Supplementary Material

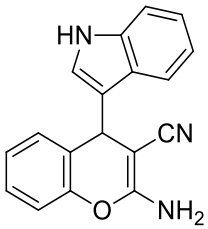
Sodium dodecyl sulfate catalyzed one-pot three-component synthesis of structurally diverse 2-amino-3-cyano-4-substitued-4*H*-chromenes in aqueous medium at room temperature

Bubun Banerjee,[a,b]* Anu Priya,[a] Aditi Sharma,[a] Arvind Singh,[a] and Manmeet Kaur[a]

[a]Department of Chemistry, Akal University, Talwandi Sabo, Bathinda, Punjab 151302, India
[b]Visiting Researcher, Eternal University, Baru Sahib, Himachal Pradesh 173101, India
Email: banerjeebubun@gmail.com

Table of Contents

Characterization data with scanned spectra of all the synthesized compounds:



4a

2-Amino-4-(1H-indol-3-yl)-4H-chromene-3-carbonitrile (**4a**). Yellow solid, yield 94%; mp 166–168 °C; 1H NMR (500 MHz, DMSO-*d*6): δ_H/ppm 10.84 (s, 1H, -NH), 7.29 (d, J 8.5 Hz, 1H, aromatic H), 7.23 (d, J 1 Hz, 1H, aromatic H), 7.20 (d, J 7.5 Hz, 1H, aromatic H), 7.15 (t, J 11 Hz, 1H, aromatic H), 7.04 (d, J 7.5 Hz, 1H, aromatic H), 6.99 (t, J 12 Hz, 2H, aromatic H), 6.95 (t, J 11.25 Hz, 1H, aromatic H), 6.82 (t, J 11.25 Hz, 1H, aromatic H), 6.70 (s, 2H, -NH_2), 4.95 (s, 1H, -CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 160.6, 148.9, 137.5, 129.8, 128.3, 125.8, 124.9 (2C), 124.3, 123.6, 121.5, 121.3, 119.2, 119.0, 116.3, 112.3, 56.9, 32.9; HRMS (ESI-TOF) *m/z*: For $C_{18}H_{13}N_3O$ Calcd. $[M+Na]^+$ 310.0956; Found $[M+Na]^+$ 310.0869.

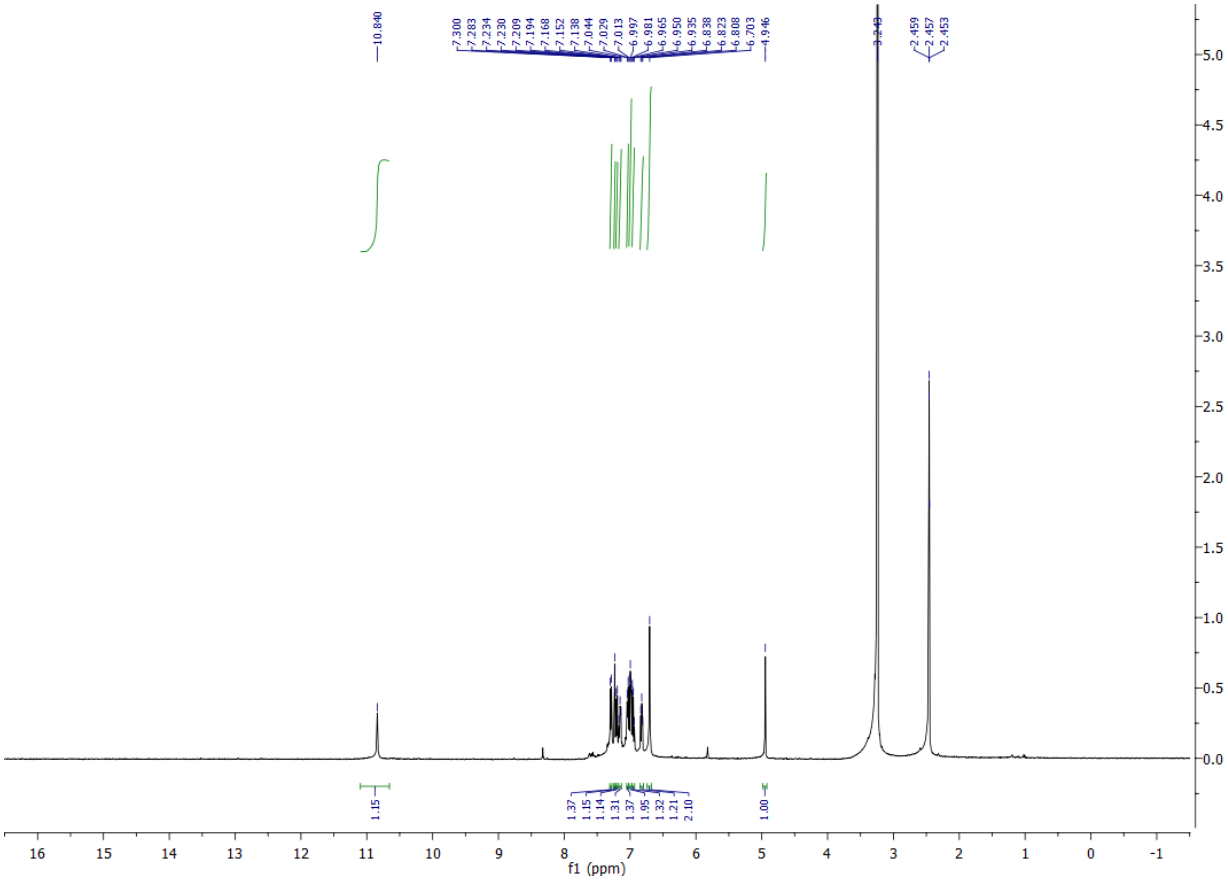


Figure S1. ^{1}H NMR spectrum of **4a**

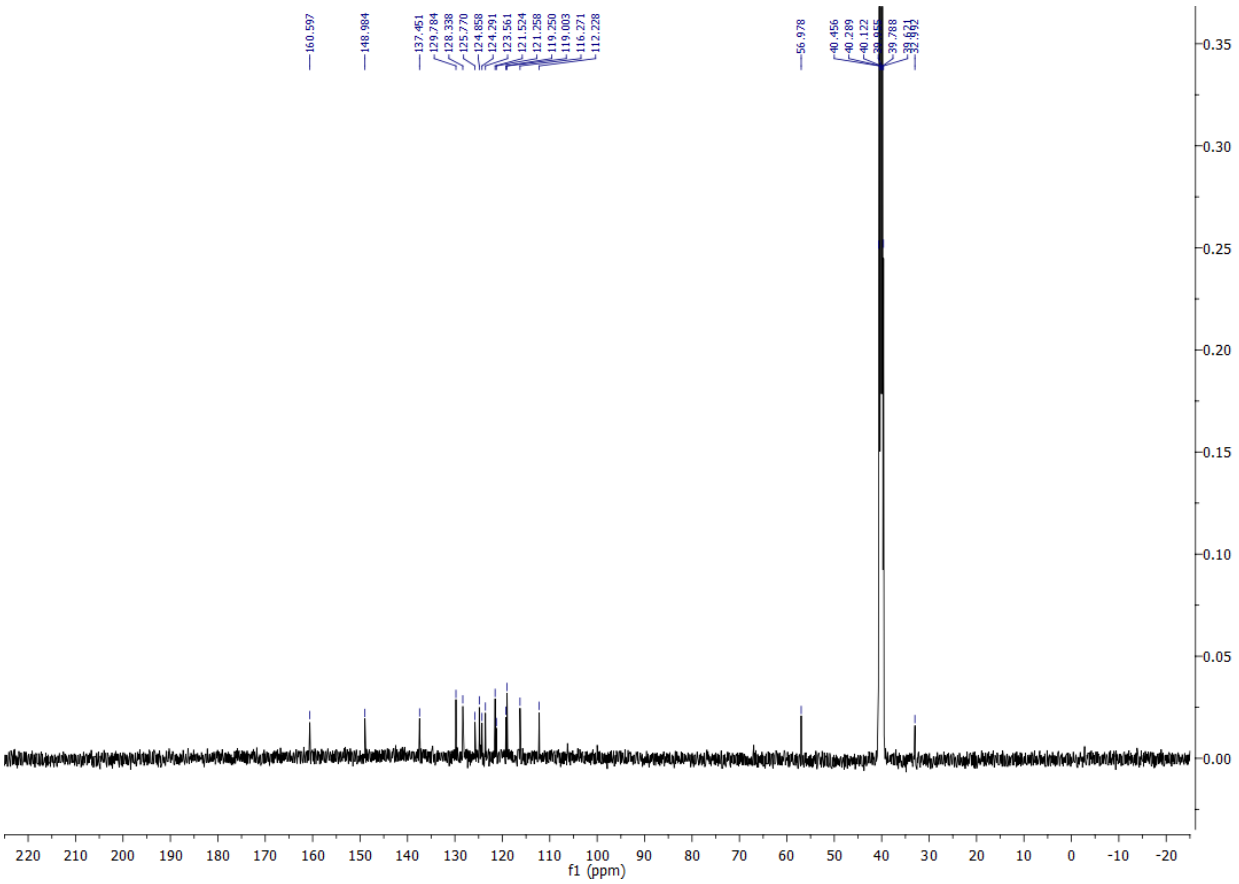


Figure S2. ^{13}C NMR spectrum of **4a**

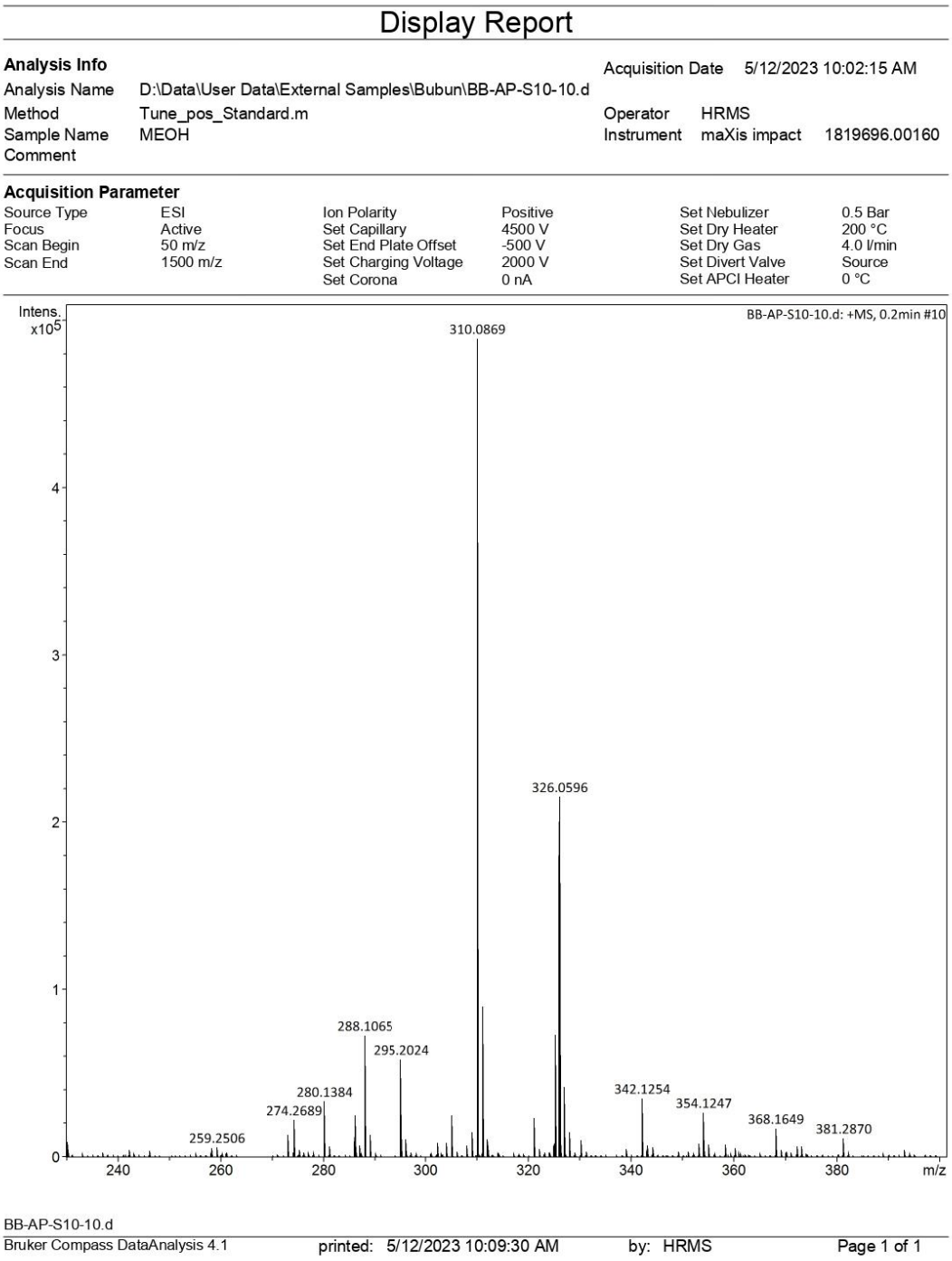
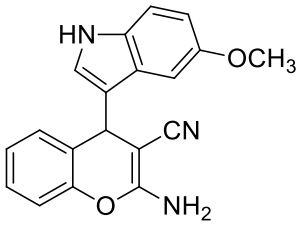


Figure S3. HRMS spectrum of **4a**



4b

2-Amino-4-(5-methoxy-1H-indol-3-yl)-4H-chromene-3-carbonitrile (**4b**). Off white solid, yield 98%; mp 185–187 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H/ppm 7.93 (s, 1H, -NH), 7.22 (d, J 9 Hz, 1H, aromatic H), 7.18 (t, J 11.25 Hz, 1H, aromatic H), 7.11 (t, J 4.25 Hz, 2H, aromatic H) 7.03-6.98 (m, 2H, aromatic H), 6.80 (dd, J 8.75 Hz, 2.5 Hz, 1H, aromatic H), 6.77 (d, J 2 Hz, 1H, aromatic H), 5.02 (s, 1H, -CH), 4.56 (s, 2H, -NH_2), 3.73 (s, 3H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C/ppm 170.4, 164.1, 158.3, 153.9, 152.1, 148.8, 132.1, 129.6, 128.1, 125.1, 123.2, 122.9, 116.1, 112.1, 112.0, 101.4, 61.5, 55.8, 32.7; HRMS (ESI-TOF) *m/z*: For $C_{19}H_{15}N_3O_2$ Calcd. $[M+Na]^+$ 340.1062; Found $[M+Na]^+$ 340.0804.

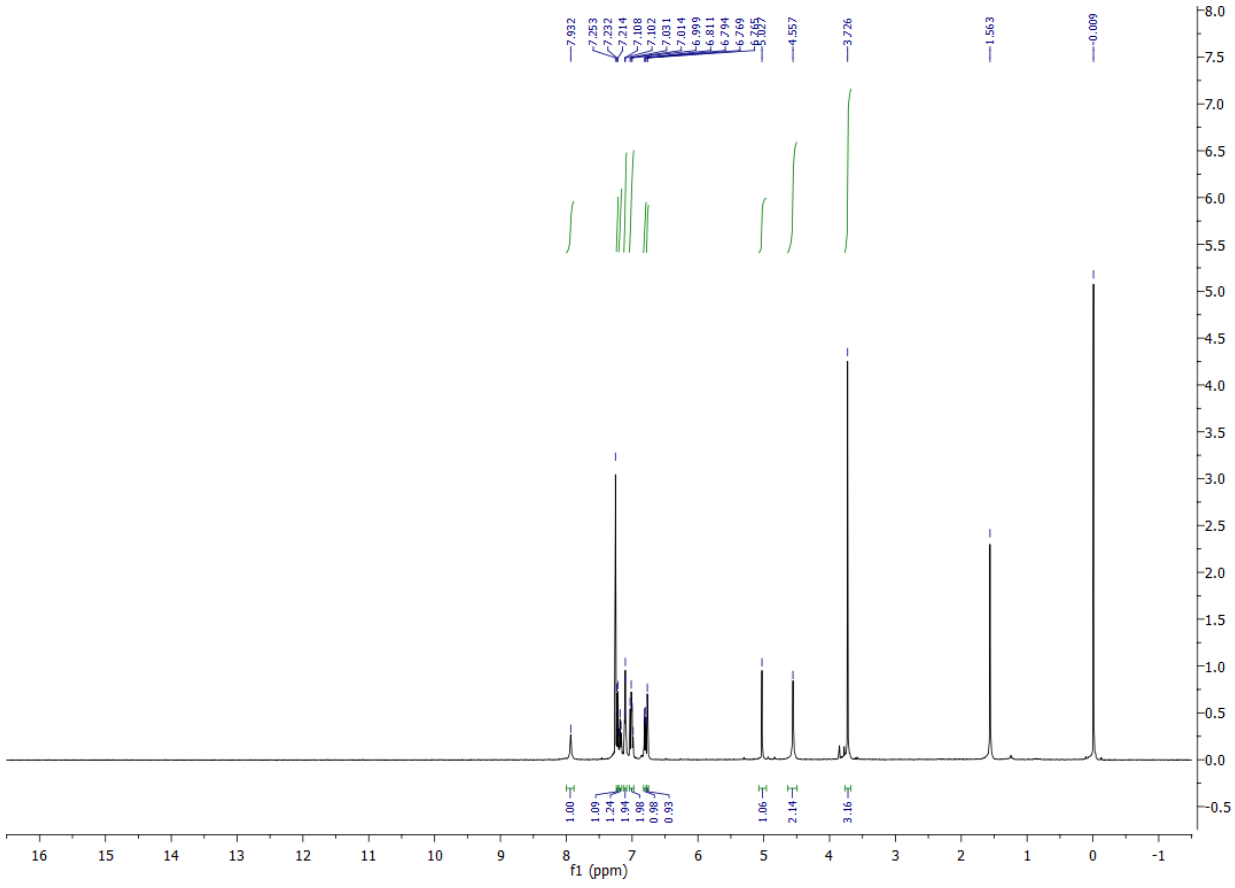


Figure S4. ^{1}H NMR spectrum of **4b**

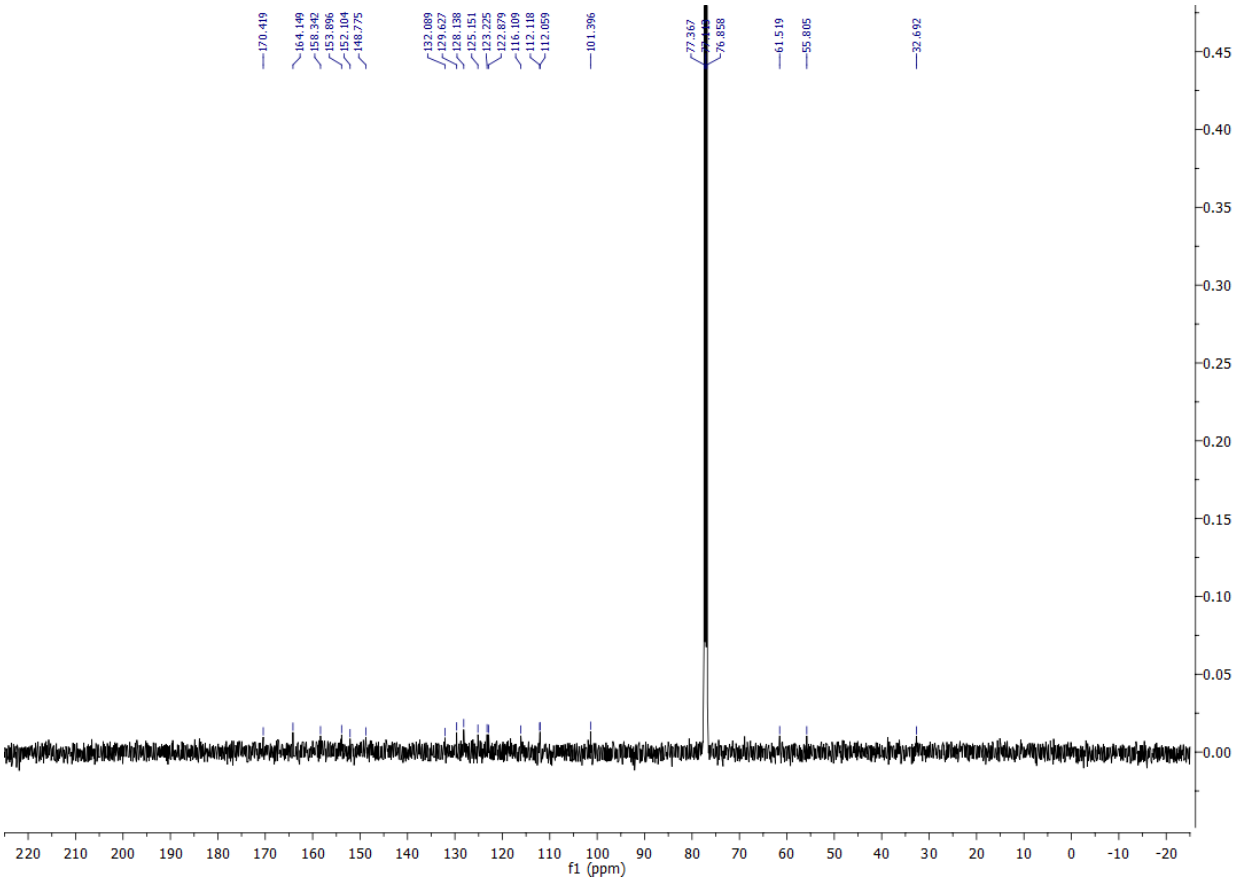


Figure S5. ^{13}C NMR spectrum of **4b**

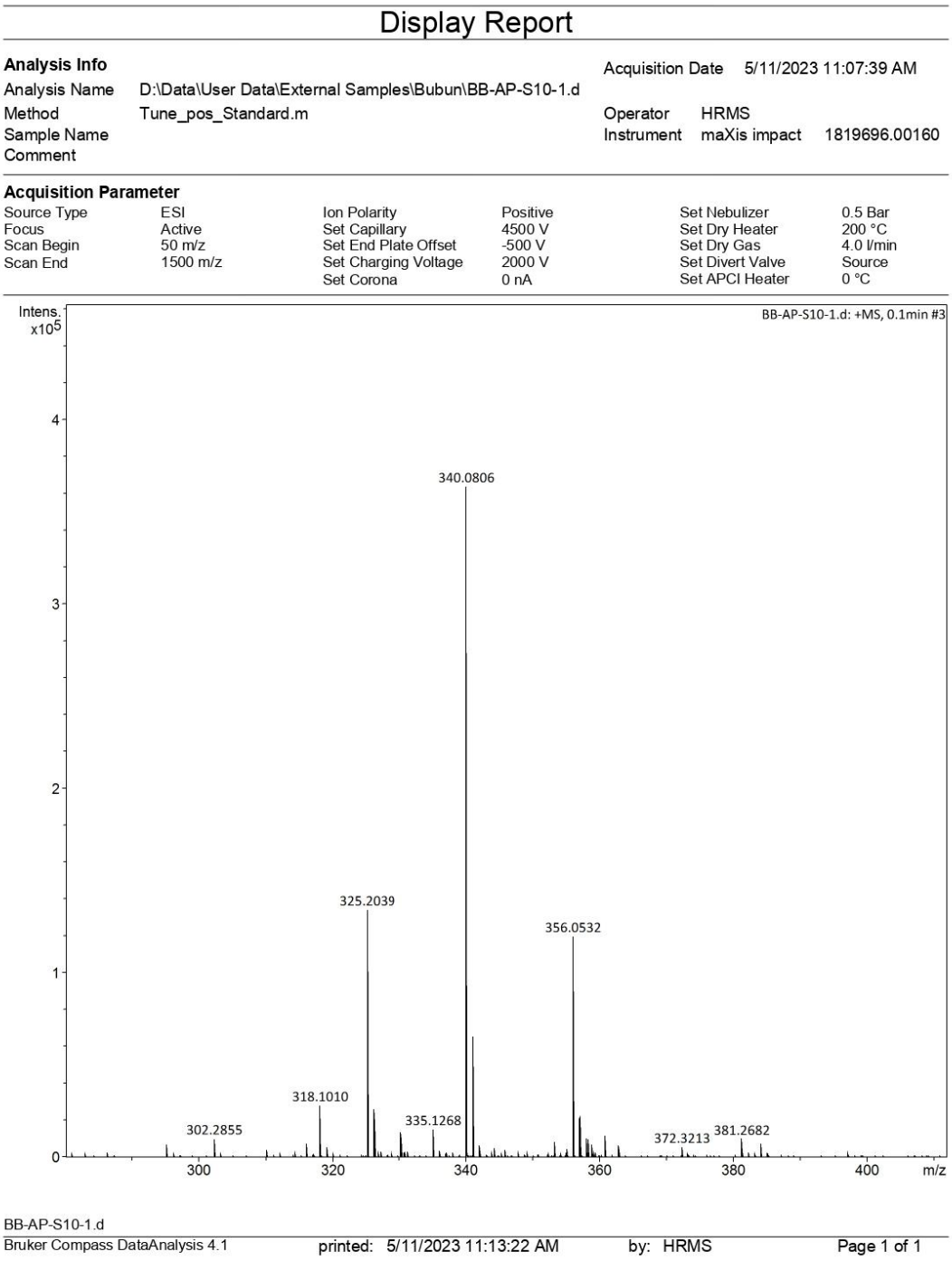
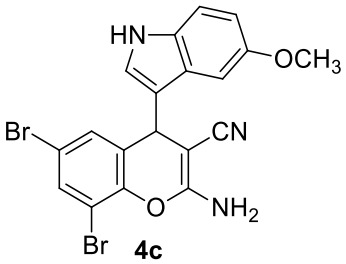


Figure S6. HRMS spectrum of **4b**



4c

2-Amino-6,8-dibromo-4-(5-methoxy-1H-indol-3-yl)-4H-chromene-3-carbonitrile (**4c**). Yellow solid, yield 91%; mp 213-215 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H/ppm 10.82 (d, J 2.5 Hz, 1H, -NH) 7.71 (d, J 2.5 Hz, 1H, aromatic H), 7.27 (d, J 3 Hz, 1H, aromatic H), 7.22 (t, J 6 Hz, 2H, aromatic H), 7.03 (s, 2H, -NH_2), 6.72 (d, J 2 Hz, 1H, aromatic H), 6.70-6.68 (m, 1H, aromatic H), 5.00 (s, 1H, -CH), 3.64 (s, 3H, -OCH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 160.2, 153.5, 145.4, 133.6, 132.5, 131.6, 128.4, 124.4, 120.6, 118.3, 116.5, 113.1, 111.3, 110.9, 100.9, 100.3, 56.8, 55.7, 33.3; HRMS (ESI-TOF) *m/z*: For $C_{19}H_{13}Br_2N_3O_2$ Calcd. $[M]^+$ 475.1334; Found $[M-H]^-$ 473.9489.

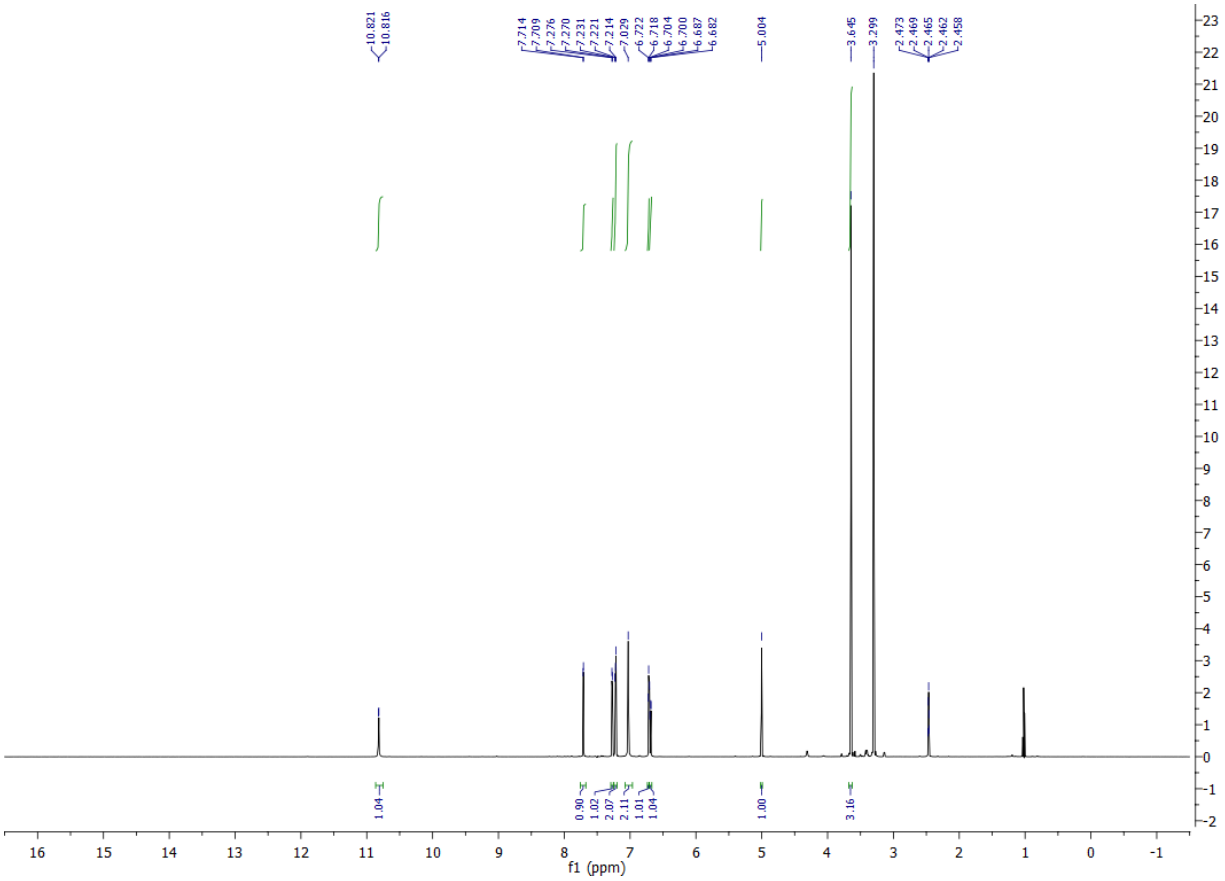


Figure S7. ^{1}H NMR spectrum of **4c**

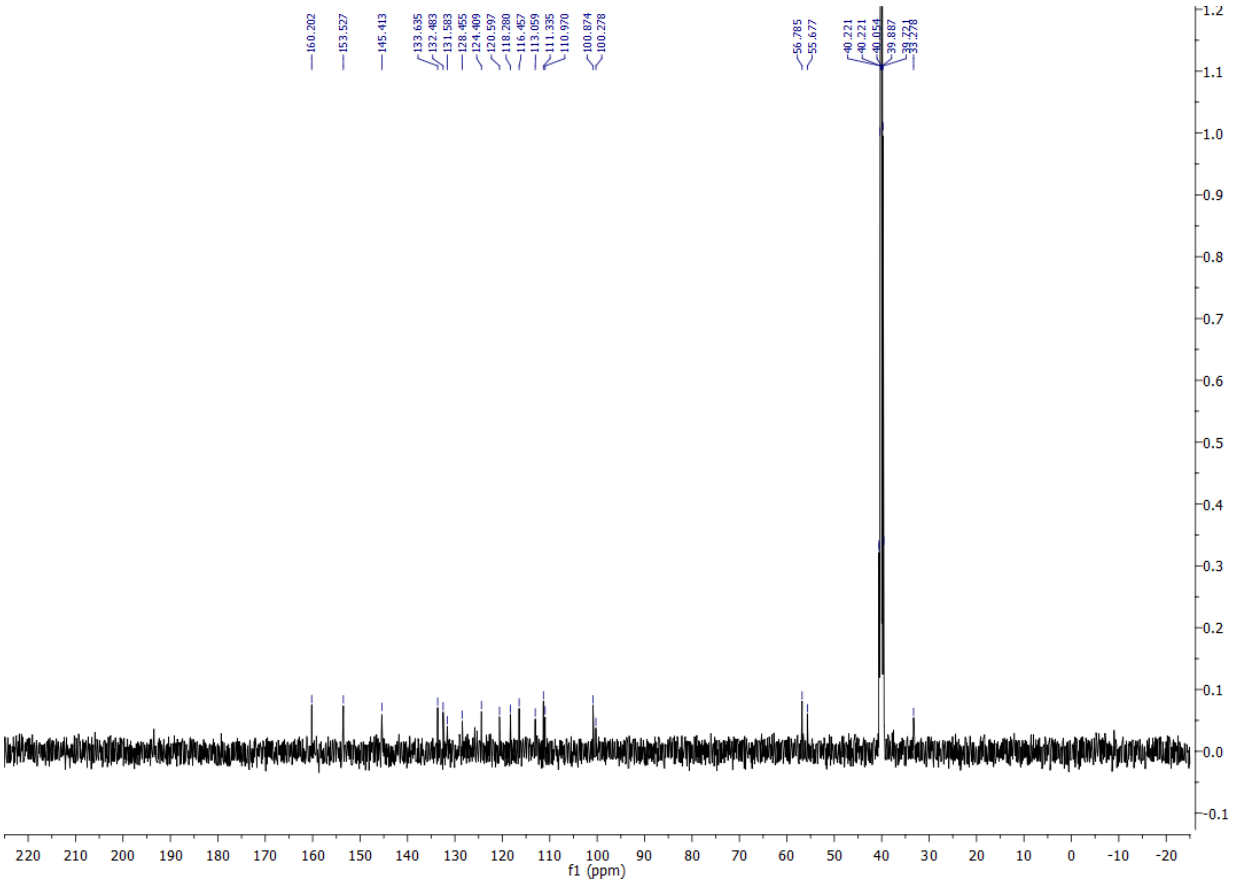


Figure S8. ^{13}C NMR spectrum of **4c**

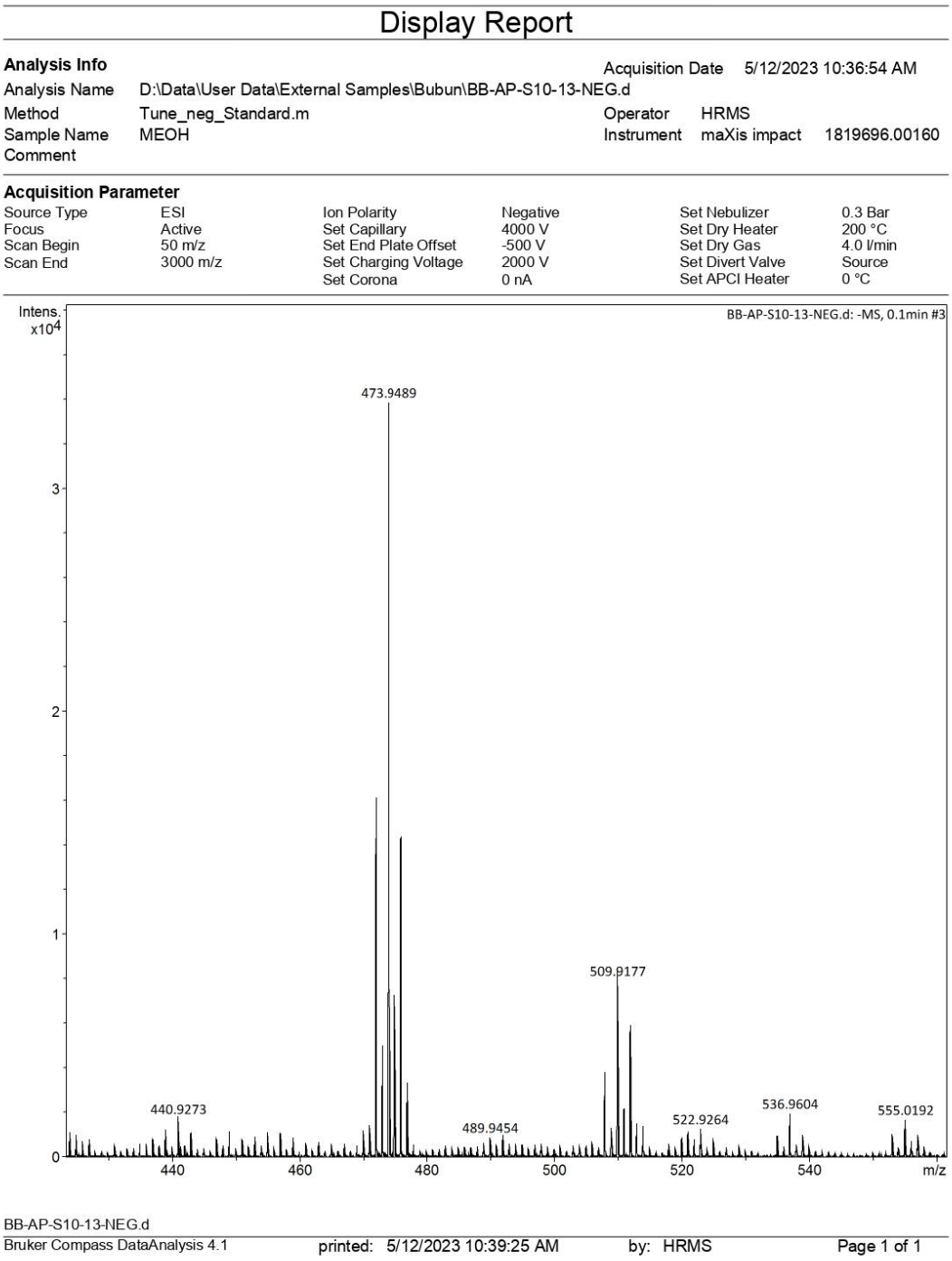
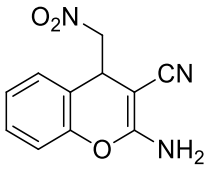


Figure S9. HRMS spectrum of **4c**



4d

2-Amino-4-(nitromethyl)-4H-chromene-3-carbonitrile (**4d**). Off white solid, yield 95%; mp 139–141°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H/ppm 7.32-7.29 (m, 1H, aromatic H), 7.18-7.13 (m, 2H, aromatic H), 7.03 (d, J 8.5 Hz, 1H, aromatic H), 4.85 (s, 2H, -NH_2), 4.61 (dd, J 12.25 Hz, 4.5 Hz, 1H, -CH_2), 4.49 (dd, J 12.5 Hz, 7.5 Hz, 1H, -CH_2), 4.36 (dd, J 7.25 Hz, 4.5 Hz, 1H, -CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C/ppm 161.8, 149.3, 129.7, 127.9, 125.8, 118. 8, 118.7, 116.9, 80.3, 54.2, 34.8; HRMS (ESI-TOF) *m/z*: For $C_{11}H_9N_3O_3$ Calcd. $[M+Na]^+$ 254.0542; Found $[M+Na]^+$ 254.0508.

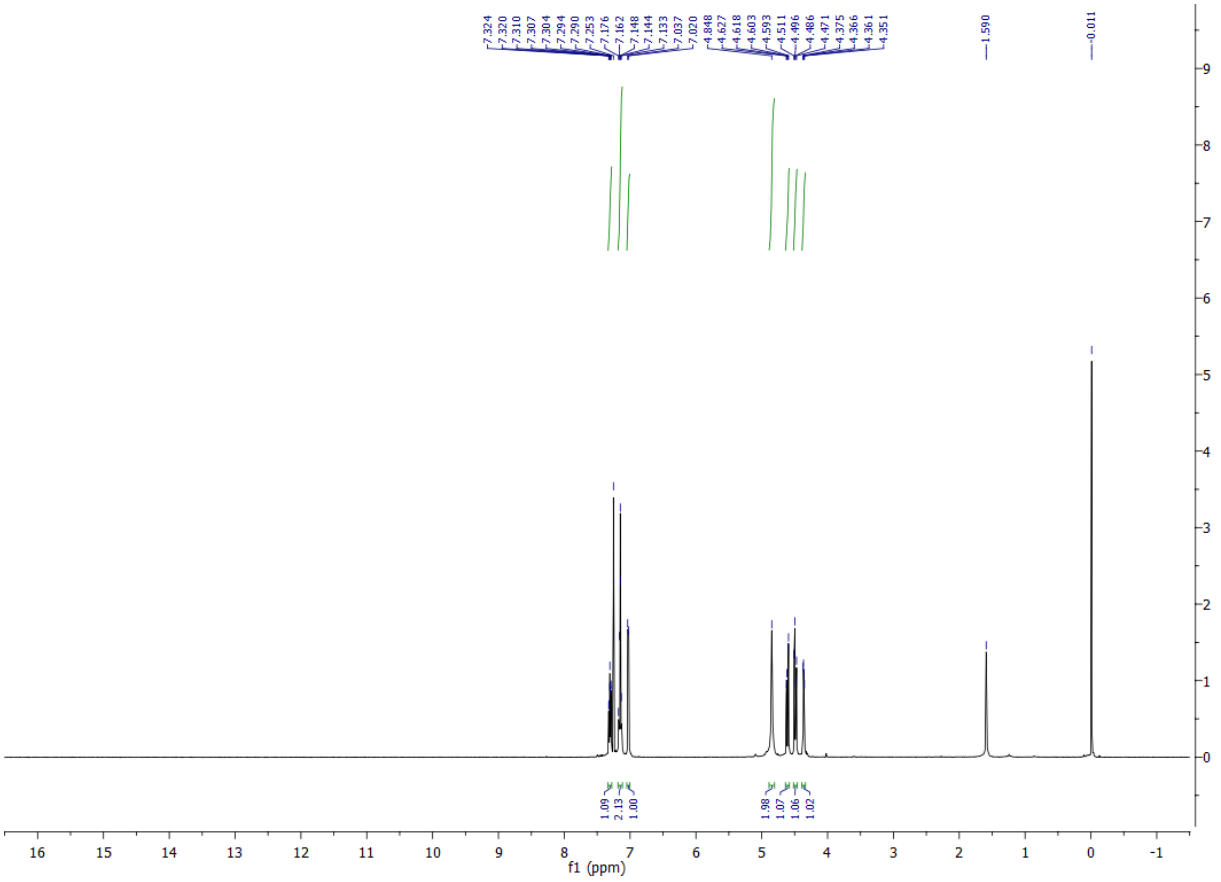


Figure S10. ^{1}H NMR spectrum of **4d**

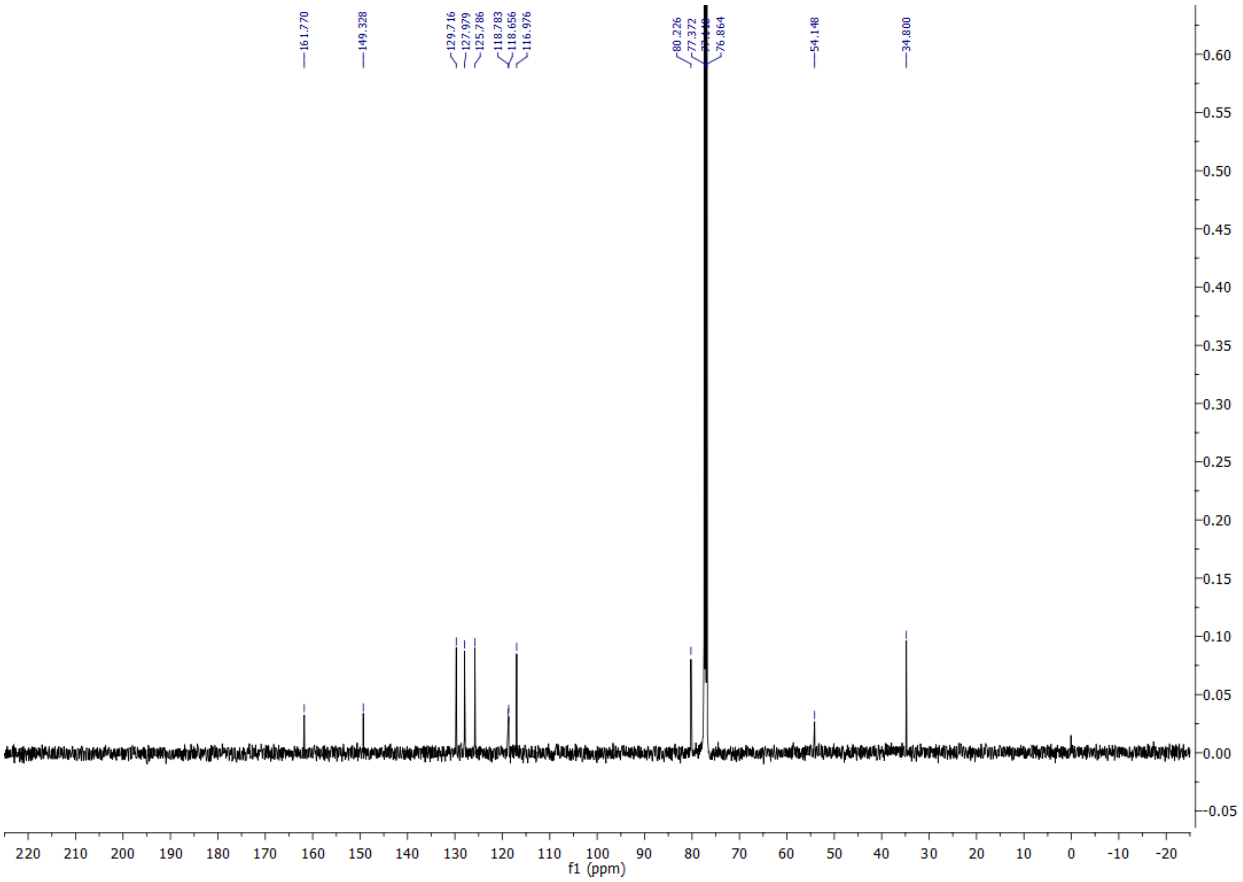


Figure S11. ^{13}C NMR spectrum of **4d**

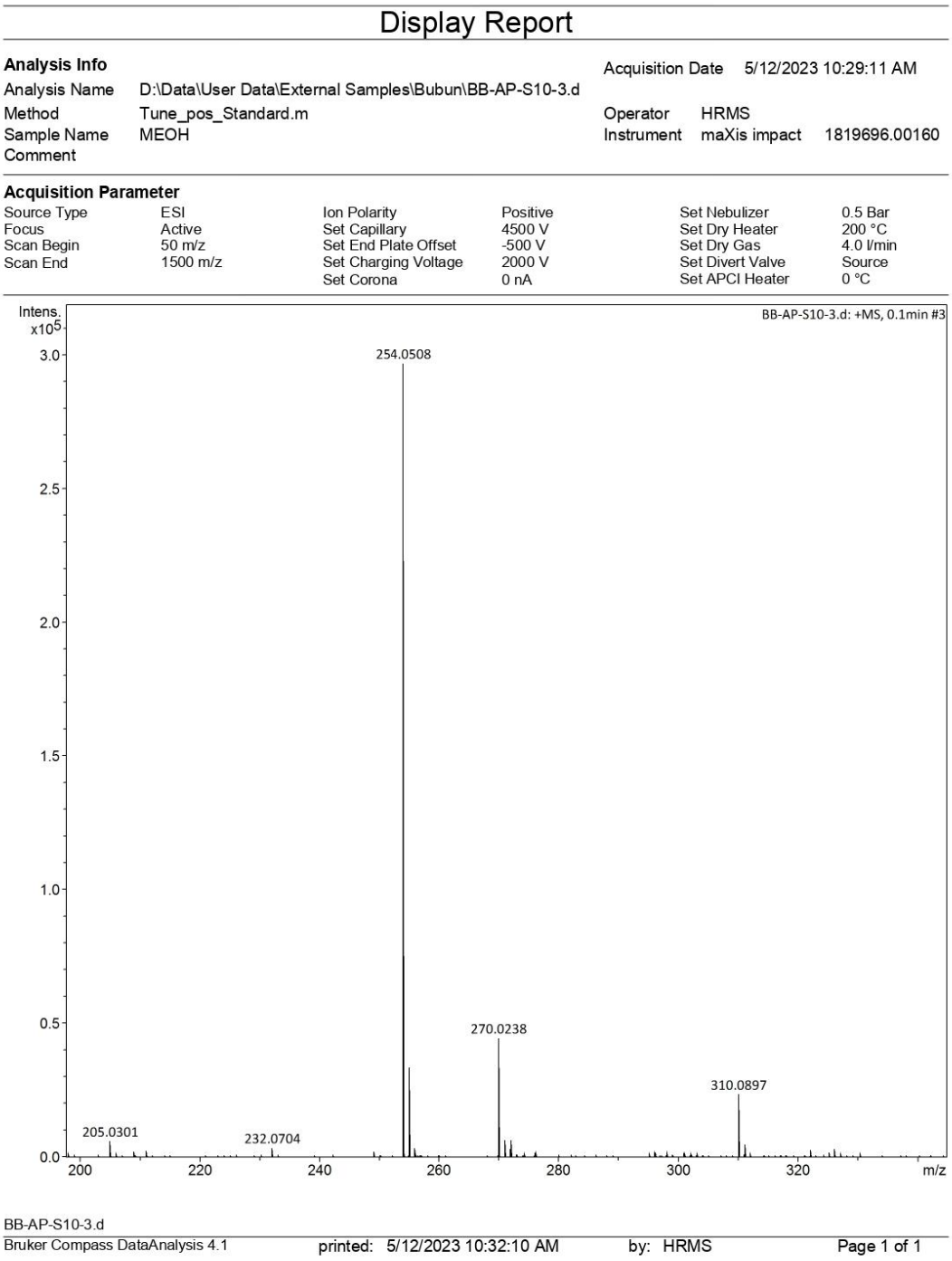
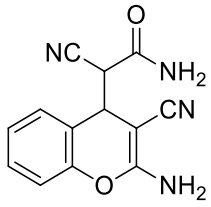


Figure S12. HRMS spectrum of **4d**



4e

*2-(2-Amino-3-cyano-4H-chromen-4-yl)-2-cyanoacetamide (***4e**). Off white solid, yield 92%; mp 168-169 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H/ppm 7.78 (s, 1H), 7.52 (s, 1H), 7.32 (t, J 11.25 Hz, 1H, aromatic H), 7.22 (d, J 7.5 Hz, 1H, aromatic H), 7.14 (s, 2H, -NH_2), 7.11 (d, J 7.5 Hz, 1H, aromatic H), 7.04 (d, J 8 Hz, 1H, aromatic H), 4.21 (d, J 5 Hz, 1H, -CH), 3.88 (d, J 5 Hz, 1H, -CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 179.2, 165.4, 163.6, 150.4, 129.8, 129.2, 124.9, 119.9, 117.3, 116.6, 51.9, 48.1, 37.3; HRMS (ESI-TOF) *m/z*: For $C_{13}H_{10}N_4O_2$ Calcd. $[M+Na]^+$ 277.0701; Found $[M+Na]^+$ 277.0937.

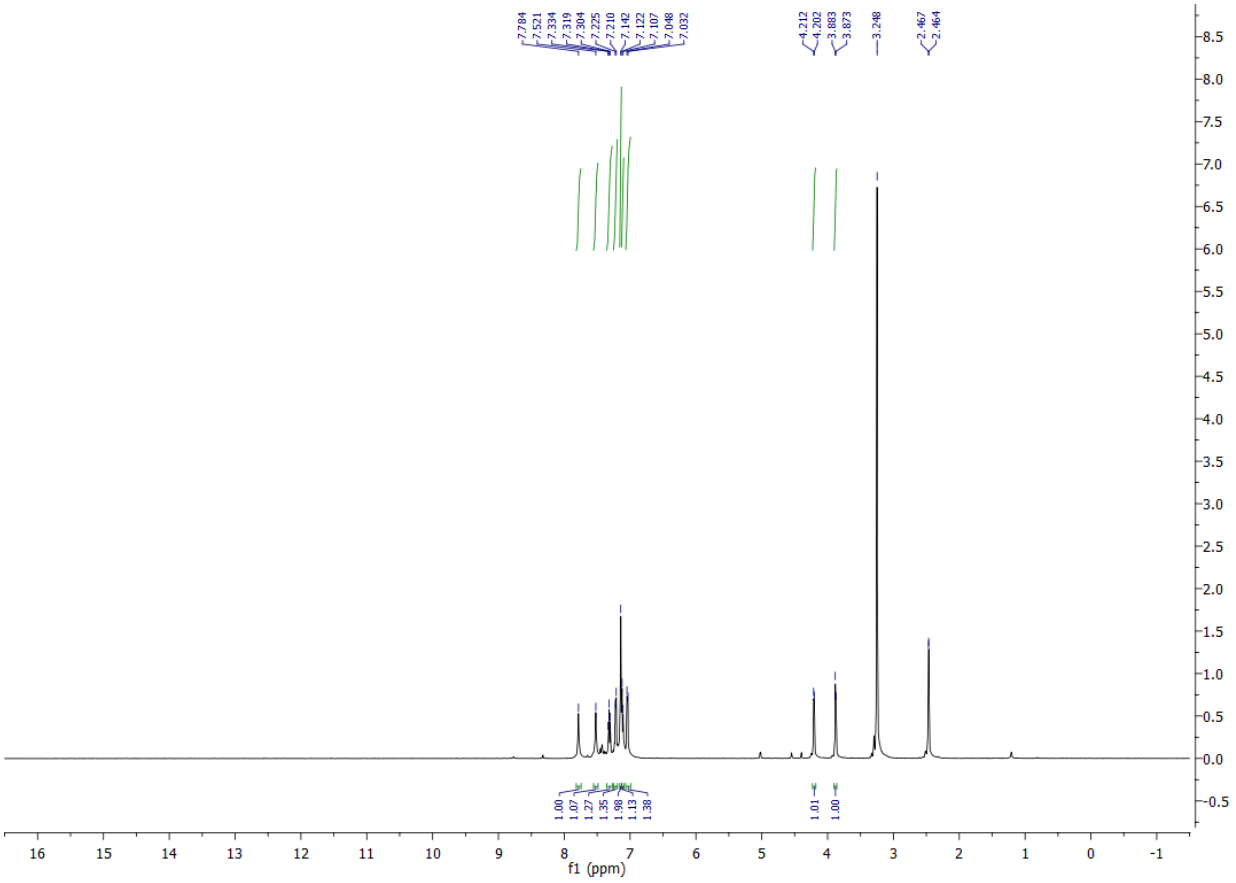


Figure S13. ^{1}H NMR spectrum of **4e**

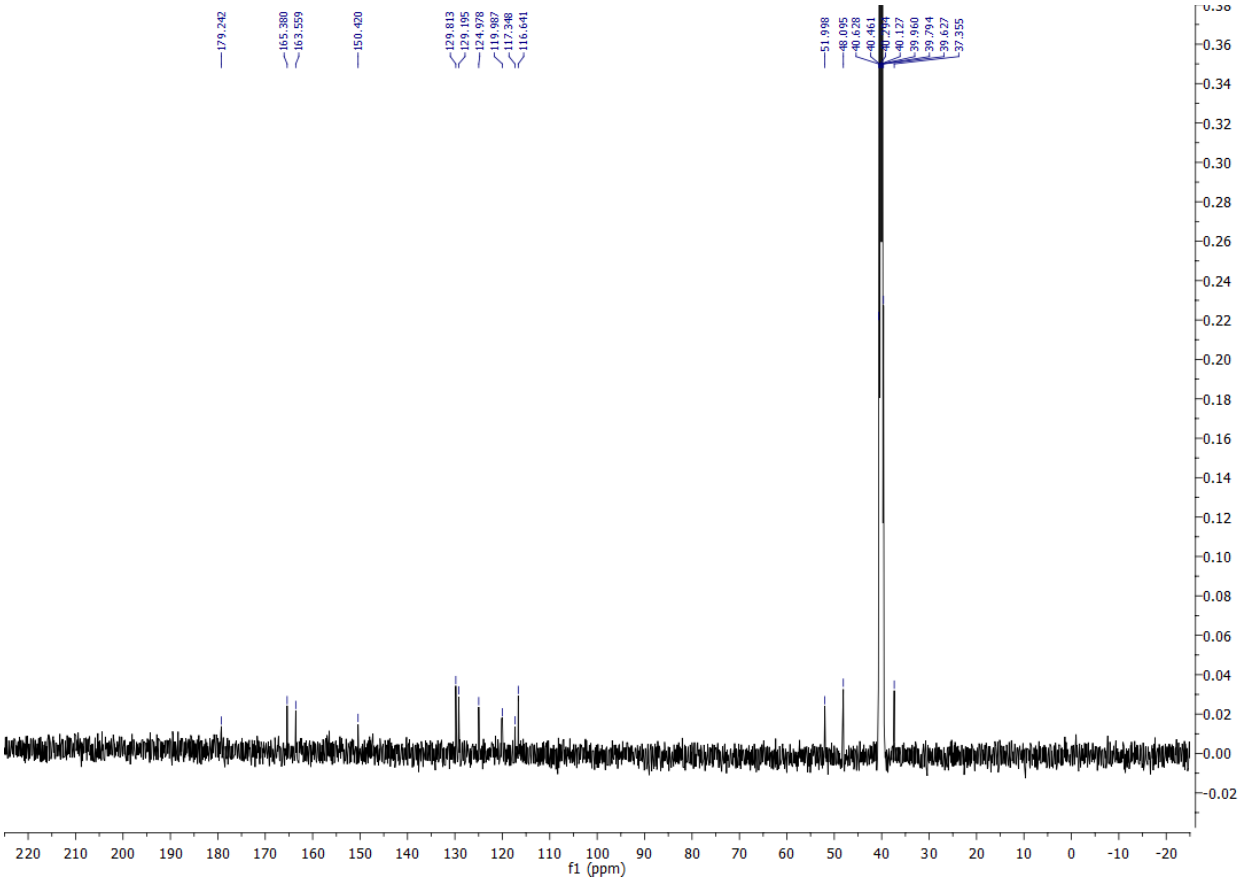


Figure S14. ^{13}C NMR spectrum of **4e**

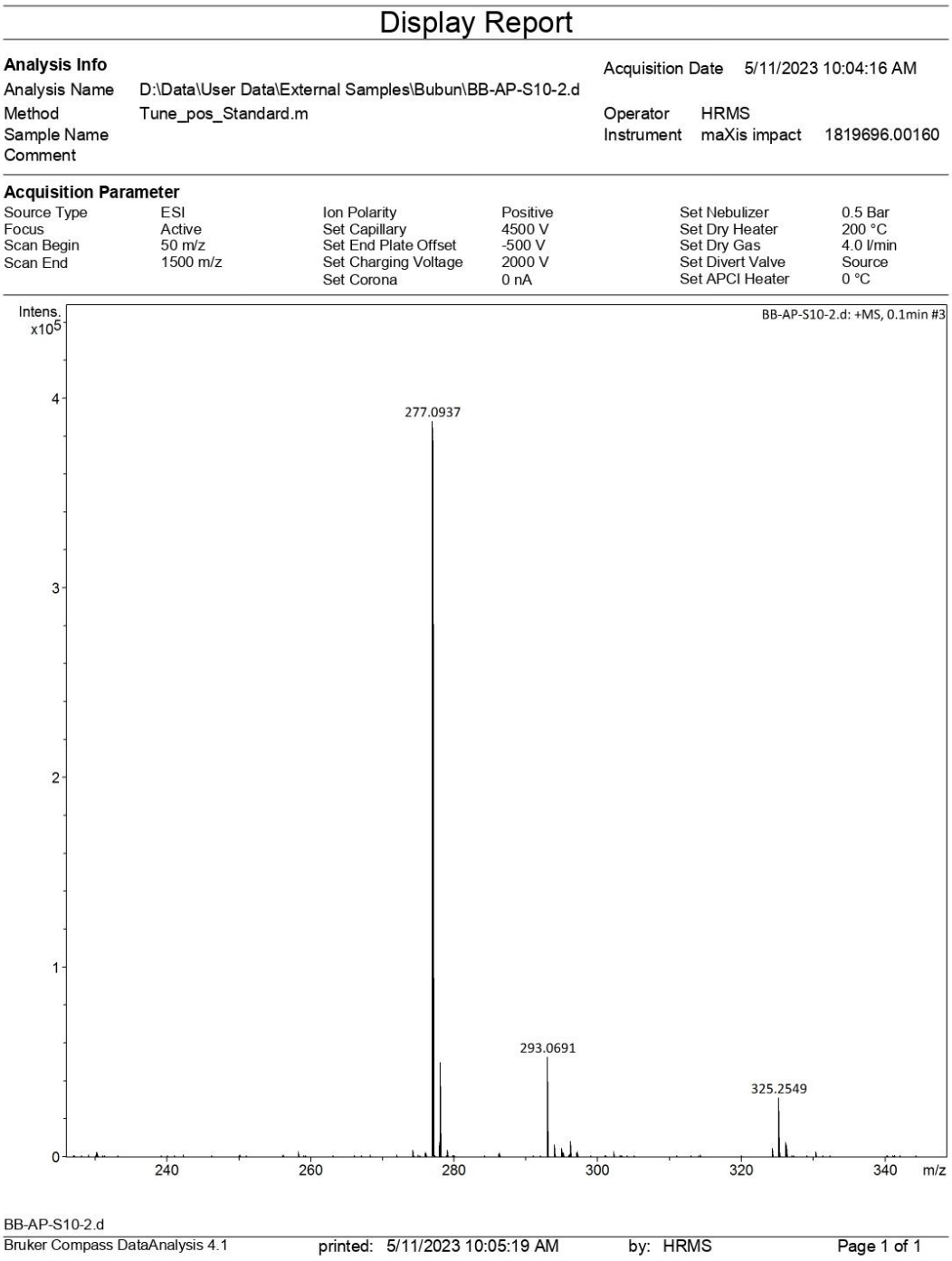
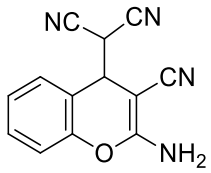


Figure S15. HRMS spectrum of **4e**



4f

2-(2-Amino-3-cyano-4H-chromen-4-yl)malononitrile (**4f**). White solid, yield 87%; mp 153-155 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H/ppm 7.53 (s, 2H, -NH_2), 7.48 (d, J 6 Hz, 1H, aromatic H), 7.43 (t, J 9.75 Hz, 1H, aromatic H), 7.28 (t, J 9. 5 Hz, 1H, aromatic H), 7.14 (d, J 7 Hz, 1H, aromatic H), 5.08 (d, J 2.5 Hz, 1H, -CH), 4.59 (d, J 2.5 Hz, 1H, -CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 163. 9, 150.2, 130.6, 129.3, 125.5, 119.8, 118.4, 116.8, 113.5, 113.4, 49.3, 37.6, 32.9; HRMS (ESI-TOF) m/z: For $C_{13}H_8N_4O$ Calcd. $[M+K]^+$ 275.0335; Found $[M+K]^+$ 275.0289.

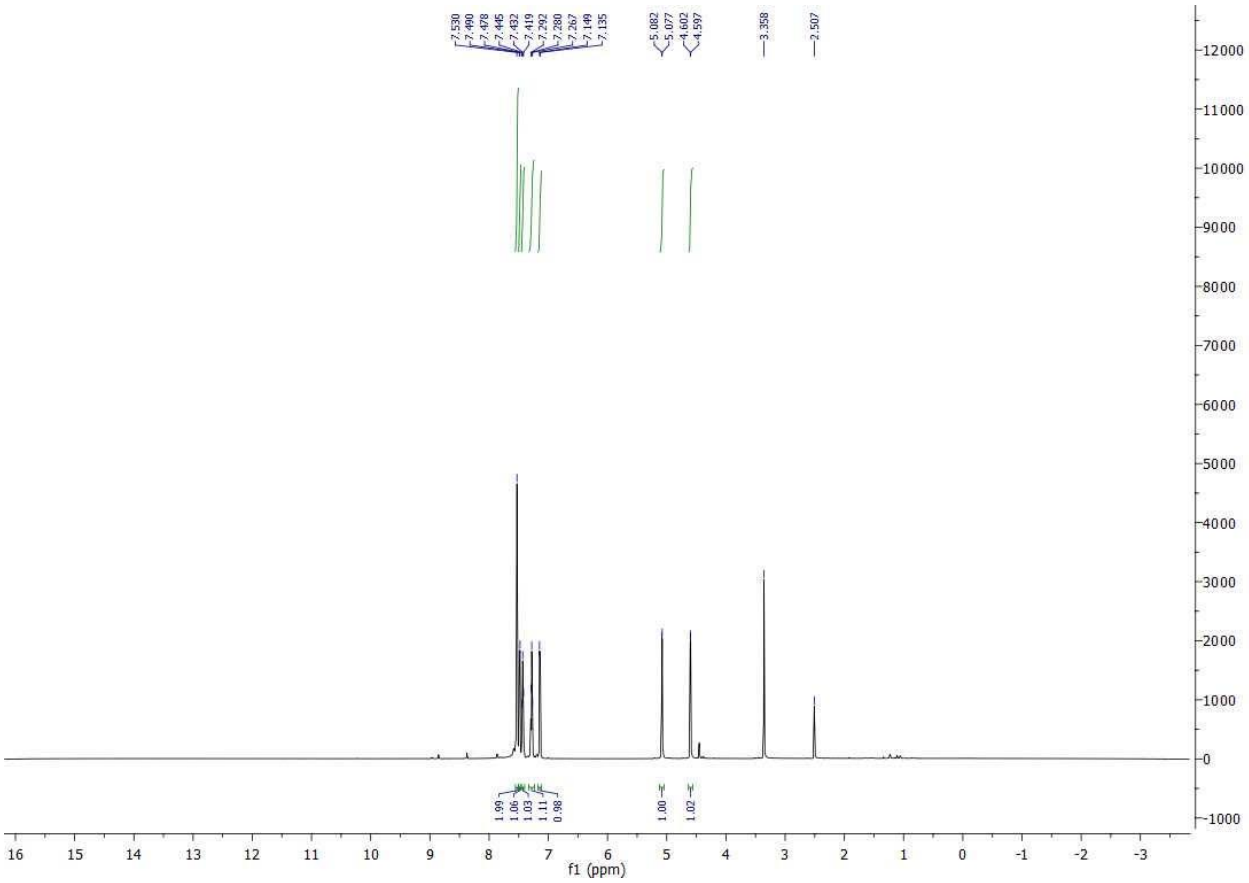


Figure S16. ^{1}H NMR spectrum of **4f**

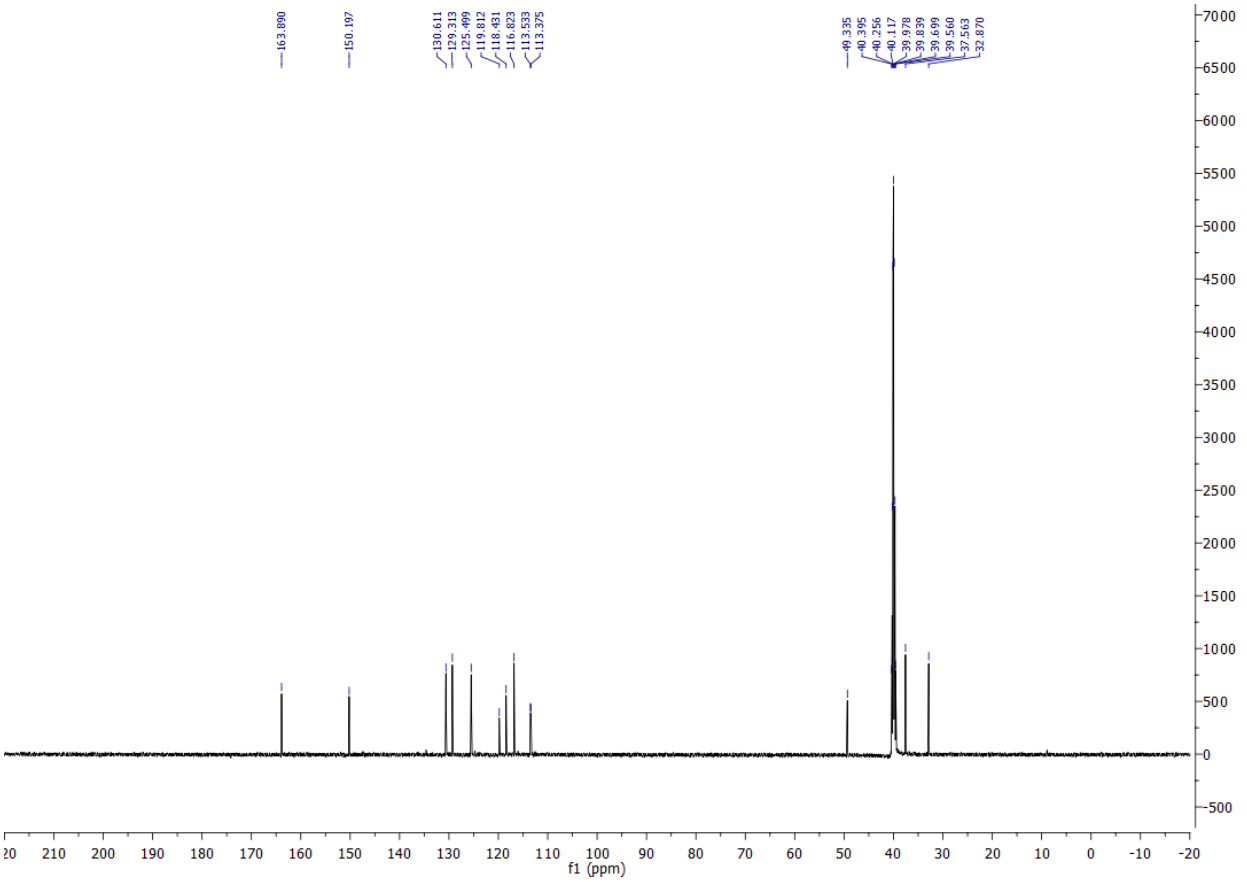


Figure S17. ^{13}C NMR spectrum of **4f**

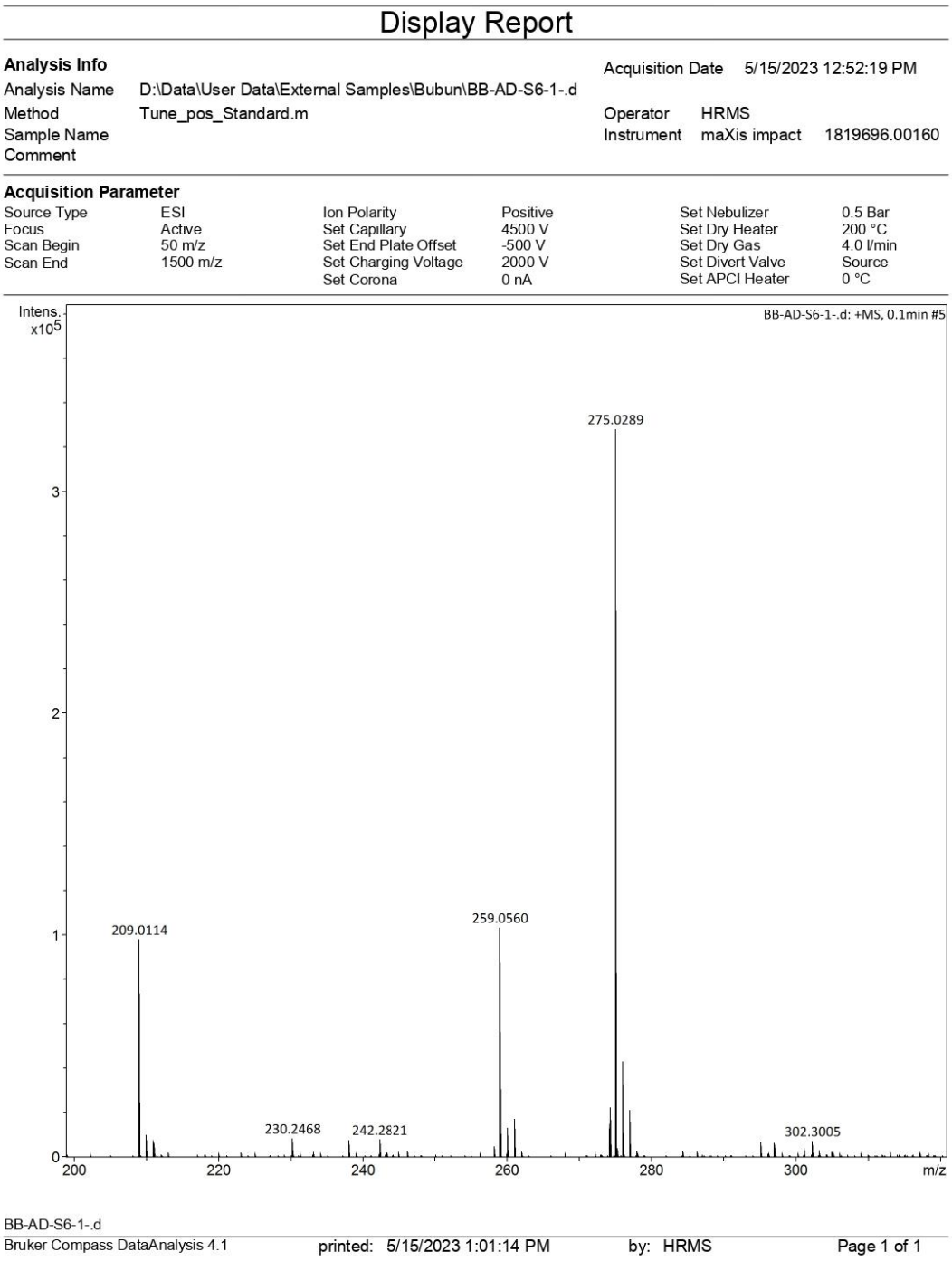
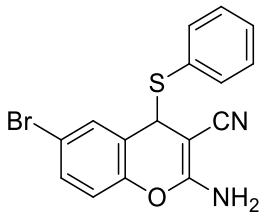


Figure S18. HRMS spectrum of **4f**



4g

2-Amino-6-bromo-4-(phenylthio)-4H-chromene-3-carbonitrile (**4g**). White solid, yield 88%; mp 181–183 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H/ppm 7.41 (d, J 2.5 Hz, 1H, aromatic H), 7.36-7.31 (m, 2H, aromatic H), 7.21 (t, J 7.5 Hz, 2H, aromatic H), 7.08 (s, 2H, -NH_2), 7.01 (dd, J 10.5 Hz, 1 Hz, 2H, aromatic H), 6.73 (d, J 9 Hz, 1H, aromatic H), 5.30 (s, 1H, -CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 162.43, 136.6, 131.8, 131.7 (2C), 129.6 (2C), 129.7 (2C), 124.4 (2C), 124.0, 118.3, 116.3, 53.6, 46.7; HRMS (ESI-TOF) *m/z*: For $C_{16}H_{11}BrN_2OS$ Calcd. $[M+Na]^+$ 380.9673; Found $[M+Na]^+$ 381.3114.

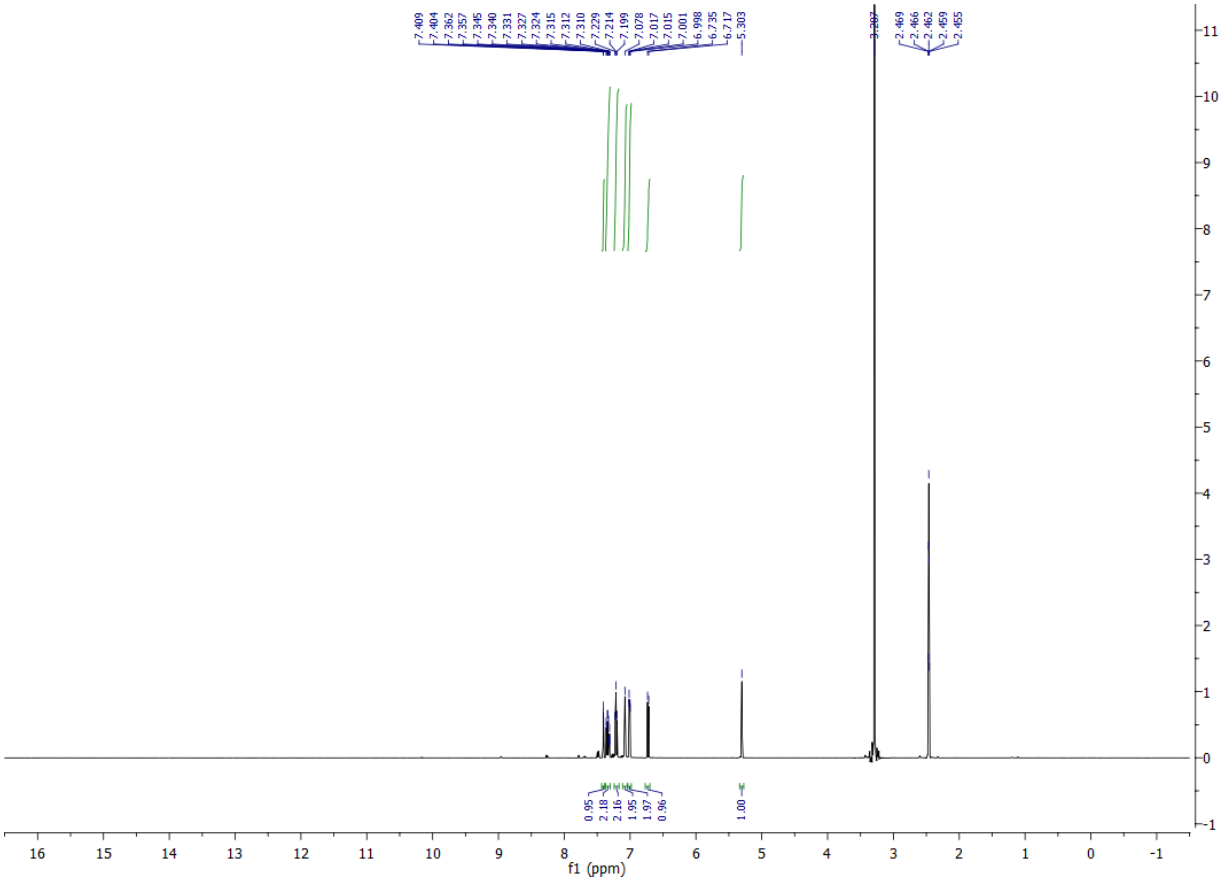


Figure S19. ^{1}H NMR spectrum of **4g**

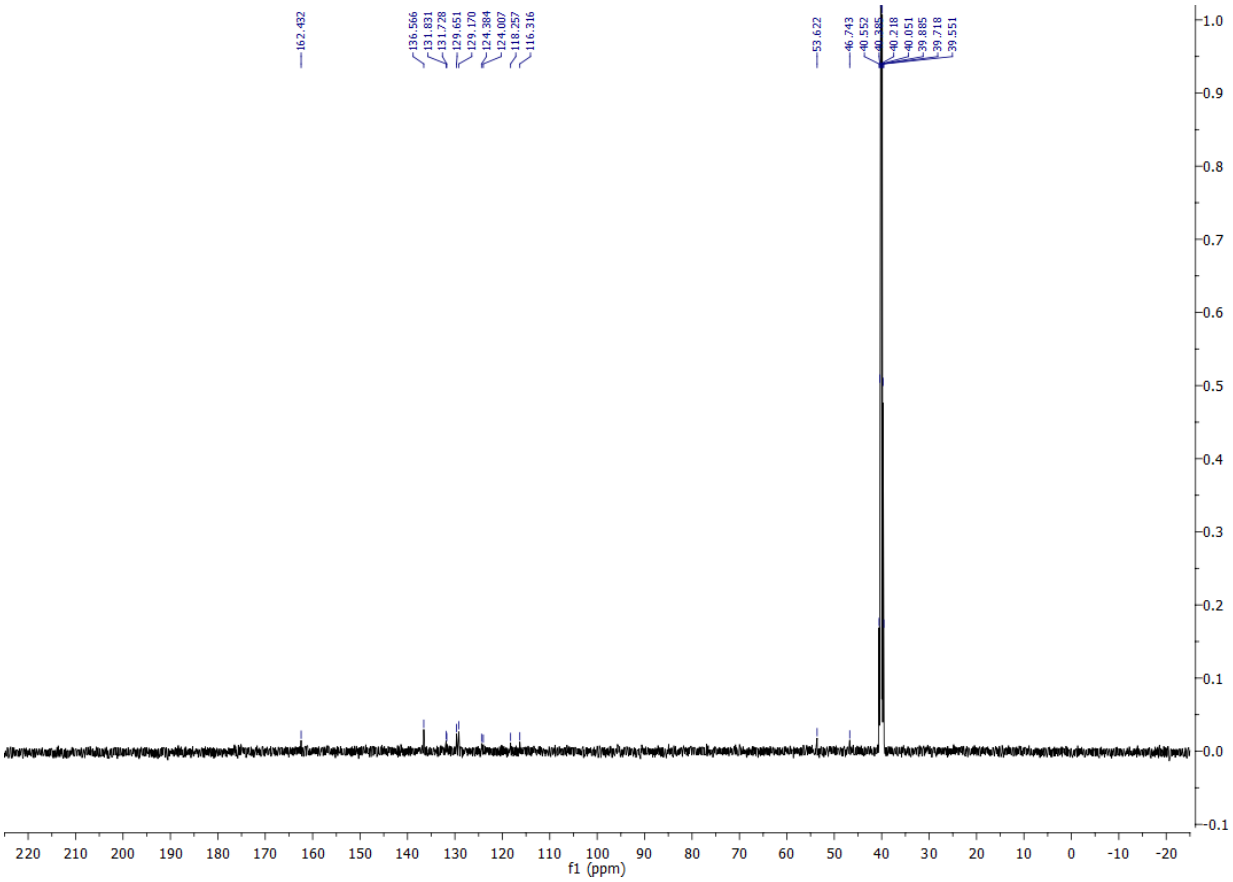


Figure S20. ^{13}C NMR spectrum of **4g**

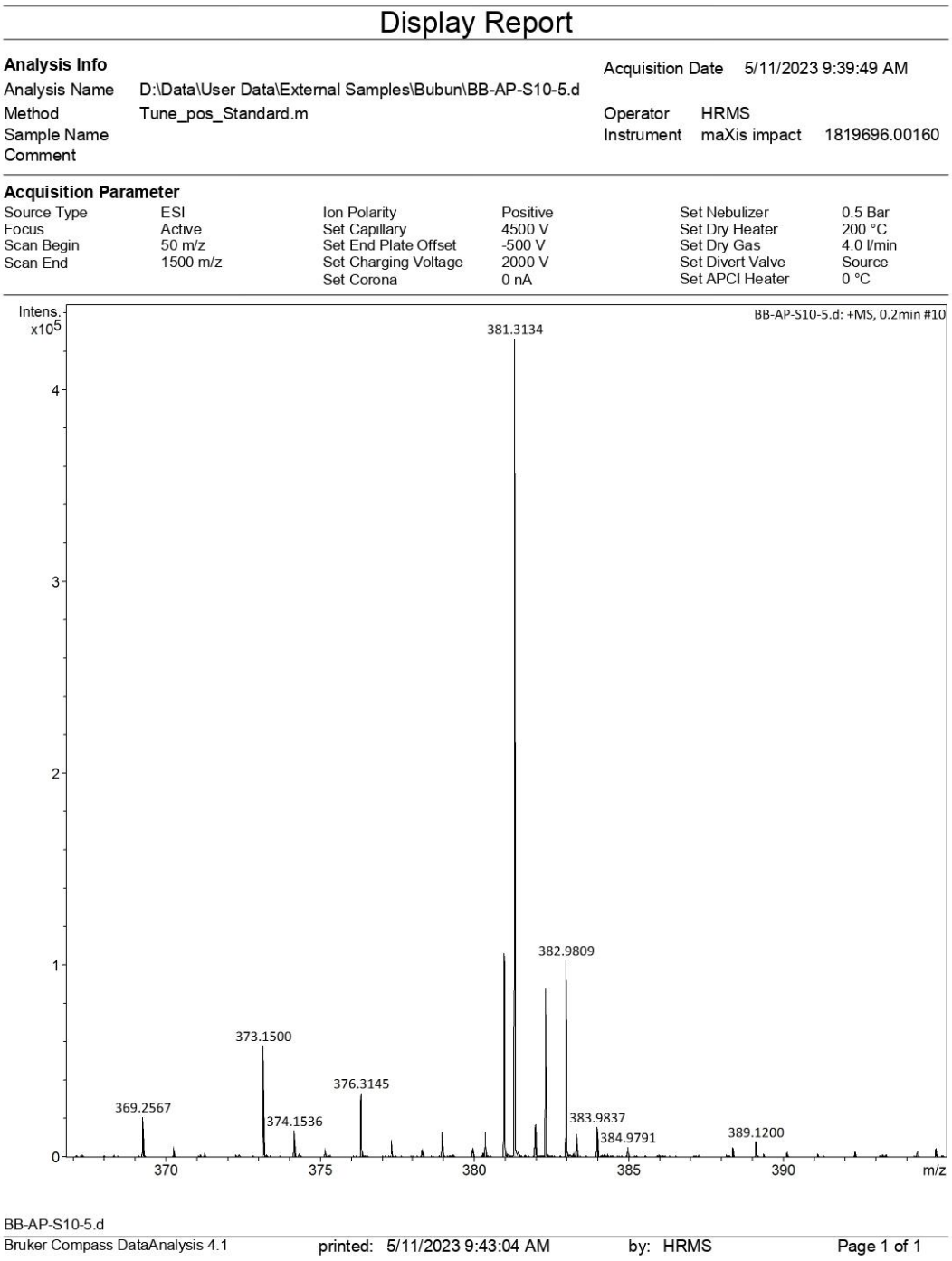
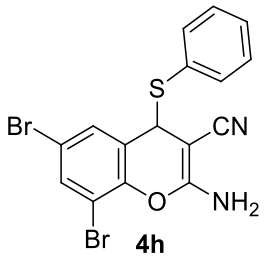


Figure S21. HRMS spectrum of **4g**



4h

2-Amino-6,8-dibromo-4-(phenylthio)-4H-chromene-3-carbonitrile (**4h**). Light Yellow solid, yield 82%; mp 171–173 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H/ppm 7.74 (d, J 2 Hz, 1H, aromatic H), 7.49 (d, J 7.5 Hz, 1H, aromatic H), 7.41 (d, J 2 Hz, 1H, aromatic H), 7.37-7.34 (m, 3H, aromatic 1H & -NH_2), 7.26-7.22 (m, 2H, aromatic H), 6.99 (dd, J 8.25 Hz, 1 Hz 1H, aromatic H), 5.34 (s, 1H, -CH), ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 162.1, 145.9, 136.7, 134.2, 130.0 (2C), 129.9, 129.2 (2C), 128.1, 127.7, 119.5, 116.4, 110.5, 53.8, 47.0; HRMS (ESI-TOF) *m/z*: For $C_{16}H_{10}Br_2N_2OS$ Calcd. $[M+H]^+$ 436.8959; Found $[M+H]^+$ 436.8742.

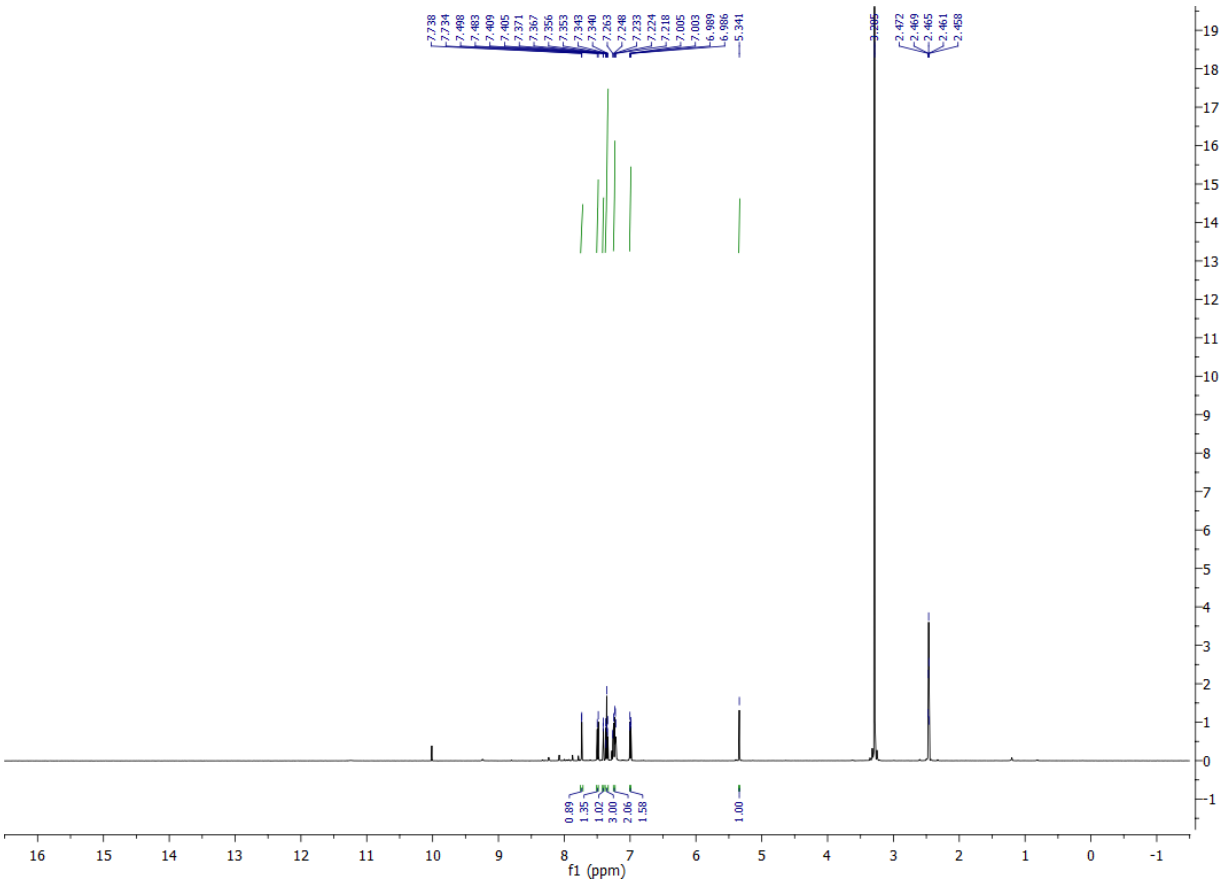


Figure S22. ^{1}H NMR spectrum of **4h**

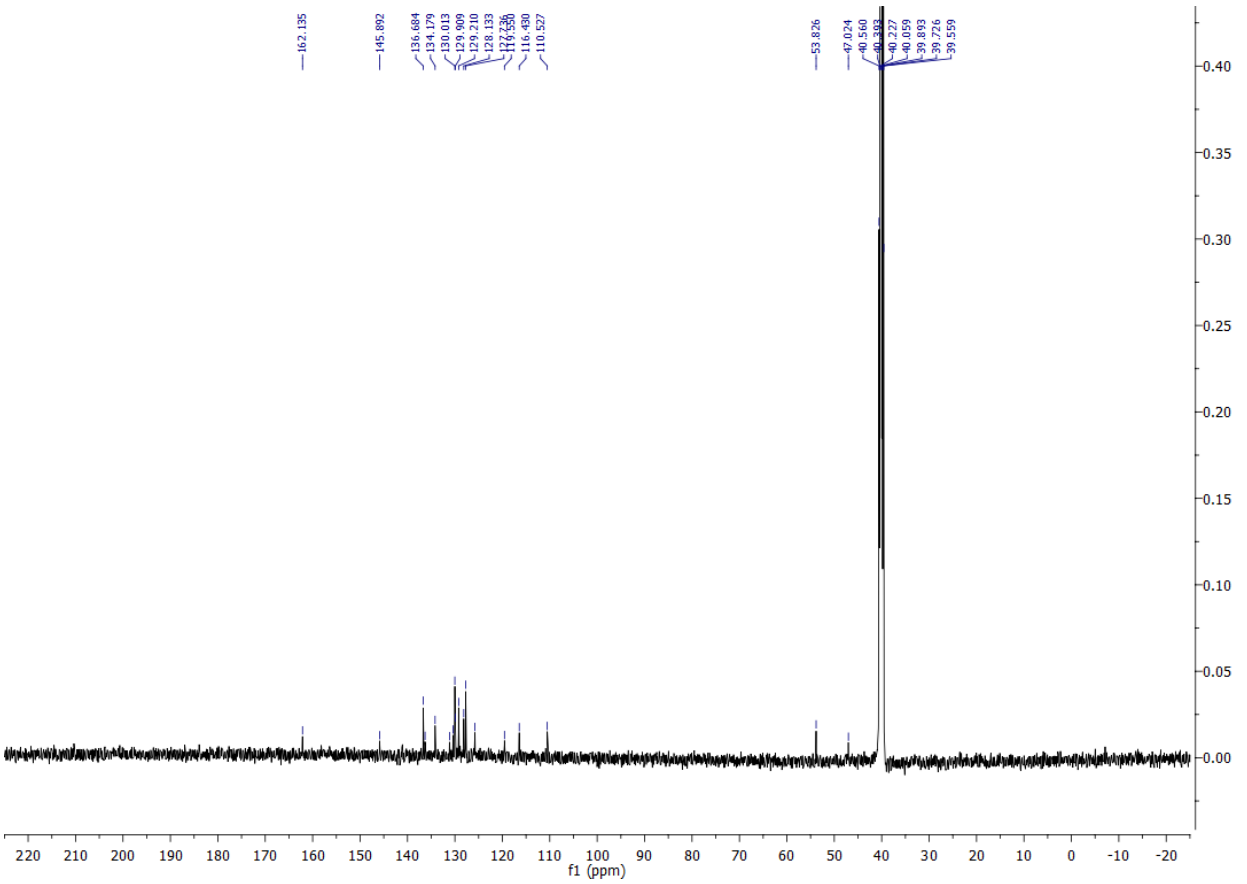


Figure S23. ^{13}C NMR spectrum of **4h**

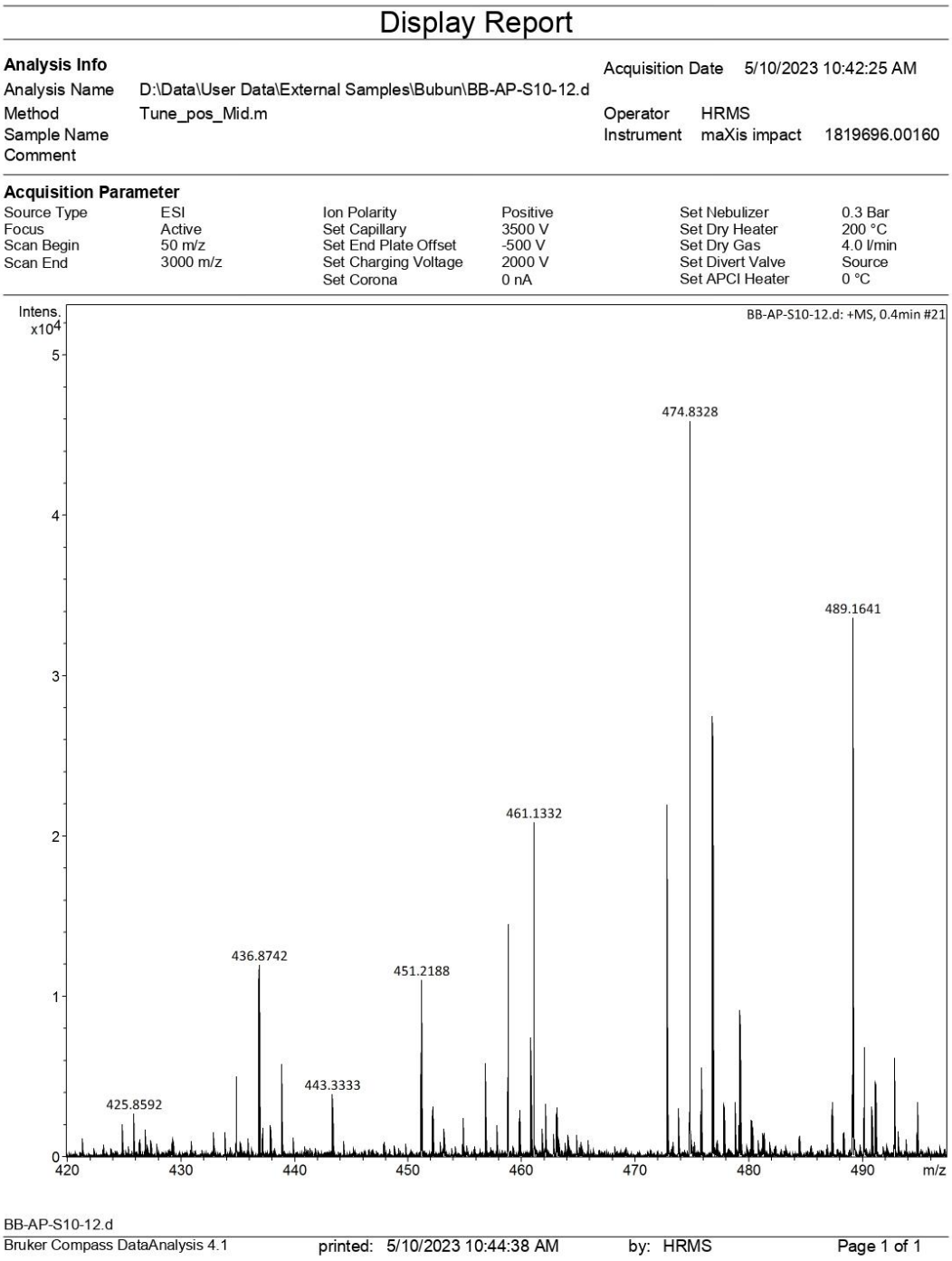
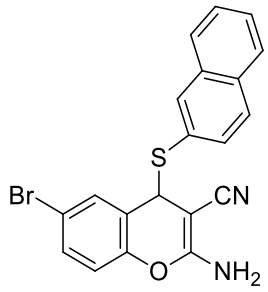


Figure S24. HRMS spectrum of **4h**



4i

2-Amino-6-bromo-4-(naphthalen-2-ylthio)-4H-chromene-3-carbonitrile (**4i**). White solid, yield 90%; mp 181-183 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H/ppm 7.87-7.86 (m, 1H, aromatic H), 7.74 (d, J 8.5 Hz, 2H, aromatic H), 7.62 (s, 1H, aromatic H), 7.51-7.48 (m, 2H, aromatic H), 7.46 (d, J 2.5 Hz, 1H, aromatic H), 7.35 (dd, J 8.5 Hz, 2.5 Hz, 1H, aromatic H), 7.09 (dd, J 8.5 Hz, 1.5 Hz, 1H, aromatic H), 7.04 (s, 2H, -NH_2), 6.66 (d, J 8.5 Hz, 1H, aromatic H); 5.40 (s, 1H, -CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 162.4, 148.8, 136.5, 133.5, 133.2, 132.9, 131.9, 131.7, 128.6, 128.4, 128.3, 128.0, 127.4, 126.9, 124.5, 119.9, 118.2, 116.4, 53.9, 47.0; HRMS (ESI-TOF) *m/z*: For $C_{20}H_{13}BrN_2OS$ Calcd. $[M+Na]^+$ 432.2888; Found $[M+Na]^+$ 432.9574.

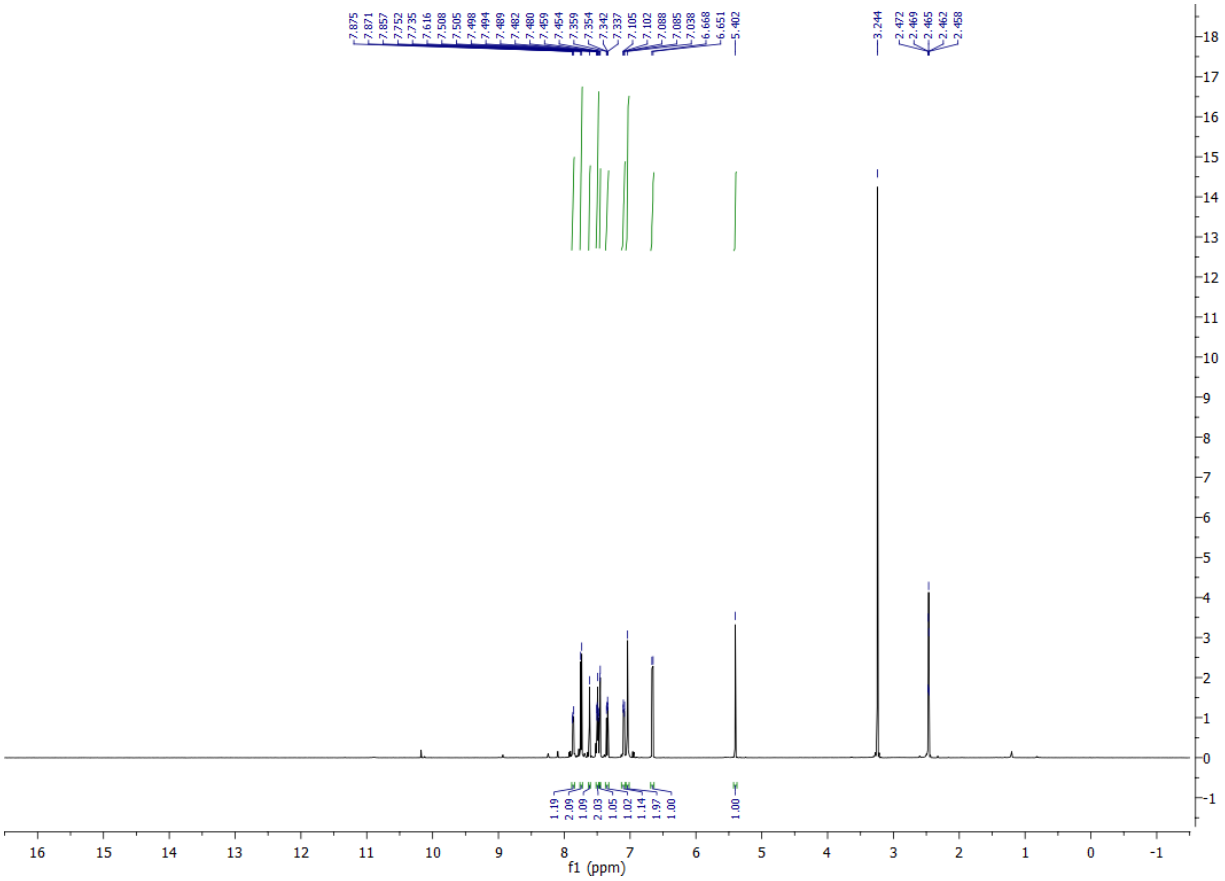


Figure S25. ^{1}H NMR spectrum of **4i**

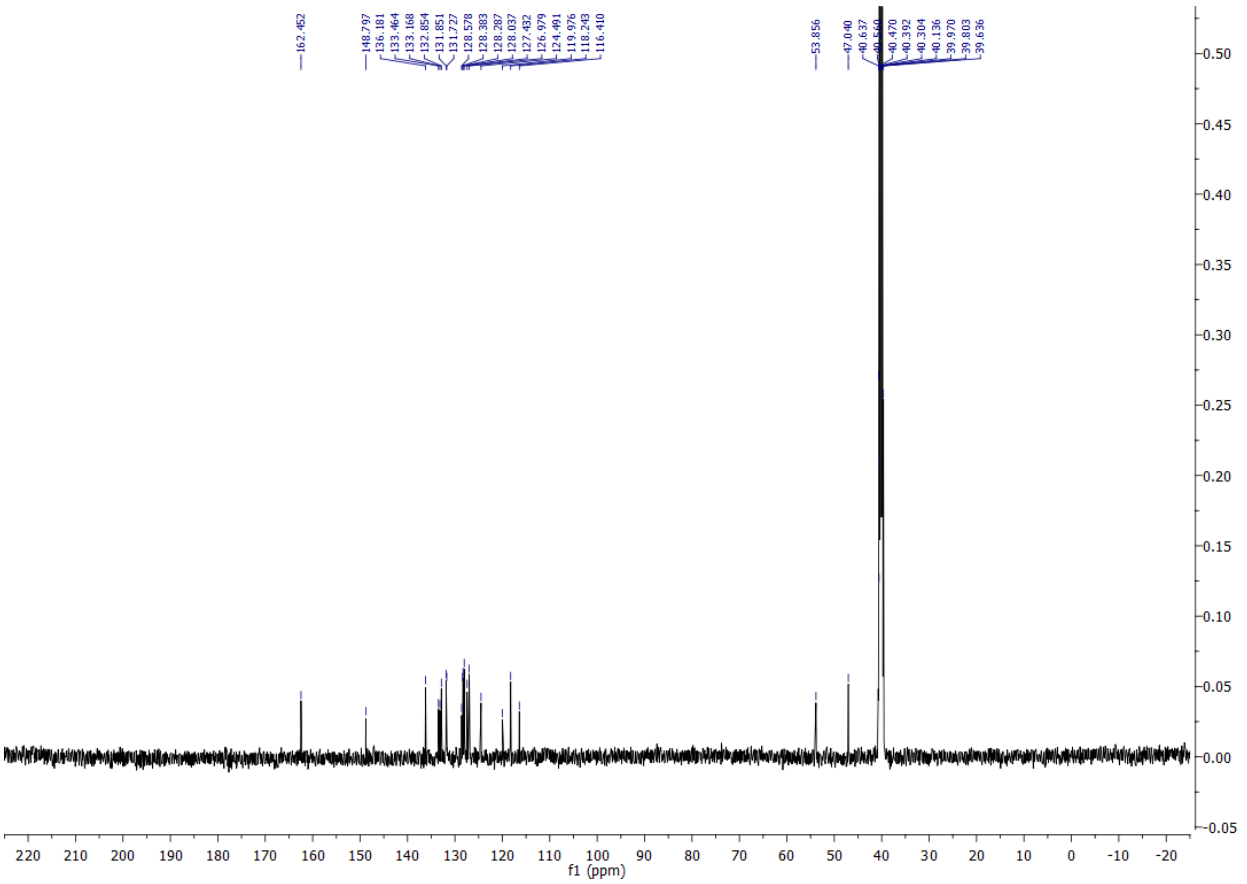


Figure S26. ^{13}C NMR spectrum of **4i**

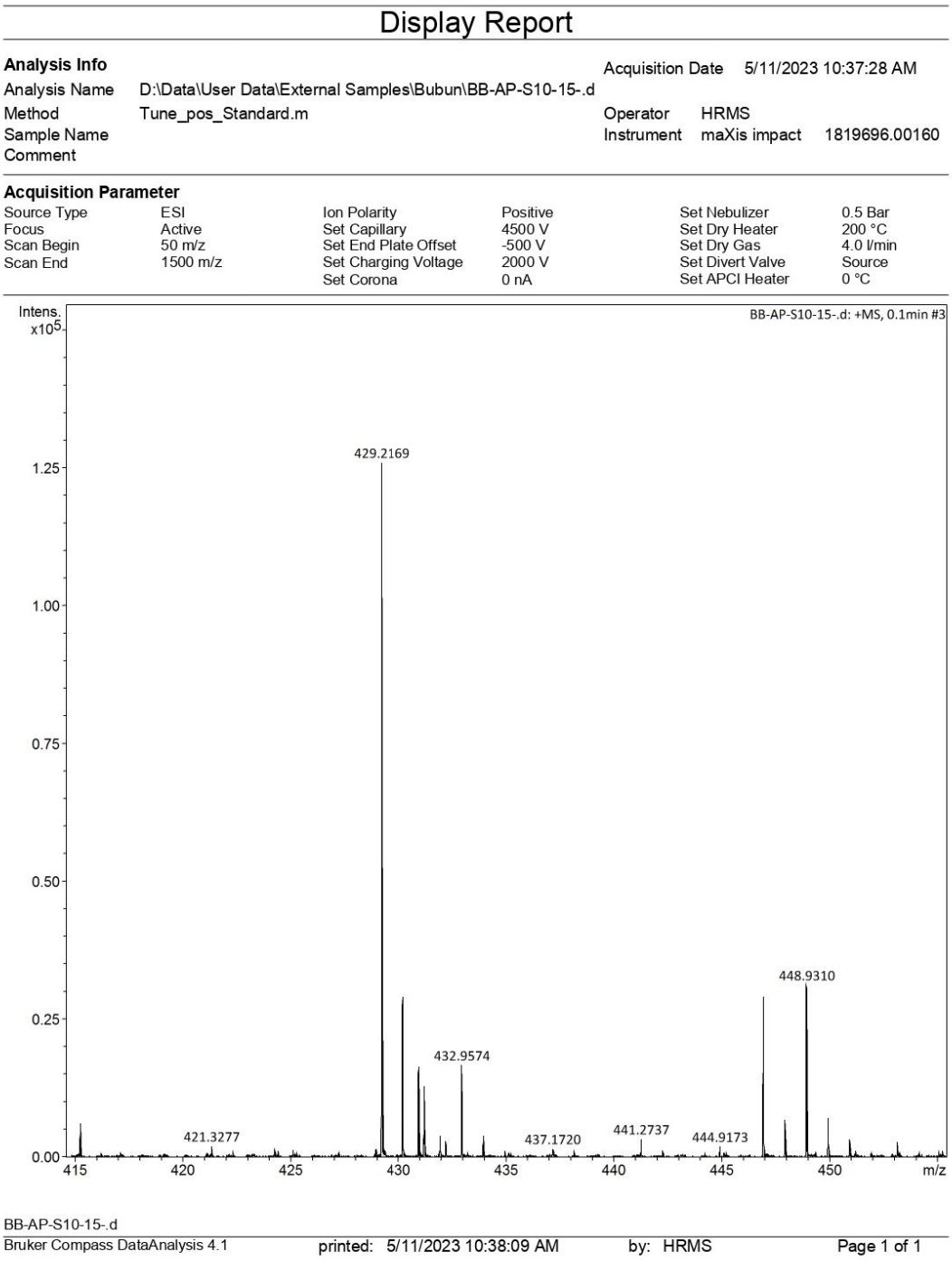
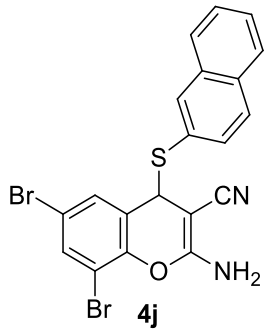


Figure S27. HRMS spectrum of **4i**



4j

2-Amino-6,8-dibromo-4-(naphthalen-2-ylthio)-4H-chromene-3-carbonitrile (**4j**). Off White solid, yield 94%; mp 173-175 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H/ppm 7.88-7.86 (m, 1H, aromatic H), 7.76 (d, J 8.5 Hz, 1H, aromatic H), 7.72 (d, J 2.5 Hz, aromatic H), 7.51-7.49 (m, 2H, aromatic H), 7.43 (d, J 2.5 Hz, 1H, aromatic H), 7.20 (s, 2H, -NH_2), 7.07 (dd, J 8.5 Hz, 1.5 Hz, 1H, aromatic H) 5.43 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C/ppm 162.1, 145.9, 136.4, 134.2, 133.5, 133.3, 132.8, 131.1, 129.8, 128.5, 128.3, 128.1, 127.6, 127.0, 125.9, 119.6, 116.5, 110.6, 53.9, 47.3; HRMS (ESI-TOF) *m/z*: For $C_{20}H_{12}Br_2N_2OS$ Calcd. $[M+Na]^+$ 511.1848; Found $[M+Na]^+$ 510.8708.

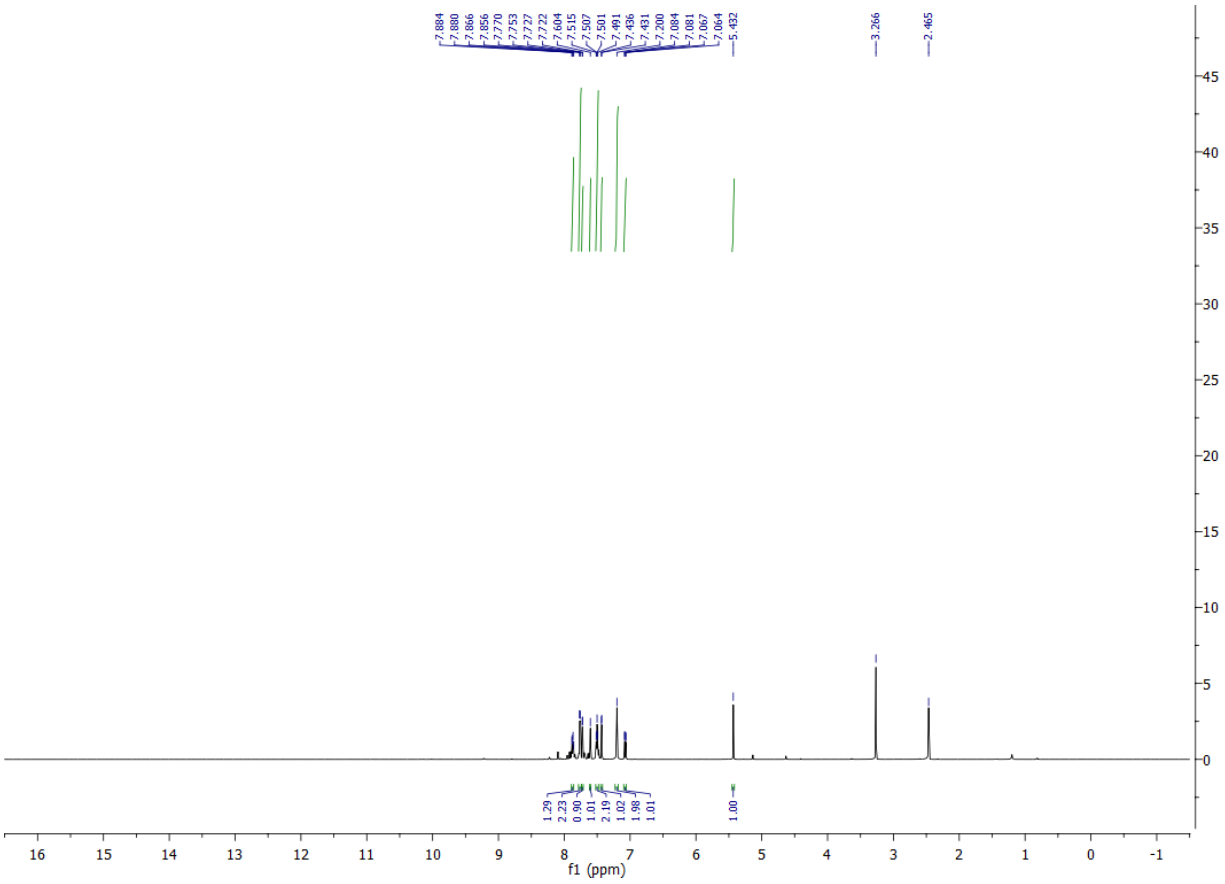


Figure S28. ^{1}H NMR spectrum of **4j**

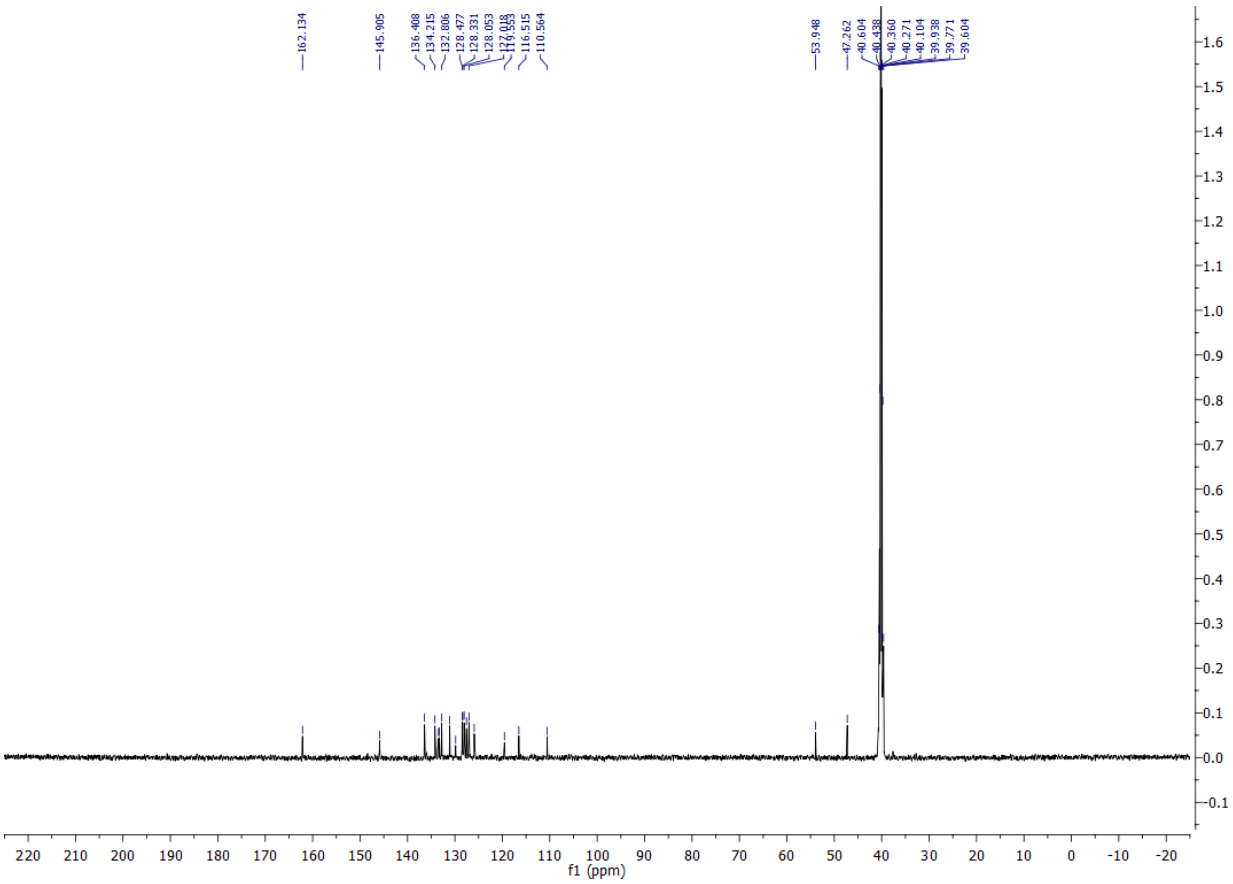


Figure S29. ^{13}C NMR spectrum of **4j**

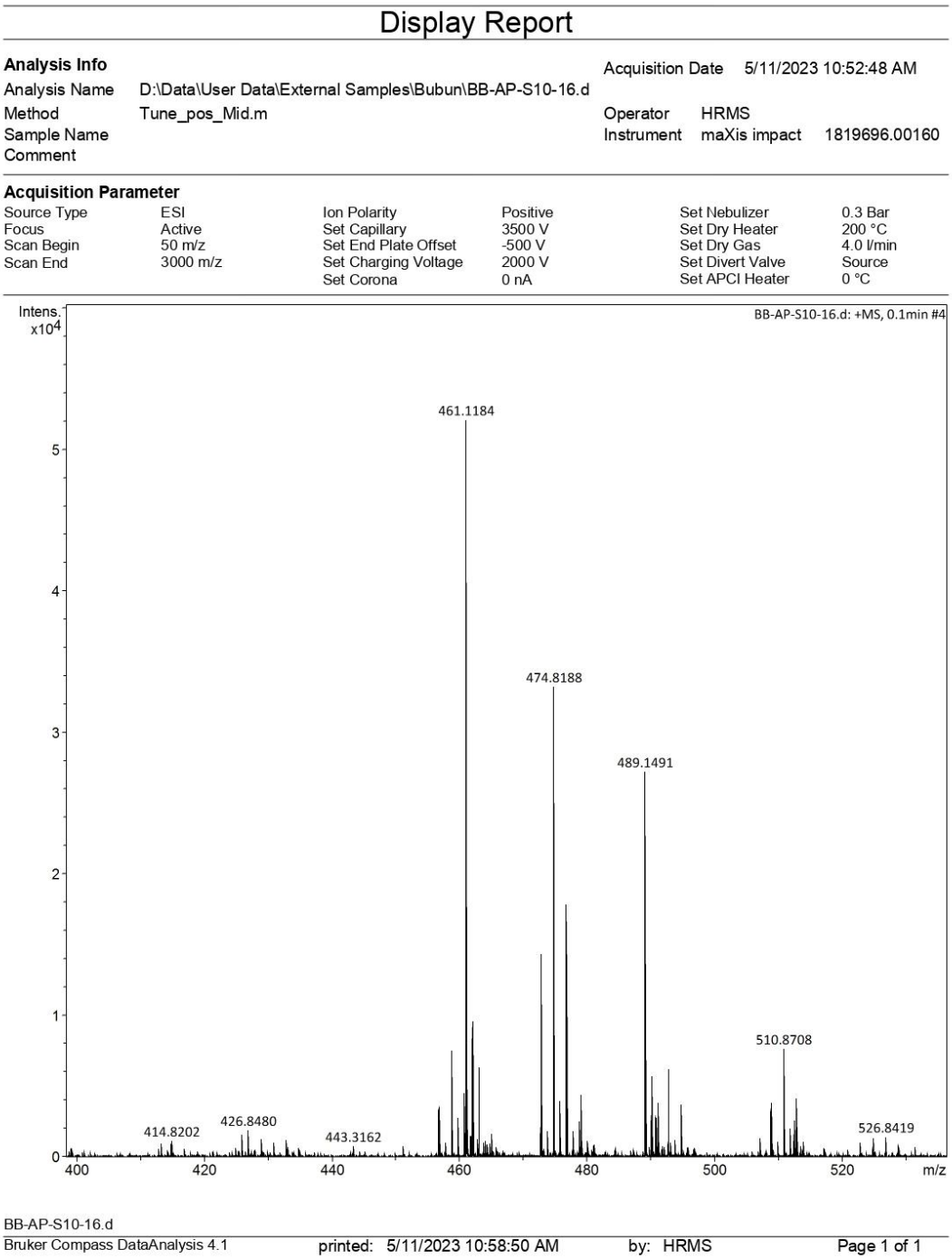


Figure S30. HRMS spectrum of **4j**

