Synthesis T. Sperger, F. Schoenebeck Special Topic

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

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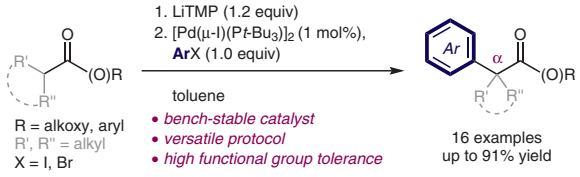

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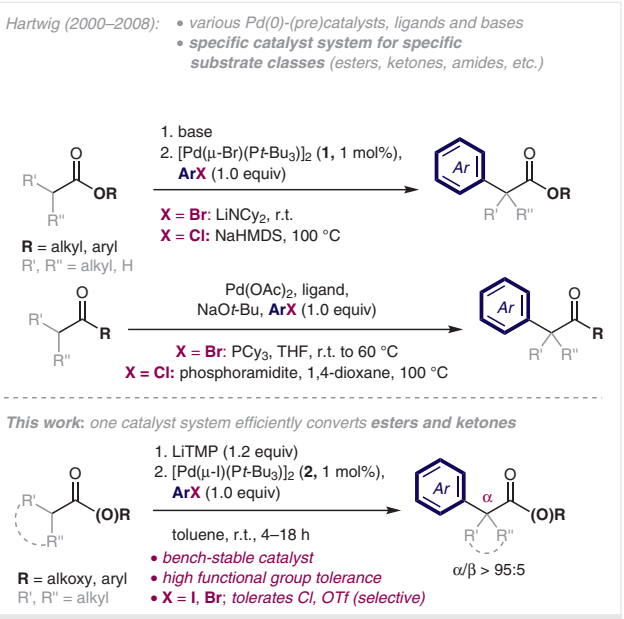
Abstract A procedure for the α-arylation of α,α-disubstituted esters and ketones to generate quaternary carbon centers is described. The developed protocol is operationally simple and employs an air- and moisture-stable dinuclear Pd(I) complex $[Pd(\mu\text{-}I)(P\textit{t}\text{-}Bu_3)]_2$ to mediate selective α-arylation of aromatic C–I/Br bonds in the presence of aromatic C–Cl and/or C–OTf sites.

Key words Pd(I) dimer, air-stable Pd catalyst, quaternary carbon, cross-coupling

α-Functionalized carbonyl compounds are a common motif in natural products and are important building blocks as well as target molecules in pharmaceutical research.[1] Therefore, the α-arylation of carbonyl and related compounds such as nitriles, sulfones, and sulfoximines via transition metal catalysis has been intensively investigated and significant advances were made within the last decades.[2] Although the vast majority of processes relies on Pd-catalysis, Cu- and Ni-catalysis methodologies were also reported.[2a] However, air- and moisture-sensitive catalysts are commonly employed in these transformations, requiring inert atmosphere in the reaction conditions and/or handling of reagents.

Seminal work in Pd-catalysis was done by Hartwig and co-workers who developed a variety of catalytic conditions to access α-arylated carbonyl compounds. This includes the transformation of ester,[3] ketone,[4] and amide[3c,5] substrates under relatively mild conditions using a number of different Pd catalysts (Scheme 1). They utilized the labile bromide-bridged Pd(I) dimer $[Pd(\mu\text{-}Br)(P\textit{t}\text{-}Bu_3)]_2$ (**1**) as a pre-catalyst to Pd(0).[6] While the bromide-bridged Pd(I) dimer is air-sensitive, its iodide analogue $[Pd(\mu\text{-}I)(P\textit{t}\text{-}Bu_3)]_2$ (**2**) is completely stable towards oxygen as a solid and can be stored on the bench.[7] Therefore, we anticipated that its use as a catalyst would greatly facilitate handling. Moreover, we envisioned that the greater overall robustness of the iodide-bridged dimer might allow for a wider set of enolates or bases to be compatible, and its recently demonstrated potential in site-selective C–C bond formations[8] might also be transferrable towards the introduction of disubstituted esters. As such we anticipated that in contrast to previous developments that primarily employed specific catalyst systems tailored to convert specific substrate classes, our dinuclear Pd(I)-based methodology might allow for a more general protocol that operates efficiently for a variety of different substrates, such as esters and ketones (Scheme 1).

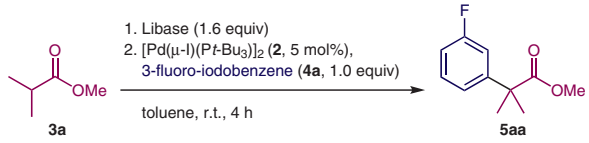


Scheme 1 Seminal work in Pd-catalyzed α-arylation and outline of this work employing a bench-stable dinuclear Pd(I) catalyst

We recently utilized the bench-stable Pd(I) iodo dimer **2** as a catalyst in a number of cross-coupling reactions[9] including the chemoselective arylation and alkylation of aryl bromides (via Negishi or Kumada cross-coupling),[8,10] Heck cross-coupling of acrylates and styrenes[11] as well as for the introduction of pharmaceutically relevant SCF_3 and $SeCF_3$ functionalities.[12] In this context, we showcased that the Pd(I) dimer **2** can act as a competent catalyst directly via dinuclear catalysis cycles.[13] We also elucidated the requirements to activate the Pd(I) iodo dimer to Pd(0) and showed that activating nucleophiles require (i) a certain nucleophilic strength and (ii) should not be capable of forming a stabilizing μ-bridge between the Pd atoms.[10]

While our previous studies showed that a nucleophilicity of 10.5 on Mayr's scale[14] is necessary to convert Pd(I) bromo dimer **1** to Pd(0), much higher nucleophilicities of 16.1 were necessary to afford this conversion for the more stable iodide analogue **2**.[10] Therefore, we anticipated that careful choice of the employed base/enolate nucleophile is essential to allow for an efficient catalytic cycle. Hence, we commenced our study with the search for an appropriate base to form the Li-enolate (Table 1) for the reaction of methyl isobutyrate (**3a**) with 3-fluoroiodobenzene (**4a**).

Table 1 Optimization of Reaction Conditions[a]

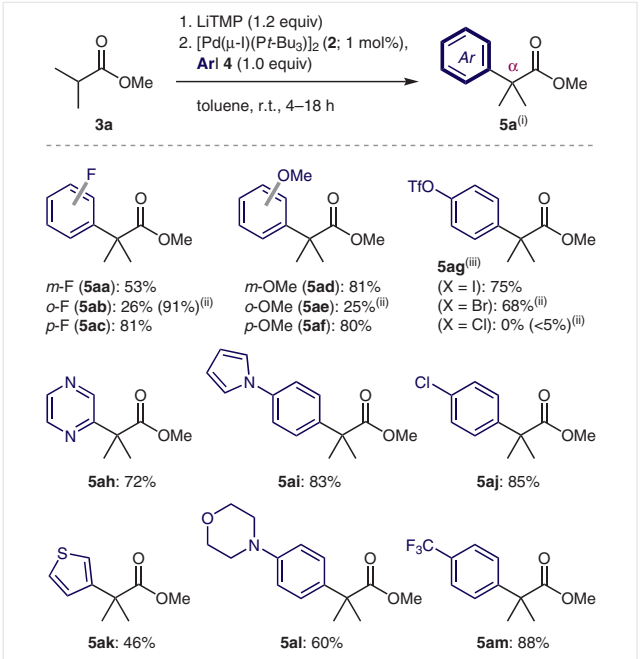


Entry	Catalyst (mol%)	Base	^{19}F NMR yield (%)[b]	Selectivity (α/β)[b]
1	**2** (5)	LiTMP	84	33:1
2	**2** (5)	$LiNCy_2$	58	29:1
3	**2** (5)	LiHMDS	29	0.8:1[c]
4	**2** (5)	–	0[d]	n.d.

[a] Reactions were conducted using Pd(I) iodo dimer **2** (5 mol%), Li-base (0.64 mmol), methyl isobutyrate (**3a**; 0.64 mmol), and 3-fluoroiodobenzene (**4a**; 0.4 mmol) in toluene (2 mL) at r.t.
[b] Yield and selectivity determined by quantitative ^{19}F NMR after 4 h using α,α,α-trifluorotoluene as an internal standard.
[c] Multiple species were detected in ^{19}F NMR spectrum.
[d] Conversion after 24 h, determined by GC-MS.

Of the different tested Li-bases, the sterically more hindered lithium 2,2,6,6-tetramethylpiperidide (LiTMP, Table 1, entry 1) afforded the product **5aa** in good yield and selectivity. The less bulky lithium dicyclohexylamide ($LiNCy_2$, entry 2) was not as efficient and lithium bis(trimethylsilyl)amide (LiHMDS, entry 3) afforded a mixture of different coupling products. Using LiTMP allowed for a decrease of the amount of enolate from 1.6 equivalents to 1.2 equivalents. Moreover, the catalyst loading could be lowered to 1 mol% without compromising the yield.

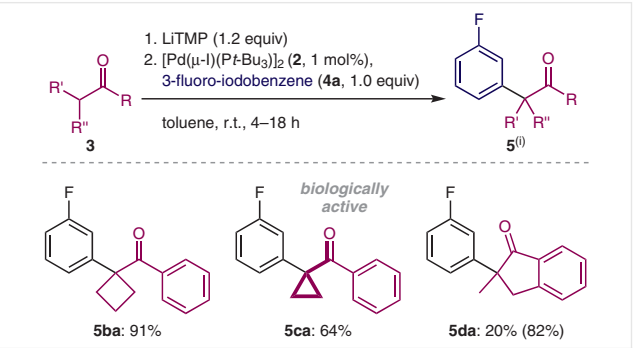
With the optimized reaction conditions in hand, we embarked on exploring the scope of the reaction (Scheme 2). A number of different aryl iodides could be coupled successfully and selectively even in the presence of potentially reactive functionalities, such as aryl chloride (**5aj**) and triflate (**5ag**). Pharmaceutically and agrochemically important heterocycles could also be efficiently transformed, and substituents were better tolerated in *meta*- or *para*-position to the coupling site than *ortho*. While aryl iodides react smoothly at ambient temperature with low catalyst loading of 1 mol% in 4–18 hours the use of aryl bromides as cross-coupling partners required prolonged reaction times of 24 hours and a higher catalyst loading of 5 mol% for high yields.



Scheme 2 Scope of aryl halides **4** in the arylation of methyl isobutyrate (**3a**). *Reagents and conditions*: (i) methyl isobutyrate (**3a**; 0.48 mmol), LiTMP (0.48 mmol), aryl iodide **4** (0.40 mmol), Pd catalyst **2** (1 mol%, 0.004 mmol) in toluene (2.0 mL). Isolated yields are given. Values in parentheses refer to conversions determined by GC-MS; (ii) reaction was conducted using Pd catalyst **2** (5 mol%) and prolonged reaction time of 24 h; (iii) reaction was conducted using 4-halophenyl triflate (X = I, Br, Cl).

Notably, the developed protocol is also compatible with various different α,α-disubstituted carbonyl compounds, such as spirocycles **5ba** and **5ca** as well as indanone **5da** (Scheme 3). In particular, cyclopropyl ketones such as **5ca** are interesting pharmaceutical targets as they have been shown to be present in a number of bioactive compounds.[15] To the best of our knowledge, these medicinally privileged building blocks have never been featured in α-arylations. As such, the herein presented method is not only operationally

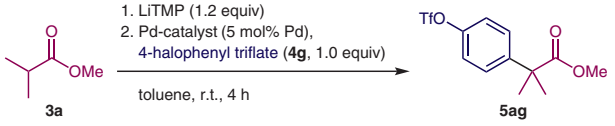
simple (air-stable catalyst), but also more general in providing easy functionalization and access to new libraries of active compounds.



Scheme 3 Scope of carbonyls **3** in the arylation with 3-fluoroiodobenzene **4a**. *Reagents and conditions*: (i) carbonyl **3** (0.48 mmol), LiTMP (0.48 mmol), **4a** (0.40 mmol), Pd catalyst **2** (1 mol%, 0.004 mmol) in toluene (2.0 mL). Isolated yields are given. Values in parentheses refer to conversions determined by GC-MS.

To gain further insight into the mechanism of the reaction, a series of control experiments were performed to explore the likely catalytically active species (Table 2).

Table 2 Test Experiments to Elucidate the Catalytically Active Species[a]



Entry	Pd catalyst	Conversion of **4g** (X = I)	Conversion of **4g** (X = Cl)
1	[Pd(μ-I)(Pt-Bu_3)]$_2$ (**2**, 2.5 mol%)	35 (96)	0 (<1)
2	[Pd(μ-Br)(Pt-Bu_3)]$_2$ (**1**, 2.5 mol%)	95 (96)	59 (61)
3	$Pd_2(dba)_3$ (2.5 mol%), Pt-Bu_3 (5 mol%)	100 (100)	100 (100)

[a] Reactions were conducted using Pd catalyst (5 mol% Pd), LiTMP (0.48 mmol), methyl isobutyrate (**3a**; 0.48 mmol), and 4-halophenyl triflate **4g** (0.4 mmol, X = I or Cl) in toluene (2 mL) at r.t. Conversions were determined by GC-MS after 1 h. Values in parentheses refer to conversions after 4 h.

Historically, labile dinuclear Pd(I) complexes, such as the bromo dimer **1**, found application as precatalysts to Pd(0). To assess whether the Pd(I) iodo dimer **2** might function as a precatalyst or even catalyst itself, the reactivities of potential active species were compared. First, using Pd(I) bromo dimer as a catalyst led to the functionalization of aryl chlorides (Table 2, entry 2). Similar reactivity is also obtained when employing $Pd_2(dba)_3$ and phosphine ligand Pt-Bu_3 in a 1:1 ratio of Pd:L (entry 3), which is generally assumed to lead to the same active species as Pd(I) bromo dimer. In contrast, using Pd(I) iodo dimer **2** as a catalyst is distinct in not functionalizing the C–Cl bond (entry 1), thus reinforcing its selectivity in poly(pseudo)halogenated arenes, namely activating C–I and C–Br over C–Cl and C–OTf, as shown above. Given the change in reactivity, a difference in mechanisms and/or active catalytic species also seems likely.[16]

While the Pd(I) iodo dimer catalyst system itself is very robust and would not require an inert atmosphere,[8] the Li-enolate coupling partner decomposes within minutes in air. However, test experiments have shown that no rigorous inert conditions are required, thus the reagents can be weighed in air and the reaction performed using standard Schlenk techniques without the necessity for a glovebox.

In summary, we have showcased the α-arylation of esters and ketones employing a bench-stable dinuclear Pd(I)-catalyst. The developed method provides access to quaternary carbon centers and high levels of α/β-selectivity. The utilized dinuclear Pd(I) catalyst is easily synthesized in a one-pot procedure, completely air-stable and thus facile to handle, while allowing for low catalyst loadings and fast reaction times. A wide range of functional groups are tolerated and allow for the chemoselective activation of aryl iodides and bromides over other potentially reactive functionalities such as aryl chlorides and triflates. Moreover, the presented method allows for easy access to pharmaceutically relevant biologically active α-arylated cyclopropyl ketones.

Starting materials are all commercially available and were used without further purification. Toluene was degassed and dried using an Innovative Technology PS-MD-5 solvent purification system. Solvents used in workup and purification were distilled prior to use. Pd(I) iodo dimer **2** was prepared from $Pd_2(dba)_3$, Pt-Bu_3 and PdI_2 according to the literature procedure.[12a] All ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Varian VNMRS 600, Varian VNMRS 400, or Varian Mercury 300 spectrometer at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) and were referenced either to residual solvent peak ($CDCl_3$; for ^{1}H and ^{13}C spectra), α,α,α-trifluorotoluene $PhCF_3$ (δ = –63.70 ppm, added as an internal standard for ^{19}F), or trimethyl phosphate $O{=}P(OMe)_3$ (δ = 3.05 ppm, added as an internal standard for ^{31}P). 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 coupled with an Agilent Technologies 7820A gas chromatograph. Preparative HPLC was performed on a Gilson-Abimed HPLC (employing UV detector model 117) using a Merck LiChrosorb Si60 column (porosity 7 μm, 250 × 25 mm). High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL spectrometer. IR spectra were recorded on a Spectrum 100 spectrophotometer with an UATR Diamond/KRS-5 crystal with attenuated total reflectance (ATR).

The analytical and spectral data of six representative α-arylated products are listed below. The data for the remaining ten products are provided in the Supporting Information.

Enolate α-Arylation Reactions; General Procedure

Inside a glovebox, lithium 2,2,6,6-tetramethylpiperidide (LiTMP, 70.7 mg, 0.48 mmol, 1.2 equiv) was dissolved in toluene (1.5 mL) and carbonyl compound **3** (0.48 mmol, 1.2 equiv) was added. After stirring for 15 min at r.t., a solution of Pd(I) iodo dimer **2** (3.5 mg, 0.004 mmol,

1 mol%) and aryl halide (iodide or bromide, 0.4 mmol, 1.0 equiv) in toluene (0.5 mL) was added. After 15 h of further stirring at r.t., the crude reaction mixture was directly adsorbed onto silica gel and purified by flash column chromatography.

Methyl 2-Methyl-2-(4-{[(trifluoromethyl)sulfonyl]oxy}phenyl)propanoate (5ag)

The title compound was obtained according to the general procedure from methyl isobutyrate (**3a**) and either 4-iodophenyl triflate or 4-bromophenyl triflate (**4g**) using 5 mol% catalyst. The crude mixture was purified by column chromatography [hexane/EtOAc 20:1; R_f = 0.30 (hexane/EtOAc 20:1)] to afford the product as a yellow oil in 75% (97.3 mg, 0.298 mmol) and 68% yield (88.9 mg, 0.272 mmol) from aryl iodide and bromide, respectively.

IR (neat): 2982, 1732, 1500, 1419, 1208, 1138, 1015, 886, 844, 784, 698 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 2 H, ArH), 7.24–7.20 (m, 2 H, ArH), 3.66 (s, 3 H, OCH_3), 1.58 (s, 6 H, 2 × CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 176.5 (C=O), 148.3 (C), 145.2 (C), 127.9 (CH), 121.3 (CH), 118.8 (q, J = 320.7 Hz, CF_3), 52.5 (d, J = 2.0 Hz, C), 46.4 (OCH_3), 26.6 (CH_3).

^{19}F NMR (564 MHz, $CDCl_3$): δ = –72.98 (s, 3 F, SO_2CF_3).

MS (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 $C_{12}H_{13}F_3O_5SNa$: 349.0328; found: 349.0327.

Methyl 2-Methyl-2-(pyrazin-2-yl)propanoate (5ah)

The title compound was obtained according to the general procedure from methyl isobutyrate (**3a**) and 2-iodopyrazine (**4h**). The crude mixture was purified by column chromatography [(hexane/EtOAc 3:1; R_f = 0.29 (hexane/EtOAc 3:1)] to afford the product as a colorless oil in 73% yield (52.8 mg, 0.293 mmol).

IR (neat): 2985, 1734, 1527, 1467, 1397, 1256, 1120, 1015, 850, 771, 676 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1 H, ArH), 8.50 (br, 1 H, ArH), 8.44 (br, 1 H, ArH), 3.67 (s, 3 H, OCH_3), 1.64 (s, 6 H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.9 (C=O), 159.2 (C), 143.6 (CH), 142.7 (CH), 142.4 (CH), 52.5 (C), 48.5 (OCH_3), 25.4 (CH_3).

MS (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 $C_9H_{13}N_2O_2$: 181.0972; found: 181.0972.

Methyl 2-[4-(1*H*-Pyrrol-1-yl)phenyl]-2-methylpropanoate (5ai)

The title compound was obtained according to the general procedure from methyl isobutyrate (**3a**) and 1-(4-iodophenyl)-1*H*-pyrrole (**4i**). The crude mixture was purified by column chromatography [hexane/EtOAc 20:1; R_f = 0.23 (hexane/EtOAc 20:1)] to afford the product as an off-white low-melting solid in 83% yield (80.7 mg, 0.332 mmol).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.31 (m, 4 H, ArH), 7.07 (dd, J = 2.2, 2.2 Hz, 2 H, HetArH), 6.34 (dd, J = 2.1, 2.1 Hz, 2 H, HetArH), 3.68 (s, 3 H, OCH_3), 1.61 (s, 6 H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.2 (C=O), 142.2 (C), 139.5 (C), 127.0 (CH), 120.6 (CH), 119.4 (CH), 110.5 (CH), 52.5 (C), 46.3 (OCH_3), 26.7 (CH_3).

MS (EI): m/z (%) = 244 (5), 243 (28, [M^+]), 185 (15), 184 (100), 169 (12), 168 (11), 167 (7), 156 (12), 143 (6), 141 (5), 115 (10), 78 (7).

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{17}NO_2Na$: 266.1152; found: 266.1151.

Methyl 2-Methyl-2-(4-morpholinophenyl)propanoate (5al)

The title compound was obtained according to the general procedure from methyl isobutyrate (**3a**) and 4-(4-iodophenyl)morpholine (**4l**). The crude mixture was purified by column chromatography [hexane/EtOAc 5:1; R_f = 0.19 (hexane/EtOAc 5:1)] to afford the product as a white solid in 60% yield (63.1 mg, 0.240 mmol); mp 53–54 °C.

IR (neat): 2965, 2855, 1720, 1613, 1514, 1451, 1379, 1241, 1117, 926, 816, 770 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.18 (m, 2 H, ArH), 6.93–6.78 (m, 2 H, ArH), 3.87–3.77 (m, 4 H, OCH_2), 3.62 (s, 3 H, OCH_3), 3.19–3.05 (m, 4 H, NCH_2), 1.54 (s, 6 H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.5 (C=O), 149.9 (C), 136.1 (C), 126.5 (CH), 115.5 (CH), 67.0 (CH_2), 52.2 (d, J = 2.7 Hz, C), 49.3 (CH_2), 45.8 (OCH_3), 26.6 (CH_3).

MS (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 $C_{15}H_{22}NO_3$: 264.1594; found: 264.1595.

[1-(3-Fluorophenyl)cyclobutyl](phenyl)methanone (5ba)

The title compound was obtained according to the general procedure from cyclobutyl phenyl ketone (**3b**) and 3-fluoroiodobenzene (**4a**). The crude mixture was purified by column chromatography [hexane/EtOAc 20:1; R_f = 0.41 (hexane/EtOAc 15:1)] and preparative HPLC (pentane/EtOAc 9:1) to afford the product as a colorless oil in 91% yield (92.6 mg, 0.364 mmol).

IR (neat): 3065, 2950, 2871, 1674, 1587, 1483, 1440, 1252, 1171, 927, 861, 783, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.67 (m, 2 H, ArH), 7.45–7.37 (m, 1 H, ArH), 7.35–7.27 (m, 3 H, ArH), 7.19–7.11 (m, 2 H, ArH), 6.95–6.86 (m, 1 H, ArH), 3.02–2.87 (m, 2 H, 2 C*H*H′), 2.61–2.47 (m, 2 H, 2 CH*H*′), 2.15–2.00 (m, 1 H, C*H*H′), 2.01–1.84 (m, 1 H, CH*H*′).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.6 (C=O), 163.4 (d, J = 246.3 Hz, C), 146.1 (d, J = 7.0 Hz, C), 134.1 (C), 132.6 (CH), 130.6 (d, J = 8.4 Hz, CH), 129.8 (CH), 128.4 (CH), 121.5 (d, J = 2.9 Hz, CH), 113.6 (d, J = 21.1 Hz, CH), 112.9 (d, J = 21.9 Hz, CH), 57.1 (d, J = 1.9 Hz, C), 32.4 (CH_2), 16.1 (CH_2).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.03 to –114.01 (m, 1 F, ArF).

MS (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 $C_{17}H_{15}FONa$: 277.0999; found: 277.1000.

[1-(3-Fluorophenyl)cyclopropyl](phenyl)methanone (5ca)

The title compound was obtained according to the general procedure from cyclopropyl phenyl ketone (**3c**) and 3-fluoroiodobenzene (**4a**). The crude mixture was purified by column chromatography [hexane/EtOAc 20:1; R_f = 0.39 (hexane/EtOAc 15:1)] and preparative HPLC (pentane/EtOAc 95:5) to afford the product as a colorless oil in 64% yield (61.7 mg, 0.257 mmol).

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, $CDCl_3$): δ = 7.80–7.72 (m, 2 H, ArH), 7.43–7.36 (m, 1 H, ArH), 7.33–7.25 (m, 2 H, ArH), 7.18 (ddd, *J* = 8.0, 8.0, 6.1 Hz, 1 H, ArH), 6.97 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1 H, ArH), 6.90 (ddd, *J* = 10.1, 2.1, 2.1 Hz, 1 H, ArH), 6.85 (dddd, *J* = 8.4, 8.4, 2.5, 1.0 Hz, 1 H, ArH), 1.71–1.65 (m, 2 H, 2 C*H*H′), 1.37–1.32 (m, 2 H, 2 CH*H*′).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.6 (C=O), 163.0 (d, *J* = 246.3 Hz, C), 143.8 (d, *J* = 7.4 Hz, C), 136.8 (C), 132.3 (CH), 130.2 (d, *J* = 8.4 Hz, CH), 129.5 (CH), 128.2 (CH), 123.9 (d, *J* = 2.8 Hz, CH), 114.7 (d, *J* = 21.8 Hz, CH), 113.7 (d, *J* = 21.0 Hz, CH), 35.0 (d, *J* = 1.8 Hz, C), 16.5 (CH_2).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.59 to –115.96 (m, 1 F, ArF).

MS (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 $C_{16}H_{13}FONa$: 263.0843; found: 263.0843.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610087.

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