Supporting Information

Table of Contents

I. General procedures2
II. General procedures for preparation of starting materials2
i. General procedures for preparation of starting materials 1a~1f, 1h~1i, 1m~1w2
ii. General procedures for preparation of starting materials 1j~1l and 1x~y2
iii. General procedures for preparation of starting material 1g 3
iv. General procedures for preparation of starting materials 1z~1ag3
III. Characterization data of starting materials3
IV. UV-vis absorption spectra of 1a15
V. General procedures for heteroaryl/aryl rearrangement16
i. General procedures for heteroaryl rearrangement
ii. General procedures for aryl rearrangement
VI. Characterization data of rearrangement products16
VII. References29
VIII. Copies of the ¹ H, ¹⁹ F and ¹³ C NMR spectra

I. General procedures

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out in argon atmosphere unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents. ¹H, ¹³C and ¹⁹F spectra were recorded at room temperature on a Varian Mercury plus 300 or Bruker AV400 or Agilent INOVA 600 MHz with TMS as an internal standard and CDCl₃ as solvent. Fourier transform infrared spectra (FT-IR) were recorded on Agilent Technologies Cary 630 instrument or Bruker TENSOR 27 instrument. HRMS analyses were made by Lanzhou University by means of ESI. Melting points were measured on micro melting point apparatus and uncorrected.

II. General procedures for preparation of starting materials

i. General procedures for preparation of starting materials 1a~1f, 1h~1i, 1m~1w

Starting materials $1a\sim1f$, $1h\sim1i$, $1m\sim1z$ were synthesized according to the literature procedures^[1]. Salicylaldehyde (1.17 g, 9.6 mmol, 1.2 equiv.), 2-bromopyridine (1.26 g, 8.0 mmol, 1.0 equiv.), CuI (76.2 mg, 0.4 mmol, 0.05 equiv.), picolinic acid (98.5 mg, 0.8 mmol, 0.1 equiv.) and K₃PO₄ (3.4 g, 16 mmol, 2.0 equiv.) in 16 mL dry DMSO were heated at 80 °C for 24 h under argon. The reaction mixture was cooled to room temperature, 16 mL H₂O was added and extracted with 3×50 mL EtOAc. The combined organic phases were washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. Purification by column chromatography on silica (PE/EA = 16/1) affords **1a**.

ii. General procedures for preparation of starting materials 1j~1l and 1x~y

Starting materials $1j\sim11$ and $1x\sim y$ were synthesized according to the literature procedures^[2]. Salicylaldehyde (977 mg, 8.0 mmol, 1.0 equiv.), 2-chloro-5-(trifluoromethyl) pyridine (1.45 g, 8.0 mmol, 1.0 equiv.) and K₂CO₃ (1.11 g, 8.0 mmol, 1.0 equiv.) in 16 mL dry DMF were heated at 150 °C for 5 h under argon. The reaction mixture was cooled to room temperature, 16 mL H₂O was added and extracted with 3 × 40 mL EtOAc. The combined organic phases were washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. Purification by column chromatography on silica (PE/EA = 25/1) affords 1j.

iii. General procedures for preparation of starting material 1g

Starting material **1g** was synthesized according to the literature procedures^[1]. 2-Bromobenzaldehyde (1.78 g, 9.6 mmol, 1.2 equiv.), 5-fluoropyridin-2-ol (0.9 g, 8.0 mmol, 1.0 equiv.), CuI (76.2 mg, 0.4 mmol, 0.05 equiv.), picolinic acid (98.5 mg, 0.8 mmol, 0.1 equiv.) and K₃PO₄ (3.4 g, 16 mmol, 2.0 equiv.) in 16 mL dry DMSO were heated at 80 °C for 24 h under argon. The reaction mixture was cooled to room temperature, 16 mL H₂O was added and extracted with 3×50 mL EtOAc. The combined organic phases were washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. Purification by column chromatography on silica (PE/EA = 20/1) affords **1g**.

iv. General procedures for preparation of starting materials 1z~1ag

Starting materials $1z \sim 1ag$ were synthesized according to the literature procedures^[2]. To a DMA (16 mL) solution containing 2-fluorobenzaldehydes (0.85 mL, 8.0 mmol, 1.0 equiv.) and 4-hydroxybenzonitrile (954 mg, 8.0 mmol, 1.0 equiv.) were added K₂CO₃ (1.10 g, 8.0 mmol, 1.0 equiv.), and the reaction mixture was stirred for 3 h at 170 °C under argon atmosphere. The reaction mixture was cooled to room temperature, diluted with H₂O (16 mL), extracted with EtOAc (40 mL x 3), and the organic layer was washed with brine, dried with anhydrous MgSO₄ and concentrated under reduced pressure. Purification by column chromatography on silica (PE/EA = 25/1) affords 1z.

III. Characterization data of starting materials



2-(Pyridin-2-yloxy)benzaldehyde (1a)

Light yellow solid, 1.37 g, 86%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.31 (s, 1H), 8.18 (d, J = 3.4 Hz, 1H), 7.98 (dd, J = 7.8, 1.6 Hz, 1H), 7.77 (td, J = 7.9, 2.0 Hz, 1H), 7.69 – 7.60 (m, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.3 Hz, 1H), 7.10 – 7.03 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 189.3, 163.5, 156.6, 147.9, 140.1, 135.7, 128.8, 128.6, 125.3, 122.6, 119.4, 112.0; ¹H and ¹³C NMR data agreed with the literature ^[3].



2-((3-Methylpyridin-2-yl)oxy)benzaldehyde (1b)

Colorless oil, 0.94 g, 55%

¹**H** NMR (300 MHz, CDCl₃) δ 10.30 (d, J = 0.6 Hz, 1H), 8.01 – 7.93 (m, 2H), 7.66 – 7.55 (m, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 7.01 – 6.93 (m, 1H), 2.41 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.4, 161.8, 156.9, 144.9, 140.4, 135.6, 128.7, 128.4, 125.0, 122.6, 121.9, 119.5, 16.1.

IR (KBr, v / cm⁻¹): 2999, 2855, 2753, 1692, 1650, 1602, 1578, 1479, 1449, 1415, 1274, 1237, 1188, 1114, 1095, 990, 892, 833, 792, 750.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0863.



2-((4-Methylpyridin-2-yl)oxy)benzaldehyde (1c)

Colorless oil, 1.16 g, 68%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.31 (d, J = 0.5 Hz, 1H), 8.00 (dd, J = 20.1, 6.2 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 8.3 Hz, 1H), 6.88 (d, J = 6.6 Hz, 2H), 2.39 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.4, 163.8, 156.8, 151.8, 147.4, 135.7, 128.7, 128.5, 125.1, 122.5, 120.8, 112.2, 21.2.

IR (KBr, v / cm⁻¹): 3008, 2856, 2757, 1693, 1603, 1562, 1478, 1455, 1394, 1288, 1273, 1215, 1149, 1096, 947, 840, 792, 752, 631.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0862.



2-((5-Methylpyridin-2-yl)oxy)benzaldehyde (1d)

Colorless oil, 1.28 g, 75%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.34 (s, 1H), 7.98 (ddd, J = 9.5, 4.8, 1.2 Hz, 2H), 7.67 – 7.54 (m, 2H), 7.37 – 7.25 (m, 1H), 7.13 (d, J = 8.3 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 2.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.5, 161.65, 157.2, 147.6, 140.9, 135.7, 128.9, 128.7, 128.5, 125.0, 122.1, 111.6, 17.7.

IR (KBr, v / cm⁻¹): 2996, 2864, 2757, 1692, 1602, 1580, 1473, 1455, 1377, 1274, 1240, 1154, 1096, 890, 832, 787, 749.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0869.



2-((5-Methoxypyridin-2-yl)oxy)benzaldehyde (1e)

Colorless oil, 1.47 g, 80%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.38 (s, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 2.6 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.41 – 7.23 (m, 2H), 7.04 (dd, J = 19.7, 8.5 Hz, 2H), 3.84 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.2, 157.4, 156.8, 152.6, 135.4, 132.6, 128.3, 127.8, 126.3, 124.3, 121.0, 112.5, 55.9.

IR (KBr, v / cm⁻¹): 3002, 2865, 2757, 1698, 1600, 1577, 1488, 1451, 1402, 1318, 1273, 1225, 1173, 1090, 955, 821, 792, 755.

HRMS (ESI): calcd. for C₁₃H₁₂NO₃ ([M+H]⁺): 230.0812, found: 230.0814.



2-((6-Methoxypyridin-2-yl)oxy)benzaldehyde (1f)

Colorless oil, 0.95 g, 52%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.34 (d, J = 0.7 Hz, 1H), 7.96 (dd, J = 7.8, 1.8 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.19 (dd, J = 8.2, 0.6 Hz, 1H), 6.51 – 6.48 (m, 2H), 3.69 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.5, 163.4, 162.0, 156.8, 142.0, 135.5, 128.8, 128.3, 125.1, 122.5, 105.2, 102.2, 53.7.

IR (KBr, v / cm⁻¹): 2987, 2858, 2757, 1694, 1604, 1574, 1473, 1428, 1318, 1275, 1231, 1187, 1143, 1097, 1035, 974, 850, 789, 732.

HRMS (ESI): calcd. for C₁₃H₁₂NO₃ ([M+H]⁺): 230.0812, found: 230.0813.



2-((5-Fluoropyridin-2-yl)oxy)benzaldehyde (1g)

Light yellow oil, 1.23 g, 71%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.30 (s, 1H), 8.01 – 7.93 (m, 2H), 7.70 – 7.59 (m, 1H), 7.52 (ddd, J = 9.0, 7.3, 3.1 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 8.3 Hz, 1H), 7.07 (dd, J = 9.0, 3.5 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 189.2, 155.8 (d, *J* = 119.6 Hz), 146.4, 135.8, 134.8 (d, *J* = 26.6 Hz), 132.8, 129.1, 128.5, 127.7 (d, *J* = 21.2 Hz), 125.5, 122.4, 112.9 (d, J = 4.8

Hz).

¹⁹**F NMR** (376 MHz, CDCl₃) δ -134.8 (s).

IR (KBr, v / cm⁻¹): 3016, 2861, 1692, 1602, 1471, 1456, 1385, 1225, 1155, 1096, 1060, 895, 838, 812, 793, 752.

HRMS (ESI): calcd. for C₁₂H₉FNO₂ ([M+H]⁺): 218.0612, found: 218.0615.



2-((5-Chloropyridin-2-yl)oxy)benzaldehyde (1h)

Colorless oil, 1.16 g, 62%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.26 (d, J = 0.5 Hz, 1H), 8.09 (dd, J = 2.6, 0.5 Hz, 1H), 7.97 (dd, J = 7.8, 1.5 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.65 (td, J = 8.2, 1.8 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.17 (dd, J = 8.2, 0.4 Hz, 1H), 7.04 (dd, J = 8.7, 0.5 Hz, 1H).

¹³**C NMR** (75 MHz, CDCl₃) *δ* 188.1, 160.9, 155.0, 145.2, 138.9, 134.8, 128.3, 127.6, 125.8, 124.7, 121.7, 111.9.

IR (KBr, v / cm⁻¹): 3034, 2860, 1692, 1603, 1558, 1454, 1396, 1371, 1241, 1209, 1155, 1110, 1062, 889, 829, 805, 766.

HRMS (ESI): calcd. for C₁₂H₉ClNO₂ ([M+H]⁺): 234.0316, found: 234.0318.



2-((5-bromopyridin-2-yl)oxy)benzaldehyde (1i)

Light yellow oil, 1.11 g, 50%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.25 (s, 1H), 8.18 (d, J = 2.5 Hz, 1H), 7.96 (dd, J = 7.8, 1.6 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.64 (ddd, J = 8.1, 7.5, 1.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.16 (dd, J = 8.2, 0.5 Hz, 1H), 6.99 (dd, J = 8.7, 0.5 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 189.0, 162.4, 155.9, 148.5, 142.6, 135.7, 129.3, 128.7, 125.7, 122.7, 114.6, 113.5.

IR (KBr, v / cm⁻¹): 3078, 2858, 1692, 1603, 1574, 1452, 1396, 1364, 1272, 1239, 1211, 1186, 1155, 1089, 1003, 888, 827, 804, 763, 638.

HRMS (ESI): calcd. for C₁₂H₉BrNO₂ ([M+H]⁺): 277.9811, found: 277.9811.



2-((4-(Trifluoromethyl)pyridin-2-yl)oxy)benzaldehyde (1j)

Colorless oil, 0.98 g, 46%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.20 (s, 1H), 8.40 (dd, J = 1.6, 0.9 Hz, 1H), 7.99 (dt, J = 4.7, 2.1 Hz, 2H), 7.73 – 7.65 (m, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.24 – 7.16 (m, 2H). ¹³**C** NMR (151 MHz, CDCl₃) δ 188.8, 165.7, 155.1, 145.6 (d, J = 4.3 Hz), 136.6 (d, J = 235.1 Hz), 129.8, 128.8, 126.3, 124.4 (d, J = 37.3 Hz), 123.2, 122.8, 122.4 (d, J = 33.8 Hz), 111.8.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -61.7 (s).

IR (KBr, v / cm⁻¹): 2996, 2865, 1696, 1606, 1478, 1456, 1393, 1328, 1281, 1254, 1210, 1162, 1126, 1077, 1013, 893, 837, 807, 780, 758.

HRMS (ESI): calcd. for C₁₃H₉F₃NO₂ ([M+H]⁺): 268.0580, found: 268.0580.



2-(Benzo[d]thiazol-2-yloxy)benzaldehyde (1k)

Orange solid, 1.67 g, 82%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.37 (d, J = 0.7 Hz, 1H), 8.01 (dd, J = 7.7, 1.8 Hz, 1H), 7.73 – 7.68 (m, 3H), 7.51 – 7.37 (m, 3H), 7.31 (td, J = 7.7, 1.3 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 188.0, 171.2, 156.1, 148.5, 135.8, 132.3, 129.2, 127.6, 126.6, 126.4, 124.5, 121.9 (d, *J* = 2.3 Hz), 121.4; ¹H and ¹³C NMR data agreed with literature^[4].



2-((3,6-Dimethylpyrazin-2-yl)oxy)benzaldehyde (11)

Yellow solid, M.p. 66 – 67 °C, 1.32 g, 72%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.25 (d, J = 0.7 Hz, 1H), 8.07 (s, 1H), 7.97 (dd, J = 7.8, 1.8 Hz, 1H), 7.63 (ddd, J = 8.3, 7.4, 1.8 Hz, 1H), 7.43 – 7.30 (m, 1H), 7.16 (dd, J = 8.3, 1.0 Hz, 1H), 2.64 (s, 3H), 2.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.1, 157.3, 155.9, 148.7, 141.4, 138.0, 135.5, 129.2, 128.5, 125.4, 122.6, 20.7, 19.0.

IR (KBr, v / cm⁻¹): 2935, 2858, 1694, 1603, 1540, 1457, 1361, 1281, 1214, 1189, 1158, 1095, 1023, 1006, 883, 851, 810, 759.

HRMS (ESI): calcd. for C₁₃H₁₃N₂O₂ ([M+H]⁺): 229.0972, found: 229.0970.



4-Methyl-2-(pyridin-2-yloxy)benzaldehyde (1m)

Light yellow oil, 1.52 g, 89%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.23 (d, J = 0.6 Hz, 1H), 8.18 (dd, J = 5.3, 2.0 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.75 (ddd, J = 8.1, 4.9, 2.0 Hz, 1H), 7.13 (dd, J = 8.0, 0.7 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.97 (d, J = 0.4 Hz, 1H), 2.41 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.0, 163.6, 156.5, 147.8, 147.3, 140.0, 128.7, 126.4, 126.2, 122.9, 119.2, 111.9, 22.1.

IR (KBr, v / cm⁻¹): 3011, 2856, 1689, 1612, 1571, 1496, 1467, 1429, 1239, 1144, 1106, 991, 949, 883, 846, 818, 805, 779, 736, 712.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0870.



3-Methyl-2-(pyridin-2-yloxy)benzaldehyde (1n)

White solid, M.p. 67 – 68 °C, 1.23 g, 72%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.15 (d, J = 0.7 Hz, 1H), 8.09 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.82 (ddd, J = 7.7, 1.7, 0.5 Hz, 1H), 7.74 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.54 (ddd, J = 7.5, 1.7, 0.8 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.05 – 6.97 (m, 2H), 2.17 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 190.0, 163.8, 154.4, 147.9, 140.1, 137.6, 132.9, 129.6, 126.7, 126.0, 118.8, 110.7, 16.4.

IR (KBr, v / cm⁻¹): 3063, 2861, 1698, 1684, 1587, 1464, 1428, 1392, 1241, 1186, 1142, 1084, 922, 880, 817, 777, 736.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0862.



3-Methoxy-2-(pyridin-2-yloxy)benzaldehyde (10)

White solid, M.p. 101 – 102 °C, 1.15 g, 63%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.24 (d, J = 0.6 Hz, 1H), 8.09 (dd, J = 5.0, 2.0 Hz, 1H), 7.73 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.56 (dd, J = 7.7, 1.6 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.24 (dd, J = 8.1, 1.6 Hz, 1H), 7.07 (d, J = 8.3 Hz, 1H), 7.00 (ddd, J = 7.2, 5.0, 0.8 Hz, 1H), 3.77 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.7, 163.8, 152.5, 147.6, 145.5, 139.8, 130.3, 126.2,

119.6, 118.8, 118.2, 110.7, 56.4.

IR (KBr, v / cm⁻¹): 2995, 2867, 1687, 1673, 1596, 1568, 1467, 1427, 1400, 1317, 1181, 1143, 1063, 991, 911, 878, 817, 779, 740.

HRMS (ESI): calcd. for C₁₃H₁₂NO₃ ([M+H]⁺): 230.0812, found: 230.0818.

5-bromo-2-(pyridin-2-yloxy)benzaldehyde (1p)

White solid, M.p. 54 – 55 °C, 1.49 g, 67%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.21 (s, 1H), 8.15 (dd, *J* = 5.4, 2.0 Hz, 1H), 8.06 (d, *J* = 2.6 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.71 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.11 – 7.06 (m, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 187.9, 163.2, 155.5, 147.8, 140.2, 138.2, 131.4, 130.0, 124.7, 119.7, 118.6, 112.0.

IR (KBr, v / cm⁻¹): 2996, 2856, 1689, 1590, 1572, 1464, 1428, 1388, 1240, 1178, 1143, 1110, 1058, 992, 893, 864, 837, 774.

HRMS (ESI): calcd. for C₁₂H₉BrNO₂ ([M+H]⁺): 277.9811, found: 277.9812.



5-Fluoro-2-(pyridin-2-yloxy)benzaldehyde (1q)

White solid, M.p. 59 – 60 °C, 0.88 g, 51%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.21 (d, J = 3.0 Hz, 1H), 8.16 – 8.13 (m, 1H), 7.77 (ddd, J = 8.3, 7.3, 2.0 Hz, 1H), 7.63 (dd, J = 8.2, 3.2 Hz, 1H), 7.34 (ddd, J = 8.9, 7.5, 3.2 Hz, 1H), 7.19 (dd, J = 9.0, 4.3 Hz, 1H), 7.09 – 7.04 (m, 2H).

¹³**C** NMR (75 MHz, CDCl₃) δ 188.2, 163.5, 159.7 (d, J = 246.3 Hz), 152.4 (d, J = 2.5 Hz), 147.7, 140.2, 129.9 (d, J = 6.5 Hz), 124.8 (d, J = 7.7 Hz), 122.7 (d, J = 24.1 Hz), 119.5, 114.3 (d, J = 23.8 Hz), 111.7.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -116.1 (s).

IR (KBr, v / cm⁻¹): 3068, 2865, 1692, 1594, 1594, 1487, 1466, 1428, 1396, 1245, 1183, 1141, 1099, 1057, 992, 965, 877, 838, 776, 734, 710.

HRMS (ESI): calcd. for C₁₂H₉FNO₂ ([M+H]⁺): 218.0612, found: 218.0613.



5-Chloro-2-(pyridin-2-yloxy)benzaldehyde (1r) Light yellow solid, M.p. 52 – 53 °C, 1.06 g, 57%. ¹**H NMR** (300 MHz, CDCl₃) δ 10.23 (d, J = 0.6 Hz, 1H), 8.20 – 8.09 (m, 1H), 7.91 (d, J = 2.7 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.57 (ddd, J = 8.7, 2.7, 0.6 Hz, 1H), 7.16 (d, J = 8.7 Hz, 1H), 7.11 – 7.04 (m, 2H).

¹³**C NMR** (75 MHz, CDCl₃) *δ* 187.9, 163.2, 154.9, 147.8, 140.2, 135.3, 131.1, 129.7, 128.3, 124.4, 119.7, 112.0.

IR (KBr, v / cm⁻¹): 2995, 2866, 1691, 1594, 1464, 1429, 1389, 1242, 1179, 1111, 1058, 992, 870, 839, 774, 736.

HRMS (ESI): calcd. for C₁₂H₉ClNO₂ ([M+H]⁺): 234.0316, found: 234.0319.



2-((5-Methoxypyridin-2-yl)oxy)-3-methylbenzaldehyde (1s)

Colorless oil, 1.65 g, 85%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.17 (d, J = 0.7 Hz, 1H), 7.81 (dd, J = 7.7, 1.7 Hz, 1H), 7.73 (d, J = 3.1 Hz, 1H), 7.53 (ddd, J = 7.5, 1.7, 0.8 Hz, 1H), 7.36 – 7.23 (m, 2H), 6.96 (dd, J = 8.9, 0.5 Hz, 1H), 3.80 (s, 3H), 2.16 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 190.0, 158.1, 154.8, 152.3, 137.5, 132.9, 132.3, 129.7, 127.2, 126.5, 125.8, 110.8, 56.3, 16.3.

IR (KBr, v / cm⁻¹): 2938, 2839, 1681, 1586, 1484, 1465, 1440, 1384, 1233, 1185, 1084, 1031, 1010, 922, 886, 831, 786, 769, 736, 716.

HRMS (ESI): calcd. for C₁₄H₁₄NO₃ ([M+H]⁺): 244.0968, found: 244.0974.



3-Methyl-2-((5-methylpyridin-2-yl)oxy)benzaldehyde (1t)

Colorless oil, 1.40 g, 77%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.15 (s, 1H), 7.89 (d, J = 0.9 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.3 Hz, 2H), 7.31 – 7.26 (m, 1H), 6.92 (d, J = 8.4 Hz, 1H), 2.26 (s, 3H), 2.16 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 190.0, 162.0, 154.6, 147.4, 140.9, 137.5, 132.8, 129.6, 127.9, 126.5, 125.8, 109.9, 17.6, 16.3.

IR (KBr, v / cm⁻¹): 2925, 2863, 1682, 1604, 1586, 1480, 1465, 1377, 1269, 1239, 1186, 1125, 1084, 1026, 922, 884, 827, 786, 739, 718.

HRMS (ESI): calcd. for C₁₄H₁₄NO₂ ([M+H]⁺): 228.1019, found: 228.1023.



3-Methyl-2-((4-methylpyridin-2-yl)oxy)benzaldehyde (1u)

White solid, M.p. 67 – 68 °C, 1.56 g, 86%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.15 (d, J = 0.4 Hz, 1H), 7.94 (dd, J = 5.0, 2.5 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 6.9 Hz, 1H), 7.30 – 7.24 (m, 1H), 6.81 (d, J = 9.1 Hz, 2H), 2.37 (s, 3H), 2.16 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.8, 163.9, 154.4, 151.6, 147.2, 137.4, 132.7, 129.5, 126.4, 125.7, 120.1, 110.6, 21.2, 16.2.

IR (KBr, v / cm⁻¹): 2956, 2858, 1698, 1682, 1611, 1588, 1564, 1467, 1390, 1289, 1250, 1188, 1149, 1085, 946, 923, 866, 819, 793, 781, 767, 734.

HRMS (ESI): calcd. for C₁₄H₁₄NO₂ ([M+H]⁺): 228.1019, found: 228.1028.



3-Methoxy-2-((5-methoxypyridin-2-yl)oxy)benzaldehyde (1v)

White solid, M.p. 64 – 65 °C, 1.43 g, 69%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.25 (d, J = 0.7 Hz, 1H), 7.72 (d, J = 3.1 Hz, 1H), 7.54 (ddd, J = 7.7, 1.6, 0.8 Hz, 1H), 7.35 – 7.18 (m, 3H), 7.00 (dd, J = 8.9, 0.5 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 189.8, 158.0, 152.6, 152.4, 146.0, 132.1, 130.5, 126.8, 126.0, 119.5, 118.3, 110.9, 56.4, 56.2.

IR (KBr, v / cm⁻¹): 2941, 2839, 1696, 1584, 1479, 1385, 1316, 1272, 1234, 1181, 1065, 1032, 1011, 886, 834, 774, 736, 715.

HRMS (ESI): calcd. for C₁₄H₁₄NO₄ ([M+H]⁺): 260.0917, found: 260.0928.



5-Fluoro-2-((5-methylpyridin-2-yl)oxy)benzaldehyde (1w)

Light yellow solid, M.p. 46 – 47 °C, 1.24 g, 67%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.23 (d, J = 3.1 Hz, 1H), 7.95 (s, 1H), 7.67 – 7.53 (m, 2H), 7.38 – 7.26 (m, 1H), 7.15 (dd, J = 9.0, 4.3 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 2.29 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 188.3, 161.7, 159.5 (d, J = 246.3 Hz), 152.9 (d, J = 2.6

Hz), 147.3, 141.0, 129.7 (d, J = 6.3 Hz), 129.0, 124.4 (d, J = 7.6 Hz), 122.6 (d, J = 24.1 Hz), 114.1 (d, J = 23.7 Hz), 111.2, 17.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -116.6 (s). IR (KBr, v / cm⁻¹): 3023, 2866, 1690, 1604, 1581, 1472, 1425, 1377, 1244, 1183, 1141, 1027, 964, 881, 824, 744, 698.

HRMS (ESI): calcd. for C₁₃H₁₁FNO₂ ([M+H]⁺): 232.0768, found: 232.0778.



2-(Isoquinolin-1-yloxy)benzaldehyde (1x)

White solid. 15%, 0.3 g.

¹**H** NMR (300 MHz, CDCl₃) δ 10.29 (s, 1H), 8.47 (d, J = 8.1 Hz, 1H), 8.03 (dd, J = 7.8, 1.7 Hz, 1H), 7.94 (d, J = 5.9 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.73 – 7.65 (m, 2H), 7.43 – 7.30 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 189.2, 160.7, 156.5, 139.8, 138.8, 135.7, 131.4, 129.2, 128.9, 127.8, 126.7, 125.8, 124.1, 123.6, 119.6, 117.4; ¹H and ¹³C NMR data agreed with literature ^[4].



2-(Quinolin-2-yloxy)benzaldehyde (1y)

Light yellow soild. 57%, 1.1 g.

¹**H NMR** (300 MHz, CDCl₃) δ 10.32 (d, J = 0.7 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 8.00 (dd, J = 7.8, 1.7 Hz, 1H), 7.74 (dd, J = 17.3, 8.1 Hz, 2H), 7.68 – 7.56 (m, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.34 (td, J = 8.5, 4.6 Hz, 2H), 7.20 (d, J = 8.8 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 189.3, 161.6, 156.3, 146.3, 140.5, 135.5, 130.2, 128.8, 128.7, 128.0, 127.6, 126.0, 125.4, 125.4, 123.1, 112.6; ¹H and ¹³C NMR data agreed with literature ^[4].



4-(2-Formylphenoxy)benzonitrile (1z)

White solid, 0.89 g, 50%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.35 (d, J = 0.7 Hz, 1H), 7.99 (dd, J = 7.8, 1.8 Hz, 1H),

7.69 – 7.64 (m, 3H), 7.39 – 7.33 (m, 1H), 7.13 – 7.06 (m, 2H), 7.05 (dd, *J* = 8.3, 0.7 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 188.6, 161.0, 157.4, 136.3, 134.6, 129.5, 128.0, 125.6, 120.7, 119.9, 118.6, 107.3; ¹H and ¹³C NMR data agreed with literature ^[4].



Methyl 4-(2-formylphenoxy)benzoate (1aa)

White solid, 0.80 g, 39%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.41 (d, J = 0.7 Hz, 1H), 8.09 – 8.03 (m, 2H), 7.97 (dd, J = 7.8, 1.8 Hz, 1H), 7.65 – 7.55 (m, 1H), 7.29 (dd, J = 8.3, 6.8 Hz, 1H), 7.12 – 6.98 (m, 3H), 3.91 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 188.9, 166.4, 161.0, 158.4, 136.1, 132.1, 128.9, 127.6, 125.7, 124.8, 120.1, 118.1, 52.3; ¹H and ¹³C NMR data agreed with literature ^[4].



2-(4-(trifluoromethyl)phenoxy)benzaldehyde (1ab)

Colorless oil, 0.92 g, 43%.

¹**H** NMR (400 MHz, CDCl₃) δ 10.42 (s, 1H), 7.98 (dd, J = 7.8, 1.4 Hz, 1H), 7.69 – 7.51 (m, 3H), 7.30 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.3 Hz, 1H). ¹³**C** NMR (101 MHz, CDCl₃) δ 188.9, 159.9, 158.5, 136.2, 129.2, 127.8, 127.7 (q, J = 3.7 Hz), 126.3 (d, J = 33.0 Hz), 124.9, 124.2 (d, J = 271.7 Hz), 119.9, 118.7; ¹H and ¹³C NMR data agreed with literature ^[5].



2-(2-Fluorophenoxy)benzaldehyde (1ac)

White solid, 0.94 g, 54%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.62 (d, J = 0.7 Hz, 1H), 7.94 (dd, J = 7.7, 1.8 Hz, 1H), 7.49 (ddd, J = 8.4, 7.3, 1.8 Hz, 1H), 7.25 – 7.11 (m, 5H), 6.79 (d, J = 8.4 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 189.2, 160.1, 154.5 (d, J = 249.6 Hz), 142.7 (d, J = 11.2 Hz), 135.9, 128.6, 126.2 (d, J = 6.9 Hz), 125.9, 125.2 (d, J = 4.0 Hz), 123.3, 122.8, 117.5 (d, J = 18.0 Hz), 116.3; ¹H and ¹³C NMR data agreed with literature ^[6].



2-(2-bromo-4-chlorophenoxy)benzaldehyde (1ad)

Colorless oil, 1.62 g, 65%.

¹**H** NMR (400 MHz, CDCl₃) δ 10.56 (s, 1H), 7.96 (dd, J = 7.7, 1.7 Hz, 1H), 7.66 (d, J = 2.3 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.41 (dd, J = 8.7, 2.3 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.7 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) *δ* 189.0, 159.2, 150.9, 136.0, 133.9, 131.6, 129.1, 127.8, 126.4, 124.0, 123.0, 118.0, 117.0.

IR (KBr, v / cm⁻¹): 3125, 2919, 2873, 1690, 1652, 1601, 1541, 1469, 1456, 1396, 1258, 1236, 1197, 1132, 1079, 1057, 823, 760, 742.

HRMS (ESI): calcd. for C₁₃H₉BrClO₂ ([M+H]⁺): 312.9448, found: 312.9455.



2-(2,6-Dimethylphenoxy)benzaldehyde (1ae)

Light yellow solid, M.p. 62 – 63 °C, 0.87 g, 48%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.78 (d, J = 0.7 Hz, 1H), 7.93 (dd, J = 7.7, 1.8 Hz, 1H), 7.49 – 7.33 (m, 1H), 7.19 – 7.11 (m, 3H), 7.07 (dd, J = 11.7, 4.2 Hz, 1H), 6.44 (d, J = 8.4 Hz, 1H), 2.15 (s, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 189.5, 160.3, 150.4, 136.1, 131.3, 129.4, 128.7, 125.9, 124.4, 121.7, 115.3, 113.6, 16.5.

IR (KBr, v / cm⁻¹): 2981, 2854, 1690, 1651, 1600, 1581, 1474, 1456, 1395, 1267, 1224, 1180, 1156, 1099, 1089, 1035, 876, 825, 800, 762.

HRMS (ESI): calcd. for C₁₅H₁₅O₂ ([M+H]⁺): 227.1607, found: 227.1068.



2-(2-Methoxyphenoxy)benzaldehyde (1af)

White solid, 0.84 g, 46%.

¹**H NMR** (300 MHz, CDCl₃) δ 10.65 (d, J = 0.8 Hz, 1H), 7.91 (dd, J = 7.7, 1.8 Hz, 1H), 7.43 (ddd, J = 8.4, 7.3, 1.8 Hz, 1H), 7.21 (ddd, J = 8.1, 7.4, 1.8 Hz, 1H), 7.14 – 6.93

(m, 4H), 6.75 – 6.67 (m, 1H), 3.78 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.7, 161.0, 151.6, 143.8, 135.7, 128.1, 126.2, 125.6, 122.5, 122.1, 121.3, 116.3, 113.0, 55.9; ¹H and ¹³C NMR data agreed with literature ^[2].



2-(2,6-Dimethoxyphenoxy)benzaldehyde (1ag)

White solid, M.p. 110 – 111 °C, 1.09 g, 53%.

¹**H** NMR (300 MHz, CDCl₃) δ 10.77 (d, J = 0.7 Hz, 1H), 7.89 (dd, J = 7.7, 1.8 Hz, 1H), 7.38 (ddd, J = 8.5, 7.3, 1.8 Hz, 1H), 7.18 (t, J = 8.4 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.72 – 6.55 (m, 3H), 3.77 (s, 6H).

¹³**C NMR** (75 MHz, CDCl₃) *δ* 190.1, 161.5, 153.5, 135.6, 132.0, 127.9, 126.2, 125.1, 121.9, 114.9, 109.9, 105.4, 56.3.

IR (KBr, v / cm⁻¹): 2996, 2832, 1684, 1599, 1480, 1444, 1397, 1303, 1280, 1257, 1235, 1184, 1157, 1033, 875, 823, 799, 768, 750, 735, 701.

HRMS (ESI): calcd. for C₁₅H₁₅O₄ ([M+H]⁺): 259.0965, found: 259.0964.

IV. UV-vis absorption spectra of 1a



Figure S1 UV-vis absorption spectra of 1a

V. General procedures for heteroaryl/aryl rearrangement

i. General procedures for heteroaryl rearrangement

The starting materials **1** (0.2 mmol), TFA (0.2 mmol) were added into 2.0 mL of ethyl acetate in an airtight quartz tube, which was then evacuated by four freeze-pump-thaw cycles and back-filled with ultra-purified argon prior to use. The reaction was stirred at room temperature under UV irradiation (254 nm) for 24 h and 5 mL saturated NaHCO₃ aqueous solution was added into the reaction solution, and extracted with 3×5 mL EtOAc. The combined organic phases were washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. Purification by column chromatography on silica (PE/EA = 20/1) affords **2**.

ii. General procedures for aryl rearrangement

The starting materials 1 (0.2 mmol) were added into 2.0 mL of ethyl acetate in an airtight quartz tube, which was then evacuated by four freeze-pump-thaw cycles and back-filled with ultra-purified argon prior to use. The reaction was stirred at room temperature under UV irradiation (254 nm) for 24 h. The reaction mixture was concentrated under reduced pressure. Purification by column chromatography on silica (PE/EA = 30/1) affords 2.

VI. Characterization data of rearrangement products



(2-Hydroxyphenyl)(pyridin-2-yl)methanone (2a)

Yellow oil. 33.1 mg, 83%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.36 (s, 1H), 8.73 (dt, J = 4.8, 1.4 Hz, 1H), 8.11 (dd, J = 8.1, 1.7 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.56 – 7.47 (m, 2H), 7.06 (dd, J = 8.4, 0.7 Hz, 1H), 6.90 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 197.4, 163.6, 155.4, 148.4, 137.6, 136.8, 134.5, 126.3, 124.8, 119.3, 119.0, 118.6; ¹H and ¹³C NMR data agreed with literature^[4].



(2-Hydroxyphenyl)(3-methylpyridin-2-yl)methanone (2b)

Light yellow oil. 34.5 mg, 81%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.08 (s, 1H), 8.52 (dd, J = 4.7, 0.7 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.40 – 7.32 (m, 2H), 7.06 (dd, J = 8.4, 1.0 Hz, 1H), 6.88 – 6.76 (m, 1H), 2.37 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 200.6, 163.9, 154.4, 146.2, 139.2, 137.2, 133.7, 132.0, 124.8, 119.2, 119.1, 118.4, 18.2.

IR (KBr, v / cm⁻¹): 3052, 2933, 1694, 1638, 1485, 1455, 1340, 1149, 1107, 1062, 1034, 944, 864, 795, 762.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0860.



(2-Hydroxyphenyl)(4-methylpyridin-2-yl)methanone (2c)

Yellow oil. 30.2 mg, 71%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.53 (s, 1H), 8.57 (d, J = 5.0 Hz, 1H), 8.09 (dd, J = 8.1, 1.7 Hz, 1H), 7.77 – 7.76 (m, 1H), 7.54 – 7.46 (m, 1H), 7.33 (ddd, J = 5.0, 1.6, 0.7 Hz, 1H), 7.05 (dd, J = 8.4, 1.1 Hz, 1H), 6.90 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 2.47 (s, 3H).

¹³**C NMR** (75 MHz, CDCl₃) *δ* 197.5, 163.3, 155.2, 149.2, 148.0, 136.7, 134.4, 127.2, 125.5, 119.7, 119.0, 118.6, 21.4.

IR (KBr, v / cm⁻¹): 3058, 2920, 1627, 1599, 1485, 1444, 1330, 1308, 1258, 1211, 1161, 954, 855, 807, 756, 661.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0861.



(2-Hydroxyphenyl)(5-methylpyridin-2-yl)methanone (2d)

Light yellow solid, M.p. 77 – 78 °C. 38.3 mg, 90%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.51 (s, 1H), 8.54 (dd, *J* = 1.4, 0.6 Hz, 1H), 8.17 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.71 (ddd, *J* = 8.0, 2.1, 0.5 Hz, 1H), 7.49 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.93 – 6.86 (m, 1H), 2.45 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 196.9, 163.3, 152.8, 148.7, 138.0, 136.9, 136.5, 134.4, 124.6, 119.6, 118.9, 118.6, 18.8.

IR (KBr, v / cm⁻¹): 3037, 2926, 1627, 1567, 1477, 1491, 1381, 1336, 1318, 1148, 1142,

1084, 943, 849, 799, 786, 691. HRMS (ESI): calcd. for $C_{13}H_{12}NO_2$ ([M+H]⁺): 214.0863, found: 214.0860.

(2-Hydroxyphenyl)(5-methoxypyridin-2-yl)methanone (2e)

Yellow oil. 44.0 mg, 96%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.46 (s, 1H), 8.38 (d, J = 2.7 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.49 (t, J = 7.1 Hz, 1H), 7.35 (dd, J = 8.7, 2.8 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 3.95 (s, 3H).

¹³**C NMR** (75 MHz, CDCl₃) *δ* 195.8, 163.3, 157.8, 147.8, 136.4 (d, *J* = 4.4 Hz), 134.5, 126.7, 120.6, 119.5, 118.8, 118.4, 56.0.

IR (KBr, v / cm⁻¹): 3013, 2970, 2942, 2844, 1623, 1570, 1477, 1442, 1395, 1272, 1148, 1026, 941, 829, 805, 758, 687.

HRMS (ESI): calcd. for C₁₃H₁₂NO₃ ([M+H]⁺): 230.0812, found: 230.0811.



(2-Hydroxyphenyl)(6-methoxypyridin-2-yl)methanone (2f)

Yellow oil. 26.1 mg, 57%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.24 (s, 1H), 8.27 (dd, J = 8.1, 1.7 Hz, 1H), 7.77 (dd, J = 8.3, 7.3 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.06 (dd, J = 8.4, 1.1 Hz, 1H), 6.96 (dd, J = 8.4, 0.7 Hz, 1H), 6.93 – 6.85 (m, 1H), 3.97 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 197.5, 164.0, 163.0, 152.8, 139.5, 136.7, 134.4, 119.0, 118.6, 118.4, 118.0, 114.4, 54.0.

IR (KBr, v / cm⁻¹): 3080, 3015, 2983, 2952, 2857, 1630, 1586, 1468, 1436, 1345, 1293, 1246, 1151, 1079, 971, 875, 825, 792, 730, 687.

HRMS (ESI): calcd. for C₁₃H₁₂NO₃ ([M+H]⁺): 230.0812, found: 230.0809.



(5-Fluoropyridin-2-yl)(2-hydroxyphenyl)methanone (2g)

Yellow solid, M.p. 72 – 73 °C. 34.7 mg, 80%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.12 (s, 1H), 8.58 (d, J = 2.6 Hz, 1H), 8.20 – 8.14 (m,

1H), 8.02 (dd, *J* = 8.7, 4.5 Hz, 1H), 7.62 (td, *J* = 8.3, 2.7 Hz, 1H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 196.0, 164.0, 160.7 (d, *J* = 263.3 Hz), 151.7, 137.0 (d, *J* = 24.2 Hz), 137.0, 134.5, 126.8 (d, *J* = 5.4 Hz), 124.2 (d, *J* = 18.5 Hz), 119.0, 118.6, 118.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -120.5 (dd, J = 8.0, 4.6 Hz).

IR (KBr, v / cm⁻¹): 2918, 2875, 2853, 1627, 1584, 1566, 1513, 1384, 1261, 1224, 1181, 1149, 1049, 1034, 941, 872, 792, 751, 690.

HRMS (ESI): calcd. for C₁₂H₉FNO₂ ([M+H]⁺): 218.0612, found: 218.0611.



(5-Chloropyridin-2-yl)(2-hydroxyphenyl)methanone (2h)

Light yellow solid, M.p. 89 – 90 °C. 33.6 mg, 72%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.09 (s, 1H), 8.69 (s, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.91 (s, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H).

¹³**C NMR** (75 MHz, CDCl₃) *δ* 196.3, 163.9, 153.3, 147.5, 137.3, 137.1, 135.2, 134.3, 125.8, 119.0, 118.5.

IR (KBr, v / cm⁻¹): 3054, 2998, 2924, 2867, 1627, 1572, 1483, 1461, 1373, 1310, 1248, 1112, 1015, 941, 851, 825, 801, 754, 734, 730, 691.

HRMS (ESI): calcd. for C₁₂H₉ClNO₂ ([M+H]⁺): 234.0316, found: 234.0321.



(5-bromopyridin-2-yl)(2-hydroxyphenyl)methanone (2i)

Light yellow solid, M.p. 103 – 104 °C. 37.3 mg, 67%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.07 (s, 1H), 8.79 (dd, J = 2.2, 0.6 Hz, 1H), 8.14 (dd, J = 8.1, 1.6 Hz, 1H), 8.05 (dd, J = 8.4, 2.3 Hz, 1H), 7.83 (dd, J = 8.4, 0.6 Hz, 1H), 7.52 (ddd, J = 8.7, 7.3, 1.6 Hz, 1H), 7.05 (dd, J = 8.4, 1.0 Hz, 1H), 6.90 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H).

¹³**C NMR** (75 MHz, CDCl₃) *δ* 196.5, 163.9, 153.8, 149.7, 140.2, 137.1, 134.3, 126.1, 124.3, 119.1, 118.6, 118.5.

IR (KBr, v / cm⁻¹): 3027, 2948, 2879, 1627, 1565, 1483, 1445, 1369, 1333, 1310, 1251,

1230, 1148, 1112, 1088, 1008, 940, 849, 824, 800, 755, 667. **HRMS (ESI)**: calcd. for C₁₂H₉BrNO₂ ([M+H]⁺): 277.9811, found: 277.9814.



(2-Hydroxyphenyl)(5-(trifluoromethyl)pyridin-2-yl)methanone (2j)

Yellow oil. 25.1 mg, 47%.

¹**H NMR** (300 MHz, CDCl₃) δ 11.97 (s, 1H), 9.01 (dd, J = 1.4, 0.7 Hz, 1H), 8.23 – 8.12 (m, 1H), 8.03 (ddd, J = 8.2, 3.6, 1.1 Hz, 2H), 7.55 (ddd, J = 8.5, 7.2, 1.7 Hz, 1H), 7.13 – 7.03 (m, 1H), 6.98 – 6.86 (m, 1H).

¹³**C NMR** (75 MHz, CDCl₃) δ 196.5, 164.2, 158.5, 145.6 (q, J = 4.0 Hz), 137.5, 134.8 (q, J = 3.5 Hz), 134.3, 128.6 (d, J = 33.5 Hz), 124.4, 123.2 (d, J = 272.9 Hz), 119.2, 118.7, 118.4.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -62.6 (s).

IR (KBr, v / cm⁻¹): 3080, 2922, 1630, 1571, 1487, 1448, 1394, 1325, 1258, 1243, 1170, 1148, 1017, 943, 815, 786.

HRMS (ESI): calcd. for C₁₃H₉F₃NO₂ ([M+H]⁺): 268.0580, found: 268.0583.



Benzo[d]thiazol-2-yl(2-hydroxyphenyl)methanone (2k)

Yellow solid, M.p. 89 – 90 °C. 29.2 mg, 57%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.10 (s, 1H), 9.25 (dd, J = 8.2, 1.7 Hz, 1H), 8.29 – 8.18 (m, 1H), 8.04 – 7.95 (m, 1H), 7.65 – 7.50 (m, 3H), 7.10 – 6.98 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 187.8, 167.2, 164.3, 153.8, 137.7, 136.9, 134.2, 128.0, 127.3, 125.9, 122.3, 119.7, 118.6, 118.3; ¹H and ¹³C NMR data agreed with literature ^[4].



(3,6-Dimethylpyrazin-2-yl)(2-hydroxyphenyl)methanone (2l)

Light yellow oil. 36.9 mg, 81%.

1H NMR (300 MHz, CDCl₃) δ 11.93 (s, 1H), 8.52 (s, 1H), 7.54 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.30 (dd, J = 8.0, 1.7 Hz, 1H), 7.08 (dd, J = 8.5, 1.0 Hz, 1H), 6.85 (ddd, J =

8.2, 7.2, 1.1 Hz, 1H), 2.60 (s, 3H), 2.55 (s, 3H).

13C NMR (75 MHz, CDCl₃) *δ* 199.4, 164.1, 150.1, 148.8, 148.6, 144.9, 137.7, 133.5, 119.3, 118.9, 118.7, 21.2, 21.1.

IR (KBr, v / cm⁻¹): 3047, 3067, 2929, 2858, 1630, 1576, 1485, 1448, 1371, 1254, 1215, 1138, 1108, 1034, 1004, 952, 885, 864, 820, 756, 736, 691.

HRMS (ESI): calcd. for C₁₃H₁₃N₂O₂ ([M+H]⁺): 229.0972, found: 229.0971.



(2-Hydroxy-4-methylphenyl)(pyridin-2-yl)methanone (2m)

Light yellow solid, M.p. 32 – 33 °C. 32.4 mg, 76%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.38 (s, 1H), 8.72 (d, J = 4.7 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 3.7 Hz, 2H), 7.49 (dd, J = 8.9, 4.7 Hz, 1H), 6.86 (s, 1H), 6.72 (d, J = 8.3 Hz, 1H), 2.37 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 196.9, 163.9, 155.6, 148.7, 148.4, 137.5, 134.3, 126.1, 124.6, 120.4, 118.6, 116.8, 22.2.

IR (KBr, v / cm⁻¹): 3060, 2985, 2924, 1641, 1584, 1556, 1504, 1345, 1308, 1261, 1171, 1047, 997, 870, 793, 785, 703.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0869.



(2-Hydroxy-3-methylphenyl)(pyridin-2-yl)methanone (2n)

Yellow solid, M.p. 42 – 45 °C. 36.2 mg, 85%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.53 (s, 1H), 8.72 (dd, J = 4.9, 1.0 Hz, 1H), 7.94 – 7.88 (m, 3H), 7.51 – 7.46 (m, 1H), 7.38 (d, J = 7.2 Hz, 1H), 6.80 (t, J = 7.7 Hz, 1H), 2.31 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 198.1, 162.2, 155.7, 148.5, 137.6, 137.4, 132.0, 127.4, 126.0, 124.6, 118.3, 118.2, 15.9.

IR (KBr, v / cm⁻¹): 3056, 3015, 2955, 2922, 1623, 1584, 1479, 1423, 1340, 1304, 1258, 1194, 1032, 995, 853, 780, 751, 687.

HRMS (ESI): calcd. for C₁₃H₁₂NO₂ ([M+H]⁺): 214.0863, found: 214.0871.



(2-Hydroxy-3-methoxyphenyl)(pyridin-2-yl)methanone (20) Yellow solid, M.p. 85 – 86 °C. 23.4 mg, 51%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.78 (s, 1H), 8.73 (d, J = 4.8 Hz, 1H), 8.01 – 7.87 (m, 2H), 7.69 (dd, J = 8.3, 1.2 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 8.1 Hz, 1H), 3.94 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) *δ* 197.3, 155.3, 153.7, 149.2, 148.2, 137.7, 126.4, 125.5, 124.8, 119.9, 118.4, 117.3, 56.4.

IR (KBr, v / cm⁻¹): 3054, 3009, 2924, 2851, 1630, 1586, 1453, 1436, 1340, 1310, 1254, 1194, 1079, 985, 842, 803, 784, 747, 698.

HRMS (ESI): calcd. for C₁₃H₁₂NO₃ ([M+H]⁺): 230.0812, found: 230.0816.



(5-bromo-2-hydroxyphenyl)(pyridin-2-yl)methanone (2p)

Yellow solid, M.p. 69 – 70 °C. 43.4 mg, 78%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.63 (s, 1H), 8.75 – 8.73(m, 1H), 8.37 (d, J = 2.5 Hz, 1H), 8.04 – 7.92 (m, 2H), 7.59 – 7.54 (m, 2H), 6.96 (d, J = 8.9 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 195.3, 162.1, 154.6, 148.2, 139.3, 138.0, 136.4, 126.9, 125.1, 121.1, 120.8, 110.7.

IR (KBr, v / cm⁻¹): 3081, 2996, 1627, 1604, 1584, 1566, 1460, 1433, 1383, 1332, 1283, 1332, 1283, 1236, 1152, 1094, 1047, 1022, 995, 947, 901, 828, 750, 676.

HRMS (ESI): calcd. for C₁₂H₉BrNO₂ ([M+H]⁺): 277.9811, found: 277.9815.



(5-Fluoro-2-hydroxyphenyl)(pyridin-2-yl)methanone (2q)

Yellow solid, M.p. 48 – 49 °C. 35.6 mg, 82%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.33 (s, 1H), 8.74 (d, J = 4.7 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.95 (td, J = 7.7, 1.7 Hz, 1H), 7.55 (ddd, J = 7.3, 4.8, 1.4 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.02 (dd, J = 9.1, 4.6 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 195.5, 159.6, 154.9 (d, J = 237.3 Hz), 154.8, 148.2,

137.9, 126.8, 125.0, 124.4 (d, *J* = 24.0 Hz), 119.9 (d, *J* = 7.4 Hz), 119.2 (d, *J* = 24.5 Hz), 119.2.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -124.3 (ddd, J = 9.8, 7.6, 4.6 Hz).

IR (KBr, v / cm⁻¹): 3093, 3060, 2920, 1641, 1615, 1584, 1485, 1422, 1343, 1284, 1252, 1138, 995, 980, 874, 833, 790, 672.

HRMS (ESI): calcd. for C₁₂H₉FNO₂ ([M+H]⁺): 218.0612, found: 218.0611.



(5-Chloro-2-hydroxyphenyl)(pyridin-2-yl)methanone (2r)

Yellow solid, M.p. 42 – 43 °C. 36.8 mg, 79%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.60 (s, 1H), 8.75 (d, J = 4.8 Hz, 1H), 8.24 (d, J = 2.7 Hz, 1H), 8.07 – 7.90 (m, 2H), 7.63 – 7.53 (m, 1H), 7.44 (dd, J = 8.9, 2.6 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 195.4, 161.7, 154.6, 148.2, 138.0, 136.5, 133.4, 126.9, 125.1, 123.7, 120.3, 120.2.

IR (KBr, v / cm⁻¹): 3019, 2968, 2920, 2799, 1632, 1587, 1567, 1463, 1435, 1390, 1336, 1287, 1237, 1157, 1130, 1025, 997, 874, 833, 752, 730, 692.

HRMS (ESI): calcd. for C₁₂H₉ClNO₂ ([M+H]⁺): 234.0316, found: 234.0316.



(2-Hydroxy-3-methylphenyl)(5-methoxypyridin-2-yl)methanone (2s)

Yellow solid, M.p. 65 – 66 °C. 46.2 mg, 95%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.63 (s, 1H), 8.38 (d, J = 2.9 Hz, 1H), 8.09 (dd, J = 8.2, 1.7 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.34 (dt, J = 8.8, 4.3 Hz, 2H), 6.86 – 6.73 (m, 1H), 3.93 (s, 3H), 2.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 196.5, 162.0, 157.6, 148.1, 137.2, 136.5, 132.1, 127.2, 126.5, 120.4, 118.5, 118.1, 55.9, 15.9.

IR (KBr, v / cm⁻¹): 3054, 2976, 2929, 2845, 1619, 1578, 1476, 1423, 1341, 1306, 1267, 1241, 1135, 1039, 1023, 978, 874, 853, 814, 740, 704.

HRMS (ESI): calcd. for C₁₄H₁₄NO₃ ([M+H]⁺): 244.0968, found: 244.0971.



(2-Hydroxy-3-methylphenyl)(5-methylpyridin-2-yl)methanone (2t) Yellow solid, M.p. 43 – 44 °C. 40.4 mg, 89%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.63 (s, 1H), 8.54 (dd, J = 1.4, 0.7 Hz, 1H), 7.95 (ddd, J = 8.2, 1.7, 0.5 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.37 (d, J = 7.2 Hz, 1H), 6.85 – 6.72 (m, 1H), 2.44 (s, 3H), 2.31 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 197.8, 162.0, 153.0, 148.9, 137.7, 137.4, 136.5, 132.0, 127.3, 124.4, 118.5, 118.2, 18.8, 15.9.

IR (KBr, v / cm⁻¹): 3025, 3012, 2931, 1633, 1575, 1497, 1412, 1367, 1304, 1222, 1180, 1032, 995, 853, 789, 751, 686.

HRMS (ESI): calcd. for C₁₄H₁₄NO₂ ([M+H]⁺): 228.1019, found: 228.1027.



(2-Hydroxy-3-methylphenyl)(4-methylpyridin-2-yl)methanone (2u)

Yellow oil. 30.9 mg, 68%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.62 (s, 1H), 8.57 (d, J = 5.0 Hz, 1H), 7.88 (ddd, J = 8.1, 1.1, 0.5 Hz, 1H), 7.76 – 7.66 (m, 1H), 7.39 – 7.35 (m, 1H), 7.30 (ddd, J = 5.0, 1.6, 0.7 Hz, 1H), 6.80 (t, J = 7.7 Hz, 1H), 2.46 (s, 3H), 2.31 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 198.3, 162.0, 155.5, 148.9, 148.2, 137.5, 132.0, 127.4, 126.9, 125.3, 118.5, 118.3, 21.3, 15.9.

IR (KBr, v / cm⁻¹): 3054, 2955, 2924, 1620, 1599, 1559, 1477, 1451, 1425, 1330, 1256, 1170, 1086, 1051, 997, 812, 799, 783, 751, 697.

HRMS (ESI): calcd. for C₁₄H₁₄NO₂ ([M+H]⁺): 228.1019, found: 228.1023.



(2-Hydroxy-3-methoxyphenyl)(5-methoxypyridin-2-yl)methanone (2v)

Yellow solid, M.p. 88 – 89 °C. 28.0 mg, 54%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.83 (s, 1H), 8.37 (d, J = 2.9 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.87 (dd, J = 8.3, 1.3 Hz, 1H), 7.37 (dd, J = 8.8, 2.9 Hz, 1H), 7.09 (d, J = 7.9 Hz, 1H), 6.86 (t, J = 8.1 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 195.8, 157.9, 153.5, 149.1, 147.8, 136.2, 126.7, 125.6, 120.8, 120.1, 118.1, 116.9, 56.4, 56.0.

IR (KBr, v / cm⁻¹): 3058, 3006, 2940, 2840, 1625, 1576, 1451, 1436, 1343, 1313, 1250, 1189, 1178, 985, 844, 779, 738, 687.

HRMS (ESI): calcd. for C₁₄H₁₄NO₄ ([M+H]⁺): 260.0917, found: 260.0917.



(5-Fluoro-2-hydroxyphenyl)(5-methylpyridin-2-yl)methanone (2w)

Yellow solid, M.p. 81 – 82 °C. 43.0 mg, 93%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.52 (s, 1H), 8.57 – 8.52 (m, 1H), 8.07 (dd, J = 9.9, 3.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.81 – 7.68 (m, 1H), 7.33 – 7.17 (m, 1H), 7.00 (dd, J = 9.1, 4.7 Hz, 1H), 2.47 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 195.1, 159.4, 154.9 (d, J = 236.8 Hz), 152.2, 148.5, 138.3, 137.5, 124.9, 124.1 (d, J = 23.9 Hz), 119.9 (d, J = 7.4 Hz), 119.6 (d, J = 6.8 Hz), 119.2 (d, J = 24.7 Hz), 18.9.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -124.5 (ddd, J = 9.8, 7.5, 4.7 Hz).

IR (KBr, v / cm⁻¹): 3037, 2965, 2931, 1638, 1612, 1593, 1479, 1422, 1384, 1343, 1287, 1218, 1136, 1034, 976, 874, 833, 784, 728, 687.

HRMS (ESI): calcd. for C₁₃H₁₁FNO₂ ([M+H]⁺): 232.0768, found: 230.0777.



4-(2-Hydroxybenzoyl)benzonitrile (2z)

Yellow solid, M.p. 121 – 122 °C. 17.0 mg, 38%.

¹**H NMR** (300 MHz, CDCl₃) δ 11.79 (s, 1H), 7.85 – 7.80 (m, 2H), 7.79 – 7.74 (m, 2H), 7.56 (ddd, J = 8.6, 7.3, 1.7 Hz, 1H), 7.45 (dd, J = 8.1, 1.6 Hz, 1H), 7.10 (dd, J = 8.4, 0.9 Hz, 1H), 6.90 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 199.7, 163.4, 141.6, 137.2, 133.0, 132.2, 129.4, 119.0, 118.8, 118.5, 117.9, 115.3; ¹H and ¹³C NMR data agreed with literature ^[4].



Methyl 4-(2-hydroxybenzoyl)benzoate (2aa)

White solid, M.p. 97 – 98 °C. 22.0 mg, 43%.

¹**H** NMR (300 MHz, CDCl₃) δ 11.93 (s, 1H), 8.21 – 8.12 (m, 2H), 7.75 – 7.68 (m, 2H), 7.57 – 7.47 (m, 2H), 7.09 (ddd, J = 8.3, 1.1, 0.6 Hz, 1H), 6.89 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H), 3.98 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 201.1, 167.0, 166.4, 163.5, 141.8, 137.0, 133.5, 133.0, 129.7, 129.1, 119.1, 118.8, 52.7; ¹H and ¹³C NMR data agreed with literature ^[4].



(2-Hydroxyphenyl)(4-(trifluoromethyl)phenyl)methanone (2ab)

White solid, M.p. 49 – 50 °C. 17.6 mg, 33%.

¹**H** NMR (300 MHz, CDCl₃) δ 11.89 (s, 1H), 7.79 (s, 4H), 7.65 – 7.46 (m, 2H), 7.10 (dd, J = 8.4, 1.1 Hz, 1H), 6.90 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 200.6, 163.6, 141.2, 137.2, 133.6 (d, J = 32.7 Hz), 133.5, 129.5, 125.6 (q, J = 3.7 Hz), 123.8 (d, J = 272.6 Hz), 119.2, 118.9, 118.9; ¹H and ¹³C NMR data agreed with literature ^[8].



(2-Fluorophenyl)(2-hydroxyphenyl)methanone (2ac)

Light yellow oil. 21.6 mg, 50%.

¹**H NMR** (300 MHz, CDCl₃) δ 11.98 (s, 1H), 7.60 – 7.38 (m, 4H), 7.30 (td, J = 7.5, 1.0 Hz, 1H), 7.21 (ddd, J = 9.5, 8.4, 0.9 Hz, 1H), 7.07 (dd, J = 8.4, 1.1 Hz, 1H), 6.87 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 198.7, 163.2, 159.3 (d, J = 251.5 Hz), 137.3, 133.6 (d, J = 2.2 Hz), 133.1 (d, J = 8.2 Hz), 130.1 (d, J = 2.9 Hz), 126.5 (d, J = 15.9 Hz), 124.6 (d, J = 3.6 Hz), 119.9, 119.2, 118.5, 116.5 (d, J = 21.3 Hz).

¹⁹**F NMR** (376 MHz, CDCl₃) δ -112.2 – -112.3 (m).

IR (KBr, v / cm⁻¹): 3063, 2920, 2862, 1630, 1615, 1580, 1485, 1451, 1336, 1269, 1246, 1220, 1146, 937, 834, 816, 754, 685.

HRMS (ESI): calcd. for C₁₃H₁₀FO₂ ([M+H]⁺): 217.0659, found: 217.0663.



(2-Bromo-4-chlorophenyl)(2-hydroxyphenyl)methanone (2ad)

Light yellow oil. 27.4 mg, 44%.

¹**H NMR** (400 MHz, CDCl₃) δ 11.83 (s, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.25 – 7.20 (m, 2H), 7.07 (dd, J = 8.4, 0.8 Hz, 1H), 6.84 (ddd, J = 8.1, 7.3, 1.1 Hz, 1H).

¹³**C NMR** (101 MHz, CDCl₃) *δ* 199.7, 163.4, 137.6, 136.4, 133.4, 133.0, 132.2, 130.3, 129.9, 124.9, 119.4, 119.3, 118.7.

IR (KBr, v / cm⁻¹): 3085, 2971, 2851, 1628, 1579, 1485, 1454, 1371, 1337, 1308, 1243, 1219, 1148, 1114, 1084, 935, 833, 777, 757, 656.

HRMS (ESI): calcd. for C₁₃H₉BrClO₂ ([M+H]⁺): 312.9448, found: 312.9458.



(2,6-Dimethylphenyl)(2-hydroxyphenyl)methanone (2ae)

White solid, M.p. 112 – 113 °C. 25.8 mg, 57%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.32 (s, 1H), 7.55 – 7.45 (m, 1H), 7.31 – 7.23 (m, 1H), 7.17 (dd, J = 8.0, 1.7 Hz, 1H), 7.12 – 7.04 (m, 3H), 6.83 – 6.75 (m, 1H), 2.16 (s, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 206.6, 163.1, 138.3, 137.2, 134.2, 132.8, 129.3, 127.8, 120.2, 119.5, 118.5, 19.5.

IR (KBr, v / cm⁻¹): 3069, 3000, 2955, 2924, 1623, 1576, 1489, 1449, 1328, 1306, 1243, 1224, 1151, 1030, 933, 827, 780, 766, 730, 690.

HRMS (ESI): calcd. for C₁₅H₁₅O₂ ([M+H]⁺): 227.1067, found: 227.1071.



(2-Hydroxyphenyl)(2-methoxyphenyl)methanone (2af)

Colorless oil. 18.3 mg, 40%.

¹**H NMR** (300 MHz, CDCl₃) δ 12.20 (s, 1H), 7.53 – 7.44 (m, 2H), 7.32 (ddd, J = 13.3, 7.7, 1.7 Hz, 2H), 7.11 – 6.98 (m, 3H), 6.87 – 6.75 (m, 1H), 3.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 202.3, 163.1, 156.7, 136.7, 134.0, 132.0, 129.0, 127.9, 120.7, 120.3, 118.9, 118.2, 111.6, 55.8.

IR (KBr, v / cm⁻¹): 3013, 2955, 2840, 1628, 1600, 1487, 1461, 1332, 1310, 1280, 1246, 1148, 1121, 1023, 944, 980, 827, 754, 687.

HRMS (ESI): calcd. for C₁₄H₁₃O₃ ([M+H]⁺): 229.0859, found: 229.0865.



(2,6-Dimethoxyphenyl)(2-hydroxyphenyl)methanone (2ag)

White solid, M.p. 117 – 118 °C. 20.1 mg, 39%.

¹**H** NMR (300 MHz, CDCl₃) δ 12.16 (s, 1H), 7.50 – 7.43 (m, 1H), 7.38 (t, J = 8.4 Hz, 1H), 7.28 (dd, J = 8.0, 1.7 Hz, 1H), 7.02 (dd, J = 8.4, 1.0 Hz, 1H), 6.83 – 6.75 (m, 1H), 6.63 (d, J = 8.4 Hz, 2H), 3.73 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 201.5, 162.7, 157.5, 136.6, 133.2, 131.5, 121.1, 119.1, 118.1, 116.6, 104.1, 56.1.

IR (KBr, v / cm⁻¹): 3011, 2963, 2842, 1630, 1593, 1474, 1448, 1332, 1306, 1254, 1220, 1146, 1112, 937, 758, 725, 678.

HRMS (ESI): calcd. for C₁₅H₁₅O₄ ([M+H]⁺): 259.0965, found: 259.0972.

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VIII. Copies of the ¹H, ¹⁹F and ¹³C NMR spectra

 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1a





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1b



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1c



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1d



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1e





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1f

 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1g




$^{19}\mathrm{F}$ NMR spectra of compound $\mathbf{1g}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1h





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1i





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1j





¹⁹F NMR spectra of compound **1j**



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1k





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 11





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1m







 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{1o}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1p





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1q





¹⁹F NMR spectra of compound **1**q



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1r





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1s





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1t





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1u





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1v





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1w





 $^{19}\mathrm{F}$ NMR spectra of compound 1w



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1x



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1y



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1z







2.08 1.01 ℓ 1.01 ₹ 3.14 1

8

7 6 fl (ppm) 3.00-

4

3

2

1

5

0

-1

¹H and ¹³C NMR spectra of compound **1aa**

0.86=

10

9

11

13

14

12





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{1ab}$











 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1ad





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1ae

40 30 20 10 0 -10

60 50

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70



$^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1af



$^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 1ag

 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2a



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2b}$







 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2d}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2e









 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2g}$

 $^{19}\mathrm{F}$ NMR spectra of compound $\mathbf{2g}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2h}$




 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2i





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2j





 $^{19}\mathrm{F}$ NMR spectra of compound 2j



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2k



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2l



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2m



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2n





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2o}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2p}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2q}$



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

 $^{19}\mathrm{F}$ NMR spectra of compound $\mathbf{2q}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2r





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2s





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2t





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2u





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2v





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2w





 $^{19}\mathrm{F}$ NMR spectra of compound $\mathbf{2w}$



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2z





¹H and ¹³C NMR spectra of compound **2aa**





¹H and ¹³C NMR spectra of compound **2ab**



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2ac





¹⁹F NMR spectra of compound **2ac**



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2ad}$





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 2ae





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2af}$





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound $\mathbf{2ag}$



