Supplementary Information

Organo-Initiator Enabled Undirected C-H Amination of Arenes

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1. General Information

All commercial materials were purchased from Sigma-Aldrich, Adamas-beta, Energy Chemical, and BidePharm. Unless otherwise noted, they were used without further purification. All reactions were conducted using oven-dried glassware. Reactions were monitored by thin-layer chromatography, which was performed on silica gel GF254 plates purchased from Xinnuo New Materials Company. Visualization was accomplished with UV light (254 nm), iodine, or phosphomolybdic acid. Product purification was done by either flash column chromatography with silica gel (200-300 mesh), or preparative thin-layer chromatography with plates (Silica, 1000 µm, 20 x 20 cm, GF254) from Xinnuo New Materials Company. ¹H, ¹³C, and ¹⁹F NMR spectra were collected on a Bruker 400MHz or Varian 400MHz spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm), coupling constants (J) are reported in Hz, and multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m =multiplet, br = broad, or combinations thereof. Regioisomeric ratios were measured by integration of ¹H NMR spectra of product mixtures. High resolution mass was obtained from Agilent 6224 Accurate-Mass TOF LC/MS spectrometer using a positive electrospray ionization (ESI⁺). Infrared spectra were collected on a Bruker Optik GmbH Tensor 27 FT-IR Spectrometer.

2. Reaction Optimization

General Procedure for Reaction Optimization:

To a oven dried 4 mL vial was added the following reagents: base (0.26 mmol, 1.3 equiv.), organo-initiator (0.03 mmol, 15 mol%), anisole (0.2 mmol, 1.0 equiv.), and a magnetic stir bar. To this mixture, 1,1,1,3,3,3-hexafluoroisopropanol (1.0 mL) was added, and the vial was cooled at -15 °C for 15 minutes. Subsequently, HOSA (0.3 mmol, 1.5 equiv.) was added, and the mixture was stirred at 30 °C for 20 hours.

After completion of the reaction, the mixture was transferred to a 20 mL vial containing a saturated aqueous solution of Na_2CO_3 (8 mL). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The isomer distribution and yield of the corresponding products was determined by ¹H NMR analysis of the crude reaction mixture using mesitylene as the internal standard.

Table S1. Evaluation of Organo-initiators



Table S2. Evaluation of Hydroxylamine Derivatives



Table S3. Control Experiments



3. General Procedures for C–H Amination Reactions

General Procedure A:

In a glove box, to a 4 mL vial was added imidazole (0.26 mmol, 1.3 equiv.), 3chloro-5-trifluoromethyl-pyridine-2-carboxylic acid (**OI-1**) or 5-trifluoromethylpyridine-2-carboxylic acid (**OI-2**) (0.03 mmol, 0.15 equiv.), arene substrate (0.2 mmol, 1.0 equiv.), and 1,1,1,3,3,3 -hexafluoroisopropanol (1.0 mL). The mixture was cooled at -15 °C for 15 minutes before HOSA (0.3 mmol, 1.5 equiv.) was added. After stirring at 30 °C for 20 hours, the reaction mixture was transferred to a 20 mL vial containing a saturated aqueous solution of Na₂CO₃ (8 mL). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude mixture was then purified by rapid column chromatography to obtain the desired product. (*Note: The reaction is not sensitive to air or moisture and proceeds smoothly when conducted in open air. However, the aminating agent HOSA is quite hygroscopic, which can cause weighing issues if used in air.*)

General Procedure B:

In a glove box, to a 4 mL vial was added BTMG (0.08 mmol, 0.4 equiv.), 3chloro-5-trifluoromethylpyridine-2-carboxylic acid (**OI-1**) (0.03 mmol, 0.15 equiv.), arene substrate (0.2 mmol, 1.0 equiv.), and 1,1,1,3,3,3 -hexafluoroisopropanol (1.0 mL). The mixture was cooled at -15 °C for 15 minutes before HOSA (0.3 mmol, 1.5 equiv.) was added. After stirring at 30 °C for 20 hours, the reaction mixture was transferred to a 20 mL vial containing a saturated aqueous solution of Na₂CO₃ (8 mL). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude mixture was then purified by rapid column chromatography to obtain the desired product.

4. Product Characterization

2a, 74%, 1.9/1.0

Following general procedure A using OI-1. *Ortho:*

Yellow oil; \mathbf{R}_{f} =0.60 (20% ethyl acetate/hexane) ¹H NMR (400 MHz, CDCl₃) δ 6.82 – 6.78 (m, 2H), 6.76 – 6.71 (m, 2H), 3.86 (s, 3H), 3.79 (brs, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 136.2, 121.2, 118.6, 115.2, 110.6, 55.6. IR (neat, cm⁻¹) v 3453, 1629, 1435, 1384, 1353, 1122, 999, 861, 776, 619, 542. HRMS: calcd. for [M+H]⁺ C₇H₁₀NO⁺ = 124.0757, found: 124.0757.

Para:

Yellow solid; \mathbf{R}_{f} =0.29 (20% ethyl acetate/hexane) ¹H NMR (400 MHz, CDCl₃) δ 6.75 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.9, 140.0, 116.6, 114.9, 55.9. IR (neat, cm⁻¹) ν 3450, 1637, 1512, 1384, 1353, 1236, 1120, 998, 949, 824, 619, 514. HRMS: calcd. for [M+H]⁺ C₇H₁₀NO⁺ = 124.0757, found: 124.0702.

The characterization data matched the ones found in the literature (*Adv. Synth. Catal.* 2021, *363*, 2783–2795).

.OF H₂N

2b, 56%, 2.7/1.0

Following general procedure A using **OI-1**. *Ortho:*

Brown oil; $\mathbf{R}_f = 0.22 \ (40\% \text{ ethyl acetate/hexane})$ ¹**H NMR** (400 MHz, CDCl₃) $\delta \ 6.83 - 6.78 \ (m, 2H), \ 6.74 - 6.70 \ (m, 2H), \ 4.15 \ (t, J = 6.0 \ \text{Hz}, 2H), \ 3.88 \ (t, J = 6.0 \ \text{Hz}, 2H), \ 2.10 - 2.04 \ (m, 2H).$ ¹³**C NMR** (101 MHz, CDCl₃) $\delta \ 146.6, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 66.0, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 66.0, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 66.0, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 66.0, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 66.0, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 66.0, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 66.0, \ 136.4, \ 121.5, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 112.0, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 115.4, \ 118.8, \ 1$ 60.5, 32.3. **IR** (neat, cm⁻¹) *v* 3454, 1599, 1505, 1384, 1353, 1268, 1221, 1081, 993, 854, 743, 621, 542. **HRMS:** calcd. for [M+H]⁺ C₉H₁₄NO₂⁺ = 168.1020, found: 168.1018.

Para:

Yellow solid; \mathbf{R}_{f} =0.29 (60% ethyl acetate/hexane) ¹**H NMR** (400 MHz, CDCl₃) δ 6.75 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.05 (t, J = 5.9 Hz, 2H), 3.84 (t, J = 5.8 Hz, 2H), 2.94 (brs, 2H), 2.03 – 1.97 (m, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 152.0, 140.3, 116.5, 115.8, 66.9, 61.0, 32.2. **IR** (neat, cm⁻¹) v 3451, 3346, 2964, 2903, 1600, 1516, 1355, 1239, 1124, 1099, 1066, 1000, 820, 519.

HRMS: calcd. for $[M+H]^+ C_9 H_{14} NO_2^+ = 168.1019$, found: 168.1016.

The characterization data matched the ones found in the literature (*Tetrahedron*. 2004, *60*, 121–130).



2c, 66%, 3.5/1.0

Following general procedure A using OI-1.

Ortho:

Brown oil;

 $\mathbf{R}_{f} = 0.31 (20\% \text{ ethyl acetate/hexane})$ ¹**H NMR** (400 MHz, CDCl₃) δ 6.82 – 6.78 (m, 2H), 6.74 – 6.69 (m, 2H), 4.28 (t, J = 6.2 Hz, 2H), 4.09 (t, J = 6.2 Hz, 2H), 2.18 – 2.12 (m, 2H), 2.06 (s, 3H).
¹³**C NMR** (101 MHz, CDCl₃) δ 171.2, 146.4, 136.4, 121.5, 118.6, 115.3, 111.6, 64.7, 61.5, 28.8, 21.1. **IR** (neat, cm⁻¹) v 3453, 2831, 1735, 1597, 1506, 1458, 1384, 1364, 1244, 1138, 1055, 776, 741, 544. **HRMS:** calcd. for [M+H]⁺ C₁₁H₁₆NO₃⁺ = 210.1125, found: 210.1122.

Para:

Brown oil;

 $\mathbf{R}_{f} = 0.10 \ (20\% \text{ ethyl acetate/hexane})$ ¹**H NMR** (400 MHz, CDCl₃) δ 6.73 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H),

4.24 (t, J = 6.4 Hz, 2H), 3.96 (t, J = 6.2 Hz, 2H), 3.25 (brs, 2H), 2.11 – 2.03 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 171.2, 152.0, 140.2, 116.5, 115.8, 65.1, 61.5,

28.8, 21.1. IR (neat, cm⁻¹) v 3449, 1732, 1602, 1511, 1385, 1356, 1233, 1126, 1002, 953, 826, 544, 518.

HRMS: calcd. for $[M+H]^+ C_{11}H_{16}NO_3^+ = 210.1125$, found: 210.1123.



Following general procedure A using OI-1.

Ortho:

Yellow oil;

 $\mathbf{R}_{f} = 0.69 \; (30\% \; \text{ethyl acetate/hexane})$

¹**H** NMR (400 MHz, CDCl₃) δ 6.84 – 6.78 (m, 2H), 6.74 – 6.68 (m, 2H), 4.46 (t, *J* = 9.2 Hz, 2H), 4.20 (t, *J* = 9.2 Hz, 2H), 3.78 (brs, 2H), 2.59 (hept, *J* = 7.2 Hz, 1H), 1.18 (d, *J* = 7.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 177.3, 146.2, 136.8, 122.0, 118.5, 115.4, 112.3, 66.9, 62.8, 34.1, 19.1.

IR (neat, cm⁻¹) *v* 3452, 1726, 1598, 1505, 1385, 1353, 1141, 1068, 1000, 542, 515.

HRMS: calcd. for $[M+H]^+ C_{12}H_{18}NO_3^+ = 224.1282$, found: 224.1281.

Para:

Brown oil; $\mathbf{R}_{f} = 0.33 (30\% \text{ ethyl acetate/hexane})$ ¹**H NMR** (400 MHz, CDCl₃) δ 6.75 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.38 – 4.36 (m, 2H), 4.10 – 4.08 (m, 2H), 3.32 (brs, 2H), 2.59 (hept, J = 7.0 Hz, 1H), 1.17 (d, J = 7.0 Hz, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 177.3, 151.8, 140.6, 116.5, 116.2, 67.0, 62.9, 34.0, 19.1. **IR** (neat, cm⁻¹) v 3423, 2972, 2943, 1727, 1634, 1512, 1468, 1385, 1349, 1238, 1122, 622, 515. **HRMS:** calcd. for [M+H]⁺ C₁₂H₁₈NO₃⁺ = 224.1281, found: 224.1278.



2e, 55%

Following general procedure A using **OI-1**. Brown solid; $\mathbf{R}_{f} = 0.52 \ (50\% \text{ ethyl acetate/hexane})$

¹**H NMR** (400 MHz, CDCl₃) δ 6.70 (d, *J* = 8.4 Hz, 1H), 6.31 (d, *J* = 2.5 Hz, 1H), 6.23 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.9, 142.3, 140.7, 113.1, 106.5, 100.8, 56.7, 55.8. IR (neat, cm⁻¹) *v* 3451, 1596, 1512, 1461, 1384, 1353, 1278, 1164, 1124, 1024, 999, 949, 846, 680, 617, 541.

HRMS: calcd. for $[M+H]^+ C_8 H_{12} NO_2^+ = 154.0863$, found: 154.0805.

The characterization data matched the ones found in the literature (*Org. Lett.* 2023, 25, 2548–2553).



2f, 58% Following general procedure **B**. Yellow oil; $\mathbf{R}_f = 0.16 (10\% \text{ methanol/ dichloromethane})$ ¹H NMR (400 MHz, CD₃OD) δ 6.78 (d, J = 8.6 Hz, 1H), 6.69 – 6.66 (m, 2H), 3.78 (s, 3H), 3.73 (s, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 152.2, 141.6, 130.2, 118.6, 116.9, 112.6, 56.1, 42.3. IR (neat, cm⁻¹) v 3454, 1637, 1502, 1384, 1352, 1094, 1115, 992, 619, 513. HRMS (ESI) *m/z* calculated for C₈H₁₃N₂O [M+H⁺]: 153.1023, found:153.1011.

The characterization data matched the ones found in the literature (ACS Med. Chem. Lett. 2019, 10, 1628–1634).



Following general procedure A using OI-1.

Yellow oil;

 $\mathbf{R}_{f} = 0.31$ (20% ethyl acetate/hexane)

¹**H NMR** (400 MHz, CDCl₃) δ 7.14 (s, 1H), 6.81 (s, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.49 (brs, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 166.9, 152.5, 139.7, 120.7, 120.4, 118.2, 114.2, 56.9, 52.1.

IR (neat, cm⁻¹) v 3444, 1612, 1502, 1436, 1384, 1319, 1137, 1080, 1002, 878, 545. **HRMS:** calcd. for [M+H]⁺ C₉H₁₂NO₃⁺ = 182.0812, found:188.0808. The characterization data matched the ones found in the literature (*Org. Lett.* 2020, 22, 2931–2934).

2h, 56%

Following general procedure **A** using **OI-1**. Brown solid; $\mathbf{R}_{f} = 0.30 (30\% \text{ ethyl acetate/hexane})$ ¹**H NMR** (400 MHz, CDCl₃) δ 6.65 (d, J = 8.4 Hz, 1H), 6.45 (d, J = 2.2 Hz, 1H), 6.35 (dd, J = 8.4, 2.1 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.51 (brs, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 153.5, 148.5, 129.9, 115.3, 104.3, 99.5, 55.9, 55.6. **IR** (neat, cm⁻¹) v 3418, 1598, 1514, 1452, 1384, 1353, 1240, 1205, 1153, 834, 619., **HRMS:** calcd. for [M+H]⁺ C₈H₁₂NO₂⁺= 154.0863, found: 154.0802.

The characterization data matched the ones found in the literature (*Chem. Eur. J.* 2017, 23, 563–567).



Following general procedure **A** using **OI-1**. Yellow solid; $\mathbf{R}_f = 0.55 (20\% \text{ ethyl acetate/hexane})$ ¹**H NMR** (400 MHz, CDCl₃) δ 6.82 – 6.79 (m, 2H), 6.62 (d, J = 7.9 Hz, 1H), 3.82 (brs, 5H). ¹³**C NMR** (101 MHz, CDCl₃) δ 146.4, 137.8, 120.7, 117.4, 113.3, 111.7, 55.7. **IR** (neat, cm⁻¹) v 3460, 3371, 1613, 1501, 1461, 1419, 1276, 1225, 1181, 1093, 1019, 855, 795, 608. **HRMS:** calcd. for [M+H]⁺ C₇H₉BrNO⁺ = 201.9863, found:201.9859.

The characterization data matched the ones found in the literature (*ACS Catal.* 2016, *6*, 8162–8165).



Following general procedure **B**.

Brown oil;

 $\mathbf{R}_{f} = 0.48 \ (10\% \text{ methanol/ dichloromethane})$

¹**H NMR** (400 MHz, CD₃OD) δ 6.78 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.65 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.82 (s, 3H), 3.55 (s, 2H), 2.34 (s, 3H).

¹³C NMR (101 MHz, CD₃OD) δ 148.5, 137.6, 132.6, 119.8, 116.9, 111.4, 56.0, 35.2. IR (neat, cm⁻¹) v3451, 2832, 1598, 1440, 1385, 1355, 1282, 1139, 1001, 618, 542. HRMS: calcd. for [M+H]⁺ C₉H₁₅N₂O⁺ = 167.1179, found:167.1176.



2k, 74%

Following general procedure B.

Brown oil;

 $\mathbf{R}_{f} = 0.21 \ (10\% \text{ methanol/ dichloromethane})$

¹**H NMR** (400 MHz, CD₃OD) δ6.79 (d, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.83 (s, 3H), 3.38 (s, 2H), 2.25 (s, 6H).

¹³**C NMR** (101 MHz, CD₃OD) δ 148.8, 137.6, 130.3, 121.1, 117.9, 111.2, 64.5, 56.0, 44.8.

IR (neat, cm⁻¹) v 3453, 1621, 1515, 1441, 1384, 1228, 1001, 619, 541. **HRMS:** calcd for $[M+H]^+$ CreH: NO⁺ = 181 1336 found: 188 1333

HRMS: calcd. for $[M+H]^+ C_{10}H_{17}N_2O^+ = 181.1336$, found: 188.1333.



2I, 93%

Following general procedure B.

Brown oil;

 $\mathbf{R}_{f} = 0.38 \ (10\% \text{ methanol/ dichloromethane})$

¹**H NMR** (400 MHz, CD₃OD) δ6.79 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.82 (s, 3H), 3.58 (s, 2H), 1.20 (s, 9H).

¹³**C NMR** (101 MHz, CD₃OD) δ 148.4, 137.7, 133.1, 119.9, 117.0, 111.4, 56.0, 52.4, 47.5, 28.4.

IR (neat, cm⁻¹) *v* 3688, 3331, 2962, 2867, 1718, 1619, 1516, 1466, 1441, 1287, 1228, 1032, 802.

HRMS: calcd. for $[M+H]^+ C_{12}H_{21}N_2O^+ = 209.1649$, found: 209.1623.



Following general procedure **B**. Brown oil;

 $\mathbf{R}_{f} = 0.50 \ (10\% \text{ methanol/ dichloromethane})$

¹**H** NMR (400 MHz, CD₃OD) $\delta 6.78$ (d, J = 8.2 Hz, 1H), 6.73 (d, J = 2.0 Hz, 1H), 6.65 (dd, J = 8.1, 2.0 Hz, 1H), 3.82 (s, 3H), 3.62 (s, 2H), 2.49 – 2.41 (m, 1H), 1.94 – 1.92 (m, 2H), 1.76 – 1.72 (m, 2H), 1.65 – 1.62 (m, 1H), 1.27 – 1.10 (m, 5H).

¹³**C NMR** (101 MHz, CD₃OD) δ 148.4, 137.6, 133.2, 119.8, 116.8, 111.4, 57.6, 56.0, 50.9, 33.6, 27.2, 26.2.

IR (neat, cm⁻¹) v 3470, 3368, 2927, 2851, 1618, 1515, 1448, 1263, 991, 738. **HRMS:** calcd. for [M+H]⁺ C₁₄H₂₃N₂O⁺ = 235.1805, found: 235.1802.



Following general procedure A using OI-1.

A 2.0 mmol scale reaction was also successfully conducted, yielding 2n with an isolated yield of 59% (215 mg).

Yellow solid;

 $\mathbf{R}_{f} = 0.38 \ (20\% \text{ ethyl acetate/hexane})$

¹**H NMR** (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.5 Hz, 1H), 7.38 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.81 (brs, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 167.3, 151.0, 136.0, 122.9, 121.1, 115.6, 109.5, 55.7, 51.9.

IR (neat, cm⁻¹) *v* 3430, 2972, 2845, 1709, 1620, 1517, 1444, 1354, 1256, 1107, 1021, 876, 820, 761, 632.

HRMS: calcd. for $[M+H]^+ C_9 H_{12} NO_3^+ = 182.0812$, found:182.0807.

The characterization data matched the ones found in the literature (*ACS Catal.* 2016, *6*, 8162–8165).

Following general procedure A using OI-1. White solid; $\mathbf{R}_f = 0.19 (80\% \text{ ethyl acetate/hexane})$ ¹H NMR (400 MHz, CD₂OD) δ 7.26 – 7.24 (m. 21)

¹**H NMR** (400 MHz, CD₃OD) δ 7.26 – 7.24 (m, 2H), 6.87 (d, *J* = 8.9 Hz, 1H), 3.89 (s, 3H).

¹³C NMR (101 MHz, CD₃OD) δ 172.8, 151.9, 137.9, 127.3, 119.5, 115.3, 110.6, 56.1.

IR (neat, cm⁻¹) v 3443, 2923, 2832, 1598, 1447, 1384, 1357, 1145, 1001, 875, 775, 622, 543.

HRMS: calcd. for $[M+H]^+ C_8 H_{11} N_2 O_2^+ = 167.0816$, found: 167.0809.

The characterization data matched the ones found in the literature (*Asian J. Chem.* 2016, **28**, 2177–2180).

2p, 75%

Following general procedure A using OI-2.

Colorless oil.

 $\mathbf{R}_{f} = 0.65 \ (20\% \text{ ethyl acetate/hexane})$

¹H NMR (400 MHz, CDCl₃) δ 6.80 (s, 2H), 3.46 (brs, 2H), 2.24 (s, 3H), 2.19 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.2, 128.9, 127.2, 122.0, 20.5, 17.7.

IR (neat, cm⁻¹) *v* 3455, 3389, 3007, 2923, 1626, 1605, 1490, 1443, 1380, 1364, 1306, 1251, 1155, 1009, 865, 561.

HRMS: calcd. for $[M+H]^+ C_9 H_{14} N^+ = 136.1121$, found: 136.1116.

The characterization data matched the ones found in the literature (*Adv. Synth. Catal.* 2021, *363*, 2783–2795).



Following general procedure **A** using **OI-1**. Yellow solid; $\mathbf{R}_f = 0.29 (30\% \text{ ethyl acetate/hexane})$ ¹**H NMR** (400 MHz, CDCl₃) δ 6.17 (s, 2H), 3.83 (s, 6H), 3.76 (s, 3H), 3.18 (brs, 2H) ¹³**C NMR** (101 MHz, CDCl₃) δ 152.6, 148.2, 118.9, 91.4, 55.9. **IR** (neat, cm⁻¹) v 3448, 2832, 1611, 1511, 1452, 1364, 1147, 1001, 853, 776, 620, 544. **HRMS:** calcd. for [M+H]⁺ C₉H₁₄NO₃⁺ = 184.0969, found:184.0908.

The characterization data matched the ones found in the literature (*Chem. Eur. J.* 2017, **23**, 563–567).



2r, 48%

Following general procedure A using OI-1.

Brown solid;

 $\mathbf{R}_{f} = 0.30 \ (20\% \text{ ethyl acetate/hexane})$

¹**H NMR** (400 MHz, CDCl₃) δ 7.26 (s, 1H), 6.45 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.27 (brs, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 166.4, 154.5, 151.9, 129.3, 117.9, 111.6, 97.3, 57.4, 55.7, 51.8.

IR (neat, cm⁻¹) *v* 3447, 2948, 2838, 1710, 1597, 1518, 1436, 1414, 1384, 1296, 1081, 1027, 782, 542.

HRMS: calcd. for $[M+H]^+ C_{10}H_{14}NO_4^+ = 212.0918$, found:212.0910.

The characterization data matched the ones found in the literature (J. Polym. Sci., Part A: Polym. Chem. 2016, 54, 1731–1741).



(from *L*-tyrosine)

Following general procedure B.

Yellow oil;

 $\mathbf{R}_{f} = 0.23 \ (80\% \text{ ethyl acetate/hexane})$

¹**H** NMR (400 MHz, CD₃OD) δ 6.75 (d, J = 8.2 Hz, 1H), 6.58 (d, J = 2.1 Hz, 1H), 6.50 (dd, J = 8.2, 2.1 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.64 (t, J = 6.4 Hz, 1H), 2.86 (dd, J = 13.5, 5.9 Hz, 1H), 2.76 (dd, J = 13.5, 6.9 Hz, 1H).

¹³**C NMR** (101 MHz, CD₃OD) δ 176.3, 148.2, 137.7, 130.5, 120.3, 117.3, 111.5, 56.7, 56.0, 52.4, 41.1.

IR (neat, cm⁻¹) *v* 3646, 3361, 2962, 1732, 1916, 1515, 1442, 1284, 1229, 1086, 1028, 799, 759.

HRMS: calcd. for $[M+H]^+ C_{11}H_{17}N_2O_3^+ = 225.1234$, found: 225.1239.



Following general procedure **B**.

Brown solid;

 $\mathbf{R}_{f} = 0.34 \ (10\% \text{ methanol/ dichloromethane})$

¹**H NMR** (400 MHz, CD₃OD) δ 7.40 – 7.34 (m, 1H), 7.26 (d, J = 7.7 Hz, 1H), 7.21 (d, J = 10.0 Hz, 1H), 7.03 (t, J = 8.6 Hz, 1H), 6.85 – 6.73 (m, 2H), 6.63 (d, J = 7.4 Hz, 1H), 5.11 (s, 2H), 3.62 (d, J = 12.6 Hz, 1H), 3.48 (d, J = 12.6 Hz, 1H), 3.24 (q, J = 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CD₃OD) δ 180.2, 164.4 (d, $J_{C-F} = 243.2$ Hz), 147.1, 141.8 (d, $J_{C-F} = 7.4$ Hz), 138.1, 133.3, 131.3 (d, $J_{C-F} = 8.3$ Hz), 124.0 (d, $J_{C-F} = 2.9$ Hz), 119.6, 117.1, 115.4(d, $J_{C-F} = 21.2$ Hz), 115.0 (d, $J_{C-F} = 22.0$ Hz), 113.3, 70.5 (d, $J_{C-F} = 1.8$ Hz), 57.5, 52.4, 19.5.

¹⁹**F NMR** (376 MHz, CD₃OD) δ -115.3.

IR (neat, cm-1) v 3673, 3299, 3183, 1678, 1619, 1515, 1489, 1449, 1382, 1257, 1169, 900, 704, 580.

HRMS: calcd. for $[M+H]^+ C_{17}H_{21}FN_3O_2^+ = 318.1613$, found: 318.1610.



Following general procedure A using **OI-1**. *Ortho:*

Brown solid;

 $\mathbf{R}_{f} = 0.20 \ (5\% \text{ methanol/ dichloromethane})$

¹**H NMR** (400 MHz, CDCl₃) δ 6.57 (s, 1H), 6.51 (s, 1H), 6.03 (brs, 1H), 5.01 – 4.95 (m, 1H), 4.19 – 4.11 (m, 2H), 3.77 (t, *J* = 8.8 Hz, 1H), 3.60 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.39 (brs, 2H), 2.23 (s, 3H), 2.13 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 159.7, 145.4, 132.1, 127.3, 124.4, 123.4, 111.0, 74.5, 69.2, 42.7, 21.0, 17.3.

IR (neat, cm⁻¹) *v* 3453, 1597, 1439, 1384, 1353, 1296, 1251, 1068, 1000, 619, 542.

HRMS: calcd. for $[M+H]^+ C_{12}H_{17}N_2O_3^+ = 237.1234$, found: 237.1233.

Para:

Brown solid;

 $\mathbf{R}_{f} = 0.10$ (2% methanol/ dichloromethane)

¹**H NMR** (400 MHz, CDCl₃) δ 6.56 (s, 2H), 5.79 (brs, 1H), 4.94 – 4.88 (m, 1H), 4.10 – 4.02 (m, 2H), 3.73 (t, *J* = 8.8 Hz, 1H), 3.59 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.37 (brs, 2H), 2.16 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 159.7, 150.6, 137.3, 123.3, 115.2, 74.5, 69.0, 42.9, 18.1.

IR (neat, cm⁻¹) v 3453, 1730, 1597, 1486, 1439, 1384, 1353, 1139, 1068, 999, 859, 542, 515.

HRMS: calcd. for $[M+H]^+ C_{12}H_{17}N_2O_3^+ = 237.1234$, found: 237.1233.

The characterization data matched the ones found in the literature (*Chem. Eur. J.* 2017, 23, 563–567).

H₂N

2v, 78%

Following general procedure A using **OI-2**. Yellow oil; **R**_f = 0.53 (20% ethyl acetate/hexane) ¹**H NMR** (400 MHz, CDCl₃) δ 7.19 (t, J = 7.8 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.71 (d, J = 7.9 Hz, 2H), 3.48 (br s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 146.5, 129.4, 118.6, 115.2. **IR** (neat, cm⁻¹) v 3450, 1637, 1384, 1353, 1094, 999, 862, 777, 619, 540.

The characterization data matched the ones found in the literature (*Adv. Synth. Catal.* 2021, 363, 2783 - 2795).

2w, 80%, 2.5/1.0/1.6 (*p/m/o*)

Following general procedure A using OI-2.

Orange oil.

 $\mathbf{R}_{f} = 0.34 \ (10\% \text{ ethyl acetate/hexane})$

o-toluidine:

¹**H** NMR (400 MHz, CDCl₃) δ 7.09 – 7.07 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 3.41 (brs, 2H), 2.19 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 144.6, 130.5, 127.1, 122.4, 118.7, 115.0, 17.5.

m-toluidine:

¹**H NMR** (400 MHz, CDCl₃) δ 7.06 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.54 – 6.51 (m, 2H), 3.41 (br s, 2H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.4, 139.2, 129.3, 119.5, 116.0, 112.3, 21.5.

p-toluidine:

¹**H NMR** (400 MHz, CDCl₃) δ 6.99 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 2H), 3.41 (br s, 2H), 2.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.9, 129.9, 128.0, 115.4, 20.6.

IR (neat, cm⁻¹) *v* 3448, 1600, 1384, 1353, 1094, 999, 862, 777, 619, 540.

HRMS: calcd. for $[M+H]^+ C_7 H_{10} N^+ = 108.0808$, found: 108.0810.

The characterization data matched the ones found in the literature (*ACS Catal.* 2016, *6*, 8162–8165).



2x, 71%, 2.5/1.0

Following general procedure A using **OI-2**. Brown oil.

 $\mathbf{R}_f = 0.65(20\% \text{ ethyl acetate/hexane})$

3-(tert-butyl)aniline:

¹**H NMR** (400 MHz, CDCl₃) δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 2.2 Hz, 1H), 6.53 (dd, *J* = 7.8, 2.2 Hz, 1H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 152.6, 146.1, 129.1, 116.0, 112.6, 112.5, 34.7, 31.4.

4-(tert-butyl)aniline:

¹**H NMR** (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 143.9, 141.6, 126.2, 115.1, 34.0, 31.7.

IR (neat, cm⁻¹) v 3670, 3343, 2962, 1719, 1621, 1516, 1363, 1265, 1189, 828, 702, 546.

HRMS: calcd. for $[M+H]^+ C_{10}H_{16}N^+ = 150.1278$, found: 150.1272.

The characterization data matched the ones found in the literature (*Org. Lett.* 2020, 22, 2931–2934).



2y, 76%, 1.4/1.2/1.0 (*p/m/o*)

Following general procedure A using OI-2. *Ortho:*

Brown solid; $\mathbf{R}_{f} = 0.24 (30\% \text{ ethyl acetate/hexane})$ ¹H NMR (400 MHz, CDCl₃) δ 9.39 (brs, 1H), 7.27 – 7.17 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.9 Hz, 1H), 3.55 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 178.4, 142.8, 128.0, 125.4, 124.7, 122.4, 110.0, 36.5. IR (neat, cm⁻¹) v 3448, 3271, 1680, 1617, 1469, 1386, 1324, 1265, 1198, 1095, 949, 901, 862, 740, 674, 597, 532. HRMS: calcd. for [M+K]⁺ C₈H₇KNO⁺ = 172.0160, found: 172.0940.

The characterization data matched the ones found in the literature (*Org. Lett.* 2009, *11*, 1345–1348).

The *meta-* and *para-* isomers were isolated as inseparable mixtures. Brown oil. \mathbf{R}_{f} =0.40 (30% ethyl acetate/hexane)

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Meta:

¹**H** NMR (400 MHz, CDCl₃) δ 7.10 (t, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.61 (s, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 3H), 3.53 (s, 2H).

Para:

¹**H NMR** (400 MHz, CDCl₃) δ 7.06 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 3.67 (s, 3H), 3.51 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 172.8, 172.3, 146.8, 145.6, 135.2, 130.2, 129.6, 123.9, 119.5, 116.0, 115.4, 114.0, 52.2, 52.1, 41.3, 40.4.

IR (neat, cm⁻¹) *v* 3459, 3236, 2962, 1730, 1622, 1518, 1495, 1463, 1360, 1265, 1144, 955, 872, 830, 772, 733, 692, 620, 521.

HRMS: calcd. for $[M+H]^+ C_9 H_{12} NO_2^+ = 166.0863$, found: 166.0858.

The characterization data matched the ones found in the literature (*Adv. Synth. Catal.* 2012, *354*, 1879–1884).

2z, 72%, 2.0/1.1/1.0 (*p/m/o*)

Following general procedure A using OI-2.

Yellow solid.

 $\mathbf{R}_{f} = 0.50 \ (40\% \ \text{ethyl acetate/hexane})$

Ortho:

¹**H** NMR (400 MHz, CDCl₃) δ 7.06 – 7.04 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 3.87 (t, *J* = 6.2 Hz, 2H), 3.58 (brs, 2H), 2.79 – 2.77 (m, 2H).

Meta:

¹**H** NMR (400 MHz, CDCl₃) δ 7.10 (t, *J* =7.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.58 – 6.53 (m, 2H), 6.55 (s, 1H), 3.81 (t, *J* = 6.6 Hz, 2H), 3.58 (brs, 2H), 2.76 – 2.73 (m, 2H).

Para:

¹**H NMR** (400 MHz, CDCl₃) δ 7.06 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 3.78 (t, *J* = 6.5 Hz, 2H), 3.58 (brs, 2H), 2.78 – 2.75 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) 146.7, 145.3, 144.9, 139.8, 130.7, 130.0, 129.6, 128.4, 127.8, 124.4, 119.4, 119.2, 116.3, 115.9, 115.5, 113.5, 64.0, 63.7, 63.3, 39.3, 38.4, 34.8.

IR (neat, cm⁻¹) v 3355, 3030, 2932, 2876, 1625, 1516, 1495, 1459, 1263, 1168, 1044, 1016, 823, 755, 698, 563, 470.

HRMS: calcd. for $[M+H]^+ C_8 H_{12} NO^+ = 138.0914$, found: 138.0910.

The characterization data matched the ones found in the literature (*ACS Catal.* 2016, *6*, 8162–8165).

2aa, 84%, 2.3/1.6/1.0 (*p/m/o*)

Following general procedure A using OI-2. *Ortho:*

Brown oil; $\mathbf{R}_{f} = 0.20 \ (10\% \text{ ethyl acetate/hexane})$ ¹**H** NMR (400 MHz, CDCl₃) δ 7.09 – 7.02 (m, 2H), 6.74 – 6.69 (m, 2H), 4.25 (t, *J* = 7.5 Hz, 2H), 3.86 (brs, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.08 (s, 3H). ¹³**C** NMR (101 MHz, CDCl₃) δ 171.6, 145.1, 130.5, 128.1, 121.6, 118.7, 115.9, 63.8, 31.1, 21.2. **IR** (neat, cm⁻¹) v 3455, 2822, 1598, 1510, 1384, 1354, 1135, 1000, 855, 776, 618. **HRMS** (ESI) *m/z* calculated for [M+H⁺] C₁₀H₁₄NO₂⁺: 180.1020, found:180.1013

The meta- and para- isomers were isolated as inseparable mixtures.

Brown oil.

 $\mathbf{R}_{f} = 0.10 \ (10\% \text{ ethyl acetate/hexane})$

Meta:

¹**H NMR** (400 MHz, CDCl₃) δ 7.08 (t, *J* = 7.7 Hz, 1H), 6.61 (d, *J* = 7.0 Hz, 1H), 6.57 – 6.54 (m, 2H), 4.26 (t, *J* = 7.2 Hz, 2H), 2.85 (t, *J* = 7.9 Hz, 2H), 2.04 (s, 3H).

Para:

¹**H NMR** (400 MHz, CDCl₃) δ 7.00 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.03 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 171.2, 146.6, 145.0, 139.1, 129.8, 129.5, 127.8, 119.2, 115.7, 115.4, 113.5, 65.5, 65.1, 35.2, 34.3, 21.1.

IR (neat, cm⁻¹) v 3415, 2957, 1731, 1620, 1518, 1386, 1365, 1243, 1032, 828, 698, 608, 481.

HRMS: calcd. for $[M+H]^+ C_{10}H_{14}NO_2^+ = 180.1020$, found: 180.1014.



2ab, 47%, 1.2/1.0

Following general procedure A using OI-2.

The products were isolated as mixtures of meta- and para- isomers.

Yellow oil.

 $\mathbf{R}_{f} = 0.25$ (40% ethyl acetate/hexane)

Meta:

¹**H** NMR (400 MHz, CDCl₃) δ 7.10 (t, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.60 – 6.55 (m, 2H), 4.39 (t, *J* = 7.0 Hz, 2H), 3.54 (brs, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.85 (s, 3H).

Para:

¹**H NMR** (400 MHz, CDCl₃) δ 7.01 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.35 (t, *J* = 7.0 Hz, 2H), 3.54 (brs, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.7, 145.2, 137.6, 130.0, 129.8, 126.3, 119.3, 115.8, 115.6, 114.0, 71.0, 70.6, 37.4, 35.7, 34.9. IR (neat, cm⁻¹) v 3474, 3413, 1639, 1618, 1384, 1351, 1114, 991, 779, 619, 477. HRMS: calcd. for [M+H]⁺ C₉H₁₄NO₃S⁺ = 216.0689, found: 216.0685.

The characterization data of *para*-isomer matched the one found in the literature (*Nat. Chem.* 2011, *3*, *146*–*153*).



Following general procedure A using OI-2 and BTMG.

The products were isolated as mixtures of regioisomers. Brown oil. $\mathbf{R}_f = 0.15$ (80% ethyl acetate/hexane)

Ortho:

¹**H** NMR (400 MHz, CDCl₃) δ 7.04 (t, *J* = 6.6 Hz, 1H), 6.99 – 6.96 (m, 1H), 6.70 – 6.65 (m, 2H), 6.25 (brs, 1H), 3.72 (brs, 2H), 3.49 – 3.34 (m, 2H), 2.73 – 2.64 (m, 2H), 1.95 (s, 3H).

Meta:

¹**H** NMR (400 MHz, CDCl₃) δ 7.07 (t, J = 7.5 Hz, 1H), 6.57 – 6.51 (m, 2H), 6.50 (s, 1H), 5.74 (brs, 1H), 3.72 (brs, 2H), 3.49 – 3.34 (m, 2H), 2.73 – 2.64 (m, 2H), 1.90 (s, 3H).

Para:

¹**H NMR** (400 MHz, CDCl₃) δ 6.95 (d, J = 7.6 Hz, 2H), 6.62 (d, J = 7.2 Hz, 2H), 5.70 (brs, 1H), 3.72 (brs, 2H), 3.49 – 3.34 (m, 2H), 2.73 – 2.64 (m, 2H), 1.90 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 171.0, 170.2, 146.8, 145.2, 145.0, 140.2, 130.2, 129.6, 128.7, 127.8, 123.0, 118.9, 118.4, 115.8, 115.5, 115.4, 113.4, 41.0, 40.6, 39.5, 35.6, 34.7, 31.7, 23.3, 23.2.

IR (neat, cm⁻¹) v 3419, 1638, 1517, 1495, 1437, 1276, 1198, 1099, 994, 699, 607. HRMS: calcd. for $[M+H]^+ C_{10}H_{15}N_2O^+ = 179.1179$, found: 179.1174.

The characterization data of *para*-isomer matched the one found in the literature (*Eur. J. Org. Chem.* 2018, 2995–3000).



2ad, 71%, 2.9/1.4/1.0 (*p/m/o*)

Following general procedure A using OI-2.

The products were isolated as mixtures of regioisomers.

Brown oil.

 $\mathbf{R}_{f} = 0.40 \ (50\% \text{ ethyl acetate/hexane})$

Ortho:

¹**H** NMR (400 MHz, CDCl₃) δ 7.05 – 7.03 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 3.68 – 3.61 (m, 2H), 3.39 (brs, 2H), 2.65 – 2.56 (m, 2H), 1.86 – 1.84 (m, 2H).

Meta:

¹**H** NMR (400 MHz, CDCl₃) δ 7.09 – 7.06 (m, 1H), 6.65 – 6.59 (m, 1H), 6.53 (s, 1H), 6.52 (d, *J* = 6.8 Hz, 1H), 3.68 – 3.61 (m, 2H), 3.39 (brs, 2H), 2.65 – 2.56 (m, 2H), 1.83 – 1.79 (m, 2H).

Para:

¹**H** NMR (400 MHz, CDCl₃) δ 6.99 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 3.68 – 3.61 (m, 2H), 3.39 (brs, 2H), 2.65 – 2.56 (m, 2H), 1.85 – 1.83 (m, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 146.5, 144.3, 143.2, 132.0, 129.9, 129.4, 129.3, 127.2, 126.6, 119.4, 118.9, 116.2, 115.5, 115.4, 112.9, 62.4, 61.6, 34.6, 34.1, 32.2, 32.1, 31.3, 26.9.

IR (neat, cm⁻¹) v 3145, 2936, 2858, 1618, 1495, 1458, 1384, 1353, 1264, 1157, 1060,827, 753, 550, 510.

HRMS: calcd. for $[M+H]^+ C_9 H_{14} NO^+ = 152.1070$, found:152.1061.

The characterization data of *ortho-* and *meta-*isomer matched the one found in the literature (*Organometallics* 2022, *41*, 1743–1747; *Angew. Chem. Int. Ed.* 2022, *61*, e202115846.).



2ae, 70%, 5.4/1.0

Following general procedure A using OI-2.

The products were isolated as mixtures of meta- and para- isomers.

Yellow oil.

 $\mathbf{R}_{f} = 0.13$ (30% ethyl acetate/hexane)

Meta:

¹**H** NMR (400 MHz, CDCl₃) δ 7.04 (t, J = 7.8 Hz, 1H), 6.50 – 6.47 (m, 2H), 6.39 (s, 1H), 3.62 – 3.53 (m, 2H), 1.75 – 1.70 (m, 1H), 1.45 – 1.40 (m, 1H), 0.94 – 0.89 (m, 2H).

Para:

¹**H NMR** (400 MHz, CDCl₃) δ 6.89 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 8.2 Hz, 2H), 3.62 – 3.53 (m, 2H), 1.75 – 1.70 (m, 1H), 1.38 – 1.30 (m, 1H), 0.86 – 0.80 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 144.3, 132.4, 129.4, 127.1, 116.3, 115.4, 112.8, 66.8, 66.6, 25.2, 24.6, 21.4, 20.8, 13.7, 13.1.

IR (neat, cm⁻¹) v 3366, 3002, 2923, 2870, 1619, 1519, 1459, 1265, 1019, 827, 546. **HRMS:** calcd. for $[M+H]^+ C_{10}H_{14}NO^+ = 164.1070$, found:164.1071.



Following general procedure A using OI-2.

Ortho:

Yellow oil;

 $\mathbf{R}_{f} = 0.20 \ (20\% \text{ ethyl acetate/hexane})$

¹**H NMR** (400 MHz, CDCl₃) δ 7.06 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.71 – 6.67 (m, 2H), 4.50 – 4.46 (m, 1H), 3.76 – 3.71 (m, 1H), 2.11 (s, 3H), 1.70 – 1.66 (m, 1H), 1.24 – 1.20 (m, 1H), 1.11 – 1.06 (m, 1H), 0.91 – 0.87 (m, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 171.1, 146.4, 128.6, 127.8, 124.9, 118.1, 114.8, 68.9, 29.8, 21.2, 18.5, 10.0.

IR (neat, cm⁻¹) v 3451, 1739, 1602, 1498, 1454, 1384, 1364, 1135, 1023, 850, 677.

HRMS (ESI) m/z calculated for [M+H⁺] C₁₂H₁₆NO₂⁺: 206.1176, found: 206.1167.

The *meta-* and *para-* isomers were isolated as inseparable mixtures.

Yellow oil.

 $\mathbf{R}_{f} = 0.36$ (40% ethyl acetate/hexane)

Meta:

¹**H** NMR (400 MHz, CDCl₃) δ 7.05 (t, J = 7.7 Hz, 1H), 6.52 – 6.45 (m, 2H), 6.40 (s, 1H), 4.03 (d, J = 7.2 Hz, 2H), 2.07 (s, 3H), 1.82 – 1.77 (m, 1H), 1.49 – 1.44 (m, 1H), 0.99 – 0.94 (m, 2H).

Para:

¹**H** NMR (400 MHz, CDCl₃) δ 6.89 (d, J = 8.2 Hz, 2H), 6.61 (d, J = 8.3 Hz, 2H), 4.03 (d, J = 7.2 Hz, 2H), 2.07 (s, 3H), 1.82 – 1.77 (m, 1H), 1.40 – 1.32 (m, 1H), 0.93 – 0.84 (m, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 171.4, 146.6, 144.5, 143.4, 131.9, 129.4, 127.2, 116.3, 115.3, 112.8, 112.8, 68.4, 68.2, 29.8, 21.9, 21.2, 21.2, 20.7, 13.9, 13.3.

IR (neat, cm⁻¹) v 3460, 3018, 2948, 1733, 1622, 1520, 1499, 1379, 1240, 1128, 1026, 826, 607.

HRMS: calcd. for $[M+H]^+ C_{12}H_{16}NO_2^+ = 206.1176$, found: 206.1179.



2ag, 85%, 1.6/3.2/1.0/1.3 (*o/m//*m'/*p*)

Following general procedure A using OI-1.



White solid;

 $\mathbf{R}_{f} = 0.69$ (20% ethyl acetate/hexane)

dibenzo[b,d]furan-1-amine:

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.32 (m, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 2.94 (brs, 2H).

dibenzo[b,d]furan-4-amine:

¹**H NMR** (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.32 (m, 3H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 2.94 (brs, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.5, 156.1, 155.6, 145.0, 142.6, 132.0, 128.2, 127.0, 125.9, 125.0, 124.7, 124.0, 123.6, 122.8, 122.7, 121.1, 120.8, 113.2, 111.8, 111.5, 110.7, 109.1, 102.1.

IR (neat, cm⁻¹) *v* 3446, 2810, 2720, 1590, 1380, 1350, 1130, 1120, 754, 664. **HRMS:** calcd. for $[M+H]^+ C_{12}H_{12}NO^+ = 184.0757$, found: 184.0754.

NH₂

dibenzo[b,d]furan-3-amine:

White solid;

 $\mathbf{R}_{f} = 0.63$ (20% ethyl acetate/hexane)

¹**H NMR** (400 MHz, CDCl₃) δ . 7.76 (dd, J = 7.2, 1.6 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.26 – 7.22 (m, 1H), 6.82 (d, J = 2.0 Hz, 1H), 6.66 (dd, J = 8.0, 2.0 Hz, 1H), 3.83 (brs, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 158.0, 156.0, 146.8, 125.3, 124.9, 122.7, 121.4, 119.4, 115.8, 111.4, 111.3, 97.6.

IR (neat, cm⁻¹) v 3600, 3452, 3410, 1630, 1595, 1380, 1350, 770, 760, 619. **HRMS:** calcd. for [M+H]⁺ C₁₂H₁₂NO⁺ = 184.0757, found: 184.0757.



dibenzo[b,d]furan-2-amine: White solid; $\mathbf{R}_f = 0.47 (20\% \text{ ethyl acetate/hexane})$ ¹H NMR (400 MHz, CDCl₃) δ . 7.86 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.24 (s, 1H), 6.83 (dd, J = 8.7, 2.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 156.9, 150.5, 142.1, 127.1, 125.0, 124.4, 122.4, 120.7, 115.9, 112.1, 111.8, 106.2. IR (neat, cm⁻¹) v 3530, 3430, 3390, 1620, 1590, 1380, 1350, 765, 690, 620. HRMS: calcd. for [M+H]⁺ C₁₂H₁₂NO⁺ = 184.0757, found: 184.0747.

Isomer characterized was according to the literature (ACS Catal. 2016, 6, 8162–8165).



2ah, 58%

Following general procedure A using OI-1.

[MsONH₃OTf] was used as the aminating agent.

Brown solid;

 $\mathbf{R}_{f} = 0.45$ (20% ethyl acetate/hexane)

¹**H NMR** (400 MHz, CDCl₃) δ 8.80 (dd, J = 4.2, 1.8 Hz, 1H), 8.51 (dd, J = 8.5, 1.8 Hz, 1H), 7.37 (dd, J = 8.5, 4.2 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 4.05 (brs, 2H), 3.92 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 148.1, 147.2, 139.1, 137.4, 131.0, 121.2, 120.5, 109.9, 105.5, 56.0.

IR (neat, cm⁻¹) v.3450, 3380, 2880, 1614, 1580, 1380, 1352, 780, 670, 650. HRMS: calcd. for $[M+H]^+ C_{10}H_{11}N_2O^+ = 175.0866$, found: 175.0897.



2ai, 50%

Following general procedure **A** using **OI-2**. [MsONH₃OTf] was used as the aminating agent. Brown solid; **R**_f=0.16 (100% ethyl acetate) ¹**H NMR** (400 MHz, CD₃OD) δ 6.95 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 2.54 (s, 3H). ¹³**C NMR** (101 MHz, CD₃OD) δ 150.7, 137.7, 137.6, 130.9, 124.5, 108.1, 103.1, 14.1. **IR** (neat, cm⁻¹) *v* 3460, 3350, 1620, 1595, 1382, 1348, 790, 680, 620. **HRMS:** calcd. for [M+H]⁺ C₈H₁₀N₃⁺ = 148.0869, found: 148.0839.

5. Mechanistic Experiments



In a glove box, to a 4 mL vial was added imidazole (17.7 mg, 0.26 mmol, 1.3 equiv.), 3-chloro-5-trifluoromethyl-pyridine-2-carboxylic acid (**OI-1**) (6.8 mg, 0.03 mmol, 0.15 equiv.), anisole (22 μ L, 0.2 mmol, 1.0 equiv.), and 1,1,1,3,3,3 - hexafluoroisopropanol (1.0 mL). The mixture was cooled at -15 °C for 15 minutes before HOSA (33.9 mg, 0.3 mmol, 1.5 equiv.) and **TEMPO** (46.9 mg, 0.3 mmol, 1.5 equiv.) was added. After stirring at 30 °C for 20 hours, the reaction mixture was transferred to a 20 mL vial containing a saturated aqueous solution of Na₂CO₃ (8 mL). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The result was analyzed by ¹H NMR spectrum of the crude reaction mixture using mesitylene as the internal standard.



In a glove box, to a 4 mL vial was added lepidine (37.2 mg, 0.26 mmol, 1.3 equiv.), 3-chloro-5-trifluoromethyl-pyridine-2-carboxylic acid (**OI-1**) (45.1 mg, 0.2 mmol, 1.0 equiv.), anisole (25 μ L, 0.2 mmol, 1.0 equiv.), **cyclohexane** (108 μ L, 1.0 mmol, 5.0 equiv.) and 1,1,1,3,3,3 -hexafluoroisopropanol (1.0 mL). The mixture was cooled at -15 °C for 15 minutes before HOSA (33.9 mg, 0.3 mmol, 1.5 equiv.). After stirring at 30 °C for 20 hours, the reaction mixture was transferred to a 20 mL vial containing a saturated aqueous solution of Na₂CO₃ (8 mL). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The result was analyzed by ¹H NMR spectrum of the crude reaction mixture using mesitylene as the internal standard, showing only trace amount of **2i**. However, a Minisci-type byproduct, 2-cyclohexanyl-lepidine, was isolated in about 10% yield via rapid column chromatography.

Yellow oil;

 $\mathbf{R}_{f} = 0.64 \ (10\% \text{ ethyl acetate/hexane})$

¹H NMR (400 MHz, CDCl3). δ 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.68-7.64 (m, 1H), 7.50-7.46 (m, 1H), 7.16 (s, 1H), 2.91-2.84 (m, 1H), 2.67 (s, 3H), 2.03-1.99 (m, 2H), 1.92-1.86 (m, 2H), 1.81-1.76 (m, 1H), 1.67-1.57 (m, 2H), 1.52-1.41 (m, 2H), 1.39-1.30 (m, 1H).
¹³C NMR (101 MHz, CDCl₃) δ 166.6, 147.7, 144.4, 129.5, 129.0, 127.1, 125.5, 123.7, 120.3, 47.7, 32.9, 26.7, 26.2, 19.0.
IR (neat, cm⁻¹) v 2922, 2850, 1598, 1446, 1380, 1288, 1030, 862, 759, 682.

HRMS: calcd. for $[M+H]^+ C_{16}H_{20}N^+ = 226.1590$, found: 226.1586.

The product characterization data matched the ones found in the literature. (ACS Catal. 2017, 7, 4057-4061).



In a glove box, to a 4 mL vial was added imidazole (5.4 mg, 0.08 mmol, 0.08 equiv.), 5-trifluoromethyl-pyridine-2-carboxylic acid (**OI-2**) (3.4 mg, 0.015 mmol,

0.015 equiv.), benzene (78 mg, 1.0 mmol, 1.0 equiv.), benzene- d_6 (84 mg, 1.0 mmol, 1.0 equiv.), and 1,1,1,3,3,3 -hexafluoroisopropanol (1.0 mL). The mixture was cooled at -15 °C for 15 minutes before HOSA (11.3 mg, 0.1 mmol, 0.1 equiv) was added. After stirring at 30 °C for **2 hours**, the reaction mixture was transferred to a 20 mL vial containing a saturated aqueous solution of Na₂CO₃ (8 mL). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum.

To the crude mixture was then diluted with DCM (1.5 mL), Ac₂O (471 μ L, 5.0 mmol) and Et₃N (695 μ L, 5.0 mmol) was added. The mixture was stirred for 2 hours at room temperture until full conversion, determined by TLC analysis. Then, a saturated aqueous solution of Na₂CO₃ (8 mL) was added, and the resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified via flash column chromatography to afford the desired N-acetylaniline. The P_H/P_D ratio were determined by ¹H NMR analysis as shown below.





In a glove box, to a 4 mL vial was added imidazole (17.7 mg, 0.26 mmol, 1.3 equiv.), 3-chloro-5-trifluoromethyl-pyridine-2-carboxylic acid (**OI-1**) (6.8 mg, 0.03 mmol, 0.15 equiv.), anisole (22 μ L, 0.2 mmol, 1.0 equiv.), and **solvent** (1.0 mL). The mixture was cooled at -15 °C for 15 minutes before HOSA (33.9 mg, 0.3 mmol, 1.5 equiv.) was added. After stirring at 30 °C for 20 hours, the reaction mixture was transferred to a 20 mL vial containing a saturated aqueous solution of Na₂CO₃ (8 mL). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The isomer distribution and yield of the corresponding products was determined by ¹H NMR analysis of the crude reaction mixture using mesitylene as the internal standard.

Proposed Reaction Mechanism

Based on the aforementioned mechanistic studies and insights from our previous work (*J. Am. Chem. Soc.*, 2024, **146**, 1735–1741.), we propose the following reaction mechanism.



Figure S1. Proposed reaction mechanism

6. NMR Spectra





¹H NMR (400 MHz, CDCl₃)









¹H NMR (400 MHz, CDCl₃)



34



¹H NMR (400 MHz, CDCl₃)


















00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -f1 (ppm)











100 90 f1 (ppm) -1 130 120



00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)









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







100 90 f1 (ppm) 140 130 120



























¹H NMR (400 MHz, CDCl₃) 7.26 CDC 3 7.26 CDC 3 7.700 7.700 6.638 6.638 6.638 6.638 6.638 6.638 6.638 6.638 6.638 6.638 6.638 6.6586 6.656 $\begin{array}{c} 3.67\\ 3.65\\ 3.66\\ 3.65\\ 1.62\\ 1.88\\$ Н Ĥ Н NH₂ H_2N OH ЮΗ .OH H₂N Н 1.4 2.9 : : 6.75 6.70 6.55 6.50 5 7.10 7.05 7.00 6.95 6.90 6.85 6.65 6.60 0.18 6.80 f1 (pr 2.00∃ 0.61 0.18 0.18 1.31 1.31 1.31 1.31 F76. 3.78 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1 f1 (ppm) ¹³C NMR (101 MHz, CDCl₃) - 77.2 CDCI3 146.5 144.3 144.3 144.3 144.3 143.2 123.9 129.9 129.9 129.9 129.9 129.9 129.9 129.4 11 62.4 61.6 34.6 34.1 32.2 32.1 32.1 31.3 26.9 ЮΗ H₂N 100 90 f1 (ppm) o -1 00 190 180 170 160 150 140 130 120 110 80 70 60 50 40 30 20 10





¹³C NMR (101 MHz, CDCl₃)














¹**H NMR** (400 MHz, CD₃OD)

