

Electronic Supplementary Information

Suzuki-Miyaura Cross-Coupling of Amides and Esters at Room Temperature: Correlation with Barriers to Rotation around C–N and C–O Bonds

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been previously described in literature and prepared by the method reported previously. Amides and esters were prepared by standard methods.¹⁻⁴ All experiments were performed using standard Schlenk techniques under nitrogen or argon unless stated otherwise. 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 sodium/benzophenone under nitrogen. 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). All products were identified using ¹H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ¹H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on Bruker spectrometers at 500 (¹H NMR) and 125 MHz (¹³C NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl₃ peak (7.26 and 77.2 ppm, ¹H NMR and ¹³C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 min). 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 aqueous potassium permanganate solutions. ¹H NMR and ¹³C NMR data are given for all compounds in the SI for characterization purposes. ¹H NMR, ¹³C NMR, MS and HRMS data are given for all new compounds. All products have been previously reported, unless stated otherwise.

Experimental Procedures and Characterization Data

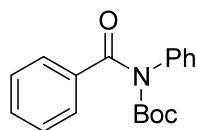
General Procedure for the Synthesis of Starting Materials. All amides used in this study have been prepared by methods described by us,¹ Garg,² and Zou.³ All esters have been prepared by standard methods.⁴ ¹H NMR and ¹³C NMR data for all amides and esters are given in the section below for characterization purposes.

General Procedure for the Suzuki-Miyaura Cross-Coupling of Amides. An oven-dried vial equipped with a stir bar was charged with an amide substrate (neat, 1.0 equiv), potassium carbonate (typically, 4.5 equiv), boronic acid (typically, 3.0 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl))⁵ (typically, 3 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (typically, 0.25 M) was added with vigorous stirring at room temperature and the reaction mixture was stirred for the indicated time. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) and GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product.

General Procedure for the Suzuki-Miyaura Cross-Coupling of Esters. An oven-dried vial equipped with a stir bar was charged with an ester substrate (neat, 1.0 equiv), potassium carbonate (typically, 7.2 equiv), boronic acid (typically, 4.5 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl)) (typically, 3 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (typically, 0.25 M) was added with vigorous stirring at room temperature and the reaction mixture was stirred for the indicated time. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) and GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product.

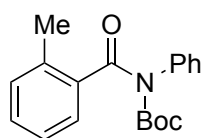
Representative Cross-Coupling Procedure. An oven-dried vial equipped with a stir bar was charged with phenyl benzoate (1.0 mmol, 198.2 mg, 1.0 equiv), potassium carbonate (4.5 mmol, 621.9 mg, 4.5 equiv), (4-methoxyphenyl)boronic acid (3.0 mmol, 455.9 mg, 3.0 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (1 mol%, 6.9 mg), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.25 M) was added with vigorous stirring at room temperature and the reaction mixture was stirred for 15 h at room temperature. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (20 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) and GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product (176.1 mg). Yield 83%. White solid. Characterization data are included in the section below.

Characterization Data for Starting Materials



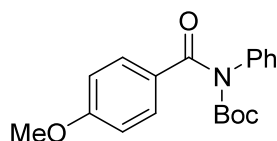
tert-Butyl benzoyl(phenyl)carbamate (2a). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 7.4$ Hz, 2 H), 7.55 (t, $J = 7.3$ Hz, 1 H), 7.46 (dd, $J = 14.1$, 7.0 Hz, 4 H), 7.37 (t, $J = 7.2$ Hz, 1 H), 7.30 (d, $J = 7.8$ Hz, 2 H), 1.26 (s, 9 H).

^{13}C NMR (125 MHz, CDCl_3) δ 172.8, 153.3, 139.1, 137.0, 131.7, 129.2, 128.3, 128.2, 128.0, 127.8, 83.5, 27.5.



tert-Butyl (2-methylbenzoyl)(phenyl)carbamate (2b). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.48 (dd, $J = 14.3$, 7.2 Hz, 3 H), 7.41-7.35 (m, 2 H), 7.32 (d, $J = 7.9$ Hz, 2 H), 7.29-7.25 (m, 2 H), 2.52 (s, 3 H), 1.19 (s, 9 H). ^{13}C NMR

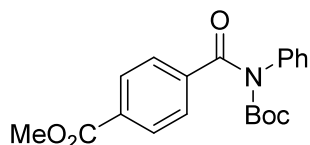
(125 MHz, CDCl_3) δ 172.6, 152.9, 138.6, 137.9, 135.7, 130.7, 129.9, 129.2, 128.1, 128.0, 126.4, 125.5, 83.6, 27.4, 19.5.



tert-Butyl (4-methoxybenzoyl)(phenyl)carbamate (2c). White solid.

^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.6$ Hz, 2 H), 7.43 (t, $J = 7.2$ Hz, 2 H), 7.33 (t, $J = 7.3$ Hz, 1 H), 7.28 (d, $J = 7.9$ Hz, 2 H), 6.95 (d, $J =$

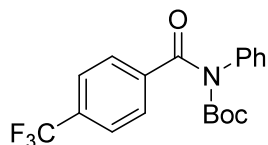
7.7 Hz, 2 H), 3.88 (s, 3 H), 1.32 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.1, 162.8, 153.6, 139.5, 130.9, 129.1, 128.7, 127.8, 127.5, 113.6, 83.1, 55.5, 27.7.



tert-Butyl (4-(methoxycarbonyl)benzoyl)(phenyl)carbamate (2d).

White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.14 (d, $J = 8.1$ Hz, 2 H), 7.78 (d, $J = 8.1$ Hz, 2 H), 7.46 (t, $J = 7.6$ Hz, 2 H), 7.38 (t, $J = 7.3$ Hz,

1 H), 7.28 (d, $J = 7.8$ Hz, 2 H), 3.97 (s, 3 H), 1.26 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 171.8, 166.2, 153.0, 141.0, 138.6, 132.5, 129.5, 129.3, 128.1, 128.0, 127.8, 84.0, 52.4, 27.5.

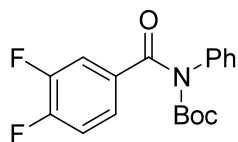


tert-Butyl phenyl(4-(trifluoromethyl)benzoyl)carbamate (2e). White

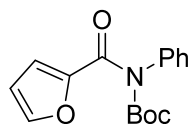
solid. ^1H NMR (500 MHz, CDCl_3) δ 7.84 (d, $J = 8.0$ Hz, 2 H), 7.74 (d, $J =$

8.2 Hz, 2 H), 7.51-7.44 (m, 2 H), 7.42-7.38 (m, 1 H), 7.31-7.27 (m, 2 H), 1.27 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 171.4, 152.9, 140.4, 138.5, 133.1 ($J^2 = 65.0$ Hz),

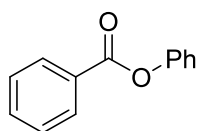
129.3, 128.2, 128.0, 125.3 ($J^3 = 7.5$ Hz), 123.7 ($J^1 = 270.0$ Hz), 84.1, 27.5. ^{19}F NMR (471 MHz, CDCl_3) δ -62.92.



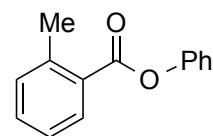
tert-Butyl (3,4-difluorobenzoyl)(phenyl)carbamate (2f). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.59 (t, $J = 8.8$ Hz, 1 H), 7.52 (s, 1 H), 7.45 (t, $J = 7.3$ Hz, 2 H), 7.38 (t, $J = 7.3$ Hz, 1 H), 7.24 (t, $J = 7.8$ Hz, 3 H), 1.33 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.3, 152.6 ($J^1 = 253.8$ Hz), 153.0, 150.07 ($J^1 = 250.0$ Hz), 138.7, 133.5 ($J^3 = 5.0$ Hz), 129.3, 128.1, 127.8, 124.9 ($J^2 = 15.0$ Hz, $J^3 = 7.5$ Hz), 117.8 ($J^2 = 18.8$ Hz), 117.3 ($J^2 = 17.5$ Hz), 84.0, 27.6. ^{19}F NMR (471 MHz, CDCl_3) δ -131.6, -136.6.



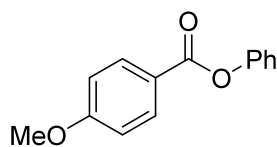
tert-Butyl (furan-2-carbonyl)(phenyl)carbamate (2g). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.58-7.53 (m, 1 H), 7.43 (dd, $J = 10.4, 4.8$ Hz, 2 H), 7.38-7.33 (m, 1 H), 7.30-7.26 (m, 2 H), 7.04 (dd, $J = 3.5, 0.6$ Hz, 1 H), 6.53 (dd, $J = 3.5, 1.7$ Hz, 1 H), 1.42 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 161.3, 152.9, 148.5, 145.1, 138.7, 129.2, 128.0, 127.9, 118.1, 112.3, 83.3, 27.7.



Phenyl benzoate (5a). White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.29-8.20 (m, 2 H), 7.67 (t, $J = 7.4$ Hz, 1 H), 7.55 (t, $J = 7.7$ Hz, 2 H), 7.47 (t, $J = 7.9$ Hz, 2 H), 7.31 (t, $J = 7.4$ Hz, 1 H), 7.25 (d, $J = 7.6$ Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ 165.2, 151.0, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.7.

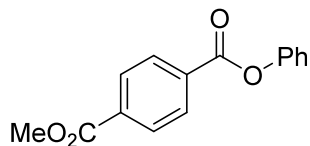


Phenyl 2-methylbenzoate (5b). Oil. ^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, $J = 7.7$ Hz, 1 H), 7.51 (t, $J = 7.5$ Hz, 1 H), 7.47 (t, $J = 7.3$ Hz, 2 H), 7.36 (t, $J = 8.0$ Hz, 2 H), 7.32-7.28 (m, 1 H), 7.25 (d, $J = 7.9$ Hz, 2 H), 2.71 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 165.9, 151.0, 141.3, 132.7, 132.0, 131.2, 129.5, 128.6, 125.9, 125.8, 121.9, 22.0.

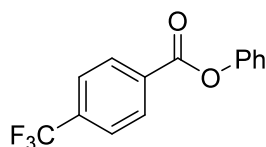


Phenyl 4-methoxybenzoate (5c). White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, $J = 8.9$ Hz, 2 H), 7.45 (t, $J = 7.9$ Hz, 2 H), 7.31-7.27 (m, 1 H), 7.24 (d, $J = 7.9$ Hz, 2 H), 7.02 (d, $J = 8.8$ Hz, 2 H), 3.92 (s, 3

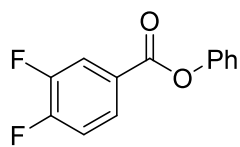
H). ^{13}C NMR (125 MHz, CDCl_3) δ 164.9, 163.9, 151.1, 132.3, 129.5, 125.7, 121.9, 121.8, 113.9, 55.5.



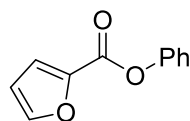
Methyl phenyl terephthalate (5d). White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.30 (d, $J = 7.5$ Hz, 2 H), 8.20 (d, $J = 7.9$ Hz, 2 H), 7.47 (t, $J = 7.3$ Hz, 2 H), 7.32 (t, $J = 7.4$ Hz, 1 H), 7.26 (d, $J = 8.0$ Hz, 2 H), 4.00 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 166.2, 164.4, 150.8, 134.5, 133.4, 130.2, 129.7, 129.6, 126.1, 121.6, 52.5.



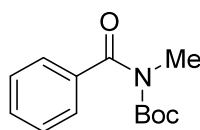
Phenyl 4-(trifluoromethyl)benzoate (5e). White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.35 (d, $J = 8.1$ Hz, 2 H), 7.81 (d, $J = 8.2$ Hz, 2 H), 7.48 (t, $J = 7.9$ Hz, 2 H), 7.33 (t, $J = 7.5$ Hz, 1 H), 7.27-7.23 (m, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ 164.0, 150.7, 135.1 ($J^2 = 32.8$ Hz), 132.9, 130.6, 129.6, 126.3, 125.6 ($J^4 = 3.7$ Hz), 123.6 ($J^1 = 272.8$ Hz), 121.6. ^{19}F NMR (471 MHz, CDCl_3) δ -63.2.



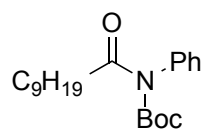
Phenyl 3,4-difluorobenzoate (5f). White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.10-7.96 (m, 2 H), 7.47 (t, $J = 7.3$ Hz, 2 H), 7.38-7.29 (m, 2 H), 7.23 (d, $J = 7.9$ Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ 163.3, 154.1 ($J^1 = 257.2$ Hz), 150.7, 150.2 ($J^1 = 250.9$ Hz), 129.6, 127.2 ($J^3 = 7.5$ Hz, $J^4 = 3.6$ Hz), 126.6 ($J^3 = 7.7$ Hz), 126.2, 121.5, 119.5 ($J^2 = 18.8$ Hz), 117.6 ($J^2 = 17.9$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -128.9, -136.0.



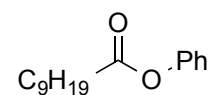
Phenyl furan-2-carboxylate (5g). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.70 (s, 1 H), 7.45 (t, $J = 7.4$ Hz, 2 H), 7.41 (d, $J = 2.3$ Hz, 1 H), 7.32-7.28 (m, 1 H), 7.24 (d, $J = 7.9$ Hz, 2 H), 6.62 (d, $J = 1.4$ Hz, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ 156.9, 150.2, 147.1, 144.1, 129.5, 126.1, 121.6, 119.4, 112.2.



tert-Butyl (benzoyl)(methyl)carbamate (2h). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.53 (d, $J = 7.2$ Hz, 2 H), 7.48 (t, $J = 7.4$ Hz, 1 H), 7.40 (t, $J = 7.5$ Hz, 2 H), 3.33 (s, 3 H), 1.17 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.6, 153.6, 137.9, 130.9, 128.0, 127.4, 83.0, 32.6, 27.4.

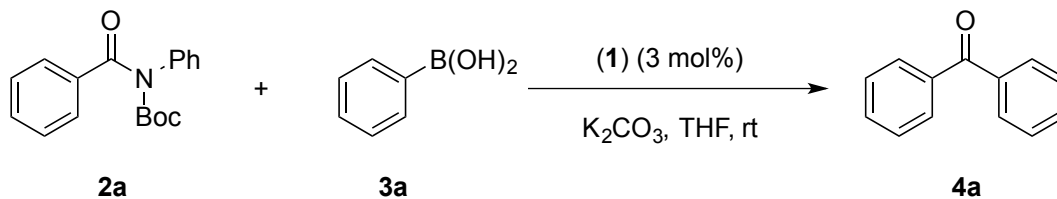


tert-Butyl decanoylphenylcarbamate (2i). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (t, $J = 7.2$ Hz, 2 H), 7.34 (t, $J = 7.3$ Hz, 1 H), 7.09 (d, $J = 7.7$ Hz, 2 H), 2.92 (t, $J = 7.4$ Hz, 2 H), 1.70 (p, $J = 7.3, 6.8$ Hz, 2 H), 1.40 (s, 9 H), 1.29 (s, 12 H), 0.90 (t, $J = 6.4$ Hz, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 176.0, 152.3, 139.2, 128.9, 128.2, 127.7, 82.9, 38.0, 31.9, 29.5, 29.3, 29.2, 27.8, 25.0, 22.7, 14.1.

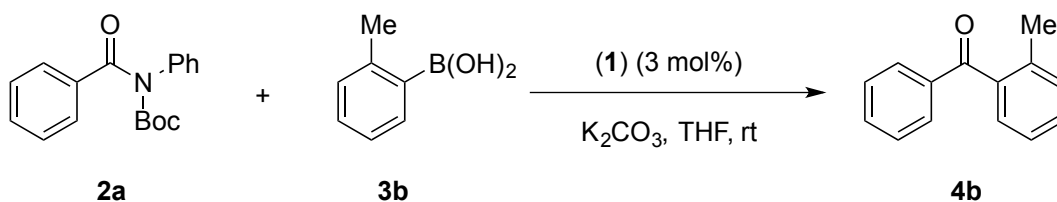


Phenyl decanoate (5h). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.40 (t, $J = 7.8$ Hz, 2 H), 7.25 (t, $J = 7.4$ Hz, 1 H), 7.10 (d, $J = 7.7$ Hz, 2 H), 2.58 (t, $J = 7.5$ Hz, 2 H), 1.85-1.73 (m, 2 H), 1.50-1.41 (m, 2 H), 1.40-1.25 (m, 10 H), 0.92 (t, $J = 6.7$ Hz, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.4, 150.8, 129.4, 125.7, 121.6, 34.4, 31.9, 29.5, 29.3, 29.1, 25.0, 22.7, 14.1.

Cross-Coupling of Amides and Esters: Variation of Boronic Acid

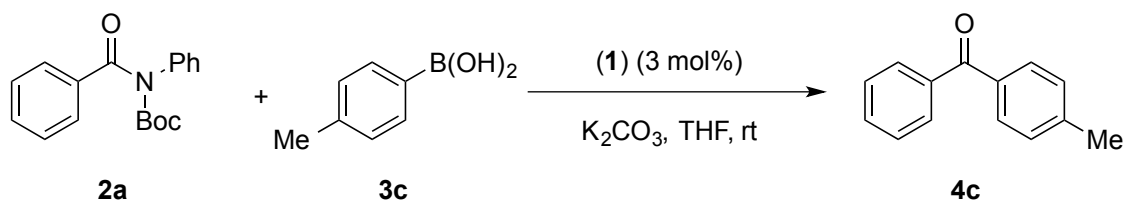
Benzophenone (4a) (Table 1, Entry 1)^{1d}

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (35.6 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.83-7.78 (m, 4 H), 7.59 (t, *J* = 7.4 Hz, 2 H), 7.48 (t, *J* = 7.7 Hz, 4 H). ¹³C NMR (125 MHz, CDCl₃) δ 196.8, 137.6, 132.4, 130.1, 128.3.

Phenyl(*o*-tolyl)methanone (4b) (Table 1, Entry 2)^{1d}

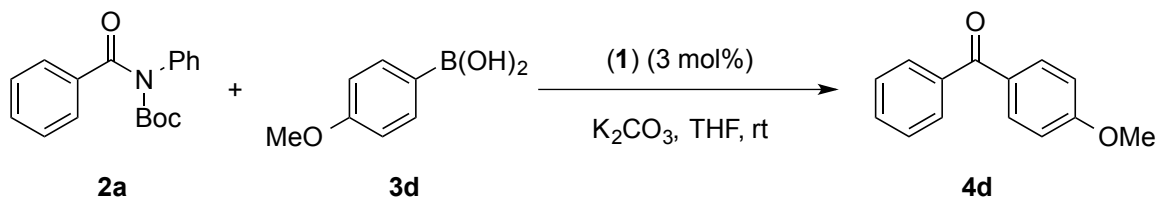
According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.20 mmol), *o*-tolylboronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 95% yield (37.3 mg). Oil. ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 7.5 Hz, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.30 (dd, *J* = 11.0, 7.6 Hz, 2 H), 7.26-7.22 (m, 1 H), 2.33 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 198.7, 138.6, 137.8, 136.8, 133.1, 131.0, 130.3, 130.2, 128.5, 128.5, 125.2, 20.0.

Phenyl(*p*-tolyl)methanone (4c) (Table 1, Entry 3)^{1d}



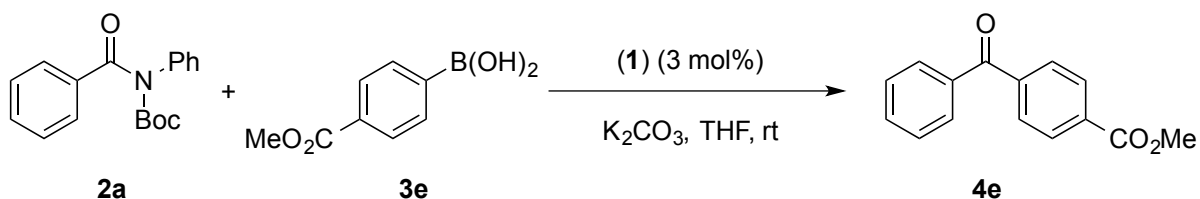
According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.20 mmol), *p*-tolylboronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 96% yield (37.5 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 7.2$ Hz, 2 H), 7.73 (d, $J = 8.1$ Hz, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ 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 196.5, 143.3, 138.0, 134.9, 132.2, 130.3, 130.0, 129.0, 128.2, 21.7.

(4-Methoxyphenyl)(phenyl)methanone (4d) (Table 1, Entry 4)^{1d}



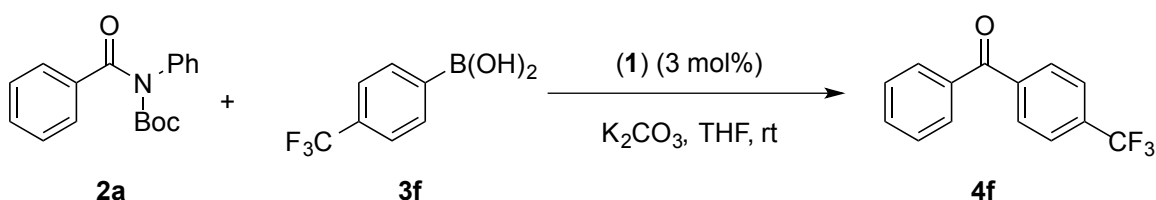
According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.20 mmol), (4-methoxyphenyl)boronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (41.7 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J = 8.8$ Hz, 2 H), 7.76 (d, $J = 7.4$ Hz, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 6.97 (d, $J = 8.8$ Hz, 2 H), 3.89 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 195.6, 163.2, 138.3, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5.

Methyl 4-benzoylbenzoate (4e) (Table 1, Entry 5)^{1d}



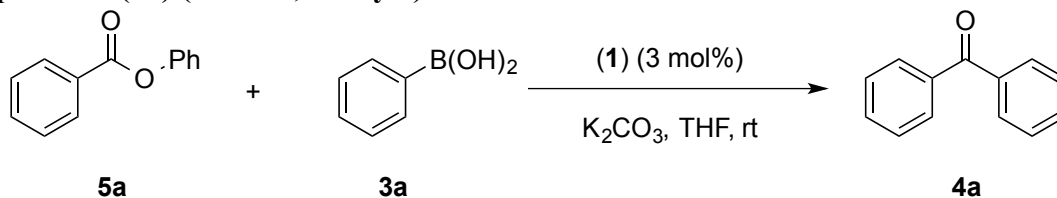
According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.20 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 95% yield (45.6 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.3 Hz, 2 H), 7.84 (d, *J* = 8.3 Hz, 2 H), 7.80 (d, *J* = 7.3 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.7 Hz, 2 H), 3.96 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 196.1, 166.3, 141.3, 137.0, 133.2, 133.0, 130.1, 129.8, 129.5, 128.5, 52.5.

Phenyl(4-(trifluoromethyl)phenyl)methanone (**4f**) (Table 1, Entry 6)^{ld}



According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.20 mmol), 4-(trifluoromethyl)phenylboronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (49.1 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 2 H), 7.81 (d, *J* = 7.3 Hz, 2 H), 7.76 (d, *J* = 8.1 Hz, 2 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.7 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 195.6, 140.7, 136.8, 133.7 (*J*² = 32.6 Hz), 133.1, 130.1 (*J*^f = 4.2 Hz), 128.6, 125.4 (*J*^f = 3.7 Hz), 123.7 (*J*^f = 272.7 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -63.0.

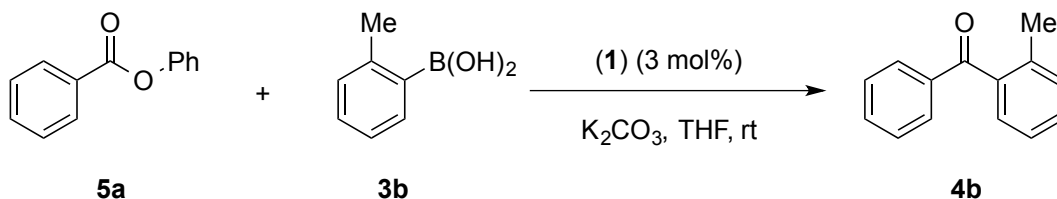
Benzophenone (**4a**) (Table 2, Entry 1)^{ld}



According to the general procedure, the reaction of phenyl benzoate (0.20 mmol), phenylboronic acid (4.5 equiv), K₂CO₃ (7.2 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 83% yield (30.2 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.83-7.78 (m, 4 H), 7.59 (t, *J*

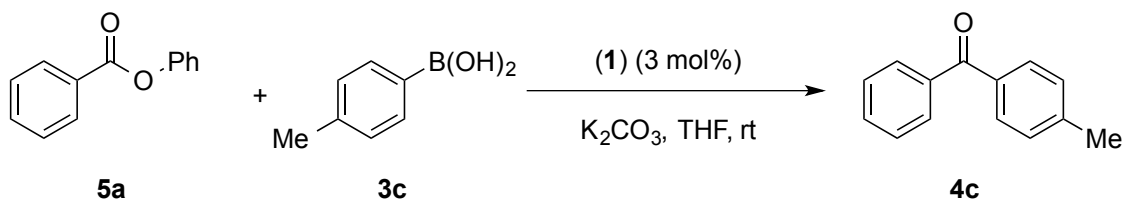
= 7.4 Hz, 2 H), 7.48 (t, $J = 7.7$ Hz, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ 196.8, 137.6, 132.4, 130.1, 128.3.

Phenyl(*o*-tolyl)methanone (4b) (Table 2, Entry 2)^{1d}



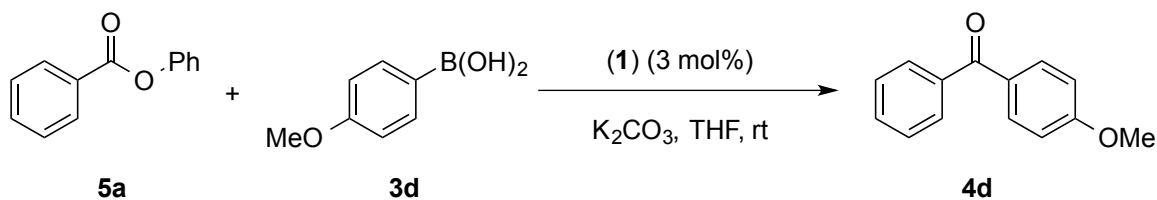
According to the general procedure, the reaction of phenyl benzoate (0.20 mmol), *o*-tolylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 72% yield (28.4 mg). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, $J = 7.5$ Hz, 2 H), 7.58 (t, $J = 7.4$ Hz, 1 H), 7.46 (t, $J = 7.7$ Hz, 2 H), 7.39 (t, $J = 7.5$ Hz, 1 H), 7.30 (dd, $J = 11.0, 7.6$ Hz, 2 H), 7.26-7.22 (m, 1 H), 2.33 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 198.7, 138.6, 137.8, 136.8, 133.1, 131.0, 130.3, 130.2, 128.5, 128.5, 125.2, 20.0.

Phenyl(*p*-tolyl)methanone (4c) (Table 2, Entry 3)^{1d}



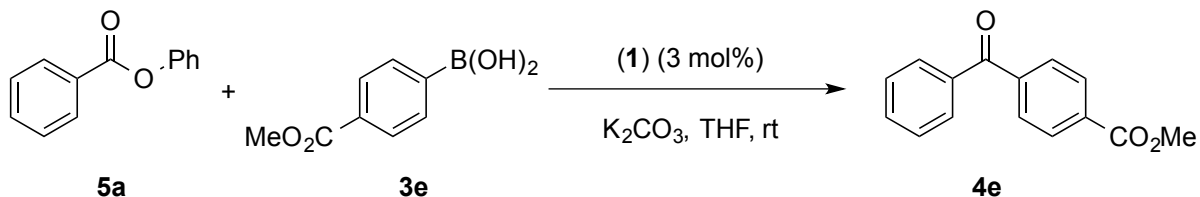
According to the general procedure, the reaction of phenyl benzoate (0.20 mmol), *p*-tolylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 80% yield (31.3 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 7.2$ Hz, 2 H), 7.73 (d, $J = 8.1$ Hz, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ 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 196.5, 143.3, 138.0, 134.9, 132.2, 130.3, 130.0, 129.0, 128.2, 21.7.

(4-Methoxyphenyl)(phenyl)methanone (4d) (Table 2, Entry 4)^{1d}



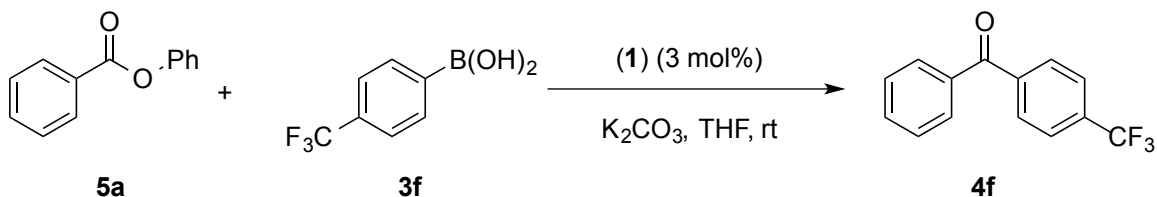
According to the general procedure, the reaction of phenyl benzoate (0.20 mmol), (4-methoxyphenyl)boronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (41.6 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J = 8.8$ Hz, 2 H), 7.76 (d, $J = 7.4$ Hz, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 6.97 (d, $J = 8.8$ Hz, 2 H), 3.89 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 195.6, 163.2, 138.3, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5.

Methyl 4-benzoylbenzoate (4e) (Table 2, Entry 5)^{1d}



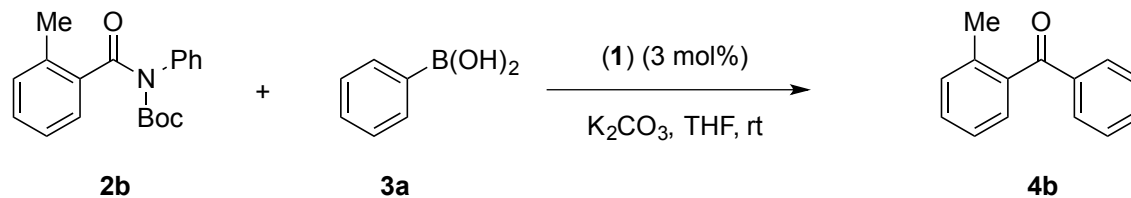
According to the general procedure, the reaction of phenyl benzoate (0.20 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration chromatography the title compound in 62% yield (29.9 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.3$ Hz, 2 H), 7.84 (d, $J = 8.3$ Hz, 2 H), 7.80 (d, $J = 7.3$ Hz, 2 H), 7.62 (t, $J = 7.4$ Hz, 1 H), 7.50 (t, $J = 7.7$ Hz, 2 H), 3.96 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 196.1, 166.3, 141.3, 137.0, 133.2, 133.0, 130.1, 129.8, 129.5, 128.5, 52.5.

Phenyl(4-(trifluoromethyl)phenyl)methanone (4f) (Table 2, Entry 6)^{1d}

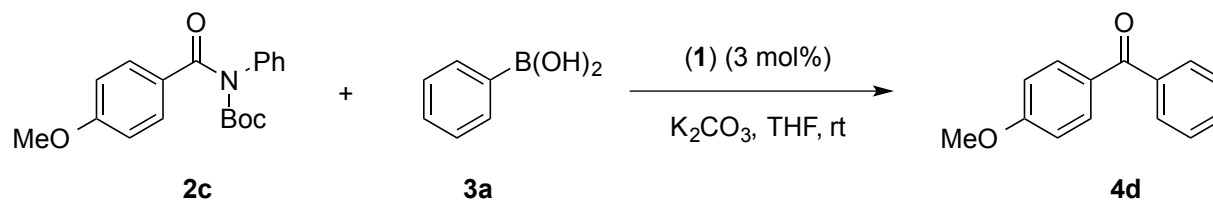


According to the general procedure, the reaction of phenyl benzoate (0.20 mmol), 4-(trifluoromethyl)phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 86% yield (43.2 mg). White solid. 1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, $J = 8.1$ Hz, 2 H), 7.81 (d, $J = 7.3$ Hz, 2 H), 7.76 (d, $J = 8.1$ Hz, 2 H), 7.63 (t, $J = 7.4$ Hz, 1 H), 7.51 (t, $J = 7.7$ Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 140.7, 136.8, 133.7 ($J^2 = 32.6$ Hz), 133.1, 130.1 ($J^4 = 4.2$ Hz), 128.6, 125.4 ($J^4 = 3.7$ Hz), 123.7 ($J^1 = 272.7$ Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.0.

Cross-Coupling of Amides and Esters: Variation of Amides and Esters

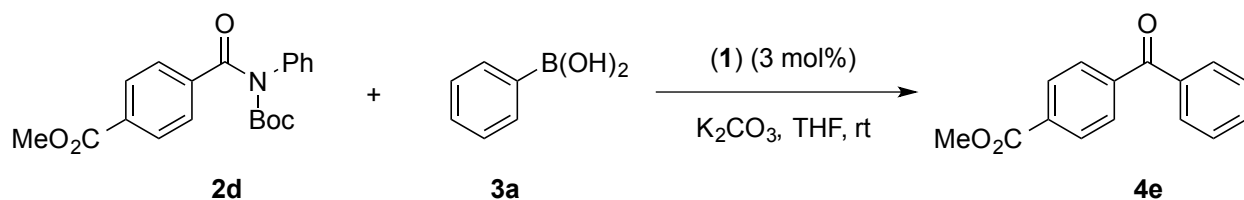
Phenyl(*o*-tolyl)methanone (4b) (Table 1, Entry 7)^{1d}

According to the general procedure, the reaction of *tert*-butyl (2-methylbenzoyl)(phenyl)carbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (1) (η³-1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 78% yield (30.7 mg). Oil. ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 7.5 Hz, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.30 (dd, *J* = 11.0, 7.6 Hz, 2 H), 7.26-7.22 (m, 1 H), 2.33 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 198.7, 138.6, 137.8, 136.8, 133.1, 131.0, 130.3, 130.2, 128.5, 128.5, 125.2, 20.0.

(4-Methoxyphenyl)(phenyl)methanone (4d) (Table 1, Entry 8)^{1d}

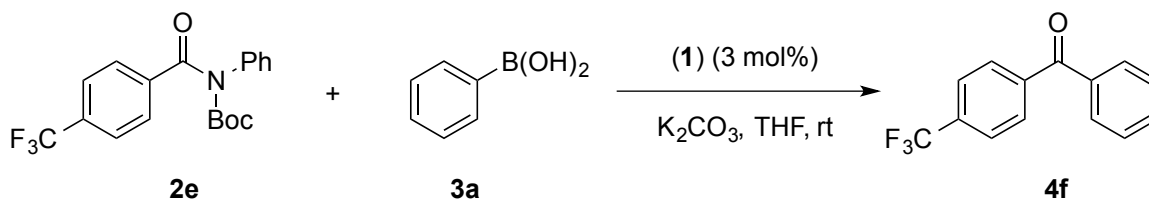
According to the general procedure, the reaction of *tert*-butyl (4-methoxybenzoyl)(phenyl)carbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (1) (η³-1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (41.4 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 8.8 Hz, 2 H), 7.76 (d, *J* = 7.4 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 195.6, 163.2, 138.3, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5.

Methyl 4-benzoylbenzoate (4e) (Table 1, Entry 9)^{1d}



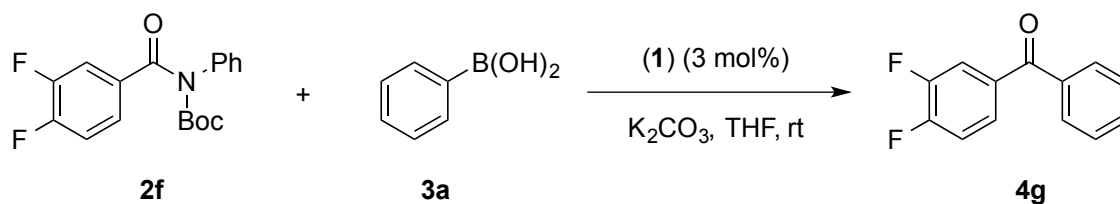
According to the general procedure, the reaction of *tert*-butyl (4-(methoxycarbonyl)benzoyl)(phenyl)carbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 80% yield (38.5 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.3$ Hz, 2 H), 7.84 (d, $J = 8.3$ Hz, 2 H), 7.80 (d, $J = 7.3$ Hz, 2 H), 7.62 (t, $J = 7.4$ Hz, 1 H), 7.50 (t, $J = 7.7$ Hz, 2 H), 3.96 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 196.1, 166.3, 141.3, 137.0, 133.2, 133.0, 130.1, 129.8, 129.5, 128.5, 52.5.

Phenyl(4-(trifluoromethyl)phenyl)methanone (4f) (Table 1, Entry 10)^{1d}



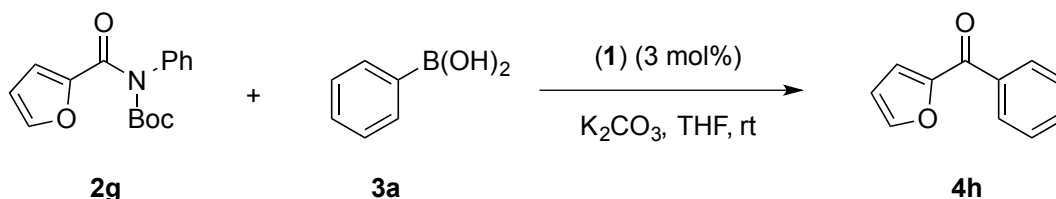
According to the general procedure, the reaction of *tert*-butyl phenyl(4-(trifluoromethyl)benzoyl)carbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (48.8 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.1$ Hz, 2 H), 7.81 (d, $J = 7.3$ Hz, 2 H), 7.76 (d, $J = 8.1$ Hz, 2 H), 7.63 (t, $J = 7.4$ Hz, 1 H), 7.51 (t, $J = 7.7$ Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ 195.6, 140.7, 136.8, 133.7 ($J^2 = 32.6$ Hz), 133.1, 130.1 ($J^f = 4.2$ Hz), 128.6, 125.4 ($J^f = 3.7$ Hz), 123.7 ($J^f = 272.7$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -63.0.

(3,4-Difluorophenyl)(phenyl)methanone (4g) (Table 1, Entry 11)⁹



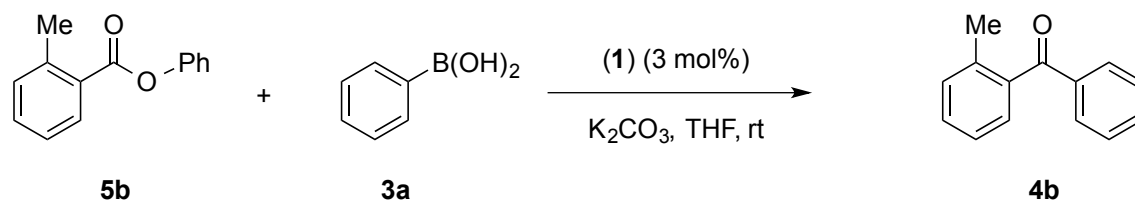
According to the general procedure, the reaction of *tert*-butyl (3,4-difluorobenzoyl)(phenyl)carbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 95% yield (41.4 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.4$ Hz, 2 H), 7.70-7.66 (m, 1 H), 7.64-7.57 (m, 2 H), 7.50 (t, $J = 7.7$ Hz, 2 H), 7.30-7.24 (m, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ 194.1, 153.3 ($J^I = 256.3$ Hz, $J^J = 12.9$ Hz), 150.2 ($J^I = 251.1$ Hz, $J^J = 12.9$ Hz), 136.9, 134.5 ($J^J = 8.0$ Hz), 132.8, 129.9, 128.5, 127.1 ($J^J = 7.3$ Hz, $J^I = 3.6$ Hz), 119.3 ($J^J = 18.1$ Hz), 117.3 ($J^J = 17.8$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -130.6, -136.2.

Furan-2-yl(phenyl)methanone (4h) (Table 1, Entry 12)^{4b}



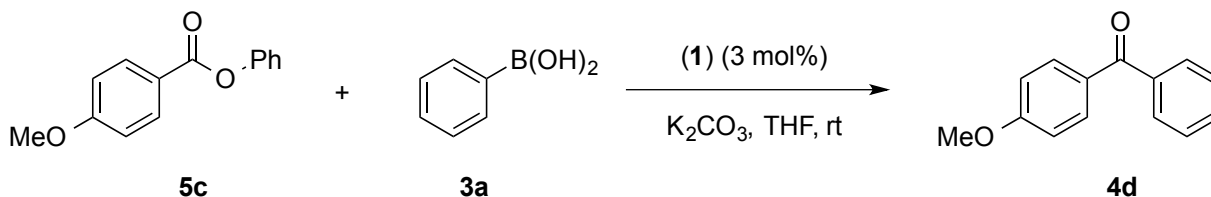
According to the general procedure, the reaction of *tert*-butyl (furan-2-carbonyl)(phenyl)carbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 91% yield (31.3 mg). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 7.3$ Hz, 2 H), 7.71 (s, 1 H), 7.60 (t, $J = 7.4$ Hz, 1 H), 7.50 (t, $J = 7.6$ Hz, 2 H), 7.24 (d, $J = 3.5$ Hz, 1 H), 6.61-6.59 (m, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ 182.6, 152.4, 147.1, 137.3, 132.6, 129.3, 128.4, 120.6, 112.2.

Phenyl(*o*-tolyl)methanone (4b) (Table 2, Entry 7)^{1d}



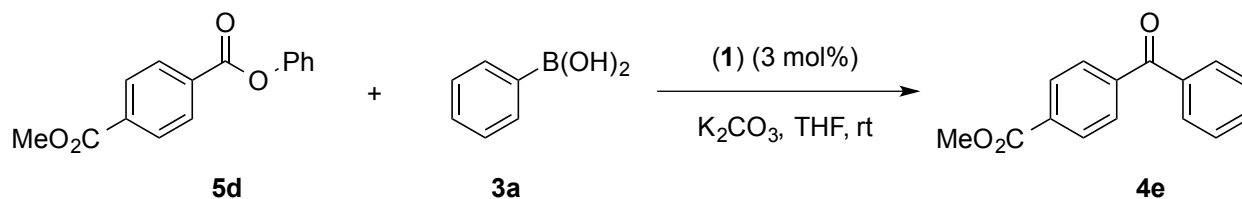
According to the general procedure, the reaction of phenyl 2-methylbenzoate (0.20 mmol), phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 75% yield (29.6 mg). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, $J = 7.5$ Hz, 2 H), 7.58 (t, $J = 7.4$ Hz, 1 H), 7.46 (t, $J = 7.7$ Hz, 2 H), 7.39 (t, $J = 7.5$ Hz, 1 H), 7.30 (dd, $J = 11.0, 7.6$ Hz, 2 H), 7.26-7.22 (m, 1 H), 2.33 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 198.7, 138.6, 137.8, 136.8, 133.1, 131.0, 130.3, 130.2, 128.5, 128.5, 125.2, 20.0.

(4-Methoxyphenyl)(phenyl)methanone (4d) (Table 2, Entry 8)^{1d}



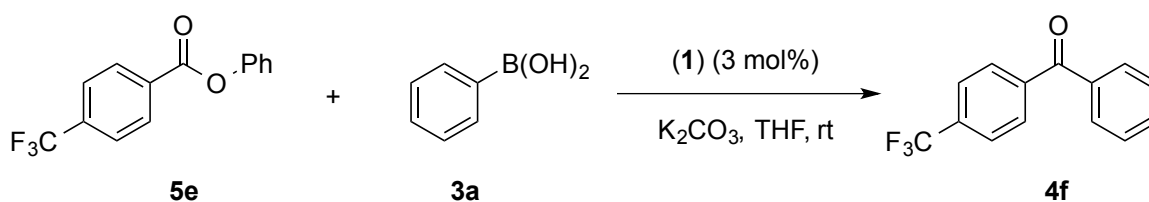
According to the general procedure, the reaction of phenyl 4-methoxybenzoate (0.20 mmol), phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 75% yield (31.9 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J = 8.8$ Hz, 2 H), 7.76 (d, $J = 7.4$ Hz, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 6.97 (d, $J = 8.8$ Hz, 2 H), 3.89 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 195.6, 163.2, 138.3, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5.

Methyl 4-benzoylbenzoate (4e) (Table 2, Entry 9)^{1d}



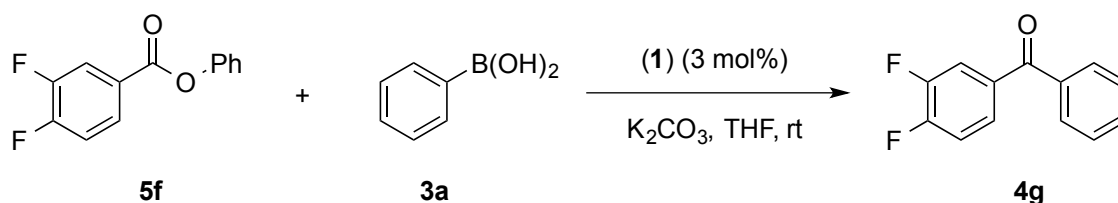
According to the general procedure, the reaction of methyl phenyl terephthalate (0.20 mmol), phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 91% yield (43.7 mg). White solid. 1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, $J = 8.3$ Hz, 2 H), 7.84 (d, $J = 8.3$ Hz, 2 H), 7.80 (d, $J = 7.3$ Hz, 2 H), 7.62 (t, $J = 7.4$ Hz, 1 H), 7.50 (t, $J = 7.7$ Hz, 2 H), 3.96 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 166.3, 141.3, 137.0, 133.2, 133.0, 130.1, 129.8, 129.5, 128.5, 52.5.

Phenyl(4-(trifluoromethyl)phenyl)methanone (4f) (Table 2, Entry 10)^{ld}



According to the general procedure, the reaction of phenyl 4-(trifluoromethyl)benzoate (0.20 mmol), phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 97% yield (48.3 mg). White solid. 1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, $J = 8.1$ Hz, 2 H), 7.81 (d, $J = 7.3$ Hz, 2 H), 7.76 (d, $J = 8.1$ Hz, 2 H), 7.63 (t, $J = 7.4$ Hz, 1 H), 7.51 (t, $J = 7.7$ Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 140.7, 136.8, 133.7 ($J^2 = 32.6$ Hz), 133.1, 130.1 ($J^f = 4.2$ Hz), 128.6, 125.4 ($J^f = 3.7$ Hz), 123.7 ($J^f = 272.7$ Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.0.

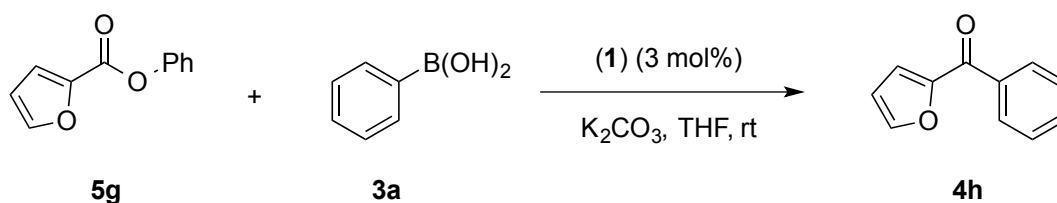
(3,4-Difluorophenyl)(phenyl)methanone (4g) (Table 2, Entry 11)⁹



According to the general procedure, the reaction of phenyl 3,4-difluorobenzoate (0.20 mmol), phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 96% yield (41.8 mg). White solid. 1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, $J =$

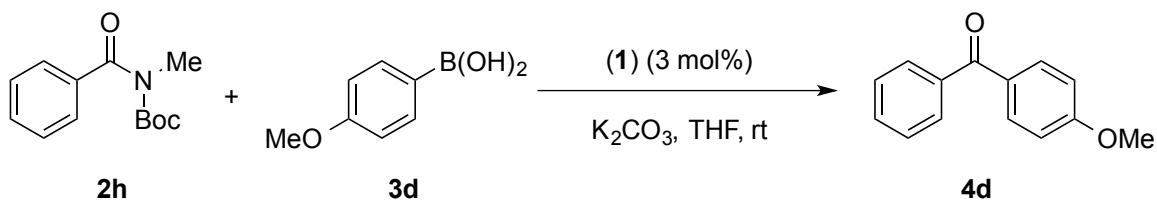
7.4 Hz, 2 H), 7.70-7.66 (m, 1 H), 7.64-7.57 (m, 2 H), 7.50 (t, $J = 7.7$ Hz, 2 H), 7.30-7.24 (m, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ 194.1, 153.3 ($J^1 = 256.3$ Hz, $J^3 = 12.9$ Hz), 150.2 ($J^1 = 251.1$ Hz, $J^3 = 12.9$ Hz), 136.9, 134.5 ($J^3 = 8.0$ Hz), 132.8, 129.9, 128.5, 127.1 ($J^3 = 7.3$ Hz, $J^4 = 3.6$ Hz), 119.3 ($J^2 = 18.1$ Hz), 117.4 ($J^2 = 17.8$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -130.6, -136.2.

Furan-2-yl(phenyl)methanone (4h) (Table 2, Entry 12)^{4b}



According to the general procedure, the reaction of phenyl furan-2-carboxylate (0.20 mmol), phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 60% yield (20.8 mg). Oil. ^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 7.3$ Hz, 2 H), 7.71 (s, 1 H), 7.60 (t, $J = 7.4$ Hz, 1 H), 7.50 (t, $J = 7.6$ Hz, 2 H), 7.24 (d, $J = 3.5$ Hz, 1 H), 6.61-6.59 (m, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ 182.6, 152.4, 147.1, 137.3, 132.6, 129.3, 128.4, 120.6, 112.2.

(4-Methoxyphenyl)(phenyl)methanone (4d) (Eq. 2, Amide = *N*-Me/Boc)^{1d}

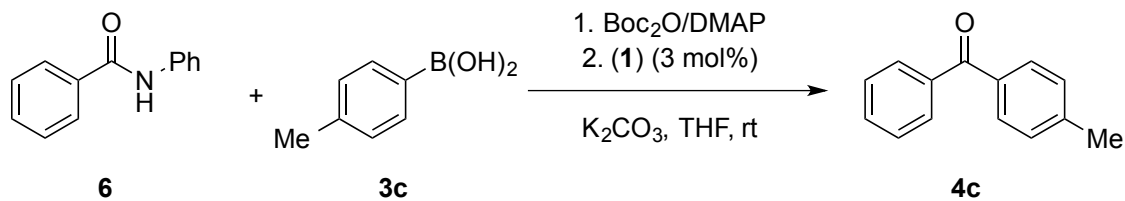


According to the general procedure, the reaction of *tert*-butyl (benzoyl)(methyl)carbamate (0.20 mmol), (4-methoxyphenyl)boronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 92% yield (39.2 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J = 8.8$ Hz, 2 H), 7.76 (d, $J = 7.4$ Hz, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 6.97 (d, $J = 8.8$ Hz, 2 H), 3.89 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ 195.6, 163.2, 138.3, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5.

One-Pot *N*-Activation/ Cross-Coupling

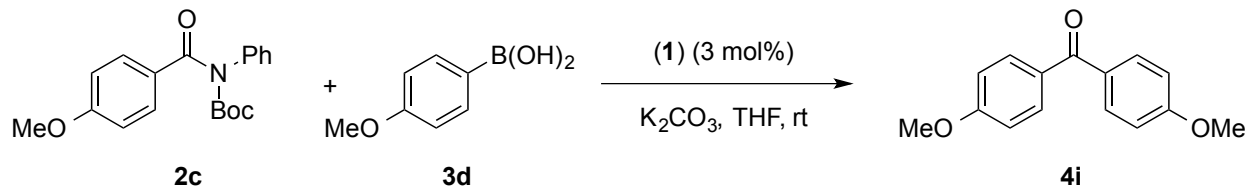
General Procedure. An oven-dried vial equipped with a stir bar was charged with *N*-phenylbenzamide (neat, 0.20 mmol, 1.0 equiv), di-*tert*-butyl-dicarbonate (1.0 equiv), and DMAP (10 mol%). Acetonitrile (0.25 M) was added with vigorous stirring and the resulting reaction mixture was stirred at room temperature for 15 h. After the indicated time, the reaction mixture was concentrated under high vacuum, 4-methylphenylboronic acid (3.0 equiv), potassium carbonate (4.5 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) were added, the reaction vial was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.25 M) was added with vigorous stirring and the resulting reaction mixture was stirred at room temperature for 15 h. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) and/or GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product. Yield 94% (36.8 mg). White solid. Characterization data matched those described above.

Scheme SI-1. One-Pot *N*-Activation/Suzuki-Miyaura Cross-Coupling at Room Temperature Catalyzed by (**1**).

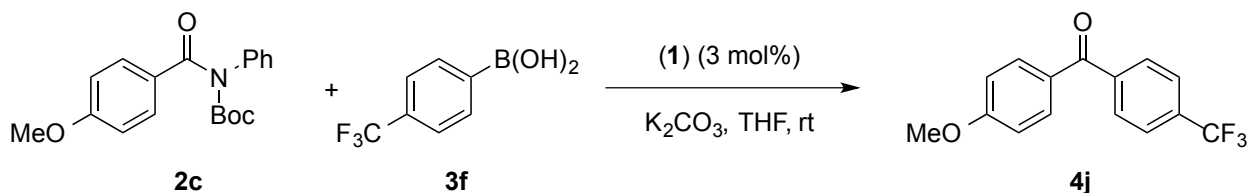


Conditions: (**1**) (3 mol%), 4-Tol-B(OH)₂ (3.0 equiv), K₂CO₃ (4.5 equiv), THF (0.25 M), 23 °C, 15 h.

Cross-Coupling of Amides and Esters: Additional Examples

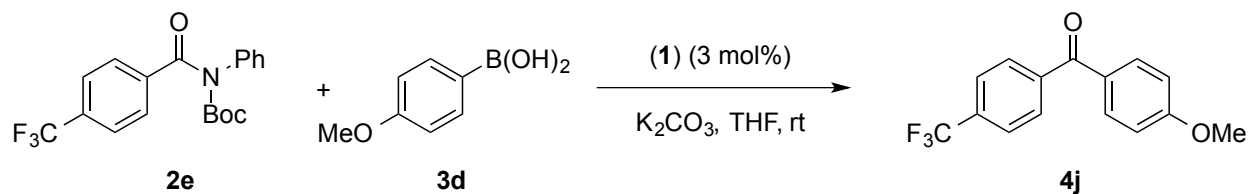
Bis(4-methoxyphenyl)methanone (**4i**) (Table 3, Entry 1)^{4b}

According to the general procedure, the reaction of *tert*-butyl (4-methoxybenzoyl) (phenyl)carbamate (0.20 mmol), (4-methoxyphenyl)boronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (47.5 mg). White solid. 1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, $J = 8.3$ Hz, 4 H), 6.99 (d, $J = 8.3$ Hz, 4 H), 3.91 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 162.9, 132.2, 130.8, 113.5, 55.5.

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (**4j**) (Table 3, Entry 2)^{4b}

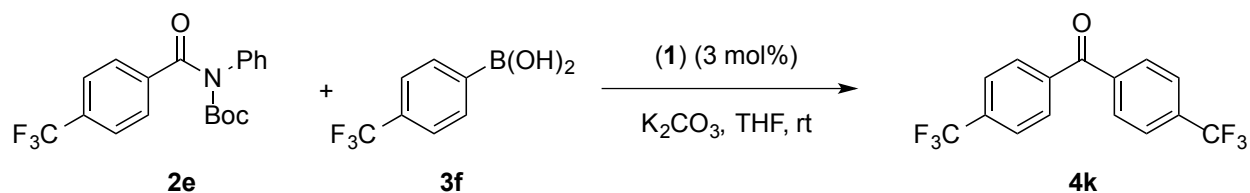
According to the general procedure, the reaction of *tert*-butyl (4-methoxybenzoyl) (phenyl)carbamate (0.20 mmol), 4-(trifluoromethyl)phenylboronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 95% yield (53.3 mg). White solid. 1H NMR (500 MHz, $CDCl_3$) δ 7.86 (t, $J = 9.0$ Hz, 4H), 7.77 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 8.3$ Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.3, 163.7, 141.5, 133.4 (t, $J = 32.7$ Hz), 132.7, 129.8, 129.4, 125.3, 123.8 (d, $J = 272.1$ Hz), 113.8, 55.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.9.

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (**4j**) (Table 3, Entry 3)^{4b}



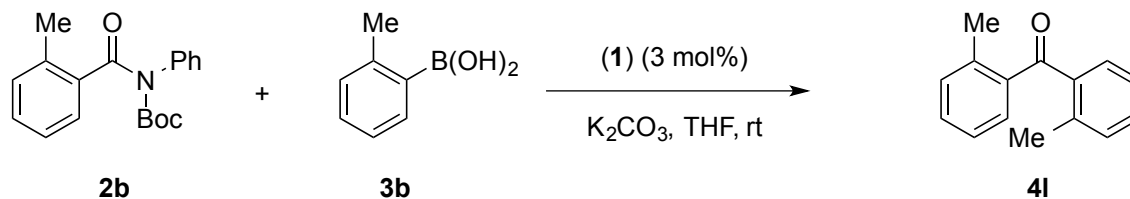
According to the general procedure, the reaction of *tert*-butyl phenyl(4-(trifluoromethyl)benzoyl)carbamate (0.20 mmol), (4-methoxyphenyl)boronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 94% yield (52.5 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.86 (t, $J = 9.0$ Hz, 4H), 7.77 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 8.3$ Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 194.3, 163.7, 141.5, 133.4 (t, $J = 32.7$ Hz), 132.7, 129.8, 129.4, 125.3, 123.8 (d, $J = 272.1$ Hz), 113.8, 55.6. ^{19}F NMR (470 MHz, CDCl_3) δ -62.9.

Bis(4-(trifluoromethyl)phenyl)methanone (4k) (Table 3, Entry 4)^{4b}



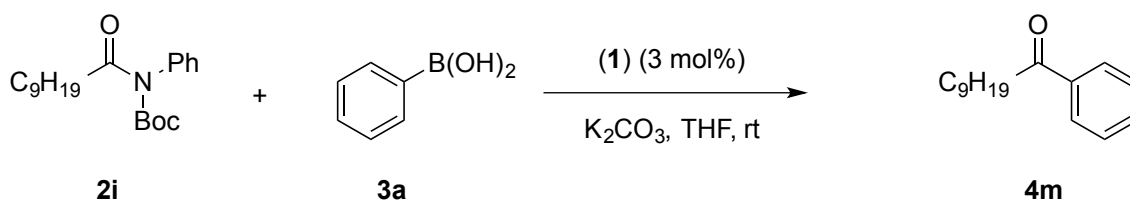
According to the general procedure, the reaction of *tert*-butyl phenyl(4-(trifluoromethyl)benzoyl)carbamate (0.20 mmol), 4-(trifluoromethyl)phenylboronic acid (3.0 equiv), K_2CO_3 (4.5 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 96% yield (61.1 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 7.4$ Hz, 4 H), 7.81 (d, $J = 7.6$ Hz, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ 194.4, 139.8, 134.4 (d, $J = 32.8$ Hz), 130.2 (s), 125.6, 123.5 (d, $J = 273.0$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -63.1.

Di-*o*-tolylmethanone (4l) (Table 3, Entry 5)³



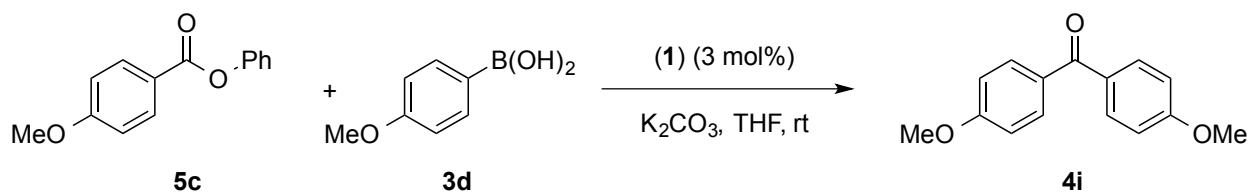
According to the general procedure, the reaction of *tert*-butyl phenyl(2-methyl benzoyl)carbamate (0.20 mmol), *o*-tolylboronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 62% yield (25.9 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (t, *J* = 7.4 Hz, 2 H), 7.32 (dt, *J* = 14.6, 7.3 Hz, 4 H), 7.23 (t, *J* = 7.4 Hz, 2 H), 2.48 (s, 6 H). ¹³C NMR (125 MHz, CDCl₃) δ 200.8, 139.0, 138.2, 131.4, 131.1, 130.3, 125.4, 20.7.

1-Phenyldecan-1-one (**4m**) (Table 3, Entry 6)^{1d}



According to the general procedure, the reaction of *tert*-butyl decanoylphenylcarbamate (0.20 mmol), phenylboronic acid (3.0 equiv), K₂CO₃ (4.5 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 76% yield (35.5 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 7.4 Hz, 2 H), 7.55 (t, *J* = 7.3 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 2.96 (t, *J* = 7.4 Hz, 2 H), 1.78-1.69 (m, 2 H), 1.40-1.22 (m, 12 H), 0.88 (t, *J* = 6.8 Hz, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 200.7, 137.1, 132.9, 128.6, 128.1, 38.7, 31.9, 29.5, 29.5, 29.4, 29.3, 24.4, 22.69, 14.1.

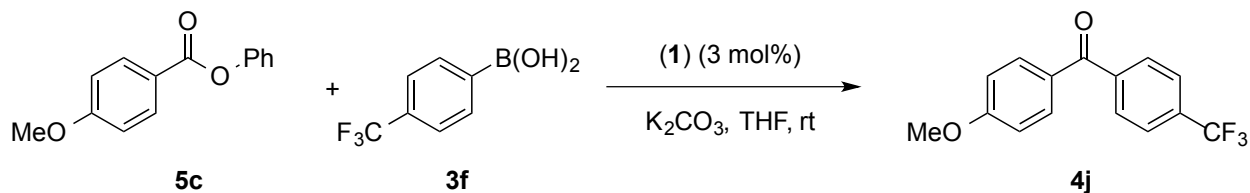
Bis(4-methoxyphenyl)methanone (**4i**) (Table 3, Entry 7)^{4b}



According to the general procedure, the reaction of phenyl 4-methoxybenzoate (0.20 mmol), (4-methoxyphenyl)boronic acid (4.5 equiv), K₂CO₃ (7.2 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 96% yield (46.5 mg). White solid. ¹H NMR (500 MHz,

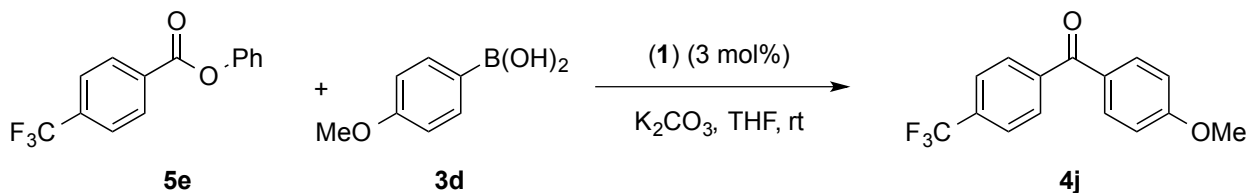
CDCl_3) δ 7.81 (d, $J = 8.3$ Hz, 4 H), 6.99 (d, $J = 8.3$ Hz, 4 H), 3.91 (s, 6 H). ^{13}C NMR (125 MHz, CDCl_3) δ 194.5, 162.9, 132.2, 130.8, 113.4, 55.5.

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (4j) (Table 3, Entry 8)^{4b}



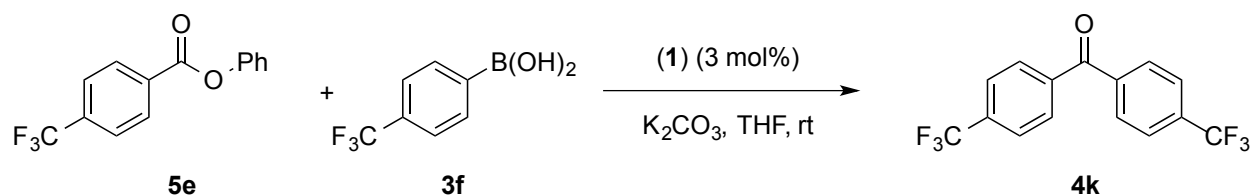
According to the general procedure, the reaction of phenyl 4-(trifluoromethyl)phenylboronic acid (0.20 mmol), (4-methoxyphenyl)boronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 94% yield (52.7 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.86 (t, $J = 9.0$ Hz, 4H), 7.77 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 8.3$ Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 194.3, 163.7, 141.5, 133.4 (t, $J = 32.7$ Hz), 132.7, 129.8, 129.4, 125.3, 123.8 (d, $J = 272.1$ Hz), 113.8, 55.6. ^{19}F NMR (470 MHz, CDCl_3) δ -62.9.

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (4j) (Table 3, Entry 9)^{4b}



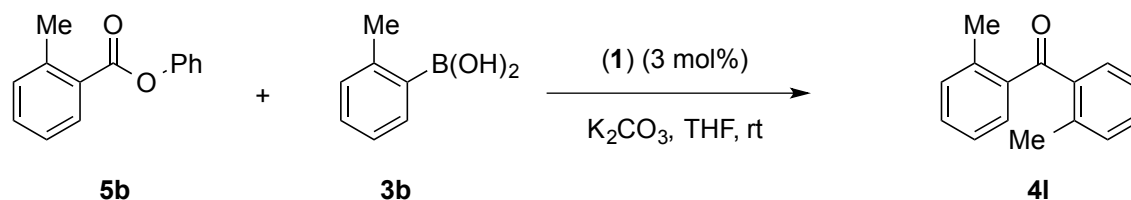
According to the general procedure, the reaction of phenyl 4-(trifluoromethyl)benzoate (0.20 mmol), (4-methoxyphenyl)boronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 98% yield (54.9 mg). White solid. White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.86 (t, $J = 9.0$ Hz, 4H), 7.77 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 8.3$ Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 194.3, 163.7, 141.5, 133.4 (t, $J = 32.7$ Hz), 132.7, 129.8, 129.4, 125.3, 123.8 (d, $J = 272.1$ Hz), 113.8, 55.6. ^{19}F NMR (470 MHz, CDCl_3) δ -62.9.

Bis(4-(trifluoromethyl)phenyl)methanone (4k) (Table 3, Entry 10)^{4b}



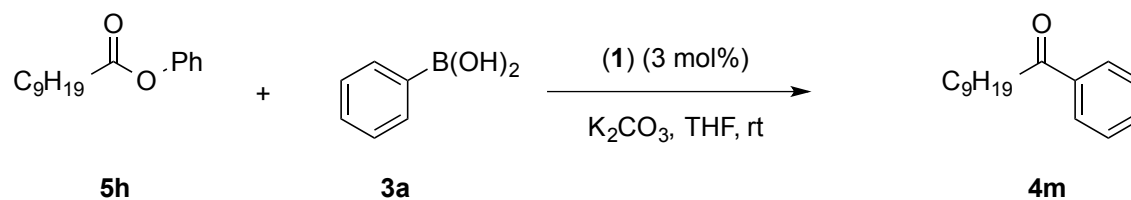
According to the general procedure, the reaction of phenyl 4-(trifluoromethyl)benzoate (0.20 mmol), (4-methoxyphenyl)boronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 93% yield (59.2 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 7.4$ Hz, 4 H), 7.81 (d, $J = 7.6$ Hz, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ 194.4, 139.8, 134.4 (d, $J = 32.8$ Hz), 130.2 (s), 125.6, 123.5 (d, $J = 273.0$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -63.1.

Di-*o*-tolylmethanone (4l) (Table 3, Entry 11)³



According to the general procedure, the reaction of phenyl 2-methylbenzoate (0.20 mmol), *o*-tolylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%) in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 49% yield (20.5 mg). White solid. ^1H NMR (500 MHz, CDCl_3) δ 7.42 (t, $J = 7.4$ Hz, 2 H), 7.32 (dt, $J = 14.6, 7.3$ Hz, 4 H), 7.23 (t, $J = 7.4$ Hz, 2 H), 2.48 (s, 6 H). ^{13}C NMR (125 MHz, CDCl_3) δ 200.8, 139.0, 138.2, 131.4, 131.1, 130.3, 125.4, 20.687

1-Phenyldecan-1-one (4m) (Table 3, Entry 12)^{1b}



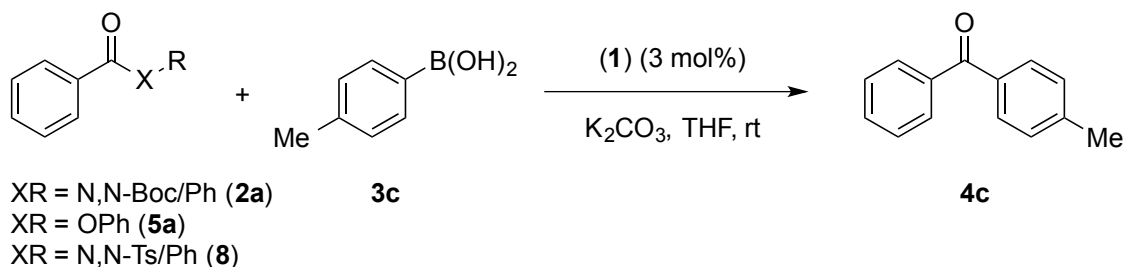
According to the general procedure, the reaction of phenyl decanoate (0.20 mmol), phenylboronic acid (4.5 equiv), K_2CO_3 (7.2 equiv), (1) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%)

in THF (0.25 M) for 15 h at room temperature, afforded after filtration and chromatography the title compound in 91% yield (42.3 mg). White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 7.4 Hz, 2 H), 7.55 (t, *J* = 7.3 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 2.96 (t, *J* = 7.4 Hz, 2 H), 1.78-1.69 (m, 2 H), 1.40-1.22 (m, 12 H), 0.88 (t, *J* = 6.8 Hz, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 200.7, 137.1, 132.9, 128.6, 128.1, 38.7, 31.9, 29.5, 29.5, 29.4, 29.3, 24.4, 22.7, 14.1.

Determination of Kinetic Profiles

General Procedure. An oven-dried vial equipped with a stir bar was charged with an amide or ester substrate (neat, 0.20 mmol, 1.0 equiv), potassium carbonate (4.5 equiv), boronic acid (3.0 equiv), **(1)** (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.25 M) was added with vigorous stirring and the reaction mixture was stirred at room temperature for the indicated time. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) and/or GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples.

Scheme SI-2. Determination of Relative Reaction Rates in the Suzuki-Miyaura Cross-Coupling Catalyzed by **(1)**.



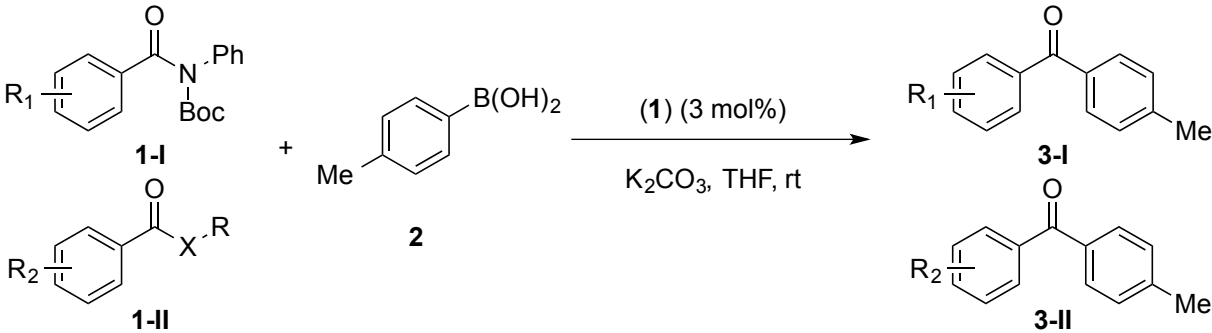
Conditions: **(1)** (3 mol%), 4-Tol-B(OH)₂ (3.0 equiv), K₂CO₃ (4.5 equiv), THF (0.25 M), 23 °C, 0-300 min.

The relative reactivity of amide and ester electrophiles in the Suzuki-Miyaura cross-coupling at room temperature was studied by determining kinetic profiles.⁶ In addition, N,N-Ts/Ph amide (**8**) was included for comparison.^{7,1-3} The observed kinetic profiles are consistent with the barrier to isomerization of the acyl bond.⁸ Note that these conditions allow for synthetically useful selectivity between **2a**, **5a** and **8**. Further studies on the mechanism of the Suzuki-Miyaura reaction are underway in our laboratory.

Selectivity Studies

General Procedure. An oven-dried vial equipped with a stir bar was charged with two carbonyl substrates (each 0.20 mmol, 1.0 equiv), potassium carbonate (4.5 equiv), 4-methylphenylboronic acid (0.50 equiv), (**1**) (η^3 -1-*t*-Bu-indenyl)Pd(IPr)(Cl) (3 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.25 M) was added with vigorous stirring and the reaction mixture was stirred at room temperature for the indicated time. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) and/or GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples.

Table SI-1. Selectivity Study in the Suzuki-Miyaura Cross-Coupling at Room Temperature Catalyzed by (**1**).



Entry	1-I (R ₁)	1-II (XR, R ₂)	Amide/Ester (equiv)	3-I:3-II (R ₁ :R ₂) ^b
1	4-Me-	N,N-Ph/Me, H	2.0	>98:2
2	4-Me-	N,N-Ph/Ts, H	2.0	>98:2
3	4-Me-	OPh, H	2.0	10:1

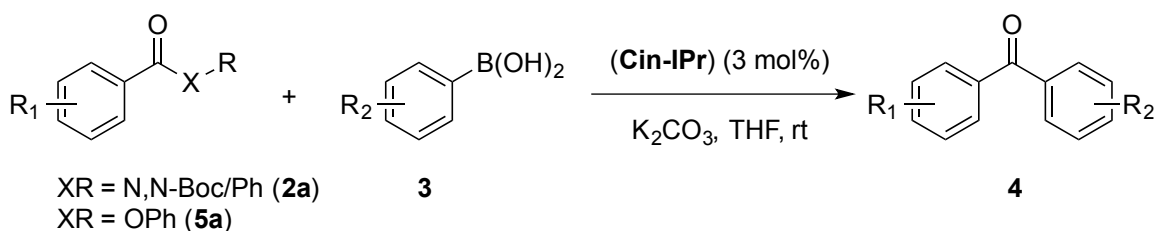
^aConditions: (**1**) (3.0 mol%), THF (0.25 M), 23 °C. All reactions carried out using standard Schlenk techniques under argon.

^bDetermined by ¹H NMR and/or GC-MS.

Comparison of Reactivity using Cin-IPr

General Procedure. An oven-dried vial equipped with a stir bar was charged with an amide or ester substrate (neat, 0.20 mmol, 1.0 equiv), potassium carbonate, boronic acid, (**Cin-IPr**) (η^3 -cinnamyl)Pd(IPr)(Cl) (3 mol%),⁹ placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.25 M) was added with vigorous stirring and the reaction mixture was stirred at room temperature for 15 h. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) and/or GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. Note that in all cases (**1**) significantly outperforms **Cin-IPr** in the coupling.¹⁰

Table SI-2. Suzuki-Miyaura Cross-Coupling Reactions at Room Temperature Catalyzed by **Cin-IPr**.^a



Entry	XR	(R ₁)	(R ₂)	yield of 4 (%) ^b
1	(2a)	4-MeO-	H-	8
2	(2a)	4-CF ₃ -	H-	7
3	(2a)	4-CO ₂ Me-	H-	<2
4	(5a)	4-MeO-	H-	<2
5	(5a)	4-CF ₃ -	H-	<2
6	(5a)	4-CO ₂ Me-	H-	<2
7	(2a)	H-	4-CF ₃ -	6
8	(2a)	H-	4-Me-	28
9	(5a)	H-	4-CF ₃ -	<2
10	(5a)	H-	4-Me-	7

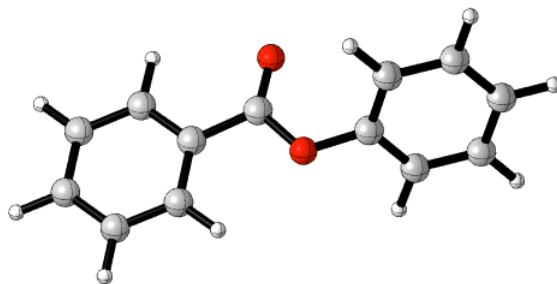
^aConditions: (**Cin-IPr**) (3.0 mol%), Ar-B(OH)₂ (**2a**: 3.0 equiv, **5a**: 4.5 equiv), K₂CO₃ (**2a**: 4.5 equiv, **5a**: 7.2 equiv), THF (0.25 M), 23 °C. All reactions carried out using standard Schlenk techniques under argon. ^bDetermined by ¹H NMR and/or GC-MS.

Computational Methods

Computational Methods. All of the calculations were performed using Gaussian 09 suite of programs. All of the geometry optimizations were performed at the B3LYP/6-311++G(d,p) level of theory in the gas phase. This level has been shown to be accurate in predicting properties and resonance energies of carboxylic acid derivatives (*J. Org. Chem.* **2012**, *77*, 5492, and references cited therein). This method was further verified by obtaining good correlations between the calculated structures and X-ray structures in the series. All conformations within 3 kcal/mol from the lowest energy conformer were explored (*J. Am. Chem. Soc.* **1996**, *118*, 8658). The absence of imaginary frequencies was used to characterize the structures as minima on the potential energy surface. All of the optimized geometries were verified as minima (no imaginary frequencies). Electronic and thermal energies were calculated for all structures. Energetic parameters were calculated under standard conditions (298.15 K and 1 atm). For geometry optimizations, we employed the structure of 4-bromophenyl benzoate as the starting geometry and performed full optimization (*Acta Crystallogr. Sect. E* **2008**, *64*, 771). Barrier to rotation in methyl acetate has been reported (13.0 kcal/mol, *J. Am. Chem. Soc.* **1987**, *109*, 5935). Phenyl benzoate isomerization barrier was determined by ester bond rotation. COSNAR method was used for determination of amide resonance energies (*J. Am. Chem. Soc.* **1996**, *118*, 8658, *J. Org. Chem.* **2016**, *81*, 8091). Optimized amide conformations were used as starting geometries for isodesmic calculations for the aza, keto, and hydrocarbon derivatives. Structural representations were generated using CYLview software (Legault, C. Y. CYLview version 1.0 BETA, University of Sherbrooke). All other representations were generated using GaussView (GaussView, version 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission, KS, 2009).

Full Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Figure SI-1. Optimized Geometry of 5a Referred to from the Main ManuscriptEster 5a (B3LYP/6-311++G(d,p))

Selected bond lengths (Å) and angles (deg): C1-C2-O1-C3 = 179.90; O1-C2-O2-C3 = 0.0; C5-C3-O1-C2 = 65.33; C4-C3-O1-C2 = -118.58; O1-C2, 1.370; C2-O2, 1.204; C1-C2, 1.489; O1-C3, 1.399.

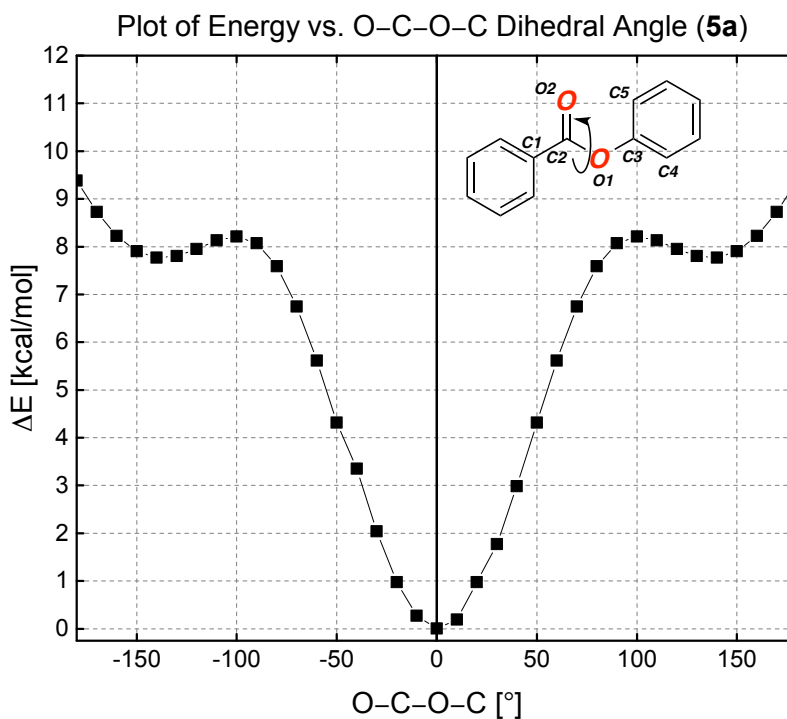
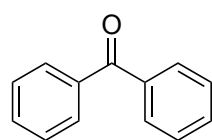
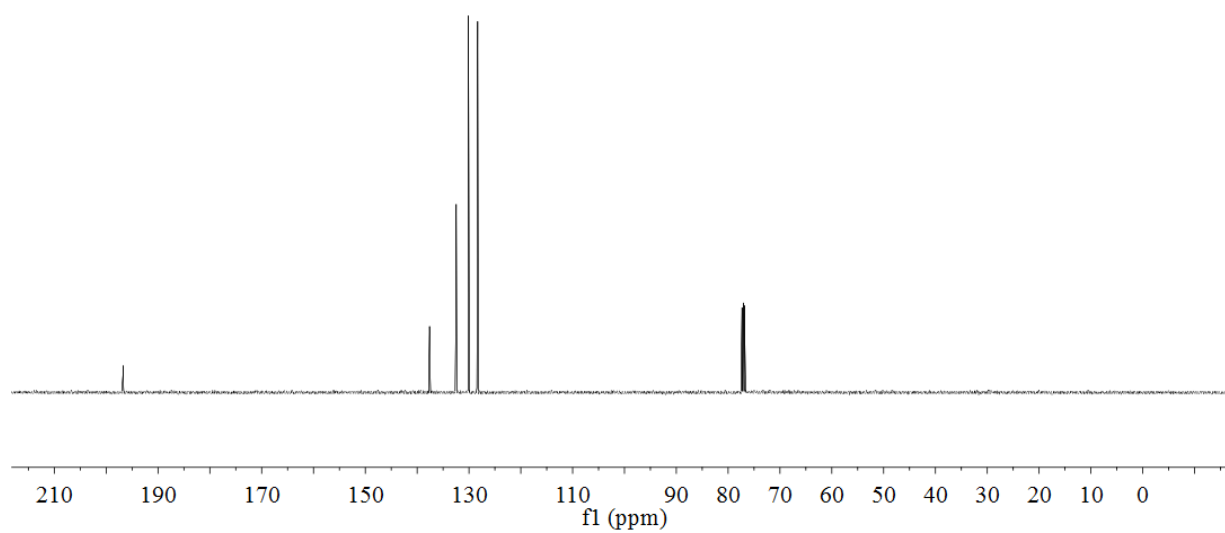
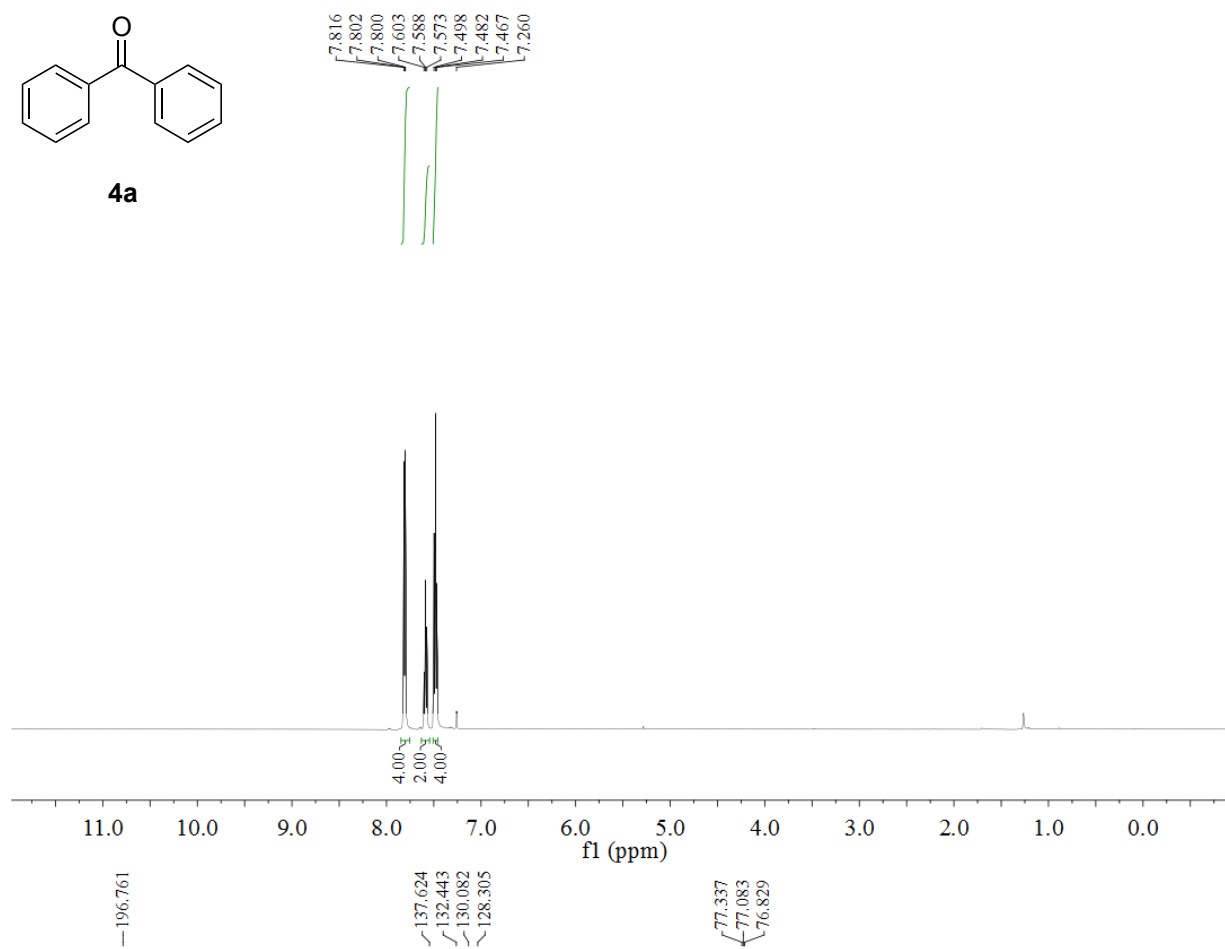
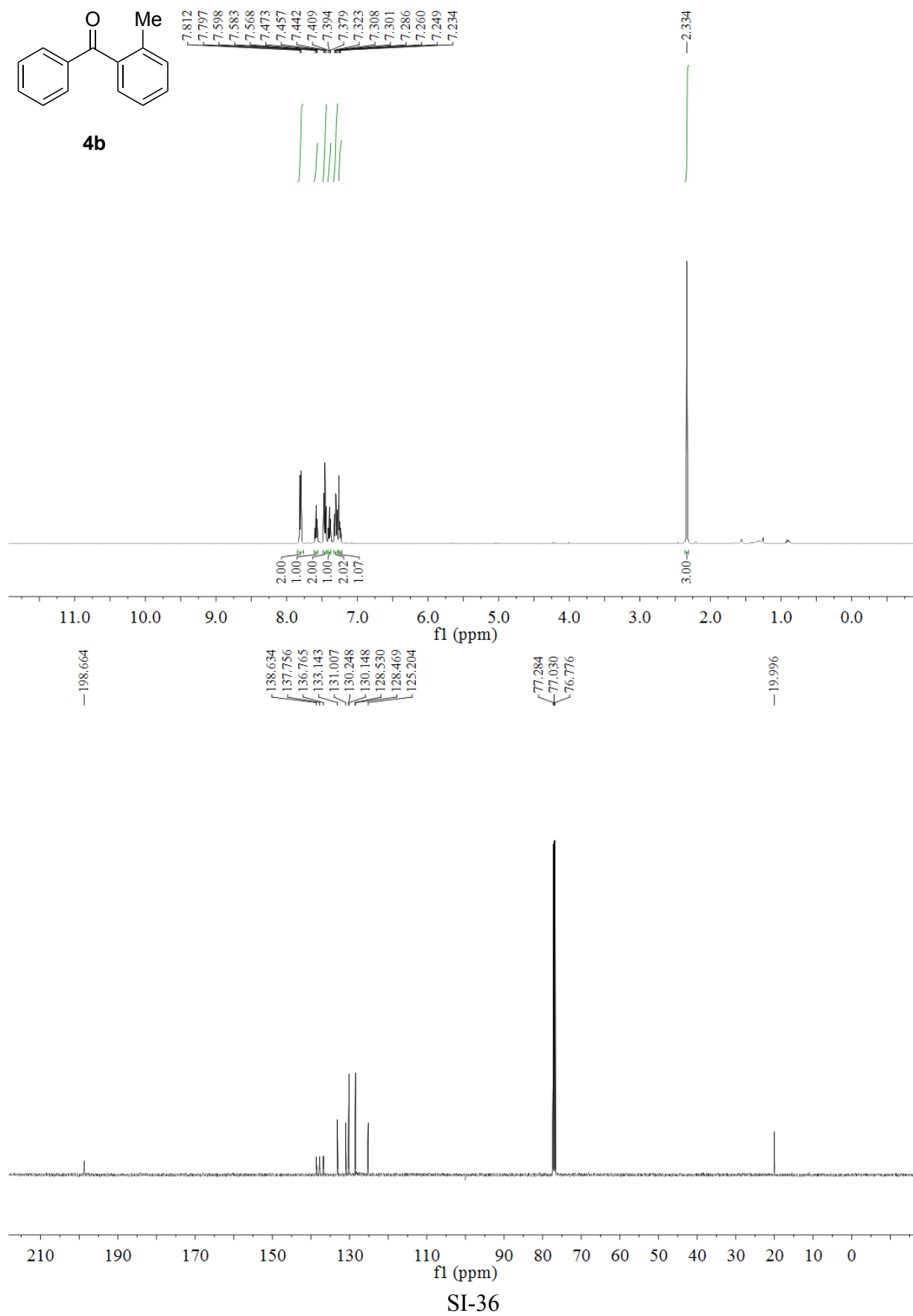
Plot of Rotational Barrier Referred to from the Main ManuscriptRotational profile of ester 5a

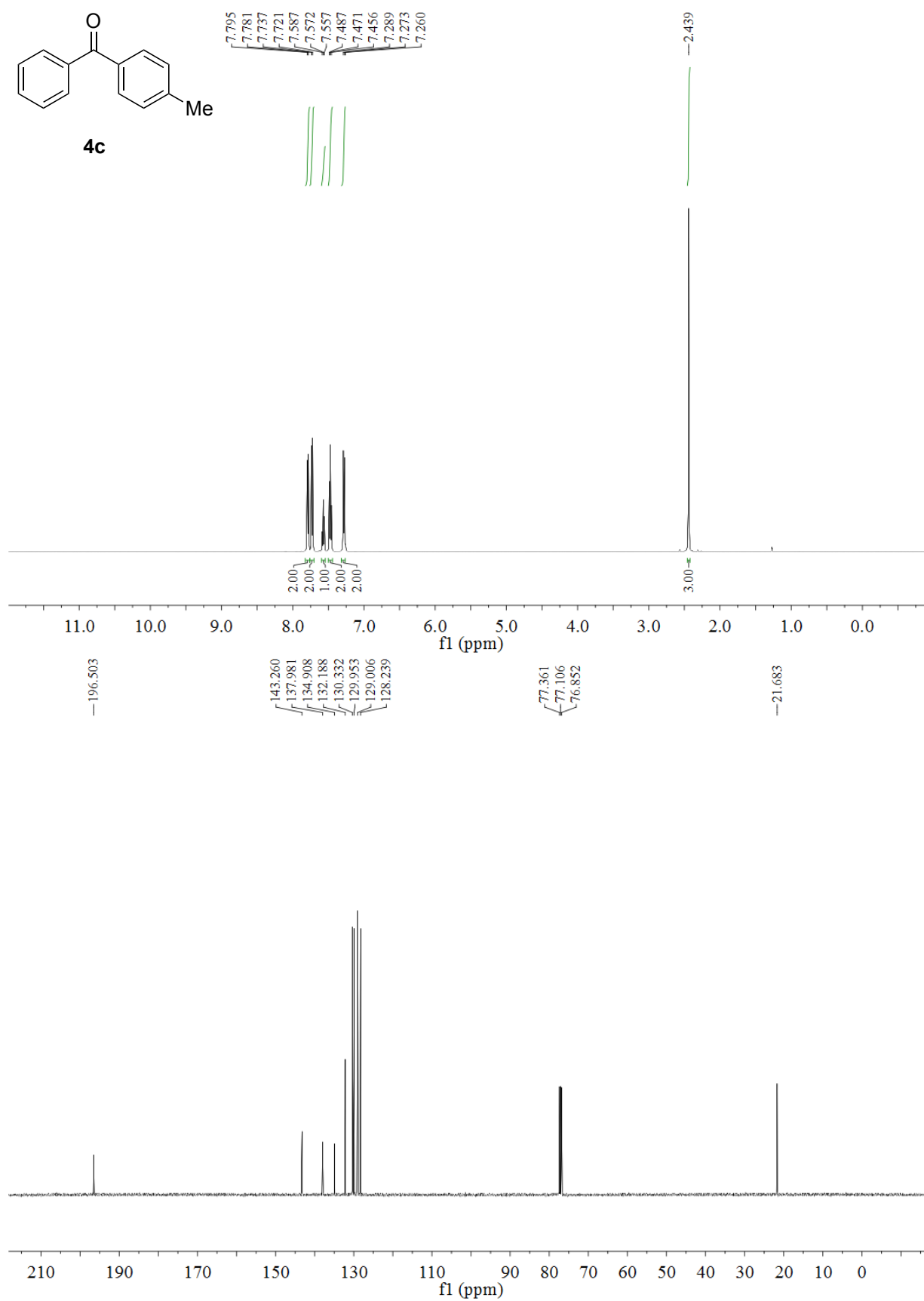
Chart SI-1. Correlation of ΔE [kcal/mol] to O-C-O-C [°] in **5a**. Note that barrier to C-O isomerization in methyl benzoate (12.8 kcal/mol, B3LYP/6-311++G(d,p)) is similar to anilides (12-14 kcal/mol, B3LYP/6-311++G(d,p)).

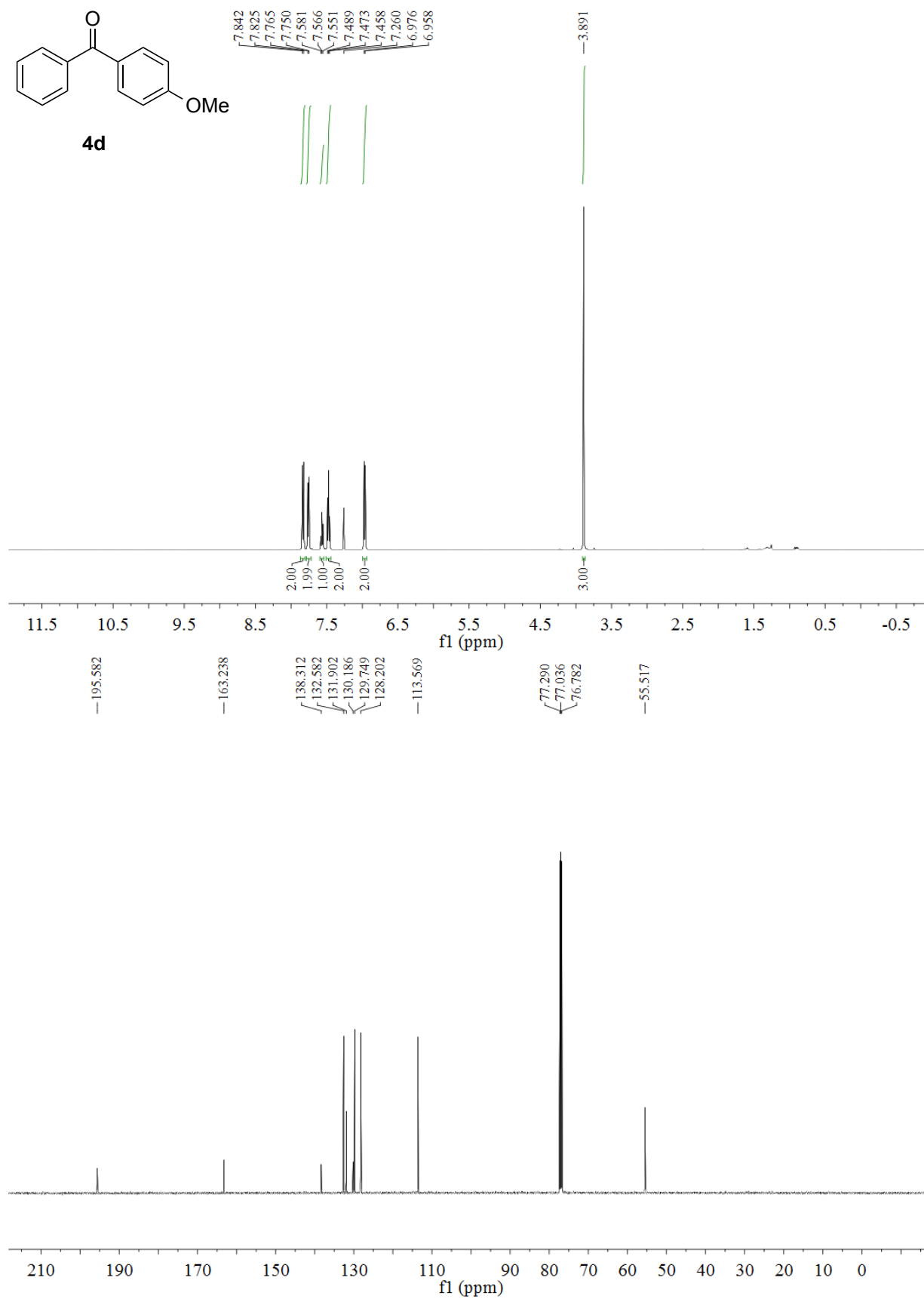
References

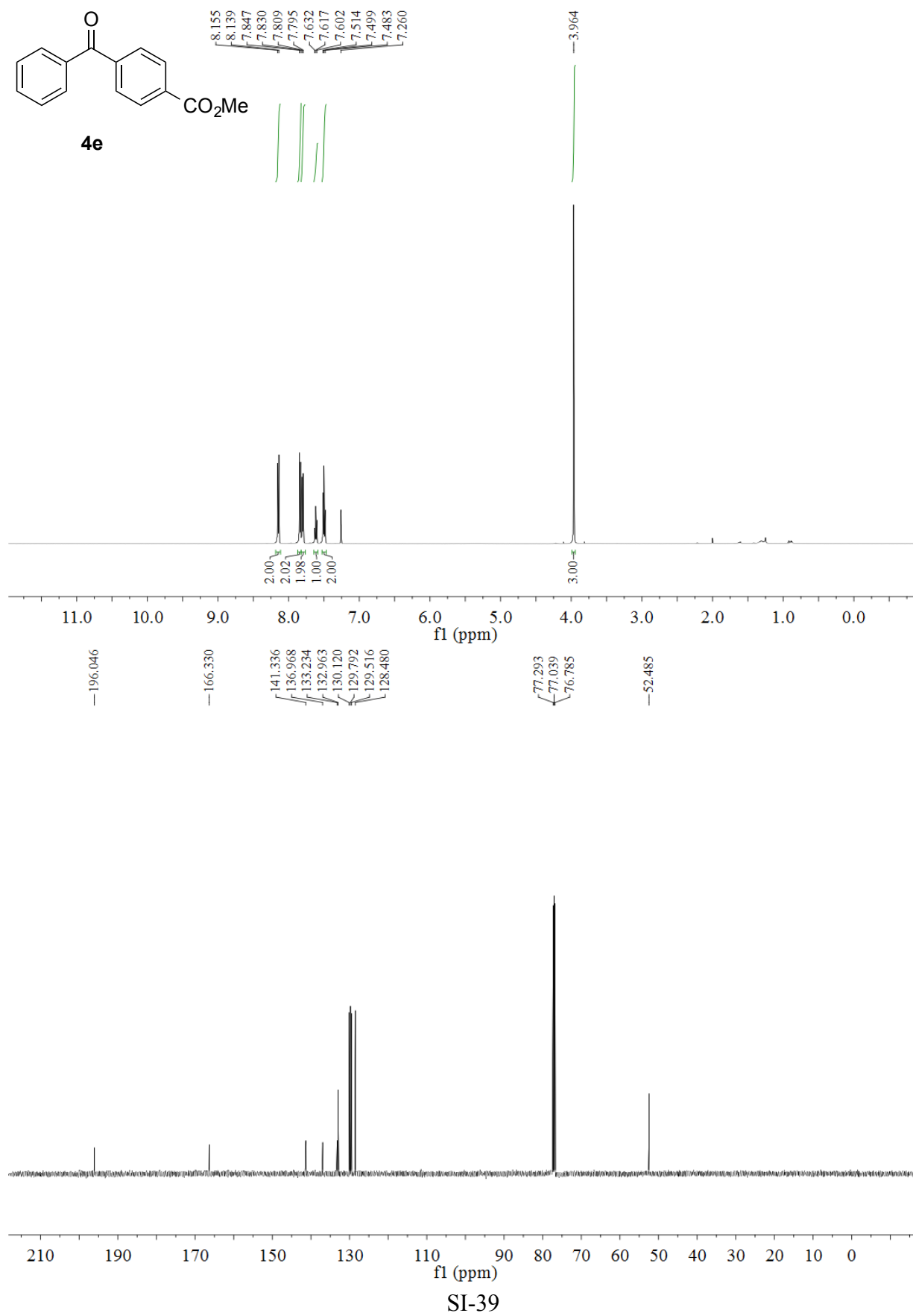
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10. Note that, in general, strong bases such as KO t -Bu are not viable in the coupling of amides and esters catalyzed by Pd-NHC complexes.

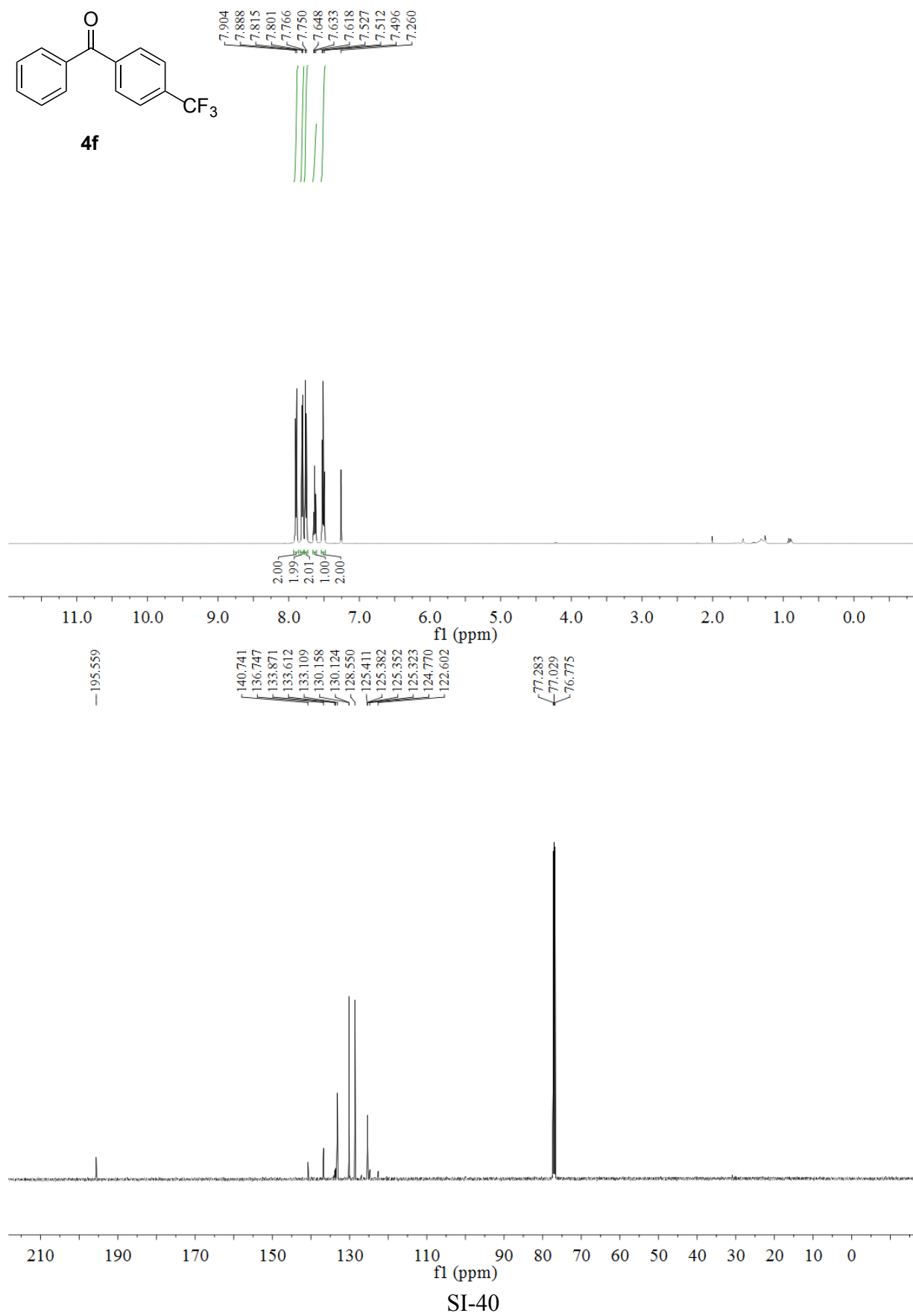
**4a**

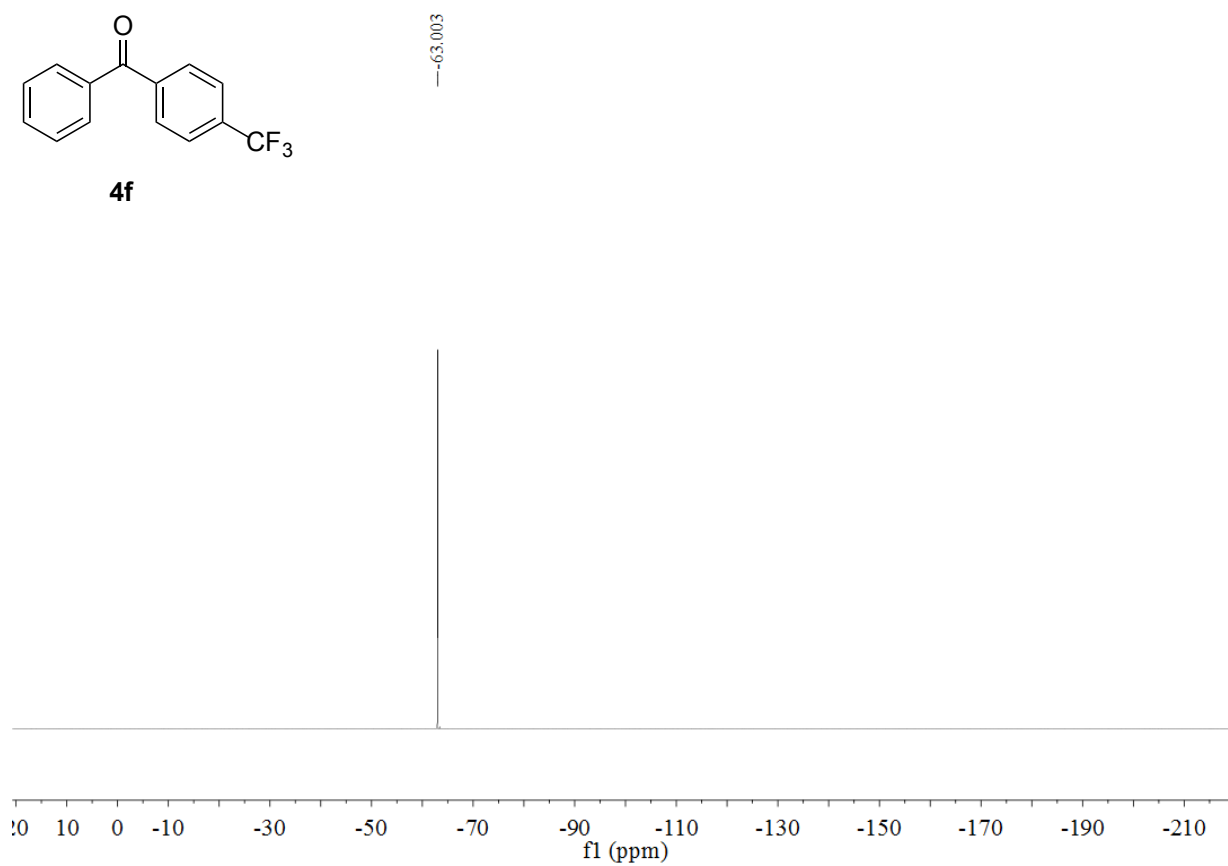


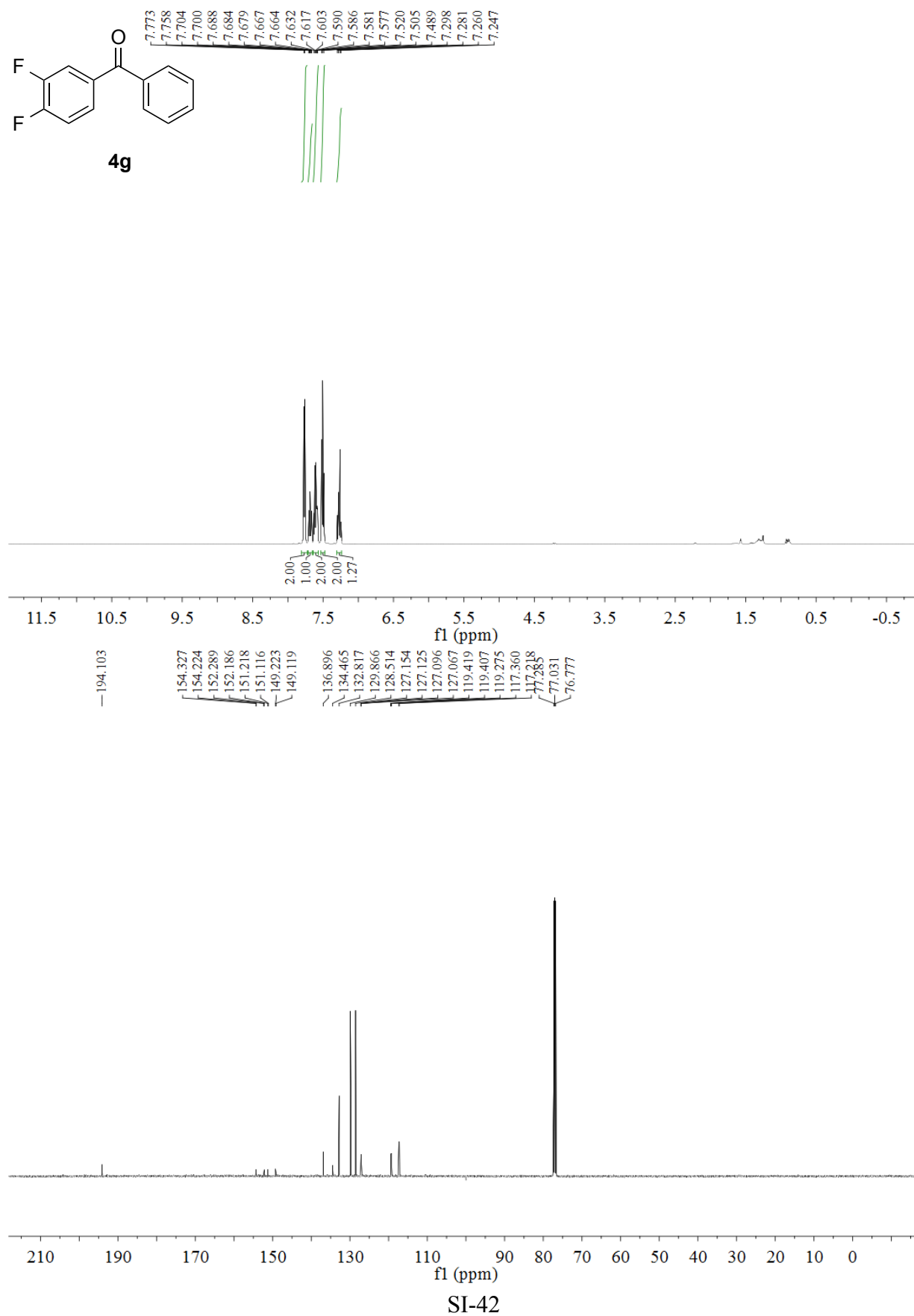


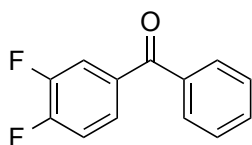












4g

130.549
130.594
136.129
136.173

