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 $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and HRMS. The known compounds were characterized by $^1$H NMR, $^{13}$C NMR, $^1$H $^{13}$C and $^{19}$F NMR data were recorded with Bruker 400 MHz with tetramethylsilane as an internal standard. Data for $^1$H $^{13}$C and $^{19}$F NMR are reported as follows: chemical shift ($\delta$ 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 ($\delta$) were reported in ppm and coupling constants ($J$) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for $^1$H), Chloroform-d (77.16 ppm for $^{13}$C), 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 

| 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     | NiCl₂ instead of NiI₂               | Trace         | Trace          | -           |
| 10    | NiBr₂ instead of NiI₂               | 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% (NiI₂/L1)  68  4  15:1
22  2 mol% (NiI₂/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 x10 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

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ 1.5 mL NMP 30 °C, 24 h

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1.5 equiv Zn²⁺ 1.5 mL NMP 30 °C, 24 h

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ 1.5 mL NMP 30 °C, 24 h

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%

C₆H₄Br  +  C₅H₈Br →  1a  3a

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ NMP, 30 °C, 24 h

1.0 equiv additive

70%, r = 27:1

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%

C₆H₄Br  +  C₅H₈Br →  1a  3a

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ NMP, 30 °C, 24 h

1.0 equiv additive

70%, r = 27:1

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%

C₆H₄Br  +  C₅H₈Br →  1a  3a

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
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1.0 equiv additive

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C₆H₄Br  +  C₅H₈Br →  1a  3a

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1.0 equiv additive

70%, r = 27:1

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%

C₆H₄Br  +  C₅H₈Br →  1a  3a

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ NMP, 30 °C, 24 h

1.0 equiv additive

70%, r = 27:1

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%

C₆H₄Br  +  C₅H₈Br →  1a  3a

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ NMP, 30 °C, 24 h

1.0 equiv additive

70%, r = 27:1

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%

C₆H₄Br  +  C₅H₈Br →  1a  3a

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ NMP, 30 °C, 24 h

1.0 equiv additive

70%, r = 27:1

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%

C₆H₄Br  +  C₅H₈Br →  1a  3a

5 mol% NiI₂ 5 mol% L1 1.5 equiv LiBr
1.5 equiv Zn²⁺ NMP, 30 °C, 24 h

1.0 equiv additive

70%, r = 27:1

Me₃C₆H₄Br  +  C₅H₈Br →  5%  8%  7%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 76% 10%

H₂N-C₆H₄Br  +  C₅H₈Br →  <5% 81% 7%
3. Synthesis of Substrates

3.1 General Procedure (B) for Synthesis of Alkyl Bromines

**General procedure for the reduction of carboxylic acid**: 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 tosylation**: 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

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).

**1-(2-bromoethyl)-3,5-dichlorobenzene** (2.8 g, 59%, a colorless liquid.): prepared according to the general procedure B. ¹H NMR (400 MHz, Chloroform-d) 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.
(3-bromopropyl-3,3-d2)benzene (0.2 g, 36%, 94% D); a colorless liquid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.32 (td, $J = 6.99, 1.54$ Hz, 2 H), 7.27 - 7.14 (m, 3 H), 2.80 (t, $J = 7.42$ Hz, 2 H), 2.18 (t, $J = 7.38$ Hz, 2 H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 140.7, 128.7, 128.6, 126.3, 34.0, 34.0, 32.80 (dt, $J = 46.46, 23.30$ Hz).
(4-bromobuty1-4,4-d2)benzene (0.2 g, 39%, 94% D): a colorless liquid. $^1$H 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).

$^{13}$C 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-phenylpropanal\(^1\): To a stirred solution of LiAlD\(_4\) (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 Et\(_3\)N (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-1-ol tosylation (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-bromopropyl-3-d)benzene (0.5 g, 48%, 96% D): a colorless liquid. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 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). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 140.7, 128.7, 128.6, 126.3, 34.2, 34.1, 33.1 (t, \(J = 23.35\) Hz).
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): 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, \( r_r = 27/1 \); X = Cl : 25.4 mg, 43% yield, \( r_r = 13/1 \)) as a colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d_2\)) \( \delta \) 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. \(^{13}\)C NMR (101 MHz, Chloroform-\(d_2\)) \( \delta \) 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, \( r_r = 10/1 \)) as a colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d_2\)) \( \delta \) 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. \(^{13}\)C NMR (101 MHz, Chloroform-\(d_2\)) \( \delta \) 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 C\(_{15}\)H\(_{24}\)O ([M+H]\(^+\)): 218.1743, measured: 218.1723.

1-(1-cyclopentylpropyl)-4-(trifluoromethyl)benzene (3c): 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, \( r_r = 14/1 \)) as a colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d_2\)) \( \delta \) 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. \(^{13}\)C NMR (101 MHz, Chloroform-\(d_2\)) \( \delta \) 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. \(^{19}\)F NMR (377 MHz, Chloroform-\(d_2\)) \( \delta \) -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, \( r_r = 10:1 \)) as a colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d_2\)) \( \delta \) 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; $^{13}$C 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 C$_{13}$H$_{23}$O ([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. $^1$H 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; $^{13}$C 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 C$_{16}$H$_{25}$O$_2$ ([M+H]+): 248.1838, measured: 248.1849.

1-(1-cyclopentylethyl)-4-fluorobenzene (3f): 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. $^1$H 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; $^{13}$C 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; $^{19}$F 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. $^1$H 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; $^{13}$C NMR (101 MHz, Chloroform-d) δ 163.0 (d, 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; $^{19}$F NMR (377 MHz, Chloroform-d) δ -110.92 ppm; HRMS (ESI) Calculated for C$_{13}$H$_{13}$F$_2$Na ([M+Na]+): 233.1096, measured: 233.1112.
1-(1-cyclopentylethyl)-3-methoxybenzene (3h): 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. \(^1\)H NMR (600 MHz, Chloroform-\(d \)) \( \delta \) 7.22 (t, \( J = 7.7 \text{ Hz}, 1 \text{ H} \)), 6.80 (d, \( J = 7.3 \text{ Hz}, 1 \text{ H} \)), 6.76 - 6.74 (m, 2 H), 3.82 (s, 3 H), 2.42 (dq, \( J = 13.3, 7.3 \text{ Hz}, 1 \text{ H} \)), 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; \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta \) 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): 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. \(^1\)H NMR (400 MHz, Chloroform-\(d \)) \( \delta \) 7.22 - 7.14 (m, 3 H), 7.06 (dt, \( J = 7.4, 1.4 \text{ Hz}, 1 \text{ H} \)), 2.41 (dq, \( J = 9.3, 6.9 \text{ Hz}, 1 \text{ H} \)), 1.98 - 1.87 (m, 2 H), 1.72 - 1.35 (m, 5 H), 1.25 (d, \( J = 6.9 \text{ Hz}, 3 \text{ H} \)), 1.22 - 1.17 (m, 1 H), 1.04 - 0.95 (m, 1 H) ppm; \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta \) 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. \(^1\)H NMR (400 MHz, Chloroform-\(d \)) \( \delta \) 7.07 - 7.03 (m, 2 H), 6.77 - 6.74 (m, 2 H), 4.94 (s, 1 H), 2.37 (dq, \( J = 9.3, 6.9 \text{ Hz}, 1 \text{ H} \)), 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, \( J = 6.9 \text{ Hz}, 3 \text{ H} \)), 1.21 - 1.14 (m, 1 H), 1.06 - 0.95 (m, 1 H) ppm; \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta \) 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 C\(_{13}\)H\(_{17}\)O (M\(-\text{H}\)) 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. \(^1\)H NMR (400 MHz, Chloroform-\(d \)) \( \delta \) 7.01 (s, 1 H), 6.92 - 6.89 (m, 1 H), 6.70 (d, \( J = 8.1 \text{ Hz}, 1 \text{ H} \)), 4.55 (t, \( J = 8.7 \text{ Hz}, 2 \text{ H} \)), 3.19 (t, \( J = 8.7 \text{ Hz}, 2 \text{ H} \)), 2.36 (dq, \( J = 9.0, 6.9 \text{ Hz}, 1 \text{ H} \)), 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, \( J = 6.9 \text{ Hz}, 3 \text{ H} \)), 1.21 - 1.14 (m, 1 H), 1.09 - 0.92 (m, 1 H) ppm; \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta \) 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 C\(_{15}\)H\(_{20}\)ONa (M+Na\(^+\)) 239.1414; measured: 239.1406.
1-cyclopentyl-2,3-dihydro-1H-indene \(31\): 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. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 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; \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta 147.5, 144.5, 126.2, 125.9, 124.6, 124.5, 50.0, 44.5, 31.5, 31.5, 30.6, 30.4, 25.7, 25.3\) ppm.

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. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 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; \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta 136.4, 127.2, 122.8, 121.8, 120.4, 119.7, 119.0, 111.2, 47.1, 36.6, 31.8, 31.5, 25.7, 25.4, 20.9\) ppm; HRMS (ESI) Calculated for \(C_{15}H_{20}N\) ([M+H]^+): 214.1590, measured: 214.1594.

1-(1-cyclopentylethyl)-2-fluorobenzene \(3n\): 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. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 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 - 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; \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta 160.6 (d, \(J = 243.8\) Hz), 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, \(J = 23.4\) 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; \(^19\)F NMR (377 MHz, Chloroform-\(d\)) \(\delta -118.71\) ppm.

1-(1-cyclopentylethyl)-3-(trifluoromethyl)benzene \(3o\): 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 \(3o\) (64.2 mg, 53% yield, \(rr = 20/1\)) as a colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 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; $^{13}$C 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; $^{19}$F NMR (377 MHz, 
Chloroform-$d$) δ -62.42 ppm.

1-chloro-4-(1-cyclopentylethyl)benzene (3p): 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. $^1$H 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; $^{13}$C 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. $^1$H 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; $^{13}$C 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 (ESI) Calculated for [C$_{13}$H$_{16}$Cl$_2$]+: 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. $^1$H 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; $^{13}$C 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 C$_{13}$H$_{22}$Na ([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. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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; $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 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 C$_{16}$H$_{24}$ONa ([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. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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; $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 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 C$_{16}$H$_{25}$ ([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. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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; $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 146.2, 128.2, 128.1, 125.7, 52.5, 46.9, 35.4, 31.9, 31.7, 31.7, 29.6, 27.7, 25.4, 25.0, 22.8, 14.2 ppm; HRMS (ESI) Calculated for C$_{18}$H$_{29}$ ([M+H$^+$]): 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. \(^1\)H NMR (400 MHz, Chloroform-\(d \)) \( \delta 7.21 - 7.17 \) (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; \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta 146.2, 128.2, 128.1, 125.7, 52.4, 46.9, 39.2, 35.6, 31.9, 31.7, 27.9, 25.4, 25.0, 23.0, 22.5 \) ppm; HRMS (ESI) Calculated for C\(_{18}\)H\(_{29}\)([M+H]\(^+\)): 218.1743, measured: 218.2262.

(1-cyclopentylpropyl)benzene (3w): 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. \(^1\)H NMR (400 MHz, Chloroform-\(d \)) \( \delta 7.28 - 7.25 \) (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. \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta 145.7, 128.2, 128.0, 125.6, 54.2, 46.5, 31.9, 31.6, 28.1, 25.3, 24.9, 12.2 \) ppm.

(1-cyclopentylbutyl)benzene (3x): 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. \(^1\)H NMR (400 MHz, Chloroform-\(d \)) \( \delta 7.28 - 7.23 \) (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), 1.26 - 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; \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta 146.1, 128.2, 128.1, 125.7, 52.2, 46.9, 37.7, 32.0, 31.8, 25.4, 25.0, 20.8, 14.3 \) 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. \(^1\)H NMR (400 MHz, Chloroform-\(d \)) \( \delta 7.32 - 7.28 \) (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; \(^{13}\)C NMR (101 MHz, Chloroform-\(d \)) \( \delta 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,
(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. $^1$H 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; $^{13}$C 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 (p, J = 19.2 Hz) ppm; HRMS (ESI) Calculated for C$_{17}$H$_{26}$Na ([M+Na]$^+$): 253.1926, measured: 253.1911.

(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. $^1$H 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; $^{13}$C 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 C$_{14}$H$_{19}$D$_2$ ([M+H]$^+$): 290.1714, measured: 290.1700.

(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. $^1$H 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; $^{13}$C 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 C$_{15}$H$_{20}$D$_2$ ([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. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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; $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 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 C$_{15}$H$_{22}$O ([M+H]$^+$): 218.1743, measured: 218.1723.

1-(1-cyclohexylpropyl)-4-methoxybenzene (4b): 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. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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; $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 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): 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. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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; $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 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): 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. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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
(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. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 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; \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 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\(_{21}\)H\(_{28}\)O\(_{Na}\) ([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. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 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; \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 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 C\(_{17}\)H\(_{27}\) ([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. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 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; \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 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 C\(_{21}\)H\(_{27}\)NONa ([M+Na\(^+\]): 332.205, 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. \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 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; \(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 159.6, 148.0, 129.2, 120.5, 113.9, 110.6, 55.2, 46.0, 45.6, 30.3, 25.5, 22.0, 12.4 ppm; HRMS (ESI) Calculated for C\(_{14}\)H\(_{22}\)O ([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. \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 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; \(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 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 C\(_{13}\)H\(_{20}\)O ([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. \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 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; \(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 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
