Supporting Information
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Supporting information for

Selective Synthesis of 2-Aryl-2H- and 4-Aryl-4H-3,5-Diformylpyrans from Acetal with Aromatic aldehydes Catalyzed by Lewis acids
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General

GLC analysis was performed with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). 1H and 13C NMR were measured at 400 and 100 MHz, respectively, in CDCl3 with Me4Si as the internal standard. The products were characterized by 1H NMR, 13C NMR, and GC-MS. The yields of products were estimated from the peak areas based on the internal standard technique using GLC. All starting materials were commercially available and used without any purification. Compound 4a was reported previously.1

3b: m.p. 112.5-113.5 °C; 1H-NMR: δ 9.57 (s, 1H, CHO), 9.38 (s, 1H, CHO), 7.54 (s, 2H, CH), 7.27 (s, 2H, Ph), 7.18 (s, 2H, Ph), 6.44 (s, 1H, CH), 2.35 (s, 3H, CH3); 13C-NMR: δ 189.69 (CHO), 185.74 (CHO), 166.85 (OCH), 140.10 (C), 134.21 (C), 133.10 (CH), 129.67 (CH), 128.56 (C), 127.42 (CH), 117.18 (C), 79.10 (CH), 21.27 (CH3); IR (neat, cm−1): 3095, 3076, 3025, 2860, 1668, 1599, 1301, 1182, 1033, 150, 690; GC-MS (EI) m/z (relative intensity) 228 (63) [M]+, 200 (100), 128 (79), 129 (75), 143 (43); Anal. Calcd. for C14H12O3: C, 73.67; H, 5.30. Found: C, 73.38; H, 5.24.

3c: 1H-NMR: δ 9.55 (s, 1H, CHO), 9.37 (s, 1H, CHO), 7.53 (s, 2H, CH), 7.29-7.31 (s, 2H, Ph), 6.87-8.89 (s, 2H, Ph), 6.42 (s, 1H, CH), 3.79 (s, 3H, CH3); 13C-NMR: δ 189.65 (CHO), 185.74 (CHO), 166.82 (OCH), 160.73 (C), 133.01 (CH), 129.21 (C), 128.98 (CH), 128.38 (C), 116.98 (CH), 114.21 (C), 78.87 (CH), 55.24 (OCH3); IR (neat, cm−1): 3329, 2935, 2838, 1662, 1609, 1562, 1419, 1308, 1250, 1133, 1033, 936, 178; GC-MS (EI) m/z (relative intensity) 244 (100) [M]+, 144 (44), 198 (35), 115 (34), 18 (33); HRMS (EI) m/z calcd for C14H12O4 [M]+ 244.0736, found 244.0747.

3d: m.p. 112.5-114.5 °C; 1H-NMR: δ 9.58 (s, 1H, CHO), 9.40 (s, 1H, CHO), 7.54-7.56 (m, 2H, CH), 7.26-7.37 (m, 4H, Ph), 6.44 (s, 1H, CH); 13C-NMR: δ 189.55 (CHO), 185.53 (CHO), 166.45 (OCH), 135.93 (C), 135.61 (C), 133.28 (CH), 129.22 (CH), 128.77 (CH), 128.24 (CH), 117.23 (C), 78.18 (CH); IR (neat, cm−1): 3026, 2842, 1682, 1636, 1560, 1421, 1202, 1135, 808, 641; GC-MS (EI) m/z (relative intensity) 248 (34) [M]+, 220 (100), 129 (71), 128 (65), 127 (46); HRMS (EI) m/z calcd for C13H9ClO3 [M]+ 248.0240, found 248.0234.

3e: 1H-NMR: δ 9.60 (s, 1H, CHO), 9.43 (s, 1H, CHO), 7.49-7.69 (m, 6H, Ph, CH), 6.52 (s, 1H, CH); 13C-NMR: δ 189.51 (CHO), 185.37 (CHO), 166.19 (OCH), 141.95 (C, C), 133.60 (CH), 132.77 (CH), 127.89 (CH), 118.08 (CN), 117.33 (C), 113.61 (C), 77.69
(CH); IR (neat, cm$^{-1}$): 2943, 2840, 2224, 1659, 1562, 1493, 1408, 1191, 1008, 825; GC-MS (EI) m/z (relative intensity) 239 (84) [M]$^+$, 137 (100), 127 (35), 154 (35), 238 (28); HRMS (EI) m/z calcd for C$_{14}$H$_9$NO$_3$ [M]$^+$ 239.0582, found 239.0579.

3f: $^1$H-NMR: $\delta$ 10.01 (s, 1H, CHO), 9.60 (s, 1H, CHO), 9.43 (s, 1H, CHO), 7.88-7.90 (m, 2H, CH), 7.55-7.65 (m, 4H, Ph), 6.55 (s, 1H, CH); $^{13}$C-NMR: $\delta$ 191.51 (CHO), 189.63 (CHO), 185.55 (CHO), 166.50 (OCH), 143.20 (C), 140.01 (C), 137.11 (C), 133.53 (CH), 130.24 (C), 127.85 (C), 117.32 (C), 78.07 (CH); IR (neat, cm$^{-1}$): 3041, 2738, 2829, 2738, 1659, 1556, 1412, 1309, 1193, 1133, 982, 894, 818; GC-MS (EI) m/z (relative intensity) 242 (28) [M]$^+$, 214 (100), 129 (68), 128 (43), 127 (20); HRMS (EI) m/z calcd for C$_{14}$H$_{10}$O$_4$ [M]$^+$ 242.0579, found 242.0583.

3g: m.p. 117.5-119.5 $^\circ$C; $^1$H-NMR: $\delta$ 9.60 (s, 1H, CHO), 9.42 (s, 1H, CHO), 7.50-7.66 (m, 6H, Ph, CH), 6.53 (s, 1H CH); $^{13}$C-NMR: $\delta$ 189.56 (CHO), 185.46 (CHO), 166.34 (OCH), 140.82 (C), 137.47 (CH), 128.14 (C), 127.65 (CH), 126.02 (CH), 117.34 (C), 77.96 (CH); IR (neat, cm$^{-1}$): 3049, 2837, 1678, 1637, 1561, 1417, 1338, 1198, 1118, 1070, 822, 641; GC-MS (EI) m/z (relative intensity) 282 (12) [M]$^+$, 254 (100), 129 (38), 177 (27), 128 (26); HRMS (EI) m/z calcd for C$_{12}$H$_9$O$_3$F$_3$ [M]$^+$ 282.0504, found 282.0514.

3h: m.p. 148-150 $^\circ$C; $^1$H-NMR: $\delta$ 9.62 (s, 1H, CHO), 9.39 (s, 1H, CHO), 7.51-7.87 (m, 9H, Naphtyl, CH, CH), 6.64 (s, 1H, CH); $^{13}$C-NMR: $\delta$ 189.68 (CHO), 185.72 (CHO), 166.79 (OCH), 134.22 (C), 133.85 (C), 133.37 (CH), 132.92 (CH), 129.12 (CH), 128.48 (CH), 128.41 (C), 127.70 (CH), 127.11 (CH), 126.99 (CH), 126.69 (CH), 124.66 (CH), 117.33 (C), 79.20 (CH); IR (neat, cm$^{-1}$): 3025, 2837, 1680, 1675, 1637, 1561, 1422, 1315, 1201, 1134, 824, 747; GC-MS (EI) m/z (relative intensity) 264 (100) [M]$^+$, 179 (54), 178 (49), 218 (48), 236 (38); HRMS (EI) m/z calcd for C$_{17}$H$_{12}$O$_3$ [M]$^+$ 264.0786, found 264.0794.

3i: $^1$H-NMR: $\delta$ 9.50 (s, 2H, CHO), 7.19-7.45 (m, 6H, Ph, OCH, CH), 6.27-6.36 (m, 2H CH), 4.39-4.41 (m, 1H, CH); $^{13}$C-NMR: $\delta$ 188.47 (CHO), 156.44 (OCH), 132.35 (C), 128.76 (CH), 128.43 (CH), 127.69 (CH), 126.41 (CH), 122.96 (CH), 77.20 (C), 28.18 (CH); IR (neat, cm$^{-1}$): 3055, 3027, 2963, 2927, 2852, 1671, 1592, 1492, 1364, 1245, 1173, 1038, 962, 746, 691; GC-MS (EI) m/z (relative intensity) 240 (100) [M]$^+$, 91 (80), 165 (76), 170 (74), 115 (57); HRMS (EI) m/z calcd for C$_{15}$H$_{12}$O$_3$ [M]$^+$ 240.0786, found 240.0791.
4b: m.p. 131-134 °C; $^1$H-NMR: δ 9.37 (s, 2H, CHO), 7.40 (s, 2H, CH), 7.17-7.19 (m, 2H, Ph), 7.05-7.07 (m, 2H, Ph), 4.71 (s, 1H, CH), 2.26 (s, 3H, CH$_3$); $^{13}$C-NMR: δ 188.51 (CHO), 155.83 (OCH), 138.97 (C), 136.96 (C), 129.13 (CH), 128.25 (CH), 124.01 (C), 31.46 (CH), 21.03 (CH$_3$); IR (neat, cm$^{-1}$): 2859, 1678, 1602, 1177, 1034, 885; GC-MS (EI) m/z (relative intensity) 228 (75) [M]$^+$, 213 (100), 137 (48), 128 (31), 199 (21); HRMS (EI) m/z calcld for C$_{14}$H$_{12}$O$_3$ [M]$^+$ 228.0786, found 228.0782.

4c: m.p. 109-111 °C; $^1$H-NMR: δ 9.35 (s, 2H, CHO), 7.39 (s, 2H, CH), 7.19-7.21 (m, 2H, Ph), 6.77-6.79 (m, 2H, Ph), 4.68 (s, 1H, CH), 3.71 (s, 3H, OCH$_3$); $^{13}$C-NMR: δ 188.67 (CHO), 158.65 (C), 155.91 (OCH), 134.23 (C), 129.42 (CH), 123.94 (CH), 55.16 (OCH$_3$), 30.96 (CH); IR (neat, cm$^{-1}$): 3058, 2836, 2733, 2354, 1684, 1601, 1514, 1293, 1248, 1173, 1038, 918, 824, 556; GC-MS (EI) m/z (relative intensity) 244 (100) [M]$^+$, 213 (61), 108 (45), 137 (36), 243 (34); HRMS (EI) m/z calcld for C$_{14}$H$_{12}$O$_4$ [M]$^+$ 244.0736, found 244.0735.

4d: $^1$H-NMR: δ 9.35 (s, 2H, CHO), 7.43 (s, 2H, CH), 7.22-7.23 (m, 4H, Ph), 4.70 (s, 1H, CH); $^{13}$C-NMR: δ 188.33 (CHO), 156.07 (OCH), 140.34 (C), 133.10 (C), 129.82 (CH), 128.55 (CH), 123.51 (C), 31.41 (CH); IR (neat, cm$^{-1}$): 3095, 3071, 2832, 2736, 1687, 1616, 1484, 1404, 1289, 1173, 1037, 886, 810; GC-MS (EI) m/z (relative intensity) 248 (27) [M]$^+$, 213 (100), 137 (51), 128 (17), 214 (14); HRMS (EI) m/z calcld for C$_{13}$H$_9$ClO$_3$ [M]$^+$ 248.0240, found 248.0244.

4e: m.p. 171-172.5 °C; $^1$H-NMR: δ 9.39 (s, 2H, CHO), 7.43-7.55 (m, 6H, Ph, CH), 4.78 (s, 1H, CH); $^{13}$C-NMR: δ 188.44 (CHO), 156.68 (OCH), 146.97 (C), 132.15 (CH), 129.39 (CH), 122.72 (C), 118.70 (CN), 110.93 (C); IR (neat, cm$^{-1}$): 3097, 3065, 2840, 2229, 1687, 1675, 1301, 1173, 1043, 929, 914; GC-MS (EI) m/z (relative intensity) 239 (84) [M]$^+$, 137 (100), 238 (28), 53 (24), 127 (23); HRMS (EI) m/z calcld for C$_{14}$H$_9$NO$_3$ [M]$^+$ 239.0582, found 239.0579; Anal. Calcd. for C$_{14}$H$_9$NO$_3$: C, 70.29; H, 3.79; N, 5.86. Found: C, 70.20; H, 3.84; N, 5.81.

4f: m.p. 143.5-144.5 °C; $^1$H-NMR: δ 9.94 (s, 1H, CHO), 9.41 (s, 2H, CHO), 7.80 (s, 2H, CH), 7.48-7.50 (m, 4H, Ph), 4.83 (s, 1H, CH); $^{13}$C-NMR: δ 191.78 (CHO), 188.33 (CHO), 156.28 (OCH), 148.23 (C), 135.40 (C), 129.87 (CH), 129.24 (CH), 123.13 (C), 32.27 (CH); IR (neat, cm$^{-1}$): 3094, 2865, 1694, 1677, 1604, 1294, 1183, 1028, 933, 800; GC-MS (EI) m/z (relative intensity) 242 (75) [M]$^+$, 213 (100), 137 (98), 53 (21), 128 (21); HRMS (EI) m/z calcld for C$_{14}$H$_{10}$O$_4$ [M]$^+$ 242.0579, found 242.0583.
4g: m.p. 96-97.5 °C; $^1$H-NMR: $\delta$ 9.36 (s, 2H, CHO), 7.43-7.52 (m, 6H, Ph, CH), 4.80 (s, 1H, CH); $^{13}$C-NMR: $\delta$ 188.28 (CHO), 156.31 (OCH), 145.57 (C), 129.28 (C), 128.74 (CH), 125.10 (CH), 122.96 (C), 77.69 (CF$_3$), 31.70 (CH); IR (neat, cm$^{-1}$): 3103, 2852, 1671, 1601, 1416, 1330, 1293, 1169, 1112, 1070, 1009, 927, 828, 762; GC-MS (EI) m/z (relative intensity) 282 (36) [M]$^+$, 137 (100), 213 (79), 53 (19), 128 (16); HRMS (EI) m/z calc for C$_{12}$H$_9$O$_3$F$_3$ [M]$^+$ 282.0504, found 282.0513.

4h: m.p. 201-205 °C; $^1$H-NMR: $\delta$ 9.41 (s, 2H, CHO), 7.26-7.78 (m, 9H, Ph, CH), 4.92 (s, 1H, CH); $^{13}$C-NMR: $\delta$ 188.37 (CHO), 155.83 (OCH), 133.26 (C), 128.14 (CH), 127.89 (CH), 127.60 (CH), 127.37 (CH), 126.56 (CH), 126.09 (CH), 125.93 (CH), 123.88 (CH), 32.03 (CH); IR (neat, cm$^{-1}$): 3058, 2849, 1670, 1599, 1180, 749; GC-MS (EI) m/z (relative intensity) 264 (100) [M]$^+$, 247 (41), 137 (33), 263 (31), 178 (25); HRMS (EI) m/z calc for C$_{17}$H$_{12}$O$_3$ [M]$^+$ 264.0786, found 264.0788.

4i: m.p. 161-162.5 °C; $^1$H-NMR: $\delta$ 9.49 (s, 2H, CHO), 7.38 (s, 2H, CH), 7.17-7.30 (m, 5H, Ph, CH), 6.23 (m, 2H CH), 4.39-4.40 (m, 1H, CH); $^{13}$C-NMR: $\delta$ 188.44 (CHO), 156.42 (OCH), 136.42 (C), 132.35 (CH), 128.79 (CH), 128.44 (CH), 127.69 (CH), 126.42 (CH), 122.98 (C), 28.20 (CH), 31.70 (CH); IR (neat, cm$^{-1}$): 3095, 3077, 3025, 2860, 2359, 1668, 1599, 1412, 1301, 1182, 1156, 1088, 963, 879, 750, 690; GC-MS (EI) m/z (relative intensity) 240 (34) [M]$^+$, 223 (100), 149 (43), 165 (21), 77 (20); HRMS (EI) m/z calc for C$_{15}$H$_{12}$O$_3$ [M]$^+$ 240.0786, found 240.0784.

Reference
The image contains a chemical structure labeled "4h" and two spectroscopic graphs. The chemical structure shows a molecule with functional groups including OH, CH, and CHO. The spectroscopic graphs display peaks at various ppm values, indicating chemical shifts in the NMR spectrum.