

Supporting Information
for
DABCO- and DBU-promoted one-pot reaction of *N*-
sulfonyl ketimines with Morita–Baylis–Hillman
carbonates: a sequential approach to
(2-hydroxyaryl)nicotinate derivatives

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Synthetic protocols, characterization data and copies of
¹H and ¹³C NMR spectra

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General information

All the reactions were carried out under air and monitored by TLC using Merck 60 F₂₅₄ pre-coated silica-gel plates (0.25 mm thickness) and the products were visualized by UV detection. Flash chromatography was carried out with silica-gel (200–300 mesh). ¹H and ¹³C NMR spectra were recorded on a BrukerAvance (III) 400 Hz spectrometer. Data for ¹H NMR are reported as a chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant *J* (Hz), integration, and assignment, data for ¹³C are reported as a chemical shift. High resolutions mass spectral analyses (HRMS) were carried out using ESI-QTOF-MS (Microtof Q-II Bruker, condition: capillary voltage = −4500V, temperature = 250 °C, N₂ gas flow = 7 lit/min, nebulizer pressure = 2 bar, instrument is calibrated using ESI tune low calibration mixture before HRMS sample analysis). Melting points were recorded on an Electro thermal melting point apparatus and are uncorrected. FT-IR spectra were recorded on a KBr plate.

Experimental procedures

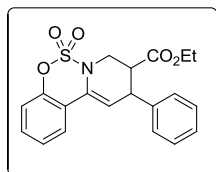
One-pot synthesis of compound 4a: A mixture of sulfonyl ketimine (**1a**, 0.2 mmol), MBH carbonates (**2a**, 0.26 mmol), and DABCO (0.04 mmol) in anhydrous toluene (1.0 mL) was heated at 60 °C for 6h. Then the crude product was directly purified by column chromatography technique to give the product **4a** as a mixture of diastereomer in 88% yield.

General procedure for the synthesis of compounds 5aa-5am: To a stirred solution of *N*-sulfonyl ketimine¹ (**1**, 0.2 mmol), MBH carbonates² (**2**, 0.26 mmol), and DABCO (0.04 mmol) in anhydrous toluene (1.0 mL) was heated at 60 °C. After completion of step I (monitored by TLC), DBU (1.2 equiv) was added to the above reaction mixture at same temperature. After 6–7 h, the reaction mixture was extracted with ethyl acetate (3 × 10 mL), washed with brined and dried over anhydrous Na₂SO₄. Afterwards, evaporation of organic solvent gave the crude product which was purified through column chromatography over silica-gel to afford the pure product.

All the obtained products (**5aa–5am**) were characterized by IR, ^1H NMR, ^{13}C NMR and HRMS data.

Characterization data

Ethyl 10-phenyl-9,10-dihydro-8*H*-benzo[*e*]pyrido[1,2-*c*][1,2,3]oxathiazine-9-carboxylate



6,6-dioxide (4a): gummy liquid; yield 88%; R_f = 0.67 (EtOAc:hexane = 1:6);

IR (KBr) ν 1731, 1596, 1537, 1488, 1474, 1391, 1366 cm^{-1} ; ^1H NMR (400

MHz, CDCl_3) δ (major isomer) 7.61 (d, J = 8.0 Hz, 1H), 7.31-7.40 (m, 3H),

7.20-7.30 (m, 4H), 7.13 (d, J = 8.2 Hz, 1H), 5.89 (d, J = 3.5 Hz, 1H), 4.11-4.16 (m, 3H), 4.03-4.07

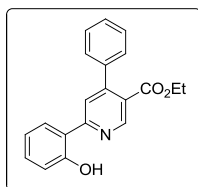
(m, 1H), 3.93-3.98 (m, 1H), 2.92-2.97 (m, 1H), 1.19 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100

MHz, CDCl_3) δ (major isomer) 171.3, 148.5, 141.9, 132.4, 130.6, 128.9, 128.2, 127.5, 126.1,

124.1, 119.2, 118.8, 108.3, 61.5, 45.6, 43.5, 41.4, 14.0 ppm; HRMS (ESI) m/z calcd for

$\text{C}_{20}\text{H}_{19}\text{NO}_5\text{S}[\text{M}+\text{H}]^+$ 386.1052, found 386.1065.

Ethyl 6-(2-hydroxyphenyl)-4-phenylnicotinate(5aa): colorless solid; mp 121-123 $^\circ\text{C}$; yield



76% (48.5 mg); R_f = 0.7 (EtOAc:hexane = 1:6); IR (KBr) ν 3433, 1698,

1593, 1530, 1499, 1376 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.99 (s, 1H),

9.00 (s, 1H), 7.86 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.46-7.46 (m, 3H), 7.35-

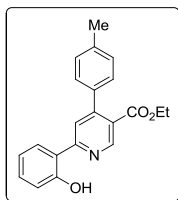
7.37 (m, 3H), 7.04-7.07 (m, 1H), 6.89-6.93 (m, 1H), 4.18 (q, J = 7.0 Hz, 2H), 1.09 (t, J = 7.0 Hz,

3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 160.6, 159.8, 152.1, 148.1, 138.9, 132.6, 128.7,

128.4, 128.0, 126.7, 124.2, 120.4, 119.1, 118.9, 118.1, 61.4, 13.7 ppm; HRMS (ESI) m/z calcd

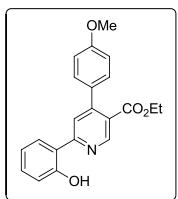
for $\text{C}_{20}\text{H}_{17}\text{NO}_3[\text{M}+\text{Na}]^+$ 342.1101, found 342.1120.

Ethyl 6-(2-hydroxyphenyl)-4-(4-methylphenyl)nicotinate (5ab): light yellow solid; mp 124-



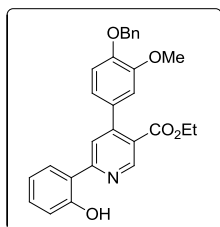
126 °C; yield 73% (48.6 mg); $R_f = 0.7$ (EtOAc:hexane = 1:6); IR (KBr) ν 3442, 1699, 1596, 1529, 1511, 1306 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 14.0 (s, 1H), 8.95 (s, 1H), 7.83 (s, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.31-7.35 (m, 1H), 7.22-7.26 (m, 4H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.87-6.91 (m, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.42 (s, 3H), 1.13 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 160.6, 159.7, 152.1, 148.0, 138.7, 135.9, 132.5, 129.1, 128.0, 126.7, 124.2, 120.4, 119.1, 118.9, 118.1, 61.4, 21.3, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_3[\text{M}+\text{Na}]^+$ 356.1257, found 356.1270

Ethyl 6-(2-hydroxyphenyl)-4-(4-methoxyphenyl)nicotinate (5ac): yellow solid; mp 131-133



°C yield 69% (48.1 mg); $R_f = 0.68$ (EtOAc:hexane = 1:6); IR (KBr) ν 3433, 1701, 1597, 1531, 1511, 1462, 1305 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 14.02 (s, 1H), 8.95 (s, 1H), 7.84 (s, 1H), 7.82-7.82 (m, 1H), 7.31-7.36 (m, 3H), 6.98-7.06 (m, 3H), 6.89-6.93 (m, 1H), 4.22 (q, $J = 7.0$ Hz, 2H), 3.87 (s, 3H), 1.16 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 160.6, 160.2, 159.7, 151.6, 148.0, 132.5, 131.0, 129.5, 126.7, 124.2, 120.3, 119.0, 118.9, 118.2, 113.9, 61.5, 55.4, 13.9 ppm; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4[\text{M}+\text{Na}]^+$ 372.1206, found 372.1220.

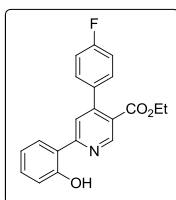
Ethyl 4-(4-(benzyloxy)-3-methoxyphenyl)-6-(2-hydroxyphenyl)nicotinate (5ad): colorless



solid; mp 140-142 °C; yield 65% (59.2 mg); $R_f = 0.60$ (EtOAc:hexane = 1:6); IR (KBr) ν 3443, 1705, 1626, 1581, 1474, 1369 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.80 (s, 1H), 8.92 (s, 1H), 7.85 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 7.3$ Hz, 2H), 7.32-7.40 (m, 4H), 7.04 (d, $J = 8.3$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.86-6.93 (m, 3H), 5.22 (s, 2H), 4.19 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 1.11 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 160.6, 159.7, 151.5, 149.5, 148.8,

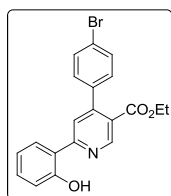
147.8, 136.8, 132.5, 131.8, 128.6, 128.0, 127.3, 126.7, 124.5, 120.7, 120.2, 119.1, 118.9, 118.2, 113.6, 111.9, 71.0, 61.5, 56.2, 13.9 ppm. HRMS (ESI) m/z calcd for $C_{28}H_{25}NO_5[M+H]^+$ 456.1805, found 456.1807.

Ethyl 4-(4-fluorophenyl)-6-(2-hydroxyphenyl)nicotinate (5ae): white solid; yield 79% (53.3



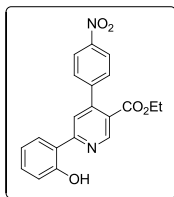
mg); mp 112-114 °C; R_f = 0.69 (EtOAc:hexane = 1:6); IR (KBr) ν 3442, 1732, 1593, 1511, 1420, 1288 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 13.9 (s, 1H), 9.0 (s, 1H), 7.82 (s, 1H), 7.81 (s, 1H), 7.34-7.35 (m, 3H), 7.14-7.19 (m, 2H), 7.05 (d, J = 8.0 Hz, 1H), 6.91-6.93 (m, 1H), 4.21 (q, J = 7.0 Hz, 2H), 1.15 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.1 (J_{C-F} = 247.2 Hz), 160.5, 160.0, 151.1, 148.3, 134.9, 132.7, 129.9 (J_{C-F} = 8.0 Hz), 126.7, 123.9, 120.4, 119.1, 119.0, 118.0, 115.4 (J_{C-F} = 21.8 Hz), 61.5, 13.9 ppm; HRMS (ESI) m/z calcd for $C_{20}H_{16}FNO_3[M+Na]^+$ 360.1006, found 360.1020.

Ethyl 4-(4-bromophenyl)-6-(2-hydroxyphenyl)nicotinate (5af): colorless solid; mp 144-146



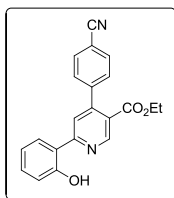
°C; yield 74% (58.9 mg); R_f = 0.7 (EtOAc:hexane = 1:6); IR (KBr) ν 3441, 1731, 1593, 1534, 1420, 1364 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 13.86 (s, 1H), 9.09 (s, 1H), 7.79-7.82 (m, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.35-7.38 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.89-6.93 (m, 1H), 4.19 (q, J = 7.0 Hz, 2H), 1.11 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 160.6, 159.9, 149.5, 147.7, 144.6, 138.3, 132.6, 126.8, 122.2, 119.2, 119.0, 118.3, 116.4, 113.2, 112.5, 62.0, 14.3 ppm; HRMS (ESI): m/z calcd for $C_{20}H_{16}^{79}BrNO_3[M+Na]^+$ 420.0206, found 420.0219; m/z calcd for $C_{20}H_{16}^{81}BrNO_3[M+Na]^+$ 422.0185, found 422.0203.

Ethyl 6-(2-hydroxyphenyl)-4-(4-nitrophenyl)nicotinate (5ag): yellow solid; mp 133-135 °C;



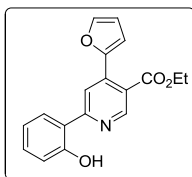
yield 76% (55.3 mg); $R_f = 0.6$ (EtOAc:hexane = 1:6); IR (KBr) ν 3427, 1720, 1591, 1516, 1420, 1348 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.90 (s, 1H), 9.03 (s, 1H), 7.81 (s, 1H), 7.79 (m, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.34-7.38 (m, 1H), 7.24 (m, 2H), 7.05 (d, $J = 8.3$ Hz, 1H), 6.90-6.93 (m, 1H), 4.21 (q, $J = 7.0$ Hz, 2H), 1.16 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 160.4, 159.8, 149.3, 147.6, 144.4, 138.2, 132.5, 126.7, 122.0, 119.1, 118.9, 118.2, 116.3, 113.1, 112.4, 61.9, 14.2 ppm; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_5[\text{M}+\text{Na}]^+$ 387.0951, found 387.0962.

Ethyl 4-(4-cyanophenyl)-6-(2-hydroxyphenyl)nicotinate (5ah): yellow solid; mp 152-154 °C



yield 79% (54.3 mg) $R_f = 0.55$ (EtOAc:hexane = 1:6); IR (KBr) ν 3404, 2224, 1713, 1599, 1534, 1474, 1302 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.80 (s, 1H), 9.11 (s, 1H), 7.78-7.80 (m, 3H), 7.75 (s, 1H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.35-7.39 (m, 1H), 7.06 (d, $J = 8.3$ Hz, 1H), 6.90-6.94 (m, 1H), 4.21 (q, $J = 7.0$ Hz, 2H), 1.16 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 164.9, 160.7, 160.4, 150.5, 148.8, 143.7, 133.1, 132.0, 128.9, 126.8, 123.0, 120.1, 119.3, 119.1, 118.4, 117.7, 112.5, 61.7, 13.9 ppm; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_3[\text{M}+\text{H}]^+$ 345.1234, found 345.1250.

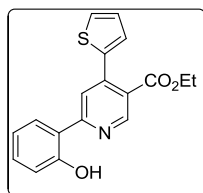
Ethyl 4-(furan-2-yl)-6-(2-hydroxyphenyl)nicotinate (5ai): brown solid; mp 119-121 °C; yield



68% (42.01 mg); $R_f = 0.7$ (EtOAc:hexane = 1:6); IR (KBr) ν 3431, 1723, 1600, 1491, 1362 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.9 (s, 1H), 8.8 (s, 1H), 8.18 (s, 1H), 7.88 (d, $J = 8$ Hz, 1H), 7.61 (s, 1H), 7.33-7.37 (m, 1H), 7.02-7.05 (m, 2H), 6.93-6.96 (m, 1H), 6.58 (s, 1H), 4.40 (q, $J = 7.0$ Hz, 2H), 1.36 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 160.4, 159.8, 149.3, 147.6, 144.4, 138.2,

132.5, 126.7, 122.0, 119.1, 118.9, 118.2, 116.3, 113.1, 112.4, 61.8, 14.1 ppm; HRMS (ESI) m/z calcd for $C_{18}H_{15}NO_4[M+Na]^+$ 332.0893, found 332.0907.

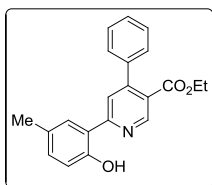
Ethyl 6-(2-hydroxyphenyl)-4-(thiophen-2-yl)nicotinate (5aj): brown solid; mp 125-127 °C



yield 70% (45.6 mg); R_f = 0.7 (EtOAc:hexane = 1:6); IR (KBr) ν 3430, 1724, 1603, 1531, 1492, 1360 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 13.8 (s, 1H), 8.89 (s, 1H), 7.95 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 6.0 Hz, 1H), 7.34-

7.37 (m, 1H), 7.23-7.27 (m, 1H), 7.13-7.15 (m, 1H), 7.05 (d, J = 8.2 Hz, 1H), 6.91-6.95 (m, 1H), 4.29 (q, J = 7.3 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 160.5, 159.8, 147.8, 143.9, 138.9, 132.6, 128.3, 127.9, 127.7, 126.7, 124.4, 120.4, 119.1, 118.9, 118.0, 61.7, 13.9 ppm; HRMS (ESI) m/z calcd for $C_{18}H_{15}NO_3S[M+Na]^+$ 348.0665, found 348.0680

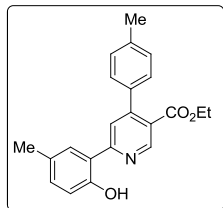
Ethyl 6-(2-hydroxy-5-methylphenyl)-4-phenylnicotinate (5ba): colorless solid; mp 129-131



°C; yield 77% (51.3 mg); R_f = 0.67 (EtOAc:hexane = 1:6); IR (KBr) ν 3457, 1720, 1594, 1532, 1497, 1396 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 13.76 (s, 1H), 8.99 (s, 1H), 7.84 (s, 1H), 7.60 (s, 1H), 7.46-7.47 (m, 3H), 7.37-7.39

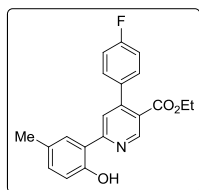
(m, 2H), 7.16 (d, J = 8.0 Hz, 1H), 6.94-6.97 (m, 1H), 4.18 (q, J = 7.0 Hz, 2H), 2.31 (s, 3H), 1.09 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.9, 158.4, 152.0, 148.2, 139.0, 133.5, 128.6, 128.3, 128.1, 128.0, 126.8, 124.0, 120.3, 118.7, 117.7, 61.4, 20.7, 13.7 ppm; HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_3[M+Na]^+$ 356.1257, found 356.1268

Ethyl 6-(2-hydroxy-5-methylphenyl)-4-(4-methylphenyl)nicotinate (5bb): colorless solid; mp



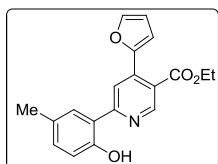
132-134 °C; yield 71% (49.3 mg); R_f = 0.67 (EtOAc:hexane = 1:6); IR (KBr) ν 3438, 1729, 1608, 1483, 1427, 1387 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.75 (s, 1H), 8.99 (s, 1H), 7.84 (s, 1H), 7.60 (s, 1H), 7.26-7.28 (m, 3H), 7.15-7.17 (m, 2H), 6.94-6.96 (m, 1H), 4.20 (q, J = 7.0 Hz, 2H), 2.82 (s, 3H), 2.31 (s, 3H), 1.14 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 158.2, 150.1, 148.8, 139.5, 139.4, 135.9, 134.8, 129.9, 129.5, 127.1, 126.9, 120.9, 120.8, 61.8, 21.3, 21.2, 14.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_3[\text{M}+\text{H}]^+$ 348.1594, found 348.1601.

Ethyl 4-(4-fluorophenyl)-6-(2-hydroxy-5-methylphenyl)nicotinate (5be): white solid; mp



110-112 °C; yield 77% (54.1 mg); R_f = 0.66 (EtOAc:hexane = 1:6); IR (KBr) ν 3439, 1730, 1597, 1491, 1366 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.70 (s, 1H), 9.0 (s, 1H), 7.80 (s, 1H), 7.59 (s, 1H), 7.34-7.37 (m, 2H), 7.14-7.19 (m, 3H), 6.94-6.97 (m, 1H), 4.20 (q, J = 7.0 Hz, 2H), 2.32 (s, 3H), 1.15 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 162.7 ($J_{\text{C-F}}$ = 247.1 Hz), 159.8, 158.1, 150.8, 148.1, 134.6, 133.3, 129.6 ($J_{\text{C-F}}$ = 8.0 Hz), 127.8, 126.4, 123.4, 120.1, 118.6, 117.3, 115.1 ($J_{\text{C-F}}$ = 22.0 Hz), 61.2, 20.4, 13.6 ppm; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{FNO}_3[\text{M}+\text{Na}]^+$ 374.1163, found 374.1174.

Ethyl 4-(furan-2-yl)-6-(2-hydroxy-5-methylphenyl)nicotinate (5bi): brown solid; mp 100-102

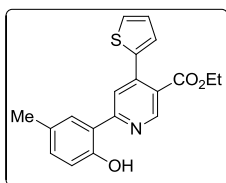


°C; yield 67% (43.3 mg); R_f = 0.68 (EtOAc:hexane = 1:6); IR (KBr) ν 3448, 1719, 1547, 1523, 1392 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.65 (s, 1H), 8.79 (s, 1H), 8.14 (s, 1H), 7.61-7.64 (m, 2H), 7.15-7.17 (m, 1H), 7.03 (d, J = 3.2 Hz, 1H), 6.94 (d, J = 8.3 Hz, 1H), 6.57-6.58 (m, 1H), 4.40 (q, J = 8.3 Hz, 2H), 2.35 (s, 3H), 1.36 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 159.9, 158.2, 149.4, 147.6,

144.4, 138.2, 133.4, 128.1, 126.7, 121.9, 118.6, 117.8, 116.2, 113.0, 112.4, 61.8, 20.7, 14.2 ppm;

HRMS (ESI) m/z calcd for $C_{19}H_{17}NO_4[M+Na]^+$ 346.1050, found 346.1062.

Ethyl 6-(2-hydroxy-5-methylphenyl)-4-(thiophen-2-yl)nicotinate (5bj): brown solid; mp 105-



107 °C; yield 72% (48.9 mg); R_f = 0.68 (EtOAc:hexane = 1:6); IR (KBr)

ν 3422, 1719, 1596, 1523, 1487, 1364 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$):

δ 13.8 (s, 1H), 8.89 (s, 1H), 7.93 (s, 1H), 7.59 (s, 1H), 7.49-7.51 (m, 1H),

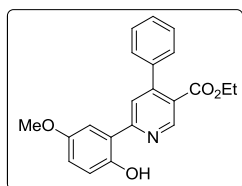
7.15-7.18 (m, 2H), 6.95 (d, J = 8.0 Hz, 1H), 4.29 (q, J = 7.3 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.9, 158.3, 147.9, 143.9, 139.1, 133.6, 128.3,

128.1, 127.8, 127.7, 126.7, 124.3, 120.4, 118.7, 117.6, 61.7, 20.7, 13.9 ppm; HRMS (ESI) m/z

calcd for $C_{19}H_{17}NO_3S[M+Na]^+$ 362.0821, found 362.0833.

Ethyl 6-(2-hydroxy-5-methoxyphenyl)-4-phenylnicotinate (5ca): colorless solid; mp 118-120



°C; yield 78% (54.5 mg); R_f = 0.68 (EtOAc:hexane = 1:6); IR (KBr) ν

3449, 1719, 1593, 1529, 1491, 1399 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ

13.49 (s, 1H), 9.00 (s, 1H), 7.79 (s, 1H), 7.46-7.47 (m, 3H), 7.36-7.38 (m,

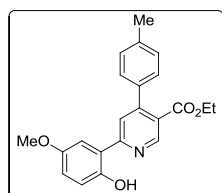
2H), 7.27-7.29 (m, 1H), 6.99-6.99 (m, 1H), 6.96-7.0 (m, 2H), 4.16 (q, J = 7.0 Hz, 2H), 3.80 (s,

3H), 1.08 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.6, 154.8, 152.4,

152.1, 148.2, 138.9, 128.7, 128.4, 128.0, 124.2, 120.5, 119.6, 119.4, 118.0, 111.0, 61.4, 56.1,

13.8 ppm; HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_4[M+Na]^+$ 372.1206, found 372.1220

Ethyl 6-(2-hydroxy-5-methoxyphenyl)-4-(4-methylphenyl)nicotinate (5cb): light yellow



solid; mp 125-127°C; yield 73% (52.3 mg); R_f = 0.65 (EtOAc:hexane = 1:6);

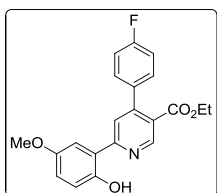
IR (KBr) ν 3438, 1721, 1595, 1514, 1462, 1387 cm^{-1} ; 1H NMR (400 MHz,

$CDCl_3$) δ 13.48 (s, 1H), 8.95 (s, 1H), 7.76 (s, 1H), 7.23-7.26 (m, 5H), 6.95-

6.96 (m, 2H), 4.17 (q, J = 7.0 Hz, 2H), 3.78 (s, 3H), 2.41 (s, 3H), 1.12 (t, J = 7.0 Hz, 3H) ppm;

^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 159.5, 154.7, 152.3, 152.2, 148.1, 138.8, 135.9, 129.0, 128.0, 124.2, 120.5, 119.5, 119.3, 118.0, 111.0, 61.4, 56.1, 21.3, 13.8 ppm; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_4[\text{M}+\text{Na}]^+$ 386.1363, found 386.1275.

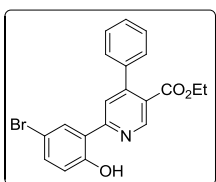
Ethyl 4-(4-fluorophenyl)-6-(2-hydroxy-5-methoxyphenyl)nicotinate (5ce): colorless solid; mp



114-116 °C; yield 80% (58.7 mg); R_f = 0.65 (EtOAc:hexane = 1:6); IR (KBr) ν 3448, 1714, 1594, 1512, 1463, 1395 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.41 (s, 1H), 9.01 (s, 1H), 7.75 (s, 1H), 7.33-7.36 (m, 2H), 7.26-

7.28 (m, 1H), 7.14-7.19 (m, 2H), 6.97-6.99 (m, 2H), 4.20 (q, J = 7.0 Hz, 2H), 3.81 (s, 3H), 1.15 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 163.1 ($J_{\text{C-F}}$ = 247.9 Hz), 159.7, 154.8, 152.4, 151.2, 148.4, 134.8, 129.9 ($J_{\text{C-F}}$ = 8.0 Hz), 124.0, 120.5, 119.6, 119.4, 117.9, 115.4 ($J_{\text{C-F}}$ = 22.0 Hz), 111.2, 61.5, 56.1, 13.8 ppm; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{FNO}_4[\text{M}+\text{Na}]^+$ 390.1112, found 390.1120

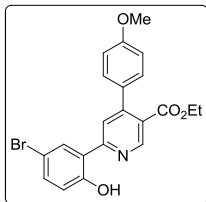
Ethyl 6-(5-bromo-2-hydroxyphenyl)-4-phenylnicotinate (5da) : colorless solid; mp 120-122



°C; yield 68% (54.1 mg); R_f = 0.7 (EtOAc:hexane = 1:6); IR (KBr) ν 3448, 1731, 1594, 1536, 1472, 1390 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 14.02 (s, 1H), 8.99 (s, 1H), 7.91 (s, 1H), 7.80 (s, 1H), 7.47-7.47 (m, 3H), 7.37-7.42

(m, 2H), 6.94 (d, J = 8.2 Hz, 2H), 4.18 (q, J = 7.0 Hz, 2H), 1.08 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 159.6, 158.4, 152.4, 148.1, 138.6, 135.1, 129.1, 128.8, 128.4, 128.0, 124.8, 120.8, 120.5, 119.7, 110.9, 61.6, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}^{79}\text{BrNO}_3[\text{M}+\text{Na}]^+$ 420.0206, found 420.0217; m/z calcd for $\text{C}_{20}\text{H}_{16}^{81}\text{BrNO}_3[\text{M}+\text{Na}]^+$ 422.0185, found 422.0197.

Ethyl 6-(5-bromo-2-hydroxyphenyl)-4-(4-methoxyphenyl)nicotinate (5dc): pale yellow solid;



mp 136-138°C; yield 65% (55.7 mg); $R_f = 0.64$ (EtOAc:hexane = 1:6); IR

(KBr) ν 3443, 1706, 1653, 1581, 1515, 1474, 1338 cm^{-1} ; ^1H NMR (400 MHz,

CDCl_3) δ 14.00 (s, 1H), 8.94 (s, 1H), 7.91 (d, $J = 2.0$ Hz, 1H), 7.78 (s, 1H),

7.41 (dd, $J_1 = 2.0$ Hz, $J_2 = 7.6$ Hz, 1H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.0 (d, $J = 8.5$ Hz, 2H), 6.94 (d,

$J = 8.0$ Hz, 1H), 4.22 (q, $J = 7.04$ Hz, 2H), 3.88 (s, 3H), 1.16 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR

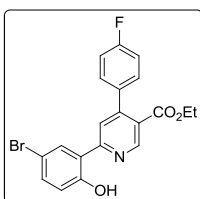
(100 MHz, CDCl_3) δ 166.1, 160.4, 159.6, 158.2, 151.9, 148.0, 135.0, 129.5, 129.1, 124.9, 120.8,

120.4, 119.8, 114.0, 110.8, 61.6, 55.4, 13.9 ppm; HRMS (ESI) m/z calcd for

$\text{C}_{21}\text{H}_{18}^{79}\text{BrNO}_4[\text{M}+\text{Na}]^+$ 450.0311, found 450.0323; m/z calcd for $\text{C}_{21}\text{H}_{18}^{81}\text{BrNO}_4[\text{M}+\text{Na}]^+$

452.0291, found 452.0309.

Ethyl 6-(5-bromo-2-hydroxyphenyl)-4-(4-fluorophenyl)nicotinate (5de): colorless solid; mp



128-130 °C; yield 70% (58.2 mg); $R_f = 0.68$ (EtOAc:hexane = 1:6); IR (KBr)

ν 3423, 1730, 1595, 1537, 1488, 1390 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ

13.96 (s, 1H), 9.0 (s, 1H), 7.90 (s, 1H), 7.76 (s, 1H), 7.40-7.43 (m, 1H), 7.34-

7.37 (m, 2H), 7.15-7.20 (m, 2H), 6.94 (d, $J = 8.8$ Hz, 1H), 4.21 (q, $J = 7.04$ Hz, 2H), 1.15 (t, $J =$

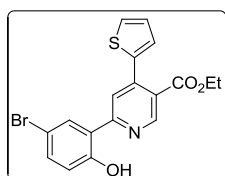
7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 163.2 ($J_{\text{C-F}} = 247.8$ Hz), 159.6, 158.4,

151.4, 148.3, 135.2, 134.5, 130.0, 129.9 ($J_{\text{C-F}} = 8.0$ Hz), 124.6, 120.9, 120.5, 119.6, 115.5 ($J_{\text{C-F}} =$

21.8 Hz), 110.9, 61.6, 13.8 ppm; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{15}^{79}\text{BrFNO}_3[\text{M}+\text{Na}]^+$ 438.0112,

found 438.0102; m/z calcd for $\text{C}_{20}\text{H}_{15}^{81}\text{BrFNO}_3[\text{M}+\text{Na}]^+$ 440.0091, found 440.0078.

6-(5-bromo-2-hydroxyphenyl)-4-(thiophen-2-yl)nicotinate (5dj): brown solid; mp 108-110



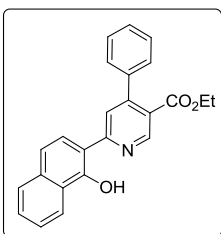
°C; yield 61% (49.3 mg); $R_f = 0.68$ (EtOAc:hexane = 1:6); IR (KBr) ν 3457,

1720, 1594, 1532, 1497, 1396 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.88 (s,

1H), 8.88 (s, 1H), 7.89 (d, $J = 7.8$ Hz, 2H), 7.51-7.52 (m, 1H), 7.42 (d, $J =$

8.0 Hz, 1H), 7.25-7.26 (m, 1H), 7.13-7.16 (m, 1H), 6.93-6.95 (m, 1H), 4.29 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 159.5, 158.3, 147.8, 144.3, 138.6, 135.2, 129.1, 128.5, 128.2, 127.8, 125.1, 120.8, 120.5, 119.6, 110.9, 61.9, 13.9 ppm; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}^{79}\text{BrNO}_3\text{S}[\text{M}+\text{H}]^+$ 403.9951, found 403.9956; m/z calcd for $\text{C}_{18}\text{H}_{14}^{81}\text{BrNO}_3\text{S}[\text{M}+\text{H}]^+$ 405.9930, found 405.9938.

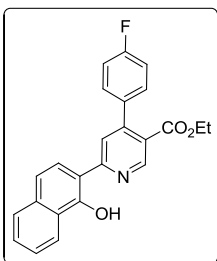
Ethyl 6-(1-hydroxynaphthalen-2-yl)-4-phenylnicotinate (5ea): colorless solid; mp 139-141



$^{\circ}\text{C}$; yield 71% (52.4 mg); $R_f = 0.65$ (EtOAc:hexane = 1:6); IR (KBr) ν 3442, 1694, 1596, 1519, 1483, 1379 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 15.49 (s, 1H), 9.04 (s, 1H), 8.50 (d, $J = 7.6$ Hz, 1H), 7.90 (s, 1H), 7.83 (d, $J = 9.0$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.47-7.57 (m, 5H), 7.33-7.40 (m,

3H), 4.18 (d, $J = 7.3$ Hz, 2H), 1.10 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 160.1, 158.9, 152.2, 147.9, 139.1, 135.7, 128.6, 128.3, 128.3, 128.0, 127.3, 128.4, 125.6, 123.9, 123.4, 122.7, 120.2, 118.6, 110.7, 61.4, 13.8 ppm; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{19}\text{NO}_3[\text{M}+\text{H}]^+$ 370.1438, found 370.1443.

Ethyl 4-(4-fluorophenyl)-6-(1-hydroxynaphthalen-2-yl)nicotinate (5ee): colorless solid; mp

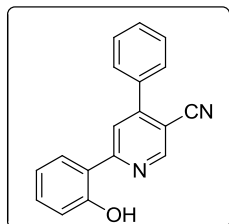


136-138 $^{\circ}\text{C}$; yield 74% (57.3 mg); $R_f = 0.65$ (EtOAc:hexane = 1:6); IR (KBr) ν 3448, 1695, 1596, 1465, 1377 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 15.45 (s, 1H), 9.05 (s, 1H), 8.50 (d, $J = 7.8$ Hz, 1H), 7.86 (s, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 7.58-7.51 (m, 2H), 7.39-7.33 (m,

3H), 7.19-7.15 (m, 2H), 4.20 (d, $J = 7.0$ Hz, 2H), 1.16 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 163.1 ($J_{\text{C-F}} = 247.0$ Hz), 160.3, 158.9, 151.2, 148.2, 135.7, 135.1, 129.9 ($J_{\text{C-F}} = 8.0$ Hz), 128.4, 127.3, 126.4, 125.6, 123.9, 123.2, 122.7, 120.3, 118.6, 115.4 ($J_{\text{C-F}} = 21.0$

Hz), 110.6, 61.5, 13.9 ppm; HRMS (ESI) m/z calcd for $C_{24}H_{18}FNO_3[M+H]^+$ 388.1343, found 388.1349.

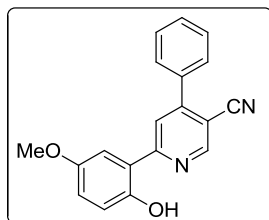
6-(2-Hydroxyphenyl)-4-phenylnicotinonitrile (5ak): light yellow solid; mp 134-136 °C; yield



73% (39.7 mg) ; R_f = 0.6 (EtOAc:hexane = 1:6); IR (KBr) ν 3443, 2225, 1595, 1529, 1497, 1371 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 13.28 (s, 1H), 8.85 (s, 1H), 7.96 (s, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.64-7.67 (m, 2H), 7.37-7.41 (m, 1H), 7.27-7.29 (m, 3H), 7.05 (d, J = 8.0 Hz, 1H), 6.92-6.96 (m, 1H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 160.7, 153.4, 151.0, 135.6, 133.5, 130.5, 129.3, 128.4, 126.9, 119.5, 119.2, 117.7, 116.5, 106.0 ppm; HRMS (ESI) m/z calcd for $C_{18}H_{12}N_2O[M+H]^+$ 273.1022, found 273.1031.

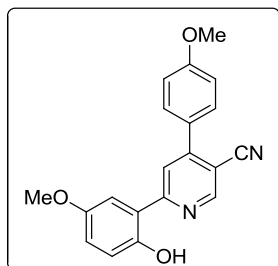
6-(2-Hydroxy-5-methoxyphenyl)-4-phenylnicotinonitrile(5ck): light yellow solid; mp 152-



154 °C; yield 74% (44.7 mg); R_f = 0.58 (EtOAc:hexane = 1:6); IR (KBr) ν 3425, 2227, 1596, 1529, 1488, 1401 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 13.77 (s, 1H), 9.14 (s, 1H), 8.36 (s, 1H), 8.33 (s, 1H), 7.79-7.81 (m, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.36-7.40 (m, 1H), 7.07 (d, J = 8.3 Hz, 1H),

6.91-6.94 (m, 1H), 3.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 154.8, 153.5, 152.5, 151.1, 135.6, 130.5, 129.3, 128.4, 120.2, 119.9, 119.3, 117.6, 116.5, 111.2, 106.0, 56.1 ppm; HRMS (ESI) m/z calcd for $C_{19}H_{14}N_2O_2[M+Na]^+$ 325.0947, found 325.0963.

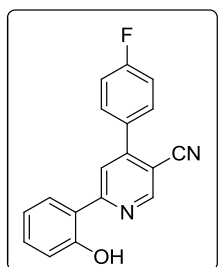
6-(2-Hydroxy-5-methoxyphenyl)-4-(4-methoxyphenyl)nicotinonitrile (5cl): light yellow



solid ; mp 146-148 °C; yield 68% (45.2 mg); R_f = 0.5 (EtOAc:hexane = 1:6); IR (KBr) ν 3442, 2223, 1609, 1588, 1494, 1369 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 12.92 (s, 1H), 8.83 (s, 1H), 7.91 (s, 1H), 7.65 (d, J

= 8.0 Hz, 2H), 7.30 (s, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.02 (m, 2H), 3.91 (s, 3H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 153.8, 153.0, 150.8, 150.4, 136.6, 132.2, 128.9, 125.4, 125.2, 121.3, 116.9, 116.4, 116.1, 112.7, 109.2, 56.0 (2C) ppm; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3[\text{M}+\text{H}]^+$ 333.1234, found 333.1245.

4-(4-Fluorophenyl)-6-(2-hydroxyphenyl)nicotinonitrile (5am): light yellow solid; mp 140-



142 °C; yield 76% (44.0 mg); R_f = 0.57 (EtOAc:hexane = 1:6); IR (KBr) ν 3443, 2223, 1601, 1513, 1417, 1362 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 13.30 (s, 1H), 8.86 (s, 1H), 7.98 (s, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.66-7.668 (m, 2H), 7.42-7.38 (m, 1H), 7.30-7.28 (m, 2H), 7.07 (d, J = 8.0 Hz, 1H), 6.97-6.94 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 164.1 ($J_{\text{C-F}}$ = 250.8 Hz), 160.9, 160.7, 152.3, 151.1, 133.6, 131.7, 130.5 ($J_{\text{C-F}}$ = 8.8 Hz), 126.9, 119.5, 119.2 ($J_{\text{C-F}}$ = 21.0 Hz), 117.6, 116.7, 116.5, 116.4, 105.8 ppm; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{11}\text{FN}_2\text{O}[\text{M}+\text{H}]^+$ 291.0928, found 291.0921.

References

1. C. A. Osborne, T. B. D. Endean, E. R. Jarvo, *Org. Lett.* **2015**, *17*, 5340.
2. S. Kayal, S. Mukherjee, *Org. Lett.* **2017**, *19*, 4944.

