Supporting Information

**Diversity-Oriented Synthesis of 3-Iodochromones and
Heteroatom Analogues via ICI-Induced Cyclization**

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General

The ^1H and ^{13}C NMR spectra were recorded at 300 MHz or 400 MHz and 75 MHz or 100 MHz, respectively. Thin layer chromatography was performed using commercially prepared 60-mesh silica gel plates, and visualization was effected with short wavelength UV light (254 nm). High resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. All melting points are uncorrected. All reagents were used as obtained commercially. The palladium salts were donated by Johnson Matthey Inc. and Kawaken Fine Chemicals Co., Ltd. The arylboronic acids were donated by Frontier Scientific Co., Ltd.

General procedure for the preparation of ynones

Method A (Sonogashira route): To a flask were added sequentially CuI (0.02 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.04 mmol), terminal acetylene (2.6 mmol), the benzoyl chloride (2 mmol) and triethylamine (20 mL). The resulting mixture was flushed with N_2 and allowed to stir at room temperature or at 50 $^\circ\text{C}$ overnight. Water (15 mL) was added, and the aqueous layer was extracted with ethyl ether 3 times (25 mL each time). The organic layers were combined, dried and concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel to afford the desired alkynone.

Method B (oxidation route): The benzaldehyde (2.0 mmol) was placed in a flask and dissolved in 15 mL of dry, oxygen-free THF. The flask was flushed with N_2 and cooled to -78 $^\circ\text{C}$. The lithium acetylide (2.2 mmol in 20 mL of THF solution) was then added dropwise. The resulting mixture was stirred at -78 $^\circ\text{C}$ for 30 min

and allowed to gradually warm to room temperature. The reaction mixture was quenched by satd aq NH_4Cl (20 mL) and extracted with ethyl ether 3 times (25 mL each time). The organic layers were combined, dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired secondary alcohol. The alcohol was then dissolved in CHCl_3 (25 mL) and activated MnO_2 (6 mmol) was added to the solution. The suspension was refluxed for 2 h, the solution was cooled and filtered through a pad of celite, and the filtrate was concentrated to afford the desired alkynone.

General procedure for the synthesis of 3-iodochromones and heteroatom analogues (Table 1)

The alkynone (0.25 mmol) and ICl (0.375 mmol) are each dissolved in 1.5 mL of dry CH_2Cl_2 in separate vials and cooled to $-78\text{ }^\circ\text{C}$. The ICl solution is added dropwise to the alkynone solution over approximately 1 min and the reaction is stirred at the indicated temperature for the indicated time. To the reaction mixture is then added 2 mL of satd aq $\text{Na}_2\text{S}_2\text{O}_3$ solution and then 20 mL of satd NaCl solution. The resulting mixture was extracted three times with ethyl ether (30 mL each time). The combined organic layers were dried over anhydrous MgSO_4 and the solvent was evaporated under reduced pressure. The residue provided the ^1H NMR pure (>95% purity) product in most cases, but sometimes the product was isolated by chromatography on a silica gel column.

Preparation of iodochromone **2** on a multi-gram scale without the use of column chromatography

2-Methoxybenzaldehyde (2.72 g, 20 mmol) was added to a 500 mL round bottom flask and dissolved in 250 mL of dry, oxygen-free THF. The flask was flushed with N₂ and allowed to cool to -78 °C. Lithium phenylacetylide (20 mL of a 1.0 M solution in THF) was then added dropwise under N₂. The resulting mixture was stirred at -78 °C for 30 min and allowed to gradually warm to room temperature. The reaction mixture was quenched by satd aq NH₄Cl (200 mL) and extracted with ethyl ether 3 times (100 mL each time). The organic layers were combined, dried and concentrated under reduced pressure. The residue was then dissolved in CHCl₃ (250 mL) and activated MnO₂ (3.6 g, 40 mmol) was added. The suspension was refluxed for 2 h, the solution was cooled and filtered through a pad of celite, and the filtrate was concentrated to afford the desired alkyne **1**. The alkyne **1** was then dissolved in 50 mL of dry CH₂Cl₂ and cooled to -78 °C. ICl (4.06 g, 25 mmol) was dissolved in 200 mL of dry CH₂Cl₂ and cooled to -78 °C. The ICl solution was slowly added to the alkyne dropwise over a period of 15 min. The reaction was then allowed to slowly warm up to room temperature. To the reaction mixture was added 50 mL of satd aq Na₂S₂O₃ solution and then 100 mL of satd aq NaCl solution. The resulting mixture was extracted 3 times with ethyl ether (100 mL each time). The combined organic layers were dried over anhydrous MgSO₄ and the solvent was evaporated under reduced pressure. The residue (6.8 g, 98% yield) proved to be chromone **2** (>95% purity by ¹H and ¹³C NMR analysis).

Characterization data:

1-(2-Methoxyphenyl)-3-phenylpropynone (1). ^1H NMR (300 MHz, CDCl_3) δ 3.92 (s, 3H), 6.96-7.02 (m, 2H), 7.30-7.62 (m, 6H), 8.04-8.08 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 56.15, 89.47, 91.88, 112.48, 120.55, 120.87, 128.85, 130.73, 132.80, 133.17, 135.33, 160.06, 176.92.

3-Iodo-2-phenylchromone (2).¹ White solid: mp 127-130 °C (lit.¹ mp 128 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.56 (m, 5H), 7.69-7.79 (m, 3H), 8.26-8.29 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 88.62, 115.56, 117.88, 120.19, 126.09, 126.95, 128.54, 129.68, 131.29, 134.45, 135.29, 156.08, 174.73; IR (CDCl_3 , cm^{-1}) 3009, 1636; MS (EI) m/z (rel intensity) 348 (M^+ , 48), 221 (12), 135 (100); HRMS (EI) calcd for $\text{C}_{15}\text{H}_9\text{IO}_2$ 347.9647, found: 347.9651.

1-(2-Methoxyphenyl)-3-(4-methylphenyl)propynone (3). Light yellow solid, obtained in a 78 % yield by Method A using *o*-anisoyl chloride and 4-ethynyltoluene: ^1H NMR (400 MHz, CDCl_3) δ 2.29 (s, 3H), 3.87 (s, 3H), 6.92-6.98 (m, 2H), 7.09-7.12 (m, 2H), 7.43-7.46 (m, 3H), 8.00, 8.04 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.94, 56.10, 89.41, 92.49, 112.47, 117.67, 120.51, 126.92, 129.69, 132.67, 133.20, 135.27, 141.43, 159.96, 176.87.

3-Iodo-2-(4-methylphenyl)chromone (4). Light yellow solid: mp 126-130 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.44 (s, 3H), 7.30-7.47 (m, 4H), 7.65-7.70 (m, 3H), 8.24 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.90, 88.29, 117.88, 120.16, 126.00, 126.88, 129.19, 129.69, 132.38, 134.38, 141.80, 156.05, 164.88, 174.73; IR (CDCl_3 , cm^{-1}) 3008, 2955, 1638; MS (EI) m/z (rel intensity) 362 (M^+ , 100), 235 (21); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{11}\text{IO}_2$ 361.9804, found: 361.9809.

1-(2-Methoxyphenyl)-3-(4-methoxyphenyl)propynone (5). Light yellow solid, obtained in an 86 % yield by Method A using *o*-anisoyl chloride and 4-ethynylanisole: ^1H NMR (400 MHz, CDCl_3) δ 3.74 (s, 3H), 3.88 (s, 3H), 6.81-6.84 (m, 2H), 6.92-6.99 (m, 2H), 7.43-7.52 (m, 3H), 8.01 (dd, $J = 7.6, 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.62, 56.11, 89.45, 93.06, 112.43, 112.51, 114.58, 120.49, 127.01, 132.61, 135.12, 135.21, 159.87, 161.72, 176.92.

3-Iodo-2-(4-methoxyphenyl)chromone (6). Light yellow solid: mp 149-151 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 3H), 7.00-7.03 (m, 2H), 7.42-7.48 (m, 2H), 7.68-7.81 (m, 3H), 8.25 (dd, $J = 8.0, 2.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.75, 87.86, 113.79, 117.78, 120.13, 125.93, 126.91, 127.33, 131.61, 134.30, 155.99, 161.86, 164.49, 174.81; IR (CDCl_3 , cm^{-1}) 3008, 2939, 1643, 1614; MS (EI) m/z (rel intensity) 378 (M^+ , 100), 251 (16); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{11}\text{IO}_3$ 377.9753, found: 377.9758.

1-(2-Methoxyphenyl)-3-(2-methylphenyl)propynone (7). White solid, obtained in a 72% yield by Method A using *o*-anisoyl chloride and 2-ethynyltoluene: ^1H NMR (400 MHz, CDCl_3) δ 2.40 (s, 3H), 3.79 (s, 3H), 6.86-6.92 (m, 2H), 7.06-7.20 (m, 3H), 7.47 (m, 2H), 7.98 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.80, 55.95, 90.80, 93.35, 112.35, 120.46, 120.53, 126.06, 129.98, 130.74, 132.50, 133.65, 135.20, 142.10, 159.82, 177.64.

3-Iodo-2-(2-methylphenyl)chromone (8). Light yellow solid: mp 118-121 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.30 (s, 3H), 7.34-7.49 (m, 6H), 7.69-7.72 (m, 1H), 8.29 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.59, 90.48, 117.99, 120.44, 126.15, 126.21, 126.89, 129.22, 130.79, 130.91, 134.50, 135.64, 136.23, 156.28, 166.42, 174.49; IR (CDCl_3 , cm^{-1}) 3008, 2966, 1638; MS (EI) m/z (rel intensity) 362 (M^+ , 100), 235 (25); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{11}\text{IO}_2$ 361.9804, found: 361.9809.

1,3-Di-(2-methoxyphenyl)propynone (9). White solid, obtained in a 75% yield by Method A using *o*-anisoyl chloride and 2-ethynylanisole: ^1H NMR (400 MHz, CDCl_3) δ 3.82 (s, 3H), 3.87 (s, 3H), 6.82-7.00 (m, 4H), 7.30-7.50 (m, 3H), 8.16 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.05, 56.09, 89.03, 93.51, 109.88, 111.09, 112.42, 120.42, 120.82, 126.88, 132.59, 133.39, 135.12, 135.21, 160.05, 161.75, 176.96.

3-Iodo-2-(2-methoxyphenyl)chromone (10). Light yellow solid: mp 133-135 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.85 (s, 3H), 7.02-7.10 (m, 2H), 7.37-7.69 (m, 5H), 8.28 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.96, 82.29, 91.40, 111.80, 118.05, 120.49, 120.71, 125.88, 126.84, 130.38, 132.56, 134.22, 156.50, 156.79, 164.45, 174.64; IR (CDCl_3 , cm^{-1}) 3007, 2939, 2839, 1643; MS (EI) m/z (rel intensity) 378 (M^+ , 100), 251 (12); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{11}\text{IO}_3$ 377.9753, found: 377.9758.

3-(2-Acetoxyphenyl)-1-(2-methoxyphenyl)propynone (11). White solid, obtained in an 81% yield by Method A using *o*-anisoyl chloride and 2-ethynylphenyl acetate: ^1H NMR (300 MHz, CDCl_3) δ 2.28 (s, 3H), 3.87 (s, 3H), 6.94-7.25 (m, 4H), 7.41-7.61 (m, 3H), 8.05 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.97, 56.12, 86.38, 93.47, 112.51, 115.23, 120.46, 122.94, 126.35, 126.62, 132.04, 133.04, 134.33, 135.48, 153.14, 160.09, 169.11, 176.49.

2-(2-Acetoxyphenyl)-3-iodochromone (12). Light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 2.08 (s, 3H), 7.22-7.45 (m, 4H), 7.51-7.68 (m, 3H), 8.22 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.25, 90.71, 117.84, 120.16, 123.54, 126.17, 126.26, 126.85, 128.56, 130.99, 132.33, 134.73, 147.98, 156.18, 162.70, 168.79, 174.33; IR (CDCl_3 , cm^{-1}) 3008, 2955, 2850, 1730, 1645; MS (EI) m/z (rel intensity) 406 (M^+ , 100), 279 (8); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{11}\text{IO}_4$ 405.9702, found: 405.9708.

1-(2-Methoxyphenyl)-3-(3-thiophenyl)propynone (13). White solid, obtained in an 80% yield by Method A using *o*-anisoyl chloride and 3-ethynylthiophene: ^1H NMR (400 MHz, CDCl_3) δ 3.90 (s, 3H), 6.95-7.02 (m, 2H), 7.20-7.30 (m, 2H), 7.45-7.51 (m, 1H), 7.71-7.73 (m, 1H), 8.02 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.14, 87.29, 89.65, 112.47, 120.10, 120.54, 126.41, 126.81, 130.46, 132.74, 133.72, 135.30, 159.98, 176.85.

3-Iodo-2-(3-thiophenyl)chromone (14). Brown solid (m.p. 103-106 °C): ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.49 (m, 3H), 7.66-7.77 (m, 2H), 8.22 (dd, J = 8.0, 1.6 Hz, 1H), 8.30-8.32 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 87.63, 117.71, 120.01, 125.88, 125.99, 126.92, 128.48, 131.30, 134.41, 135.29, 155.72, 159.65, 174.70; IR (CDCl_3 , cm^{-1}) 3008, 1638; MS (EI) m/z (rel intensity) 354 (M^+ , 75), 353 (100), 135(40); HRMS (EI) calcd for $\text{C}_{13}\text{H}_7\text{IO}_2\text{S}$ 353.9211, found: 353.9217.

1-(2-Methoxyphenyl)-3-(3-pyridyl)propynone (15). White solid, obtained in an 86% yield by Method A using *o*-anisoyl chloride and 3-ethynylpyridine: ^1H NMR (400 MHz, CDCl_3) δ 3.78 (s, 3H), 6.84-6.90 (m, 2H), 7.16-7.20 (m, 1H), 7.35-7.38 (m, 1H), 7.71-7.74 (m, 1H), 7.88 (dd, J = 7.6, 1.6 Hz, 1H), 8.48 (dd, J = 8.8, 1.6 Hz, 1H), 8.66 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.02, 87.64, 91.90, 112.42, 118.08, 120.54, 123.48, 126.24, 132.52, 135.66, 139.88, 150.60, 153.24, 160.03, 176.06.

1-(2-Methoxyphenyl)-3-[3,5-bis(trifluoromethyl)phenyl]propynone (17). Yellow solid, obtained in an 85% yield by Method A using *o*-anisoyl chloride and 1-ethynyl-3,5-bis(trifluoromethyl)benzene: ^1H NMR (400 MHz, CDCl_3) δ 3.96 (s, 3H), 7.02-7.06 (m, 2H), 7.56-7.57 (m, 1H), 7.91 (s, 1H), 8.02-8.06 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.07, 86.75, 91.15, 112.46, 115.57, 118.83, 120.69, 121.54, 123.55, 123.68, 123.71, 123.75, 123.78, 124.26, 126.15, 126.97, 132.02, 132.36, 132.66, 132.70, 132.73, 133.04, 135.93, 160.28, 175.80.

3-Iodo-2-[3,5-bis(trifluoromethyl)phenyl]chromone (18). Yellow solid: ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.55 (m, 2H), 7.75-7.78 (m, 1H), 8.06 (s, 1H), 8.28-8.31 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 90.04, 117.88, 120.08, 121.69, 124.78, 124.82, 124.86, 126.67, 127.14, 130.22, 132.07, 132.40, 134.98, 137.03, 155.99, 161.05, 174.14; IR (CDCl_3 , cm^{-1}) 3008, 1638; MS (EI) m/z (rel intensity) 484 (M^+ , 100), 357 (22); HRMS (EI) calcd for $\text{C}_{17}\text{H}_7\text{F}_6\text{IO}_2$ 483.9395, found: 483.9400.

3-(1-Cyclohexenyl)-1-(2-methoxyphenyl)propynone (19). Yellow solid, obtained in an 88% yield by Method A using *o*-anisoyl chloride and 1-ethynylcyclohexene: ^1H NMR (400 MHz, CDCl_3) δ 1.52-1.62 (m, 4H), 2.07-2.17 (m, 4H), 3.84 (s, 3H), 6.42 (d, J = 1.6 Hz, 1H), 6.89-6.96 (m, 2H), 7.41-7.43 (m, 1H), 7.92 (dd, J = 8.0, 1.6 Hz, 1H);

^{13}C NMR (100 MHz, CDCl_3) δ 21.36, 22.20, 26.36, 28.64, 56.02, 87.80, 94.34, 112.37, 119.63, 120.37, 127.08, 132.61, 134.93, 142.17, 159.79, 177.06.

2-(1-Cyclohexenyl)-3-iodochromone (20). Light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.68-1.82 (m, 4H), 2.15-2.39 (m, 4H), 6.29-6.32 (m, 1H), 7.36-7.44 (m, 2H), 7.63-7.68 (m, 1H), 8.18-8.21 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.64, 22.39, 25.28, 26.34, 87.02, 117.72, 120.35, 125.73, 126.78, 134.15, 134.20, 136.05, 155.81, 167.29, 174.93; IR (CDCl_3 , cm^{-1}) 3050, 3009, 1643, 1614; MS (EI) m/z (rel intensity) 352 (M^+ , 100), 225 (11); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{13}\text{IO}_2$ 351.9960, found: 351.9966.

1-(2-Methoxyphenyl)-2-octyn-1-one (21). Colorless oil, obtained in an 82% yield by Method A using *o*-anisoyl chloride and 1-heptyne: ^1H NMR (300 MHz, CDCl_3) δ 0.84 (t, J = 7.2 Hz, 3H), 1.25-1.58 (m, 6H), 2.35 (t, J = 7.2 Hz, 2H), 3.81 (s, 3H), 6.88-6.96 (m, 2H), 7.38-7.42 (m, 1H), 7.92 (dd, J = 7.8, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.09, 19.37, 22.31, 27.72, 31.22, 55.98, 82.00, 95.46, 112.32, 120.30, 126.97, 132.98, 134.91, 159.80, 177.23.

3-Iodo-2-(*n*-pentyl)chromone (22). Light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 0.93 (t, J = 6.8 Hz, 3H), 1.40-1.81 (m, 6H), 3.03 (dt, J = 7.6, 0.8 Hz, 2H), 7.26-7.46 (m, 2H), 7.67-7.69 (m, 1H), 8.22 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.20, 22.60, 26.90, 31.50, 38.90, 88.57, 117.62, 120.26, 125.77, 126.75, 134.08, 155.77, 169.52, 174.17; IR (CDCl_3 , cm^{-1}) 3007, 2939, 1639; MS (EI) m/z (rel intensity) 342 (M^+ , 100), 293 (12); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{15}\text{IO}_2$ 342.0117, found: 342.0122.

6-Chloro-1-(2-methoxyphenyl)-2-hexyn-1-one (23). Colorless oil, obtained in an 80% yield by Method A using *o*-anisoyl chloride and 5-chloro-1-pentyne: ^1H NMR (300 MHz, CDCl_3) δ 1.96-2.03 (m, 2H), 2.59 (t, J = 6.9 Hz, 2H), 3.63 (t, J = 6.3 Hz, 2H), 3.84 (s, 3H), 6.90-6.97 (m, 2H), 7.41-7.45 (m, 1H), 7.90 (dd, J = 7.8, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.85, 30.72, 43.64, 56.06, 82.62, 92.93, 112.38, 120.43, 126.75, 132.82, 135.18, 159.86, 176.95.

2-(3-Chloropropyl)-3-iodochromone (24). Light yellow solid: mp 75-78 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.24-2.32 (m, 2H), 3.22 (t, J = 7.2 Hz, 2H), 3.67 (t, J = 6.4 Hz, 2H), 7.39-7.46 (m, 2H), 7.67-7.71 (m, 1H), 8.21 (dd, J = 8.0, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.95, 36.52, 44.04, 89.22, 117.61, 120.26, 126.00, 126.84, 134.26, 155.73, 167.62, 173.97; IR (CDCl_3 , cm^{-1}) 3007, 2839, 1645; MS (EI) m/z (rel intensity) 348 (M^+ , 100), 185 (11); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{10}\text{ClIO}_2$ 347.9414, found: 347.9419.

1-(2-Methoxyphenyl)-3-(trimethylsilyl)propynone (27). Colorless oil, obtained in a 95% yield by the modified Sonogashira method² using *o*-anisoyl chloride and trimethylsilylacetylene: ^1H NMR (300 MHz, CDCl_3) δ 0.12 (s, 9H), 3.72 (s, 3H), 6.80-6.87 (m, 2H), 7.32-7.36 (m, 1H), 7.82 (dd, J = 7.8, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 0.01, 56.30, 98.80, 103.80, 112.96, 120.92, 126.87, 133.17, 135.90, 160.52, 176.55.

1-(5-Bromo-2-methoxyphenyl)-3-phenylpropynone (29). White solid, obtained in an 86% overall yield by Method B using 5-bromo-2-methoxybenzaldehyde and lithium phenylacetylide: ^1H NMR (300 MHz, CDCl_3) δ 3.82 (s, 3H), 6.80 (d, $J = 9.0$ Hz, 1H) 7.28-7.52 (m, 6H), 7.97-7.99 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 56.36, 89.18, 92.79, 112.71, 114.52, 120.45, 128.17, 128.88, 130.97, 133.21, 134.53, 137.65, 158.97, 175.12.

6-Bromo-3-iodo-2-phenylchromone (30). Light yellow solid: mp 143-146 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.40 (m, 1H), 7.52-7.55 (m, 3H), 7.75-7.79 (m, 3H), 8.36 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 88.33, 119.30, 119.91, 121.32, 128.59, 129.36, 129.68, 131.50, 134.90, 137.44, 154.84, 164.95, 173.54; IR (CDCl_3 , cm^{-1}) 3007, 1638; MS (EI) m/z (rel intensity) 427 (42), 425 (M^+ , 63), 348 (100); HRMS (EI) calcd for $\text{C}_{15}\text{H}_8\text{BrIO}_2$ 425.0752, found: 425.0760.

1-(5-Fluoro-2-methoxyphenyl)-3-phenylpropynone (31). White solid, obtained in an 88% overall yield by Method B using 5-fluoro-2-methoxybenzaldehyde and lithium phenylacetylide: ^1H NMR (400 MHz, CDCl_3) δ 3.87 (s, 3H), 6.90-7.66 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.71, 89.20, 92.63, 114.01, 114.08, 118.07, 118.31, 120.56, 121.66, 121.89, 127.48, 128.88, 130.95, 133.24, 133.52, 155.22, 156.30, 157.63, 175.45.

6-Fluoro-3-iodo-2-phenylchromone (32). Light yellow solid: mp 131-133 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.54 (m, 5H), 7.75-7.78 (m, 2H), 7.87 (dd, J = 8.0, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 87.72, 111.54, 111.78, 120.12, 120.20, 121.15, 121.23, 122.67, 122.92, 128.57, 129.66, 131.44, 135.00, 152.35, 152.37, 158.76, 161.22, 165.01, 174.12; IR (CDCl_3 , cm^{-1}) 3007, 1639; MS (EI) m/z (rel intensity) 366 (M^+ , 100), 348 (10), 221 (34); HRMS (EI) calcd for $\text{C}_{15}\text{H}_8\text{FIO}_2$ 365.9553, found: 365.9558.

1-(2,3-Dimethoxyphenyl)-3-(4-methylphenyl)propynone (33). White solid, obtained in a 95% overall yield by Method B using 2,3-dimethoxybenzaldehyde and lithium 4-methylphenylacetylide: ^1H NMR (400 MHz, CDCl_3) δ 2.34 (s, 3H), 3.86 (s, 3H), 3.97 (s, 3H), 7.08-7.17 (m, 4H), 7.49-7.52 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.97, 56.35, 61.89, 89.69, 92.57, 117.24, 117.60, 122.46, 124.06, 129.67, 132.40, 133.26, 141.55, 149.93, 153.66, 177.16.

3-Iodo-2-(4-methylphenyl)-8-methoxychromone (34). Light yellow solid: mp 166-168 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.42 (s, 3H), 3.90 (s, 3H), 7.12-7.14 (m, 1H), 7.27-7.31 (m, 3H), 7.70-7.75 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.92, 56.64, 88.41, 114.76, 117.36, 121.11, 125.70, 129.16, 129.89, 132.24, 141.73, 146.45, 148.71,

164.51, 174.66; IR (CDCl₃, cm⁻¹) 3007, 2939, 2839, 1642; MS (EI) m/z (rel intensity) 392 (M⁺, 100), 265 (22); HRMS (EI) calcd for C₁₇H₁₃IO₃ 391.9909, found: 391.9915.

1-(2,4-Dimethoxyphenyl)-3-phenylpropynone (35). White solid, obtained in a 96% overall yield by Method B using 2,4-dimethoxybenzaldehyde and lithium phenylacetylide; ¹H NMR (300 MHz, CDCl₃) δ 3.56 (s, 3H), 3.63 (s, 3H), 6.19-6.29 (m, 2H), 7.09-7.12 (m, 3H), 7.31-7.35 (m, 2H), 7.83 (d, *J* = 8.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 55.60, 55.76, 89.38, 90.61, 98.46, 105.58, 119.87, 120.82, 128.70, 130.38, 132.80, 135.03, 162.12, 165.75, 174.64.

3-Iodo-7-methoxy-2-phenylchromone (36). Light yellow solid: mp 173-175 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 6.82 (s, 1H), 6.94-6.97 (m, 1H), 7.50-7.74 (m, 5H), 8.11 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 56.22, 88.87, 99.86, 114.04, 115.58, 128.27, 128.78, 129.66, 131.17, 135.27, 157.81, 164.21, 164.63, 173.89; IR (CDCl₃, cm⁻¹) 3007, 1623; MS (EI) m/z (rel intensity) 378 (M⁺, 100), 251 (22); HRMS (EI) calcd for C₁₆H₁₁IO₃ 377.9753, found: 377.9760.

1-(2,4,5-Trimethoxyphenyl)-3-phenylpropynone (37). White solid, obtained in an 88% overall yield by Method B using 2,4,5-trimethoxybenzaldehyde and lithium phenylacetylide; ¹H NMR (300 MHz, CDCl₃) δ 3.73 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 6.39 (s, 1H), 7.23-7.48 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 56.34, 56.37, 56.78,

90.02, 91.15, 97.04, 113.38, 118.50, 121.10, 128.77, 130.44, 132.97, 143.01, 155.46, 157.01, 174.28.

3-Iodo-6,7-dimethoxy-2-phenylchromone (38). Light yellow solid: mp 253-255 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.96 (s, 3H), 3.99 (s, 3H), 6.89 (s, 1H), 7.52-7.77 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.69, 56.77, 99.39, 105.40, 128.48, 129.64, 131.06, 135.43, 148.33, 152.28, 155.06, 164.01, 174.39; IR (CDCl_3 , cm^{-1}) 3007, 2939, 2839, 1619; MS (EI) m/z (rel intensity) 408 (M^+ , 100), 281 (25); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{13}\text{IO}_4$ 407.9859, found: 407.9866.

3-Iodo-7-nitro-2-phenylchromone (42). Yellow solid: mp 163-165 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.82 (m, 6H), 8.53-8.55 (m, 1H), 9.09-9.12 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 88.77, 119.80, 120.05, 123.69, 128.72, 129.05, 129.71, 131.89, 134.28, 145.37, 158.80, 165.19, 173.53; IR (CDCl_3 , cm^{-1}) 3007, 1657, 1625; MS (EI) m/z (rel intensity) 393 (M^+ , 100), 364 (18); HRMS (EI) calcd for $\text{C}_{15}\text{H}_8\text{INO}_4$ 392.9498, found: 392.9504.

1-(2-Methoxy-1-naphthyl)-3-phenylpropynone (43). White solid, obtained in an 85% overall yield by Method B using 2-methoxy-1-naphthaldehyde and lithium phenylacetylide: ^1H NMR (400 MHz, CDCl_3) δ 3.99 (s, 3H), 7.26-7.58 (m, 8H), 7.78 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 9.2 Hz, 1H), 8.16 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz,

CDCl₃) δ 57.09, 90.90, 91.52, 113.70, 120.69, 123.41, 124.00, 124.64, 128.43, 128.62, 128.88, 129.04, 130.89, 131.17, 133.30, 133.56, 156.77, 180.62.

3-Iodo-2-phenylnaphtho[2,1-*b*]pyran-1-one (44). Yellow solid: mp 182-185 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.44-7.88 (m, 9H), 8.05 (d, *J* = 9.0 Hz, 1H), 10.03 (d, *J* = 9.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 93.15, 113.51, 117.15, 127.19, 127.48, 128.56, 129.76, 129.81, 130.21, 130.98, 131.24, 134.90, 136.30, 157.28, 162.64, 175.70; IR (CDCl₃, cm⁻¹) 3010, 1630; MS (EI) *m/z* (rel intensity) 398 (*M*⁺, 100), 271 (32); HRMS (EI) calcd for C₁₉H₁₁IO₂ 397.9804, found: 397.9810.

1-(2-Methoxy-3-pyridyl)-3-phenylpropynone (45). White solid, obtained in an 80% overall yield by Method B using 2-methoxy-3-pyridinecarboxaldehyde and lithium phenylacetylide: ¹H NMR (400 MHz, CDCl₃) δ 3.99 (s, 3H), 6.90-6.92 (m, 1H) 7.26-7.52 (m, 5H), 8.23-8.27 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 54.25, 88.76, 92.91, 116.90, 120.39, 120.70, 128.86, 130.98, 133.23, 141.78, 152.10, 162.52, 175.48.

3-Iodo-2-phenyl-4H-pyrano[2,3-*b*]pyridin-4-one (46). Light yellow solid: mp 131-133 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.54 (m, 4H), 7.82-7.85 (m, 2H), 8.63-8.73 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 88.41, 114.79, 123.04, 128.51, 129.90,

131.62, 134.52, 137.64, 154.08, 160.53, 165.05, 175.43; IR (CDCl₃, cm⁻¹) 3007, 1653; MS (EI) m/z (rel intensity) 349 (M⁺, 100), 222 (20); HRMS (EI) calcd for C₁₄H₈NIO₂ 348.9600, found: 348.9605.

3-(1-Cyclohexenyl)-1-[2-(methylthio)phenyl]propynone (49). White solid, obtained in a 72% overall yield by Method B using 2-(methylthio)benzaldehyde and lithium 1-cyclohexenylacetylide: ¹H NMR (300 MHz, CDCl₃) δ 1.50-1.78 (m, 4H), 2.05-2.25 (m, 4H), 2.40 (s, 3H), 6.40-6.45 (m, 1H), 7.12-7.23 (m, 2H), 7.39-7.46 (m, 1H), 8.23 (dd, *J* = 7.8, 1.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 15.68, 21.33, 22.17, 26.35, 28.57, 85.71, 95.40, 119.31, 123.37, 124.34, 133.32, 136.66, 142.33, 144.58, 178.02.

2-(1-Cyclohexenyl)-3-iodothiophene (50). Light yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 1.64-1.82 (m, 4H), 2.21-2.43 (m, 4H), 5.88-5.89 (m, 1H), 7.51-7.61 (m, 3H), 8.54 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.61, 22.61, 25.44, 28.10, 101.18, 123.36, 125.40, 127.65, 128.39, 130.10, 131.67, 131.85, 137.97, 139.64, 157.05, 176.96; IR (CDCl₃, cm⁻¹) 3025, 3007, 1617; MS (EI) m/z (rel intensity) 368 (M⁺, 100), 241 (25); HRMS (EI) calcd for C₁₅H₁₃IOS 367.9732, found: 367.9736.

3-(2-Methoxyphenyl)-1-[2-(methylthio)phenyl]propynone (51). White solid, obtained in an 88% overall yield by Method B using 2-(methylthio)benzaldehyde and lithium 2-methoxyphenylacetylide: ¹H NMR (300 MHz, CDCl₃) δ 2.39 (s, 3H), 3.87 (s,

3H), 6.85-6.93 (m, 2H), 7.17-7.54 (m, 5H), 8.57 (dd, $J = 8.0, 1.5$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.66, 56.14, 90.30, 91.75, 109.58, 111.10, 120.86, 123.48, 124.28, 132.78, 133.36, 133.46, 134.92, 135.38, 144.77, 161.97, 177.99.

3-Iodo-2-(2-methoxyphenyl)thiochromenone (52). Light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 3.77 (s, 3H), 6.93-7.19 (m, 3H), 7.42-7.56 (m, 4H), 8.53 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.03, 105.38, 111.93, 120.97, 125.46, 127.67, 128.45, 129.78, 130.22, 131.92, 131.96, 138.19, 152.30, 155.77, 176.44; IR (CDCl_3 , cm^{-1}) 3007, 2945, 2839, 1618; MS (EI) m/z (rel intensity) 394 (M^+ , 100), 267 (18); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{11}\text{IO}_3$ 393.9796, found: 393.9800.

3-(3,5-Dimethoxyphenyl)-1-[2-(methylthio)phenyl]propynone (53). White solid, obtained in a 72% overall yield by Method B using 2-(methylthio)benzaldehyde and lithium 3,5-dimethoxyphenylacetylide: ^1H NMR (300 MHz, CDCl_3) δ 2.44 (s, 3H), 3.79 (s, 6H), 6.54-6.56 (m, 1H), 6.78 (d, $J = 2.4$ Hz, 2H), 7.22-7.32 (m, 2H), 7.48-7.55 (m, 1H), 8.38 (dd, $J = 7.7, 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.68, 55.78, 86.70, 92.88, 104.23, 110.74, 121.66, 123.49, 124.45, 133.17, 133.59, 134.93, 145.01, 160.87, 177.78.

2-(3,5-Dimethoxyphenyl)-3-iodothiochromenone (54). Light yellow solid: mp 93-96 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.81 (s, 6H), 6.55-6.59 (m, 3H), 7.58-7.66 (m, 3H), 8.60 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.82, 102.18, 103.00, 106.95, 110.76, 125.36, 127.59, 128.65, 130.28, 132.16, 137.55, 142.47, 154.27, 161.00, 176.50; IR (CDCl_3 , cm^{-1}) 3009, 2961, 2938, 2839, 1617; MS (EI) m/z (rel intensity) 424 (M^+ , 100), 297 (22); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{13}\text{IO}_3\text{S}$ 423.9630, found: 423.9630.

3-Iodo-1,1-dimethyl-4-oxo-2-phenyl-1,4-dihydroquinolinium chloride (56). Light yellow solid: ^1H NMR (400 MHz, CDCl_3) δ 2.83 (s, 6H), 6.96-7.04 (m, 2H), 7.35-7.40 (m, 4H), 7.52-7.59 (m, 2H), 7.69-7.74 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 39.48, 89.49, 115.96, 123.20, 124.73, 128.11, 128.50, 129.48, 130.00, 132.88, 139.65, 141.00, 155.50, 174.30; IR (CDCl_3 , cm^{-1}) 3007, 1630; MS (EI) m/z (rel intensity) 376 (M^+ , 1), 361 (100), 234 (35); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{15}\text{INO}$ 376.0198, found: 376.0205.

3-(1-Cyclohexenyl)-1-[2-(dimethylamino)phenyl]propynone (57). Colorless oil, obtained in a 66% overall yield by Method B using 2-(dimethylamino)benzaldehyde and lithium 1-cyclohexenylacetylide: ^1H NMR (300 MHz, CDCl_3) δ 1.55-1.66 (m, 4H), 2.12-2.20 (m, 4H), 2.86 (s, 6H), 6.43-6.45 (m, 1H), 6.80-6.92 (m, 2H), 7.31-7.34 (m, 1H), 8.00 (dd, $J = 8.0, 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.42, 22.26, 26.36, 28.72, 44.19, 87.19, 93.28, 116.57, 117.97, 119.62, 133.69, 133.90, 141.70, 152.68, 178.20.

2-(1-Cyclohexenyl)-3-iodo-N-methyl-4(1H)-quinolinone (58). Light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.60-2.40 (m, 8H), 3.84 (s, 3H), 5.83 (s, 1H), 7.34-7.38 (m, 1H), 7.47-7.50 (m, 1H), 7.62-7.67 (m, 1H), 8.45 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.60, 22.50, 25.25, 28.01, 38.04, 88.02, 115.77, 123.07, 124.41, 127.97, 132.23, 132.55, 137.57, 140.72, 156.90, 174.45; IR (CDCl_3 , cm^{-1}) 3007, 2942, 1615; MS (EI) m/z (rel intensity) 365 (M^+ , 100), 238 (32); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{INO}$ 365.0277, found: 365.0283.

7-Methoxy-3-(4-methylphenyl)-2-phenylchromone (59). White solid: mp 163-166 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 2.33 (s, 3H), 3.91 (s, 3H), 6.91-7.00 (m, 2H), 7.05-7.15 (m, 4H), 7.21-7.42 (m, 5H), 8.18 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.56, 56.07, 82.29, 100.24, 114.73, 117.62, 128.01, 128.28, 129.24, 129.73, 130.03, 130.08, 131.28, 133.73, 137.43, 158.00, 161.08, 164.34, 177.73; IR (CDCl_3 , cm^{-1}) 3007, 2941, 2839, 1639; MS (EI) m/z (rel intensity) 342 (M^+ , 100), 329 (25); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3$ 342.1256, found: 342.1262.

Benzofuro[3,2-*b*][1]chromone (60).³ White solid: ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.79 (m, 6H), 7.98 (d, $J = 8.0$ Hz, 1 H), 8.48 (dd, $J = 8.0, 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 113.69, 118.26, 120.80, 124.41, 125.11, 126.77, 128.67, 128.80, 130.73,

132.43, 132.54, 133.66, 155.31, 156.05, 176.68; MS (EI) m/z (rel intensity) 236 (M^+ , 100), 208 (23); HRMS (EI) calcd for $C_{15}H_8O_3$ 236.0473, found: 236.0477.

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