Rh(III)-Catalyzed [5+1] Annulation of 2-Alkenylanilides and 2-Alkenylphenols with Allenyl Acetates

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1. General information:

All reactions were performed in a 15 mL reaction tube. Unless otherwise noted, starting materials, reagents and solvents were purchased from common commercial sources and used without further purification. Starting materials were prepared according to the existing literature procedures. $^1$H NMR spectra were recorded at 400 MHz and 500 MHz using TMS as internal standard. $^{13}$C NMR spectra were recorded at 100 MHz and 125 MHz using TMS as internal standard. High resolution mass measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was performed on pre-coated 0.2 mm thick Merck 60 F$_245$ silica plates and various combinations of ethyl acetate and petroleum ether were used as eluent. Visualization of spots of allene and final product was accomplished by subjecting to KMnO$_4$ stain. All compounds were purified using silica gel (100-200 mesh) column chromatography and gave spectroscopic data consistent with being ≥95% the assigned structure.

2. General procedure for the synthesis of 2-alkenyl anilides.$^{1,2}$

Step 1:

To a solution of methyltriphenylphosphonium bromide (2.04 g, 2.3 equiv) and potassium tert-butoxide (0.699 g, 2.3 equiv) in THF (26 mL) under Ar atmosphere was added the 2-aminoacetophenone derivative (0.50 g, 4.09 mmol). The reaction was heated at 30 °C and stirred for 12 hours and then cooled to room temperature. Solvents were removed in vacuo and the resulting mixture was extracted with diethyl ether. The combined organic layers were washed with brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification by flash chromatography on silica gel (hexanes:diethylether; 4:6) gave the 2-alkenyl aniline derivatives.

Aniline (5 mmol) A, phenylacetylene (0.51 g, 5 mmol) B and montmorillonite KSF S4 (0.51 g) are introduced in a round bottomed flask equipped with magnetic stirrer and a reflux condenser. The reaction mixture is heated at 140 °C for 5 hours and then cooled to room temperature. The products was dissolved with dichloromethane and filtered. Then the solvent were concentrated in vacuo and the crude was purified by column chromatography (silica gel, appropriate mixture of petroleum ether /ethyl acetate) to give corresponding 2-alkenyl aniline.

Step 2:
To a solution of o-isopropenylaniline (1 mL, 7.34 mmol) in dichloromethane (25 mL) under Ar atmosphere was added triethylamine (1.228 ml, 1.2 equiv) at °C. Then trifluoromethanesulfonic anhydride (1.489 ml, 1.2 equiv) was added dropwise. The reaction was stirred at 0 °C for 1.5 hours and quenched with saturated NH₄Cl aqueous solution. The resulting mixture was extracted with dichloromethane and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification column flash chromatography on silica gel (hexanes:diethyl ether; 8:2) affording corresponding products.

General procedure for the synthesis of Allenyl Acetate.³,⁴

Step 1:
To a two-necked round bottom-flask equipped with a magnetic stir bar were added under argon propargylic alcohol (10 mmol), 15 mL dioxane, 0.72 g of cuprous bromide, 0.74 g of paraformaldehyde, and 1.85 g of diisopropylamine. The reaction mixture was refluxed for 2 h and then cooled to room temperature. To mixture was filtered through a Celite plug. The filtrate is diluted with water followed by diethyl ether and acidified with 6 N HCl to pH 2. The organic layer was separated and the aqueous phase was extracted with diethyl ether for additional two times. The organic phase was then washed with saturated NaHCO₃, brine and dried over MgSO₄. After filtration and evaporation under reduced pressure, the residue was subjected directly for the next step.
Step 2: To a round bottom-flask equipped with a magnetic stir bar were added under argon allenylic carbinol, DMAP (122 mg, 1.0 mmol, 0.2 equiv), pyridine (790 mg, 10 mmol, 2.0 equiv) and dichloromethane (0.3 M). The mixture was cooled to 0 °C and the chloro methyl formate (708.8 mg, 7.5 mmol, 1.5 equiv) was slowly added. The reaction was allowed to stir at room temperature until completion (typically 1 – 16 h). The mixture was diluted with dichloromethane and washed successively with 1 N HCl, saturated NaHCO₃, and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography to yield the desired product.

3. Optimization of reaction conditions:

To achieve further enhancement in yield, different solvents were screened. DCE proved to be best solvent for developed protocol delivering the product 7a in 93% yield, while other solvents like toluene, 1,4 dioxane, MeOH and DMF were found less efficient hence lowered yield were observed (entry 3-6). The presence of other additives like Cu(OAc)₂, CsOAc and AgOAc did not exhibit any significant improvement in reaction yield (entry 7-9). Surprisingly, silver salts like AgSbF₆ and AgBF₄, having non-coordinating counter anions which are known to enhance the reactivity of the Rh(III) catalyst, gave the product 3a only in 70% and 68%, respectively (entries 10 and 11). After carefully examination of optimization, we found that loading of NaOAc could be further lower down to 30 mol% in DCE solvent (entry 12). In the absence of NaOAc, diminished yield of 7a (20%) was observed (entry 11). When reaction was also carried out at elevated temperature at 70 °C, formation of 7a was noticed within 20 minute with 86% yield (entry 12). Other metal catalyst like Pd(OAc)₂, [Cp*RhCl₂]₂, [Cp*IrCl₂]₂ and [Ru(p-cymene)Cl₂]₂ were found completely ineffect when used instead of Rh(III) (entry 13). Absence of Rh catalyst did not furnish the cyclized product (entry 14).

| entry | catalyst | solvent | base | yield (%) |
|-------|----------|---------|------|-----------|
| 3-6   |          |         |      |           |
| 7-9   |          |         |      |           |
| 10-11 |          |         |      |           |
| 12    |          |         |      |           |
| 11    |          |         |      |           |
| 12    |          |         |      |           |
| 13    |          |         |      |           |
| 14    |          |         |      |           |
| Entry | Precatalyst | Solvent | Base | Yield [%] [b] |
|-------|-------------|---------|------|--------------|
| 1     | [Cp*RhCl₂]₂ | CH₃CN   | NaOAc | 45 (42)      |
| 2     | [Cp*RhCl₂]₂ | DCE     | NaOAc | 93 (89)      |
| 3     | [Cp*RhCl₂]₂ | Toluene | NaOAc | 75           |
| 4     | [Cp*RhCl₂]₂ | 1,4-dioxane | NaOAc | 25           |
| 5     | [Cp*RhCl₂]₂ | MeOH    | NaOAc | 64           |
| 6     | [Cp*RhCl₂]₂ | DMF     | NaOAc | 43           |
| 7     | [Cp*RhCl₂]₂ | DCE     | Cu(OAc)₂ | 73      |
| 8     | [Cp*RhCl₂]₂ | DCE     | CsOAc | 68           |
| 9     | [Cp*RhCl₂]₂ | DCE     | AgOAc | 68           |
| 10    | [Cp*RhCl₂]₂ | DCE     | AgSbF₆ | 70       |
| 11    | [Cp*RhCl₂]₂ | DCE     | AgBF₄ | 68           |
| 12    | [Cp*RhCl₂]₂ | DCE     | NaOAc | 91 [c]      |
| 13    | [Cp*RhCl₂]₂ | DCE     | -     | 10           |
| 14    | [Cp*RhCl₂]₂ | DCE     | NaOAc | 87[d]       |
| 15    | [Ru(p-cymene)Cl₂]₂ | DCE | NaOAc | -           |
| 16    | Pd(OAc)₂ | DCE     | NaOAc | -           |
| 17    | [Cp*IrCl₂]₂ | DCE     | NaOAc | -           |
| 18    | [Cp*Co(CO)I₂]₂ | DCE | NaOAc | -           |

[a] Reaction condition: 1a (0.2 mmol), 2a (0.18 mmol), solvent 2 ml, 36 h. [b] isolated yield. [c] Used 30 mol % NaOAc. [d] T= 70 oC.

3. General procedure for Rh(III) -catalyzed [5+1] annulation of o-alkenylanilides with allenic acetates.

A sealed tube containing [Cp*RhCl₂]₂ (2.5 mol %), NaOAc (30 mol %) was evacuated and purged with nitrogen gas three times. Then, o-alkenylanilides 1 (0.20 mmol) and allenic acetate 4 (0.18 mmol) in CH₃CN (2 ml) were added via syringe under nitrogen atmosphere and the reaction mixture was allowed to stir at r.t. for 24 h. Then, the mixture was diluted with CH₂Cl₂ (10 mL). The mixture was filtered through a celite pad and washed with CH₂Cl₂ (3 x 10 mL). The filtrate was concentrated under reduced.
pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired annulated pure product 7.

4. Spectroscopic data:

(E)-2,4-dimethyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

![Chemical structure of 7a, 91%]

64.4 mg, 91%, colorless liquid;

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 – 7.53 (m, 1H), 7.35 (dd, $J = 7.4$, 1.9 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.27 – 7.22 (m, 3H), 6.44 (d, $J = 15.9$ Hz, 1H), 6.17 (d, $J = 15.9$ Hz, 1H), 5.97 (s, 1H), 2.25 (d, $J = 1.4$ Hz, 3H), 1.88 (s, 3H).

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) $\delta$ 136.16, 134.27, 132.87, 132.17, 131.27, 130.68, 129.61, 128.55, 128.06, 127.93, 127.89, 127.72, 126.59, 123.09, 120.45 (q, $J = 325.9$ Hz), 64.29, 26.56, 17.95.

HRMS (ESI-TOF) $m/z$ [M + Na]$^+$ calcd for C$_{20}$H$_{18}$F$_3$NNaO$_2$S 416.0903, found 416.0907.

(E)-4-ethyl-2-methyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

![Chemical structure of 7b, 81%]

59.407 mg, 81%, colorless liquid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (dd, $J = 7.6$, 1.5 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.29 – 7.18 (m, 7H), 6.39 (d, $J = 15.9$ Hz, 1H), 6.12 (d, $J = 15.9$ Hz, 1H), 5.97 – 5.85 (m, 1H), 2.62 (q, $J = 7.4$ Hz, 2H), 1.86 (s, 3H), 1.23 (q, $J = 7.2$ Hz, 3H).

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 138.47, 136.16, 134.57, 131.45, 131.33, 129.60, 129.20, 128.52, 128.32, 127.90, 127.74, 127.70, 126.57, 122.85, 121.96, 120.45 (q, $J = 326.1$ Hz) 26.63, 24.45, 12.56.

HRMS (ESI-TOF) $m/z$ [M + Na]$^+$ calcd for C$_{21}$H$_{20}$F$_3$NNaO$_2$S 430.1059, found 430.1063.

(E)-4-isopropyl-2-methyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

![Chemical structure of 7c, 78%]

57.5 mg, 78%, sticky brown solid.
**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.7$ Hz, 1H), 7.36 (d, $J = 9.2$ Hz, 1H), 7.28 – 7.25 (m, 2H), 7.25 – 7.19 (m, 3H), 7.19 – 7.15 (m, 2H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.08 (d, $J = 15.9$ Hz, 1H), 5.85 (s, 1H), 3.12 – 2.99 (sept, $J = 6.7$ Hz, 1H), 1.86 (s, 3H), 1.31 (d, $J = 6.7$ Hz, 3H), 1.16 (d, $J = 6.9$ Hz, 3H).

**13C{1H} NMR** (100 MHz, CDCl$_3$) $\delta$ 142.92, 136.12, 134.70, 131.45, 131.41, 129.55, 128.47, 127.89, 127.84, 127.66, 127.61, 126.55, 126.57, 125.05, 124.25 (q, $J = 325.3$ Hz), 64.26, 27.96, 26.70, 22.09, 21.40.

**HRMS** (ESI-TOF) $m/z$ [M + H]$^+$ calcld for C$_{22}$H$_{23}$F$_3$NO$_2$S 422.1396, found 422.1392.

(E)-4-butyl-2-methyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

64.5 mg, 82%, Brown sticky solid.

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 7.3$ Hz, 1H), 7.29 – 7.17 (m, 7H), 6.38 (d, $J = 15.9$ Hz, 1H), 6.12 (d, $J = 15.9$ Hz, 1H), 5.90 (s, 1H), 2.67 – 2.46 (m, 2H), 1.85 (s, 3H), 1.62 – 1.44 (m, 4H), 1.00 (t, $J = 7.1$ Hz, 3H).

**13C{1H} NMR** (100 MHz, CDCl$_3$) $\delta$ 137.29, 136.15, 134.57, 131.51, 131.31, 129.87, 129.59, 128.53, 128.26, 127.90, 127.72, 127.65, 126.57, 122.97, 120.45 (q, $J = 325.8$ Hz), 64.27, 31.32, 30.44, 26.60, 22.80, 13.95.

**HRMS** (ESI-TOF) $m/z$ [M + H]$^+$ calcld for C$_{23}$H$_{25}$F$_3$NO$_2$S 436.1553, found 436.1548.

(E)-2-methyl-4-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

69.9 mg, 85%, colorless liquid;

**1H NMR** (500 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.0$ Hz, 1H), 7.53 – 7.44 (m, 5H), 7.33 – 7.28 (m, 3H), 7.27 – 7.20 (m, 4H), 7.13 (dd, $J = 7.7, 1.3$ Hz, 1H), 6.55 (d, $J = 16.0$ Hz, 1H), 6.23 (d, $J = 16.0$ Hz, 1H), 6.20 (s, 1H), 1.97 (s, 3H).


\[ {^1}\text{H} \text{NMR} \ (125 \text{ MHz, CDCl}_3) \ \delta \ 139.61, 137.63, 136.03, 135.04, 131.55, 131.25, 130.83, 129.94, 129.41, 128.71, 128.58, 128.57, 128.51, 128.44, 128.38, 128.27, 128.06, 127.64, 126.93, 126.64, 125.98, 120.45 (q, \ J = 326 \text{ Hz}), 64.33, 26.64. \]

**HRMS** (ESI-TOF) \[ m/z \ [M + Na]^+ \text{ calcld for C}_{25}\text{H}_{20}\text{F}_{3}\text{N}_{2}\text{O}_{2} \text{S} 478.1059, \text{ found 478.1051.} \]

\[ (E)-2,6\text{-dimethyl-4-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline} \]

76.3 mg, 90%, yellowish liquid.

\[ {^1}\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.55 - 7.38 (m, 6H), 7.33 - 7.20 (m, 5H), 7.08 (dd, \ J = 8.2, 1.3 \text{ Hz}, 1H), 6.89 (d, \ J = 1.1 \text{ Hz}, 1H), 6.53 (d, \ J = 16.0 \text{ Hz}, 1H), 6.22 (d, \ J = 16.0 \text{ Hz}, 1H), 6.15 (s, 1H), 2.24 (s, 3H), 1.93 (s, 3H). \]

\[ {^{13}}\text{C}(^{1}\text{H}) \text{NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 139.66, 137.81, 137.59, 136.09, 132.47, 131.24, 131.20, 131.11, 129.72, 129.12, 128.70, 128.59, 128.44, 128.18, 128.03, 126.67, 126.46, 120.45 (q, \ J = 326.1 \text{ Hz}), 64.24, 26.71, 21.17. \]

**HRMS** (ESI-TOF) \[ m/z \ [M + Na]^+ \text{ calcld for C}_{26}\text{H}_{22}\text{F}_{3}\text{N}_{2}\text{NaO}_{2} \text{S} 492.1216, \text{ found 492.1214.} \]

\[ (E)-6\text{-methoxy-2-methyl-4-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline} \]

74.5 mg, 85%, white solid.

\[ {^1}\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.55 (d, \ J = 8.9 \text{ Hz}, 1H), 7.49 - 7.44 (m, 5H), 7.33 - 7.24 (m, 5H), 6.81 (dd, \ J = 8.9, 2.9 \text{ Hz}, 1H), 6.63 (d, \ J = 2.9 \text{ Hz}, 1H), 6.54 (d, \ J = 16.0 \text{ Hz}, 1H), 6.23 (d, \ J = 16.0 \text{ Hz}, 1H), 6.20 (s, 1H), 3.70 (s, 3H), 1.95 (s, 3H). \]

\[ {^{13}}\text{C}(^{1}\text{H}) \text{NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 158.56, 139.62, 137.56, 136.07, 132.61, 131.77, 131.12, 129.77, 129.56, 128.74, 128.60, 128.56, 128.30, 128.07, 127.85, 126.68, 120.45 (q, \ J = 326.3 \text{ Hz}), 113.00, 111.80, 64.27, 55.38. \]
HRMS (ESI-TOF) m/z [M + Na]+ calcd for C_{26}H_{23}F_{3}NO_{3}S 486.1345, found 486.1340.

**(E)-6-fluoro-2-methyl-4-phenyl-2-steryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline**

71 mg, 83%, solid, m.p. 123-126 °C.

**H NMR** (400 MHz, CDCl₃) δ 7.58 (dd, J = 8.9, 5.1 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.44 – 7.38 (m, 2H), 7.30 – 7.20 (m, 5H), 7.01 – 6.90 (m, 1H), 6.80 (dt, J = 12.7, 6.4 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H), 6.22 (s, J = 7.4 Hz, 1H), 6.17 (d, J = 16.0 Hz, 1H), 1.95 (s, 3H).

**C{H} NMR** (100 MHz, CDCl₃) δ 161.34 (d, J = 247.8 Hz), 139.07 (s), 136.92 (s), 133.42 (d, J = 8.5 Hz), 132.40 (s), 130.85 (d, J = 3.1 Hz), 130.48 (s), 130.25 (s, J = 8.7 Hz), 130.14 (d, J = 4.9 Hz), 128.89 (s), 128.81 (s), 128.63 (s), 128.44 (s), 128.22 (s), 126.65 (s), 120.45 (q, J = 326.0 Hz), 115.16 (d, J = 23.1 Hz), 112.75 (d, J = 24.5 Hz), 64.42 (s), 24.47.

HRMS (ESI-TOF) m/z [M + H]+ calcd for C_{25}H_{20}F_{4}NO_{2}S 474.1145, found 474.1141.

**(E)-6-chloro-2-methyl-4-phenyl-2-steryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline**

69.8 mg, 79%, colorless liquid.

**H NMR** (500 MHz, CDCl₃) δ 7.56 (d, J = 8.6 Hz, 1H), 7.50 (m, 3H), 7.44 – 7.36 (m, 2H), 7.33 – 7.28 (m, 3H), 7.28 – 7.24 (m, 3H), 7.09 (d, J = 2.1 Hz, 1H), 6.52 (d, J = 15.9 Hz, 1H), 6.21 (s, 1H), 6.18 (d, J = 16.0 Hz, 1H), 1.96 (s, 3H).

**C{H} NMR** (125 MHz, CDCl₃) δ 138.85, 136.86, 135.72, 133.49, 133.47, 132.99, 132.51, 130.34, 130.23, 129.67, 128.91, 128.81, 128.63, 128.45, 128.32, 128.25, 126.67, 125.80, 120.45 (q, J = 325.9 Hz), 64.44, 26.58.

HRMS (ESI-TOF) m/z [M + Na]+ calcd for C_{25}H_{19}ClF_{3}NNaO_{2}S 512.0669, found 512.0661.
(E)-6-bromo-2-methyl-4-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

78 mg, 81%, brown oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 – 7.44 (m, 4H), 7.44 – 7.36 (m, 3H), 7.33 – 7.21 (m, 6H), 6.51 (d, $J$ = 16.0 Hz, 1H), 6.23 – 6.13 (m, 2H), 1.94 (s, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 138.76, 136.85, 135.71, 134.02, 133.30, 132.56, 131.31, 130.25, 129.96, 128.95, 128.84, 128.72, 128.66, 128.47, 128.28, 126.70, 121.94, 120.45 (q, $J$ = 325.8 Hz), 64.42, 26.61.

HRMS (ESI-TOF) $m/z$ [M + H]$^+$ calcd for C$_{25}$H$_{20}$BrF$_3$NO$_2$S 534.0345, found 534.0331.

(E)-6-bromo-2,4-dimethyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

69.8 mg, 82%, sticky solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.32 (m, 3H), 7.31 – 7.18 (m, 5H), 6.38 (d, $J$ = 15.9 Hz, 1H), 6.10 (d, $J$ = 15.9 Hz, 1H), 5.97 (s, 1H), 2.19 (s, 3H), 1.84 (s, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 135.85, 133.88, 133.31, 132.03, 131.98, 130.76, 129.93, 129.52, 128.64, 128.59, 128.12, 126.61, 126.19, 121.56, 120.45 (q, $J$ = 325.8 Hz), 64.37, 26.50, 17.84.

HRMS (ESI-TOF) $m/z$ [M + K]$^+$ calcd for C$_{20}$H$_{17}$BrF$_3$KNO$_2$S 509.9747 found 509.9747.

(E)-methyl 2-methyl-4-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline-6 carboxylate

81%, 75.2 mg, white solid.
**1H NMR (500 MHz, CDCl₃)** δ 7.96 (d, J = 8.5 Hz, 1H), 7.82 (s, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.44 (m, 2H), 7.27 (m, 5H), 6.51 (d, J = 15.9 Hz, 1H), 6.23 (s, 1H), 6.17 (d, J = 15.9 Hz, 1H), 3.85 (s, 3H), 1.98 (s, 3H).

**13C[1H] NMR (100 MHz, CDCl₃)** δ 166.02, 139.28, 138.98, 137.01, 135.63, 132.03, 131.67, 130.34, 130.19, 129.39, 129.32, 128.93, 128.80, 128.60, 128.44, 128.24, 127.14, 126.66, 120.45 (q, J = 326.50 Hz), 64.68, 52.30, 26.59.

**HRMS (ESI-TOF) m/z** [M + H]+ calcld for C₂₇H₂₃F₃NO₅S 514.1294, found 514.1286.

(E)-8-fluoro-2-methyl-4-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

89%, 76.1 mg, colorless oil.

**1H NMR (500 MHz, CDCl₃)** δ 7.55 – 7.43 (m, 6H), 7.31 – 7.20 (m, 5H), 7.08 (t, J = 8.8 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 6.21 (s, 1H), 6.09 (d, J = 15.9 Hz, 1H), 2.07 (s, 3H).

**13C[1H] NMR (125 MHz, CDCl₃)** δ 158.95 – 157.14 (d, J = 259.92 Hz), 139.70, 137.06, 135.71, 134.04, 132.73, 130.17, 130.11, 128.97, 128.90, 128.78, 128.73, 128.59, 128.47, 128.16, 126.64, 120.45 (q, J = 125.8), 116.72-116.47(q, J = 21.14Hz), 64.55, 25.97.

**HRMS (ESI-TOF) m/z** [M + H]+ calcld for C₂₅H₂₀F₄NO₂S 474.1145, found 474.1142.

(E)-2,6,8-trimethyl-4-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

74.2 mg, 85%, colorless oil.

**1H NMR (500 MHz, CDCl₃)** δ 7.49 (s, J = 26.3 Hz, 5H), 7.31 – 7.23 (m, 3H), 7.18 (d, J = 7.2 Hz, 2H), 6.97 (s, J = 27.2 Hz, 1H), 6.72 (s, J = 28.5 Hz, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.12 (s, 1H), 6.09 (d, J = 16.0 Hz, 1H), 2.50 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H).
1H NMR (125 MHz, CDCl$_3$) δ 140.74, 137.76, 137.64, 135.99, 132.35, 132.05, 131.60, 131.10, 129.73, 128.62, 128.56, 128.39, 127.99, 126.59, 124.37, 120.45 (q, $J$ = 327.3 Hz), 64.13, 26.11, 21.12, 19.42.

HRMS (ESI-TOF) $m/z$ [M + H]$^+$ calcd for C$_{27}$H$_{34}$F$_3$NO$_2$S 484.1553 found 484.1542.

(E)-6,8-dimethyl-6-arylyl-5-((trifluoromethyl)sulfonyl)-5,6-dihydro-[1,3]dioxolo[4,5-g]quinoline

61.6 mg, 78%, sticky liquid.

1H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.23 (m, 1H), 7.04 (s, $J$ = 16.6 Hz, 1H), 6.77 (s, 1H), 6.41 (d, $J$ = 15.9 Hz, 1H), 6.14 (d, $J$ = 15.9 Hz, 1H), 5.99 (dd, $J$ = 10.3, 1.2 Hz, 1H), 5.83 (s, 1H), 2.16 (s, $J$ = 1.2 Hz, 3H), 1.84 (s, 3H).

13C{1H} NMR (125 MHz, CDCl$_3$) δ 147.09, 146.59, 136.13, 132.76, 131.60, 129.36, 128.79, 128.55, 128.39, 127.93, 127.07, 126.62, 120.45 (q, $J$ = 125.3 Hz), 109.59, 102.84, 101.80, 64.38, 26.54, 18.25.

HRMS (ESI-TOF) $m/z$ [M + K]$^+$ calcd for C$_{21}$H$_{18}$F$_3$KNO$_2$S 476.0540 found 476.0537.

(E)-2,4-dimethyl-2-(4-methylstyryl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

64.5 mg, 89%, colorless liquid.

1H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, $J$ = 8.1 Hz, 1H), 7.35 – 7.24 (m, 3H), 7.20 – 7.16 (m, 1H), 7.13 – 7.03 (m, 3H), 6.57 (d, $J$ = 15.8 Hz, 1H), 5.91 (s, 1H), 5.88 (d, $J$ = 15.8 Hz, 1H), 2.22 (s, 3H), 2.02 (s, 3H), 1.89 (s, 3H).

13C{1H} NMR (100 MHz, CDCl$_3$) δ 135.59, 134.47, 132.99, 132.38, 132.28, 130.70, 130.03, 128.17, 127.88, 127.76, 127.65, 126.06, 123.04, 121.97(q, $J$ = 325.1), 64.49, 26.51, 19.47, 17.89.

HRMS (ESI-TOF) $m/z$ [M + H]$^+$ calcd for C$_{21}$H$_{30}$F$_3$NNO$_2$S 408.1240 found 408.1240.
(E)-2-(4-chlorostyryl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

![Chemical structure](image)

66.8 mg, 87%, yellowish liquid;

**$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.55 (d, $J = 7.6$ Hz, 1H), 7.39 (d, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 7.4$ Hz, 1H), 7.33 – 7.25 (m, 2H), 7.10 (d, $J = 7.9$ Hz, 2H), 6.37 (d, $J = 15.9$ Hz, 1H), 6.15 (d, $J = 15.9$ Hz, 1H), 5.95 (s, 1H), 2.23 (s, 3H), 1.85 (s, 3H).

**$^{13}$C{$^1$H} NMR** (125 MHz, CDCl$_3$) δ 135.06, 134.18, 133.03, 132.08, 131.99, 131.65, 130.40, 128.48, 128.11, 128.03, 127.96, 127.79, 123.13, 121.78, 125.45(q, $J = 326$), 64.14, 26.43, 17.95.

**HRMS (ESI-TOF)** $m/z$ [M + Na]$^+$ calcd for C$_{20}$H$_{17}$ClF$_3$N$_2$O$_2$S 450.0513, found 450.0519.

(E)-2-(4-bromostyryl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

![Chemical structure](image)

71.21 mg, 84%, colorless liquid.

**$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.56 (dd, $J = 7.8$, 1.3 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 (d, $J = 8.5$ Hz, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 6.39 (d, $J = 16.0$ Hz, 1H), 6.14 (d, $J = 15.9$ Hz, 1H), 5.96 (s, 1H), 2.24 (d, $J = 1.2$ Hz, 3H), 1.86 (s, 3H).

**$^{13}$C{$^1$H} NMR** (125 MHz, CDCl$_3$) δ 134.63, 134.18, 133.62, 133.01, 132.10, 131.87, 130.44, 128.70, 128.43, 128.03, 127.95, 127.81, 123.13, 120.25 (q, $J = 325.8$), 64.16, 26.46, 17.94.

**HRMS (ESI-TOF)** $m/z$ [M + H]$^+$ calcd for C$_{20}$H$_{18}$BrF$_3$NO$_2$S 472.0188, found 472.0189.

(E)-2-(4-fluorostyryl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

![Chemical structure](image)

61.27 mg, 83%, colorless liquid.
\( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \): 7.55 (dd, \( J = 7.7, 1.3 \) Hz, 1H), 7.36 – 7.33 (m, 1H), 7.33 – 7.25 (m, 2H), 7.24 – 7.17 (m, 2H), 6.96 (t, \( J = 8.7 \) Hz, 2H), 6.39 (d, \( J = 16.0 \) Hz, 1H), 6.08 (d, \( J = 15.9 \) Hz, 1H), 5.95 (s, 1H), 2.23 (d, \( J = 1.3 \) Hz, 3H), 1.85 (s, 3H).

\( ^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \): 162.50 (d, \( J = 247.5 \) Hz), 134.21 (s), 132.91 (s), 132.28 (d, \( J = 3.3 \) Hz), 132.12 (s), 130.96 (s), 130.55 (s), 128.47 (s), 128.17 (s), 128.11 (s), 128.04 (s), 127.92 (s), 127.75 (s), 123.10 (s), 120.25 (q, \( J = 325.8 \) Hz), 64.18 (s), 26.52 (s), 17.94 (s).

HRMS (ESI-TOF) m/z \([M + H]^+\) calcd for C\(_{20}\)H\(_{18}\)F\(_4\)NO\(_2\)S 412.0989 found 412.0995.

\((E)-4-(2,4\text{-dimethyl-1-}((\text{trifluoromethyl)sulfonyl})\text{-1,2-dihydroquinolin-2-yl}viny]benzonitrile\)

58.68 mg, 78%, sticky solid.

\( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \): 7.55 (d, \( J = 8.0 \) Hz, 3H), 7.37 – 7.26 (m, 5H), 6.44 (d, \( J = 16.0 \) Hz, 1H), 6.28 (d, \( J = 16.0 \) Hz, 1H), 5.95 (s, 1H), 2.23 (s, 3H), 1.85 (s, 3H).

\( ^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \): 140.61 (s), 135.18 (s), 134.08 (s), 133.33 (s), 132.36 (s), 131.93 (s), 129.95 (s), 128.10 (s), 127.99 (s), 127.96 (s), 127.90 (s), 127.08 (s), 123.22 (s), 120.25 (q, \( J = 325.8 \) Hz), 118.75 (s), 111.21 (s), 63.90 (s), 26.34 (s), 17.97 (s).

HRMS (ESI-TOF) m/z \([M + H]^+\) calcd for C\(_{21}\)H\(_{18}\)F\(_3\)N\(_2\)O\(_2\)S 419.1036 found 419.1030.

\((E)-2,4\text{-dimethyl-2-}((\text{trifluoromethyl})styryl)-1\text{-}((\text{trifluoromethyl)sulfonyl})\text{-1,2-dihydroquinoline}\)

63.0 mg, 76%, brown oil.

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \): 7.55 – 7.45 (m, 3H), 7.35 – 7.21 (m, 5H), 6.42 (d, \( J = 16.0 \) Hz, 1H), 6.22 (d, \( J = 16.0 \) Hz, 1H), 5.93 (s, 1H), 2.21 (d, \( J = 1.3 \) Hz, 3H), 1.83 (s, 3H).

\( ^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \): 140.08, 134.32 (s), 134.08 (s), 133.37 (s), 132.19 (s), 130.36 (s), 129.90, 128.44 (s), 128.19 (d, \( J = 1.5 \) Hz), 128.00 (s), 126.91 (s), 125.66 (q, \( J = 3.9 \) Hz), 123.32 (s), 120.45 (q, \( J = 125.2 \) Hz), 64.18 (s), 26.57 (s), 18.12 (s).
HRMS (ESI-TOF) m/z [M + K]^+ calcd for C_{21}H_{17}F_6KNO_2S 500.0516, found 500.0508.

(E)-2-(3-fluorostyryl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

60.53 mg, 82%, colorless liquid.

^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.47 (m, 1H), 7.34 – 7.29 (m, 1H), 7.29 – 7.22 (m, 2H), 7.22 – 7.16 (m, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.94 – 6.85 (m, J = 8.8 Hz, 2H), 6.37 (d, J = 15.9 Hz, 1H), 6.14 (d, J = 15.9 Hz, 1H), 5.92 (d, J = 0.9 Hz, 1H), 2.21 (d, J = 1.4 Hz, 3H), 1.83 (s, 3H).

^13C{^1H} NMR (100 MHz, CDCl_3) δ 162.95 (d, J = 245.6 Hz), 138.45 (d, J = 7.8 Hz), 134.18 (s), 133.06 (s), 132.65 (s), 132.06 (s), 130.37 (s), 129.99 (d, J = 8.4 Hz), 128.53 (d, J = 2.4 Hz), 128.02 (s), 127.97 (s), 127.79 (s), 123.13 (s), 122.44 (d, J = 2.7 Hz), 120.45 (q, J = 325.8 Hz), 114.73 (d, J = 21.4 Hz), 113.08 (d, J = 21.8 Hz), 64.07 (s), 26.45 (s), 17.94 (s).

HRMS (ESI-TOF) m/z [M + H]^+ calcd for C_{20}H_{16}F_2NO_2S 412.0989, found 412.0986.

(E)-2-(3-chlorostyryl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

63.8 mg, 83%, colorless liquid.

^1H NMR (400 MHz, CDCl_3) δ 7.51 (m, 1H), 7.33 – 7.22 (m, 1H), 7.20 – 7.14 (m, 3.65H), 7.11 – 7.01 (m, 3H), 6.33 (d, J = 15.9 Hz, 1H), 6.12 (d, J = 15.9 Hz, 1H), 5.90 (d, J = 1.1 Hz, 1H), 2.20 (d, J = 1.5 Hz, 3H), 1.82 (s, 3H).

^13C{^1H} NMR (100 MHz, CDCl_3) δ 137.96 (s), 134.48 (s), 134.18 (s), 133.09 (s), 132.76 (s), 132.03 (s), 130.32 (s), 129.74 (s), 128.31 (s), 128.01 (s), 127.99 (s), 127.85 (s), 127.78 (s), 126.52 (s), 124.71 (s), 123.12 (s), 120.45 (q, J = 325.8 Hz), 64.06 (s), 26.48 (s), 17.93 (s).

HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{20}H_{16}ClF_3NNaO_2S 450.0513 found 450.0507.
(E)-2-(2-chloro-6-fluorostyryl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

63.0 mg, 79%, colorless liquid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.58 – 7.51 (m, 1H), 7.36 – 7.24 (m, 3H), 7.13 – 7.03 (m, 2H), 6.91 (m, 1H), 6.47 (d, $J$ = 16.3 Hz, 1H), 6.27 (d, $J$ = 16.3 Hz, 1H), 5.92 (d, $J$ = 0.9 Hz, 1H), 2.23 (d, $J$ = 1.4 Hz, 3H), 1.93 (s, 3H).

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) $\delta$ 160.81 (d, $J$ = 252.2 Hz), 138.71 (d, $J$ = 10.5 Hz), 134.43 (d, $J$ = 5.3 Hz), 134.37 (s), 133.56 (s), 132.16 (s), 130.09 (s), 128.46 (d, $J$ = 10.0 Hz), 128.21 (s), 127.88 (s), 127.68 (s), 125.33 (d, $J$ = 3.5 Hz), 123.15 (s), 123.04 (s), 120.45 (q, $J$ = 325.6 Hz), 120.26 (s), 114.44 (d, $J$ = 23.4 Hz), 64.65 (s), 26.31 (s), 17.90 (s).

HRMS (ESI-TOF) $m/z$ [M + H]$^+$ calcd for C$_{20}$H$_{17}$ClF$_4$NO$_2$S 446.0599 found 446.0597.

(E)-2-(2,4-dichlorostyryl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

67.2 mg, 81%, sticky solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 – 7.45 (m, 1H), 7.36 – 7.24 (m, 4H), 7.19 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.08 (t, $J$ = 7.9 Hz, 1H), 6.78 (d, $J$ = 15.9 Hz, 1H), 6.06 (d, $J$ = 15.9 Hz, 1H), 5.94 (s, 1H), 2.22 (d, $J$ = 1.4 Hz, 3H), 1.84 (s, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 137.02 (s), 135.00 (s), 134.16 (s), 133.36 (s), 133.20 (s), 132.08 (s), 131.38 (s), 130.01 (s), 129.51 (s), 128.09 (s), 128.00 (s), 127.84 (s), 127.19 (s), 126.61 (s), 125.46 (s), 123.27 (s), 120.45 (q, $J$ = 325.7 Hz), 64.10 (s), 26.29 (s), 17.94 (s).

HRMS (ESI-TOF) $m/z$ [M + H]$^+$ calcd for C$_{20}$H$_{17}$Cl$_2$F$_3$NO$_2$S 462.0304 found 462.0294.

(E)-2-(4-bromostyryl)-2-methyl-4-phenyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

16
83.6 mg, 87%, white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 (dd, $J = 8.1$, 1.1 Hz, 1H), 7.53 – 7.44 (m, 5H), 7.43 – 7.39 (m, 2H), 7.31 (td, $J = 7.8$, 1.6 Hz, 1H), 7.23 (td, $J = 7.6$, 1.2 Hz, 1H), 7.16 – 7.08 (m, 3H), 6.49 (d, $J = 16.0$ Hz, 1H), 6.23 (d, $J = 16.0$ Hz, 1H), 6.19 (s, 1H), 1.96 (s, 3H).

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$) δ 139.75, 137.52, 134.99, 134.95, 131.71, 131.56, 131.50, 130.95, 128.82, 128.74, 128.58, 128.55, 128.46, 128.43, 128.16, 127.70, 126.03, 121.96, 120.45 (q, $J = 326$ Hz), 64.22, 26.51.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{25}$H$_{19}$BrF$_3$NNaO$_2$S 556.0164 found 556.0151.

(E)-2-(4-chlorostyryl)-2,6-dimethyl-4-phenyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

70 mg, 78%, viscous liquid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.46 (m, 4H), 7.45 – 7.40 (m, 2H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 9.7$ Hz, 1H), 6.89 (s, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 6.19 (d, $J = 16.0$ Hz, 1H), 6.13 (s, 1H), 2.25 (s, 3H), 1.91 (s, 3H), 1.61 (s, 3H).

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$) δ 139.74, 137.68, 137.63, 134.54, 133.74, 132.39, 131.67, 131.11, 130.94, 129.15, 128.73, 128.68, 128.54, 128.46, 128.14, 127.84, 126.46, 121.69, 119.09 (q, $J = 326$ Hz), 64.08, 26.57, 21.15.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{27}$H$_{25}$ClF$_3$NNaO$_2$S 542.1139, found 542.1145.

(E)-2,4-dimethyl-2-(2-(naphthalen-2-yl)vinyl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

67.0 mg, 84%, yellowish liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J = 8.1$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.62 – 7.57 (m, 1H), 7.48 – 7.44 (m, 1H), 7.43 – 7.39 (m, 3H), 7.39 – 7.33 (m, 2H), 7.33 – 7.25 (m, 2H), 7.07 (d, $J = 15.7$ Hz, 1H), 6.04 (d, $J = 15.7$ Hz, 1H), 6.01 (s, $J = 1.0$ Hz, 1H), 2.28 (d, $J = 1.4$ Hz, 3H), 1.97 (s, 3H).
\(^{13}\)C\(^{1}H\) NMR (100 MHz, CDCl\(_3\)) δ 134.58 (s), 134.34 (s), 134.25 (s), 133.37 (s), 133.25 (s), 132.43 (s), 131.14 (s), 130.73 (s), 128.44 (s), 128.29 (s), 128.14 (s), 127.98 (d, J = 6.4 Hz), 127.94 (s), 127.74 (s), 125.96 (s), 125.84 (s), 125.54 (s), 124.26 (s), 123.76 (s), 123.17 (s), 120.45 (q, J = 325.8 Hz), 64.54 (s), 26.43 (s), 17.97 (s).

HRMS (ESI-TOF) \(m/z\) [M + H]\(^+\) calcd for C\(_{26}\)H\(_{32}\)F\(_3\)N\(_2\)O\(_2\)S 444.1240 found 444.1235.

\((E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinoline\)

CCDC: 2074148

68.3 mg, 81%, colorless liquid.

\(^1H\) NMR (500 MHz, CDCl\(_3\)) δ 7.58 (d, J = 7.5 Hz, 3H), 7.52 (d, J = 8.1 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.39 – 7.34 (m, 2H), 6.47 (d, J = 15.9 Hz, 1H), 6.21 (d, J = 15.9 Hz, 1H), 5.98 (s, 1H), 2.25 (s, 3H), 1.89 (s, 3H).

\(^{13}\)C\(^{1}H\) NMR (125 MHz, CDCl\(_3\)) δ 140.80 (s), 140.56 (s), 135.16 (s), 134.30 (s), 132.90 (s), 132.17 (s), 131.31 (s), 130.68 (s), 129.17 (s), 128.81 (s), 128.07 (s), 127.92 (s), 127.73 (s), 127.42 (s), 127.24 (s), 127.01 (s), 126.94 (s), 123.09 (s), 120.45 (q, J = 326.0 Hz), 64.32 (s), 26.58 (s), 17.95 (s).

HRMS (ESI-TOF) \(m/z\) [M + H]\(^+\) calcd for C\(_{26}\)H\(_{32}\)F\(_3\)N\(_2\)O\(_2\)S 470.1396 found 470.1389.

\((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl 4-((E)-2-(4,2-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinolin-2-yl)vinyl)benzoate\)

86 mg, 75%, sticky white solid.

\(^1H\) NMR (400 MHz, CDCl\(_3\)) δ 7.92 (d, J = 8.3 Hz, 2H), 7.58 – 7.46 (m, 1H), 7.34 – 7.28 (m, 1H), 7.28 – 7.21 (m, 4H), 6.43 (d, J = 16.0 Hz, 1H), 6.32 – 6.15 (m, 1H), 5.93 (s, 1H), 4.90 (td, J = 10.8, 4.3 Hz, 1H), 2.21 (d, J = 1.4 Hz, 3H), 2.14 – 2.05 (m, 1H), 1.95 – 1.88 (m, 1H), 1.84 (s, 3H), 1.77 – 1.67 (m, 2H), 1.59 – 1.47 (m, 2H), 1.18 – 1.05 (m, 2H), 0.98 – 0.85 (m, 7H), 0.77 (d, J = 6.9 Hz, 3H).

\(^{13}\)C\(^{1}H\) NMR (100 MHz, CDCl\(_3\)) δ 165.70, 140.39, 134.18, 133.73, 133.67, 133.15, 132.06, 130.30, 130.07, 129.84, 128.78, 128.74, 128.02, 127.98, 127.80, 126.40, 123.13, 120.45 (q, J = 325.8 Hz),
HRMS (ESI-TOF) m/z [M + K]^+ calcld for C$_{31}$H$_{36}$F$_3$KNO$_4$S 614.1949 found 614.1944.

(E)-2-isopropyl-5-methylphenyl4-(2-(2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2 dihydroquinoalin-2-yl)vinyl)benzoate

81%, 92 mg, colorless liquid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, $J = 8.3$ Hz, 1H), 7.57 (d, $J = 7.5$ Hz, 1H), 7.39 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 7.27 – 7.24 (m, 1H), 7.08 (d, $J = 7.8$ Hz, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 6.31 (d, $J = 15.9$ Hz, 1H), 5.97 (s, 1H), 3.07 – 2.97 (m, 1H), 2.36 (s, $J = 7.2$ Hz, 3H), 2.25 (d, $J = 1.0$ Hz, 3H), 1.88 (s, 3H), 1.21 (d, $J = 6.9$ Hz, 6H).

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) δ 164.96, 148.10, 141.24, 137.13, 136.67, 134.33, 134.19, 133.22, 132.04, 130.45, 130.23, 129.55, 128.80, 128.61, 128.04, 127.85, 127.21, 126.69, 126.50, 123.18, 122.84, 120.45 (q, $J = 325.7$ Hz), 64.08, 27.31, 26.41, 23.02, 20.87, 17.98.

HRMS (ESI-TOF) m/z [M + Na]^+ calcld for C$_{31}$H$_{38}$F$_3$NNaO$_4$S 592.1740 found 592.1748.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((E)-2-(2,4-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydroquinolin-2-yl)vinyl)benzoate

112 mg, 70%, sticky solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J = 8.1$ Hz, 2H), 7.53 (d, $J = 7.4$ Hz, 1H), 7.35 – 7.20 (m, 5H), 6.43 (d, $J = 16.0$ Hz, 1H), 6.23 (d, $J = 16.0$ Hz, 1H), 5.93 (s, 1H), 5.41 (d, $J = 3.7$ Hz, 1H), 4.93 – 4.73 (m, 1H), 2.44 (d, $J = 7.7$ Hz, 2H), 2.21 (s, 3H), 2.08 – 1.90 (m, 4H), 1.84 (s, 3H), 1.78 – 1.66 (m, 1H), 1.65 – 1.44 (m, 7H), 1.31 (m, 5H), 1.25 – 1.08 (m, 7H), 1.06 (s, 3H), 1.03 – 0.96 (m, 2H), 0.93 (d, $J = 6.4$ Hz, 3H), 0.88 (d, $J = 6.4$ Hz, 7H), 0.69 (s, 3H).
\[^{13}\text{C}\{^1\text{H}\}\text{ NMR}\] (100 MHz, CDCl\textsubscript{3}) δ 165.59, 140.38, 139.62, 134.18, 133.67, 133.13, 132.05, 130.31, 130.07, 129.82, 128.77, 128.03, 127.98, 126.37, 123.14, 122.81, 120.45 (q, \(J = 325.7\) Hz), 74.60, 64.11, 56.70, 56.15, 50.05, 42.33, 39.75, 39.54, 38.21, 37.03, 36.65, 36.21, 35.83, 31.95, 31.89, 28.26, 28.04, 27.88, 26.39, 24.32, 23.86, 22.86, 22.60, 21.07, 19.39, 18.75, 17.95, 11.89.

HRMS (ESI-TOF) \(m/z\) [M + H]\(^+\) calcd for C\textsubscript{48}H\textsubscript{63}F\textsubscript{3}NO\textsubscript{2}S 806.4424 found 806.4428.

\((E)-3,7\text{-dimethyloct-6-en-1-yl}\ 4\text{-}(2\text{-}(2,4\text{-dimethyl-1-((trifluoromethyl)sulfonyl)}\text{-}1,2\text{-dihydroquinolin-2-yl)}vinyl)benzoate\)

82%, 94 mg, colorless liquid

\(^1\text{H}\) NMR (500 MHz, CDCl\textsubscript{3}) δ 7.93 (d, \(J = 8.2\) Hz, 2H), 7.55 (d, \(J = 7.6\) Hz, 1H), 7.34 (d, \(J = 7.9\) Hz, 1H), 7.32 – 7.24 (m, 4H), 6.46 (d, \(J = 16.0\) Hz, 1H), 6.26 (d, \(J = 16.0\) Hz, 1H), 5.95 (s, 1H), 5.12 (t, \(J = 6.8\) Hz, 1H), 4.42 – 4.25 (m, 2H), 2.23 (s, 3H), 2.02 (m, 2H), 1.86 (s, 3H), 1.80 (m, 1H), 1.70 (s, 3H), 1.66 (m, 1H), 1.62 (s, 3H), 1.58 (m, 1H), 1.47 – 1.38 (m, 1H), 1.29 – 1.22 (m, 1H), 0.98 (d, \(J = 6.5\) Hz, 3H).

\(^{13}\text{C}\{^1\text{H}\}\text{ NMR}\) (125 MHz, CDCl\textsubscript{3}) δ 166.26, 140.49, 134.20, 133.78, 131.37, 130.33, 129.80, 129.76, 128.75, 128.01, 127.98, 127.78, 126.42, 124.56, 123.13, 120.25 (q, \(J = 325.7\) Hz). 64.10, 63.52, 36.98, 35.50, 29.60, 26.37, 25.69, 25.40, 19.49, 17.91, 17.65.

HRMS (ESI-TOF) \(m/z\) [M + Na]\(^+\) calcd for C\textsubscript{31}H\textsubscript{36}F\textsubscript{3}NO\textsubscript{4}S 598.2209 found 598.2198.

\((E)-2,4\text{-dimethyl-2-((4-methylstyryl)}-2\text{H-chromene}\)

44.49mg, 88%, colorless sticky liquid

\(^1\text{H}\) NMR (500 MHz, CDCl\textsubscript{3}) δ 7.27 (d, \(J = 8.2\) Hz, 2H), 7.21 – 7.15 (m, 2H), 7.12 (d, \(J = 7.8\) Hz, 2H), 6.91 (m, 2H), 6.57 (d, \(J = 16.0\) Hz, 1H), 6.27 (d, \(J = 16.2\) Hz, 1H), 5.51 (d, \(J = 1.5\) Hz, 1H), 2.34 (s, 3H), 2.11 (d, \(J = 1.5\) Hz, 3H).

\(^{13}\text{C}\{^1\text{H}\}\text{ NMR}\) (126 MHz, CDCl\textsubscript{3}) δ 153.00, 137.55, 134.00, 131.68, 129.30, 129.21, 128.89, 128.86, 126.64, 124.93, 123.56, 120.79, 116.39, 77.50, 27.68, 21.31, 18.21.

HRMS (ESI-TOF) \(m/z\) [M + H]\(^+\) calcd for C\textsubscript{20}H\textsubscript{21}O\textsubscript{2} 277.1587, found 277.1582.
(E)-2-(4-chlorostyryl)-2,4-dimethyl-2H-chromene

\[
\begin{align*}
\text{Me} & \quad \text{Cl} \\
\text{O} & \quad \text{Me}
\end{align*}
\]

47.36mg, 80%, colorless sticky liquid

\(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta \) 7.29 – 7.26 (m, 4H), 7.17 (m, 2H), 6.91 (t, \(J = 7.6\) Hz, 1H), 6.89 (d, \(J = 8.1\) Hz, 1H), 6.54 (d, \(J = 16.0\) Hz, 1H), 6.27 (d, \(J = 16.0\) Hz, 1H), 5.49 (d, \(J = 1.5\) Hz, 1H), 2.10 (d, \(J = 1.5\) Hz, 3H), 1.63 (s, 3H).

\(^{13}\text{C}[^1\text{H}]\text{NMR (125 MHz, CDCl}_3\) \(\delta \) 152.89, 135.35, 133.38, 133.33, 129.33, 129.14, 128.75, 127.96, 127.68, 124.53, 123.64, 122.94, 120.93, 116.37, 77.36, 27.69, 18.22.

HRMS (ESI-TOF) \(m/z\) [M+H]^+ calcd for C\(_{19}\)H\(_{18}\)ClO\(_2\) 297.1041, found 297.1031.

(E)-2,4-dimethyl-2-(2-(napthalen-1-yl)vinyl)-2H-chromene

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{O} & \quad \text{C}_8\text{H}_7
\end{align*}
\]

49.29mg, 79%, colorless liquid

\(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta \) 7.96 – 7.89 (m, 1H), 7.85 (dd, \(J = 6.3, 3.2\) Hz, 1H), 7.78 (d, \(J = 8.2\) Hz, 1H), 7.57 (d, \(J = 8.1\) Hz, 1H), 7.50 (m, 2H), 7.46 – 7.41 (m, 1H), 7.38 (d, \(J = 15.7\) Hz, 1H), 7.24 (m, 2H), 7.02 – 6.94 (m, 2H), 6.30 (d, \(J = 15.7\) Hz, 1H), 5.61 (s, 1H), 2.16 (d, \(J = 1.3\) Hz, 3H), 1.75 (s, 3H).

\(^{13}\text{C}[^1\text{H}]\text{NMR (125 MHz, CDCl}_3\) \(\delta \) 153.03, 135.43, 134.68, 133.57, 131.29, 129.24, 129.22, 128.45, 127.89, 126.21, 125.97, 125.73, 125.55, 124.79, 123.84, 123.55, 123.21, 120.86, 116.42, 77.51, 27.66, 18.12.

HRMS (ESI-TOF) \(m/z\) [M + H]^+ calcd for C\(_{23}\)H\(_{21}\)O 331.1587, found 331.1575.

(E)-2-(2-cyclohexylvinyl)-2,4-dimethyl-2H-chromene

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{O} & \quad \text{C}_8\text{H}_7
\end{align*}
\]

42.90, 81%, colorless liquid

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta \) 7.15 – 7.08 (m, 2H), 6.86 (td, \(J = 7.5, 1.2\) Hz, 1H), 6.80 (dd, \(J = 7.9, 0.9\) Hz, 1H), 5.60 (dd, \(J = 15.7, 6.3\) Hz, 1H), 5.51 (dd, \(J = 15.8, 0.9\) Hz, 1H), 5.38 (d, \(J = 1.4\) Hz, 1H), 2.03
(d, J = 1.4 Hz, 3H), 1.95 – 1.85 (m, 1H), 1.65 (dd, J = 14.5, 6.9 Hz, 4H), 1.48 (s, 6H), 1.29 – 0.94 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.91, 136.12, 130.41, 128.85, 128.14, 125.65, 123.24, 123.10, 120.43, 116.25, 77.28, 40.19, 32.74, 27.22, 26.15, 25.99, 18.03.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{19}$H$_{25}$O 269.1900, found 269.1960.

(E)-2-methyl-4-phenyl-2-styryl-2H-chromene

53.78mg, 83%, colorless liquid

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.33 (m, 7H), 7.29 (t, J = 7.4 Hz, 2H), 7.22 (t, J = 7.8 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 7.7 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.82 (t, J = 6.9 Hz, 1H), 6.68 (d, J = 16.1 Hz, 1H), 6.36 (d, J = 16.1 Hz, 1H), 5.69 (s, 1H), 1.71 (s, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 153.30, 138.29, 136.58, 136.00, 131.94, 129.51, 129.43, 128.78, 128.53, 128.40, 127.87, 127.75, 126.68, 126.25, 125.79, 122.29, 120.78, 116.82, 77.27, 27.38.

HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{24}$H$_{21}$O$_3$ 325.1587, found 325.1584.

(E)-2-(3,7-dimethylocta-1,6-dien-1-yl)-2,4-dimethyl-2H-chromene

46.18mg, 78%, colorless liquid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.16 – 7.08 (m, 2H), 6.86 (t, J = 8.2 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 5.65 – 5.56 (m, 1H), 5.52 (d, J = 16.8 Hz, 1H), 5.40 (s, 1H), 5.10 – 4.96 (m, 1H), 2.04 (s, 3H), 2.01 – 1.76 (m, 4H), 1.68 (s, 3H), 1.58 (s, 3H), 1.50 (s, 3H), 1.41 (m, 1H), 1.27 – 1.15 (m, 1H), 1.10 – 0.98 (m, 1H), 0.75 (d, 6.6 Hz, 3H).

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) δ 153.12, 134.19, 134.13, 131.18, 131.16, 129.35, 129.32, 129.02, 128.67, 128.64, 126.88, 125.63, 125.01, 125.00, 123.42, 123.40, 123.38, 120.69, 120.65, 116.44, 77.16, 39.64, 36.67, 36.52, 32.63, 27.52, 27.49, 25.86, 25.65, 25.62, 19.44, 19.32, 18.13, 17.77.

HRMS (ESI-TOF) m/z [M + K]$^+$ calcd for C$_{22}$H$_{30}$KO 349.1928, found 349.1930.
(E)-3,7-dimethyloct-6-en-1-yl 4-(2-(2,4-dimethyl-2H-chromen-2-yl)vinyl)benzoate

71mg, 83%, colorless liquid

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.3$ Hz, 2H), 7.16 (t, $J = 9.3$ Hz, 2H), 6.90 (t, $J = 8.9$ Hz, 2H), 6.61 (d, $J = 16.1$ Hz, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 5.48 (s, 1H), 5.10 (t, $J = 8.3$ Hz, 1H), 4.40 – 4.28 (m, 2H), 2.08 (d, $J = 1.4$ Hz, 3H), 2.06 – 1.91 (m, 2H), 1.86 – 1.76 (m, 1H), 1.70 – 1.55 (m, 11H), 1.46 – 1.36 (m, 1H), 1.25 (m, $J = 16.4$, 6.7 Hz, 1H), 0.97 (d, $J = 6.5$ Hz, 3H).

$^{13}$C{$_^1$H} NMR (100 MHz, CDCl$_3$) δ 166.46, 152.74, 152.17, 151.16, 135.15, 131.40, 129.79, 129.37, 129.26, 129.13, 127.78, 126.47, 124.58, 124.20, 123.54, 122.76, 120.86, 116.24, 77.26, 63.50, 37.00, 35.51, 29.58, 27.57, 25.74, 25.41, 19.53, 18.09, 17.69.

HRMS (ESI-TOF) $m/z$ [M + H]$^+$ calcd for C$_{30}$H$_{37}$O$_3$ 445.2737, found 445.2732.

(E)-2-(hept-1-en-1-yl)-4-methyl-2-(4-methylbenzyl)-2H-chromene (10 h)

40.8 mg, 59%, colorless liquid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.21 – 7.03 (m, 6H), 6.88 (dd, $J = 12.2$, 7.6 Hz, 2H), 5.67 – 5.56 (m, 1H), 5.53 – 5.41 (m, 2H), 3.04 (d, $J = 13.5$ Hz, 1H), 2.99 (d, $J = 13.5$ Hz, 1H), 2.34 (s, 3H), 2.04 (s, 3H), 1.99 (dd, $J = 14.2$, 7.1 Hz, 2H), 1.32 – 1.25 (m, 5H), 1.17 (m, 1H), 0.87 (t, $J = 7.2$ Hz, 3H).

$^{13}$C{$_^1$H} NMR (125 MHz, CDCl$_3$) δ 152.89, 135.69, 133.23, 131.84, 131.64, 130.83, 128.93, 128.73, 128.41, 124.06, 123.30, 123.24, 120.43, 116.32, 79.62, 46.39, 32.25, 31.22, 28.72, 22.49, 21.07, 18.09, 14.02.

HRMS (ESI-TOF) $m/z$ [M + H]$^+$ calcd for C$_{25}$H$_{31}$O 347.2369, found 347.2379.
(E)-2-isobutyl-4-methyl-2-(4-methylstyrlyl)-2H-chromene(10i)

![Chemical Structure Image]

28.62 mg, 45%, colorless liquid.

\[^{1}H\text{ NMR (500 MHz, CDCl}_3\text{)} \delta 7.25 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.91 \text{–} 6.86 \text{ (m, 2H), 6.55 (d, J = 16.0 Hz, 1H), 6.14 (d, J = 16.0 Hz, 1H), 5.47 (s, 1H), 2.33 (s, 3H), 2.09 (s, 3H), 2.01 (m, 1H), 1.75 (d, J = 6.1 Hz, 2H), 1.00 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H).} \]

\[^{13}C\{^{1}H\} \text{ NMR (125 MHz, CDCl}_3\text{)} \delta 152.96, 142.61, 137.21, 134.13, 131.60, 129.14, 129.02, 128.49, 128.45, 126.41, 124.29, 123.36, 120.39, 116.13, 80.35, 49.23, 24.43, 24.37, 24.20, 21.14, 18.13. \]

HRMS (ESI-TOF) \text{m/z [M + H]^+ calecd for C}_{23}H_{27}O 319.2056, found 319.2068.}

**Functionalization:**

To a solution of 7g (50 mg, 0.10mmol) in MeOH (2 mL) was added Pd/C (10 mol%) and H\(_2\) gas was bubbled from a balloon at room temperature. After 10 h, mixture was diluted with DCM and filtered through a pad of celite bad. The combined organic phase was dried with Na\(_2\)SO\(_4\). After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel mesh100-200; hexane: ethyl acetate; 80:20) to give the product 8 (41 mg, 82% yield).

\[^{1}H\text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.39 (d, J = 8.9 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 7.28 \text{–} 7.23 (m, 2H), 7.22 \text{–} 7.15 (m, 4H), 6.92 (d, J = 7.4 Hz, 2H), 6.82 (dd, J = 9.0, 2.8 Hz, 1H), 6.45 (d, J = 2.6 Hz, 1H), 4.13 (t, J = 9.8 Hz, 1H), 3.69 (s, 3H), 2.76 (td, J = 12.9, 5.1 Hz, 1H), 2.58 (td, J = 12.8, 3.8 Hz, 1H), 2.49 \text{–} 2.38 (m, 1H), 2.28 (dd, J = 14.5, 8.7 Hz, 1H), 1.97 (t, J = 15.1 Hz, 1H), 1.82 (s, 3H), 1.62 \text{–} 1.58 (m, 1H). \]

\[^{13}C\{^{1}H\} \text{ NMR (100 MHz, CDCl}_3\text{)} \delta 158.34, 144.47, 141.24, 136.38, 129.08, 128.97, 128.48, 128.36, 128.24, 126.86, 126.07, 121.17-119.02 (q, J = 326.0 Hz) 114.71, 112.89, 66.01, 55.38, 46.38, 42.22, 41.20, 30.02, 25.08. \]

HRMS (ESI-TOF) \text{m/z [M + Na]^+ calecd for C}_{29}H_{30}F_{3}NNaO_{3}S 512.1478 found 512.1470.}
(E)-2,4-dimethyl-2-(2-(phenylethynyl)styryl)-I-(trifluoromethyl)sulfonyl)-1,2-dihydroquinoline

![Chemical Structure](image)

73.5 mg, 75 %, colorless liquid.

1H NMR (400 MHz, CDCl3) δ 7.55 (dd, J = 7.8, 1.8 Hz, 2H), 7.49 (d, J = 7.0 Hz, 1H), 7.43 (m, 4H), 7.37 (d, J = 7.9 Hz, 1H), 7.25 – 7.15 (m, 5H), 7.02 (d, J = 16.1 Hz, 1H), 6.20 (d, J = 16.1 Hz, 1H), 5.94 (s, 1H), 2.13 (s, 3H), 1.88 (s, 3H).

13C{1H} NMR (100 MHz, CDCl3) δ 137.73, 134.35, 133.13, 132.82, 132.44, 132.21, 131.58, 130.68, 128.67, 128.64, 128.59, 128.19, 128.06, 127.98, 127.80, 127.72, 125.28, 123.39, 123.23, 122.25, 122.08 (q, J = 325.8 Hz) 94.23, 87.62, 64.59, 26.68, 17.98.

HRMS (ESI-TOF) m/z [M + K]+ calcd for C28H22F3KNO2S 532.0955, found 532.0944.

(E)-2,4-dimethyl-2-(2-(phenylethynyl)styryl)-2H-chromene

![Chemical Structure](image)

52.8 mg, 73 %, colorless liquid.

1H NMR (500 MHz, CDCl3) δ 7.55 (m, 3H), 7.51 (d, J = 7.8 Hz, 1H), 7.41 (m, 3H), 7.30 – 7.28 (m, 1H), 7.23 (m, 2H), 7.16 (d, J = 7.5 Hz, 1H), 7.10 (t, J = 7.7 Hz, 1H), 6.92 – 6.85 (m, 2H), 6.42 (d, J = 14.2 Hz, 1H), 5.55 (s, 1H), 2.08 (s, 3H), 1.69 (s, 3H).

13C{1H} NMR (125 MHz, CDCl3) δ 153.08, 138.44, 134.37, 133.08, 132.59, 131.76, 129.37, 129.25, 128.60, 128.55, 127.50, 127.29, 125.32, 124.71, 123.68, 123.62, 123.05, 122.38, 120.92, 116.49, 94.36, 88.05, 77.73, 27.95, 18.30.

HRMS (ESI-TOF) m/z [M + H]+ calcd for C27H23O 363.1743, found 363.1755.

Mechanistic Study:

A sealed tube containing [Cp*RhCl2]2 (2.5 mol %), NaOAc (30 mol%) was evacuated and purged with nitrogen gas three times. Then, α-alkenylanilides 1 (0.20 mmol) and allenic acetate 2 (0.30 mmol) in DCE (2 ml) were added via syringe under nitrogen atmosphere and the reaction mixture was allowed to stir at rt for 24 h. Then, the mixture diluted with CH2Cl2 (10 mL). The mixture was filtered through a Celite pad and washed with CH2Cl2 (3 × 10 mL). The filtrate was concentrated under reduced pressure.
The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford recovered substrate 1a.

A sealed tube containing \([\text{Cp}^*\text{RhCl}_2]_2\) (2.5 mol %), NaOAc (30 mol%) was evacuated and purged with nitrogen gas three times. Then, \(\alpha\)-alkenylanilides 1 (0.20 mmol) and allenic acetate 2 (0.30 mmol) in CH\(_3\)CN (2 ml) were added via syringe under nitrogen atmosphere and the reaction mixture was allowed to stir at rt for 24 h. Then, the mixture diluted with CH\(_2\)Cl\(_2\) (10 mL). The mixture was filtered through a Celite pad and washed with CH\(_2\)Cl\(_2\) (3 \times 10 \text{ mL}) The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford annulated product 3a.
Competitive experiment: A sealed tube containing \([\text{Cp}^*\text{RhCl}_2]\)\(_2\) (2.5 mol %), NaOAc (30 mol%) was evacuated and purged with nitrogen gas three times. Then, \(\text{o-alkenylanilides 1g (0.10 mmol)}\) and \(\text{1l (0.10 mmol)}\) and allenic acetate \(2a\) (0.12 mmol) in CH\(_3CN\) (2 ml) were added via syringe under nitrogen atmosphere and the reaction mixture was allowed to stir at rt for 1 h. Then, the mixture diluted with CH\(_2\)Cl\(_2\) (10 mL). The mixture was filtered through a Celite pad and washed with CH\(_2\)Cl\(_2\) (3 \(\times\) 10 mL). The filtrate was concentrated under reduced pressure and crude NMR of mixture on recorded.
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2. Chen, P.; Nan, J.; Hu, Y.; Ma, Q.; Ma. Y. Org. Lett. 2019, 21, 4812-4815.

3. Shukla, R. K, Nair, A. M.; Khan, S.; Volla, C. M. R. Cobalt-Catalyzed C8-Dienylation of Quinoline-N-Oxides. Angew.Chem.Int. Ed. 2020, 59, 17042 –17048.

$^1$H and $^{13}$C spectra
7e, 85%
7f, 90%
Me

75, 83%
7ab, 84%
10f, 78%, dr = 1:1

Citronellal
