Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling of Carboxylic-Phosphoric Anhydrides via C–O Bond Cleavage

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been prepared according to the method reported previously.[1-2] Unless stated otherwise, all compounds reported in this manuscript have been previously reported. Spectroscopic data matched literature values. All experiments involving palladium were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 400/600 (^{1}H NMR) and 101/125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting point was measured on MeltEMP (laboratory devices). All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Information. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds.

Experimental Procedures and Characterization Data

General Procedure A for the Synthesis of Carboxylic-Phosphoric Anhydrides.[1] An oven-dried flask (50 mL) equipped with a stir bar was charged with acyl chlorides (typically, 10.0 mmol, 1.0 equiv), hydrogen phosphates (2.2 equiv), silver oxide (1.0 equiv) in acetonitrile (20 mL). The reaction mixture was stirred for 15 h at room temperature. After the indicated time, the reaction mixture was filtrated, washed with water (30 mL) and CH_2Cl_2 (30 mL), dried, filtrated, concentrated to get crude product. Unless stated otherwise, the crude product was purified by chromatography (ethyl acetate/hexane = 1/10 to 1/2) to give analytically pure product.

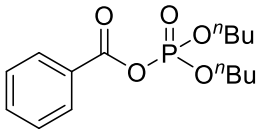
General Procedure B for the Synthesis of Carboxylic-Phosphoric Anhydrides.[2] An oven-drie d flask (50 mL) equipped with a stir bar was charged with carboxylic acids (typically, 10.0 mmol, 1.0 equiv), phosphites (3.0 equiv), Cu_2O (0.1 equiv), dicumyl peroxide (4.0 equiv) and acetonitri le (30 mL). The mixture was allowed to stir at 70 °C for 12 h under air atmosphere. Upon comple tion as shown by TLC, the reaction mixture was cooled to room temperature. After the indicated time, the reaction mixture was diluted with acetonitrile (30 mL), filtrated, concentrated to get cru de product. Unless stated otherwise, the crude product was purified by chromatography (ethyl ac etate/hexane = 1/10 to 1/2) to give analytically pure product.

General Procedure for Suzuki-Miyaura Cross-Coupling of Carboxylic-Phosphoric Anhydrides. An oven-dried vial equipped with a stir bar was charged with carboxylic-phosphoric anhydrides (neat, 1.0 equiv), arylboronic acid (typically, 2.0 equiv), $Pd(OAc)_2$ (typically, 3 mol%), PCy_3HBF_4 (typically, 12 mol%) and Et_3N (typically, 2.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (typically, 0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 120 °C, and stirred for the indicated time at 120 °C. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz), ^1H NMR ($CDCl_3$, 600 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product.

Representative Procedure for Suzuki-Miyaura Cross-Coupling of Carboxylic-Phosphoric Anhydrides. An oven-dried vial equipped with a stir bar was charged with benzoic (dibutyl phosphoric) anhydride (neat, 31.4 mg, 0.10 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (30.4 mg, 0.2 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.7 mg, 0.003 mmol, 3 mol %), PCy_3HBF_4 (4.4 mg, 0.012 mmol, 12 mol%) and Et_3N (neat, 25.3 mg, 0.25 mmol, 2.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (0.5 mL, 0.20 M) was added with vigorous stirring at room temperature, and the reaction mixture was placed in a preheated oil bath at 120 °C and stirred for 15 h at 120 °C. After the indicated time, the reaction mixture was cooled down to room temperature. Purification by chromatography on silica gel (hexanes/dichloromethane) afforded the title product. Yield 82% (17.4 mg, 0.082 mmol). White solid. Characterization data are included in the section below.

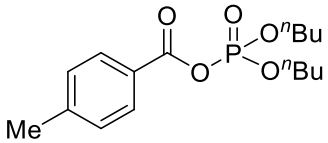
Characterization Data for Starting Materials

Note: All starting materials have been prepared according to the previously published procedure.[1-2] The yields have not been optimized.



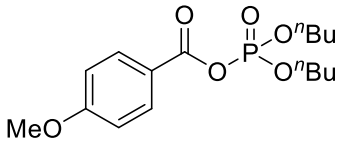
1a

Benzoic (dibutyl phosphoric) anhydride (1a).[1] This compound was synthesized using procedure A. Yield 83% (2.609 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 6H), 1.38-1.48 (m, 4H), 1.68-1.75 (m, 4H), 4.25-4.30 (m, 4H), 7.44-7.49 (m, 2H), 7.60-7.65 (m, 1H), 8.02-8.05 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.65, 18.71, 32.30 (d, *J* = 6.9 Hz), 69.10 (d, *J* = 6.1 Hz), 128.31 (d, *J* = 8.4 Hz), 128.85, 130.75, 134.60, 161.16 (d, *J* = 8.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -6.80.



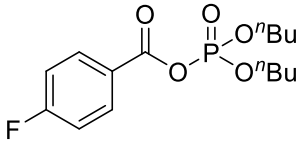
1b

(Dibutyl phosphoric) 4-methylbenzoic anhydride (1b). [1] This compound was synthesized using procedure A. Yield 90% (2.955 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 7H), 1.38-1.48 (m, 4H), 1.68-1.75 (m, 4H), 2.42 (s, 3H), 4.24-4.29 (m, 4H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.66, 18.71, 21.92, 32.31 (d, *J* = 6.9 Hz), 69.03 (d, *J* = 6.2 Hz), 125.54 (d, *J* = 8.3 Hz), 129.58, 130.83, 145.71, 161.15 (d, *J* = 8.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -6.74.



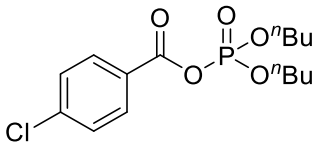
1c

(Dibutyl phosphoric) 4-methoxybenzoic anhydride (1c). This compound was synthesized using procedure A. Yield 82% (2.823 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 6H), 1.40-1.46 (m, 4H), 1.66-1.75 (m, 4H), 3.87 (s, 3H), 4.23-4.29 (m, 4H), 6.92-6.94 (m, 2H), 7.97-8.01 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.66, 18.72, 32.32 (d, *J* = 7.0 Hz), 55.68, 68.97 (d, *J* = 6.2 Hz), 114.15, 120.46 (d, *J* = 8.5 Hz), 133.06, 160.73 (d, *J* = 8.4 Hz), 164.72. **^{31}P NMR (162 MHz, CDCl3)** δ -6.70. **HRMS (ESI)** Calcd for $[M+H]^+$: 345.1467; Found $[M+H]^+$: 345.1484.



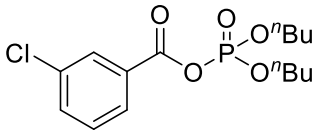
1d

(Dibutyl phosphoric) 4-fluorobenzoic anhydride (1d). This compound was synthesized using procedure A. Yield 78% (2.592 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 6H), 1.38-1.47 (m, 4H), 1.67-1.76 (m, 4H), 4.23-4.30 (m, 4H), 7.14 (t, *J* = 8.6 Hz, 2H), 8.03-8.08 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.63, 18.69, 32.29 (d, *J* = 6.9 Hz), 69.16 (d, *J* = 6.1 Hz), 116.19 (d, *J* = 22.4 Hz), 124.60 (dd, *J* = 8.6, 2.7 Hz), 133.49 (d, *J* = 9.7 Hz), 160.18 (d, *J* = 8.2 Hz), 167.17 (d). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -6.87. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -102.32. **HRMS (ESI)** Calcd for $[M+H]^+$: 333.1267; Found $[M+H]^+$: 333.1285.



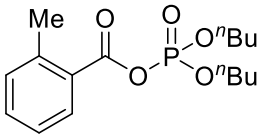
1e

(Dibutyl phosphoric) 4-chlorobenzoic anhydride (1e). This compound was synthesized using procedure A. Yield 81% (2.825 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 6H), 1.43 (h, *J* = 7.5 Hz, 4H), 1.71 (p, *J* = 6.9 Hz, 4H), 4.24-4.30 (m, 4H), 7.14 (t, *J* = 8.7 Hz, 2H), 8.04-8.08 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.64, 18.70, 32.30 (d, *J* = 6.9 Hz), 69.16 (d, *J* = 6.1 Hz), 116.20 (d, *J* = 22.2 Hz), 124.60 (d, *J* = 11.5 Hz), 133.49 (d, *J* = 9.7 Hz), 160.19 (d, *J* = 8.2 Hz), 165.47. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -6.87. **HRMS (ESI)** Calcd for $[M+H]^+$: 349.0972; Found $[M+H]^+$: 349.0975.



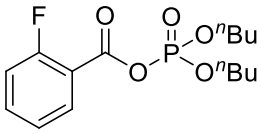
1f

(Dibutyl phosphoric) 3-chlorobenzoic anhydride (1f). This compound was synthesized using procedure A. Yield 75% (2.616 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 6H), 1.40-1.48 (m, 4H), 1.66-1.75 (m, 4H), 4.24-4.30 (m, 4H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.58-7.61 (m, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.99 (t, *J* = 2.0 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 13.58, 18.65, 32.24 (d, *J* = 6.8 Hz), 69.25 (d, *J* = 6.2 Hz), 128.77, 130.12, 130.59, 134.55, 134.80, 135.01, 159.98 (d, *J* = 8.3 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -6.99. **HRMS (ESI)** Calcd for $[M+H]^+$: 349.0972; Found $[M+H]^+$: 349.0983.



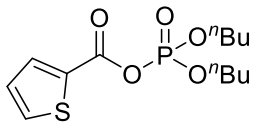
1g

(Dibutyl phosphoric) 2-methylbenzoic anhydride (1g). This compound was synthesized using procedure A. Yield 77% (2.528 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.94 (t, *J* = 7.4 Hz, 6H), 1.44 (h, *J* = 7.4 Hz, 4H), 1.72 (p, *J* = 6.8 Hz, 4H), 2.63 (s, 3H), 4.23-4.31 (m, 4H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.45-7.49 (m, 1H), 7.97 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.67, 18.72, 22.19, 32.33 (d, *J* = 6.9 Hz), 68.97 (d, *J* = 6.2 Hz), 126.14, 131.92, 132.29, 133.84, 142.81, 161.09 (d, *J* = 8.5 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -6.75. **HRMS (ESI)** Calcd for $[M+H]^+$: 329.1518; Found $[M+H]^+$: 329.1526.



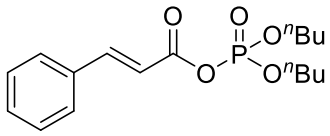
1h

(Dibutyl phosphoric) 2-fluorobenzoic anhydride (1h). This compound was synthesized using procedure A. Yield 79% (2.625 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 6H), 1.43 (h, *J* = 14.7, 7.4 Hz, 4H), 1.67-1.75 (m, 4H), 4.22-4.33 (m, 4H), 7.13-7.18 (m, 1H), 7.23-7.25 (m, 1H), 7.57-7.63 (m, 1H), 7.94-7.98 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.64, 18.68, 32.25 (d, *J* = 7.1 Hz), 69.25 (d, *J* = 6.2 Hz), 116.83 (t, *J* = 8.5 Hz), 117.46 (d, *J* = 22.1 Hz), 124.43 (d, *J* = 4.0 Hz), 133.12, 136.42 (d, *J* = 9.4 Hz), 158.47 (d, *J* = 11.9 Hz), 162.68 (d, *J* = 263.4 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -7.53. **^{19}F (376 MHz, $CDCl_3$)** δ -108.28. **HRMS (ESI)** Calcd for $[M+H]^+$: 333.1267; Found $[M+H]^+$: 333.1268.



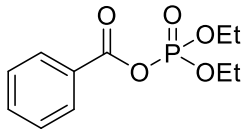
1i

(Dibutyl phosphoric) thiophene-2-carboxylic anhydride (1i). This compound was synthesized using procedure A. Yield 87% (2.787 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 7H), 1.38-1.47 (m, 4H), 1.67-1.74 (m, 4H), 4.23-4.29 (m, 4H), 7.13 (t, 1H), 7.67-7.69 (m, 1H), 7.87-7.88 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 13.59, 18.64, 32.21 (d, *J* = 6.7 Hz), 69.14 (d, *J* = 6.2 Hz), 128.43, 131.64 (d, *J* = 9.9 Hz), 135.26, 136.17, 156.08 (d, *J* = 7.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -7.58. **HRMS (ESI)** Calcd for $[M+H]^+$: 321.0926; Found $[M+H]^+$: 321.0931.



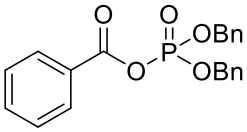
1j

(*E*)-(Dibutyl phosphoric) cinnamic anhydride (1j). This compound was synthesized using procedure A. Yield 54% (1.838 g). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.93 (t, *J* = 7.4 Hz, 6H), 1.37-1.46 (m, 4H), 1.66-1.73 (m, 4H), 4.20-4.26 (m, 4H), 6.38 (dd, *J* = 15.9, 2.1 Hz, 1H), 7.38-7.42 (m, 3H), 7.50-7.53 (m, 2H), 7.76 (d, *J* = 15.9 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 13.65, 18.69, 32.28 (d, *J* = 7.1 Hz), 68.96 (d, *J* = 6.1 Hz), 116.15 (d, *J* = 9.1 Hz), 128.66, 129.17, 131.44, 133.62, 149.13, 160.93 (d, *J* = 8.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -7.09. **HRMS (ESI)** Calcd for $[M+H]^+$: 341.1512; Found $[M+H]^+$: 341.1512.



1k

Benzoic (diethyl phosphoric) anhydride (1k).[1] This compound was synthesized using procedure A. Yield 84% (2.169 g). Colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 1.35 (t, *J* = 7.1 Hz, 6H), 4.28-4.33 (m, 4H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 7.4 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 16.17 (d, *J* = 7.0 Hz), 65.40 (d, *J* = 5.9 Hz), 128.21 (d, *J* = 8.2 Hz), 128.81, 130.71, 134.58, 161.09 (d, *J* = 8.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -7.06.



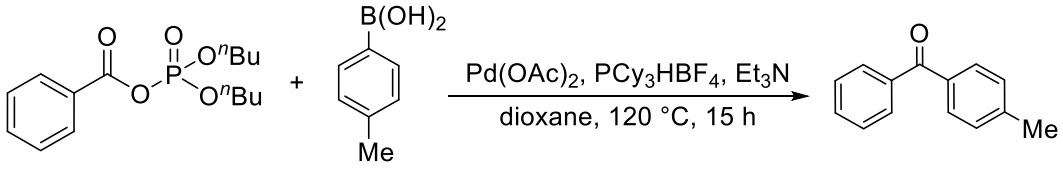
1l

Benzoic (dibenzyl phosphoric) anhydride (1l).[1] This compound was synthesized using procedure A. Yield 72% (2.753 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.28 (d, *J* = 8.9 Hz, 4H), 7.32-7.44 (m, 12H), 7.58-7.63 (m, 1H), 7.84-7.87 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 70.67 (d, *J* = 5.7 Hz), 127.92, 128.00, 128.29, 128.77, 128.84, 130.84, 134.66, 135.41 (d, *J* = 6.7 Hz), 161.09 (d, *J* = 8.4 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -6.69.

Characterization Data for Suzuki-Miyaura Products

Suzuki-Miyaura Cross-Coupling: Variation of Arylboronic acids

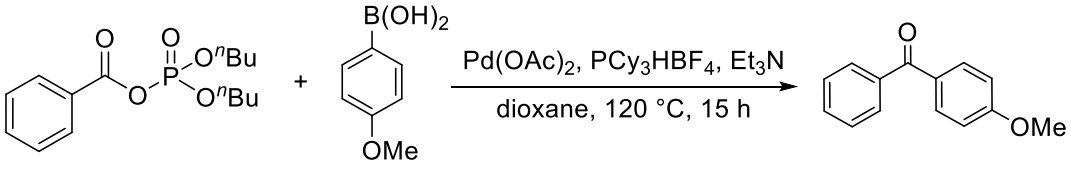
Phenyl(*p*-tolyl)methanone (Scheme 1, 3a)[3]



1a 2a 3a

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), *p*-tolylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 77% yield (15.1 mg). White solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 2.37 (s, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 21.77, 128.31, 129.08, 130.05, 130.42, 132.27, 134.96, 138.04, 143.36, 196.66.

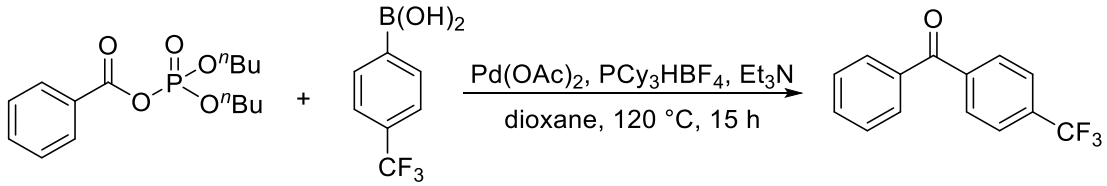
(4-Methoxyphenyl)(phenyl)methanone (Scheme 1, 3b)[3]



1a 2b 3b

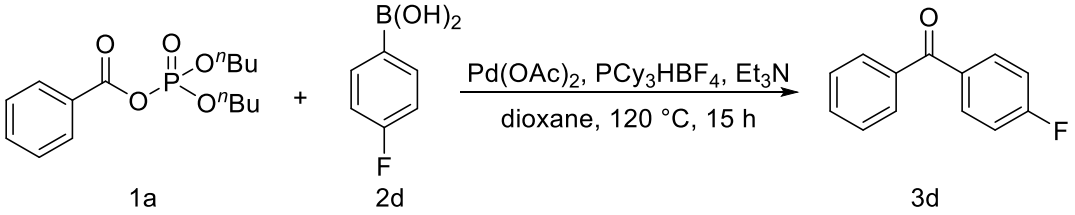
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 82% yield (17.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.88 (s, 3H), 6.94-6.97 (m, 2H), 7.44-7.49 (m, 2H), 7.54-7.58 (m, 1H), 7.73-7.76 (m, 2H), 7.80-7.84 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 55.60, 113.65, 128.29, 129.84, 130.25, 132.00, 132.68, 138.37, 163.32, 195.72.

Phenyl(4-(trifluoromethyl)phenyl)methanone (Scheme 1, 3c)[3]



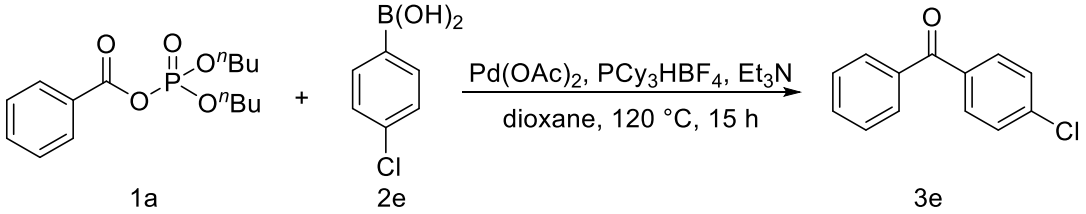
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-(trifluoromethyl)phenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 75% yield (18.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (t, *J* = 7.7 Hz, 2H), 7.60-7.65 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.78-7.81 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 125.45 (d, *J* = 3.7 Hz), 126.24 (q, *J*=3.4 Hz)), 128.63, 130.23 (d, *J* = 3.3 Hz), 133.20, 133.66, 133.99, 136.82, 140.81, 195.68. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.88.

(4-Fluorophenyl)(phenyl)methanone (Scheme 1, 3d)[3]



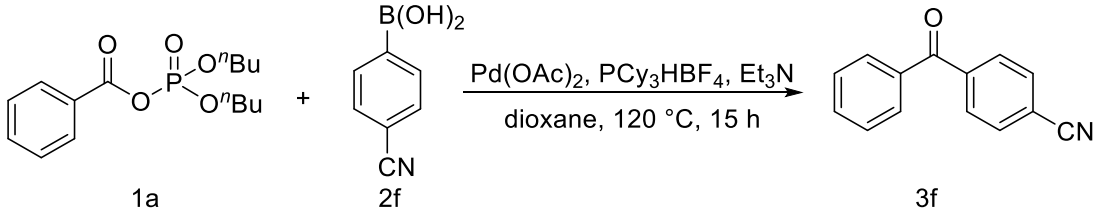
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-fluorophenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 74% yield (14.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.12-7.18 (m, 2H), 7.46-7.50 (m, 2H), 7.57-7.61 (m, 1H), 7.75-7.78 (m, 2H), 7.81-7.86 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 115.46, 115.68, 128.47, 129.99, 132.59, 132.79 (d, *J* = 9.3 Hz), 137.58, 166.76, 195.43. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -105.83.

(4-Chlorophenyl)(phenyl)methanone (Scheme 1, 3e)[3]



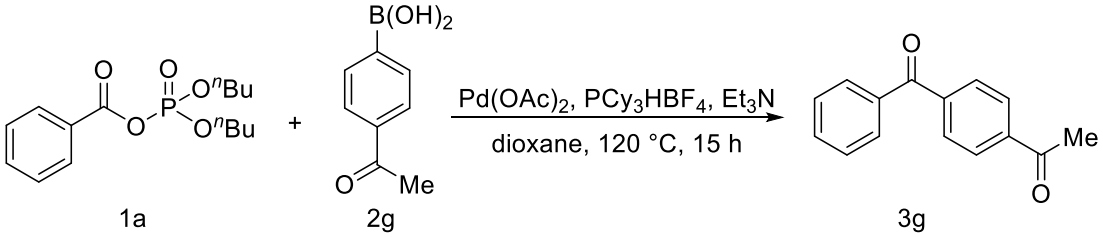
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-chlorophenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 63% yield (13.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.51 (m, 4H), 7.56-7.62 (m, 1H), 7.73-7.78 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.51, 128.74, 130.04, 131.57, 132.75, 135.96, 137.33, 139.00, 195.64.

4-Benzoylbenzonitrile (Scheme 1, 3f)[3]



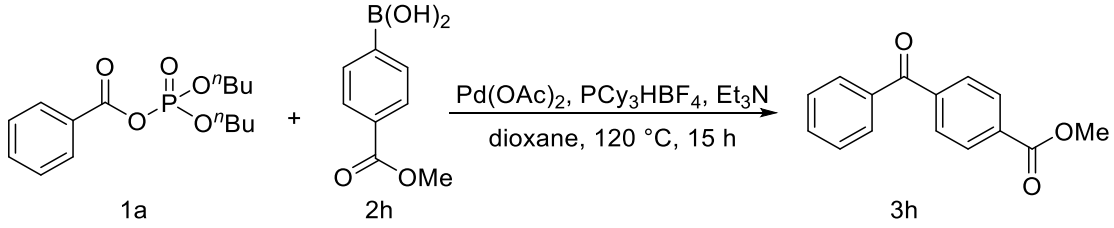
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-cyanophenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 51% yield (10.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (t, J = 7.7 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.76-7.79 (m, 4H), 7.87 (d, J = 8.3 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 115.76, 118.12, 128.74, 130.18, 130.35, 132.28, 133.45, 136.41, 141.33, 195.18.

1-(4-Benzoylphenyl)ethan-1-one (Scheme 1, 3g)[3]



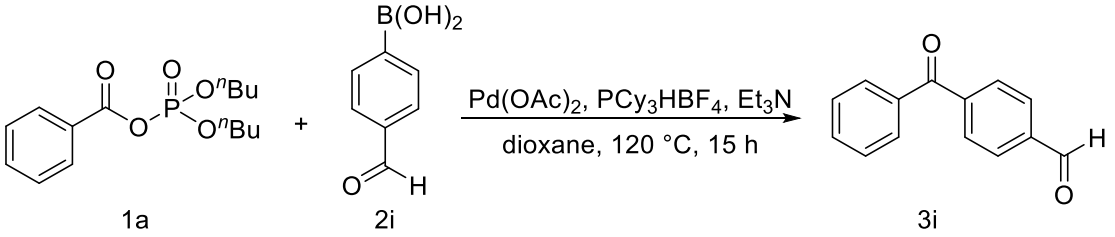
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-acetylphenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 90% yield (20.2 mg). White solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 2.61 (s, 3H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 27.01, 128.27, 128.59, 130.16, 130.21, 133.11, 137.00, 139.65, 141.43, 196.09, 197.67.

Methyl 4-benzoylbenzoate (Scheme 1, 3h)[3]



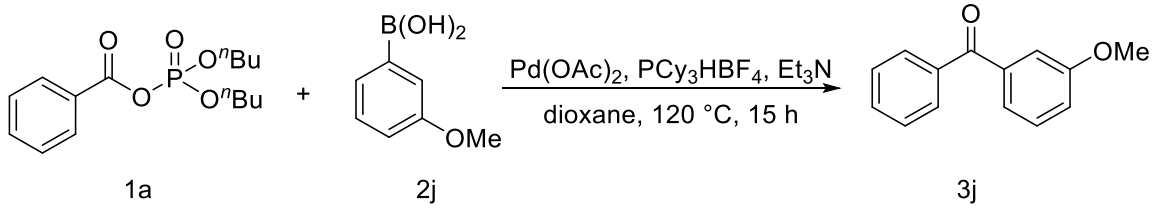
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-(methoxycarbonyl)phenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 74% yield (17.8 mg). White solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 3.90 (s, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 52.58, 128.57, 129.60, 129.89, 130.21, 133.06, 133.30, 137.03, 141.41, 166.43, 196.18.

4-Benzoylbenzaldehyde (Scheme 1, 3i)[3]



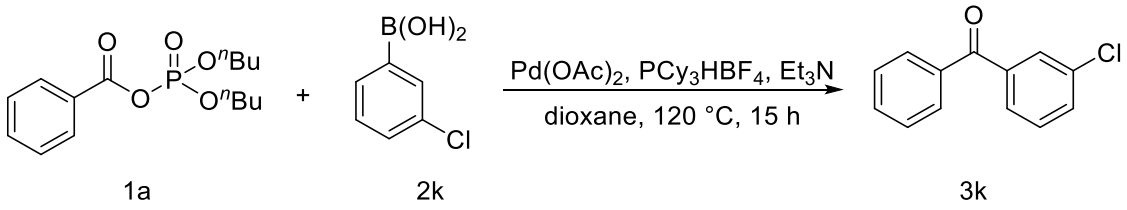
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (4-formylphenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 52% yield (10.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (t, *J* = 7.7 Hz, 2H), 7.60-7.65 (m, 1H), 7.79-7.82 (m, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.3 Hz, 2H), 10.12 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.65, 129.62, 130.23, 130.44, 133.26, 136.82, 138.56, 142.66, 191.79, 195.98.

(3-Methoxyphenyl)(phenyl)methanone (Scheme 1, 3j)[3]



According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (3-methoxyphenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 90% yield (19.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.85 (s, 3H), 7.11-7.14 (m, 1H), 7.32-7.38 (m, 3H), 7.45-7.49 (m, 2H), 7.56-7.60 (m, 1H), 7.79-7.81 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 55.57, 114.39, 118.99, 122.99, 128.36, 129.32, 130.15, 132.55, 137.70, 138.98, 159.66, 196.68.

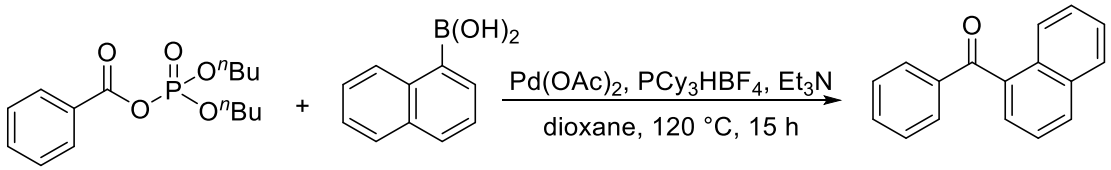
(3-Chlorophenyl)(phenyl)methanone (Scheme 1, 3k)[4]



1a 2k 3k

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (3-chlorophenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 58% yield (12.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.54-7.57 (m, 1H), 7.58-7.63 (m, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.76-7.80 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.21, 128.56, 129.74, 130.01, 130.13, 132.47, 132.95, 134.67, 137.04, 139.35, 195.40.

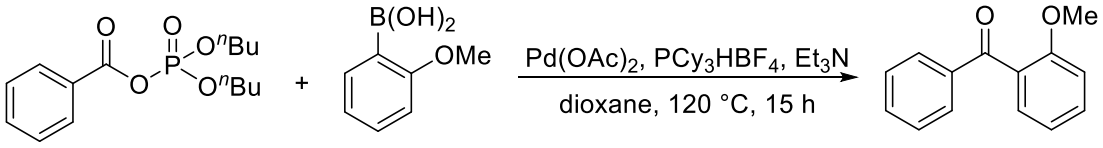
Naphthalen-1-yl(phenyl)methanone (Scheme 1, 3l)[3]



1a 2l 3l

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), naphthalen-1-ylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 85% yield (19.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43-7.61 (m, 7H), 7.85-7.88 (m, 2H), 7.91-7.93 (m, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 124.43, 125.78, 126.56, 127.36, 127.88, 128.50, 128.55, 130.52, 131.05, 131.38, 133.35, 133.81, 136.43, 138.40, 198.17.

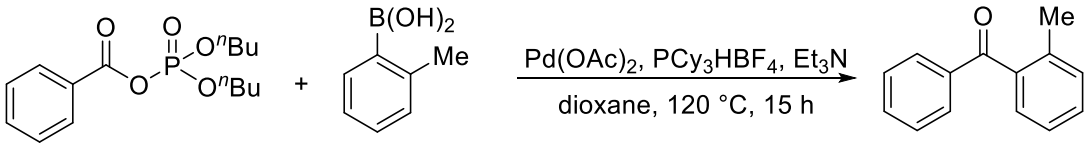
(2-Methoxyphenyl)(phenyl)methanone (Scheme 1, 3m)[4]



1a 2m 3m

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (2-methoxyphenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 58% yield (12.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.72 (s, 3H), 6.97-7.05 (m, 2H), 7.34-7.36 (m, 1H), 7.40-7.48 (m, 3H), 7.52-7.56 (m, 1H), 7.79-7.82 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 55.69, 111.53, 120.58, 128.31, 128.93, 129.69, 129.94, 131.98, 133.03, 137.89, 157.45, 196.60.

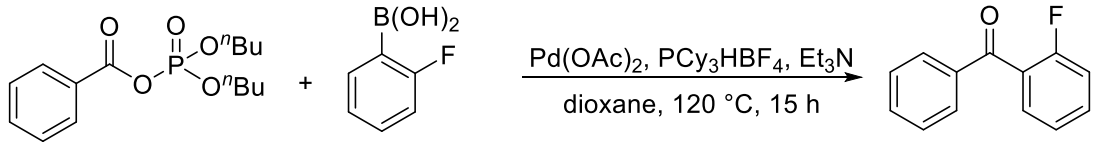
Phenyl*(o*-tolyl*)*methanone (Scheme 1, 3n)[3]



1a 2n 3n

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), *o*-tolylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 75% yield (14.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.32 (s, 3H), 7.22-7.32 (m, 4H), 7.36-7.40 (m, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.55-7.59 (m, 1H), 7.78-7.80 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 20.08, 125.29, 128.56, 128.62, 130.24, 130.35, 131.09, 133.25, 136.85, 137.81, 138.69, 198.80.

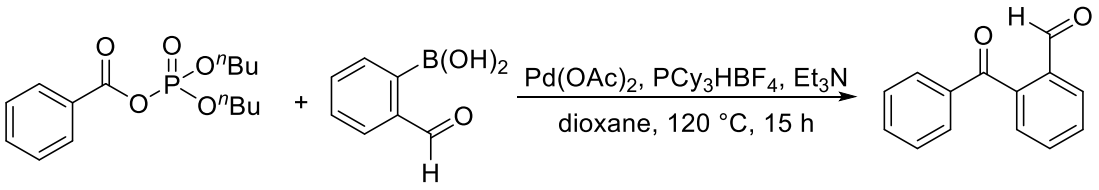
(2-Fluorophenyl)(phenyl)methanone (Scheme 1, 3o)[3]



1a 2o 3o

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (2-fluorophenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 55% yield (11.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.13-7.18 (m, 1H), 7.24-7.28 (m, 1H), 7.45-7.62 (m, 5H), 7.82-7.85 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 116.38 (d, J = 21.7 Hz), 124.38 (d, J = 3.7 Hz), 127.12 (d, J = 14.7 Hz), 128.56, 129.92, 130.86 (d, J = 2.8 Hz), 133.17 (d, J = 8.3 Hz), 133.52, 137.48, 160.19 (d, J = 252.5 Hz), 193.61. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.91.

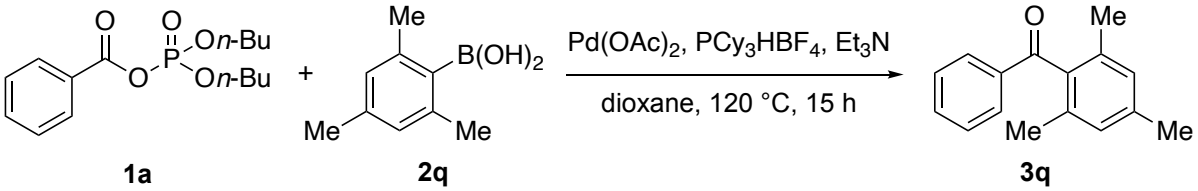
2-Benzoylbenzaldehyde (Scheme 1, 3p)[5]



1a 2p 3p

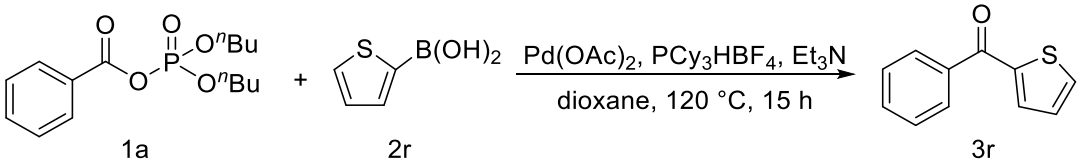
According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), (2-formylphenyl)boronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 50% yield (10.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.51 (m, 3H), 7.58-7.62 (m, 1H), 7.67-7.69 (m, 2H), 7.78-7.81 (m, 2H), 8.01-8.04 (m, 1H), 10.02 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.76, 128.98, 130.11 (d, J = 9.1 Hz), 130.72, 133.45, 133.79, 135.49, 137.15, 141.50, 190.71, 196.64.

Mesityl(phenyl)methanone (Scheme 1, 3q)[6]



According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), mesitylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 96% yield (21.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.07 (s, 6H), 2.32 (s, 3H), 6.88 (s, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.53 – 7.60 (m, 1H), 7.75 – 7.83 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 19.45, 21.25, 128.42, 128.88, 129.51, 133.65, 134.30, 136.96, 137.39, 138.60, 200.92.

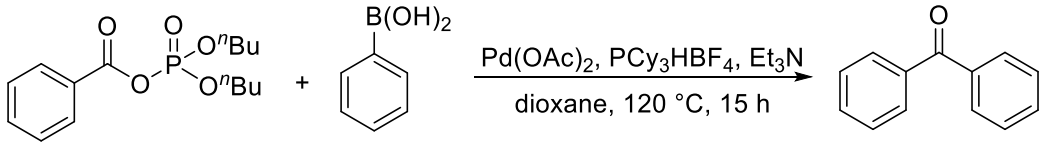
Phenyl(thiophen-2-yl)methanone (Scheme 1, 3r)[3]



According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), thiophen-2-ylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 71% yield (13.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.16 (t, *J* = 4.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 3.8 Hz, 1H), 7.72 (d, *J* = 4.9 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.06, 128.52, 129.28, 132.38, 134.33, 134.97, 138.24, 143.74, 188.38.

Suzuki-Miyaura Cross-Coupling: Variation of Carboxylic-Phosphoric Anhydrides

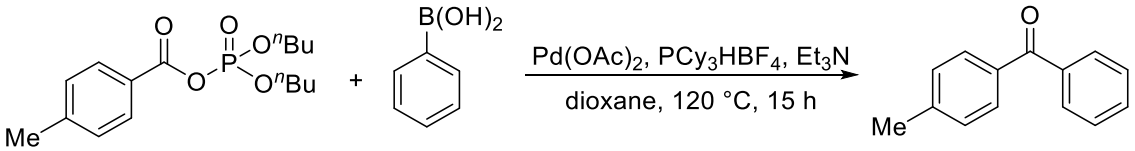
Benzophenone (Scheme 2, 3s)[3]



1a 2s 3s

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 98% yield (17.9 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (t, *J* = 7.6 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 7.0 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.38, 130.17, 132.53, 137.69, 196.91.

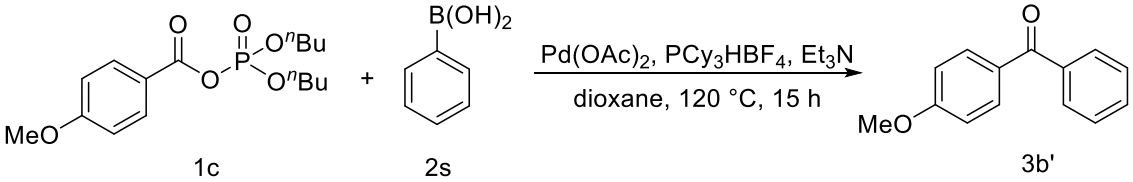
Phenyl(*p*-tolyl)methanone (Scheme 2, 3a')[3]



1b 2s 3a'

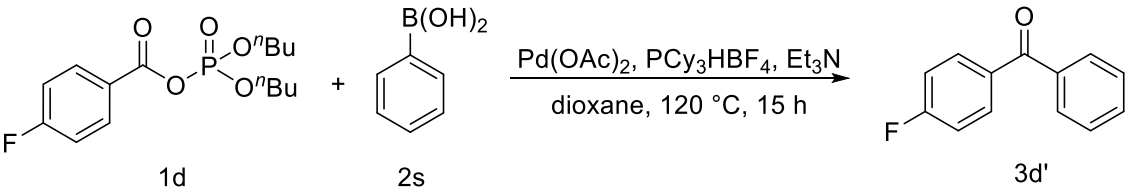
According to the general procedure, the reaction of (dibutyl phosphoric) 4-methylbenzoic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 71% yield (13.9 mg). White solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.80-7.75 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.60-7.54 (m, 1H), 7.49-7.43 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.66, 143.36, 138.04, 134.96, 132.27, 130.42, 130.05, 129.08, 128.31, 21.77.

(4-Methoxyphenyl)(phenyl)methanone (Scheme 2, 3b')[3]



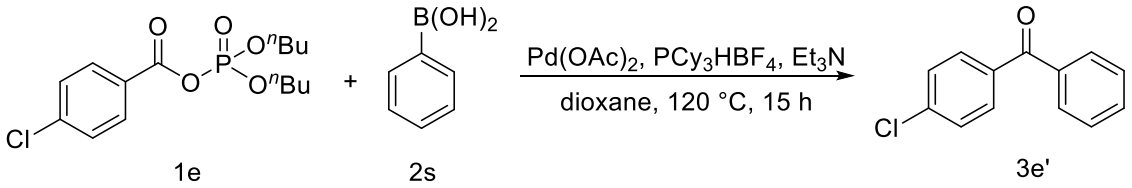
According to the general procedure, the reaction of (dibutyl phosphoric) 4-methoxybenzoic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 89% yield (18.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.88 (s, 3H), 6.94-6.97 (m, 2H), 7.44-7.49 (m, 2H), 7.54-7.58 (m, 1H), 7.73-7.76 (m, 2H), 7.80-7.84 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 55.60, 113.65, 128.29, 129.84, 130.25, 132.00, 132.68, 138.37, 163.32, 195.72.

(4-Fluorophenyl)(phenyl)methanone (Scheme 2, 3d')[3]



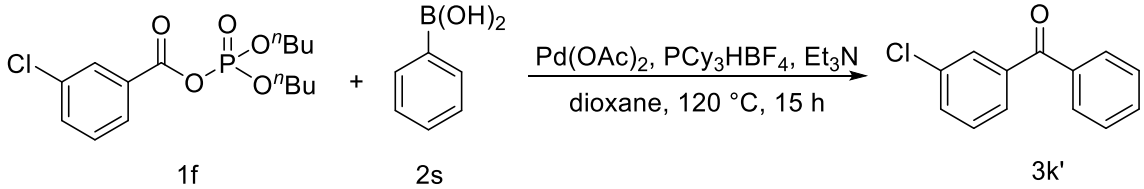
According to the general procedure, the reaction of (dibutyl phosphoric) 4-fluorobenzoic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 93% yield (18.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.12-7.18 (m, 2H), 7.46-7.50 (m, 2H), 7.57-7.61 (m, 1H), 7.75-7.78 (m, 2H), 7.81-7.86 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 115.46, 115.68, 128.47, 129.99, 132.59, 132.79 (d, J = 9.3 Hz), 137.58, 166.76, 195.43. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -105.83.

(4-Chlorophenyl)(phenyl)methanone (Scheme 2, 3e')[3]



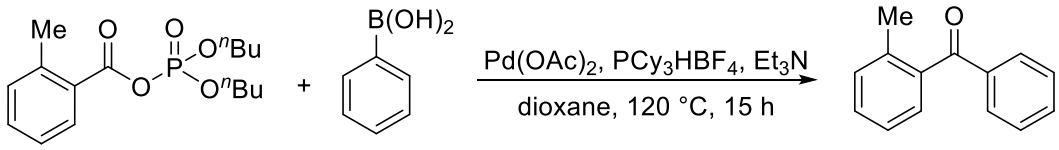
According to the general procedure, the reaction of (dibutyl phosphoric) 4-chlorobenzoic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 83% yield (18.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.51 (m, 4H), 7.56-7.62 (m, 1H), 7.73-7.78 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.51, 128.74, 130.04, 131.57, 132.75, 135.96, 137.33, 139.00, 195.64.

(3-Chlorophenyl)(phenyl)methanone (Scheme 2, 3k')[4]



According to the general procedure, the reaction of (dibutyl phosphoric) 3-chlorobenzoic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 67% yield (14.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (t, J = 7.8 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.54-7.57 (m, 1H), 7.58-7.63 (m, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.76-7.80 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.21, 128.56, 129.74, 130.01, 130.13, 132.47, 132.95, 134.67, 137.04, 139.35, 195.40.

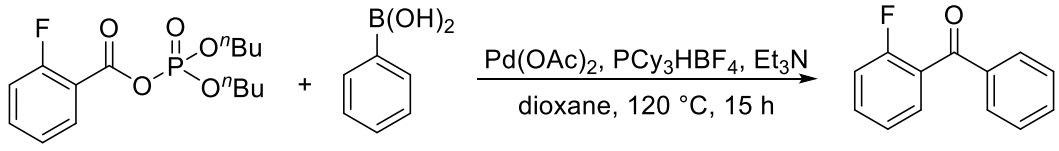
Phenyl(*o*-tolyl)methanone (Scheme 2, 3n')[3]



1g 2s 3n'

According to the general procedure, the reaction of (dibutyl phosphoric) 2-methylbenzoic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 53% yield (10.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.32 (s, 3H), 7.22-7.32 (m, 4H), 7.36-7.40 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.55-7.59 (m, 1H), 7.78-7.80 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 20.08, 125.29, 128.56, 128.62, 130.24, 130.35, 131.09, 133.25, 136.85, 137.81, 138.69, 198.80.

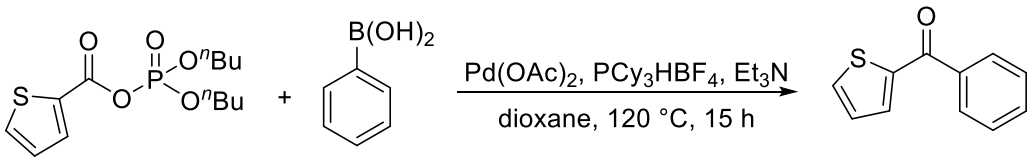
(2-Fluorophenyl)(phenyl)methanone (Scheme 2, 3o')[3]



1h 2s 3o'

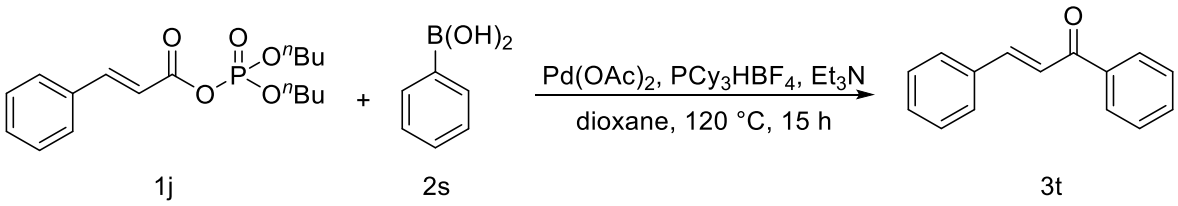
According to the general procedure, the reaction of (dibutyl phosphoric) 2-fluorobenzoic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 35% yield (7.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.13-7.18 (m, 1H), 7.24-7.28 (m, 1H), 7.45-7.62 (m, 5H), 7.82-7.85 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 116.38 (d, *J* = 21.7 Hz), 124.38 (d, *J* = 3.7 Hz), 127.12 (d, *J* = 14.7 Hz), 128.56, 129.92, 130.86 (d, *J* = 2.8 Hz), 133.17 (d, *J* = 8.3 Hz), 133.52, 137.48, 160.19 (d, *J* = 252.5 Hz), 193.61. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.91.

Phenyl(thiophen-2-yl)methanone (Scheme 2, 3r')[3]



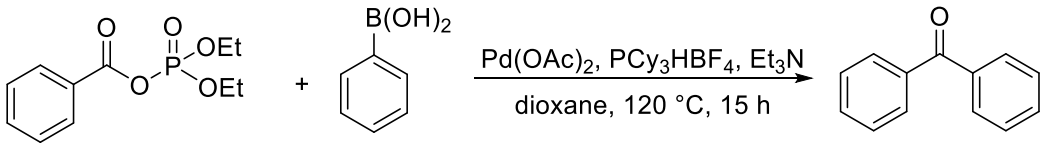
According to the general procedure, the reaction of (dibutyl phosphoric) thiophene-2-carboxylic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 46% yield (8.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.16 (t, *J* = 4.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 3.8 Hz, 1H), 7.72 (d, *J* = 4.9 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.06, 128.52, 129.28, 132.38, 134.33, 134.97, 138.24, 143.74, 188.38.

(*E*)-Chalcone (Scheme 3, 3t)[7]



According to the general procedure, the reaction of (E)-(dibutyl phosphoric) cinnamic anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 74% yield (15.41 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01-7.92 (m, 2H), 7.75 (d, *J* = 15.7 Hz, 1H), 7.57-7.60 (m, 2H), 7.55-7.50 (m, 1H), 7.49 (s, 1H), 7.47-7.42 (m, 2H), 7.39-7.31 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.71, 144.98, 138.30, 134.98, 132.91, 130.67, 129.07, 128.74, 128.62, 128.56, 122.18.

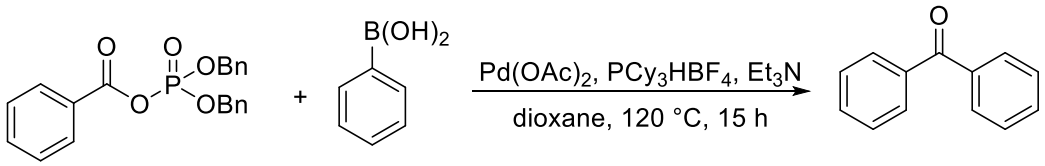
Benzophenone (Scheme 4, 3s)[3]



1k 2s 3s

According to the general procedure, the reaction of benzoic (diethyl phosphoric) anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 67% yield (12.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (t, *J* = 7.6 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 7.0 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.38, 130.17, 132.53, 137.69, 196.91.

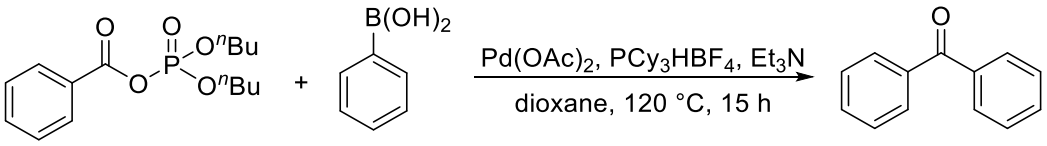
Benzophenone (Scheme 4, 3s)[3]



1l 2s 3s

According to the general procedure, the reaction of benzoic (dibenzyl phosphoric) anhydride (0.10 mmol, 1.0 equiv), phenylboronic acid (0.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.003 mmol, 3 mol%), PCy_3HBF_4 (0.012 mmol, 12 mol%) and Et_3N (0.25 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 88% yield (16.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (t, *J* = 7.6 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 7.0 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.38, 130.17, 132.53, 137.69, 196.91.

Benzophenone (Scheme 4, 3s)[3]



1a 2s 3s

According to the general procedure, the reaction of benzoic(dibutyl phosphoric)anhydride (1.0 mmol, 1.0 equiv), phenylboronic acid (2.0 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.3 mmol, 3 mol%), PCy_3HBF_4 (1.2 mmol, 12 mol%) and Et_3N (2.5 mmol, 2.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 120 °C, afforded after work-up and chromatography the title product in 92% yield (167.6 mg). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (t, *J* = 7.6 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 7.0 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 128.38, 130.17, 132.53, 137.69, 196.91.

References

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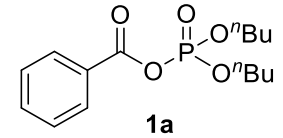
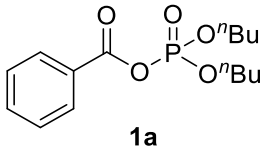
^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR Spectra



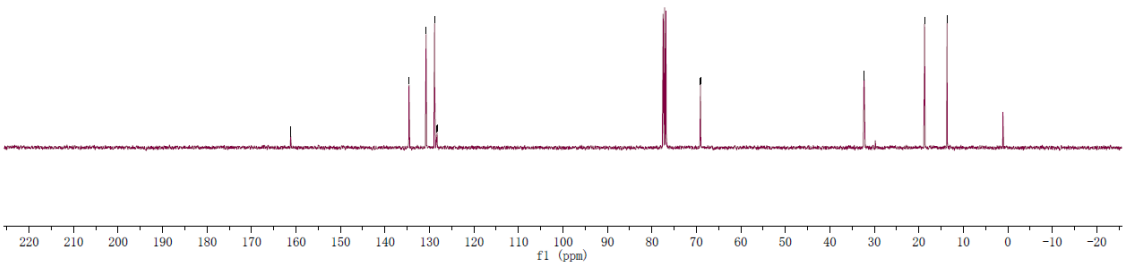
1a

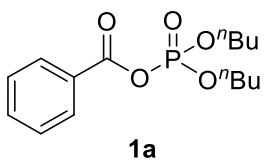
^{1}H NMR (400 MHz, $CDCl_3$)



1a

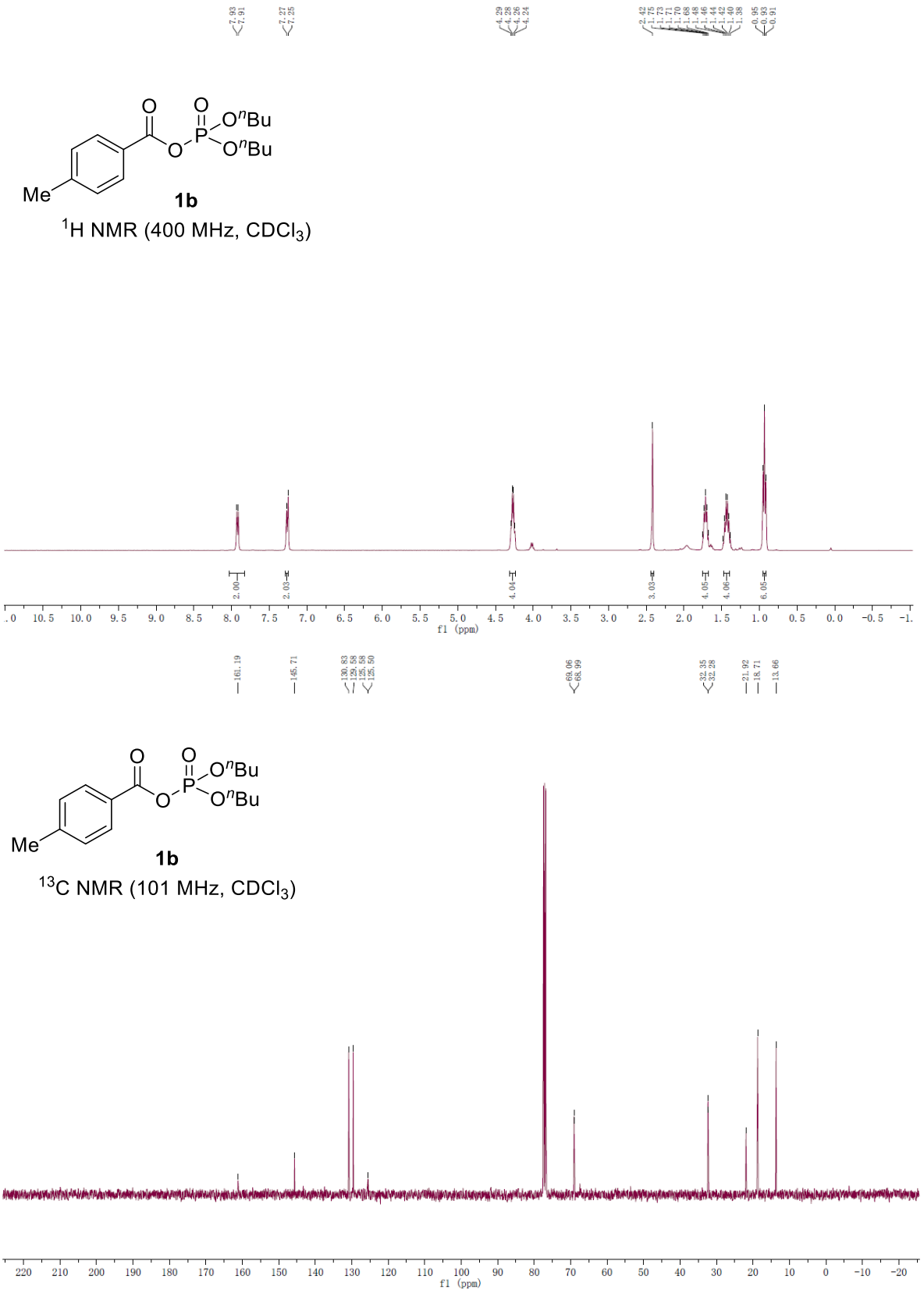
^{13}C NMR (101 MHz, $CDCl_3$)





1a

^{31}P NMR (162 MHz, $CDCl_3$)


Me
1b
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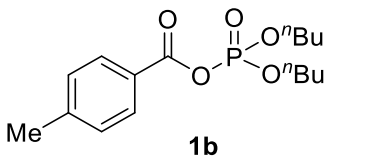
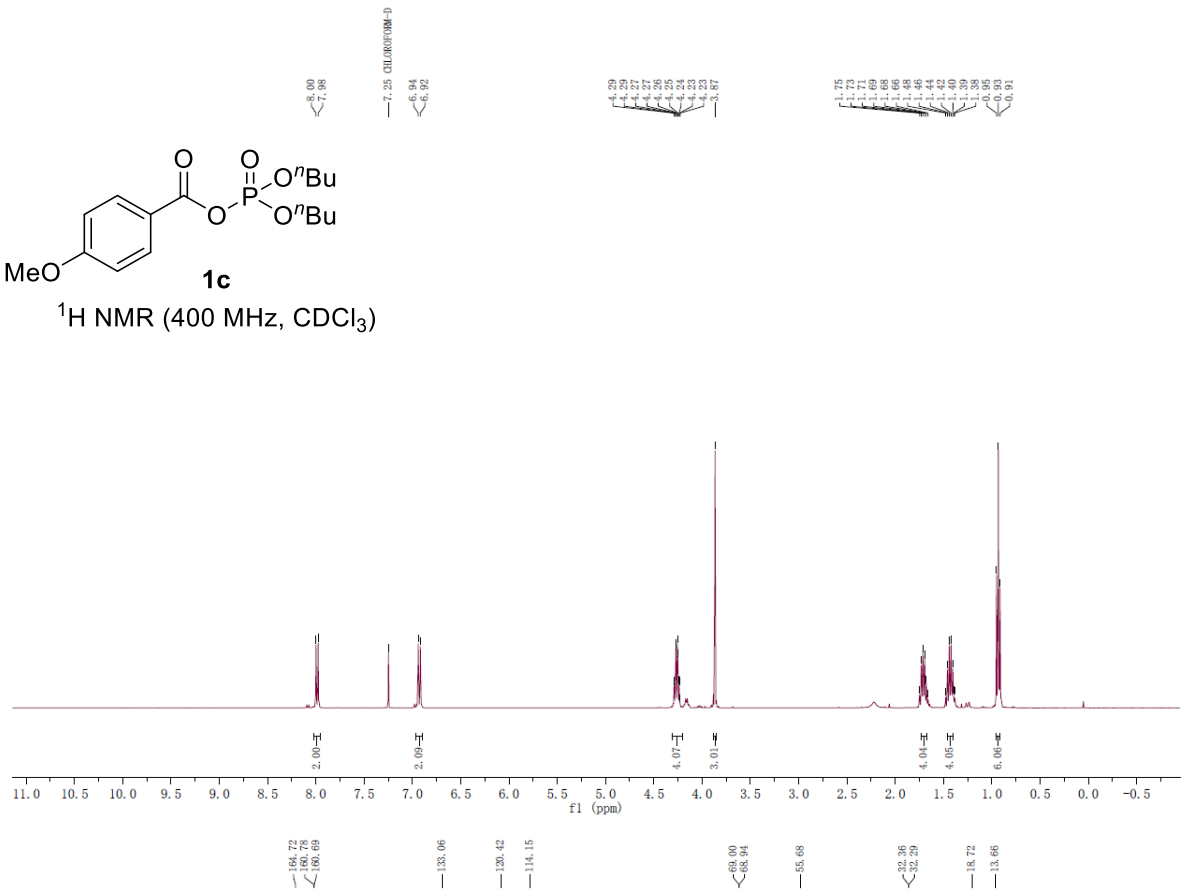
f1 (ppm)
Me
1b
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)



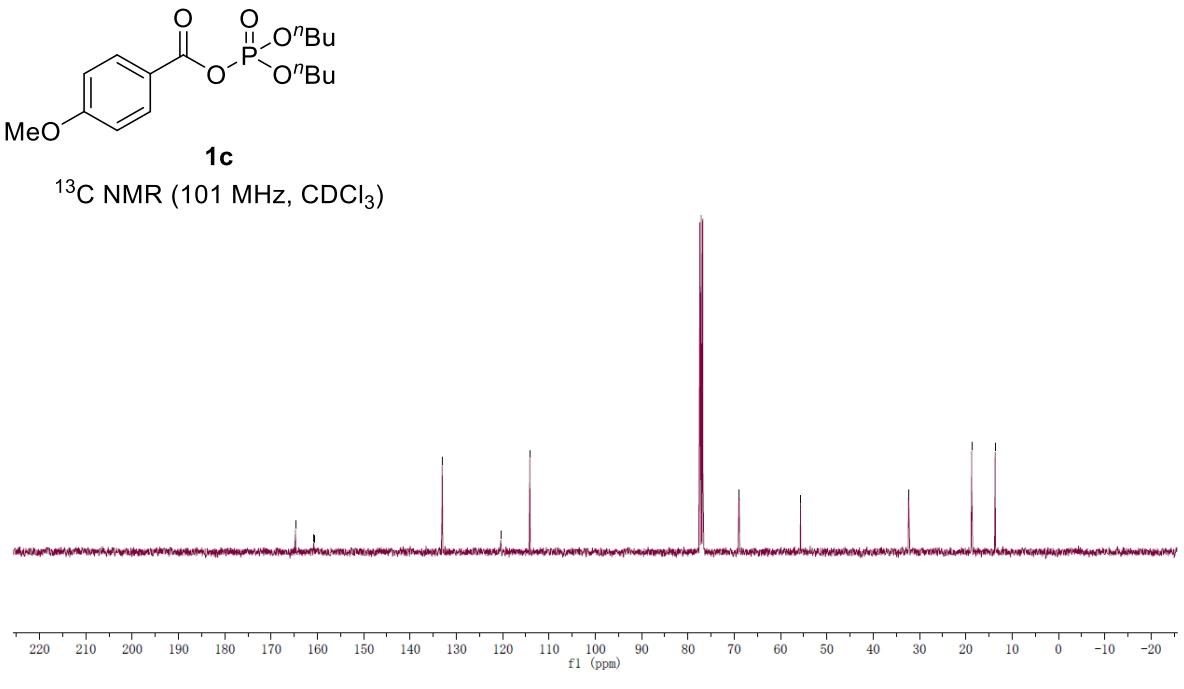
1b

^{31}P NMR (162 MHz, $CDCl_3$)



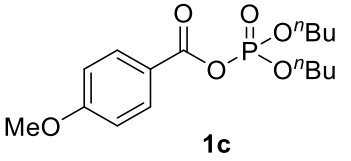
1c

^{1}H NMR (400 MHz, $CDCl_3$)



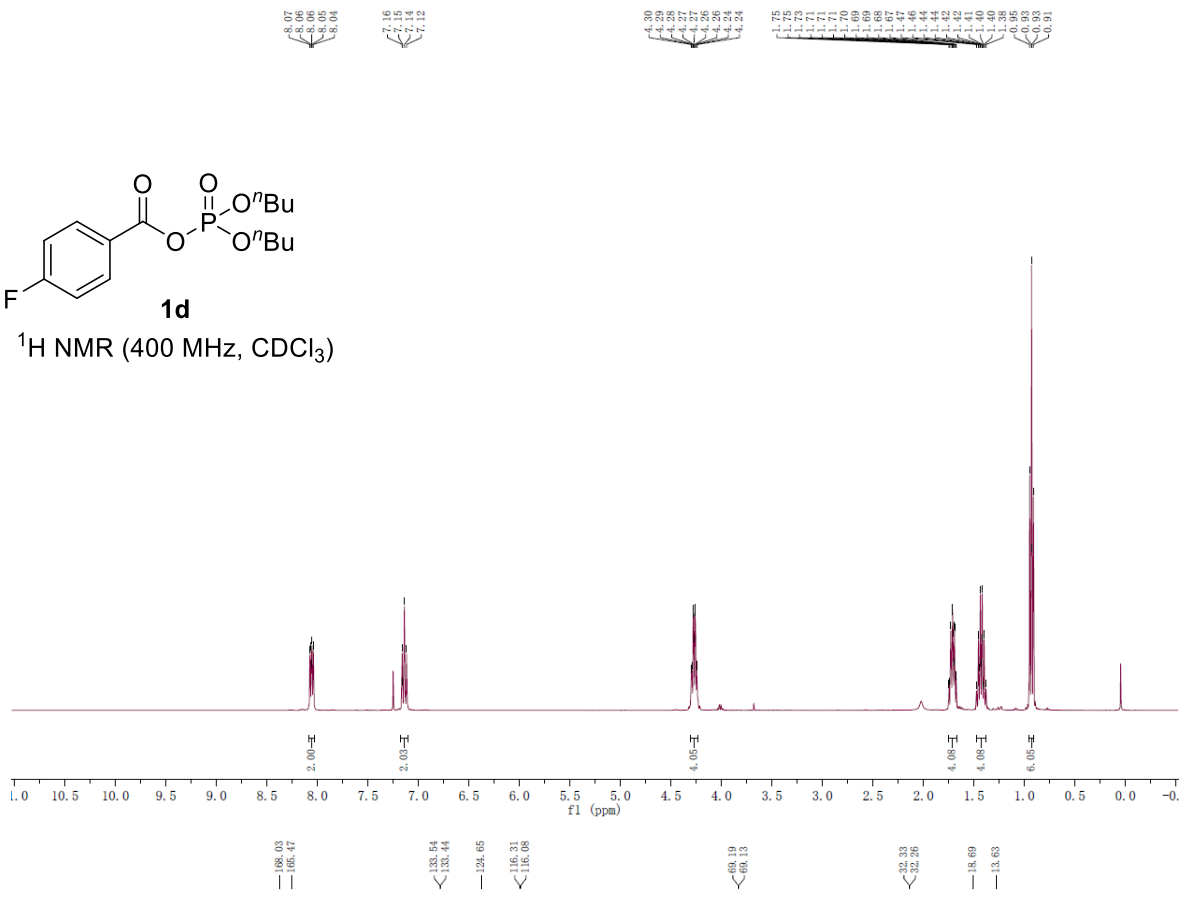
1c

^{13}C NMR (101 MHz, $CDCl_3$)



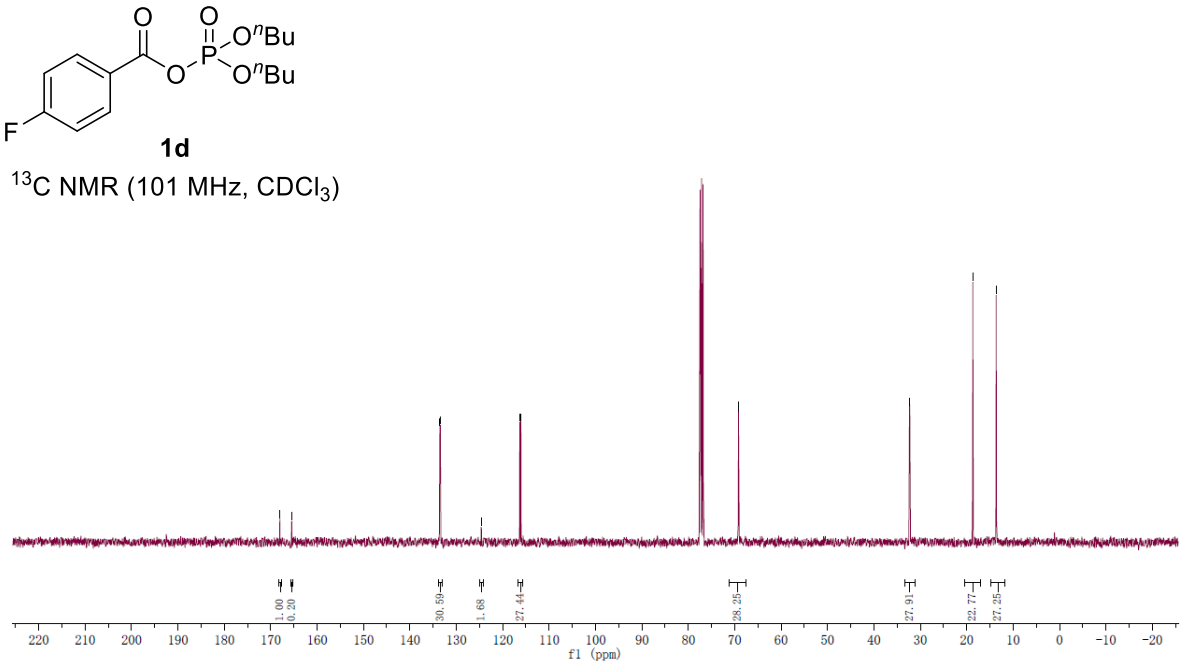
1c

^{31}P NMR (162 MHz, $CDCl_3$)



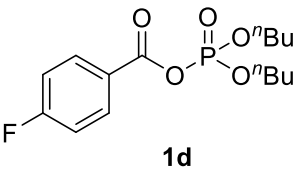
1d

^{1}H NMR (400 MHz, $CDCl_3$)



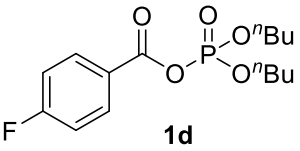
1d

^{13}C NMR (101 MHz, $CDCl_3$)



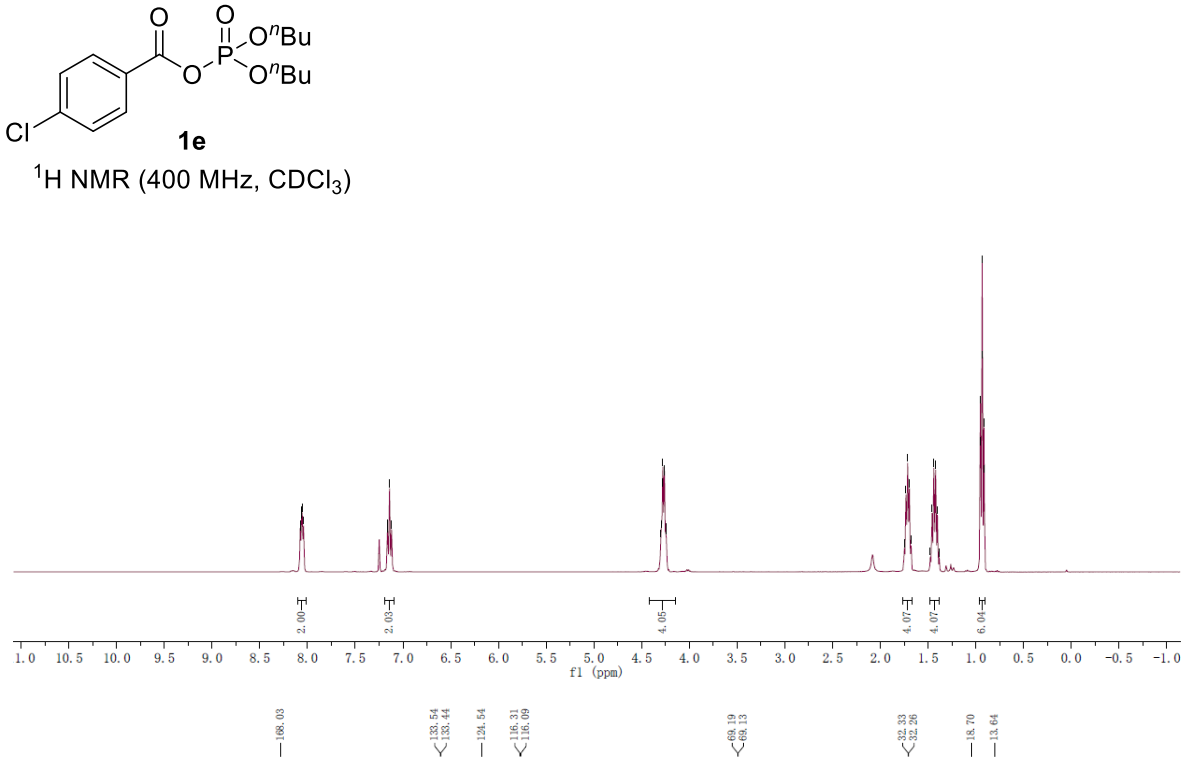
1d

^{31}P NMR (162 MHz, $CDCl_3$)



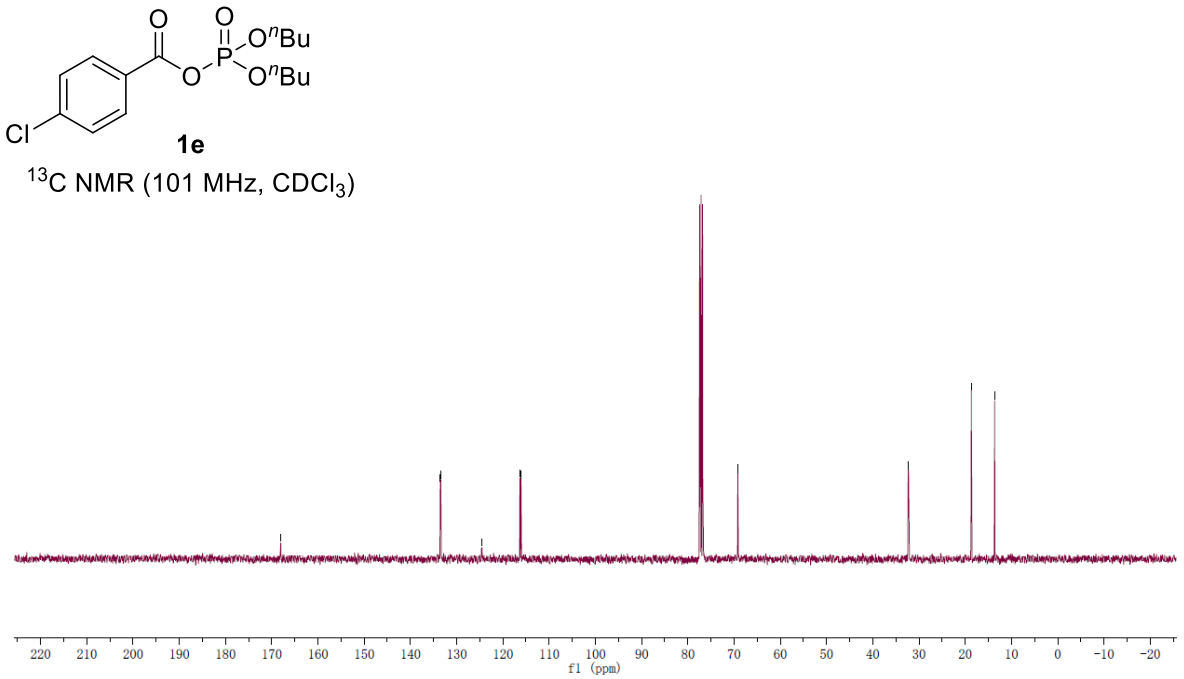
1d

^{19}F NMR (376 MHz, $CDCl_3$)



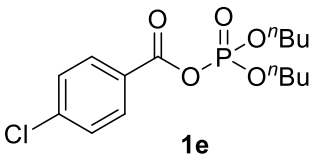
1e

^{1}H NMR (400 MHz, $CDCl_3$)



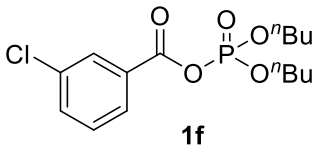
1e

^{13}C NMR (101 MHz, $CDCl_3$)



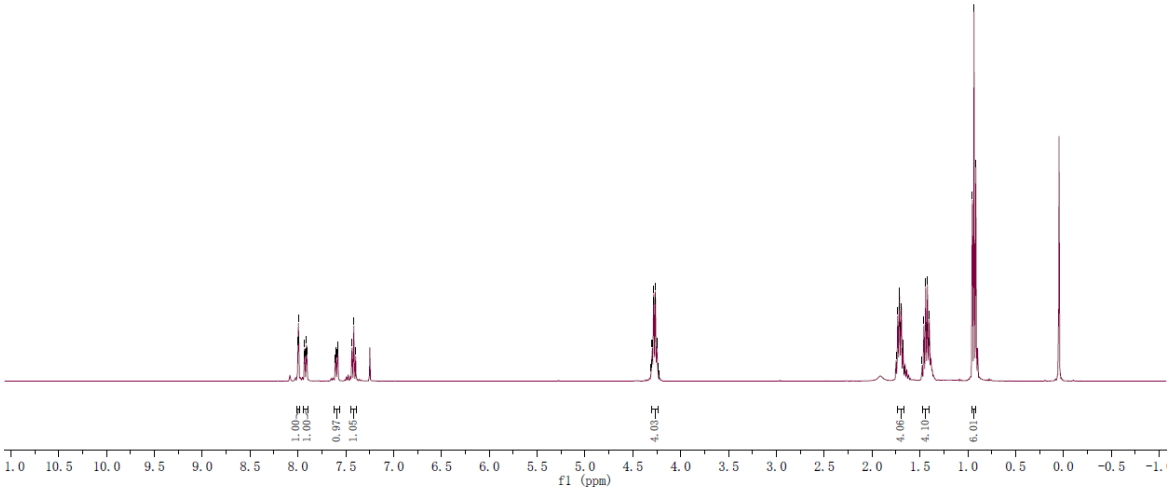
1e

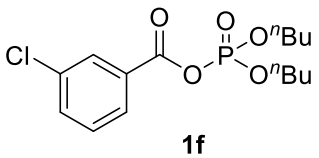
^{31}P NMR (162 MHz, $CDCl_3$)



1f

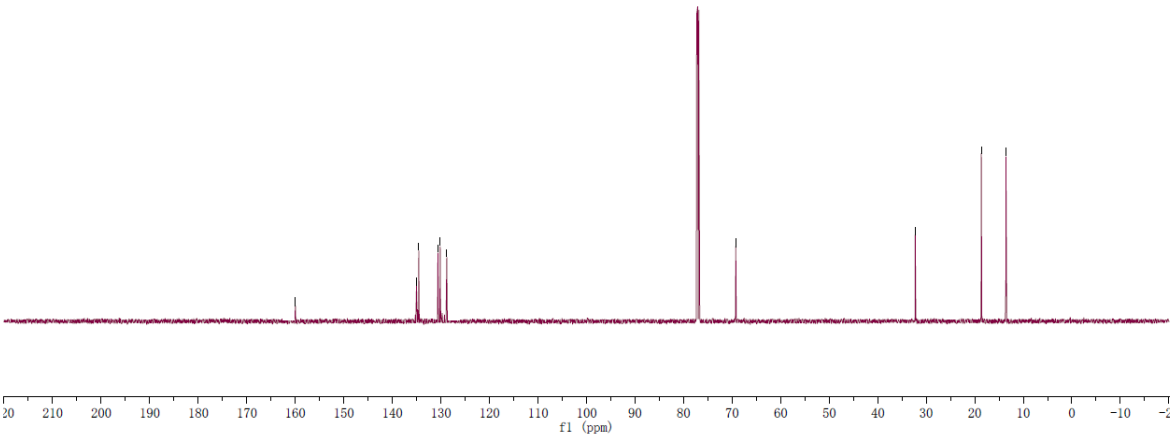
^{1}H NMR (400 MHz, $CDCl_3$)

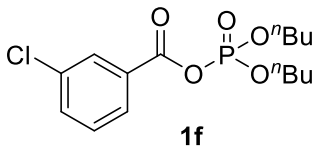




1f

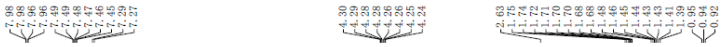
^{13}C NMR (101 MHz, $CDCl_3$)

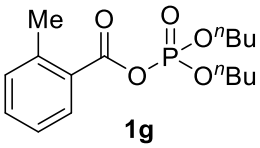




1f

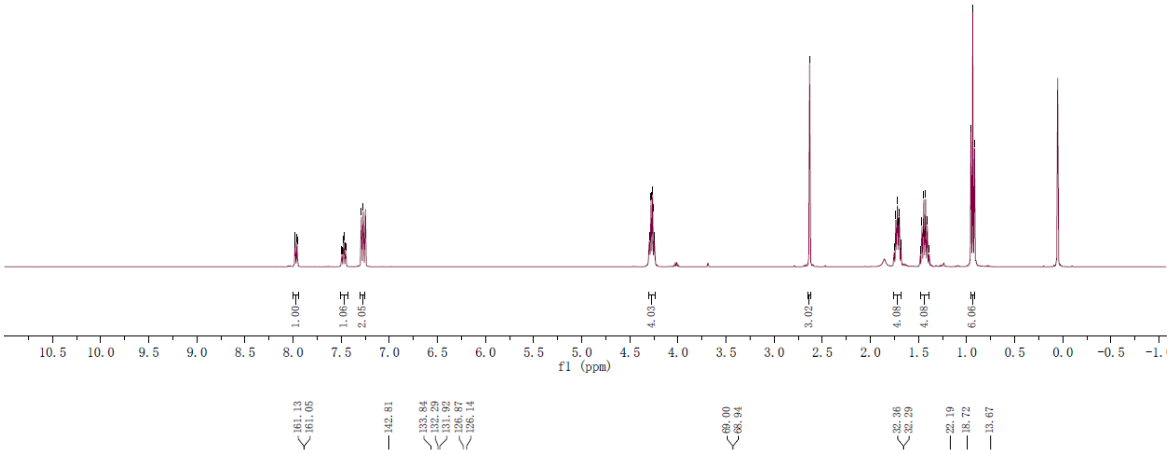
^{31}P NMR (162 MHz, $CDCl_3$)

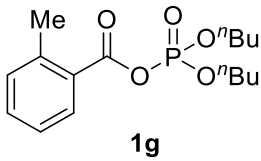




1g

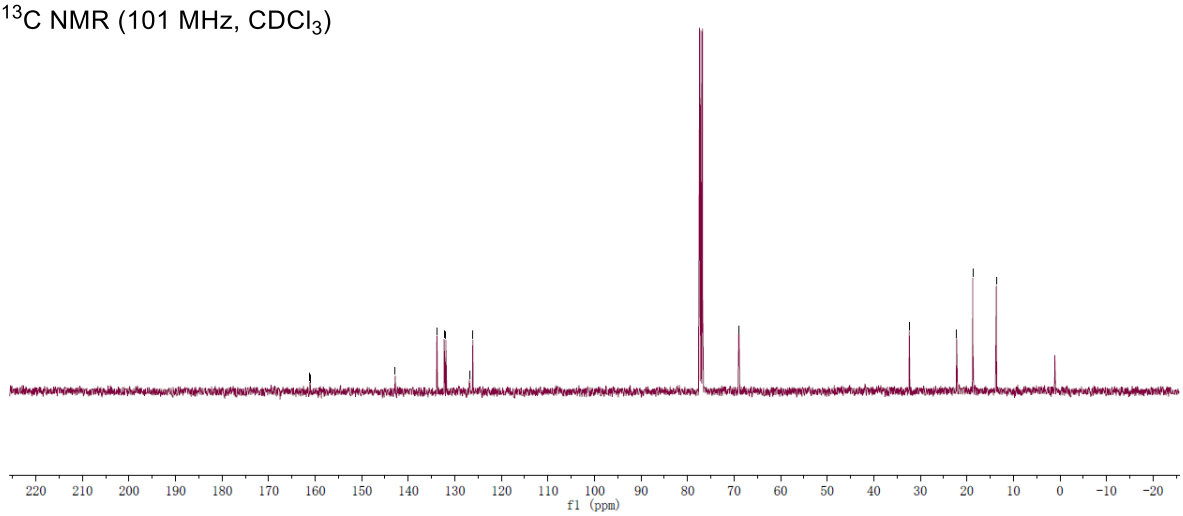
^{1}H NMR (400 MHz, $CDCl_3$)

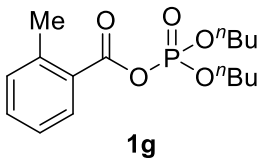




1g

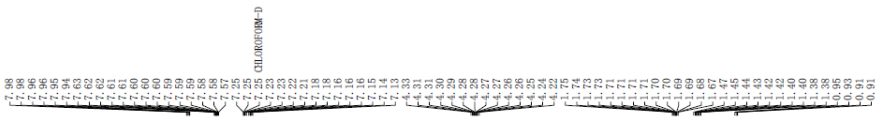
^{13}C NMR (101 MHz, $CDCl_3$)

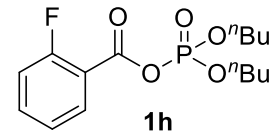




1g

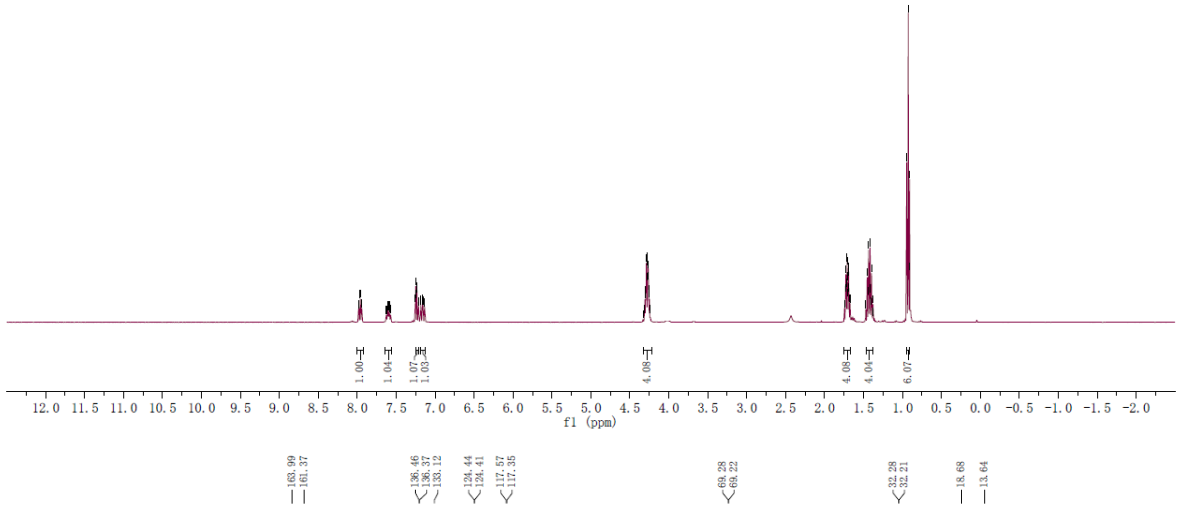
^{31}P NMR (162 MHz, $CDCl_3$)

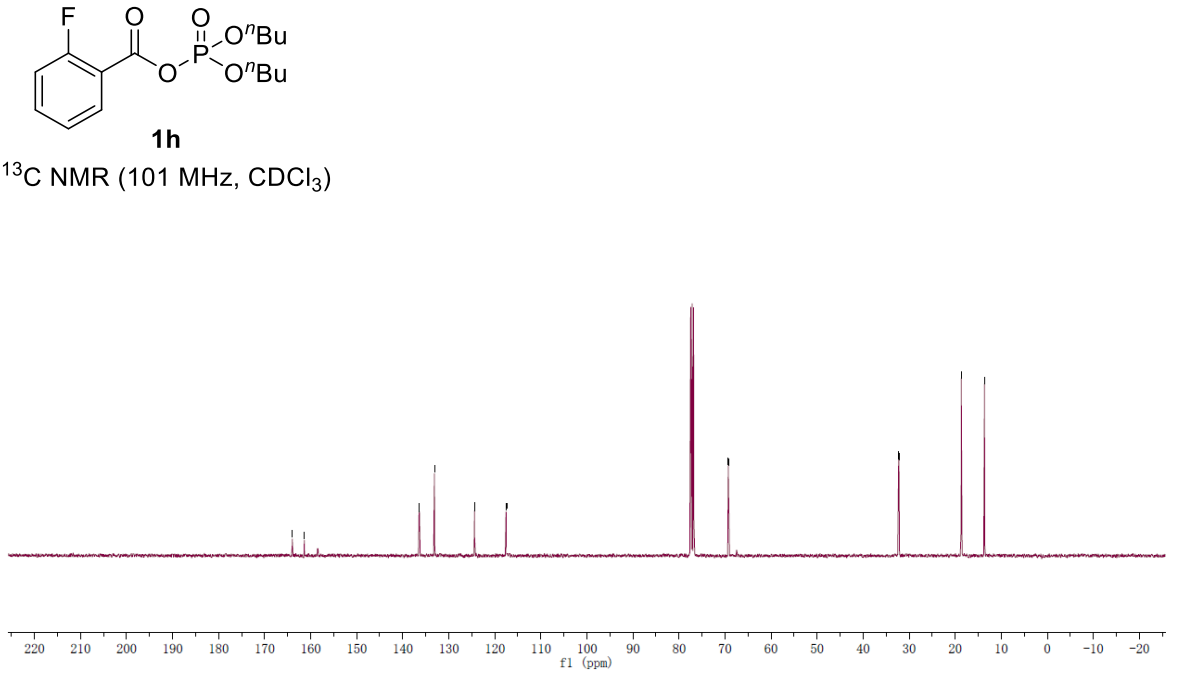




1h

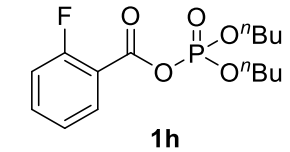
^{1}H NMR (400 MHz, $CDCl_3$)





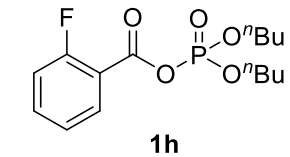
1h

^{13}C NMR (101 MHz, $CDCl_3$)



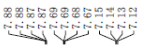
1h

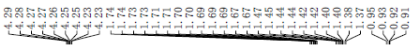
^{31}P NMR (162 MHz, $CDCl_3$)

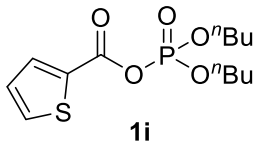


1h

^{19}F NMR (376 MHz, $CDCl_3$)

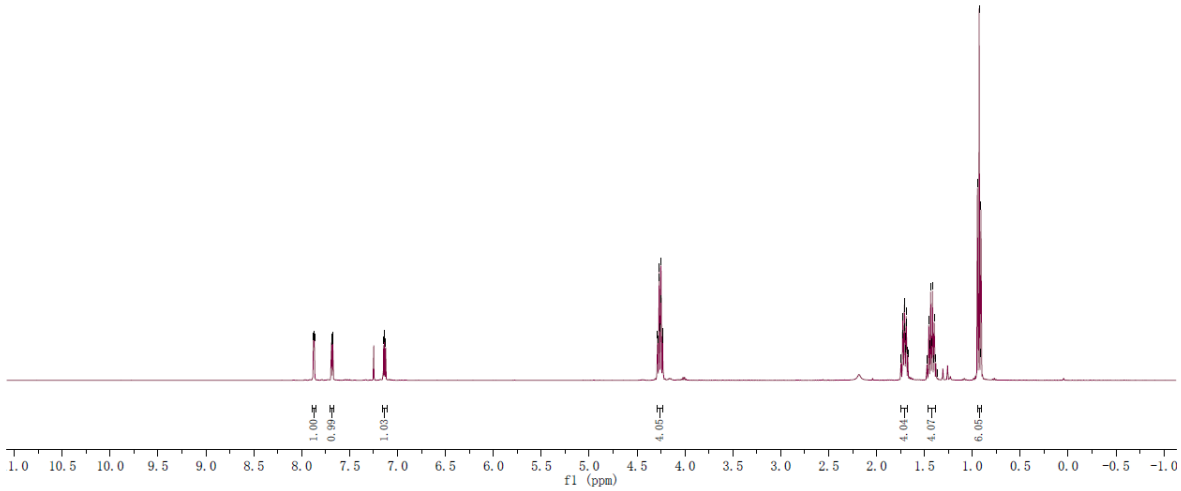


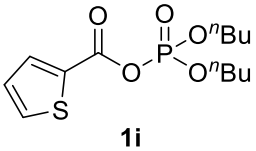




1i

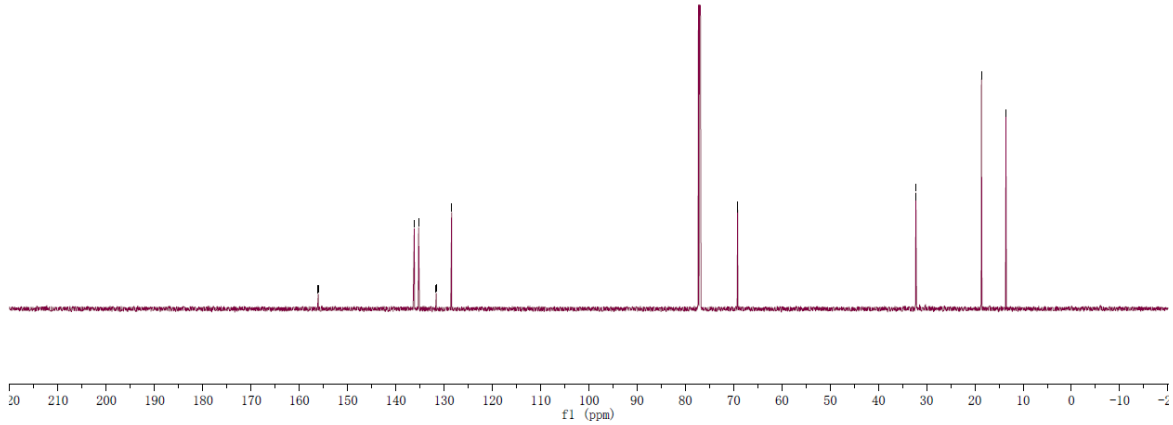
^{1}H NMR (400 MHz, $CDCl_3$)

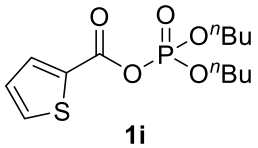




1i

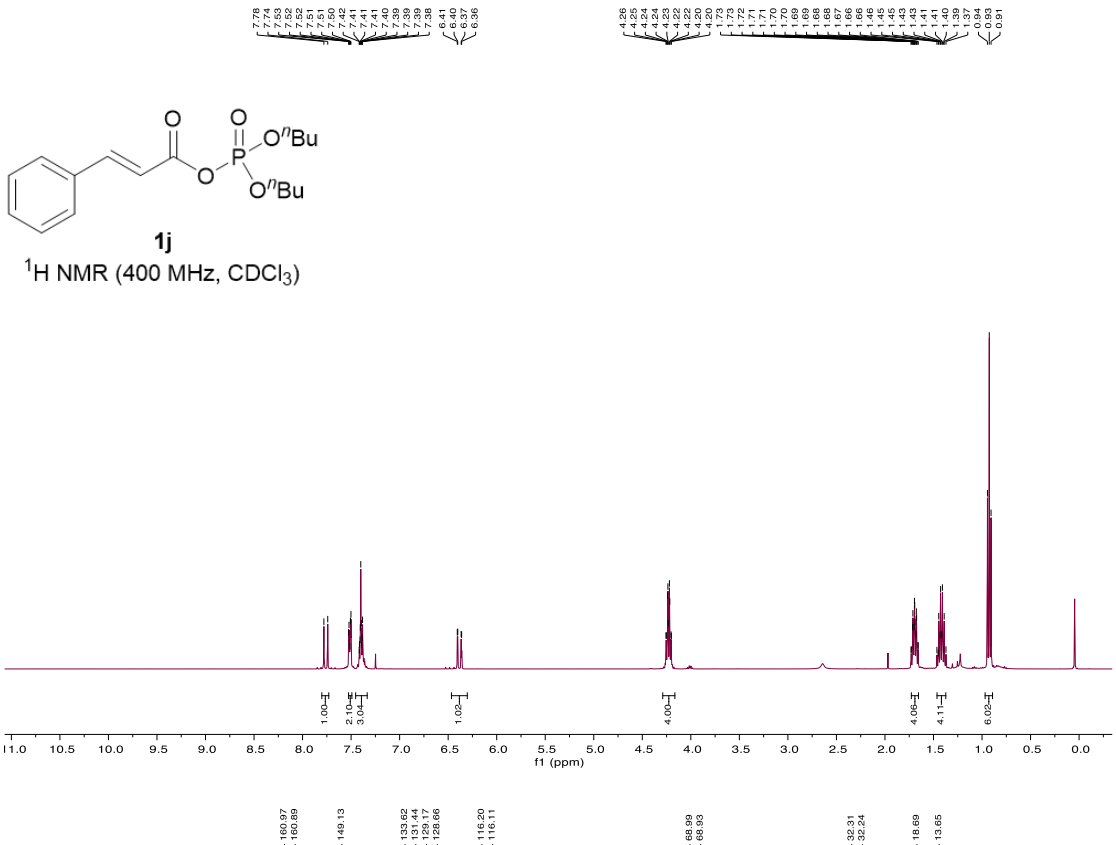
^{13}C NMR (101 MHz, $CDCl_3$)

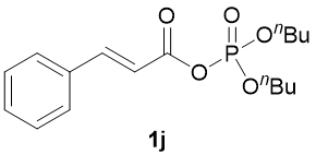




1i

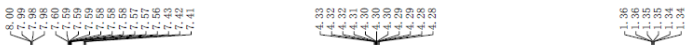
^{31}P NMR (162 MHz, $CDCl_3$)

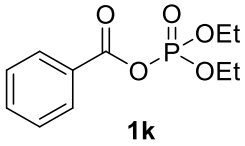

7.78
7.74
7.53
7.52
7.52
7.51
7.50
7.48
7.41
7.41
7.41
7.40
7.39
7.39
7.39
7.38
6.41
6.40
6.37
6.36
4.26
4.25
4.24
4.24
4.23
4.22
4.22
4.20
4.20
1.73
1.72
1.71
1.71
1.71
1.70
1.70
1.69
1.69
1.68
1.68
1.67
1.66
1.66
1.46
1.45
1.45
1.43
1.43
1.41
1.40
1.39
1.37
0.94
0.93
0.91
O
O
O
P
O
O
O
O
O
O
P
O
O
1j
1H NMR (400 MHz, CDCl3)
1.00
2.10
3.04
1.02
4.00
4.06
4.11
6.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
160.97
160.89
149.13
133.62
131.44
129.17
128.66
116.20
116.11
68.99
68.93
32.31
32.24
18.69
13.65
1j
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



1j

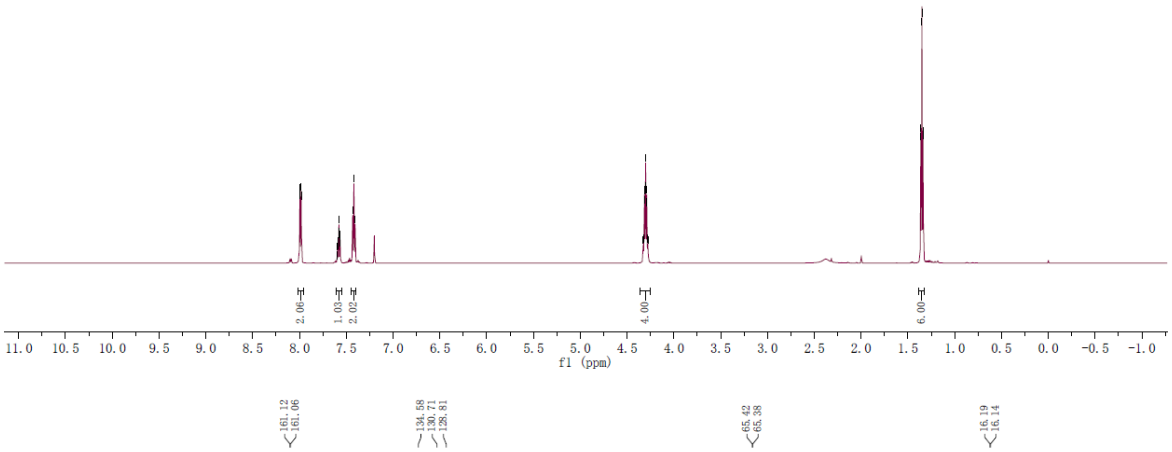
^{31}P NMR (162 MHz, $CDCl_3$)

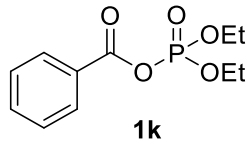




1k

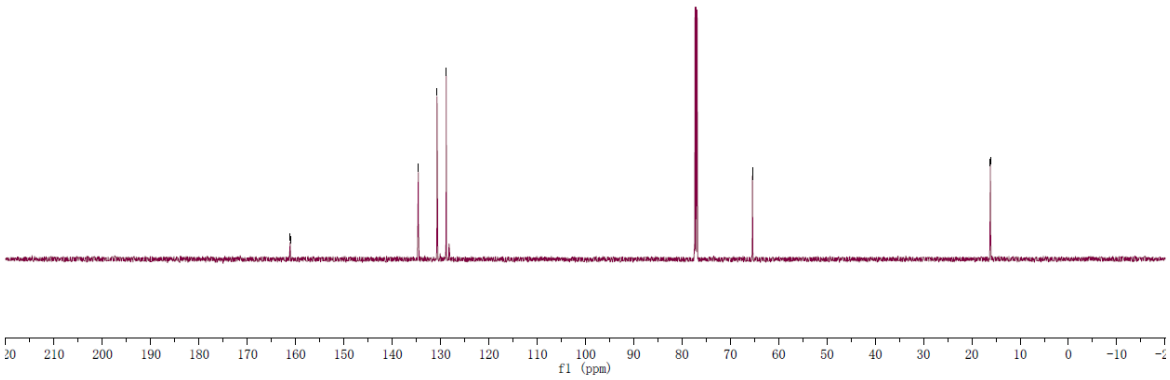
^{1}H NMR (600 MHz, $CDCl_3$)

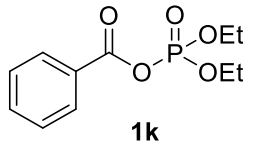




1k

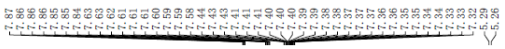
^{13}C NMR (101 MHz, $CDCl_3$)

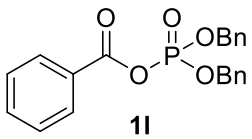




1k

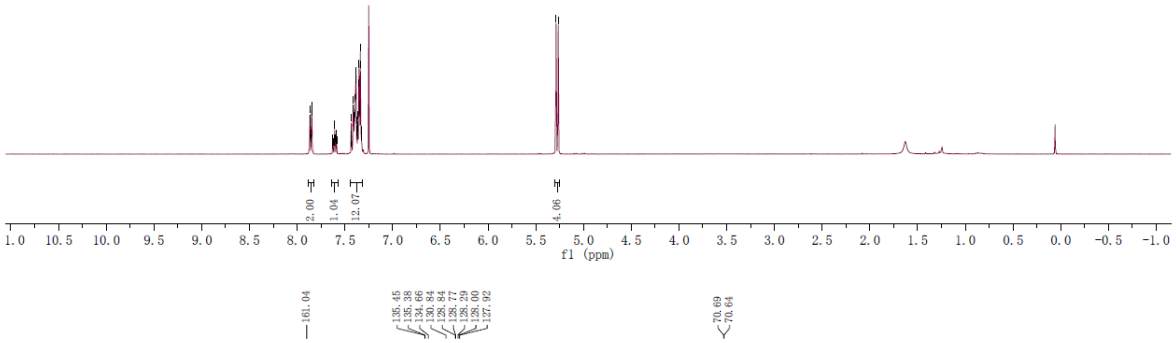
^{31}P NMR (162 MHz, $CDCl_3$)

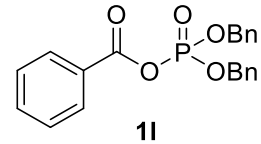




1l

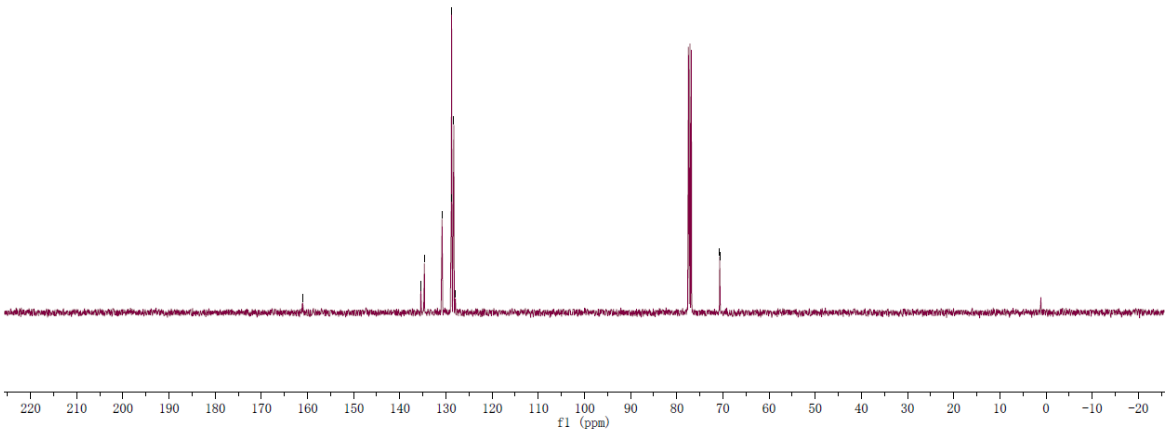
^{1}H NMR (400 MHz, $CDCl_3$)

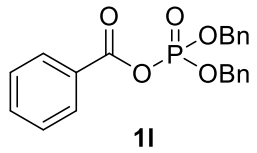




1l

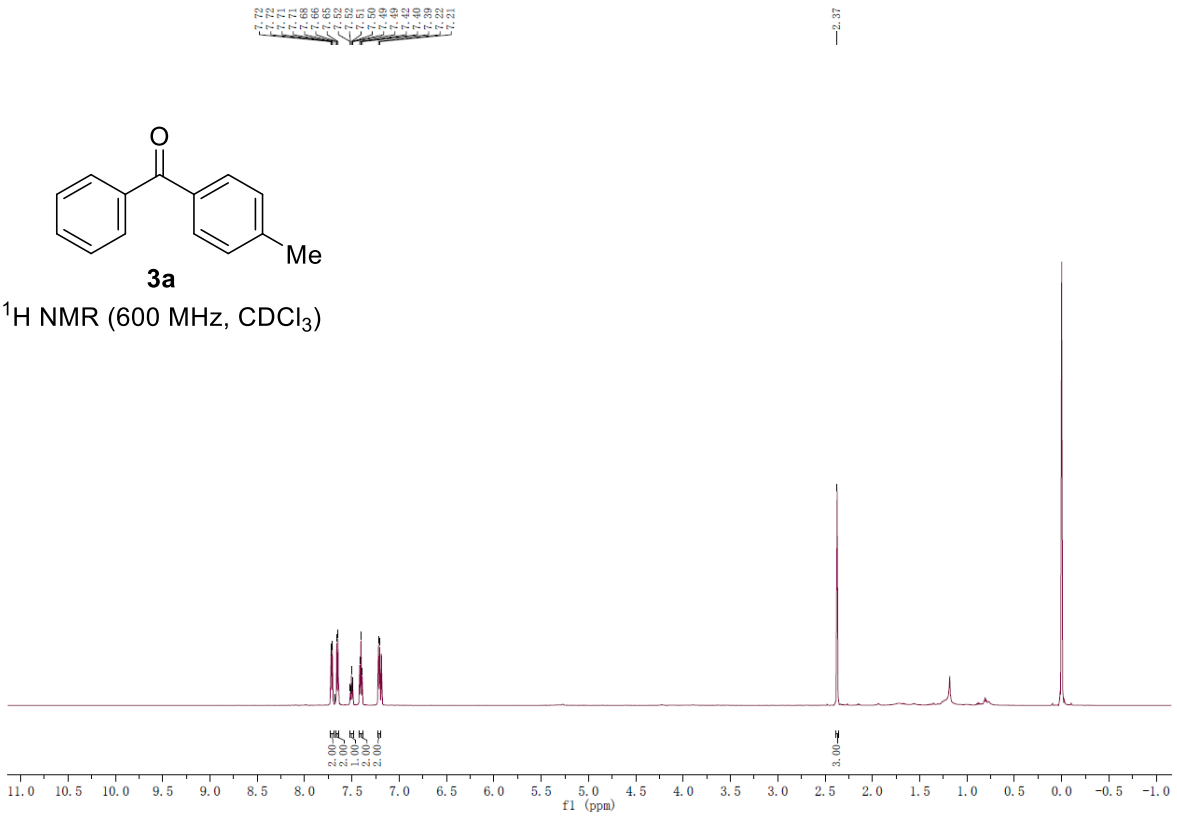
^{13}C NMR (101 MHz, $CDCl_3$)

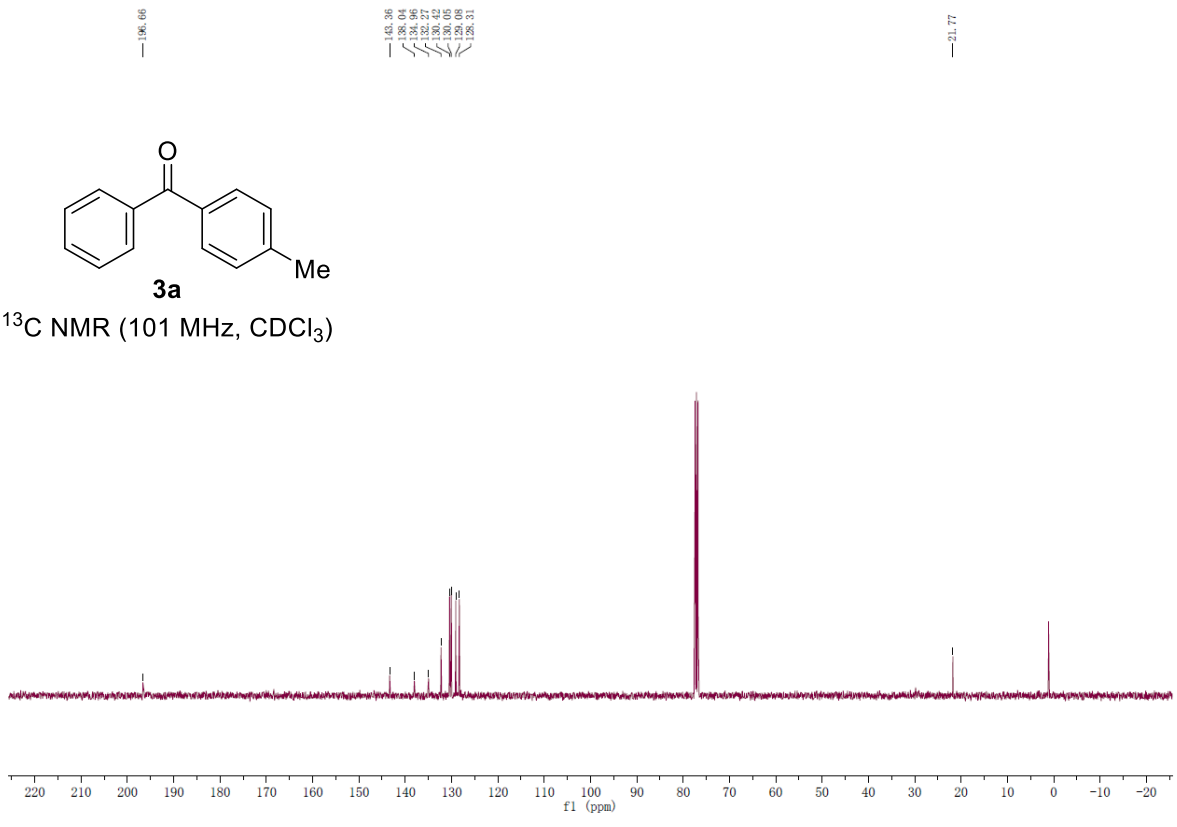


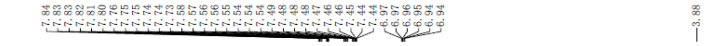


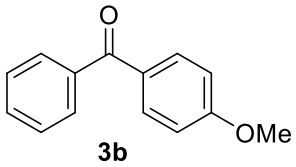
1l

^{31}P NMR (162 MHz, $CDCl_3$)


7.72
7.72
7.71
7.71
7.68
7.66
7.65
7.52
7.51
7.50
7.49
7.42
7.40
7.39
7.22
7.21
2.37
O
Me
3a
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
2.00
1.00
2.00
2.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

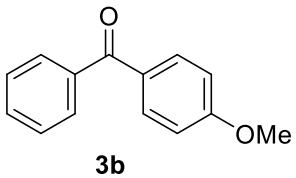

196.66
143.36
138.04
134.96
132.27
130.42
130.05
129.08
128.31
21.77
O
Me
3a
^{13}C NMR (101 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)





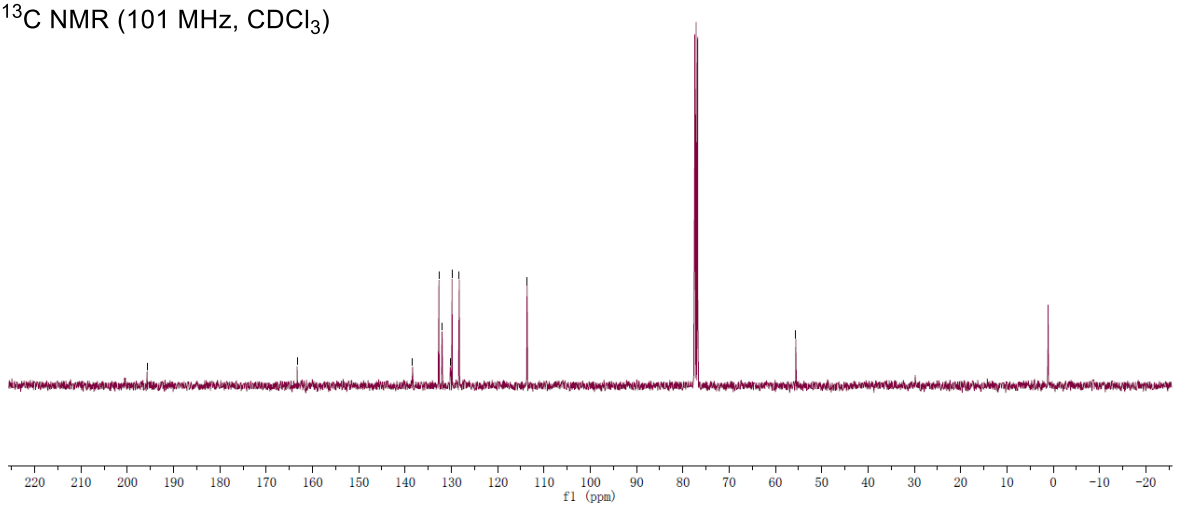
3b

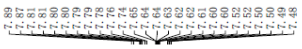
^{1}H NMR (400 MHz, $CDCl_3$)

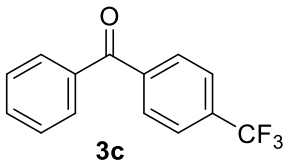


3b

^{13}C NMR (101 MHz, $CDCl_3$)

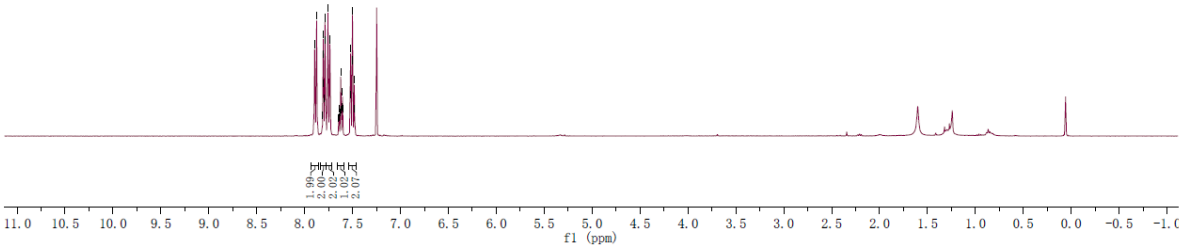


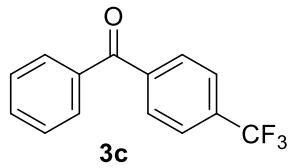




3c

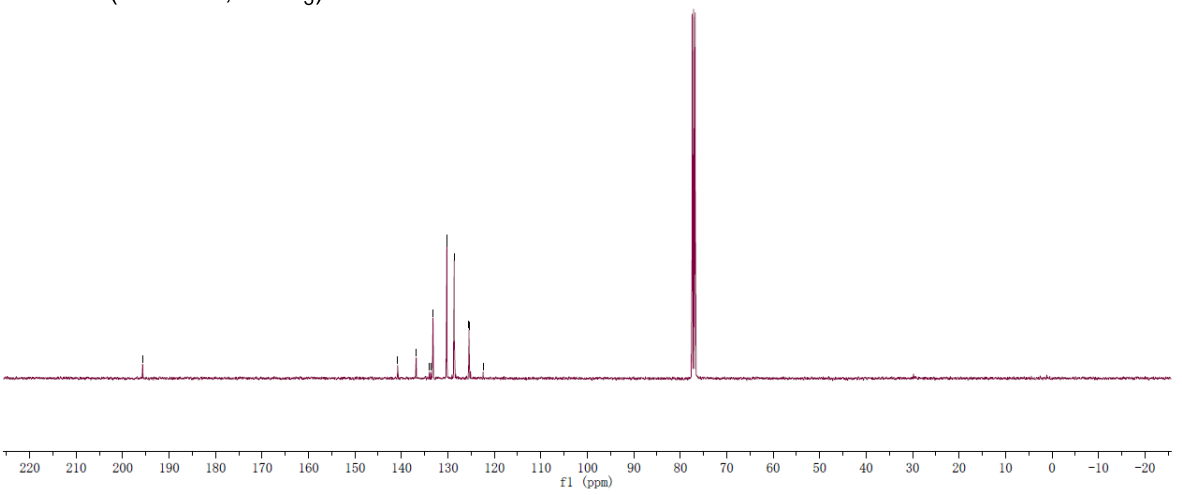
^{1}H NMR (400 MHz, $CDCl_3$)

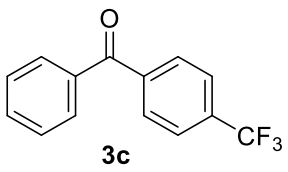




3c

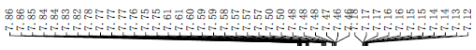
^{13}C NMR (101 MHz, $CDCl_3$)

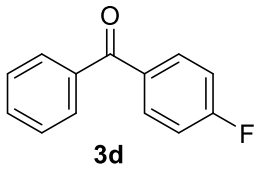




3c

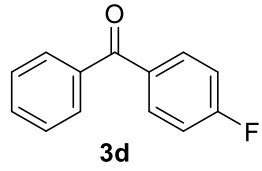
^{19}F NMR (376 MHz, $CDCl_3$)





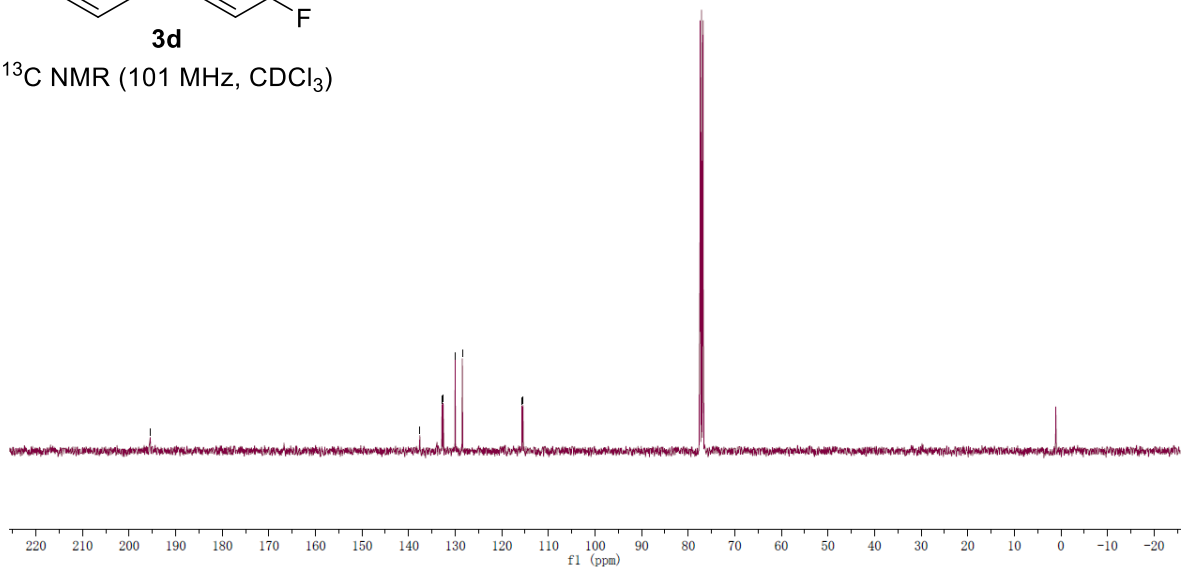
3d

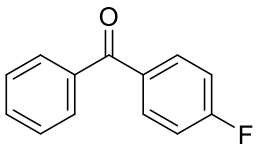
^{1}H NMR (400 MHz, $CDCl_3$)



3d

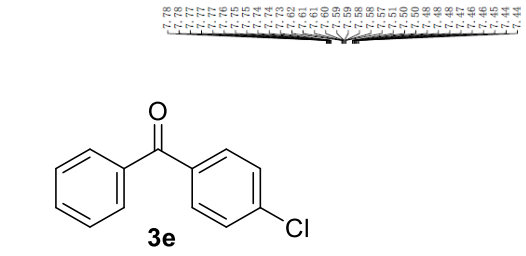
^{13}C NMR (101 MHz, $CDCl_3$)





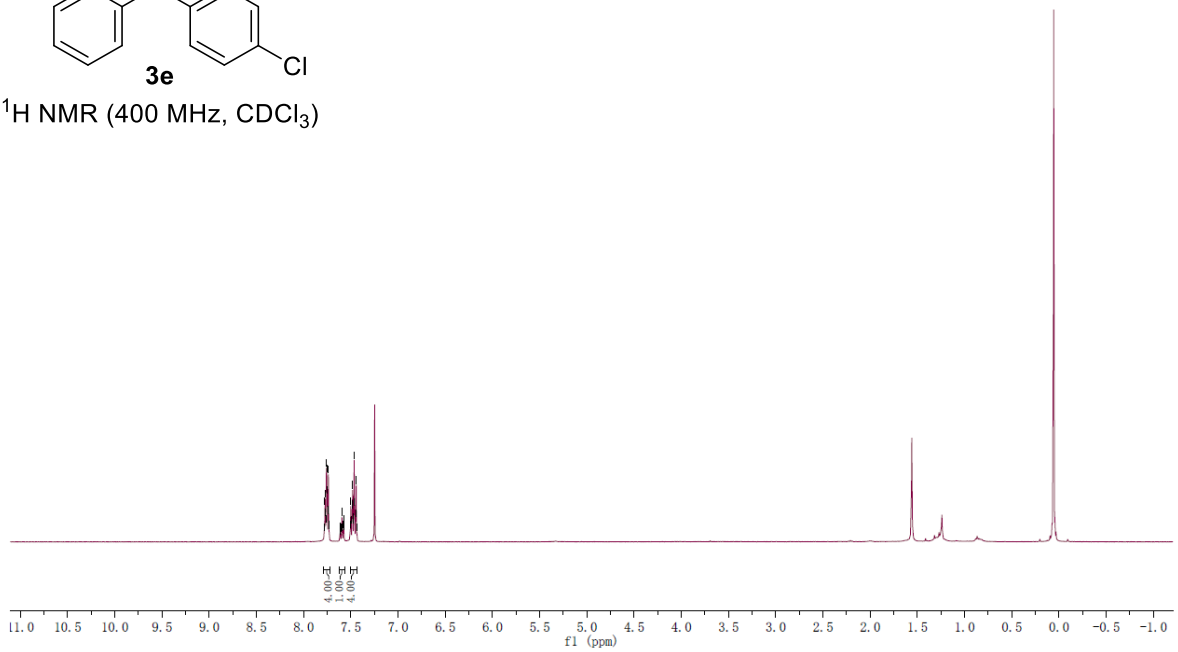
3d

^{19}F NMR (376 MHz, $CDCl_3$)



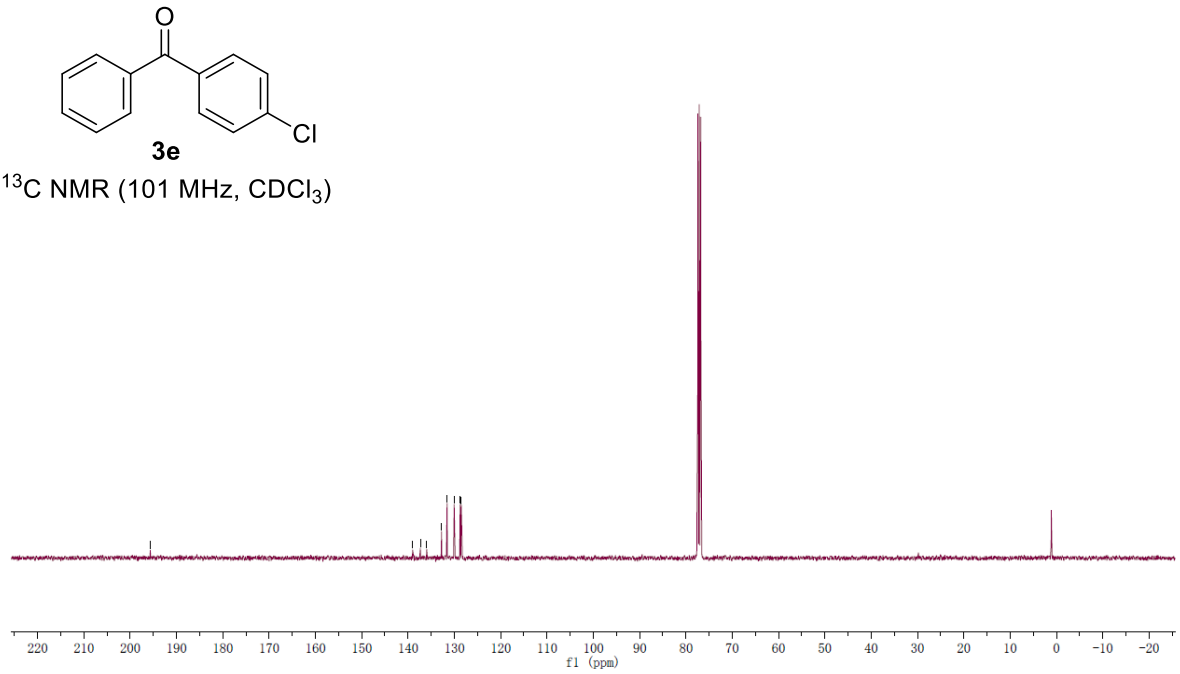
3e

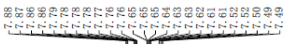
^{1}H NMR (400 MHz, $CDCl_3$)

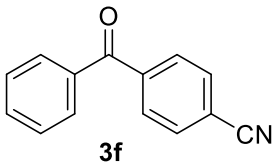


3e

^{13}C NMR (101 MHz, $CDCl_3$)

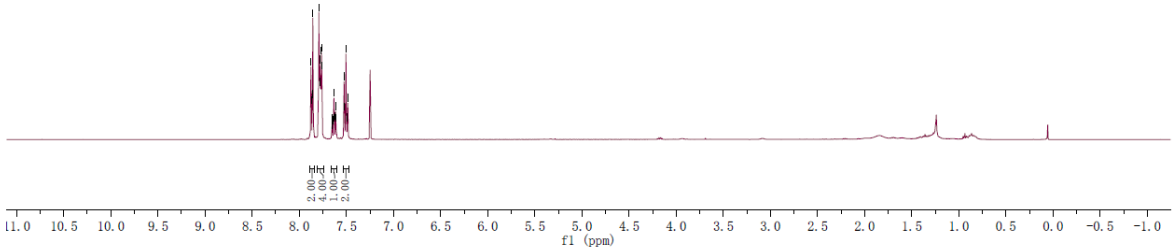


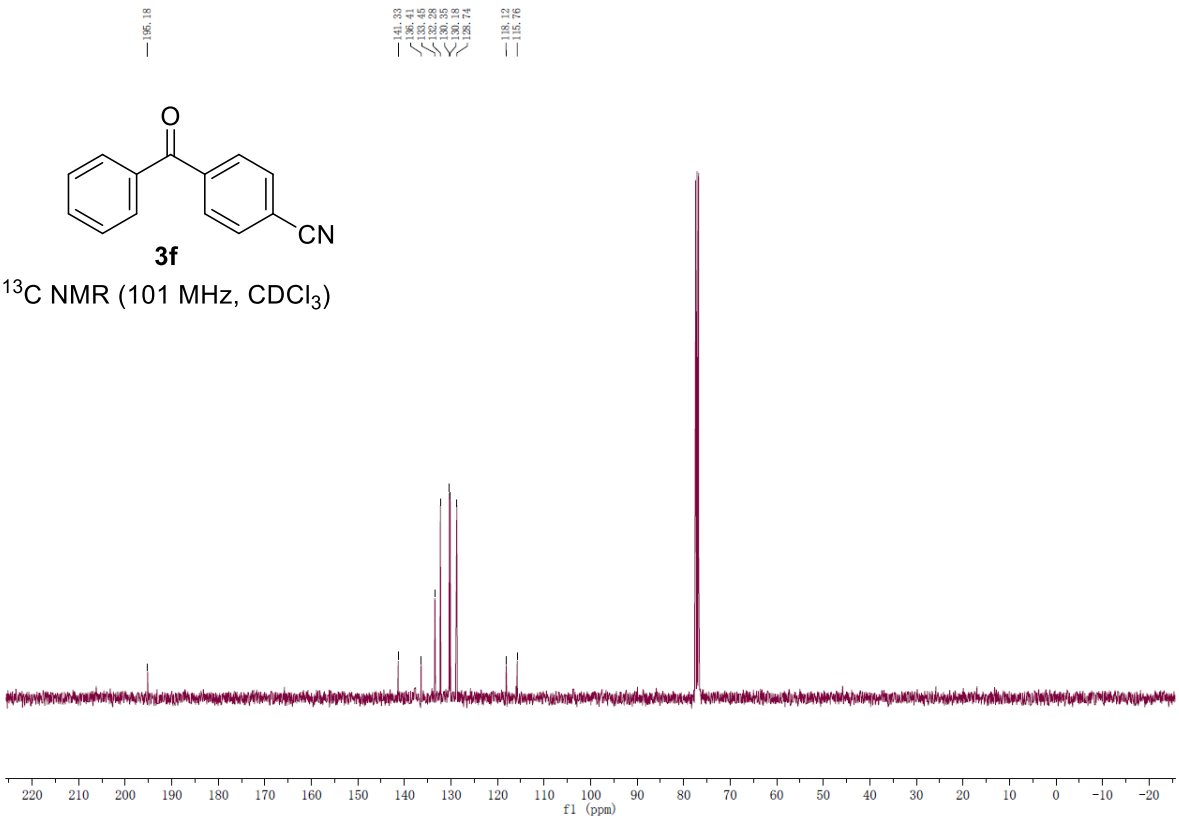




3f

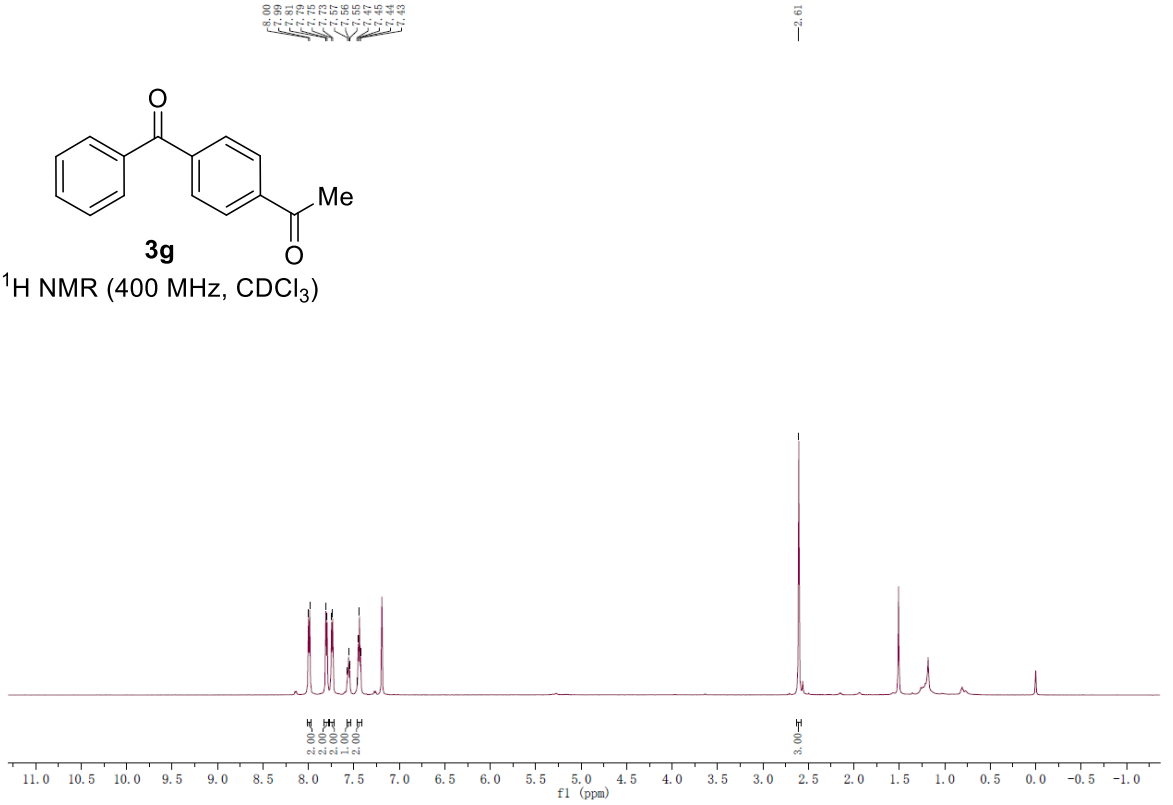
^{1}H NMR (400 MHz, $CDCl_3$)

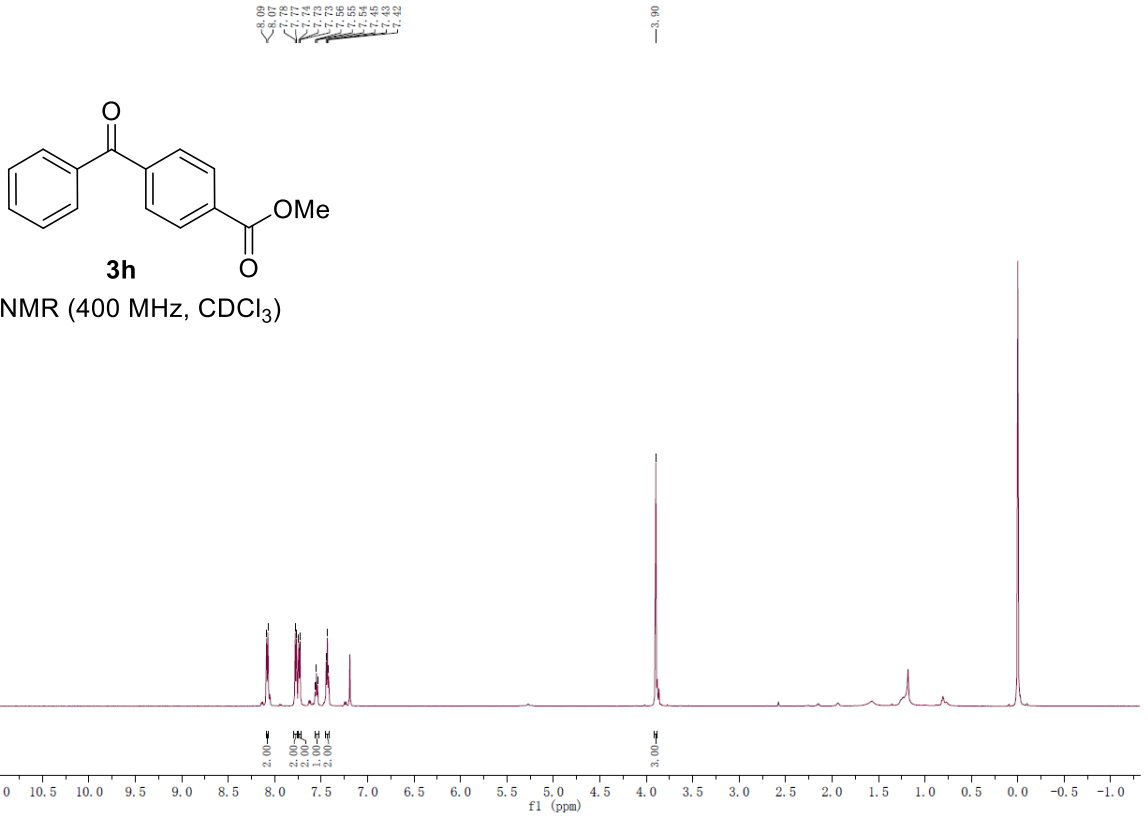




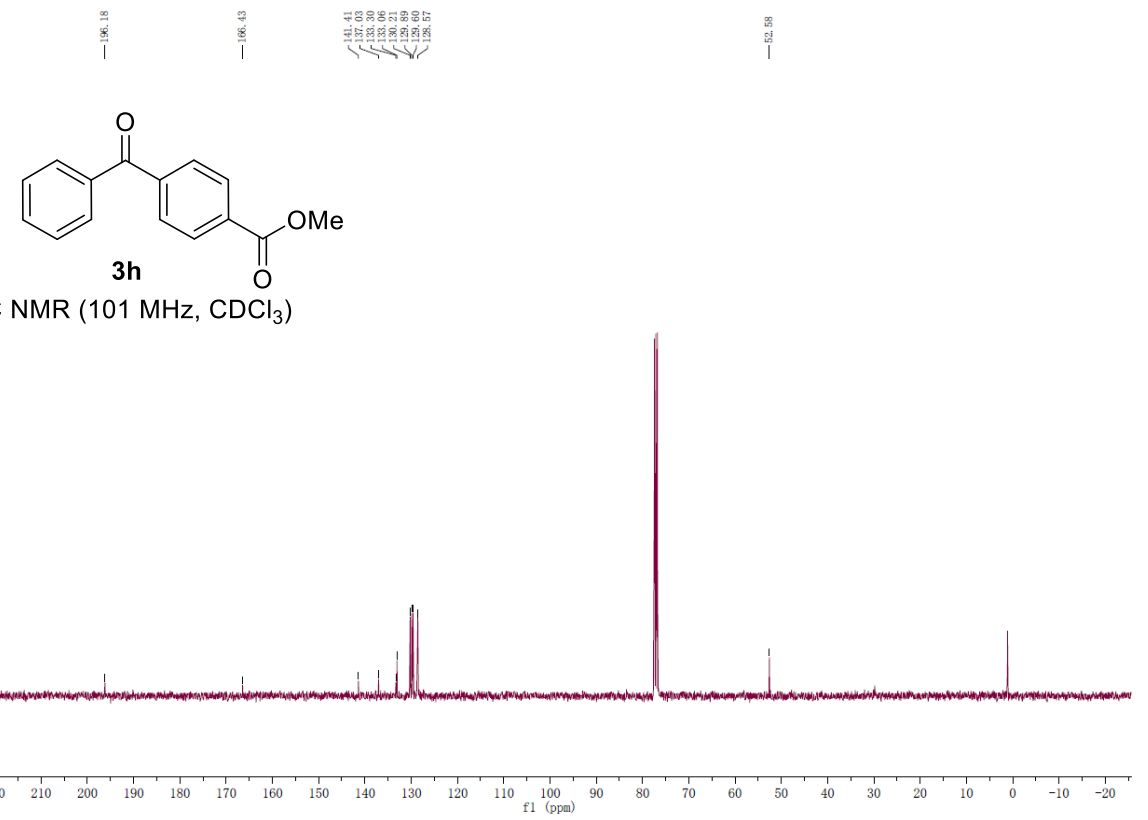
3f

^{13}C NMR (101 MHz, $CDCl_3$)

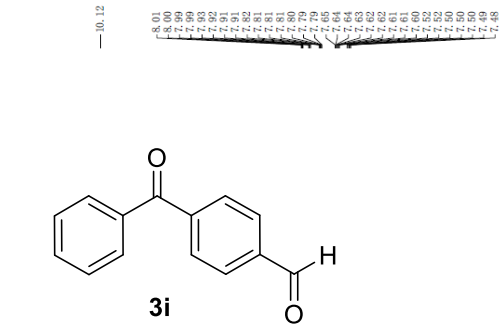

Me
O
3g
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)
Me
O
3g
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)

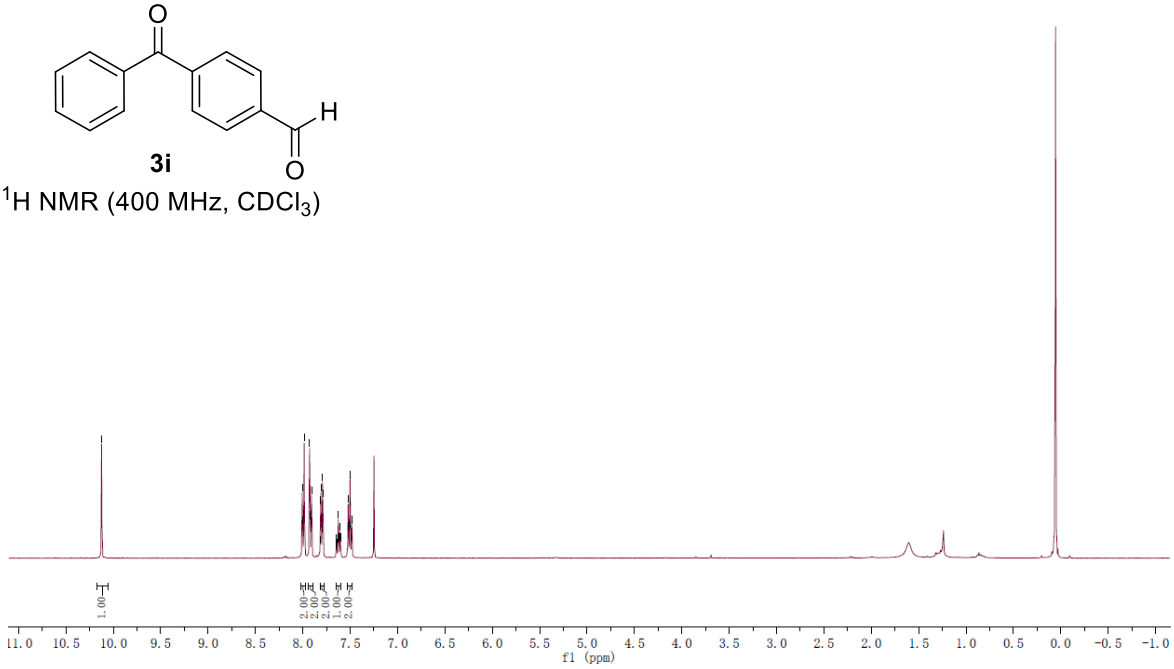


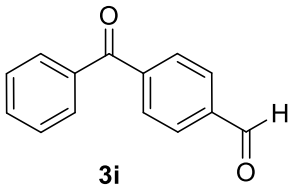
^{13}C NMR (101 MHz, $CDCl_3$)



3i

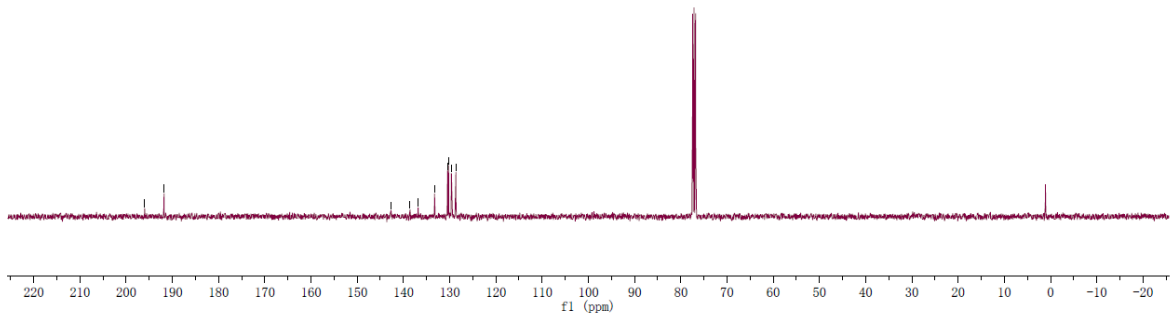
^{1}H NMR (400 MHz, $CDCl_3$)

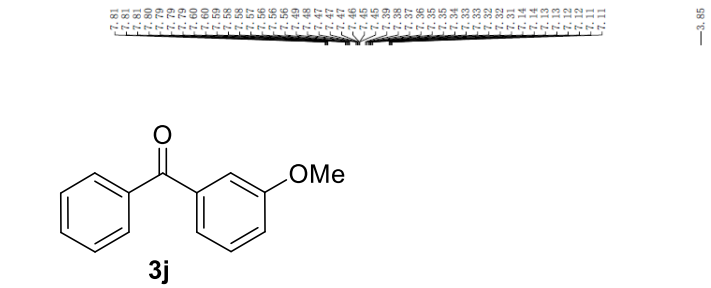




3i

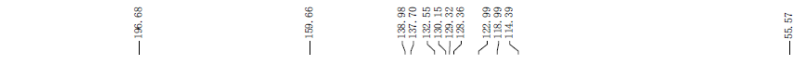
^{13}C NMR (101 MHz, $CDCl_3$)

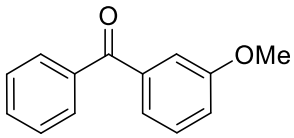




3j

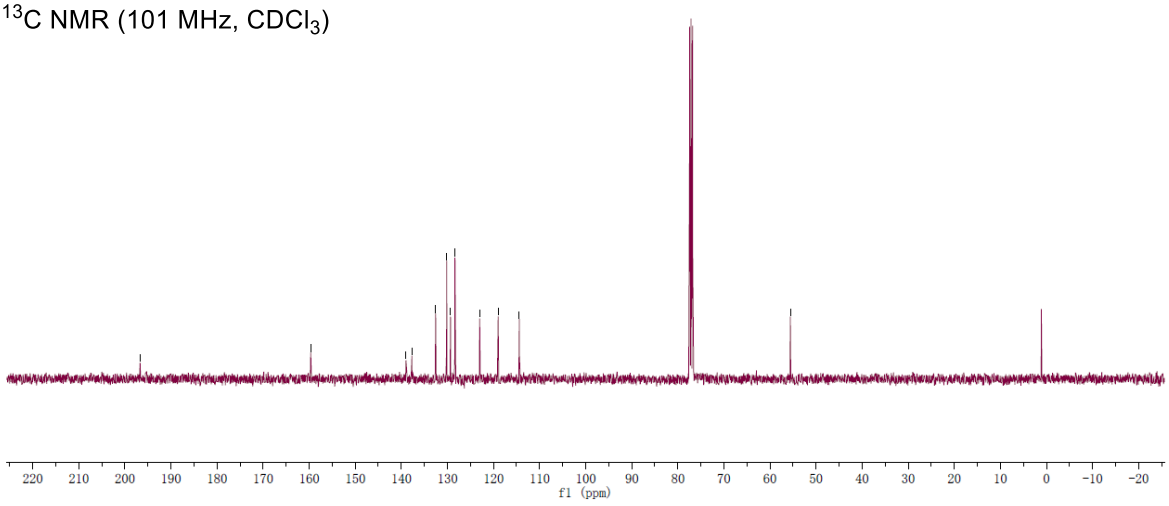
^{1}H NMR (400 MHz, $CDCl_3$)

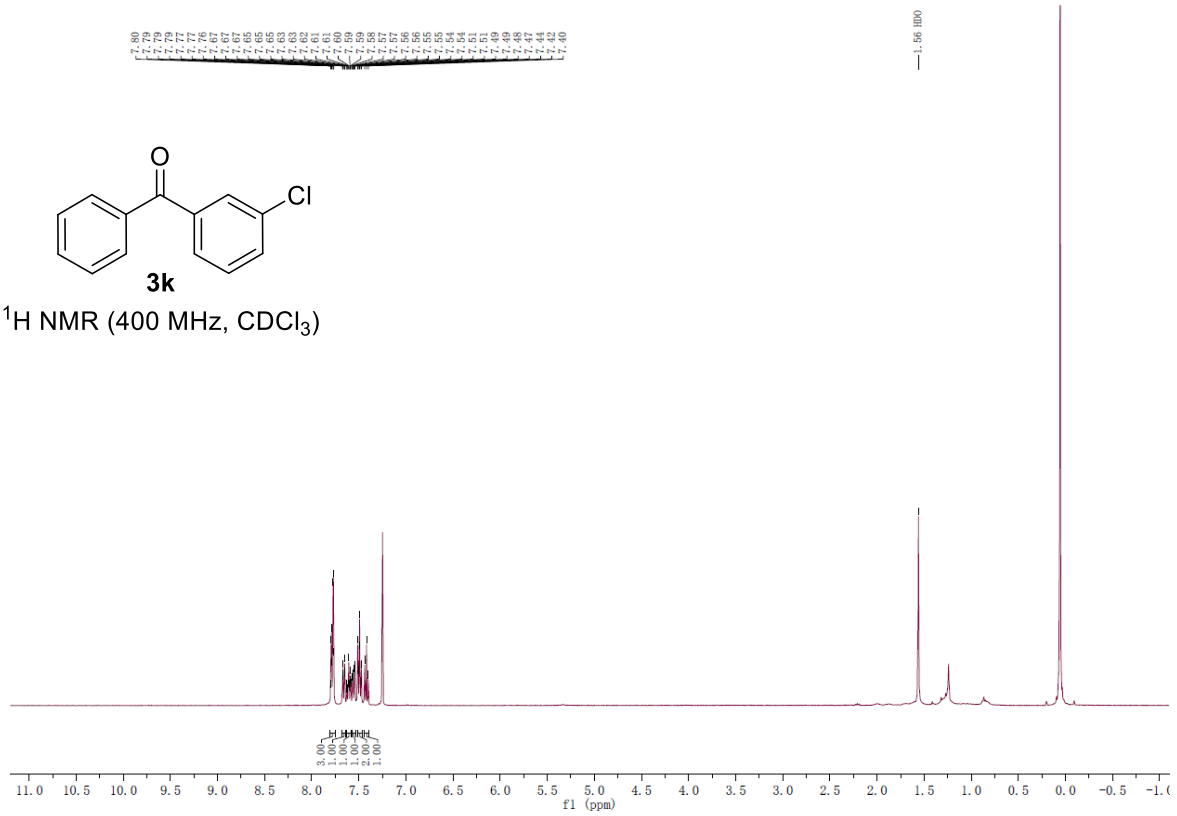


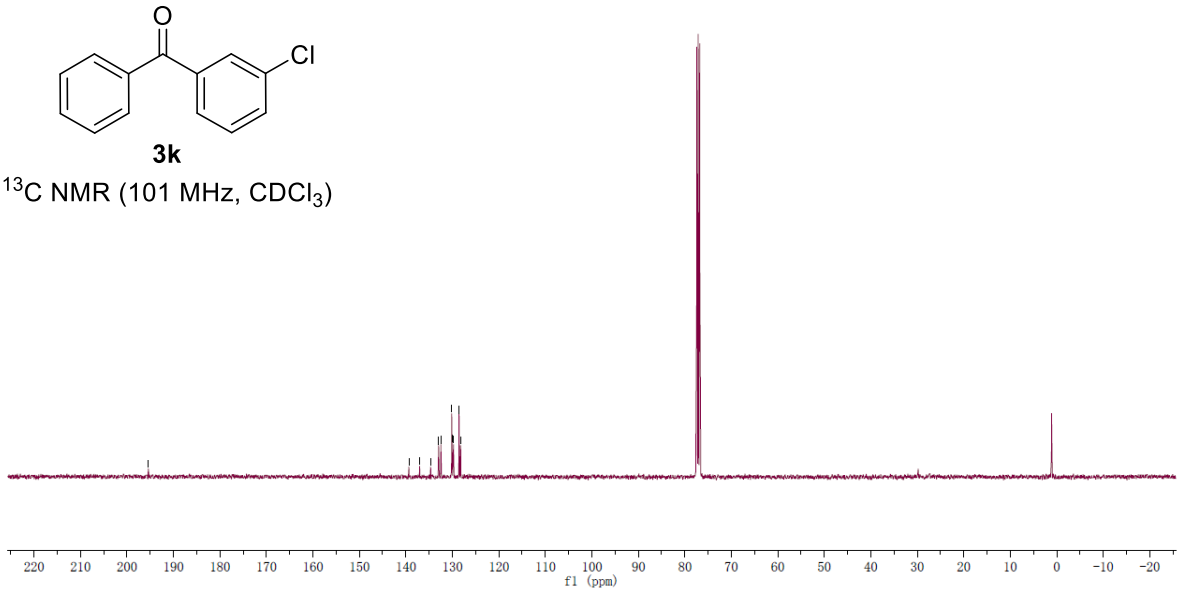


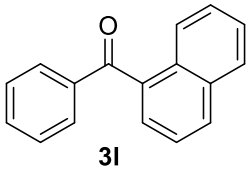
3j

^{13}C NMR (101 MHz, $CDCl_3$)



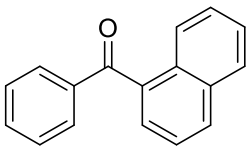

O
Cl
3k
1H NMR (400 MHz, CDCl3)
f1 (ppm)


O
Cl
3k
13C NMR (101 MHz, CDCl3)
f1 (ppm)



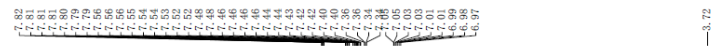
3l

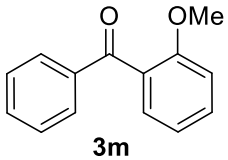
^{1}H NMR (400 MHz, $CDCl_3$)



3l

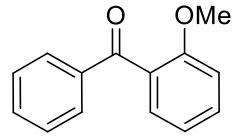
^{13}C NMR (101 MHz, $CDCl_3$)





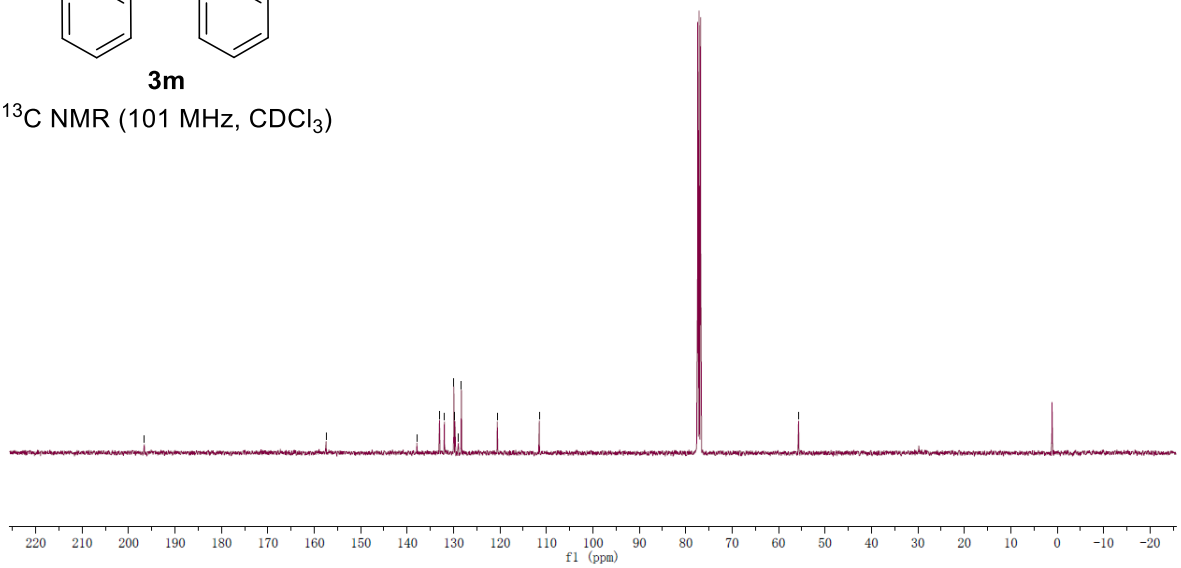
3m

^{1}H NMR (400 MHz, $CDCl_3$)



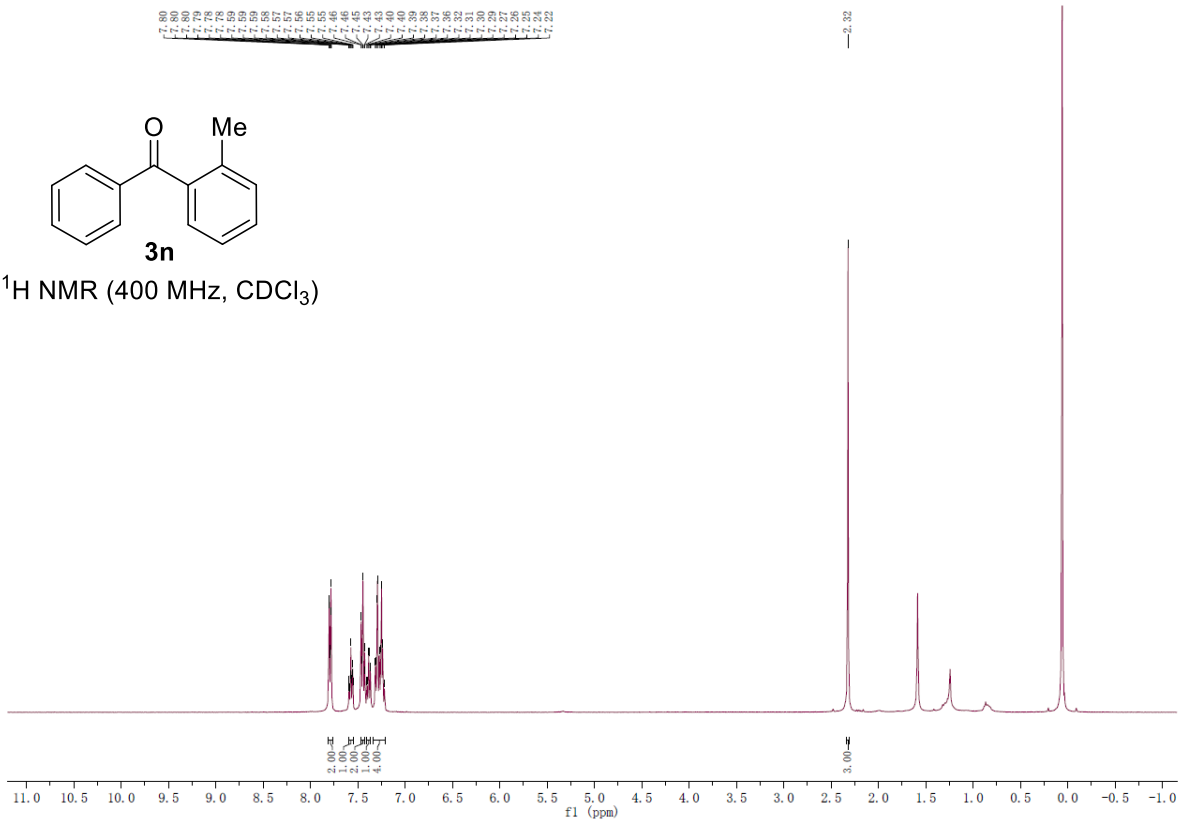
3m

^{13}C NMR (101 MHz, $CDCl_3$)



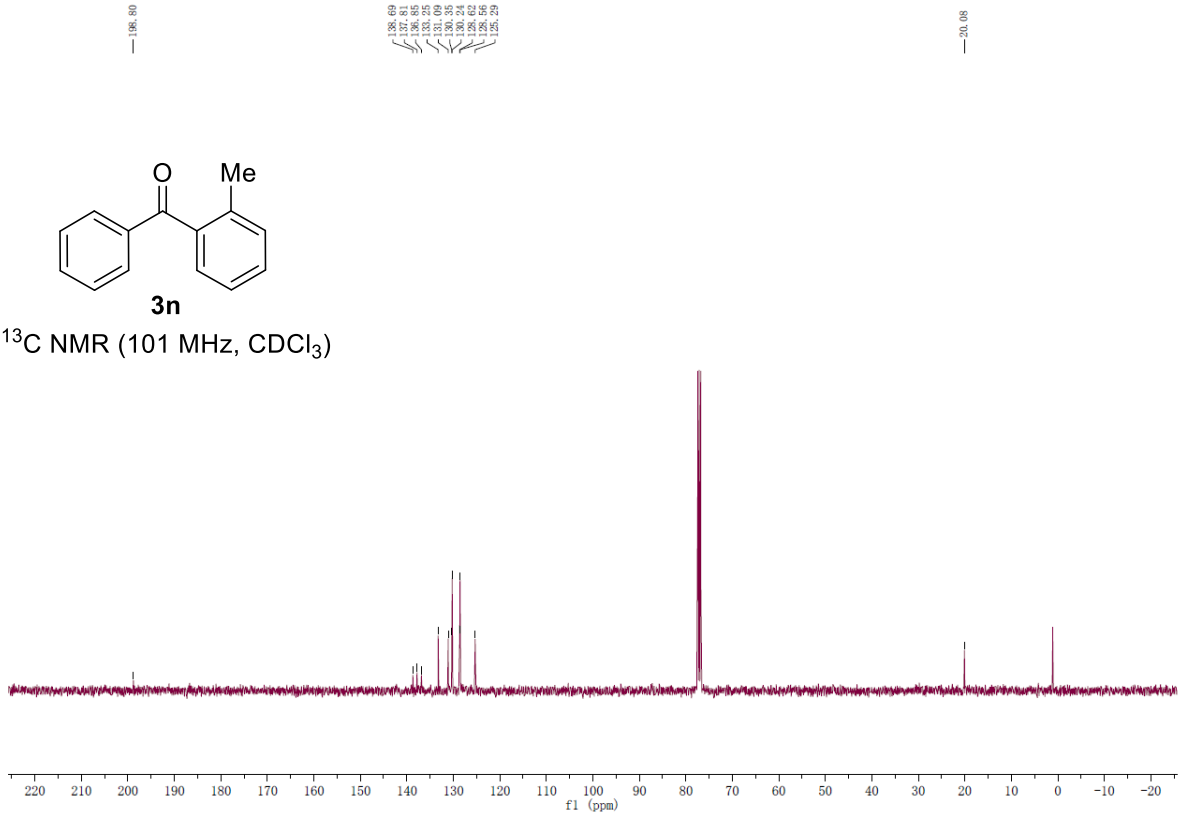
3n

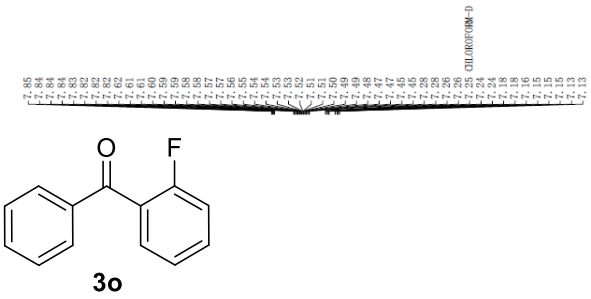
^{1}H NMR (400 MHz, $CDCl_3$)



3n

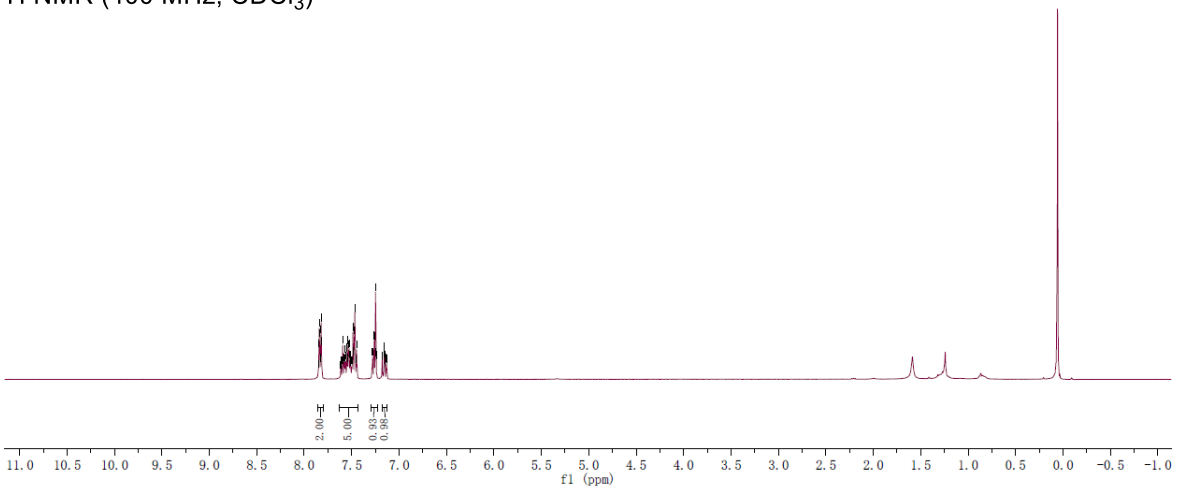
^{13}C NMR (101 MHz, $CDCl_3$)

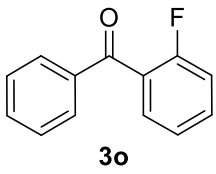




3o

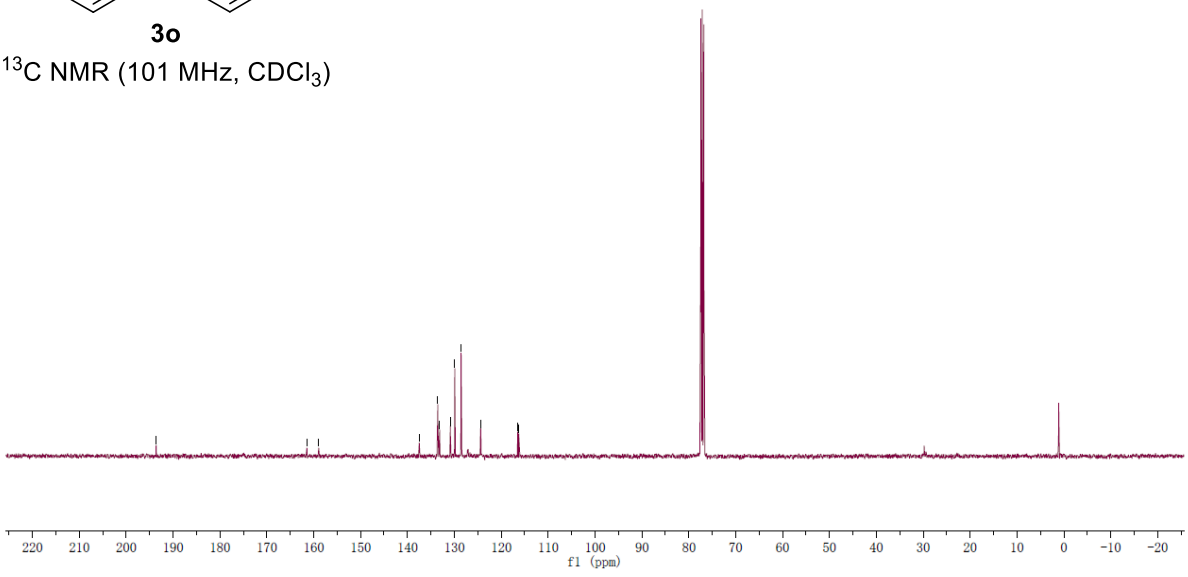
^{1}H NMR (400 MHz, $CDCl_3$)

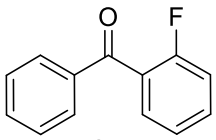




3o

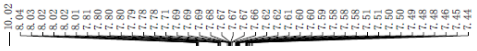
^{13}C NMR (101 MHz, $CDCl_3$)

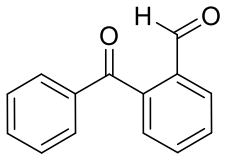




3o

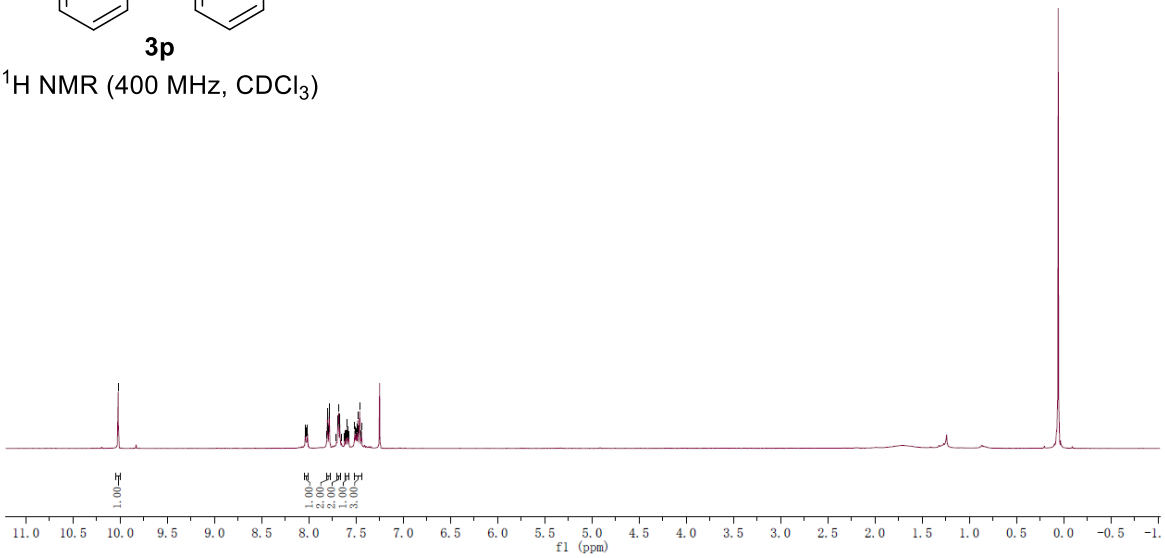
^{19}F NMR (376 MHz, $CDCl_3$)

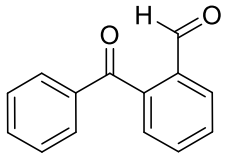




3p

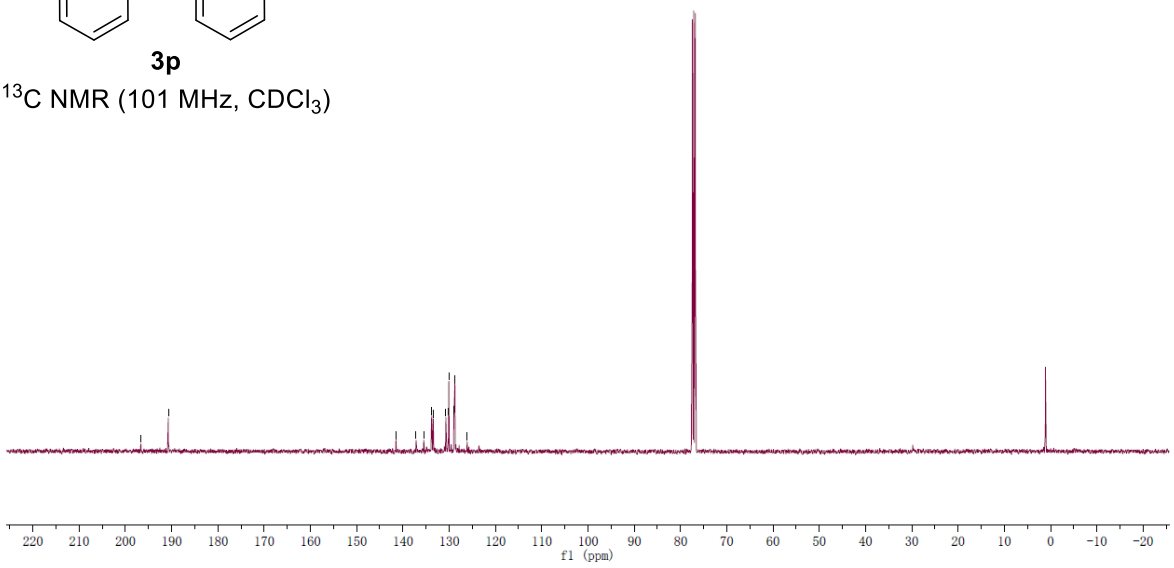
^{1}H NMR (400 MHz, $CDCl_3$)

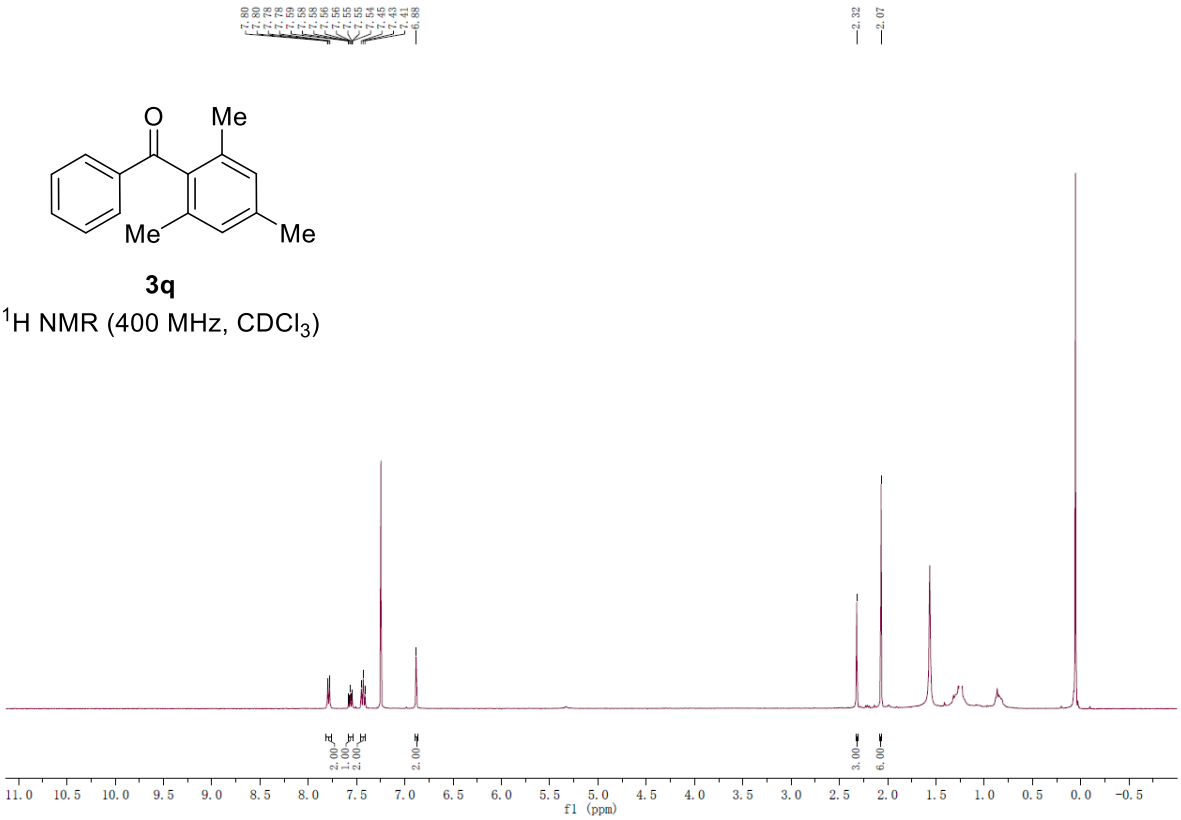




3p

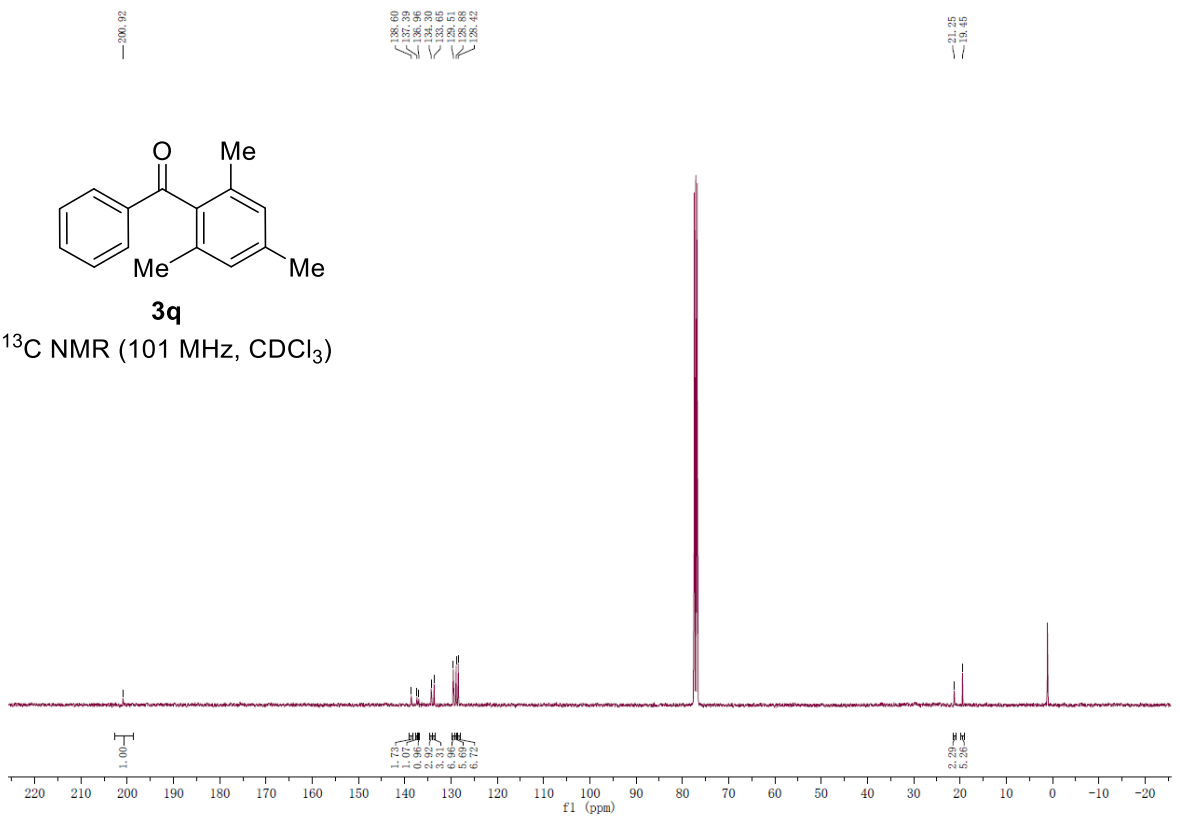
^{13}C NMR (101 MHz, $CDCl_3$)





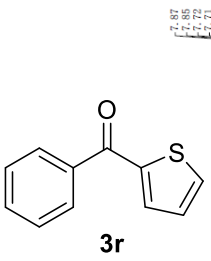
3q

^{1}H NMR (400 MHz, $CDCl_3$)



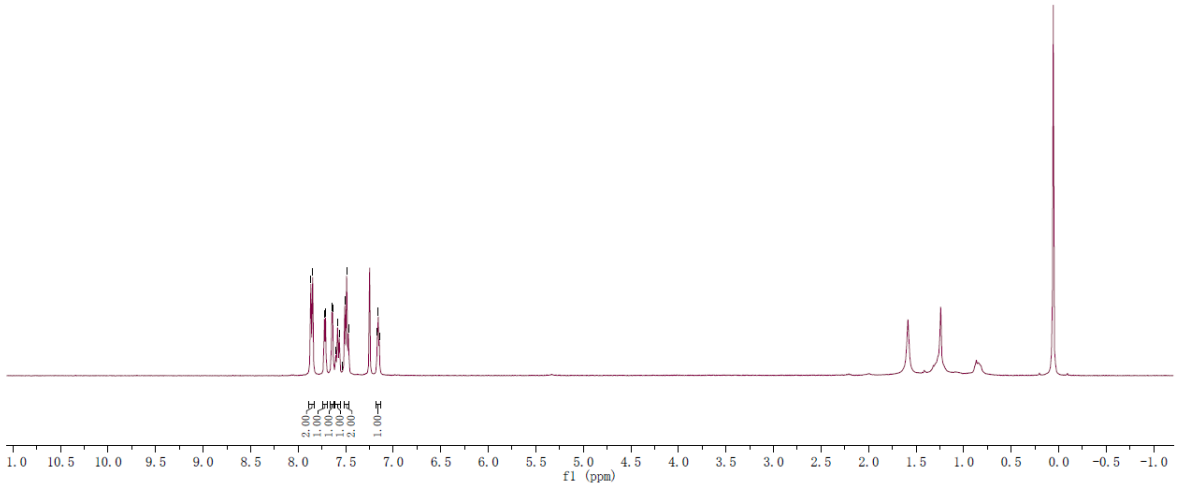
3q

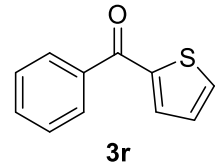
^{13}C NMR (101 MHz, $CDCl_3$)



3r

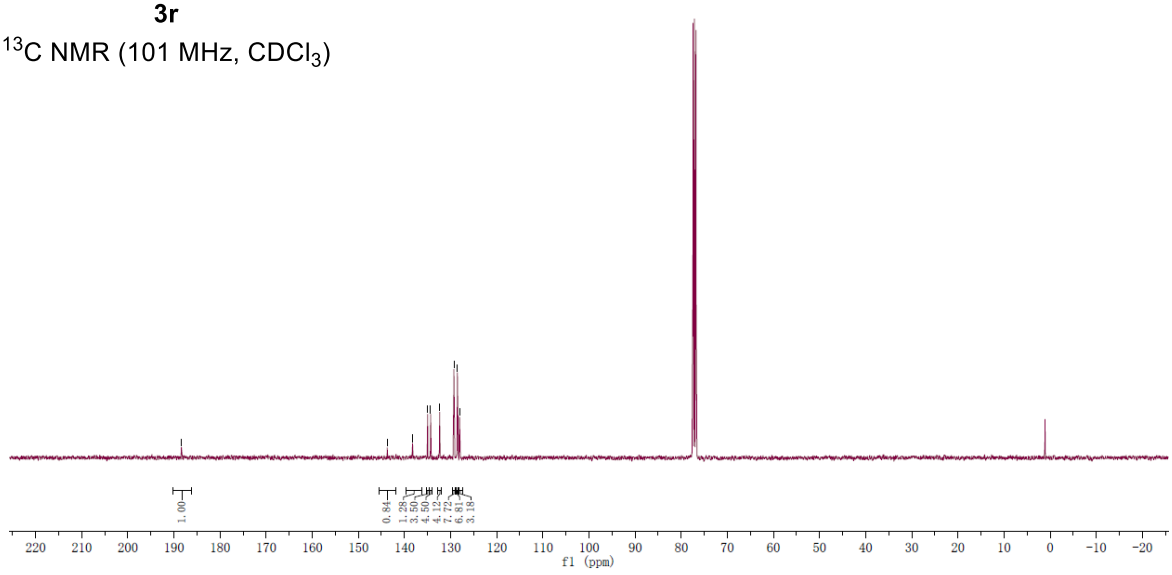
^{1}H NMR (400 MHz, $CDCl_3$)

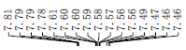


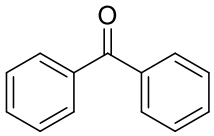


3r

^{13}C NMR (101 MHz, $CDCl_3$)

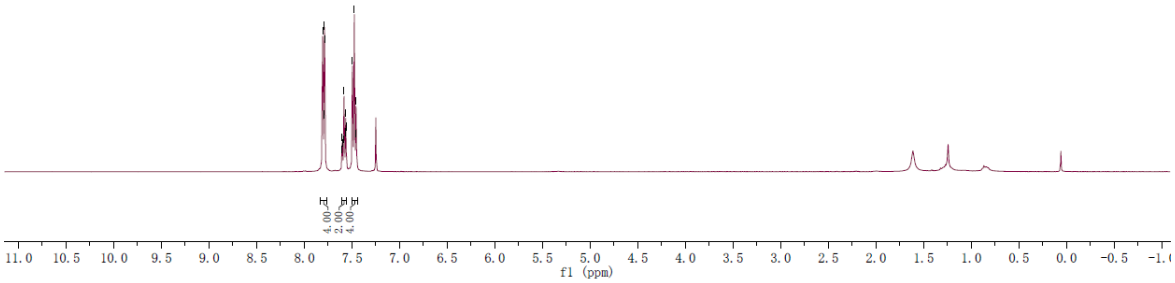


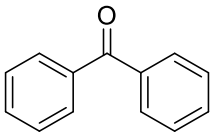




3s

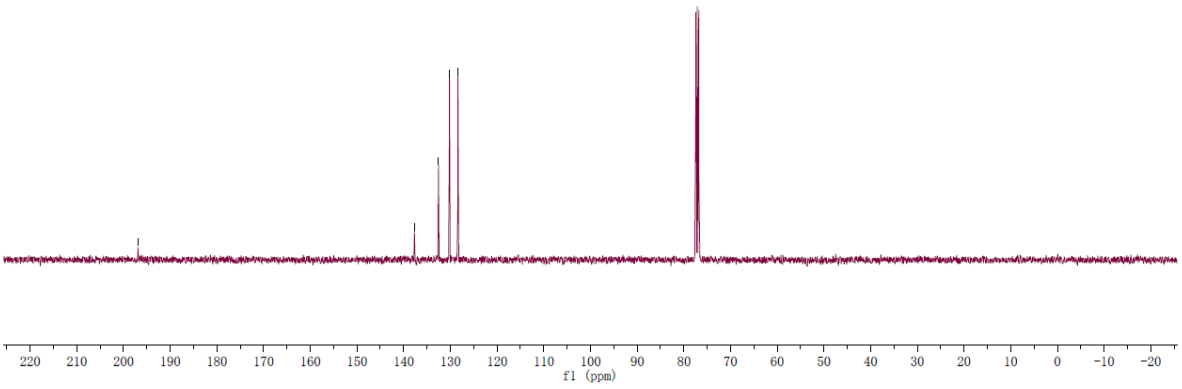
^{1}H NMR (400 MHz, $CDCl_3$)

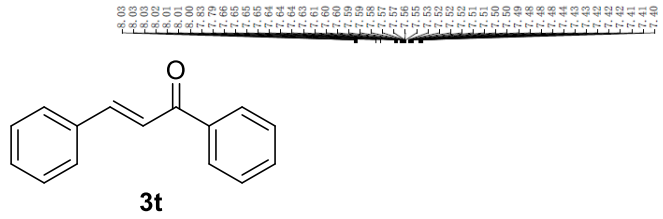




3s

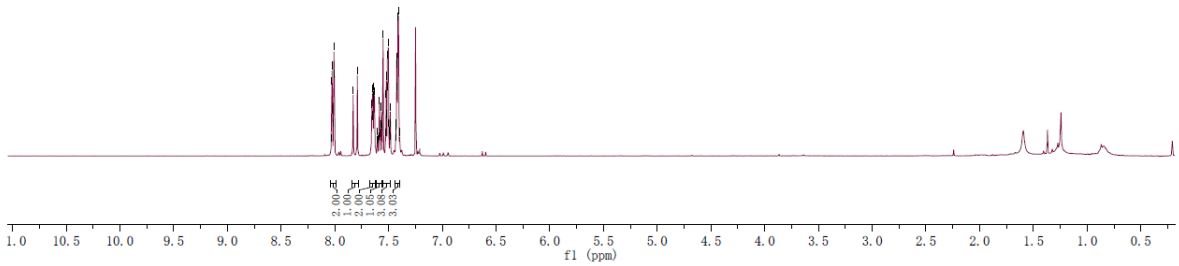
^{13}C NMR (101 MHz, $CDCl_3$)

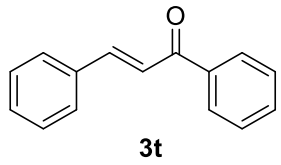




3t

^{1}H NMR (400 MHz, $CDCl_3$)





3t

^{13}C NMR (101 MHz, $CDCl_3$)