– Supporting Information –

Transition-Metal-Free, Ambient-Pressure Carbonylative Cross- Coupling Reactions of Aryl Halides with Potassium Aryltrifluoroborates

Fengli Jin, and Wei Han*

Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of Biofunctional Materials, Key Laboratory of Applied Photochemistry, School of Chemistry and Materials Science, Nanjing Normal University
Wenyuan Road No.1, 210023 Nanjing (China)

Fax: (+)86-(0)25-8589-1455
E-mail: hanwei@njnu.edu.cn; whhanwei@gmail.com

Table of Contents

1. General Information

Instruments. ^{1}H (400 MHz) and ^{13}C NMR spectra (100 MHz) of solutions in $CDCl_3$ or DMSO-*d*$_6$ were recorded on a Bruker Avance 400 NMR spectrometer. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals ($CDCl_3$: δ_H 7.24 and δ_C 77.0 ppm; DMSO-*d*$_6$: δ_H 2.50 and δ_C 39.50 ppm). The signals of water were observed at about 1.58 ppm in $CDCl_3$ and 3.33 ppm in DMSO-*d*$_6$, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, *J,* were reported in hertz unit (Hz). HRMS was performed on a Q-TOF mass spectrometer. Infrared spectra of neat substances were recorded on a Thermo Nicolet Corporation GC-FTIR NEXUS670 spectrometer.

Materials. All the aryl halides and the Potassium Aryltrifluoroborates were purchased from Alfa Aesar, Adamas, Aladdin, Acros, and Accela ChemBio Co., Ltd. and were used as received. PEG-400 was bought from Aladdin and was pre-dried by using toluene azeotrope.

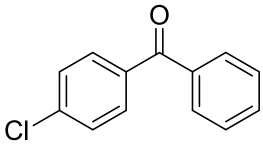
The following acid and base were used: PivOH (99%, Alfa Aesar); Na_2CO_3 (99.5%, Alfa Aesar).

2. Products from Transition-Metal-Free Carbonylative Cross Couplings

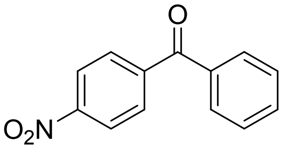
General Procedure A: A 25 mL Schlenk flask was charged with aryl iodide (0.25 mmol), potassium aryl trifluoroborate (0.375 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), and PivOH (12. 9 mg, 0.125 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 100 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was cooled to room temperature, poured into a saturated aqueous NaCl solution (15 mL), and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel.

General Procedure B: A 25 mL Schlenk flask was charged with aryl iodide (0.25 mmol), potassium aryl trifluoroborate (0.375 mmol), Na_2CO_3 (80.0 mg, 0.75 mmol), and PivOH (12.9 mg, 0.125 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 120 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was cooled to room temperature, and poured into a saturated aqueous NaCl solution (15 mL). The water phase was then acidified to pH 3 with 3 N HCl aqueous solution, and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel.

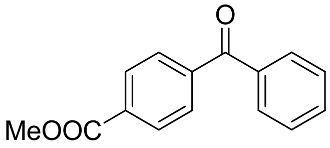
General Procedure C: A 25 mL Schlenk flask was charged with aryl bromide (0.25 mmol), potassium aryl trifluoroborate (0.375 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), KI (21.0 mg, 0.125 mmol), and PivOH (12.9 mg, 0.125 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 120 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was cooled to room temperature, poured into a saturated aqueous NaCl solution (15 mL), and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel.



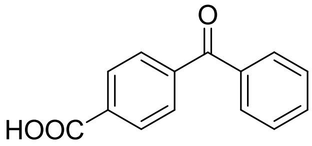
(4-Chlorophenyl)(phenyl)methanone (3aa): Following *general procedure A*, **3aa** was isolated as a white solid (48 mg, 89%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77–7.72 (m, 4 H), 7.58 (tt, *J* = 7.2, 1.2 Hz, 1 H), 7.50–7.43 ppm (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 138.9, 137.2, 135.9, 132.6, 131.4, 129.9, 128.6, 128.4 ppm; mp 71.1–71.6 °C.



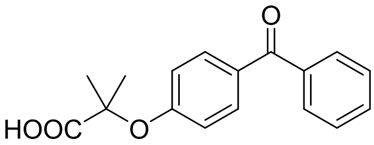
(4-Nitrophenyl)(phenyl)methanone (3ba): Following *general procedure A*, **3ba** was isolated as a light pink solid (49 mg, 86%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 7.79–7.77 (m, 2 H), 7.65-7.61 (m, 1 H), 7.50 ppm (t, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 149.8, 142.9, 136.3, 133.4, 130.7, 130.1, 128.7, 123.5 ppm; mp 136.7–136.9 °C.



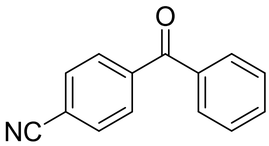
Methyl 4-Benzoylbenzoate (3ca): Following *general procedure A*, **3ca** was isolated as a white solid (47 mg, 78%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.13 (d, *J* = 8.4 Hz, 2 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.79−7.77 (m, 2 H), 7.60 (tt, *J* = 7.2 Hz, J = 1.2 Hz, 1 H), 7.50−7.46 (m, 2 H), 3.95 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.0, 166.3, 141.3, 136.9, 133.2, 132.9, 130.1, 129.8, 129.5, 128.4, 52.5 ppm; mp 105.4−106.1 °C.



4-Benzoylbenzoic acid (3da): Following *general procedure B*, **3da** was isolated as a white solid (44 mg, 77%), known compound. The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.22 (d, *J* = 8.4 Hz, 2 H), 7.86 (d, *J* = 8.4 Hz, 2 H), 7.82–7.79 (m, 2 H), 7.62 (tt, *J* = 7.2, 1.3 Hz, 1 H), 7.51–7.48 ppm (m, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.4, 166.7, 140.4, 136.5, 134.0, 133.1, 129.7, 129.6, 129.4, 128.7 ppm; mp 193.2–193.5 °C.

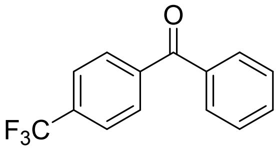


2-(4-Benzoylphenoxy)-2-methylpropanoic acid (3ea): Following *general procedure B*, was isolated as a brown solid (46 mg, 65%), known compound. The NMR spectroscopic data agree with those described in ref.[S19]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.61 (br s, 1 H), 7.77–7.72 (m, 4 H), 7.55 (tt, *J* = 7.2, 1.2 Hz, 1 H), 7.46–7.42 (m, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 1.69 ppm (s, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.0, 178.4, 159.0, 137.8, 132.2, 132.18, 131.1, 129.8, 128.2, 118.0, 79.2, 25.3 ppm; mp 91.6–92.5 °C.

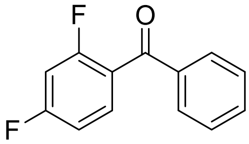


4-Benzoylbenzonitrile (3fa): Following *general procedure A* except that the reaction temperature is 120 °C, **3fa** was isolated as a white solid (45 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S3]. ^{1}H NMR

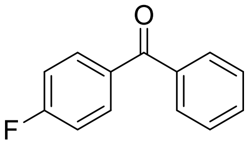
(400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2 H), 7.78–7.75 (m, 4 H), 7.62 (tt, *J*= 7.6, 1.2 Hz, 1 H), 7.51–7.47 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 141.2, 136.3, 133.3, 132.1, 130.2, 130.0, 128.6, 118.0, 115.6 ppm; mp 110.8–111.1 °C.



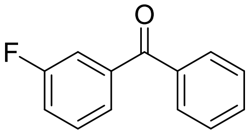
Phenyl(4-(trifluoromethyl)phenyl)methanone (3ga): Following *general procedure A*, 3**ga** was isolated as a white solid (51 mg, 81%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 2 H), 7.80–7.78 (m, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.61 (tt, *J* = 7.6, 1.6 Hz, 1H), 7.51–7.47 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 140.7, 136.7, 133.7 (q, *J* = 32 Hz), 133.1, 130.11, 130.08, 128.5, 125.3 (q, *J* = 4 Hz), 123.7 ppm (q, *J* = 271 Hz); mp 113.4–114.3 °C.



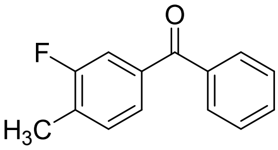
(2,4-Difluorophenyl)(phenyl)methanone (3ha): Following *general procedure A*, **3ha** was isolated as a light yellow oil (38 mg, 70%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2 H), 7.61–7.56 (m, 2 H), 7.49–7.44 (m, 2 H), 7.01–6.96 (m, 1H), 6.92–6.86 ppm (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 164.9 (dd, *J* = 253, 12 Hz), 160.9 (dd, *J* = 254, 12 Hz), 137.4, 133.5, 132.5 (dd, *J* = 10, 4 Hz), 129.7, 128.5, 123.3 (dd, *J* = 15, 4 Hz), 111.9 (dd, *J* = 21, 4 Hz), 104.7 ppm (t, *J* = 25 Hz).



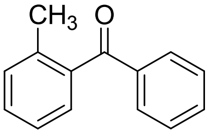
(4-Fluorophenyl)(phenyl)methanone (3ia): Following *general procedure A*, **3ia** was isolated as a light yellow oil (45 mg, 91%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.84–7.81 (m, 2 H),7.76–7.74 (m, 2 H), 7.58 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.49–7.45 (m, 2 H); 7.17–7.11 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 165.4 (d, *J* = 252 Hz), 137.5, 133.8 (d, *J* = 3 Hz), 132.7, 132.5 (d, *J* = 15 Hz), 129.9, 128.3, 115.4 ppm (d, *J* = 22 Hz).



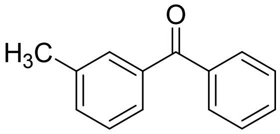
(3-Fluorophenyl)(phenyl)methanone (3ja): Following *general procedure A*, **3ja** was isolated as a light yellow oil (45 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.77 (m, 2 H),7.61–7.54 (m, 2 H), 7.50–7.43 (m, 4 H), 7.29–7.24 ppm (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3 (d, $J = 2$ Hz), 162.5 (d, $J = 247$ Hz), 139.6 (d, $J = 6$ Hz), 137.0, 132.8, 130.0, 129.9, 128.4, 125.8 (d, $J = 3$ Hz), 119.4 (d, $J = 21$ Hz), 116.7 ppm (d, $J = 22$ Hz).



(3-Fluoro-4-methylphenyl)(phenyl)methanone (3ka): Following *general procedure A*, **3ka** was isolated as a light yellow solid (46 mg, 86%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.75 (m, 2 H), 7.57 (tt, $J = 7.6$, 1.2 Hz, 1H),7.48–7.46 (m, 3 H), 7.45 (s, 1 H), 7.29–7.25 (m, 1 H), 2.35 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2 (d, $J = 2$ Hz), 160.9 (d, $J = 245$ Hz), 137.4, 137.1 (d, $J = 6.5$ Hz), 132.5, 131.3 (d, $J = 4.9$ Hz), 130.2 (d, $J = 17.3$ Hz), 129.9, 128.3, 125.8 (d, $J = 3.4$ Hz), 116.5 (d, $J = 23.3$ Hz), 14.8 ppm (d, $J = 3.5$ Hz); mp 40.0–40.7 °C.

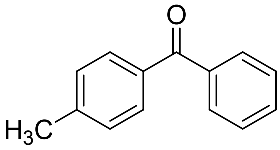


Phenyl(*o*-tolyl)methanone (3la): Following *general procedure A*, **3la** was isolated as a light yellow oil (42 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.77 (m, 2 H), 7.56 (tt, $J = 7.6$, 1.2 Hz, 1 H), 7.46–7.42 (m, 2 H), 7.38 (td, $J = 7.6$, 1.2 Hz, 1 H), 7.31–7.21 (m, 3 H), 2.32 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 138.6, 137.7, 136.7, 133.1, 131.0, 130.2, 130.1, 128.5, 128.4, 125.2, 19.9 ppm.

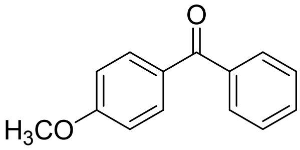


Phenyl(*m*-tolyl)methanone (3ma): Following *general procedure A*, **3ma** was isolated as a light yellow oil (45 mg, 92%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–

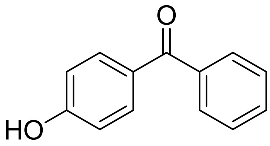
7.77 (m, 2 H), 7.61 (s, 1 H), 7.60–7.54 (m, 2 H), 7.48–7.44 (m, 2 H); 7.39–7.32 (m, 2 H), 2.40 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 138.1, 137.8, 137.6, 133.2, 132.3, 130.4, 130.0, 128.2, 128.1, 127.4, 21.3 ppm.



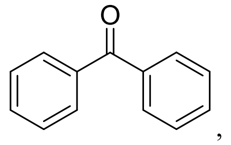
Phenyl(*p*-tolyl)methanone (3na): Following *general procedure A*, **3na** was isolated as a white solid with low melting point (46 mg, 94%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.75 (m, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.56 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.48–7.43 (m, 2 H), 7.27–7.25 (m, 2 H), 2.42 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 143.2, 138.0, 134.9, 132.2, 130.3, 129.9, 129.0, 128.2, 21.6 ppm.



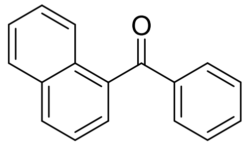
(4-Methoxyphenyl)(phenyl)methanone (3oa): Following *general procedure A*, **3oa** was isolated as light white solid (42 mg, 80%), known compound. The NMR spectroscopic data agree with those described in ref.[S4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 9.2 Hz, 2 H), 7.75–7.72 (m, 2 H), 7.54 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.47–7.43 (m, 2 H), 6.94 (d, *J* = 9.2 Hz, 2 H), 3.86 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 163.2, 138.2, 132.5, 131.8, 130.1, 129.7, 128.1,113.5, 55.4 ppm; mp 55.3–56.3 °C.



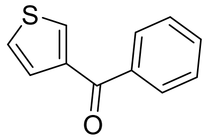
(4-Hydroxyphenyl)(phenyl)methanone (3pa): Following *general procedure B* except that the amounts of Na_2CO_3 and PivOH are 0.5 mmol and 0.25 mmol, respectively, **3pa** was isolated as a light yellow solid (32 mg, 65%), known compound. The NMR spectroscopic data agree with those described in ref.[S6]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 2 H), 7.74 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.56 (tt, *J* = 8.8, 1.6 Hz, 1H), 7.48–7.44 (m, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.30 ppm (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 160.1, 138.1, 133.0, 132.1, 130.0, 129.8, 128.2, 115.2 ppm; mp 116.0–116.7 °C.



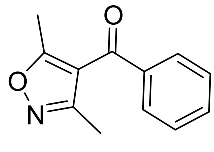
Benzophenone (3qa): Following *general procedure A*, **3qa** was isolated as a white solid with low melting point (42 mg, 93%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80–7.78 (m, 4 H), 7.57 (tt, *J* = 8.4, 1.2 Hz, 2H), 7.49–7.44 ppm (m, 4 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.8, 137.6, 132.4, 130.1, 128.3 ppm.



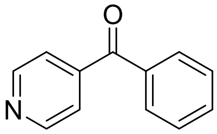
Naphthalen-1-yl(phenyl)methanone (3ra): Following *general procedure A*, **3ra** was isolated as a light yellow oil (52 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.09–8.07 (m, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.92–7.90 (m, 1 H), 7.87–7.84 (m, 2 H), 7.60–7.56 (m, 2 H), 7.54–7.48 (m, 3 H), 7.47–7.42 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.0, 138.3, 136.3, 133.7, 133.2, 131.2, 130.9, 130.4, 128.4, 128.37, 127.7, 127.2, 126.4, 125.7, 124.3 ppm.



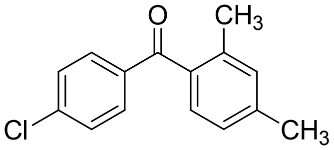
Phenyl(thiophen-3-yl)methanone (3sa): Following *general procedure A*, **3sa** was isolated as a light yellow oil (40 mg, 85%), known compound. The NMR spectroscopic data agree with those described in ref.[S5].^{1}H NMR (400 MHz, CDCl$_3$): δ 7.91 (dd, *J* = 2.8, 1.2 Hz, 1 H), 7.84–7.82 (m, 2 H), 7.59–7.55 (m, 2 H), 7.49–7.45 (m, 2 H); 7.36 ppm (dd, *J* = 5.2, 2.8 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.0, 141.3, 138.6, 133.9, 132.3, 129.3, 128.6, 128.4, 126.2 ppm.



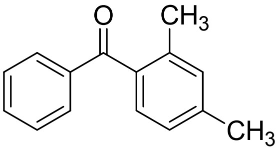
(3,5-Dimethylisoxazol-4-yl)(phenyl)methanone (3ta): Following *general procedure A*, **3ta** was isolated as a colorless liquid (45 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S2].^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70–7.68 (m, 2 H), 7.59 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.50–7.46 (m, 2 H), 2.31 (s, 3 H), 2.28 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.4, 172.3, 159.6, 138.4, 133.2, 128.9, 128.8, 116.5, 13.3, 11.3 ppm.



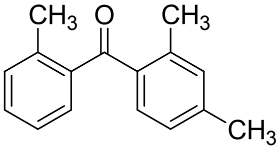
Phenyl(pyridin-4-yl)methanone (3ua): Following *general procedure A* except that the amount of PivOH is 0.25 mmol, **3ua** was isolated as a light yellow solid (32 mg, 72%), known compound. The NMR spectroscopic data agree with those described in ref.[S7]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 4.8 Hz, 2 H), 7.80 (d, J = 7.2 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.57 (d, J = 5.6 Hz, 2 H), 7.49 ppm (t, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 150.2, 144.5, 135.8, 133.6, 130.1, 128.6, 122.9 ppm; mp 63.7–64.4 °C.



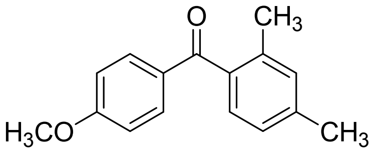
(4-Chlorophenyl)(2,4-dimethylphenyl)methanone (3ab): Following *general procedure A*, **3ab** was isolated as a light yellow oil (52 mg, 85%), known compound (CAS 57800-67-6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.8 Hz, 2 H), 7.40 (d, J = 8.8 Hz, 2 H), 7.19 (d, J = 8.8 Hz, 1 H), 7.09 (s, 1 H), 7.03 (d, J = 8.8 Hz, 1 H), 2.36 (s, 3 H), 2.30 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 141.0,139.3, 137.3, 136.5, 135.1, 132.0, 131.4, 129.1, 128.7, 125.9, 21.4, 20.1 ppm.



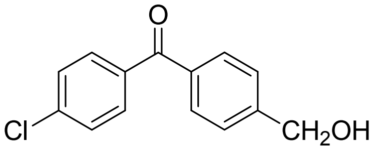
(2,4-Dimethylphenyl)(phenyl)methanone (3qb): Following *general procedure A*, **3qb** was isolated as a light yellow oil (42 mg, 81%), known compound. The NMR spectroscopic data agree with those described in ref.[S8].^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.76 (m, 2 H), 7.55 (tt, J = 7.2, 2.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 1 H), 7.09 (s, 1 H),7.03 (d, J = 8.0 Hz, 1 H), 2.37 (s, 3 H), 2.31 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 140.6, 138.2, 137.3, 135.6, 132.8, 131.9, 130.1, 129.2, 128.3, 125.8, 21.4, 20.1 ppm.



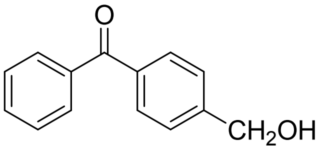
(2,4-Dimethylphenyl)(*o*-tolyl)methanone (3lb): Following *general procedure A*, **3lb** was isolated as a light yellow oil (48 mg, 86%), known compound (CAS 13152-98-2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (td, J = 7.2, 1.6 Hz, 1H), 7.28–7.23 (m, 2 H), 7.23–7.16 (m, 2 H), 7.08 (s, 1 H), 6.97 (d, J = 8.0 Hz, 1 H), 2.44 (s, 3 H), 2.38 (s, 3 H), 2.35 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 141.8, 139.7, 138.8, 137.6, 135.8, 132.4, 132.2, 131.2, 130.6, 129.7, 126.0, 125.3, 21.4, 20.9, 20.4 ppm.



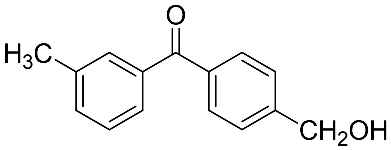
(2,4-Dimethylphenyl)(4-methoxyphenyl)methanone (3ob): Following *general procedure A*, **3ob** was isolated as a light yellow oil (48 mg, 81%), known compound (CAS 57800-66-5). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.76 (d, J = 8.8 Hz, 2 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.07 (s, 1 H), 7.02 (d, *J* = 7.6 Hz, 1 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H), 2.36 (s, 3 H), 2.27 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.4, 163.5, 140.1, 136.6, 136.2,132.5,131.7, 130.9, 128.6, 125.8, 113.6, 55.5, 21.4, 19.9 ppm.



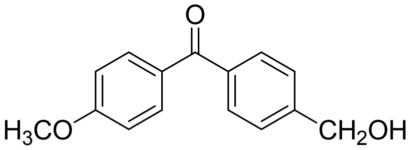
(4-Chlorophenyl)(4-(hydroxymethyl)phenyl)methanone (3ac): Following *general procedure A*, **3ac** was isolated as a light white solid (49 mg, 80%), known compound (CAS 183171-01-9). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.47–7.42 (m, 4 H), 4.78 (s, 2 H), 2.26ppm (s, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.2, 145.8, 138.9, 136.4, 135.9, 131.4, 130.2, 128.6, 126.5, 64.6 ppm; mp 127.6–128.2 °C.



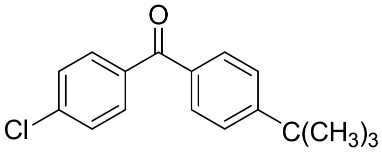
(4-(Hydroxymethyl)phenyl)(phenyl)methanone (3qc): Following *general procedure A*, **3qc** was isolated as a yellow solid with low melting point (41 mg, 79%), known compound. The NMR spectroscopic data agree with those described in ref.[S9]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80–7.76 (m, 4 H), 7.57 (tt, *J* = 8.8, 1.2 Hz, 1 H), 7.49–7.44 (m, 4 H), 4.79 (s, 2 H), 1.77 ppm (s, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.5, 145.5, 137.6, 136.8, 132.4, 130.4, 130.0, 128.3, 126.4, 64.7 ppm.



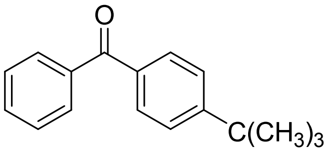
(4-(Hydroxymethyl)phenyl)(*m*-tolyl)methanone (3mc): Following *general procedure A*, **3mc** was isolated as a light brown oil (40 mg, 72%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.78 (d, *J* = 8.4 Hz, 2 H), 7.59 (s, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.39–7.32 (m, 2 H), 4.79 (s, 2 H), 2.40 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.8, 145.5, 138.2, 137.6, 136.9, 133.2, 130.4, 130.35, 128.1, 127.3, 126.4, 64.7, 21.3 ppm; HRMS (ESI) calcd for $C_{15}H_{14}NO_2$ [M+H] m/z 249.088601, found m/z 249.088632; IR: ν_{max} = 3410, 3056, 2918, 2854, 1650, 1598, 1580, 1562, 1502, 1450, 1412, 1376, 1320, 1282, 1216, 1174, 1042, 1010, 952, 844, 808, 796, 746, 712 cm^{-1}.



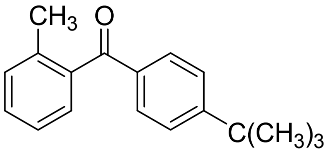
(4-(Hydroxymethyl)phenyl)(4-methoxyphenyl)methanone (3oc): Following *general procedure A*, **3oc** was isolated as a light white solid (43 mg, 71%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (d, *J* = 8.8 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 4.77 (s, 2 H), 3.87 (s, 3 H),1.86 ppm (s, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.3, 163.2, 144.9, 137.4, 132.5, 130.2, 130.1, 126.4, 113.6, 64.7, 55.5 ppm; HRMS (ESI) calcd for $C_{15}H_{14}NO_3$ [M+H] m/z 265.083515, found m/z 265.082937; IR: ν_{max} = 3462, 3186, 3020, 2970, 2914, 2850, 1648, 1598, 1510, 1464, 1412, 1372, 1316, 1260, 1164, 1142, 1050, 1018, 934, 848, 760, 686 cm^{-1}; mp 113.5–114.3 °C.



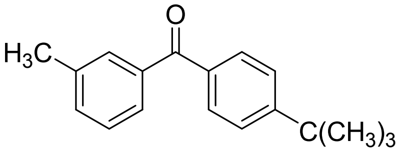
(4-(*Tert*-butyl)phenyl)(4-chlorophenyl)methanone (3ad): Following *general procedure A*, **3ad** was isolated as a light yellow solid (61 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S14]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75–7.70 (m, 4 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 8.8 Hz, 2 H), 1.35 ppm (s, 9 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.2, 156.4, 138.6, 136.2, 134.4, 131.4, 130.0, 128.5, 125.3, 35.1, 31.1 ppm; mp 74.6–75.6 °C.



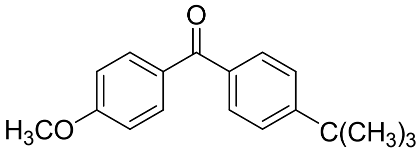
(4-(*Tert*-butyl)phenyl)(phenyl)methanone (3qd): Following *general procedure A*, **3qd** was isolated as a light yellow oil (50 mg, 85%), known compound. The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80–7.74 (m, 4 H), 7.56 (tt, *J* = 7.6, 1.2 Hz, 1 H), 7.49–744 (m, 4 H), 1.35 ppm (s, 9 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.4, 156.2, 137.9, 134.8, 132.1, 130.1, 129.9, 128.2, 125.2, 35.1, 31.1 ppm.



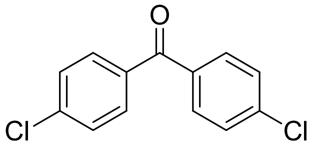
(4-(Tert-butyl)phenyl)(*o*-tolyl)methanone (3ld): Following *general procedure A*, **3ld** was isolated as a light yellow oil (56 mg, 90%), known compound. (CAS 14252-16-5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.8 Hz, 4 H), 7.36 (dd, *J* = 7.2, 1.2 Hz, 1 H), 7.30–7.20 (m, 3 H), 2.31 (s, 3 H), 1.33 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 157.0, 138.9, 136.5, 135.0, 130.9, 130.1, 130.0, 128.3, 125.4, 125.1, 35.1, 31.1, 19.9 ppm.



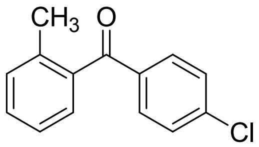
(4-(*Tert*-butyl)phenyl)(*m*-tolyl)methanone (3md): Following *general procedure A*, **3md** was isolated as a yellow oil (56 mg, 90%), known compound (CAS 55709-37-0). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.8 Hz, 2 H), 7.61 (s, 1 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 8.8 Hz, 2 H),7.38–7.32 (m, 2 H), 2.40 (s, 3 H), 1.35 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 156.1, 138.0, 137.9, 134.9, 132.9, 130.3, 130.1, 128.0, 127.3, 125.2, 35.1, 31.1, 21.3 ppm.



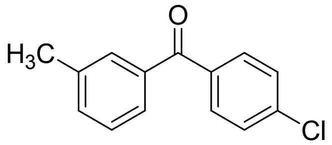
(4-(*Tert*-butyl)phenyl)(4-methoxyphenyl)methanone (3od): Following *general procedure A*, **3od** was isolated as a colorless oil (50 mg, 75%), known compound. The NMR spectroscopic data agree with those described in ref.[S16].^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.8 Hz, 2 H), 7.70 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H), 1.35 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 163.0, 155.5, 135.4, 132.4, 130.4, 129.8, 125.1, 113.4, 55.4, 35.0, 31.1 ppm.



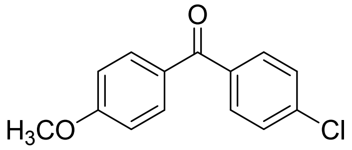
Bis(4-chlorophenyl)methanone (3ae): Following *general procedure A*, **3ae** was isolated as a light white solid (51 mg, 82%), known compound. The NMR spectroscopic data agree with those described in ref.[S10]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.8 Hz, 4 H), 7.45 ppm (d, *J* = 8.8 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 139.1, 135.5, 131.3, 128.7 ppm.; mp 144.6–145.4 °C.



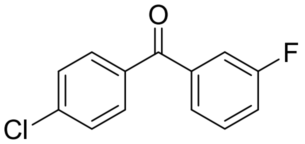
(4-Chlorophenyl)(*o*-tolyl)methanone (3le): Following *general procedure A*, **3le** was isolated as a colorless liquid (46 mg, 80%), known compound. The NMR spectroscopic data agree with those described in ref.[S11]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.8 Hz 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.38–7.36 (m, 1 H), 7.29–7.21 (m, 3 H), 2.30 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 139.7, 138.1, 136.8, 136.1, 131.5, 131.1, 130.5, 128.8, 128.4, 125.3, 19.9 ppm.



(4-Chlorophenyl)(*m*-tolyl)methanone (3me): Following *general procedure A*, **3me** was isolated as a light white solid (50 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S11]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz 2 H), 7.57 (s, 1 H);7.52 (d, *J* = 7.6 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.40–7.33 (m, 2 H), 2.40 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 138.8, 138.3, 137.3, 136.0, 133.4, 131.4, 130.3, 128.6, 128.2, 127.2, 21.3 ppm; mp 102.6–102.8 °C.

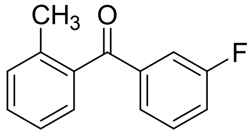


(4-Chlorophenyl)(4-methoxyphenyl)methanone (3oe): Following *general procedure A*, **3oe** was isolated as a light white solid (45 mg, 74%), known compound. The NMR spectroscopic data agree with those described in ref.[S12].^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz 2 H), 7.68 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.87 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 163.4, 138.2, 136.5, 132.4, 131.1, 129.8, 128.5, 113.7, 55.5 ppm; mp 123.8–124.1 °C.

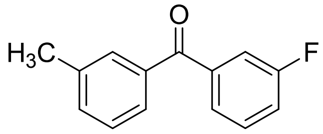


(4-Chlorophenyl)(3-fluorophenyl)methanone (3af): Following *general procedure A*, **3af** was isolated as a light white solid (48 mg, 83%), known compound (CAS 46698-36-6).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.8 Hz, 2 H), 7.52 (dt, *J* = 7.6, 1.2 Hz, 1 H), 7.47–7.42 (m, 4 H), 7.28 ppm (tdd, *J* = 8.4, 2.4, 1.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0 (d, *J* = 2.2

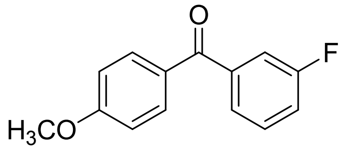
Hz), 162.5 (d, $J = 247$ Hz), 139.3, 139.2, 135.3, 131.4, 130.1 (d, $J = 7.7$ Hz), 128.8, 125.7 (d, $J = 3$ Hz), 119.6 (d, $J = 21.2$ Hz), 116.6 ppm (d, $J = 22.4$ Hz); mp 76.6–77.3 °C.



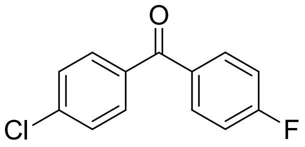
(3-Fluorophenyl)(*o*-tolyl)methanone (3lf): Following *general procedure A*, **3lf** was isolated as a light yellow oil (42 mg, 80%), known compound (CAS 68295-41-0). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 (dt, $J = 8.0$, 1.2 Hz, 1 H), 7.51–7.48 (m, 1 H), 7.44–7.37 (m, 2 H), 7.30–7.22 (m, 4 H), 2.32 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.2 (d, $J = 2.1$ Hz), 162.7 (d, $J = 246.6$ Hz), 139.9 (d, $J = 6.2$ Hz), 137.9, 136.9, 131.2, 130.6, 130.1 (d, $J = 7.6$ Hz), 128.6, 126.0 (d, $J = 3$ Hz), 125.3, 120.1 (d, $J = 21.4$ Hz), 116.6 (d, $J = 22.1$ Hz), 20.0 ppm.



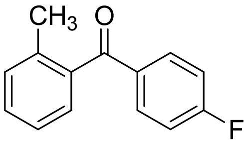
(3-Fluorophenyl)(*m*-tolyl)methanone (3mf): Following *general procedure A*, **3mf** was isolated as a light yellow oil (49 mg, 93%), known compound (CAS 864087-22-9). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60 (s, 1 H), 7.56 (dt, $J = 7.6$, 1.2 Hz, 2 H), 7.49–7.42 (m, 2 H), 7.41–7.33 (m, 2 H), 7.26 (tdd, $J = 8.4$, 2.8, 1.2 Hz, 1 H), 2.41 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.5 (d, $J = 2.0$ Hz), 162.5 (d, $J = 246.5$ Hz), 139.8 (d, $J = 6.4$ Hz), 138.3, 137.1, 133.5, 130.4, 129.9 (d, $J = 7.6$ Hz), 128.2, 127.3, 125.8 (d, $J = 3$ Hz), 119.3 (d, $J = 21.3$ Hz), 116.7 (d, $J = 22.3$ Hz), 21.3 ppm.



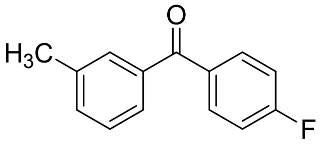
(3-Fluorophenyl)(4-methoxyphenyl)methanone (3of): Following *general procedure A*, **3of** was isolated as a light white solid (43 mg, 76%), known compound (CAS 96719-99-2). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80 (d, $J = 9.2$ Hz, 2 H), 7.50 (dt, $J = 7.6$, 1.2 Hz, 1 H), 7.45–7.40 (m, 2 H), 7.24 (tdd, $J = 8.4$, 2.8, 1.2 Hz, 1 H), 6.95 (d, $J = 9.2$ Hz, 2 H), 3.87 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 194.0 (d, $J = 2.0$ Hz), 163.5, 162.4 (d, $J = 246$ Hz), 140.4 (d, $J = 6.2$ Hz), 132.5, 129.9, 129.7 (d, $J = 23.6$ Hz), 125.4 (d, $J = 2.9$ Hz), 118.8 (d, $J = 21.2$ Hz), 116.5 (d, $J = 22.2$ Hz), 113.7, 55.5 ppm; mp 68.1–68.6 °C.



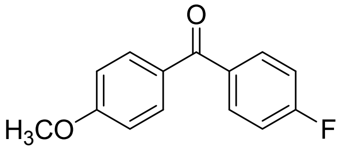
(4-Chlorophenyl)(4-fluorophenyl)methanone (3ag): Following *general procedure A*, **3ag** was isolated as a light white solid (53 mg, 91%), known compound. The NMR spectroscopic data agree with those described in ref.[S14]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.78 (m, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.15 ppm (t, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 165.5 (d, *J* = 253.1 Hz), 139.0, 135.8, 133.4 (d, *J* = 3 Hz), 132.5 (d, *J* = 9.1 Hz), 131.3, 128.7, 115.6 ppm (d, *J* = 21.8 Hz); mp 112.1–112.7 °C.



(4-Fluorophenyl)(*o*-tolyl)methanone (3lg): Following *general procedure A*, **3lg** was isolated as a light yellow oil (48 mg, 90%), known compound (CAS 68295-42-1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.79 (m, 2 H), 7.40–7.36 (m, 1 H), 7.28–7.21 (m, 3 H), 7.13–7.09 (m, 2 H), 2.30 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 165.8 (d, *J* = 253.7 Hz), 138.4, 136.6, 134.1 (d, *J* = 3 Hz), 132.7 (d, *J* = 9 Hz), 131.1, 130.3, 128.3, 125.3, 115.6 (d, *J* = 22 Hz), 19.9 ppm.

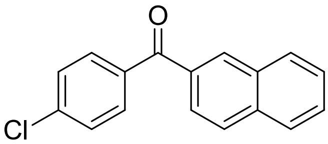


(4-Fluorophenyl)(*m*-tolyl)methanone (3mg): Following *general procedure A*, **3mg** was isolated as a light yellow oil (48 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S17]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2 H), 7.57 (s, 1 H), 7.52 (d, *J* = 7.6 Hz, 1 H), 7.40–7.33 (m, 2 H), 7.16–7.11 (m, 2 H), 2.41 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 165.3 (d, *J* = 252.5 Hz), 138.3, 137.5, 133.9 (d, *J* = 3.1 Hz), 133.2, 132.6 (d, *J* = 9.1 Hz), 130.3, 128.1, 127.1, 115.4 (d, *J* = 21.7 Hz), 21.3 ppm.

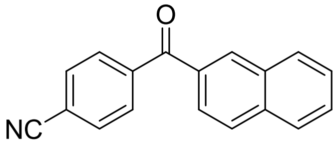


(4-Fluorophenyl)(4-methoxyphenyl)methanone (3og): Following *general procedure A*, **3og** was isolated as a light white solid (53 mg, 91%), known compound. The NMR spectroscopic data agree with those described in ref.[S18]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dt, *J* = 8.8, 2.8 Hz, 4 H), 7.13 (t, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.87 ppm (s, 3 H); ^{13}C NMR

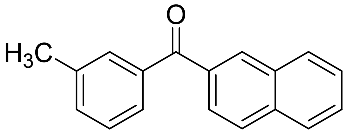
(100 MHz, CDCl$_3$): δ 194.1, 165.0 (d, *J* = 251.5 Hz), 163.2, 134.4 (d, *J* = 3.1 Hz), 132.4, 132.3 (d, *J* = 8.9 Hz), 130.0, 115.3 (d, *J* = 21.6 Hz), 113.6, 55.5 ppm; mp 92.0–92.5 °C.



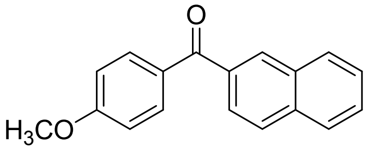
(4-Chlorophenyl)(naphthalen-2-yl)methanone (3ah): Following *general procedure A*, **3ah** was isolated as a light white solid (51 mg, 77%), known compound. The NMR spectroscopic data agree with those described in ref.[S13]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 (s, 1 H), 7.95–7.88 (m, 4 H), 7.79 (d, *J* = 8.8 Hz, 2 H), 7.63–7.53 (m, 2 H), 7.48 ppm (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.5, 138.8, 136.2, 135.3, 134.5, 132.2, 131.7, 131.5, 129.4, 128.7, 128.5, 128.4, 127.8, 126.9, 125.6 ppm; mp 122.3–123.1 °C.



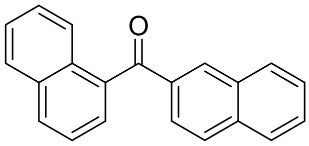
4-(2-Naphthoyl)benzonitrile (3fh): Following *general procedure A*, **3fh** was isolated as a light white solid (52 mg, 81%), known compound. (CAS 194939-76-9). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.19 (d, *J* = 1.2 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.91–7.89 (m, 5 H), 7.79 (d, *J* = 8.4 Hz, 2 H), 7.65–7.60 (m, 1 H), 7.58–7.54 ppm (m, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.0, 141.5, 135.5, 133.5, 132.21, 132.16, 132.1, 130.2, 129.5, 128.9, 128.7, 127.8, 127.1, 125.2, 118.0, 115.5 ppm; mp 121.7–122.3 °C.



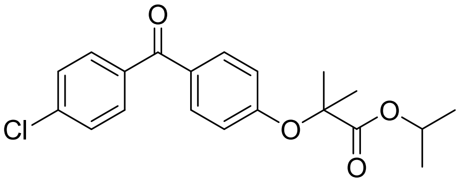
Naphthalen-2-yl(*m*-tolyl)methanone (3mh): Following *general procedure A*, **3mh** was isolated as a light white solid (43 mg, 70%), known compound (CAS 418770-90-8). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.25 (d, *J* = 0.8 Hz, 1 H), 7.93–7.89 (m, 4 H), 7.67 (s, 1 H), 7.63–7.58 (m, 2 H), 7.56–7.52 (m, 1 H), 7.43–7.36 (m, 2 H), 2.43 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.0, 138.2, 137.9, 135.2, 135.0, 133.1, 132.3, 131.8, 130.5, 129.4, 128.3, 128.2, 128.1, 127.8, 127.4, 126.7, 125.8, 21.4 ppm; mp 72.3–73.3 °C.



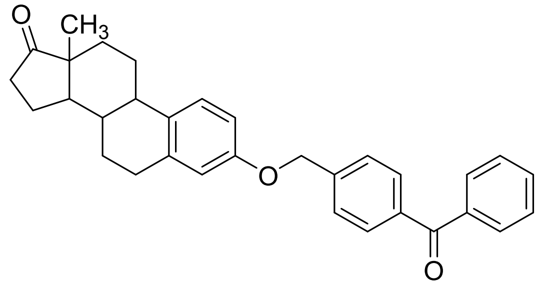
(4-Methoxyphenyl)(naphthalen-2-yl)methanone (3oh): Following *general procedure A*, **3oh** was isolated as a light white solid (47 mg, 73%), known compound. The NMR spectroscopic data agree with those described in ref.[S14]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 (s, 1 H), 7.93–7.85 (m, 6 H), 7.60–7.51 (m, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 3.88 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.5, 163.2, 135.5, 135.0, 132.6, 132.2, 131.1, 130.4, 129.2, 128.1, 128.0, 127.8, 126.7, 125.8, 113.6, 55.5 ppm; mp 85.9–86.5 °C.



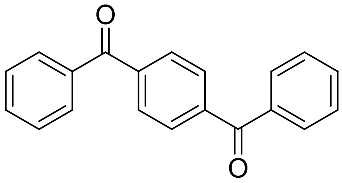
Naphthalen-1-yl(naphthalen-2-yl)methanone (3rh): Following *general procedure A*, **3rh** was isolated as a light yellow solid (57 mg, 82%), known compound. The NMR spectroscopic data agree with those described in ref.[S3]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.24 (s, 1 H), 8.11 (d, J = 8.4 Hz, 1 H), 8.07 (dd, J = 8.4, 2.0 Hz, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 7.95–7.92 (m, 2 H), 7.89 (d, J = 8.4 Hz, 1 H), 7.82 (d, J = 8.4 Hz, 1 H), 7.64 (dd, J = 7.2, 1.2 Hz, 1 H), 7.61–7.57 (m, 1 H), 7.56–7.47 ppm (m, 4 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.0, 136.6, 135.7, 135.6, 133.7, 132.9, 132.3, 131.2, 131.0, 129.6, 128.6, 128.41, 128.4, 127.8, 127.7, 127.3, 126.8, 126.5, 125.7, 125.3, 124.4 ppm; mp 131.0–131.8 °C.



***I*sopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (3ve):** Following *general procedure A* except that the reaction temperature is 120°C, **3ve** was isolated as a light yellow solid (72 mg, 80%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (d, J = 8.8 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 5.10−5.04 (m, 1 H), 1.64 (s, 6 H), 1.18 ppm (d, J = 6.0 Hz, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 194.3, 173.1, 159.7, 138.3, 136.4, 131.9, 131.1, 130.2, 128.5, 117.2, 79.4, 69.3, 25.3, 21.5 ppm; mp 74.2−75.2 °C.



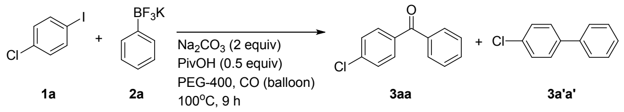
3-((4-Benzoylbenzyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopentaphenanthren-17-one (3wa): Following *general procedure A* except that the reaction temperature is 120°C, **3wa** was isolated as a light yellow solid (92 mg, 80%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.83−7.78 (m, 4 H), 7.58 (tt, *J* = 7.2, 1.2 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 1 H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.72 (d, *J* = 2.8 Hz, 1 H), 5.12 (s, 2 H), 2.88 (dd, *J* = 11.2, 4.8 Hz, 2 H), 2.49 (dd, *J* = 18.8, 8.8 Hz, 1 H), 2.41−2.36 (m, 1 H), 2.78−2.21 (m, 1 H), 2.17−1.92 (m, 4 H), 1.66−1.37 (m, 6 H), 0.89 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 220.9, 196.3, 156.5, 142.0, 137.9, 137.5, 137.0, 132.6, 132.4, 130.4, 130.0, 128.3, 126.9, 126.4, 114.9, 112.3, 69.3, 50.4, 48.0, 44.0, 38.3, 35.8, 31.5, 29.6, 26.5, 25.9, 21.6, 13.8 ppm; IR: ν_{max} = 3088,3050, 3028, 2960, 2930, 2864, 1739, 1652, 1612, 1570, 1500, 1454, 1414, 1376, 1274, 1254, 1164, 1056, 922, 856, 796, 738, 704 cm^{-1}; mp 170.0−170.8 °C.



1,4-Phenylenebis(phenylmethanone) (3xa): A 25 mL Schlenk flask was charged with **3x** (84.2 mg, 0.25 mmol), **2a** (142.3 mg, 0.75 mmol), Na$_2$CO$_3$ (106.6 mg, 1.0 mmol), and PivOH (25.8 mg, 0.25 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 100 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was cooled to room temperature, poured into a saturated aqueous NaCl solution (15 mL), and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel to give a light yellow solid **3xa** (50 mg, 70%). The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.87 (s, 4 H), 7.83−7.81 (m, 4 H), 7.61 (tt, *J* = 7.2, 1.2 Hz, 2 H), 7.52–7.48 ppm (m, 4 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.0, 140.6, 136.9, 133.0, 130.1, 129.7, 128.5 ppm; mp 158.3−159.3 °C.

3. Effect of Transition Metals on The Carbonylative Cross Coupling

Table S1 The effect of transition metals on the carbonylative Suzuki coupling.[a]



Entry	catalyst	yield of **3aa** (%)	yield of **3a'a'** (%)
1	-	89	5
2	$PdCl_2$	39	56
3	$Pd(OAc)_2$	54	41
4	Cu	86	9
5	$NiCl_2$	84	10
6	$FeCl_2$	87	8

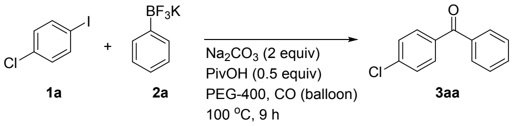
[a] Reaction conditions: catalyst (2 mol %), **1a** (0.25 mmol), **2a** (0.375 mmol), CO (balloon), Na_2CO_3 (0.5 mmol), PivOH (0.125 mmol), PEG-400 (2.0 mL), 100 °C, and 9 h.

As per *general procedure A*, four reactions of **1a** (60.8 mg, 0.25 mmol), **2a** (71.1 mg, 0.375 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) were carried out, one as a control. A transition-metal catalyst [$Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Cu powder (0.3 mg, 0.005 mmol), $NiCl_2$ (0.7 mg, 0.005 mmol) , or $FeCl_2$ (0.6 mg, 0.005 mmol)] was introduced to the reactions. All reaction mixtures were stirred at 100 °C and ambient pressure for 9 h.

Furthermore**,** ICP was carried out to analyze the model reaction system (inlcuding the solvent) and showed that the concentrations of Pd, Ni, and Fe were lower than the detection limits of the machine. Although 10 ppm Cu was observed, the addition of 2–6 times this amount of Cu (nanocopper) to the reaction system did not obviously affect the reaction rate. These result suggest that the potential catalysts such as Pd, Cu, Ni, and Fe are not involved in this transformation, discarding the slightest doubt of a transition-metal catalyzed process.

4. Mechanistic investigations

4.1 Effect of radical scavengers.

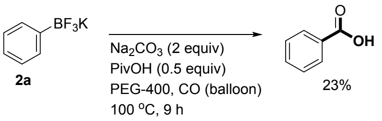


No scavenger	89%
TEMPO (1.0 equiv)	89%
TEMPO (2.0 equiv)	87%
1,1-Diphenylethylene (1.0 equiv)	80%

Scheme S1 Effect of radical scavengers.

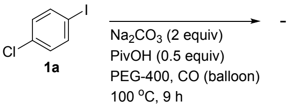
As per *general procedure A*, three reactions of **1a** (60.8 mg, 0.25 mmol), **2a** (71.1 mg, 0.375 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) were carried out, one as a control. A radical scavenger [TEMPO (39.9 mg, 0.25 mmol), TEMPO (79.7 mg, 0.5 mmol), or 1,1-Diphenylethylene (40 μL, 0.25 mmol)] was introduced to the reactions. All reaction mixtures were stirred at 100 °C and ambient pressure for 9 h.

Control experiments



(S1)

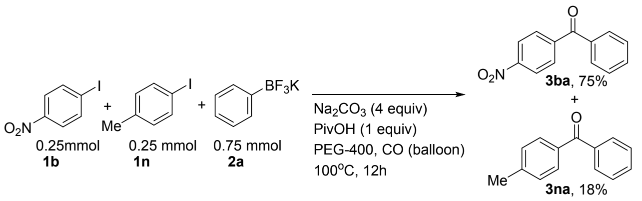
Following *general procedure B*, a reaction of **2a** (71.1 mg, 0.375 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 °C and ambient pressure for 9 h.



(S2)

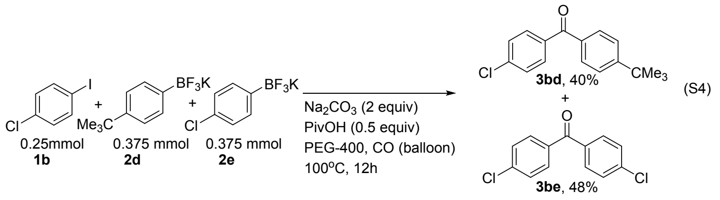
Following *general procedure B*, a reaction of **1a** (60.8 mg, 0.25 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 °C and ambient pressure for 9 h.

Competition Experiments.



(S3)

Following *general procedure A*, a reaction of **1b** (63.5 mg, 0.25 mmol), **1n** (55.6 mg, 0.25 mmol), **2a** (142.3 mg, 0.75 mmol), Na_2CO_3 (106.6 mg, 1.0 mmol), and PivOH (25.8 mg, 0.25 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 °C and ambient pressure for 12 h.



Following *general procedure A*, a reaction of **1b** (60.8 mg, 0.25 mmol), **2d** (93.8 mg, 0.375 mmol), **2e** (85.3 mg, 0.375 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 ^oC and ambient pressure for 12 h.

Reaction time profile studies.

According to the below Figure S1, in first one hour, the reaction ran much fast and gave the desired product in 80% yield. And no induction period was observed.

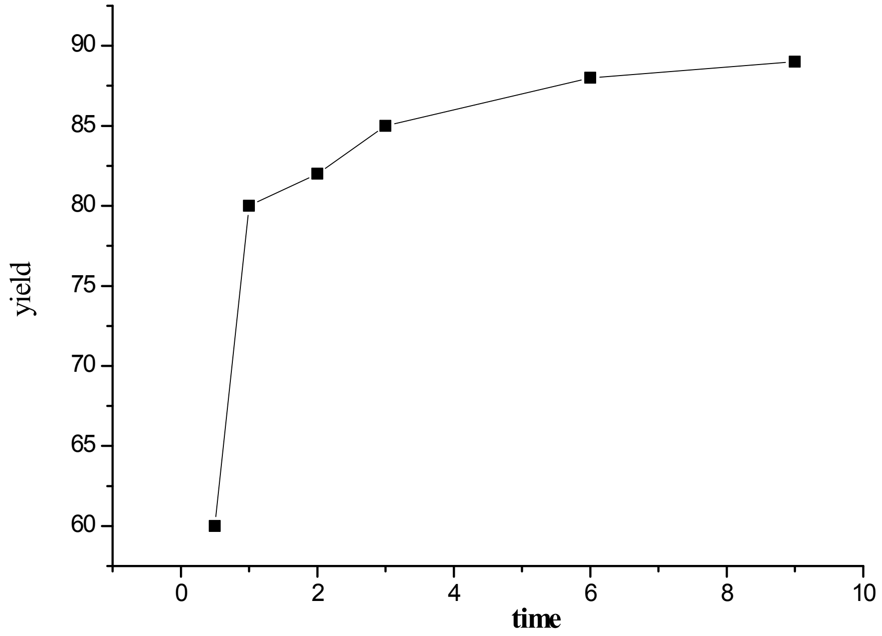
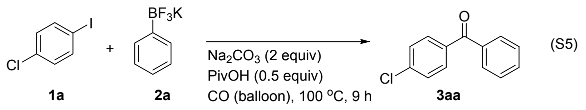


Figure S1 Yield versus time curve of the model reaction under normal conditions.

Effect of solvents

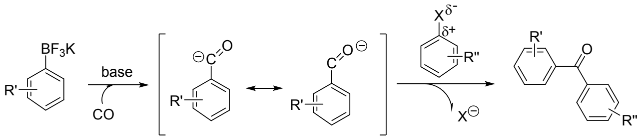


PEG-400	89%
PEM-250	10%

As per *general procedure A*, two reactions of **1a** (60.8 mg, 0.25 mmol), **2a** (71.1 mg, 0.375 mmol), Na_2CO_3 (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in solvents [PEG-400 (2.0 mL) and PEM-250 (2.0 mL)] were carried out, one as a control. All reaction mixtures were stirred at 100 °C and ambient pressure for 9 h.

A proposed mechanism:

In view of our findings and previous studies (See: R. Luque, D. J. Macquarrie, *Org. Biomol. Chem.*__2009__, *7*, 1627–1632), a tentative mechanism might be proposed for the carbonylative transformation (Scheme S2). Initially, a potassium aryl trifluoroborate in the presence of a base reacts with CO to form aryl acyl anion. Thereafter, the aryl acyl anion undergoes nucleophilic attack of an aryl halide to yield the desired product upon elimination of a halide anion. The above mentioned competition experiments reveal that the nucleophilic attack of an aryl halide is likely to be the rate limiting step. Meanwhile, such a mechanism would explain the decreased efficiency of electron-rich aryl halides, as they could stabilize the positive charge engendered in the C–X bond via an inductive effect. When CO doesn't insert into the potassium aryl trifluoroborate in time, biaryl side product will be formed. Indeed, Suzuki coupling was reported to proceed successfully in the absence of a metal catalyst (See: N. E. Leadbeater, M. Marco, *Angew. Chem. Int. Ed.*, **2003**, *42*, 1407-1409).



Scheme S2 Proposed mechanism of the transition-metal-free carbonylative Suzuki coupling.

5. References

[S1] Q. Zhou, S. H. Wei, W. Han, *J. Org. Chem*. **2014**, *79*, 1454–1460.

[S2] T. Ohishi, M. Nishiura, Z. M Hou, *Angew. Chem. Int. Ed.* **2008**, *47*, 5792–5795.

[S3] L. J. Cheng, Y. Z. Zhong, Z. C Ni, H. Y. Du, F. L. Jin, Q. Rong, W. Han. *RSC Adv.* **2014**, *4*, 44312–44316.

[S4] Y. Z. Zhong, W. Han. *Chem. Commun.* **2014**, *50*, 3874–3877.

[S5] A. T. Biju, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 9761–9764.

[S6] M. Javier, M. H. Chen, J. D. Clark, T. Nussbaumer, *J. Org. Chem* **2006**, *71*, 7103–7105.

[S7] J. Karthikeyan, K. Parthasarathy, C. H. Cheng, *Chem. Commun.* **2011**, *47*, 10461–10463.

[S8] F. Jafarpour, P. Rashidi-Ranjbar, A. O. Kashani, *Eur. J. Org. Chem*. 2**011**, 2128–2132.

[S9] D. Mitchell, M. Lukeman, D. Lehnherr, P. Wan, *Org. Lett*. **2005**, *7*, 3387–3389.

[S10] M. Z. Cai, J Peng, W. Y. Hao, G. D. Ding, *Green. Chem*. **2011**, *13*, 190–196.

[S11] L. Zhang, J. L. Wu, L. J. Shi, C. G. Xia, F. W. Li, *Tetrahedron. Lett.* **2011**, *52*, 3897–3901.

[S12] G. M. Zheng, P. P.Wang, M. Z. Cai, *Chin. J. Chem.* **2009**, *27*, 1420–1426.

[S13] M. Al-Masum, M. C. Wai, H. Dunnenberger, *Synth. Commun.* **2011**, *41*, 2888–2898.

[S14] H. Li, Y. Xu, E. B. Shi, W. Wei, X. Q. Suo, X. B. Wan, *Chem. Commun.* **2011**, *47*, 7880–7882.

[S15] K. Ito, H. Tamashima, N. Iwasawa, H. Kusama, *J. Am. Chem. Soc.* **2011**, *133*, 3716–3719.

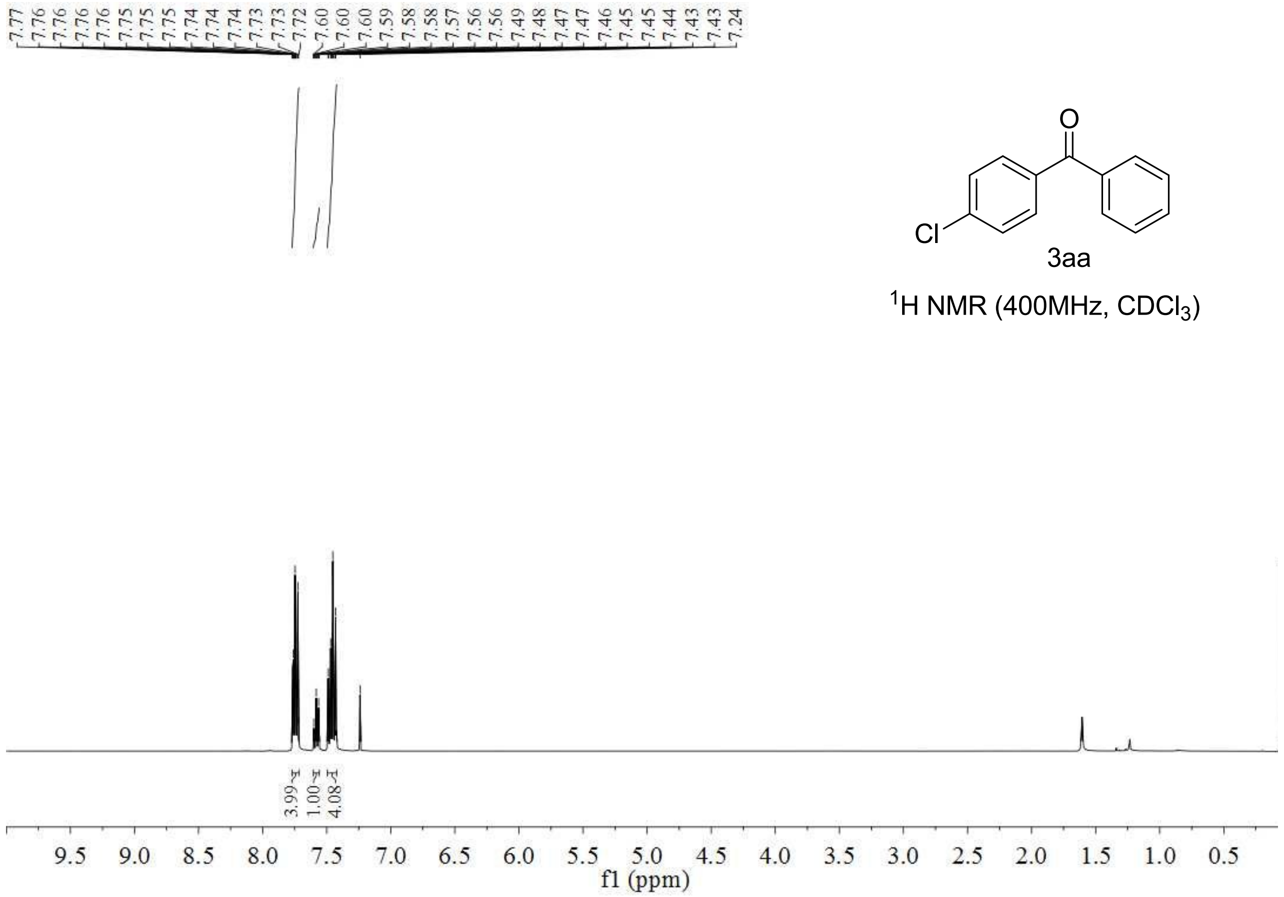
[S16] J. Y. Chen, S. C. Chen, Y. J. Tang, C. Y. Mou, F. Y. Tsai, *J. Mol. Catal. A-Chem.* **2009**, *307*, 88–92.

[S17] Y. X. Liao, C. H. Xing, M. Israel, Q. S. Hu, *J. Org. Chem.* **2010**, *75*, 6986–6989.

[S18] R. Bayles, *Synthesis*, **1977**, 31–33.

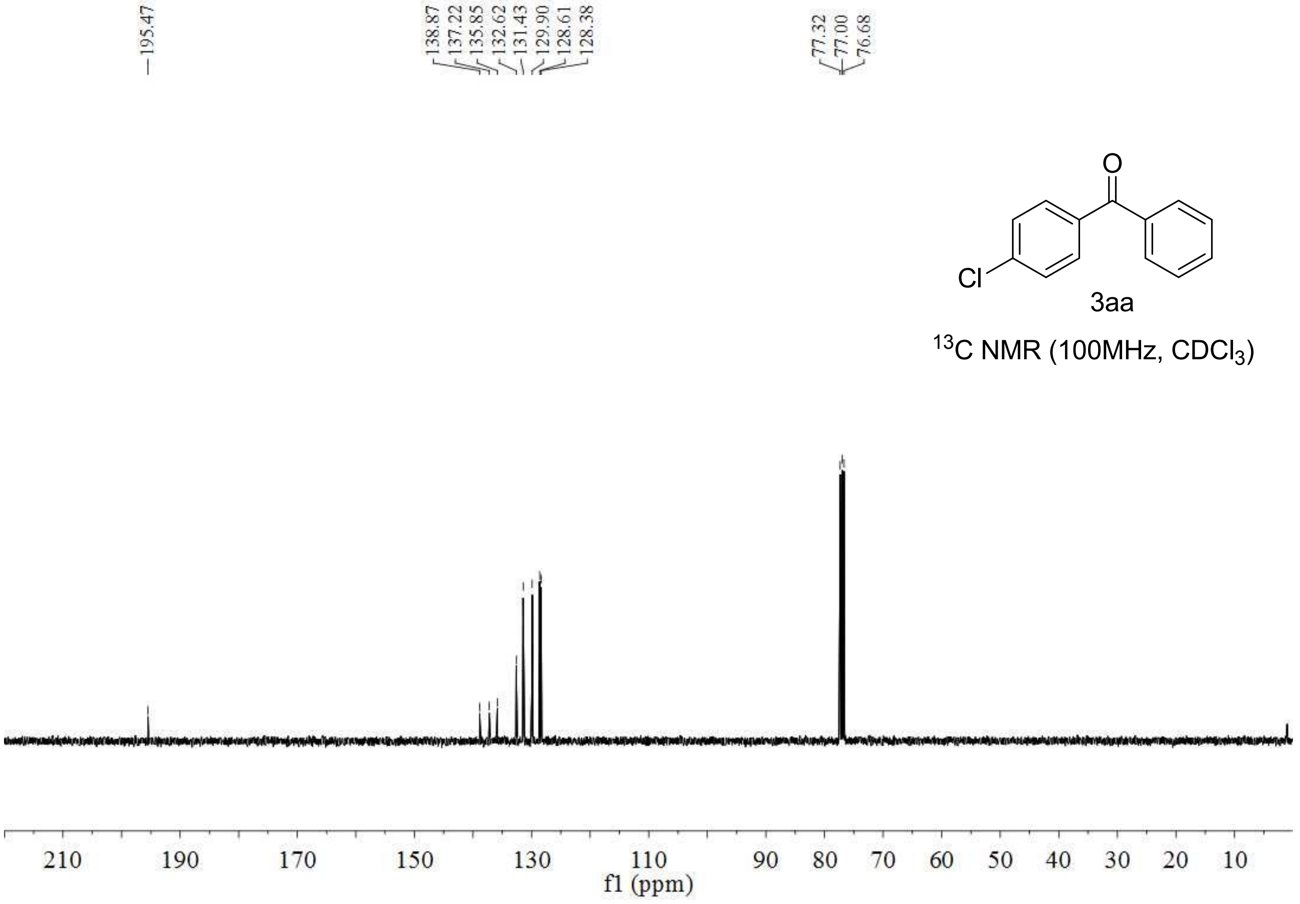
[S19] M. Z. Rehman, *J. Chem. Soc. Pakistan.* **2007**, *29*, 352–356.

6. Copies of NMR Spectra



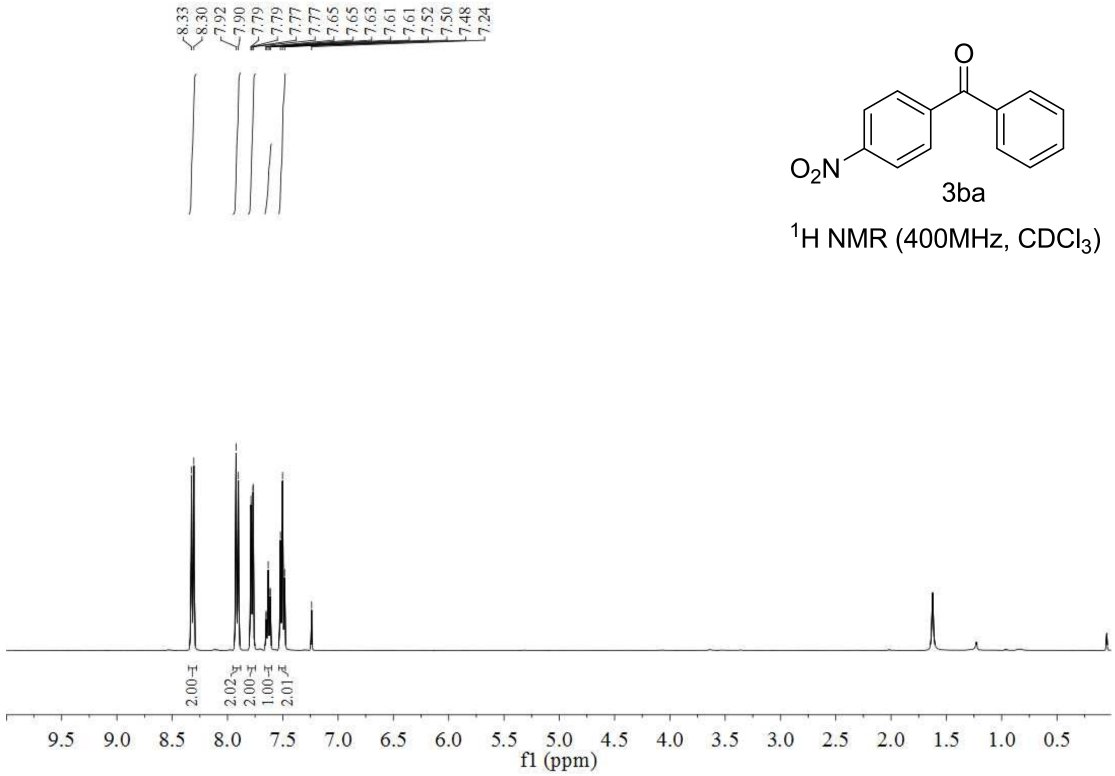
3aa

^{1}H NMR (400MHz, CDCl$_3$)



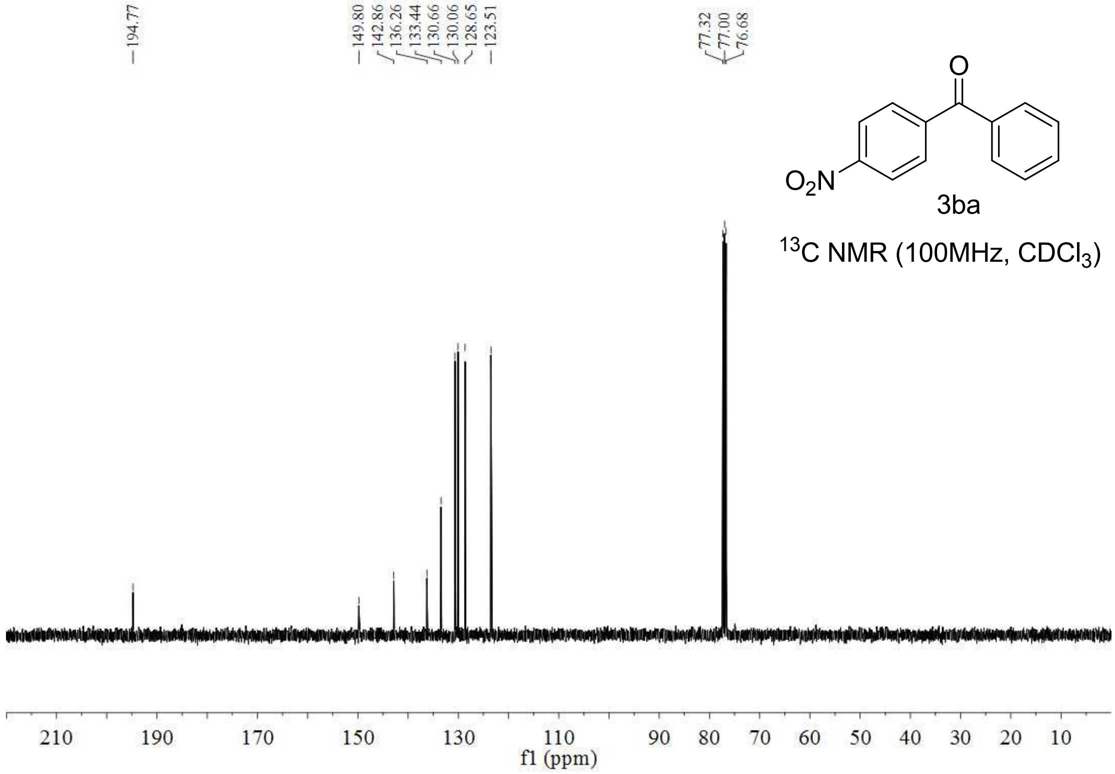
3aa

^{13}C NMR (100MHz, CDCl$_3$)



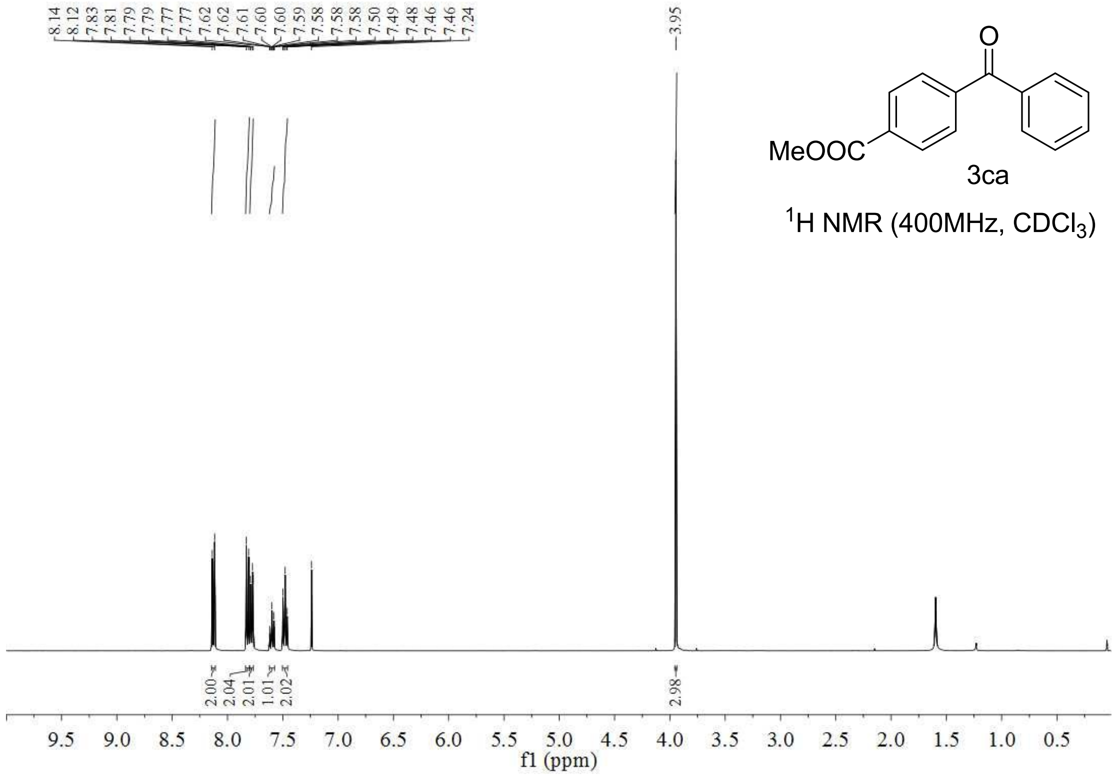
3ba

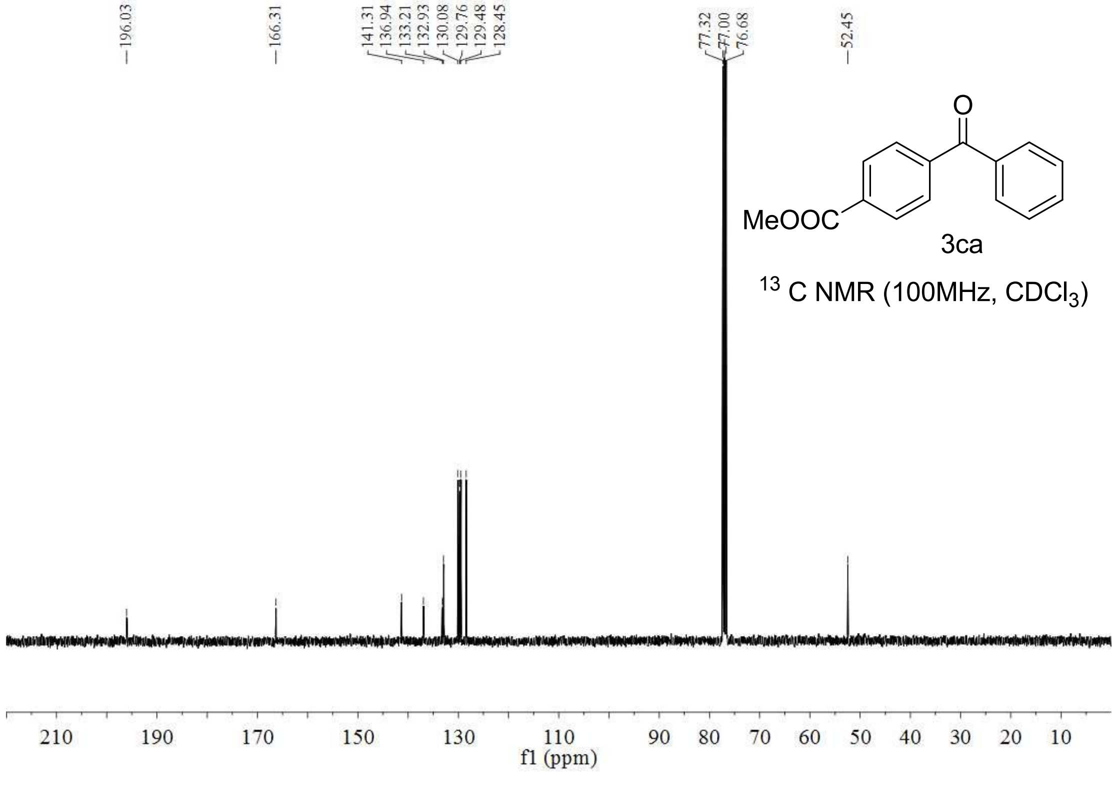
^{1}H NMR (400MHz, $CDCl_3$)

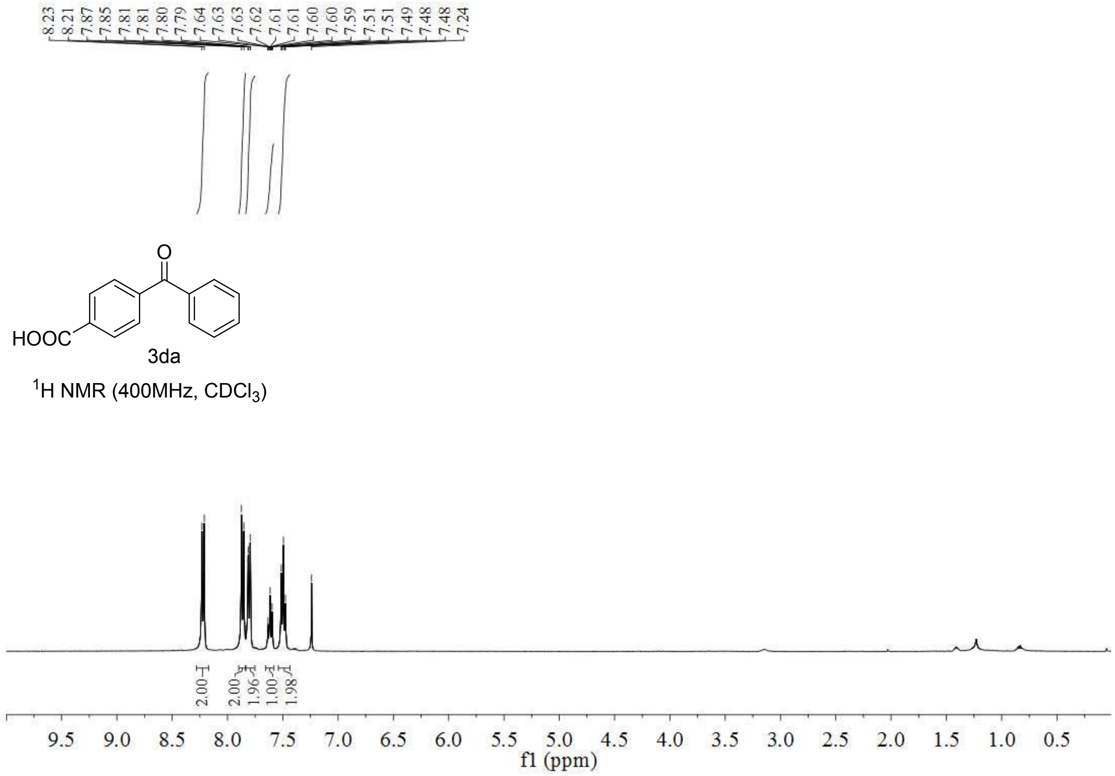


3ba

^{13}C NMR (100MHz, $CDCl_3$)

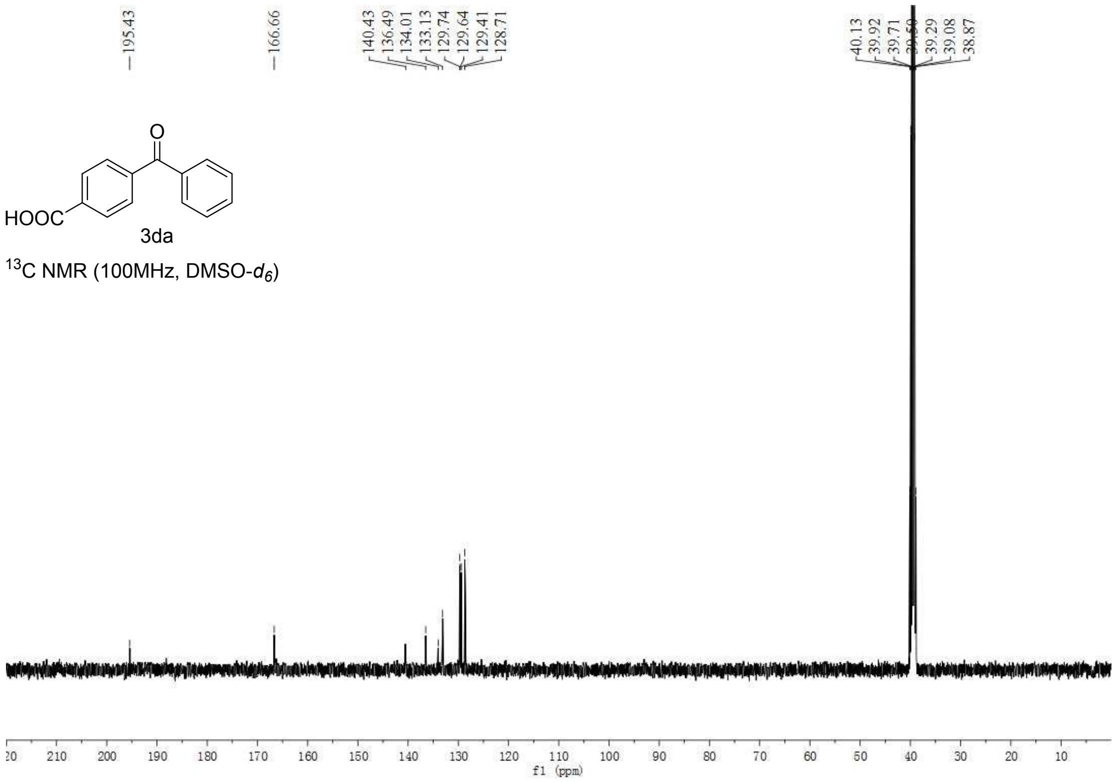

8.14
8.12
7.83
7.81
7.79
7.79
7.77
7.77
7.62
7.62
7.61
7.60
7.60
7.59
7.58
7.58
7.58
7.50
7.49
7.48
7.46
7.46
7.24
3.95
O
MeOOC
3ca
^{1}H NMR (400MHz, CDCl$_3$)
2.00
2.04
2.01
1.01
2.02
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


196.03
166.31
141.31
136.94
133.21
132.93
130.08
129.76
129.48
128.45
77.32
77.00
76.68
52.45
O
MeOOC
3ca
^{13} C NMR (100MHz, CDCl$_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)



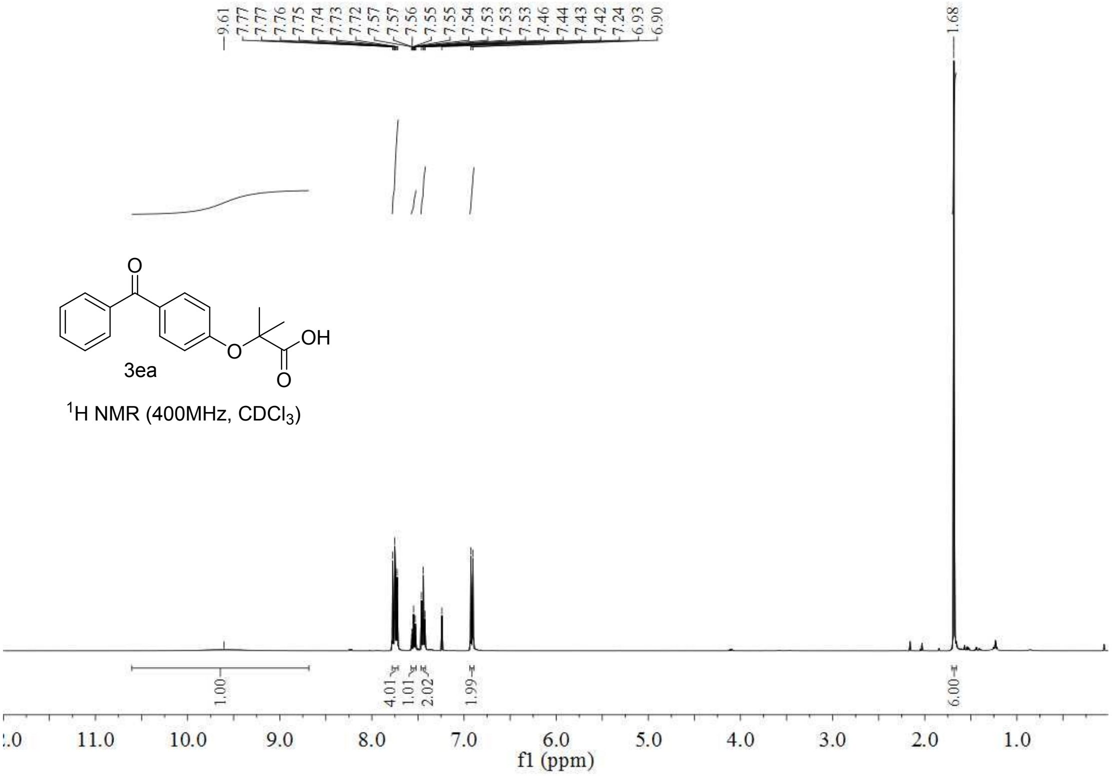
3da

^{1}H NMR (400MHz, CDCl$_3$)



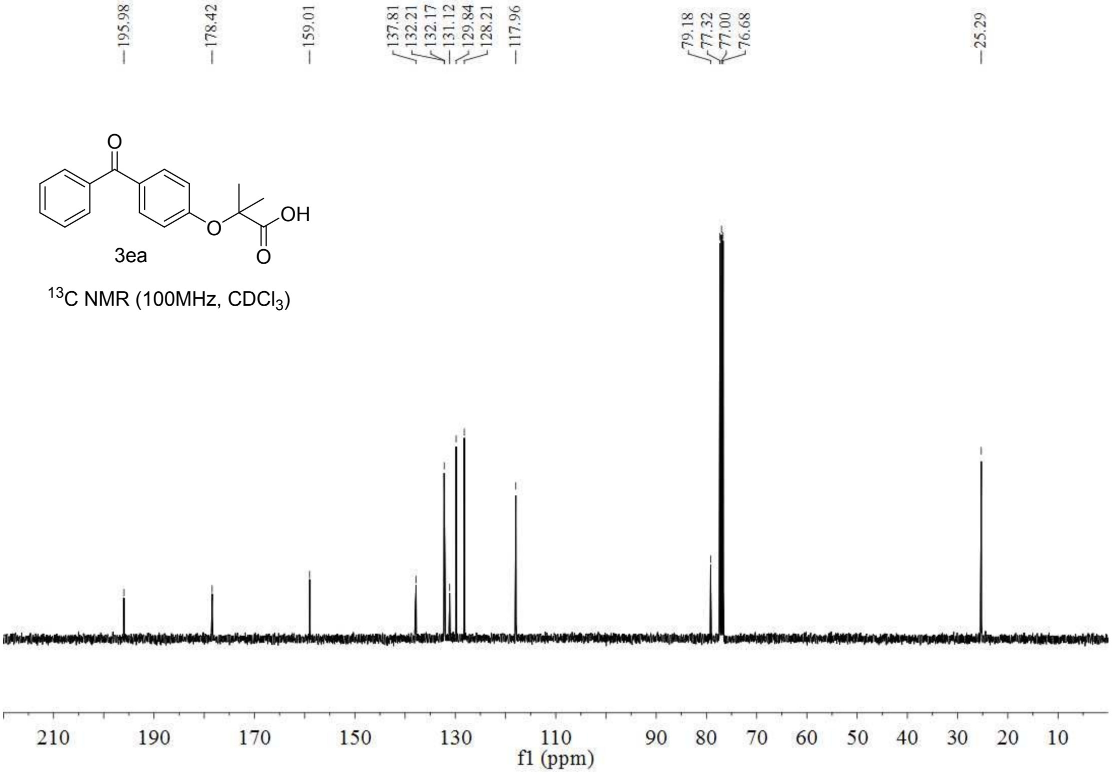
3da

^{13}C NMR (100MHz, DMSO-d_6)



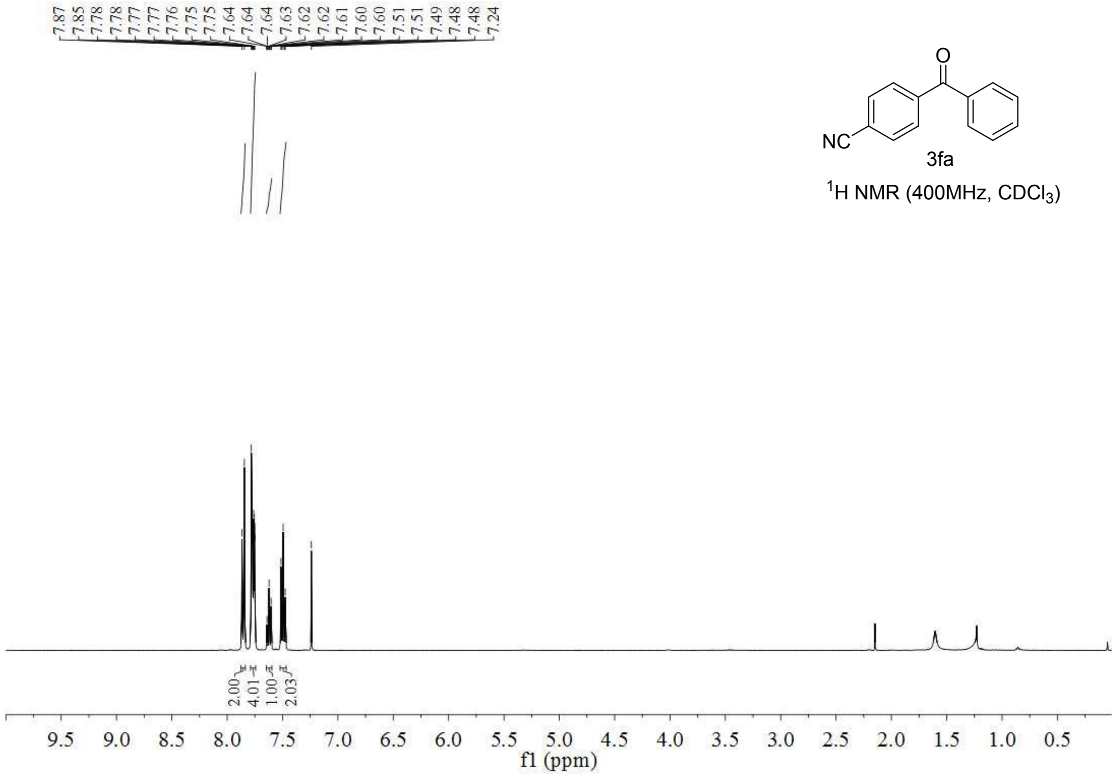
3ea

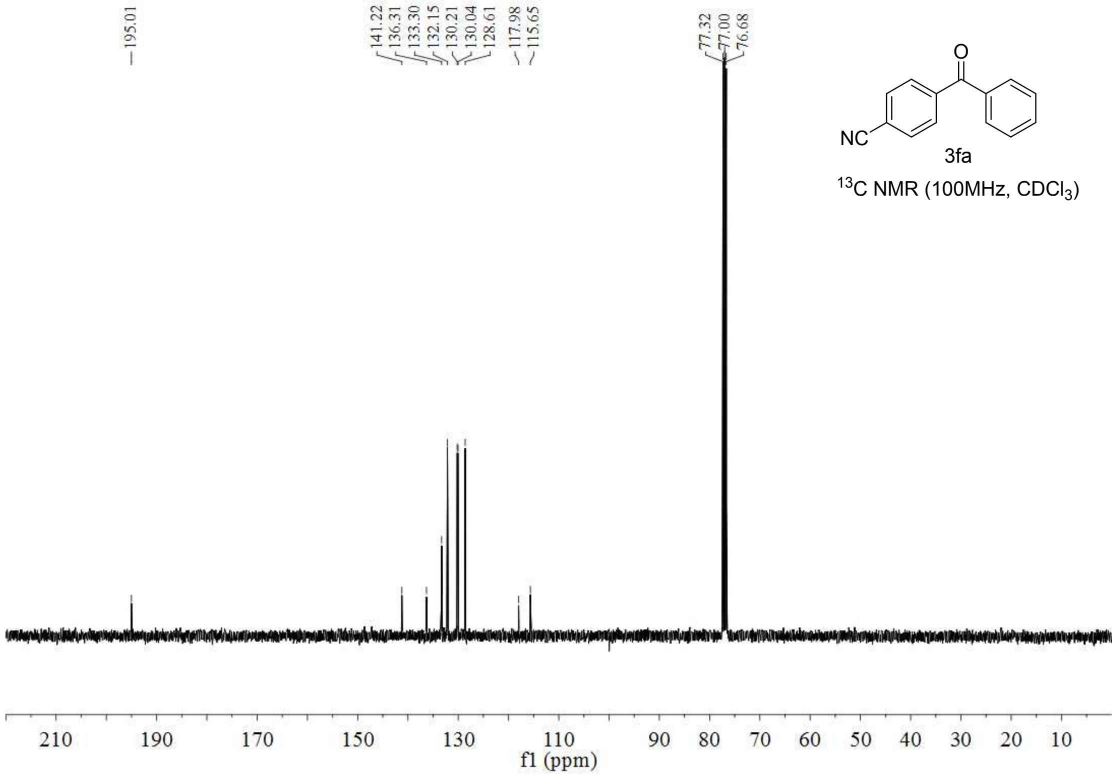
^{1}H NMR (400MHz, $CDCl_3$)

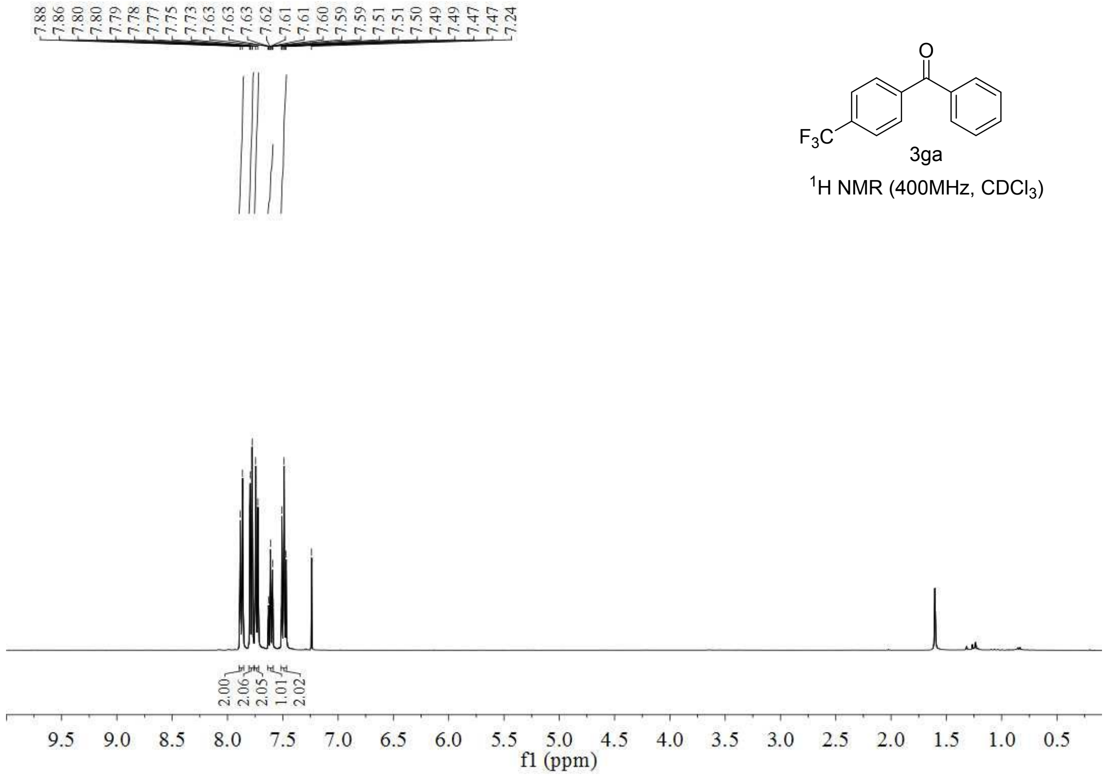


3ea

^{13}C NMR (100MHz, $CDCl_3$)

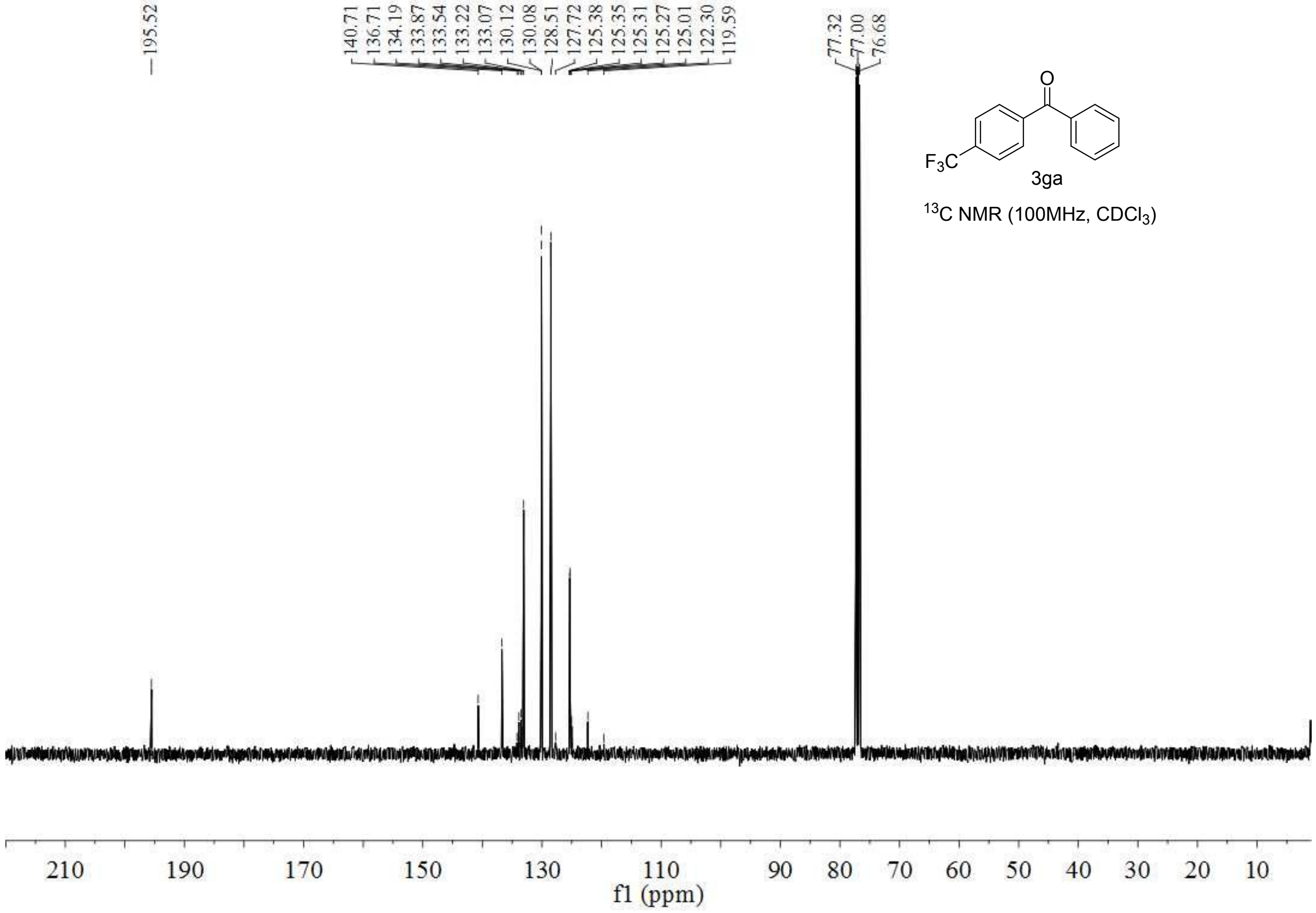

7.87
7.85
7.78
7.78
7.77
7.77
7.76
7.75
7.75
7.64
7.64
7.63
7.62
7.62
7.61
7.60
7.60
7.51
7.51
7.49
7.48
7.48
7.24
O
NC
3fa
^{1}H NMR (400MHz, CDCl$_3$)
2.00
4.01
1.00
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


195.01
141.22
136.31
133.30
132.15
130.21
130.04
128.61
117.98
115.65
77.32
77.00
76.68
O
NC
3fa
^{13}C NMR (100MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)



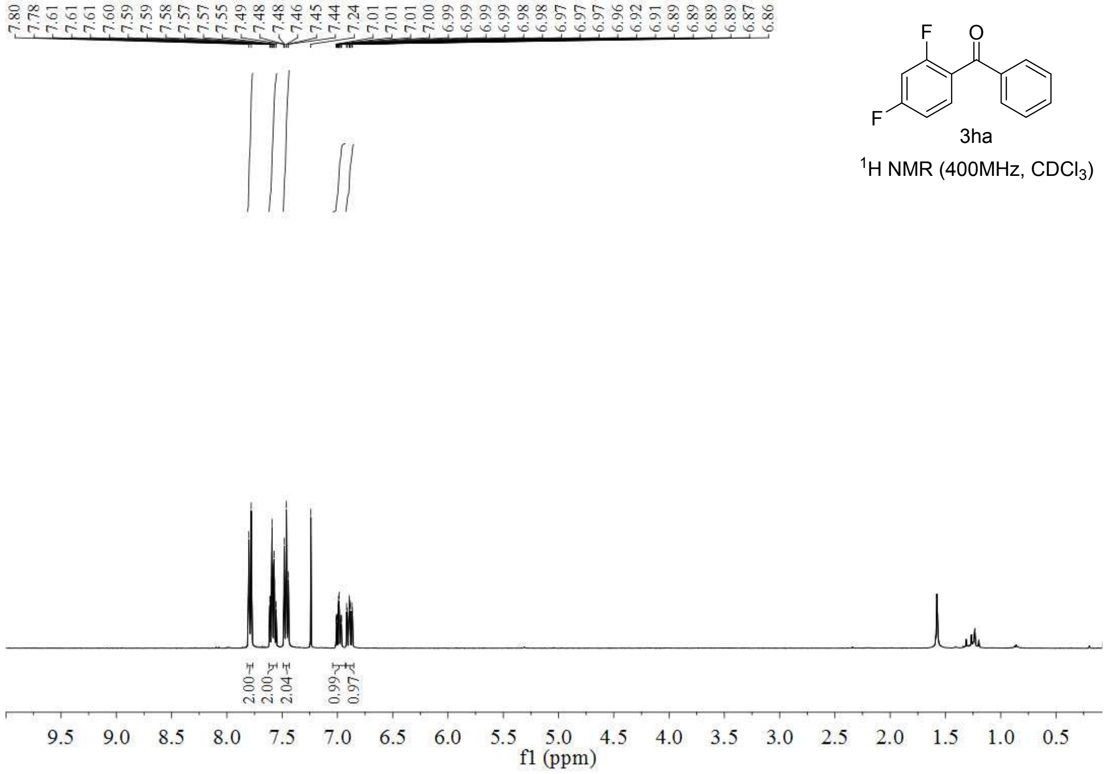
3ga

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



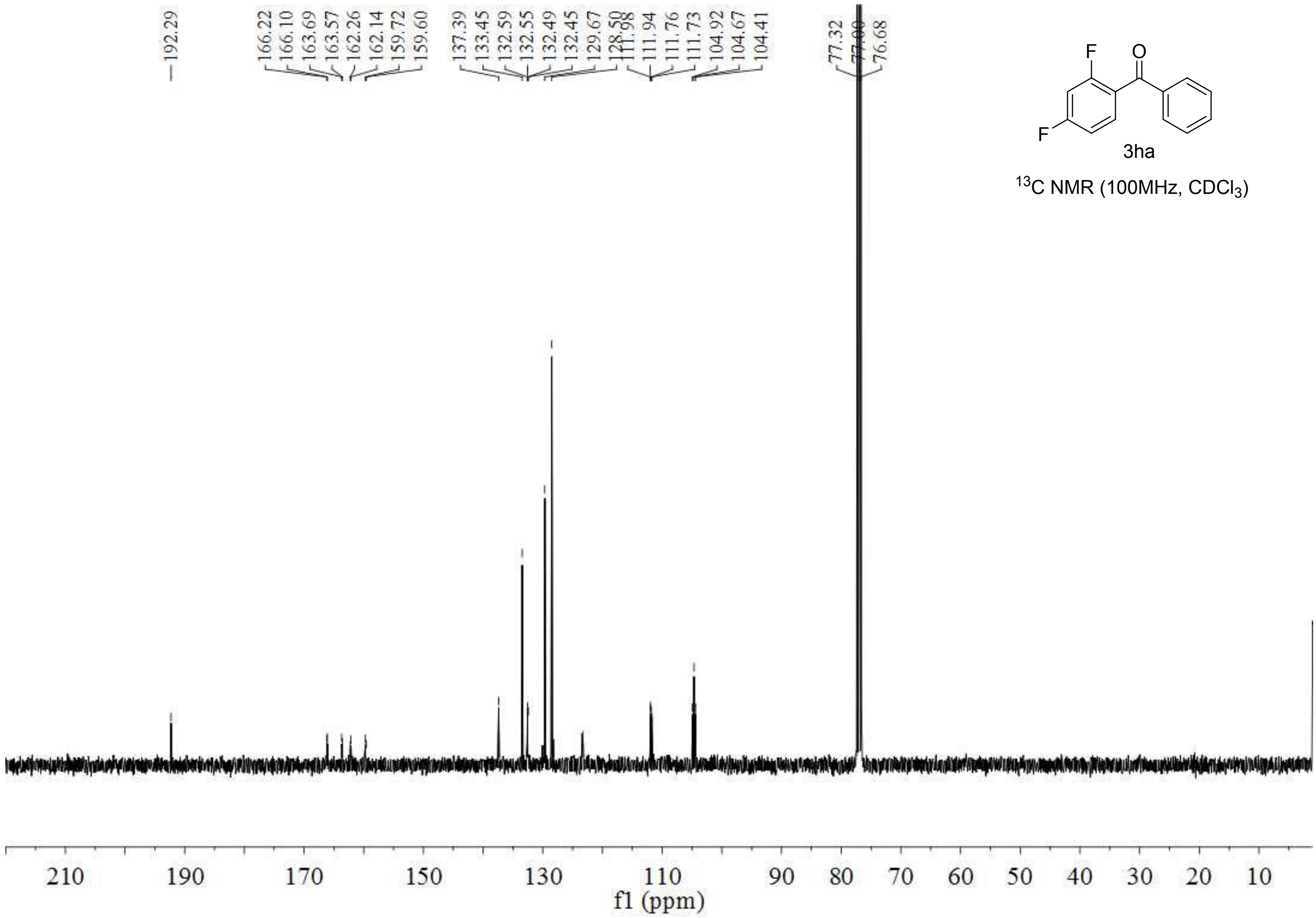
3ga

^{13}C NMR (100MHz, $CDCl_3$)



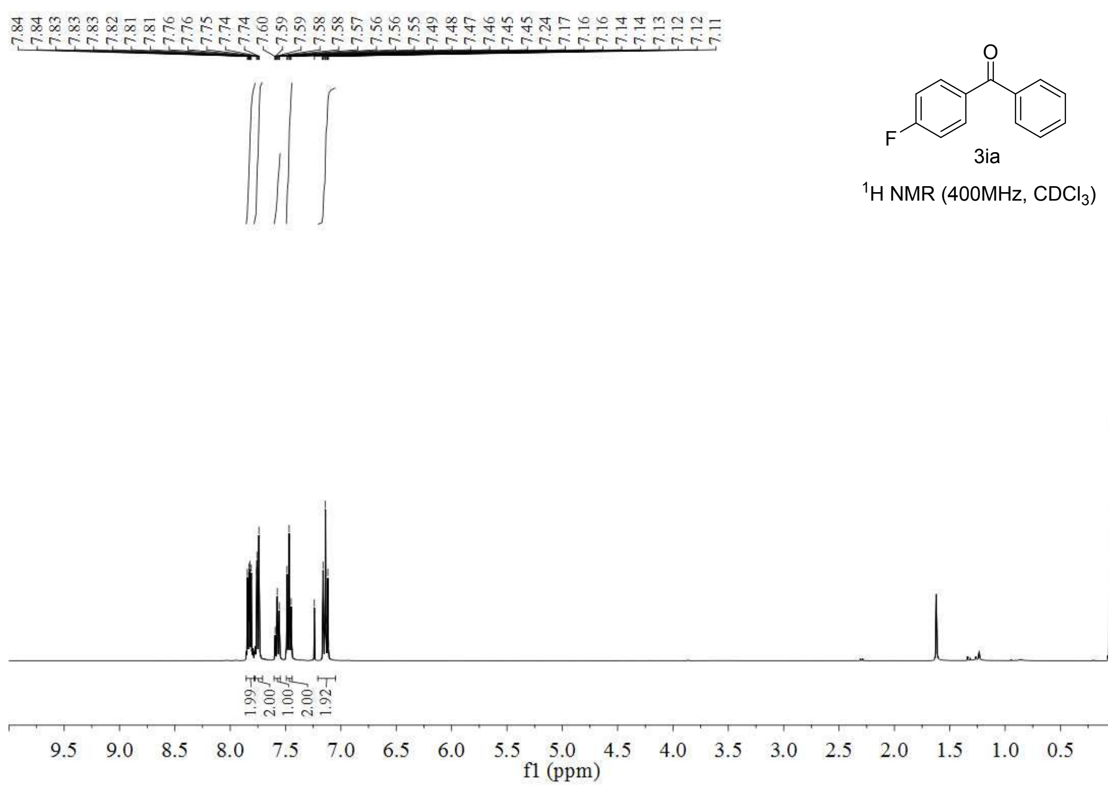
3ha

^{1}H NMR (400MHz, CDCl$_3$)



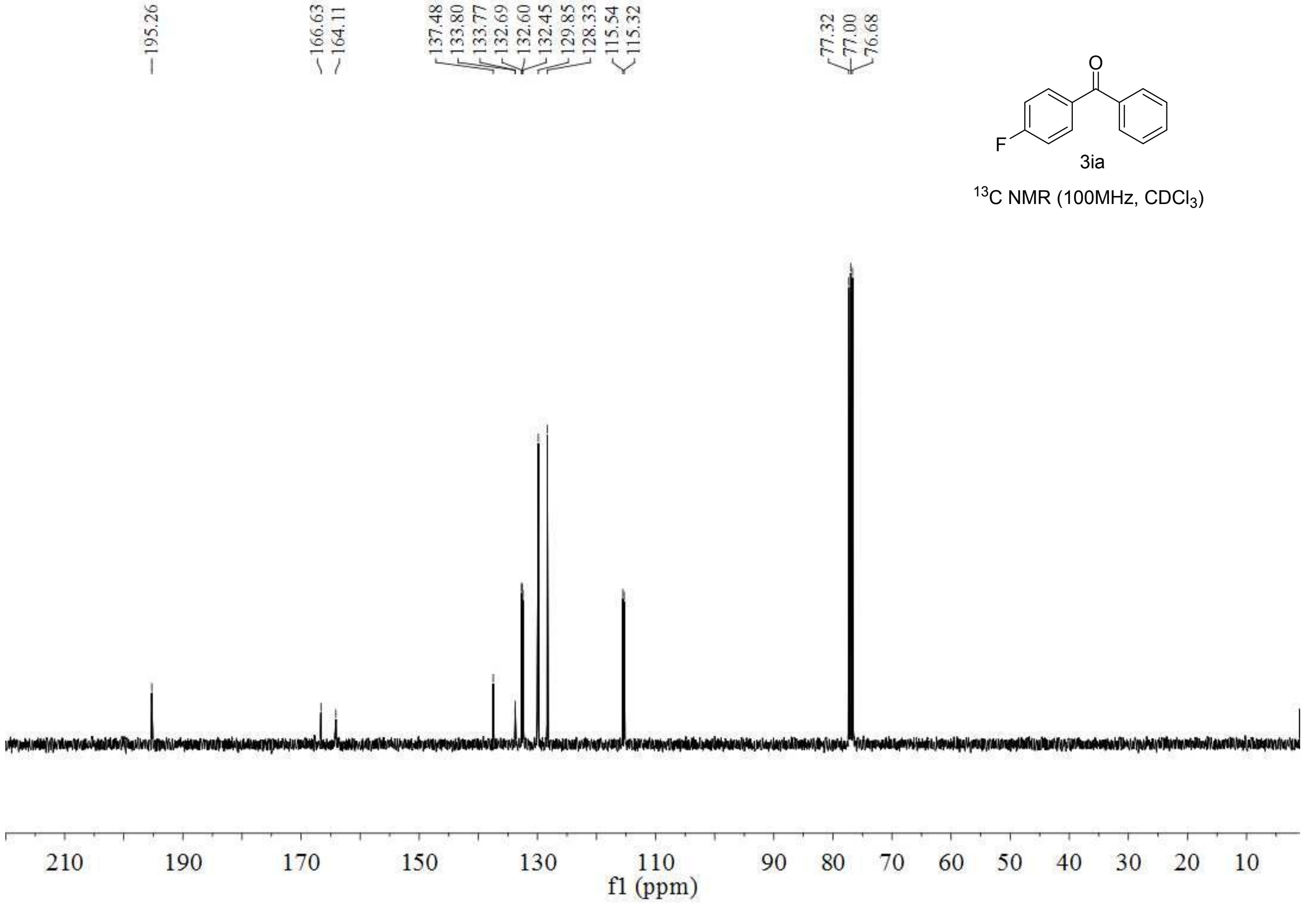
3ha

^{13}C NMR (100MHz, $CDCl_3$)



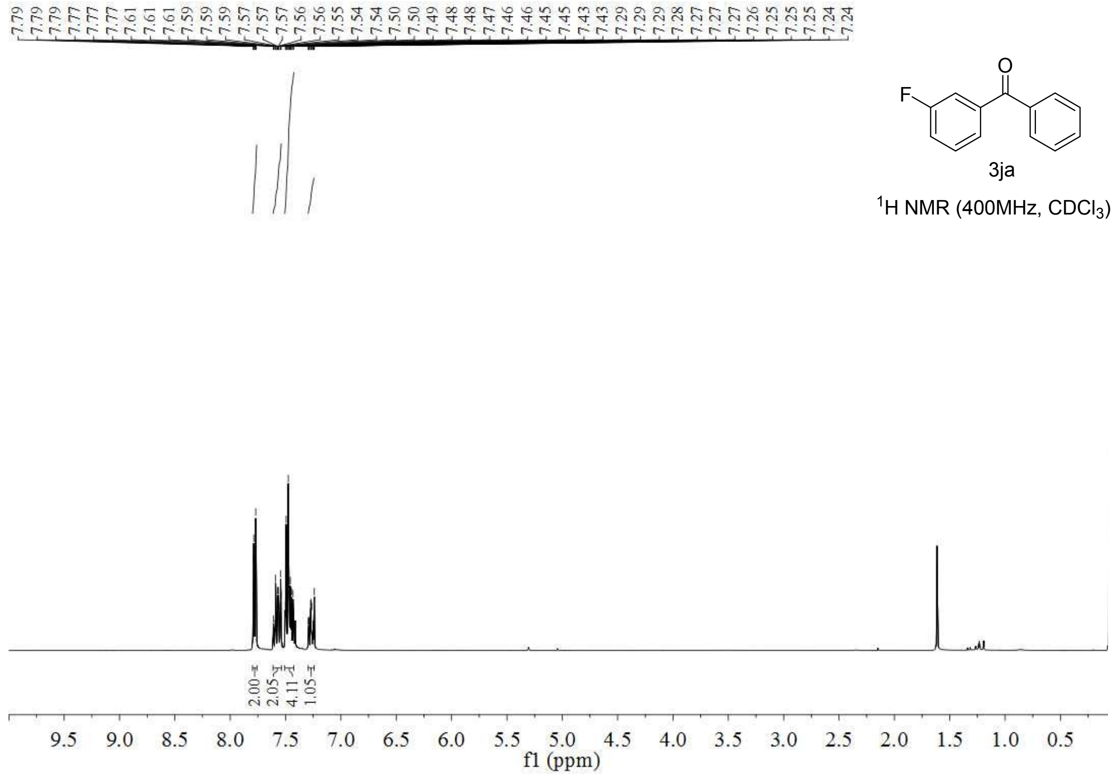
3ia

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



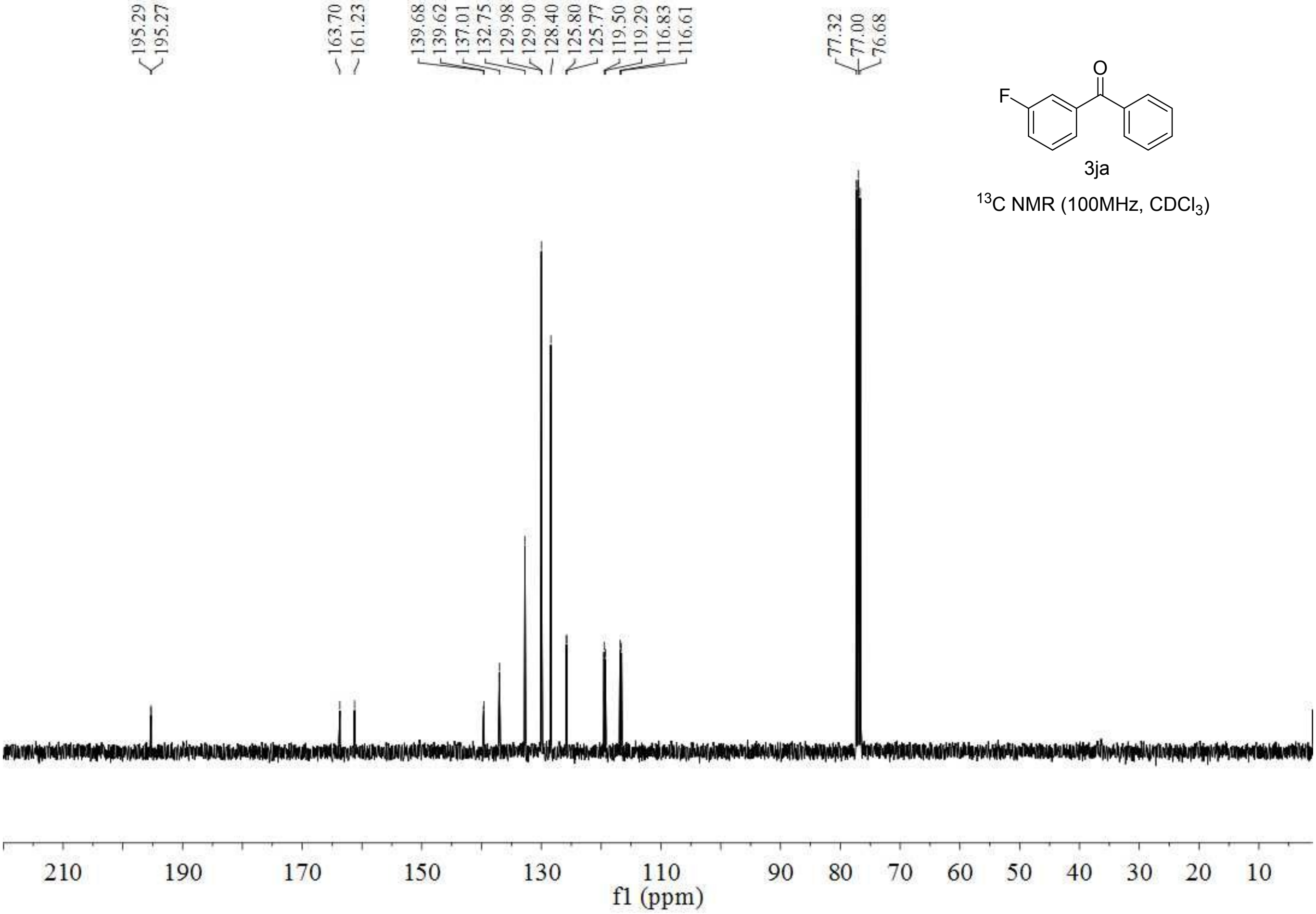
3ia

^{13}C NMR (100MHz, $CDCl_3$)



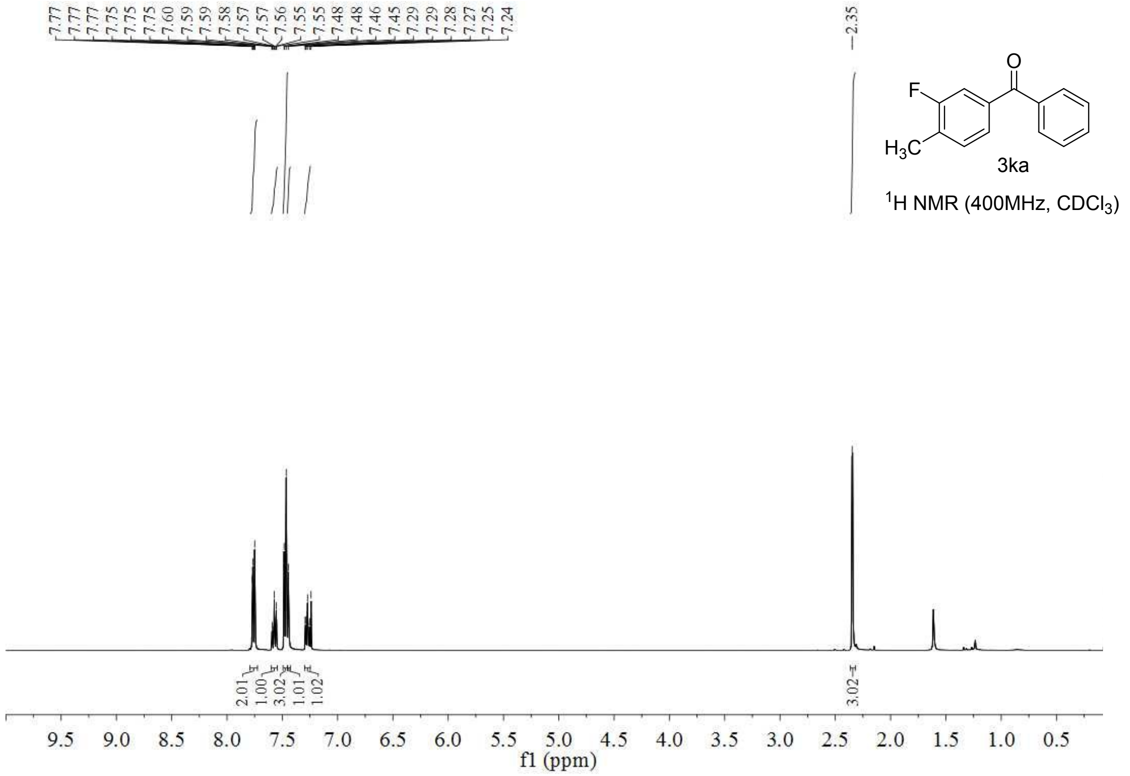
3ja

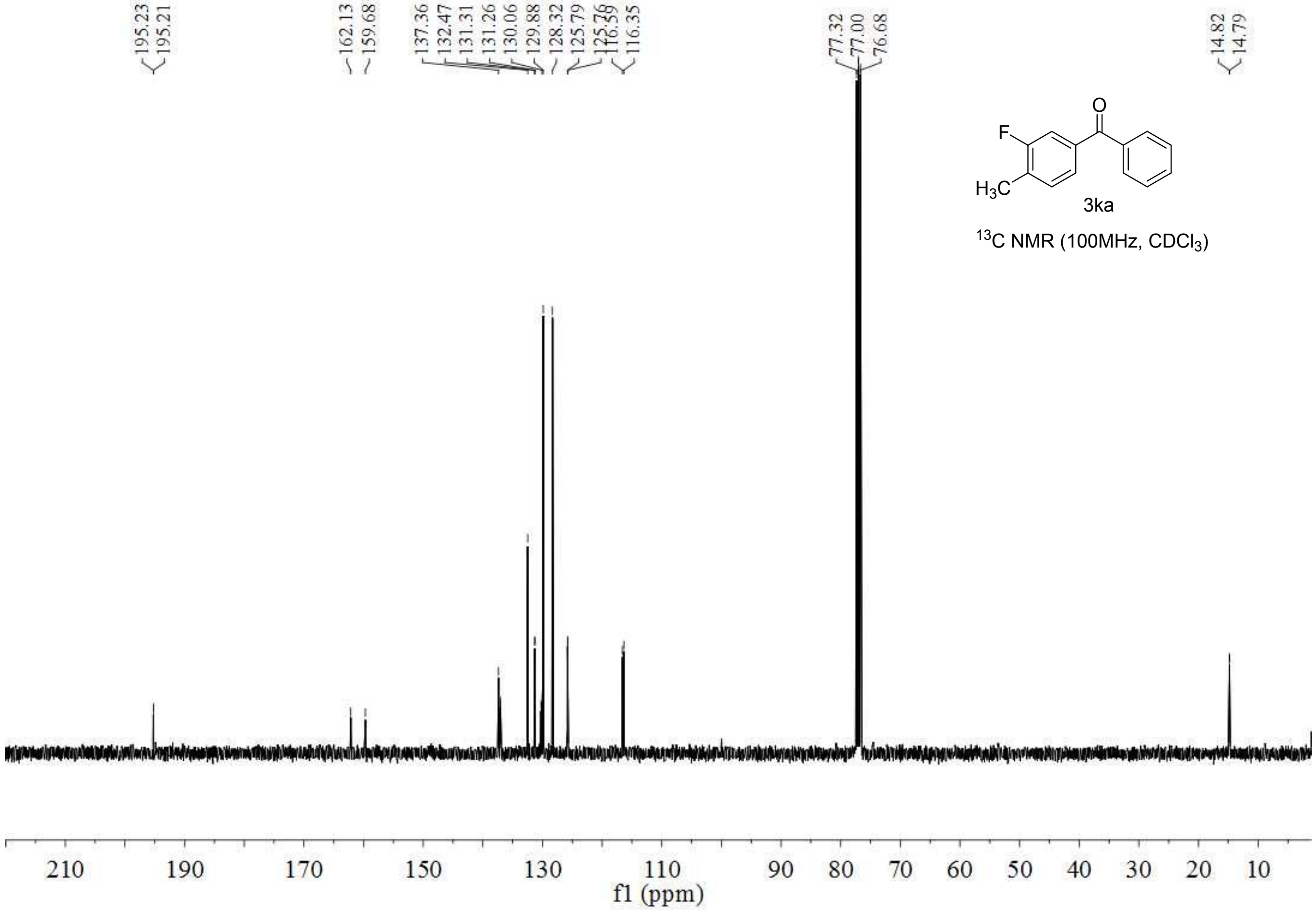
^{1}H NMR (400MHz, $CDCl_3$)

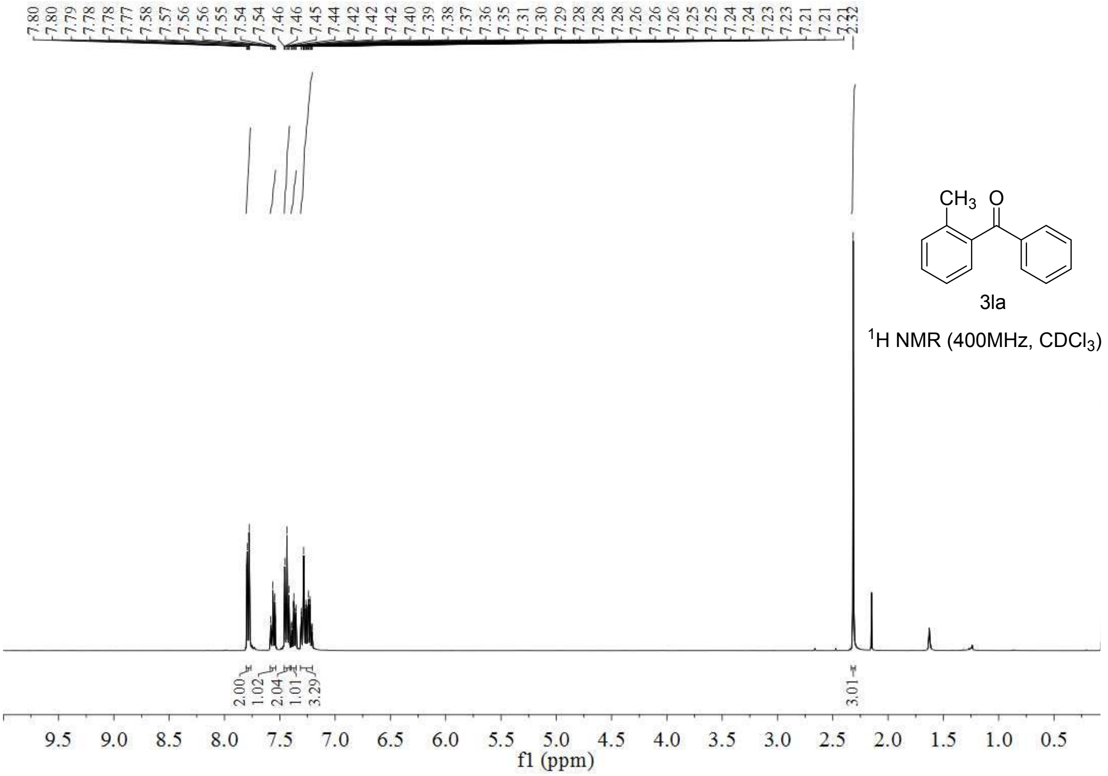


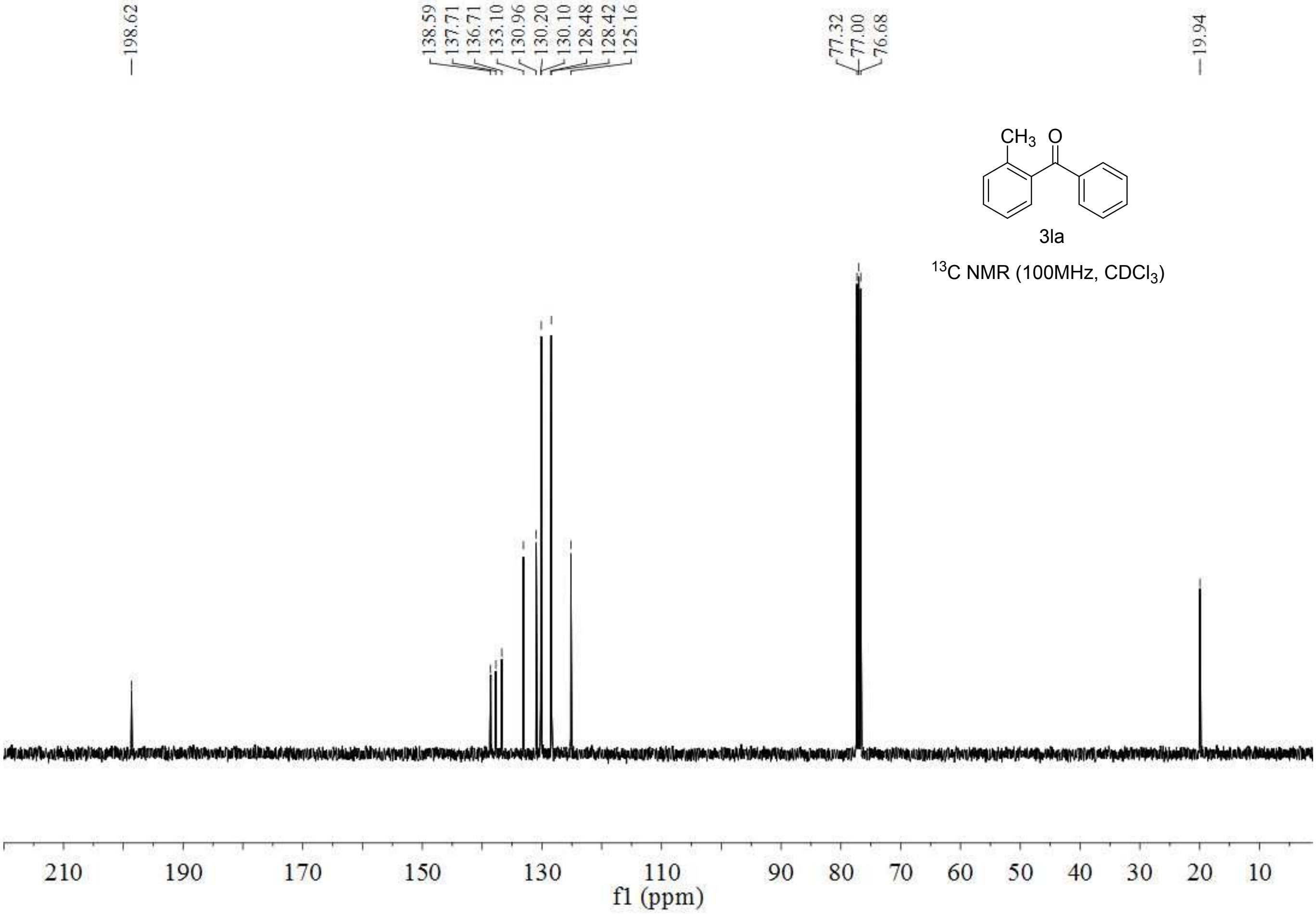
3ja

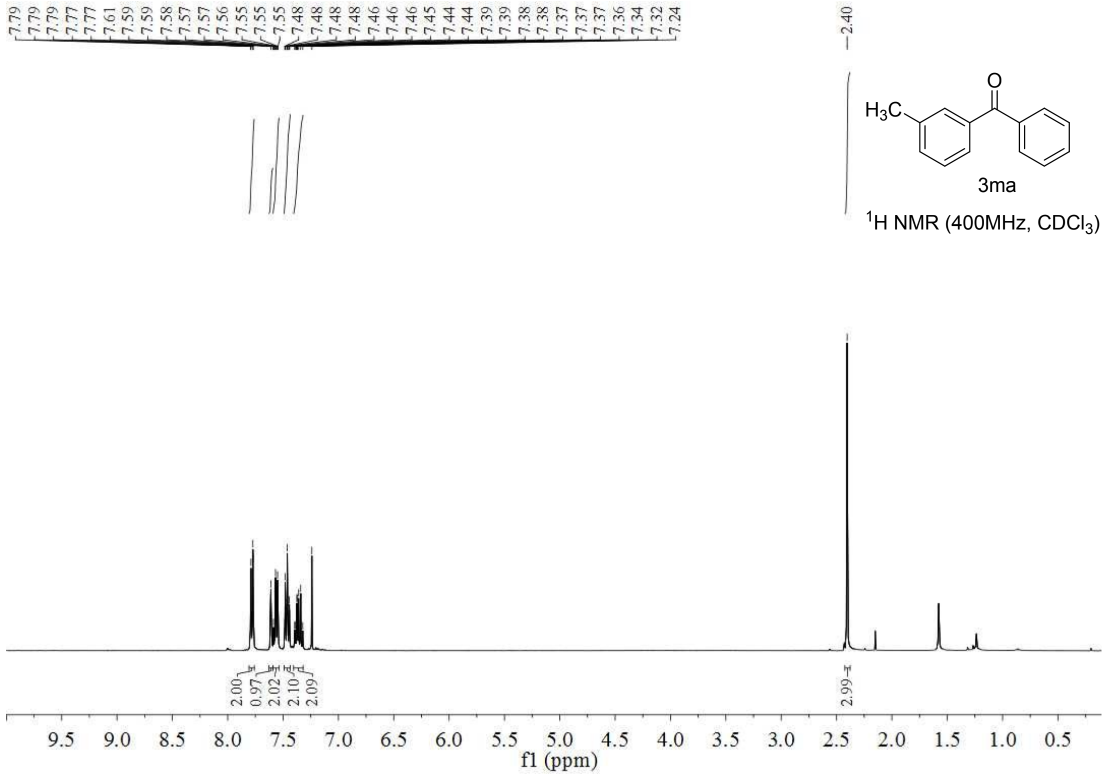
^{13}C NMR (100MHz, $CDCl_3$)

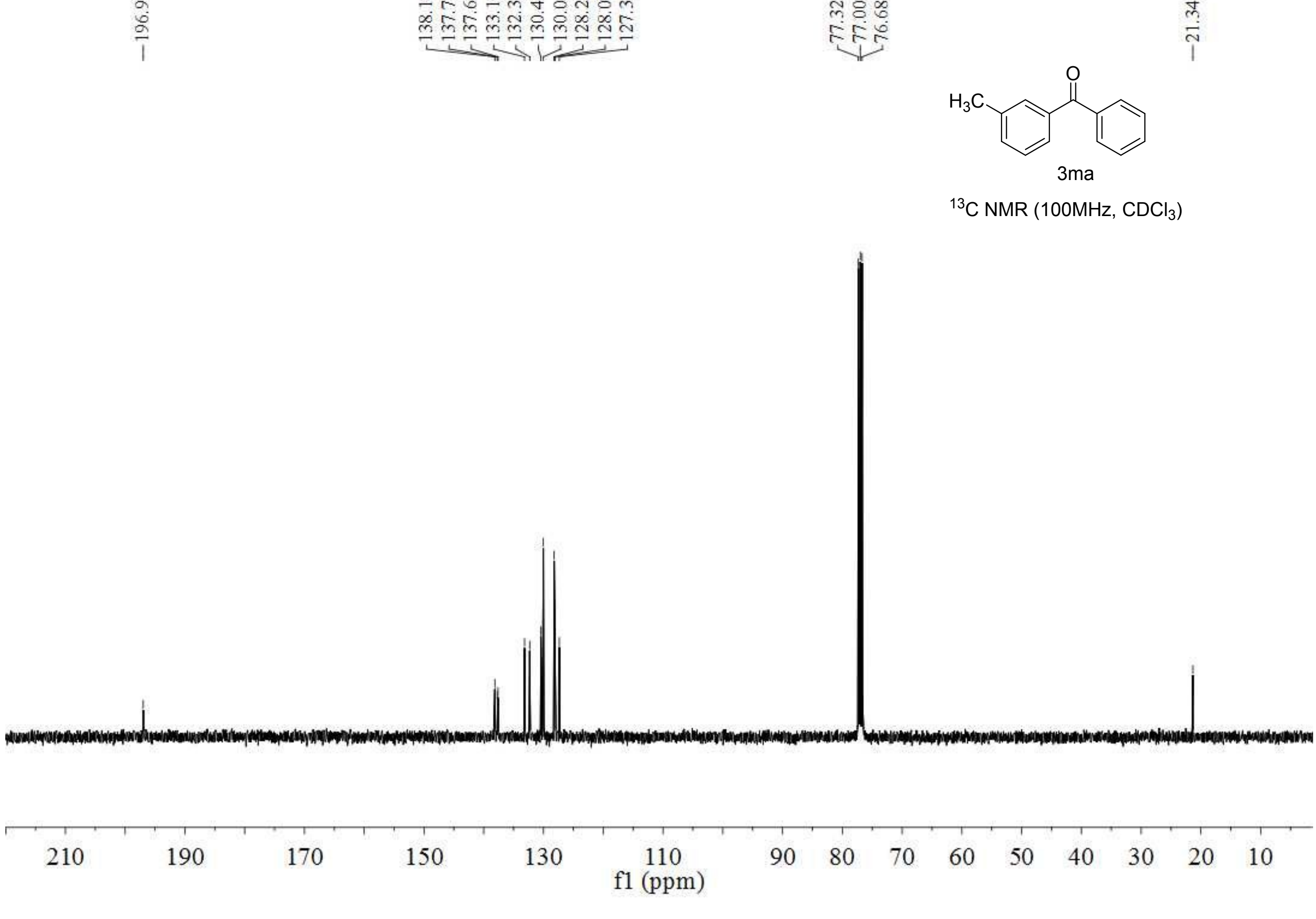

7.77
7.77
7.77
7.75
7.75
7.75
7.60
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.48
7.46
7.45
7.29
7.29
7.28
7.27
7.25
7.24
2.35
3ka
^{1}H NMR (400MHz, CDCl$_3$)
2.01
1.00
3.02
1.01
1.02
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

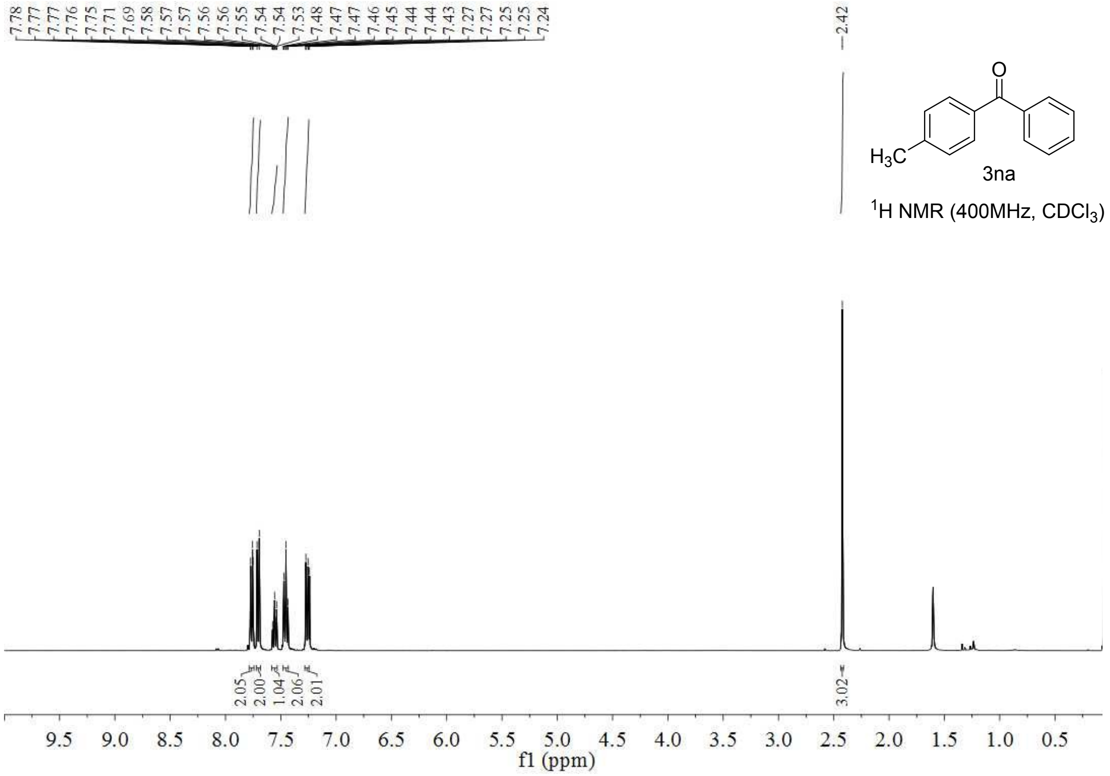

195.23
195.21
162.13
159.68
137.36
132.47
131.31
131.26
130.06
129.88
128.32
125.79
125.76
116.59
116.35
77.32
77.00
76.68
14.82
14.79
3ka
^{13}C NMR (100MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.80
7.80
7.79
7.78
7.78
7.77
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.46
7.46
7.45
7.44
7.42
7.42
7.42
7.40
7.39
7.38
7.37
7.36
7.35
7.31
7.30
7.29
7.28
7.28
7.28
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.21
7.21
2.32
CH3
O
3la
1H NMR (400MHz, CDCl3)
2.00
1.02
2.04
1.01
3.29
3.01
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
f1 (ppm)


198.62
138.59
137.71
136.71
133.10
130.96
130.20
130.10
128.48
128.42
125.16
77.32
77.00
76.68
19.94
CH3
O
3la
13C NMR (100MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

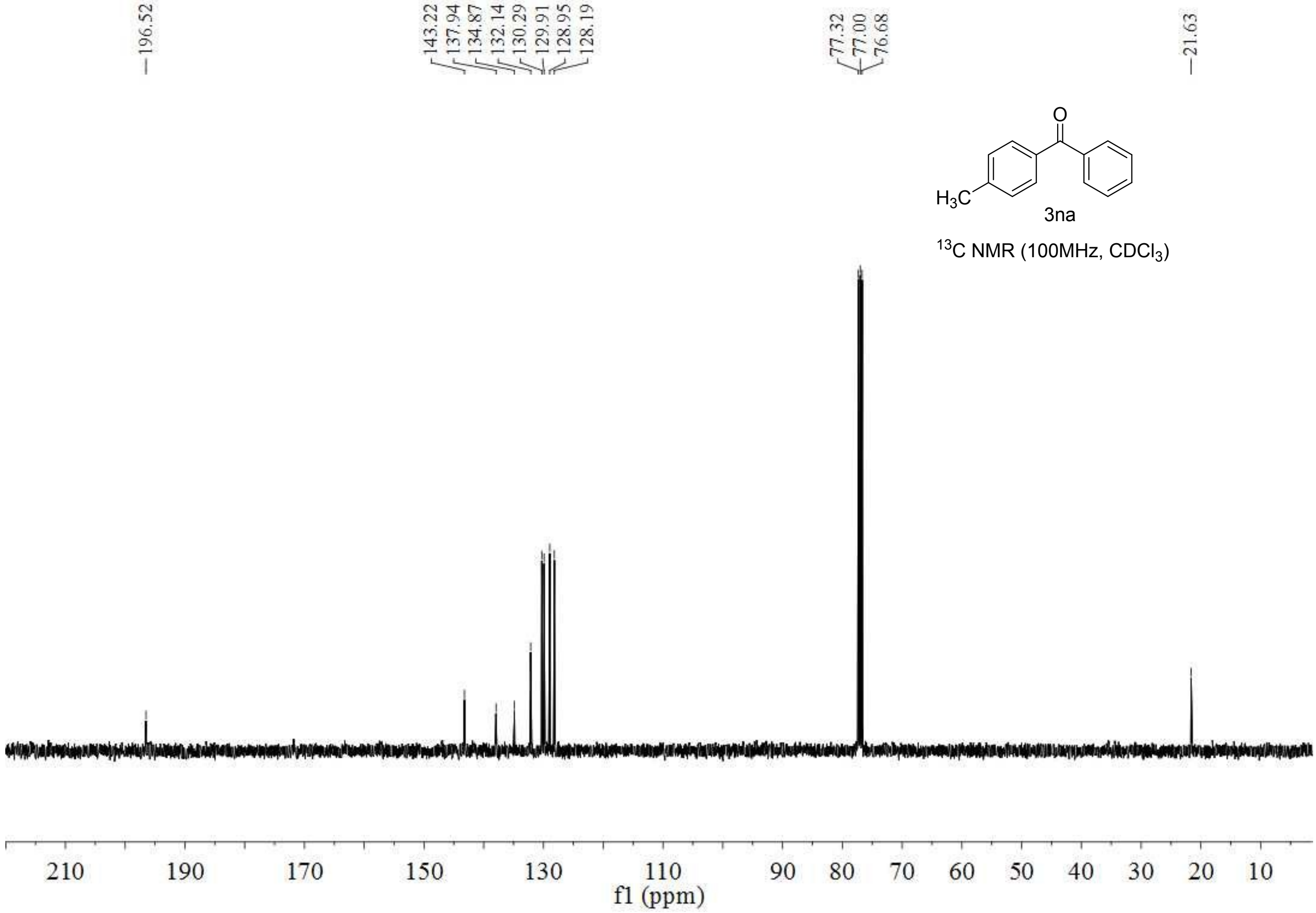

7.79 7.79 7.79 7.77 7.77 7.61 7.59 7.59 7.58 7.57 7.57 7.56 7.55 7.55 7.55 7.48 7.48 7.48 7.46 7.46 7.46 7.45 7.44 7.44 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.34 7.32 7.24
2.40
H_3C
O
3ma
^1H NMR (400MHz, $CDCl_3$)
2.00
0.97
2.02
2.10
2.09
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


196.97
138.14 137.75 137.62 133.17 132.31 130.44 130.02 128.22 128.07 127.35
77.32 77.00 76.68
21.34
H_3C
O
3ma
^{13}C NMR (100MHz, $CDCl_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)



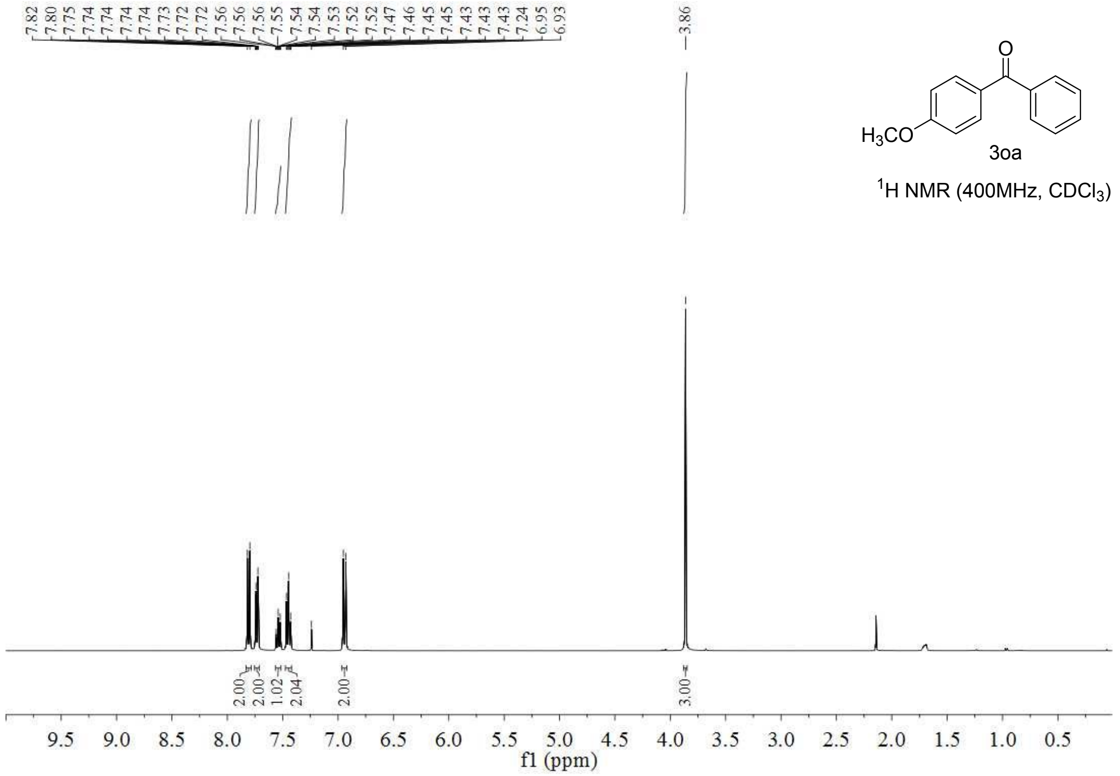
3na

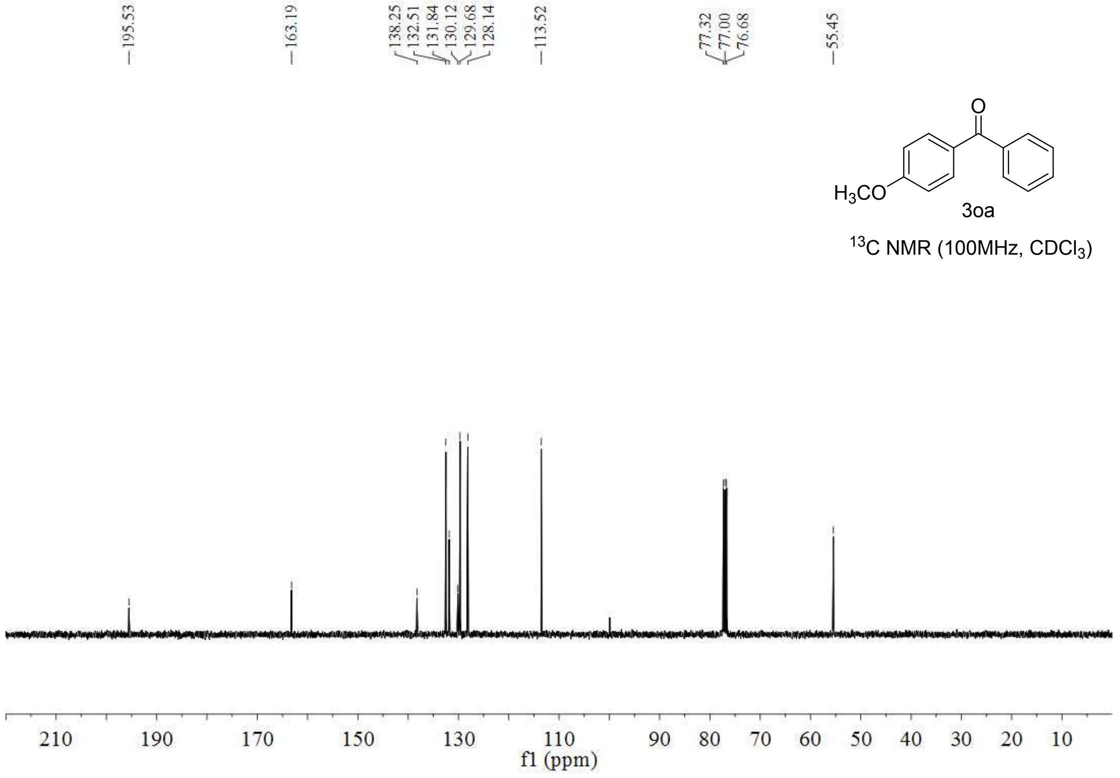
^{1}H NMR (400MHz, $CDCl_3$)

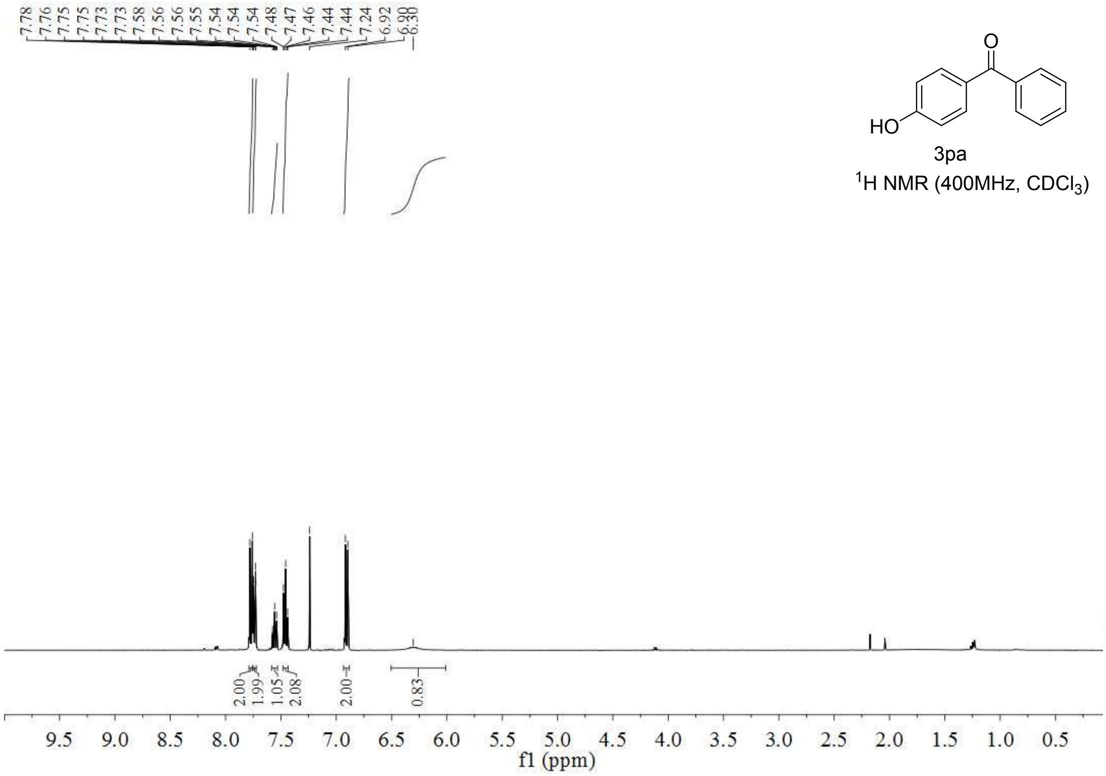


3na

^{13}C NMR (100MHz, $CDCl_3$)

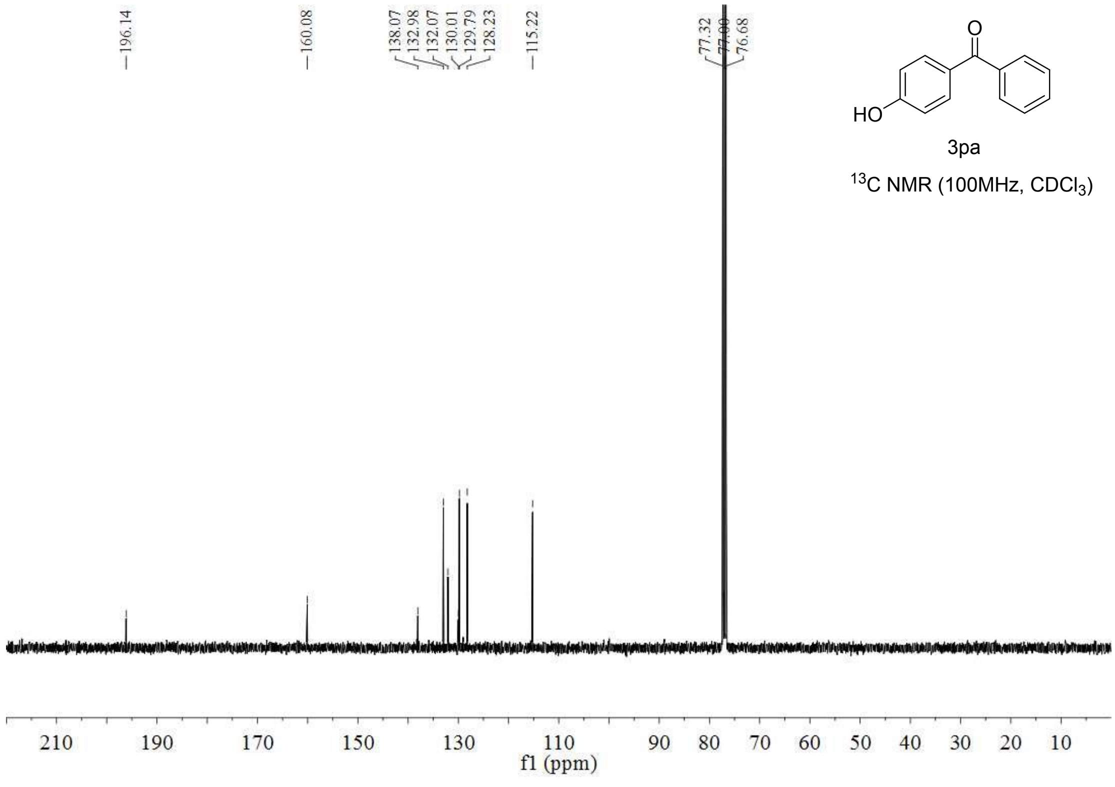

7.82
7.80
7.75
7.74
7.74
7.74
7.74
7.73
7.72
7.72
7.56
7.56
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.47
7.46
7.45
7.45
7.43
7.43
7.43
7.24
6.95
6.93
3.86
O
H3CO
3oa
1H NMR (400MHz, CDCl3)
2.00
2.00
1.02
2.04
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


195.53
163.19
138.25
132.51
131.84
130.12
129.68
128.14
113.52
77.32
77.00
76.68
55.45
O
H3CO
3oa
13C NMR (100MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)



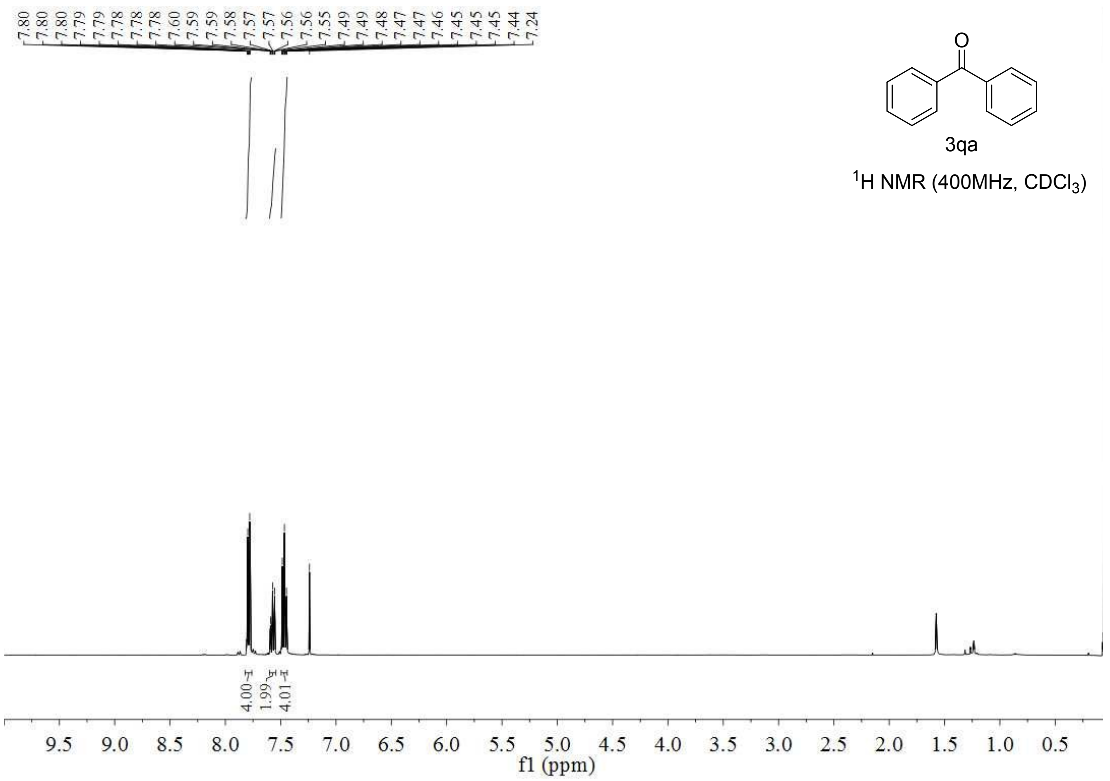
3pa

^{1}H NMR (400MHz, CDCl$_3$)



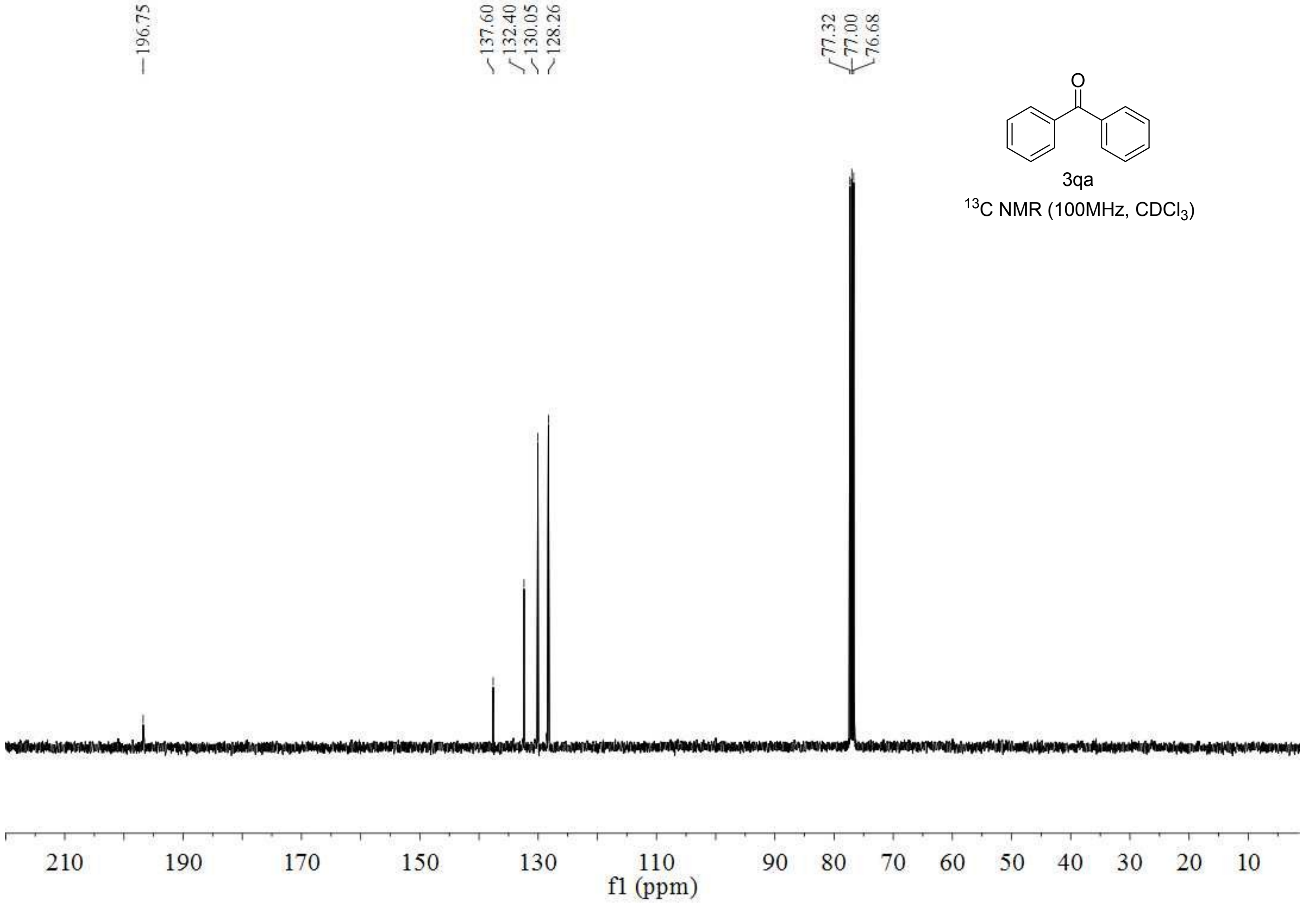
3pa

^{13}C NMR (100MHz, CDCl$_3$)



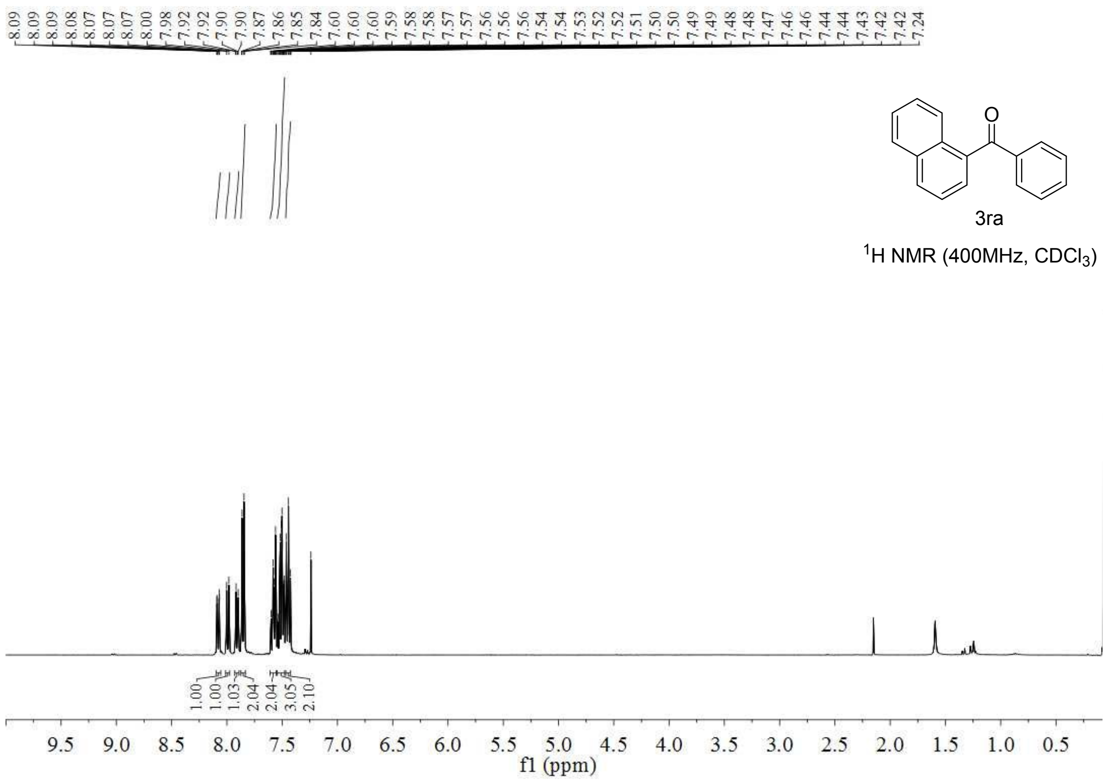
3qa

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



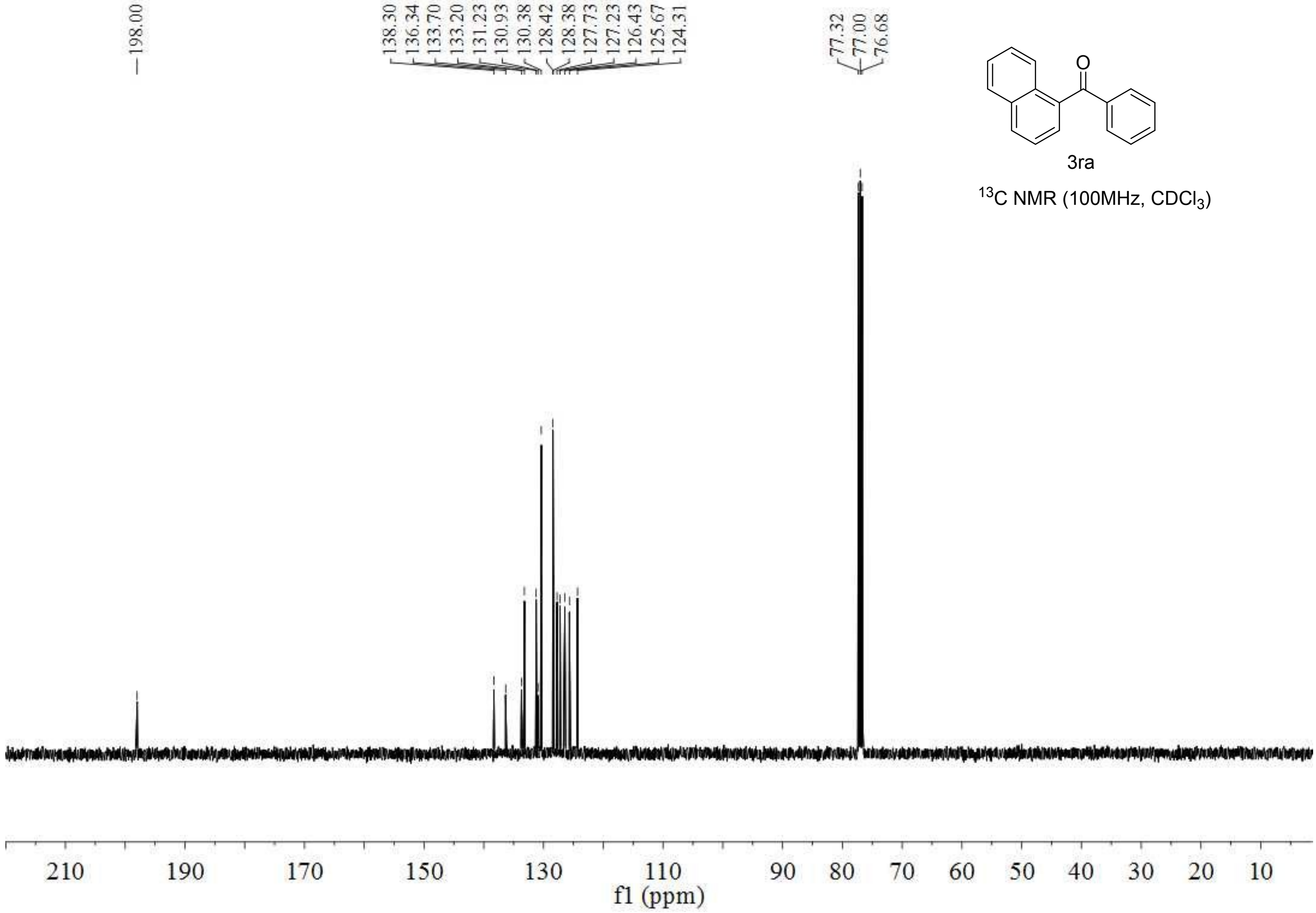
3qa

^{13}C NMR (100MHz, $CDCl_3$)



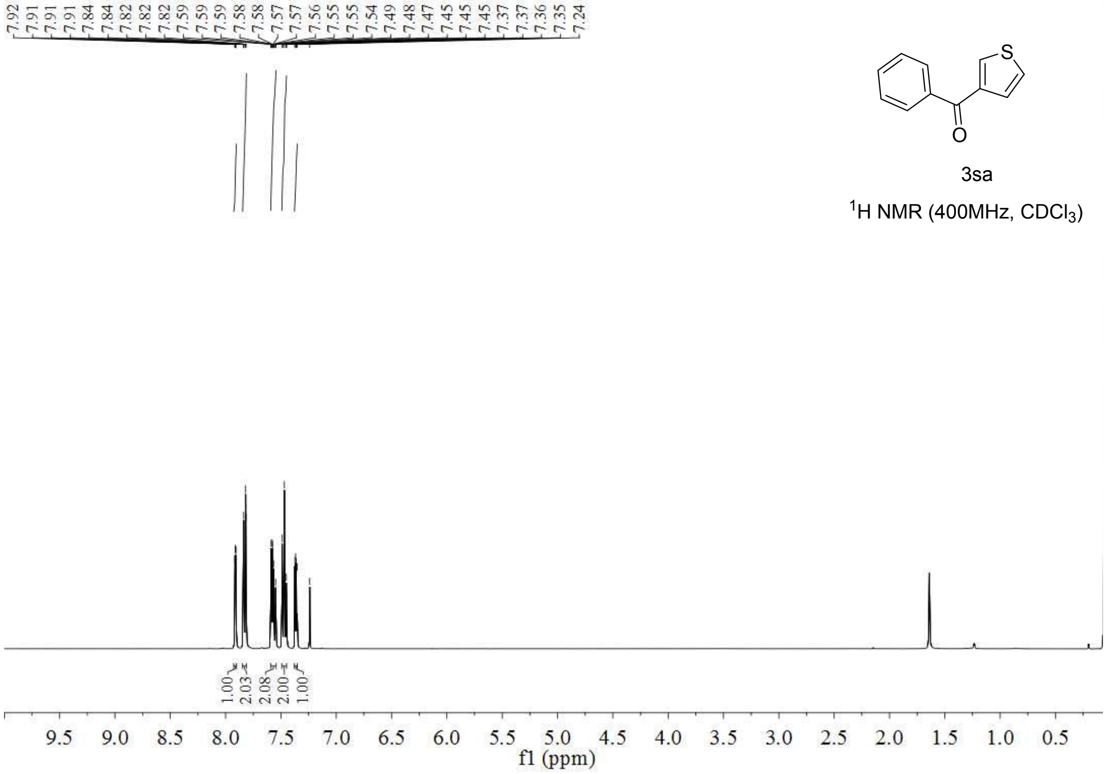
3ra

^{1}H NMR (400MHz, CDCl$_3$)



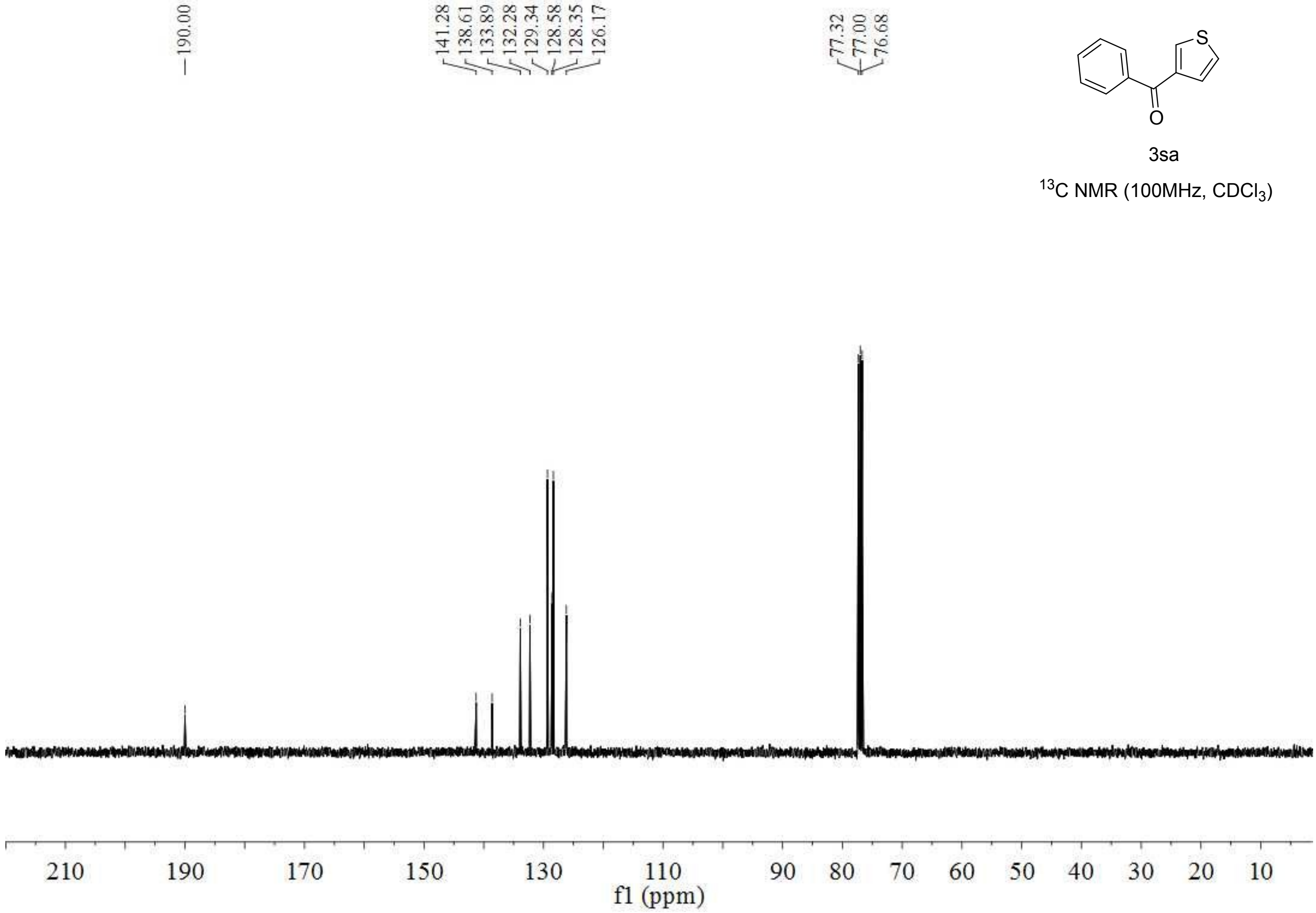
3ra

^{13}C NMR (100MHz, CDCl$_3$)



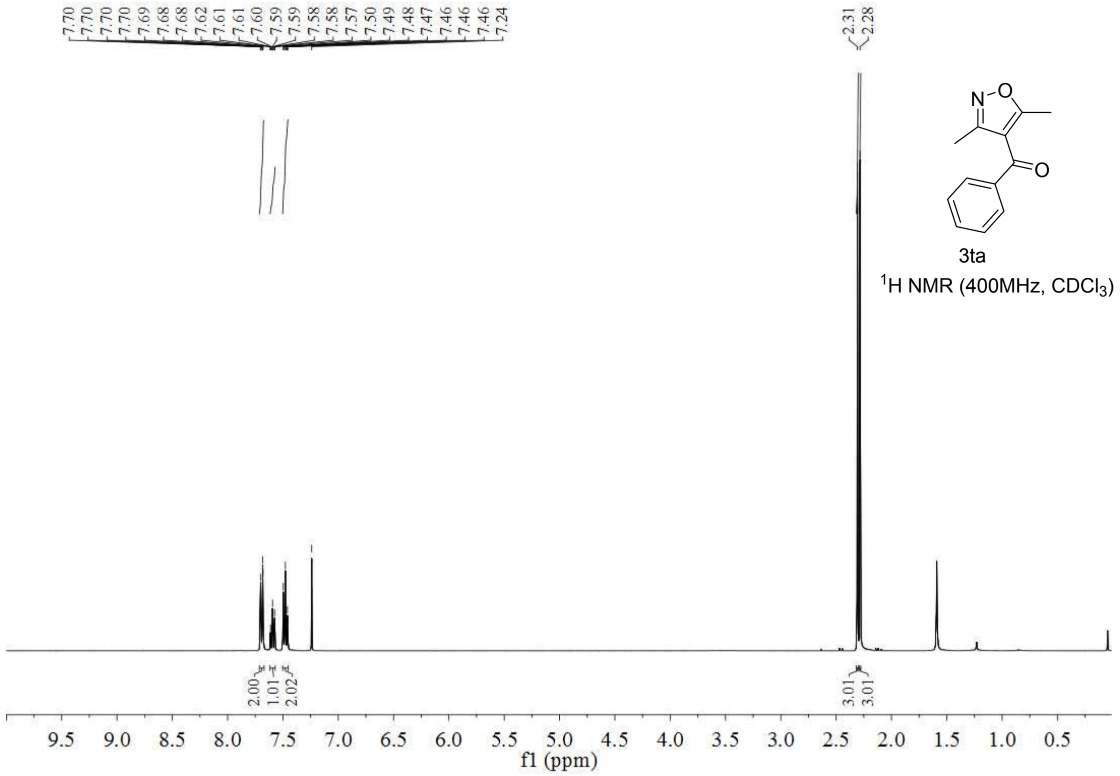
3sa

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



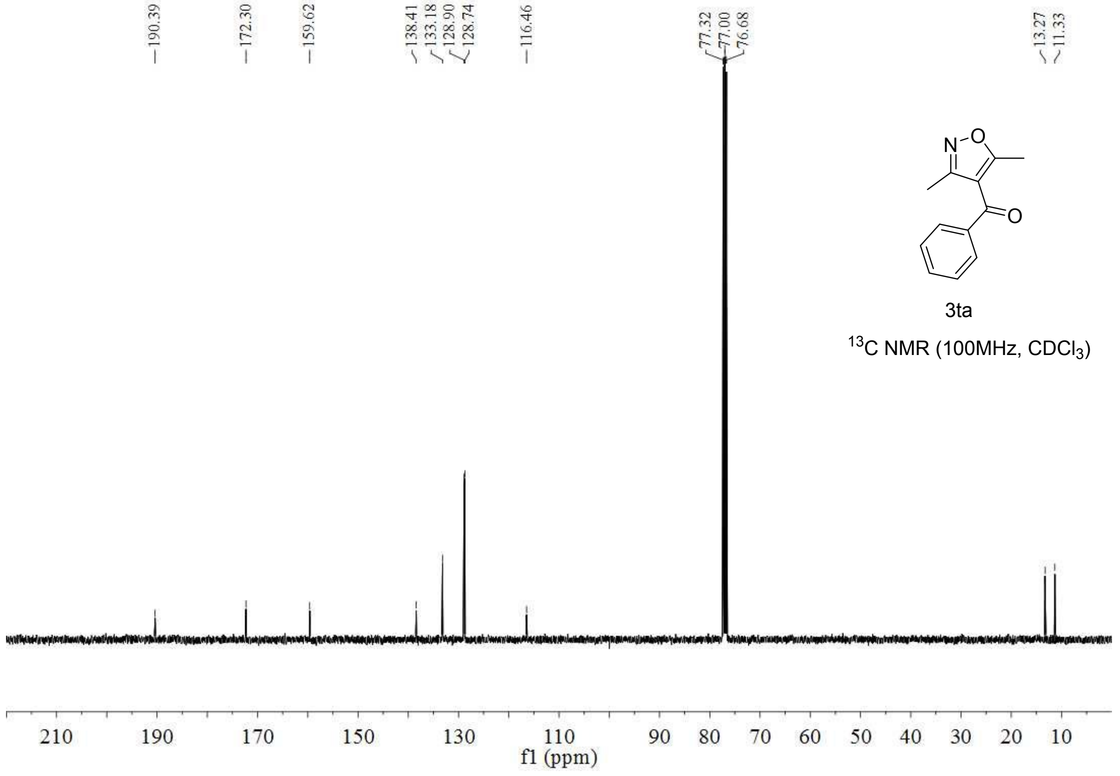
3sa

^{13}C NMR (100MHz, $CDCl_3$)



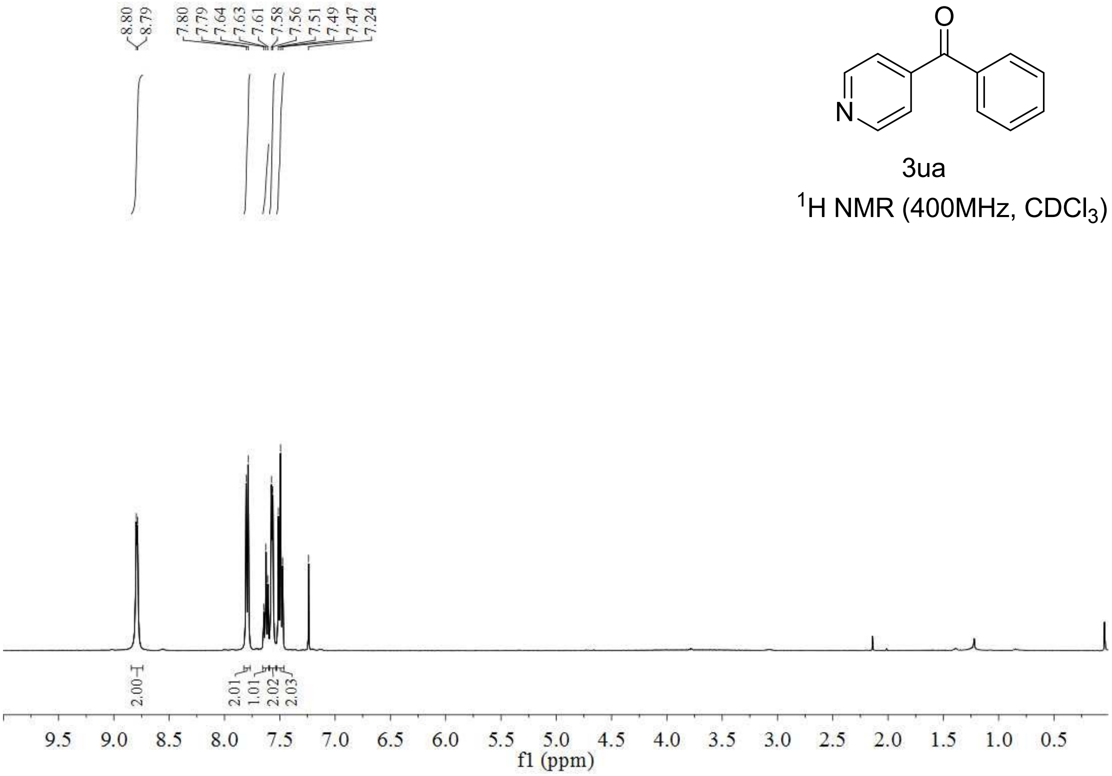
3ta

^{1}H NMR (400MHz, CDCl$_3$)



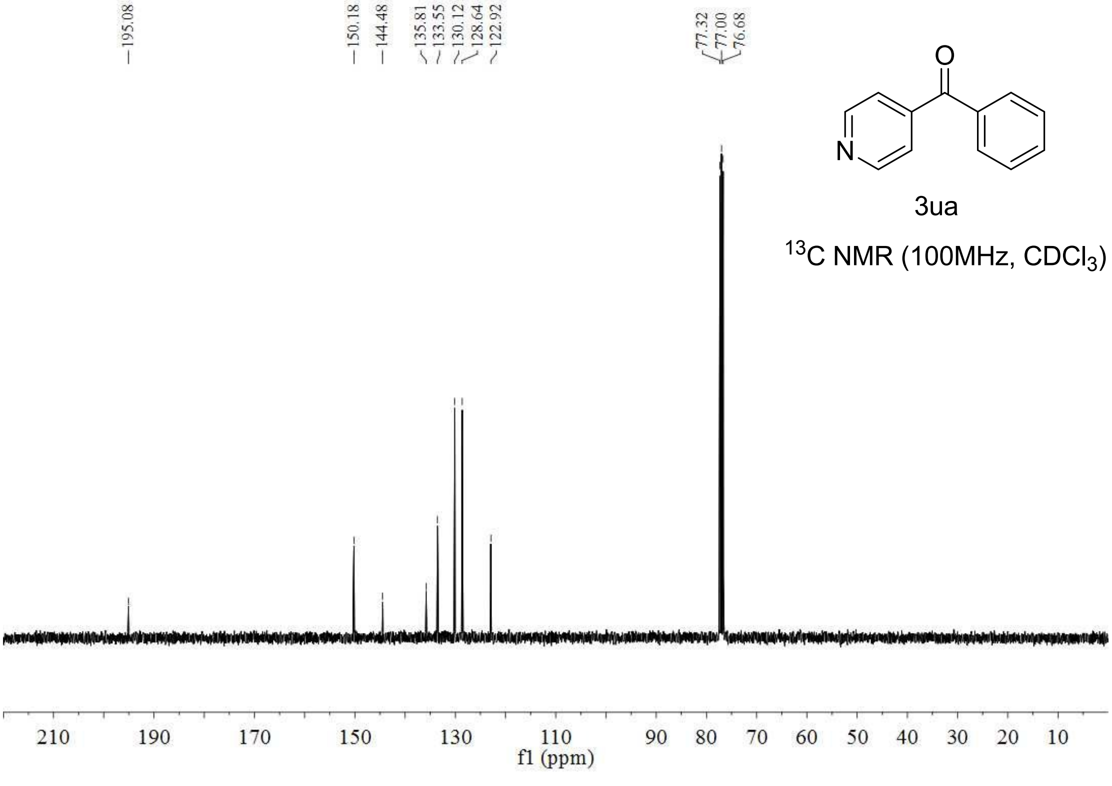
3ta

^{13}C NMR (100MHz, CDCl$_3$)



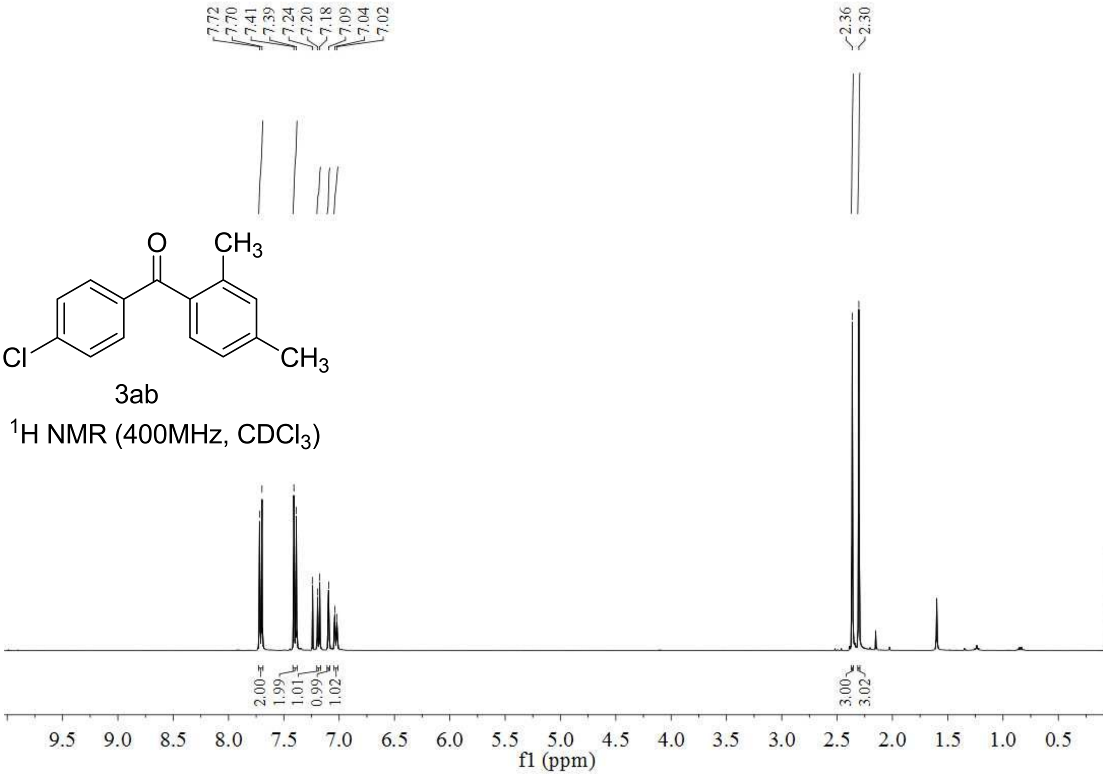
3ua

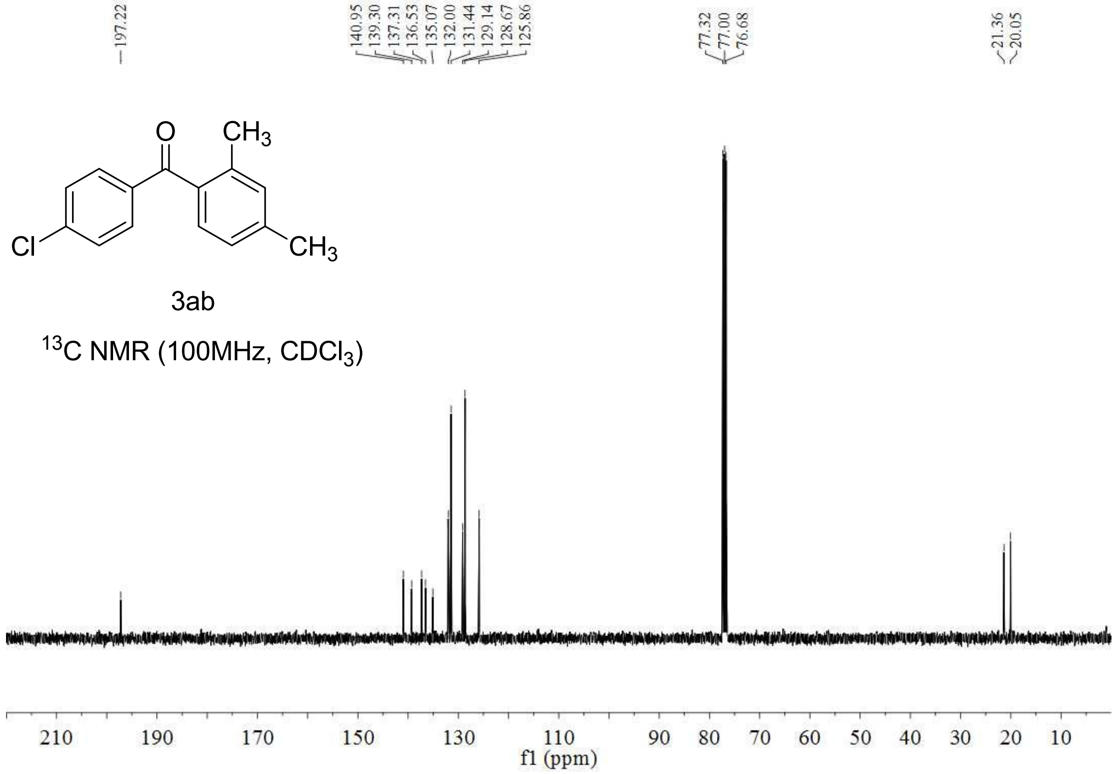
^{1}H NMR (400MHz, $CDCl_3$)

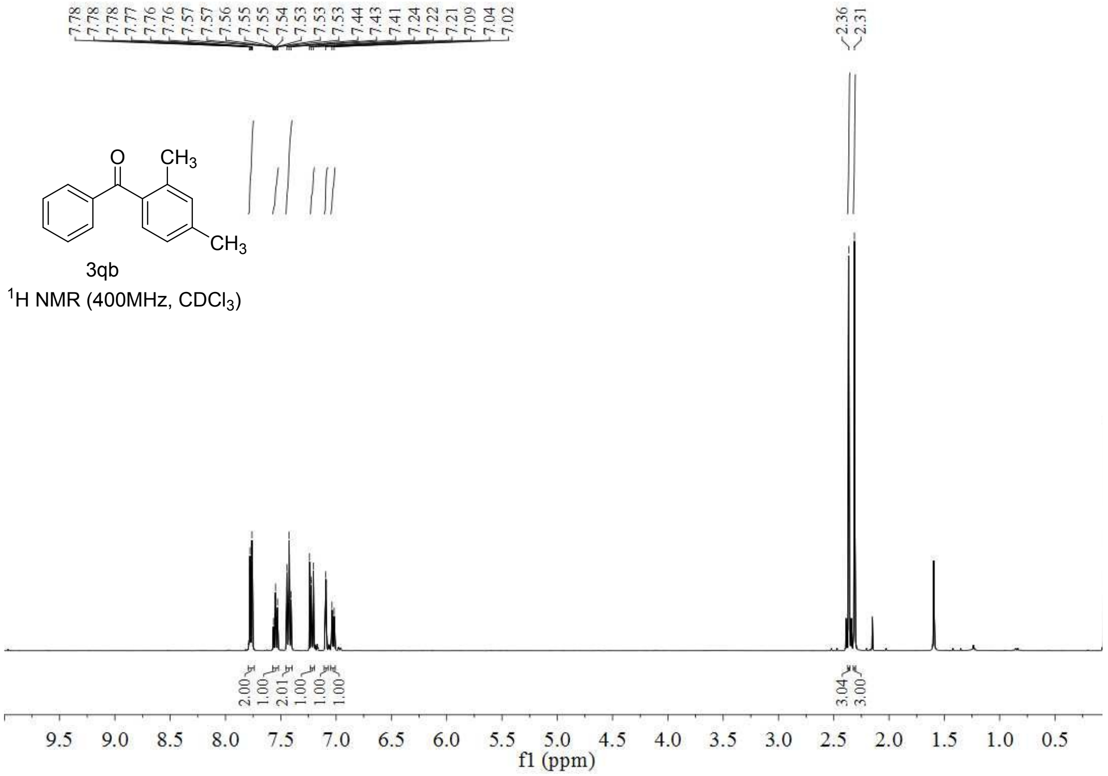


3ua

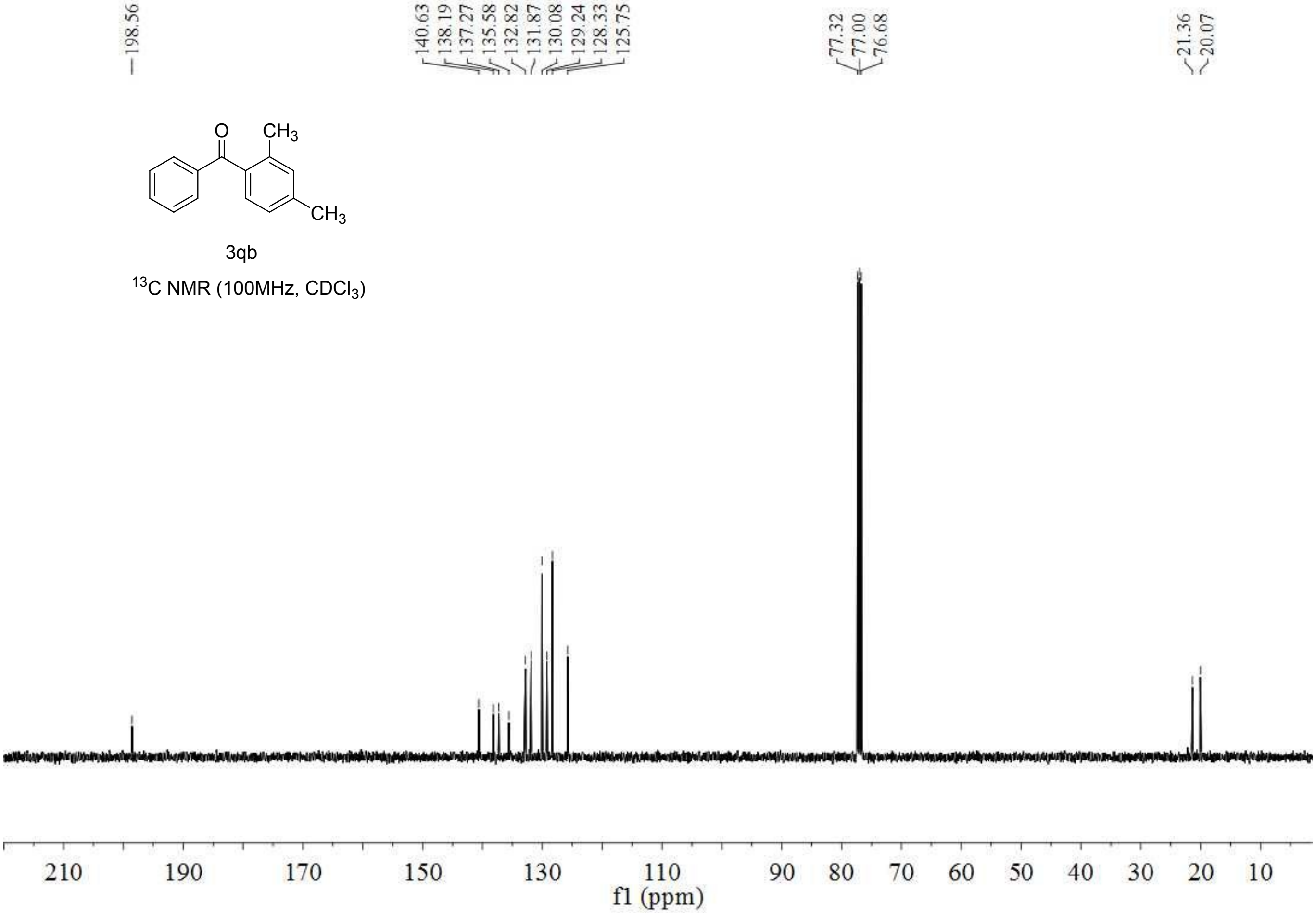
^{13}C NMR (100MHz, $CDCl_3$)


7.72
7.70
7.41
7.39
7.24
7.20
7.18
7.09
7.04
7.02
2.36
2.30
O
CH3
Cl
CH3
3ab
¹H NMR (400MHz, CDCl3)
2.00
1.99
1.01
0.99
1.02
3.00
3.02
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
f1 (ppm)

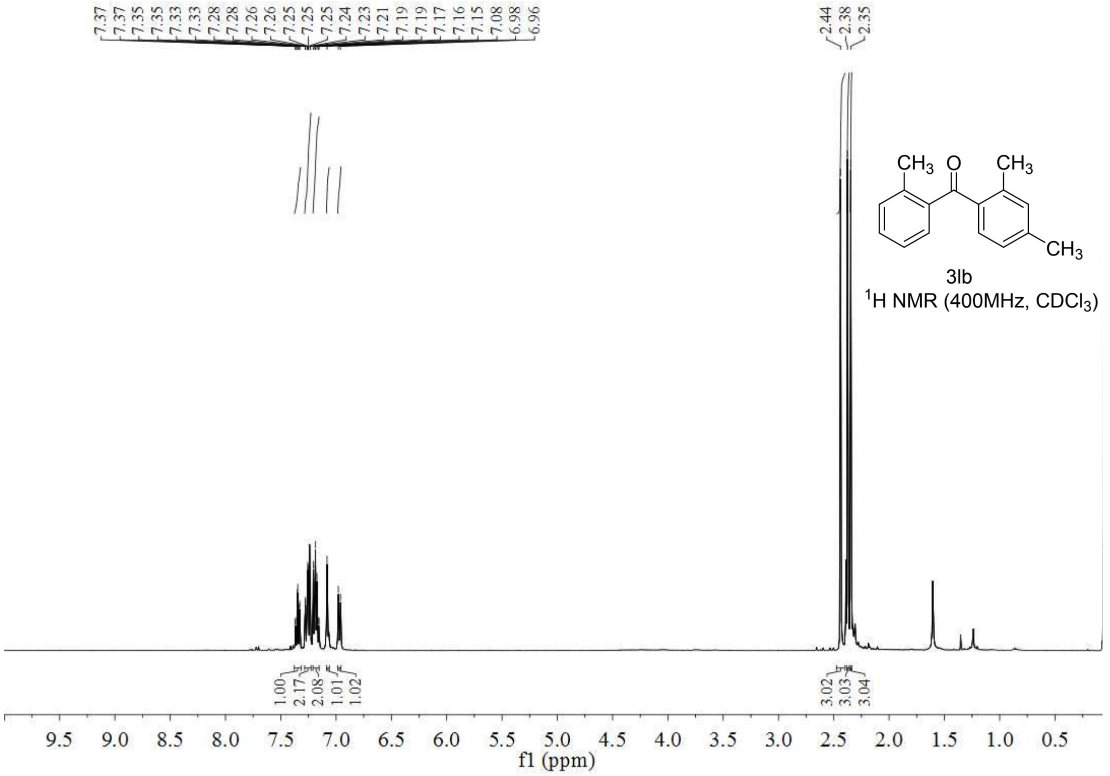

197.22
140.95
139.30
137.31
136.53
135.07
132.00
131.44
129.14
128.67
125.86
77.32
77.00
76.68
21.36
20.05
O
CH3
Cl
CH3
3ab
¹³C NMR (100MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

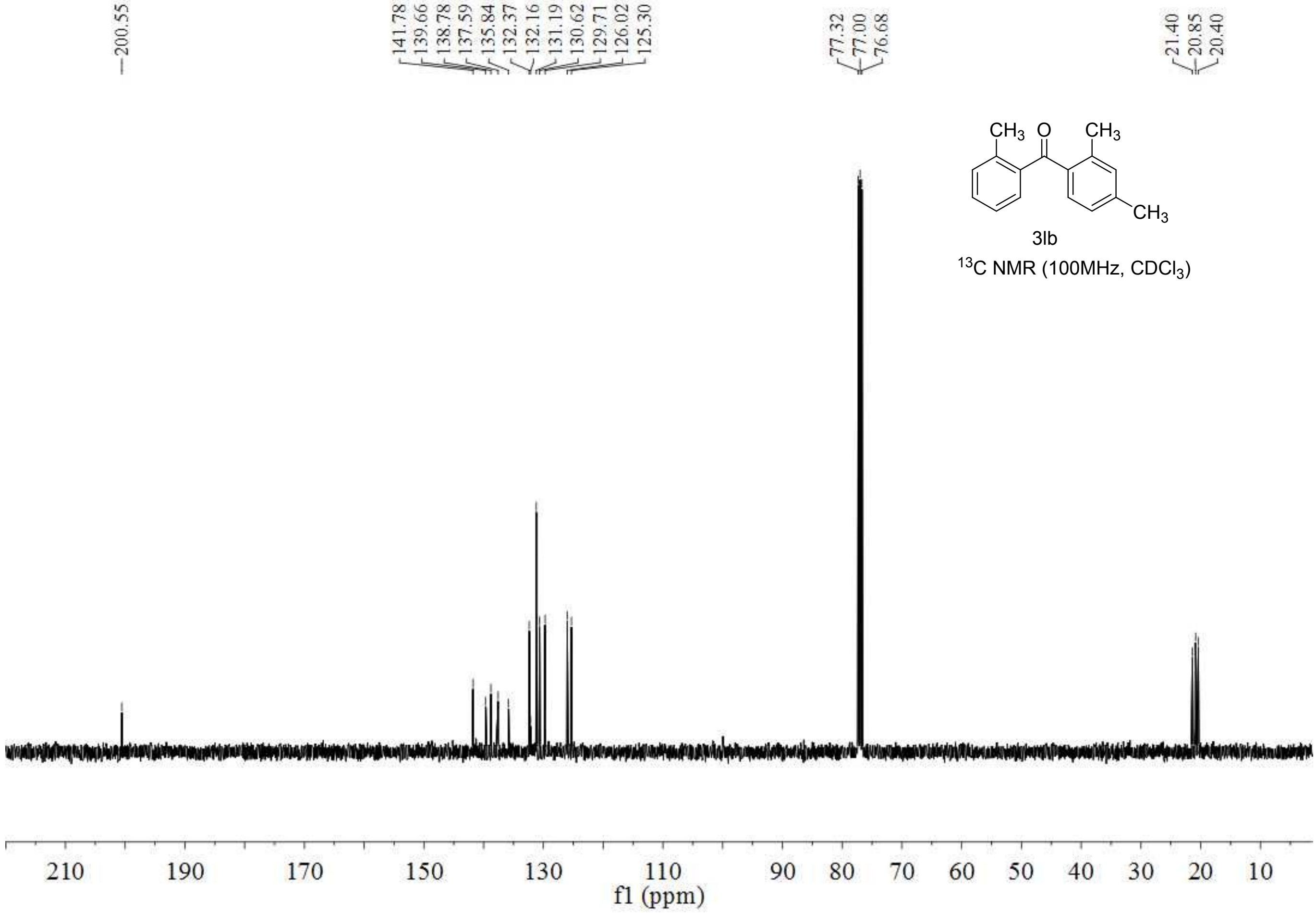

3qb

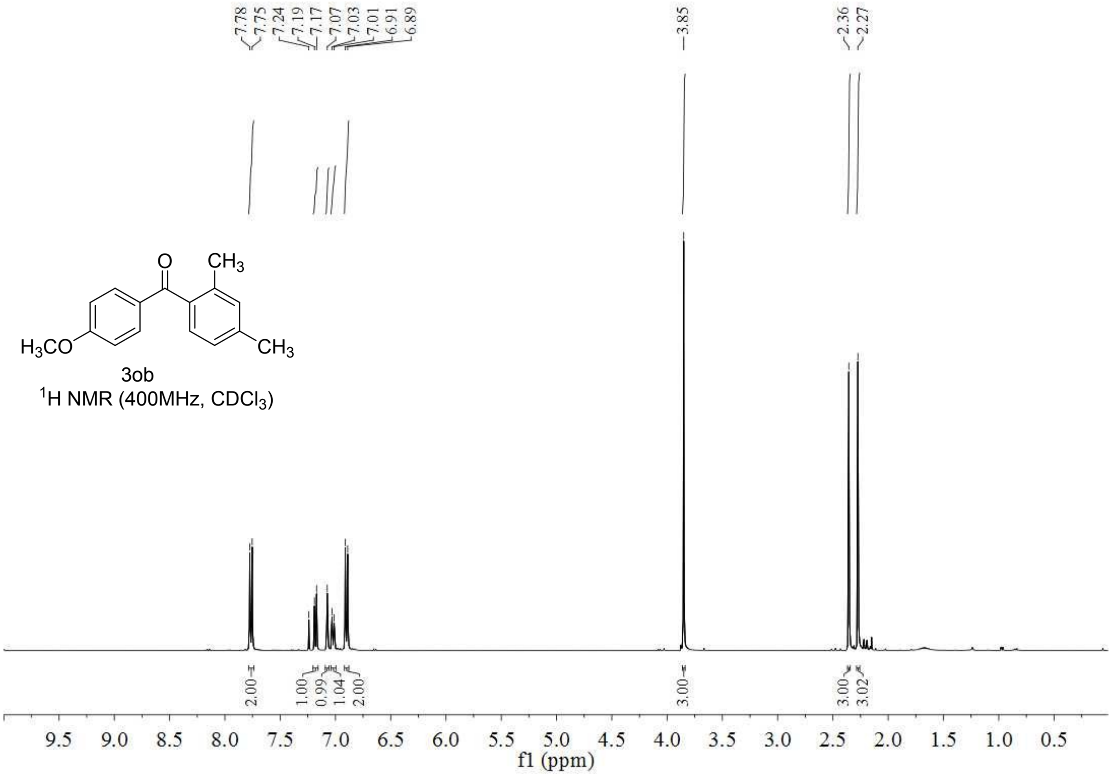
^{1}H NMR (400MHz, $CDCl_3$)


3qb

^{13}C NMR (100MHz, $CDCl_3$)

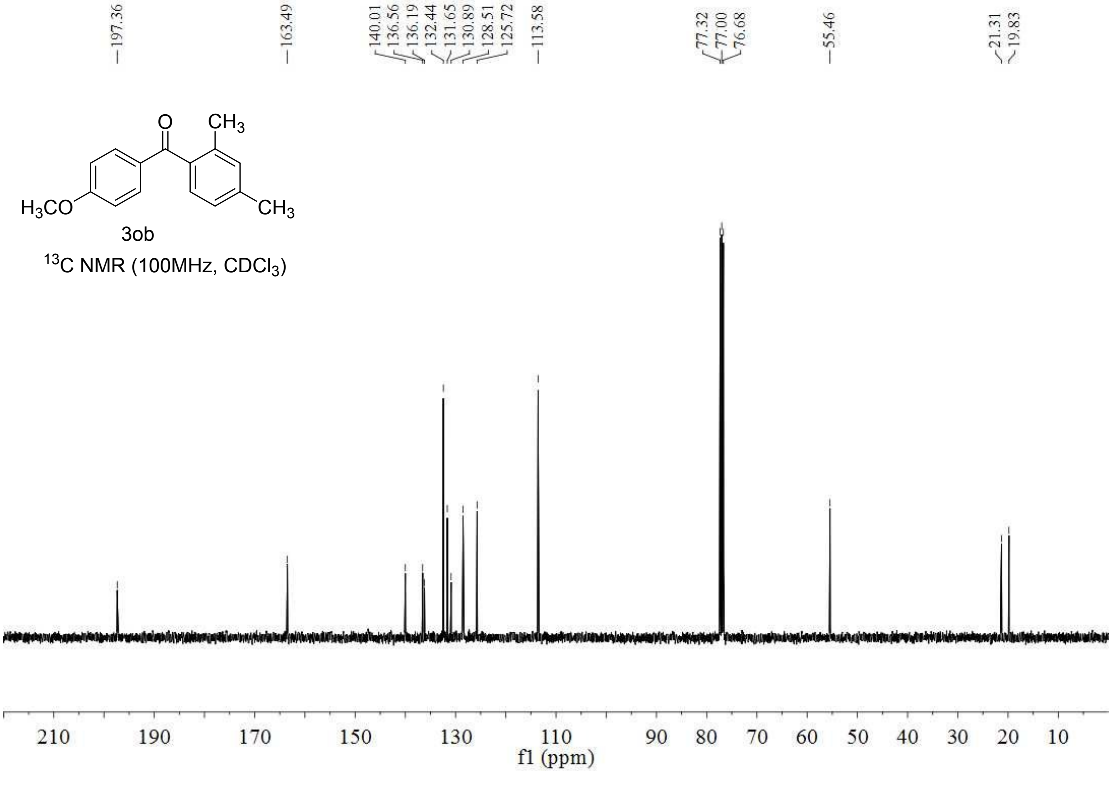

7.37 7.37 7.35 7.35 7.33 7.33 7.28 7.28 7.26 7.26 7.25 7.25 7.25 7.24 7.23 7.21 7.19 7.19 7.17 7.16 7.15 7.08 6.98 6.96
2.44 2.38 2.35
CH3
O
CH3
CH3
3lb
^{1}H NMR (400MHz, CDCl$_3$)
1.00 2.17 2.08 1.01 1.02
3.02 3.03 3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


200.55
141.78 139.66 138.78 137.59 135.84 132.37 132.16 131.19 130.62 129.71 126.02 125.30
77.32 77.00 76.68
21.40 20.85 20.40
CH3
O
CH3
CH3
3lb
^{13}C NMR (100MHz, CDCl$_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)



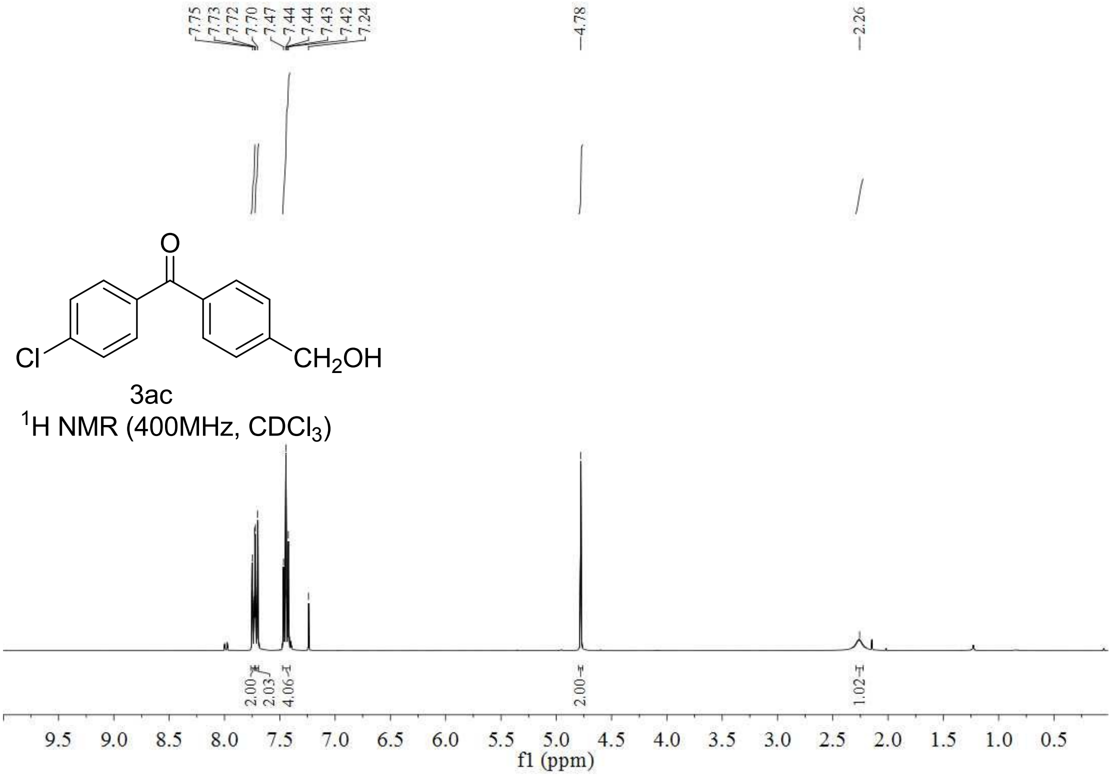
3ob

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



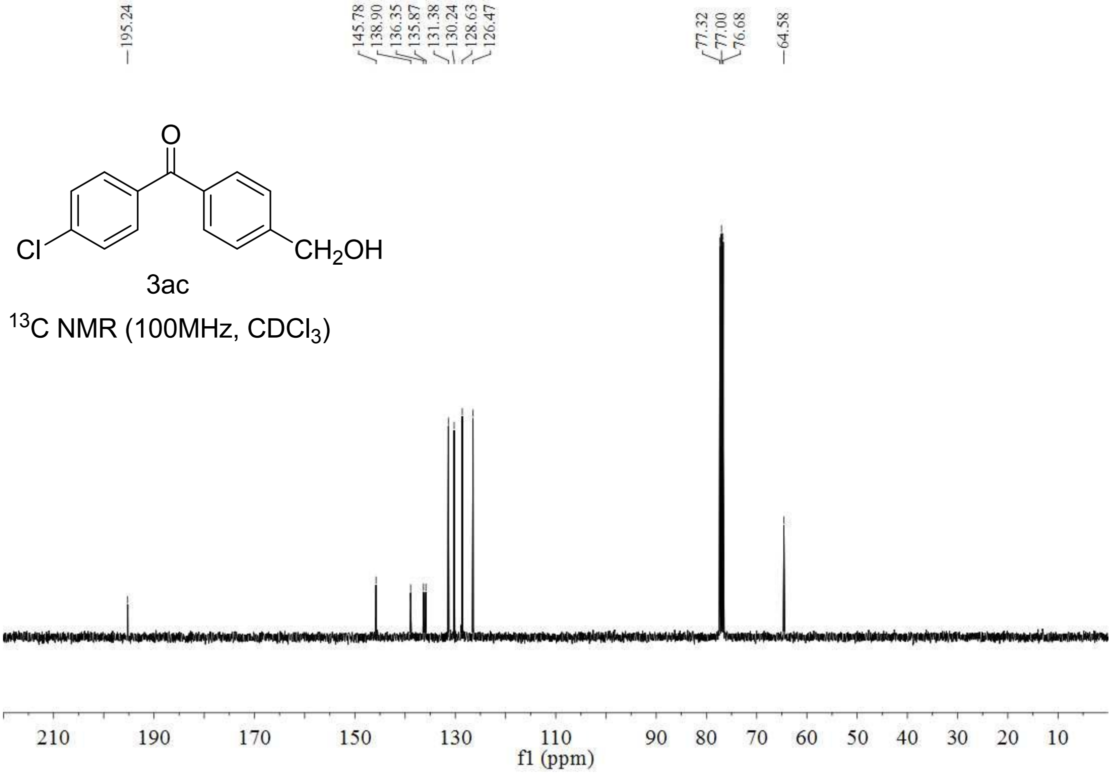
3ob

^{13}C NMR (100MHz, $CDCl_3$)



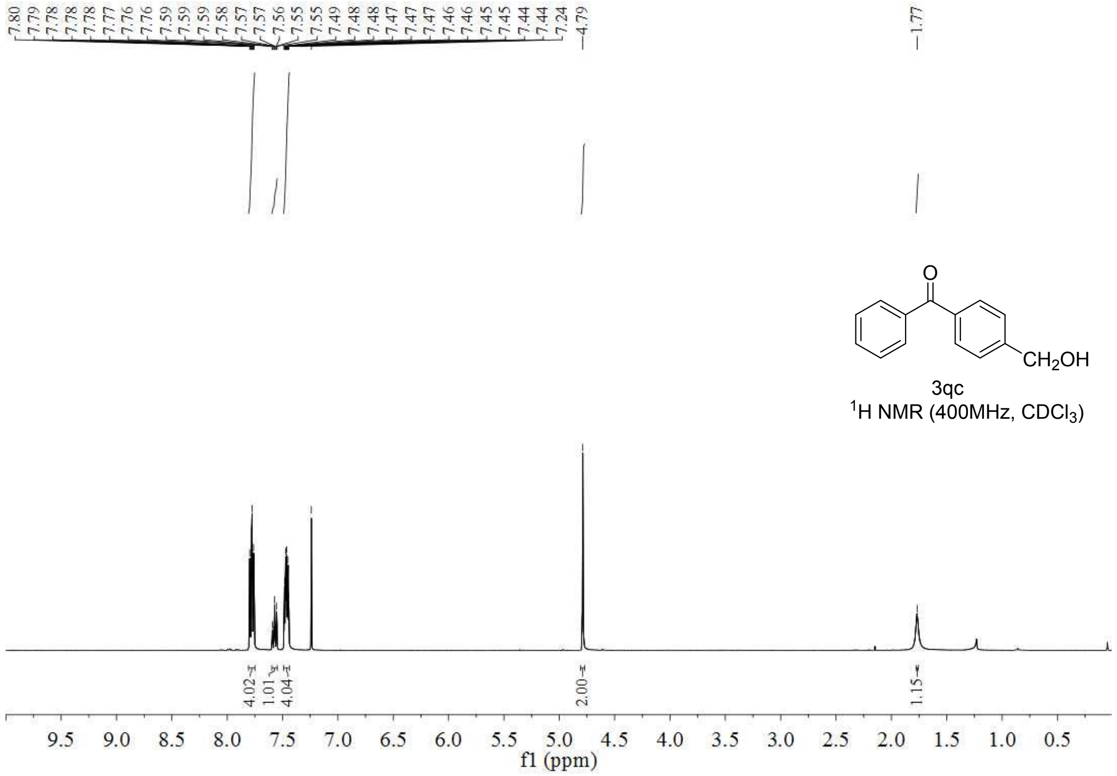
3ac

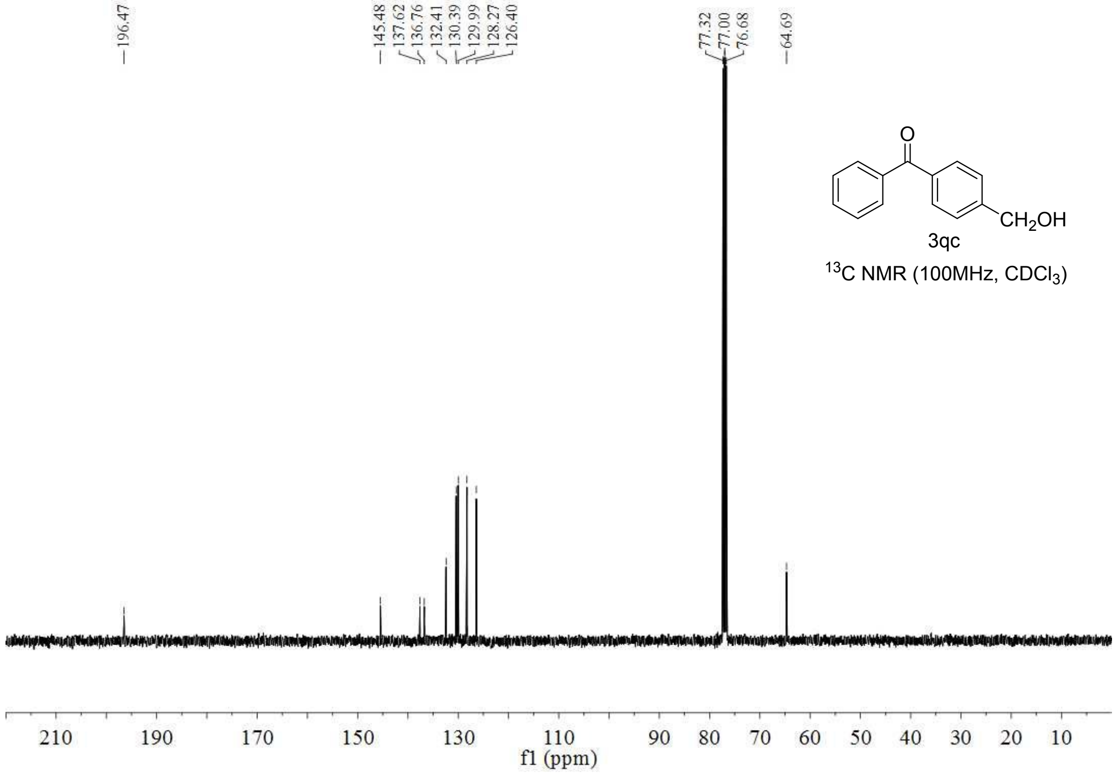
^{1}H NMR (400MHz, $CDCl_3$)

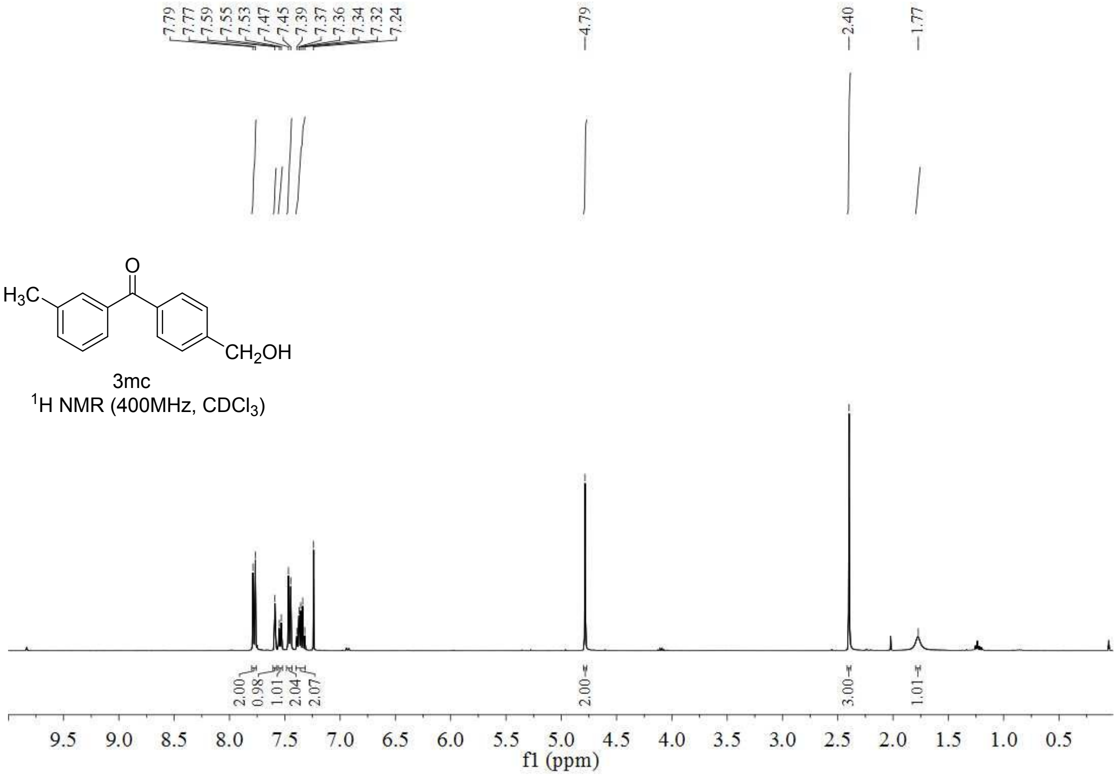


3ac

^{13}C NMR (100MHz, $CDCl_3$)

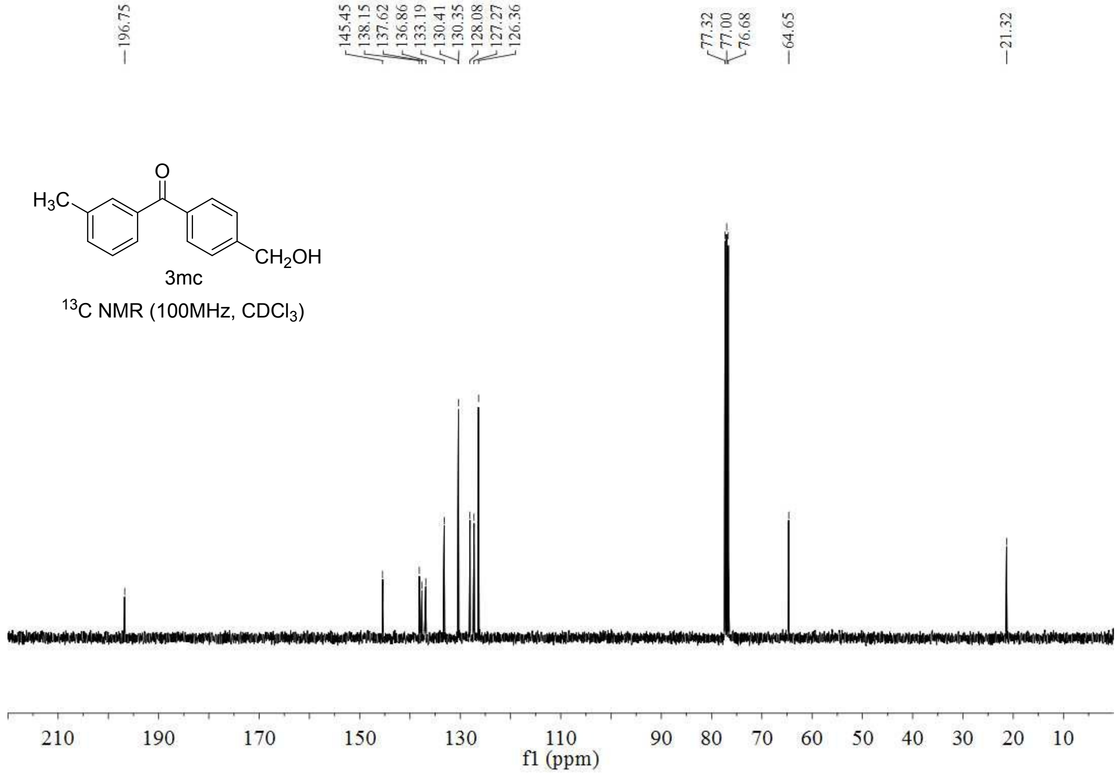

7.80
7.79
7.78
7.78
7.78
7.77
7.76
7.76
7.59
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.24
4.79
1.77
O
CH2OH
3qc
1H NMR (400MHz, CDCl3)
4.02
1.01
4.04
2.00
1.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


196.47
145.48
137.62
136.76
132.41
130.39
129.99
128.27
126.40
77.32
77.00
76.68
64.69
O
CH2OH
3qc
13C NMR (100MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)



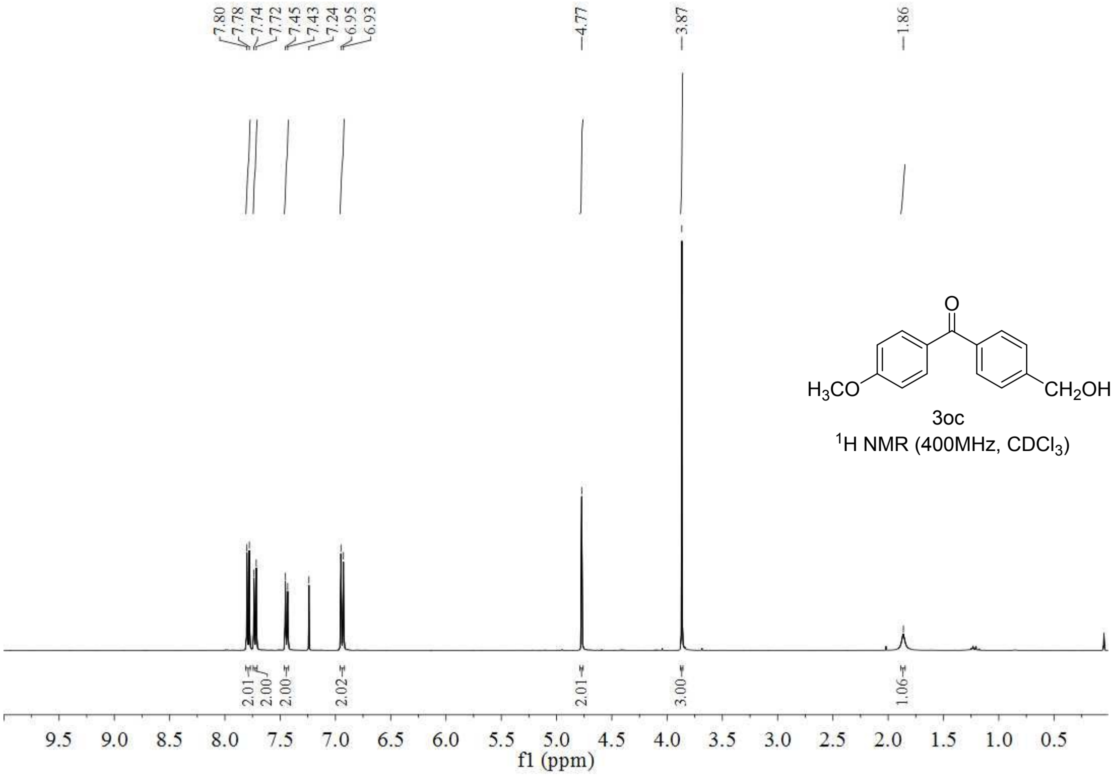
3mc

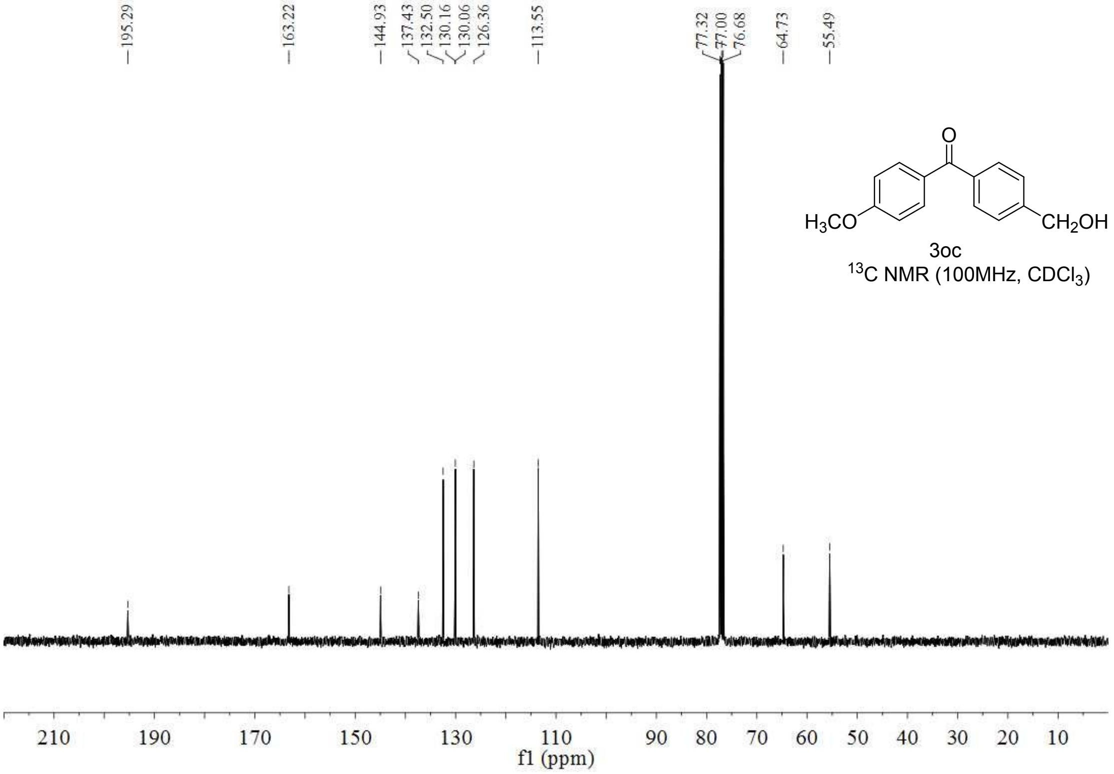
^{1}H NMR (400MHz, CDCl$_3$)

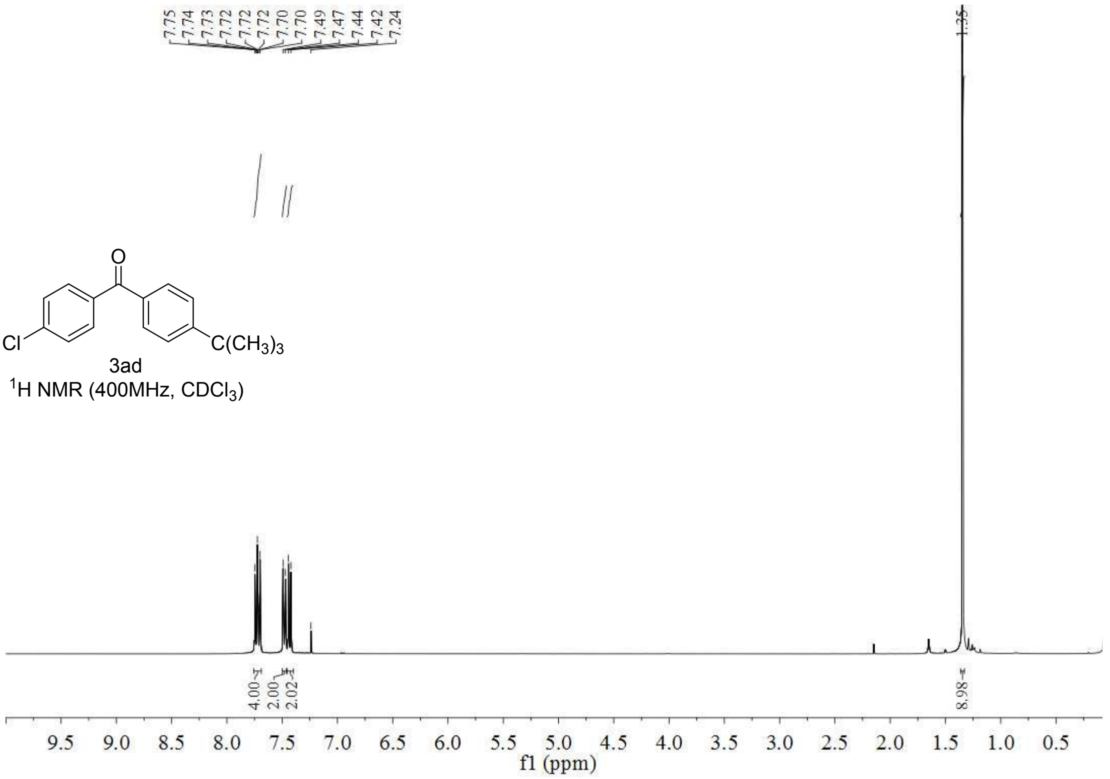


3mc

^{13}C NMR (100MHz, CDCl$_3$)

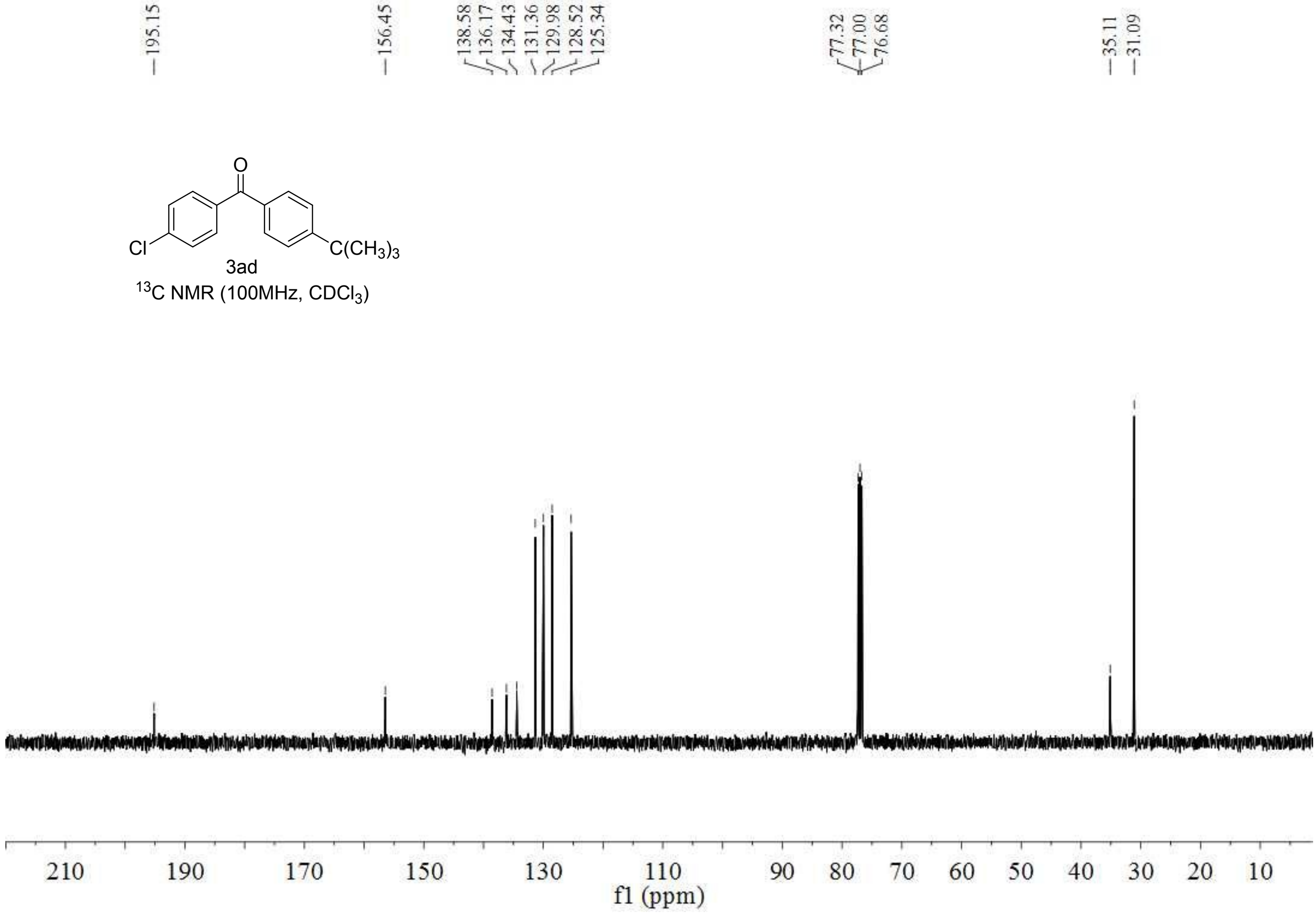

7.80
7.78
7.74
7.72
7.45
7.43
7.24
6.95
6.93
4.77
3.87
1.86
O
H_3CO
CH_2OH
3oc
^1H NMR (400MHz, $CDCl_3$)
2.01
2.00
2.00
2.02
2.01
3.00
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


195.29
163.22
144.93
137.43
132.50
130.16
130.06
126.36
113.55
77.32
77.00
76.68
64.73
55.49
O
H_3CO
CH_2OH
3oc
^{13}C NMR (100MHz, $CDCl_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)



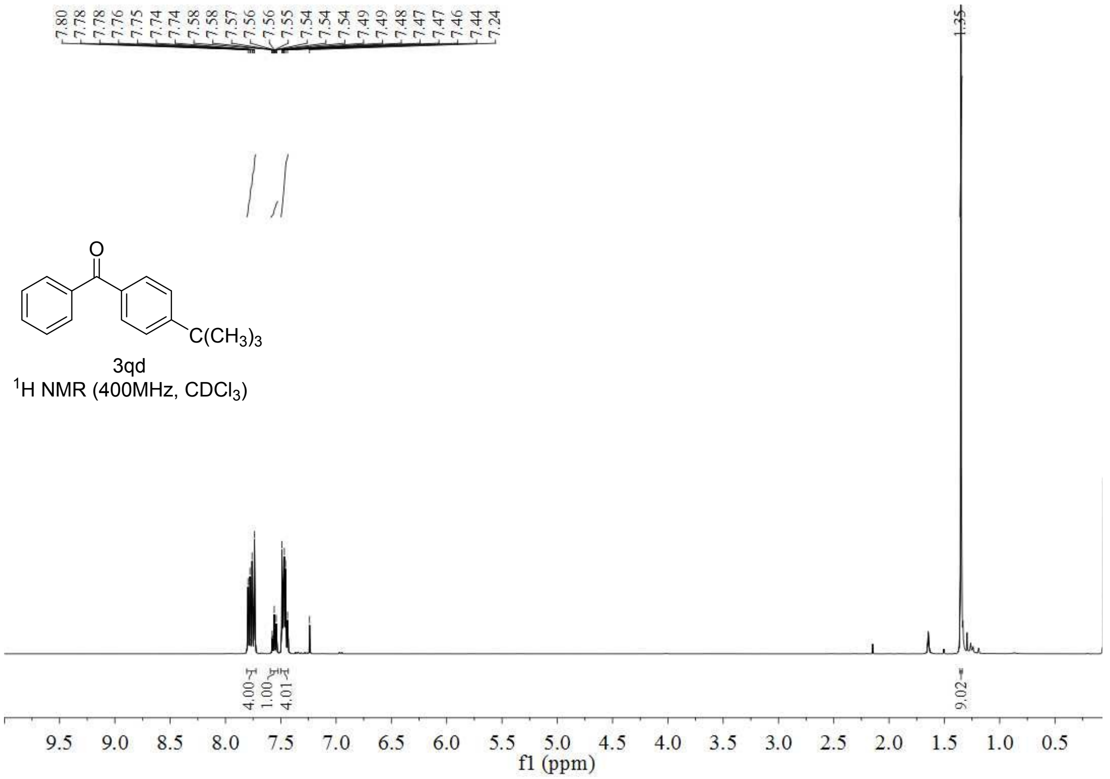
3ad

^{1}H NMR (400MHz, CDCl$_3$)



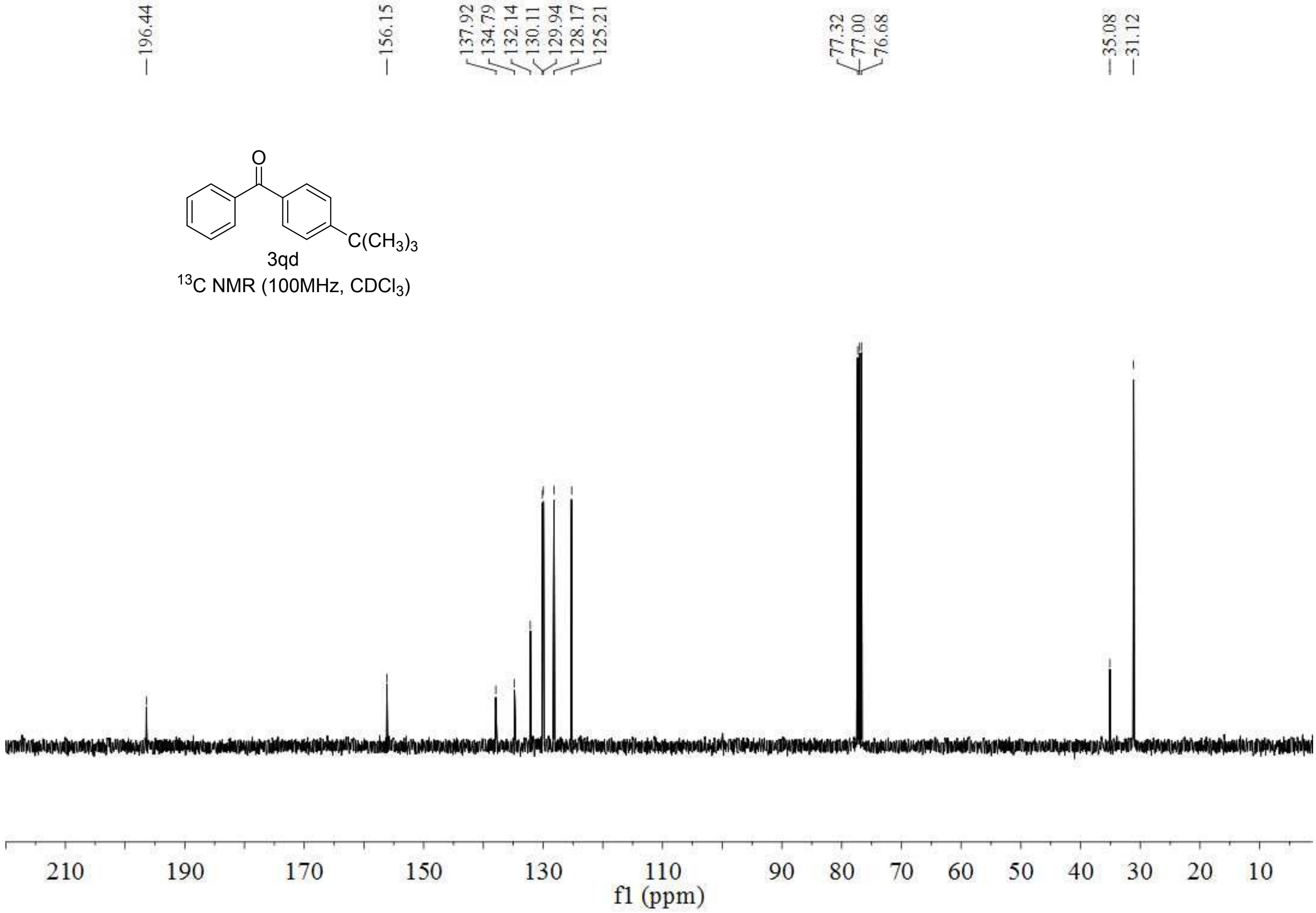
3ad

^{13}C NMR (100MHz, CDCl$_3$)



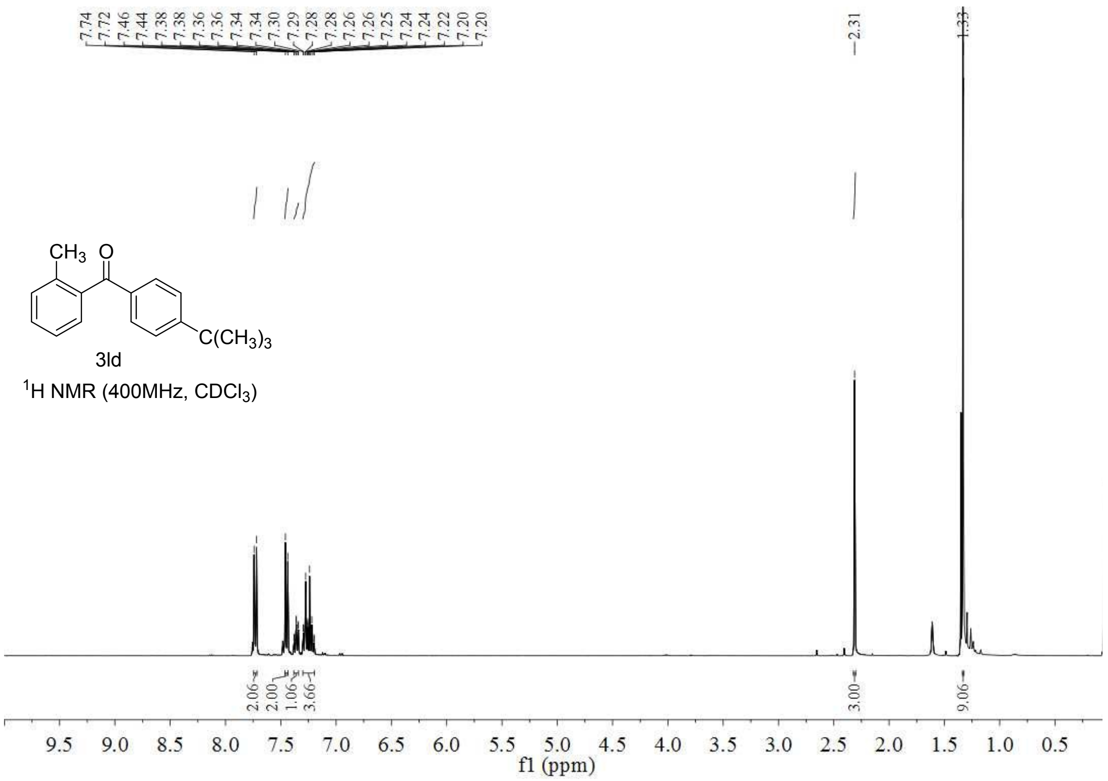
3qd

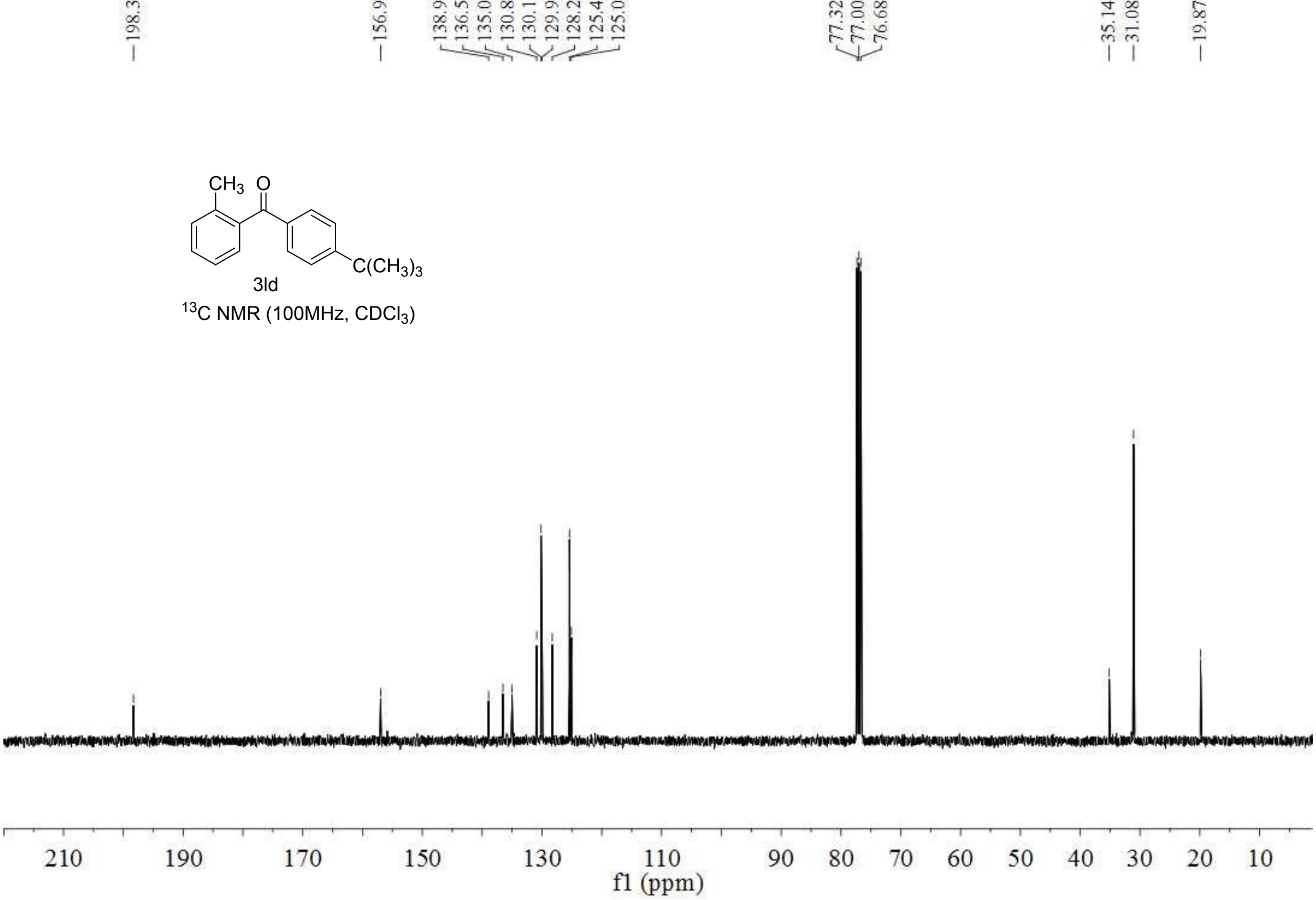
^{1}H NMR (400MHz, CDCl$_3$)

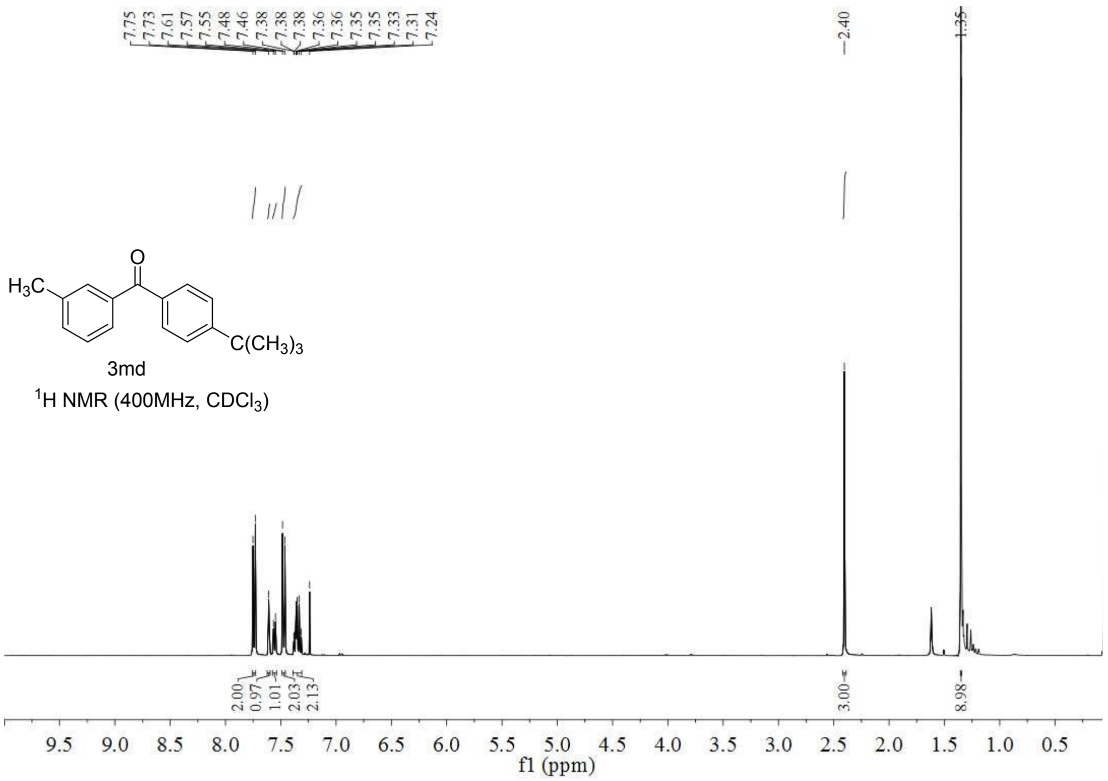


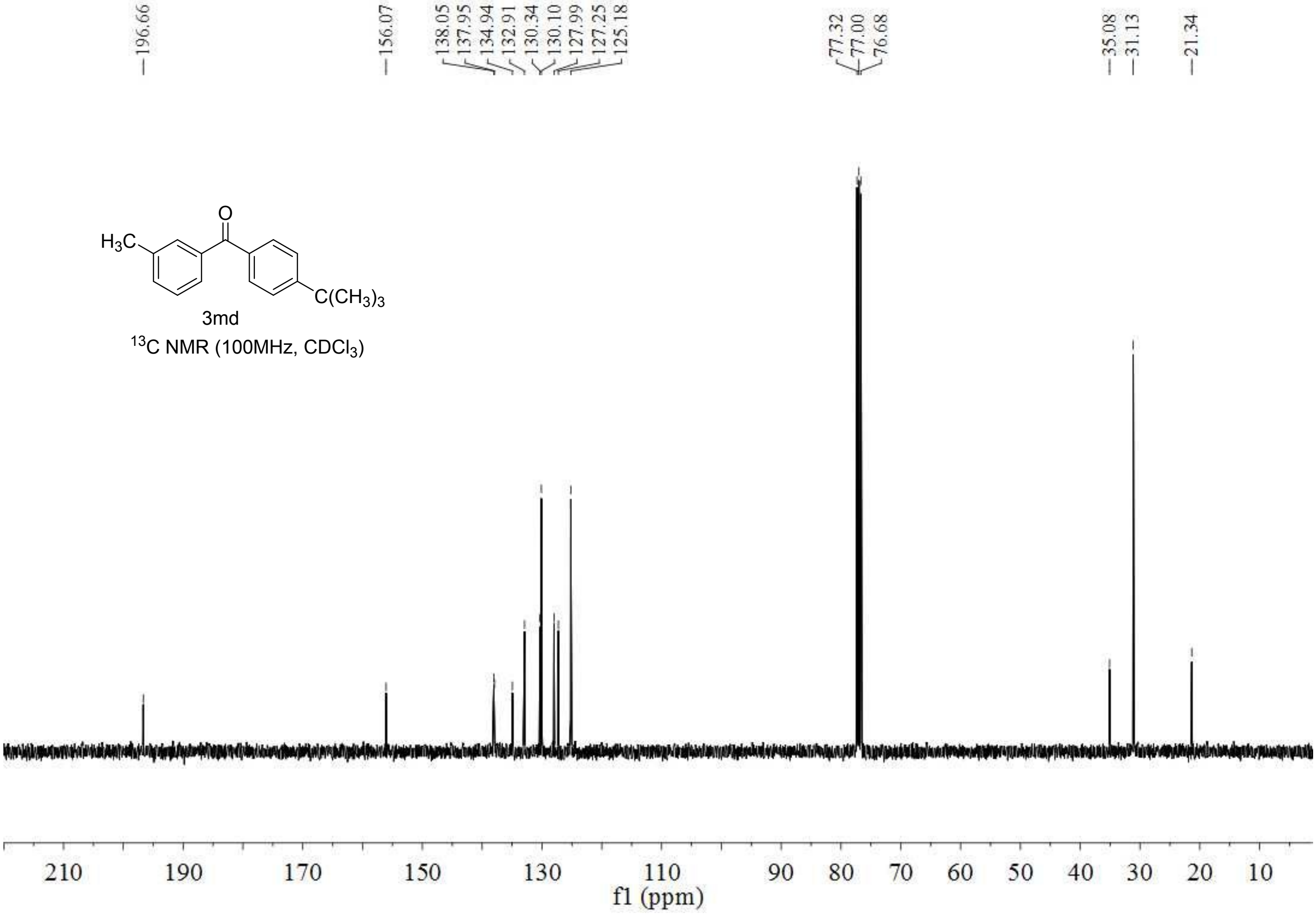
3qd

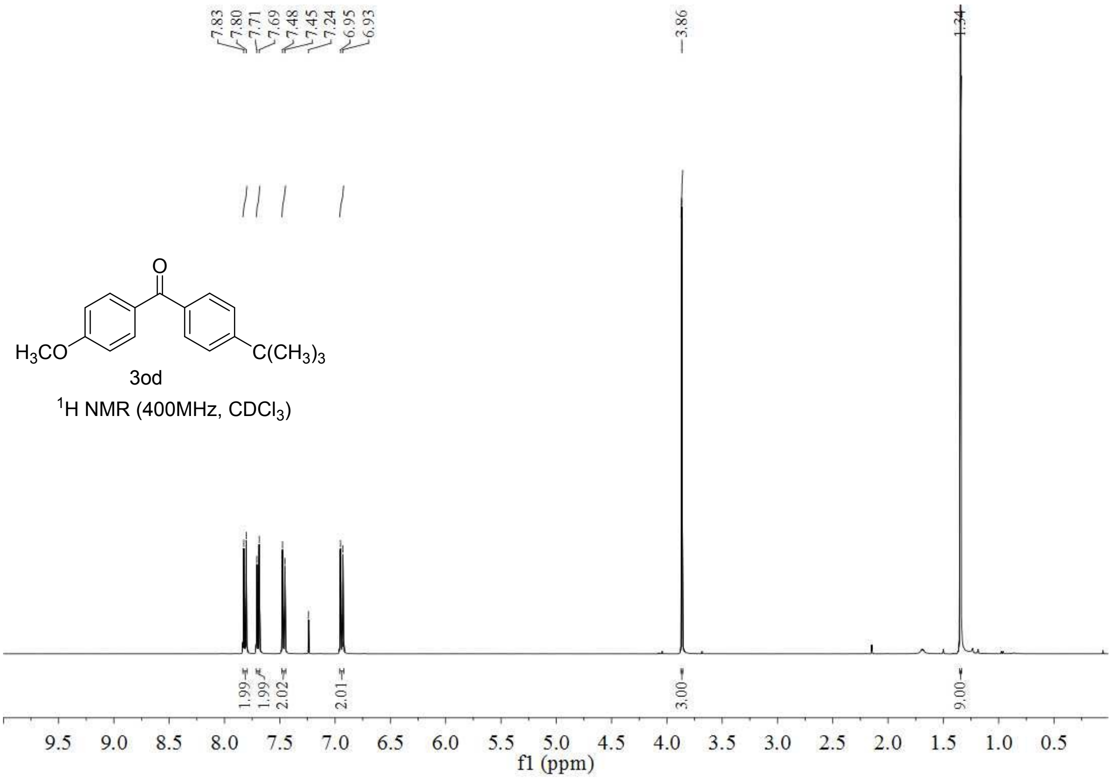
^{13}C NMR (100MHz, CDCl$_3$)


7.74
7.72
7.46
7.44
7.38
7.38
7.36
7.36
7.34
7.34
7.30
7.29
7.28
7.28
7.26
7.26
7.25
7.24
7.24
7.22
7.20
7.20
2.31
1.33
CH3
O
C(CH3)3
3ld
1H NMR (400MHz, CDCl3)
2.06
2.00
1.06
3.66
3.00
9.06
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
f1 (ppm)


198.30
156.97
138.93
136.52
135.00
130.87
130.15
129.96
128.28
125.40
125.08
77.32
77.00
76.68
35.14
31.08
19.87
CH3
O
C(CH3)3
3ld
13C NMR (100MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

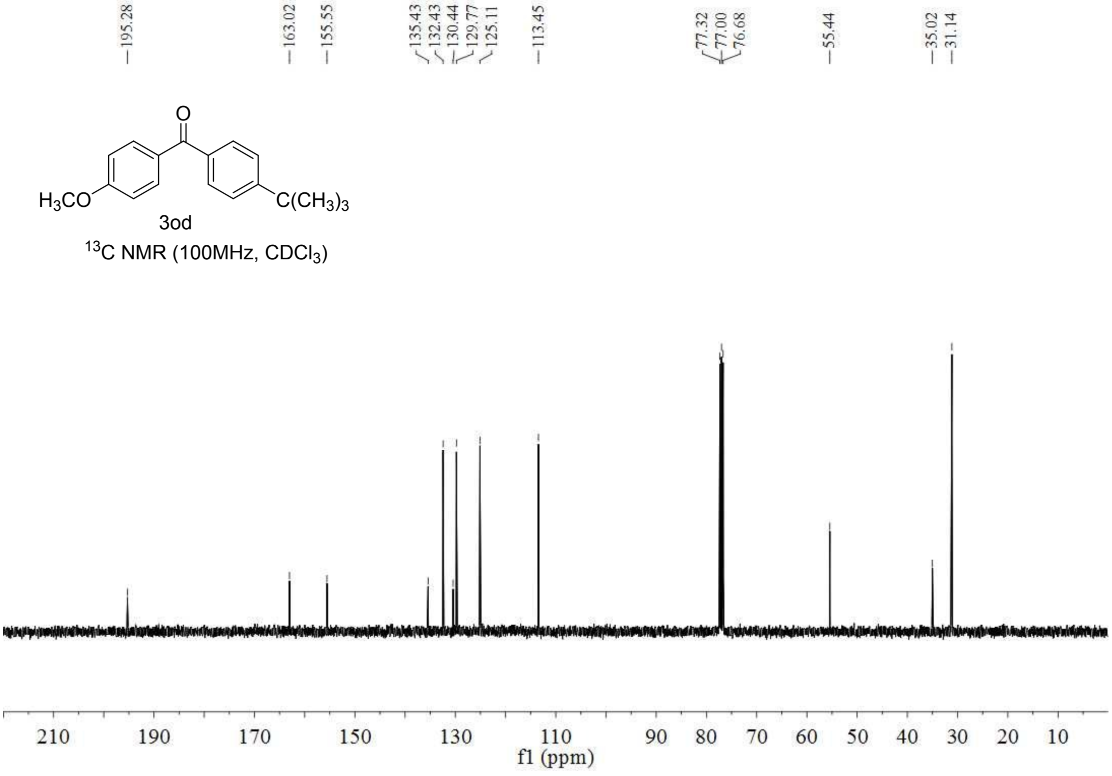

7.75
7.73
7.61
7.57
7.55
7.48
7.46
7.38
7.38
7.38
7.36
7.36
7.35
7.35
7.33
7.31
7.24
2.40
1.35
O
H_3C
$C(CH_3)_3$
3md
^1H NMR (400MHz, $CDCl_3$)
2.00
0.97
1.01
2.03
2.13
3.00
8.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


196.66
156.07
138.05
137.95
134.94
132.91
130.34
130.10
127.99
127.25
125.18
77.32
77.00
76.68
35.08
31.13
21.34
O
H_3C
$C(CH_3)_3$
3md
^{13}C NMR (100MHz, $CDCl_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)



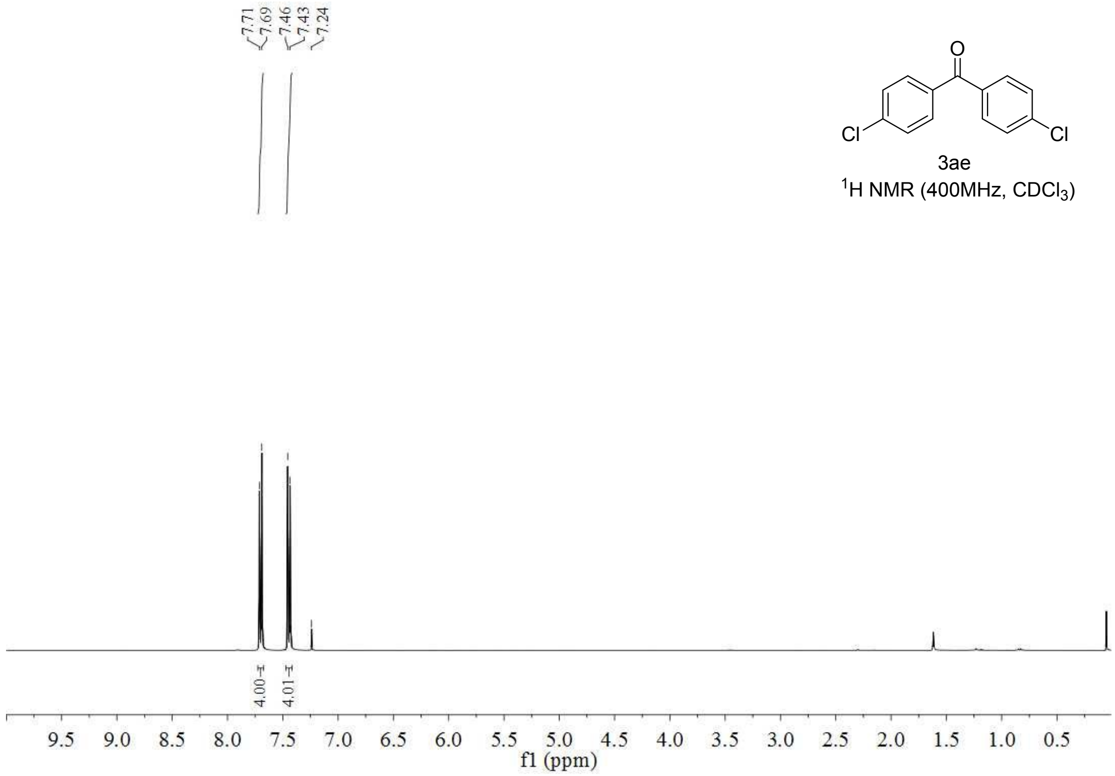
3od

^{1}H NMR (400MHz, CDCl$_3$)



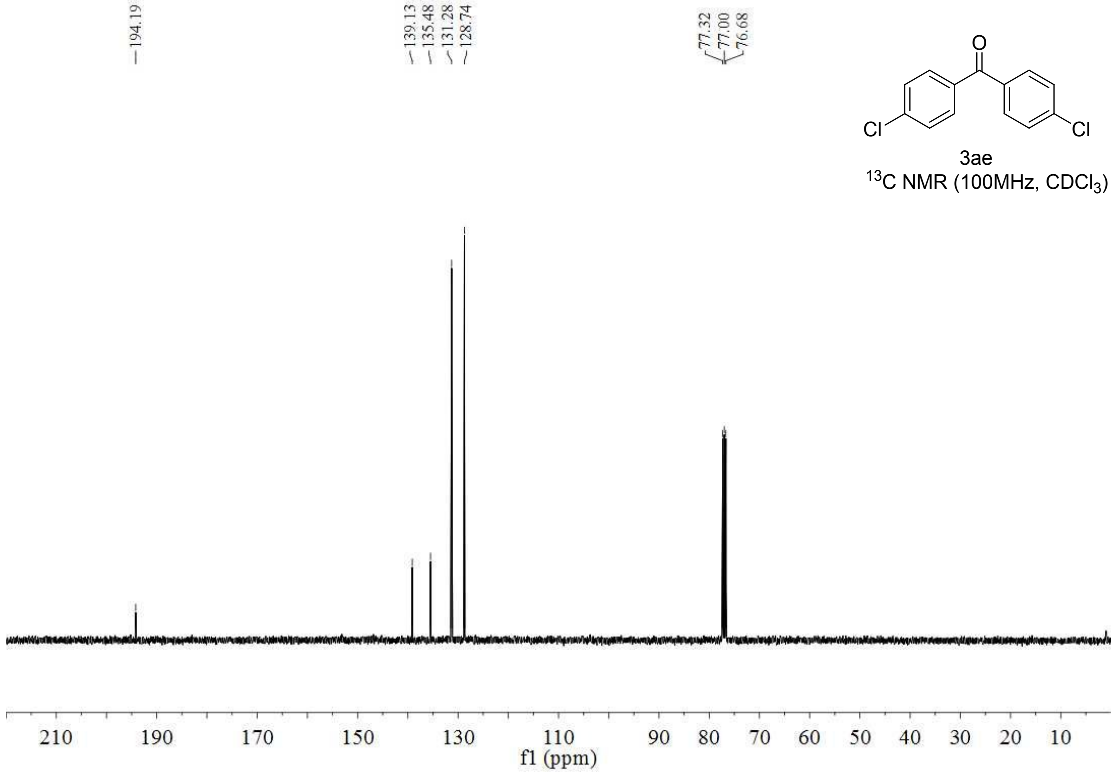
3od

^{13}C NMR (100MHz, CDCl$_3$)



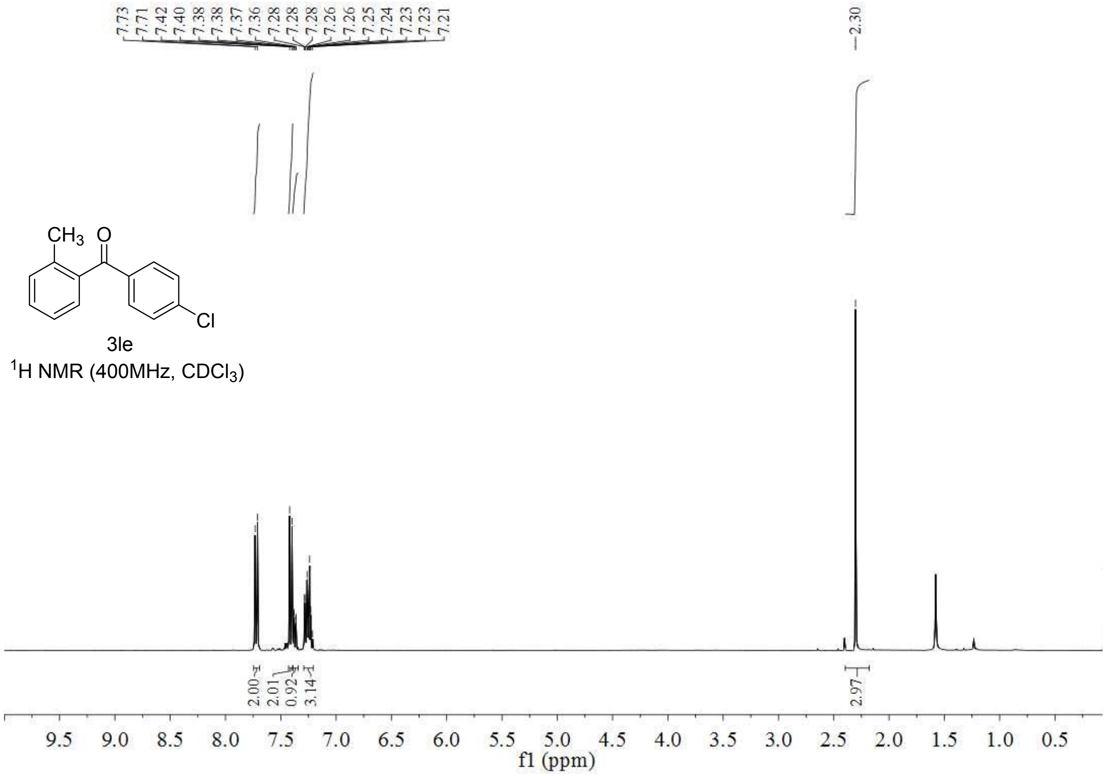
3ae

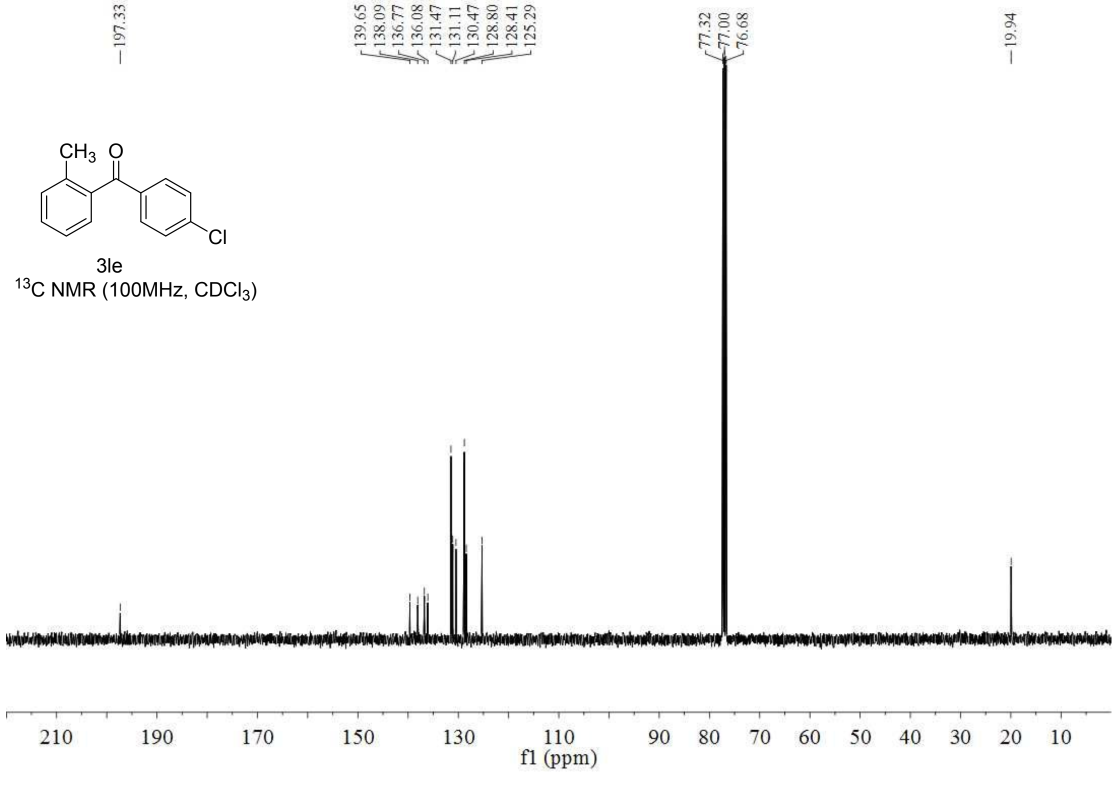
^{1}H NMR (400MHz, $CDCl_3$)

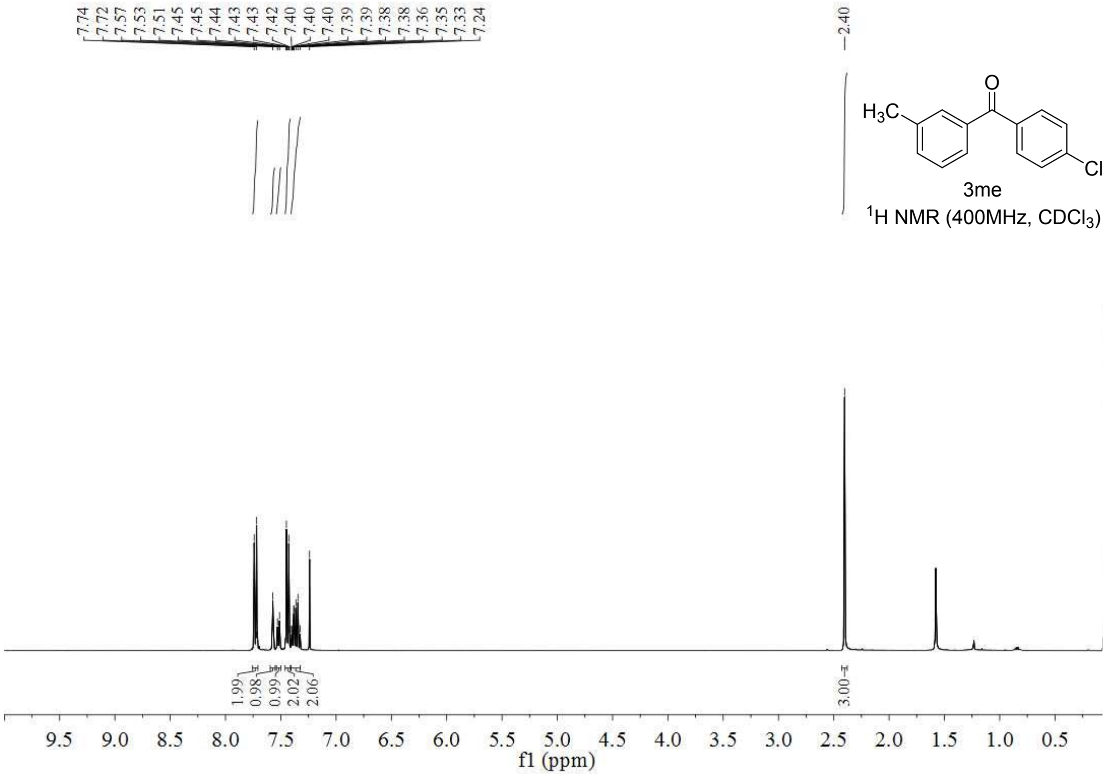


3ae

^{13}C NMR (100MHz, $CDCl_3$)

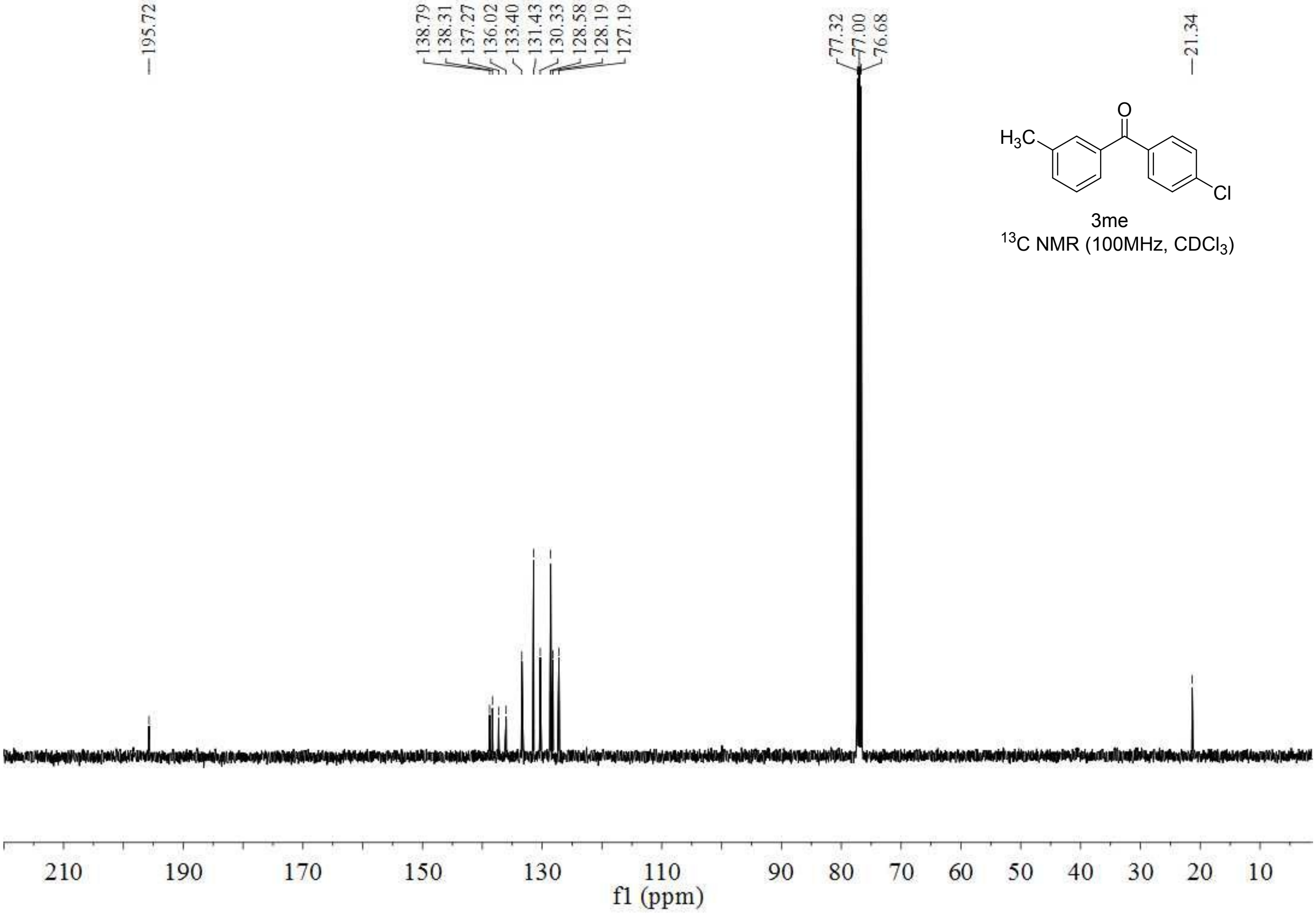

7.73
7.71
7.42
7.40
7.38
7.38
7.37
7.36
7.28
7.28
7.28
7.26
7.26
7.25
7.24
7.23
7.23
7.21
2.30
CH3
O
Cl
3le
^{1}H NMR (400MHz, CDCl$_3$)
2.00
2.01
0.92
3.14
2.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


197.33
139.65
138.09
136.77
136.08
131.47
131.11
130.47
128.80
128.41
125.29
77.32
77.00
76.68
19.94
CH3
O
Cl
3le
^{13}C NMR (100MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)



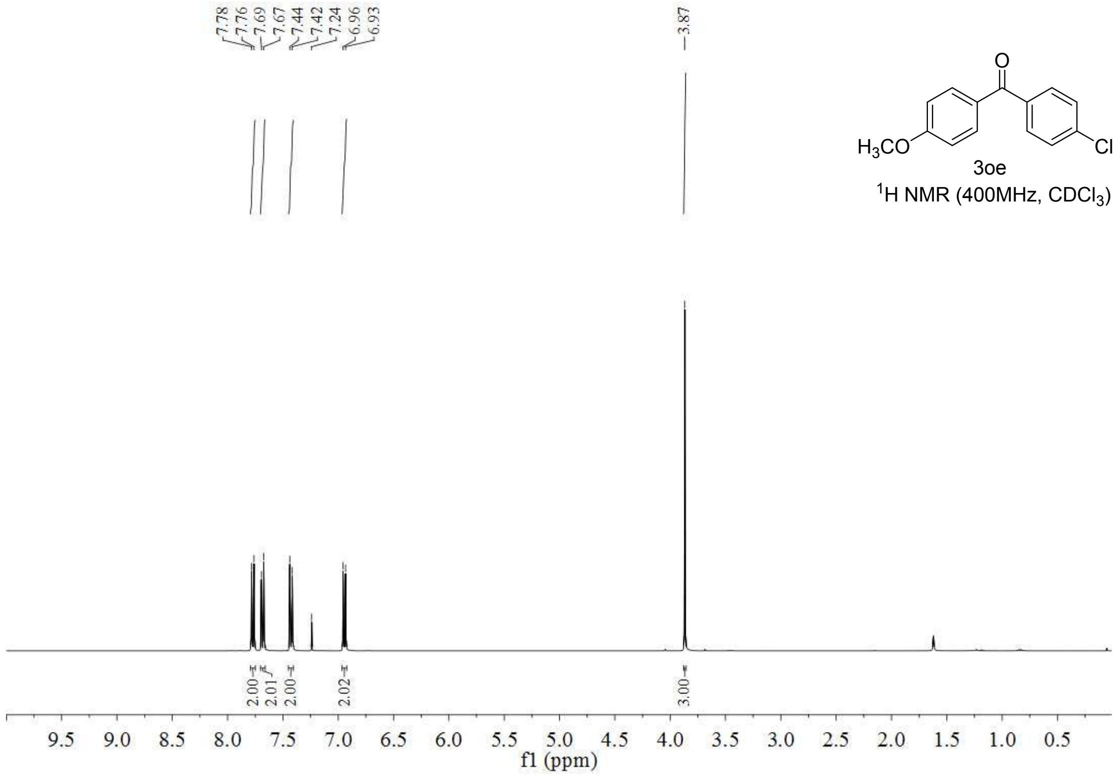
3me

^{1}H NMR (400MHz, CDCl$_3$)



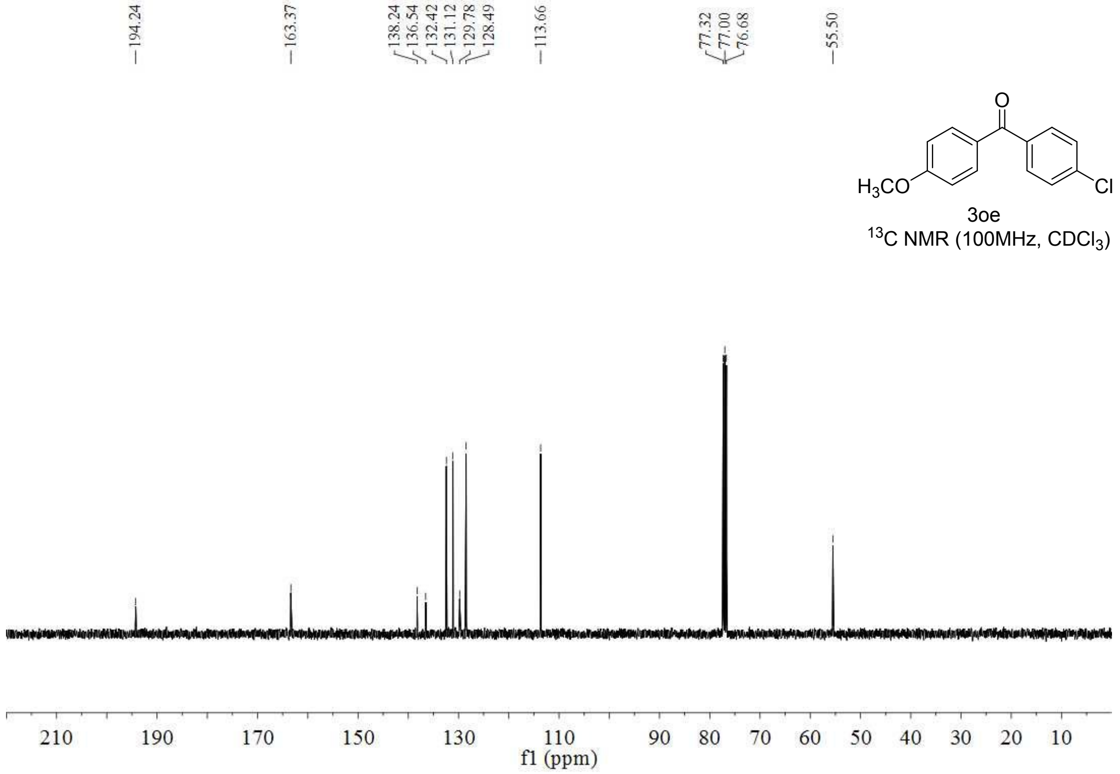
3me

^{13}C NMR (100MHz, CDCl$_3$)



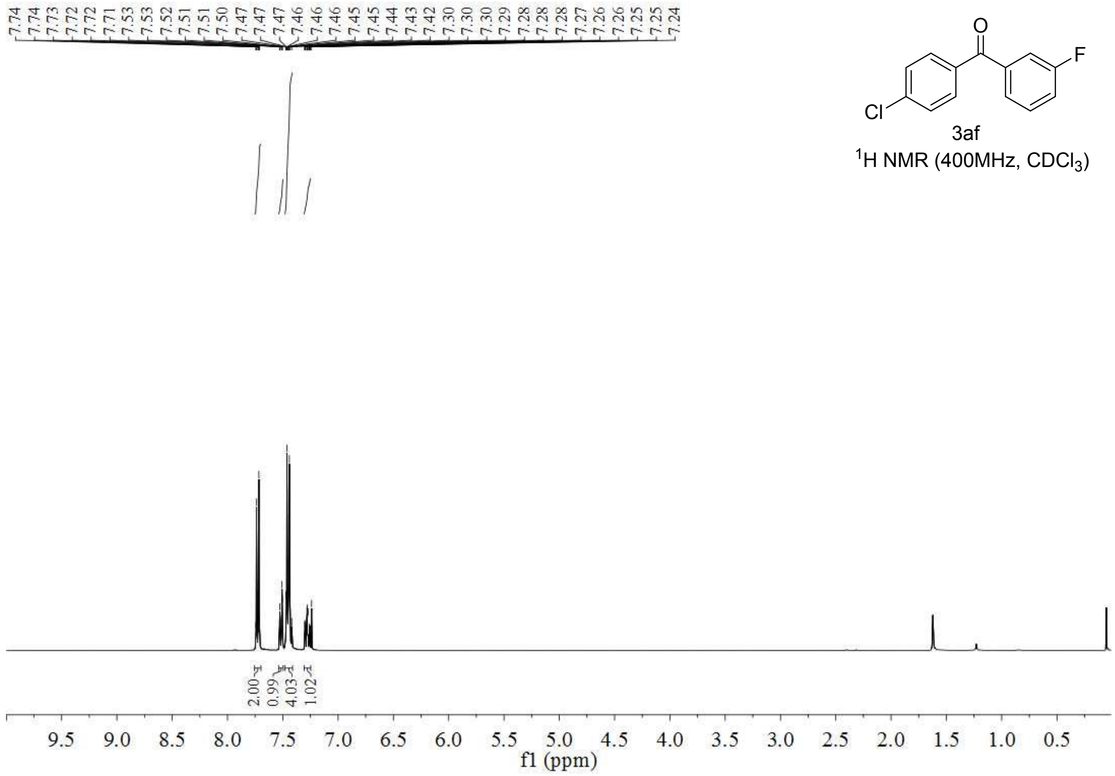
3oe

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



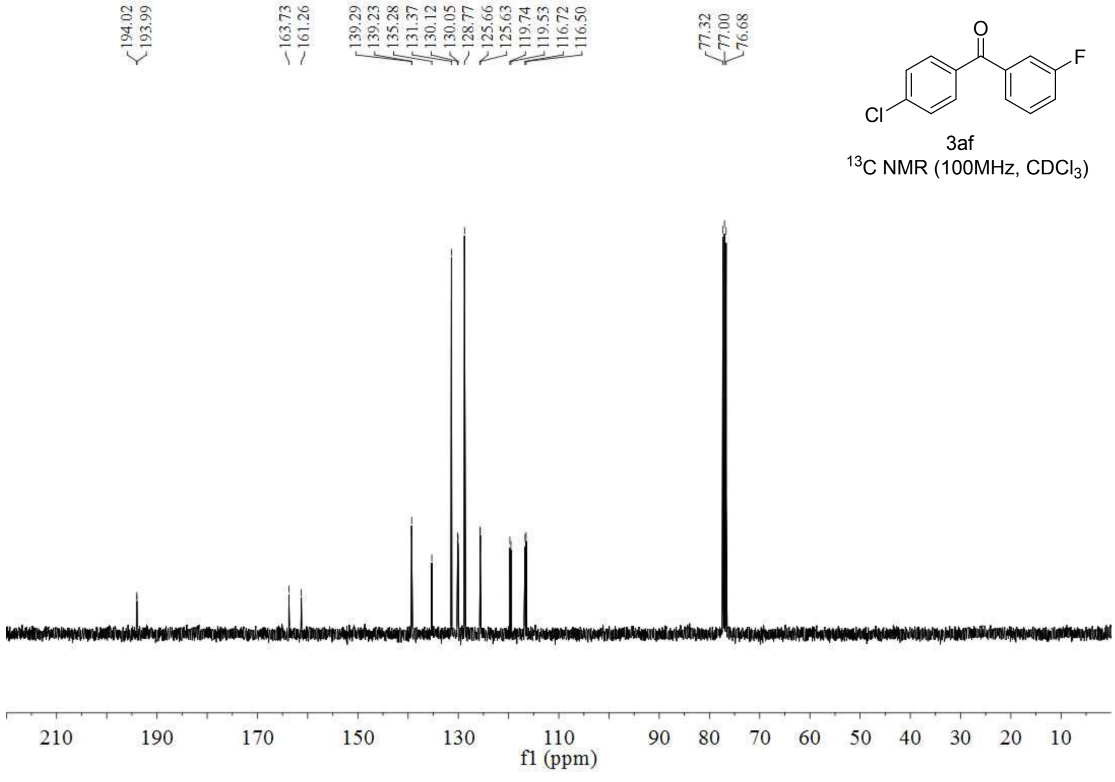
3oe

^{13}C NMR (100MHz, $CDCl_3$)



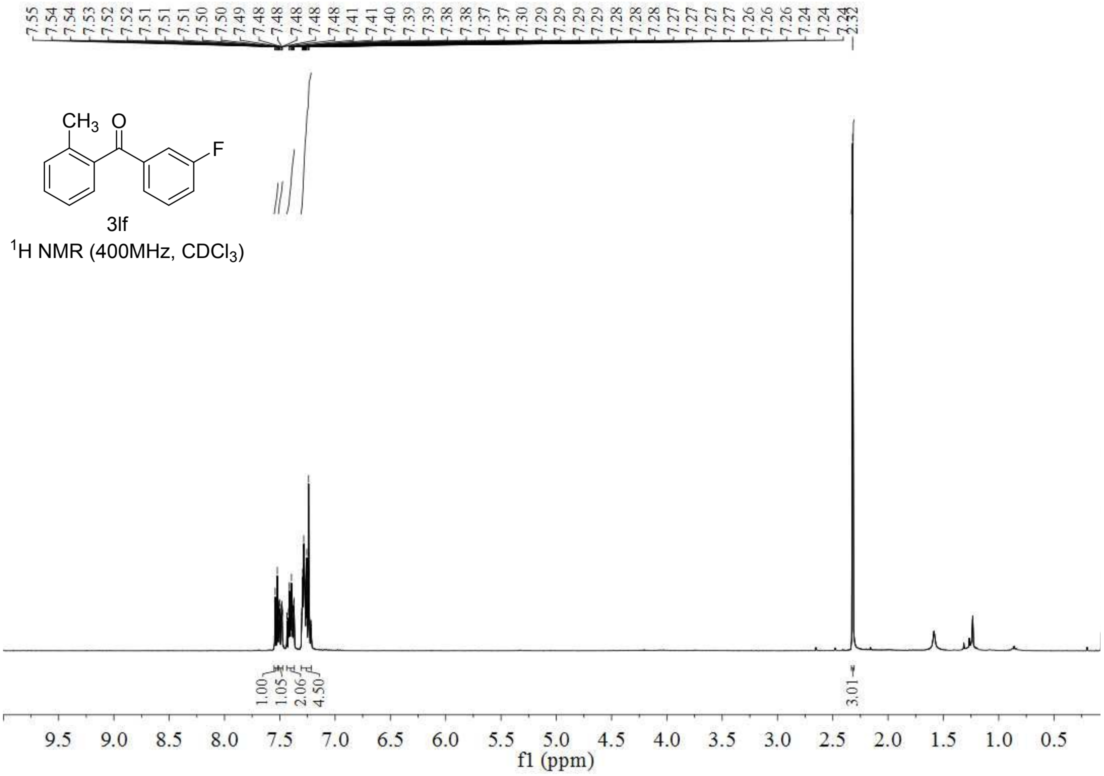
3af

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



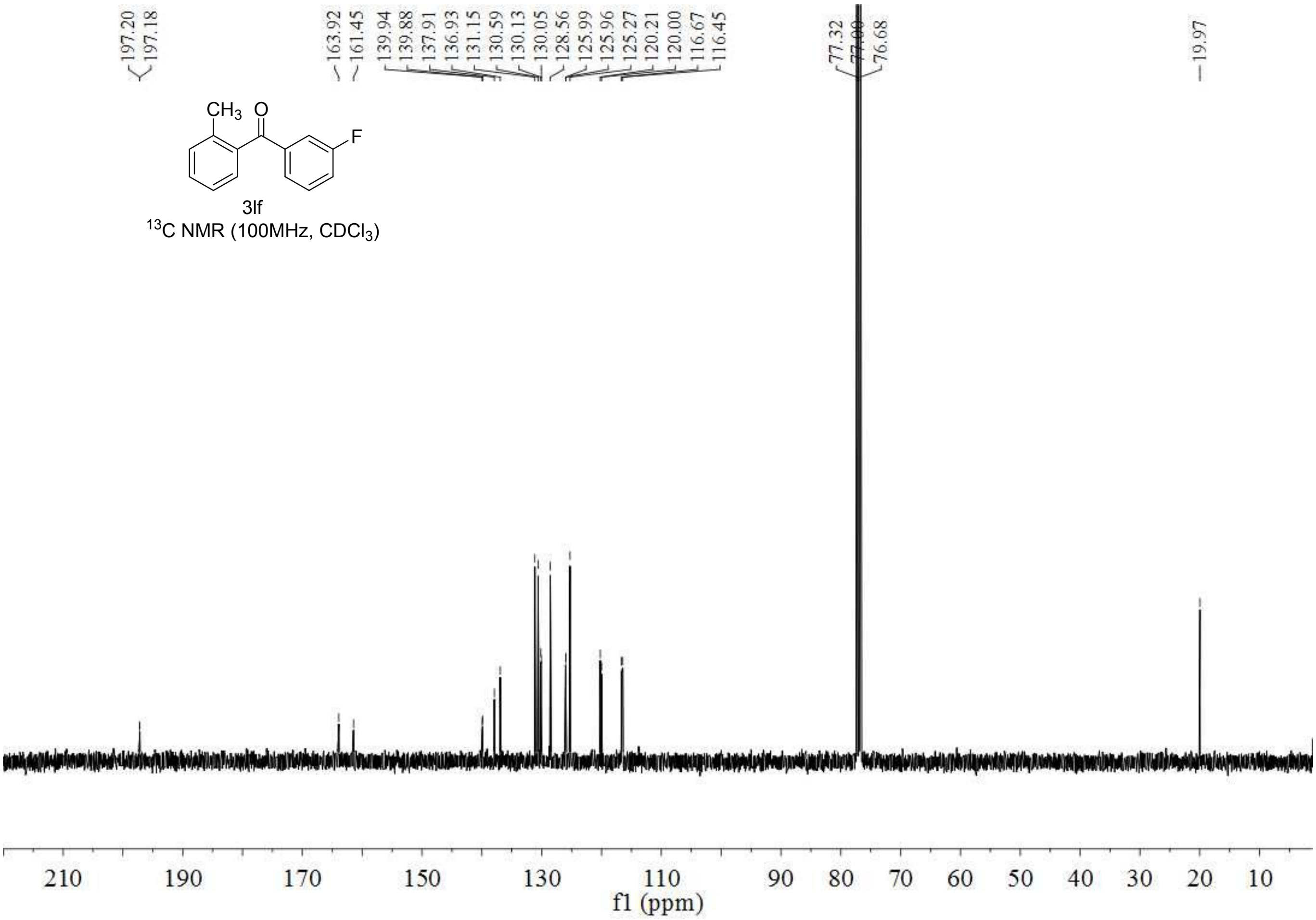
3af

^{13}C NMR (100MHz, $CDCl_3$)



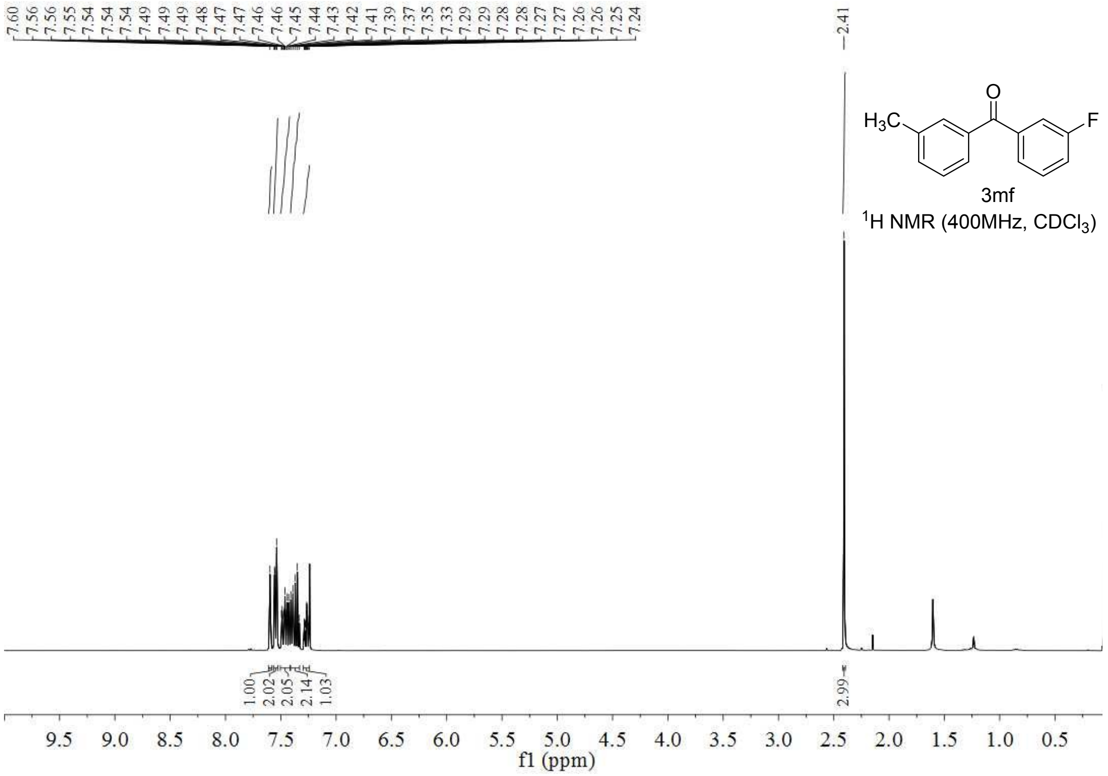
3lf

^{1}H NMR (400MHz, CDCl$_3$)



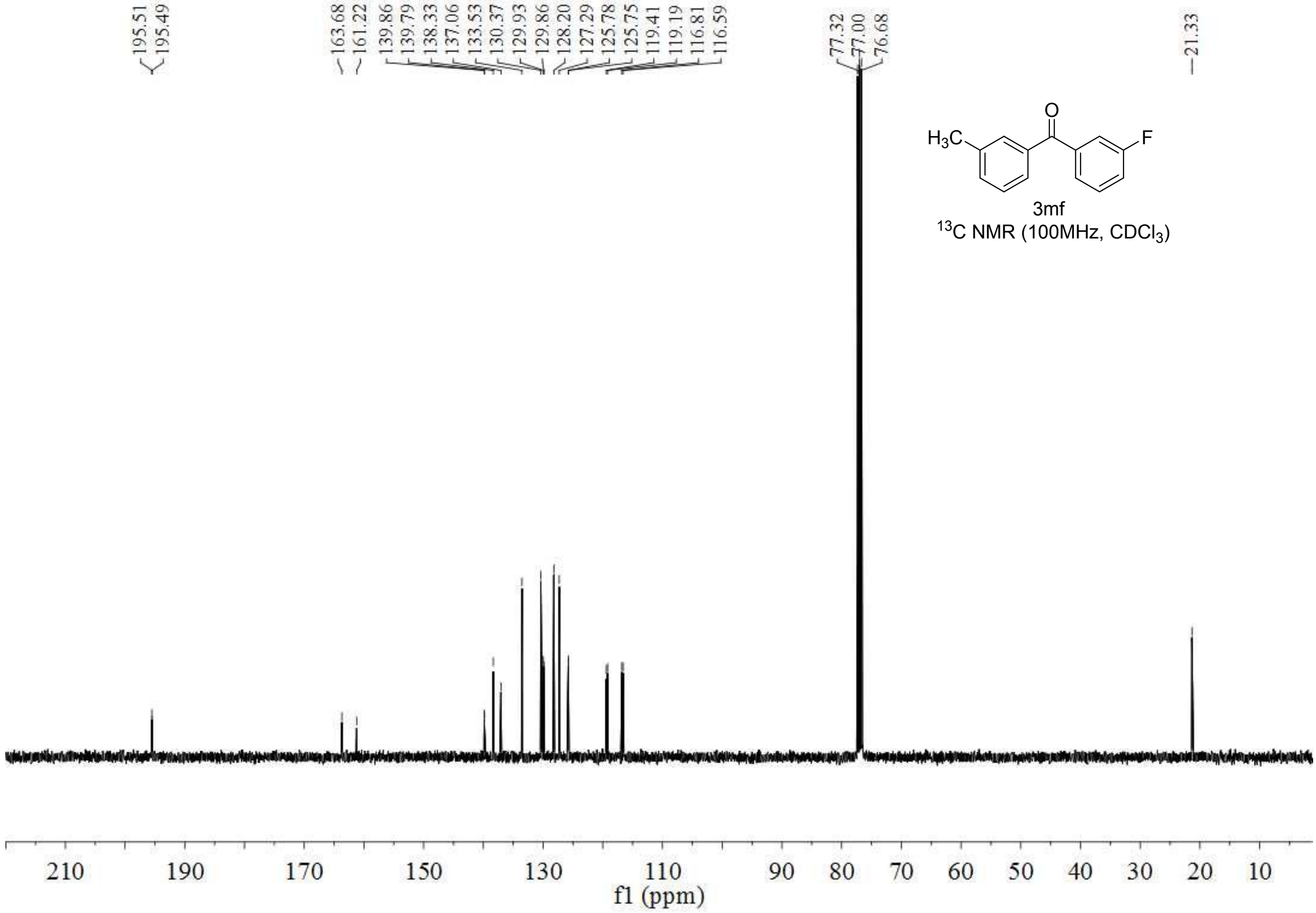
3lf

^{13}C NMR (100MHz, CDCl$_3$)



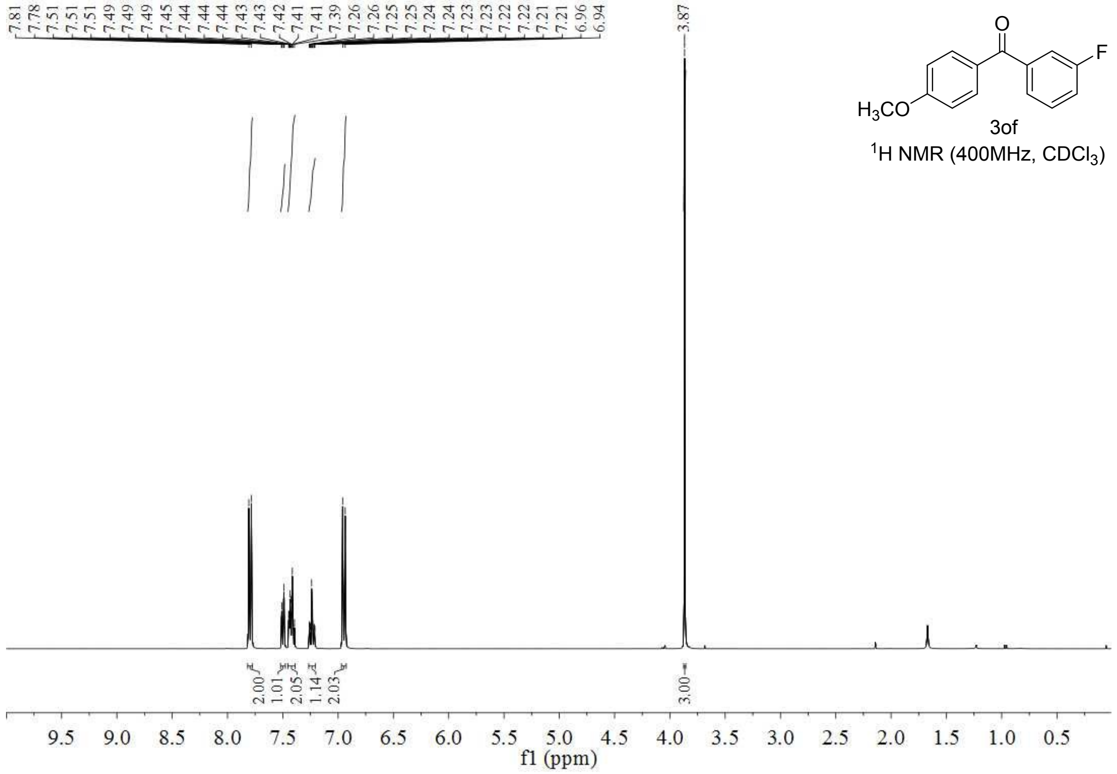
3mf

^{1}H NMR (400MHz, CDCl$_3$)



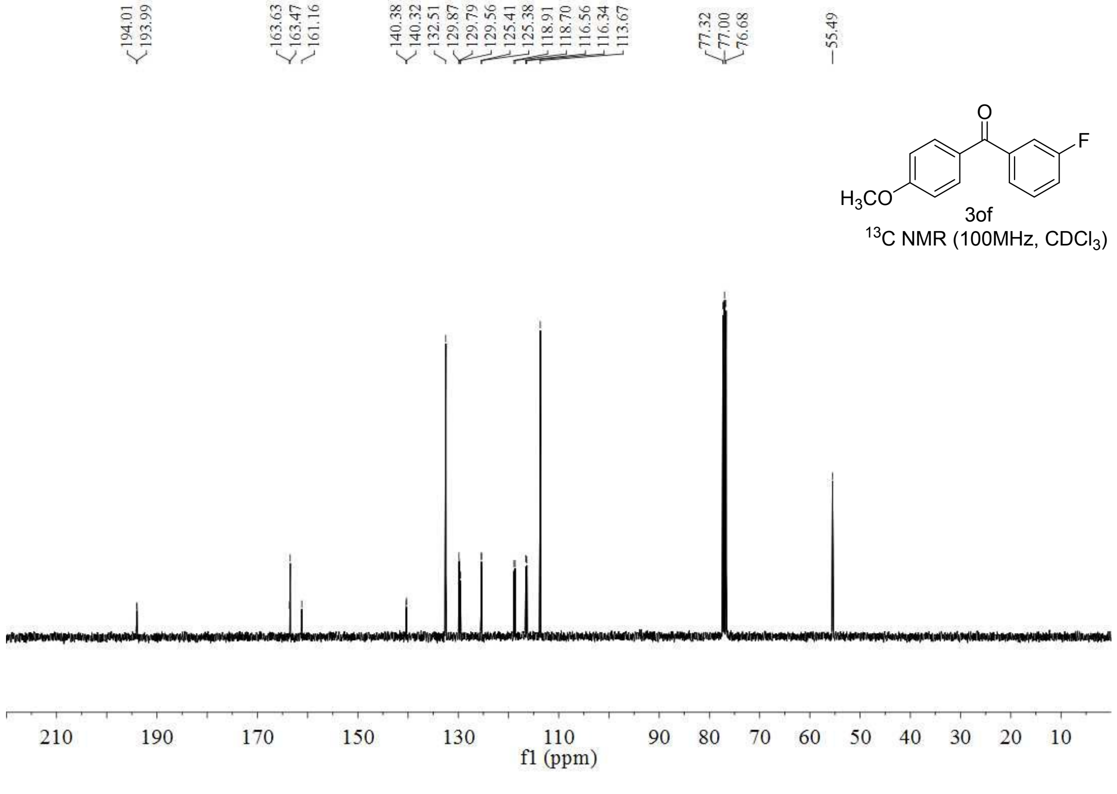
3mf

^{13}C NMR (100MHz, CDCl$_3$)



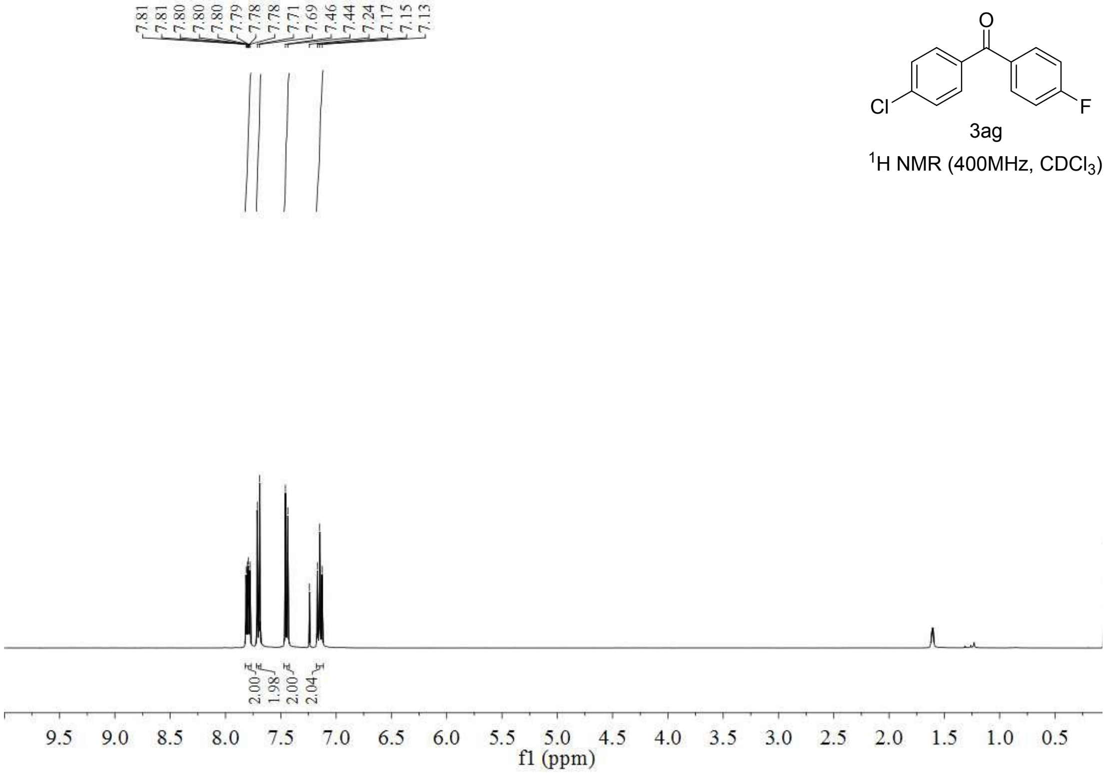
3of

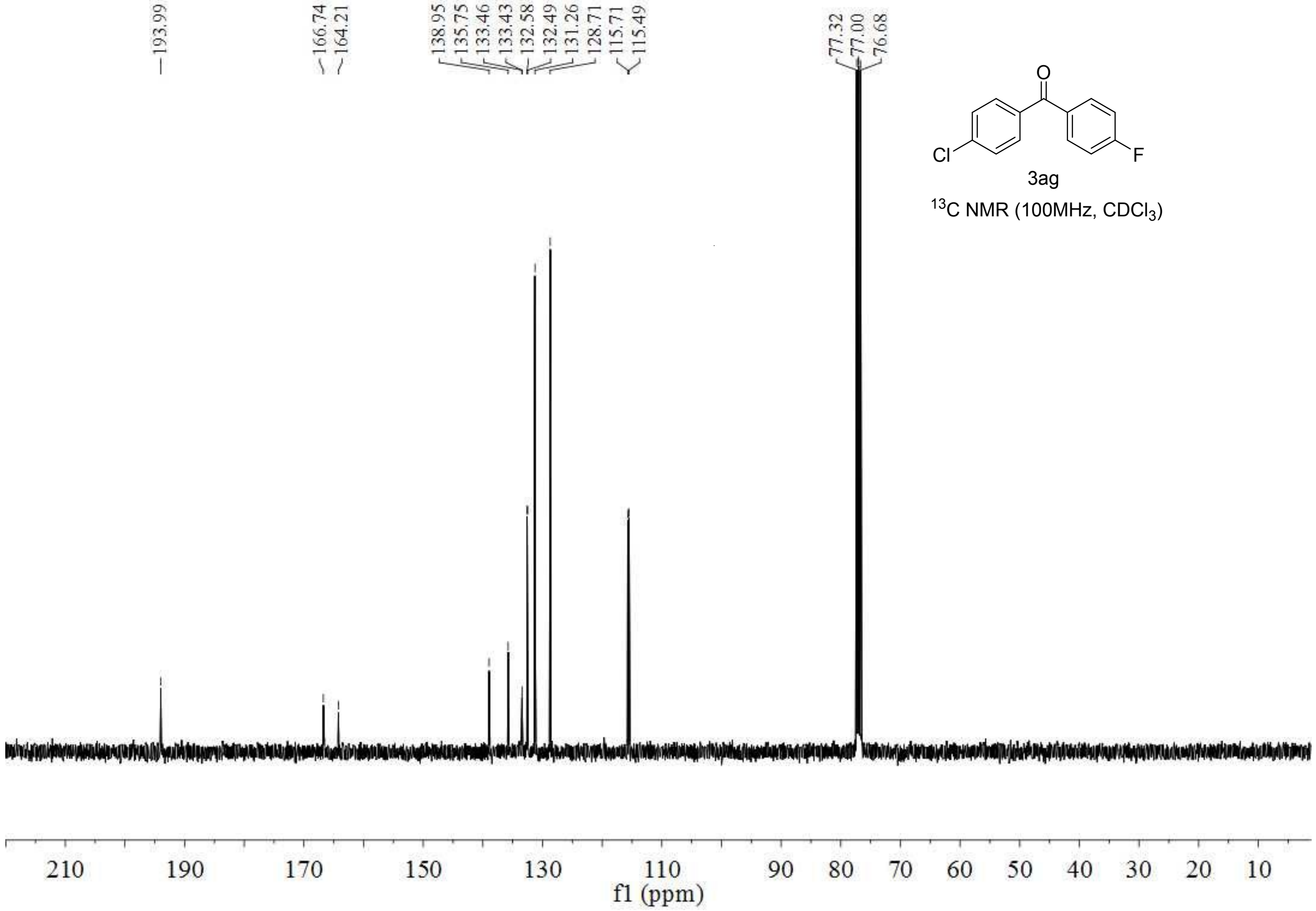
^1H NMR (400MHz, $CDCl_3$)

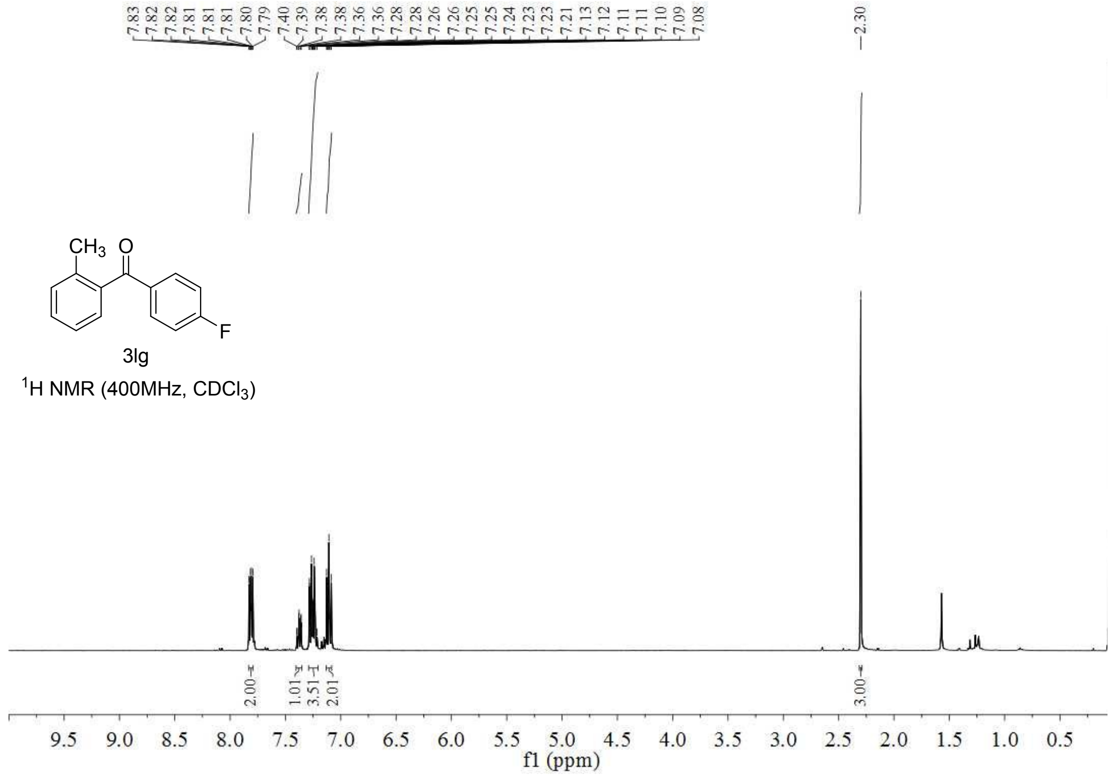


3of

^{13}C NMR (100MHz, $CDCl_3$)

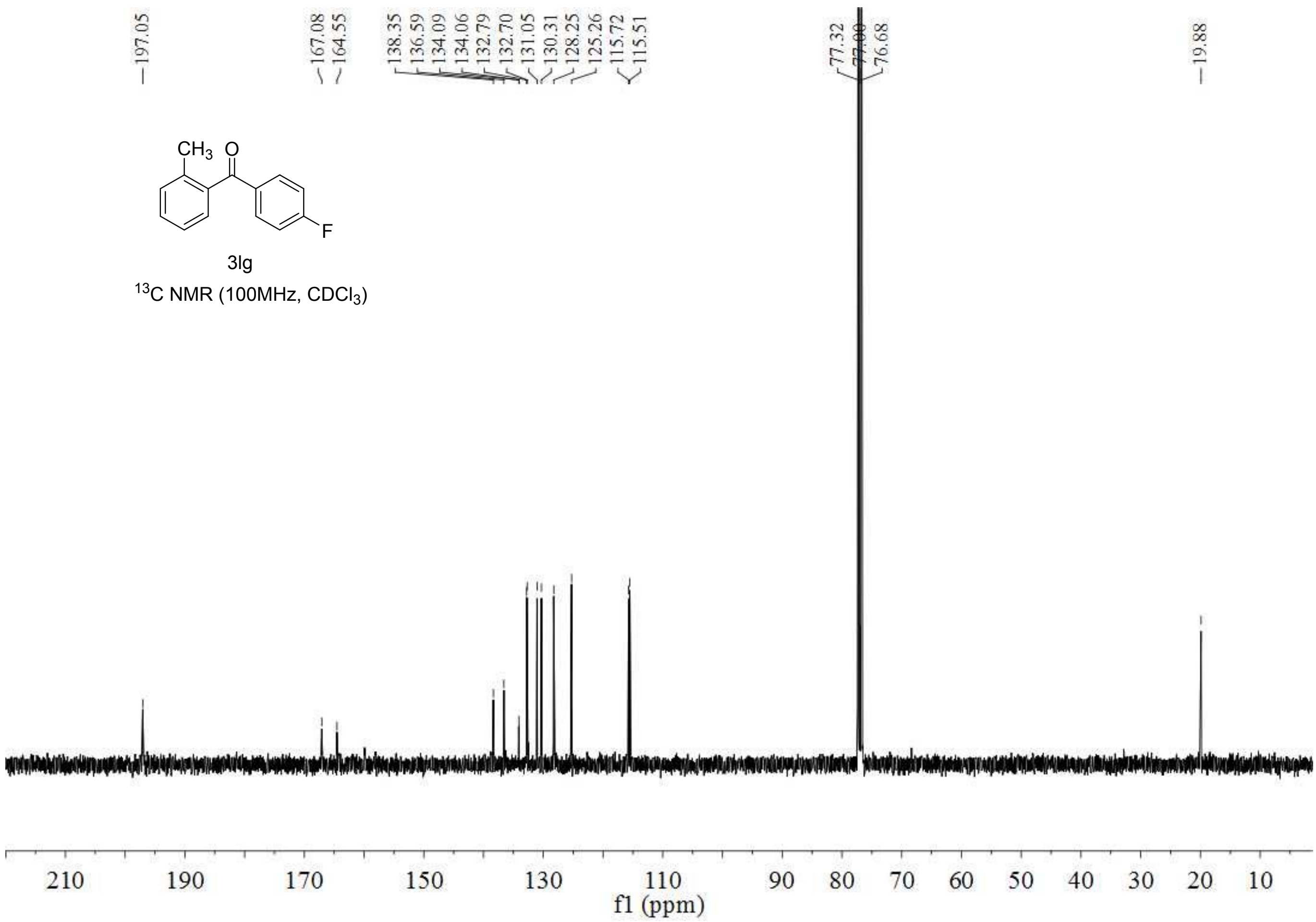

7.81
7.81
7.80
7.80
7.80
7.79
7.78
7.78
7.71
7.69
7.46
7.44
7.24
7.17
7.15
7.13
O
Cl
F
3ag
^{1}H NMR (400MHz, CDCl$_3$)
2.00
1.98
2.00
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


193.99
166.74
164.21
138.95
135.75
133.46
133.43
132.58
132.49
131.26
128.71
115.71
115.49
77.32
77.00
76.68
O
Cl
F
3ag
^{13}C NMR (100MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)



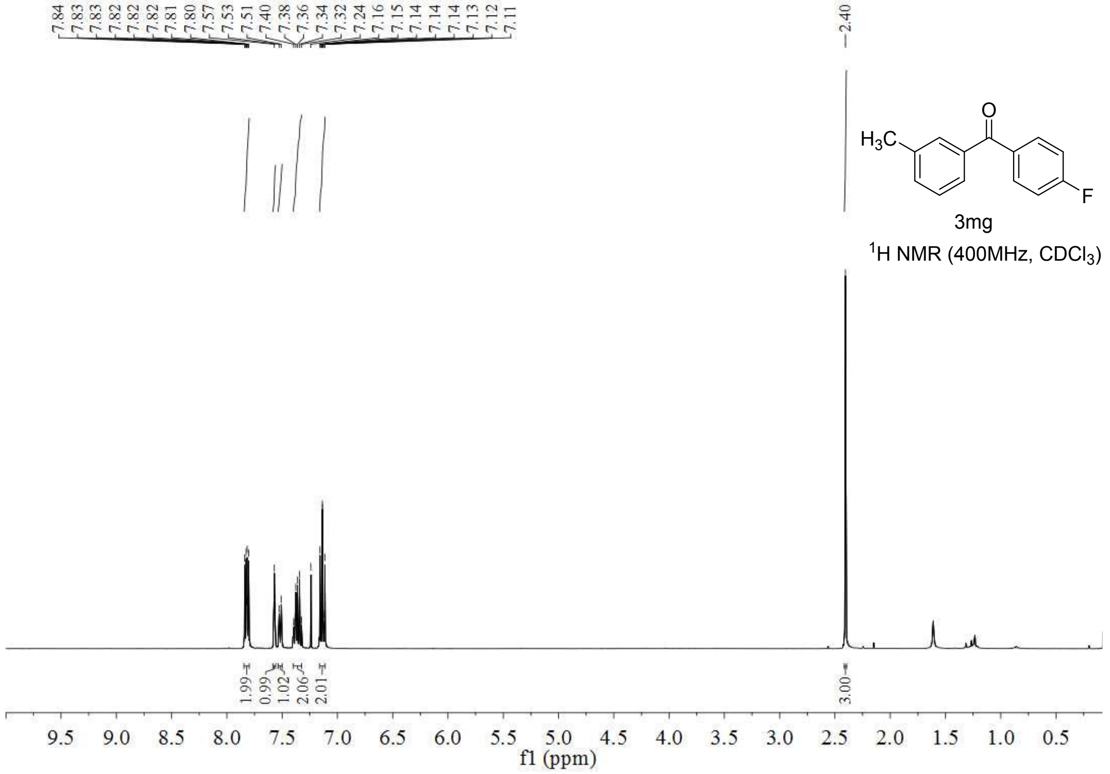
3lg

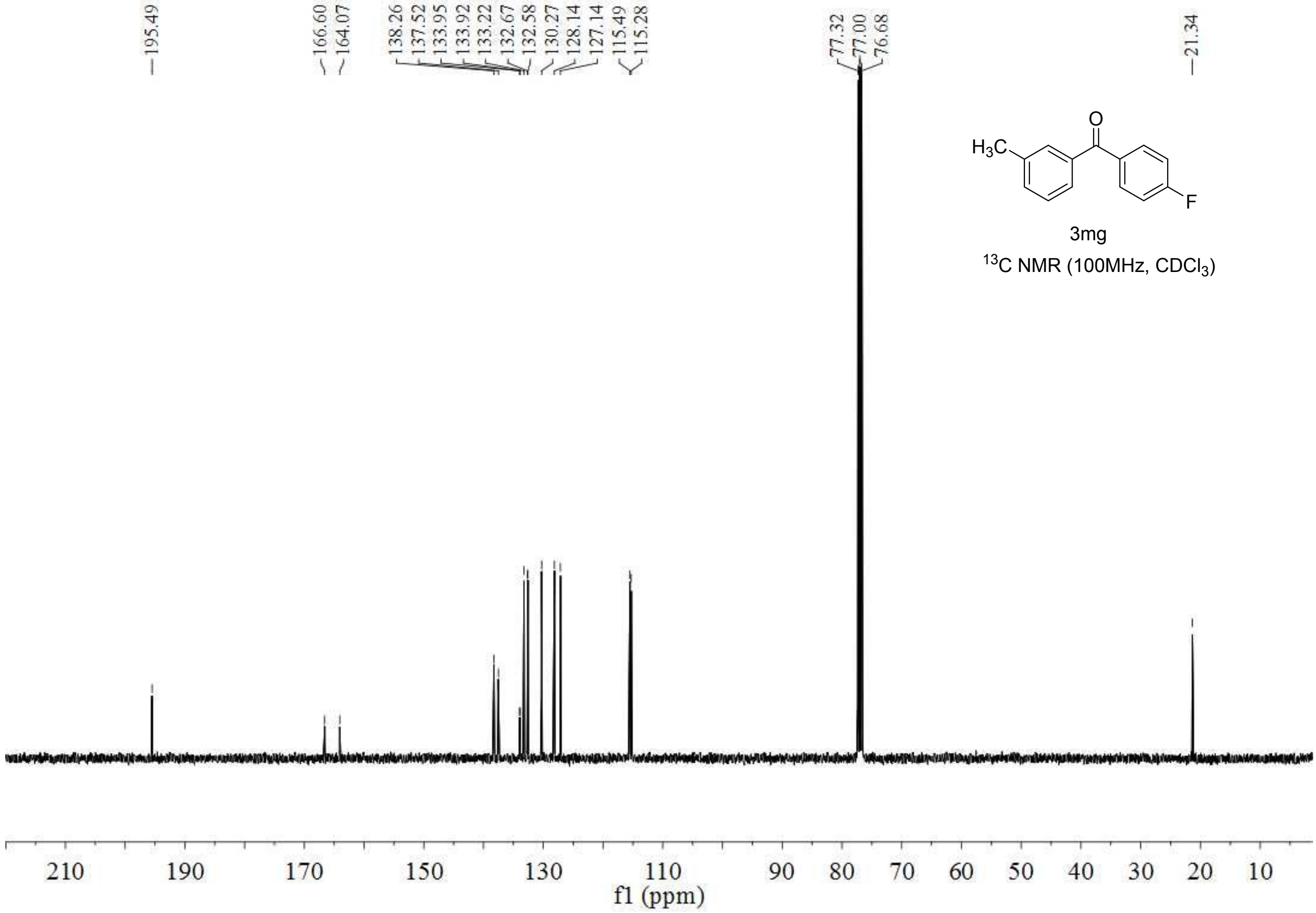
^{1}H NMR (400MHz, CDCl$_3$)

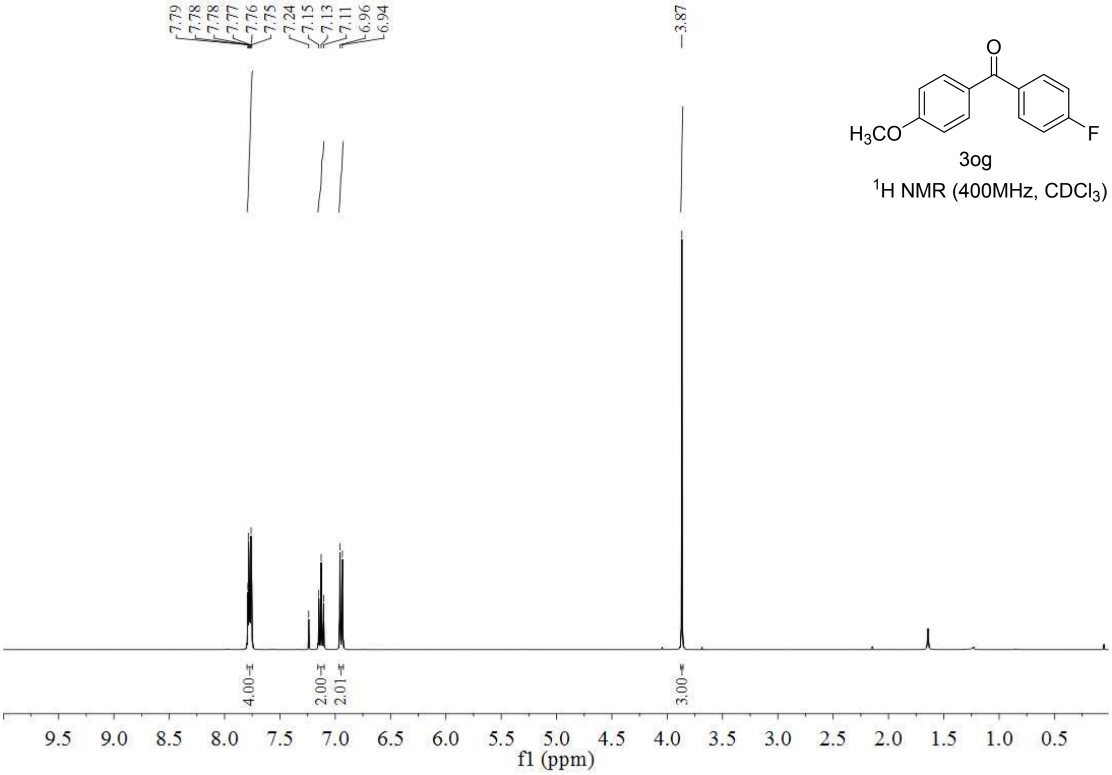


3lg

^{13}C NMR (100MHz, CDCl$_3$)

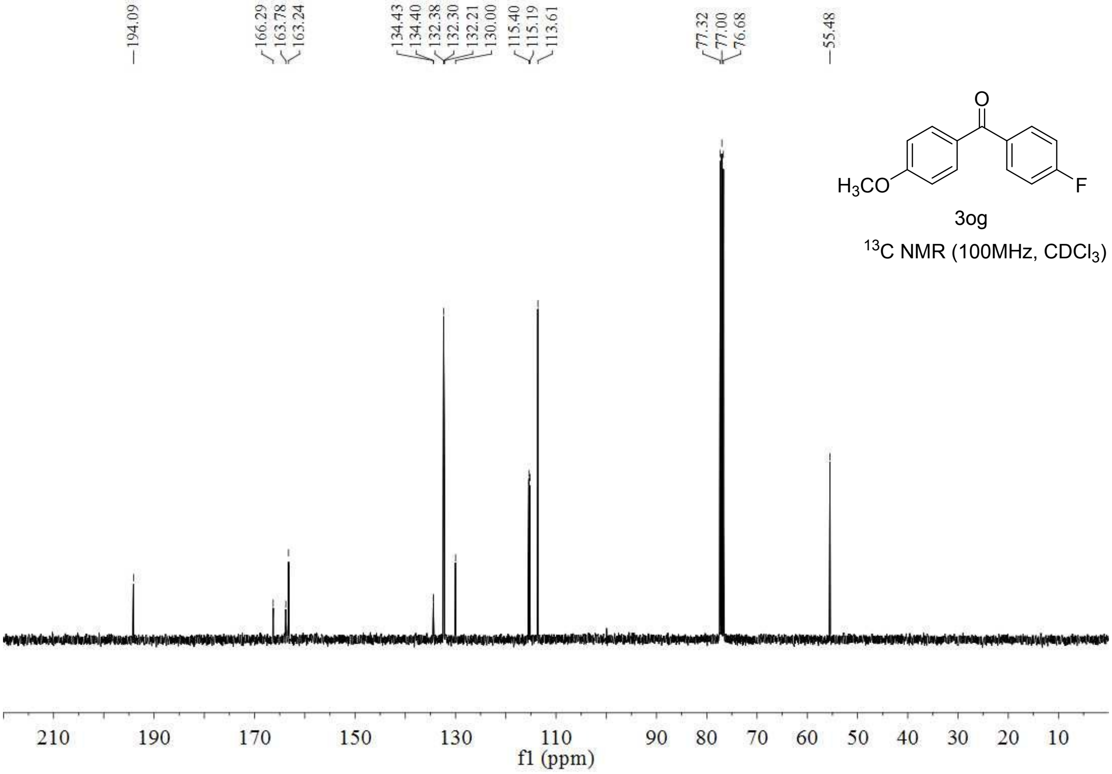

7.84
7.83
7.83
7.82
7.82
7.82
7.81
7.80
7.57
7.53
7.51
7.40
7.38
7.36
7.34
7.32
7.24
7.16
7.15
7.14
7.14
7.14
7.13
7.12
7.11
2.40
H_3C
O
F
3mg
^{1}H NMR (400MHz, CDCl$_3$)
1.99
0.99
1.02
2.06
2.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


195.49
166.60
164.07
138.26
137.52
133.95
133.92
133.22
132.67
132.58
130.27
128.14
127.14
115.49
115.28
77.32
77.00
76.68
21.34
H_3C
O
F
3mg
^{13}C NMR (100MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)



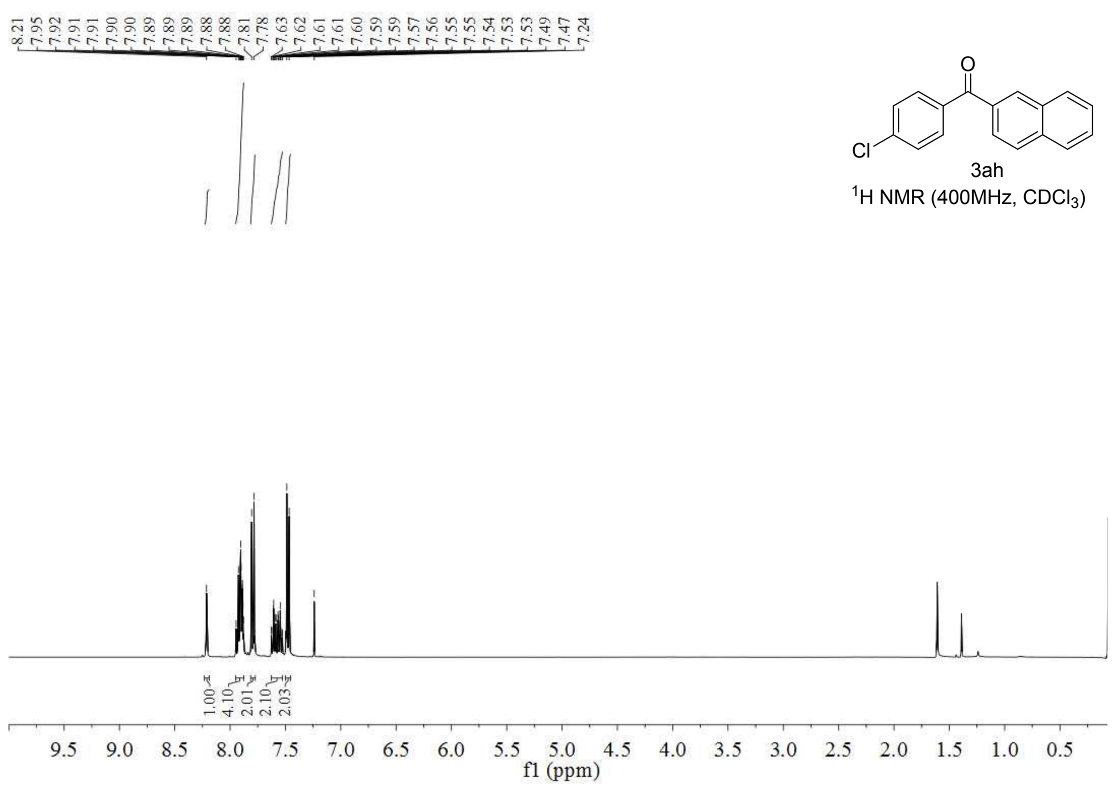
3og

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



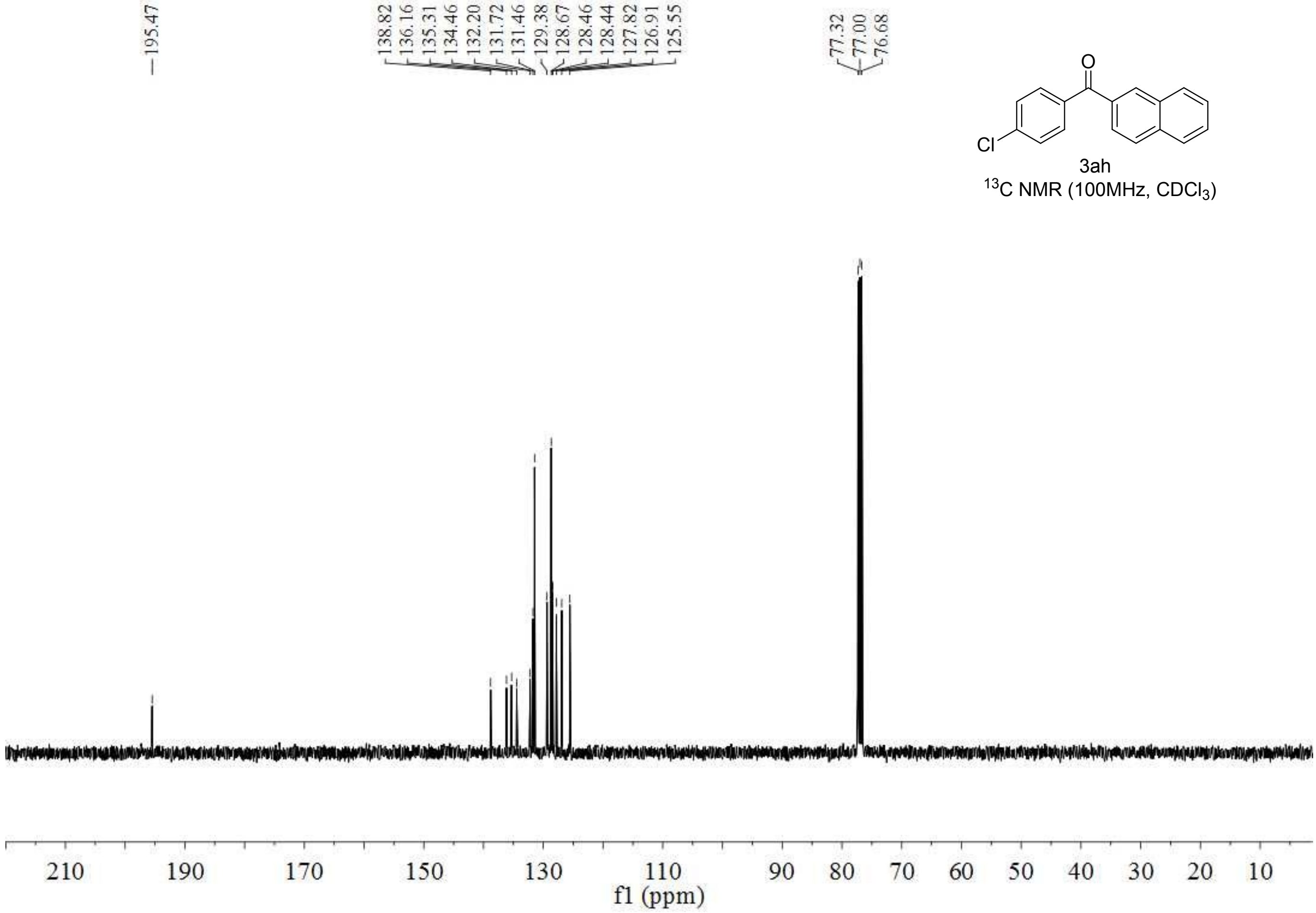
3og

^{13}C NMR (100MHz, $CDCl_3$)



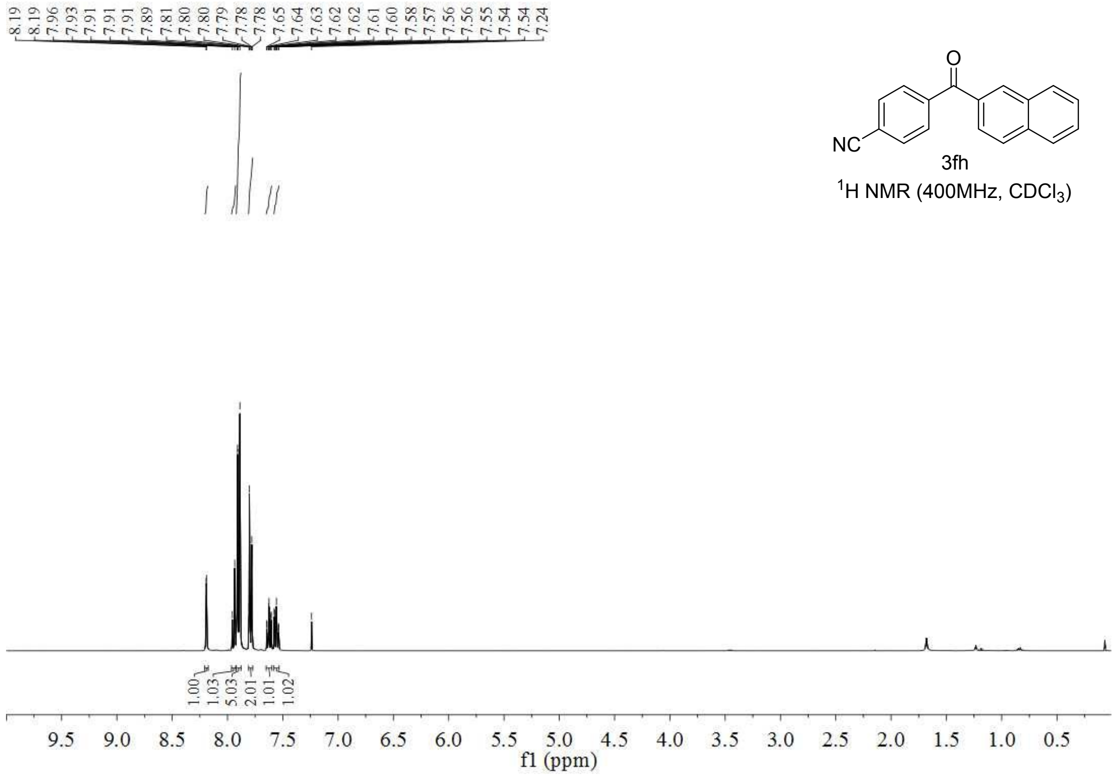
3ah

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



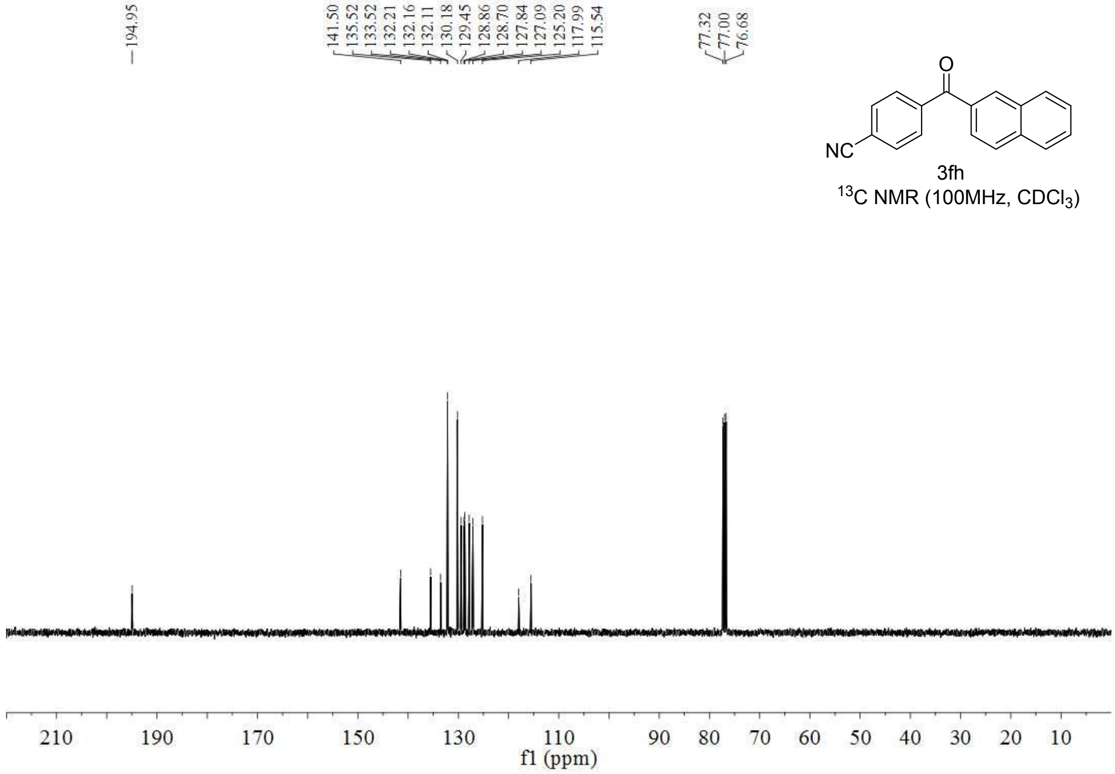
3ah

^{13}C NMR (100MHz, $CDCl_3$)



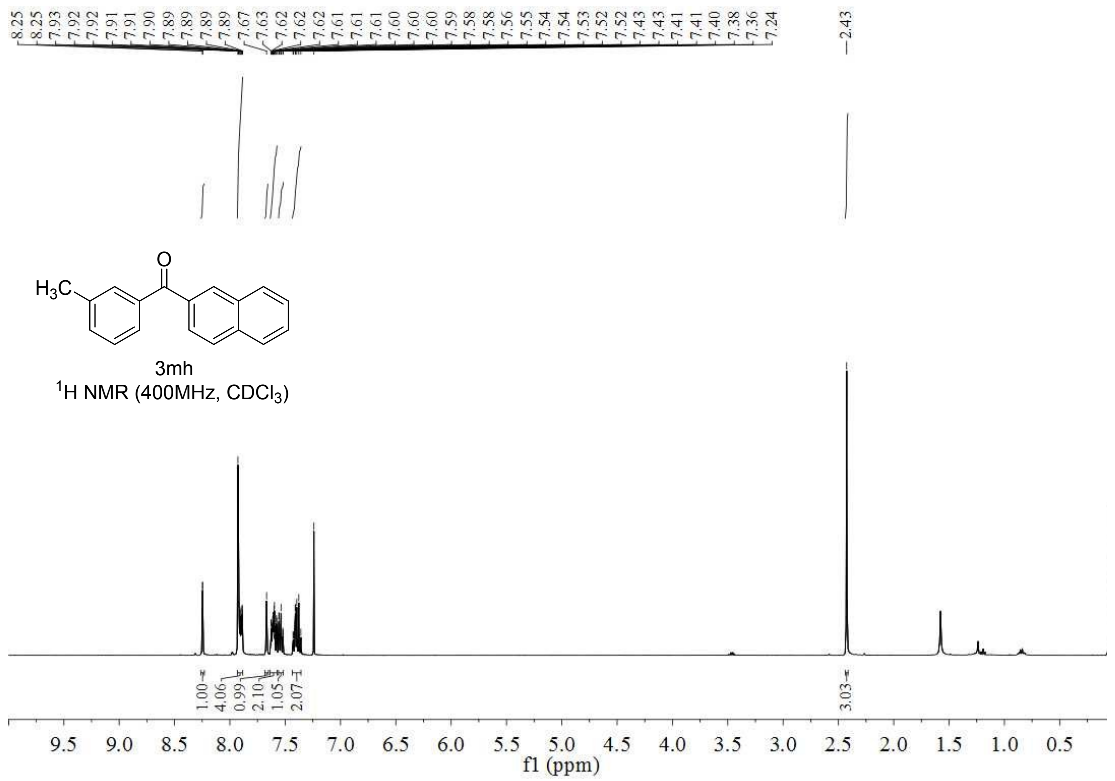
3fh

^{1}H NMR (400MHz, CDCl$_3$)



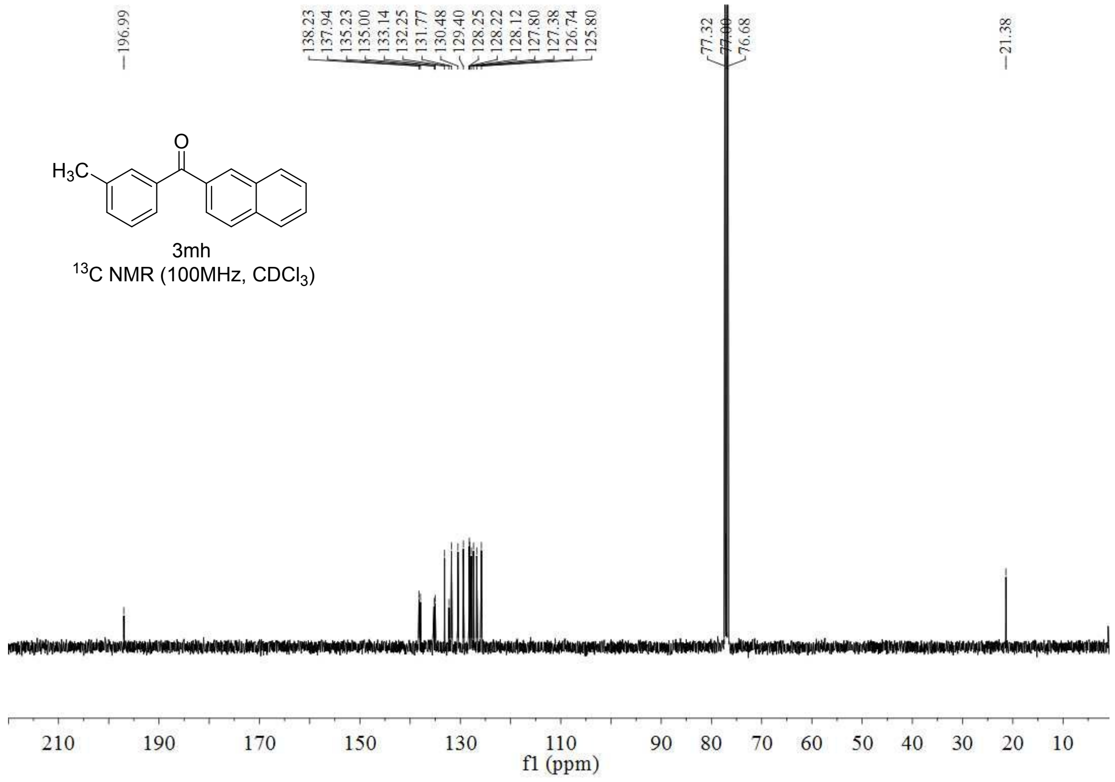
3fh

^{13}C NMR (100MHz, CDCl$_3$)



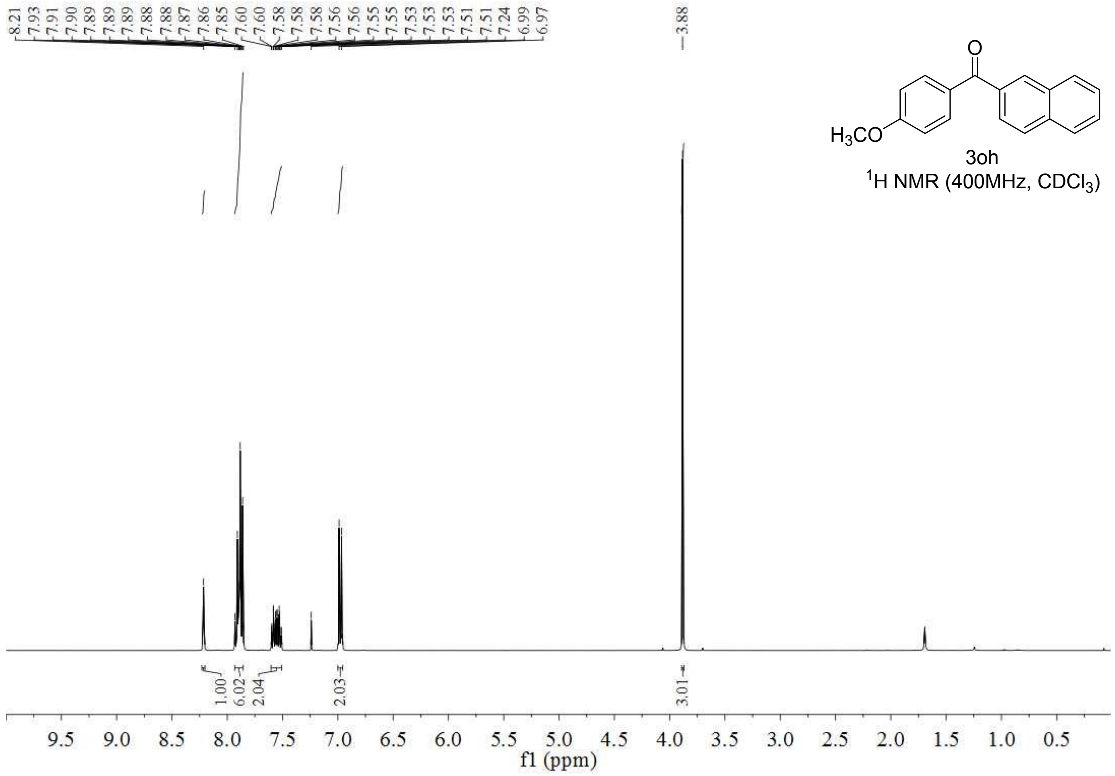
3mh

^{1}H NMR (400MHz, CDCl$_3$)



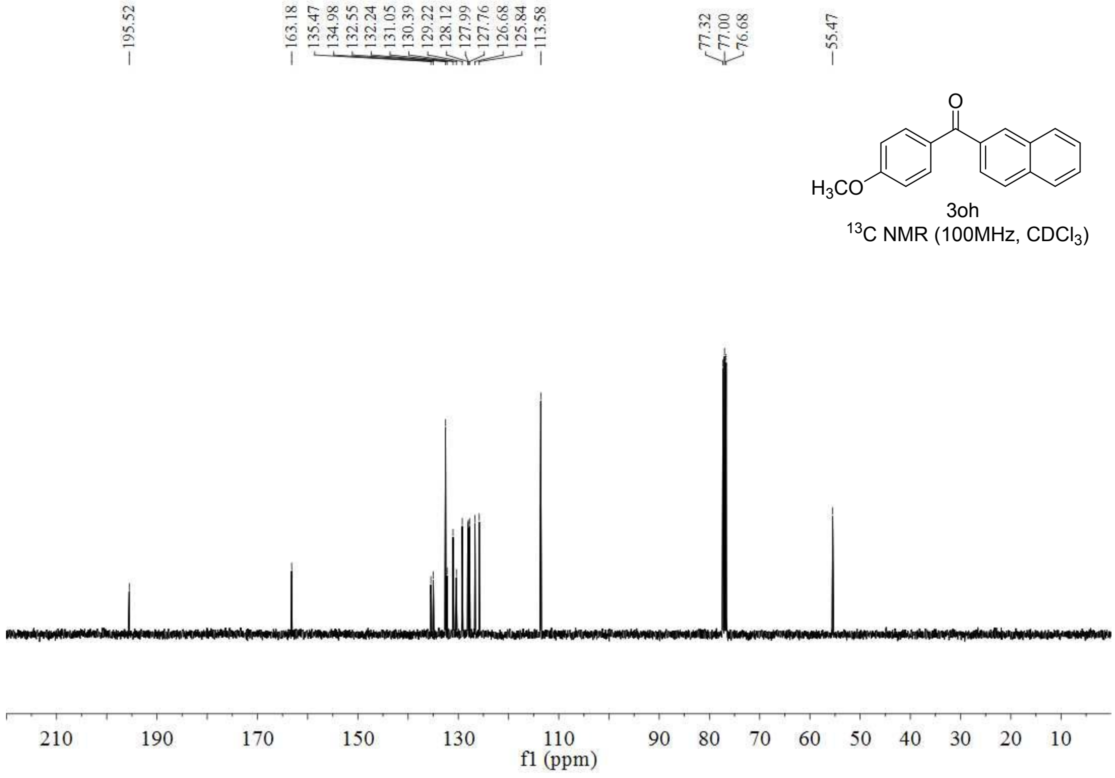
3mh

^{13}C NMR (100MHz, CDCl$_3$)



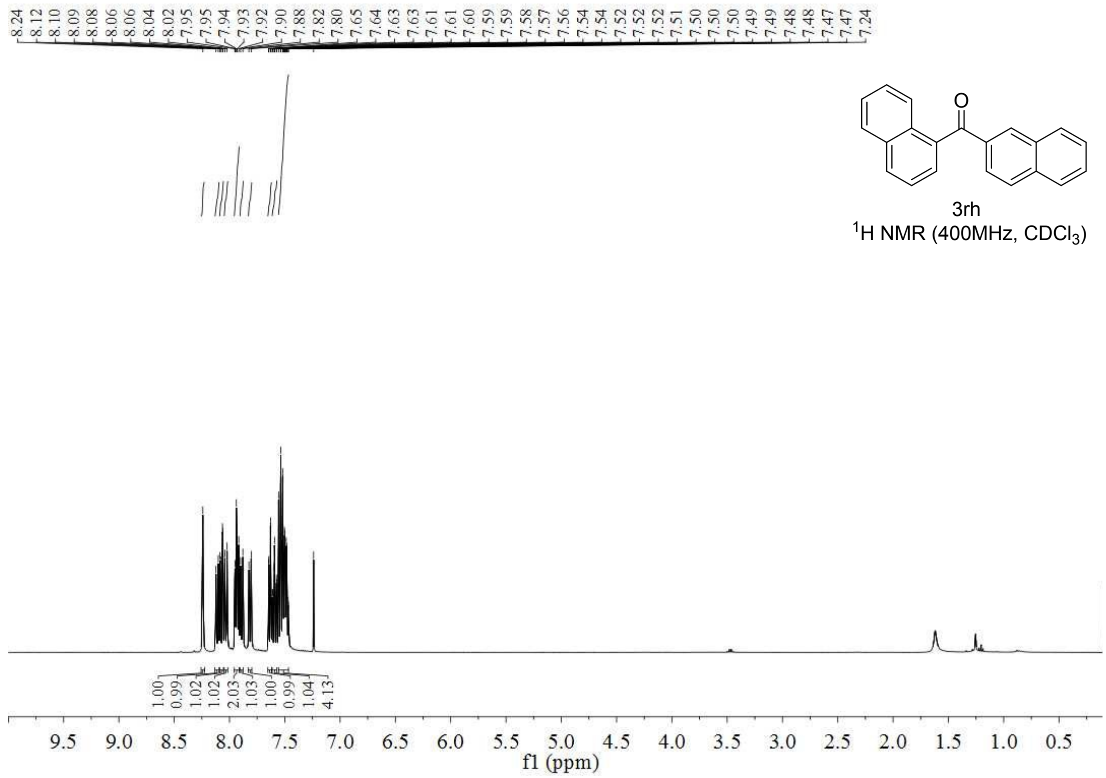
3oh

^{1}H NMR (400MHz, CDCl$_3$)



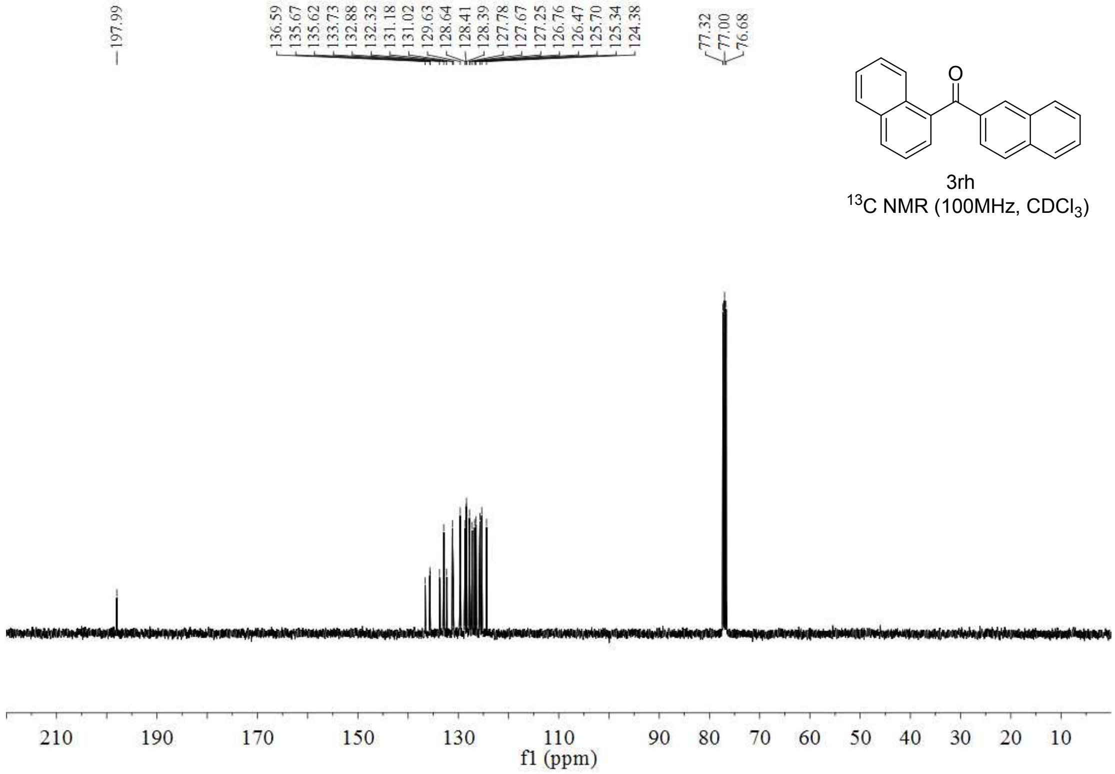
3oh

^{13}C NMR (100MHz, CDCl$_3$)



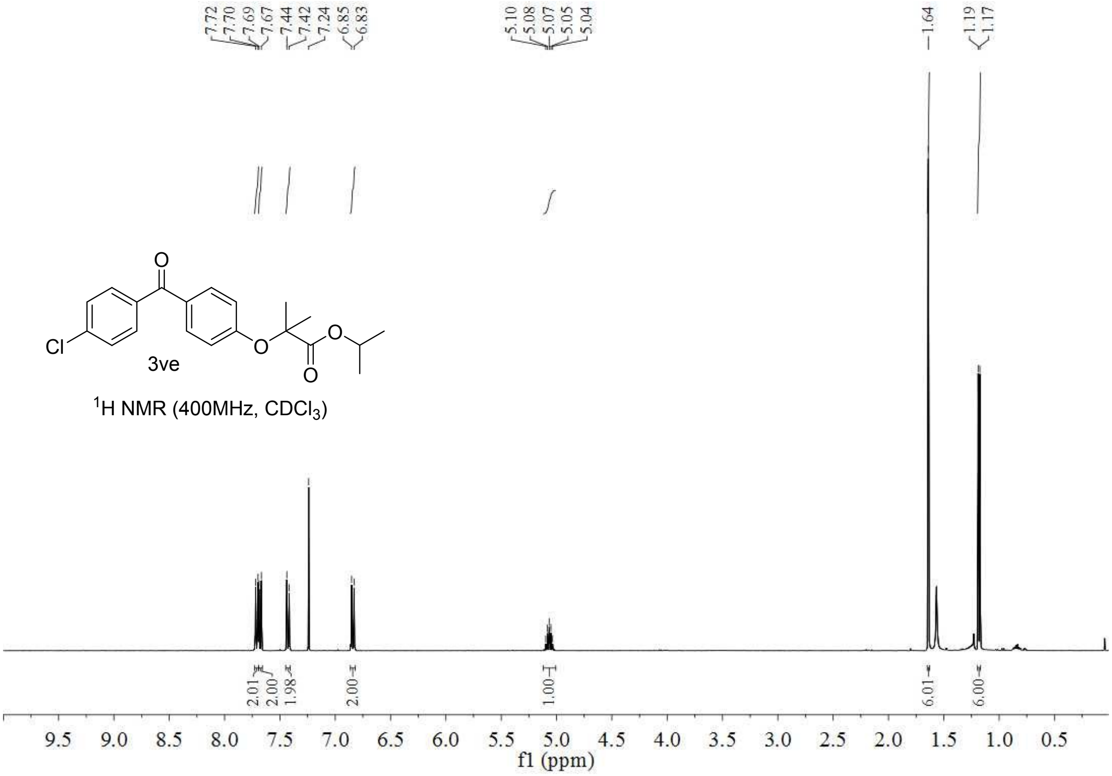
3rh

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



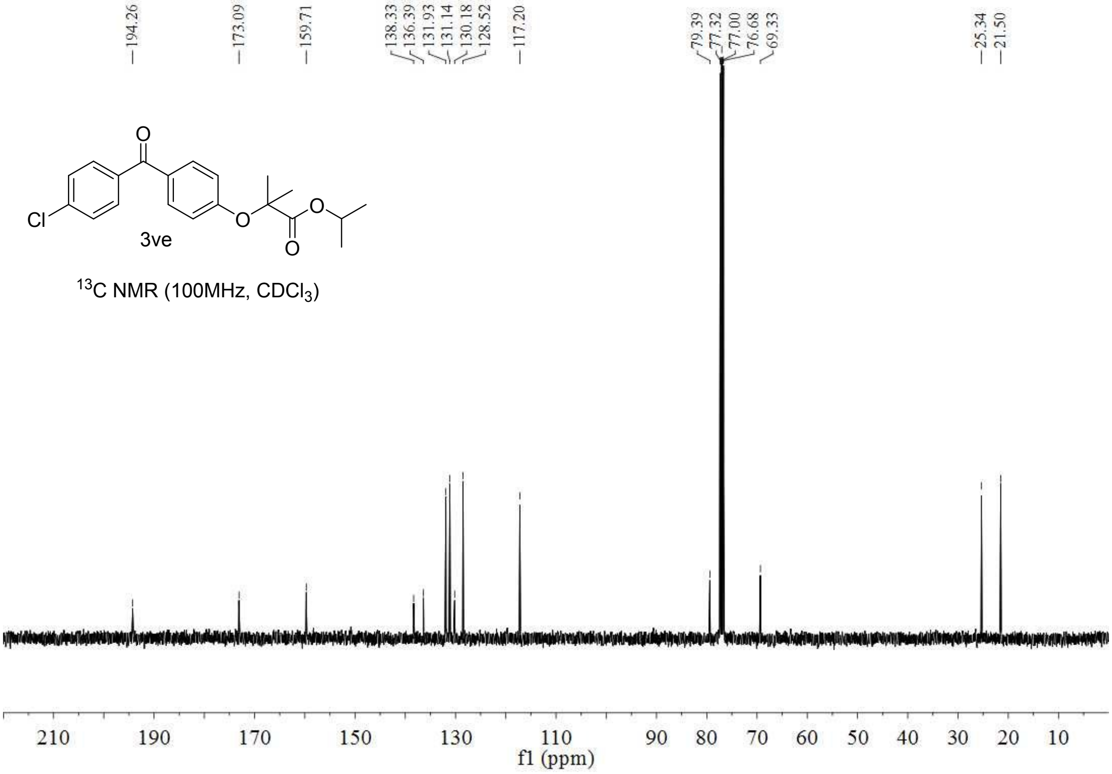
3rh

^{13}C NMR (100MHz, $CDCl_3$)



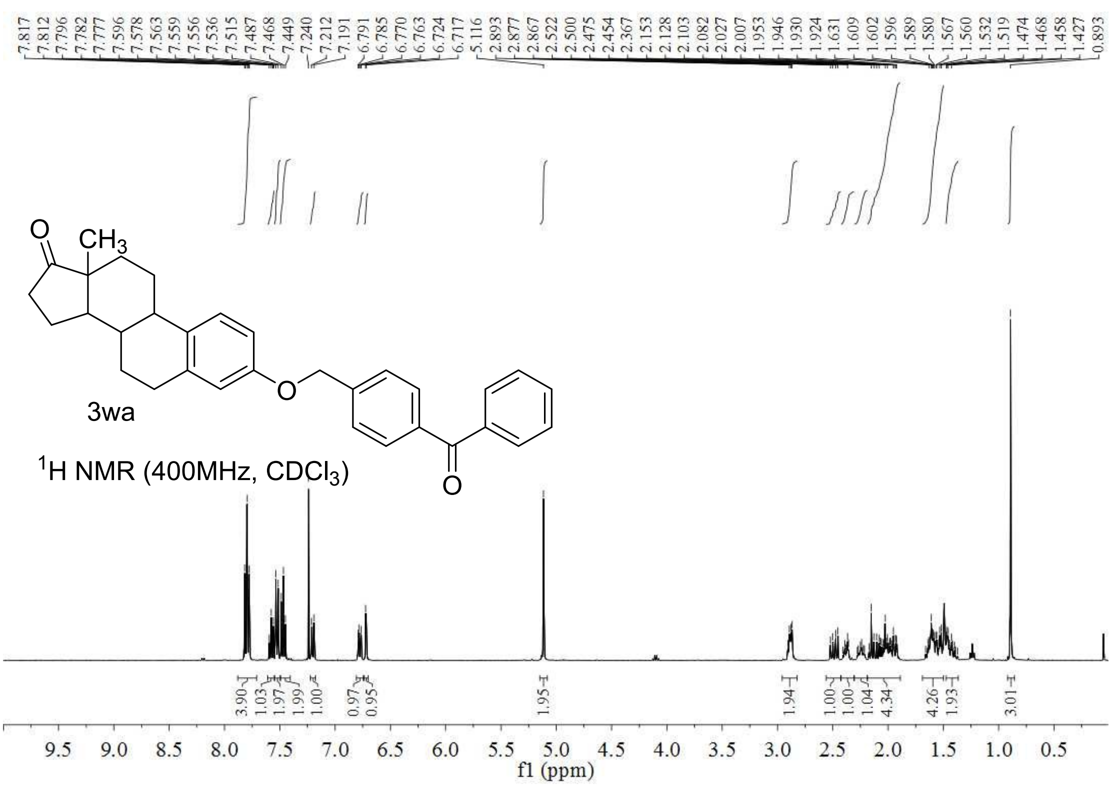
3ve

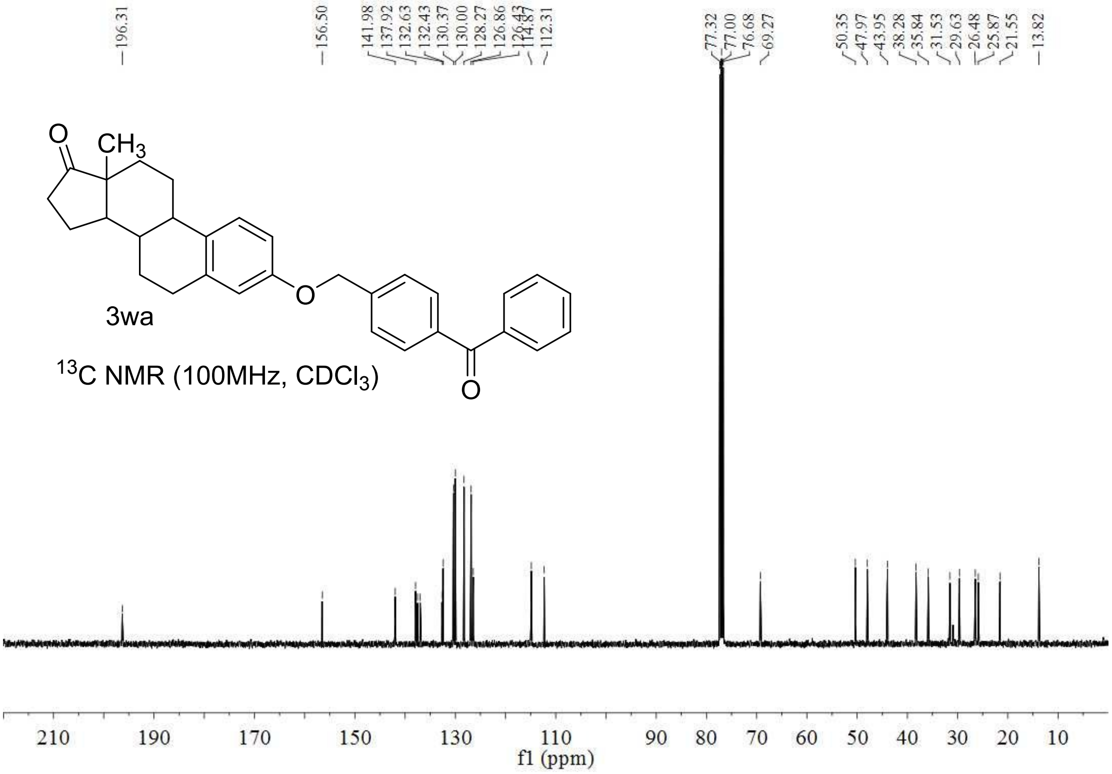
^{1}H NMR (400MHz, CDCl$_3$)

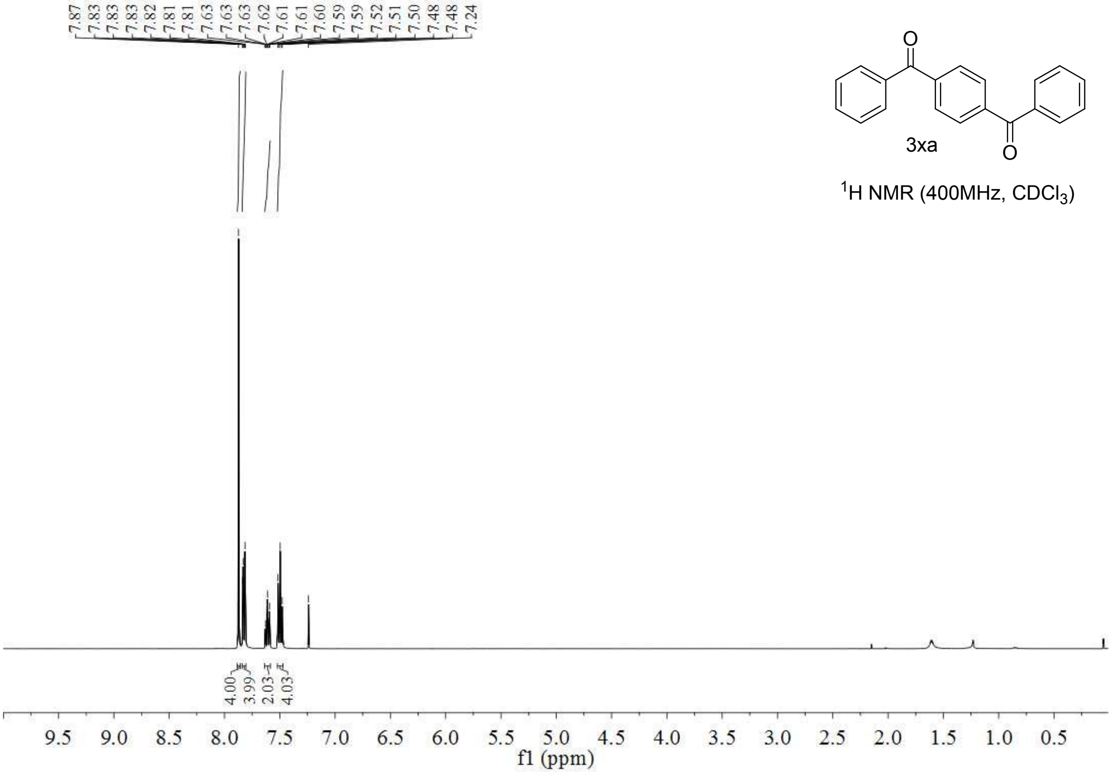


3ve

^{13}C NMR (100MHz, CDCl$_3$)

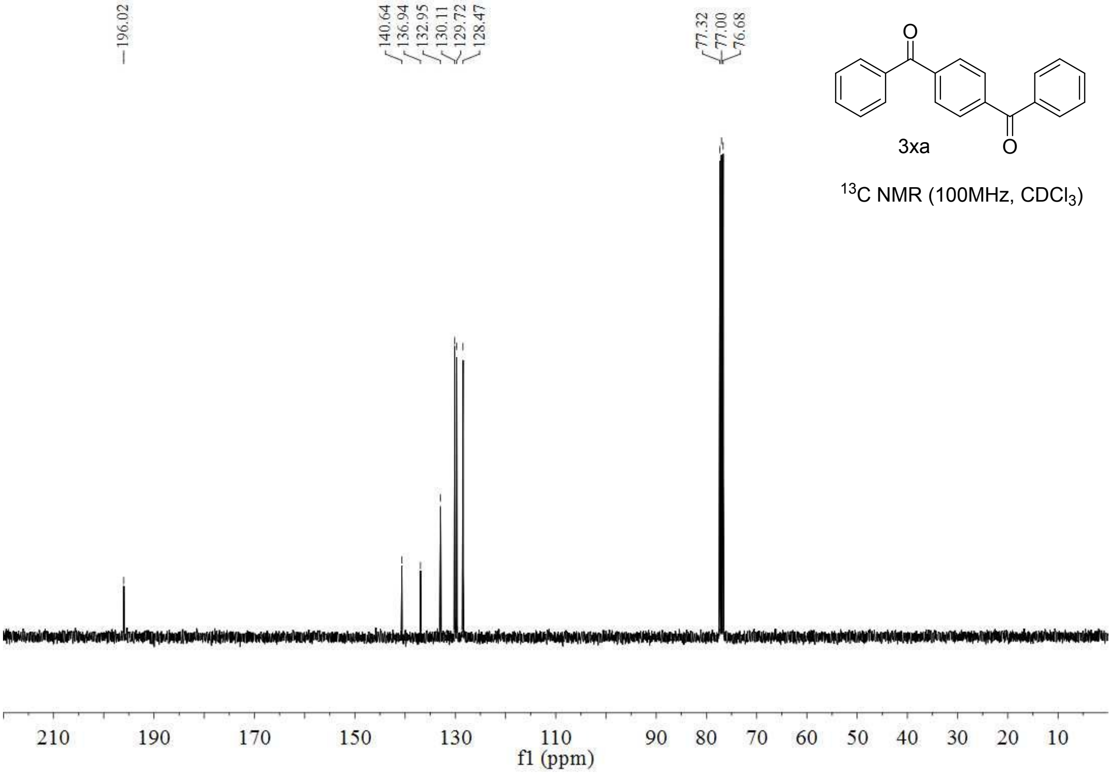

7.817
7.812
7.796
7.782
7.777
7.596
7.578
7.563
7.559
7.556
7.536
7.515
7.487
7.468
7.449
7.240
7.212
7.191
6.791
6.785
6.770
6.763
6.724
6.717
5.116
2.893
2.877
2.867
2.522
2.500
2.475
2.454
2.367
2.153
2.128
2.103
2.082
2.027
2.007
1.953
1.946
1.930
1.924
1.631
1.609
1.602
1.596
1.589
1.580
1.567
1.560
1.532
1.519
1.474
1.468
1.458
1.427
0.893
O
CH3
O
O
3wa
1H NMR (400MHz, CDCl3)
3.90
1.03
1.97
1.99
1.00
0.97
0.95
1.95
1.94
1.00
1.00
1.04
4.34
4.26
1.93
3.01
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
f1 (ppm)


196.31
156.50
141.98
137.92
132.63
132.43
130.37
130.00
128.27
126.86
126.43
114.87
112.31
77.32
77.00
76.68
69.27
50.35
47.97
43.95
38.28
35.84
31.53
29.63
26.48
25.87
21.55
13.82
O
CH3
O
O
3wa
13C NMR (100MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)



3xa

^{1}H NMR (400MHz, CDCl$_3$)



3xa

^{13}C NMR (100MHz, CDCl$_3$)