Electronic Supplementary Information

Nickel-Catalyzed Reductive Migratory Alkyl-Alkyl Cross-Coupling Reaction

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1. General Information

General information: All reactions were run under a dry argon atmosphere fitted on 8 mL vials unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. All new compounds were characterized by ¹H NMR, ¹³C NMR, ¹⁹F NMR and HRMS. The known compounds were characterized by ¹H NMR, ¹³C and ¹⁹F NMR data were recorded with Bruker 400 MHz with tetramethylsilane as an internal standard. Data for ¹H ¹³C and ¹⁹F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, m = multiplet), integration, and coupling constant (Hz). All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ¹H), Chloroform-d (77.16 ppm for ¹³C), respectively. GC analyses were performed on an Agilent 7890B gas chromatograph with an FID detector using a *J* & W DB-1 column (10 m, 0.1 mm I.D.). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument.

Materials: NiI₂ (CAS Nu: 13462-90-3) was purchased from sigma-aldrich. Bathocuproine (BC, CAS Nu: 4733-39-5) and anhydrous NMP and LiBr were purchased from Adamas-beta®. *n*-Bu₄NBr (TBAB, CAS Nu:1643-19-2) was purchased from Tokyo Chemical Industry. LiAlD₄ (95% D) was purchased from AMEKO. Unless otherwise noted, alkyl acids, and alkyl bromides were obtained from commercial suppliers (Energy Chemical, Adamas-beta®, *J*&K and so on) and used without further purification.

2. Reaction Optimization

Table S1. Preliminary Reaction Optimization ^a

| | | | \bigtriangledown | | |
|-------|------------------------------------|---|----------------------|---------------------|--|
| | ∽ _{Br +} | 5 mol% Nil ₂ 5 mol% L1 1.5 equiv LiBr | \bigcirc | H 3a | |
| 12 | + Y Br 1a 2a | 1.5 equiv Zn ⁰ 1.5 mL NMP 30 °C, 24 h | Û | 3a' | |
| entry | deviation from standard conditions | 3a Yield [%] | 3a' Yield [%] | rr [3a/3a'] | |
| 1 | no | 74(70) ^[b] | 3 | 27:1 | |
| 2 | L2 instead of L1 | 52 | 5 | 10:1 | |
| 3 | L3 instead of L1 | 4 | Trace | - | |
| 4 | L4 instead of L1 | Trace | Trace | - | |
| 5 | L5 instead of L1 | Trace | Trace | - | |
| 6 | L6 instead of L1 | Trace | 67 | 1:>20 | |
| 7 | L7 instead of L1 | Trace | 53 | 1:>20 | |
| 8 | no ligand | 0 | 0 | - | |
| 9 | $NiCl_2$ instead of NiI_2 | Trace | Trace | - | |
| 10 | $NiBr_2$ instead of NiI_2 | 5 | Trace | - | |
| 11 | DMF instead of NMP | Trace | Trace | - | |
| 12 | DMA instead of NMP | 50 | 6 | 8:1 | |
| 13 | THF instead of NMP | Trace | Trace | - | |
| 14 | MeCN instead of NMP | Trace | Trace | - | |
| 15 | NMP (2.0 mL) | 51 | 5 | 10:1 | |
| 16 | Mn instead of Zn | 24 | 6 | 4:1 | |

| 17 | n-BuN4Br instead of LiBr | 30 | 3 | 11:1 |
|----|--------------------------------|-------|-------|------|
| 18 | NaBr instead of LiBr | Trace | Trace | - |
| 19 | LiI instead of LiBr | Trace | Trace | - |
| 20 | no LiBr | Trace | Trace | - |
| 21 | 10 mol% (NiI ₂ /L1) | 68 | 4 | 15:1 |
| 22 | 2 mol% (NiI ₂ /L1) | 14 | 3 | 4:1 |



^{*a*} **Standard conditions**: NiI₂ (7.8 mg, 0.05 mmol, 5 mol %), L1 (7.2 mg, 0.05 mmol, 5 mol %), 1a (75 ul, 0.5 mmol, 1.0 equiv), 2a (80 mg, 0.75 mmol, 1.5 equiv), LiBr (65 mg, 0.75 mmol, 1.5 equiv), Zn (49 mg, 0.75 mmol, 1.5 equiv), NMP (1.5 mL). Yields were determined by GC with naphthalene as the internal standard. ^[b] Isolated yield.

General procedure A : Under Nitrogen atmosphere, into an oven-dried 10 mL reaction tube equipped with a magnetic stir bar and sealed with a rubber stopper sequentially added NiI₂ (7.8 mg, 0.05 mmol, 5 mol %), **L1** (7.2 mg, 0.05 mmol, 5 mol %), **1a** (75 ul, 0.5 mmol, 1.0 equiv), **2a** (80 mg, 0.75 mmol, 1.5 equiv), LiBr (65 mg, 0.75 mmol, 1.5 equiv), Zn (49 mg, 0.75 mmol, 1.5 equiv), NMP (1.5 mL). The mixture was stirred at 30 °C for 24 h. The reaction was extracted with acetate (3 ×10 mL), and then the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the products.

Table S2. Ineffective Substrates



Functional group tolerance studies



3. Synthesis of Substrates

3.1 General Procedure (B) for Synthesis of Alkyl Bromines



General procedure for the reduction of carboxylic acid¹: To a stirred solution of LiAlH₄ (1.0 equiv) in THF (0.4 M) was added a solution of carboxylic acid (1.0 equiv) in THF dropwise at 0 °C. The mixture was stirred at 0 °C for another 1 h and then allowed to warm to room temperature for 12 h. The reaction progress was monitored by thin-layer chromatography (TLC). The reaction was quenched with 10% NaOH, then the mixture was extracted with EtOAc (3 × 40 mL), and the organic layers were combined and concentrated in vacuo to give a crude material of alcohol, which was used directly in the next step without further purification.

General procedure for the alcohol tosylation²: To a solution of corresponding starting alcohol (1.0 equiv) in DCM (0.4 M), TsCl (1.2 equiv), DMAP (10 mol %) and Et₃N (2 equiv) were added. The reaction mixture was stirred rapidly at room temperature for 12 h. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was extracted with DCM (3 × 40 mL), and the organic layers were combined and concentrated in vacuo to give a crude material of alkyl tosylate. The crude product was purified via flash chromatography over silica gel.

General procedure for the alkyl bromines: To a solution of corresponding starting alcohol tosylate (1.0 equiv) in Acetone (0.4 M), TBAB (1.2 equiv) was added. The reaction mixture was stirred rapidly at 40 °C for 2 h. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was concentrated in vacuo to give a crude material of alkyl tosylate. The crude product was then purified via flash chromatography over silica gel.

3.2 General Procedure (C) for Synthesis of Alkyl Bromines

Br₂ (1.3 equiv) PPh₃ (1.3 equiv) R-CH₂OH imidazole (1.3 equiv) DCM (0.4 M)

To a solution of PPh₃ (1.3 equiv) and imidazole (1.3 equiv) in anhydrous DCM (0.4 M), Br₂ was added slowly. The reaction mixture was stirred rapidly at 0 °C. Then alcohol was added dropwise. The mixture was stirred at 0 °C for another 1 h and then allowed to warm to room temperature for 12 h. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, the

mixture was quenched with saturated aqueous NaHCO₃ and extracted with DCM (3×40 mL), and the organic layers were combined and concentrated in vacuo to give a crude material of alkyl bromine. The crude product was purified via flash chromatography over silica gel.



1-(2-bromoethyl)-3,5-difluorobenzene (2.2 g, 51 %, a colorless liquid.): prepared according to the **general procedure B.** ¹H NMR (400 MHz, Chloroform-*d*) δ 6.80 - 6.66 (m, 3 H), 3.55 (t, *J* = 7.3 Hz, 2 H), 3.15 (t, *J* = 7.3 Hz, 2 H).

Cl Br 1-(2-bromoethyl)-3,5-dichlorobenzene (2.8 g, 59%, a colorless liquid.): prepared according to the general procedure B. ¹H NMR (400 MHz, Chloroformd) δ 7.39 (d, J = 8.21 Hz, 1 H), 7.31 (d, J = 2.08 Hz, 1 H), 7.06 (dd, J = 8.19, 2.10 Hz, 1 H), 3.54 (t, J = 7.25 Hz, 2 H), 3.12 (t, J = 7.25 Hz, 2 H).



1-(4-bromobutyl)-4-methoxybenzene (2.5 g, 54%, a colorless liquid.): prepared according to the general procedure **B**. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.28 Hz, 2 H), 6.85 (d, *J* = 8.26 Hz, 2 H), 3.80 (s,

3 H), 3.43 (t, *J* = 6.82 Hz, 2 H), 2.61 (t, *J* = 7.58 Hz, 2 H), 1.90 (p, *J* = 7.06 Hz, 2 H), 1.76 (p, *J* = 7.60 Hz, 2 H).



(**3-bromobutyl)benzene** (2.0 g, 96%, a colorless liquid.): prepared according to the **general procedure** C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 (m, 2 H), 7.12 (m, 3 H), 4.01 (m, 1 H), 2.80 (m, 1 H), 2.67 (m, 1 H), 2.11 - 2.02 (m, 1 H), 2.01 - 1.92 (m, 1 H), 1.65 (d, *J* = 6.7 Hz, 3 H).

3.3 Synthesis of Dueterium-Labeled Alkyl Bromides



General procedure for the dueterium-labeled alkyl bromides: According to the general procedure B.



(4-bromobutyl-4,4-d2)benzene (0.2 g, 39%, 94% D): a colorless liquid. ¹H NMR (600 MHz, Chloroform-d) δ 7.30 (dd, J = 8.44, 6.36 Hz, 2 H), 7.25 - 7.14 (m, 3 H), 2.65 (t, J = 7.50 Hz, 2 H), 1.89 (dd, J = 8.90, 5.83 Hz, 2 H), 1.83 - 1.73 (m, 2 H). ¹³C NMR (151 MHz, Chloroform-d) δ 141.9, 128.5, 126.0, 35.1, 33.7 (tt, J = 13.41 Hz), 32.1, 29.9. Note: one aryl carbon signal is missing due to overlapping, which is consistent with a precedent report (Org. Lett. 2012, 14, 4842–4845. See: SI page 2)



3.4 Synthesis of (3-Bromopropyl-3-d)benzene



Procedure for the reduction of 3-phenylpropanal¹: To a stirred solution of LiAlD₄ (210 mg, 5 mmol, 1.0 equiv) in THF (20 mL) was added a solution of 3-phenylpropanal (0.7 mL, 5 mmol, 1.0 equiv) in THF dropwise at 0 °C. The mixture was stirred at 0 °C for another 1 h and then allowed to warm to room temperature for 12 h. The reaction progress was monitored by thin-layer chromatography (TLC). The reaction was quenched with 10% NaOH, then the mixture was extracted with EtOAc (3 × 40 mL), and the organic layers were combined and concentrated in vacuo to give a crude material of 3-phenylpropan-1-*d*-1-ol, which was used without further purification.

Procedure for 3-phenylpropan-1-*d***-1-ol tosylation**² **:** To a solution of 3-phenylpropan-1-d-1-ol (0.7 mL, 5 mmol, 1.0 equiv) in DCM (20 mL), TsCl (1.2 g, 6 mmol, 1.2 equiv), DMAP (61 mg, 0.5 mmol, 10 mol %) and Et₃N (1.4 mL, 10 mmol, 2 equiv) were added. The reaction mixture was stirred rapidly at room temperature for 12 h. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was extracted with DCM (3 × 40 mL), and the organic layers were combined and concentrated in vacuo to give a crude material. The crude product was purified via flash chromatography over silica gel.

Procedure for (3-bromopropyl-3-d)benzene: To a solution of corresponding 3-phenylpropan-1-d-1ol tosylation (1.0 equiv) in Acetone (0.4 M), TBAB (1.2 equiv) was added. The reaction mixture was stirred rapidly at 40 $^{\circ}$ C for 2 h. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was concentrated in vacuo to give a crude material of alkyl tosylate. The crude product was then purified via flash chromatography over silica gel.



(3-bromopropyl-3-d)benzene (0.5 g, 48%, 96% D): a colorless liquid. ¹H NMR (400 MHz, Chloroform-d) δ 7.36 - 7.26 (m, 2 H), 7.22 (td, J = 6.43, 1.64 Hz, 3 H), 3.39 (tt, J = 6.53, 1.65 Hz, 1 H), 2.79 (t, J = 7.36 Hz, 2 H), 2.17 (q, J = 7.18 Hz, 2 H).¹³C NMR (101 MHz, Chloroform-d) δ 140.7, 128.7, 128.6, 126.3, 34.2, 34.1,

33.1 (t, J = 23.35 Hz).

7.332 7.330 7.317 7.317 7.317 7.314 7.314 7.314 7.314 7.299 7.299 7.299 7.293 7.225 7.225 7.225 7.209 3.413 3.409 3.3406 3.3406 3.3377 3.3377 3.3377 3.3377 3.3377 3.3377 2.333 2.2721 2.772 2.772 2.772 2.7148 2





3.5 Synthesis of 1-Bromocyclopentane-1-d

Procedure method according to 3.4

cyclopentyl-1-d 4-methylbenzenesulfonate (0.8 g, 65%, 98% D) 1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 7.75 Hz, 2 H), 7.40 (d, J = 7.82 Hz, 2 H), 2.52 (s, 3 H), 1.91 -1.73 (m, 6 H), 1.67 - 1.56 (m, 2 H).



4. Synthesis of Ligands



Synthesis of 6-methoxyquinoline-2-carbonitrile : Under O2, a 200 mL of Schlenk flask equipped with a stir bar was charged with 6-methoxy-2-methylquinoline (5.2 g ,30 mmol), I2 (10.2 mg, 0.04 mmol), NH4F (4.5 g, 120 mmol), TBHP (70% in water, 48.6 mL, 260 mmol), DMSO (50 mL). The reaction mixture was stirred at 70 °C for 48 h in oil bath. After the completion of the reaction (monitored by TLC), the solvent was extracted by EtOAc (3×40 mL) and the organic layers were combined and concentrated in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product(3.0 g, 54%, a white solid).



Synthesis of 6-methoxyquinoline-2-carbonitrile : a 10 mL of microwave tube equipped with a stir bar was charged with 6-methoxyquinoline-2-carbonitrile (921 mg, 5 mmol), 2-amino-3,3-dimethylbutan-1-ol (879 mg, 7.5 mmol), Zn(OAc)2.2H2O (43.9 mg, 0.2 mmol), PhMe (5 mL). The reaction mixture was stirred at 140 °C for 30 min. After the completion of the reaction (monitored by TLC), the solvent was extracted by EtOAc (3×40 mL) and the organic layers were combined and concentrated in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product(924 mg, 65%, a white solid). 1H NMR (400 MHz, Chloroform-d) δ 8.24 - 8.05 (m, 3H), 7.39 (dd, J = 9.27, 2.78 Hz, 1H), 7.09 (d, J = 2.77 Hz, 1H), 4.52 (dd, J = 10.25, 8.74 Hz, 1H), 4.38 (t, J = 8.46 Hz, 1H), 4.16 (dd, J = 10.26, 8.18 Hz, 1H), 3.94 (s, 3H), 1.00 (s, 9H). ¹³C NMR (101 MHz, Chloroform-d) δ 162.9, 158.9, 144.7, 143.7, 135.3, 131.9, 130.2, 123.0, 121.5, 105.0, 76.6, 69.6, 55.7, 34.2, 26.1. HRMS (ESI) Calculated for C₁₇H₂₀N₂O₂ ([M+H]⁺): 285.1598, measured: 285.1599.



5. Analytical Data of Compounds



(1-cyclopentylpropyl)benzene (3a) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3a** (X = Br : 41.4 mg, 70% yield, rr = 27/1; X= Cl : 25.4 mg, 43% yield, rr = 13/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 - 7.25 (m, 2 H), 7.18 - 7.16 (m, 1 H), 7.15 - 7.11 (m, 2

H), 2.15 (td, *J* = 10.3, 3.6 Hz, 1 H), 2.05 - 1.78 (m, 3 H), 1.66 - 1.55 (m, 2 H), 1.54 - 1.28 (m, 4 H), 1.26 - 1.15 (m, 1 H), 1.00 - 0.90 (m, 1 H), 0.68 (t, *J* = 7.4 Hz, 3 H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.7, 128.2, 128.0, 125.6, 54.2, 46.5, 31.9, 31.6, 28.1, 25.3, 24.9, 12.2 ppm.



1-(1-cyclopentylpropyl)-4-methoxybenzene (3b): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3b** (77.5 mg, 71% yield, rr = 10/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.06 - 7.02 (m, 2 H), 6.84 - 6.80 (m, 2 H), 3.79 (s, 3 H), 2.11

(td, J = 10.18, 3.61 Hz, 1 H), 2.01 - 1.86 (m, 2 H), 1.83 - 1.75 (m, 1 H), 1.68 - 1.58 (m, 1 H), 1.55 - 1.43 (m, 3 H), 1.42 - 1.29 (m, 2 H), 1.23 - 1.13 (m, 1 H), 1.01 - 0.88 (m, 1 H), 0.68 (t, J = 7.37 Hz, 3 H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.6, 137.9, 129.0, 113.4, 55.3, 53.4, 46.7, 31.9, 31.7, 28.2, 25.5, 25.0, 12.3 ppm. HRMS (ESI) Calculated for C₁₅H₂₄O ([M+H]⁺): 218.1743, measured: 218.1723.



1-(1-cyclopentylpropyl)-4-(trifluoromethyl)benzene (3c) ³: The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 3c (92.3 mg, 72% yield, rr = 14/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, J = 7.98 Hz, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 2.24 (td,

J = 10.3, 3.6 Hz, 1 H), 2.05 - 1.82 (m, 3 H), 1.68 - 1.58 (m, 1 H), 1.55 - 1.50 (m, 2 H), 1.49 - 1.16 (m, 4 H), 0.97 - 0.87 (m, 1 H), 0.67 (t, *J* = 7.4 Hz, 3 H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.1 (q, *J* = 1.08 Hz), 128.5, 128.1 (q, *J* = 32.8 Hz), 125.1 (q, *J* = 3.79 Hz), 124.6 (q, *J* = 271.7 Hz), 54.3, 46.4, 31.9, 31.7, 28.1, 25.3, 25.0, 12.2 ppm. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -62.15 ppm.



1-(1-cyclopentylpropyl)-3-methoxybenzene (**3d**): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether to afford the product **3d** (66.6 mg, 61% yield, rr = 10:1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, J = 7.8 Hz, 1 H), 6.73 (t, J = 9.1 Hz,

2 H), 6.69 (s, 1 H), 3.80 (s, 3 H), 2.13 (td, J = 10.4, 3.2 Hz, 1 H), 2.00 - 1.89 (m, 2 H), 1.84 - 1.79 (m, 1 H), 1.65 - 1.60 (m, 1 H), 1.56 - 1.47 (m, 3 H), 1.45 - 1.34 (m, 2 H), 1.23 - 1.16 (m, 1 H), 1.00 - 0.94 (m, 1 H), 0.70 (t, J = 7.3 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.4, 147.6, 128.9, 120.9, 114.3, 110.5, 55.2, 54.4, 46.6, 32.0, 31.7, 28.1, 25.4, 25.0, 12.3 ppm; HRMS (ESI) Calculated for C₁₅H₂₃O ([M+H]⁺): 218.1743, measured: 218.1723.



1-(1-cyclopentylpropyl)-3,5-dimethoxybenzene (3e): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3e** (59.6 mg, 48% yield, rr = 35/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.31 - 6.29 (m, 3 H), 3.78 (s, 6 H), 2.08 (td, J = 10.2, 3.6 Hz, 1 H), 2.00 - 1.87 (m, 2 H), 1.84 - 1.74 (m, 1 H), 1.57 - 1.35 (m, 6 H), 1.22 -

1.12 (m, 1 H), 1.04 - 0.93 (m, 1 H), 0.70 (t, J = 7.4 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.5, 148.6, 106.5, 97.2, 55.3, 54.7, 46.5, 31.9, 31.7, 28.1, 25.4, 25.0, 12.4 ppm; HRMS (ESI) Calculated for C₁₆H₂₅O₂ ([M+H]⁺): 248.1838, measured: 248.1849.



1-(1-cyclopentylethyl)-4-fluorobenzene (3f) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3f** (X = Br : 77.1 mg, 74 % yield, rr = 29/1; X = Cl : 47.1 mg, 49 % yield, rr = 14/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.14 - 7.11 (m, 2 H), 6.98 - 6.94 (m, 2 H), 2.42 (dq, J =

14.0, 6.9 Hz, 1 H), 1.94 - 1.86 (m, 2 H), 1.70 - 1.52 (m, 3 H), 1.49 - 1.35 (m, 2 H), 1.28 - 1.17 (m, 4 H), 1.04 - 0.94 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.2 (d, J = 242.70 Hz), 143.7 (d, J = 3.17 Hz), 128.6 (d, J = 7.57 Hz), 114.9 (d, J = 20.87 Hz), 47.9, 45.6, 31.9, 31.5, 25.5, 25.2, 21.8 ppm; ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -118.08.



1-(1-cyclopentylethyl)-3,5-difluorobenzene (3g): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3g** (53.6 mg, 51% yield, rr = 27/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.72 - 6.58 (m, 3 H), 2.41 (dq, J = 13.5, 6.7 Hz, 1 H), 1.94 - 1.83 (m, 2 H), 1.69 - 1.38 (m, 5 H), 1.27

- 1.14 (m, 4 H), 1.05 - 0.95 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.0 (dd, J = 247.2, 12.9 Hz), 152.3 (t, J = 8.2 Hz), 110.1 (dd, J = 18.0, 5.8 Hz), 101.2 (t, J = 25.4 Hz), 47.8, 46.4 (t, J = 1.8 Hz), 31.8, 31.4, 25.4, 25.2, 21.3 ppm; ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -110.92 ppm; HRMS (ESI) Calculated for C₁₃H₁₆F₂Na ([M+Na]⁺): 233.1096, measured: 233.1112.



1-(1-cyclopentylethyl)-3-methoxybenzene (3h) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3h** (81.7 mg, 80% yield, rr = 24/1) as a colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.22 (t, J = 7.7 Hz, 1 H), 6.80 (d, J = 7.3 Hz, 1 H), 6.76 - 6.74 (m, 2 H), 3.82 (s, 3 H),

2.42 (dq, *J* = 13.3, 7.3 Hz, 1 H), 1.98 - 1.91 (m, 2 H), 1.70 - 1.65 (m, 1 H), 1.61 - 1.54 (m, 2 H), 1.50 - 1.41 (m, 2 H), 1.30 - 1.20 (m, 4 H), 1.08 - 1.01 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.5, 149.9, 129.1, 119.9, 113.4, 110.6, 55.2, 47.6, 46.4, 31.9, 31.6, 25.5, 25.2, 21.6.



1-chloro-3-(1-cyclopentylethyl)benzene (3i) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3i** (73.1 mg, 70% yield, rr = 14/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 - 7.14 (m, 3 H), 7.06 (dt, J = 7.4, 1.4 Hz, 1 H), 2.41 (dq, J = 9.3, 6.9 Hz, 1 H), 1.98

- 1.87 (m, 2 H), 1.72 - 1.35 (m, 5 H), 1.25 (d, *J* = 6.9 Hz, 3 H), 1.22 - 1.17 (m, 1 H), 1.04 - 0.95 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.4, 134.1, 129.6, 127.6, 126.1, 125.8, 47.7, 46.3, 32.0, 31.6, 25.4, 25.2, 21.5 ppm.



4-(1-cyclopentylethyl)phenol (3j): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3j** (48.5 mg, 51% yield, rr = 8/1) as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.07 - 7.03 (m, 2 H), 6.77 - 6.74 (m, 2 H), 4.94 (s, 1 H), 2.37 (dq, J = 9.3, 6.9 Hz, 1 H), 1.93 - 1.84 (m,

2 H), 1.70 - 1.59 (m, 1 H), 1.59 - 1.49 (m, 2 H), 1.49 - 1.34 (m, 2 H), 1.22 (d, J = 6.9 Hz, 3 H), 1.21 - 1.14 (m, 1 H), 1.06 - 0.95 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.4, 140.5, 128.4, 115.0, 47.9, 45.4, 31.9, 31.5, 25.5, 25.2, 21.8 ppm; HRMS (ESI) Calculated for C₁₃H₁₇O ([M-H]⁻): 189.1286, measured: 189.1285.



5-(1-cyclopentylethyl)-2,3-dihydrobenzofuran (3k): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3k** (81.1 mg, 75% yield, rr = 27/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.01 (s, 1 H),

6.92 - 6.89 (m, 1 H), 6.70 (d, J = 8.1 Hz, 1 H), 4.55 (t, J = 8.7 Hz, 2 H), 3.19 (t, J = 8.7 Hz, 2 H), 2.36 (dq, J = 9.0, 6.9 Hz, 1 H), 1.93 - 1.84 (m, 2 H), 1.71 - 1.62 (m,1 H), 1.60 - 1.49 (m, 2 H), 1.49 - 1.36 (m, 2 H), 1.22 (d, J = 6.9 Hz, 3 H), 1.21 - 1.14 (m, 1 H), 1.09 - 0.92 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.1, 140.4, 126.8, 126.7, 123.7, 108.8, 71.2, 48.0, 45.7, 32.0, 31.6, 30.0, 25.5, 25.2, 22.0 ppm; HRMS (ESI) Calculated for C₁₅H₂₀ONa ([M+Na]⁺): 239.1414, measured: 239.1406.



1-cyclopentyl-2,3-dihydro-1H-indene (31) ³: The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **31** (86.6 mg, 93% yield, rr = 20/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-d) & 7.29 - 7.23 (m, 1 H), 7.22 - 7.17 (m, 1 H), 7.15 - 7.08 (m, 2 H), 3.06 (td, J = 7.9, 5.9 Hz, 1 H), 2.96 - 2.88 (m, 1 H), 2.83

- 2.75 (m, 1 H), 2.23 - 2.12 (m, 1 H), 2.10 - 1.98 (m, 1 H), 1.92 - 1.78 (m, 2 H), 1.78 - 1.69 (m, 1 H), 1.68 - 1.58 (m, 2 H), 1.58 - 1.48 (m, 2 H), 1.41 - 1.32 (m, 1 H), 1.27 - 1.18 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-d) δ 147.5, 144.5, 126.2, 125.9, 124.6, 124.5, 50.0, 44.5, 31.52, 31.50, 30.6, 30.4, 25.7, 25.3 ppm.



3n

F₃C

30

3-(1-cyclopentylethyl)-1H-indole (3m): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3m** (23.5 mg, 22% yield, rr = 13/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-d) δ 7.88 (s, 1 H), 7.66 (d, J = 7.9 Hz, 1 H), 7.34 (d, J = 8.1 Hz, 1 H), 7.19 - 7.15 (m, 1 H), 7.11 - 7.07 (m, 1 H), 6.95 (d, *J* = 2.3 Hz, 1 H), 2.89 - 2.76 (m, 1 H), 2.21 - 2.14 (m, 1 H), 1.92 - 1.83 (m, 1 H), 1.66 -

1.58 (m, 1 H), 1.55 - 1.48 (m, 2 H), 1.34 (d, J = 7.0 Hz, 3 H), 1.32 - 1.24 (m, 2 H), 1.21 - 1.11 (m, 2 H) ppm; ¹³C NMR (101 MHz, Chloroform-d) δ 136.4, 127.2, 122.8, 121.8, 120.4, 119.7, 119.0, 111.2, 47.1, 36.6, 31.8, 31.5, 25.7, 25.4, 20.9 ppm; HRMS (ESI) Calculated for C₁₅H₂₀N ([M+H]⁺): 214.1590, measured: 214.1594.

1-(1-cyclopentylethyl)-2-fluorobenzene (3n)³: The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3n** (64.4 mg, 67% yield, rr = 16/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-d) δ 7.27 (td, J = 7.4, 1.9 Hz, 1 H), 7.15 - 7.09 (m, 1 H), 7.07 - 7.03 (m, 1 H), 7.01 - 6.95 (m, 1 H), 2.89 (dq, J = 9.9, 6.9 Hz, 1 H), 2.06 - 7.09 (m, 1 H), 7.07 - 7.03 (m, 1 H), 7.01 - 6.95 (m, 1 H), 2.89 (dq, J = 9.9, 6.9 Hz, 1 H), 2.06 - 7.03 (m, 1 H), 7.07 - 7.03 (m, 1 H), 7.01 - 6.95 (m, 1 H), 7.07 - 7.03 (m, 1 H), 7.01 - 6.95 (m, 1 H), 7.

1.98 (m, 1 H), 1.94 - 1.87 (m, 1 H), 1.76 - 1.66 (m, 1 H), 1.64 - 1.55 (m, 2 H), 1.55 - 1.43 (m, 2 H), 1.26 - 1.18 (m, 4 H), 1.08 - 0.98 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-d) δ 160.6 (d, J = 243.8Hz), 134.4 (d, J = 14.8 Hz), 128.5 (d, J = 5.5 Hz), 126.9 (d, J = 8.4 Hz), 123.9 (d, J = 3.5 Hz), 115.2 (d, J = 3.5 Hz), 125.2 (d, J = 3. *J* = 23.4 Hz), 46.6 (d, *J* = 1.2 Hz), 38.5 (d, *J* = 1.4 Hz), 31.7, 31.6, 25.5, 25.2, 20.3 (d, *J* = 1.2 Hz) ppm; ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -118.71 ppm.

> 1-(1-cyclopentylethyl)-3-(trifluoromethyl)benzene) (30) ³: The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 30 (64.2 mg, 53% yield, rr = 20/1) as a colorless oil. ¹H NMR (400 MHz,

Chloroform-d) δ 7.47 - 7.43 (m, 2 H), 7.41 - 7.35 (m, 2 H), 2.51 (dq, J = 9.4, 6.9 Hz, 1 H), 2.02 - 1.85

(m, 2 H), 1.74 - 1.62 (m, 1 H), 1.60 - 1.51 (m, 2 H), 1.51 - 1.42 (m, 1 H), 1.42 - 1.32 (m, 1 H), 1.28 (d, J = 6.9 Hz, 3 H), 1.26 - 1.18 (m, 1 H), 1.05 - 0.93 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.9, 130.7 (d, J = 1.5 Hz), 130.42 (q, J = 31.7 Hz), 128.6, 124.4 (q, J = 272.2 Hz) 124.0 (q, J = 3.7 Hz), 122.6 (q, J = 3.9 Hz), 47.5, 46.2, 31.9, 31.5, 25.4, 25.2, 21.4 ppm; ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -62.42 ppm.



1-chloro-4-(1-cyclopentylethyl)benzene) (**3p**) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3p** (88.5 mg, 79% yield, rr = 30/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 - 7.21 (m, 2 H), 7.11 - 7.07 (m, 2 H), 2.39 (dq, J = 9.0, 6.9 Hz, 1 H), 1.93 - 1.84 (m, 2 H),

1.67 - 1.32 (m, 5 H), 1.26 - 1.14 (m, 4 H), 1.01 - 0.91 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform*d*) δ 146.6, 131.3, 128.7, 128.4, 47.7, 45.8, 31.9, 31.5, 25.5, 25.2, 21.6 ppm.

1,2-dichloro-4-(1-cyclopentylethyl)benzene (3q): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3q** (91.2 mg, 75% yield, rr = 36/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, J = 8.2 Hz, 1 H), 7.27 - 7.25 (m, 1 H), 7.03 - 7.00 (m, 1 H), 2.43 - 2.36 (m, 1 H), 1.93 - 1.84 (m, 2 H), 1.70 - 1.62 (m, 1 H), 1.59 - 1.35 (m, 4 H), 1.23 (d, J = 6.9 Hz, 3 H), 1.21 - 1.14 (m, 1 H), 1.03 - 0.93 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.5, 132.1, 130.2, 129.5, 129.3, 126.9, 47.5, 45.7, 31.8, 31.5, 25.4, 25.2, 21.5 ppm; HRMS (EI) Calculated for [C₁₃H₁₆Cl₂]⁺: 242.0629, [M+2]⁺: 244.0594, [M+4]⁺: 246.0565, measured: [M]⁺: 242.0648, [M+2]⁺: 244.0608, [M+4]⁺: 246.0570.



(1-cyclopentylbutyl)benzene (3r): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 3r (78.9 mg, 78% yield, rr = 20/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 - 7.22 (m, 2 H), 7.18 - 7.11 (m, 3 H), 2.25 (td, J = 10.7, 3.6 Hz, 1 H), 2.03 - 1.83 (m, 2 H), 1.77 -

1.60 (m, 2 H), 1.60 - 1.46 (m, 3 H), 1.43 - 1.26 (m, 2 H), 1.24 - 1.13 (m, 1 H), 1.13 - 0.99 (m, 2 H), 0.99 - 0.87 (m, 1 H), 0.81 (t, J = 7.3 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.1, 128.2, 128.1, 125.7, 52.3, 46.9, 37.7, 32.0, 31.8, 25.4, 25.0, 20.8, 14.3 ppm; HRMS (ESI) Calculated for C₁₅H₂₂Na ([M+Na]⁺): 225.1613, measured: 225.1593.



1-(1-cyclopentylbutyl)-4-methoxybenzene (3s): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 3s (128.0 mg, 81% yield, rr = 16/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.06 - 7.03 (m, 2 H), 6.84 - 6.81 (m, 2 H), 3.79 (s, 3

H), 2.21 (td, J = 10.3, 3.6 Hz, 1 H), 1.95 - 1.90 (m, 2 H), 1.72 - 1.62 (m, 2 H), 1.56 - 1.46 (m, 3 H), 1.45 - 1.37 (m, 1 H), 1.36 - 1.26 (m, 1 H), 1.23 - 1.13 (m, 1 H), 1.12 - 1.00 (m, 2 H), 0.99 - 0.89 (m, 1 H), 0.81 (t, J = 7.4 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.6, 138.2, 128.9, 113.4, 55.3, 51.3, 47.0, 37.8, 31.9, 31.7, 25.4, 25.0, 20.8, 14.3 ppm; HRMS (ESI) Calculated for C₁₆H₂₄ONa ([M+Na]⁺): 255.1719, measured: 218.1723.



(1-cyclopentylpentyl)benzene (3t): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 3t (77.9 mg, 72% yield, rr = 17/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 - 7.24 (m, 2)

H), 7.19 - 7.15 (m, 1 H), 7.14 - 7.11 (m, 2 H), 2.26 - 2.20 (m, 1 H), 2.04 - 1.88 (m, 2 H), 1.80 - 1.70 (m, 1 H), 1.65 - 1.52 (m, 3 H), 1.51 - 1.36 (m, 2 H), 1.34 - 1.25 (m, 2 H), 1.24 - 1.13 (m, 2 H), 1.06 - 0.92 (m, 3 H), 0.79 (t, J = 7.3 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.1, 128.1, 128.0, 125.6, 52.4, 46.8, 35.0, 31.8, 31.7, 29.8, 25.3, 24.9, 22.9, 14.1 ppm; HRMS (ESI) Calculated for C₁₆H₂₅ ([M+H]⁺): 217.1960, measured: 217.1951.



(1-cyclopentylheptyl)benzene (3u): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3u** (85.6 mg, 70% yield, rr = 15/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 - 7.17 (m, 2 H), 7.12 - 7.04 (m, 3 H), 2.16 (td, J =

10.2, 3.7 Hz, 1 H), 1.95 - 1.81 (m, 2 H), 1.72 - 1.61 (m, 1 H), 1.58 - 1.50 (m, 1 H), 1.47 - 1.38 (m, 3 H), 1.25 - 1.19 (m, 2 H), 1.16 - 1.04 (m, 7 H), 0.99 - 0.88 (m, 3 H), 0.76 (t, J = 6.9 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.2, 128.2, 128.1, 125.7, 52.5, 46.9, 35.4, 31.94, 31.92, 31.7, 29.6, 27.7, 25.4, 25.0, 22.8, 14.2 ppm; HRMS (ESI) Calculated for C₁₈H₂₉ ([M+H]⁺): 218.1743, measured: 245.2262.



(1-cyclopentyl-5-methylhexyl)benzene (3v): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 3v (48.9 mg, 40 % yield, rr = 6/1) as a colorless oil. ¹H NMR (400 MHz, Chloroformd) δ 7.21 - 7.17 (m, 2 H), 7.11 - 7.04 (m, 3 H), 2.19 - 2.13 (m, 1 H), 1.93 - 1.82

(m, 2 H), 1.69 - 1.56 (m, 2 H), 1.49 - 1.42 (m, 3 H), 1.37 - 1.29 (m, 2 H), 1.26 - 1.13 (m, 2 H), 1.06 - 0.94 (m, 4 H), 0.91 - 0.83 (m, 1 H), 0.70 (dd, J = 8.4, 6.6 Hz, 6 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.2, 128.2, 128.1, 125.7, 52.4, 46.9, 39.2, 35.6, 31.9, 31.7, 27.9, 25.4, 25.4, 25.0, 23.0, 22.5 ppm; HRMS (ESI) Calculated for C₁₈H₂₉ ([M+H]⁺): 218.1743, measured: 245.2262.



(1-cyclopentylpropyl)benzene (3w) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3w** (26.1 mg, 44% yield, rr = 17/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 - 7.25 (m, 2 H), 7.18 - 7.16 (m, 1 H), 7.15 - 7.11 (m, 2 H), 2.15 (td, J = 10.3, 3.6 Hz, 1 H), 2.05 - 1.78 (m, 3 H),

1.66 - 1.55 (m, 2 H), 1.54 - 1.28 (m, 4 H), 1.26 - 1.15 (m, 1 H), 1.00 - 0.90 (m, 1 H), 0.68 (t, *J* = 7.4 Hz, 3 H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.7, 128.2, 128.0, 125.6, 54.2, 46.5, 31.9, 31.6, 28.1, 25.3, 24.9, 12.2 ppm.



(1-cyclopentylbutyl)benzene (3x) ³: The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 3x (63.7 mg, 63% yield, rr = 7/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 - 7.23 (m, 2 H), 7.19 - 7.11 (m, 3 H), 2.28 - 2.22 (m, 1 H), 2.03 - 1.88 (m, 2 H), 1.76 - 1.56 (m, 3 H), 1.54

- 1.45 (m, 2 H), 1.42 - 1.26 (m, 2 H), 1.24 - 1.13 (m, 1 H), 1.11 - 0.99 (m, 2 H), 0.98 - 0.89 (m, 1 H), 0.81 (t, J = 7.3 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.1, 128.2, 128.1, 125.7, 52.2, 46.9, 37.7, 32.0, 31.8, 25.4, 25.0, 20.8, 14.3 ppm.



(1-cyclopentyl-3-methylpentyl)benzene (3y): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3y** (49.5 mg, 43% yield, rr = 8/1, dr = 1/1) as a colorless oil.¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 - 7.28 (m, 2 H), 7.23 - 7.15 (m, 3 H), 2.44 - 2.36 (m, 1 H), 2.02 - 1.90 (m,

2 H), 1.75 - 1.62 (m, 2 H), 1.58 - 1.52 (m, 2 H), 1.50 - 1.40 (m, 2 H), 1.36 - 1.22 (m, 2 H), 1.21 - 1.09 (m, 2 H), 1.06 - 0.92 (m, 2 H), 0.86 - 0.76 (m, 6 H) ppm; ¹³C NMR (101 MHz, Chloroform- *d*) δ 146.3, 146.0, 128.17, 128.16, 128.1, 125.7, 49.79, 49.77, 47.7, 47.5, 42.5, 42.2, 32.0, 31.9, 31.78, 31.76, 31.7,

31.4, 31.0, 27.5, 25.4, 25.04, 25.02, 20.5, 18.6, 11.5, 10.7. HRMS (ESI) Calculated for $C_{17}H_{26}Na$ ([M+Na]⁺): 253.1926, measured: 253.1911.



(1-cyclopentylpropyl-3-d)benzene (3ac): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3ac** (46.4 mg, 49% yield, 95% D, rr = 15/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 - 7.29 (m, 2 H), 7.23 - 7.20 (m, 1 H), 7.19 - 7.16 (m, 2 H), 2.19 (td, J = 10.3, 3.6 Hz, 1 H), 2.09 -

1.93 (m, 2 H), 1.90 - 1.82 (m, 1 H), 1.73 - 1.63 (m, 1 H), 1.58 - 1.52 (m, 2 H), 1.51 - 1.28 (m, 3 H), 1.28 - 1.18 (m, 1 H), 1.04 - 0.94 (m, 1 H), 0.74 - 0.68 (m, 2 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.8, 128.3, 128.1, 125.8, 54.3, 46.6, 32.0, 31.7, 28.1, 25.4, 25.0, 12.0 (t, *J* = 19.2 Hz) ppm; HRMS (ESI) Calculated for C₁₄H₂₀D ([M+H]⁺): 290.1714, measured: 290.1700.

(1-cyclopentylpropyl-3,3-d2)benzene (3ad): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether to afford the product **3ad** (70.4 mg, 74% yield, 94% D, rr = 21/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform*d*) δ 7.32 - 7.26 (m, 2 H), 7.23 - 7.13 (m, 3 H), 2.18 (td, J = 10.3, 3.6 Hz, 1 H), 2.08 - 1.90 (m, 2 H), 1.88 - 1.82 (m, 1 H), 1.71 - 1.62 (m, 1 H), 1.60 - 1.49 (m, 3 H), 1.48 - 1.31 (m, 2 H), 1.29 - 1.18 (m, 1 H), 1.05 - 0.94 (m, 1 H), 0.72 - 0.65 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.8, 128.3, 128.1, 125.8, 54.3, 46.6, 32.0, 31.7, 28.0, 25.4, 25.0, 11.7 (p, J = 38.2, 19.1 Hz) ppm; HRMS (ESI) Calculated for C₁₄H₁₉D₂ ([M+H]⁺): 191.1762, measured: 191.1763.



(1-cyclopentylbutyl-4,4-d2)benzene (3ae): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3ae** (43.9 mg, 43% yield, 93% D, rr = 22/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 - 7.24 (m, 2 H), 7.18 - 7.11 (m, 3 H), 2.25 (td, J = 10.3, 3.2 Hz, 1 H), 2.03 - 1.88 (m, 2 H),

1.76 - 1.67 (m, 1 H), 1.65 - 1.46 (m, 4 H), 1.44 - 1.27 (m, 2 H), 1.24 - 1.15 (m, 1 H), 1.12 - 0.91 (m, 3 H), 0.81 - 0.75 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.2, 128.2, 128.1, 125.7, 52.3, 46.9, 37.6, 32.0, 31.8, 25.4, 25.0, 20.7, 13.74 (p, J = 19.0 Hz) ppm; HRMS (ESI) Calculated for C₁₅H₂₀D₂ ([M+Na]⁺): 227.1739, measured: 227.1705.



1-(1-cyclohexylethyl)-3-methoxybenzene (4a): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **4a** (69.9 mg, 64% yield, rr = 10/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 (t, J = 7.8 Hz, 1 H), 6.76 - 6.70 (m, 3 H), 3.81 (s, 3 H), 2.44 - 2.37 (m, 1 H), 1.90 -

1.86 (m, 1 H), 1.77 - 1.72 (m, 1 H), 1.64 - 1.59 (m, 3 H), 1.45 - 1.34 (m, 2 H), 1.22 (d, J = 7.1 Hz, 3 H), 1.14 - 1.07 (m, 2 H), 1.00 - 0.79 (m, 2 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.5, 149.1, 129.0, 120.4, 113.9, 110.5, 55.2, 46.2, 44.2, 33.4, 31.6, 30.7, 26.7, 26.6, 19.0 ppm; HRMS (ESI) Calculated for C₁₅H₂₂O ([M+H]⁺): 218.1743, measured: 218.1723.



1-(1-cyclohexylpropyl)-4-methoxybenzene (4b) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 4b (52.3 mg, 45% yield, rr = 12/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.05 - 7.02 (m, 2 H), 6.87 - 6.84 (m, 2 H), 3.83 (s, 3 H), 2.20

- 2.15 (m, 1 H), 1.93 - 1.81 (m, 2 H), 1.78 - 1.72 (m, 1 H), 1.56 - 1.39 (m, 4 H), 1.31 - 1.04 (m, 4 H), 0.97 - 0.87 (m, 1 H), 0.83 - 0.76 (m, 1 H), 0.72 (t, J = 7.3 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.6, 136.7, 129.5, 113.3, 55.3, 53.3, 43.2, 31.6, 31.1, 26.80, 26.78, 26.7, 25.5, 12.6 ppm.



(1-(3-methoxyphenyl)ethyl)cycloheptane (4c) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 4c (73.2 mg, 63% yield, rr = 20/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 (t, J = 8.1 Hz, 1 H), 6.79 (d, J = 7.8 Hz, 1 H), 6.74 - 6.72 (m, 2 H), 3.81 (s, 3 H),

2.62 - 2.54 (m, 1 H), 1.82 - 1.75 (m, 1 H), 1.71 - 1.62 (m, 2 H), 1.61 - 1.53 (m, 4 H), 1.50 - 1.40 (m, 3 H), 1.40 - 1.28 (m, 2 H), 1.22 (d, J = 7.0 Hz, 3 H), 1.19 - 1.11 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.5, 149.2, 129.0, 120.4, 113.9, 110.5, 55.2, 46.0, 45.5, 32.7, 31.3, 28.6, 28.4, 26.9, 26.7, 18.5 ppm.



1-cycloheptyl-2,3-dihydro-1H-indene (4d) ³: The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **4d** (65.4 mg, 61% yield, rr = 11/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 - 7.10 (m, 4 H), 3.27 - 3.18 (m, 1 H), 2.97 - 2.75 (m, 2 H), 2.18 - 2.07 (m, 1 H), 2.07 - 1.97 (m, 1 H), 1.92 - 1.81 (m, 1 H), 1.80 - 1.72 (m, 2 H), 1.69 - 1.59 (m, 2 H), 1.59 - 1.49 (m, 3 H), 1.48 - 1.27

(m, 4 H), 1.26 - 1.16 (m, 1 H) ppm; ¹³C NMR (101 MHz, CDCl₃ Chloroform-*d*) δ 146.6, 144.9, 126.2, 126.0, 124.4, 124.0, 52.0, 42.3, 34.2, 31.9, 29.3, 28.6, 27.8, 27.7, 27.2 ppm.



(1-(4-methoxyphenyl)butyl)cycloheptane (4e): The reaction was conducted following the general procedure **A** in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **4e** (65.1 mg, 50% yield, rr = 14/1) as a colorless oil. 1H NMR (400 MHz, Chloroform-d) δ 7.07 (d, J = 8.6 Hz, 2 H), 6.85 (d, J = 8.6 Hz, 2 H), 3.83 (s, 3 H), 2.39 - 2.34 (m, 1 H), 1.81 - 1.75 (m, 1 H), 1.70 - 1.59 (m, 3 H),

1.57 - 1.50 (m, 4 H), 1.45 - 1.37 (m, 3 H), 1.34 - 1.02 (m, 6 H), 0.86 (t, J = 7.3 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.6, 137.1, 129.5, 113.3, 55.3, 51.2, 44.9, 35.3, 32.6, 31.8, 28.6, 28.3, 27.0, 26.9, 21.2, 14.4 ppm; HRMS (ESI) Calculated for $C_{18}H_{28}ONa$ ([M+Na]⁺): 283.2032, measured: 283.2033.



(1-phenylbutyl)cycloheptane (4f): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product 4f (56.4 mg, 49 % yield, rr = 3/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 - 7.23 (m, 2 H), 7.19 - 7.15 (m, 1 H), 7.14 - 7.11 (m, 2 H), 2.45 - 2.37 (m, 1 H), 1.85 - 1.78 (m, 1

H), 1.73 - 1.61 (m, 3 H), 1.61 - 1.54 (m, 3 H), 1.46 - 1.35 (m, 4 H), 1.35 - 1.14 (m, 3 H), 1.13 - 0.99 (m, 3 H), 0.82 (t, J = 7.3 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.2, 128.8, 128.0, 125.7, 52.2, 44.8, 35.2, 32.5, 32.0, 28.6, 28.3, 26.9, 26.8, 21.2, 14.4 ppm; HRMS (ESI) Calculated for C₁₇H₂₇ ([M+H]⁺): 231.2107, measured: 231.2101.



1-benzyl-4-(1-(3-methoxyphenyl)ethyl)piperidine (4g): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **4g** (54.2 mg, 35 % yield, rr = 4/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 - 7.17 (m, 6 H), 6.78 - 6.67 (m, 3 H), 3.78 (s, 3 H), 3.45 (d, J = 1.82 Hz, 2 H), 2.96 - 2.74 (m, 2 H), 2.45 - 2.35 (m, 1 H), 1.97 - 1.74 (m, 3 H),

1.38 - 1.25 (m, 3 H), 1.22 (d, J = 6.98 Hz, 3 H), 1.20 - 1.12 (m, 1 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.5, 148.5, 138.5, 129.4, 129.2, 128.2, 127.0, 120.2, 113.7, 110.7, 63.5, 55.2, 54.2, 54.1, 45.7, 42.5, 30.9, 30.2, 19.1 ppm; HRMS (ESI) Calculated for C₂₁H₂₇NONa ([M+Na]⁺): 332.2005, measured: 332.2011.



1-methoxy-3-(5-methylhexan-3-yl)benzene (**4h**): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **4h** (25.8 mg, 25 % yield, rr = 6/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 - 7.14 (m, 1 H), 6.91 - 6.49 (m, 3 H), 3.81 (s, 3 H), 2.50

- 2.34 (m, 1 H), 1.67 - 1.44 (m, 3 H), 1.43 - 1.26 (m, 2 H), 0.83 (dd, J = 14.68, 5.83 Hz, 6 H), 0.76 (t, J = 7.27 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.6, 148.0, 129.2, 120.5, 113.9, 110.6, 55.2, 46.0, 45.6, 30.3, 25.5, 23.7, 22.0, 12.4 ppm; HRMS (ESI) Calculated for C₁₄H₂₂O ([M+H]⁺): 207.1752, measured: 207.1743.



1-methoxy-4-(4-methylpentan-2-yl)benzene (4i): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **4i** (30.0 mg, 27 % yield, rr = 7/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.13 - 7.08 (m, 2 H), 6.86 - 6.82 (m, 2 H), 3.79 (s, 3 H), 2.78 - 2.69 (m, 1 H), 1.51 - 1.31

(m, 3 H), 1.18 (d, J = 6.90 Hz, 3 H), 0.85 (dd, J = 11.48, 6.22 Hz, 6 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.7, 140.2, 127.9, 113.8, 55.4, 48.1, 36.8, 25.7, 23.2, 22.5 ppm; HRMS (ESI) Calculated for C₁₃H₂₀O ([M+Na]⁺): 215.1406, measured: 215.1403.



(1-(cyclopentyl-d)propyl)benzene (3ah): The reaction was conducted following the general procedure A in a 0.5 mmol scale. The residue was purified by column chromatography on silica gel to afford the product **3ah** (61.5 mg, 65 % yield, rr = 21/1) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 - 7.17 (m, 2 H), 7.11 - 7.04 (m, 3 H), 2.11 - 2.05 (m, 1 H), 1.95 - 1.72 (m, 3 H), 1.55 - 1.52 (m, 1 H), 1.47 - 1.42 (m, 2 H), 1.35 - 1.21 (m, 2 H), 1.20 - 1.07 (m, 2 H), 0.90 -

0.83 (m, 1 H), 0.61 (t, *J* = 7.36 Hz, 3 H) ppm; ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.8, 128.3, 128.1, 125.8, 54.3, 46.6 (d, *J* = 9.06 Hz), 31.9 (d, *J* = 13.16 Hz), 31.7 (d, *J* = 9.91 Hz), 28.2, 25.4 (d, *J* = 9.98 Hz), 25.0 (d, *J* = 10.04 Hz), 12.3 ppm.

6. References

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7. NMR Spectra

7,281 7,77,7184 7,7157 7,7157 7,7157 7,7157 7,7157 7,7157 7,7157 7,1151 1,151 1,151 1,1550 1,1524 1,1524 1,1524 1,1524 1,1524 1,1524 1,1524 1,1524 1,1524 1,1524 1,1524 1,1556 1,























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)





















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)







































140 130 120 110 100 90 f1 (ppm) - (















5.0 4.5 f1 (ppm)).0 4.0 3.5 2.5 2.0 1.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 3.0 1.0 0.5 0



















