Supporting Information

Air-Stable Pd\textsuperscript{I} Dimer Enabled Remote Functionalization: Access to Fluorinated 1,1-Diaryl Alkanes with Unprecedented Speed

Gourab Kundu, Filip Opincal, Theresa Sperger, and Franziska Schoenebeck*

anie_202113667_sm_misellaneous_information.pdf
Contents

1. General experimental details ................................................................. S2
2. Synthesis and characterization data of the products ................................ S3
   2.1. General experimental procedure for remote functionalization .......... S3
   2.2. Characterization data ..................................................................... S3
3. Mechanistic tests and Comparisons ....................................................... S12
   3.1. Direct coupling .............................................................................. S12
       3.1.1. GC-MS comparison of PdI dimers ........................................... S12
   3.2. Comparison to known catalytic systems ........................................ S13
4. Synthesis and characterization data for the starting materials ................ S15
   4.1. General experimental procedures for the synthesis of the alkyl bromides .......... S15
   4.2. Characterization data of alkyl bromides ........................................ S16
   4.3. General experimental procedures for the synthesis of the aryl triflates .......... S20
   4.4. Characterization data of aryl triflates ........................................... S21
5. Crystallographic data ........................................................................... S23
6. Computational details ........................................................................... S24
   6.1. Full computed pathways and energies .......................................... S25
   6.2. Distortion/Interaction Analysis ..................................................... S28
   6.3. NCI analysis .................................................................................. S28
   6.4. Coordinates of the computed structures ....................................... S29
       6.4.1. Structures for pathway using L = PCy2Bu and Aryl = 2-fluoro-4-chlorophenyl .......... S29
       6.4.2. Structures for pathway using L = PBu3 and Aryl = 2-fluoro-4-chlorophenyl .......... S37
7. NMR spectra ....................................................................................... S41
8. References ............................................................................................ S97
1. General experimental details

Reagents, starting materials and solvents

Unless otherwise stated, all reagents and starting materials were commercially available and used as received. All anhydrous solvents were either purchased from Acros or dried using an Innovative Technology PS-MD-5 solvent purification system. Technical grade solvents were distilled prior to use for chromatography and extraction.

Purification

Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F254 aluminium plates with unmodified silica and visualized either under UV light or stained with iodine. Flash column chromatography was performed with Merck silica gel 60 (35 – 70 mesh). Preparative HPLC was performed on a Gilson-Abimed HPLC (employing UV detector model 117) using a Merck LiChrosorb Si60 column (porosity 7 μm, 250 x 25 mm).

Characterization

All ¹H, ¹³C and ¹⁹F NMR spectra were recorded on Varian VNMRS 600, Varian VNMRS 400 or Bruker Avance Neo 600 spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) and were referenced either to residual solvent peak (CDCl₃; for ¹H and ¹³C spectra). Coupling constants (J) are given in Hertz (Hz).

Gas chromatography coupled with mass spectrometry (GC-MS) was performed on an Agilent Technologies 5975 series MSD mass spectrometer under electrospray ionization (EI) mode coupled with an Agilent Technologies 7820A gas chromatograph employing an Agilent 19091s-433 HP-5MS column (30 m x 0.250 μm x 0.250 μm).

High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL spectrometer. Low-resolution masses of known compounds were extracted from their GC-MS chromatograms. IR spectra were recorded on a Spectrum 100 spectrometer with an UATR Diamond/KRS-5 crystal with attenuated total reflectance (ATR).
2. Synthesis and characterization data of the products

2.1. General experimental procedure for remote functionalization

Under an argon atmosphere, a solution of alkyl bromide (0.5 mmol) in THF (0.5 mL) was added to a 4 mL vial containing Mg turnings (0.6 mmol, 14.6 mg) and stirred vigorously for 10 minutes. After that, an aliquot of the freshly prepared alkyl magnesium bromide (0.1 mL) was titrated with I₂ to determine the concentration. The Grignard solution (0.24 mmol, 1.2 equiv.) and ZnCl₂ (1M in THF, 0.3 mL) were added to a 16 mL vial and stirred for 10 minutes. NMP (0.5 mL) was added to dissolve the formed suspension of alkyl-ZnCl₂ and a solution of the aryl triflate (0.2 mmol, 1 equiv.) and [Pd(µ-I)(PCy₂Bu)]₂ (4.9 mg, 0.005 mmol, 0.025 equiv.) in NMP (0.5 mL) was added, followed by NMP (0.5 mL) used to wash the vial containing the mixture at room temperature under Ar atmosphere. The reaction mixture was stirred for 10 minutes, an aliquot was analyzed by GC-MS (to determine the b/l ratio) and afterwards the crude reaction mixture was directly subjected to column chromatography on silica for purification.

2.2. Characterization data

**1-chloro-2-fluoro-3-(1-phenylpropyl)benzene (1):** Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulphonate (1a) (b/l 94:6, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (45.8 mg, 0.18 mmol, 91%). \( R_t = 0.43 \) (Hexane). \( ^1H \) NMR (400 MHz, CDCl₃): \( δ = 7.32 – 7.15 \) (m, 7H), 7.04 – 7.00 (m, 1H), 4.18 (t, \( J = 7.8 \) Hz, 1H), 2.16 – 2.00 (m, 2H), 0.93 (t, \( J = 7.3 \) Hz, 3H). \( ^{13}C \) NMR (101 MHz, CDCl₃): \( δ = 156.3 \) (d, \( J = 247.4 \) Hz), 143.4, 134.0 (d, \( J = 14.7 \) Hz), 128.6, 128.4, 128.1, 126.9 (d, \( J = 4.0 \) Hz), 126.6, 124.5 (d, \( J = 4.6 \) Hz), 121.2 (d, \( J = 18.9 \) Hz), 45.71 – 45.70 (m, 1C), 27.8, 12.7. \( ^{19}F \) NMR (376 MHz, CDCl₃): \( δ = -119.85 \) (t, \( J = 6.5 \) Hz). IR (neat, cm⁻¹): 2966, 2871, 1605, 1502, 775, 727, 698. MS (70 eV, EI): \( m/z \) (%): 250 (7) \(^{13}Cl-M^+\), 248 (23) \(^{13}Cl-M^+\), 221 (34), 220 (15), 219 (100), 184 (55), 183 (65). HRMS (ESI) calculated for C₁₅H₁₄ClF: 248.0763 [M]⁺, found: 248.0761.

**1-chloro-3-(1-(2,4-difluorophenyl)propyl)-2-fluorobenzene (2):** Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulphonate (1a) (b/l 74:26, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (22.6 mg, 0.08 mmol, 39%). \( R_t = 0.56 \) (Hexane). \( ^1H \) NMR (400 MHz, CDCl₃): \( δ = 7.27 – 7.13 \) (m, 3H), 7.05 – 7.00 (m, 1H), 6.85 – 6.80 (m, 1H), 6.78 – 6.73 (m, 1H), 4.39 (t, \( J = 7.9 \) Hz, 1H), 2.05 (p, \( J = 7.4 \) Hz, 2H), 0.93 (t, \( J = 7.3 \) Hz, 3H). \( ^{13}C \) NMR (101 MHz, CDCl₃): \( ^{19}F \) decoupled: \( δ = 161.8, 160.9, 156.4, 132.4, 129.6, 128.8, 127.2, 126.1, 124.5, 121.4, 111.2, 104.0, 38.7, 26.9, 12.5. \( ^{19}F \) NMR (376 MHz, CDCl₃): \( δ = -112.9 \) (p, \( J = 7.6 \) Hz), -113.06 – -113.10 (m), -119.3 (s, br). IR (neat, cm⁻¹): 2935, 2871, 1605, 1502.
1458, 1217, 1135, 1095. MS (70 eV, EI): \(m/z\) (%): 286 (5) \([^{37}\text{Cl-M}^+]\), 284 (15) \([^{35}\text{Cl-M}^+]\), 257 (32), 256 (12), 255 (100), 220 (17), 219 (37). HRMS (ESI) calculated for \(\text{C}_{15}\text{H}_{12}\text{ClF}_3\): 284.0574 [M]+, found: 284.0571.

2-{1-[3-chloro-2-fluorophenyl]propyl}napthalene (3): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) \(b/l\ 96:4\), based on GC-MS of the crude. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (54.2 mg, 0.18 mmol, 85%). \(R_t = 0.41\) (Hexane). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.83 – 7.75 (m, 4H), 7.50 – 7.43 (m, 2H), 7.38 (dd, \(J = 8.5, 1.7\ Hz, 1H\)), 7.26 – 7.20 (m, 2H), 7.05 – 7.01 (m, 1H), 4.37 (t, \(J = 7.8\ Hz, 1H\)), 2.29 – 2.10 (m, 2H), 0.99 (t, \(J = 7.3\ Hz, 3H\)). \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) 156.4 (d, \(J = 247.4\ Hz\)), 140.8, 133.9 (d, \(J = 14.7\ Hz\)), 133.6, 132.4, 128.5, 128.3, 127.9, 127.7, 127.1 (d, \(J = 3.9\ Hz\)), 126.7, 126.4, 126.2, 125.7, 124.6 (d, \(J = 4.6\ Hz\)), 121.3 (d, \(J = 19.1\ Hz\)), 45.74 - 45.73 (m, 1C), 27.7, 12.7. \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)): \(\delta\) -119.75 (t, \(J = 6.8\ Hz\)). IR (neat, \(cm^{-1}\)): 2964, 2932, 2873, 1454, 1228, 815, 779, 745. MS (70 eV, EI): \(m/z\) (%): 300 (13) \([^{37}\text{Cl-M}^+]\), 298 (39) \([^{35}\text{Cl-M}^+]\), 271 (35), 270 (18), 269 (100), 234 (50), 233 (72). HRMS (ESI) calculated for \(\text{C}_{16}\text{H}_{13}\text{ClF}_2\): 298.0919 [M]+, found: 298.0913.

1-chloro-2-fluoro-3-(1-(4-(trifluoromethyl)phenyl)propyl)benzene (4): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) \(b/l\ 92:8\), based on GC-MS of the crude. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (51.6 mg, 0.16 mmol, 81%). \(R_t = 0.51\) (Hexane). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.55 (d, \(J = 8.2\ Hz, 2H\)), 7.36 (d, \(J = 8.1\ Hz, 2H\)), 7.28 – 7.24 (m, 1H), 7.19 – 7.15 (m, 1H), 7.07 – 7.03 (m, 1H), 4.22 (t, \(J = 7.8\ Hz, 1H\)), 2.09 (p, \(J = 7.4\ Hz, 2H\)), 0.93 (t, \(J = 7.3\ Hz, 3H\)). \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) 156.3, 147.4, 133.0, 128.9 (128.94), 128.9 (128.87), 128.4, 126.7, 125.6, 124.7, 124.3, 121.5, 45.7, 27.6, 12.6. \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)): \(\delta\) -62.46 (s, 3F), -119.52 (t, \(J = 6.5\ Hz, 1F\)). IR (neat, \(cm^{-1}\)): 2968, 2936, 2878, 1455, 1324, 1163, 1120, 1068. MS (70 eV, EI): \(m/z\) (%): 318 (6) \([^{37}\text{Cl-M}^+]\), 316 (19) \([^{35}\text{Cl-M}^+]\), 289 (34), 288 (16), 287 (100), 252 (22), 251 (21), 183 (43). HRMS (ESI) calculated for \(\text{C}_{16}\text{H}_{13}\text{ClF}_4\): 316.0636 [M]+, found: 316.0637.

1-chloro-2-fluoro-3-(1-(m-tolyl)propyl)benzene (5): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) \(b/l\ 97:3\), based on GC-MS of the crude. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (44.7 mg, 0.17 mmol, 85%). \(R_t = 0.55\) (Hexane). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.24 – 7.16 (m, 3H), 7.08 – 7.01 (m, 4H), 4.15 (t, \(J = 7.8\ Hz, 1H\)), 3.33 (s, 3H), 2.13 – 2.01 (m, 2H), 0.93 (t, \(J = 7.3\ Hz, 3H\)). \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) 156.3 (d, \(J = 247.2\ Hz\)), 143.3, 138.2, 134.1 (d, \(J = 14.6\ Hz\)), 128.9, 128.5, 128.3, 127.4, 126.97 - 126.93 (m, 1C), 125.0, 124.5 (d, \(J = 4.6\ Hz\)), 121.2 (d, \(J = 19.2\ Hz\)), 46.6 – 45.6 (m, 1C), 27.8, 21.6, 12.7. \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)): \(\delta\) -119.92 (t, \(J = 6.5\ Hz\)). IR (neat, \(cm^{-1}\)): 2965, 2931, 2874, 1603, 1453, 1228, 778, 706. MS (70 eV, EI): \(m/z\) (%): 264 (5) \([^{37}\text{Cl-M}^+]\), 262 (35) \([^{35}\text{Cl-M}^+]\), 235 (35), 234 (16), 233 (100), 207 (24), 198 (32), 197 (12), 196 (13), 183 (44). HRMS (ESI) calculated for \(\text{C}_{16}\text{H}_{16}\text{ClF}_2\): 262.0919 [M]+, found: 262.0917.
1-chloro-2-fluoro-3-(1-(o-tolyl)propyl)benzene (6): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) (b/l 90:10, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (42.6 mg, 0.16 mmol, 77%). $R_t = 0.56$ (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29 (d, $J = 7.6$ Hz, 1H), 7.24 – 7.19 (m, 2H), 7.17 – 7.12 (m, 2H), 7.06 – 7.02 (m, 1H), 6.98 (dd, $J = 7.9$, 7.9 Hz, 1H), 4.39 (t, $J = 7.7$ Hz, 1H), 2.29 (s, 3H), 2.10 – 1.98 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 156.4 (d, $J = 246.9$ Hz), 141.3, 136.8, 133.7 (d, $J = 15.1$ Hz), 130.7, 128.3, 127.4 – 127.3 (m, 1C), 126.8, 126.5, 126.1, 124.5 (d, $J = 4.6$ Hz), 121.0 (d, $J = 19.2$ Hz), 41.09 – 41.08 (m, 1C), 28.5, 19.7, 12.6. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –120.00 (t, $J = 6.8$ Hz). IR (neat, cm$^{-1}$): 2965, 2933, 2874, 1453, 1228, 729. MS (70 eV, EI): $m$/z (%): 264 (9) [$^{19}$Cl-M$^+$], 262 (25) [$^{35}$Cl-M$^+$], 235 (34), 234 (16), 233 (100), 198 (35), 197 (32), 196 (24), 183 (32). HRMS (ESI) calculated for C$_{18}$H$_{16}$ClF: 262.0919 [M]$^+$, found: 262.0925.

1-chloro-2-fluoro-3-(1-(2-isoproplyphenyl)propyl)benzene (7): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) (b/l 86:14, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (40.3 mg, 0.14 mmol, 69%). $R_t = 0.48$ (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31 – 7.15 (m, 5H), 7.06 – 6.96 (m, 2H), 4.54 (t, $J = 7.6$ Hz, 1H), 3.25 (hept, $J = 6.9$ Hz, 1H), 2.08 – 1.97 (m, 2H), 1.26 (d, $J = 6.8$ Hz, 3H), 1.01 (d, $J = 6.8$ Hz, 3H), 0.96 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$). $^{19}$F decoupled: $\delta$ 156.2, 147.3, 139.5, 134.3, 128.3, 127.5, 127.0, 126.9, 125.9, 125.7, 124.5, 121.0, 40.2, 28.9, 28.3, 24.4, 23.8, 12.8. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -119.78 (t, $J = 6.4$ Hz). IR (neat, cm$^{-1}$): 2965, 2932, 2873, 1452, 1228, 756, 728. MS (70 eV, EI): $m$/z (%): 292 (12) [$^{19}$Cl-M$^+$], 290 (35) [$^{35}$Cl-M$^+$], 263 (23), 262 (12), 261 (67), 196 (28), 183 (26), 143 (28), 131 (100), 91 (22). HRMS (ESI) calculated for C$_{18}$H$_{16}$F: 290.1232 [M]$^+$, found: 290.1233.

2-(1-(2-fluoro-4-pentylphenyl)propyl)naphthalene (8): Prepared, following the general procedure from 2-fluoro-4-pentylphenyl trifluoromethanesulfonate (8a) (b/l 73:27, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (41.1 mg, 0.12 mmol, 65%). $R_t = 0.39$ (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 – 7.75 (m, 4H), 7.48 – 7.38 (m, 3H), 7.20 (dd, $J = 7.9$, 7.9 Hz, 1H), 6.91 – 6.89 (m, 1H), 6.85 – 6.82 (m, 1H), 4.31 (t, $J = 7.8$ Hz, 1H), 2.57 – 2.53 (m, 2H), 2.26 – 2.09 (m, 2H), 1.59 (p, $J = 7.5$ Hz, 2H), 1.39 – 1.26 (m, 4H), 0.97 (t, $J = 7.3$ Hz, 3H), 0.89 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 160.7 (d, $J = 244.8$ Hz), 143.0 (d, $J = 7.6$ Hz), 141.7, 133.5, 132.1, 128.9 (d, $J = 14.7$ Hz), 128.2 (d, $J = 5.1$ Hz), 127.9, 127.7, 127.5, 126.8, 126.0, 125.8, 125.3, 124.0 (d, $J = 2.8$ Hz), 115.1 (d, $J = 22.4$ Hz), 45.18 – 45.17 (m, 1C), 35.3, 31.4, 30.8, 27.6, 22.5, 14.0, 12.7. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -118.83 – -118.88 (m). IR (neat, cm$^{-1}$): 2928, 2862, 1503, 1458, 1423, 1257, 1113, 811, 743. MS (70 eV, EI): $m$/z (%): 334 (16) [M]$^+$, 306 (25), 305 (100), 233 (17). HRMS (ESI) calculated for C$_{20}$H$_{17}$F: 334.2091 [M]$^+$, found: 334.2095.

1-(1-(4-(tert-butyl)phenyl)propyl)-4-chloro-2-fluorobenzene (9): Prepared, following the general procedure from 4-chloro-2-fluorophenyl trifluoromethanesulfonate (9a) (b/l 93:7, based on GC-MS of the crude). The title
product was obtained after purification by column chromatography (Hexane) as a colorless oil (52.2 mg, 0.17 mmol, 82%). \( R_t = 0.6 \) (Hexane). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): 7.30 (d, \( J = 8.3 \) Hz, 2H), 7.21 – 7.16 (m, 3H), 7.09 – 7.02 (m, 2H), 4.10 (t, \( J = 7.8 \) Hz, 1H), 2.13 – 1.96 (m, 2H), 1.30 (s, 9H), 0.91 (t, \( J = 7.3 \) Hz, 3H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)), \( ^19F \) decoupled: \( \delta \) 160.7, 149.3, 140.4, 132.3, 131.2, 129.6, 127.6, 125.5, 124.6, 116.3, 44.6, 34.5, 31.5, 27.8, 12.7. \( ^19F \) NMR (376 MHz, CDCl\(_3\)): \( \delta \) -115.4 (t, \( J = 8.8 \) Hz). IR (neat, cm\(^{-1}\)):\( 2961, 2872, 1484, 1408, 1266, 896, 850, 811. \) MS (70 eV, EI): \( m/z \) (%): 304 (13) \([^{35}Cl-M^*] \), 291 (7), 289 (21), 277 (37), 276 (21), 275 (100), 260 (20), 245 (15), 143 (11). HRMS (ESI) calculated for C\(_{19}\)H\(_{12}\)CIF: 304.1389 \([M]^+ \), found: 304.1387.

2-fluoro-3-(1-(4-(trifluoromethyl)phenyl)propyl)pyridine (10): Prepared, following the general procedure from 2-fluoropyridin-3-yl trifluoromethanesulfonate (2a) \( (b:/l = 97:3) \), based on GC-MS of the crude). The title product was obtained after purification by column chromatography (98:2 Hexane/EtOAc) as a colorless oil (50.2 mg, 0.18 mmol, 88%). \( R_t = 0.25 \) (95:5 Hexane/EtOAc). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): 8.07 (d, \( J = 4.3 \) Hz, 1H), 7.69 – 7.64 (m, 1H), 7.55 (d, \( J = 8.2 \) Hz, 2H), 7.35 (d, \( J = 8.1 \) Hz, 2H), 7.18 – 7.15 (m, 1H), 4.13 (t, \( J = 7.8 \) Hz, 1H), 2.10 (p, \( J = 7.4 \) Hz, 2H), 0.93 (t, \( J = 7.3 \) Hz, 3H). \( ^13C \) NMR (101 MHz, CDCl\(_3\), \( ^19F \) decoupled): \( \delta \) 161.7, 146.7, 145.7, 138.9, 129.2, 128.4, 126.3, 125.7, 124.3, 121.8, 45.6, 27.3, 12.5. \( ^19F \) NMR (376 MHz, CDCl\(_3\)): \( \delta \) -62.53 (s, 3F), -71.34 (s, 1F). IR (neat, cm\(^{-1}\)): 2970, 1432, 1323, 1163, 1118, 1067, 800. MS (70 eV, EI): \( m/z \) (%): 283 (14) \([M]^+ \), 255 (15), 254 (100), 234 (8), 185 (18). HRMS (ESI) calculated for C\(_{19}\)H\(_{12}\)F\(_4\): 283.0979 \([M]^+ \), found: 283.0973.

4-(1-(3-chloro-2-fluorophenyl)propyl)-1,1'-biphenyl (11): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) \( (b:/l = 97:3) \), based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a white solid (61.6 mg, 0.19 mmol, 94%). \( R_t = 0.31 \) (Hexane). M.p. = 71 – 73 \( ^\circ \)C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.59 – 7.53 (m, 4H), 7.45 – 7.41 (m, 2H), 7.35 – 7.32 (m, 3H), 7.27 – 7.20 (m, 2H), 7.07 – 7.03 (m, 1H), 4.24 (t, \( J = 7.8 \) Hz, 1H), 2.20 – 2.04 (m, 2H), 0.97 (t, \( J = 7.3 \) Hz, 3H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 156.3 (d, \( J = 247.4 \) Hz), 142.5, 141.0, 139.5, 133.9 (d, \( J = 14.6 \) Hz), 128.9, 128.5 (br, 2C), 127.4, 127.3, 127.2, 127.0 (d, \( J = 4.0 \) Hz), 124.6 (d, \( J = 4.7 \) Hz), 121.3 (d, \( J = 18.9 \) Hz), 45.4 (d, \( J = 1.8 \) Hz), 27.8, 12.8. \( ^19F \) NMR (376 MHz, CDCl\(_3\)): \( \delta \) -115.77 (t, \( J = 6.5 \) Hz). IR (neat, cm\(^{-1}\)): 2964, 2928, 1485, 1454, 1224, 1128, 818, 765, 741, 692. MS (70 eV, EI): \( m/z \) (%): 326 (11) \([^{35}Cl-M^*] \), 324 (31) \([^{35}Cl-M^*] \), 297 (34), 296 (16), 295 (100), 260 (18), 259 (23). HRMS (ESI) calculated for C\(_{21}\)H\(_{18}\)ClF: 324.1076 \([M]^+ \), found: 324.1068. White crystals of 11 were obtained by slow evaporation from a hexane solution. A suitable crystal was selected and analysed by single crystallography.

4-chloro-2-fluoro-1-(1-phenylpentyl)benzene (12): Prepared, following the general procedure from 4-chloro-2-fluorophenyl trifluoromethanesulfonate (9a) \( (b:/l = 91:9) \), based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (46.0 mg, 0.17 mmol, 83%). \( R_t = 0.52 \) (Hexane). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.31 – 7.18 (m, 6H), 7.09 – 7.02 (m, 2H), 4.22 (t, \( J = 7.8 \) Hz, 1H), 2.09 – 1.95 (m, 2H), 1.40 – 1.21 (m, 4H), 0.88 (t, \( J = 7.2 \) Hz, 3H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 160.6 (d, \( J = 248.6 \) Hz), 143.7, 132.4 (d, \( J = 10.6 \) Hz), 131.2 (d, \( J = 14.6 \) Hz), 129.5 (d, \( J = 5.5 \) Hz), 128.6, 128.0, 126.5, 124.6 (d, \( J = 3.6 \) Hz), 116.3 (d, \( J = 26.6 \) Hz), 43.22 – 43.21 (m, 1C), 34.5,
30.1, 22.7, 14.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -115.29 (t, $J = 9.0$ Hz). IR (neat, cm$^{-1}$): 2930, 2863, 1605, 1576, 1485, 1454, 1407, 1222, 1076, 895, 856, 697. MS (70 eV, EI): $m/z$ (%): 278 (7) [${}^{35}$Cl-M$^+$], 276 (23) [${}^{37}$Cl-M$^+$], 221 (35), 220 (14), 219 (100), 184 (45), 183 (56). HRMS (ESI) calculated for C$_{17}$H$_{15}$ClF: 276.1076 [M]$^+$, found: 276.1068.

3-fluoro-4-(1-phenylpentyl)benzonitrile (13): Prepared, following the general procedure from 4-cyano-2-fluorophenyl trifluoromethanesulfonate (4a) ($b$:l 75:25, based on GC-MS of the crude). The title product was obtained after purification by preparative HPLC (70:30 Hexane/ EtOAc) as a colorless oil (32.1 mg, 0.12 mmol, 60%). $R_f$ = 0.43 (96:4 Hexane/EtOAc). $^1$H NMR (400 MHz, CDCl$_3$): 7.41 – 7.36 (m, 2H), 7.32 – 7.20 (m, 6H), 4.29 (t, $J = 7.8$ Hz, 1H), 2.12 – 1.96 (m, 2H), 1.40 – 1.31 (m, 2H), 1.29 – 1.17 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 160.2 (d, $J = 248.9$ Hz), 142.5, 138.8 (d, $J = 14.7$ Hz), 129.8 (d, $J = 5.2$ Hz), 128.8, 128.4 (d, $J = 3.7$ Hz), 128.0, 126.9, 119.3 (d, $J = 26.8$ Hz), 117.9, 111.3 (d, $J = 9.8$ Hz), 43.71 – 43.70 (m, 1C), 34.3, 30.1, 22.7, 14.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -114.52 (dd, $J = 9.0$, 5.9 Hz). IR (neat, cm$^{-1}$): 2931, 2864, 2233, 1567, 1494, 1455, 1413, 1255, 944, 875, 735, 699. MS (70 eV, EI): $m/z$ (%): 267 (16) [M]$^+$, 211 (20), 210 (100), 208 (16), 190 (11). HRMS (ESI) calculated for C$_{18}$H$_{19}$NF: 267.1418 [M]$^+$, found: 267.1419.

2,4-difluoro-1-(1-phenylpentyl)benzene (14): Prepared, following the general procedure from 2,4-difluorophenyl trifluoromethanesulfonate (5a) ($b$:l 90:10, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (42.5 mg, 0.16 mmol, 81%). $R_t$ = 0.63 (hexane). $^1$H NMR (400 MHz, CDCl$_3$): 7.31 – 7.17 (m, 6H), 6.84 – 6.72 (m, 2H), 4.21 (t, $J = 7.9$ Hz, 1H), 2.09 – 1.95 (m, 2H), 1.40 – 1.31 (m, 2H), 1.29 – 1.21 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $^{19}$F decoupled: $\delta$ 161.4, 160.7, 144.0, 129.3, 128.6, 128.3, 128.0, 126.4, 111.2, 103.9, 43.1, 34.7, 30.2, 22.8, 14.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -113.8 – -113.9 (m, 2F). IR (neat, cm$^{-1}$): 2931, 2863, 1604, 1499, 1456, 1427, 1274, 1138, 1110, 964, 848, 738, 697. MS (70 eV, EI): $m/z$ (%): 260 (9) [M]$^+$, 204 (15), 203 (100), 201 (17), 183 (25). HRMS (ESI) calculated for C$_{15}$H$_{13}$F$_2$: 260.1371 [M]$^+$, found: 260.1382.

2-fluoro-4-pentyl-1-(1-phenylpentyl)benzene (15): Prepared, following the general procedure from 2-fluoro-4-pentylphenyl trifluoromethanesulfonate (8a) ($b$:l 71:29, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (36.1 mg, 0.12 mmol, 60%). $R_t$ = 0.66 (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): 7.30 – 7.27 (m, 4H), 7.21 – 7.14 (m, 2H), 6.89 (dd, $J = 7.9$, 1.3 Hz, 1H), 6.81 (dd, $J = 11.4$, 1.4 Hz, 1H), 4.21 (t, $J = 7.9$ Hz, 1H), 2.56 – 2.52 (m, 2H), 2.03 (q, $J = 8.1$ Hz, 2H), 1.58 (p, $J = 7.6$ Hz, 2H), 1.40 – 1.22 (m, 8H), 0.91 – 0.86 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 160.8 (d, $J = 244.6$ Hz), 144.6, 143.0 (d, $J = 7.6$ Hz), 129.3 (d, $J = 14.9$ Hz), 128.5, 128.3 (d, $J = 5.0$ Hz), 128.1, 126.2, 124.2 (d, $J = 2.8$ Hz), 115.3 (d, $J = 22.5$ Hz), 43.40 – 43.39 (m, 1C), 35.4, 34.7, 31.6, 31.0, 30.3, 22.8, 22.7, 14.2, 14.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -118.96 (dd, $J = 10.9$, 8.3 Hz). IR (neat, cm$^{-1}$): 2928, 2960, 1499, 1456, 1424, 1251, 1116, 734, 697. MS (70 eV, EI): $m/z$ (%): 312 (8) [M]$^+$, 256 (30), 255 (100), 198 (12), 183 (13). HRMS (ESI) calculated for C$_{19}$H$_{19}$F: 312.2248 [M]$^+$, found: 312.2253.
2-(3-fluoro-4-(1-phenylpentyl)phenyl)thiophene (16): Prepared, following the general procedure from 2-fluoro-4-(thiophen-2-yl)phenyl trifluoromethanesulfonate (7a) (b:l 83:17, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (53.1 mg, 0.16 mmol, 80%). Rf = 0.36 (Hexane). 1H NMR (400 MHz, CDCl3): 7.36 – 7.18 (m, 10H), 7.08 – 7.06 (m, 1H), 4.27 (t, J = 7.9 Hz, 1H), 2.07 (q, J = 8.3 Hz, 2H), 1.43 – 1.26 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ117.63 (dd, J = 11.2, 7.7 Hz). IR (neat, cm−1): 2929, 2861, 1492, 1418, 867, 816, 695. MS (70 eV, EI): m/z (%): 324 (20) [M]+, 268 (21), 267 (100), 233 (19). HRMS (ESI) calculated for C21H22FS: 325.1421 [M+H]+, found: 325.1431.

6-(1-(4-chloro-2-fluorophenyl)pentyl)-2,3-dihydrobenzo[b][1,4]dioxine (17): Prepared, following the general procedure from 4-chloro-2-fluorophenyl trifluoromethanesulfonate (9a) (b:l 96:4, based on GC-MS of the crude). The title product was obtained after purification by preparative HPLC (90:10 Hexane/EtOAc) as a colorless oil (53.4 mg, 0.16 mmol, 79%). Rf = 0.5 (6:94 EtOAc/Hexane). 1H NMR (400 MHz, CDCl3): 7.17 (dd, J = 8.1, 8.1 Hz, 1H), 7.06 (dd, J = 8.4, 1.7 Hz, 1H), 7.01 (dd, J = 9.9, 2.0 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 6.74 – 6.69 (m, 2H), 4.22 (s, 4H), 4.10 (t, J = 7.8 Hz, 1H), 2.02–1.88 (m, 2H), 1.38 – 1.29 (m, 2H), 1.28 – 1.18 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ160.5 (d, J = 248.6 Hz), 143.5, 142.1, 137.1, 132.3 (d, J = 10.6 Hz), 131.3 (d, J = 14.8 Hz), 129.4 (d, J = 5.4 Hz), 124.6 (d, J = 3.5 Hz), 121.0, 117.3, 116.5, 116.3 (d, J = 26.5 Hz), 64.5, 64.4, 42.46 – 42.45 (m, 1C), 34.6, 30.1, 22.7, 14.1. 19F NMR (376 MHz, CDCl3): δ -115.5 (t, J = 8.9 Hz). IR (neat, cm−1): 2929, 2867, 1587, 1504, 1460, 1285, 1254, 1069, 890, 812. MS (70 eV, EI): m/z (%): 336 (6) [19Cl-M]+, 334 (17) 336 (6) [19Cl-M]+, 279 (35), 278 (18), 277 (100), 170 (12). HRMS (ESI) calculated for C19H18O2ClF: 335.1209 [M+H]+, found: 335.1203.

3-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)pentyl)-2-fluoropyridine (18): Prepared, following the general procedure from 2-fluoropyridin-3-yl trifluoromethanesulfonate (2a) (b:l 94:6, based on GC-MS of the crude). The title product was obtained after purification by preparative HPLC (6:4 Hexane/EtOAc) as a colorless oil (45.6 mg, 0.15 mmol, 75%). Rf = 0.27 (90:10 Hexane/EtOAc). 1H NMR (400 MHz, CDCl3): 8.02 (d, J = 3.6 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.11 (dd, J = 8.9, 3.2 Hz, 1H), 6.78 (d, J = 8.2 Hz, 1H), 6.74 – 6.70 (m, 2H), 4.22 (s, 4H), 4.06 (t, J = 7.8 Hz, 1H), 2.00 – 1.94 (m, 2H), 1.37 – 1.18 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ161.6 (d, J = 238.5 Hz), 145.1 (d, J = 15.1 Hz), 143.6, 142.3, 138.9 (d, J = 5.4 Hz), 136.2, 127.7 (d, J = 29.2 Hz), 121.7 – 121.6 (m, 1C), 121.1, 117.4, 116.6, 64.5, 64.4, 43.0 (br), 34.4, 30.1, 22.7, 14.1. 19F NMR (376 MHz, CDCl3): δ -72.1 (d, J = 9.8 Hz). IR (neat, cm−1): 2930, 2868, 1589, 1504, 1430, 1285, 1247, 1066, 885, 794. MS (70 eV, EI): m/z (%): 301 (18) [M]+, 245 (15), 244 (100). HRMS (ESI) calculated for C18H12O2NF: 302.1551 [M+H]+, found: 302.1551.
4-cyclopropyl-2-fluoro-1-(1-phenylpentyl)benzene (19): Prepared, following the general procedure from 4-cyclopropyl-2-fluorophenyl trifluoromethanesulfonate (6a) (b/: 66:34, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (28.5 mg, 0.10 mmol, 54%). Rf = 0.46 (Hexane). 1H NMR (400 MHz, CDCl3): δ 7.30 – 7.26 (m, 4H), 7.21 – 7.13 (m, 2H), 6.82 (dd, J = 8.0, 1.6 Hz, 1H), 6.68 (dd, J = 11.6, 1.6 Hz, 1H), 4.21 (t, J = 7.9 Hz, 1H), 2.03 (q, J = 8.0 Hz, 2H), 1.84 (dd, J = 13.5, 8.5, 5.1 Hz, 1H), 1.41 – 1.33 (m, 2H), 1.31 – 1.23 (m, 2H), 0.98 – 0.93 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H), 0.68 – 0.64 (m, 2H). 13C NMR (101 MHz, CDCl3): δ 161.0 (d, J = 244.4 Hz), 144.6, 144.3 (d, J = 7.9 Hz), 129.1 (d, J = 14.9 Hz), 128.5, 128.4 (d, J = 5.3 Hz), 128.0, 126.2, 121.6 (d, J = 2.7 Hz), 112.5 (d, J = 23.5 Hz), 43.4 – 43.3 (m, 1C), 34.7, 30.3, 22.8, 15.1 (15.09), 15.1 (15.08), 14.1, 9.5. 19F NMR (376 MHz, CDCl3): δ -118.82 (dd, J = 11.3, 8.2 Hz). IR (neat, cm⁻¹): 3027, 2930, 2863, 1625, 1571, 1457, 1423, 950, 698. MS (70 eV, EI): m/z (%): 282 (14) [M]+, 226 (24), 225 (100), 196 (11), 183 (17). HRMS (ESI) calculated for C20H12F: 282.1778 [M]+, found: 282.1779.

2-fluoro-3-(1-phenylpentyl)pyridine (20): Prepared, following the general procedure from 2-fluoropyridin-3-yl trifluoromethanesulfonate (2a) (b/: 92:8, based on GC-MS of the crude). The title product was obtained after purification by preparative HPLC (9:1 Hexane/ EtOAc) as a colorless oil (38.7 mg, 0.16 mmol, 78%). Rf = 0.35 (95:5 Hexane/EtOAc). 1H NMR (400 MHz, CDCl3): 8.05 (s, 1H), 7.67 (dd, J = 8.3, 8.3 Hz, 1H), 7.32 – 7.19 (m, 5H), 7.15 – 7.12 (m, 1H), 4.18 (t, J = 7.8 Hz, 1H), 2.11 – 1.98 (m, 2H), 1.40 – 1.21 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 161.7 (d, J = 237.6 Hz), 145.1 (br), 142.8, 139.0 (d, J = 5.2 Hz), 128.7, 128.1, 127.5 (d, J = 30.5 Hz), 126.8, 121.7 (br), 43.8 (br), 34.3, 30.1, 22.7, 14.1. 19F NMR (376 MHz, CDCl3): δ -71.87 (s). IR (neat, cm⁻¹): 2930, 2863, 1600, 1576, 1431, 1242, 797, 751, 698. MS (70 eV, EI): m/z (%): 243 (12) [M]+, 187 (16), 186 (100), 185 (15), 166 (10). HRMS (ESI) calculated for C16H19NF: 244.1496 [M+H]+, found: 244.1495.

1-chloro-2-fluoro-3-(1-phenyloctyl)benzene (21): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) (b/: 90:10, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (52.1 mg, 0.16 mmol, 81%). Rf = 0.43 (Hexane). 1H NMR (400 MHz, CDCl3): δ 7.31 – 7.16 (m, 7H), 7.04 – 7.00 (m, 1H), 4.27 (t, J = 7.8 Hz, 1H), 2.10 – 1.96 (m, 2H), 1.32 – 1.25 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 156.2 (d, J = 247.2 Hz), 143.6, 134.2 (d, J = 14.7 Hz), 128.6, 128.3, 128.0, 126.9 (d, J = 3.9 Hz), 126.6, 124.5 (d, J = 4.6 Hz), 121.2 (d, J = 19.0 Hz), 43.87 – 43.85 (m, 1C), 34.8, 32.0, 29.6, 29.3, 28.0, 22.8, 14.2. 19F NMR (376 MHz, CDCl3): δ -119.89 (t, J = 6.5 Hz). IR (neat, cm⁻¹): 2926, 2856, 1454, 1229, 771, 726, 698. MS (70 eV, EI): m/z (%): 320 (4) [37Cl-M]+, 318 (12) [37Cl-M]+, 221 (35), 220 (16), 219 (100), 184 (30), 183 (35). HRMS (ESI) calculated for C20H14ClF: 318.1545 [M]+, found: 318.1541.

4-chloro-2-fluoro-1-(1-phenyloctyl)benzene (22): Prepared, following the general procedure from 4-chloro-2-fluorophenyl trifluoromethanesulfonate (9a) (b/: 86:14, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (47.2 mg, 0.15 mmol, 74%). Rf = -S9-
0.54 (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31 – 7.17 (m, 6H), 7.09 – 7.01 (m, 2H), 4.21 (t, $J$ = 7.8 Hz, 1H), 2.08 – 1.94 (m, 2H), 1.28 – 1.24 (m, 10H), 0.87 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 160.6 (d, $J$ = 248.7 Hz), 143.7, 132.4 (d, $J$ = 10.6 Hz), 131.2 (d, $J$ = 14.7 Hz), 129.5 (d, $J$ = 5.5 Hz), 128.6, 128.0, 126.5, 124.6 (d, $J$ = 3.5 Hz), 116.3 (d, $J$ = 26.5 Hz), 43.24 – 43.23 (m, 1C), 34.8, 32.0, 29.6, 29.3, 28.0, 22.8, 14.2. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -115.28 (t, $J$ = 8.9 Hz). IR (neat, cm$^{-1}$): 2926, 2856, 1605, 1576, 1485, 1456, 1407, 1222, 1076, 895, 856, 697. MS (70 eV, EI): $m/z$ (%): 320 (3) [37Cl-M$^+$], 318 (10) [35Cl-M$^+$], 221 (40), 220 (18), 219 (100), 184 (27), 183 (34). HRMS (ESI) calculated for C$_{20}$H$_{20}$ClF: 318.1545 [M$^+$], found: 318.1549.

1-chloro-2-fluoro-3-(1-phenylundecyl)benzene (23): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) ($b/l$ 90:10, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (56.2 mg, 0.16 mmol, 77%). $R_t$ = 0.45 (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30 – 7.14 (m, 7H), 7.00 (dd, $J$ = 7.9 Hz, 1H), 4.25 (t, $J$ = 7.8 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.28 – 1.23 (m, 16H), 0.87 (t, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 156.3 (d, $J$ = 247.4 Hz), 143.6, 134.2 (d, $J$ = 14.6 Hz), 128.6, 128.3, 128.1, 127.0 (d, $J$ = 4.0 Hz), 126.6, 124.5 (d, $J$ = 4.6 Hz), 121.2 (d, $J$ = 19.0 Hz), 43.9 (d, $J$ = 1.8 Hz), 34.8, 32.1, 29.7 (29.74), 29.7 (29.66), 29.6, 29.5, 28.0, 22.8, 14.3. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -119.88 (t, $J$ = 6.3 Hz). IR (neat, cm$^{-1}$): 2924, 2854, 1454, 1229, 770, 726, 698. MS (70 eV, EI): $m/z$ (%): 362 (3) [37Cl-M$^+$], 360 (10) [35Cl-M$^+$], 221 (34), 220 (15), 219 (100), 184 (21), 183 (19). HRMS (ESI) calculated for C$_{23}$H$_{22}$ClF: 360.2015 [M$^+$], found: 360.2029.

2-fluoro-3-(3-methyl-1-phenylpentyl)pyridine (24): Prepared, following the general procedure from 2-fluoropyridin-3-yl trifluoromethanesulfonate (2a) ($b/l$ 75:25, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (33.4 mg, 0.13 mmol, 65%) of the 1:1 mixture of two inseparable diastereomers. $R_t$ = 0.35 (95:5 Hexane/EtOAc). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05 – 8.02 (m, 1H), 8.70 – 8.62 (m, 1H), 7.33 – 7.18 (m, 5H), 7.15 – 7.09 (m, 1H), 4.36 – 4.30 (m, 1H), 2.13 – 2.05 (m, 1H), 1.82 – 1.72 (m, 1H), 1.44 – 1.35 (m, 1H), 1.28 – 1.16 (m, 2H), 0.93 – 0.82 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $^{19}$F decoupled: $\delta$ 145.2, 145.1, 143.3, 142.4, 139.2, 139.0, 128.8 (128.77), 128.8 (128.75), 128.3, 128.0, 126.3 (126.82), 126.8 (126.75), 121.7, 121.6, 41.6, 41.5, 41.2, 32.0, 31.9, 29.7, 29.4, 19.3, 19.0, 11.2, 11.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -71.99 (s). IR (neat, cm$^{-1}$): 2925, 2861, 1603, 1578, 1435, 1242, 1114, 1063, 796, 745, 697. MS (70 eV, EI): $m/z$ (%): 257 (9) [M$^+$], 187 (33), 186 (100). HRMS (ESI) calculated for C$_{20}$H$_{20}$FN: 280.1472 [M+Na$^+$], found: 280.1464.

1-chloro-2-fluoro-3-(1-phenylpropyl)benzene (25): Prepared, following the general procedure from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) ($b/l$ 95:5, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (48.1 mg, 0.18 mmol, 88%). $R_t$ = 0.43 (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 – 7.26 (m, 4H), 7.24 – 7.16 (m, 3H), 7.02 (dd, $J$ = 7.9, 7.9 Hz, 1H), 4.30 (t, $J$ = 7.9 Hz, 1H), 2.10 – 1.95 (m, 2H), 1.35 – 1.26 (m, 2H), 0.94 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 156.3 (d, $J$ = 247.3 Hz), 143.5, 134.2 (d, $J$ = 14.6 Hz), 128.6, 128.4, 128.1, 127.0 (d, $J$ = 4.0 Hz), 126.6, 124.5 (d, $J$ = 4.5 Hz), 121.2 (d, $J$ = 19.0 Hz), 43.58 – 43.57 (m, 1C), 37.0,
$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –119.91 (t, $J = 6.8$ Hz). IR (neat, cm$^{-1}$): 2931, 2957, 1453, 1229, 769, 727, 698. MS (70 eV, EI): $m/z$ (%): 264 (5) [Cl-M']$, 262 (16) [Cl-M'], 221 (33), 220 (15), 219 (100), 184 (52), 183 (64). HRMS (ESI) calculated for C$_{16}$H$_{16}$ClF: 262.0919 [M]$^+$, found: 262.0919.
3. Mechanistic tests and Comparisons

3.1. Direct coupling

1-chloro-2-fluoro-3-(3-phenylpropyl)benzene (26): Prepared, following the general procedure but employing [Pd(μ-I)(PtBu₃)]₂ as the catalyst from 3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a) (b/l 2:98, based on GC-MS of the crude). The title product was obtained after purification by column chromatography (Pentane) as a colorless oil (40.6 mg, 0.16 mmol, 80%). Rf = 0.42 (Hexane).

1H NMR (400 MHz, CDCl₃): δ 7.32 – 7.19 (m, 6H), 7.10 – 7.06 (m, 1H), 7.01 – 6.97 (m, 1H), 2.73 – 2.66 (m, 4H), 1.96 (p, J = 7.7 Hz, 2H). 13C NMR (151 MHz, CDCl₃): δ 156.6 (d, J = 247.1 Hz), 141.9, 131.0 (d, J = 4.5 Hz), 128.5 (128.54), 128.5 (128.51), 128.3, 126.0, 124.4 (d, J = 4.6 Hz), 121.1 (d, J = 18.4 Hz), 35.6, 33.6 (m), 29.0 (d, J = 2.1 Hz). 19F NMR (376 MHz, CDCl₃): δ –120.74 (t, J = 7.0 Hz). IR (neat, cm⁻¹): 2927, 2855, 1458, 774, 741, 698. MS (70 eV, EI): m/z (%): 250 (21) [Cl-M⁺], 248 (65) [Cl-M⁺], 144 (30), 105 (53), 92 (100). HRMS (ESI) calculated for C₁₅H₁₄ClF: 248.0763 [M⁺], found: 248.0760.

3.1.1. GC-MS comparison of Pdª dimers

- S12 -
3.2. Comparison to known catalytic systems

**Test-1**[2]: In an argon filled glove box, NiCl$_2$ (0.7 mg, 0.005 mmol, 0.05 equiv.), L (1.1 mg, 0.006 mmol, 0.06 equiv.) and CsF (30.4 mg, 0.2 mmol, 2.0 equiv.) were dissolved in anhydrous THF (0.5 mL) and stirred for 10 minutes. After that, poly(methylhydrosiloxane) (PMHS, CAS 63148-57-2, 59.1 mg, 0.25 mmol, 2.5 equiv) was added to the reaction mixture and stirred for another 5 min. Alkene (0.1 mmol, 1.0 equiv.) and aryl iodide (0.15 mmol, 1.5 equiv.) were added to the reaction mixture consecutively. After 14 hours of further stirring at ambient temperature diphenylmethane (16.8 mg, 0.1 mmol) was added as an internal standard to the reaction mixture, aliquots were taken and analyzed by GC-MS. *Note: Other examples (see 3.1.) were analyzed with quantitative $^1$H NMR as well and the obtained results were within a 5% error range with the result obtained from GC-MS analysis.*

**Test-2**[3]: In an argon filled glove box, (NiClO$_4$)$_2$ (3.7 mg, 0.005 mmol, 0.05 equiv.), and L (1.1 mg, 0.006 mmol, 0.06 equiv.) were dissolved in anhydrous DMA (1.0 mL) and stirred for 10 minutes. After that, aryl bromide (2.0 equiv, 0.40 mmol), alkyl bromide (1.0 equiv, 0.20 mmol) and Mn (22.0 mg, 2.0 equiv, 0.40 mmol) were added to the resulting mixture in this order and the resulting mixture was stirred for 8h. Then n-PrBr (9.0 μL, 0.50 equiv, 0.10 mmol) was added. After 24 hours of further stirring at ambient temperature diphenylmethane (33.7 mg, 0.2 mmol) was added as an internal standard to the reaction mixture and aliquots were taken, and analyzed by GC-MS. *Note: Other examples (see 3.1.) were analyzed with quantitative $^1$H NMR as well and the obtained results were within a 5% error range with the result obtained from GC-MS analysis.*

*Previously reported results from ref [2].

*Previously reported results from ref [3].
**Test-3**\(^{[4]}\): In an argon filled glove box, NiI\(_2\) (3.1 mg, 0.1 mmol, 0.05 equiv.), bathocuproine (3.6 mg, 10 mol%), \(n\)-Bu\(_4\)NBr (32.2 mg, 1.0 equiv.) and Zn dust (9.8 mg, 1.5 equiv.) were suspended in anhydrous DMA (1.0 mL) and stirred for 5 minutes. After that, alkyl bromide (1.0 equiv, 0.1 mmol), and aryl bromide (1.2 equiv, 0.12 mmol) were added to the resulting mixture in this order. After 24 hours of further stirring at ambient temperature diphenylmethane (16.8 mg, 0.1 mmol) was added as an internal standard to the reaction mixture and aliquots were taken, and analyzed by GC-MS. Note: Other examples (see 3.1.) were analyzed with quantitative \(^1\)H NMR as well and the obtained results were within a 5% error range with the result obtained from GC-MS analysis.
4. Synthesis and characterization data for the starting materials

4.1. General experimental procedures for the synthesis of the alkyl bromides

**Method A**

\[
\text{R-COOH} \xrightarrow{\text{LiAlH}_4 (2 \text{ equiv.})} \text{R-COH} \xrightarrow{\text{PPh}_3 (1.5 \text{ equiv.})} \text{R-CBr}
\]

Under Ar atmosphere, carboxylic acid (5.0 mmol, 1.0 equiv) was dissolved in 5 mL THF and slowly added to a suspension of LiAlH\(_4\) (380 mg, 10.0 mmol, 2.0 equiv) in THF (20 mL) at 0 °C. Then the reaction mixture was allowed to warm at room temperature and was stirred until all starting material was consumed (typically 2 h, monitored by TLC). After completion the reaction mixture was cooled in an ice bath and EtOAc (20 mL) was slowly added and the resulting mixture was stirred at room temperature for 10 minutes. The formed white suspension was filtered through a pad of celite and the resulting filtrate was acidified with 1 N HCl (20 mL) to get a clear solution. The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed with NaHCO\(_3\) and dried over Na\(_2\)SO\(_4\). The crude mixture was concentrated under reduced pressure.

Without further purification, the crude material (5.0 mmol, 1 equiv.) was dissolved in DCM (5 mL) and added to a solution of CBr\(_4\) (2.5 g, 7.5 mmol, 1.5 equiv.) in DCM (10 mL) at 0 °C under Ar atmosphere. Then, PPh\(_3\) (2.0 g, 7.5 mmol, 1.5 equiv.) was dissolved in DCM (5 mL) and slowly added to the reaction mixture. The resulting mixture was allowed to warm to room temperature and further stirred for 4 hours. After completion, the solvent was removed under reduced pressure and the residue was subjected to column chromatography on silica for further purification.

**Method B**

\[
\text{R-B} \xrightarrow{\text{tBuLi (1.1 equiv.)}} \text{R-B} \xrightarrow{\text{1,3-dibromopropane (3.0 equiv.)}} \text{R-BBr}
\]

Under Ar atmosphere, tBuLi (2.1 mL of 2.7 M in hexane, 5.5 mmol, 1.1 equiv.) was added drop-wise to a flame dried round-bottom flask containing aryl bromide (5.0 mmol, 1.0 equiv.) dissolved in THF (20 mL) at -78 °C. After 10 minutes of stirring at the same temperature 1,3-dibromopropane (1.5 mL, 15.0 mmol, 3.0 equiv) was slowly added. The resulting mixture was then allowed to warm to room temperature and further stirred for 2 hours. After that, the reaction mixture was cooled in an ice bath and was slowly quenched with water (20 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL) and the combined organic phases were dried over Na\(_2\)SO\(_4\) and volatiles were removed under reduced pressure. The obtained crude was further purified by column chromatography.
4.2. Characterization data of alkyl bromides

1-(3-bromopropyl)-4-(trifluoromethyl)benzene (1b): Prepared, following method A from 3-(4-(trifluoromethyl)phenyl)propanoic acid. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (1.0 g, 3.75 mmol, 75%). $R_t = 0.42$ (Hexane). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 7.7$ Hz, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 3.39 (t, $J = 6.4$ Hz, 2H), 2.85 (t, $J = 7.3$ Hz, 2H), 2.19 (p, $J = 6.8$ Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 144.8, 129.0, 128.8 (q, $J = 32.3$ Hz), 125.6 (q, $J = 3.8$ Hz), 124.4 (q, $J = 271.8$ Hz), 33.9 (33.91), 33.9 (33.88), 32.8. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.4 (s). MS (70 eV, EI): m/z (%): 268 (33) $^{[81}\text{Br-M}^\text{-}]$, 266 (33) $^{[79}\text{Br-M}^\text{-}]$, 186 (12), 159 (100), 117 (17), 109 (21).

1-(3-bromopropyl)-2,4-difluorobenzene (2b): Prepared, following method A from 3-(2,4-difluorophenyl)propanoic acid. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (920 mg, 3.9 mmol, 78%). $R_t = 0.45$ (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.21 – 7.15 (m, 1H), 6.84 – 6.76 (m, 2H), 3.39 (t, $J = 6.6$ Hz, 2H), 2.78 (t, $J = 7.3$ Hz, 2H), 2.17 – 2.10 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$, $^{19}$F decoupled): $\delta$ 161.8, 161.2, 131.5, 123.3, 111.2, 103.9, 32.9 (32.88), 32.9 (32.85), 27.2. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -113.04 (p, $J = 7.4$ Hz), -114.25 (q, $J = 8.5$ Hz). MS (70 eV, EI): m/z (%): 236 (19) $^{[81}\text{Br-M}^\text{-}]$, 234 (19) $^{[79}\text{Br-M}^\text{-}]$, 127 (100).

1-(3-bromopropyl)-2-methylbenzene (3b): Prepared, following method B from 1-bromo-2-methylbenzene. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (480 mg, 2.23 mmol, 45%). $R_t = 0.47$ (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17 – 7.10 (m, 4H), 3.45 (t, $J = 6.6$ Hz, 2H), 2.79 – 2.76 (m, 2H), 2.33 (s, 3H), 2.17 – 2.10 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 139.0, 136.1, 130.5, 129.2, 126.5, 126.2, 33.6, 33.2, 31.7, 19.4. MS (70 eV, EI): m/z (%): 214 (22) $^{[81}\text{Br-M}^\text{-}]$, 212 (22) $^{[79}\text{Br-M}^\text{-}]$, 105 (100).

1-(3-bromopropyl)-3-methylbenzene (4b): Prepared, following method B from 1-bromo-3-methylbenzene. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (554 mg, 2.60 mmol, 52%). $R_t = 0.45$ (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.19 (dd, $J = 7.3$, 7.3 Hz, 1H), 7.03 – 7.00 (m, 3H), 3.40 (t, $J = 6.5$ Hz, 2H), 2.74 (t, $J = 7.3$ Hz, 2H), 2.34 (s, 3H), 2.17 (p, $J = 6.8$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 140.7, 138.2, 129.5, 128.5, 127.0, 125.7, 34.4, 34.1, 33.3, 21.5. MS (70 eV, EI): m/z (%): 214 (28) $^{[81}\text{Br-M}^\text{-}]$, 212 (28) $^{[79}\text{Br-M}^\text{-}]$, 105 (100), 91 (14).

4-(3-bromopropyl)-1,1’-biphenyl (5b): Prepared, following method B from 4-bromo-1,1’-biphenyl. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (592 mg, 2.2 mmol, 43%). $R_t = 0.31$ (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 – 7.58 (m, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.44 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.34 (dd, $J = 7.3$, 7.3 Hz, 1H), 7.28 (d, $J = 8.1$ Hz, 2H), 3.44 (t, $J = 6.6$ Hz, 2H), 2.83 (t, $J = 7.4$ Hz, 2H), 2.21 (p, $J = 6.7$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 141.1, 139.8, 138.9, 129.1, 128.9, 127.4, 127.3, 127.1, 34.3, 33.7, 33.3. MS (70 eV, EI): m/z (%): 276 (27) $^{[81}\text{Br-M}^\text{-}]$, 274 (28) $^{[79}\text{Br-M}^\text{-}]$, 167 (100), 152 (14). These data are in agreement with those reported previously in the literature.\[6\]
2-(3-bromopropyl)naphthalene (6b): Prepared, following method B from 2-bromonaphthalene. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (760 mg, 3.1 mmol, 61%). Rf = 0.35 (Hexane). 1H NMR (400 MHz, CDCl3): δ 7.80 (dd, J = 9.1 Hz, 3H), 7.65 – 7.63 (m, 1H), 7.49 – 7.41 (m, 2H), 7.34 (dd, J = 8.4, 1.8 Hz, 1H), 3.43 (t, J = 6.6 Hz, 2H), 2.95 (t, J = 7.3 Hz, 2H), 2.30 – 2.23 (m, 2H). 13C NMR (101 MHz, CDCl3): δ 138.1, 133.7, 132.3, 128.3, 127.8, 127.6, 127.3, 126.9, 126.2, 125.5, 34.3, 34.2, 33.3. MS (70 eV, EI): m/z (%):250 (32) [81Br-M*], 248 (33) [79Br-M*], 141 (100), 115 (25). These data are in agreement with those reported previously in the literature.[6]

1-(3-bromopropyl)-2-isopropylbenzene (7b): Prepared, following method B from 1-bromo-2-isopropylbenzene. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (362 mg, 1.5 mmol, 30%). Rf = 0.56 (Hexane). 1H NMR (400 MHz, CDCl3): δ 7.28 (dd, J = 8.0, 8.0 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.16 – 7.10 (m, 2H), 3.46 (t, J = 6.5 Hz, 2H), 3.23 – 3.13 (m, 1H), 2.84 – 2.81 (m, 2H), 2.17 – 2.10 (m, 2H), 1.25 (d, J = 6.9 Hz, 6H). 13C NMR (101 MHz, CDCl3): δ 146.8, 137.5, 129.7, 126.9, 125.8, 125.6, 34.6, 33.6, 31.2, 28.8, 24.2. MS (70 eV, EI): m/z (%):242 (37) [81Br-M*], 240 (38) [79Br-M*], 227 (62), 225 (64), 145 (45), 133 (36), 119 (100).

1-(3-bromopropyl)-4-(tert-butyl)benzene (8b): Prepared, following method B from 1-bromo-4-(tert-butyl)benzene. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (510 mg, 2.0 mmol, 40%). Rf = 0.6 (Hexane). 1H NMR (400 MHz, CDCl3): δ 7.33 – 7.31 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 3.41 (t, J = 6.6 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 2.17 (p, J = 6.8 Hz, 2H), 1.32 (s, 9H). 13C NMR (101 MHz, CDCl3): δ 149.1, 137.6, 128.4, 125.5, 34.5, 34.3, 33.6, 33.4, 31.5. MS (70 eV, EI): m/z (%):256 (15) [81Br-M*], 254 (15) [79Br-M*], 241 (100), 239 (97), 131 (22), 117 (27), 91 (20). These data are in agreement with those reported previously in the literature.[7]

6-(5-bromopentyl)-2,3-dihydrobenzo[b][1,4]dioxine (9b): Prepared, following method B from 6-bromo-2,3-dihydrobenzo[b][1,4]dioxine. The title product was obtained after purification by column chromatography (94:6 Hexane/EtOAc) as a colorless oil (742 mg, 2.6 mmol, 52%). Rf = 0.53 (94:6 Hexane/EtOAc). 1H NMR (400 MHz, CDCl3): δ 6.77 (d, J = 8.2 Hz, 1H), 6.68 (s, 1H), 6.65 – 6.63 (m, 1H), 4.24 (s, 4H), 3.40 (t, J = 6.9 Hz, 2H), 2.52 (t, J = 7.6 Hz, 2H), 1.88 (p, J = 7.0 Hz, 2H), 1.60 (p, J = 7.5 Hz, 2H), 1.50 – 1.42 (m, 2H). 13C NMR (101 MHz, CDCl3): δ 143.4, 141.7, 135.8, 121.4, 117.1, 117.0, 64.6, 64.5, 35.1, 33.9, 32.8, 30.8, 27.9. MS (70 eV, EI): m/z (%):286 (28) [81Br-M*], 284 (28) [79Br-M*], 150 (22), 149 (100).

(3-bromobutyl)benzene (10b): Prepared, following method A from 4-phenylbutan-2-ol. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (1.0 g, 3.75 mmol, 75%). Rf = 0.44 (Hexane). 1H NMR (400 MHz, CDCl3): δ 7.31 (dd, J = 7.5, 7.5 Hz, 2H), 7.23 – 7.21 (m, 3H), 4.12 – 4.07 (m, 1H), 2.90 – 2.86 (m, 1H), 2.79 – 2.74 (m, 1H), 2.18 – 2.12 (m, 1H), 2.09 – 2.03 (m, 1H), 1.75 (d, J = 6.6 Hz, 3H). 13C NMR
(101 MHz, CDCl$_3$): δ 141.1, 128.7, 128.6, 126.2, 51.0, 42.8, 34.1, 26.7. MS (70 eV, El): $m/z$ (%): 214 (18) [${}^{81}\text{Br-M}^+\] 212 (15) [${}^{79}\text{Br-M}^+\], 132 (16), 117 (26), 91(100). These data are in agreement with those reported previously in the literature.\[8\]

(8-bromooctyl)benzene (11b): Prepared, following method A from 8-phenyloctan-1-ol. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil (1.2 g, 4.3 mmol, 86%). $R_l$ = 0.53 (Hexane). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.31 – 7.27 (m, 2H), 7.20 – 7.17 (m, 3H), 3.41 (t, $J$ = 6.9 Hz, 2H), 2.64 – 2.60 (m, 2H), 1.86 (p, $J$ = 6.9 Hz, 2H), 1.63 (p, $J$ = 7.3 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.37 – 1.30 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 143.0, 128.5, 128.4, 125.7, 36.1, 34.1, 33.0, 31.6, 29.4, 29.3, 28.8, 28.3. MS (70 eV, EI): $m/z$ (%): [${}^{81}\text{Br-M}^+\] 270 (22), [${}^{79}\text{Br-M}^+\] 268 (22), 133 (8), 105 (12), 92 (91), 91 (100). These data are in agreement with those reported previously in the literature.\[9\]

(11-bromoundecyl)benzene (12b):

To a solution of 11-bromoundecan-1-ol (1.3 g, 5.2 mmol, 1.0 equiv.) and p-toluenesulfonic acid (90 mg, 0.52 mmol, 0.1 equiv.) in DCM (20 mL) 3,4-dihydro-2H-pyran (0.69 mL, 7.5 mmol, 1.5 equiv.) was added slowly at 0 °C. The resulting reaction mixture was slowly warmed to room temperature and stirred until all starting material was consumed (typically 4 h, monitored by TLC). After completion, the mixture was slowly quenched with water (20 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL) and the combined organic phases were dried over Na$_2$SO$_4$ and volatiles were removed under reduced pressure. The crude mixture was then filtered through a pad of silica using diethyl ether as an eluent and then concentrated under reduced pressure.

The obtained crude material (5.0 mmol, 1 equiv.) was dissolved in THF (10 mL) and cooled to -78 °C under Ar atmosphere. After that, PhLi solution in THF (3.2 mL 1.9 M, 6.1 mmol, 1.2 equiv.) was slowly added and the resulting mixture was allowed to warm to room temperature and stirred for 2h. The reaction mixture was cooled in an ice bath and was slowly quenched with water (20 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL) and the combined organic phases were dried over Na$_2$SO$_4$ and volatiles were removed under reduced pressure. The crude mixture was then filtered through a pad of silica using diethyl ether as an eluent and then concentrated under reduced pressure.

Without further purification, the crude material (5.0 mmol, 1 equiv.) was dissolved in MeOH (30 mL) and added to a round bottom flask containing p-toluenesulfonic acid (88 mg, 0.5 mmol, 0.1 equiv.) and the resulting mixture was stirred at room temperature overnight. After completion, the reaction mixture was concentrated under reduced pressure and further purified by column chromatography (hexane/EtOAc 1:1) to afford 11-phenylundecan-1-ol (1.0 g, 4.1 mmol, 82%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.27 – 7.25 (m, 2H), 7.18 (d, $J$ = 7.0 Hz, 3H), 3.65 (t, $J$ = 6.7 Hz, 2H), 2.62 – 2.58 (m, 2H), 1.66 – 1.50 (m, 4H), 1.45 (s, 1H), 1.30 – 1.27 (m, 14H). Spectroscopic data match with those reported previously in the literature.\[10\]
11-phenylundecan-1-ol (4.0 mmol, 1 equiv.) was dissolved in DCM (5 mL) and added to a solution of CBr₄ (2.0 g, 6.0 mmol, 1.5 equiv.) in DCM (10 mL) at 0 °C under Ar atmosphere. Then, PPh₃ (1.6 g, 6.0 mmol, 1.5 equiv.) was dissolved in DCM (5 mL) and slowly added to the reaction mixture. The resulting mixture was allowed to warm to room temperature and was further stirred for 4 hours. After completion, the solvent was removed under reduced pressure. The crude was purified by column chromatography (Hexane) to afford (11-bromoundecyl)benzene (900 mg, 2.9 mmol, 72%) as a colorless oil. 

H NMR (400 MHz, CDCl₃): δ 7.28 (d, J = 7.4 Hz, 2H), 7.18 (d, J = 7.0 Hz, 3H), 3.41 (t, J = 6.9 Hz, 2H), 2.63 – 2.59 (m, 2H), 1.86 (p, J = 7.0 Hz, 2H), 1.62 (p, J = 7.3 Hz, 2H), 1.42 (p, J = 7.0 Hz, 2H), 1.31 – 1.28 (m, 12 H). 

C NMR (101 MHz, CDCl₃): δ 143.1, 128.5, 128.4, 125.7, 36.1, 34.2, 33.0, 31.7, 29.7, 29.6 (29.62), 26.6 (29.58), 29.6 (29.56), 29.5, 28.9, 28.3.

The isolated compound contains impurities (ca. 28% by GC-MS) that could not be separated by column chromatography nor preparative HPLC. The obtained mixture was used without further purification.

(5-bromo-3-methylpentyl)benzene (13b):

Under Ar atmosphere, to a suspension of NaH (144 mg, 6.0 mmol, 1.2 equiv.) in THF (10 mL) ethyl 2-(diethoxyphosphoryl)acetate (1.2 mL, 6.0 mmol, 1.2 equiv) was added drop-wise at 0 °C. The resulting mixture was slowly allowed to warm to room temperature and stirred for 10 minutes. After that, 4-phenylbutan-2-one (0.75 mL, 5.0 mmol, 1.0 equiv.) was dissolved in THF (10 mL) and added drop-wise at 0 °C. The reaction mixture was further stirred for 4h at room temperature and was then slowly quenched with water (20 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL) and the combined organic phases were dried over Na₂SO₄ and volatiles were removed under reduced pressure.

Without further purification, the crude material (5.0 mmol, 1 equiv.) was dissolved in MeOH (30 mL) and was added to a round bottom flask containing 10% palladium on activated carbon (500 mg) under H₂ atmosphere and the resulting suspension was stirred at room temperature overnight. Then, volatiles were removed under reduced pressure, the crude redissolved in diethyl ether, filtered through a small column of celite using diethyl ether as eluent and concentrated under reduced pressure.

Without further purification, the crude material (5.0 mmol, 1 equiv.) was dissolved in THF (20 mL) and cooled to 0 °C under Ar atmosphere. Then, LiAlH₄ solution in THF (2.4 M, 4.2 mL, 10.0 mmol, 2.0 equiv.) was slowly added and the resulting mixture was allowed to warm to room temperature and further stirred for 2h. After completion, the reaction mixture was cooled in an ice bath and EtOAc (20 mL) was slowly added and the resulting mixture stirred at room temperature for 10 minutes. The obtained white suspension was filtered through a pad of celite and the resulting filtrate was acidified with 1 N HCl (20 mL) to get a clear solution. The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed with NaHCO₃ and dried over Na₂SO₄. The crude
mixture was concentrated under reduced pressure. The crude was further purified by column chromatography (hexane/EtOAc 1:1) to afford 3-methyl-5-phenylpentan-1-ol (766 mg, 4.3 mmol, 86%) as a colorless oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.32 – 7.25 \text{ (m, 2H)}\), \(7.20 – 7.15 \text{ (m, 3H)}\), \(3.75 – 3.64 \text{ (m, 2H)}\), \(2.73 – 2.54 \text{ (m, 2H)}\), \(1.72 – 1.58 \text{ (m, 3H)}\), \(1.54 – 1.40 \text{ (m, 3H)}\), \(1.26 \text{ (s, 1H)}\), \(0.98 \text{ (d, } J = 6.3 \text{ Hz, 3H)}\). Spectroscopic data match with those reported previously in the literature.\(^{[11]}\)

3-methyl-5-phenylpentan-1-ol (766 mg, 4.3 mmol, 1 equiv.) was dissolved in DCM (5 mL) and added to a solution of CBr\(_4\) (2.2 g, 6.5 mmol, 1.5 equiv.) in DCM (10 mL) at 0 °C under Ar atmosphere. Then, PPh\(_3\) (1.7 g, 6.5 mmol, 1.5 equiv.) was dissolved in DCM (5 mL) and slowly added to the reaction mixture. The resulting mixture was allowed to warm to room temperature and was further stirred for 4 hours. After completion, the solvent was removed under reduced pressure. The crude was purified by column chromatography (hexane) to afford (5-bromo-3-methylpentyl)benzene (1 g, 4.1 mmol, 96%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.29 \text{ (dd, } J = 7.5, 7.5 \text{ Hz, 2H)}\), \(7.23 – 7.19 \text{ (m, 3H)}\), \(3.50 – 3.46 \text{ (m, 1H)}\), \(3.44 – 3.40 \text{ (m, 1H)}\), \(2.71 – 2.66 \text{ (m, 1H)}\), \(2.63 – 2.58 \text{ (m, 1H)}\), \(1.99 – 1.93 \text{ (m, 1H)}\), \(1.77 – 1.64 \text{ (m, 3H)}\), \(1.53 – 1.47 \text{ (m, 1H)}\), \(0.98 \text{ (d, } J = 6.0 \text{ Hz, 3H)}\). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 142.7, 128.5 \text{ (128.49), 128.5 (128.45), 125.9, 40.1, 38.5, 33.4, 32.0, 31.6, 19.0. MS (70 eV, EI): } m/z \%: 242 (18) [\text{\(^{81}\)Br-M}]^+, 240 (15) [\text{\(^{79}\)Br-M}]^+, 105 (17), 92 (100), 91 (84).\)

4.3. General experimental procedures for the synthesis of the aryl triflates

**Method C**

![Diagram of Method C](image)

To a stirred solution of substituted phenol (5.0 mmol, 1.0 equiv) in dry DCM (10 mL) NEt\(_3\) (1.5 mL, 10.5 mmol, 2.1 equiv.) was added slowly under Ar atmosphere. Then the mixture was cooled to -78 °C and Tf\(_2\)O (0.93 mL, 5.5 mmol, 1.1 equiv) was added drop-wise and the mixture was stirred at room temperature overnight. The obtained reaction mixture was cooled in an ice bath and quenched with water (20 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL) and the combined organic phases were dried over Na\(_2\)SO\(_4\). Solvents were removed under reduced pressure and the concentrated crude was subjected to column chromatography on silica for further purification.

**Method D**

![Diagram of Method D](image)

To a suspension of 4-bromo-2-fluorophenyl trifluoromethanesulfonate (323 mg, 1.0 mmol, 1.0 equiv.) and [Pd(µ-I)PtBu\(_3\)]\(_2\) (22 mg, 0.025 mmol, 0.025 equiv.) in THF (5 mL), the appropriate Grignard reagent (1.5 mmol, 1.5 equiv.) was added in air and the reaction mixture was stirred for 5 minutes in an open flask. After that, all volatiles were removed under reduced pressure and the obtained crude was subjected to column chromatography on silica for further purification.
4.4. Characterization data of aryl triflates

4-chloro-2-fluorophenyl trifluoromethanesulfonate (9a) was prepared as previously reported and analyses matched previously reported data.\[[12]\]

3-chloro-2-fluorophenyl trifluoromethanesulfonate (1a): Prepared, following method C from 3-chloro-2-fluorophenol. The title product was obtained after purification by column chromatography (Pentane) as a colourless liquid (1.1 g, 3.9 mmol, 79%). R<sub>t</sub> = 0.52 (Pentane).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.47 - 7.43 (m, 1H), 7.30 - 7.26 (m, 1H), 7.20 - 7.15 (m, 1H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 150.6 (d, J = 242.2 Hz), 146.9 (d, J = 13.5 Hz), 133.9, 132.5 (d, J = 28.8 Hz), 122.8 (d, J = 4.9 Hz), 118.7 (d, J = 320.9 Hz).<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -73.12 (d, J = 5.1 Hz, 3F), -127.83 (q, J = 5.7 Hz, 1F). MS (70 eV, EI): m/z (%) : 280 (27) [<sup>37</sup>Cl-M<sup>+</sup>], 278 (70) [<sup>35</sup>Cl-M<sup>+</sup>], 216 (53), 214 (17), 145 (55), 119 (33), 117 (100).

2-fluoropyridin-3-yl trifluoromethanesulfonate (2a): Prepared, following method C from 2-fluoropyridin-3-ol. The title product was obtained after purification by column chromatography (Pentane/Et<sub>2</sub>O 95:5) as a colourless liquid (1.0 g, 4.1 mmol, 82%). R<sub>t</sub> = 0.57 (Pentane/Et<sub>2</sub>O 90:10).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.25 - 8.23 (m, 1H), 7.81 - 7.76 (m, 1H), 7.35 - 7.31 (m, 1H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 154.8 (d, J = 2.3 Hz), 146.9 (d, J = 13.5 Hz), 133.9, 132.5 (d, J = 28.8 Hz), 122.8 (d, J = 4.9 Hz), 118.7 (d, J = 320.9 Hz).<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -73.08 (d, J = 5.4 Hz, 3F), -79.12 - -79.14 (m, 1F). MS (70 eV, EI): m/z (%) : 245 (46) [M<sup>+</sup>], 181 (52), 153 (23), 93 (52), 84 (100), 69 (80).

4-bromo-2-fluorophenyl trifluoromethanesulfonate (3a): Prepared, following method C from 4-bromo-2-fluorophenol. The title product was obtained after purification by column chromatography (Pentane) as a colourless liquid (1.5 g, 4.9 mmol, 96%). R<sub>t</sub> = 0.51 (Pentane).<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.46 (dd, J = 9.1, 2.0 Hz, 1H), 7.38 - 7.36 (m, 1H), 7.23 (dd, J = 8.2, 8.2 Hz, 1H).<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 153.8 (d, J = 258.1 Hz), 136.2 (d, J = 13.3 Hz), 128.5 (d, J = 4.0 Hz), 124.8, 122.3 (d, J = 7.9 Hz), 121.5 (d, J = 21.1 Hz), 118.8 (q, J = 320.7 Hz).<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -73.12 (d, J = 5.1 Hz, 3F), -124.09 - -124.10 (m, 1F). HRMS (EI) calculated for C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>BrF<sub>4</sub>S: 321.08917 [M<sup>+</sup>]<sup>+</sup>, found: 321.8920.

4-cyano-2-fluorophenyl trifluoromethanesulfonate (4a): Prepared, following method C from 3-fluoro-4-hydroxybenzonitrile. The title product was obtained after purification by column chromatography (Pentane/Et<sub>2</sub>O 95:5) as a colourless liquid (800 mg, 3.0 mmol, 62%). R<sub>t</sub> = 0.38 (Pentane/Et<sub>2</sub>O 95:5).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.63 - 7.57 (m, 2H), 7.52 - 7.48 (m, 1H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 153.7 (d, J = 258.3 Hz), 140.2 (d, J = 13.2 Hz), 129.6 (d, J = 4.6 Hz), 125.2, 121.8 (d, J = 21.6 Hz), 118.7 (q, J = 320.8 Hz), 116.2 (d, J = 2.3 Hz), 114.0 (d, J = 8.1 Hz).<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -72.97 (d, J = 4.9 Hz, 3F), -123.08 - -123.10 (m, 1F). MS (70 eV, EI): m/z (%) : 269 (29) [M<sup>+</sup>], 205 (33), 136 (21), 108 (52), 69 (100). These data are in agreement with those reported previously in the literature.\[[13]\]
2,4-difluorophenyl trifluoromethanesulfonate (5a): Prepared, following method C from 4,2,4-difluorophenol. The title product was obtained after purification by column chromatography (Pentane) as a colourless liquid (1.2 g, 4.6 mmol, 92%). $R_t = 0.56$ (Pentane).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.36 – 7.32 (m, 1H), 7.05 – 7.01 (m, 1H), 6.97 – 6.94 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.7 (dd, $J = 252.2, 10.1$ Hz), 154.2 (dd, $J = 256.3, 12.8$ Hz), 133.4 (dd, $J = 13.4, 4.3$ Hz), 124.6 (d, $J = 10.3$ Hz), 118.8 (q, $J = 320.8$ Hz), 112.3 (dd, $J = 23.8, 4.0$ Hz), 106.3 (dd, $J = 27.3, 21.8$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -73.13 (d, $J = 5.1$ Hz, 3F), -107.44 – -107.49 (m, 1F), -122.11 – 122.17 (m, 1F). MS (70 eV, El): $m/z$ (%): 262 (39) [$M^+$], 198 (11), 129 (100), 101 (90), 69 (35).

These data are in agreement with those reported previously in the literature.[14]

4-cyclopropyl-2-fluorophenyl trifluoromethanesulfonate (6a): Prepared, following method D from 4-bromo-2-fluorophenyl trifluoromethanesulfonate. The title product was obtained after purification by column chromatography (Pentane) as a colourless liquid (213 mg, 0.75 mmol, 75%). $R_t = 0.41$ (Pentane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (dd, $J = 8.8, 7.7$ Hz, 1H), 6.93 – 6.88 (m, 2H), 1.90 (ddd, $J = 13.4, 8.5, 5.0$ Hz, 1H), 1.08 – 1.03 (m, 2H), 0.73 – 0.69 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 153.7 (d, $J = 252.2$ Hz), 147.33 (d, $J = 7.0$ Hz), 134.4 (d, $J = 13.4$ Hz), 123.2, 122.2 (d, $J = 3.5$ Hz), 118.8 (q, $J = 320.8$ Hz), 114.5 (d, $J = 18.4$ Hz), 15.3, 10.2. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -73.30 (d, $J = 5.4$ Hz, 3F), -128.32 – -128.37 (m, 1F). HRMS (EI) calculated for C$_{10}$H$_8$O$_3$F$_4$S: 284.0125 [$M^+$], found: 283.0126.

2-fluoro-4-(thiophen-2-yl)phenyl trifluoromethanesulfonate (7a): Prepared, following method D from 4-bromo-2-fluorophenyl trifluoromethanesulfonate. The title product was obtained after purification by column chromatography (Pentane) as a green liquid (281 mg, 0.86 mmol, 86%). $R_t = 0.34$ (Pentane). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.48 (dd, $J = 10.8, 2.2$ Hz, 1H), 7.43 – 7.41 (m, 1H), 7.37 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.35 – 7.32 (m, 2H), 7.11 (dd, $J = 5.1, 3.6$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 153.9 (d, $J = 253.4$ Hz), 141.2 (d, $J = 2.2$ Hz), 136.7 (d, $J = 7.2$ Hz), 135.8 (d, $J = 13.6$ Hz), 128.6, 126.9, 125.1, 124.1, 122.3 (d, $J = 3.6$ Hz), 118.9 (q, $J = 320.8$ Hz), 114.8 (d, $J = 19.8$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -73.15 (d, $J = 5.0$ Hz, 3F), -126.75 – -126.81 (m, 1F). HRMS (EI) calculated for C$_{11}$H$_6$O$_3$F$_3$S: 325.9689 [$M^+$], found: 325.9687.

2-fluoro-4-pentylphenyl trifluoromethanesulfonate (8a): Prepared, following method D from 4-bromo-2-fluorophenyl trifluoromethanesulfonate. The title product was obtained after purification by column chromatography (Pentane) as a colourless liquid (248 mg, 0.79 mmol, 79%). $R_t = 0.52$ (Pentane). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.22 (dd, $J = 8.0, 8.0$ Hz, 1H), 7.07 (d, $J = 10.8$ Hz, 1H), 7.00 (d, $J = 8.6$ Hz, 1H), 2.62 (t, $J = 7.7$ Hz, 2H), 1.63 – 1.60 (m, 2H), 1.35 – 1.31 (m, 4H), 0.91 – 0.89 (m, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 153.5 (d, $J = 252.6$ Hz), 145.8 (d, $J = 6.5$ Hz), 134.8 (d, $J = 13.5$ Hz), 124.9 (d, $J = 3.2$ Hz), 123.2, 118.9 (q, $J = 320.8$ Hz), 117.4 (d, $J = 17.6$ Hz), 35.5, 31.4, 30.8, 22.6, 14.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -73.31 (d, $J = 5.1$ Hz, 3F), -128.33 – -128.39 (m, 1F). HRMS (EI) calculated for C$_{12}$H$_8$O$_3$F$_4$S: 314.0594 [$M^+$], found: 314.0599.
5. Crystallographic data

Single crystal X-ray data were collected on a Bruker-Nonius Kappa CCD diffractometer with an APEX-II detector with graphite-monochromatized Mo-Kα (λ = 0.71073 Å) radiation at 293 K. Data collection and reduction were performed using the program SAINT[15] and the intensities were corrected for absorption using SADABS.[16] The structure was solved with intrinsic phasing using SHELXT[17] and refined by full-matrix least squares on $F^2$ using the OLEX2 software,[18] which utilises the SHELXL-2015 module.[19] The main details of crystal data collection and refinement parameters are presented in Table S1.

| Table S1. Crystal data and structure refinement for 11. |
|--------------------------------------------------------|
| Compound | 11 |
| CCDC Number | 2107414 |
| Formula | C$_{21}$H$_{18}$ClF |
| Formula Weight [g/mol] | 324.8 |
| Colour | colourless |
| Shape | plate |
| Crystal System | monoclinic |
| Space Group | $P2_1/c$ |
| $a$ [Å] | 7.111(3) |
| $b$ [Å] | 7.774(3) |
| $c$ [Å] | 30.715(11) |
| $\alpha$ [Å] | 90 |
| $\beta$ [Å] | 94.691(8) |
| $\gamma$ [Å] | 90 |
| $V$ [Å$^3$] | 1692.3(10) |
| $Z$ | 4 |
| $\rho$ calc [g/cm$^3$] | 1.275 |
| $F(000)$ | 680 |
| $\mu$ [mm$^{-1}$] | 0.232 |
| $\theta_{max}$ [°] | 24.996 |
| Total Refl. | 69472 |
| Unique Refl. | 2977 |
| Reflections with $I_0 > 2\sigma(I_0)$ | 2671 |
| $R_{int}$ | 0.0631 |
| Parameters | 209 |
| Restraints | 0 |
| GooF on $F^2$ | 1.168 |
| $R_1$ ($I_0 > 2\sigma(I_0)$) | 0.0813 |
| $wR_2$ ($I_0 > 2\sigma(I_0)$) | 0.1937 |
| $R_1$ (all reflections) | 0.0873 |
| $wR_2$ (all reflections) | 0.1991 |
| Largest Peak [e/Å$^3$] | 0.392 |
| Largest Hole [e/Å$^3$] | -0.561 |
6. Computational details

All the DFT calculations were carried out in Gaussian 16 (A.03) program package.\cite{20} For optimisations and frequency calculations the MN15 with D3(BJ) correction was used. The values for D3(BJ) parameters were taken from the literature,\cite{21} and were input through the following option: IOp(3/174=1000000,3/175=0786200,3/177=2097100,3/178=7592300). For single point corrections M06-2X with the D3 dispersion correction was used. The basis sets of choice were def-SVP for geometries and frequencies, and def2-TZVP for single points corrections. Those basis sets automatically involve the use of the def2-ECP pseudopotential for palladium. For all calculations implicit solvation was introduced using the SMD model with N,N-dimethylacetamide as the solvent, as it is the closest one to NMP that is included in Gaussian. Frequency calculations were analysed to characterize the nature of the stationary point as minima (no imaginary frequency) or transition state (one imaginary frequency). Additionally, relaxation of transition states towards previous and next intermediates and IRC analysis, when needed, were used to verify the connectivity of the transition states. Finally, the GoodVibes program\cite{22} was used to apply quasi-harmonic corrections as well as correct the thermochemistry values to represent the solvated state at standard conditions (1 M concentration, 298.15 K, and 1 atm). The approach from Cramer and Truhlar\cite{23} was used for the quasi-harmonic approximation, with the cut-off value set at 100 cm\(^{-1}\). The reported energies are a sum of potential energies calculated at the M06-2X/def-TZVP level and the thermochemistry corrections obtained using GoodVibes.\cite{22} Computational figures were created with CYLview.\cite{24}
6.1. Full computed pathways and energies

**Figure S1.** Full pathway for $L = PCy_2$Bu and Aryl = 2-fluoro-4-chlorophenyl. Calculated at the SMD(DMAc) M06-2X-D3/def2-TZVP//MN15-D3(BJ)/def2-SVP level. Quasi-harmonic and corrections for concentration (1 M) applied using GoodVibes (qs Truhlar, cut off at 100 cm$^{-1}$). The values represent $\Delta G$ (kcal/mol) relative to Int I.
Figure S2. Full pathway for $L = P^tBu_3$ and Aryl = 2-fluoro-4-chlorophenyl. Calculated at the SMD(DMAc) M06-2X-D3/def2-TZVP//MN15-D3(BJ)/def2-SVP level. Quasi-harmonic and corrections for concentration (1 M) applied using GoodVibes (qs Truhlar, cut off at 100 cm$^{-1}$). The values represent $\Delta G$ (kcal/mol) relative to Int I.
| Structure | E | ZPE | H | T.S | T qb-S | G(T) | qb-G(T) | im freq | E M06-2X/def2-TZVP | G M06-2X/def2-TZVP |
|-----------|---|-----|---|-----|-------|------|--------|---------|-------------------|-------------------|
| Int_I     | -2234.243766 | 0.691561 | -2233.513881 | 0.104397 | 0.096643 | -2233.618278 | -2233.610524 | -2237.561638 | -2236.928396 |
| Int_II    | -2234.235030 | 0.689771 | -2233.509693 | 0.103414 | 0.096469 | -2233.610376 | -2233.603431 | -2237.549583 | -2236.917984 |
| Int_III   | -2234.235886 | 0.689603 | -2233.507830 | 0.103951 | 0.096849 | -2233.611781 | -2233.604679 | -2237.551223 | -2236.920016 |
| Int_IV    | -2234.245956 | 0.690818 | -2233.516539 | 0.104633 | 0.096995 | -2233.613534 | -2233.613534 | -2237.642979 | -2236.931952 |
| Int_V     | -2234.259118 | 0.692189 | -2233.520802 | 0.105211 | 0.098003 | -2233.633233 | -2233.626025 | -2237.579847 | -2236.945354 |
| Int_VI    | -2234.242911 | 0.690607 | -2233.513505 | 0.106266 | 0.097447 | -2233.619770 | -2233.610952 | -2237.561676 | -2236.929717 |
| Int_VII   | -2234.241394 | 0.689288 | -2233.513335 | 0.104322 | 0.097455 | -2233.617657 | -2233.610790 | -2237.555355 | -2236.924751 |
| Int_VIII  | -2234.240176 | 0.689301 | -2233.512111 | 0.105052 | 0.097212 | -2233.617163 | -2233.609323 | -2237.555359 | -2236.924506 |
| Int_IX    | -2234.229437 | 0.691028 | -2233.499136 | 0.110758 | 0.098552 | -2233.609894 | -2233.597688 | -2237.558443 | -2236.926694 |
| Int_X     | -2234.382666 | 0.691126 | -2233.508333 | 0.105147 | 0.097764 | -2233.613480 | -2233.606097 | -2237.636372 | -2236.931203 |
| Prod_C1   | -1138.433977 | 0.249596 | -1138.168304 | 0.057053 | 0.053990 | -1138.225357 | -1138.222294 | -1140.057934 | -1139.847851 |
| Prod_C2   | -1138.434832 | 0.249534 | -1138.169250 | 0.057158 | 0.053941 | -1138.226408 | -1138.223191 | -1140.060858 | -1139.849217 |
| Prod_C3   | -1138.350501 | 0.250012 | -1138.169966 | 0.058906 | 0.054091 | -1138.227773 | -1138.223058 | -1140.062339 | -1139.850396 |
| Ts_bHE_I  | -2234.33724 | 0.691101 | -2233.505017 | 0.101143 | 0.095017 | -2233.606250 | -2233.600214 | -439.74 | -2237.547782 | -2236.914272 |
| Ts_bHE_II | -2234.321503 | 0.687887 | -2233.505440 | 0.103914 | 0.096249 | -2233.609354 | -2233.601689 | -556.29 | -2237.545953 | -2236.916139 |
| Ts_bHE_III| -2234.323173 | 0.687509 | -2233.507069 | 0.105163 | 0.096986 | -2233.612232 | -2233.604055 | -664.14 | -2237.546778 | -2236.917660 |
| Ts_bHE_IV | -2234.327915 | 0.688273 | -2233.511362 | 0.103353 | 0.096427 | -2233.614715 | -2233.607789 | -533.63 | -2237.552788 | -2236.922662 |
| Ts_RE_C1  | -2234.29358 | 0.691648 | -2233.499394 | 0.103707 | 0.096888 | -2233.630310 | -2233.596282 | -265.44 | -2237.551376 | -2236.918300 |
| Ts_RE_C2  | -2234.223330 | 0.69195 | -2233.493070 | 0.103000 | 0.096245 | -2233.596100 | -2233.589315 | -323.73 | -2237.547221 | -2236.914067 |
| Ts_RE_C3  | -2234.215711 | 0.690660 | -2233.486379 | 0.109507 | 0.097397 | -2233.595886 | -2233.583777 | -365.62 | -2237.544177 | -2236.912243 |
| NMP       | -325.286624 | 0.139094 | -325.139683 | 0.035594 | 0.035594 | -325.175277 | -325.175277 | -325.937083 | -325.825376 |
| Prod[PCy2Bu](NMP) | -142.1128732 | 0.584309 | -1420.514040 | 0.087663 | 0.082005 | -1420.61703 | -1420.596045 | -1423.482606 | -1422.949919 |

**Table S2.** Energies of all computed structures. All energies in the table are in \( E_{\text{h}} \).
6.2. Distortion/Interaction Analysis

The transition states for reductive elimination and β-H elimination with \( L = \text{PCy}_2^t\text{Bu} \) and \( \text{P}^t\text{Bu}_3 \) were analyzed with regard to their distortion and interaction.\(^{25}\) Single-point energy calculations at the SMD(DMAc) M06-2X-D3/def2-TZVP level of theory were performed for: (i) the whole structure, (ii) just the ligand fragment (frag1) and (iii) just the Ar-Pd-(CH\(_2\))\(_3\)Ph fragment (i.e. the remaining fragment after removing the ligand; frag2). The contributions of distortion and interaction were then calculated as follows:

\[
\text{Potential energy surface (\( \Delta E \))} = E(\text{TS}) - E(\text{Int I})
\]
\[
\Delta E(\text{distortion}) = [E(\text{fragment 1}) + E(\text{fragment 2})] - E(\text{Int I})
\]
\[
\Delta E(\text{interaction}) = \Delta E - \Delta E(\text{distortion})
\]

Table S3. Single point energies used for the distortion/interaction analysis and resulting \( \Delta E \) values. All energies in the table are in kcal/mol.

| Structure | E(\text{Int I}) | E(\text{TS}) | E(\text{frag1}) | E(\text{frag2}) | \( \Delta E \) | \( \Delta E_{\text{dist}} \) | \( \Delta E_{\text{int}} \) |
|-----------|----------------|--------------|----------------|----------------|----------------|---------------------|---------------------|
| \text{TS}_\text{RE-C3} | | | | | | | |
| \( L = \text{PCy}_2^t\text{Bu} \) | -1404091.2 | -1404080.2 | -608475.5 | -795571.1 | 11.0 | 44.5 | -33.5 |
| \( L = \text{P}^t\text{Bu}_3 \) | -1306915.9 | -1306905.4 | -511301.4 | -795571.4 | 10.5 | 43.0 | -32.5 |
| \( \Delta \Delta E \) | -0.5 | -1.5 | 1.0 | | | | |
| \text{TS}_\text{bHE-I} | | | | | | | |
| \( L = \text{PCy}_2^t\text{Bu} \) | -1404091.2 | -1404082.5 | -608474.7 | -795559.2 | 8.7 | 57.2 | -48.6 |
| \( L = \text{P}^t\text{Bu}_3 \) | -1306915.9 | -1306902.7 | -511299.3 | -795559.0 | 13.2 | 57.5 | -44.3 |
| \( \Delta \Delta E \) | 4.5 | 0.3 | 4.2 | | | | |

6.3. NCI analysis

Noncovalent interactions were analyzed graphically using the Multiwfn software (Figure S3).\(^{26}\) The high quality grid setting was used to create reduced density gradient (RDG) and \( \text{sign}(\lambda_2)\rho \) cube files, which were then plotted using Chimera.\(^{27}\) Using an isosurface value of 0.05 the RDG surface was plotted and colored according to the \( \text{sign}(\lambda_2)\rho \) values ranging from -0.035 (blue, H-bonding) via 0.0 (green, VdW/dispersion) to 0.02 (red, steric interactions).\(^{26, 28}\)

Figure S3. Noncovalent interaction analysis for transition states of reductive elimination (left) and β-H elimination (right) with \( L = \text{PCy}_2^t\text{Bu} \) (a, c) and \( L = \text{P}^t\text{Bu}_3 \) (b, d), respectively. Calculated at the SMD(DMAc) M06-2X-D3/def2-TZVP level of theory.
6.4. Coordinates of the computed structures

6.4.1. Structures for pathway using L = PCy3/But and Aryl = 2-fluoro-4-chlorophenyl
6.4.2. Structures for pathway using L = PBU₃ and Aryl = 2-fluoro-4-chlorophenyl
|     | X     | Y     | Z     |     | X     | Y     | Z     |
|-----|-------|-------|-------|-----|-------|-------|-------|
| H   | -2.93366 | 0.71760 | -2.37990 | H   | -1.42815 | -2.06712 | 2.48122 |
| C   | -0.24105 | 1.10662 | -2.02858 | H   | -2.67970 | -1.28532 | 3.47027 |
| H   | -0.30573 | 2.03888 | -2.61573 | C   | -1.18401 | 0.63560 | 2.69082 |
| H   | 0.76223  | 1.06492 | -1.57650 | H   | -0.91578 | 1.63925 | 2.34224 |
| H   | -0.33998 | 0.26905 | -2.72825 | C   | -1.68110 | 0.74480 | 3.67015 |
| C   | -2.36122 | -1.47884 | 2.44007 | H   | -0.25218 | 0.06361 | 2.84261 |
| H   | -3.14489 | -2.08358 | 1.96484 | C   | -3.47677 | 0.61370 | 1.67569 |
7. NMR spectra

$^1$H (400 MHz, CDCl$_3$)

![NMR spectrum of $^1$H](image)

$^{13}$C (101 MHz, CDCl$_3$)

![NMR spectrum of $^{13}$C](image)
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}$C (101 MHz, CDCl$_3$)

$^{19}$F (376 MHz, CDCl$_3$)
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}\text{C} \ (101 \text{ MHz, CDCl}_3, ^{19}\text{F decoupled})$

$^{19}\text{F} \ (376 \text{ MHz, CDCl}_3)$
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)
$^{19}\text{F} \ (376 \text{ MHz, CDCl}_3)$

$^1\text{H} \ (400 \text{ MHz, CDCl}_3)$
$^{13}C$ (101 MHz, CDCl$_3$)

$^{19}F$ (376 MHz, CDCl$_3$)
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$, $^{19}$F decoupled)
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^1$H (400 MHz, CDCl$_3$)

$^1$H NMR spectrum showing peaks at various ppm values.

$^13$C (101 MHz, CDCl$_3$, $^{19}$F decoupled)

$^13$C NMR spectrum showing peaks at various ppm values.

-S53-
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}$C (101 MHz, CDCl$_3$, $^{19}$F decoupled)

$^{19}$F (376 MHz, CDCl$_3$)
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)
\textsuperscript{19}F (376 MHz, CDCl\textsubscript{3})

\textsuperscript{1}H (400 MHz, CDCl\textsubscript{3})
$^{13}$C (101 MHz, CDCl$_3$)

$^{19}$F (376 MHz, CDCl$_3$)
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)
$^{19}F$ (376 MHz, CDCl$_3$)

$^1H$ (400 MHz, CDCl$_3$)
$^{13}\text{C} \ (101 \text{ MHz, CDCl}_3)$

$^{19}\text{F} \ (376 \text{ MHz, CDCl}_3)$
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}$C (101 MHz, CDCl$_3$, $^{19}$F decoupled)

19F (376 MHz, CDCl$_3$)
$^{1}H$ (400 MHz, CDCl$_3$)

- B (dd) 7.06 (J(8.41, 1.73))
- A (dd) 7.17 (J(8.12))
- C (dd) 7.01 (J(9.88, 2.09))

$^{13}C$ (101 MHz, CDCl$_3$)

- A (d) 160.51 (J(248.59))
- B (d) 124.58 (J(3.51))
- D (d) 131.32 (J(14.75))
- F (d) 116.28 (J(26.54))
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}$C (101 MHz, CDCl$_3$)

$^{19}$F (376 MHz, CDCl$_3$)
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)

-S68-
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)
$^{19}\text{F (376 MHz, CDCl}_3)$

$^{1}\text{H (400 MHz, CDCl}_3)$
$^1$H (400 MHz, CDCl₃)

$^{13}$C (101 MHz, CDCl₃)
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}$C (101 MHz, CDCl$_3$)

$^{19}$F (376 MHz, CDCl$_3$)
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (151 MHz, CDCl$_3$)

-S77-
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}$C (151 MHz, CDCl$_3$)

$^{19}$F (376 MHz, CDCl$_3$)
$^1$H (600 MHz, CDCl$_3$)

- A (d) 7.56 $J$(7.72)
- B (d) 7.32 $J$(7.78)
- C (t) 3.39 $J$(6.38)
- D (p) 2.19 $J$(6.80)
- E (t) 2.85 $J$(7.30)

$^{13}$C (151 MHz, CDCl$_3$)

- A (q) 128.79 $J$(32.32)
- B (q) 124.43 $J$(271.82)
- C (q) 125.80 $J$(3.82)
- D (p) 2.14 $J$(6.80)
$^{19}$F (565 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^{13}$C (101 MHz, CDCl$_3$, $^{19}$F decoupled)

$^{19}$F (376 MHz, CDCl$_3$)
$^{1}H$ (400 MHz, CDCl$_3$)

$^{13}C$ (101 MHz, CDCl$_3$)

-S83-
$^1$H (600 MHz, CDCl$_3$)

$^1$C (151 MHz, CDCl$_3$)

-S84-
$^1$H (400 MHz, CDCl$_3$)

| Peak | ppm |
|------|-----|
| A    | 7.28 (dd) |
| B    | 3.46 (t) |
| C    | 1.25 (t) |

$^13$C (101 MHz, CDCl$_3$)

| Peak | ppm |
|------|-----|
| A    | 146.84 |
| B    | 137.47 |
| C    | 125.64 |
| D    | 75.63 |
| E    | 31.22 |

-S85-
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)
$^1$H (600 MHz, CDCl$_3$)

| δ (ppm) | J (Hz) |
|---------|--------|
| 7.29    | 7.45   |

$^13$C (151 MHz, CDCl$_3$)

| δ (ppm) |
|---------|
| 142.66  |
| 128.87  |
| 31.01   |
| 19.01   |
$^1$H (400 MHz, CDCl$_3$)

$^{13}$C (101 MHz, CDCl$_3$)
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (400 MHz, CDCl$_3$)
$^1$H (600 MHz, CDCl$_3$)

$^{13}$C (151 MHz, CDCl$_3$)
$^{19}\text{F} \ (565 \text{ MHz, CDCl}_3)$

A (d)
-73.07
$\gamma(5.09)$

$^{1}\text{H} \ (400 \text{ MHz, CDCl}_3)$

A (dd)
7.18
$\gamma(8.80, 7.71)$

B (ddd)
1.90
$\gamma(13.39, 8.48, 5.04)$
$^{13}$C (101 MHz, CDCl$_3$)

$^{19}$F (376 MHz, CDCl$_3$)
$^1$H (600 MHz, CDCl$_3$)

- A (dd) 7.11  \( \nu(5.08, 3.64) \)
- B (dd) 7.48  \( \nu(10.81, 2.18) \)

$^{13}$C (151 MHz, CDCl$_3$)

- A (q) 118.86  \( \nu(320.77) \)
- B (d) 114.83  \( \nu(19.79) \)
- C (d) 122.28  \( \nu(3.61) \)

- G (d) 141.18  \( \nu(2.21) \)
- D (d) 153.94  \( \nu(253.40) \)
- E (d) 136.68  \( \nu(7.17) \)
$^{19}$F (376 MHz, CDCl$_3$)

$^1$H (600 MHz, CDCl$_3$)
$^{13}$C (151 MHz, CDCl$_3$)

$^{19}$F (376 MHz, CDCl$_3$)
8. References

[1] A. Krasovskiy, P. Knochel, Synthesis 2006, 2006, 0890-0891.
[2] Y. He, Y. Cai, S. Zhu, J. Am. Chem. Soc. 2017, 139, 1061-1064.
[3] F. Chen, K. Chen, Y. Zhang, Y. He, Y.-M. Wang, S. Zhu, J. Am. Chem. Soc. 2017, 139, 13929-13935.
[4] L. Peng, Y. Li, Y. Li, W. Wang, H. Pang, G. Yin, ACS Catal. 2018, 8, 310-313.
[5] S. Ni, H. Wei, B. Li, F. Chen, Y. Liu, W. Chen, Y. Xu, X. Qiu, X. Li, Y. Lu, W. Liu, L. Hu, D. Lin, M. Wang, X. Zheng, F. Mao, J. Zhu, L. Lan, J. Li, J. Med. Chem. 2017, 60, 8145-8159.
[6] L. Zimmermann, A. Bussière, M. Ouberaï, I. Baussanne, C. Jolivalt, M.-P. Mingeot-Leclercq, J.-L. Décout, J. Med. Chem. 2013, 56, 7691-7705.
[7] P. Franzmann, S. B. Beil, D. Schollmeyer, S. R. Waldvogel, Chem. Eur. J. 2019, 25, 1936-1940.
[8] C.-T. Yang, Z.-Q. Zhang, J. Liang, J.-H. Liu, X.-Y. Lu, H.-H. Chen, L. Liu, J. Am. Chem. Soc. 2012, 134, 11124-11127.
[9] B. E. Tiedemann, K. N. Raymond, Angew. Chem. Int. Ed. 2005, 45, 83-86.
[10] L. S. Li, H. Jiang, B. W. Messmore, S. R. Bull, S. I. Stupp, Angew. Chem. Int. Ed. 2007, 46, 5873-5876.
[11] D. A. Gandamana, B. Wang, C. Tejo, B. Bolte, F. Gagosz, S. Chiba, Angew. Chem. Int. Ed. 2018, 57, 6181-6185.
[12] S. T. Keaveney, G. Kundu, F. Schoenebeck, Angew. Chem. Int. Ed. 2018, 57, 12573-12577.
[13] K. G. Lalwani, A. Sudalai, Synlett 2016, 27, 1339-1343.
[14] J. T. Joseph, A. M. Sajith, R. C. Ningegowda, S. Shashikanth, Adv. Synth. Catal. 2017, 359, 419-425.
[15] Bruker AXS Inc., SAINT, 2017, Madison, WI.
[16] G. M. Sheldrick, SADABS, Version 2008/2, 1996, University of Göttingen, Germany.
[17] G. M. Sheldrick, Acta Crystallogr. Sect. A 2015, 71, 3–8.
[18] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
[19] G. M. Sheldrick, Acta Crystallogr. Sect. C 2015, 71, 3–8.
[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparrini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision A.03, 2016, Gaussian, Inc., Wallingford, CT.
[21] L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi, S. Grimme, Phys. Chem. Chem. Phys. 2017, 19, 32184-32215.
[22] G. Luchini, J. Alegre-Requena, I. Funes-Ardoiz, R. Paton, F1000Research 2020, 9.
[23] R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. A 2011, 115, 14556-14562.
[24] C. Y. Legault, CYLview, Version 1.0b, 2009, Université de Sherbrooke, (http://www.cylview.org).
[25] F. M. Bickelhaupt, K. N. Houk, Angew. Chem. Int. Ed. 2017, 56, 10070-10086.
[26] T. Lu, F. Chen, J. Comput. Chem. 2012, 33, 580-592.
[27] E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng, T. E. Ferrin, J. Comput. Chem. 2004, 25, 1605-1612.
[28] E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. Yang, J. Am. Chem. Soc. 2010, 132, 6498-6506.