 21.0 and 20.0, 16.3 and 14.7. HRMS (ESI) for $C_{12}H_{17}ClNOS(M+H)^+$: calcd. 258.0714, found 258.0714.

_N_-(1-(benzylthio)ethyl)-_N_-ethylacetamide (3u)



Light-yellow oil, yield: 61%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.34-7.32 (m, 2H), 7.30-7.29 (m, 3H), 6.21 and 4.91 (2×q, 1H), 3.72 and 3.64 (2×m, 2H), 3.52-3.42 and 3.01-2.92 (2×m, 2H), 1.96 and 1.82 (2×s, 3H), 1.45 and 1.34 (2×d, 3H), 1.20 (2×t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 172.8 and 171.1, 138.6 and 137.3, 134.2 and 133.7, 131.8 and 130.5, 129.6 and 128.8, 128.6 and 128.4, 128.0 and 127.4, 126.8, 58.6 and 55.2, 37.5 and 36.1, 35.8 and 35.1, 21.8, 20.9 and 20.5, 16.7 and 15.0. HRMS (ESI) for $C_{13}H_{20}NOS(M+H)^+$: calcd. 238.1260, found 238.1263.

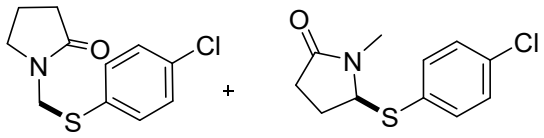
1-((phenylthio)methyl)pyrrolidin-2-one (a) and 1-methyl-5-(phenylthio)pyrrolidin-2-one (b) (a : b = 0.17 : 1) (3w)



a **b**

Light-yellow oil, yield: 61%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.45-7.42 (m, 2H), 7.36-7.34 (m, 3H), 4.81 (m, 1H), 4.77 (s, 2H), 3.44 (t, 2H), 2.99 (s, 3H), 2.52-2.44 (m, 1H), 2.32-2.28 (m, 2H), 2.22-2.16 (m, 1H), 2.13-2.06 (m, 1H), 1.98-1.93 (m, 2H), 1.73-1.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 174.5 and 174.2, 161.1 and 160.8, 136.0 and 135.2, 131.0 and 130.6, 129.3 and 129.1, 129.0, 127.2, 69.6, 46.8 and 46.0, 29.7 and 29.1, 28.1, 26.6, 17.7. HRMS (ESI) for $C_{11}H_{14}NOS(M+H)^+$: calcd. 208.0791, found 208.0791.

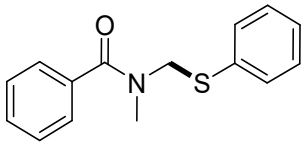
1-(((4-chlorophenyl)thio)methyl)pyrrolidin-2-one (a) and 5-((4-chlorophenyl)thio)-1-methyl-pyrrolidin-2-one (b) (a : b = 0.27 : 1) (3x)



a **b**

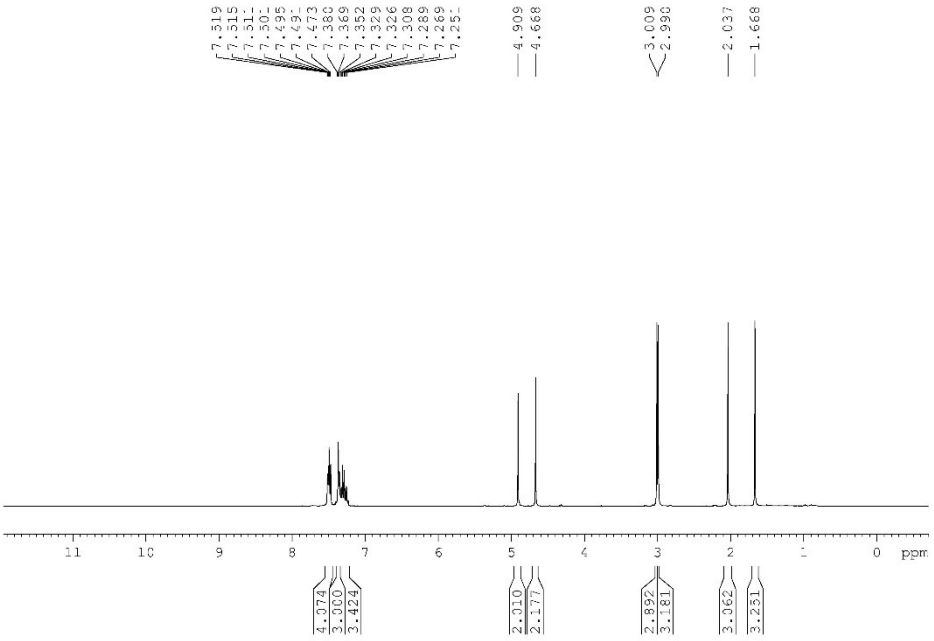
Light-yellow oil, yield: 73%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.37-7.28 (m, 4H), 4.79 (m, 1H), 4.75 (s, 2H), 3.44 (t, 2H), 2.98 (s, 3H), 2.53-2.47 (m, 1H), 2.33-2.29 (m, 2H), 2.19-2.10 (m, 2H), 1.99-1.96 (m, 2H), 1.80-1.71 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 174.4 and 173.7, 156.8 and 156.0, 136.4 and 135.6, 132.2, 129.6, 129.24 and 129.16, 69.7, 46.8 and 45.9, 30.8 and 29.1, 28.1 and 26.4, 17.6. HRMS (ESI) for $C_{11}H_{13}ClNOS(M+H)^+$: calcd. 242.0401, found 242.0402.

***N*-methyl-*N*-((phenylthio)methyl)benzamide (3y)**

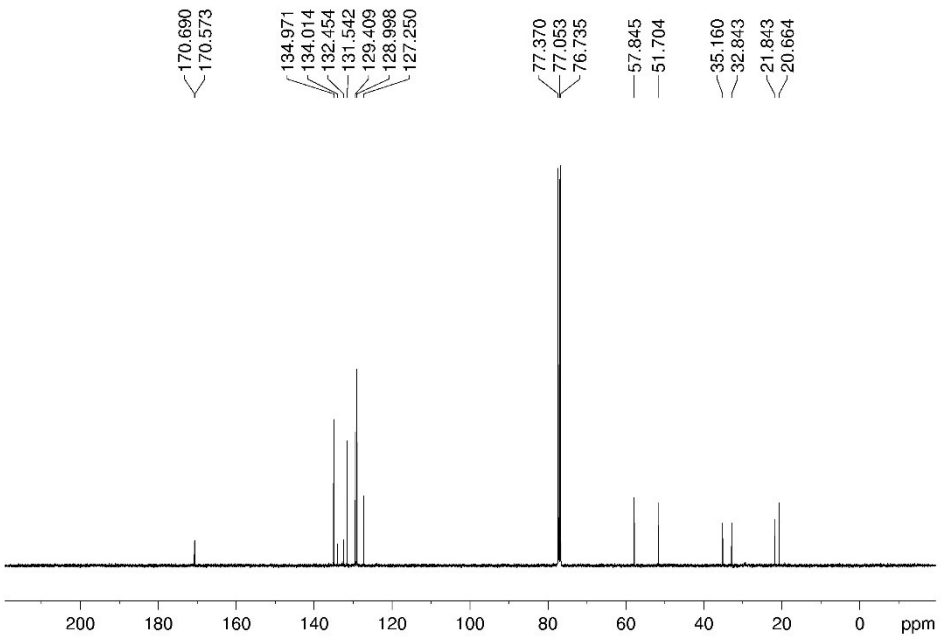


Light-yellow oil, yield: 30%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ:7.54 (2×s, 1H), 7.30 (2×s, 8H), 7.97 (2×s, 1H), 5.06 and 4.69 (2×s, 2H), 3.18 and 2.96 (2×s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 171.8 and 171.7, 134.4, 133.5, 132.3, 132.0 and 129.7, 129.5 and 129.3, 129.1 and 128.6, 128.3, 127.5, 126.9, 58.3 and 51.6, 32.6 and 29.7. HRMS (ESI) for $C_{15}H_{15}NNaOS$ $(M+Na)^+$: calcd. 280.0767, found 280.0778.

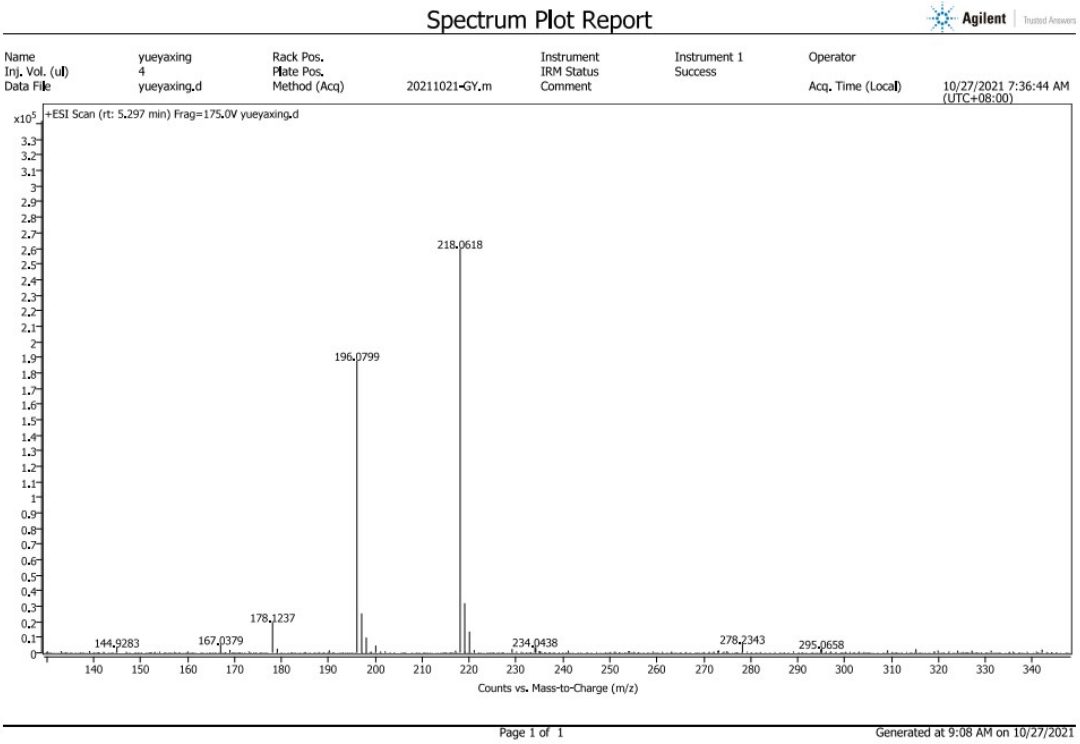
7. ^{1}H NMR, ^{13}C NMR and HRMS copies of compounds 3a-h, 3k-u and 3w-y.



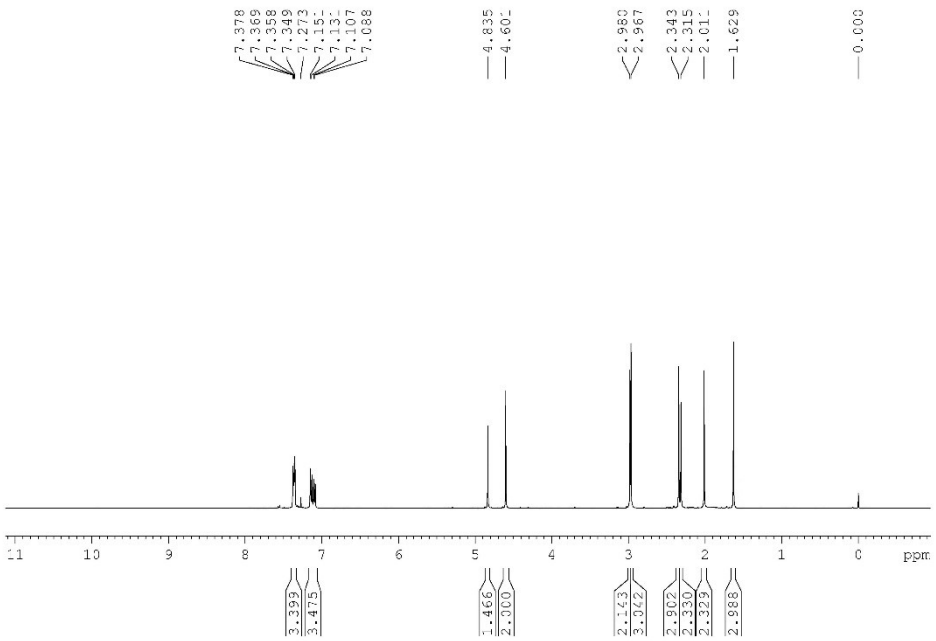
^{1}H NMR spectrum of compound **3a**



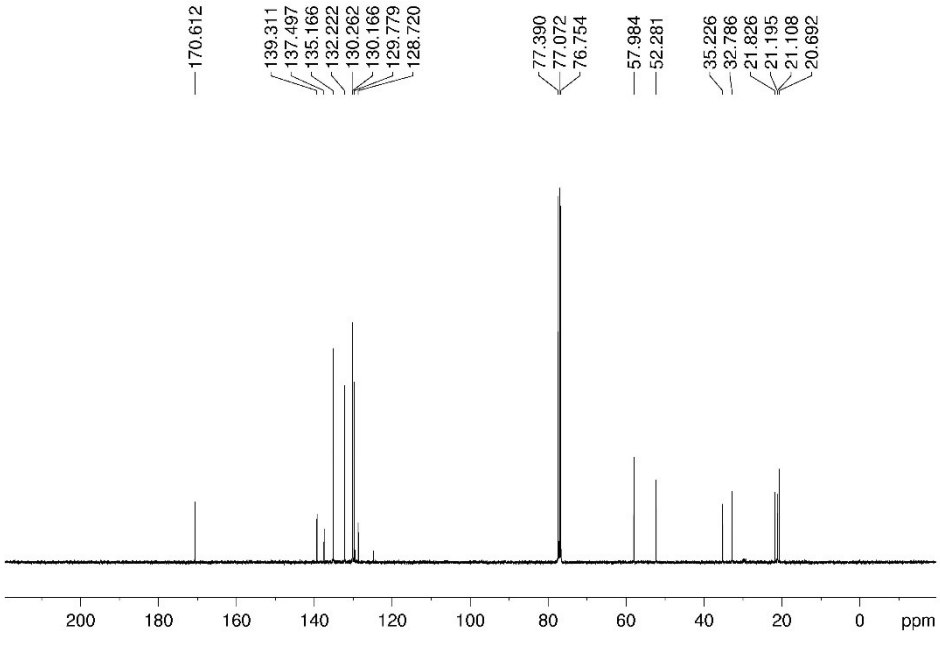
^{13}C NMR spectrum of compound **3a**



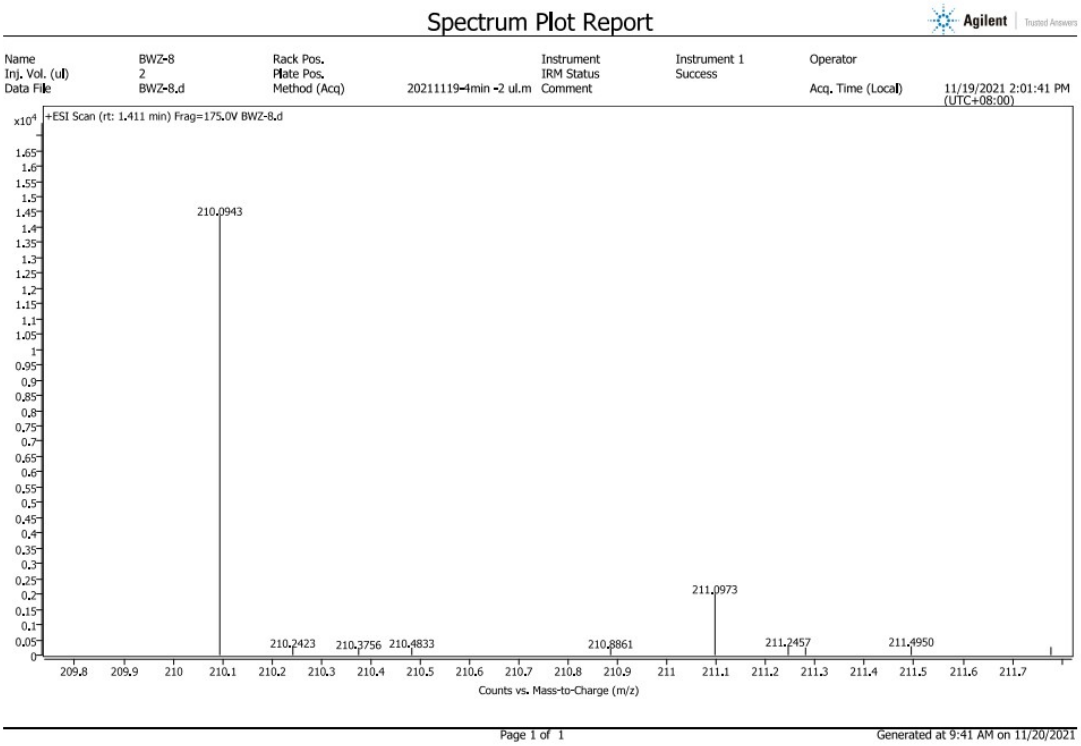
HRMS spectrum of compound **3a**



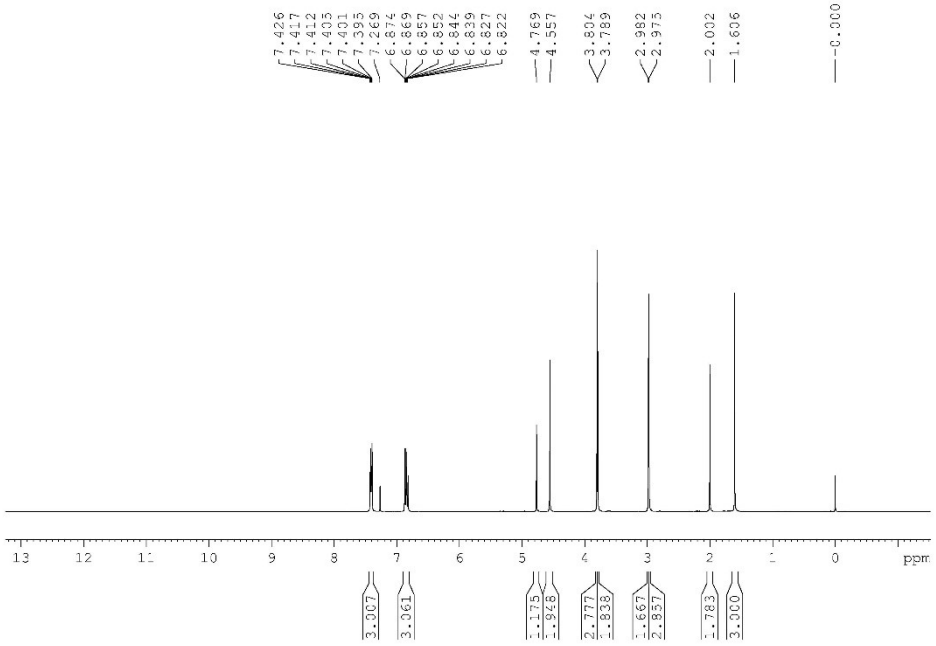
^{1}H NMR spectrum of compound **3b**



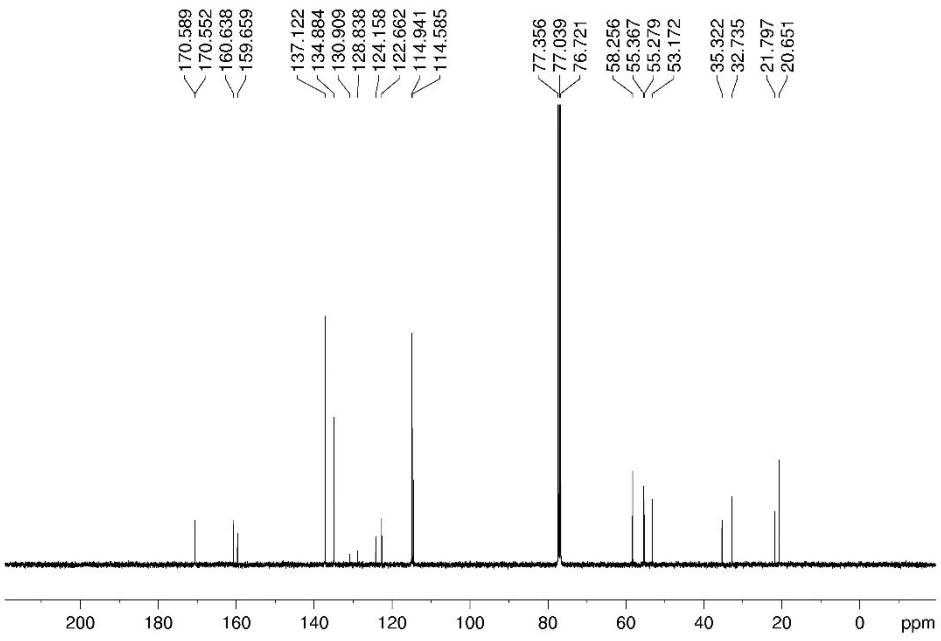
^{13}C NMR spectrum of compound **3b**



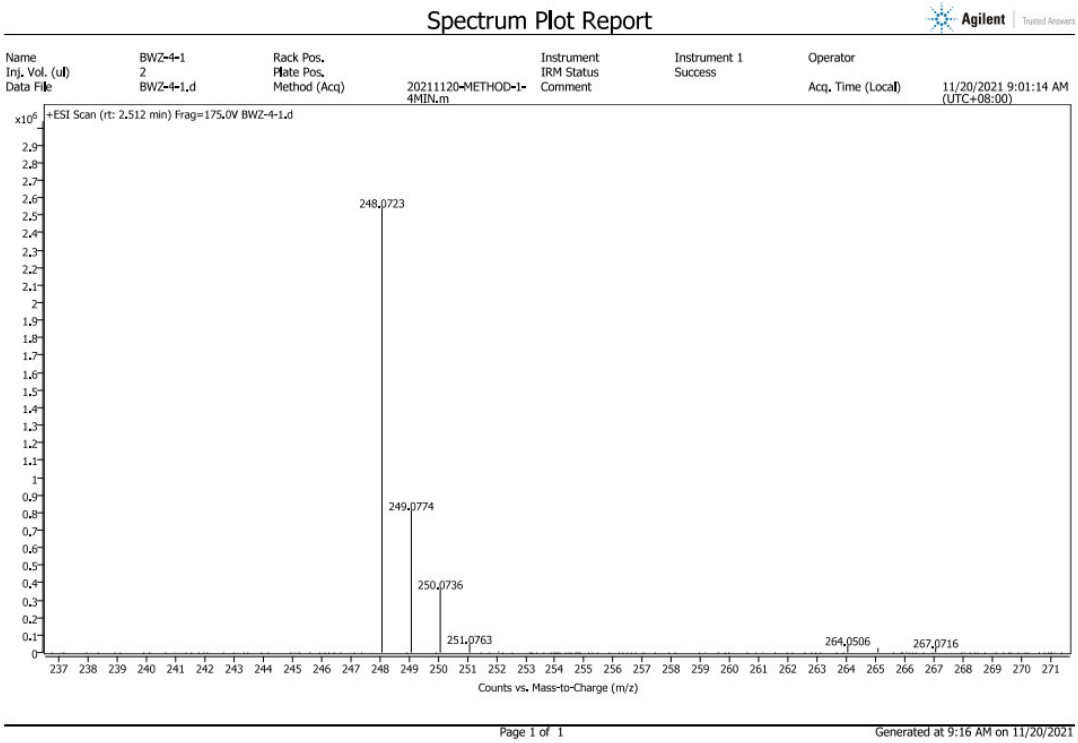
HRMS spectrum of compound **3b**



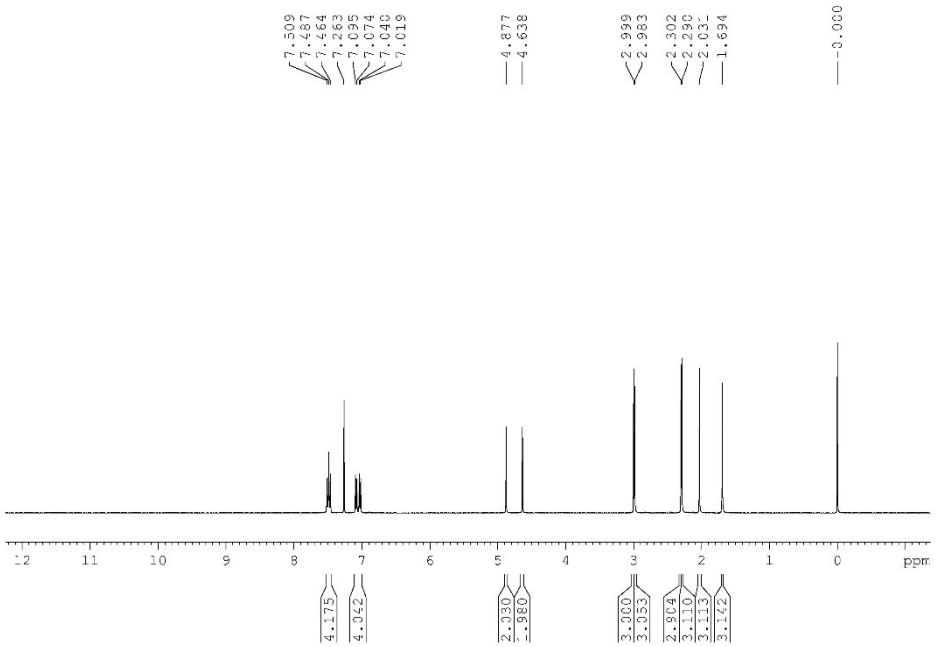
^{1}H NMR spectrum of compound **3c**



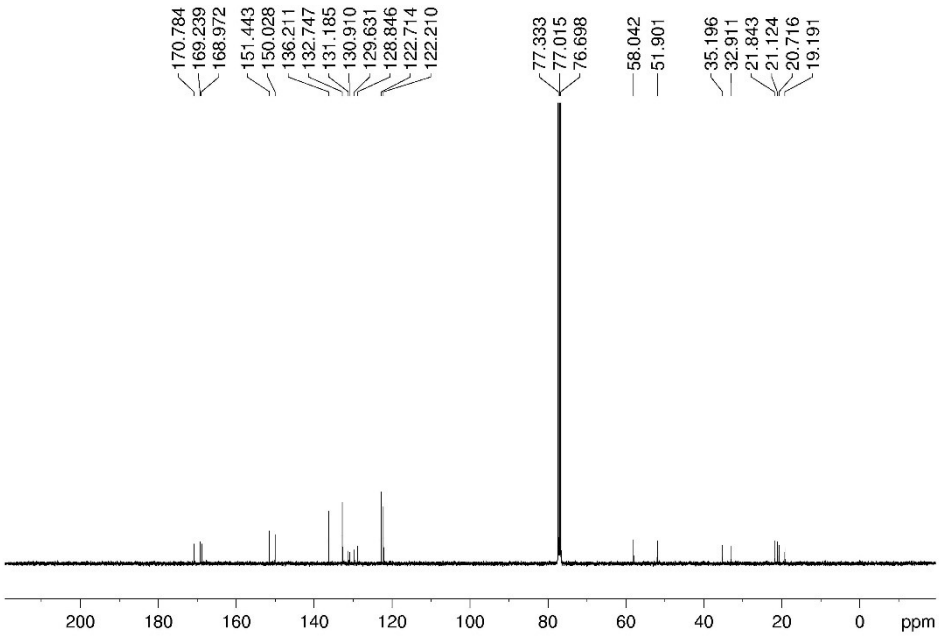
^{13}C NMR spectrum of compound **3c**



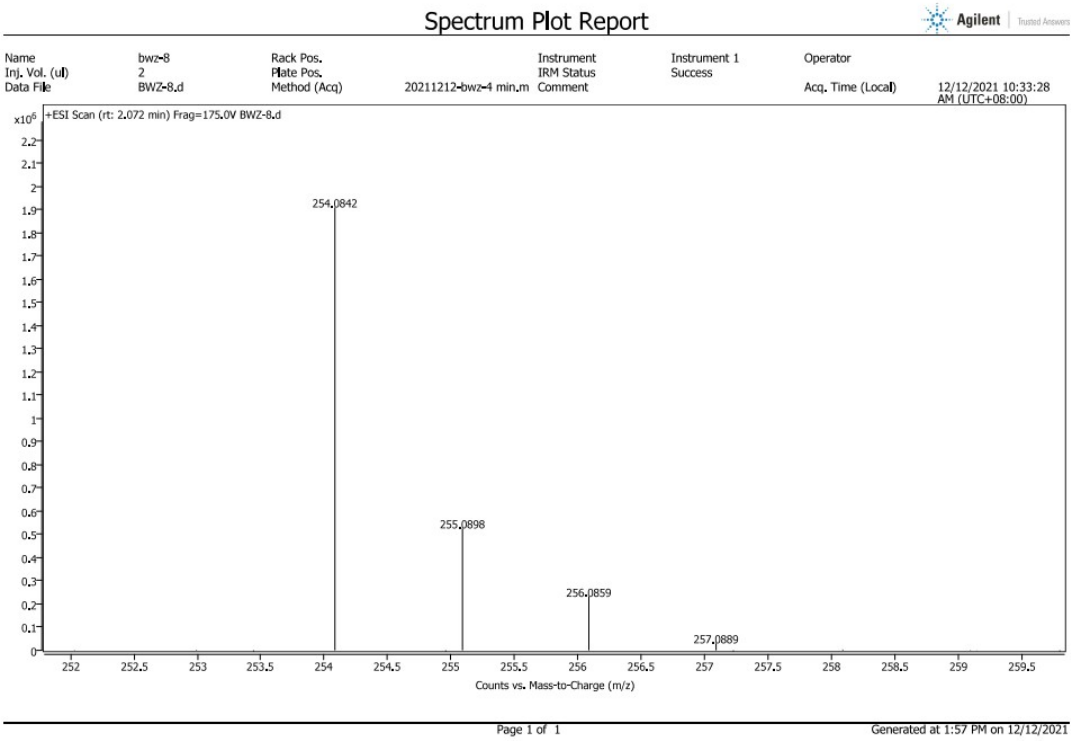
HRMS spectrum of compound **3c**



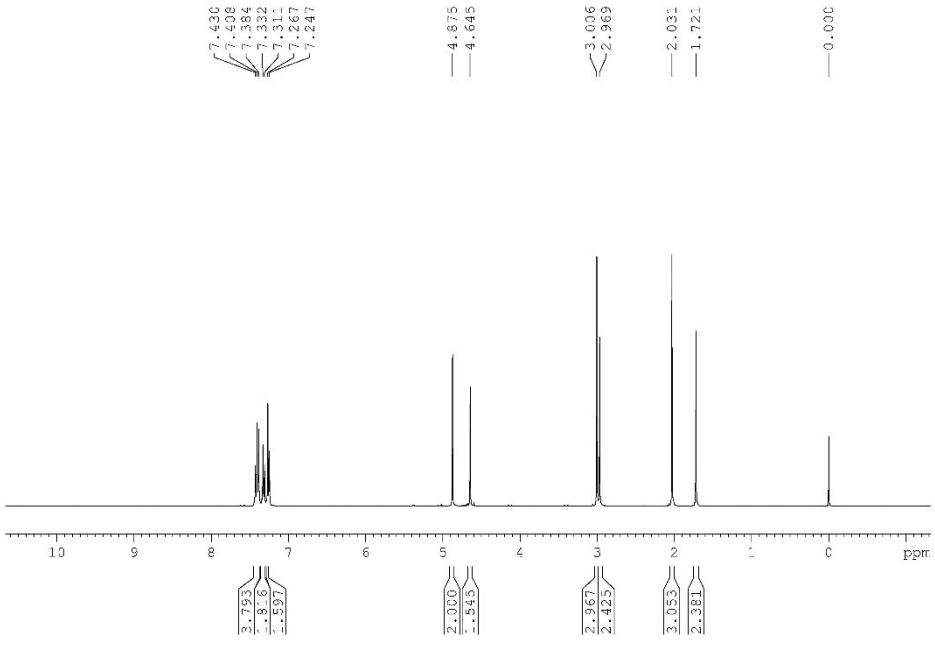
^{1}H NMR spectrum of compound **3d**



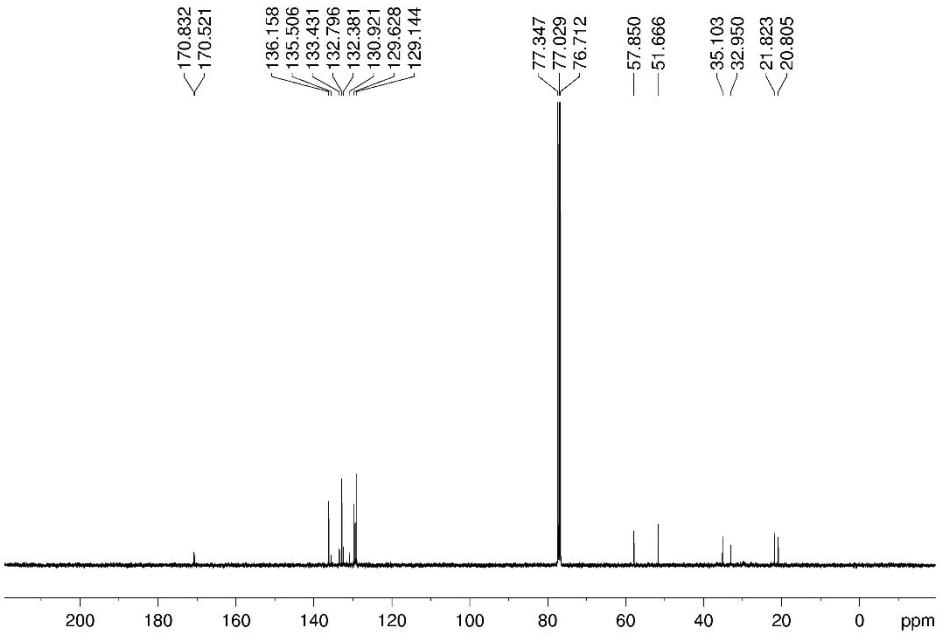
^{13}C NMR spectrum of compound **3d**



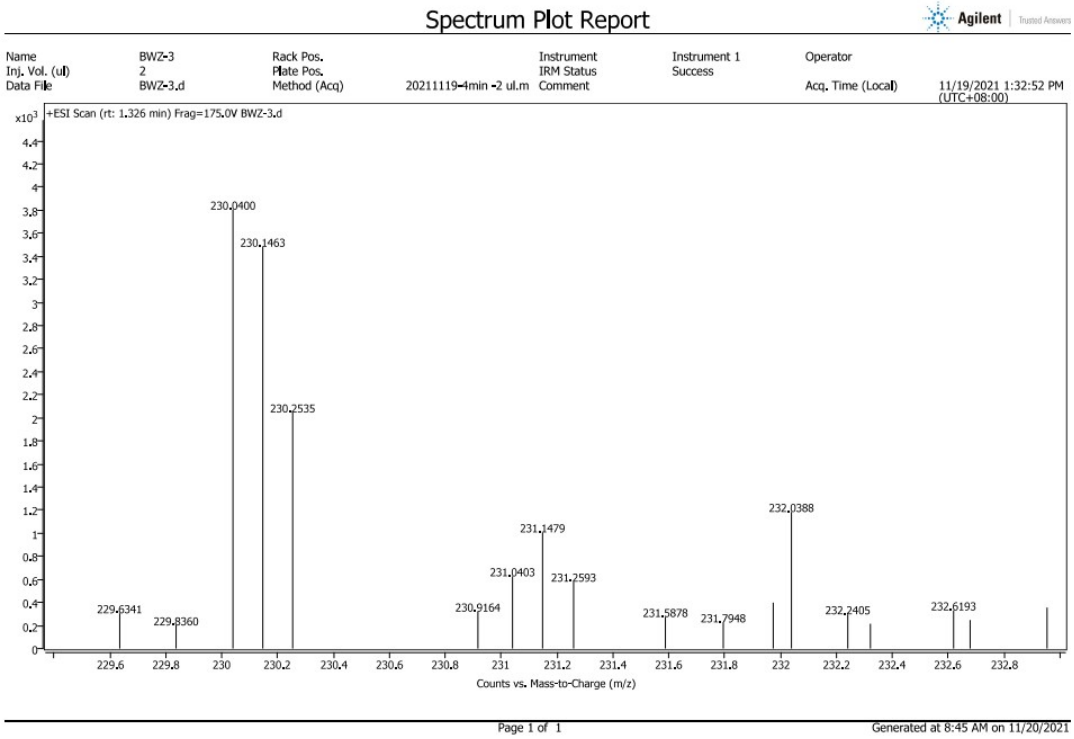
HRMS spectrum of compound **3d**



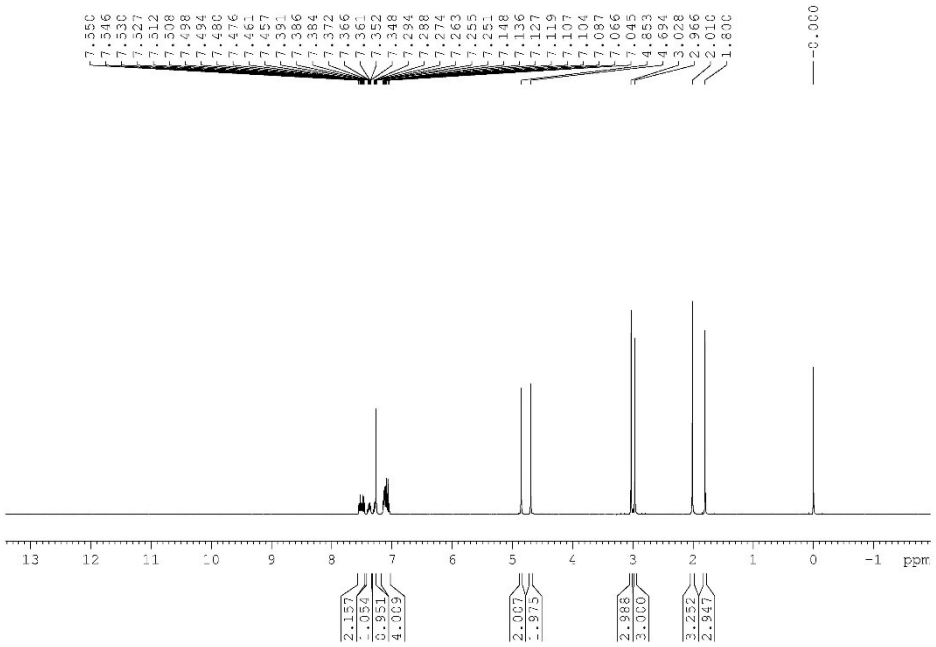
^{1}H NMR spectrum of compound **3e**



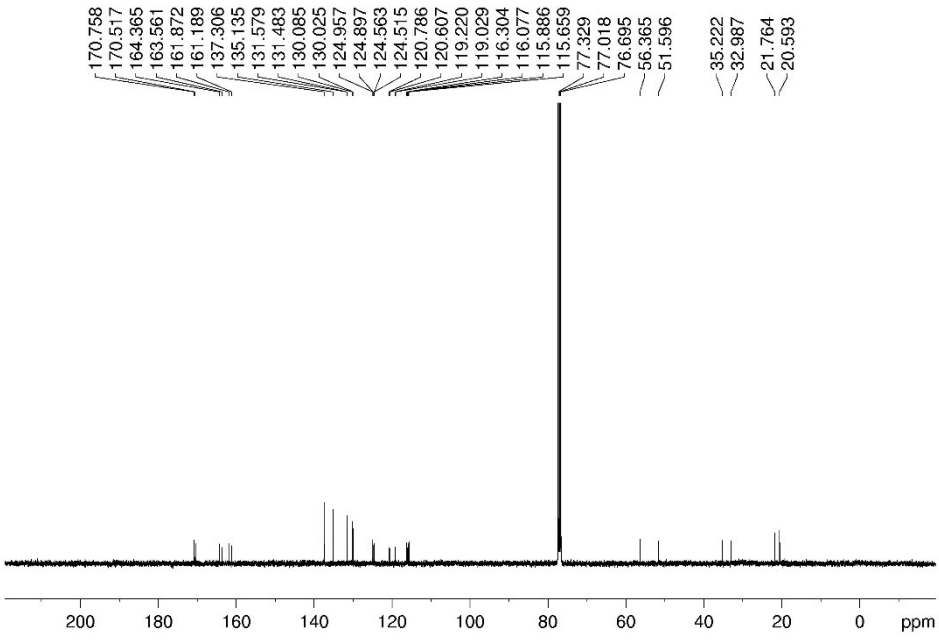
^{13}C NMR spectrum of compound **3e**



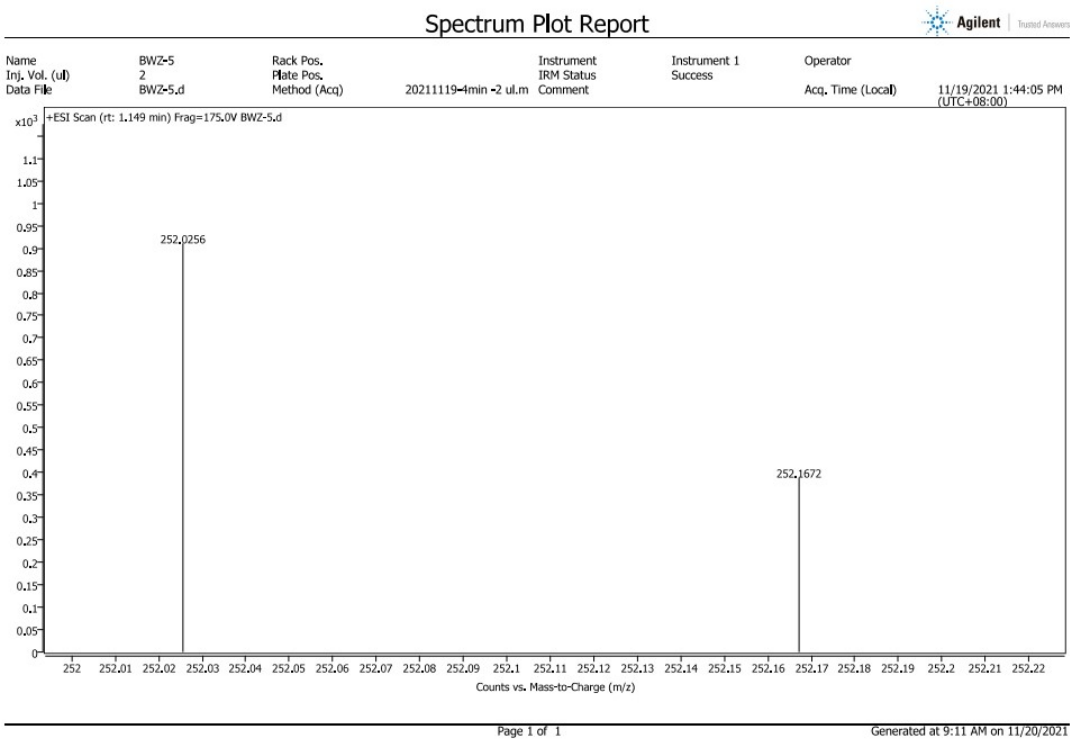
HRMS spectrum of compound **3e**



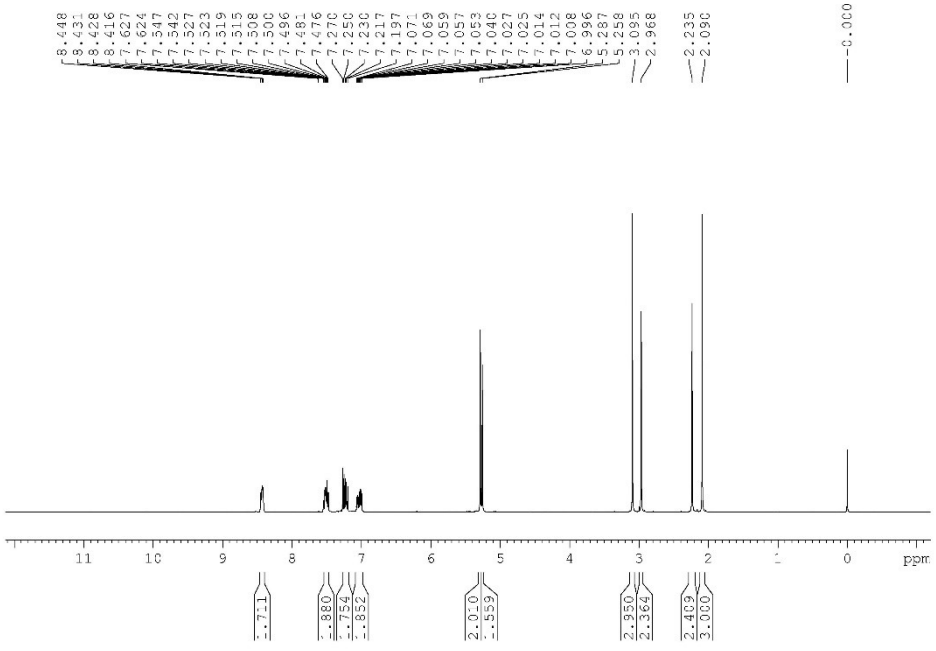
^{1}H NMR spectrum of compound **3f**



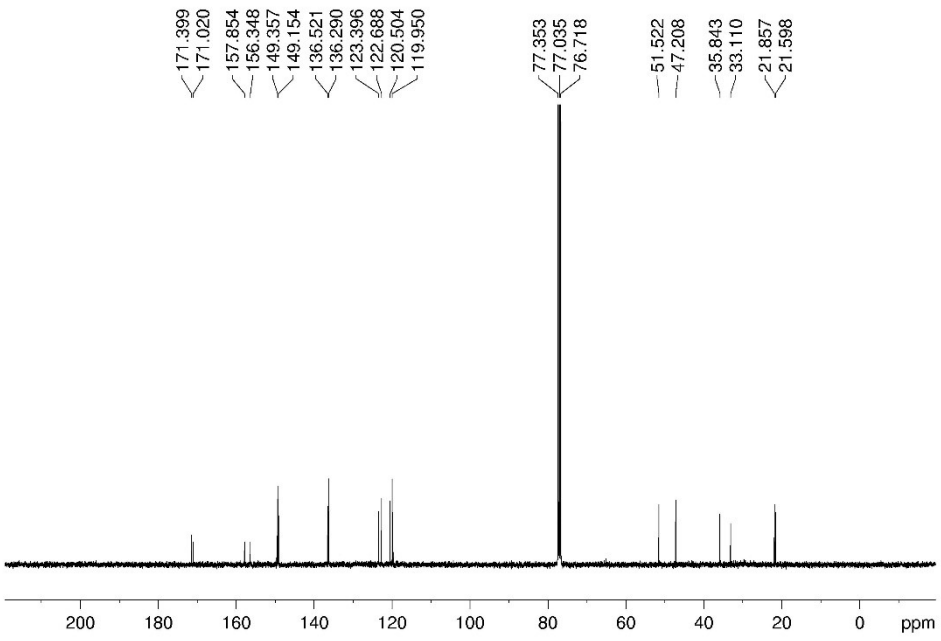
^{13}C NMR spectrum of compound **3f**



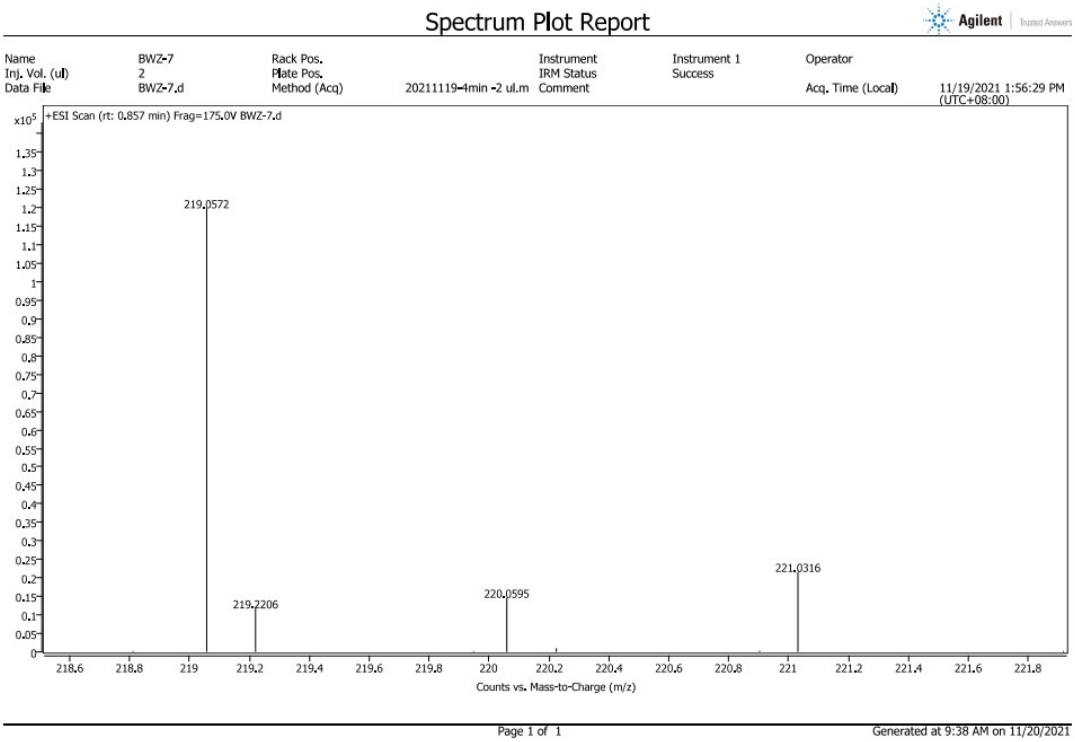
HRMS spectrum of compound **3f**



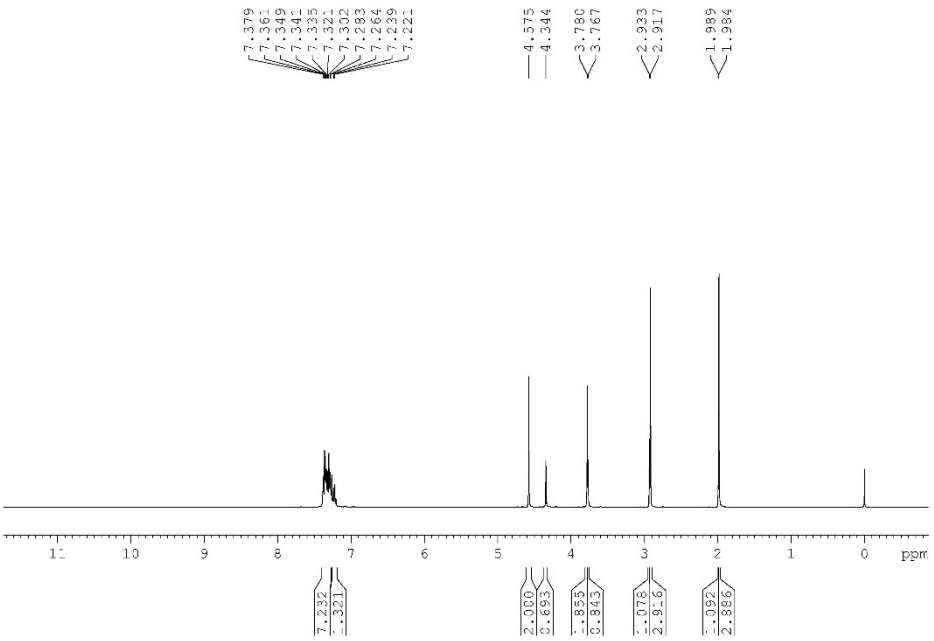
^{1}H NMR spectrum of compound **3g**



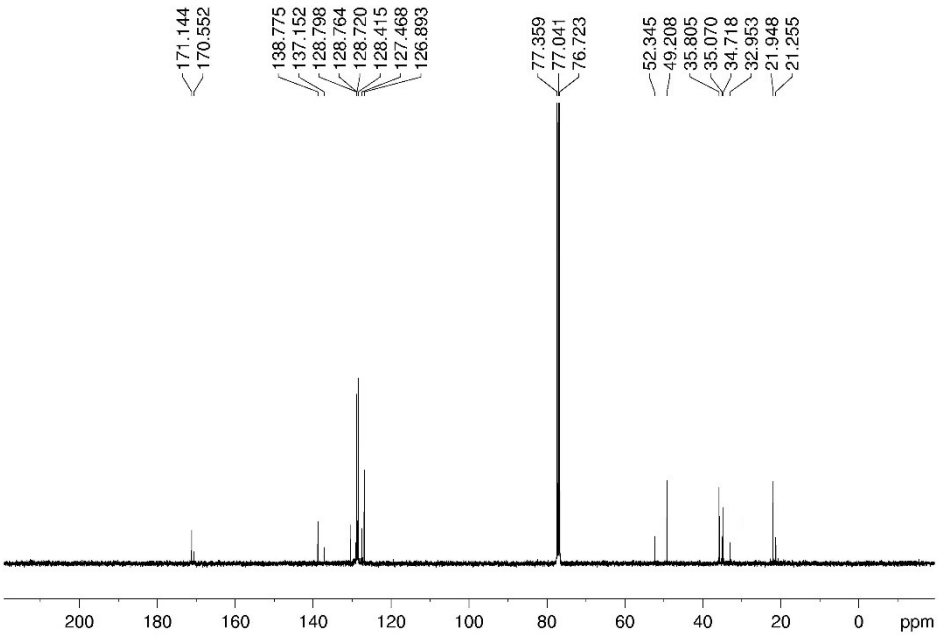
^{13}C NMR spectrum of compound **3g**



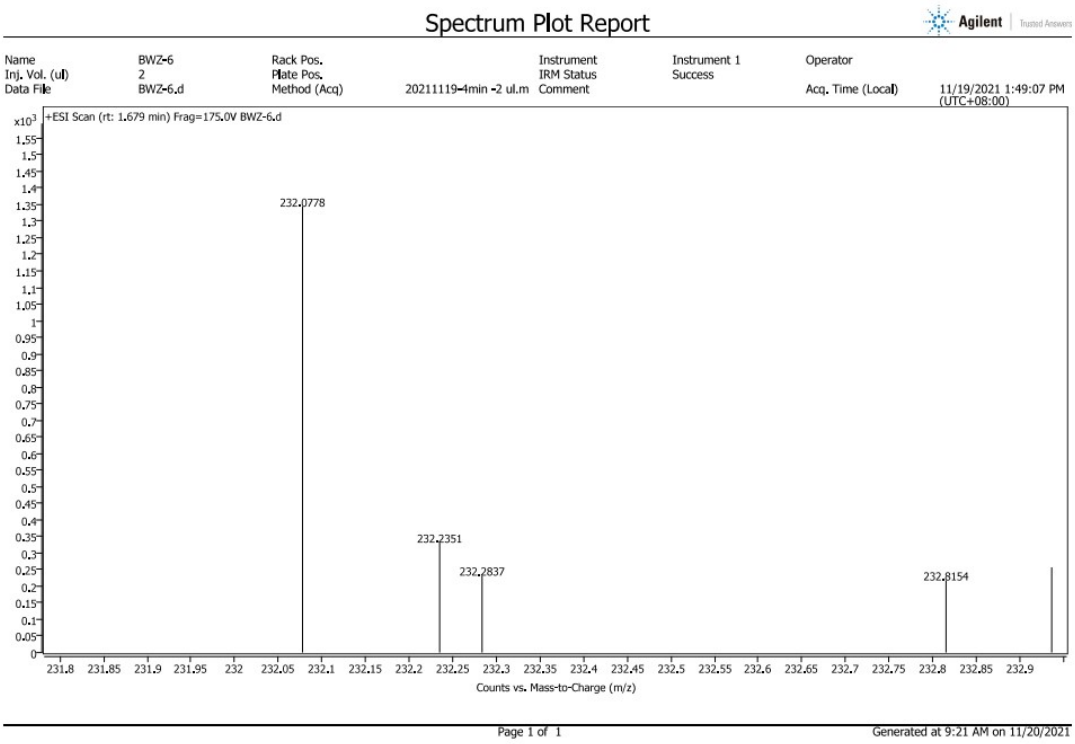
HRMS spectrum of compound **3g**



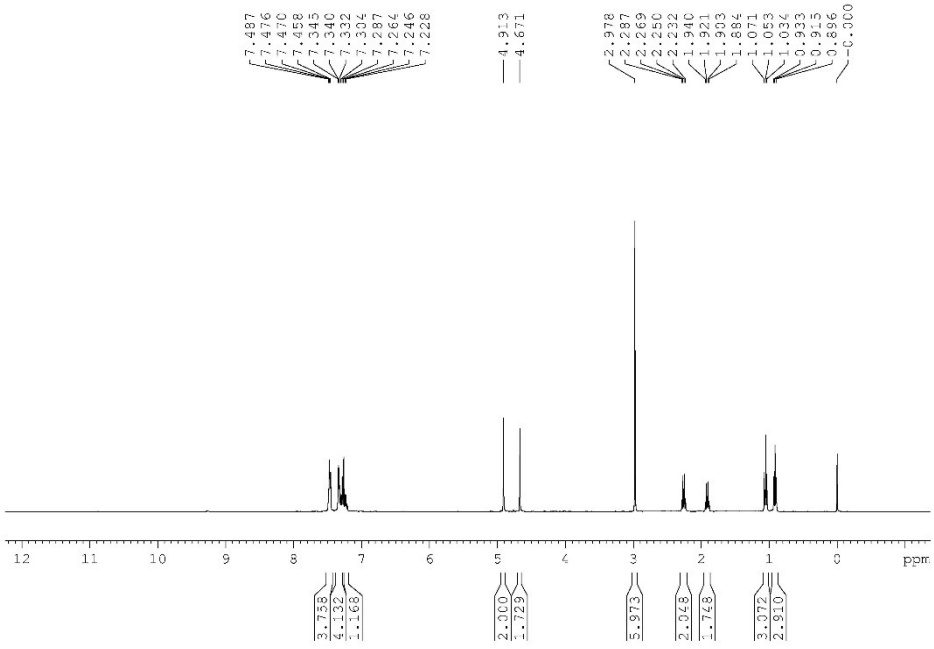
^{1}H NMR spectrum of compound **3h**



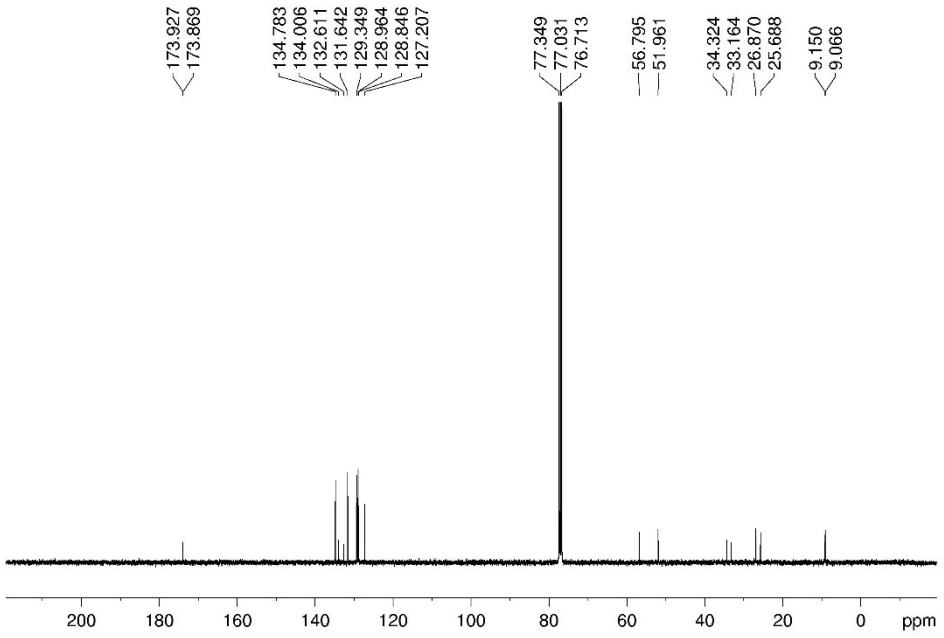
^{13}C NMR spectrum of compound **3h**



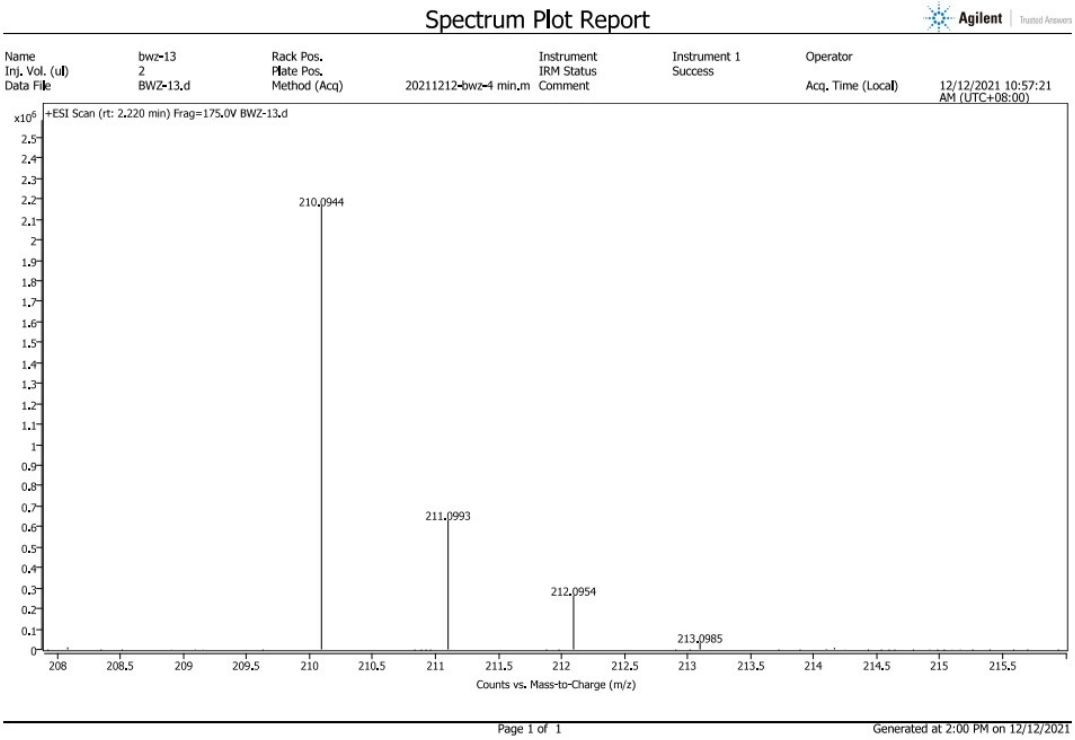
HRMS spectrum of compound **3h**



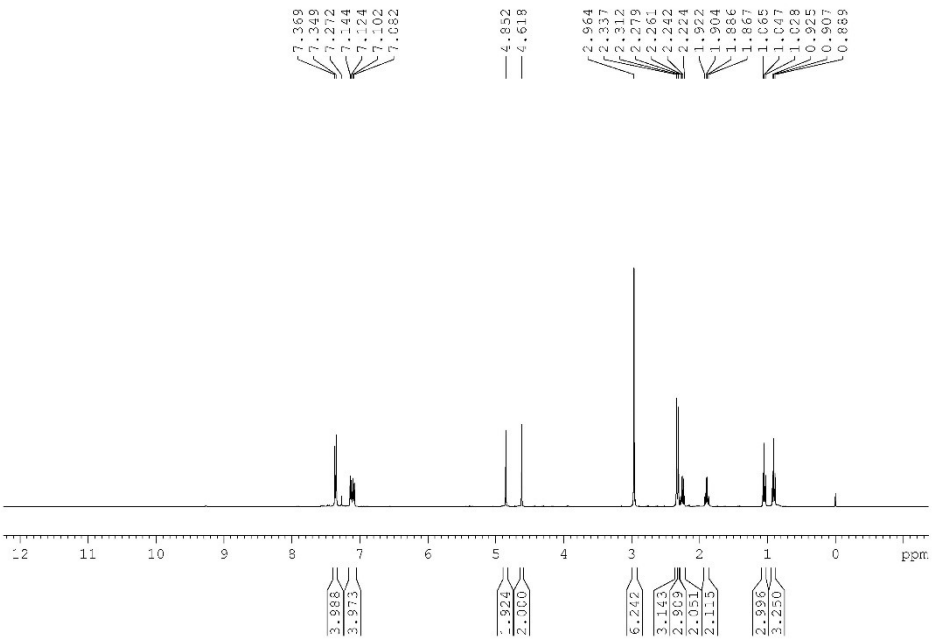
^{1}H NMR spectrum of compound **3k**



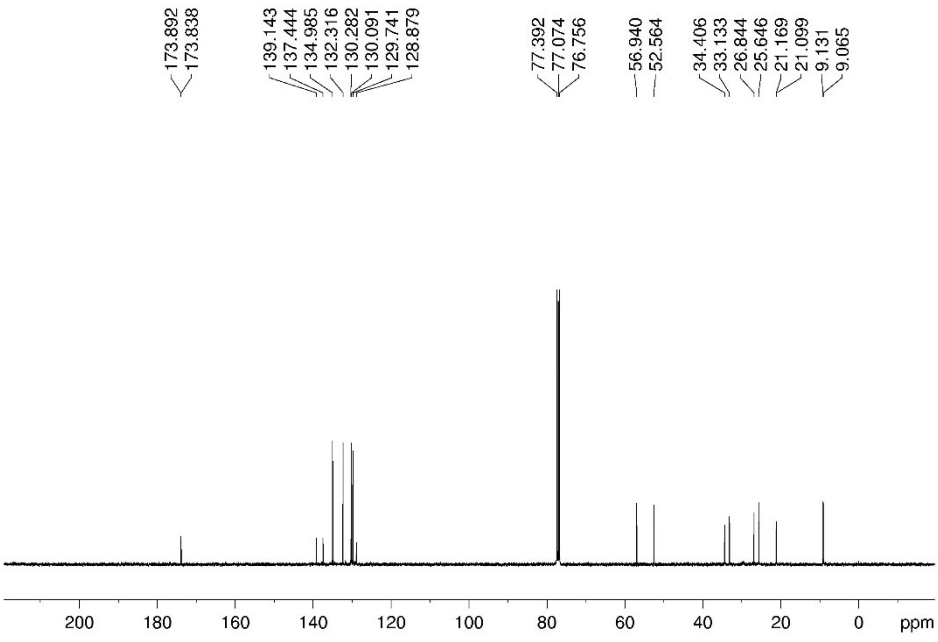
^{13}C NMR spectrum of compound **3k**



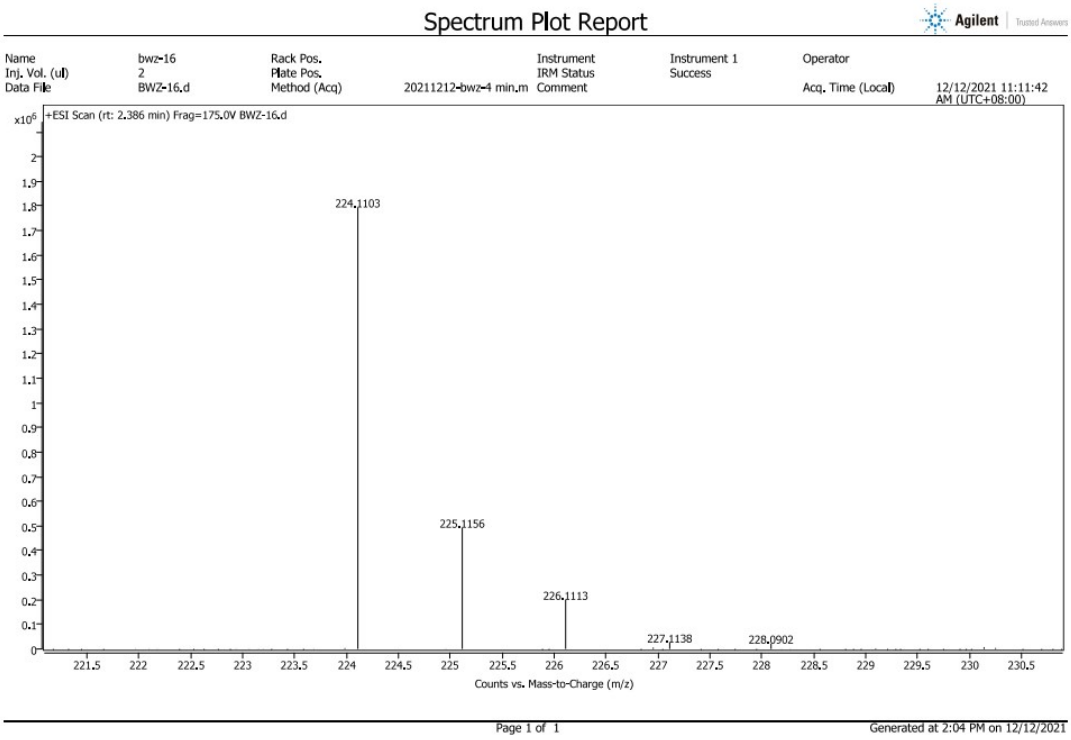
HRMS spectrum of compound **3k**



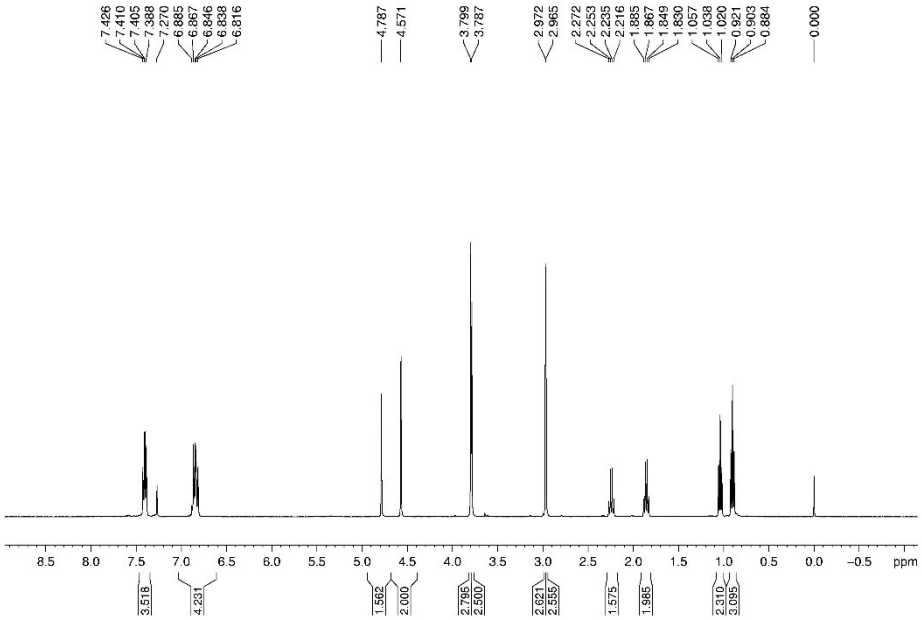
^{1}H NMR spectrum of compound **3l**



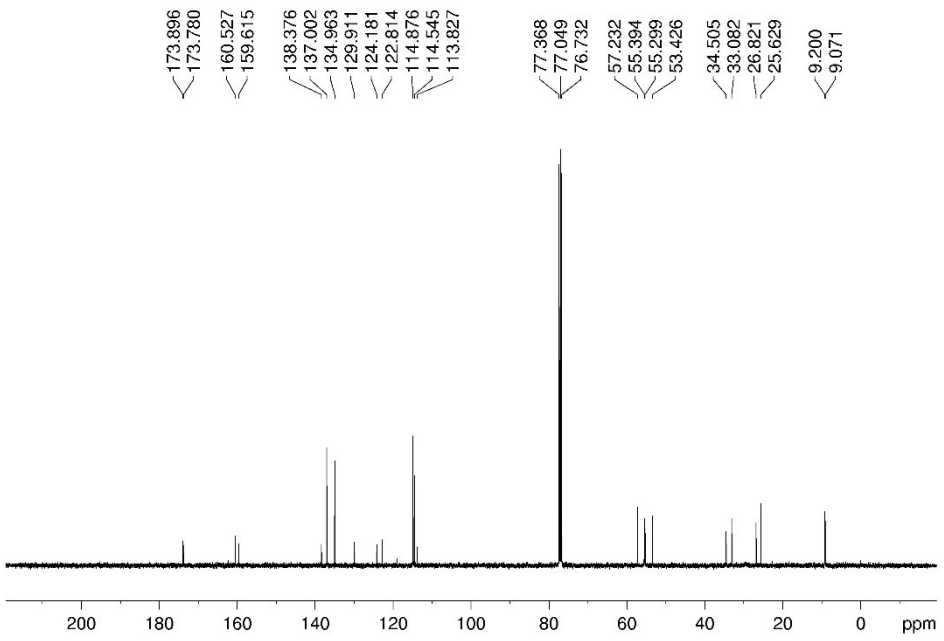
^{13}C NMR spectrum of compound **3l**



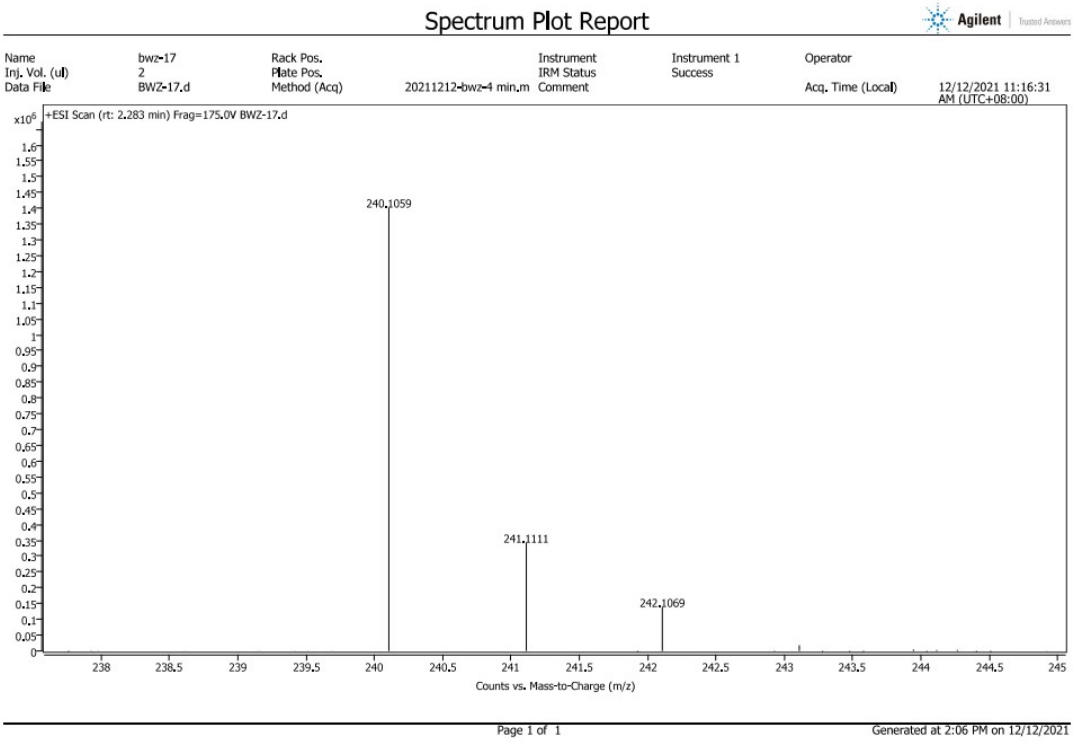
HRMS spectrum of compound **3l**



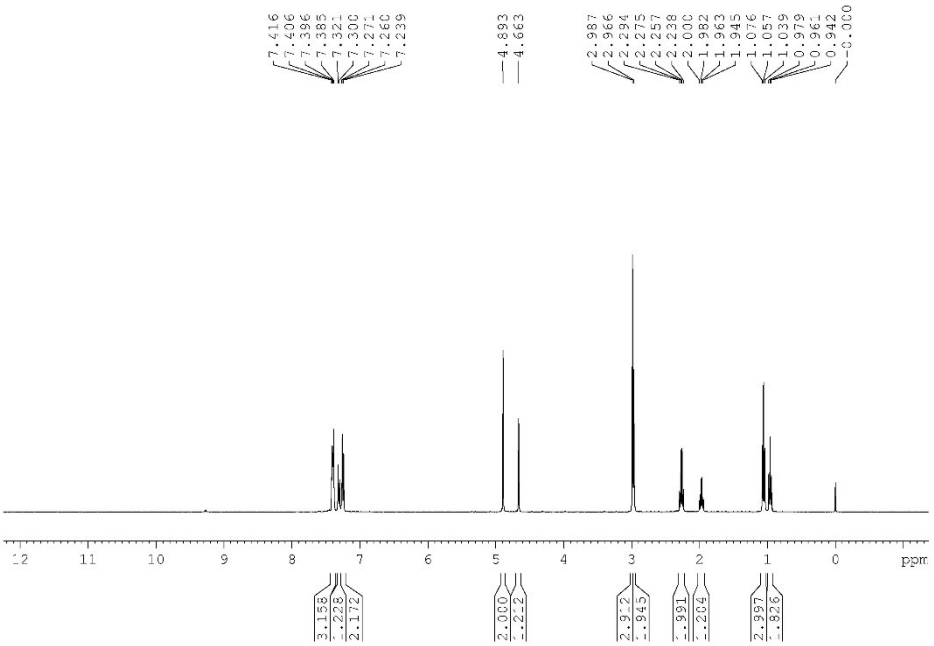
^{1}H NMR spectrum of compound **3m**



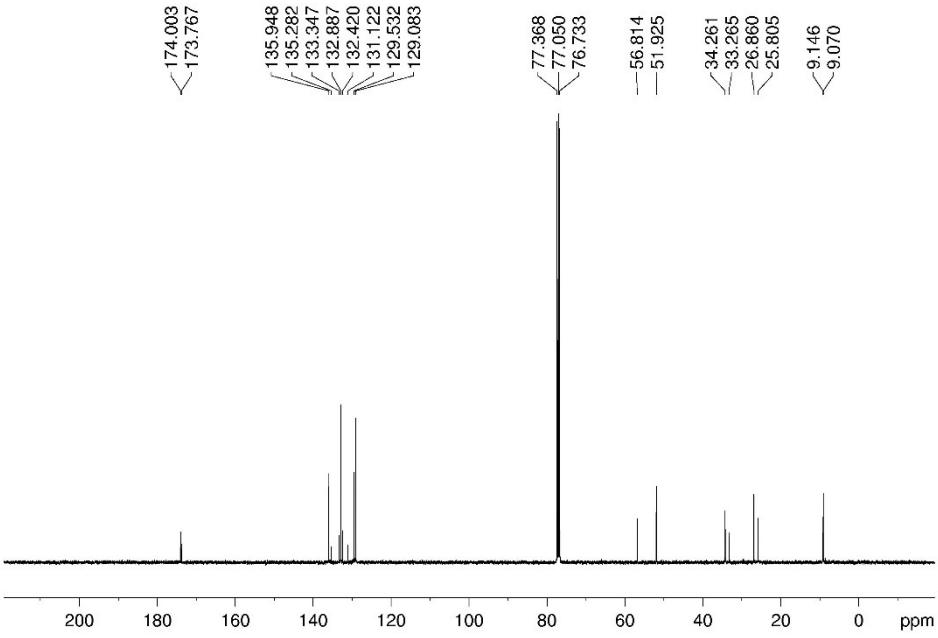
^{13}C NMR spectrum of compound **3m**



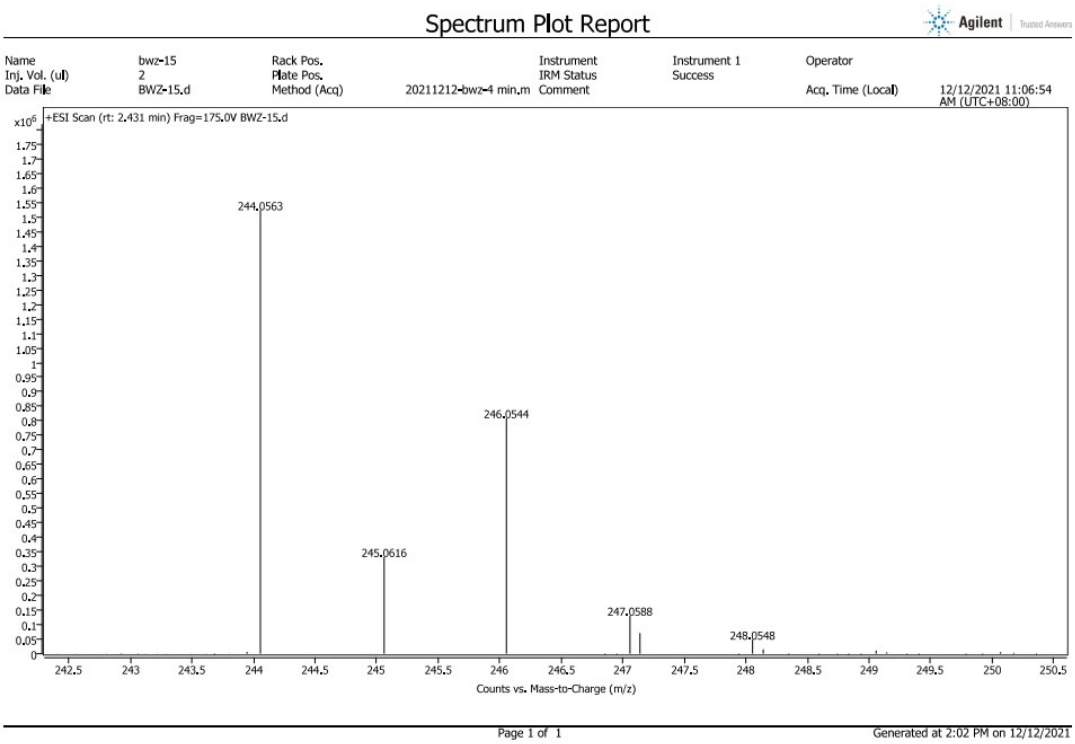
HRMS spectrum of compound **3m**



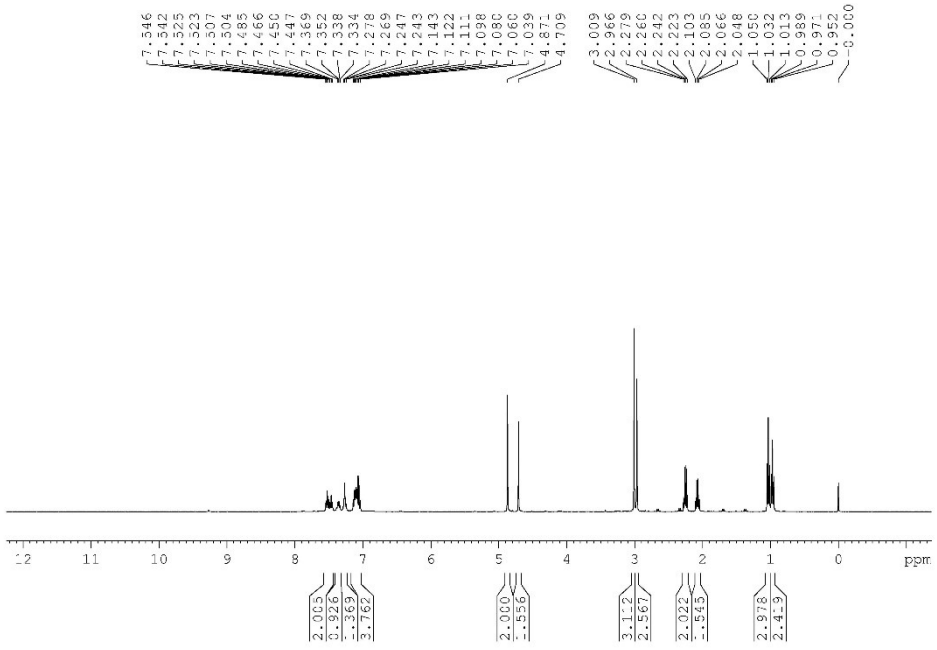
^{1}H NMR spectrum of compound **3n**



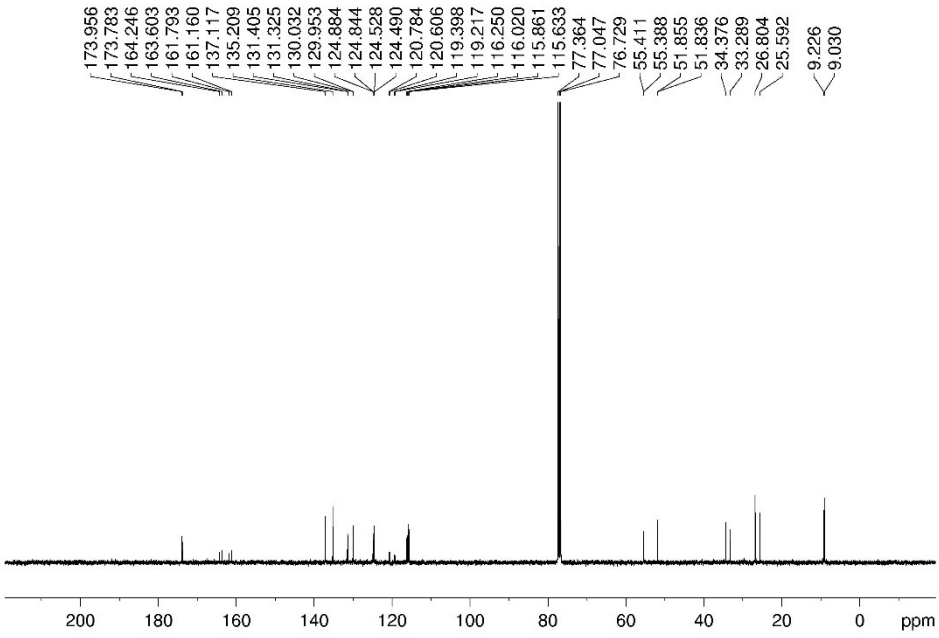
^{13}C NMR spectrum of compound **3n**



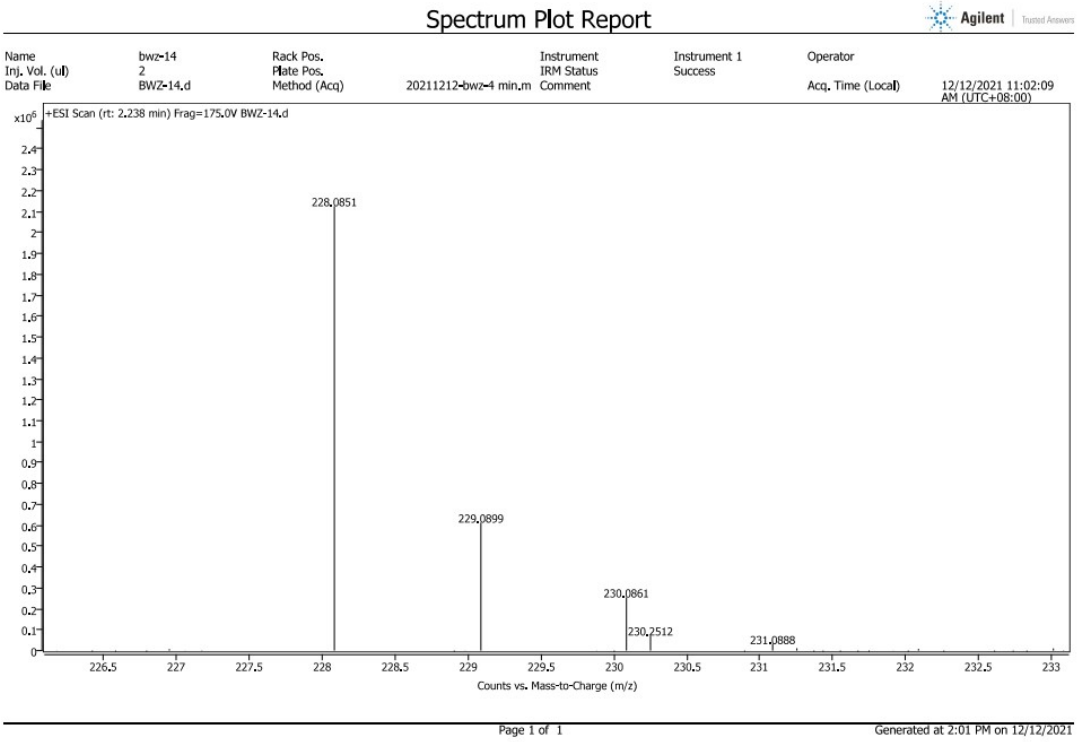
HRMS spectrum of compound **3n**



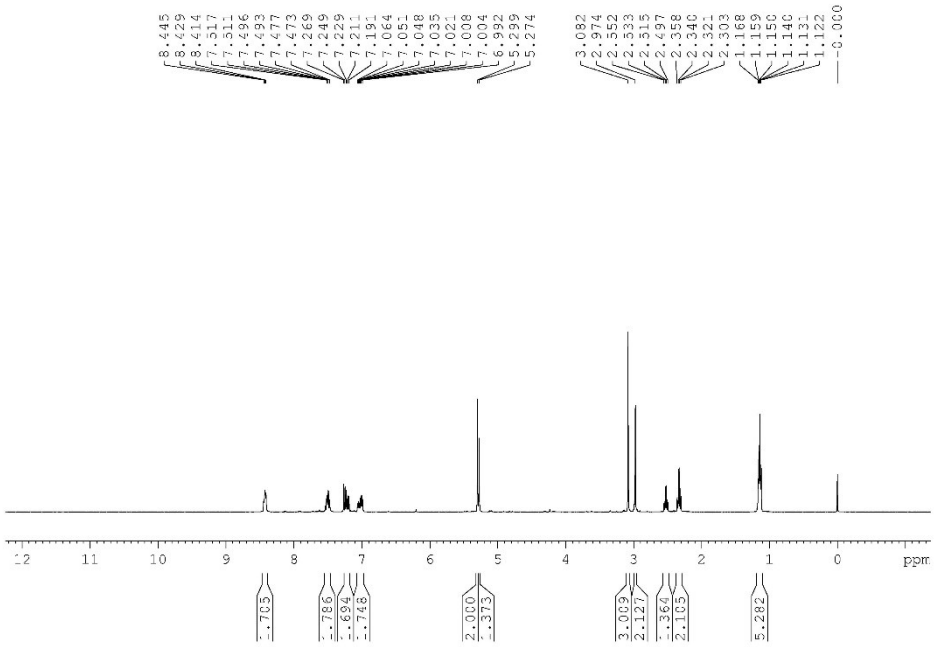
^{1}H NMR spectrum of compound **3o**



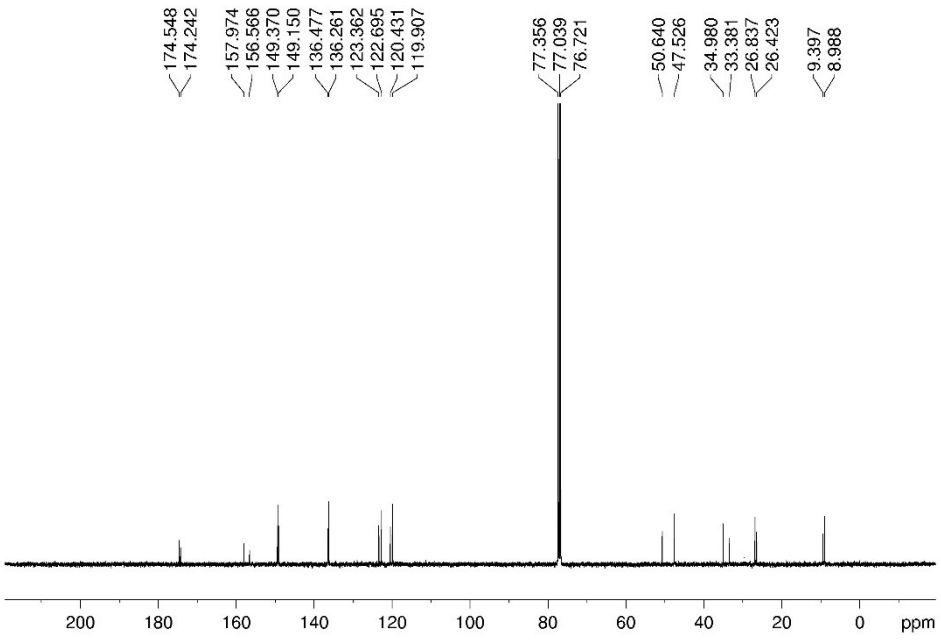
^{13}C NMR spectrum of compound **3o**



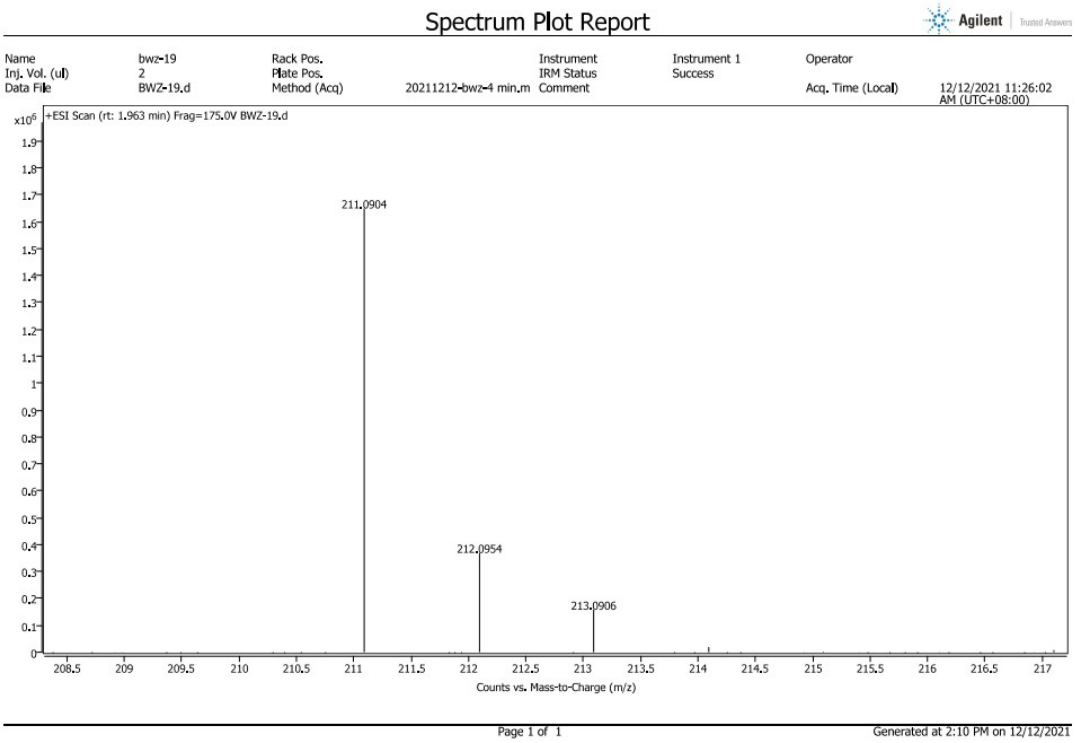
HRMS spectrum of compound **3o**



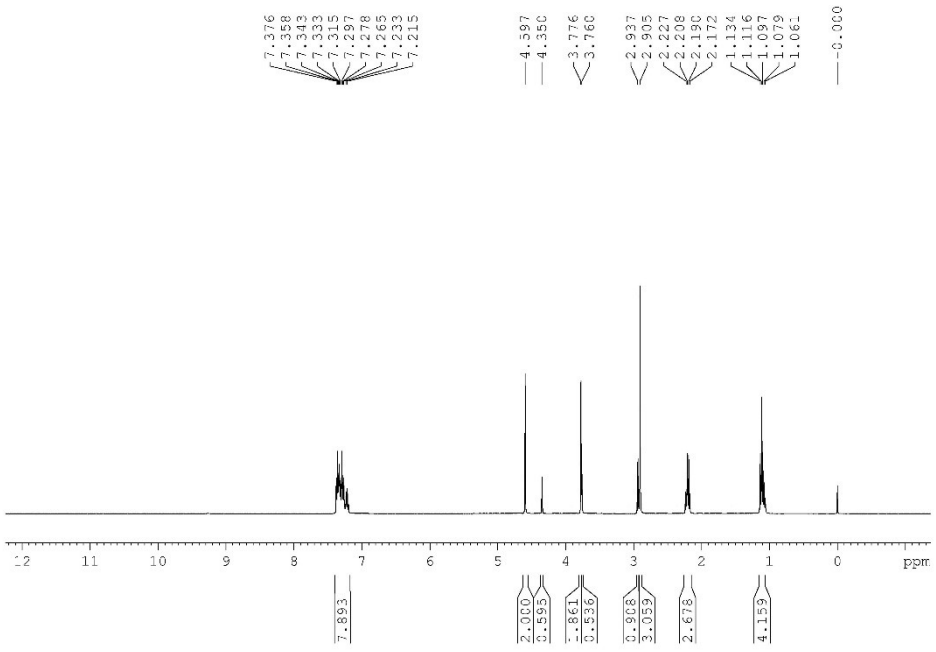
^{1}H NMR spectrum of compound **3p**



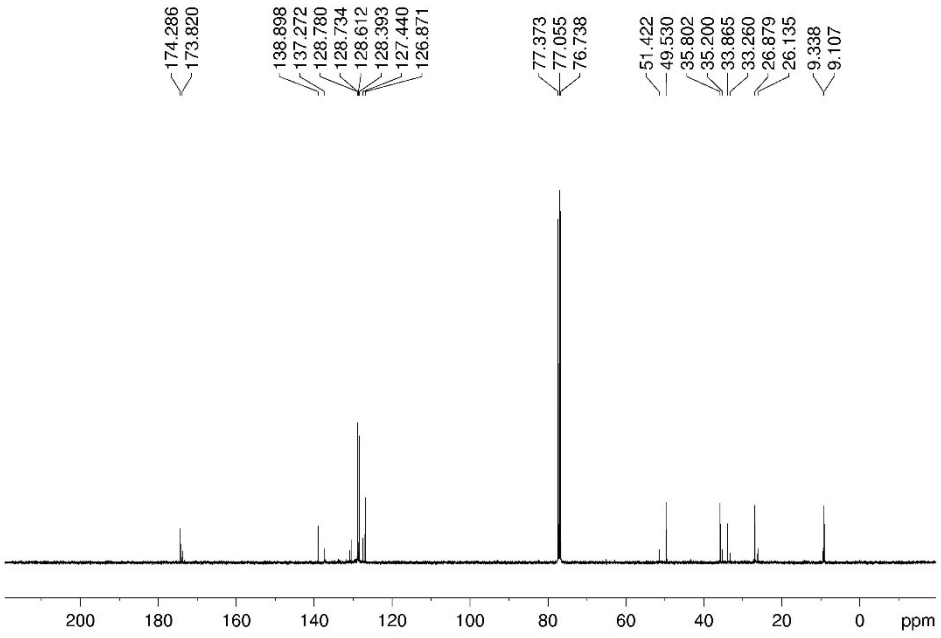
^{13}C NMR spectrum of compound **3p**



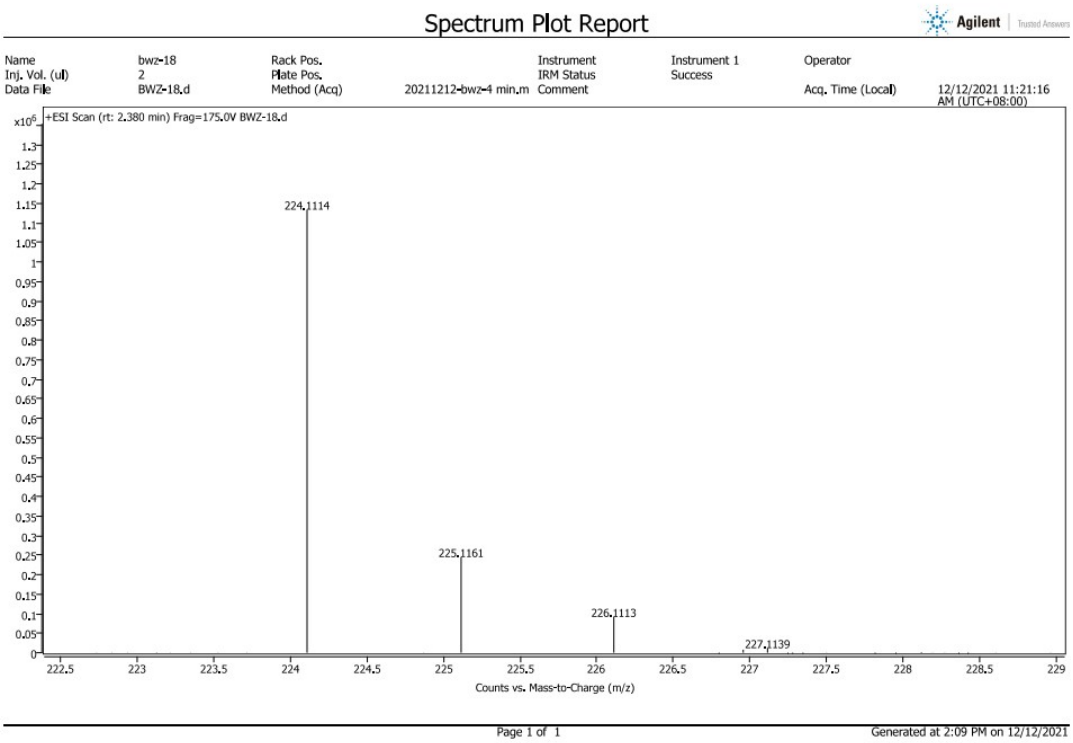
HRMS spectrum of compound **3p**



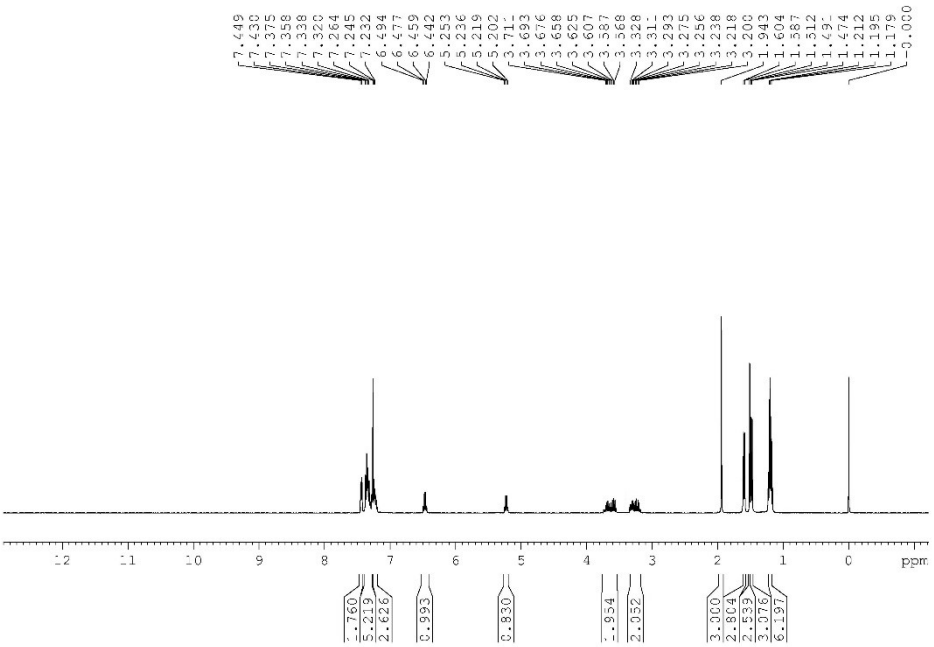
^{1}H NMR spectrum of compound **3q**



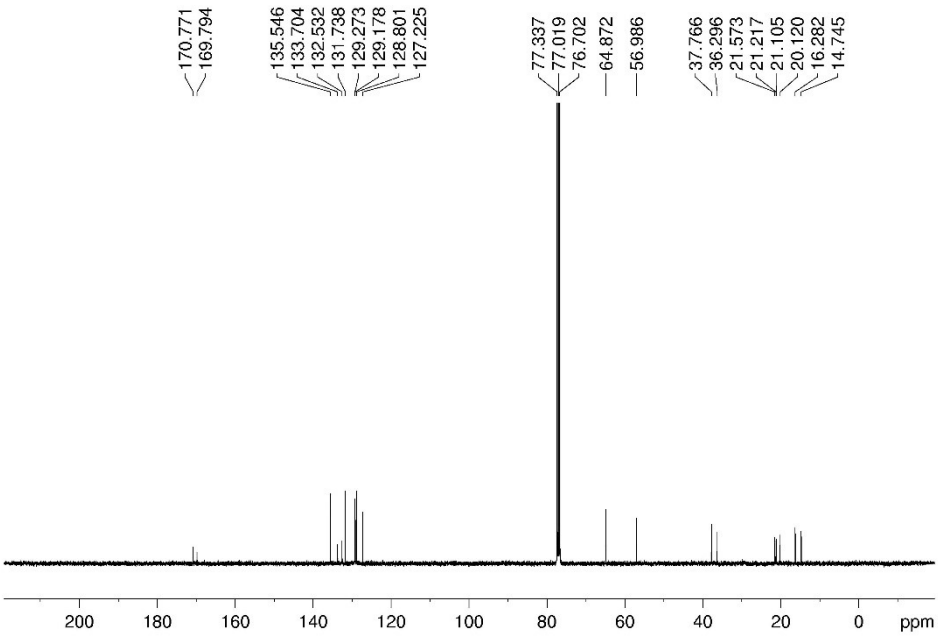
^{13}C NMR spectrum of compound **3q**



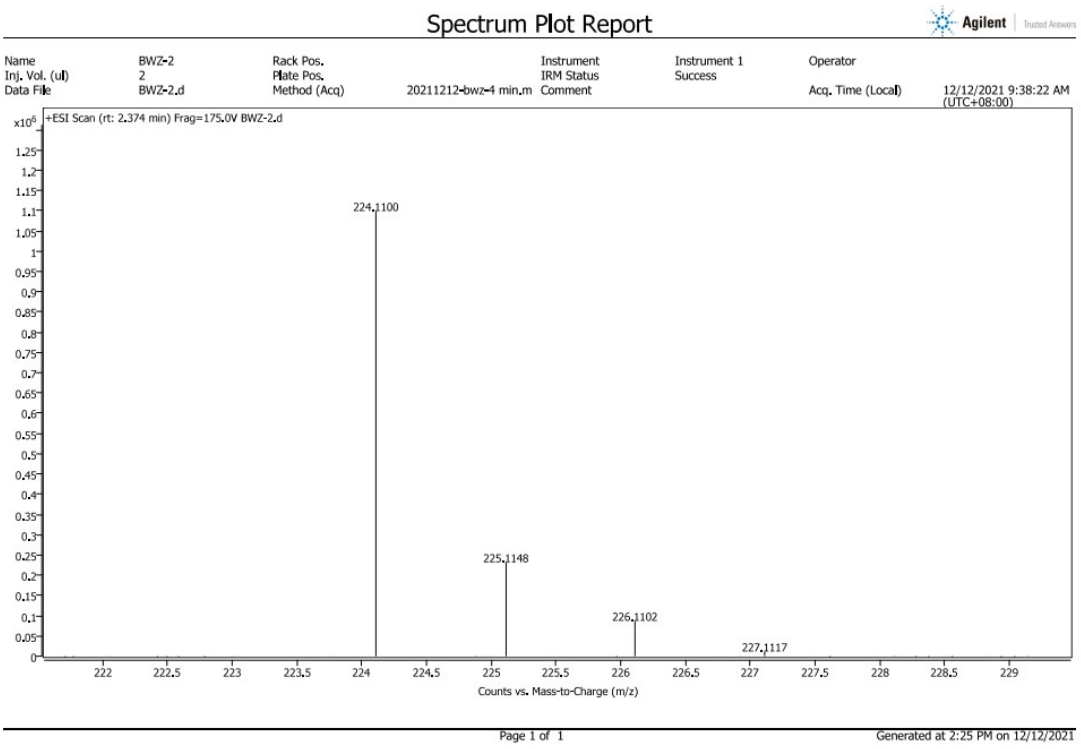
HRMS spectrum of compound **3q**



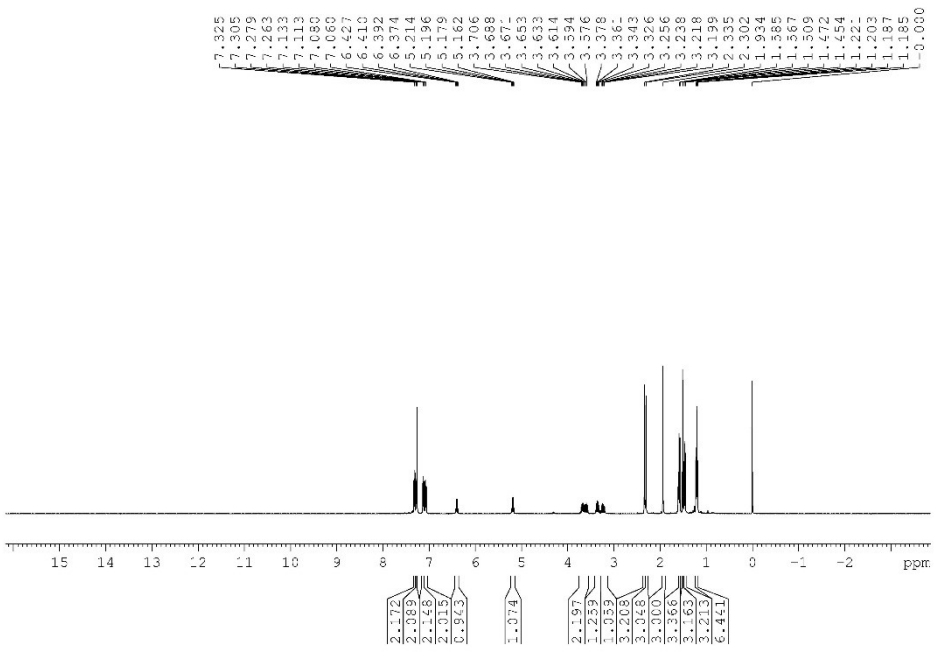
^{1}H NMR spectrum of compound **3r**



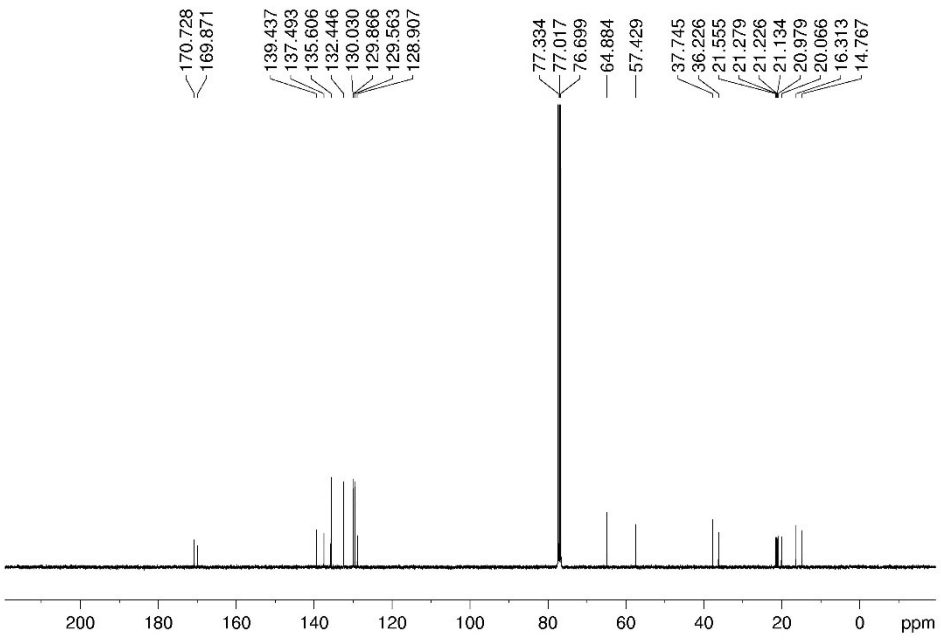
^{13}C NMR spectrum of compound **3r**



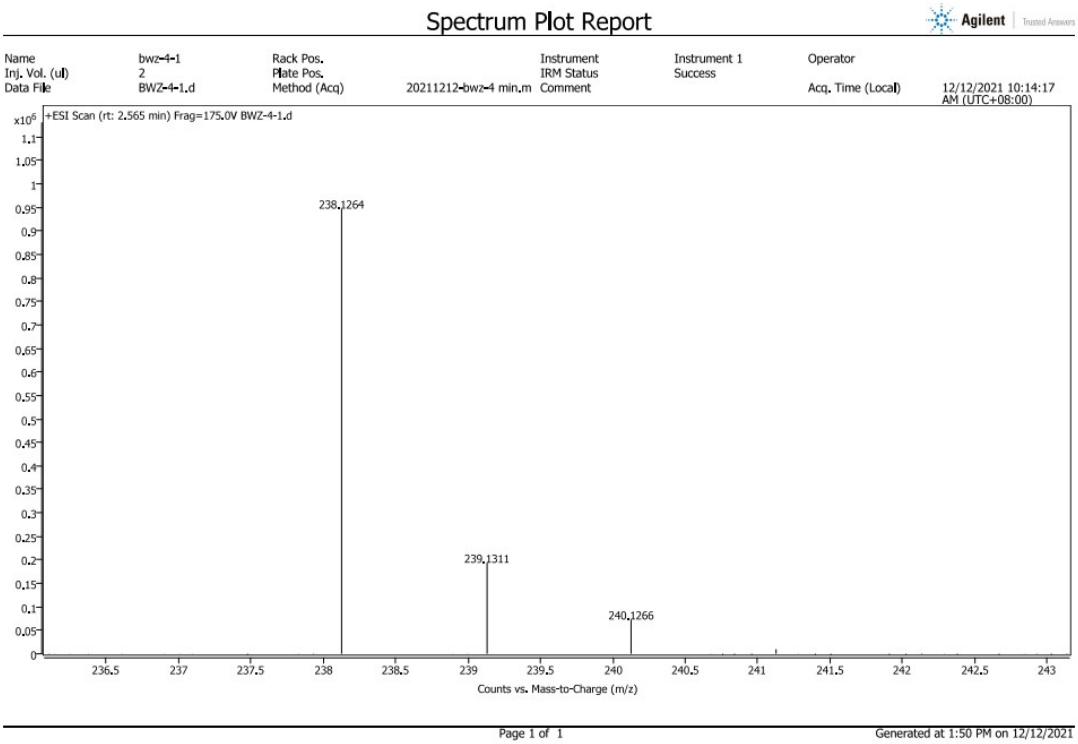
HRMS spectrum of compound **3r**



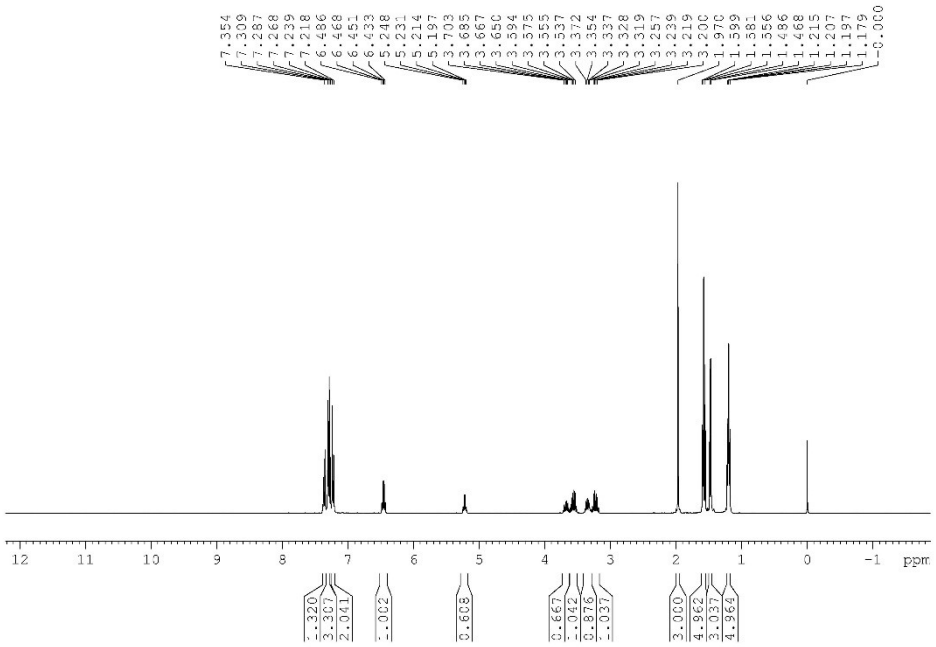
^{1}H NMR spectrum of compound **3s**



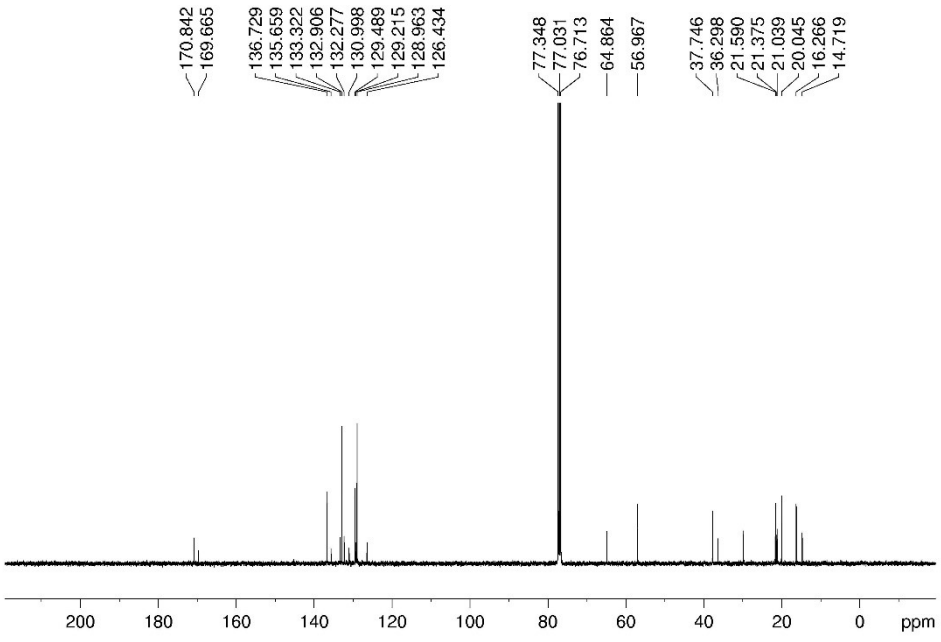
^{13}C NMR spectrum of compound **3s**



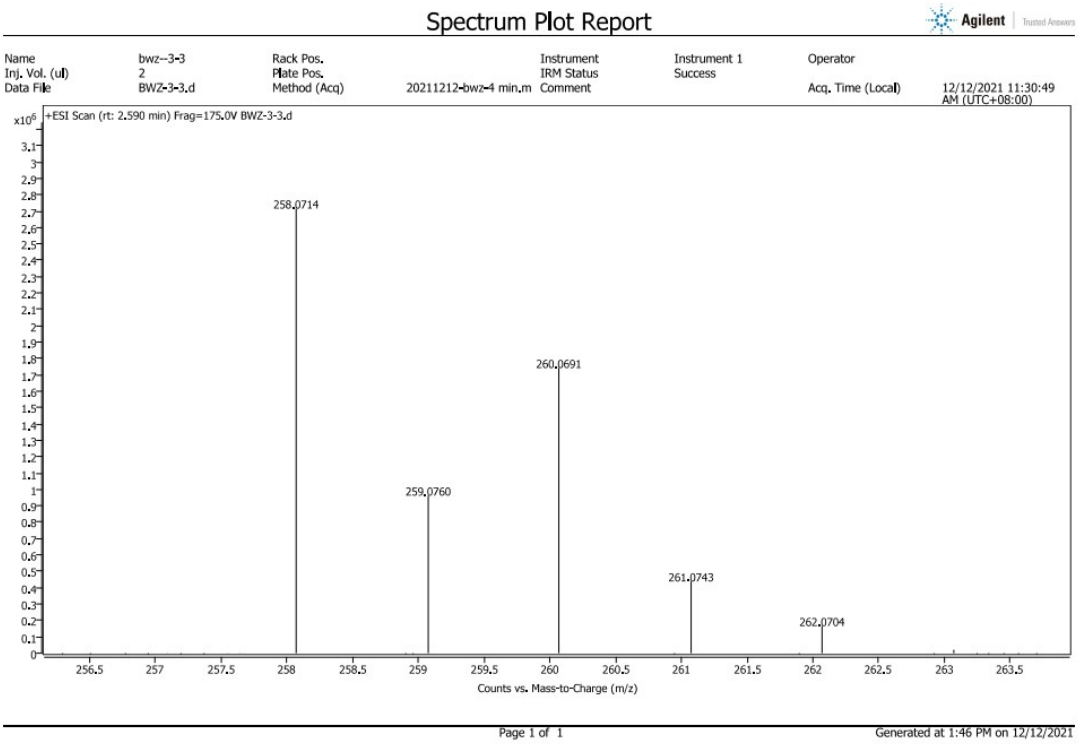
HRMS spectrum of compound **3s**



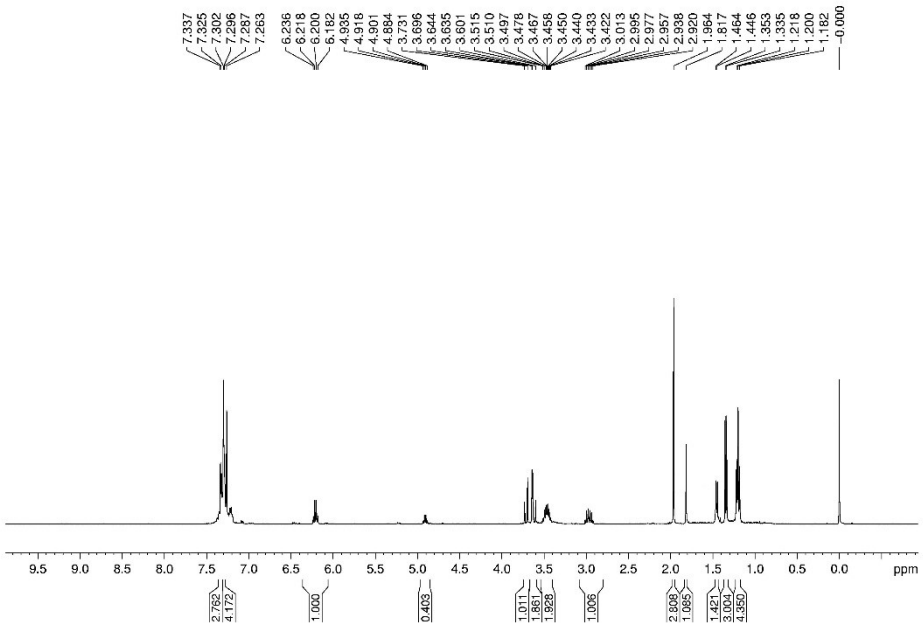
^{1}H NMR spectrum of compound **3t**



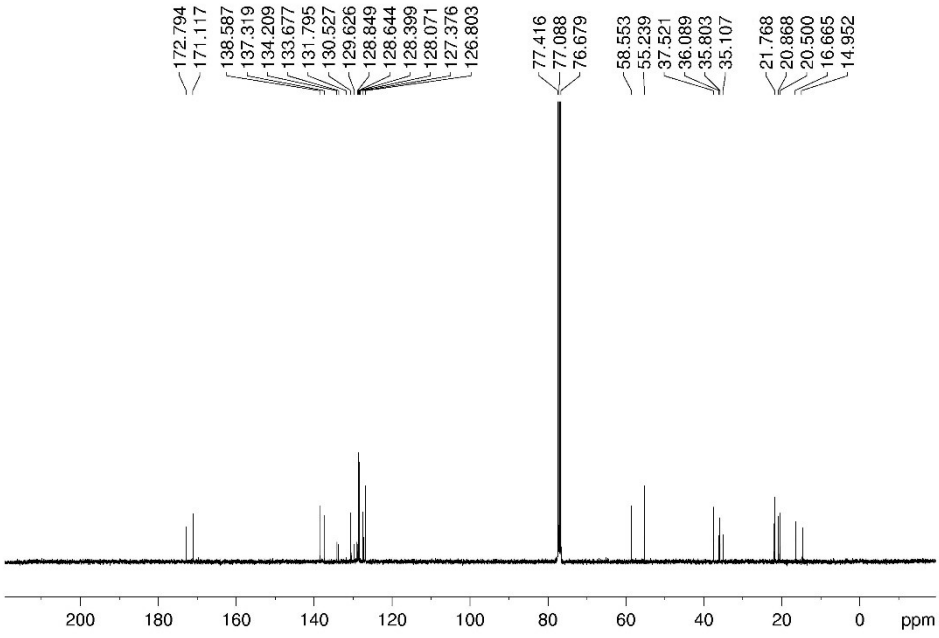
^{13}C NMR spectrum of compound **3t**



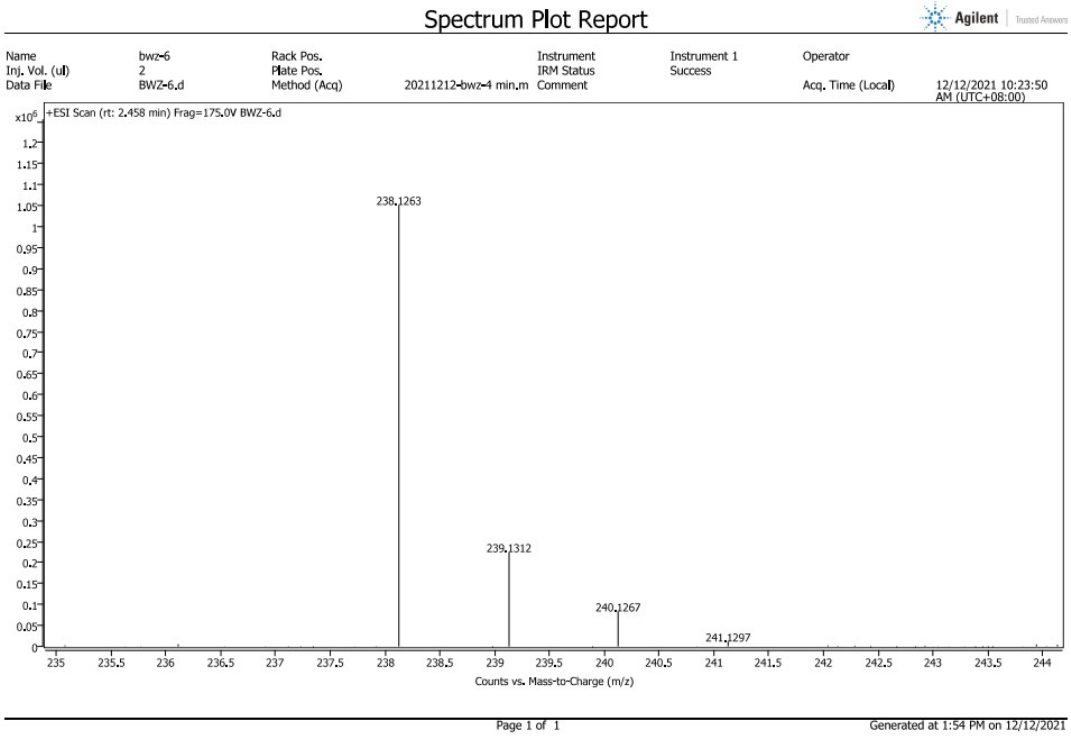
HRMS spectrum of compound **3t**



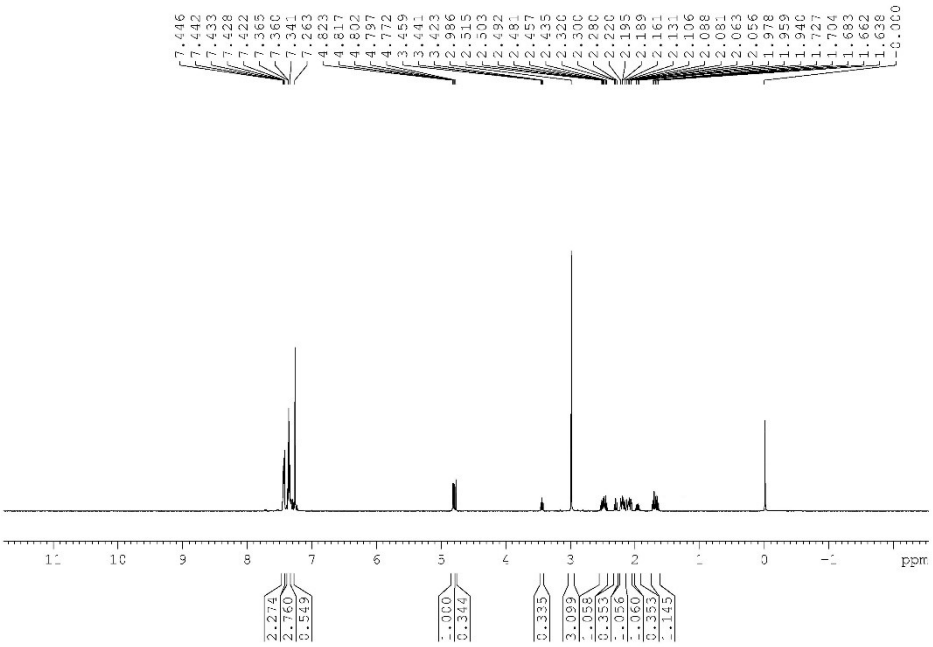
^{1}H NMR spectrum of compound **3u**



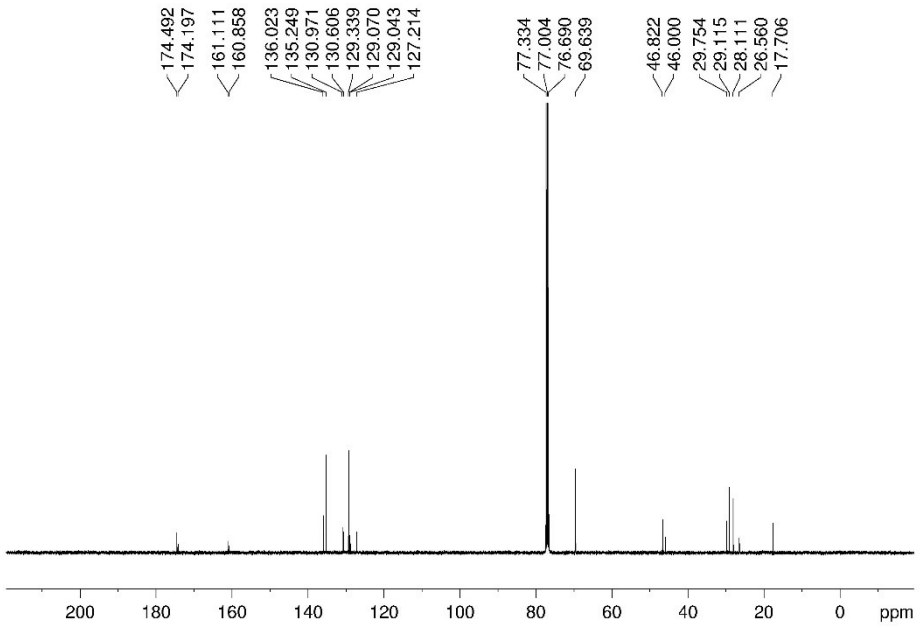
^{13}C NMR spectrum of compound **3u**



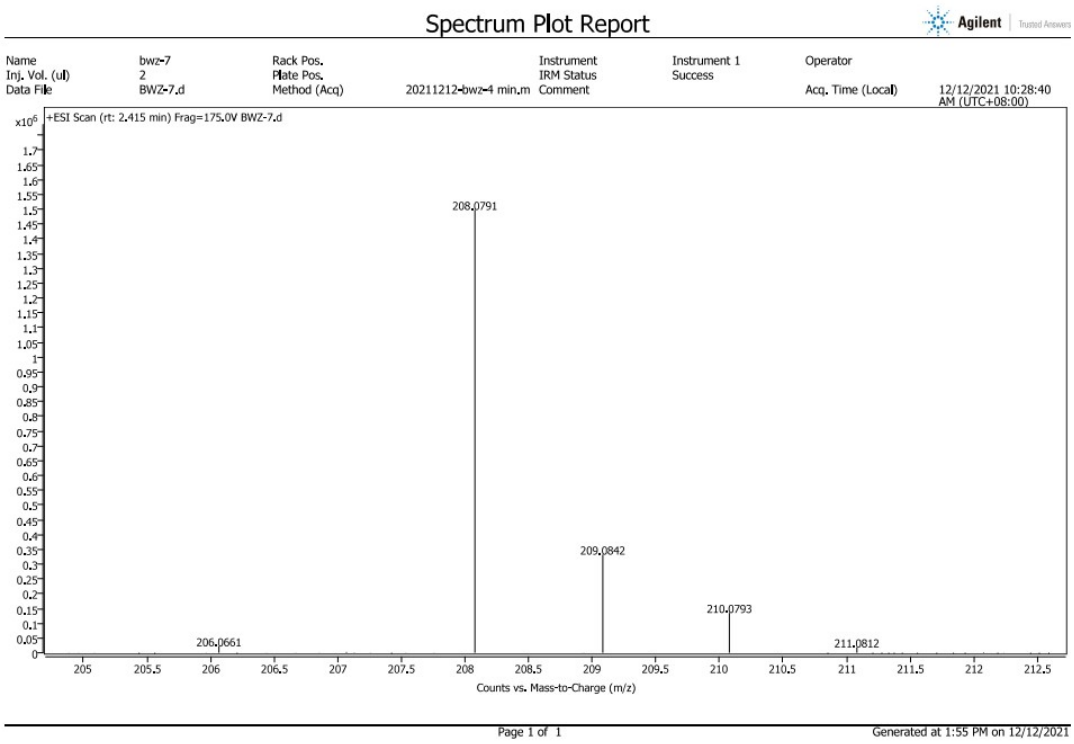
HRMS spectrum of compound **3u**



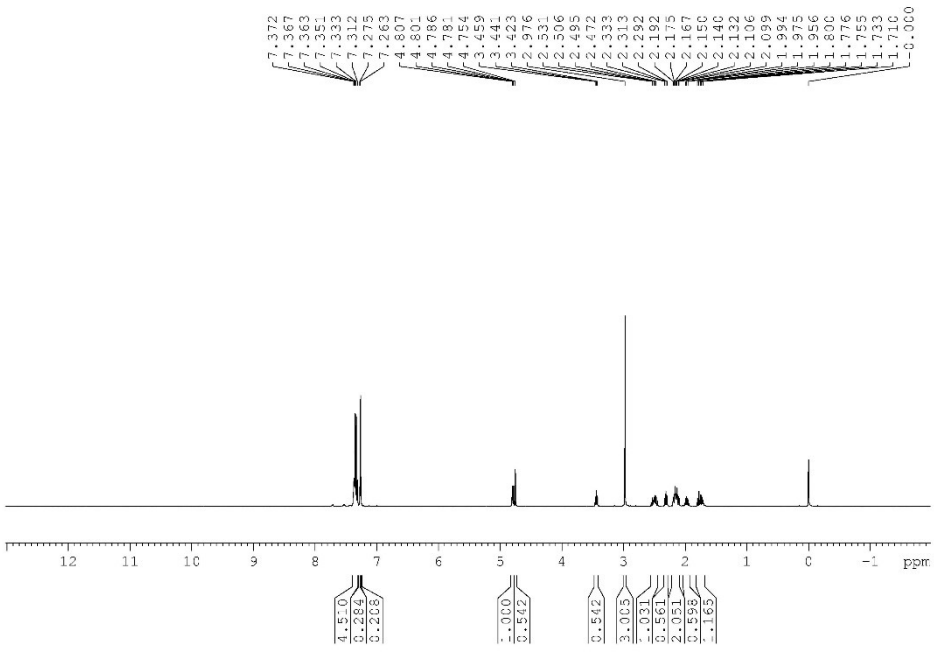
^{1}H NMR spectrum of compound **3w**



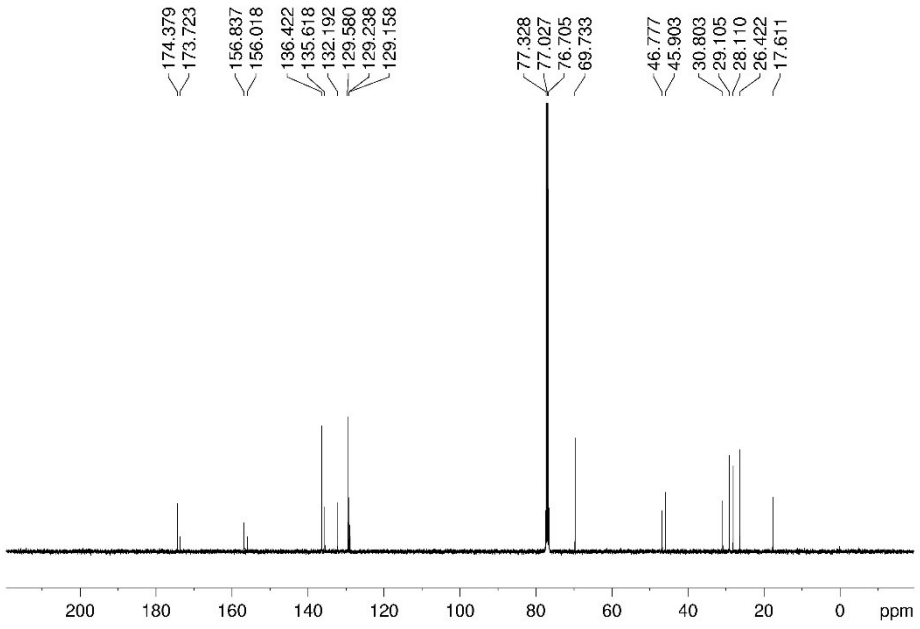
^{13}C NMR spectrum of compound **3w**



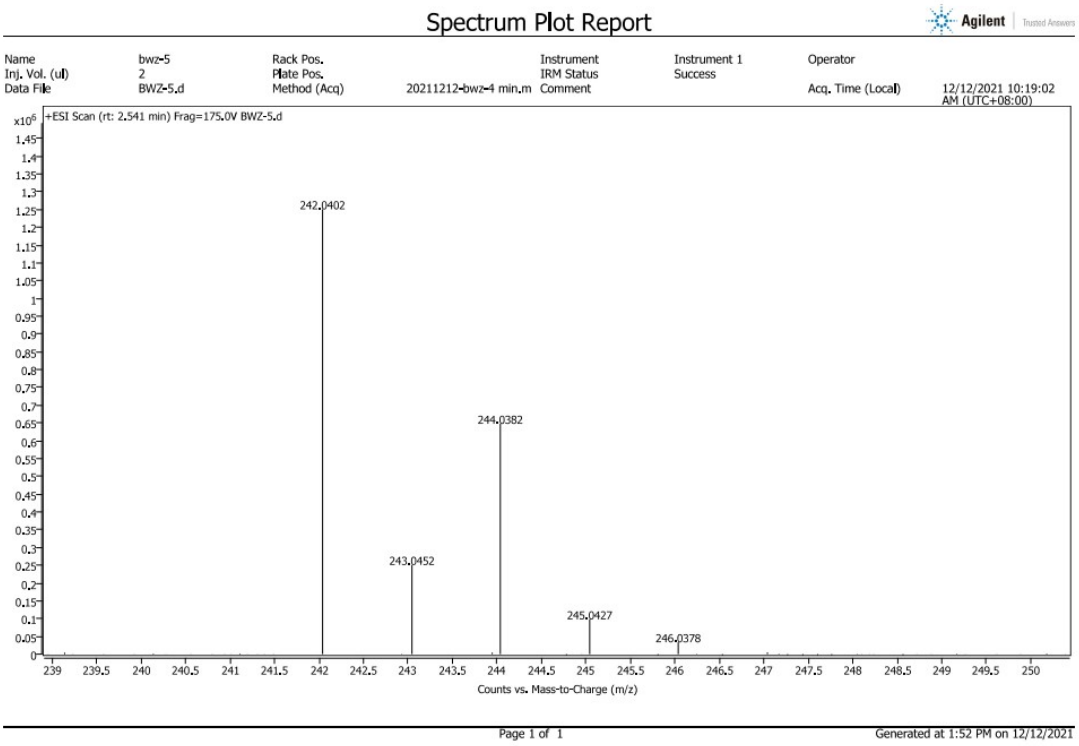
HRMS spectrum of compound **3w**



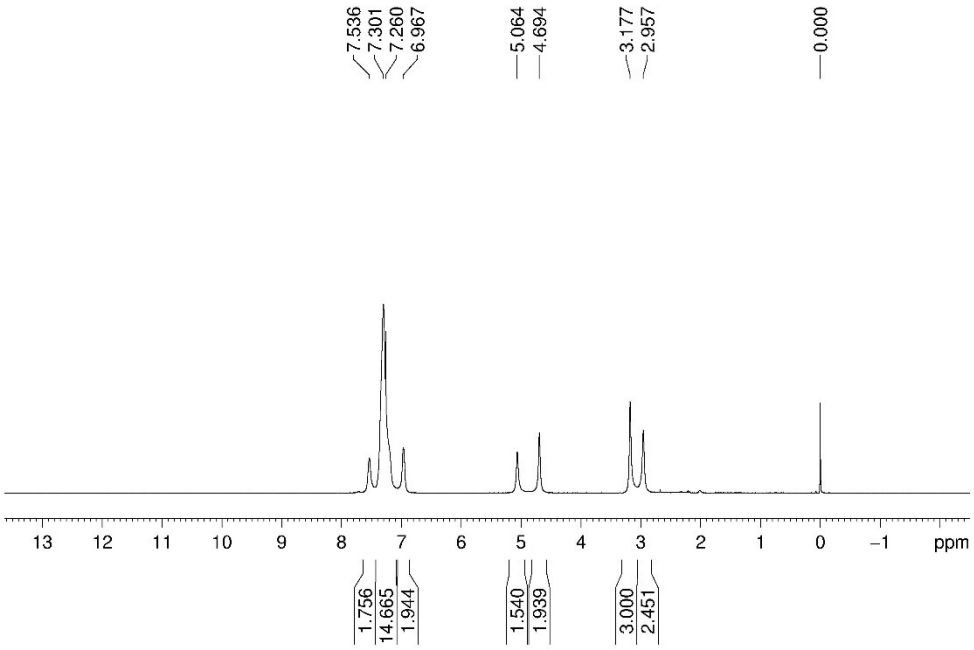
^{1}H NMR spectrum of compound **3x**



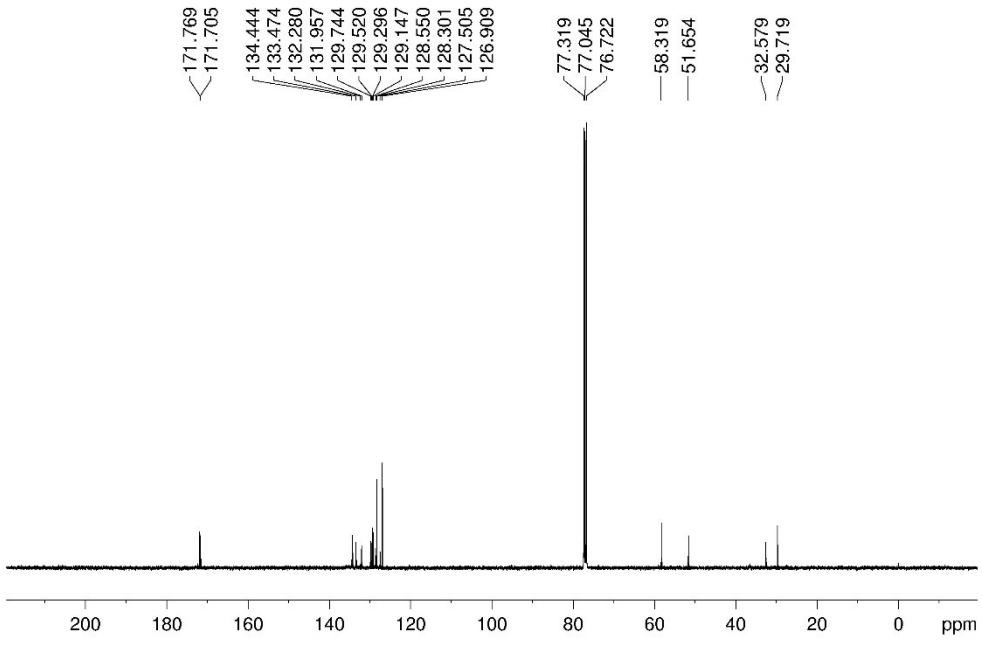
^{13}C NMR spectrum of compound **3x**



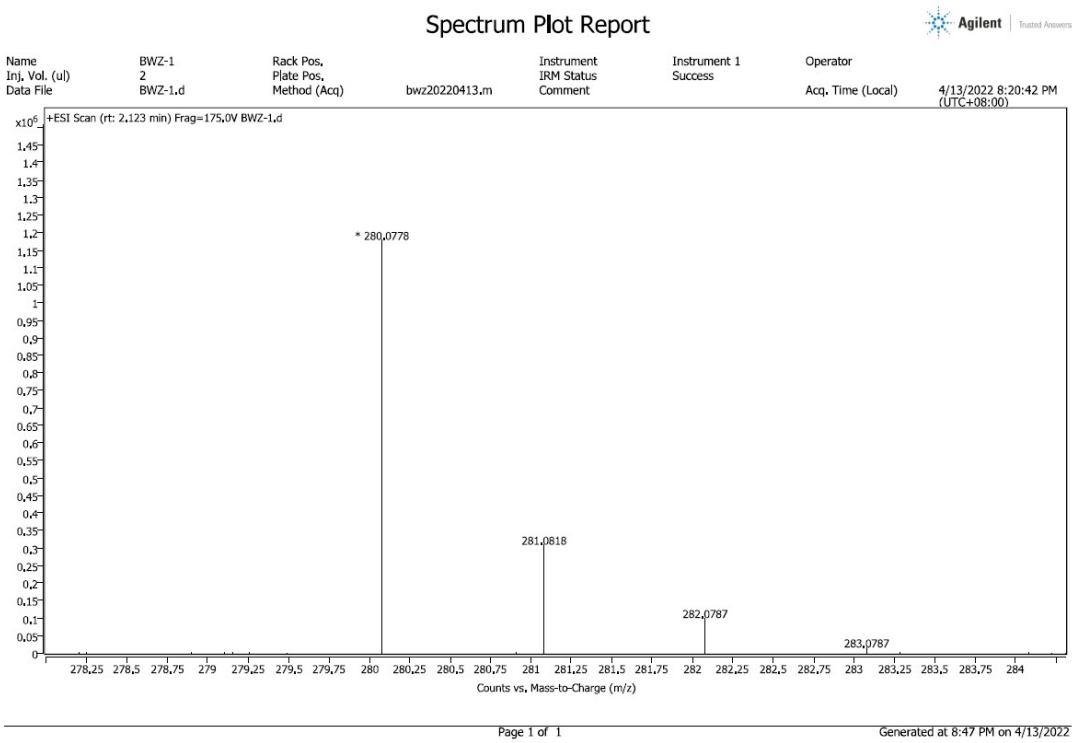
HRMS spectrum of compound **3x**



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



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



HRMS spectrum of compound **3y**