Supporting Information

α-Arylation of Esters and Ketones Enabled by a Bench-Stable Pd(I) Dimer Catalyst

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Contents

1. General Experimental Details ................................................................. S3
2. General Procedures ........................................................................ S4
3. Compound Characterization Data ....................................................... S5
4. NMR spectra ...................................................................................... S10
5. References ....................................................................................... S20
1. General Experimental Details

All reagents and starting materials were commercially available and used as received. Anhydrous toluene was dried using an Innovative Technology PS-MD-5 solvent purification system. Solvents used in work up and purification were distilled prior to use. 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 potassium permanganate. 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).

All ¹H, ¹³C and ¹⁹F NMR spectra were recorded on Varian VNMRS 600 or Varian VNMRS 400 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) or α,α,α-trifluorotoluene PhCF₃ (δ = -63.70 ppm, added as an internal standard for ¹⁹F). 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. General Procedures

*General procedure for the dinuclear Pd(I)-mediated enolate arylation*

Inside the glovebox, lithium 2,2,6,6-tetramethylpiperidide (LiTMP, 70.7 mg, 0.48 mmol, 1.2 eq.) was dissolved in toluene (1.5 mL) and carbonyl compound (3, 0.48 mmol, 1.2 eq.) was added. After 15 min of stirring at ambient temperature a solution of Pd(I) iodo dimer (2, 3.5 mg, 0.004 mmol, 1 mol% for aryl iodides; 17.4 mg, 0.02 mmol, 5 mol% for aryl bromides) and aryl halide (4, X = I or Br, 0.4 mmol, 1.0 eq.) in toluene (0.5 mL) was added. After 4-18 h of further stirring at ambient temperature (reaction progress was monitored by GC-MS), the crude was directly adsorbed onto silica (washing with diethyl ether) and purified by flash column chromatography.

*General procedure for mechanistic control experiments*

Inside the glovebox, lithium 2,2,6,6-tetramethylpiperidide (LiTMP, 70.7 mg, 0.48 mmol, 1.2 eq.) was dissolved in toluene (1.6 mL) and methyl isobutyrate (49.0 mg, 0.48 mmol, 1.2 eq.) was added. After 15 min of stirring at ambient temperature a solution of Pd-catalyst (5 mol% Pd) and aryl halide (4-iodophenyl triflate or 4-chlorophenyl triflate, 0.4 mmol, 1.0 eq.) in toluene (0.5 mL) was added. The reaction mixtures were analyzed via GC-MS after 1 h and 4 h.
3. Compound Characterization Data

**Methyl 2-(3-fluorophenyl)-2-methylpropanoate (5aa):** Prepared, following the general procedure from methyl isobutyrate (3a) and 3-fluoriodobenzene (4a). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a colorless oil (41.4 mg, 0.211 mmol, 53%). \( R_f = 0.39 \) (Hexane/EtOAc 20:1). ¹H NMR (600 MHz, CDCl₃): \( \delta = 7.28 \) (ddd, \( J = 8.1, 6.2, 6.2 \) Hz, 1H), 7.14 – 7.06 (m, 1H), 7.05 (ddd, \( J = 10.7, 2.4, 2.1 \) Hz, 1H), 6.96 – 6.91 (m, 1H), 3.66 (s, 3H), 1.57 (s, 6H). ¹³C NMR (151 MHz, CDCl₃): \( \delta = 176.8, 163.0 \) (d, \( J = 245.4 \) Hz), 147.4 (d, \( J = 6.8 \) Hz), 129.9 (d, \( J = 8.5 \) Hz), 121.5 (d, \( J = 2.8 \) Hz), 113.7 (d, \( J = 20.8 \) Hz), 113.1 (d, \( J = 22.9 \) Hz), 52.5, 46.6 (d, \( J = 2.1 \) Hz), 26.6. ¹⁹F NMR (564 MHz, CDCl₃): \( \delta = -112.82 \) – -112.90 (m). MS (70eV, EI): m/z (%): 196 (16) [M⁺], 138 (10), 137 (100), 121 (6), 109 (53), 101 (6), 97 (5), 96 (5). These data are in agreement with those reported previously in the literature.¹

**Methyl 2-(2-fluorophenyl)-2-methylpropanoate (5ab):** Prepared, following the general procedure from methyl isobutyrate (3a) and 2-fluoriodobenzene (4b), using 5 mol% catalyst and a reaction time of 24 h. The title product was obtained as an inseparable mixture of \( \alpha \)- and \( \beta \)-isomers (\( \alpha:\beta = 12:1 \)) after purification by column chromatography (Hexane/EtOAc 20:1) as a yellowish oil (20.6 mg, 0.105 mmol, 26%). \( R_f = 0.33 \) (Hexane/EtOAc 20:1). IR (neat): 2955, 2330, 2096, 1919, 1730, 1590, 1438, 1385, 1253, 1192, 1144, 991, 943, 890, 783, 695 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): \( \delta = 7.33 \) (ddd, \( J = 7.9, 7.9, 1.7 \) Hz, 1H), 7.29 – 7.21 (m, 1H), 7.14 (ddd, \( J = 7.6, 7.6, 1.2 \) Hz, 1H), 7.02 (ddd, \( J = 11.5, 8.1, 1.2 \) Hz, 1H), 3.68 (s, 3H), 1.57 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): \( \delta = 177.3, 160.8 \) (d, \( J = 246.7 \) Hz), 132.7 (d, \( J = 13.5 \) Hz), 128.6 (d, \( J = 8.6 \) Hz), 126.5 (d, \( J = 4.7 \) Hz), 124.2 (d, \( J = 3.3 \) Hz), 115.8 (d, \( J = 22.4 \) Hz), 52.4, 44.2, 25.9. ¹⁹F NMR (376 MHz, CDCl₃): \( \delta = -113.43 \) – -114.35 (m, major), -117.85 – -118.34 (m, minor, \( \beta \)-arylation). MS (70eV, EI): m/z (%): 196 (15) [M⁺], 138 (10), 137 (100), 121 (6), 115 (7), 110 (6), 109 (70), 101 (8). HRMS (ESI): m/z [M+Na⁺] calcd for C₁₁H₁₃FNaO₂: 219.0792; found: 219.0791.

**Methyl 2-(4-fluorophenyl)-2-methylpropanoate (5ac):** Prepared, following the general procedure from methyl isobutyrate (3a) and 4-fluoriodobenzene (4c). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a colorless oil (63.4 mg, 0.323 mmol, 81%). \( R_f = 0.32 \) (Hexane/EtOAc 20:1). ¹H NMR (600 MHz, CDCl₃): \( \delta = 7.34 – 7.27 \) (m, 2H), 7.02 – 6.98 (m, 2H), 3.65 (s, 3H), 1.57 (s, 6H). ¹³C NMR (151 MHz, CDCl₃): \( \delta = 177.1, 161.7 \) (d, \( J = 245.2 \) Hz), 140.5 (d, \( J = 3.2 \) Hz), 127.4 (d, \( J = 8.3 \) Hz), 115.2 (d, \( J = 21.4 \) Hz), 52.4, 46.1, 26.8. ¹⁹F NMR (564 MHz, CDCl₃): \( \delta = -116.34 \) – -116.61 (m). MS (70eV, EI): m/z (%): 196 (9) [M⁺], 138 (10), 137 (100), 121 (7), 109 (42), 101 (6), 97 (4). These data are in agreement with those reported previously in the literature.¹

**Methyl 2-(3-methoxyphenyl)-2-methylpropanoate (5ad):** Prepared, following the general procedure from methyl isobutyrate (3a) and 3-iodoanisole (4d). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a colorless oil (67.4 mg, 0.324 mmol, 81%). \( R_f = 0.44 \) (Hexane/EtOAc 10:1). ¹H NMR (600 MHz, CDCl₃): \( \delta = 7.75 \) (dd, \( J = 8.0, 8.0 \) Hz, 1H), 6.92 (ddd, \( J = 7.8, 1.8, 0.8 \) Hz, 1H), 6.90 – 6.87 (m, 1H), 6.81 – 6.77 (m,
The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a colorless oil (20.9 mg, 0.100 mmol, 25%). $R_t = 0.28$ (Hexane/EtOAc 20:1). $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 7.30$ (dd, $J = 7.7, 1.6$ Hz, 1H), 7.25 (ddd, $J = 8.1, 7.5, 1.6$ Hz, 1H), 6.97 (ddd, $J = 7.6, 6.1, 1$ Hz, 1H), 6.87 (dd, $J = 8.1, 0.9$ Hz, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 1.52 (s, 6H). $^{13}C$ NMR (101 MHz, CDCl$_3$): $\delta = 178.6, 156.8, 134.2, 128.0, 125.5, 120.8, 111.1, 55.4, 52.0, 44.3, 25.8$. MS (70eV, EI): $m/z$ (%): 208 (21) [M$^+$], 150 (11), 149 (100), 121 (36), 115 (9), 105 (6), 91 (26), 77 (7). These data are in agreement with those reported previously in the literature.$^1$

Methyl 2-(2-methoxyphenyl)-2-methylpropanoate (5ae): Prepared, following the general procedure from methyl isobutyrate (3a) and 2-iodoisooanisole (4e), using 5 mol% catalyst and a reaction time of 24 h. The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a colorless oil (66.3 mg, 0.318 mmol, 80%). $R_t = 0.44$ (Hexane/EtOAc 10:1). $^1H$ NMR (600 MHz, CDCl$_3$): $\delta = 7.30 - 7.25$ (m, 2H), 6.89 - 6.84 (m, 2H), 3.79 (s, 3H), 3.65 (s, 3H), 1.57 (s, 6H). $^{13}C$ NMR (151 MHz, CDCl$_3$): $\delta = 177.5, 158.3, 136.9, 126.8, 113.8, 55.3, 52.3, 45.8, 26.7$. MS (70eV, EI): $m/z$ (%): 208 (9) [M$^+$], 150 (11), 149 (100), 121 (36), 115 (9), 105 (6), 91 (26), 77 (7). These data are in agreement with those reported previously in the literature.$^2$

Methyl 2-(2-methyl-2-(4-((trifluoromethyl)sulfonyl)oxy)phenyl) propanoate (5ag): Prepared, following the general procedure from methyl isobutyrate (3a) and 4-halophenyltriflate (4g, X = I or Br). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a yellow oil using either 4-iodophenyl triflate (97.3 mg, 0.298 mmol, 75%) or 4-bromophenyl triflate (88.9 mg, 0.272 mmol, 68%). $R_t = 0.30$ (Hexane/EtOAc 20:1). IR (neat): 2982, 1732, 1500, 1419, 1208, 1138, 1015, 886, 844, 784, 698 cm$^{-1}$. $^1H$ NMR (600 MHz, CDCl$_3$): $\delta = 7.44 - 7.40$ (m, 2H), 7.24 - 7.20 (m, 2H), 3.66 (s, 3H), 1.58 (s, 6H). $^{13}C$ NMR (151 MHz, CDCl$_3$): $\delta = 176.5, 148.3, 145.2, 127.9, 121.3, 118.8$ (q, $J = 320.7$ Hz), 52.5 (d, $J = 2.0$ Hz), 46.4, 26.6. $^{19}F$ NMR (564 MHz, CDCl$_3$): $\delta = -72.98$ (s). MS (70eV, EI): $m/z$ (%): 326 (4) [M$^+$], 269 (6), 268 (12), 267 (100), 175 (13), 134 (10), 106 (6), 91 (10), 77 (3), 69 (6). HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{12}$H$_{13}$F$_3$NaO$_5$S: 349.0328; found: 349.0327.

Methyl 2-methyl-2-(pyrazin-2-yl)propanoate (5ah): Prepared, following the general procedure from methyl isobutyrate (3a) and 2-iodopyrazine (4h). The title product was obtained after purification by column chromatography (Hexane/EtOAc 3:1) as a colorless oil (52.8 mg, 0.293 mmol, 72%). $R_t = 0.29$ (Hexane/EtOAc 3:1). IR (neat): 2985, 1734, 1527, 1467, 1397, 1256, 1120, 1015, 850, 771, 676 cm$^{-1}$. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 8.61$ (s, 1H), 8.50 (br, 1H), 8.44 (br, 1H), 3.67 (s, 3H), 1.64 (s, 6H). $^{13}C$ NMR (101 MHz, CDCl$_3$): $\delta = 175.9, 159.2, 143.6, 142.7, 142.4, 52.5, 48.5, 25.4$. MS (70eV, EI): $m/z$ (%): 180 (9) [M$^+$], 165 (7), 148 (12), 122 (9), 121 (100), 120 (17), 119 (21), 94 (5), 93 (18), 79 (6), 59 (6), 52 (8). HRMS (ESI): $m/z$ [M+H]$^+$ calcd for C$_{19}$H$_{24}$O$_3$N$_2$: 338.1729; found: 338.1727.
**Methyl 2-(4-(1H-pyrrol-1-yl)phenyl)-2-methylpropanoate (5ai):** Prepared, following the general procedure from methyl isobutyrate (3a) and 1-(4-iodophenyl)-1H-pyrrole (4i). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as an off-white, low-melting solid (80.7 mg, 0.332 mmol, 83%). \( R_t = 0.23 \) (Hexane/EtOAc 20:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.43 - 7.31 \) (m, 4H), 7.07 (dd, \( J = 2.2, 2.2 \) Hz, 2H), 6.34 (dd, \( J = 2.1, 2.1 \) Hz, 2H), 3.68 (s, 3H), 1.61 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta = 177.2, 142.2, 139.5, 127.0, 120.6, 119.4, 110.5, 52.5, 46.3, 26.7. \) MS (70eV, EI): \( m/z \) (%): 244 (5), 243 (28) \([M^+]\), 185 (15), 184 (100), 169 (12), 168 (11), 167 (7), 156 (12), 146 (3), 145 (5), 115 (10), 78 (7). HRMS (ESI): \( m/z [M+Na]^+ \) calc for C\(_{15}\)H\(_{19}\)NNaO\(_2\): 266.1152; found: 266.1151.

**Methyl 2-(4-chlorophenyl)-2-methylpropanoate (5aj):** Prepared, following the general procedure from methyl isobutyrate (3a) and 4-chloriodobenzene (4j). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a brown oil (72.0 mg, 0.339 mmol, 85%). \( R_t = 0.39 \) (Hexane/EtOAc 20:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.43 - 7.22 \) (m, 4H), 3.63 (s, 3H), 1.55 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta = 176.9, 143.2, 132.7, 128.6, 127.3, 52.4, 46.3, 26.6. \) MS (70eV, EI): \( m/z \) (%): 214 (3) \([^{37}\text{Cl-M}^-]\), 212 (10) \([^{35}\text{Cl-M}^-]\), 155 (33), 154 (11), 153 (100), 127 (11), 125 (35), 103 (4), 102 (5), 101 (5), 91 (3), 77 (5), 75 (4). These data are in agreement with those reported previously in the literature.\(^1\)

**Methyl 2-methyl-2-(thiophen-3-yl)propanoate (5ak):** Prepared, following the general procedure from methyl isobutyrate (3a) and 3-iodothiophene (4k). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a colorless oil (34.1 mg, 0.185 mmol, 46%, volatile compound). \( R_t = 0.20 \) (Hexane/EtOAc 20:1). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.26 \) (dd, \( J = 5.0, 3.0 \) Hz, 1H), 7.11 (dd, \( J = 3.0, 1.4 \) Hz, 1H), 7.08 (dd, \( J = 5.0, 1.4 \) Hz, 1H), 3.66 (s, 3H), 1.59 (s, 2H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta = 176.7, 145.9, 126.7, 125.6, 120.0, 52.4, 44.4, 26.7. \) MS (70eV, EI): \( m/z \) (%): 184 (21) \([M^-]\), 127 (5), 126 (9), 125 (100), 109 (7), 97 (17), 85 (10). These data are in agreement with those reported previously in the literature.\(^3\)

**Methyl 2-methyl-2-(4-morpholinophenyl)propanoate (5al):** Prepared, following the general procedure from methyl isobutyrate (3a) and 4-(iodophenyl)morpholine (4i). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a white solid (63.1 mg, 0.240mmol, 60%); mp 53-54°C. \( R_t = 0.19 \) (Hexane/EtOAc 5:1). IR (neat): 2965, 2855, 1720, 1613, 1514, 1451, 1379, 1241, 1117, 926, 816, 770 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.29 - 7.18 \) (m, 2H), 6.93 - 6.78 (m, 2H), 3.87 - 3.77 (m, 4H), 3.62 (s, 3H), 3.19 - 3.05 (m, 4H), 1.54 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta = 177.5, 149.9, 136.1, 126.5, 115.5, 67.0, 52.2 (d, \( J = 2.7 \) Hz), 49.3, 45.8, 26.6. MS (70eV, EI): \( m/z \) (%): 263 (19) \([M^-]\), 205 (15), 204 (100), 146 (12), 145 (3), 131 (4), 130 (4), 118 (6), 117 (4), 91 (3), 77 (3). HRMS (ESI): \( m/z [M+H]^+ \) calcd for C\(_{15}\)H\(_{22}\)O\(_3\)N: 264.1594; found: 264.1595.

**Methyl 2-methyl-2-(4-(trifluoromethyl)phenyl)propanoate (5am):** Prepared, following the general procedure from methyl isobutyrate (3a) and 4-
(trifluoromethyl)iodobenzene (4m). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) as a colorless oil (87.0 mg, 0.353 mmol, 88%). $R_t = 0.21$ (Hexane/EtOAc 20:1). $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.58$ (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 3.66 (s, 3H), 1.60 (s, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 176.7, 148.7, 129.1$ (q, $J = 32.6$ Hz), 126.3, 125.5 (q, $J = 3.7$ Hz), 124.3 (q, $J = 272.0$ Hz), 52.5, 46.8, 26.5. $^{19}$F NMR (564 MHz, CDCl$_3$): $\delta = -62.58$. MS (70eV, EI): $m/z$ (%): 246 (8) [M$^+$], 227 (5), 188 (11), 187 (100), 159 (54), 151 (7). These data are in agreement with those reported previously in the literature.¹

![1-{(3-Fluorophenyl)cyclobutyl}(phenyl)methanone (5ba)](image)

(1-{(3-Fluorophenyl)cyclobutyl}(phenyl)methanone (5ba): Prepared, following the general procedure from cyclobutyl phenyl ketone (3b) and 3-fluoriodobenzene (4a). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) and preparative HPLC (Pentane/EtOAc 9:1) as a colorless oil (92.6 mg, 0.364 mmol, 91%). $R_t = 0.41$ (Hexane/EtOAc 15:1). IR (neat): 3065, 2950, 2871, 1674, 1587, 1483, 1440, 1252, 1171, 927, 861, 783, 696 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.75 - 7.67$ (m, 2H), 7.45 - 7.37 (m, 1H), 7.35 - 7.27 (m, 3H), 7.19 - 7.11 (m, 2H), 6.95 - 6.86 (m, 1H), 3.02 - 2.87 (m, 2H), 2.61 - 2.47 (m, 2H), 2.15 - 2.00 (m, 1H), 2.01 - 1.84 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 200.6, 163.4$ (d, $J = 246.3$ Hz), 146.1 (d, $J = 7.0$ Hz), 134.1, 132.6, 130.6 (d, $J = 8.4$ Hz), 129.8, 128.4, 121.5 (d, $J = 2.9$ Hz), 113.6 (d, $J = 21.1$ Hz), 112.9 (d, $J = 21.9$ Hz), 57.1 (d, $J = 1.9$ Hz), 32.4, 16.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -111.03 - -114.01$ (m). MS (70eV, EI): $m/z$ (%): 254 (1) [M$^+$], 149 (8), 121 (8), 109 (7), 106 (8), 105 (100), 101 (6), 77 (24), 51 (5). HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{13}$H$_{11}$FNaO: 277.0999; found: 277.1000.

![1-{(3-Fluorophenyl)cyclopropyl}(phenyl)methanone (5ca)](image)

(1-{(3-Fluorophenyl)cyclopropyl}(phenyl)methanone (5ca): Prepared, following the general procedure from cyclopropyl phenyl ketone (3c) and 3-fluoriodobenzene (4a). The title product was obtained after purification by column chromatography (Hexane/EtOAc 20:1) and preparative HPLC (Pentane/EtOAc 95:5) as a colorless oil (61.7 mg, 0.257 mmol, 64%). $R_t = 0.39$ (Hexane/EtOAc 15:1). IR (neat): 3066, 3014, 2328, 2095, 1818, 1672, 1586, 1487, 1439, 1299, 1197, 1034, 990, 925, 858, 782, 697 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.80 - 7.72$ (m, 2H), 7.43 - 7.36 (m, 1H), 7.33 - 7.25 (m, 2H), 7.18 (ddd, $J = 8.0, 8.0, 6.1$ Hz, 1H), 6.97 (ddd, $J = 7.8, 1.8, 0.9$ Hz, 1H), 6.90 (ddd, $J = 10.1, 2.1$, 2.1 Hz, 1H), 6.85 (ddd, $J = 8.4, 8.4, 2.5$, 1.0 Hz, 1H), 1.71 - 1.65 (m, 2H), 1.37 - 1.32 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 199.6, 163.0$ (d, $J = 246.3$ Hz), 143.8 (d, $J = 7.4$ Hz), 136.8, 132.3, 130.2 (d, $J = 8.4$ Hz), 129.5, 128.2, 123.9 (d, $J = 2.8$ Hz), 114.7 (d, $J = 21.8$ Hz), 113.7 (d, $J = 21.0$ Hz), 35.0 (d, $J = 1.8$ Hz), 16.5. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -111.59 - -115.96$ (m). MS (70eV, EI): $m/z$ (%): 241 (8), 240 (46) [M$^+$], 133 (10), 115 (5), 109 (5), 106 (8), 105 (100), 77 (44), 51 (8). HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{16}$H$_{13}$FNaO: 263.0843; found: 263.0843.

![2-(3-Fluorophenyl)-2-methyl-1-indanone (5da)](image)

(2-(3-Fluorophenyl)-2-methyl-1-indanone (5da): Prepared, following the general procedure from 2-methyl-1-indanone (3d) and 3-fluoriodobenzene (4a). The racemic title product was obtained after purification by preparative HPLC (Pentane/EtOAc 9:1) as a yellowish oil (19.1 mg, 0.079 mmol, 20%, volatile compound). $R_t = 0.39$ (20:1 Hexane/EtOAc). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.85$ (d, $J = 7.6$ Hz, 1H), 7.72 - 7.64 (m, 1H), 7.56 - 7.49 (m, 1H), 7.49 - 7.41 (m, 1H), 7.31 - 7.22 (m, 1H), 7.13 - 7.03 (m, 3H), 6.97 - 6.89 (m, 1H), 3.59 (d, $J = 17.4$ Hz, 1H), 3.34 (d, $J = 17.4$ Hz, 1H), 1.67 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 208.0, 164.3, 161.8, 152.4, 146.6$ (d, $J = 7.1$ Hz), 135.4 (d, $J = 4.1$ Hz).
Hz), 130.1 (d, \( J = 8.3 \) Hz), 128.0, 126.5, 125.1, 121.9 (d, \( J = 2.9 \) Hz), 113.7 (d, \( J = 7.7 \) Hz), 113.5 (d, \( J = 9.1 \) Hz), 53.0 (d, \( J = 1.4 \) Hz), 44.8, 24.7. \(^{19}\text{F NMR} \) (376 MHz, CDCl\(_3\)): \( \delta = -112.55 \) – \(-112.70 \) (m). \( \text{MS} \) (70eV, EI): \( m/z \) (%): 241 (18), 240 (100) \([\text{M}^+],\) 239 (16), 226 (17), 225 (98), 222 (17), 211 (12), 209 (7), 197 (23), 196 (46), 183 (11), 177 (11), 145 (13), 133 (6), 131 (9), 118 (6), 115 (13), 101 (7), 91 (7), 75 (6). These data are in agreement with those reported previously in the literature.\(^4\)
4. NMR spectra

Methyl 2-[(2-fluorophenyl)-2-methylpropanoate (5ab):

1H NMR (399.97 MHz, CDCl3)
13C NMR (100.58 MHz, CDCl3)

19F NMR (376.33 MHz, CDCl3)

α:β = 12:1
Methyl 2-methyl-2-((4-(((trifluoromethyl)sulfonyl)oxy)phenyl) propanoate (5ag):

1H NMR (599.86 MHz, CDCl3)

13C NMR (150.85 MHz, CDCl3)
Methyl 2-methyl-2-(pyrazin-2-yl)propanoate (5ah):
Methyl 2-(4-(1H-pyrrolo-1-yl)phenyl)-2-methylpropanoate (5ai):

1H NMR
(399.97 MHz, CDCl3)

13C NMR
(100.58 MHz, CDCl3)
Methyl 2-methyl-2-(4-morpholinophenyl)propanoate (5a1):
(1-(3-Fluorophenyl)cyclobutyl)(phenyl)methanone (5ba):

1H NMR
(399.97 MHz, CDCl3)

13C NMR
(100.58 MHz, CDCl3)
(1-(3-Fluorophenyl)cyclopropyl)(phenyl)methanone (5ca):

**1H NMR**

(399.97 MHz, CDCl₃)

![1H NMR spectrum](image)

**13C NMR**

(100.58 MHz, CDCl₃)

![13C NMR spectrum](image)
19F NMR
(376.33 MHz, CDCl3)
5. References