Supporting Information

Rh(III)-Catalyzed Regioselective C–H [4+2] C-Annulation of Vinyl Enaminones with Alkynes to Form Polysubstituted Salicylaldehydes

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I. General Remarks

All commercial available reagents were used without further purification unless otherwise noted. DCE was dried through manual solvent purification system from Innovative Technology. DME were dried by refluxing over sodium and freshly distilled prior to use. [Cp*RhCl$_2$]$_2$, enaminones 1$^2$ and alkynes 2$^3$ were prepared according to previous reports.

NMR spectra were measured on a Agilent DD2 400-MR MHz. The $^1$H NMR (400 MHz) chemical shifts were recorded relative to CDCl$_3$ as the internal reference (CDCl$_3$: $\delta$ 7.26 ppm, (CD$_3$)$_2$CO: $\delta$ 2.05 ppm). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ as the internal standard (CDCl$_3$: $\delta$ 77.16 ppm). High resolution mass spectra (HRMS) were collected on Shimadzu LCMS-IT-TOF (ESI). X-Ray single-crystal diffraction data were obtained on an Agilent Technologies Gemini single crystal diffractometer. Melting points were measured with SGW®X-4/4A/4B and are uncorrected.

II. Preparation of Exocyclic Enones$^2$

To a magnetically stirred mixture of an $\alpha,\beta$-enone$^4$ (2.5 mmol) and DMF-DMA (0.66 mL, 5 mmol) at 80 °C was added L-proline (29 mg, 10 mol%) under an N$_2$ atmosphere. The mixture was stirred until the completion of the reaction (Detected by TLC). After the reaction mixture was cooled down to room temperature, it was concentrated under vacuum and the residue was purified by flash chromatography on silica gel column (PE/EA = 1/1-1:4, v/v) to provide the desired enaminone.

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\text{O} \quad \text{MeO} \quad \text{NMe}_2 \quad \text{O}
\]

(E)-1-(Dimethylamino)-4-(4-methoxyphenyl)penta-1,4-dien-3-one: Viscous brown oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.79 (bs, 3H), 3.08 (bs, 3H), 3.81 (s, 3H), 5.22 (d, $J$ = 12.8 Hz, 1H), 5.56 (s, 1H), 5.63 (s, 1H), 6.86 (d, $J$ = 8.4 Hz, 2H), 7.58 (s, 1H), 7.72 (d, $J$ = 12.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.4, 37.3, 45.1, 55.3, 95.0, 114.2, 128.9, 130.6, 131.1, 131.2, 133.4, 134.5, 138.1, 141.2, 154.1, 158.8, 189.3 ppm. HRMS (ESI$^+$): calcd for C$_{14}$H$_{18}$NO$_2$ [M+H]$^+$ 232.1338, found 232.1339.
(E)-4-([1,1'-Biphenyl]-4-yl)-1-(dimethylamino)penta-1,4-dien-3-one: Off-white solid, 106-108 °C.  
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.81$ (bs, 3H), 3.10 (bs, 3H), 5.26 (d, $J = 12.4$ Hz, 1H), 5.69 (s, 1H), 5.76 (s, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.42-7.51 (m, 4H), 7.56-7.62 (m, 3H), 7.68 (d, $J = 12.8$ Hz, 1H) ppm.  
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 37.3$, 45.2, 96.1, 117.8, 127.0, 127.1, 127.4, 128.2, 128.9, 137.5, 140.6, 140.9, 150.6, 154.9, 195.0 ppm. HRMS (ESI$^+$): calcd for C$_{19}$H$_{20}$NO [M+H]$^+$ 278.1539, found 278.1548.

(IE,4E)-5-(Dimethylamino)-2-(4-methoxyphenyl)-1-(p-tolyl)penta-1,4-dien-3-one: Viscous brown oil.  
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.25$ (s, 3H), 2.66 (bs, 3H), 3.06 (bs, 3H), 3.85 (s, 3H), 4.96 (d, $J = 12.4$ Hz, 1H), 6.89-6.94 (m, 6H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.58 (s, 1H), 7.72 (d, $J = 12.8$ Hz, 1H) ppm.  
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.4$, 37.2, 45.1, 55.3, 95.0, 114.2, 128.9, 130.6, 131.1, 131.2, 133.4, 134.5, 138.1, 141.2, 154.1, 158.8, 189.3 ppm. HRMS (ESI$^+$): calcd for C$_{21}$H$_{24}$NO$_2$ [M+H]$^+$ 322.1802, found 322.1798.

(IE,4E)-2-Benzyl-5-(dimethylamino)-1-phenylpenta-1,4-dien-3-one: Viscous yellow oil.  
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.83$ (bs, 3H), 3.05 (bs, 3H), 4.02 (s, 2H), 5.48 (d, $J = 12.4$ Hz, 1H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.23-7.38 (m, 9H), 7.59 (s, 1H), 7.68 (d, $J = 12.4$ Hz, 1H) ppm.  
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 33.6$, 37.4, 45.0, 93.0, 125.9, 127.9, 128.3, 128.5, 128.6, 129.1, 135.1, 136.7, 140.4, 141.5, 154.2, 190.9 ppm. HRMS (ESI$^+$): calcd for C$_{20}$H$_{22}$NO [M+H]$^+$ 292.1696, found 292.1696.

III. Rh-Catalyzed Annulation of Enaminones with Alkynes

General procedure: A Schlenk tube containing an enaminone 1 (0.3 mmol), an alkyne 2 (0.2 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 2.5 mol%), AgSbF$_6$ (6.8 mg, 10 mol %), AgOAc (66.4 mg, 0.4 mmol), H$_2$O
(0.1 mol) and DCE (2.0 mL) was sealed with a teflon-coated screw cap and the mixture was stirred at 90 °C under N₂ for 15-20 h. After cooled down to room temperature, the mixture was filtered through a celite pad and washed with DCM. The filtrate was then concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/EA=25:1–5:1) to provide the final product.

4'-Hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3a): 15 h, 63.1 mg, 83%, yellow solid. M.p.: 130-132 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.87 (s, 3H), 7.00-7.06 (m, 4H), 7.15-7.18 (m, 5H), 7.26-7.29 (m, 3H), 7.62-7.65 (m, 3H), 9.74 (s, 1H), 12.59 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 113.9, 118.8, 126.6, 127.87, 127.94, 128.0, 128.7, 129.5, 130.0, 130.6, 131.4, 133.4, 135.9, 139.3, 140.1, 143.8, 159.4, 159.5, 198.4 ppm. HRMS (ESI⁺): calcd for C₂₆H₂₀O₃Na [M+Na]⁺ 403.1305, found 403.1310.

4'-Hydroxy-5'-(4-methoxyphenyl)-4,4''-dimethyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3b): 20 h, 69.4 mg, 85%, M.p.: 132-134 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.28 (s, 3H), 2.35 (s, 3H), 3.86 (s, 3H), 6.93-7.01 (m, 6H), 7.04 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.61-7.63 (m, 3H), 9.72 (s, 1H), 12.58 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 21.4, 55.5, 113.9, 119.0, 128.7, 128.8, 128.9, 129.2, 129.8, 130.6, 131.3, 132.9, 133.3, 136.1, 137.3, 137.5, 139.5, 143.9, 159.32, 159.34, 198.6 ppm. HRMS (ESI⁺): calcd for C₂₈H₂₄O₃Na [M+Na]⁺ 431.1618, found 431.1620.
4'-Hydroxy-4,4''-dimethoxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3c): 20 h, 70.4 mg, 80%, yellow solid. M.p.: 183-185 ºC. ¹H NMR (400 MHz, CDCl₃): δ = 3.76 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 6.72 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.61-7.63 (m, 3H), 9.75 (s, 1H), 12.56 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.3, 55.4, 55.5, 113.4, 113.6, 113.9, 119.0, 128.1, 128.8, 129.1, 130.6, 131.0, 132.6, 133.1, 139.4, 143.6, 158.2, 159.15, 159.24, 159.3, 198.6 ppm. HRMS (ESI⁺): calcd for C₂₈H₂₄O₅Na [M+Na]⁺ 463.1516, found 463.1515.

4,4''-Difluoro-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3d): 20 h, 71.5 mg, 86%, yellow solid. M.p.: 118-120 ºC. ¹H NMR (400 MHz, CDCl₃): δ = 3.86 (s, 3H), 6.97-7.02 (m, 6H), 7.10-7.14 (m, 2H), 7.60-7.62 (m, 3H), 9.73 (s, 1H), 12.58 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.3, 114.0, 115.1 (d, J₉CF = 21.3 Hz), 115.3 (d, J₉CF = 21.5 Hz), 118.8, 128.4, 129.9, 130.6, 131.4 (d, J₉CF = 7.9 Hz), 131.63 (d, J₉CF = 3.4 Hz), 132.5, 132.9 (d, J₉CF = 8.0 Hz), 135.8 (d, J₉CF = 3.4 Hz), 139.2, 142.6, 159.4. HRMS (ESI⁺): calcd for C₂₆H₁₈F₂O₃Na [M+Na]⁺ 439.1116, found 439.1123.

4,4''-Dichloro-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3e): 20 h, 71.5 mg, 71.7%, yellow solid. M.p.: 167-169 ºC. ¹H NMR (400 MHz, CDCl₃): δ = 3.86 (s, 3H), 6.96 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H),
7.29 (d, J = 8.4 Hz, 2H), 7.58-7.61 (m, 3H), 9.71 (s, 1H), 12.58 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 114.0, 118.7, 128.3, 128.4, 128.6, 130.2, 130.6, 131.2, 132.1, 132.6, 133.0, 134.1, 134.4, 138.2, 139.1, 142.3, 159.5, 159.8, 197.7 ppm. HRMS (ESI⁺): calcd for C₂₆H₁₈Cl₂O₃Na [M+Na]⁺ 471.0531, found 471.0530.

**4,4''-Dibromo-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3f):** 15 h, 83.4 mg, 78%, yellow solid. M.p.: 195-197 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.86 (s, 3H), 6.90 (d, J = 8.4 Hz, 2H), 6.99-7.04 (m, 4H), 7.32 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.58-7.61 (m, 3H), 9.70 (s, 1H), 12.59 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 114.0, 118.6, 122.6, 122.6, 128.3, 130.2, 130.6, 131.4, 131.5, 131.6, 132.0, 132.9, 134.5, 138.7, 139.1, 142.2, 159.5, 159.8, 197.7 ppm. HRMS (ESI⁺): calcd for C₂₆H₁₉Br₂O₃ [M+H]⁺ 536.9695, found 536.9695.

**4,4''-Diacetyl-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3g):** 18 h, 65.0 mg, 70%, yellow solid. M.p.: 189-191 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.55 (s, 3H), 2.61 (s, 3H), 3.87 (s, 3H), 7.01 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.61-7.64 (m, 3H), 7.76 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 9.69 (s, 1H), 12.62 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 26.76, 26.82, 55.5, 114.0, 118.5, 128.1, 128.20, 128.24, 130.1, 130.56, 130.60, 132.1, 135.4, 136.5 138.9, 140.6, 142.4, 144.7, 159.6, 160.1, 197.4, 197.5, 197.8 ppm. HRMS (ESI⁻): calcd for C₃₀H₂₄O₅Na [M+Na]⁻ 487.1516, found 487.1514.
Diethyl 3'-formyl-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4,4''-dicarboxylate (3h): 15 h, 75.3 mg, 72%, yellow solid. M.p.: 144-146 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.37\) (t, \(J = 7.2\) Hz, 3H), 1.40 (t, \(J = 7.2\) Hz, 3H), 3.86 (s, 3H), 4.34 (q, \(J = 7.2\) Hz, 3H), 4.38 (q, \(J = 7.2\) Hz, 3H), 7.01 (d, \(J = 8.8\) Hz, 2H), 7.10 (d, \(J = 8.4\) Hz, 2H), 7.25 (d, \(J = 8.0\) Hz), 7.61-7.64 (m, 3H), 7.84 (d, \(J = 8.4\) Hz, 2H), 7.97 (d, \(J = 8.4\) Hz, 2H), 9.69 (s, 1H), 12.61 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 14.4, 55.5, 61.2, 61.4, 114.0, 118.5, 128.2, 128.9, 129.39, 129.40, 129.9, 130.2, 130.4, 131.4, 132.3, 138.9, 140.3, 142.6, 144.4, 159.6, 160.0, 166.1, 166.4, 197.6 ppm. HRMS (ESI\(^+\)): calcd for C\(_{32}\)H\(_{28}\)O\(_7\)Na [M+Na]\(^+\) 547.177, found 547.1725.

4'-Hydroxy-5'-(4-methoxyphenyl)-4,4''-dinitro-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3i): 15 h, 47.0 mg, 50%, yellow solid. M.p.: 239-241 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.87\) (s, 3H), 7.02 (d, \(J = 8.8\) Hz, 2H), 7.13 (d, \(J = 9.2\) Hz, 2H), 7.29 (d, \(J = 8.8\) Hz, 2H), 7.61 (d, \(J = 9.2\) Hz, 2H), 7.64 (s, 1H), 8.06 (d, \(J = 8.8\) Hz, 2H), 8.20 (d, \(J = 8.8\) Hz, 2H), 9.68 (s, 1H), 12.64 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 55.5, 114.1, 118.3, 123.6, 123.7, 127.6, 130.6, 130.7, 131.0, 131.6, 132.3, 138.6, 140.9, 142.2, 146.1, 147.7, 159.8, 160.6, 196.6 ppm. HRMS (ESI\(^+\)): calcd for C\(_{26}\)H\(_{17}\)N\(_2\)O\(_7\) [M-H]\(^-\) 469.1041, found 469.1038.

4'-Hydroxy-5'-(4-methoxyphenyl)-3,3''-dimethyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3j): 24 h, 67.7 mg, 83%, yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.22\) (s, 3H), 2.28 (s, 3H), 3.86 (s, 3H),
6.80 (d, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 6.90-7.04 (m, 6H), 7.08 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.15 (t, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.61-7.63 (m, 3H), 9.74 (s, 1H), 12.57 (s, 1H) ppm. \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3): \delta = 21.47, 21.49, 55.5, 113.9, 118.8, 127.0, 127.2, 127.7, 127.8, 128.5, 128.8, 129.2, 130.6, 130.7, 132.2, 133.4, 133.9, 135.8, 137.4, 137.6, 139.3, 140.0, 144.0, 159.31, 159.33, 198.6 ppm. HRMS (ESI\(^+\)): calcld for C\(_{28}\)H\(_{25}\)O\(_3\)Na [M+Na]\(^+\) 431.1623, found 431.1619.

4'-Hydroxy-3,3''-dimethoxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3k):
16 h, 74.0 mg, 84%, yellow solid. M.p.: 125-127 °C. \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3): \delta = 3.61 (s, 3H), 3.68 (s, 3H), 3.86 (s, 1H), 6.69-6.72 (m, 3H), 6.80-6.85 (m, 2H), 7.01 (d, \( J = 8.4 \text{ Hz}, 2\text{H} \)), 7.10 (t, \( J = 8.0 \text{ Hz}, 1\text{H} \)), 7.22 (t, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.62 (d, \( J = 8.8 \text{ Hz}, 2\text{H} \)), 7.66 (s, 1H), 9.77 (s, 1H), 12.58 (s, 1H) ppm. \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3): \delta = 55.2, 55.4, 55.5, 112.8, 113.8, 113.9, 115.1, 116.8, 118.7, 122.3, 124.1, 128.6, 129.0, 129.1, 129.5, 130.6, 133.0, 137.2, 139.1, 141.4, 143.5, 159.1, 159.2, 159.37, 159.45, 198.4 ppm. HRMS (ESI\(^+\)): calcld for C\(_{28}\)H\(_{25}\)O\(_5\) [M+H]\(^+\) 441.1697, found 441.1697.

3,3''-Difluoro-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3l):
20 h, 66.5 mg, 80%, yellow solid. M.p.: 121-123 °C. \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3): \delta = 3.87 (s, 3H), 6.77 (d, \( J = 8.4 \text{ Hz}, 1\text{H} \)), 6.82 (d, \( J = 8.4 \text{ Hz}, 1\text{H} \)), 6.85-6.90 (m, 2H), 7.97-7.05 (m, 4H), 7.12-7.17 (m, 1H), 7.26-7.32 (m, 1H), 7.60-7.62 (m, 3H), 9.73 (s, 1H), 12.59 (s, 1H) ppm. \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3): \delta = 55.5, 113.9 (d, \( J_{CF} = 21.0 \text{ Hz} \)), 114.0, 115.3 (d, \( J_{CF} = 21.0 \text{ Hz} \)), 117.8 (d, \( J_{CF} = 21.8 \text{ Hz} \)), 118.3 (d, \( J_{CF} = 21.7 \text{ Hz} \)), 118.5, 125.6 (d, \( J_{CF} = 2.8 \text{ Hz} \)), 127.2 (d, \( J_{CF} = 3.1 \text{ Hz} \)), 128.3, 129.5 (d, \( J_{CF} = 8.3 \text{ Hz} \)), 129.9 (d, \( J_{CF} = 8.5 \text{ Hz} \)), 130.2, 130.6, 132.0 (d, \( J_{CF} = 2.0 \text{ Hz} \)), 137.7 (d, \( J_{CF} = 8.9 \text{ Hz} \)), 139.0, 141.9 (d, \( J_{CF} = 7.8 \text{ Hz} \)), 142.1 (d, \( J_{CF} = 1.9 \text{ Hz} \)), 159.5, 159.8, 162.37 (d, \( J_{CF} = 247.0 \text{ Hz} \)), 162.42 (d, \( J_{CF} = 245.0 \text{ Hz} \)), 197.7 ppm. HRMS (ESI\(^+\)): calcld for C\(_{26}\)H\(_{18}\)F\(_2\)O\(_3\)Na [M+Na]\(^+\) 439.1116, found 439.1113.
Dimethyl 3'-formyl-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3,3''-dicarboxylate
(3m): 15 h, 79.3 mg, 80%, yellow solid. M.p.: 134-136 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.87 (brs, 6H), 3.90 (s, 3H), 7.01 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.18 (t, $J = 8.0$ Hz, 1H), 7.30-7.37 (m, 2H), 7.62-7.65 (m, 3H), 7.82 (d, $J = 6.4$ Hz, 2H), 7.92 (s, 1H), 7.97 (d, $J = 7.2$ Hz, 1H), 9.70 (s, 1H), 12.61 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 52.3, 52.5, 55.5, 114.0, 118.6, 128.0, 128.1, 128.3, 128.5, 129.3, 130.1, 130.2, 130.3, 130.6, 131.0, 132.3, 132.4, 134.5, 135.5, 136.0, 139.1, 140.0, 142.6, 159.5, 159.9, 166.5, 166.9, 197.6 ppm. HRMS (ESI$^+$): calcd for C$_{30}$H$_{24}$O$_7$Na [M+Na]$^+$ 519.1414, found 519.1412.

2-Hydroxy-4'-methoxy-4,5-di(naphthalen-2-yl)-[1,1'-biphenyl]-3-carbaldehyde (3n): 20 h, 87.0 mg, 90%, yellow solid. M.p.: 148-150 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.88 (s, 3H), 7.02-7.08 (m, 3H), 7.28 (s, 1H), 7.37-7.43 (m, 2H), 7.46-7.50 (m, 3H), 7.66-7.79 (m, 10H), 9.76 (s, 1H), 12.67 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.5, 114.0, 119.0, 126.0, 126.2, 126.7, 126.8, 127.3, 127.6, 127.9, 128.0, 128.07, 128.14, 128.7, 128.9, 129.7, 130.6, 131.0, 132.0, 132.55, 132.64, 133.33, 133.34, 137.8, 139.7, 143.7, 159.4, 159.6, 198.3 ppm. HRMS (ESI$^+$): calcd for C$_{34}$H$_{24}$O$_3$ [M+Na]$^+$ 503.1623, found 503.1627.

2-Hydroxy-4'-methoxy-4,5-di(thiophen-2-yl)-[1,1'-biphenyl]-3-carbaldehyde (3o): 16 h, 57.2 mg, 73%, yellow solid. M.p.: 117-119 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.87 (s, 3H), 6.83 (d, $J = 1.2$ Hz, 1H), 6.91 (t, $J = 3.6$ Hz, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 7.06-7.10 (m, 2H), 7.44 (d, $J = 5.2$ Hz, 1H),
7.60 (d, J = 8.4 Hz, 2H), 7.78 (s, 1H), 9.86 (s, 1H), 12.60 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$):
$\delta = 55.5, 114.0, 120.0, 126.3, 126.8, 127.2, 127.8, 128.18, 128.22, 130.6, 130.9, 131.2, 135.7, 135.9, 138.8, 141.3, 159.6, 159.7, 198.0$ ppm. HRMS (ESI$^+$): calcd for C$_{22}$H$_{16}$O$_3$S$_2$Na [M+Na]$^+$ 415.0433, found 415.0436.

2-Hydroxy-4'-methoxy-4,5-bis(5-methylthiophen-2-yl)-[1,1'-biphenyl]-3-carbaldehyde (3p): 16 h, 65.5 mg, 78%, yellow solid. M.p.: 115-117 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.42$ (s, 3H), 2.51 (s, 3H), 3.86 (s, 3H), 6.58 (d, $J = 3.2$ Hz, 1H), 6.74 (s, 1H), 6.83 (d, $J = 3.2$ Hz, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.74 (s, 1H), 9.89 (s, 1H), 12.57 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 15.4, 15.5, 55.5, 114.0, 120.1, 125.2, 125.4, 126.6, 128.0, 128.4, 130.6, 131.2, 133.5, 135.7, 138.7, 139.0, 140.7, 142.8, 159.4, 159.5, 198.3$ ppm. HRMS (ESI$^+$): calcd for C$_{24}$H$_{21}$O$_3$S$_2$Na [M+Na]$^+$ 443.0746, found 443.0749.

2-Hydroxy-4'-methoxy-4,5-di(thiophen-3-yl)-[1,1'-biphenyl]-3-carbaldehyde (3q): 15 h, 59.6 mg, 76%, yellow solid. M.p.: 152-154 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.87$ (s, 3H), 6.68 (d, $J = 4.8$ Hz, 1H), 6.91-6.92 (m, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 7.13-7.15 (m, 2H), 7.35 (t, $J = 3.6$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.70 (s, 1H), 9.83 (s, 1H), 12.55 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 55.5, 113.9, 119.3, 122.9, 124.9, 126.1, 126.2, 128.5, 128.55, 128.61, 129.8, 130.3, 130.6, 136.0, 138.5, 138.8, 140.4, 159.37, 159.39, 198.2$ ppm. HRMS (ESI$^+$): calcd for C$_{22}$H$_{16}$O$_3$S$_2$Na [M+Na]$^+$ 415.0433, found 415.0435.
3'-Hydroxy-4''-methoxy-6'-methyl-[1,1':4',1''-terphenyl]-2'-carbaldehyde (3r): 16 h, 43.2 mg, 68%, yellow solid. M.p.: 87-89 °C. 1H NMR (400 MHz, CDCl₃): δ = 2.05 (s, 3H), 3.87 (s, 3H), 7.00-7.02 (m, 2H), 7.26-7.28 (m, 2H), 7.42-7.50 (m, 4H), 7.58-7.60 (m, 2H), 9.59 (s, 1H), 12.33 (s, 1H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 19.4, 55.5, 113.9, 119.1, 127.3, 128.1, 128.6, 129.0, 129.1, 130.0, 130.5, 136.7, 139.4, 144.7, 158.1, 159.2, 198.0 ppm. HRMS (ESI⁺): calcd for C₂₁H₁₉O₃ [M+H]+ 319.1329, found 319.1329.

6'-Ethyl-3'-hydroxy-4''-methoxy-[1,1':4',1''-terphenyl]-2'-carbaldehyde (3s): 24 h, 36.0 mg, 54%, viscous yellow oil. 1H NMR (400 MHz, CDCl₃): δ = 1.05 (t, J = 7.2 Hz, 3H), 2.37 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 7.01 (d, J = 8.4 Hz, 2H), 7.26-7.30 (m, 2H), 7.44-7.51 (m, 4H), 7.59 (d, J = 8.4 Hz, 2H), 9.54 (s, 1H), 12.36 (s, 1H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 16.0, 25.5, 55.5, 113.9, 119.0, 128.1, 128.4, 129.1, 129.5, 130.2, 130.6, 133.7, 136.3, 138.1, 144.2, 158.2, 159.3, 198.1 ppm. HRMS (ESI⁺): calcd for C₂₂H₂₀NaO₃ [M+Na]+ 355.1305, found 355.1311.

4'-Hydroxy-6'-phenyl-[1,1':3',1''-4'',1'''-quaterphenyl]-5'-carbaldehyde (3t): 20 h, 75.0 mg, 88%, yellow solid. M.p.: 157-159 °C. 1H NMR (400 MHz, CDCl₃): δ = 7.06-7.08 (m, 2H), 7.17-7.20 (m, 5H), 7.29-7.31 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.66-7.74 (m, 5H), 7.78 (d, J = 8.4 Hz, 2H), 9.77 (s, 1H), 12.67 (s, 1H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 118.8, 126.7, 127.2, 127.3, 127.5, 127.9, 128.0, 128.1, 128.9, 129.4, 129.8, 130.0, 131.4, 133.5, 135.3, 135.8, 139.5, 140.0, 140.7, 140.9, 144.4, 159.6, 198.4 ppm. HRMS (ESI⁺): calcd for C₃₁H₂₃O₂ [M+H]+ 427.1693, found 427.1697.
4'-Hydroxy-4-methoxy-6'-(4-methoxyphenyl)-[1,1':3',1''':4'',1''''-quaterphenyl]-5'-carbaldehyde (3u): 20 h, 76.8 mg, 79%, yellow solid. M.p.: 105-107 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.77 (s, 3H), 3.82 (s, 3H), 6.73 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.65-7.71 (m, 5H), 7.78 (d, J = 8.4 Hz, 2H), 9.78 (s, 1H), 12.62 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.3, 55.4, 113.5, 113.6, 119.1, 127.2, 127.3, 127.5, 128.0, 128.9, 129.0, 129.8, 131.0, 132.5, 132.6, 133.3, 135.5, 139.6, 140.6, 140.9, 144.2, 158.3, 159.2, 159.3, 198.6 ppm. HRMS (ESI⁺): calcd for C₃₃H₂₆O₄Na [M+Na]⁺ 509.1723, found 509.1719.

4'-Hydroxy-5'-(6-methoxynaphthalen-2-yl)-[1,1':2',1'''-terphenyl]-3'-carbaldehyde (3v): 20 h, 77.4 mg, 92%, yellow solid. M.p.: 145-147 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.95 (s, 3H), 7.07-7.09 (m, 2H), 7.17-7.20 (m, 2H), 7.29-7.31 (m, 3H), 7.78-7.83 (m, 4H), 8.07 (s, 1H), 9.78 (s, 1H), 12.66 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 105.7, 118.8, 119.2, 126.6, 126.7, 127.91, 127.95, 127.97, 128.1, 128.3, 129.0, 129.8, 129.9, 130.0, 131.4, 131.7, 133.5, 134.1, 135.8, 139.7, 140.1, 144.2, 158.1, 159.7, 198.4 ppm. HRMS (ESI⁺): calcd for C₃₀H₂₂O₃Na [M+Na]⁺ 453.1467, found 453.1466.

5'-(Benzo[d][1,3]dioxol-5-yl)-4'-hydroxy-[1,1':2',1'''-terphenyl]-3'-carbaldehyde (3w): 20 h, 67.8 mg, 86%, yellow solid. M.p.: 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ = 6.02 (s, 2H), 6.91 (d, J = 8.4 Hz, 1H), 7.03-7.05 (m, 2H), 7.11-7.17 (m, 6H), 7.22 (s, 1H), 7.26-7.29 (m, 3H), 7.63 (s, 1H), 9.74 (s, 1H), 12.61 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 101.3, 108.5, 110.1, 118.7, 123.0, 126.6, 127.9, 128.0, 128.1, 129.4, 129.9, 130.2, 131.4, 133.4, 135.8, 139.4, 140.0, 144.1, 147.3, 147.6, 159.4,
198.4 ppm. HRMS (ESI⁺): calcd for C_{26}H_{19}O_{4} [M+H]^+ 395.1278, found 395.1278.

![Chemical Structure](image)

4'-Hydroxy-5'-{(4-methoxyphenyl)-6'-(p-tolyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3x): 24 h, 47.9 mg, 51%, yellow solid. M.p.: 120-122 ºC. \[\text{^1H NMR (400 MHz, CDCl}_3\text{): } \delta = 2.10 (s, 3H), 3.76 (s, = 3H), 6.63-6.73 (m, 8H), 6.85 (s, 3H), 7.06 (d, J = 8.4 Hz, 2H), 7.12-7.19 (m, 5H), 9.68 (s, 1H), 12.44 (s, 1H) ppm. \[\text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta = 21.2, 55.2, 113.3, 117.8, 125.6, 126.9, 127.4, 127.6, 127.8, 127.9, 129.8, 130.5, 131.2, 131.7, 132.1, 133.6, 135.6, 136.2, 136.5, 138.9, 145.1, 150.2, 158.3, 159.8, 197.9 ppm. HRMS (ESI⁺): calcd for C_{33}H_{27}O_{3} [M+H]^+ 471.1955, found 471.1957.

IV. H/D exchange experiment

H/D exchange in the reaction of 1e using CD₃OD as the co-solvent without 2a: A solution of [Cp*RhCl₂]₂ (3.1 mg, 2.5 mol%), AgSbF₆ (6.8 mg, 10 mol%), 1e (96.3 mg, 0.3 mmol), AgOAc (66.4 mg, 0.4 mmol), H₂O (0.1 mol) in the mixture of DCE (1.8 mL) and CD₃OD (0.2 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 90 ºC for 12 h under N₂. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/EA) to provide recovered 1e (41.4 mg, 60%) as an off-white solid. The D-incorporation in recovered 1e was estimated by \[\text{^1H NMR spectroscopy, and 55% of } \alpha\text{-arylvinylic } C\text{–H and 65% of } 2\text{-}(\text{dimethylamino})\text{vinylic } C\text{–H were deuterated, respectively.}
V. Transformation of 3a into compounds 4-7

1. The reaction of 3a with TsCl\(^5\)

To a rapidly stirred solution of 3a (38.0 mg, 0.1 mmol) in DCM (2 mL) was added Et\(_3\)N (0.3 mL). The mixture was cooled to 0 °C, and a solution of TsCl (22.8 mg, 1.2 eq.) in DCM (1 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/EA = 10:1-5:1, v/v) to provide sulfonate 4 (50.7 mg, 95% yield) as a white solid.

\[\text{3'-formyl-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4'-yl 4-methylbenzenesulfonate (4):}\]

50.7 mg, 95%, a white solid. M.p.: 161-163 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.38\) (s, 3H),
3.84 (s, 3H), 6.75 (d, J = 8.4 Hz, 2H), 7.03-7.26 (m, 14H), 7.37 (d, J = 8.4 Hz, 2H), 7.48 (s, 1H), 9.89 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 20.8, 54.4, 112.7, 126.2, 126.9, 127.0, 127.1, 127.3, 127.7, 128.4, 128.8, 129.7, 130.2, 131.3, 131.9, 134.88, 134.91, 135.1, 140.5, 141.0, 144.0, 158.4, 190.3 ppm. HRMS (ESI+): calcd for C$_{33}$H$_{26}$O$_5$SNa [M+Na]$^+$ 557.1393, found 557.1396.

2. The reaction of 3a with NH$_2$OH·HCl

A solution of 3a (38.0 mg, 0.1 mmol), NH$_2$OH·HCl (1.5 eq.), NaHCO$_3$ (2.0 eq.) in DCM (1 mL)/EtOH (3 mL) was stirred at room temperature for 3h. The resulting solution was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/EA = 5:1-2:1, v/v) to provide oxime 5 (35.5 mg, 90% yield) as a white solid.

4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde oxime: 73.6 mg, 88%, yellow solid. M.p.: 233-235 ºC. 1H NMR (400 MHz, CDCl$_3$): δ = 3.86 (s, 3H), 6.99-7.04 (m, 4H), 7.08-7.14 (m, 5H), 7.24-7.26 (m, 3H), 7.42 (s, 1H), 7.44 (s, 1H), 7.62 (d, J = 8.8 Hz, 2H), 9.12 (s, 1H), 11.03 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 55.5, 113.8, 115.1, 126.2, 127.4, 127.7, 128.1, 128.6, 129.99, 130.04, 130.6, 131.2, 133.6, 134.1, 137.8, 140.9, 141.1, 153.2, 154.4, 159.0 ppm. HRMS (ESI+): calcd for C$_{26}$H$_{21}$NO$_3$Na [M+Na]$^+$ 418.1414, found 418.1413.

3. The reaction of 3a with acrylaldehyde to form 2H-chromene product 6

A solution of 3a (38.0 mg, 0.1 mmol), acrylaldehyde (1.2 eq.), K$_2$CO$_3$ (2.0 eq.) in dioxane (1 mL) was stirred at 100 ºC for 3h under N$_2$ atmosphere. The resulting solution was concentrated under reduced
pressure and the residue was purified by flash chromatography on silica gel column (PE/EA = 10:1-5:1, v/v) to provide 2H-chromene 6 (73.6 mg, 88% yield) as a yellow solid.

8-(4-methoxyphenyl)-5,6-diphenyl-2H-chromene-3-carbaldehyde: 41.8 mg, 88%, yellow solid. M.p.: 112-114 °C. 1H NMR (400 MHz, CDCl3): δ = 3.87 (s, 3H), 5.01 (s, 2H), 6.99 (d, J = 8.0 Hz, 2H), 7.06-7.17 (m, 8H), 7.30 (brs, 3H), 7.48 (s, 1H), 7.55 (d, J = 7.2 Hz, 2H), 9.45 (s, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ = 55.5, 62.4, 113.8, 120.6, 126.5, 127.6, 127.9, 128.1, 129.0, 129.2, 129.9, 130.6, 131.31, 131.34, 135.2, 135.7, 137.4, 139.6, 140.6, 141.3, 152.6, 159.3, 190.0 ppm. HRMS (ESI+): calcd for C29H22O3Na [M+Na]+ 441.1460, found 441.1460.

4. The reaction of 3a with dimethyl malonate to form 2H-chromen-2-one product 7

A solution of 3a (38.0 mg, 0.1 mmol), dimethyl malonate (1.2 eq.), piperidine (5 mol%) in DCM (1 mL)/CH3CN (2 mL) was stirred at room temperature for 12 h. The resulting solution was concentrated under reduced pressure to provide 2H-chromen-2-one 7 (42.0 mg, 91% yield) as a yellow solid through recrystallization (PE/DCM).

methyl 8-(4-methoxyphenyl)-2-oxo-5,6-diphenyl-2H-chromene-3-carboxylate: 42.0 mg, 91%, yellow solid. M.p.: 233-235 °C. 1H NMR (400 MHz, CDCl3): δ = 3.87 (s, 3H), 3.88 (s, 3H), 7.03-7.13 (m, 6H), 7.18-7.20 (m, 3H), 7.32-34 (m, 3H), 7.64 (d, J = 8.8 Hz, 2H), 7.75 (s, 1H), 8.44 (s, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ = 53.0, 55.5, 114.3, 117.5, 117.6, 127.1,
127.4, 128.1, 128.2, 128.5, 129.0, 129.8, 130.9, 131.2, 135.9, 137.0, 138.2, 139.7, 139.8, 148.5, 159.8, 164.2 ppm. HRMS (ESI+): calcd for C_{30}H_{22}O_5Na [M+Na]^+ 485.1359, found 485.1358.

VI. References
VII. Copies of $^1$H and $^{13}$C NMR Spectra

![NMR Spectra of 1a](image)