

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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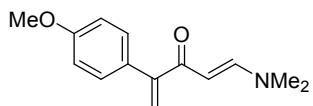
I. General Remarks

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. $[\text{Cp}^*\text{RhCl}_2]_2$,¹ enaminones **1**² and alkynes **2**³ were prepared according to previous reports.

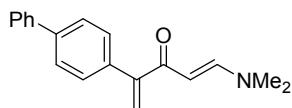
NMR spectra were measured on a Agilent DD2 400-MR MHz. The ¹H NMR (400 MHz) chemical shifts were recorded relative to CDCl_3 as the internal reference (CDCl_3 : δ 7.26 ppm, $(\text{CD}_3)_2\text{CO}$: δ 2.05 ppm). The ¹³C NMR (100 MHz) chemical shifts were given using CDCl_3 as the internal standard (CDCl_3 : δ 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 Enones²

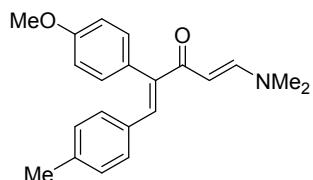
To a magnetically stirred mixture of an α,β -enone⁴ (2.5 mmol) and DMF-DMA (0.66 mL, 5 mmol) at 80 °C was added L-proline (29 mg, 10 mol%) under an N_2 atmosphere. The mixture was stirred until the completion of the reaction (Detected by TLC). After the reaction mixture was cooled down to room temperature, 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.



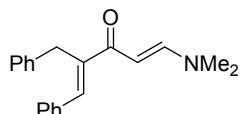
(E)-1-(Dimethylamino)-4-(4-methoxyphenyl)penta-1,4-dien-3-one: Viscous brown oil. ¹H NMR (400 MHz, CDCl_3): δ = 2.79 (bs, 3H), 3.08 (bs, 3H), 3.81 (s, 3H), 5.22 (d, J = 12.8 Hz, 1H), 5.56 (s, 1H), 5.63 (s, 1H), 6.86 (d, J = 8.4 Hz, 2H), 7.58 (s, 1H), 7.72 (d, J = 12.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl_3): δ = 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 $\text{C}_{14}\text{H}_{18}\text{NO}_2$ [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.
¹H NMR (400 MHz, CDCl₃): δ = 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.
¹³C NMR (100 MHz, CDCl₃): δ = 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 C₁₉H₂₀NO [M+H]⁺ 278.1539, found 278.1548.



(1E,4E)-5-(Dimethylamino)-2-(4-methoxyphenyl)-1-(p-tolyl)penta-1,4-dien-3-one: Viscous brown oil.
¹H NMR (400 MHz, CDCl₃): δ = 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.
¹³C NMR (100 MHz, CDCl₃): δ = 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 C₂₁H₂₄NO₂ [M+H]⁺ 322.1802, found 322.1798.

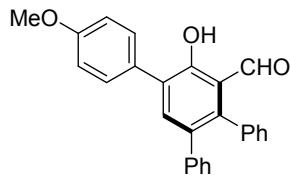


(1E,4E)-2-Benzyl-5-(dimethylamino)-1-phenylpenta-1,4-dien-3-one: Viscous yellow oil.
¹H NMR (400 MHz, CDCl₃): δ = 2.83 (bs, 3H), 3.05 (bs, 3H), 4.02 (s, 2H), 5.48 (d, *J* = 12.4 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.23-7.38 (m, 9H), 7.59 (s, 1H), 7.68 (d, *J* = 12.4 Hz, 1H) ppm.
¹³C NMR (100 MHz, CDCl₃): δ = 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 C₂₀H₂₂NO [M+H]⁺ 292.1696, found 292.1696.

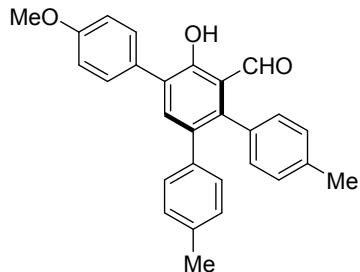
III. Rh-Catalyzed Annulation of Enaminones with Alkynes

General procedure: A Schlenk tube containing an enaminone **1** (0.3 mmol), an alkyne **2** (0.2 mmol), [Cp^{*}RhCl₂]₂ (3.1 mg, 2.5 mol%), AgSbF₆ (6.8 mg, 10 mol %), AgOAc (66.4 mg, 0.4 mmol), H₂O

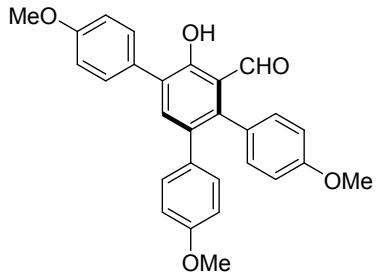
(0.1 mol) and DCE (2.0 mL) was sealed with a teflon-coated screw cap and the mixture was stirred at 90 °C under N₂ for 15-20 h. After cooled down to room temperature, the mixture was filtered through a celite pad and washed with DCM. The filtrate was then concentrated under reduced pressure and the residue 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.

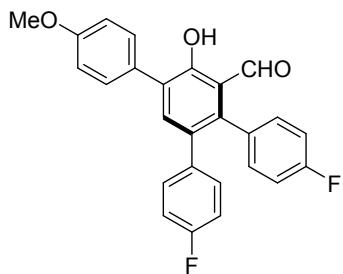


4'-Hydroxy-5'-(4-methoxyphenyl)-4,4''-dimethyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3b): 20 h, 69.4 mg, 85%, M.p.: 132-134 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.28 (s, 3H), 2.35 (s, 3H), 3.86 (s, 3H), 6.93-7.01 (m, 6H), 7.04 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.61-7.63 (m, 3H), 9.72 (s, 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.

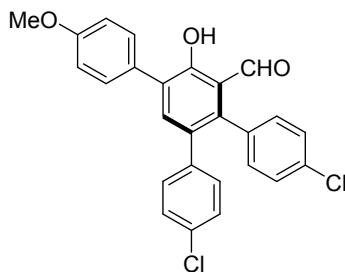


4'-Hydroxy-4,4''-dimethoxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3c):

20 h, 70.4 mg, 80%, yellow solid. M.p.: 183-185 °C. ^1H NMR (400 MHz, CDCl_3): 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. ^{13}C NMR (100 MHz, CDCl_3): 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 $\text{C}_{28}\text{H}_{24}\text{O}_5\text{Na} [\text{M}+\text{Na}]^+$ 463.1516, found 463.1515.

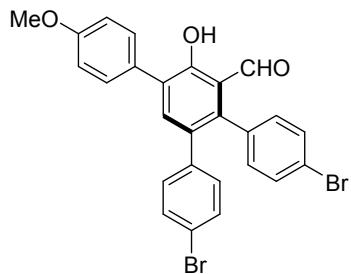


4,4''-Difluoro-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3d): 20 h, 71.5 mg, 86%, yellow solid. M.p.: 118-120 °C. ^1H NMR (400 MHz, CDCl_3): δ = 3.86 (s, 3H), 6.88 (t, J = 8.4 Hz, 2H), 6.97-7.02 (m, 6H), 7.10-7.14 (m, 2H), 7.60-7.62 (m, 3H), 9.73 (s, 1H), 12.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 55.5, 114.0, 115.1 (d, J_{CF} = 21.3 Hz), 115.3 (d, J_{CF} = 21.5 Hz), 118.8, 128.4, 129.9, 130.6, 131.4 (d, J_{CF} = 7.9 Hz), 131.63 (d, J_{CF} = 3.4 Hz), 132.5, 132.9 (d, J_{CF} = 8.0 Hz), 135.8 (d, J_{CF} = 3.4 Hz), 139.2, 142.6, 159.4, 159.6, 161.7 (d, J_{CF} = 245.3 Hz), 162.4 (d, J_{CF} = 247.2 Hz), 197.9 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{26}\text{H}_{18}\text{F}_2\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$ 439.1116, found 439.1123.

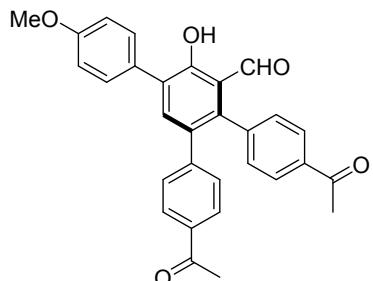


4,4''-Dichloro-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3e): 20 h, 71.5 mg, 71.7%, yellow solid. M.p.: 167-169 °C. ^1H NMR (400 MHz, CDCl_3): δ = 3.86 (s, 3H), 6.96 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H),

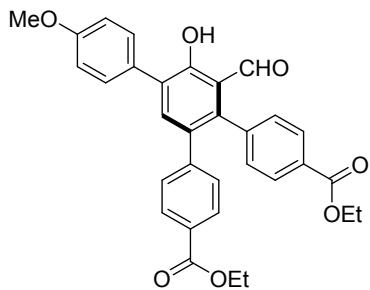
7.29 (d, $J = 8.4$ Hz, 2H), 7.58-7.61 (m, 3H), 9.71 (s, 1H), 12.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.5, 114.0, 118.7, 128.3, 128.4, 128.6, 130.2, 130.6, 131.2, 132.1, 132.6, 133.0, 134.1, 134.4, 138.2, 139.1, 142.3, 159.5, 159.8, 197.7$ ppm. HRMS (ESI $^+$): calcd for $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$ 471.0531, found 471.0530.



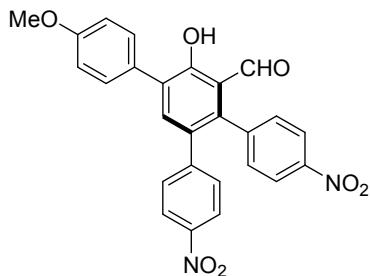
4,4''-Dibromo-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3f): 15 h, 83.4 mg, 78%, yellow solid. M.p.: 195-197 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 3.86$ (s, 3H), 6.90 (d, $J = 8.4$ Hz, 2H), 6.99-7.04 (m, 4H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.58-7.61 (m, 3H), 9.70 (s, 1H), 12.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.5, 114.0, 118.6, 121.2, 122.6, 128.3, 130.2, 130.6, 131.4, 131.5, 131.6, 132.0, 132.9, 134.5, 138.7, 139.1, 142.2, 159.5, 159.8, 197.7$ ppm. HRMS (ESI $^+$): calcd for $\text{C}_{26}\text{H}_{19}\text{Br}_2\text{O}_3 [\text{M}+\text{H}]^+$ 536.9695, found 536.9695.



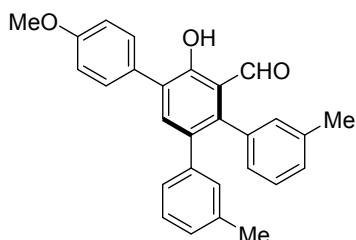
4,4''-Diacetyl-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3g): 18 h, 65.0 mg, 70%, yellow solid. M.p.: 189-191 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 2.55$ (s, 3H), 2.61 (s, 3H), 3.87 (s, 3H), 7.01 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 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. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 26.76, 26.82, 55.5, 114.0, 118.5, 128.1, 128.20, 128.24, 130.1, 130.56, 130.60, 132.1, 135.4, 136.5, 138.9, 140.6, 142.4, 144.7, 159.6, 160.1, 197.4, 197.5, 197.8$ ppm. HRMS (ESI $^+$): calcd for $\text{C}_{30}\text{H}_{24}\text{O}_5\text{Na} [\text{M}+\text{Na}]^+$ 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 °C. ^1H NMR (400 MHz, CDCl_3): δ = 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): δ = 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 $\text{C}_{32}\text{H}_{28}\text{O}_7\text{Na} [\text{M}+\text{Na}]^+$ 547.177, found 547.1725.

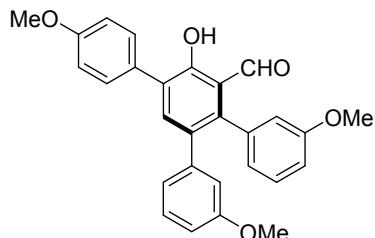


4'-Hydroxy-5'-(4-methoxyphenyl)-4,4''-dinitro-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3i): 15 h, 47.0 mg, 50%, yellow solid. M.p.: 239-241 °C. ^1H NMR (400 MHz, CDCl_3): δ = 3.87 (s, 3H), 7.02 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 9.2 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 9.2 Hz, 2H), 7.64 (s, 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): δ = 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 $\text{C}_{26}\text{H}_{17}\text{N}_2\text{O}_7 [\text{M}-\text{H}]^-$ 469.1041, found 469.1038.

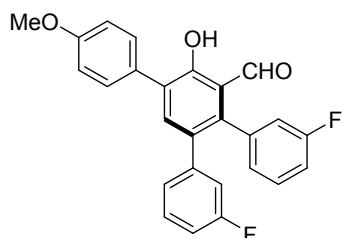


4'-Hydroxy-5'-(4-methoxyphenyl)-3,3''-dimethyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3j): 24 h, 67.7 mg, 83%, yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 2.22 (s, 3H), 2.28 (s, 3H), 3.86 (s, 3H),

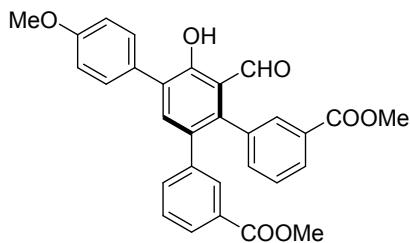
6.80 (d, $J = 7.2$ Hz, 1H), 6.90-7.04 (m, 6H), 7.08 (d, $J = 7.6$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.61-7.63 (m, 3H), 9.74 (s, 1H), 12.57 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 21.47, 21.49, 55.5, 113.9, 118.8, 127.0, 127.2, 127.7, 127.8, 128.5, 128.8, 129.2, 130.6, 130.7, 132.2, 133.4, 133.9, 135.8, 137.4, 137.6, 139.3, 140.0, 144.0, 159.31, 159.33, 198.6$ ppm. HRMS (ESI $^+$): calcd for $\text{C}_{28}\text{H}_{25}\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$ 431.1623, found 431.1619.



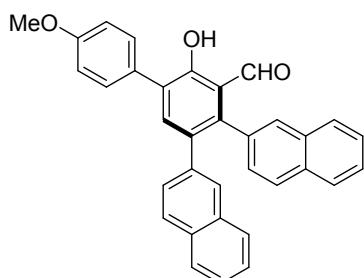
4'-Hydroxy-3,3''-dimethoxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3k): 16 h, 74.0 mg, 84%, yellow solid. M.p.: 125-127 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 3.61$ (s, 3H), 3.68 (s, 3H), 3.86 (s, 3H), 6.59 (s, 1H), 6.69-6.72 (m, 3H), 6.80-6.85 (m, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 7.10 (t, $J = 8.0$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 2H), 7.66 (s, 1H), 9.77 (s, 1H), 12.58 (s, 1H) ppm. ^{13}C NMR (100 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 $^+$): calcd for $\text{C}_{28}\text{H}_{25}\text{O}_5 [\text{M}+\text{H}]^+$ 441.1697, found 441.1697.



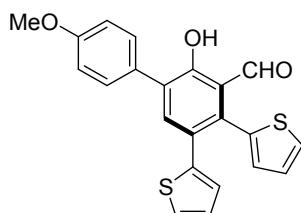
3,3''-Difluoro-4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3l): 20 h, 66.5 mg, 80%, yellow solid. M.p.: 121-123 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 3.87$ (s, 3H), 6.77 (d, $J = 8.4$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 6.85-6.90 (m, 2H), 7.97-7.05 (m, 4H), 7.12-7.17 (m, 1H), 7.26-7.32 (m, 1H), 7.60-7.62 (m, 3H), 9.73 (s, 1H), 12.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.5, 113.9$ (d, $J_{CF} = 21.0$ Hz), 114.0, 115.3 (d, $J_{CF} = 21.0$ Hz), 117.8 (d, $J_{CF} = 21.8$ Hz), 118.3 (d, $J_{CF} = 21.7$ Hz), 118.5, 125.6 (d, $J_{CF} = 2.8$ Hz), 127.2 (d, $J_{CF} = 3.1$ Hz), 128.3, 129.5 (d, $J_{CF} = 8.3$ Hz), 129.9 (d, $J_{CF} = 8.5$ Hz), 130.2, 130.6, 132.0 (d, $J_{CF} = 2.0$ Hz), 137.7 (d, $J_{CF} = 8.9$ Hz), 139.0, 141.9 (d, $J_{CF} = 7.8$ Hz), 142.1 (d, $J_{CF} = 1.9$ Hz), 159.5, 159.8, 162.37 (d, $J_{CF} = 247.0$ Hz), 162.42 (d, $J_{CF} = 245.0$ Hz), 197.7 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{26}\text{H}_{18}\text{F}_2\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$ 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 °C. ^1H NMR (400 MHz, CDCl_3): δ = 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): δ = 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 $\text{C}_{30}\text{H}_{24}\text{O}_7\text{Na}$ [M+Na] $^+$ 519.1414, found 519.1412.

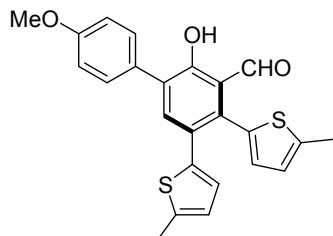


2-Hydroxy-4'-methoxy-4,5-di(naphthalen-2-yl)-[1,1'-biphenyl]-3-carbaldehyde (3n): 20 h, 87.0 mg, 90%, yellow solid. M.p.: 148-150 °C. ^1H NMR (400 MHz, CDCl_3): δ = 3.88 (s, 3H), 7.02-7.08 (m, 3H), 7.28 (s, 1H), 7.37-7.43 (m, 2H), 7.46-7.50 (m, 3H), 7.66-7.79 (m, 10H), 9.76 (s, 1H), 12.67 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 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 $\text{C}_{34}\text{H}_{24}\text{O}_3$ [M+Na] $^+$ 503.1623, found 503.1627.

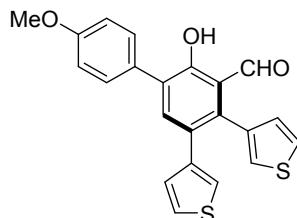


2-Hydroxy-4'-methoxy-4,5-di(thiophen-2-yl)-[1,1'-biphenyl]-3-carbaldehyde (3o): 16 h, 57.2 mg, 73%, yellow solid. M.p.: 117-119 °C. ^1H NMR (400 MHz, CDCl_3): δ = 3.87 (s, 3H), 6.83 (d, J = 1.2 Hz, 1H), 6.91 (t, J = 3.6 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.06-7.10 (m, 2H), 7.44 (d, J = 5.2 Hz, 1H),

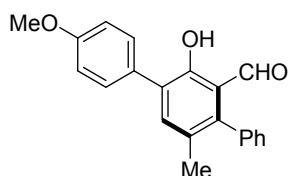
7.60 (d, $J = 8.4$ Hz, 2H), 7.78 (s, 1H), 9.86 (s, 1H), 12.60 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.5, 114.0, 120.0, 126.3, 126.8, 127.2, 127.8, 128.18, 128.22, 130.6, 130.9, 131.2, 135.7, 135.9, 138.8, 141.3, 159.6, 159.7, 198.0$ ppm. HRMS (ESI $^+$): calcd for $\text{C}_{22}\text{H}_{16}\text{O}_3\text{S}_2\text{Na} [\text{M}+\text{Na}]^+$ 415.0433, found 415.0436.



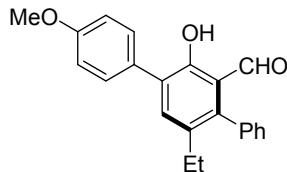
2-Hydroxy-4'-methoxy-4,5-bis(5-methylthiophen-2-yl)-[1,1'-biphenyl]-3-carbaldehyde (3p): 16 h, 65.5 mg, 78%, yellow solid. M.p.: 115-117 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 2.42$ (s, 3H), 2.51 (s, 3H), 3.86 (s, 3H), 6.58 (s, 1H), 6.65 (d, $J = 3.2$ Hz, 1H), 6.74 (s, 1H), 6.83 (d, $J = 3.2$ Hz, 1H), 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 $\text{C}_{24}\text{H}_{21}\text{O}_3\text{S}_2\text{Na} [\text{M}+\text{Na}]^+$ 443.0746, found 443.0749.



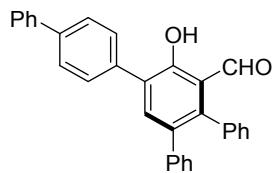
2-Hydroxy-4'-methoxy-4,5-di(thiophen-3-yl)-[1,1'-biphenyl]-3-carbaldehyde (3q): 15 h, 59.6 mg, 76%, yellow solid. M.p.: 152-154 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 3.87$ (s, 3H), 6.68 (d, $J = 4.8$ Hz, 1H), 6.91-6.92 (m, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 7.13-7.15 (m, 2H), 7.35 (t, $J = 3.6$ Hz, 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 $\text{C}_{22}\text{H}_{16}\text{O}_3\text{S}_2\text{Na} [\text{M}+\text{Na}]^+$ 415.0433, found 415.0435.



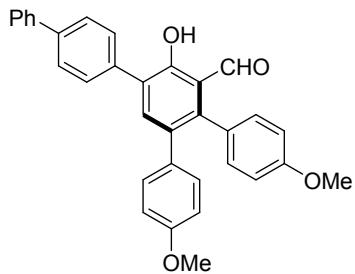
3'-Hydroxy-4''-methoxy-6'-methyl-[1,1':4',1''-terphenyl]-2'-carbaldehyde (3r): 16 h, 43.2 mg, 68%, yellow solid. M.p.: 87-89 °C. ^1H NMR (400 MHz, CDCl_3): δ = 2.05 (s, 3H), 3.87 (s, 3H), 7.00-7.02 (m, 2H), 7.26-7.28 (m, 2H), 7.42-7.50 (m, 4H), 7.58-7.60 (m, 2H), 9.59 (s, 1H), 12.33 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): 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 $\text{C}_{21}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$ 319.1329, found 319.1329.



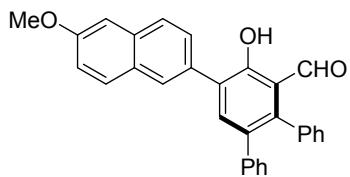
6'-Ethyl-3'-hydroxy-4''-methoxy-[1,1':4',1''-terphenyl]-2'-carbaldehyde (3s): 24 h, 36.0 mg, 54%, viscous yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.05 (t, J = 7.2 Hz, 3H), 2.37 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 7.01 (d, J = 8.4 Hz, 2H), 7.26-7.30 (m, 2H), 7.44-7.51 (m, 4H), 7.59 (d, J = 8.4 Hz, 2H), 9.54 (s, 1H), 12.36 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): 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 $\text{C}_{22}\text{H}_{20}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 355.1305, found 355.1311.



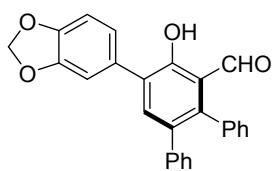
4'-Hydroxy-6'-phenyl-[1,1':3',1''-4'',1'''-quaterphenyl]-5'-carbaldehyde (3t): 20 h, 75.0 mg, 88%, yellow solid. M.p.: 157-159 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.06-7.08 (m, 2H), 7.17-7.20 (m, 5H), 7.29-7.31 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.66-7.74 (m, 5H), 7.78 (d, J = 8.4 Hz, 2H), 9.77 (s, 1H), 12.67 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): 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 $\text{C}_{31}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$ 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, CDCl_3): 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. ^{13}C NMR (100 MHz, CDCl_3): 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 $\text{C}_{33}\text{H}_{26}\text{O}_4\text{Na}$ [M+Na] $^+$ 509.1723, found 509.1719.

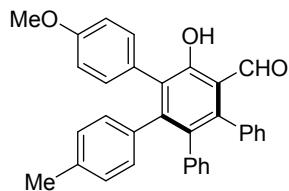


4'-Hydroxy-5'-(6-methoxynaphthalen-2-yl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (3v): 20 h, 77.4 mg, 92%, yellow solid. M.p.: 145-147 °C. ^1H NMR (400 MHz, CDCl_3): δ = 3.95 (s, 3H), 7.07-7.09 (m, 2H), 7.17-7.20 (m, 7H), 7.29-7.31 (m, 3H), 7.78-7.83 (m, 4H), 8.07 (s, 1H), 9.78 (s, 1H), 12.66 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): 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 $\text{C}_{30}\text{H}_{22}\text{O}_3\text{Na}$ [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, CDCl_3): 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. ^{13}C NMR (100 MHz, CDCl_3): 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,

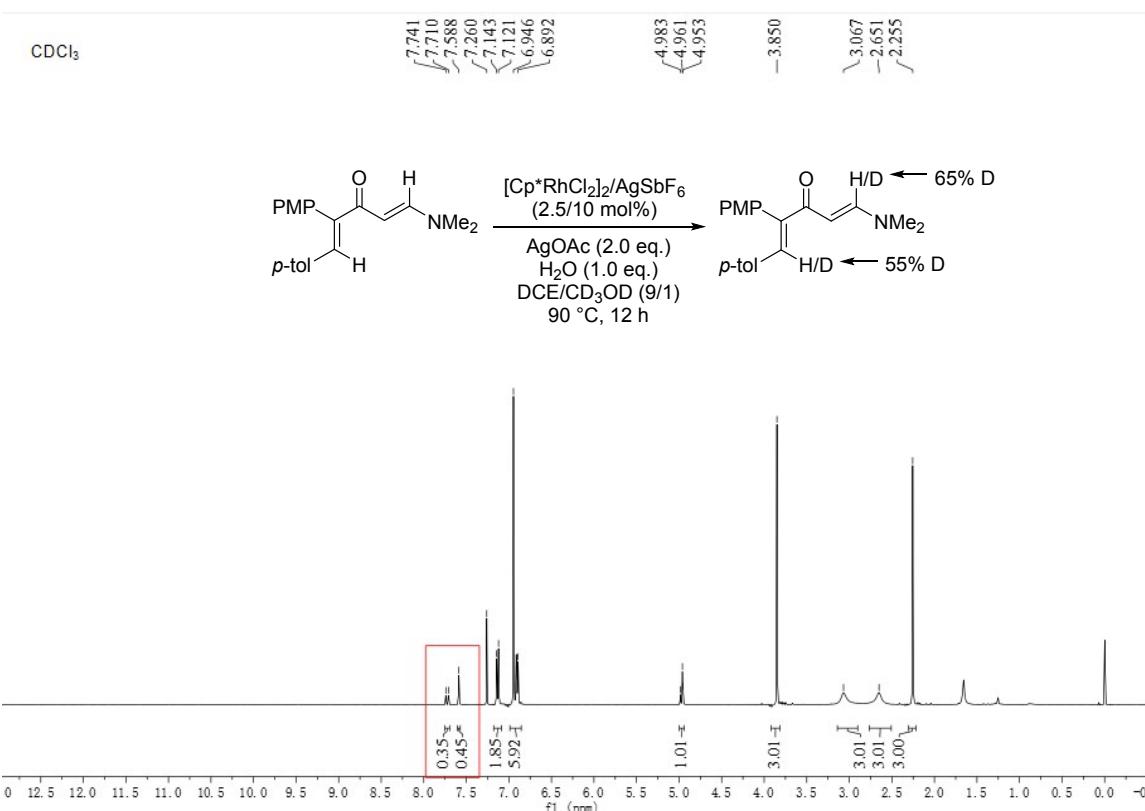
198.4 ppm. HRMS (ESI⁺): calcd for C₂₆H₁₉O₄ [M+H]⁺ 395.1278, found 395.1278.



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 °C. ¹H NMR (400 MHz, CDCl₃): δ = 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. ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₃₃H₂₇O₃ [M+H]⁺ 471.1955, found 471.1957.

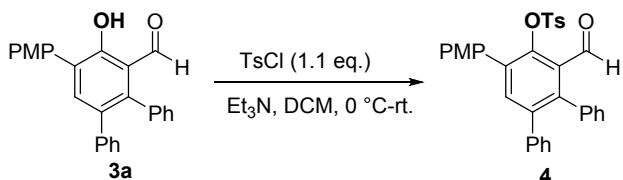
IV. H/D exchange experiment

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 °C 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 ¹H NMR spectroscopy, and 55% of α -arylvinylic C–H and 65% of 2-(dimethylamino)vinylic C–H were deuterated, respectively.

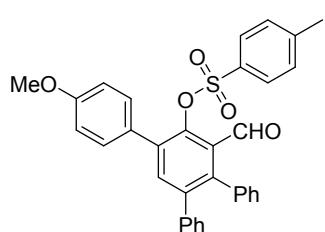


V. Transformation of 3a into compounds 4-7

1. The reaction of 3a with TsCl⁵



To a rapidly stirred solution of **3a** (38.0 mg, 0.1 mmol) in DCM (2 mL) was added Et₃N (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.

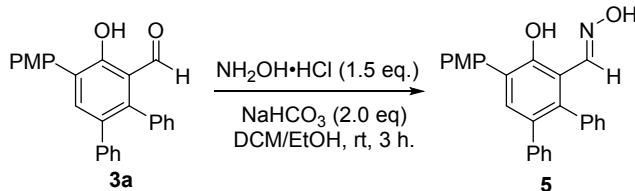


3'-formyl-5'-(4-methoxyphenyl)-[1,1':2',1"-terphenyl]-4'-yl 4-methylbenzenesulfonate (4):

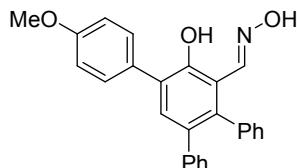
50.7 mg, 95%, a white solid. M.p.: 161-163 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.38 (s, 3H),

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 $\text{C}_{33}\text{H}_{26}\text{O}_5\text{SNa}$ [M+Na] $^+$ 557.1393, found 557.1396.

2. The reaction of **3a** with $\text{NH}_2\text{OH}\cdot\text{HCl}$ ⁶

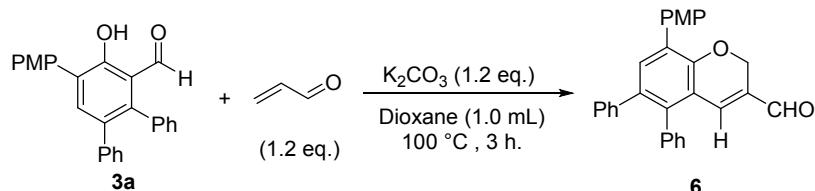


A solution of **3a** (38.0 mg, 0.1 mmol), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1.5 eq.), NaHCO_3 (2.0 eq.) in DCM (1 mL)/EtOH (3 mL) was stirred at room temperature for 3h. The resulting solution was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/EA = 5:1-2:1, v/v) to provide oxime **5** (35.5 mg, 90% yield) as a white solid.



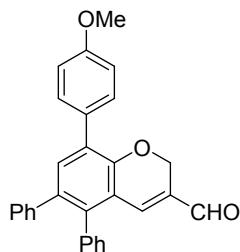
4'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde oxime: 73.6 mg, 88%, yellow solid. M.p.: 233-235 °C. ^1H NMR (400 MHz, CDCl_3): δ = 3.86 (s, 3H), 6.99-7.04 (m, 4H), 7.08-7.14 (m, 5H), 7.24-7.26 (m, 3H), 7.42 (s, 1H), 7.44 (s, 1H), 7.62 (d, J = 8.8 Hz, 2H), 9.12 (s, 1H), 11.03 (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 $\text{C}_{26}\text{H}_{21}\text{NO}_3\text{Na}$ [M+Na] $^+$ 418.1414, found 418.1413.

3. The reaction of **3a** with acrylaldehyde to form 2*H*-chromene product **6**⁷



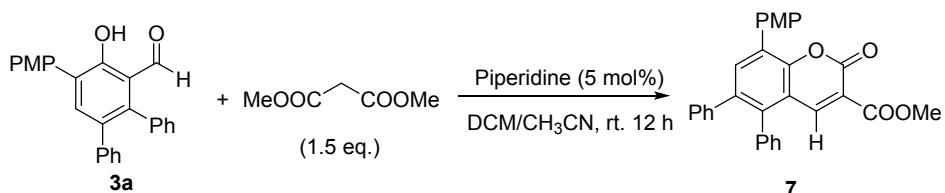
A solution of **3a** (38.0 mg, 0.1 mmol), acrylaldehyde (1.2 eq.), K_2CO_3 (2.0 eq.) in dioxane (1 mL) was stirred at 100 °C for 3h under N_2 atmosphere. The resulting solution was concentrated under reduced

pressure and the residue was purified by flash chromatography on silica gel column (PE/EA = 10:1-5:1, v/v) to provide 2*H*-chromene **6** (73.6 mg, 88% yield) as a yellow solid.

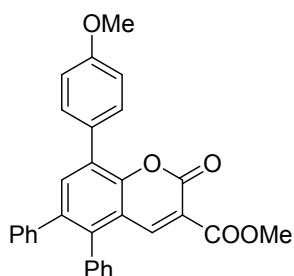


8-(4-methoxyphenyl)-5,6-diphenyl-2*H*-chromene-3-carbaldehyde: 41.8 mg, 88%, yellow solid. M.p.: 112-114 °C. ^1H NMR (400 MHz, CDCl₃): δ = 3.87 (s, 3H), 5.01 (s, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.06-7.17 (m, 8H), 7.30 (brs, 3H), 7.48 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 9.45 (s, 1H) ppm. ^{13}C NMR (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 2*H*-chromen-2-one product **7**⁸



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 2*H*-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-2*H*-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. ^{13}C 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 C₃₀H₂₂O₅Na [M+Na]⁺ 485.1359, found 485.1358.

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

