Supplementary Material

Synthesis and insecticidal activity of novel benzothiazole derivatives containing the coumarin moiety

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Table of contents

I. Data of key intermediates

7-Hydroxy-2*H*-chromen-2-one(**2a**)

White power; yield 74.2%; mp 233–235 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.59 (s, 1H,OH), 7.94 (d, *J* 9.5 Hz, 1H, Coumarin-4-H), 7.53 (d, *J* 8.5 Hz, 1H, Coumarin-5-H), 6.80 (dd, *J* 8.5, 2.3 Hz, 1H, Coumarin-6-H), 6.72 (d, *J* 2.2 Hz, 1H, Coumarin-8-H), 6.21 (d, *J* 9.5 Hz, 1H, Coumarin-3-H); EI-MS, *m/z*: 162 $[M]^+$; Anal Calcd. for $C_9H_6O_3$ (162.03).

7-Hydroxy-4-methyl-2*H*-chromen-2-one(**2b**)

Light yellow power; yield 87.6%; mp 187–188 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.54 (s, 1H,OH), 7.59 (t, *J* 8.4 Hz, 1H, Coumarin-4-H), 6.81 (dd, *J* 8.7, 2.3 Hz, 1H, Coumarin-6-H), 6.71 (d, *J* 2.3 Hz, 1H, Coumarin-8-H), 6.13 (s, 1H, Coumarin-3-H), 2.37 (s, 3H,CH_3); EI-MS, *m/z*: 176 $[M]^+$; Anal Calcd. for $C_{10}H_8O_3$ (176.05).

4-(Benzothiazole-2-yl)phenol(**4a**)

White power; yield 67.1%; mp 223–225 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.24 (s, 1H,OH), 8.12–8.06 (m, 1H, Benzothiazole-4-H), 8.01–7.91 (m, 3H, Benzothiazole-5,6,7-3H), 7.54–7.48 (m, 1H, Benzothiazol-2-phenyl-2-H), 7.44–7.37 (m, 1H, Benzothiazol-2-phenyl-6-H), 6.97–6.90 (m, 2H, Benzothiazol-2-phenyl-3,5-2H); EI-MS, *m/z*: 227 $[M]^+$; Anal Calcd. for $C_{13}H_9NOS$ (227.04).

4-(Benzothiazol-2-yl)-2-methoxyphenol(**4b**)

White power; yield 73.4%; mp 172–174 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.87 (s, 1H,OH), 8.09 (d, *J* 7.8 Hz, 1H, Benzothiazole-4-H), 8.00 (d, *J* 8.0 Hz, 1H, Benzothiazole-7-H), 7.64 (d, *J* 2.0 Hz, 1H, Benzothiazole-5-H), 7.55–7.47 (m, 2H, Benzothiazole-6-H, Benzothiazol-2-phenyl-6-H), 7.45–7.37 (m, 1H, Benzothiazol-2-phenyl-2-H), 6.95 (d, *J* 8.2 Hz, 1H, Benzothiazol-2-phenyl-5-H), 3.91 (s, 3H,OCH_3); EI-MS, *m/z*: 257 $[M]^+$; Anal Calcd. for $C_{14}H_{11}NO_2S$ (257.05).

3-(Benzothiazol-2-yl)phenol(**4c**)

White power; yield 60.2%; mp 165–167 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.92 (s, 1H,OH), 8.14 (d, *J* 7.8 Hz, 1H, Benzothiazole-4-H), 8.06 (d, *J* 8.0 Hz, 1H, Benzothiazole-7-H), 7.51 (dq, *J* 15.1, 7.2 Hz, 4H, Benzothiazole-5,6-2H, Benzothiazol-2-phenyl-5,6-2H), 7.38 (dd, *J* 10.6, 5.6 Hz, 1H, Benzothiazol-2-phenyl-2-H), 7.01–6.94 (m, 1H, Benzothiazol-2-phenyl-4-H); EI-MS, *m/z*: 227 $[M]^+$; Anal Calcd. for $C_{13}H_9NOS$ (227.04).

2-(4-(2-Bromoethoxy)phenyl)benzothiazole(**5a**)

White power; yield 71.5%; mp 131–133 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.12 (d, *J* 7.9 Hz, 1H, Benzothiazole-4-H), 8.09–8.00 (m, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.53 (t, *J* 7.6 Hz, 1H, Benzothiazole-5-H), 7.44 (t, *J* 7.5 Hz, 1H, Benzothiazole-6-H), 7.16 (d, *J* 8.7 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.44 (t, *J* 10.4 Hz, 2H,CH_2), 3.86 (t, *J* 10.4 Hz, 2H,CH_2-Br).

2-(4-(3-Bromopropoxy)phenyl)benzothiazole(**5b**)

White power; yield 74.2%; mp 115–116 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.12 (d, *J* 7.8 Hz, 1H, Benzothiazole-4-H), 8.03 (dd, *J* 11.2, 8.4 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.53 (t, *J* 7.2 Hz, 1H, Benzothiazole-5-H), 7.44 (t, *J* 7.2 Hz, 1H, Benzothiazole-6-H), 7.15 (d, *J* 8.8 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.20 (t, *J* 6.0 Hz, 2H,CH_2), 3.70 (t, *J* 6.5 Hz, 2H, CH_2-Br), 2.33–2.27 (m, 2H, CH_2).

2-(4-(4-Bromobutoxy)phenyl)benzothiazole(**5c**)

Yellow-white powder; yield 78.3%; mp 112–114 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.15–8.08 (m, 1H, Benzothiazole-4-H), 8.03 (t, *J* 8.3 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.57–7.49 (m, 1H, Benzothiazole-5-H), 7.46–7.39 (m, 1H, Benzothiazole-6-H), 7.13 (d, *J* 8.9 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.12 (t, *J* 6.2 Hz, 2H, CH_2), 3.64 (t, *J* 6.6 Hz, 2H, CH_2-Br), 2.04–1.94 (m, 2H, CH_2), 1.95–1.83 (m, 2H, CH_2).

2-(4-((5-Bromopentyl)oxy)phenyl)benzothiazole(**5d**)

Off-white power; yield 80.8%; mp 109–111 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.10 (t, *J* 6.6 Hz, 1H, Benzothiazole-4-H), 8.02 (dd, *J* 8.2, 6.3 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.52 (dd, *J*

11.3, 4.1 Hz, 1H, Benzothiazole-5-H), 7.42 (dd, *J* 11.1, 4.0 Hz, 1H, Benzothiazole-6-H), 7.14–7.07 (m, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.09 (dd, *J* 13.1, 6.7 Hz, 2H, CH_2), 3.57 (q, *J* 7.0 Hz, 2H, CH_2-Br), 1.94–1.83 (m, 2H, CH_2), 1.83–1.72 (m, 2H, CH_2), 1.55 (dq, *J* 14.7, 7.8 Hz, 2H, CH_2).

2-(4-((6-Bromohexyl)oxy)phenyl)benzothiazole(**5e**)

Grey Powder; yield 85.2%; mp 95–96 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.11 (d, *J* 7.9 Hz, 1H, Benzothiazole-4-H), 8.02 (dd, *J* 8.3, 6.5 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.56–7.49 (m, 1H, Benzothiazole-5-H), 7.46–7.40 (m, 1H, Benzothiazole-6-H), 7.11 (d, *J* 8.8 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.07 (t, *J* 6.4 Hz, 2H, CH_2), 3.55 (t, *J* 6.7 Hz, 2H, CH_2-Br), 1.90–1.66 (m, 4H, 2xCH_2), 1.53–1.30 (m, 4H, 2xCH_2).

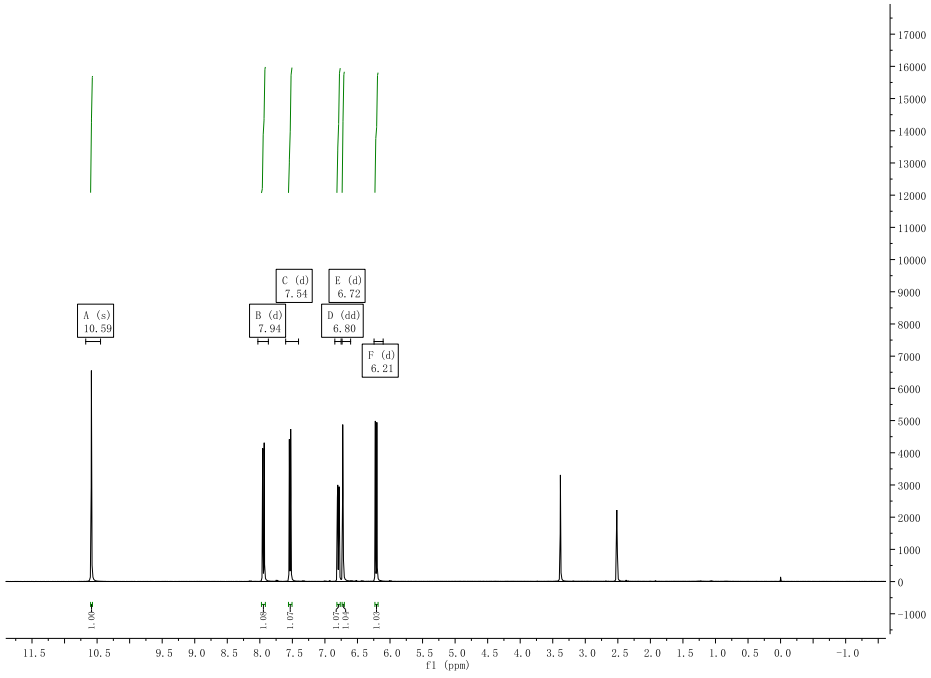
II. Crystallographic data of compound **6v**

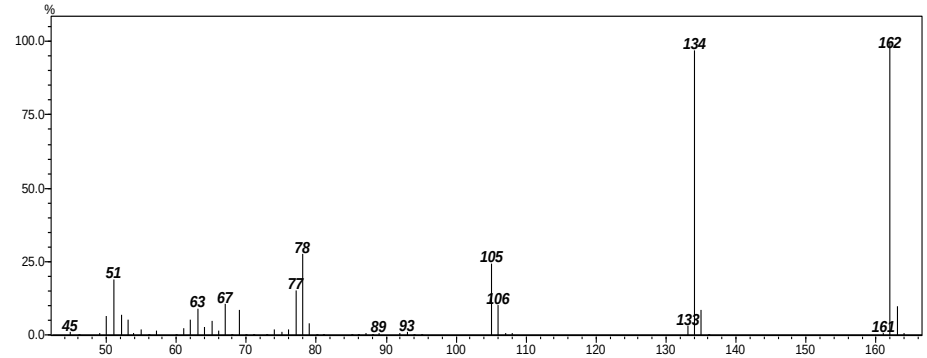
Table 1. Crystallographic data of compound **6v**

Chemical formula	$C_{25}H_{19}NO_4S$
Formula weight	429.47
Temperature[K]	100.00(10)
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	6.5984(9)
b [Å]	7.2742(12)
c [Å]	22.5363(19)
α [°]	90.238(10)
β [°]	91.143(9)
γ [°]	115.337(15)
V[Å^3]	977.4(3)
Z	2
ρ (calculated)[g/cm^3]	1.459
μ [mm^{-1}]	0.201
F(000)	448
Crystal size [mm^3]	0.11 × 0.12 × 0.13
Colour,shape	Colourless, block
Radiation [Å]	MoKα (*λ* = 0.71073)
Theta Min-Max [°]	2.7, 26.4
h,k,l	-8 ≤ *h* ≤ 6, -8 ≤ *k* ≤ 9, -23 ≤ *l* ≤ 28
Reflections collected	7766
Independent reflections	4000
Data/restraints/parameters	2947/12/293
Goodness-of-fit	1.097
Final R indexes [*I*>=2*σ* (*I*)]	R_1= 0.0806, wR_2= 0.1916
Final R indexes [all data]	R_1= 0.1078, wR_2= 0.2119
Min. and Max. Resd. Dens [e Å^{-3}]	-0.49, 0.51

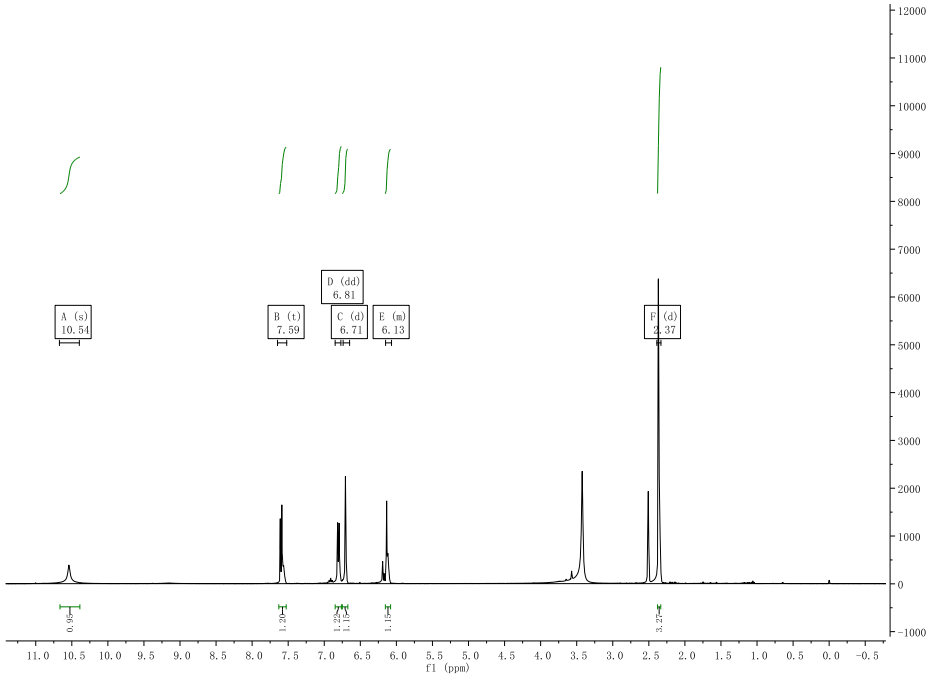
III Spectrograms of key intermediates and all title compounds

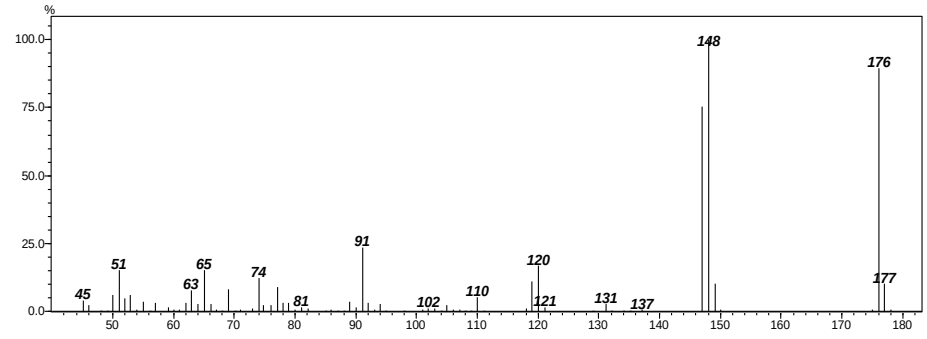
^{1}H NMR, and MS spectra of the compound **2a**



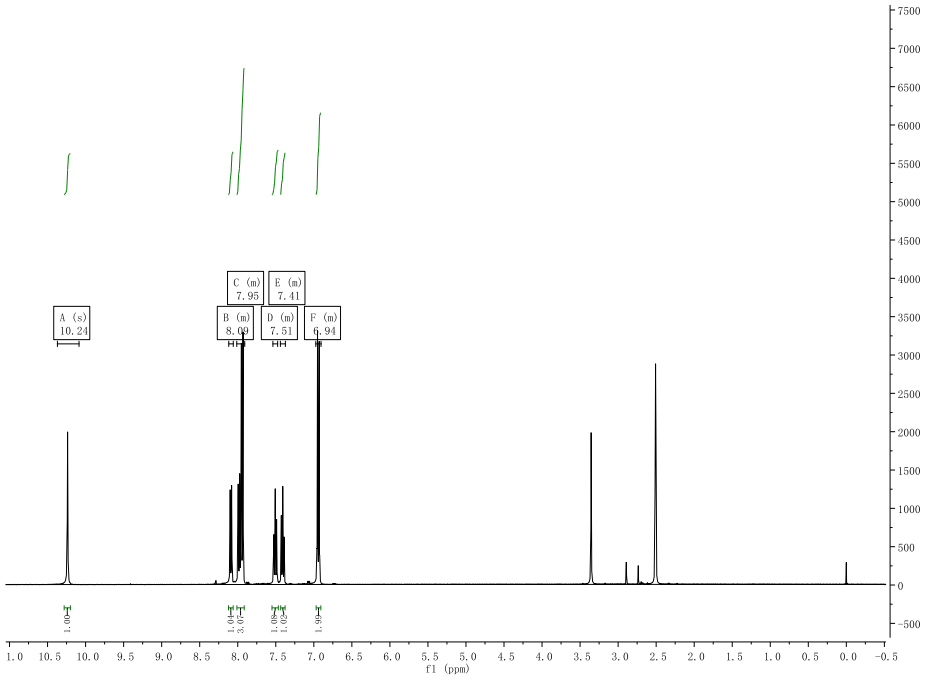


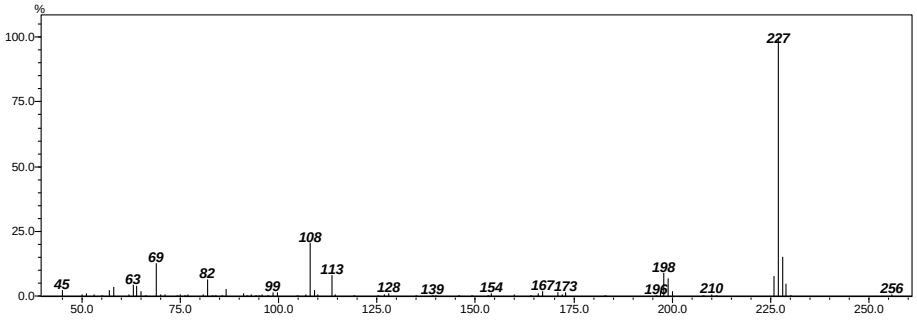
^{1}H NMR, and MS spectra of the compound **2b**



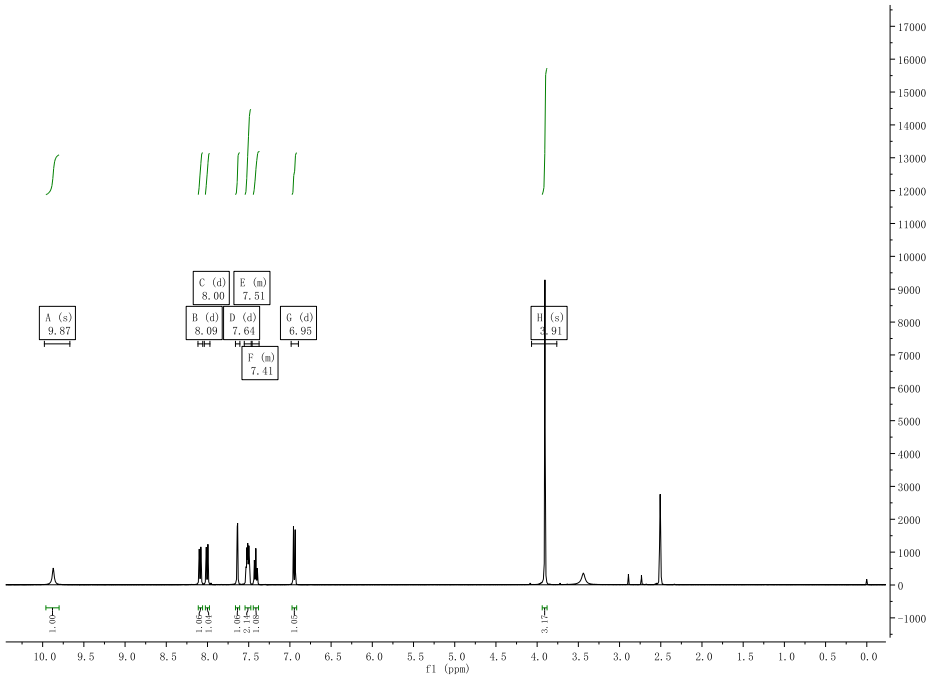


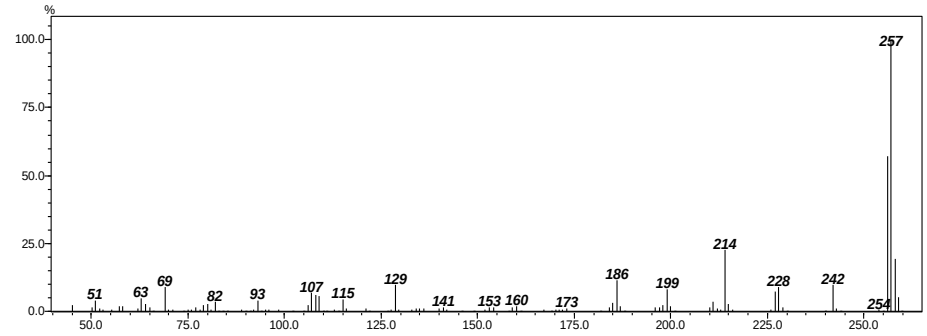
^{1}H NMR, and MS spectra of the compound **4a**



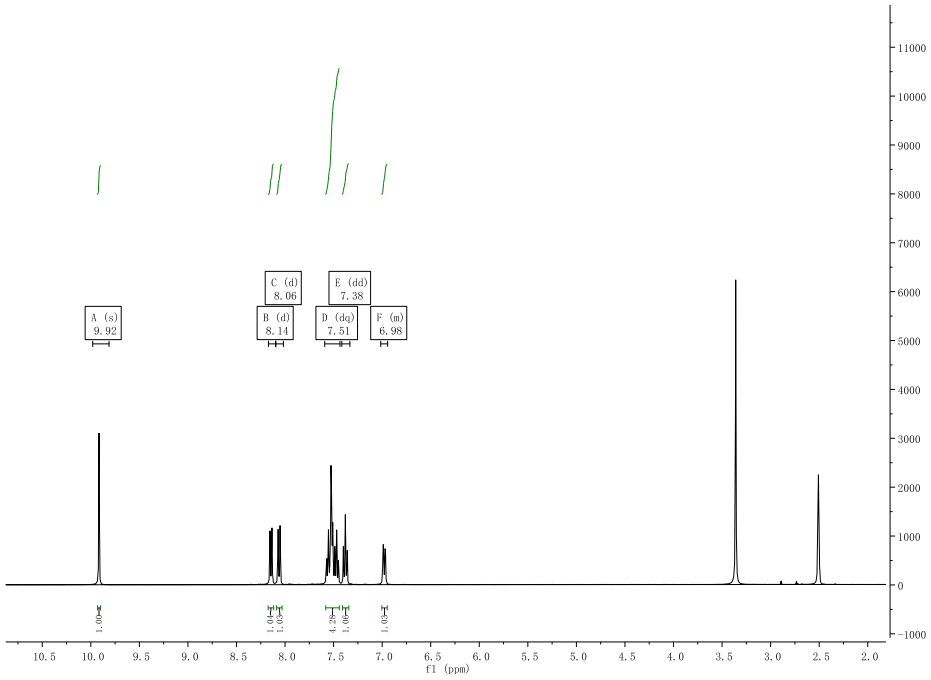


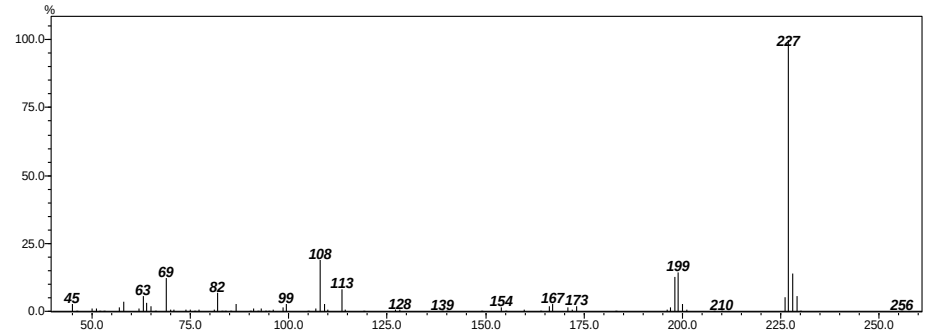
^{1}H NMR, and MS spectra of the compound **4b**



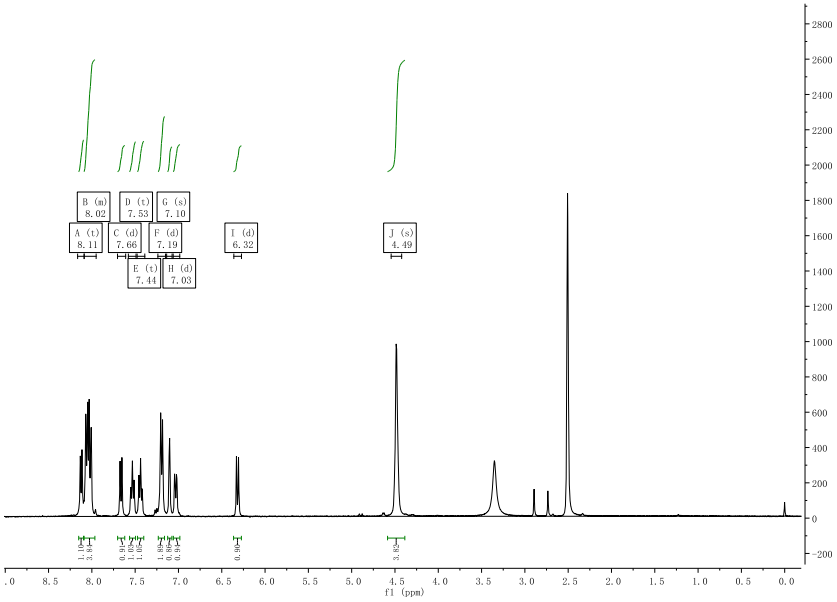


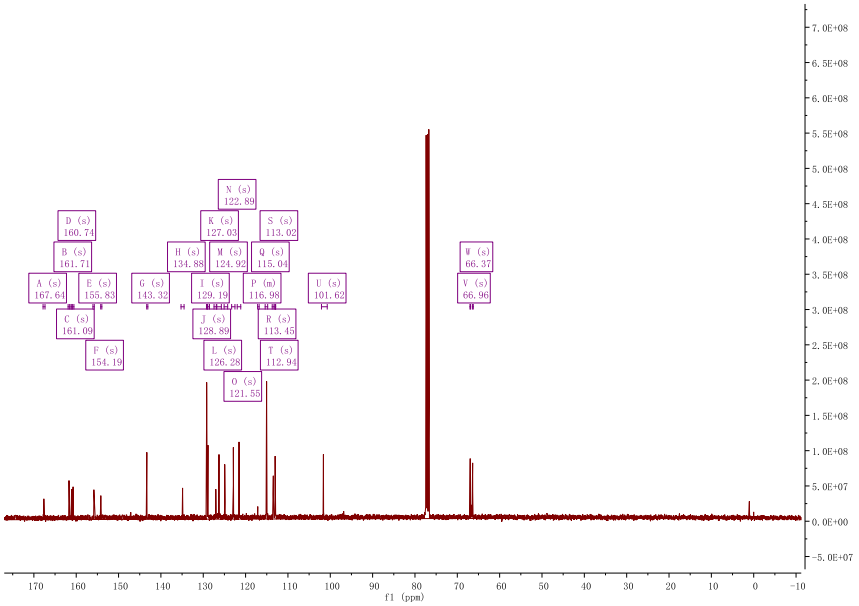
^{1}H NMR, and MS spectra of the compound **4c**

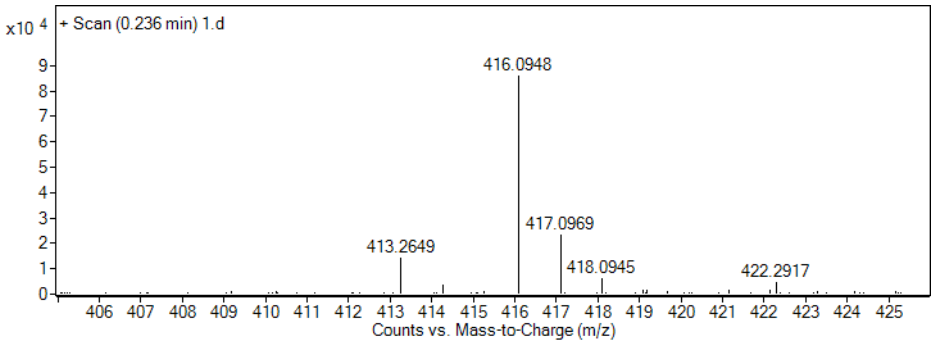




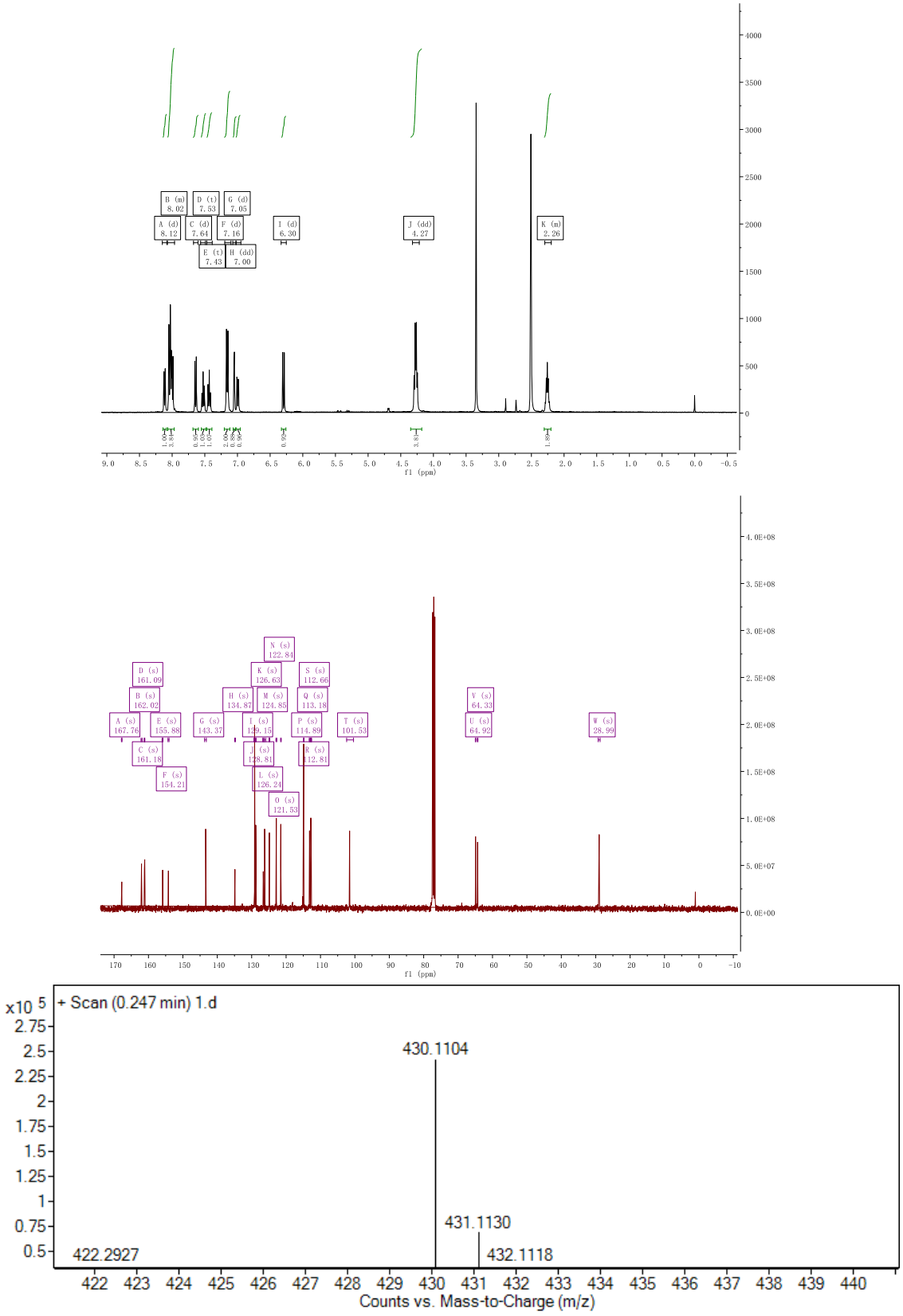
^{1}H NMR,^{13}C NMR and HRMS spectra of the compound **6a**



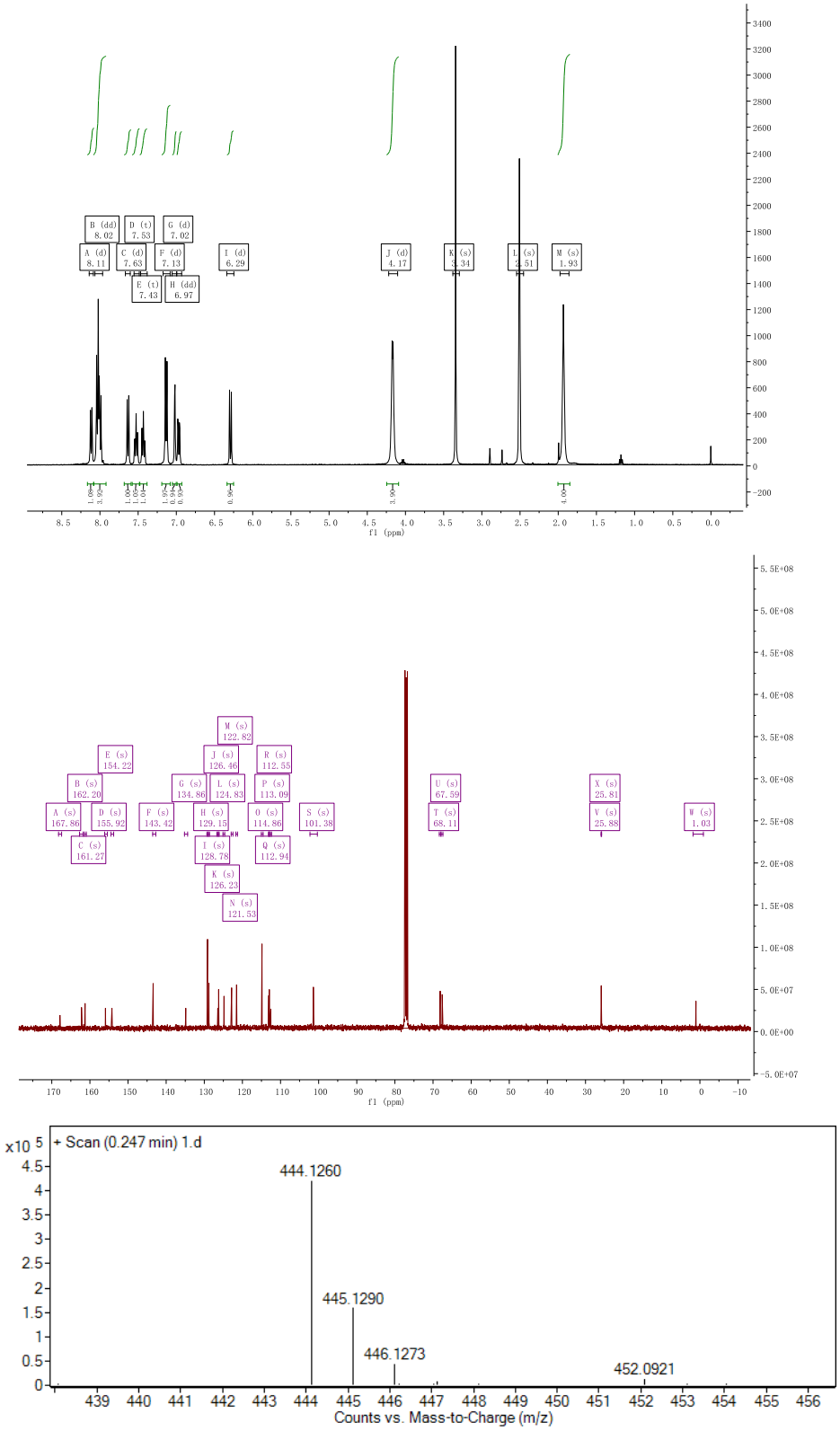




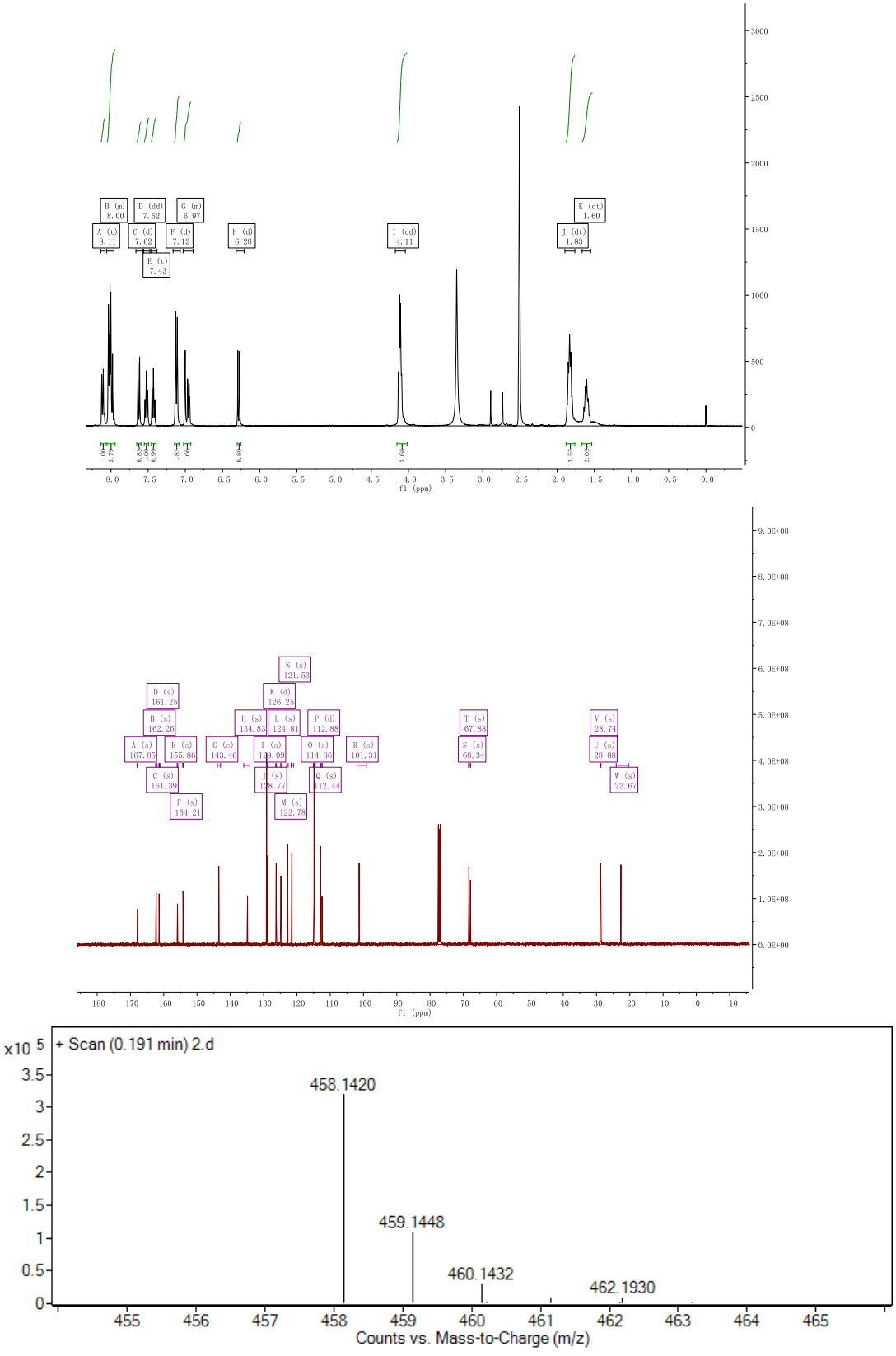
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6b**



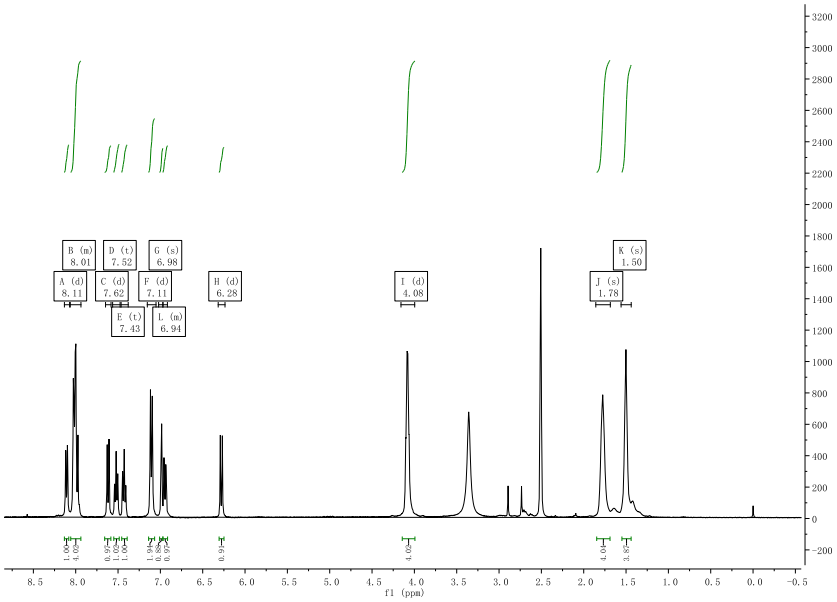
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6c**

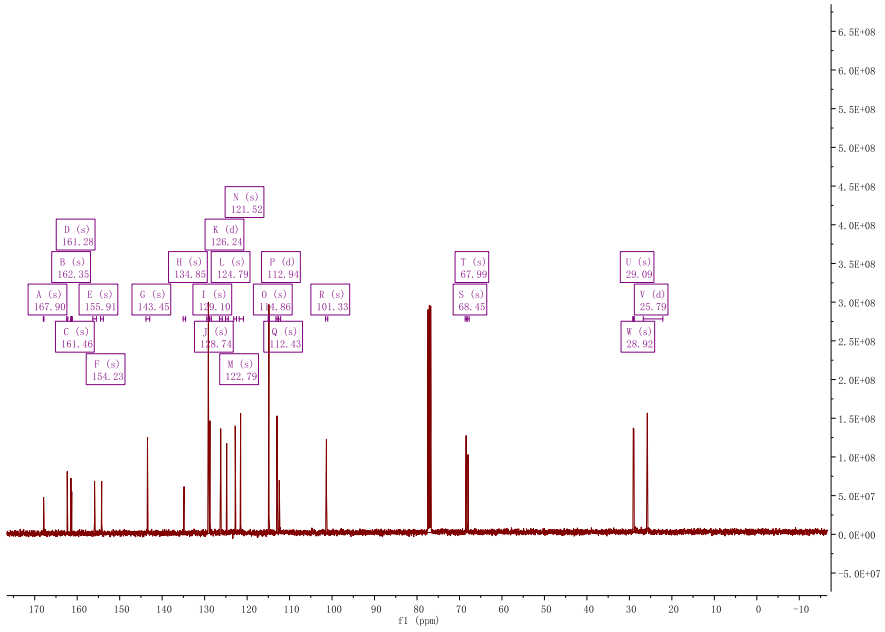


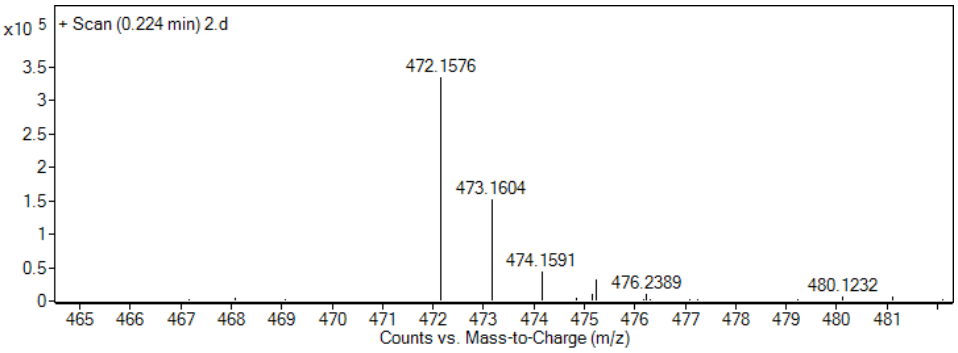
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6d**



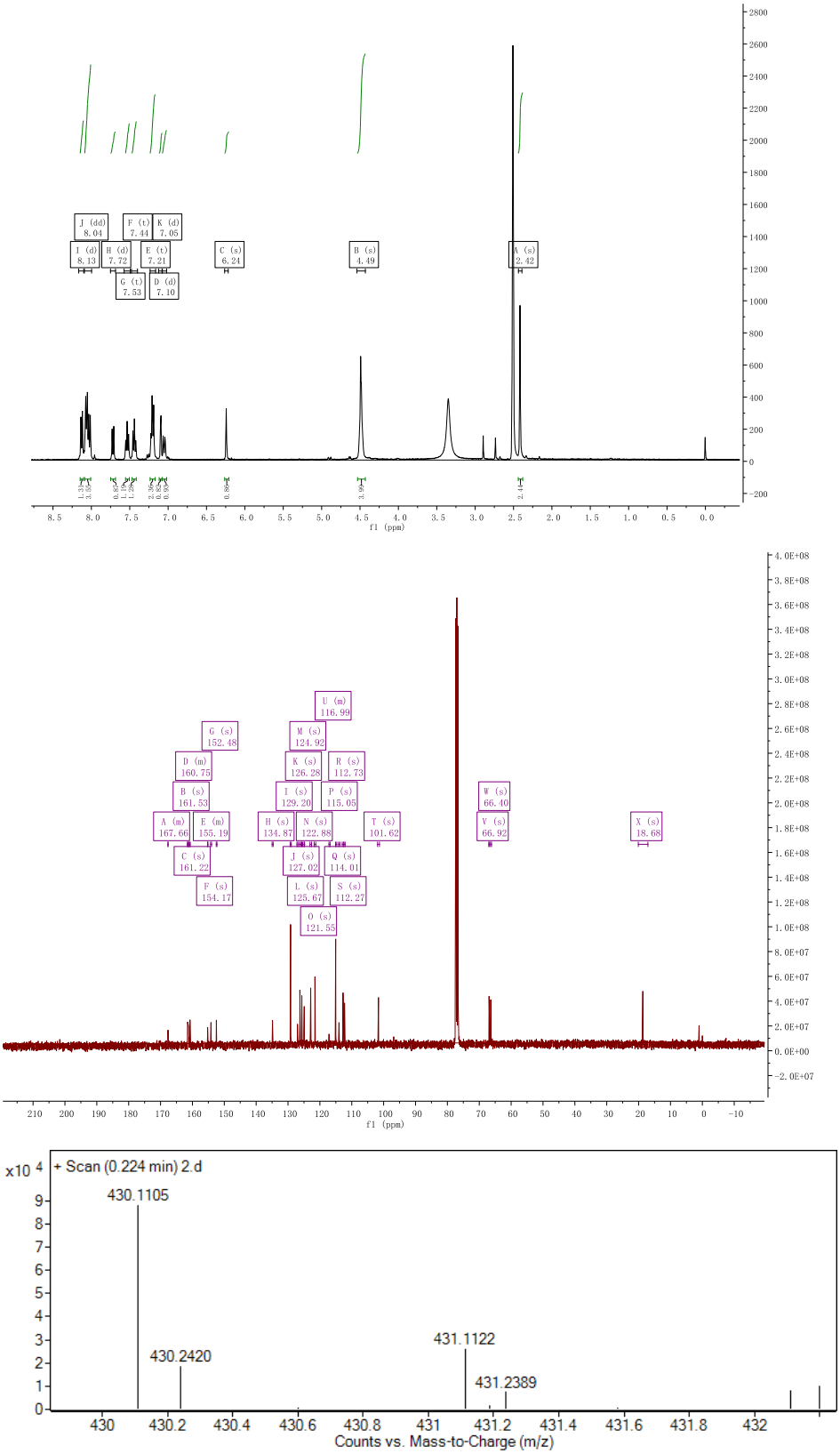
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6e**



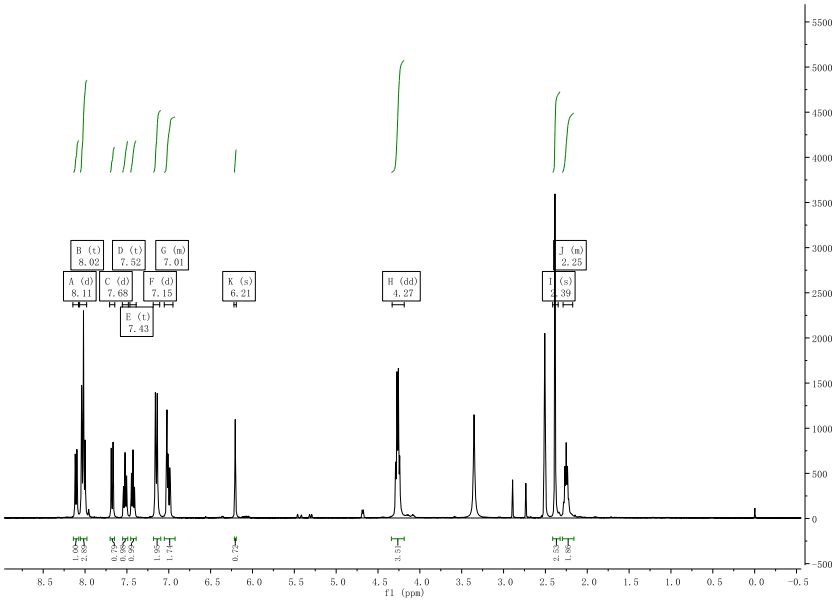


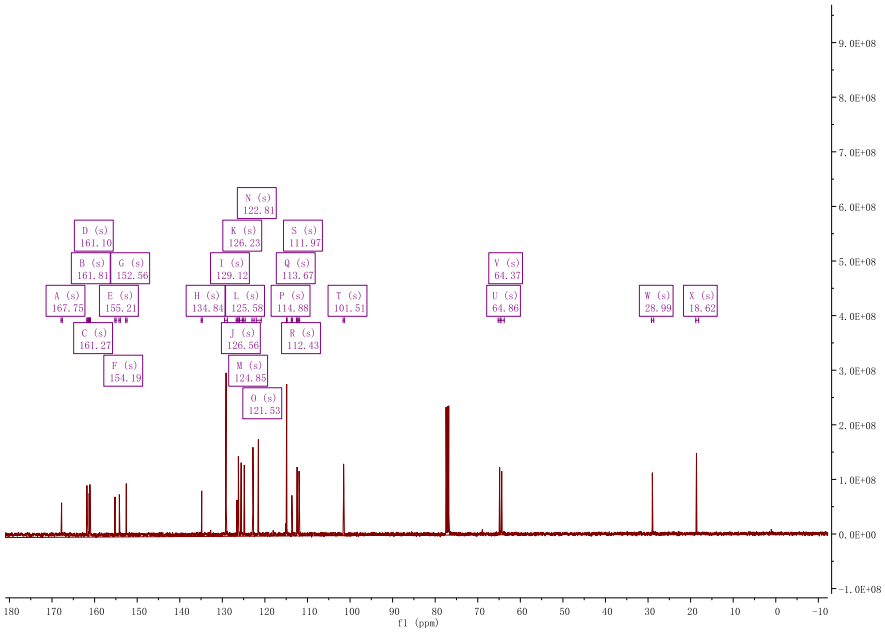


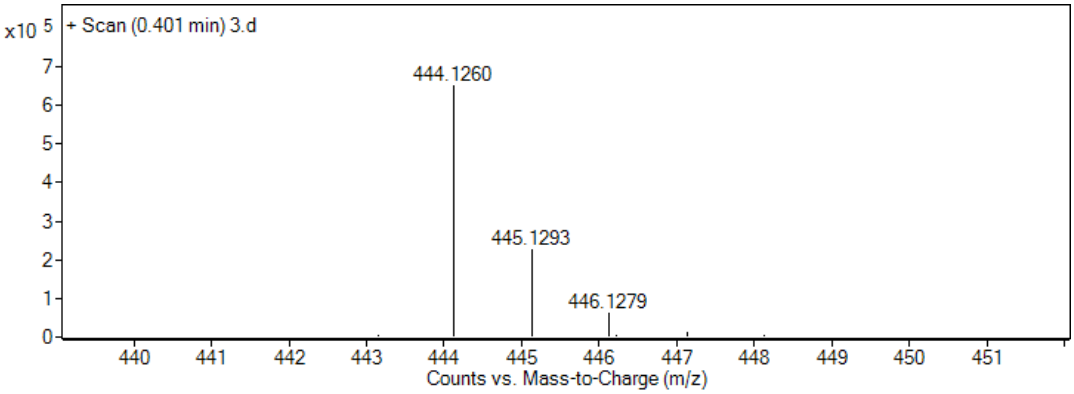
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6f**



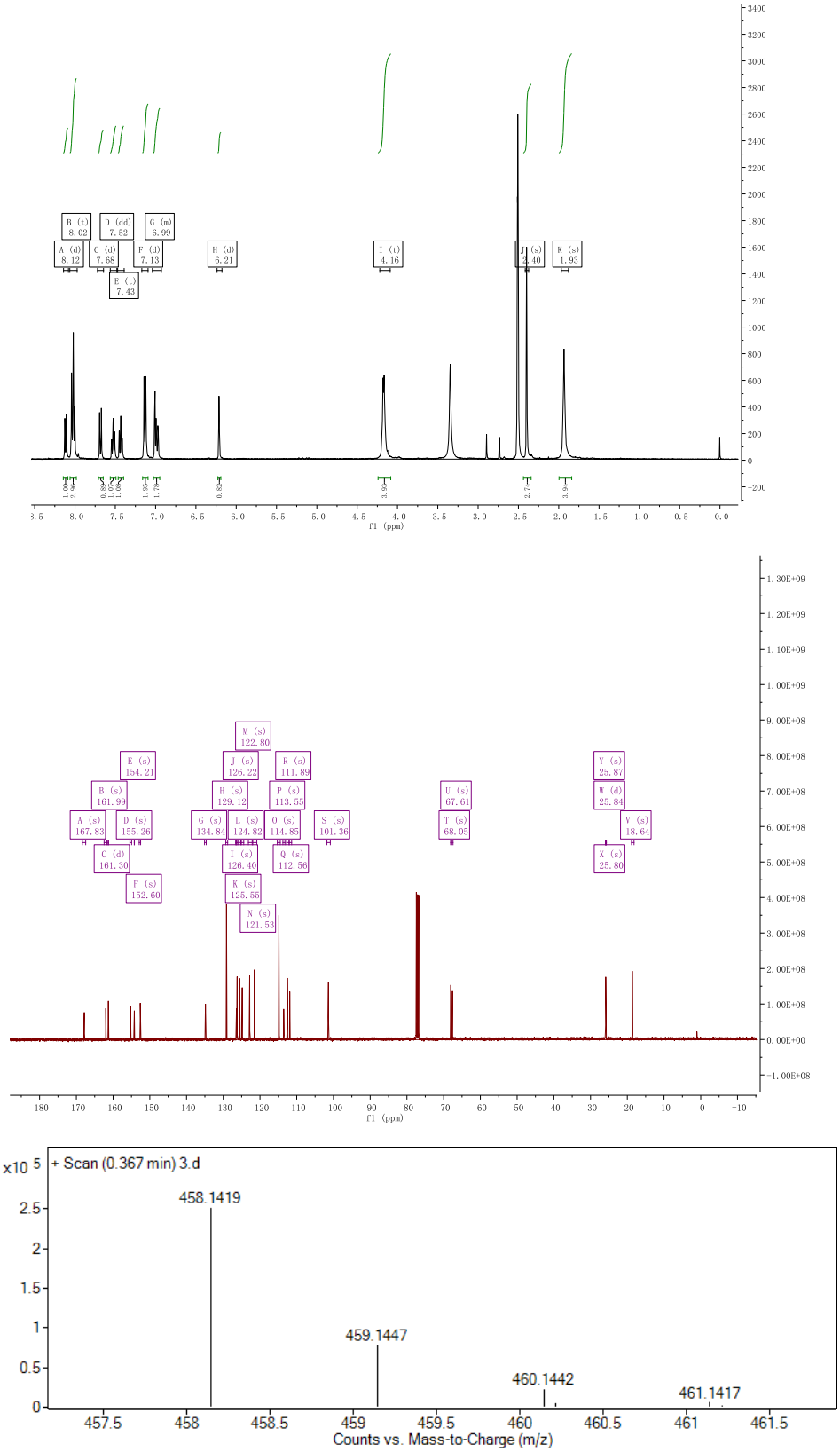
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6g**



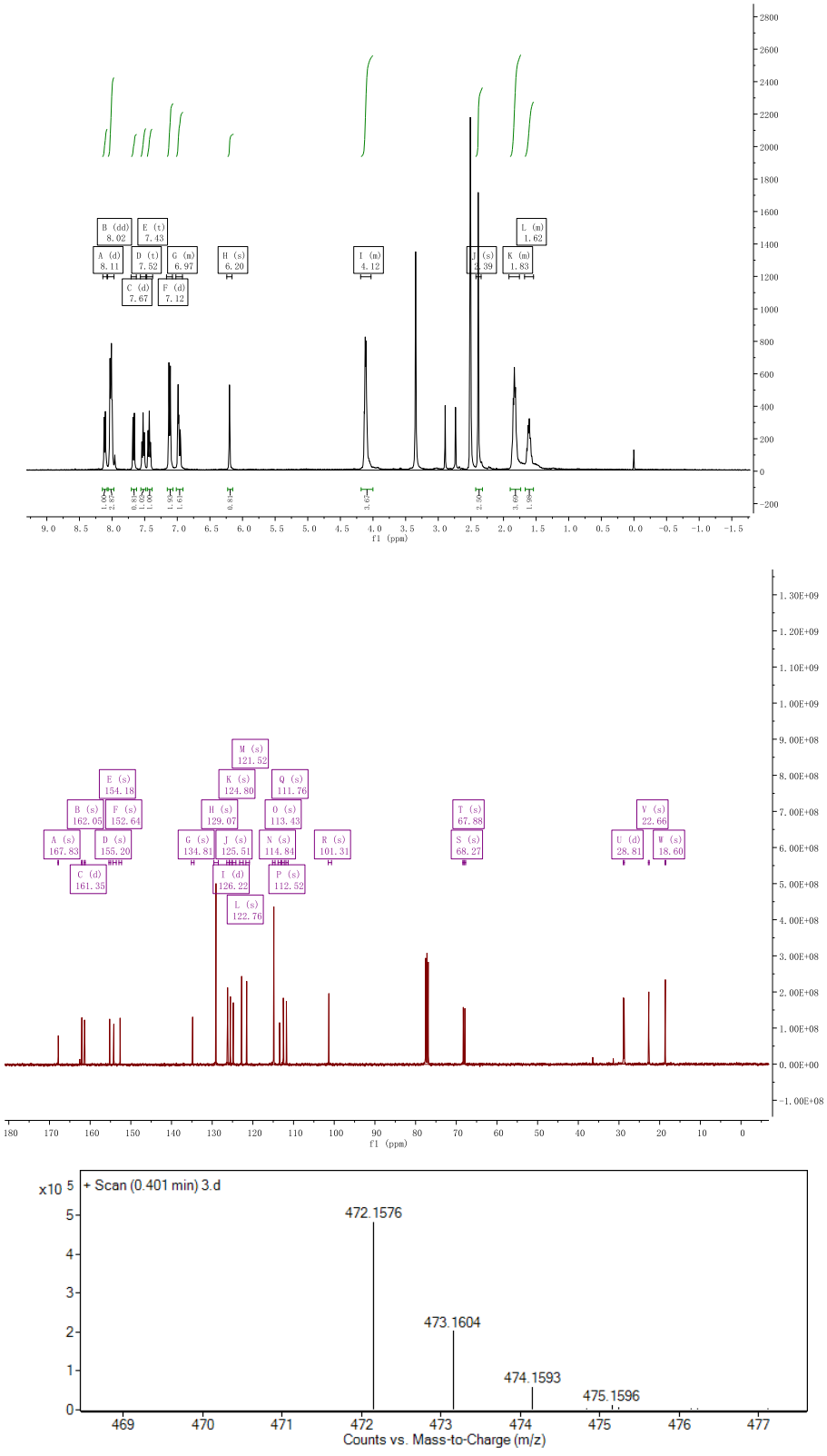




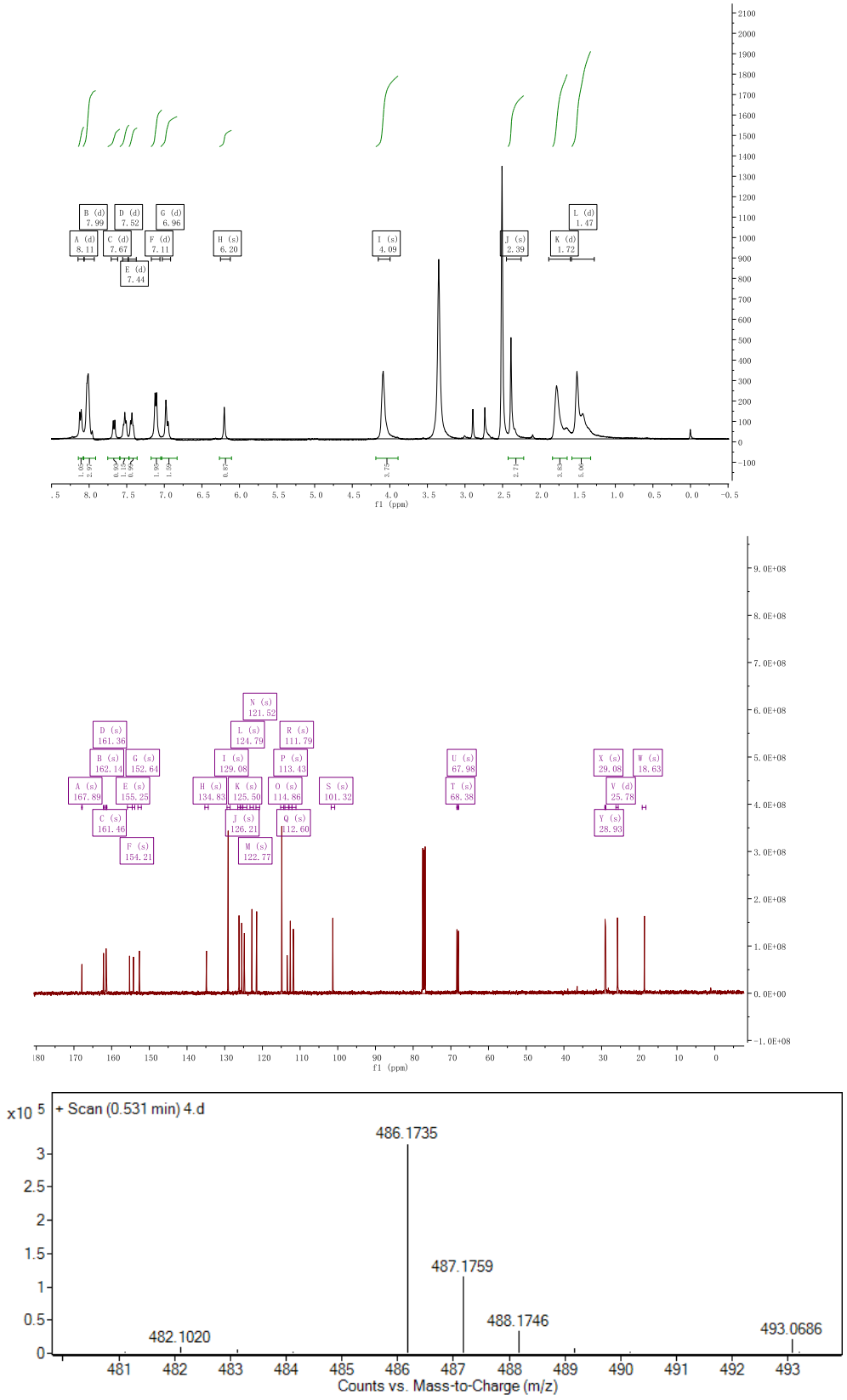
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6h**



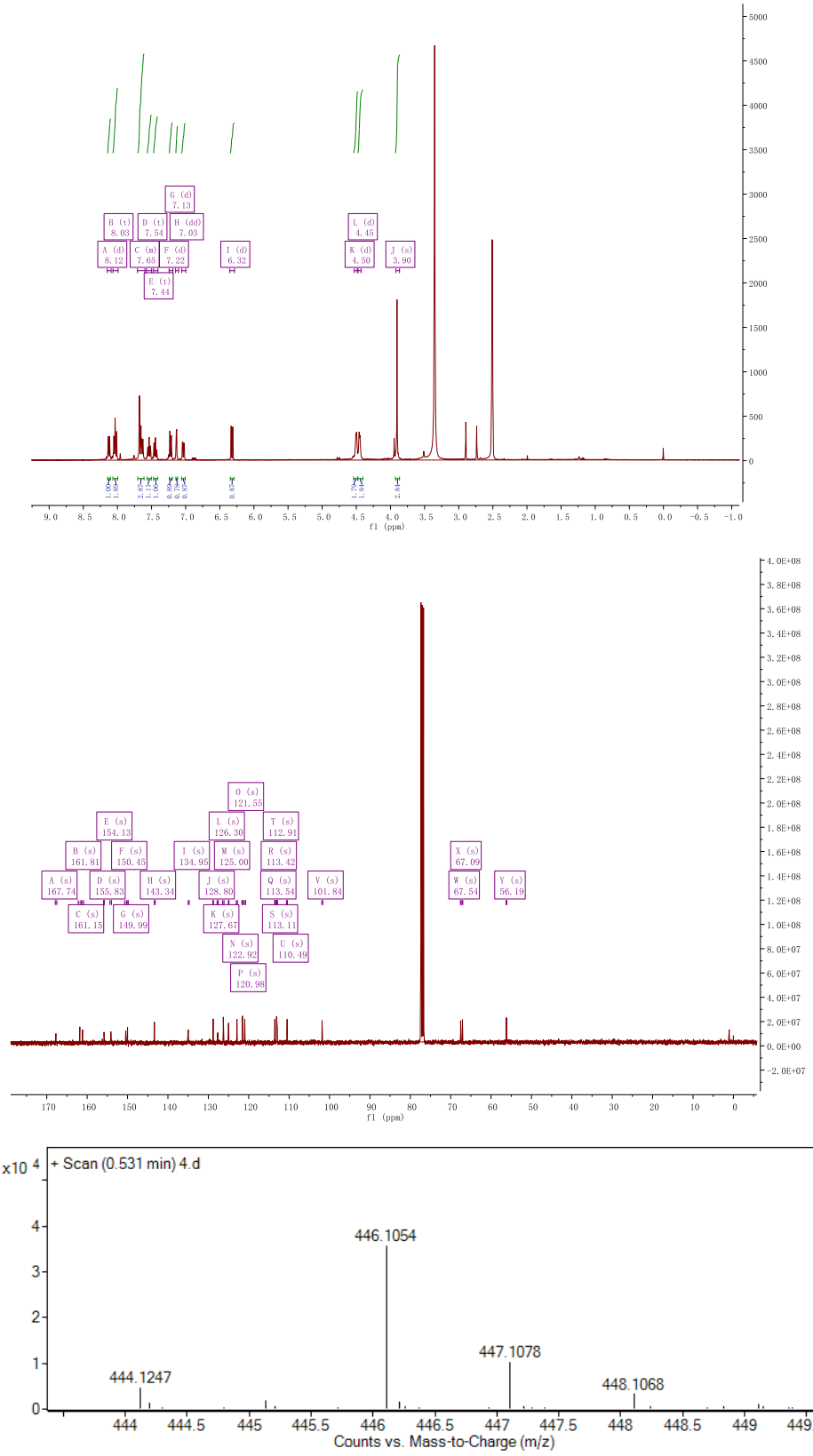
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6i**



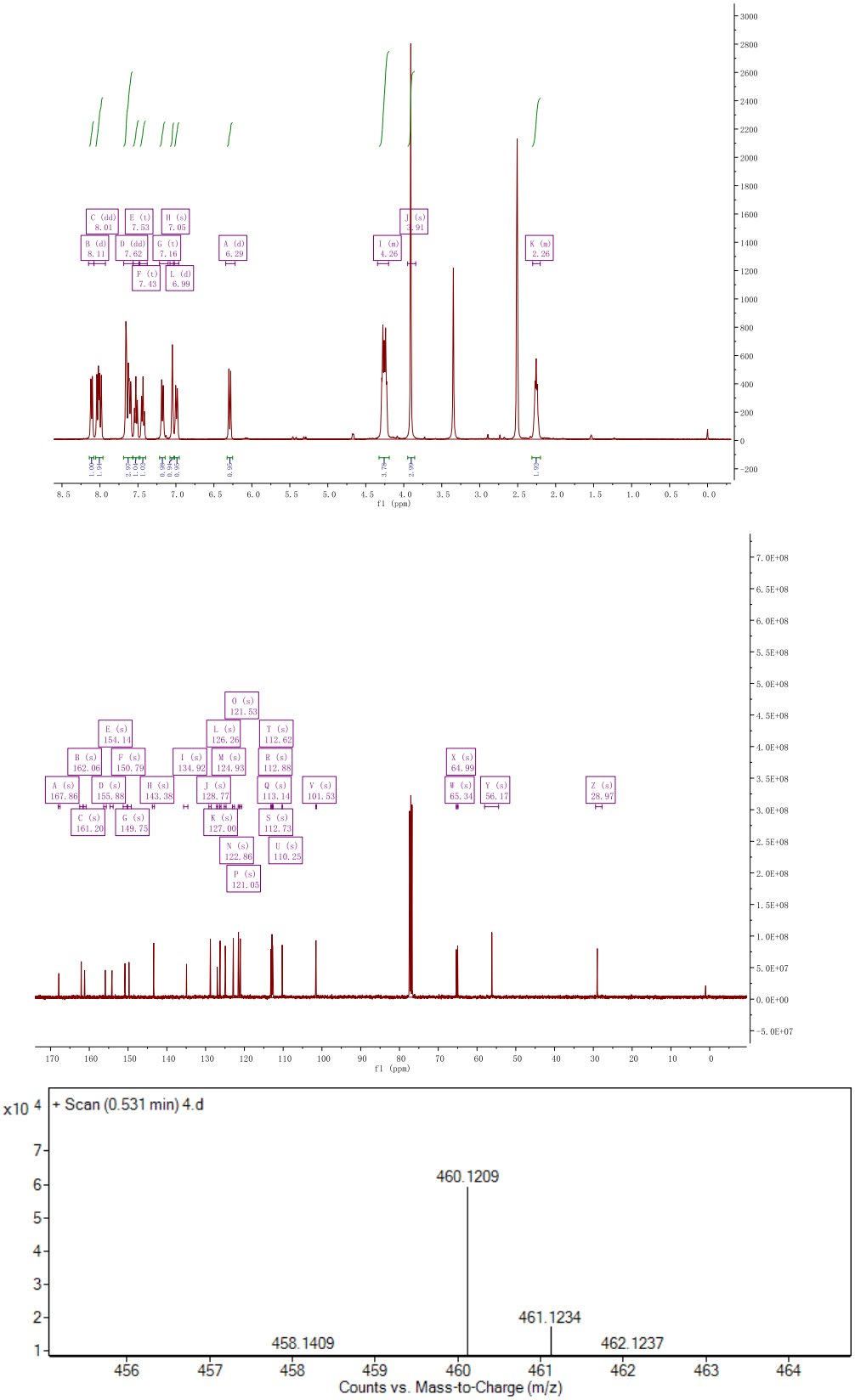
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6j**



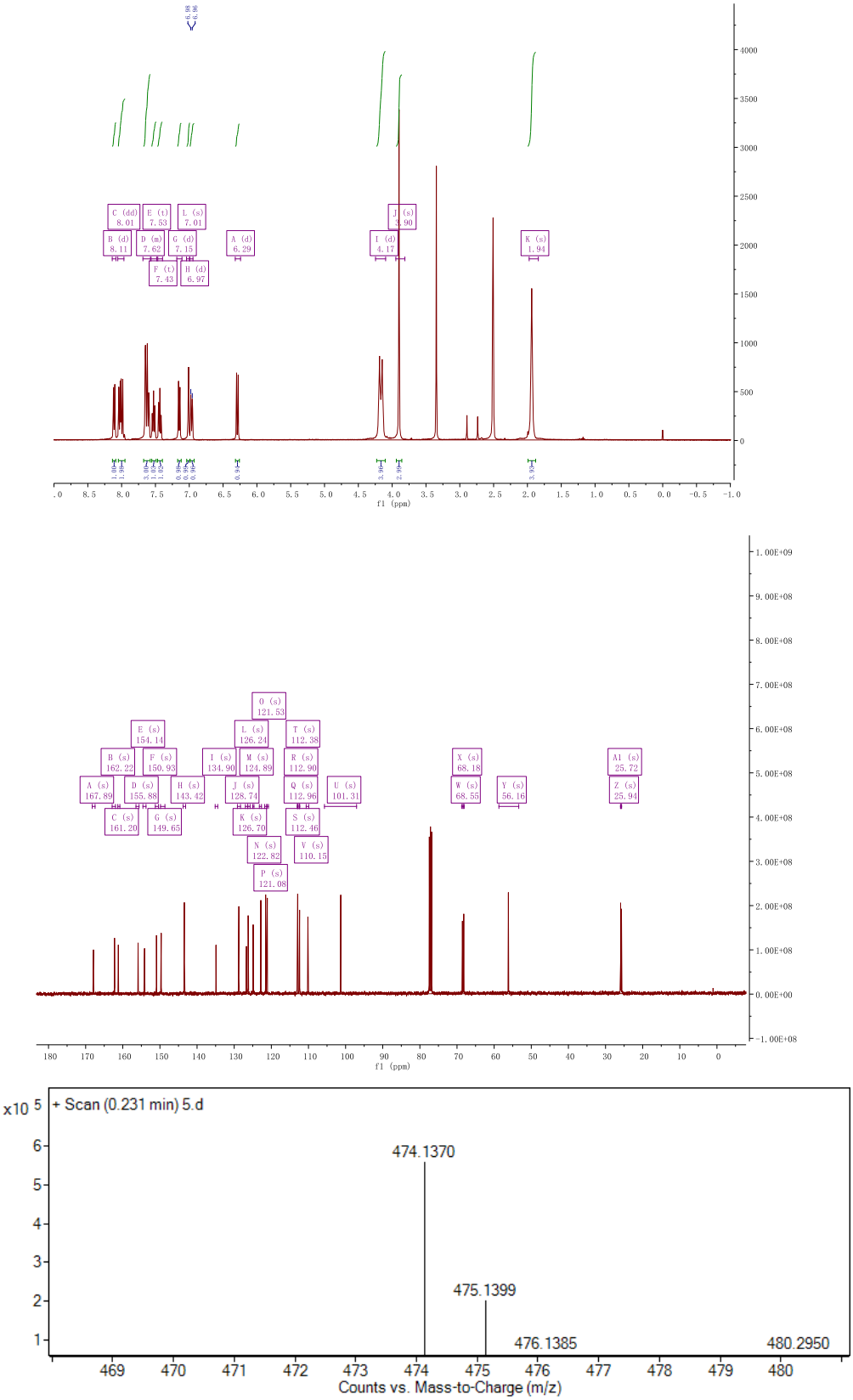
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6k**



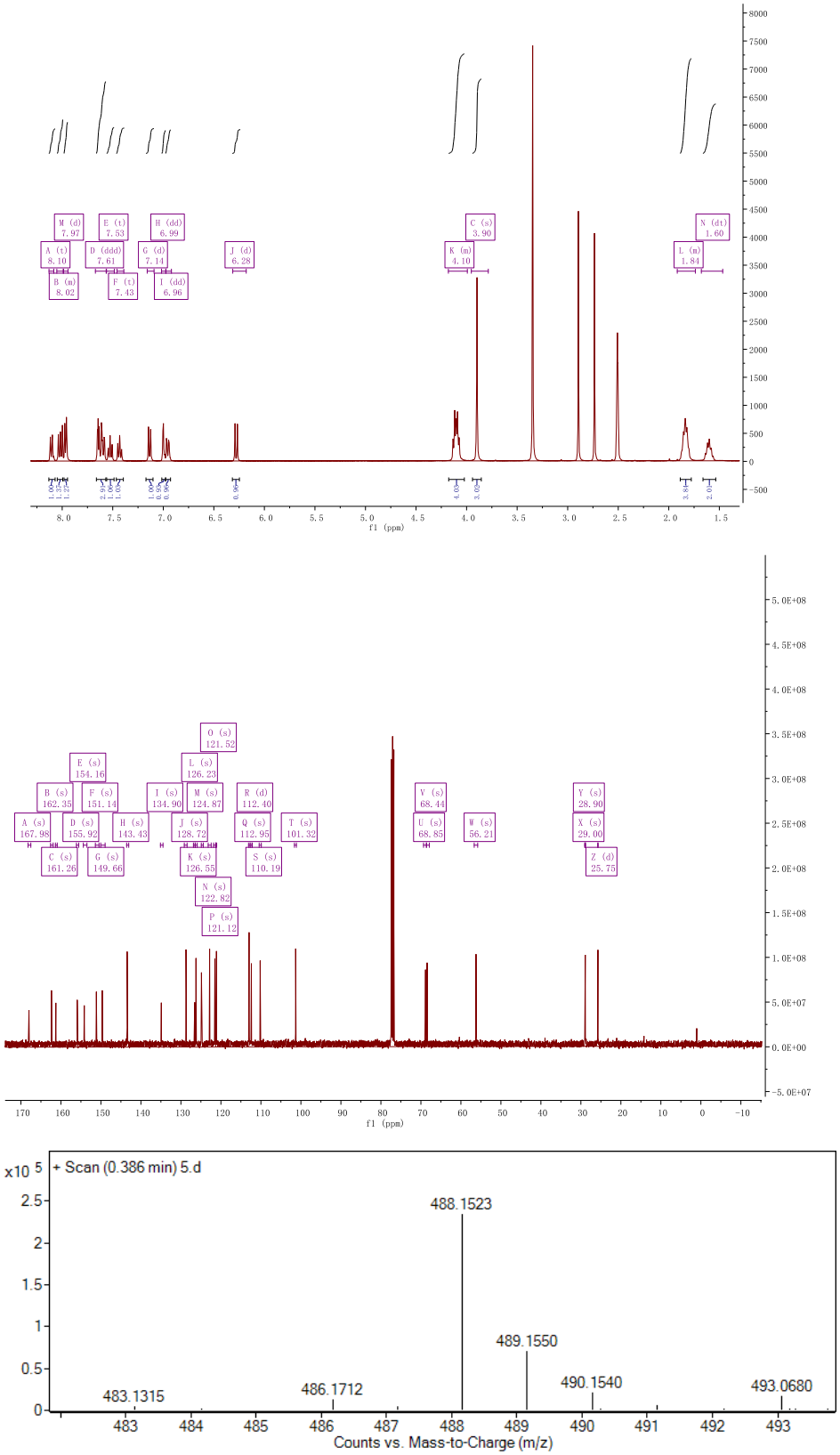
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6l**



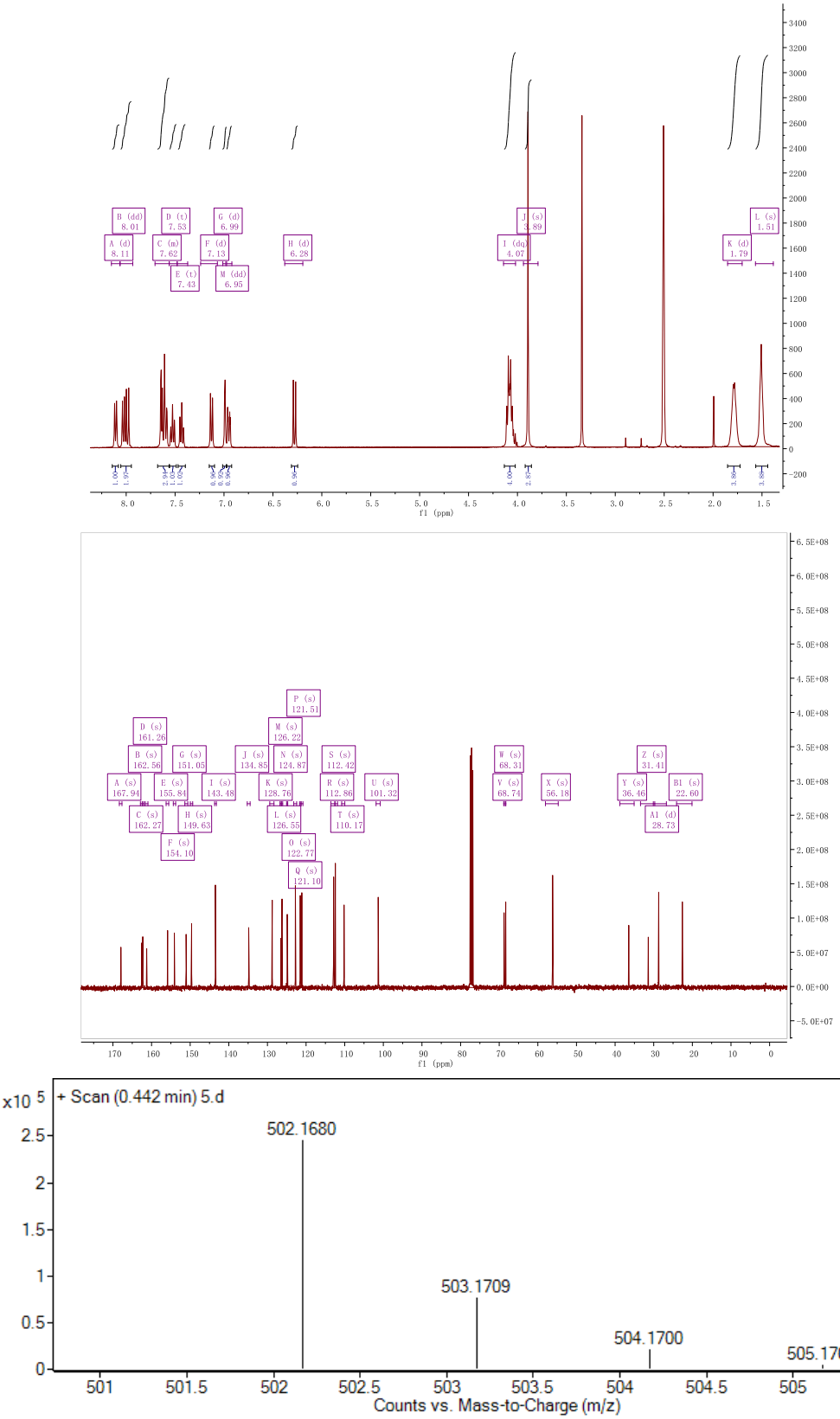
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6m**



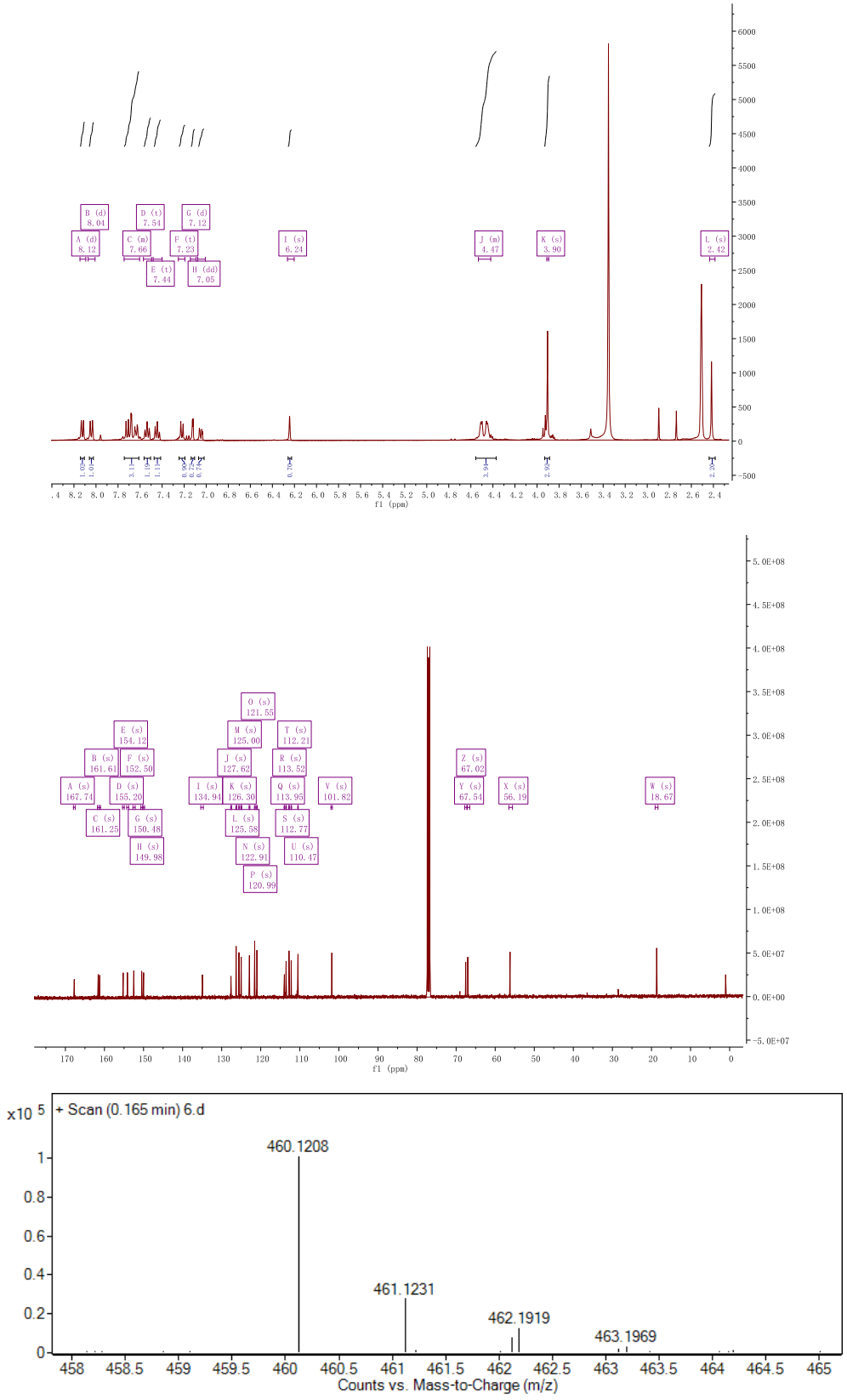
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6n**



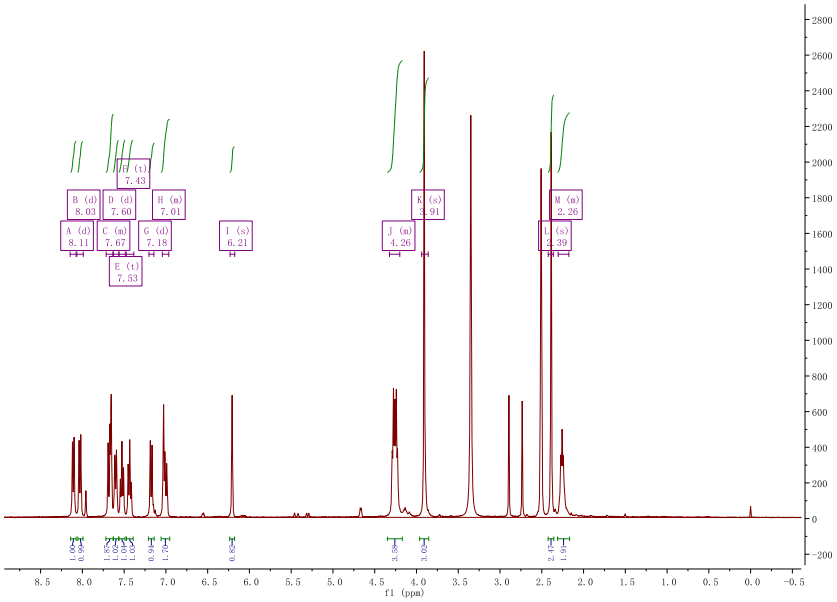
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6o**

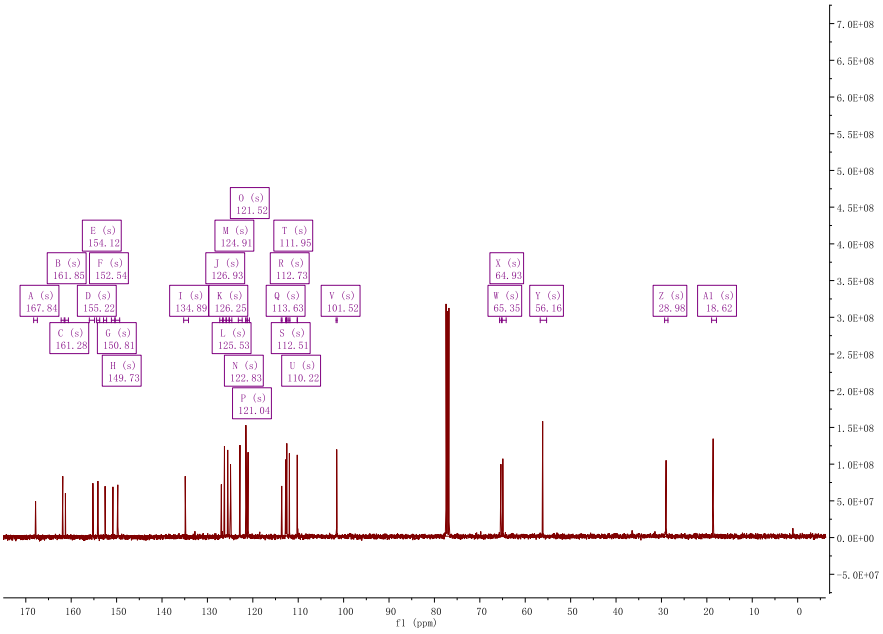


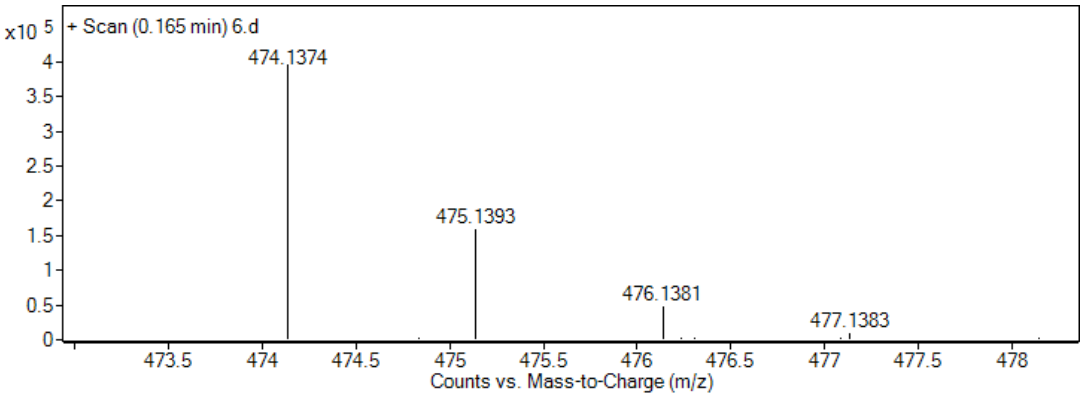
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6p**



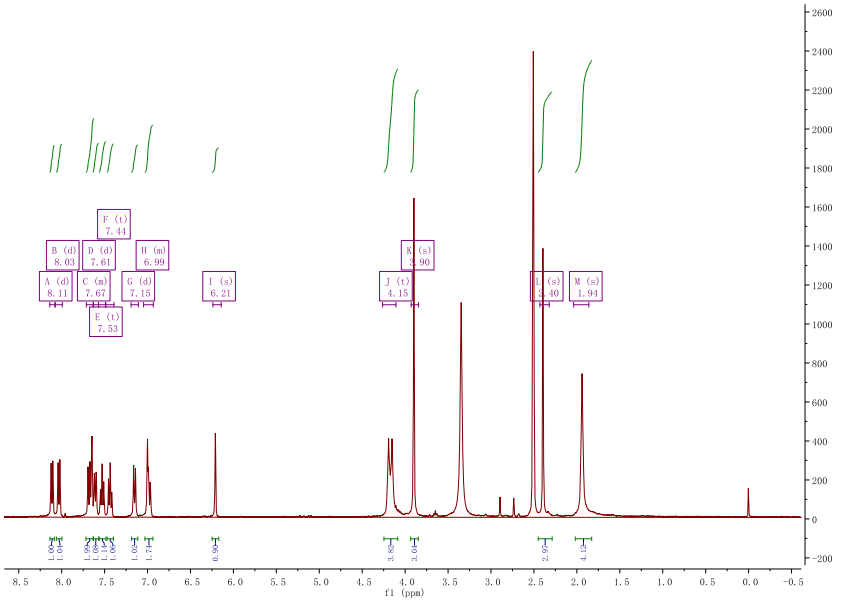
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6q**

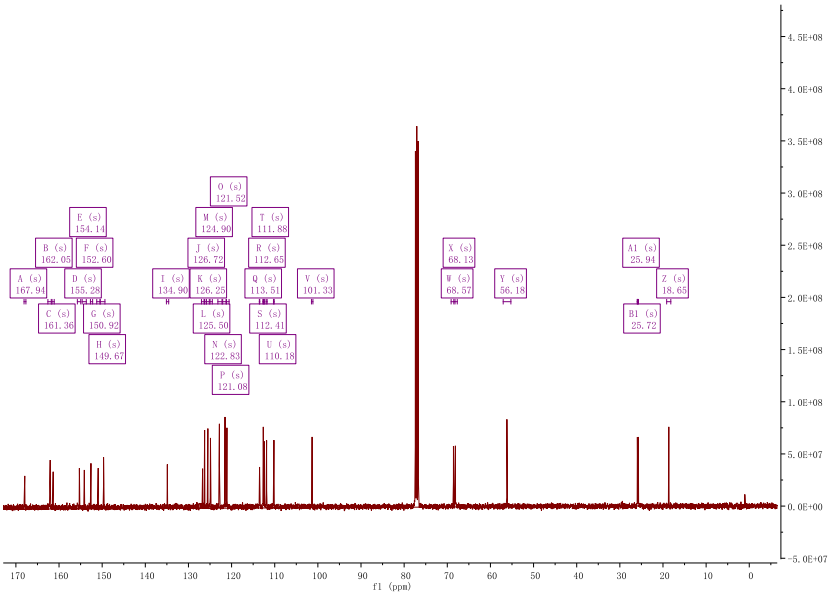


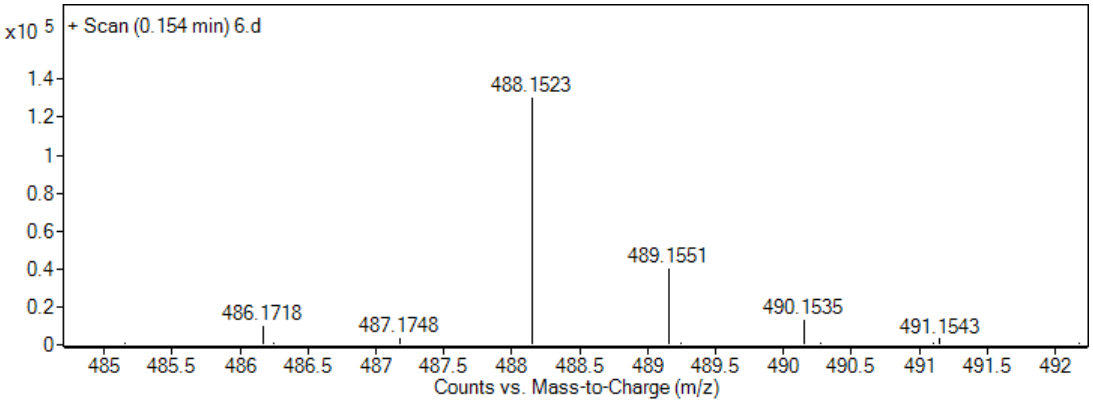




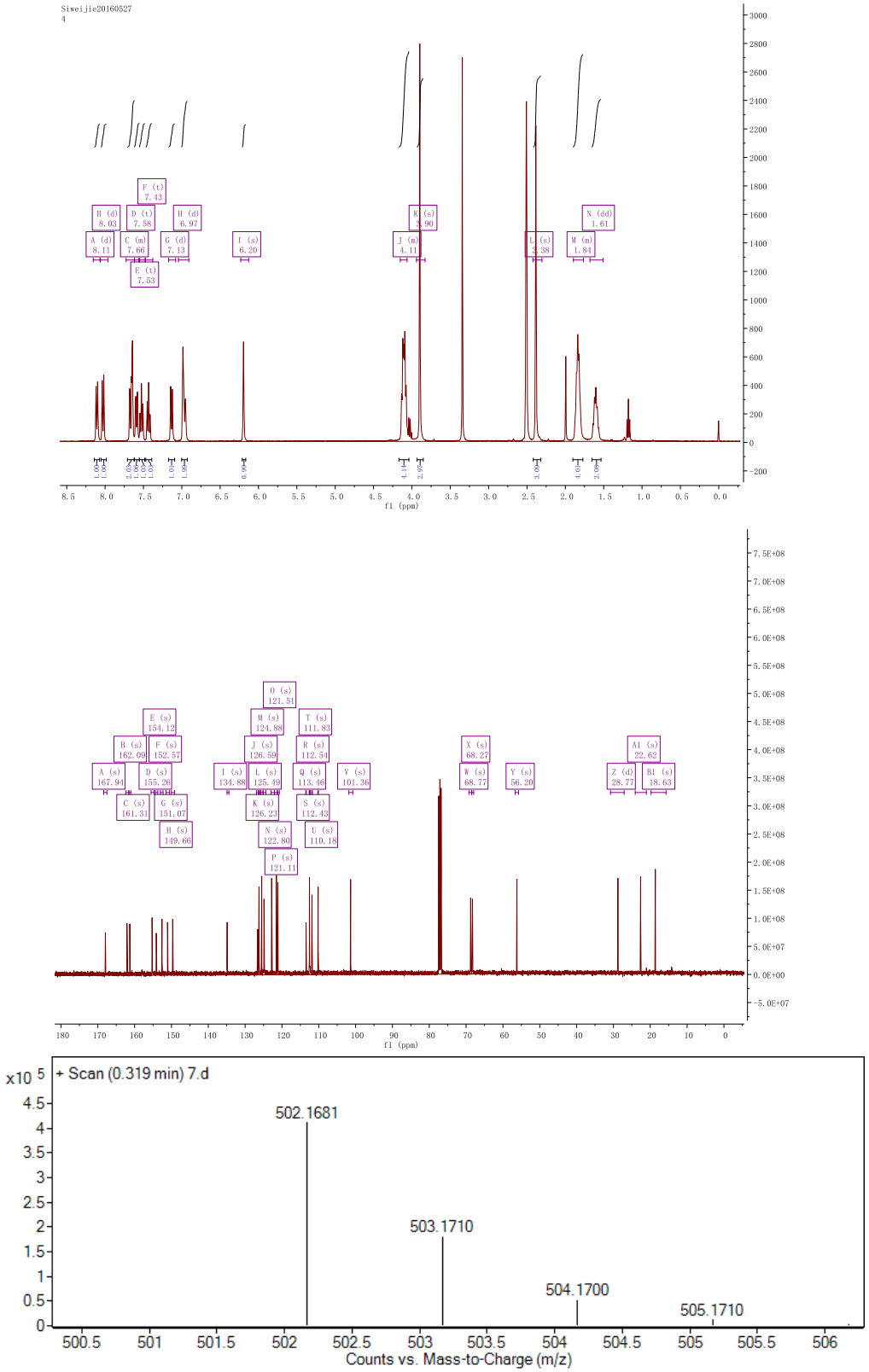
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6r**



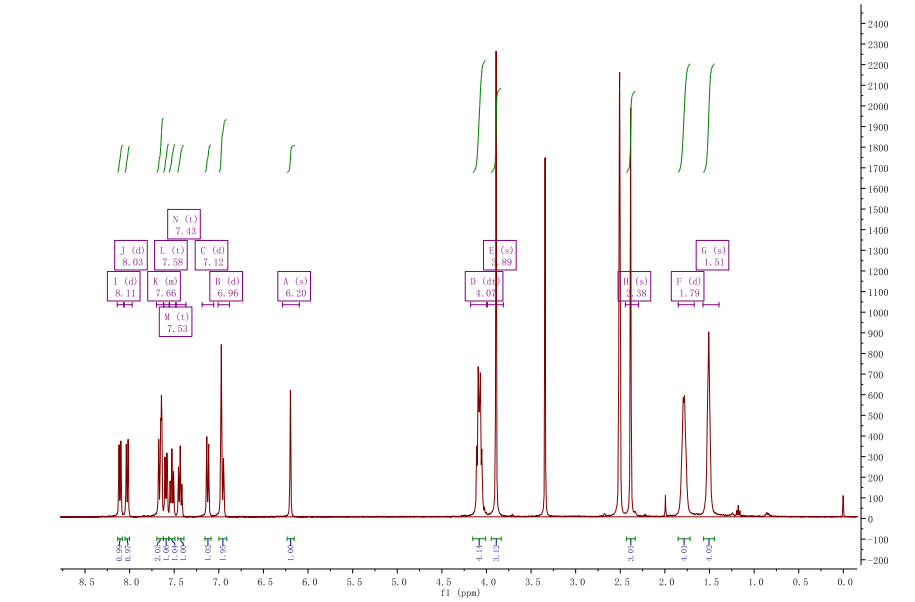


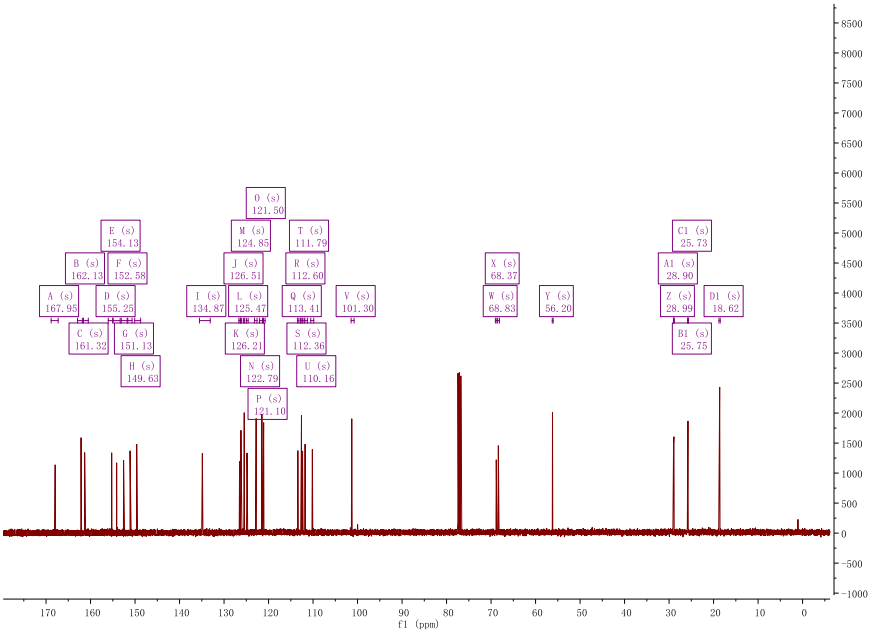


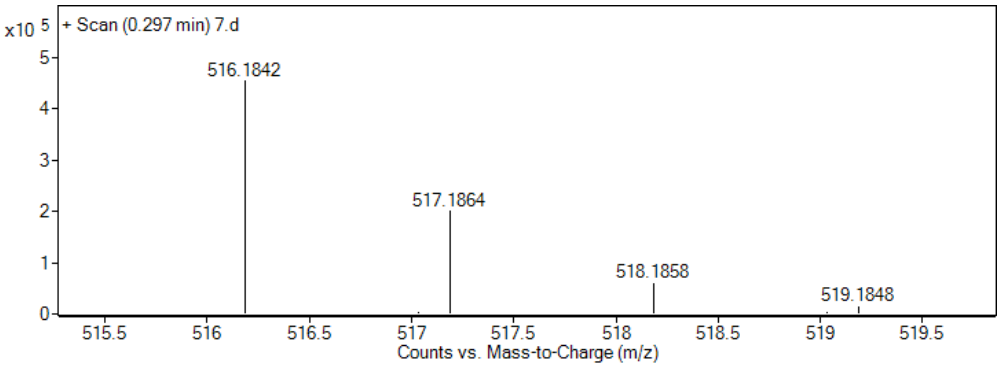
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6s**



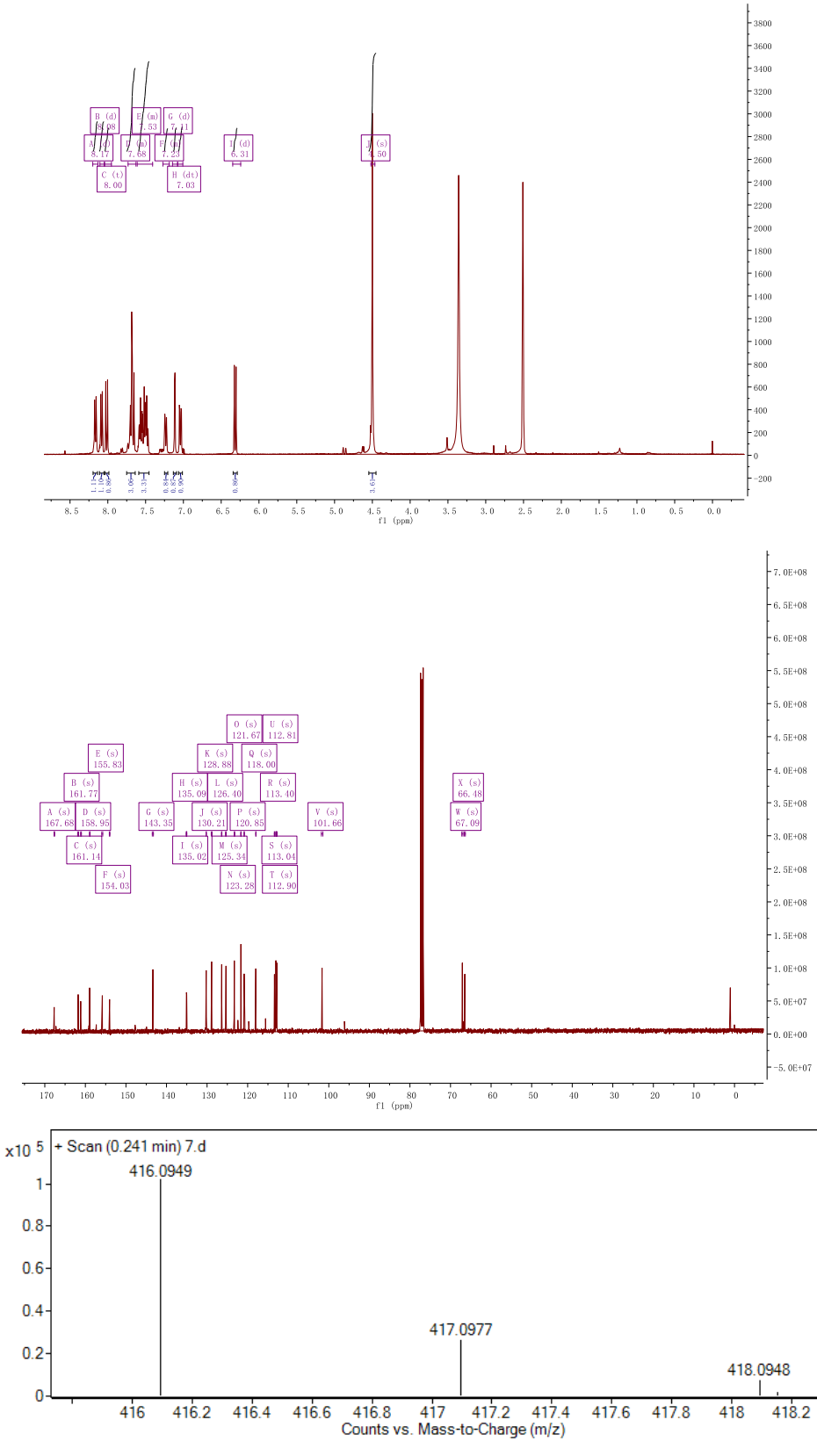
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6t**



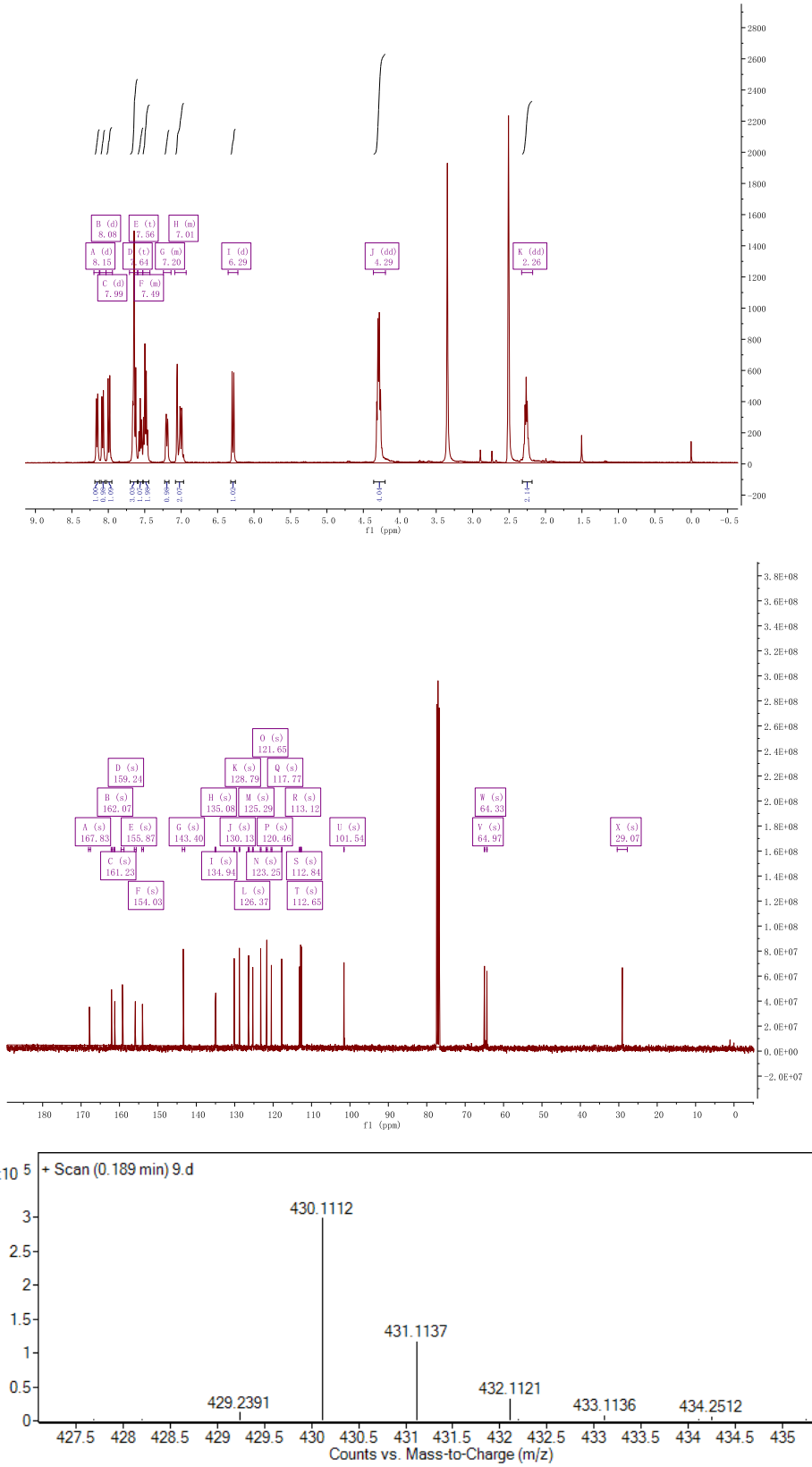




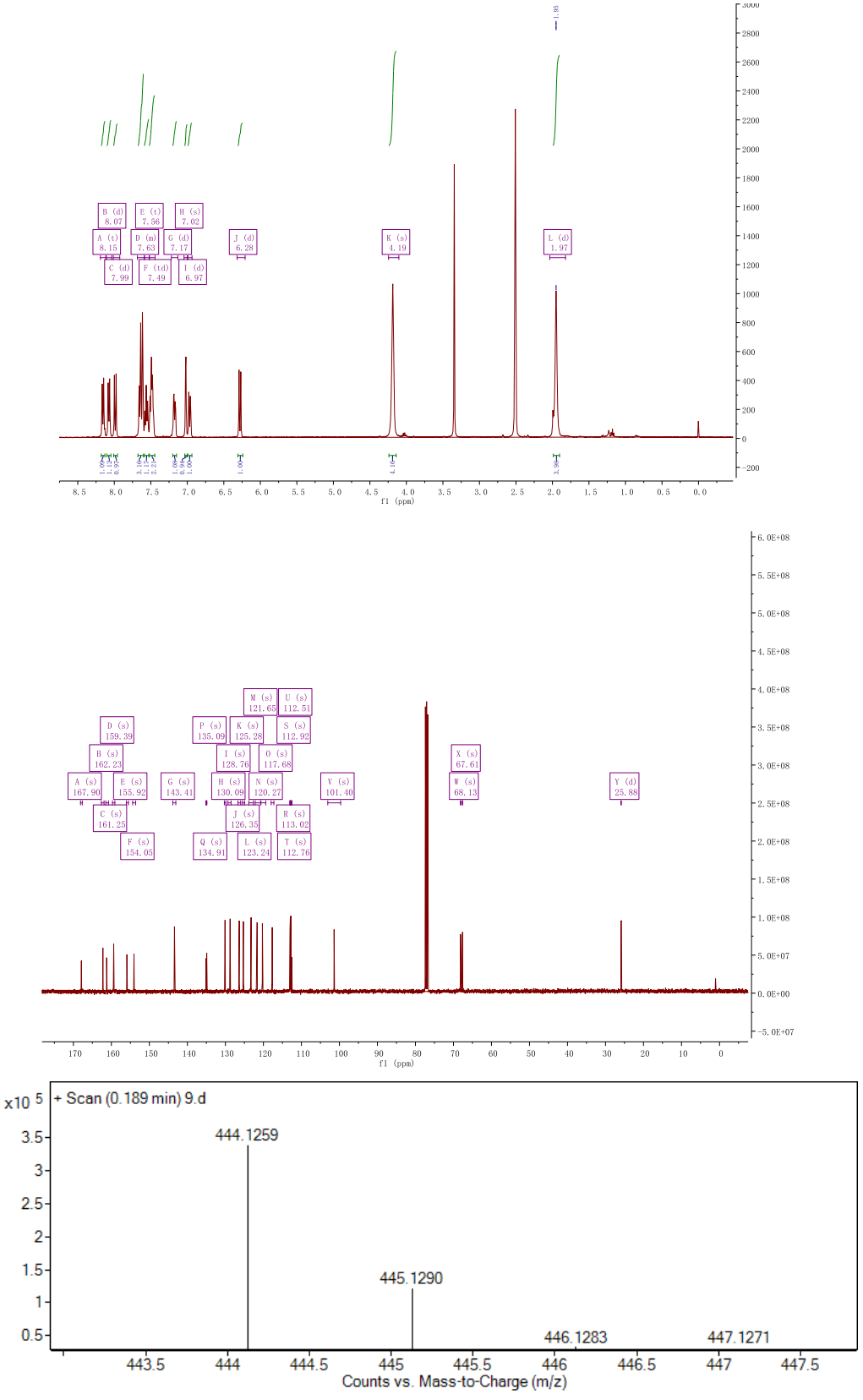
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6u**



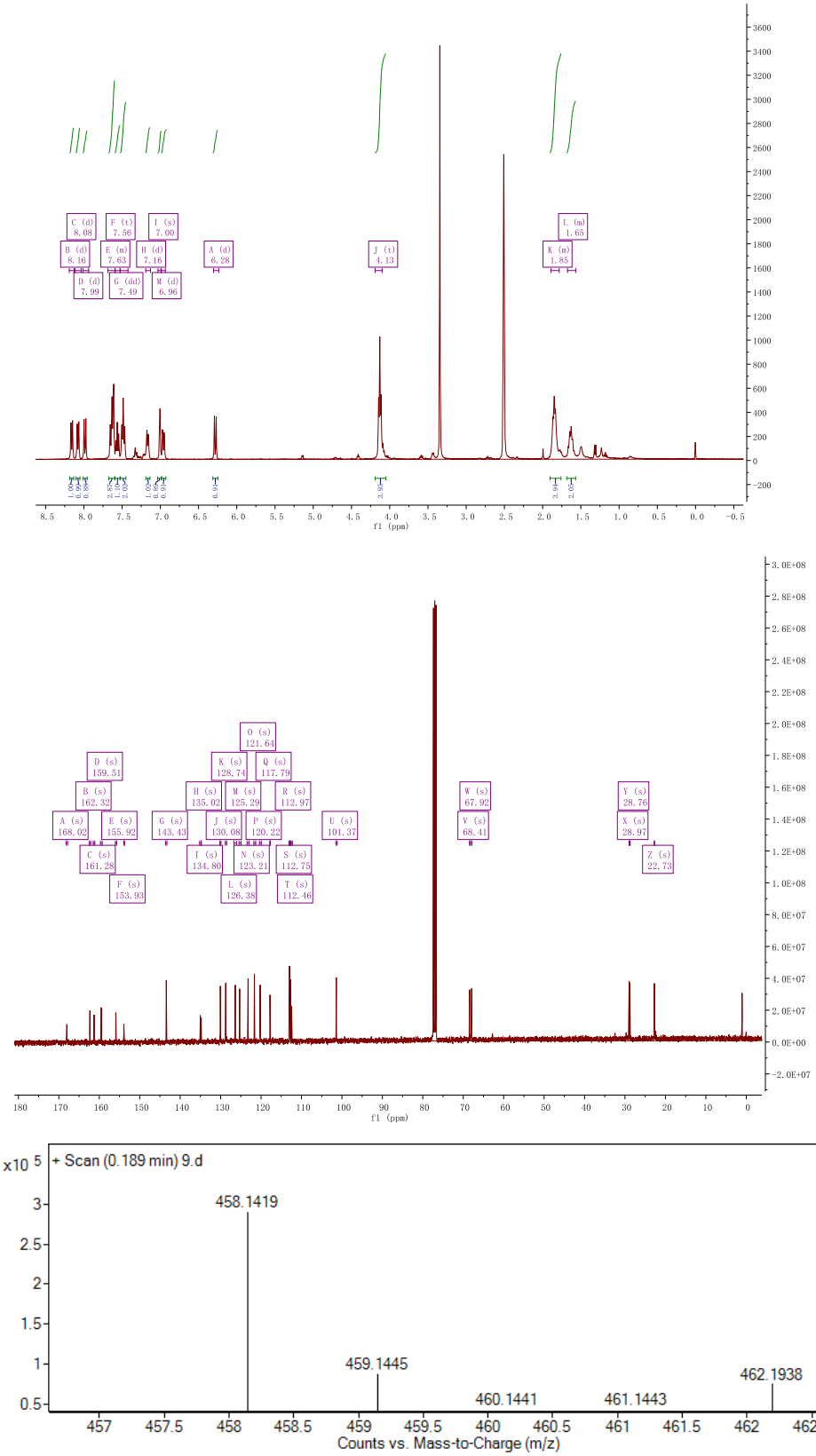
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6v**



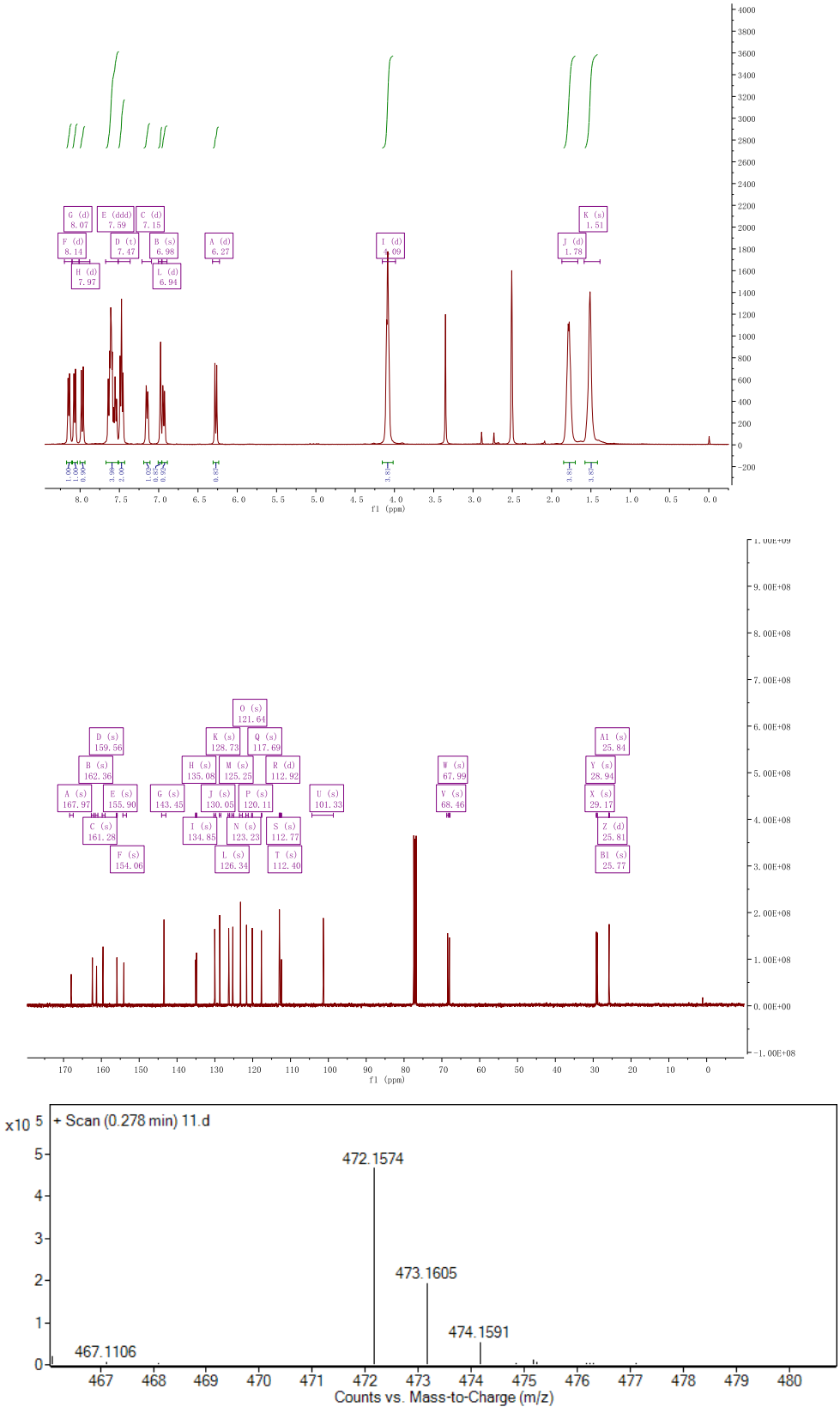
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6w**



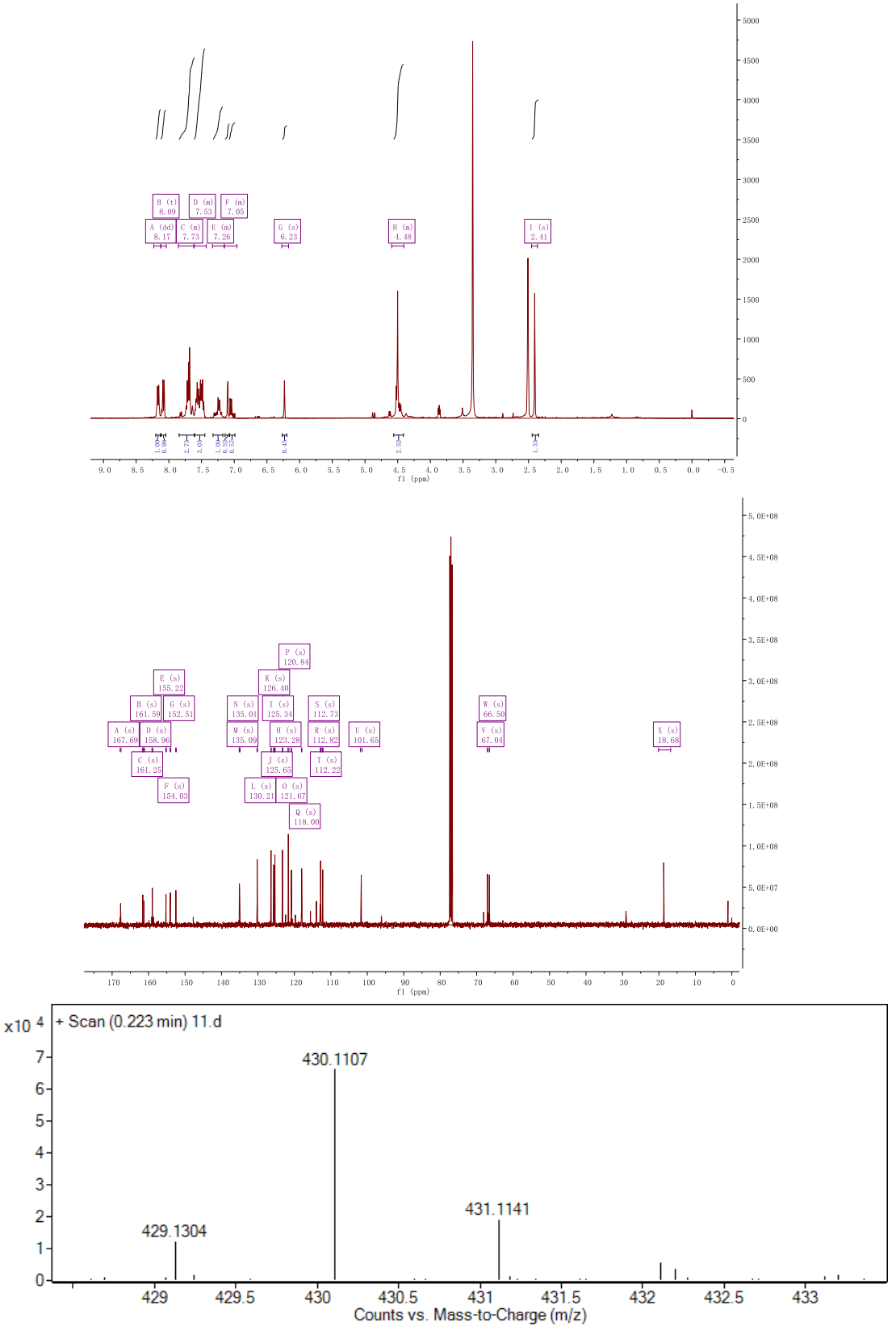
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6x**



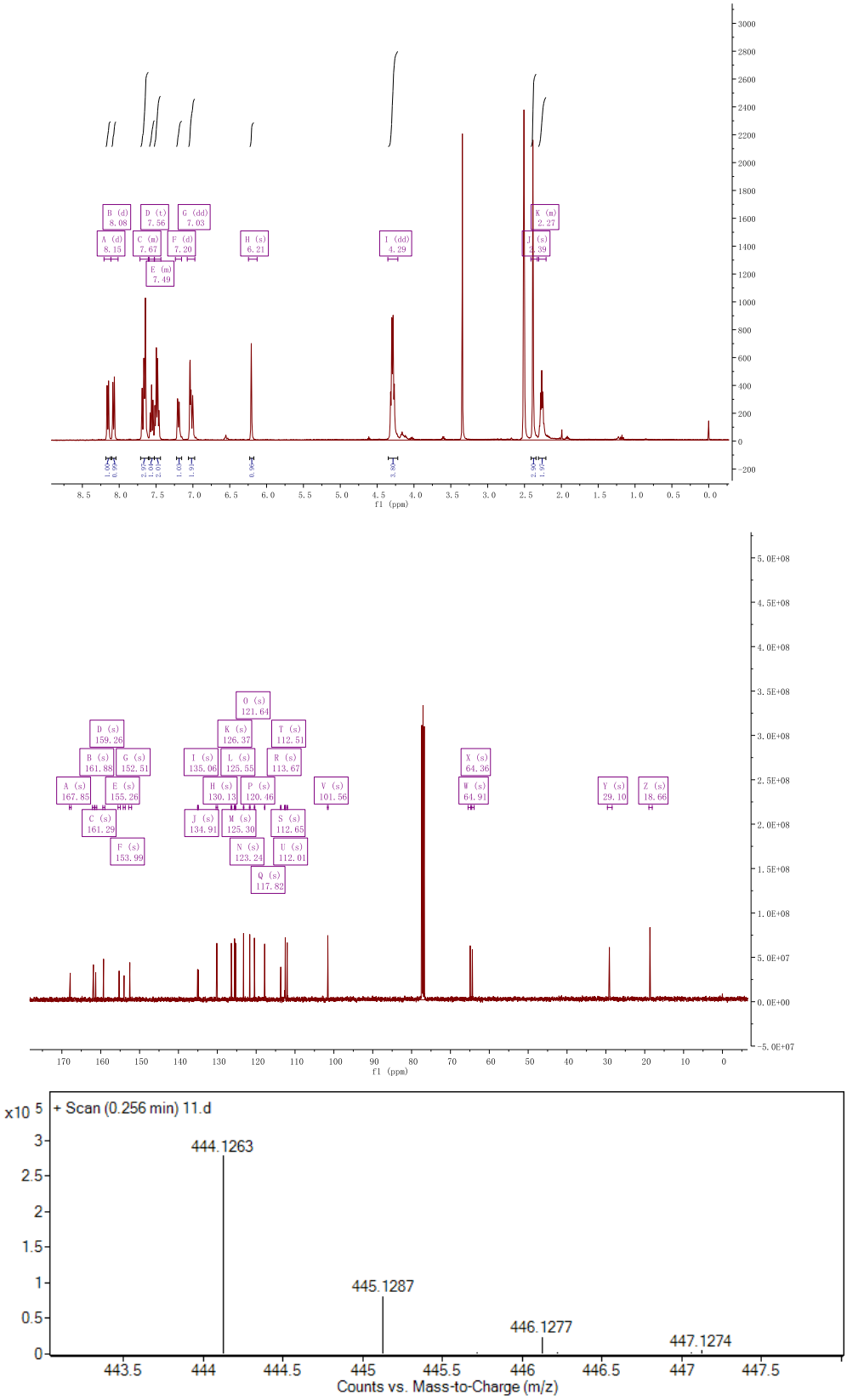
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6y**



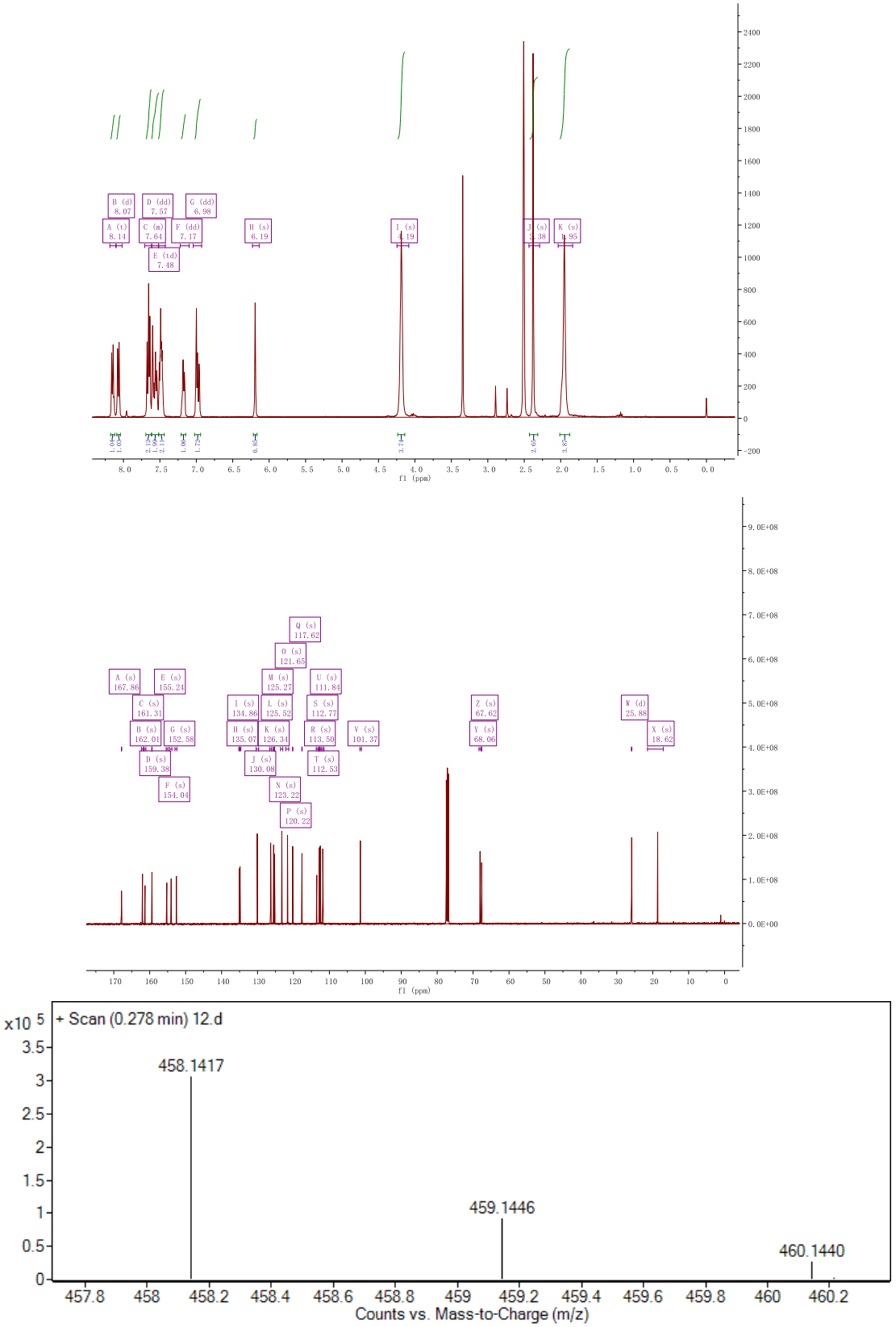
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6z**



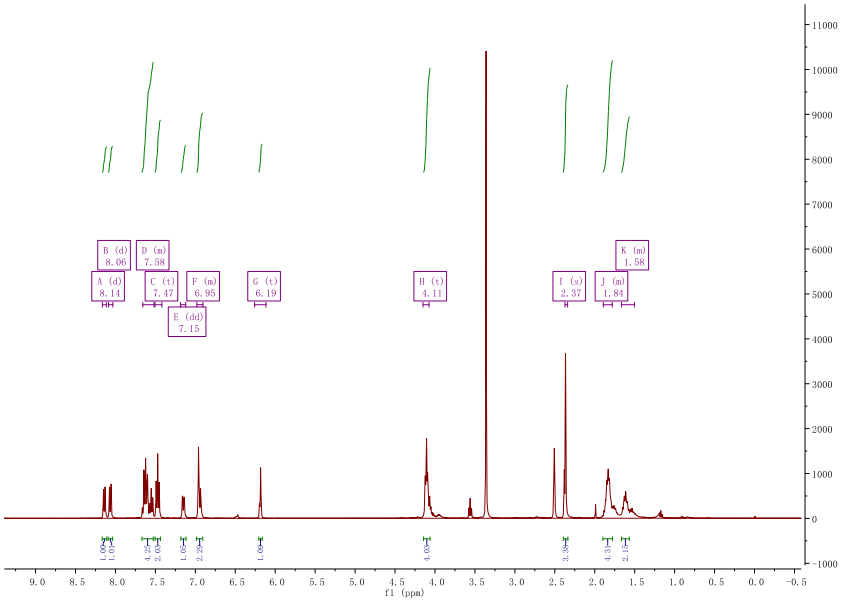
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6aa**

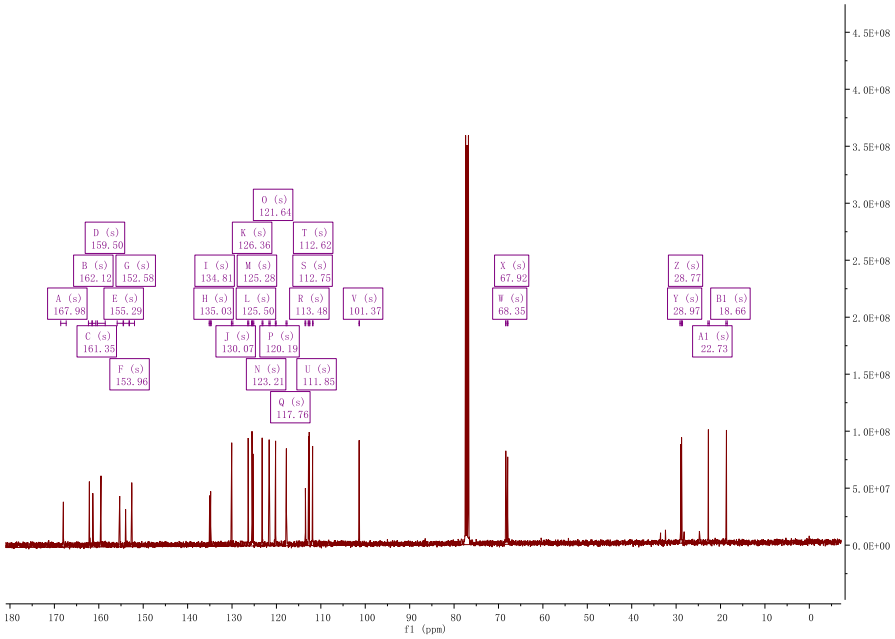


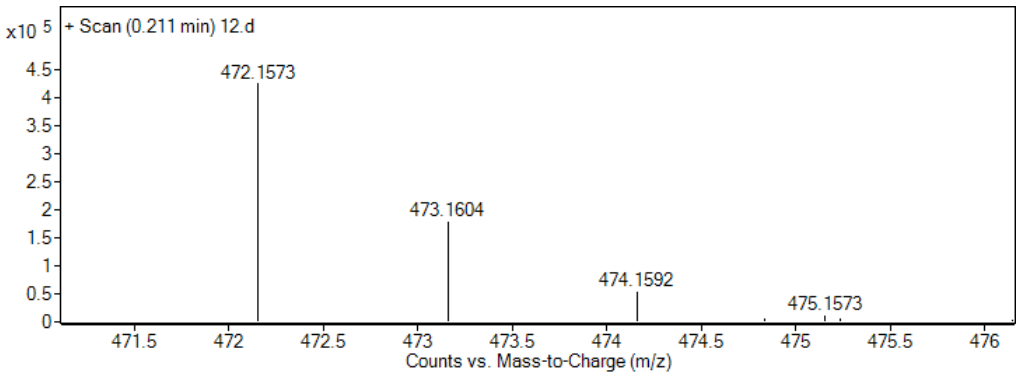
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6bb**



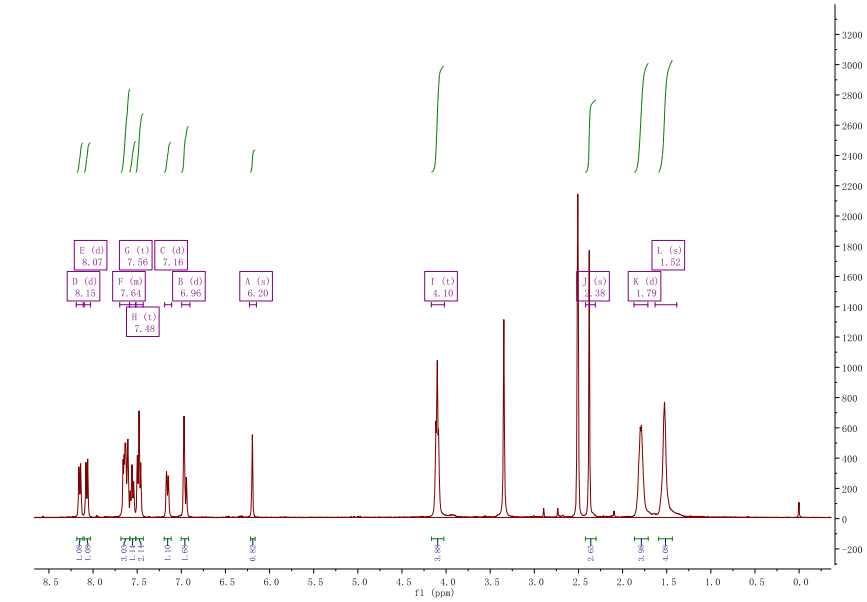
^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6cc**

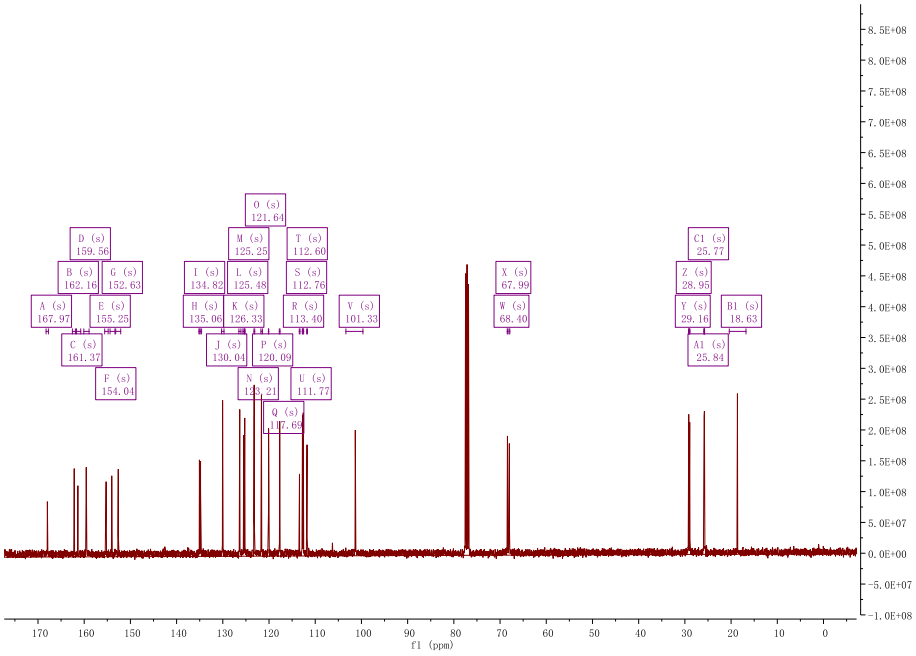


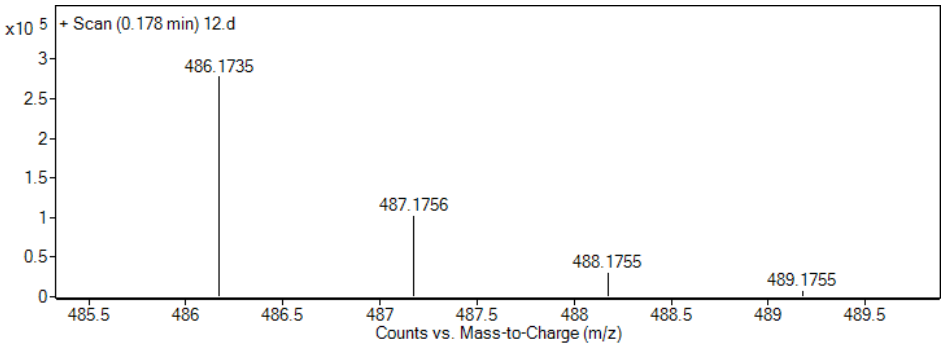




^{1}H NMR, ^{13}C NMR and HRMS spectra of the compound **6dd**


E (d) 8.07
G (t) 7.56
C (d) 7.16
D (d) 8.15
F (m) 7.64
B (d) 6.96
A (s) 6.20
I (t) 4.10
J (s) 2.38
K (d) 1.79
L (s) 1.52
H (t) 7.48
f1 (ppm)


O (s) 121.64
M (s) 125.25
T (s) 112.60
D (s) 159.56
B (s) 162.16
G (s) 152.63
I (s) 134.82
L (s) 125.48
S (s) 112.76
X (s) 67.99
C1 (s) 25.77
Z (s) 28.95
A (s) 167.97
E (s) 155.25
H (s) 135.06
K (s) 126.33
R (s) 113.40
V (s) 101.33
W (s) 68.40
Y (s) 29.16
B1 (s) 18.63
C (s) 161.37
J (s) 130.04
P (s) 120.09
A1 (s) 25.84
F (s) 154.04
N (s) 123.21
U (s) 111.77
Q (s) 117.69
f1 (ppm)


x10 5
+ Scan (0.178 min) 12.d
486.1735
487.1756
488.1755
489.1755
Counts vs. Mass-to-Charge (m/z)