Supporting Information

Mechanochemical Synthesis of Ketones via Chemoselective Suzuki–Miyaura Cross-Coupling of Acyl Chlorides

Jin Zhang,[†,*] Pei Zhang,[†] Yangmin Ma,[†] Michal Szostak[‡,*]

[†]College of Chemistry and Chemical Engineering, Key Laboratory of Chemical Additives for China National Light Industry, Shaanxi University of Science and Technology, Xi'an 710021, China
phone: (+ 86)-029-8161-8312 E-mail: zhangjin@sust.edu.cn

[‡]Department of Chemistry, Rutgers University, 73 Warren Street, Newark, NJ 07102, United States
phone: (+ 1)-973-353-5329 E-mail: michal.szostak@rutgers.edu

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1. General Information

All mechanochemical reactions were carried out using grinding vessels in a Retsch MM400 mill. Both bowls (5 mL and 10 mL) and balls are made of stainless. The heat gun DELIXI ELECTRIC with temperature control function was used for high-temperature ball-milling reactions. 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 other chemicals were purchased at the highest commercial grade and used as received. All products were identified using ^{1}H NMR analysis and comparison with authentic samples. All yields refer to yields determined by ^{1}H NMR using an internal standard (optimization) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Ascend spectrometers at 400 (^{1}H NMR) and 100 MHz (^{13}C NMR) or 600 (^{1}H NMR) and 150 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.16 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet. Dibromomethane was used as an internal standard to determine NMR yields. 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.

2. Mechanochemical Set-up

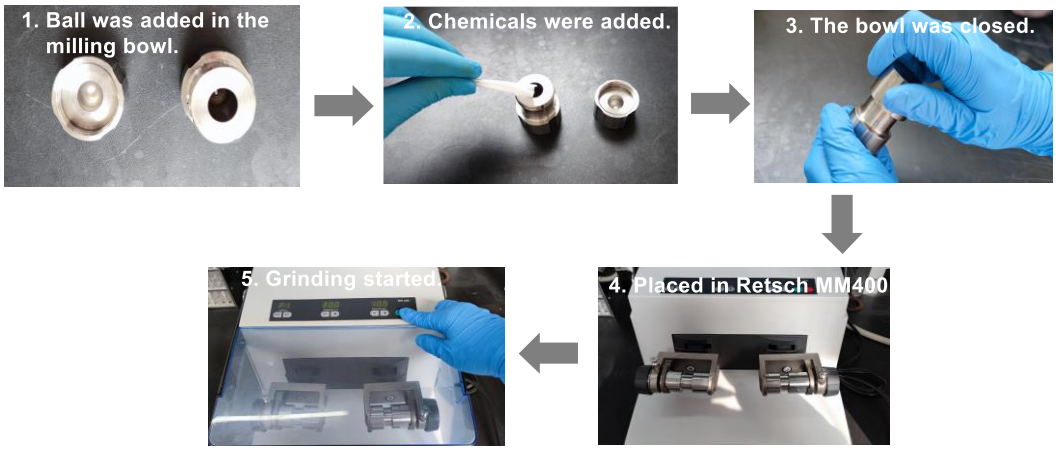


Chart S1. The mechanochemical set-up.

3. Experimental Procedures and Characterization Data

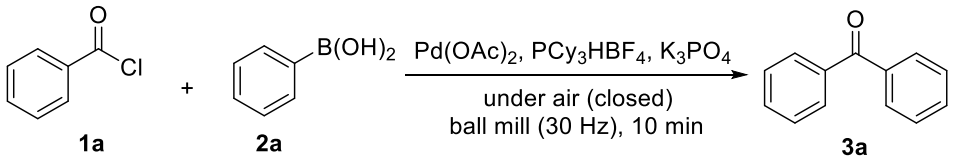
General Procedure for Acyl C(O)–Cl Cleavage Using a Ball Mill. Acyl chlorides (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples. Unless stated otherwise, purification by chromatography on silica gel afforded the title product.

General Procedure for High Temperature Ball Milling. The heat gun was fixed with clamps and placed directly above the ball milling bowl (distance between the heat gun and ball milling bowl: ca. 1 cm). First, one grinding ball (stainless, diameter: 5 mm) was loaded in a ball milling bowl (stainless, 5 mL or 10 mL). Then solid and liquid materials were added to the bowl. After the ball milling bowl was closed, the bowl was placed in the ball mill (Retsch MM400) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C).

Representative Procedure for Acyl C(O)–Cl Cleavage. 1.0 Mmol Scale. 1l (1.0 mmol, 191 mg), **2ac** (1.5 mmol, 318 mg, 1.5 equiv), $Pd(OAc)_2$ (0.05 mmol, 11.2 mg, 5 mol%), PCy_3HBF_4 (0.06 mmol, 22.1 mg, 6 mol%), and K_3PO_4 (1.0 mmol, 212 mg, 1.0 equiv) were placed in a ball milling bowl (stainless, 10 mL) loaded with one grinding ball (stainless, diameter: 9 mm). the bowl was placed in the ball mill (Retsch MM400, 30 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). After 30 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. Purification by chromatography on silica gel afforded the title product. Yield 61% (196.7 mg). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.01-7.88 (m, 4H), 7.59 (dt, J = 21.6, 7.1 Hz, 2H), 3.97 (s, 3H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) 195.8, 152.9, 142.0, 135.2, 135.1, 132.9, 132.3, 131.5, 129.4, 128.3, 128.3, 127.9, 126.9, 125.9, 107.8, 61.0, 56.4. This compound showed identical spectroscopic properties to those reported previously.[1]

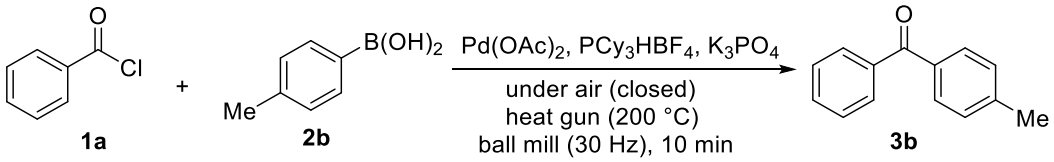
Cross-Coupling of Acyl Chlorides: Variation of Boronic Acids

Benzophenone (Scheme 1, **3a**)



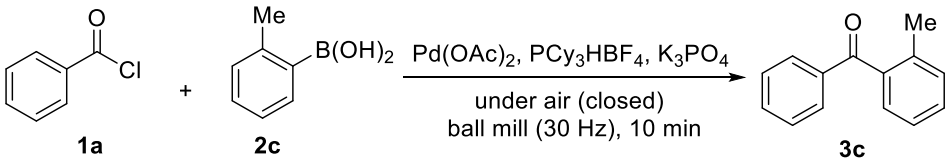
According to the general procedure, Benzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 92% yield (33.5 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.6, 132.4, 130.1, 128.3. This compound showed identical spectroscopic properties to those reported previously.[1-4]

Phenyl(*p*-tolyl)methanone (Scheme 1, **3b**)



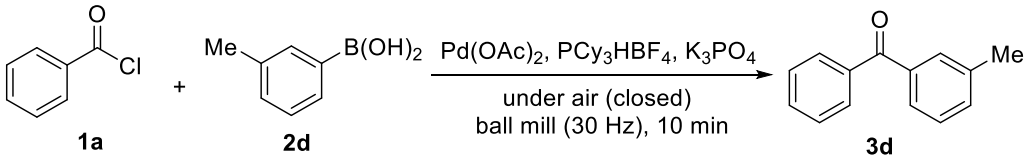
According to the general procedure, Benzoyl chloride (0.2 mmol), *p*-Tolylboronic Acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 82% yield (32.2 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 143.3, 138.0, 134.9, 132.2, 130.4, 130.0, 129.0, 128.3, 21.7. This compound showed identical spectroscopic properties to those reported previously.[5]

Phenyl(*o*-tolyl)methanone (Scheme 1, **3c**)



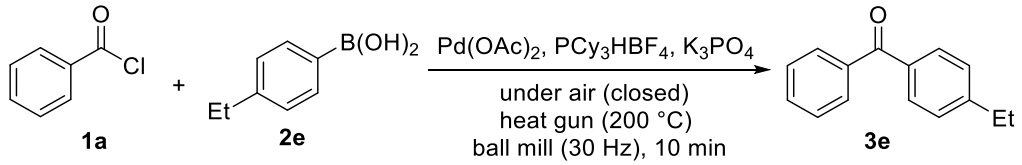
According to the general procedure, Benzoyl chloride (0.2 mmol), *o*-Tolylboronic Acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 90% yield (35.3 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.26 (dt, *J* = 21.9, 8.0 Hz, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 138.6, 137.7, 136.8, 133.2, 131.0, 130.3, 130.2, 128.5, 128.5, 125.2, 20.0. This compound showed identical spectroscopic properties to those reported previously.[6]

Phenyl(*m*-tolyl)methanone (Scheme 1, **3d**)



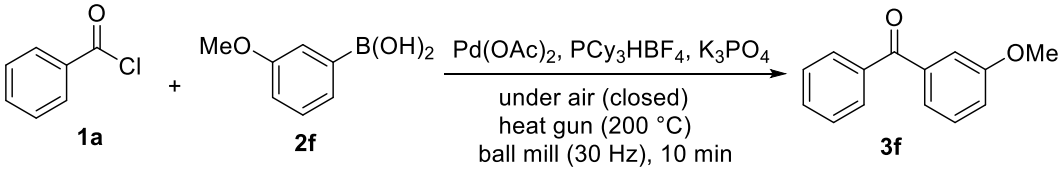
According to the general procedure, Benzoyl chloride (0.2 mmol), *m*-Tolylboronic Acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 80% yield (31.4 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.63 (s, 1H), 7.58 (d, *J* = 6.6 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.42-7.31 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 138.2, 137.8, 137.6, 133.2, 132.4, 130.5, 130.1, 128.3, 128.1, 127.4, 21.4. This compound showed identical spectroscopic properties to those reported previously.[7]

(4-Ethylphenyl)(phenyl)methanone (Scheme 1, **3e**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (*p*-Ethylphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 92% yield (38.7 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.27 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 149.4, 138.0, 135.1, 132.2, 130.4, 130.0, 128.2, 127.8, 29.0, 15.3. This compound showed identical spectroscopic properties to those reported previously.[8]

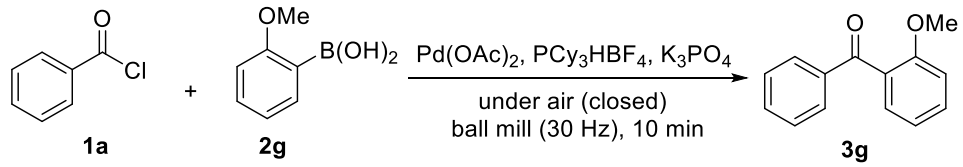
(3-Methoxyphenyl)(phenyl)methanone (Scheme 1, **3f**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (3-Methoxyphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 83% yield (35.2 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.36 (p, *J* = 7.5 Hz, 3H), 7.13 (d, *J* = 8.9 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 159.6, 138.9, 137.6, 132.4, 130.1, 129.2, 128.3, 122.9, 118.9, 114.3, 55.5. This compound showed identical spectroscopic properties to those reported

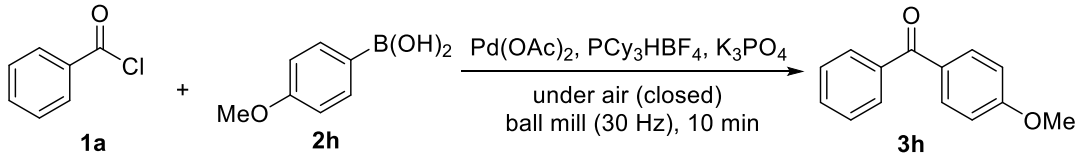
previously.[9]

(2-Methoxyphenyl)(phenyl)methanone (Scheme 1, **3g**)



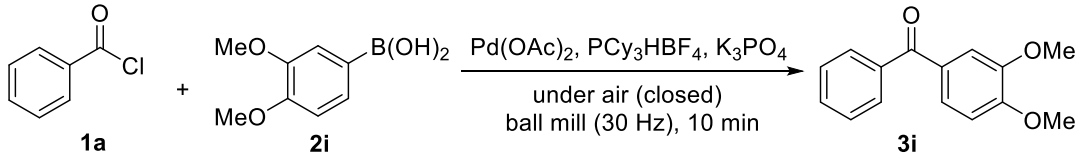
According to the general procedure, Benzoyl chloride (0.2 mmol), (*o*-Methoxyphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 78% yield (33.1 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (dt, *J* = 25.3, 8.4 Hz, 3H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.06-6.97 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 157.4, 137.8, 132.9, 131.9, 129.8, 129.6, 128.9, 128.2, 120.5, 111.5, 55.6. This compound showed identical spectroscopic properties to those reported previously.[9]

(4-Methoxyphenyl)(phenyl)methanone (Scheme 1, **3h**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (*p*-Methoxyphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 81% yield (34.4 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 163.3, 138.4, 132.5, 131.8, 130.3, 129.7, 128.2, 113.6, 55.5. This compound showed identical spectroscopic properties to those reported previously.[9]

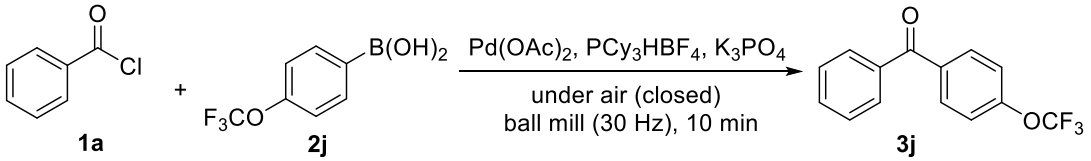
(3,4-Dimethoxyphenyl)(phenyl)methanone (Scheme 1, **3i**)



1a **2i** **3i**

According to the general procedure, Benzoyl chloride (0.2 mmol), (3,4-Dimethoxyphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 75% yield (36.3 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 14.1, 6.5 Hz, 3H), 7.39 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.6, 153.0, 149.0, 138.3, 131.9, 130.2, 129.7, 128.2, 125.5, 112.7, 109.7, 56.1, 56.1. This compound showed identical spectroscopic properties to those reported previously.[9]

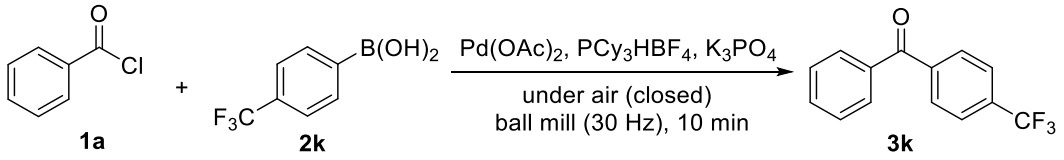
Phenyl(4-(trifluoromethoxy)phenyl)methanone (Scheme 1, **3j**)



1a **2j** **3j**

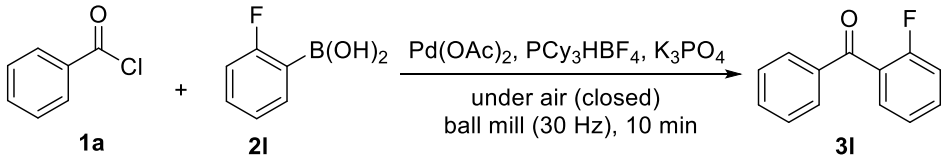
According to the general procedure, Benzoyl chloride (0.2 mmol), (4-(Trifluoromethoxy)phenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 77% yield (41.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 137.1, 135.9, 132.8, 132.0, 130.0, 128.5, 121.6, 120.2, 119.1. ^{19}F (376 MHz, $CDCl_3$) δ -57.5. This compound showed identical spectroscopic properties to those reported previously.[10]

Phenyl(4-(trifluoromethyl)phenyl)methanone (Scheme 1, **3k**)



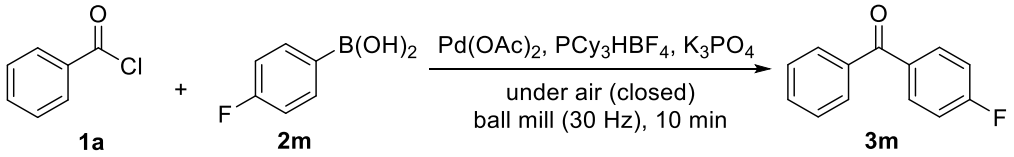
According to the general procedure, Benzoyl chloride (0.2 mmol), (4-(Trifluoromethyl)phenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 68% yield (34.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.87 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 140.7, 136.7, 133.9, 133.6, 133.1, 130.2 (d, *J* = 3.5 Hz), 128.5, 125.4 (q, *J* = 20.0 Hz), 122.3. ^{19}F (376 MHz, $CDCl_3$) δ -63.0. This compound showed identical spectroscopic properties to those reported previously.[11]

(2-Fluorophenyl)(phenyl)methanone (Scheme 1, **3l**)



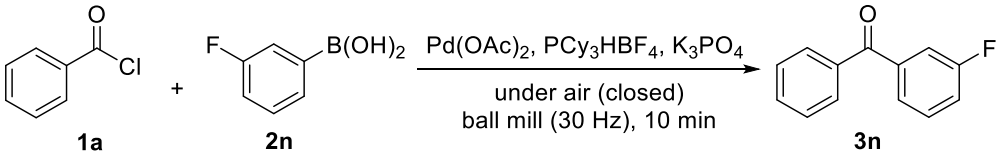
According to the general procedure, Benzoyl chloride (0.2 mmol), (2-Fluorophenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 80% yield (32.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (q, *J* = 6.6, 6.1 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.29-7.24 (m, 1H), 7.19-7.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 160.1 (d, *J* = 260.0 Hz), 137.4, 133.4, 133.1 (d, *J* = 10.0 Hz), 130.8, 129.8, 128.5, 127.1 (d, *J* = 10.0 Hz), 124.3, 116.3 (d, *J* = 20.0 Hz). ^{19}F (376 MHz, $CDCl_3$) δ -111.0. This compound showed identical spectroscopic properties to those reported previously.[11]

(4-Fluorophenyl)(phenyl)methanone (Scheme 1, **3m**)



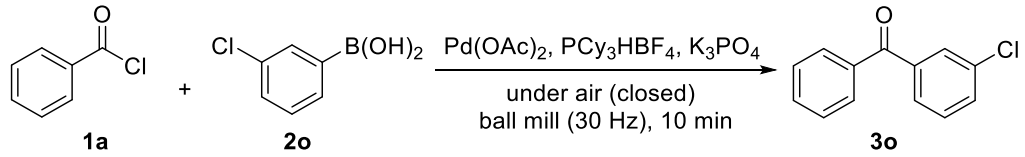
According to the general procedure, Benzoyl chloride (0.2 mmol), (4-Fluorophenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 83% yield (33.2 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.77 (d, *J* = 7.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 165.4 (d, *J* = 260.0 Hz), 137.5, 133.8 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 10.0 Hz), 132.5, 129.9, 128.4, 115.5 (d, *J* = 20.0 Hz). ^{19}F (376 MHz, $CDCl_3$) δ -105.9. This compound showed identical spectroscopic properties to those reported previously.[12]

(3-Fluorophenyl)(phenyl)methanone (Scheme 1, **3n**)



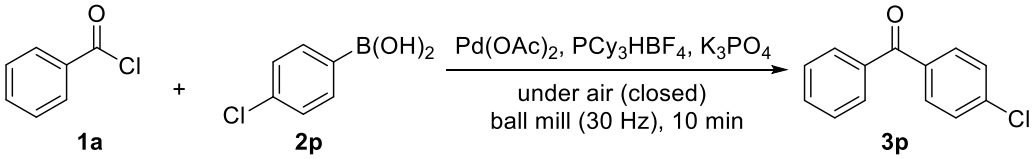
According to the general procedure, Benzoyl chloride (0.2 mmol), (3-Fluorophenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 82% yield (32.8 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.77 (m, 2H), 7.64-7.54 (m, 2H), 7.50 (t, *J* = 7.9 Hz, 4H), 7.29 (t, *J* = 9.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 162.5 (d, *J* = 240.0 Hz), 139.7 (d, *J* = 10.0 Hz), 137.0, 132.8, 130.0, 129.9, 128.4, 125.8 (d, *J* = 2.0 Hz), 119.4 (d, *J* = 20.0 Hz), 116.8 (d, *J* = 30.0 Hz). ^{19}F (376 MHz, $CDCl_3$) δ -111.9. This compound showed identical spectroscopic properties to those reported previously.[13]

(3-Chlorophenyl)(phenyl)methanone (Scheme 1, **3o**)



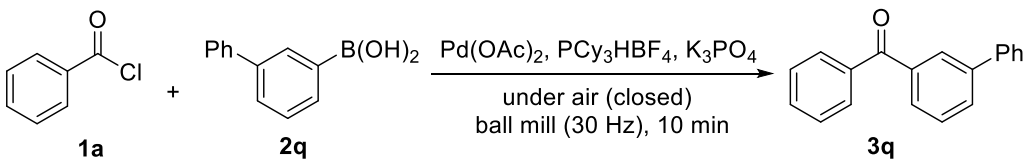
According to the general procedure, Benzoyl chloride (0.2 mmol), (3-Chlorophenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 77% yield (33.4 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 3H), 7.67 (d, J = 7.7 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 139.3, 136.9, 134.6, 132.9, 132.4, 130.0, 129.9, 129.6, 128.5, 128.1. This compound showed identical spectroscopic properties to those reported previously.[13]

(4-Chlorophenyl)(phenyl)methanone (Scheme 1, **3p**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (4-Chlorophenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 80% yield (34.7 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (t, J = 7.0 Hz, 4H), 7.59 (t, J = 7.0 Hz, 1H), 7.52-7.42 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.5, 138.9, 137.2, 135.9, 132.6, 131.5, 129.9, 128.6, 128.4. This compound showed identical spectroscopic properties to those reported previously.[14]

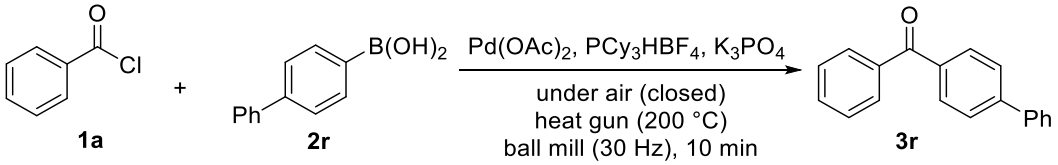
Phenyl(*m*-tolyl) methanone (Scheme 1, **3q**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (3-Biphenyl)boronic acid

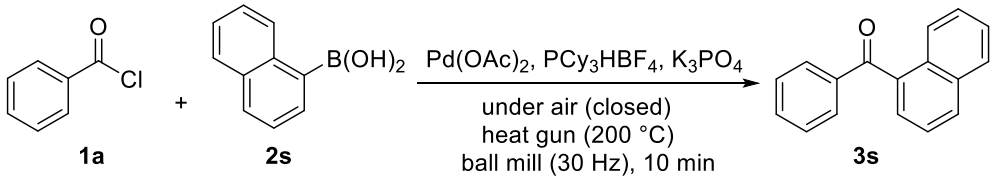
(typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 71% yield (36.7 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.88-7.77 (m, 4H), 7.60 (dd, *J* = 20.7, 7.5 Hz, 4H), 7.49 (dt, *J* = 15.9, 7.8 Hz, 4H), 7.39 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 141.4, 140.2, 138.2, 137.6, 132.6, 131.1, 130.2, 129.0, 128.8, 128.7, 128.4, 127.8, 127.3. This compound showed identical spectroscopic properties to those reported previously.[15]

Phenyl(*p*-tolyl) methanone (Scheme 1, **3r**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (4-Biphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 71% yield (36.7 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.66 (td, *J* = 23.9, 22.8, 7.6 Hz, 5H), 7.55-7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 145.3, 140.0, 137.8, 136.3, 132.4, 130.8, 130.1, 129.0, 128.4, 128.2, 127.4, 127.0. This compound showed identical spectroscopic properties to those reported previously.[11]

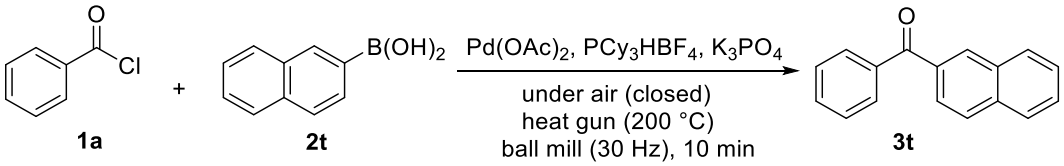
Naphthalen-1-yl(phenyl)methanone (Scheme 1, **3s**)



According to the general procedure, Benzoyl chloride (0.2 mmol), Naphthalen-1-ylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and

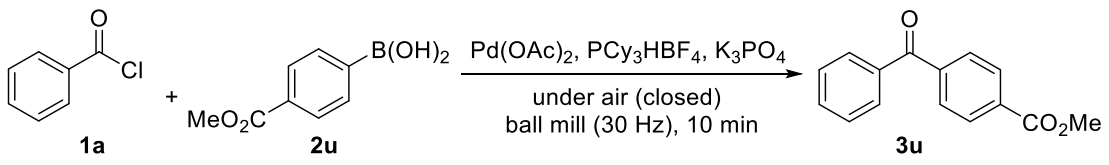
K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 72% yield (33.4 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.86-7.83 (m, 2H), 7.58-7.53 (m, 2H), 7.51-7.45 (m, 3H), 7.41 (t, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.0, 138.4, 136.4, 133.8, 133.3, 131.3, 131.0, 130.4, 128.5, 128.5, 127.8, 127.3, 126.5, 125.7, 124.4. This compound showed identical spectroscopic properties to those reported previously.[7]

Naphthalen-2-yl(phenyl)methanone (Scheme 1, **3t**)



According to the general procedure, Benzoyl chloride (0.2 mmol), Naphthalen-2-ylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 70% yield (32.5 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.95 (s, 2H), 7.93 (d, J = 3.6 Hz, 1H), 7.91 (d, J = 3.8 Hz, 1H), 7.88-7.85 (m, 2H), 7.64-7.60 (m, 2H), 7.57-7.51 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.8, 137.9, 135.3, 134.8, 132.4, 132.3, 131.9, 130.1, 129.4, 128.3, 128.3, 128.3, 127.8, 126.8, 125.8. This compound showed identical spectroscopic properties to those reported previously.[7]

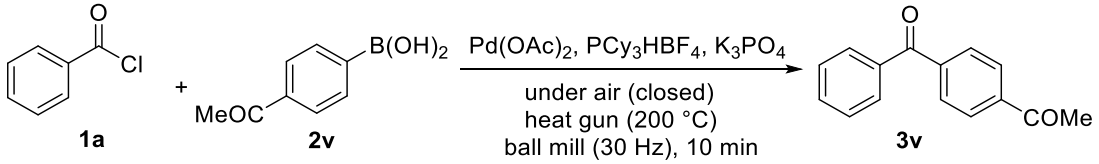
Methyl 4-benzoylbenzoate (Scheme 1, **3u**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (4-

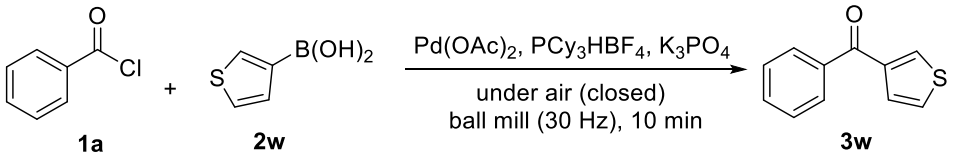
(Methoxycarbonyl)phenyl)boronic Acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 55% yield (26.4 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 166.3, 141.3, 136.9, 133.2, 133.0, 130.0, 129.8, 129.5, 128.5, 52.5. This compound showed identical spectroscopic properties to those reported previously.[16]

1-(4-Benzoylphenyl)ethan-1-one (Scheme 1, **3v**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (4-Acetylphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 70% yield (31.4 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 196.0, 141.3, 139.6, 136.9, 133.0, 130.1, 130.1, 128.5, 128.2, 26.9. This compound showed identical spectroscopic properties to those reported previously.[17]

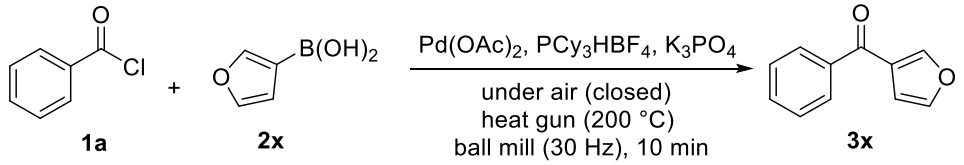
Phenyl(thiophen-3-yl)methanone (Scheme 1, **3w**)



According to the general procedure, Benzoyl chloride (0.2 mmol), 3-Thienylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and

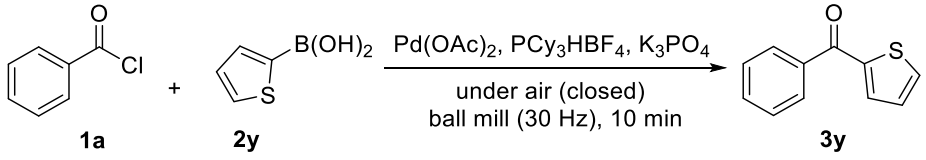
K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 75% yield (28.2 mg). Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.8 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.59 (dd, *J* = 10.1, 6.1 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 5.0, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 141.3, 138.6, 134.0, 132.3, 129.4, 128.6, 128.4, 126.2. This compound showed identical spectroscopic properties to those reported previously.[17]

Furan-3-yl(phenyl)methanone (Scheme 1, **3x**)



According to the general procedure, Benzoyl chloride (0.2 mmol), Furan-3-ylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 70% yield (24.1 mg). Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.53-7.45 (m, 3H), 6.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 148.6, 144.0, 138.8, 132.5, 18.8, 128.6, 126.5, 110.2. This compound showed identical spectroscopic properties to those reported previously.[18]

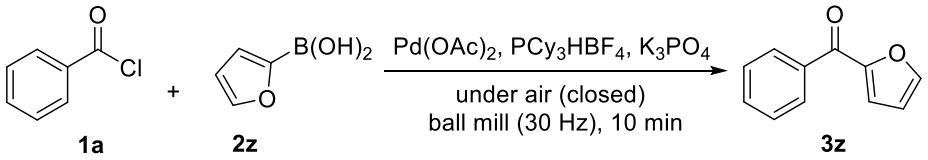
Phenyl(thiophen-2-yl)methanone (Scheme 1, **3y**)



According to the general procedure, Benzoyl chloride (0.2 mmol), 2-Thienylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch

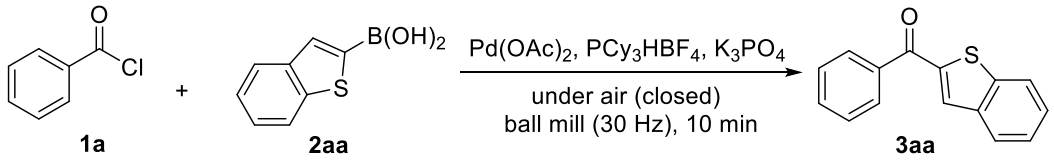
MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 90% yield (33.9 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.0 Hz, 2H), 7.72 (s, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 6.3 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.16 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 143.6, 138.1, 134.9, 134.3, 132.3, 129.2, 128.4, 128.0. This compound showed identical spectroscopic properties to those reported previously.[6]

Furan-2-yl(phenyl)methanone (Scheme 1, **3z**)



According to the general procedure, Benzoyl chloride (0.2 mmol), Furan-2-ylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 77% yield (26.5 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.4 Hz, 2H), 7.71 (s, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.60 (dd, J = 3.2, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ182.7, 152.2, 147.2, 137.3, 132.6, 129.3, 128.5, 120.7, 112.3. This compound showed identical spectroscopic properties to those reported previously.[19]

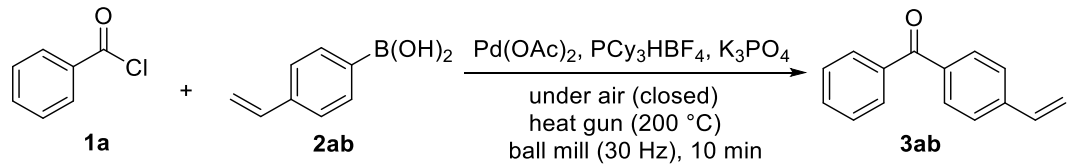
Benzo[*b*]thiophen-2-yl(phenyl)methanone (Scheme 1, **3aa**)



According to the general procedure, Benzoyl chloride (0.2 mmol), 1-Benzothiophen-2-ylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 85% yield (40.5 mg). Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.85 (m, 5H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 143.1, 142.7, 139.1, 137.9, 132.5, 132.3, 129.3,

128.6, 127.5, 126.1, 125.1, 123.0. This compound showed identical spectroscopic properties to those reported previously.[20]

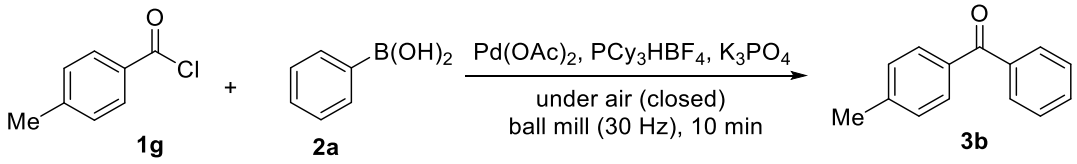
(4-Ethenylphenyl)phenylmethanone (Scheme 1, **3ab**)



According to the general procedure, Benzoyl chloride (0.2 mmol), (4-Ethenylphenyl)boronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 67% yield (27.9 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 4H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.54-7.45 (m, 4H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.89 (d, *J* = 17.6 Hz, 1H), 5.41 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 141.6, 137.8, 136.7, 136.0, 132.3, 130.5, 129.9, 128.3, 126.0, 116.5. This compound showed identical spectroscopic properties to those reported previously.[21]

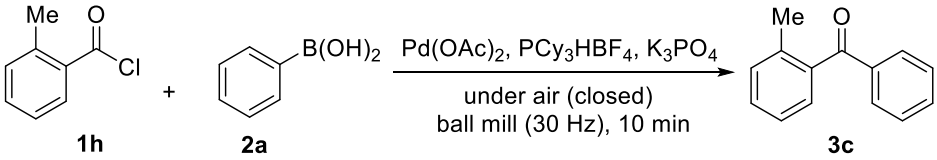
Cross-Coupling of Acyl Chlorides: Variation of Acyl Chlorides

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



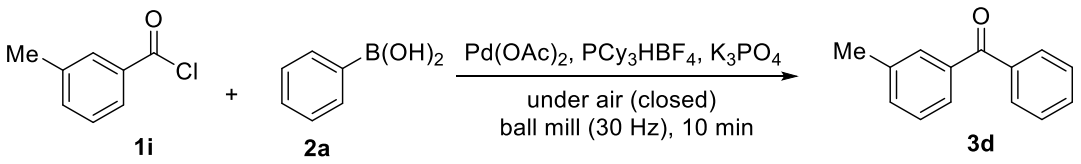
According to the general procedure, *p*-Toluoyl Chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 85% yield (33.4 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 143.3, 138.0, 134.9, 132.2, 130.4, 130.0, 129.0, 128.3, 21.7. This compound showed identical spectroscopic properties to those reported previously.[5]

Phenyl(*o*-tolyl)methanone (Scheme 2, **3c**)



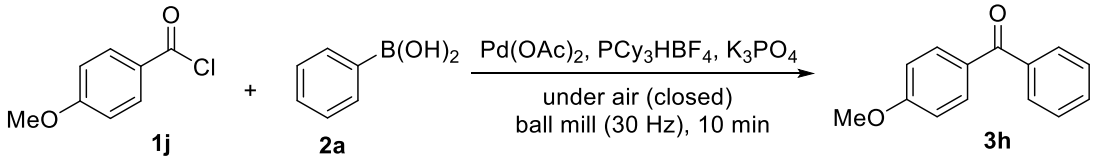
According to the general procedure, *o*-Toluoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 55% yield (21.6 mg). White solid. White solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.26 (dt, *J* = 21.9, 8.0 Hz, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 138.6, 137.7, 136.8, 133.2, 131.0, 130.3, 130.2, 128.5, 128.5, 125.2, 20.0. This compound showed identical spectroscopic properties to those reported previously.[6]

Phenyl(*m*-tolyl)methanone (Scheme 2, **3d**)



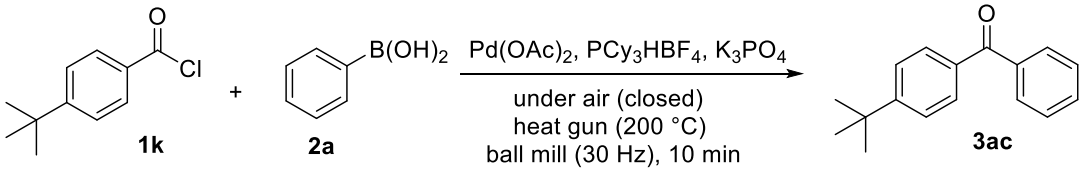
According to the general procedure, *m*-Toluoyl Chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), Pcy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). Afforded after work-up and chromatography the title compound in 83% yield (32.6 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.63 (s, 1H), 7.58 (d, *J* = 6.6 Hz, 2 H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.42-7.31 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 138.2, 137.8, 137.6, 133.2, 132.4, 130.5, 130.1, 128.3, 128.1, 127.4, 21.4. This compound showed identical spectroscopic properties to those reported previously.[7]

(4-Methoxyphenyl)(phenyl)methanone (Scheme 2, **3h**)



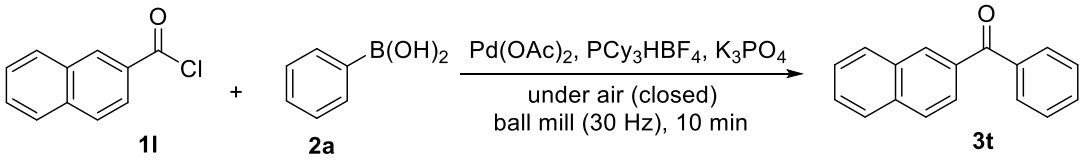
According to the general procedure, *p*-Anisoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(Oac)_2$ (typically, 5 mol%), Pcy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). Afforded after work-up and chromatography the title compound in 76% yield (32.3 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 163.3, 138.4, 132.5, 131.8, 130.3, 129.7, 128.2, 113.6, 55.5. This compound showed identical spectroscopic properties to those reported previously.[9]

4-*tert*-Butylbenzophenone (Scheme 2, **3ac**)



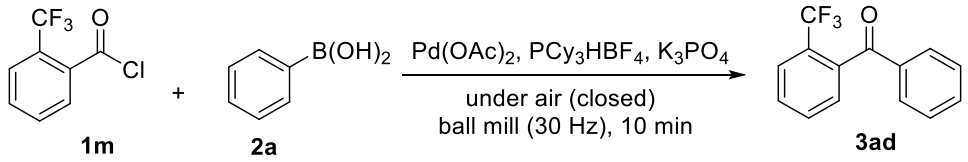
According to the general procedure, 4-tert-Butylbenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 76% yield (36.2 mg). Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.1 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 7.4 Hz, 1H), 7.52-7.45 (m, 4H), 1.37 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 156.2, 137.9, 134.8, 132.2, 130.2, 130.0, 128.2, 125.3, 35.1, 31.2. This compound showed identical spectroscopic properties to those reported previously.[22]

Naphthalen-2-yl(phenyl)methanone (Scheme 2, **3t**)



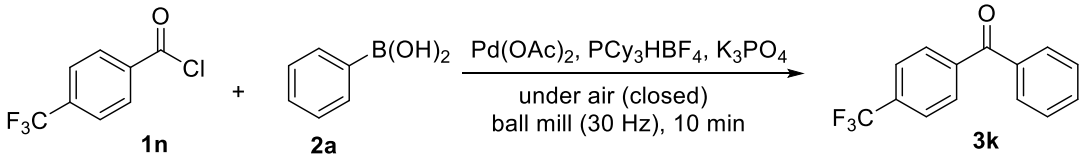
According to the general procedure, 2-Naphthoyl Chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 70% yield (32.5 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.95 (s, 2H), 7.93 (d, J = 3.6 Hz, 1H), 7.91 (d, J = 3.8 Hz, 1H), 7.88-7.85 (m, 2H), 7.64-7.60 (m, 2H), 7.57-7.51 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.8, 137.9, 135.3, 134.8, 132.4, 132.3, 131.9, 130.1, 129.4, 128.3, 128.3, 128.3, 127.8, 126.8, 125.8. This compound showed identical spectroscopic properties to those reported previously.[7]

Phenyl(2-(trifluoromethyl)phenyl)methanone (Scheme 2, **3ad**)



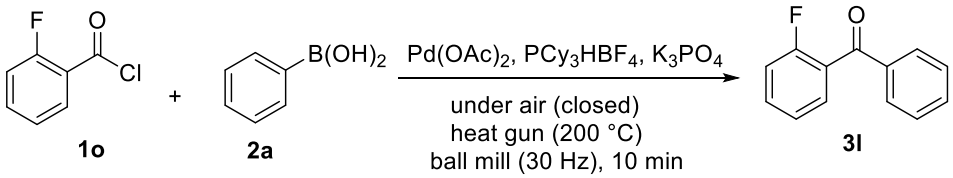
According to the general procedure, 2-(Trifluoromethyl)benzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 85% yield (42.5 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 3H), 7.61 (dt, *J* = 10.6, 5.8 Hz, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.41-7.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 138.3, 136.4, 133.9, 131.4, 130.2, 129.8, 128.5, 128.1, 126.7 (q, *J* = 10.0 Hz), 125.0, 122.2. ^{19}F (376 MHz, $CDCl_3$) δ -58.0. This compound showed identical spectroscopic properties to those reported previously.[23]

Phenyl(4-(trifluoromethyl)phenyl)methanone (Scheme 2, **3k**)



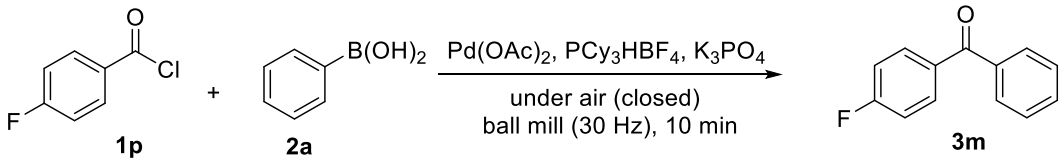
According to the general procedure, 4-(Trifluoromethyl)benzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 83% yield (41.5 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.87 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 140.7, 136.7, 133.9, 133.6, 133.1, 130.2 (d, *J* = 3.5 Hz), 128.5, 125.4 (q, *J* = 20.0 Hz), 122.3. ^{19}F (376 MHz, $CDCl_3$) δ -63.0. This compound showed identical spectroscopic properties to those reported previously.[11]

(2-Fluorophenyl)(phenyl)methanone (Scheme 2, **3l**)



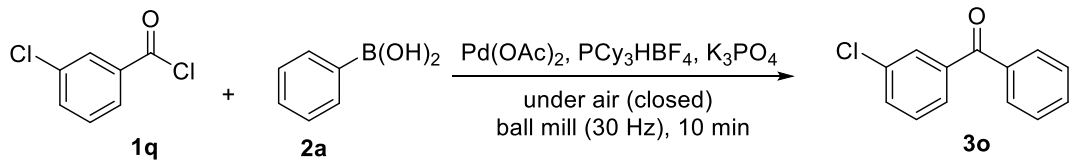
According to the general procedure, 2-Fluorobenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 67% yield (26.8 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (q, *J* = 6.6, 6.1 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.29-7.24 (m, 1H), 7.19-7.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 160.1 (d, *J* = 260.0 Hz), 137.4, 133.4, 133.1 (d, *J* = 10.0 Hz), 130.8, 129.8, 128.5, 127.1 (d, *J* = 10.0 Hz), 124.3, 116.3 (d, *J* = 20.0 Hz). ^{19}F (376 MHz, $CDCl_3$) δ -111.0. This compound showed identical spectroscopic properties to those reported previously.[11]

(4-Fluorophenyl)(phenyl)methanone (Scheme 2, **3m**)



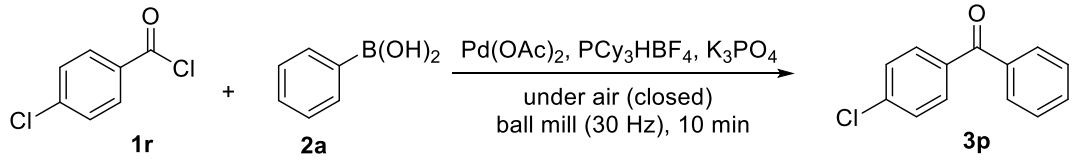
According to the general procedure, 4-Fluorobenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 90% yield (36.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.77 (d, *J* = 7.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 165.4 (d, *J* = 260.0 Hz), 137.5, 133.8 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 10.0 Hz), 132.5, 129.9, 128.4, 115.5 (d, *J* = 20.0 Hz). ^{19}F (376 MHz, $CDCl_3$) δ -105.9. This compound showed identical spectroscopic properties to those reported previously.[12]

(3-Chlorophenyl)(phenyl)methanone (Scheme 2, **3o**)



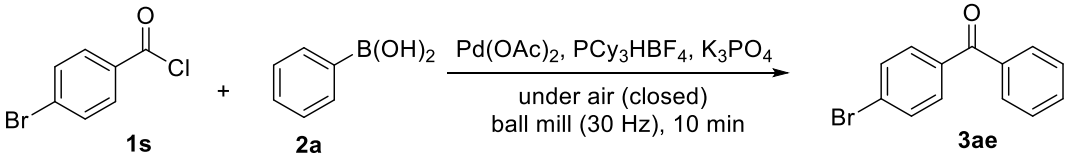
According to the general procedure, 3-Chlorobenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 83% yield (36.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 3H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 139.3, 136.9, 134.6, 132.9, 132.4, 130.0, 129.9, 129.6, 128.5, 128.1. This compound showed identical spectroscopic properties to those reported previously.[13]

(4-Chlorophenyl)(phenyl)methanone (Scheme 2, **3p**)



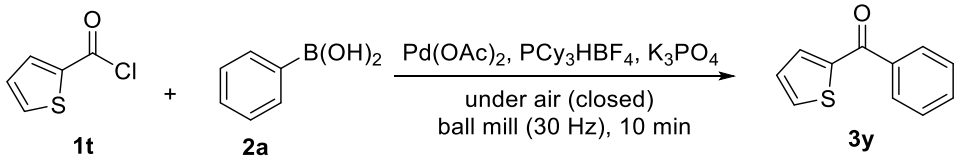
According to the general procedure, 4-Chlorobenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 82% yield (35.5 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.0 Hz, 4H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.52-7.42 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.5, 138.9, 137.2, 135.9, 132.6, 131.5, 129.9, 128.6, 128.4. This compound showed identical spectroscopic properties to those reported previously.[14]

(4-Bromophenyl)phenylmethanone (Scheme 2, **3ae**)



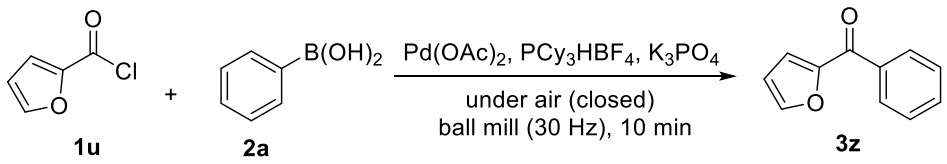
According to the general procedure, 4-Bromobenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 80% yield (41.8 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.61 (dd, *J* = 18.8, 7.9 Hz, 3H), 7.49 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.7, 137.2, 136.3, 132.7, 131.6, 131.6, 130.0, 128.4, 127.5. This compound showed identical spectroscopic properties to those reported previously.[13]

Phenyl(thiophen-2-yl)methanone (Scheme 2, **3y**)



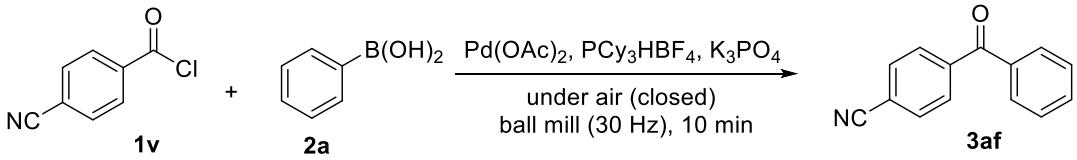
According to the general procedure, 2-Thiophenecarbonyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 85% yield (32.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.0 Hz, 2H), 7.72 (s, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 6.3 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.16 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 143.6, 138.1, 134.9, 134.3, 132.3, 129.2, 128.4, 128.0. This compound showed identical spectroscopic properties to those reported previously.[6]

Furan-2-yl(phenyl)methanone (Scheme 2, **3z**)



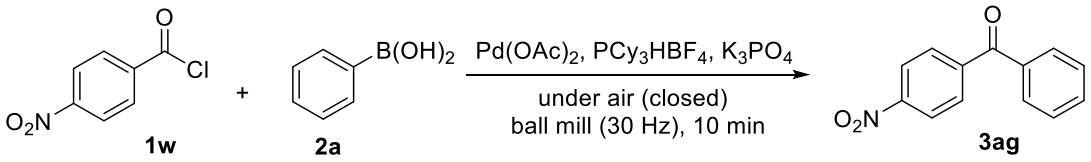
According to the general procedure, 2-Furoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 80% yield (26.5 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.71 (s, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.25-7.21 (m, 1H), 6.60 (dd, *J* = 3.2, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ182.7, 152.2, 147.2, 137.3, 132.6, 129.3, 128.5, 120.7, 112.3. This compound showed identical spectroscopic properties to those reported previously.[19]

4-Benzoylbenzonitrile (Scheme 2, **3af**)



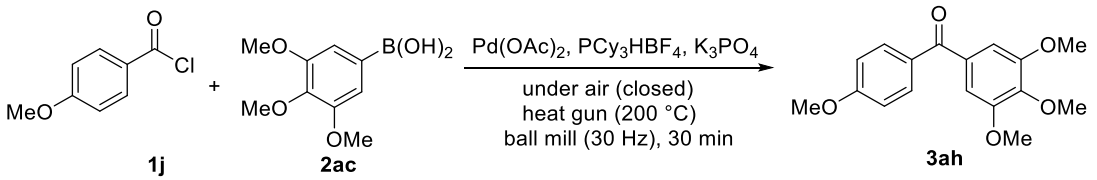
According to the general procedure, 4-Cyanobenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 60% yield (24.9 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.78 (dd, *J* = 9.1, 2.8 Hz, 4H), 7.67-7.61 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 141.2, 136.3, 133.4, 132.2, 130.3, 130.1, 128.3, 118.1, 115.7. This compound showed identical spectroscopic properties to those reported previously.[13]

(4-Nitrophenyl)(phenyl)methanone (Scheme 2, **3ag**)



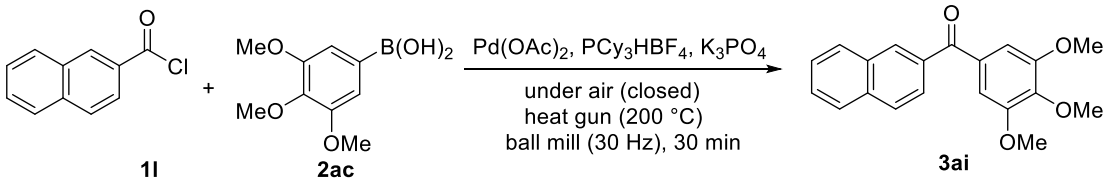
According to the general procedure, 4-Nitrobenzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). afforded after work-up and chromatography the title compound in 43% yield (19.5 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 149.8, 142.9, 136.3, 133.5, 130.7, 130.1, 128.7, 123.5. This compound showed identical spectroscopic properties to those reported previously.[13]

(4-Methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (Scheme 4, **3ah**)



According to the general procedure, *p*-Anisoyl chloride (0.2 mmol), 3,4,5-Trimethoxyphenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 30 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 60% yield (36.3 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.94 (s, 3H), 3.89 (d, *J* = 11.0 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.7, 163.1, 152.8, 141.6, 133.4, 132.4, 130.3, 113.6, 107.5, 61.0, 56.3, 55.5. This compound showed identical spectroscopic properties to those reported previously.[24]

Naphthylphenstatin (Scheme 4, 3ai)



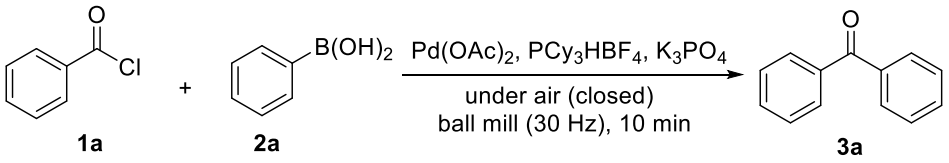
According to the general procedure, 2-Naphthoyl Chloride (0.2 mmol), 3,4,5-Trimethoxyphenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 30 min at 30 Hz) and a heat gun was placed directly above the ball-milling bowl. The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling bowl (the preset temperature at 200 °C). afforded after work-up and chromatography the title compound in 70% yield (45.1 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.01-7.88 (m, 4H), 7.59 (dt, *J* = 21.6, 7.1 Hz, 2H), 7.13 (s, 2H), 3.97 (s, 3H), 3.87 (s, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 152.9,

142.0, 135.2, 135.1, 132.9, 132.3, 131.5, 129.4, 128.3, 128.3, 127.9, 126.9, 125.9, 107.8, 61.0, 56.4. This compound showed identical spectroscopic properties to those reported previously.[1]

4. Mechanistic Studies

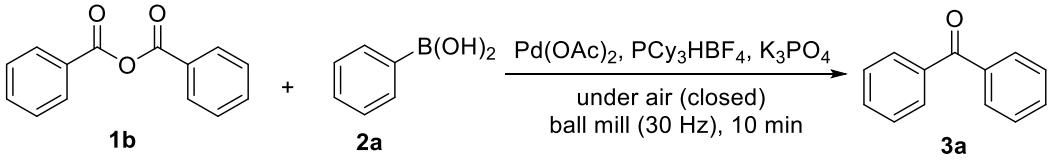
4.1. Effect of Acyl Electrophiles

Benzoyl chloride (Scheme 5A)



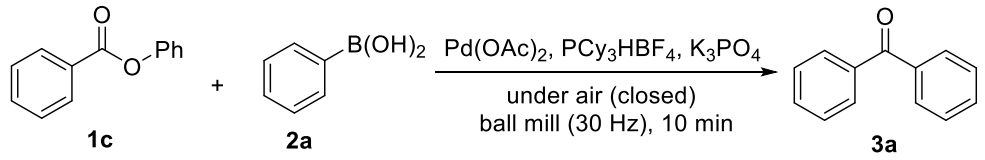
According to the general procedure, Benzoyl chloride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM 400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) to obtain yield using internal standard: yield of **3a** 92%, indicating a superior reactivity of **1a** in the cross-coupling under these conditions.

Benzoic anhydride (Scheme 5A)



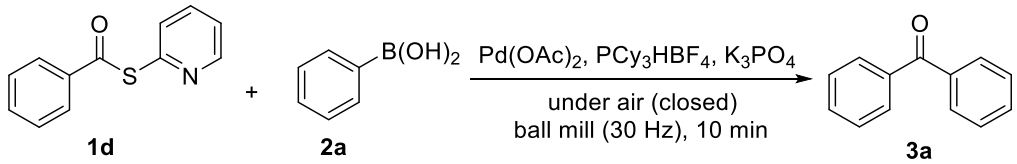
According to the general procedure, Benzoic anhydride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM 400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) to obtain yield using internal standard: yield of **3a** 40%. At this stage, further optimization of the cross-coupling of **1b** was not performed.

Phenyl benzoate (Scheme 5A)



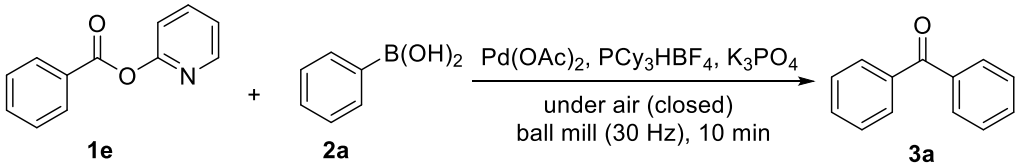
According to the general procedure, Phenyl benzoate (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM 400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) to obtain yield using internal standard: yield of **3a** <5%. At this stage, further optimization of the cross-coupling of **1c** was not performed.

***S*-2-Pyridyl-4-benzothioate** (Scheme 5A)



According to the general procedure, S-2-Pyridyl-4-benzothioate (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM 400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) to obtain yield using internal standard: yield of **3a** <5%. At this stage, further optimization of the cross-coupling of **1d** was not performed.

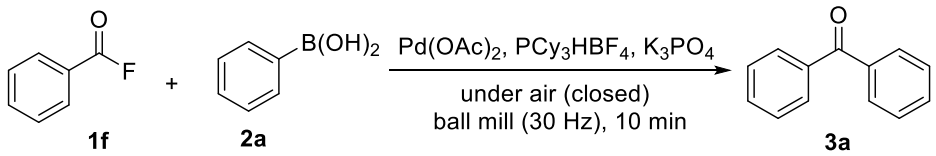
Pyridin-2-yl Benzoate (Scheme 5A)



According to the general procedure, Pyridin-2-yl Benzoate (0.2 mmol), phenylboronic acid

(typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM 400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) to obtain yield using internal standard: yield of **3a** 60%. At this stage, further optimization of the cross-coupling of **1e** was not performed.

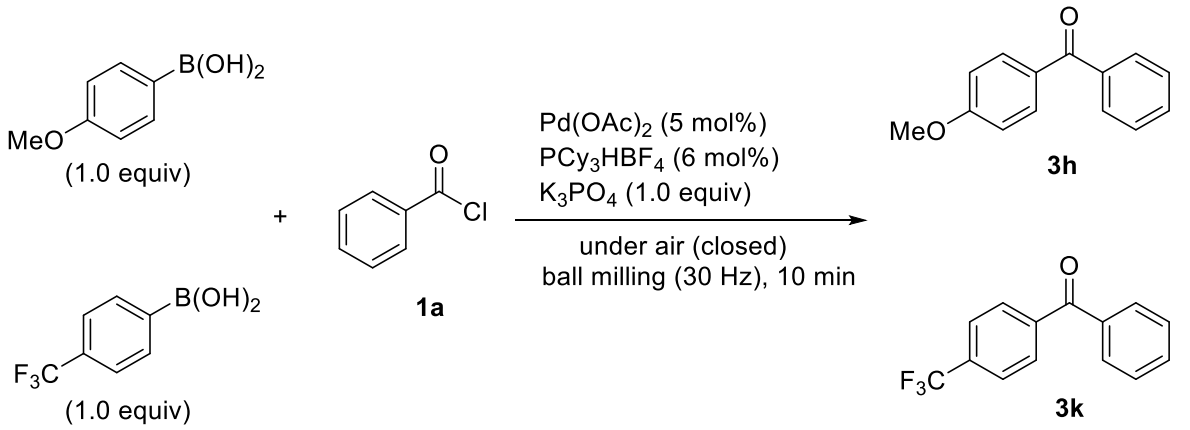
Benzoyl fluoride (Scheme 5A)



According to the general procedure, Benzoyl fluoride (0.2 mmol), phenylboronic acid (typically, 1.5 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM 400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) to obtain yield using internal standard: yield of **3a** 42%. At this stage, further optimization of the cross-coupling of **1f** was not performed.

4.2. Selectivity Studies – Boronic Acids

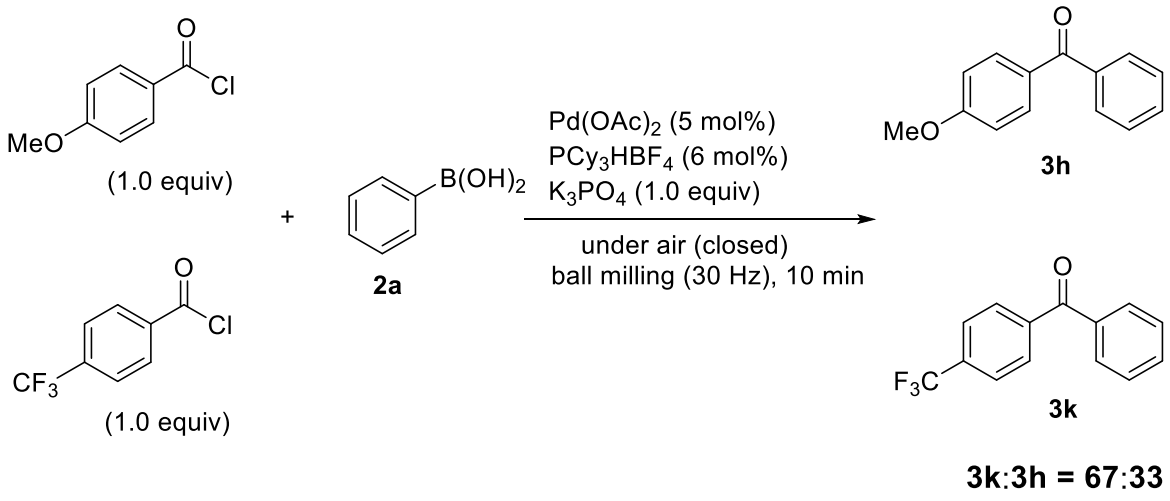
General Procedure. Benzoyl chloride (0.2 mmol, 1.0 equiv), Two Boronic acid substrates (each 1.0 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 600 MHz) to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.



3h:3k = 67:33

4.3. Selectivity Studies – Acyl Chlorides

General Procedure. Two Acyl chlorides (each 0.2 mmol, 1.0 equiv), boronic acid (1.0 equiv), $Pd(OAc)_2$ (typically, 5 mol%), PCy_3HBF_4 (typically, 6 mol%), and K_3PO_4 (typically, 1.0 equiv) were placed in a ball milling bowl (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 5 mm). the bowl was placed in the ball mill (Retsch MM400, 10 min at 30 Hz). After 10 min, the reaction mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 600 MHz) to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.



5. NMR Spectra

Benzophenone (3a).

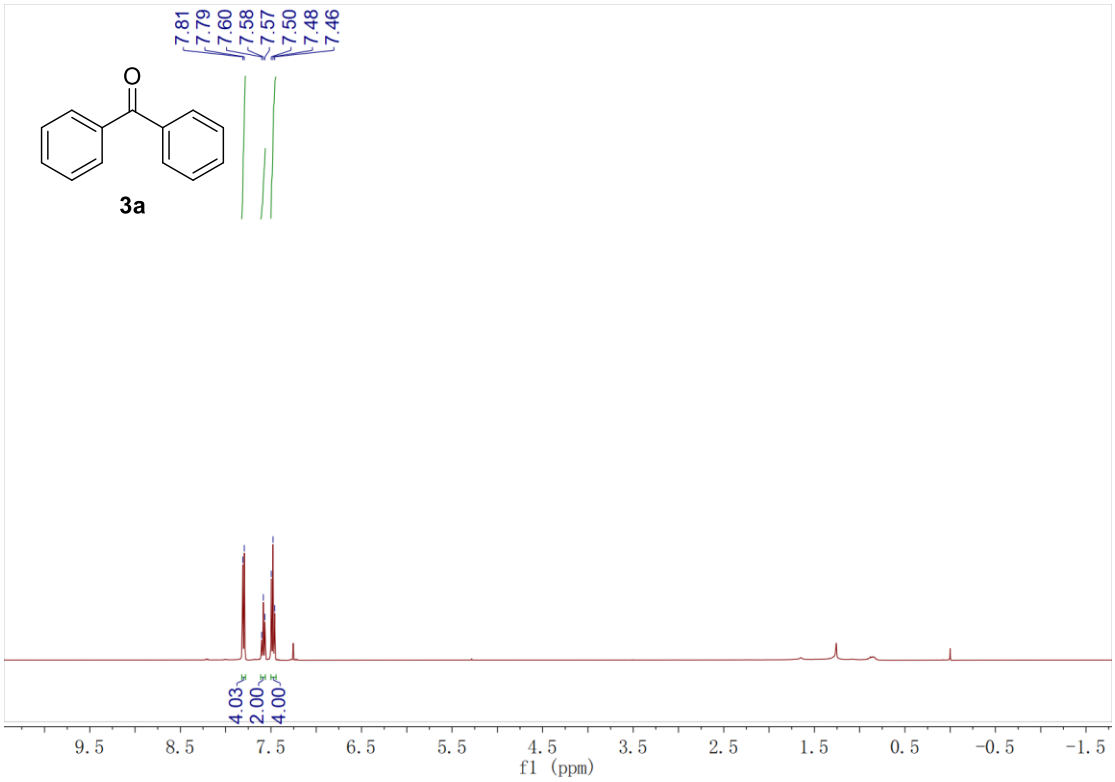


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3a**

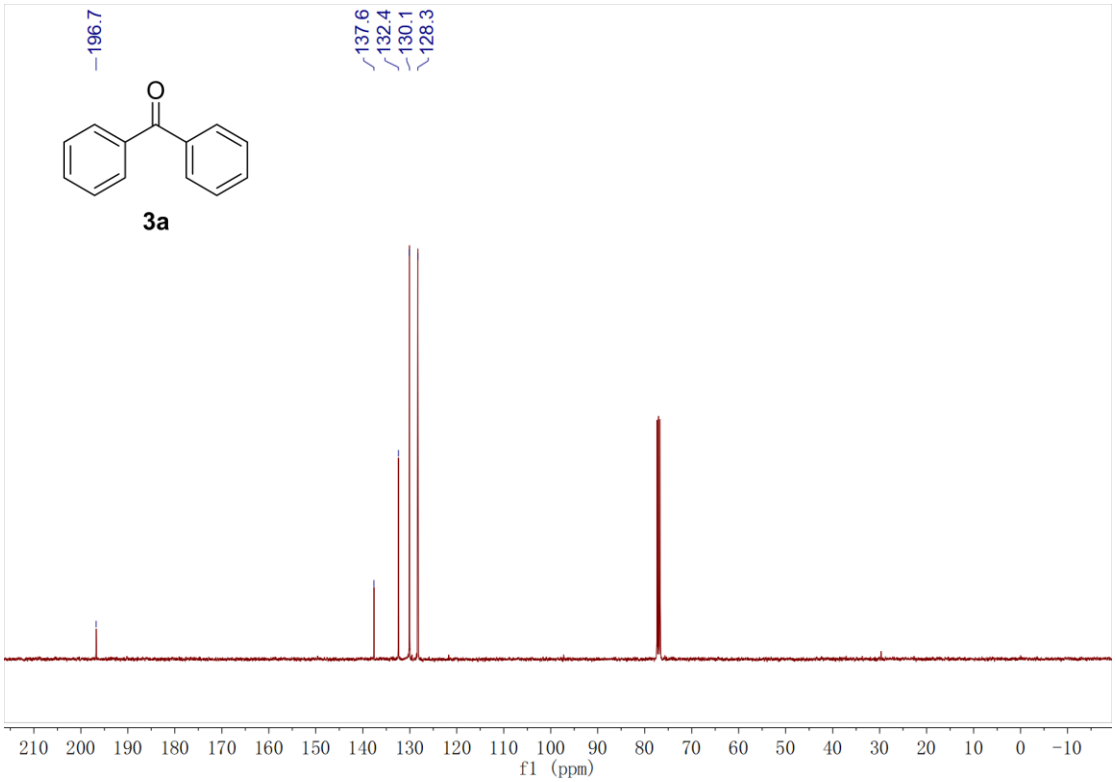


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3a**

Phenyl(*p*-tolyl)methanone (3b).

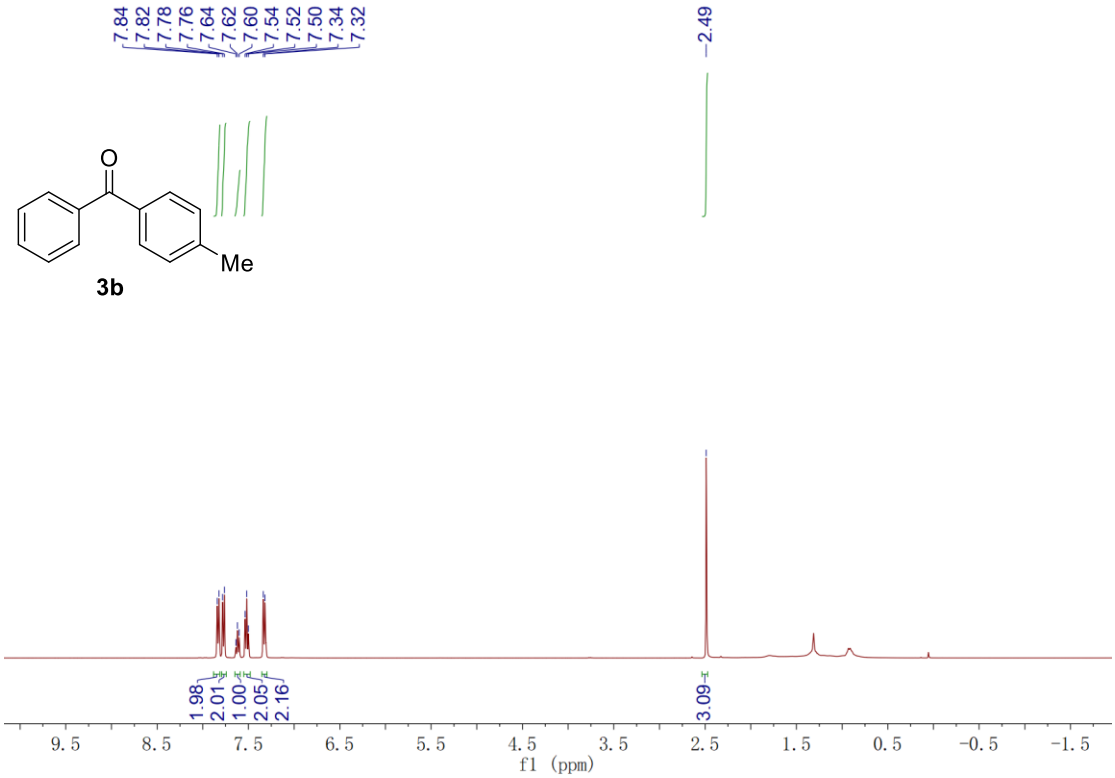


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3b**

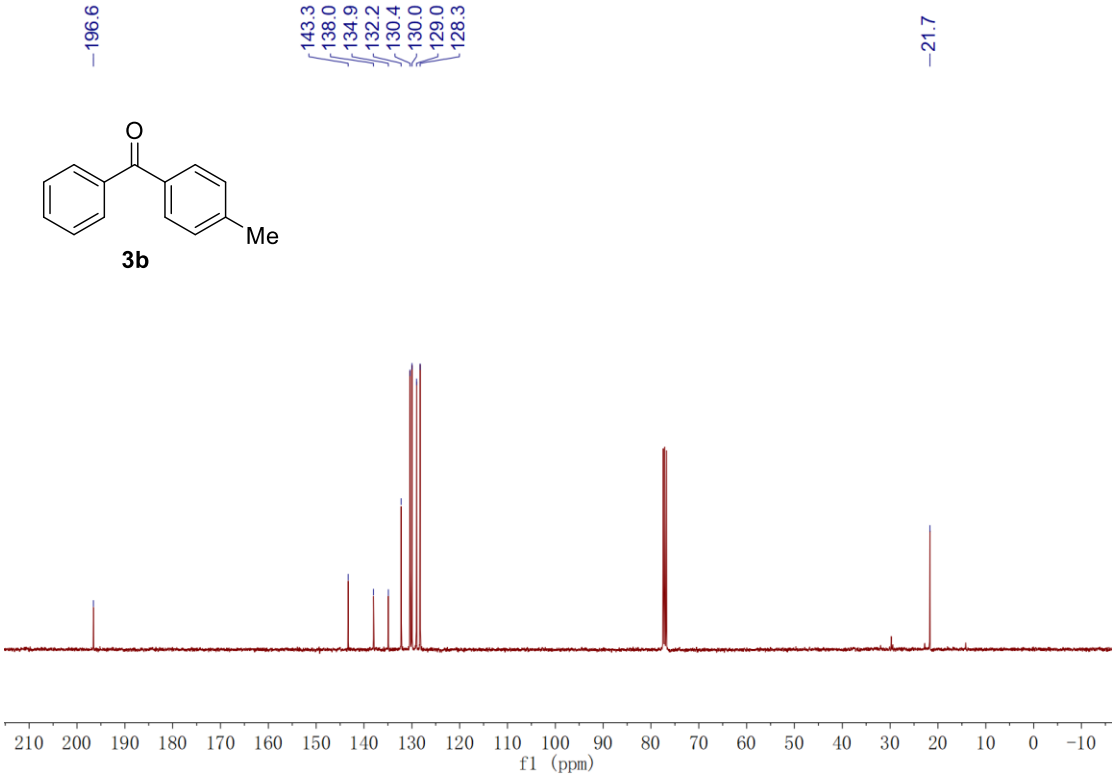


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3b**

Phenyl(*o*-tolyl)methanone (3c).

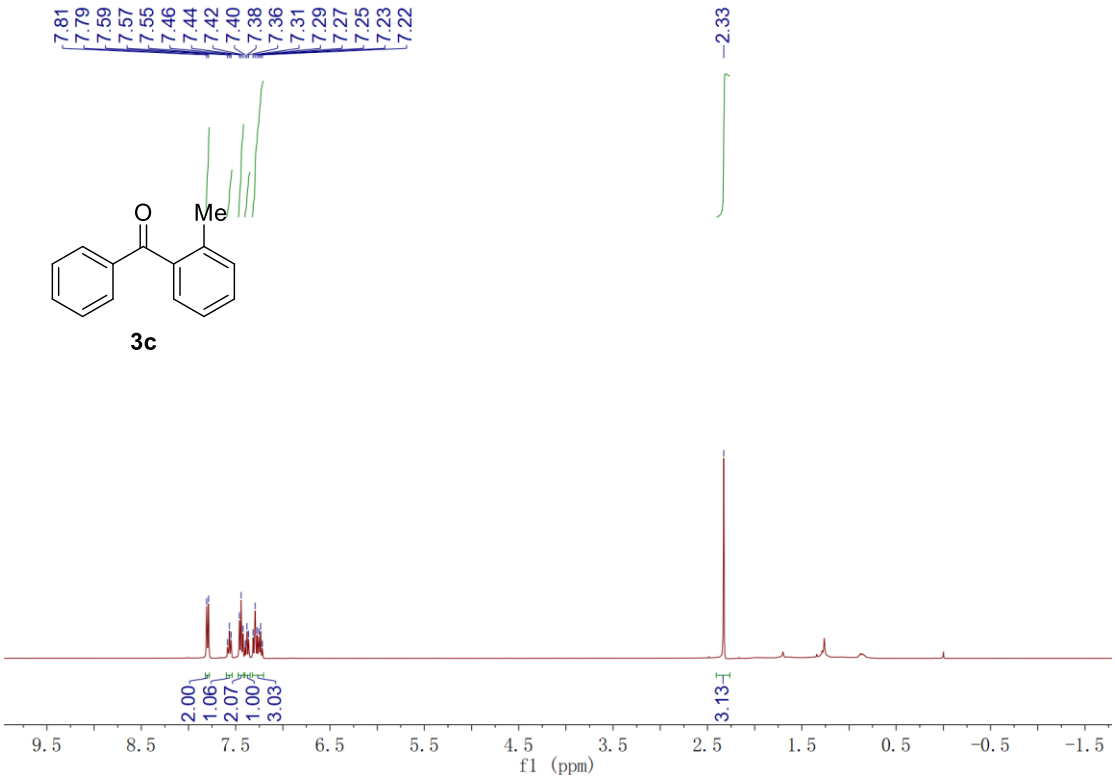


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3c**

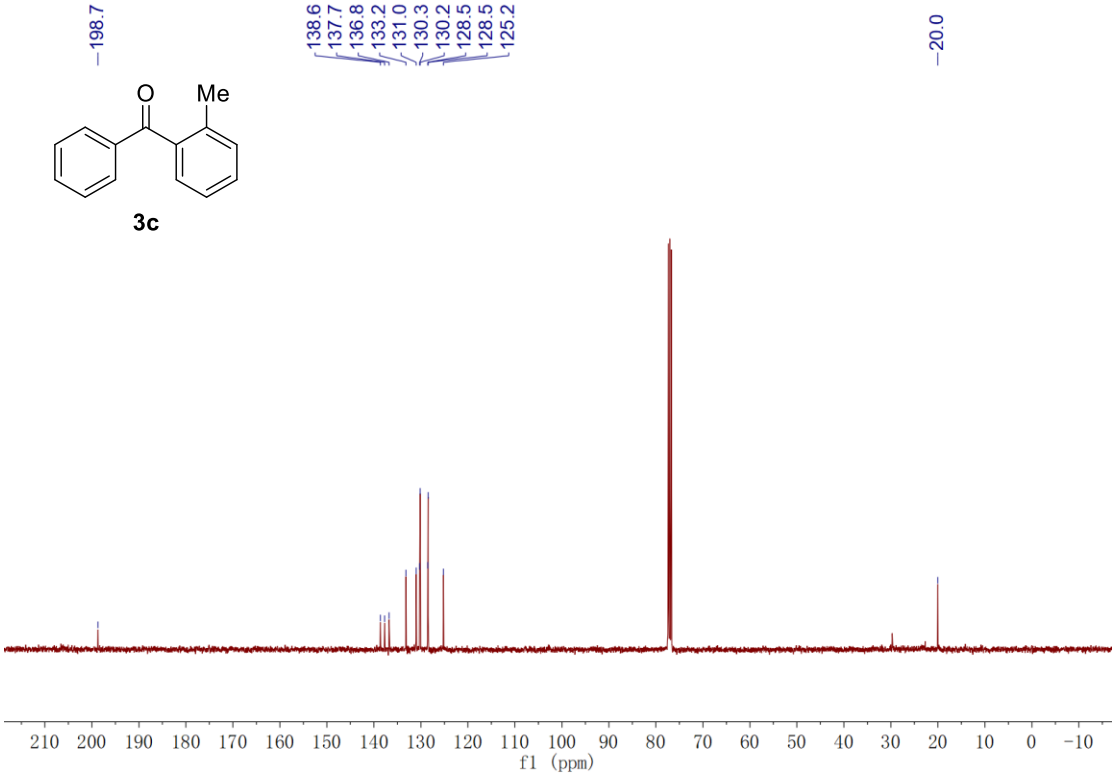


Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3c**

Phenyl(*m*-tolyl)methanone (3d).

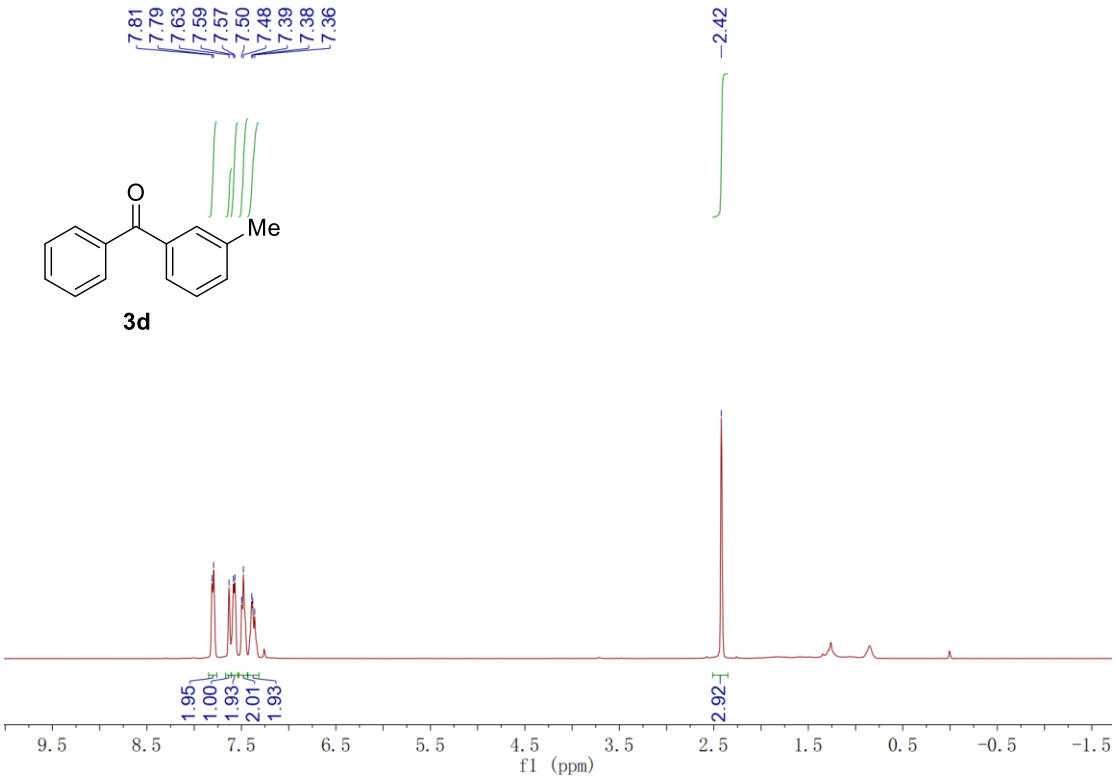


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3d**

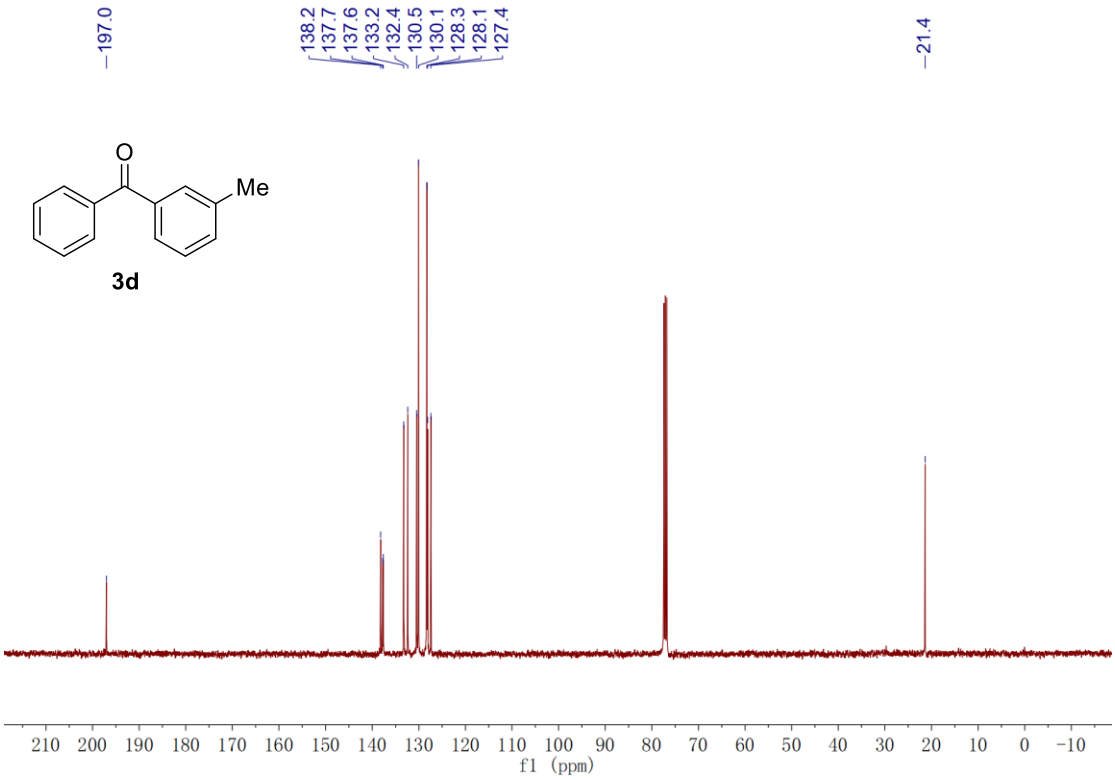


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3d**

(4-Ethylphenyl)(phenyl)methanone (3e).

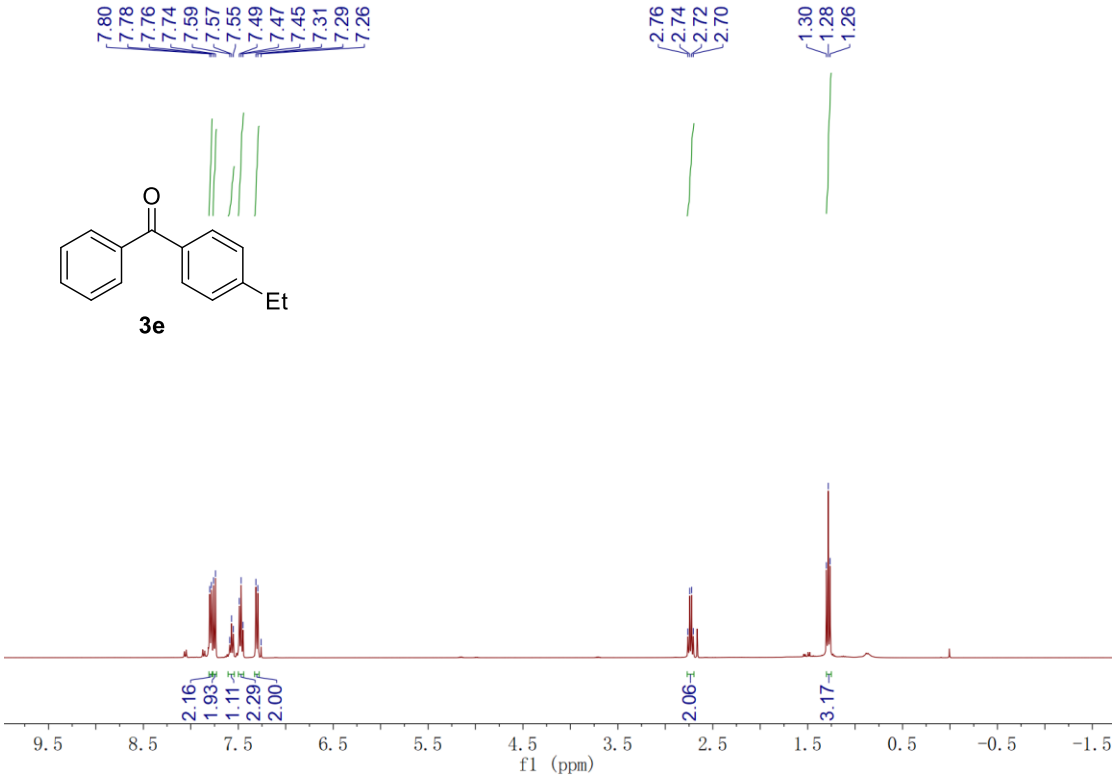


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3e**

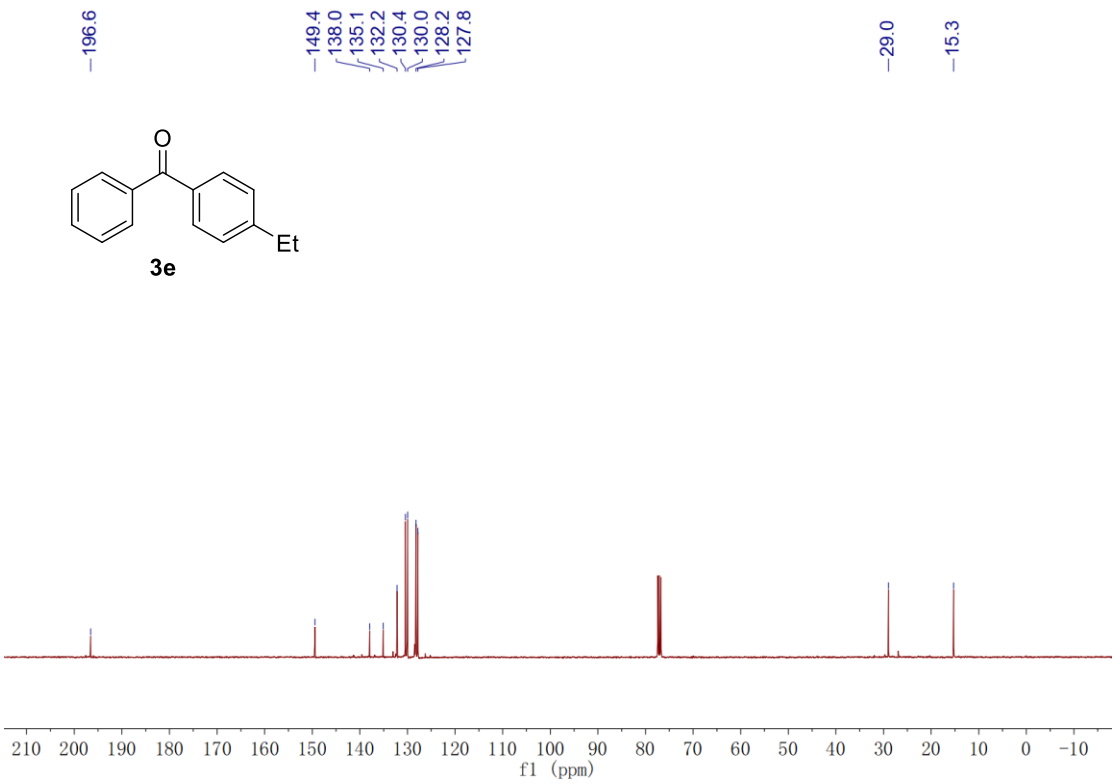


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3e**

(3-Methoxyphenyl)(phenyl)methanone (3f).

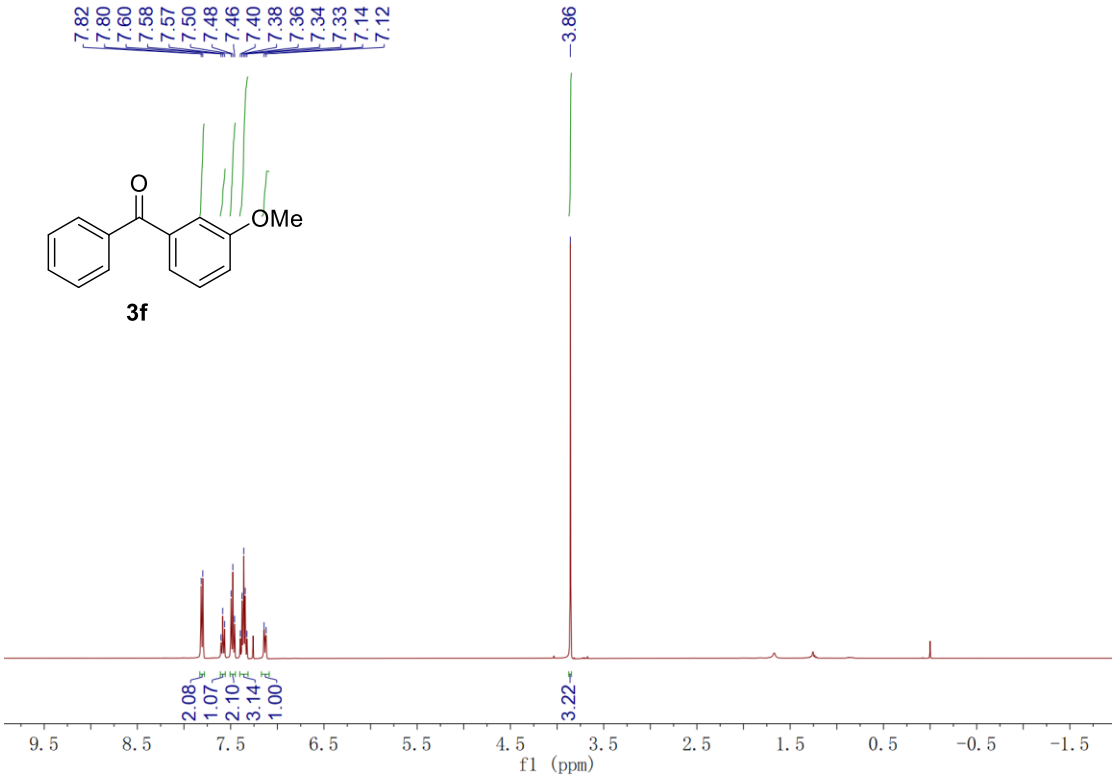


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3f**

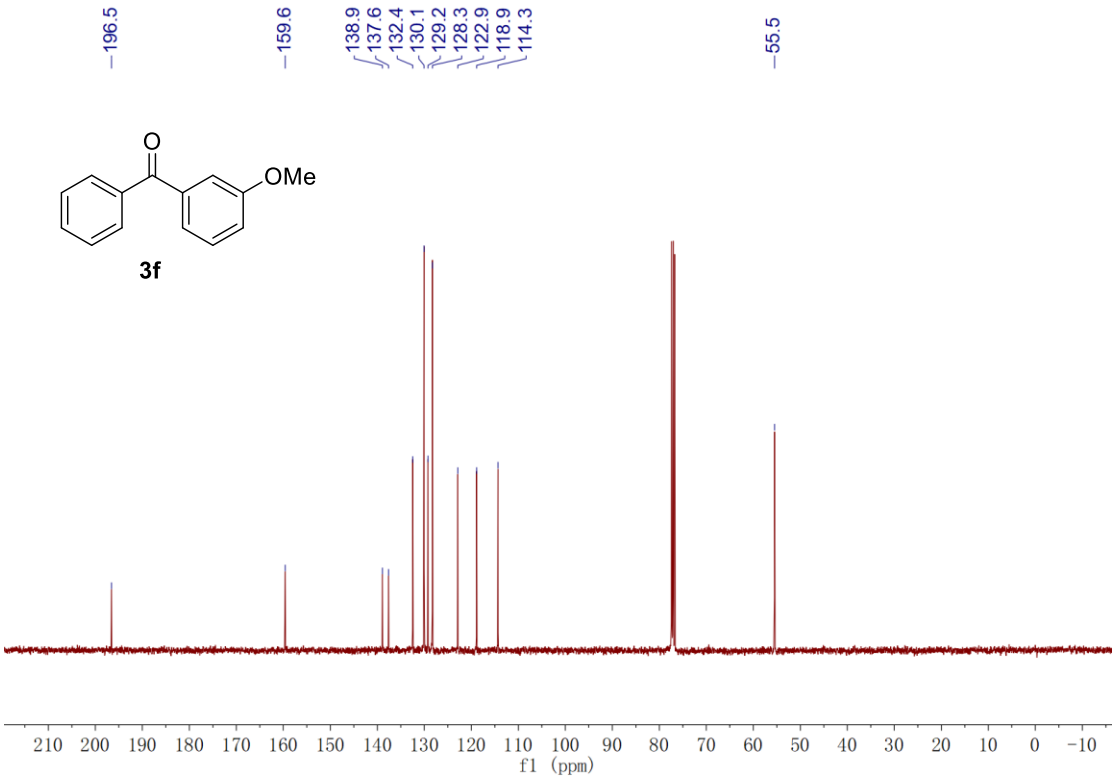


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3f**

(2-Methoxyphenyl)(phenyl)methanone (3g).

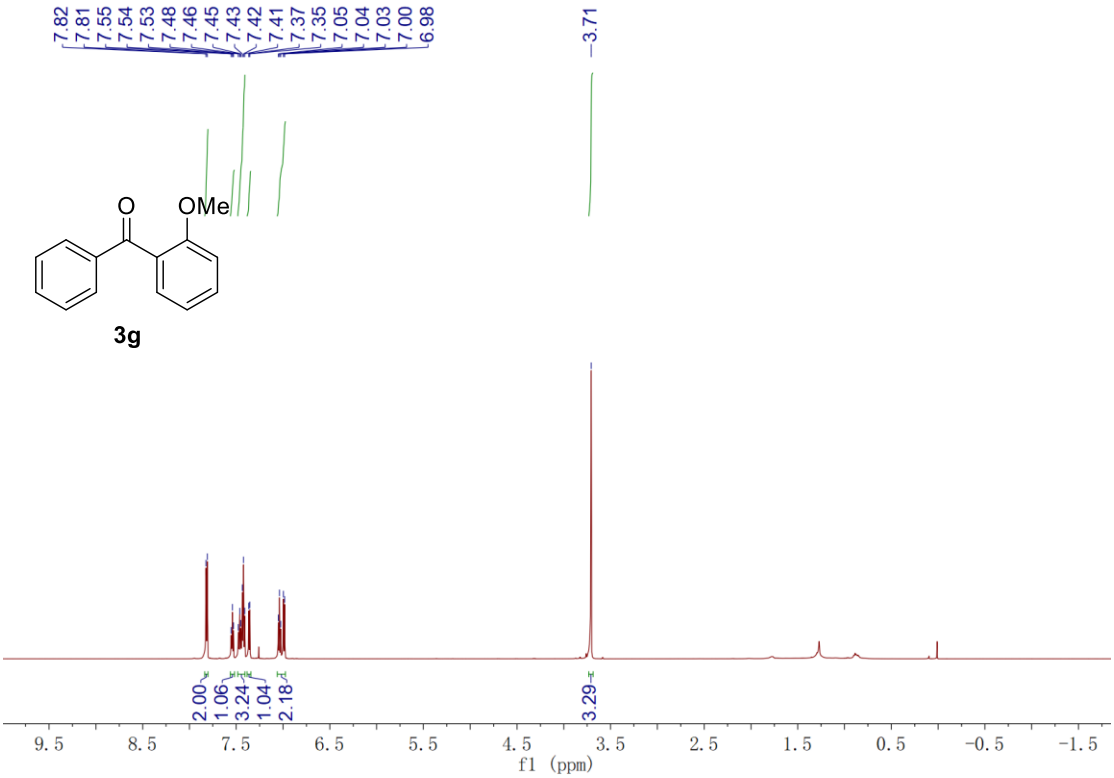


Figure S13. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3g**

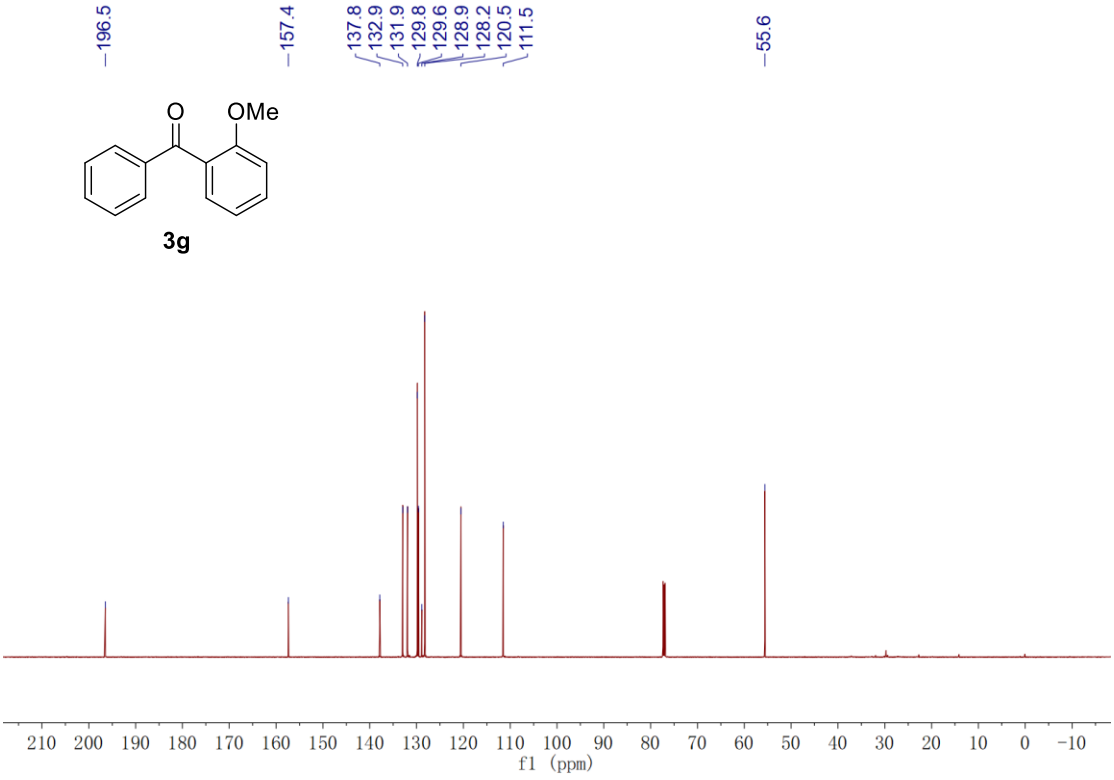


Figure S14. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3g**

(4-Methoxyphenyl)(phenyl)methanone (3h).

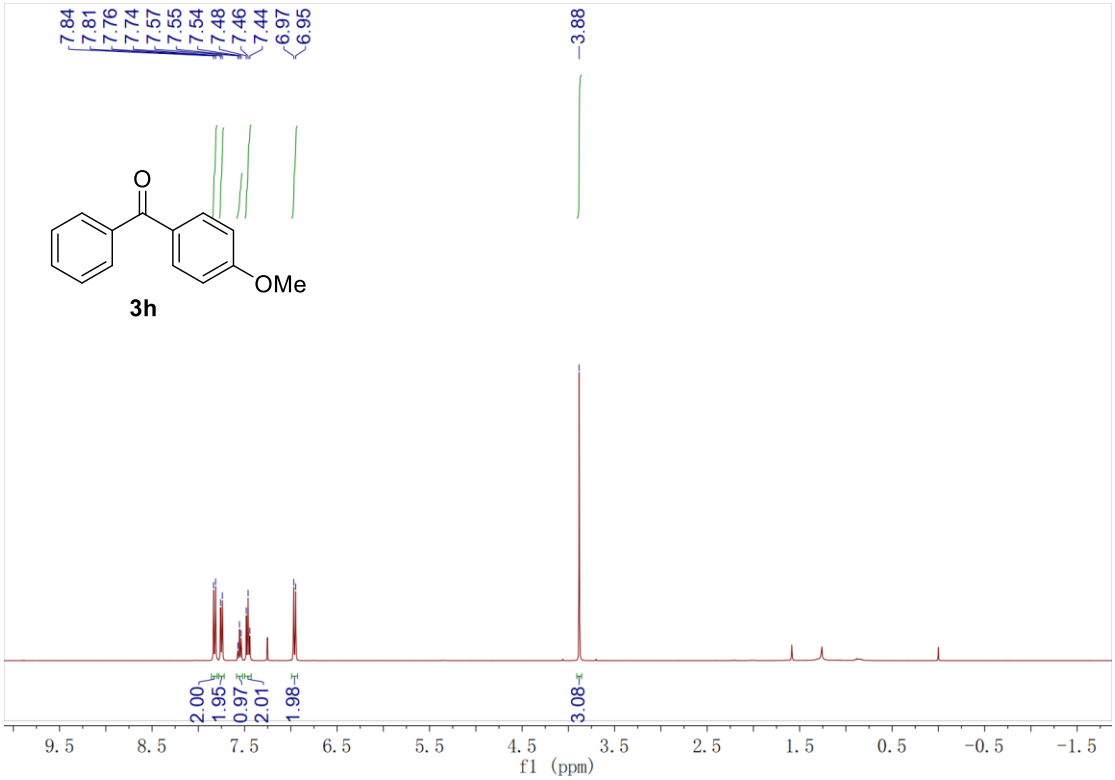


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3h**

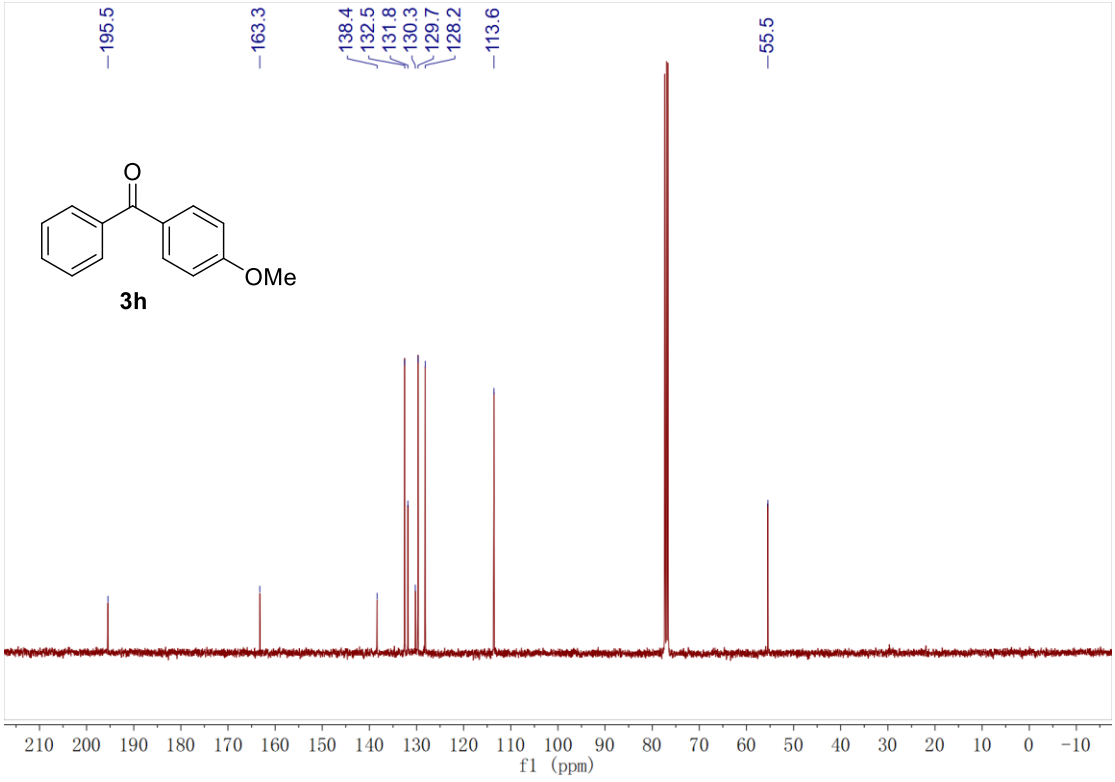


Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3h**

(3,4-Dimethoxyphenyl)(phenyl)methanone (3i).

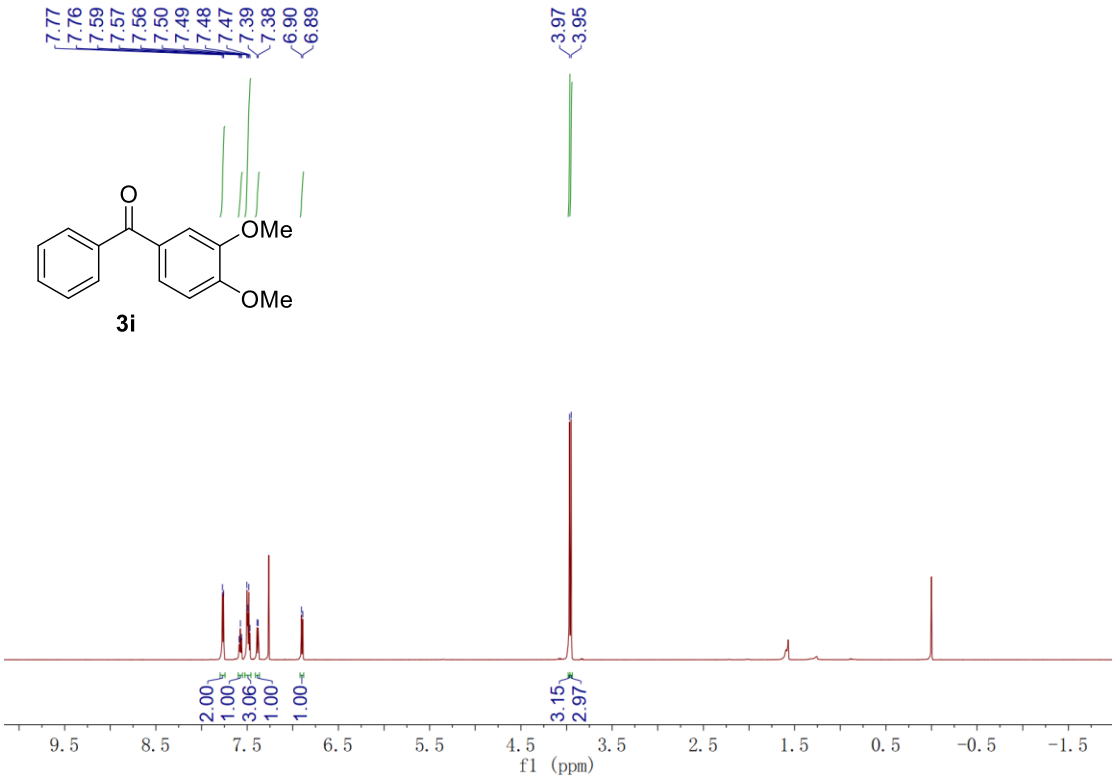


Figure S17. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3i**

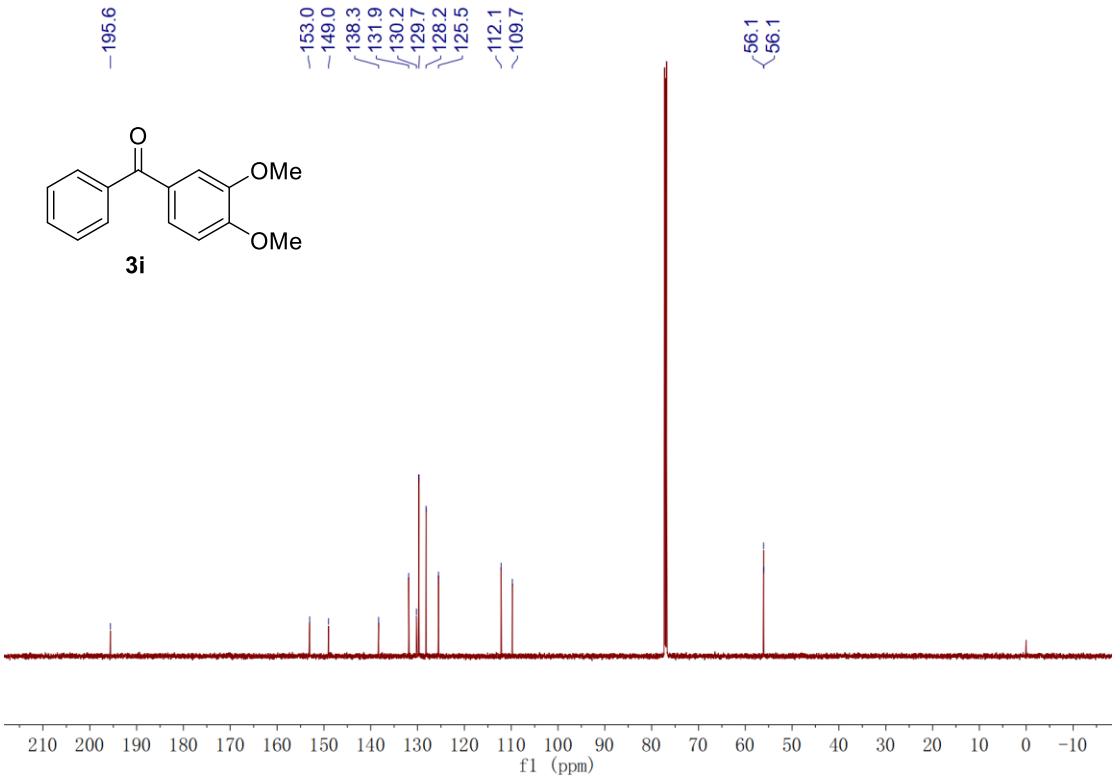


Figure S18. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3i**

Phenyl(4-(trifluoromethoxy)phenyl)methanone (3j).

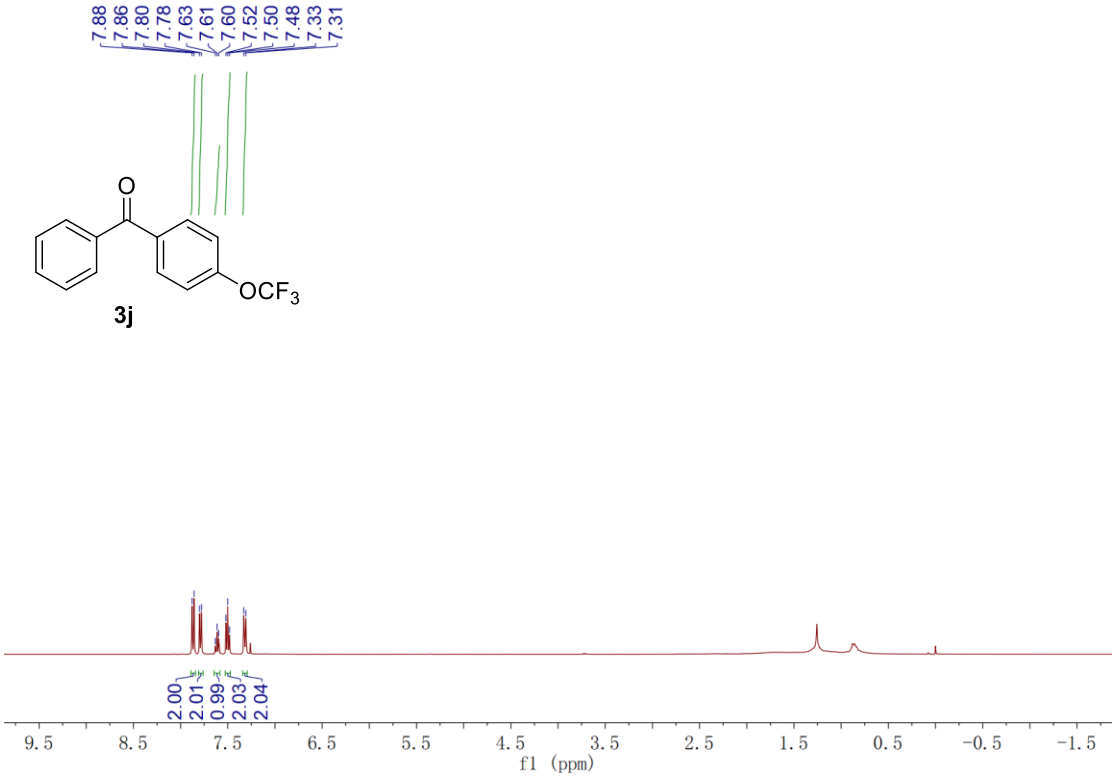


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3j**

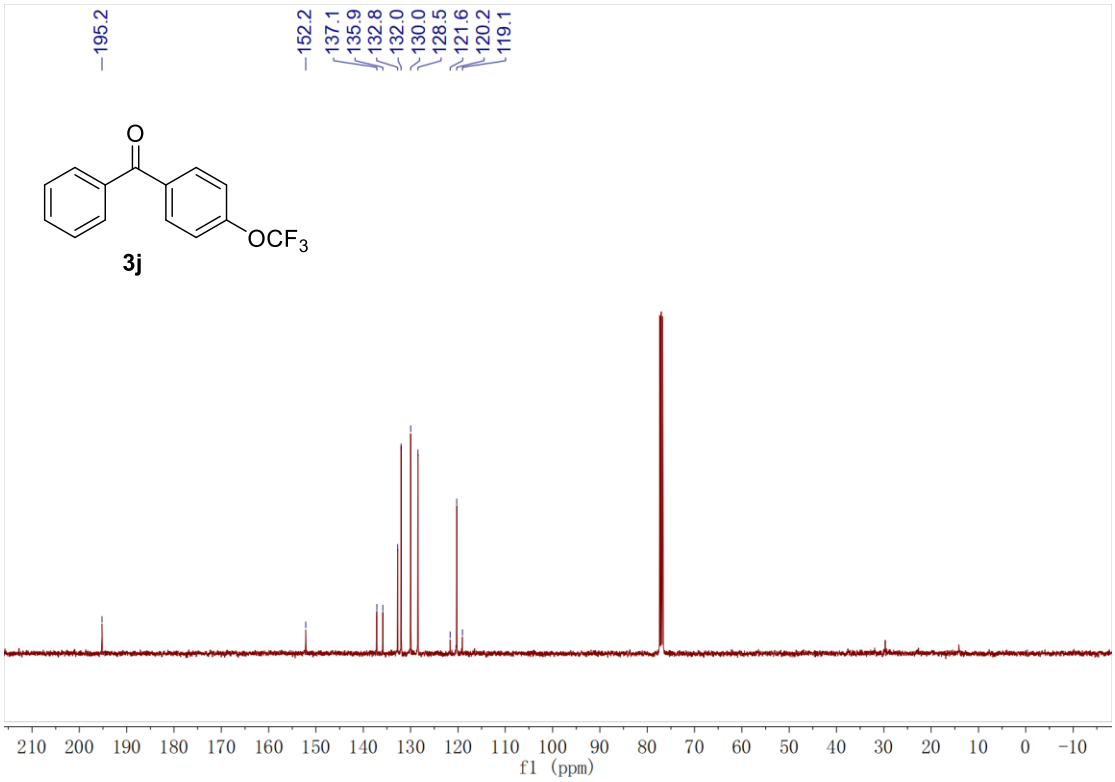


Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3j**

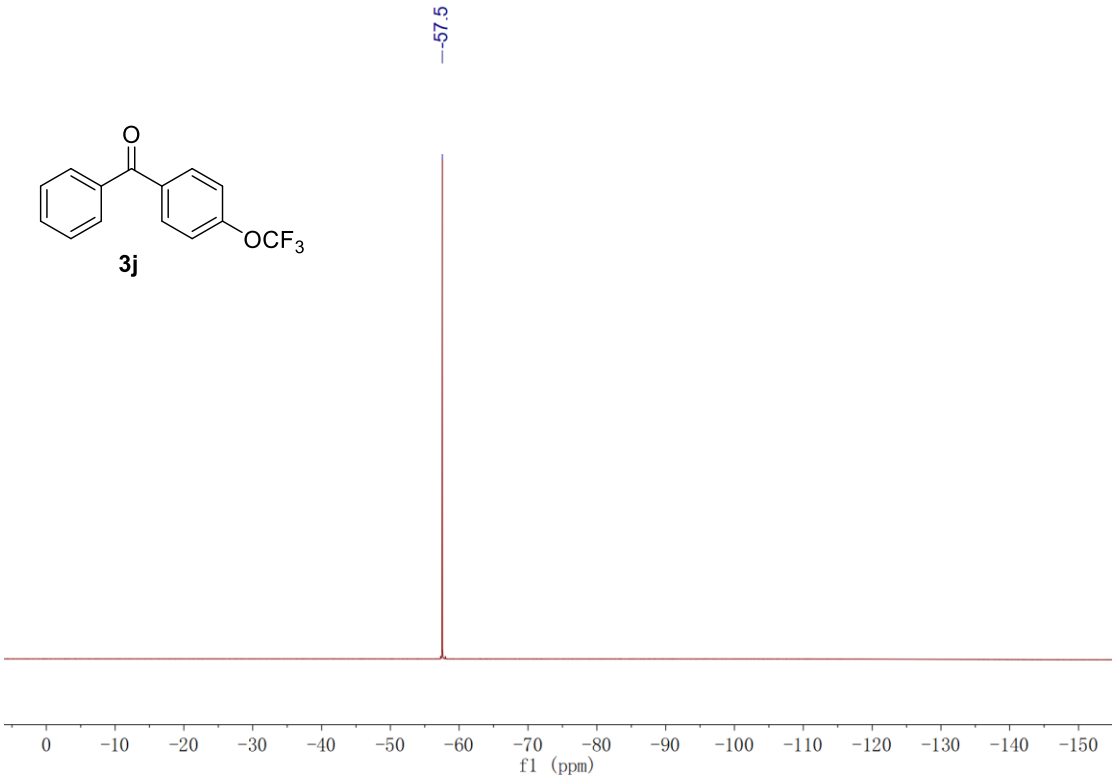


Figure S21. ^{19}F (376 MHz, $CDCl_3$) Spectrum of Compound **3j**

Phenyl(4-(trifluoromethyl)phenyl)methanone (3k).

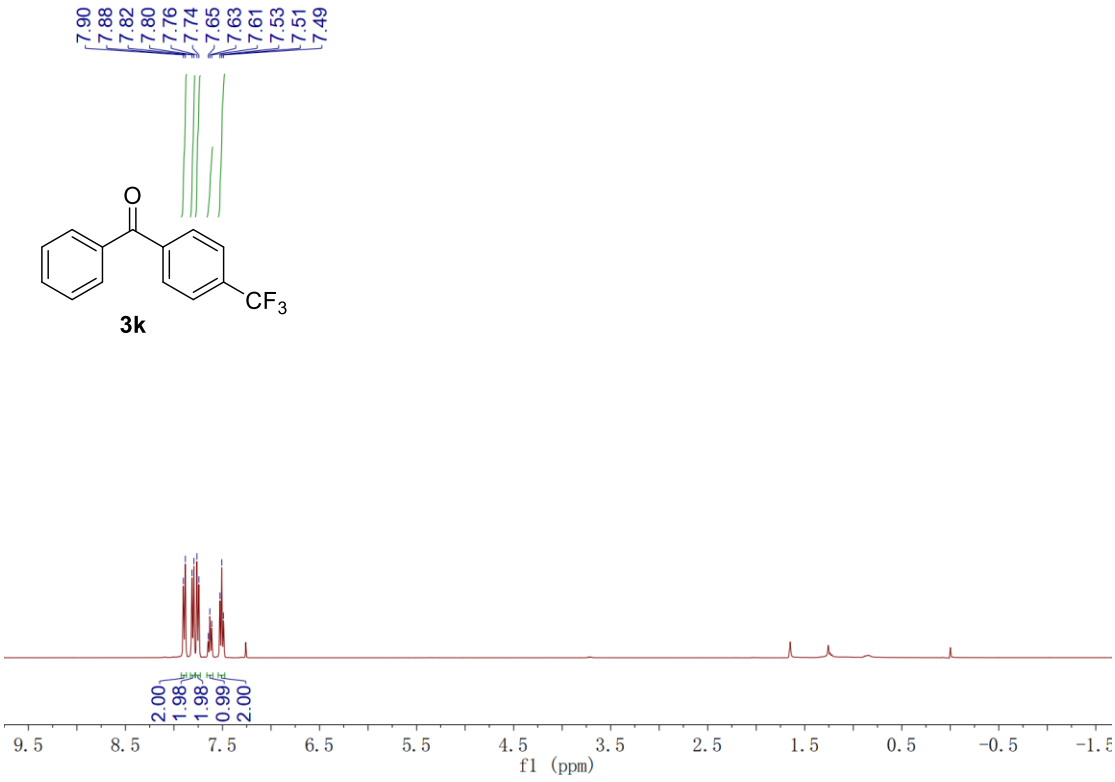


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3k**

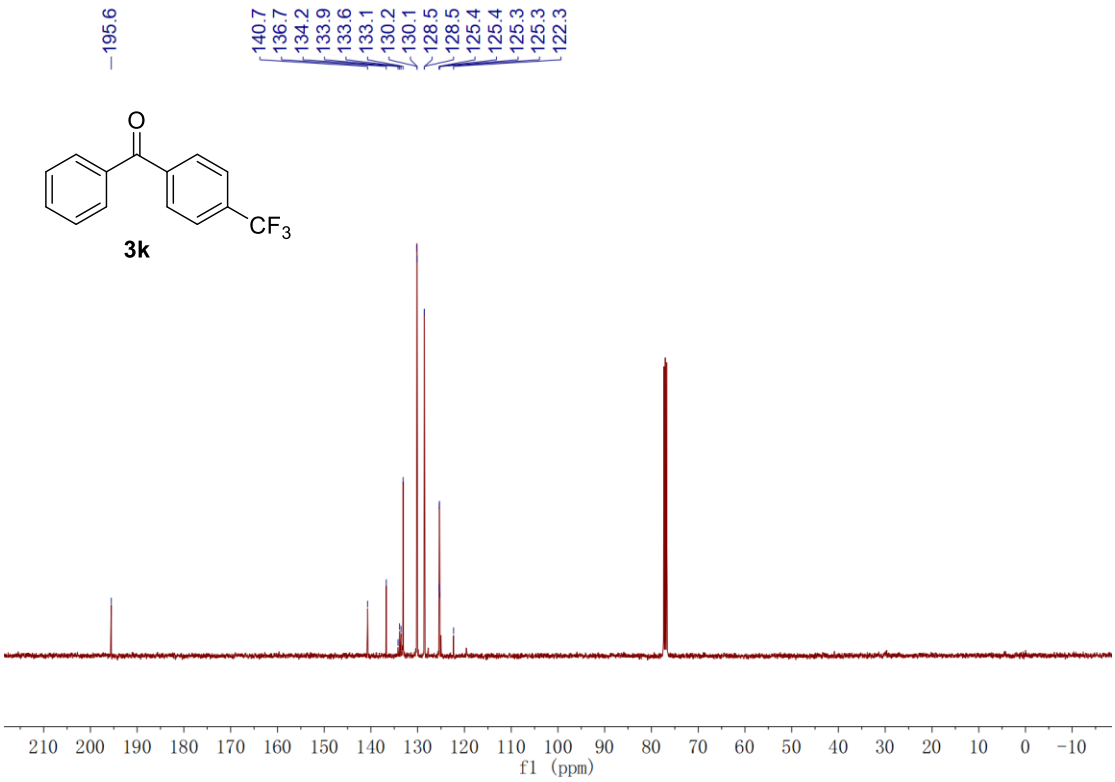


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3k**

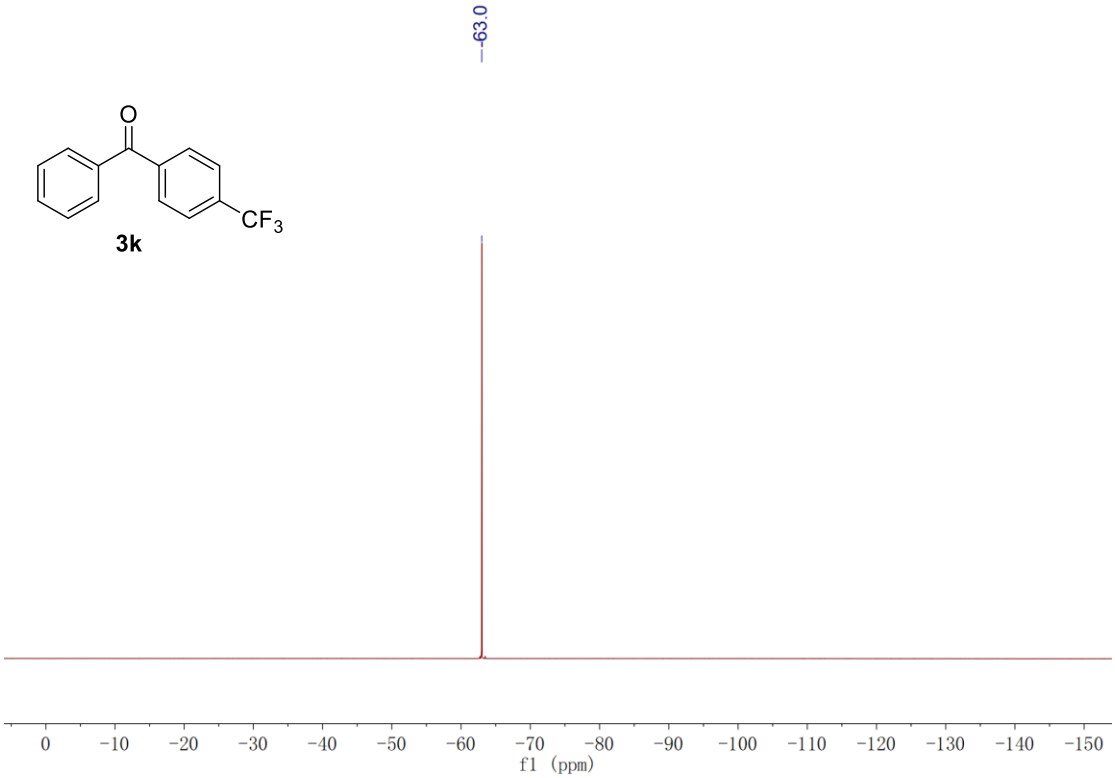


Figure S24. ^{19}F (376 MHz, $CDCl_3$) Spectrum of Compound **3k**

(2-Fluorophenyl)(phenyl)methanone (3l).

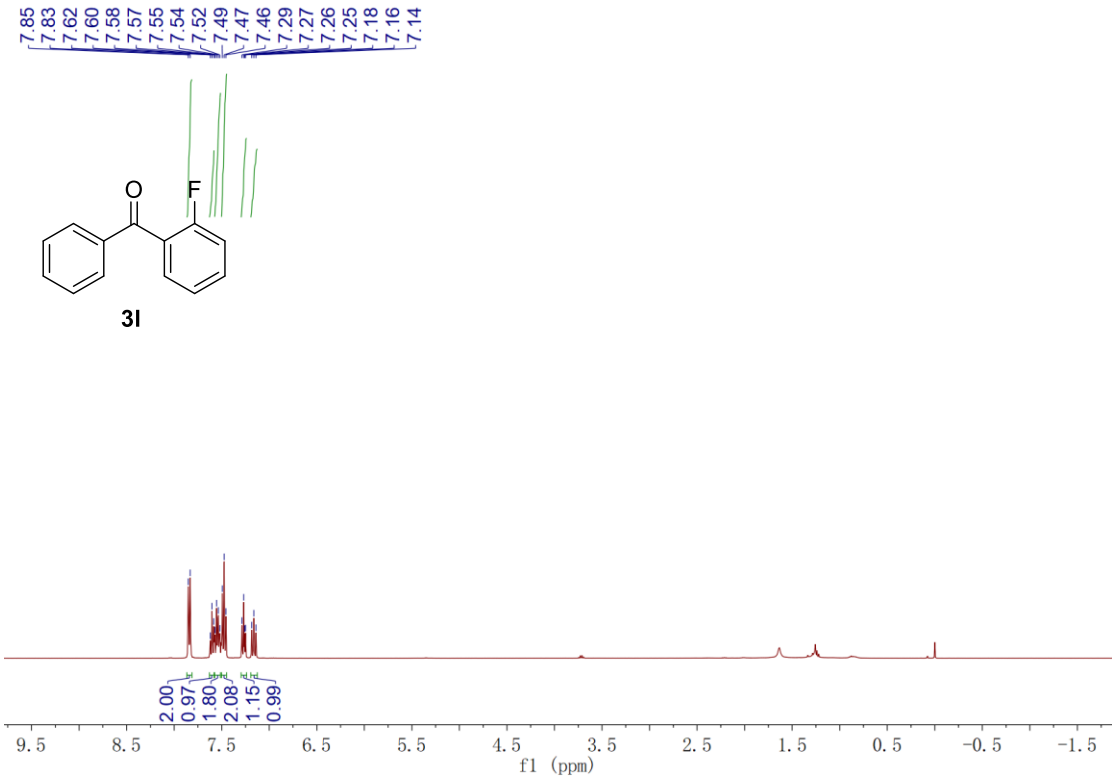


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3l**

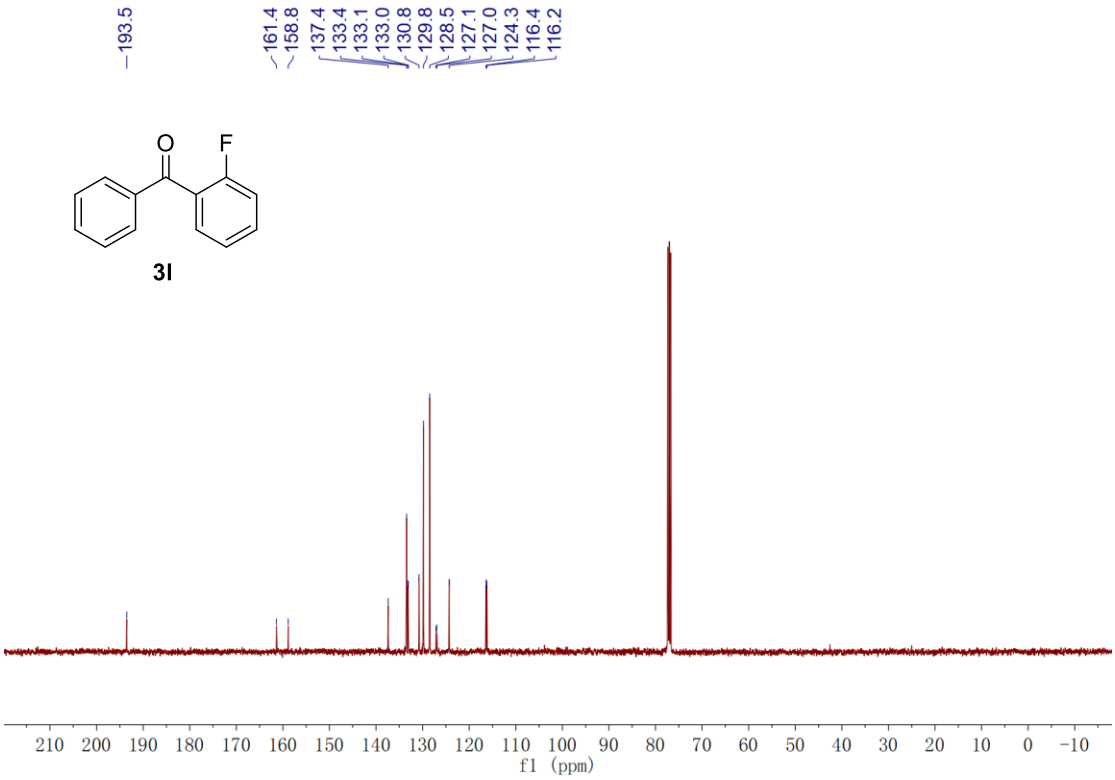


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3l**

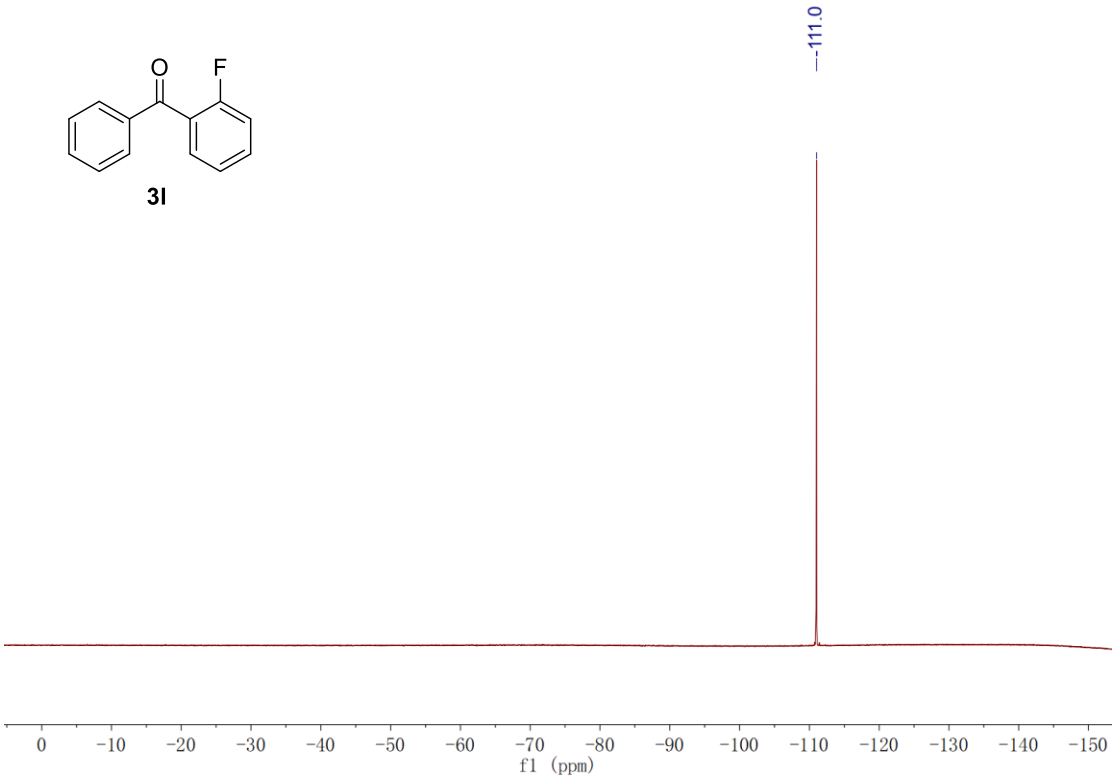


Figure S27. ^{19}F (376 MHz, $CDCl_3$) Spectrum of Compound **3l**

(4-Fluorophenyl)(phenyl)methanone (3m).

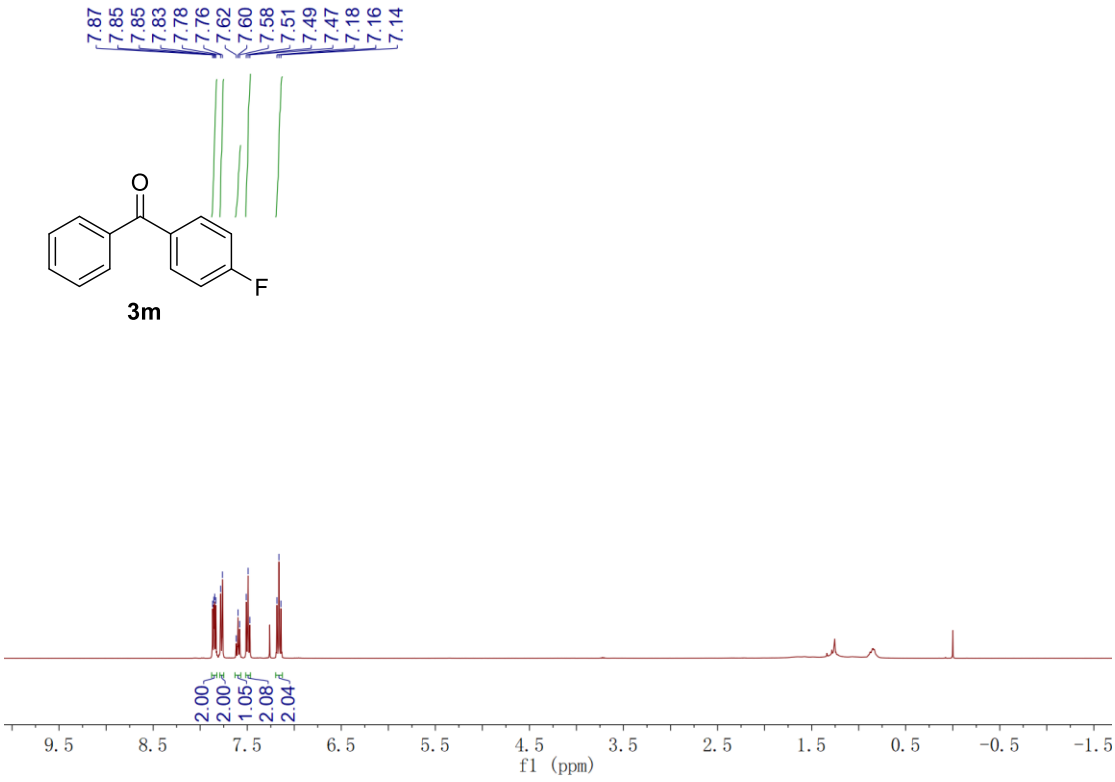


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3m**

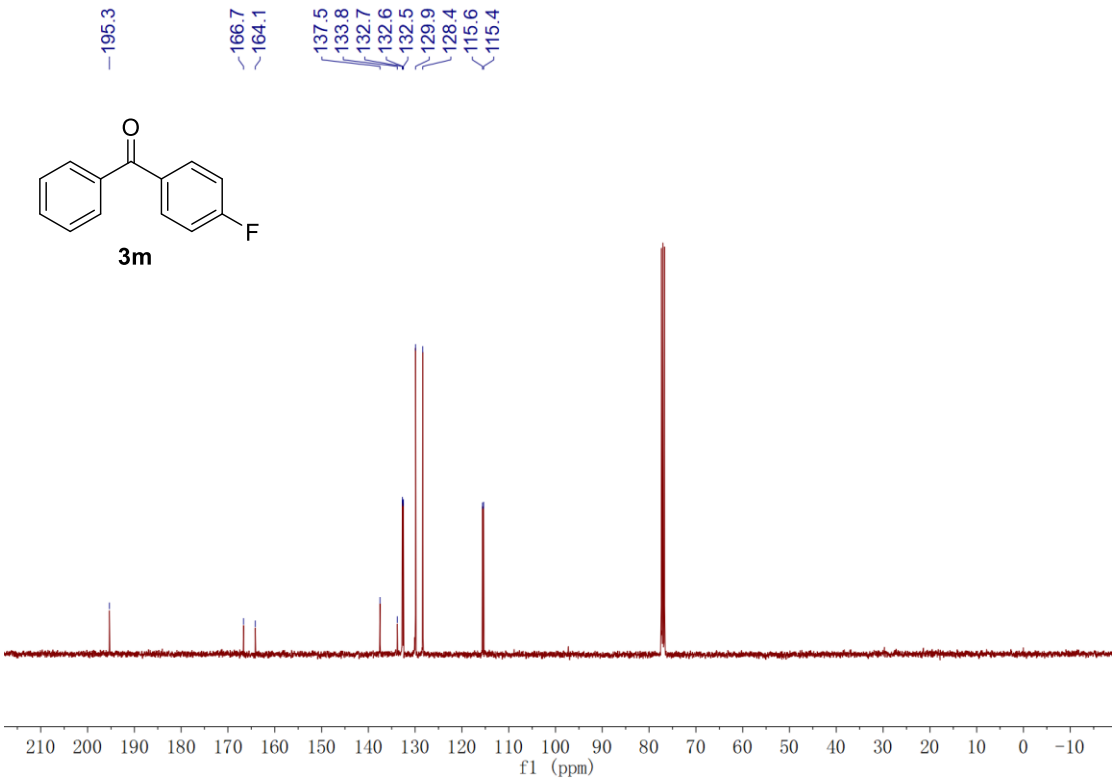


Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3m**

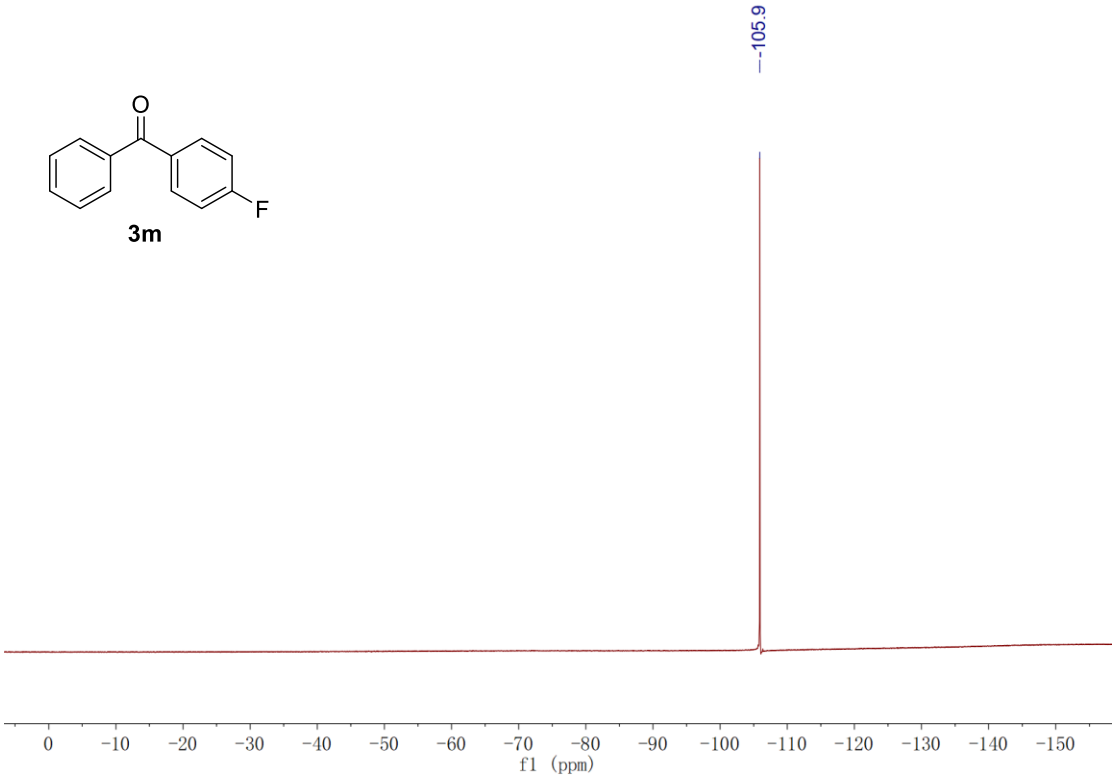


Figure S30. ^{19}F (376 MHz, $CDCl_3$) Spectrum of Compound **3m**

(3-Fluorophenyl)(phenyl)methanone (3n).

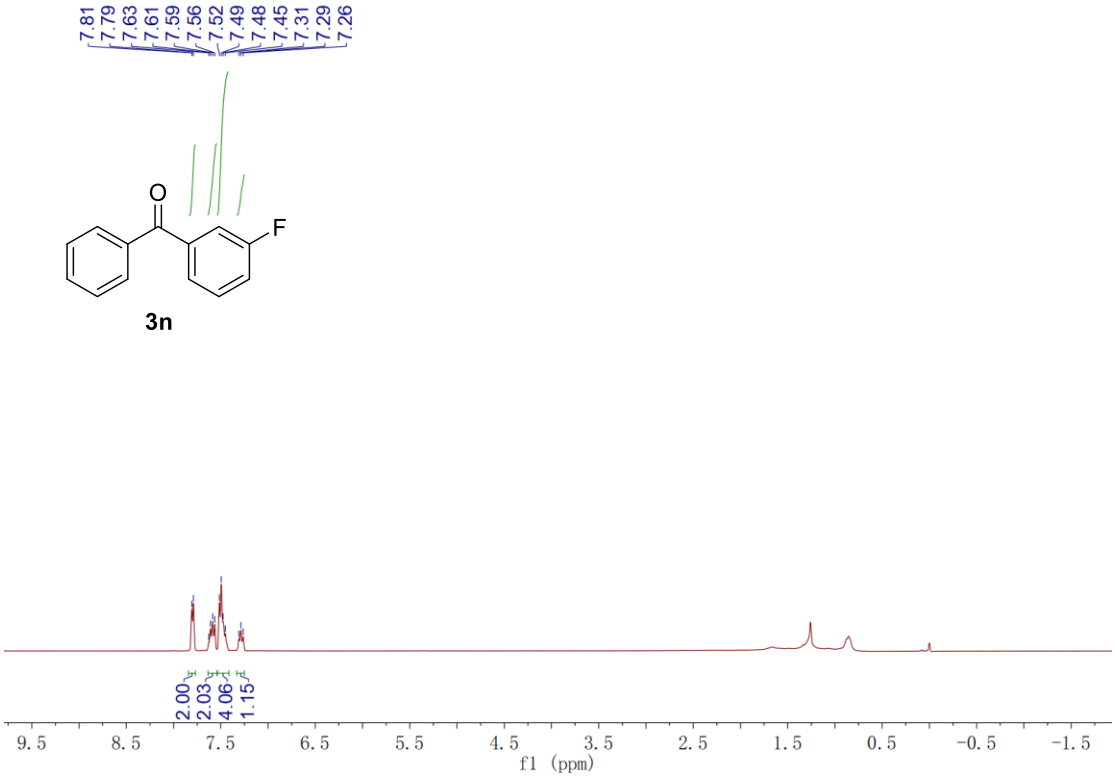


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3n**

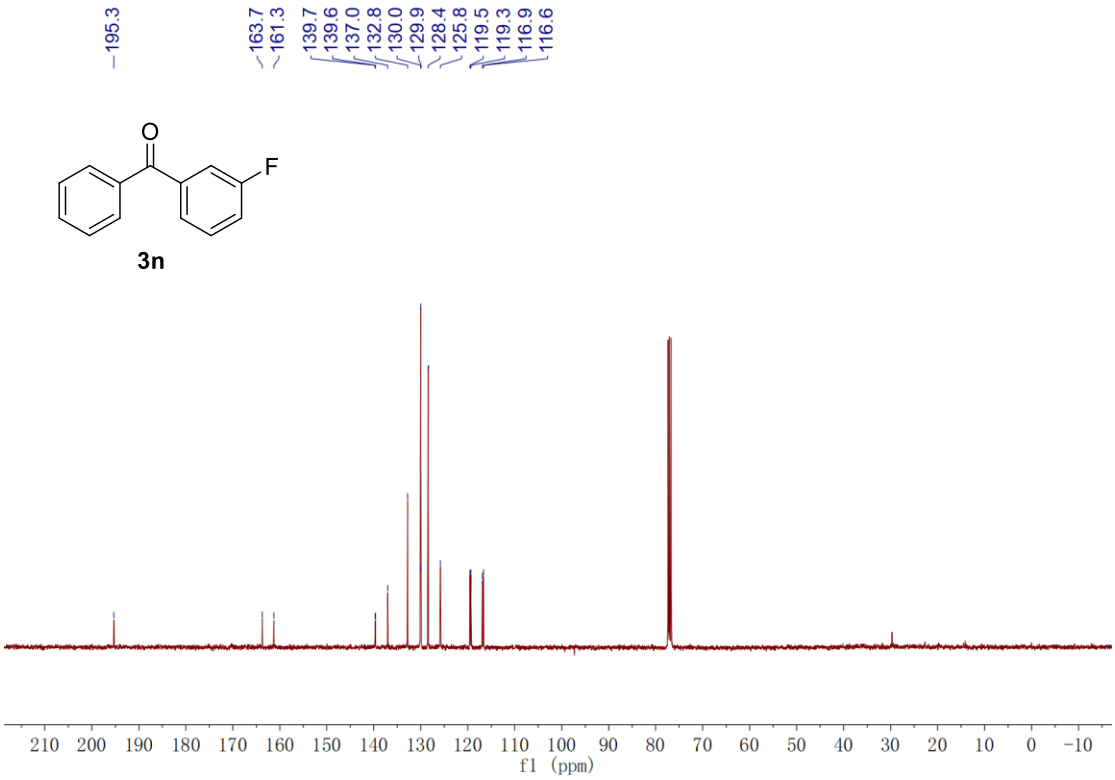


Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3n**

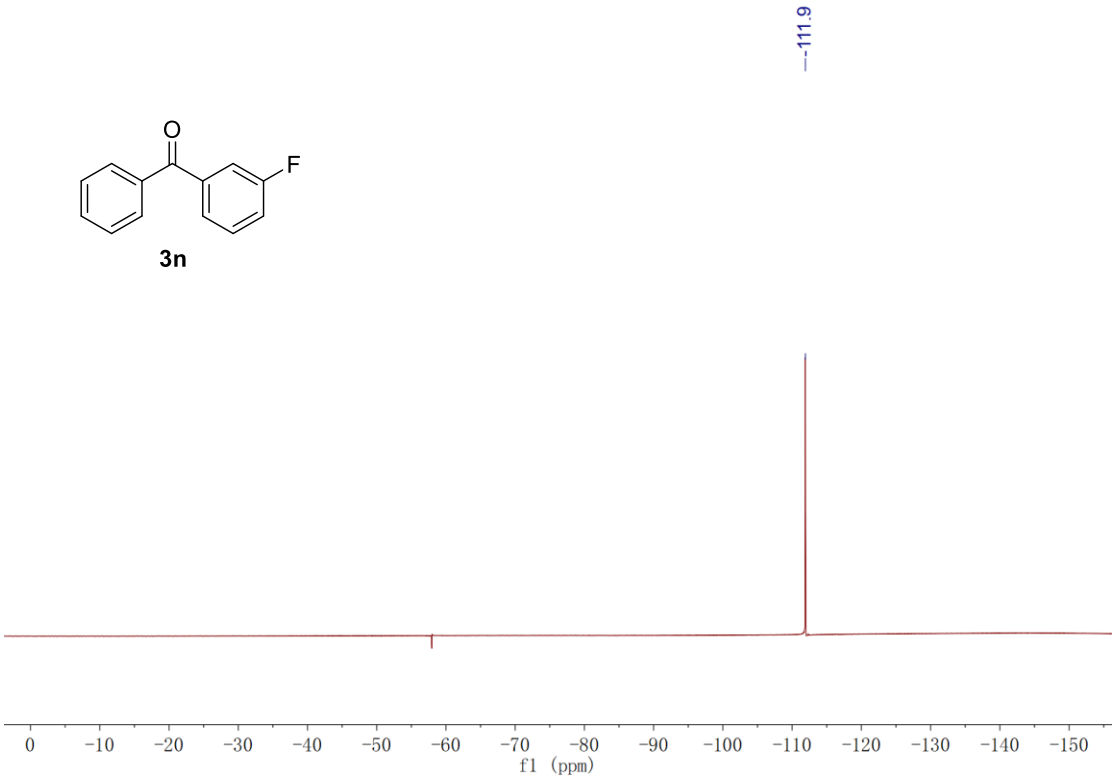


Figure S33. ^{19}F (376 MHz, $CDCl_3$) Spectrum of Compound **3n**

(3-Chlorophenyl)(phenyl)methanone (3o).

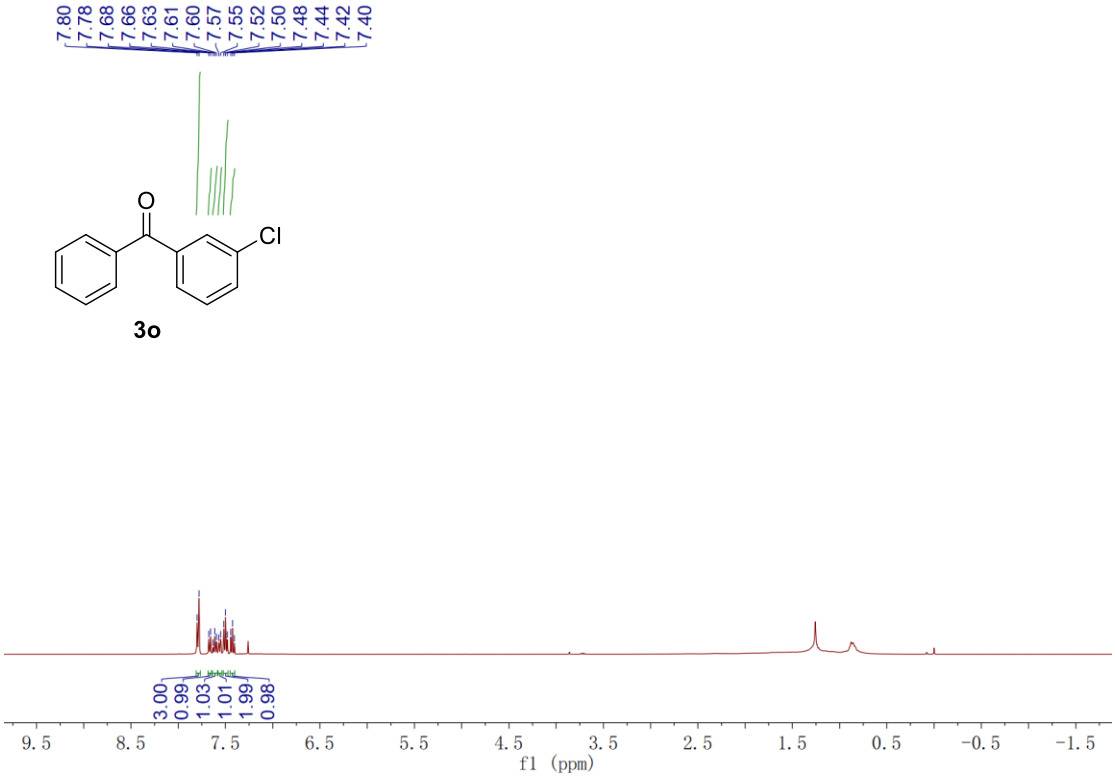


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3o**

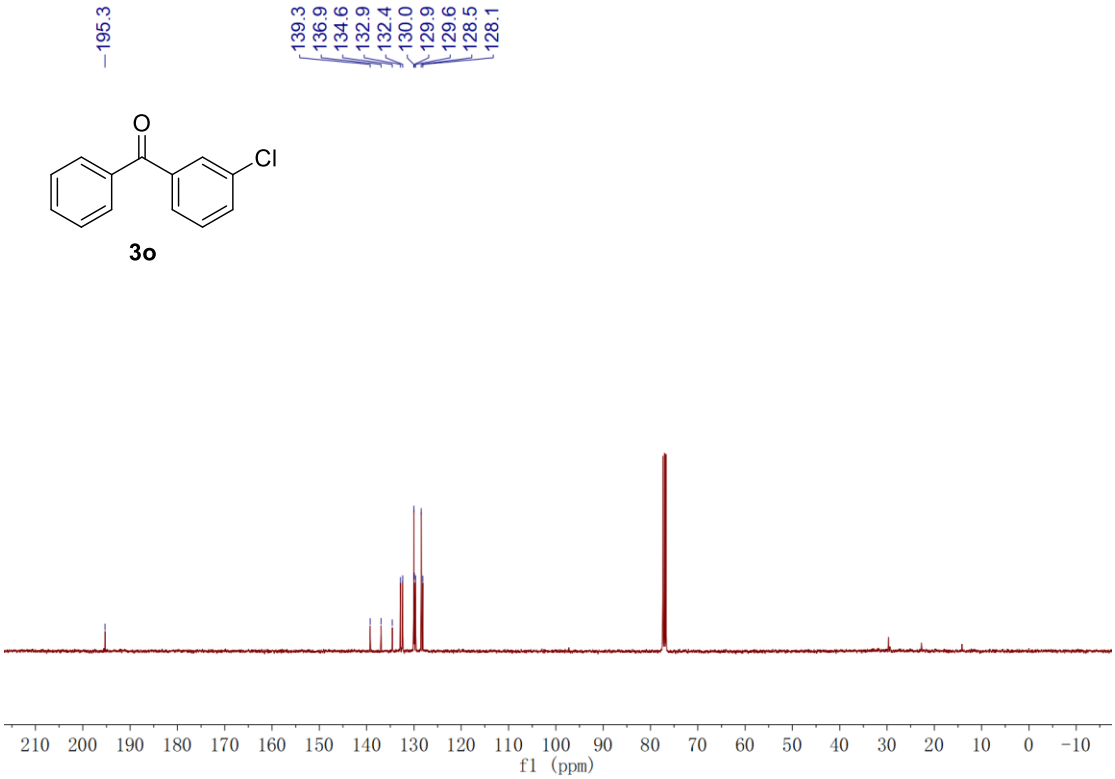


Figure S35. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3o**

(4-Chlorophenyl)(phenyl)methanone (3p).

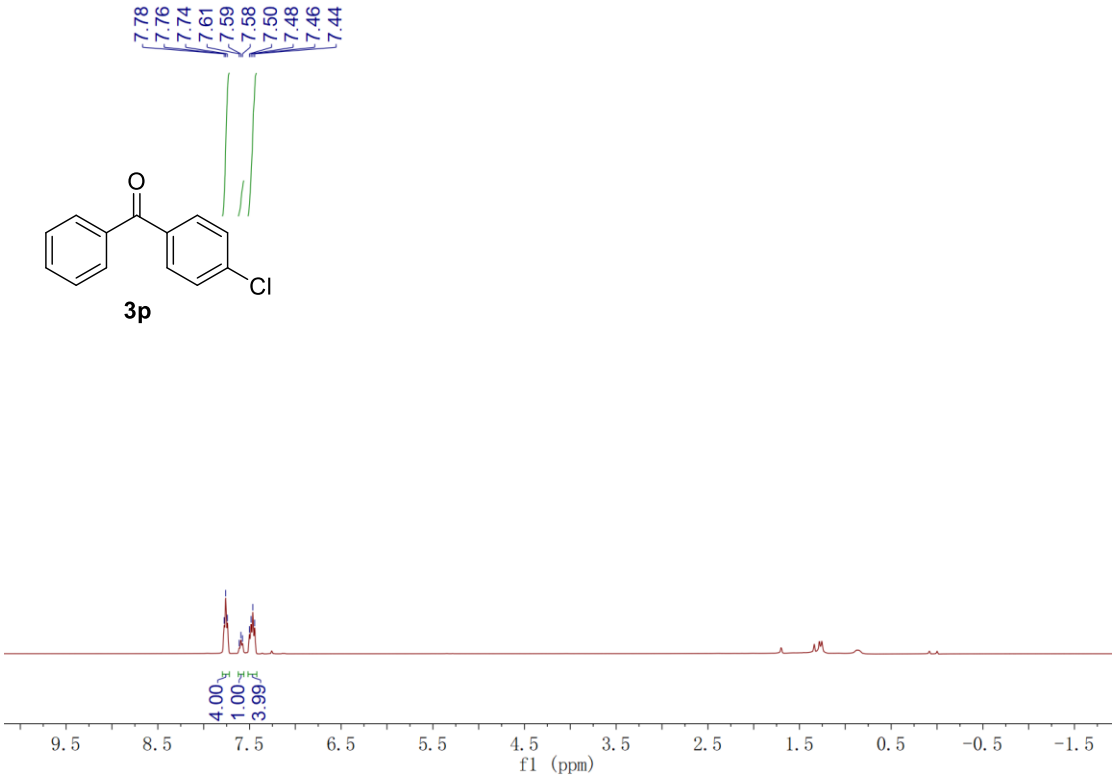


Figure S36 . ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3p**

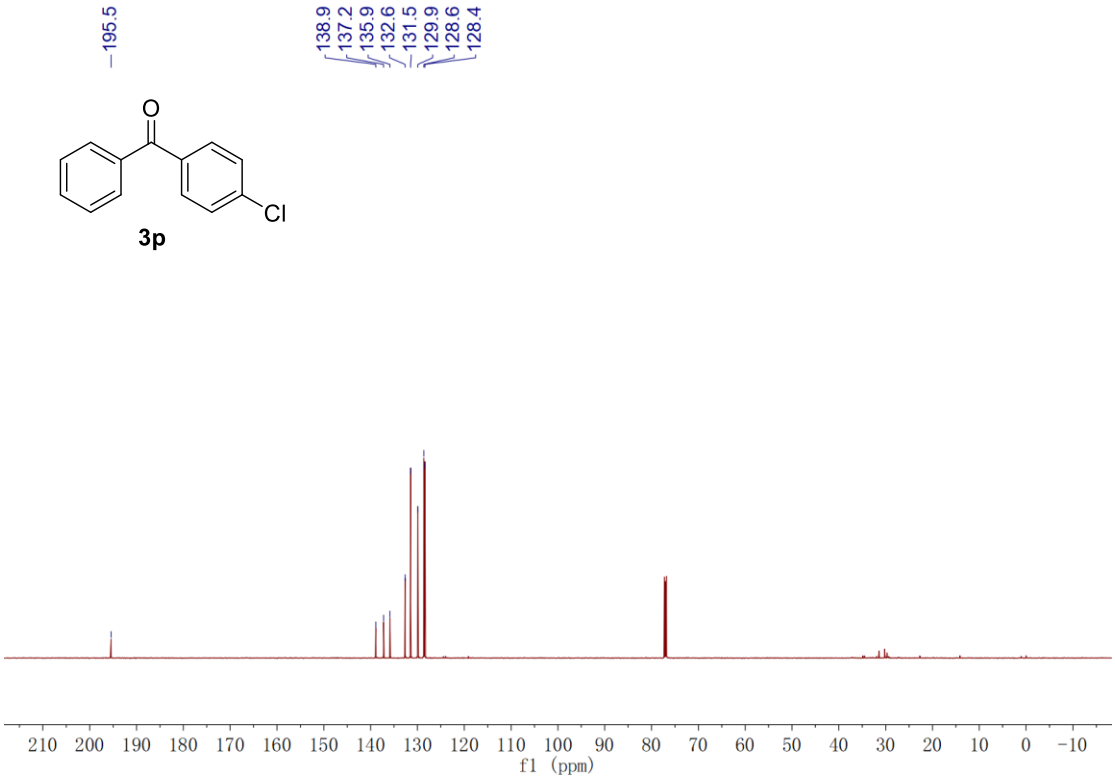


Figure S37. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3p**

Phenyl(*m*-tolyl) methanone (3q).

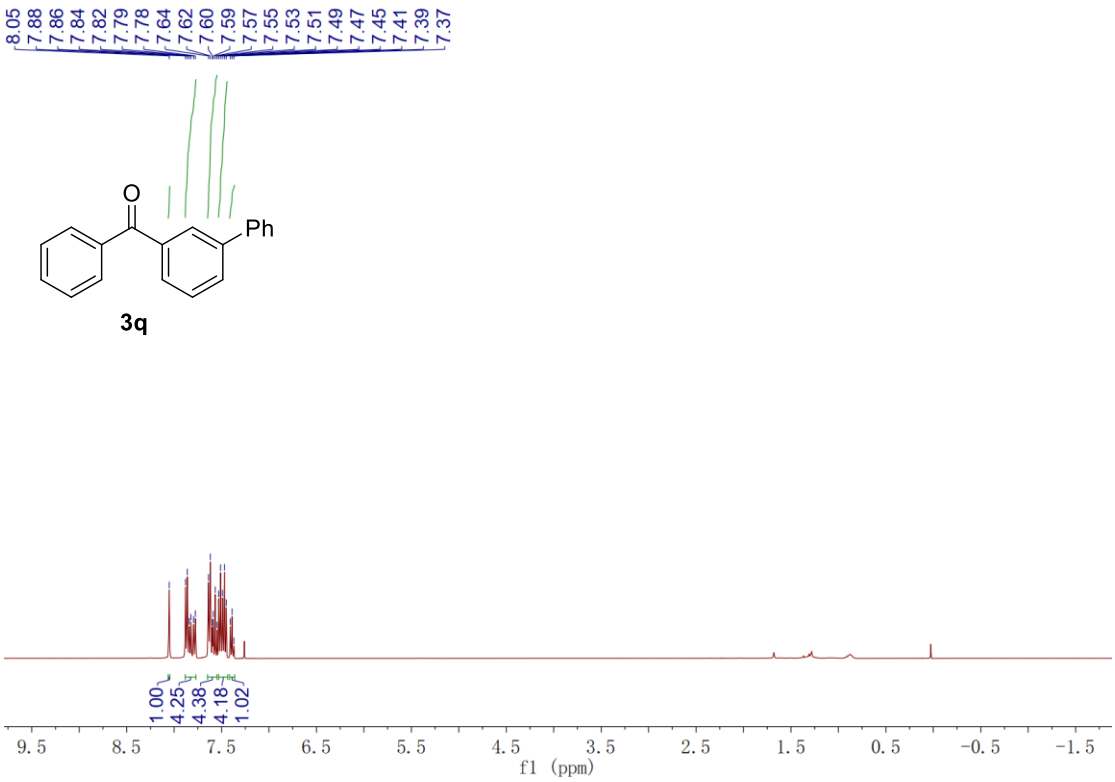


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3q**

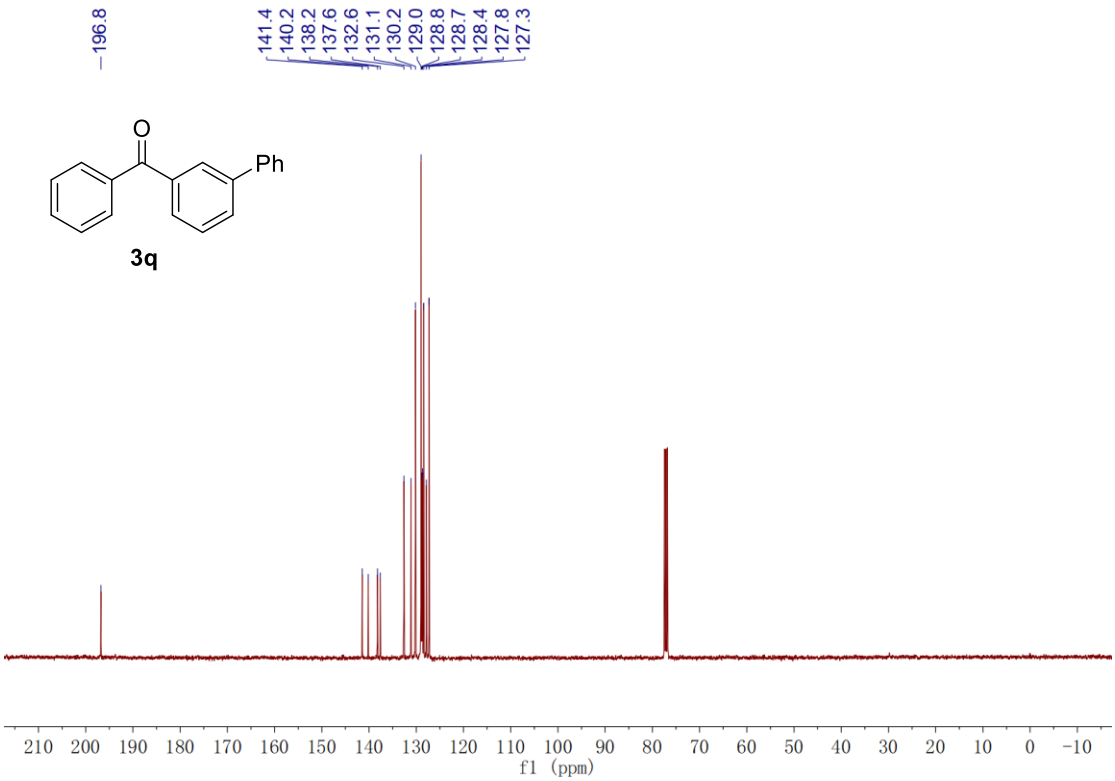


Figure S39 . ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3q**

Phenyl(*p*-tolyl) methanone (3r).

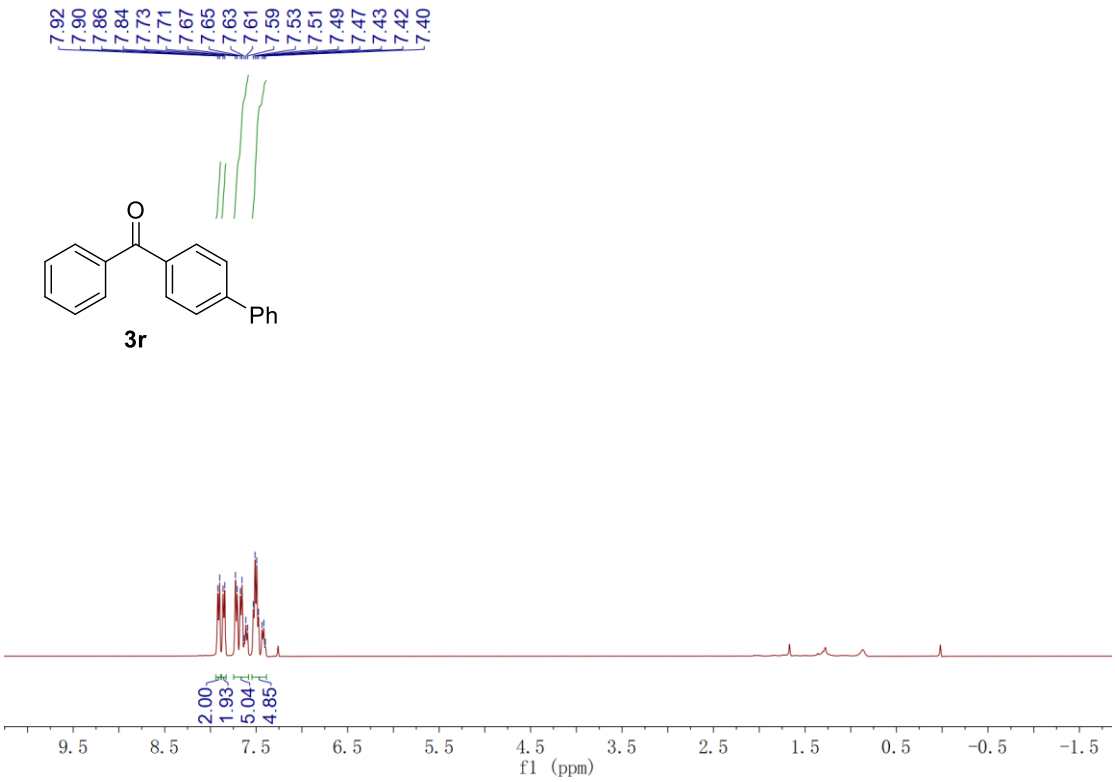


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3r**

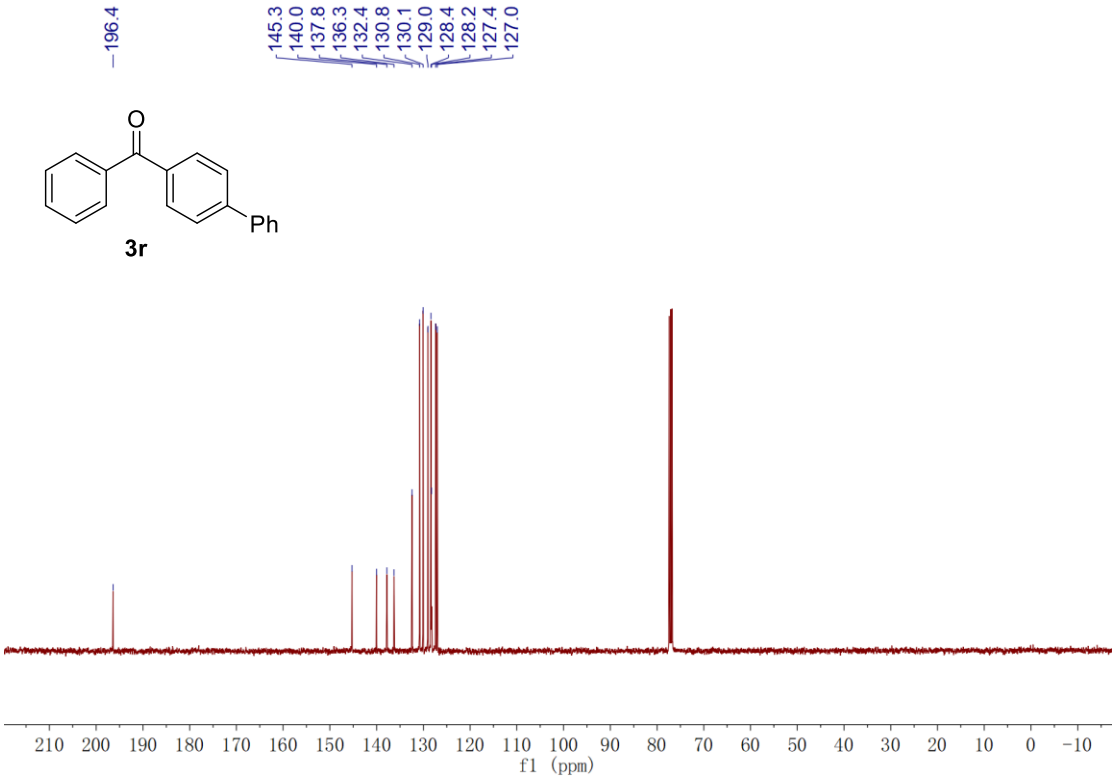


Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3r**

Naphthalen-1-yl(phenyl)methanone (3s).

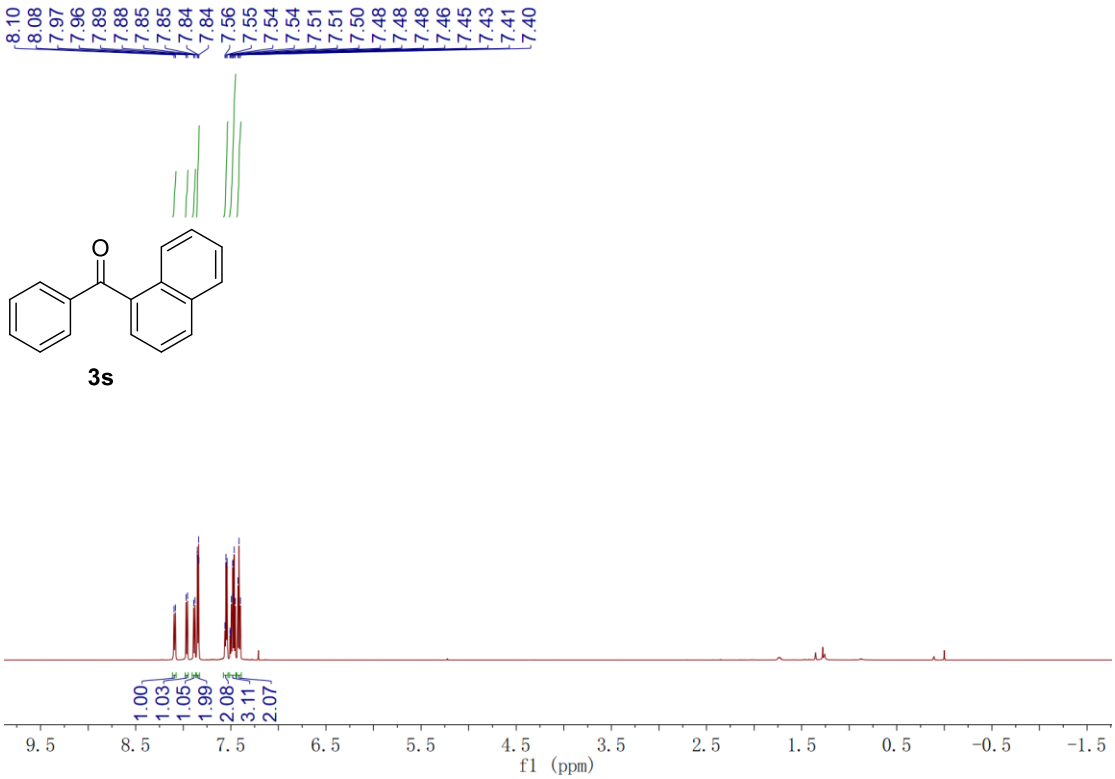


Figure S42. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3s**

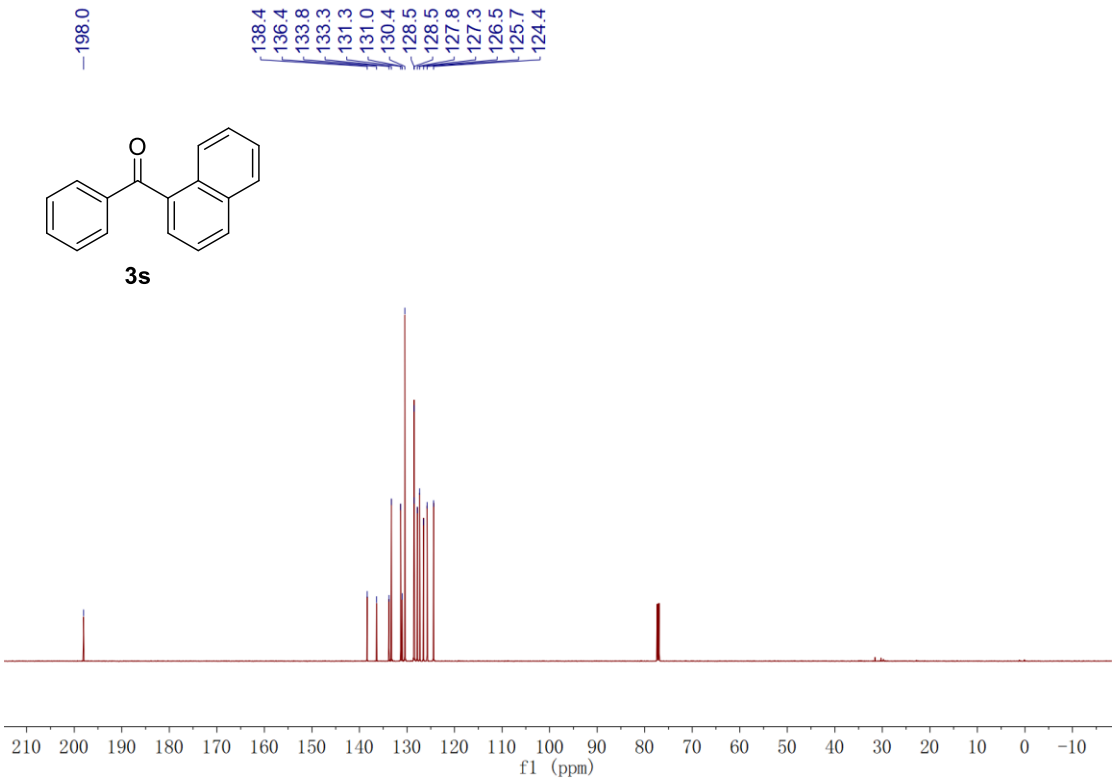


Figure S43. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3s**

Naphthalen-2-yl(phenyl)methanone (3t).

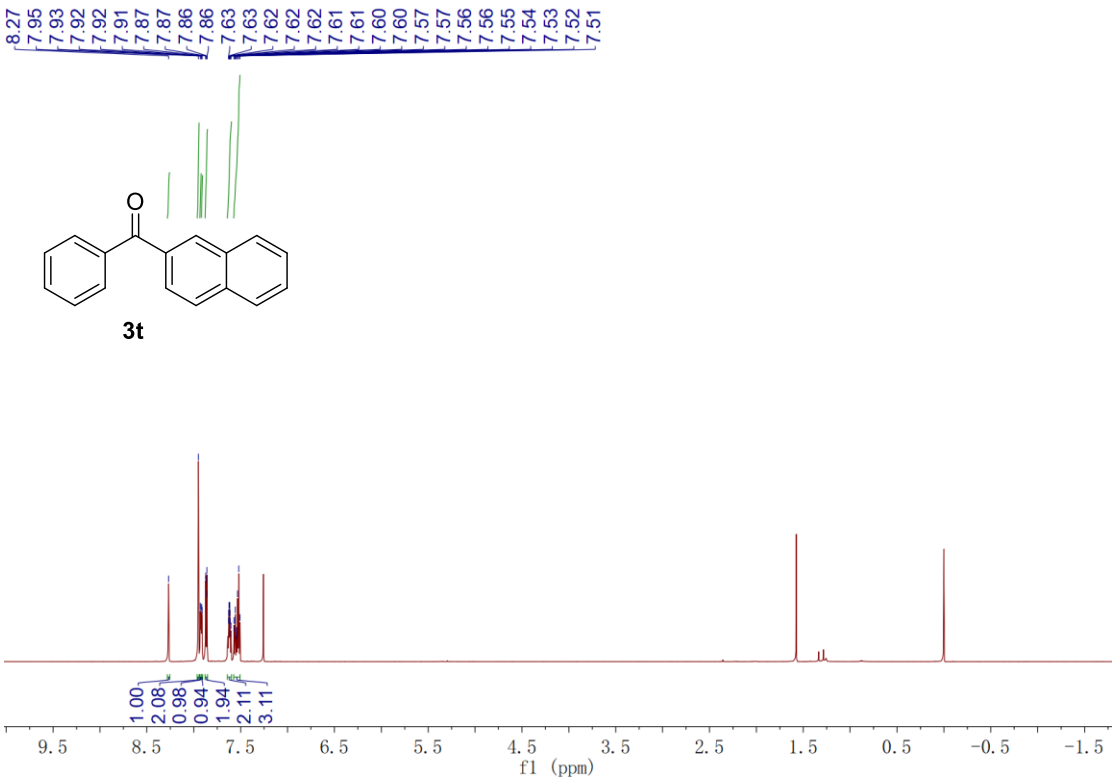


Figure S44. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3t**

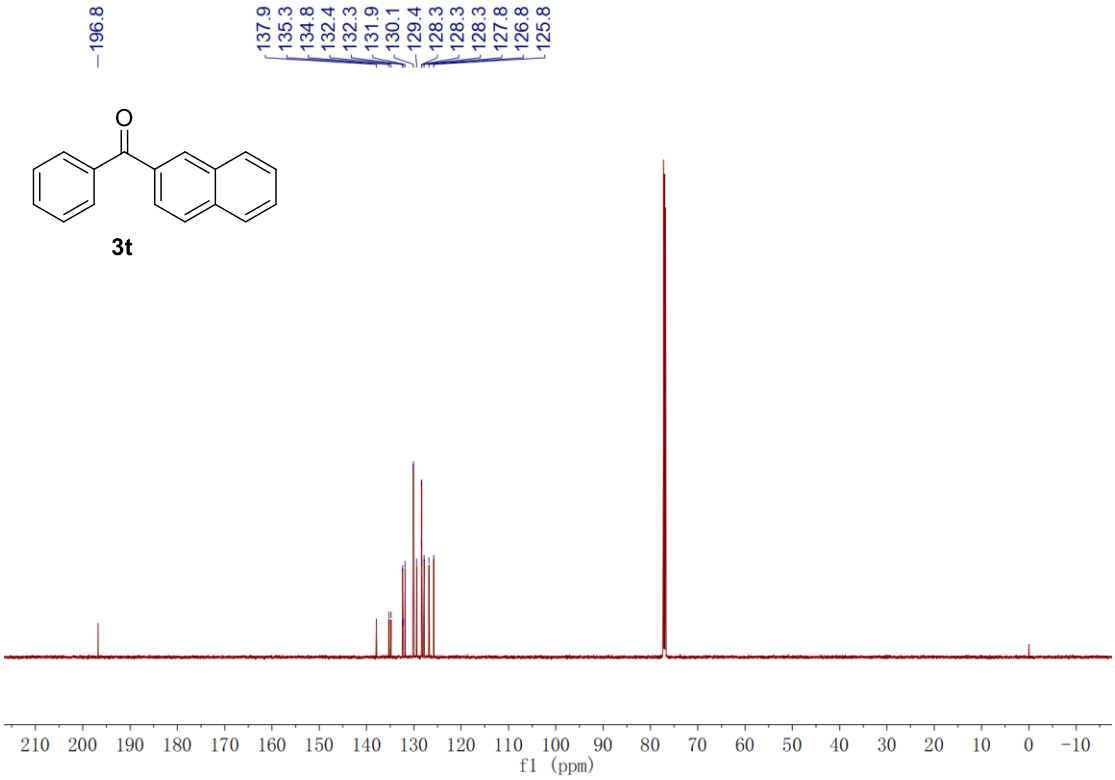


Figure S45. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3t**

Methyl 4-benzoylbenzoate (3u).

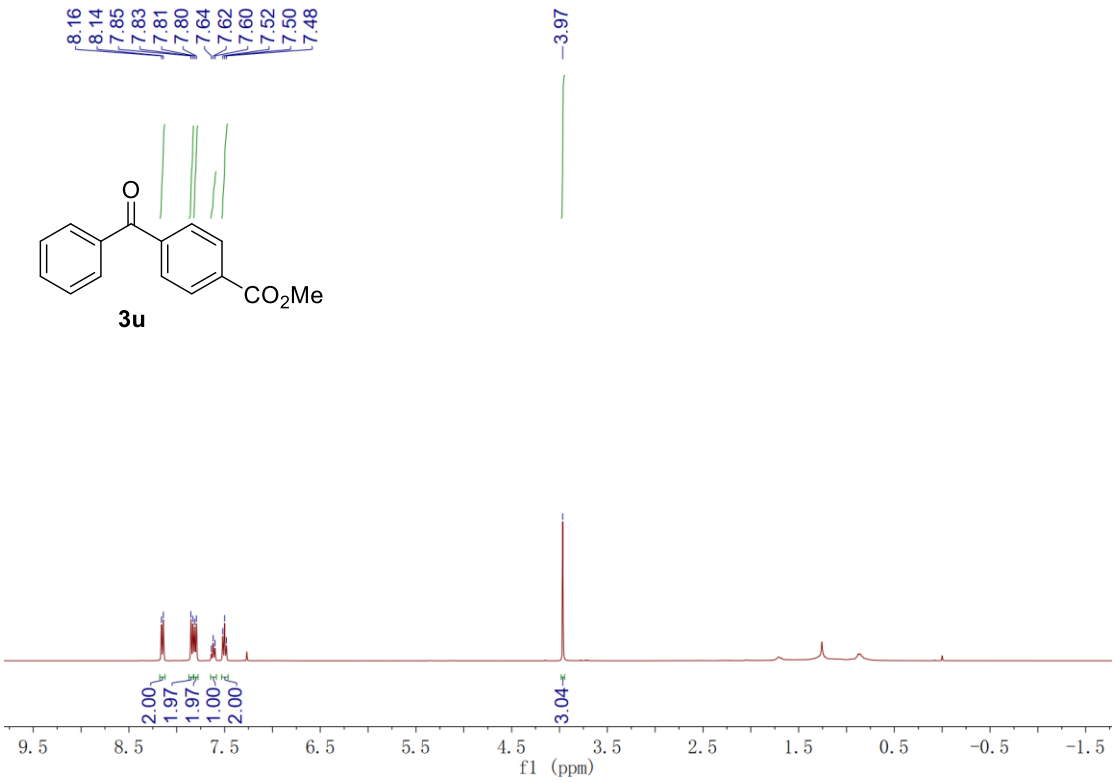


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3u**

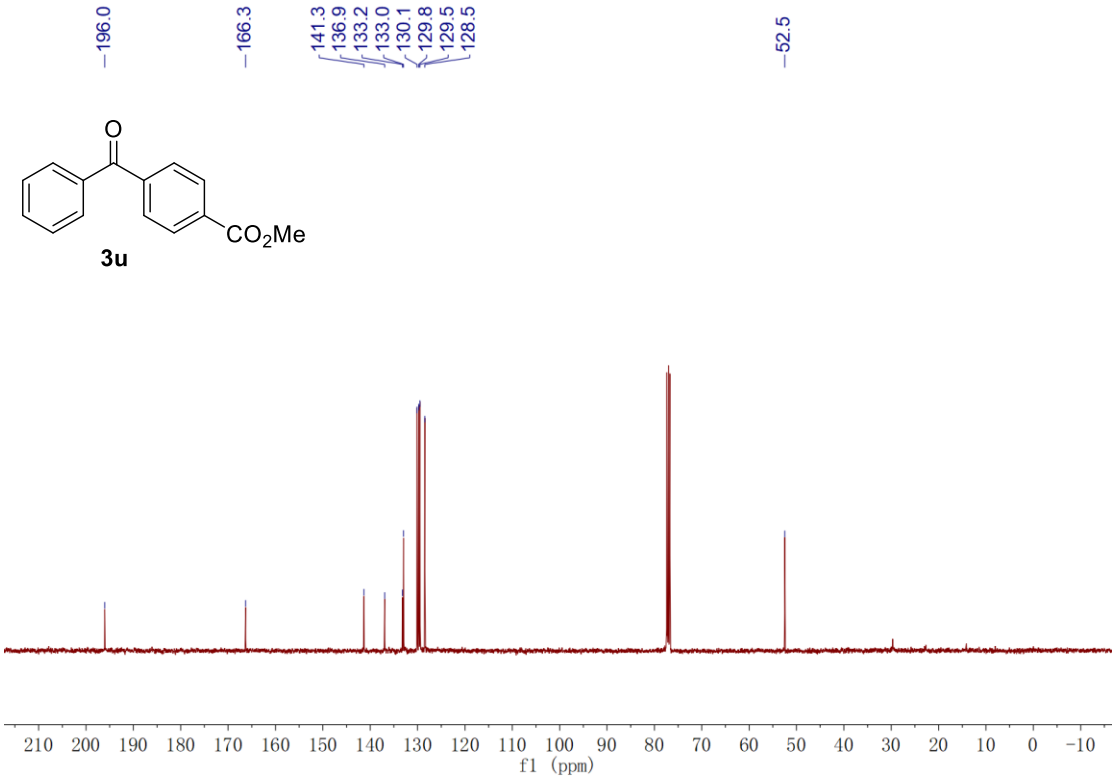


Figure S47. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3u**

1-(4-Benzoylphenyl)ethan-1-one (3v).

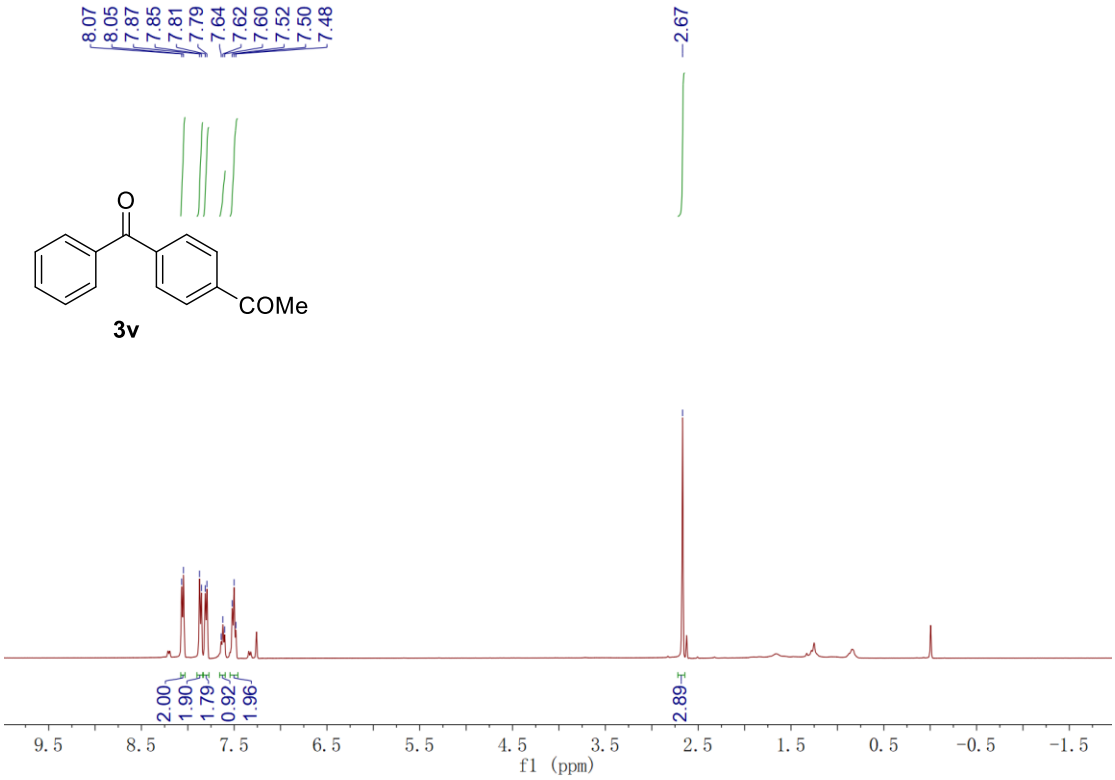


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3v**

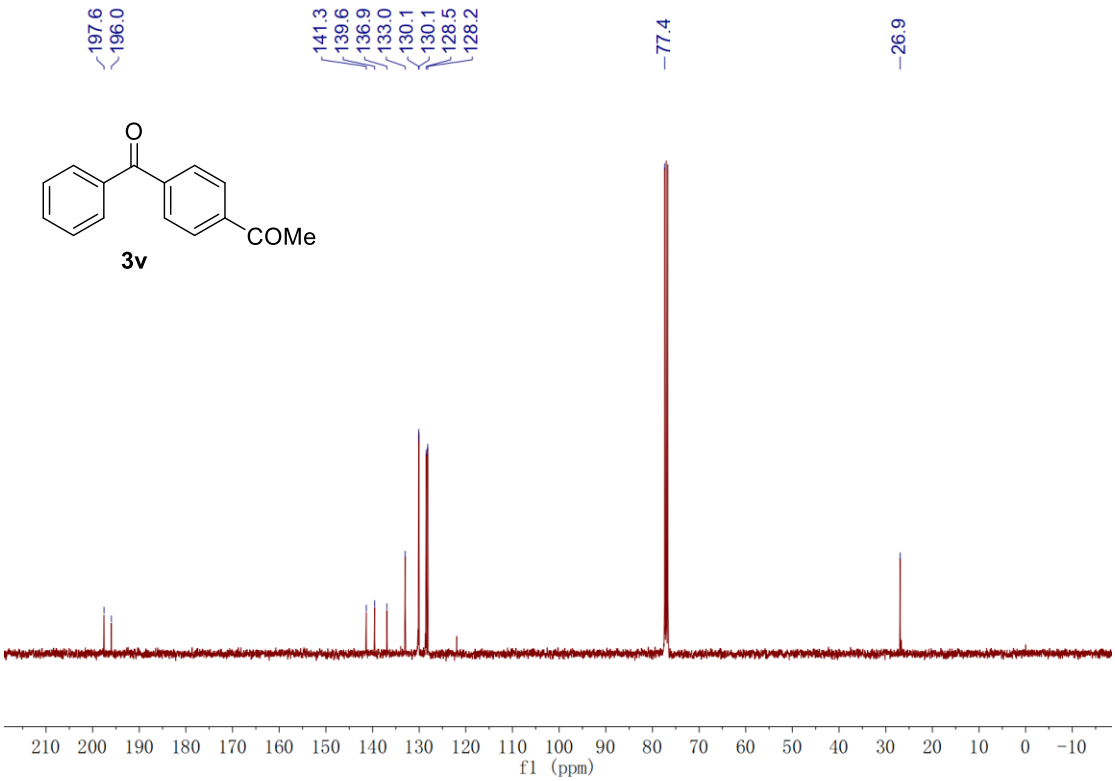


Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3v**

Phenyl(thiophen-3-yl)methanone (3w).

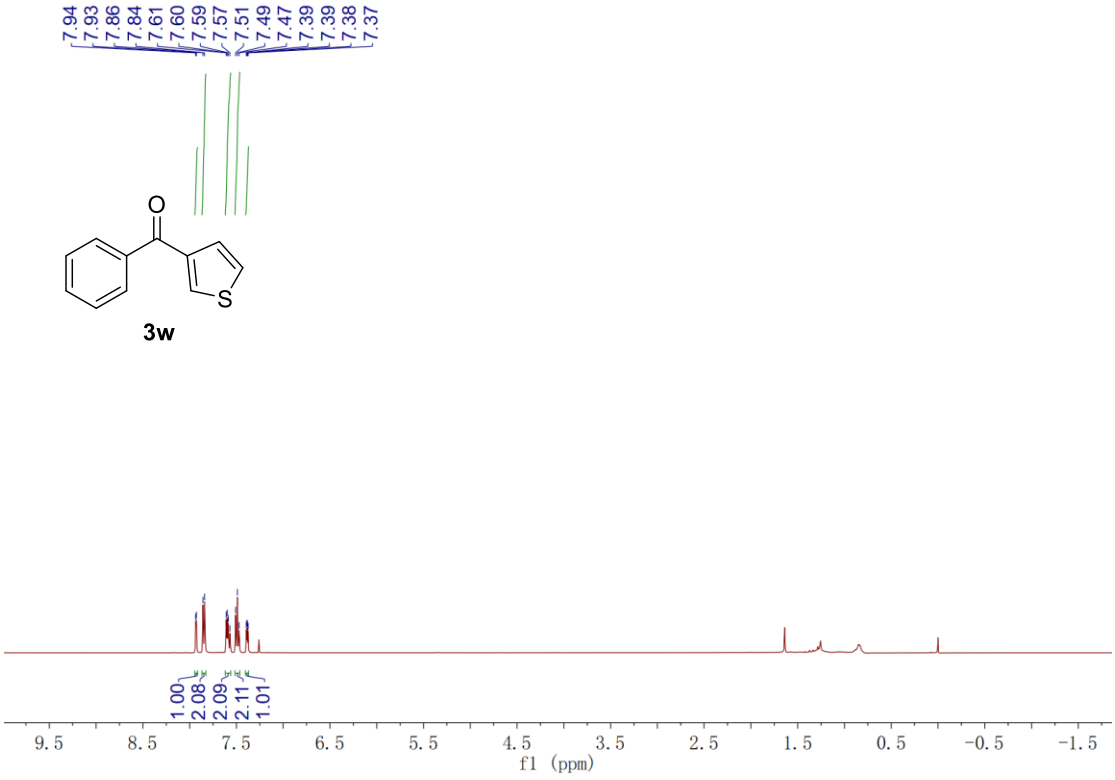


Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3w**

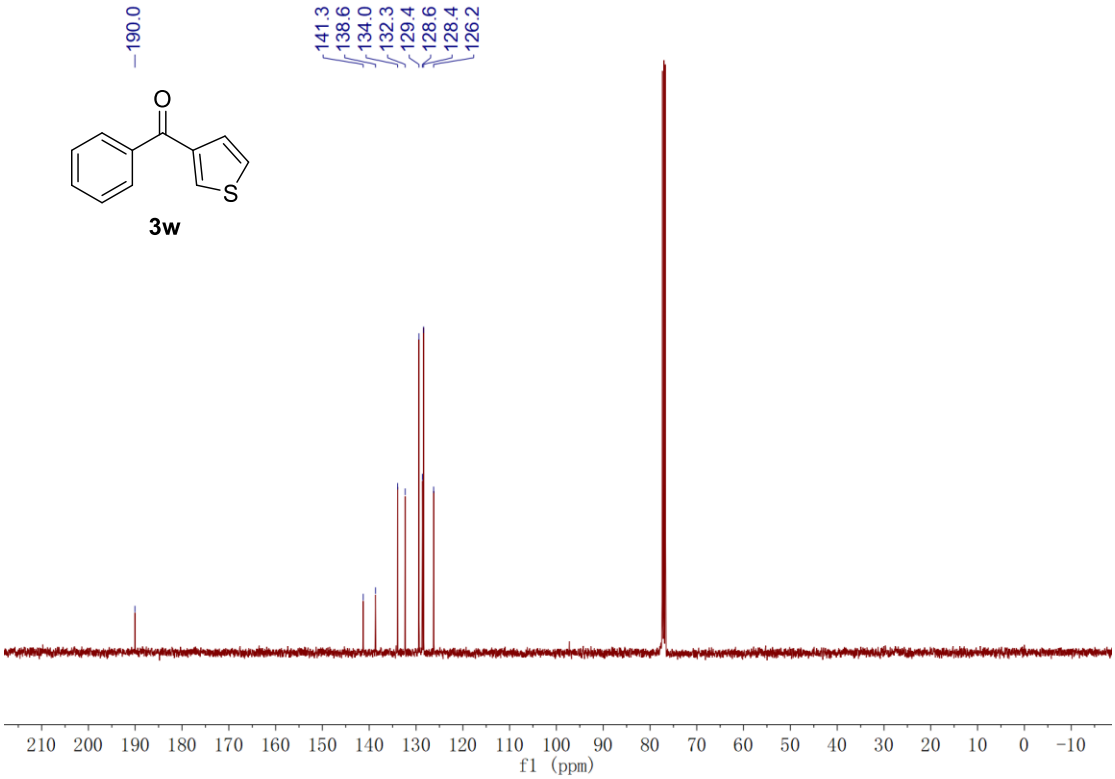


Figure S51. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3w**

Furan-3-yl(phenyl)methanone (3x).

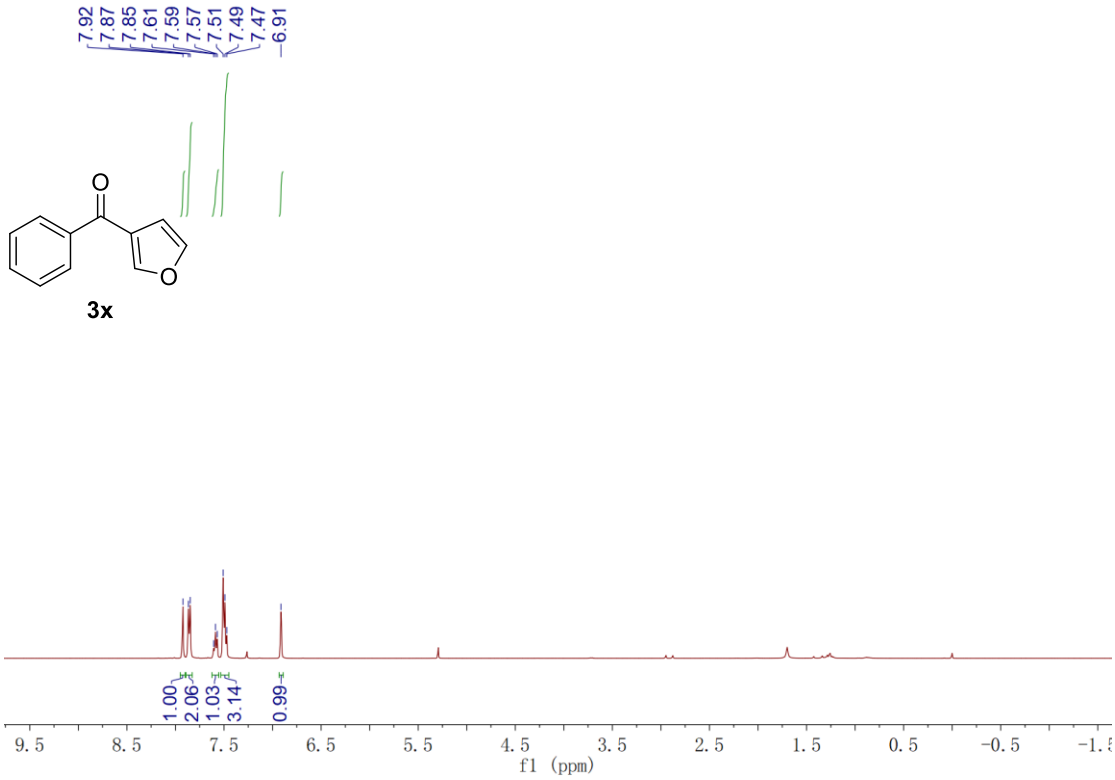


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3x**

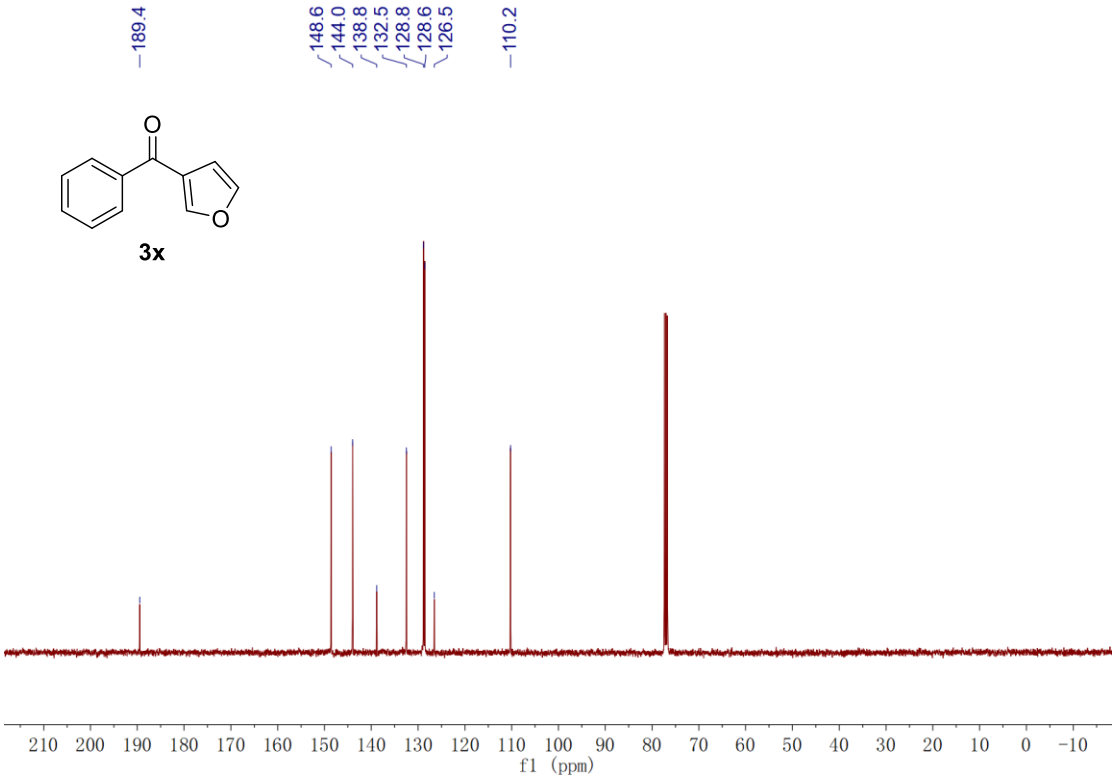


Figure S53. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3x**

Phenyl(thiophen-2-yl)methanone (3y).

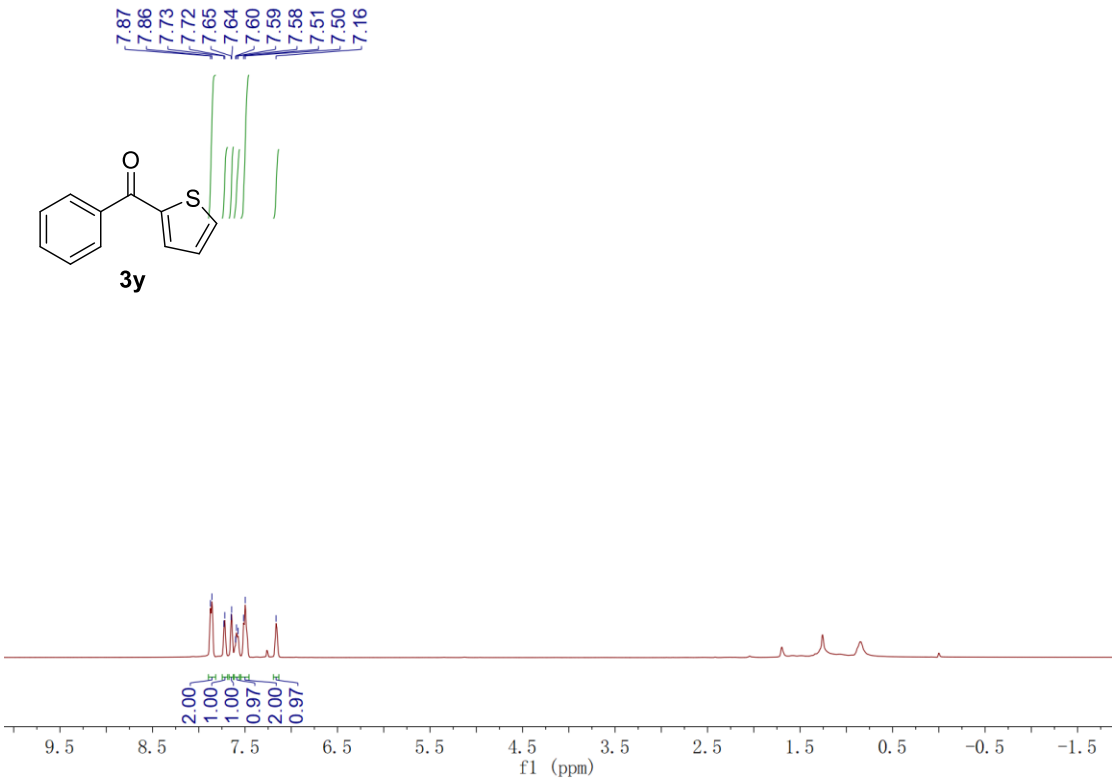


Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3y**

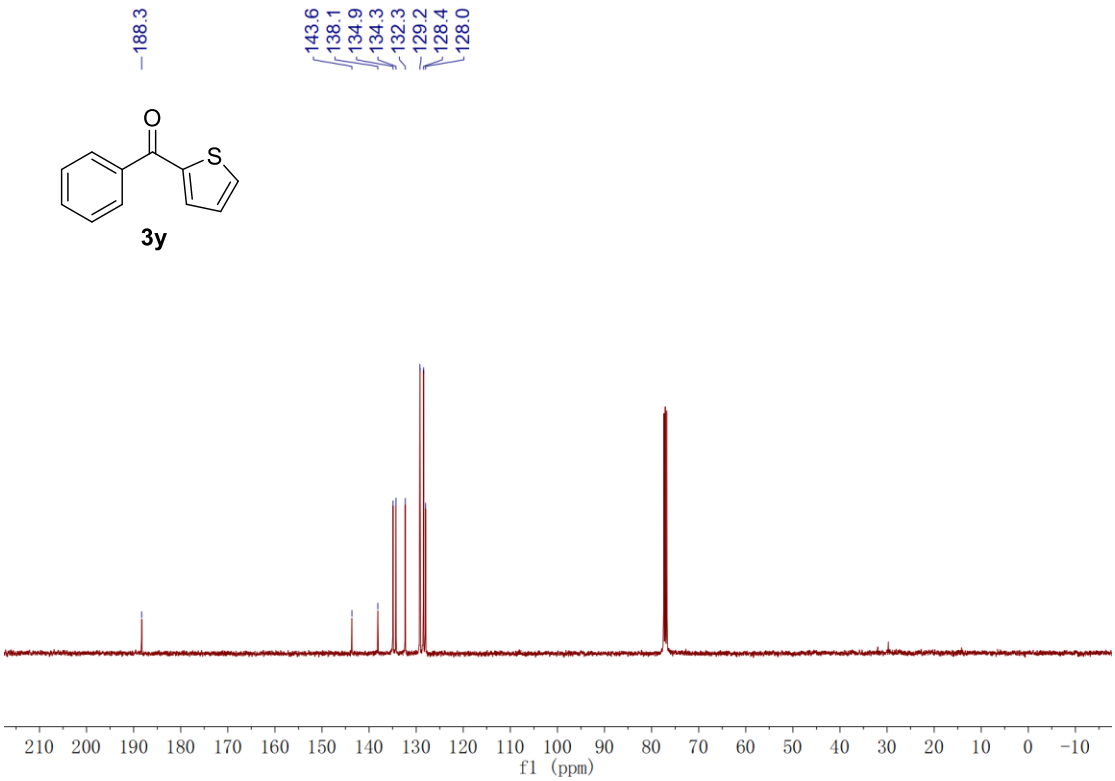


Figure S55. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3y**

Furan-2-yl(phenyl)methanone (3z).

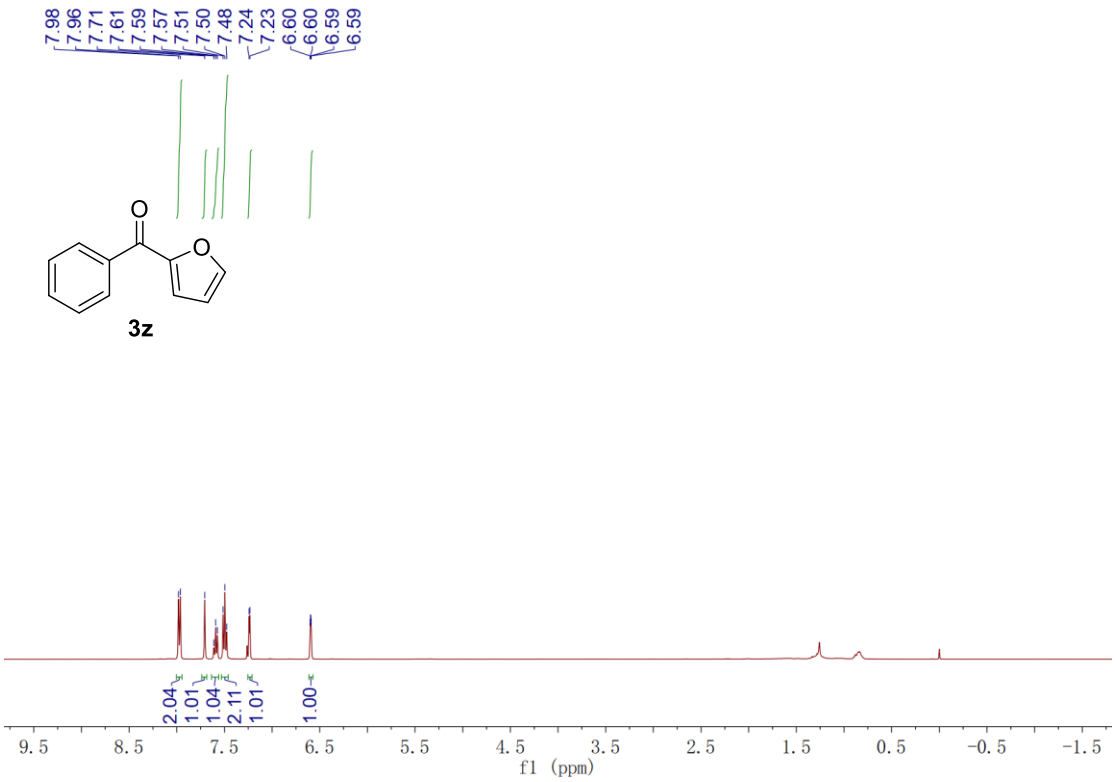


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3z**

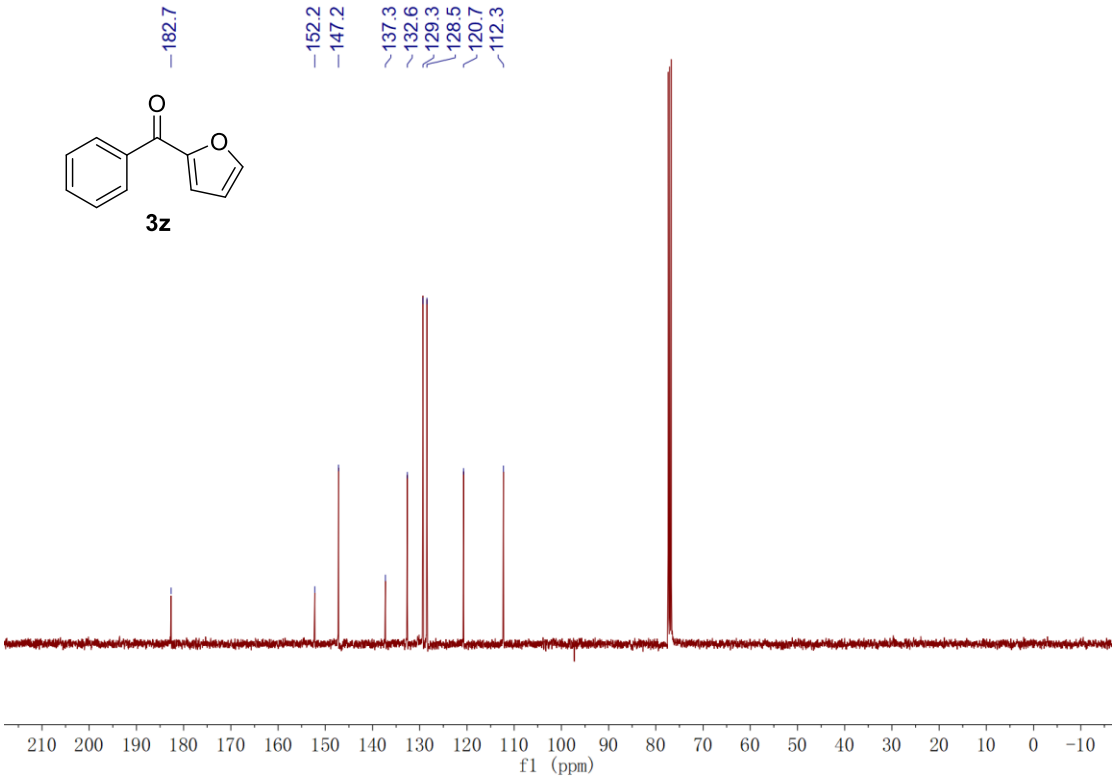


Figure S57. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3z**

Benzo[*b*]thiophen-2-yl(phenyl)methanone (3aa).

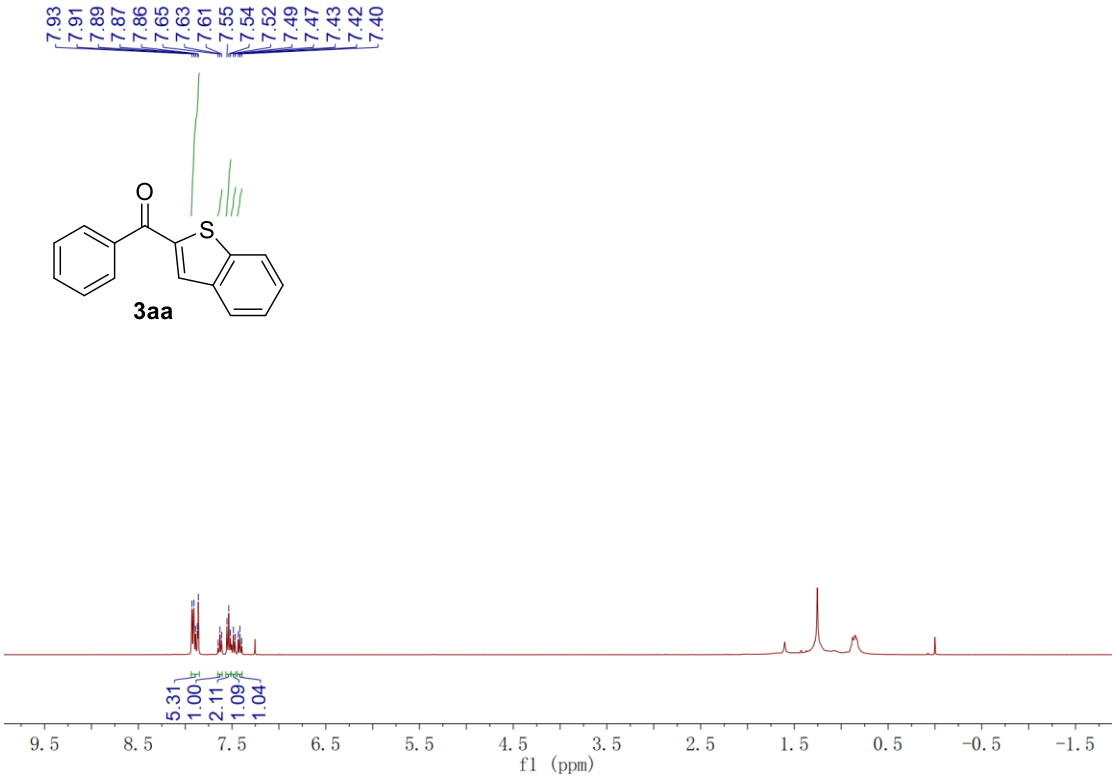


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3aa**

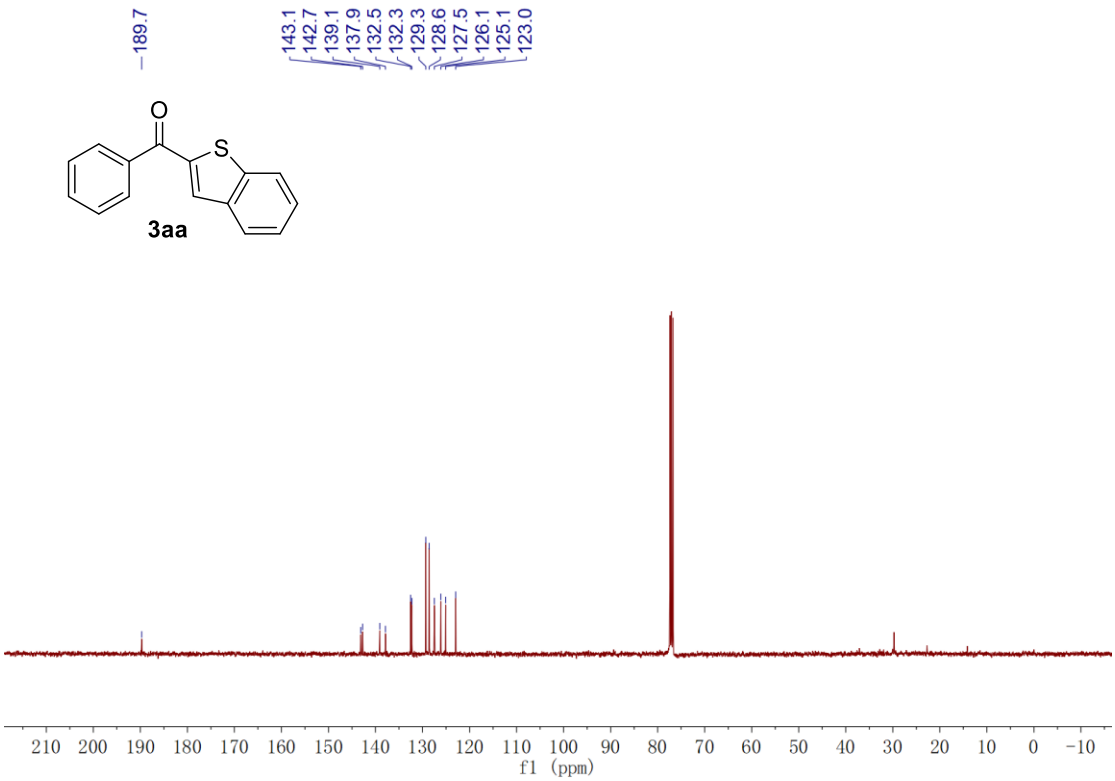


Figure S59. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3aa**

(4-Ethenylphenyl)phenylmethanone (3ab).

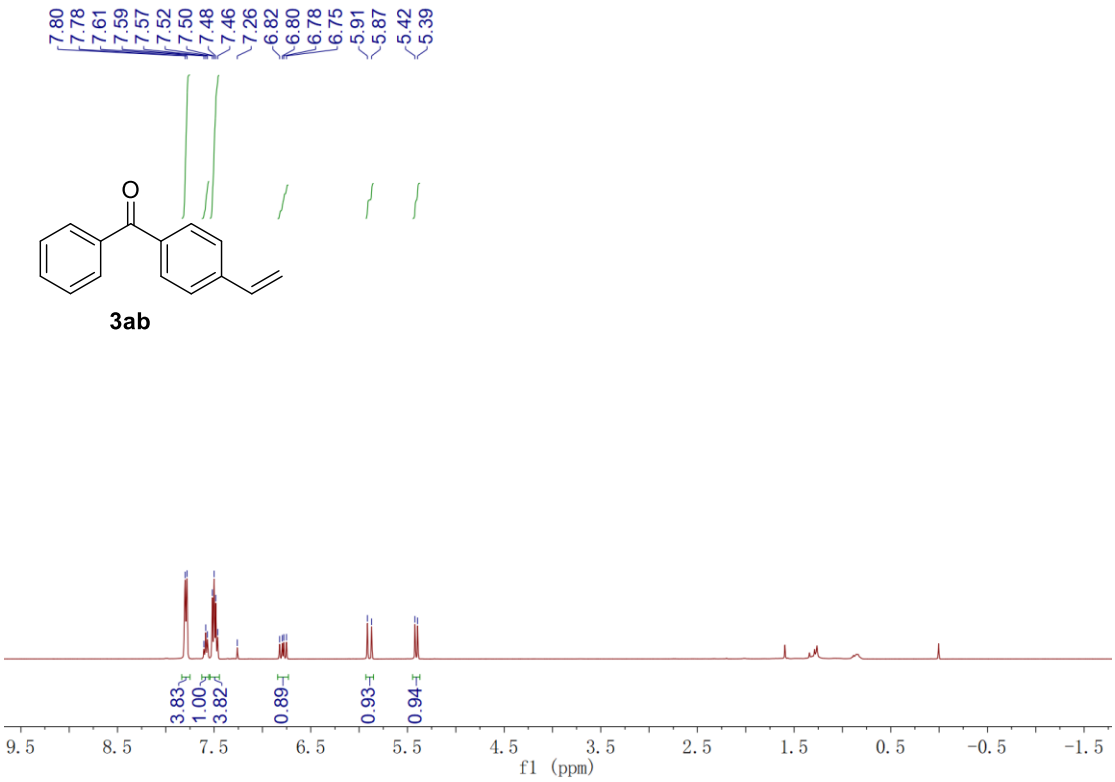


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3ab**

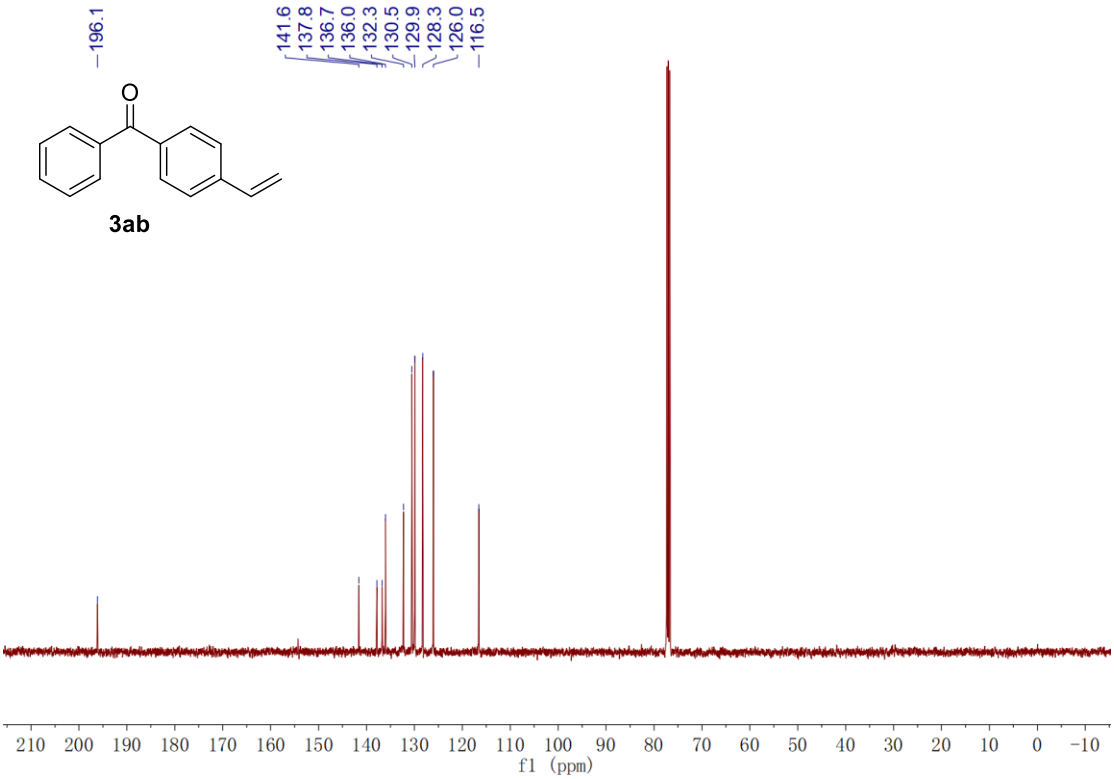


Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3ab**

4-tert-Butylbenzophenone (3ac).

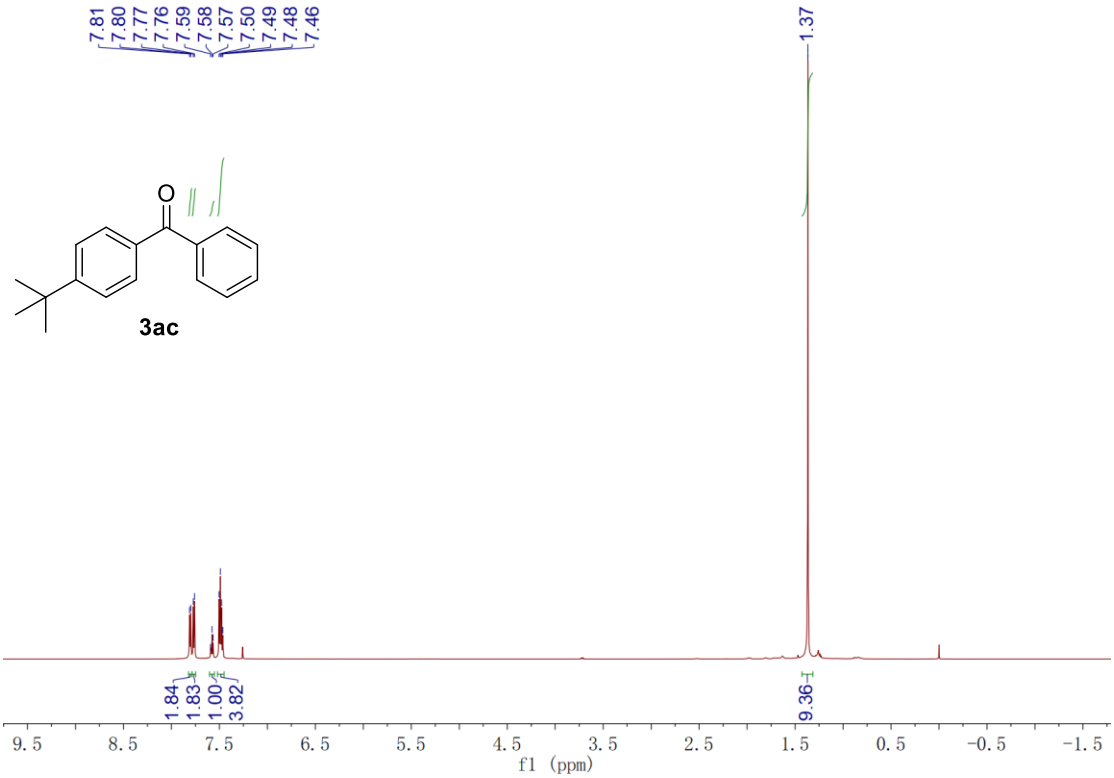


Figure S62. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3ac**

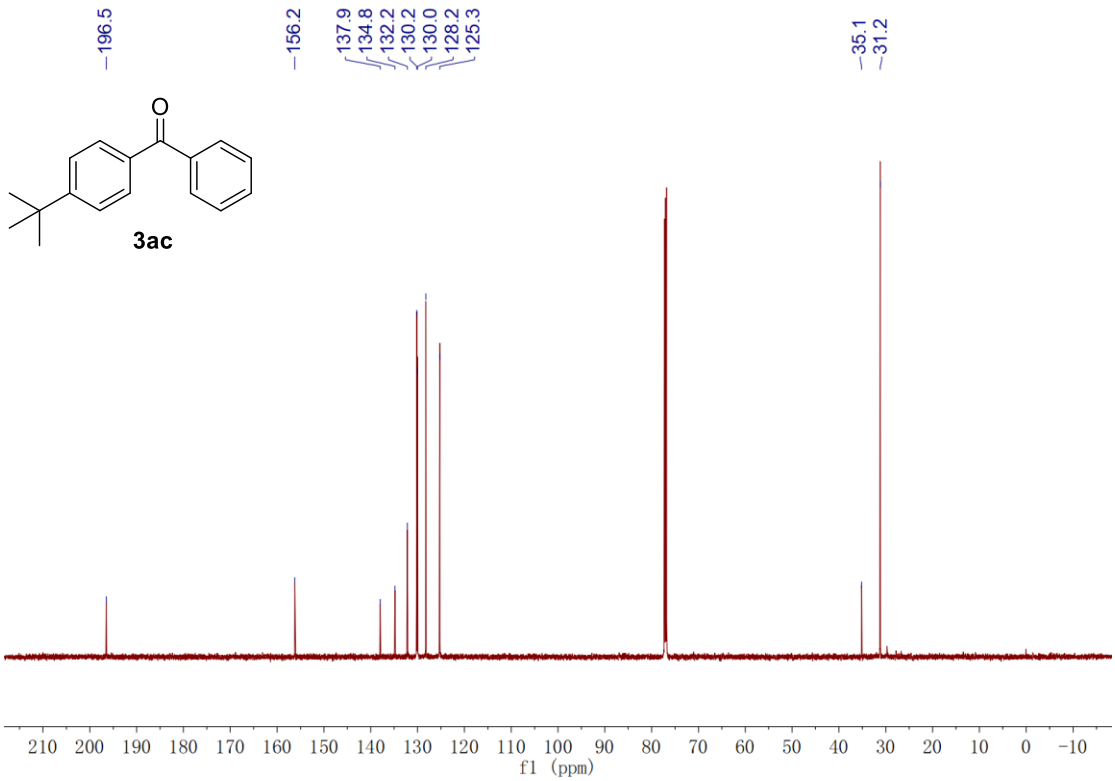


Figure S63. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3ac**

Phenyl(2-(trifluoromethyl)phenyl)methano (3ad).

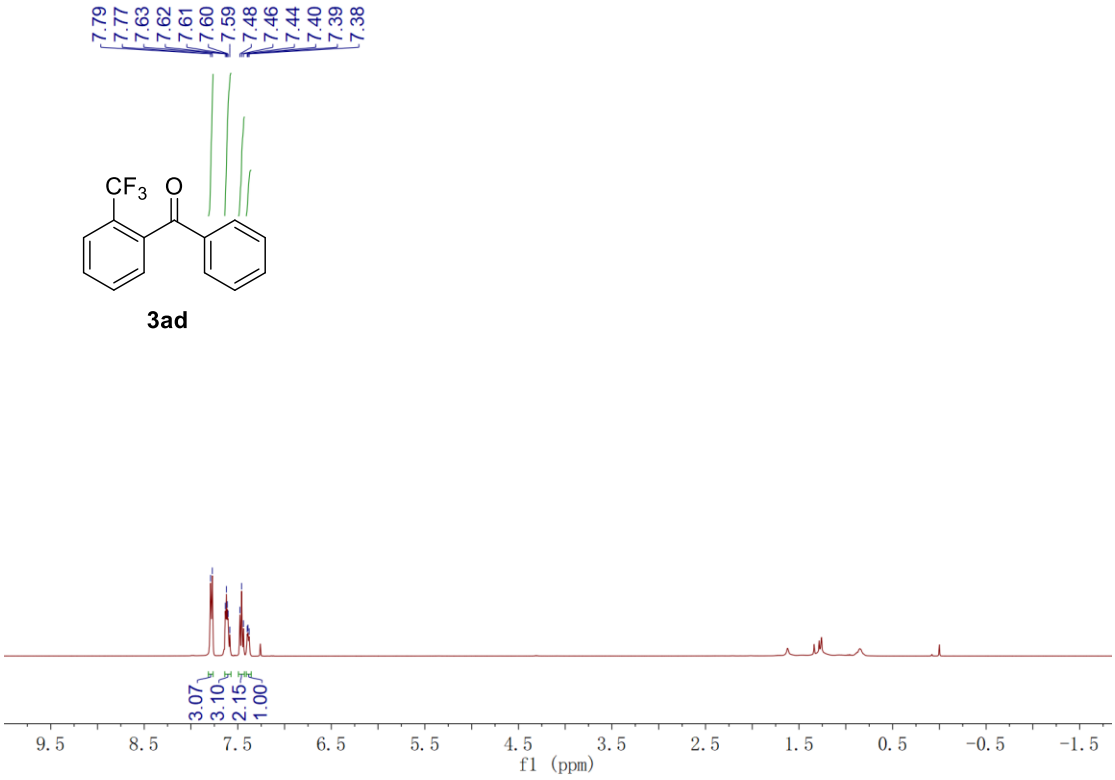


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3ad**

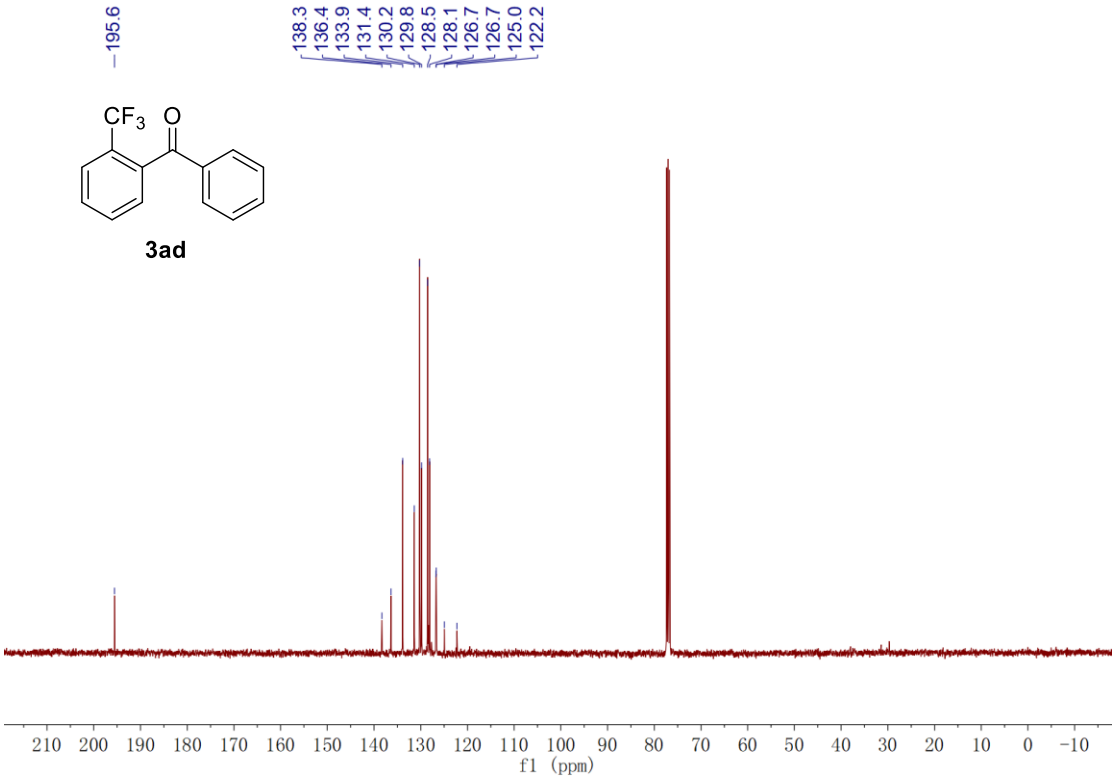


Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3ad**

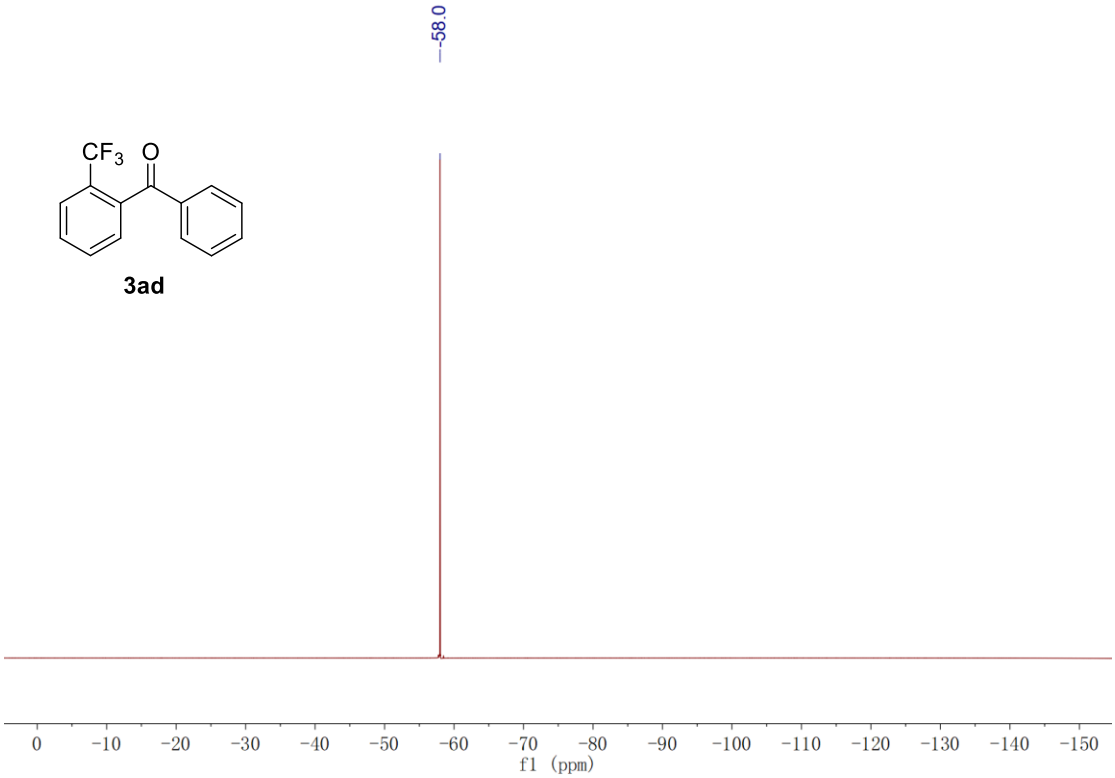


Figure S66. ^{19}F (376 MHz, $CDCl_3$) Spectrum of Compound **3ad**

(4-Bromophenyl)phenylmethanone (3ae).

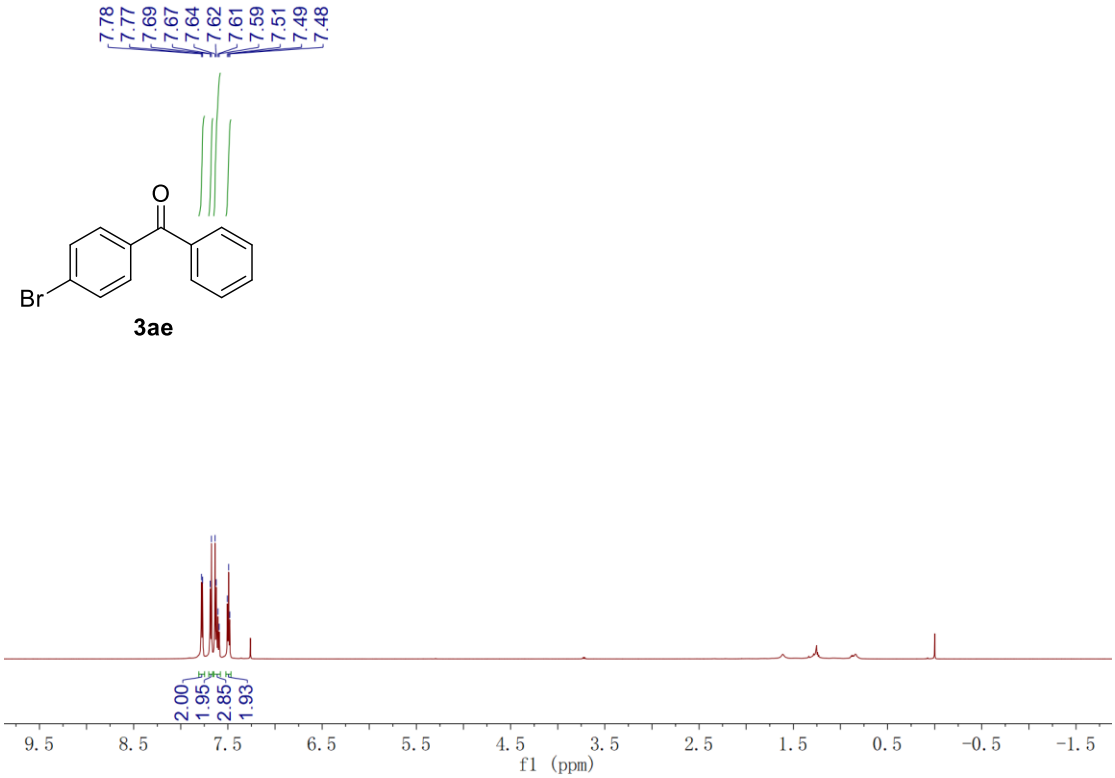


Figure S67. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3ae**

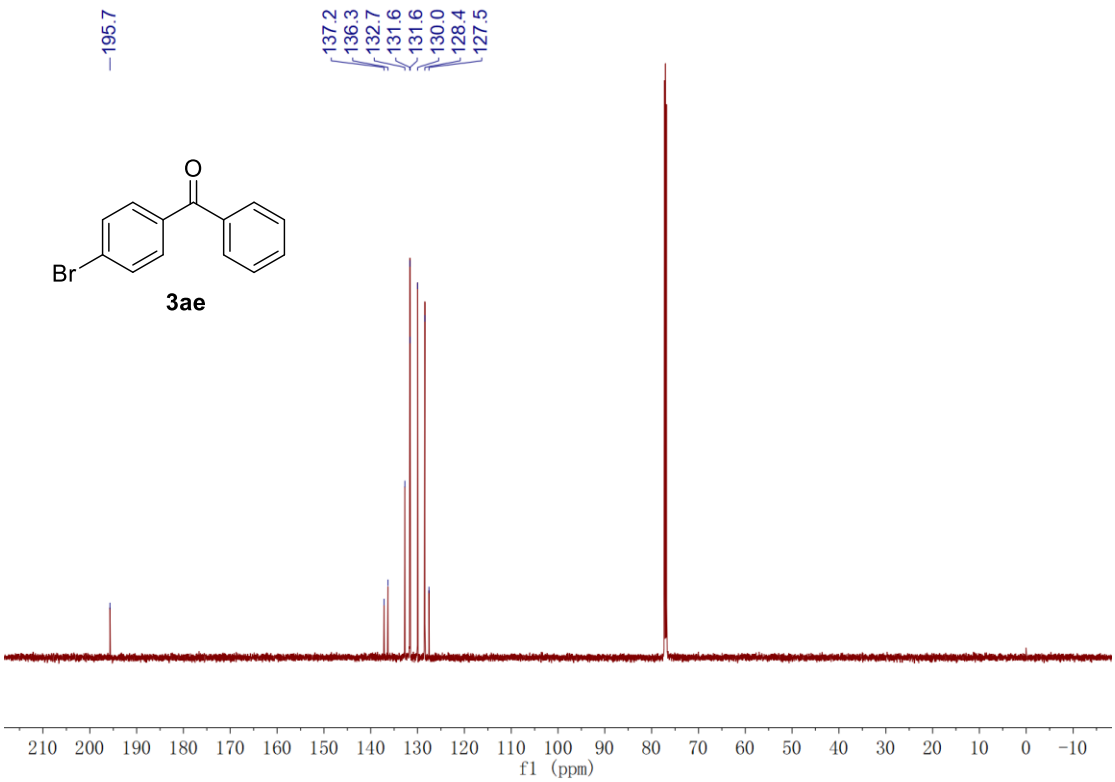


Figure S68. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3ae**

4-Benzoylbenzonitrile (3af).

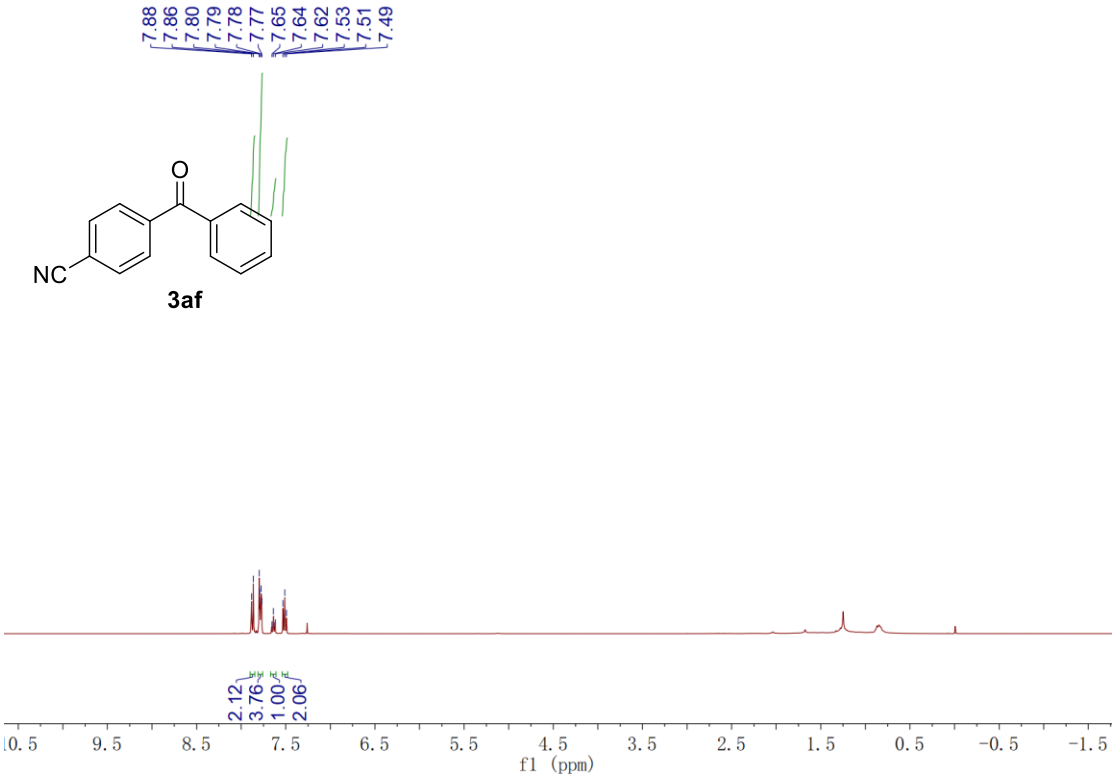


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3af**

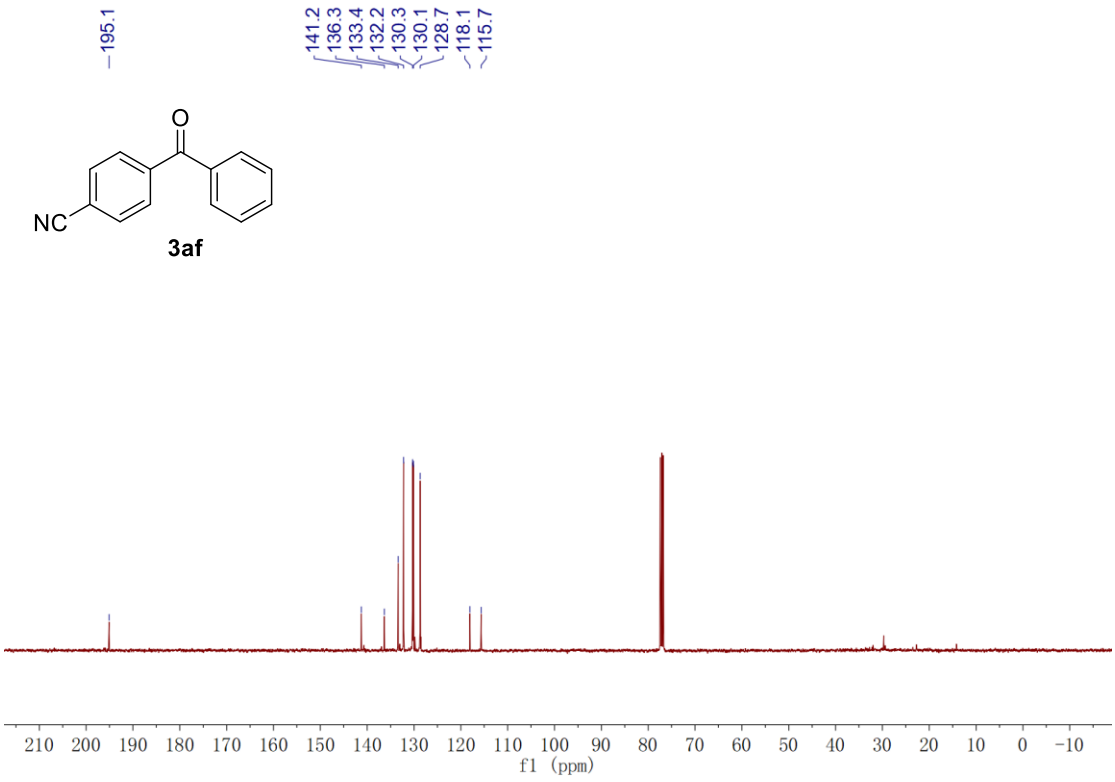


Figure S70. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3af**

(4-Nitrophenyl)(phenyl)methanone (3ag).

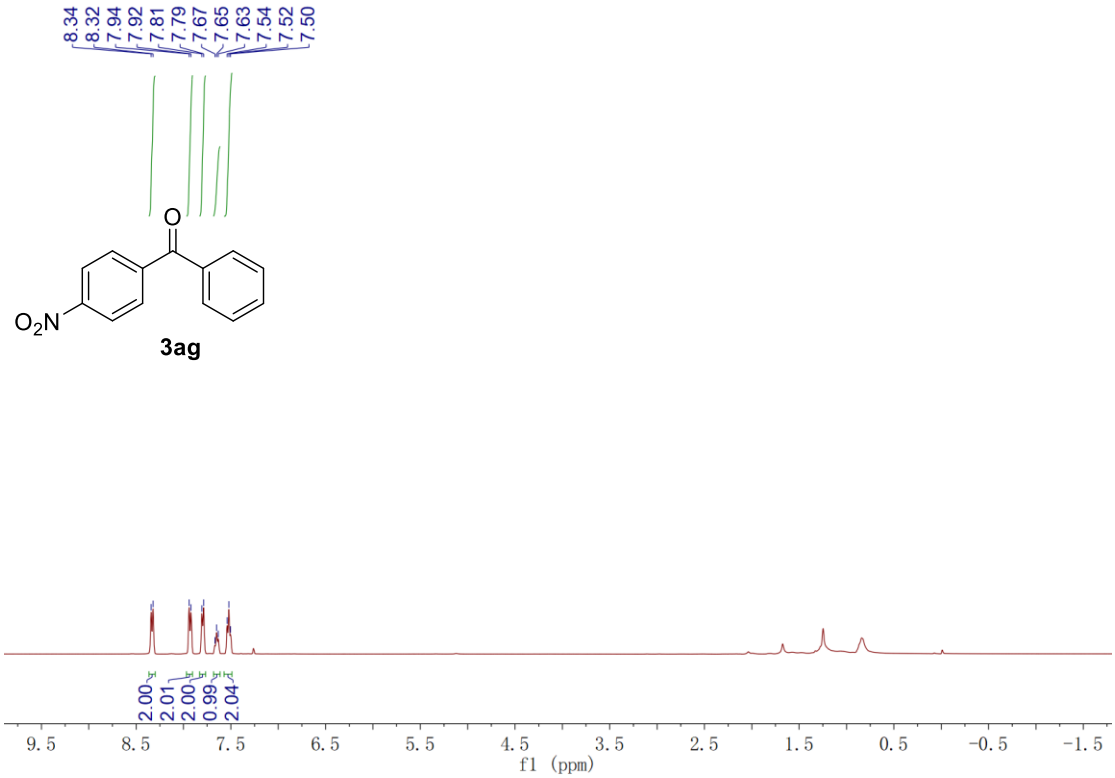


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3ag**

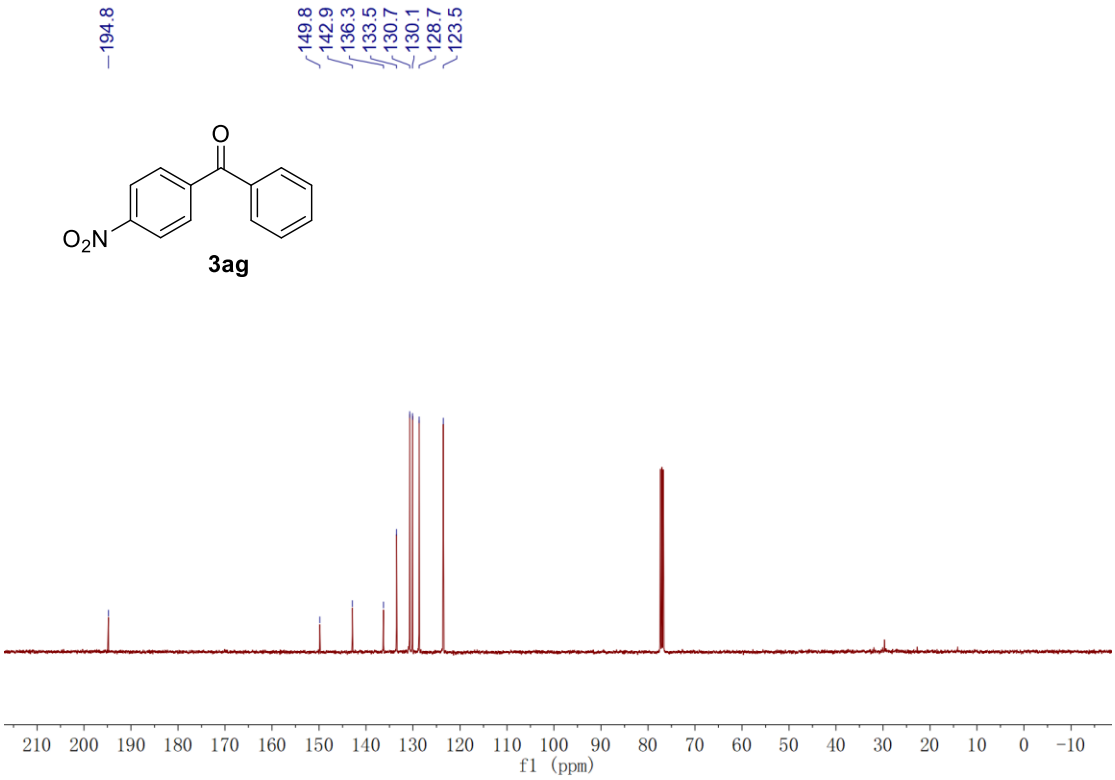


Figure S72. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3ag**

(4-methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (3ah).

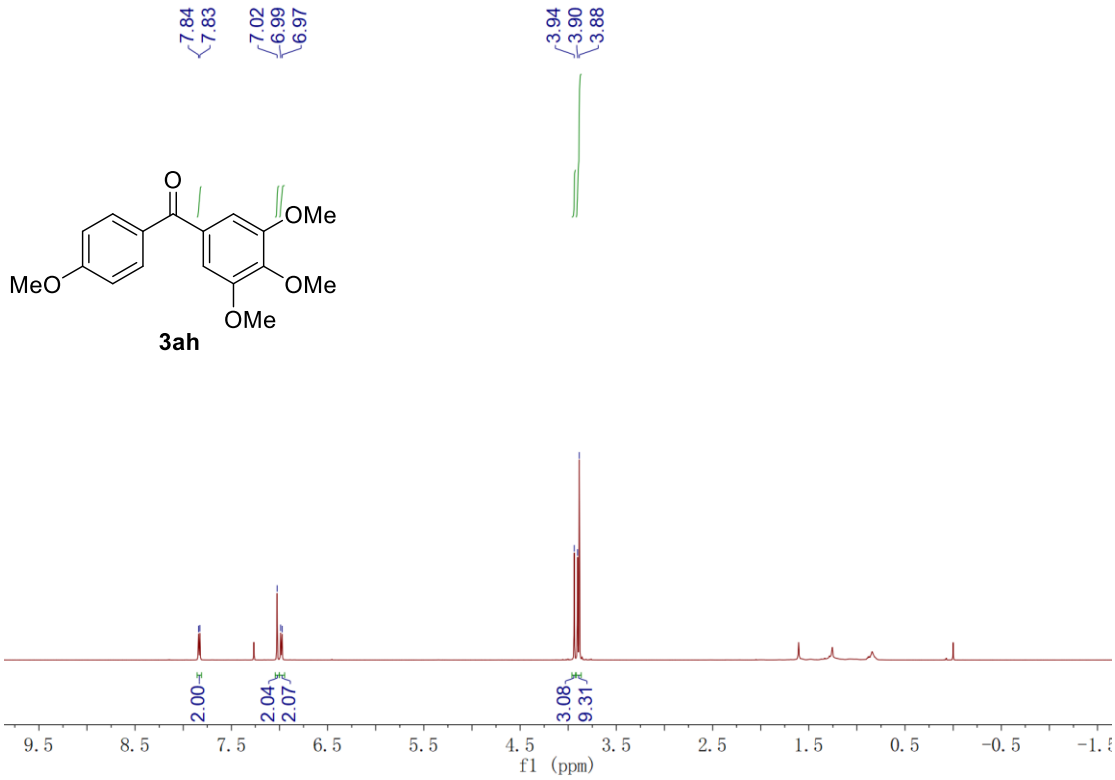


Figure S73. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **3ah**

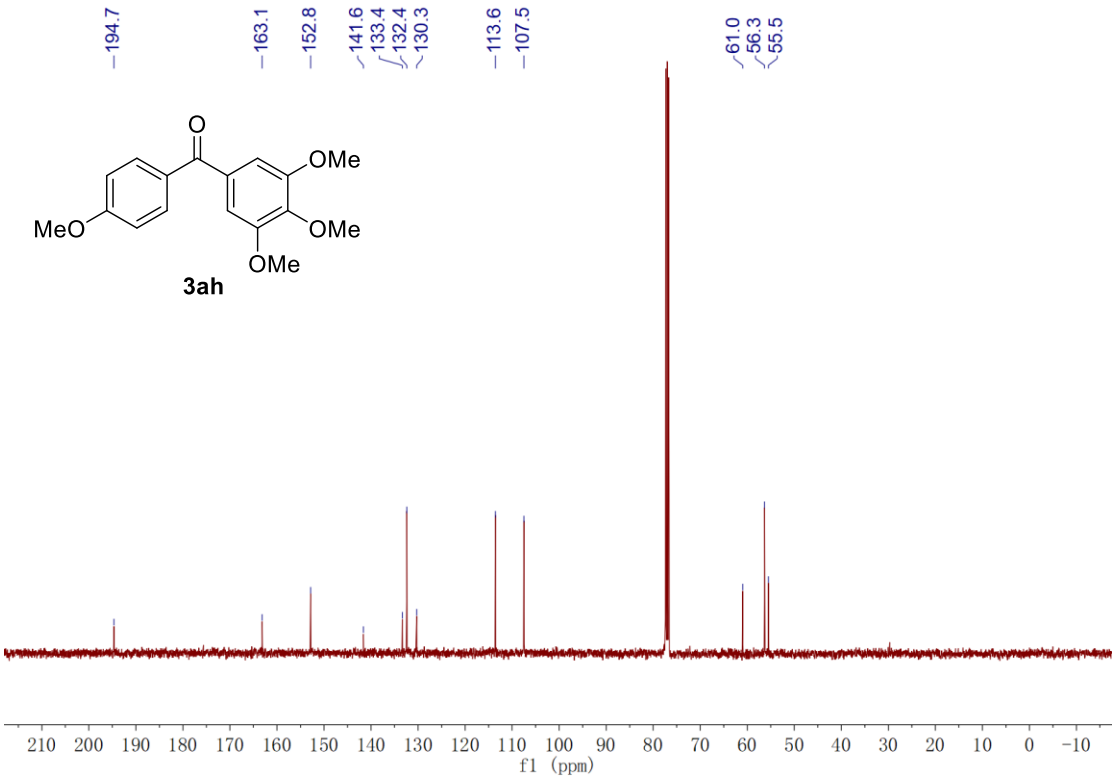


Figure S74. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **3ah**

Naphthylphenstatin (3ai).

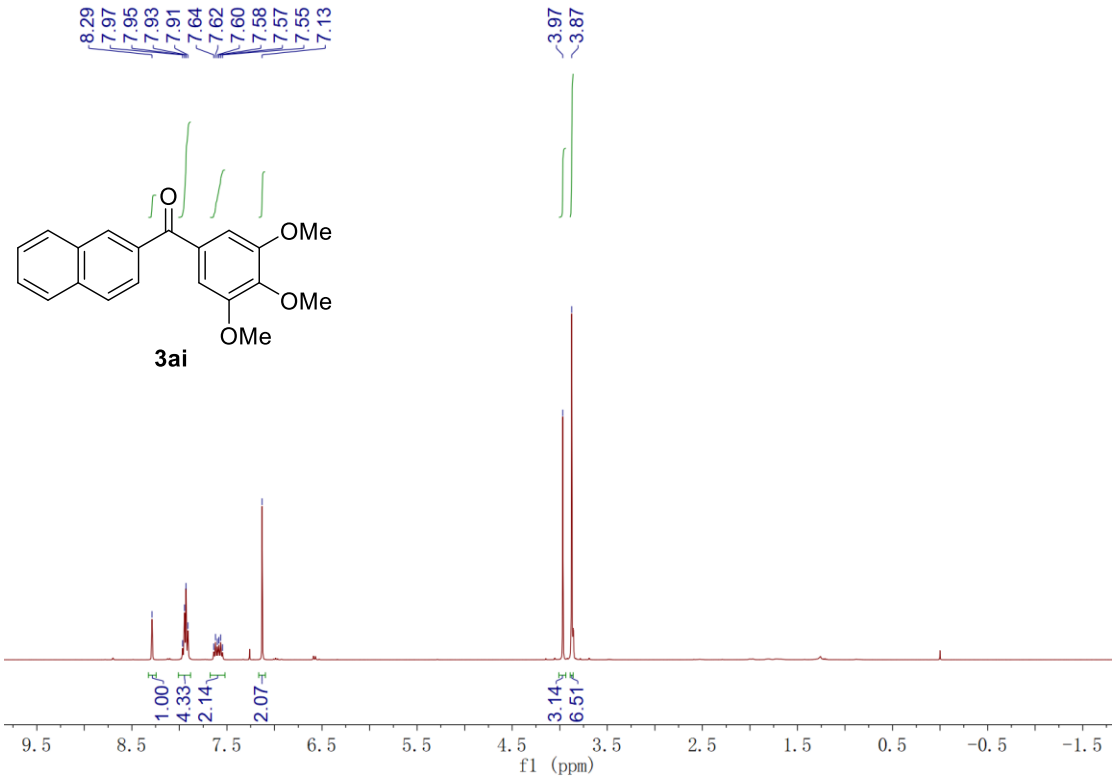


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3ai**

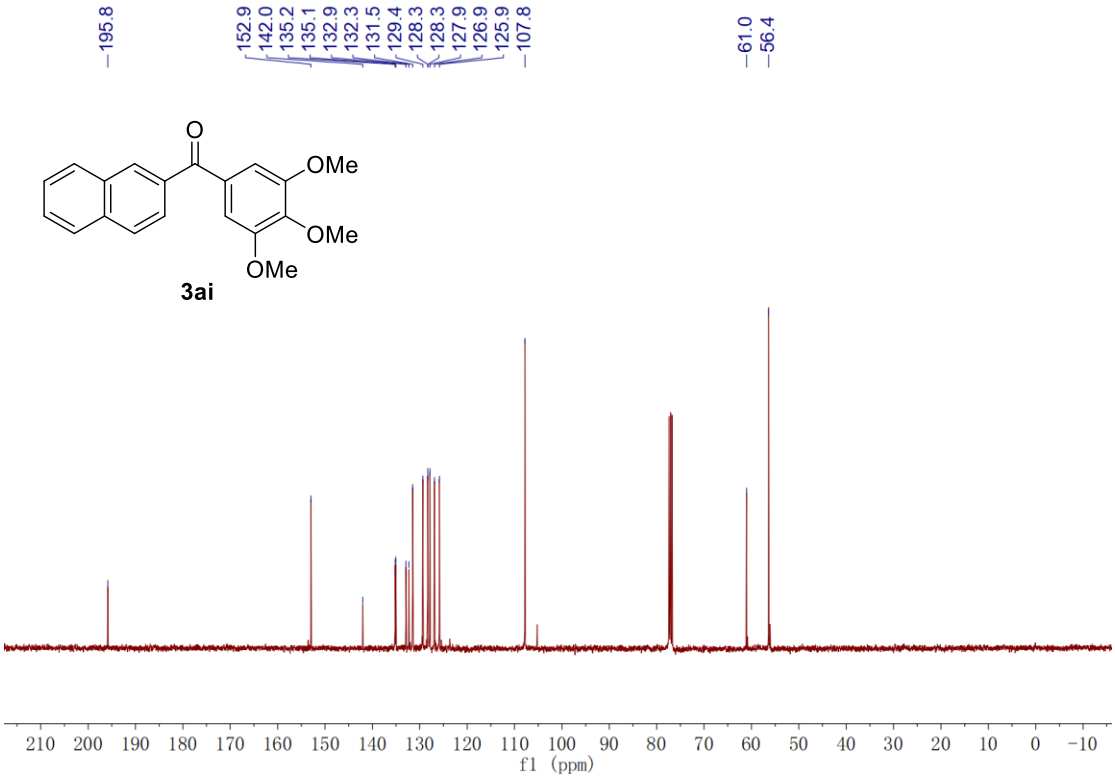


Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3ai**

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