Supplementary Information

for

Ligand-Enabled Ni-Catalyzed Hydroarylation and Hydroalkenylation of Internal Alkenes with Organoborons

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**Supplementary Methods**

1. **General Information**

Ni(2-NH$_2$-5-MeC$_6$H$_3$SO$_3$)$_2$ were purchased from Alfa Aesar. Other reagents were purchased from TCI, Sigma-Aldrich, Acros, Adamas-beta, J&K, 9-Ding, Bidepharm and Energy Chemical of the highest purity grade and used without further purification, unless otherwise indicated. Tetrahydrofuran (THF), acetonitrile (CH$_3$CN), dichloromethane (CH$_2$Cl$_2$) and N, N-dimethylformamide (DMF) were dried using the solvent purification system, and stored in the glovebox before use. 2-Methyl-2-butanol (t-AmylOH) was dried using sodium. Other anhydrous solvents were purchased from J&K. The extent of reaction was monitored by thin–layer chromatography (TLC), performed on 0.25 mm silica gel HSGF254. The TLC plates were visualized by ultraviolet light (254 nm) or treatment with potassium permanganate stain followed by gentle heating.

NMR spectra were recorded on Varian 400, Bruker 400 and Agilent 400 (400 MHz for $^1$H; 375 MHz for $^{19}$F; 100 MHz for $^{13}$C) spectrometer. The chemical shifts (δ) were quoted in parts per million (ppm) referenced to TMS (0.0 ppm for $^1$H NMR) and CDCl$_3$ (77.0 ppm for $^{13}$C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad. Coupling constants, $J$, were reported in Hertz unit (Hz). High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer and Thermo Fisher Scientific LTQ FTICR-MS using ESI–TOF, DART or EI. The selectivity of the products was recorded on a Thermo Fisher gas chromatography-mass spectrometer (GC).
2. Experimental Section

2.1 Preparation of Substrates

Substrates 4a, 4b, 4c, 4d, 4e, 4f, 4g, 4i, 4k, 4l, 4m, 4n, 4o, 4p, 4r, 4u were prepared according to the following Wittig-olefination procedure.

**General Procedure A for the Synthesis of Internal Alkenes**

A suspension of the alkyltriphenylphosphonium bromide (1.1 equiv) and t-BuOK (2.0 equiv) in dry THF (0.5 M) was stirred at 0 °C under nitrogen for 30 min. Then, the solution of aldehyde (1.0 equiv) in THF (5.0 mL) was added dropwise over 5 min. The reaction mixture was stirred for 30 min at 0 °C, then allowed to warm up to room temperature overnight. The reaction mixture was quenched with water and extracted with Et₂O. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude reaction mixture was purified by flash chromatography on silica gel to afford the corresponding internal alkene.

4a was prepared according to general procedure A using 4-biphenylcarboxaldehyde (1.82 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.08 g, 11 mmol, 1.1 equiv), t-BuOK (2.24 g, 20 mmol, 2.0 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a mixture of alkenes as a white solid (760.9 mg, 40% yield, E/Z = 97/3). ¹H NMR (400 MHz, CDCl₃) δ 7.64–7.56 (m, 2H), 7.56–7.49 (m, 2H), 7.46–7.36 (m, 4H), 7.36–7.28 (m, 1H), 6.44 (dd, J = 15.6, 1.8 Hz, 1H), 6.29 (dq, J = 15.8, 6.4 Hz, 0.97H), 5.90–5.74 (m, 0.03H), 1.95 (dd, J = 7.2, 1.6 Hz, 0.13H), 1.91 (dd, J = 6.6, 1.6 Hz, 2.9H).

4b was prepared according to general procedure B using 4-fluorobenzaldehyde (1.24 g, 10.0 mmol, 1.0 equiv),
ethyltriphenylphosphonium bromide (4.5 g, 12 mmol, 1.2 equiv), n-butyllithium (4.8 mL, 2.5 M in hexane, 12 mmol, 1.2 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (671 mg, 49% yield, \( E/Z = 79/21 \)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) δ 7.30–7.26 (m, 2H), 7.07–6.84 (m, 2H), 6.42–6.28 (m, 1H), 6.23–6.05 (m, 0.79H), 5.82–5.71 (dm, 0.21H), 1.89–1.82 (m, 3H).

4c was prepared according to general procedure A using 4-(trifluoromethyl)benzaldehyde (1.74 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.08 g, 11 mmol, 1.1 equiv), t-BuOK (2.24 g, 20 mmol, 2.0 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (583.3 mg, 31% yield, \( E/Z = 99/1 \)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) δ 7.53 (d, \( J = 8.2 \) Hz, 2H), 7.40 (d, \( J = 8.2 \) Hz, 2H), 6.51–6.22 (m, 2H), 1.91 (dd, \( J = 6.4, 1.2 \) Hz, 3H).

4d was prepared according to general procedure B using methyl 4-formylbenzoate (1.64 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (3.9 g, 10.5 mmol, 1.05 equiv), n-butyllithium (4.2 mL, 2.5 M in hexane, 10.5 mmol, 1.05 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a yellow liquid (1.14 g, 65% yield, \( E/Z = 33/67 \)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) δ 8.04–7.96 (m, 1.29H), 7.99–7.91 (m, 0.61H), 7.39–7.33 (m, 2H), 6.53–6.23 (m, 1.33H), 5.90 (dq, \( J = 11.6, 7.2 \) Hz, 0.67H), 3.91 (s, 1.94H), 3.90 (s, 1.02H), 1.93–1.88 (m, 2H).

4e was prepared according to general procedure B using 4-(trifluoromethoxy)benzaldehyde (1.64 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.5 g, 12 mmol, 1.2 equiv), n-butyllithium (4.8 mL, 2.5 M in hexane, 12 mmol, 1.2 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a yellow liquid (1.76 g, 87% yield, \( E/Z = 52/48 \)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) δ 7.33–7.25 (m, 2H), 7.18–7.14 (m, 1H), 7.13–7.09 (m, 1H), 6.44–6.30 (m, 1H), 6.20 (dq, \( J = 15.8, 6.4 \) Hz, 0.52H), 5.81 (dq, \( J = 11.6, 7.2 \) Hz, 0.48H), 1.86 (dd, \( J = 7.0, 1.8 \) Hz, 3H).

4f was prepared according to general procedure B using 4-formylphenylboronic acid pinacol cyclic ester (2.32 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.5 g, 12 mmol, 1.2 equiv), n-butyllithium (4.8 mL, 2.5 M in hexane, 12 mmol, 1.2 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE/EtOAc = 20/1) gave a mixture of alkenes as a colourless oil (2.15 g, 88% yield, \( E/Z = 62/38 \)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) δ
7.78 (d, \( J = 7.6 \) Hz, 0.8H), 7.73 (d, \( J = 7.6 \) Hz, 1.13H), 7.35–7.27 (m, 2H), 6.51–6.36 (m, 1H), 6.31 (dq, \( J = 15.8, 6.4 \) Hz, 1H), 5.82 (dq, \( J = 11.4, 7.2 \) Hz, 0H), 1.93–1.82 (m, 3H), 1.36–1.30 (m, 12H).

4g was prepared according to general procedure B using 3-hydroxybenzaldehyde (3.66 g, 30.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (22.3 g, 60 mmol, 2.0 equiv), \( n \)-butyllithium (24 mL, 2.5 M in hexane, 60 mmol, 2.0 equiv) in dry THF (60 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a mixture of alkenes as a colourless oil (3.44 g, 86% yield, E/Z = 69/31).

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.27–7.08 (m, 1H), 6.93–6.84 (m, 1H), 6.82–6.76 (m, 1H), 6.73–6.62 (m, 1H), 6.40–6.29 (m, 1H), 6.20 (dq, \( J = 15.8, 6.4 \) Hz, 0.69H), 5.78 (dq, \( J = 11.6, 7.2 \) Hz, 0.31H), 5.29 (s, 1H), 1.92–1.83 (t, \( J = 8.0 \) Hz, 3H).

4i was prepared according to general procedure B using 3-fluorobenzaldehyde (1.24 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.5 g, 12 mmol, 1.2 equiv), \( n \)-butyllithium (4.8 mL, 2.5 M in hexane, 12 mmol, 1.2 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (1.0 g, 76% yield, E/Z = 55/45).

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.36–7.16 (m, 1H), 7.10–6.97 (m, 2H), 6.94–6.84 (m, 1H), 6.44–6.32 (m, 1H), 6.25 (dq, \( J = 15.8, 6.4 \) Hz, 0.55H), 5.83 (dq, \( J = 11.4, 7.2 \) Hz, 0.45H), 1.92–1.85 (m, 3H).

4k was prepared according to general procedure A using 3,4,5-trimethoxybenzaldehyde (1.96 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.08 g, 11 mmol, 1.1 equiv), \( t \)-BuOK (2.24 g, 20 mmol, 2.0 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a mixture of alkenes as a colourless oil (1.38 g, 66 % yield, E/Z = 60/40).

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 6.56 (s, 1.18H), 6.52 (s, 0.82H), 6.41–6.29 (m, 1H), 6.15 (dq, \( J = 15.8, 6.6 \) Hz, 0.60H), 5.76 (dq, \( J = 11.6, 7.2 \) Hz, 0.40H), 3.89–3.81 (m, 9H), 1.92 (dd, \( J = 7.2, 2.0 \) Hz, 1.24H), 1.88 (dd, \( J = 6.4, 1.6 \) Hz, 1.76H).

4l was prepared according to general procedure A using 1-naphthaldehyde (1.56 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.08 g, 11 mmol, 1.1 equiv), \( t \)-BuOK (2.24 g, 20 mmol, 2.0 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (1.17
g, 70% yield, $E/Z = 90/10$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 7.6$ Hz, 1H), 8.01–7.97 (m, 0.12H), 7.87–7.79 (m, 1.12H), 7.77–7.70 (m, 1.12H), 7.56–7.30 (m, 4.5H), 7.12 (d, $J = 15.6$ Hz, 1H), 6.90 (d, $J = 11.4$ Hz, 0.12H), 6.24 (dq, $J = 15.6$, 6.6 Hz, 1H), 6.04 (dq, $J = 11.6$, 6.8 Hz, 0.12H), 2.00 (dd, $J = 6.8$, 1.6 Hz, 3.0H), 1.75 (dd, $J = 7.0$, 1.6 Hz, 0.36H).

$^4$m was prepared according to general procedure A using 2-naphthaldehyde (1.56 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.08 g, 11 mmol, 1.1 equiv), t-BuOK (2.24 g, 20 mmol, 2.0 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (1.28 g, 76% yield, $E/Z = 98/2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81–7.74 (m, 3H), 7.65 (s, 1H), 7.59–7.53 (m, 1H), 7.48–7.34 (m, 2H), 6.56 (dd, $J = 15.8$, 2.0 Hz, 1H), 6.37 (dq, $J = 15.8$, 6.6 Hz, 0.98H), 5.98–5.79 (m, 0.02H), 2.00–1.96 (m, 0.6H), 1.94 (dd, $J = 6.6$, 1.6 Hz, 3H).

$^4$n was prepared according to general procedure B using ferrocenecarboxaldehyde (1.5 g, 10.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (4.08 g, 11 mmol, 1.1 equiv), t-BuOK (2.24 g, 20 mmol, 2.0 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a yellow liquid (1.94 g, 86% yield, $E/Z = 18/82$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.09 (dd, $J = 11.2$, 1.6 Hz, 1.22H), 5.80 (dq, $J = 15.6$, 6.6 Hz, 0.22H), 5.56 (dq, $J = 11.4$, 7.2 Hz, 1H), 4.33 (t, $J = 2.0$ Hz, 2H), 4.26 (t, $J = 2.0$ Hz, 0.46H), 4.19 (t, $J = 1.8$ Hz, 2H), 4.14 (t, $J = 2.0$ Hz, 0.48H), 4.10 (s, 5H), 4.09 (s, 1.2H), 1.82 (dd, $J = 7.2$, 1.6 Hz, 3H), 1.73 (dd, $J = 6.4$, 1.6 Hz, 0.67H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 127.61, 126.83, 123.49, 122.89, 82.33, 69.03, 68.98, 68.94, 68.84, 68.18, 68.03, 66.14, 18.47, 14.80; HRMS (ESI-TOF) $m/z$ Calcd for $C_{13}H_{14}Fe$ [M]+: 226.0439, found: 226.0438.

$^4$o was prepared according to general procedure B using benzaldehyde (530.6 mg, 5.0 mmol, 1.0 equiv), isopropyltriphenylphosphonium bromide (2.2 g, 5.5 mmol, 1.1 equiv), $n$-butyllithium (2.2 mL, 2.5 M in hexane, 5.5 mmol, 1.1 equiv) in dry THF (10 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (570.3 mg, 78% yield, $E/Z = 28/72$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48–7.10 (m, 5H), 6.38–6.26 (m, 1H), 6.19 (ddd, $J = 15.8$, 6.6, 2.0 Hz, 0.28H), 5.47 (ddd, $J = 11.8$, 10.4, 2.2 Hz, 0.72H), 2.97–2.82 (m, 0.72H), 2.57–2.28 (m, 0.28H), 1.12–1.07 (m, 1.68H), 1.06–1.02 (m, 4.32H).
4p was prepared according to general procedure B using cyclohexanecarboxaldehyde (560.8 mg, 5.0 mmol, 1.0 equiv), benzyltriphenylphosphonium bromide (2.4 g, 5.5 mmol, 1.1 equiv), n-butyllithium (2.2 mL, 2.5 M in hexane, 5.5 mmol, 1.1 equiv) in dry THF (10 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (902.5 mg, 97% yield, E/Z = 70/30). 1H NMR (400 MHz, CDCl3) δ 7.37–7.09 (m, 5H), 6.39–6.27 (m, 1H), 6.17 (dd, J = 16.0, 6.8 Hz, 0.7H), 5.48 (dd, J = 11.6, 10.4 Hz, 0.30H), 2.64–2.51 (m, 0.30H), 2.20–2.03 (m, 0.70H), 1.83–1.58 (m, 5H), 1.40–1.08 (m, 5H).

4r was prepared according to general procedure B using 2-pyridinecarboxaldehyde (1.07 g, 10.0 mmol, 1.0 equiv), benzyltriphenylphosphonium bromide (5.2 g, 12 mmol, 1.2 equiv), n-butyllithium (4.8 mL, 2.5 M in hexane, 12 mmol, 1.2 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a mixture of alkenes as a yellow solid (1.67 g, 92% yield, E/Z = 60/40). 1H NMR (400 MHz, CDCl3) δ 8.62–8.55 (m, 1H), 7.67–7.61 (m, 1.3H), 7.60–7.55 (m, 1.3H), 7.45–7.33 (m, 2.50H), 7.31–7.21 (m, 2.8H), 7.17–7.10 (m, 1.30H), 7.09–7.04 (m, 0.40H), 6.82 (d, J = 12.4 Hz, 0.40H), 6.69 (d, J = 12.4 Hz, 0.40H).

4u was prepared according to general procedure B using benzaldehyde (1.07 g, 10.0 mmol, 1.0 equiv), n-butylltriphenylphosphonium bromide (4.2 g, 10.5 mmol, 1.05 equiv), n-butyllithium (4.2 mL, 2.5 M in hexane, 10.5 mmol, 1.05 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (1.12 g, 77% yield, E/Z = 56/44). 1H NMR (400 MHz, CDCl3) δ 7.37–7.26 (m, 4H), 7.24–7.14 (m, 1H), 6.49–6.33 (m, 1H), 6.23 (dt, J = 15.8, 6.8 Hz, 0.56H), 5.67 (dt, J = 11.8, 7.2 Hz, 0.44H), 2.36–2.27 (m, 0.88H), 2.19 (q, J = 7.2 Hz, 1.12H), 1.59–1.44 (m, 2H), 1.06–0.88 (m, 3H).

4x was prepared according to general procedure B using 3-furaldehyde (0.48 g, 5.0 mmol, 1.0 equiv), n-butylltriphenylphosphonium bromide (2.2 g, 5.5 mmol, 1.1 equiv), n-butyllithium (2.2 mL, 2.5 M in hexane, 5.5 mmol, 1.1 equiv) in dry THF (10 mL). Purification by flash chromatography on silica gel (PE) gave a mixture of alkenes as a colourless oil (0.43 g, 64% yield, E/Z = 36/64). 1H NMR (400 MHz, CDCl3) δ 7.43 (s, 0.51H), 7.40–7.36 (m, 0.50H), 7.34 (s, 0.59H), 6.50 (s, 0.31H), 6.46 (s, 0.53H), 6.22 (d, J = 15.8 Hz, 0.32H), 6.15 (d, J = 11.4 Hz, 0.55H), 5.94 (dt, J = 15.6, 7.0 Hz, 0.33H), 5.57 (dt, J = 11.4, 7.2 Hz, 0.56H), 2.25 (qd, J = 7.4, 1.8 Hz, 1.2H), 2.13 (q, J = 7.2 Hz, 0.7H), 1.48 (tq, J = 12.4, 6.9 Hz, 2H), 0.95 (dt, J = 10.2, 7.4 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 143.25, 142.58, 140.75, 139.29, 131.99, 130.59, 124.53, 122.64, 119.36, 118.71, 110.98, 107.53, 34.98, 31.25, 22.72, 22.52, 13.88, 13.70; HRMS (El) m/z Calcd for C9H12O [M]+: 136.0883, found: 136.0884.
4y was prepared according to general procedure B using 1-tosyl-1H-indole-3-carbaldehyde (1.5 g, 5.0 mmol, 1.0 equiv), ethyltriphenylphosphonium bromide (2.2 g, 6.0 mmol, 1.2 equiv), n-butyllithium (2.4 mL, 2.5 M in hexane, 6.0 mmol, 1.2 equiv) in dry THF (20 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a mixture of alkenes as a white solid (1.47 g, 94% yield, E/Z = 50/50). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.00–7.94 (m, 1H), 7.79–7.71 (m, 2H), 7.68 (d, J = 8.0 Hz, 0.5H), 7.54 (s, 1H), 7.53–7.48 (m, 1H), 7.35–7.27 (m, 1H), 7.26–7.21 (m, 1H), 7.20–7.15 (m, 2H), 6.53–6.36 (m, 1H), 6.34–6.20 (m, 0.5H), 5.93 (dq, J = 11.4, 7.2 Hz, 0.5H), 2.31–2.27 (m, 3H), 1.94–1.88 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 144.87, 144.82, 135.45, 135.14, 134.53, 130.79, 129.81, 129.79, 129.30, 128.44, 127.37, 126.74, 126.73, 124.81, 124.71, 123.52, 123.29, 123.19, 122.52, 122.52, 121.32, 121.10, 120.27, 119.53, 119.09, 118.70, 113.70, 113.53, 21.49, 18.91, 15.63; HRMS (EI) m/z Calcd for C\(_{18}\)H\(_{17}\)NO\(_2\)S [M]$: 311.0975, found: 311.0983.

A Schlenk flask was charged with the naproxen (268.2 mg, 2.0 mmol, 1.0 equiv), DCC (618.9 mg, 3.0 mmol, 1.5 equiv), DMAP (244.3 mg, 2.0 mmol, 1.0 equiv) and anhydrous DCM (10 mL) under N\(_2\), followed by addition of S1 (506.7 mg, 2.2 mmol, 1.1 equiv, E/Z = 93/7). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed under vacuum, and the crude residue was purified by silica gel column chromatography (PE/EA = 20/1 to 10/1) to afford the product 4z as a white solid (307.9 mg, 44% yield, E/Z = 95/5). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.80–7.68 (m, 3H), 7.49 (dt, J = 8.4, 2.0 Hz, 1H), 7.27–7.22 (m, 2H), 7.18–7.09 (m, 2H), 7.00–6.82 (m, 2H), 6.34 (dt, J = 15.8, 1.8 Hz, 1H), 6.21–6.08 (m, 0.95H), 5.83–5.69 (m, 0.05H), 4.08 (qd, J = 7.2, 2.0 Hz, 1H), 3.92–3.91 (m, 3H), 1.84 (dt, J = 6.4, 1.8 Hz, 3H), 1.71–1.63 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 173.20, 157.70, 149.52, 135.64, 135.15, 133.77, 130.02, 129.66, 129.30, 128.96, 127.33, 126.55, 126.11, 125.85, 121.32, 120.98, 119.07, 55.29, 45.54, 18.51, 18.41; HRMS (ESI-TOF) m/z Calcd for C\(_{23}\)H\(_{22}\)O\(_3\)Na [M+Na]**: 369.1461, found: 369.1454.

A Schlenk flask was charged with the lbufrofen (412.6 mg, 2.0 mmol, 1.0 equiv), EDCI (460.1 mg, 2.4 mmol, 1.2 equiv), DMAP (48.9 mg, 0.4 mmol, 0.2 equiv) and anhydrous DCM (10 mL) under N\(_2\), followed by addition of S1 (506.7 mg, 2.2 mmol, 1.1 equiv, E/Z = 93/7). The reaction mixture was stirred at room temperature for 12 h. Upon
completion, the solvent was removed under vacuum, and the crude residue was purified by silica gel column chromatography (PE/EA = 40/1) to afford the product 4aa as a colourless oil (365.7 mg, 57% yield, E/Z = 92/8). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.21 (m, 4H), 7.16–7.08 (m, 2H), 6.96 (d, $J$ = 8.6 Hz, 0.17H), 6.93–6.87 (m, 1.76H), 6.47–6.29 (m, 1H), 6.15 (dq, $J$ = 15.8, 6.6 Hz, 0.92H), 5.76 (dq, $J$ = 11.6, 7.2 Hz, 0.08H), 3.92 (q, $J$ = 7.2 Hz, 1H), 2.46 (d, $J$ = 7.2 Hz, 2H), 1.93–1.77 (m, 4H), 1.51–1.58 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.23, 149.56, 140.75, 137.23, 135.58, 130.05, 129.64, 129.46, 127.18, 126.54, 125.80, 121.32, 120.99, 45.22, 45.01, 30.16, 22.37, 18.52, 18.42; HRMS (ESI-TOF) $m/z$ Calcd for C$_{22}$H$_{26}$O$_2$Na [M+Na]$^+$: 345.1825, found: 345.1820.

A Schlenk flask was charged with the flurbiprofen (488.5 mg, 2.0 mmol, 1.0 equiv), DCC (618.9 mg, 3.0 mmol, 1.5 equiv), DMAP (293.3 mg, 2.4 mmol, 1.2 equiv) and anhydrous DCM (10 mL) under N$_2$, followed by addition of S1 (618.9 mg, 2.4 mmol, 1.2 equiv, $E/Z$ = 93/7). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed under vacuum, and the crude residue was purified by silica gel column chromatography (PE/EA = 20/1 to 10/1) to afford the product 4ab as a colourless oil (278.9 mg, 39% yield, E/Z = 95/5). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J$ = 7.6 Hz, 2H), 7.46–7.40 (m, 3H), 7.37 (t, $J$ = 7.4 Hz, 1H), 7.29 (d, $J$ = 8.4 Hz, 2H), 7.26–7.18 (m, 2H), 7.00 (d, $J$ = 8.2 Hz, 0.2H), 6.97–6.92 (m, 1.8H), 6.36 (d, $J$ = 15.6 Hz, 1H), 6.25–6.08 (m, 0.95H), 5.84–5.67 (m, 0.05H), 3.98 (q, $J$ = 7.2 Hz, 1H), 1.86 (dd, $J$ = 6.8, 1.6 Hz, 3H), 1.64 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.49, 159.74 (d, $J$ = 248.7 Hz), 149.38, 141.27 (d, $J$ = 7.9 Hz), 135.81, 135.38, 130.97 (d, $J$ = 4.0 Hz), 129.98, 128.93 (d, $J$ = 3.0 Hz), 128.44, 127.70, 126.62, 126.02, 123.57 (d, $J$ = 3.3 Hz), 121.26, 115.30 (d, $J$ = 23.8 Hz), 45.11, 34.90, 18.44, 18.41; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ -117.31; HRMS (ESI-TOF) $m/z$ Calcd for C$_{24}$H$_{21}$O$_2$FNa [M+Na]$^+$: 383.1418, found: 383.1424.

A Schlenk flask was charged with the $L$-menthol (781.5 mg, 5.0 mmol, 1.0 equiv), EDCI (1.15 g, 6.0 mmol, 1.2 equiv), DMAP (122.2 mg, 1.0 mmol, 0.2 equiv) and anhydrous DCM (20 mL) under N$_2$, followed by addition of $p$-hydroxybenzaldehyde (825.6 mg, 5.5 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed under vacuum, and the crude residue was purified by silica gel column chromatography (PE/EA = 20/1) to afford the product S2 as a colourless oil (620.1 mg, 43% yield). To a suspension of the ethyltriphenylphosphonium bromide (913.4 mg, 2.46 mmol, 1.2 equiv) in dry THF (10 mL) at 0 °C under nitrogen was added n-butyllithium (2.46 mmol, 2.5 M in hexane, 1.2 equiv) dropwise. After stirring at
the same temperature for 30 min, the solution of the corresponding aldehyde (590.1 mg, 2.05 mmol, 1.0 equiv) in THF (5.0 mL) was added dropwise over 5 min. The reaction mixture was stirred for 30 min at 0 °C, and was allowed to warm up to room temperature overnight. Upon completion, the reaction mixture was quenched with water and extracted with EtO. The combined organic layers were dried over anhydrous Na2SO4 and concentrated in vacuum. The crude reaction mixture was purified by flash chromatography on silica gel (PE/EA = 40/1) to afford the product 4ac as a colourless oil (539.6 mg, 88% yield, E/Z = 23/77). 1H NMR (400 MHz, CDCl3) δ 8.04–7.99 (m, 1.51H), 7.96 (dd, J = 8.4, 1.6 Hz, 0.43H), 7.39–7.31 (m, 2H), 6.50–6.29 (m, 1.19H), 5.89 (dq, J = 11.7, 7.2 Hz, 0.73H), 4.92 (tt, J = 10.4, 5.0 Hz, 1H), 2.17–2.09 (m, 1H), 2.04–1.87 (m, 4H), 1.76–1.68 (m, 2H), 1.61–1.48 (m, 2H), 1.22–1.03 (m, 2H), 0.99–0.85 (m, 7H), 0.82–0.76 (m, 3H); 13C NMR (100 MHz, CDCl3) δ 165.96, 142.21, 142.07, 130.39, 129.83, 129.40, 129.16, 128.86, 128.66, 128.63, 128.53, 125.56, 74.68, 47.27, 40.97, 34.32, 31.42, 26.48, 23.63, 22.03, 20.75, 18.61, 16.51, 14.72; HRMS (ESI-TOF) m/z Calcd for C20H28O2Na [M+Na]+: 323.1981, found: 323.1974.

A Schlenk flask was charged with the lithocholic acid (753.2 mg, 2.0 mmol, 1.0 equiv), EDCI (460.1 mg, 2.4 mmol, 1.2 equiv), DMAP (48.9 mg, 0.4 mmol, 0.2 equiv) and anhydrous DCM (10 mL) under N2, followed by addition of S1 (483.6 mg, 2.1 mmol, 1.05 equiv, E/Z = 93/7). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed in vacuum, and the crude residue was purified by silica gel column chromatography (PE/EA = 3/1) to afford the product 4ad as a white solid (845.3 mg, 86% yield, E/Z = 94/6). 1H NMR (400 MHz, CDCl3) δ 7.31 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.4 Hz, 0.12H), 6.99 (d, J = 8.6 Hz, 1.88H), 6.42–6.31 (m, 1H), 6.18 (dq, J = 15.4, 6.4 Hz, 0.94H), 5.87–5.71 (m, 0.06H), 3.67–3.55 (m, 1H), 2.59 (ddd, J = 14.8, 9.8, 4.8 Hz, 1H), 2.45 (ddd, J = 15.6, 8.8, 6.8 Hz, 1H), 2.01–1.70 (m, 9H), 1.72–1.54 (m, 3H), 1.54–1.21 (m, 12H), 1.19–1.02 (m, 5H), 1.01–0.97 (m, 4H), 0.92 (s, 3H), 0.66 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 172.76, 149.45, 143.57, 130.05, 129.71, 126.61, 125.79, 121.46, 121.14, 71.77, 56.46, 55.92, 42.72, 42.04, 40.38, 40.13, 36.38, 35.80, 35.33, 35.31, 34.52, 31.35, 30.92, 30.48, 28.19, 27.15, 26.37, 24.16, 23.33, 20.78, 18.41, 18.28, 12.02; HRMS (ESI-TOF) m/z Calcd for C33H48O3Na [M+Na]+: 515.3496, found: 515.3502.

A Schlenk flask was charged with the gemfibrozil (250.3 mg, 1.0 mmol, 1.0 equiv), DCC (309.5 mg, 1.5 mmol, 1.5 equiv), DMAP (122.2 mg, 1.0 mmol, 1.0 equiv) and anhydrous DCM (10 mL) under N2, followed by addition of S1
(161.1 mg, 1.2 mmol, 1.2 equiv, E/Z = 93/7). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed in vacuum, and the crude residue was purified by silica gel column chromatography (PE/EA = 20/1) to afford the product 4ae as a colourless oil (237.4 mg, 65% yield, E/Z = 98/2). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.28 (m, 2H), 7.00 (d, $J = 7.4$ Hz, 1H), 6.97–6.91 (m, 2H), 6.66 (d, $J = 7.4$ Hz, 1H), 6.62 (d, $J = 1.8$ Hz, 1H), 6.38 (dd, $J = 15.8$, 1.8 Hz, 1H), 6.18 (dq, $J = 15.8$, 6.6 Hz, 0.98H), 5.83–5.71 (m, 0.02H), 3.98 (p, $J = 2.8$ Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.90–1.84 (m, 7H), 1.36 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.40, 156.85, 149.70, 136.46, 135.56, 130.31, 130.08, 126.62, 125.82, 123.60, 121.46, 120.70, 111.90, 67.75, 42.40, 37.13, 25.24, 25.14, 21.39, 18.45, 15.79; HRMS (ESI-TOF) $m/z$ Calcd for C$_{24}$H$_{30}$O$_3$Na [M+Na]$^+$: 389.2087, found: 389.2080.
### 2.2 Experimental Optimization

#### 2.2.1 Base Effect

| Entry | Base        | 3a (%) | 3a' (%) | 1 (%) | 3a/3a' | Entry | Base       | 3a (%) | 3a' (%) | 1 (%) | 3a/3a' |
|-------|-------------|--------|---------|-------|--------|-------|-----------|--------|---------|-------|--------|
| 1     | Li₂CO₃      | --     | --      | 76    | --     | 11    | Na₂HPO₄   | --     | --      | 74    | --     |
| 2     | Na₂CO₃      | 16     | 52      | --    | 12     | 12    | CsF       | --     | 84      | --    | --     |
| 3     | K₂CO₃       | 2      | 6       | 52    | 25/75  | 13    | KF        | --     | 76      | --    | --     |
| 4     | Cs₂CO₃      | --     | 64      | --    | 14     | 14    | CsOAc     | --     | 84      | --    | --     |
| 5     | NaHCO₃      | --     | 82      | --    | 15     | 15    | NaOAc     | --     | 86      | --    | --     |
| 6     | KHCO₃       | 11     | 2       | 63    | 85/15  | 16    | KOMe      | --     | 84      | --    | --     |
| 7     | CsHCO₃      | 3      | 6       | 64    | 33/67  | 17    | KODBu     | --     | 84      | --    | --     |
| 8     | K₂PO₄       | 3      | 4       | 66    | 43/57  | 18    | CsOPh     | --     | 90      | --    | --     |
| 9     | Na₂PO₄      | 31     | 2       | 36    | 94/6   | 19    | KOH       | --     | 80      | --    | --     |
| 10    | NaH₂PO₄     | --     | 82      | --    | --     | --    | --        | --     | --      | --    | --     |

*Reaction conditions: 1 (0.1 mmol, 1.0 equiv), 2a (0.2 mmol, 2.0 equiv), Base (0.2 mmol, 2.0 equiv), Ni(O₂Tf)₂ (10 mol %), L (10 mol %), N₂, 80 °C, 10 h, L-AmyOH (0.5 mL). Yield was determined by 'H NMR using CH₂Cl₂ as an internal standard.

#### 2.2.2 Evaluation of Ligands

| Ligand | 3a (%) | 3a' (%) | 1 (%) | 3a'/% |
|--------|--------|---------|-------|-------|
| L₁     | 65%    | 85%     | 90%   | 84%   |
| L₂     | 90%    | 90%     | 90%   | 90%   |
| L₃     | 90%    | 90%     | 90%   | 90%   |
| L₄     | 90%    | 90%     | 90%   | 90%   |
| L₅     | 90%    | 90%     | 90%   | 90%   |

*Reaction conditions: 1 (0.1 mmol, 1.0 equiv), 2a (0.2 mmol, 2.0 equiv), Ni(O₂Tf)₂ (10 mol %), L (10 mol %), N₂, 80 °C, 10 h. Yield was determined by 'H NMR using CH₂Cl₂ as an internal standard.
2.2.3 Evaluation of Nickel Sources

| Entry | Ni          | 3a (%) | 3a' (%) | 1 (%) | 3a/3a' |
|-------|-------------|--------|---------|-------|--------|
| 1     | NiF₂        | --     | 96      | --    | 3a     |
| 2     | NiCl₂       | --     | 99      | --    | 3a     |
| 3     | NiBr₂       | 60     | 51      | 32/33 | 3a     |
| 4     | Ni(Clo)₂    | --     | 97      | --    | 3a     |
| 5     | Ni(Clo)₂DME | --     | 97      | --    | 3a     |
| 6     | NiBr₂DME    | 60     | 55      | 32/33 | 3a     |
| 7     | NiCl₂dialysis | 26   | 63      | --    | 3a     |
| 8     | Ni(OAc)₂    | --     | 100     | --    | 3a     |
| 9     | Ni(OD)₂    | 20     | 10      | --    | 3a     |
| 10    | Ni(OD)₂    | 58     | 33      | 33/33 | 3a     |

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*Reaction conditions: 1 (0.1 mmol, 1.0 equiv), 2a (0.2 mmol, 2.0 equiv), Ni cat. (10 mol %), L14 (10 mol %), Na₂PO₄ (2.0 equiv), i-AmyOH, 80 °C, 10 h. Yield was determined by 'H NMR using CH₃Br₂ as an internal standard. ² 20 mg 4Å MS was added.

2.2.4 Solvent Effect

| Entry | Solvent | 3a (%) | 3a' (%) | 1 (%) | 3a/3a' |
|-------|---------|--------|---------|-------|--------|
| 1     | THF     | 29     | 64      | --    | 3a     |
| 2     | dioxane | 62     | 38      | --    | 3a     |
| 3     | Toluene | 30     | 52      | --    | 3a     |
| 4     | DMF     | --     | 16      | --    | 3a     |
| 5     | DMSO    | --     | 24      | --    | 3a     |
| 6     | MeOH    | --     | 100     | --    | 3a     |

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*Reaction conditions: 1 (0.1 mmol, 1.0 equiv), 2a (0.2 mmol, 2.0 equiv), Na₂PO₄ (0.2 mmol, 2 equiv), Ni(2-NH₂-5-MeC₆H₄SO₃)₂ (10 mol %), L14 (10 mol %), N₂, 80 °C, 10 h, solvent (0.5 mL). Yield was determined by 'H NMR using CH₃Br₂ as an internal standard. ³ 24 h.
2.2.5 Loading of Arylboronic Acid and Base

![Chemical reaction diagram]

| Entry | Condition        | 3a (%) | 3a' (%) | 1 (%) | 3a/3a' |
|-------|------------------|--------|---------|-------|--------|
| 1     | None             | 80     | --      | 18    | --     |
| 2     | 2a (1.2 equiv)  | 44     | --      | 30    | --     |
| 3     | 2a (1.5 equiv)  | 58     | --      | 22    | --     |
| 4     | 2a (2.0 equiv)  | 80     | --      | 14    | --     |
| 5     | 2a (2.5 equiv)  | 76     | --      | 14    | --     |
| 6     | 2a (3.0 equiv)  | 76     | --      | 6     | --     |
| 7     | 2a (3.0 equiv), Na_2PO_4 (2.5 equiv) | 84 | -- | 8 | -- |
| 8     | 2a (3.0 equiv), Na_2PO_4 (3.0 equiv) | 92 | -- | -- | -- |
| g     | 2a (3.0 equiv), Na_2PO_4 (3.0 equiv) | 96 (91%) | -- | -- | -- |

*Reaction conditions: 1 (0.1 mmol, 1.0 equiv), 2a (0.2 mmol, 2.0 equiv), Na_2PO_4 (0.2 mmol, 2 equiv), Ni(2-NH_2-5-MeC_6H_4SO_3H) (10 mol %), L14 (10 mol %), N_2, 80 °C, 10 h, t-AmylOH (0.5 mL). Yield was determined by ^1H NMR using CH_3Br_2 as an internal standard. g 1 (0.2 mmol, 1.0 equiv), 2a (0.6 mmol, 3.0 equiv), Na_2PO_4 (0.6 mmol, 3.0 equiv), Ni(2-NH_2-5-MeC_6H_4SO_3H) (10 mol %), L14 (10 mol %), N_2, 80 °C, 10 h, t-AmylOH (1.0 mL). g Isolated yield.

2.2.6 Control Experiments

![Chemical reaction diagram]

| Entry | Condition     | 3a (%) | 3a' (%) | 1 (%) | 3a/3a' |
|-------|---------------|--------|---------|-------|--------|
| 1     | None          | 92     | --      | --    | --     |
| 2     | No L14       | --     | --      | 80    | --     |
| 3     | No Base      | --     | --      | 92    | --     |
| 4     | No Ni        | --     | --      | 86    | --     |

*Reaction conditions: 1 (0.1 mmol, 1.0 equiv), 2a (0.3 mmol, 3.0 equiv), Na_2PO_4 (0.3 mmol, 3 equiv), Ni(2-NH_2-5-MeC_6H_4SO_3H) (10 mol %), L14 (10 mol %), N_2, 80 °C, 10 h, t-AmylOH (0.5 mL). Yield was determined by ^1H NMR using CH_3Br_2 as an internal standard.
2.2.7 The Reactivities of cis- and trans-Alkenes

The experimental results unveiled that the configuration of the alkenes didn’t affect the reactivity of this Ni-catalyzed hydroarylation reaction. The E-1, Z-1, and the mixture with a ratio of 28/72 (E/Z) all resulted in similar yields. Accordingly, we evaluated our reaction scope using the alkenes with the configurational mixtures.

2.2.8 The Reaction Rates of Z-Alkene and E-Alkene

Experimental Procedure: In a nitrogen-filled glovebox, substrate 1 (Z/E = 55/45), 2a, Ni(2-NH₂-5-MeC₆H₃SO₃)₂, L14, Na₃PO₄ were charged in a 10-mL tube, and added 3.0 µL dodecane as internal standard. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (1.0 mL). The tube was sealed again with parafilm and heated to 80 °C. The reaction progress was monitored by removing aliquots (~10 µL) from the reaction mixture via syringe under N₂. Each aliquot was quenched by EA (4.0 mL) in an 8.0 mL tube. The mixture was filtered with a filter head into 2.0 mL GC vial and analyzed by gas chromatography. The kinetic experiments with respect to the consumption of E-1 and Z-1 were investigated, indicating a similar reaction rate for cis- and trans- internal alkenes in our reaction.

Supplementary Figure 1. Time-course profile for the reaction using the mixed 1 (Z/E=45:55)
2.3 General Procedure for Ni-Catalyzed Hydroarylation of Internal Alkenes

**General Procedure**: In a nitrogen-filled glovebox, substrate 1 or 4 (0.2 mmol, 1.0 equiv), 2 (0.6 mmol, 3.0 equiv), Ni(2-NH$_2$-5-MeC$_6$H$_3$SO$_3$)$_2$ (8.6 mg, 10 mol %), L14 (6.8 mg, 10 mol %), Na$_3$PO$_4$ (98.4 mg, 0.6 mmol, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (1.0 mL). The tube was sealed again with parafilm and heated to 80 °C for 24 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with EtOAc as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by silica gel chromatography or preparative thin-layer chromatography to afford the hydroarylated product 3 or 5.

![Chemical Structure](image)

1-Methoxy-4-(1-phenylpropyl)benzene$^{10}$

3a was synthesized following the general procedure with $E$-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3a was obtained in 90% yield (40.6 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.17 (m, 4H), 7.17–7.10 (m, 3H), 6.81 (d, $J$ = 8.8 Hz, 2H), 3.75 (s, 3H), 3.72 (t, $J$ = 8.0 Hz, 1H), 2.0–1.99 (m, 2H), 0.88 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.78, 145.55, 137.32, 128.75, 128.30, 127.79, 125.88, 113.70, 55.16, 52.35, 28.72, 12.77.

![Chemical Structure](image)

1-Methoxy-4-(1-(p-tolyl)propyl)benzene$^{11}$

3b was synthesized following the general procedure with $E$-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3b was obtained in 75% yield (35.8 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16–7.03 (m, 6H), 6.84–6.77 (m, 2H), 3.74 (s, 3H), 3.70 (t, $J$ = 7.8 Hz, 1H), 2.28 (s, 3H), 2.05–1.96 (m, 2H), 0.88 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.71, 142.54, 137.58, 135.30, 129.00, 128.68, 127.63, 113.68, 55.15, 51.93, 28.74, 20.93, 12.79.
4,4’-(Propane-1,1-diyl)bis(methoxybenzene)\textsuperscript{12}

3c was synthesized following the general procedure with \textit{E-1}. After purification by preparative thin-layer chromatography using PE as the eluent, 3c was obtained in 73\% yield (37.5 mg) as a colourless liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.12 (d, \( J = 8.6 \) Hz, 4H), 6.81 (d, \( J = 8.8 \) Hz, 4H), 3.75 (s, 6H), 3.68 (t, \( J = 7.8 \) Hz, 1H), 2.04–1.95 (m, 2H), 0.87 (t, \( J = 7.2 \) Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 157.70, 137.71, 128.64, 113.67, 55.15, 51.46, 28.87, 12.77.

4,4’-(Propane-1,1-diyl)bis(methoxybenzene)

3d was synthesized following the general procedure with \textit{E-1}. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3d was obtained in 54\% yield (34.4 mg) as a colourless liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.34–7.26 (m, 2H), 7.15 (t, \( J = 8.4 \) Hz, 4H), 7.06 (t, \( J = 7.3 \) Hz, 1H), 6.97 (d, \( J = 8.0 \) Hz, 2H), 6.91 (d, \( J = 8.4 \) Hz, 2H), 6.83 (d, \( J = 8.8 \) Hz, 2H), 3.77 (s, 3H), 3.72 (t, \( J = 7.8 \) Hz, 1H), 2.05–1.98 (m, 2H), 0.89 (t, \( J = 7.2 \) Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 157.80, 157.44, 155.12, 140.56, 137.31, 129.61, 128.92, 128.71, 122.93, 118.80, 118.61, 113.72, 55.17, 51.67, 28.88, 12.77; HRMS (El) \( m/z \) Calcd for C\textsubscript{22}H\textsubscript{22}O\textsubscript{2} [M]+: 318.1614, found: 318.1619.

1-Methoxy-4-(1-(4-(trifluoromethoxy)phenyl)propyl)benzene

3e was synthesized following the general procedure with \textit{E-1}. After purification by preparative thin-layer chromatography using PE as the eluent, 3e was obtained in 79\% yield (48.9 mg) as a colourless liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.26–7.18 (m, 2H), 7.14–7.05 (m, 4H), 6.83 (d, \( J = 8.8 \) Hz, 2H), 3.76 (s, 3H), 3.73 (t, \( J = 7.8 \) Hz, 1H), 2.05–1.96 (m, 1H), 0.88 (t, \( J = 7.4 \) Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 157.99, 147.33 (d, \( J = 1.9 \) Hz), 144.33, 136.60, 128.97, 128.71, 120.82, 120.49 (d, \( J = 255.2 \) Hz), 113.84, 55.17, 51.70, 28.74, 12.67; \textsuperscript{19}F NMR (375 MHz, CDCl\textsubscript{3}) \( \delta \) -57.90; HRMS (El) \( m/z \) Calcd for C\textsubscript{17}H\textsubscript{17}F\textsubscript{3}O\textsubscript{2} [M]+: 310.1175, found: 310.1182.
1-Fluoro-4-(1-(4-methoxyphenyl)propyl)benzene

3f was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3f was obtained in 92% yield (45.1 mg) as a colourless liquid.

\[ ^1H \text{NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 7.15 (dd, J = 8.4, 5.6 \text{ Hz}, 2H), 7.11 (d, J = 8.6 \text{ Hz}, 2H), 6.94 (t, J = 8.6 \text{ Hz}, 2H), 6.82 (d, J = 8.8 \text{ Hz}, 2H), 3.76 (s, 3H), 3.72 (t, J = 7.8 \text{ Hz}, 1H), 2.06–1.93 (m, 2H), 0.87 (t, J = 7.4 \text{ Hz}, 3H); \]
\[ ^{13}C \text{NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 161.17 (d, J = 243.8 \text{ Hz}), 157.87, 141.23 (d, J = 3.2 \text{ Hz}), 137.10, 129.10 (d, J = 7.6 \text{ Hz}), 128.65, 115.02 (d, J = 21.2 \text{ Hz}), 113.77, 55.17, 51.54, 28.84, 12.69; \]
\[ ^{19}F \text{NMR} (375 \text{ MHz}, \text{CDCl}_3) \delta -117.67. \]

1-Methoxy-4-(1-(4-(trifluoromethyl)phenyl)propyl)benzene

3g was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3g was obtained in 80% yield (47.1 mg) as a colourless liquid.

\[ ^1H \text{NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 7.51 (d, J = 8.0 \text{ Hz}, 2H), 7.32 (d, J = 8.0 \text{ Hz}, 2H), 7.12 (d, J = 8.2 \text{ Hz}, 2H), 6.83 (d, J = 9.2 \text{ Hz}, 2H), 3.80 (t, J = 7.8 \text{ Hz}, 1H), 3.77 (s, 3H), 2.09–1.99 (m, 1H), 0.89 (t, J = 7.4 \text{ Hz}, 3H); \]
\[ ^{13}C \text{NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 158.07, 149.67, 136.18, 128.74, 128.08, 127.00 (q, J = 271.0 \text{ Hz}), 125.28 (q, J = 3.8 \text{ Hz}), 113.90, 55.18, 52.19, 28.51, 12.63; \]
\[ ^{19}F \text{NMR} (375 \text{ MHz}, \text{CDCl}_3) \delta -62.32. \]

Methyl-4-(1-(4-methoxyphenyl)propyl)benzoate

3h was synthesized following the general procedure with E-1. Ni(OTf)_2 (10 mol%) instead of Ni(2-NH_2-5-MeC_6H_3SO_3)_2 as catalyst. After purification by preparative thin-layer chromatography using PE as the eluent, 3h was obtained in 56% yield (32.0 mg) as a colourless liquid.

\[ ^1H \text{NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 7.97–7.91 (m, 2H), 7.31–7.25 (m, 2H), 7.16–7.09 (m, 2H), 6.86–6.79 (m, 2H), 3.88 (s, 3H), 3.79 (t, J = 8.0 \text{ Hz}, 1H), 3.76 (s, 3H), 2.09–2.00 (m, 2H), 0.88 (t, J = 7.2 \text{ Hz}, 3H); \]
\[ ^{13}C \text{NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 167.04, 157.99, 150.96, 136.30, 129.70, 128.73, 127.86, 127.81, 113.83, 55.15, 52.33, 51.91, 28.47, 12.63; \]
\[ \text{HRMS (EI)} \ m/z \text{ Calcd for C}_{19}H_{20}O_3 [M]^+: 284.1407, \text{ found: 284.1414.} \]
1-Methoxy-3-(1-(4-methoxyphenyl)propyl)benzene

3i was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3i was obtained in 88% yield (45.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.22–7.08 (m, 3H), 6.85–6.77 (m, 3H), 6.77–6.76 (m, 1H), 6.69 (dd, $J = 8.2$, 2.4 Hz, 1H), 3.75 (s, 3H), 3.70 (t, $J = 7.8$ Hz, 1H), 2.07–1.96 (m, 2H), 0.88 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.53, 157.79, 147.24, 137.12, 129.21, 128.69, 120.26, 113.92, 113.69, 110.71, 55.14, 55.04, 52.36, 28.64, 12.76; HRMS (EI) m/z Calcd for C$_{17}$H$_{20}$O$_2$ [M]+: 256.1461, found: 256.1460.

1-(1-(4-Methoxyphenyl)propyl)-3-methylbenzene

3j was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3j was obtained in 86% yield (41.5 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.17–7.12 (m, 3H), 7.03–7.00 (m, 2H), 6.96 (d, $J = 7.6$ Hz, 1H), 6.86–6.76 (m, 2H), 3.75 (s, 3H), 3.69 (t, $J = 8.0$ Hz, 1H), 2.29 (s, 3H), 2.06–1.97 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.73, 145.47, 137.76, 137.42, 128.72, 128.61, 128.17, 126.66, 124.72, 113.67, 55.14, 52.32, 28.73, 21.49, 12.81; HRMS (EI) m/z Calcd for C$_{17}$H$_{20}$O [M]+: 240.1509, found: 240.1513.

(3-(1-(4-Methoxyphenyl)propyl)phenyl)trimethylsilane

3k was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3k was obtained in 62% yield (37.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (s, 1H), 7.32 (dt, $J = 7.2$, 1.2 Hz, 1H), 7.24 (t, $J = 4.0$ Hz, 1H), 7.21–7.11 (m, 3H), 6.82 (d, $J = 8.8$ Hz, 2H), 3.76 (s, 3H), 3.74 (t, $J = 7.6$ Hz, 1H), 2.08–1.99 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H), 0.24 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.75, 144.61, 140.26, 137.27, 132.82, 130.94, 128.78, 128.13, 127.71, 113.69, 55.16, 52.54, 28.92, 12.82, -1.09; HRMS (EI) m/z Calcd for C$_{19}$H$_{26}$OSi [M]+: 298.1747, found: 298.1753.
1-Fluoro-3-(1-(4-methoxyphenyl)propyl)benzene

3l was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3l was obtained in 91% yield (44.5 mg) as a colourless liquid.

\[ ^1 \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.26–7.17 \text{ (m, 1H)}, 7.16–7.08 \text{ (m, 2H)}, 6.99 \text{ (dt, } J = 7.6, 1.6 \text{ Hz, 1H}), 6.91 \text{ (dt, } J = 10.4, 2.0 \text{ Hz, 1H}), 6.89–6.77 \text{ (m, 3H)}, 3.76 \text{ (s, 3H)}, 3.73 \text{ (t, } J = 8.0 \text{ Hz, 1H}), 2.05–1.97 \text{ (m, 2H)}, 0.88 \text{ (t, } J = 7.2 \text{ Hz, 3H}); ^{13} \text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 162.90 \text{ (d, } J = 245.1 \text{ Hz)}, 157.95, 148.28 \text{ (d, } J = 6.7 \text{ Hz)}, 136.53, 129.66 \text{ (d, } J = 8.3 \text{ Hz)}, 128.70, 123.48 \text{ (d, } J = 2.7 \text{ Hz)}, 114.53 \text{ (d, } J = 21.1 \text{ Hz}), 113.80, 112.74 \text{ (d, } J = 21.1 \text{ Hz}), 55.16, 52.06 \text{ (d, } J = 1.6 \text{ Hz)}, 28.57, 12.66; ^{19} \text{F NMR} (375 \text{ MHz, CDCl}_3) \delta -113.56; \text{HRMS } (\text{EI}) \text{ } m/z \text{ Calcd for C}_{16}H_{17}OF [M]^+: 244.1258, \text{found: 244.1264.}

1-(1-(4-Methoxyphenyl)propyl)-3-(trifluoromethyl)benzene

3m was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3m was obtained in 82% yield (48.0 mg) as a colourless liquid.

\[ ^1 \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.48 \text{ (s, 1H)}, 7.45–7.32 \text{ (m, 3H)}, 7.16–7.08 \text{ (m, 2H)}, 6.88–6.79 \text{ (m, 2H)}, 3.79 \text{ (t, } J = 8.0 \text{ Hz, 1H}), 3.76 \text{ (s, 3H)}, 2.11–1.97 \text{ (m, 2H), 0.89 (t, } J = 7.2 \text{ Hz, 3H}); ^{13} \text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 158.06, 146.55, 136.21, 131.23, 130.56 \text{ (q, } J = 31.9 \text{ Hz)}, 128.76, 128.74, 124.42 \text{ (q, } J = 3.8 \text{ Hz)}, 124.27 \text{ (q, } J = 270.6 \text{ Hz)}, 122.85 \text{ (q, } J = 3.9 \text{ Hz)}, 113.91, 55.17, 52.18, 28.64, 12.63; ^{19} \text{F NMR} (375 \text{ MHz, CDCl}_3) \delta -62.41.

1-(1-(4-Methoxyphenyl)propyl)-2-methylbenzene

3n was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3n was obtained in 74% yield (35.8 mg) as a colourless liquid.

\[ ^1 \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.32–7.26 \text{ (m, 1H)}, 7.23–7.13 \text{ (m, 1H)}, 7.12–7.06 \text{ (m, 2H)}, 6.82–6.75 \text{ (m, 2H)}, 3.92 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 3.74 \text{ (s, 3H)}, 2.25 \text{ (s, 3H)}, 2.05–1.94 \text{ (m, 2H), 0.90 (t, } J = 7.4 \text{ Hz, 3H}); ^{13} \text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 157.62, 143.19, 136.81, 136.28, 130.39, 129.08, 126.41, 125.91, 125.79, 113.55, 55.13, 47.87, 29.16, 19.86, 12.78; \text{HRMS } (\text{EI}) \text{ } m/z \text{ Calcd for } C_{17}H_{20}O [M]^+: 240.1509, \text{found: 240.1502.} \]
1-(1-(4-Methoxyphenyl)propyl)-3,5-dimethylbenzene

3o was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3o was obtained in 68% yield (34.7 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.18–7.11 (m, 2H), 6.85–6.78 (m, 5H), 3.76 (s, 3H), 2.26 (s, 6H), 2.05–1.95 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.70, 145.45, 137.64, 137.53, 128.71, 127.60, 125.58, 113.66, 55.16, 52.30, 28.75, 21.37, 12.85.

1-(1-(4-Methoxyphenyl)propyl)-3,5-bis(trifluoromethyl)benzene

3p was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE as the eluent, 3p was obtained in 51% yield (37.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (s, 1H), 7.65 (s, 2H), 7.15–7.09 (m, 2H), 6.89–6.83 (m, 2H), 3.87 (t, $J = 7.8$ Hz, 1H), 3.79 (s, 3H), 2.14–1.98 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.40, 148.23, 134.96, 131.54 (q, $J = 33.0$ Hz), 128.74, 127.88 (d, $J = 3.2$ Hz), 126.86, 123.43 (q, $J = 272.6$ Hz), 120.12 (p, $J = 4.0$ Hz), 114.19, 55.20, 52.09, 28.59, 12.52; $^{19}$F NMR (375 MHz, CDCl$_3$) δ -62.76; HRMS (EI) m/z Calcd for C$_{18}$H$_{16}$F$_6$O [M]$^+$: 362.1100, found: 362.1111.

Fluoro-4-methoxy-1-(1-(4-methoxyphenyl)propyl)benzene

3q was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3q was obtained in 67% yield (36.9 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.15–7.06 (m, 2H), 6.97–6.89 (m, 2H), 6.86 (d, $J = 8.3$ Hz, 1H), 6.84–6.79 (m, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 3.66 (t, $J = 7.8$ Hz, 1H), 2.02–1.93 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.87, 152.25 (d, $J = 245.0$ Hz), 145.59 (d, $J = 10.9$ Hz), 138.87 (d, $J = 5.5$ Hz), 136.95, 128.59, 123.19 (d, $J = 3.3$ Hz), 115.33 (d, $J = 18.1$ Hz), 113.76, 113.22 (d, $J = 2.2$ Hz), 56.23, 55.15, 51.36 (d, $J = 1.3$ Hz), 28.69, 12.65; $^{19}$F NMR (375 MHz, CDCl$_3$) δ -135.36 (dd, $J = 12.6$, 8.5 Hz); HRMS (EI) m/z Calcd for C$_{18}$H$_{19}$FO$_2$ [M]$^+$: 274.1364, found: 274.1363.
2-Fluoro-1-methoxy-4-(1-(4-methoxyphenyl)propyl)benzene

3r was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3r was obtained in 64% yield (35.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.15–7.07 (m, 2H), 6.96–6.89 (m, 2H), 6.86 (d, $J$ = 8.4 Hz, 1H), 6.85 – 6.79 (m, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.66 (t, $J$ = 7.8 Hz, 1H), 2.02–1.93 (m, 2H), 0.87 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.89, 152.27 (d, $J$ = 245.1 Hz), 145.61 (d, $J$ = 10.8 Hz), 138.89 (d, $J$ = 5.4 Hz), 136.97, 128.61, 123.20 (d, $J$ = 3.3 Hz), 115.35 (d, $J$ = 18.1 Hz), 113.78, 113.25 (d, $J$ = 2.2 Hz), 56.28, 55.19, 51.38 (d, $J$ = 1.3 Hz), 28.71, 12.67; $^{19}$F NMR (375 MHz, CDCl$_3$) δ -135.37; HRMS (EI) m/z Calcd for C$_{17}$H$_{19}$FO$_2$ [M$^+$]: 274.1364, found: 274.1369.

2-(1-(4-Methoxyphenyl)propyl)naphthalene

3s was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 3s was obtained in 90% yield (49.7 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 (t, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 8.4 Hz, 1H), 7.68 (s, 1H), 7.46 – 7.36 (m, 2H), 7.31 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.18 (d, $J$ = 8.4 Hz, 2H), 6.81 (d, $J$ = 8.4 Hz, 2H), 3.90 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.83, 142.95, 137.15, 133.51, 132.06, 128.89, 127.93, 127.66, 127.52, 126.79, 125.83, 125.74, 125.22, 113.73, 55.17, 52.35, 28.49, 12.80.

6-(1-(4-Methoxyphenyl)propyl)-2,3-dihydrobenzo[b][1,4]dioxine

3t was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 3t was obtained in 63% yield (35.8 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.16–7.08 (m, 2H), 6.83–6.78 (m, 2H), 6.75 (d, $J$ = 8.2 Hz, 1H), 6.72 (d, $J$ = 2.0 Hz, 1H), 6.68 (dd, $J$ = 8.0, 2.0 Hz, 1H), 4.19 (s, 4H), 3.75 (s, 3H), 3.62 (t, $J$ = 7.6 Hz, 1H), 2.01–1.97 (m, 2H), 0.87 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.73, 143.16, 141.58, 139.06, 137.45, 128.60, 120.70, 116.91,
116.27, 113.68, 64.33, 64.24, 55.15, 51.63, 28.75, 12.76; HRMS (EI) m/z Calcd for C_{18}H_{20}O_{3} [M]^+: 284.1407, found: 284.1409.

4-(1-(4-Methoxyphenyl)propyl)dibenzo[b,d]furan

4u was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using PE/EA (50/1) as the eluent, 4u was obtained in 45% yield (28.2 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (dd, $J = 7.6$, 1.2 Hz, 1H), 7.77 (dd, $J = 7.4$, 1.6 Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.43 (ddd, $J = 8.4$, 7.4, 1.2 Hz, 1H), 7.39–7.23 (m, 5H), 6.84–6.78 (m, 2H), 4.46 (t, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 2.34–2.11 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.88, 155.98, 154.34, 136.24, 129.72, 128.94, 126.85, 125.34, 124.58, 123.99, 122.86, 122.49, 120.57, 118.22, 113.68, 111.69, 55.16, 46.15, 27.94, 12.82; HRMS (EI) m/z Calcd for C$_{22}$H$_{20}$O$_2$ [M]^+: 316.1470, found: 316.1458.

4-(1-Phenylpropyl)-1,1'-biphenyl

5a was synthesized following the general procedure with 4a ($E/Z = 97/3$). After purification by preparative thin-layer chromatography using PE as the eluent, 5a was obtained in 81% yield (44.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.59–7.52 (m, 2H), 7.52–7.47 (m, 2H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.33–7.23 (m, 6H), 7.19–7.14 (m, 1H), 3.82 (t, $J = 7.8$ Hz, 1H), 2.14–2.04 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.02, 144.28, 140.96, 138.87, 128.66, 128.40, 128.26, 127.90, 127.07, 126.99, 126.96, 126.07, 52.90, 28.58, 12.81; HRMS (EI) m/z Calcd for C$_{21}$H$_{20}$ [M]^+: 272.1561, found: 272.1560.

1-Fluoro-4-(1-phenylpropyl)benzene

5b was synthesized following the general procedure with 4b ($E/Z = 79/21$). After purification by preparative thin-layer chromatography using PE as the eluent, 5b was obtained in 74% yield (31.8 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32–7.24 (m, 2H), 7.23–7.12 (m, 5H), 6.99–6.88 (m, 2H), 3.76 (t, $J = 7.8$ Hz, 1H), 2.09–1.97 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.23 (d, $J = 243.9$ Hz), 144.94, 140.81 (d, $J = 3.2$ Hz), 129.21 (d, $J = 7.8$ Hz), 128.40, 127.77, 126.12, 115.06 (d, $J = 21.0$ Hz), 52.40, 28.67, 12.69; $^{19}$F NMR (375 MHz, CDCl$_3$) δ -117.45.
1-(1-Phenylpropyl)-4-(trifluoromethyl)benzene\(^{13}\)

5c was synthesized following the general procedure with 4c \((E/Z = 99/1)\). After purification by preparative thin-layer chromatography using PE as the eluent, 5c was obtained in 70% yield (37.1 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.52 (d, \(J = 8.0\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 7.30–7.26 (m, 2H), 7.24–7.14 (m, 3H), 3.84 (t, \(J = 7.8\) Hz, 1H), 2.14–2.08 (m, 2H), 0.90 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 149.2, 149.25, 144.06, 128.55, 128.20, 127.85, 126.41, 125.31 (q, \(J = 3.8\) Hz), 124.30 (q, \(J = 270\) Hz), 53.06, 28.37, 12.62; \(^{19}\)F NMR (375 MHz, CDCl\(_3\)) δ -62.34.

Methyl-4-(1-phenylpropyl)benzoate\(^{13}\)

5d was synthesized following the general procedure with 4d \((E/Z = 33/67)\). After purification by preparative thin-layer chromatography using PE as the eluent, 5d was obtained in 85% yield (43.0 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.01–7.88 (m, 2H), 7.34–7.24 (m, 4H), 7.23–7.10 (m, 3H), 3.87 (s, 3H), 3.84 (t, \(J = 7.8\) Hz, 1H), 2.14–2.01 (m, 2H), 0.89 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 167.02, 150.52, 144.16, 129.71, 128.46, 127.95, 127.91, 127.83, 126.28, 53.17, 51.93, 28.31, 12.62.

1-(1-Phenylpropyl)-4-(trifluoromethoxy)benzene\(^{13}\)

5e was synthesized following the general procedure with 4e \((E/Z = 52/48)\). After purification by preparative thin-layer chromatography using PE as the eluent, 5e was obtained in 66% yield (36.8 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.33–7.16 (m, 7H), 7.11 (d, \(J = 8.2\) Hz, 2H), 3.79 (t, \(J = 7.8\) Hz, 1H), 2.13–1.97 (m, 2H), 0.89 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 147.41, 144.47, 143.90, 129.08, 128.49, 127.83, 126.29, 120.85, 120.48 (q, \(J = 255\) Hz), 52.56, 28.59, 12.67; \(^{19}\)F NMR (375 MHz, CDCl\(_3\)) δ -57.86.

4,4,5,5-Tetramethyl-2-(4-(1-phenylpropyl)phenyl)-1,3-dioxolane\(^{13}\)

5f was synthesized following the general procedure with 4f \((E/Z = 62/38)\). After purification by preparative thin-layer chromatography using PE/Aetone (50/1) as the eluent, 5f was obtained in 53% yield (34.1 mg) as a colourless liquid.
\[\text{S25}\]

**3-(1-Phenylpropyl)phenol**

5g was synthesized following the general procedure with 4g (E/Z = 69/31). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5g was obtained in 73% yield (30.8 mg) as a colourless liquid.

\[\text{1H NMR (400 MHz, CDCl}_3\] δ 7.31–7.20 (m, 4H), 7.19–7.07 (m, 2H), 6.82 (d, \(J = 7.6\) Hz, 1H), 6.79 (d, J = 2.0 Hz, 1H), 6.64 (dt, \(J = 7.8, 2.0\) Hz, 1H), 3.72 (t, \(J = 7.8\) Hz, 1H), 2.08–1.98 (m, 2H), 0.95 (s, 9H), 0.89 (t, \(J = 7.2\) Hz, 3H); \[\text{13C NMR (100 MHz, CDCl}_3\] δ 155.57, 146.69, 145.07, 129.13, 128.28, 127.85, 126.07, 120.50, 114.80, 112.93, 53.02, 28.48, 25.71, 18.21, 12.75; HRMS (EI) \(m/z\) Calcd for \(\text{C}_{15}\text{H}_{16}\text{O}\ [\text{M}]^+: 212.1193, \text{found: 212.1196.}\]

**tert-Butyldimethyl(3-(1-phenylpropyl)phenoxy)silane**

5h was synthesized following the general procedure with 4h (E/Z = 69/31). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5h was obtained in 76% yield (49.8 mg) as a colourless liquid.

\[\text{1H NMR (400 MHz, CDCl}_3\] δ 7.29–7.18 (m, 4H), 7.18–7.04 (m, 2H), 6.81 (dt, \(J = 7.6, 1.2\) Hz, 1H), 6.71 (t, \(J = 2.0\) Hz, 1H), 6.64 (dt, \(J = 7.8, 2.0\) Hz, 1H), 3.72 (t, \(J = 7.8\) Hz, 1H), 2.08–1.98 (m, 2H), 0.95 (s, 9H), 0.89 (t, \(J = 7.2\) Hz, 3H), 0.15 (s, 6H); \[\text{13C NMR (100 MHz, CDCl}_3\] δ 155.57, 146.69, 145.07, 129.13, 128.28, 127.85, 125.96, 121.05, 119.71, 117.64, 53.02, 28.48, 25.71, 18.21, 12.75, -4.43; HRMS (EI) \(m/z\) Calcd for \(\text{C}_{21}\text{H}_{30}\text{OSi}[\text{M}]^+: 326.2067, \text{found: 326.2060.}\]

**1-Fluoro-3-(1-phenylpropyl)benzene**

5i was synthesized following the general procedure with 4i (E/Z = 55/45). After purification by preparative thin-layer chromatography using PE as the eluent, 5i was obtained in 68% yield (29.0 mg) as a colourless liquid.

\[\text{1H NMR (400 MHz, CDCl}_3\] δ 7.28 (t, \(J = 7.6\) Hz, 2H), 7.25–7.14 (m, 4H), 7.01 (d, \(J = 7.8\) Hz, 1H), 6.93 (dd, \(J = 10.4, 2.4\) Hz, 1H), 6.85 (dd, \(J = 8.4, 2.4\) Hz, 1H), 3.78 (t, \(J = 7.8\) Hz, 1H), 2.10–1.99 (m, 2H), 0.89 (t, \(J = 7.2\) Hz, 3H); \[\text{13C NMR (100 MHz, CDCl}_3\] δ 162.92 (d, \(J = 245.1\) Hz), 147.84 (d, \(J = 6.7\) Hz), 144.40, 129.69 (d, \(J = 8.3\) Hz), 128.46, 127.82, 126.26, 123.61 (d, \(J = 2.7\) Hz), 114.66 (d, \(J = 21.2\) Hz), 112.86 (d, \(J = 21.1\) Hz), 52.94 (d, \(J = 1.7\) Hz).
Hz), 28.43, 12.66; \(^{19}\text{F NMR}\) (375 MHz, CDCl\(_3\)) \(\delta -113.52\) (td, \(J = 9.7, 6.3\) Hz); HRMS (EI) \(m/z\) Calcd for C\(_{15}\)H\(_{15}\)F [M]+: 214.1147, found: 214.1152.

**1-Fluoro-2-(1-phenylpropyl)benzene**

5j was synthesized following the general procedure with 4j (E/Z = 58/42). After purification by preparative thin-layer chromatography using PE as the eluent, 5j was obtained in 43% yield (18.3 mg) as a colourless liquid.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta 7.31–7.22\) (m, 5H), 7.21–7.11 (m, 2H), 7.07 (td, \(J = 7.4, 1.4\) Hz, 1H), 6.98 (ddd, \(J = 9.8, 8.0, 1.4\) Hz, 1H), 4.16 (t, \(J = 7.8\) Hz, 1H), 2.13–1.98 (m, 2H), 0.91 (t, \(J = 7.2\) Hz, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta 160.79\) (d, \(J = 244.8\) Hz), 143.94, 132.01 (d, \(J = 14.4\) Hz), 128.51 (d, \(J = 4.5\) Hz), 128.33, 127.96, 127.49 (d, \(J = 8.3\) Hz), 126.16, 124.02 (d, \(J = 3.6\) Hz), 115.34 (d, \(J = 22.8\) Hz), 45.26 (d, \(J = 2.2\) Hz), 27.69, 12.61. \(^{19}\text{F NMR}\) (375 MHz, CDCl\(_3\)) \(\delta -117.94\); HRMS (EI) \(m/z\) Calcd for C\(_{15}\)H\(_{15}\)F [M]+: 214.1152, found: 214.1151.

**1,2,3-Trimethoxy-5-(1-phenylpropyl)benzene**

5k was synthesized following the general procedure with 4k (E/Z = 60/40). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5k was obtained in 87% yield (50.1 mg) as a colourless liquid.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta 7.36–7.22\) (m, 4H), 7.21–7.14 (m, 1H), 6.45 (s, 2H), 3.82 (s, 6H), 3.81 (s, 3H), 3.72 (t, \(J = 7.6\) Hz, 1H), 2.10–1.97 (m, 2H), 0.91 (t, \(J = 7.2\) Hz, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta 152.98, 144.87, 140.82, 136.18, 128.32, 127.69, 126.07, 104.86, 60.73, 55.99, 53.46, 28.69, 12.75.

**1-(1-Phenylpropyl)naphthalene**

5l was synthesized following the general procedure with 4l (E/Z = 90/10). After purification by preparative thin-layer chromatography using PE as the eluent, 5l was obtained in 83% yield (40.8 mg) as a colourless liquid.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta 8.14–8.08\) (m, 1H), 7.85–7.77 (m, 1H), 7.70 (dd, \(J = 7.4, 2.0\) Hz, 1H), 7.52–7.34 (m, 4H), 7.29–7.18 (m, 4H), 7.15–7.06 (m, 1H), 4.59 (t, \(J = 7.4\) Hz, 1H), 2.30–2.08 (m, 2H), 0.98 (t, \(J = 7.2\) Hz, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta 144.98, 140.49, 134.03, 132.04, 128.79, 128.29, 128.10, 126.82, 125.96, 125.80, 125.38, 125.23, 124.23, 123.73, 48.15, 29.27, 12.98.
2-(1-Phenylpropyl)naphthalene\textsuperscript{11}

5m was synthesized following the general procedure with 4m (E/Z = 98/2). After purification by preparative thin-layer chromatography using PE as the eluent, 5m was obtained in 80% yield (39.2 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82–7.65 (m, 4H), 7.41 (p, $J = 7.0$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.28–7.22 (m, 4H), 7.16 (dt, $J = 9.2$, 5.4 Hz, 1H), 3.94 (t, $J = 7.8$ Hz, 1H), 2.23–2.08 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.99, 142.54, 133.50, 132.10, 128.36, 128.01, 127.96, 127.68, 127.53, 126.81, 126.06, 125.90, 125.86, 125.28, 53.22, 28.34, 12.80.

(1-Phenylpropyl)ferrocene

5n was synthesized following the general procedure with 4n (E/Z = 18/82). After purification by preparative thin-layer chromatography using PE as the eluent, 5n was obtained in 60% yield (36.4 mg) as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 (t, $J = 7.4$ Hz, 2H), 7.20–7.12 (m, 3H), 4.17 (s, 1H), 4.08 (s, 1H), 4.05–4.01 (m, 6H), 3.93 (s, 1H), 3.46 (dd, $J = 10.8$, 4.4 Hz, 1H), 2.17–2.04 (m, 1H), 1.87–1.73 (m, 1H), 0.83 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.37, 128.07, 127.95, 125.98, 94.45, 68.54, 67.49, 67.40, 66.93, 66.78, 47.89, 29.85, 12.71; HRMS (EI) m/z Calcd for C$_{19}$H$_{20}$Fe [M]$^+$: 304.0909, found: 304.0913.

(3-Methylbutane-1,1-diyl) dibenzene\textsuperscript{15}

5o was synthesized following the general procedure with 4o (E/Z = 28/72). After purification by preparative thin-layer chromatography using PE as the eluent, 5o was obtained in 71% yield (32.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30–7.20 (m, 8H), 7.17–7.12 (m, 2H), 4.01 (t, $J = 8.0$ Hz, 1H), 1.94–1.88 (m, 2H), 1.48–1.39 (m, 1H), 0.91 (dd, $J = 6.6$, 1.2 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.27, 128.07, 127.95, 125.98, 94.45, 68.54, 67.49, 67.40, 66.93, 66.78, 47.89, 29.85, 12.71; HRMS (EI) m/z Calcd for C$_{19}$H$_{20}$Fe [M]$^+$: 304.0909, found: 304.0913.

(2-Cyclohexylethane-1,1-diyl) dibenzene\textsuperscript{15}

5p was synthesized following the general procedure with 4p (E/Z = 70/30). After purification by preparative thin-layer chromatography using PE as the eluent, 5p was obtained in 66% yield (34.8 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.19 (m, 8H), 7.17–7.10 (m, 2H), 4.06 (t, $J = 8.0$ Hz, 1H), 1.91 (t, $J = 7.2$ Hz, 2H), 1.80–1.72 (m, 2H), 1.68–1.56 (m, 3H), 1.22–1.03 (m, 4H), 0.99–0.88 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.43, 128.34, 127.87, 125.92, 47.93, 43.59, 34.83, 33.40, 26.62, 26.12.
Ethane-1,1,2-triyltribenzeno\textsuperscript{16}  
5q was synthesized following the general procedure with \textit{E}-4q. After purification by preparative thin-layer chromatography using PE as the eluent, 5q was obtained in 89\% yield (46.2 mg) as a colourless liquid.  
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.27–7.17 (m, 8H), 7.16–7.06 (m, 5H), 7.01–6.95 (m, 2H), 4.22 (t, \( J = 7.8 \) Hz, 1H), 3.35 (d, \( J = 7.8 \) Hz, 2H).  
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 144.42, 140.23, 129.04, 129.02, 128.31, 128.29, 128.02, 128.00, 126.15, 126.14, 125.85, 53.06, 42.07.

2-(2,2-Diphenylethyl)pyridine\textsuperscript{17}  
5r was synthesized following the general procedure with 4r (\( EI/Z = 60/40 \)). After purification by preparative thin-layer chromatography using PE/EA (10/1) as the eluent, 5r was obtained in 72\% yield (37.2 mg) as a colourless liquid.  
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.54–8.47 (m, 1H), 7.39 (td, \( J = 7.8, 2.0 \) Hz, 1H), 7.25–7.19 (m, 8H), 7.16–7.19 (m, 2H), 7.01 (ddd, \( J = 7.6, 4.8, 1.2 \) Hz, 1H), 6.86 (d, \( J = 7.8 \) Hz, 1H), 4.61 (t, \( J = 8.0 \) Hz, 1H), 3.52 (d, \( J = 8.0 \) Hz, 2H);  
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 159.85, 149.15, 144.17, 135.92, 128.29, 127.98, 126.13, 123.72, 121.06, 51.00, 44.28.

1-Phenyl-1,2,3,4-tetrahydronaphthalene\textsuperscript{18}  
5s was synthesized following the general procedure with 4s. After purification by preparative thin-layer chromatography using PE as the eluent, 5s was obtained in 77\% yield (31.9 mg) as a colourless liquid.  
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.27 (t, \( J = 7.4 \) Hz, 2H), 7.18 (t, \( J = 7.2 \) Hz, 1H), 7.13–7.06 (m, 4H), 7.05–6.97 (m, 1H), 6.83 (d, \( J = 7.8 \) Hz, 1H), 4.11 (t, \( J = 6.8 \) Hz, 1H), 2.95–2.79 (m, 2H), 2.19–2.12 (m, 1H), 1.97–1.81 (m, 2H), 1.80–1.67 (m, 1H);  
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 147.49, 139.35, 137.55, 130.15, 128.93, 128.82, 128.19, 125.90, 125.86, 125.61, 45.59, 33.23, 29.76, 20.93.

5-Phenyl-6,7,8,9-tetrahydro-5\( H \)-benzo[7]annulene  
5t was synthesized following the general procedure with 4t. After purification by preparative thin-layer chromatography using PE as the eluent, 5t was obtained in 49\% yield (21.9 mg) as a colourless liquid.
\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 7.33 (t, \(J = 7.4\) Hz, 2H), 7.26–7.21 (m, 1H), 7.18 (d, \(J = 7.6\) Hz, 2H), 7.15–7.05 (m, 2H), 7.01 (td, \(J = 7.4, 1.6\) Hz, 1H), 6.65 (d, \(J = 7.6\) Hz, 1H), 4.27 (dd, \(J = 8.2, 2.8\) Hz, 1H), 3.02–2.87 (m, 1H), 2.81–2.72 (m, 1H), 2.19–2.06 (m, 2H), 2.02–1.94 (m, 1H), 1.86–1.76 (m, 2H), 1.59–1.45 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 145.26, 144.67, 142.85, 129.56, 128.46, 128.35, 126.05, 125.92, 49.76, 36.42, 33.88, 29.96, 27.75; HRMS (EI) \(m/z\) Calcd for C\(_{17}\)H\(_{18}\)[M]+: 222.1403, found: 222.1403.

**Pentane-1,1-diyl dibenzene**\(^{19}\)

5u was synthesized following the general procedure with 4u (\(E/Z = 56/44\)). After purification by preparative thin-layer chromatography using PE as the eluent, 5u was obtained in 80% yield (35.7 mg) as a colourless liquid.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 7.30–7.21 (m, 8H), 7.17–7.11 (m, 2H), 3.87 (t, \(J = 7.8\) Hz, 1H), 2.03 (q, \(J = 7.8\) Hz, 2H), 1.38–1.29 (m, 2H), 1.28–1.18 (m, 2H), 0.86 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 145.33, 128.33, 127.83, 125.95, 51.34, 35.44, 30.23, 22.69, 13.98.

**3-(3,3-Diphenylpropoxy)triisopropylsilane**

5v was synthesized following the general procedure with \(E\)-4v. After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5v was obtained in 61% yield (45.3 mg) as a colourless liquid.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 7.35–7.23 (m, 8H), 7.18–7.14 (m, 2H), 4.20 (t, \(J = 7.8\) Hz, 1H), 3.61 (t, \(J = 6.4\) Hz, 2H), 2.31–2.24 (m, 2H), 1.08–0.97 (m, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 144.83, 128.35, 128.00, 126.04, 61.12, 46.87, 38.66, 18.03, 18.00, 11.95; HRMS (DAST) \(m/z\) Calcd for C\(_{24}\)H\(_{37}\)OSi[M+H]\(^{+}\): 369.2604, found: 369.2608.

**5-(Benzyloxy)pentane-1,1-diyl dibenzene**

5w was synthesized following the general procedure with 4w (\(E/Z = 93/7\)). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5w was obtained in 47% yield (31.1 mg) as a colourless liquid.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 7.36–7.20 (m, 13H), 7.19–7.06 (m, 2H), 4.45 (s, 2H), 3.88 (t, \(J = 7.8\) Hz, 1H), 3.42 (t, \(J = 6.6\) Hz, 2H), 2.11–2.00 (m, 2H), 1.65 (p, \(J = 6.8\) Hz, 2H), 1.40–1.26 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 145.10, 138.56, 128.36, 128.30, 127.82, 127.60, 127.45, 126.01, 72.82, 70.19, 51.29, 35.48, 29.66, 24.63; HRMS (DAST) \(m/z\) Calcd for C\(_{24}\)H\(_{27}\)O[M+H]\(^{+}\): 331.2056, found: 331.2056.
3-(1-Phenylpentyl)furan

5x was synthesized following the general procedure with 4x (E/Z = 36/64). After purification by preparative thin-layer chromatography using PE as the eluent, 5x was obtained in 42% yield (18.1 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.39–7.15\) (m, 7H), 6.22 (d, \(J = 1.8\) Hz, 1H), 3.73 (t, \(J = 7.6\) Hz, 1H), 2.02–1.80 (m, 2H), 1.39–1.12 (m, 4H), 0.86 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 144.81, 142.78, 138.76, 129.39, 128.33, 127.75, 126.16, 110.39, 42.34, 35.70, 29.96, 22.61, 13.98\); HRMS (EI) \(m/z\) Calcd for C\(_{15}\)H\(_{18}\)O \([M]^+\): 214.1352, found: 214.1353.

3-(1-Phenylpropyl)-1-tosyl-1H-indole

5y was synthesized following the general procedure with 4y (E/Z = 50/50). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5y was obtained in 45% yield (35.2 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.97–7.90\) (m, 1H), 7.78–7.69 (m, 2H), 7.45 (d, \(J = 1.2\) Hz, 1H), 7.27–7.11 (m, 9H), 7.11–7.03 (m, 1H), 3.90 (t, \(J = 7.6\) Hz, 1H), 2.32 (s, 3H), 2.22–2.10 (m, 1H), 2.05–1.90 (m, 1H), 0.92 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 144.69, 143.30, 135.58, 135.16, 130.70, 129.73, 128.35, 127.85, 126.79, 126.68, 126.35, 124.54, 122.99, 122.67, 120.12, 113.72, 44.43, 28.50, 21.51, 12.51; HRMS (EI) \(m/z\) Calcd for C\(_{24}\)H\(_{23}\)NO\(_2\)S \([M]^+\): 389.1444, found: 389.1454.

4-(1-Phenylpropyl)phenyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate

5z was synthesized following the general procedure with 4z (E/Z = 95/5). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5z was obtained in 74% yield (63.1 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.76–7.67\) (m, 3H), 7.47 (dd, \(J = 8.5, 1.9\) Hz, 1H), 7.28–7.19 (m, 2H), 7.19–7.09 (m, 7H), 6.92–6.80 (m, 2H), 4.06 (q, \(J = 7.2\) Hz, 1H), 3.89 (s, 3H), 3.74 (t, \(J = 7.8\) Hz, 1H), 2.06–1.94 (m, 2H), 1.66 (d, \(J = 7.2\) Hz, 3H), 0.85 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 173.20, 157.67, 148.93, 144.75, 142.57, 135.15, 133.74, 129.27, 128.93, 128.66, 128.32, 127.81, 127.28, 126.10, 126.07, 126.04, 121.06, 119.04, 105.53, 55.26, 52.52, 45.51, 28.55, 18.47, 12.67; HRMS (ESI) \(m/z\) Calcd for C\(_{29}\)H\(_{28}\)O\(_3\) \([M]^+\): 424.2041, found: 424.2033.
5aa was synthesized following the general procedure with 4aa (E/Z = 92/8). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5aa was obtained in 52% yield (41.7 mg) as a colourless liquid.

1H NMR (400 MHz, CDCl3) δ 7.31–7.22 (m, 4H), 7.20–7.14 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 6.93–6.86 (m, 2H), 3.90 (q, J = 7.2 Hz, 1H), 3.76 (t, J = 7.8 Hz, 1H), 2.45 (d, J = 7.2 Hz, 2H), 2.08–1.95 (m, 2H), 1.91–1.79 (m, 1H), 1.58 (d, J = 7.2 Hz, 3H), 0.93–0.83 (m, 9H); 13C NMR (100 MHz, CDCl3) δ 173.26, 148.97, 144.80, 142.53, 140.73, 137.24, 129.43, 128.66, 128.34, 127.83, 127.17, 126.06, 121.08, 52.55, 45.21, 45.01, 30.16, 28.57, 22.37, 18.46, 12.69; HRMS (EI) m/z Calcd for C32H32O2 [M]+: 439.2038, found: 439.2037.

4-(1-Phenylpropyl)phenyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate

5ab was synthesized following the general procedure with 4ab (E/Z = 95/5). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 5ab was obtained in 41% yield (35.8 mg) as a colourless liquid.

1H NMR (400 MHz, CDCl3) δ 7.54 (d, J = 7.6 Hz, 2H), 7.46–7.34 (m, 4H), 7.27–7.17 (m, 9H), 6.94 (d, J = 8.0 Hz, 2H), 3.96 (q, J = 7.2 Hz, 1H), 3.77 (t, J = 7.8 Hz, 1H), 2.09–1.95 (m, 2H), 1.63 (d, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 172.50, 159.72 (d, J = 23.7 Hz), 159.72 (d, J = 23.7 Hz), 135.38, 130.94 (d, J = 3.9 Hz), 128.94, 128.92, 128.75, 128.44, 128.36, 127.84, 127.69, 126.10, 123.56 (d, J = 3.4 Hz), 121.01, 115.28 (d, J = 23.7 Hz), 52.56, 45.10, 28.58, 18.36, 12.70; 19F NMR (375 MHz, CDCl3) δ -117.35; HRMS (ESI-TOF) m/z Calcd for C51H38F2O2 [M+H]+: 439.2073, found: 439.2068.

(1R,2S,5R)-2-isopropyl-5-methycyclohexyl 4-(1-phenylpropyl)benzoate

5ac was synthesized following the general procedure with 4ac (E/Z = 23/77). After purification by preparative thin-layer chromatography using PE/EA (40/1) as the eluent, 5ac was obtained in 65% yield (49.1 mg) as a colourless liquid. The dr (1:1) was determined by GC.

1H NMR (400 MHz, CDCl3) δ 7.95 (d, J = 8.2 Hz, 2H), 7.33–7.25 (m, 4H), 7.24–7.15 (m, 3H), 4.90 (td, J = 10.8, 4.4 Hz, 1H), 3.85 (t, J = 7.8 Hz, 1H), 2.14–2.03 (m, 3H), 1.98–1.89 (m, 1H), 1.75–1.67 (m, 2H), 1.60–1.46 (m, 2H), 1.19–1.00 (m, 2H), 0.90 (t, J = 6.8 Hz, 10H), 0.77 (d, J = 7.0 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.02, 150.33, 150.30, 144.28, 144.25, 129.72, 128.71, 128.48, 127.86, 127.83, 126.29, 74.58, 53.22, 47.26, 40.96, 34.31, 31.41, 28.33, 28.29, 26.43, 26.41, 23.59, 23.57, 22.03, 20.76, 16.47, 16.46, 12.66; HRMS (DAST) m/z Calcd for C26H36O2 [M+H]+: 379.2629, found: 379.2632.
4-(1-phenylpropyl)phenyl (4R)-4-((3R, 8R, 9S, 10S, 13R, 14S, 17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate

5ad was synthesized following the general procedure with 4ad (E/Z = 94/6). After purification by preparative thin-layer chromatography using PE/Acetone (10/1) as the eluent, 5ad was obtained in 69% yield (78.8 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.30–7.24 (m, 2H), 7.23–7.19 (m, 4H), 7.17 (td, $J = 7.0, 1.6$ Hz, 1H), 7.02–6.92 (m, 2H), 3.78 (t, $J = 7.8$ Hz, 1H), 3.67–3.57 (m, 1H), 2.62–2.52 (m, 1H), 2.50–2.39 (m, 1H), 2.10–2.01 (m, 2H), 1.99–1.94 (m, 1H), 1.93–1.70 (m, 5H), 1.69–1.63 (m, 1H), 1.61–1.00 (m, 20H), 0.97 (d, $J = 6.4$ Hz, 3H), 0.92 (s, 3H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.65 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.84, 148.87, 144.79, 142.54, 128.73, 128.37, 127.89, 126.09, 121.27, 71.86, 56.47, 55.95, 52.60, 42.74, 42.05, 40.39, 40.15, 36.42, 35.82, 35.34, 35.31, 34.55, 31.36, 30.94, 30.52, 28.62, 28.21, 27.16, 26.39, 24.19, 23.35, 20.80, 18.28, 12.73, 12.05; HRMS (ESI-TOF) m/z Calcd for C$_{93}$H$_{54}$O$_3$Na [M+Na]$^+$: 593.3965, found: 593.3965.

4-(1-Phenylpropyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate

5ae was synthesized following the general procedure with 4ae (E/Z = 98/2). After purification by preparative thin-layer chromatography using PE/Acetone (50/1) as the eluent, 5ae was obtained in 39% yield (34.6 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31–7.23 (m, 2H), 7.23–7.11 (m, 5H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.96–6.91 (m, 2H), 6.65 (d, $J = 7.4$ Hz, 1H), 6.61 (s, 1H), 4.00–3.92 (m, 2H), 3.78 (t, $J = 7.8$ Hz, 1H), 2.29 (s, 3H), 2.16 (s, 3H), 2.09–2.01 (m, 2H), 1.86–1.84 (m, 4H), 1.34 (s, 6H), 0.89 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.38, 156.84, 149.08, 144.84, 142.47, 136.44, 130.29, 128.74, 128.35, 127.85, 126.07, 123.58, 121.21, 120.69, 111.89, 67.75, 52.56, 42.36, 37.13, 28.60, 25.23, 25.13, 21.38, 15.78, 12.71; HRMS (ESI-TOF) m/z Calcd for C$_{33}$H$_{40}$O$_3$ [M+H]$^+$: 445.2745, found: 445.2737.
Other Substrates[^a,b]

![Chemical Reaction Image]

[^a]: Reaction conditions: 4 (0.2 mmol, 1.0 equiv), 2a (0.6 mmol, 3.0 equiv), Ni(OTf)_2 (10 mol %), L14 (10 mol%), Na_3PO_4 (0.6 mmol, 3.0 equiv), t-Amy/OH (1.0 mL), 80 °C, N_2, 24 h. [^b]: Isolated yield, and the regioselectivity was determined by analysis of the crude ^1^H NMR. [^c]: Ni(2-NH_2-C_6H_5SO_3)_2 instead of Ni(OTf)_2.
2.4 General Procedure for Ni-Catalyzed Hydroalkenylation of Internal Alkenes

**General Procedure:** In a nitrogen-filled glovebox, substrate 4 (0.2 mmol, 1.0 equiv), 6 (0.6 mmol, 3.0 equiv), Ni(OTf)$_2$ (7.1 mg, 10 mol %), L14 (6.8 mg, 10 mol %), Na$_3$PO$_4$ (98.4 mg, 0.6 mmol, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (1.0 mL). The tube was sealed again with parafilm and heated to 80 °C for 24 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with EtOAc as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by silica gel chromatography or preparative thin-layer chromatography to afford the hydroarylated product 7.

1-(1-(Cyclohex-1-en-1-yl)propyl)-4-methoxybenzene

7a was synthesized following the general procedure with E-1. After purification by preparative thin-layer chromatography using n-hexane as the eluent, 7a was obtained in 69% yield (31.6 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.13–7.06 (m, 2H), 6.86–6.78 (m, 2H), 5.60–5.56 (m, 1H), 3.78 (s, 3H), 2.93 (t, $J$ = 7.6 Hz, 1H), 2.04 (q, $J$ = 3.4 Hz, 2H), 1.87–1.55 (m, 4H), 1.51 (p, $J$ = 3.2 Hz, 4H), 0.82 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.66, 140.31, 136.67, 128.72, 120.97, 113.32, 55.16, 54.00, 26.45, 25.59, 25.34, 23.03, 22.68, 12.58; HRMS (EI) $m/z$ Calcd for C$_{16}$H$_{22}$O [M]+: 230.1671, found: 230.1663.

Methyl-4-(1-(cyclohex-1-en-1-yl)propyl)benzoate

7b was synthesized following the general procedure with 4d (E/Z = 33/67). After purification by preparative thin-layer chromatography using PE/EA (40/1) as the eluent, 7b was obtained in 60% yield (30.9 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.98–7.91 (m, 2H), 7.29–7.22 (m, 2H), 5.65–5.61 (m, 1H), 3.90 (s, 3H), 3.04 (t, $J$ = 7.6 Hz, 1H), 2.67–2.62 (m, 2H), 1.93–1.79 (m, 1H), 1.74–1.60 (m, 3H), 1.51 (p, $J$ = 3.0 Hz, 4H), 0.83 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.21, 150.24, 139.30, 129.38, 127.93, 127.79, 122.00, 54.90, 51.93, 26.59, 25.32, 25.27, 22.93, 22.53, 12.45; HRMS (EI) $m/z$ Calcd for C$_{17}$H$_{22}$O$_2$ [M]+: 258.1620, found: 258.1615.
2-(1-(Cyclohex-1-en-1-yl)propyl)naphthalene

7c was synthesized following the general procedure with 4m (E/Z = 98/2). After purification by preparative thin-layer chromatography using PE as the eluent, 7c was obtained in 75% yield (37.6 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79 (dd, \(J = 7.6, 1.8\) Hz, 2H), 7.74 (d, \(J = 8.4\) Hz, 1H), 7.61 (d, \(J = 1.6\) Hz, 1H), 7.48–7.37 (m, 2H), 7.34 (dd, \(J = 8.4, 1.8\) Hz, 1H), 5.70–5.66 (m, 1H), 3.14 (t, \(J = 7.6\) Hz, 1H), 2.07 (p, \(J = 3.6\) Hz, 2H), 2.00–1.84 (m, 1H), 1.87–1.70 (m, 3H), 1.54–1.46 (m, 4H), 0.86 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.04, 139.94, 133.41, 132.14, 127.59, 127.51, 126.75, 126.07, 125.67, 125.03, 121.51, 54.95, 26.64, 25.39, 25.30, 23.01, 22.65, 12.61; HRMS (EI) \(m/z\) Calcd for C\(_{19}\)H\(_{22}\)NO\(_2\)S [M]\(^+\): 250.1722, found: 250.1718.

5-(1-(Cyclohex-1-en-1-yl)propyl)-1,2,3-trimethoxybenzene

7d was synthesized following the general procedure with 4k (E/Z = 60/40). After purification by preparative thin-layer chromatography using PE/Ea (40/1) as the eluent, 7d was obtained in 55% yield (32.0 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.40 (s, 2H), 5.60 (q, \(J = 3.4\) Hz, 1H), 3.84 (s, 6H), 3.83 (s, 3H), 2.91 (t, \(J = 7.6\) Hz, 1H), 2.06 (s, 2H), 1.89–1.38 (m, 8H), 0.85 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.76, 140.46, 139.83, 136.03, 121.41, 104.83, 60.82, 56.04, 55.12, 26.58, 25.62, 25.37, 23.07, 22.65, 12.62; HRMS (EI) \(m/z\) Calcd for C\(_{18}\)H\(_{26}\)O\(_3\) [M]\(^+\): 290.1882, found: 290.1882.

(1-(Cyclohex-1-en-1-yl)-3-methylbutyl)benzene

7e was synthesized following the general procedure with 4o (E/Z = 28/72). After purification by preparative thin-layer chromatography using PE as the eluent, 7e was obtained in 60% yield (27.6 mg) as a colourless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30–7.22 (m, 2H), 7.22–7.12 (m, 3H), 5.61 (s, \(J = 4.0\) Hz, 1H), 3.22 (t, \(J = 8.0\) Hz, 1H), 2.09–1.93 (m, 2H), 1.86–1.70 (m, 2H), 1.70–1.48 (m, 6H), 1.47–1.37 (m, 1H), 0.90 (d, \(J = 6.6\) Hz, 3H), 0.86 (d, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.75, 140.27, 127.99, 127.88, 125.74, 121.14, 50.33, 41.86, 26.58, 25.37, 25.32, 23.04, 22.92, 22.63, 22.61; HRMS (EI) \(m/z\) Calcd for C\(_{17}\)H\(_{34}\) [M]\(^+\): 228.1878, found: 228.1871.
(1-(Cyclohex-1-en-1-yl)penty1)benzene

7f was synthesized following the general procedure with 4u (E/Z = 56/44). After purification by preparative thin-layer chromatography using n-hexane as the eluent, 7f was obtained in 85% yield (39.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.30–7.22 (m, 2H), 7.21–7.12 (m, 3H), 5.61 (t, $J = 4.0$ Hz, 1H), 3.07 (t, $J = 7.6$ Hz, 1H), 2.06–2.01 (m, 2H), 1.87–1.60 (m, 4H), 1.55–1.46 (m, 4H), 1.37–1.06 (m, 3H), 0.86 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.81, 140.27, 127.98, 127.87, 125.74, 121.10, 52.96, 32.37, 30.13, 26.58, 25.35, 23.03, 22.80, 22.64, 14.07; HRMS (EI) m/z Calcd for C$_{17}$H$_{24}$ [M]+: 228.1878, found: 228.1873.

1-(Cyclohex-1-en-1-yl)-1,2,3,4-tetrahydronaphthalene

7g was synthesized following the general procedure with 4s. After purification by preparative thin-layer chromatography using n-hexane as the eluent, 7g was obtained in 77% yield (32.7 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.14–7.01 (m, 4H), 5.39 (tt, $J = 3.6, 1.6$ Hz, 1H), 3.44–3.36 (m, 1H), 2.90–2.53 (m, 2H), 2.19–1.97 (m, 2H), 1.96–1.68 (m, 5H), 1.65–1.49 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.81, 140.27, 127.98, 127.87, 125.74, 121.10, 52.96, 32.37, 30.13, 26.58, 25.35, 23.03, 22.80, 22.64, 14.07; HRMS (EI) m/z Calcd for C$_{16}$H$_{20}$ [M]+: 212.1565, found: 212.1560.

4-(1,2,3,4-Tetrahydronaphthalen-1-yl)-3,6-dihydro-2H-pyran

7h was synthesized following the general procedure with 4s. After purification by preparative thin-layer chromatography using PE as the eluent, 7h was obtained in 44% yield (19.0 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.15–7.04 (m, 4H), 5.35 (tt, $J = 2.4$ Hz, 1H), 4.23–4.10 (m, 2H), 3.81 (dt, $J = 10.6, 5.2$ Hz, 1H), 3.72 (ddd, $J = 11.2, 6.6, 4.6$ Hz, 1H), 3.51–3.43 (m, 1H), 2.85–2.68 (m, 2H), 2.10–2.00 (m, 1H), 1.99–1.83 (m, 3H), 1.82–1.65 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.14, 137.71, 137.60, 129.10, 129.03, 125.87, 125.53, 122.99, 65.63, 64.50, 46.73, 29.68, 28.02, 26.04, 21.12; HRMS (EI) m/z Calcd for C$_{15}$H$_{16}$O [M]+: 214.1358, found: 214.1351.
1-(Cyclopent-1-en-1-yl)-1,2,3,4-tetrahydronaphthalene

7i was synthesized following the general procedure with 4s. After purification by preparative thin-layer chromatography using PE as the eluent, 7i was obtained in 60% yield (25.6 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.10–7.04 (m, 4H), 5.25 (t, $J$ = 2.4 Hz, 1H), 3.65 (t, $J$ = 5.8 Hz, 1H), 2.82–2.70 (m, 2H), 2.40–2.27 (m, 2H), 2.22–2.12 (m, 2H), 1.94–1.77 (m, 5H), 1.80–1.67 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.29, 138.67, 137.09, 129.25, 128.91, 126.88, 125.61, 125.30, 41.22, 32.45, 32.23, 29.64, 28.21, 23.73, 20.91;

HRMS (EI) m/z Calcd for C$_{15}$H$_{18}$ [M]+: 198.1409, found: 198.1402.

(E)-1-(Hex-1-en-1-yl)-1,2,3,4-tetrahydronaphthalene

7j was synthesized following the general procedure with 4s. After purification by preparative thin-layer chromatography using PE as the eluent, 7j was obtained in 15% yield (6.3 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.19–7.14 (m, 1H), 7.13–7.02 (m, 3H), 5.57–5.36 (m, 2H), 3.38 (q, $J$ = 6.4 Hz, 1H), 2.84–2.72 (m, 2H), 2.10–1.98 (m, 2H), 1.99–1.82 (m, 2H), 1.80–1.58 (m, 2H), 1.48–1.22 (m, 4H), 0.90 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.21, 136.93, 134.66, 131.24, 129.42, 129.00, 125.69, 125.40, 42.52, 32.19, 31.74, 30.58, 29.72, 22.22, 20.92, 13.97; HRMS (EI) m/z Calcd for C$_{16}$H$_{22}$ [M]+: 214.1722, found: 214.1712.

4-(1-(Cyclohex-1-en-1-yl)propyl)phenyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate

7k was synthesized following the general procedure with 4z ($E/Z$ = 95/5). After purification by preparative thin-layer chromatography using PE/EA (20/1) as the eluent, 7k was obtained in 40% yield (34.5 mg) as a colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.85–7.62 (m, 3H), 7.50 (dd, $J$ = 8.4, 2.0 Hz, 1H), 7.20–7.02 (m, 4H), 6.96–6.76 (m, 2H), 5.71–5.37 (m, 1H), 4.08 (q, $J$ = 7.2 Hz, 1H), 3.91 (s, 3H), 2.94 (t, $J$ = 7.6 Hz, 1H), 2.04–1.96 (m, 2H), 1.87–1.58 (m, 7H), 1.52–1.44 (m, 4H), 0.79 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.29, 157.67, 148.84, 142.00, 139.76, 135.21, 133.75, 129.29, 128.95, 128.60, 127.28, 126.14, 126.09, 121.44, 120.68, 119.03, 105.54, 55.27, 54.22, 45.54, 26.39, 25.43, 25.30, 22.93, 22.57, 18.48, 12.48; HRMS (EI) m/z Calcd for C$_{29}$H$_{42}$O$_3$ [M]+: 428.2351, found: 428.2364.
3. Mechanistic Study

3.1 Kinetics Data

**General Kinetics Experimental Procedure:** In a nitrogen-filled glovebox, substrate 1, 2a, Ni(2-NH₂-5-MeC₆H₃SO₃)₂, L14, Na₃PO₄ were charged in a 10-mL tube, and added 5.0 µL dodecane as internal standard. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (1.0 mL). The tube was sealed again with parafilm and heated to 80 °C. The reaction progress was monitored by removing aliquots (~10 µL) from the reaction mixture via syringe under N₂. Each aliquot was quenched by EA (4.0 mL) in an 8.0 mL tube. The mixture was filtered with a filter head into 2.0 mL GC vial and analyzed by gas chromatography.

**3.1.1 Kinetic Plots for “Different Excess” Experiment**

**Supplementary Figure 2.** Time-course for the reaction shown in eq S1. Reaction conditions: [Ni(2-NH₂-5-MeC₆H₃SO₃)₂] = 0.02 M, [L14] = 0.02 M, Na₃PO₄ = 0.6 mmol, solvent = t-AmylOH. [1]₀ = 0.20 M; [2a]₀ = 0.60 M.

**Supplementary Figure 3.** Time-course for the reaction shown in eq S1. Reaction conditions: [Ni(2-NH₂-5-MeC₆H₃SO₃)₂] = 0.02 M, [L14] = 0.02 M, Na₃PO₄ = 0.6 mmol, solvent = t-AmylOH. [1]₀ = 0.20 M; [2a]₀ = 0.70 M.
Supplementary Figure 4. Time-course for the reaction shown in eq S1. Reaction conditions: [Ni(2-NH$_2$-5-MeC$_6$H$_4$SO$_3$)$_2$] = 0.02 M, [L14] = 0.02 M, Na$_3$PO$_4$ = 0.6 mmol, solvent = t-AmylOH. [1]$_0$ = 0.10 M; [2a]$_0$ = 0.60 M.

Supplementary Figure 5. Time-course for the reaction shown in eq S1. Reaction conditions: [Ni(2-NH$_2$-5-MeC$_6$H$_4$SO$_3$)$_2$] = 0.02 M, [L14] = 0.02 M, Na$_3$PO$_4$ = 0.6 mmol, solvent = t-AmylOH. [1]$_0$ = 0.15 M; [2a]$_0$ = 0.60 M.

Supplementary Figure 6. Time-course for the reaction shown in eq S1. Reaction conditions: [Ni(2-NH$_2$-5-MeC$_6$H$_4$SO$_3$)$_2$] = 0.02 M, [L14] = 0.02 M, Na$_3$PO$_4$ = 0.6 mmol, solvent = t-AmylOH. [1]$_0$ = 0.20 M; [2a]$_0$ = 0.65 M.
Supplementary Figure 7. “Different excess” experiments reveal that this reaction is zero-order dependence on alkene concentration and arylboronic acid concentration.

3.1.2 Kinetic Plots with Different [Ni] loading

The study of kinetic orders in the catalyst was completed following the general procedure described above.

Supplementary Figure 8. Time-course for the reaction shown in eq S1. Reaction conditions: [Ni(2-NH$_2$-5-MeC$_6$H$_3$SO$_3$)$_2$] = 0.02 M, [L14] = 0.02 M, Na$_3$PO$_4$ = 0.6 mmol, solvent = t-AmyLOH. [1]$_0$ = 0.20 M; [2a]$_0$ = 0.60 M.

Supplementary Figure 9. Time-course for the reaction shown in eq S1. Reaction conditions: [Ni(2-NH$_2$-5-MeC$_6$H$_3$SO$_3$)$_2$] = 0.03 M, [L14] = 0.03 M, Na$_3$PO$_4$ = 0.6 mmol, solvent = t-AmyLOH. [1]$_0$ = 0.20 M; [2a]$_0$ = 0.60 M.
**Supplementary Figure 10.** Time-course for the reaction shown in eq S1. Reaction conditions: \([\text{Ni}(2\text{-NH}_2\text{-5-MeC}_8\text{H}_3\text{SO}_3)_2] = 0.04 \text{ M}, [\text{L14}] = 0.04 \text{ M}, \text{Na}_3\text{PO}_4 = 0.6 \text{ mmol}, \text{solvent} = \text{t-AniolOH}. [1]_0 = 0.20 \text{ M}; [2a]_0 = 0.60 \text{ M}.

**Supplementary Figure 11.** Various normalization analysis of product vs. Time.

**Supplementary Figure 12.** Various normalization analysis of product vs. [catalyst].-(time).

The experiments with different concentration of [Ni] were performed to evaluate the order of [Ni] catalyst. When normalizing the rates as a function of [Ni] catalyst, good overlay of the curves indicates the first order with regard to [Ni] catalyst (Supplementary Figure 12).
3.2 Deuteration Experiments

3.2.1 Deuterium-Scrambling Reactions

Following the general procedure, in a nitrogen-filled glovebox, substrate 1 (0.1 mmol, 1.0 equiv), Ni(2-NH₂-5-MeC₆H₃SO₃)₂ (4.3 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na₃PO₄ (49.2 mg, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (1.0 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with DCM as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by preparative thin-layer chromatography to give 1 as a colourless liquid in 94% yield.

Supplementary Figure 13. ¹H NMR (400 MHz, CDCl₃) spectrum of 1

Following the general procedure, in a nitrogen-filled glovebox, substrate 3a (0.1 mmol, 1.0 equiv), D-2a (0.3 mmol, 3.0 equiv), Ni(2-NH₂-5-MeC₆H₃SO₃)₂ (4.3 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na₃PO₄ (49.2 mg, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside
of the glovebox, followed by the addition of tert-amyl alcohol (0.5 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with DCM as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by preparative thin-layer chromatography as a colourless liquid in 98% yield.

Supplementary Figure 14. 1H NMR (400 MHz, CDCl3) spectrum of 3a

Following the general procedure, in a nitrogen-filled glovebox, substrate 1 (0.1 mmol, 1.0 equiv), D-2a (0.3 mmol, 3.0 equiv), Ni(2-NH2-5-MeC6H5SO3)2 (4.3 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na3PO4 (49.2 mg, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (0.5 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with DCM as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by preparative thin-layer chromatography as a colourless liquid in 83% yield.
Following the general procedure, in a nitrogen-filled glovebox, substrate 1 (0.1 mmol, 1.0 equiv), D-2a (0.3 mmol, 3.0 equiv), Ni(2-NH2-5-MeCd3H5SO3)2 (4.3 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na3PO4 (49.2 mg, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (0.5 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with DCM as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by preparative thin-layer chromatography as a colourless liquid in 83% yield.
3.2.2 KIE Study

Following the general procedure, in a nitrogen-filled glovebox, substrate 1 (0.1 mmol, 1.0 equiv), 2a (0.3 mmol, 3.0 equiv), Ni(2-NH$_2$-5-MeC$_6$H$_3$SO$_3$)$_2$ (4.3 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na$_3$PO$_4$ (49.2 mg, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (0.5 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with DCM as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by preparative thin-layer chromatography as a colourless liquid in 80% yield.

Supplementary Figure 16. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of D-3a
Supplementary Figure 17. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3a

3.2.3 Identification of Active Ar-Ni(II)-H

Following the general procedure, in a nitrogen-filled glovebox, substrate 1 (0.1 mmol, 1.0 equiv), Ni(COD)$_2$ (2.8 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na$_3$PO$_4$ (49.2 mg, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (0.5 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with DCM as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by preparative thin-layer chromatography.
Supplementary Figure 18. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1

Following the general procedure, in a nitrogen-filled glovebox, substrate (Z)-1 (0.1 mmol, 1.0 equiv), Ni(COD)$_2$ (2.8 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na$_3$PO$_4$ (49.2 mg, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (0.5 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with DCM as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by preparative thin-layer chromatography.
**Supplementary Figure 19.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of (Z)-1

**General Procedure:** In a nitrogen-filled glovebox, substrate 8 (0.1 mmol, 1.0 equiv), 2a (0.3 mmol, 3.0 equiv), Ni(2-NH$_2$-5-MeC$_6$H$_3$SO$_3$)$_2$ (4.3 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na$_3$PO$_4$ (49.2 mg, 0.6 mmol, 3.0 equiv) were charged in a 10-mL tube. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (0.5 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with EtOAc as the eluent to remove the nickel and the insoluble precipitate. The resulting solution was concentrated. The residue was then purified by silica gel chromatography or preparative thin-layer chromatography to afford the hydroarylated product 9 as a colourless oil (11.9 mg, 47 % yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30–7.19 (m, 4H), 7.19–7.13 (m, 1H), 6.71 (s, 3H), 5.89 (d, J = 1.4 Hz, 2H), 3.82 (t, J = 7.8 Hz, 1H), 1.96 (q, J = 7.6 Hz, 2H), 1.34–1.20 (m, J = 7.1 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.59, 145.64, 145.40, 139.37, 128.36, 127.30, 126.00, 120.72, 108.21, 108.00, 100.76, 50.67, 37.96, 21.09, 14.04; HRMS (EI) m/z Calcd for C$_{17}$H$_{18}$O$_2$ [M]$^+$: 254.1301, found: 254.1302.
General Experimental Procedure: In a nitrogen-filled glovebox, substrate 1 (0.1 mmol, 1.0 equiv), 2c (0.3 mmol, 3.0 equiv), Ni(2-NH_{2}-5-MeC_{6}H_{3}SO_{3})_{2} (4.3 mg, 10 mol %), L14 (3.4 mg, 10 mol %), Na_{3}PO_{4} (49.2 mg, 3.0 equiv) were charged in a 10-mL tube, and added 5.0 µL dodecane as internal standard. The tube was sealed using an open-top cap with PTFE cap liner, and moved outside of the glovebox, followed by the addition of tert-amyl alcohol (1.0 mL). The tube was sealed again with parafilm and heated to 80 °C for 10 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with EtOAc as the eluent to remove the nickel and the insoluble precipitate. The mixture was filtered with a filter head into 2.0 mL GC vial and analyzed by gas chromatography.

| Apex RT | Start RT | End RT | Area       | %Area   | Height   | %Height |
|---------|----------|--------|------------|---------|----------|---------|
| 4.93    | 4.88     | 4.99   | 597894.435 | 44.05   | 589603.5 | 51.21   |
| 7.14    | 7.11     | 7.2    | 185072.453 | 13.64   | 169447.5 | 14.72   |
| 7.84    | 7.81     | 7.92   | 186404.691 | 13.73   | 175421.7 | 15.23   |
| 12.8    | 12.73    | 12.88  | 387815.496 | 28.57   | 216975.8 | 18.84   |
To demonstrate the ligand effect on stabilizing the Ar-Ni(II)-H intermediate, we carried out the experiments with ligand L4 and L14, as other ligands resulted in no reaction. The control experiments unveiled that our ligand L14 could inhibit the formation of protonation byproduct from aryloboric acid, which supports our hypothesis.

\[
\text{Ni(II)} + \text{Ar} + \text{Ligand} \rightarrow \text{Ar-Ni(II)-H intermediate}
\]

with L14 vs. with L4 = 3.23/4.25

The formation of 2c' (determined by GC)
3.3 Synthesis of Ni(Adacac)$_2^{20}$

To a dry Schlenk flask was subsequentially added the ligand L14 (1.4 g, 4.1 mmol, 2.05 equiv), Ni(OAc)$_2$ (353.6 mg, 2.0 mmol, 1.0 equiv), and dry EtOH (10 mL). Then Et$_3$N (0.84 mL, 6.0 mmol, 3.0 equiv) was added. The reaction mixture was heated to 80 °C and stirred for 12 h. After cooling to room temperature, the mixture was filtered and the precipitate was subsequentially washed with H$_2$O, EtOH and THF to afford a green solid. After remove the THF under vacuum at 80 °C, a purple solid [Ni(Adacac)$_2$(THF)] was obtained in 74% yield (1.2 g). The green solid was assigned to the Ni(Adacac)$_2$(THF). Anal. calcd for [Ni(Adacac)$_2$(THF)] $C_{50}H_{70}NiO_5$ (808.46): C, 74.16; H, 8.71. Found: C, 73.92; H, 8.52.

We also checked the efficiency of the Ni(Adacac)$_2$ in the Ni-catalyzed hydroarylation of internal alkenes, and this new Ni(II) precursor showed better reactivity than commercially available Ni(acac)$_2$ and Ni(Hfacac)$_2$. 

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4. X-Ray Structure of Ni(Adacac)$_2$(THF)$_2$

Single crystals of Ni(Adacac)$_2$(THF)$_2$ (green) were obtained by recrystallization from THF. The molecular structure and X-ray diffractional data/refinement of Ni(Adacac)$_2$(THF)$_2$ were shown below.

Bond precision: \( \text{C-C} = 0.0082 \text{ Å} \)

Wavelength=1.34139

Cell:
\[
\begin{align*}
\text{a} &= 26.6950(6) \\
\text{b} &= 9.1351(2) \\
\text{c} &= 19.8265(5) \\
\alpha &= 90 \\
\beta &= 90 \\
\gamma &= 90
\end{align*}
\]

Temperature: 214 K

Temperature correction method=

# Reported T Limits:

\( \text{Tmin}=0.522 \quad \text{Tmax}=0.751 \quad \text{AbsCorr} = \text{MULTI-SCAN} \)

Data completeness= 0.993

Theta(max)= 54.956

\( R(\text{reflections})= 0.0734(1965) \quad \text{wR2( reflections)}= 0.2423(2346) \)

\( S = 1.093 \quad \text{Npar}= 148 \)
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6. NMR Spectra

Supplementary Figure 20. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4a

Supplementary Figure 21. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4b
Supplementary Figure 22. $^1$H NMR (400 MHz, CDCl₃) spectrum of 4c

Supplementary Figure 23. $^1$H NMR (400 MHz, CDCl₃) spectrum of 4d
Supplementary Figure 24. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4e

Supplementary Figure 25. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4f
Supplementary Figure 26. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4g

Supplementary Figure 28. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4i
Supplementary Figure 29. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4k

Supplementary Figure 30. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4l
Supplementary Figure 31. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4m

Supplementary Figure 32. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4n
Supplementary Figure 33. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4n

Supplementary Figure 34. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4o
Supplementary Figure 35. \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum of 4p

Supplementary Figure 36. \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum of 4r
Supplementary Figure 37. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4u

Supplementary Figure 38. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4x
**Supplementary Figure 39.** $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4x

**Supplementary Figure 40.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4y
Supplementary Figure 41. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4y

Supplementary Figure 42. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4z
Supplementary Figure 43. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4z

Supplementary Figure 44. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4aa
Supplementary Figure 45. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4aa

Supplementary Figure 46. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4ab
Supplementary Figure 47. $^{13}$C NMR (400 MHz, CDCl$_3$) spectrum of 4ab

Supplementary Figure 48. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 4ab
Supplementary Figure 49. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4ac

Supplementary Figure 50. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4ac
Supplementary Figure 51. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4ad

Supplementary Figure 52. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4ad
Supplementary Figure 53. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4ae

Supplementary Figure 54. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4ae
Supplementary Figure 55. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3a

Supplementary Figure 56. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3a
Supplementary Figure 57. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3b

Supplementary Figure 58. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3b
Supplementary Figure 59. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3c

Supplementary Figure 60. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3c
Supplementary Figure 61. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3d

Supplementary Figure 62. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3d
Supplementary Figure 63. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3e

Supplementary Figure 64. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3e
Supplementary Figure 65. $^{19}$F NMR (375 MHz, CDCl₃) spectrum of 3e

Supplementary Figure 66. $^1$H NMR (400 MHz, CDCl₃) spectrum of 3f
Supplementary Figure 67. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3f

Supplementary Figure 68. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 3f
Supplementary Figure 69. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3g

Supplementary Figure 70. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3g
Supplementary Figure 71. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 3g

Supplementary Figure 72. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3h
Supplementary Figure 73. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3h

Supplementary Figure 74. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3i
Supplementary Figure 75. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3i

Supplementary Figure 76. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3j
Supplementary Figure 77. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3j

Supplementary Figure 78. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3k
Supplementary Figure 81. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3l

Supplementary Figure 82. $^{19}$F NMR (100 MHz, CDCl$_3$) spectrum of 3l
Supplementary Figure 83. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3m

Supplementary Figure 84. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3m
Supplementary Figure 85. $^{19}$F NMR (100 MHz, CDCl$_3$) spectrum of 3m

Supplementary Figure 86. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3n
Supplementary Figure 87. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3n

Supplementary Figure 88. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3o
Supplementary Figure 89. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3o

Supplementary Figure 90. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3p
Supplementary Figure 91. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3p

Supplementary Figure 92. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 3p
Supplementary Figure 93. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3q

Supplementary Figure 94. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3q
Supplementary Figure 95. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 3q

Supplementary Figure 96. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3r
Supplementary Figure 97. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3r

Supplementary Figure 98. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 3r
Supplementary Figure 99. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3s

Supplementary Figure 100. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3s
Supplementary Figure 101. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3t

Supplementary Figure 102. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3t
Supplementary Figure 103. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3u

Supplementary Figure 104. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3u
Supplementary Figure 105. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5a

Supplementary Figure 106. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5a
Supplementary Figure 107. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5b

Supplementary Figure 108. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5b
Supplementary Figure 109. $^{17}$F NMR (375 MHz, CDCl$_3$) spectrum of 5b

Supplementary Figure 110. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5c
Supplementary Figure 111. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5c

Supplementary Figure 112. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 5c
Supplementary Figure 113. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5d

Supplementary Figure 114. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5d
Supplementary Figure 115. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5e

Supplementary Figure 116. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5e
Supplementary Figure 117. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 5e

Supplementary Figure 118. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5f
Supplementary Figure 119. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5f

Supplementary Figure 120. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5g
Supplementary Figure 121. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5g

Supplementary Figure 122. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5h
Supplementary Figure 123. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5h

Supplementary Figure 124. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5i
Supplementary Figure 125. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5i

Supplementary Figure 126. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 5i
Supplementary Figure 127. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5j

Supplementary Figure 128. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5j
Supplementary Figure 129. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 5j

Supplementary Figure 130. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5k
Supplementary Figure 131. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5k

Supplementary Figure 132. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5l
Supplementary Figure 133. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5l

Supplementary Figure 134. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5m
Supplementary Figure 135. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5m.

Supplementary Figure 136. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5m.

[Chemical structures and spectra images are present in the figure.]
Supplementary Figure 137. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5n

Supplementary Figure 138. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5o
Supplementary Figure 139. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5o

Supplementary Figure 140. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5p
Supplementary Figure 141. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5p

Supplementary Figure 142. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5q
Supplementary Figure 143. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5q

Supplementary Figure 144. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5r
Supplementary Figure 145. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5r

Supplementary Figure 146. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5s
Supplementary Figure 147. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5s

Supplementary Figure 148. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5t
Supplementary Figure 149. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5t

Supplementary Figure 150. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5u
Supplementary Figure 151. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5u

Supplementary Figure 152. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5v
Supplementary Figure 153. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5v

Supplementary Figure 154. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5w
Supplementary Figure 155. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5w

Supplementary Figure 156. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5x
Supplementary Figure 157. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5x

Supplementary Figure 158. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5y
Supplementary Figure 159. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5y

Supplementary Figure 160. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5z
Supplementary Figure 161. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5z

Supplementary Figure 162. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5aa
Supplementary Figure 163. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5aa

Supplementary Figure 164. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5ab
Supplementary Figure 165. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5ab

Supplementary Figure 166. $^{19}$F NMR (375 MHz, CDCl$_3$) spectrum of 5ab
Supplementary Figure 167. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5ac

Supplementary Figure 168. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5ac
Supplementary Figure 169. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5ad

Supplementary Figure 170. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5ad
Supplementary Figure 171. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5ae

Supplementary Figure 172. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 5ae
Supplementary Figure 173. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7a

Supplementary Figure 174. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7a
Supplementary Figure 175. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7b

Supplementary Figure 176. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7b
Supplementary Figure 177. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7c

Supplementary Figure 178. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7c
Supplementary Figure 179. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7d

Supplementary Figure 180. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7d
Supplementary Figure 181. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7e

Supplementary Figure 182. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7e
Supplementary Figure 183. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7f

Supplementary Figure 184. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7f
Supplementary Figure 185. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7g

Supplementary Figure 186. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7g
Supplementary Figure 187. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7h

Supplementary Figure 188. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7h
Supplementary Figure 189. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7i

Supplementary Figure 190. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7i
Supplementary Figure 191. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7j

Supplementary Figure 192. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7j
Supplementary Figure 193. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7k

Supplementary Figure 194. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7k
Supplementary Figure 195. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 9

Supplementary Figure 196. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 9