Supporting Information
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Supporting Information

For

Carbonylative Synthesis of Thiochromenones via Palladium-Catalyzed tert-Butyl Isocyanide Insertion

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1. General Information:

Reactants and reagents were purchased from commercial suppliers and used without special instructions. All solvents were dried and freshly distilled. TLC was performed on silica HSGF254 plates. Melting points were determined with a digital melting-point apparatus. $^1$H and $^{13}$C NMR spectra were obtained from a solution in CDCl$_3$ with TMS as internal standard using a 400/101 MHz ($^1$H/$^{13}$C) spectrometer. High-resolution mass spectra (HRMS) analyses were carried out on a chemical ionization (CI) apparatus using time-of-flight (TOF) mass spectrometry. Infrared (IR) data were obtained using KBr tablets, and wave numbers are reported in cm$^{-1}$.

2. Condition Optimization and General Procedure for the Synthesis of Thiochromenones.

Condition Optimization

In our preliminary investigation, 1-bromo-2-fluorobenzene (1a) and phenylacetylene (2a) reacted with tert-butyl isocyanide utilizing Pd(OAc)$_2$ and DPEPhos as the catalysts in dimethyl sulfoxide (DMSO) at 100 °C for 2 h under argon. Subsequently, the Na$_2$S$\cdot$9H$_2$O was added in the same system for 2 h, followed by hydrochloric acid hydrolysis for 8 h. To our delight, the desired product 2-phenyl-4H-thiochromen-4-one (3a) was produced in 28% yield (Table 1, entry 1). Solvent screening revealed that DMF appeared as the optimal solvent (Table 1, entries 2 and 3). Higher temperature gave a lower yield (Table 1, entry 4); nevertheless, because of the side reaction of phenylacetylene, 1-bromo-2-fluorobenzene could not be converted totally. Fortunately, side reaction of phenylacetylene was controlled by reducing the amount of phenylacetylene (Table 1, entries 5-9). Then, the amount of base for the activity of the reaction was examined. To our delight, the yield was improved to 74% when decreasing the amount of Cs$_2$CO$_3$ to 0.8 equiv (Table 1, entries 10-14). In comparison with Na$_2$S$\cdot$9H$_2$O, other sulfur sources such as K$_2$S and NaHS resulted in diminished yields.
Further extension of the reaction temperature for Na$_2$S$\cdot$9H$_2$O exhibited that lower temperature led to a better yield (Table 1, entry 17). As hydrolysis step, oxalic acid resulted in a better yield in comparison to hydrochloric acid (Table 1, entry 18). Other palladium catalysts were tested to improve the yield further. However, none of them were found to compete with Pd(OAc)$_2$ (Table 1, entries 19-22). After many trials with other commercially available bidentate and monodentate ligands (Table 1, entries 23-25), DPEPhos gave the best yield of thiochromone. Several other commonly applied inorganic and organic bases were not able to achieve higher yields than Cs$_2$CO$_3$ (Table 1, entries 26-27). Further screening of reaction temperature showed temperature lower than the proposed reaction temperature (100°C) resulted in diminished yields (Table 1, entries 28-30). Therefore, using Pd(OAc)$_2$ and DPEPhos as the catalyst system, Cs$_2$CO$_3$ (0.8 equiv) as base, Na$_2$S$\cdot$9H$_2$O as sulfur source in DMF at 100 °C was selected as the optimal reaction condition. Then, oxalic acid hydrolysis could make the generation of thiochromone-4-one (3a) in high yield (Table 1, entry 18).

**Table 1.** Condition Optimization

<table>
<thead>
<tr>
<th>Entry</th>
<th>2a (equiv)</th>
<th>Base (equiv)</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Ligand</th>
<th>T (°C)</th>
<th>Yield (%)</th>
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<td>Pd(OAc)$_2$</td>
<td>DPEPhos</td>
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<tr>
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<td>Pd(OAc)$_2$</td>
<td>DPEPhos</td>
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<td>32</td>
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<tr>
<td>6</td>
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<td>Pd(OAc)$_2$</td>
<td>DPEPhos</td>
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<td>Cs$_2$CO$_3$ (1.5)</td>
<td>DMF</td>
<td>Pd(OAc)$_2$</td>
<td>DPEPhos</td>
<td>100</td>
<td>54</td>
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11 0.8 Cs₂CO₃ (1.2) DMF Pd(OAc)₂ DPEPhos 100 60
12 0.8 Cs₂CO₃ (1.0) DMF Pd(OAc)₂ DPEPhos 100 63
13 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 100 74
14 0.8 Cs₂CO₃ (0.6) DMF Pd(OAc)₂ DPEPhos 100 65
15 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 100 Traceᵇ
16 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 100 65ᶜ
17 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 100 70ᵈ
18 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 100 82ᵃ
19 0.8 Cs₂CO₃ (0.8) DMF PdCl₂ DPEPhos 100 48ᵉ
20 0.8 Cs₂CO₃ (0.8) DMF Pd₂(dba)₃ DPEPhos 100 36ᵉ
21 0.8 Cs₂CO₃ (0.8) DMF PdCl₂(dpff)₂ — 100 41ᵉ
22 0.8 Cs₂CO₃ (0.8) DMF PdCl₂(PPh₃)₄ — 100 32ᵉ
23 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ (R)-BINAP 100 54ᵉ
24 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ BuPAd₂ 100 52ᵉ
25 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ Xantphos 100 68ᵉ
26 0.8 K₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 100 68ᵉ
27 0.8 NEt₃ (0.8) DMF Pd(OAc)₂ DPEPhos 100 0ᵉ
28 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 80 75ᵉ
29 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 60 43ᵉ
30 0.8 Cs₂CO₃ (0.8) DMF Pd(OAc)₂ DPEPhos 40 Traceᵉ

ᵃReaction condition: (1) 1a (1 mmol), 2a (1.2 mmol), tert-butyl isocyanide (1.2 mmol), Pd(OAc)₂ (0.03 mmol), DPEPhos (0.06 mmol), in 2.0 mL of solvent under argon at 100 °C for 2 h. Then Na₂S·9H₂O (1.2 mmol) at 100 °C for 2 h. (2) Refluxed in THF/hydrochloric acid for 8 h. Isolated yields. Abbreviations: DPEPhos = bis[2-(diphenylphosphino)phenyl] ether, (R)-BINAP=(R)-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl, Xantphos = 4,5-bis-(diphenylphosphino)-9,9-dimethylxanthene, BuPAd₂ = Di(1-adamantyl)-n-butylphosphine. ᵇK₂S (1.2 mmol). ᶜNaHS (1.2 mmol). ᵈReaction temperature for Na₂S·9H₂O changed to 120 °C. ᵉOxalic acid instead of hydrochloric acid.
General Procedure:

In a 15 mL sealed tube equipped with a magnetic stirring bar were added 1 (1 mmol), 2 (0.8 mmol), tert-butyl isocyanide (1.2 mmol, 136 μL), Pd(OAc)$_2$ (0.03 mmol, 7 mg), DPEPhos (0.06 mmol, 32 mg), Cs$_2$CO$_3$ (0.8 mmol, 261 mg), and anhydrous DMF (2.0 mL). The tube was purged with argon, and the contents were stirred at 100 °C for 2 h. Then Na$_2$S·9H$_2$O (1.2 mmol, 240 mg) was added for 2 h. After reaction completion, the mixture was filtered through a pad of Celite, and DMF was removed by a vacuum. The combined filtrates were refluxed in THF (15 mL) and oxalic acid (1 M, 3 mL) for 8 h. The solvents were removed under reduced pressure, then poured into brine (20 mL) and extracted by ethyl acetate (3 × 30 mL). The combined organic layers were dried (Na$_2$SO$_4$) and evaporated. The residue was purified on a silica gel column using petroleum ether/ethyl acetate as the eluent to give the pure target product.

3. Characterization of Compounds

3a: 2-phenyl-4H-thiochromen-4-one

White solid (156 mg, 82%). Mp: 123–125 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, $J$ = 8.0 Hz, 1H), 7.74 – 7.49 (m, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.1 (s), 153.2 (s), 137.8 (s), 136.7 (s), 131.7 (s), 131.0 (s), 130.9 (s), 129.4 (s), 128.7 (s), 127.9 (s), 127.1 (s), 126.6 (s), 123.6 (s). IR (KBr): ν 1725, 1619, 1587, 1272, 1131, 1072, 863, 758, 730, 696, 653 cm$^{-1}$. m/z calcd for C$_{15}$H$_{11}$OS [M + H]$^+$, 239.0531; found, 239.0535.

3b: 2-(p-tolyl)-4H-thiochromen-4-one

Yellow solid (138 mg, 66%). Mp: 124–126 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (d, $J$ = 8.0 Hz, 1H), 7.75 – 7.49 (m, 6H), 7.31 (d, $J$ = 7.9 Hz, 2H), 2.43 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 181.1 (s), 153.4 (s), 141.5 (s), 137.9 (s), 133.8 (s), 131.7 (s), 131.1 (s),
3c: 2-(m-tolyl)-4H-thiochromen-4-one
Yellow solid (93 mg, 46%). Mp: 132–135 °C. 1H NMR (400 MHz, CDCl₃) δ 8.54 (d, J = 7.9 Hz, 1H), 7.63 (dt, J = 14.8, 7.3 Hz, 2H), 7.54 (t, J = 7.0 Hz, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.38 (2H, 3H), 7.34 (2H, 3H), 2.44 (s, 3H). IR (KBr): ν 2924, 1726, 1624, 1270, 1123, 1071, 836, 778, 741 cm⁻¹. m/z calcd for C₁₆H₁₃OS [M + H]⁺, 253.0688; found, 253.0689.

3d: 2-(4-methoxyphenyl)-4H-thiochromen-4-one
Yellow solid (148 mg, 69%). Mp: 126–128 °C. 1H NMR (400 MHz, CDCl₃) δ 8.58 (d, J = 8.2 Hz, 1H), 7.64 (ddd, J = 29.1, 16.3, 9.0 Hz, 6H), 7.06 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H). IR (KBr): ν 2922, 2850, 1624, 1601, 1550, 1264, 1243, 1019, 830, 773, 730, 620 cm⁻¹. m/z calcd for C₁₆H₁₃O₂S [M + H]⁺, 269.0637; found, 269.0641.

3e: 2-(4-(tert-butyl)phenyl)-4H-thiochromen-4-one
Yellow oil (120 mg, 51%). 1H NMR (400 MHz, CDCl₃) δ 8.55 (d, J = 7.9 Hz, 1H), 7.69 – 7.59 (5H, 1H), 7.54 (dd, J = 12.1, 8.3 Hz, 3H), 1.37 (s, 9H). IR (KBr): ν 2960, 1723, 1620, 1270, 1123, 1071, 836, 778, 741 cm⁻¹. m/z calcd for C₉H₁₉OS [M + H]⁺, 295.1157; found, 295.1154.

3f: 2-(4-ethylphenyl)-4H-thiochromen-4-one
Yellow solid (63 mg, 30%). Mp: 74–76 °C. 1H NMR (400 MHz, CDCl₃) δ 8.55 (d, J = 7.9 Hz, 1H), 7.65 (dd, J = 14.6, 7.7 Hz, 4H), 7.55 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.25 (2H, 3H), 2.73 (q, J = 7.5 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). IR (KBr): ν 2921, 1726, 1614, 1544, 1216, 815, 778, 734 cm⁻¹. m/z calcd for C₁₆H₁₃OS [M + H]⁺, 253.0688; found, 253.0692.
128.7 (s), 127.8 (s), 127.1 (s), 126.6 (s), 123.1 (s), 28.9 (s), 15.5 (s). IR (KBr): ν 2961, 2928, 1587, 1543, 1329, 1103, 779, 738, 685 cm⁻¹. m/z calcd for C_{17}H_{15}OS [M + H]^+, 267.0844; found, 267.0840.

3g: 2-(4-pentyphenyl)-4H-thiochromen-4-one
Yellow solid (91 mg, 37%). Mp: 68–70 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.55 (d, J = 7.9 Hz, 1H), 7.64 (dd, J = 18.6, 7.7 Hz, 4H), 7.55 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 2.67 (t, J = 7.7 Hz, 2H), 1.67 (dd, J = 14.2, 7.1 Hz, 2H), 1.35 (s, 4H), 0.91 (t, J = 6.4 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 181.1 (s), 153.3 (s), 146.5 (s), 137.9 (s), 134.0 (s), 131.7 (s), 131.1 (s), 129.5 (s), 128.7 (s), 127.8 (s), 127.0 (s), 126.6 (s), 123.0 (s), 35.9 (s), 31.6 (s), 31.1 (s), 22.7 (s), 14.2 (s). IR (KBr): ν 2923, 2852, 1613, 1587, 1327, 1101, 777, 727 cm⁻¹. m/z calcd for C_{20}H_{21}OS [M + H]^+, 309.1314; found, 309.1311.

3h: 2-[(1,1'-biphenyl)-4-yl]-4H-thiochromen-4-one
Yellow solid (108 mg, 42%). Mp: 162–164 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.57 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.72 (dd, J = 15.1, 8.0 Hz, 3H), 7.65 (d, J = 7.3 Hz, 3H), 7.58 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.35 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 181.0 (s), 152.7 (s), 143.9 (s), 139.9 (s), 137.8 (s), 135.5 (s), 131.8 (s), 131.1 (s), 129.1 (s), 128.8 (s), 128.3 (s), 128.1 (s), 128.0 (s), 127.5 (s), 127.3 (s), 126.7 (s), 123.3 (s). IR (KBr): ν 2922, 1702, 1608, 1586, 1104, 1108, 835, 762, 687 cm⁻¹. m/z calcd for C_{21}H_{15}OS [M + H]^+, 315.0844; found, 315.0851.

3i: 2-(4-fluorophenyl)-4H-thiochromen-4-one
White solid (135 mg, 66%). Mp: 162–166 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 7.8 Hz, 1H), 7.65 (dt, J = 14.1, 5.5 Hz, 4H), 7.56 – 7.51 (m, 1H), 7.17 (dd, J = 11.1, 5.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 180.9 (s), 165.7 (s), 163.2 (s), 151.9 (s), 137.5 (s), 132.8 (d, J_C-F = 3.3 Hz), 131.8 (s), 130.9 (s), 129.1 (d, J_C-F = 8.6 Hz), 128.7 (s), 128.0 (s), 126.6 (s), 123.5 (s), 116.7 (s), 116.4 (s). IR (KBr): ν 2922, 1703, 1628, 1595, 1499, 1229, 1097, 835, 779, 723 cm⁻¹. m/z calcd for C_{15}H_{10}FOS [M + H]^+, 257.0437; found, 257.0434.

3j: 2-(2-fluorophenyl)-4H-thiochromen-4-one
Yellow solid (116 mg, 57%). Mp: 128–130 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, J = 7.9 Hz, 1H), 7.65 (d, J = 3.1 Hz, 2H), 7.56 (dd, J = 13.0, 5.6 Hz, 2H), 7.48 (dd, J = 13.2,
7.1 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.21 (d, J = 12.4 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.6 (s), 160.6 (s), 158.1 (s), 147.1 (s), 138.2 (s), 132.2 (d, $J_{CF} = 8.4$ Hz), 131.8 (s), 131.0 (s), 130.3 (d, $J_{CF} = 1.9$ Hz), 128.8 (s), 128.0 (s), 127.0 (d, $J_{CF} = 3.7$ Hz), 126.5 (s), 124.9 (d, $J_{CF} = 3.8$ Hz), 124.6 (d, $J_{CF} = 13.1$ Hz), 117.0 (s), 116.8 (s). IR (KBr): ν 1627, 1593, 1439, 1325, 1098, 758, 732, 685 cm$^{-1}$. m/z calcd for C$_{15}$H$_{10}$FOS [M + H]$^+$, 257.0437; found, 257.0428.

3k: 2-(4-chlorophenyl)-4H-thiochromen-4-one

Yellow solid (117 mg, 54%). Mp: 168–170 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (d, $J = 8.0$ Hz, 1H), 7.68 – 7.61 (m, 4H), 7.57 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.21 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.9 (s), 151.7 (s), 137.5 (s), 137.3 (s), 135.2 (s), 131.9 (s), 131.0 (s), 129.7 (s), 128.8 (s), 128.4 (s), 128.1 (s), 126.6 (s), 123.7 (s). IR (KBr): ν 3016, 1629, 1589, 1327, 1088, 829, 777, 731 cm$^{-1}$. m/z calcd for C$_{15}$H$_{10}$ClOS [M + H]$^+$, 273.0142; found, 273.0148.

3l: 2-(2-chlorophenyl)-4H-thiochromen-4-one

White solid (128 mg, 59%). Mp: 140–145 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.58 (d, J = 7.8 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.60 – 7.55 (m, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.47 – 7.36 (m, 3H), 7.03 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.6 (s), 150.6 (s), 138.3 (s), 135.4 (s), 132.8 (s), 131.8 (s), 131.2 (s), 131.1 (s), 130.9 (s), 130.6 (s), 128.9 (s), 128.0 (s), 127.4 (s), 127.2 (s), 126.5 (s). IR (KBr): ν 3016, 1590, 1437, 1327, 1031, 863, 764, 733 cm$^{-1}$. m/z calcd for C$_{15}$H$_{10}$ClOS [M + H]$^+$, 273.0142; found, 273.0136.

3m: 2-heptyl-4H-thiochromen-4-one

Yellow oil (48 mg, 23%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.51 (d, J = 8.0 Hz, 1H), 7.60 – 7.49 (m, 3H), 6.88 (s, 1H), 2.68 (t, J = 7.6 Hz, 2H), 1.73 (dd, J = 14.8, 7.3 Hz, 3H), 1.30 (d, J = 9.3 Hz, 7H), 0.88 (t, J = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.9 (s), 156.8 (s), 137.9 (s), 131.5 (s), 131.1 (s), 128.7 (s), 127.6 (s), 126.4 (s), 124.2 (s), 37.6 (s), 31.5 (s), 30.0 (s), 29.2 (s), 29.0 (s), 22.7 (s), 14.2 (s). IR (KBr): ν 2925, 2854, 1625, 1593, 1439, 1334, 1099, 777, 737 cm$^{-1}$. m/z calcd for C$_{16}$H$_{21}$OS [M + H]$^+$, 261.1314; found, 261.1320.

3n: 2-(thiophen-3-yl)-4H-thiochromen-4-one

Yellow solid (78 mg, 40%). Mp: 135–140 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.53 (d, J =
8.0 Hz, 1H), 7.78 (s, 1H), 7.65 – 7.43 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 181.2 (s), 147.0 (s), 137.8 (s), 137.3 (s), 131.8 (s), 131.2 (s), 128.7 (s), 127.9 (s), 127.7 (s), 126.5 (s), 125.4 (s), 125.2 (s), 122.2 (s). IR (KBr): ν 3094, 1605, 1582, 1543, 1329, 1101, 774, 738, 631 cm$^{-1}$. $m/z$ calcd for C$_{13}$H$_9$OS$_2$ [M + H]$^+$, 245.0096; found, 245.0093.

4a: 8-fluoro-2-phenyl-4H-thiochromen-4-one

Yellow solid (164 mg, 80%). Mp: 134–137 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 (d, $J = 8.0$ Hz, 1H), 7.71 (dd, $J = 7.4, 1.7$ Hz, 2H), 7.51 (dd, $J = 7.3, 5.5$ Hz, 4H), 7.38 (t, $J = 8.8$ Hz, 1H), 7.23 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.0 (d, $J_{C-F} = 3.3$ Hz), 159.2 (s), 156.8 (s), 152.1 (s), 151.6 (s), 136.6 (s), 131.2 (s), 129.5 (s), 127.0 (s, $J_{C-F} = 7.8$ Hz), 127.2 (s), 124.3 (d, $J_{C-F} = 3.2$ Hz), 123.5 (s), 117.2 (d, $J_{C-F} = 19.5$ Hz). IR (KBr): ν 2924, 1734, 1632, 1329, 1242, 1138, 750, 684, 614 cm$^{-1}$. $m/z$ calcd for C$_{15}$H$_{10}$FOS [M + H]$^+$, 257.0437; found, 257.0429.

4b: 7-fluoro-2-phenyl-4H-thiochromen-4-one

Yellow solid (166 mg, 81%). Mp: 145–148 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 (dd, $J = 8.9, 5.9$ Hz, 1H), 7.67 (dd, $J = 7.9, 1.4$ Hz, 2H), 7.51 (d, $J = 6.8$ Hz, 3H), 7.34 (dd, $J = 8.5, 2.1$ Hz, 1H), 7.29 – 7.22 (m, 1H), 7.21 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.0 (s), 165.5 (s), 162.9 (s), 151.1 (s), 139.9 (d, $J_{C-F} = 9.8$ Hz), 136.3 (s), 131.8 (d, $J_{C-F} = 9.7$ Hz), 131.1 (s), 129.5 (s), 127.0 (s), 123.6 (s), 116.6 (s), 116.37 (s), 112.6 (s), 112.3 (s). IR (KBr): ν 1727, 1620, 1593, 1474, 1241, 1205, 840, 755, 690 cm$^{-1}$. $m/z$ calcd for C$_{15}$H$_{10}$FOS [M + H]$^+$, 257.0437; found, 257.0429.

4c: 7-chloro-2-phenyl-4H-thiochromen-4-one

Yellow solid (154 mg, 71%). Mp: 139–143 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.47 (d, $J = 8.7$ Hz, 1H), 7.67 (dd, $J = 7.9, 3.9$ Hz, 3H), 7.50 (dd, $J = 11.8, 4.2$ Hz, 4H), 7.22 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.2 (s), 153.0 (s), 139.2 (s), 138.5 (s), 136.3 (s), 131.2 (s), 130.4 (s), 129.5 (s), 129.4 (s), 128.6 (s), 127.1 (s), 125.9 (s), 123.7 (s). IR (KBr): ν 3058, 1612, 1586, 1322, 1099, 858, 822, 750, 734, 690 cm$^{-1}$. $m/z$ calcd for C$_{15}$H$_{10}$ClOS [M + H]$^+$, 273.0142; found, 273.0139.

4d: 8-methyl-2-phenyl-4H-thiochromen-4-one

Yellow solid (102 mg, 51%). Mp: 124–126 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 7.6$ Hz, 1H), 7.75 – 7.72 (m, 2H), 7.50 (dd, $J = 16.7, 6.6$ Hz, 5H), 7.28 (s, 1H), 2.59 (s,
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 181.6 (s), 152.3 (s), 137.3 (s), 137.1 (s), 134.9 (s), 132.9 (s), 131.4 (s), 130.9 (s), 129.4 (s), 127.2 (s), 127.1 (s), 126.6 (s), 123.5 (s), 19.7 (s). IR (KBr): $\nu$ 2963, 1612, 1582, 1335, 1058, 894, 759, 691 cm$^{-1}$. $m/z$ calcd for C$_{16}$H$_{13}$OS [M + H]$^+$, 253.0688; found, 253.0694.

4e: 6-methyl-2-phenyl-4H-thiochromen-4-one

Yellow solid (78 mg, 39%). Mp: 144–146 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.39 (s, 1H), 7.73 – 7.69 (m, 2H), 7.60 (d, $J$ = 8.3 Hz, 1H), 7.54 – 7.48 (m, 4H), 7.35 (s, 1H), 2.51 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 181.1 (s), 153.1 (s), 138.3 (s), 136.8 (s), 134.8 (s), 133.2 (s), 130.9 (s), 129.4 (s), 128.5 (s), 127.1 (s), 127.0 (s), 126.5 (s), 123.5 (s), 21.5 (s). IR (KBr): $\nu$ 2921, 1620, 1591, 1323, 1100, 864, 806, 775, 695 cm$^{-1}$. $m/z$ calcd for C$_{16}$H$_{13}$OS [M + H]$^+$, 253.0688; found, 253.0686.

4f: 2-phenyl-4H-thiopyrano [2, 3-b] pyridin-4-one

Yellow solid (80 mg, 42%). Mp: 118–122 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.82 (dd, $J$ = 4.5, 1.7 Hz, 1H), 8.77 (dd, $J$ = 8.1, 1.8 Hz, 1H), 7.72 (dd, $J$ = 7.4, 2.0 Hz, 2H), 7.56 – 7.50 (m, 4H), 7.27 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 181.5 (s), 159.2 (s), 155.0 (s), 153.0 (s), 136.9 (s), 136.5 (s), 131.3 (s), 129.6 (s), 128.2 (s), 127.2 (s), 123.7 (s), 123.1 (s). IR (KBr): $\nu$ 2922, 2847, 1630, 1577, 1399, 1127, 746, 685 cm$^{-1}$. $m/z$ calcd for C$_{14}$H$_{10}$NOS [M + H]$^+$, 240.0484; found, 240.0481.

5a: 8-fluoro-2-(p-tolyl)-4H-thiochromen-4-one

Yellow solid (143 mg, 66%). Mp: 160–164 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (d, $J$ = 8.0 Hz, 1H), 7.62 (d, $J$ = 8.0 Hz, 2H), 7.52 (dd, $J$ = 13.4, 7.9 Hz, 1H), 7.39 (t, $J$ = 8.7 Hz, 1H), 7.32 (d, $J$ = 7.8 Hz, 2H), 7.24 (s, 1H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.2 (s), 159.3 (s), 156.8 (s), 152.2 (s), 141.8 (s), 133.8 (s), 132.7 (s), 132.6 (s), 130.2 (s), 127.9 (d, $J_{C-F}$ = 7.8 Hz), 127.0 (s), 124.3 (s), 123.0 (s), 117.2 (d, $J_{C-F}$ = 19.6 Hz), 21.5 (s). IR (KBr): $\nu$ 2922, 2847, 1630, 1577, 1399, 1127, 746, 685 cm$^{-1}$. $m/z$ calcd for C$_{16}$H$_{12}$FOS [M + H]$^+$, 271.0594; found, 271.0598.

5b: 7-chloro-2-(4-fluorophenyl)-4H-thiochromen-4-one

White solid (192 mg, 83%). Mp: 159–162 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.47 (d, $J$ = 8.7 Hz, 1H), 7.67 (dd, $J$ = 8.8, 5.2 Hz, 3H), 7.51 (d, $J$ = 8.7 Hz, 1H), 7.21 (t, $J$ = 8.5 Hz, 2H), 7.16 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.1 (s), 165.8 (s), 163.3 (s), 151.7 (s), 141.8 (s), 141.8 (s), 133.8 (s), 132.7 (s), 132.6 (s), 130.2 (s), 127.9 (d, $J_{C-F}$ = 7.8 Hz), 127.0 (s), 124.3 (s), 123.0 (s), 117.2 (d, $J_{C-F}$ = 19.6 Hz), 21.5 (s). IR (KBr): $\nu$ 2922, 2847, 1630, 1577, 1399, 1127, 746, 685 cm$^{-1}$. $m/z$ calcd for C$_{16}$H$_{12}$FOS [M + H]$^+$, 271.0594; found, 271.0598.
138.9 (s), 138.6 (s), 132.5 (d, J = 3.4 Hz), 130.4 (s), 129.5 – 129.0 (m), 128.7 (s), 125.9 (s), 123.7 (s), 116.8 (s), 116.6 (s). IR (KBr): ν 1630, 1598, 1504, 1236, 1107, 823, 755 cm\(^{-1}\). m/z calcd for C\(_{15}\)H\(_9\)ClFOS [M + H]\(^{+}\), 291.0047; found, 291.0045.

5c: 7-fluoro-2-(m-tolyl)-4H-thiochromen-4-one

Yellow solid (149 mg, 69%). Mp: 130–132 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.57 (dd, J = 9.0, 5.9 Hz, 1H), 7.48 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.8 Hz, 1H), 7.34 (dd, J = 6.5, 1.9 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.21 (s, 1H), 2.44 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 180.1 (s), 165.5 (s), 163.0, 153.1 (s), 140.0 (d, \(J_{CF} = 9.8\) Hz), 139.4 (s), 136.3 (s), 131.9 (d, \(J_{CF} = 3.7\) Hz), 131.8 (s), 129.4 (s), 127.8 (d, \(J_{CF} = 2.2\) Hz), 127.7 (s), 124.2 (s), 123.5 (s), 116.6 (s), 116.4 (s), 112.6 (s), 112.3 (s), 21.6 (s). IR (KBr): ν 2922, 1622, 1589, 1478, 1240, 835, 793, 699 cm\(^{-1}\). m/z calcd for C\(_{16}\)H\(_{12}\)FOS [M + H]\(^{+}\), 271.0594; found, 271.0600.

intermediate 8: N-(tert-butyl)-1-(2-fluorophenyl)-3-phenylprop-2-yn-1-imine

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (t, J = 8.6 Hz, 1H), 7.53 (d, J = 7.8 Hz, 2H), 7.43 – 7.33 (m, 4H), 7.17 (t, J = 7.5 Hz, 1H), 7.13 – 7.05 (m, 1H), 1.58 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.9 (s), 159.4 (s), 144.6 (s), 133.4 (s), 131.8 (s), 131.0 (d, \(J_{CF} = 8.4\) Hz), 130.4 (d, \(J_{CF} = 2.4\) Hz), 129.8 (s), 129.4 (d, \(J_{CF} = 11.0\) Hz), 128.7 (s), 124.2 (d, \(J_{CF} = 3.7\) Hz), 122.0 (s), 116.5 (s), 116.3 (s), 98.9 (d, \(J_{CF} = 2.9\) Hz), 85.0 (s), 57.9 (s), 29.6 (s). IR (KBr): ν 2968, 1609, 1590, 1485, 1305, 1222, 752, 648. m/z calcd for C\(_{19}\)H\(_{18}\)FN [M + H]\(^{+}\), 280.1502; found, 280.1509.
4. NMR Spectra for Compounds

$^1$H NMR spectrum of compound 3a

$^{13}$C NMR spectrum of compound 3a
$^1$H NMR spectrum of compound 3b

$^{13}C$ NMR spectrum of compound 3b
$^1$H NMR spectrum of compound 3c

$^{13}$C NMR spectrum of compound 3c
$^1$H NMR spectrum of compound 3d

$^{13}$C NMR spectrum of compound 3d
$^1$H NMR spectrum of compound 3e

$^{13}$C NMR spectrum of compound 3e
$^1$H NMR spectrum of compound 3f

$^{13}$C NMR spectrum of compound 3f
$^1$H NMR spectrum of compound 3g

$^{13}$C NMR spectrum of compound 3g
$^1$H NMR spectrum of compound 3h

$^{13}$C NMR spectrum of compound 3h
$^1$H NMR spectrum of compound 3i

$^{13}$C NMR spectrum of compound 3i
\[ ^1H \text{NMR spectrum of compound } 3j \]

\[ ^{13}C \text{NMR spectrum of compound } 3j \]
$^1$H NMR spectrum of compound 3k

$^{13}$C NMR spectrum of compound 3k
$^1$H NMR spectrum of compound 3l

$^{13}$C NMR spectrum of compound 3l
$^1$H NMR spectrum of compound 3m

$^{13}$C NMR spectrum of compound 3m
$^1$H NMR spectrum of compound 3n

$^{13}$C NMR spectrum of compound 3n
$^1$H NMR spectrum of compound 4a

$^{13}$C NMR spectrum of compound 4a
$^1$H NMR spectrum of compound 4b

$^{13}$C NMR spectrum of compound 4b
$^1$H NMR spectrum of compound 4c

$^{13}$C NMR spectrum of compound 4c
$^1$H NMR spectrum of compound 4d

$^{13}$C NMR spectrum of compound 4d
$^1$H NMR spectrum of compound 4e

$^{13}$C NMR spectrum of compound 4e
$^1$H NMR spectrum of compound 4f

$^{13}$C NMR spectrum of compound 4f
$^1$H NMR spectrum of compound 5a

$^{13}$C NMR spectrum of compound 5a
$^1$H NMR spectrum of compound 5b

$^{13}$C NMR spectrum of compound 5b
$^1$H NMR spectrum of compound 5c

$^{13}$C NMR spectrum of compound 5c
$^1$H NMR spectrum of compound 8

$^{13}$C NMR spectrum of compound 8