Synthesis S. Shi, M. Szostak Special Topic

Nickel-Catalyzed Negishi Cross-Coupling of *N*-Acylsuccinimides: Stable, Amide-Based, Twist-Controlled Acyl-Transfer Reagents via N–C Activation

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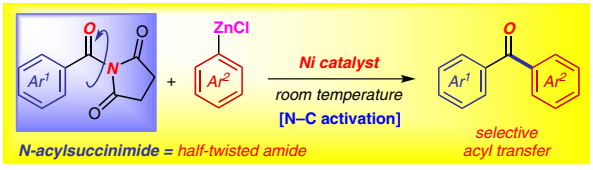

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Abstract This paper reports a room temperature, nickel-catalyzed Negishi cross-coupling of *N*-acylsuccinimides with arylzinc reagents via selective N–C bond cleavage enabled by amide bond twist. The reaction proceeds using a commercially available, air-stable Ni(II) precatalyst in the absence of additives under exceedingly mild conditions. Of broad interest, this report introduces *N*-acylsuccinimides as stable, crystalline, electrophilic, cost-effective, benign, amide-based acyl transfer reagents via acyl metal intermediates. The reaction selectivity is governed by half-twist of the amide bond in *N*-acylsuccinimides, thus opening the door for applications in metal-catalyzed manifolds via redox-neutral reaction pathways tuneable by amide bond distortion.

Key words nickel, Negishi cross-coupling, N–C activation, succinimide, twisted amides, amide cross-coupling, acyl transfer

The catalytic functionalization of amide N–C bonds has emerged as a new paradigm in organic synthesis (Figure 1 A).[1,2] In this reactivity manifold, amides serve as stable acyl or aryl synthetic equivalents under redox neutral reaction conditions. The breakthrough study was reported by Garg and co-workers in 2015, and focused on Ni-catalyzed esterification of amides under mild conditions.[3] Our group has pioneered decarbonylative cross-couplings of amides.[4] We were the first to establish the working model for amide bond cross-coupling in that *amide bond destabilization* (steric or electronic) is required to enable selective metal insertion into the resonance weakened amide bond ($n_N \rightarrow \pi^*_{C=O}$ conjugation, 15–20 kcal/mol in planar amides),[5] and developed a range of amide bond activation methods.[6] Significant progress has been made in the field,[7–9] providing the necessary driving force for further advances using amides as N–C electrophiles in generic transition-metal-catalyzed manifolds.[10,11]

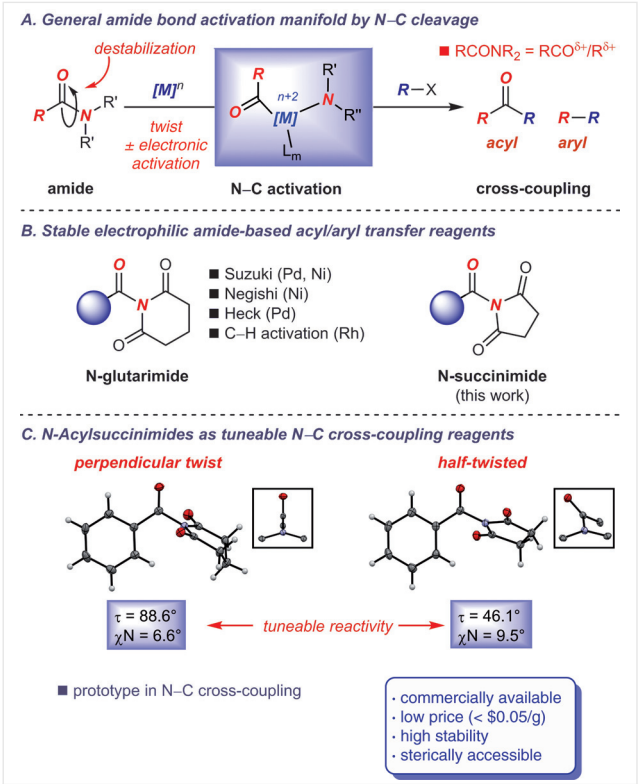


Figure 1 Cross-coupling of amides by N–C bond activation (previous and this work)

Despite the advances, the development of new amide-based reagents for selective N–C functionalization with rational design of the N–C bond cleavage selectivity remains a challenge in the field.[1b,5] Herein, we establish for the first time a room temperature, nickel-catalyzed Negishi cross-coupling of *N*-acylsuccinimides with arylzinc reagents via selective N–C bond cleavage enabled by amide bond twist.

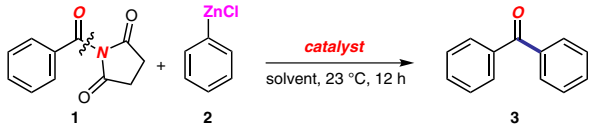
Notably, this report introduces *N*-acylsuccinimides as stable, crystalline, electrophilic, cost-effective, benign, amide-based acyl transfer reagents via acyl metal intermediates. The reaction selectivity is governed by *half-twist of the amide bond*[12] in *N*-acylsuccinimides, thus opening the door for applications in metal-catalyzed manifolds via redox-neutral reaction pathways tuneable by amide bond distortion (Figure 1 B, C).

The use of amide derivatives in cross-coupling is of broad importance because (1) generic acyl-metal intermediates can be generated under mild, chemoselective conditions by tuning amidic resonance; (2) halide waste is not generated during the transition-metal-catalyzed protocols, avoiding the handling of moisture sensitive and corrosive acyl halides; and (3) the amide bond activation manifold can potentially be employed in molecular biology and medicinal chemistry in late-stage derivatization.

Previous studies showed that *N*-glutarimide amides introduced by us represent the most reactive amide derivatives reported in N–C cross-coupling to date.[1,4–6,8g,h] *Mechanistically, the high reactivity of N-glutarimides results from perpendicular amide bond twist, irrespective of the R substitution.*[5e] To further advance the concept, we considered the use of *N*-succinimides as attractive precursors for selective acyl-transfer by N–C bond cleavage. On the basis of structural studies, the amide bond in *N*-succinimide amides is *half-twisted* (cf. fully perpendicular as in *N*-glutarimide amides),[5e] offering a strategic advantage of tuneable N–C insertion reactivity controlled by nonplanar geometry of the amide bond. *N*-Acylsuccinimides offer several additional major advantages in amide bond cross-coupling: (1) succinimide is a cheap, widely available chemical, with a price of < $ 0.05/g);[13] (2) the parent benzoylsuccinimide is commercially available; (3) *N*-acylsuccinimides are bench-stable, easily purified crystalline solids; (4) lower bond twist corresponds to higher stability of the amide *N*–acyl bond in acylsuccinimides (cf. *N*-glutarimide amides); (5) the compact five-membered ring is more sterically accessible for metal insertion (cf. *N*-glutarimide amides); and (6) the cyclic activating ring prevents undesired cleavage of the σ N–C bond adjacent to the amide bond (cf. saccharins or acyclic amides).[1,3–9,14]

We selected Ni-catalyzed Negishi cross-coupling to demonstrate the concept because of (1) the importance of Negishi cross-coupling,[15] (2) advantages of Ni-catalysis,[16] and (3) potentially mild reaction conditions for the coupling.[17] Our investigations commenced with an evaluation of the coupling of *N*-benzoylsuccinimide with arylzinc chloride in the presence of various Ni catalysts (Table 1). Various nickel catalysts were tested (Table 1, entries 1–5) and $NiCl_2(PPh_3)_2$ proved the most effective, delivering the cross-coupling product in excellent yield (entry 5). Importantly, other Ni(II) precatalysts such as $NiCl_2$(dppe), $NiCl_2$(dppf), $NiCl_2(PCy_3)_2$, and $Ni(acac)_2$ also showed good to high reactivity (entries 1–4), suggesting superior reactivity of *N*-succinimide amides versus *N*-glutarimide amides[6a] (vide infra). Likewise, a brief solvent screen demonstrated that although Et_2O is the preferred solvent for the coupling (entry 5), good to high yields can be obtained with 1,4-dioxane, THF, MeCN, and toluene (entries 6–9), indicating high reactivity and/or stability of *N*-benzoylsuccinimides. Finally, the use of $PdCl_2(PPh_3)_2$ clearly indicated that nickel is the preferred catalyst for the Negishi coupling of amides via N–C activation (entry 10). Importantly, the developed reaction proceeds with a commercially available, air-stable Ni(II) precatalyst in the absence of additives under exceedingly mild room temperature conditions.

Table 1 Optimization of Ni-Catalyzed Negishi Cross-Coupling of *N*-Acylsuccinimides by N–C Activation[a]



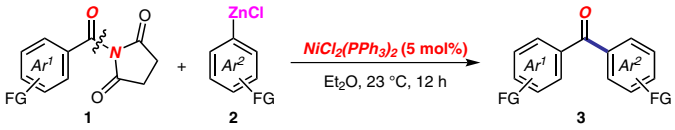
Entry	Catalyst	Solvent	Yield (%)[b]
1	$Ni(dppe)Cl_2$	Et_2O	42
2	$Ni(dppf)Cl_2$	Et_2O	40
3	$Ni(PCy_3)_2Cl_2$	Et_2O	88
4	$Ni(acac)_2$	Et_2O	45
5	$Ni(PPh_3)_2Cl_2$	Et_2O	90[c]
6	$Ni(PPh_3)_2Cl_2$	1,4-dioxane	75
7	$Ni(PPh_3)_2Cl_2$	THF	68
8	$Ni(PPh_3)_2Cl_2$	MeCN	72
9	$Ni(PPh_3)_2Cl_2$	toluene	59
10	$Pd(PPh_3)_2Cl_2$	Et_2O	<5

[a] Conditions: amide (1.0 equiv), Ph–ZnCl (1.5 equiv), catalyst (5 mol%), solvent (0.20 M), 23 °C, 12 h.
[b] GC/^{1}H NMR yields.
[c] Isolated yield.

With the optimized conditions in hand, the scope of the reaction was next examined (Table 2). We were pleased to find that the developed coupling is general, providing a versatile platform to generate a range of diaryl ketones.[18] Amide substrates containing neutral (Table 2, entry 1), electron-donating (entries 2–3) and electron-withdrawing (entry 4) substituents at the 4-position were well-tolerated. Importantly, the cross-coupling of a sterically demanding *ortho*-substituted amide afforded the desired product in good yield (Table 2, entry 5). Both electron-rich (entry 6) and electron-deficient (entry 7) arylzinc reagents can be employed in this coupling. The higher efficiency using electron-rich nucleophiles is consistent with the transmetalation as the slow step in the Negishi coupling.[19] Metal insertion may be the rate limiting step in the case of less electrophilic amide cross-coupling partners. The reaction could be further extended to the coupling of sterically demanding

amide precursors with electronically differentiated arylzincs (entries 8, 9). Finally, the reaction of electronically differentiated amides with electron-rich and electron-poor arylzinc reagents also proceeded smoothly and gave the diaryl ketone products in 70–82% yields (entries 10–12). The mild conditions and operational-simplicity using a single Ni(II) precatalyst in the absence of additives compare favorably with the Suzuki coupling of amides by N–C activation.

Table 2 Substrate Scope of Ni-Catalyzed Negishi Cross-Coupling of *N*-Acylsuccinimides[a]



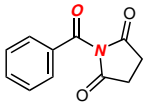
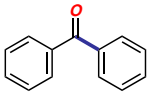
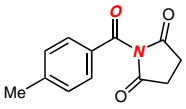
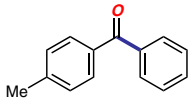
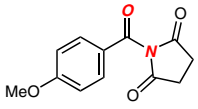
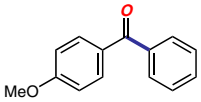
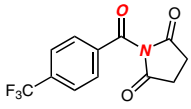
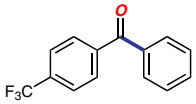
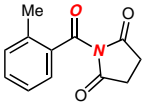
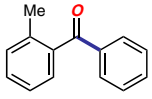
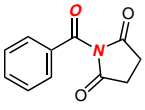
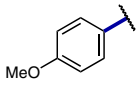
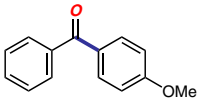
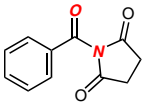
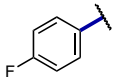
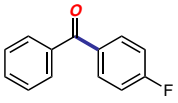
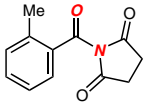
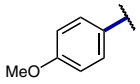
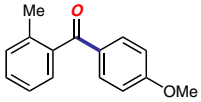
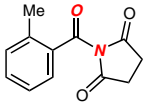
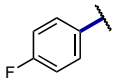
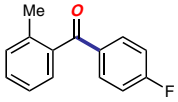
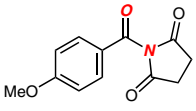
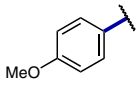
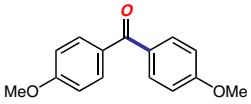
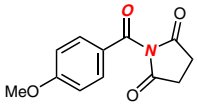
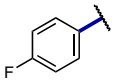
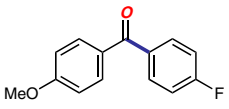
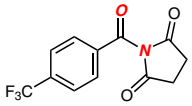
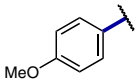
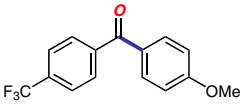
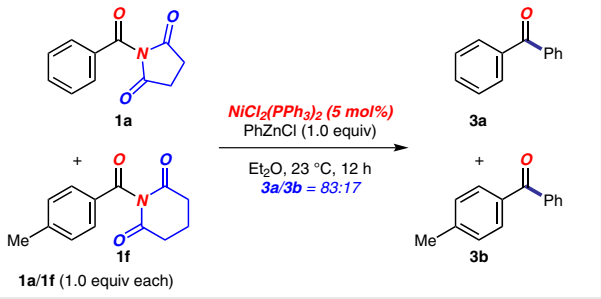
Entry	Amide **1**	ArZnCl **2** (Ar^2)	Product **3**	**3**	Yield (%)
1				**3a**	90
2				**3b**	87
3				**3c**	73
4				**3d**	71
5				**3e**	62
6				**3c′**	78
7				**3f**	56
8				**3g**	61
9				**3h**	56
10				**3i**	77

Table 2 (continued)

Entry	Amide **1**	ArZnCl **2** (Ar^2)	Product **3**	**3**	Yield (%)
11				**3j**	70
12				**3k**	82

[a] Conditions: amide (1.0 equiv), R–ZnCl (1.5 equiv), $Ni(PPh_3)_2Cl_2$ (5 mol%), Et_2O (0.20 M), 23 °C, 12 h.
[b] Isolated yields.

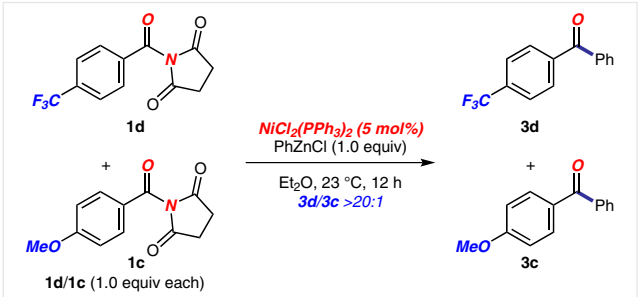
Interestingly, the reaction is more selective for the cross-coupling of *N*-acylsuccinimides (cf. *N*-acylglutramides) (Scheme 1). We hypothesize that the higher reactivity of *N*-succinimide amides results from (1) more sterically accessible amide bond and (2) higher stability under the reaction conditions. This finding bodes well for the development of a range of N–C activation protocols with *N*-acylsuccinimides, especially in cases when stability of *N*-glutarimide amides is problematic.[8j] Note that the higher reactivity of **1a** may also be partially attributed to the presence of a slightly electron-donating methyl group (**1f**).



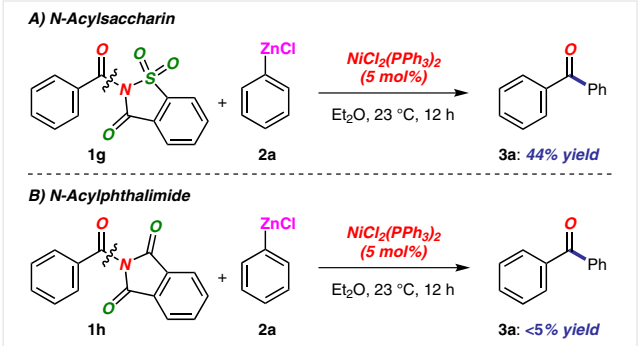
Scheme 1 Selectivity study in the Ni-catalyzed Negishi cross-coupling of *N*-acylsuccinimides: Effect of N-substitution

Preliminary mechanistic studies demonstrate that electron-deficient amides are inherently more reactive substrates, consistent with the facility of metal insertion (Scheme 2). This appears to be a common feature in the amide cross-coupling.[1,2]

The potential of using other five-membered *N*-acylimides as precursors to afford acyl metal intermediates was briefly evaluated (Scheme 3 A, B). Interestingly, our results demonstrate that *N*-acylsaccharins pioneered by our group[4d,6d] and Zeng and co-workers[8b–d] may become suitable cross-coupling partners in the reaction (Scheme 3 A). However, the capacity for unselective N–C vs. N–SO_2 insertion using Ni should be noted.



Scheme 2 Selectivity study in the Ni-catalyzed Negishi cross-coupling of *N*-acylsuccinimides: Effect of amides



Scheme 3 Ni-catalyzed Negishi cross-coupling of *N*-acylsaccharins and *N*-acylphthalimides

In contrast, *N*-acylphthalimides are not suitable amide-based acyl transfer reagents for the cross-coupling under various Ni-conditions (Scheme 3 B). We hypothesize that the electron-withdrawing fused benzene ring activates the phthalimide imide bonds towards unselective addition. Overall, these results highlight the beneficial use of N-succinimide amides as selective acyl-transfer reagents.[20]

In conclusion, we have developed *N*-acylsuccinimides as new, amide-based, electrophilic acyl transfer reagents in which the selectivity of metal insertion is controlled by amide bond twist. *N*-Acylsuccinimides contain *half-twisted amide bonds* (cf. fully perpendicular *N*-glutarimide amides). This results in higher stability under the reaction condi-

tions, while preserving the beneficial features of the imide activating group. Notably, these reagents are considerably cheaper than other amide-based electrophiles reported to date. The high selectivity for metal insertion, tuneable twist, ease of purification, and high bench-stability are other synthetically appealing features of *N*-acylsuccinimides.

In a broader context, our results demonstrate that the use of cheap and readily available carboxylic acid amides represents a valuable strategy for the selective formation of acyl-metal intermediates.[10] Studies on general activation of amide bonds and other applications of *N*-acylsuccinimides[21] are ongoing and these results will be reported in due course.

All starting materials reported in the manuscript have been previously described in the literature or prepared by a method reported previously. All experiments involving Ni were performed using standard techniques under argon atmosphere. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from Na/benzophenone. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum, and purged with argon (three cycles). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker and Varian spectrometers at 500 and 600 MHz (^{1}H NMR) and 125 and 150 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations are used to denote signal multiplicities. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using He as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aq $KMnO_4$ solutions.

The preparations of starting materials **1** and arylzinc reagents **2** are described in the Supporting Information.

Ni-Catalyzed Negishi Cross-Coupling; General Procedure

An oven-dried vial equipped with a stir bar was charged with an amide substrate **1** (neat, 1.0 equiv) and $Ni(PPh_3)_2Cl_2$ (0.05 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under vacuum. Et_2O (0.20 M) was added with vigorous stirring at r.t. and the reaction was stirred at r.t. for 5 min. A solution of arylzinc reagent **2** (THF solution, 1.5 equiv) was added with vigorous stirring and the reaction mixture was stirred for the indicated time at 23 °C. After the indicated time, the mixture was diluted with aq 1 N HCl (10 mL), the aqueous layer was extracted with EtOAc (3 × 20 mL), organic layers were combined, dried, filtered, and concentrated. Purification by chromatography on silica gel afforded the desired product.

Ni-Catalyzed Negishi Cross-Coupling; (4-Methoxyphenyl)(phenyl)-methanone (3c′); Typical Procedure

An oven-dried 100 mL round-bottomed flask equipped with a stir bar was charged with 1-benzoylpyrrolidine-2,5-dione (**1a**; 0.46 g, 2.0 mmol, 1.0 equiv) and $Ni(PPh_3)_2Cl_2$ (0.10 mmol, 0.05 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Et_2O (15.0 mL) was added at r.t. and the reaction mixture stirred for 5 min at r.t. A solution of 4-$MeOC_6H_4ZnCl$ (3.0 mmol, 1.50 equiv) was added with vigorous stirring and the reaction mixture was stirred overnight at 23 °C. After the indicated time, the reaction was quenched with aq 1 N HCl (30 mL), the aqueous layer was extracted with EtOAc (3 × 40 mL), organic layers were combined, dried, filtered, and concentrated. Purification by chromatography afforded the title product; yield: 0.33 g (78%, 1.56 mmol); white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.0 Hz, 2 H), 7.76 (d, *J* = 7.6 Hz, 2 H), 7.56 (t, *J* = 7.3 Hz, 1 H), 7.47 (t, *J* = 7.4 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 3.89 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.70, 163.35, 138.42, 132.69, 132.02, 130.29, 129.86, 128.32, 113.68, 55.63.

Characterization data for all other products are included in the section below. All products have been previously reported.[6a,c]

Benzophenone (Table 2, 3a)

White solid; yield: 32.9 mg (90%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.7 Hz, 2 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.89, 137.73, 132.54, 130.19, 128.41.

Phenyl(*p*-tolyl)methanone (Table 2, 3b)

White solid; yield: 34.2 mg (87%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.2 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H), 7.58 (t, *J* = 7.3 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 2 H), 7.28 (d, *J* = 7.9 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.65, 143.37, 138.09, 135.01, 132.29, 130.44, 130.07, 129.11, 128.34, 21.80.

(4-Methoxyphenyl)(phenyl)methanone (Table 2, 3c)

White solid; yield: 30.9 mg (73%).

For NMR data of **3c**, see the entries under **3c′**.

Phenyl[4-(trifluoromethyl)phenyl]methanone (Table 2, 3d)

White solid; yield: 35.4 mg (71%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.0 Hz, 2 H), 7.81 (dd, *J* = 8.3, 1.2 Hz, 2 H), 7.76 (d, *J* = 8.1 Hz, 2 H), 7.66–7.61 (m, 1 H), 7.51 (t, *J* = 7.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.68, 140.87, 136.87, 133.87 (q, $J_{C,F}$ = 32.5 Hz), 133.24, 130.28, 130.25, 128.68, 125.49 (q, *J* = 3.8 Hz), 123.82 (q, $J_{C,F}$ = 271.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.01.

Phenyl(*o*-tolyl)methanone (Table 2, 3e)

White solid; yield: 24.4 mg (62%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87–7.78 (m, 2 H), 7.63–7.59 (m, 1 H), 7.48 (t, *J* = 7.7 Hz, 2 H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.36–7.30 (m, 2 H), 7.29–7.27 (m, 1 H), 2.36 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.77, 138.74, 137.86, 136.87, 133.25, 131.12, 130.36, 130.26, 128.64, 128.58, 125.32, 20.12.

(4-Fluorophenyl)(phenyl)methanone (Table 2, 3f)

White solid; yield: 22.3 mg (56%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89–7.81 (m, 2 H), 7.77 (d, *J* = 7.7 Hz, 2 H), 7.60 (t, *J* = 7.3 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.16 (t, *J* = 8.4 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.41, 165.52 (d, $J_{C,F}$ = 252.5 Hz), 137.63, 133.94 (d, $J_{C,F}$ = 3.8 Hz), 132.80 (d, $J_{C,F}$ = 8.8 Hz), 132.61, 130.01, 128.49, 115.68 (d, $J_{C,F}$ = 21.2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –105.99.

(4-Methoxyphenyl)(*o*-tolyl)methanone (Table 2, 3g)

White solid; yield: 27.5 mg (61%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.6 Hz, 2 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 7.28 (t, *J* = 6.1 Hz, 2 H), 7.26–7.22 (m, 1 H), 6.93 (d, *J* = 8.5 Hz, 2 H), 3.88 (s, 3 H), 2.31 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.51, 163.84, 139.34, 136.29, 132.64, 130.95, 130.67, 129.92, 128.06, 125.30, 113.84, 55.65, 19.93.

(4-Fluorophenyl)(*o*-tolyl)methanone (Table 2, 3h)

White solid; yield: 24.0 mg (56%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 8.2, 6.0 Hz, 2 H), 7.42 (t, *J* = 7.5 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.29–7.28 (m, 1 H), 7.15 (d, *J* = 8.5 Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.06, 165.84 (d, $J_{C,F}$ = 253.6 Hz), 138.39, 136.62, 134.11 (d, $J_{C,F}$ = 3.0 Hz), 131.08, 130.34, 128.28, 125.29, 115.64 (d, $J_{C,F}$ = 21.8 Hz), 21.63.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –104.94.

Bis(4-methoxyphenyl)methanone (Table 2, 3i)

White solid; yield: 37.4 mg (77%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.4 Hz, 4 H), 6.96 (d, *J* = 8.4 Hz, 4 H), 3.89 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.60, 162.98, 132.37, 130.93, 113.61, 55.62.

(4-Fluorophenyl)(4-methoxyphenyl)methanone (Table 2, 3j)

White solid; yield: 32.1 mg (70%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86–7.74 (m, 4 H), 7.15 (t, *J* = 8.5 Hz, 2 H), 6.97 (d, *J* = 8.6 Hz, 2 H), 3.89 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.23, 165.20 (q, $J_{C,F}$ = 252.5 Hz), 163.40, 134.59 (d, $J_{C,F}$ = 2.5 Hz), 132.54, 132.42 (d, $J_{C,F}$ = 8.8 Hz), 130.18, 115.46 (d, $J_{C,F}$ = 22.5 Hz), 113.78, 55.66.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –106.94.

(4-Methoxyphenyl)[4-(trifluoromethyl)phenyl]methanone (Table 2, 3k)

White solid; yield: 46.0 mg (82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87–7.79 (m, 4 H), 7.74 (d, *J* = 8.1 Hz, 2 H), 6.98 (d, *J* = 8.9 Hz, 2 H), 3.90 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.40, 163.86, 141.65, 133.39 (q, $J_{C,F}$ = 32.5 Hz), 132.77, 129.92, 129.49, 125.79 (q, $J_{C,F}$ = 3.8 Hz), 123.87 (q, $J_{C,F}$ = 217.3 Hz), 113.95, 55.71.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –62.94.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588845.

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