

Supporting Information

A Facile Strategy for Accessing 3-Alkynylchromones through Gold-Catalyzed Alkyneation/Cyclization of *o*-Hydroxyarylenaminones

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1. General information

1.1 Practical considerations

All reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere, unless otherwise specified. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining KMnO₄ and charring on a hot plate. Solvents were removed in vacuum and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

1.2 Instrumentation

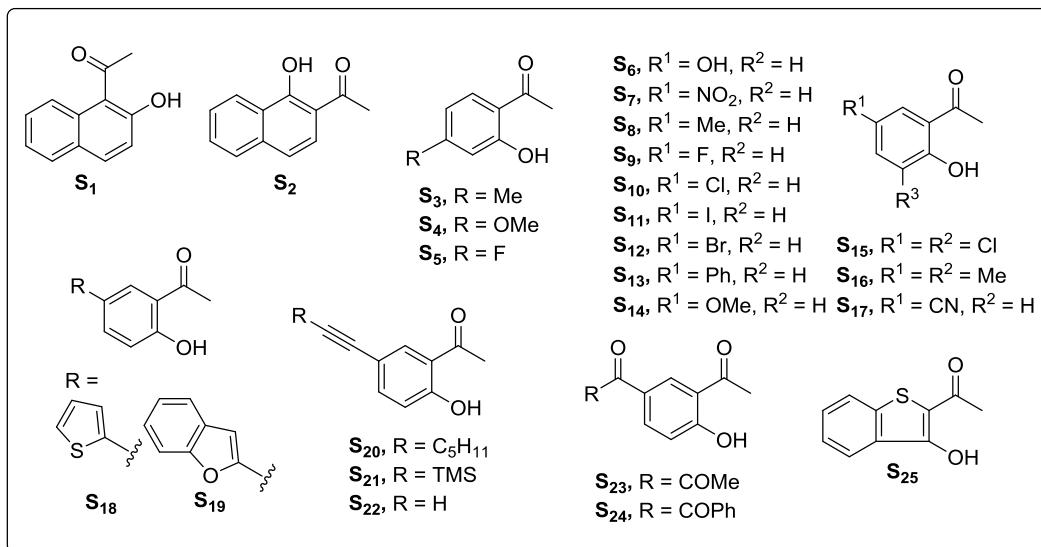
Melting points are uncorrected and recorded using digital Büchi Melting Point Apparatus B-540. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AV, 400/500, JEOL 400 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ¹H NMR signals are designated as s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), t (triplet), q (quartet), m (multiplet)... etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Single-crystal data was collected on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with CCD area detector.

1.3 Materials

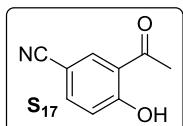
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was distilled from Na/benzophenone under an atmosphere of dry N₂. DCE, toluene, chloroform, DCM were dried using standard protocol under N₂. Gold and silver salts were purchased from Sigma-Aldrich and stored under inert atmosphere.

2. General procedures

2.1 Preparation of substituted *o*-hydroxy acetophenones



Compounds S₁, S₂, S₃, S₄, S₅, S₆, S₇ have been used from commercial sources. Substituted *o*-hydroxy acetophenones S₈, S₉, S₁₀, S₁₁, S₁₂, S₁₃, S₁₄, S₁₅, S₁₆ and S₂₅ have been synthesized using literature known methods.¹ Compounds S₁₇, S₁₈, S₁₉, S₂₀, S₂₁, S₂₂, S₂₃ and S₂₄ were not exist in the literature and those were synthesized by the following literature known procedures.



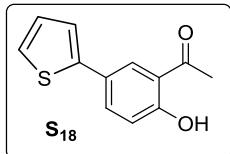
• Synthesis of compound S₁₇

Compound S₁₇ was prepared by using literature known procedure.² A solution of 5-bromo-2-hydroxyacetophenone (S₁₂) (215 mg, 1.00 mmol, 1 equiv) in 10 mL anhydrous DMF was mixed with of copper cyanide (98 mg, 1.10 mmol, 1.1 equiv) and the resulting mixture was heated for 24 h at 160 °C. The reaction mixture was cooled to room temperature and mixed with ether and mixture was filtered through celite. The filtrate was concentrated and purified by flash column chromatography with silica using pet. ether/EtOAc as eluent to afford compound S₁₇.

¹ (a) R. Murashige, Y. Hayashi, S. Ohmori, A. Torii, Y. Aizu, Y. Muto, Y. Murai, Y. Oda, M. Hashimoto, *Tetrahedron* 2011, **67**, 641-649. (b) S. L.-F. Chan, K.-H. Low, C. Yang, S. H.-F. Cheung, C.-M. Che, *Chem. Eur. J.* 2011, **17**, 4709-4714.

² A. V. Nizovtsev, A. Scheurer, B. Kosog, F. W. Heinemann, K. Meyer, *Eur. J. Inorg. Chem.* 2013, 2538-2548.

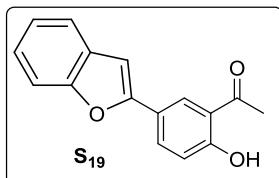
R_f: 0.60 (pet. ether/EtOAc = 80/20); 111 mg, **Yield**: 69%; **Physical appearance**: Reddish solid; **M. P.**: 171 °C; **¹H NMR**: (500 MHz, CDCl₃) δ = 12.69 (s, 1 H), 8.09 (d, J = 2.3 Hz, 1 H), 7.70 (d, J = 8.8 Hz, 1 H), 7.05 (d, J = 8.8 Hz, 1 H), 2.67 (s, 3 H); **¹³C NMR**: (125 MHz, CDCl₃) δ = 203.6, 165.3, 138.7, 135.7, 120.0, 119.7, 118.1, 102.6, 26.6; **HRMS**: calcd 162.0550 for C₉H₈NO₂ [M+H]⁺ found 162.0550.



- **Synthesis of compound S₁₈**

Compound **S₁₇** was prepared by using literature known procedure.³ A 50 mL oven-dried round bottom flask was evacuated and back-filled with argon and charged with Compound **S₁₁** (262 mg, 1.00 mmol), thiophen-2-ylboronic acid (254 mg, 2.00 mmol), K₂CO₃ (552 mg, 4 mmol), degassed THF (25 mL), and Pd(PPh₃)₄ (92 mg, 0.08 mmol) were added. The reaction mixture was stirred at 60 °C for 10h. The reaction profile was monitored by TLC. The reaction mixture was cooled to room temperature and mixed with ether and the mixture was filtered through celite. The filtrate was concentrated and purified by flash column chromatography through silica using pet. ether/EtOAc as eluent to yield compound **S₁₈**.

R_f: 0.60 (pet. ether/EtOAc = 95/05); 191 mg, **Yield**: 88%; **Physical appearance**: Yellow solid; **M. P.**: 53 °C; **¹H NMR**: (500 MHz, CDCl₃) δ = 12.31 (s, 1 H), 7.90 (d, J = 2.3 Hz, 1 H), 7.69 (dd, J = 2.3, 8.8 Hz, 1 H), 7.31 - 7.24 (m, 1 H), 7.22 (dd, J = 1.0, 3.6 Hz, 1 H), 7.09 (dd, J = 3.6, 5.1 Hz, 1 H), 7.00 (d, J = 8.8 Hz, 1 H), 2.67 (s, 3 H); **¹³C NMR**: (125 MHz, CDCl₃) δ = 204.3, 161.7, 142.9, 134.1, 128.0, 127.7, 125.6, 124.3, 122.6, 119.5, 118.8, 26.5; **HRMS**: calcd 218.0396 for C₁₂H₁₀O₂S [M+H]⁺ found 218.0397.

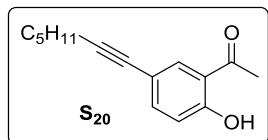


³ Y. Xie, Y. Liu, G. Gong, A. Rinderspacher, S. X. Deng, D. H. Smith, U. Toebben, E. Tzilianos, L. Branden, D. Vidovic, C. Chung, S. Schurer, L. Tautz, D. W. Landry, *Bioorg. Med. Chem. Lett.* 2008, **18**, 2840-2844.

- **Synthesis of compound S₁₉**

Compound **S₁₉** was prepared by using literature known procedure.³ A 50 mL oven-dried round bottom flask was evacuated and back-filled with argon and charged with compound **S₄** (262 mg, 1.00 mmol), benzofuran-2-ylboronic acid (322 mg, 2.00 mmol), K₂CO₃ (552 mg, 4 mmol), degassed THF (25 mL), and Pd(PPh₃)₄ (92 mg, 0.08 mmol) were added. The reaction mixture was stirred at 60 °C for 12h. The reaction profile was monitored by TLC. The reaction mixture was cooled to room temperature and mixed with ether. The mixture was filtered through celite and the filtrate was concentrated and purified by flash column chromatography with silica gel using pet. ether/EtOAc as eluent to afford compound **S₁₉**.

R_f: 0.60 (pet. ether/EtOAc = 95/05); 204 mg, **Yield:** 81%; **Physical appearance:** Yellow solid; **M. P.:** 134 °C; **¹H NMR:** (**500 MHz**, CDCl₃) δ = 12.45 (s, 1 H), 8.19 - 8.12 (m, 1 H), 7.86 (dd, *J* = 1.9, 8.8 Hz, 1 H), 7.60 - 7.55 (m, 1 H), 7.55 - 7.49 (m, 1 H), 7.30 (dt, *J* = 1.3, 7.7 Hz, 1 H), 7.28 - 7.22 (m, 1 H), 7.04 (d, *J* = 8.4 Hz, 1 H), 6.87 (s, 1 H), 2.69 (s, 3 H); **¹³C NMR:** (**125 MHz**, CDCl₃) δ = 204.5, 162.5, 154.6, 154.6, 132.8, 129.1, 126.7, 124.1, 123.0, 121.7, 120.7, 119.5, 119.0, 110.9, 100.2, 26.6; **HRMS:** calcd 252.0781 for C₁₆H₁₂O₃ [M]⁺ found 252.0781.

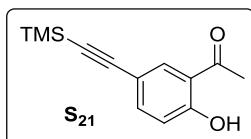


- **Synthesis of compounds S₂₀**

Compound **S₂₀** was prepared by using literature known procedure.⁴ In a 30 mL sealed tube, a solution of 1-(2-hydroxy-5-iodophenyl)ethan-1-one (**S₄**) (262 mg, 1.00 mmol), Pd(PPh₃)₂Cl₂ (14 mg, 0.02 mmol) and CuI (3.8 mg, 0.02 mmol) in dry Et₃N/THF (10 mL, 1:1) was degassed. After 10 min, 1-heptyne (290 μL, 1.10 mmol) was added slowly and mixture was left to stir for 12 h. After completion of reaction (as monitored by TLC) the reaction mixture was filtered through a celite pad. The organic layer was evaporated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography using pet. ether/EtOAc as eluent.

⁴ S. H. Lee, Y. B. Kwon, C. M. Yoon, *Synth. Commun.* 2009, **39**, 4069-4078.

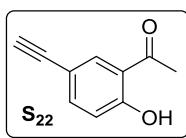
R_f: 0.60 (pet. ether/EtOAc = 98/02); 177 mg, **Yield**: 86%; **Physical appearance**: Yellow liquid; **¹H NMR**: (**500 MHz**, **CDCl₃**) δ = 12.29 (s, 1 H), 7.79 (s, 1 H), 7.49 (d, *J* = 8.8 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 1 H), 2.63 (s, 3 H), 2.40 (t, *J* = 7.1 Hz, 2 H), 1.66 - 1.58 (m, 2 H), 1.47 - 1.33 (m, 4 H), 0.93 (t, *J* = 7.1 Hz, 3 H); **¹³C NMR**: (**125 MHz**, **CDCl₃**) δ = 204.2, 161.7, 139.4, 133.8, 119.4, 118.6, 114.9, 89.4, 79.2, 31.2, 28.5, 26.7, 22.2, 19.3, 14.0; **HRMS**: (**ESI**) calcd 210.0925 for 231.1380 C₁₅H₁₉O₂ [M+H]⁺ found 231.1380.



- **Synthesis of compounds S₂₁**

Compound **S₂₀** was prepared by using literature known procedure.⁴ In a 50 mL round bottom flask, a solution of 1-(2-hydroxy-5-iodophenyl)ethan-1-one (**S₄**) (524 mg, 2.00 mmol), Pd(PPh₃)₂Cl₂ (28 mg, 0.04 mmol) and CuI (7.6 mg, 0.04 mmol) in dry Et₃N/THF (20 mL, 1:1) was degassed. After 10 min, trimethylsilylacetylene (313 μL, 2.20 mmol) was added slowly and mixture was left to stir for 12 h. After completion of reaction (as monitored by TLC) the reaction mixture was filtered through a celite pad. The organic layer was evaporated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography using pet. ether/ EtOAc as eluent.

R_f: 0.50 (pet. ether/EtOAc = 98/02); 366 mg, **Yield**: 79%; **Physical appearance**: Yellow liquid; **¹H NMR**: (**500 MHz**, **CDCl₃**) δ = 12.37 (s, 1 H), 7.86 (d, *J* = 1.9 Hz, 1 H), 7.55 (dd, *J* = 2.1, 8.6 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 1 H), 2.64 (s, 3 H), 0.26 (s, 9 H); **¹³C NMR**: (**125 MHz**, **CDCl₃**) δ = 204.1, 162.4, 139.6, 134.5, 119.4, 118.7, 113.9, 103.8, 93.1, 26.6, -0.1; **HRMS**: (**ESI**) calcd 233.0992 for C₁₃H₁₆O₂Si [M]⁺ found 233.0994.

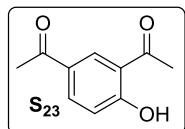


- **Synthesis of compound S₂₂**

Compound **S₁₉** (323 mg, 1.0 mmol) was dissolved in dry THF, cooled to 0 °C, then 1equiv 1(M) TBAF (1 mL, 1.0 mmol) was slowly added, stirred for 1h. After completion of the reaction (as monitored by TLC) water was added, the combined organic layer was washed with brine,

dried over Na_2SO_4 and the resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired products **S₂₂**.

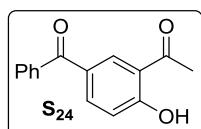
R_f: 0.45 (pet. ether/EtOAc = 98/02); 150 mg, **Yield**: 94%; **Physical appearance**: Yellow solid; **M. P.**: 105 °C; **¹H NMR**: (500 MHz, CDCl_3) δ = 12.39 (s, 1 H), 7.90 (s, 1 H), 7.57 (d, J = 8.5 Hz, 1 H), 6.94 (d, J = 9.2 Hz, 1 H), 3.03 (s, 1 H), 2.64 (s, 3 H); **¹³C NMR**: (125 MHz, CDCl_3) δ = 204.0, 162.6, 139.6, 134.8, 119.4, 118.8, 112.8, 82.4, 76.3, 26.6; **HRMS**: (ESI) calcd 160.0591 for $\text{C}_{10}\text{H}_8\text{O}_2$ [$\text{M}+\text{H}]^+$ found 160.0591.



- **Synthesis of compound S₂₃**⁵

Compound **S₂₂** (107 mg, 0.60 mmol) was taken in a 30 mL sealed tube, AcOH/H₂O (10 mL, 1:1) was added, followed by AgBF₄ (12 mg, 0.06 mmol, 0.1 equiv). The reaction mixture was heated at 80 °C for 12 h. After completion of reaction, acetic acid was quenched by NaHCO₃. The combined organic layer was washed with brine, dried over Na_2SO_4 and the resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired product **S₂₃**.

R_f: 0.50 (pet. ether/EtOAc = 80/20); 90 mg, **Yield**: 84%; **Physical appearance**: White solid; **M. P.**: 136 °C; **¹H NMR**: (500 MHz, CDCl_3) δ = 12.67 (s, 1 H), 8.42 (s, 1 H), 8.05 (d, J = 8.5 Hz, 1 H), 7.01 (d, J = 8.5 Hz, 1 H), 2.70 (s, 3 H), 2.58 (s, 3 H); **¹³C NMR**: (125 MHz, CDCl_3) δ = 204.7, 195.6, 166.0, 136.2, 131.8, 128.6, 119.1, 118.5, 26.6, 26.2; **HRMS**: (ESI) calcd 178.2070 for $\text{C}_{10}\text{H}_{10}\text{O}_3$ [$\text{M}+\text{H}]^+$ found 178.2061.



- **Synthesis of 1-(5-benzoyl-2-hydroxyphenyl)ethan-1-one (S₂₄)¹**

Compound **S₂₀** was prepared by Fries rearrangement of *o*-hydroxyacetophenone. To a cooled (0 °C) solution of *o*-hydroxy acetophenone (1.09 g, 8 mmol) in a 30 mL sealed tube, was added triflic acid (15 mL) followed by slow addition of benzoyl chloride (0.9 mL, 8 mmol) over 10 min

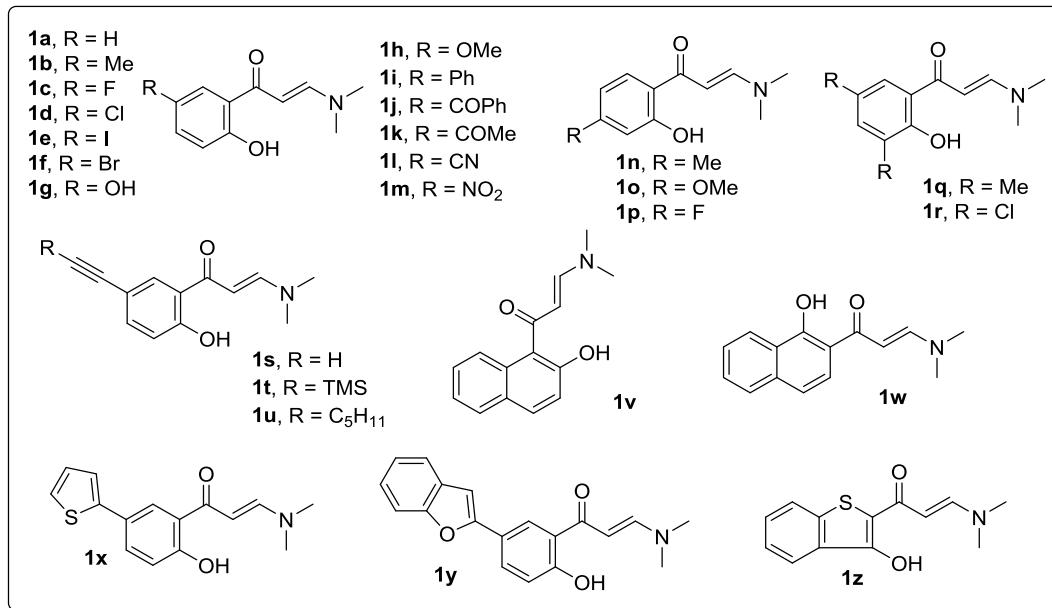
⁵ Z.-W. Chen, D.-N. Ye, Y.-P. Qian, M. Ye, L.-X. Liu, *Tetrahedron* 2013, **69**, 6116-6120.

under N₂ atmosphere. The reaction was kept at room temperature for 12h. The reaction mixture was allowed to cool to 0 °C and quenched with ice-cold water. The reaction mixture was diluted with EtOAc (20 mL). The organic layer was washed two times with 2(N) HCl. Then the organic layer was washed thoroughly with saturated sodium bicarbonate solution and dried over Na₂SO₄. The solvent was removed under reduced pressure and resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to afford S₂₄.

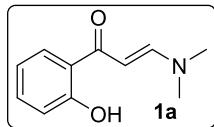
R_f: 0.50 (pet. ether/EtOAc = 90/10); 326 mg, **Yield:** 17%; **Physical appearance:** Pale brown solid; **M. P.:** 85 °C; **¹H NMR:** (**500 MHz, CDCl₃**) δ = 12.68 (br. s., 1 H), 8.32 (d, *J* = 1.9 Hz, 1 H), 7.91 (dd, *J* = 2.3, 8.8 Hz, 1 H), 7.78 - 7.68 (m, 2 H), 7.61 - 7.54 (m, 1 H), 7.51 - 7.45 (m, 2 H), 7.00 (d, *J* = 8.8 Hz, 1 H), 2.64 (s, 3 H); **¹³C NMR:** (**125 MHz, CDCl₃**) δ = 204.6, 194.3, 165.6, 137.9, 137.4, 133.7, 132.2, 129.5, 128.4, 128.3, 119.0, 118.2, 26.5; **HRMS:** (**ESI**) calcd 241.0859 for C₁₅H₁₃O₃ [M+H]⁺ found 241.0855.

2.2 General procedure for the synthesis of *o*-hydroxyarylenaminones

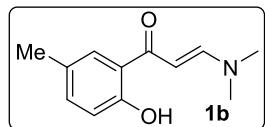
An oven dried sealed tube equipped with a stirring bar, filled with ketones (0.5 mmol), followed by of *N,N*-Dimethylformamide dimethyl acetal (DMF-DMA) (2.0 mmol) in toluene (5 mL). The reaction was allowed to stir at 80 °C for 6-8h until the complete conversion of starting material as monitored by TLC. The reaction mixture was then concentrated and was purified by flash column chromatography (silica gel, pet. ether/EtOAc) to afford the desired products **1**. Compounds **1i**, **1v**, **1z** were used as such for next step, without further purification.



- Characterization data

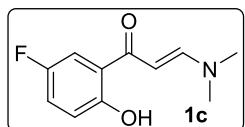


Compound 1a: R_f : 0.30 (pet. ether/EtOAc = 70/30); 87 mg, Yield: 91%; **Physical appearance:** Yellow solid; **M. P.:** 130 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 13.98 (s, 1 H), 7.87 (d, *J* = 12.2 Hz, 1 H), 7.70 (dd, *J* = 1.1, 8.0 Hz, 1 H), 7.41 - 7.30 (m, 1 H), 7.03 - 6.87 (m, 1 H), 6.87 - 6.71 (m, 1 H), 5.77 (d, *J* = 12.2 Hz, 1 H), 3.17 (br. s., 3 H), 2.95 (br. s., 3 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 191.4, 162.9, 154.7, 133.9, 128.2, 120.3, 118.1, 117.9, 90.0, 45.3, 37.3; **HRMS:** (ESI) calcd 192.1019 for C₁₁H₁₃NO₂ [M+H]⁺ found 192.1021.

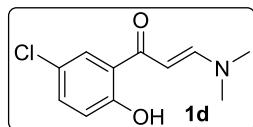


Compound 1b: R_f : 0.40 (pet. ether/EtOAc = 70/30); 91 mg, Yield: 89%; **Physical appearance:** Yellow solid; **M. P.:** 138 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 13.75 (s, 1 H), 7.85 (d, *J* = 12.2 Hz, 1 H), 7.47 (s, 1 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 5.76 (d, *J* = 12.2 Hz, 1 H), 3.16 (br. s., 3 H), 2.96 (br. s., 3 H), 2.29 (s, 3 H); **¹³C NMR:** (125 MHz, CDCl₃) δ =

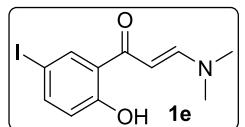
191.4, 160.7, 154.6, 134.8, 128.1, 126.8, 119.9, 117.8, 90.0, 45.3, 37.4, 20.6; **HRMS: (ESI)** calcd 206.1176 for $C_{12}H_{15}NO_2$ $[M+H]^+$ found 206.1178.



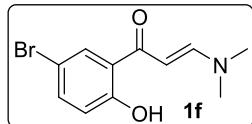
Compound 1c: R_f : 0.40 (pet. ether/EtOAc = 70/30); 94 mg, Yield: 90%; **Physical appearance:** Brown solid; **M. P.:** 144 °C; **1H NMR:** (500 MHz, CDCl₃) δ = 13.67 (s, 1 H), 7.89 (d, J = 11.8 Hz, 1 H), 7.35 (dd, J = 3.1, 9.5 Hz, 1 H), 7.07 (dt, J = 3.1, 8.6 Hz, 1 H), 6.87 (dd, J = 4.8, 9.0 Hz, 1 H), 5.65 (d, J = 12.2 Hz, 1 H), 3.20 (s, 3 H), 2.97 (s, 3 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 190.2, 158.9, 155.6-153.7 (d, J = 12.2 Hz), 155.2, 121.1-120.9 (d, J = 12.2 Hz), 120.1-120.0 (d, J = 5.7 Hz), 119.1-119.0 (d, J = 7.6 Hz), 113.5-113.3 (d, J = 23.8 Hz), 89.7, 45.5, 37.4; **HRMS: (ESI)** calcd 210.0925 for $C_{11}H_{12}FNO_2$ $[M+H]^+$ found 210.0916.



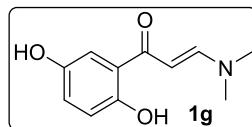
Compound 1d: R_f : 0.40 (pet. ether/EtOAc = 70/30); 105 mg, Yield: 94%; **Physical appearance:** Yellow solid; **M. P.:** 142 °C; **1H NMR:** (500 MHz, CDCl₃) δ = 13.93 (s, 1 H), 7.89 (d, J = 12.2 Hz, 1 H), 7.63 (d, J = 2.3 Hz, 1 H), 7.29 (dd, J = 2.7, 8.8 Hz, 1 H), 6.88 (d, J = 8.8 Hz, 1 H), 5.68 (d, J = 11.8 Hz, 1 H), 3.21 (s, 3 H), 2.99 (s, 3 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 190.1, 161.4, 155.2, 133.6, 127.5, 122.5, 121.1, 119.7, 89.7, 45.5, 37.5; **HRMS: (ESI)** calcd 226.0629 for $C_{11}H_{13}O_2NCl$ $[M+H]^+$ found 226.0633.



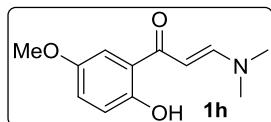
Compound 1e: R_f : 0.40 (pet. ether/EtOAc = 70/30); 148 mg, Yield: 94%; **Physical appearance:** Yellow solid; **M. P.:** 145 °C; **1H NMR:** (500 MHz, CDCl₃) δ = 14.02 (s, 1 H), 7.93 (d, J = 1.5 Hz, 1 H), 7.88 (d, J = 11.8 Hz, 1 H), 7.57 (dd, J = 1.5, 8.8 Hz, 1 H), 6.71 (d, J = 8.8 Hz, 1 H), 5.65 (d, J = 12.2 Hz, 1 H), 3.20 (s, 3 H), 2.99 (s, 3 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 189.8, 162.6, 155.3, 142.1, 136.5, 122.6, 120.7, 89.6, 79.0, 45.5, 37.6; **HRMS: (ESI)** calcd 317.9985 for $C_{11}H_{13}O_2NI$ $[M+H]^+$ found 317.9986.



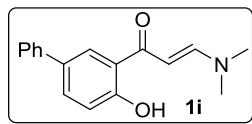
Compound 1f: R_f : 0.40 (pet. ether/EtOAc = 70/30); 124 mg, Yield: 92%; **Physical appearance:** Yellow solid; **M. P.:** 152 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 13.97 (s, 1 H), 7.89 (d, J = 12.2 Hz, 1 H), 7.77 (d, J = 2.7 Hz, 1 H), 7.41 (dd, J = 2.3, 8.8 Hz, 1 H), 6.83 (d, J = 8.8 Hz, 1 H), 5.67 (d, J = 12.2 Hz, 1 H), 3.21 (s, 3 H), 2.99 (s, 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.0, 161.9, 155.3, 136.4, 130.5, 121.7, 120.1, 109.5, 89.7, 45.5, 37.6; **HRMS:** (ESI) calcd 270.0124 for C₁₁H₁₃O₂NBr [M+H]⁺ found 270.0129.



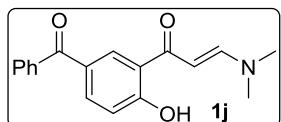
Compound 1g: R_f : 0.30 (pet. ether/EtOAc = 40/60); 66 mg, Yield: 64%; **Physical appearance:** Yellow solid; **M. P.:** 205 °C; **$^1\text{H NMR}$:** (500 MHz, DMSO-d₆) δ = 13.23 (s, 1 H), 8.28 (br. s., 1 H), 7.76 (d, J = 11.8 Hz, 1 H), 7.09 (br. s., 1 H), 6.90 - 6.73 (m, 1 H), 6.65 (d, J = 8.8 Hz, 1 H), 5.63 (d, J = 12.2 Hz, 1 H), 3.12 (br. s., 3 H), 2.88 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.6, 155.3, 154.2, 148.1, 121.9, 119.7, 117.7, 113.2, 89.6, 44.9, 36.9; **HRMS:** (ESI) calcd 208.0968 for C₁₁H₁₄O₃N [M+H]⁺ found 208.0970.



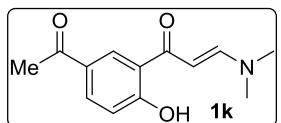
Compound 1h: R_f : 0.40 (pet. ether/EtOAc = 60/40); 93 mg, Yield: 85%; **Physical appearance:** Yellow solid; **M. P.:** 107 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 13.41 (s, 1 H), 7.88 (d, J = 12.2 Hz, 1 H), 7.24 - 7.15 (m, 1 H), 7.00 (dd, J = 2.4, 8.8 Hz, 1 H), 6.88 (d, J = 8.8 Hz, 1 H), 5.71 (d, J = 12.2 Hz, 1 H), 3.80 (s, 3 H), 3.18 (br. s., 3 H), 2.96 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 191.0, 157.0, 154.8, 151.2, 120.6, 120.1, 118.6, 112.7, 90.0, 56.1, 45.4, 37.4; **HRMS:** (ESI) calcd 222.1125 for C₁₂H₁₆O₃N [M+H]⁺ found 222.1126.



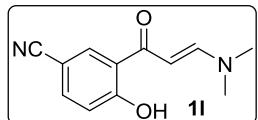
Compound 1i: The compound **1i** was found to be unstable and used as such without further purification.



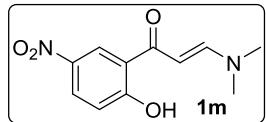
Compound 1j: **R_f:** 0.30 (pet. ether/EtOAc = 70/30); 103 mg, Yield: 70%; **Physical appearance:** Reddish solid; **M. P.:** 142 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 14.81 (br. s., 1 H), 8.36 (br. s., 1 H), 7.94 (d, *J* = 12.2 Hz, 1 H), 7.86 - 7.64 (m, 3 H), 7.64 - 7.53 (m, 1 H), 7.53 - 7.39 (m, 2 H), 6.95 (d, *J* = 8.5 Hz, 1 H), 5.81 (d, *J* = 11.6 Hz, 1 H), 3.22 (br. s., 3 H), 2.99 (br. s., 3 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 195.2, 190.8, 167.1, 155.4, 138.1, 136.2, 131.9, 131.2, 129.6, 128.2, 127.4, 120.0, 117.8, 89.7, 45.6, 37.6; **HRMS:** (ESI) calcd 296.1281 for C₁₈H₁₈O₃N [M+H]⁺ found 296.1283.



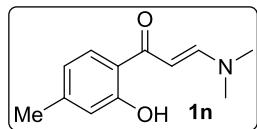
Compound 1k: **R_f:** 0.30 (pet. ether/EtOAc = 60/40); 90 mg, Yield: 77%; **Physical appearance:** Yellow solid; **M. P.:** 112 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 14.80 (br. s., 1 H), 8.35 (br. s., 1 H), 7.90 (br. s., 2 H), 6.91 (br. s., 1 H), 5.82 (d, *J* = 11.8 Hz, 1 H), 3.19 (br. s., 3 H), 2.99 (br. s., 3 H), 2.54 (br. s., 3 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 196.4, 190.7, 167.3, 155.4, 134.2, 129.1, 127.6, 119.7, 118.0, 89.5, 45.5, 37.6, 26.2; **HRMS:** (ESI) calcd 234.1125 for C₁₃H₁₆O₃N [M+H]⁺ found 234.1125.



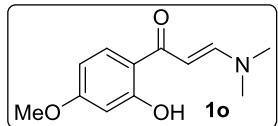
Compound 1l: **R_f:** 0.30 (pet. ether/EtOAc = 70/30); 96 mg, Yield: 89%; **Physical appearance:** Yellow solid; **M. P.:** 176 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 8.04 - 7.96 (m, 1 H), 7.93 (d, *J* = 11.6 Hz, 1 H), 7.55 (d, *J* = 8.5 Hz, 1 H), 6.95 (d, *J* = 8.5 Hz, 1 H), 5.68 (d, *J* = 12.2 Hz, 1 H), 3.24 (s, 3 H), 3.02 (s, 3 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 189.3, 166.6, 155.7, 136.3, 133.2, 120.5, 119.5, 119.2, 100.9, 89.2, 45.7, 37.6; **HRMS:** (ESI) calcd 217.0972 for C₁₂H₁₃O₂N₂ [M+H]⁺ found 217.0972.



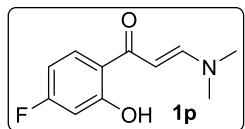
Compound 1m: R_f : 0.30 (pet. ether/EtOAc = 60/40); 99 mg, Yield: 84%; **Physical appearance:** Yellow solid; **M. P.:** 188 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 15.23 (s, 1 H), 8.65 - 8.60 (m, 1 H), 8.22 (dd, J = 2.3, 8.8 Hz, 1 H), 7.98 (d, J = 11.8 Hz, 1 H), 6.98 (d, J = 9.2 Hz, 1 H), 5.79 (d, J = 11.8 Hz, 1 H), 3.27 (s, 3 H), 3.07 (s, 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 189.4, 168.8, 156.0, 138.8, 128.8, 124.7, 119.1, 119.0, 89.1, 45.8, 37.8; **HRMS:** (ESI) calcd 237.0870 for C₁₁H₁₃O₄N₂ [M+H]⁺ found 237.0870.



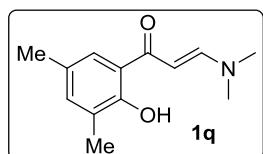
Compound 1n: R_f : 0.40 (pet. ether/EtOAc = 70/30); 86 mg, Yield: 84%; **Physical appearance:** Greenish-yellow solid; **M. P.:** 129 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.04 - 13.90 (m, 1 H), 7.85 (d, J = 12.2 Hz, 1 H), 7.58 (d, J = 8.4 Hz, 1 H), 6.74 (s, 1 H), 6.63 (d, J = 8.0 Hz, 1 H), 5.74 (d, J = 12.2 Hz, 1 H), 3.16 (br. s., 3 H), 2.95 (br. s., 3 H), 2.32 (s, 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 191.2, 163.0, 154.4, 145.0, 128.1, 119.2, 118.3, 117.8, 89.9, 45.2, 37.3, 21.7; **HRMS:** (ESI) calcd 206.1176 for C₁₂H₁₆O₂N [M+H]⁺ found 206.1175.



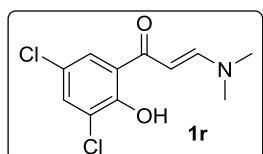
Compound 1o: R_f : 0.40 (pet. ether/EtOAc = 60/40); 78 mg, Yield: 71%; **Physical appearance:** Yellow solid; **M. P.:** 140 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.49 (s, 1 H), 7.83 (d, J = 12.2 Hz, 1 H), 7.61 (d, J = 9.2 Hz, 1 H), 6.41 (d, J = 2.3 Hz, 1 H), 6.38 (dd, J = 2.3, 8.8 Hz, 1 H), 5.67 (d, J = 12.2 Hz, 1 H), 3.81 (s, 3 H), 3.16 (br. s., 3 H), 2.94 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.5, 165.5, 164.3, 154.0, 129.7, 113.8, 106.3, 101.0, 89.7, 55.3, 45.2, 37.3; **HRMS:** (ESI) calcd 222.1125 for C₁₂H₁₆O₃N [M+H]⁺ found 222.1117.



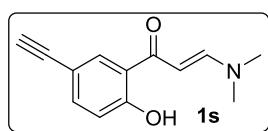
Compound 1p: R_f : 0.40 (pet. ether/EtOAc = 70/30); 92 mg, **Yield:** 88%; **Physical appearance:** Yellow solid; **M. P.:** 134 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.47 - 14.42 (m, 1 H), 7.87 (d, *J* = 11.8 Hz, 1 H), 7.70 - 7.65 (m, 1 H), 6.60 (d, *J* = 10.7 Hz, 1 H), 6.57 - 6.46 (m, 1 H), 5.67 (d, *J* = 11.8 Hz, 1 H), 3.19 (br. s., 3 H), 2.97 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.4, 167.0-165.0 (d, *J* = 252.7 Hz), 165.4-165.2 (d, *J* = 13.4 Hz), 154.7, 130.2-130.1 (d, *J* = 11.4 Hz), 117.0 (d, *J* = 2.9 Hz), 105.8-105.7 (d, *J* = 21.9 Hz), 104.7-104.5 (d, *J* = 22.9 Hz), 89.7, 45.4, 37.4; **HRMS:** (ESI) calcd 210.0925 for C₁₁H₁₃O₂NF [M+H]⁺ found 210.0917.



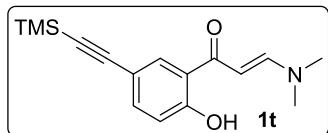
Compound 1q: R_f : 0.30 (pet. ether/EtOAc = 80/20); 101 mg, **Yield:** 92%; **Physical appearance:** Golden-yellow solid; **M. P.:** 126 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.04 (s, 1 H), 7.86 (d, *J* = 12.2 Hz, 1 H), 7.34 (s, 1 H), 7.07 (s, 1 H), 5.78 (d, *J* = 12.2 Hz, 1 H), 3.16 (br. s., 3 H), 2.96 (br. s., 3 H), 2.24 (s, 3 H), 2.27 (s, 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 191.8, 159.2, 154.5, 135.9, 126.6, 126.0, 125.6, 119.1, 90.2, 45.2, 37.4, 20.6, 15.6; **HRMS:** (ESI) calcd 220.1332 for C₁₃H₁₈O₂N [M+H]⁺ found 220.1322.



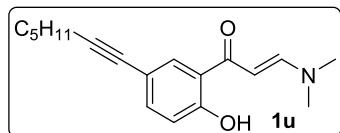
Compound 1r: R_f : 0.30 (pet. ether/EtOAc = 80/20); 110 mg, **Yield:** 85%; **Physical appearance:** Yellow solid; **M. P.:** 159 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.92 (s, 1 H), 7.91 (d, *J* = 11.7 Hz, 1 H), 7.54 (d, *J* = 2.0 Hz, 1 H), 7.42 (d, *J* = 2.0 Hz, 1 H), 5.63 (d, *J* = 12.2 Hz, 1 H), 3.22 (s, 3 H), 3.00 (s, 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 189.2, 157.6, 155.9, 133.1, 126.1, 123.2, 122.0, 121.5, 89.4, 45.7, 37.6; **HRMS:** (ESI) calcd 260.0240 for C₁₁H₁₂O₂NCl₂ [M+H]⁺ found 260.0228.



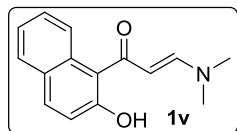
Compound 1s: R_f : 0.30 (pet. ether/EtOAc = 40/60); 65 mg, **Yield:** 61%; **Physical appearance:** Yellow solid; **M. P.:** 160 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.30 (s, 1 H), 7.87 (d, J = 12.2 Hz, 1 H), 7.84 (s, 1 H), 7.45 (d, J = 8.4 Hz, 1 H), 6.87 (d, J = 8.4 Hz, 1 H), 5.72 (d, J = 11.8 Hz, 1 H), 3.18 (br. s., 3 H), 3.00 (s, 1 H), 2.96 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.4, 163.5, 155.1, 137.2, 132.4, 120.1, 118.5, 111.3, 89.6, 83.6, 75.3, 45.4, 37.5; **HRMS:** (ESI) calcd 216.1019 for C₁₃H₁₄O₂N [M+H]⁺ found 216.1019.



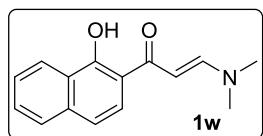
Compound 1t: R_f : 0.30 (pet. ether/EtOAc = 70/30); 119 mg, **Yield:** 83%; **Physical appearance:** Yellow solid; **M. P.:** 193 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.30 (br. s., 1 H), 7.87 (d, J = 11.8 Hz, 1 H), 7.81 (br. s., 1 H), 7.44 (d, J = 8.8 Hz, 1 H), 6.85 (d, J = 8.4 Hz, 1 H), 5.74 (d, J = 12.2 Hz, 1 H), 3.18 (br. s., 3 H), 2.98 (br. s., 3 H), 0.25 (br. s., 9 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.5, 163.4, 155.1, 137.3, 132.1, 120.0, 118.4, 112.5, 105.1, 91.9, 89.8, 45.4, 37.5, 0.0; **HRMS:** (ESI) calcd 288.1414 for C₁₆H₂₂O₂NSi [M+H]⁺ found 288.1414.



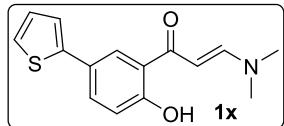
Compound 1u: R_f : 0.30 (pet. ether/EtOAc = 80/20); 130 mg, **Yield:** 91%; **Physical appearance:** Yellow solid; **M. P.:** 104 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.13 (s, 1 H), 7.88 (d, J = 11.7 Hz, 1 H), 7.74 (s, 1 H), 7.38 (d, J = 8.8 Hz, 1 H), 6.85 (d, J = 8.3 Hz, 1 H), 5.75 (d, J = 12.2 Hz, 1 H), 3.19 (s, 3 H), 2.98 (s, 3 H), 2.39 (t, J = 7.1 Hz, 2 H), 1.61 (quin, J = 7.2 Hz, 2 H), 1.49 - 1.32 (m, 4 H), 0.93 (t, J = 7.1 Hz, 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.7, 162.5, 155.0, 137.0, 131.4, 120.0, 118.3, 113.5, 89.9, 88.3, 80.1, 45.4, 37.5, 31.2, 28.6, 22.2, 19.3, 14.0; **HRMS:** (ESI) calcd 286.1802 for C₁₈H₂₄O₂N [M+H]⁺ found 286.1801.



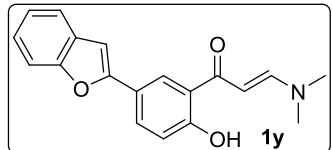
Compound 1v: The compound 1v was found to be unstable and used as such without further purification.



Compound 1w: R_f : 0.30 (pet. ether/EtOAc = 70/30); 113 mg, **Yield:** 94%; **Physical appearance:** Brown solid; **M. P.:** 171 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 15.98 (s, 1 H), 8.46 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 12.2 Hz, 1 H), 7.74 (d, J = 8.0 Hz, 1 H), 7.67 (d, J = 9.2 Hz, 1 H), 7.59 - 7.53 (m, 1 H), 7.52 - 7.46 (m, 1 H), 7.22 (d, J = 8.8 Hz, 1 H), 5.81 (d, J = 11.8 Hz, 1 H), 3.13 (br. s., 3 H), 2.93 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 191.2, 162.5, 154.5, 136.4, 128.7, 127.1, 125.9, 125.2, 123.9, 117.0, 113.1, 90.1, 45.3, 37.3; **HRMS:** (ESI) calcd 242.1176 for C₁₅H₁₆O₂N [M+H]⁺ found 242.1165.

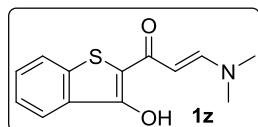


Compound 1x: R_f : 0.30 (pet. ether/EtOAc = 70/30); 114 mg, **Yield:** 84%; **Physical appearance:** Yellow solid; **M. P.:** 120 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.09 (br. s., 1 H), 7.90 (d, J = 12.2 Hz, 1 H), 7.88 (d, J = 2.3 Hz, 1 H), 7.60 (dd, J = 2.1, 8.6 Hz, 1 H), 7.26 - 7.15 (m, 2 H), 7.06 (dd, J = 3.8, 5.0 Hz, 1 H), 6.96 (d, J = 8.8 Hz, 1 H), 5.80 (d, J = 12.2 Hz, 1 H), 3.18 (br. s., 3 H), 2.98 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 191.0, 162.6, 155.0, 144.2, 131.9, 127.9, 125.7, 124.7, 123.7, 122.2, 120.3, 118.6, 89.8, 45.4, 37.4; **HRMS:** (ESI) calcd 274.0896 for C₁₅H₁₆O₂N [M+H]⁺ found 274.0882.

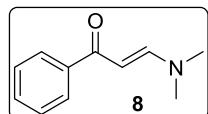


Compound 1y: R_f : 0.30 (pet. ether/EtOAc = 70/30); 136 mg, **Yield:** 89%; **Physical appearance:** Yellow solid; **M. P.:** 175 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 14.36 (br. s., 1 H), 8.17 (d, J = 1.9 Hz, 1 H), 7.93 (d, J = 12.2 Hz, 1 H), 7.81 (dd, J = 2.1, 8.6 Hz, 1 H), 7.60 - 7.48 (m, 2 H), 7.29 - 7.19 (m, 2 H), 7.02 (d, J = 8.4 Hz, 1 H), 6.89 (s, 1 H), 5.88 (d, J = 12.2 Hz, 1 H), 3.19 (br. s., 3 H), 3.02 (br. s., 3 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 190.9, 163.6, 155.8,

155.2, 154.6, 130.7, 129.4, 124.6, 123.7, 122.8, 120.7, 120.5, 120.2, 118.8, 110.9, 99.5, 89.8, 45.4, 37.6; **HRMS: (ESI)** calcd 308.1281 for $C_{19}H_{18}O_3N$ $[M+H]^+$ found 308.1265.



Compound 1z: The compound **1z** was found to be unstable and used as such without further purification.

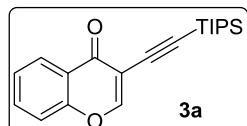


Compound 8: R_f : 0.30 (pet. ether/EtOAc = 40/60); 70 mg, **Yield:** 81%; **Physical appearance:** Yellow solid; **M. P.:** 89 °C; **1H NMR:** (500 MHz, CDCl₃) δ = 7.88 (d, J = 6.5 Hz, 2 H), 7.78 (dd, J = 2.1, 10.1 Hz, 1 H), 7.48 - 7.34 (m, 3 H), 5.75 - 5.63 (m, 1 H), 3.10 (br. s., 3 H), 2.89 (br. s., 3 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 188.5, 154.1, 140.4, 130.7, 128.0, 127.4, 44.9, 37.2; **HRMS: (ESI)** calcd 176.1070 for $C_{11}H_{14}ON$ $[M+H]^+$ found 176.1061.

2.3 Procedure for the synthesis of 3-alkynyl chromones (3):

An oven dried sealed tube equipped with a stirring bar, filled with argon *o*-hydroxyarylenaminones (0.2 mmol, 1.0 equiv), TIPS-EBX (0.24 mmol, 1.2 equiv), AuCl (5 mol %), dry DCE (2.0 mL) were added under a stream of argon flow in the reaction vessel. The reaction was allowed to stir at room temperature for 12h until and unless noted in the specific examples. The reaction mixture was then concentrated and resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired products **3** (33-96% yield).

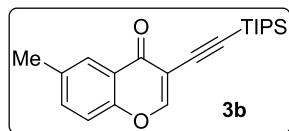
- **Characterization Data:**



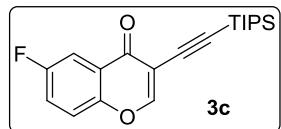
Compound 3a: R_f : 0.50 (pet. ether/EtOAc = 95/05); 61 mg, Yield: 93%; **Physical appearance:** Brown liquid; **1H NMR:** (500 MHz, CDCl₃) δ = 8.25 (dd, J = 1.5, 8.0 Hz, 1 H), 8.18 (s, 1 H), 7.68 (ddd, J = 1.5, 7.2, 8.5 Hz, 1 H), 7.46 (d, J = 8.4 Hz, 1 H), 7.44 - 7.40 (m, 1 H), 1.16 (s, 21

H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 175.4, 158.4, 155.9, 133.8, 126.1, 125.7, 123.7, 118.1, 111.6, 97.8, 96.6, 18.6, 11.2; **HRMS:** (ESI) calcd 327.1775 for C₂₀H₂₇O₂Si [M+H]⁺ found 327.1759.

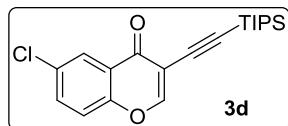
Compound **3a** was synthesized in large scale in decent yield. An oven dried 2-neck round bottom flask was equipped with a stirring bar, filled with argon *o*-hydroxyphenylenaminone (0.764 g, 4 mmol, 1.0 equiv), TIPS-EBX (2.05g, 4.8 mmol, 1.2 equiv), AuCl (46 mg, 5 mol%), dry DCE (40.0 mL) were added under a stream of argon flow in the reaction vessel. The reaction was allowed to stir at room temperature for 12 h. The reaction mixture was then concentrated and resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired products **3a** in 83% yield (1.08 g).



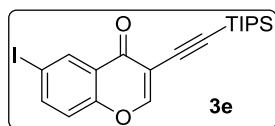
Compound 3b: R_f: 0.50 (pet. ether/EtOAc = 95/05); 65 mg, **Yield:** 96%; **Physical appearance:** White solid; **M. P.:** 94 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 8.14 (s, 1 H), 8.03 - 7.97 (m, 1 H), 7.46 (dd, J = 2.1, 8.6 Hz, 1 H), 7.34 (d, J = 8.4 Hz, 1 H), 2.44 (s, 3 H), 1.15 (s, 21 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 175.5, 158.3, 154.2, 135.7, 135.0, 125.4, 123.3, 117.9, 111.3, 97.5, 96.8, 21.0, 18.6, 11.2; **HRMS:** (ESI) calcd 341.1931 for C₂₁H₂₉O₂Si [M+H]⁺ found 341.1909.



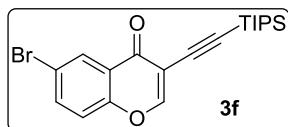
Compound 3c: R_f: 0.50 (pet. ether/EtOAc = 95/05); 58 mg, Yield: 84%; **Physical appearance:** White solid; **M. P.:** 95 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 8.18 (s, 1 H), 7.87 (dd, J = 3.1, 8.4 Hz, 1 H), 7.48 (dd, J = 4.2, 9.2 Hz, 1 H), 7.40 (dt, J = 3.1, 8.4 Hz, 1 H), 1.15 (s, 21 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 174.7, 160.7-158.7 (d, J = 247.0 Hz), 158.5, 152.1, 124.9-124.8 (d, J = 7.6 Hz), 122.2-122.0 (d, J = 25.8 Hz), 120.4-120.3 (d, J = 7.6 Hz), 111.1-110.9 (d, J = 23.8 Hz), 111.0, 98.3, 96.1, 18.6, 11.2; **HRMS:** (ESI) calcd 345.1681 for C₁₂H₁₃O₂N₂ (M⁺ + H) found 345.1675.



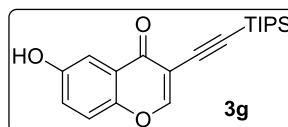
Compound 3d: R_f : 0.50 (pet. ether/EtOAc = 95/05); 66 mg, Yield: 91%; **Physical appearance:** Pale yellow solid; **M. P.:** 91 °C; **^1H NMR:** (500 MHz, CDCl₃) δ = 8.19 (d, J = 2.7 Hz, 1 H), 8.17 (s, 1 H), 7.61 (dd, J = 2.5, 9.0 Hz, 1 H), 7.42 (d, J = 8.8 Hz, 1 H), 1.16 - 1.14 (m, 21 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 174.3, 158.4, 1514.2, 134.1, 131.6, 125.5, 124.5, 119.9, 111.7, 98.5, 96.0, 18.6, 11.2; **HRMS:** (ESI) calcd 361.1385 for C₂₀H₂₆O₂ClSi [M+H]⁺ found 361.1382.



Compound 3e: R_f : 0.40 (pet. ether/EtOAc = 98/02); 79 mg, Yield: 87%; **Physical appearance:** Pale yellow solid; **M. P.:** 92 °C; **^1H NMR:** (400 MHz, CDCl₃) δ = 8.55 (d, J = 2.0 Hz, 1 H), 8.16 (s, 1 H), 7.92 (dd, J = 2.4, 8.8 Hz, 1 H), 7.22 (d, J = 8.8 Hz, 1 H), 1.15 (s, 21 H); **^{13}C NMR:** (100 MHz, CDCl₃) δ = 173.9, 158.4, 155.3, 142.4, 135.0, 125.2, 120.2, 111.9, 98.6, 96.0, 89.5, 18.6, 11.2; **HRMS:** (ESI) calcd 453.0741 for C₂₀H₂₆O₂ISi [M+H]⁺ found 453.0732.

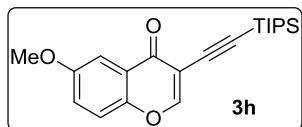


Compound 3f: R_f : 0.40 (pet. ether/EtOAc = 98/02); 75 mg, Yield: 92%; **Physical appearance:** White solid; **M. P.:** 88 °C; **^1H NMR:** (500 MHz, CDCl₃) δ = 8.36 (d, J = 2.7 Hz, 1 H), 8.17 (s, 1 H), 7.75 (dd, J = 2.5, 9.0 Hz, 1 H), 7.36 (d, J = 8.8 Hz, 1 H), 1.15 (s, 21 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 174.1, 158.4, 154.6, 136.8, 128.7, 124.9, 120.1, 119.1, 111.8, 98.6, 96.0, 18.6, 11.2; **HRMS:** (ESI) calcd 405.0880 for C₂₀H₂₆O₂BrSi [M+H]⁺ found 405.0877.

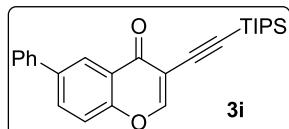


Compound 3g: R_f : 0.50 (pet. ether/EtOAc = 80/20); 51 mg, Yield: 76%; **Physical appearance:** White solid; **M. P.:** 137 °C; **^1H NMR:** (500 MHz, CDCl₃) δ = 8.21 (s, 1 H), 8.05 (d, J = 2.7 Hz, 1 H), 7.73 (br. s., 1 H), 7.39 (d, J = 9.2 Hz, 1 H), 7.29 (dd, J = 3.1, 9.2 Hz, 1 H), 1.16 (s, 21 H);

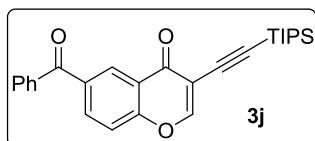
¹³C NMR: (125 MHz, CDCl₃) δ = 176.5, 158.8, 154.9, 150.5, 124.1, 123.9, 119.5, 110.4, 109.5, 97.7, 96.4, 18.6, 11.2; **HRMS:** (ESI) calcd 343.1724 for C₂₀H₂₇O₃Si [M+H]⁺ found 343.1717.



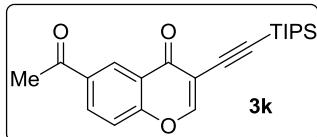
Compound 3h: R_f: 0.50 (pet. ether/EtOAc = 90/10); 58 mg, Yield: 82%; **Physical appearance:** White solid; **M. P.:** 101 °C; **¹H NMR:** (400 MHz, CDCl₃) δ = 8.17 (s, 1 H), 7.68 - 7.53 (m, 1 H), 7.39 (d, J = 8.8 Hz, 1 H), 7.28 - 7.22 (m, 1 H), 3.88 (s, 3 H), 1.16 (s, 21 H); **¹³C NMR:** (100 MHz, CDCl₃) δ = 175.4, 158.1, 157.2, 150.7, 124.3, 123.9, 119.6, 110.7, 105.0, 97.6, 96.8, 55.9, 18.6, 11.2; **HRMS:** (ESI) calcd 357.1880 for C₂₁H₂₉O₃Si [M+H]⁺ found 357.1879.



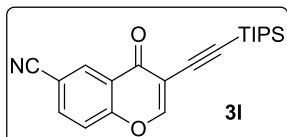
Compound 3i: R_f: 0.60 (pet. ether/EtOAc = 95/05); 52 mg, Yield: 65%; **Physical appearance:** White solid; **M. P.:** 85 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 8.47 (d, J = 2.3 Hz, 1 H), 8.20 (s, 1 H), 7.92 (dd, J = 2.1, 8.6 Hz, 1 H), 7.64 (d, J = 7.6 Hz, 2 H), 7.53 (d, J = 8.8 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 2 H), 7.43 - 7.37 (m, 1 H), 1.17 (s, 21 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 175.5, 158.3, 155.3, 139.1, 138.8, 132.7, 129.0, 128.0, 127.1, 123.9, 123.8, 118.7, 111.6, 98.0, 96.6, 18.6, 11.2; **HRMS:** (ESI) calcd 403.2088 for C₁₂H₁₃O₂N₂ (M⁺ + H) found 403.2065.



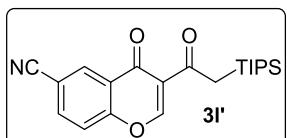
Compound 3j: R_f: 0.40 (pet. ether/EtOAc = 95/05); 61 mg, Yield: 71%; **Physical appearance:** Reddish brown solid; **M. P.:** 103 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 8.59 (d, J = 2.3 Hz, 1 H), 8.26 (dd, J = 2.3, 8.8 Hz, 1 H), 8.22 (s, 1 H), 7.79 (dd, J = 1.3, 8.2 Hz, 2 H), 7.65 - 7.60 (m, 2 H), 7.53 - 7.48 (m, 2 H), 1.16 - 1.14 (m, 21 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 194.7, 175.0, 158.3, 158.0, 136.8, 134.8, 132.9, 129.9, 129.1, 128.6, 122.8, 119.1, 112.3, 99.0, 95.8, 18.6, 11.2; **HRMS:** (ESI) calcd 431.2037 for C₂₇H₃₁O₃Si [M+H]⁺ found 431.2039.



Compound 3k: R_f : 0.50 (pet. ether/EtOAc = 90/10); 47 mg, Yield: 64%; **Physical appearance:** White solid; **M. P.:** 93 °C; **^1H NMR:** (500 MHz, CDCl₃) δ = 8.79 (d, J = 1.9 Hz, 1 H), 8.34 - 8.28 (m, 1 H), 8.20 (s, 1 H), 7.53 (d, J = 8.8 Hz, 1 H), 2.68 (s, 3 H), 1.16 (s, 21 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 196.2, 175.0, 158.3, 158.3, 134.3, 132.9, 127.6, 123.1, 119.0, 112.2, 99.1, 95.7, 26.6, 18.6, 11.2; **HRMS:** (ESI) calcd 369.1880 for C₂₂H₂₉O₃Si [M+H]⁺ found 369.1878.

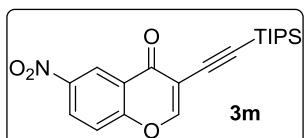


Compound 3l: R_f : 0.55 (pet. ether/EtOAc = 95/05); 23 mg, Yield: 33%; **Physical appearance:** White solid; **M. P.:** 113 °C; **^1H NMR:** (500 MHz, CDCl₃) δ = 8.56 (d, J = 2.3 Hz, 1 H), 8.20 (s, 1 H), 7.90 (dd, J = 1.9, 8.8 Hz, 1 H), 7.59 (d, J = 8.8 Hz, 1 H), 1.16 - 1.14 (m, 21 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 173.6, 158.4, 157.5, 136.1, 131.8, 124.0, 119.9, 117.3, 112.7, 110.0, 99.8, 95.2, 18.6, 11.2; **HRMS:** (ESI) calcd 352.1727 for C₂₁H₂₆O₂NSi [M+H]⁺ found 352.1717.

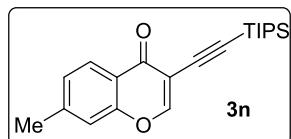


Compound 3l': Hydration product **3l'** was obtained alongwith with **3l**.

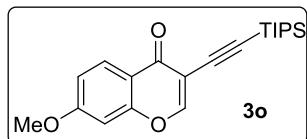
R_f : 0.50 (pet. ether/EtOAc = 95/05); 15 mg, Yield: 21%; **Physical appearance:** White solid; **M. P.:** 152 °C; **^1H NMR:** (500 MHz, CDCl₃) δ = 10.54 (s, 1 H), 8.57 (d, J = 1.9 Hz, 1 H), 7.93 (dd, J = 2.1, 8.6 Hz, 1 H), 7.48 (d, J = 8.8 Hz, 1 H), 1.23 - 1.16 (m, 3 H), 1.10 - 1.07 (m, 18 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 190.2, 180.5, 175.5, 157.0, 136.8, 131.5, 124.5, 119.1, 117.2, 116.0, 110.2, 19.0, 18.4, 11.9; **HRMS:** (ESI) calcd 370.1833 for C₂₁H₂₈O₃NSi [M+H]⁺ found 370.1823.



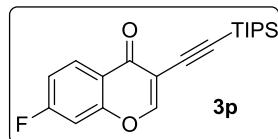
Compound 3m: R_f : 0.60 (pet. ether/EtOAc = 90/10); 36 mg, Yield: 49%; **Physical appearance:** White solid; **M. P.:** 110 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 9.12 (d, J = 2.7 Hz, 1 H), 8.51 (dd, J = 2.7, 9.2 Hz, 1 H), 8.22 (s, 1 H), 7.63 (d, J = 9.2 Hz, 1 H), 1.17 - 1.15 (m, 21 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 173.9, 158.6, 158.3, 145.1, 128.2, 123.7, 122.9, 120.0, 112.5, 100.2, 95.0, 18.6, 11.2; **HRMS:** (ESI) calcd 372.1626 for C₂₀H₂₆O₄NSi [M+H]⁺ found 372.1627.



Compound 3n: R_f : 0.50 (pet. ether/EtOAc = 98/02); 58 mg, Yield: 85%; **Physical appearance:** Brown solid; **M. P.:** 84 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 8.18 - 8.08 (m, 2 H), 7.26 - 7.17 (m, 2 H), 2.48 (s, 3 H), 1.15 (s, 21 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 175.3, 158.2, 156.0, 145.3, 127.2, 125.9, 121.5, 117.9, 111.5, 97.5, 96.8, 21.8, 18.6, 11.3; **HRMS:** (ESI) calcd 341.1931 for C₂₁H₂₉O₂Si [M+H]⁺ found 341.1930.

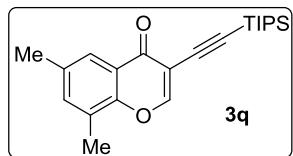


Compound 3o: R_f : 0.50 (pet. ether/EtOAc = 95/05); 58 mg, Yield: 81%; **Physical appearance:** White solid; **M. P.:** 76 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 8.14 (d, J = 9.2 Hz, 1 H), 8.11 (s, 1 H), 7.03 - 6.93 (m, 1 H), 6.83 (br. s., 1 H), 3.90 (s, 3 H), 1.15 (s, 21 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 174.7, 164.1, 158.0, 157.6, 127.5, 117.5, 114.9, 111.5, 100.4, 97.5, 96.7, 55.8, 18.6, 11.2; **HRMS:** (ESI) calcd 357.1880 for C₂₁H₂₉O₃Si [M+H]⁺ found 357.1881.

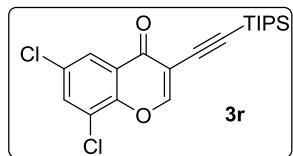


Compound 3p: R_f : 0.60 (pet. ether/EtOAc = 98/02); 60 mg, Yield: 87%; **Physical appearance:** Yellow liquid; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 8.30 - 8.21 (m, 1 H), 8.15 (br. s., 1 H), 7.14 (d, J = 8.4 Hz, 2 H), 1.15 (br. s., 21 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 174.5, 166.6-164.6 (d, J = 256.5 Hz), 158.4, 156.9-156.8 (d, J = 13.4 Hz), 128.8-128.7 (d, J = 11.4 Hz), 120.5,

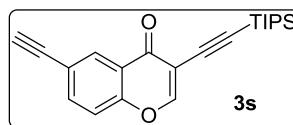
114.6-114.4 (d, $J = 22.9$ Hz), 111.9, 105.0-104.8 (d, $J = 25.8$ Hz), 98.4, 96.0, 18.6, 11.2; **HRMS:** (ESI) calcd 345.1681 for $C_{12}H_{13}O_2N_2$ ($M^+ + H$) found 345.1679.



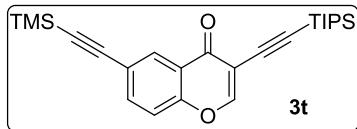
Compound 3q: R_f : 0.50 (pet. ether/EtOAc = 98/02); 63 mg, Yield: 89%; **Physical appearance:** White solid; **M. P.:** 126 °C; **1H NMR:** (400 MHz, CDCl₃) δ = 8.19 (s, 1 H), 7.84 (s, 1 H), 7.31 (s, 1 H), 2.42 (s, 3 H), 2.40 (s, 3 H), 1.15 (s, 21 H); **^{13}C NMR:** (100 MHz, CDCl₃) δ = 175.8, 158.1, 152.7, 136.1, 135.1, 127.2, 123.3, 123.0, 111.1, 97.3, 97.0, 20.9, 18.6, 15.3, 11.2; **HRMS:** (ESI) calcd 355.2088 for C₂₂H₃₁O₂Si [M+H]⁺ found 355.2086.



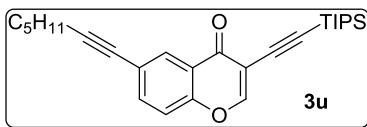
Compound 3r: R_f : 0.40 (pet. ether/EtOAc = 98/02); 66 mg, Yield: 84%; **Physical appearance:** White solid; **M. P.:** 83 °C; **1H NMR:** (500 MHz, CDCl₃) δ = 1H NMR (500MHz, CHLOROFORM-d) δ = 8.23 (s, 1 H), 8.11 (d, $J = 2.3$ Hz, 1 H), 7.72 (d, $J = 2.3$ Hz, 1 H), 1.15 (s, 21 H); **^{13}C NMR:** (125 MHz, CDCl₃) δ = 173.7, 158.2, 150.3, 134.1, 131.4, 125.4, 124.5, 124.2, 112.1, 99.5, 95.4, 18.6, 11.2; **HRMS:** (ESI) calcd 395.0995 for C₂₀H₂₅O₂Cl₂Si [M+H]⁺ found 395.0995.



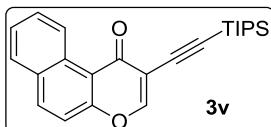
Compound 3s: R_f : 0.60 (pet. ether/EtOAc = 95/05); 33 mg, Yield: 47%; **Physical appearance:** White solid; **M. P.:** 99 °C; **1H NMR:** (500MHz, CDCl₃) δ = 88.36 (d, $J = 1.9$ Hz, 1 H), 8.16 (s, 1 H), 7.74 (dd, $J = 1.9, 8.8$ Hz, 1 H), 7.42 (d, $J = 8.8$ Hz, 1 H), 3.15 (s, 1 H), 1.15 (s, 21 H); **^{13}C NMR:** (125MHz, CDCl₃) δ = 174.5, 158.3, 155.5, 137.0, 130.2, 123.5, 120.0, 118.6, 111.9, 98.4, 96.1, 81.8, 78.6, 18.6, 11.2; **HRMS:** (ESI) calcd 351.1775 for C₁₂H₁₃O₂N₂ ($M^+ + H$) found 351.1777.



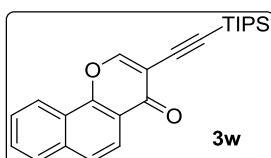
Compound 3t: R_f : 0.60 (pet. ether/EtOAc = 98/02); 64 mg, Yield: 76%; **Physical appearance:** Yellow liquid; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 8.32 (d, J = 1.9 Hz, 1 H), 8.14 (s, 1 H), 7.70 (dd, J = 2.1, 8.6 Hz, 1 H), 7.38 (d, J = 8.8 Hz, 1 H), 1.15 (s, 21 H), 0.27 (s, 9 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 174.5, 158.3, 155.3, 136.8, 129.9, 123.5, 121.1, 118.4, 111.8, 103.0, 98.3, 96.2, 96.0, 18.6, 11.2, -0.2; **HRMS:** (ESI) calcd 423.2170 for C₂₅H₃₅O₂Si₂ [M+H]⁺ found 423.2162.



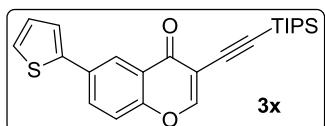
Compound 3u: R_f : 0.70 (pet. ether/EtOAc = 98/02); 75 mg, Yield: 89%; **Physical appearance:** Yellow liquid; **$^1\text{H NMR}$:** (400 MHz, CDCl₃) δ = 8.23 (d, J = 2.0 Hz, 1 H), 8.14 (s, 1 H), 7.63 (dd, J = 2.0, 8.8 Hz, 1 H), 7.36 (d, J = 8.3 Hz, 1 H), 2.41 (t, J = 7.1 Hz, 2 H), 1.47 - 1.33 (m, 4 H), 0.93 (t, J = 7.1 Hz, 3 H); **$^{13}\text{C NMR}$:** (100 MHz, CDCl₃) δ = 174.7, 158.2, 154.8, 136.7, 129.0, 123.5, 122.1, 118.2, 111.6, 98.0, 96.4, 92.1, 79.0, 31.1, 28.2, 22.2, 19.3, 18.6, 14.0, 11.2; **HRMS:** (ESI) calcd 420.6781 for C₂₇H₃₇O₂Si [M+H]⁺ found 420.6780.



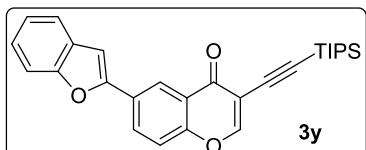
Compound 3v: R_f : 0.60 (pet. ether/EtOAc = 98/02); 48 mg, Yield: 64%; **Physical appearance:** White solid; M. P.: 94 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 10.07 (d, J = 8.4 Hz, 1 H), 8.22 (s, 1 H), 8.08 (d, J = 9.2 Hz, 1 H), 7.90 (d, J = 8.0 Hz, 1 H), 7.78 - 7.72 (m, 1 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.49 (d, J = 9.2 Hz, 1 H), 1.19 (s, 21 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 176.9, 157.1, 156.2, 135.7, 130.7, 130.4, 129.5, 128.2, 127.4, 126.9, 117.4, 117.1, 114.2, 98.0, 97.0, 18.7, 11.3; **HRMS:** (ESI) calcd 377.1931 for C₁₂H₁₃O₂N₂ (M⁺ + H) found 377.1915.



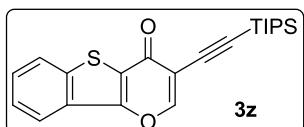
Compound 3w: R_f : 0.60 (pet. ether/EtOAc = 98/02); 61 mg, Yield: 81%; **Physical appearance:** Pale yellow liquid solid; **M. P.:** 109 °C; **$^1\text{H NMR}$:** (500 MHz, CDCl₃) δ = 8.45 (d, J = 8.0 Hz, 1 H), 8.36 (s, 1 H), 8.17 (d, J = 8.8 Hz, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.78 (d, J = 8.8 Hz, 1 H), 7.75 - 7.65 (m, 2 H), 1.18 (s, 21 H); **$^{13}\text{C NMR}$:** (125 MHz, CDCl₃) δ = 175.3, 157.6, 153.3, 135.8, 129.5, 128.1, 127.3, 125.8, 123.8, 122.2, 120.8, 120.0, 112.9, 98.5, 96.5, 18.7, 11.2; **HRMS: (ESI)** calcd 377.1931 for C₂₄H₂₉O₂Si [M+H]⁺ found 377.1906.



Compound 3x: R_f : 0.40 (pet. ether/EtOAc = 95/05); 56 mg, Yield: 68%; **Physical appearance:** White solid; **M. P.:** 169 °C; **$^1\text{H NMR}$:** (400 MHz, CDCl₃) δ = 8.42 (d, J = 2.4 Hz, 1 H), 8.14 (s, 1 H), 7.87 (dd, J = 2.1, 8.9 Hz, 1 H), 7.44 (d, J = 9.2 Hz, 1 H), 7.37 (d, J = 3.1 Hz, 1 H), 7.32 (d, J = 4.9 Hz, 1 H), 7.09 (dd, J = 3.7, 4.9 Hz, 1 H), 1.17 (s, 21 H); **$^{13}\text{C NMR}$:** (100 MHz, CDCl₃) δ = 175.2, 158.2, 154.9, 142.1, 132.2, 131.3, 128.3, 125.9, 124.1, 123.8, 122.1, 118.8, 111.5, 98.1, 96.4, 18.6, 11.2; **HRMS: (ESI)** calcd 409.1652 for C₂₄H₂₉O₂SSi [M+H]⁺ found 409.1625.

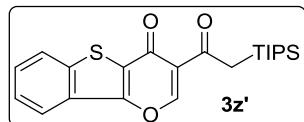


Compound 3y: R_f : 0.40 (pet. ether/EtOAc = 95/05); 71 mg, Yield: 79%; **Physical appearance:** White solid; **M. P.:** 205 °C; **$^1\text{H NMR}$:** (400 MHz, CDCl₃) δ = 8.67 (s, 1 H), 8.23 - 8.03 (m, 2 H), 7.60 (d, J = 7.8 Hz, 1 H), 7.52 (dd, J = 2.2, 8.1 Hz, 2 H), 7.35 - 7.28 (m, 1 H), 7.28 - 7.21 (m, 1 H), 7.09 (s, 1 H), 1.18 (s, 21 H); **$^{13}\text{C NMR}$:** (100 MHz, CDCl₃) δ = 175.1, 158.2, 155.5, 155.0, 153.8, 130.1, 128.9, 128.3, 124.8, 123.8, 123.2, 122.0, 121.2, 118.9, 111.7, 111.3, 102.6, 98.3, 96.4, 18.6, 11.2; **HRMS: (ESI)** calcd 443.2037 for C₂₈H₃₁O₃Si [M+H]⁺ found 443.2038.



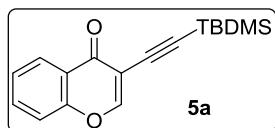
Compound 3z: R_f : 0.45 (pet. ether/EtOAc = 95/05); 28 mg, Yield: 37% (over two steps); **Physical appearance:** White solid; **M. P.:** 97 °C; **$^1\text{H NMR}$:** (200 MHz, CDCl₃) δ = 8.28 (s, 1 H), 8.11 - 8.01 (m, 1 H), 7.91 (dd, J = 1.5, 6.9 Hz, 1 H), 7.57 (m, 2 H), 1.17 (s, 21 H); **$^{13}\text{C NMR}$:**

(**125 MHz, CDCl₃**) δ = 172.0, 156.9, 153.3, 147.0, 139.4, 129.1, 125.4, 123.8, 122.0, 113.4, 111.0, 99.7, 95.7, 18.6, 11.2; **HRMS: (ESI)** calcd 383.1496 for C₂₂H₂₇O₂SSi [M+H]⁺ found 383.1496.

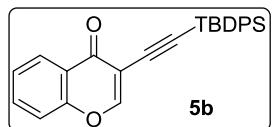


Compound 3z': Hydration product **3z'** was obtained alongwith **3z**.

R_f: 0.40 (pet. ether/EtOAc = 95/05); 20 mg, Yield: 25% (over two steps); **Physical appearance:** White solid; **M. P.:** 139 °C; **¹H NMR:** (**500 MHz, CDCl₃**) δ = 10.63 (s, 1 H), 7.99 (d, J = 8.0 Hz, 1 H), 7.94 (d, J = 8.0 Hz, 1 H), 7.64 - 7.60 (m, 1 H), 7.58 - 7.54 (m, 1 H), 3.22 (s, 2 H), 1.27 - 1.20 (m, 3 H), 1.12 (d, J = 7.2 Hz, 18 H); **¹³C NMR:** (**125 MHz, CDCl₃**) δ = 190.9, 178.6, 174.4, 152.7, 139.7, 129.1, 128.6, 125.6, 125.0, 124.0, 121.6, 116.4, 18.5, 17.9, 11.8; **HRMS: (ESI)** calcd 401.1601 for C₂₂H₂₉O₃SSi [M+H]⁺ found 401.1595.

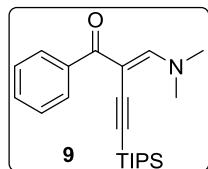


Compound 5a: **R_f:** 0.50 (pet. ether/EtOAc = 98/02); 43 mg, Yield: 76%; **Physical appearance:** White solid; **M. P.:** 91 °C; **¹H NMR:** (**500 MHz, CDCl₃**) δ = 8.25 (dd, J = 1.9, 8.0 Hz, 1 H), 8.17 (s, 1 H), 7.68 (ddd, J = 1.5, 7.1, 8.6 Hz, 1 H), 7.46 (d, J = 8.4 Hz, 1 H), 7.44 - 7.41 (m, 1 H), 1.02 (s, 9 H), 0.21 (s, 6 H); **¹³C NMR:** (**125 MHz, CDCl₃**) δ = 175.3, 158.6, 155.9, 133.9, 126.2, 125.7, 123.7, 118.2, 111.4, 99.6, 95.3, 26.1, 16.7, -4.7; **HRMS: (ESI)** calcd 285.1305 for C₁₇H₂₁O₂Si [M+H]⁺ found 285.1305.



Compound 5b: **R_f:** 0.50 (pet. ether/EtOAc = 98/02); 55 mg, Yield: 68%; **Physical appearance:** White solid; **M. P.:** 131 °C; **¹H NMR:** (**500 MHz, CDCl₃**) δ = 8.30 (dd, J = 1.5, 8.0 Hz, 1 H), 8.28 (s, 1 H), 7.93 - 7.89 (m, 4 H), 7.70 (ddd, J = 1.9, 7.1, 8.6 Hz, 1 H), 7.48 (d, J = 8.4 Hz, 1 H), 7.47 - 7.44 (m, 1 H), 7.44 - 7.41 (m, 6 H), 1.20 (s, 9 H); **¹³C NMR:** (**125 MHz, CDCl₃**) δ =

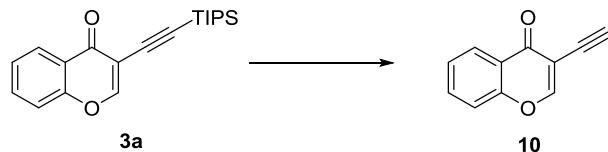
175.3, 158.8, 155.9, 135.7, 134.0, 132.9, 129.5, 127.7, 126.1, 125.8, 123.7, 118.2, 111.3, 98.9, 96.6, 27.1, 18.7; **HRMS: (ESI)** calcd 409.1618 for $C_{27}H_{25}O_2Si$ $[M+H]^+$ found 409.1615.



Compound 9: Compound **9** was found to be highly unstable. R_f : 0.50 (pet. ether/EtOAc = 50/50); 50 mg, Yield: 68%; **Physical appearance:** Yellow liquid; **1H NMR:** (500 MHz, $CDCl_3$) δ = 7.71 - 7.58 (m, 3 H), 7.28 - 7.16 (m, 3 H), 3.47 (br. s., 3 H), 3.07 (br. s., 3 H), 0.83 (s, 21 H); **^{13}C NMR:** (125 MHz, $CDCl_3$) δ = 194.8, 156.1, 140.3, 130.0, 128.5, 127.4, 105.0, 98.1, 91.0, 47.4, 38.5, 18.5, 11.4; **HRMS: (ESI)** calcd 356.2404 for $C_{22}H_{34}ONSi$ $[M+H]^+$ found 356.2400.

2.4 Procedure for synthetic transformations

a) Procedure for synthesis of 3-ethynyl-4H-chromen-4-one (10)

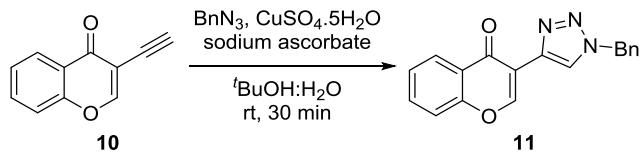


Entry	Reagent	Additives (1 equiv)	Temp	Time (h)	Yield (%)
1	K_2CO_3	-	rt	3	-
2	TBAF	-	0 °C	1	-
3	TBAF	HF.py	0 °C	12	-
4	TBAF	CF_3SO_3H	0 °C – rt	6	trace
5	TBAF	$MsOH$	0 °C – rt	6	-
6	TBAF	$TsOH$	0 °C – rt	6	-
7	TBAF	CH_3COOH	0 °C – rt	6	trace
8	TBAF	CF_3COOH	0 °C – rt	6	trace
9	TBAF	CSA	0 °C – rt	3	79

To a stirred solution of **3a** (978 mg, 3.00 mmole) and CSA (696 mg, 3.00 mmole) in THF (15 mL) was added TBAF (1.0 M in THF, 3.3 mL, 3.30 mmol) at 0 °C. The reaction mixture was stirred for 3h at room temperature. The mixture was quenched by addition of water, extracted with EtOAc (3×5 mL) and the combined organic layer was evaporated in vacuo. Obtained crude product was purified by column chromatography (silica gel, pet. ether/EtOAc) to afford **10**.

R_f: 0.40 (pet. ether/EtOAc = 80/20); 403 mg, Yield: 79%; **Physical appearance:** White solid; **M. P.:** 123 °C; **¹H NMR:** (**500 MHz**, CDCl₃) δ = 8.29 - 8.25 (m, 1 H), 8.20 (s, 1 H), 7.70 (ddd, *J* = 1.5, 7.1, 8.6 Hz, 1 H), 7.49 - 7.43 (m, 2 H), 3.29 (s, 1 H); **¹³C NMR:** (**125 MHz**, CDCl₃) δ = 175.4, 159.0, 155.9, 134.1, 126.2, 125.9, 123.5, 118.2, 110.3, 83.2, 74.0; **HRMS:** (ESI) calcd 171.0441 for C₁₁H₇O₂ [M+H]⁺ found 171.0433.

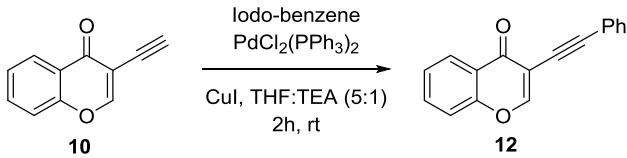
c) Procedure for synthesis of triazole **11**



To a solution of CuSO₄.5H₂O (10.0 mg, 0.04 mmol), sodium ascorbate (15.8 mg, 0.08 mmol), in ¹BuOH/H₂O (1:1 v/v, 2.0 mL) was added a mixture of alkyne **10** (40 mg, 0.22 mmol) and benzyl azide (30 mg, 0.22 mmol) at room temperature. The resultant mixture was stirred for 1 h. Then CH₂Cl₂ (5 mL) was added to dissolve the crude product. The organic layer was washed with H₂O followed by brine, dried over Na₂SO₄ and evaporated in vacuo. The crude product was purified by a column chromatography (silica gel, pet. ether/EtOAc) to give triazole **11**.

R_f: 0.30 (pet. ether/EtOAc = 80/20); 34 mg, Yield: 89%; **Physical appearance:** White solid; **M. P.:** 123 °C; **¹H NMR:** (**500 MHz**, CDCl₃) δ = 8.29 - 8.25 (m, 1 H), 8.20 (s, 1 H), 7.70 (ddd, *J* = 1.5, 7.1, 8.6 Hz, 1 H), 7.49 - 7.43 (m, 2 H), 3.29 (s, 1 H); **¹³C NMR:** (**125 MHz**, CDCl₃) δ = 175.4, 159.0, 155.9, 134.1, 126.2, 125.9, 123.5, 118.2, 110.3, 83.2, 74.0; **HRMS:** (ESI) calcd 304.1081 for C₁₈H₁₄O₂N₃ [M+H]⁺ found 304.1081.

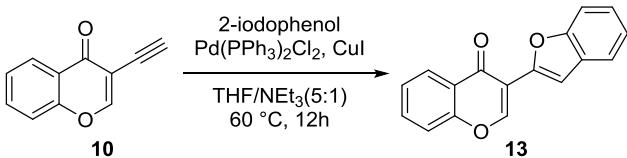
b) Procedure for synthesis of internal alkyne **12**



To a stirred solution of iodobenzene (40 mg, 0.20 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (2.8 mg, 0.004 mmol, 2 mol %), CuI (1.15 mg, 0.006 mmol, 3 mol%) in dry THF:NEt₃ (5:1, 2 mL) was added **10** (35 mg, 0.20 mmol). The mixture was stirred at room temperature for 2h. After completion of the reaction, the reaction mixture was filtered through celite pad and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired product **12**.

R_f: 0.40 (pet. ether/EtOAc = 90/10); 46 mg, Yield: 94%; **Physical appearance:** White solid; **M. P.:** 123 °C; **¹H NMR:** (**500 MHz**, CDCl₃) δ = 8.29 - 8.25 (m, 1 H), 8.20 (s, 1 H), 7.70 (ddd, *J* = 1.5, 7.1, 8.6 Hz, 1 H), 7.49 - 7.43 (m, 2 H), 3.29 (s, 1 H); **¹³C NMR:** (**125MHz**, CDCl₃) δ = 175.4, 159.0, 155.9, 134.1, 126.2, 125.9, 123.5, 118.2, 110.3, 83.2, 74.0; **HRMS:** (ESI) calcd 247.0754 for C₁₇H₁₁O₂ [M+H]⁺ found 247.0744.

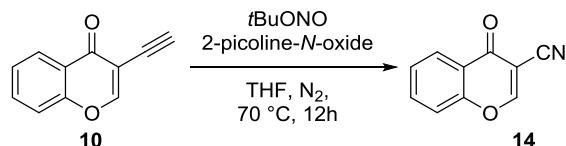
d) Procedure for synthesis of 3-(benzofuran-2-yl)-chromone **13**



To a stirred solution of 2-iodophenol (40 mg, 0.20 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2.8 mg, 0.004mmol, 2 mol %), CuI (1.15 mg, 0.006 mmol, 3 mol%) in dry THF:NEt₃ (5:1, 2 mL) was added **10** (35 mg, 0.20 mmol). The mixture was stirred at 60 °C for 12h. After completion of the reaction, the reaction mixture was filtered through celite pad and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired a product **13**.

R_f: 0.20 (pet. ether/EtOAc = 90/10); 35 mg, Yield: 67%; **Physical appearance:** White solid; **M. P.:** 123 °C; **¹H NMR:** (**500 MHz**, CDCl₃) δ = 8.29 - 8.25 (m, 1 H), 8.20 (s, 1 H), 7.70 (ddd, *J* = 1.5, 7.1, 8.6 Hz, 1 H), 7.49 - 7.43 (m, 2 H), 3.29 (s, 1 H); **¹³C NMR:** (**125 MHz**, CDCl₃) δ = 175.4, 159.0, 155.9, 134.1, 126.2, 125.9, 123.5, 118.2, 110.3, 83.2, 74.0; **HRMS:** (ESI) calcd 263.0703 for C₁₇H₁₁O₃ [M+H]⁺ found 263.0696.

e) Procedure for synthesis of 3-cyanochromone **14**⁶



An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, **10** (0.5 mmol), *t*BuONO (1.0 mmol, 103 mg, 119 μ L) and 2-picoline-*N*-oxide (1.0 mmol, 109 mg) under N_2 atmosphere. Then, 2 mL of dry THF was added using syringe at the end. The reaction mixture was stirred vigorously on a preheated oil bath at 70 $^\circ\text{C}$ for 12h (monitored by TLC). After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired a product **14**.

R_f: 0.50 (pet. ether/EtOAc = 70/30); 37 mg, Yield: 44%; **Physical appearance:** White solid; **M. P.:** 123 $^\circ\text{C}$; **¹H NMR:** (**500 MHz, CDCl₃**) δ = 8.29 - 8.25 (m, 1 H), 8.20 (s, 1 H), 7.70 (ddd, *J* = 1.5, 7.1, 8.6 Hz, 1 H), 7.49 - 7.43 (m, 2 H), 3.29 (s, 1 H); **¹³C NMR:** (**125 MHz, CDCl₃**) δ = 175.4, 159.0, 155.9, 134.1, 126.2, 125.9, 123.5, 118.2, 110.3, 83.2, 74.0; **HRMS:** (**ESI**) calcd 172.0393 for C₁₀H₆NO₂ [M+H]⁺ found 172.0385.

3. X-ray crystallography

Compound Structure	ORTEP Diagram
<p>CCDC 1498524</p>	

⁶ Dutta, U.; Lupton, D. W.; Maity, D. *Org. Lett.* **2016**, *18*, 860-863.

4. NMR Data

