

Supplementary Information

Thallium(III) *p*-tosylate (TTS) mediated oxidative rearrangement of 2-naphthyl and 2-heteroarylchromanones

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Content:

1. General Procedure for the synthesis of 2'-Hydroxy-3-(2''- & 1''-naphthyl)-1-acrylophenones (2aa - 2bc): -----S2
2. General procedure: Synthesis of 2-(2'- & 1'-Naphthyl) chromanones (3a- 6c):
..... S3
3. General Procedure: Oxidation of 2-(2'- & 1'-Naphthyl) chromanones with Thallium(III) *p*-tosylate: Synthesis of 3-(2'- & 1'-Naphthyl) chromones (4a-7c):
..... S4
4. General Procedure: Oxidation of 2-(2'- & 1'-Naphthyl) chromanones with Thallium(III) acetate: Synthesis of 2-(2'- & 1'-Naphthyl) chromones (5a-8c):
..... S5
5. General procedure for the synthesis of *chalcone* (containing thiophenyl/ furyl / Pyridyl groups)-----S6
6. General procedure for the synthesis of *flavanones* with *hetero aryl* groups (thiophenyl/ furyl / Pyridyl) -----
-----S9.
7. General procedure for the synthesis of *chromones* with *hetero aryl* group (thiophenyl/ furyl / Pyridyl) using *Thallium(III)Acetate*.
..... S10
8. Copies of ¹HNMR and ¹³CNMR -----S12
9. References -----S25

Experimental Section

General Procedure: Synthesis of 2'-Hydroxy-3-(2''- & 1''-naphthyl)-1-acrylophenones (2aa - 2bc): To a cooled solution of potassium hydroxide (1.23 g, 22 mmol) in methanol (50 mL) was added substituted 2'-hydroxyacetophenone (3 a-e; 10 mmol) and 2- or 1-naphthaldehyde (1.56 g; 10 mmol). The reaction mixture was stirred at room temperature for 24 hrs and then poured into ice-cold water containing conc. hydrochloric acid (5 mL). The yellow solid, so obtained, was filtered off, washed with water, dried and recrystallized with ethanol to obtained 2'-hydroxy-3-(2''- & 1''-naphthyl)-1-acrylophenones (2aa - 2bc).

1-(2-Hydroxyphenyl)-3-(naphthalen-2-yl)prop-2-en-1-one(2aa): as off-white solid, m.p.: 156-158°C (Lit¹. m.p.: 155-156°C), Yield (220 mg) 74%; ¹H-NMR (CDCl₃) δ: 12.98 (s, 1H, D₂O exchangeable), 8.08 (d, 1H, *J*=15.36 Hz), 8.06 (brs, 1H), 7.93 – 7.83 (m, 4H), 7.80 (dd, 1H, *J*=8.56 & 1.45 Hz), 7.79 (d, 1H, *J*=15.34 Hz), 7.63 – 7.53 (m, 3H), 7.45 (ddd, 1H, *J*=8.85, 7.98 & 2.56 Hz), 7.00 (dd, 1H, *J*=8.88 & 2.42 Hz).MS, m/z:275.30 [M+H]⁺.

1-(2-Hydroxy-5-methylphenyl)-3-(naphthalen-2-yl) prop-2-en-1-one(2ab): As yellow crystalline solid, Yield (220 mg) 76%, IR (KBr) cm⁻¹: 3392, 1639; ¹H-NMR (CDCl₃) δ: 12.68 (s, 1H, D₂O exchangeable), 8.08 (d, 1H, *J*=15.34 Hz), 8.07(brs, 1H), 7.92 – 7.82 (m, 4H), 7.77 (d, 1H, *J*=15.64 Hz), 7.75 (d, 1H, *J*=2.02 Hz), 7.57 – 7.52 (m, 2H), 7.33 (dd, 1H, *J*=2.05 & 8.5 Hz), 6.95 (d, 1H, *J*=8.45 Hz), 2.38 (s, 3H); MS (ES) m/z: 289.2. [M+H]⁺.

(5-Chloro-2-hydroxyphenyl)-3-(naphthalen-2-yl)prop-2-en-1-one (2ac):As pale yellow solid, m.p.: 164-166°C, Yield (210 mg), 71%; ¹H-NMR (CDCl₃) δ: 12.76 (s, 1H, D₂O exchangeable), 8.08 (d, 1H, *J*=15.36 Hz), 8.07 (brs, 1H), 7.92 – 7.83 (m, 4H), 7.80 (dd, 1H, *J*=8.58 & 1.50 Hz), 7.78 (d, 1H, *J*=15.60 Hz), 7.57 – 7.52 (m, 2H), 7.46 (dd, 1H, *J*=2.58 & 8.85 Hz), 7.01 (d, 1H, *J*=8.86 Hz); MS (ES) m/z: 309.2 [M+H]⁺.

1-(2-Hydroxy-4-methoxyphenyl)-3-(naphthalen-2-yl)prop-2-en-1-one (2ad)²: ¹H-NMR (CDCl₃) δ: 13.48 (s, 1H, D₂O exchangeable), 8.05 (d, 1H, *J*=15.37 Hz), 7.90 – 7.84 (m, 4H), 8.05 (brs, 1H), 7.80 (dd, 1H, *J*=8.58 & 1.50 Hz), 7.70 (d, 1H, *J*=15.45 Hz), 7.56 – 7.52 (m, 2H), 6.53 – 6.49 (m, 2H), 3.87 (s, 3H); MS (ESI) /z: 305.2 [M+H]⁺; Data matches with literature values.

1-(2-Hydroxyphenyl)-3-(naphthalen-1-yl)prop-2-en-1-one (2ba):As white solid, m.p.: 110-112°C (Lit¹. m.p.: 110.6-111.3°C), Yield (98 mg) 71%; ¹H-NMR (CDCl₃) δ: 12.79 (s, 1H, D₂O exchangeable), 8.83 (d, 1H, *J*=15.26 Hz), 8.27 (d, 1H, *J*=8.38 Hz), 7.99 – 7.91 (m, 4H), 7.67 (d, 1H, *J*=15.28 Hz), 7.65 – 7.53 (m, 4H), 7.43 (ddd, 1H, *J*=8.84, 7.88 & 2.26 Hz), 7.00 (dd, 1H, *J*=8.86 & 2.48Hz).MS m/z: 275.10 [M+H]⁺.

1-(2-Hydroxy-5-methylphenyl)-3-(naphthalen-1-yl) prop-2-en-1-one (2bb): as off-white solid, m.p.: 132-134°C, (Lit³. m.p.: 133°C), Yield (130 mg) 66%, IR (KBr) cm⁻¹: 3398, 1640; ¹H-NMR (CDCl₃) δ: 12.67 (s, 1H, D₂O exchangeable), 8.77 (d, 1H, *J*=15.23 Hz), 8.28

(d, 1H, $J=8.41$ Hz), 7.96 – 7.90 (m, 3H), 7.77 – 7.73 (m, 2H), 7.63 – 7.53 (m, 3H), 7.33 (dd, 1H, $J=8.38$ & 2.04 Hz), 6.96 (d, 1H, $J=8.36$ Hz), 2.35 (s, 3H); HRMS (ESI) $[M+H]^+$ Calc. for $C_{20}H_{16}O_2$: 289.1150, found: 289.118.

1-(5-Chloro-2-hydroxyphenyl)-3-(naphthalen-1-yl)prop-2-en-1-one (2bc): As white solid, m.p.: 148-150°C (Lit⁴. m.p.: 152°C), Yield (180 mg) 71%; ¹H-NMR (CDCl₃) δ : 12.76 (s, 1H, D₂O exchangeable), 8.82 (d, 1H, $J=15.19$ Hz), 8.27 (d, 1H, $J=8.41$ Hz), 7.99 – 7.91 (m, 4H), 7.67 (d, 1H, $J=15.20$ Hz), 7.65 – 7.54 (m, 3H), 7.46 (dd, 1H, $J=8.94$ & 2.54 Hz), 7.02 (d, 1H, $J=8.92$ Hz). MS m/z : 309.06 $[M+H]^+$.

General procedure: Synthesis of 2-(2'- & 1'-Naphthyl) chromanones (3a- 6c):

A solution of 2'-hydroxy-3-(2''- & 1''-naphthyl)-1-acrylophenones (**2aa** to **2bc**; 5 mmol) in acetic acid (50 mL) was refluxed on a heating mantle and conc. hydrochloric acid was added from top of condenser till turbidity appears and the resultant solution was further refluxed for 8 hrs. The reddish solution cooled to room temperature and poured into ice cold water with constant stirring. The above mixture was extracted with dichloromethane (2 x 50 mL); organic layer was washed with 2% sodium hydroxide solution (2 x 50 mL) followed by with water till neutral and dried over anhydrous sodium sulfate. The solvent was distilled under reduced pressure and the solid was purified by passing through a column of basic alumina using ethyl acetate-hexane (1: 15) as eluent to afford 2-(2'- & 1'-naphthyl) chromanones (3aa -3bc).

2-(Naphthalen-2-yl) chroman-4-one (3a): As pale ash solid, m.p.: 120-122°C, (Lit⁵. m.p.: 122-124°C), Yield (45 mg) 59%; ¹H-NMR (CDCl₃) δ (ppm): 7.97 – 7.86 (m, 5H), 7.60 (dd, 1H, $J=1.75$ & 8.48 Hz), 7.55 – 7.50 (m, 3H), 7.12 – 7.06 (m, 2H), 5.66 (dd, 1H, $J=2.85$ & 13.2 Hz), 3.20 (dd, 1H, $J=13.21$ & 16.88 Hz), 2.99 (dd, 1H, $J=2.95$ & 16.86 Hz). HRMS Calc. for $C_{19}H_{14}O_2$: 275.102, found: 275.102.

6-Methyl-2-(naphthalen-2-yl)chroman-4-one⁶ (3b): As white solid, m.p.: 126-128°C, (Lit⁶. m.p.: 129-131°C), Yield (69 mg) 66%; IR (KBr) cm^{-1} : 1689; ¹H-NMR (CDCl₃) δ (ppm): 7.93-7.84 (m, 4H), 7.75 – 7.74 (m, 1H), 7.59 (dd, 1H, $J=1.8$ & 8.4 Hz), 7.58 – 7.49 (m, 2H), 7.34 (dd, 1H, $J=2.2$ & 8.4 Hz), 7.00 (d, 1H, $J=8.4$ Hz), 5.64 (dd, 1H, $J=3.0$ & 12.9 Hz), 3.17 (dd, 1H, $J=12.9$ & 16.8 Hz), 2.96 (dd, 1H, $J=3.0$ & 16.8 Hz), 2.38 (s, 3H); ¹³C NMR (CDCl₃): δ = 192.2, 159.8, 137.6, 135.9, 133.8, 133.6, 130.5, 127.9, 129.8, 127.1, 126.9, 126.0, 124.8, 123.0, 120.8, 117.0, 79.5, 43.9, 20.6. MS (ES): m/z : 288.1 $[M+H]^+$. Data matches with literature values.

6-Chloro-2-(naphthalen-2-yl)chroman-4-one (3c): As pale pink solid, m.p.: 132-134°C, Yield (29 mg), 51%; ¹H-NMR (CDCl₃) δ (ppm): 7.94 – 7.86 (m, 5H), 7.57 (dd, 1H, $J=1.8$ & 8.5 Hz), 7.55 – 7.51 (m, 2H), 7.46 (dd, 1H, $J=2.7$ & 8.8 Hz), 7.05 (d, 1H, $J=8.8$ Hz), 5.64 (dd, 1H, $J=3.0$ & 12.9 Hz), 3.17 (dd, 1H, $J=12.9$ & 16.8 Hz), 2.96 (dd, 1H, $J=3.0$ & 16.8 Hz). MS (ES) m/z : 309.0 $[M+H]^+$

7-Methoxy-2-(naphthalen-2-yl) chroman-4-one (3d): As off-white solid, m.p.: 130-132°C, Yield (25 mg) 49%; ¹H-NMR (CDCl₃) δ (ppm): 7.9486 7.94 (m, 5H), 7.59 (dd, 1H, $J=1.8$ & 8.5 Hz), 7.54 – 7.49 (m, 2H), 6.64 (dd, 1H, $J=2.4$ & 9.0 Hz), 6.54 (d, 1H, $J=2.4$ Hz), 5.64 (dd,

1H, $J=3.0$ & 13.2 Hz), 3.84 (s, 3H), 3.14 (dd, 1H, $J=13.2$ & 17.0 Hz), 2.92 (dd, 1H, $J=3.0$ & 17.0 Hz).MS (ES) m/z : 305.1 $[M+H]^+$;

2-(Naphthalen-1-yl) chroman-4-one (6a):As white solid, Yield (45 mg), 69%; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 8.07 - 7.99 (m, 2H), 7.94 - 7.88 (m, 2H), 7.75 (brd, 1H, $J=6.9$ Hz), 7.59 - 7.51 (m, 4H), 7.13 - 7.07 (m, 2H), 6.23 (dd, 1H, $J=3.0$ & 13.2 Hz), 3.27 (dd, 1H, $J=13.2$ & 16.8 Hz), 3.11 (dd, 1H, $J=3.3$ & 16.8 Hz).MS (ES) m/z : 275.1.

6-Methyl-2-(naphthalen-1-yl) chroman-4-one (6b): As off-white solid, m.p.: $134-136^\circ\text{C}$, (Lit⁶. m.p.: $137-138^\circ\text{C}$), Yield (110 mg) 61%; IR (KBr) cm^{-1} : 1692; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 8.05 (dd, 1H, $J=8.1$ & 2.4 Hz), 7.93 - 7.87 (m, 2H), 7.80 - 7.77 (m, 2H), 7.57 - 7.52 (m, 3H), 7.35 (dd, 1H, $J=2.4$ & 8.48 Hz), 7.00 (d, 1H, $J=8.7$ Hz), 6.19 (dd, 1H, $J=2.7$ & 13.2 Hz), 3.21 (dd, 1H, $J=13.2$ & 16.8 Hz), 3.08 (dd, 1H, $J=2.7$ & 16.8 Hz), 2.38 (s, 3H); ^{13}C NMR (CDCl_3): $\delta = 191.2, 158.6, 136.5, 133.8, 133.2, 130.5, 130.0, 129.8, 128.7, 126.6, 126.0, 125.1, 124.9, 123.8, 122.9, 120.1, 116.9, 76.0, 44.8, 20.2$; MS (ES) m/z : 289.1 $[M+H]^+$; Data matches with literature values.

6-Chloro-2-(naphthalen-1-yl)chroman-4-one(6c):As Pale yellow solid, m.p.: $134-136^\circ\text{C}$, (Lit⁷. m.p.: $137-138^\circ\text{C}$), yield (39 mg), 69%; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 8.02 (dd, 1H, $J=6.6$ & 2.4 Hz), 7.95 (d, 1H, $J=2.7$ Hz), 7.94 - 7.89 (m, 2H), 7.75 (brd, 1H, $J=6.6$ Hz), 7.60 - 7.51 (m, 3H), 7.43 (dd, 1H, $J=2.7$ & 8.85 Hz), 7.05 (d, 1H, $J=8.85$ Hz), 6.22 (dd, 1H, $J=3.0$ & 12.9 Hz), 3.25 (dd, 1H, $J=12.9$ & 16.8 Hz), 3.11 (dd, 1H, $J=3.3$ & 17.1 Hz), MS m/z : 309.76 $[M+H]^+$. Data matches with literature values.

General Procedure: Oxidation of 2-(2'- & 1'-naphthyl)chromanones with Thallium(III) *p*-tosylate: Synthesis of 3-(2'- & 1'-naphthyl)chromones (4a-d & 7a-c):

To a solution of 2-(2'- & 1'-naphthyl)chromanones (1 eq) in acetonitrile (15 mL) was added thallium(III) *p*-tosylate (1.1 eq) and the resultant mixture was heated on water bath for 2 hrs. The reaction mixture was cooled to room temperature and dichloromethane (25 mL) was added. The precipitated thallium(I) *p*-tosylate was filtered off, washed well with dichloromethane (2 x 15 mL) and whole combined filtrate was washed with water (2 x 25 mL) followed by saturated sodium bicarbonate solution (25 mL) and dried over anhydrous sodium sulfate. The solvent was distilled off and the residue was purified by passing through a small bed of basic alumina using ethyl acetate-hexane (1: 10) as eluent to afford 3-(2'- & 1'-naphthyl) chromones (4a-7c).

3-(2'-Naphthyl)chromone (4a):As pale pink solid, m.p.: $186-188^\circ\text{C}$, (Lit⁸. m.p.: $184-486^\circ\text{C}$); Yield (29 mg) 79%; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 8.35 (dd, 1H, $J=1.8$ & 8.4 Hz), 8.14 (d, 1H, $J=1.2$ Hz), 8.06 (s, 1H), 7.93 - 7.85 (m, 3H), 7.73- 7.68 (m, 2H), 7.53 - 7.42 (m, 4H); MS: m/z : 273.2 $[M+H]^+$. Data matches with literature values.

6-Methyl-3-(2'-naphthyl)chromone (4b): As off-white solid, m.p.: $196-197^\circ\text{C}$, Yield: (21 mg) 94%; IR (KBr) cm^{-1} : 1639; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 8.13 - 8.12(m, 1H), 8.1 (s, 1H), 8.05 (d, 1H, $J=1.5$ Hz), 7.83 - 7.92 (m, 3H), 7.70 (dd, 1H, $J=1.5$ & 8.6 Hz), 7.53 - 7.47 (m, 3H), 7.41 (d, 1H, $J=8.4$ Hz), 2.48 (s, 3H); HRMS (ESI) $[M+H]^+$ Calc. for $\text{C}_{20}\text{H}_{14}\text{O}_2$: 287.0994, found: 287.098; Data matches with literature values.

6-Chloro-3-(2'-naphthyl)chromone (4c): As pale brown solid, m.p.: 188-190°C, Yield (18 mg) 75%; ¹H-NMR (CDCl₃) δ(ppm): 8.25 (d, 1H, *J*=1.9 Hz), 8.12 (d, 1H), 8.05 (s, 1H), 7.93 – 7.83 (m, 3H), 7.71 (dd, 1H, *J*=1.6 & 8.48 Hz), 7.55 – 7.46 (m, 4H); MS (ESI) *m/z*: 307.0;

7-Methoxy-3-(2'-naphthyl)chromone (4d): As off-white solid, Yield: (14 mg) 72%; ¹H-NMR (CDCl₃) δ(ppm): 8.25 (d, 1H, *J*=9.0 Hz), 8.06 (s, 1H), 8.05 (d, 1H, *J*=1.8 Hz), 7.91 – 7.83 (m, 3H), 7.69 (dd, 1H, *J*=1.8 & 8.4 Hz), 7.52 – 7.46 (m, 2H), 7.02 (dd, 1H, *J*=8.9 & 2.4 Hz), 6.88 (d, 1H, *J*=2.4 Hz), 3.88 (s, 3H); MS (ES) *m/z*: 303.0 [M+H]⁺.

3-(Naphthalen-1-yl)-4H-chromen-4-one(7a): As off-white solid, m.p.: 174-176°C, (Lit⁹. m.p.: 177-179°C), Yield: (21mg) 70%; ¹H-NMR (CDCl₃) δ (ppm): 8.26 (dd, 1H, *J*=2.55 & 8.52 Hz), 8.02 (s, 1H), 7.97– 7.89 (m, 2H), 7.71 – 7.67 (m, 2H), 7.58 – 7.40 (m, 6H). ¹³C NMR (CDCl₃) δ 175.0, 154.9, 153.0, 133.2, 133.0, 131.9, 128.8, 128.1, 127.4, 127.0, 125.6, 125.1, 125.0, 124.9, 124.5, 124.6, 124.1, 123.6, 118.0. MS: *m/z*: 273.01 [M+H]⁺. Data matches with literature values.

6-Methyl-3-(1'-naphthyl)chromone (7b): As pale yellow solid, m.p.: 130-131°C, Yield: (28 mg) 76%; IR (KBr) cm⁻¹: 1641; ¹H-NMR (CDCl₃) δ(ppm): 8.15 (d, 1H, *J*=2.55 Hz), 8.03 (s, 1H), 7.97 – 7.89 (m, 2H), 7.71 – 7.67 (m, 2H), 7.57 – 7.42 (m, 4H), 7.41 (d, 1H, *J*=8.50 Hz), 2.48 (s, 3H); MS (ESI) *m/z*: 287.1 [M+H]⁺.

6-Chloro-3-(1'-naphthyl)chromone(7c): As white solid, m.p.: 159-162°C, Yield: (12mg) 69%; ¹H-NMR (CDCl₃) δ(ppm): 8.30 (d, 1H, *J*=2.55 Hz), 8.03 (s, 1H), 7.96 – 7.89 (m, 2H), 7.71– 7.66 (m, 2H), 7.57 – 7.41 (m, 5H); MS (ES) *m/z*: 307.1 [M+H]⁺.

General Procedure: Oxidation of 2-(2'- & 1'-Naphthyl) chromanones with Thallium(III) acetate: Synthesis of 2-(2'- & 1'-Naphthyl) chromones (5a-8c):

To a solution of 2-(2'- & 1'-naphthyl) chromanones (3a-d, 6a-c; 1 eq.) in acetic acid (10 vol.) was added Thallium(III) acetate (1.4 eq) and the resultant mixture was refluxed on hot plate for 2 hrs. The reaction mixture was cooled to room temperature, poured into water and extracted with dichloromethane (2 x 50 mL). The organic phase was washed with water (2 x 50 mL) followed by saturated sodium bicarbonate solution (25 mL) and dried over anhydrous sodium sulfate. The solvent was distilled off and the residue was purified by passing through a small bed of basic alumina using ethyl acetate-hexane (1: 10) as eluent to afford 2-(2'- & 1'-naphthyl)chromones (5a-8c).

2-(2'-Naphthyl) chromone (5a): The compound was obtained as off-white solid, Yield: 81%; m.p.: 156-158°C, (Lit⁵. m.p.: 152-154°C); ¹H-NMR (CDCl₃) δ (ppm): 8.49 (brs, 1H), 8.26 (dd, 1H, *J*=1.60 & 7.94 Hz), 7.99 – 7.87 (m, 4H), 7.62 – 7.56 (m, 4H), 7.45 (dd, 1H, *J*=1.54 & 8.06 Hz), 6.96 (s, 1H). ¹³C NMR (CDCl₃) δ(ppm): 179.01, 163.29, 155.21, 134.01, 133.07, 132.90, 129.38, 128.30, 128.35, 127.90, 124.12, 123.52, 122.74, 118.10 & 108.01; HRMS (ESI) Calc. for C₁₉H₁₂O₂ [M+ H]⁺: 273.09.

6-Methyl-2-(2'-naphthyl) chromone (5b): As white solid, m.p.: 186-187°C, Yield: (10 mg) 90%; IR (KBr) cm⁻¹: 1640; ¹H-NMR (CDCl₃) δ(ppm): (08.48 (d, 1H, *J*=1.2 Hz), 8.04 - 7.87 (m, 5H), 7.61 – 7.53 (m, 4H), 6.94 (s, 1H), 2.48 (s, 3H); MS (ES) *m/z*: 287.1 [M+H]⁺.

6-Chloro-2-(2'-naphthyl) chromone (5c): As brown solid, m.p.: 162-165°C, Yield: (26 mg) 79%; ¹H-NMR (CDCl₃) δ(ppm): 8.48 (brs, 1H), 8.22 (d, 1H, *J*=2.48 Hz), 8.05 - 7.90 (m, 4H), 7.67 (dd, 1H, *J*=8.8 & 2.55 Hz), 7.62 - 7.59 (m, 3H), 6.96 (s, 1H); MS (ES) *m/z*: 307.2 [M+H]⁺.

7-Methoxy-2-(2'-naphthyl) chromones (5d): As brown solid, m.p.: 178-180°C, Yield: (20 mg) 74%; ¹H-NMR (CDCl₃) δ(ppm): 8.46 (brs, 1H), 8.15 (d, 1H, *J*=8.81 Hz), 7.99 - 7.94 (m, 2H), 7.91 - 7.88 (m, 2H), 7.61 - 7.55 (m, 2H), 7.04 (d, 1H, *J*=2.31 Hz), 7.00 (dd, 1H, *J*=8.8 & 2.38 Hz), 6.89 (s, 1H), 3.96 (s, 3H); MS: *m/z*: 303.2 [M+H]⁺. MS (ESI) *m/z*: 303.2 [M+H]⁺.

2-(1'-Naphthyl)chromone(8a): As white solid, m.p.: 140-142°C, (Lit¹⁰. m.p.: 142-143°C); Yield: (19 mg) 39%; ¹H-NMR (CDCl₃) δ(ppm): 8.31 (dd, 1H, *J*=7.94 & 1.70 Hz), 8.15 - 8.13 (m, 1H), 8.03 (d, 1H, *J*=8.31 Hz), 7.97 - 7.94 (m, 1H), 7.77 (dd, 1H, *J*=7.12 & 1.16 Hz), 7.72 (ddd, 1H, *J*=7.92, 7.76 & 1.70 Hz), 7.61 - 7.53 (m, 4H), 7.46 - 7.49 (m, 1H), 6.69 (s, 1H); MS: *m/z*: 273.05 [M+H]⁺. Data matches with literature values.

6-Methyl-2-(1'-naphthyl) chromone (8b): As brown solid, m.p.: 114-116°C, Yield: (16 mg) 38%; IR (KBr) cm⁻¹: 1639; ¹H-NMR (CDCl₃) δ(ppm): 8.14 - 8.09 (m, 2H), 8.02 (d, 1H, *J*=8.30 Hz), 7.98 - 7.94 (m, 1H), 7.76 (dd, 1H, *J*=7.12 & 1.12 Hz), 7.60 - 7.52 (m, 4H), 7.43 (d, 1H, *J*=8.50 Hz), 6.67 (s, 1H), 2.50 (s, 3H); MS: *m/z*: 288.5 [M+H]⁺ and 6-methyl-3-(1'-naphthyl) chromone (7bb), R_f 0.42 (benzene), yield 64 mg (45%); m.p.: 130-131°C.

6-Chloro-2-(1'-naphthyl) chromone (8c): As white solid, Yield: (14 mg) 41%; ¹H-NMR (CDCl₃) δ(ppm): 8.27 (d, 1H, *J*=2.60 Hz), 8.11 - 8.09 (m, 1H), 8.04 (d, 1H, *J*=8.28 Hz), 7.97 - 7.94 (m, 1H), 7.76 (dd, 1H, *J*=7.12 & 1.13 Hz), 7.66 (dd, 1H, *J*=8.88 & 2.60 Hz), 7.61 - 7.57 (m, 3H), 7.49 (d, 1H, *J*=8.88 Hz), 6.69 (s, 1H); MS (ES) *m/z*: 307.2.

General procedure for the preparation of flavanones with hetero aryl group using Thallium(III) Acetate.

General procedure for the synthesis of chalcone (containing thiophenyl/ furyl / Pyridyl groups).

Potassium hydroxide (3 eq) was added to methanol (30 vol) under nitrogen. The reaction mixture was vigorously stirred for 20 min to dissolve the KOH. The reaction mixture was cooled to 0-5°C, added 2'-hydroxy acetophenones (1 eq). After 5 min added heteroaryl aldehyde (1.05 eq) and stirred for 20h at room temperature. TLC showed complete conversion of starting materials. The reaction mixture was evaporated under vacuum, added water (10 vol). The pH of the residue was adjusted to 6 using acetic acid, the solids were filtered, washed with water, hexane and dried under vacuum to afford the respective chalcone.

(E)-1-(2-hydroxyphenyl)-3-(thiophen-2-yl) prop-2-en-1-one (2ac) was prepared from above described general procedure from 1-(2-hydroxyphenyl) ethanone as dark brown solid, m.p.: 94-96°C, (Lit¹¹. m.p.: 96-98°C), Yield (300 mg) 76%; ¹H-NMR (CDCl₃) δ(ppm): 12.84

(s, 1H), 8.05 (d, 1H, $J = 14.8$ Hz), 7.89 (d, 1H, $J = 8.0$ Hz), 7.52- 7.46 (m, 3H), 7.42-7.40 (m, 1H), 7.13- 7.10 (m, 1H), 7.02 (d, 1H, $J = 8.4$ Hz), 6.95 (t, 1H, $J = 7.6$ Hz); LCMS: 99.9%, m/z :231.0, $[M+H]^+$.

(E)-1-(2-hydroxyphenyl)-3-(thiophen-3-yl) prop-2-en-1-one (2ad) was prepared from above described general procedure 2 from 1-(2-hydroxyphenyl) ethanone as brown solid, m.p.: 72-74 °C, (Lit¹². m.p.: 74-76°C), Yield (280 mg) 79%; ¹H NMR (CDCl₃): δ (ppm)= 12.84(s, 1H), 7.93-7.88(m, 2H), 7.66 (d, 1H, $J = 2.0$ Hz), 7.51- 7.39 (m, 4H), 7.02 (d, 1H, $J = 8.4$ Hz), 6.94 (t, 1H, $J = 7.6$ Hz); LCMS: (ESI)94.4%, m/z :231.0, $[M+H]^+$.

(E)-1-(2-hydroxyphenyl)-3-(pyridin-3-yl) prop-2-en-1-one (2ae) was prepared from above described general procedure from 1-(2-hydroxyphenyl) ethanone as pale yellow semi solid, m.p.: 118-121°C, (Lit¹³. m.p.: 120-122°C), Yield (240 mg) 71%; ¹H NMR (CDCl₃): δ (ppm)= 12.65(s, 1H), 8.89 (s, 1H), 8.66 (d, 1H, $J = 3.6$ Hz), 7.97 (d, 1H, $J = 7.6$ Hz), 7.92- 7.88 (m, 2H), 7.72 (d, 1H, $J = 15.6$ Hz), 7.52 (t, 1H, $J = 7.2$ Hz), 7.40-7.37 (m, 1H), 7.04 (d, 1H, $J = 8.4$ Hz), 6.96 (t, 1H, $J = 7.6$ Hz); LCMS: (ESI) 81.6%, m/z :226.0, $[M+H]^+$. Data matches with literature values.

(E)-1-(2-hydroxyphenyl)-3-(2-methoxypyridin-4-yl) prop-2-en-1-one (2af) was prepared from above described general procedure from 1-(2-hydroxyphenyl) ethanone as yellow solid, m.p.:130-131°C, Yield (245 mg) 77%; ¹H NMR (CDCl₃) δ (ppm): 12.57(s, 1H), 8.22 (d, 1H, $J = 5.2$ Hz), 7.87 (d, 1H, $J = 7.2$ Hz), 7.78-7.68 (m, 2H), 7.52 (t, 1H, $J = 6.4$ Hz), 7.09- 6.91 (m, 4H), 3.96 (s, 3H); LCMS: (ESI) 93.4%, m/z : 256.1, $[M+H]^+$.

(E)-1-(2-hydroxy-4-methoxyphenyl)-3-(thiophen-2-yl) prop-2-en-1-one¹⁴, (2dc) was prepared from above described general procedure from 1-(2-hydroxy-4-methoxyphenyl)ethanone as yellow solid, m.p.: 130-132°C, Yield (290 mg), 82%; ¹H NMR (CDCl₃) δ (ppm): 13.45 (s, 1H), 8.01 (d, 1H, $J = 15.2$ Hz), 7.79 (d, 1H, $J = 8.8$ Hz), 7.44-7.43(d, 1H, $J = 4.8$ Hz), 7.37-7.33(m, 2H), 7.10 (t, 1H, $J = 4$ Hz), 6.50-6.43(m, 2H), 3.86 (s, 3H); HRMS (ESI) Calc. for C₁₄H₁₂O₃S: 260.055, found 260.078; Data matches with literature values.

(E)-1-(2-hydroxy-4-methoxyphenyl)-3-(thiophen-3-yl) prop-2-en-1-one¹⁴, (2dd) was prepared from above described general procedure from 1-(2-hydroxy-4-methoxyphenyl) ethanone yield as off-white solid. ¹H NMR (CDCl₃) δ (ppm): 13.41 (s, 1H), 7.86 (d, 1H, $J = 15.2$ Hz, 1H), 7.68 (d, 1H, $J = 8.7$ Hz), 7.60 (d, 1H, $J = 1.8$ Hz), 7.40-7.31 (m, 3H), 6.50-6.41 (m, 2H), 3.80 (s, 1H); ¹³C (CDCl₃) δ 192.6, 166.5, 166.8, 132.9, 138.8, 131.3, 129.7, 126.9, 125.0, 120.2, 114.2, 107.8, 101.8; LCMS: (ESI) 98%, m/z :261.0, $[M+H]$. Data matches with literature values.

(E)-1-(2-hydroxy-4-methoxyphenyl)-3-(pyridin-3-yl) prop-2-en-1-one, (2de) was prepared from above described general procedure from 1-(2-hydroxy-4-methoxyphenyl) ethanone as brown solid, m.p.: 126-128°C, (Lit¹³. m.p.: 128-129°C), Yield (240 mg) 82%; ¹H NMR (CDCl₃) δ (ppm): 13.28 (s, 1H), 8.87 (s, 1H), 8.64 (d, 1H, $J = 4.4$ Hz), 7.95 (d, 1H, $J = 8$ Hz), 7.87-7.80 (m, 2H), 7.65- 7.61(d, 1H, $J = 15.6$ Hz), 7.39-7.36 (m, 1H), 6.52-6.48 (m, 2H), 3.86 (s, 3H); LCMS: 98.9 %, m/z :256.1, $[M+H]^+$.

(E)-1-(2-hydroxy-4-methoxyphenyl)-3-(2-methoxypyridin-4-yl) prop-2-en-1-one, (2df) was prepared from above described general procedure from 1-(2-hydroxy-4-methoxyphenyl) ethanone as white solid, m.p.: 148-149°C; ¹HNMR (CDCl₃) δ(ppm): 13.20 (s, 1H), 8.22 (d, 1H, *J*=5.2 Hz), 7.79 (d, 1H, *J*= 8.8 Hz), 7.74- 7.73 (m, 2H), 7.09 (d, 1H, *J*= 5.2 Hz), 6.91 (s, 1H), 6.51-6.49 (m, 2H), 3.97 (s, 3H), 3.87 (s, 3H); LCMS: (ESI) 90.3 %, m/z:286.1, [M+H⁺].

1-(2-hydroxy-5-methylphenyl)-3-(thiophen-2-yl) prop-2-en-1-one¹⁵, (2bc) was prepared from above described general procedure from 1-(2-hydroxy-5-methylphenyl) ethanone and purified by silica-gel column as white solid, m.p.: 126-128°C; Yield (210 mg) 71%; ¹HNMR (CDCl₃) δ(ppm): 12.66 (s, 1H), 8.03 (d, 1H, *J*= 15.2 Hz), 7.64 (s, 1H), 7.47- 7.40 (m, 3H), 7.32-7.30 (m, 1H), 7.13-7.10 (m, 1H), 6.93 (d, 1H, *J*= 8.4 Hz), 2.36 (s, 3H); MS: (ES) m/z:245, [M+H⁺]. Data matches with literature values.

(E)-1-(2-hydroxy-5-methylphenyl)-3-(thiophen-3-yl) prop-2-en-1-one¹⁵, (2bd) was prepared from above described general procedure from 1-(2-hydroxy-5-methylphenyl) ethanone as dark brown solid, m.p.: 130-132°C; ¹HNMR (CDCl₃) δ(ppm): 12.66 (s, 1H), 7.90 (d, 1H, *J*= 15.2 Hz), 7.65 (br s, 2H), 7.48-7.44 (m, 2H), 7.40-7.39 (m, 1H), 7.31 (d, 1H, *J*= 8.4 Hz), 6.93 (d, 1H, *J*= 8.4 Hz), 2.35 (s, 3H); LCMS: (ESI) 99.5 %, m/z:245.0, [M+H⁺]. Data matches with literature values.

(E)-1-(2-hydroxy-5-methylphenyl)-3-(pyridin-3-yl) prop-2-en-1-one, (2be)¹⁵ was prepared from above described general procedure from 1-(2-hydroxy-5-methylphenyl) ethanone as off-white solid, m.p.: 96-98°C, Yield (210 mg) 71%; ¹HNMR (CDCl₃) δ(ppm): 12.46 (s, 1H), 8.92 (s, 1H), 8.66 (d, 1H, *J*= 3.6 Hz), 8.02 (d, 1H, *J*= 8 Hz), 7.88 (d, 1H, *J*= 15.6 Hz), 7.75-7.67 (m, 2H), 7.44-7.41 (m, 1H), 7.35 (d, 1H, *J*= 8.4 Hz), 6.95 (d, 1H, *J*= 8.4 Hz), 2.36 (s, 3H). LCMS: (ESI) 99.2%, m/z:240.1, [M+H⁺].

3-(Furan-2-yl)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one(2dg) was prepared same as above described procedure from 1-(2-hydroxy-4-methoxyphenyl)ethanone as off-white solid, m.p.: 114-116°C, (Lit¹⁶. m.p.: 116°C), Yield 66%; ¹HNMR (CDCl₃) δ(ppm): 13.48 (s, 1H), 7.82 (d, 1H, *J*= 8.8 Hz), 7.64 (d, 1H, *J*= 15.2 Hz), 7.54-7.45 (m, 2H), 6.73 (d, 1H, *J*= 3.2 Hz), 6.53- 6.46 (m, 3H), 3.85 (s, 3H); LCMS: (ESI) 98 %, m/z:245.1, [M+H⁺].

3-(Furan-2-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one (2ag) was prepared same as above described procedure from 1-(2-hydroxyphenyl)ethanone as pale brown solid, m.p.: 102-104°C, (Lit¹. m.p.: 99.8°C), Yield 71%; ¹H NMR (CDCl₃) δ(ppm): 12.81 (s, 1H), 7.89 (d, 1H, *J*= 8.0 Hz), 7.60 (d, 1H, *J*= 15.3 Hz), 7.60-7.50 (m, 2H), 7.46 (t, 1H, *J*= 7.3 Hz), 7.05 (d, 1H, *J*= 8.4 Hz), 6.89 (t, 1H, *J*= 7.4 Hz), 6.75 (d, 1H, *J*= 3.0 Hz), 6.52 (m, 1H); ¹³C NMR (CDCl₃): δ 193.0, 163.1, 152.1, 145.0, 135.9, 131.0, 129.1, 121.9, 118.5, 118.3, 117.4, 117.0, 113.0; LCMS: 98.4 %, m/z:215.0, [M+H⁺]. Data matches with literature values.

3-(Furan-3-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one (2ah) was prepared same as above described procedure from 1-(2-hydroxyphenyl) as off-white solid, m.p.: 105-107°C, (Lit¹. m.p.: 106.9-108.5°C) Yield 72%; ¹HNMR (CDCl₃) δ(ppm): 12.83 (s, 1H), 7.89-7.78 (m, 3H), 7.51-7.47 (m, 2H), 7.37 (d, 1H, *J*= 15.2 Hz), 7.02 (d, 1H, *J*= 8.4 Hz), 6.95-6.92 (m, 1H), 6.73 (s, 1H); LCMS: (ESI) 98.8%, m/z:215.0, [M+H⁺].

General procedure for the synthesis of flavanones with hetero aryl groups (thiophenyl/furyl / pyridyl).

The *chalcone* (1 eq) was dissolved in acetone (10vol), added potassium carbonate (3 eq) and was refluxed for 3 h. TLC of the reaction mixture showed ~50-60% conversion. Reaction mixture was evaporated under vacuum, added water, extracted into ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated under vacuum. The crude was purified by flash column chromatography over silica-gel using ethyl acetate-hexane as eluting solvent to afford corresponding *flavanone*.

2-(Thiophen-2-yl)chroman-4-one(9a) was prepared from compound (2ac) using above described procedure as yellow gummy liquid solidifies on standing, m.p.: 87-88°C, (Lit¹⁷. m.p.: 86-88°C), Yield (110 mg) 81% ¹HNMR (CDCl₃) δ(ppm): 7.92 (dd, 1H, *J*= 1.6 Hz, 8 Hz), 7.52-7.48 (m, 1H), 7.37 (d, 1H, *J*= 5.2 Hz), 7.13 (d, 1H, *J*= 3.2Hz), 7.07-7.02 (m, 3H), 5.75 (dd, 1H, *J*= 3.2 Hz, 11.6 Hz), 3.23- 3.16 (m, 1H), 3.09-3.04 (m, 1H); LCMS: (ESI) 98.1%, m/z:231.0, [M+H⁺].

6-Methyl-2-(thiophen-2-yl)chroman-4-one¹⁵, (9b) was prepared from compound (2bc) using above described procedure as white solid, m.p.: 124-126°C, Yield (32 mg) 60%; Data matches with the literature¹² values. LCMS: (ESI) 91%, m/z:245.1, [M+H⁺].

7-Methoxy-2-(thiophen-2-yl)chroman-4-one¹⁴, (9c) was prepared from compound (2dc) using above described procedure as pale yellow gummy liquid. ¹HNMR (CDCl₃) δ(ppm): 7.86 (d, 1H, *J*= 8.8 Hz), 7.37 (d, *J*= 5.2 Hz, 1H), 7.13 (d, 1H, *J*= 3.6 Hz), 7.04- 7.02 (m, 1H), 6.61 (dd, 1H, *J*= 2 Hz, 8.8 Hz), 6.49 (d, 1H, *J*= 2.4 Hz), 5.73 (dd, 1H, *J*= 3.6 Hz, 12 H), 3.83 (s, 3H), 3.18-3.13 (m, 1H), 3.02-2.97 (m, 1H); LCMS: (ESI) 93 %, m/z: 261.0, [M+H⁺]. Data was consistency with literature¹⁴ values

2-(Thiophen-3-yl)chroman-4-one, (12a) was prepared from compound (2ad) using above described procedure as white solid, m.p.: 76-78 °C, (Lit¹⁸. m.p.: 76-78°C), Yield 67%. ¹HNMR (CDCl₃) δ(ppm): 7.93-7.91 (dd, 1H, *J*= 1.6 Hz, 8 Hz), 7.52-7.48 (m, 1H), 7.40-7.38 (m, 2H), 7.21- 7.19 (m, 1H), 7.06-7.03 (m, 2H), 5.60 (dd, 1H, *J*= 3.2 Hz, 12 Hz), 3.15-3.08 (m, 1H), 3.01-3.29 (m, 1H); LCMS: (ESI) 97.2 %, m/z:231.0, [M+H⁺].

6-Methyl-2-(thiophen-3-yl)chroman-4-one, (12b) was prepared from compound (2bd) using above described procedure and purified by Silica-gel column chromatography to afford the desired product as yellow gummy liquid. ¹HNMR (CDCl₃) δ(ppm): 7.70 (d, 1H, *J*= 1.6 Hz), 7.39-7.37 (m, 2H), 7.31 (dd, 1H, *J*= 2Hz, 8.4 Hz), 7.20- 7.18 (m, 1H), 6.94 (d, 1H, *J*= 8.8 Hz), 5.55 (dd, 1H, *J*= 3.6Hz, 12 Hz), 3.12-3.05 (m, 1H), 2.98-2.93(m, 1H), 2.31 (s, 3H); LCMS: (ESI) 91%, m/z:245.1, [M+H⁺].

7-Methoxy-2-(thiophen-3-yl)chroman-4-one¹⁴, (12c) was prepared from compound (2dd) using above described procedure in as white solid, m.p.: 130-132°C, Yield (110 mg) 68%; ¹HNMR (CDCl₃) δ(ppm): 7.85 (d, 1H, *J*= 8.8 Hz), 7.39- 7.37 (m, 2H), 7.20- 7.18 (m, 1H), 6.61(dd, 1H, *J*= 2.4 Hz, 8.8 Hz), 6.49 (d, 1H, *J*= 2 Hz), 5.57 (dd, 1H, *J*= 3.6 Hz, 12 Hz), 3.83

(s, 3H), 3.09-3.02 (m, 1H), 2.94-2.89 (m, 1H): LCMS: (ESI) 96.6%, m/z:261.0, [M+H⁺]. Data was consistent with literature¹⁴ values.

2-(Pyridin-3-yl)chroman-4-one, (15a) was prepared from compound (**2ae**) using above described procedure as dark brown gummy compound. ¹HNMR (CDCl₃) δ(ppm): 8.75 (s, 1H), 8.70-8.62 (m, 1H), 7.94 (d, 1H, *J*=1.6 Hz), 7.92 (d, 1H, *J*=1.2 Hz), 7.54-7.50 (m, 1H), 7.40-7.37 (m, 1H), 7.09-7.04 (m, 2H), 5.54 (dd, 1H, *J*= 2.8 Hz, 13.2 Hz), 3.07-3.03 (m, 1H), 2.94- 2.89 (m, 1H); LCMS: 96 %, m/z:226.0, [M+H⁺]. LCMS: (ESI) 96 %, m/z:226.0, [M+H⁺].

6-Methyl-2-(pyridin-3-yl)chroman-4-one, (15b) was prepared from compound (**2be**) using above described procedure as brown gummy liquid solidifies on standing, m.p.: 88-90°C, (Lit¹⁹. m.p.: 89-90°C), Yield (60 mg) 52%; ¹HNMR (CDCl₃) δ(ppm): 8.74 (s, 1H), 8.63 (d, 1H, *J*= 4 Hz), 7.85 (d, 1H, *J*= 8 Hz), 7.72 (s, 1H), 7.40-7.32 (m, 2H), 6.93 (d, 1H, *J*= 8.4 Hz), 5.51 (dd, 1H, *J*= 2.8 Hz, 13.2 Hz), 3.09- 3.01 (m, 1H), 2.92-2.87 (m, 1H), 2.33 (s, 3H); LCMS: 96%, m/z: 240.1, [M+H⁺].

7-Methoxy-2-(pyridin-3-yl)chroman-4-one, (15c) was prepared from compound (**2de**) using above described procedure in as white solid, m.p. 138-140°C, Yield (90 mg) 61%; ¹HNMR (CDCl₃) δ(ppm): 8.75 (s, 1H), 8.65 (s, 1H), 7.88-7.85 (m, 2H), 7.42- 7.38 (m, 1H), 6.65-6.62 (m, 1H), 6.50- 6.49 (m, 1H), 5.53 (d, 1H, *J*= 12.8 Hz), 3.88 (s, 3H), 3.06-3.02 (m, 1H), 2.98-2.83 (m, 1H); HRMS (ESI) [M+H]⁺ Calc. for C₁₅H₁₃NO₃: 256.0895, found: 256.091;

2-(2-Methoxy-4-yl)pyridin-3-yl)chroman-4-one(18a) was prepared from compound (**2af**) using above described procedure as yellow solid. ¹HNMR (CDCl₃) δ(ppm): 8.22 (d, 1H, *J*= 5.2 Hz), 7.92 (dd, 1H, *J*= 1.6 Hz, 8 Hz), 7.55- 7.47 (m, 1H), 7.09-7.06 (m, 2H), 7.00-6.95 (m, 1H), 6.87 (s, 1H), 5.45 (dd, 1H, *J*= 4.4 Hz, 12 Hz), 3.96 (s, 3H), 3.02- 2.90 (m, 2H); LCMS: 93.2%, m/z:256.1, [M+H⁺]. LCMS: (ESI) 93.7 %, m/z: 256.1, [M+H⁺].

7-Methoxy-2-(2-methoxy-4-yl)pyridin-3-yl)chroman-4-one(18c) was prepared from compound (**2df**) using above described procedure in as pale yellow solid, m.p.: 136-138°C, Yield (60 mg) 61%; ¹HNMR (CDCl₃) δ(ppm): 8.20 (d, 1H, *J*= 5.2 Hz), 7.86 (d, 1H, *J*= 8.8 Hz), 6.94 (d, 1H, *J*= 5.2 Hz), 6.85 (s, 1H), 6.63 (dd, 1H, *J*= 2.4 Hz, 8.8 Hz), 6.51 (d, 1H, *J*= 2.4 Hz), 5.43 (dd, 1H, *J*= 4 Hz, 11.6 Hz), 3.96 (s, 3H), 3.85 (s, 3H), 2.96-2.83 (m, 2H); LCMS: (ESI)98.3%, m/z: 286.1, [M+H⁺].

2-(Furan-2-yl)-7-methoxychroman-4-one(21) was prepared from the respective chalcone (**2dg**) same as above sighted procedure as brown solid, m.p.: 86-88°C, (Lit²⁰. m.p.: 88°C), Yield (45 mg) 66%; ¹HNMR (CDCl₃) δ(ppm): 7.85 (d, 1H, *J*= 9.2 Hz), 7.47 (d, 1H, *J*= 1.2 Hz), 6.61-6.58 (m, 1H), 6.46-6.44 (m, 2H), 6.40-6.31 (m, 1H), 5.52 (dd, 1h, *J*= 3.6 Hz, 11.6 Hz), 3.81 (s, 3H), 3.24-3.17 (m, 1H), 2.93-2.88 (m, 1H); LCMS: (ESI) 99.4%, m/z:245.1, [M+H⁺].

2-(Furan-2-yl) chroman-4-one²²(22) was prepared from the respective chalcone (**2ag**) as same procedure explained above, m.p.:70-72°C, (Lit¹⁴. m.p.: 72-74°C), Yield (31 mg) 66%; ¹HNMR matches with literature data; LCMS: (ESI) 99.54 %, m/z:215.0, [M+H⁺].

General procedure for the synthesis of chromones with hetero aryl group (thiophenyl/furyl / Pyridyl) using Thallium(III)Acetate.

The compound **2-substituted chroman-4-one** (1 eq) was dissolved in acetonitrile, added thallium(III)*p*-tosylate (1.2 eq.) and was refluxed for 3h. TLC showed almost conversion of starting material. Reaction mixture was added with water, extracted into ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated under vacuum. The crude was purified by flash column chromatography over silica-gel using ethyl acetate-hexane as eluting solvent to afford corresponding **3-substituted -4H-chromen-4-one**.

3-(Thiophen-2-yl)-4H-chromen-4-one(10a) was prepared from compound **(9a)** using above described procedure in as off-white solid, m.p.: 131-133°C, (Lit²². m.p.: 126.6-127.8°C), Yield (12 mg) 61%; ¹HNMR (CDCl₃) δ(ppm): 8.36-8.32(m, 2H), 7.69 (t, 1H, *J*=7.2 Hz), 7.51- 7.40 (m, 4H), 7.11 (t, 1H, *J*= 4.4 Hz); HRMS (ESI) Calc. for C₁₃H₈O₂S: 228.021, found: 228.025: 99.54%, m/z:228.9, [M+H⁺].

6-Methyl-3-(thiophen-2-yl)-4H-chromen-4-one(10b) was prepared from compound **9b** using above described procedure in as pale brown solid, m.p.: 172-174°C (Lit²². m.p.: 169.2-170.5°C); Yield (11 mg) 35%; ¹HNMR (CDCl₃) δ(ppm): 8.33 (s, 1H), 8.10 (s, 1H), 7.50-7.48 (m, 2H), 7.39- 7.37 (m, 2H), 7.11-7.09(m, 1H), 2.47(s, 3H); ¹³C NMR (CDCl₃) δ_c(ppm): 175.1, 154.1, 151.5, 135.4, 134.99, 132.6, 126.6, 126.4, 125.7, 124.4, 123.5, 117.8 & 21.01; LCMS: (ESI) 99.83%, m/z:243.0, [M+H⁺]; Data matches with literature values.

7-Methoxy-3-(thiophen-2-yl)-4H-chromen-4-one(10c): was prepared from compound **9c** using above described procedure as pale brown solid, m.p.: 174-176°C, (Lit²². m.p.: 170.6-172.3°C); Yield (22 mg) 52%; ¹HNMR (CDCl₃): δ(ppm)= 8.28 (s, 1H), 8.23 (d, 1H, *J*= 9.2 Hz), 7.49 (d, 1H, *J*=3.6 Hz), 7.40 (d, 1H, *J*= 5.2 Hz), 7.11- 7.09 (m, 1H), 7.00 (dd, 1H, *J*= 2 Hz, 8.8 Hz), 6.87-6.86 (d, 1H, *J*= 2.4 Hz), 3.92 (s,3H); LCMS: (ESI) 96.03%, m/z:259.0, [M+H⁺]. Data matches with literature values.

3-(Thiophen-3-yl)-4H-chromen-4-one⁹ (13a) was prepared from compound **12a** using above described procedure as pale yellow solid, m.p.: 136-138°C, Yield (20 mg) 58%; ¹HNMR (CDCl₃): δ(ppm)= 8.32 (dd, 1H, *J*= 1.2 Hz, 8 Hz), 8.23 (s, 1H), 8.00 (t, 1H, *J*= 2Hz),7.70-7.66 (m, 1H), 7.49-7.39 (m,4H); LCMS: (ESI) 98.16%, m/z:229, [M+H⁺].Data matches with literature values.

6-Methyl-3-(thiophen-3-yl)-4H-chromen-4-one(13b) was prepared from compound **12b** using above described procedure in as off-white solid, m.p.: 180-182°C, Yield (22 mg) 52% ¹HNMR (CDCl₃) δ(ppm): 8.21 (s, 1H), 8.10 (s, 1H), 7.99 (t, 1H, *J*= 3.6 Hz), 7.49 (dd, 1H, *J*= 2Hz, 8.4 Hz), 7.39- 7.37 (m, 3H), 2.48 (s, 3H); LCMS: 98.3%, m/z: 243.0, [M+H⁺]; LCMS: (ESI) 98.3%, m/z: 243.0, [M+H⁺];

7-Methoxy-3-(thiophen-3-yl)-4H-chromen-4-one(13c): The compound was obtained as white solid, m.p. 181-183°C; Yield (41 mg) 65%; ¹HNMR (CDCl₃) δ(ppm): 8.21 (d, 1H, *J*=8.8 Hz), 8.14 (s, 1H), 7.98 (t, 1H, *J*= 2.0 Hz), 7.37 (d, 2H, *J*=2.0 Hz), 6.99 (dd, 1H, *J*= 2.4 Hz, 8.8 Hz), 6.85-6.84 (d, 1H, *J*=2.4 Hz), 3.91 (s,3H); ¹³C NMR (CDCl₃) δ_c(ppm): 175.4,

164.09, 157.7, 152.1, 131.7, 127.9, 126.3, 125.4, 124.2, 120.3, 118.39, 114.7, 100.1 & 55.8; LCMS: (ESI) 99.47%, m/z:259.0, [M+H⁺];

2-(Pyridin-3-yl)-4H-chromen-4-one(17a) was prepared from compound **15a** using above described procedure in as pale brown solid, m.p.: 118-120°C, (Lit²³ m.p.: 116-118°C); Yield (21 mg) 52% ¹HNMR (CDCl₃): δ(ppm)= 9.13 (s, 1H), 8.78 (d, 1H, *J*= 3.6 Hz), 8.23 (t, 2H, *J*=8.4 Hz), 7.73 (t, 1H, *J*=7.2 Hz), 7.59 (d, 1H, *J*= 8.4 Hz), 7.51-7.43 (m, 2H), 6.85 (s, 1H); LCMS: (ESI) 99.40%, m/z:224.0, [M+H⁺]. Data matches with literature values.

6-Methyl-2-(pyridin-3-yl)-4H-chromen-4-one(17b) was prepared from compound 18b using above described procedure as white solid, m.p.; 154-156°C, Yield (10 mg) 39% ¹HNMR (CDCl₃): δ(ppm): 9.18 (s, 1H), 8.77 (s, 1H), 8.21 (d, 1H, *J*= 8 Hz), 8.02 (s, 1H), 7.55-7.47 (m, 3H), 6.83 (s, 1H), 2.47 (s, 3H); LCMS: (ESI) 96.03%, m/z:238.0, [M+H⁺].

-Methoxy-2-(pyridin-3-yl)-4H-chromen-4-one, (17c) was prepared from compound 15d using above described procedure as gummy liquid solidifies on standing, m.p.: 180-182°C, (Lit²⁴ m.p.: 182-184°C); Yield (12 mg) 59%; ¹HNMR (CDCl₃): δ(ppm): 9.16 (s, 1H), 8.76 (s, 1H), 8.18- 8.12 (m, 2H), 7.49-7.45 (m, 1H), 7.02-6.97 (m, 2H), 6.78 (s, 1H), 3.94 (s, 3H); LCMS: (ESI) 96.03%, m/z:254.1, [M+H⁺]. Data matches with literature values.

2-(2-Methoxypyridin-4-yl)-4H-chromen-4-one (20a), was prepared from compound 18a using above described procedure in as ash colour solid, m.p.: 176-178°C, Yield (15 mg) 54%; ¹HNMR (CDCl₃): δ(ppm)= 8.33 (d, 1H, *J*= 5.6 Hz), 8.23 (dd, 1H, *J*= 1.2 Hz, 8 Hz), 7.75-7.71 (m, 1H), 7.58 (d, 1H, *J*= 8.4 Hz), 7.45 (t, 1H, *J*= 7.6 Hz), 7.31 (d, 1H, *J*= 5.6 Hz), 7.27-7.26 (m, 1H), 6.86 (s, 1H), 4.01 (s, 3H); LCMS: 98.3%, m/z:243.0, [M+H⁺]. LCMS: (ESI) 96.03%, m/z:238.0, [M+H⁺].

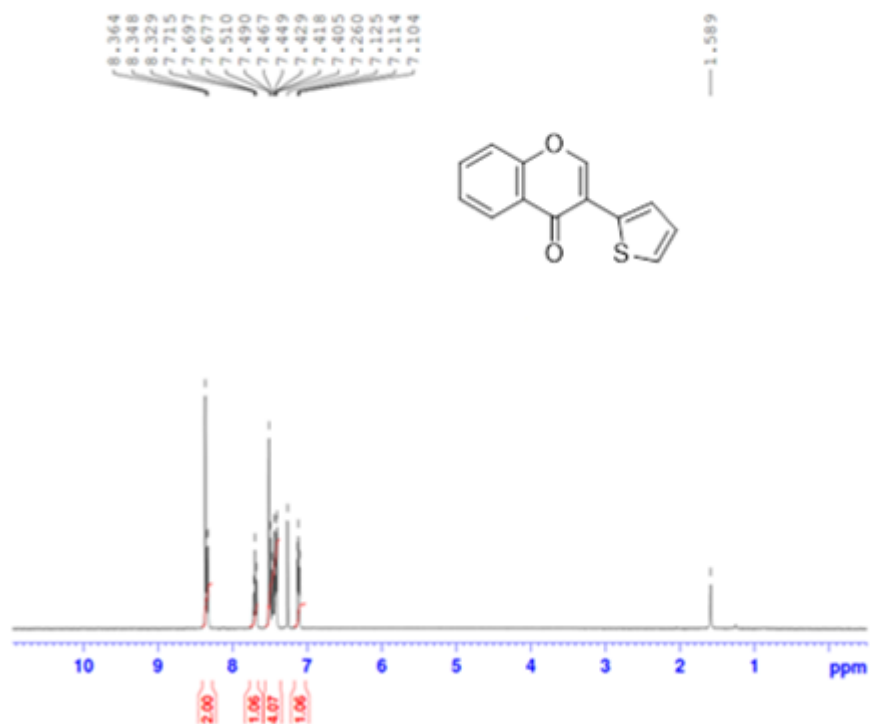
7-Methoxy-2-(2-methoxypyridin-4-yl)-4H-chromen-4-one(20c) was prepared from compound **18d** using above described procedure as off-white solid, m.p.: 198-200°C, Yield (12 mg) 78%; ¹HNMR (CDCl₃): δ(ppm): 8.31 (d, 1H, *J*= 5.2 Hz), 8.13 (d, 1H, *J*= 9.2 Hz), 7.29(d, 1H, *J*= 4.4 Hz), 7.26- 7.24 (m, 1H), 7.01 (dd, 1H, *J*= 2 Hz, Hz, 8.8 Hz), 6.96(d, 1H, *J*= 2 Hz, 1H), 6.80 (s, 1H), 4.01 (s, 3H), 3.94 (s, 3H); LCMS :(ESI) 93.23%, m/z:284.1, [M+H⁺]; Data matches with literature values.

2-(Thiophen-2-yl)-4H-chromen-4-one, 11a: To a solution of **2-(thiophen-2-yl) chroman-4-one** (1.0 eq.) in acetic acid (10 vol) was added thallium(III) acetate (1.4 eq.) and the resultant reaction mixture was allowed stir 110°C for 2 hrs. The reaction mixture was cooled to room temperature, poured into water and extracted with ethyl acetate (2 x 20 mL). The organic phase was washed with saturated sodium bicarbonate solution (10 mL) followed by brine solution (10 mL) and dried over anhydrous sodium sulfate. The solvent was distilled off and the residue was purified by combiflash (silica-gel column) using ethyl acetate-hexane (2: 8) as eluent to afford 2-(thiophen-2-yl)-4H-chromen-4-one, 11, as off-white solid, m.p.: 90-92°C., (Lit¹ m.p.: 93-95°C), Yield (110 mg) 62%. ¹HNMR (CDCl₃) δ (ppm): 8.20 (dd, 1H, *J*₁= 8.0 & *J*₂=1.5 Hz), 7.71 (d, 1H, *J*=3.1 Hz), 7.70-7.63 (m, 1H), 7.60 (d, 1H, *J*=5.1 Hz), 7.54 (d, 1H, *J*= 8.4 Hz), 7.40 (t, 1H, *J*=7.6 Hz), 7.20-7.15 (m, 1H), 6.70 (s, 1H); ¹³C NMR (CDCl₃) δ (ppm): 176.58, 157.87, 154.93, 134.99, 133.11, 130.52, 12.99, 128.40, 125.44,

125.13, 123.63, 116.65 & 106.94; LCMS(ESI): 96% m/z: 229.1 [M+H]⁺. Data matches with the literature²⁵ values.

2-(Thiophen-3-yl)-4H-chromen-4-one, 14a was synthesized as per the above procedure using 2-(thiophen-3-yl) chroman-4-one, 12a, as white solid, m.p: 116-118°C, Yield (105 mg), 59%; ¹H-NMR (CDCl₃) δ (ppm): 8.14 (dd, 1H, *J*₁= 8.1 Hz, *J*₂= 1.6 Hz), 7.98-7.90 (m, 1H), 7.65-7.50 (m, 1H), 7.28-7.54 (m, 4H), 6.58 (s, 1H); ¹³C NMR (CDCl₃) δ (ppm): 178.0, 159.0, 156.3, 133.9, 133.5, 127.6, 126.9, 125.4, 125.0, 124.9, 123.8, 117.9, 107.0; LCMS (ESI): 97%, m/z: 229.2 [M+H]⁺. Data matches with the literature values²⁶.

Compound 9a
 1HNMR-CDCl3



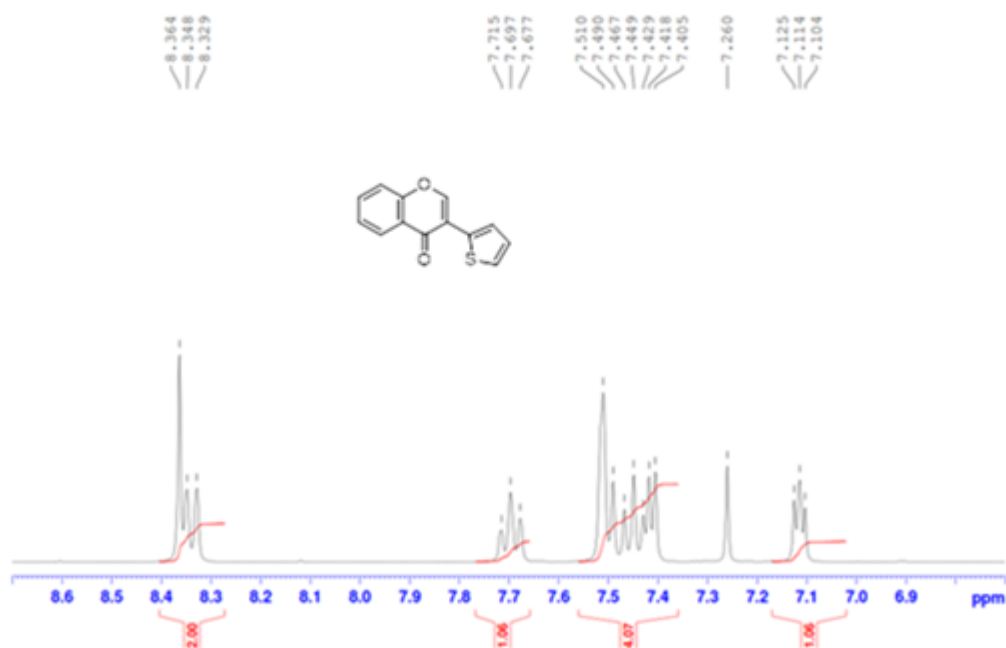
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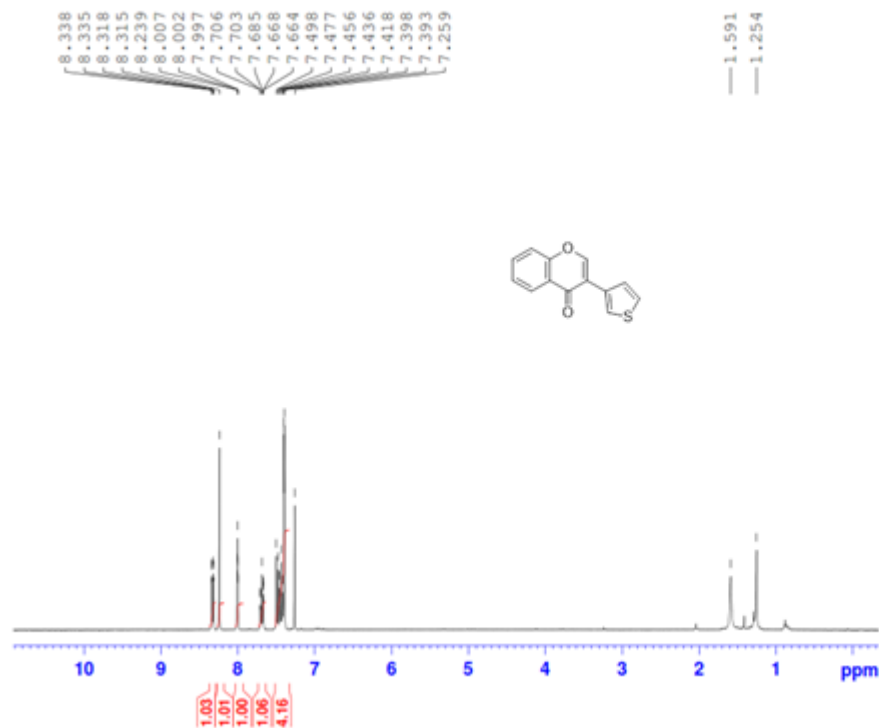
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Compound-9a
 1HNMR-Expansion



1HNMR-CDCl3



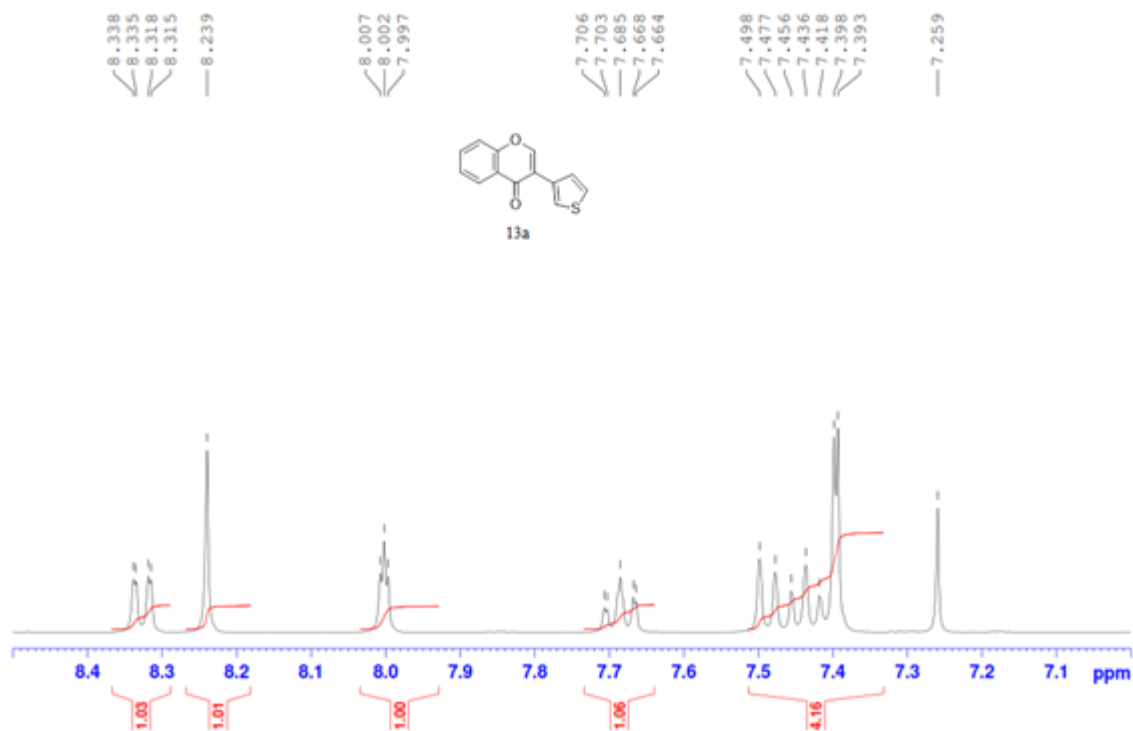
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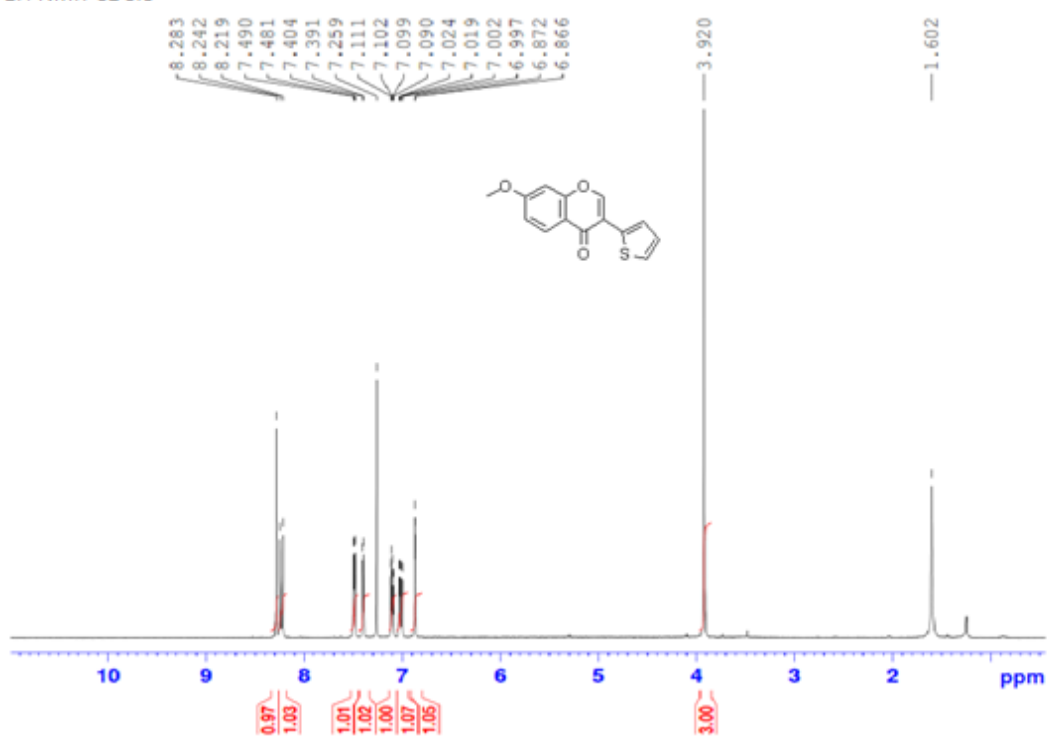
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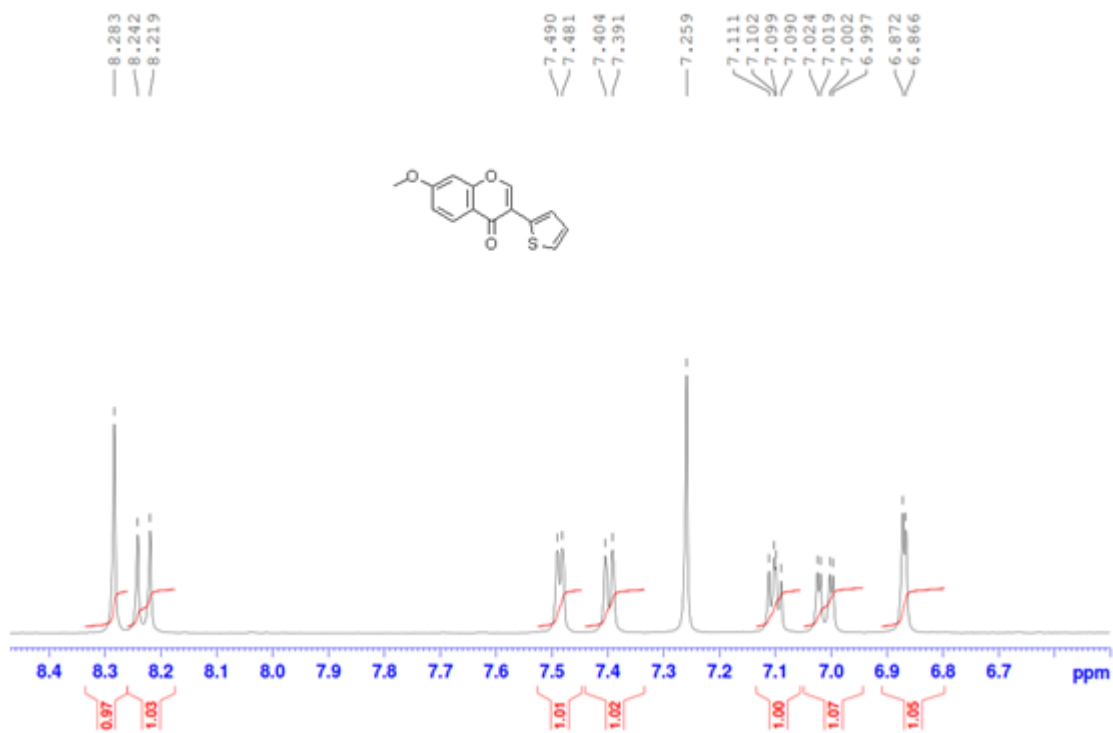
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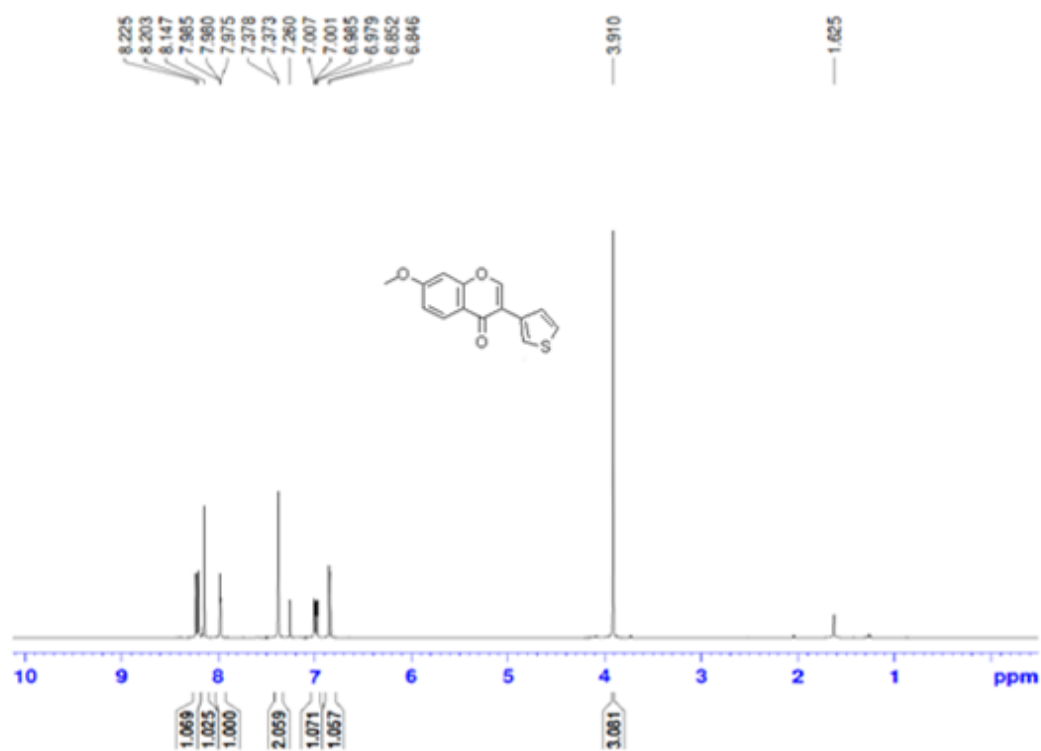
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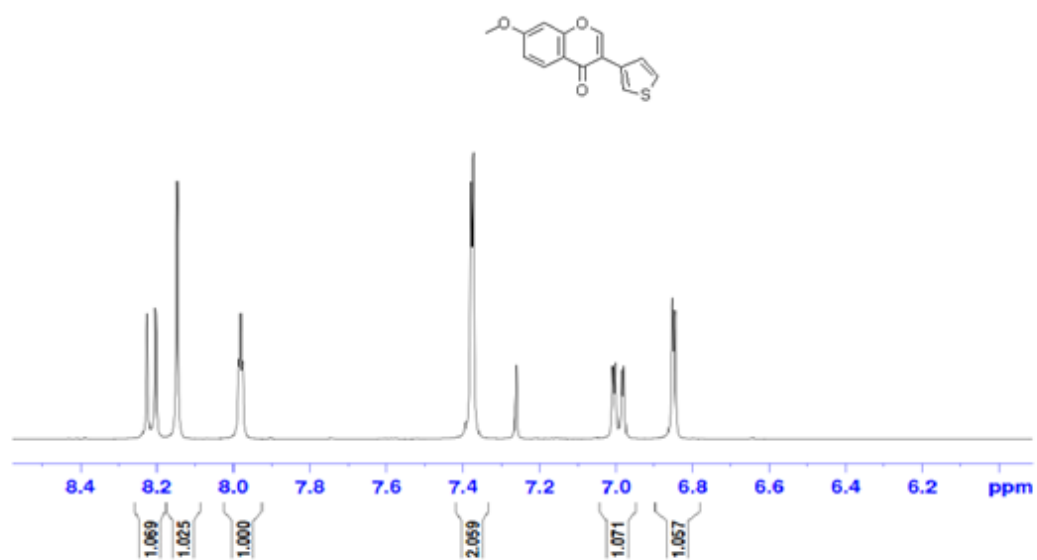
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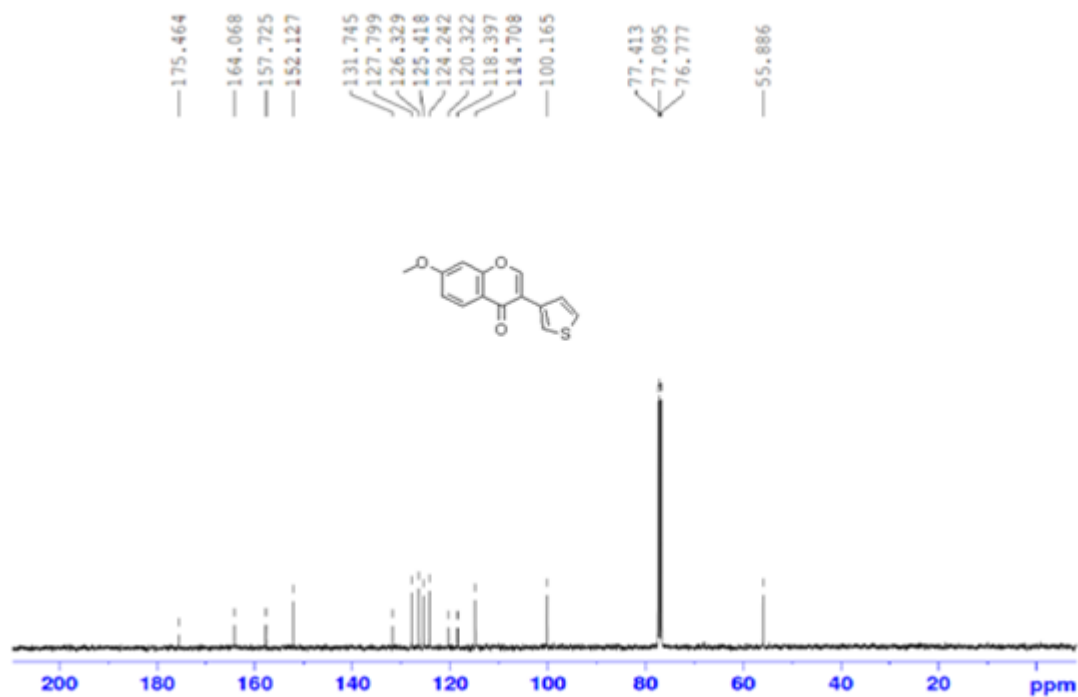
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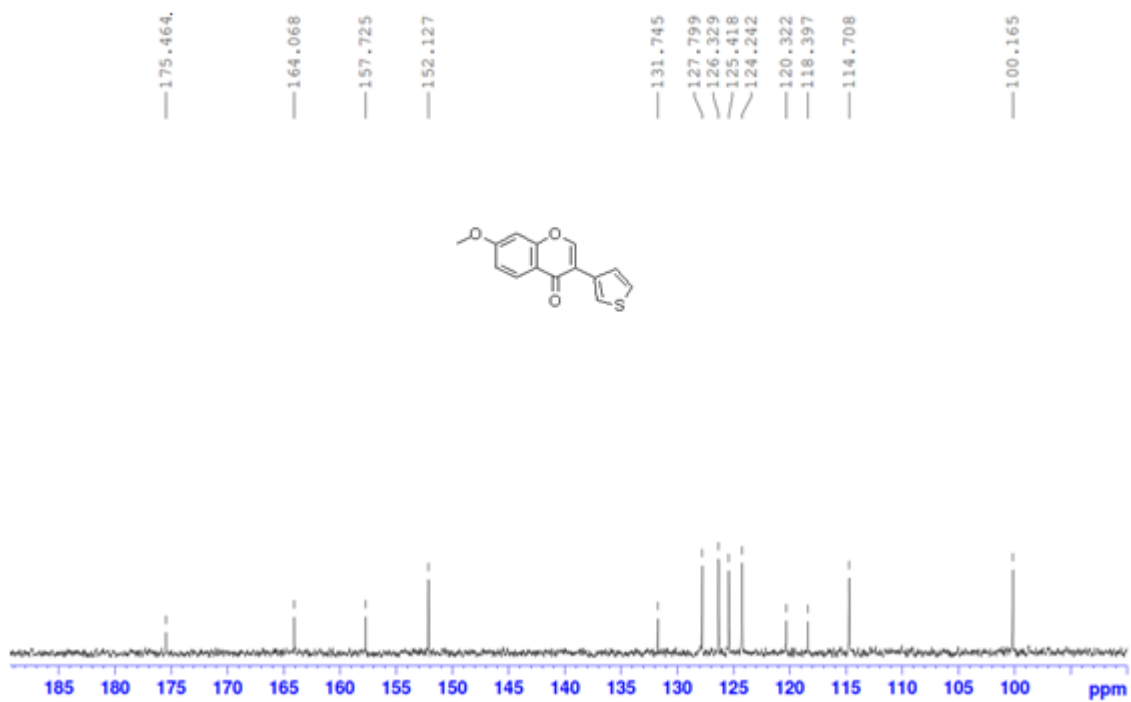
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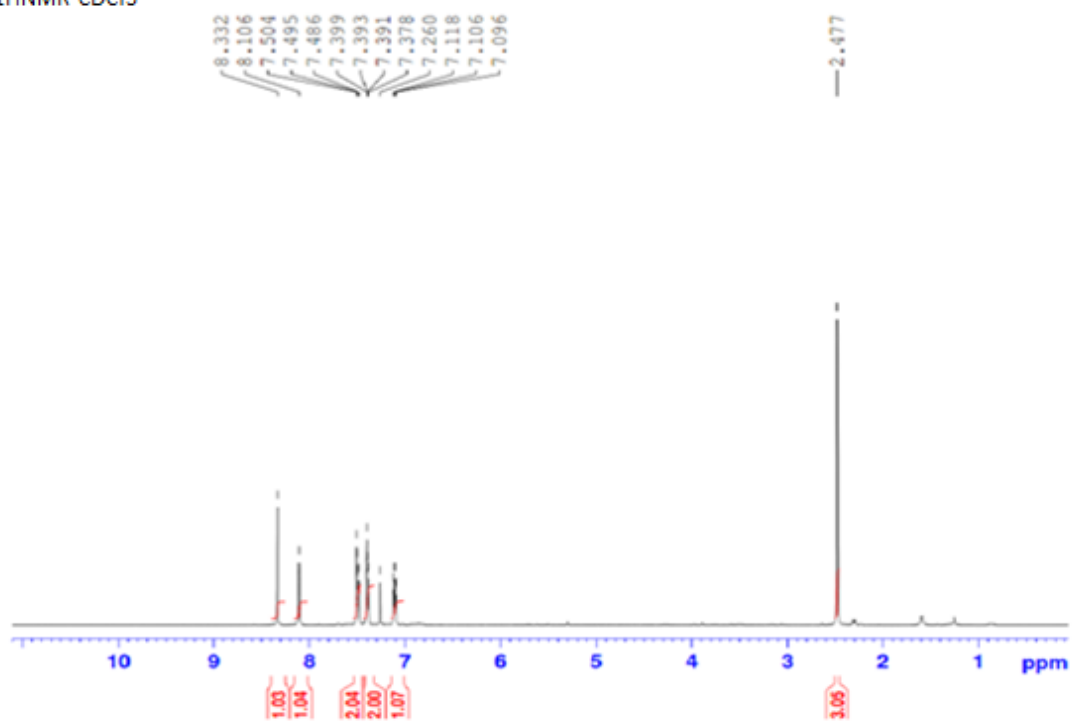
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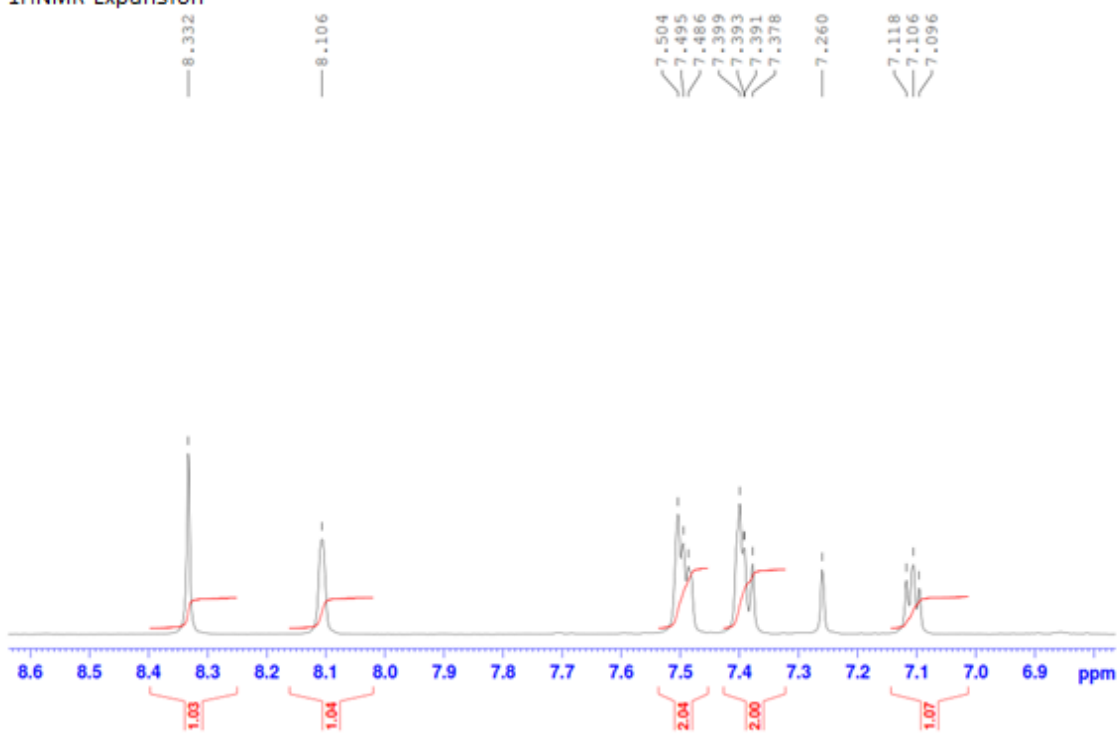
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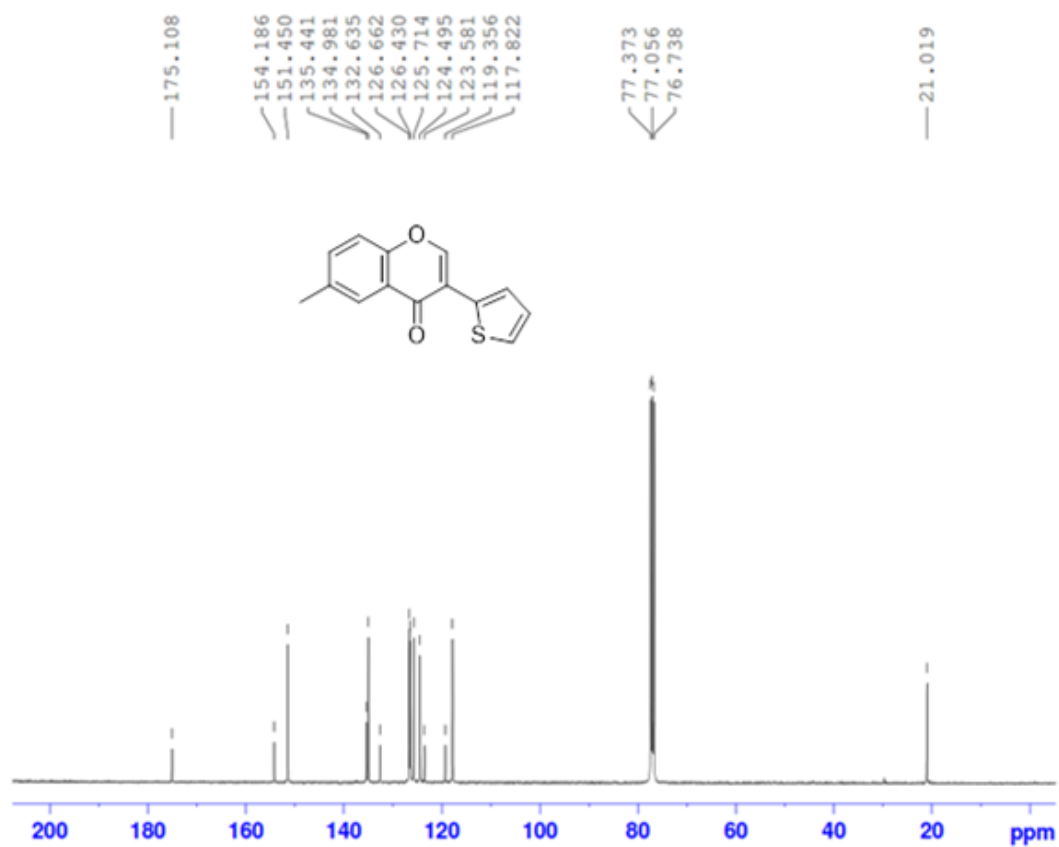
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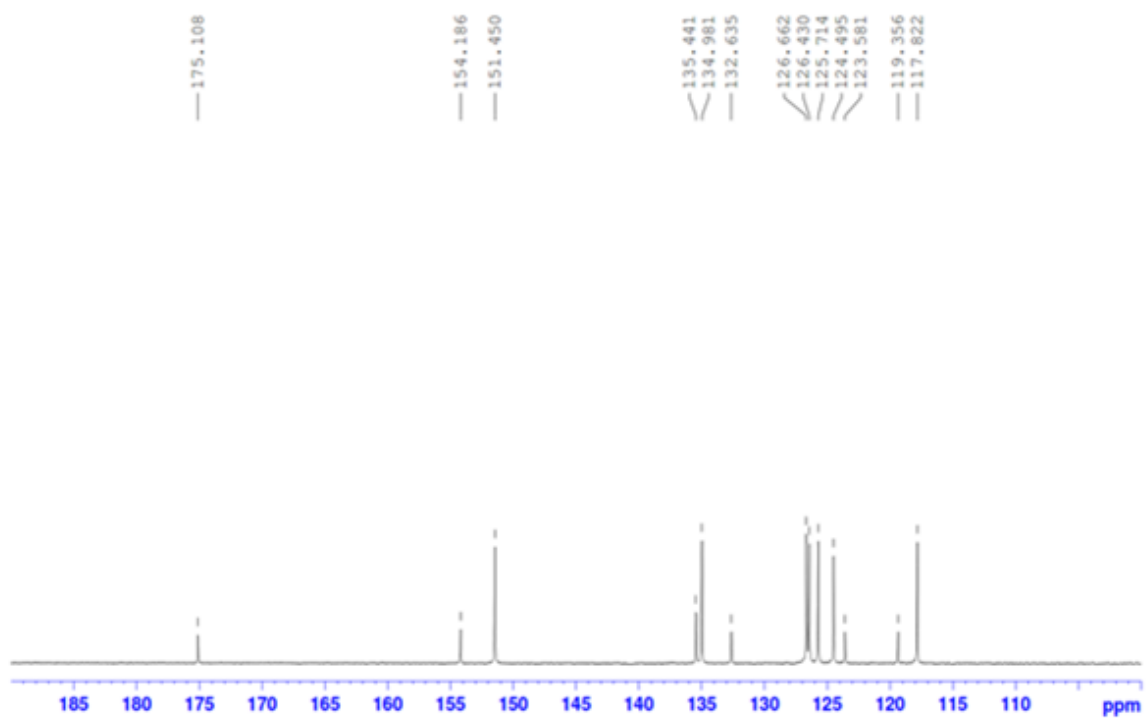
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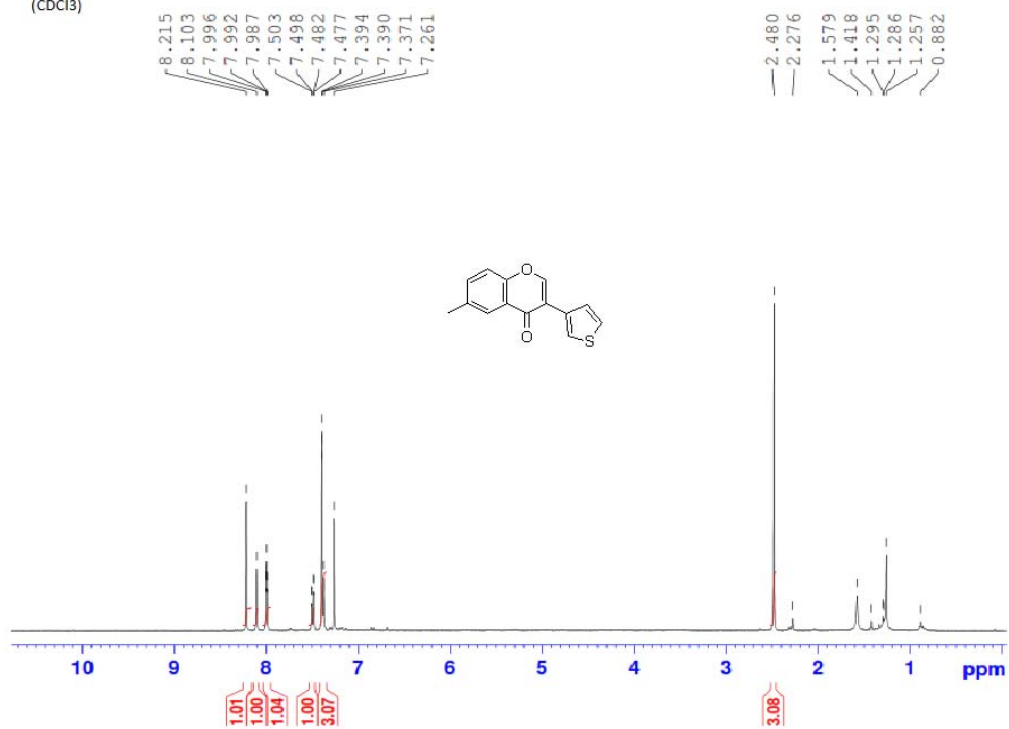
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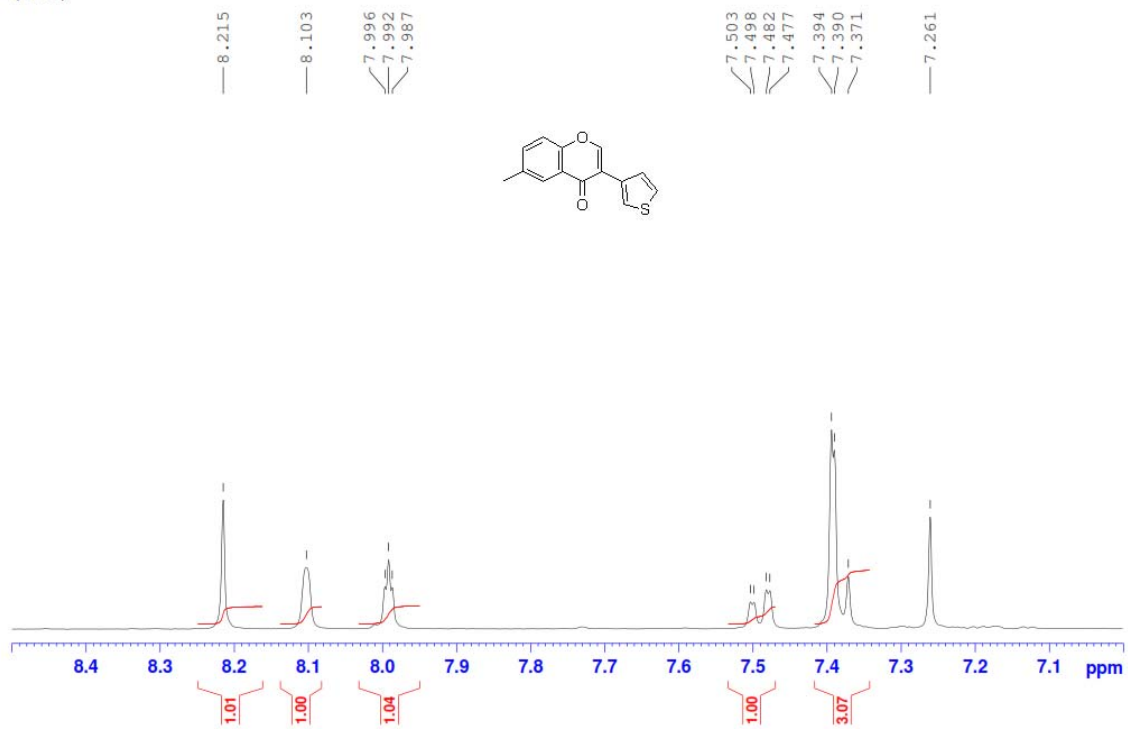
Compound 10b
13C NMR-Expansion



Compound 13b
(CDCl₃)



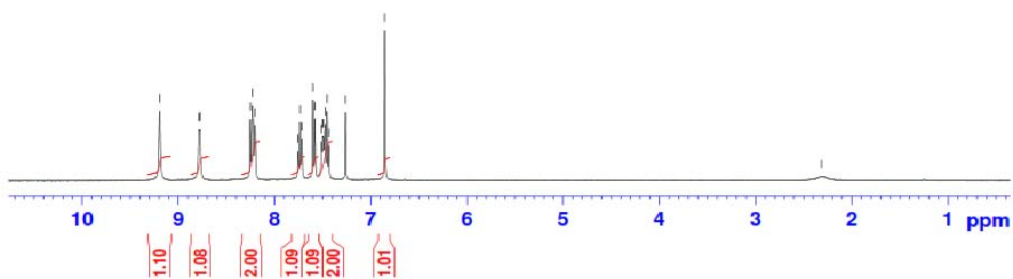
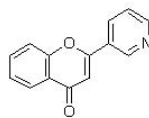
Compound 13b
(CDCl₃)



Compound 17a
(CDCl₃)

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8.784
8.775
8.251
8.230
8.201
7.753
7.715
7.600
7.579
7.510
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7.491
7.473
7.453
7.435
7.261
6.854

— 2.314



Compound 17a
(CDCl₃)

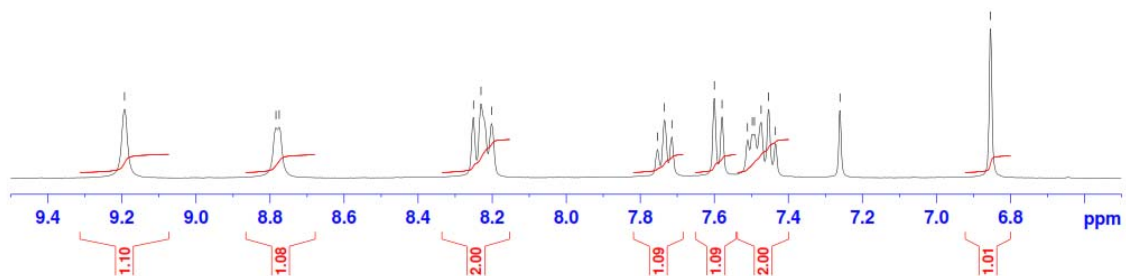
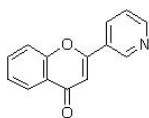
— 9.193

8.784
8.775

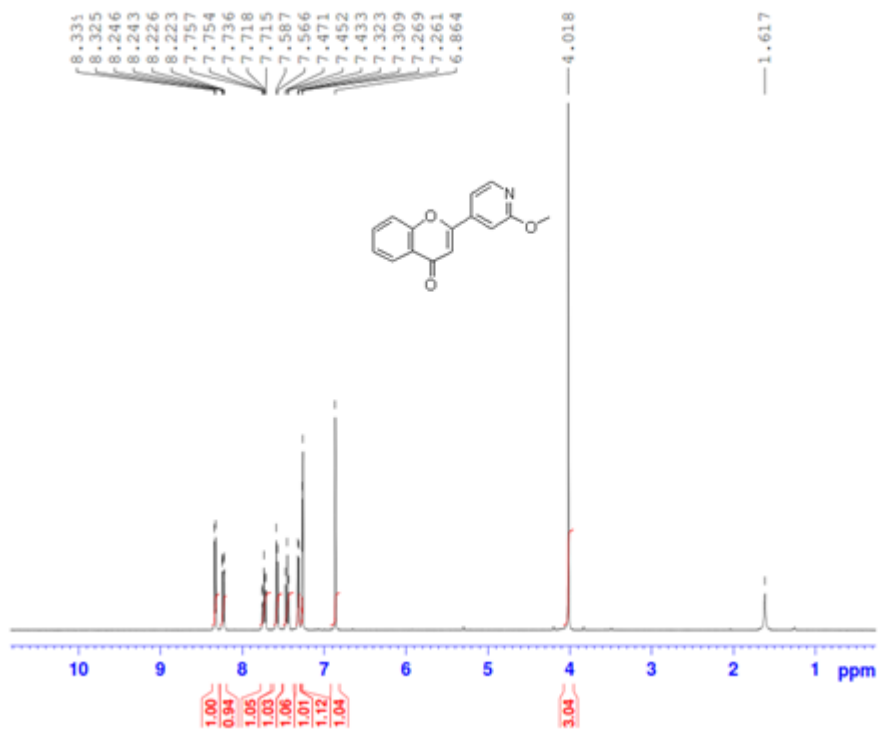
8.251
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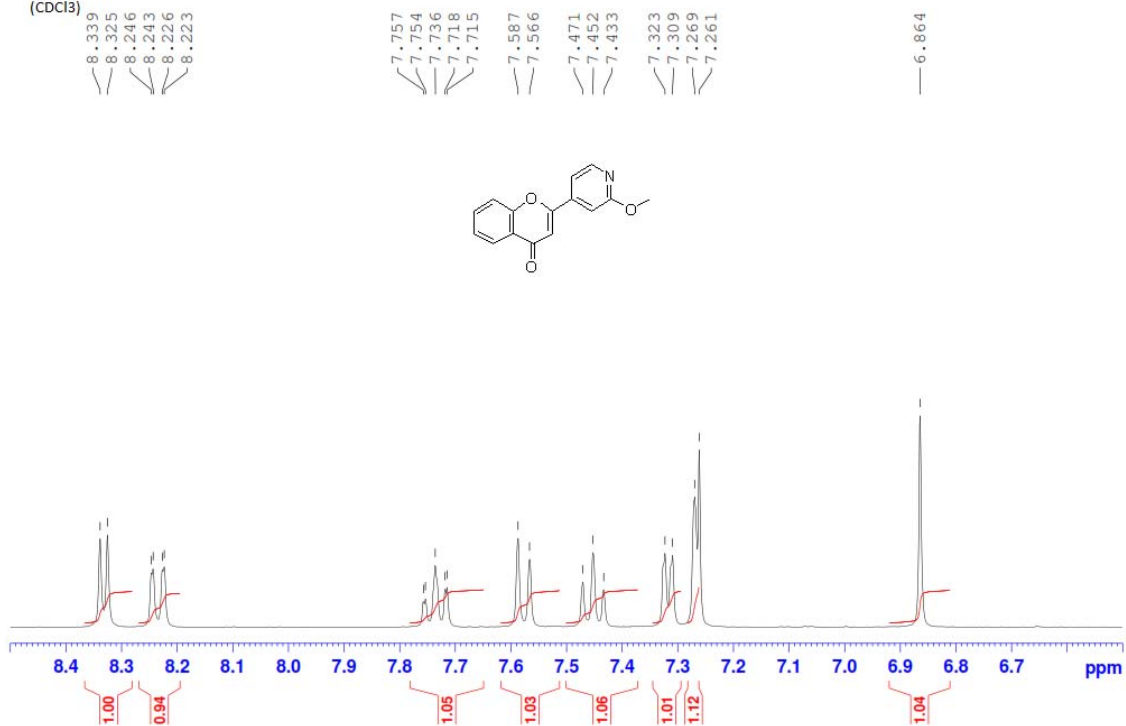
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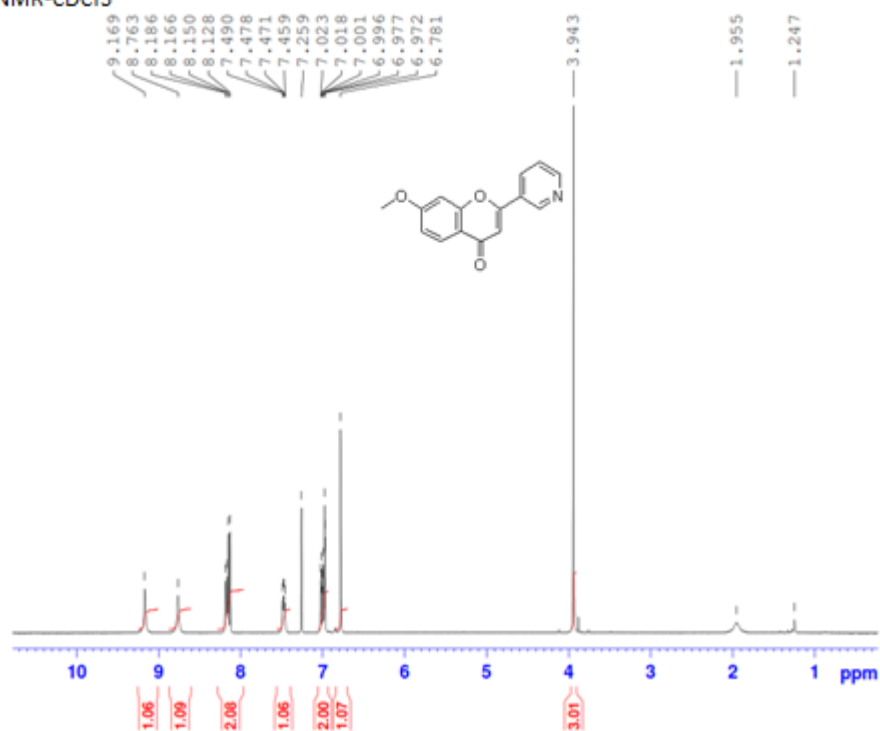
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¹HNMR-CDCl₃



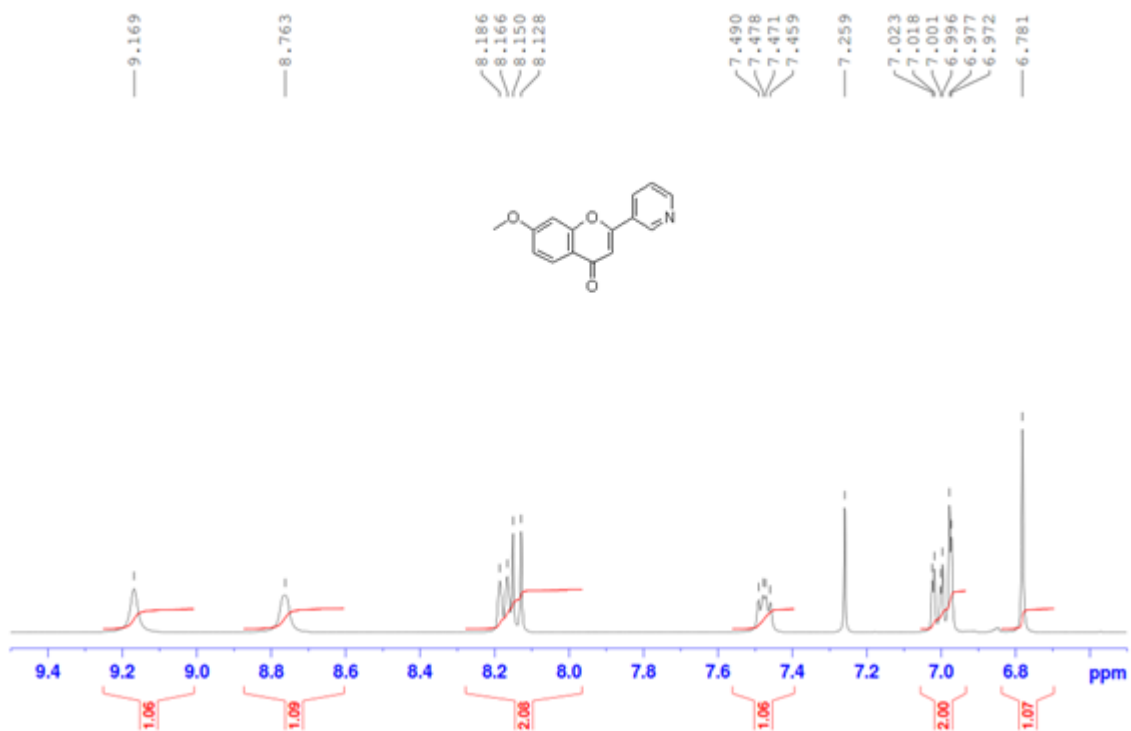
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(CDCl₃)



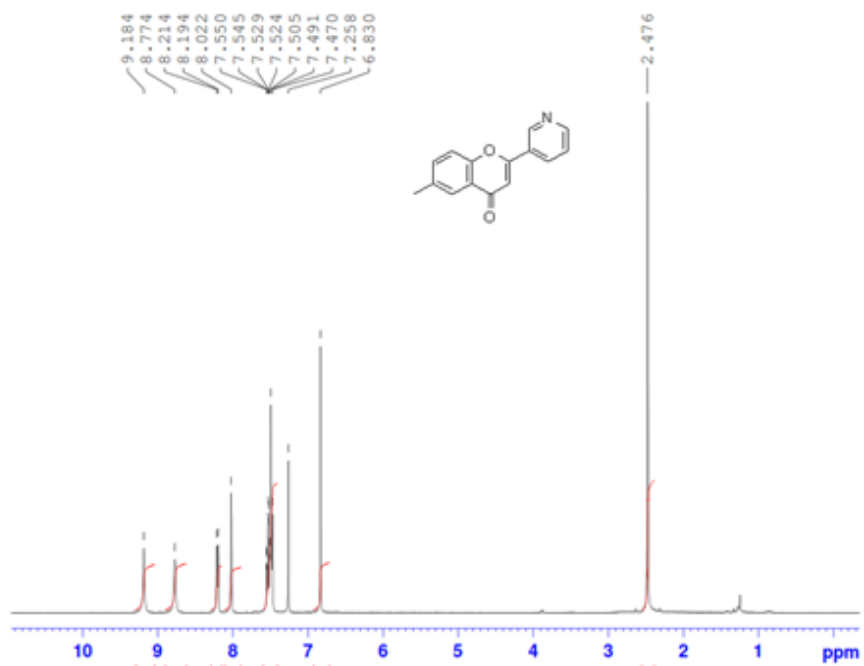
Compound 17c
 1H NMR-CDCl₃



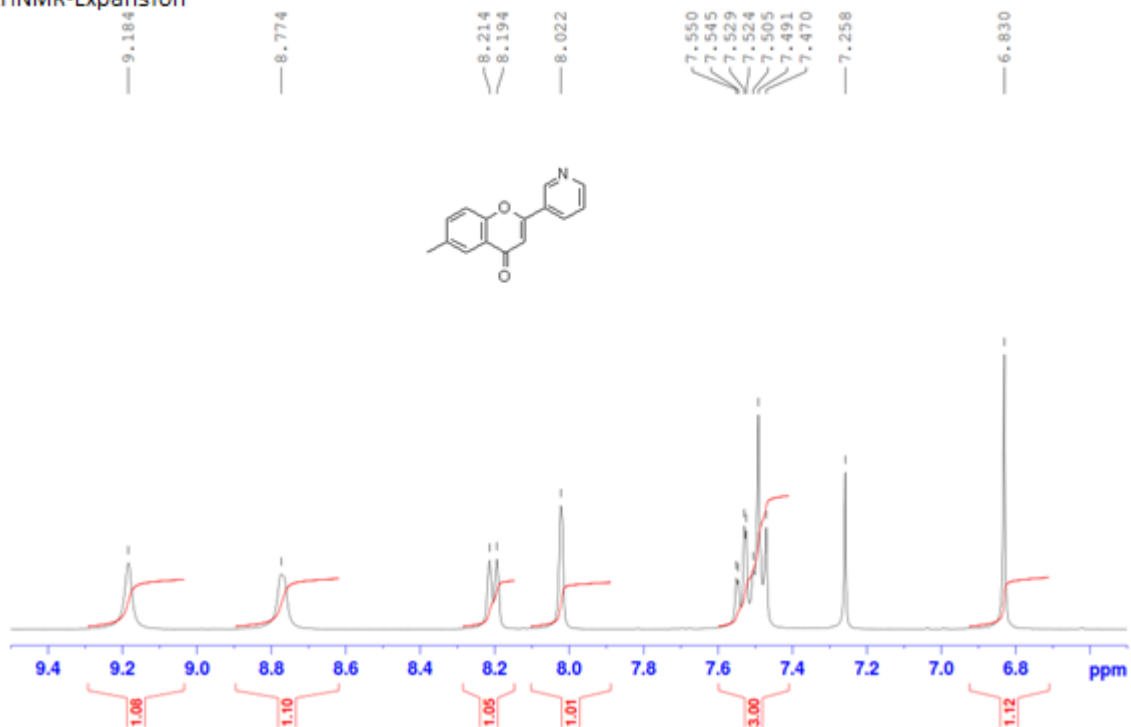
Compound 17c
 1H NMR-Expansion



Compound-17b
1HNMR-CDCl3



Compound 17b
1HNMR-Expansion



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