Supporting Information

Copper-Catalyzed Imino C-N bond formation with Aryl Boronic acids under Aerobic Conditions
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1. General Methods:
NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. $^1$HNMR spectra were recorded at 400 MHz, and $^{13}$C NMR spectra were recorded at 100MHz. Chemical shifts ($\delta$) are reported in ppm downfield from CDCl$_3$ ($\delta = 7.26$ ppm) or DMSO-D6 ($\delta = 2.49$ ppm) for $^1$H NMR and relative to the central CDCl$_3$ resonance ($\delta = 77.0$ ppm) or DMSO-D$_6$ ($\delta = 39.5$ ppm) for $^{13}$C NMR spectroscopy. Coupling constants ($J$) are given in Hz. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals.
2. Experimental Procedures.

Activation of Amberlite IRA-900(Cl), ion exchange resin:
A glass column packed with Amberlite IRA-900 (Cl) was first washed with deionized water, then later with 5% NaOH solution. The pH of the eluent was checked during the washing process. This was continued till all the chloride got replaced with hydroxide ions as seen by the pH of the eluent (pH 7). The resin was again washed with deionized water. The resin was air dried and stored in a dessicator.

Synthesis of 3-phenyl-2H-chromen-2-imine (1a):-

A solution of 2-hydroxybenzaldehyde (500 mg, 4.09 mmol), IRA 900 resin (500 mg, 4.09 mmol OH\(^{-}\)), and toluene (20 mL) was introduced into a 100 mL, three-neck flask equipped with a condenser and stirred for 3 h at 85 °C under a nitrogen atmosphere. After that, 2-phenylacetonitrile (480 mg, 4.09 mmol) was added, and the mixture was refluxed for 12 h. After completion of the reaction, the organic compound was separated from the solid catalyst and concentrated under reduced pressure. The solid phase was recrystallized from toluene to furnish the pure compound as pale (750 mg, 83%). yellow solid.

M.p.: 105–106 °C

\(^{1}\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.49 – 7.21 (m, 8H), 7.11 – 7.00 (m, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 153.2, 153.1, 136.2, 133.2, 130.5, 128.7, 128.6, 128.5, 127.4, 127.4, 123.4, 123.4, 119.9, 115.5.

Synthesis of 3-(3-(trifluoromethyl)phenyl)-2H-chromen-2-imine (1b):-

A solution of 2-hydroxybenzaldehyde (500 mg, 4.09 mmol), IRA 900 resin (500 mg, 4.09 mmol OH\(^{-}\)), and toluene (20 mL) was introduced into a 100 mL, three-neck flask equipped with a condenser and stirred for 3 h at 85 °C under a nitrogen atmosphere. After that, 2-(3-(trifluoromethyl)phenyl)acetonitrile (639 mg, 4.09 mmol) was added, and the mixture was refluxed for 24 h. After completion of the reaction, the organic compound was separated from the solid catalyst and concentrated under reduced pressure. The solid phase was recrystallized from toluene to furnish the pure compound as (985 mg, 83%) pale green solid.

M.p.: 98-99°C.

IR (KBr) \(\nu/cm\(^{-1}\)): 1735, 1647, 1600, 1489, 1442, 1373, 1336, 1298, 1219, 1201, 1165, 1074.
\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.90 (s, 2H), 7.69 – 7.51 (m, 3H), 7.37 (dd, \(J = 19.1, 7.6\) Hz, 2H), 7.24 (s, 1H), 7.15 (t, \(J = 7.2\) Hz, 2H).
\(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 141.1, 125.0, 122.18, 120.0, 118.6, 116.5, 115.5, 113.4, 113.0, 111.4, 107.5, 103.1.
HRMS (ESI): Calc. For C\(_{16}\)H\(_{11}\)F\(_3\)NO [M+H]\(^+\): 290.0787; Found: 290.0798.

**Synthesis of 3-(4-nitrophenyl)-2\(H\)-chromen-2-imine (1c):**

A solution of 2-hydroxybenzaldehyde (500 mg, 4.09 mmol), IRA 900 resin (500 mg, 4.09 mmol OH\(^-\)), and toluene (20 mL) was introduced into a 100 mL, three-neck flask equipped with a condenser and stirred for 3 h at 85 °C under a nitrogen atmosphere. After that, 2-2-(4-nitrophenyl)acetonitrile (664 mg, 4.09 mmol) was added, and the mixture was refluxed for 12 h. After completion of the reaction, the organic compound was separated from the solid catalyst and concentrated under reduced pressure. The solid phase was recrystallized from toluene to furnish the pure compound as (950 mg, 87%) pale yellow solid. 

M.p.: 165-166°C.

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 8.26 (d, \(J = 8.2\) Hz, 2H), 7.85 (s, 2H), 7.60 (s, 1H), 7.40 (dd, \(J = 19.0, 7.7\) Hz, 2H), 7.31 (s, 1H), 7.15 (dd, \(J = 14.8, 7.4\) Hz, 2H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 157.4, 153.5, 147.6, 143.0, 135.3, 131.4, 129.8, 128.0, 123.9, 123.8, 123.5, 119.5, 115.5.

**Synthesis of 3-(4-chlorophenyl)-2\(H\)-chromen-2-imine (1d):**

A solution of 2-hydroxybenzaldehyde (500 mg, 4.09 mmol), IRA 900 resin (500 mg, 4.09 mmol OH\(^-\)), and toluene (20 mL) was introduced into a 100 mL, three-neck flask equipped with a condenser and stirred for 3 h at 85 °C under a nitrogen atmosphere. After that, 2-(4-chlorophenyl)acetonitrile (523 mg, 4.09 mmol) was added, and the mixture was refluxed for 6 h. After completion of the reaction, the organic compound was separated from the solid catalyst and concentrated under reduced pressure. The solid phase was recrystallized from toluene to furnish the pure compound as pale (800 mg, 80%) yellow solid. Obtained data was matched with the literature data.

\(^4\)
Synthesis of 3-(2-fluorophenyl)-2H-chromen-2-imine (1e):

A solution of 2-hydroxybenzaldehyde (500 mg, 4.09 mmol), IRA 900 resin (500 mg, 4.09 mmol OH⁻), and toluene (20 mL) was introduced into a 100 mL, three-neck flask equipped with a condenser and stirred for 3 h at 85 °C under a nitrogen atmosphere. After that, 2-(2-fluorophenyl)acetonitrile (553 mg, 4.09 mmol) was added, and the mixture was refluxed for 24 h. After completion of the reaction, the organic compound was separated from the solid catalyst and concentrated under reduced pressure. The solid phase was recrystallized from toluene to furnish the pure compound as white solid (510 mg, 52%).

M.p.: 115–116 °C.

IR (KBr) ν/cm⁻¹: 1732, 1693, 1651, 1598, 1494, 1373, 1311 1217, 1118, 1103, 1068.

¹H NMR (CDCl3, 400 MHz) δ: 7.85 (s, 1H), 7.62 – 7.38 (m, 4H), 7.33 (d, J = 7.6 Hz, 1H), 7.20 (ddd, J = 22.7, 15.0, 7.4 Hz, 4H).

¹³C NMR (CDCl3, 100 MHz) δ: 161.2, 158.7, 153.4, 142.6, 142.6, 135.5, 131.8, 131.3, 130.9, 128.1, 127.6, 124.5, 123.5, 116.6, 116.1, 115.9.


Synthesis of 2-imino-2H-chromene-3-carbonitrile (1f):

25 mL round bottom flask 2-hydroxybenzaldehyde (100 mg, 0.81 mmol) and malononitrile (54 mg, 0.81 mmol) were added in ethanol (5 mL) with a drop of piperidine. The reaction mixture was stirred for 30 min at room temperature. The product was precipitated from the reaction mixture and collected after filtration. Solid product recrystallized from an appropriate solvent to furnish the pure compound as (101 mg, 73%) pale yellow solid. Obtained data was matched with the literature data.¹ ² ³

Synthesis of 6,8-di-tert-butyl-2-imino-2H-chromene-3-carbonitrile (1g)¹⁻:

25 mL round bottom flask 3,5-di-tert-butyl-2-hydroxybenzaldehyde (100 mg, 0.42 mmol) and malononitrile (28 mg, 0.42 mmol) were added in ethanol (5 mL) with a drop of piperidine. The reaction mixture was stirred for 30 min at room temperature. The product was precipitated from the reaction mixture and collected after filtration. It was recrystallized from an appropriate solvent to furnish the pure compound as (80 mg, 67%) pale yellow solid.

M.p.: 173–173°C.
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.77 (s, 1H), 7.58 (d, $J = 20.0$ Hz, 2H), 7.18 (d, $J = 2.2$ Hz, 1H), 1.45 (s, 9H), 1.32 (s, 9H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 153.9, 150.6, 147.3, 146.9, 136.6, 129.5, 123.7, 117.1, 114.6, 104.0, 35.0, 34.6, 31.2, 29.8.

Synthesis of 7-diethylamino-2-imino-2H-chromene-3-carbonitrile (1h):

25 mL round bottom flask 4-(diethylamino)-2-hydroxybenzaldehyde (100 mg, 0.51 mmol) and malononitrile (34 mg, 0.51 mmol) were added in ethanol (5 mL) with a drop of piperidine. The reaction mixture was stirred for 30 min at room temperature. The product was precipitated from the reaction mixture and collected after filtration. Solid product recrystallized from an appropriate solvent to furnish the pure compound as (108 mg, 86%) yellow solid. Obtained data was matched with the literature data.$^{1,2,3}$

Synthesis of 2-imino-7-methoxy-2H-chromene-3-carbonitrile (1i):

25 mL round bottom flask 2-hydroxy-4-methoxybenzaldehyde (100 mg, 0.65 mmol) and malononitrile (43 mg, 0.65 mmol) were added in ethanol (5 mL) with a drop of piperidine. The reaction mixture was stirred for 30 min at room temperature. The product was precipitated from the reaction mixture and collected after filtration. Solid product recrystallized from an appropriate solvent to furnish the pure compound as (43 mg, 57%) yellow solid. Obtained data was matched with the literature data.$^{3}$

Synthesis of 6-Chloro-2-imino-2H-chromene-3-carbonitrile (1j):

25 mL round bottom flask 4-chloro-2-hydroxybenzaldehyde (100 mg, 0.63 mmol) and malononitrile (34 mg, 0.63 mmol) were added in ethanol (5 mL) with a drop of piperidine. The reaction mixture was stirred for 30 min at room temperature. The product was precipitated from the reaction mixture and collected after filtration. Solid product recrystallized from an appropriate solvent to furnish the pure compound as (105 mg, 81%) yellow solid. Obtained data was matched with the literature data.$^{1}$

Synthesis of $N,N$-diethyl-2-imino-3-(4-nitrophenyl)-2H-chromen-7-amine (1k)$^5$:

![Synthesis of $N,N$-diethyl-2-imino-3-(4-nitrophenyl)-2H-chromen-7-amine (1k)](image-url)
A solution of 4-(diethylamino)-2-hydroxybenzaldehyde (500 mg, 3.08 mmol), IRA 900 resin (500 mg, 4.09 mmol OH⁻), and toluene (20 mL) was introduced into a 100 mL, three-neck flask equipped with a condenser and stirred for 3 h at 85 °C under a nitrogen atmosphere. After that, 2-phenylacetonitrile (596 mg, 3.08 mmol) was added, and the mixture was refluxed for 12 h. After completion of the reaction, the organic compound was separated from the solid catalyst and concentrated under reduced pressure. The solid phase was recrystallized from toluene to furnish the pure compound as (850 mg, 85%) red solid.

M.p.: 157–158°C.

¹H NMR (CDCl₃, 400 MHz) δ: 8.26 – 8.18 (m, 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.21 (s, 1H), 7.15 (d, J = 8.7 Hz, 1H), 6.44 (dd, J = 8.7, 2.6 Hz, 1H), 6.34 (d, J = 1.9 Hz, 1H), 3.40 (q, J = 7.1 Hz, 4H), 1.20 (t, J = 7.1 Hz, 6H).

¹³C NMR (CDCl₃, 100 MHz) δ: 155.8, 150.6, 146.8, 144.2, 136.0, 129.4, 129.0, 123.6, 108.5, 107.7, 96.8, 44.8, 12.6.

General procedure for Cu(II) catalyzed coupling of iminochromene with aryl boronic acids:

To a round bottomed flask equipped with stir bar iminochromene (a, 1 mmol), Cu(OAc)₂·H₂O (20 mol %) and arylboronic acid (2.07 mmol) were added. Ethanol (5 mL) was added and the reaction mixture was stirred for 24 h at room temperature. After completion of the reaction as monitored by TLC, the organic phase was concentrated under reduced pressure and the solid residue was fractioned in ethyl acetate (20 mL) and water (10 mL) thrice. The organic phase was separated and dried on anhydrous Na₂SO₄. The solvent was removed in vacuum and the crude residue was purified by column chromatography with ethyl acetate/petroleum ether to afford the respective N-arylated chromene.
Synthesis of (Z)-N-3-diphenyl-2H-chromen-2-imine (3a):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3a 200 mg scale reaction (249 mg, 93%) as yellow solid.

**M.p.:** 112-113°C.

**IR (KBr) v/cm⁻¹:** 1737, 1643, 1587, 1485, 1365, 1230, 1116.

**¹H NMR (CDCl₃, 400MHz)** δ: 7.79 – 7.72 (m, 2H), 7.46 – 7.30 (m, 7H), 7.29 (s, 1H), 7.20 – 7.13 (m, 2H), 7.13 – 7.05 (m, 1H), 7.02 (d, J = 8.2 Hz, 1H).

**¹³C NMR (CDCl₃, 100MHz)** δ: 152.9, 148.9, 146.6, 136.7, 133.6, 133.3, 132.1, 130.1, 129.1, 128.7, 128.4, 128.3, 128.0, 127.2, 123.9, 123.4, 122.8, 122.5, 120.4, 115.6, 115.3.

**HRMS (ESI):** Calc. For C₂₁H₁₃NO [M+H]⁺: 298.1226; Found: 298.1277.

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Synthesis of (Z)-N-(4-bromophenyl)-3-phenyl-2H-chromen-2-imine (3b):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3b 200 mg scale reaction (289 mg, 85%) as yellow solid.

**M.p.:** 127-128°C.

**IR (KBr) v/cm⁻¹:** 1643, 1597, 1481, 1226, 1141, 1072, 1002, 756, 694.

**¹H NMR (CDCl₃, 400MHz)** δ: 7.81 – 7.74 (m, 2H), 7.54 – 7.33 (m, 8H), 7.18 (t, J = 7.5 Hz, 1H), 7.09 (dd, J = 11.2, 8.4 Hz, 3H).

**¹³C NMR (CDCl₃, 100MHz)** δ: 152.7, 149.4, 145.7, 136.4, 133.7, 131.9, 131.5, 130.3, 129.0, 128.5, 128.1, 127.4, 124.5, 123.9, 120.3, 116.4, 115.3.

**HRMS (ESI):** Calc. For C₂₁H₁₅BrNO [M+H]⁺: 376.0332; Found: 378.0326.

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Synthesis of (Z)-N-(4-chlorophenyl)-3-phenyl-2H-chromen-2-imine (3c):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3c 200 mg scale reaction (300 mg, 82%) as yellow solid.

**M.p.:** 117-118°C.

**IR (KBr) v/cm⁻¹:** 1739, 1643, 1481, 1365, 1217, 1141, 1089, 1010, 842, 767.

**¹H NMR (CDCl₃, 400MHz)** δ: 7.73 (dd, J = 8.0, 1.2 Hz, 2H), 7.46 – 7.26 (m, 8H), 7.17 – 7.08 (m, 3H), 7.03 (d, J = 8.1 Hz, 1H).
Synthesis of (Z)-N-(4-fluorophenyl)-3-phenyl-2H-chromen-2-imine (3d):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3d 200 mg scale reaction (224 mg, 79%) as yellow solid

M.p.: 108-109°C.

IR (KBr) ν/cm⁻¹: 1732, 1656, 1500, 1454, 1365, 1228, 1153, 1116, 1026.

¹H NMR (CDCl₃, 400MHz) δ: 7.76 – 7.70 (m, 2H), 7.46 – 7.30 (m, 5H), 7.28 (s, 1H), 7.21 – 7.10 (m, 3H), 7.02 (ddd, J = 8.9, 7.3, 3.9 Hz, 3H).

¹³C NMR (CDCl₃, 100MHz) δ: 152.7, 150.0 (C-F), 149.9, 136.3, 134.2, 131.7, 130.5, 129.0, 128.6, 128.2, 127.5, 125.8, 125.8, 124.1, 122.5, 120.4, 115.4.


Synthesis of (Z)-3-phenyl-N-(m-tolyl)-2H-chromen-2-imine (3e):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3e 200 mg scale reaction (246 mg, 82%) as yellow solid.

M.p.: 108-109°C.

IR (KBr) ν/cm⁻¹: 3055, 2970, 1739, 1647, 1593, 1483, 1375, 1261 1155, 1116, 1031.

¹H NMR (CDCl₃, 400MHz) δ: 7.82 (d, J = 7.4 Hz, 2H), 7.52 – 7.41 (m, 3H), 7.33 (ddd, J = 17.6, 9.4, 4.6 Hz, 4H), 7.17 (t, J = 7.4 Hz, 1H), 7.11 – 7.04 (m, 3H), 6.98 (d, J = 7.3 Hz, 1H).

¹³C NMR (CDCl₃, 100MHz) δ: 152.9, 148.7, 146.5, 138.2, 136.7, 133.2, 132.2, 130.1, 129.1, 128.4, 128.4, 128.1, 127.3, 124.4, 123.6, 123.3, 120.4, 119.4, 115.4, 21.5.


Synthesis of (Z)-N-(naphthalen-2-yl)-3-phenyl-2H-chromen-2-imine (3f):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure
compound 3f 200 mg scale reaction (261 mg, 83%) as yellow solid; M.p.:112-123°C.

IR (KBr) v/cm\(^{-1}\):1734, 1648, 1593, 1454, 1369, 1230, 1139.

\(^1\)H NMR (CDCl\(_3\), 400MHz) \(\delta\): 7.92 – 7.77 (m, 5H), 7.63 (s, 1H), 7.55 – 7.31 (m, 9H), 7.17 (td, \(J = 7.5, 0.7\) Hz, 1H), 7.04 (d, \(J = 8.2\) Hz, 1H).

\(^1\)C NMR (CDCl\(_3\), 100MHz) \(\delta\): 152.9, 149.3, 144.3, 136.6, 134.2, 133.5, 132.1, 130.7, 130.2, 129.1, 128.5, 128.1, 128.0, 127.6, 127.5, 127.4, 125.8, 124.4, 123.7, 123.4, 120.4, 118.9, 115.4.;

HRMS (ESI): Calc. For C\(_{25}\)H\(_{18}\)NO [M+H]\(^+\): 348.1383; Found: 348.1395.

Synthesis of (Z)-N-(naphthalen-1-yl)-3-phenyl-2\(H\)-chromen-2-imine (3g):

\[ \text{A obtain residue which was purified by column chromatography over} \]
\[ \text{silica gel using EtOAc/petroleum ether (5:95) to furnish the pure} \]
\[ \text{compound 3g 200 mg scale reaction (249 mg, 79%) as yellow soli} \]
\[ \text{d; M.p.:159-160°C.} \]

IR (KBr) v/cm\(^{-1}\):1737, 1645, 1598, 1454, 1365, 1228, 1139.

\(^1\)H NMR (CDCl\(_3\), 400MHz) \(\delta\): 8.06 (d, \(J = 8.2\) Hz, 1H), 7.92 – 7.81 (m, 3H), 7.62 (d, \(J = 8.2\)
Hz, 1H), 7.53 – 7.36 (m, 8H), 7.34 – 7.26 (m, 2H), 7.13 (td, \(J = 7.5, 1.0\) Hz, 1H), 6.92 (d, \(J = 8.2\)
Hz, 1H).

\(^1\)C NMR (CDCl\(_3\), 100MHz) \(\delta\): 152.9, 149.5, 143.2, 136.8, 134.3, 133.7, 132.2, 130.3, 129.2,
128.6, 128.5, 128.2, 127.9, 127.4, 125.9, 125.8, 125.2, 124.2, 123.8, 123.5, 120.4, 116.64, 115.5.

HRMS (ESI): Calc. For C\(_{25}\)H\(_{18}\)NO [M+H]\(^+\): 348.1383; Found: 348.1490.

Synthesis of (Z)-N-(benzo[d][1,3]dioxol-5-yl)-3-phenyl-2\(H\)-chromen-2-imine (3h):

\[ \text{A obtain residue which was purified by column chromatography over} \]
\[ \text{silica gel using EtOAc/petroleum ether (5:95) to furnish the pure} \]
\[ \text{compound 3h 200 mg scale reaction (243 mg, 76 %) as yellow soli} \]
\[ \text{d; M.p.:103-104°C.} \]

IR (KBr) v/cm\(^{-1}\):1726, 1647, 1595, 1500, 1481, 1456, 1365, 1330,
1238, 1184, 1155, 1116, 1034.

\(^1\)H NMR (CDCl\(_3\), 400MHz) \(\delta\): 7.76 (dd, \(J = 5.2, 3.2\) Hz, 2H), 7.49 – 7.33 (m, 6H), 7.21 – 7.10
(m, 2H), 6.92 (s, 1H), 6.82 (d, \(J = 8.2\) Hz, 1H), 6.76 (dd, \(J = 8.2, 1.9\) Hz, 1H), 5.99 (s, 2H).

\(^1\)C NMR (CDCl\(_3\), 100MHz) \(\delta\): 152.9, 148.4, 147.4, 143.9, 140.5, 136.7, 132.9, 132.3, 130.1,
129.10, 128.5, 128.5, 128.3, 128.0, 127.3, 123.7, 120.4, 116.5, 115.3, 107.9, 104.6, 100.9.

HRMS (ESI): For C\(_{22}\)H\(_{16}\)NO\(_3\) [M+H]\(^+\):342.1125; Found: 342.1162.
Synthesis of (Z)-3-phenyl-N-(4-vinylphenyl)-2H-chromen-2-imine (3i):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (2:98) to furnish the pure compound 3i 200 mg scale reaction (229 mg, 78 %) as yellow solid; M.p.:112-123°C.

IR (KBr) ν/cm\(^{-1}\):1724, 1643, 1591, 1492, 1402, 1325, 1230, 1150, 1116, 1031.

\(^1\)H NMR (CDCl\(_3\), 400MHz) δ: 7.78 – 7.72 (m, 2H), 7.48 – 7.37 (m, 5H), 7.33 (ddd, \(J = 12.4, 6.9, 3.9\) Hz, 2H), 7.29 (s, 1H), 7.14 (ddd, \(J = 8.9, 8.5, 4.7\) Hz, 3H), 7.04 (d, \(J = 8.2\) Hz, 1H), 6.72 (dd, \(J = 17.6, 10.9\) Hz, 1H), 5.71 (d, \(J = 17.7\) Hz, 1H), 5.18 (d, \(J = 10.9\) Hz, 1H).

\(^13\)C NMR (CDCl\(_3\), 100MHz) δ: 152.9, 149.0, 146.3, 136.8, 136.6, 133.5, 133.1, 132.2, 130.3, 129.1, 128.5, 128.20, 127.4, 126.5, 126.3, 123.0, 120.4, 115.4, 112.2.

HRMS (ESI): Calc. For C\(_{23}\)H\(_{18}\)NO \([M+H]\)^+: 324.1383; Found: 324.1500.

Synthesis of (Z)-3-phenyl-N-(4-(trifluoromethoxy)phenyl)-2H-chromen-2-imine (3j):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (2:98) to furnish the pure compound 3j 200 mg scale reaction (253 mg, 73%) as yellow solid.

M.p.:110-111°C

IR (KBr) ν/cm\(^{-1}\):1737, 1645, 1595, 1500, 1458, 1366, 1259, 1197.

\(^1\)H NMR (CDCl\(_3\), 400MHz) δ: 7.75 – 7.71 (m, 1H), 7.45 – 7.33 (m, 3H), 7.32 (s, 1H), 7.18 – 7.12 (m, 3H), 7.05 (d, \(J = 8.2\) Hz, 1H).

\(^13\)C NMR (CDCl\(_3\), 100MHz) δ: 152.7, 149.0, 146.3, 136.8, 136.4, 134.0, 133.7, 131.9, 130.3, 129.1, 128.3, 128.1, 127.3, 123.6, 121.5, 121.2, 120.3, 115.62, 115.3.

HRMS (ESI): Calc. For C\(_{22}\)H\(_{15}\)F\(_3\)NO\(_2\) \([M+H]\)^+: 382.1049; Found: 382.1117.

Synthesis of (Z)-N-(3-methoxyphenyl)-3-phenyl-2H-chromen-2-imine (3k):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound 3k 200 mg scale reaction (200 mg, 68 %) as yellow solid; M.p.:110-111°C.
IR (KBr) ν/cm$^{-1}$: 2833, 1726, 1651, 1589, 1485, 1325, 1280, 1232, 1116, 1043.

$^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.83 – 7.76 (m, 2H), 7.50 – 7.35 (m, 5H), 7.33 (s, 1H), 7.31 – 7.27 (m, 1H), 7.16 (td, J = 7.5, 1.0 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 6.82 (ddd, J = 7.8, 1.7, 0.8 Hz, 1H), 6.78 – 6.75 (m, 1H), 6.70 (ddd, J = 8.2, 2.5, 0.8 Hz, 1H), 3.84 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100MHz) δ: 160.0, 152.9, 148.9, 147.8, 136.6, 133.4, 132.0, 130.1, 129.2, 129.0, 128.4, 128.1, 127.3, 123.7, 120.3, 115.4, 115.0, 109.6, 108.0, 55.2.

HRMS (ESI): Calc. For C$_{22}$H$_{18}$NO$_2$ [M+H]$^+$:328.1332; Found: 328.1415.

Synthesis of (Z)-3-phenyl-N-(3-(trifluoromethoxy)phenyl)-2H-chromen-2-imine (3l):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (2:98) to furnish the pure compound 3l 200 mg scale reaction (217 mg, 63%) as yellow solid.

M.p.:78-79°C.

IR (KBr) ν/cm$^{-1}$:1737, 1651, 1593, 1485, 1365, 1295, 1157.

$^1$H NMR (CDCl$_3$, 400MHz) δ: 7.79 (d, J = 7.0 Hz, 2H), 7.53 – 7.34 (m, 7H), 7.24 – 7.13 (m, 3H), 7.08 (d, J = 8.1 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz) δ: 152.6, 149.8, 149.5, 148.1, 136.3, 134.0, 131.8, 130.4, 129.5, 129.0, 128.5, 128.1, 127.5, 124.0, 121.4, 120.31, 115.9, 115.5, 115.3.

HRMS (ESI): Calc. For C$_{22}$H$_{15}$F$_3$NO$_2$ [M+H]$^+$: 382.1049; Found: 382.1051.

Synthesis of ethyl (Z)-4-((3-phenyl-2H-chromen-2-ylidene)amino)benzoate (3m):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound 3m 200 mg scale reaction (236 mg, 71 %) as yellow solid; M.p.:125-126°C.

IR (KBr) ν/cm$^{-1}$:2980, 1708, 1647, 1589, 1456, 1365, 1274, 1168, 1099, 1016.

$^1$H NMR (CDCl$_3$, 400 MHz) δ: 8.06 (d, J = 8.4 Hz, 2H), 7.80 – 7.75 (m, 2H), 7.50 – 7.34 (m, 6H), 7.22 – 7.15 (m, 3H), 7.03 (d, J = 8.2 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100MHz) δ: 166.7, 152.7, 151.4, 136.3, 134.1, 131.7, 130.46, 130.3, 129.0, 128.6, 128.2, 127.4, 125.4, 123.9, 122.1, 120.2, 115.4, 60.6, 14.4.

HRMS (ESI): Calc. For C$_{24}$H$_{20}$NO$_3$ [M+H]$^+$:370.1438; Found: 370.1563.
Synthesis of (Z)-3-phenyl-\(\text{N}-(4\text{-(trifluoromethyl)phenyl})\)-2\(\text{H}\)-chromen-2-imine (3n):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3n.

200 mg scale reaction (213 mg, 64%) as yellow solid.

\text{M.p.:} 101-102^\circ\text{C}.

\text{IR (KBr) v/cm}^{-1}:1651, 1595, 1456, 1323, 1226, 1116.

\text{^1H NMR (CDCl}_3, \text{ 400MHz}) \delta: 7.73 (d, J = 6.9 \text{ Hz, 2H}), 7.57 (d, J = 8.3 \text{ Hz, 2H}), 7.47 – 7.30 (m, 6H), 7.17 (dd, J = 16.3, 8.1 \text{ Hz, 3H}), 7.02 (d, J = 8.2 \text{ Hz, 1H}).

\text{^13C NMR (CDCl}_3, \text{ 100MHz}) \delta: 152.7, 150.2, 149.9, 136.3, 134.2, 131.7, 130.5, 129.0, 128.6, 128.2, 127.5, 125.8, 125.8, 124.1, 122.51, 120.3, 115.4.

\text{HRMS (ESI)}: \text{Calc. For C}_{22}\text{H}_15\text{F}_3\text{NO} [\text{M+H}]^+: 366.1100; \text{Found: 366.1101}.

Synthesis of (Z)-3-phenyl-\(\text{N}-(2\text{-(trifluoromethyl)phenyl})\)-2\(\text{H}\)-chromen-2-imine (3o):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3o.

200 mg scale reaction (183 mg, 55%) as yellow solid.

\text{M.p.:} 103-104^\circ\text{C}.

\text{IR (KBr) v/cm}^{-1}:1753, 1643, 1323, 1217, 1116.

\text{^1H NMR (CDCl}_3, \text{ 400MHz}) \delta: 7.80 – 7.73 (m, 1H), 7.64 (d, J = 7.7 \text{ Hz, 1H}), 7.50 – 7.35 (m, 3H), 7.34 – 7.28 (m, 1H), 7.14 (dt, J = 13.5, 3.9 \text{ Hz, 1H}), 7.07 (d, J = 8.0 \text{ Hz, 1H}), 6.96 (d, J = 8.2 \text{ Hz, 1H}).

\text{^13C NMR (CDCl}_3, \text{ 100MHz}) \delta: 152.8, 150.1, 145.8, 136.2, 134.2, 132.1, 131.8, 130.4, 129.1, 128.6, 128.2, 127.5, 126.3, 126.2, 124.0, 122.8, 120.2, 115.4.

\text{HRMS (ESI)}: \text{Calc. For C}_{22}\text{H}_15\text{F}_3\text{NO} [\text{M+H}]^+: 366.1100; \text{Found: 366.1107}.

Synthesis of (Z)-\text{N}-(4\text{-nitrophenyl})\text{-3-phenyl-2H-chromen-2-imine (3p)}:

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (2:98) to furnish the pure compound 3p.

200 mg scale reaction (130 mg, 42 %) as yellow solid.

\text{M.p.:} 164-165^\circ\text{C}.

\text{IR (KBr) v/cm}^{-1}:1724, 1647, 1577, 1508, 1454, 1336, 1261, 1224, 1157, 1109.
**Synthesis of (Z)-4-((3-phenyl-2H-chromen-2-ylidene)amino)benzonitrile (3q):**

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (2:98) to furnish the pure compound 3q 200 mg scale reaction (215 mg, 74%) as yellow solid.

**M.p.:** 120-121°C.

**IR (KBr) ν/cm⁻¹:** 2222, 1726, 1645, 1587, 1492, 1327, 1228, 1168, 1116, 1076.

**¹H NMR (CDCl₃, 400MHz) δ:** 7.74 – 7.70 (m, 2H), 7.65 – 7.60 (m, 2H), 7.56 – 7.51 (m, 6H), 7.19 (ddd, J = 8.7, 7.1, 1.5 Hz, 3H), 7.03 (d, J = 8.2 Hz, 1H).

**¹³C NMR (CDCl₃, 100MHz) δ:** 152.5, 151.4, 150.1, 136.0, 134.6, 132.8, 130.6, 128.9, 128.7, 128.5, 128.2, 127.6, 124.24, 123.1, 120.2, 115.4.

**HRMS (ESI):** Calc. For C₂₂H₁₅N₂O [M+H]⁺: 323.1179; Found: 323.1196.

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**Synthesis of (Z)-N-([1,1′-biphenyl]-4-yl)-3-phenyl-2H-chromen-2-imine (3r):**

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (2:98) to furnish the pure compound 3r 200 mg scale reaction (391 mg, 73%) as yellow solid.

**M.p.:** 109-110°C.

**IR (KBr) ν/cm⁻¹:** 1734, 1651, 1591, 1483, 1365, 1261, 1155, 1116, 1055.

**¹H NMR (CDCl₃, 400MHz) δ:** 7.82 (d, J = 7.1 Hz, 2H), 7.66 (dd, J = 16.4, 7.8 Hz, 4H), 7.53 – 7.31 (m, 11H), 7.22 – 7.09 (m, 2H).

**¹³C NMR (CDCl₃, 100MHz) δ:** 152.9, 145.8, 141.1, 136.66, 136.4, 133.4, 132.2, 130.2, 129.1, 128.7, 128.4, 128.1, 127.4, 127.2, 126.8, 126.8, 123.7, 123.27, 120.4, 115.4.

**HRMS (ESI):** Calc. For C₂₇H₂₀NO [M+H]⁺: 374.1539; Found: 374.1638.
Synthesis of (Z)-3-phenyl-N-(pyren-1-yl)-2H-chromen-2-imine (3s):

A obtain residue which was purified by column chromatography over silica using EtOAc/petroleum ether (5:95) to furnish the pure compound 3s 200 mg scale reaction (281 mg, 73 %) as orange solid.

**M.p.**: 140-141°C.

**IR (KBr) v/cm⁻¹**: 1735, 1645, 1587, 1485, 1365, 1230, 1141, 1116, 1058.

**¹H NMR (CDCl₃, 400MHz) δ**: 8.15 (d, J = 9.1 Hz, 1H), 8.07 – 7.76 (m, 11H), 7.36 (dt, J = 29.9, 7.2 Hz, 3H), 7.23 (d, J = 7.4 Hz, 1H), 7.11 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H).

**¹³C NMR (CDCl₃, 100MHz) δ**: 152.9, 141.4, 136.8, 133.8, 132.3, 131.6, 131.5, 130.3, 129.2, 128.5, 128.2, 127.8, 127.4, 127.4, 126.4, 125.8, 125.7, 125.6, 125.1, 125.1, 124.4, 124.3, 123.9, 123.8, 123.8, 120.4, 119.6, 115.4.

**HRMS (ESI)**: Calc. For C₃₁H₂₀N₂O [M+H]⁺: 422.1539; Found: 422.1541.

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Synthesis of (Z)-3-phenyl-N-(pyridin-3-yl)-2H-chromen-2-imine (3t):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (20:80) to furnish the pure compound 3t 200 mg scale reaction (198 mg, 73%) as yellow solid.

**M.p.**: 104-105°C.

**IR (KBr) v/cm⁻¹**: 1735, 1653, 1598, 1456, 1363, 1228, 1143.

**¹H NMR (CDCl₃, 400MHz) δ**: 8.50 (d, J = 2.4 Hz, 1H), 8.32 (dd, J = 4.7, 1.5 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.54 – 7.31 (m, 7H), 7.26 (dd, J = 6.4, 1.8 Hz, 1H), 7.16 (td, J = 7.5, 1.0 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H).

**¹³C NMR (CDCl₃, 100MHz) δ**: 152.6, 141.4, 136.8, 133.8, 132.3, 131.6, 131.5, 130.3, 129.2, 128.5, 128.2, 127.8, 127.4, 127.4, 126.4, 125.8, 125.7, 125.6, 125.1, 125.1, 124.4, 124.3, 123.9, 123.8, 123.8, 120.4, 119.6, 115.4.

**HRMS (ESI)**: Calc. For C₂₀H₁₅N₂O [M+H]⁺: 299.1179; Found: 299.1181.

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Synthesis of (Z)-N-((E)-4-fluorostyryl)-3-phenyl-2H-chromen-2-imine (3u):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound 3u 200 mg scale reaction (235 mg, 76%) as pale orange solid.

**M.p.**: 158-159°C.
IR (KBr) ν/cm$^{-1}$: 1739, 1641, 1558, 1506, 1454, 1365, 1228, 1157, 1116.; $^1$H NMR (CDCl$_3$, 400MHz) δ 8.10 (d, $J = 13.6$ Hz, 1H), 7.78 – 7.69 (m, 2H), 7.55 – 7.33 (m, 7H), 7.28 (s, 1H), 7.19 (dd, $J = 10.8$, 4.2 Hz, 2H), 7.05 (t, $J = 8.7$ Hz, 2H), 6.71 (d, $J = 13.6$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz) δ: 162.0 (C-F) 153.2, 149.9, 136.4, 133.6, 133.5, 132.8, 132.2, 130.9, 130.9, 130.1, 129.2, 128.4, 128.0, 127.9, 127.8, 127.5, 127.1, 123.8, 120.8, 115.64, 115.4, 115.1.

HRMS (ESI): Calc. For C$_{23}$H$_{17}$FNO [M+H]$^+$: 342.1289; Found: 342.1298.

Synthesis of (Z)-3-phenyl-N-((E)-styryl)-2H-chromen-2-imine (3v):

A residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3v 200 mg scale reaction (221 mg, 72 %) as yellow solid.

M.p.: 112-113°C.

IR (KBr) ν/cm$^{-1}$: 1735, 1670, 1627, 1560, 1436, 1365, 1217, 1141, 1033.; $^1$H NMR (CDCl$_3$, 400MHz) δ 8.18 (d, $J = 13.6$ Hz, 1H), 7.78 – 7.70 (m, 2H), 7.62 – 7.33 (m, 10H), 7.31 – 7.22 (m, 2H), 7.18 (s, 1H), 6.75 (d, $J = 13.6$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz) δ: 153.3, 149.9, 139.8, 137.4, 136.4, 132.7, 132.3, 131.4, 131.1, 130.1, 129.1, 128.8, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.4, 127.0, 126.4, 124.5, 123.8, 120.8, 116.5, 115.1.

HRMS (ESI): Calc. For C$_{23}$H$_{18}$FNO [M+H]$^+$: 324.1383; Found: 324.1420.

Synthesis of (Z)-N-phenyl-3-(3-(trifluoromethyl)phenyl)-2H-chromen-2-imine (3w):

A residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound 3w 200 mg scale reaction (252 mg, 94 %) as yellow solid; M.p.: 110-111°C.

IR (KBr) ν/cm$^{-1}$: 1739, 1645, 1587, 1485, 1336, 1230, 1155, 1074.

$^1$H NMR (CDCl$_3$, 400MHz) δ: 8.05 – 7.97 (m, 2H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.37 (dd, $J = 14.0$, 7.9 Hz, 5H), 7.25 – 7.11 (m, 4H), 7.07 (d, $J = 8.1$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz) δ: 153.1, 149.4, 146.1, 137.4, 134.1, 132.7, 130.9, 130.8, 128.7, 128.5, 127.6, 126.0, 126.0, 125.2, 125.1, 124.0, 124.0, 122.8, 120.1, 115.6.

HRMS (ESI): Calc. For C$_{22}$H$_{15}$F$_3$NO [M+H]$^+$: 366.1100; Found: 366.1100.
Synthesis of (Z)-3-(4-nitrophenyl)-N-phenyl-2H-chromen-2-imine (3x):

A obtain residue which was purified by column chromatography over silica gel (using EtOAc/petroleum ether (5:95) to furnish the pure compound 3x 200 mg scale reaction (210 mg, 82%) as yellow solid.

**M.p.:** 160-162°C.

**IR (KBr) v/cm⁻¹:** 1739, 1647, 1604, 1581, 1521, 1340, 1217, 1130.

**¹H NMR (CDCl₃, 400 MHz) δ:** 8.27 (d, J = 8.7 Hz, 2H), 7.94 (d, J = 8.7 Hz, 2H), 7.43 – 7.34 (m, 5H), 7.24 – 7.11 (m, 4H), 7.07 (d, J = 8.3 Hz, 1H).

**¹³C NMR (CDCl₃, 100MHz) δ:** 153.1, 147.6, 145.9, 143.3, 134.9, 131.2, 130.1, 128.7, 127.9, 124.1, 124.1, 123.3, 122.7, 119.8, 115.6.

**HRMS (ESI):** Calc. For C₂₁H₁₅N₂O₃ [M+H]⁺: 343.1077; Found: 343.1083.

Synthesis of (Z)-3-(4-chlorophenyl)-N-phenyl-2H-chromen-2-imine (3y):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound 3y 200 mg scale reaction (209 mg, 81%) as yellow solid; **M.p.:** 107-108°C.

**IR (KBr) v/cm⁻¹:** 1737, 1643, 1587, 1485, 1366, 1230, 1139, 823.

**¹H NMR (CDCl₃, 400MHz) δ:** 7.72 (d, J = 8.5 Hz, 2H), 7.37 (dt, J = 17.1, 8.9 Hz, 6H), 7.28 (s, 1H), 7.15 (ddd, J = 14.7, 12.1, 7.5 Hz, 4H), 7.04 (d, J = 8.1 Hz, 1H).

**¹³C NMR (CDCl₃, 100MHz) δ:** 153.0, 148.6, 146.4, 135.1, 134.4, 133.5, 131.0, 130.5, 128.7, 128.4, 127.5, 123.9, 123.8, 122.7, 120.2, 115.5.

**HRMS (ESI):** Calc. For C₂₁H₁₅ClNO [M+H]⁺: 332.0837; Found: 332.0847.

Synthesis of (Z)-3-(2-fluorophenyl)-N-phenyl-2H-chromen-2-imine (3z):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (1:99) to furnish the pure compound 3z 200 mg scale reaction (203 mg, 77%) as brown solid. **M.p.:** 105-106°C.

**IR (KBr) v/cm⁻¹:** 1801, 1651, 1062, 1589, 1485, 1371, 1267, 1205, 1159, 1118, 1072.
**1H NMR (CDCl₃, 400MHz)** \(\delta\): 7.62 (td, \(J = 7.4, 1.4\) Hz, 1H), 7.43 – 7.31 (m, 6H), 7.27 – 7.03 (m, 7H).

**13C NMR (CDCl₃, 100MHz)** \(\delta\): 160.15(C-F), 158.9, 153.1, 148.2, 146.4, 135.2, 131.4, 131.4, 130.5, 130.0, 129.9, 128.5, 127.4, 127.2, 124.6, 124.4, 123.8, 123.8, 123.7, 123.6, 122.5, 119.9, 115.9, 115.7, 115.5.

**HRMS (ESI)**: Calc. For C₂₁H₁₅FNO \([M+H]^+\):316.1132; Found: 316.1169.

**Synthesis of (Z)-2-(phenylimino)-2H-chromene-3-carbonitrile (3aa):**

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound **3aa** 200 mg scale reaction (263 mg, 91%) as yellow solid.

**M.p.**: 128-129°C.

**IR (KBr)** \(\nu/cm\): 2231, 1647, 1604, 1589, 1566, 1485, 1375, 1219, 1193, 1055.

**1H NMR (CDCl₃, 400MHz)** \(\delta\): 7.89 (s, 1H), 7.59 (t, \(J = 7.8\) Hz, 1H), 7.49 (t, \(J = 8.6\) Hz, 3H), 7.41 – 7.27 (m, 4H), 7.19 (d, \(J = 8.3\) Hz, 1H).

**13C NMR (CDCl₃, 100MHz)** \(\delta\): 153.6, 144.7, 144.68, 144.5, 134.0, 128.8, 128.8, 125.0, 124.8, 123.1, 117.7, 116.4, 114.7, 107.4.

**HRMS (ESI)**: Calc. For C₁₆H₁₁N₂O \([M+H]^+\):247.0866; Found: 247.0877.

**Synthesis of (Z)-6,8-di-tert-butyl-2-(phenylimino)-2H-chromene-3-carbonitrile (3ab):**

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound **3ab** 200 mg scale reaction (200 mg, 79%) as yellow solid;

**M.p.**: 176-177°C.

**IR (KBr)** \(\nu/cm\): 2233, 1654, 1577, 1487, 1363, 1244, 1201, 1126, 1066.

**1H NMR (CDCl₃, 400MHz)** \(\delta\): 7.82 (s, 1H), 7.48 (d, \(J = 2.4\) Hz, 1H), 7.38 – 7.30 (m, 2H), 7.18 (d, \(J = 2.3\) Hz, 1H), 7.14 – 7.06 (m, 1H), 7.01 – 6.94 (m, 2H), 1.31 (s, 9H), 1.04 (s, 9H).

**13C NMR (CDCl₃, 100MHz)** \(\delta\): 150.5, 147.0, 146.6, 146.6, 146.0, 137.4, 129.5, 128.8, 123.8, 123.6, 121.1, 117.3, 114.8, 105.1, 34.6, 34.5, 31.2, 29.2.

**HRMS (ESI)**: Calc. For C₂₄H₂₇N₂O \([M+H]^+\): 359.2118; Found: 359.2168.
Synthesis of (Z)-7-(diethylamino)-2-(phenylimino)-2H-chromene-3-carbonitrile (3ac):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (5:95) to furnish the pure compound 3ac 200 mg scale reaction (284 mg, 86 %) as brown solid; M.p.:138-139°C.

IR (KBr) v/cm⁻¹:2974, 2220, 1724, 1598, 1487, 1354, 1276, 1193, 1076.;¹H NMR (CDCl₃,400 MHz) δ 7.63 (s, 1H), 7.43 – 7.36 (m, 2H), 7.27 – 7.22 (m, 2H), 7.19 – 7.12 (m, 2H), 6.48 (dd, J = 8.9, 2.5 Hz, 1H), 6.20 (d, J = 2.3 Hz, 1H), 3.41 (q, J = 7.1 Hz, 4H), 1.21 (t, J = 7.1 Hz, 6H).

¹³C NMR (CDCl₃,100MHz) δ: 156.3, 152.3, 145.5, 144.6, 129.9, 128.6, 123.9, 122.9, 108.4, 106.8, 97.1, 44.8, 12.5.


Synthesis of (Z)-7-methoxy-2-(phenylimino)-2H-chromene-3-carbonitrile (3ad):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (10:90) to furnish the pure compound 3ad 200 mg scale reaction (223mg, 81%) as brown solid; M.p.:205-506°C.

IR (KBr) v/cm⁻¹:3076, 2227, 1734, 1653, 1602, 1552, 1552, 1440, 1367, 1350, 1274, 1201, 1165, 1026.

¹H NMR (CDCl₃,400MHz) δ: 7.75 (s, 1H), 7.44 – 7.37 (m, 2H), 7.29 (d, J = 5.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.15 (m, 1H), 6.79 (dd, J = 8.6, 2.4 Hz, 1H), 6.59 (d, J = 2.3 Hz, 1H), 3.86 (s, 3H).

¹³C NMR (CDCl₃,100MHz) δ: 164.6, 155.5, 144.8, 144.5, 135.6, 129.7, 128.7, 128.0, 124.6, 122.9, 112.5, 111.2, 103.3, 100.9, 56.0.


Synthesis of (Z)-6-chloro-2-(phenylimino)-2H-chromene-3-carbonitrile (3ae):

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (2:98) to furnish the pure compound 3ae 200 mg scale reaction (329 mg, 80%) as brown solid; M.p.:105-106°C.

IR (KBr) v/cm⁻¹:2341, 1735, 1649, 1589, 1477, 1365, 1217, 1055.
**1H NMR (CDCl₃, 400MHz)** δ: 7.87 – 7.79 (m, 1H), 7.60 – 7.44 (m, 4H), 7.43 – 7.27 (m, 3H), 7.24 – 7.10 (m, 1H).

**13C NMR (CDCl₃, 100MHz)** δ: 152.0, 144.1, 143.2, 133.6, 130.0, 128.8, 127.9, 125.3, 123.1, 118.7, 117.8, 114.3, 108.7.


**Synthesis of (Z)-N,N-diethyl-3-(4-nitrophenyl)-2-(phenylimino)-2H-chromen-7-amine (3af):**

A obtain residue which was purified by column chromatography over silica gel using EtOAc/petroleum ether (10:90) to furnish the pure compound 3af 200 mg scale reaction (207 mg, 84%) as red solid.

**M.p.:** 161-162°C.

**IR (KBr) v/cm⁻¹:** 1749, 1647, 1581, 1521, 1373, 1217, 1130.

**1H NMR (CDCl₃, 400 MHz)** δ: 8.25 – 8.20 (m, 2H), 7.98 – 7.91 (m, 2H), 7.35 (dd, J = 8.1, 7.5 Hz, 2H), 7.30 (s, 1H), 7.20 – 7.14 (m, 2H), 7.13 – 7.06 (m, 1H), 6.46 (dd, J = 8.7, 2.5 Hz, 1H), 6.22 (d, J = 2.4 Hz, 1H), 3.36 (d, J = 7.1 Hz, 4H), 1.17 (t, J = 7.1 Hz, 6H).

**13C (CDCl₃, 100MHz)** δ: 155.4, 150.5, 149.0, 146.7, 146.7, 144.4, 135.9, 129.7, 128.9, 128.7, 123.3, 123.3, 122.8, 122.7, 108.8, 108.0, 96.9, 44.6, 12.6.

**HRMS (ESI)**: Calc. For C₂₅H₂₄N₃O₃ [M+H]^+: 414.1812; Found: 414.1891.

**One pot procedure:**

**Synthesis of (Z)-2-(phenylimino)-2H-chromene-3-carbonitrile (4aa):**

To a round bottomed flask equipped with stir bar was added salicylaldehyde (200 mg, 1.63 mmol), malonitrile (108 mg, 1.63 mmol) and DABCO (10 mol %) under the nitrogen atmosphere at room temperature for 1 hr. After the complete consumption of salicylaldehyde as monitored by TLC, Cu(OAc)₂.H₂O (20 mol %), phenylboronic acid (457 mg, 2.3 mmol) were added to the reaction mixture and stirred for 24 h at temperature in open flask conditions. After
completion of the reaction, the organic phase was concentrated under reduced pressure and the solid residue was fractioned in ethyl acetate (20 mL) and water (10 mL) thrice. The combined organic phases were dried on anhydrous Na$_2$SO$_4$ and solvent was removed in vacuum. The crude residue upon purification by column chromatography with ethyl acetate/petroleum ether (5:95) furnished the pure compound 4aa (360 mg, 89 %) as yellow solid.

M.p.: 128-129°C.

$^1$H NMR (CDCl$_3$, 400MHz) $\delta$: 7.88 (s, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.48 (t, J = 8.0 Hz, 3H), 7.40 – 7.26 (m, 4H), 7.18 (d, J = 8.3 Hz, 1H).

$^{13}$C (CDCl$_3$, 100MHz) $\delta$: 153.6, 144.7, 144.6, 144.5, 134.0, 128.8, 128.7, 124.9, 124.8, 123.1, 117.6, 116.3, 114.7, 107.3.

Crystal Structure Parameters.

Crystal structure of (Z)-3-phenyl-N-(3-(trifluoromethoxy)phenyl)-2$H$-chromen-2-imine:-

<table>
<thead>
<tr>
<th>Table 1. Crystal data and structure refinement for PM-01-027.</th>
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<tbody>
<tr>
<td>Identification code</td>
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<td>Empirical formula</td>
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<td>Unit cell dimensions</td>
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<td>Volume</td>
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<td>Theta range for data collection</td>
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<td>Index ranges</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Completeness to theta = 67.722°</td>
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<tr>
<td>Absorption correction</td>
</tr>
</tbody>
</table>
Max. and min. transmission 0.865 and 0.793
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 3127 / 0 / 253
Goodness-of-fit on F^2 1.034
Final R indices [I>2sigma(I)] R1 = 0.0295, wR2 = 0.1087
R indices (all data) R1 = 0.0335, wR2 = 0.1152
Extinction coefficient n/a
Largest diff. peak and hole 0.231 and -0.155 e.Å^-3
MALDI-ESI mass spectra (TiO$_2$ as the matrix) of Cu(OAc)$_2$. H$_2$O and 3-Phenyliminochromene stirred at room temperature in ethanol solvent for 24h.
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3-phenyl-2H-chromen-2-imine (1a)
3-(3-(trifluoromethyl)phenyl)-2H-chromen-2-imine (1b)
3-(4-nitrophenyl)-2H-chromen-2-imine (1c)
3-(2-fluorophenyl)-2H-chromen-2-imine (1e)
6,8-di-tert-butyl-2-imino-2$H$-chromene-3-carbonitrile (1g)
N,N-diethyl-2-imino-3-(4-nitrophenyl)-2H-chromen-7-amine (1k)
(Z)-N, 3-diphenyl-2H-chromen-2-imine (3a)
(Z)-N-(4-bromophenyl)-3-phenyl-2H-chromen-2-imine (3b)
(Z)-N-(4-chlorophenyl)-3-phenyl-2H-chromen-2-imine (3c)
(Z)-N-(4-fluorophenyl)-3-phenyl-2H-chromen-2-imine (3d)
(Z)-3-phenyl-N-(m-tolyl)-2H-chromen-2-imine (3e)
(Z)-N-(naphthalen-2-yl)-3-phenyl-2H-chromen-2-imine (3f)
(Z)-N-(naphthalen-1-yl)-3-phenyl-2H-chromen-2-imine (3g)
(Z)-N-(benzo[d][1,3]dioxol-5-yl)-3-phenyl-2H-chromen-2-imine (3h)
(Z)-3-phenyl-N-(4-vinylphenyl)-2H-chromen-2-imine (3i)
(Z)-3-phenyl-N-(4-(trifluoromethoxy)phenyl)-2H-chromen-2-imine (3j)
(Z)-N-(3-methoxyphenyl)-3-phenyl-2H-chromen-2-imine (3k)
(Z)-3-phenyl-N-(3-(trifluoromethoxy)phenyl)-2H-chromen-2-imine (3l)
ethyl (Z)-4-((3-phenyl-2H-chromen-2-ylidene)amino)benzoate (3m)
(Z)-3-phenyl-N-(4-(trifluoromethyl)phenyl)-2H-chromen-2-imine (3n)
(Z)-3-phenyl-N-(2-(trifluoromethyl)phenyl)-2H-chromen-2-imine (3o)
(Z)-\(N\)-(4-nitrophenyl)-3-phenyl-2\(H\)-chromen-2-imine (3p)
(Z)-4-((3-phenyl-2H-chromen-2-ylidene)amino)benzonitrile (3q)
(Z)-N-([1,1'-biphenyl]-4-yl)-3-phenyl-2H-chromen-2-imine (3r)
(Z)-3-phenyl-N-(pyren-1-yl)-2H-chromen-2-imine (3s)
(Z)-3-phenyl-N-(pyridin-3-yl)-2H-chromen-2-imine (3t)
(Z)-N-((E)-4-fluorostyryl)-3-phenyl-2H-chromen-2-imine (3u)
(Z)-3-phenyl-N-((E)-styryl)-2H-chromen-2-imine (3v)
(Z)-N-phenyl-3-(3-(trifluoromethyl)phenyl)-2H-chromen-2-imine (3w)
(Z)-3-(4-nitrophenyl)-N-phenyl-2H-chromen-2-imine (3x)
(Z)-3-(4-chlorophenyl)-N-phenyl-2H-chromen-2-imine (3y)
(Z)-3-(2-fluorophenyl)-N-phenyl-2H-chromen-2-imine (3z)
(Z)-2-(phenylimino)-2H-chromene-3-carbonitrile (3aa)
(Z)-6,8-di-tert-butyl-2-(phenylimino)-2H-chromene-3-carbonitrile (3ab)
(Z)-7-(diethylamino)-2-(phenylimino)-2H-chromene-3-carbonitrile (3ac)
(Z)-7-methoxy-2-(phenylimino)-2H-chromene-3-carbonitrile (3ad)
(Z)-6-chloro-2-(phenylimino)-2H-chromene-3-carbonitrile (3ae)
(Z)-N,N-diethyl-3-(4-nitrophenyl)-2-(phenylimino)-2H-chromen-7-amine (3af)
(Z)-2-(phenylimino)-2H-chromene-3-carbonitrile (4aa):
3-(3-(trifluoromethyl)phenyl)-2H-chromen-2-imine (1b)

3-(2-fluorophenyl)-2H-chromen-2-imine (1e)
(Z)-N, 3-diphenyl-2H-chromen-2-imine (3a)

(Z)-N-(4-bromophenyl)-3-phenyl-2H-chromen-2-imine (3b)
(Z)-N-(4-chlorophenyl)-3-phenyl-2H-chromen-2-imine (3c):

(Z)-N-(4-fluorophenyl)-3-phenyl-2H-chromen-2-imine (3d)
(Z)-3-phenyl-N-(m-tolyl)-2H-chromen-2-imine (3e)

(Z)-N-(naphthalen-2-yl)-3-phenyl-2H-chromen-2-imine (3f)
(Z)-N-(naphthalen-1-yl)-3-phenyl-2H-chromen-2-imine (3g):

(Z)-N-(benzo[d][1,3]dioxol-5-yl)-3-phenyl-2H-chromen-2-imine (3h):
(Z)-3-phenyl-N-(4-vinylphenyl)-2H-chromen-2-imine (3i)

(Z)-3-phenyl-N-(4-(trifluoromethoxy)phenyl)-2H-chromen-2-imine (3j)
(Z)-N-(3-methoxyphenyl)-3-phenyl-2H-chromen-2-imine (3k)

(Z)-3-phenyl-N-(3-(trifluoromethoxy)phenyl)-2H-chromen-2-imine (3l)
(Z)-4-((3-phenyl-2H-chromen-2-ylidene)amino)benzoate (3m)

(Z)-3-phenyl-N-(4-(trifluoromethyl)phenyl)-2H-chromen-2-imine (3n)
(Z)-3-phenyl-N-(2-(trifluoromethyl)phenyl)-2H-chromen-2-imine (3o)

(Z)-N-(4-nitrophenyl)-3-phenyl-2H-chromen-2-imine (3p)
(Z)-4-((3-phenyl-2H-chromen-2-ylidene)amino)benzonitrile (3q)

(Z)-N-([1,1’-biphenyl]-4-yl)-3-phenyl-2H-chromen-2-imine (3r)
(Z)-3-phenyl-N-(pyren-1-yl)-2H-chromen-2-imine (3s)

(Z)-3-phenyl-N-(pyridin-3-yl)-2H-chromen-2-imine (3t)
\[(Z)-N-N-((E)-4\text{-fluorostyryl})-3\text{-phenyl-}2H\text{-chromen-2-imine (3u)}\]

\[(Z)-3\text{-phenyl-N-}((E)\text{-styryl})-2H\text{-chromen-2-imine (3v)}\]
(Z)-N-phenyl-3-(3-(trifluoromethyl)phenyl)-2H-chromen-2-imine (3w)

(Z)-3-(4-nitrophenyl)-N-phenyl-2H-chromen-2-imine (3x)
(Z)-3-(4-chlorophenyl)-N-phenyl-2H-chromen-2-imine (3y)

(Z)-3-(2-fluorophenyl)-N-phenyl-2H-chromen-2-imine (3z)
(Z)-2-(phenylimino)-2H-chromene-3-carbonitrile (3aa)

(Z)-6,8-di-tert-butyl-2-(phenylimino)-2H-chromene-3-carbonitrile (3ab)
(Z)-7-(diethylamino)-2-(phenylimino)-2H-chromene-3-carbonitrile (3ac)

(Z)-7-methoxy-2-(phenylimino)-2H-chromene-3-carbonitrile (3ad)
(Z)-6-chloro-2-(phenylimino)-2H-chromene-3-carbonitrile (3ae)

(Z)-N,N-diethyl-3-(4-nitrophenyl)-2-(phenylimino)-2H-chromen-7-amine (3af)
References: