Supporting Information

Effect of the Substituents of New Coumarin-imidazo[1,2-*a*]heterocyclic-3-acrylate Derivatives on Nonlinear Optical Properties: A combined experimental-theoretical approach

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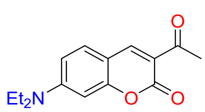
1. General Method

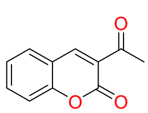
All melting points were determined on Electrothermal 9100 Melting point apparatus and were not corrected. Microwave irradiation was carried out in a Discover SP CEM microwave. Reactions were monitored by thin layer chromatography (TLC) using Sigma Aldrich TLC plates 20 x 20 locating the spots using UV light as the visualizing agent. Column chromatography was performed on silica gel 230-400 mesh. Standard work up: organic layers were dried with Na_2SO_4 and concentrated in vacuum. Infrared spectra were recorded on Spectrum 100 Perkin Elmer instrument and values are reported in cm^{-1} units. UV spectra were recorded on Perkin Elmer lambda 50, and the emission spectra were recorded on Fluorescence spectrophotometer HITACHI F-7000. ^{1}H and ^{13}C NMR spectra were recorded on Nuclear Magnetic resonance spectrometer Bruker Avance III HD with the magnet Bruker Ascent 400 MHz or Bruker Avance III HD with the magnet Bruker Ultra Shield 500 MHz HD at 25 °. Chemical shifts are given in δ values relative to TMS (tetramethylsilane) as internal standard. Mass spectra were recorded on Spectrometer Maxis Impact ESI-QTOF-MS, Bruker Daltonics mass spectrometer.

2. Synthetic procedures and spectroscopic data of compounds 1a-c, 2a-c and 4a-g

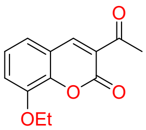
Compounds **1 a-c, 2 a-c** and **4a-g** were synthesized using literature procedure previously.[1,2]



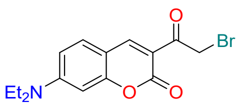
3-acetyl-7-(diethylamino)-2H-chromen-2-one (1a): Yield 82%, m.p. 150 – 151 ºC; RMN ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS) δ = 8.40 (s, 1H, –CH=C–), 7.38 (d, *J* (H,H) = 8.9 Hz, 1H, Ar), 6.62 (dd, *J* (H,H) = 8.9, 1.8 Hz, 1H, Ar), 6.44 (d, *J* (H,H) = 1.4 Hz, 1H, Ar), 3.46 (q, *J* (H,H) = 7.0 Hz, 4H, $–\underline{CH_2}CH_3$), 2.67 (s, 3H, CH_3), 1.25 (t, *J* (H,H) = 7.1 Hz, 6H, $–CH_2\underline{CH_3}$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS) δ = 195.50, 160.78, 158.68, 153.00, 147.75, 131.87, 115.93, 109.87, 108.07, 96.46, 45.11, 30.51, 12.48; FT-IR (KBr) ν_{max} = 1725 cm^{-1} (C=O), 1664 cm^{-1} (C=O lactone); UV–Vis (MeOH) λ_{max} = 243 nm, 312 nm.



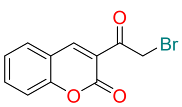
3-acetyl-2H-chromen-2-one (1b): Yield 90%, m.p. 107 – 109 ºC, ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS) δ = 8.52 (s, 1H, –CH=C–), 7.66 (d, *J* (H,H) = 2.8 Hz, 2H, Ar), 7.41 – 7.33 (m, 2H, Ar), 2.74 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS) δ = 195.5, 159.2,155.3, 147.4, 134.3, 130.2,125.0, 124.9, 118.3, 116.7, 30.5; FT-IR (KBr) ν_{max} = 1741 cm^{-1} (C=O), 1678 cm^{-1} (C=O lactone); UV–Vis (MeOH) λ_{max} = 245 nm.



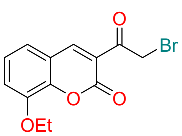
3-acetyl-8-ethoxy-2H-chromen-2-one (1c): Rendimiento: 95%, solido de amarillo claro, p.f. = 133 – 136 ºC, RMN ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS) δ = 8.461(s, 1H, –CH=C–), 7.170-7.242 (m, 3H, Ar), 4.206 (q, *J* (H,H) = 7 Hz, 2H, H-8a), 2.726 (s, 3H, H-3b), 1.518 (t, *J* (H,H) = 7 Hz, 3H, H-8b); RMN ^{13}C (125 MHz, $CDCl_3$, 25 ºC, TMS) δ = 195.74, 158.97, 147.80, 146.48, 145.28, 124.89, 124.66, 121.36, 119.02, 117.21, 65.21, 30.66, 14.78; FT-IR (KBr) ν_{max} = 1730 cm^{-1} (C=O), 1716 cm^{-1} (C=O lactone); UV–Vis (MeOH) λ_{max} = 315.



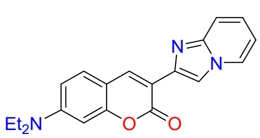
3-(2-bromoacetyl)-7-(diethylamino)-2H-chromen-2-one (2a): Yield 73%, m.p. 211 – 213 ºC; ^{1}H NMR (500 MHz, DMSO-d_6, 25 ºC, TMS) δ = 8.53 (s, 1H, –CH=C–), 7.48 – 7.37 (m, 1H, Ar), 6.69 – 6.60 (m, 1H, Ar), 6.48 (d, *J* (H,H) = 2.4 Hz, 1H, Ar), 4.77 (s, 2H, –$\underline{CH_2}$Br), 3.48 (q, *J* (H,H) = 7.1 Hz, 4H, –$\underline{CH_2}CH_3$), 1.26 (t, *J* (H,H) = 7.1 Hz, 6H, –$CH_2\underline{CH_3}$); ^{13}C NMR (125 MHz, DMSO-d_6, 25 ºC, TMS) δ = 188.57, 160.55, 159.00, 153.59, 149.44, 132.22, 113.98, 112.71, 110.22, 108.44, 96.69, 45.28, 36.77, 12.45; FT-IR (KBr) ν_{max} = 1735 cm^{-1} (C=O), 1675 cm^{-1} (C=O lactone); UV–Vis (CH_2Cl_2) λ_{max} = 245 nm, 270 nm.



3-(2-bromoacetyl)-2H-chromen-2-one (2b): Yield 95%, m.p. 163 – 164 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS) δ = 8.64 (1H, s, –CH=C–), 7.71 (t, *J* (H,H) = 7.2 Hz, 2H, Ar), 7.44 – 7.35 (m, 2H, Ar), 4.76 (s, 2H, –$\underline{CH_2}$Br); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS) δ = 188.90, 158.88, 155.43, 149.54, 135.12, 130.43, 125.31, 122.19, 118.15, 116.91, 35.59; FT-IR (KBr) ν_{max} = 1727 cm^{-1} (C=O), 1685 cm^{-1} (C=O lactone); UV–Vis (CH_2Cl_2) λ_{max} = 247 nm.

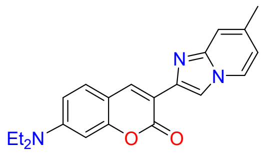


3-(2-bromoacetyl)-8-ethoxy-2H-chromen-2-one (2c): gray powder; yield 79%; m.p. 180 – 182 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS) δ = 8.60 (s, 1H, –CH=C–), 7.19–7.32 (m, 3H, Ar), 4.77 (s, 2H, CH2), 4.23 (q, *J* (H,H) = 7.2 Hz, 2H, –$\underline{CH_2}CH_3$), 1.54 (t, *J* (H,H) = 7.2 Hz, 3H, –$CH_2\underline{CH_3}$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS) δ = 173.03, 162.70, 154.19, 151.42, 145.53, 127.92, 125.75, 120.01, 118.43, 115.47, 62.13, 35.10, 13.73; FT-IR (KBr) ν_{max} = 1,722 cm^{-1} (C=O), 1,692 cm^{-1} (C=O lactone).

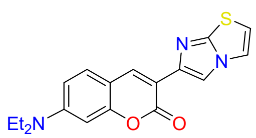


7-(diethylamino)-3-(imidazo[1,2-a]pyridin-2-yl)-2H-chromen-2-one (4a): Yield 92%; dark yellow powder; m.p. 167.6 – 169 °C; ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.65 (s,1H, −$\underline{CH}$=C−), 8.44 (s, 1H, −$\underline{CH}$=C−), 8.11 (d, *J* (H,H) = 7,1 Hz,1H, Ar), 7.56 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 7.41 (d, *J* (H,H) = 8.5, 1,5 Hz, 1H, Ar), 7.16 (t, *J* (H,H) = 7.5 Hz, 1H, Ar), 6.74 (t, *J* (H,H) = 7.5 Hz, 1H, Ar), 6.62 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.54 (s, 1H, Ar), 3.44 (q, *J* (H,H) = 7 Hz, 4H, −$\underline{CH_2}$−CH_3), 1.22 (t, *J* (H,H) = 7 Hz, 6H, −CH_2−$\underline{CH_3}$) RMN^{13}C (125 MHz, $CDCl_3$, TMS) δ (ppm): 161.1, 175.8, 176.5, 164.8, 159.5, 158.8, 149.3, 145.8, 144.9, 136.6, 133.6, 132.2, 131.9, 109.3, 109.2, 97.1, 44.9, 12.6; FT-IR (KBr) ν_{max} = 1705 cm^{-1} (C=O lactone), 1619 cm^{-1} (C=C Ar);

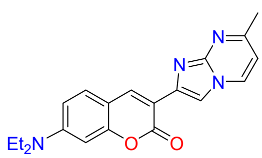
UV−Vis (MeOH) λ_{max} = 421 nm; HRMS (ESI m/z) Calcd. for $C_{20}H_{19}N_3O_2$ $[M+H]^+$ 334.1550, found 334.1564.



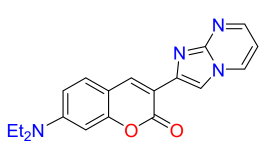
7-(diethylamino)-3-(7-methylimidazo[1,2-a]pyridin-2-yl)-2H-chromen-2-one (4b): Yield 87%; dark yellow powder; m.p. 200.6 – 202°C; RMN ^1H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.62 (s, 1H, −<u>CH</u>=C−), 8.36 (s, 1H, −<u>CH</u>=C−), 7.98 (d, *J* (H,H) = 7 Hz, 1H, Ar), 7.41 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 7.31 (s, 1H, Ar), 6.62 (dd, *J* (H,H) = 8.5, 2 Hz, 1H, Ar), 6.59 (dd, *J* (H,H) = 7, 1.5 Hz, 1H, Ar), 6.54 (s, *J* (H,H) = 2 Hz, 1H, Ar), 3.44 (q, *J* (H,H) = 7 Hz, 4H, −<u>CH₂</u>−CH₃), 2.39 (s, 3H), 1.23 (t, *J* (H,H) = 7 Hz, 6H, −CH₂−<u>CH₃</u>); RMN ^{13}C (125 MHz, $CDCl_3$, TMS) δ (ppm): 161.3, 155.88, 150.8, 145.7, 139,5, 139.1, 136.4, 129.7, 126.4, 115.4, 115.1, 114.2, 112.1, 109.5, 97.4, 45.2, 21.7,12.8; FT-IR (KBr) ν_{max} = 1712 cm^{-1} (C=O lactone), 1621 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 422 nm; HRMS (ESI m/z) Calcd. for $C_{21}H_{21}N_3O_2$ $[M+H]^+$ 348.1707, found 348.1725.



7-(diethylamino)-3-(imidazo[2,1-b]thiazol-6-yl)-2H-chromen-2-one (4c): Yield 78%; dark brown powder; m.p. 173 – 175°C; RMN ^1H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.45 (s, 1H, −<u>CH</u>=C−), 8.30 (s, 1H, −<u>CH</u>=C−), 7.41 (d *J* (H,H) = 4.5 Hz, 1H, Ar), 7.37 (d, *J* (H,H) = 9 Hz, 1, Ar), 6.78 (d, *J* (H,H) = 4.5 Hz, 1H, Ar), 6.61 (dd, *J* (H,H) = 9, 2.5 Hz, 1H, Ar), 6.52 (s, *J* (H,H) = 2.5 Hz, 1H, Ar), 3.43 (q, *J* (H,H) = 7 Hz, 4H, −<u>CH₂</u>−CH₃), 1.22 (t, *J* (H,H) = 7 Hz, 6H, −CH₂−<u>CH₃</u>); RMN^{13}C (125 MHz, $CDCl_3$, TMS) δ (ppm): 161.0, 155.6, 150.5, 15.15, 141.9, 137.89, 129.4, 119.0, 114.4, 112.5, 112.3, 109.5, 109.4, 97.3, 45.1, 12.8; FT-IR (KBr) ν_{max} = 1710 cm^{-1} (C=O lactone), 1618 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 415 nm; HRMS (ESI m/z) Calcd. for $C_{18}H_{17}N_3O_2$ $[M+H]^+$ 340.1114, found 340.1118.

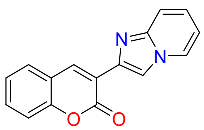


7-(diethylamino)-3-(7-methylimidazo[1,2-a]pyrimidin-2-yl)-2H-chromen-2-one (4d): Yield 98%; yellow powder; m.p. 229.4 – 231 °C; RMN ^1H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.72 (s, 1H, −<u>CH</u>=C−), 8.26 (s, 1H, −<u>CH</u>=C−), 8.24 (d, *J* (H,H) = 7 Hz, 1H, Ar), 7.38 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 6.65 (d, *J* (H,H) = 7 Hz, 1H, Ar), 6.58 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.48 (s, 1H, <u>CH₃</u>), 3.40 (q, *J* (H,H) = 7 Hz, 4H, −<u>CH₂</u>−CH₃), 2.57 (t, *J* (H,H) = 7 Hz, 6H, −CH₂−<u>CH₃</u>); RMN ^{13}C (125 MHz, $CDCl_3$, TMS) δ (ppm) = 161.0, 160.4, 156.1, 150.9, 148.2, 140.6, 140.2, 132.8, 129.7, 113.4, 109.8, 109.4, 109.2, 97.8, 45.0, 25.1, 12.6; FT-IR (KBr) ν_{max} = 1714 cm^{-1} (C=O lactone), 1620 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 433 nm; HRMS (ESI m/z) Calcd. for $C_{20}H_{20}N_4O_2$ $[M+H]^+$ 349.1659, found 349.1671.

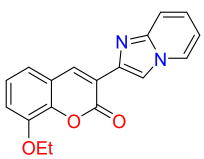


7-(diethylamino)-3-(imidazo[1,2-a]pyrimidin-2-yl)-2H-chromen-2-one (4e): Yield 94%; yellow powder; m.p. 158 – 160°C; RMN ^1H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.78 (s, 1H, −<u>CH</u>=C−), 8.50 (dd, *J* (H,H) = 4, 2 Hz, 1H, Ar), 8.41 (d, *J* (H,H) = 2 Hz, 1H, Ar), 8.40 (s, 1H, −<u>CH</u>=C−), 7.42 (d, *J* (H,H) = 7.59 Hz, 1H, Ar), 6.82 (t, *J* (H,H) = 4, 2.5 Hz, 1H, Ar), 6.662

(dd, *J* (H,H) = 9, 2.5 Hz, 1H, Ar1) , 6.51 (s, *J* (H,H) = 2Hz, 1H, Ar), 3.43 (q, *J* (H,H) = 7 Hz, 4H, −$\underline{CH_2}$−CH_3), 1.22 (t, *J* (H,H) = 7 Hz, 6H, −CH_2−$\underline{CH_3}$); RMN ^{13}C (125 MHz, $CDCl_3$, TMS) δ (ppm) = 161.2, 156.4, 151.2, 150.40, 148.3, 141.7, 140.9, 133.7, 130.0, 113.2, 110.4, 109.6, 109.4, 108.7, 97.3, 45.2, 12.7, FT-IR (KBr) ν_{max} = 1702 cm^{-1} (C=O lactone), 1613 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 436 nm; HRMS (ESI m/z) Calcd. for $C_{19}H_{18}N_4O_2$ $[M+H]^+$ 335.1503, found 335.1522.



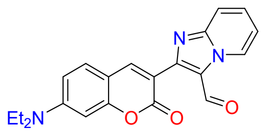
3-(imidazo[1,2-a]pyridin-2-yl)-2H-chromen-2-one (4f): Yield 70%; brown powder; m.p. 297 – 300 °C; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.76 (s, 1H, −$\underline{CH}$=C−), 8.53 (s, 1H, −$\underline{CH}$=C−), 8.13 (d, *J* (H,H) = 7 Hz, 1H, Ar), 7.62 (d, *J* (H,H) = 7.5, 1H, Ar), 7.58 (d, *J* (H,H) = 9.5 Hz, 1H, Ar), 7.52 (t, *J* (H,H) = 7.5 Hz, 1H, Ar), 7.37 (d, *J* (H,H) = 8 Hz, 1H, Ar), 7.31 (t, *J* (H,H) = 7.5 Hz, 1H, Ar), 7.21 (t, *J* (H,H) = 6.5 Hz, 1H, Ar), 6.79 (t, *J* (H,H) = 6.5 Hz, 1H, Ar); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 160.2, 153.3, 145.4, 138.5, 138.3, 131.63, 128.6, 126.5, 126.0, 124.9, 121.1, 120.0, 117.4, 116.7, 114.2, 112.8; FT-IR (KBr) ν_{max} = 1726 cm^{-1} (C=O lactone), 1636 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 345 nm; HRMS (ESI m/z) Calcd. for $C_{16}H_{10}N_2O_2$ $[M+H]^+$ 263.0815, found 263.0820.



8-ethoxy-3-(imidazo[1,2-a]pyridin-2-yl)-2H-chromen-2-one (4g): Yield: 41%, dark brown powder; m.p. = 157 – 159 ºC, RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.75 (s, 1H, −$\underline{CH}$=C−), 8.57 (s, 1H, −$\underline{CH}$=C−), 7.14 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 7.59 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 7.20 (m, 3H, Ar), 7.07 (d, 1H, Ar), 6.78 (t, *J* (H,H) = 6.5 Hz, 1H, Ar), 4.21 (q, *J* (H,H) = 7 Hz, 2H, −$\underline{CH_2}$−CH_3), 1.52 (t, *J* (H,H) = 7 Hz, 3H, −CH_2−$\underline{CH_3}$); RMN ^{13}C (1 25 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 159.65, 146.40, 145.20, 143.01, 138.36, 138.33, 126.28, 125.80, 124.53, 121.09, 120.54, 119.86, 117.21, 114.56, 114.07, 112.62, 65.07, 14.90. FT-IR (KBr) ν_{max} = 1724 cm^{-1} (C=O lactone); UV−Vis (MeOH) λ_{max} = 340 nm; HRMS (ESI m/z) Calcd. for $C_{18}H_{15}N_2O_3$ $[M+H]^+$ 307.1077, found 307.1068.

3. General procedure for coumarin-imidazo[1,2-a]pyridine-3-carbaldehyde derivatives 5a-e.

Synthesis of **5a-e** was carried out using the Vilsmeier-Haack formilation.[3] In a 50 mL round bottom flask was added **4a-e** derivatives (1mmol), then was purged with nitrogen, 15 mL of DMF was added and placed in agitation. In a second 50 mL round bottom flask with nitrogen atmosphere DMF was added and placed in an ice bath for 10 min (2.2 mmol). $POCl_3$ were slowly added (2.4 mmol) and the mixture was kept in constant agitation in an ice bath for 15 min. Finally, the solution from the first flask was transferred to the second flask through a steel cannula and heated to 60 °C for 1 h. The reaction was treated with 10% NaOH solution and a solid product was formed. The product was filtered and purified using a chromatographic column with an Hex/AcOEt 70:30 elution system.


2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)imidazo[1,2-a]pyridine-3-carbaldehyde **(5a):** Yield 94%; yellow powder; m.p. 228 – 229.6 °C; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 10.22 (s, 1H, −COH), 9.61 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 8.24 (s, 1H, −CH=C−), 7.70 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.50 (t, *J* (H,H) = 8.5-1.5 Hz, 1H, Ar), 7.36 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.05 (t, *J* (H,H) = 6,1 Hz, 1H, Ar), 6.60 (d, *J* (H,H) = 9, 2.5 Hz, 1H, Ar), 6.50 (s, *J* (H,H) = 2.5, 1H, −CH=C−), 3.43 (q, *J* (H,H) = 7.5 Hz, 4H, $-CH_2-CH_3$), 1.21 (t, *J* (H,H) = 7.5 Hz, 6H, CH_3); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 181.5, 177.2, 171.7, 171.1, 167.6, 165.6, 150.1, 149.9, 148.8, 141.0, 137.0, 135.1, 132,6, 129.5, 128.7, 97.1, 45.2, 12.7; FT-IR (KBr) ν_{max} = 2736 cm^{-1} (H−C=O), 1698 cm^{-1} (C=O lactone), 1647 cm^{-1} (H−C=O); UV−Vis (MeOH) λ_{max} = 422 nm; HRMS (ESI m/z) Calcd. for $C_{20}H_{18}N_4O_3$ $[M+H]^+$ 362.1499, found 362.1495.

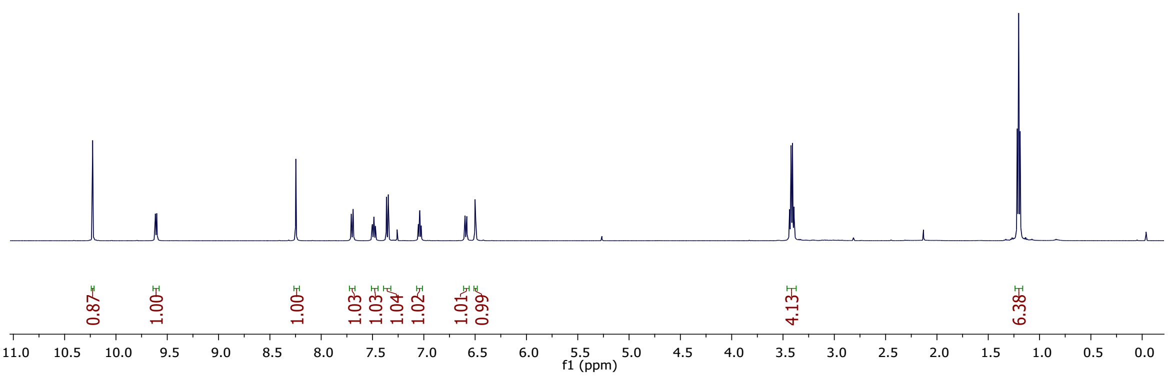


Figure SI-1. ^{1}H NMR spectra of **5a** on $CDCl_3$ 500 MHz

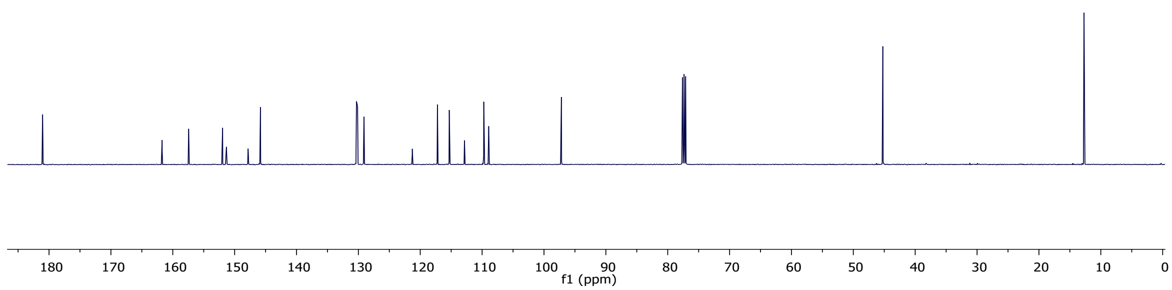


Figure SI-2. ^{13}C NMR spectra of **5a** on $CDCl_3$ 125 MHz.

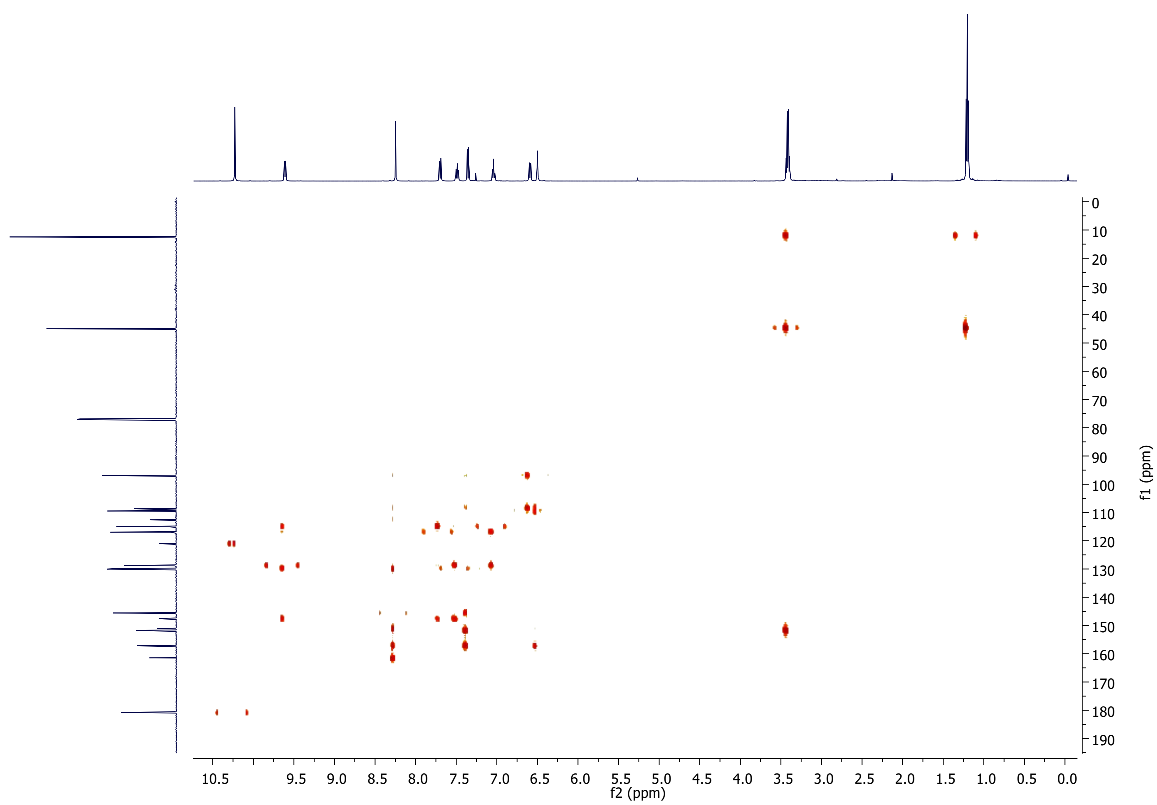


Figure SI-3. HMBC NMR spectra of **5a** on $CDCl_3$

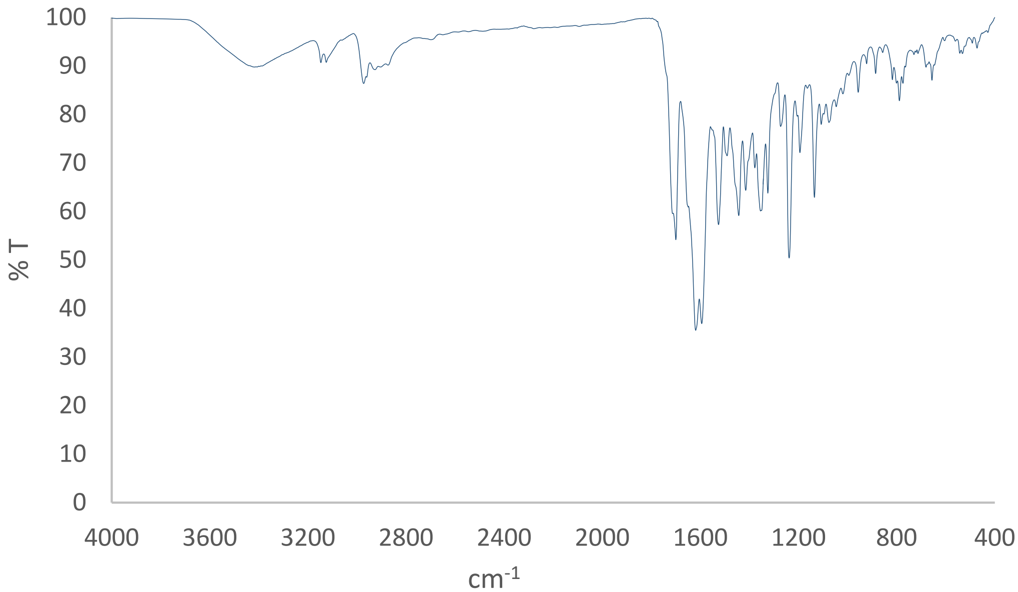


Figure SI-4. IR spectra for **5a** in KBr.

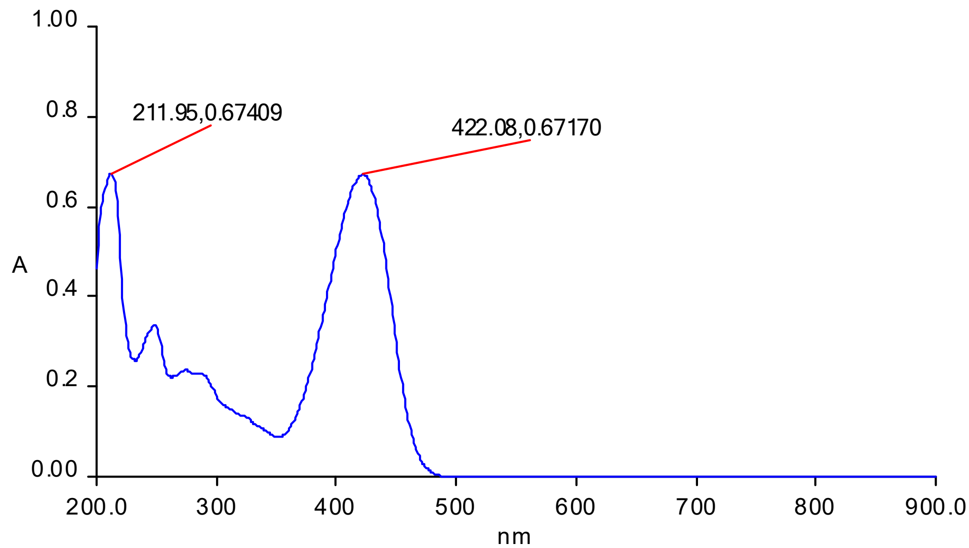


Figure SI-5. UV-Vis spectra of **5a** in MeOH.

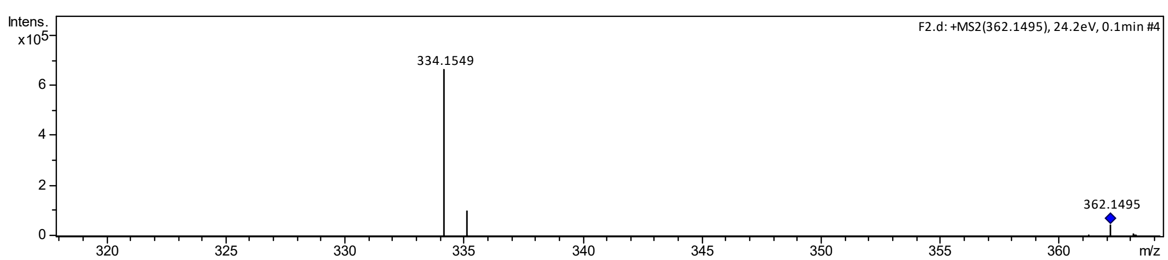
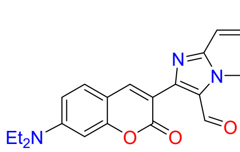


Figure SI-6. ESI-MS chromatogram of **5a**.



2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-7-methylimidazo[1,2-a]pyridine-3-carbaldehyde (5b): Yield 97%; yellow powder; m.p. 174 – 176°C; RNM ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 10.35 (s, 1H, −CO<u>H</u>), 9.65 (d, *J* (H,H) = 7 Hz, 1H, Ar), 8.79 (s, 1H, −<u>CH</u>=C−), 8.01 (s, 1H, Ar), 7.50 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.20 (d, *J* (H,H) = 7 Hz, 1H, Ar), 6.67 (dd, *J* (H,H) = 9, 2.5 Hz, 1H, Ar), 6.51 (sd, *J* (H,H) = 2 Hz, 1H, Ar), 3.49 (q, *J* (H,H) = 7 Hz, 4H, −$\underline{CH_2}$−CH_3), 2.59 (s, 3H, $\underline{CH_3}$), 1.26 (t, *J* (H,H) = 7 Hz, 6H, $\underline{CH_3}$); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 181.6. 160.9, 158.1, 153.3, 148.1, 131.9, 128.8, 120.5, 119.3, 113.4, 110.5, 109.0, 97.1, 45.5, 29.2, 12.8. FT-IR (KBr) ν_{max} = 2687 cm^{-1} (<u>H−C</u>=O), 1716 cm^{-1} (C=O lactone), 1600 cm^{-1} (−O−<u>C=O</u>); UV−Vis (MeOH) λ_{max} = 422 nm.

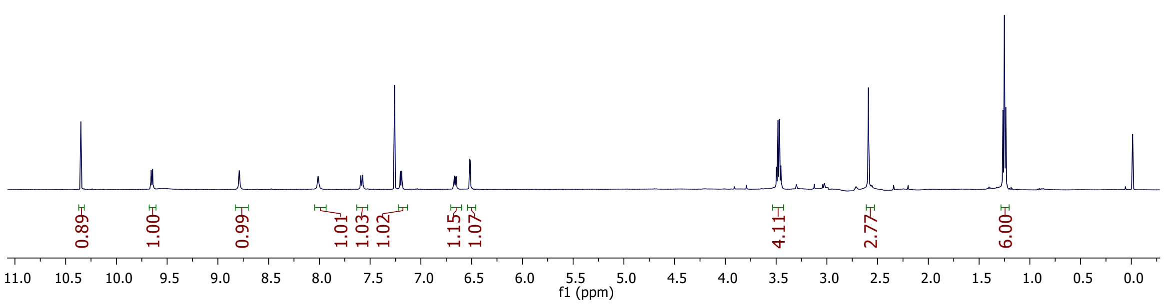


Figure SI-7. ^{1}H NMR spectra of **5b** on $CDCl_3$ 500 MHz

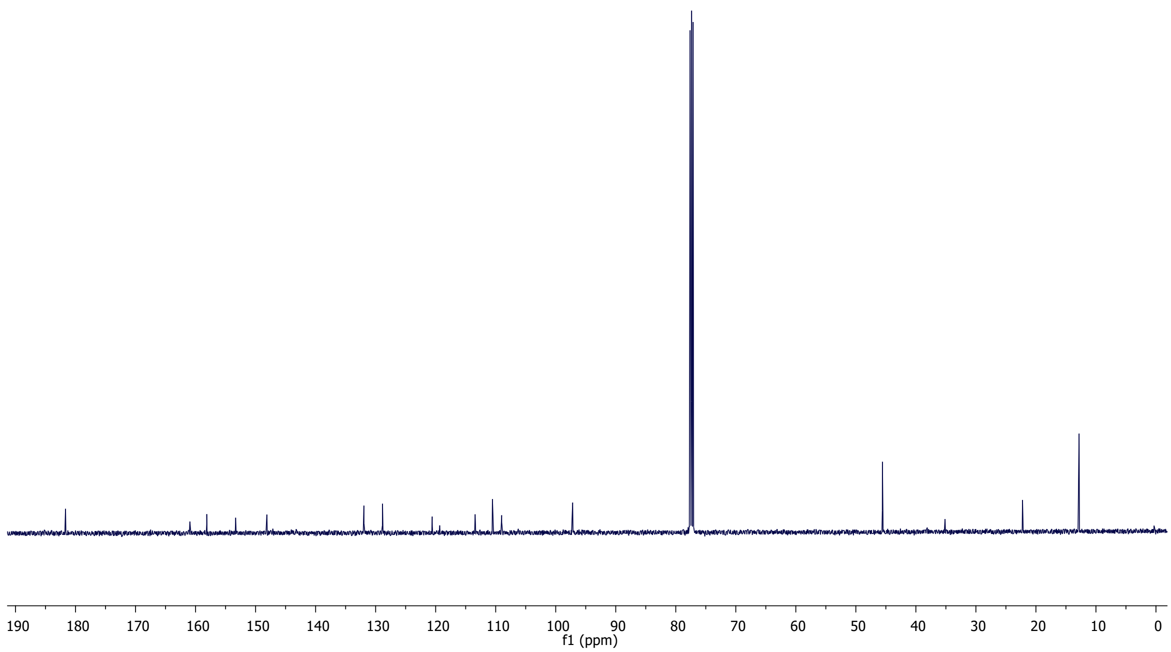


Figure SI-8. ^{13}C NMR spectra of **5b** on $CDCl_3$ 125 MHz.

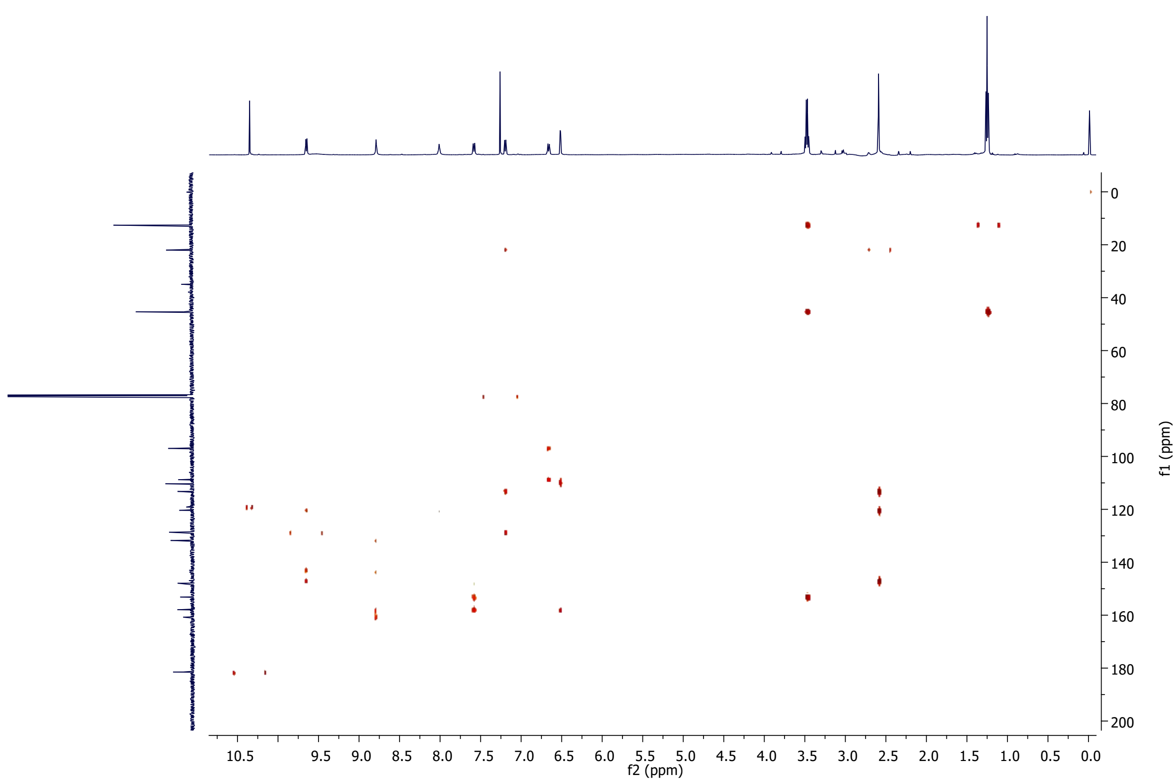


Figure SI-9. HMBC NMR spectra of **5b** on $CDCl_3$

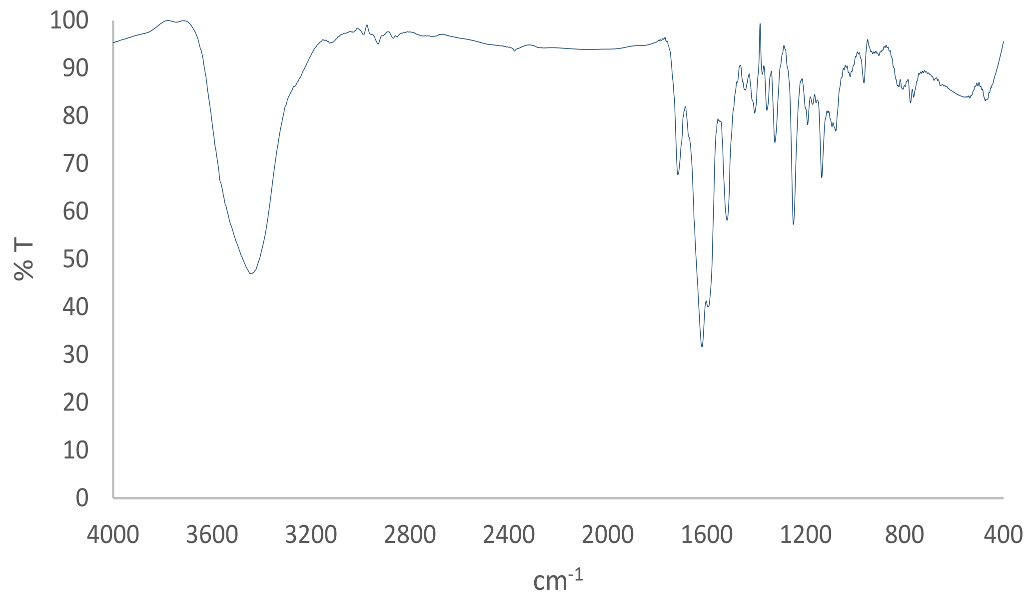


Figure SI-10. IR spectra for **5b** in KBr.

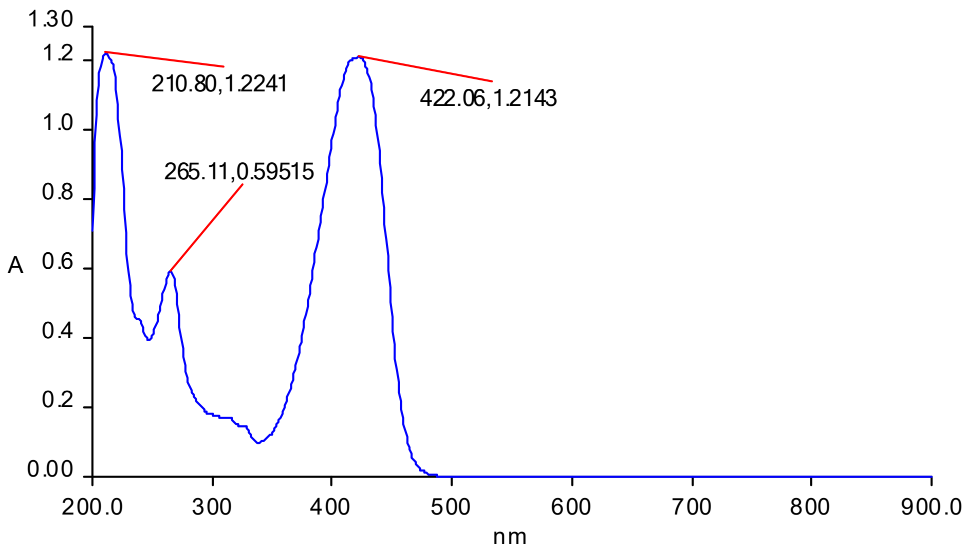
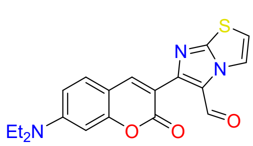


Figure SI-11. UV-Vis spectra of **5b** in MeOH.



6-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)imidazo[2,1-b]thiazole-5-carbaldehyde (5c): Yield 60%; brown powder; m.p. 194 – 196°C; ^{1}H RMN (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 10.20 (s, 1H, −CO<u>H</u>), 8.38 (d, *J* (H,H) = 4.5 Hz, 1H, −<u>CH</u>=C−), 8.26 (s, 1H, −<u>CH</u>=C−), 7.35 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.98 (d, *J* (H,H) = 4.5 Hz, 1H, −<u>CH</u>=C−), 6.60 (dd, *J* (H,H) = 9, 2 Hz, 1H, Ar), 6.49 (sd, *J* = 2 Hz, 1H, Ar) , 3.43 (q, *J* (H,H) = 7 Hz, 4H, −<u>CH_2</u>−CH_3), 1.21 (t, *J* (H,H) = 7 Hz, 6H, <u>CH_3</u>); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 180.5, 161.4, 157.1, 155.0, 151.8, 150.3, 144.8, 130.2, 124,7, 122.0, 114.4, 113.0, 109.7, 108.9, 97.1, 45.2, 12.7; FT-IR (KBr) ν_{max} = 2743 cm^{-1} (<u>H−C</u>=O), 1699 cm^{-1} (C=O lactone), 1619 cm^{-1} (H−<u>C=O</u>); UV–Vis (MeOH) λ_{max} = 425 nm; HRMS (ESI m/z) Calcd. for $C_{19}H_{17}N_3O_3S$ $[M+H]^+$ 368.1063, found 368.1062.

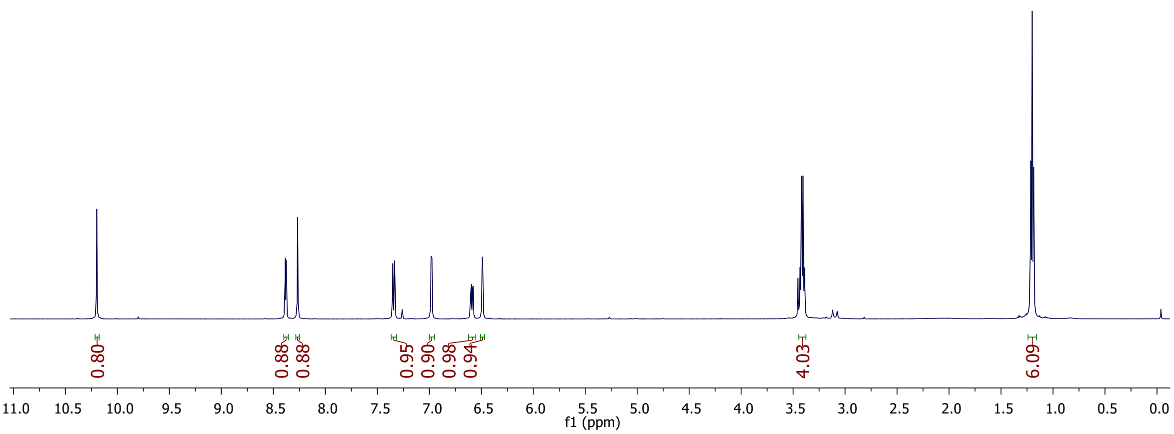


Figure SI-12. ^{1}H NMR spectra of **5c** on $CDCl_3$ 500 MHz

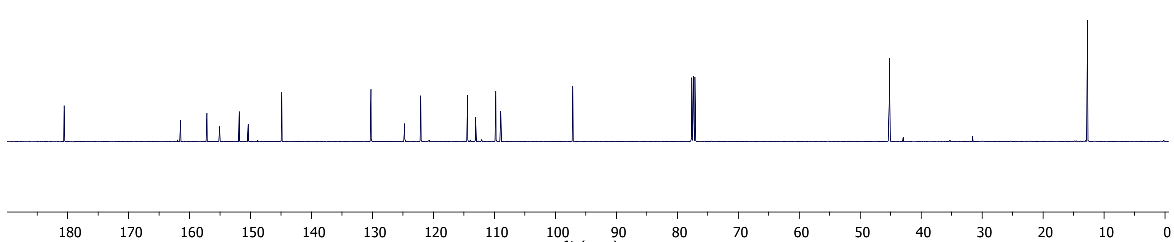


Figure SI-13. ^{13}C NMR spectra of **5b** on $CDCl_3$ 125 MHz.

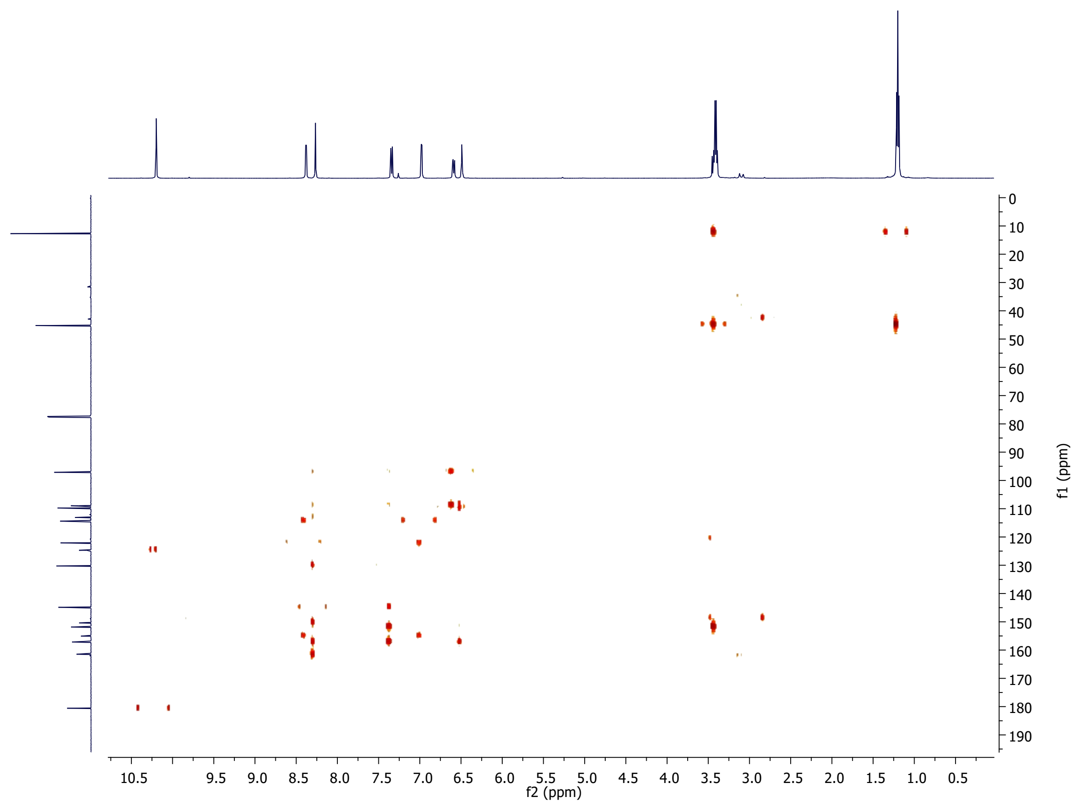


Figure SI-14. HMBC NMR spectra of **5c** on $CDCl_3$

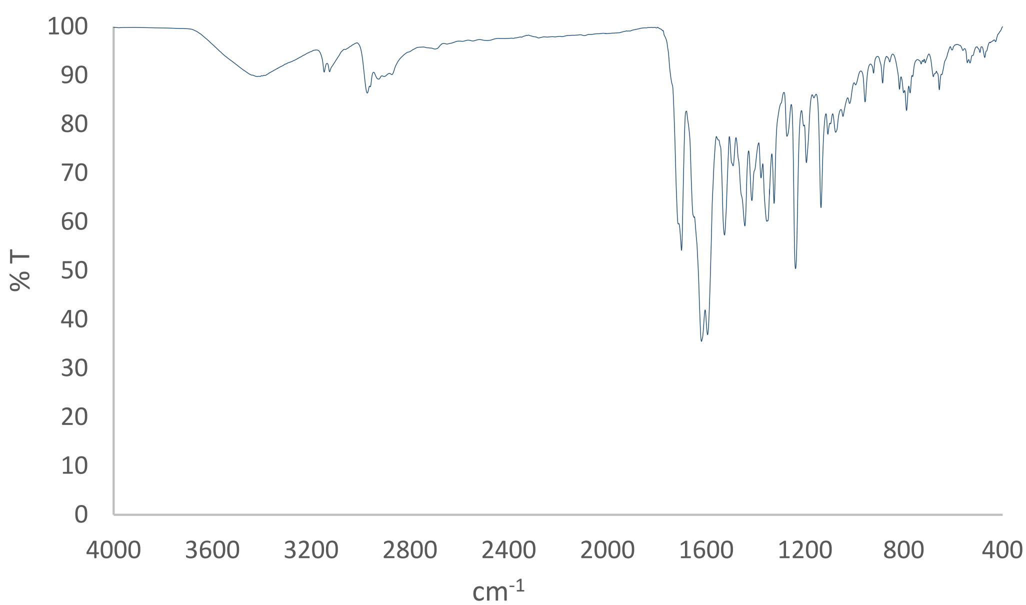


Figure SI-15. IR spectra for **5c** in KBr.

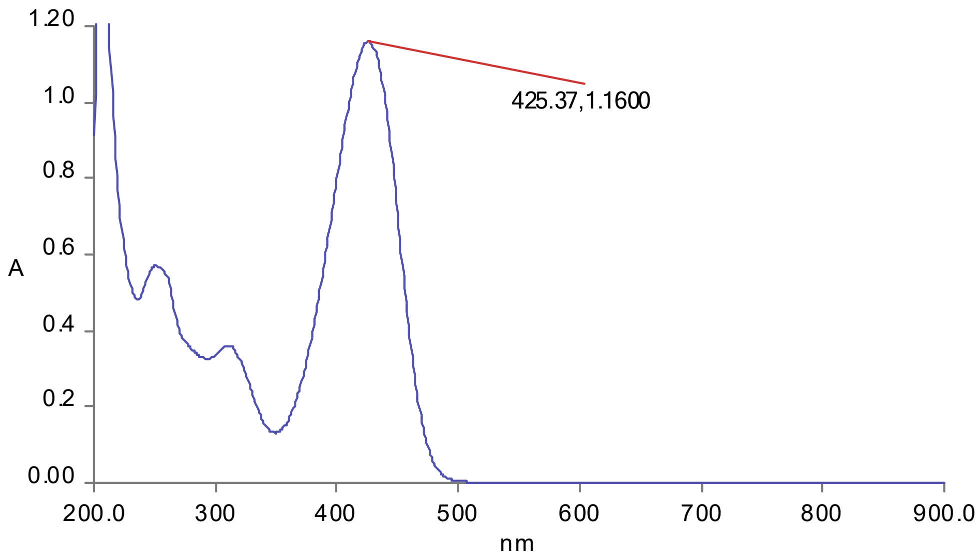


Figure SI-16. UV-Vis spectra of **5c** in MeOH.

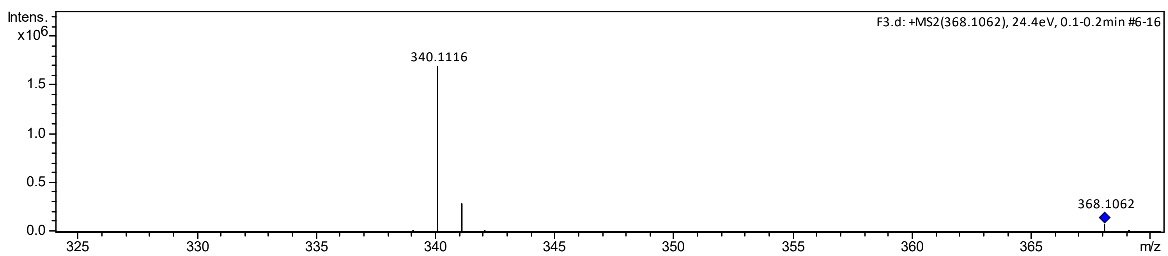
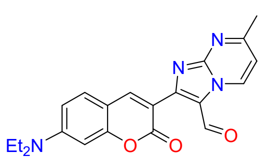


Figure SI-17. ESI-MS chromatogram of **5c**.



2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-7-methylimidazo[1,2-a]pyrimidine-3-carbaldehyde (5d): Yield 76%; orange powder; m.p. 778-779.3°C; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 10.41 (s, 1H, −CO<u>H</u>), 9.66 (d, *J* (H,H) = 7.5 Hz, 1H, Ar), 8.52 (d, *J* (H,H) = 7.5 Hz, 1H, Ar), 8.43 (s, 1H, −<u>CH</u>=C−), 7.44 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.66 (dd, *J* (H,H) = 9, 2.5 Hz, 1H, Ar), 6.52 (sd, *J* = 2.5 Hz, 1H, Ar), 3.49 (q, *J* (H,H) = 7.5 Hz, 4H, −<u>CH_2</u>−CH_3), 2.16 (s, 3H, <u>CH_3</u>), 1.26 (t, *J* (H,H) = 7.5 Hz, 6H, <u>CH_3</u>); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 182.6, 161.3, 161.3, 157.7, 152.6, 146.7, 138.6, 130.9, 111.3, 110.2, 109.0, 107.1, 97.2, 53.7, 45.4, 19.8; FT-IR (KBr) ν_{max} = 1711 cm^{-1} (C=O lactone), 1619 cm^{-1} (H−<u>C=O</u>); UV−Vis (MeOH) λ_{max} = 431 nm; HRMS (ESI m/z) Calcd. for $C_{21}H_{20}N_4O_3$ $[M+H]^+$ 376.1635, found 376.1638.

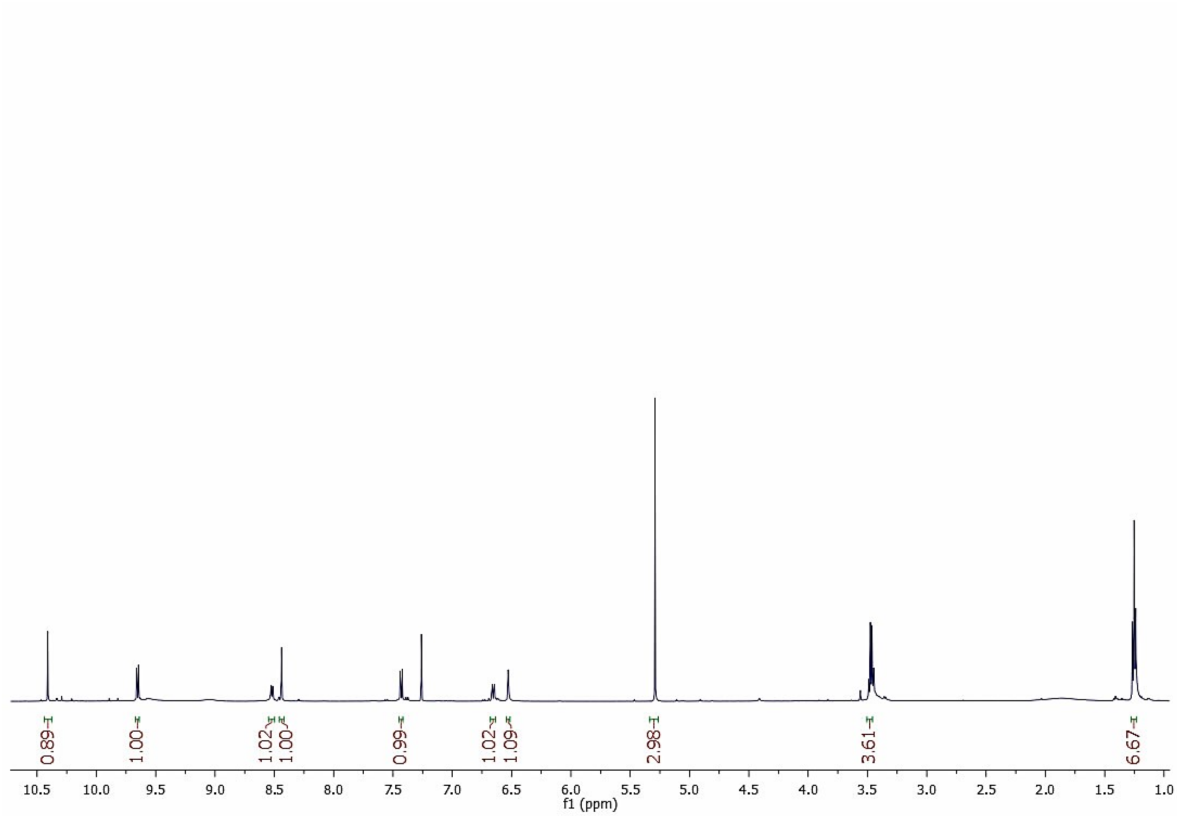


Figure SI-18. ^{1}H NMR spectra of **5d** on $CDCl_3$ 500 MHz

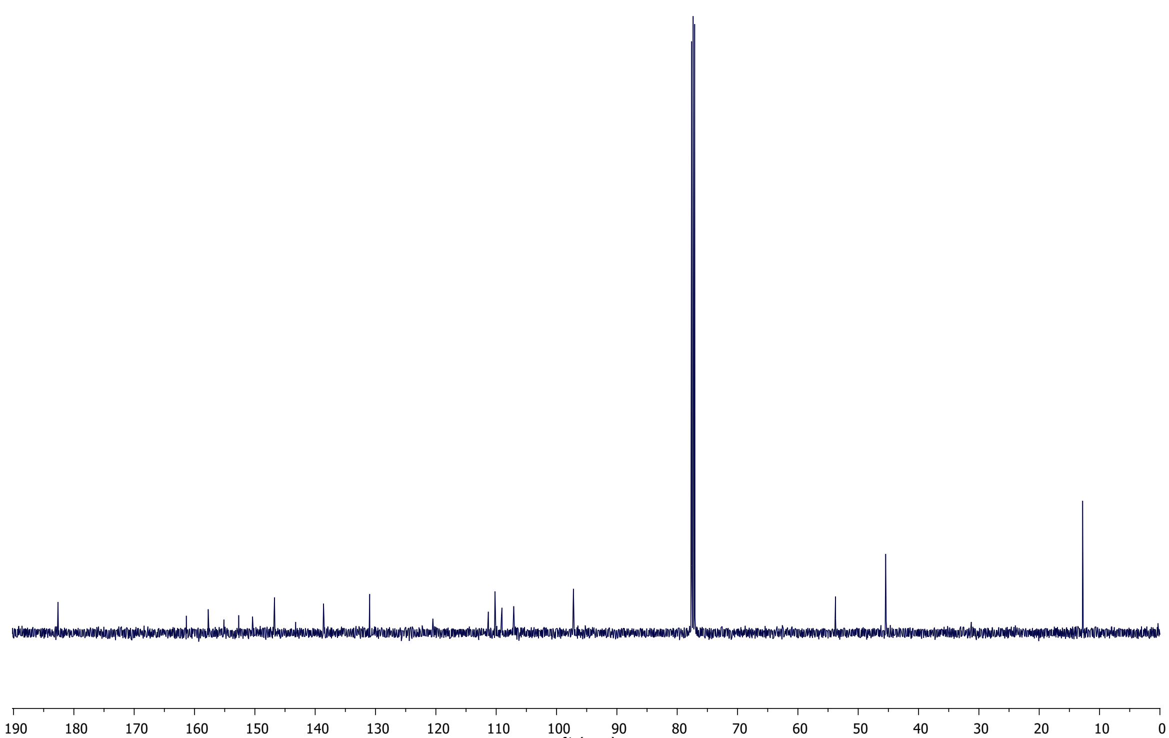


Figure SI-19. ^{13}C NMR spectra of **5d** on $CDCl_3$ 125 MHz.

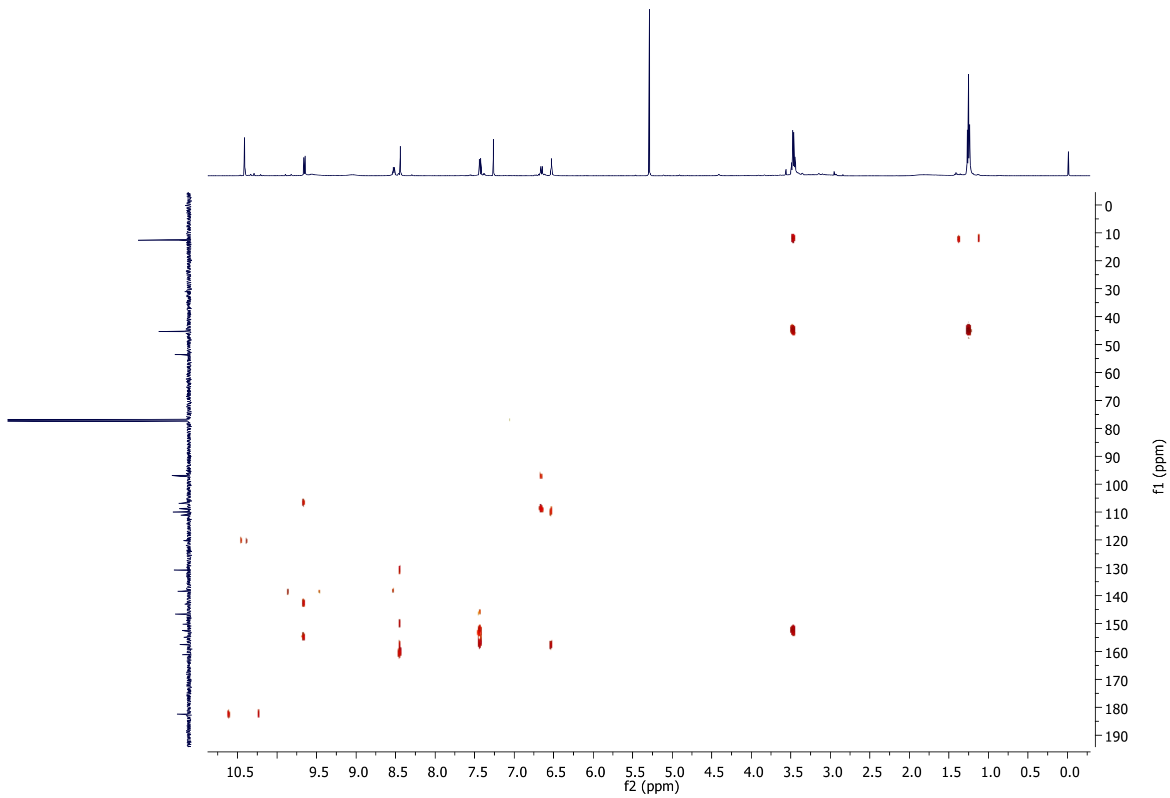


Figure SI-20. HMBC NMR spectra of **5d** on $CDCl_3$

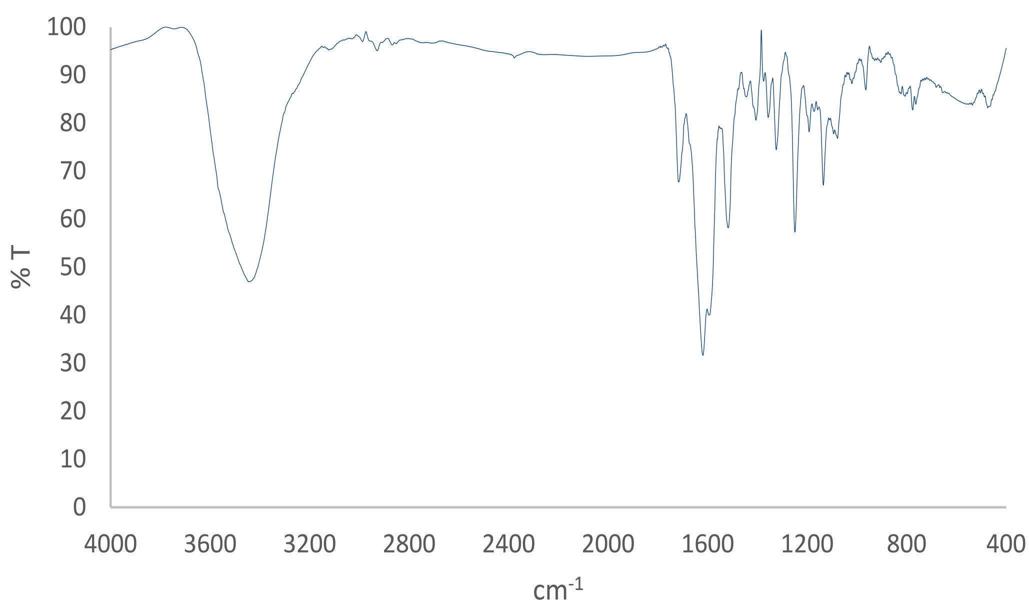


Figure SI-21. IR spectra for **5b** in KBr.

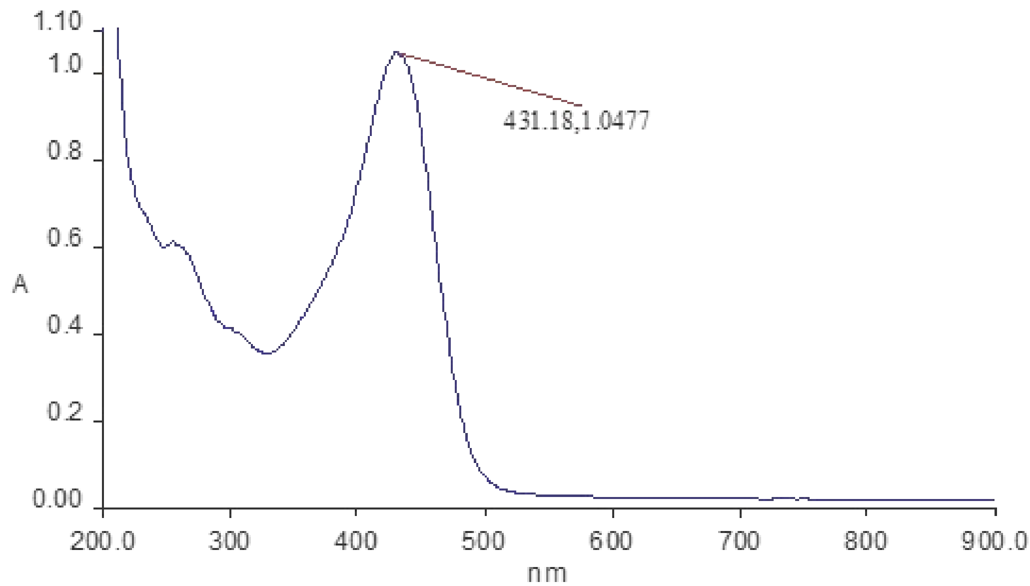


Figure SI-22. UV-Vis spectra of **5d** in MeOH.

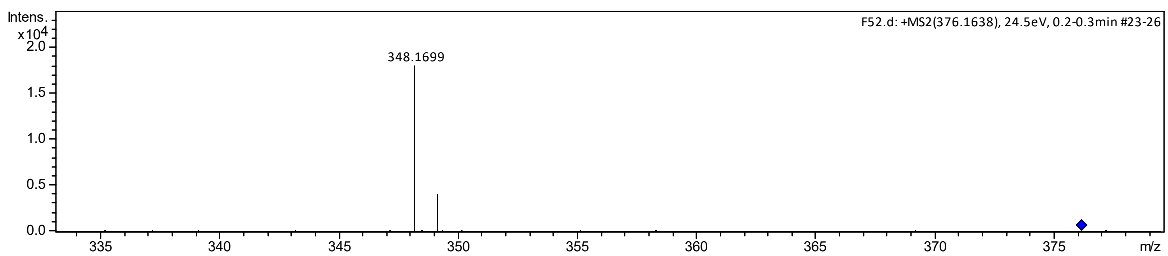
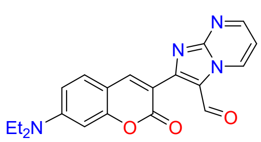


Figure SI-23. ESI-MS chromatogram of **5e**.



2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)imidazo[1,2-a]pyrimidine-3-carbaldehyde (5e): Yield 63%; orange powder; m.p. 263 – 264.5°C; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 10.43 (s, 1H, −CO<u>H</u>), 9.93 (dd, *J* (H,H) = 7, 2 Hz, 1H, Ar), 8.76 (d, *J* (H,H) = 2 Hz, 1H, Ar), 8.57 (s, 1H, −<u>CH</u>=C−), 7.43 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.13 (m, 1H, Ar), 6.65 (dd, *J* (H,H) = 9, 2.5 Hz, 1H, Ar), 6.54 (sd, *J* (H,H) = 2.5 Hz, 1H, Ar), 3.48 (q, *J* (H,H) = 7 Hz, 4H, −$\underline{CH_2}$−CH_3), 1.26 (t, *J* (H,H) = 7 Hz, 6H, $\underline{CH_3}$); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 182.8. 161.7, 157.7, 154.2, 152.3, 151.7, 150.4, 147.0, 136.9, 130.8, 119.3, 112.3, 111.3, 110.1, 109.2, 97.2, 45.3, 12.8. FT-IR (KBr) ν_{max} = 2700 cm^{-1} (<u>H−C</u>=O), 1714 cm^{-1} (C=O lactone), 1618 cm^{-1} (H−<u>C=O</u>); UV–Vis (MeOH) λ_{max} = 431 nm.

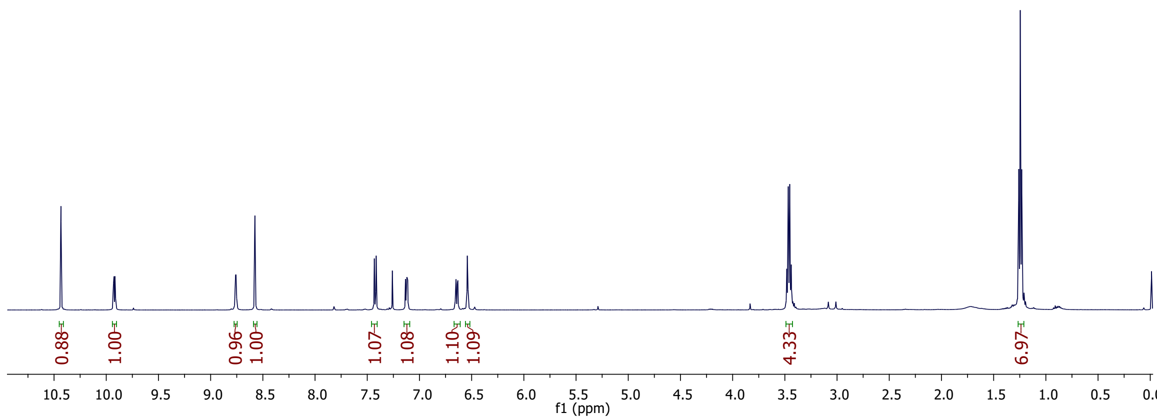


Figure SI-24. ^{1}H NMR spectra of **5e** on $CDCl_3$ 500 MHz

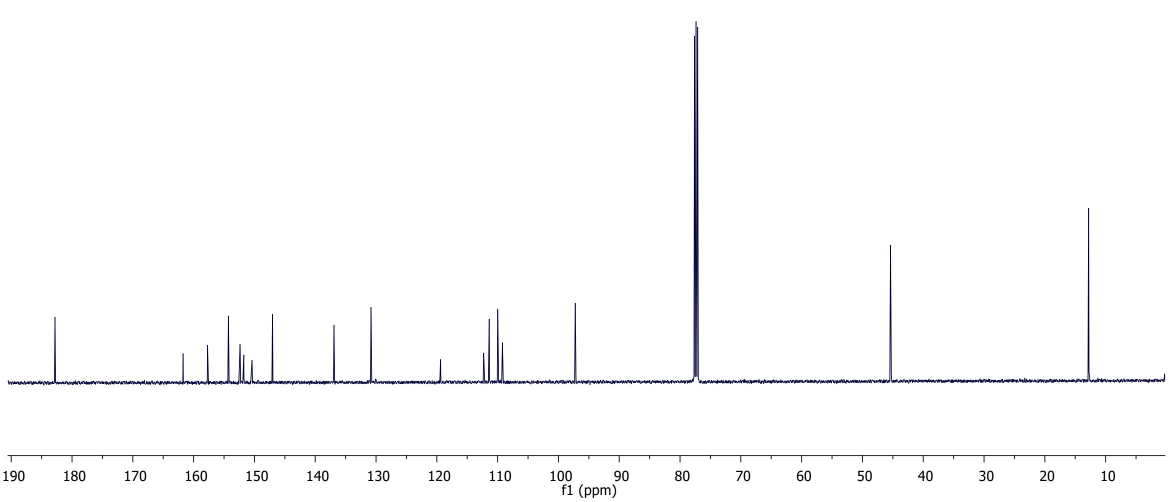


Figure SI-25. ^{13}C NMR spectra of **5e** on $CDCl_3$ 125 MHz.

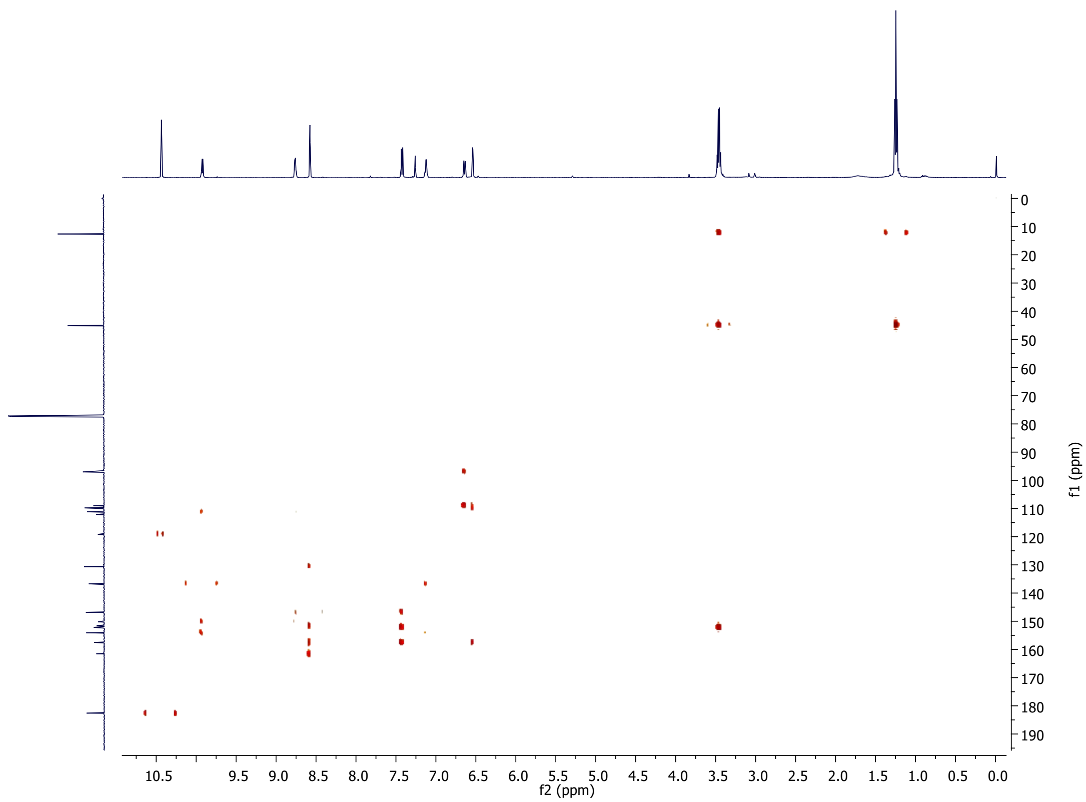


Figure SI-26. HMBC NMR spectra of **5e** on $CDCl_3$

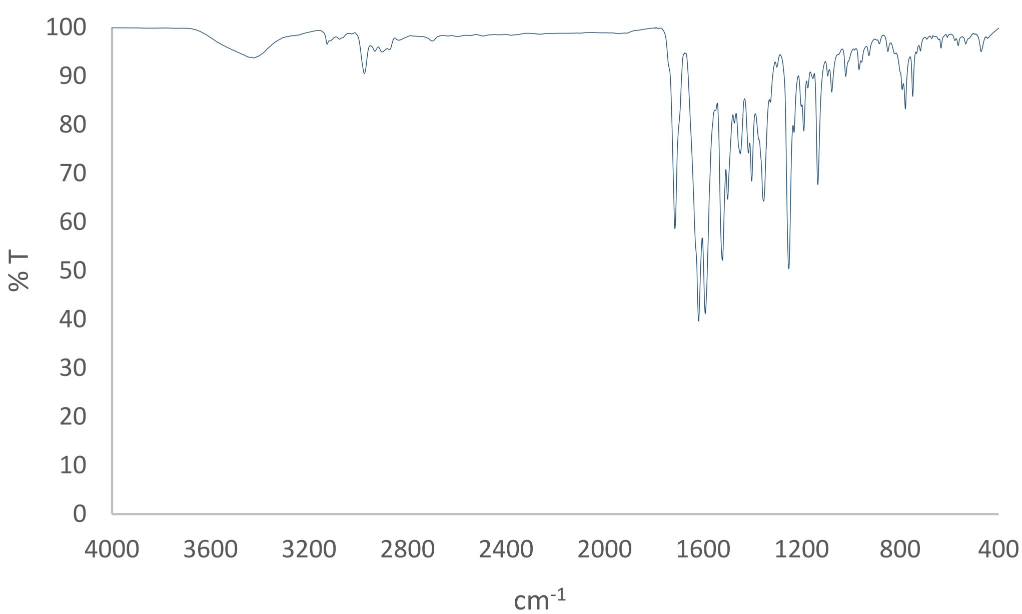


Figure SI-27. IR spectra for **5e** in KBr.

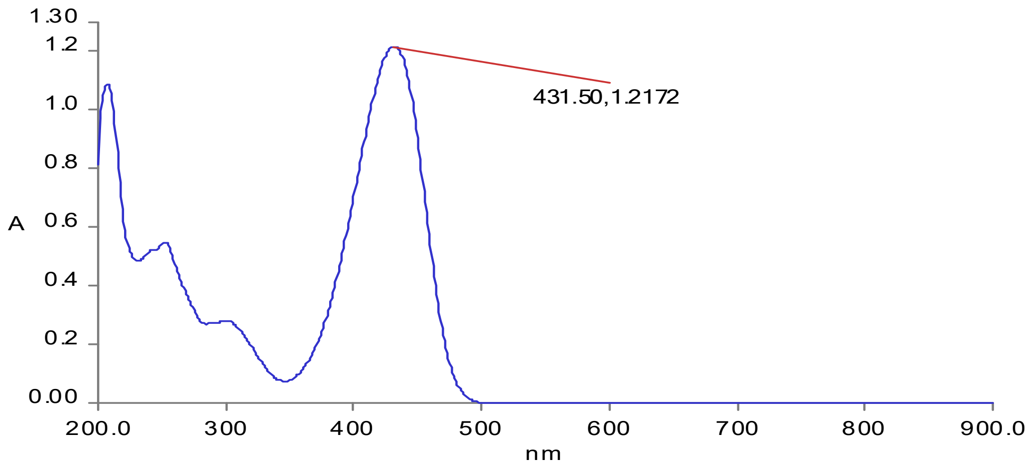
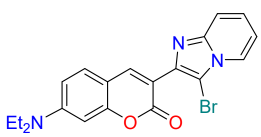


Figure SI-28. UV-Vis spectra of **5e** in MeOH.

4. General procedure for 3-bromo-2-(cumarin-3-il)imidazo[1,2-*a*]pyridine derivatives 6a-h

In a 15 mL round bottom flask, **4a-h** derivatives (0.6 mmol) and acetic acid was added (4 mL), the solution was maintained in agitation and heating at 50 °C for 5 minutes. Later, Br_2 were added (0.7 mmol) and a brown precipitate was generated. The solid was filtered, dissolved in dichloromethane and washed with a saturated solution of $NaHCO_3$. The organic phase was concentrated and purified by chromatographic column in Hex/AcOEt 80:20 elution system.



3-(3-bromoimidazo[1,2-a]pyridin-2-yl)-7-(diethylamino)-2H-chromen-2-one (6a): Yield 97%; yellow powder; m.p. = 160 – 163 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.155 (d, *J* (H,H) = 8 Hz, 1H, Ar), 8.029 (s, 1H, −CH=C−), 7.625 (d, *J* (H,H) = 7.5 Hz, 1H, Ar), 7.339 (d, *J* (H,H) = 7 Hz, 1H, Ar), 7.25 (t, *J* (H,H) = 7 Hz, 1H, Ar), 6.932 (t, *J* (H,H) = 7 Hz, 1H, Ar), 6.604 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.535 (s, 1H, Ar), 3.427 (q, *J* (H,H) = 7 Hz, 4H, $-CH_2-CH_3$), 1.221 (t, *J* (H,H) = 7 Hz, 6H, CH_3), RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 160.128, 156.883, 151.098, 145.350, 144.370, 139.570, 129.495, 125.103, 123.997, 117.613, 113.432, 113.196, 109.111, 108.688, 97.151, 44.935, 12.522; FT-IR (KBr) ν_{max} = 3027 cm^{-1} (C−H Ar), 2968 cm^{-1} (C−H Aliphatic), 1711 cm^{-1} (C=O lactone), 1598 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 402.41 nm; HRMS (ESI m/z) Calcd. for $C_{20}H_{19}BrN_3O_2$ $[M+H]^+$ 412.0655, found 412.0640.

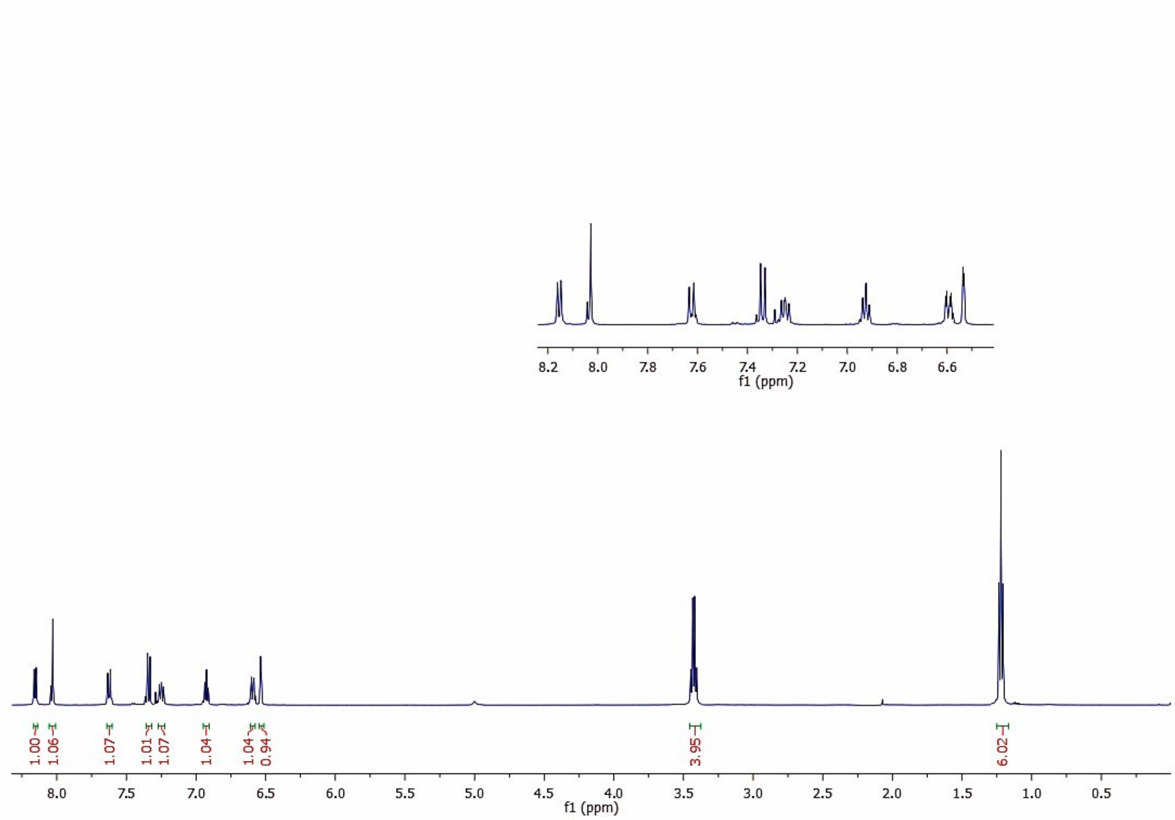


Figure SI-29. ^{1}H NMR spectra of **6a** on $CDCl_3$ 500 MHz

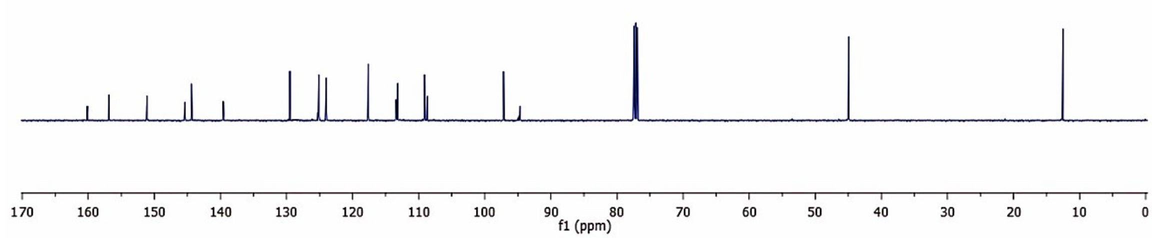


Figure SI-30. ^{13}C NMR spectra of **6a** on $CDCl_3$ 125 MHz.

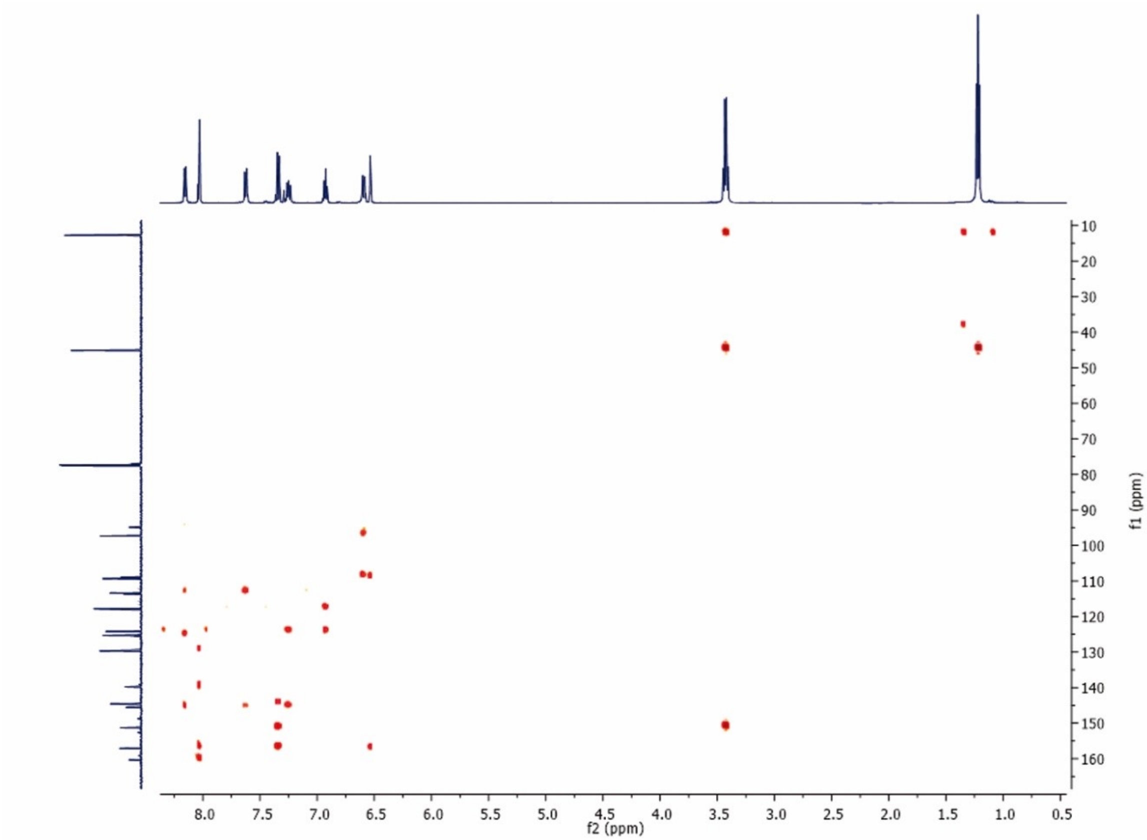


Figure SI-31. HMBC NMR spectra of **6a** on $CDCl_3$

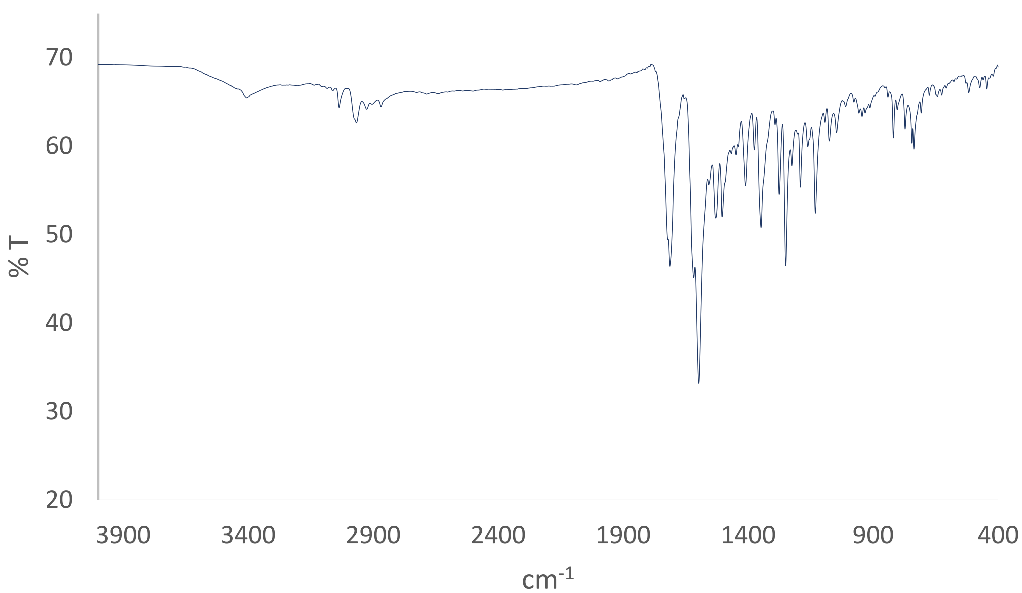


Figure SI-32. IR spectra for **6a** in KBr.

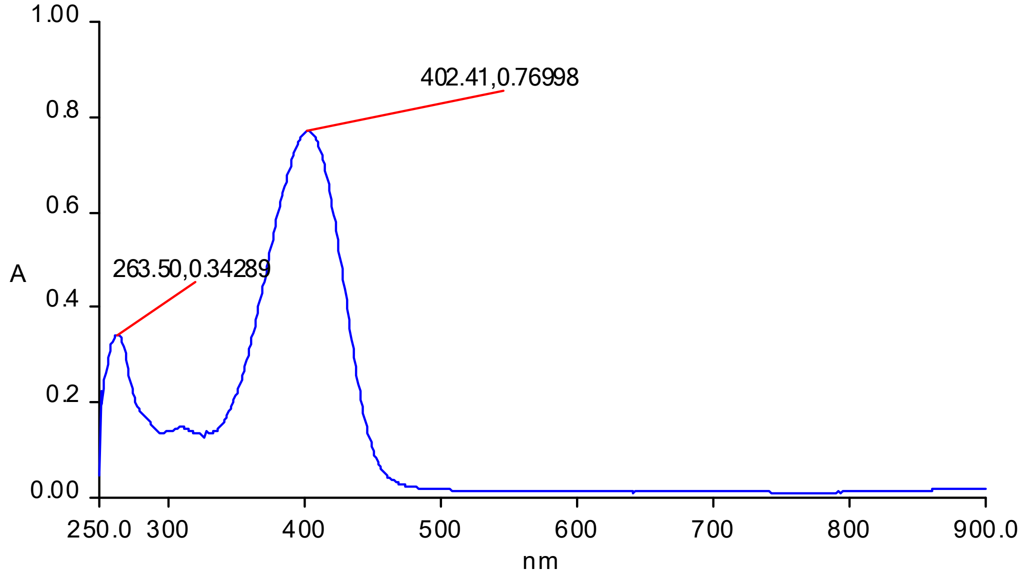


Figure SI-33. UV-Vis spectra of **6a** in MeOH.

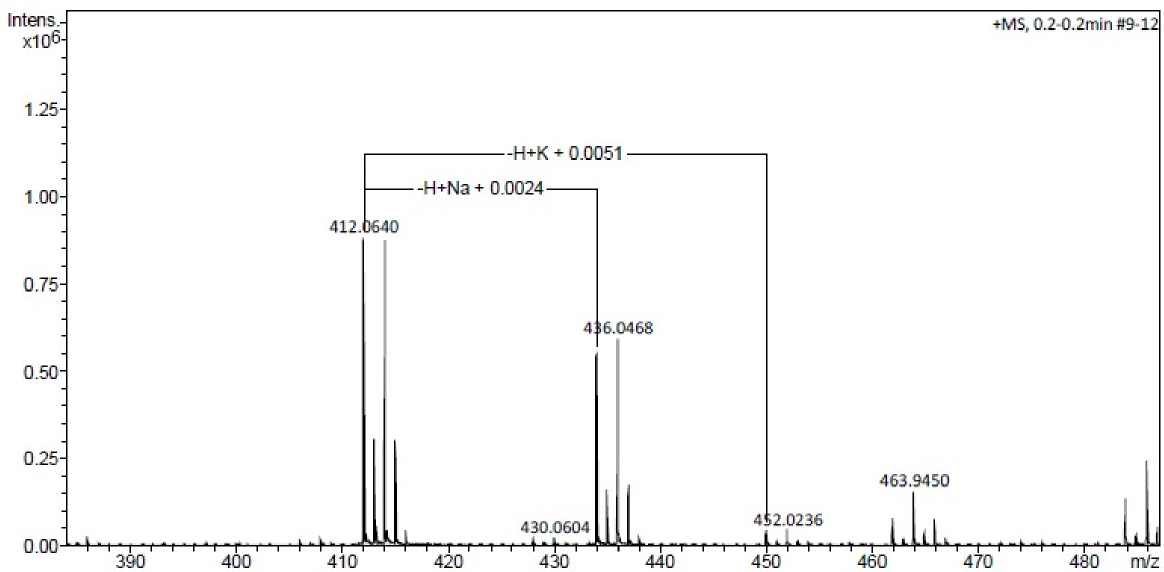
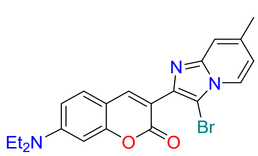


Figure SI-34. ESI-MS chromatogram of **6a**.



3-(3-bromo-7-methylimidazo[1,2-a]pyridin-2-yl)-7-(diethylamino)-2H-chromen-2-one (6b): Yield 95%; yellow powder; m.p. = 171 – 174 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.004 – 7.988 (m, 2H, Ar), 7.335 – 7.297 (m, 2H, Ar), 6.726 (d, *J* (H,H) = 7 Hz, 1H, Ar), 6.576 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.509 (s, 1H, Ar), 3.407 (q, *J* (H,H) = 7 Hz, 4H, −$\underline{CH_2}$−CH_3), 2.396 (s, 3H, $\underline{CH_3}$), 1.194 (t, *J* (H,H) = 7 Hz, 6H, $\underline{CH_3}$); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 160.116, 0156.874, 151.064, 145.778, 144.159, 139.287, 136.121, 129.449 , 123.179, 116.035, 115.786, 113.825, 109.101, 108.804, 97.238, 93.792, 44.946 , 21.409, 12.556; FT-IR (KBr) ν_{max} = 3079 cm^{-1} (C−H Ar), 2925 cm^{-1} (C−H Aliphatic), 1723 cm^{-1} (C=O lactone), 1608 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 406.16 nm; HRMS (ESI m/z) Calcd. for $C_{21}H_{21}BrN_3O_2$ $[M+H]^+$ 426.0812, found 426.0844.

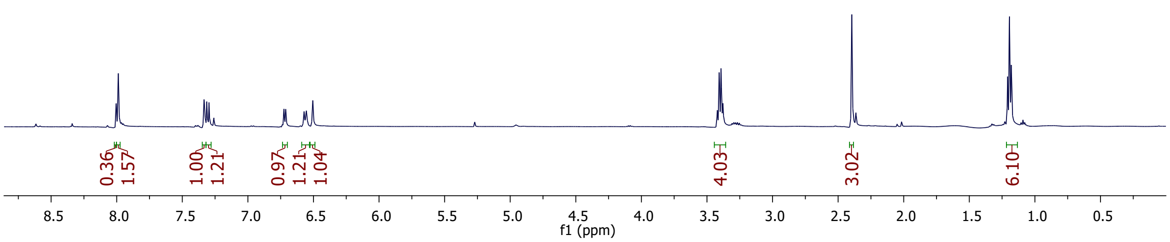


Figure SI-35. ^{1}H NMR spectra of **6b** on $CDCl_3$ 500 MHz

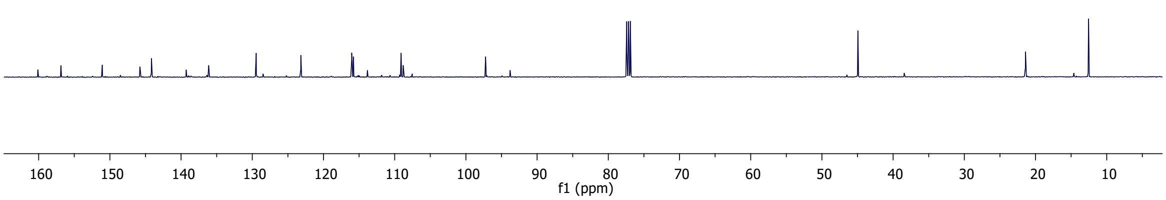


Figure SI-36. ^{13}C NMR spectra of **6b** on $CDCl_3$ 125 MHz.

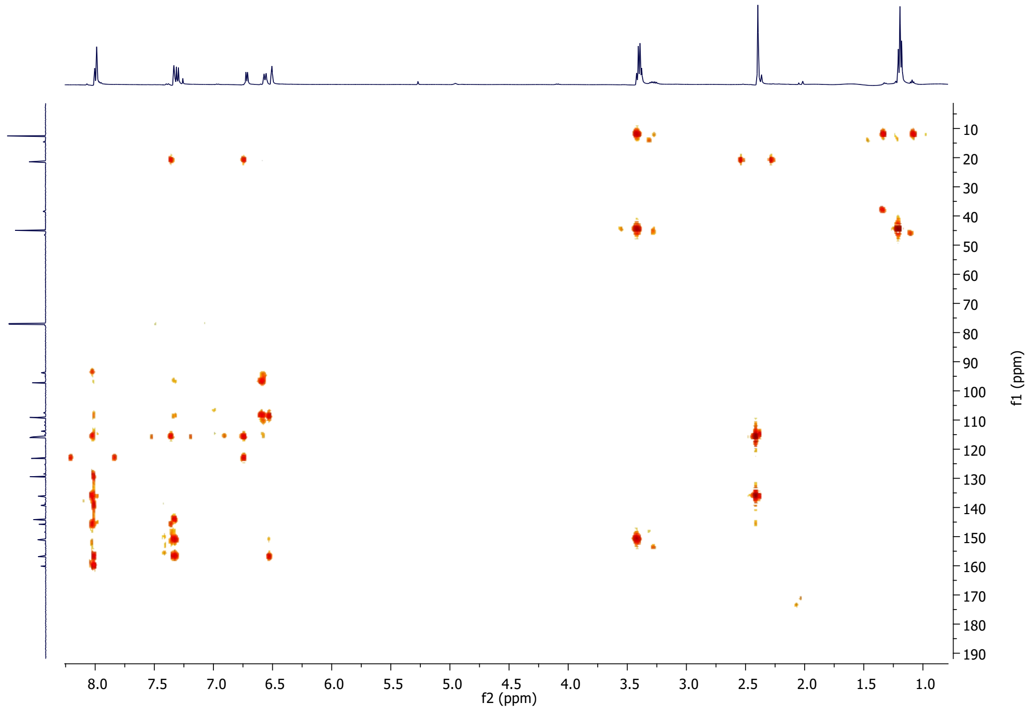


Figure SI-37. HMBC NMR spectra of **6b** on $CDCl_3$

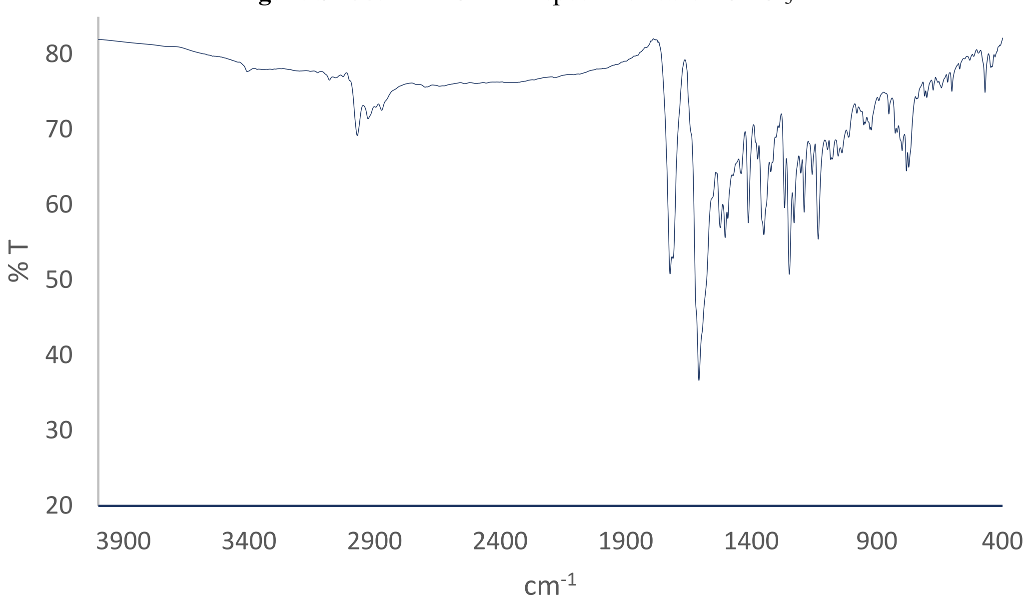


Figure SI-38. IR spectra for **6b** in KBr.

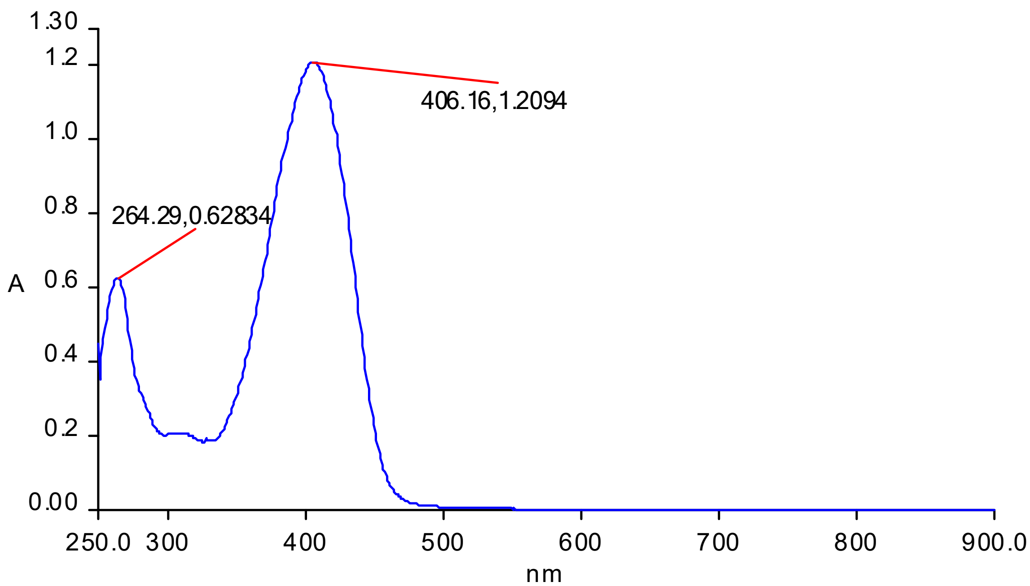


Figure SI-39. UV-Vis spectra of **6b** in MeOH.

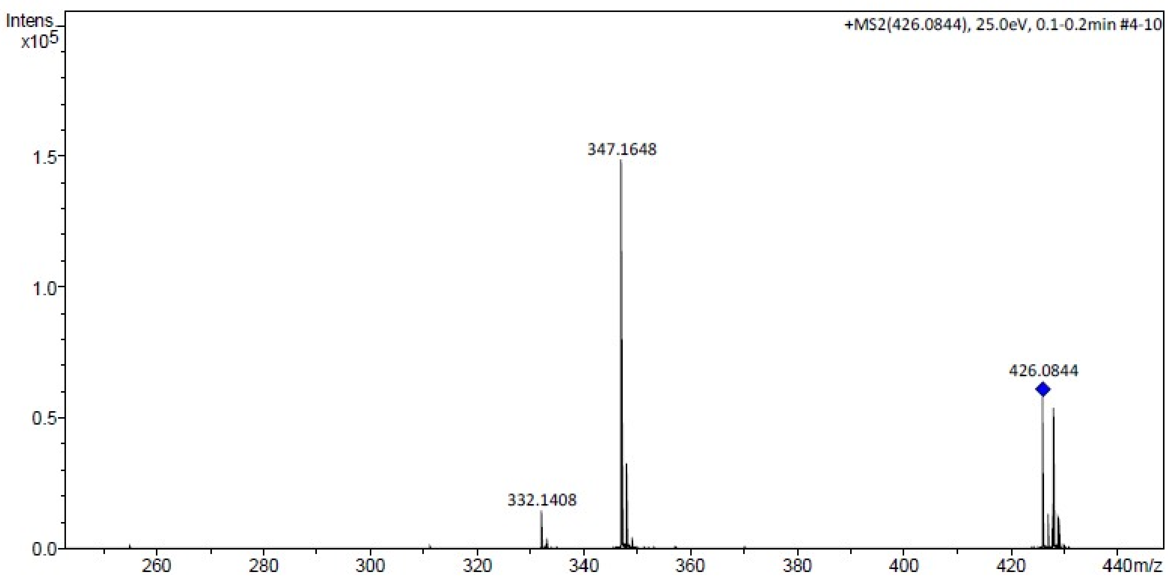
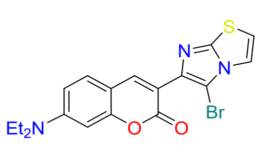


Figure SI-40. ESI-MS chromatogram of **6b**.



3-(5-bromoimidazo[2,1-b]thiazol-6-yl)-7-(diethylamino)-2H-chromen-2-one (6c): Yield 80%; yellow powder; m.p. = 140 – 142 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 7.886 (s, 1H, −CH=C−), 7.352 (d, *J* (H,H) = 4.5 Hz, 1H, −CH=C−), 7.276 (d, *J* (H,H) =9 Hz, 1H, Ar), 6.889 (d, *J* (H,H) = 4.5 Hz, 1H, −CH=C−), 6.547 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.473 (s, 1H, Ar), 3.380 (q, *J* (H,H) = 7.5 Hz, 4H, $-CH_2-CH_3$), 1.174 (t, *J* (H,H) = 7.5 Hz, 6H, CH_3); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 160.075, 156.649, 150.957, 148.642, 143.399, 140.435, 129.312, 117.579, 113.499, 113.250, 109.089, 108.600, 97.132, 93.159, 44.884, 12.488; FT-IR (KBr) ν_{max} = 3089 cm^{-1} (C−H Ar), 2928 cm^{-1} (C−H Aliphatic), 1719 cm^{-1} (C=O lactone), 1605 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 404.87 nm; HRMS (ESI m/z) Calcd. for $C_{18}H_{17}BrN_3O_2S$ $[M+H]^+$ 418.0219, found 418.0150.

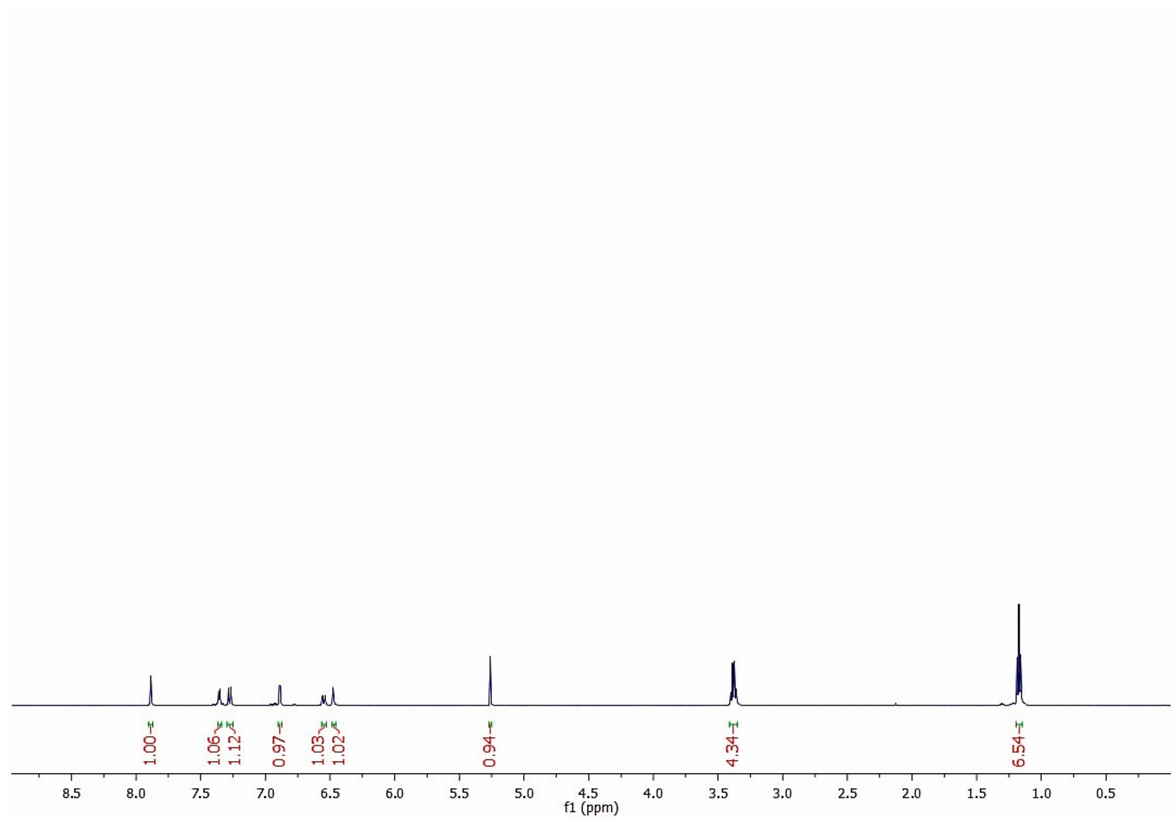


Figure SI-41. ^{1}H NMR spectra of **6c** on $CDCl_3$ 500 MHz

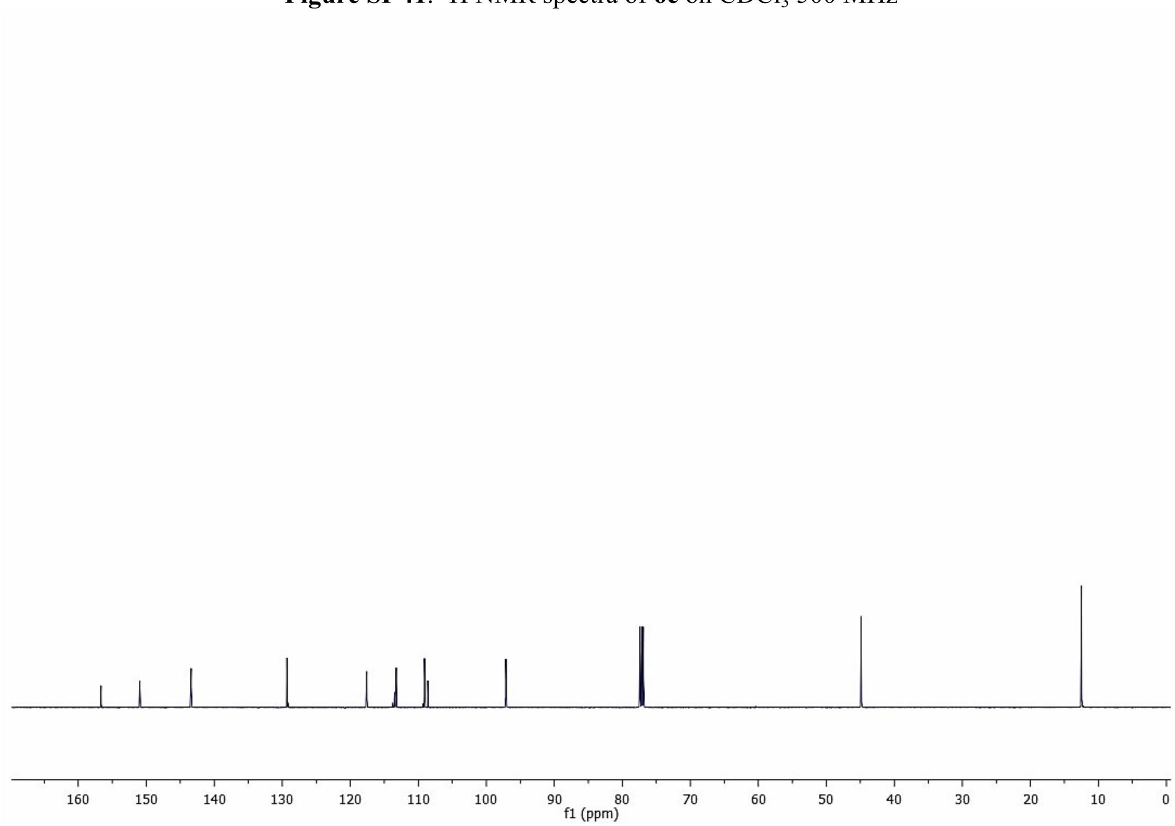


Figure SI-42. ^{13}C NMR spectra of **6c** on $CDCl_3$ 125 MHz.

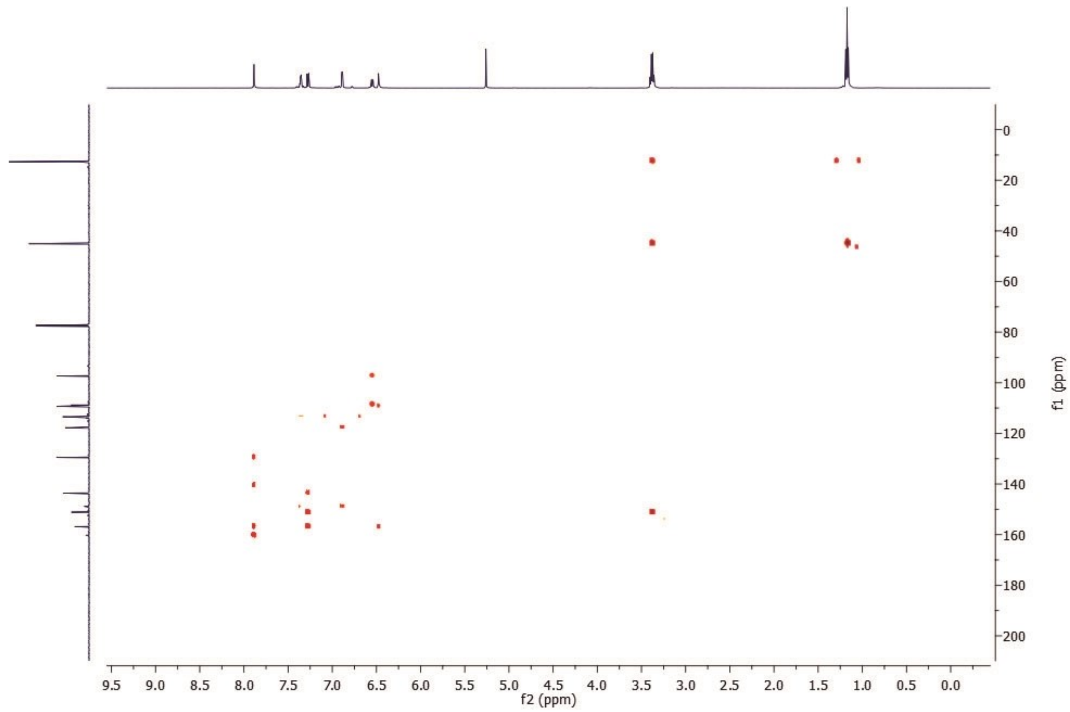


Figure SI-43. HMBC NMR spectra of **6c** on $CDCl_3$

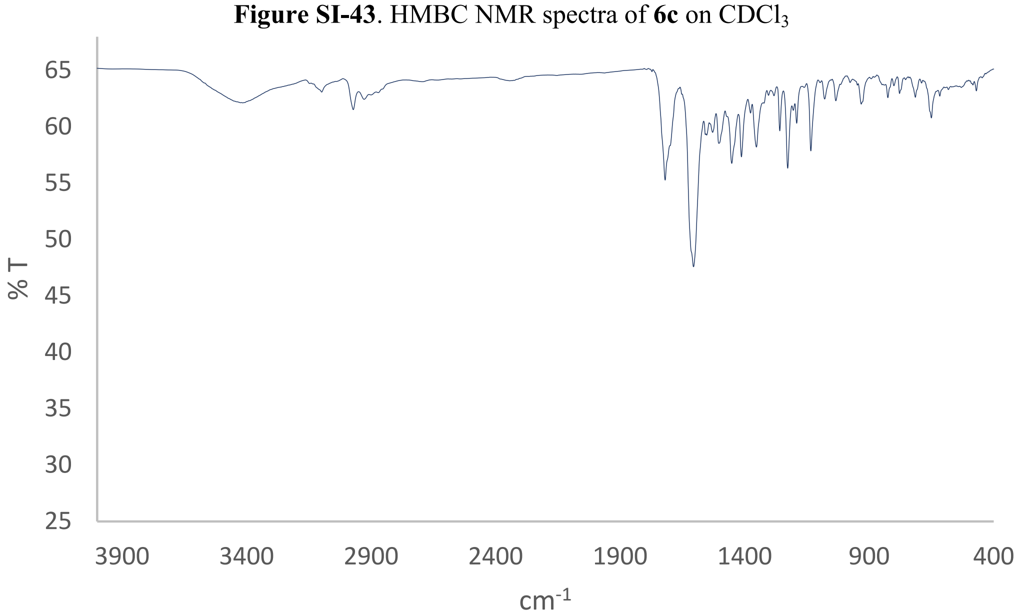


Figure SI-44. IR spectra for **6c** in KBr.

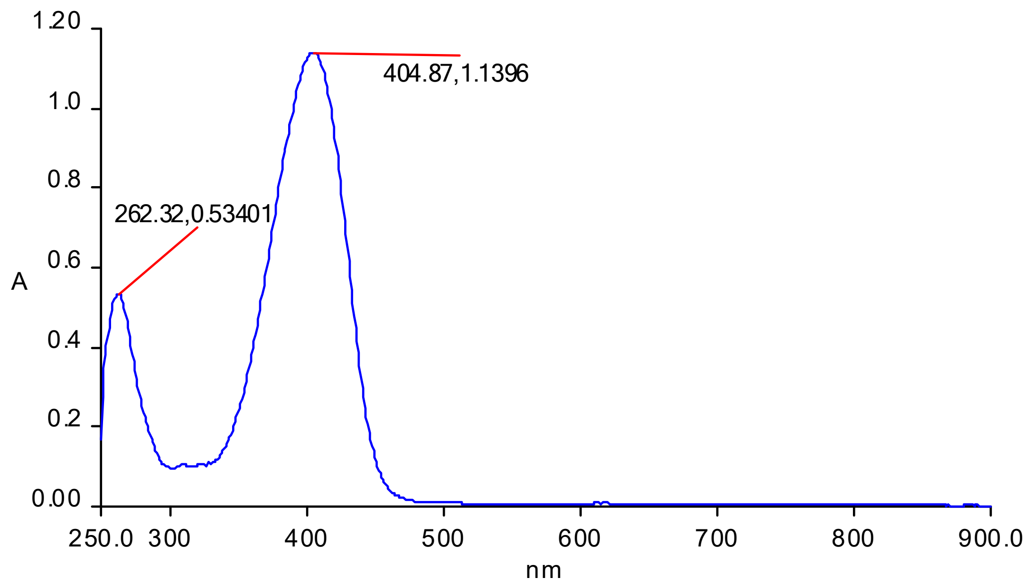


Figure SI-45. UV-Vis spectra of **6c** in MeOH.

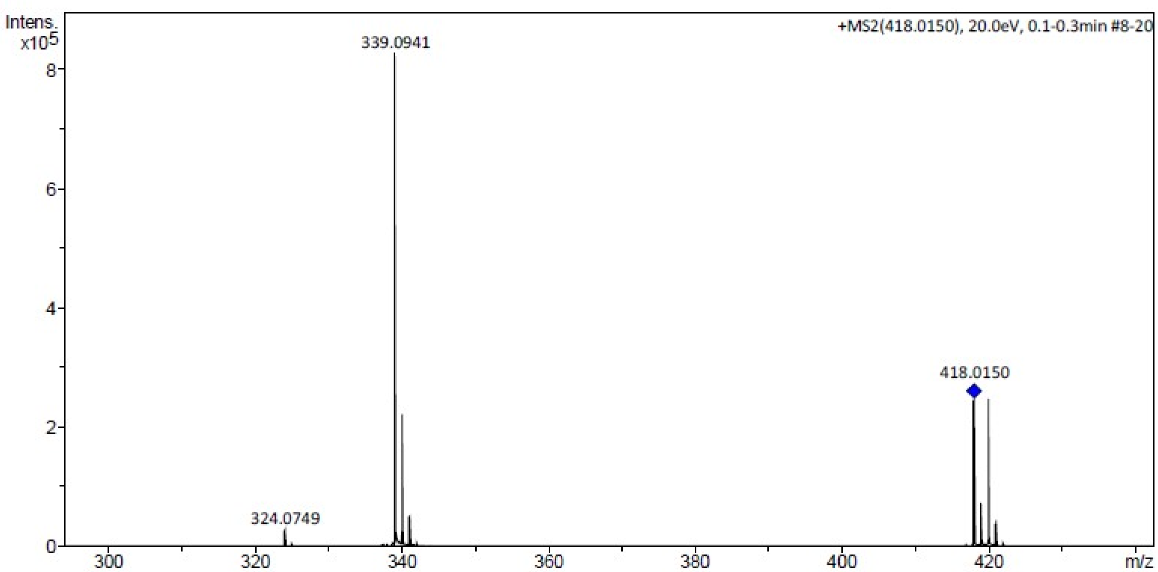
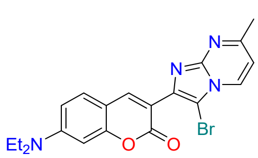


Figure SI-46. ESI-MS chromatogram of **6c**.



3-(3-bromo-7-methylimidazo[1,2-a]pyrimidin-2-yl)-7-(diethylamino)-2H-chromen-2-one ***(6d):*** Yield 92%; yellow powder; m.p. = 218 – 220 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.269 (d, *J* (H,H) = 7 Hz, 1H, Ar), 8.144 (s, 1H, −CH=C−), 7.310 (d, *J* (H,H)= 9 Hz, 1H, Ar), 6.574 (d, *J* (H,H) = 7 Hz, 1H, Ar), 6.558 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.476 (s, 1H, Ar), 3.394 (q, *J* (H,H) = 7.5 Hz, 4H, $-CH_2-CH_3$), 2.619 (s, 3H, CH_3), 1.184 (t, *J* (H,H) = 7.5 Hz, 6H, CH_3); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 160.569, 159.694, 156.941, 151.218, 148.026, 144.926 , 140.505, 130.778, 129.712, 113.245, 110.340, 108.852, 97.078, 92.515, 44.949, 24.963, 12.527; FT-IR (KBr) ν_{max} = 3083 cm^{-1} (C−H Ar), 2972 cm^{-1} (C−H Aliphatic), 1711 cm^{-1} (C=O lactone), 1620 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 423.00 nm; HRMS (ESI m/z) Calcd. for $C_{20}H_{20}BrN_4O_2$ $[M+H]^+$ 427.0764, found 427.0769.

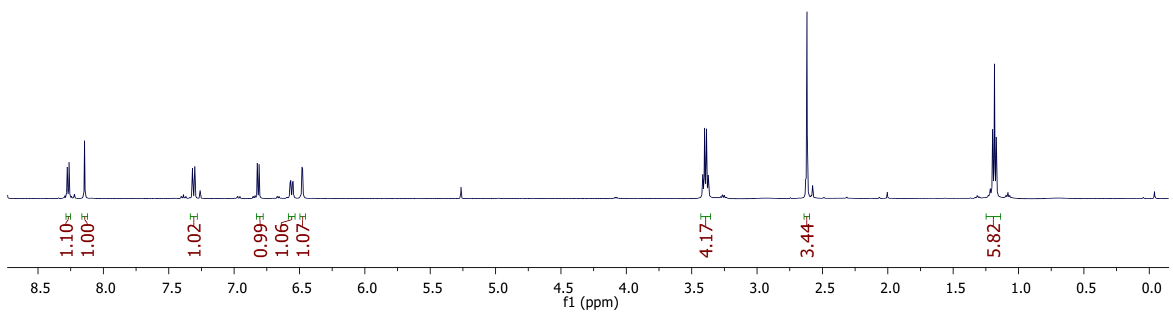


Figure SI-47. ^{1}H NMR spectra of **6d** on $CDCl_3$ 500 MHz

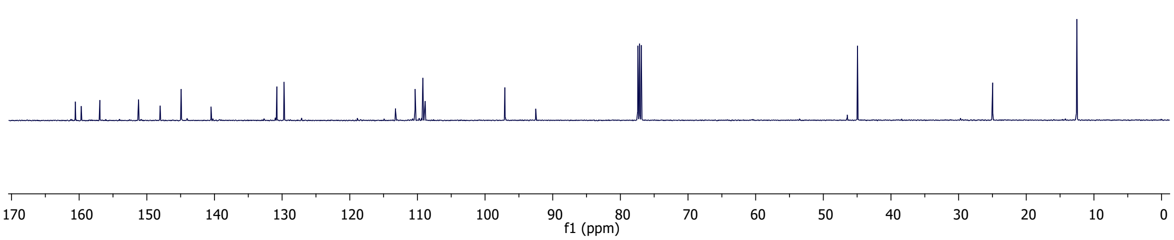


Figure SI-48. ^{13}C NMR spectra of **6d** on $CDCl_3$ 125 MHz.

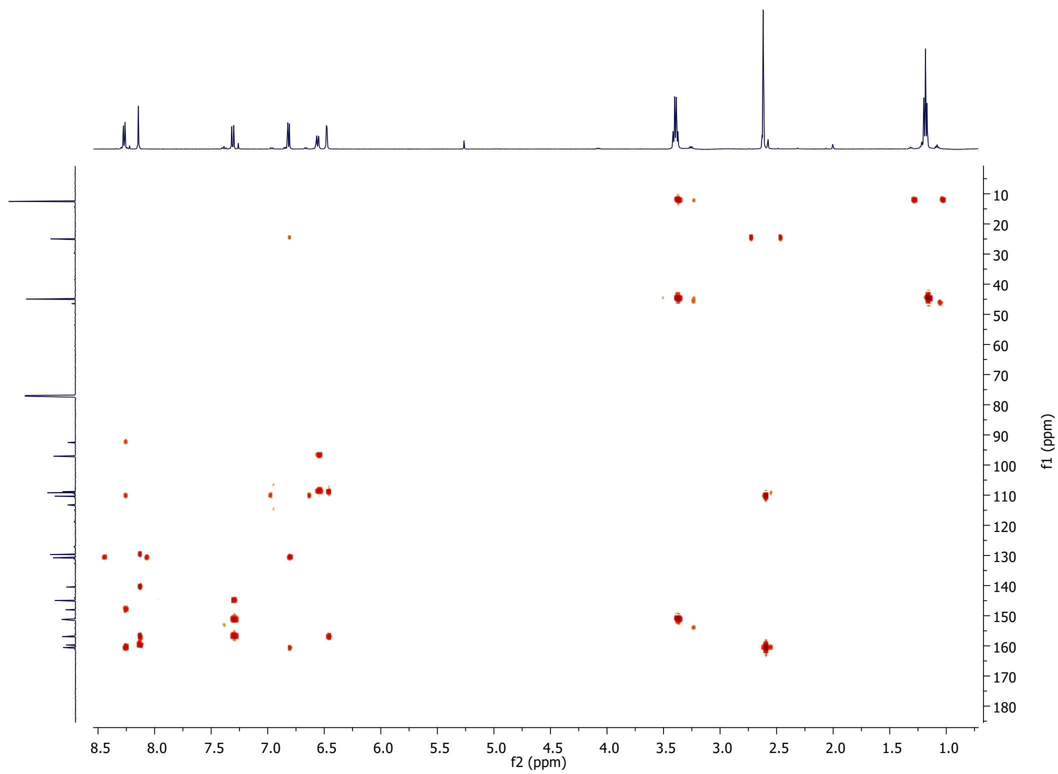


Figure SI-49. HMBC NMR spectra of **6d** on $CDCl_3$

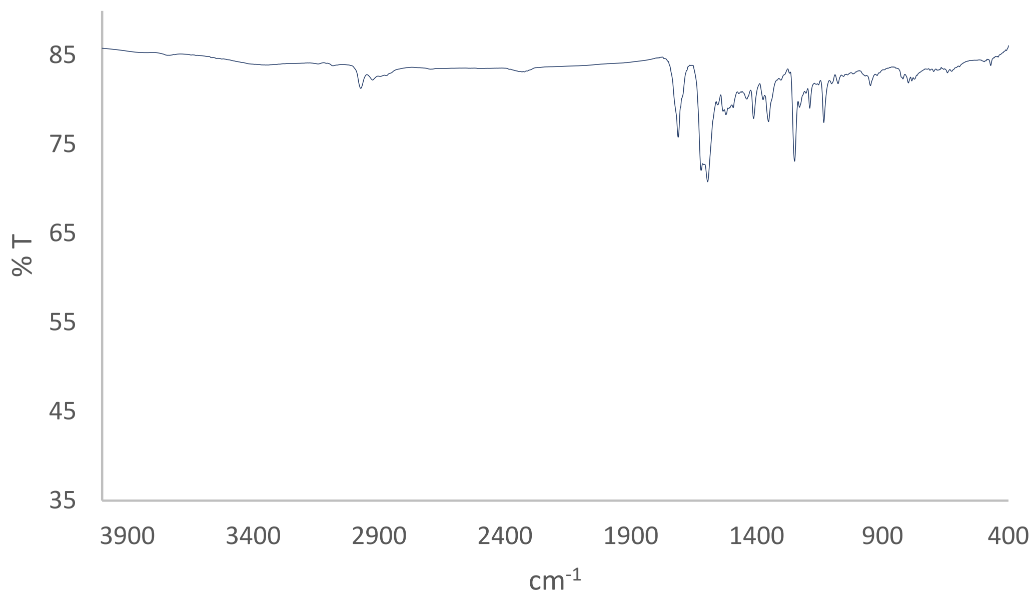


Figure SI-50. IR spectra for **6d** in KBr.

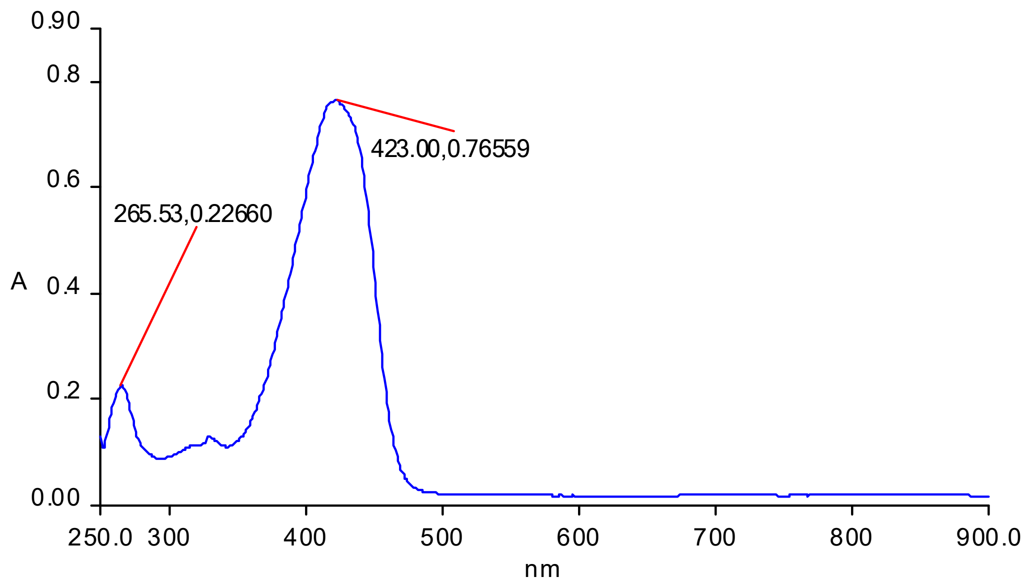


Figure SI-51. UV-Vis spectra of **6d** in MeOH.

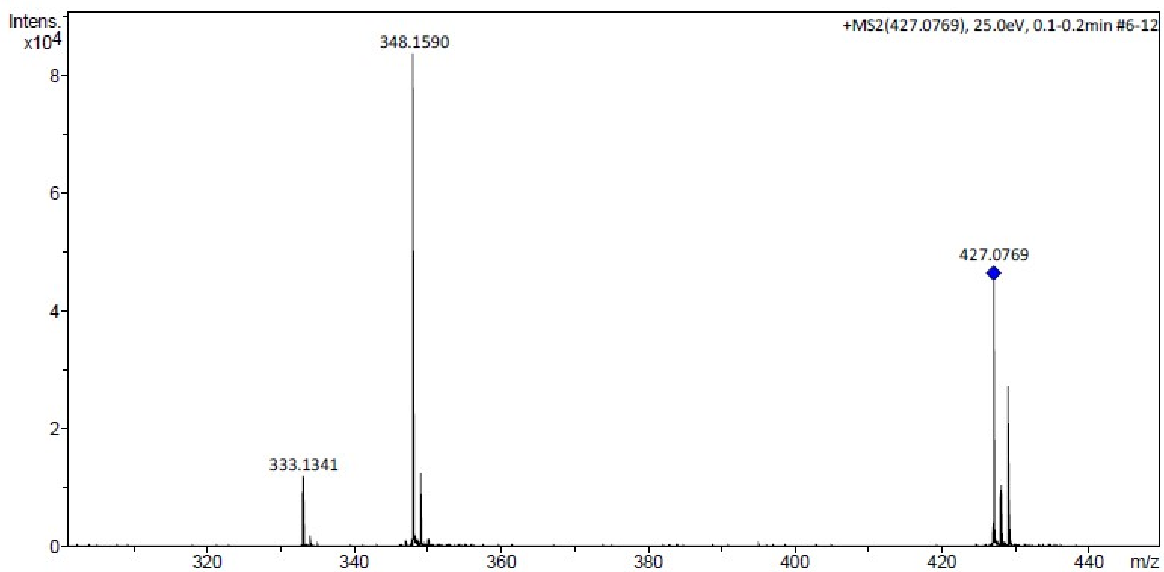
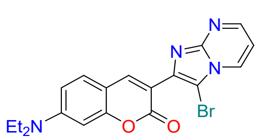


Figure SI-52. ESI-MS chromatogram of **6d**.



3-(3-bromoimidazo[1,2-a]pyrimidin-2-yl)-7-(diethylamino)-2H-chromen-2-one (6e): Yield 81%; yellow powder; m.p. = 121 – 125 ºC; RMN [1]H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.565 (d, *J* (H,H) = 4 Hz, 1H, Ar), 8.458 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 8.165 (s, 1H, −<u>CH</u>=C−), 7.338 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 7.000 (t, *J* (H,H) = 6 Hz, 1H, Ar), 6.581 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 6.501 (s, 1H, Ar), 3.415 (q, *J* (H,H) = 7.5 Hz, 4H, −<u>CH_2</u>−CH_3), 1.203 (t, *J* (H,H) = 7.5 Hz, 6H, <u>CH_3</u>); RMN [13]C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 159.756, 157.059, 151.376, 150.348, 147.958, 145.349, 141.283, 131.542, 129.859, 112.617, 109.566, 109.302, 108.753, 97.066, 93.628, 45.006, 12.338; FT-IR (KBr) ν_{max} = 3085 cm^{-1} (C−H Ar), 2971 cm^{-1} (C−H

Aliphatic), 1717 cm^{-1} (C=O lactone), 1598 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 408.14 nm; HRMS (ESI m/z) Calcd. for $C_{19}H_{18}BrN_4O_2$ $[M+H]^+$ 413.0608, found 413.0614.

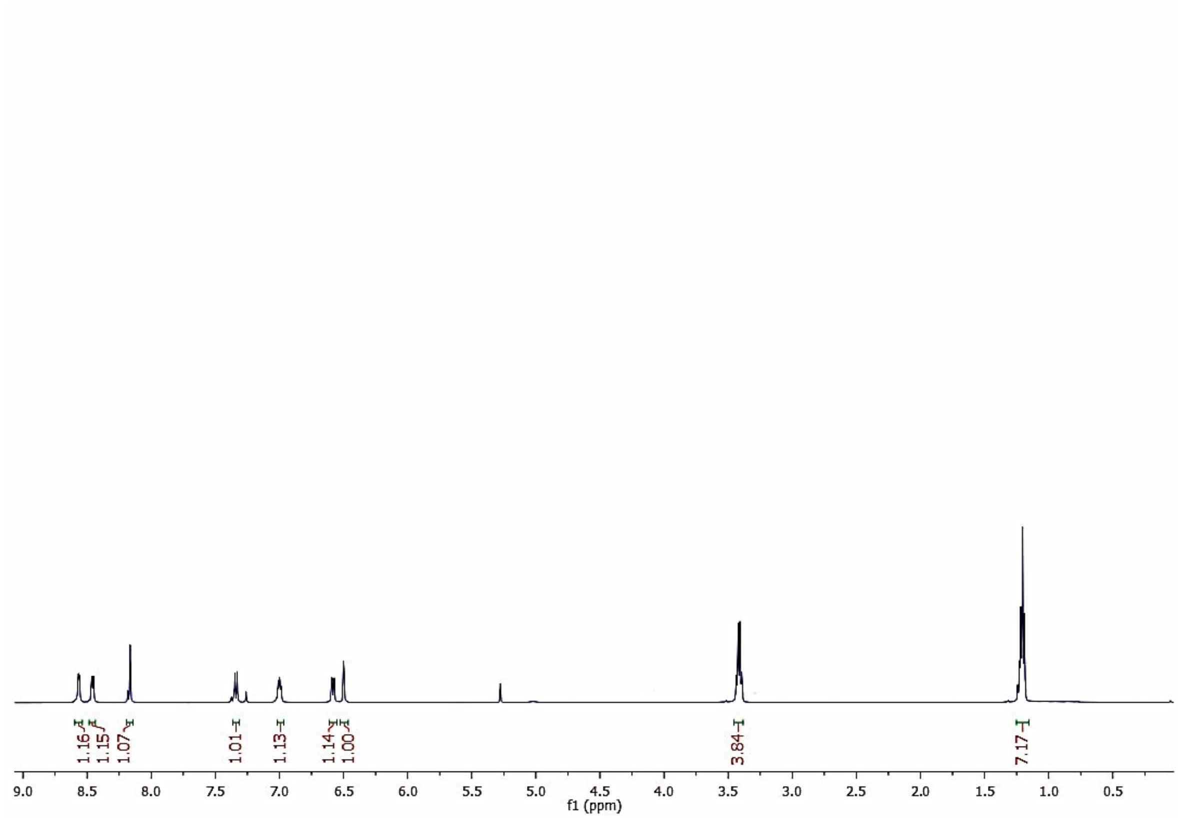


Figure SI-53. ^{1}H NMR spectra of **6e** on $CDCl_3$ 500 MHz

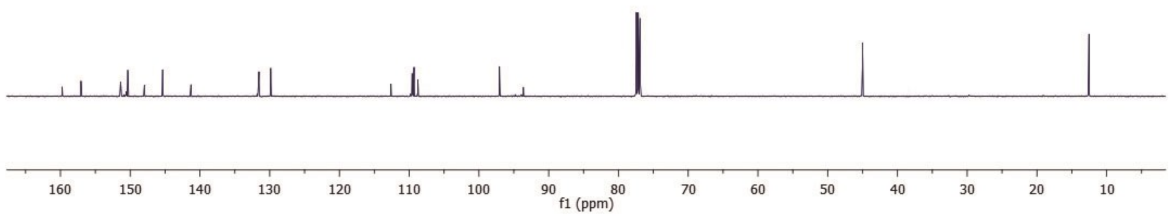


Figure SI-54. ^{13}C NMR spectra of **6e** on $CDCl_3$ 125 MHz.

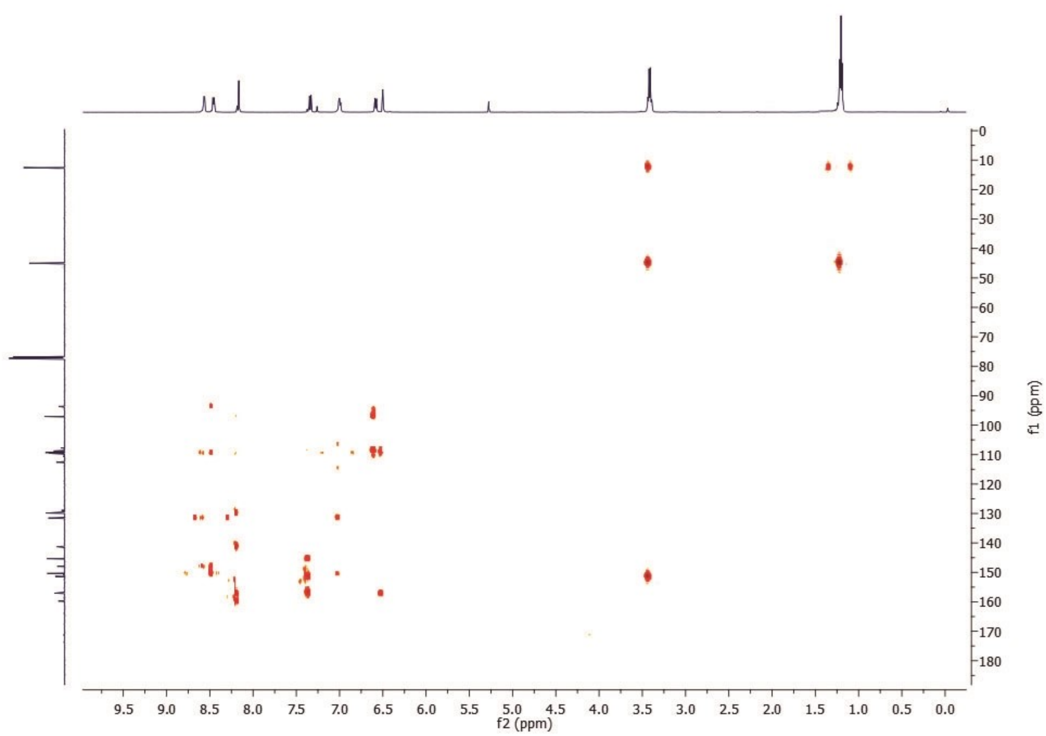


Figure SI-55. HMBC NMR spectra of **6e** on $CDCl_3$

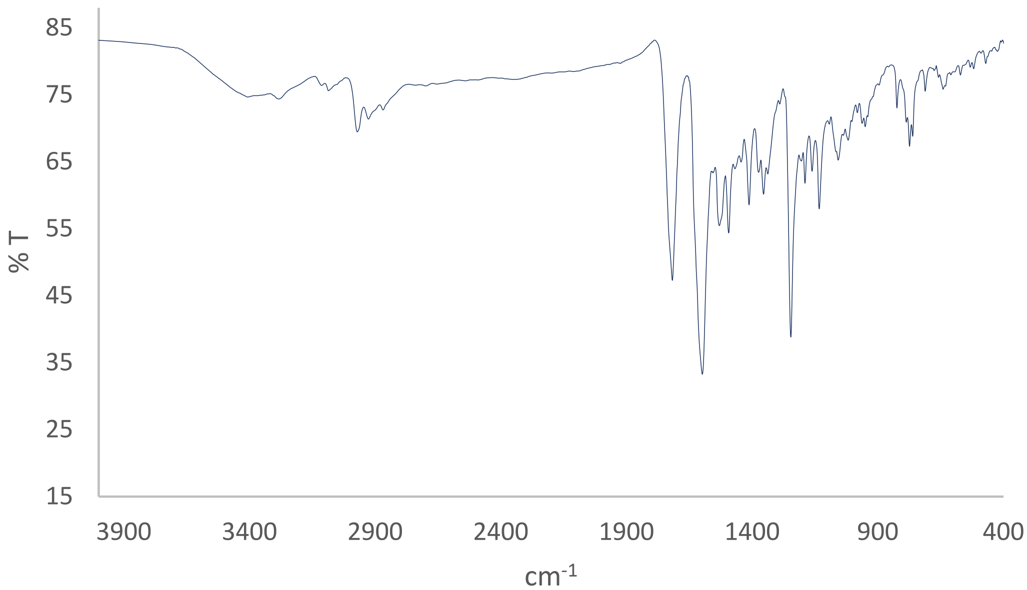


Figure SI-56. IR spectra for **6e** in KBr.

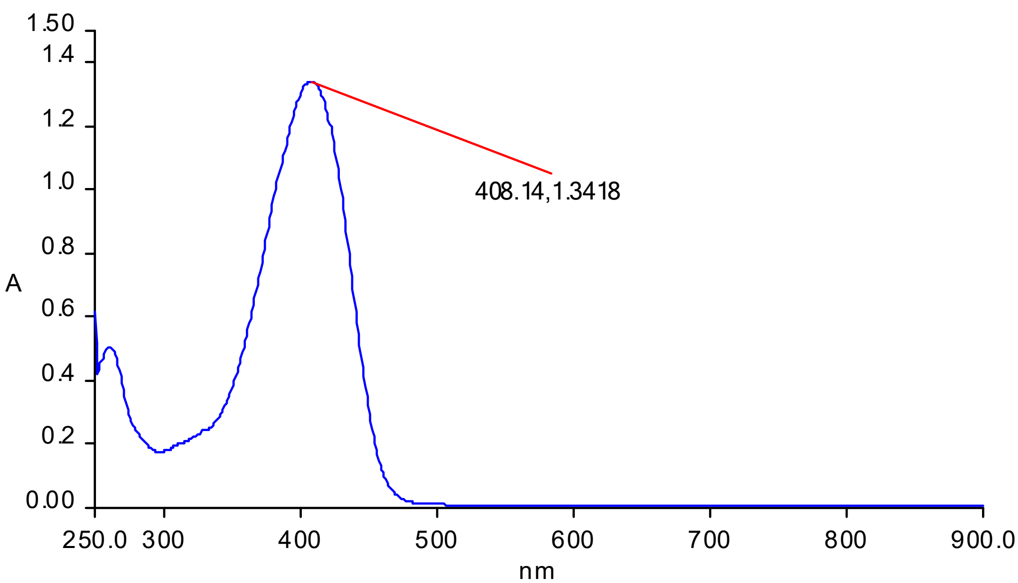


Figure SI-57. UV-Vis spectra of **6e** in MeOH.

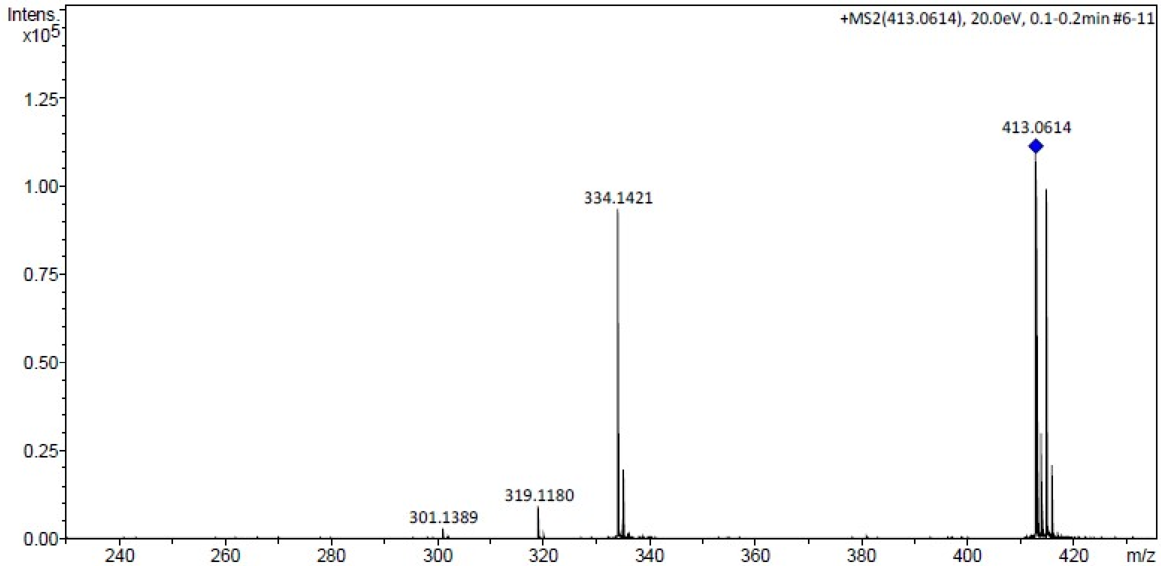
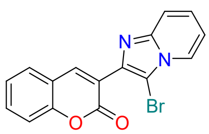


Figure SI-58. ESI-MS chromatogram of **6e**.



3-(3-bromoimidazo[1,2-a]pyridin-2-yl)-2H-chromen-2-one ***(6f):*** Yield 98%; brown powder; m.p. = 195 – 197 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.200 (m, 2H, Ar), 7.664 (d, *J* (H,H) = 7 Hz, 1H, Ar), 7.592 – 7.557 (m, 2H, Ar), 7.419 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.320 – 7.310 (m, 2H, Ar), 6.986 (t, *J* (H,H) = 7 Hz, 1H, Ar); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 158.909, 154.018, 145.469, 143.842, 138.235, 132.138, 128.376, 125.639, 00, 124.156, 121.382, 119.166, 117.860, 116.691, 113.609, 95.432; FT-IR (KBr) ν_{max} = 3040 cm^{-1} (C−H Ar), 2922 cm^{-1} (C−H Aliphatic), 1722 cm^{-1} (C=O lactone), 1632 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 335.14 nm; HRMS (ESI m/z) Calcd. for $C_{16}H_{10}BrN_2O_2$ $[M+H]^+$ 340.9920, found 340.9923.

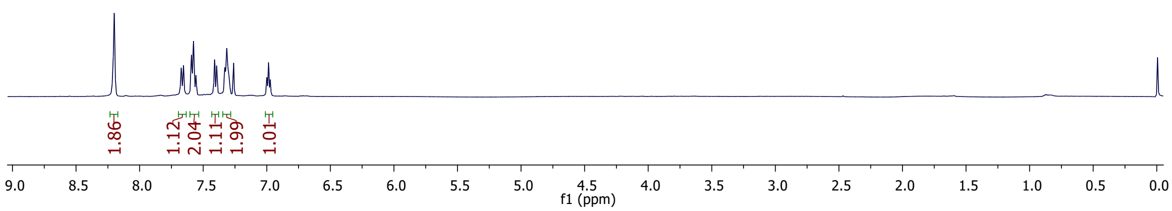


Figure SI-59. ^{1}H NMR spectra of **6f** on $CDCl_3$ 500 MHz

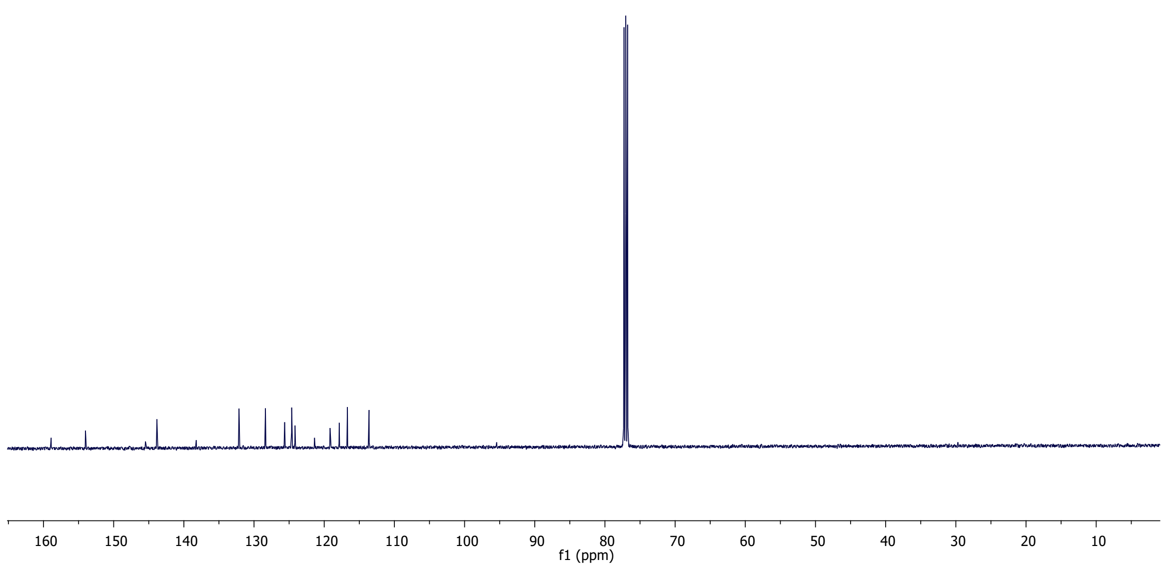


Figure SI-60. ^{13}C NMR spectra of **6f** on $CDCl_3$ 125 MHz.

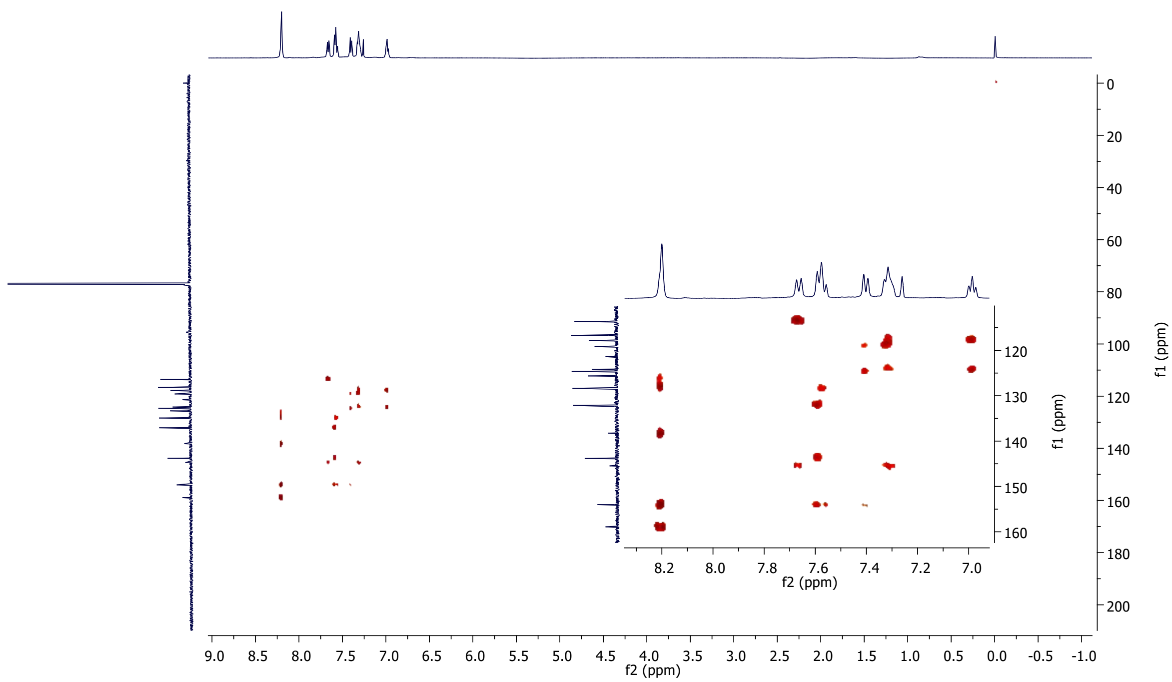


Figure SI-61. HMBC NMR spectra of **6f** on $CDCl_3$

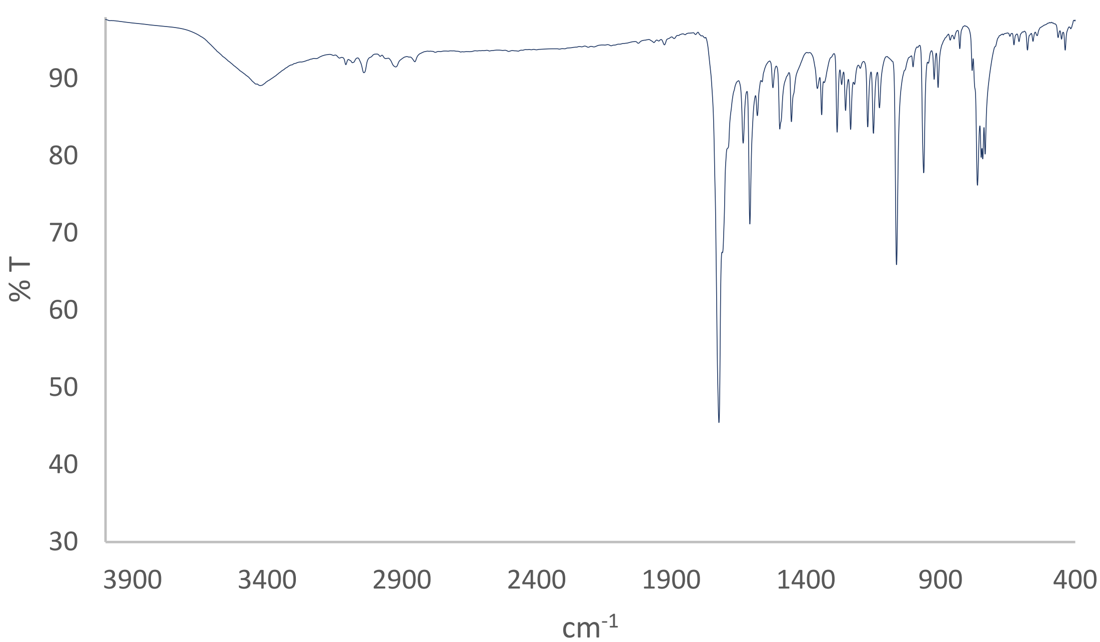


Figure SI-62. IR spectra for **6f** in KBr.

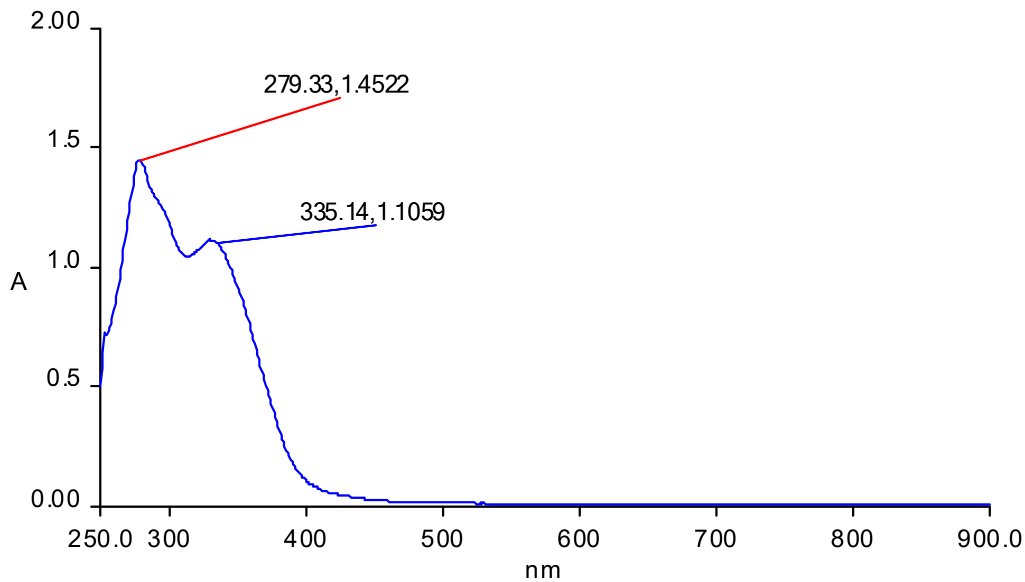


Figure SI-63. UV-Vis spectra of **6f** in MeOH.

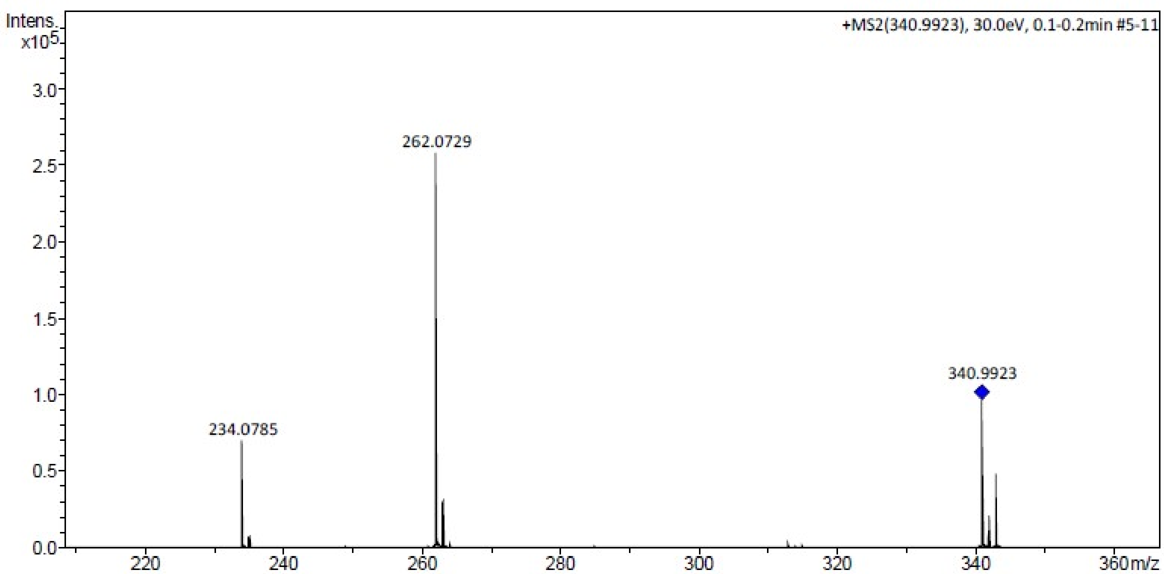
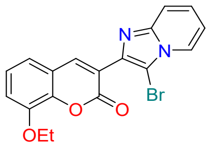
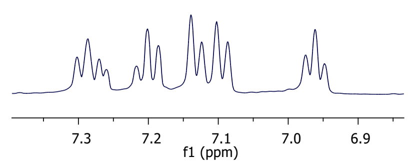


Figure SI-64. ESI-MS chromatogram of **6f**.



3-(3-bromoimidazo[1,2-a]pyridin-2-yl)-8-ethoxy-2H-chromen-2-one ***(6g):*** Yield 56%; dark brown powder; m.p. = 158 – 161 ºC; RMN [1]H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.184 – 8.168 (m, 2H, Ar), 7.638 (sd, *J* (H,H) = 9 Hz, 1H, Ar), 7.287 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 7.201 (t, *J* (H,H) = 7.5 Hz, 1H, Ar), 7.132 (d, *J* (H,H) = 8 Hz, 1H, Ar), 7.094 (d, *J* (H,H) = 8 Hz, 1H, Ar), 6.962 (t, *J* (H,H) = 7 Hz, 1H, Ar), 4.203 (q, *J* (H,H) = 7.5 Hz, 1H, $-\underline{CH_2}-CH_3$), 1.513 (t, *J* (H,H) = 7.5 Hz, 1H, $\underline{CH_3}$); RMN [13]C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 158.620, 146.580, 145.542, 144.212, 143.985, 138.401, 125.674, 124.574, 124.124, 121.668, 119.997, 119.829, 117.889, 115.319, 113.649,95.590, 65.144, 14.911; FT-IR (KBr) ν_{max} = 3040 cm^{-1} (C−H Ar), 2922 cm^{-1} (C−H Aliphatic), 1722 cm^{-1} (C=O lactone), 1632 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 340.05 nm; HRMS (ESI m/z) Calcd. for $C_{18}H_{14}BrN_2O_3$ $[M+H]^+$ 385.0182, found 385.0214.



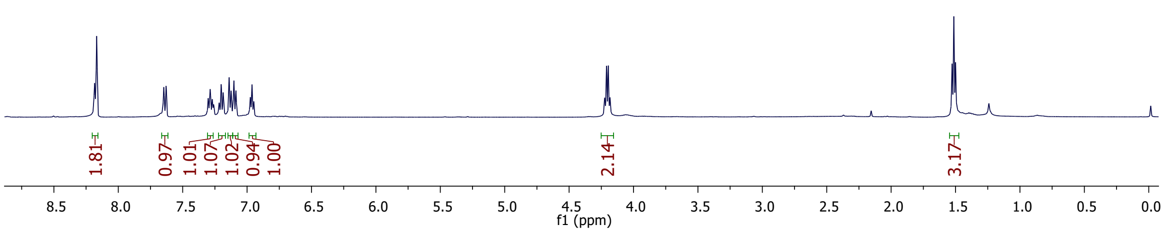


Figure SI-65. [1]H NMR spectra of **6g** on $CDCl_3$ 500 MHz

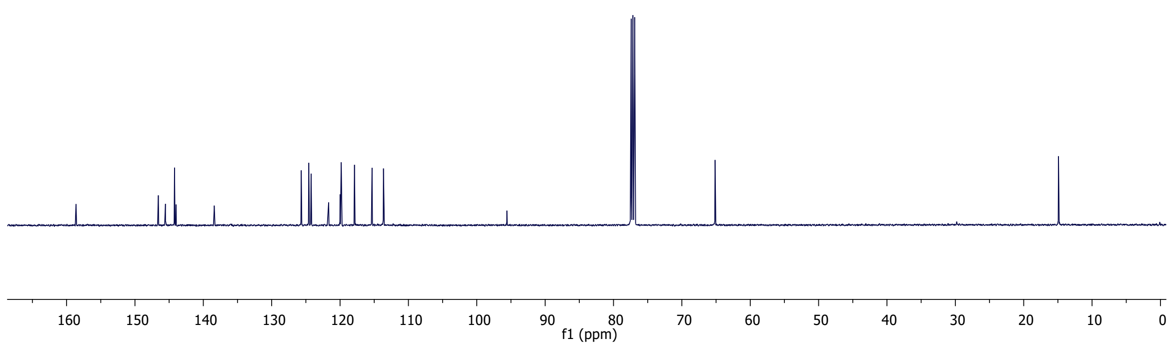


Figure SI-66. ^{13}C NMR spectra of **6g** on $CDCl_3$ 125 MHz.

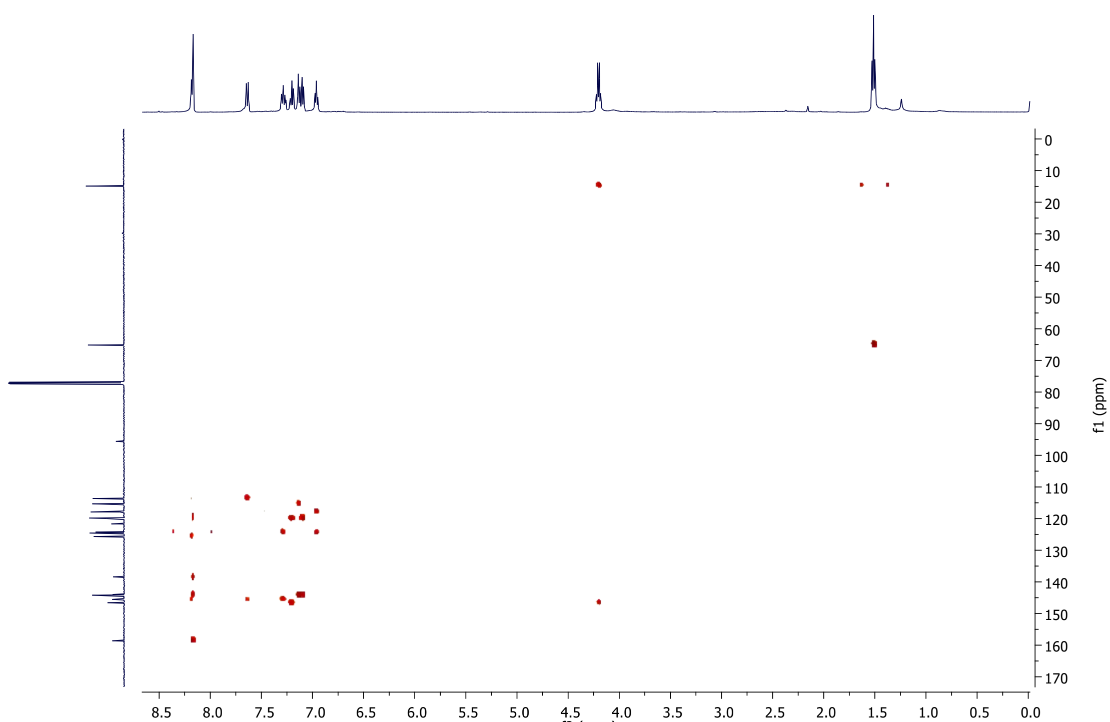


Figure SI-67. HMBC NMR spectra of **6g** on $CDCl_3$

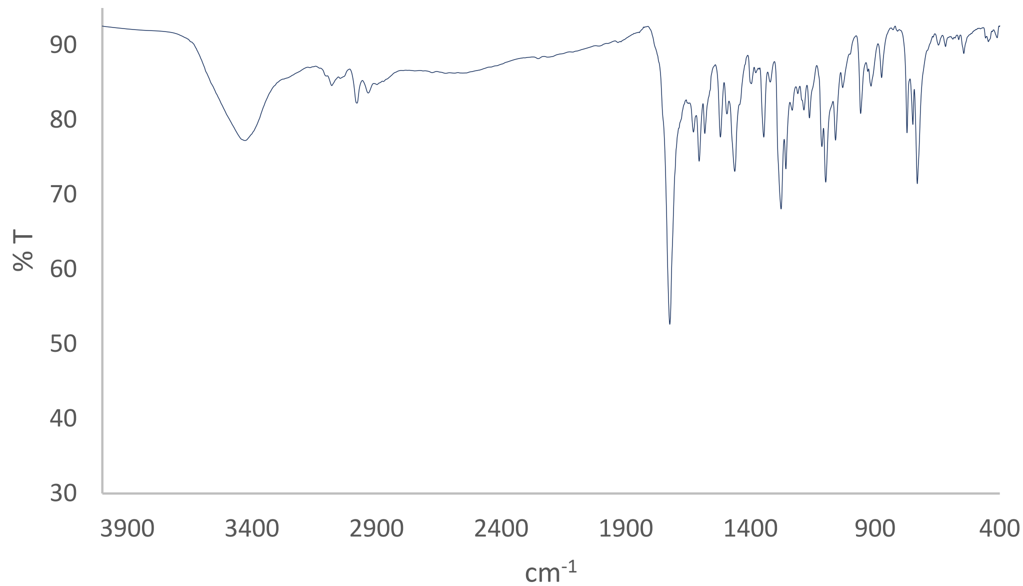


Figure SI-68. IR spectra for **6g** in KBr.

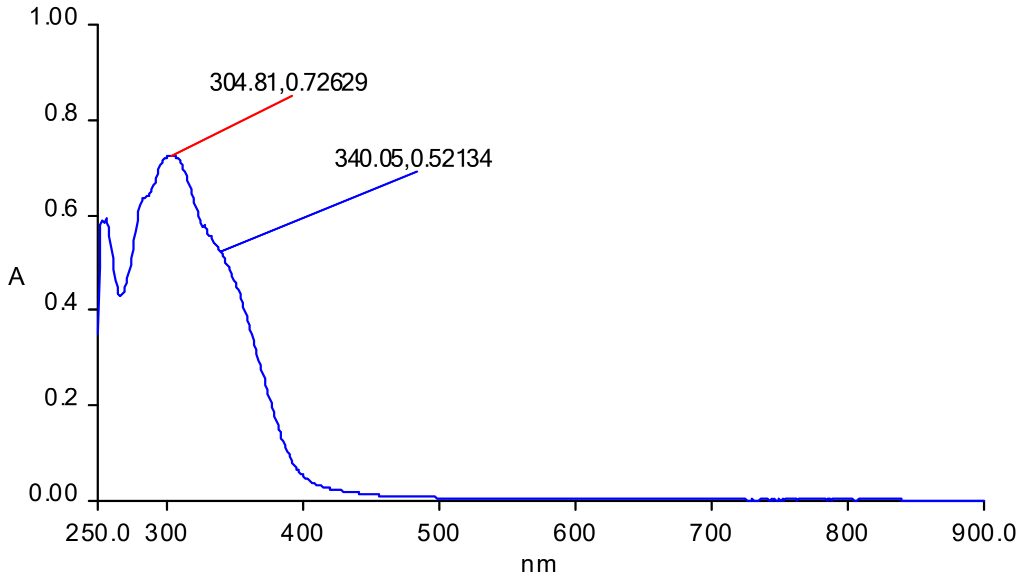


Figure SI-69. UV-Vis spectra of **6g** in MeOH.

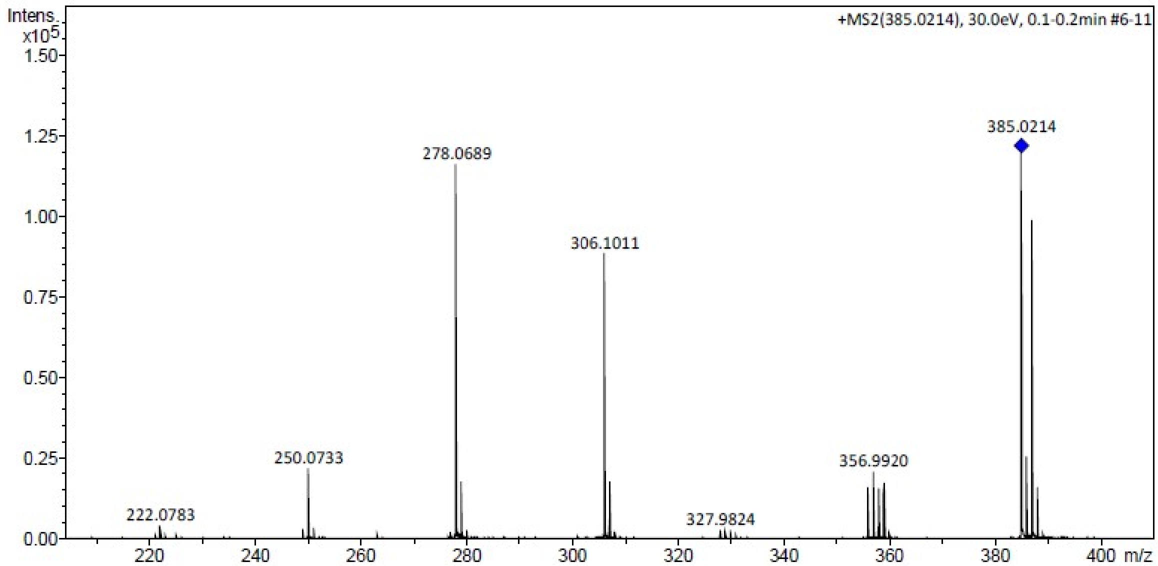
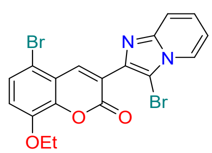


Figure SI-70. ESI chromatogram of **6g**.



5-bromo-3-(3-bromoimidazo[1,2-a]pyridin-2-yl)-8-ethoxy-2H-chromen-2-one (6h): Yield 89%; reddish brown; m.p. = 165 – 167 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.480 (s, 1H, −CH$_2$−CH$_3$), 8.192 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 7.676 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.427 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.308 (t, *J* (H,H) = 7 Hz, 1H, Ar), 6.983 – 6.952 (m, 2H, H-6, Ar), 4.188 (q, *J* (H,H) = 7.5 Hz, 1H, −CH$_2$−CH$_3$), 1.517 (t, *J* (H,H) = 7.5 Hz, 1H, CH$_3$); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 157.960, 146.215, 145.619, 144.729, 143.090, 138.033, 128.023, 125.776, 124.232, 122.606, 119.450, 118.080, 115.698, 113.785, 112.302, 95.780, 65.374, 14.807; FT-IR (KBr) ν_{max} = 29.24 cm^{-1} (C−H Aliphatic), 1728 cm^{-1} (C=O lactone), 1573 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 316.850 nm; HRMS (ESI m/z) Calcd. for $C_{18}H_{13}Br_2N_2O_3$ $[M+H]^+$ 461.9215, found 462.9295.

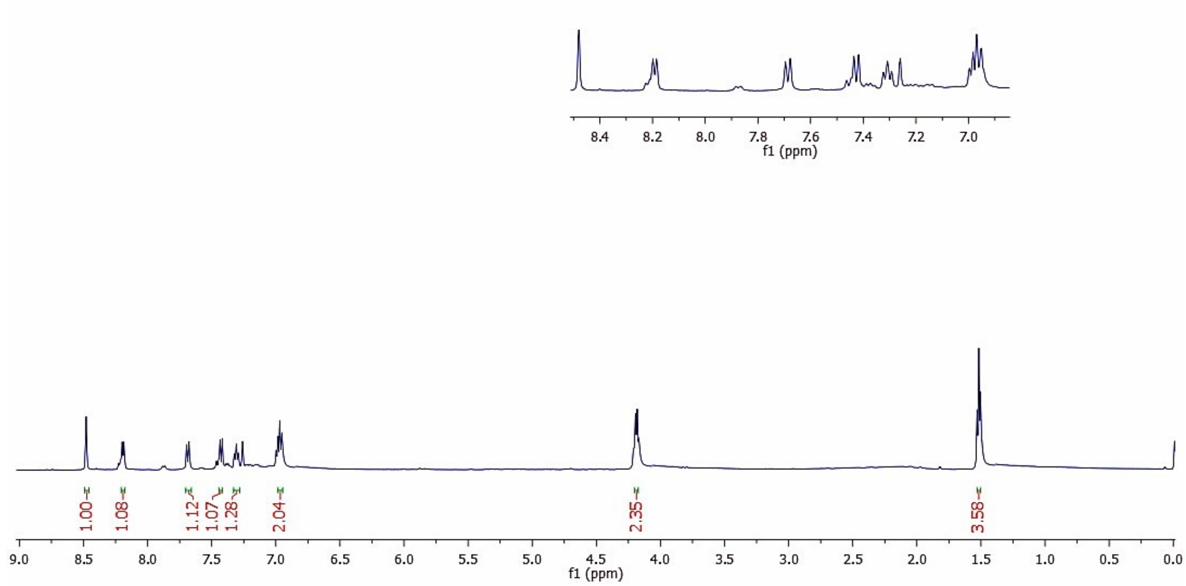


Figure SI-71. ^{1}H NMR spectra of **6h** on $CDCl_3$ 500 MHz

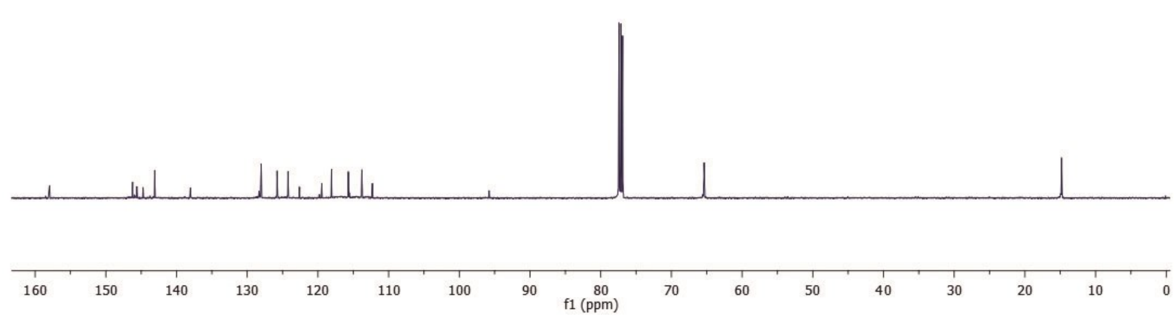


Figure SI-72. ^{13}C NMR spectra of **6h** on $CDCl_3$ 125 MHz.

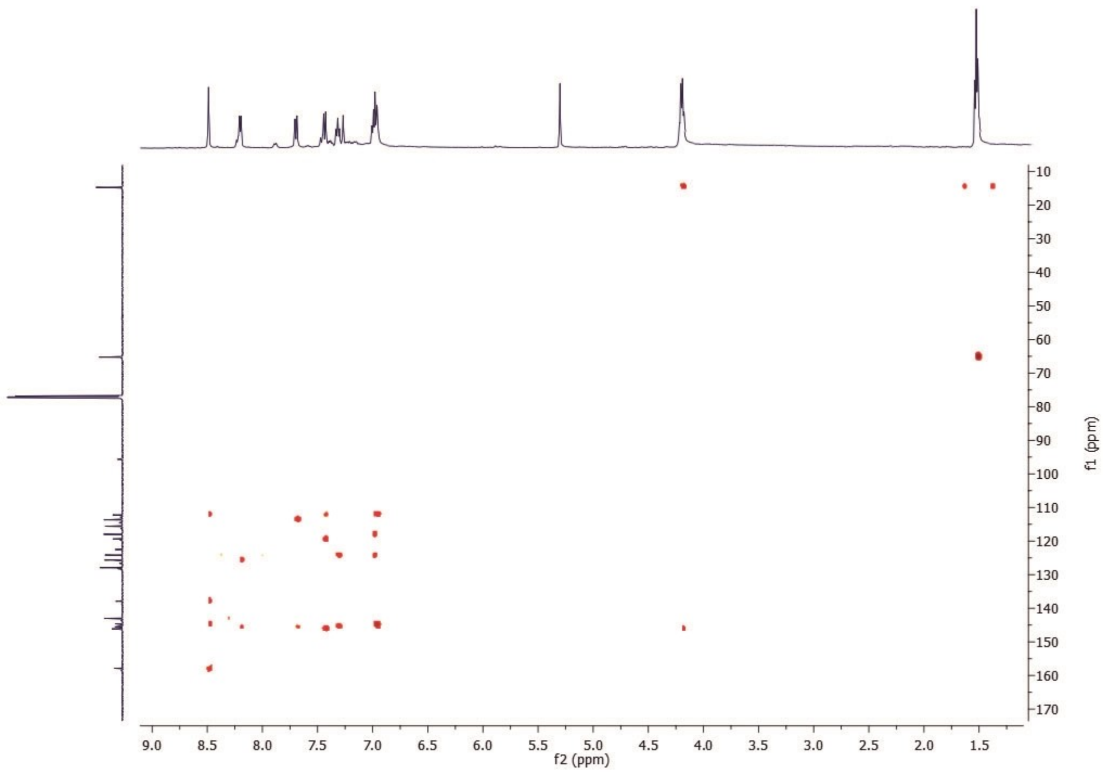


Figure SI-73. HMBC NMR spectra of **6h** on $CDCl_3$

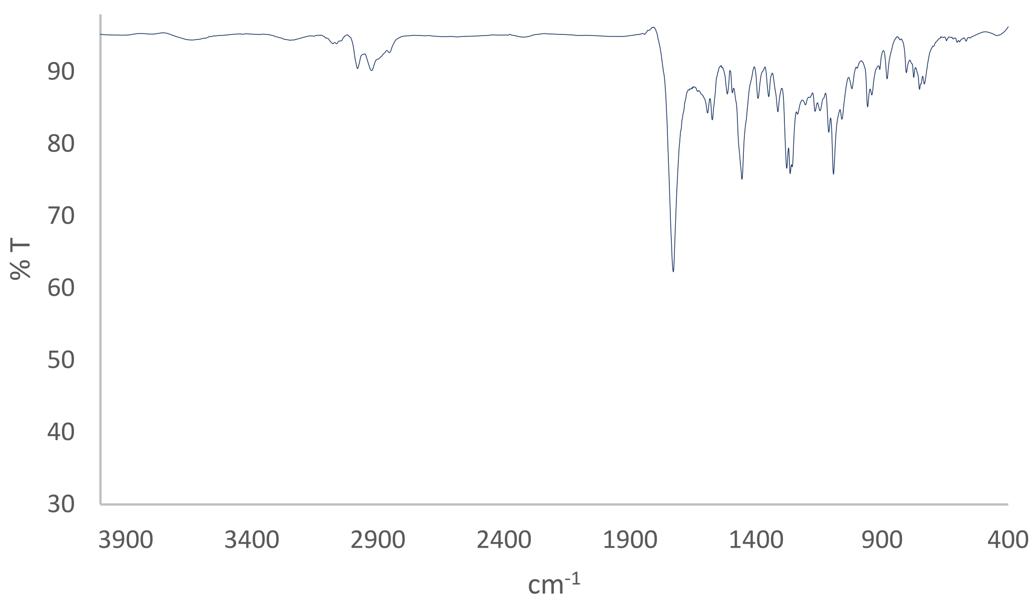


Figure SI-74. IR spectra for **6h** in KBr.

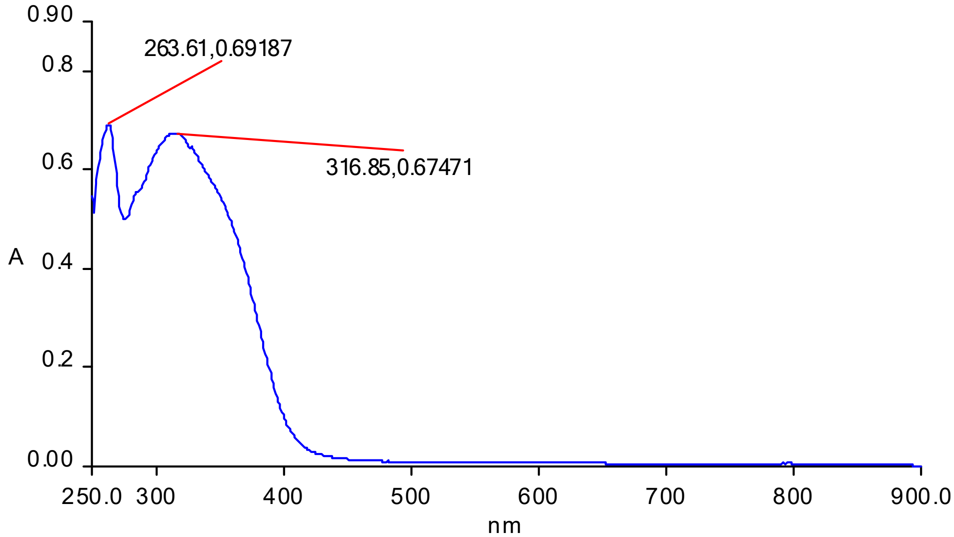


Figure SI-75. UV-Vis spectra of **6h** in MeOH.

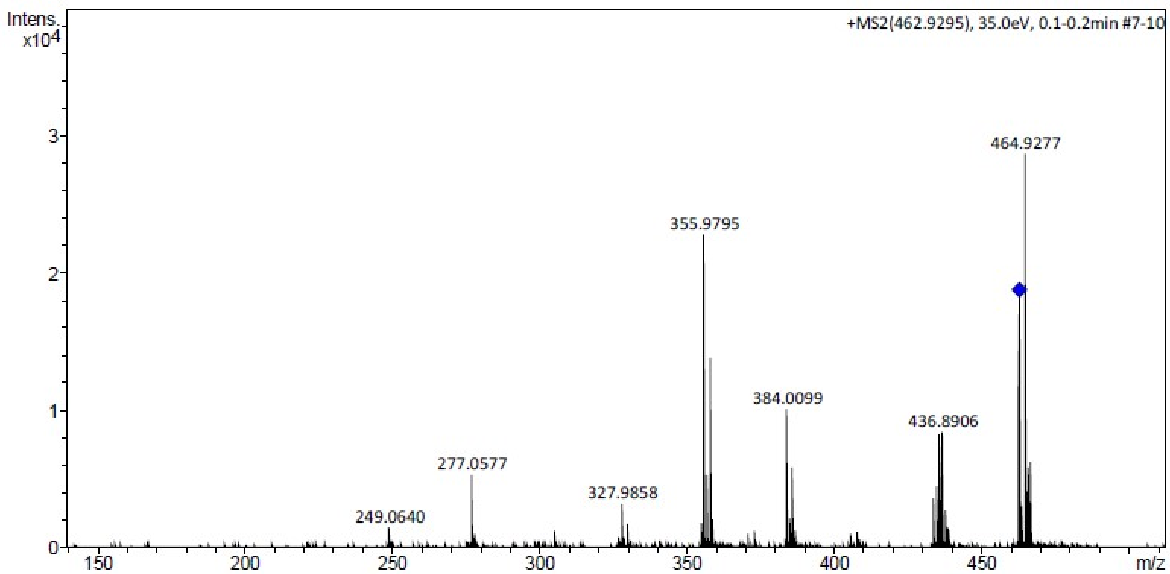
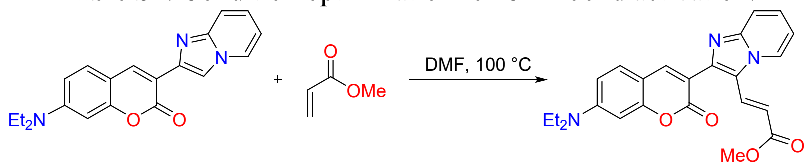


Figure SI-76. ESI-MS chromatogram of **6h**.

5. General procedure of coumarin-imidazo[1,2-*a*]pyridine-3-acrylates derivatives 7a-h
Method A: Alkenylation by C−H bond activation.

In a 15 mL round bottom flask **4a** (0.5 mmol), catalyst (15% mol), phase transfer agent (TA, 1 mmol), and base (1 mmol) were added according to the reagents shown in Table 1, the flask was sealed and purged with nitrogen, 5 mL of DMF and 2 mmol of methyl acrylate were injected into the flask. The flask was kept at 100 °C and shaken constantly for 7 days. The reaction crude was treated by adding distilled water, which caused the precipitation of the medium, the solid was filtered and redissolved in dichloromethane, the solution was filtered again through a buchner funnel packed with celite, the collected solution was washed with three volumes of $NaHCO_3$ saturated solution, the organic phase was concentrated and the solid was purified by chromatographic column in Hex/AcOEt 80:20 elution system.

Table S1. Condition optimization for C−H bond activation.



4 7

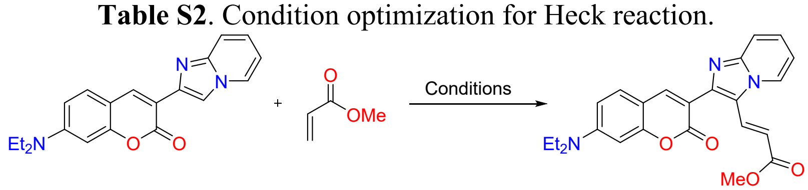
Entry	Catalyst	Base	TA[a]	t (days)	(%) R
1	$Pd(OAc)_2$ (15%)			2	30
2	$PdCl_2$ (15%)	$NaHCO_3$		7	22
3	Palladium Dichloro-N,N,N'N'-(Tetramethylethylenediamine) (II) (15%)		Hexadecyltrimethylammonium Bromide ($C_{19}H_{42}BrN$)	7	18
4		$CaCO_3$		7	18
5		*t*-BuOK		7	15
6	$Pd(OAc)_2$ (15%)		Tetrabutylammonium acetate	7	------
7		$NaHCO_3$	--------	7	------

[a]TA : Transfer agent

Method B: Method B: Heck reaction

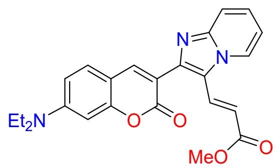
In a 15 mL round bottom flask, **6a-j** (0.5 mmol), catalyst (15% mol), BINAP (30% mol), base (1 mmol) and AgOAc (1 mmol) were added. Table 2 shows the reagents used. The flask was sealed and purged with nitrogen, then solvent (5 mL) and methyl acrylate (2 mmol) were injected, the flask was kept at 100 °C and stirred (2-7 days). The reaction was treated by adding distilled water which caused the precipitation of the medium, the solid was filtered and redissolved in dichloromethane, the collected solution was washed with three volumes of $NaHCO_3$ saturated solution, the organic phase was concentrated and purified by chromatographic column in Hex/AcOEt 80:20 elution system.

Table S2. Condition optimization for Heck reaction.



6 7

Entry	Catalyst	Solvent	Base	Aditive	T (°C)	%R	t (days)
1		DMF		----		70	2
2	$Pd(OAc)_2$ (15%)				100	78	2
3		Dioxane				85	2
4		THF			66	60	7
5	$PdCl_2$ (15%)		$NaHCO_3$	$Ag(OAc)_2$		80	7
6	Palladium Dichloro-N,N,N'N'-(Tetramethylethylenediamine) (II) (15%)	Dioxane			100	66	7
7	$Pd(OAc)_2$ (15%)		$CaCO_3$			85	2
8	$Pd(OAc)_2$ (15%)		*t*-BuOK			67	2
9	$Pd(OAc)_2$ (15%)		$CaCO_3$			87	2



Methyl (E)-3-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)imidazo[1,2-a]pyridin-3-yl)acrylate (7a): Yield 87%; yellow powder; m.p. = 219 – 223 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.391 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 8.013 – 7.999 (m, 2H, Ar), 7.659 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.329 – 7.311 (m, 2H, Ar), 6.965 (d, *J* (H,H) = 7 Hz, 1H, Ar), 6.587 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.525 (s, 1H, Ar), 7.206 (d, *J* (H,H) = 16 Hz, 1H, −<u>CH</u>=C−), 3.758 (s, 1H, <u>CH_3</u>), 3.417 (q, *J* (H,H) = 7.5 Hz, 4H, −<u>CH_2</u>−CH_3), 1.210 (t, *J* (H,H) = 7.5 Hz, 6H, <u>CH_3</u>); RMN ^{13}C (125 MHz, $CDCl_3$, TMS) δ (ppm): $CDCl_3$, 25 °C, TMS) δ (ppm) = 167.734, 160.559, 157.095, 151.356, 147.035, 145.191, 145.160, 130.231, 129.705, 126.609, 125.141, 118.770, 118.095, 114.177, 114.067, 113.992, 109.283, 108.727, 97.157, 51.772, 44.985, 12.532; FT-IR (KBr) ν_{max} = 3020 cm^{-1} (C−H Ar), 2969 cm^{-1} (C−H Aliphatic), 1714 cm^{-1} (C=O lactone), 1619 cm^{-1} (−O−<u>C=O</u>), 1595 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 415.15 nm; HRMS (ESI m/z) Calcd. for $C_{24}H_{24}N_3O_4$ $[M+H]^+$ 418.1761, found 418.1770.

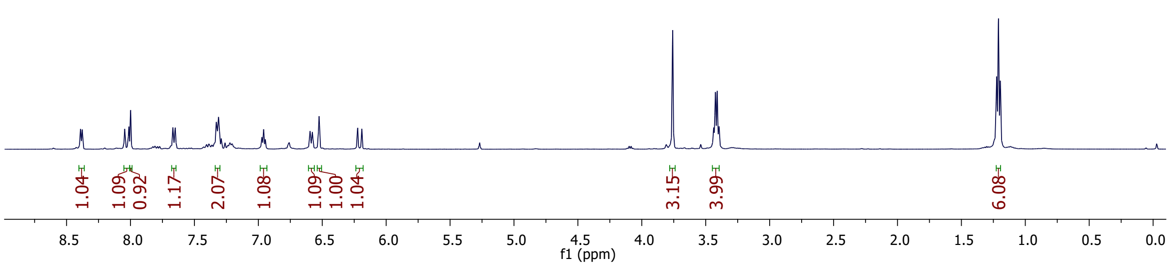


Figure SI-77. ^{1}H NMR spectra of **7a** on $CDCl_3$ 500 MHz

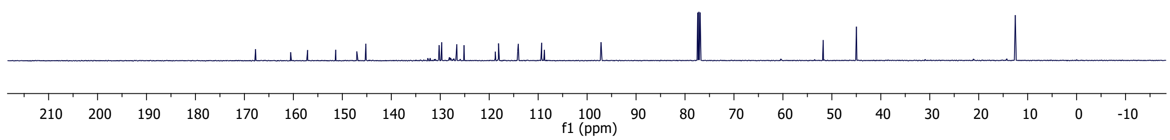


Figure SI-78. ^{13}C NMR spectra of **7a** on $CDCl_3$ 125 MHz.

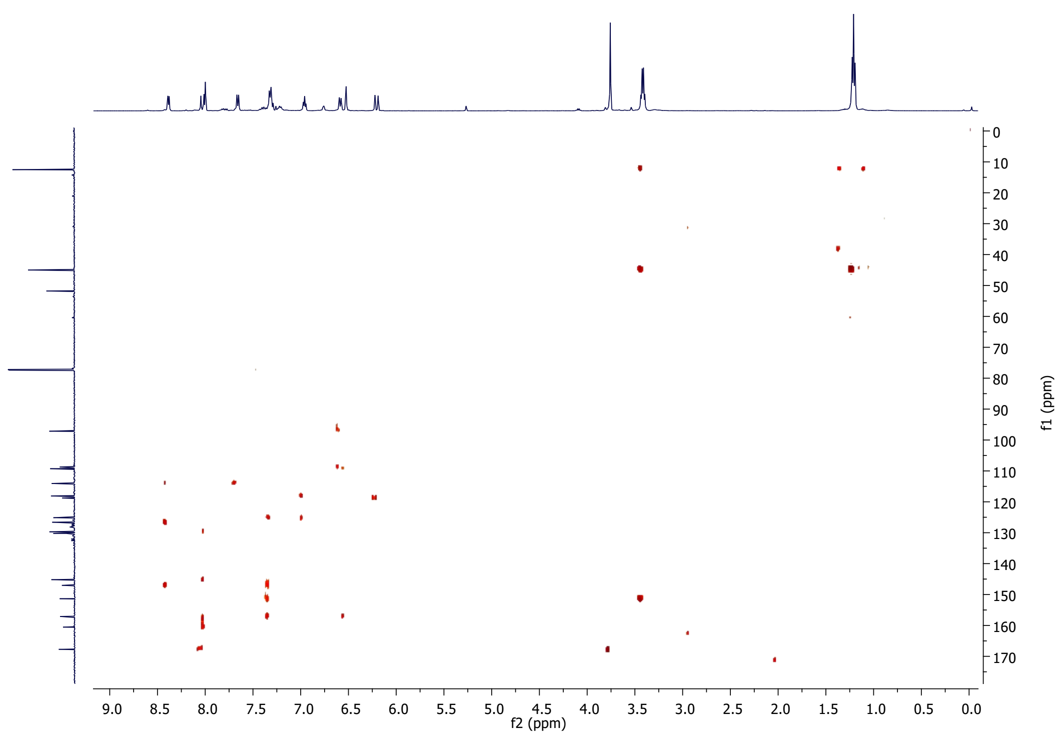


Figure SI-79. HMBC NMR spectra of **7a** on $CDCl_3$

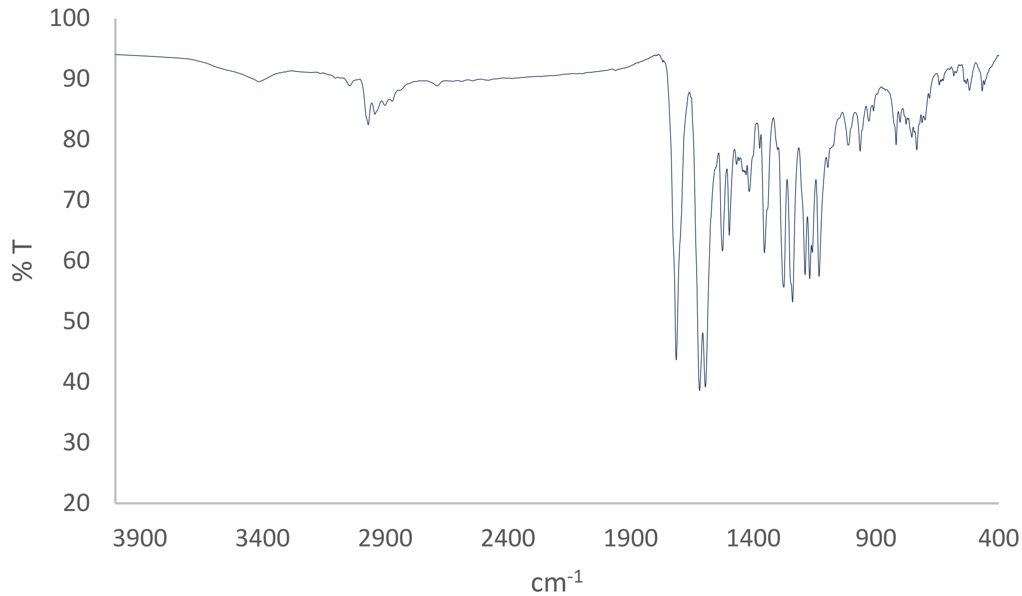


Figure SI-80. IR spectra for **7a** in KBr.

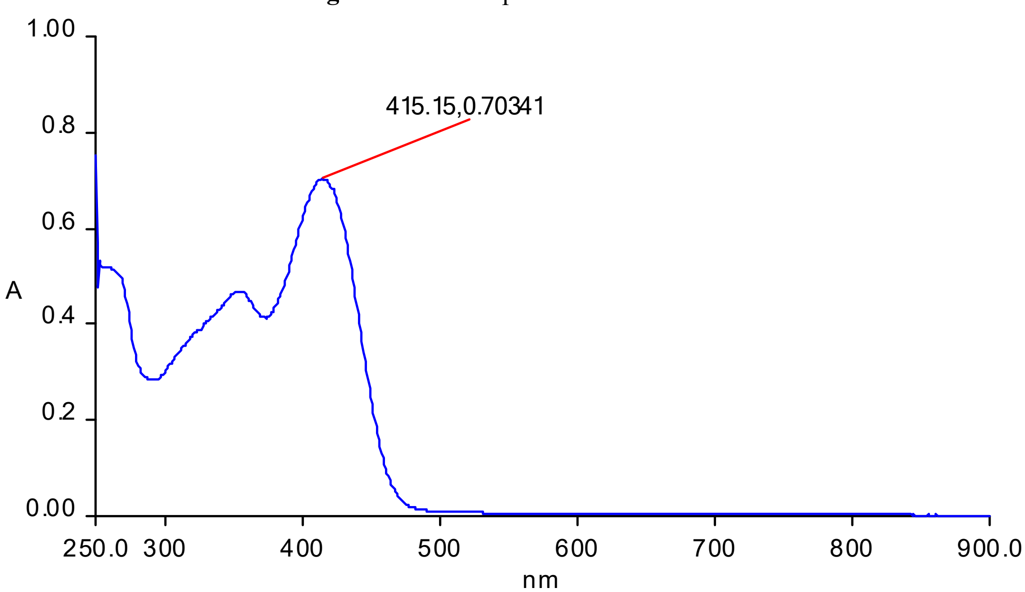


Figure SI-81. UV-Vis spectra of **7a** in MeOH.

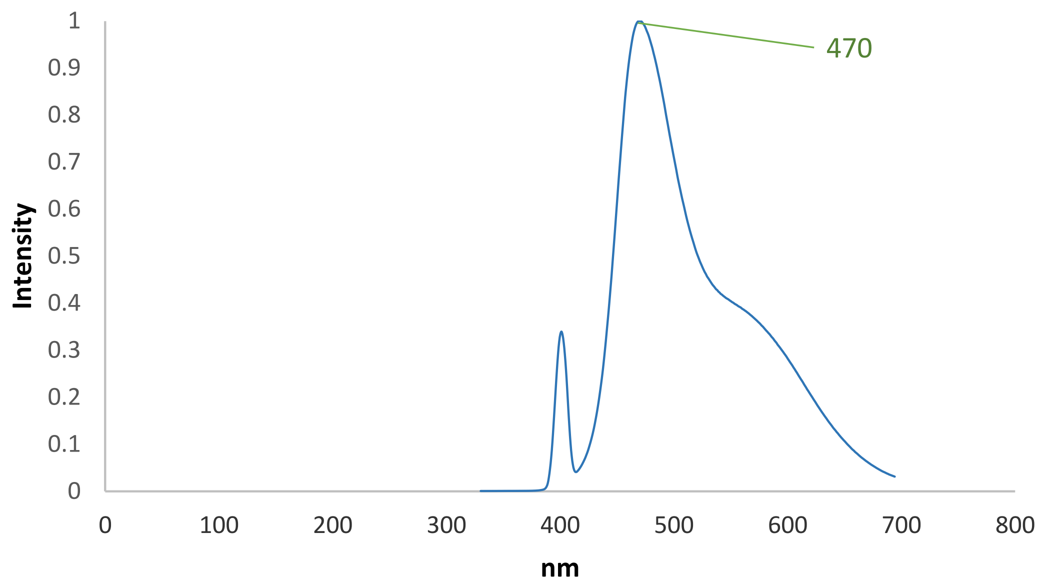


Figure SI-82. Emission spectra of **7a** in MeOH.

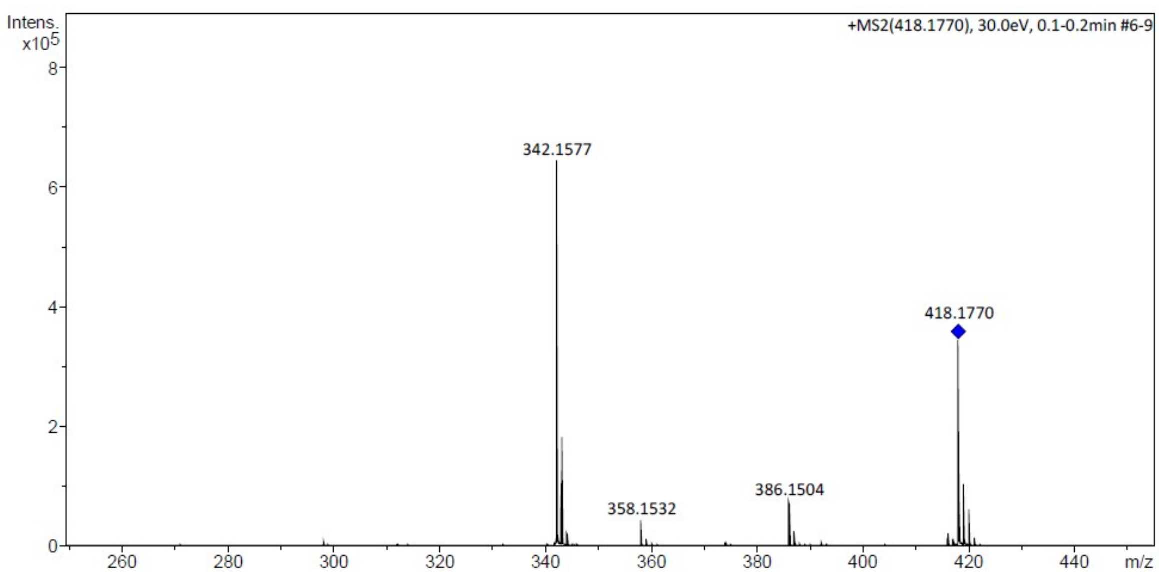
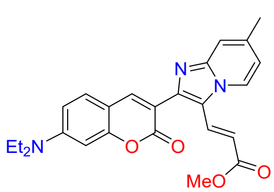


Figure SI-83. ESI-MS chromatogram of **7a**.



Methyl (E)-3-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-7-methylimidazo[1,2-a]pyridin-3-yl)acrylate (7b): Yield 85%; yellow powder; m.p. = 188 – 190 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.276 (d, *J* (H,H) = 7 Hz, 1H, Ar), 8.026 – 7.991 (m, 1H, Ar), 7.420 (s, 1H, Ar), 7.323 (d, *J* (H,H) = 8 Hz, 1H, Ar), 8.000 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 6.600 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.532 (s, 1H, Ar), 6.159 (d, *J* (H,H) = 16 Hz, 1H, −CH=C−), 3.761 (s, 3H, CH_3), 3.426 (q, *J* (H,H) = 7 Hz, 4H, $-CH_2-CH_3$), 2.431 (s, 3H, CH_3), 1.220 (t, *J* (H,H) = 7.5 Hz, 6H, H-7b'); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 167.900, 160.632, 157.099, 151.338, 147.631, 145.387, 145.111, 138.060, 130.413, 129.705, 124.513, 118.396, 116.651, 116.575, 114.370, 113.056 , 109.274, 108.7996, 97.207, 51.854, 45.119, 21.562, 12.670; FT-IR (KBr) ν_{max} = 2925 cm^{-1} (C−H Aliphatic), 1708 cm^{-1} (C=O lactone), 1619 cm^{-1} (−O−C=O), 1608 cm^{-1} (C=C Ar); UV−Vis (MeOH) λ_{max} = 415.81 nm; HRMS (ESI m/z) Calcd. for $C_{25}H_{26}N_3O_4$ $[M+H]^+$ 432.1918, found 432.1919.

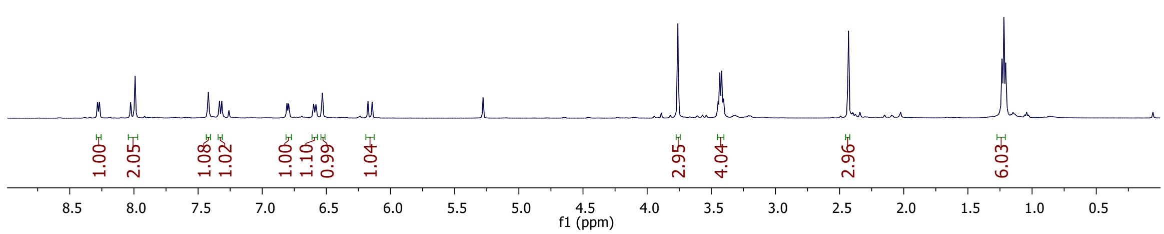


Figure SI-84. ^{1}H NMR spectra of **7b** on $CDCl_3$ 500 MHz

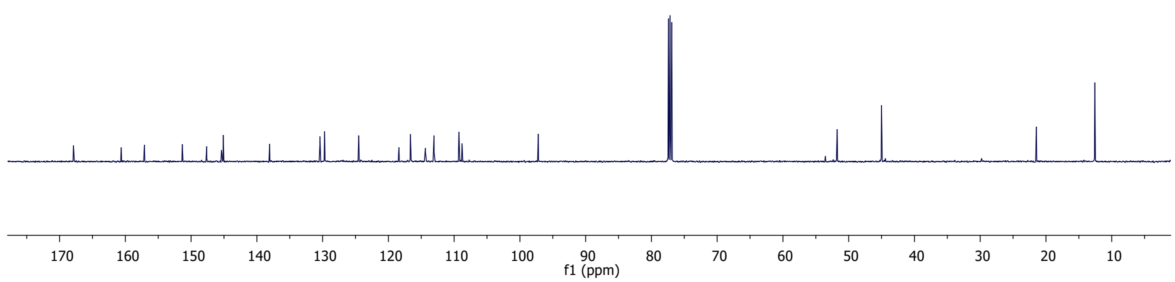


Figure SI-85. ^{13}C NMR spectra of **7b** on $CDCl_3$ 125 MHz.

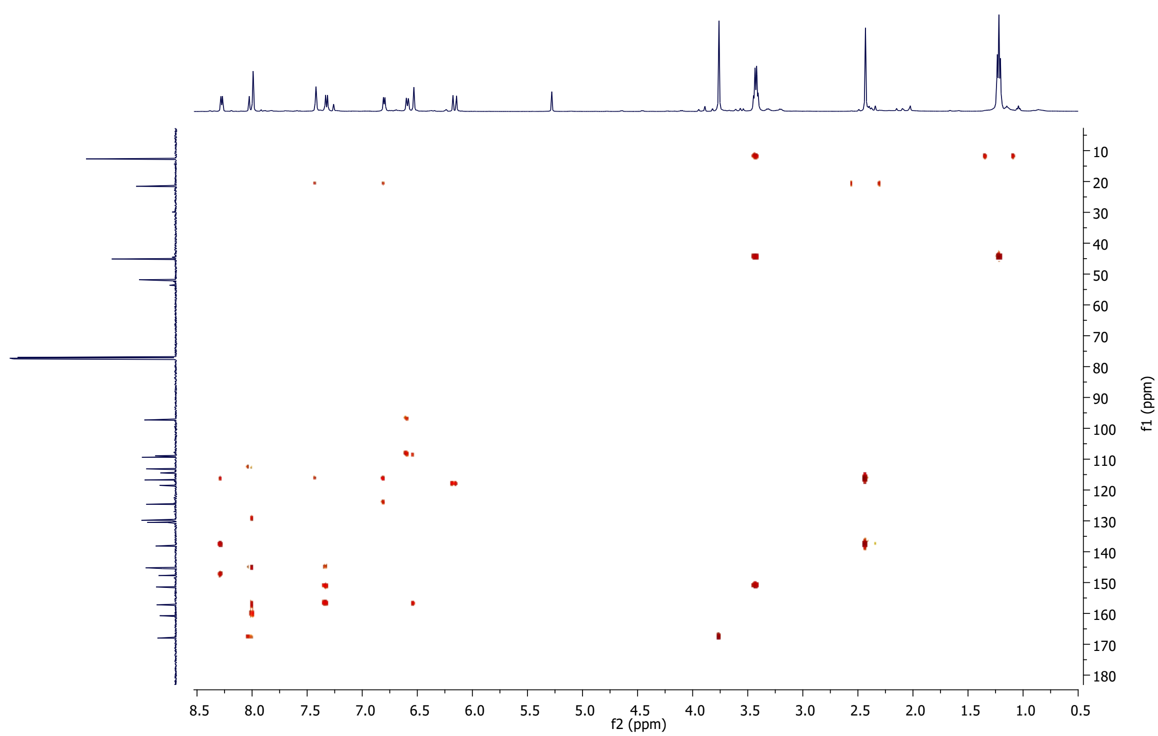


Figure SI-86. HMBC NMR spectra of **7b** on $CDCl_3$

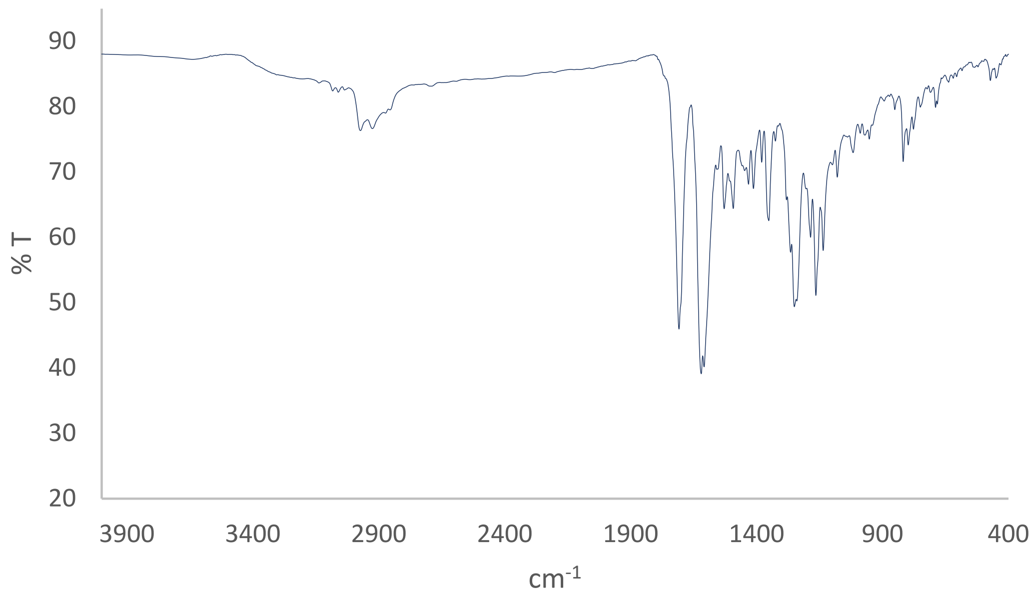


Figure SI-87. IR spectra for **7b** in KBr.

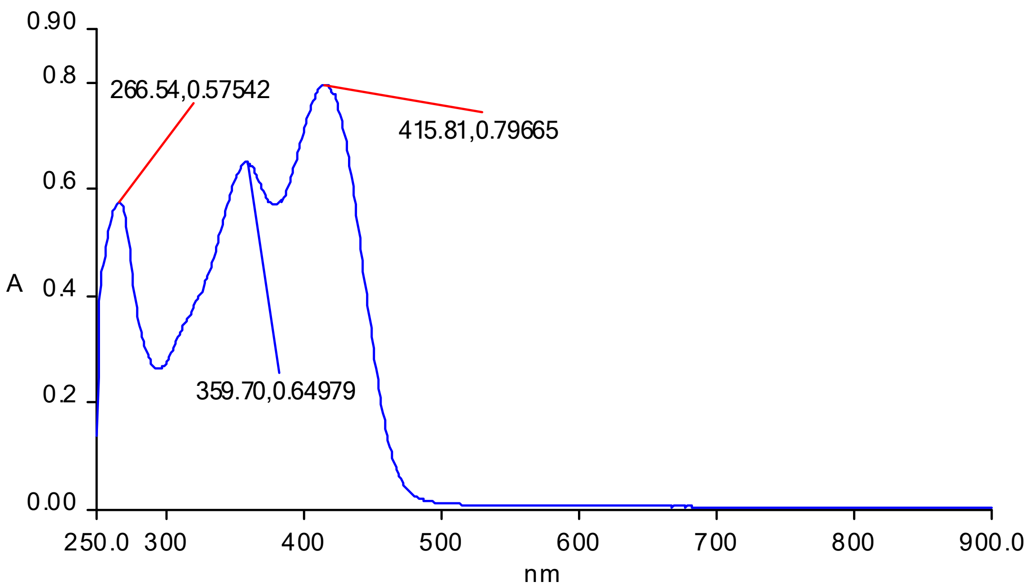


Figure SI-88. UV-Vis spectra of **7a** in MeOH.

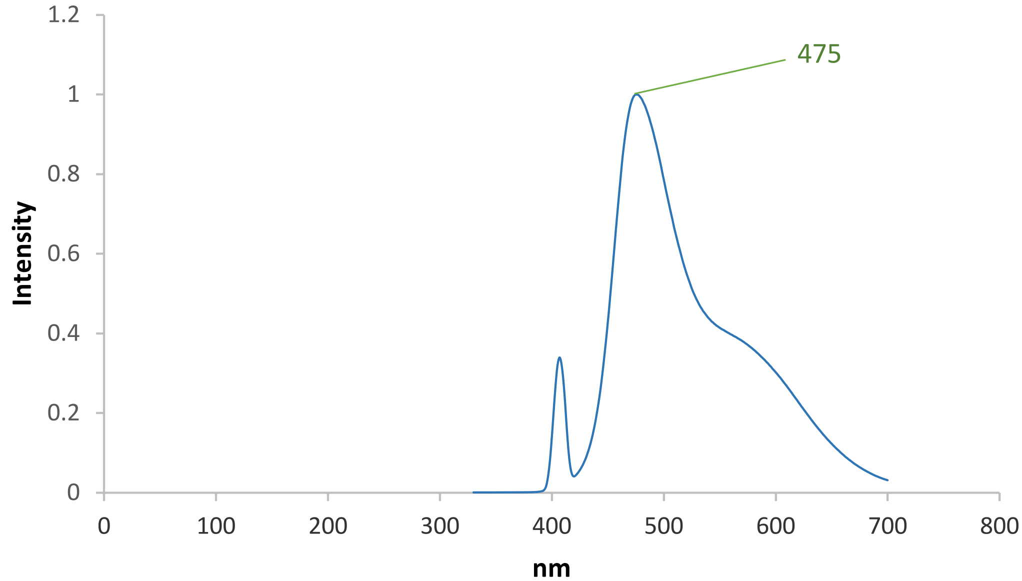


Figure SI-89. Emission spectra of **7b** in MeOH.

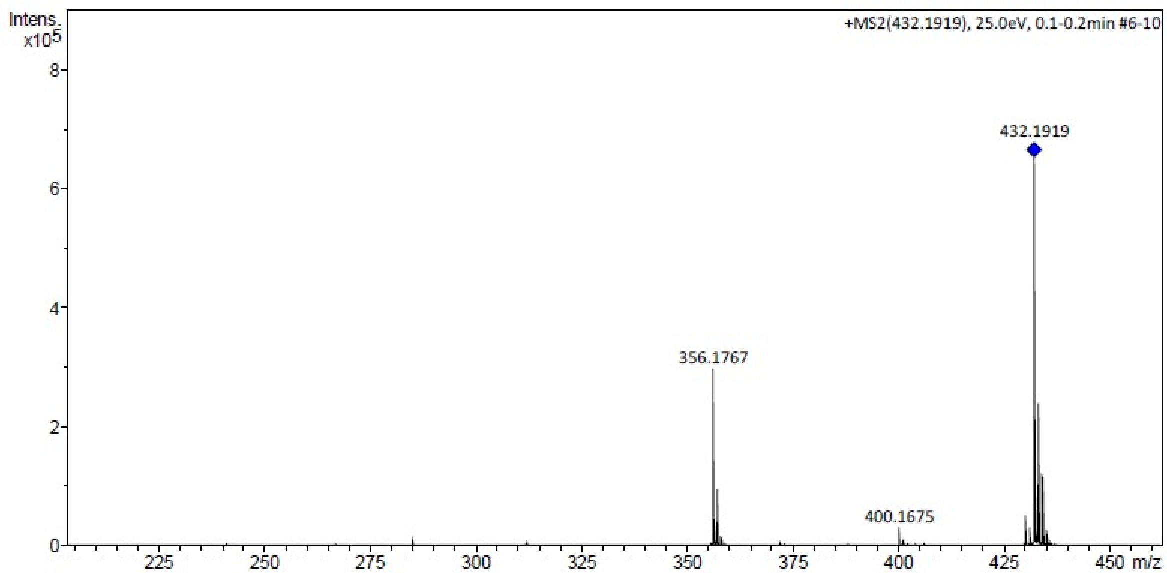
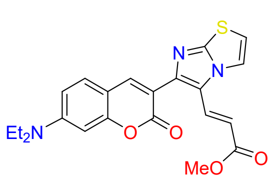


Figure SI-90. ESI-MS chromatogram of **7a**.



Methyl (E)-3-(6-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)imidazo[2,1-b]thiazol-5-yl)acrylate (7c): Yield 46%; yellow powder; m.p. = 185 – 188 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 7.962 – 7.929 (m, 2H, H-3a, Ar), 7.739 (d, *J* (H,H) = 4.5 Hz, 1H, −CH=C−), 7.327 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.009 (6, *J* (H,H) = 4.5 Hz, 1H, −CH=C−), 6.598 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.521 (s, 1H, Ar), 6.068 (d, *J* (H,H) = 16 Hz, 1H, −CH=C−), 3.762 (s, 1H, CH_3), 3.432 (q, *J* (H,H) = 7.5 Hz, 1H, $-CH_2-CH_3$), 1.216 (t, *J* (H,H) = 7.5 Hz, 1H, CH_3); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 167.537, 160.860, 156.948, 153.227, 151.315, 146.719, 144.502, 131.192, 129.682, 121.207, 119.429, 114.080, 113.924, 112.264, 109.320, 108.320, 97.174, 51.809, 45.023, 12.565; FT-IR (KBr) ν_{max} = 3115 cm^{-1} (C−H Ar), 2972 cm^{-1} (C−H

Aliphatic), 1709 cm^{-1} (C=O lactone), 1617 cm^{-1} (−O−<u>C=O</u>), 1595 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 416.21 nm; HRMS (ESI m/z) Calcd. for $C_{22}H_{22}N_3O_4S$ $[M+H]^+$ 424.1326, found 424.1332.

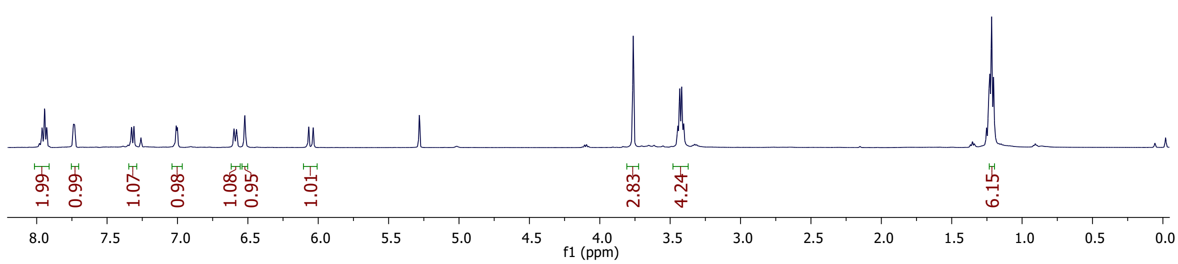


Figure SI-91. ^{1}H NMR spectra of **7c** on $CDCl_3$ 500 MHz

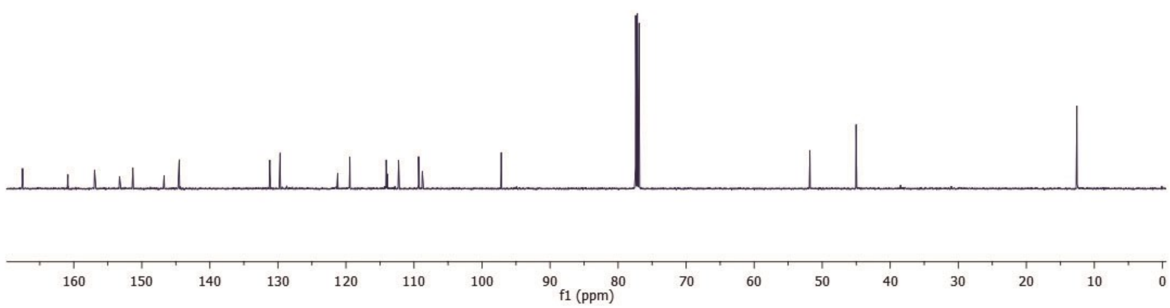


Figure SI-92. ^{13}C NMR spectra of **7c** on $CDCl_3$ 125 MHz.

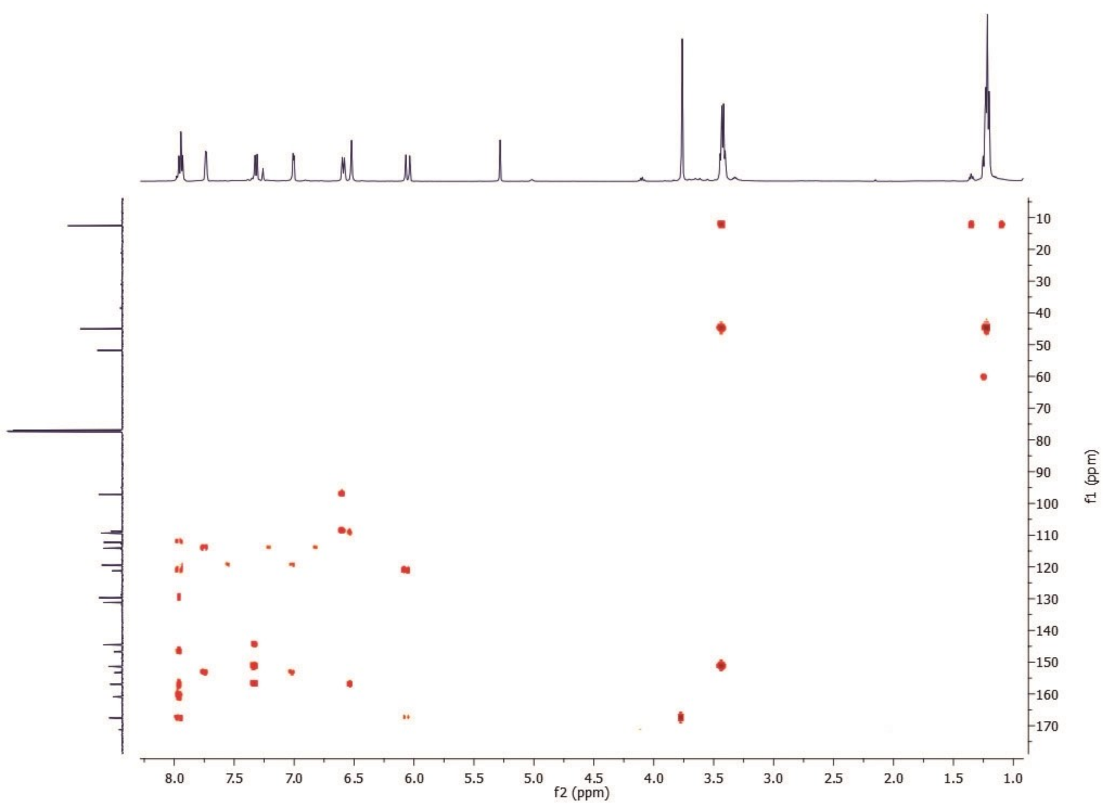


Figure SI-93. HMBC NMR spectra of **7c** on $CDCl_3$

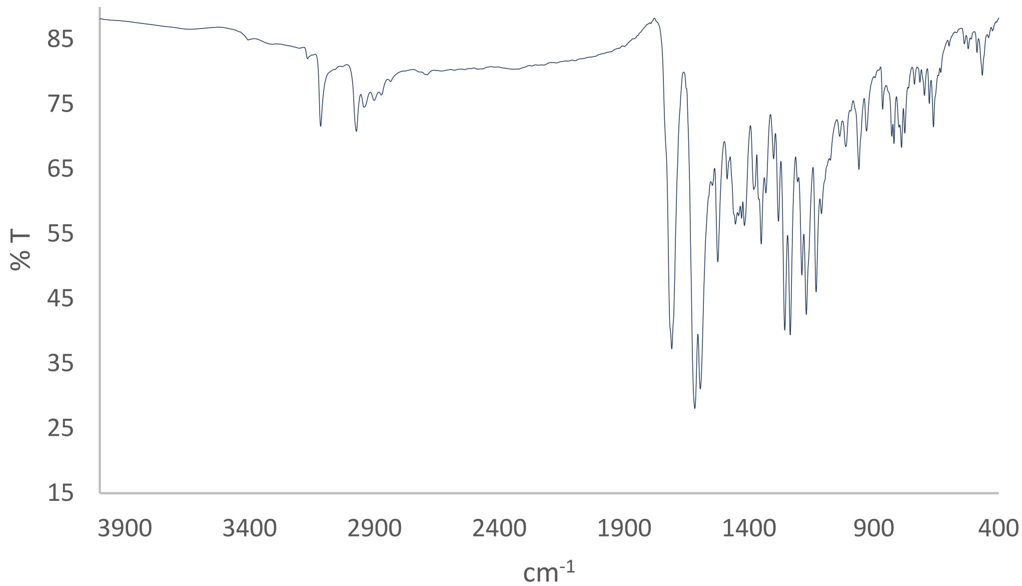


Figure SI-94. IR spectra for **7c** in KBr.

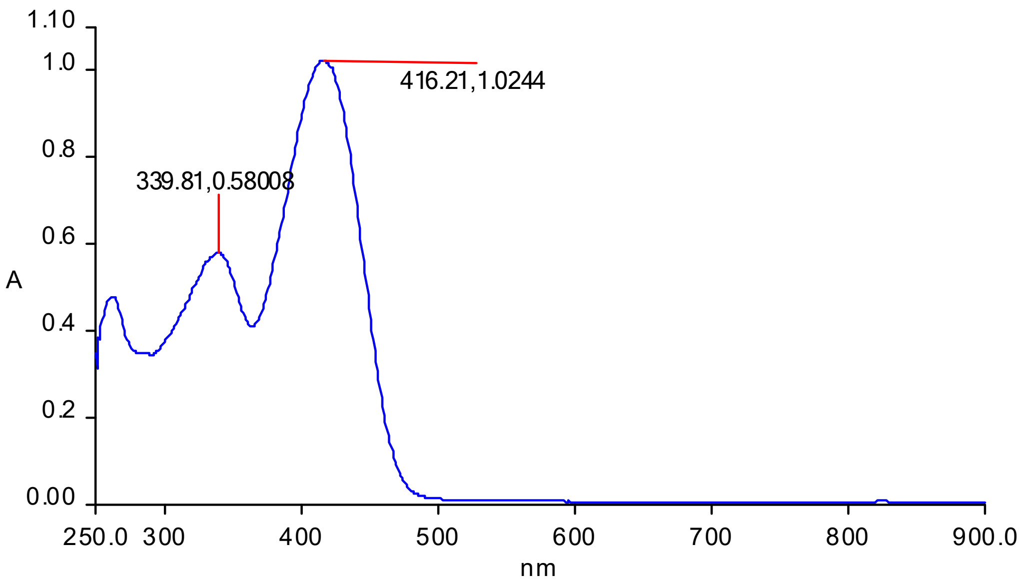


Figure SI-95. UV-Vis spectra of **7c** in MeOH.

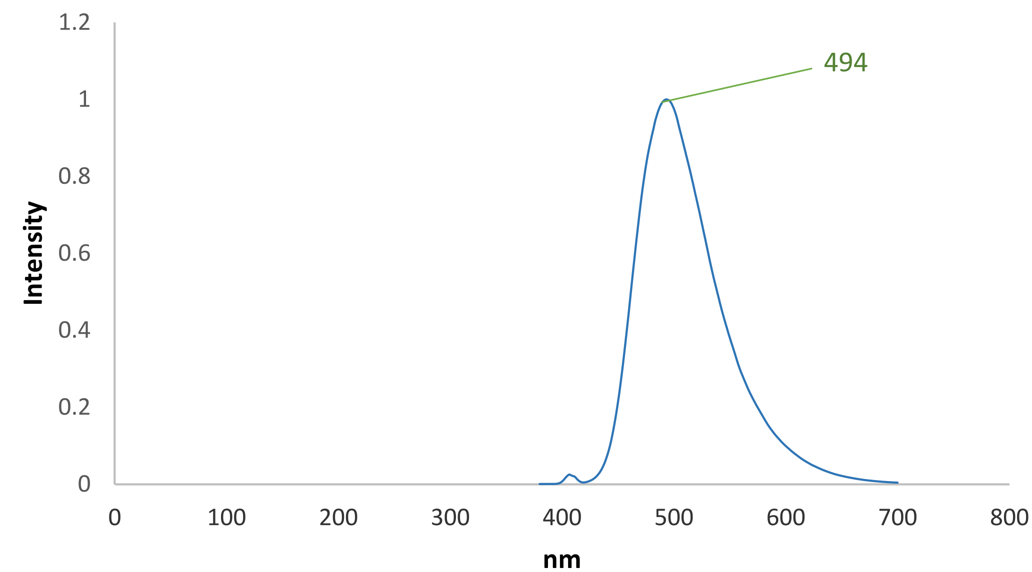


Figure SI-96. Emission spectra of **7c** in MeOH.

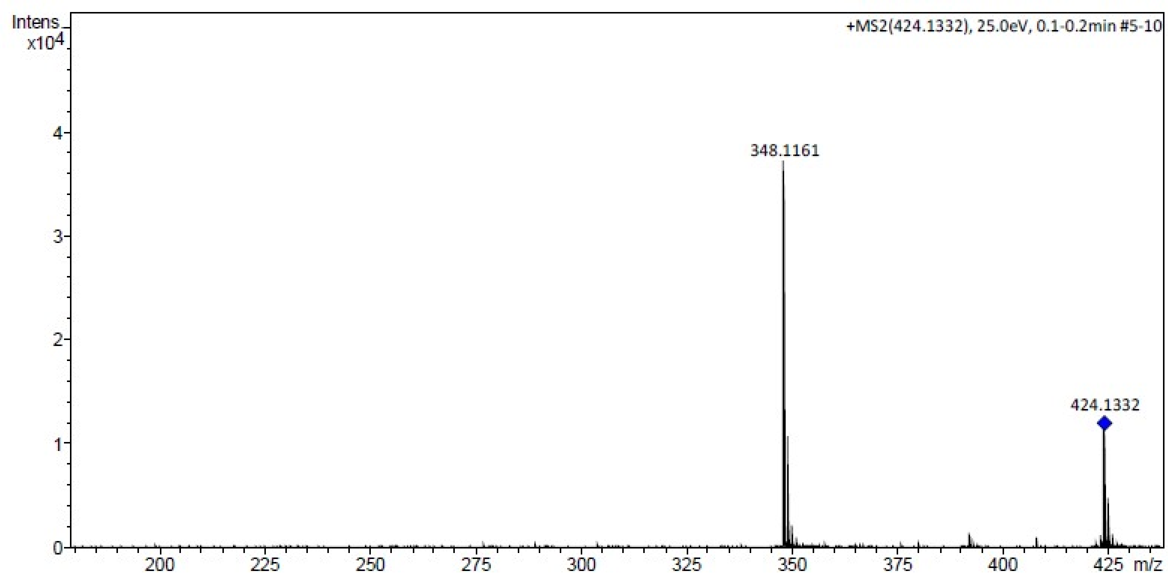
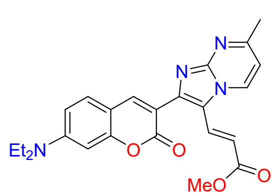


Figure SI-97. ESI-MS chromatogram of **7c**.



Methyl (E)-3-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-7-methylimidazo[1,2-a]pyrimidin-3-yl)acrylate (7d): Yield 65%; yellow powder; m.p. = 229 – 231 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.567 (d, *J* (H,H) = 6 Hz, 1H, Ar), 8.249 (s, 1H, −<u>CH</u>=C−), 8.113 (d, *J* (H,H) = 16.5 Hz, 1H, −<u>CH</u>=C−), 7.357 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 6.892 (t, *J* (H,H) = 7 Hz, 1H, Ar), 6.620 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.531 (s, 1H, Ar), 6.129 (d, *J* (H,H) = 16.5 Hz, 1H, −<u>CH</u>=C−), 3.779 (s, 3H, <u>CH_3</u>), 3.442 (q, *J* (H,H) = 7 Hz, 4H, −<u>CH_2</u>−CH_3), 2.663 (s, 3H, <u>CH_3</u>), 1.231 (t, *J* (H,H) = 7 Hz, 6H, <u>CH_3</u>); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 167.511, 161.84, 160.494, 157.221, 151.546, 149.904, 146.012, 145.938, 132.288, 130.688, 130.044, 116.767, 114.395, 113.772, 110.816, 109.434, 108.975, 97.105, 51.922, 45.082, 25.145, 12.593; FT-IR (KBr) ν_{max} = 3046 cm^{-1} (C−H Ar), 2963 cm^{-1} (C−H Aliphatic), 1719 cm^{-1} (C=O lactone), 1621 cm^{-1} (−O−C=O), 1593 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 423.07 nm; HRMS (ESI m/z) Calcd. for $C_{24}H_{25}N_4O_4$ $[M+H]^+$ 433.1870, found 433.1872.

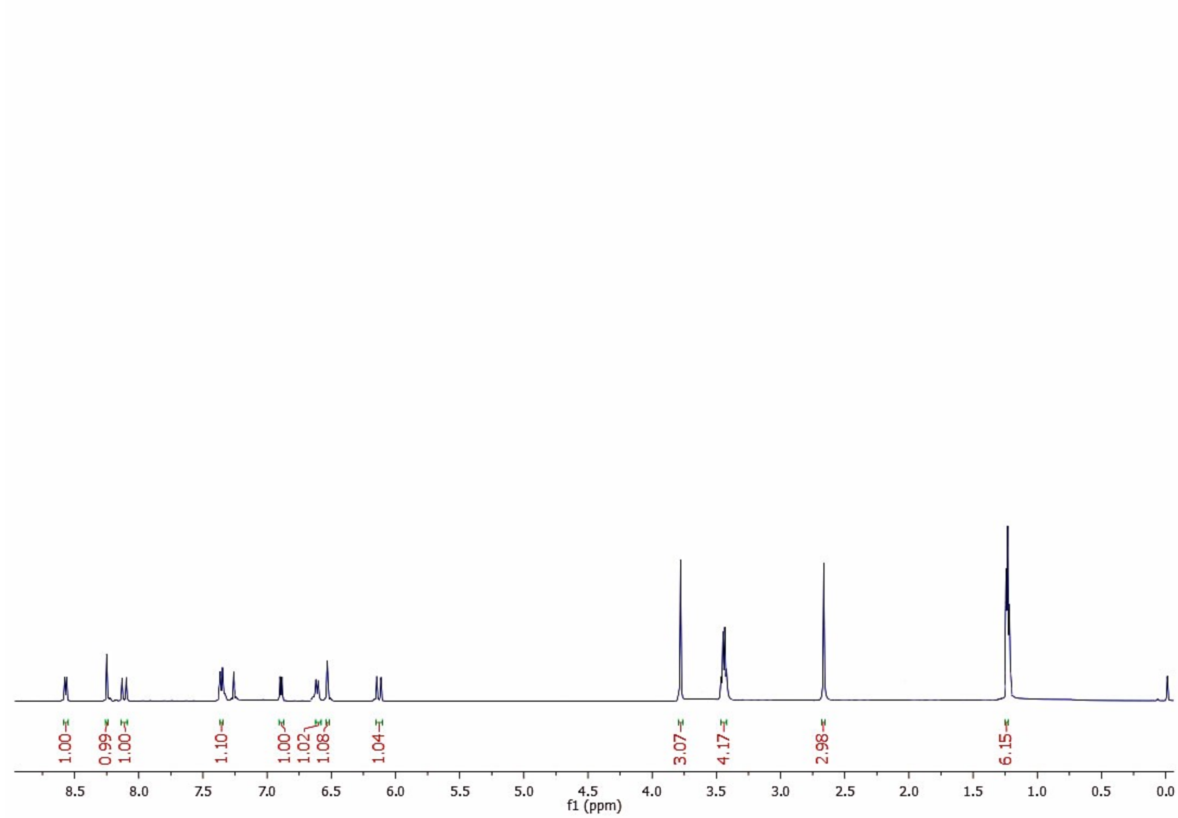


Figure SI-98. ^{1}H NMR spectra of **7d** on $CDCl_3$ 500 MHz

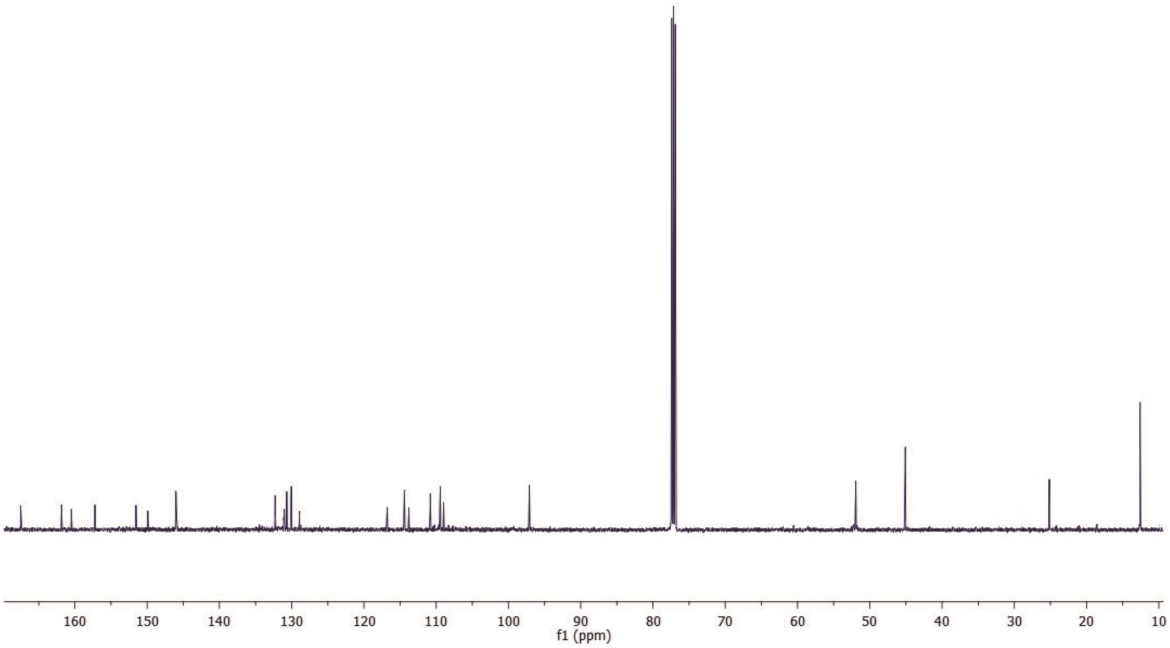


Figure SI-99. ^{13}C NMR spectra of **7d** on $CDCl_3$ 125 MHz.

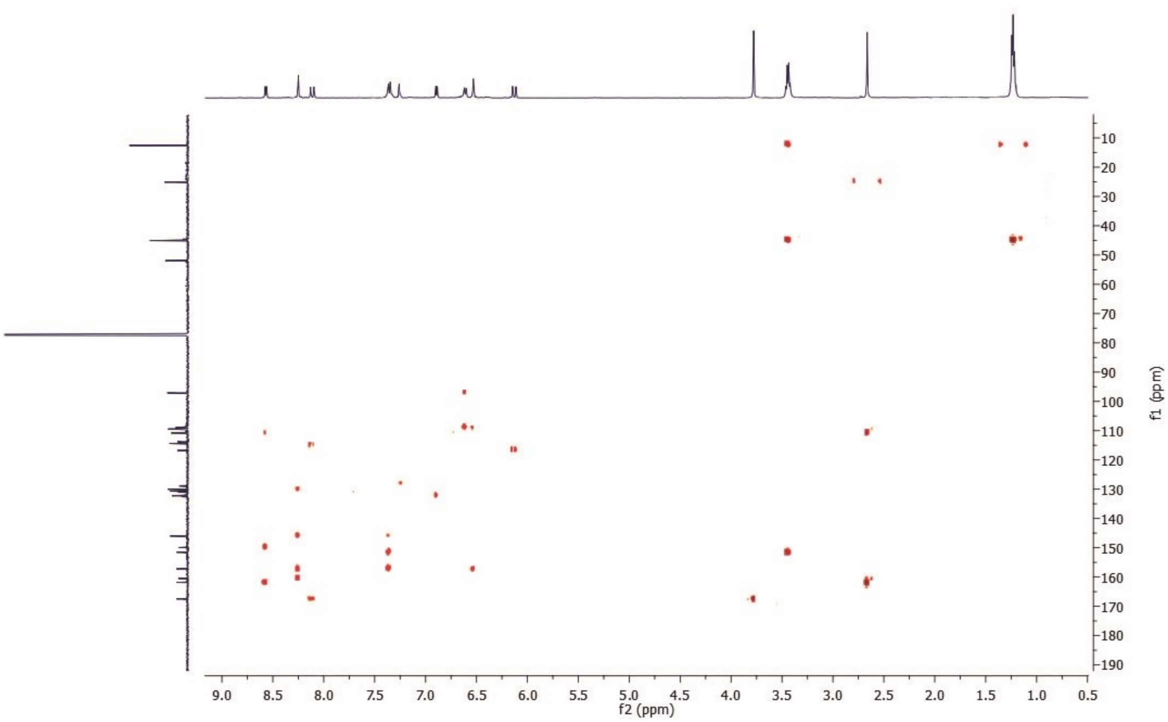


Figure SI-100. HMBC NMR spectra of **7d** on $CDCl_3$

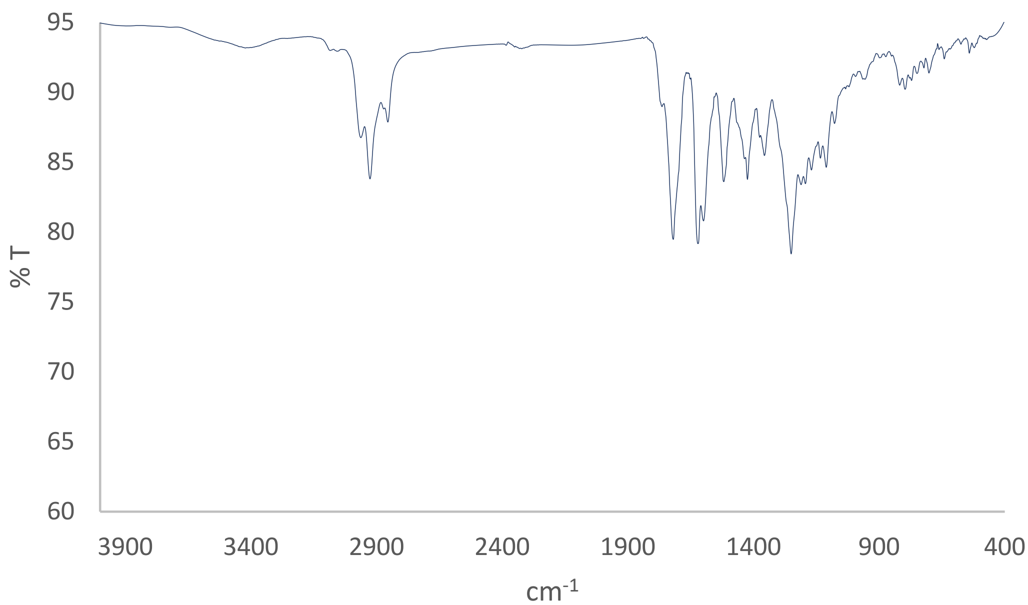


Figure SI-101. IR spectra for **7d** in KBr.

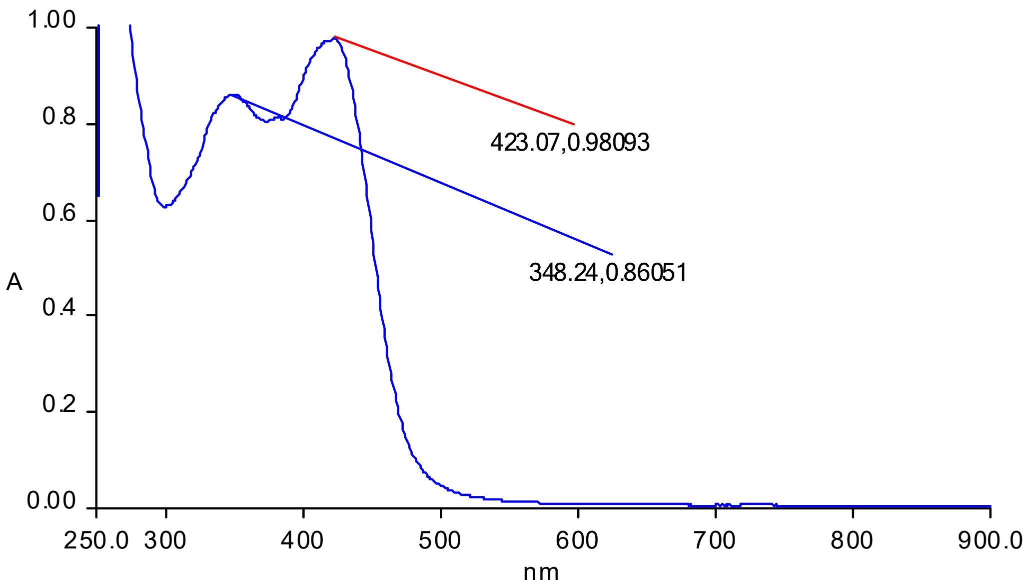


Figure SI-102. UV-Vis spectra of **7d** in MeOH.

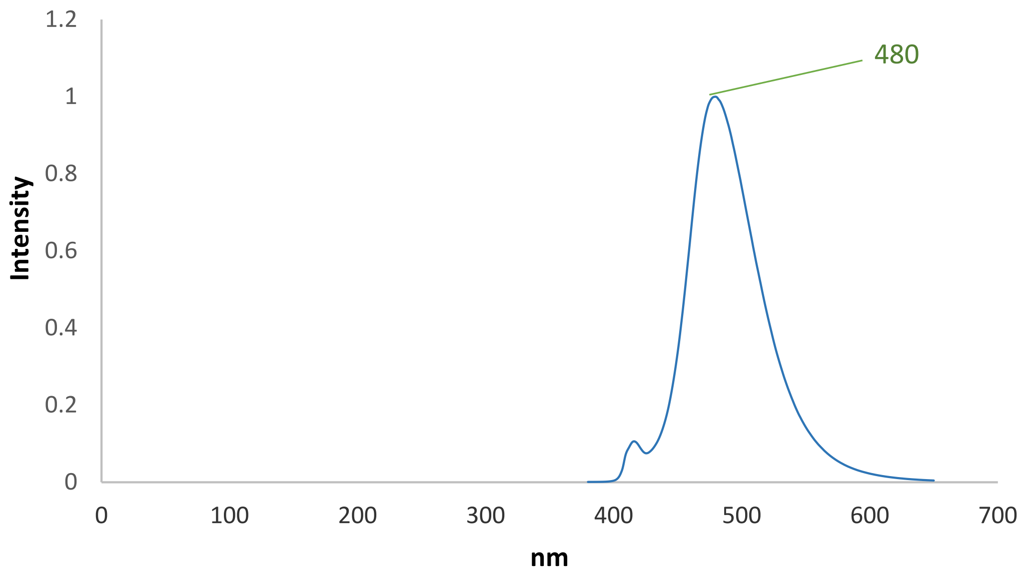


Figure SI-103. Emission spectra of **7d** in MeOH.

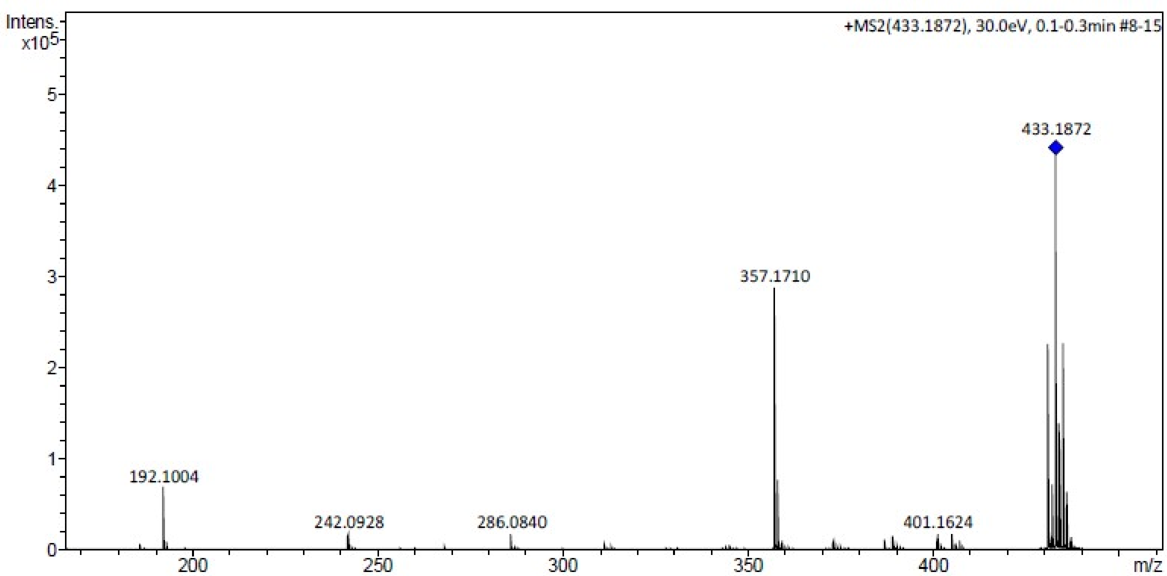
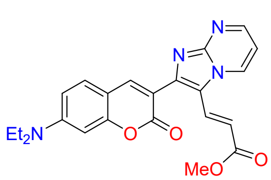


Figure SI-104. ESI-MS chromatogram of **7d**.



Methyl (E)-3-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)imidazo[1,2-a]pyrimidin-3-yl)acrylate (7e): Yield 43%; yellow powder; m.p. = 262 – 264 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.732 (d, *J* (H,H) = 6 Hz, 1H, Ar), 8.602 (d, *J* (H,H) = 4.5 Hz, 1H, Ar), 8.206 (s, 1H, −CH=C−), 8.069 (d, *J* (H,H) = 16.5 Hz, 1H, −CH=C−), 7.342 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.036 (t, *J* (H,H) = 7 Hz, 1H, Ar), 6.593 (d, *J* (H,H) = 9 Hz, 1H, Ar), 6.500 (s, *J* (H,H) = 7 Hz, 1H, Ar), 6.173 (d, *J* (H,H) = 16.5 Hz, 1H, −CH=C−), 3.744 (s, 1H, CH_3), 3.420 (q, *J* (H,H) = 7 Hz, 4H, CH_2−CH_3), 1.208 (t, *J* (H,H) = 7 Hz, 6H, CH_3); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 167.278, 160.372, 157.201, 151.571, 151.207, 149.626, 146.19, 146.091, 132.891, 130.199, 130.019, 117.050, 115.356, 113.361, 109.953, 109.441, 108.783, 96.988, 51.895, 45.023, 12.525; FT-IR (KBr) ν_{max} = 3067 cm^{-1} (C−H Ar), 2968 cm^{-1} (C−H Aliphatic), 1711 cm^{-1} (C=O lactone), 1616 cm^{-1} (−O−C=O), 1588 cm^{-1} (C=C Ar); UV–Vis (MeOH) λ_{max} = 422.98 nm; HRMS (ESI m/z) Calcd. for $C_{23}H_{23}N_4O_4$ $[M+H]^+$ 419.1714, found 419.1625.

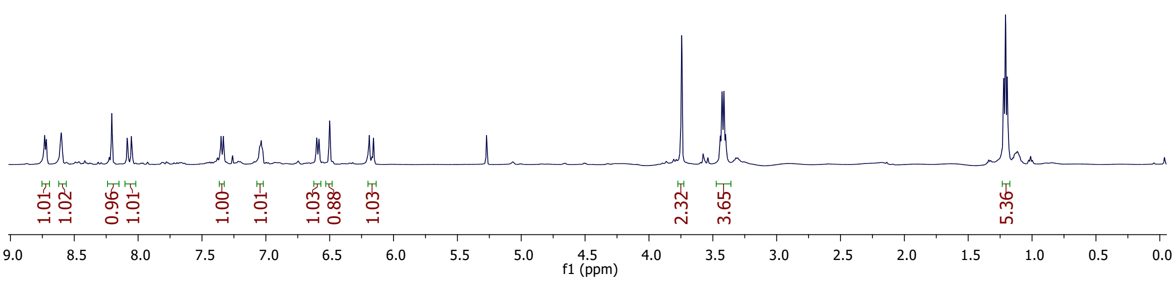


Figure SI-105. ^{1}H NMR spectra of **7e** on $CDCl_3$ 500 MHz

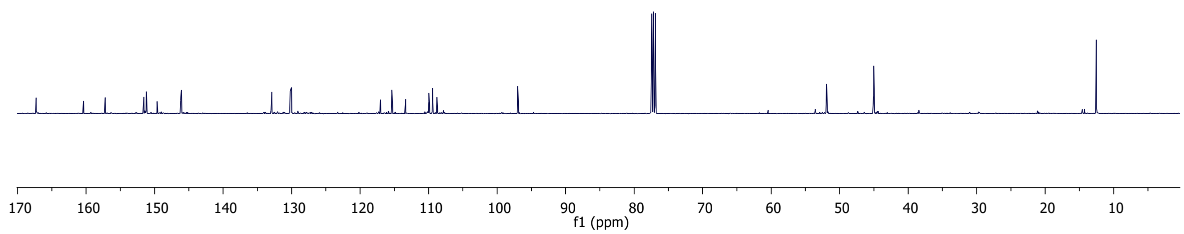


Figure SI-106. ^{13}C NMR spectra of **7e** on $CDCl_3$ 125 MHz.

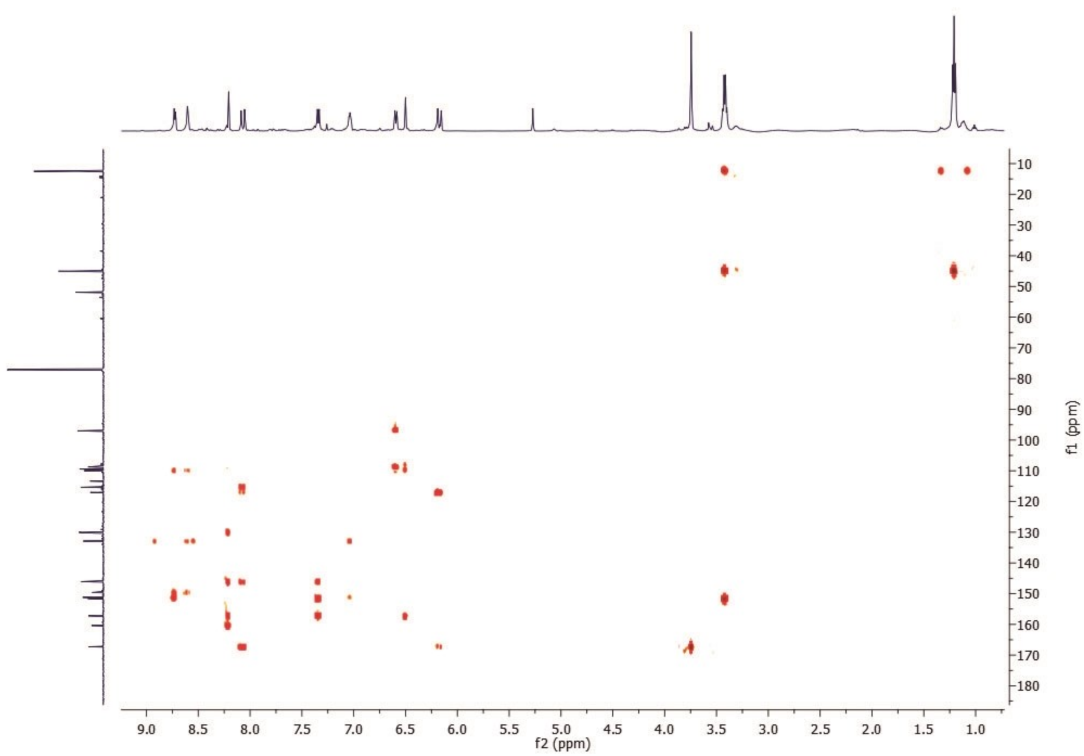


Figure SI-107. HMBC NMR spectra of **7e** on $CDCl_3$

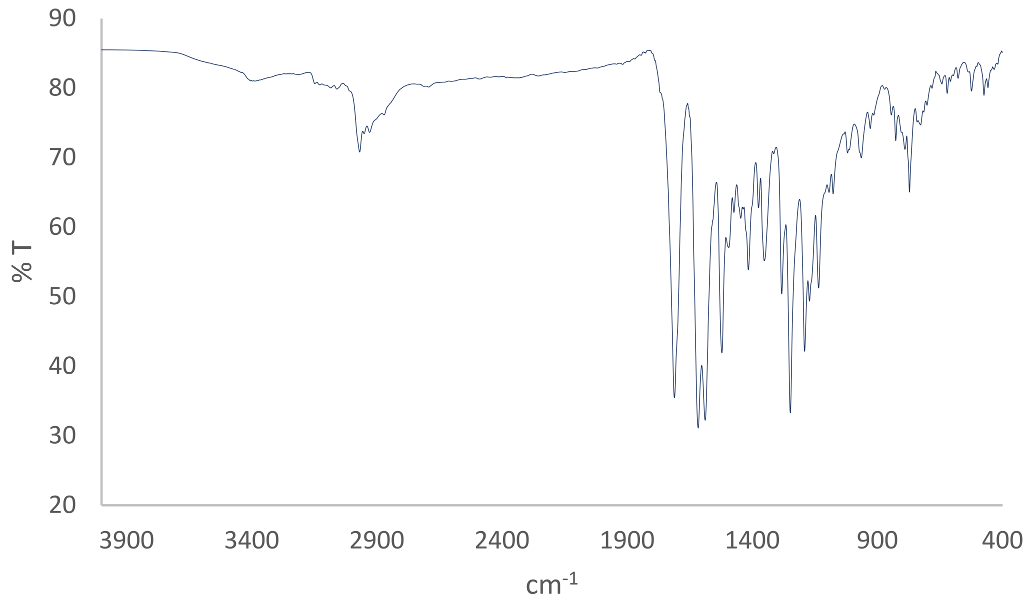


Figure 108. IR spectra for **7e** in KBr.

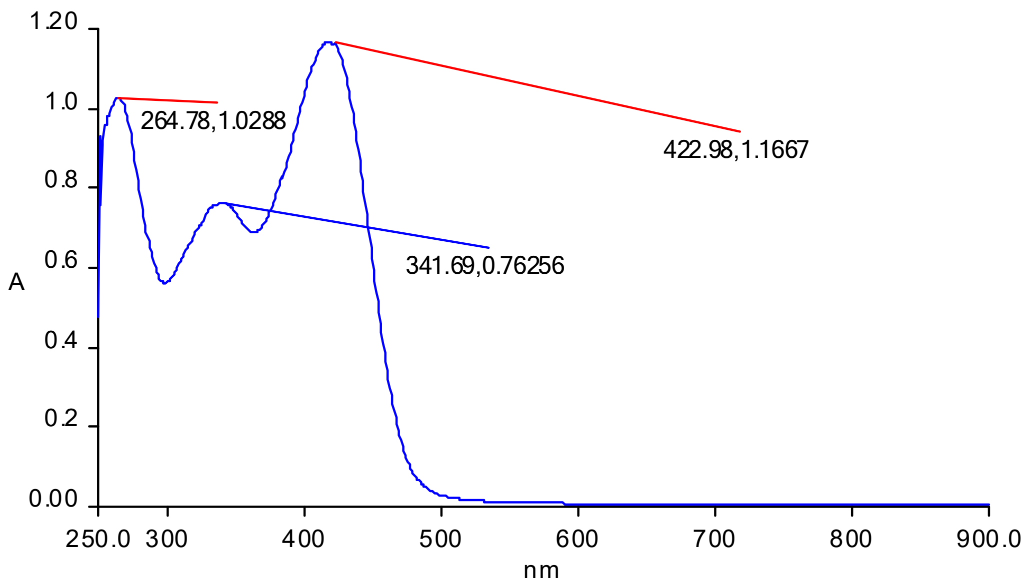


Figure SI-109. UV-Vis spectra of **7e** in MeOH.

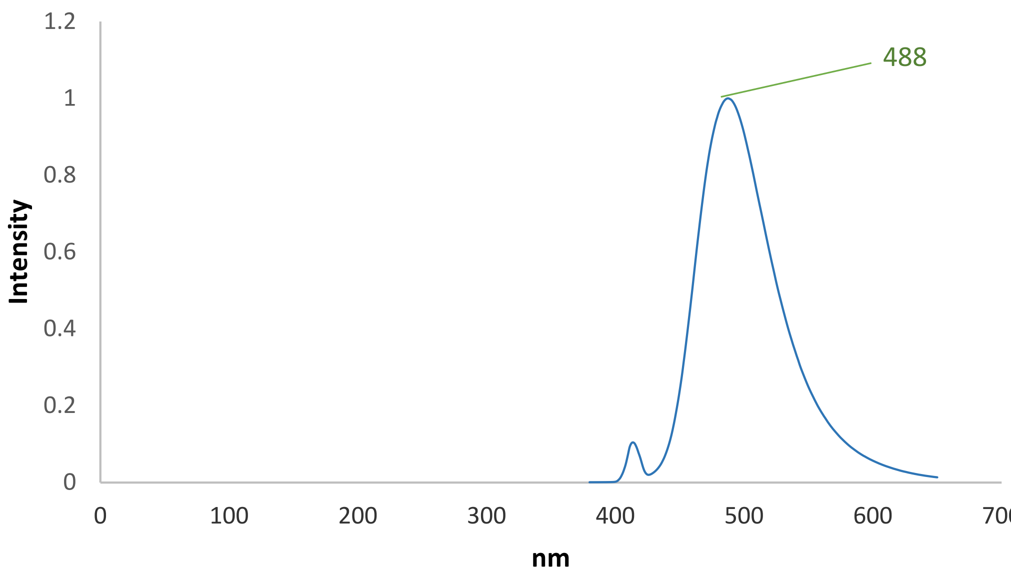


Figure SI-110. Emission spectra of **7e** in MeOH.

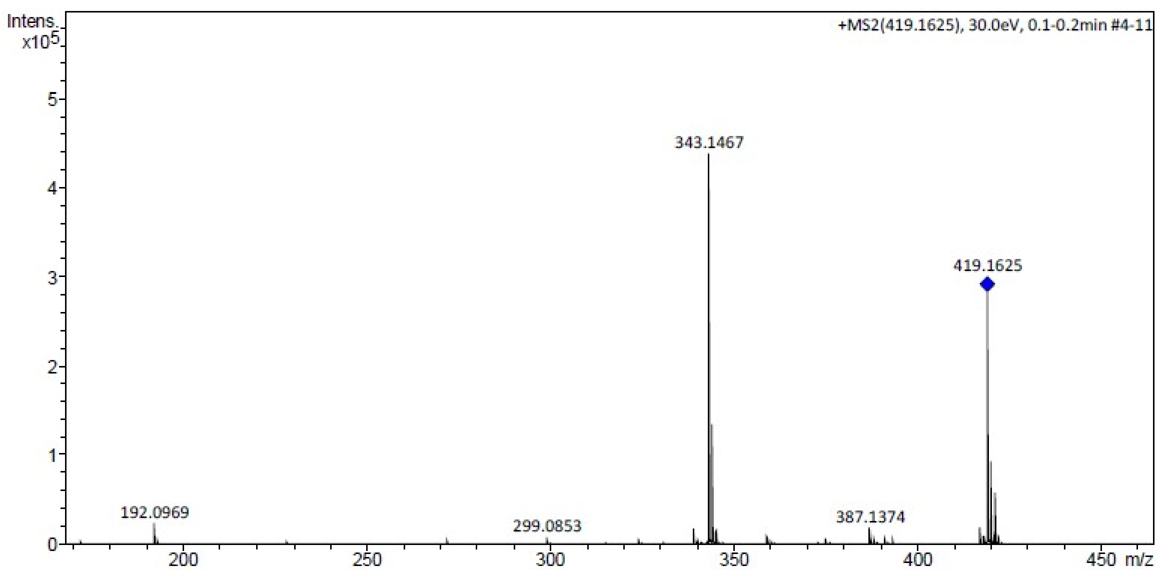
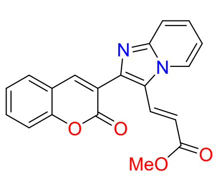


Figure SI-111. ESI-MS chromatogram of **7e**.



Methyl (E)-3-(2-(2-oxo-2H-chromen-3-yl)imidazo[1,2-a]pyridin-3-yl)acrylate (7f): Yield 81%; light brown powder; m.p. = 208 – 210 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.399 (d, *J* (H,H) = 7 Hz, 1H, Ar), 8.162 (s, 1H, −CH=C−), 7.999 (d, *J* (H,H) = 16 Hz, 1H, −CH=C−), 7.684 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.571 (m, 2H, H-7', Ar), 7.395 – 7.303 (m, 3H, Ar), 7.001 (t, *J* (H,H) = 7 Hz, 1H, Ar), 6.221 (d, *J* (H,H) = 16 Hz, 1H, −CH=C−), 3.762 (s, 1H, CH_3); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 167.425, 159.441, 154.189, 147.052, 144.749, 143.339, 132.505, 129.849, 128.572, 126.983, 125.198, 124.850, 122.441, 119.378, 119.153, 118.373, 116.802, 115.267, 114.399, 51.909; FT-IR (KBr) ν_{max} = 3071 cm^{-1} (C−H Ar), 2940 cm^{-1} (C−H Aliphatic), 1724 cm^{-1} (C=O lactone), 1705 cm^{-1} (−O−C=O), 1623 cm^{-1} (C=C Ar);

UV–Vis (MeOH) λ_{max} = 330.17 nm; HRMS (ESI m/z) Calcd. for $C_{20}H_{15}N_2O_4$ $[M+H]^+$ 347.1026, found 347.1032.

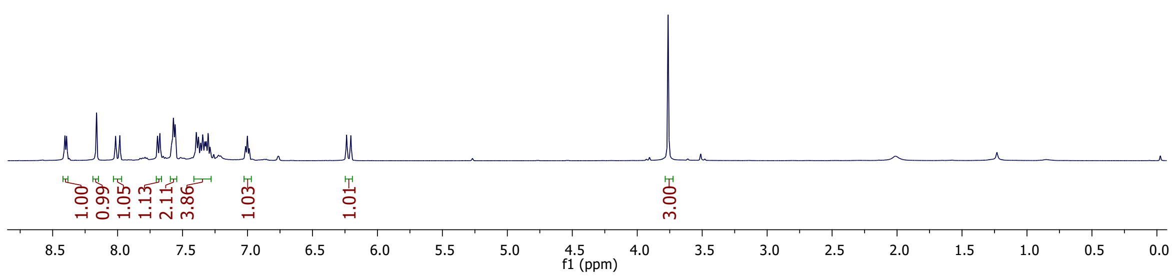


Figure SI-112. ^{1}H NMR spectra of **7f** on $CDCl_3$ 500 MHz

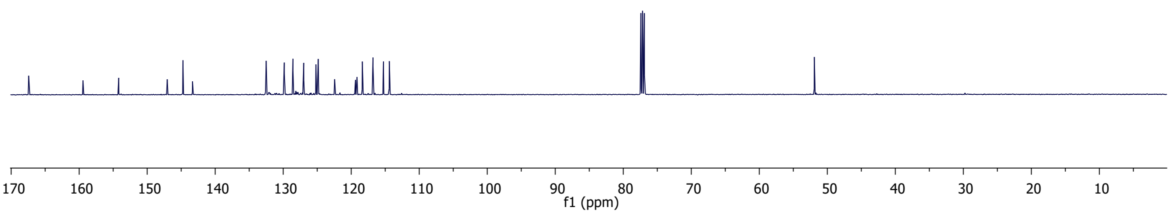


Figure SI-113. ^{13}C NMR spectra of **7f** on $CDCl_3$ 125 MHz.

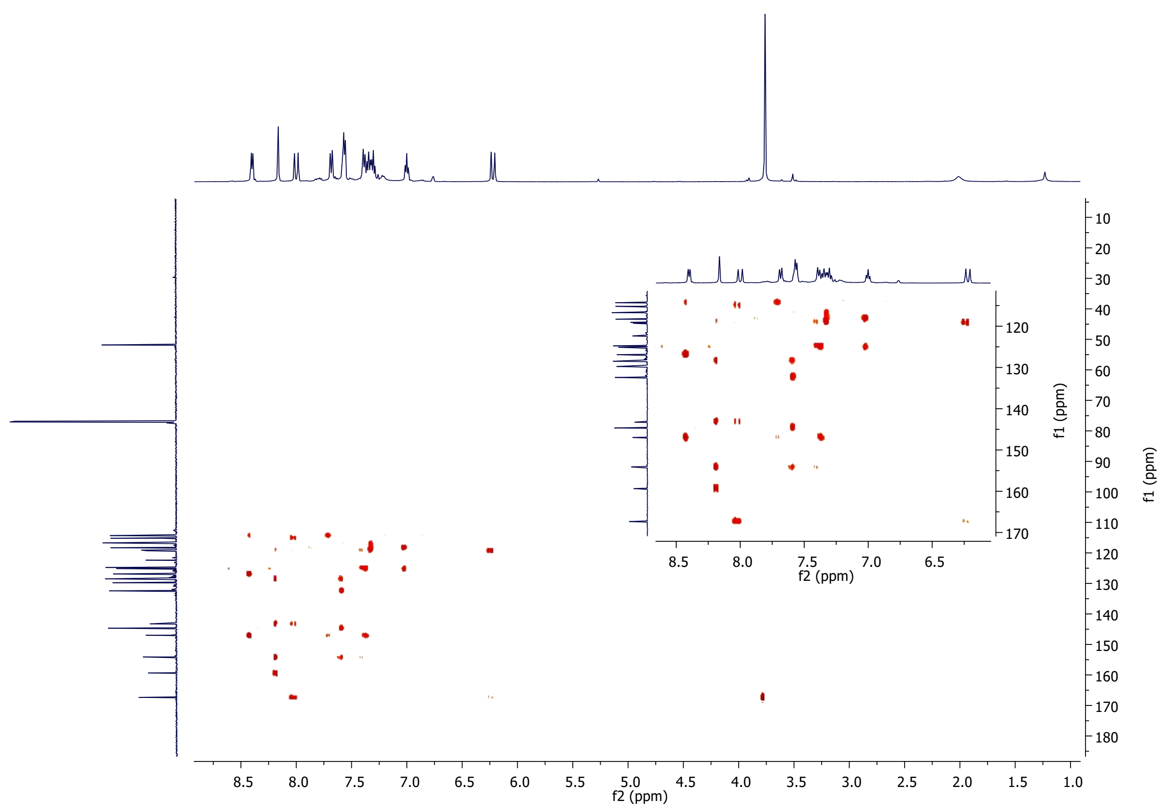


Figure SI-114. HMBC NMR spectra of **7f** on $CDCl_3$

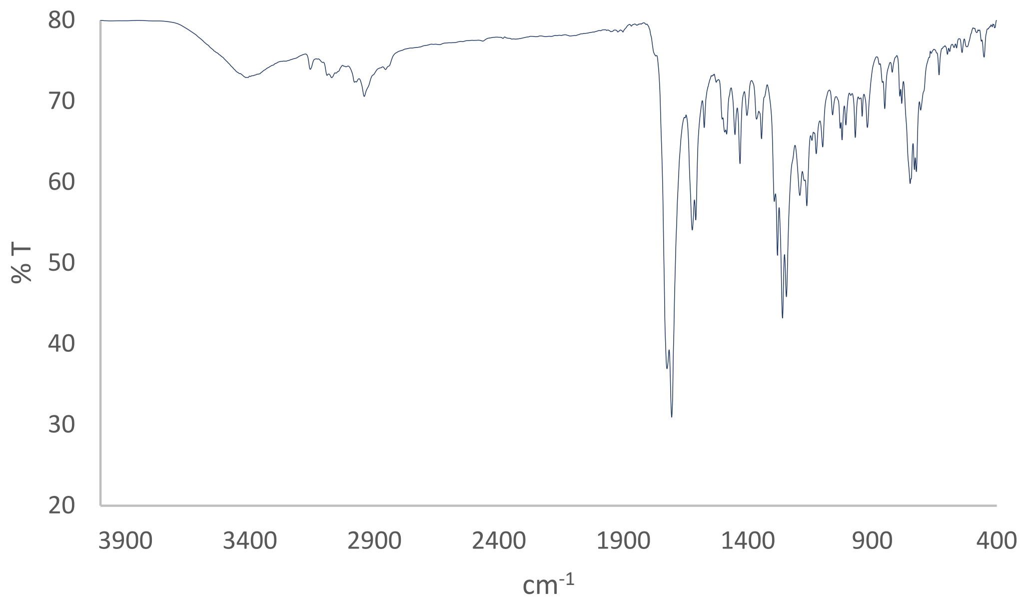


Figure SI-115. IR spectra for **7f** in KBr.

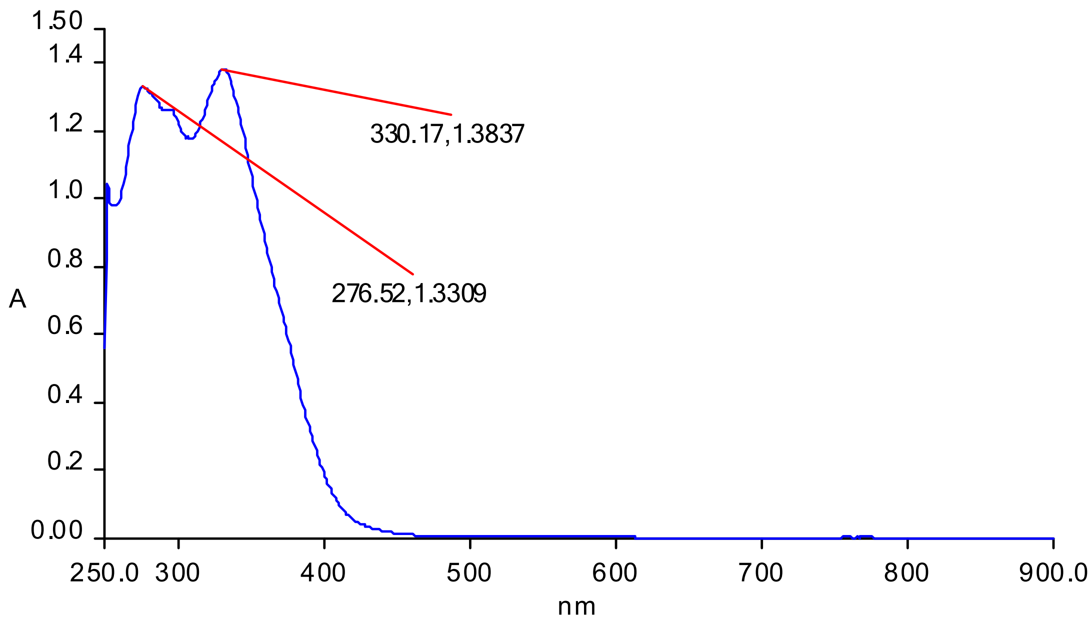


Figure SI-116. UV-Vis spectra of **7f** in MeOH.

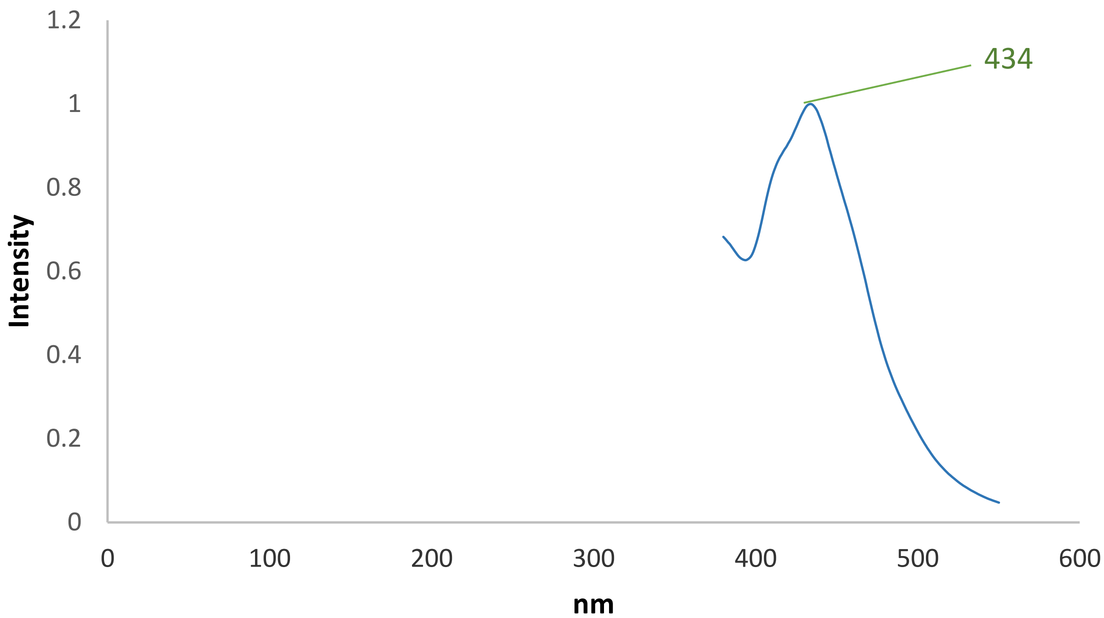


Figure SI-117. Emission spectra of **7f** in MeOH.

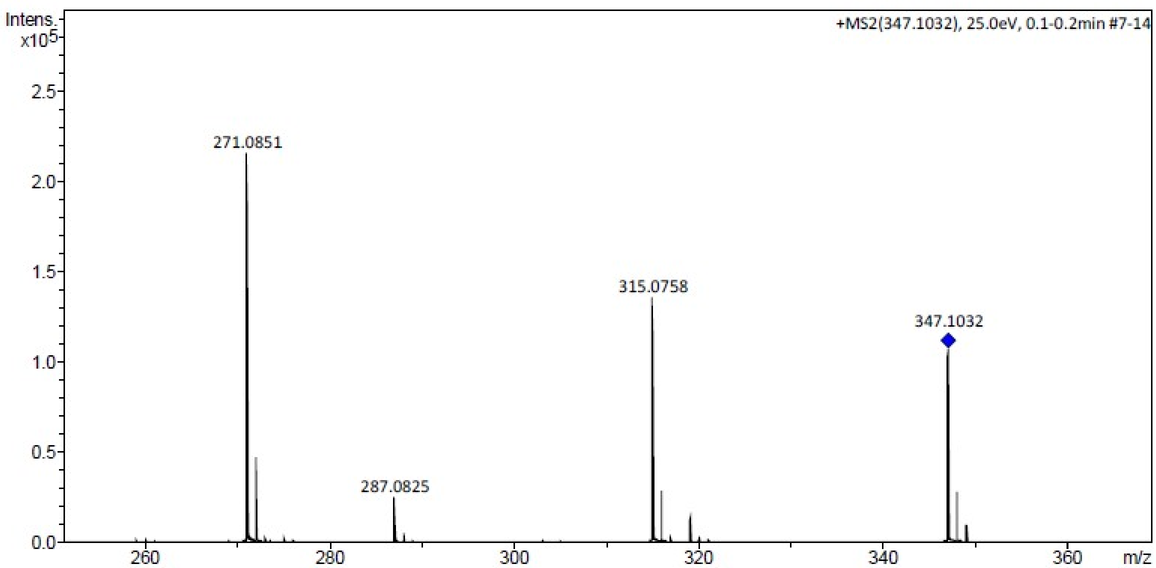
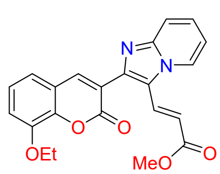


Figure SI-118. ESI-MS chromatogram of **7f**.



Methyl (E)-3-(2-(8-ethoxy-2-oxo-2H-chromen-3-yl)imidazo[1,2-a]pyridin-3-yl)acrylate (7g): Yield 71%; dark brown powder; m.p. = 137 – 141 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.428 (d, *J* (H,H) = 6.5 Hz, 1H, Ar), 8.180 (s, 1H, −<u>CH</u>=C−), 8.019 (d, *J* (H,H) = 16 Hz, 1H, −<u>CH</u>=C−), 7.713 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.373 (d, *J* (H,H) = 7 Hz, 1H, Ar), 7.227 (d, *J* (H,H) = 8 Hz, 1H, Ar), 7.157 – 7.140 (m, 2H, Ar), 7.027 (t, *J* (H,H) = 7 Hz, 1H, Ar), 7.231 (d, *J* (H,H) = 16 Hz, 1H, −<u>CH</u>=C−), 4.226 (q, *J* (H,H) = 7 Hz, 2H, <u>CH_2</u>−CH_3), 3.788 (s, 1H, <u>CH_3</u>), 1.538 (t, *J* (H,H) = 7 Hz, 3H, <u>CH_3</u>); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 167.460, 159.120, 147.080, 146.631, 145.059, 144.059, 143.303, 129.954, 126.950, 125.220, 124.732, 122.701, 119.957, 119.914, 119.463, 118.408, 115.499, 114.322, 65.173, 51.940, 14.909; FT-IR (KBr) ν_{max} = 2926 cm^{-1} (C−H Aliphatic), 1720 cm^{-1} (C=O lactone), 1621 cm^{-1} (−O−C=O); UV−Vis (MeOH) λ_{max} = 314.90 nm; HRMS (ESI m/z) Calcd. for $C_{22}H_{19}N_2O_5$ $[M+H]^+$ 391.1288, found 391.1299.

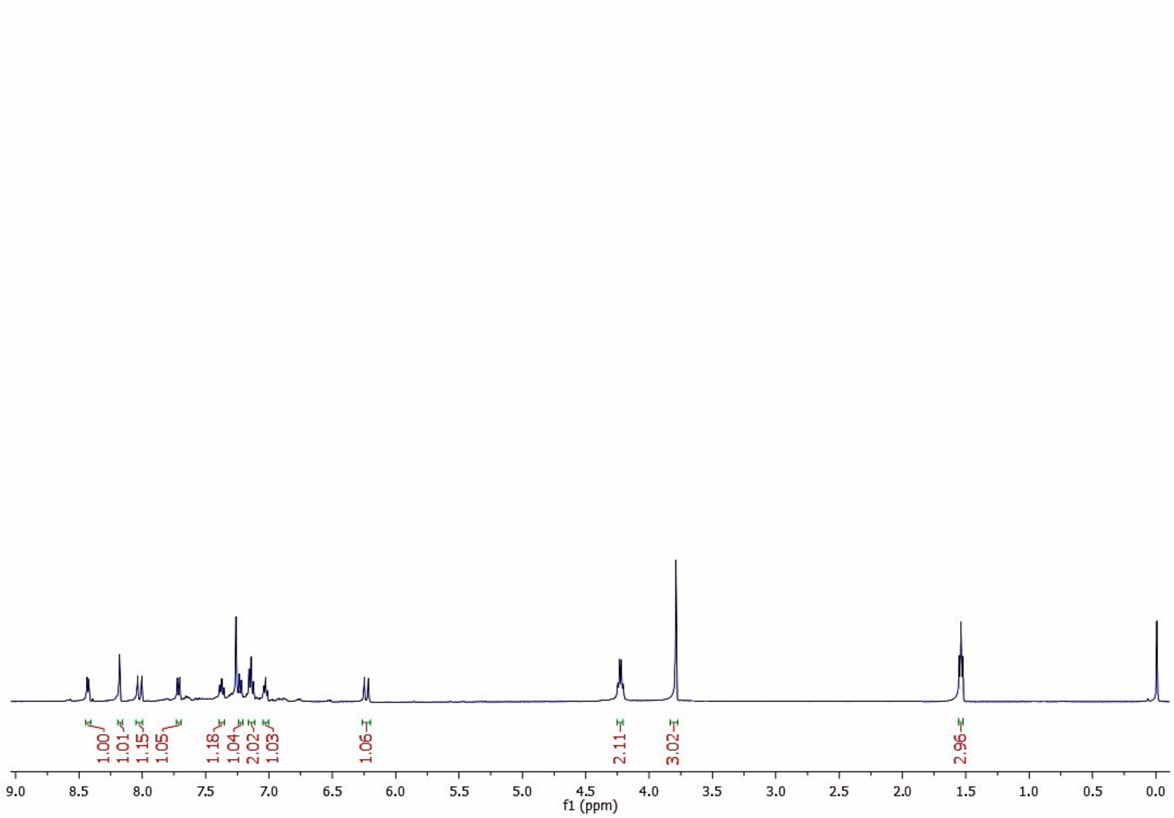


Figure SI-119. ^1H NMR spectra of **7g** on $CDCl_3$ 500 MHz

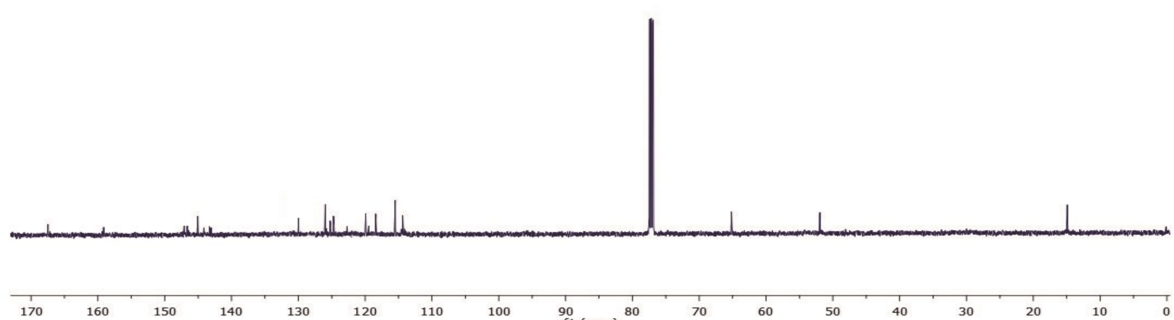


Figure SI-120. ^{13}C NMR spectra of **7g** on $CDCl_3$ 125 MHz.

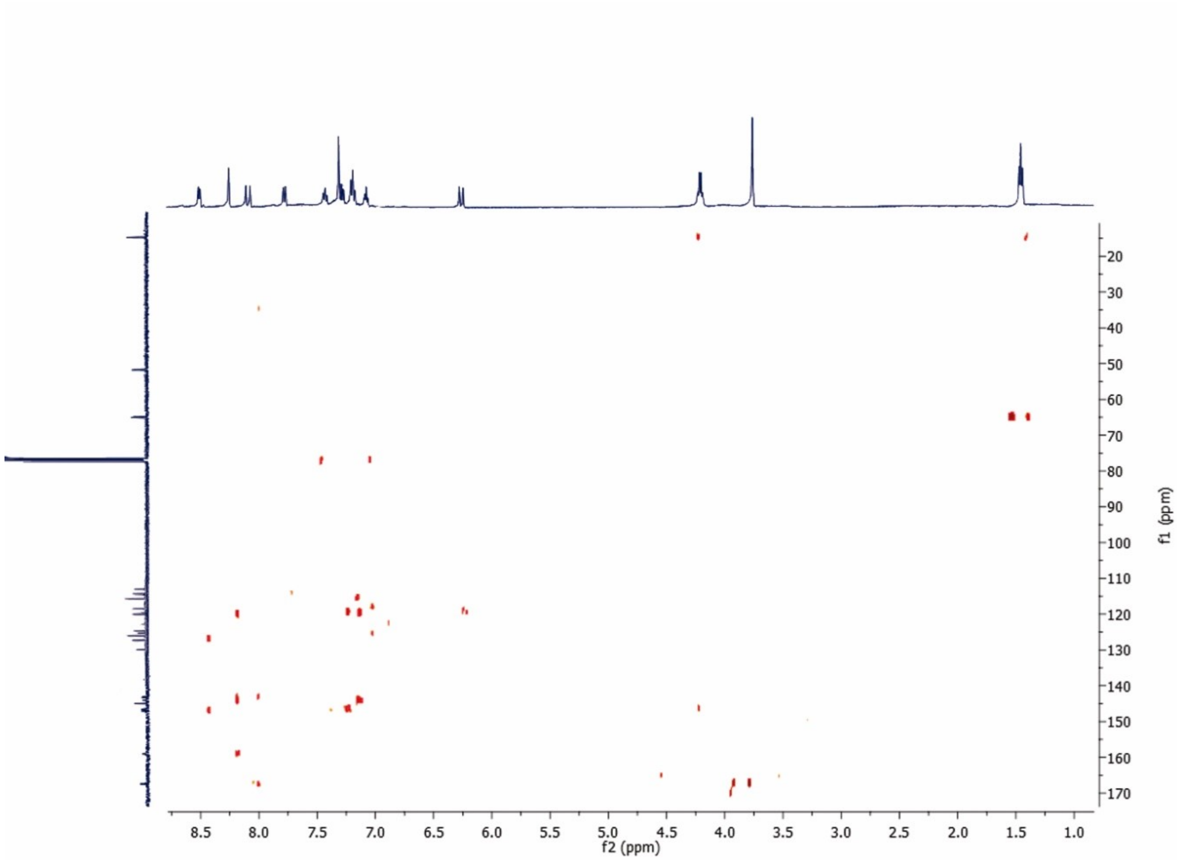


Figure SI-121. HMBC NMR spectra of **7g** on $CDCl_3$

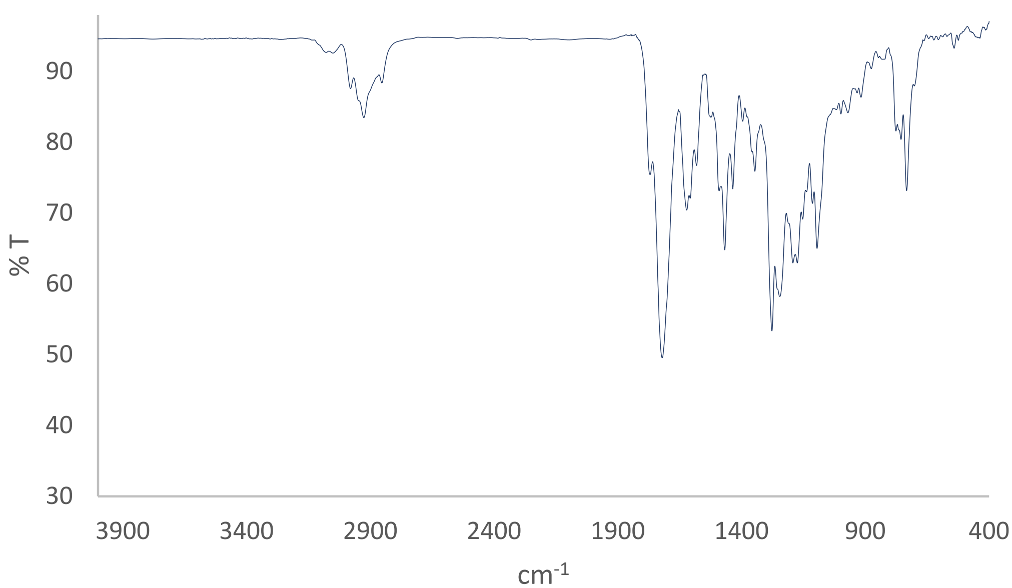


Figure SI-122. IR spectra for **7g** in KBr.

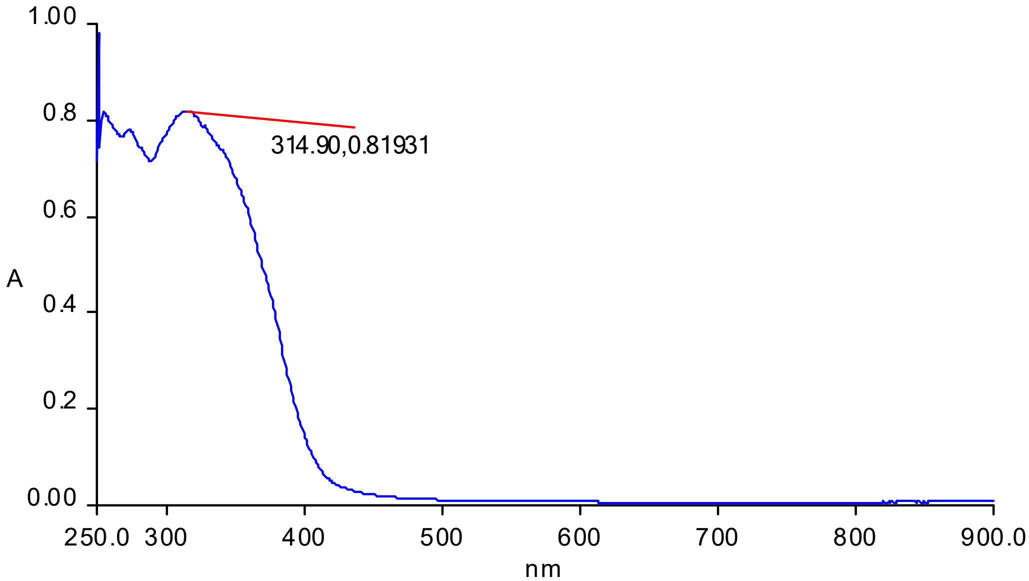


Figure SI-123. UV-Vis spectra of **7g** in MeOH.

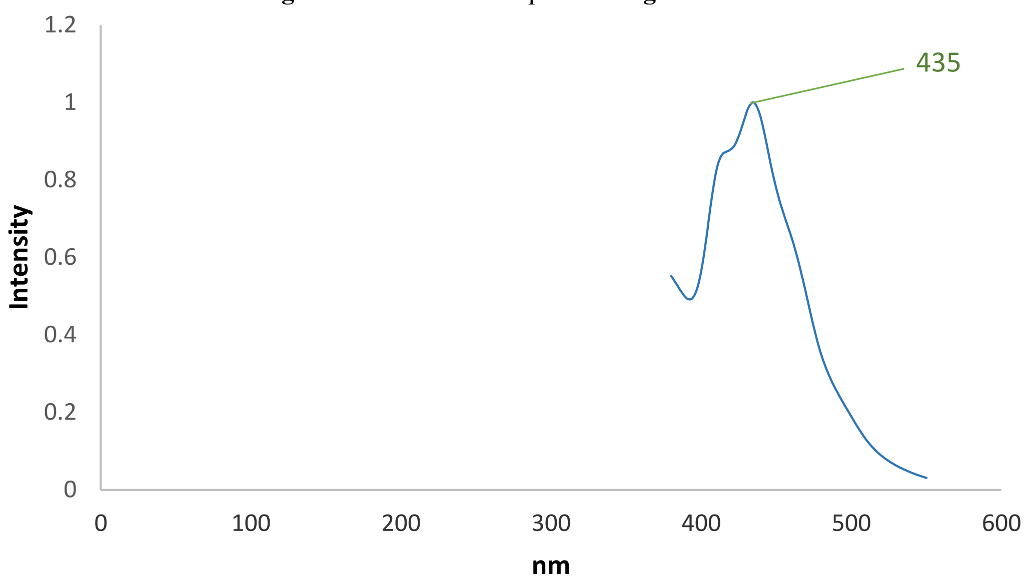


Figure SI-124. Emission spectra of **7g** in MeOH.

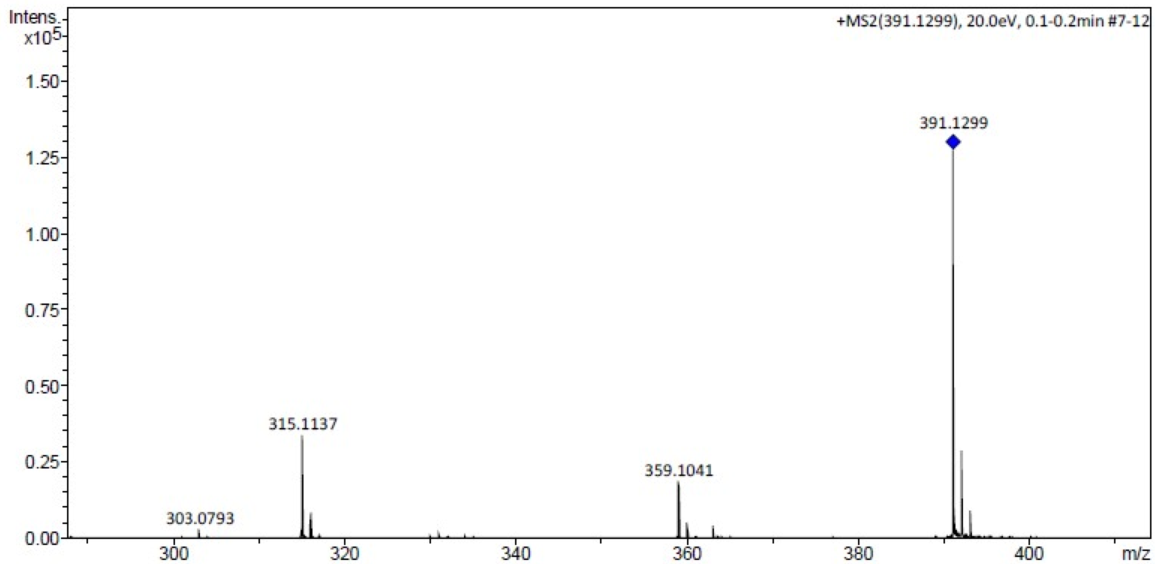
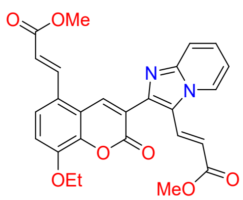


Figure SI-125. ESI-MS chromatogram of **7g**.



Methyl (E)-3-(8-ethoxy-3-(3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)imidazo[1,2-a]pyridin-2-yl)-2-oxo-2H-chromen-5-yl)acrylate (7h): Yield 61%; dark brown powder; m.p. = 179 – 181 ºC; RMN ^{1}H (500 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 8.557 (s, 1H, −CH=C−), 8.432 (d, *J* (H,H) = 7 Hz, 1H, Ar), 8.121 (d, *J* (H,H) = 15.5 Hz, 1H, −CH=C−), 8.015 (d, *J* (H,H) = 16.5 Hz, 1H, −CH=C−), 7.729 (d, *J* (H,H) = 9 Hz, 1H, Ar), 7.532 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 7.393 (t, *J* (H,H) = 8 Hz, 1H, Ar), 7.134 (d, *J* (H,H) = 8.5 Hz, 1H, Ar), 7.042 (t, *J* (H,H) = 7 Hz, 1H, Ar), 6.414 (d, *J* (H,H) = 15.5 Hz, 1H, −CH=C−), 6.224 (d, *J* (H,H) = 16.5 Hz, 1H, −CH=C−), 4.256 (q, *J* (H,H) = 7 Hz, 2H, CH_2−CH_3), 3.796 (s, 3H, CH_3), 3.788 (s, 3H, CH_3), 1.553 (t, *J* (H,H) = 7 Hz, 3H, CH_3); RMN ^{13}C (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) = 123.428, 167.384, 166.963, 158.365, 147.943, 147.103, 144.360, 142.923, 140.950, 138.753, 129.872, 127.096, 125.203, 124.553, 123.406, 120.420, 119.650, 118.514, 118.493, 115.786, 114.875, 114.517, 65.281, 51.988, 14.823; FT-IR (KBr) ν_{max} = 3045 cm^{-1} (C−H Ar), 2978 cm^{-1} (C−H Aliphatic), 1718 cm^{-1} (C=O lactone), 1631 cm^{-1} (−O−C=O); UV–Vis (MeOH) λ_{max} = 328.33 nm. HRMS (ESI m/z) Calcd. for $C_{26}H_{22}N_2O_7$ $[M+H]^+$ 475.1500, found 475.1526.

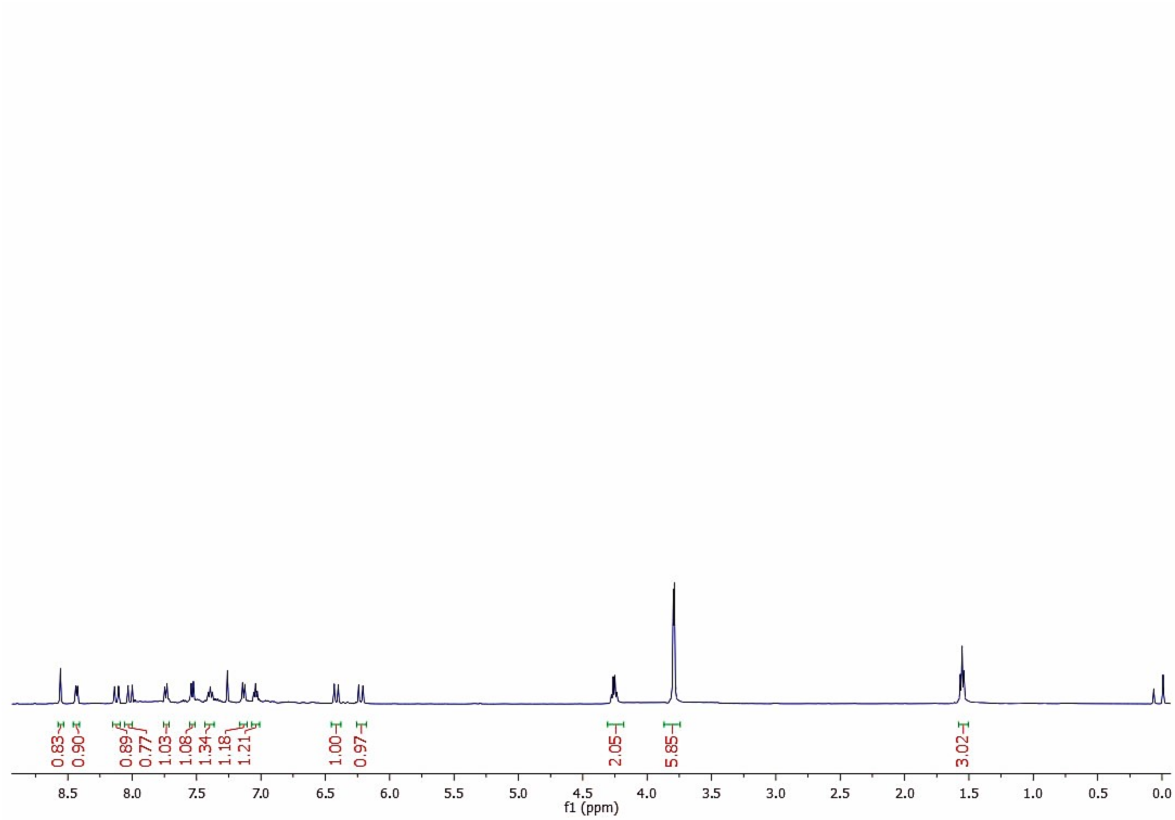


Figure SI-126. ^{1}H NMR spectra of **7h** on $CDCl_3$ 500 MHz

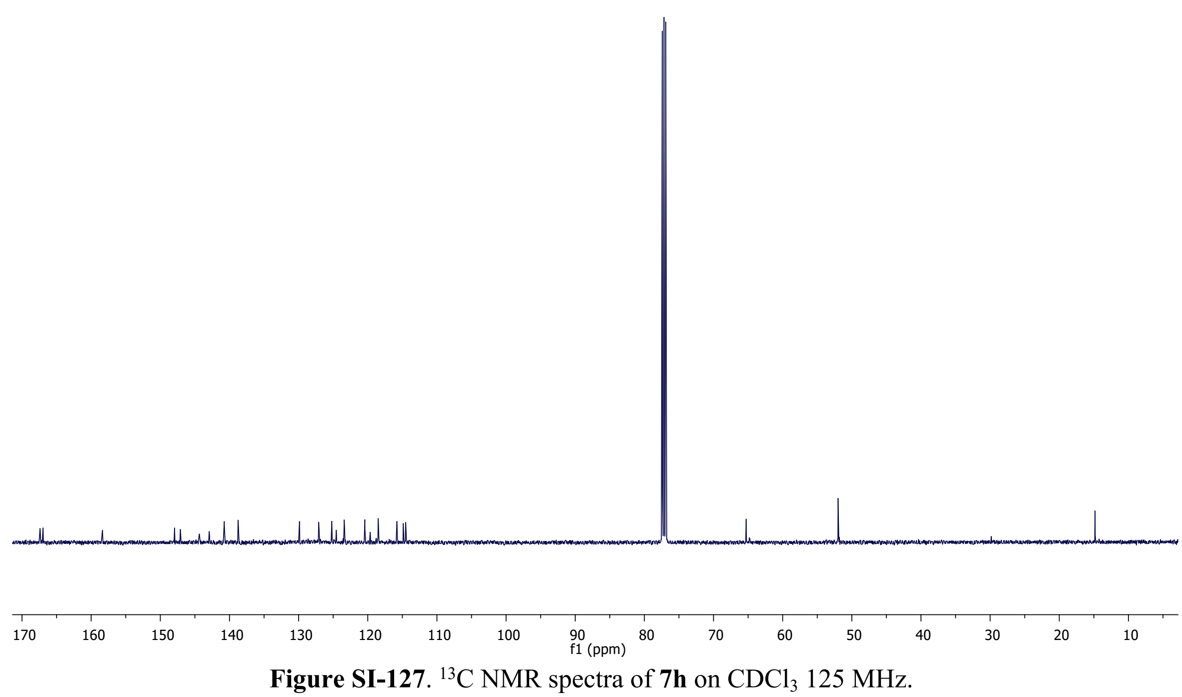


Figure SI-127. ^{13}C NMR spectra of **7h** on $CDCl_3$ 125 MHz.

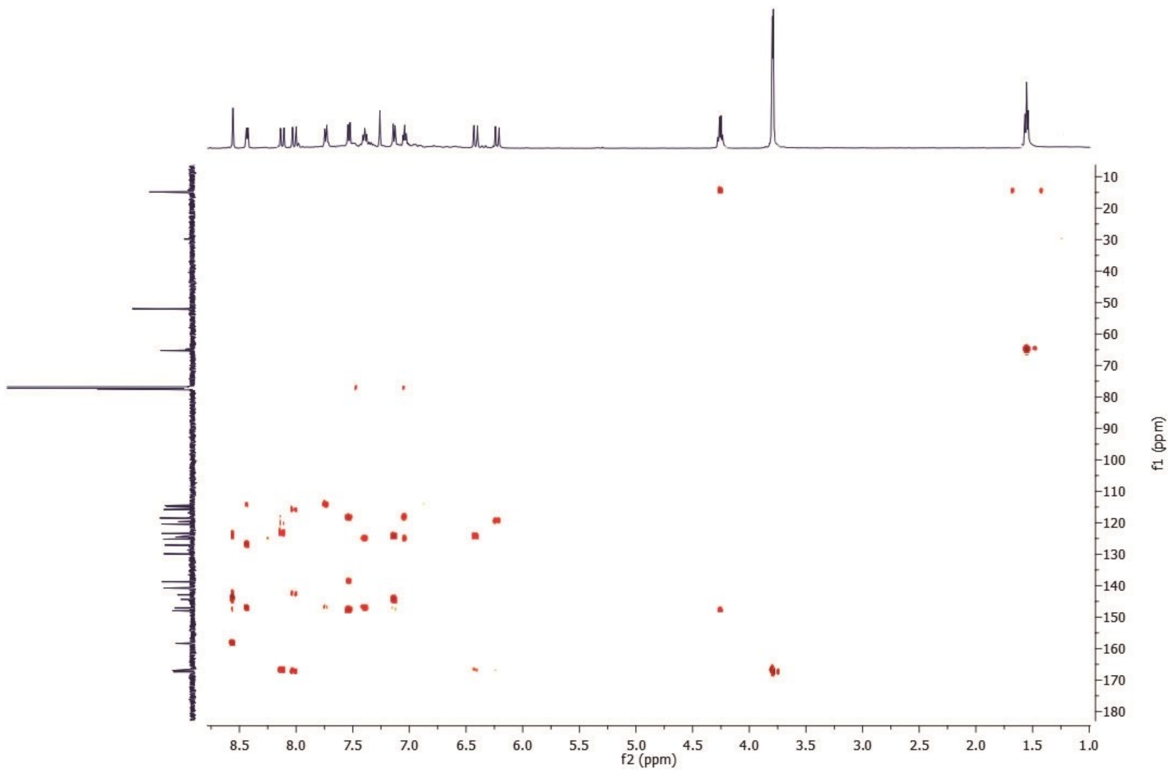


Figure SI-128. HMBC NMR spectra of **7h** on $CDCl_3$

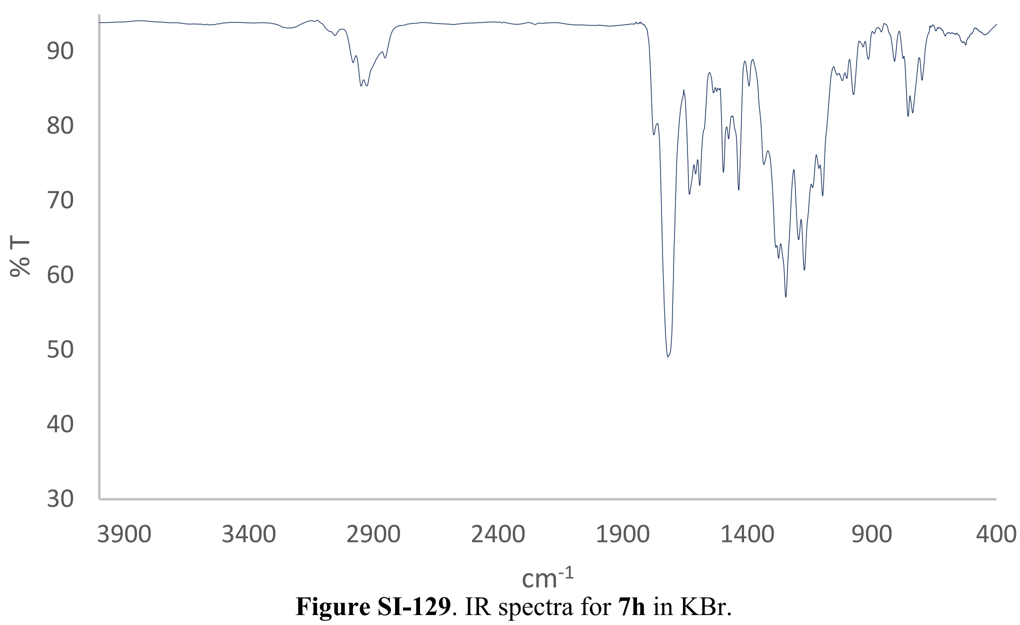


Figure SI-129. IR spectra for **7h** in KBr.

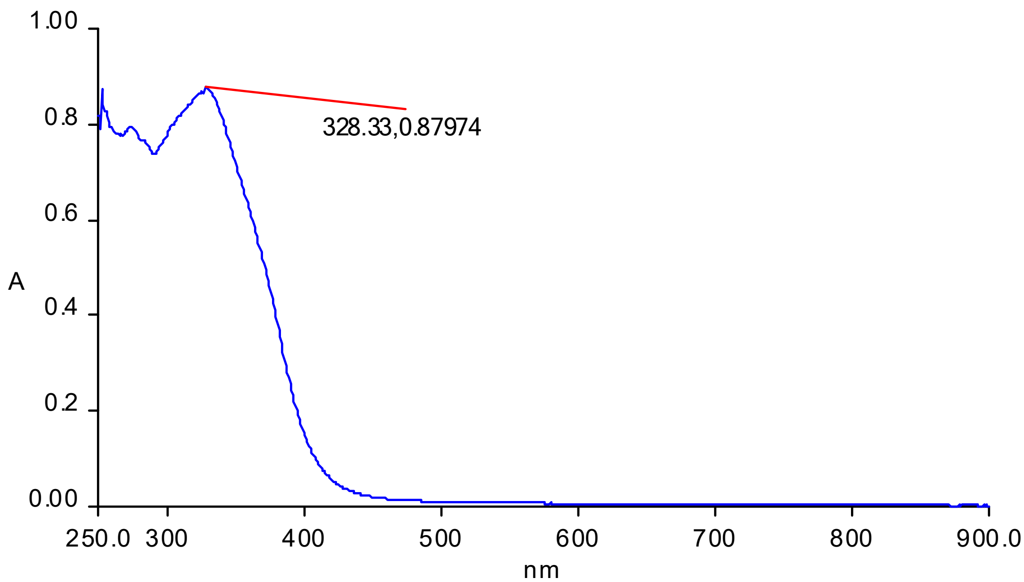


Figure SI-130. UV-Vis spectra of **7h** in MeOH.

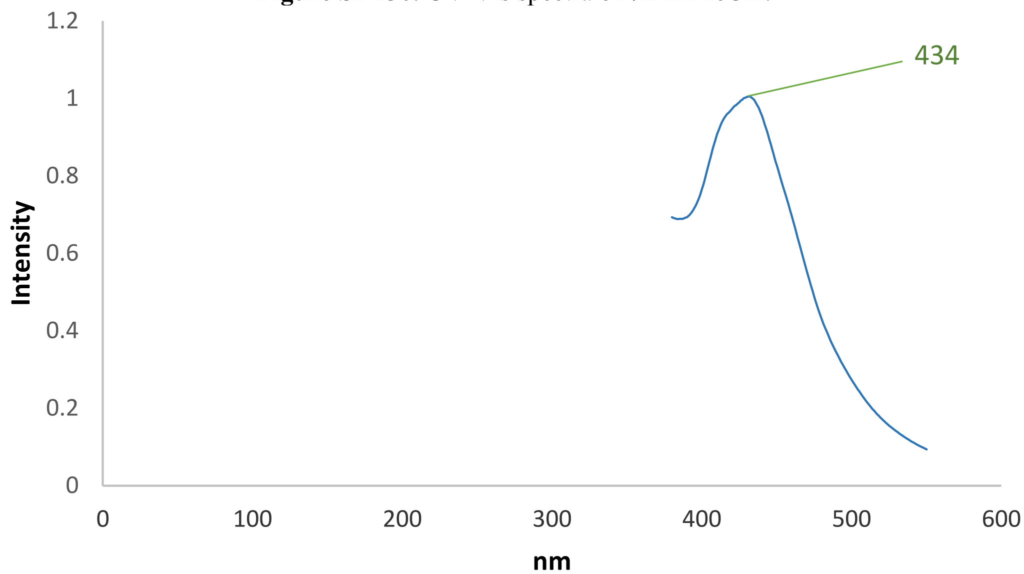


Figure SI-131. Emission spectra of **7h** in MeOH.

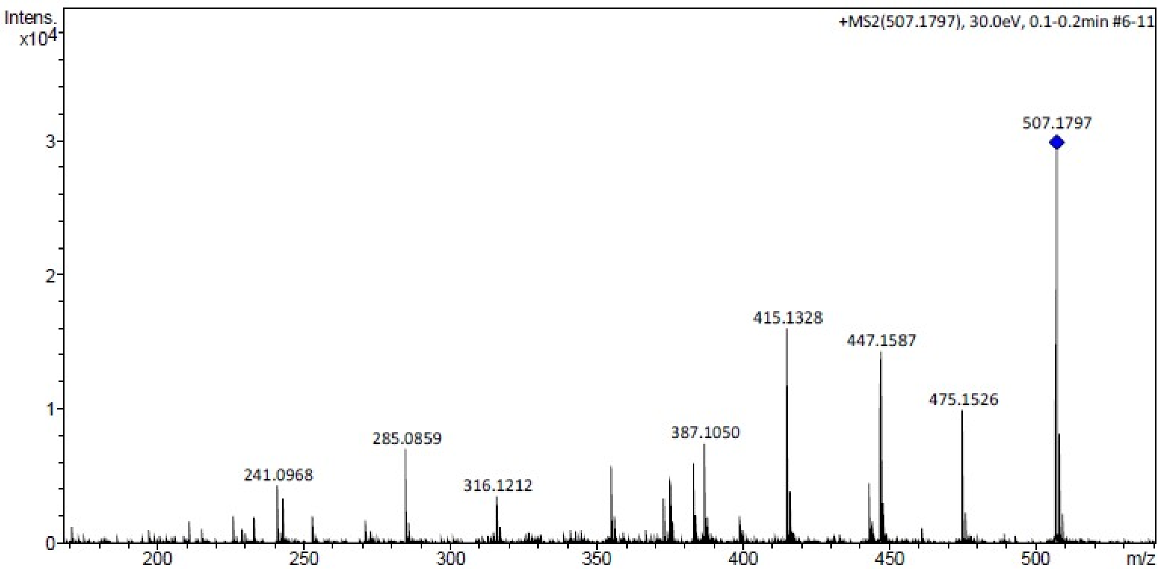


Figure SI-132. ESI chromatogram of **7h**.

6. Nonlinear optical properties

Table S3. Non-linear refractive index values of coumarin-imidazo[1,2-*a*]heterocyclic-3-acrylate **7a-h.**

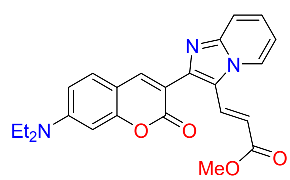
				Nonlinear refraction index n_2 (W/cm^2)						
Power (mW)	**4a**	**5a**	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**	**7h**
1	-7.403e^{-7}									
3	-1.22e^{-7}									
4	-7.7218e^{-8}									
5	-6.332e^{-8}			-1.994e^{-9}						
7	-1.179e^{-8}			-1.616e^{-08}						
10				-7.514e^{-09}	-2.622e^{-09}	-9.499e^{-10}	-1.324e^{-08}			-2.188e^{-09}
15			-2.486e^{-09}	-4.133e^{-09}	-2.215e^{-09}	-4.557^{-10}	-3.252e^{-09}			-1.198e^{-09}
20			-1.507e^{-09}		-1.210e^{-09}	-8.254e^{-10}	-1.656e^{-09}			-6.373e^{-10}
25		-2.1424e^{-10}	-1.184e^{-09}							-4.795e^{-10}
30		-1.1188e^{-10}	-8.832e^{-10}	-9.553e^{-10}	-8.475e^{-10}				-2.267e^{-10}	-3.688e^{-10}
35		-2.6887e^{-10}	-7.719e^{-10}	-5.532e^{-10}					-1.634e^{-10}	
40		-1.824e^{-10}			-5.721e^{-10}			-1.569e^{-10}	-1.290e^{-10}	-3.146e^{-10}
45		-1.621e^{-10}						-1.254e^{-10}	-1.491e^{-10}	
50								-1.112e^{-10}	-1.243e^{-10}	
55									-9.896e^{-11}	

7.- Theoretical calculations

Computational Details.

The stationary points of all molecules were obtained by Berny geometry optimization using the Density Functional Theory (DFT). To test the performance of the level of theory against the experimental absorption-emission data, four DFT functionals were used: B3LYP [4,5], CAM-B3LYP [6], PBE [7] (PBEPBE) and M062XR [8] with the basis set 6-311++g(d,p) [9], the Polarizable Continuum Model (PCM) [10,11]. with methanol as solvent was used, all stationary points were confirmed with a frequency analysis. The theoretical characterization of the optical properties were performed using the Time Dependent Density Functional Theory (TD-DFT) [12]. We have performed vertical excitation of all the molecules using TD-DFT at the corresponding theory level of the respective optimization calculation. In addition, the relaxation of the brighter excited states in the gas phase was performed using TD-DFT at corresponding level to that of its fundamental geometry stationary point. Similarly, the theorical calculation of polarizability and hyperpolarizability was made. All calculations were done using the Gaussian09 software [13].

8.- Equilibrium Geometry in Ground State, Equilibrium Geometry in Excited states, Excitation energies and oscillator strength of compound 7a (B3LYP)



7a

B3LYP

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.597339	-0.346524	-0.178995
2	6	0	3.583912	0.318825	0.554517
3	6	0	2.268361	-0.084203	0.434986
4	6	0	1.862884	-1.146831	-0.394390
5	6	0	2.877632	-1.806859	-1.123080
6	6	0	4.194480	-1.428834	-1.025876
7	1	0	3.805590	1.130209	1.231006
8	1	0	2.603404	-2.625927	-1.778838
9	1	0	4.927516	-1.955642	-1.618172
10	6	0	0.485667	-1.464123	-0.444542
11	6	0	-0.454689	-0.770254	0.277149
12	6	0	-0.021404	0.291737	1.168878
13	8	0	1.335559	0.589138	1.177980
14	1	0	0.158558	-2.280675	-1.078849
15	6	0	-3.027309	-0.388957	0.112442
16	6	0	-3.497975	-2.586482	0.120210
17	7	0	-2.166051	-2.505354	0.208726
18	6	0	-1.866769	-1.183860	0.224975
19	7	0	-4.077286	-1.315349	0.067458
20	6	0	-4.325147	-3.724454	0.097533

21	6	0	-5.688427	-3.562735	0.040586
22	1	0	-6.340033	-4.427247	0.022118
23	6	0	-6.247793	-2.261400	0.019436
24	1	0	-7.319826	-2.120225	-0.003066
25	6	0	-5.441514	-1.157981	0.037674
26	1	0	-5.827184	-0.153799	0.054233
27	1	0	-3.858535	-4.700019	0.131391
28	7	0	5.906144	0.029228	-0.085610
29	6	0	6.985196	-0.716984	-0.746046
30	1	0	7.879597	-0.594592	-0.131336
31	1	0	6.753502	-1.782982	-0.727618
32	6	0	7.274185	-0.248563	-2.175503
33	1	0	6.406162	-0.384561	-2.824586
34	1	0	7.549601	0.809045	-2.192309
35	1	0	8.106368	-0.821646	-2.593407
36	6	0	6.323831	1.199206	0.696113
37	1	0	7.224350	1.596096	0.222435
38	1	0	5.568170	1.981576	0.606294
39	6	0	6.610079	0.887014	2.168433
40	1	0	6.939113	1.793533	2.683595
41	1	0	5.721413	0.508379	2.678208
42	1	0	7.400998	0.138515	2.262169
43	8	0	-0.712994	0.946098	1.925777
44	6	0	-3.097529	1.024236	-0.071681
45	6	0	-4.130102	1.822256	-0.439024
46	6	0	-4.001493	3.270839	-0.613564
47	8	0	-4.919373	3.987816	-0.983967
48	8	0	-2.773355	3.755437	-0.329057
49	6	0	-2.585766	5.175471	-0.485894
50	1	0	-1.552327	5.363071	-0.204557
51	1	0	-2.756959	5.471473	-1.521500
52	1	0	-3.263138	5.724856	0.168668
53	1	0	-5.121531	1.462274	-0.668467
54	1	0	-2.149062	1.517457	0.096685

Rotational constants (GHZ): 0.2218649 0.0648972 0.0538852

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.9247 eV 423.92 nm f=0.6876 <S**2>=0.000
110 ->111 0.69871
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1393.85529913
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1591 eV 392.46 nm f=0.2270 <S**2>=0.000
109 ->111 -0.27309
110 ->112 0.64086

Excited State 3: Singlet-A 3.4174 eV 362.81 nm f=0.3052 <S**2>=0.000
109 ->111 0.60016

```
      109 ->112         0.22260
      110 ->112         0.27381

 Excited State   4:      Singlet-A      3.6365 eV  340.94 nm  f=0.2581  <S**2>=0.000
      109 ->111        -0.19047
      109 ->112         0.59655
      110 ->113         0.30221

 Excited State   5:      Singlet-A      3.7336 eV  332.08 nm  f=0.1596  <S**2>=0.000
      109 ->111         0.12601
      109 ->112        -0.29031
      109 ->113        -0.14217
      110 ->113         0.60006

 Excited State   6:      Singlet-A      4.0594 eV  305.42 nm  f=0.0272  <S**2>=0.000
      107 ->111        -0.11886
      107 ->112         0.10333
      108 ->111        -0.25097
      108 ->112         0.10133
      109 ->113         0.59225
      110 ->113         0.19319

 Excited State   7:      Singlet-A      4.0893 eV  303.19 nm  f=0.0118  <S**2>=0.000
      107 ->111        -0.37913
      107 ->112        -0.12616
      108 ->111         0.43196
      108 ->112         0.15045
      110 ->114         0.33212

 Excited State   8:      Singlet-A      4.2893 eV  289.05 nm  f=0.0787  <S**2>=0.000
      107 ->111         0.20125
      108 ->111         0.46235
      109 ->113         0.22319
      110 ->114        -0.40788

 Excited State   9:      Singlet-A      4.4064 eV  281.37 nm  f=0.0643  <S**2>=0.000
      107 ->111         0.51700
      109 ->113         0.10946
      110 ->114         0.42094

 Excited State  10:      Singlet-A      4.4980 eV  275.64 nm  f=0.0617  <S**2>=0.000
      108 ->112         0.65434
      109 ->113        -0.15040

 Excited State  11:      Singlet-A      4.6091 eV  269.00 nm  f=0.0004  <S**2>=0.000
      105 ->111         0.57057
      105 ->112        -0.37659

 Excited State  12:      Singlet-A      4.6305 eV  267.76 nm  f=0.1150  <S**2>=0.000
      107 ->111        -0.12069
      107 ->112         0.65544
```

```
                109 ->113        -0.10713
                110 ->114         0.10348

Excited State  13:      Singlet-A      4.7459 eV  261.25 nm  f=0.0167  <S**2>=0.000
                110 ->115         0.55740
                110 ->116         0.34334
                110 ->117         0.16316
                110 ->118         0.11489

Excited State  14:      Singlet-A      4.8314 eV  256.62 nm  f=0.0367  <S**2>=0.000
                107 ->113         0.11523
                108 ->113         0.13886
                109 ->115         0.13746
                109 ->116        -0.10647
                110 ->115        -0.34197
                110 ->116         0.50094
                110 ->117         0.18859

Excited State  15:      Singlet-A      4.8430 eV  256.01 nm  f=0.0034  <S**2>=0.000
                104 ->111         0.53853
                104 ->112         0.32439
                104 ->113        -0.14132
                106 ->111         0.20195

Excited State  16:      Singlet-A      4.9228 eV  251.86 nm  f=0.1442  <S**2>=0.000
                106 ->111         0.11497
                108 ->113        -0.12714
                110 ->116        -0.22092
                110 ->117         0.60734

Excited State  17:      Singlet-A      4.9826 eV  248.83 nm  f=0.0119  <S**2>=0.000
                109 ->114         0.15247
                109 ->116         0.11492
                110 ->118         0.62705
                110 ->120         0.11290

Excited State  18:      Singlet-A      5.0062 eV  247.66 nm  f=0.0010  <S**2>=0.000
                106 ->111         0.19133
                109 ->114         0.63399
                110 ->118        -0.12571

Excited State  19:      Singlet-A      5.0462 eV  245.70 nm  f=0.0689  <S**2>=0.000
                103 ->111         0.26245
                106 ->111        -0.37355
                108 ->113         0.37938
                109 ->114         0.21346
                110 ->116        -0.11629
                110 ->117         0.13217

Excited State  20:      Singlet-A      5.1038 eV  242.93 nm  f=0.0258  <S**2>=0.000
                102 ->111         0.10510
```

103 ->111 0.52201
105 ->112 -0.10536
108 ->113 -0.31813
109 ->115 -0.12730
109 ->116 0.12885
110 ->116 0.12105

SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 LETran= 370.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.713993	-0.266004	-0.108189
2	6	0	3.643156	0.555039	0.345878
3	6	0	2.351388	0.085758	0.310142
4	6	0	2.005743	-1.204021	-0.168585
5	6	0	3.087034	-2.016732	-0.617565
6	6	0	4.385604	-1.575014	-0.589771
7	1	0	3.812320	1.545085	0.741805
8	1	0	2.867446	-3.008204	-0.996329
9	1	0	5.162049	-2.229278	-0.957170
10	6	0	0.654532	-1.582992	-0.189927
11	6	0	-0.368421	-0.705257	0.250444
12	6	0	0.025970	0.571237	0.837500
13	8	0	1.370600	0.920278	0.781920
14	1	0	0.373117	-2.555581	-0.567012
15	6	0	-2.992746	-0.424924	0.171754
16	6	0	-3.268043	-2.670565	0.093500
17	7	0	-1.960009	-2.497881	0.116732
18	6	0	-1.730889	-1.145132	0.221194
19	7	0	-3.954642	-1.444656	0.143841
20	6	0	-4.015955	-3.872116	0.052720
21	6	0	-5.383133	-3.814199	0.101841
22	1	0	-5.968037	-4.725269	0.072932
23	6	0	-6.045115	-2.559595	0.213696
24	1	0	-7.122252	-2.507123	0.292854
25	6	0	-5.325437	-1.400235	0.238454
26	1	0	-5.779907	-0.433122	0.366745
27	1	0	-3.476858	-4.808276	-0.006437
28	7	0	6.002679	0.181332	-0.087665
29	6	0	7.136585	-0.677869	-0.452473
30	1	0	7.996061	-0.326455	0.121553
31	1	0	6.939603	-1.696852	-0.118651
32	6	0	7.466297	-0.645916	-1.949730
33	1	0	6.631378	-1.013691	-2.549551
34	1	0	7.704622	0.368503	-2.277595
35	1	0	8.335516	-1.279464	-2.143586

36	6	0	6.346821	1.554845	0.301387
37	1	0	7.260130	1.816524	-0.236335
38	1	0	5.572930	2.235022	-0.056039
39	6	0	6.568402	1.721886	1.809766
40	1	0	6.850409	2.756126	2.022559
41	1	0	5.663605	1.488777	2.374563
42	1	0	7.371326	1.070511	2.162289
43	8	0	-0.685733	1.372034	1.409415
44	6	0	-3.245467	0.950118	-0.027541
45	6	0	-4.395621	1.590280	-0.441195
46	6	0	-4.490019	3.022298	-0.631611
47	8	0	-5.485973	3.600179	-1.068191
48	8	0	-3.364322	3.706266	-0.282071
49	6	0	-3.396813	5.131605	-0.458869
50	1	0	-2.424385	5.488517	-0.125978
51	1	0	-3.553093	5.388442	-1.507943
52	1	0	-4.188624	5.578581	0.144406
53	1	0	-5.302010	1.071603	-0.716091
54	1	0	-2.385304	1.579054	0.143149

Rotational constants (GHZ): 0.2250089 0.0635153 0.0517698

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.4729 eV 501.37 nm f=1.4063 <S**2>=0.000
110 ->111 0.70410
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1393.86578184
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.9807 eV 415.95 nm f=0.0278 <S**2>=0.000
109 ->111 -0.38970
110 ->112 0.58164

Excited State 3: Singlet-A 3.1268 eV 396.52 nm f=0.5942 <S**2>=0.000
109 ->111 0.57982
110 ->112 0.39249

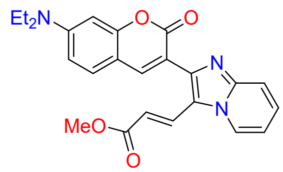
Excited State 4: Singlet-A 3.5456 eV 349.68 nm f=0.1535 <S**2>=0.000
109 ->112 0.67461
110 ->113 0.18019

Excited State 5: Singlet-A 3.6383 eV 340.77 nm f=0.1601 <S**2>=0.000
108 ->111 0.15513
109 ->112 -0.18544
109 ->113 -0.10925
110 ->113 0.64474

```
Excited State   6:      Singlet-A      3.8330 eV  323.46 nm  f=0.0202  <S**2>=0.000
      107 ->111        -0.28106
      108 ->111         0.61067
      110 ->113        -0.15208

Excited State   7:      Singlet-A      3.9491 eV  313.96 nm  f=0.0055  <S**2>=0.000
      107 ->111        -0.57770
      108 ->111        -0.27240
      109 ->113         0.11986
      110 ->114         0.23122

Excited State   8:      Singlet-A      4.1748 eV  296.99 nm  f=0.0946  <S**2>=0.000
      107 ->111         0.11625
      108 ->111         0.10505
      108 ->112         0.19060
      109 ->113         0.63896
      110 ->113         0.11851

Excited State   9:      Singlet-A      4.2408 eV  292.36 nm  f=0.0504  <S**2>=0.000
      107 ->111         0.24295
      110 ->114         0.64251

Excited State  10:      Singlet-A      4.3444 eV  285.39 nm  f=0.1182  <S**2>=0.000
      108 ->112         0.65649
      109 ->113        -0.20745

Excited State  11:      Singlet-A      4.3951 eV  282.10 nm  f=0.0005  <S**2>=0.000
      106 ->111         0.60940
      106 ->112        -0.31908

Excited State  12:      Singlet-A      4.6496 eV  266.66 nm  f=0.0601  <S**2>=0.000
      104 ->111        -0.33284
      105 ->111         0.20514
      107 ->112         0.55126

Excited State  13:      Singlet-A      4.6538 eV  266.41 nm  f=0.0148  <S**2>=0.000
      104 ->111         0.52661
      104 ->112         0.11578
      105 ->111        -0.15754
      107 ->112         0.37080

Excited State  14:      Singlet-A      4.6843 eV  264.68 nm  f=0.0193  <S**2>=0.000
      110 ->115         0.59434
      110 ->116         0.32475
      110 ->120        -0.10968
```

```
Excited State  15:      Singlet-A      4.7652 eV  260.19 nm  f=0.0916  <S**2>=0.000
      103 ->111         0.29423
      105 ->111        -0.16267
      110 ->115         0.27893
      110 ->116        -0.49363
      110 ->117         0.13131

Excited State  16:      Singlet-A      4.7850 eV  259.11 nm  f=0.0338  <S**2>=0.000
      102 ->111         0.20198
      103 ->111        -0.43573
      105 ->111         0.30085
      108 ->113         0.16271
      110 ->115         0.14633
      110 ->116        -0.24506
      110 ->117         0.12624

Excited State  17:      Singlet-A      4.7943 eV  258.61 nm  f=0.1174  <S**2>=0.000
      105 ->111        -0.10980
      109 ->116         0.11696
      110 ->115        -0.11059
      110 ->116         0.18938
      110 ->117         0.61623

Excited State  18:      Singlet-A      4.8750 eV  254.33 nm  f=0.0104  <S**2>=0.000
      109 ->115         0.11524
      110 ->117         0.10043
      110 ->118         0.66326

Excited State  19:      Singlet-A      4.8886 eV  253.62 nm  f=0.0048  <S**2>=0.000
      102 ->111        -0.13481
      103 ->111         0.33989
      104 ->111         0.21791
      105 ->111         0.48057
      108 ->113         0.19753

Excited State  20:      Singlet-A      4.9787 eV  249.03 nm  f=0.0445  <S**2>=0.000
      108 ->113         0.28155
      109 ->114         0.61597
      110 ->114        -0.10530
```

9.- Equilibrium Geometry in Ground State, Equilibrium Geometry in Excited states, Excitation energies and oscillator strength of compound 7a´ (B3LYP)



7a'

B3LYP

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.347400	-0.159664	-0.317349
2	6	0	-3.529237	-0.946293	0.530643
3	6	0	-2.161164	-0.973037	0.340286
4	6	0	-1.513834	-0.239777	-0.671300
5	6	0	-2.333920	0.539650	-1.515930
6	6	0	-3.697819	0.583632	-1.354030
7	1	0	-3.938027	-1.523668	1.346030
8	1	0	-1.871852	1.109836	-2.314460
9	1	0	-4.280309	1.180685	-2.039542
10	6	0	-0.104699	-0.349562	-0.777760
11	6	0	0.632032	-1.132807	0.072036
12	6	0	-0.040832	-1.870347	1.131860
13	8	0	-1.424954	-1.752366	1.193825
14	1	0	0.396908	0.192422	-1.572786
15	6	0	3.019715	-0.193440	-0.065759
16	6	0	4.006622	-2.190575	-0.341782
17	7	0	2.700369	-2.452998	-0.220668
18	6	0	2.094595	-1.256780	-0.052922
19	7	0	4.257874	-0.815648	-0.260347
20	6	0	5.083095	-3.077763	-0.526603
21	6	0	6.360152	-2.577717	-0.606295
22	1	0	7.199881	-3.246461	-0.747586
23	6	0	6.585020	-1.183241	-0.494855
24	1	0	7.586971	-0.778848	-0.542235
25	6	0	5.538313	-0.322035	-0.322264
26	1	0	5.668374	0.740937	-0.219275
27	1	0	4.870347	-4.136437	-0.593693
28	7	0	-5.702516	-0.114019	-0.155769
29	6	0	-6.557784	0.770380	-0.957319
30	1	0	-7.418524	1.029869	-0.337036
31	1	0	-6.033521	1.708166	-1.148014
32	6	0	-7.037090	0.140770	-2.268730
33	1	0	-6.198245	-0.105586	-2.923663
34	1	0	-7.601195	-0.775943	-2.078872

35	1	0	-7.691772	0.837716	-2.799062
36	6	0	-6.393532	-0.946387	0.836337
37	1	0	-7.396241	-1.140541	0.449610
38	1	0	-5.901950	-1.919086	0.897207
39	6	0	-6.490399	-0.299986	2.221862
40	1	0	-7.035209	-0.959067	2.903229
41	1	0	-5.501533	-0.112809	2.646120
42	1	0	-7.024931	0.652079	2.171648
43	8	0	0.474071	-2.565748	1.983340
44	6	0	2.734549	1.191380	0.126810
45	6	0	3.508632	2.292985	-0.026646
46	6	0	3.030015	3.653513	0.230913
47	8	0	3.710285	4.651667	0.047910
48	8	0	1.762135	3.714195	0.691987
49	6	0	1.232200	5.028181	0.956508
50	1	0	0.221518	4.863695	1.322206
51	1	0	1.831697	5.536251	1.712461
52	1	0	1.213346	5.623416	0.042951
53	1	0	4.527412	2.269209	-0.382975
54	1	0	1.711075	1.364359	0.442470

Rotational constants (GHZ): 0.2194130 0.0680333 0.0566899

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.9950 eV 413.97 nm f=0.2820 <S**2>=0.000
110 ->111 0.69613
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1393.85193139
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1782 eV 390.10 nm f=0.4993 <S**2>=0.000
109 ->111 -0.19910
110 ->112 0.66022

Excited State 3: Singlet-A 3.4726 eV 357.03 nm f=0.1361 <S**2>=0.000
109 ->111 0.42083
109 ->112 0.52434
110 ->112 0.19119

Excited State 4: Singlet-A 3.6092 eV 343.52 nm f=0.5724 <S**2>=0.000
109 ->111 0.50476
109 ->112 -0.45108
110 ->113 0.13116

Excited State 5: Singlet-A 3.7604 eV 329.71 nm f=0.0423 <S**2>=0.000
109 ->111 -0.10785
109 ->113 -0.12787
110 ->113 0.66700

Excited State 6: Singlet-A 4.0234 eV 308.16 nm f=0.0057 <S**2>=0.000

```
      107 ->111        -0.19320
      108 ->111        -0.16929
      109 ->113         0.61336
      110 ->113         0.16770

Excited State   7:      Singlet-A      4.1442 eV  299.18 nm  f=0.0106  <S**2>=0.000
      107 ->111         0.20256
      107 ->112         0.19286
      108 ->111        -0.37194
      108 ->112        -0.31203
      110 ->114         0.41411

Excited State   8:      Singlet-A      4.3475 eV  285.19 nm  f=0.1022  <S**2>=0.000
      107 ->112         0.10873
      108 ->111         0.49380
      108 ->112         0.11238
      109 ->113         0.14275
      110 ->114         0.43550

Excited State   9:      Singlet-A      4.4429 eV  279.06 nm  f=0.0574  <S**2>=0.000
      107 ->111         0.21393
      108 ->111        -0.24655
      108 ->112         0.59170

Excited State  10:      Singlet-A      4.4747 eV  277.08 nm  f=0.0484  <S**2>=0.000
      107 ->111         0.53900
      107 ->112         0.18465
      108 ->111         0.10108
      108 ->112        -0.10333
      109 ->113         0.17417
      110 ->114        -0.30443
      110 ->117         0.10451

Excited State  11:      Singlet-A      4.5513 eV  272.42 nm  f=0.1594  <S**2>=0.000
      107 ->111        -0.23459
      107 ->112         0.61583
      109 ->113        -0.15995
      110 ->114        -0.11604

Excited State  12:      Singlet-A      4.6202 eV  268.35 nm  f=0.0028  <S**2>=0.000
      104 ->111         0.22478
      104 ->112        -0.11786
      105 ->111         0.54268
      105 ->112        -0.22100
      106 ->111         0.23685

Excited State  13:      Singlet-A      4.7560 eV  260.69 nm  f=0.0127  <S**2>=0.000
      110 ->115         0.66669
      110 ->118        -0.18060

Excited State  14:      Singlet-A      4.8105 eV  257.73 nm  f=0.0009  <S**2>=0.000
```

103 ->112 -0.14543
104 ->111 0.32837
104 ->112 0.44689
104 ->113 0.10354
105 ->111 -0.10247
105 ->112 -0.22584
106 ->111 -0.15272
106 ->112 -0.20121

Excited State 15: Singlet-A 4.8892 eV 253.59 nm f=0.0916 <S**2>=0.000
107 ->113 0.10515
109 ->116 -0.17417
110 ->116 0.49895
110 ->117 0.38688

Excited State 16: Singlet-A 4.9208 eV 251.96 nm f=0.1131 <S**2>=0.000
106 ->111 -0.11079
107 ->113 -0.15308
108 ->113 -0.15535
109 ->116 0.10652
110 ->116 -0.35744
110 ->117 0.52082

Excited State 17: Singlet-A 5.0094 eV 247.50 nm f=0.0195 <S**2>=0.000
103 ->111 0.12488
104 ->111 0.15977
104 ->112 -0.13548
106 ->111 -0.26616
109 ->114 0.41973
110 ->118 0.34843
110 ->119 -0.11605

Excited State 18: Singlet-A 5.0178 eV 247.09 nm f=0.0043 <S**2>=0.000
103 ->111 -0.10262
104 ->111 -0.13601
104 ->112 0.10841
106 ->111 0.20059
109 ->114 -0.23841
110 ->115 0.12904
110 ->118 0.51445
110 ->119 -0.16507

Excited State 19: Singlet-A 5.0303 eV 246.47 nm f=0.0294 <S**2>=0.000
103 ->111 -0.17060
104 ->111 -0.24862
104 ->112 0.17739
106 ->111 0.28835
106 ->112 -0.11252
109 ->114 0.49822

Excited State 20: Singlet-A 5.0586 eV 245.10 nm f=0.0589 <S**2>=0.000

```
                     104 ->111         0.11749
                     107 ->113         0.24178
                     108 ->113         0.46712
                     109 ->116        -0.28401
                     110 ->116        -0.27497
 SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 LETran=     370.

**********************************************************************

 Excited State   5:      Singlet-A      3.9152 eV  316.68 nm  f=0.1530  <S**2>=0.000
                      99 ->104         0.10166
                     100 ->103         0.15302
                     100 ->104        -0.31073
                     101 ->104        -0.14061
                     102 ->105         0.57426

 Excited State   6:      Singlet-A      4.0080 eV  309.34 nm  f=0.0497  <S**2>=0.000
                     101 ->103         0.10329
                     101 ->104         0.67847
                     102 ->105         0.10456

 Excited State   7:      Singlet-A      4.1436 eV  299.22 nm  f=0.0124  <S**2>=0.000
                      99 ->103         0.20258
                     100 ->104         0.59085
                     102 ->105         0.30570

 Excited State   8:      Singlet-A      4.4361 eV  279.49 nm  f=0.0085  <S**2>=0.000
                      99 ->103         0.62904
                      99 ->104        -0.11501
                     100 ->104        -0.12300
                     101 ->105        -0.11804
                     101 ->106         0.12855
                     102 ->105        -0.14001

 Excited State   9:      Singlet-A      4.5620 eV  271.77 nm  f=0.0002  <S**2>=0.000
                      98 ->103         0.49825
                      98 ->104         0.47510

 Excited State  10:      Singlet-A      4.6563 eV  266.27 nm  f=0.0521  <S**2>=0.000
                      99 ->103         0.10040
                     101 ->105         0.67740

 Excited State  11:      Singlet-A      4.7110 eV  263.18 nm  f=0.0035  <S**2>=0.000
                      95 ->103         0.17882
                      96 ->103         0.21550
                      97 ->103         0.58154
                      97 ->104        -0.16276
```

```
Excited State  12:      Singlet-A      4.7660 eV  260.14 nm  f=0.1354  <S**2>=0.000
     100 ->105         0.64899
     102 ->107        -0.14278
     102 ->108         0.11278

Excited State  13:      Singlet-A      4.8196 eV  257.25 nm  f=0.1297  <S**2>=0.000
      99 ->104         0.47650
     102 ->106         0.48526

Excited State  14:      Singlet-A      4.9004 eV  253.01 nm  f=0.1685  <S**2>=0.000
      99 ->103         0.11082
      99 ->104         0.47126
     102 ->106        -0.45767
Excited State  15:      Singlet-A      4.9611 eV  249.91 nm  f=0.0112  <S**2>=0.000
      95 ->103        -0.13543
      96 ->103         0.58885
      97 ->103        -0.16551
      98 ->103        -0.19250
      98 ->104         0.19847
Excited State  16:      Singlet-A      5.1227 eV  242.03 nm  f=0.1911  <S**2>=0.000
      99 ->105        -0.19596
     100 ->106         0.16453
     101 ->106         0.43981
     102 ->106        -0.15034
     102 ->107        -0.17720
     102 ->108         0.32570
     102 ->109        -0.11755
Excited State  17:      Singlet-A      5.1565 eV  240.44 nm  f=0.0059  <S**2>=0.000
      96 ->103        -0.20335
      97 ->103         0.13046
      98 ->103        -0.40341
      98 ->104         0.41062
     101 ->106         0.14177
     102 ->107         0.21832
Excited State  18:      Singlet-A      5.1661 eV  240.00 nm  f=0.0103  <S**2>=0.000
      96 ->103         0.11561
      98 ->103         0.19612
      98 ->104        -0.19269
      99 ->105         0.19858
     100 ->105         0.13526
     101 ->106         0.21207
     102 ->107         0.48329

Excited State  19:      Singlet-A      5.2275 eV  237.18 nm  f=0.0046  <S**2>=0.000
      99 ->105        -0.11432
     101 ->106        -0.15409
     102 ->108         0.41337
```

102 ->109 0.37135
102 ->110 0.31802
Excited State 20: Singlet-A 5.3686 eV 230.95 nm f=0.0632 <S**2>=0.000
96 ->104 -0.12113
97 ->104 0.29231
101 ->106 0.14406
102 ->107 -0.27284
102 ->108 -0.25432
102 ->109 0.41206
102 ->110 0.14264
SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 LETran= 370.

10. Benchmark of both vertical excitation and emission energy

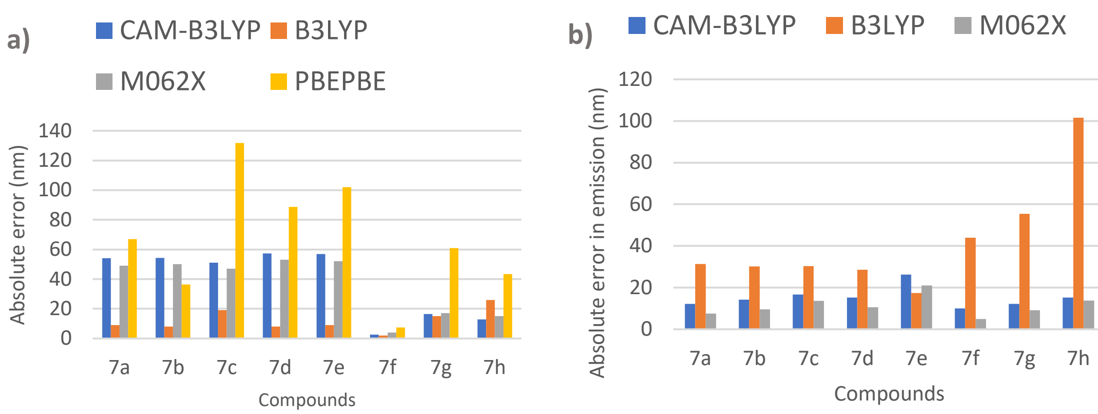


Figure SI-133. Absolute error in nm between the experimental data and theorical data of compounds **7a-h**. a) absorption. b) emission.

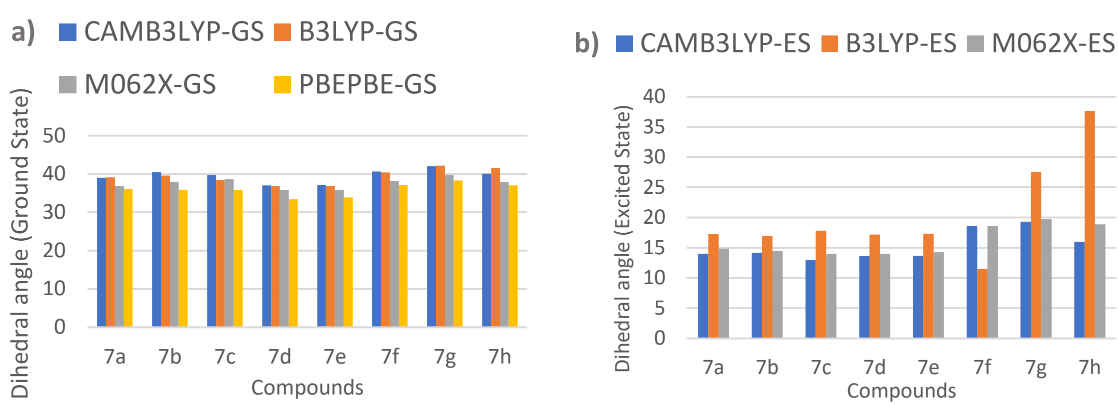


Figure SI-134. Dihedral angles of compound **7a-h.** a) Ground State and b) Excited State**.**

Theorical lineal and non-lineal properties analysis.

The total static dipole moment μ was determined by the squad of the quadratic sum of the components of the dipole moment. (Ec. 1)

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \qquad (1).$$

The isotropic polarizability α was be calculated from the trace of the polarization tensor (Ec. 2)

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (2).$$

The mean/static first hyperpolarizability $\beta_0$is expressed by (Ec. 3 and Ec. 4):

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right) \qquad (3).$$

$$\beta_0 = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yxx} + \beta_{yyy} + \beta_{yzz})^2 + (\beta_{zxx} + \beta_{zyy} + \beta_{zzz})^2 \qquad (4).$$

$\beta_x, \beta_y, \beta_z$ are the components of the second order polarizability tensor along the x, y and z axes.

The mean second hyperpolarizability γ is expressed by (Ec. 5):

$$\gamma = \frac{1}{5}[(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}) + 2\,(\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{zzxx})] \qquad (5)$$

Where, $\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}$ are the second order tensor components.

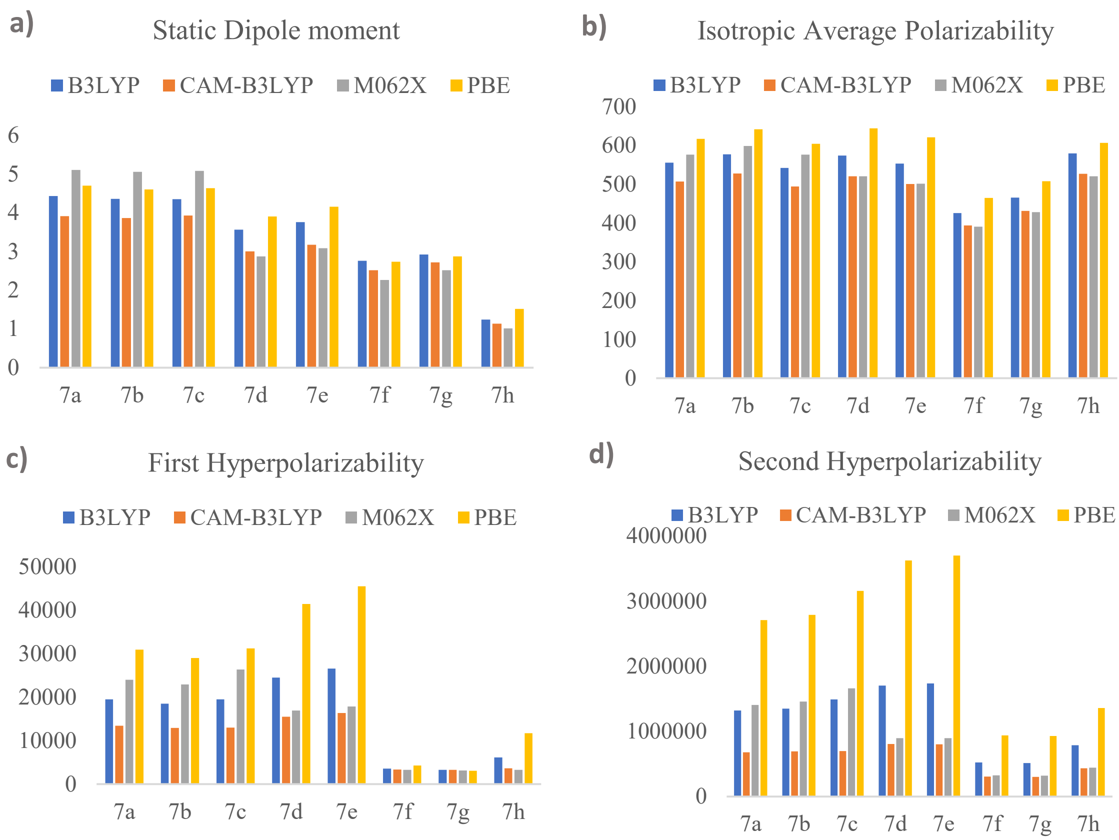


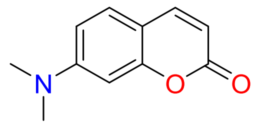
Figure SI-135. Theoretical calculations of the nonlinear properties of compounds **7a-h**. a) static dipole moment, b) isotropic average polarizability, c) first hyperpolarizability, d) second hyperpolarizability.

11. Static dipole moment, isotropic average polarizability, first hyperpolarizability and second hyperpolarizability of compound 7a-h

Molecule	Method	$\mu^{[a]}$	$\alpha_0^{[b]}$	$\beta_0^{[c]}$	$\gamma_0^{[d]}$

		a.u.	a.u.	a.u.	a.u.
7a	B3LYP	4.432623	555.63933	19543.4411	1321884
	CAM-B3LYP	3.914257	507.35733	13443.4485	680356
	M062X	5.104336	576.77467	24036.2611	1407060
	PBE	4.700977	616.73933	30914.4481	2710851
7b	B3LYP	4.354041	577.35967	18479.5701	1347974
	CAM-B3LYP	3.862711	527.47567	12915.161	690913
	M062X	5.057873	598.66267	22914.8533	1458239
	PBE	4.602749	642.04333	28973.818	2787777
7c	B3LYP	4.353766	542.43967	19527.8854	1490650
	CAM-B3LYP	3.926845	494.01667	13051.1336	696898
	M062X	5.081003	576.205	26380.3665	1658576
	PBE	4.630039	604.64	31186.907	3157246
7d	B3LYP	3.565883	573.94967	24516.1865	1703297
	CAM-B3LYP	3.004084	520.55433	15506.4538	804267
	M062X	2.875138	520.797	16935.3404	897191
	PBE	3.906009	644.51933	41423.9897	3622888
7e	B3LYP	3.759327	553.42	26601.8673	1737046
	CAM-B3LYP	3.17446	501.02	16338.8322	801496
	M062X	3.079435	501.34867	17861.6618	897517
	PBE	4.156943	620.923	45514.066	3697776
7f	B3LYP	2.759275	426.01	3559.797	524577
	CAM-B3LYP	2.514013	393.61833	3413.61965	303890
	M062X	2.265561	390.99467	3323.69175	323841
	PBE	2.733683	464.72633	4317.22768	939318
7g	B3LYP	2.918466	465.27867	3283.88806	514166
	CAM-B3LYP	2.714823	431.443	3289.8928	302766
	M062X	2.513504	428.53033	3187.23534	318663
	PBE	2.869619	507.986	3077.76374	928800
7h	B3LYP	1.241644	579.221	6172.80369	786579
	CAM-B3LYP	1.136127	526.82333	3654.19197	434853
	M062X	1.011368	520.54533	3329.57635	444456
	PBE	1.516401	607.08767	11720.1685	1359374
Coumarin	B3LYP	4.269110	263.95367	7500.13424	207626
Imidazo	B3LYP	0.923603	240.06700	4884.65540	170203

12. Equilibrium Geometry in Ground State, Excitation energies and oscillator strength of coumarin fragment (B3LYP)



Coumarin

B3LYP
ABSORPTION

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.3739 eV 367.48 nm f=0.5454 <S**2>=0.000
58 -> 59 0.69967
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -709.706366173
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.2085 eV 294.60 nm f=0.0181 <S**2>=0.000
57 -> 59 0.41631
58 -> 60 0.55516

Excited State 3: Singlet-A 4.4967 eV 275.72 nm f=0.0552 <S**2>=0.000
57 -> 59 0.56148
58 -> 60 -0.41520

Excited State 4: Singlet-A 4.7538 eV 260.81 nm f=0.0133 <S**2>=0.000
58 -> 61 0.69482

Excited State 5: Singlet-A 4.8825 eV 253.93 nm f=0.0005 <S**2>=0.000
55 -> 59 0.69032
55 -> 62 0.12182

Excited State 6: Singlet-A 4.9091 eV 252.56 nm f=0.1407 <S**2>=0.000
56 -> 59 -0.18291
58 -> 62 0.66426

Excited State 7: Singlet-A 5.0593 eV 245.06 nm f=0.0061 <S**2>=0.000
58 -> 63 0.69700

Excited State 8: Singlet-A 5.2139 eV 237.79 nm f=0.0347 <S**2>=0.000
56 -> 59 -0.38800
58 -> 64 0.57477

Excited State 9: Singlet-A 5.2975 eV 234.04 nm f=0.0372 <S**2>=0.000
56 -> 59 0.37490

```
                    58 -> 64         0.22879
                    58 -> 65         0.52308

Excited State  10:      Singlet-A      5.3889 eV  230.07 nm  f=0.0963  <S**2>=0.000
                    56 -> 59        -0.36790
                    58 -> 62        -0.15460
                    58 -> 64        -0.29676
                    58 -> 65         0.45725
                    58 -> 67        -0.10574

Excited State  11:      Singlet-A      5.4754 eV  226.44 nm  f=0.0012  <S**2>=0.000
                    58 -> 66         0.68575

Excited State  12:      Singlet-A      5.6555 eV  219.23 nm  f=0.0079  <S**2>=0.000
                    57 -> 60        -0.10205
                    58 -> 67         0.67129

Excited State  13:      Singlet-A      5.8526 eV  211.84 nm  f=0.0037  <S**2>=0.000
                    58 -> 67        -0.11033
                    58 -> 68         0.34019
                    58 -> 69         0.58380

Excited State  14:      Singlet-A      5.9180 eV  209.50 nm  f=0.0182  <S**2>=0.000
                    56 -> 60        -0.10057
                    57 -> 62         0.17209
                    58 -> 68         0.57137
                    58 -> 69        -0.31883

Excited State  15:      Singlet-A      5.9854 eV  207.14 nm  f=0.3450  <S**2>=0.000
                    56 -> 60         0.26332
                    57 -> 60         0.58389
                    57 -> 62        -0.14658
                    58 -> 68         0.16004

Excited State  16:      Singlet-A      6.0995 eV  203.27 nm  f=0.0146  <S**2>=0.000
                    57 -> 61         0.62651
                    57 -> 63         0.15764
                    57 -> 66        -0.12056
                    58 -> 70         0.18022
                    58 -> 71        -0.10156

Excited State  17:      Singlet-A      6.1123 eV  202.84 nm  f=0.5304  <S**2>=0.000
                    56 -> 60        -0.24477
                    57 -> 60         0.27064
                    57 -> 62         0.54671
                    58 -> 68        -0.13627
```

Excited State 18: Singlet-A 6.1584 eV 201.33 nm f=0.0028 <S**2>=0.000
57 -> 61 0.14126
58 -> 70 -0.12316
58 -> 71 0.66363

Excited State 19: Singlet-A 6.1835 eV 200.51 nm f=0.0046 <S**2>=0.000
57 -> 61 -0.13097
58 -> 70 0.57038
58 -> 71 0.12969
58 -> 72 -0.32991

Excited State 20: Singlet-A 6.1896 eV 200.31 nm f=0.0045 <S**2>=0.000
58 -> 70 0.30620
58 -> 72 0.61437

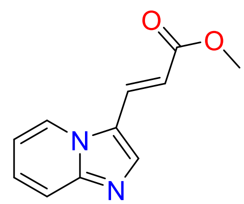
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.135459	-0.228016	-0.061026
2	6	0	-0.040185	0.649861	0.124883
3	6	0	1.254569	0.168681	0.056631
4	6	0	1.555276	-1.182723	-0.199396
5	6	0	0.460237	-2.051662	-0.385482
6	6	0	-0.838276	-1.602757	-0.319391
7	1	0	-0.177760	1.705531	0.304413
8	1	0	0.652317	-3.101601	-0.578298
9	1	0	-1.638209	-2.315810	-0.451852
10	6	0	2.925275	-1.565119	-0.251566
11	6	0	3.917651	-0.652470	-0.062990
12	6	0	3.613049	0.731886	0.195745
13	8	0	2.266443	1.077893	0.243544
14	1	0	3.172393	-2.603763	-0.446637
15	7	0	-2.426145	0.218586	0.005710
16	6	0	-3.571352	-0.651367	-0.287618
17	1	0	-4.361749	-0.014407	-0.691051
18	1	0	-3.306458	-1.342458	-1.089462
19	6	0	-4.096116	-1.413374	0.933321
20	1	0	-3.335905	-2.081341	1.344707
21	1	0	-4.404193	-0.722253	1.722117
22	1	0	-4.964549	-2.015787	0.652726
23	6	0	-2.749528	1.602749	0.368163
24	1	0	-3.729567	1.587984	0.850063
25	1	0	-2.047197	1.951109	1.127866
26	6	0	-2.777310	2.563260	-0.825383
27	1	0	-3.048486	3.567879	-0.489450

28	1	0	-1.803624	2.619386	-1.317159
29	1	0	-3.514634	2.243299	-1.566077
30	8	0	4.410899	1.634218	0.377850
31	1	0	4.964911	-0.918457	-0.098382

Rotational constants (GHZ): 1.1060997 0.2905825 0.2396559

13. Equilibrium Geometry in Ground State, Excitation energies and oscillator strength of imidazo fragment (B3LYP)



Imidazo

B3LYP

ABSOPRTION

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.980758	0.176590	0.000032
2	6	0	4.062846	-1.195364	0.000032
3	6	0	2.882014	-1.977729	0.000014
4	6	0	1.652806	-1.380841	-0.000002
5	6	0	2.716010	0.790382	0.000015
6	1	0	4.858829	0.808767	0.000046
7	1	0	5.029256	-1.683542	0.000045
8	1	0	2.934361	-3.058031	0.000015
9	1	0	0.732745	-1.938832	-0.000014
10	7	0	1.565486	-0.010476	-0.000002
11	7	0	2.397931	2.095358	0.000015
12	6	0	1.053889	2.133583	-0.000013
13	1	0	0.509481	3.067786	-0.000021
14	6	0	0.471534	0.862944	-0.000014
15	6	0	-0.928200	0.586611	-0.000030
16	1	0	-1.520847	1.496603	-0.000037
17	6	0	-1.614474	-0.581104	-0.000039
18	1	0	-1.147329	-1.554412	-0.000033
19	6	0	-3.077898	-0.653983	-0.000060
20	8	0	-3.699273	-1.705800	-0.000016
21	8	0	-3.689292	0.549934	-0.000004
22	6	0	-5.130567	0.544647	0.000047

23	1	0	-5.510512	0.044036	0.891178
24	1	0	-5.423117	1.591875	0.000094
25	1	0	-5.510574	0.044099	-0.891093

Rotational constants (GHZ): 1.5654195 0.2803146 0.2381013

Excitation energies and oscillator strengths:

```
Excited State   1:      Singlet-A      3.6384 eV  340.76 nm  f=0.6873  <S**2>=0.000
      53 -> 54         0.69900
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) =  -685.201122417
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:      Singlet-A      3.9443 eV  314.34 nm  f=0.0267  <S**2>=0.000
      52 -> 54         0.27018
      53 -> 55         0.64457

Excited State   3:      Singlet-A      4.6482 eV  266.74 nm  f=0.0001  <S**2>=0.000
      51 -> 54         0.68424
      51 -> 56        -0.10735

Excited State   4:      Singlet-A      4.6790 eV  264.98 nm  f=0.3301  <S**2>=0.000
      52 -> 54         0.63920
      53 -> 55        -0.25919

Excited State   5:      Singlet-A      5.0662 eV  244.73 nm  f=0.1370  <S**2>=0.000
      52 -> 55        -0.48198
      53 -> 56         0.49989

Excited State   6:      Singlet-A      5.2135 eV  237.81 nm  f=0.0001  <S**2>=0.000
      50 -> 54         0.68910

Excited State   7:      Singlet-A      5.2274 eV  237.18 nm  f=0.0010  <S**2>=0.000
      53 -> 57         0.68208

Excited State   8:      Singlet-A      5.5356 eV  223.98 nm  f=0.2040  <S**2>=0.000
      49 -> 54        -0.38802
      52 -> 55         0.41116
      53 -> 56         0.40119

Excited State   9:      Singlet-A      5.5672 eV  222.71 nm  f=0.0009  <S**2>=0.000
      53 -> 58         0.67844
      53 -> 59        -0.12009
      53 -> 60         0.10180

Excited State  10:      Singlet-A      5.6753 eV  218.46 nm  f=0.0062  <S**2>=0.000
```

53 -> 58 0.10502
53 -> 59 0.68657

Excited State 11: Singlet-A 5.7042 eV 217.36 nm f=0.0004 <S**2>=0.000
50 -> 55 0.60363
51 -> 55 -0.35137

Excited State 12: Singlet-A 5.8283 eV 212.73 nm f=0.0100 <S**2>=0.000
48 -> 54 0.57118
49 -> 54 -0.36324
52 -> 55 -0.13463

Excited State 13: Singlet-A 5.9410 eV 208.69 nm f=0.0024 <S**2>=0.000
53 -> 57 0.12091
53 -> 60 0.67668

Excited State 14: Singlet-A 6.0028 eV 206.54 nm f=0.0000 <S**2>=0.000
50 -> 55 0.35123
51 -> 55 0.60473

Excited State 15: Singlet-A 6.1239 eV 202.46 nm f=0.1697 <S**2>=0.000
48 -> 54 0.36924
49 -> 54 0.40474
52 -> 55 0.21413
52 -> 56 0.16368
53 -> 56 0.19734
53 -> 63 -0.10855
53 -> 65 0.17915

Excited State 16: Singlet-A 6.1652 eV 201.10 nm f=0.0010 <S**2>=0.000
53 -> 61 0.67692
53 -> 64 0.15342

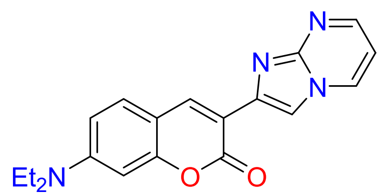
Excited State 17: Singlet-A 6.2067 eV 199.76 nm f=0.0047 <S**2>=0.000
48 -> 55 0.11054
49 -> 55 0.52314
52 -> 56 0.43980

Excited State 18: Singlet-A 6.3439 eV 195.44 nm f=0.0060 <S**2>=0.000
52 -> 57 0.60775
52 -> 58 0.20696
53 -> 62 -0.25394

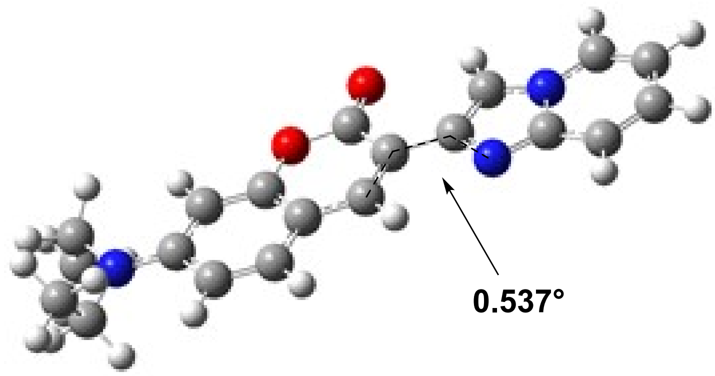
Excited State 19: Singlet-A 6.3882 eV 194.08 nm f=0.0001 <S**2>=0.000
52 -> 57 0.15897
53 -> 62 0.53833
53 -> 64 -0.40002

Excited State 20: Singlet-A 6.4025 eV 193.65 nm f=0.0019 <S**2>=0.000
53 -> 63 0.62761
53 -> 67 -0.29728

14. Equilibrium Geometry in Ground State and Dihedral angles of compound 4a



4a



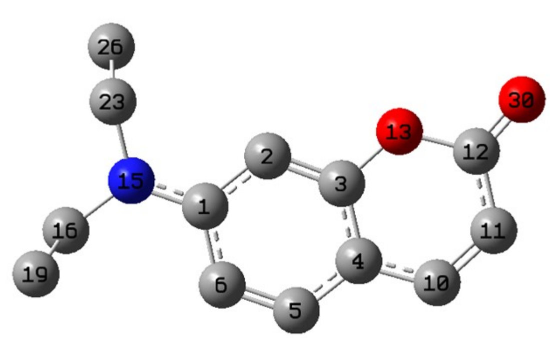
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.740944	-0.315076	0.045668
2	6	0	2.851468	0.766559	-0.099312
3	6	0	1.491022	0.543357	-0.076026
4	6	0	0.926653	-0.722617	0.091625
5	6	0	1.819570	-1.798305	0.237187
6	6	0	3.176096	-1.612291	0.214872
7	1	0	3.196482	1.782854	-0.210486
8	1	0	1.418796	-2.797682	0.362100
9	1	0	3.818071	-2.474413	0.311164
10	6	0	-0.487771	-0.829106	0.103495
11	6	0	-1.295159	0.255570	-0.038531
12	6	0	-0.691950	1.566656	-0.207903
13	8	0	0.679408	1.632157	-0.216894
14	1	0	-0.944557	-1.803531	0.230652
15	6	0	-3.708580	1.111227	-0.140156

16	1	0	-3.631890	2.174385	-0.267940
17	6	0	-4.642046	-0.890921	0.102121
18	7	0	-3.337984	-1.103576	0.126392
19	6	0	-2.753926	0.127695	-0.022724
20	7	0	-4.918979	0.461073	-0.060355
21	6	0	-5.729119	-1.790122	0.211223
22	6	0	-7.000577	-1.305611	0.154069
23	1	0	-7.842775	-1.980674	0.235992
24	6	0	-7.238972	0.087606	-0.013386
25	1	0	-8.248448	0.471442	-0.058542
26	6	0	-6.198925	0.949304	-0.118028
27	1	0	-6.301855	2.017289	-0.246290
28	1	0	-5.517767	-2.843316	0.337636
29	7	0	5.090699	-0.131927	0.022857
30	6	0	6.027454	-1.218959	0.292482
31	1	0	6.920834	-0.770655	0.730736
32	1	0	5.615636	-1.873142	1.061717
33	6	0	6.409705	-2.017304	-0.949455
34	1	0	5.538406	-2.498039	-1.397616
35	1	0	6.863701	-1.369485	-1.702314
36	1	0	7.132748	-2.793774	-0.690256
37	6	0	5.684755	1.170471	-0.260766
38	1	0	6.654692	0.987500	-0.726526
39	1	0	5.085348	1.685924	-1.012471
40	6	0	5.864264	2.041835	0.978301
41	1	0	6.330274	2.991476	0.706595
42	1	0	4.907176	2.256299	1.456794
43	1	0	6.505837	1.547143	1.710565
44	8	0	-1.280195	2.616793	-0.343393

Rotational constants (GHZ): 0.7725879 0.0793274 0.0728829

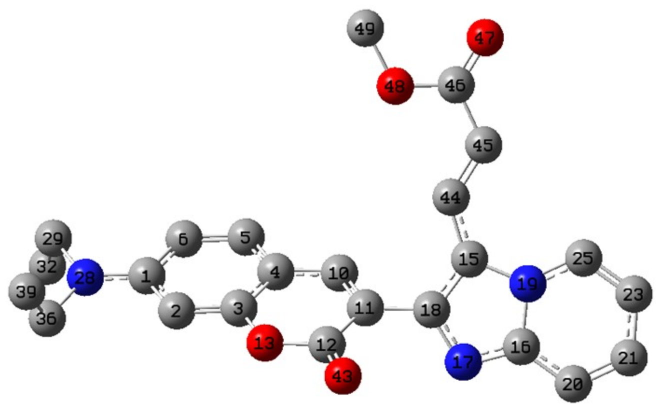
Mulliken and Hirshfeld charges for the coumarin and imidazo[1,2-a]pyridine moieties



Coumarin moiety

		Charge*	
Number	Atom	Mulliken	Hirshfeld
1	C	-0.014534	0.066341
2	C	-0.347231	-0.033362
3	C	-1.495054	0.079459
4	C	1.512279	-0.042438
5	C	0.203971	0.024677
6	C	0.006306	-0.018571
10	C	-0.005721	0.063879
11	C	0.156157	-0.020614
12	C	0.16769	0.184711
13	O	-0.160629	-0.12186
15	N	0.238834	-0.070163
16	C	0.070358	0.107409
19	C	-0.007207	0.022907
23	C	0.087413	0.107233
26	C	-0.011412	0.023069
30	O	-0.401219	-0.372356

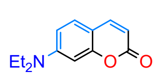
*Hydrogens charges summed into heavy atoms



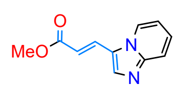
		7a		7a'	
		Charge*		Charge*	
		Mulliken	Hirshfeld	Mulliken	Hirshfeld
1	C	-0.174924	0.069881	0.014796	0.069088
2	C	-0.487775	-0.029374	-0.392624	-0.03
3	C	-1.043379	0.08248	-1.000349	0.08181
4	C	0.908072	-0.040431	0.725183	-0.040741
5	C	-0.088182	0.030438	0.037988	0.029593
6	C	0.167453	-0.013922	0.117326	-0.015042
10	C	0.414935	0.057506	0.206209	0.062593

11	C	0.63653	-0.038746	0.212857	-0.035184
12	C	-0.201706	0.193732	0.18416	0.190963
13	O	-0.122641	-0.11682	-0.147803	-0.118446
15	C	0.047747	0.014117	0.189537	0.016497
16	C	0.379125	0.100394	0.544243	0.100456
17	N	-0.037396	-0.252668	-0.048593	-0.256217
18	C	-0.12706	0.044478	-0.125209	0.0442
19	N	0.237738	-0.002802	0.24777	-0.002864
20	C	0.101523	0.026456	-0.02953	0.027236
21	C	-0.394565	0.037992	-0.345713	0.039083
23	C	0.062369	0.023529	0.001833	0.024274
25	C	0.004743	0.107857	0.016487	0.108161
28	N	0.248835	-0.066262	0.247505	-0.067192
29	C	0.081937	0.110137	0.085623	0.109515
32	C	-0.000301	0.02543	-0.002232	0.024834
36	C	0.080079	0.10996	0.084605	0.109419
39	C	-0.004009	0.025776	-0.003341	0.025022
43	O	-0.375488	-0.339651	-0.36087	-0.35796
44	C	0.070057	0.012359	-0.27982	0.023446
45	C	-0.107701	-0.038254	0.103909	-0.033608
46	C	-0.046217	0.199018	-0.055513	0.199992
47	O	-0.358131	-0.347282	-0.352068	-0.345343
48	O	-0.136235	-0.133012	-0.140274	-0.13273
49	C	0.264567	0.147413	0.263904	0.149186

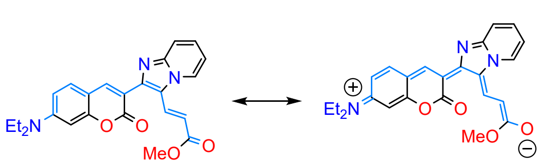
*Hydrogens charges summed into heavy atoms



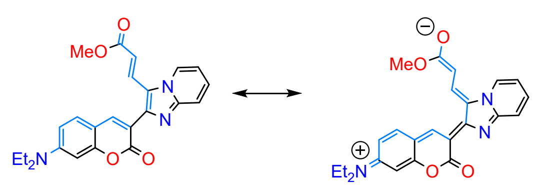
Mulliken: 0.238834
Hirshfeld: -0.070163



Mulliken: O -0.349022
Hirshfeld: O -0.339052



7a



7a'

Mulliken: N 0.247505
Hirshfeld: N -0.067192
Mulliken: O -0.358131
Hirshfeld: O -0.347282

Mulliken: N 0.248835
Hirshfeld N -0.066262
Mulliken: O -0.352068
Hirshfeld: O -0.345343

Scheme S1. Resonances structures of the ICT, The N charges refers to Nitrogen in diethylamino in coumarin and the O chargers refers to carbonylic oxygen in acrylate.

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