

Supplementary Material

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

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I. Data of key intermediates

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

White power; yield 74.2%; mp 233–235 °C; ^1H 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 $\text{C}_9\text{H}_6\text{O}_3$ (162.03).

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

Light yellow power; yield 87.6%; mp 187–188 °C; ^1H 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 $\text{C}_{10}\text{H}_8\text{O}_3$ (176.05).

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

White power; yield 67.1%; mp 223–225 °C; ^1H 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 $\text{C}_{13}\text{H}_9\text{NOS}$ (227.04).

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

White power; yield 73.4%; mp 172–174 °C; ^1H 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 $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}$ (257.05).

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

White power; yield 60.2%; mp 165–167 °C; ^1H 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 $\text{C}_{13}\text{H}_9\text{NOS}$ (227.04).

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

White power; yield 71.5%; mp 131–133 °C; ^1H 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, $\text{CH}_2\text{-Br}$).

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

White power; yield 74.2%; mp 115–116 °C; ^1H 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, $\text{CH}_2\text{-Br}$), 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; ^1H 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, $\text{CH}_2\text{-Br}$), 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; ^1H 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, CH₂), 3.57 (q, *J* 7.0 Hz, 2H, CH₂-Br), 1.94–1.83 (m, 2H, CH₂), 1.83–1.72 (m, 2H, CH₂), 1.55 (dq, *J* 14.7, 7.8 Hz, 2H, CH₂).

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

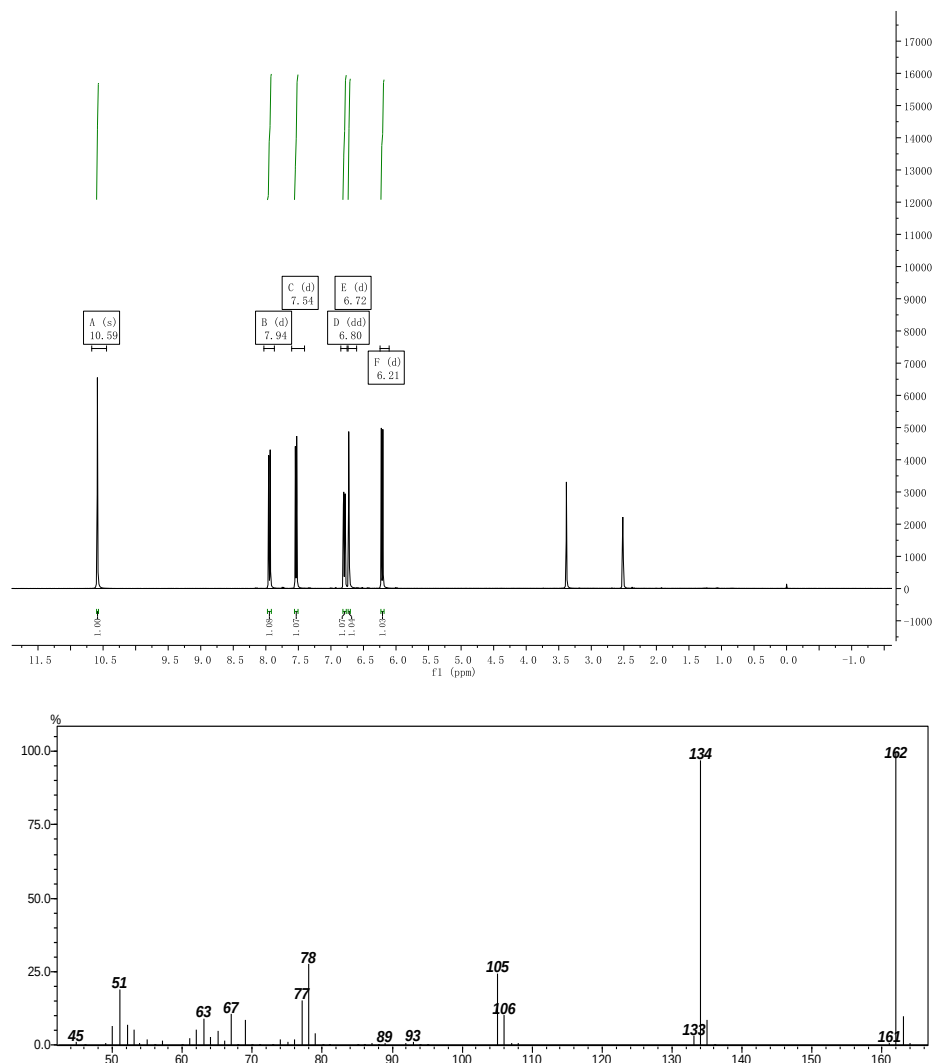
Grey Powder; yield 85.2%; mp 95–96 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.11 (d, *J* 7.9 Hz, 1H, Benzothiazole-4-H), 8.02 (dd, *J* 8.3, 6.5 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.56–7.49 (m, 1H, Benzothiazole-5-H), 7.46–7.40 (m, 1H, Benzothiazole-6-H), 7.11 (d, *J* 8.8 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.07 (t, *J* 6.4 Hz, 2H, CH₂), 3.55 (t, *J* 6.7 Hz, 2H, CH₂-Br), 1.90–1.66 (m, 4H, 2xCH₂), 1.53–1.30 (m, 4H, 2xCH₂).

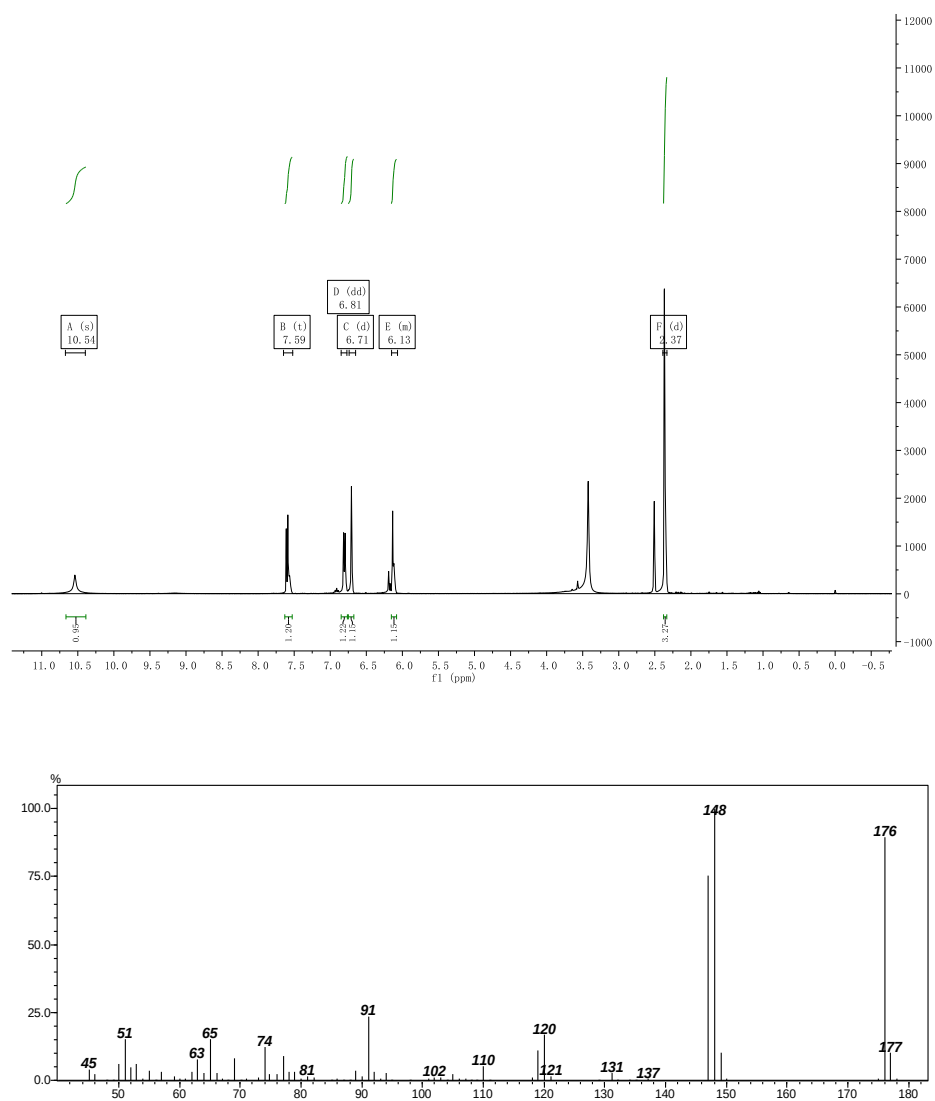
II. Crystallographic data of compound **6v**

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

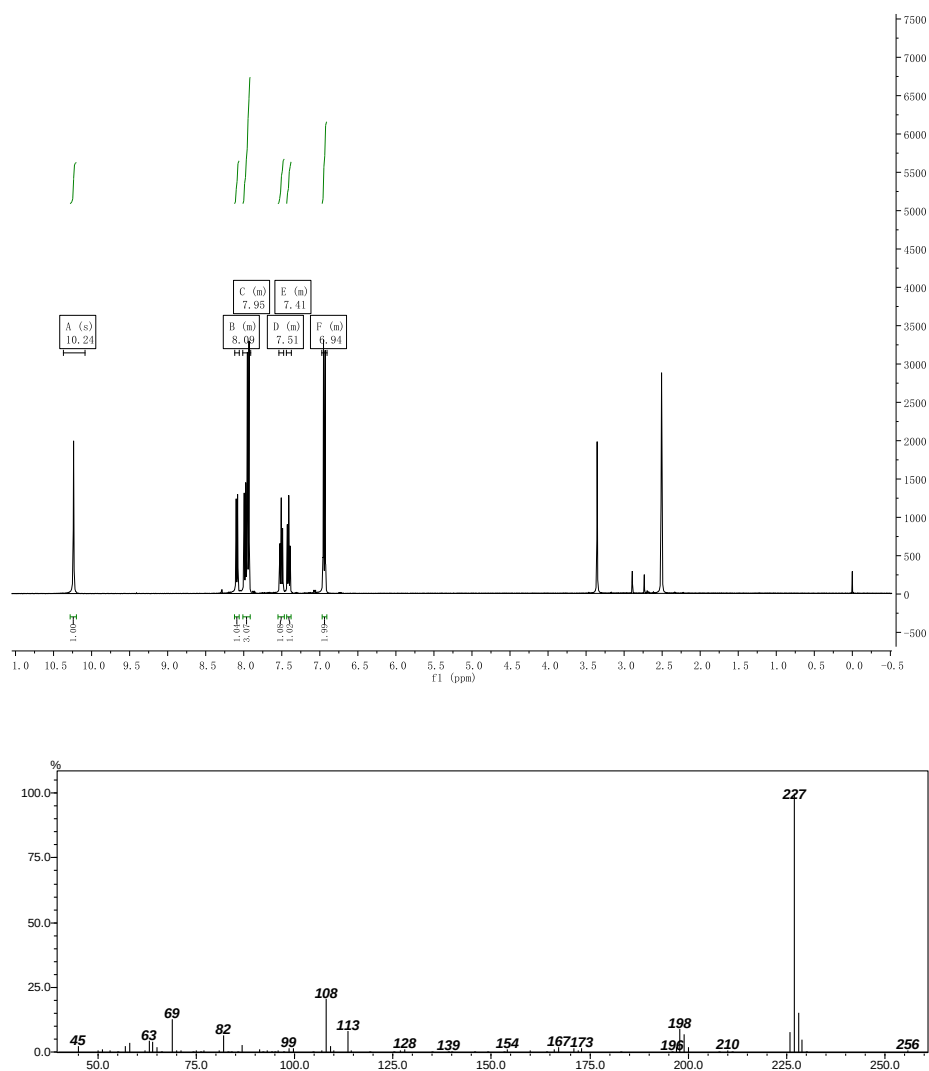
Chemical formula	C ₂₅ H ₁₉ NO ₄ S
Formula weight	429.47
Temperature[K]	100.00(10)
Crystal system	triclinic
Space group	P1
<i>a</i> [Å]	6.5984(9)
<i>b</i> [Å]	7.2742(12)
<i>c</i> [Å]	22.5363(19)
α [°]	90.238(10)
β [°]	91.143(9)
γ [°]	115.337(15)
<i>V</i> [Å ³]	977.4(3)
<i>Z</i>	2
ρ (calculated)[g/cm ³]	1.459
μ [mm ⁻¹]	0.201
<i>F</i> (000)	448
Crystal size [mm ³]	0.11 × 0.12 × 0.13
Colour,shape	Colourless, block
Radiation [Å]	MoK α (λ = 0.71073)
Theta Min-Max [°]	2.7, 26.4
<i>h,k,l</i>	-8 ≤ <i>h</i> ≤ 6, -8 ≤ <i>k</i> ≤ 9, -23 ≤ <i>l</i> ≤ 28
Reflections collected	7766
Independent reflections	4000
Data/restraints/parameters	2947/12/293
Goodness-of-fit	1.097
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0806, <i>wR</i> ₂ = 0.1916
Final R indexes [all data]	<i>R</i> ₁ = 0.1078, <i>wR</i> ₂ = 0.2119
Min. and Max. Resd. Dens [e Å ⁻³]	-0.49, 0.51

III Spectrograms of key intermediates and all title compounds

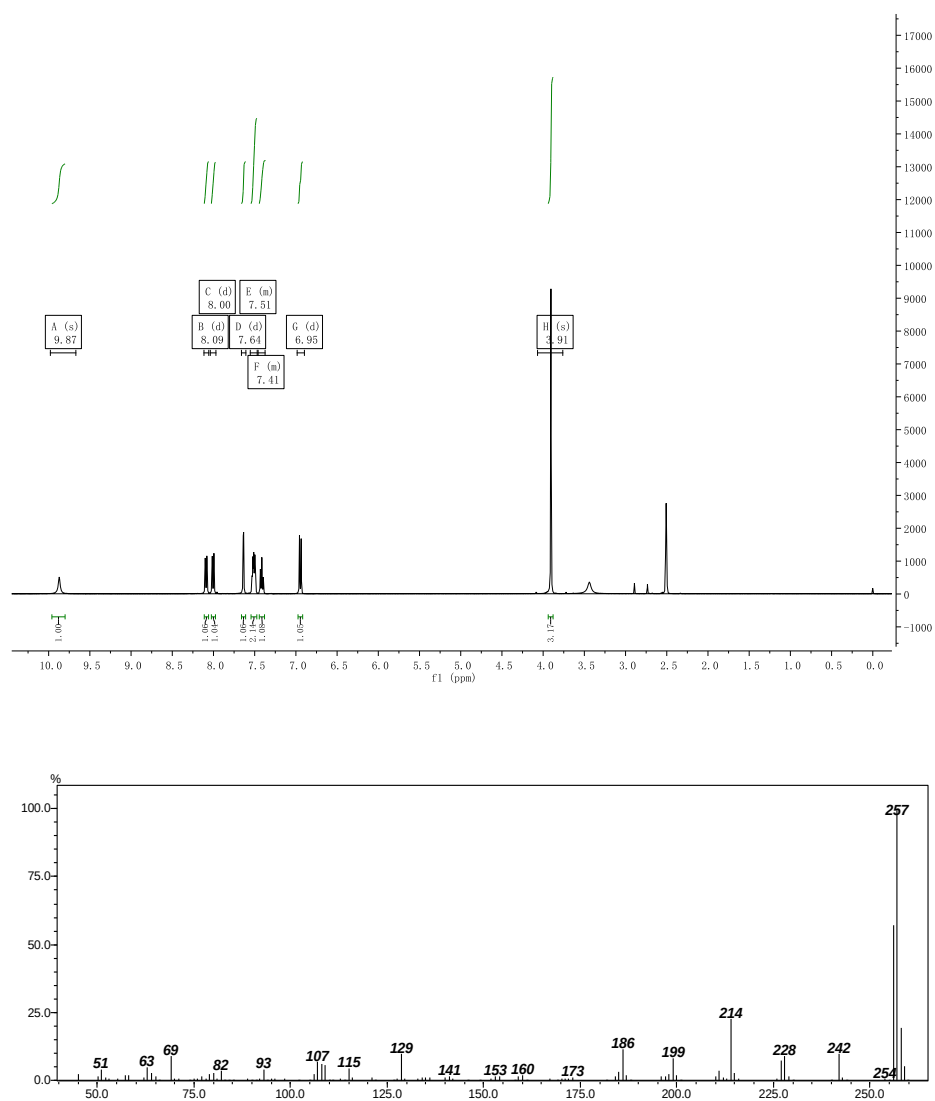
¹H NMR, and MS spectra of the compound **2a**¹H NMR, and MS spectra of the compound **2b**



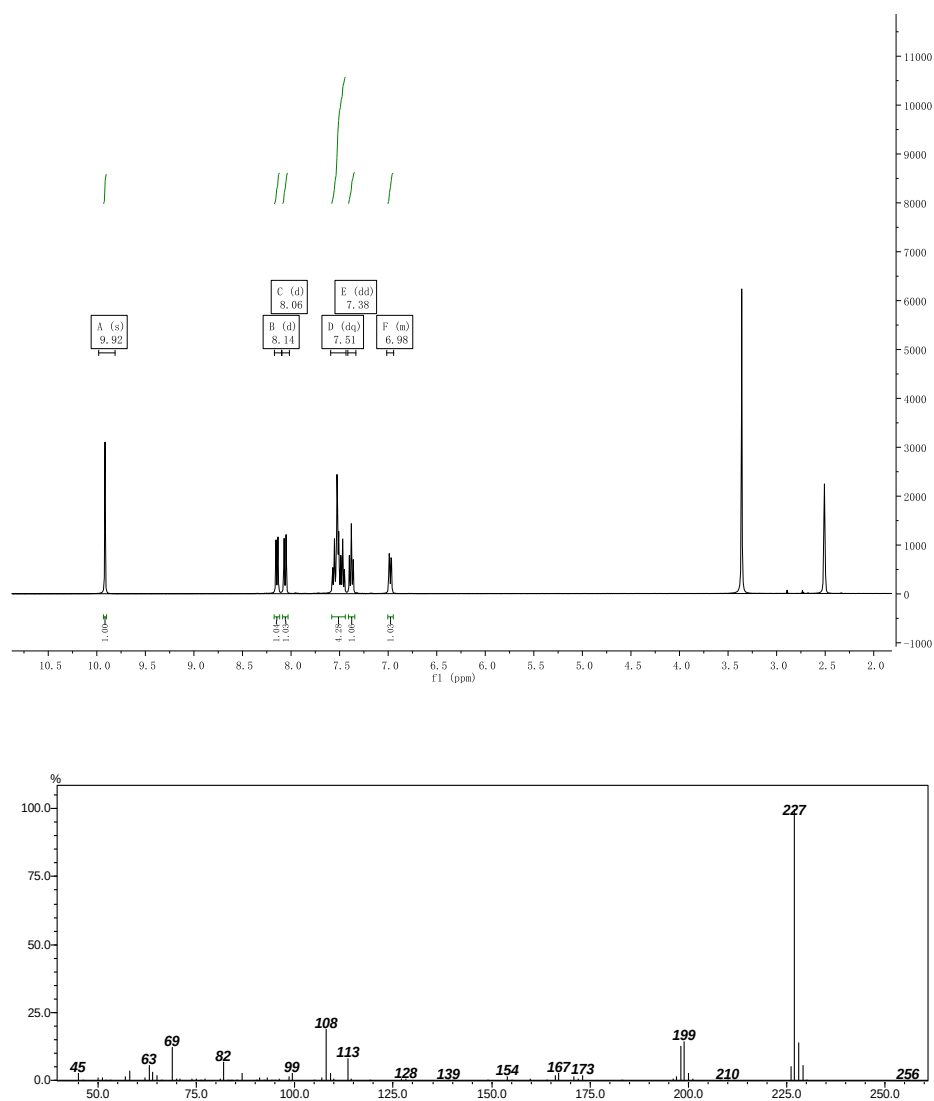
^1H NMR, and MS spectra of the compound **4a**



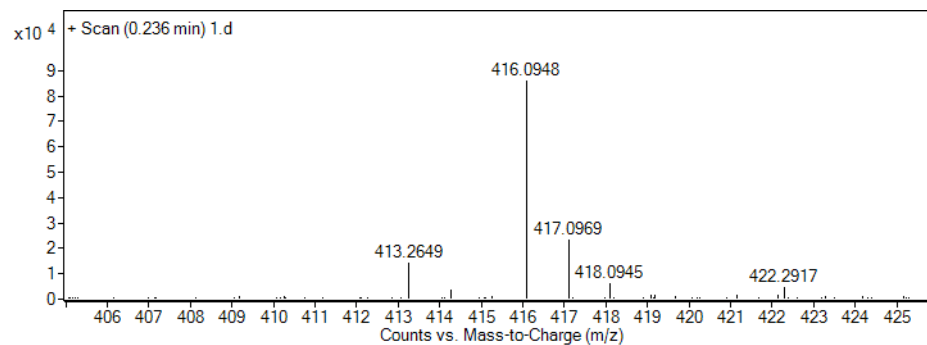
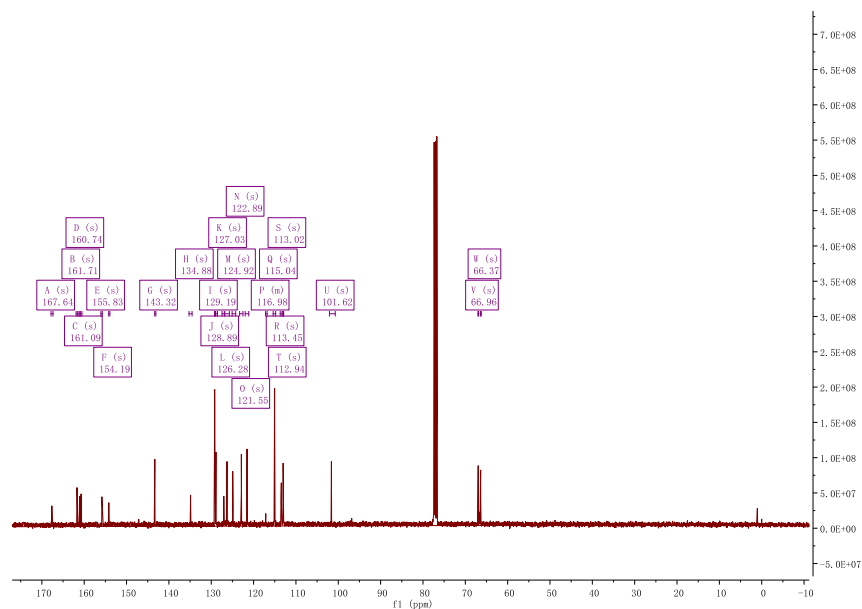
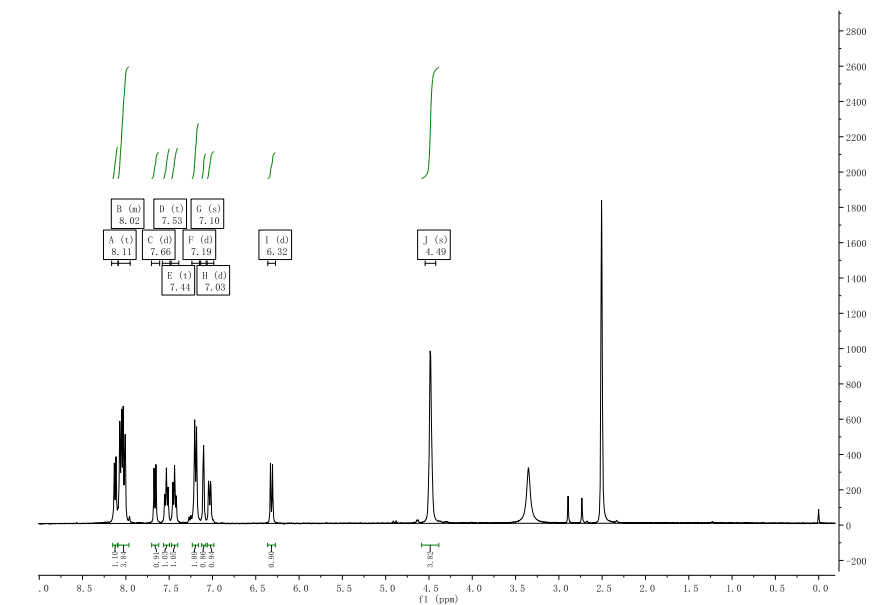
¹H NMR, and MS spectra of the compound **4b**



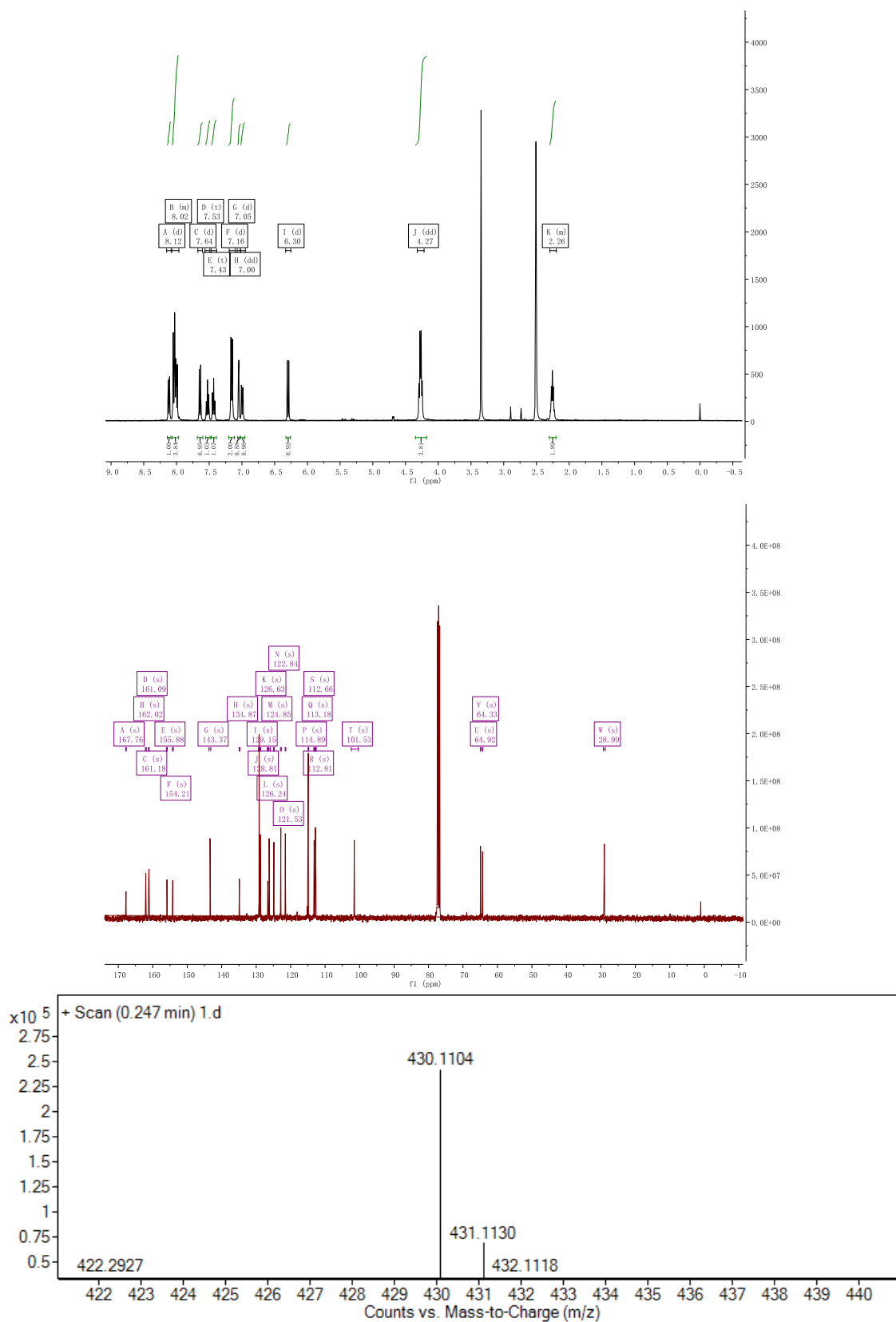
^1H NMR, and MS spectra of the compound **4c**



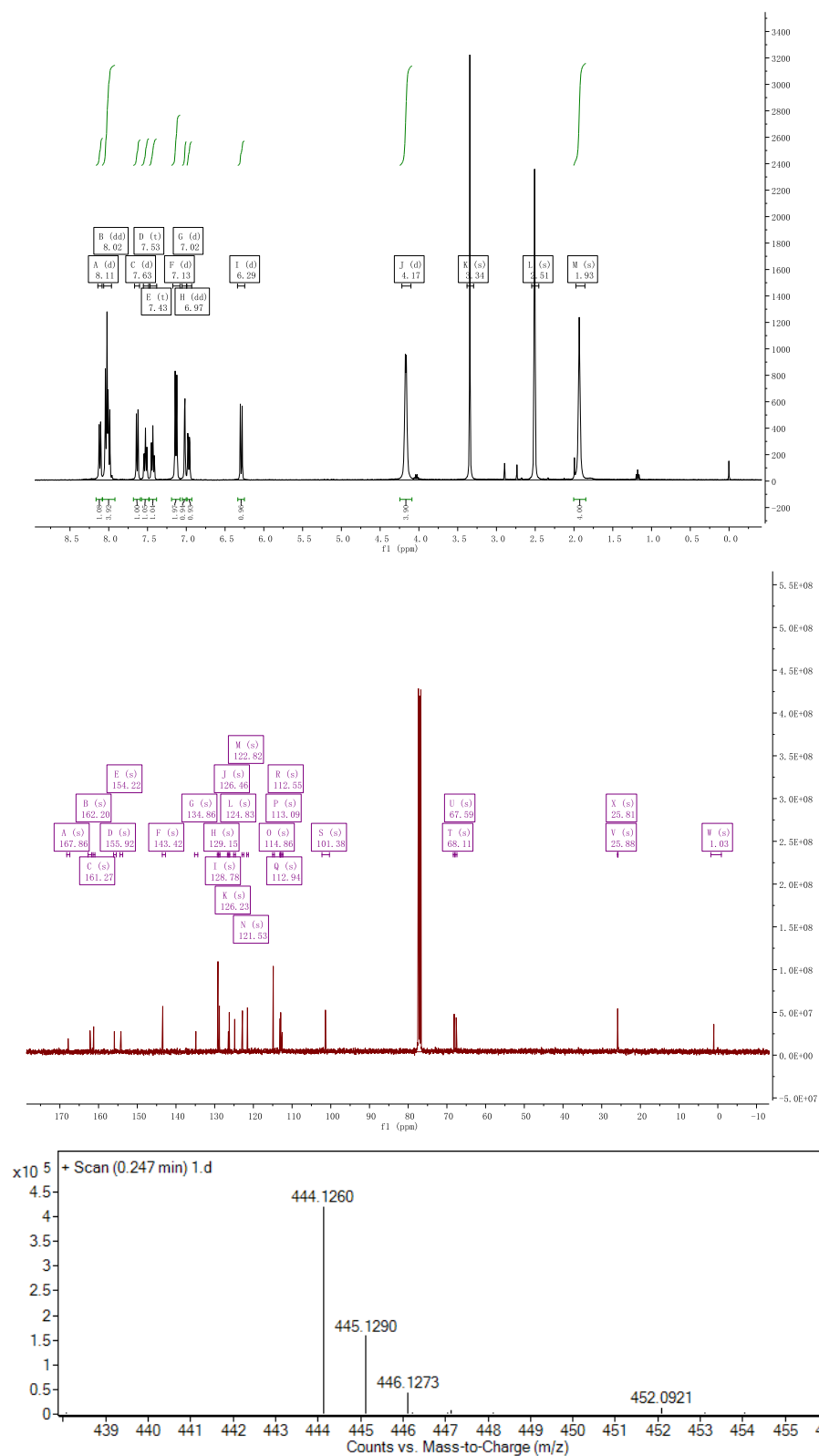
^1H NMR, ^{13}C NMR and HRMS spectra of the compound 6a



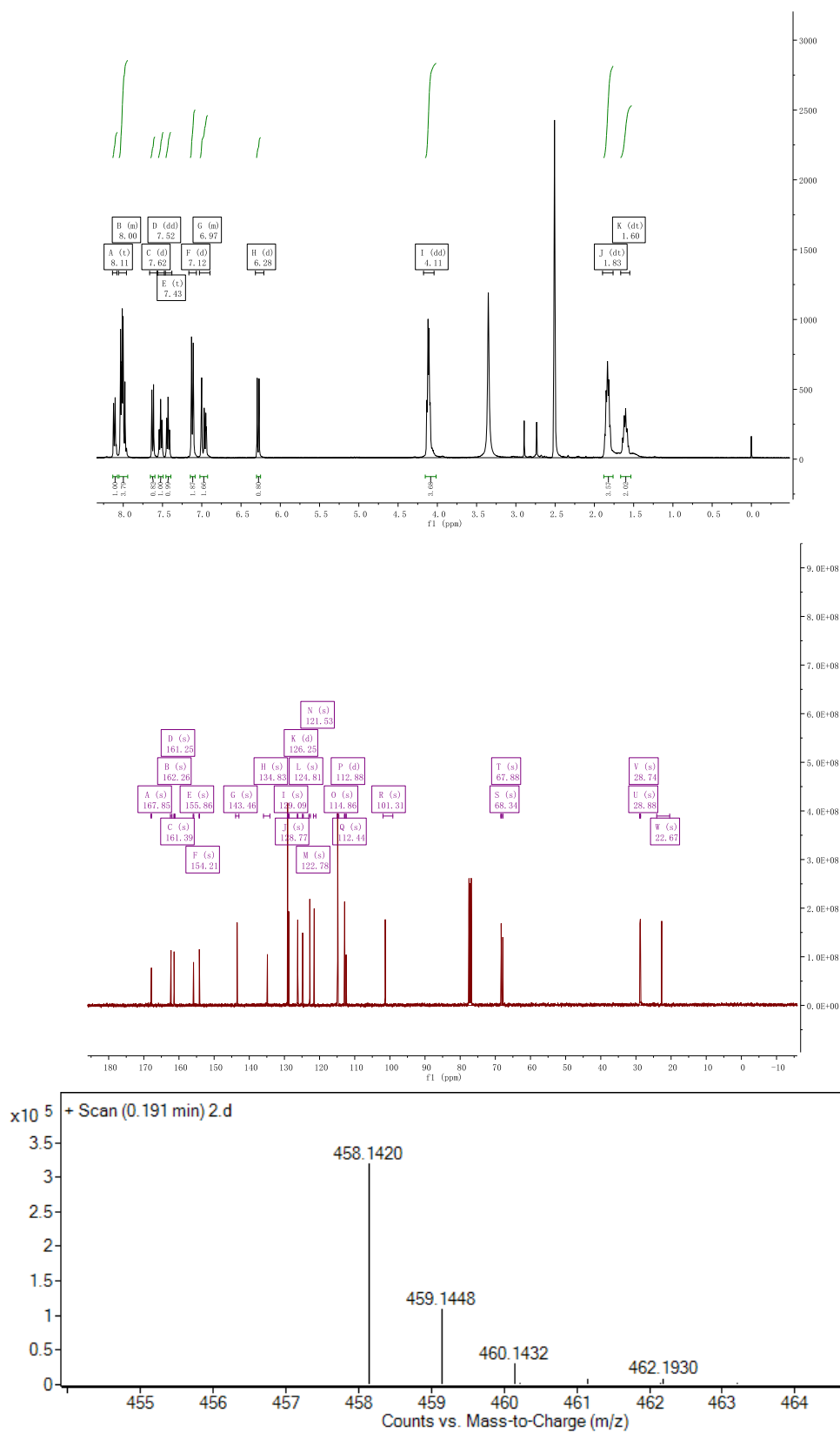
¹H NMR, ¹³C NMR and HRMS spectra of the compound **6b**



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

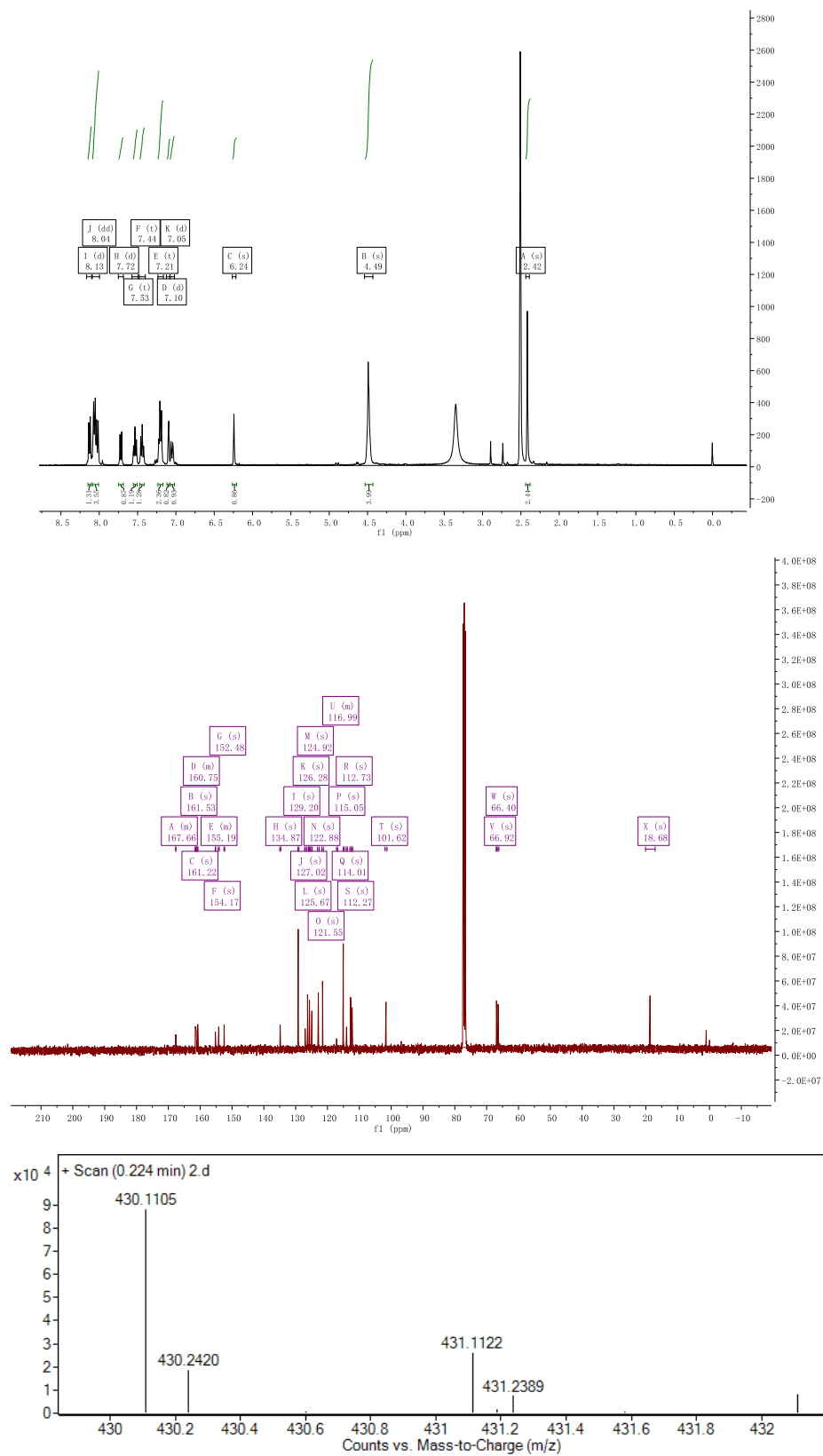


^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6d**

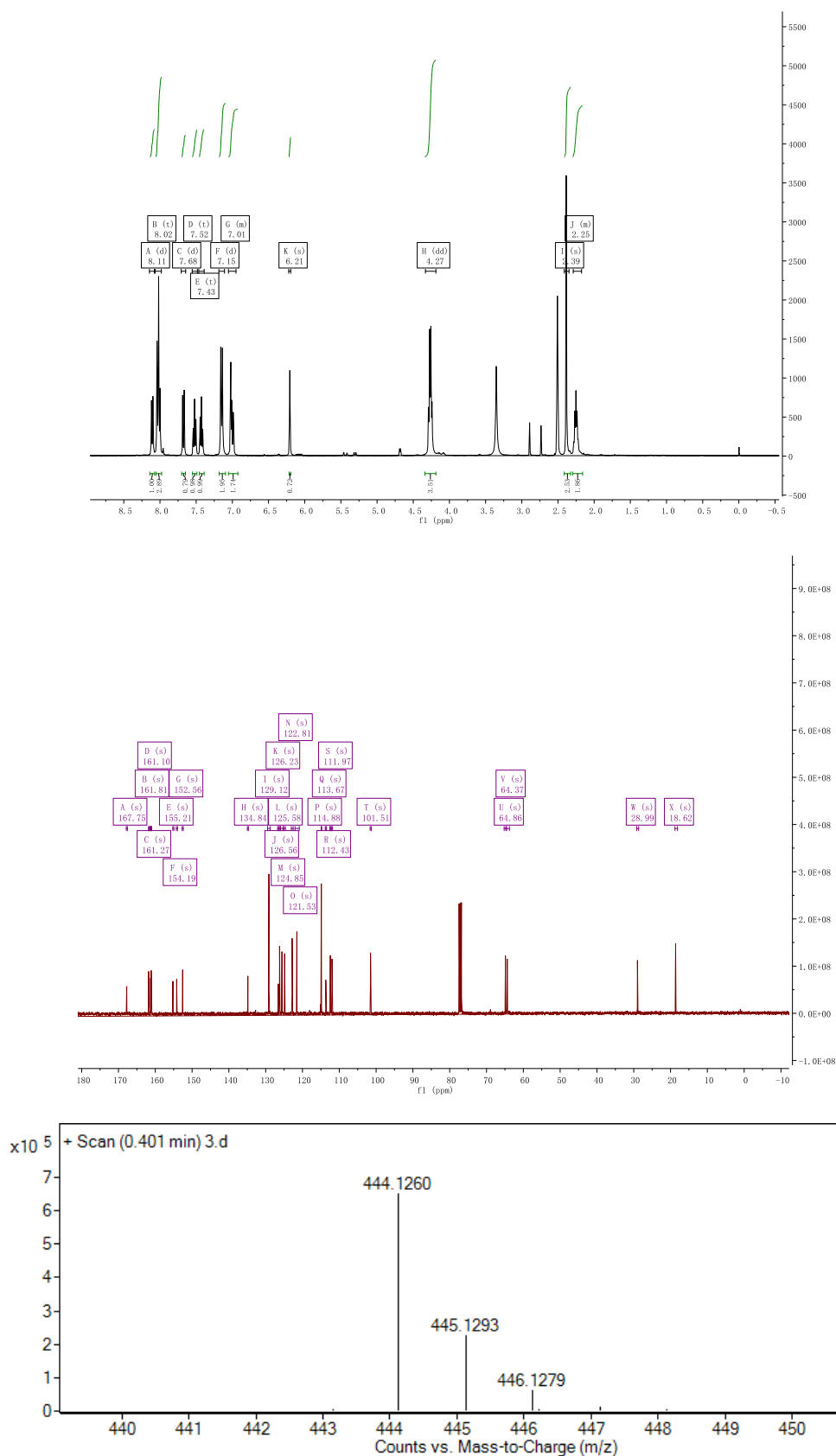


¹H NMR, ¹³C NMR and HRMS spectra of the compound **6e**

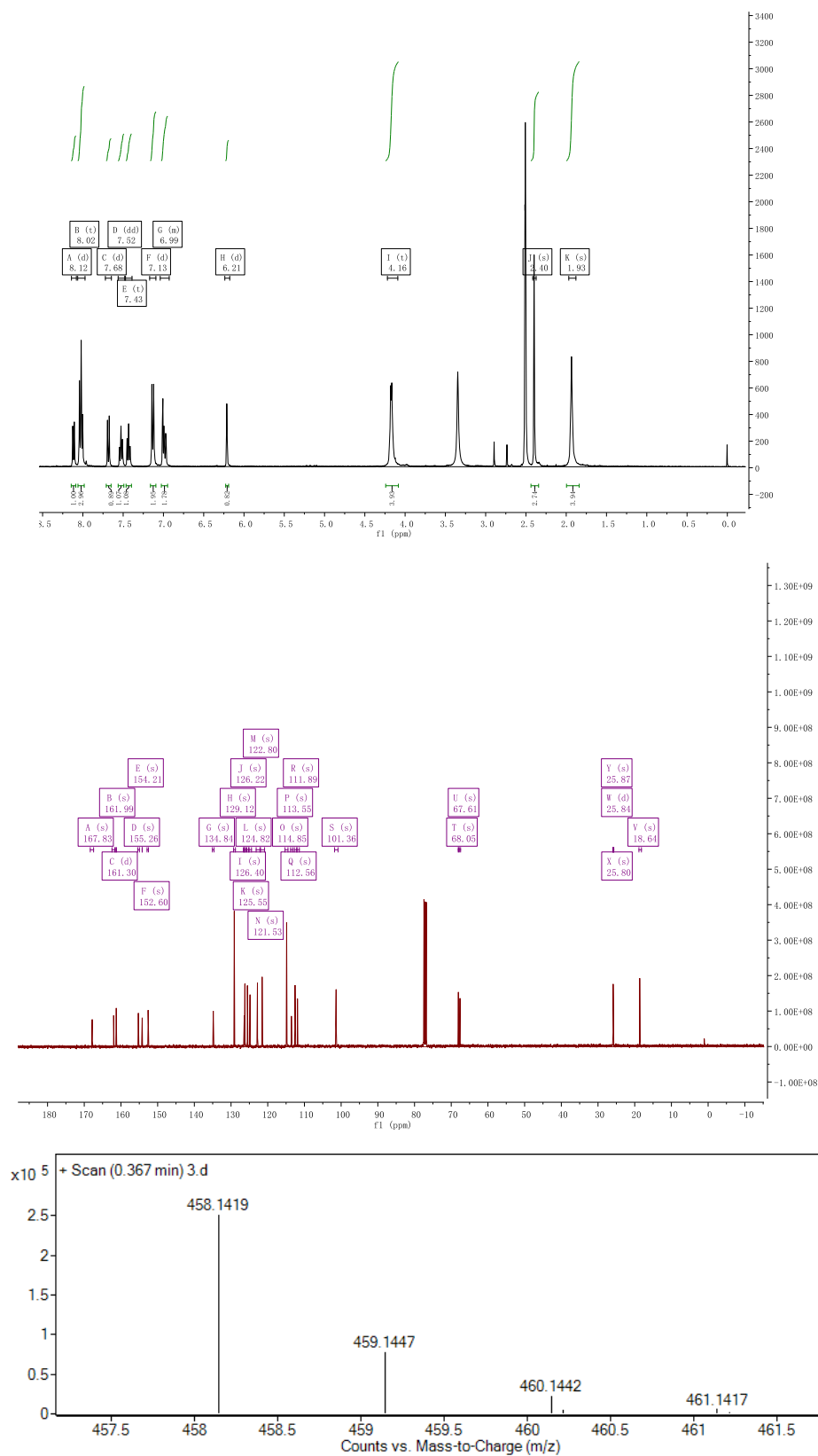




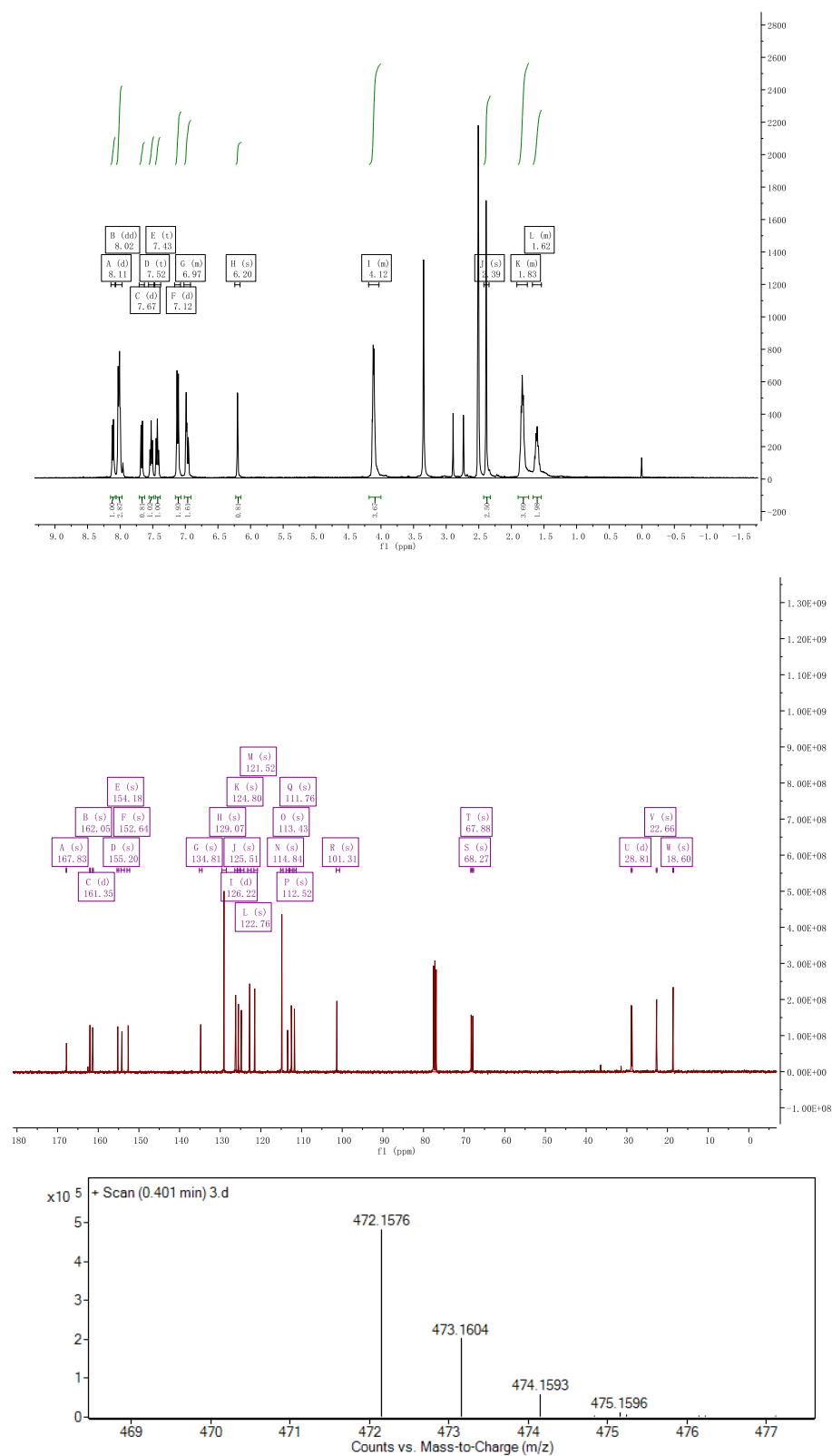
¹H NMR, ¹³C NMR and HRMS spectra of the compound **6g**



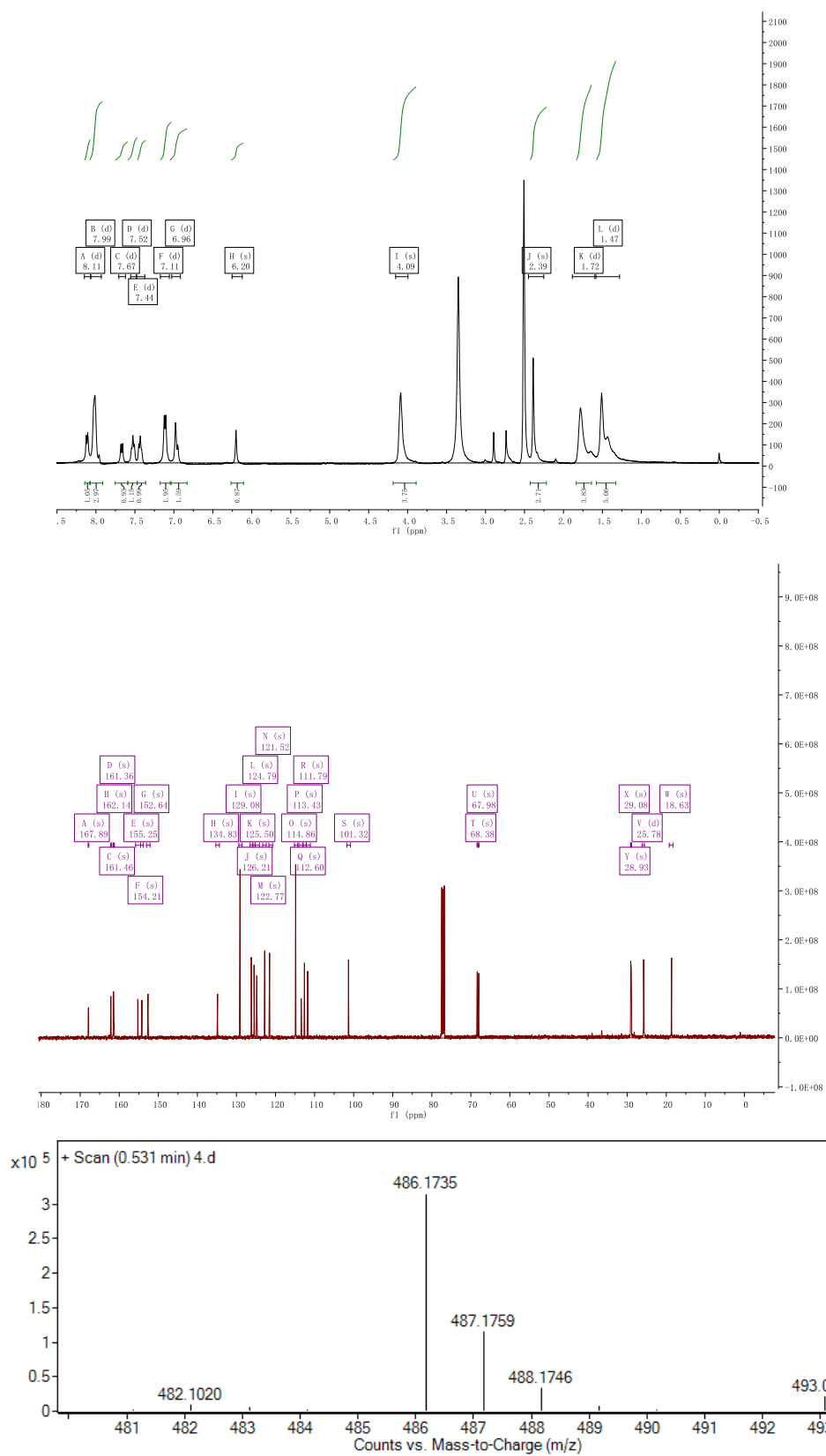
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6h**



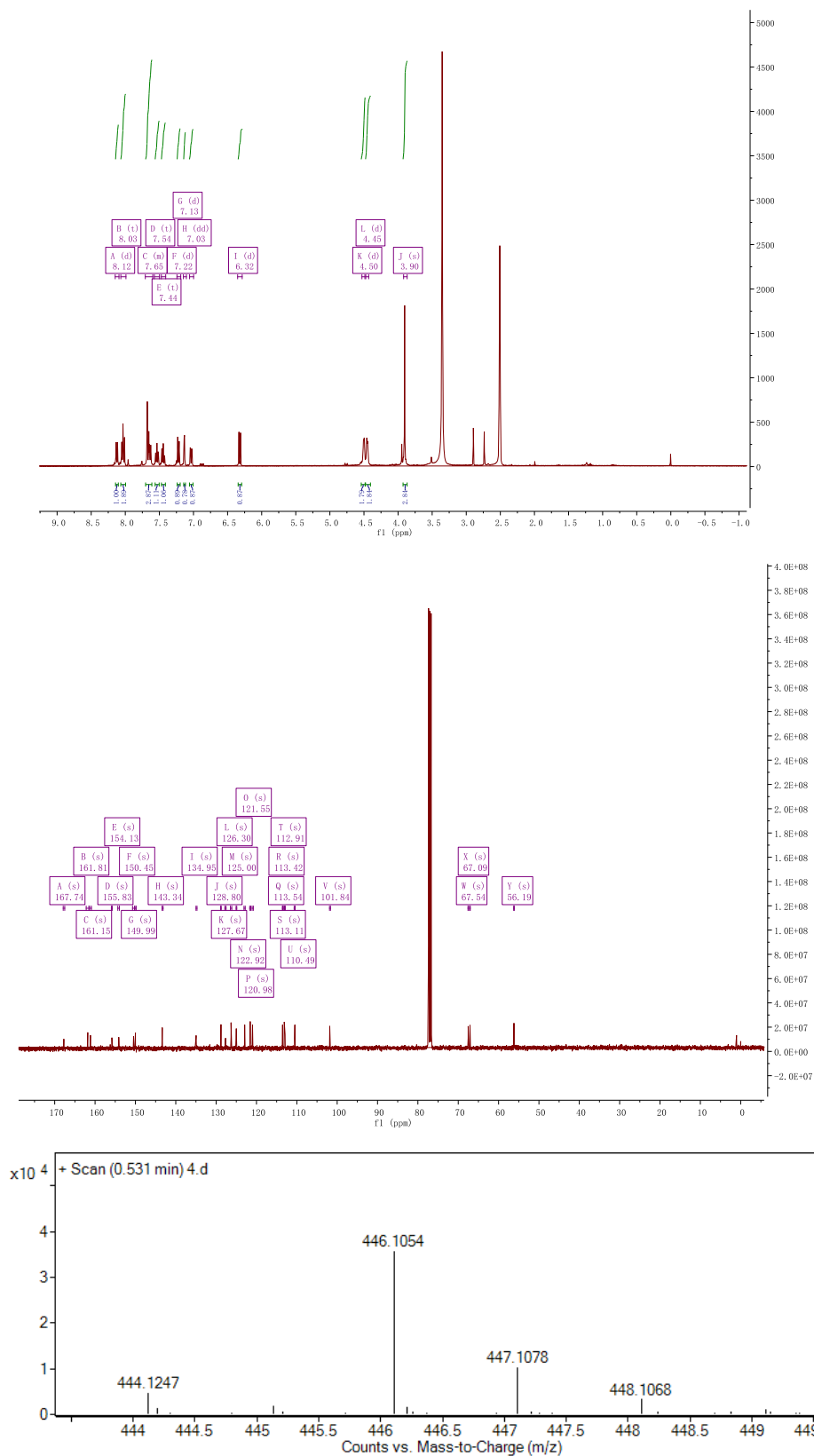
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6i**



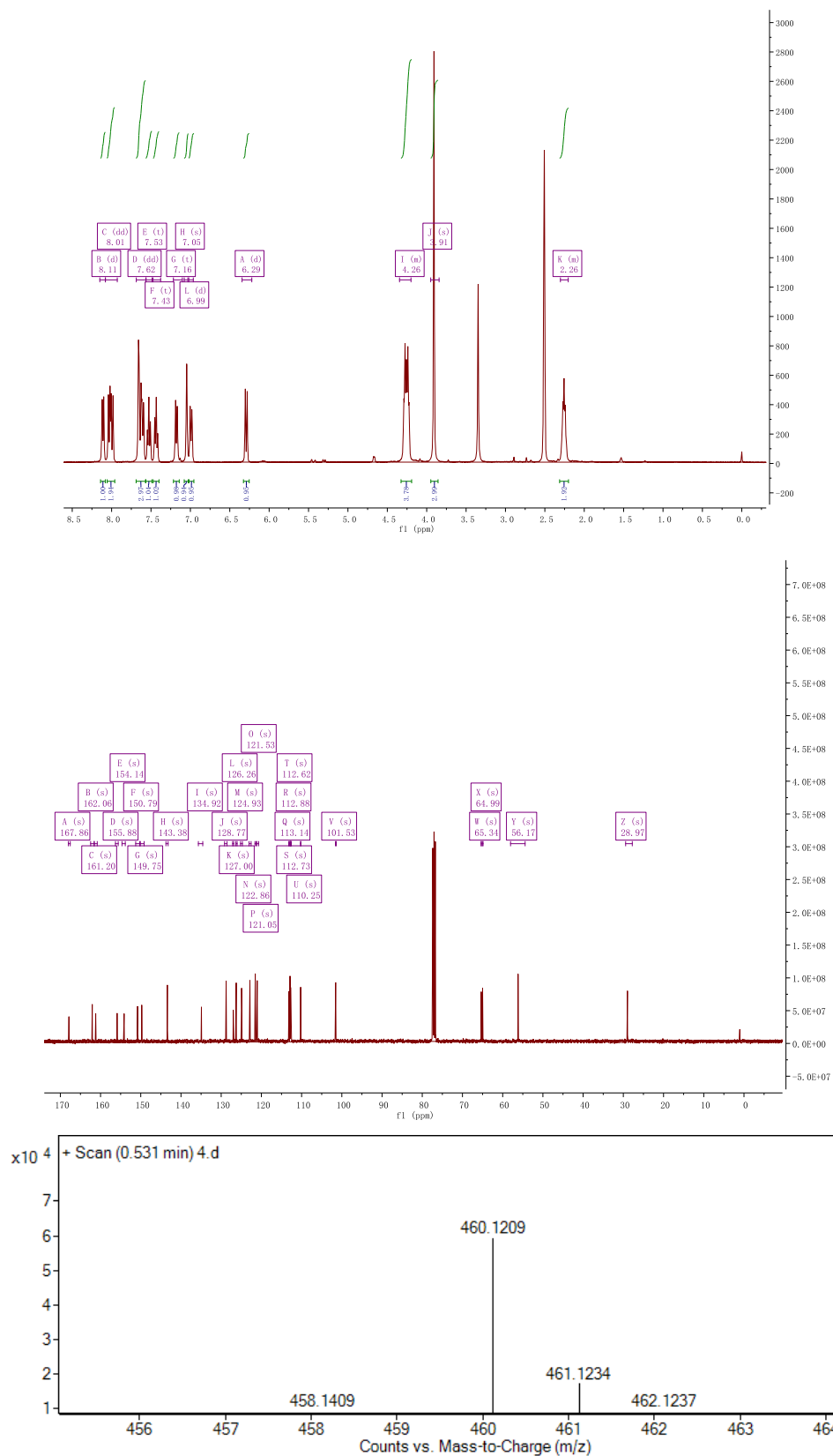
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6j**



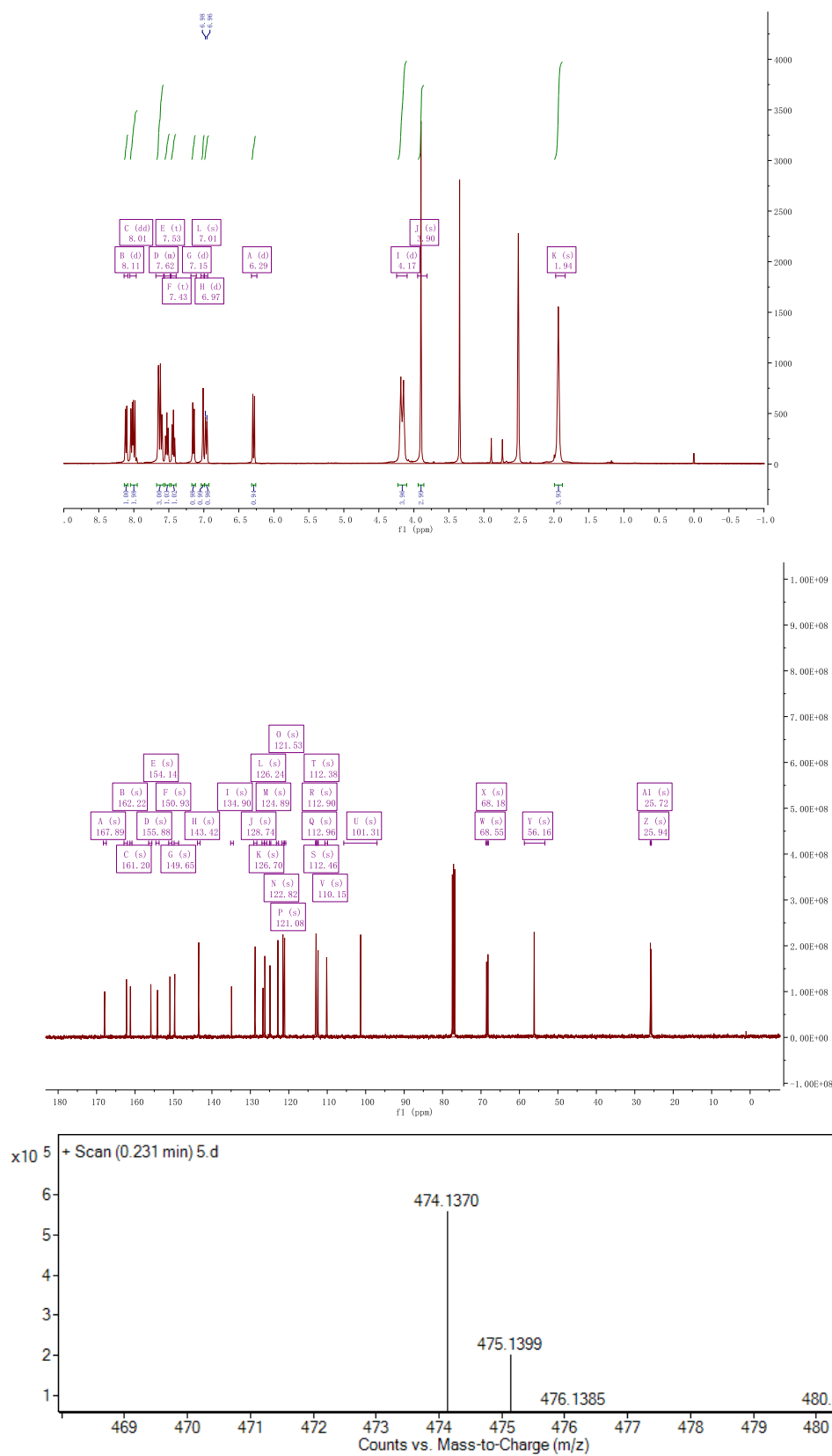
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6k**



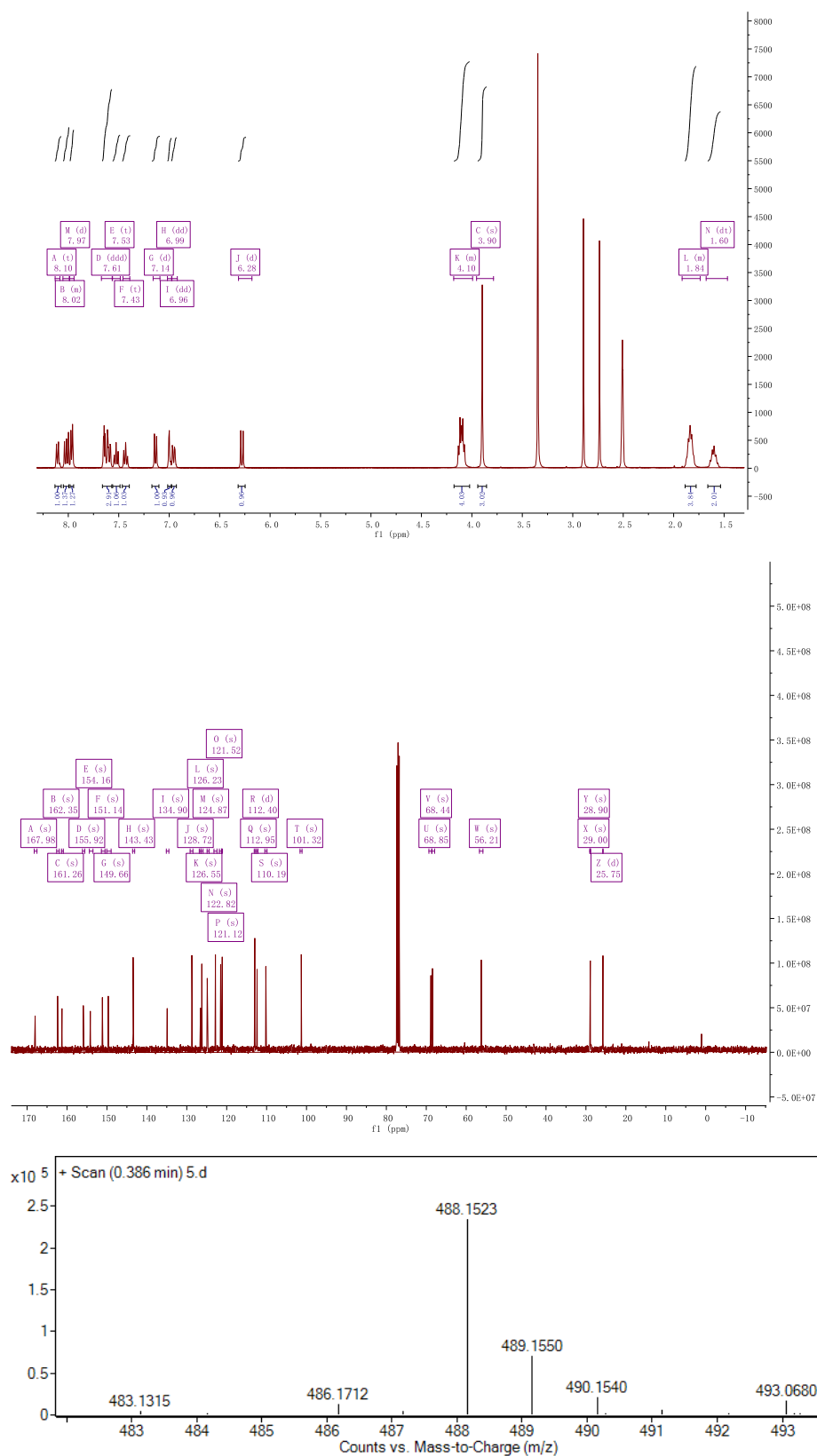
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **61**



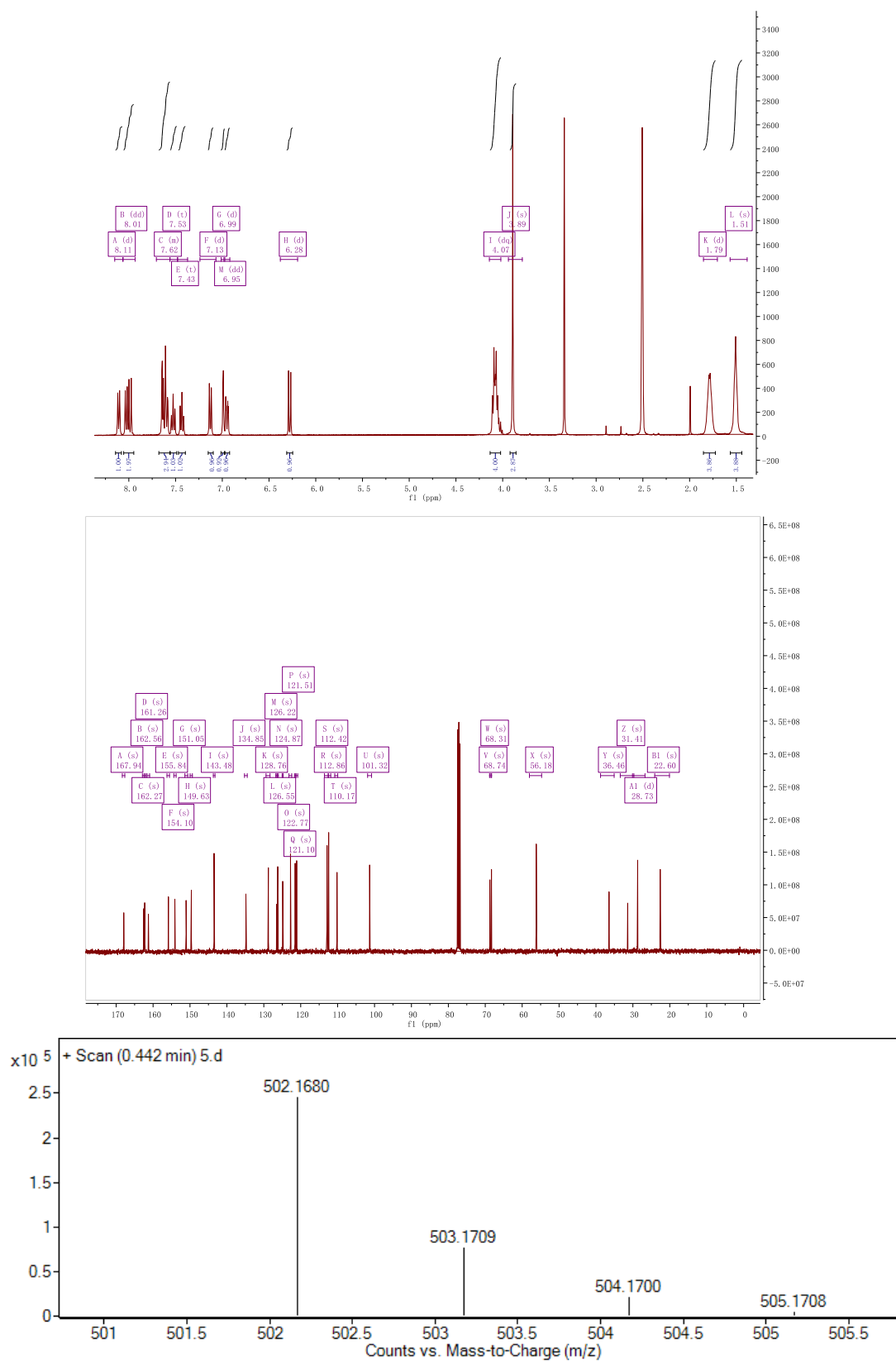
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6m**



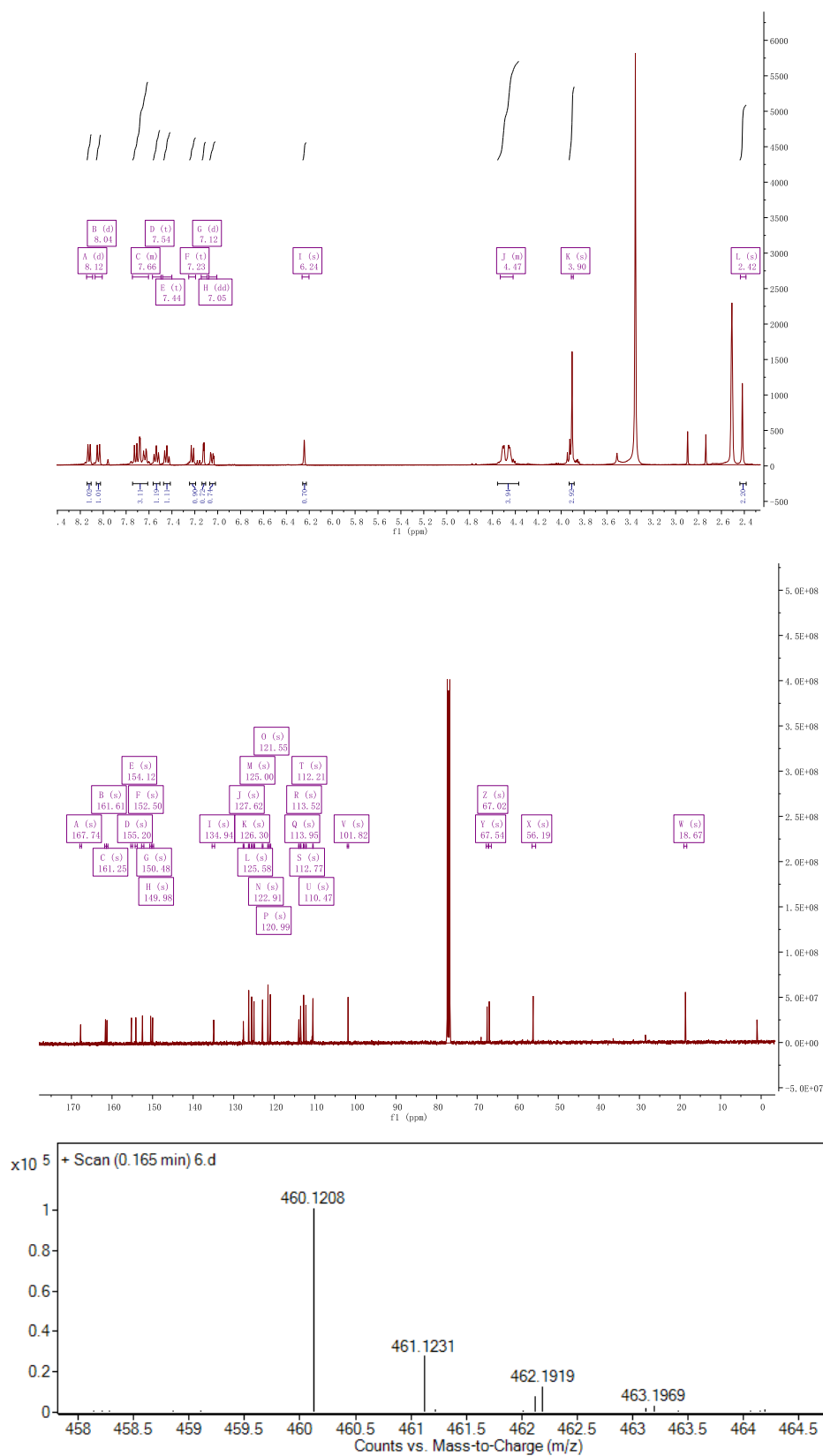
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6n**



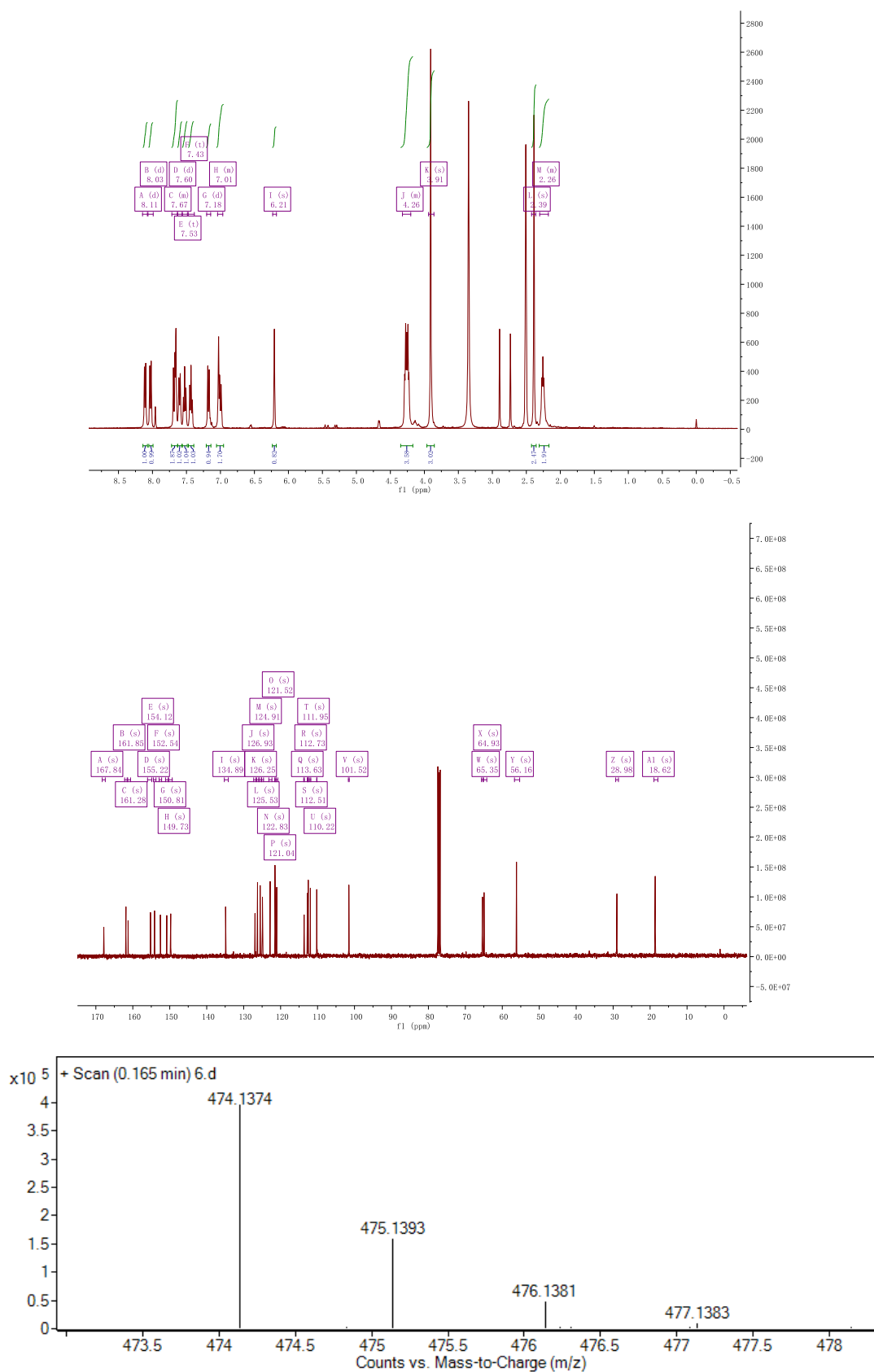
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **60**



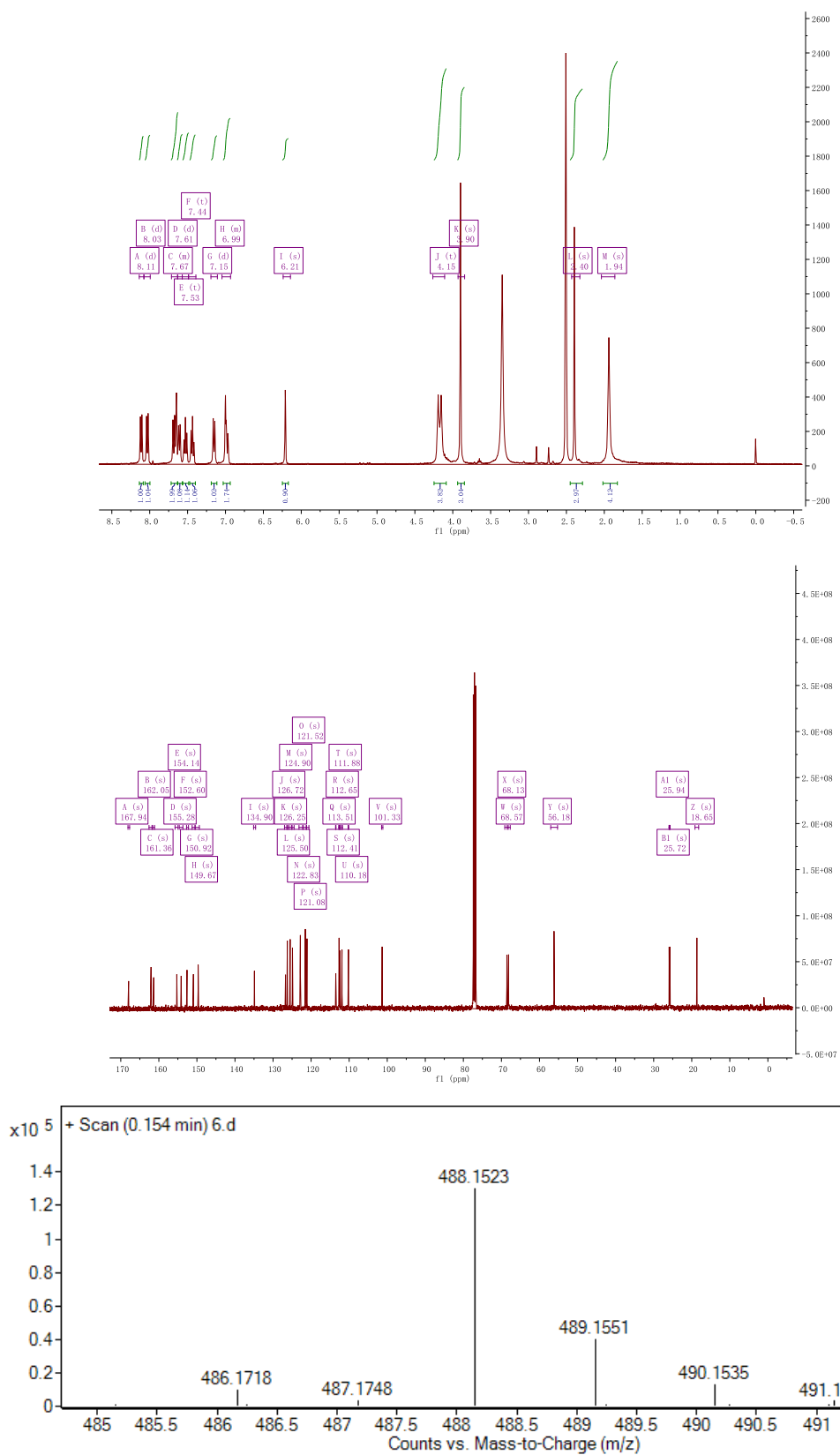
¹H NMR, ¹³C NMR and HRMS spectra of the compound **6p**



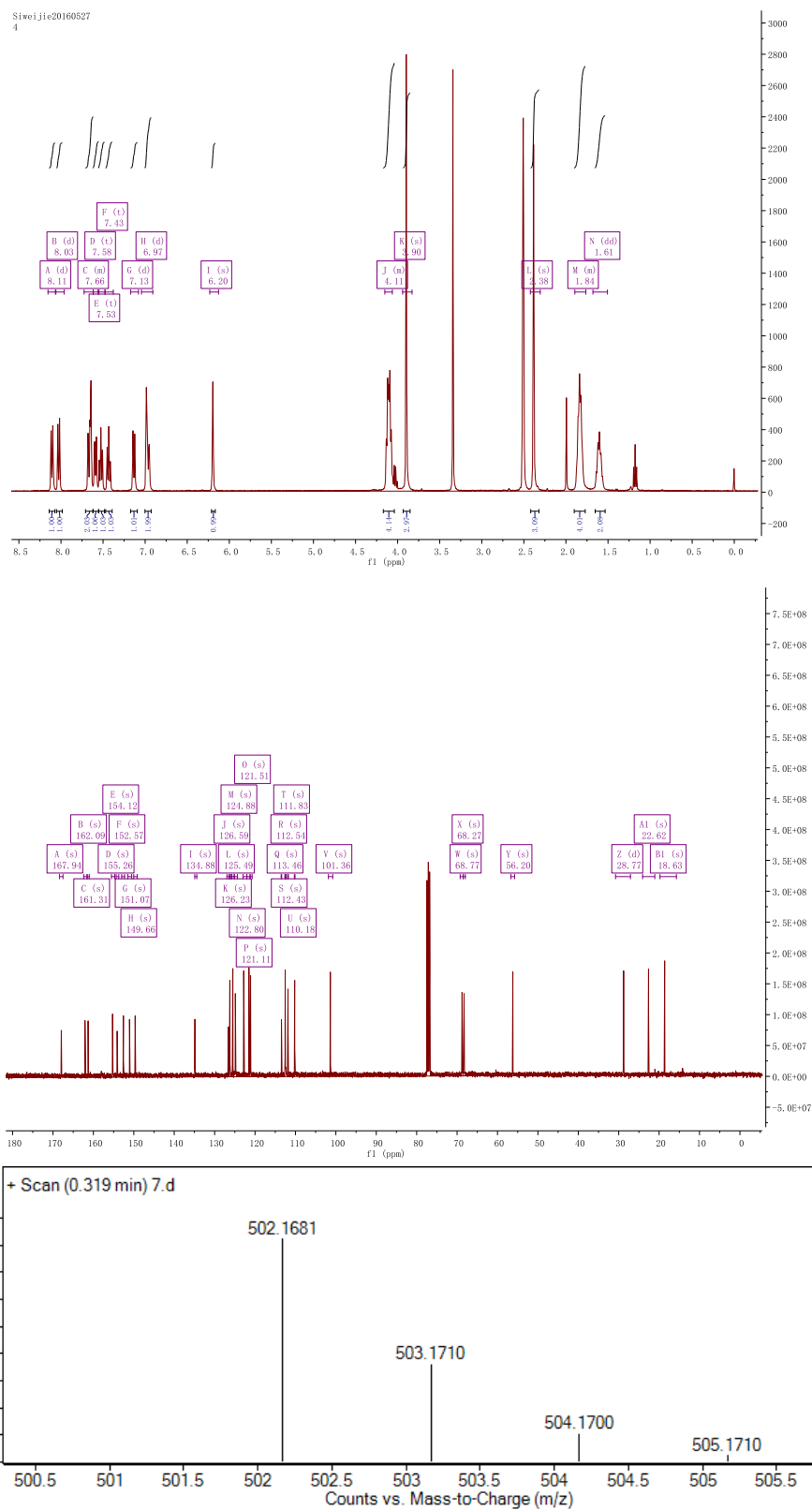
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6q**



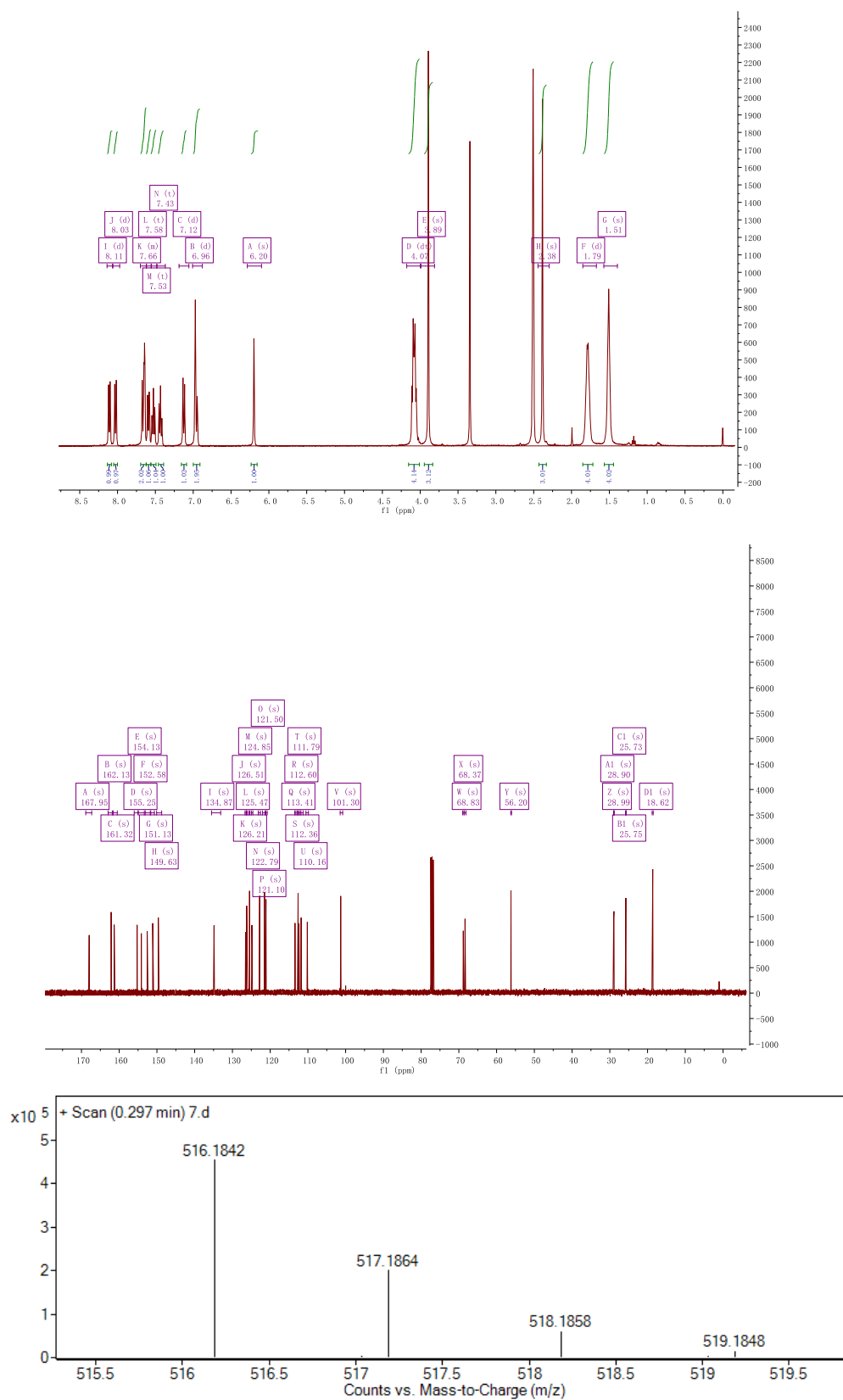
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6r**



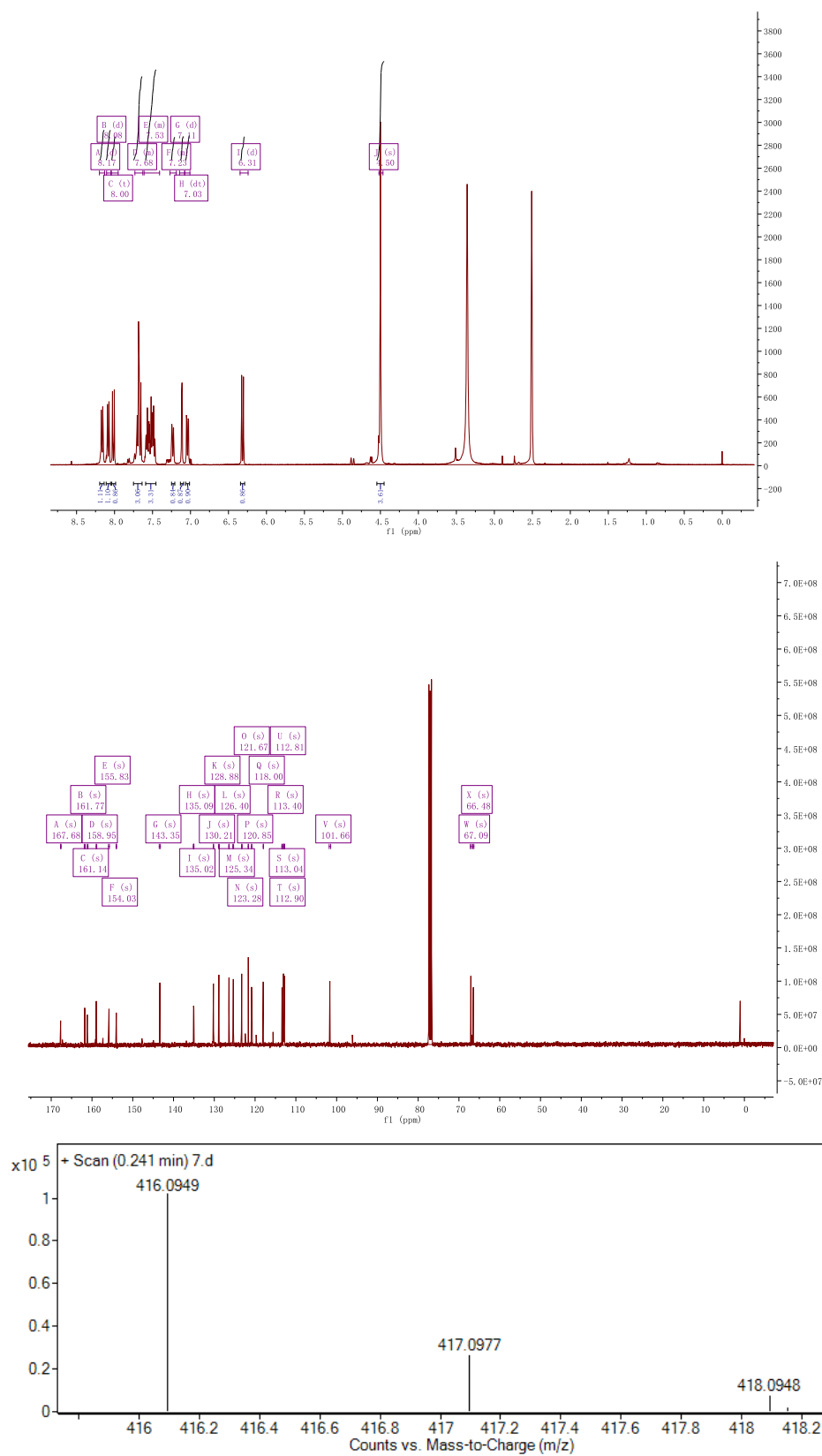
¹H NMR, ¹³C NMR and HRMS spectra of the compound **6s**



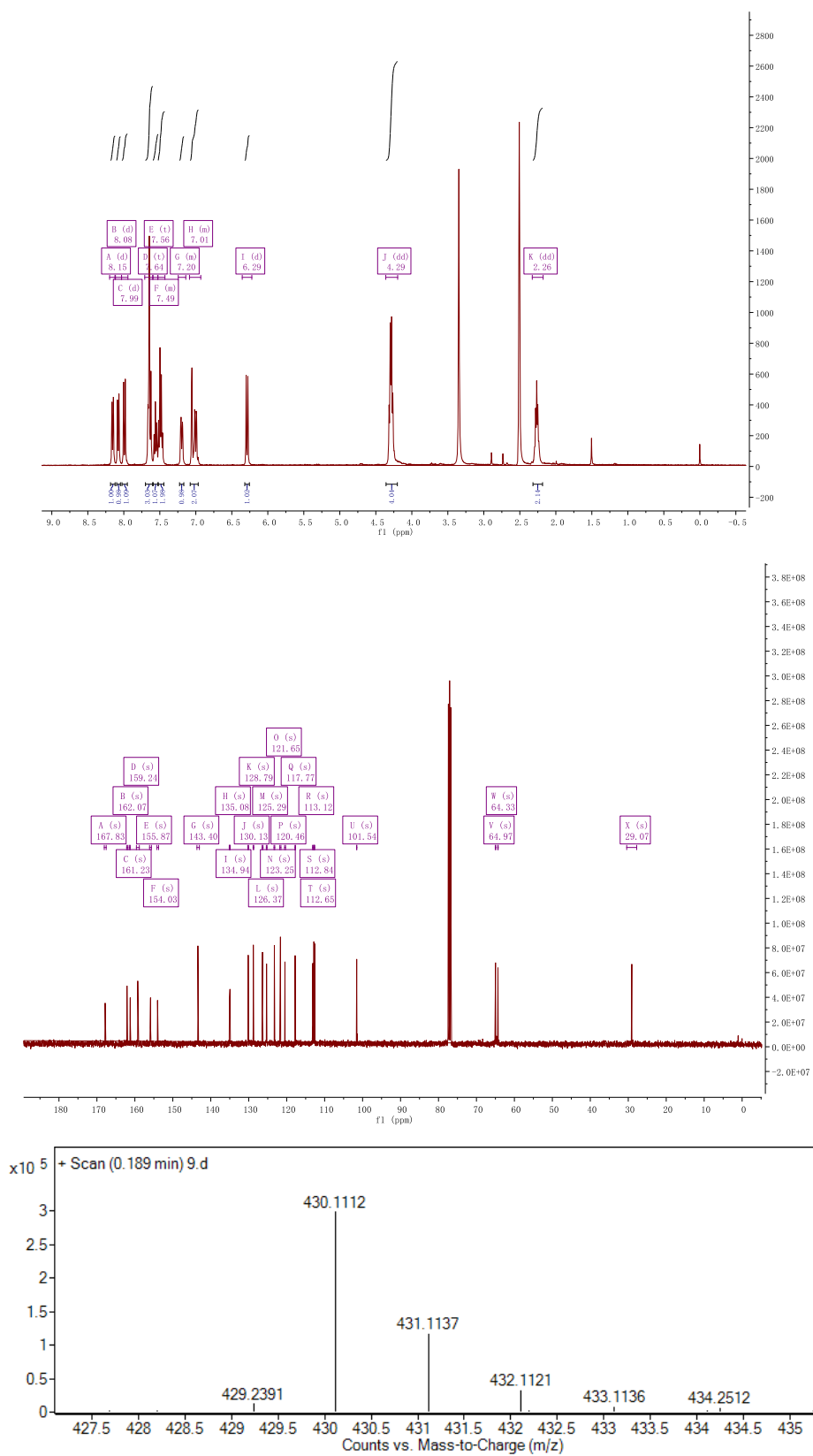
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6t**



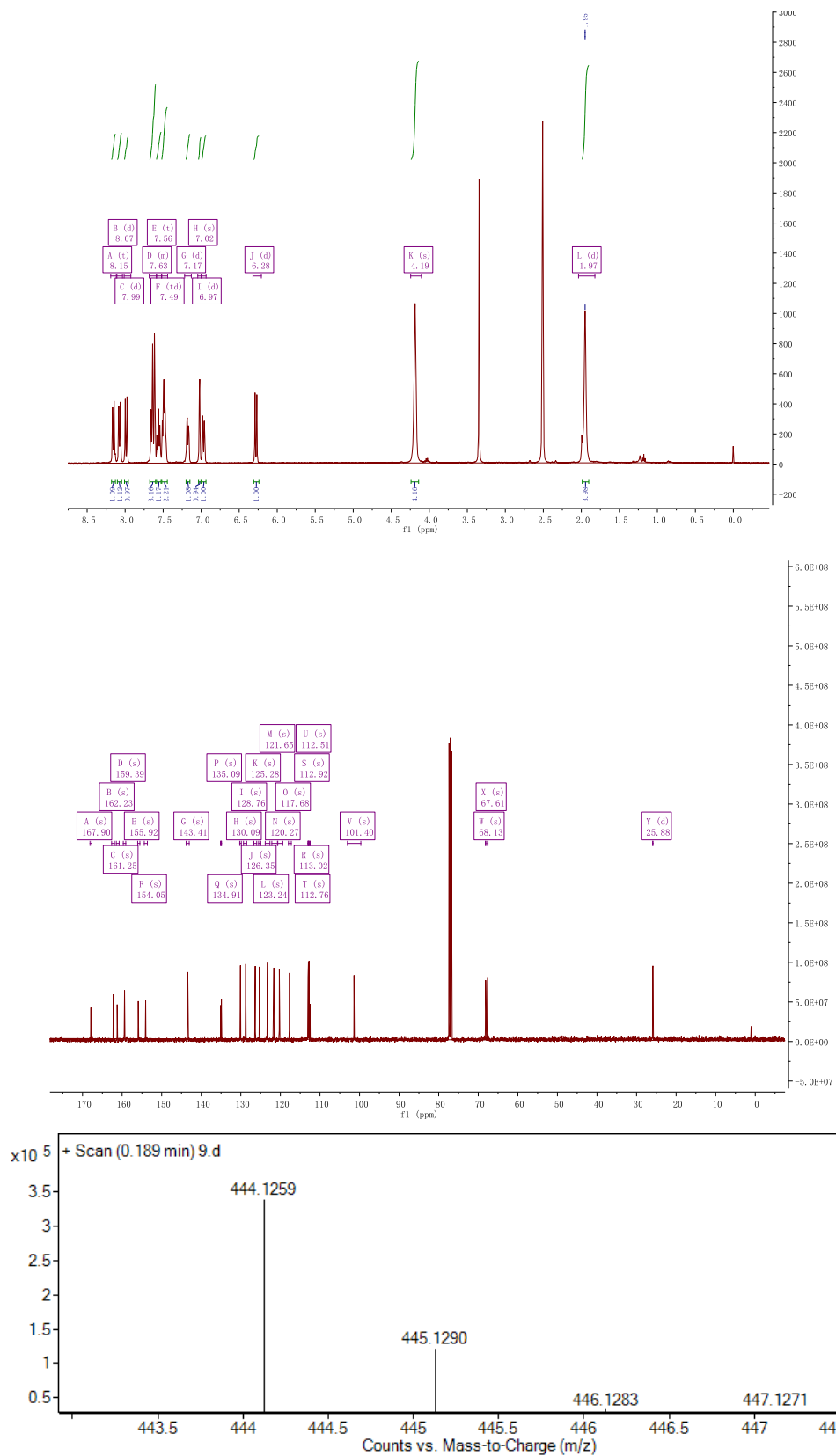
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6u**



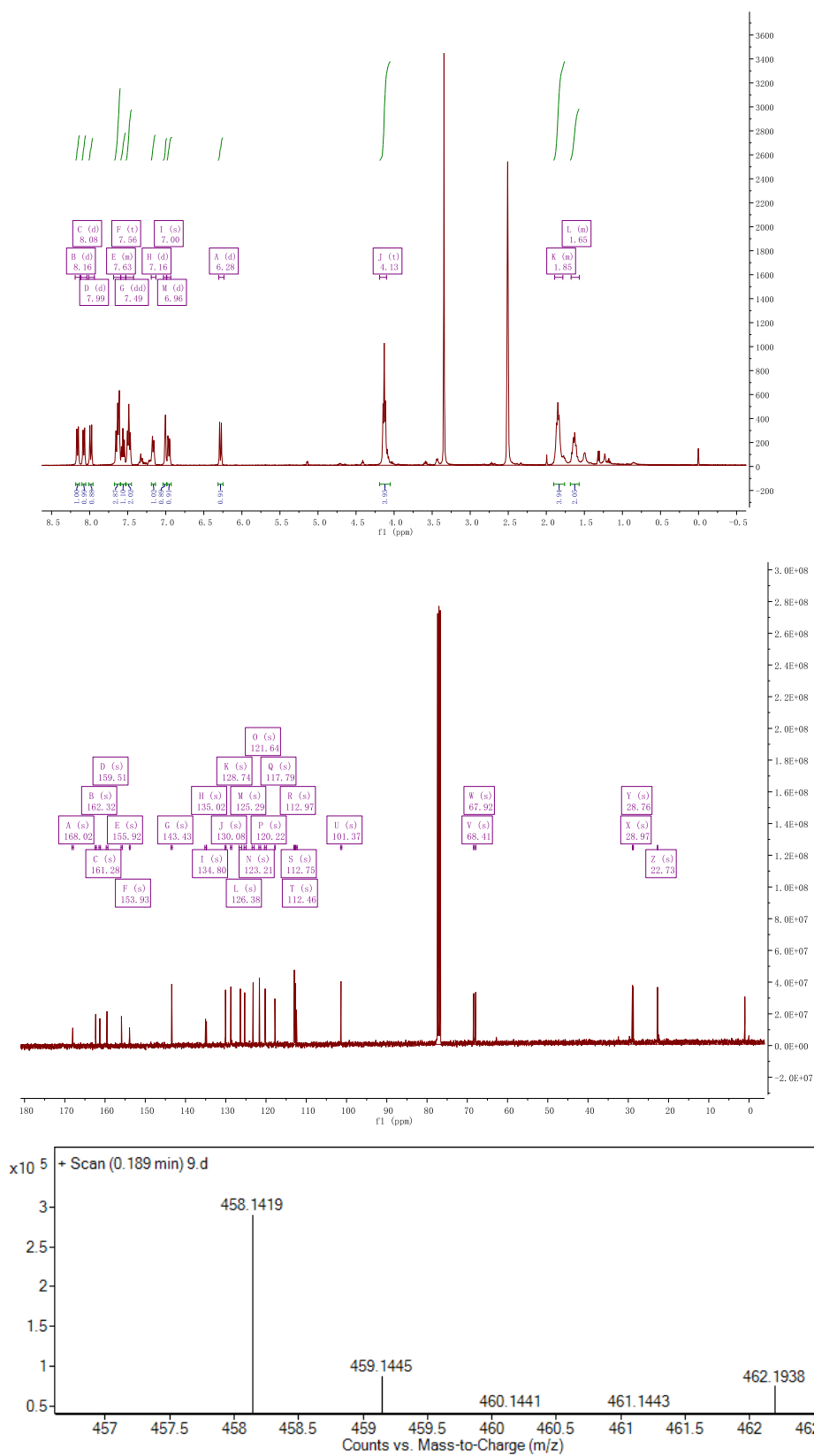
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6v**



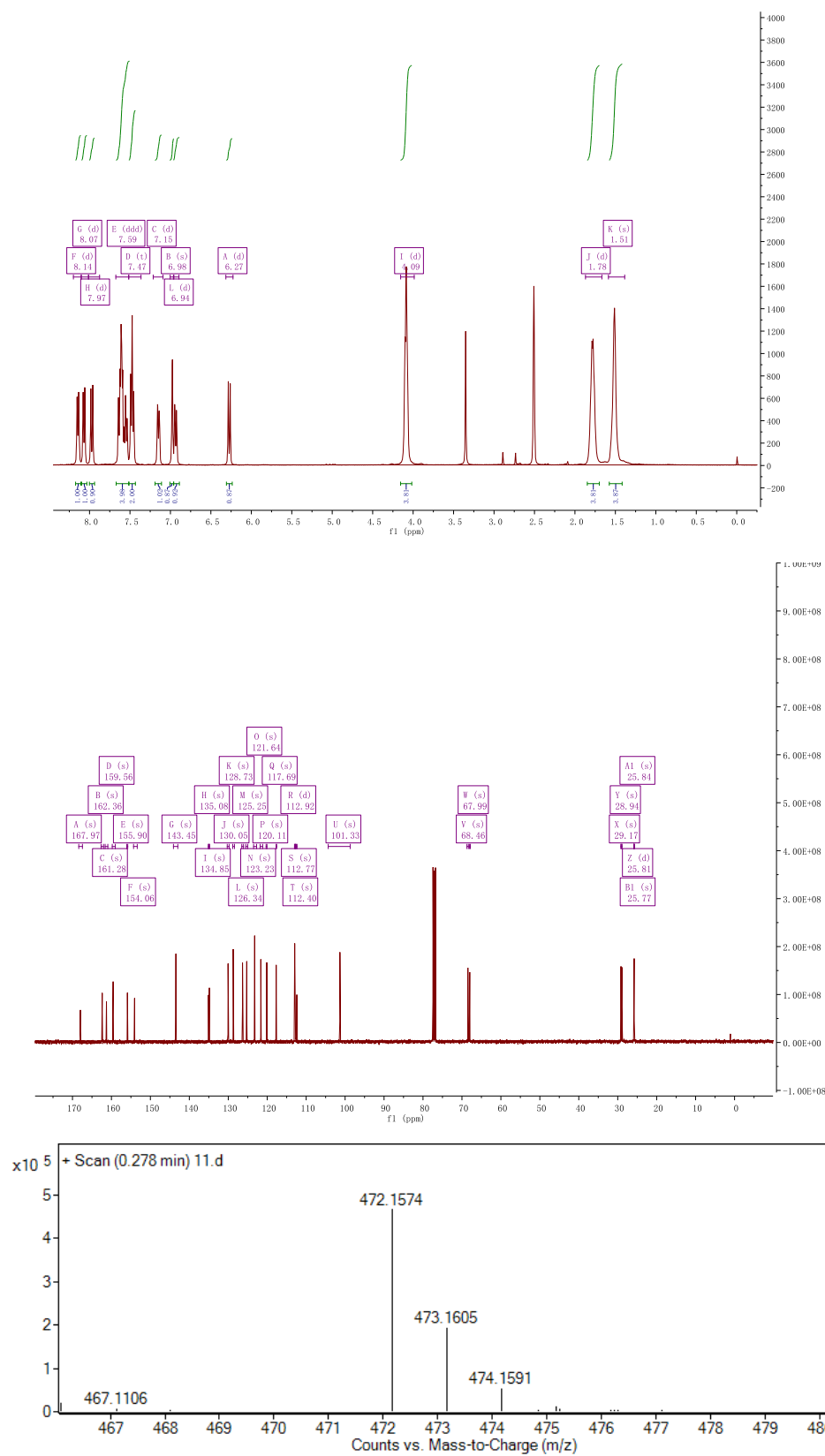
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6w**



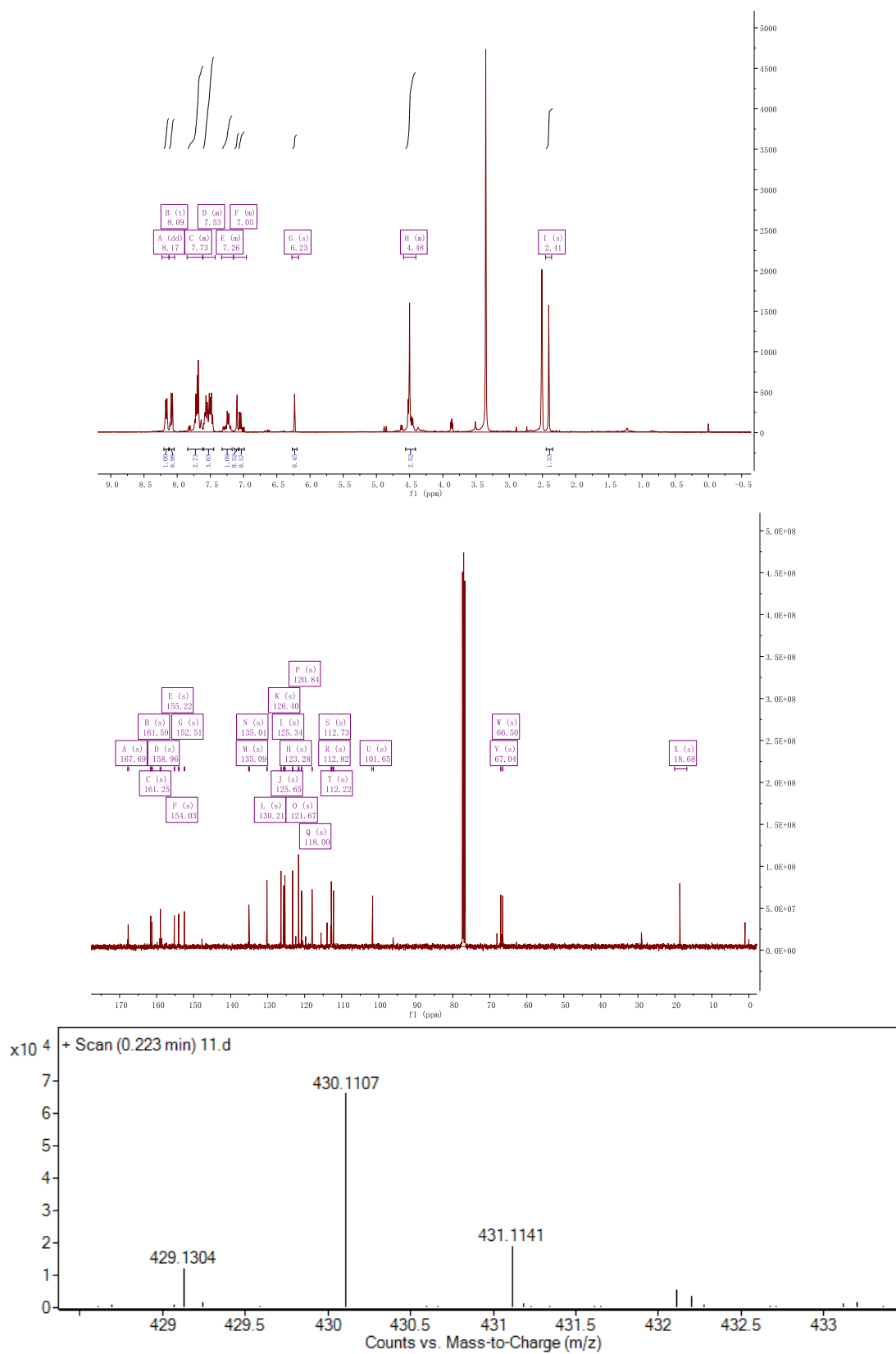
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6x**



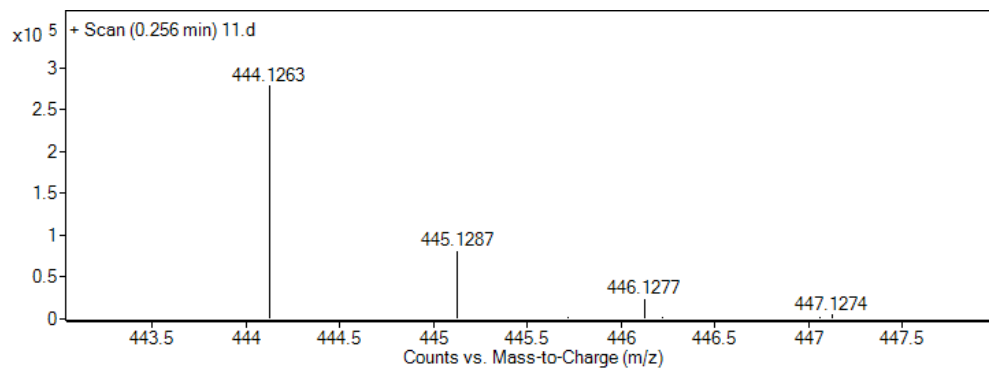
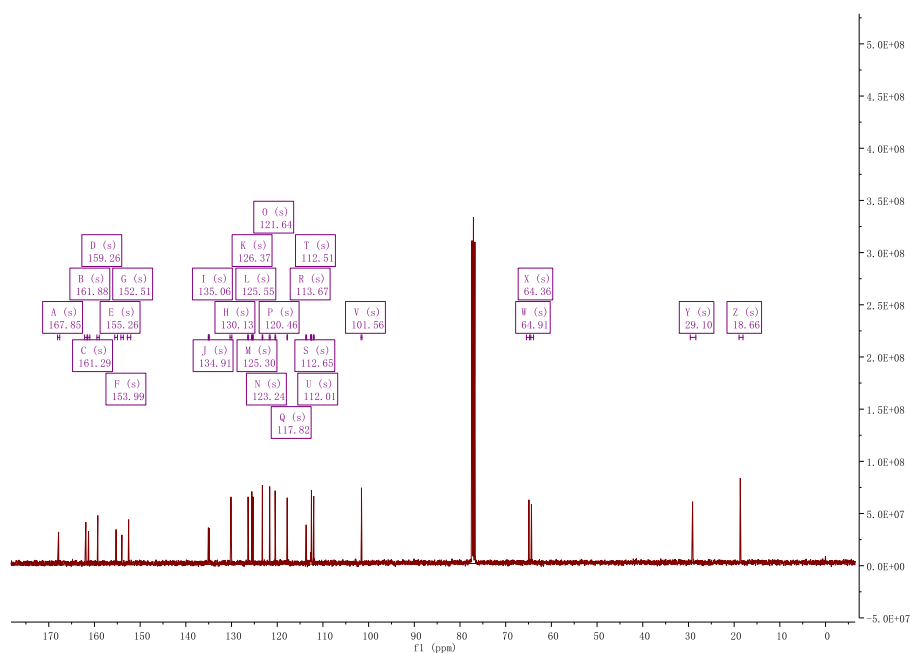
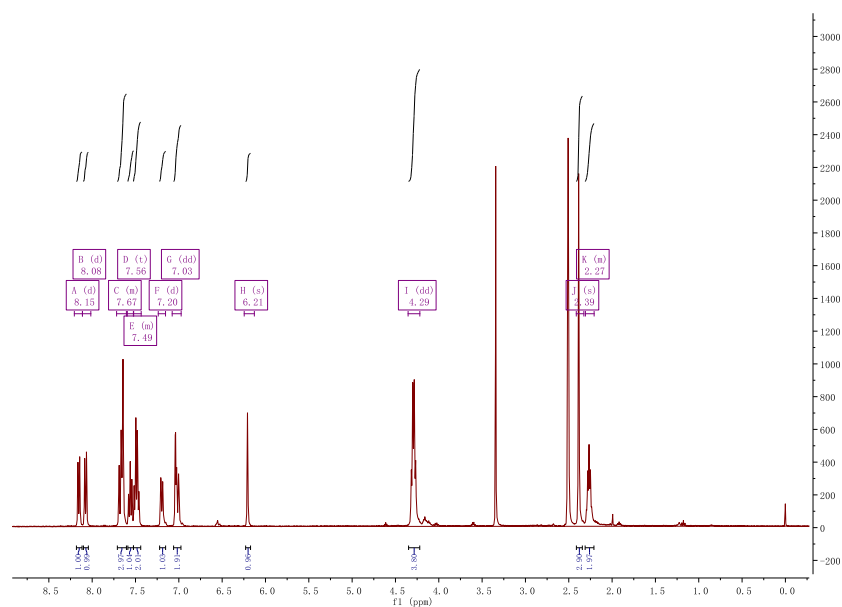
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6y**



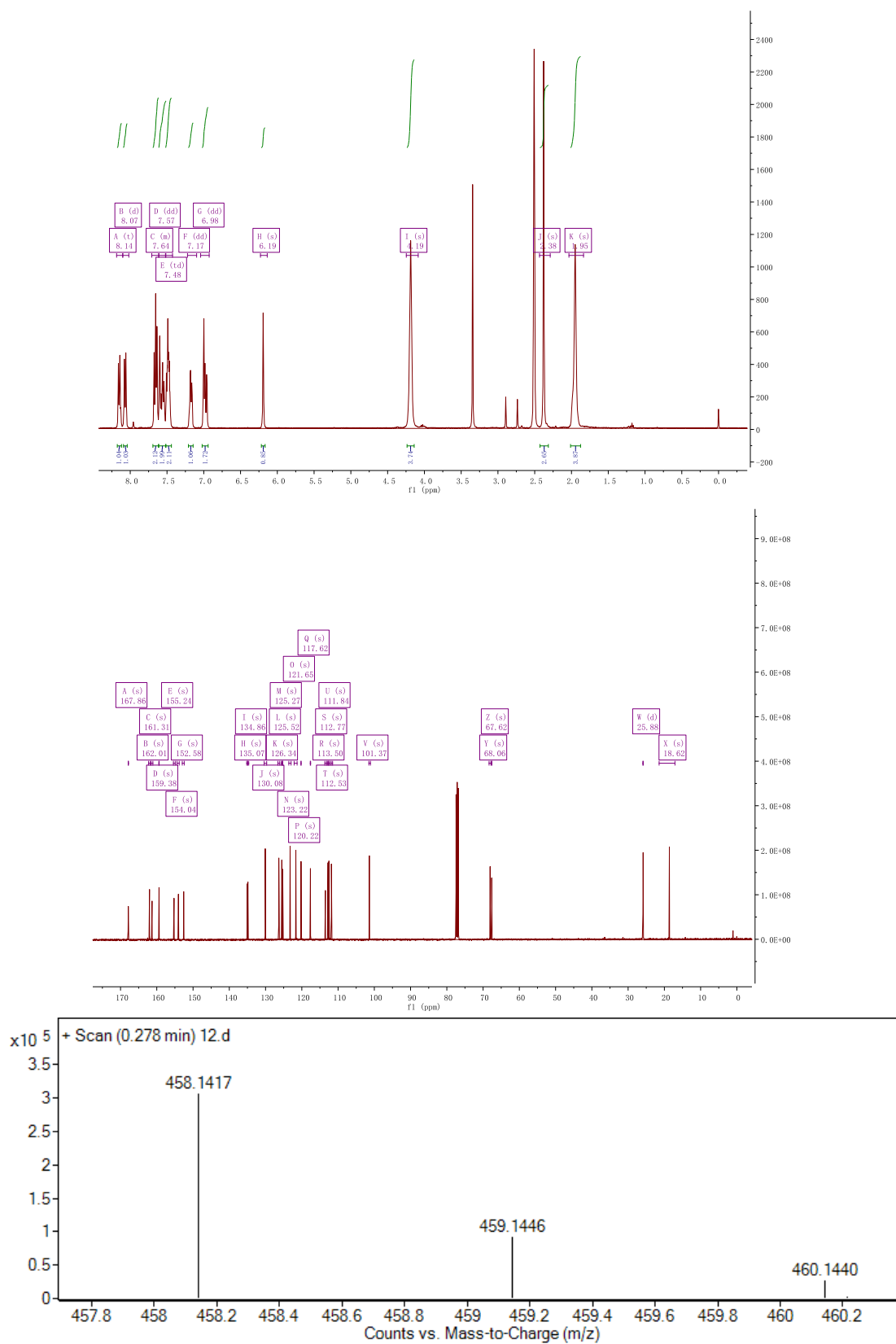
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6z**



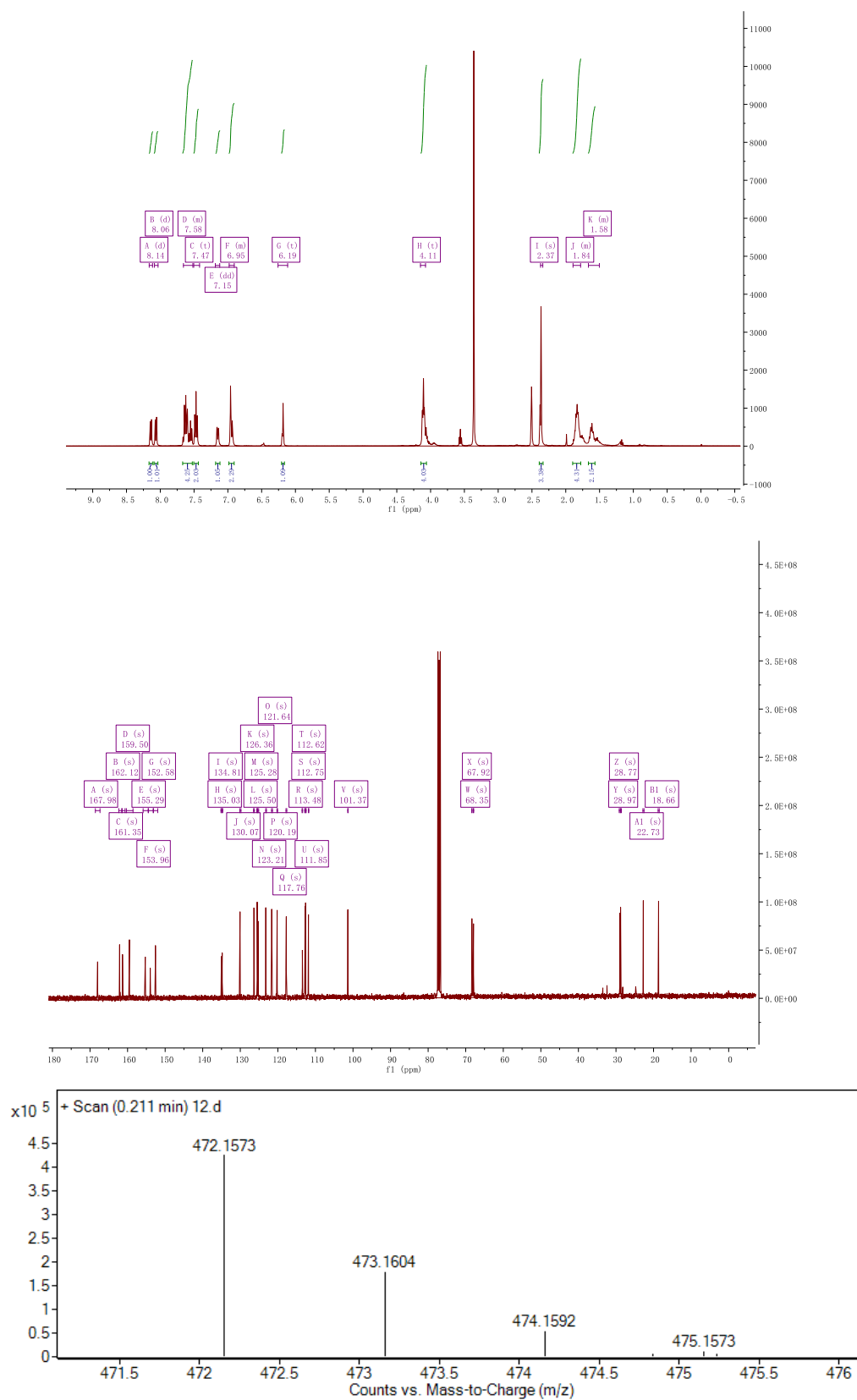
^1H NMR, ^{13}C NMR and HRMS spectra of the compound **6aa**



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



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



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

