

Electronic Supporting Information

Reactivity Study of 4-Hydroxydithiocoumarin/4-Hydroxythiocoumarin with Vinyl Ether /Cyclic Vinyl Ether: Synthesis of Fused Novel Thiophene Derivatives Using CuO Nanoparticles

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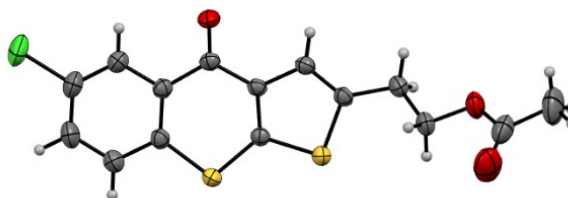
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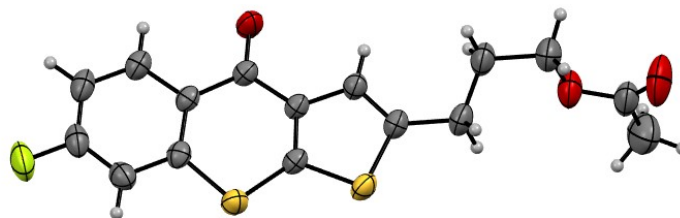
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S1: X-ray crystallographic data of compound 8a and 10c



ORTEP Diagram of compound **8a** with CCDC number [2513822](#)

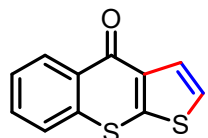
Entry	Identification Code	Compound 8a
01	Empirical formula	C ₁₅ H ₁₁ ClO ₃ S ₂
02	Formula weight	338.81
03	Temperature	298 K
04	Wavelength	0.71073
05	Crystal system	Monoclinic
06	Space group	p-1
07	Cell length	a 17.1285 (14) b 4.0509 (3) c 22.3190 (18)
08	Cell angle	$\alpha = 90$ $\beta = 106.564 (2)$ $\gamma = 90$
09	Cell volume	1484.4 (2)
10	Density	1.516 g/cm ³
11	Completeness to theta	0.997
12	Index ranges	h = 20 k = 4 l = 26
13	Theta (Max)	24.995
14	Cell formula units Z	4
15	CCDC no	2513822



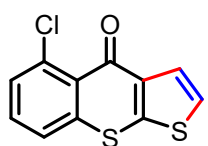
ORTEP Diagram of compound **10c** with CCDC number [2518535](#)

Entry	Identification Code	Compound 10c
01	Empirical formula	C ₁₆ H ₁₃ FO ₃ S ₂
02	Formula weight	336.38
03	Temperature	299 K
04	Wavelength	0.71073
05	Crystal system	Triclinic
06	Space group	p-1
07	Cell length	a 7.4957 (4) b 7.5172 (4) c 13.7183 (7)
08	Cell angle	α = 91.097 (2) β = 90.856 (1) γ = 101.684 (2)
09	Cell volume	756.69 (7)
10	Density	1.476 g/cm ³
11	Completeness to theta	0.995
12	Index ranges	h = 9 k = 9 l = 16
13	Theta (Max)	26.029
14	Cell formula units Z	2
15	CCDC no	2518535

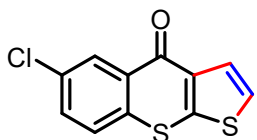
S2: Characterization Table



4H-thieno[2,3-*b*]thiochromen-4-one (4a). A brown solid (33 mg, yield 74%), mp 154 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.69 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 5.2$ Hz, 1H), 7.63 (s, 2H), 7.57 – 7.53 (m, 1H), 7.37 (d, $J = 5.2$ Hz, 1H), ^{13}C NMR (125 MHz, CDCl_3) δ 175.8, 144.6, 136.5, 134.7, 131.5, 129.8, 129.6, 126.9, 126.7, 126.0, 123.5. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2918 (C–H), 1632 (C=O); HRMS (ESI): m/z ($M + \text{H}^+$) calculated for $\text{C}_{11}\text{H}_7\text{OS}_2$ 218.9933; found 218.9933.

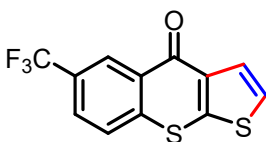


5-chloro-4H-thieno[2,3-*b*]thiochromen-4-one (4b). A brown solid (37 mg, yield 72%), mp 174 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, $J = 3.8$ Hz, 1H), 7.55 – 7.53 (d, 2H), 7.46 (t, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 3.9$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.5, 141.7, 139.8, 137.4, 136.3, 131.2, 131.0, 127.4, 126.7, 125.4, 124.0. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2919 (C–H), 1633 (C=O); HRMS (ESI): m/z ($M + \text{H}^+$) calculated for $\text{C}_{11}\text{H}_6\text{ClOS}_2$ 252.9543; found 252.9536.



6-chloro-4H-thieno[2,3-*b*]thiochromen-4-one (4c). A brown solid (35 mg, yield 70%), mp 175 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.65 (s, 1H), 7.87 – 7.85 (m, 1H), 7.58 (t, 2H), 7.40 – 7.39 (m, 1H), ^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 144.7, 134.7, 134.6, 133.5, 132.0, 131.2, 129.3, 127.5, 126.8, 124.2. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2923 (C–H), 1627 (C=O); HRMS (ESI): m/z ($M + \text{H}^+$) calculated for $\text{C}_{11}\text{H}_6\text{ClOS}_2$ 252.9543; found 252.9532.

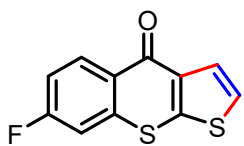
7-chloro-4H-thieno[2,3-*b*]thiochromen-4-one (4d). A yellowish brown solid (35 mg, yield 69%), mp 180 °C ^1H NMR (500 MHz, CDCl_3) δ 8.60 (d, $J = 8.7$ Hz, 1H), 7.85 (d, $J = 5.4$ Hz, 1H), 7.62 (d, $J = 2.0$ Hz, 1H), 7.49 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.39 (d, $J = 5.4$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.1, 144.1, 138.4, 138.0, 134.8, 131.2, 128.4, 127.7, 126.8, 125.5, 124.2. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2920 (C–H), 1640 (C=O); HRMS (ESI): m/z ($M + \text{H}^+$) calculated for $\text{C}_{11}\text{H}_6\text{ClOS}_2$ 252.9543; found 252.9528.



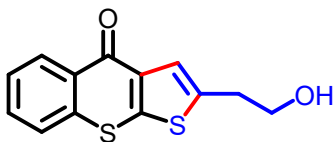
6-(trifluoromethyl)-4H-thieno[2,3-*b*]thiochromen-4-one (4e). A yellow solid (38 mg, yield 75%), mp 168 °C ^1H NMR (500 MHz, CDCl_3) δ 8.95 (s, 1H), 7.88 (s, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.44 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.8, 144.2, 140.2, 134.9, 130.1, 129.5 (q, $J = 33.4$ Hz), 127.6, (q, $J = 3.4$ Hz), 127.2 (q, $J = 4$ Hz), 127.1, 126.9, 124.6.

123.7 (q, $J = 270.1$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -62.56. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2922 (C–H), 1661 (C=O), 1264 (C–O); HRMS (ESI): m/z ($\text{M} + \text{H}^+$) calculated for $\text{C}_{12}\text{H}_6\text{F}_3\text{OS}_2$ 286.9807; found 286.9797.

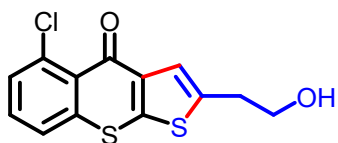
7-fluoro-4*H*-thieno[2,3-*b*]thiochromen-4-one (4f). A light yellow solid (39 mg, yield 78%), mp 159 °C ^1H NMR (500 MHz, CDCl_3) δ 8.70 (t, $J = 6.8$ Hz, 1H), 7.85 (d, $J = 3.8$ Hz, 1H), 7.39 (d, $J = 4.7$ Hz, 1H), 7.32 (d, $J = 8.6$ Hz, 1H), 7.24 (s, 1H), ^{13}C NMR (125 MHz, CDCl_3) δ 175.0, 164.1 (d, $J = 253.7$ Hz), 144.0, 138.8 (d, $J = 10$ Hz), 134.8, 132.7 (d, $J = 10$ Hz), 126.8, 126.7 (d, $J = 1.2$ Hz), 124.0, 115.6 (d, $J = 21$ Hz), 112.1 (d, $J = 25$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -105.78. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2920 (C–H), 1643 (C=O); HRMS (ESI): m/z ($\text{M} + \text{H}^+$) calculated for $\text{C}_{11}\text{H}_6\text{FOS}_2$ 236.9839; found 236.9828.



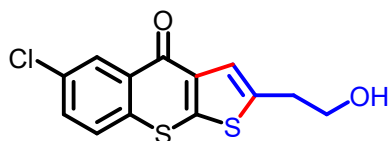
2-(2-hydroxyethyl)-4*H*-thieno[2,3-*b*]thiochromen-4-one (7a). A brown solid (35 mg, yield 74%), mp 142 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.66 – 8.64 (m, 1H), 7.60 (d, $J = 5.9$ Hz, 3H), 7.53 (ddd, $J = 8.2, 5.7, 2.6$ Hz, 1H), 3.95 (t, $J = 6.1$ Hz, 2H), 3.13 (t, $J = 6.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.5, 143.9, 140.1, 136.7, 134.8, 131.5, 129.9, 129.7, 126.9, 126.2, 124.3, 62.9, 33.4. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3417 (O–H), 2925 (C–H), 1622 (C=O); HRMS (ESI): m/z ($\text{M} + \text{H}^+$) calculated for $\text{C}_{13}\text{H}_{11}\text{O}_2\text{S}_2$ 263.0195; found 263.0187.



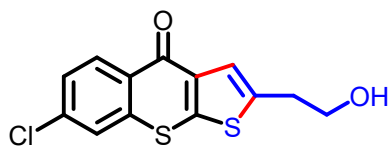
5-chloro-2-(2-hydroxyethyl)-4*H*-thieno[2,3-*b*]thiochromen-4-one (7b). A brown solid (46 mg, yield 77%), mp 155 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.0$ Hz, 2H), 7.49 (d, $J = 1.3$ Hz, 1H), 7.45 – 7.41 (m, 1H), 3.93 (t, $J = 6.1$ Hz, 2H), 3.11 (t, $J = 5.8$ Hz, 2H), 1.78 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.1, 140.8, 140.4, 139.8, 137.3, 136.3, 131.1, 130.8, 126.7, 125.4, 124.8, 62.8, 33.4. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3428 (O–H), 2925 (C–H), 1622 (C=O); HRMS (ESI): m/z ($\text{M} + \text{H}^+$) calculated for $\text{C}_{13}\text{H}_{10}\text{ClO}_2\text{S}_2$ 296.9805; found 296.9811.



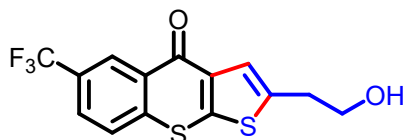
6-chloro-2-(2-hydroxyethyl)-4*H*-thieno[2,3-*b*]thiochromen-4-one (7c). A yellow solid (46 mg, yield 78%), mp 195 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.62 – 8.62 (m, 1H), 7.59 (s, 1H), 7.57 – 7.53 (m, 2H), 3.95 (t, $J = 6.0$ Hz, 2H), 3.13 (t, $J = 6.1$ Hz, 2H), 1.82 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.3, 143.8, 140.7, 134.8, 134.6, 133.4, 131.8, 131.2, 129.2, 127.5, 124.3, 62.8, 33.4. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3402 (O–H), 2921 (C–H), 1624 (C=O); HRMS (ESI): m/z ($\text{M} + \text{H}^+$) calculated for $\text{C}_{13}\text{H}_{10}\text{ClO}_2\text{S}_2$ 296.9805; found 296.9796.



7-chloro-2-(2-hydroxyethyl)-4*H*-thieno[2,3-*b*]thiochromen-4-one (7d). A yellow solid (45 mg, yield 75%), mp 190 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.57 (d, $J = 8.7$ Hz, 1H), 7.58 (d, $J = 5.9$ Hz, 2H), 7.47 (d, $J = 9.1$ Hz, 1H), 3.95 (t, $J = 6.1$ Hz, 2H),

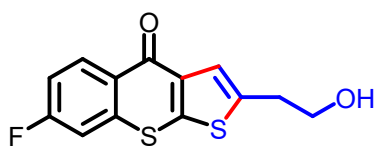


3.13 (t, $J = 5.9$ Hz, 2H), 1.85 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 143.2, 140.7, 138.2, 138.0, 134.8, 131.2, 128.4, 127.6, 125.4, 124.3, 62.8, 33.4. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3418 (O–H), 2921 (C–H), 1623 (C=O); HRMS (ESI): m/z ($M + H^+$) calculated for $\text{C}_{13}\text{H}_{10}\text{ClO}_2\text{S}_2$ 296.9805; found 296.9794.

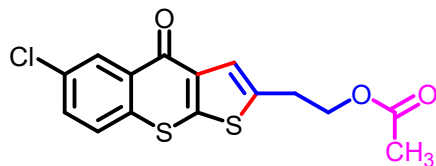


2-(2-hydroxyethyl)-6-(trifluoromethyl)-4H-thieno[2,3-*b*]thiochromen-4-one (7e). A light yellow solid (51 mg, yield 77%), mp 144 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.92 (s, 1H), 7.81 (dd, $J = 8.5$, 1.8 Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 1H), 7.61 (s, 1H), 3.96 (t, $J = 5.9$ Hz, 2H), 3.15 (t, $J = 6.3$ Hz, 2H), 1.88 (s, 1H), ^{13}C NMR (125 MHz, CDCl_3) δ 174.4, 143.3, 141.2, 140.3, 134.8, 130.1, 129.4 (q, $J = 33.5$ Hz), 127.4, (q, $J = 3.4$ Hz), 127.1 (q, $J = 4.2$ Hz), 127.1, 124.3, 123.7 (q, $J = 272.4$ Hz), 62.8, 33.4. ^{19}F NMR (377 MHz, CDCl_3) δ -62.76. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3418 (O–H), 2922 (C–H), 1623 (C=O); HRMS (ESI): m/z ($M + H^+$) calculated for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{O}_2\text{S}_2$ 331.0069; found 331.0069.

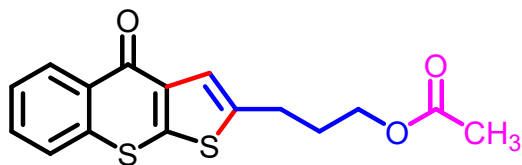
7-fluoro-2-(2-hydroxyethyl)-4H-thieno[2,3-*b*]thiochromen-4-one (7f). A white solid (44 mg, yield 78%), mp 160 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.65 (dd, $J = 8.9$, 6.0 Hz, 1H), 7.57 (s, 1H), 7.29 – 7.26 (m, 1H), 7.23 (td, $J = 9.0$, 2.3 Hz, 1H), 3.95 (s, 2H), 3.13 (t, $J = 5.9$ Hz, 2H), 1.97 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 164.0, (d, $J = 256.1$ Hz), 143.1, 140.6, 138.8 (d, $J = 10$ Hz), 134.8, 132.6 (d, $J = 9.8$ Hz), 126.6 (d, $J = 2.3$ Hz), 124.3, 115.5 (d, $J = 22.3$ Hz), 112.1, (d, $J = 24.9$ Hz),, 62.8, 33.4. ^{19}F NMR (377 MHz, CDCl_3) δ -106.03. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3421 (O–H), 2922 (C–H), 1625 (C=O); HRMS (ESI): m/z ($M + H^+$) calculated for $\text{C}_{13}\text{H}_{10}\text{FO}_2\text{S}_2$ 281.0101; found 281.0096.



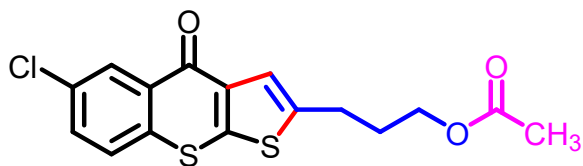
2-(6-chloro-4-oxo-4H-thieno[2,3-*b*]thiochromen-2-yl)ethyl acetate (8a). A light yellow solid (53 mg, yield 78%), mp 160 °C ^1H NMR (400 MHz, CDCl_3) 8.62 (d, $J = 1.6$ Hz, 1H), 7.60 – 7.54 (m, 3H), 4.34 (t, $J = 6.3$ Hz, 2H), 3.21 (t, $J = 6.3$ Hz, 2H), 2.09 (s, 3H), ^{13}C NMR (125 MHz, CDCl_3) δ 174.3, 170.9, 143.8, 139.6, 134.7, 134.6, 133.5, 131.8, 131.2, 129.2, 127.6, 124.6, 63.8, 29.6, 21.1. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2924 (C–H), 1744 (O–CO–CH₃), 1631 (C=O); HRMS (ESI): m/z ($M + H^+$) calculated for $\text{C}_{15}\text{H}_{12}\text{ClO}_3\text{S}_2$ 338.9911; found 338.9878.



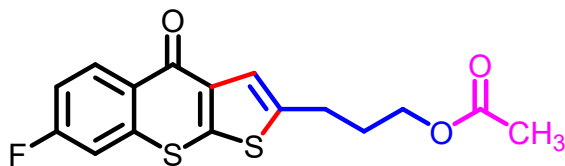
3-(4-oxo-4H-thieno[2,3-*b*]thiochromen-2-yl)propyl acetate (10a). A brown solid (45 mg, yield 71%), mp 105 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, $J = 8.0$ Hz, 1H), 7.62 – 7.61 (m, 2H), 7.56 – 7.52 (m, 2H), 4.16 (t, $J = 6.3$ Hz, 2H), 2.97 (t, $J = 7.3$ Hz, 2H), 2.11 – 2.04 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.6, 171.2, 143.2, 142.7, 136.7, 135.0, 131.4, 130.0, 129.7, 126.9, 126.2, 123.5, 63.2, 30.0, 26.6, 21.0. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2925 (C–H), 1745 (O–CO–CH₃), 1642 (C=O); HRMS (ESI): m/z ($M + H^+$) calculated for $\text{C}_{16}\text{H}_{15}\text{O}_3\text{S}_2$ 319.0457; found 319.0439.



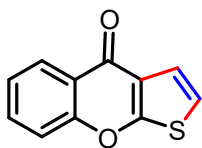
3-(6-chloro-4-oxo-4H-thieno[2,3-b]thiochromen-2-yl)propyl acetate (10b). A brown solid (51 mg, 72%), mp 135 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.59 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.54 (s, 1H), 7.48 (dd, *J* = 8.7, 2.0 Hz, 1H), 4.15 (t, *J* = 6.3 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.10 – 2.04 (m, 5H). ¹³C NMR (125 MHz, CDCl₃) δ 174.7, 171.1, 143.2, 142.5, 138.2, 138.0, 135.0, 131.2, 128.4, 127.6, 125.5, 123.5, 63.1, 30.0, 26.6, 21.0. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2924 (C–H), 1744 (O–CO–CH₃) 1639 (C=O); HRMS (ESI): *m/z* (M + H⁺) calculated for C₁₆H₁₄ClO₃S₂ 353.0067; found 353.0061.



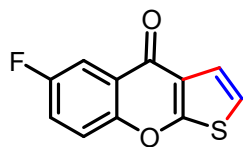
3-(7-fluoro-4-oxo-4H-thieno[2,3-b]thiochromen-2-yl)propyl acetate (10c). A light brown solid (47 mg, yield 70%), mp 112 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.68 (dd, *J* = 9.0, 5.9 Hz, 1H), 7.54 (s, 1H), 7.30 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.23 (dd, *J* = 8.1, 2.4 Hz, 1H), 4.15 (t, *J* = 6.3 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.10 – 2.05 (m, 5H). ¹³C NMR (125 MHz, CDCl₃) δ 174.6, 171.1, 164.0 (d, *J* = 255.9 Hz), 143.1, 142.4, 138.8 (d, *J* = 9.9 Hz) 135.0, 132.6 (d, *J* = 9.7 Hz), 126.7, 123.5, 115.5 (d, *J* = 22.2 Hz), 112.1 (d, *J* = 25.2 Hz), 63.1, 30.0, 26.6, 21.0. ¹⁹F NMR (471 MHz, CDCl₃) δ -106.32. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2935 (C–H), 1744 (O–CO–CH₃), 1638 (C=O); HRMS (ESI): *m/z* (M + H⁺) calculated for C₁₆H₁₄FO₃S₂ 337.0363; found 337.0351.



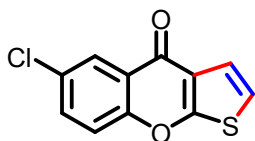
4H-thieno[2,3-b]chromen-4-one (11a). A yellow brown solid (30 mg, yield 74%), mp 121 °C ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 2H), 6.92 (d, *J* = 5.9 Hz, 1H), ¹³C NMR (125 MHz, CDCl₃) δ 173.0, 168.0, 156.8, 133.5, 126.7, 124.8, 123.4, 122.5, 121.3, 117.5, 115.2. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2920 (C–H), 1638 (C=O); HRMS (ESI): *m/z* (M + H⁺) calculated for C₁₁H₇O₂S 203.0161; found 203.0162.



6-fluoro-4H-thieno[2,3-b]chromen-4-one (11b). A brown solid (31 mg, yield 71%), mp 129 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.01 (dd, *J* = 8.2, 2.8 Hz, 1H), 7.55 (dd, *J* = 9.1, 4.0 Hz, 1H), 7.45-7.41 (m, 2H), 6.94 (d, *J* = 5.9 Hz, 1H), ¹³C NMR (150 MHz, CDCl₃) δ 172.4, 168.5, 159.5, (d, *J* = 246.6 Hz) 153.2, 124.0 (d, *J* = 7.1 Hz), 123.0, 121.8 (d, *J* = 25.5 Hz), 119.7 (d, *J* = 7.9 Hz), 115.9, 111.9 (d, *J* = 23.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -114.54. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2924 (C–H), 1656 (C=O); HRMS (ESI): *m/z* (M + H⁺) calculated for C₁₁H₆FO₂S 221.0067; found 221.0059.

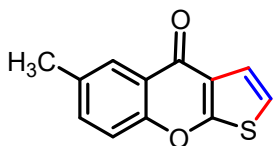


6-chloro-4H-thieno[2,3-b]chromen-4-one (11c). A brown solid (35 mg, yield 73%), mp 137 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 2.6 Hz, 1H), 7.65 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.45 (d, *J* = 6.0 Hz, 1H), 6.94 (d, *J* = 6.0 Hz, 1H). ¹³C

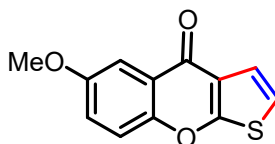


NMR (125 MHz, CDCl₃) δ 172.0, 168.4, 155.3, 133.8, 131.0, 126.4, 123.8, 123.5, 121.5, 119.4, 116.0. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2928 (C–H), 1656 (C=O); HRMS (ESI): m/z (M + H⁺) calculated for C₁₁H₅ClO₂S 236.9772; found 236.9752.

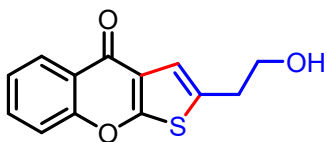
6-methyl-4H-thieno[2,3-b]chromen-4-one (11d). A yellow brown solid (30 mg, yield 69%), mp 130 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.15 (s, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 6.90 (d, J = 5.9 Hz, 1H), 2.49 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 173.4, 168.3, 155.4, 135.0, 134.9, 126.3, 123.5, 122.4, 121.6, 117.4, 115.3, 21.0. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2923 (C–H), 1653 (C=O); HRMS (ESI): m/z (M + H⁺) calculated for C₁₂H₉O₂S 217.0318; found 217.0315.



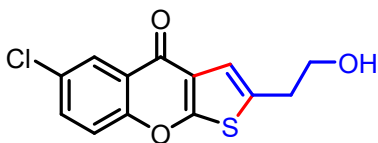
6-Methoxy-4H-thieno[2,3-b]chromen-4-one (11e). A yellow brown solid (33 mg, yield 69%), mp 117 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.73 (s, 1H), 7.46 (t, J = 8.6 Hz, 2H), 7.29 (d, J = 9.1 Hz, 1H), 6.90 (d, J = 5.7 Hz, 1H), 3.93 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 173.1, 168.2, 156.8, 151.9, 123.5, 123.3, 123.1, 121.5, 119.0, 115.4, 106.2, 56.1. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2923 (C–H), 1649 (C=O); HRMS (ESI): m/z (M + H⁺) calculated for C₁₂H₉O₃S 233.0267; found 233.0267.



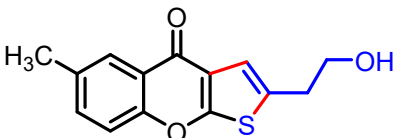
2-(2-hydroxyethyl)-4H-thieno[2,3-b]chromen-4-one (12a). A yellowish brown solid, (37 mg, 74%), mp 134 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.34 (dd, J = 8.0, 1.8 Hz, 1H), 7.68 (ddd, J = 8.7, 7.1, 1.8 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.43 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 7.20 (s, 1H), 3.94 (t, J = 6.0 Hz, 2H), 3.06 (t, J = 6.5 Hz, 2H), 1.86 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 172.8, 167.3, 156.9, 133.5, 131.7, 126.9, 124.9, 123.7, 122.9, 118.8, 117.7, 62.8, 33.7. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3416 (O–H), 1634 (C=O), 1462 (C–O); HRMS (ESI) calculated for C₁₃H₁₁O₃S 247.0423 (M + H⁺); found 247.0422



6-chloro-2-(2-hydroxyethyl)-4H-thieno[2,3-b]chromen-4-one (12c). A brown solid (43 mg, yield 77%), mp 149 °C ¹H NMR (500 MHz, CDCl₃) δ 8.31 (s, 1H), 7.63 (d, J = 11.0 Hz, 1H), 7.48 (d, J = 8.9 Hz, 1H), 7.19 (s, 1H), 3.94 (t, J = 6.0 Hz, 2H), 3.07 (t, J = 6.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 171.6, 167.4, 155.2, 133.6, 132.3, 130.9, 126.3, 124.0, 123.5, 119.4, 118.7, 62.8, 33.7. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3426 (O–H), 2925 (C–H), 1642 (C=O); HRMS (ESI): m/z (M + H⁺) calculated for C₁₃H₁₀ClO₃S 281.0034; found 281.0028.

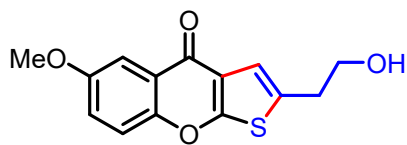


2-(2-hydroxyethyl)-6-methyl-4H-thieno[2,3-b]chromen-4-one (12d). A yellowish brown solid, (41 mg, yield 75%), mp 138.3 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.12 (s, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.19 (s, 1H), 3.93 (t, J = 7.2 Hz,



2H), 3.05 (t, $J = 6.8$ Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.0, 167.3, 155.3, 134.9, 134.7, 131.4, 126.2, 123.6, 122.5, 118.8, 117.4, 62.8, 33.7, 21.0. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3421 (O–H), 2921 (C–H), 1638 (C=O); HRMS (ESI): m/z ($M + H^+$) calculated for $\text{C}_{14}\text{H}_{13}\text{O}_3\text{S}$ 261.0580; found 261.0581.

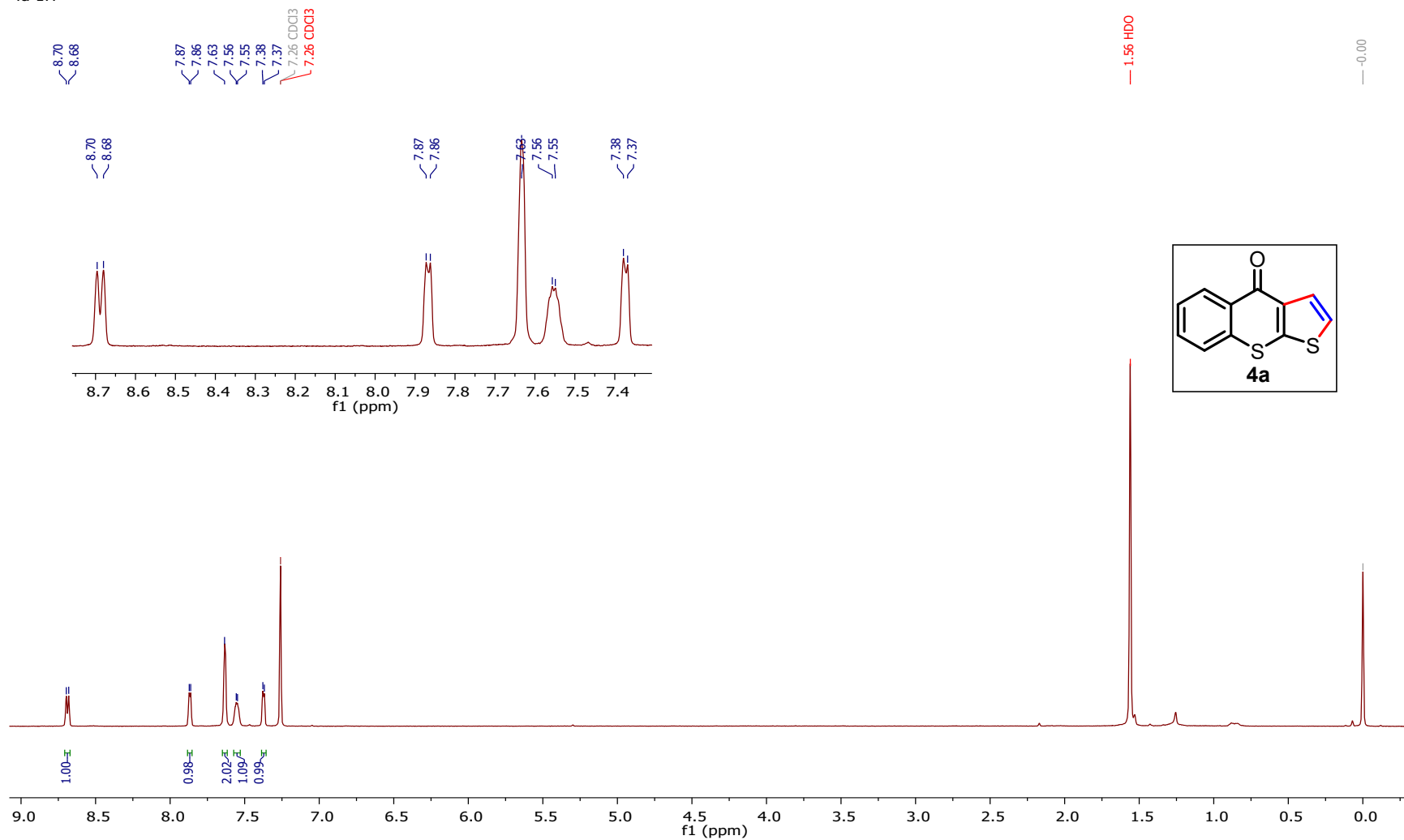
2-(2-hydroxyethyl)-6-methoxy-4*H*-thieno[2,3-*b*]chromen-4-one (12e). A brown solid, (41 mg, yield 75%), mp 135.2 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 3.0$ Hz, 1H), 7.41 (d, $J = 9.1$ Hz, 1H), 7.24 (dd, $J = 5.9, 3.1$ Hz, 1H), 7.17 (s, 1H), 3.94-3.90 (m, 2H), 3.04 (t, $J = 5.9$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.7, 167.3, 156.7, 151.8, 131.6, 123.4, 123.3, 123.1, 119.0, 118.7, 106.1, 62.8, 56.1, 33.7. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3411 (O–H), 2923 (C–H), 1642 (C=O); HRMS (ESI): m/z ($M + H^+$) calculated for $\text{C}_{14}\text{H}_{13}\text{O}_4\text{S}$ 277.0529; found 277.0529.



S3: ^1H , ^{13}C NMR and HRMS data of each synthesised Compounds.

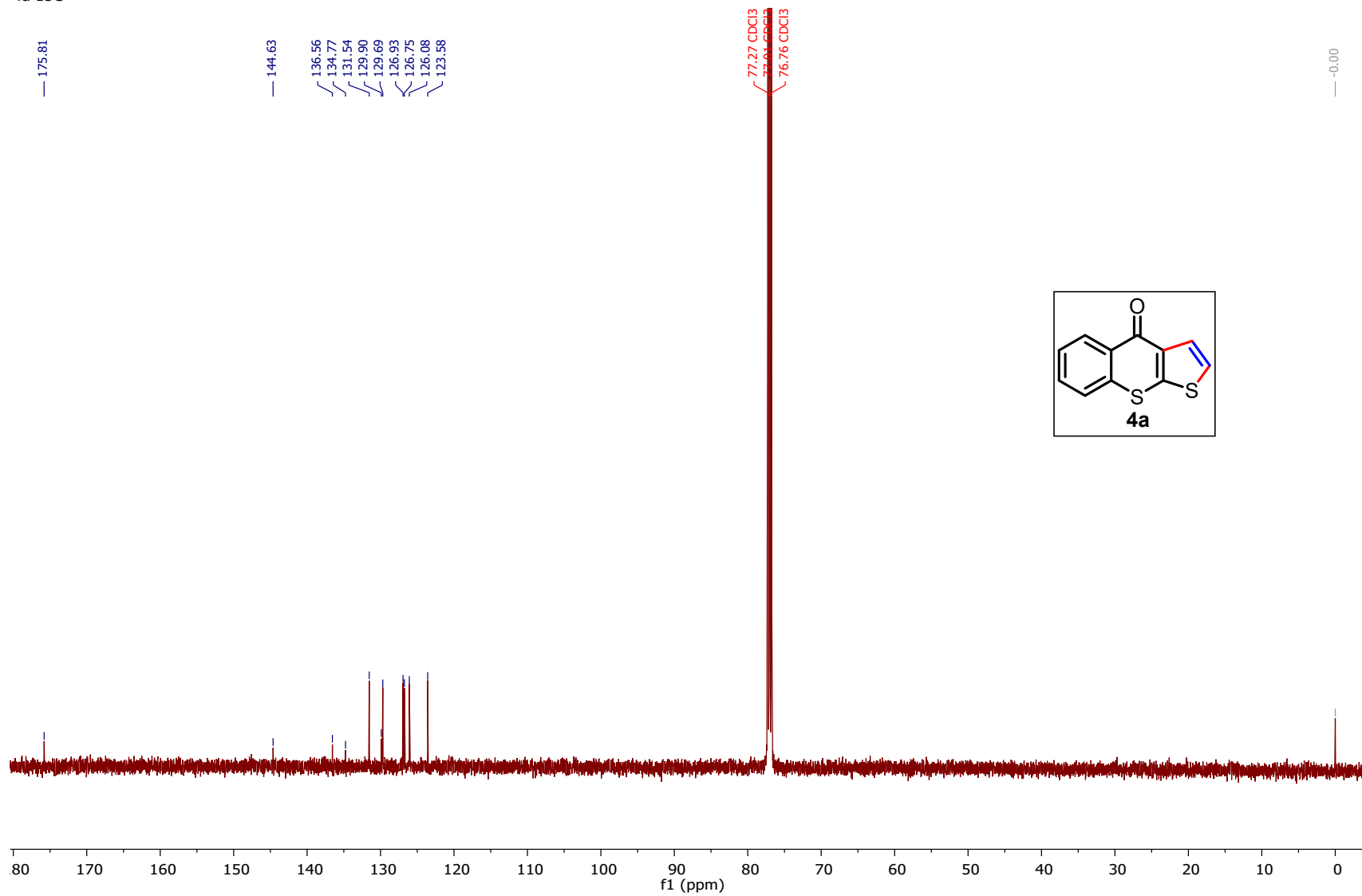
^1H NMR (500 MHz, CDCl_3) spectrum of Compound 4a

4a 1H



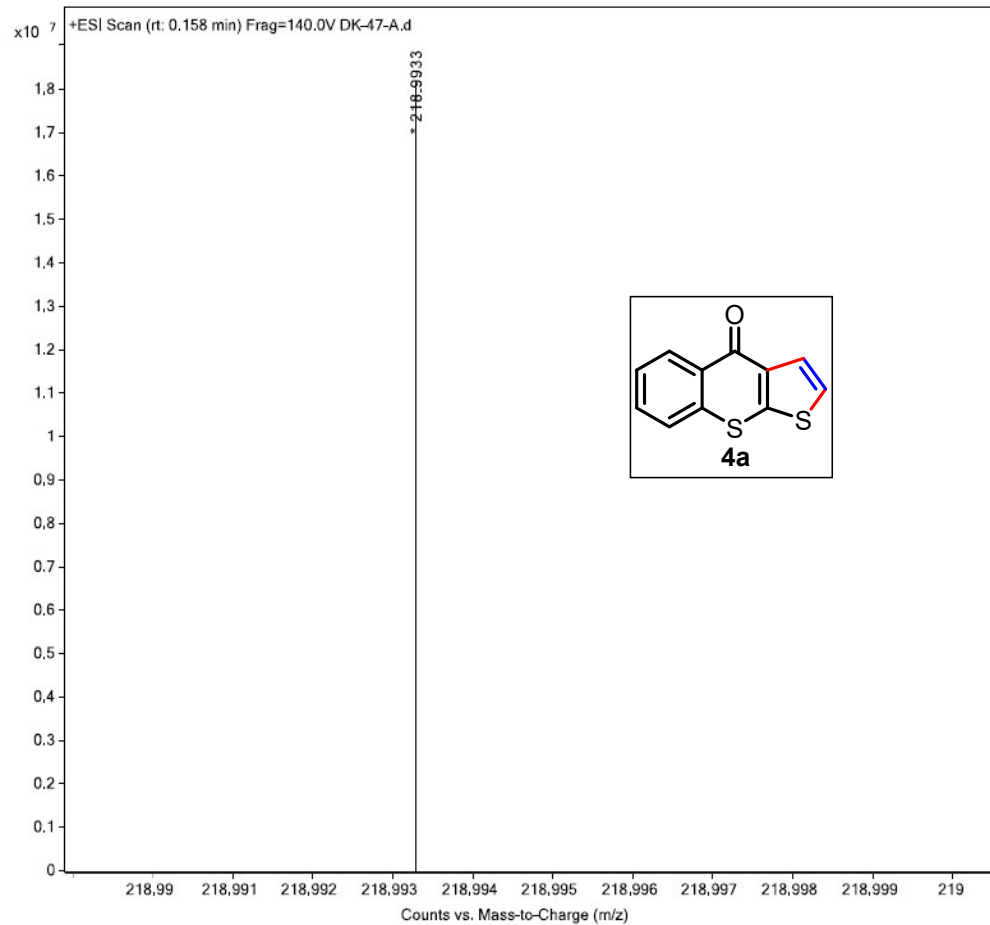
$^{13}\text{C} \{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Compound 4a

4a 13C



HRMS of compound 4a

Sample Name	Sample12	Position	P1-B1	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DK-47-A,d
ACQ Method	DIRECT MASS_POSITIVE_01_1500.m	Comment		Acquired Time	07-04-2025 15:01:31 (UTC+05:30)



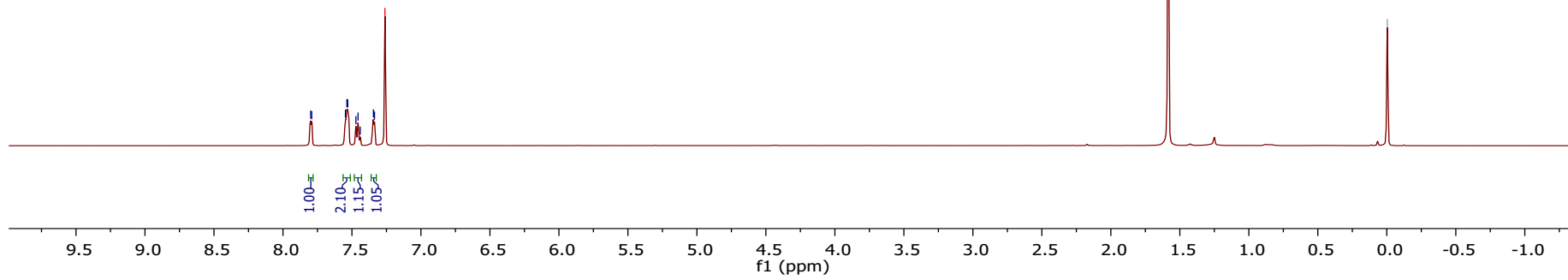
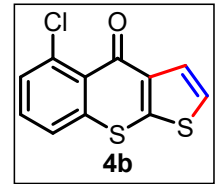
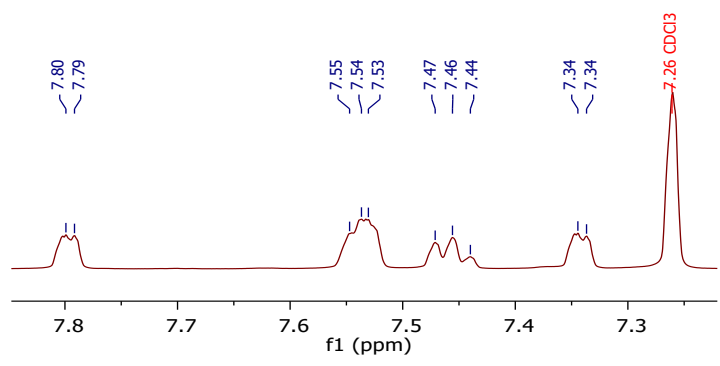
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 4b

4b 1H

7.80
7.79
7.55
7.54
7.53
7.47
7.46
7.44
7.34
7.34
7.26 CDCl3

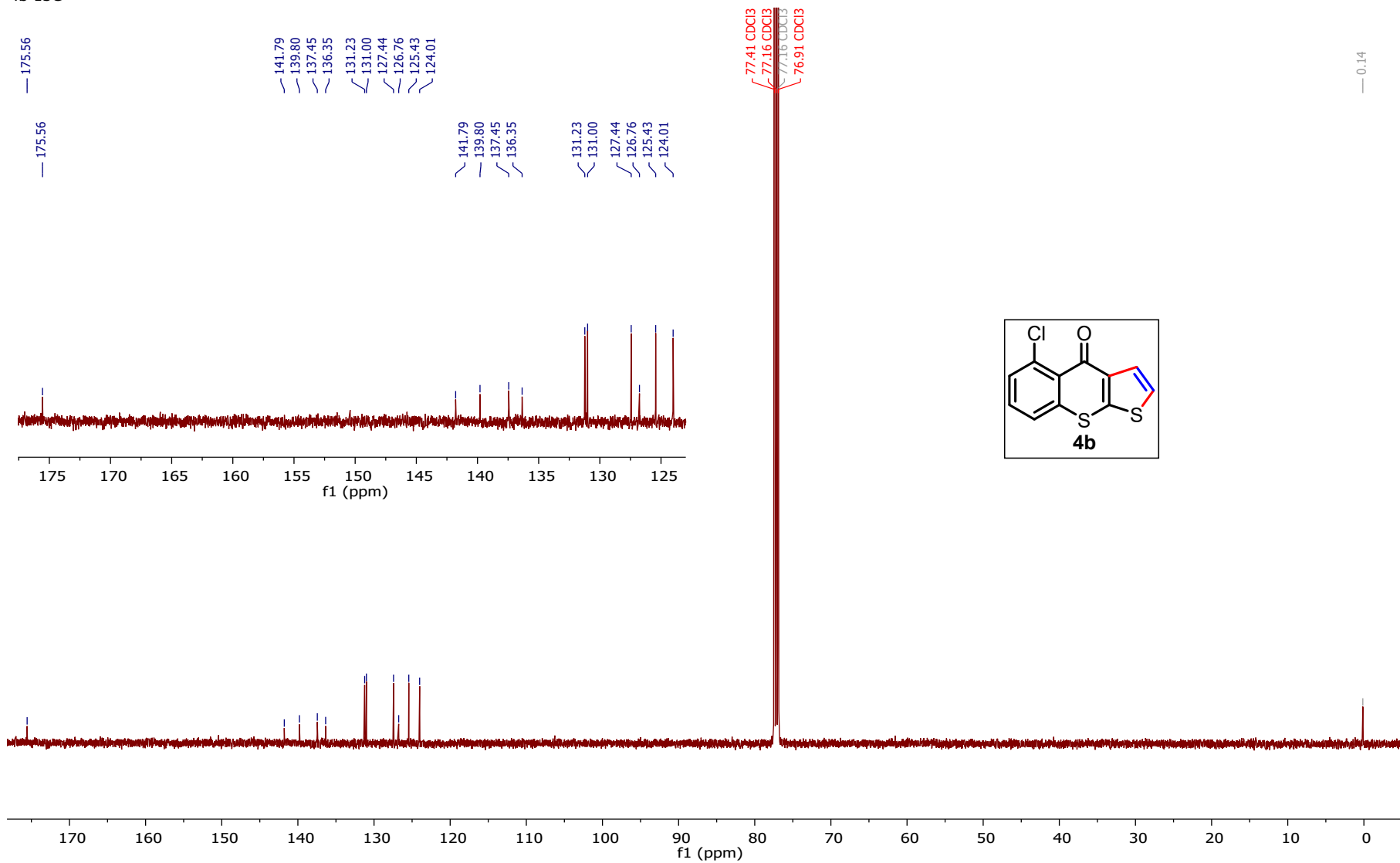
1.58 H2O

-0.00



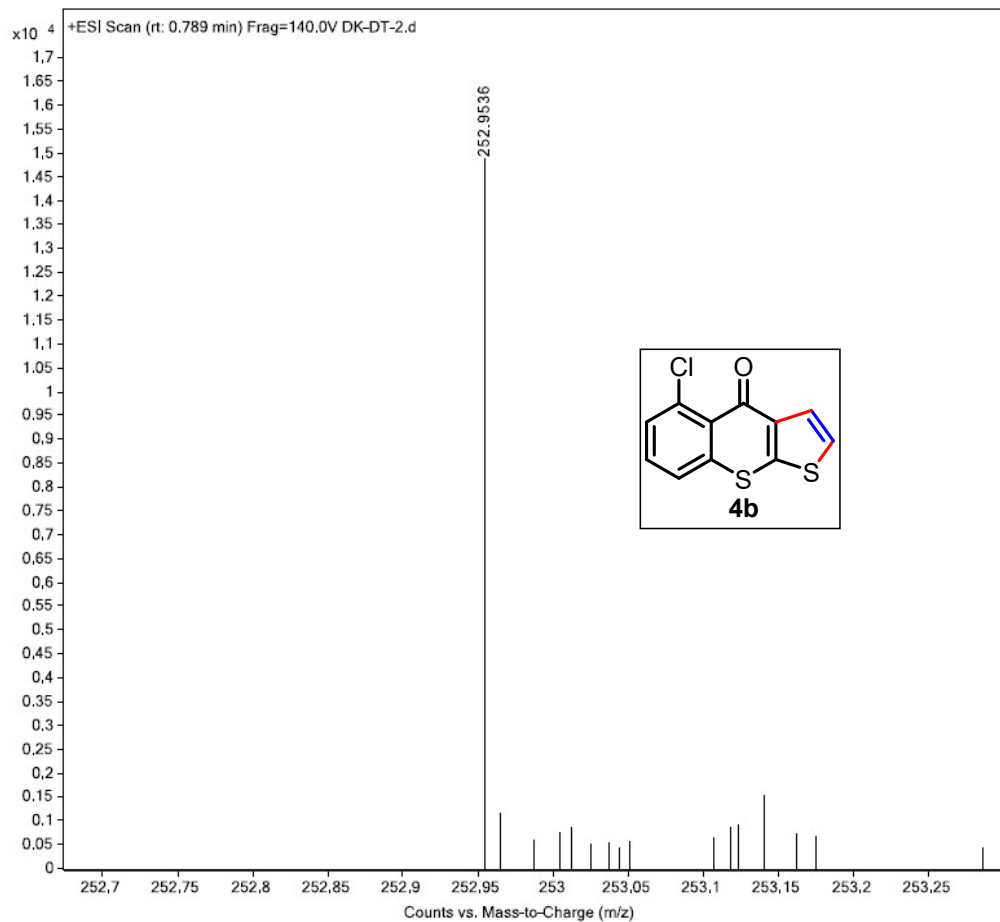
$^{13}\text{C} \{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Compound 4b

4b 13C



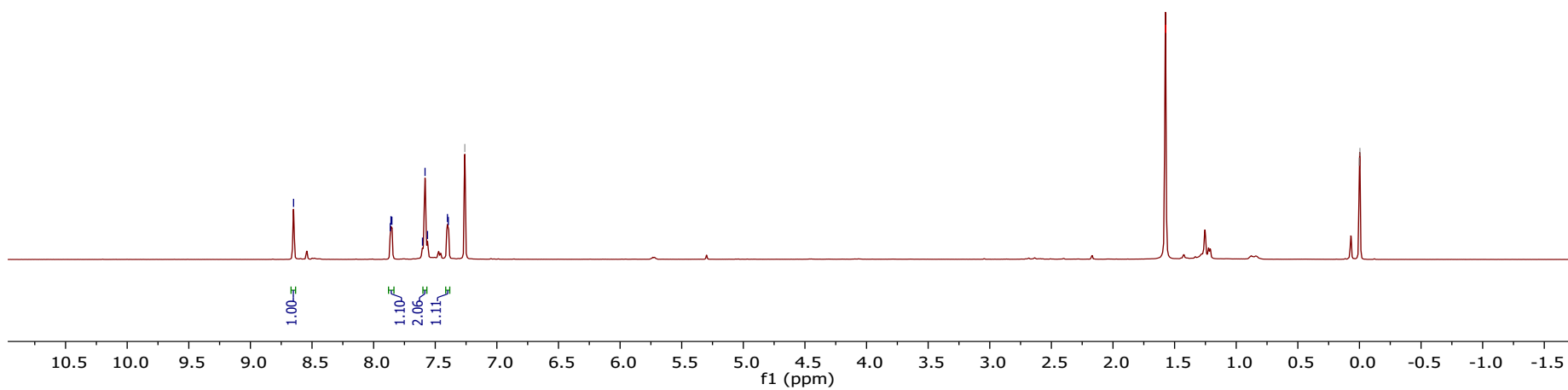
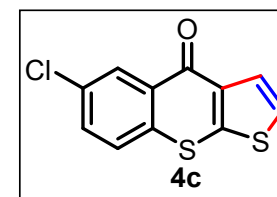
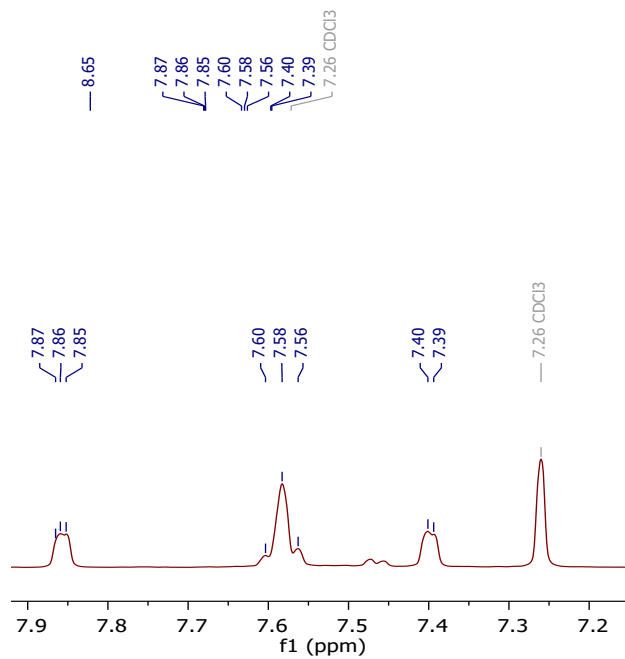
HRMS of compound 4b

Sample Name	Sample2	Position	P1-A2	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DK-DT-2,d
ACQ Method	DIRECT MASS_POSITIVE_50_1500,m	Comment		Acquired Time	28-07-2025 10:17:04 (UTC+05:30)



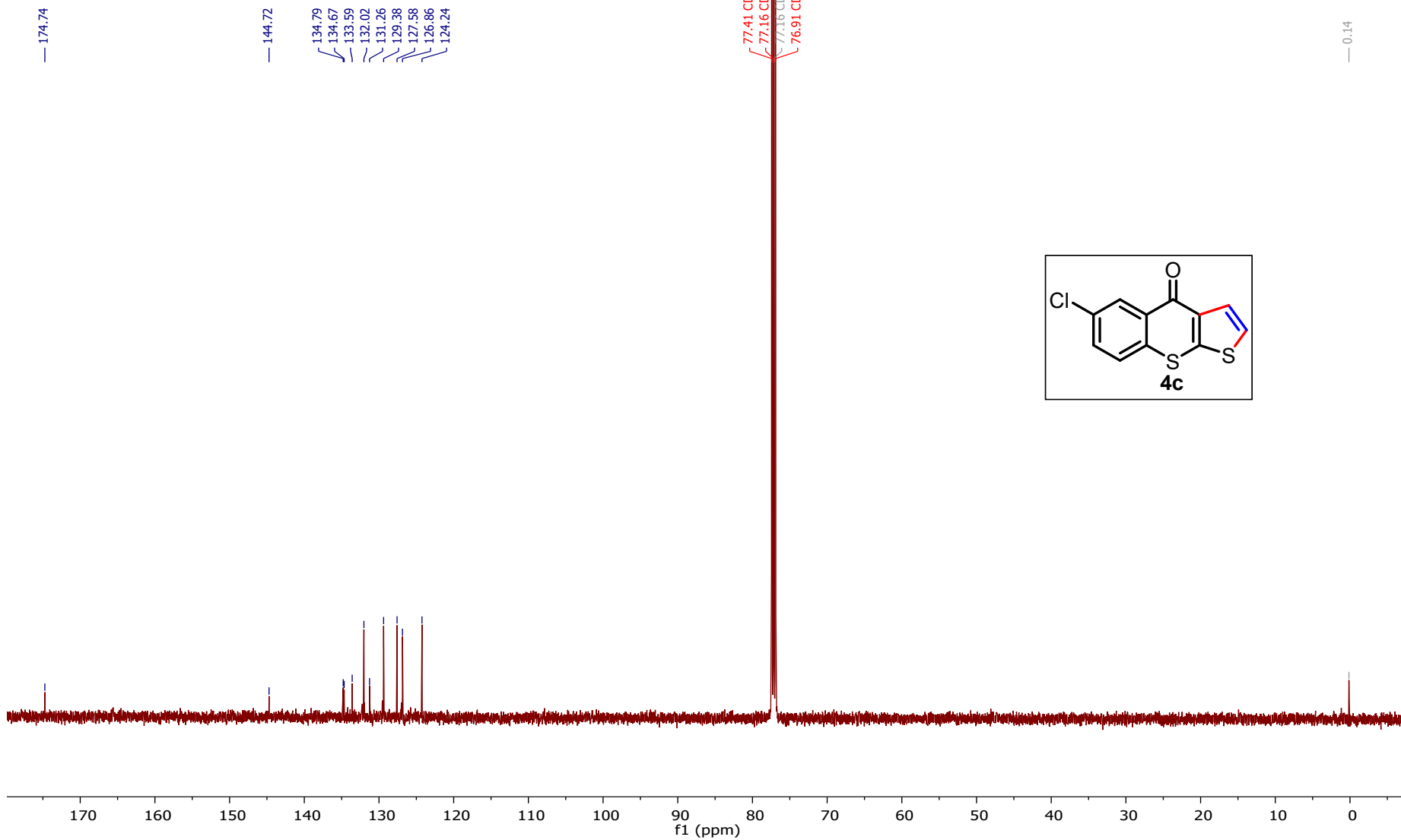
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 4c

4c 1H

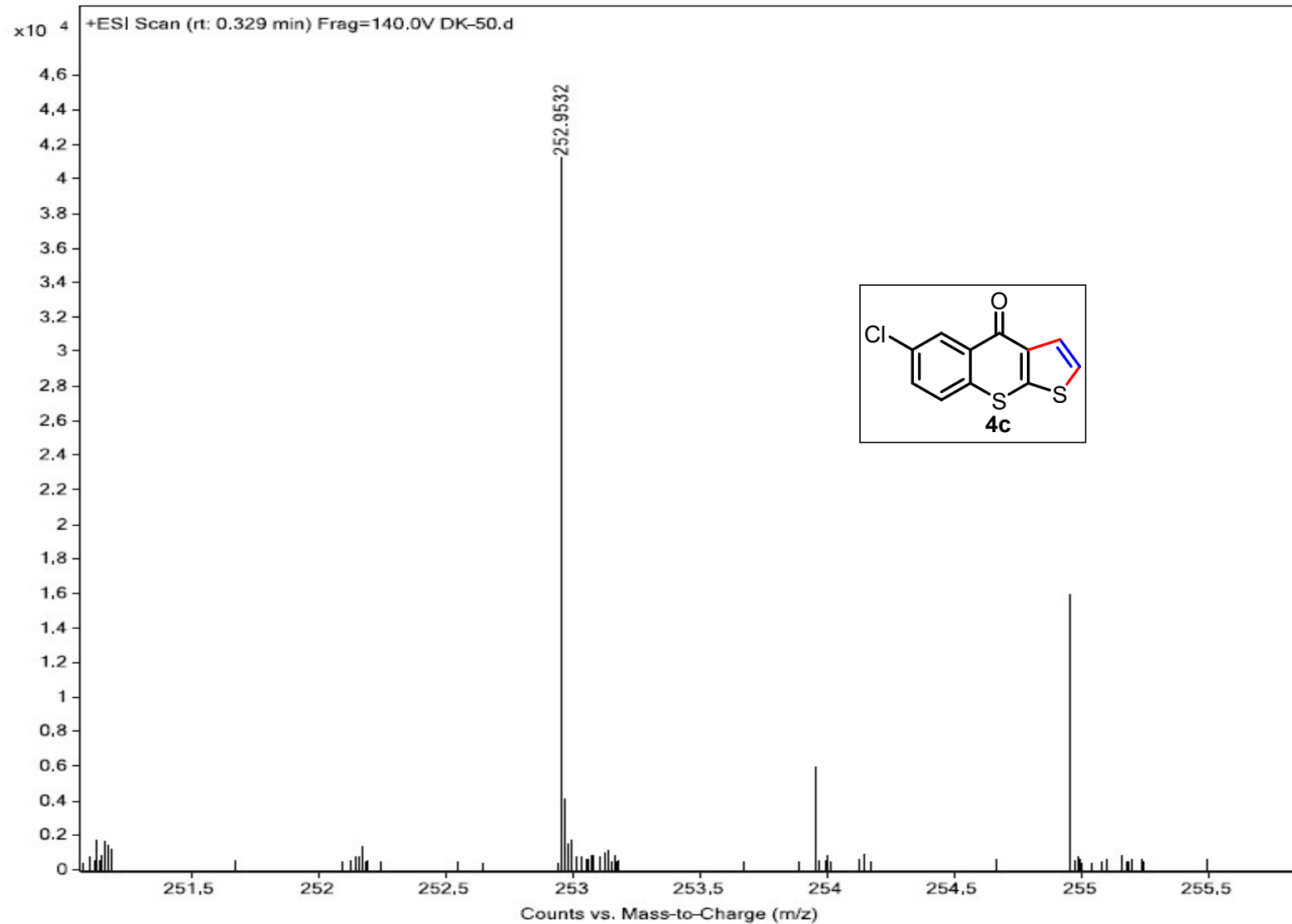


¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 4c

4c 13C

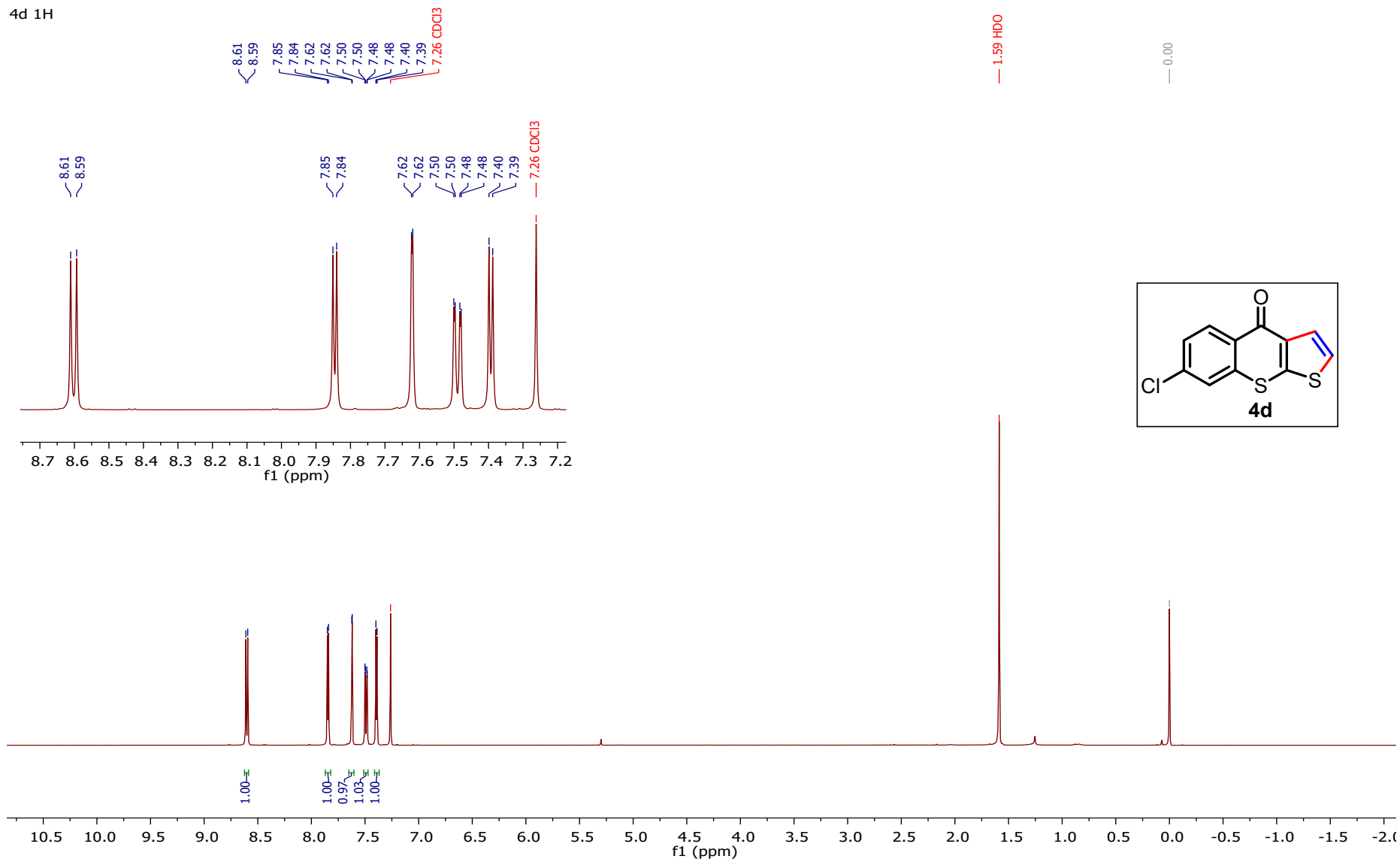


HRMS of compound 4c

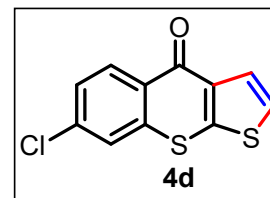
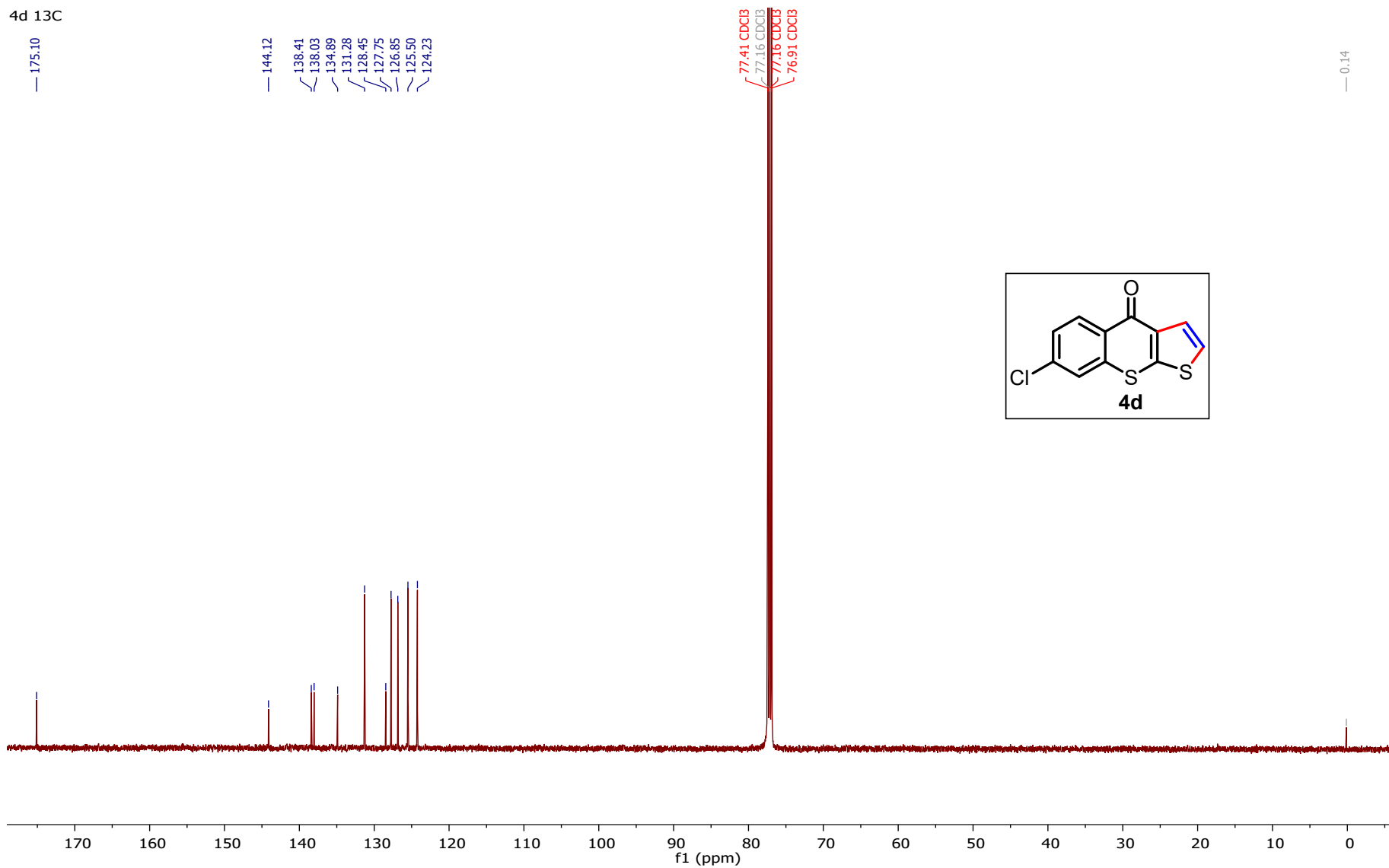


¹H NMR (500 MHz, CDCl₃) spectrum of Compound 4d

4d 1H



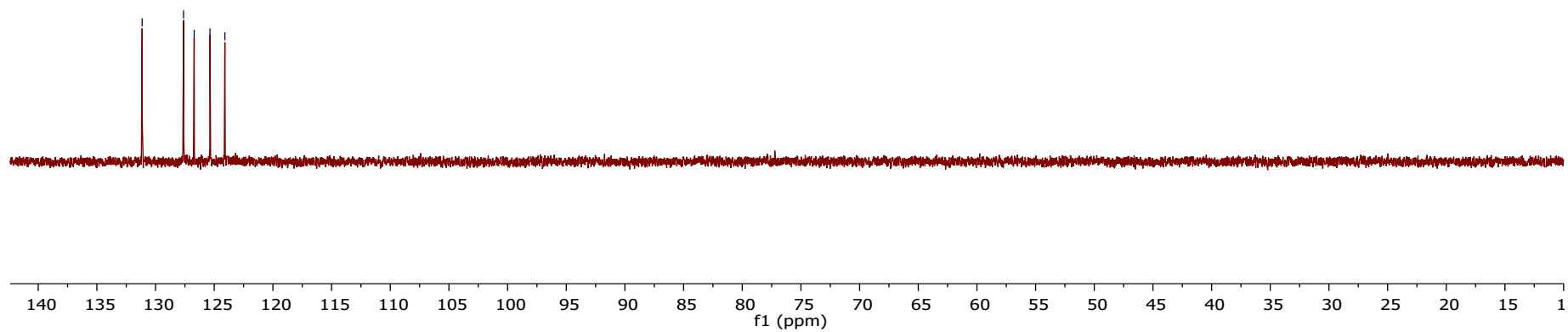
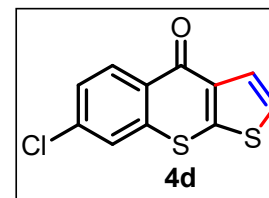
4d ¹³C



DEPT-135 ¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 4d

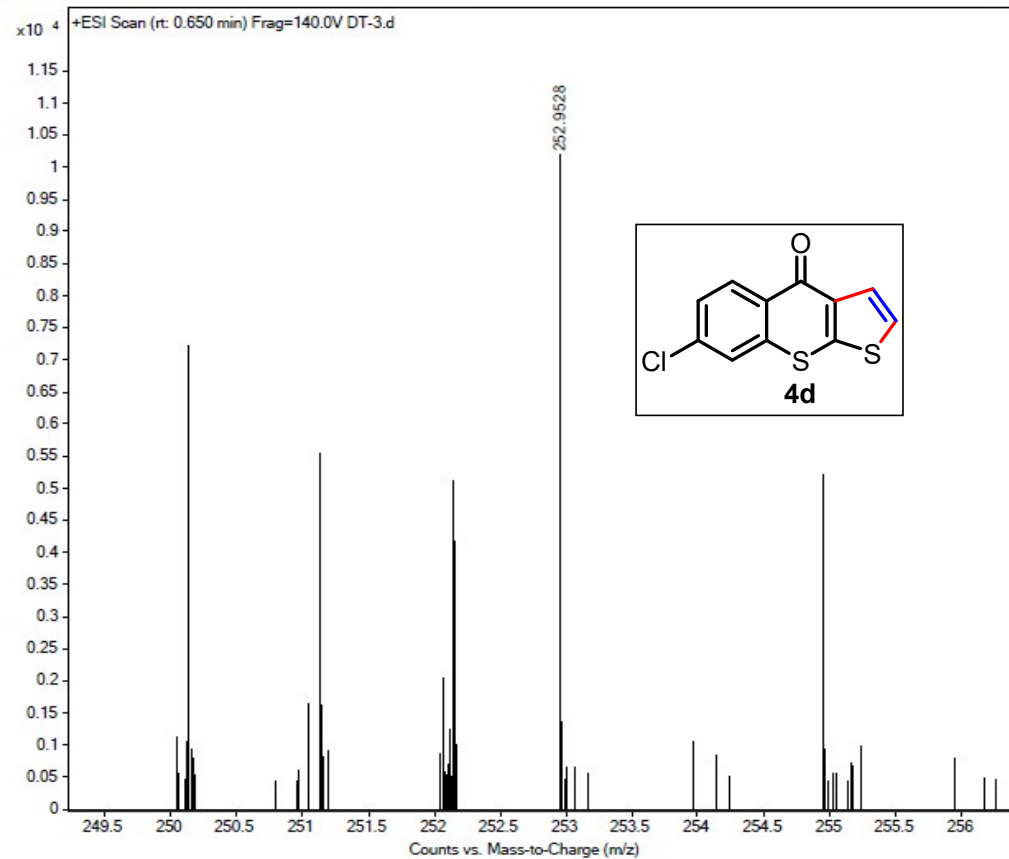
— 131.15
— 127.62
— 126.71
— 125.36
— 124.10

4d DEPT-135



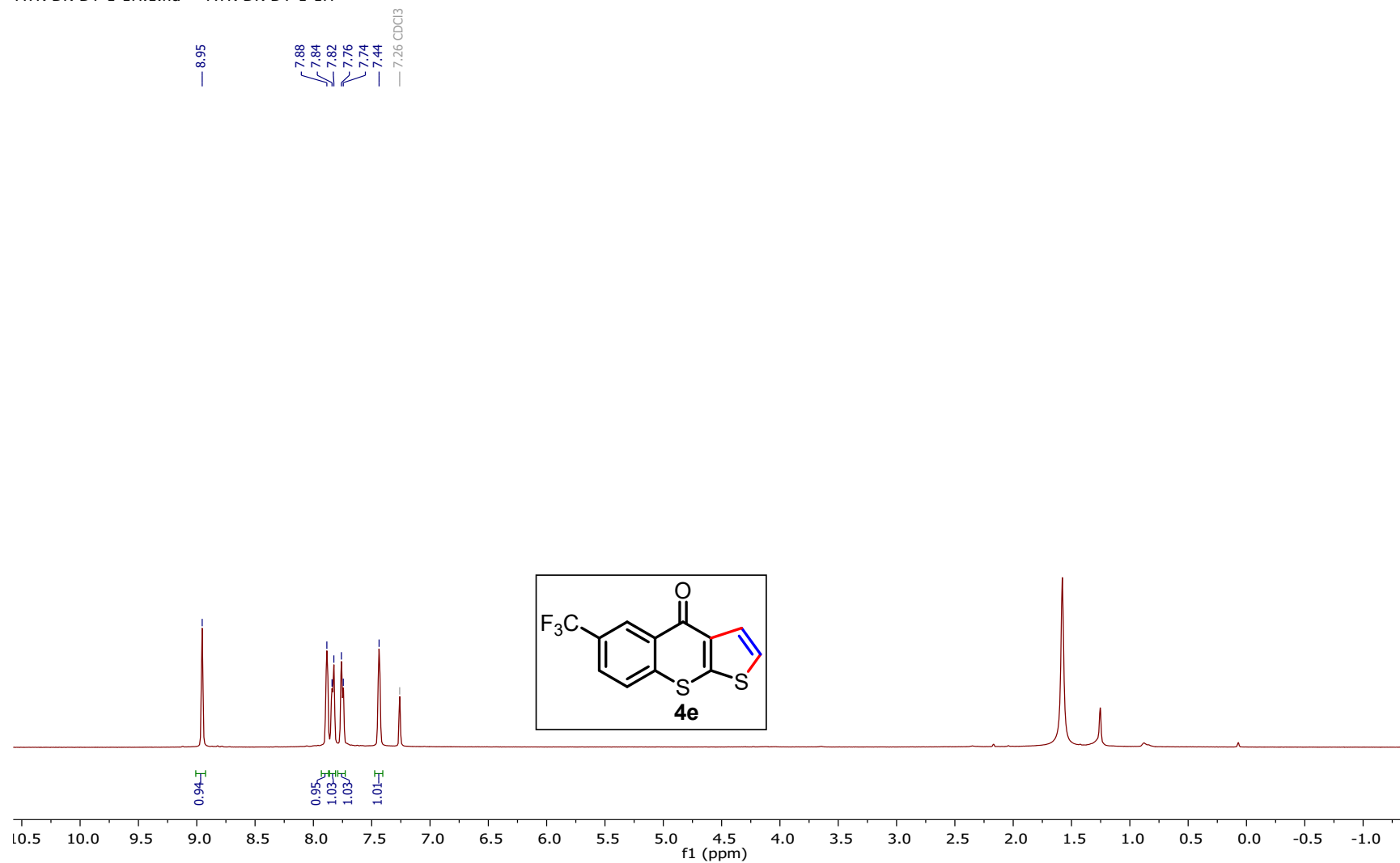
HRMS of compound 4d

Sample Name		Position	P1-A9	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DT-3.d
ACQ Method	DIRECT MASS_POSITIVE_01_1.m	Comment		Acquired Time	19-08-2025 15:48:20 (UTC+05:30)



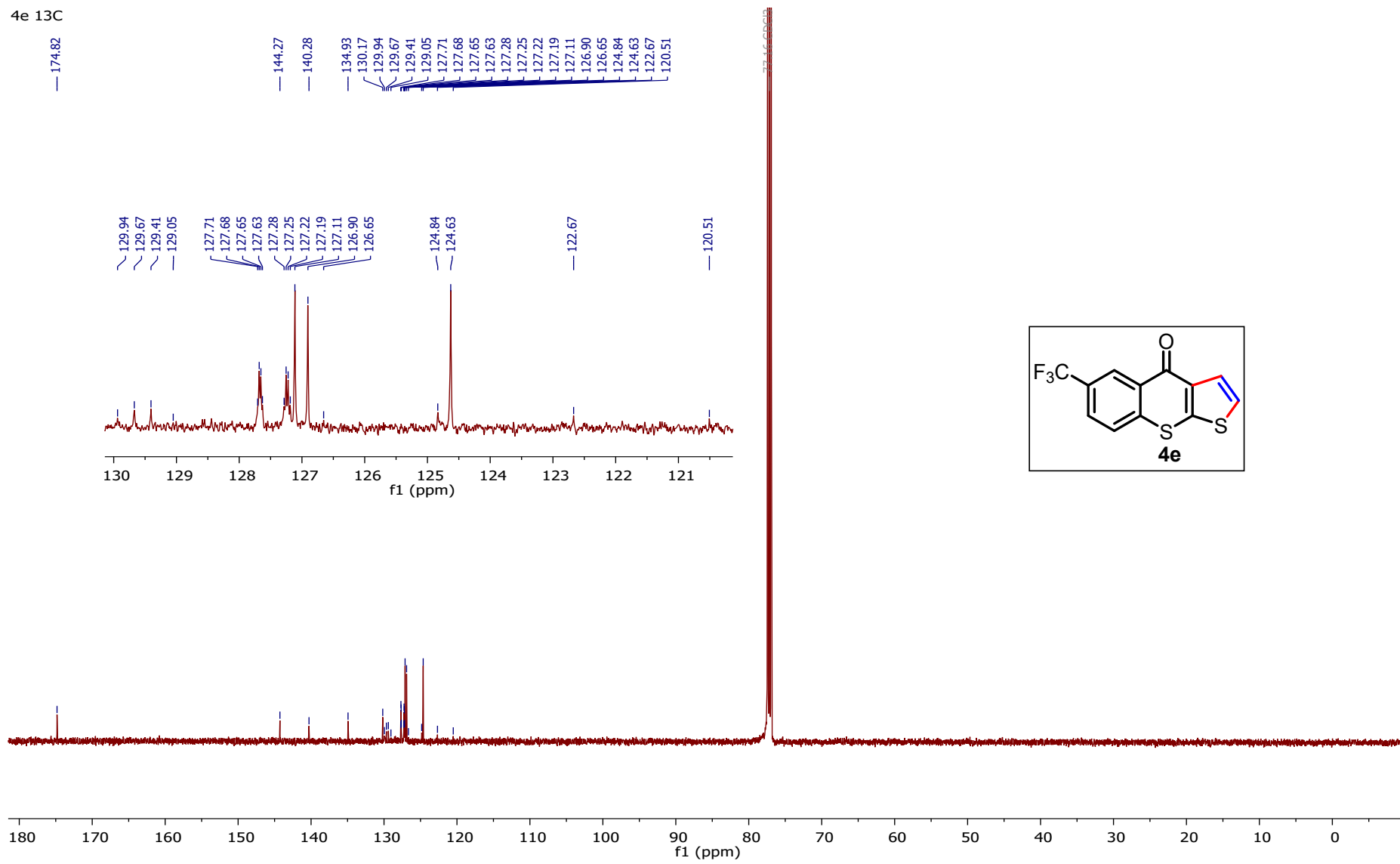
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 4e

ATK-DK-DT-1-1H.1.fid — ATK-DK-DT-1-1H



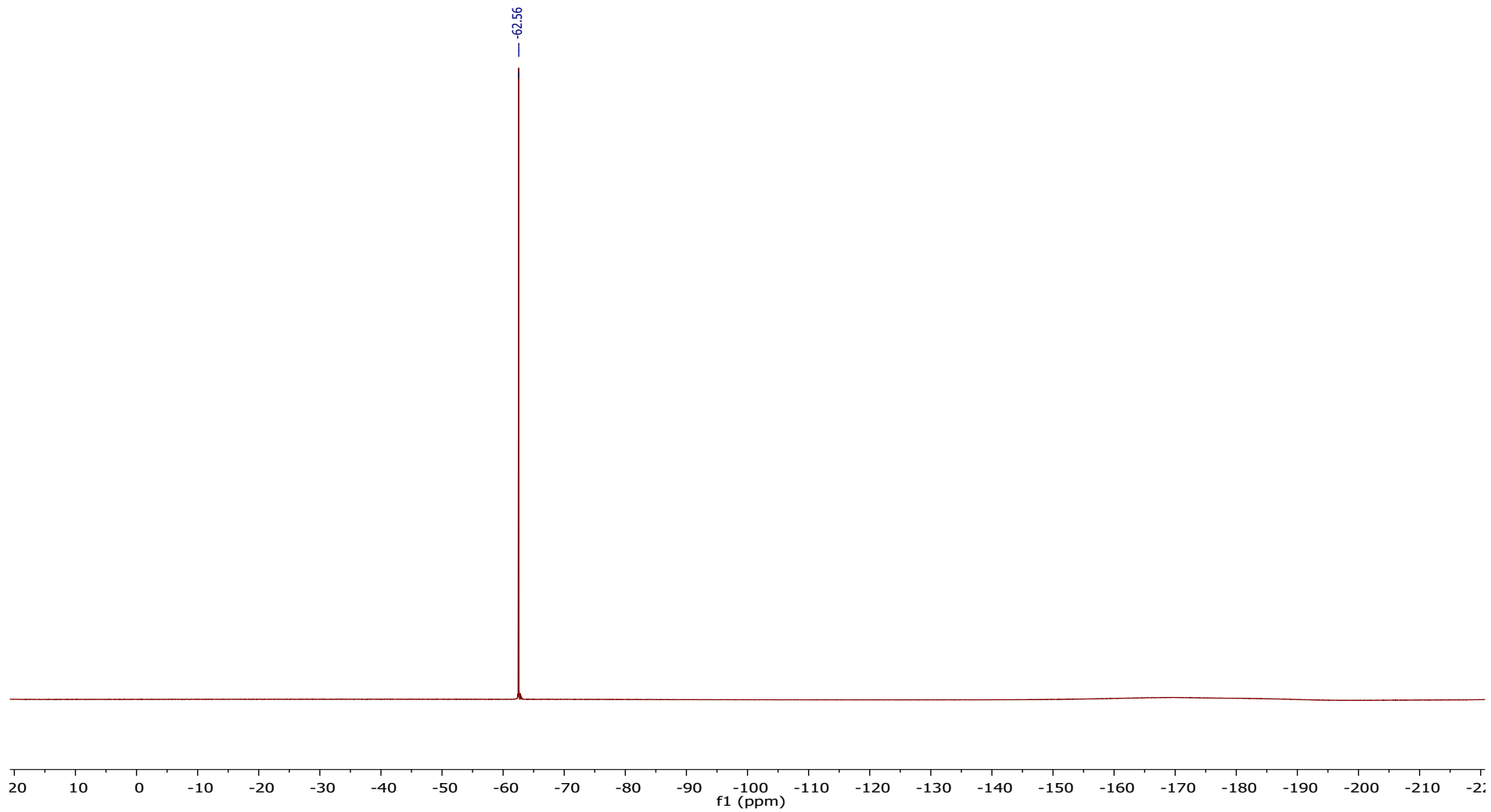
¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 4e

4e 13C



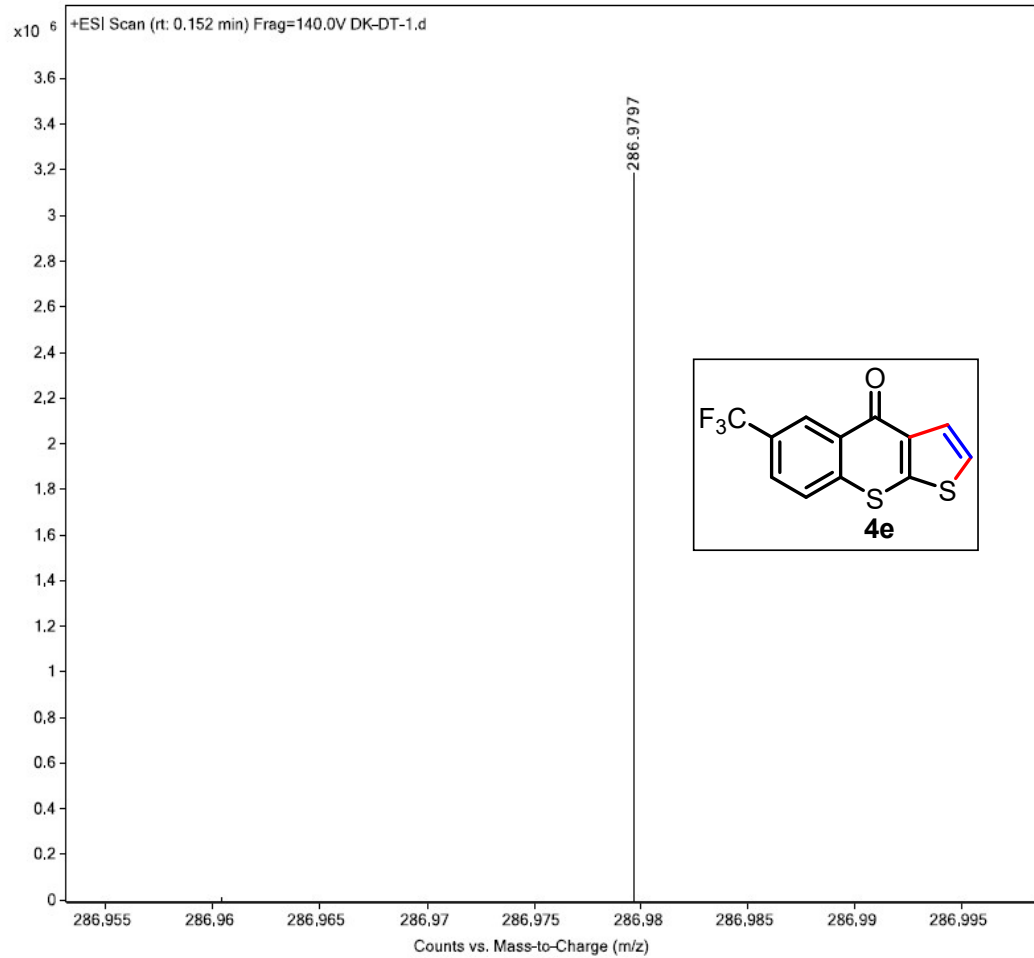
¹⁹F NMR of compound 4e

ATK-DK-DT-1-19F.3.fid — ATK-DK-DT-1-19F



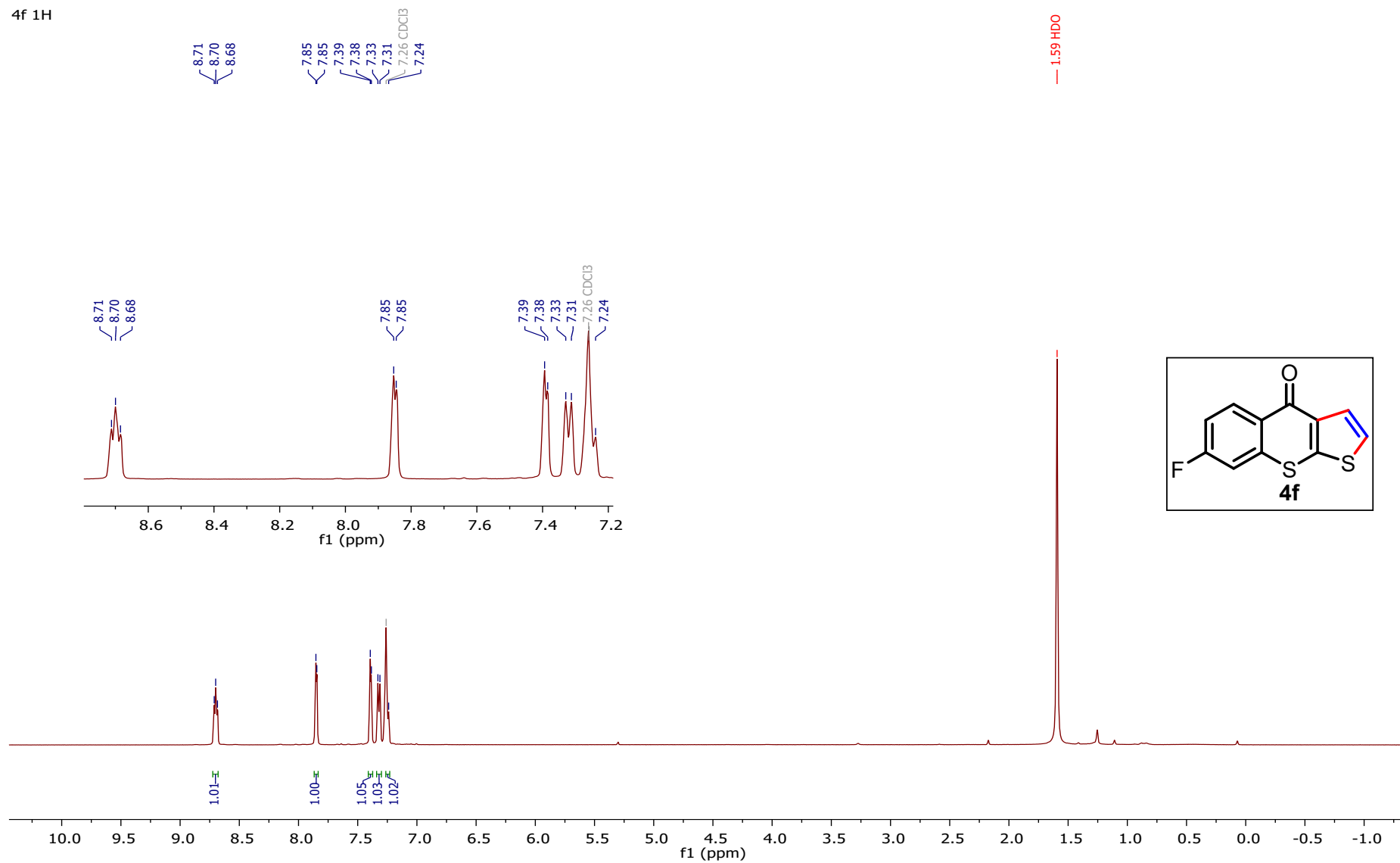
HRMS of compound 4e

Sample Name	Sample17	Position	P1-B5	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DK-DT-1,d
ACQ Method	DIRECT MASS_POSITIVE_50_1500.m	Comment		Acquired Time	23-06-2025 10:47:06 (UTC+05:30)



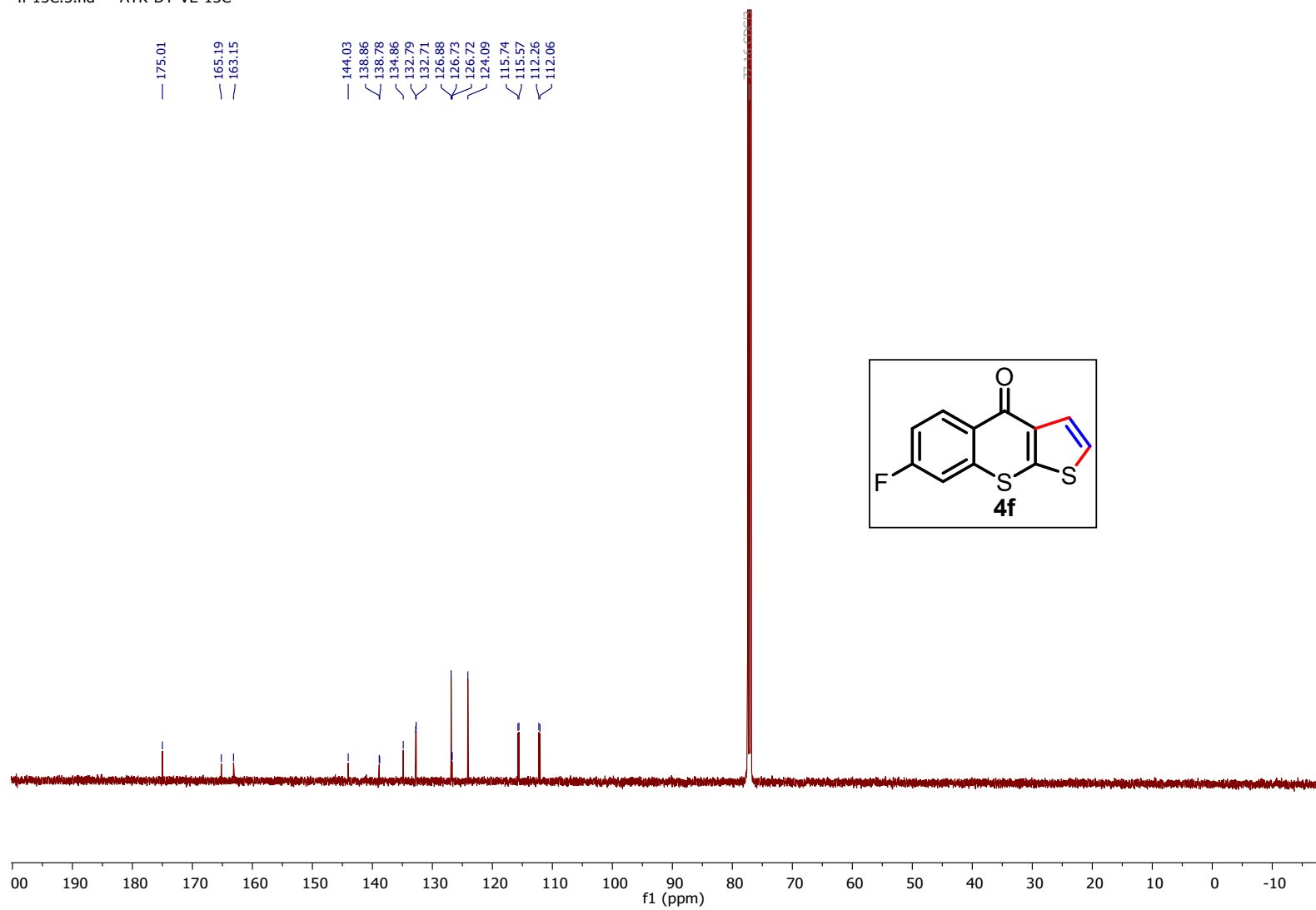
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 4f

4f 1H



^{13}C { ^1H } NMR (125 MHz, CDCl_3) spectrum of Compound 4f

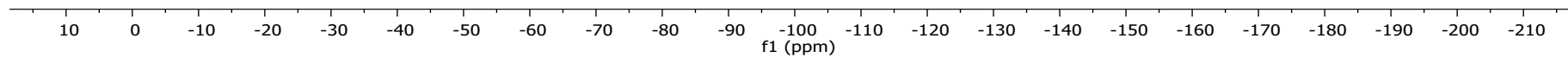
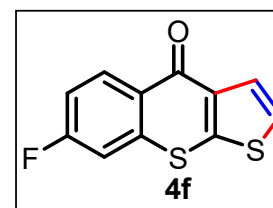
4f 13C.5.fid — ATK-DT-VE-13C



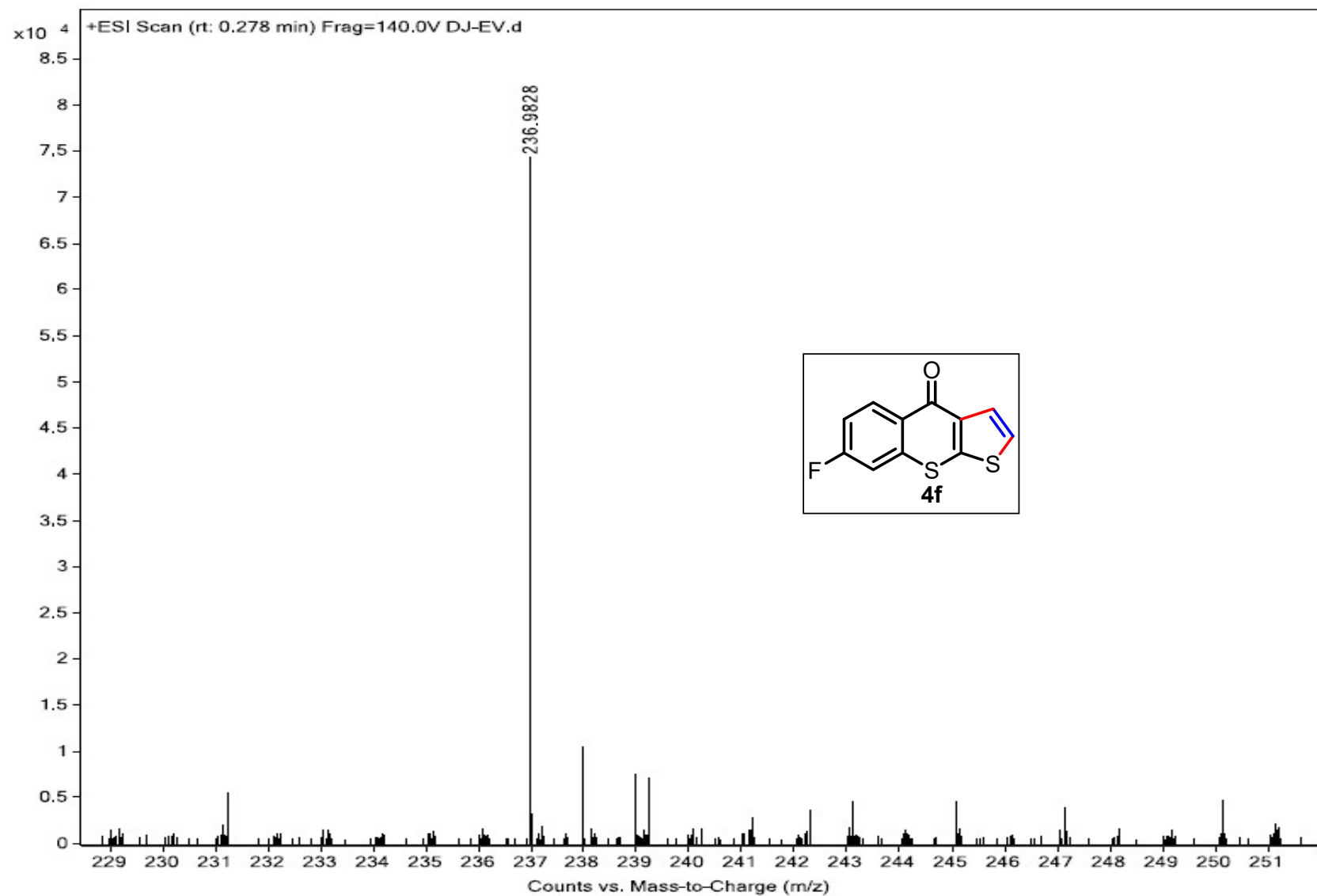
¹⁹F NMR of Compound 4f

4f 19F

-105.78

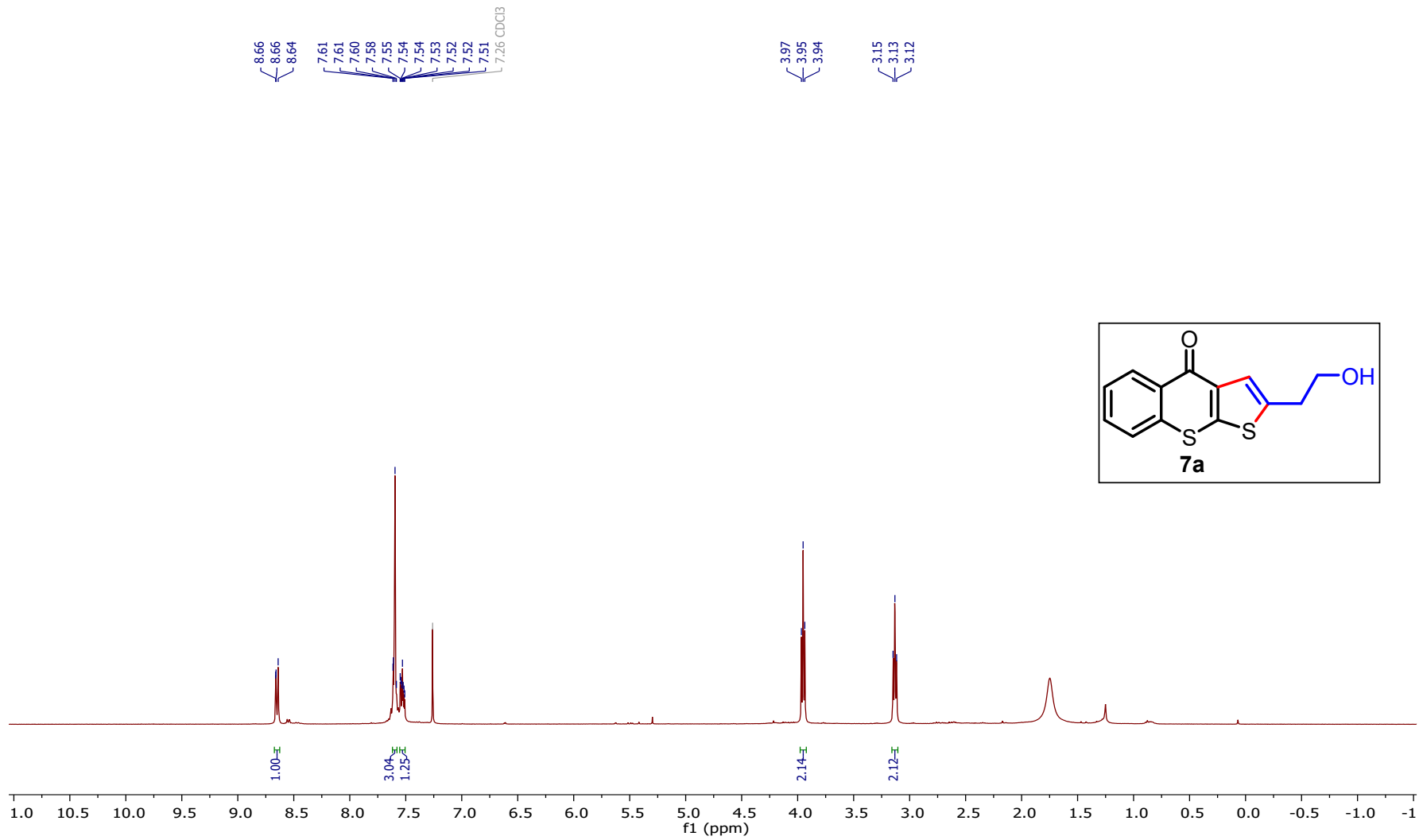


HRMS of compound 4f



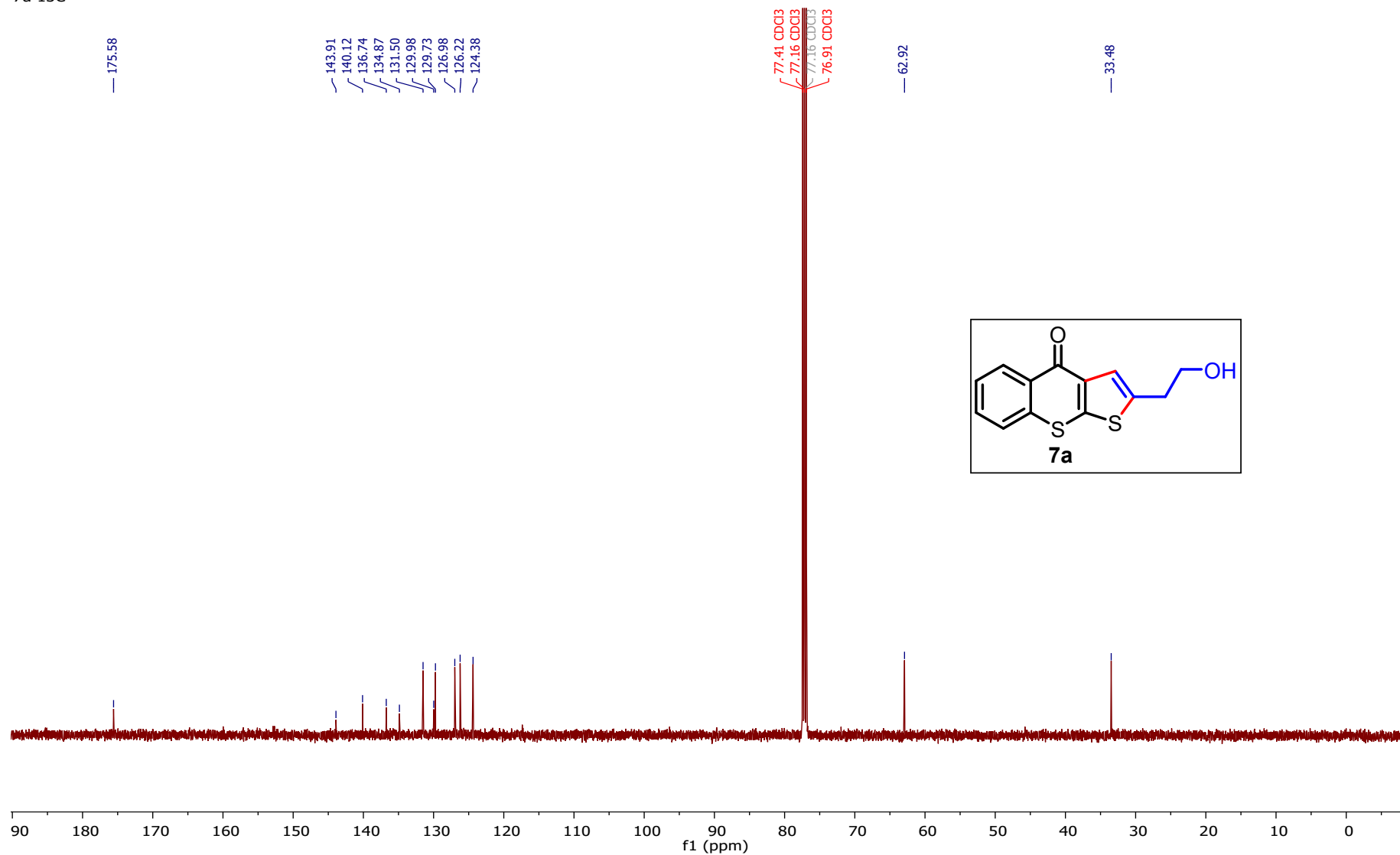
¹H NMR (400 MHz, CDCl₃) spectrum of Compound 7a

7a 1H



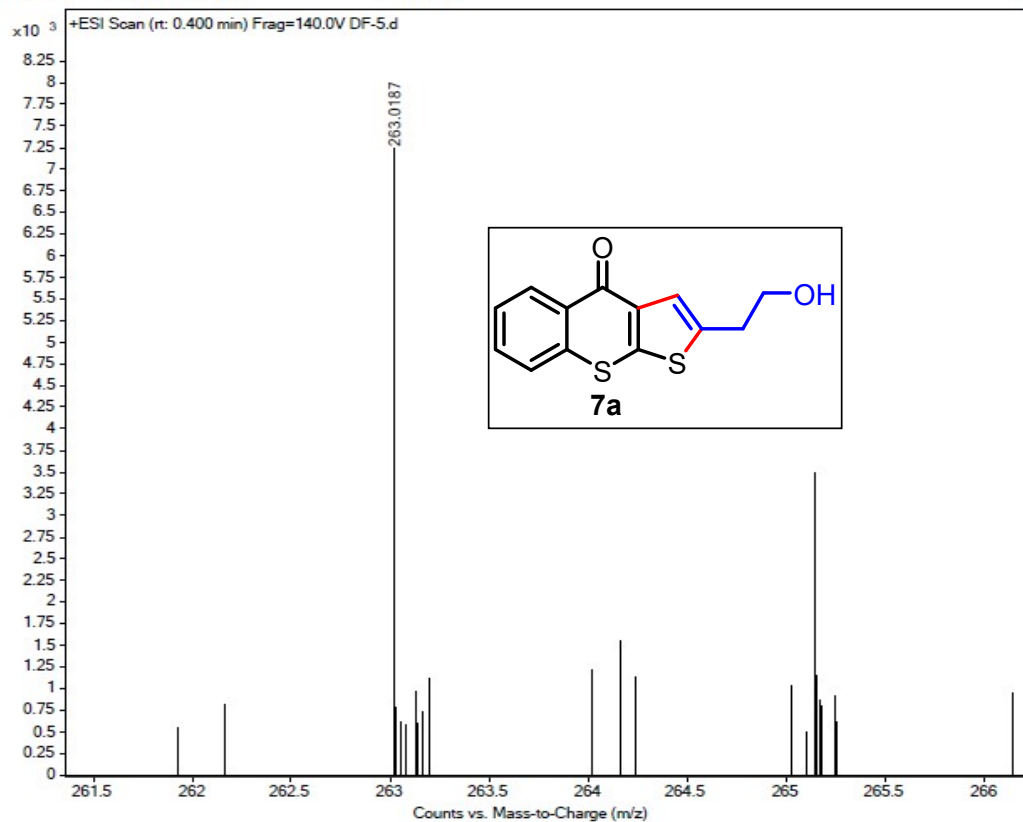
¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 7a

7a 13C



HRMS of compound 7a

Sample Name	Sample34	Position	P1-D1	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DF-5.d
ACQ Method	DIRECT MASS_POSITIVE_01_1.m	Comment		Acquired Time	28-08-2025 12:29:56 (UTC+05:30)



^1H NMR (400 MHz, CDCl_3) spectrum of Compound 7b

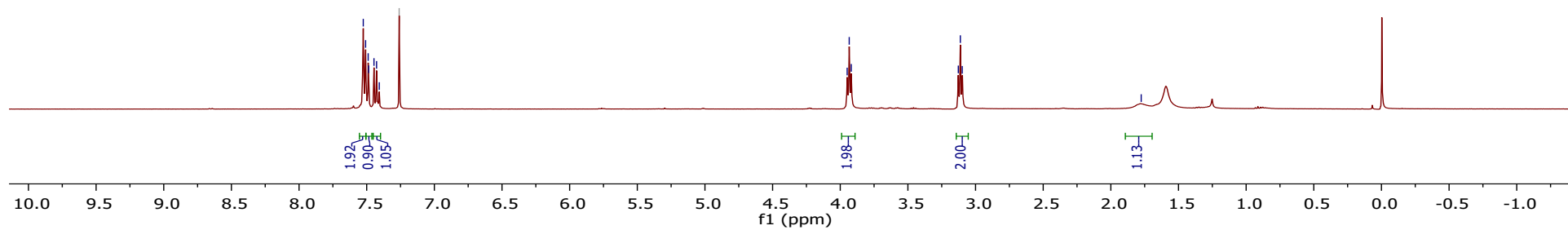
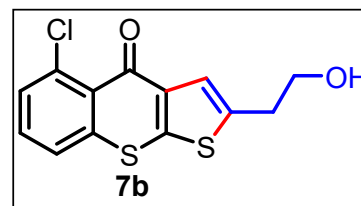
ATK-DF-D-1-1H.1.fid — ATK-DF-D-1-1H

7.53
7.51
7.49
7.49
7.45
7.43
7.41
7.26 CDCl₃

3.95
3.93
3.92

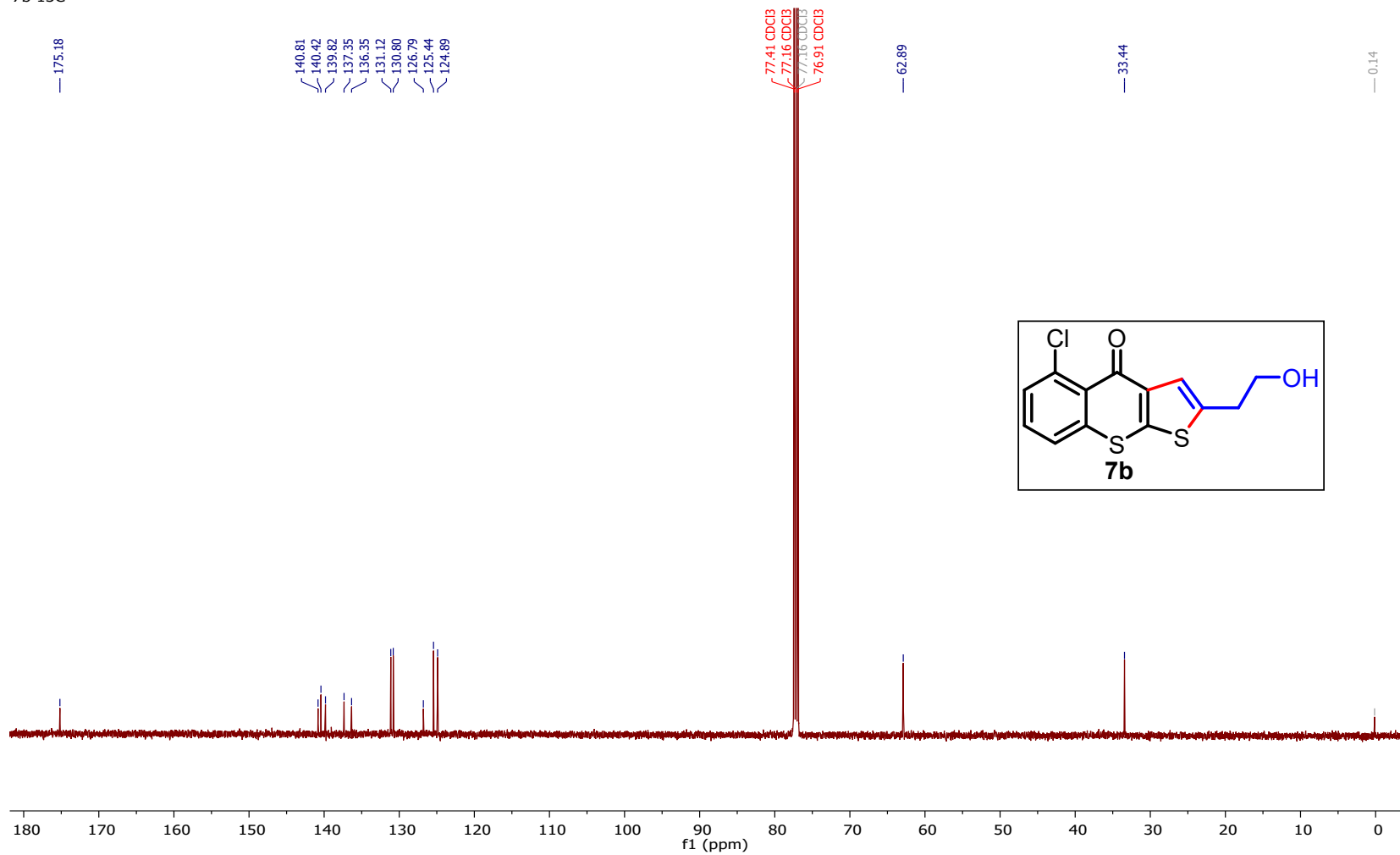
3.13
3.11
3.10

— 1.78



^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Compound 7b

7b 13C



HRMS of compound 7b

Sample Name
User Name
Sample Type
ACQ Method

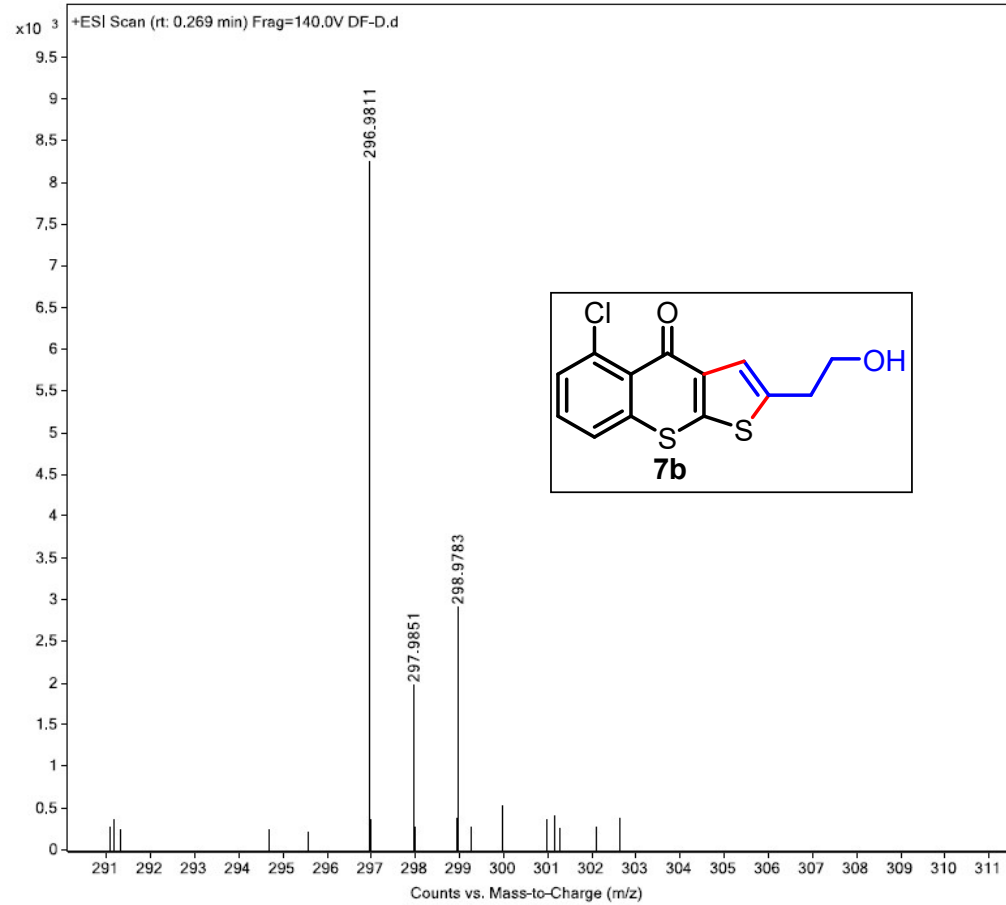
Sample17
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_50_1500.m

Position
Inj Vol
IRM Calibration Status
Comment

P1-B6
5
Success

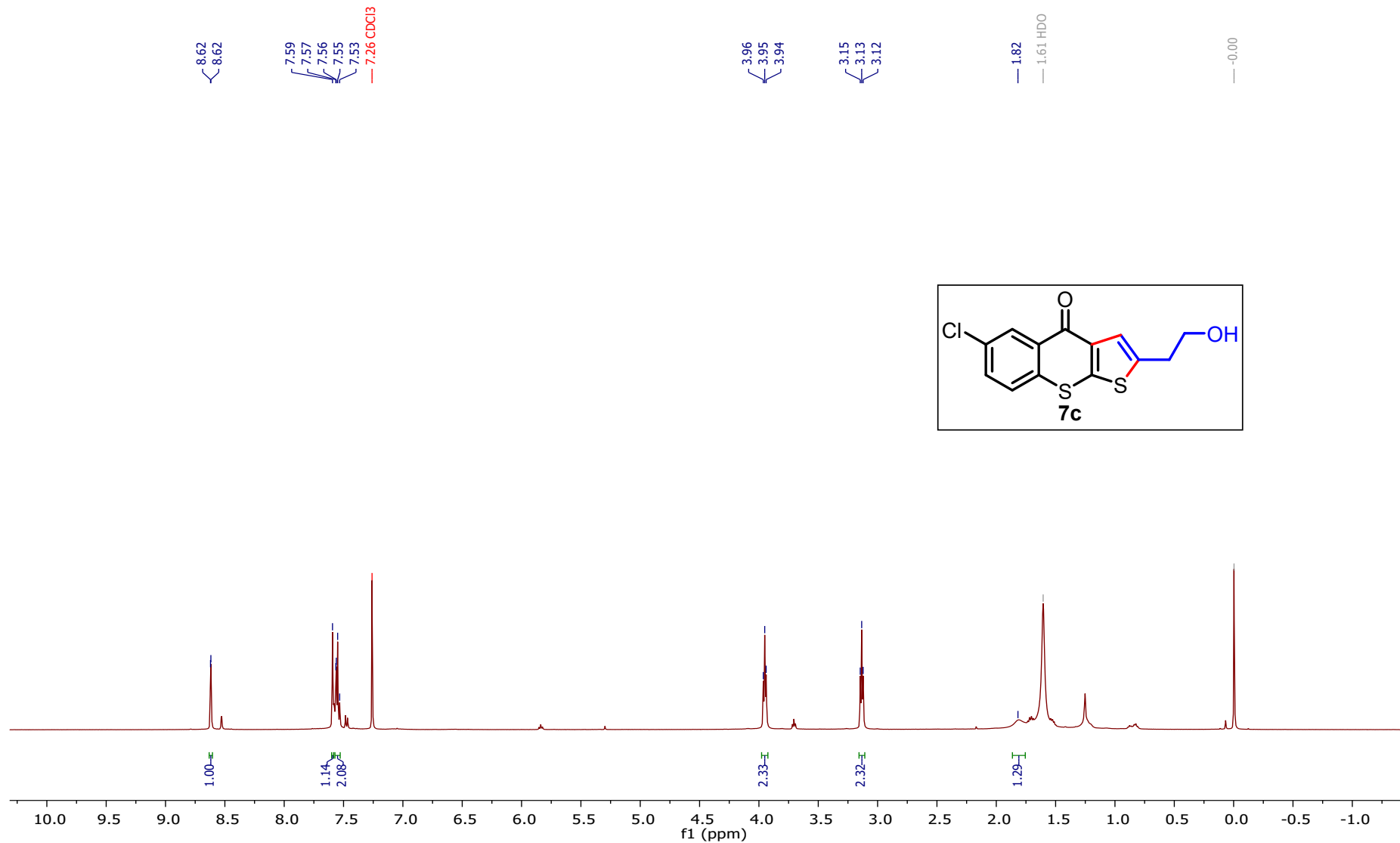
Instrument Name
InjPosition
Data Filename
Acquired Time

QTOF
DF-D,d
28-08-2025 17:00:18 (UTC+05:30)



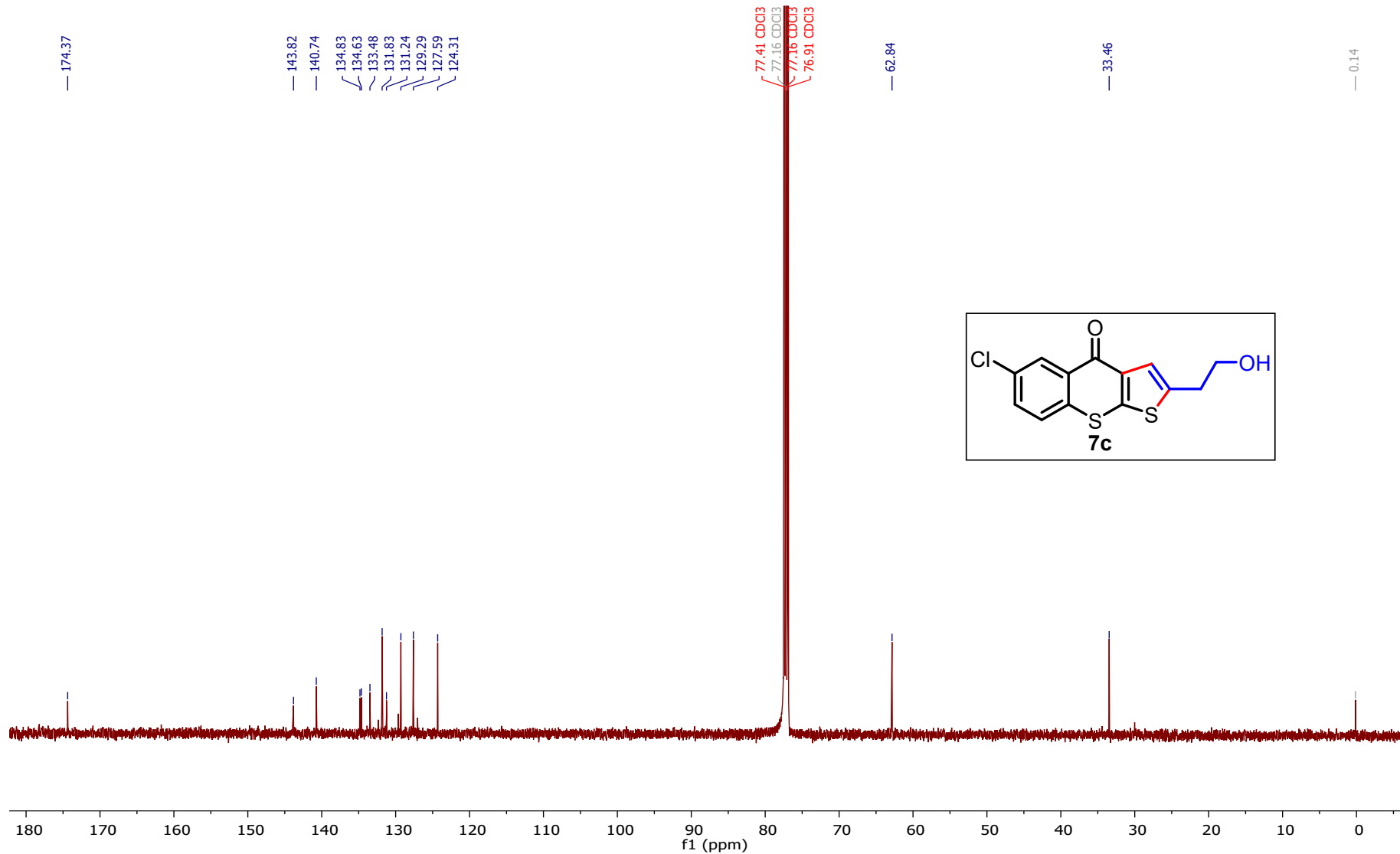
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 7c

7c 1H



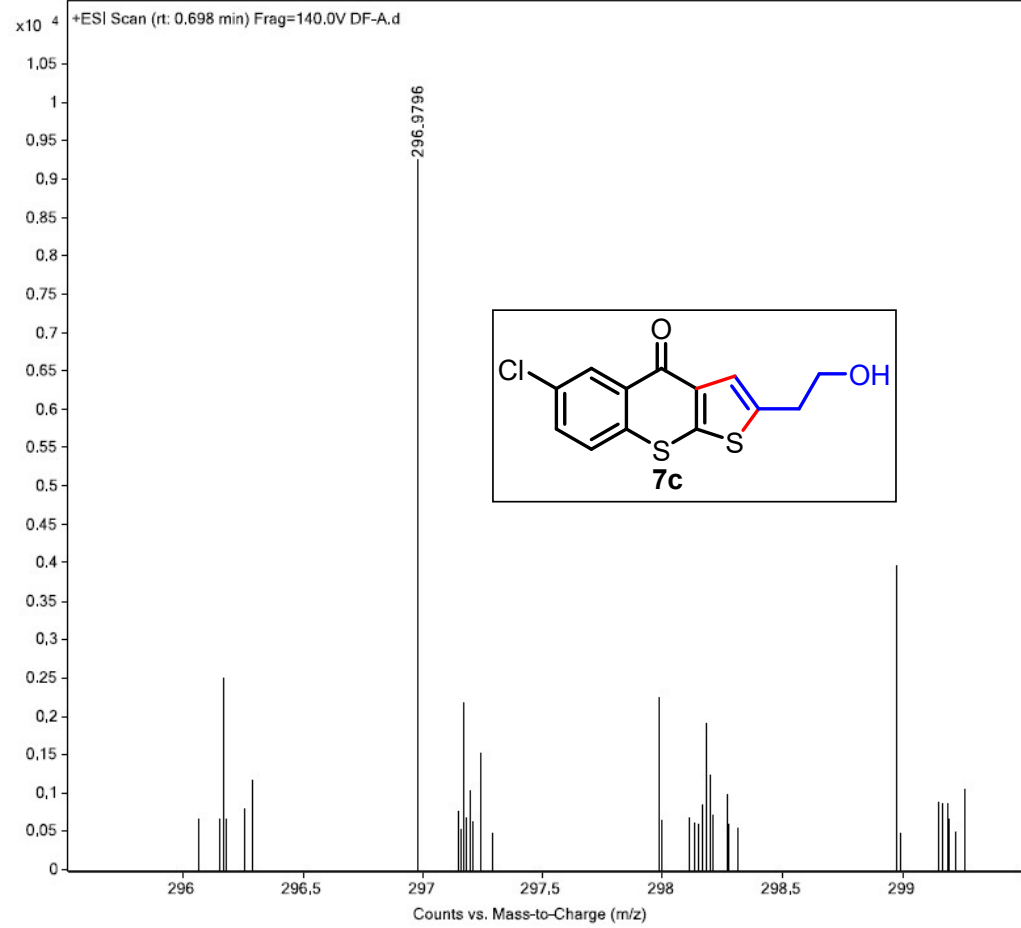
¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 7c

7c 13C



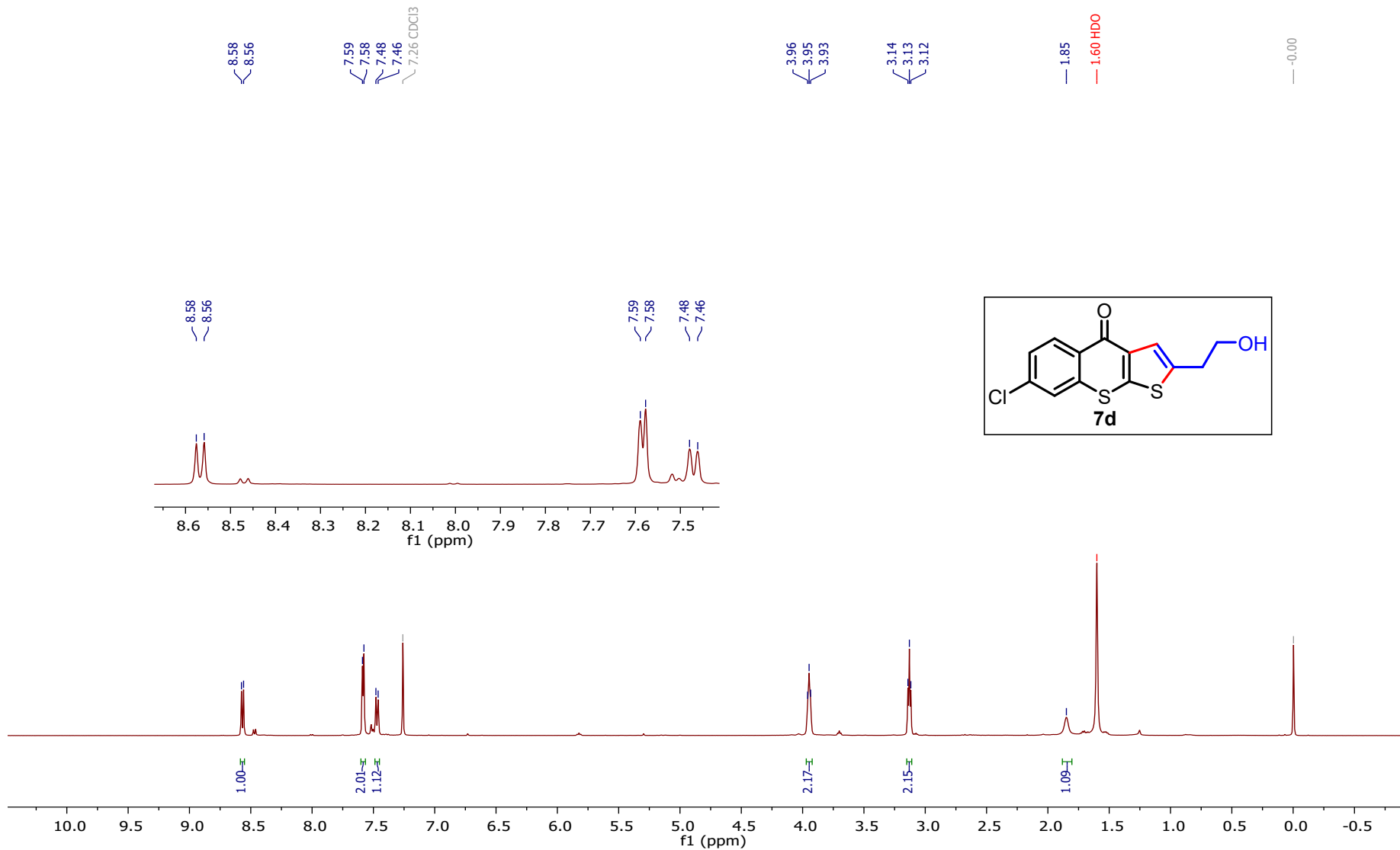
HRMS of compound 7c

Sample Name	Sample31	Position	P1-C9	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DF-A,d
ACQ Method	DIRECT MASS_POSITIVE_01_1.m	Comment		Acquired Time	28-08-2025 12:24:30 (UTC+05:30)



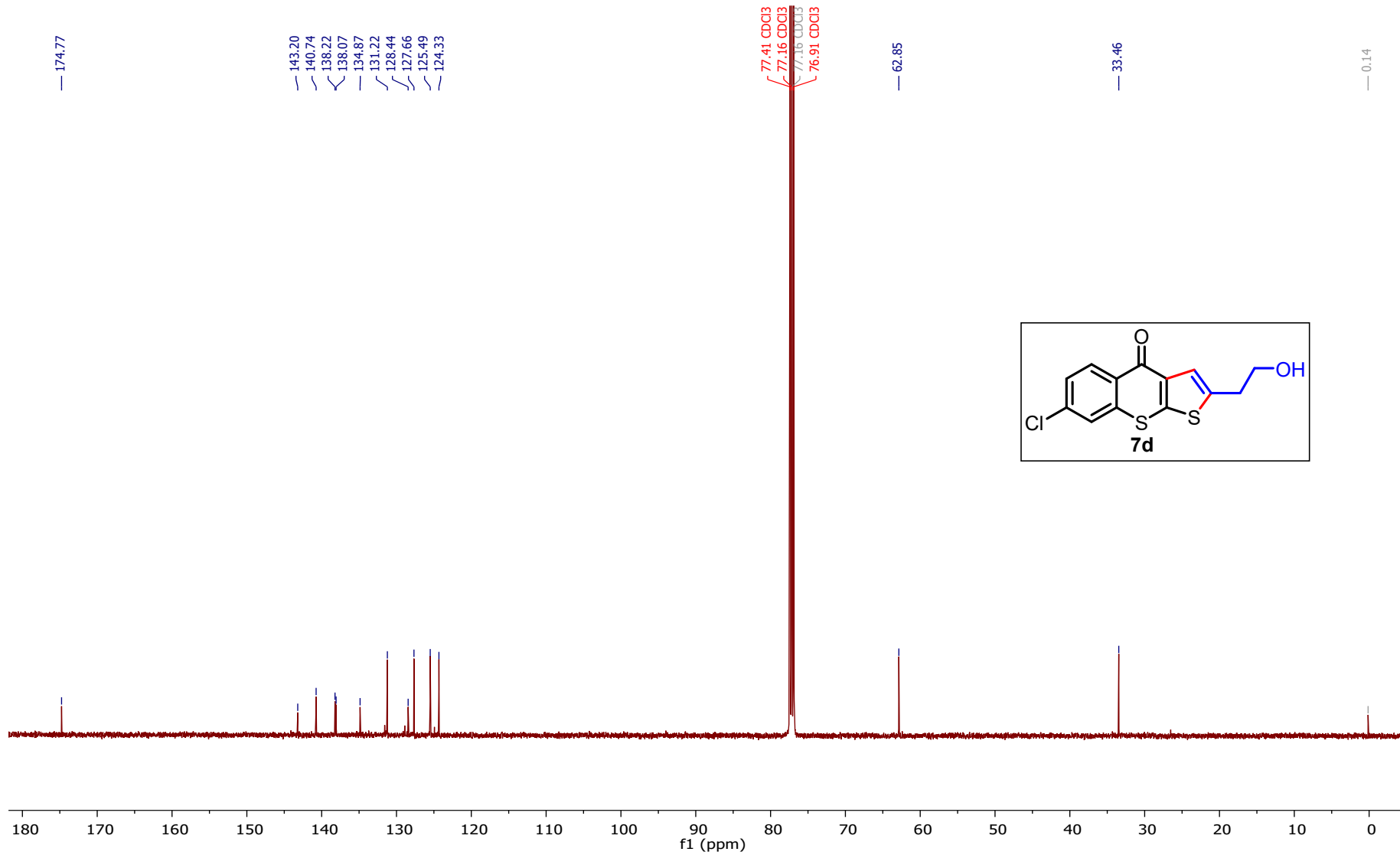
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 7d

7d 1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 7d

7d 13d



DEPT-135 ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Compound 7d

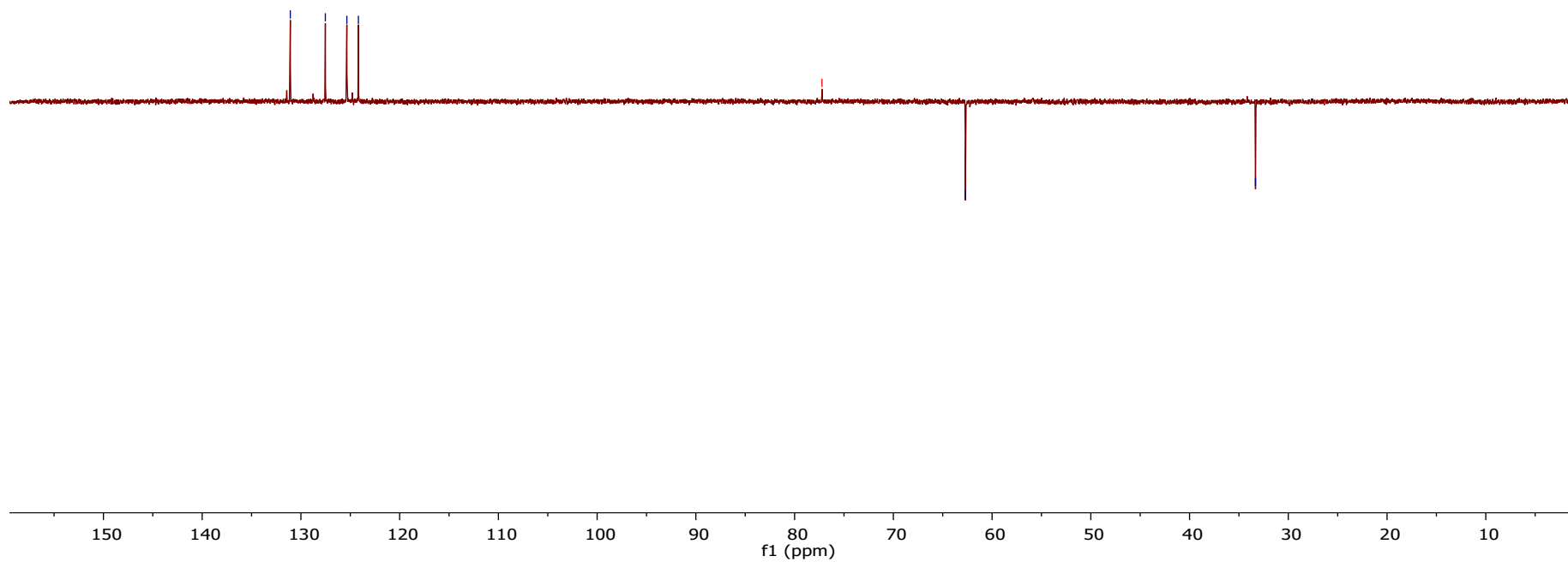
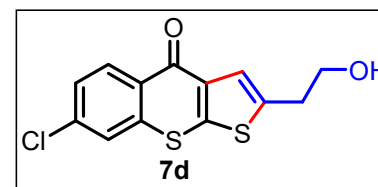
7d DEPT-135

131.07
127.52
125.35
124.18

77.23 CDCl_3

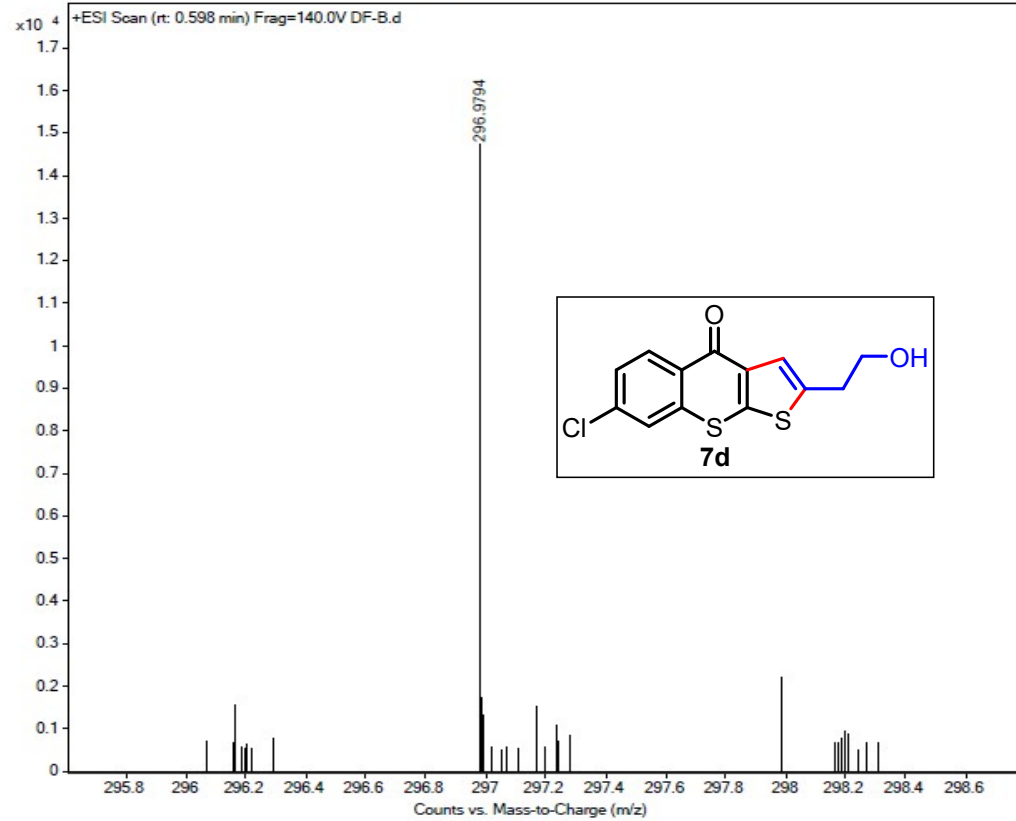
62.71

33.32



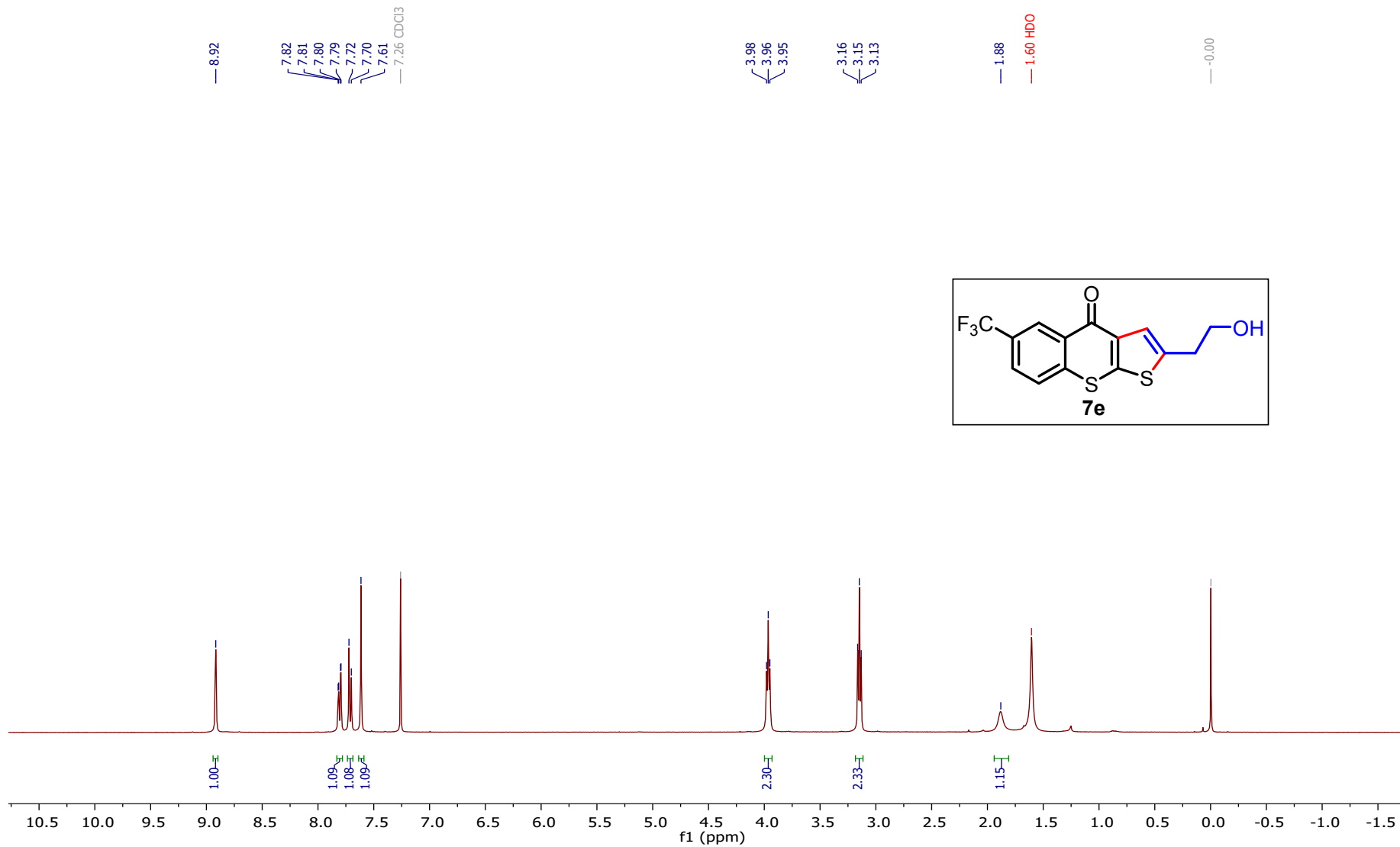
HRMS of compound 7d

Sample Name	Sample32	Position	P1-C10	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DF-B.d
ACQ Method	DIRECT MASS_POSITIVE_01_1.m	Comment		Acquired Time	28-08-2025 12:26:19 (UTC+05:30)



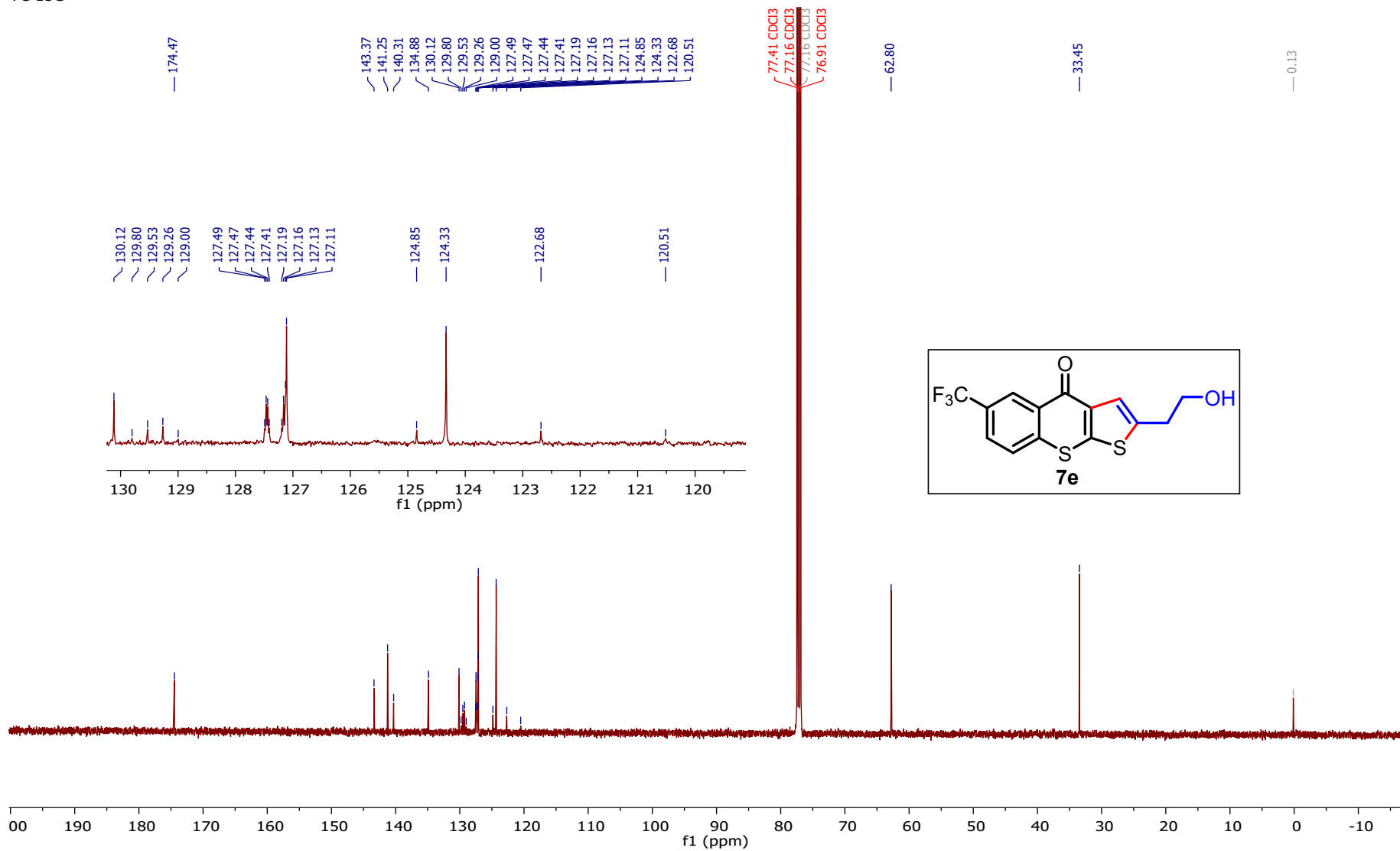
¹H NMR (400 MHz, CDCl₃) spectrum of Compound 7e

7e 1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 7e

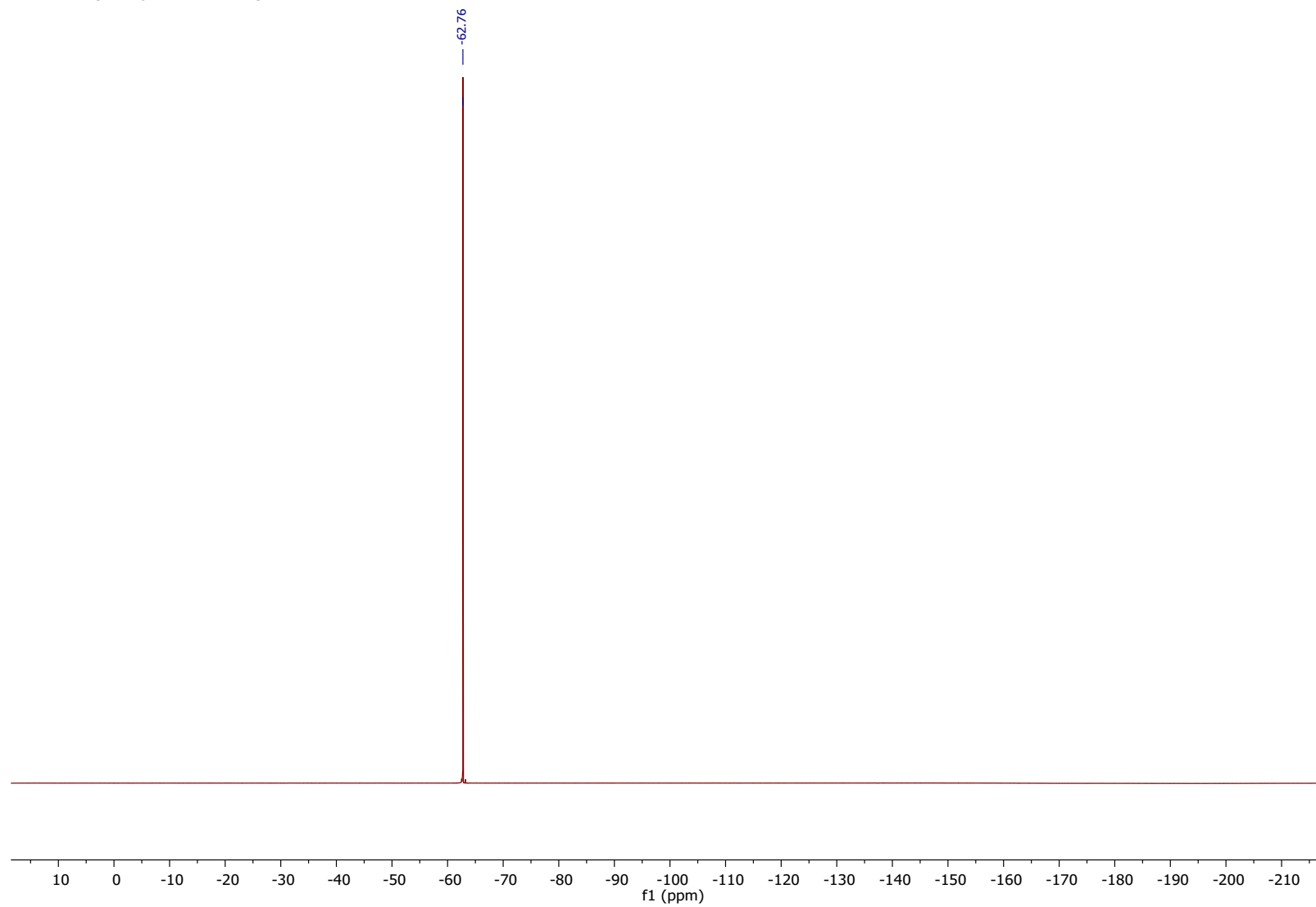
7e 13C



¹⁹F NMR

of

ATK-DF-2-19F.1.fid — ATK-DF-2-19F



Compound 7e

HRMS of compound 7e

Sample Name
User Name
Sample Type
ACQ Method

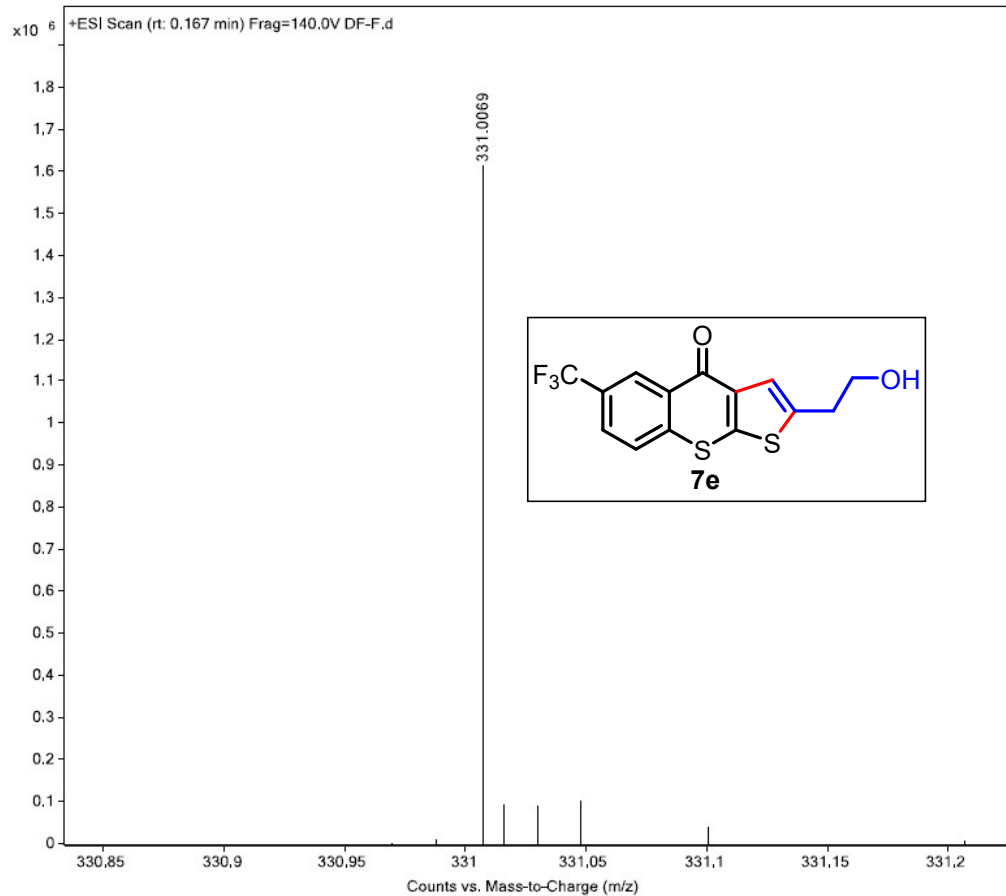
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_01_1.m

Position
Inj Vol
IRM Calibration Status
Comment

P1-A4
5
Success

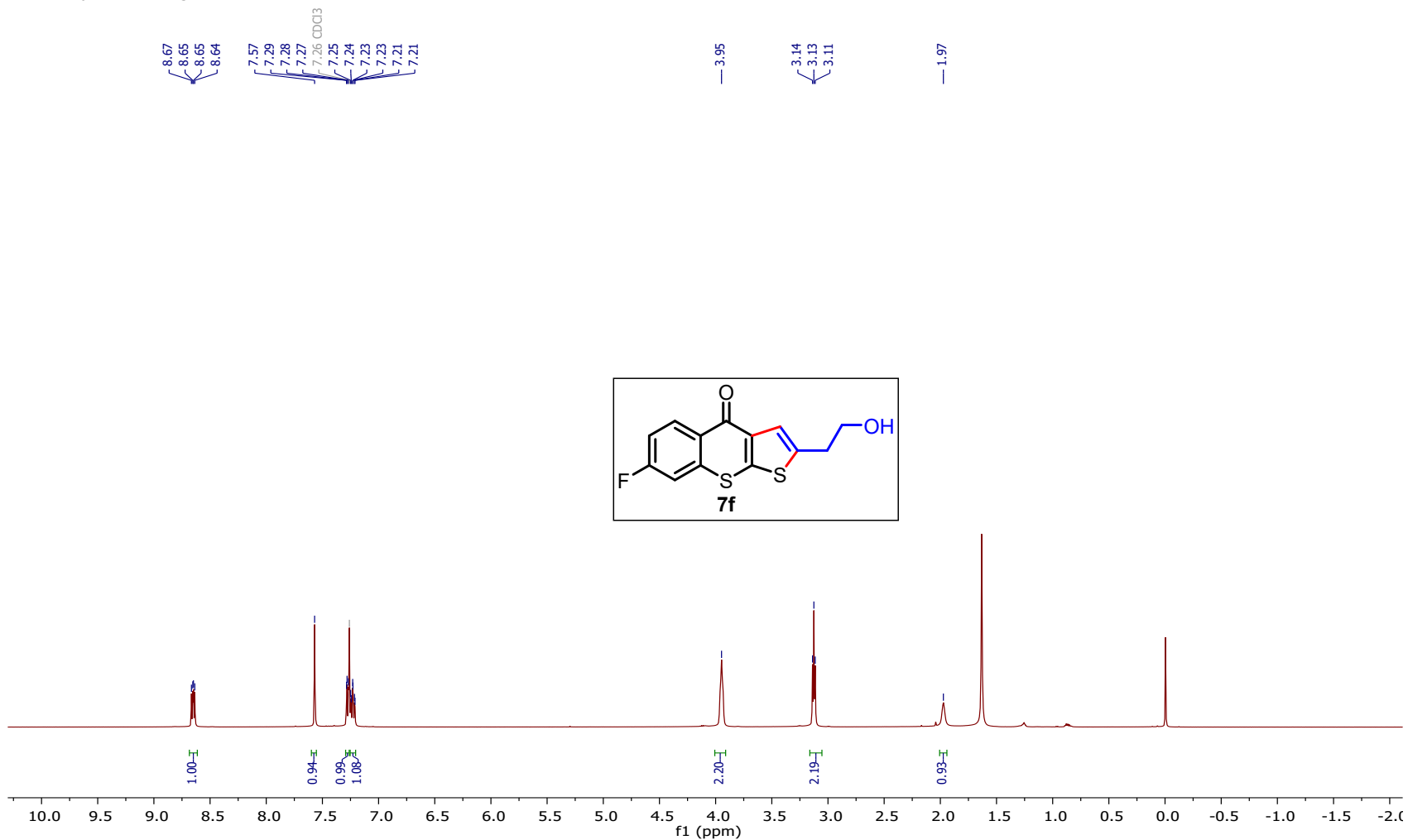
Instrument Name
InjPosition
Data Filename
Acquired Time

QTOF
DF-F,d
29-07-2025 14:59:13 (UTC+05:30)



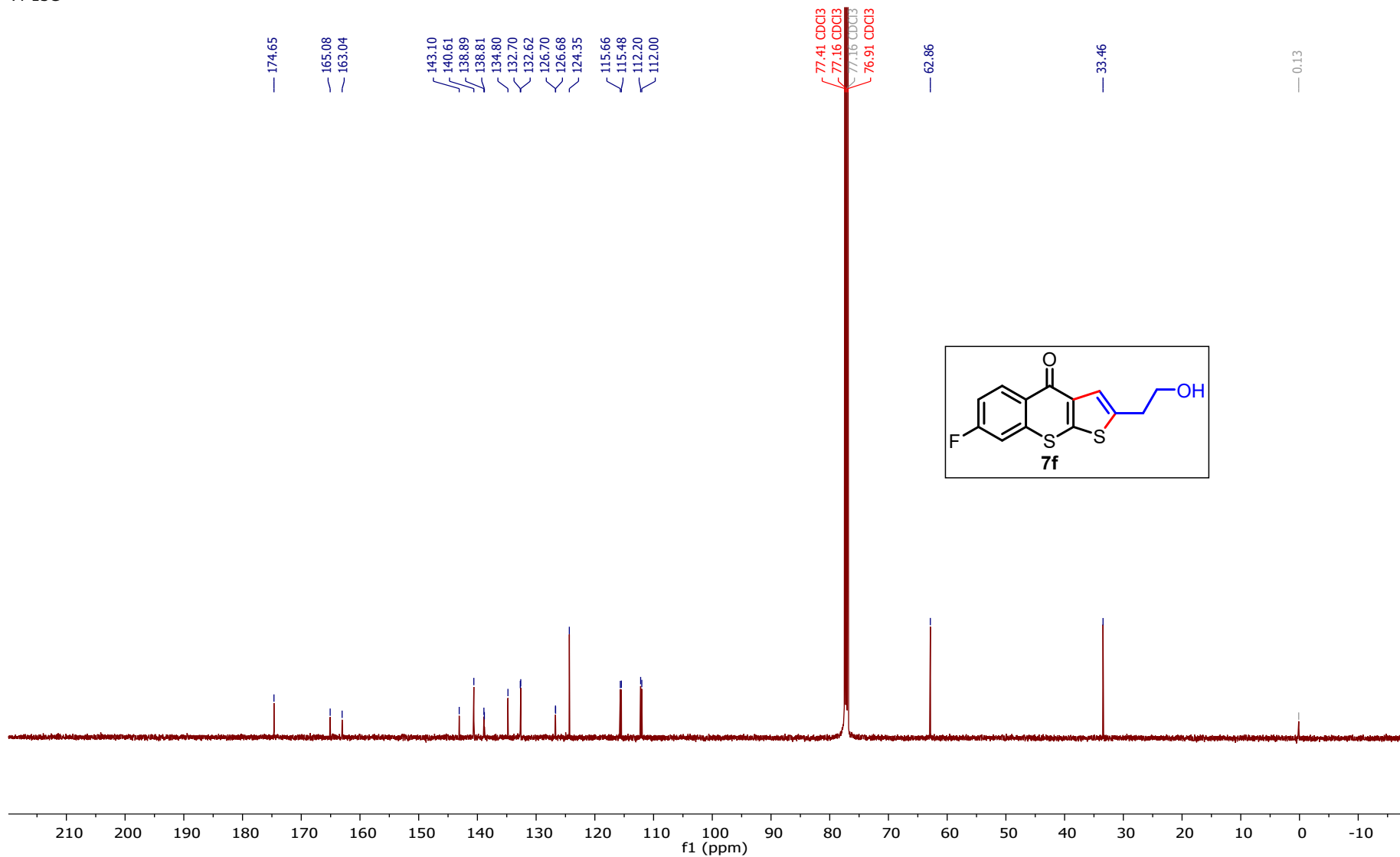
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 7f

7f 1H.1.fid — ATK-DF-G-1H

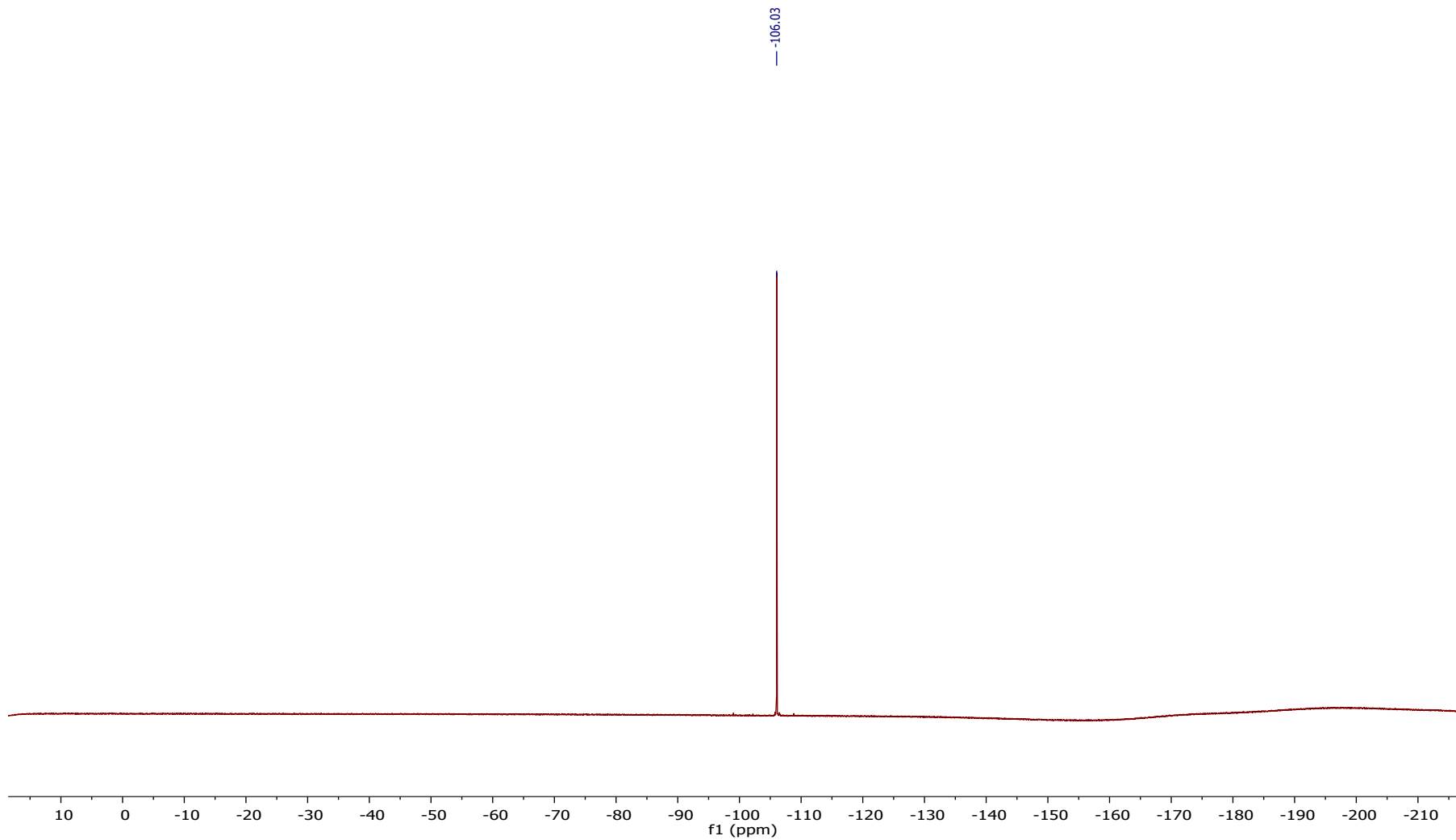


¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 7f

7f 13C

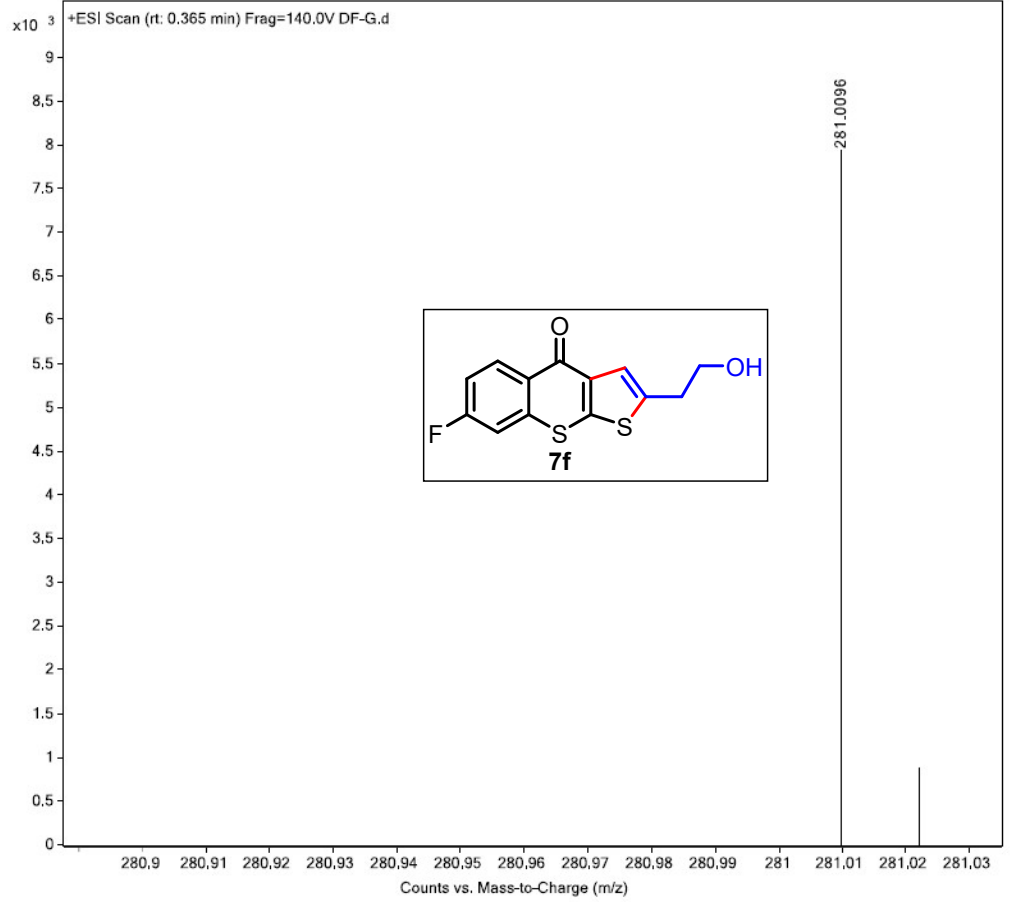


^{19}F NMR of Compound 7f



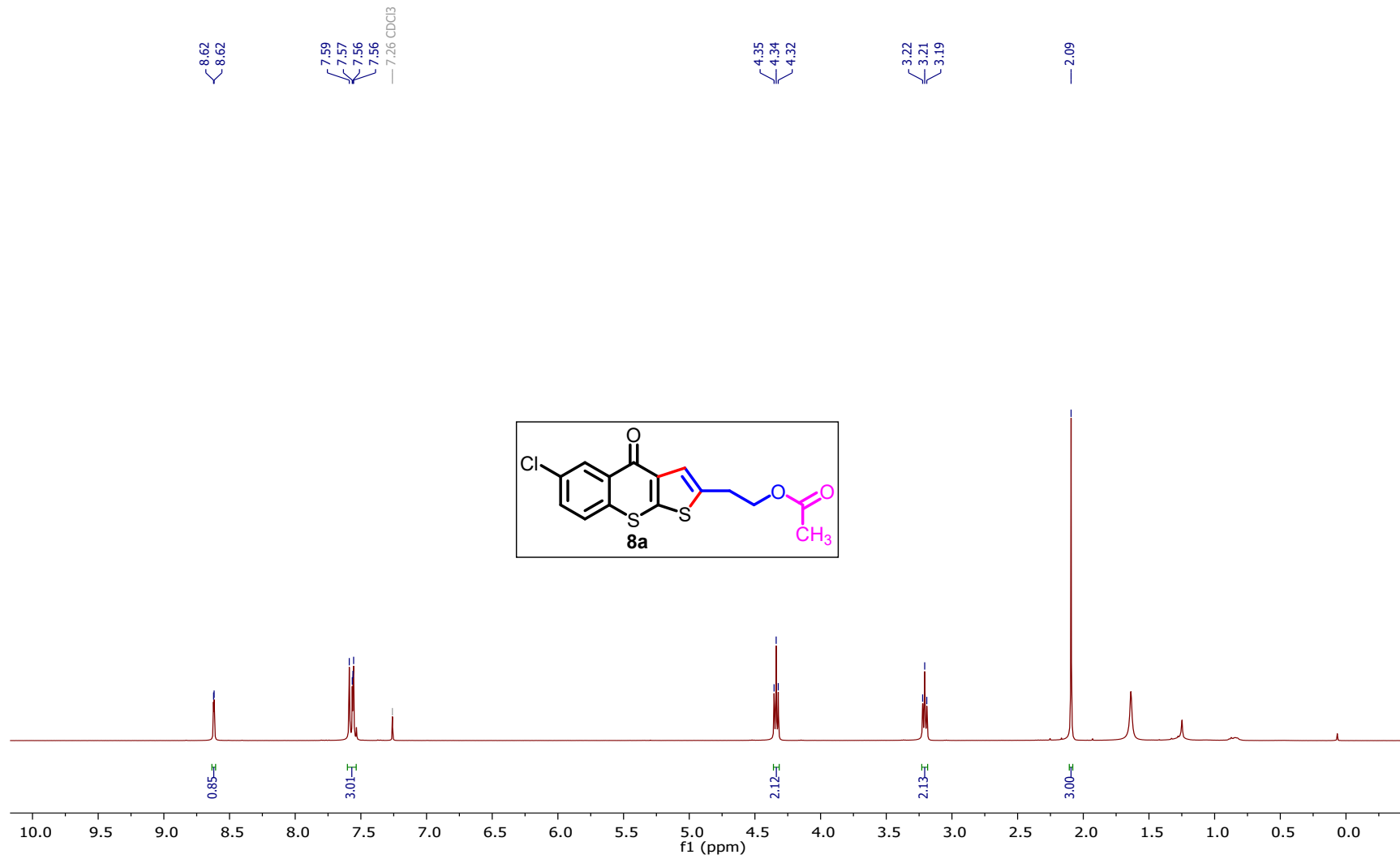
HRMS of compound 7f

Sample Name	Sample16	Position	P1-B5	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DF-G,d
ACQ Method	DIRECT MASS_POSITIVE_01_1500.m	Comment		Acquired Time	11-09-2025 17:09:47 (UTC+05:30)



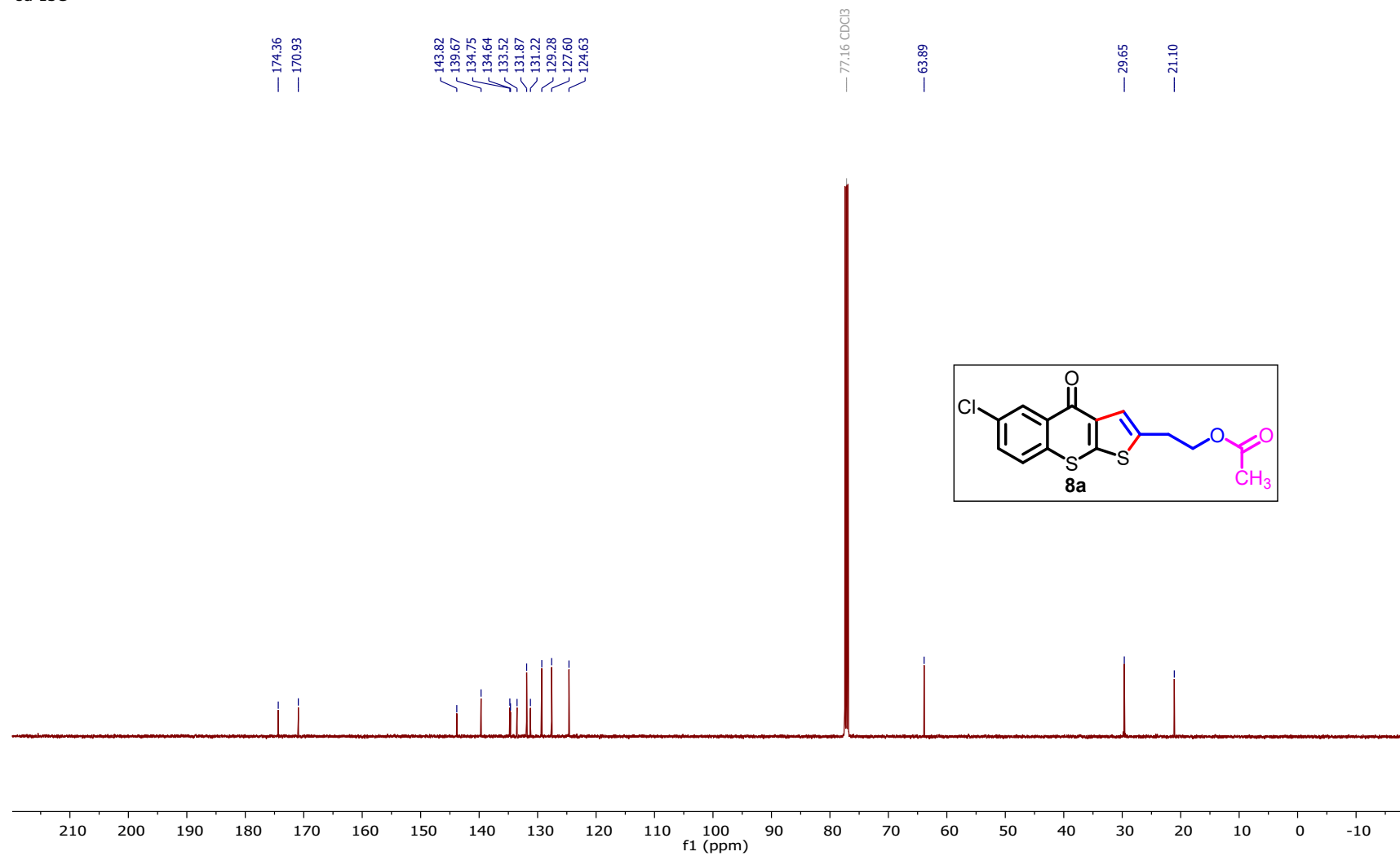
¹H NMR (400 MHz, CDCl₃) spectrum of Compound 8a

ATK-DK-AC-01-1H.1.fid — ATK-DK-AC-01-1H



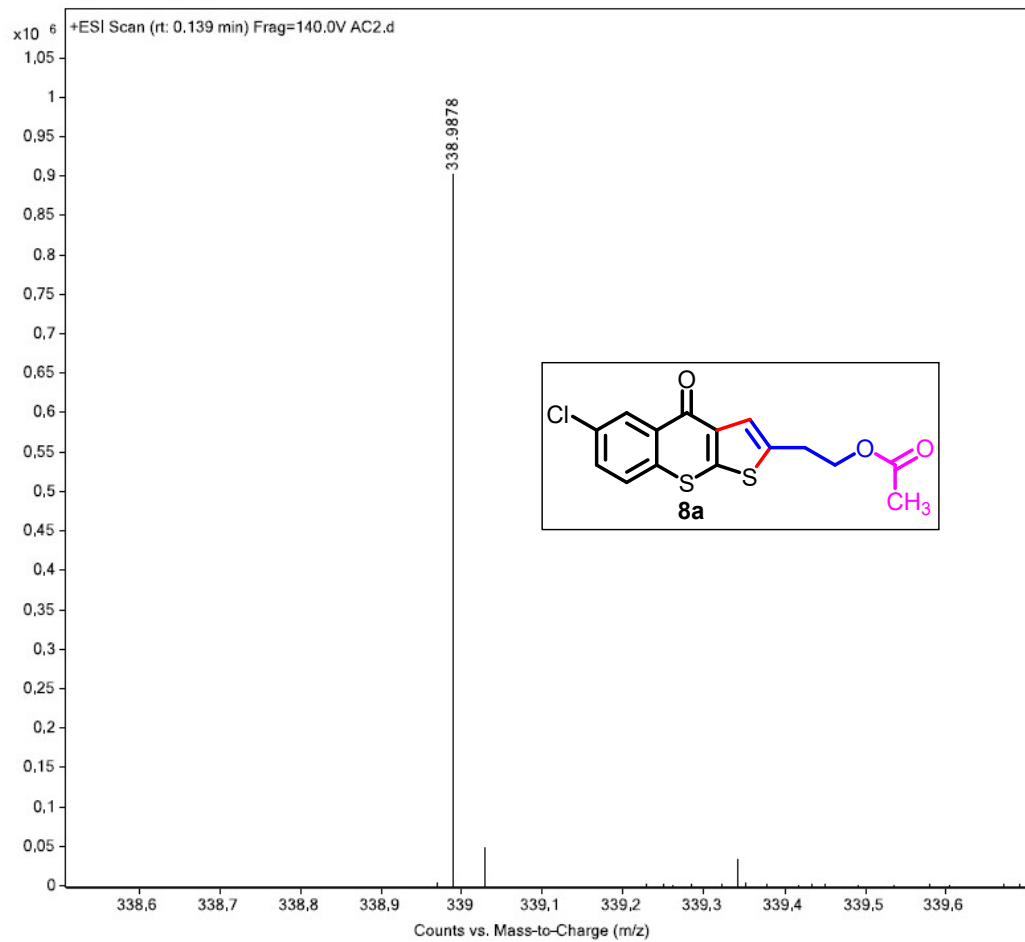
^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Compound 8a

8a 13C



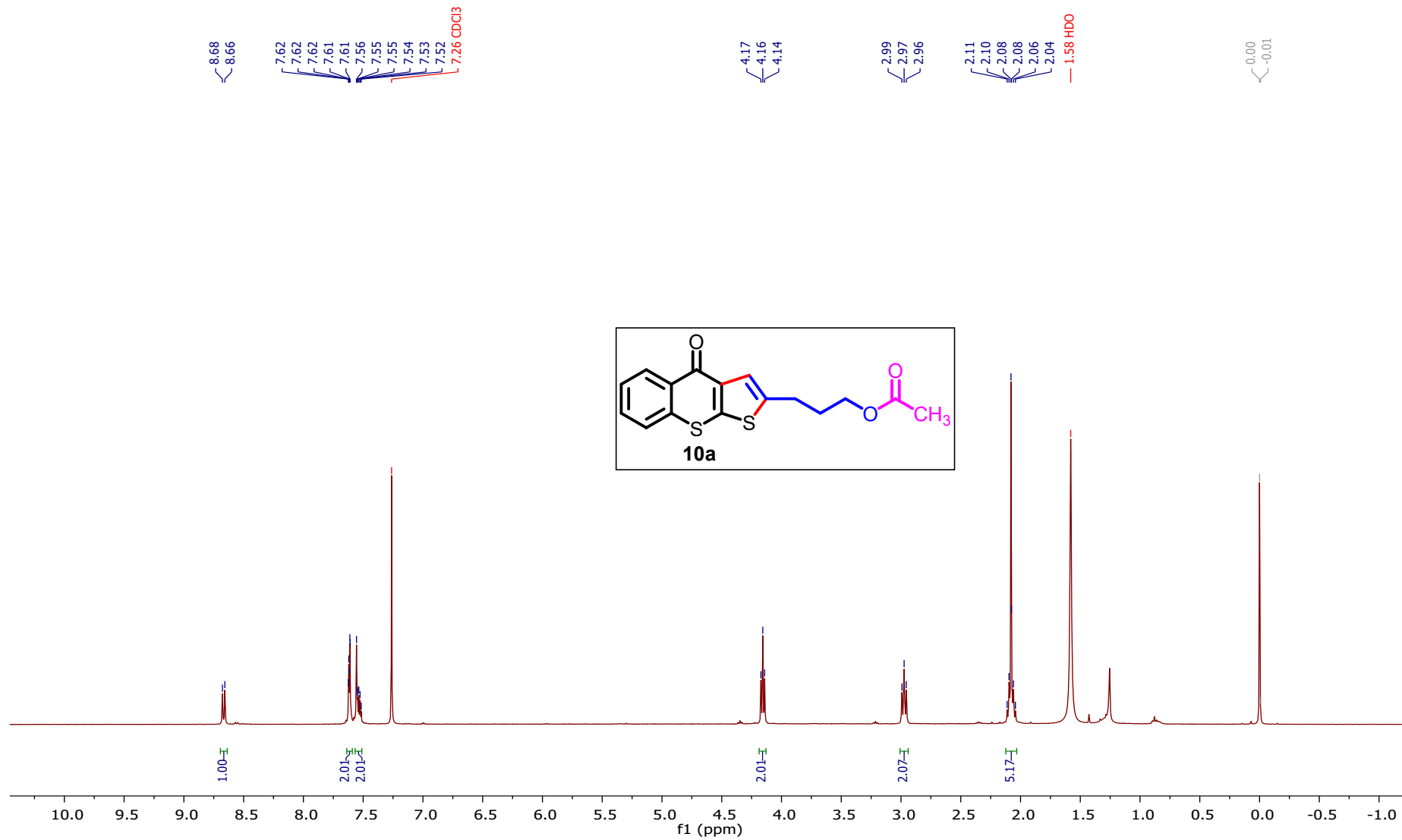
HRMS of compound 8a

Sample Name	Sample12	Position	P1-B1	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	AC2,d
ACQ Method	DIRECT MASS_POSITIVE_50_3200,m	Comment		Acquired Time	11-07-2025 15:07:20 (UTC+05:30)



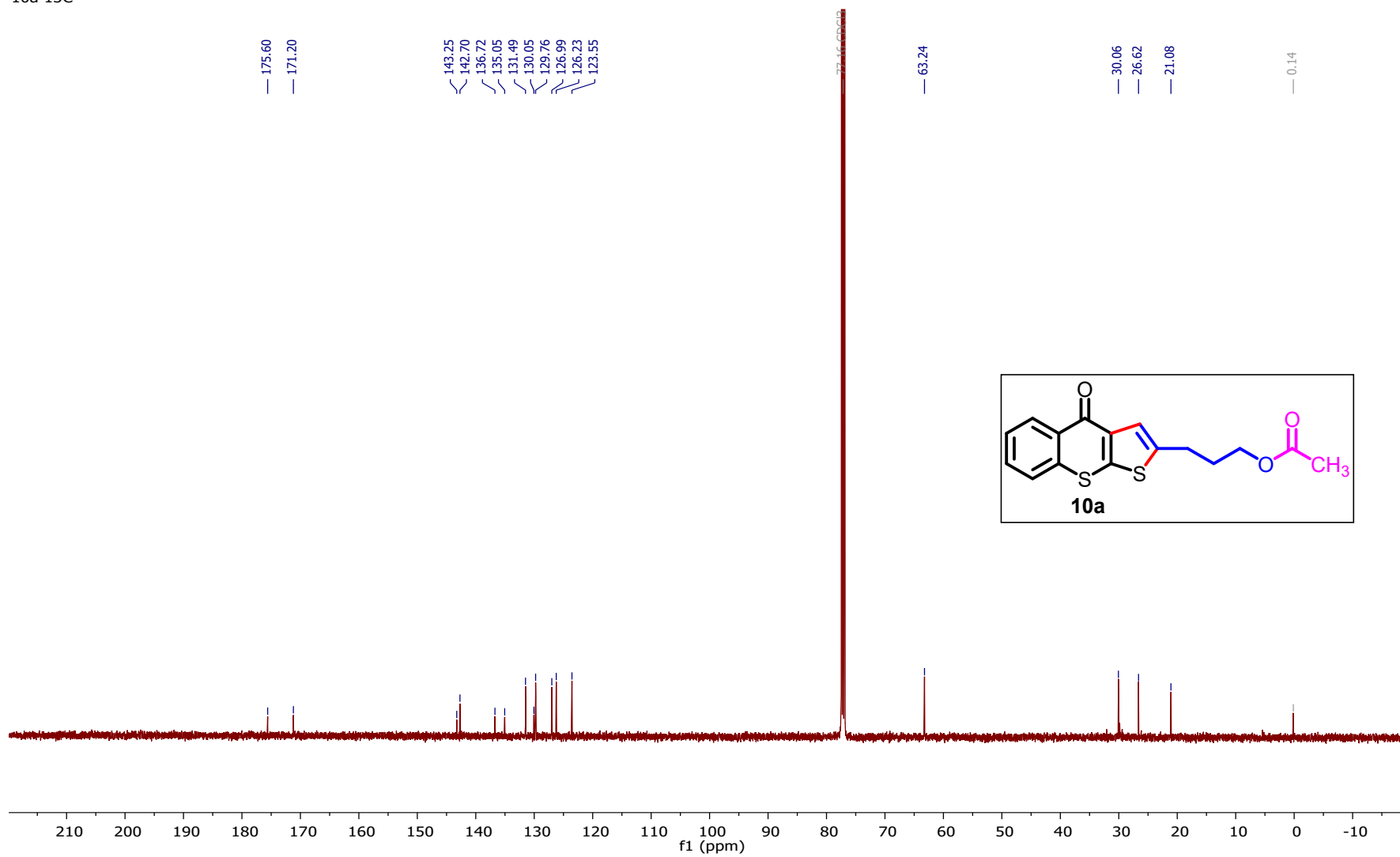
¹H NMR (400 MHz, CDCl₃) spectrum of Compound 10a

10a 1H



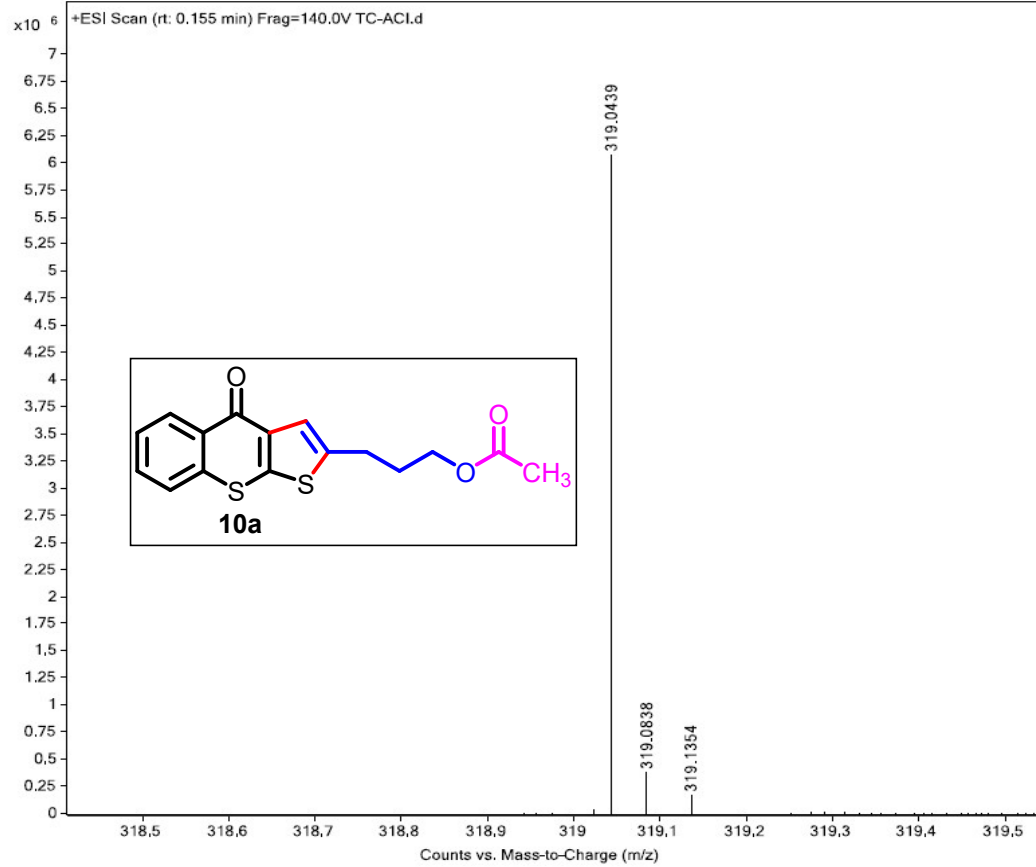
^{13}C { ^1H } NMR (125 MHz, CDCl_3) spectrum of Compound 10a

10a 13C



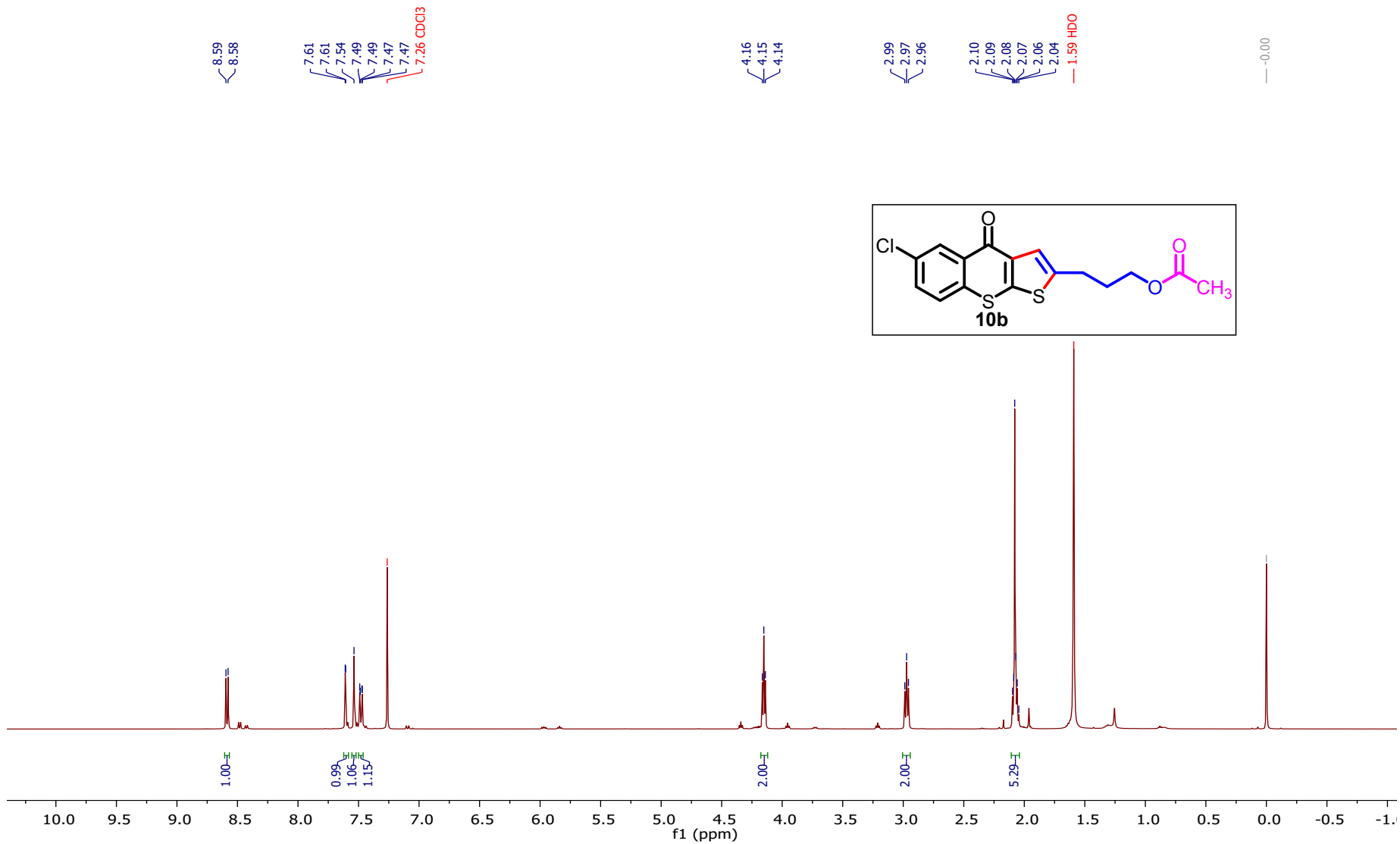
HRMS of compound 10a

Sample Name	Sample34	Position	P1-D1	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	TC-ACI,d
ACQ Method	DIRECT MASS_POSITIVE_50_1500.m	Comment		Acquired Time	15-09-2025 11:21:55 (UTC+05:30)



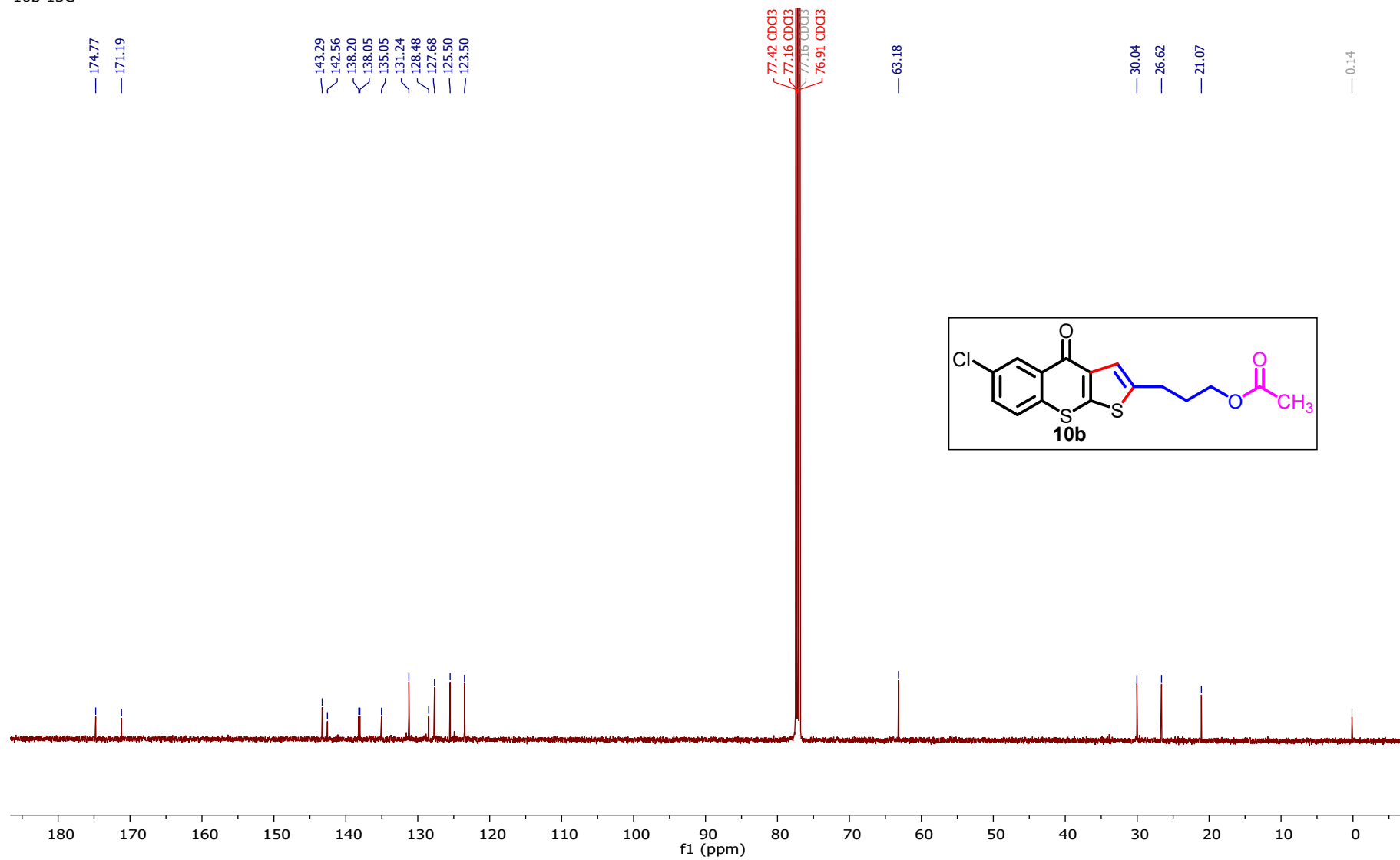
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 10b

10b 1H



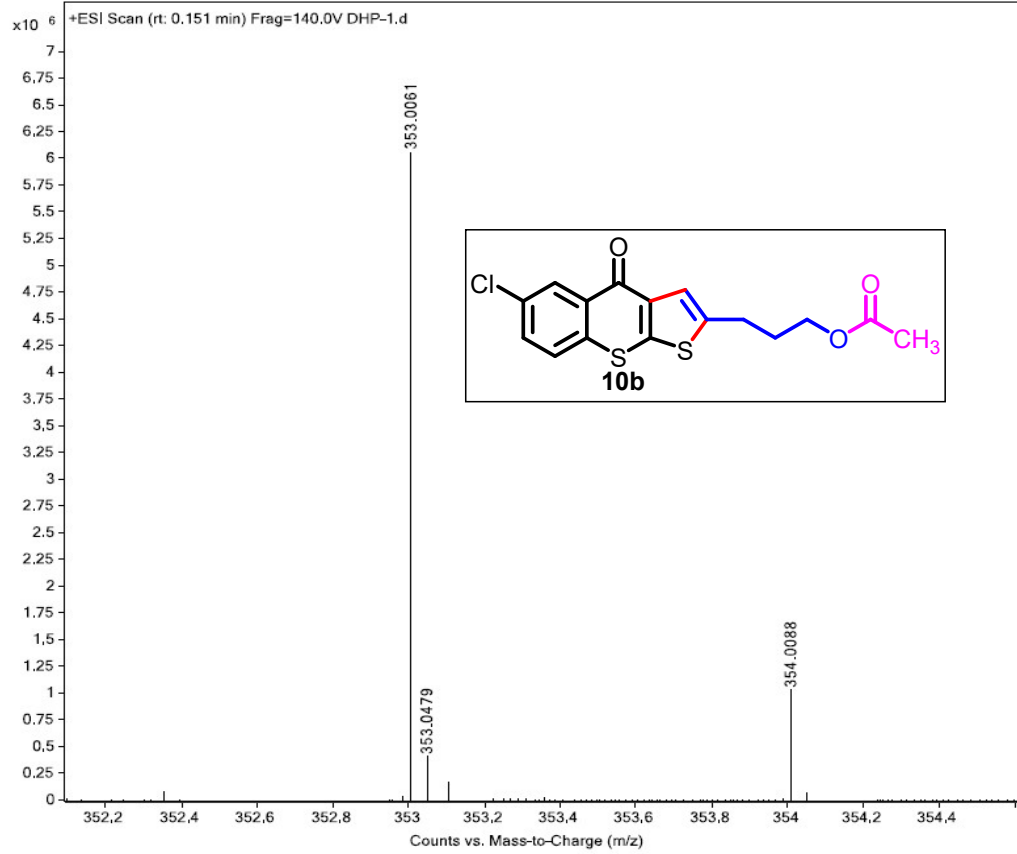
¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 10b

10b 13C



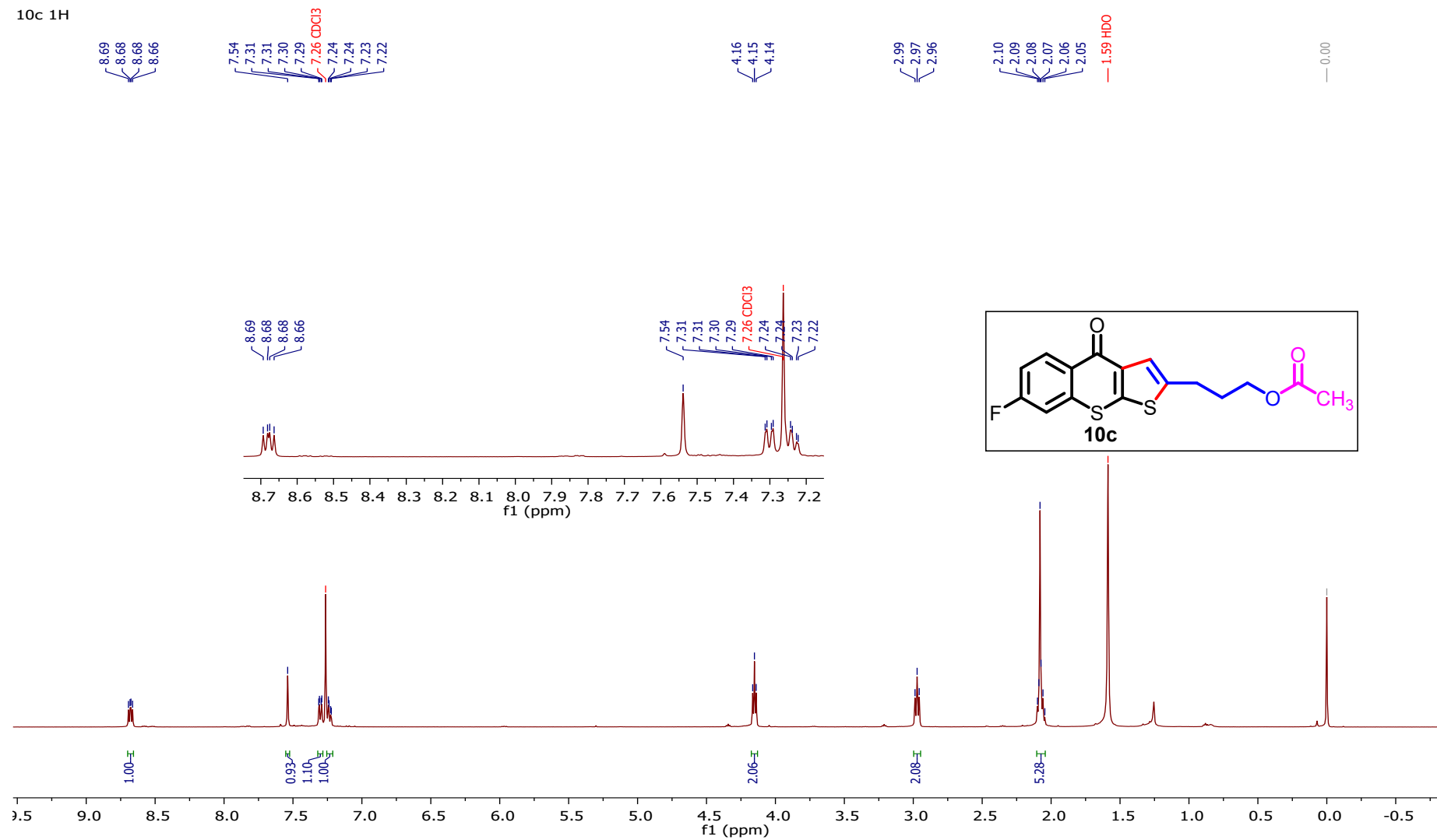
HRMS of compound 10b

Sample Name	Sample29	Position	P1-C7	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DHP-1,d
ACQ Method	DIRECT MASS_POSITIVE_01_1.m	Comment		Acquired Time	11-09-2025 12:19:34 (UTC+05:30)



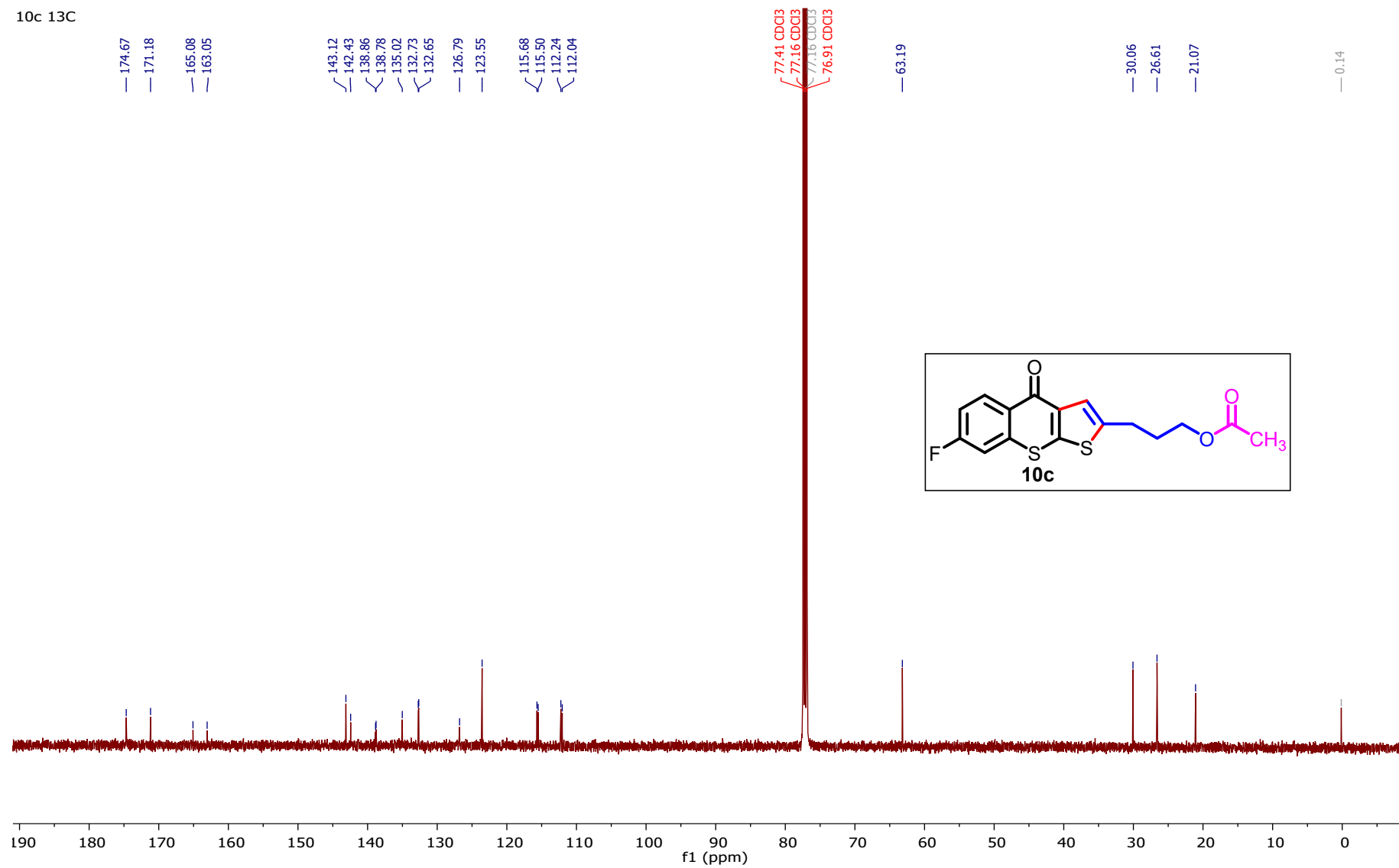
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 10c

10c 1H



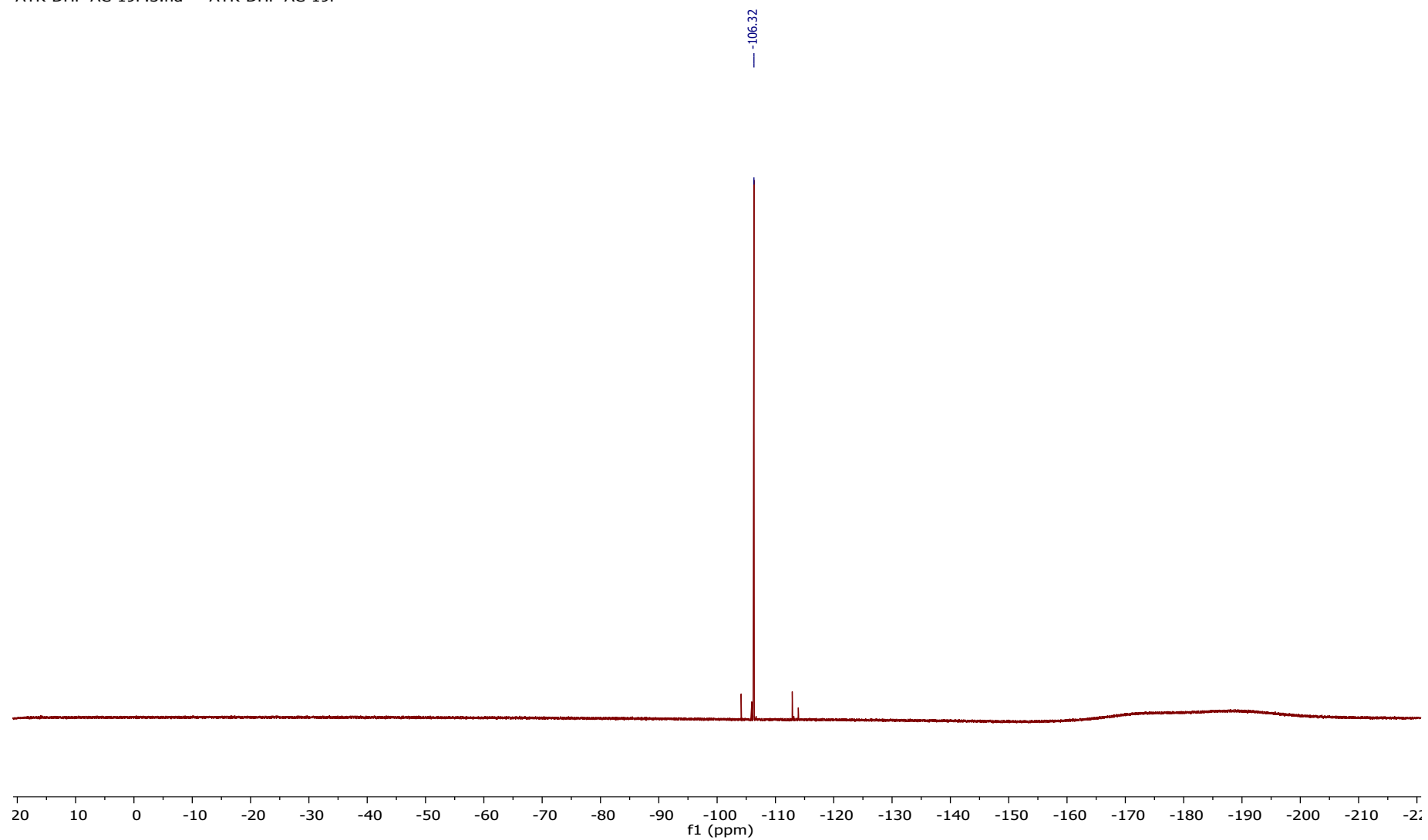
^{13}C { ^1H } NMR (125 MHz, CDCl_3) spectrum of Compound 10c

10c 13C



¹⁹F of Compound 10c

ATK-DHP-AC-19F.3.fid — ATK-DHP-AC-19F



DEP
T-
135
¹³C
{¹H}
NM
R
(125
MHz
,
CDC
l₃)
spec
tru
m of
Com
pou
nd
10c

10c DEPT-135

132.59

123.41

115.54

115.37

112.11

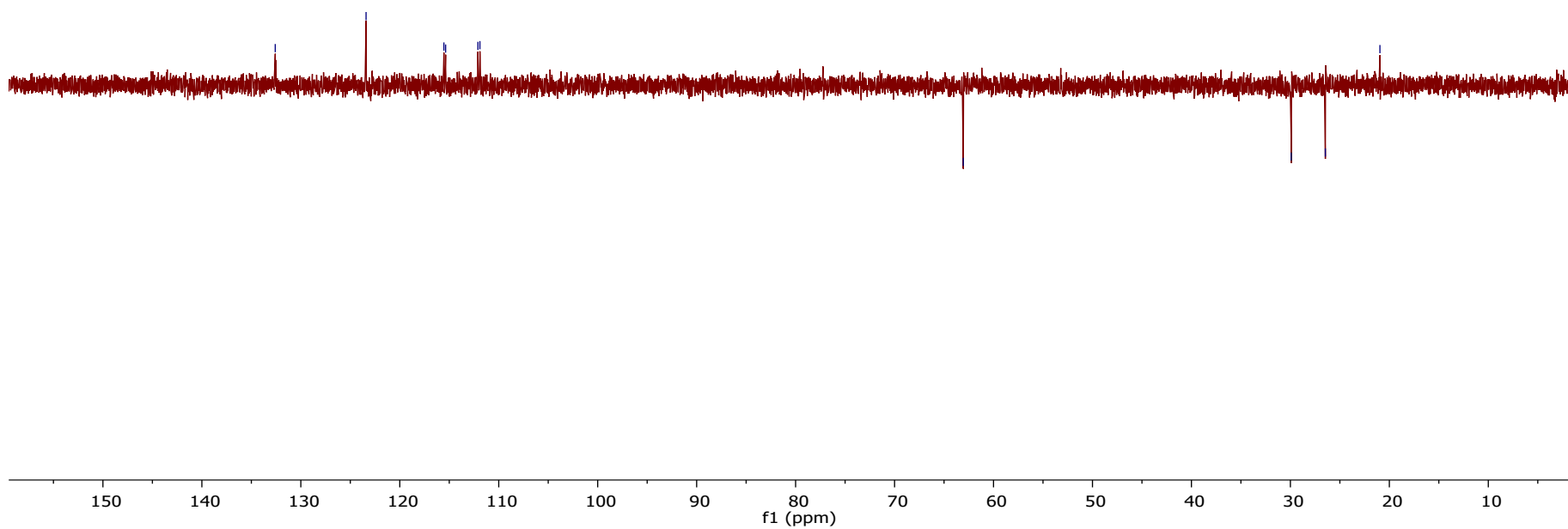
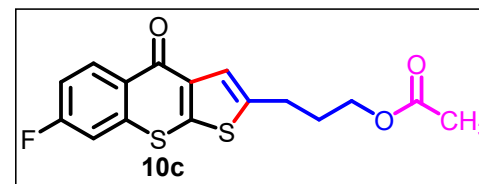
111.90

63.05

29.91

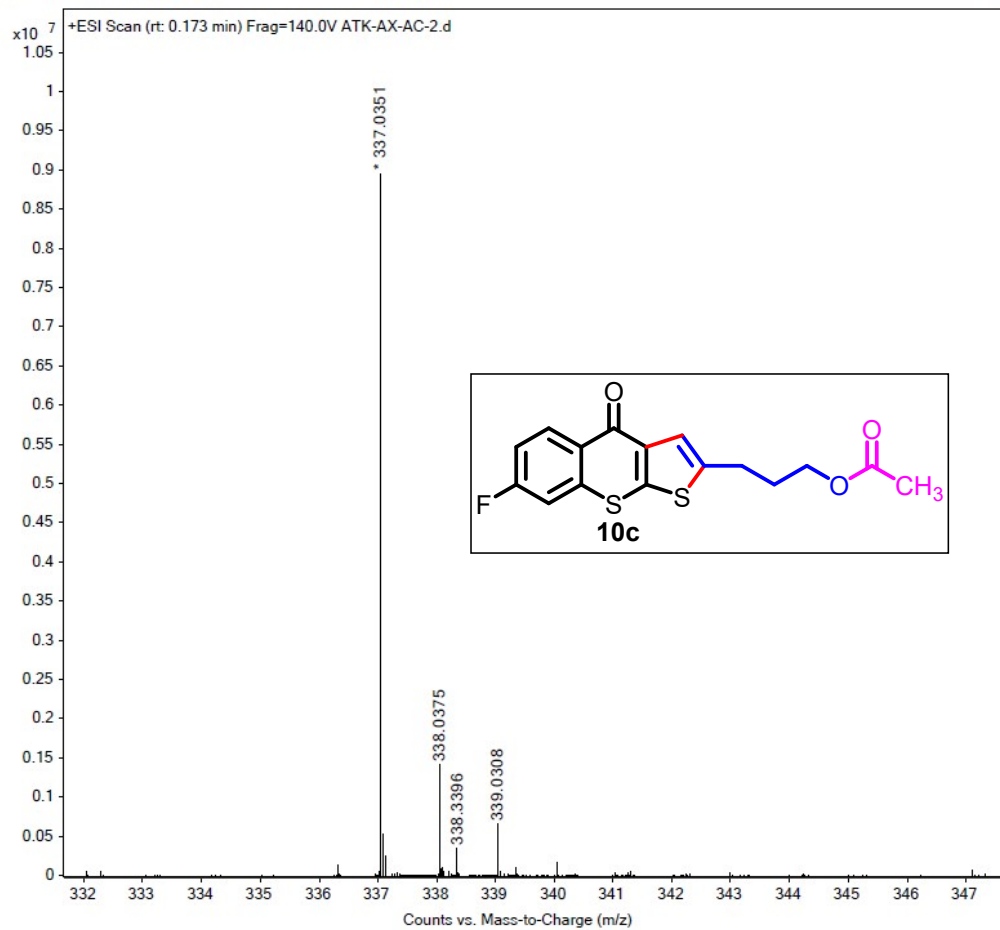
26.47

20.95



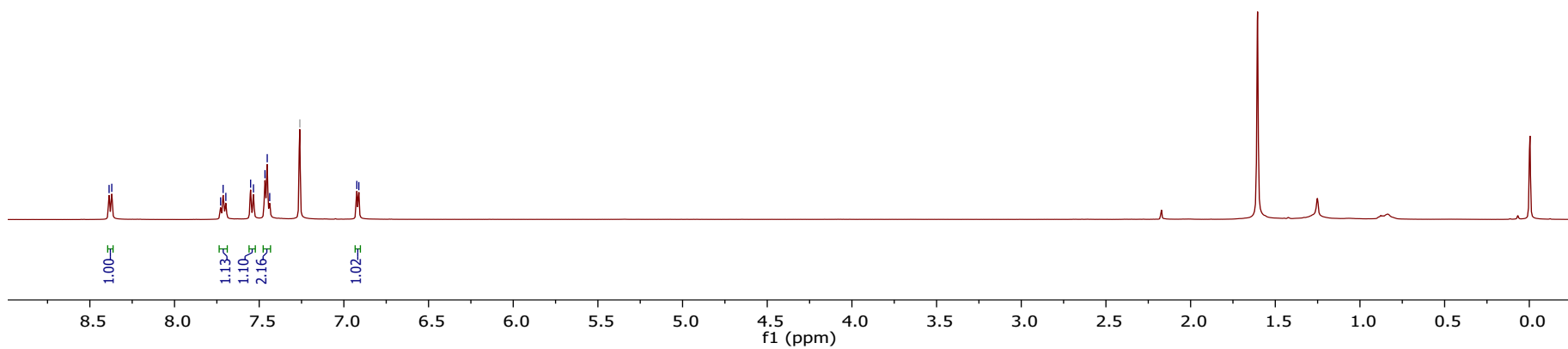
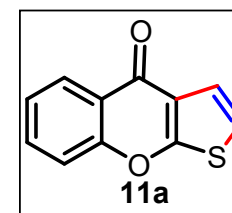
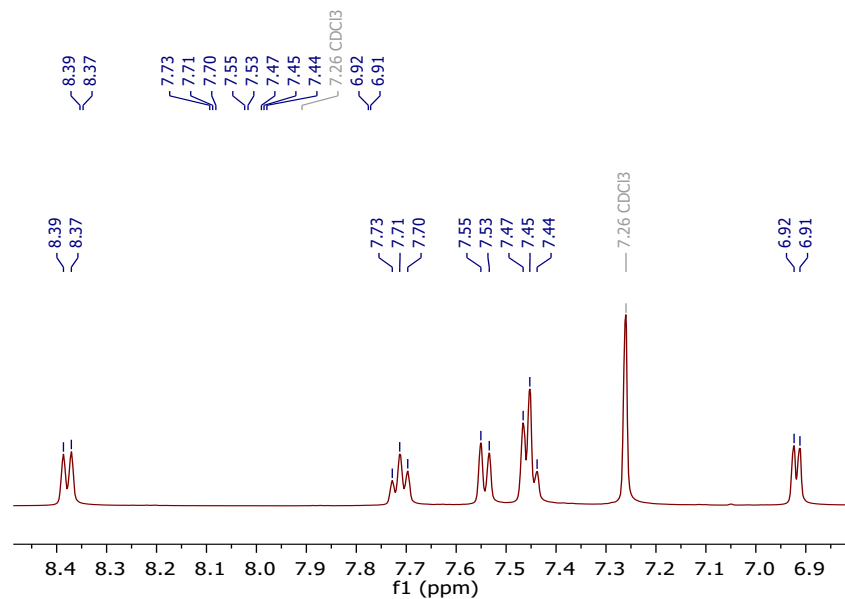
HRMS of compound 10c

Sample Name	Sample14	Position	P1-B3	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	ATK-AX-AC-2.d
ACQ Method	DIRECT MASS_POSITIVE_01_1.m	Comment		Acquired Time	14-08-2025 12:32:56 (UTC+05:30)



¹H NMR (500 MHz, CDCl₃) spectrum of Compound 11a

11a 1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 11a

11a 13C

— 173.04

— 168.05

— 156.80

— 133.52

— 126.72

— 124.81

— 123.42

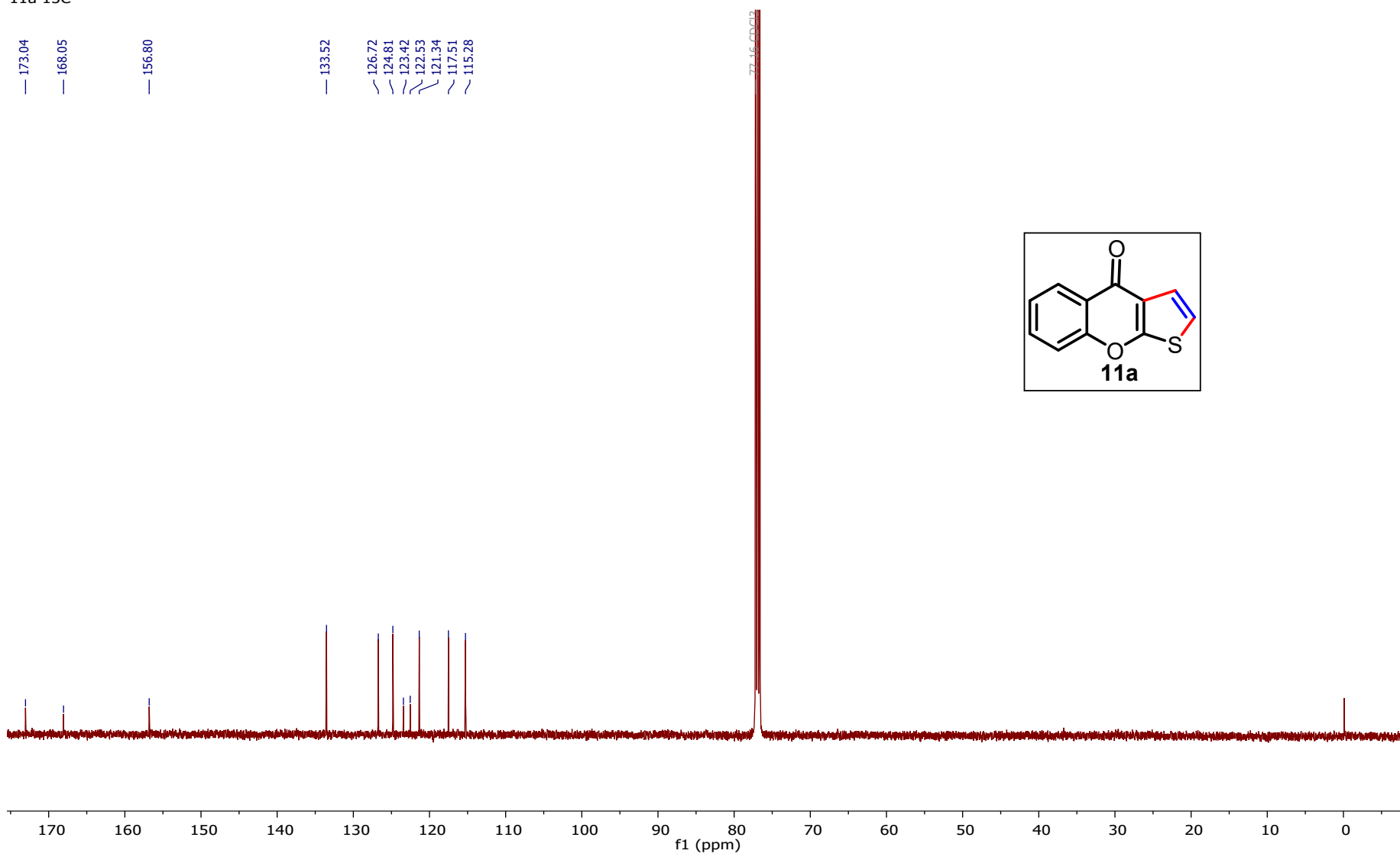
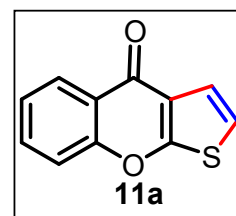
— 122.53

— 121.34

— 117.51

— 115.28

77.16 CDCl3

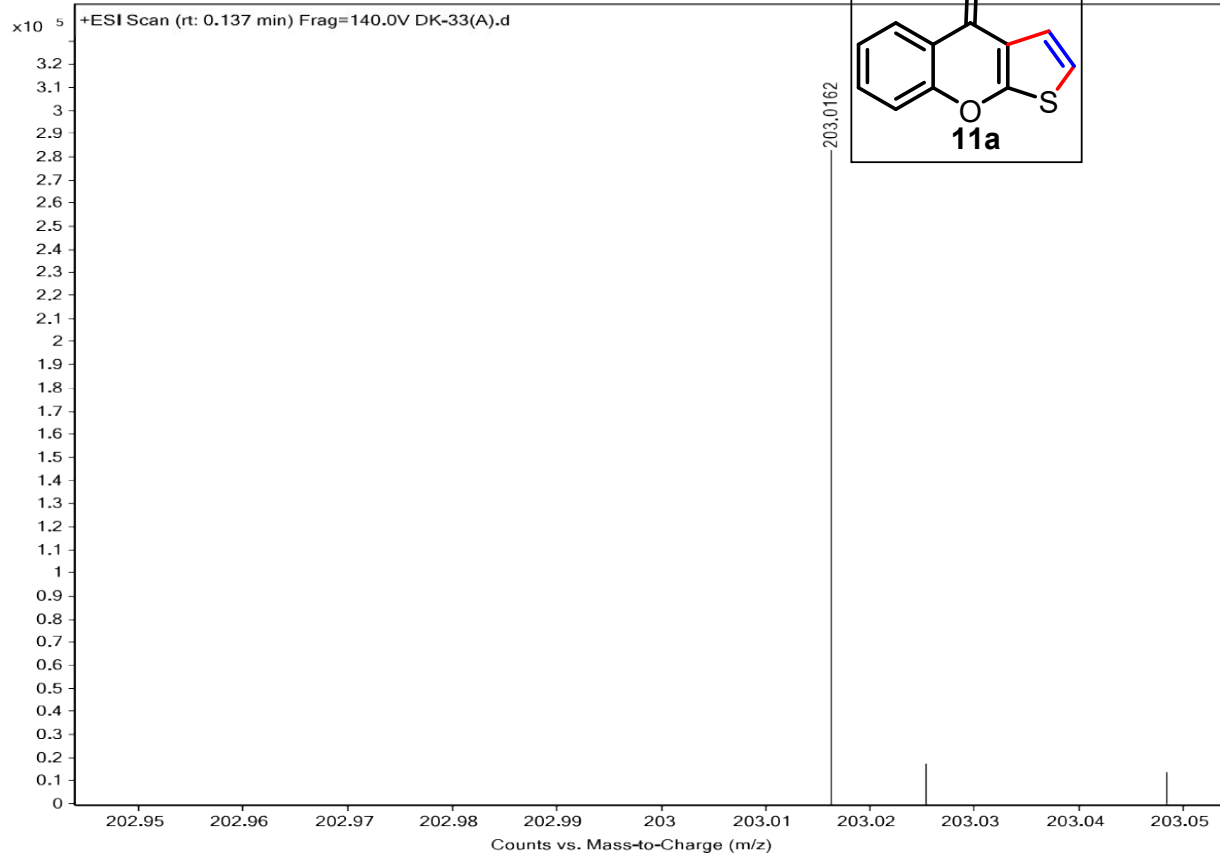


HRMS of compound 11a

Sample6
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_01_1.m

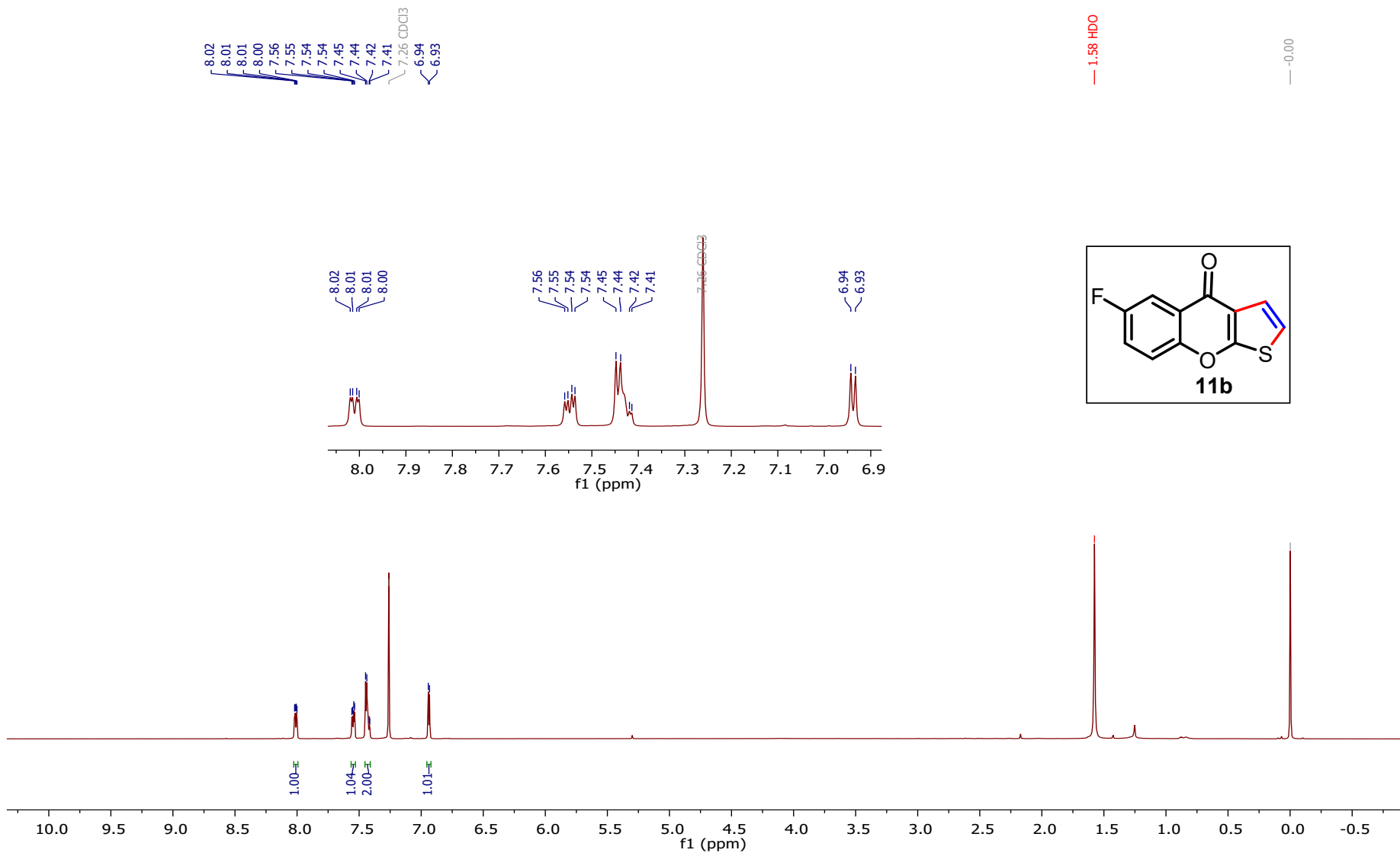
Position P1-A4
Inj Vol 5
IRM Calibration Status Success
Comment

Instrument Name
InjPosition
Data Filename
Acquired Time



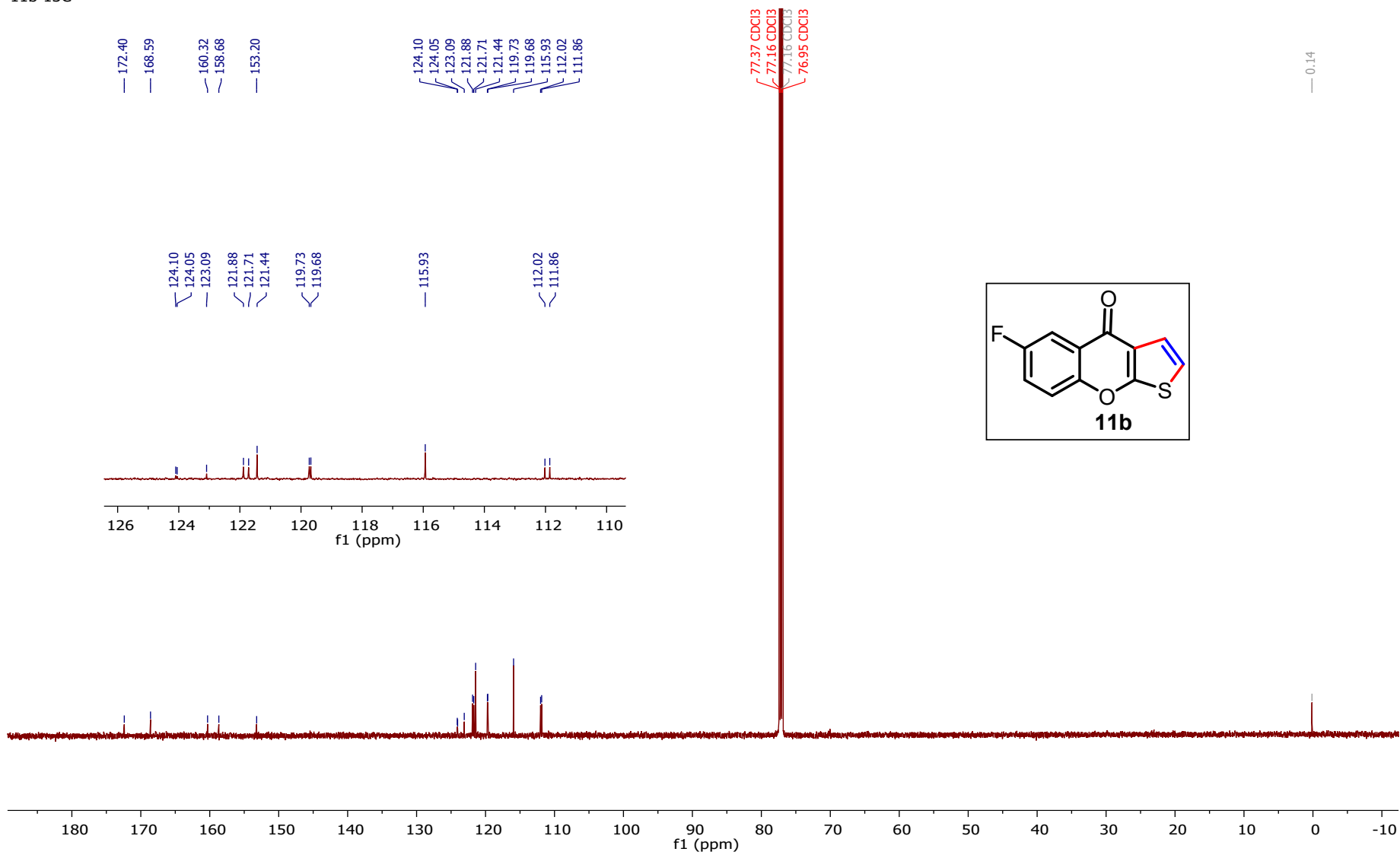
^1H NMR (600 MHz, CDCl_3) spectrum of Compound 11b

11b 1H



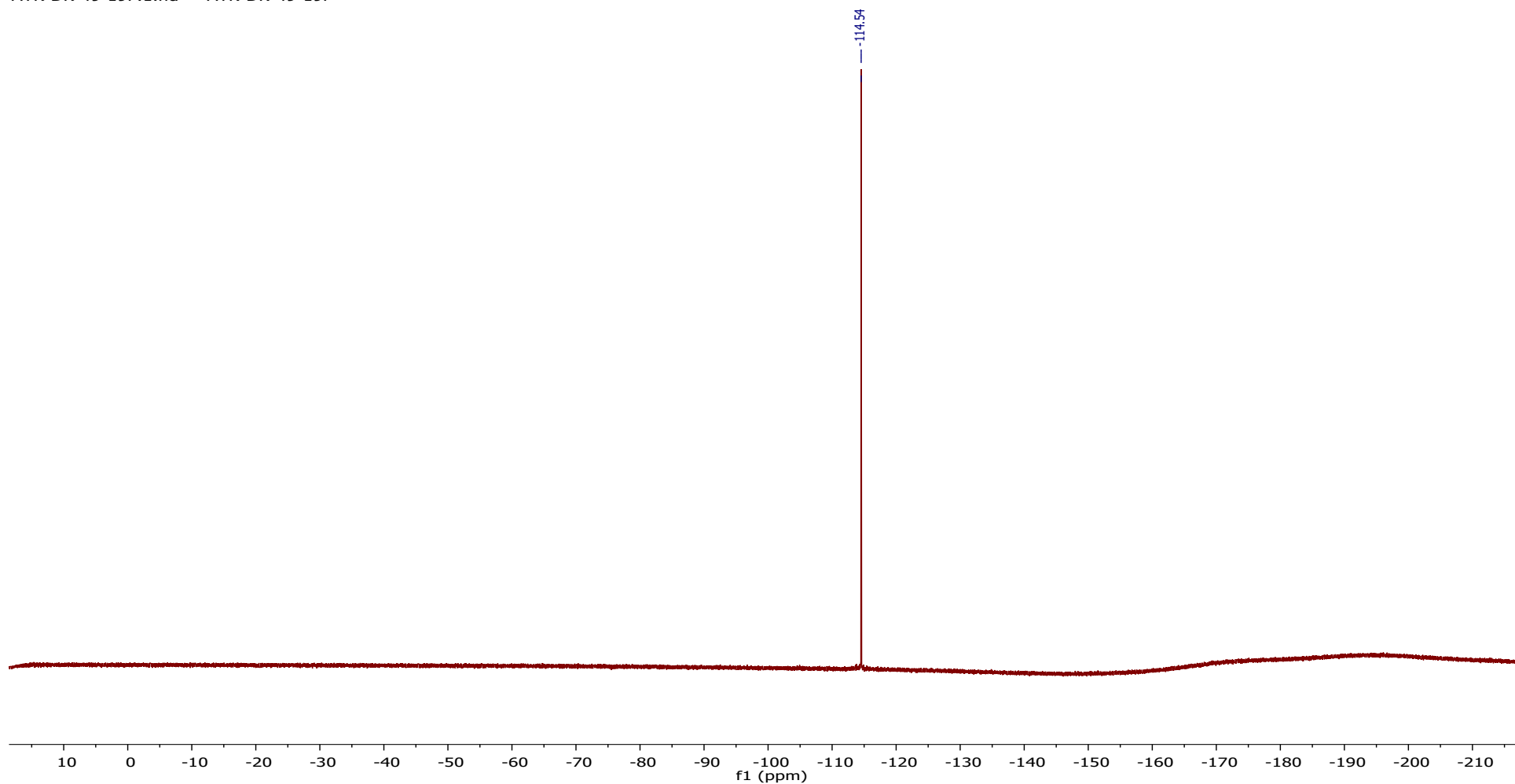
$^{13}\text{C} \{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of Compound 11b

11b 13C



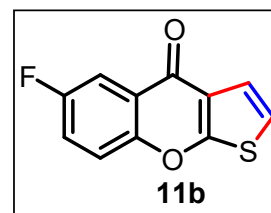
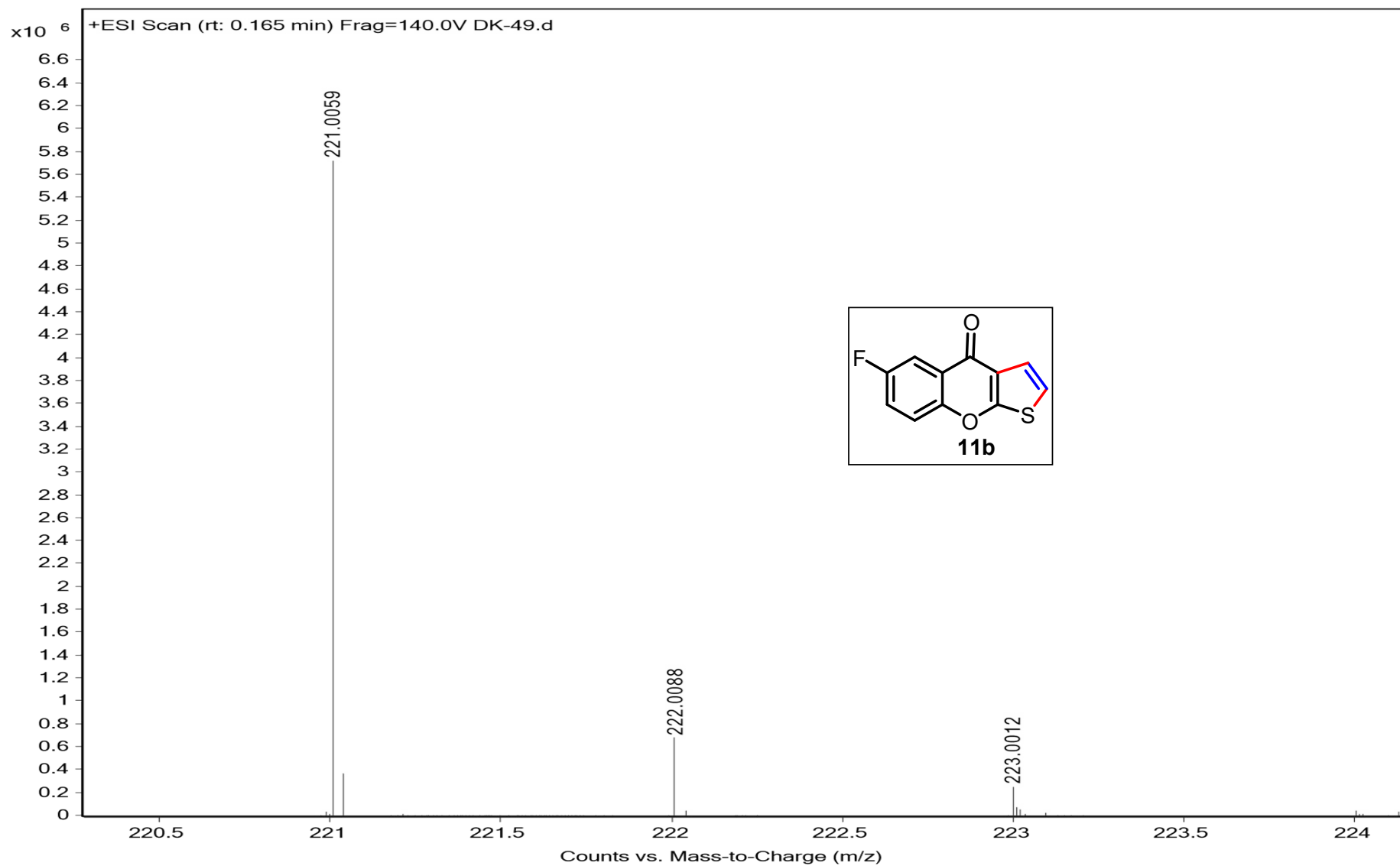
¹⁹F NMR of Compound 11b

ATK-DK-49-19F.1.fid — ATK-DK-49-19F



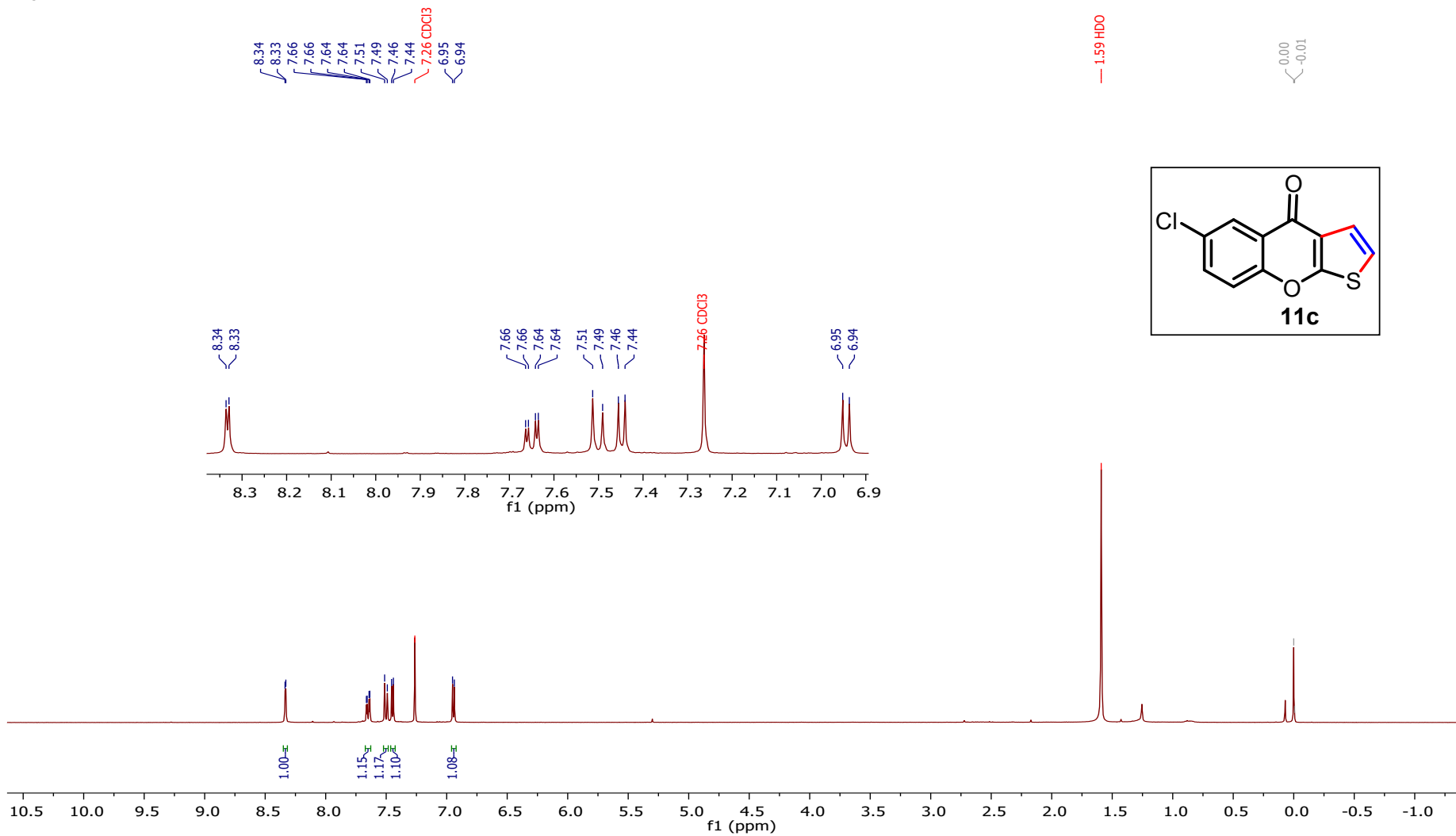
HRMS of compound 11b

75



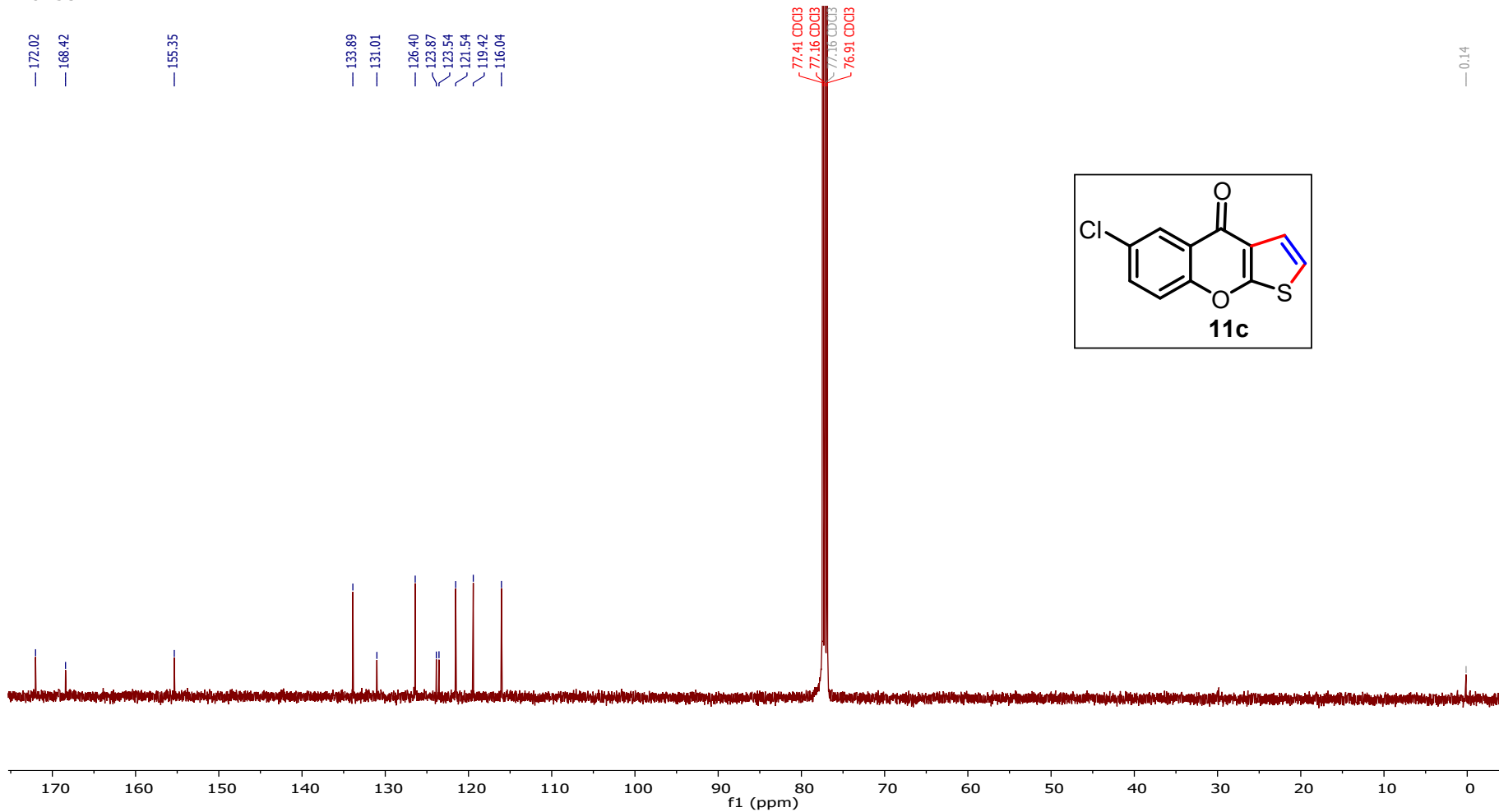
¹H NMR (400 MHz, CDCl₃) spectrum of Compound 11c

11c 1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 11c

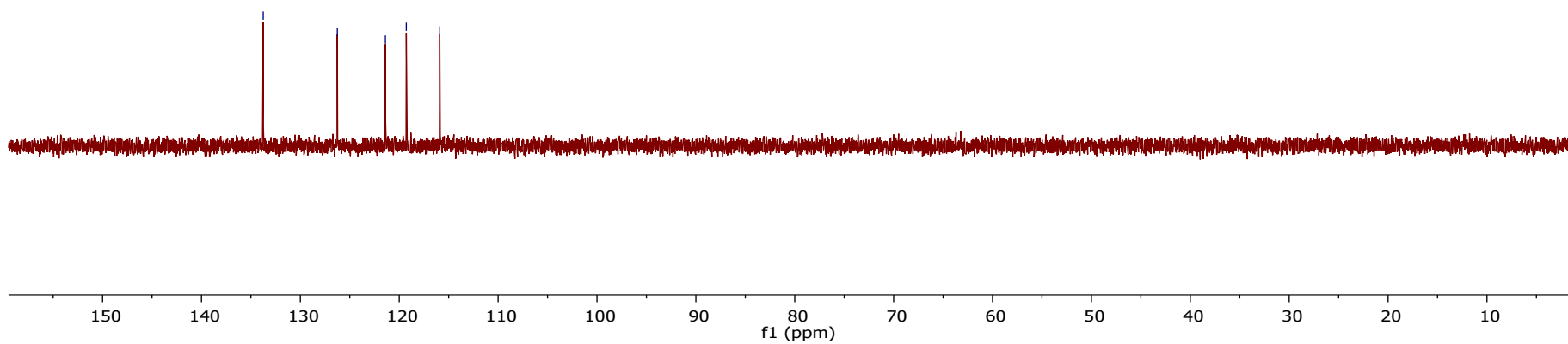
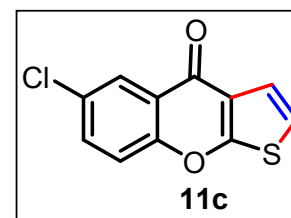
11c 13C



DEPT-135 ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Compound 11c

11c DEPT-135

— 133.75
— 126.26
— 121.40
— 119.28
— 115.90



HRMS of compound 11c

Sample Name
User Name
Sample Type
ACQ Method

Sample23
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_01_1,m

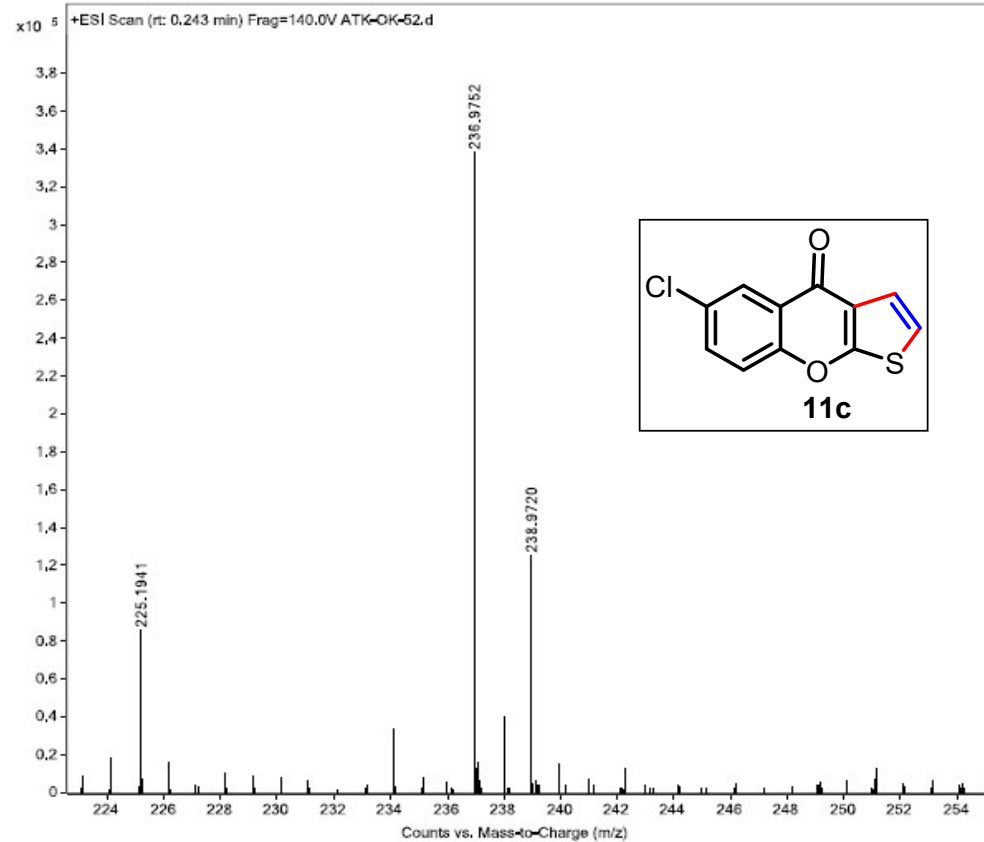
Position
Inj Vol
IRM Calibration Status
Comment

P1-C1
5
Success

Instrument Name
InjPosition
Data Filename
Acquired Time

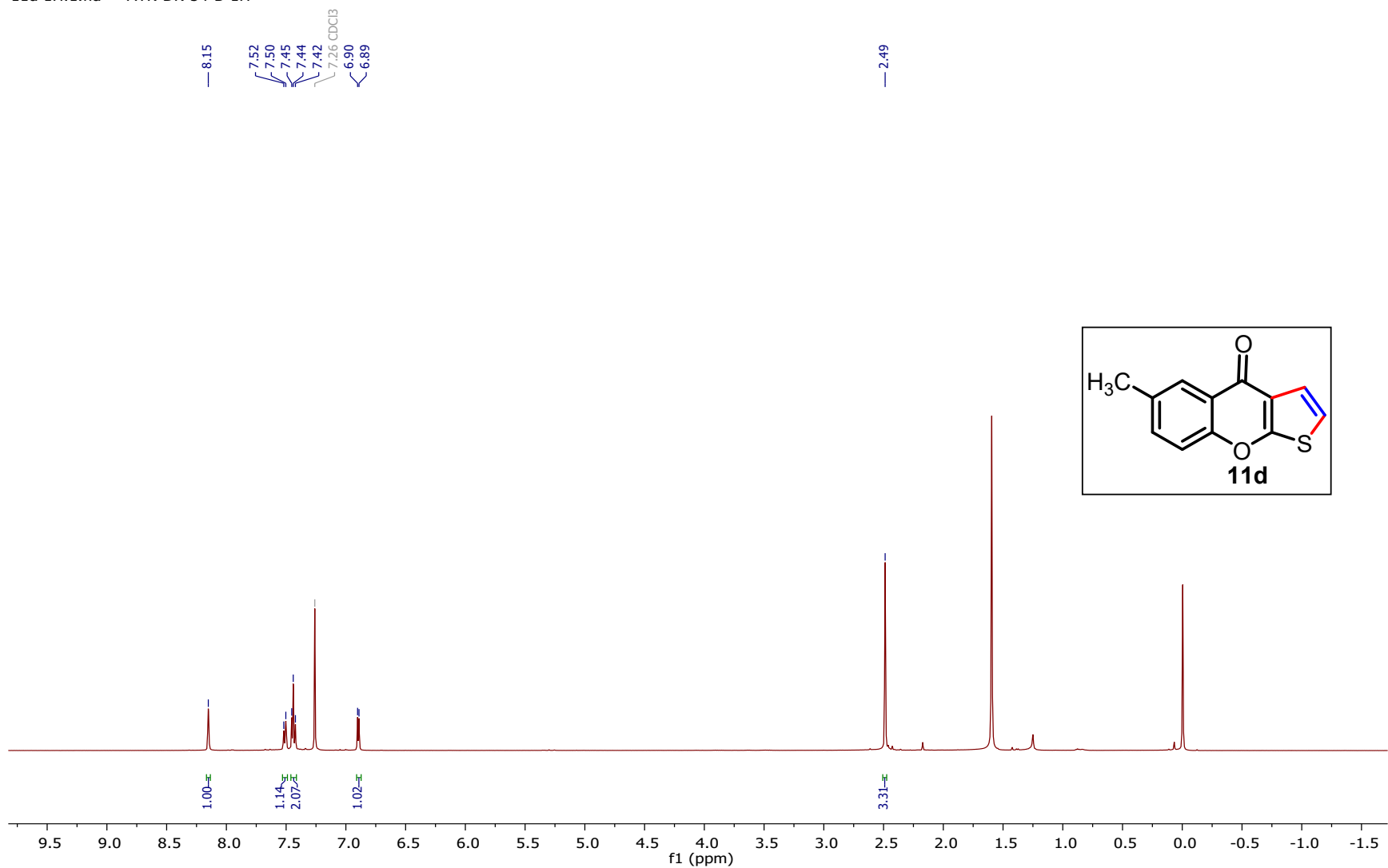
QTOF

ATK-OK-52,d
24-11-2025 15:33:50 (UTC+05:30)



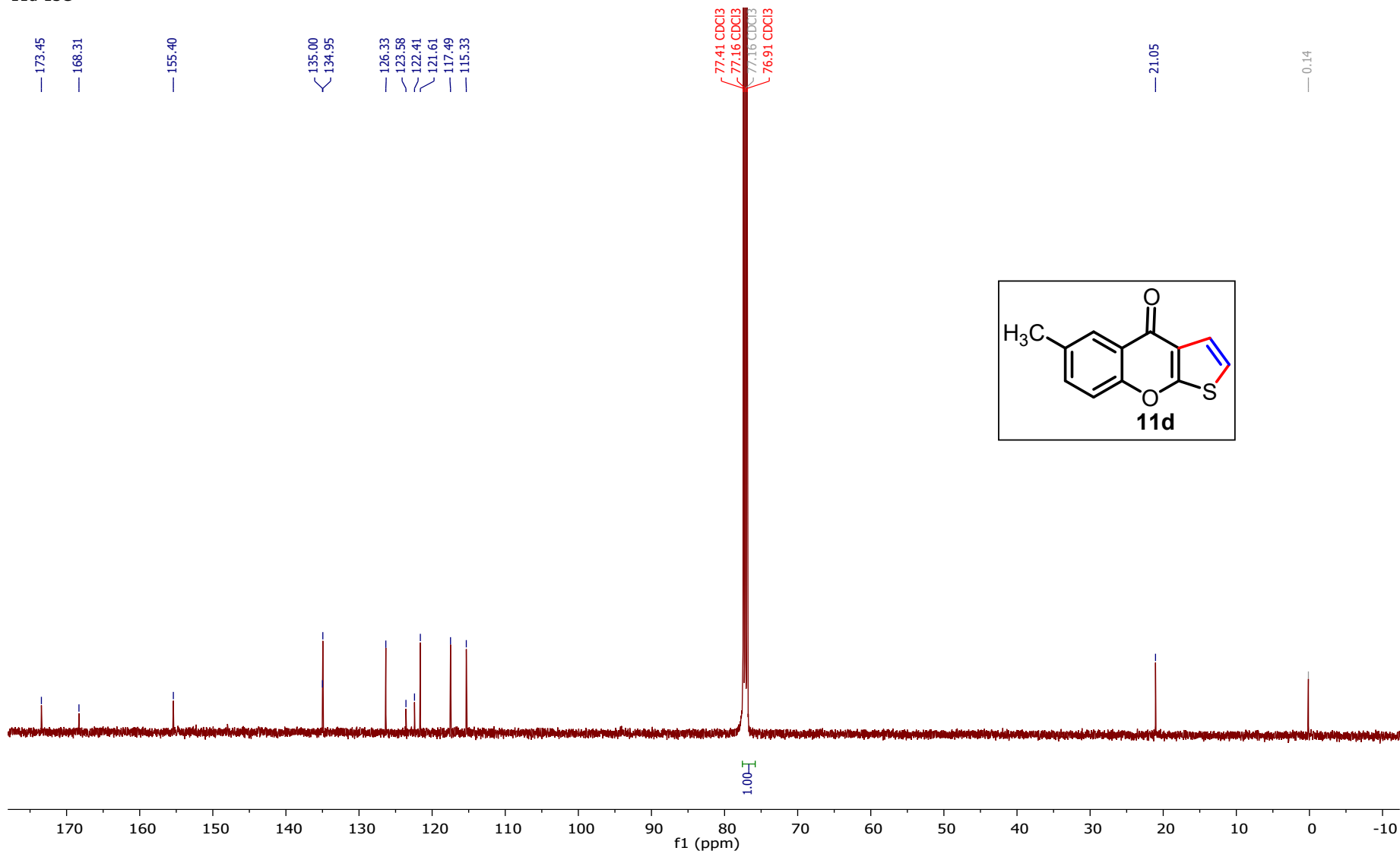
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 11d

11d 1H.1.fid — ATK-DK-54-B-1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 11d

11d 13C



HRMS of compound 11d

Sample Name
User Name
Sample Type
ACQ Method

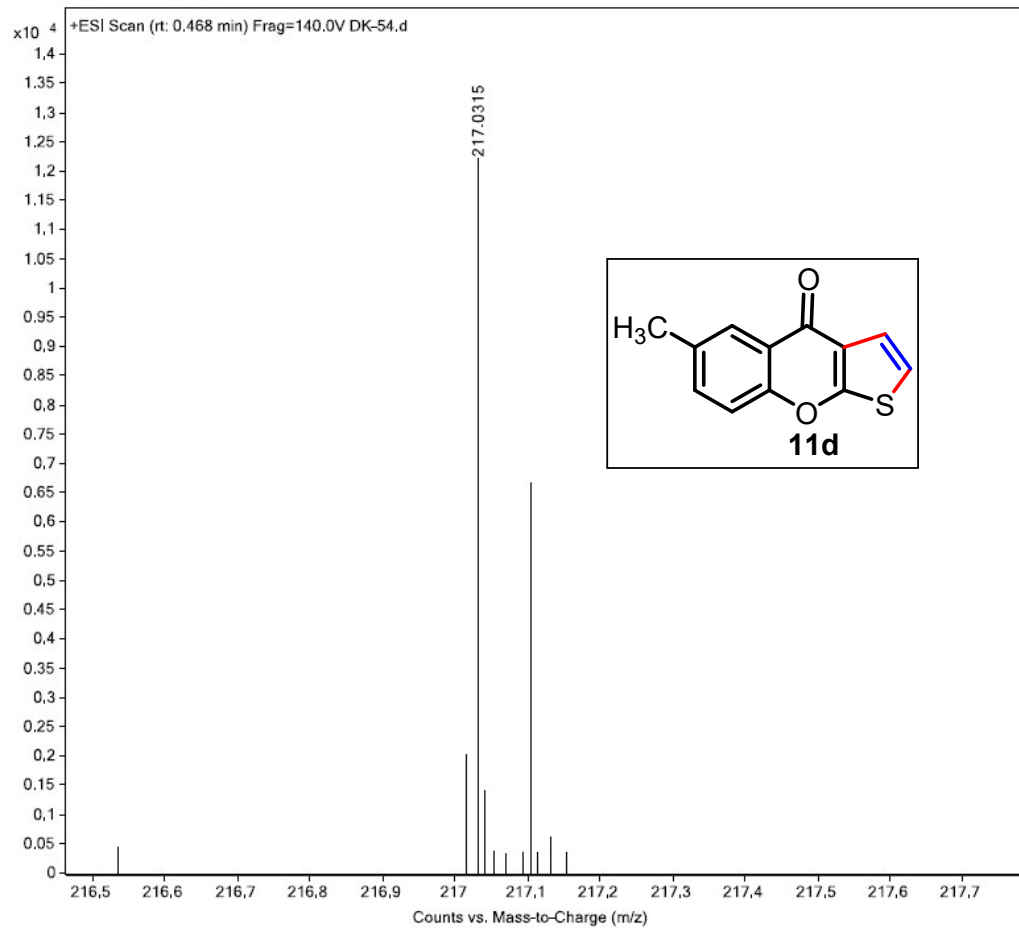
Sample13
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_50_1500.m

Position
Inj Vol
IRM Calibration Status
Comment

P1-B2
5
Success

Instrument Name
InjPosition
Data Filename
Acquired Time

QTOF
DK-54,d
01-05-2025 15:22:28 (UTC+05:30)



¹H NMR (500 MHz, CDCl₃) spectrum of Compound 11e

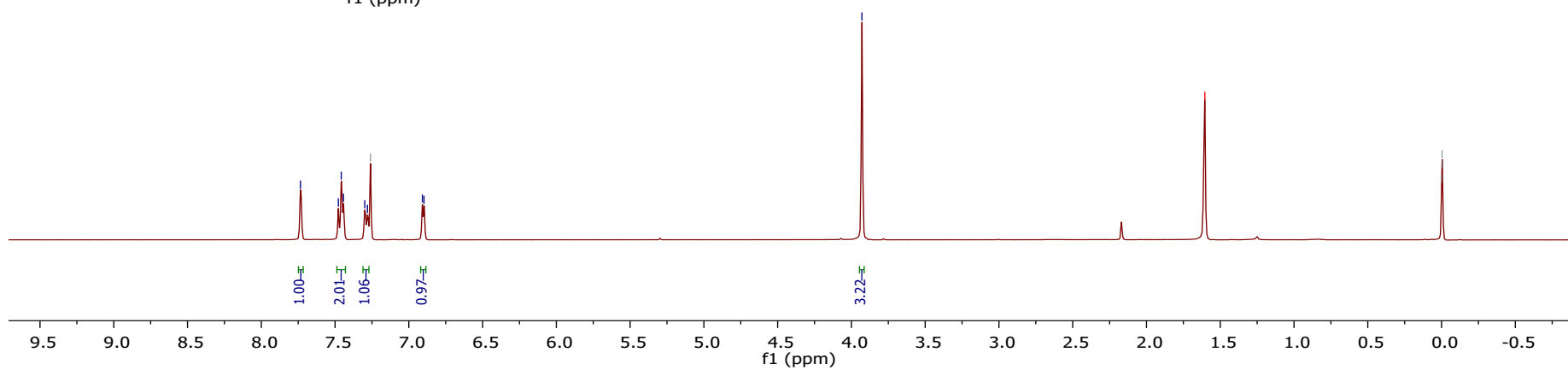
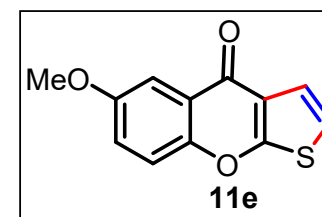
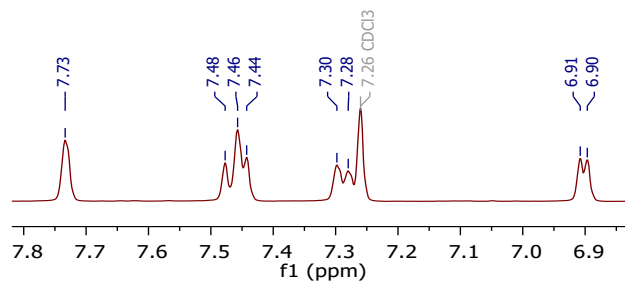
11e 1H

7.73
7.48
7.46
7.44
7.30
7.28
7.26 CDCl3
6.91
6.90

3.93

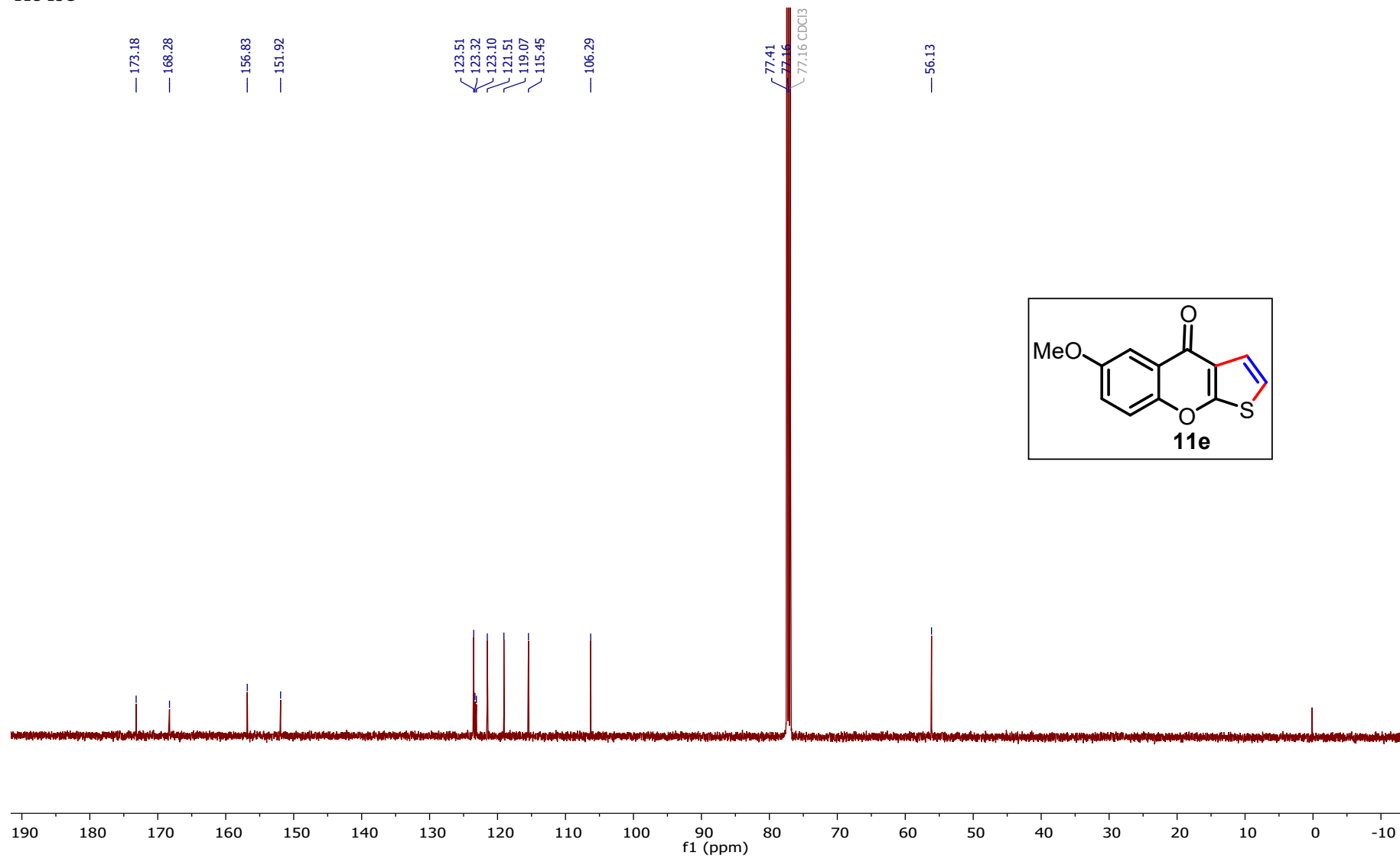
1.60 H2O

-0.00
-0.00
-0.01



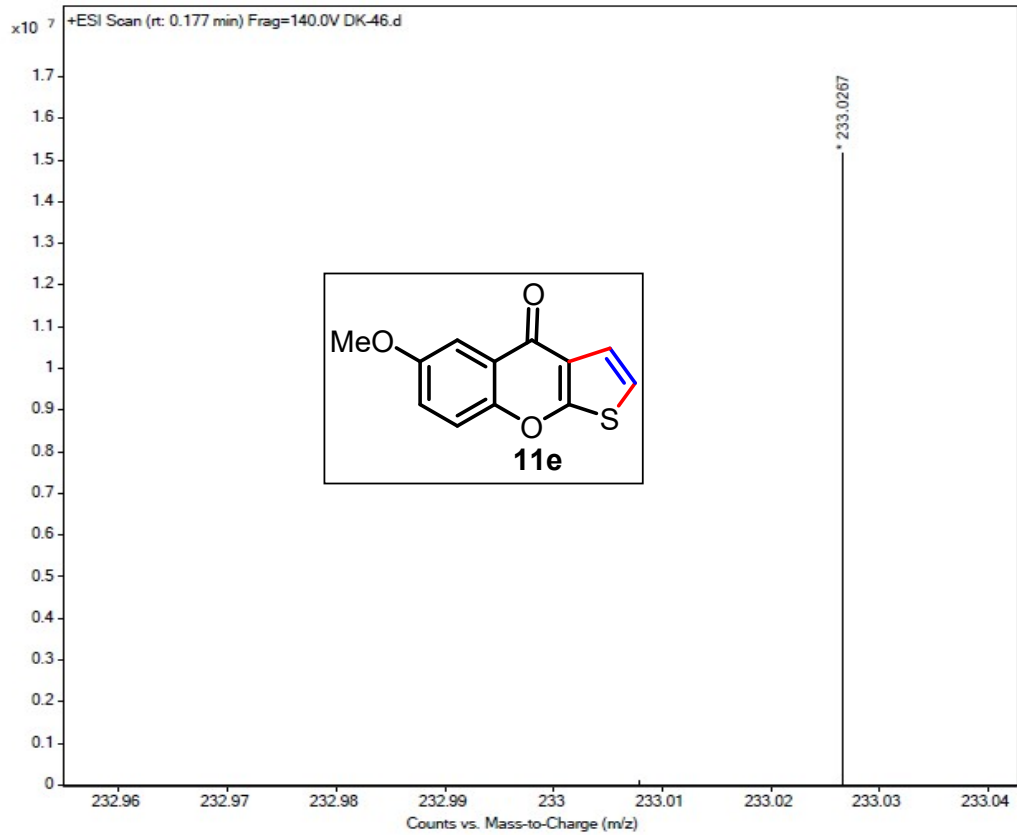
$^{13}\text{C} \{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Compound 11e

11e 13C



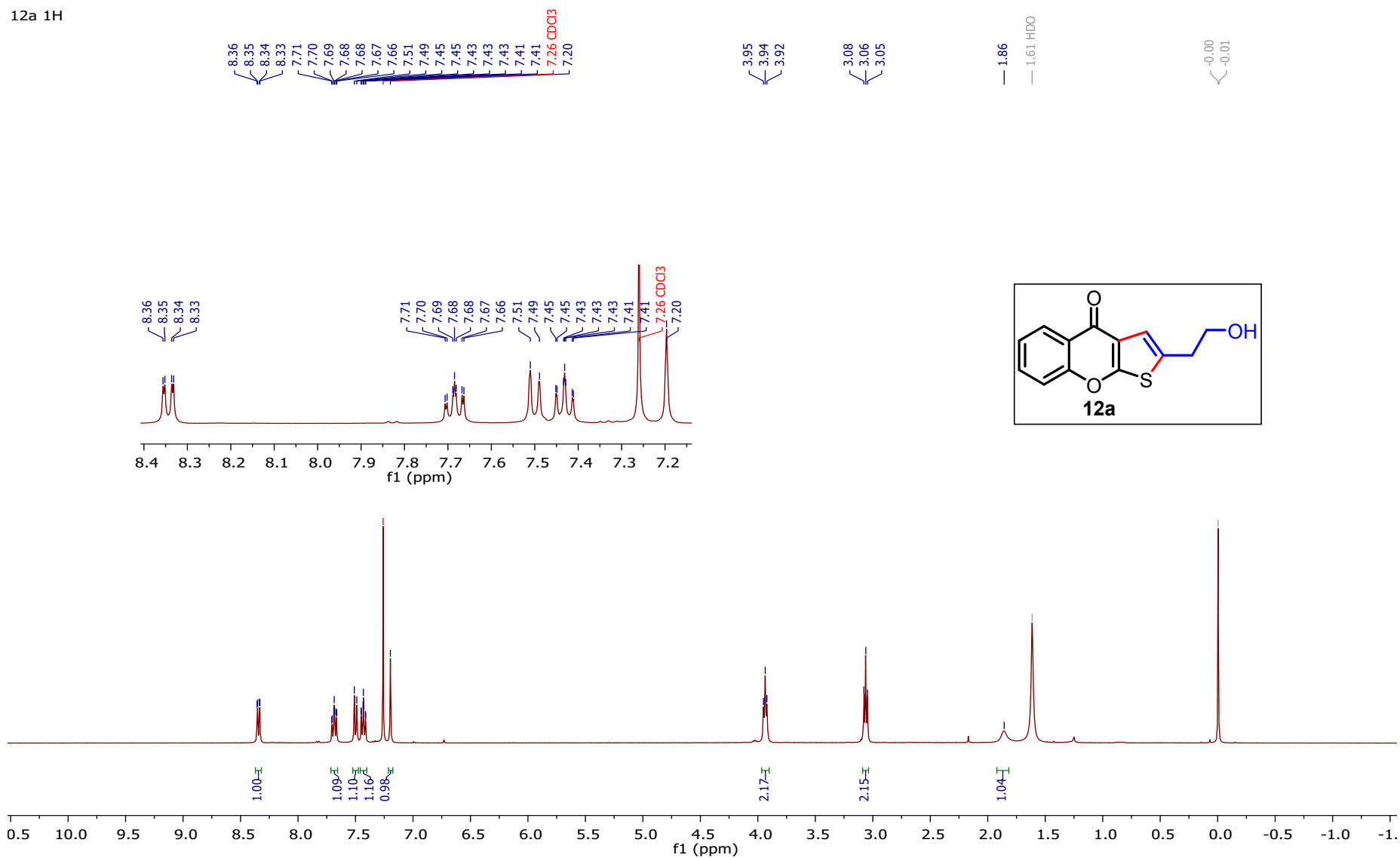
HRMS of compound 11e

Sample Name	Sample17	Position	P1-B6	Instrument Name	QTOF
User Name	SYSTEM (SYSTEM)	Inj Vol	5	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	DK-46.d
ACQ Method	DIRECT MASS_POSITIVE_01_1.m	Comment		Acquired Time	03-04-2025 11:22:06 (UTC+05:30)



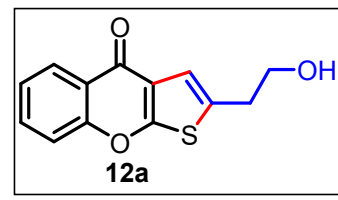
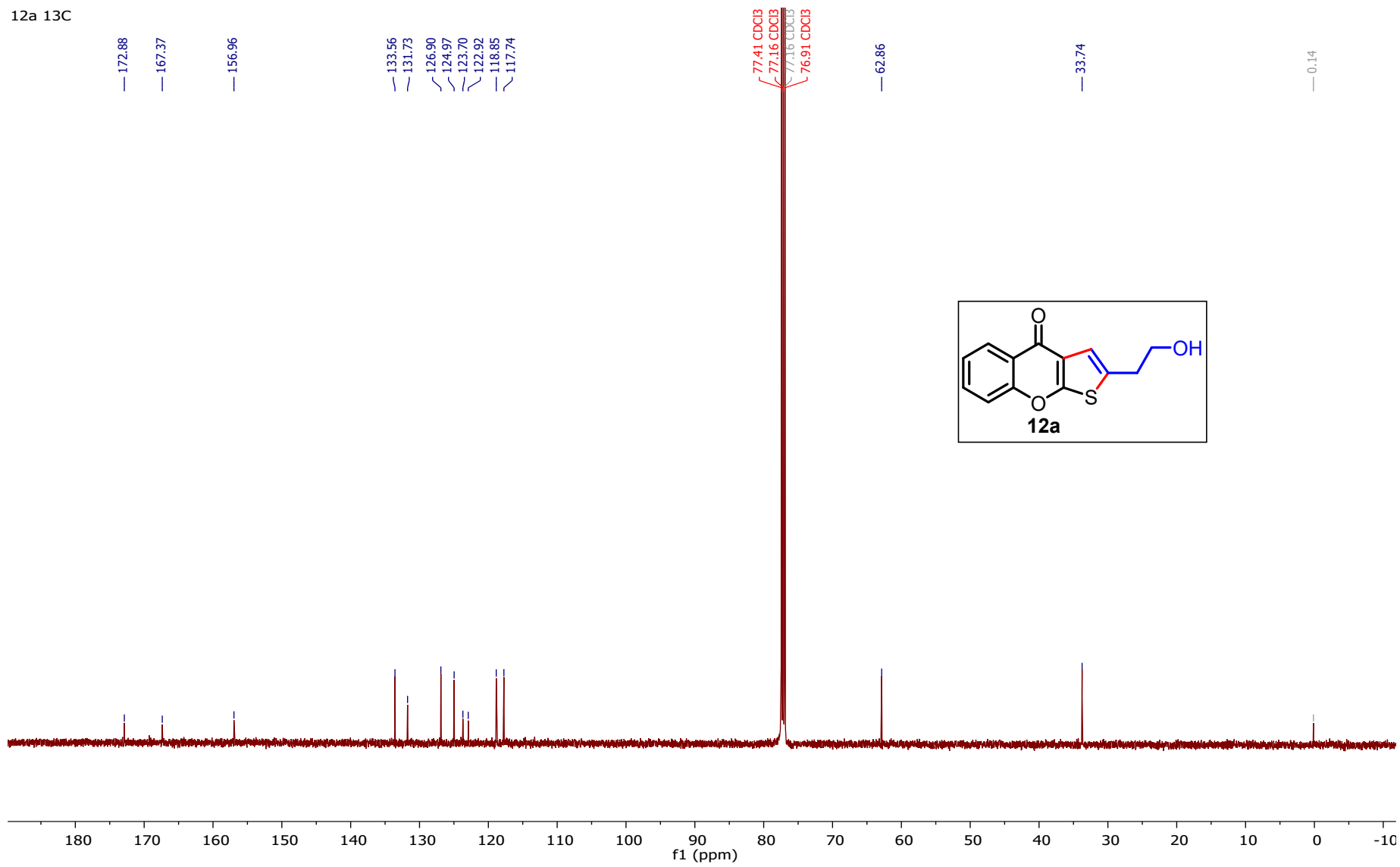
¹H NMR (400 MHz, CDCl₃) spectrum of Compound 12a

12a 1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 12a

12a 13C



HRMS of compound 12a

Sample Name
User Name
Sample Type
ACQ Method

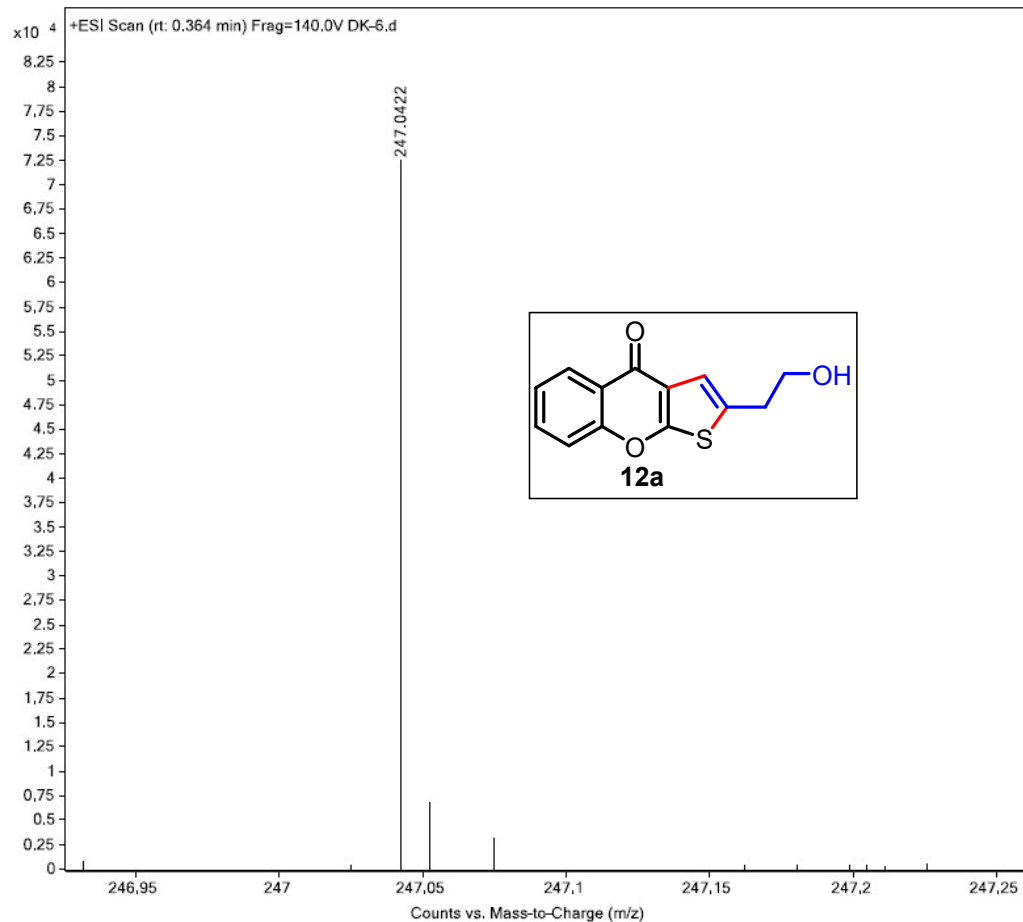
Sample6
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_50_1500.m

Position
Inj Vol
IRM Calibration Status
Comment

P1-A6
5
Success

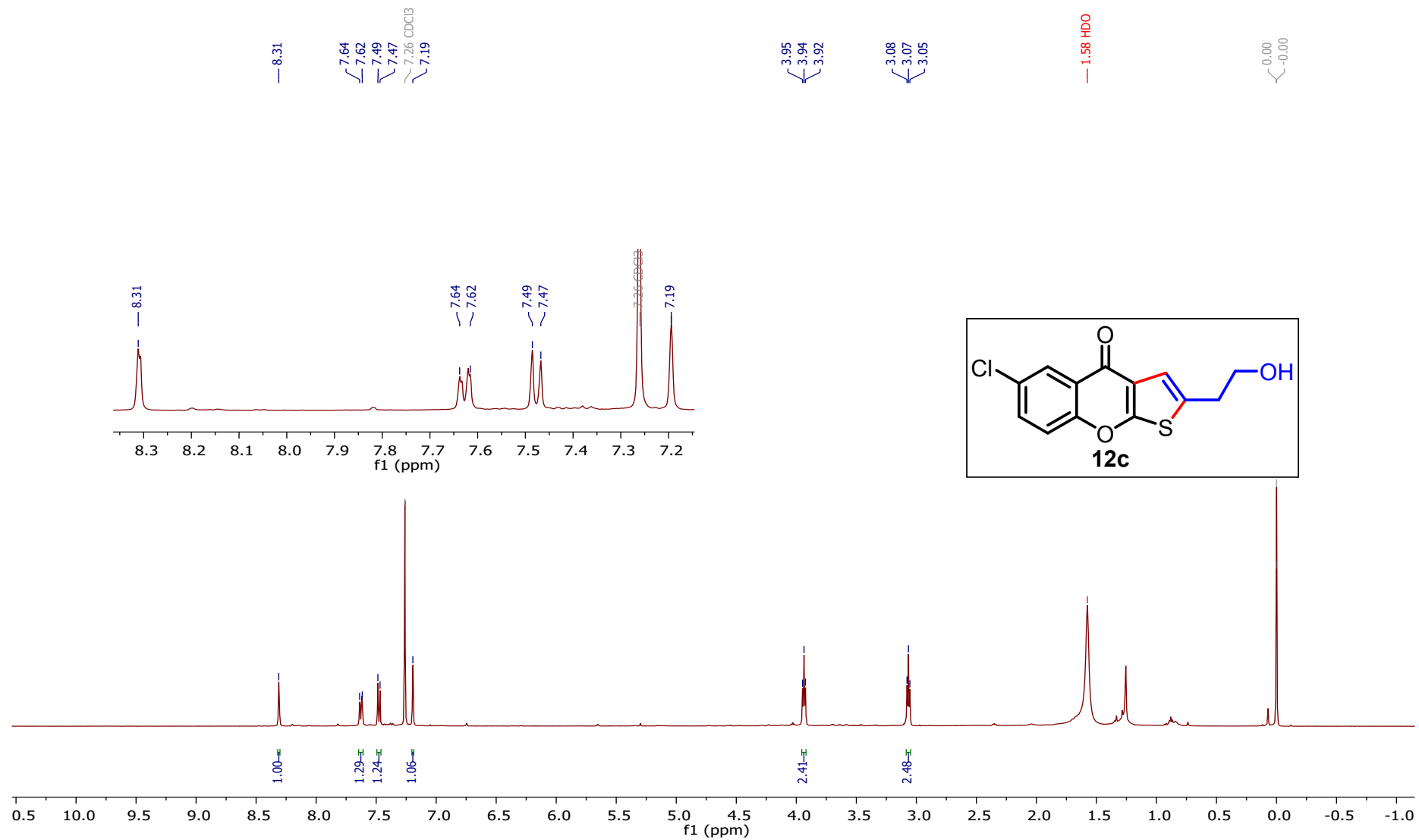
Instrument Name
InjPosition
Data Filename
Acquired Time

QTOF
DK-6,d
10-06-2025 10:47:09 (UTC+05:30)



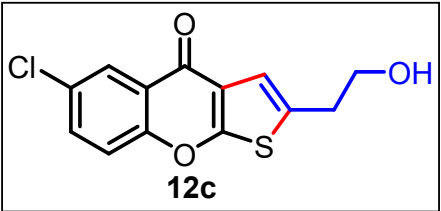
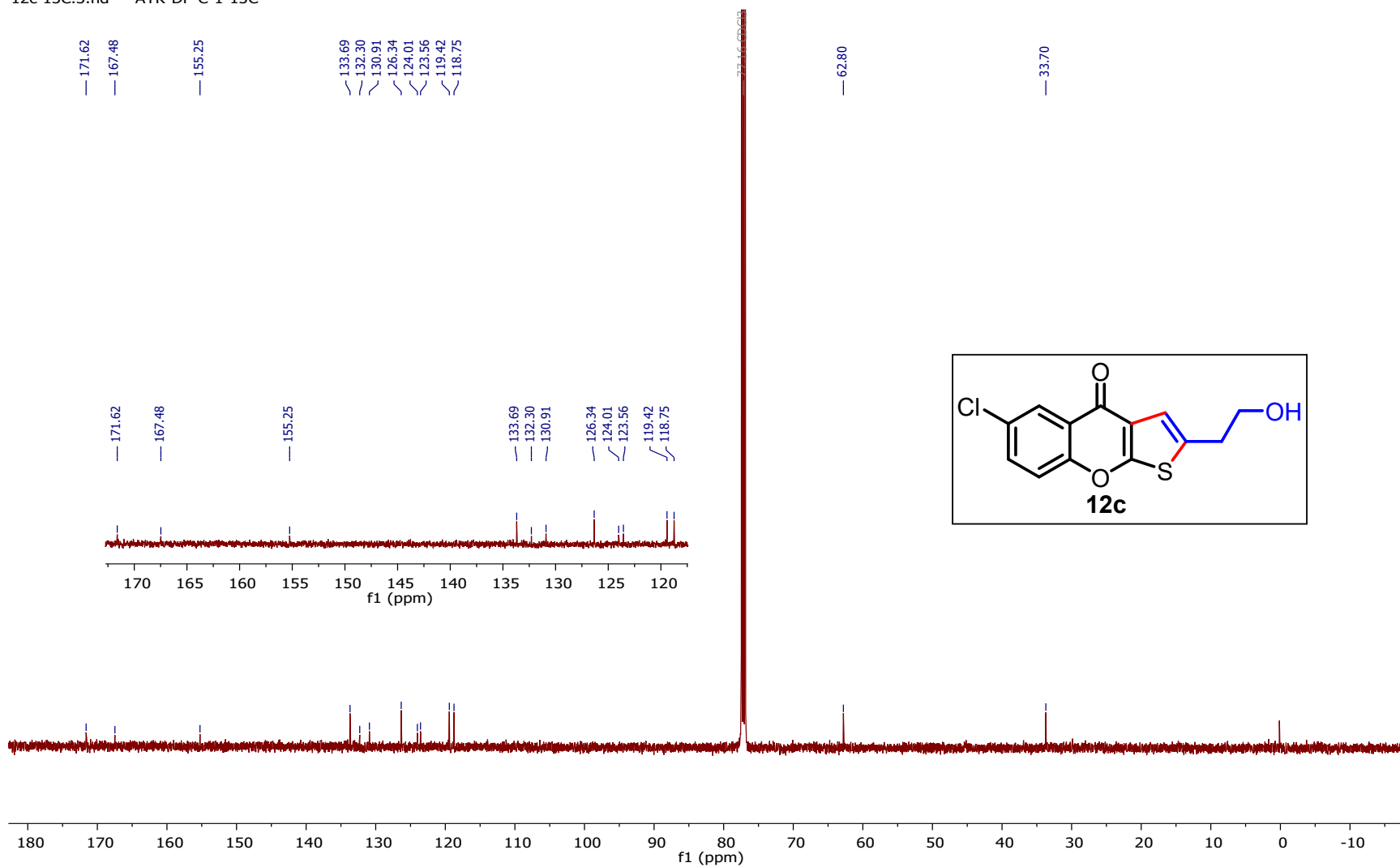
¹H NMR (500 MHz, CDCl₃) spectrum of Compound 12c

12c 1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 12c

12c 13C.3.fid — ATK-DF-C-1-13C



HRMS of compound 12c

Sample Name
User Name
Sample Type
ACQ Method

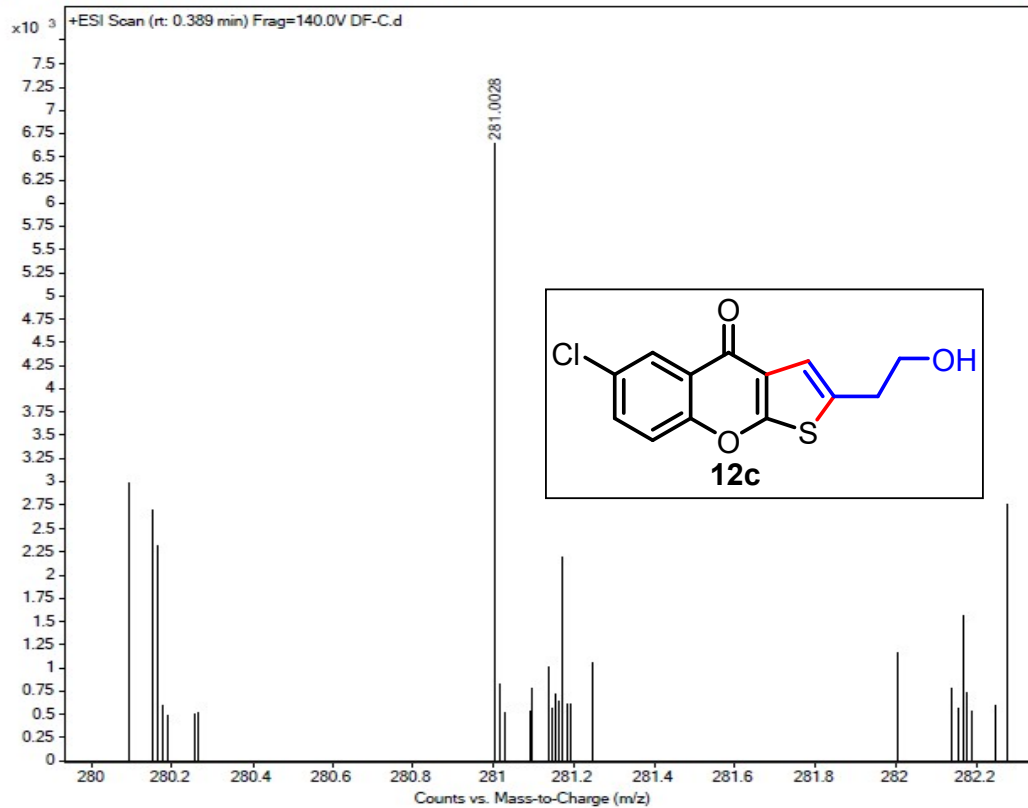
Sample33
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_01_1.m

Position
Inj Vol
IRM Calibration Status
Comment

P1-C11
5
Success

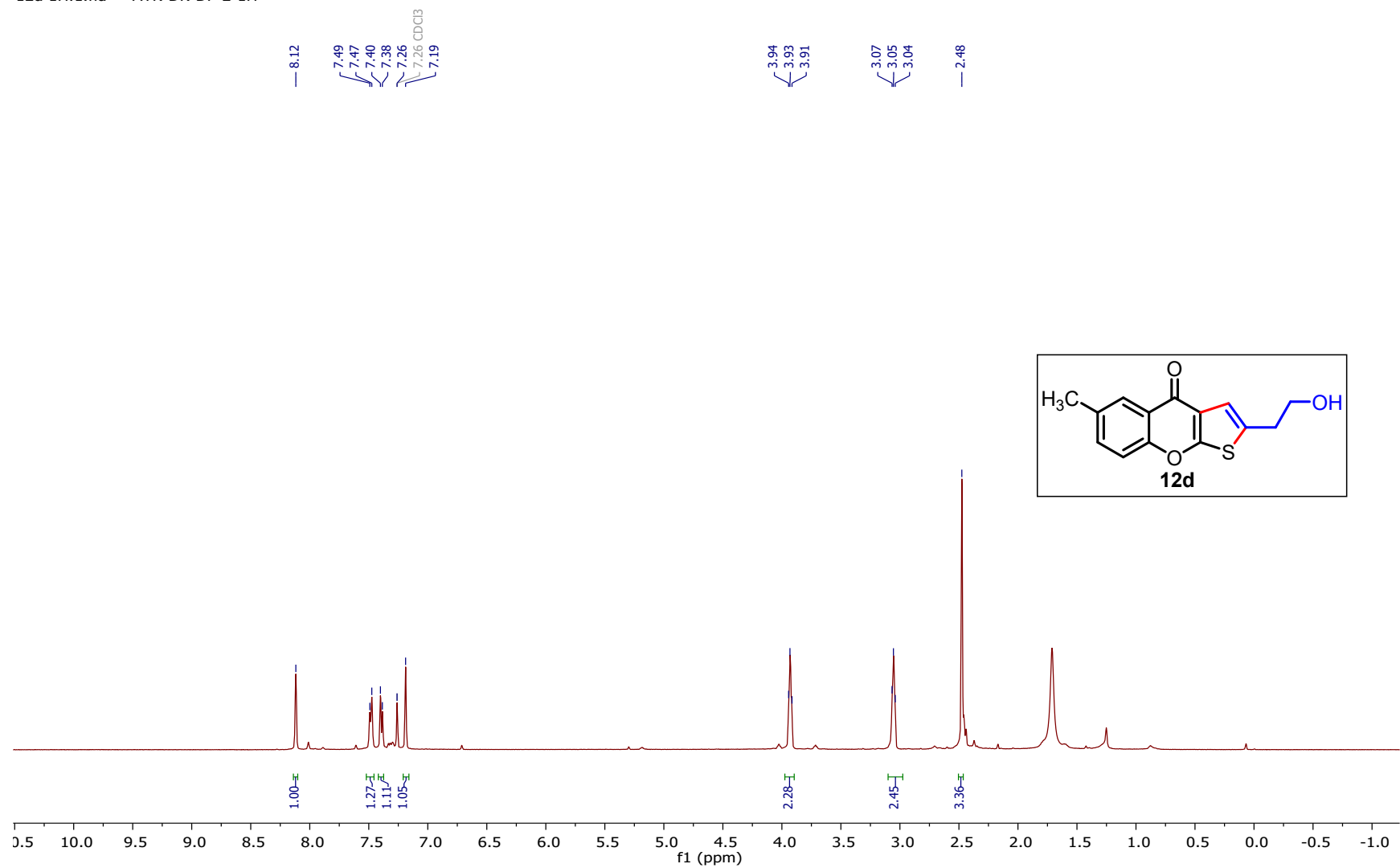
Instrument Name
InjPosition
Data Filename
Acquired Time

QTOF
DF-C.d
28-08-2025 12:28:06 (UTC+05:30)



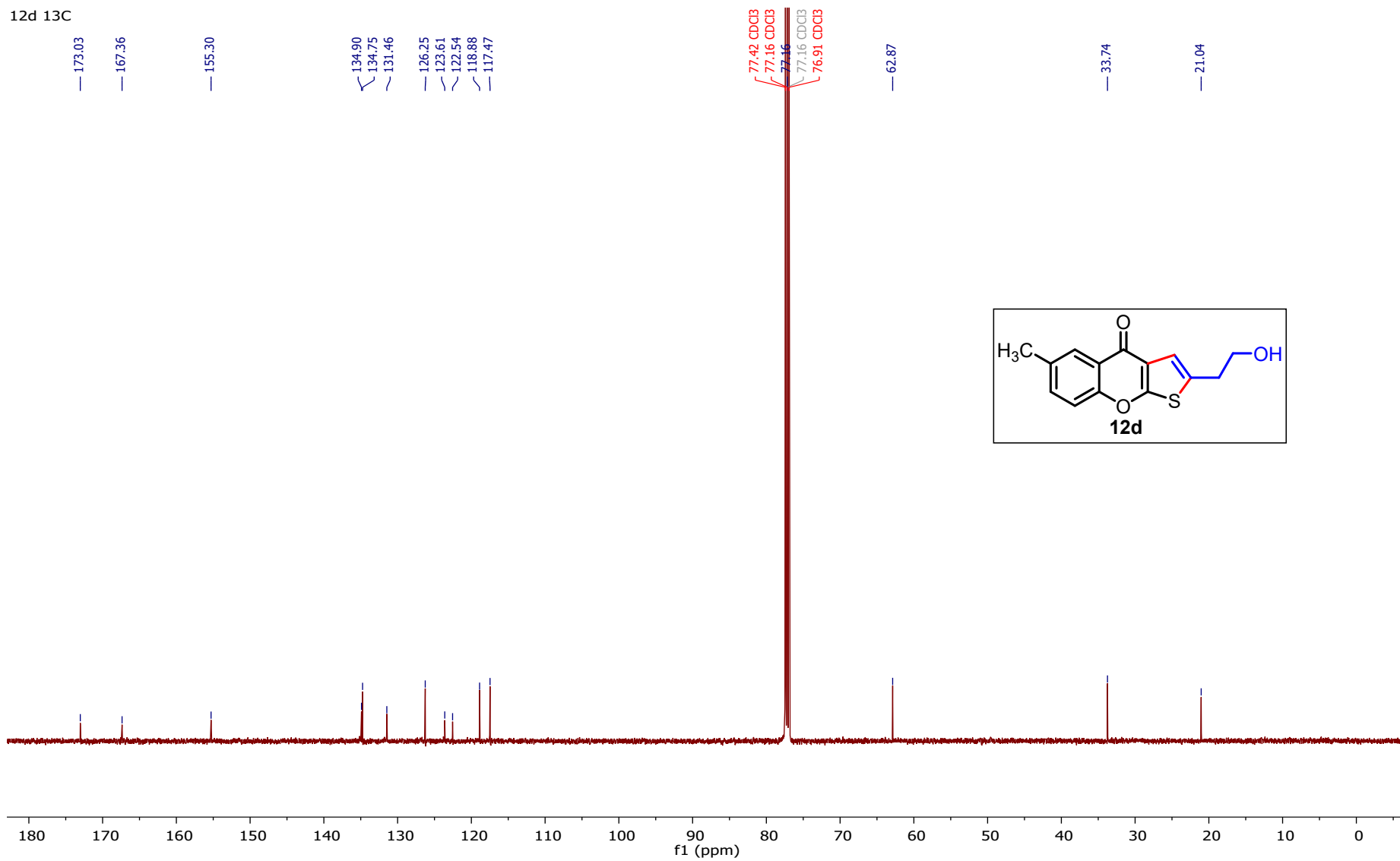
^1H NMR (500 MHz, CDCl_3) spectrum of Compound 12d

12d 1H.1.fid — ATK-DK-DF-2-1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 12d

12d 13C



HRMS of compound 12d

Sample Name
User Name
Sample Type
ACQ Method

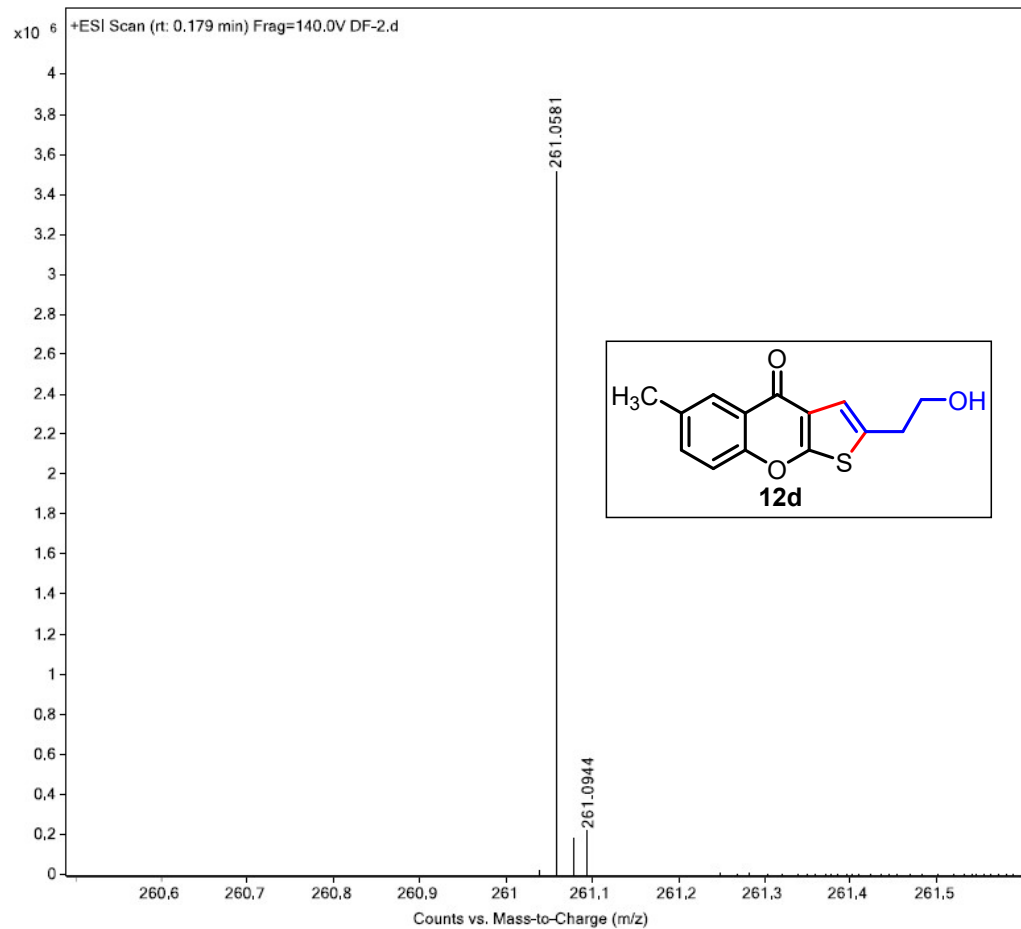
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_01_1.m

Position
Inj Vol
IRM Calibration Status
Comment

P1-A5
5
Success

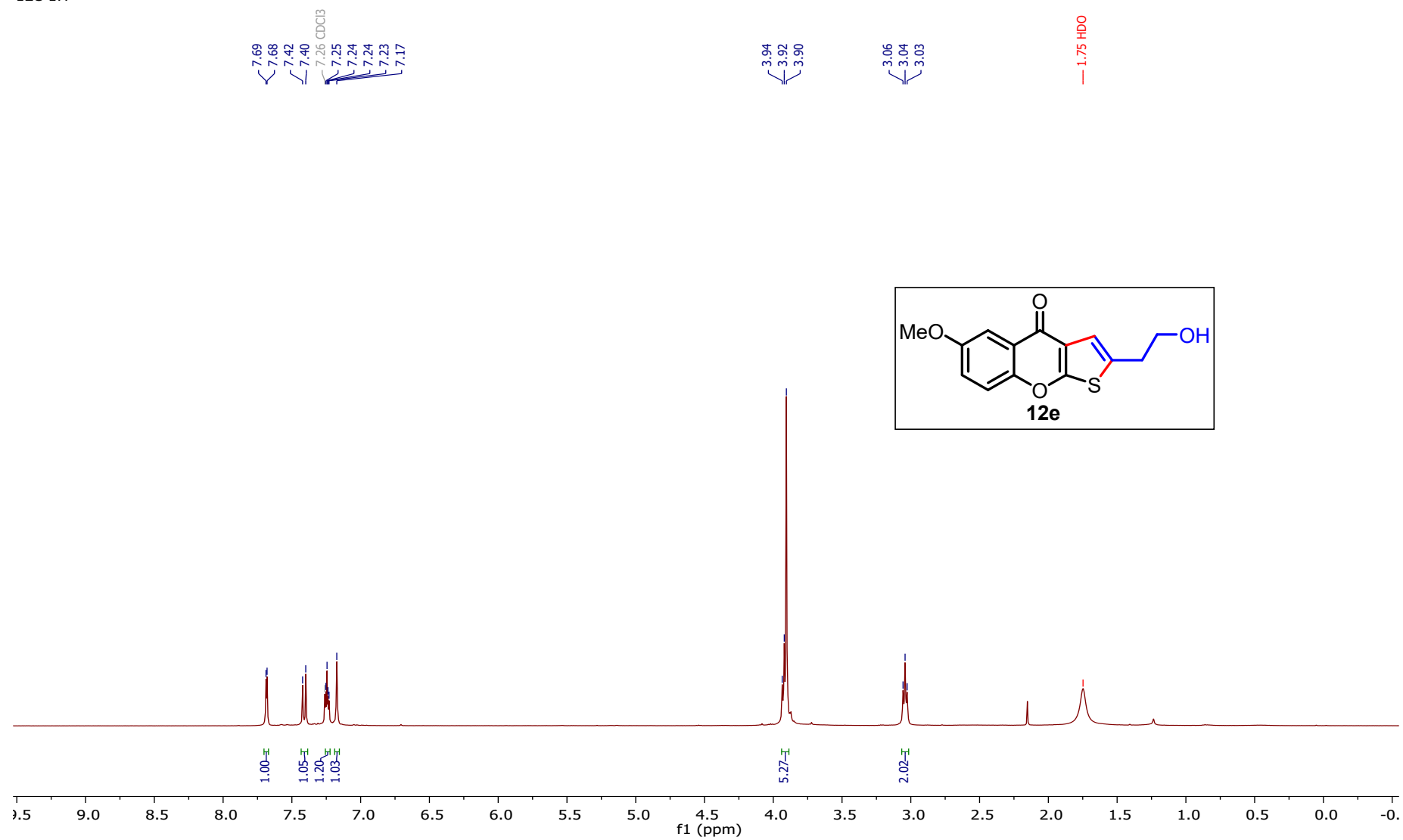
Instrument Name
InjPosition
Data Filename
Acquired Time

QTOF
DF-2,d
29-07-2025 15:01:01 (UTC+05:30)



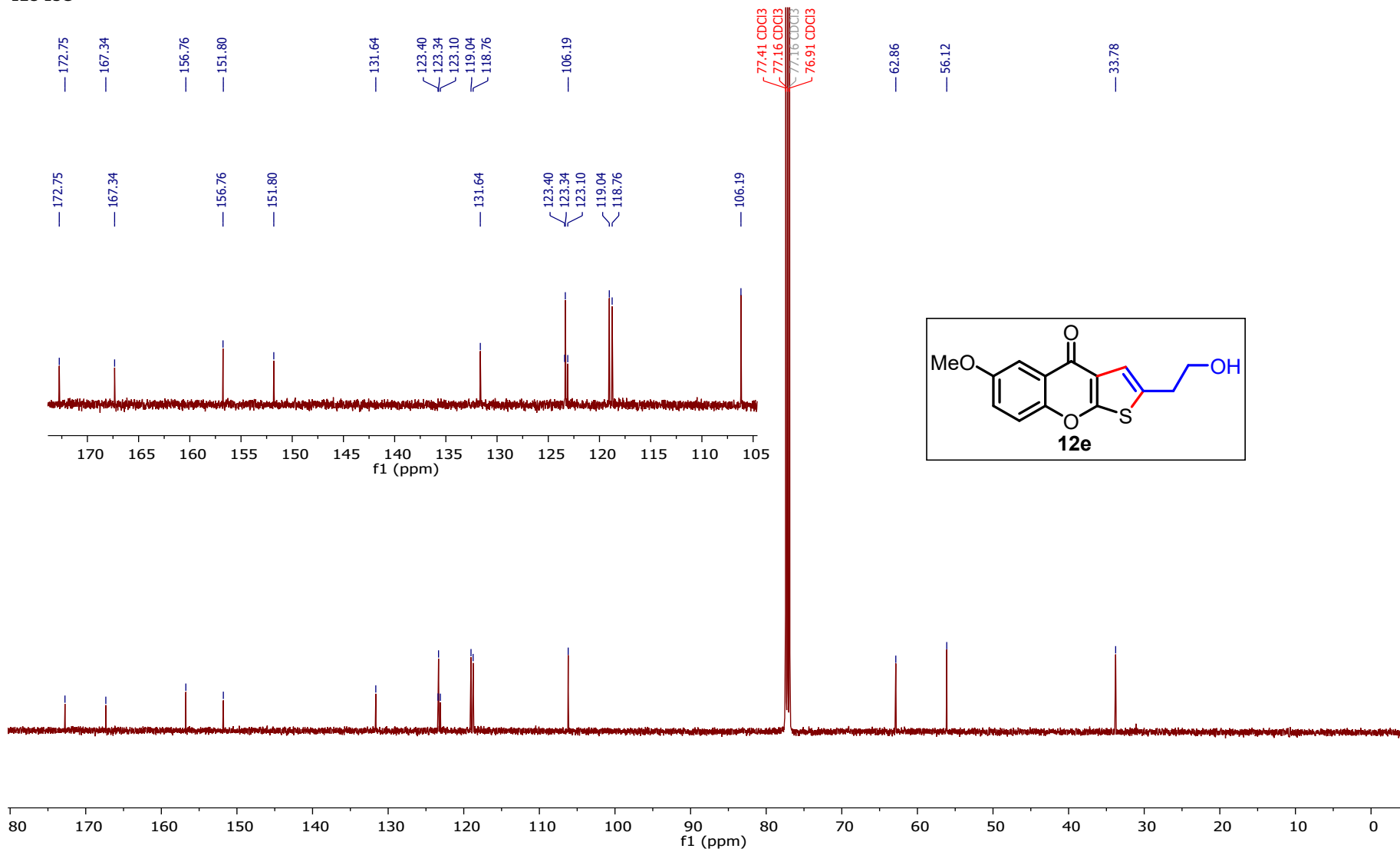
¹H NMR (400 MHz, CDCl₃) spectrum of Compound 12e

12e 1H



¹³C {¹H} NMR (125 MHz, CDCl₃) spectrum of Compound 12e

12e 13C



HRMS of compound 12e

Sample Name
User Name
Sample Type
ACQ Method

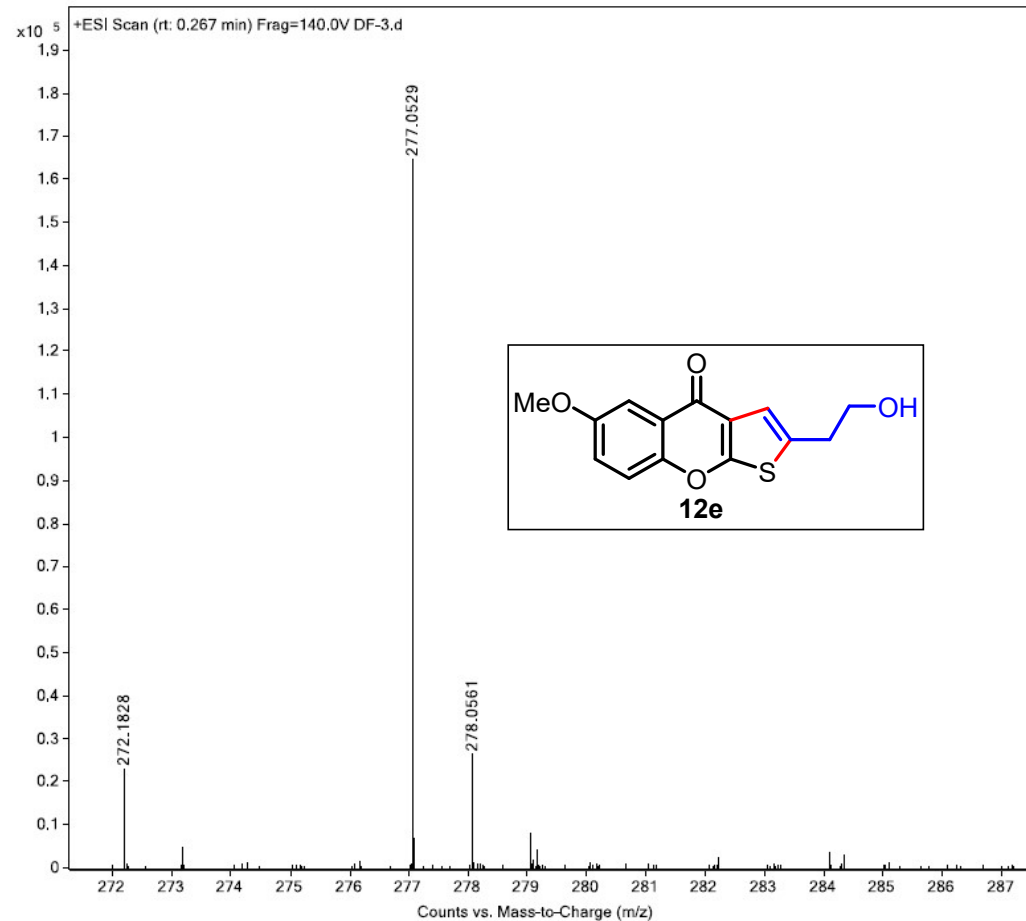
Sample5
SYSTEM (SYSTEM)
Sample
DIRECT MASS_POSITIVE_50_1500.m

Position
Inj Vol
IRM Calibration Status
Comment

P1-A5
5
Success

Instrument Name
InjPosition
Data Filename
Acquired Time

QTOF
DF-3,d
10-06-2025 10:40:04 (UTC+05:30)

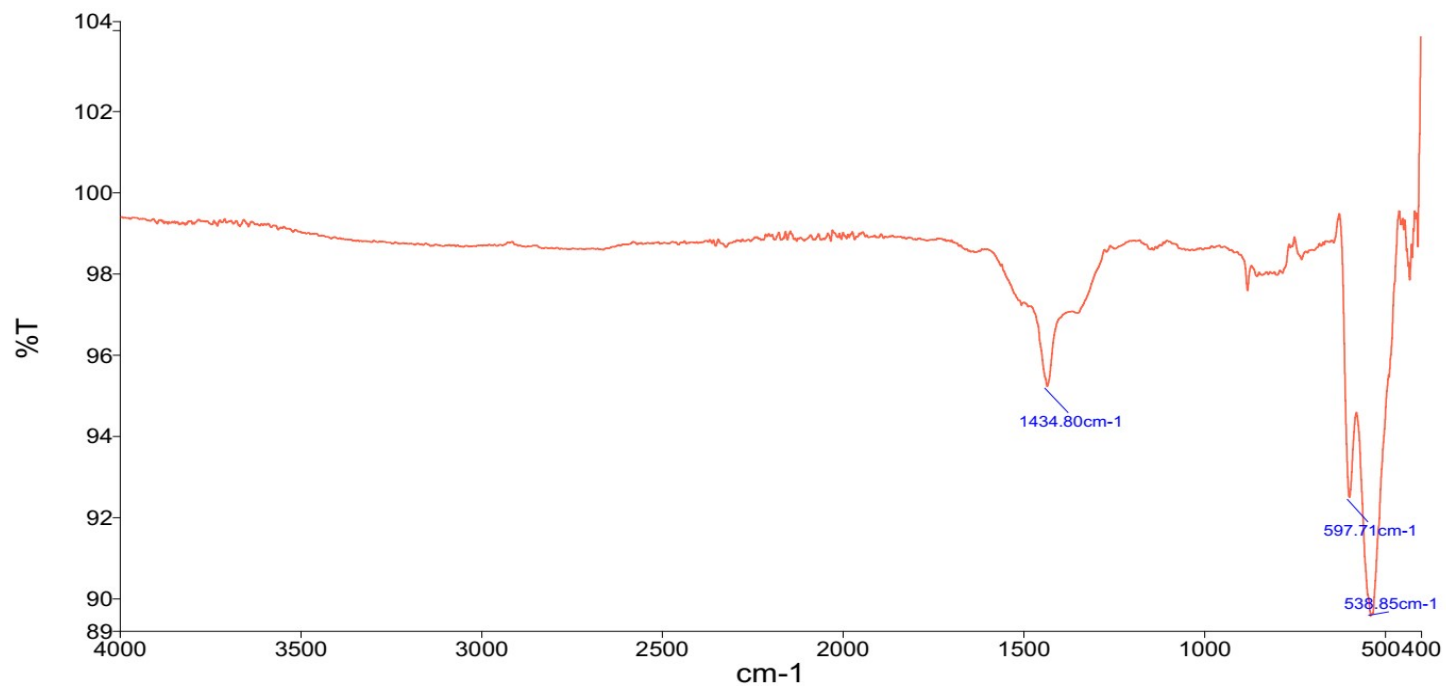


IR Spectrum of the CuO NPs before reaction (pure)

PerkinElmer Spectrum IR Version 10.6.1
10 March 2026 21:33

Analyst Date
Date

Analyst
10 March 2026 21:33



Analyst 30448_1_1 Sample 30448 By Analyst Date Tuesday, March 10 2026

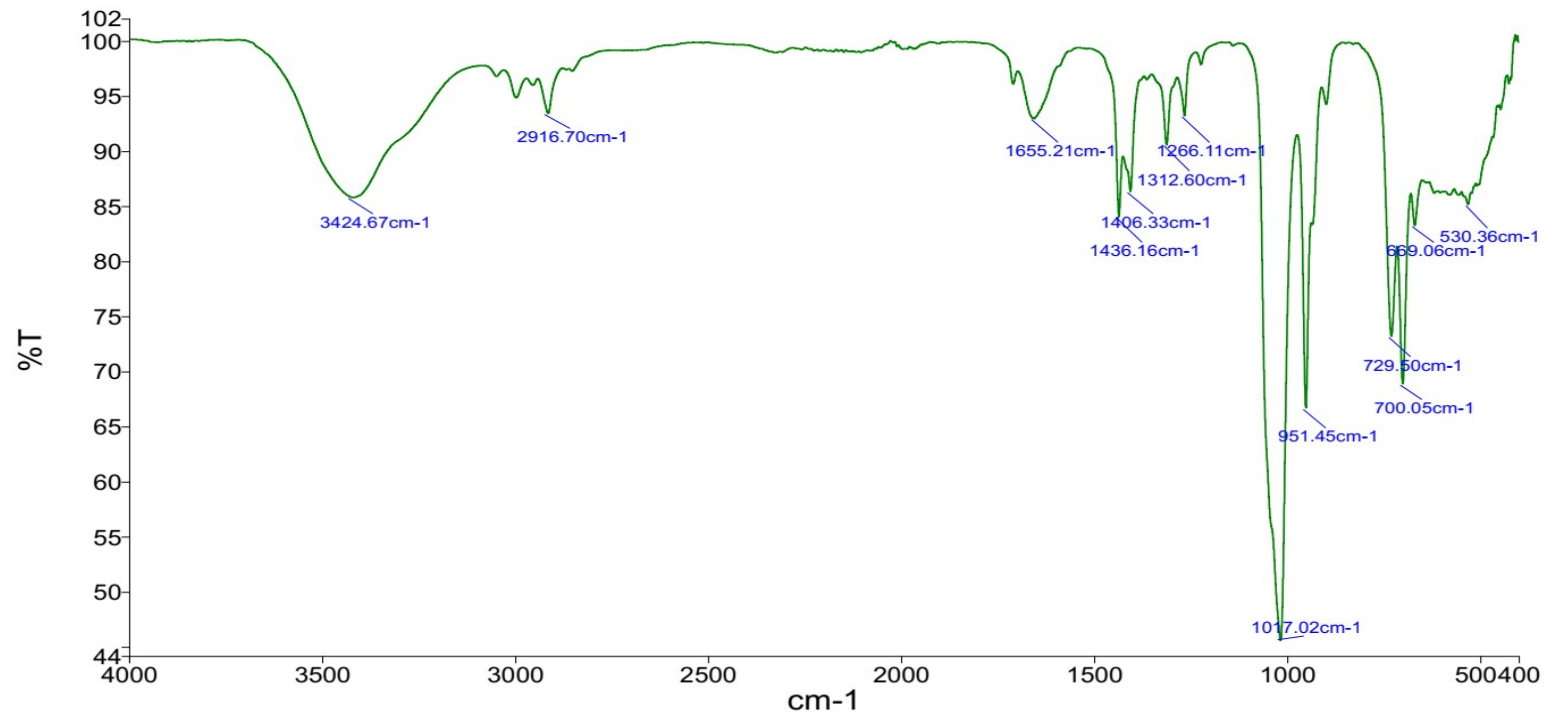
Source Spectra Results	
Spectrum Name	Number Of Peaks
Analyst 30448_1_1	3

IR Spectrum of the CuO NPs during reaction

PerkinElmer Spectrum IR Version 10.6.1
10 March 2026 21:45

Analyst
Date

Analyst
10 March 2026 21:45

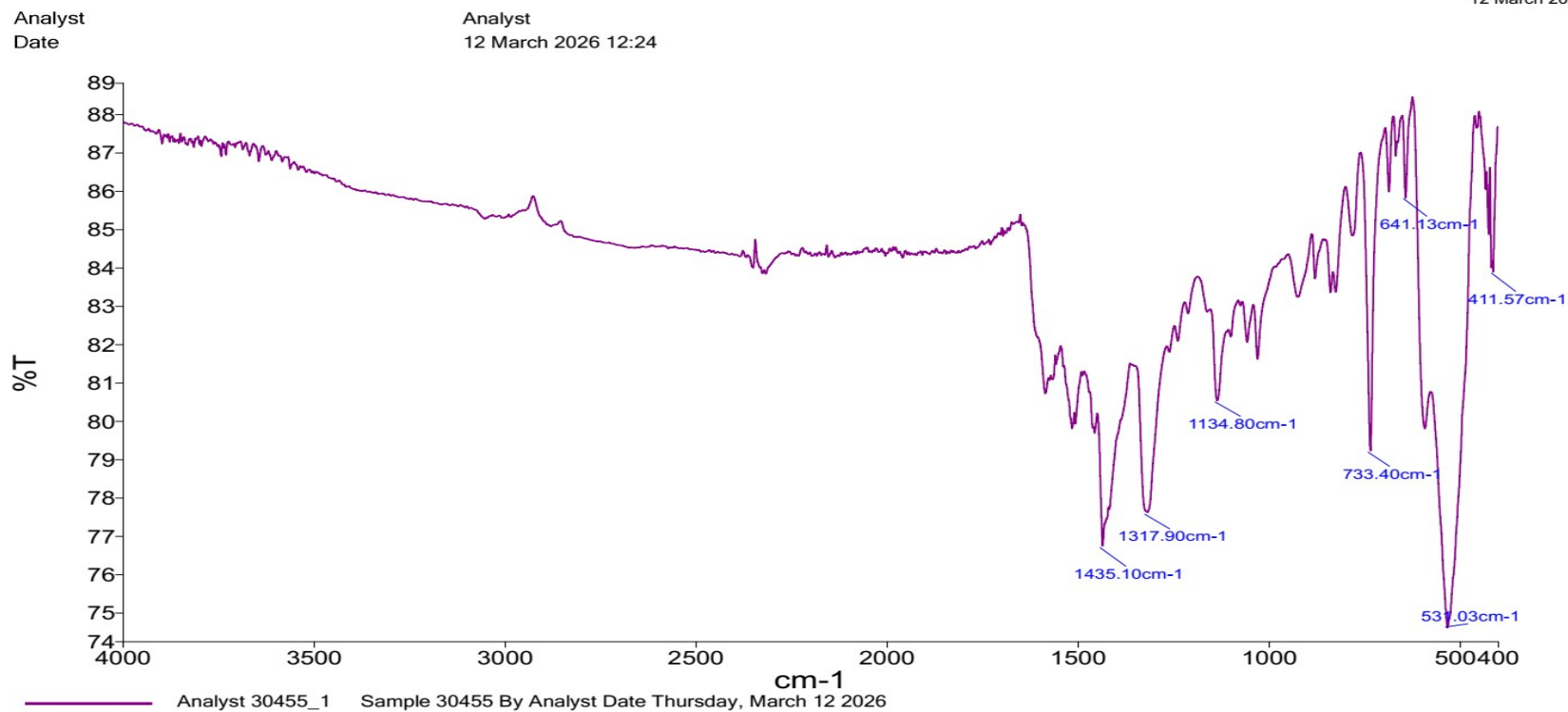


— Analyst 30450_1_1 Sample 30450 By Analyst Date Tuesday, March 10 2026

Source Spectra Results	
Spectrum Name	Number Of Peaks
Analyst 30450_1_1	13

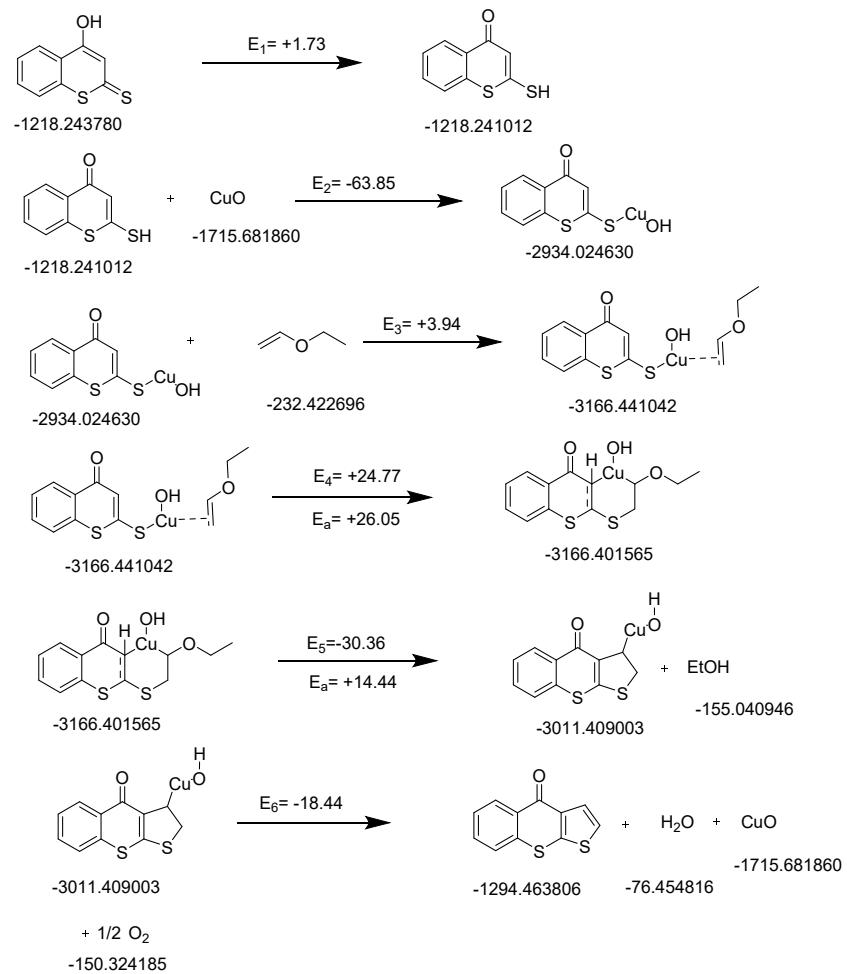
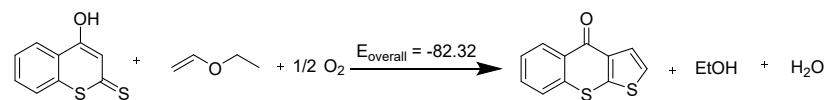
IR Spectrum of the CuO NPs after the reaction

PerkinElmer Spectrum IR Version 10.6.1
12 March 2026 12:24

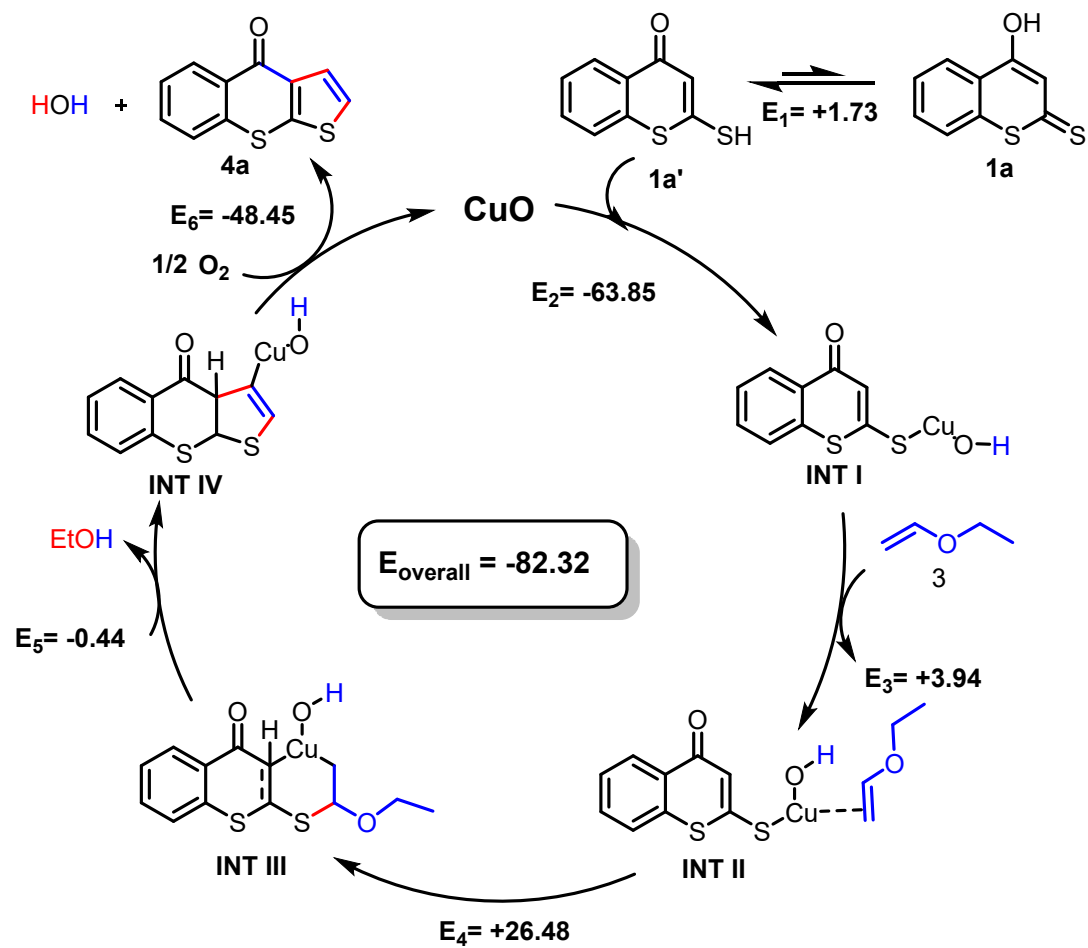


Source Spectra Results	
Spectrum Name	Number Of Peaks
Analyst 30455_1	7

S4: Detailed Stepwise Mechanism.



Alternative pathway of the reaction mechanism.

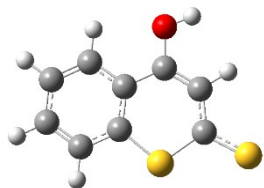


ESI Quantum Chemical Analysis

Gaussian 16.0 software³ was employed to perform quantum chemical analysis. All the 3D structures (given in Scheme 5 in the manuscript) were optimized using density functional [B3LYP/6 311+G(d,p)]^{1,2} level of theory. The analytical frequencies for all the species were obtained to establish the character of the saddle points along the reaction path (0 to negative frequencies for all minima and one negative frequency for the TS). Free energy corrected absolute values are employed in the calculation of ΔG values for all individual reactions along the reaction path. The activation energy (E_a) for the C-S and two C-C bond formations from the intermediate to give the final products has been estimated using Berny optimisation procedures (OPT=TS option).

Codes	Energy values (in Hartrees)
1a	-1218.243780
1a'	-1218.241012
3	-232.422696
CuO	-1715.681860
INT I	-2934.024630
INT II	-3166.441042
INT III	-3166.401565
INT IV	-3011.409003
H₂O	-76.454816
EtOH	-155.040946
½ O₂	-75.162095 (O ₂ : -150.324185)
TS I	-3166.399531
TS II	-3166.378543

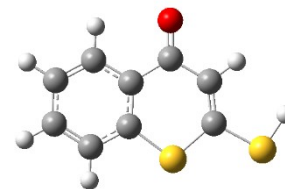
1a



0 1

C	-3.15376800	-1.30941700	-0.00037100
C	-1.83650200	-1.74016500	-0.00073700
C	-0.78825000	-0.80899900	-0.00022400
C	-1.07505900	0.57137900	0.00025500
C	-2.42165700	0.98574900	0.00077700
C	-3.44917700	0.05883900	0.00063300
H	-3.95487300	-2.03956800	-0.00087300
H	-1.60950800	-2.80031000	-0.00143000
C	0.00038900	1.54504100	-0.00031000
H	-2.63848800	2.04524800	0.00129500
H	-4.47960500	0.39324800	0.00129200
C	1.33335400	1.24845200	-0.00036400
C	1.91816400	-0.05351800	-0.00004500
O	-0.42592600	2.83272800	-0.00043700
S	3.55696500	-0.33658900	0.00025100
S	0.85213800	-1.45976700	0.00020100
H	0.33067500	3.43080000	-0.00097700
H	2.04859300	2.06627000	-0.00070400

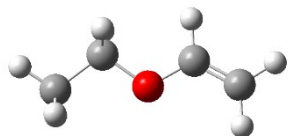
1a'



0 1

C	3.18440900	-1.29423300	-0.00128900
C	1.86328900	-1.71142000	-0.00038100
C	0.83017400	-0.76177600	0.00040400
C	1.12269000	0.61081600	0.00033600
C	2.47159800	1.00528200	-0.00066400
C	3.49268100	0.07149300	-0.00142600
H	3.97733700	-2.03336700	-0.00194700
H	1.62531600	-2.76939400	-0.00034300
C	0.08199800	1.67777100	0.00075700
H	2.67584000	2.06882000	-0.00079100
H	4.52681700	0.39512500	-0.00217100
C	-1.32352100	1.28832900	-0.00086300
C	-1.80307000	0.02373300	-0.00009300
O	0.39648900	2.86504000	0.00158800
S	-3.53259500	-0.39438700	-0.00229100
S	-0.81184400	-1.42091600	0.00277200
H	-2.01550900	2.12363600	-0.00285300
H	-3.97218400	0.87973400	0.00702300

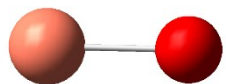
3



0 1

C	-2.30074600	-0.35225600	-0.01357300
H	-2.31642800	-0.93525400	-0.93697600
H	-2.31098500	-1.04377800	0.83166600
H	-3.20730600	0.25752600	0.02698100
C	-1.07472600	0.53736700	0.03729100
H	-1.05732300	1.12619700	0.96312200
H	-1.06175100	1.23349300	-0.81113200
O	0.08792800	-0.29833800	-0.01623300
C	1.28442300	0.34752300	-0.02582300
H	1.22806400	1.43348400	-0.07796400
C	2.44948600	-0.29535100	0.01476600
H	3.37234500	0.26701700	-0.00922100
H	2.49934200	-1.37567500	0.06742500

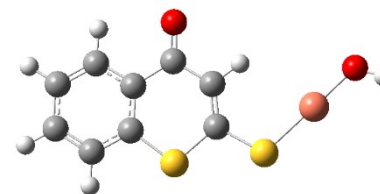
CuO



0 2

Cu	0.00000000	0.00000000	0.38212000
O	0.00000000	0.00000000	-1.38518600

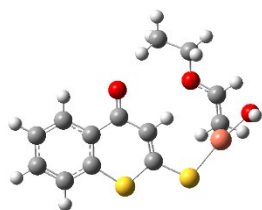
INT I



0 2

C	-4.82043000	-0.58756300	-0.01288900
C	-3.64547700	-1.32050000	-0.01046800
C	-2.40682700	-0.65929200	-0.00302700
C	-2.35124700	0.74425100	0.00190600
C	-3.55944700	1.46332700	-0.00067800
C	-4.77986400	0.81279300	-0.00796700
H	-5.77254500	-1.10570100	-0.01861800
H	-3.67871600	-2.40437800	-0.01429500
C	-1.08052500	1.51702200	0.00983100
H	-3.49381300	2.54428900	0.00324000
H	-5.70119600	1.38300900	-0.00988200
C	0.18959900	0.79059900	0.01272000
C	0.34845500	-0.56036300	0.00883600
O	-1.08028300	2.74460900	0.01415000
S	1.90118600	-1.40052400	0.01473800
Cu	3.46392500	0.05050900	-0.00222900
O	4.75157600	1.27889100	-0.02653800
S	-0.98128000	-1.70556700	-0.00079400
H	5.67243500	0.99598500	-0.02857600
H	1.06573800	1.42984300	0.01917500

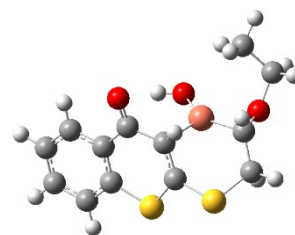
INT II



0 2			
C	-5.44759600	-0.04856200	-0.49867300
C	-4.43925000	-0.98599800	-0.64735800
C	-3.13375200	-0.68807300	-0.22330400
C	-2.84329600	0.56133100	0.35041400
C	-3.88595300	1.49417500	0.49003800
C	-5.17197100	1.19992100	0.07421500
H	-6.45260800	-0.28830700	-0.82696800
H	-4.65402700	-1.95258100	-1.08973700
C	-1.48839000	0.94768400	0.82764900
H	-3.63988000	2.44967900	0.93647500
H	-5.96355100	1.93071800	0.19125300
C	-0.42080600	-0.03882800	0.78439800
C	-0.47547200	-1.27891100	0.22851000
O	-1.27084000	2.08044700	1.26512100
S	0.87697600	-2.40998600	0.13096100
C	3.17928400	0.99613900	-1.05704800
C	3.02533400	-0.21090400	-1.68140800
H	3.91053300	-0.81505600	-1.83924100
H	2.14301200	-0.41467800	-2.27473600
Cu	2.66878000	-1.14953000	0.32007800
O	4.16896000	-0.44334900	1.12917400
H	4.09292800	1.22386700	-0.51397900
S	-1.92678000	-1.95109700	-0.49156000
O	2.22291500	1.90633400	-1.04772500
C	2.43995200	3.07885100	-0.20256300
H	2.57135400	2.73108400	0.82509700

H	3.36264700	3.56317500	-0.53628300
C	1.23964500	3.98726600	-0.33822400
H	1.09473900	4.28688200	-1.37869400
H	0.33697800	3.49703200	0.03039100
H	1.40573900	4.88867000	0.25800800
H	4.25212600	-0.70503100	2.05217200
H	0.50761000	0.28621900	1.24112500

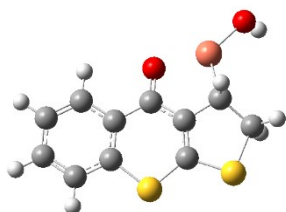
INT III



0 2			
C	4.85313300	-0.34404200	-0.84832000
C	3.91060100	0.67480300	-0.91715600
C	2.68676400	0.52203700	-0.25716500
C	2.39479800	-0.64227600	0.47624000
C	3.36886600	-1.64698700	0.53964600
C	4.58203400	-1.50555600	-0.12117200
H	5.80064700	-0.22891900	-1.36053600
H	4.12547700	1.57895000	-1.47556400
C	1.13146400	-0.83872900	1.23507500
H	3.14493700	-2.53414900	1.11911500
H	5.31989900	-2.29678500	-0.07006800
C	0.03624900	0.18035500	1.09974100
C	0.20328200	1.43126500	0.47474200
O	0.96600100	-1.77413100	1.99115800
S	-0.97042300	2.77138600	0.66863800
C	-2.72185600	0.61975100	0.21439800
C	-2.44630700	2.04406300	-0.16683900

H	-3.28459600	2.68549500	0.13080600
H	-2.32056400	2.13397800	-1.24743500
Cu	-1.22748700	-0.53695100	-0.35775800
O	-0.63054400	-1.86703000	-1.42016500
H	-3.04342000	0.39208000	1.22981800
S	1.56696800	1.88995500	-0.42587100
O	-3.25704700	-0.12147900	-0.78043800
C	-4.25531400	-1.20772800	-0.49471500
H	-5.08988600	-0.70370400	-0.00481600
H	-4.54426000	-1.50958000	-1.49826600
C	-3.68126400	-2.35180600	0.30804100
H	-2.82262200	-2.79715500	-0.20068500
H	-3.40280400	-2.05882600	1.32375000
H	-4.45477900	-3.11971600	0.39867000
H	0.25841000	-2.22685900	-1.38762400
H	-0.63601900	0.16552500	1.95401000

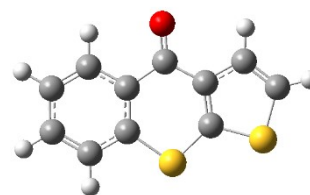
INT IV



0 2			
C	4.48587200	-1.15821800	-0.07742000
C	3.92822100	0.10831400	-0.13012900
C	2.53596300	0.26721900	-0.05699600
C	1.69964900	-0.86345600	0.06839900
C	2.29454700	-2.13978600	0.11061300
C	3.66646900	-2.28923200	0.04210300
H	5.56272900	-1.26901900	-0.13012100
H	4.56527400	0.98028600	-0.22772100

C	0.24436100	-0.74994900	0.15654100
H	1.63784500	-2.99573300	0.20181400
H	4.10836700	-3.27765000	0.08100500
C	0.24682200	1.72703500	0.04686700
O	-0.49992700	-1.77863700	0.15486400
S	-0.84084100	3.10437900	0.04148300
C	-1.84144700	0.59958000	0.50970300
C	-2.33102900	1.91177400	-0.05171400
H	-3.14833800	2.36268500	0.50809900
H	-2.58678500	1.87606000	-1.11091400
Cu	-2.45291700	-1.26582200	-0.03640400
O	-4.17636800	-1.73984400	-0.31722700
H	-2.03491700	0.52510800	1.58829400
S	1.94704100	1.93044400	-0.20096700
C	-0.37939100	0.52307400	0.24334600
H	-4.55864900	-1.52034200	-1.17196900

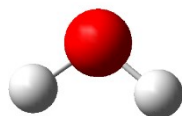
3a



0 1			
C	-3.75741400	-0.80137800	-0.00012600
C	-2.55314100	-1.48441100	0.00008000
C	-1.34051500	-0.77615600	0.00011800
C	-1.33879500	0.63086900	0.00001400
C	-2.57887700	1.29598000	-0.00017400
C	-3.77298900	0.59898900	-0.00027900
H	-4.68715400	-1.35877800	-0.00014600
H	-2.54246200	-2.56887300	0.00024100
C	-0.10992100	1.47741400	0.00017600

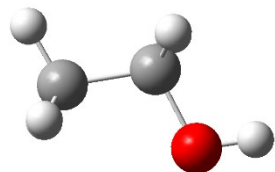
H	-2.55673300	2.37870500	-0.00020900
H	-4.71582700	1.13296400	-0.00048700
C	1.36038200	-0.56863100	0.00003400
O	-0.18584100	2.70150800	0.00035300
S	3.04393200	-1.01419400	-0.00011500
C	2.44497000	1.49998800	-0.00010000
C	3.51586500	0.66967100	-0.00018700
H	4.56626500	0.91687400	-0.00028500
H	2.50141500	2.57932000	-0.00014000
S	0.11618300	-1.78317100	0.00015500
C	1.19033100	0.80192200	0.00003800

H₂O



0 1			
O	0.00000000	0.00000000	0.11702500
H	0.00000000	-0.76350200	-0.46810100
H	0.00000000	0.76350200	-0.46810100

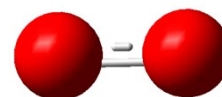
EtOH



0 1			
C	1.17761300	-0.40046800	0.00000000
H	1.15176400	-1.03993800	0.88567700
H	1.15176400	-1.03993800	-0.88567700
H	2.12018400	0.15445000	0.00000000
C	0.00000000	0.55575100	0.00000000

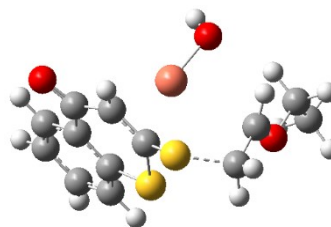
H	0.03688200	1.20197800	-0.88776800
H	0.03688200	1.20197800	0.88776800
O	-1.20072100	-0.22264800	0.00000000
H	-1.95738800	0.37095300	0.00000000

O₂



0 1			
O	0.00000000	0.00000000	0.60272000
O	0.00000000	0.00000000	-0.60272000

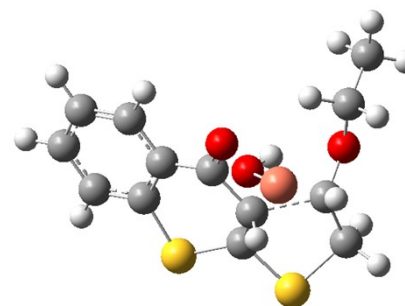
TS I



0 2			
C	-3.69819300	2.35788400	-0.82196900
C	-2.49986300	1.88349000	-1.33187400
C	-1.97248800	0.66853500	-0.86947100
C	-2.65120200	-0.06824800	0.11737800
C	-3.86396800	0.43553700	0.61672100
C	-4.38592200	1.63225700	0.15766600
H	-4.09738500	3.29787600	-1.18539700
H	-1.96730800	2.44893200	-2.08834000

C	-2.15691900	-1.36021600	0.66855900
H	-4.37161500	-0.14845000	1.37446700
H	-5.32041800	2.00768100	0.55719300
C	-0.79000900	-1.80848700	0.31606700
C	0.00743200	-1.25811400	-0.68343400
O	-2.84504300	-2.04406700	1.41182800
S	1.33531100	-2.24472400	-1.35568300
C	3.09249500	-0.22229100	-0.38852700
C	2.74555700	-0.99122000	-1.58933100
H	3.53657100	-1.67315300	-1.91851100
H	2.49433400	-0.32767700	-2.41590500
Cu	0.61394000	-0.58216500	1.20955000
O	1.49158300	0.25584400	2.56641100
H	3.58439600	-0.65632600	0.47434400
S	-0.47996500	0.13054300	-1.65864400
O	3.04908100	1.12161000	-0.50515800
C	3.51365200	1.87043400	0.64886800
H	2.97352600	1.50533000	1.52784100
H	4.58588400	1.67238200	0.76535800
C	3.25273800	3.33873300	0.38713100
H	3.76394400	3.67999200	-0.51660900
H	2.18261600	3.52745400	0.27572400
H	3.61656700	3.92990000	1.23187700
H	0.93226100	0.69656200	3.21207300
H	-0.52799300	-2.78768200	0.70679300

TS II



0.2			
C	4.45174900	-0.58729400	-0.68314500
C	3.65307600	0.52371900	-0.45802500
C	2.40068000	0.37899000	0.15144100
C	1.94864700	-0.89719600	0.54496300
C	2.78320400	-2.00408400	0.31091800
C	4.01787900	-1.85985700	-0.29735900
H	5.41136500	-0.46237000	-1.17209600
H	3.98638200	1.50613000	-0.77285300
C	0.66756100	-1.13820600	1.26079900
H	2.42266700	-2.97515500	0.62728400
H	4.64290400	-2.72691400	-0.47576100
C	-0.34628800	-0.02262000	1.41286200
C	-0.10648800	1.28072100	0.71923300
O	0.42375900	-2.21266500	1.79026200
S	-1.37956500	2.47858800	0.95059600
C	-2.18644800	-0.22989200	0.89558400
C	-2.70318800	1.16686300	0.72096800