– Supporting Information –

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1. General Information

All reactions were carried out under air atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial suppliers such as $FeCl_2$ (anhydrous, 99.99% pure) from Aldrich, PMHS [CAS:9004-73-3, 15 to 40 mPa.s (at 20°C)] from Acros, and used without further purification. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm Yantai silica plates (GF-254), using shortwave UV light (254nm) as the visualizing agent or iodine (mixed with silica gel) stain in case of no UV activity. Flash column chromatography was performed using Yantai silica gel (300-400 mesh). ^1H (400 MHz), ^{19}F (400 MHz), and ^{13}C NMR spectra (100 MHz) of solutions in $CDCl_3$ or CD_3COCD_3-*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 7.26 and δ_C 77.0 ppm; CD_3COCD_3-*d*$_6$: δ_H 2.05 and δ_C 29.8 ppm). The signals of water were observed at about 1.58 ppm in $CDCl_3$ and 2.84 ppm in CD_3COCD_3-*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. ICP-AES analysis was measured on a Prodigy (LEEMAN LABS INC.) machine. GC-MS were determined with Agilent 7890-5975C. The gaseous products was detected using a GC-7920 Gas Chromatograph (Beijing Zhong Jiao Jin Yuan Technology Co., Ltd., Beijing, China) equipped with a FID detector (N_2 as carrier gas).

2. General procedure for the synthesis of (*E*)-3-substituted-acrylic acid compounds

To a degassed solution of aldehyde (0.5 mmol) in pyridine (2 mL) was added piperidine (25 µL, 0.25 mmol) and malonic acid (132.7 mg, 1.25 mmol). The resulting mixture was refluxed under N_2 for 12 h. The solvent was removed under reduced pressure. The residue was taken up in water that was acidified (pH = 2) with concentrated HCl; the resulting precipitate was collected, washed with water, and dried under reduced pressure to afford corresponding (*E*)-3-substituted-acrylic acid. The crude product was used in the next step without further purification.

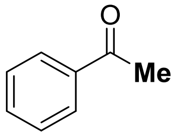
Gram-scale experiment: To a degassed solution of 4-methoxybenzaldehyde (1.36 g, 10 mmol) in pyridine (40 mL) was added piperidine (500 μL, 5 mmol) and malonic acid (2.65 g, 25 mmol). The resulting mixture was refluxed under N_2 for 12 h. The solvent was removed under reduced pressure. The residue was taken up in water that was acidified (pH = 2) with concentrated HCl; the resulting precipitate was collected by filtration and recrystallized from anhydrous ethanol to afford product. The residue was taken up in anhydrous ethanol and recrystallized to afford product **2e** in 88% yield.

3. Products from Iron-Catalyzed Domino Decarboxylation-Oxidation of α,β-Unsaturated Carboxylic Acids

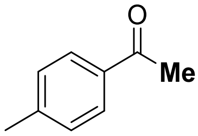
General Procedure A: A 25 mL flask was charged with $FeCl_2$ (0.025 mmol, 3.2 mg), cinnamic acid (0.25 mmol), EtOH (2 mL), and PMHS (0.75 mmol, 170 μL). The reaction mixture was stirred under air atmosphere at 80 °C until the reaction was complete (observed by TLC). After the mixture was cooled to room temperature, filtered through Celite and then washed with ethyl acetate (3 x 5 mL). The organic phases were combined and concentrated to give the crude product. The residue was purified by column chromatography (Petroleum ether/ ethyl acetate) on silica gel to afford the corresponding product.

General Procedure B: A 25 mL flask was charged with $FeCl_2$ (0.050 mmol, 6.4 mg), cinnamic acid (0.25 mmol), *t*BuOH (2 mL), and PMHS (0.75 mmol, 170 μL). The reaction mixture was stirred under air atmosphere at 80 °C until the reaction was complete (observed by TLC). After the mixture was cooled to room temperature, filtered through Celite and then washed with ethyl acetate (3 x 5 mL). The organic phases were combined and concentrated to give the crude product. The residue was purified by column chromatography (Petroleum ether/ ethyl acetate) on silica gel to afford the corresponding product.

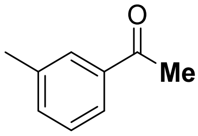
General Procedure C: A 25 mL flask was charged with $FeCl_2$ (0.075 mmol, 9.6 mg), cinnamic acid (0.25 mmol), EtOH (2 mL), and PMHS (0.75 mmol, 170 μL). The reaction mixture was stirred under air atmosphere at 80 °C until the reaction was complete (observed by TLC). After the mixture was cooled to room temperature, filtered through Celite and then washed with ethyl acetate (3 x 5 mL). The organic phases were combined and concentrated to give the crude product. The residue was purified by column chromatography (Petroleum ether/ ethyl acetate) on silica gel to afford the corresponding product.



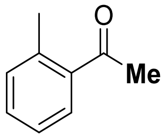
Acetophenone (3a): Following *general procedure A*, **3a** was isolated as a colorless liquid (28.5 mg, 95%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 2 H), 2.60 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.2, 137.0, 133.1, 128.5, 128.2, 26.6 ppm.



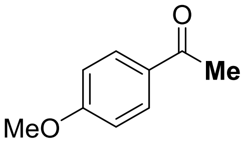
1-(*p*-Tolyl)ethanone (3b): Following *general procedure A*, **3b** was isolated as a yellow liquid (29.1 mg, 87%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.87 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 2.59 (s, 3 H), 2.42 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.8, 143.8, 134.6, 129.2, 128.4, 26.5, 21.6 ppm.



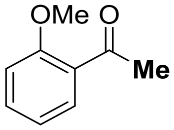
1-(*m*-Tolyl)ethanone (3c): Following *general procedure A*, **3c** was isolated as a yellow liquid (30.2 mg, 90%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.77-7.74 (m, 2 H), 7.38-7.32 (m, 2 H), 2.59 (s, 3 H), 2.40 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.4, 138.3, 137.0, 133.8, 128.7, 128.4, 125.5, 26.6, 21.3 ppm.



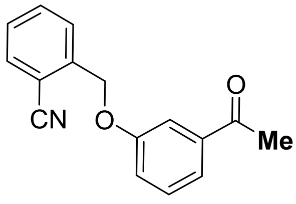
1-(*o*-Tolyl)ethanone (3d): Following *general procedure A*, **3d** was isolated as a yellow liquid (29.8 mg, 89%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (dd, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.38 (td, *J* = 7.2 Hz, 1.2 Hz, 1 H), 7.28-7.23 (m, 2 H), 2.58 (s, 3 H), 2.53 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 201.7, 138.4, 137.5, 132.0, 131.5, 129.3, 125.6, 29.5, 21.6 ppm.



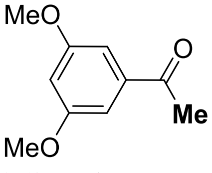
1-(4-Methoxyphenyl)ethanone (3e): Following *general procedure A*, **3e** was isolated as a yellow liquid (34.1 mg, 91%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94 (dt, J = 8.8 Hz, 2.4 Hz, 2 H), 6.93 (dt, J = 8.8 Hz, 2.4 Hz, 2 H), 3.87 (s, 3 H), 2.55 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.8, 163.4, 130.6, 130.3, 113.6, 55.4, 26.3 ppm.



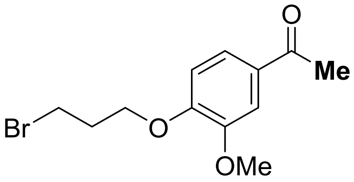
1-(2-Methoxyphenyl)ethanone (3f): Following *general procedure A*, **3f** was isolated as a yellow liquid (33.8 mg, 90%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74 (dd, J = 7.6 Hz, 1.6 Hz, 1 H), 7.49-7.44 (m, 1 H), 7.02-6.96 (m, 2 H), 3.91 (s, 3 H), 2.62 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 199.9, 158.9, 133.7, 130.3, 128.2, 120.5, 111.5, 55.4, 31.9 ppm.



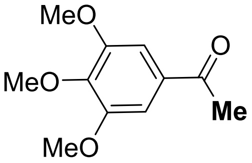
2-((3-Acetylphenoxy)methyl)benzonitrile (3g): Following *general procedure A*, **3g** was isolated as a yellow liquid (50.8 mg, 90%), known compound (CAS: 1016691-05-6); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, J = 7.6 Hz, 1 H), 7.68 (d, J = 7.6 Hz, 1 H), 7.64 (td, J = 7.2 Hz, 1.2 Hz, 1 H), 7.60-7.59 (m, 2 H), 7.46 (td, J = 7.6 Hz, 1.6 Hz, 1 H), 7.41 (t, J = 8.0 Hz, 1 H), 7.22 (ddd, J = 8.0 Hz, 2.4 Hz, 0.8 Hz, 1 H), 5.30 (s, 2 H), 2.60 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.7, 158.4, 140.0, 138.6, 133.1, 133.0, 129.8, 128.65, 128.62, 121.9, 120.0, 117.0, 113.8, 111.4, 67.8, 26.7 ppm.



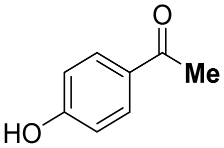
1-(3,5-Dimethoxyphenyl)ethanone (3h): Following *general procedure A*, **3h** was isolated as a yellow solid with low melting point (41.4 mg, 92%), known compound; The NMR spectroscopic data agree with those described in ref.[S3]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.07 (d, J = 2.0 Hz, 2 H), 6.63 (t, J = 2.0 Hz, 1 H), 3.81 (s, 6 H), 2.55 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.7, 160.8, 139.0, 106.1, 105.2, 55.5, 26.6 ppm.



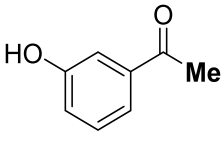
1-(4-(3-Bromopropoxy)-3-methoxyphenyl)ethanone (3i): Following *general procedure A*, **3i** was isolated as a yellow oil (21.8 mg, 75%), known compound; The NMR spectroscopic data agree with those described in ref.[S4]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.47 (d, *J* = 7.6 Hz, 1 H), 7.44 (s, 1 H), 6.84 (d, *J* = 7.2 Hz, 1 H), 4.14-4.13 (m, 2 H), 3.82 (s, 3 H), 3.55-3.54 (m, 2 H), 3.48 (s, 3 H), 2.30 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.8, 152.4, 149.3, 130.7, 123.2, 111.4, 110.5, 66.4, 56.0, 32.0, 29.8, 26.2 ppm.



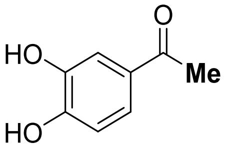
1-(3,4,5-Trimethoxyphenyl)ethanone (3j): Following *general procedure A*, **3j** was isolated as a white solid (49.4 mg, 94%), known compound; The NMR spectroscopic data agree with those described in ref.[S5]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.21 (s, 2 H), 3.92 (s, 6 H), 3.91 (s, 3 H), 2.59 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.9, 153.0, 142.5, 132.4, 105.8, 60.9, 56.3, 26.4 ppm; Mp: 72.2-72.9 °C.



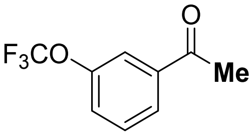
1-(4-Hydroxyphenyl)ethanone (3k): Following *general procedure A*, **3k** was isolated as a white solid (30.3 mg, 89%), known compound; The NMR spectroscopic data agree with those described in ref.[S6]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.92 (dt, *J* = 8.8 Hz, 2.4 Hz, 2 H), 6.94 (dt, *J* = 8.8 Hz, 2.4 Hz, 2 H), 2.59 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.4, 161.1, 131.2, 129.6, 115.5, 26.3 ppm; Mp: 109.5-110.4 °C.



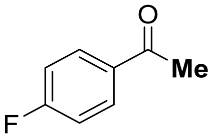
1-(3-Hydroxyphenyl)ethanone (3l): Following *general procedure A*, **3l** was isolated as a yellow solid (28.9 mg, 85%), known compound; The NMR spectroscopic data agree with those described in ref.[S7]. ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): δ 8.76 (s, 1 H), 7.47 (ddd, *J* = 7.6 Hz, 1.6 Hz, 1.2 Hz, 1 H), 7.42 (dd, *J* = 2.0 Hz, 1.6 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.09 (ddd, *J* = 8.4 Hz, 2.4 Hz, 1.2 Hz, 1 H), 2.53 ppm (s, 3 H); ^{13}C NMR (100 MHz, CD$_3$COCD$_3$): δ 197.8, 158.4, 139.6, 130.5, 120.8, 120.5, 115.2, 26.8 ppm; Mp: 95.3-96.5 °C.



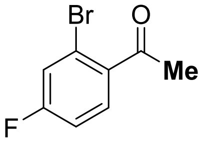
1-(3,4-Dihydroxyphenyl)ethanone (3m): Following *general procedure A*, **3m** was isolated as a brown solid (28.1 mg, 74%), known compound; The NMR spectroscopic data agree with those described in ref.[S8]. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.75 (s, 1 H), 8.39 (s, 1 H), 7.45 (td, J = 8.0 Hz, 2.0 Hz, 2 H), 6.90 (d, J = 8.4 Hz, 1 H), 2.46 ppm (s, 3 H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 196.4, 150.9, 145.7, 130.9, 122.8, 115.6, 115.5, 26.3 ppm; Mp: 118.2-119.4 °C.



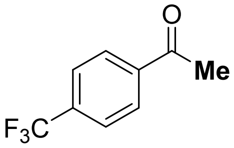
1-(3-(Trifluoromethoxy)phenyl)ethanone (3n): Following *general procedure A*, **3n** was isolated as a yellow liquid (47.4 mg, 93%), known compound; The NMR spectroscopic data agree with those described in ref.[S9]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 7.6 Hz, 1 H), 7.79 (s, 1 H), 7.51 (t, J = 8.0 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 1 H), 2.62 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 149.4, 138.8, 130.1, 126.7, 125.4, 120.6, 120.0 (q, J = 256 Hz), 26.7 ppm; ^{19}F NMR (400 MHz, $CDCl_3$): -57.9 ppm.



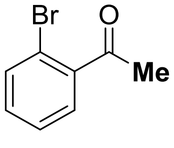
1-(4-Fluorophenyl)ethanone (3o): Following *general procedure A*, **3o** was isolated as a yellow liquid (31.7 mg, 92%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.95 (m, 2 H), 7.15-7.09 (m, 2 H), 2.58 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 165.7 (d, J = 253 Hz), 133.5 (d, J = 3 Hz), 130.9 (d, J = 9 Hz), 115.6 (d, J = 22 Hz), 26.5 ppm; ^{19}F NMR (400 MHz, $CDCl_3$): -105.3 ppm.



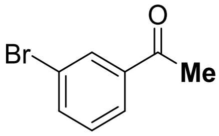
1-(2-Bromo-4-fluorophenyl)ethanone (3p): Following *general procedure A*, **3p** was isolated as a yellow liquid (48.6 mg, 90%), known compound (CAS: 1006-39-9); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, J = 8.4 Hz, 6.0 Hz, 1 H), 7.37 (dd, J = 8.0 Hz, 2.4 Hz, 1 H), 7.11-7.06 (m, 1 H), 2.63 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 163.3 (d, J = 254 Hz), 137.3 (d, J = 3 Hz), 131.2 (d, J = 9 Hz), 121.3 (d, J = 25 Hz), 120.3 (d, J = 10 Hz), 114.7 (d, J = 21 Hz), 30.2 ppm; ^{19}F NMR (400 MHz, $CDCl_3$): -106.9 ppm.



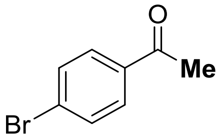
1-(4-(Trifluoromethyl)phenyl)ethanone (3q): Following *general procedure A*, **3q** was isolated as a yellow solid (39.0 mg, 82%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (d, *J* = 8.0 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 2.65 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.0, 139.6 (d, *J* = 1 Hz), 134.4 (d, *J* = 33 Hz), 128.6, 125.6 (d, *J* = 4 Hz), 123.6 (d, *J* = 271 Hz), 26.8 ppm; ^{19}F NMR (400 MHz, CDCl$_3$): -63.1 ppm; Mp: 31.3-31.9 °C.



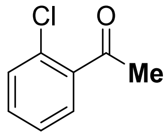
1-(2-Bromophenyl)ethanone (3r): Following *general procedure A*, **3r** was isolated as a yellow liquid (44.8 mg, 90%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 7.46 (dd, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.36 (td, *J* = 7.6 Hz, 1.2 Hz, 1 H), 7.29 (td, *J* = 7.6 Hz, 1.6 Hz, 1 H), 2.63 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 201.5, 141.4, 133.9, 131.8, 128.9, 127.5, 118.9, 30.4 ppm.



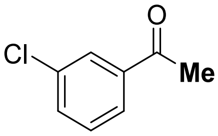
1-(3-Bromophenyl)ethanone (3s): Following *general procedure A*, **3s** was isolated as a yellow liquid (45.8 mg, 92%), known compound; The NMR spectroscopic data agree with those described in ref.[S10]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (t, *J* = 2.0 Hz, 1 H), 7.86 (dt, *J* = 7.6 Hz, 1.2 Hz, 1 H), 7.68-7.65 (m, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 2.58 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.6, 138.6, 135.9, 131.3, 130.1, 126.8, 122.8, 26.6 ppm.



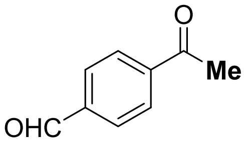
1-(4-Bromophenyl)ethanone (3t): Following *general procedure A*, **3t** was isolated as a white solid with low melting point (45.3 mg, 92%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (dt, *J* = 8.4 Hz, 2.0 Hz, 2 H), 7.61 (dt, *J* = 8.4 Hz, 2.0 Hz, 2 H), 2.59 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.0, 135.7, 131.9, 129.8, 128.3, 26.6 ppm.



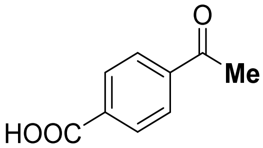
1-(2-Chlorophenyl)ethanone (3u): Following *general procedure A*, **3u** was isolated as a yellow liquid (33.1 mg, 86%), known compound; The NMR spectroscopic data agree with those described in ref.[S11]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 1 H), 7.42-7.29 (m, 3 H), 2.64 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 139.0, 132.0, 131.2, 130.6, 129.3, 126.9, 30.7 ppm.



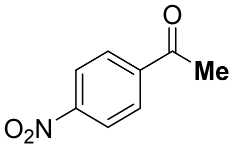
1-(3-Chlorophenyl)ethanone (3v): Following *general procedure A*, **3v** was isolated as a yellow liquid (35.0 mg, 91%), known compound; The NMR spectroscopic data agree with those described in ref.[S11]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (t, J = 2.0 Hz, 1 H), 7.82 (dt, J = 7.6 Hz, 1.2 Hz, 1 H), 7.53-7.51 (m, 1 H), 7.40 (t, J = 8.0 Hz, 1 H), 2.59 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 138.5, 134.8, 133.0, 129.9, 128.3, 126.4, 26.6 ppm.



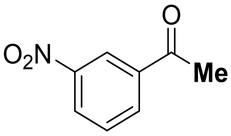
4-Acetylbenzaldehyde (3w): Following *general procedure B*, **3w** was isolated as a low melting point (22.8 mg, 62%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1 H), 8.11 (d, J = 8.4 Hz, 2 H), 7.99 (d, J = 8.4 Hz, 2 H), 2.67 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 191.6, 141.2, 139.0, 129.8, 128.8, 27.0 ppm.



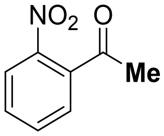
4-Acetylbenzoic acid (3x): Following *general procedure A*, **3x** was isolated as a white solid (34.4 mg, 84%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.17-8.09 (m, 4 H), 2.65 ppm (s, 3 H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 197.7, 166.9, 141.3, 135.0, 130.6, 129.1, 27.0 ppm; Mp: 207.7-208.5 °C.



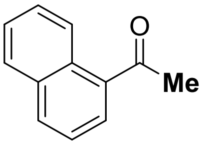
1-(4-Nitrophenyl)ethanone (3y): Following *general procedure A*, **3y** was isolated as a yellow solid (35.5 mg, 86%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.8 Hz, 2 H), 8.11 (d, J = 9.2 Hz, 2 H), 2.68 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 150.3, 141.3, 129.3, 123.8, 27.0 ppm; Mp: 81.5-82.8 °C.



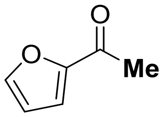
1-(3-Nitrophenyl)ethanone (3z): Following *general procedure A*, **3z** was isolated as a yellow solid (31.4 mg, 76%), known compound; The NMR spectroscopic data agree with those described in ref.[S10]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (t, J = 2.0 Hz, 1 H), 8.44-8.41 (m, 1 H), 8.29 (d, J = 7.6 Hz, 1 H), 7.69 (t, J = 8.0 Hz, 1 H), 2.69 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 148.4, 138.2, 133.8, 129.9, 127.4, 123.2, 26.8 ppm; Mp: 80.7-81.3 °C.



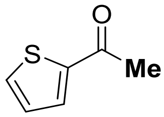
1-(2-Nitrophenyl)ethanone (3aa): Following *general procedure A*, **3aa** was isolated as a yellow liquid (21.9 mg, 53%), known compound; The NMR spectroscopic data agree with those described in ref.[S12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.0 Hz, 1 H), 7.72 (td, J = 7.6 Hz, 1.2 Hz, 1 H), 7.61 (td, J = 8.0 Hz, 1.2 Hz, 1 H), 7.43 (dd, J = 7.6 Hz, 1.6 Hz, 1 H), 2.56 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 145.7, 138.0, 134.2, 130.6, 127.3, 124.4, 30.2 ppm.



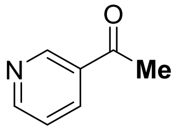
1-(Naphthalen-1-yl)ethanone (3ab): Following *general procedure A*, **3ab** was isolated as a yellow liquid (31.5 mg, 74%), known compound; The NMR spectroscopic data agree with those described in ref.[S12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J = 8.8 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 1 H), 7.95 (dd, J = 7.2 Hz, 1.2 Hz, 1 H), 7.88 (dd, J = 8.4 Hz, 0.8 Hz, 1 H), 7.63-7.59 (m, 1 H), 7.56-7.49 (m, 2 H), 2.76 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 135.4, 133.9, 133.0, 130.1, 128.7, 128.4, 128.1, 126.4, 126.0, 124.3, 30.0 ppm.



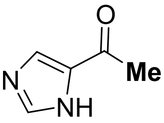
1-(Furan-2-yl)ethanone (3ac): Following *general procedure A*, **3ac** was isolated as a yellow liquid (21.8 mg, 79%), known compound; The NMR spectroscopic data agree with those described in ref.[S2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, J = 2.0 Hz, 0.8 Hz, 1 H), 7.18 (dd, J = 3.6 Hz, 0.8 Hz, 1 H), 6.53 (dd, J = 3.6 Hz, 1.6 Hz, 1 H), 2.47 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.9, 152.8, 146.5, 117.3, 112.3, 26.1 ppm.



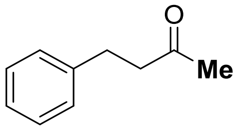
1-(Thiophen-2-yl)ethanone (3ad): Following *general procedure A*, **3ad** was isolated as a yellow liquid (27.7 mg, 88%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 3.6 Hz, 0.8 Hz, 1 H), 7.63 (dd, *J* = 5.2 Hz, 0.8 Hz, 1 H), 7.11 (dd, *J* = 5.2 Hz, 3.6 Hz, 1 H), 2.55 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 144.5, 133.7, 132.4, 128.0, 26.8 ppm.



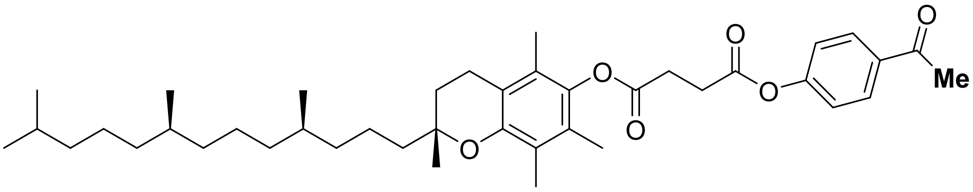
1-(Pyridin-3-yl)ethanone (3ae): Following *general procedure C*, **3ae** was isolated as a yellow liquid (16.0 mg, 53%), known compound; The NMR spectroscopic data agree with those described in ref.[S12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (dd, *J* = 2.4 Hz, 0.8 Hz, 1 H), 8.72 (dd, *J* = 4.8 Hz, 1.6 Hz, 1 H), 8.18 (dt, *J* = 8.0 Hz, 4.8 Hz, 0.8 Hz, 1 H), 7.37 (ddd, *J* = 8.4 Hz, 0.8 Hz, 1 H), 2.59 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 153.4, 149.8, 135.3, 132.1, 123.5, 26.6 ppm.



1-(1*H*-imidazol-5-yl)ethan-1-one (3af): Following *general procedure C*, **3af** was isolated as a yellow solid (17.6 mg, 64%), known compound (CAS: 61985-25-9); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 11.99 (s, 1H), 7.81 (s, 1 H), 7.79 (s, 1 H), 2.43 ppm (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.2, 138.0, 129.2, 127.7, 26.6 ppm; Mp: 169.7-170.1 °C.

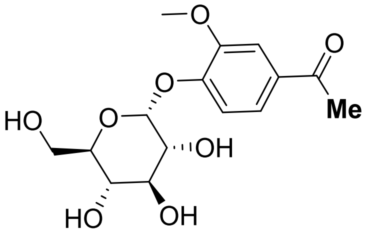


4-Phenylbutan-2-one (3ai): Following *general procedure A*, **3ai** was isolated as a colorless liquid (21.8 mg, 75%), known compound; The NMR spectroscopic data agree with those described in ref.[S13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2 H), 7.23-7.20 (m, 3 H), 2.92 (t, *J* = 7.2 Hz, 2 H), 2.77 (t, *J* = 8.0 Hz, 2 H), 2.15 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 140.8, 128.2, 128.0, 125.8, 44.8, 29.8, 29.5 ppm.

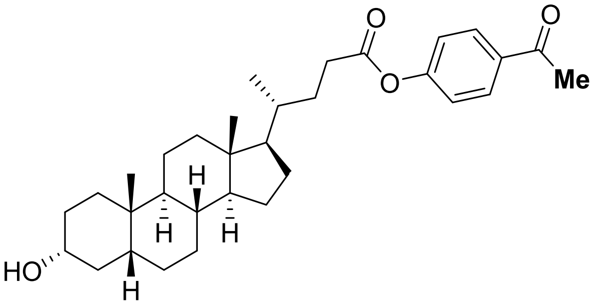


4-Acetylphenyl ((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)

succinate (6a): Following *general procedure A*, **6a** was isolated as a white solid (99.2 mg, 70%), unknown compound; ^{1}H NMR (400 MHz, DMSO): δ 8.01 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 3.01-3.00 (m, 4 H), 2.57 (s, 3 H), 2.00 (s, 4 H), 1.90 (d, *J* = 19.6 Hz, 6 H), 1.72 (s, 2 H), 1.51-1.33 (m, 8 H), 1.20 (d, *J* = Hz, 9 H), 1.12-1.03 (m, 8 H), 0.83-0.79 ppm (m, 12 H); ^{13}C NMR (100 MHz, DMSO): δ 196.8, 170.8, 170.6, 154.0, 148.6, 140.2, 134.5, 130.7, 129.9, 126.3, 121.9, 117.3, 115.1, 74.8, 36.7, 36.3, 32.0, 28.9, 28.3, 27.4, 26.7, 24.1, 23.7, 22.5, 22.4, 20.3, 19.9, 19.6, 19.5, 12.7, 11.8, 11.5 ppm. HRMS (ESI) calcd. for $C_{41}H_{61}O_6^+$ [M + H]$^+$ m/z 649.6448, found 649.6451. IR(KBr): 3423, 2973, 2893, 1834, 1653, 1434, 1178, 1043, 934, 877, 654, 562 cm^{-1}; Mp: 245.2-245.7 °C.



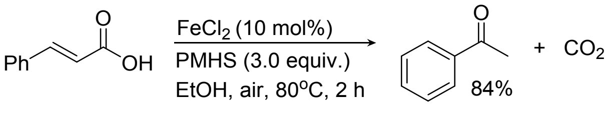
1-(3-Methoxy-4-(((2R,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)phenyl)ethanone (6b): Raw materials **5b** was synthesized by the method from this article.[S14] Following *general procedure A*, **6b** was synthesized by the method from this article[S14] and was isolated as a white solid (99.2 mg, 70%), unknown compound; ^{1}H NMR (400 MHz, DMSO): δ 7.58 (dd, *J* = 8.4 Hz, 2.0 Hz, 1 H), 7.46 (d, *J* = 2.0 Hz, 1 H), 7.18 (d, *J* = 8.4 Hz, 1 H), 5.35 (d, *J* = 4.4 Hz, 1 H), 5.17 (s, 1 H), 5.07 (dd, *J* = 14.8 Hz, 4.8 Hz, 2 H), 4.57 (t, *J* = 5.6 Hz, 1 H), 3.82 (s, 3 H), 3.68-3.64 (m, 1 H), 3.38-3.42 (m, 2 H), 3.29-3.27 (m, 2 H), 3.20-3.17 (m, 1 H), 2.53 ppm (s, 3 H); ^{13}C NMR (100 MHz, DMSO): δ 196.5, 150.6, 148.7, 130.8, 122.7, 114.1, 110.9, 99.4, 77.1, 76.8, 73.1, 69.5, 60.5, 55.6, 26.4 ppm; HRMS (ESI) calcd. for $C_{15}H_{21}O_8^+$ [M + H]$^+$ m/z 329.1236, found 329.1240. IR(KBr):3152, 2374, 1829, 1744, 1554, 1120, 973, 752, 732, 657, 612 cm^{-1}; Mp: 231.3-231.8 °C.



(*R*)-4-Acetylphenyl 4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethyl -hexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (6c): Following *general procedure A*, **6c** was isolated as a white solid (99.2 mg, 78%), unknown compound; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98 (dt, *J* = 8.4 Hz, 2.0 Hz, 2 H), 7.17 (dt, *J* = 8.4 Hz, 2.0 Hz, 2 H), 3.61 (m, 1 H), 2.66-2.43 (m, 2 H), 2.59 (s, 3 H), 1.98-1.74 (m, 7 H), 1.66-1.05 (m, 19 H), 0.97 (d, *J* = 6.4 Hz, 3 H), 0.91 (s, 3 H), 0.65 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.9, 172.2, 154.4, 134.5, 129.9, 121.7, 71.7, 56.4, 55.8, 42.7, 42.0, 40.3, 40.1, 36.3, 35.8, 35.29, 35.27, 34.5, 31.3, 30.8, 30.4, 28.2, 27.1, 26.6, 26.3, 24.1, 23.3, 20.7, 18.3, 12.0 ppm; HRMS (ESI) calcd. for $C_{32}H_{47}O_4^+$ [M + H]$^+$ m/z 495.3468, found 495.3473. IR(KBr):3397, 2940, 2854, 1789, 1654, 1463, 1421, 970, 775, 711, 603 cm^{-1}; Mp: 237.5-237.9 °C.

4. Preliminary Mechanistic Studies

(1) CO_2 detection



2a **3a**

Following *general procedure A*, a 25mL flask was charge with $FeCl_2$ (0.025 mmol), **2a** (0.25 mmol), and PMHS (0.75 mmol) in EtOH (2.0 mL), and sealed with a rubber stopper. The reaction was stirred at 80 °C for 12 h. Head space sampling was taken from the reaction flask and analyzed by GC (gas chromatography) (Figure S1, black trace). The rest peak is identical to the GC of the CO_2 standard sample, indicating that CO_2 is generated in the reaction. [GC analysis was performed on an TDX-01(GC-7920 (Beijing Zhong Jiao Jin Yuan Technology Co., Ltd., Beijing, China), 1.5 m × 3 mm)] capillary column.

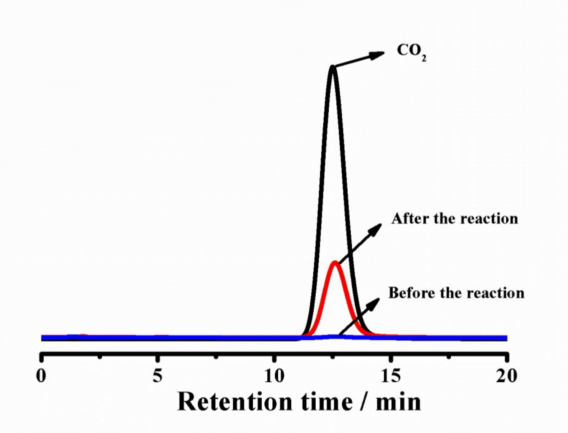
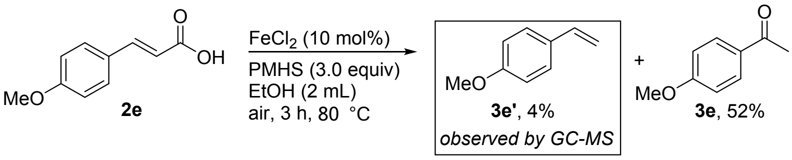


Figure S1. GC analysis of acetaldehyde in the reaction mixture

(2) Alkene intermediate detection



Following *general procedure A*, a 25mL flask was charge with $FeCl_2$ (0.025 mmol), **2e** (0.25 mmol), and PMHS (0.75 mmol) in EtOH (2.0 mL), and sealed with a rubber stopper. The reaction was stirred at 80 °C for 3 h. Then, the resulting reaction mixture was analyzed by GC-MS (gas chromatography-mass spectrometer) (Figure S2). Minor 4-methoxystyrene was observed and its mass spectra [M: 134] is consistant with a previous report.[S15].

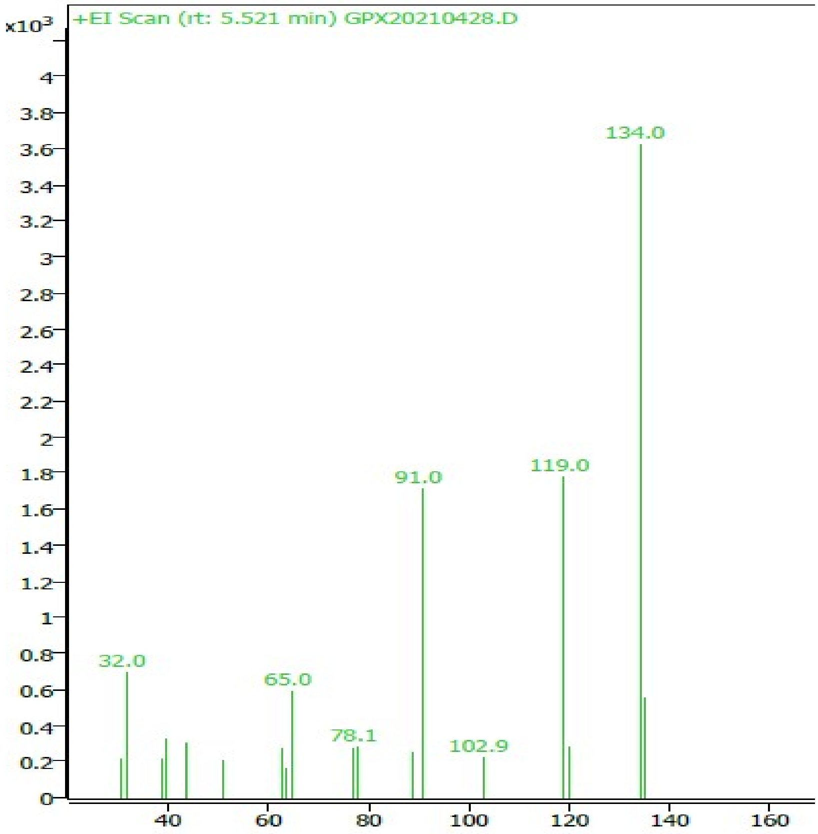


Figure S2. GC-MS analysis of 4-methoxystyrene in the reaction mixture

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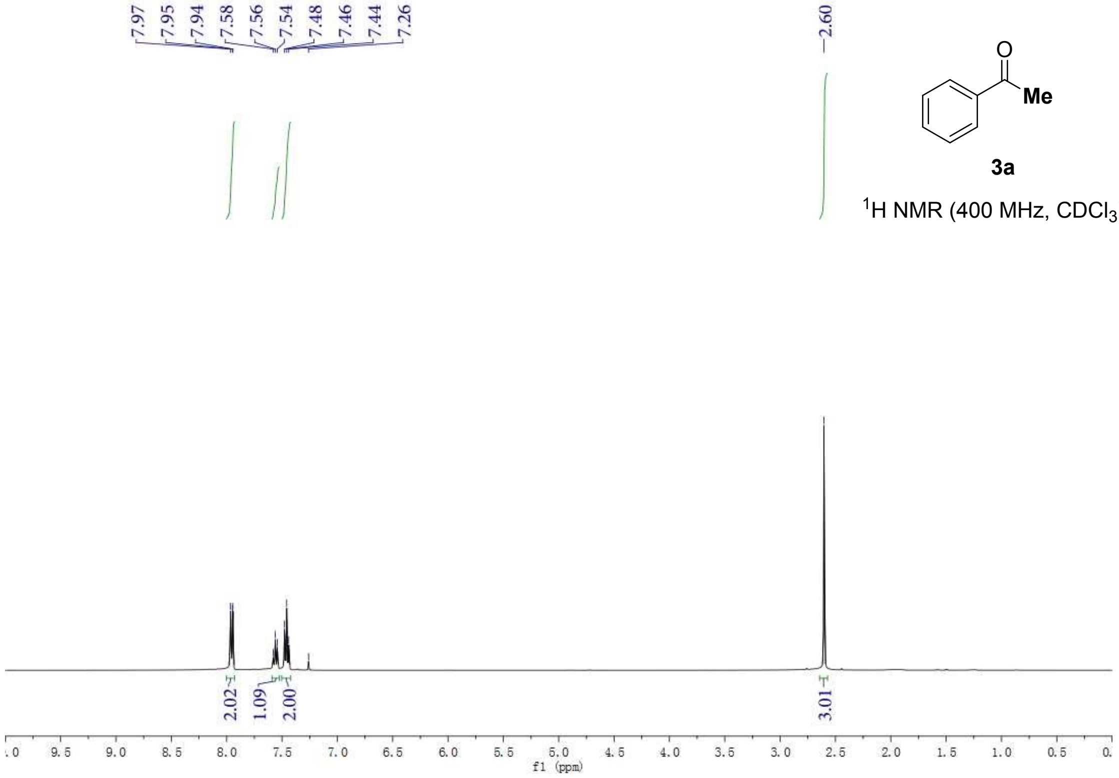
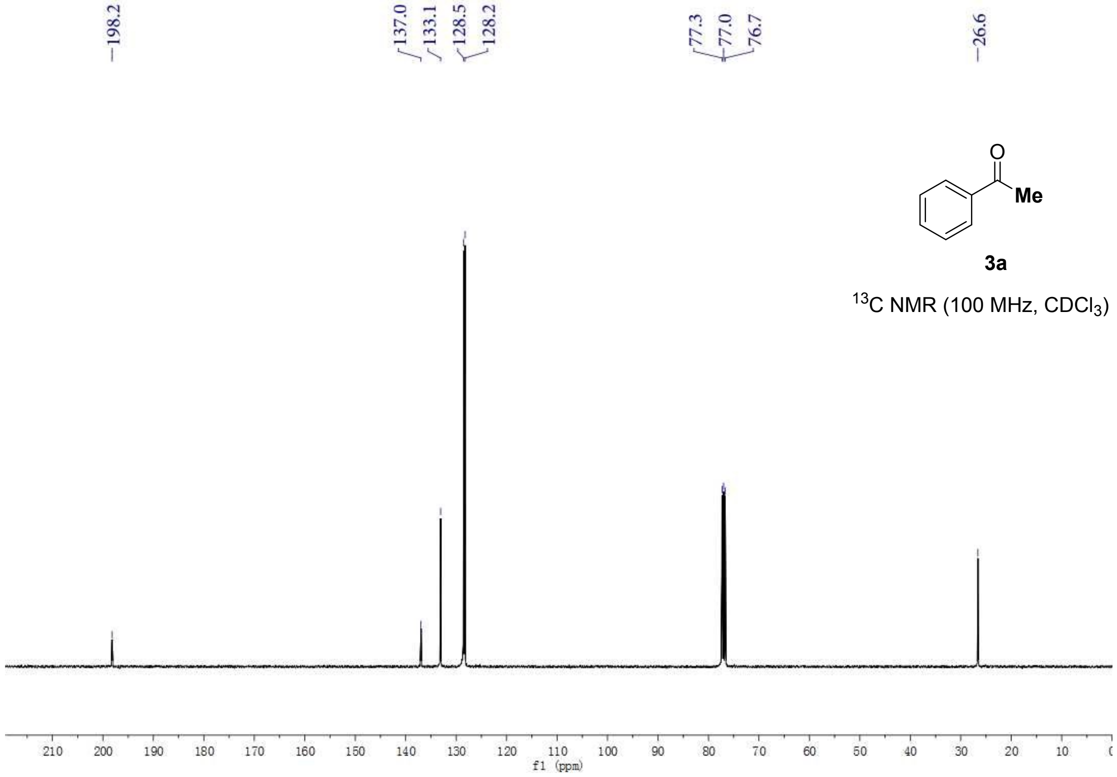
6. Copies of NMR Spectra



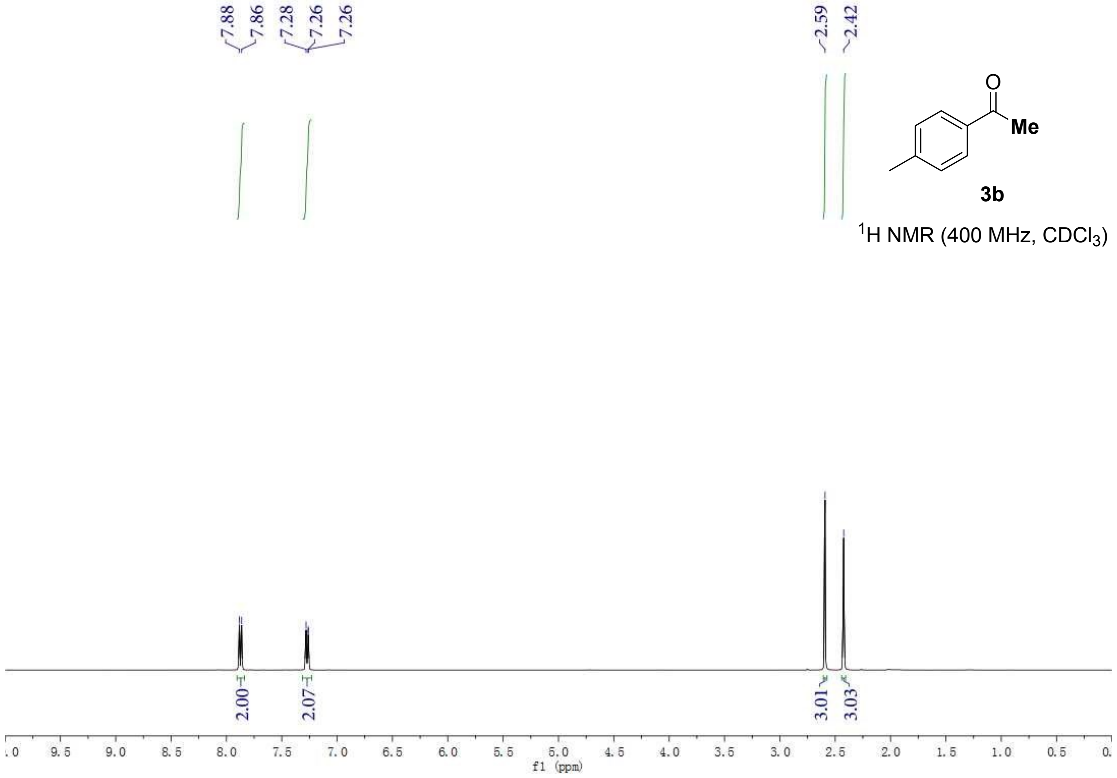
3a

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



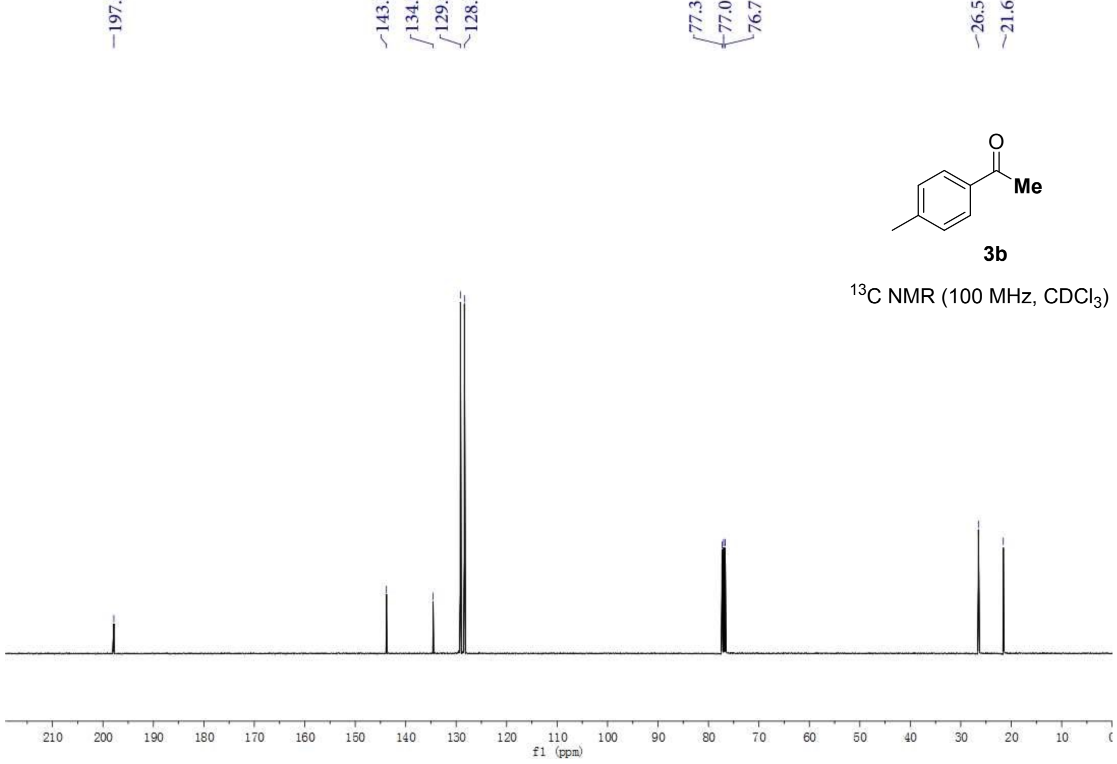
3a

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



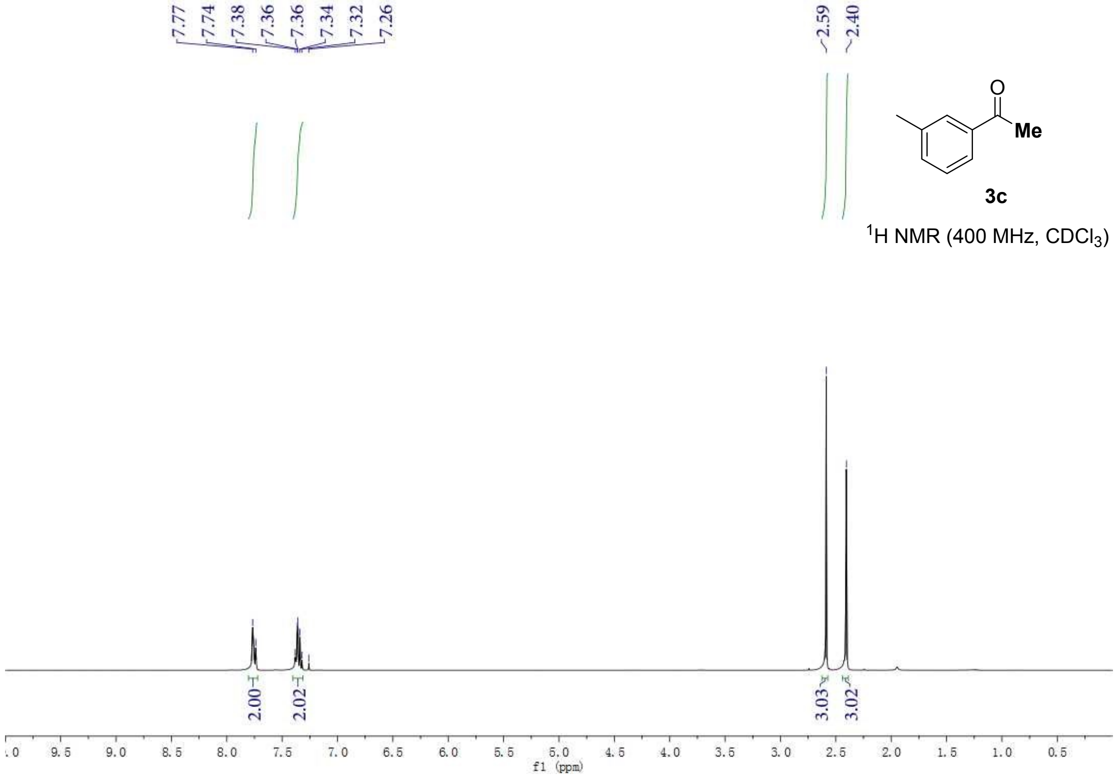
3b

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



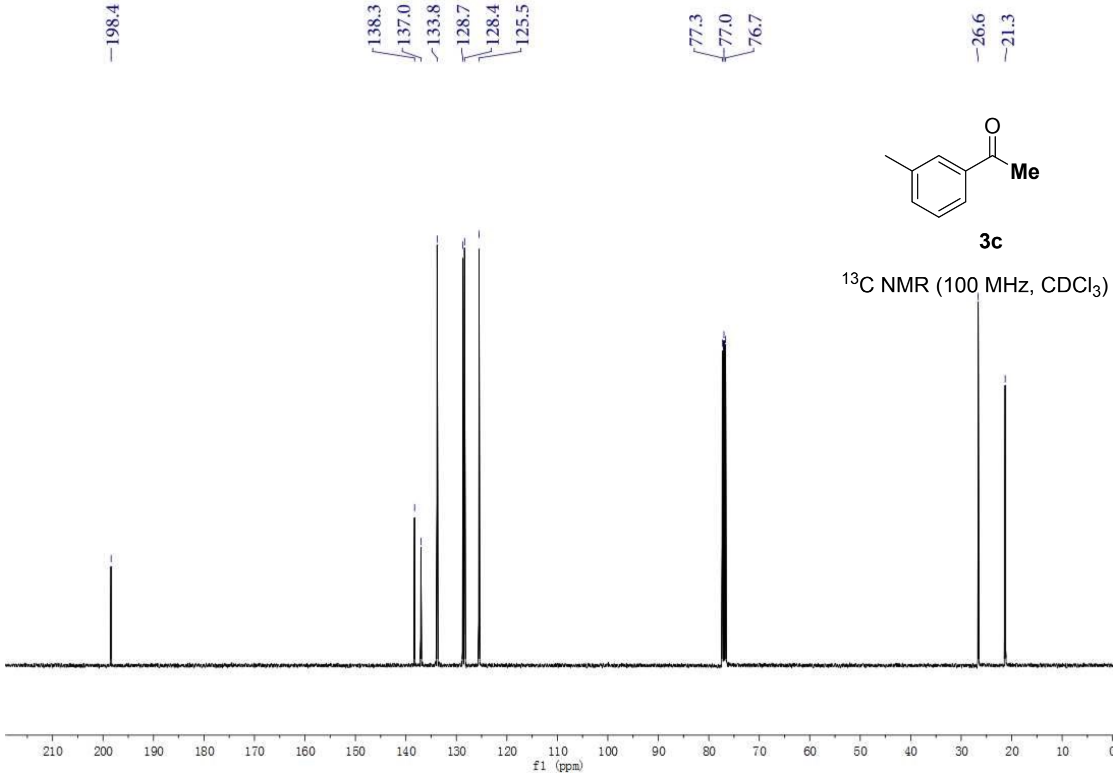
3b

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



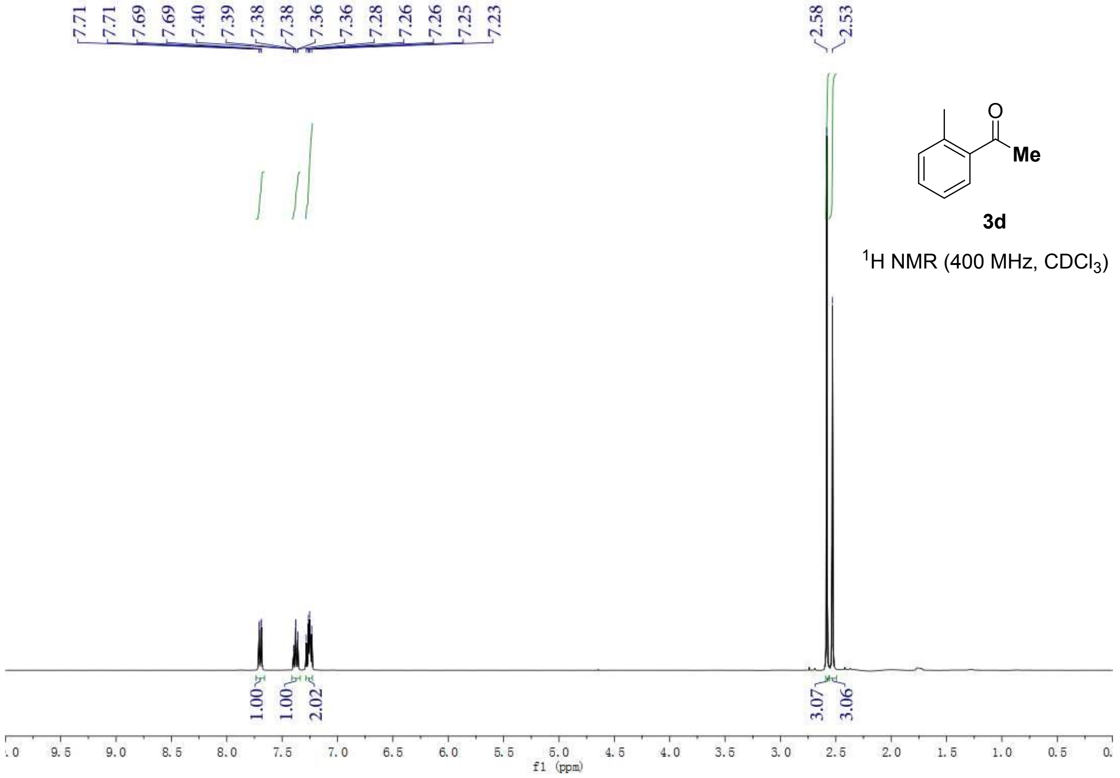
3c

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



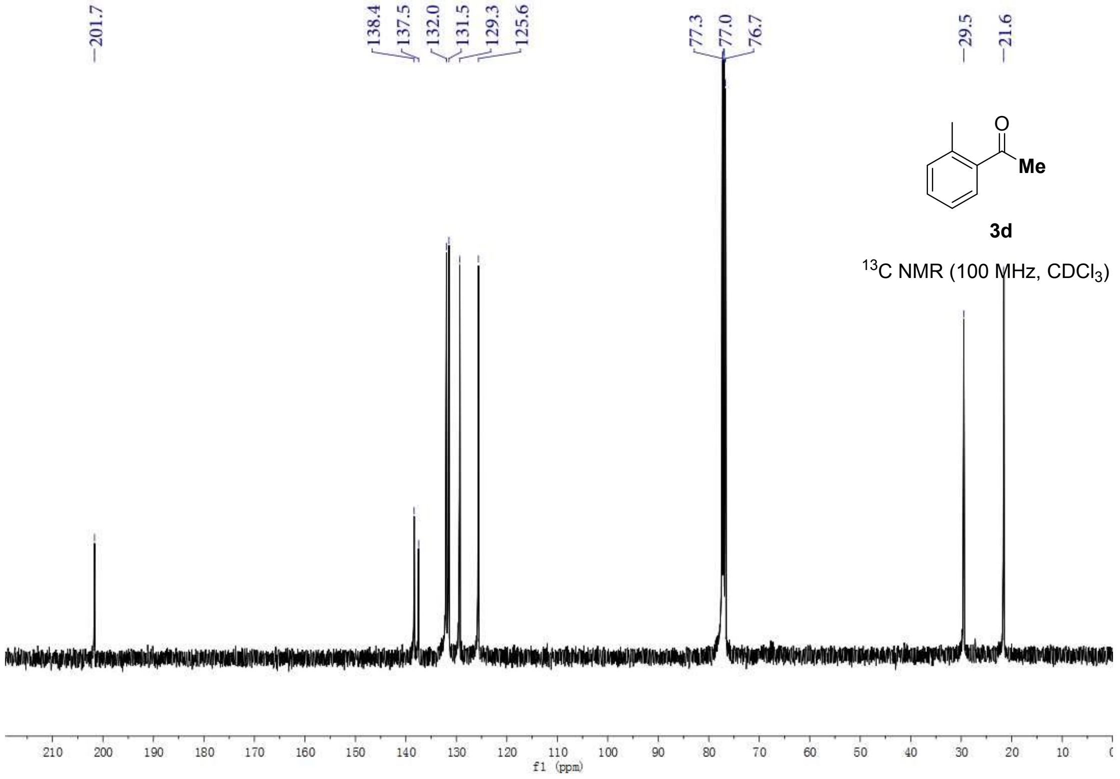
3c

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



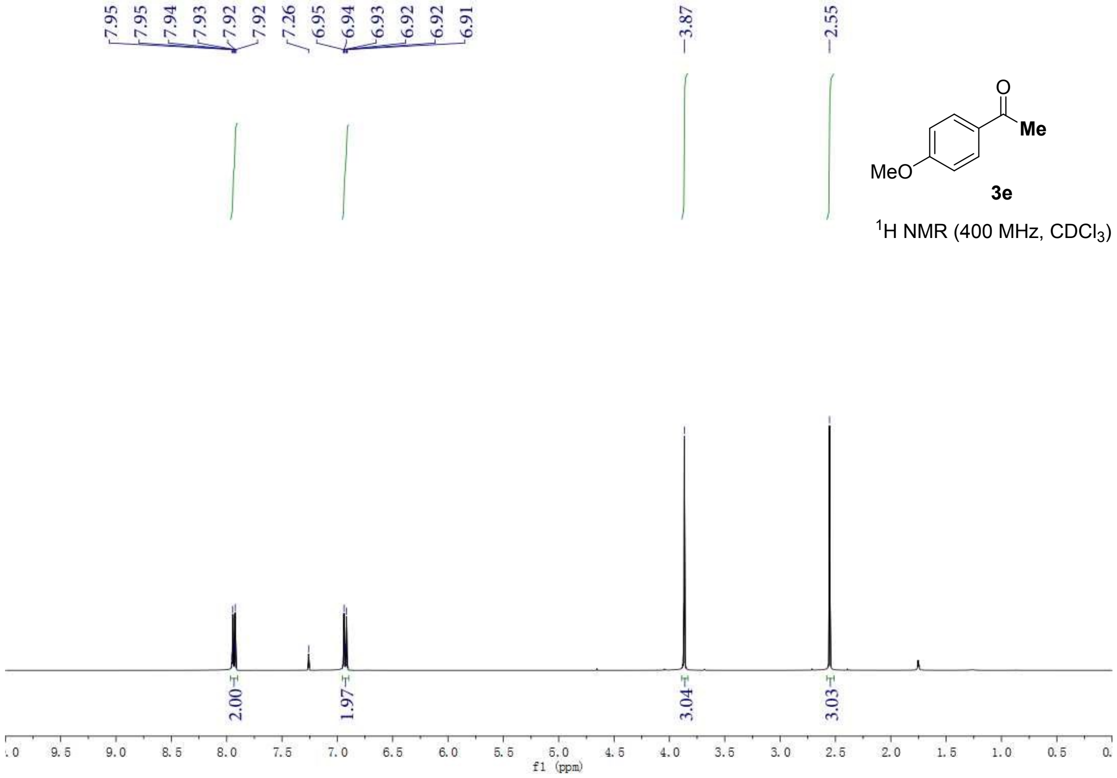
3d

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



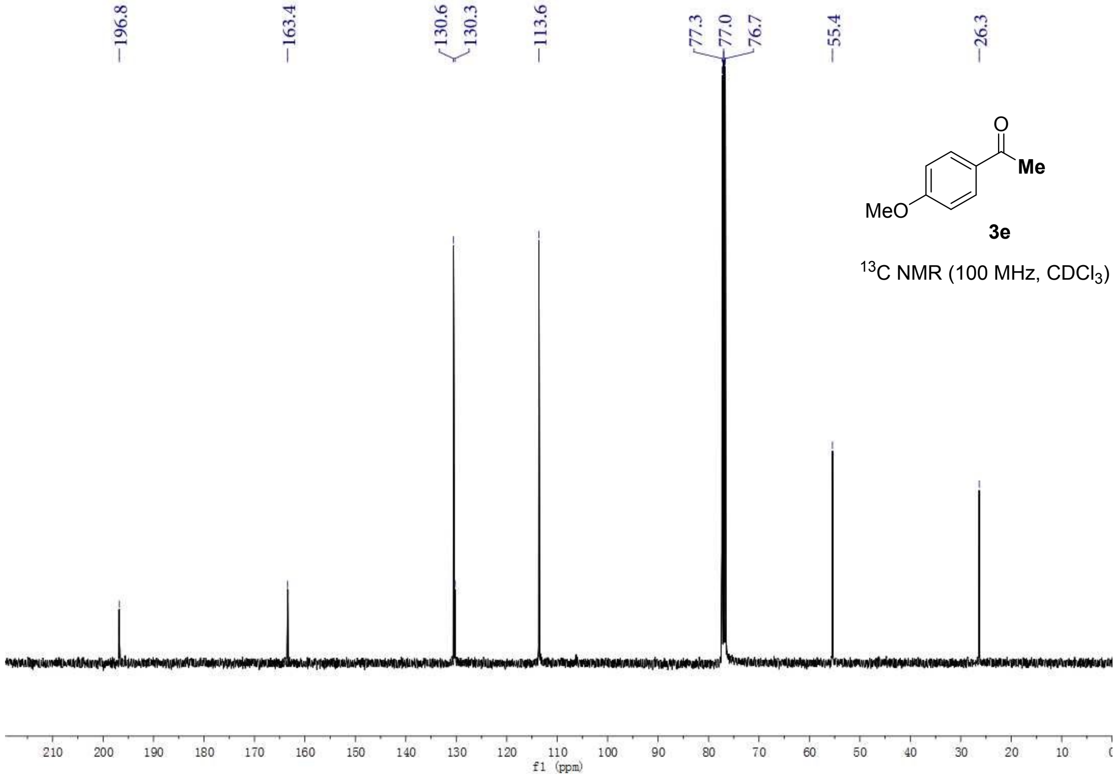
3d

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



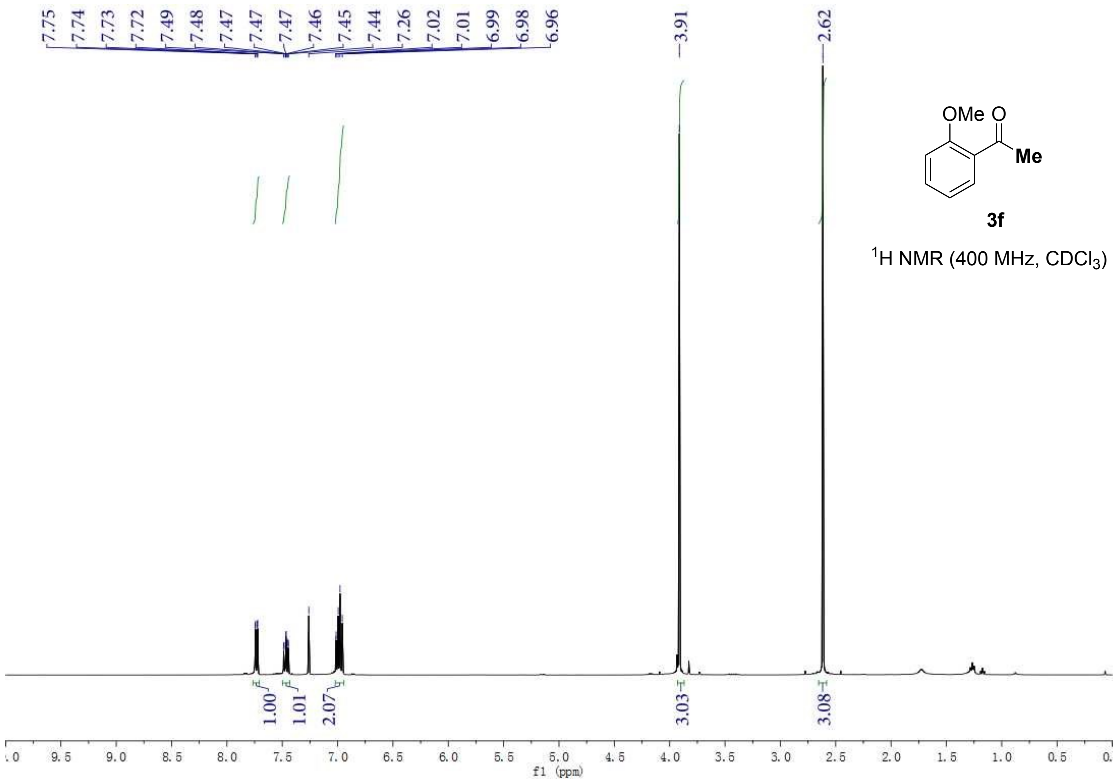
3e

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



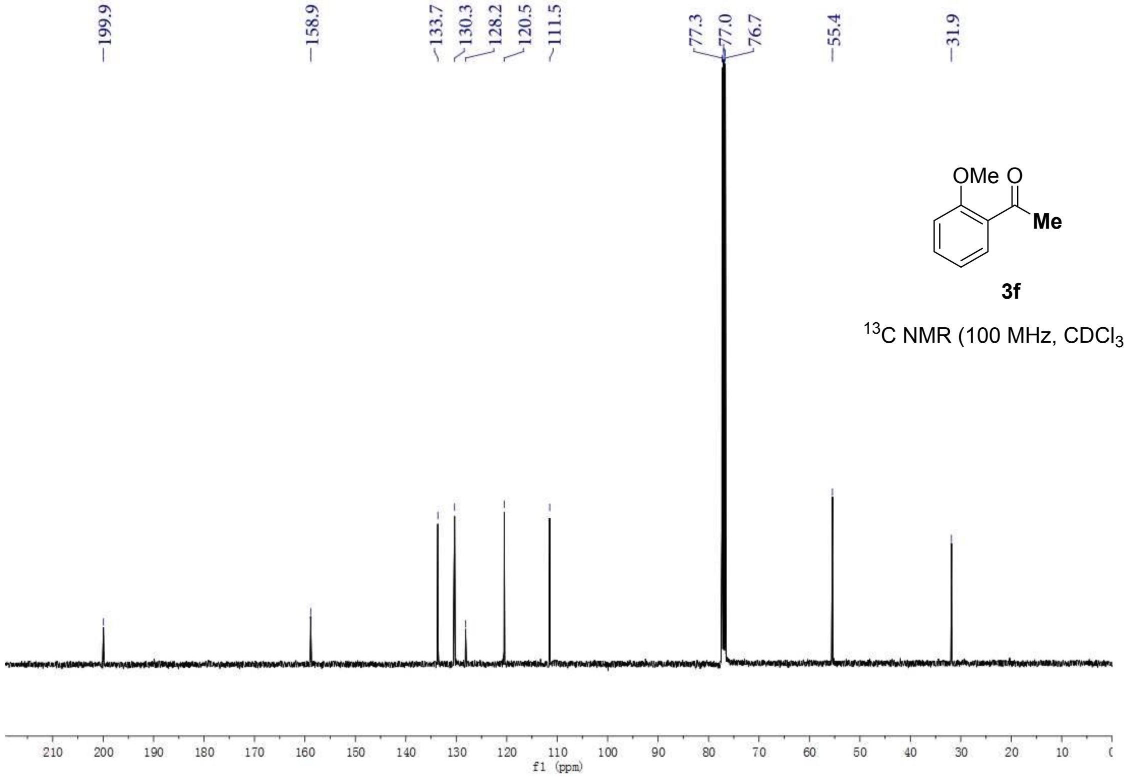
3e

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



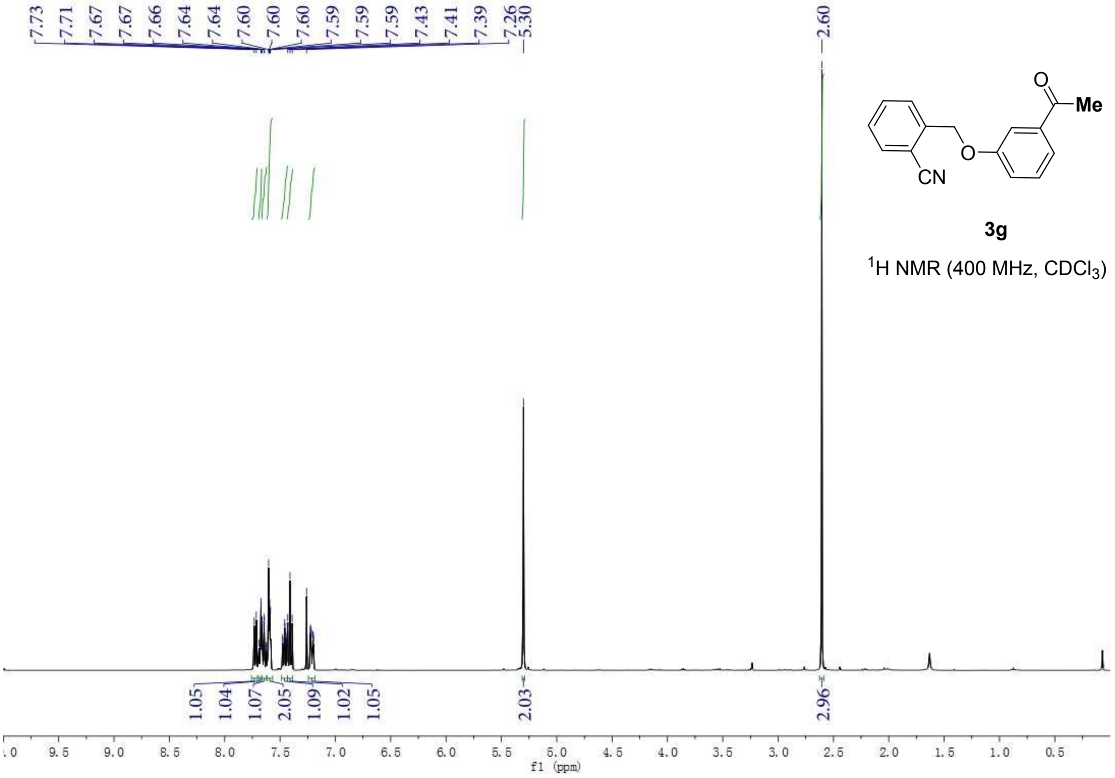
3f

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



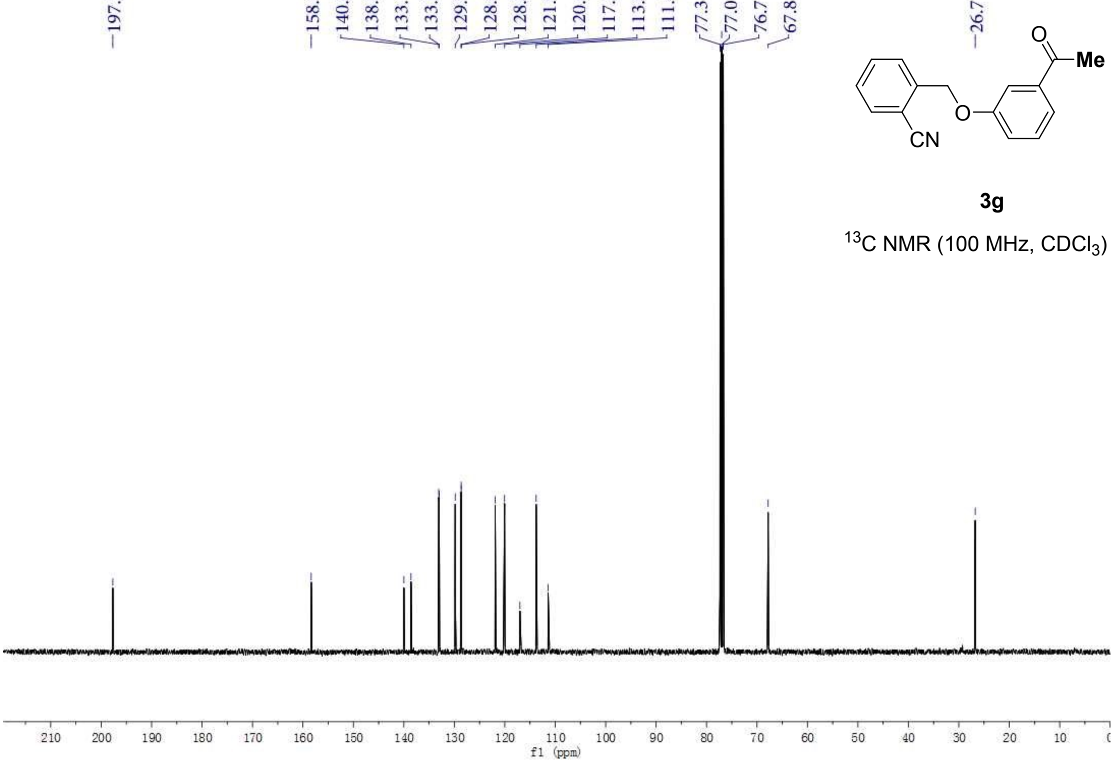
3f

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



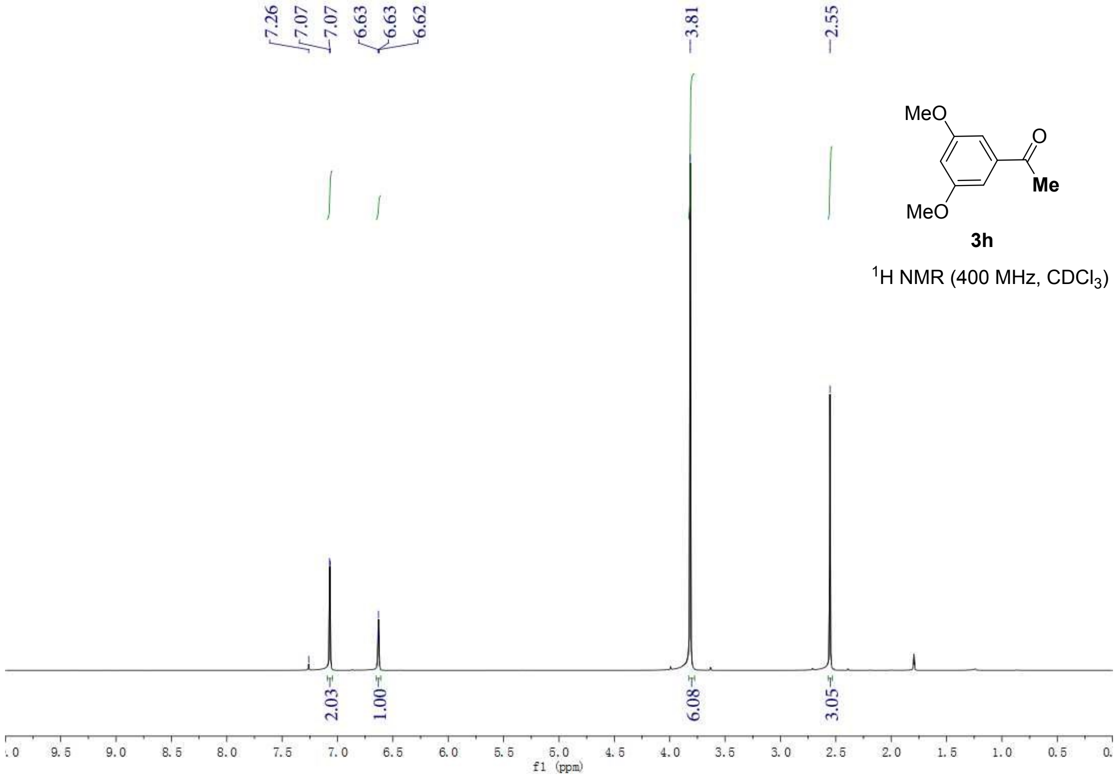
3g

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



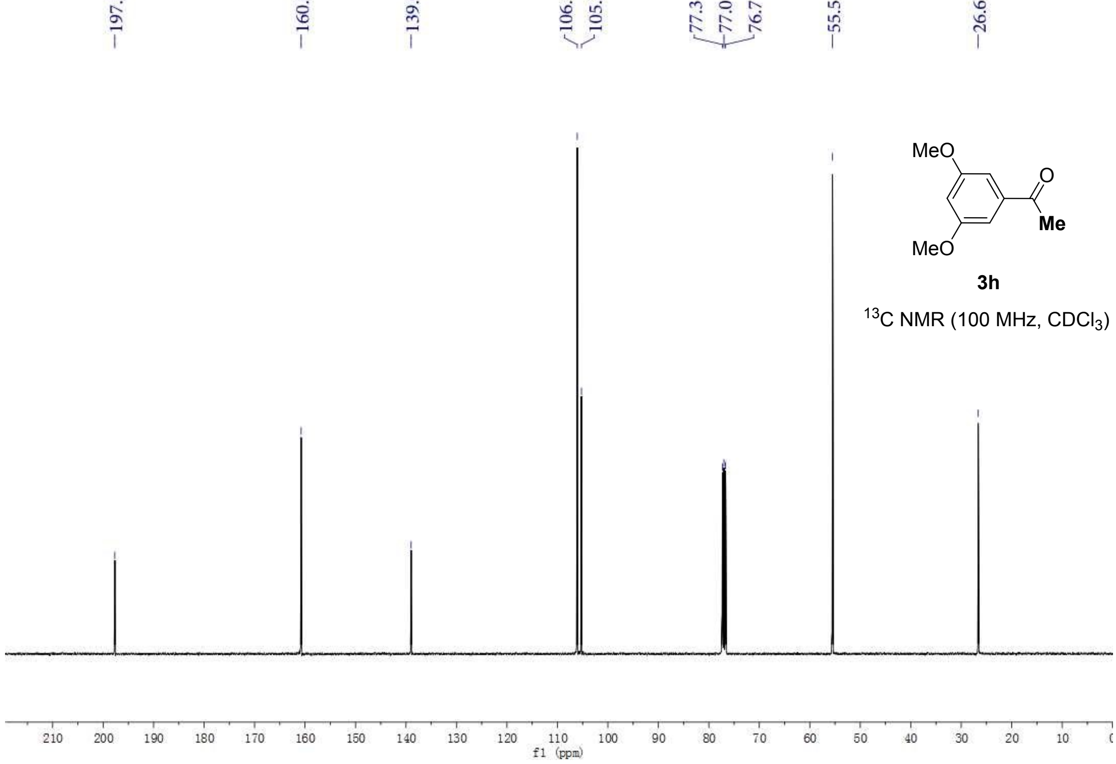
3g

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



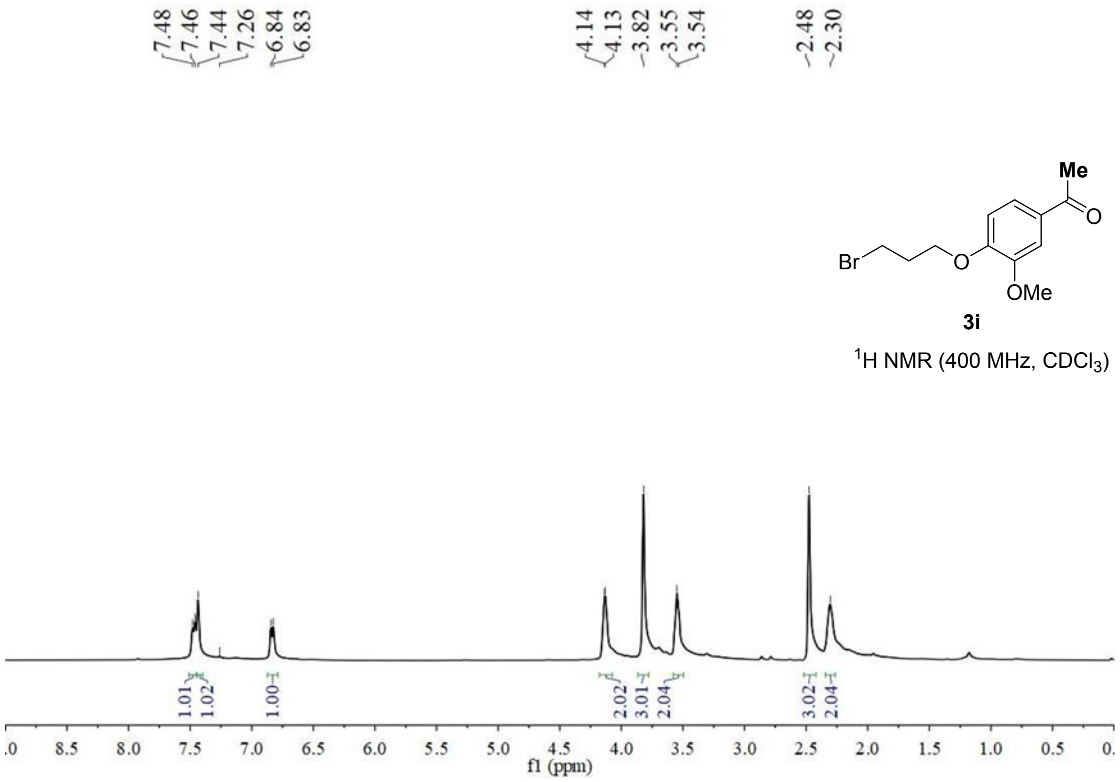
3h

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



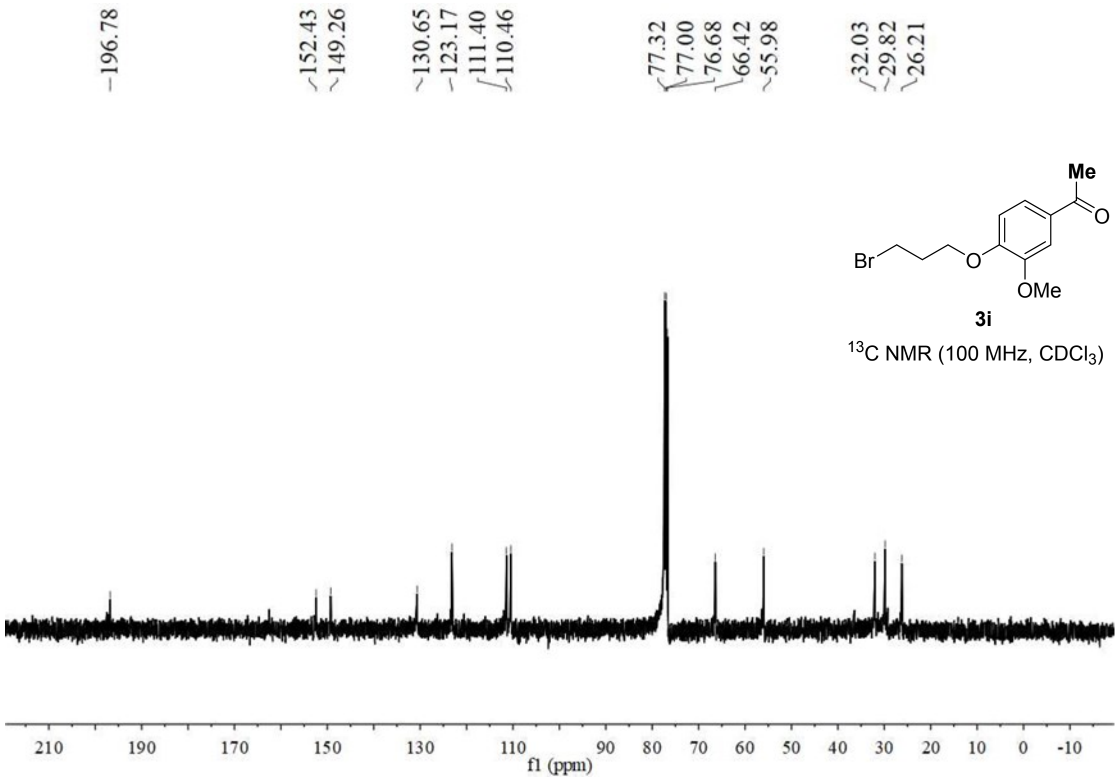
3h

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



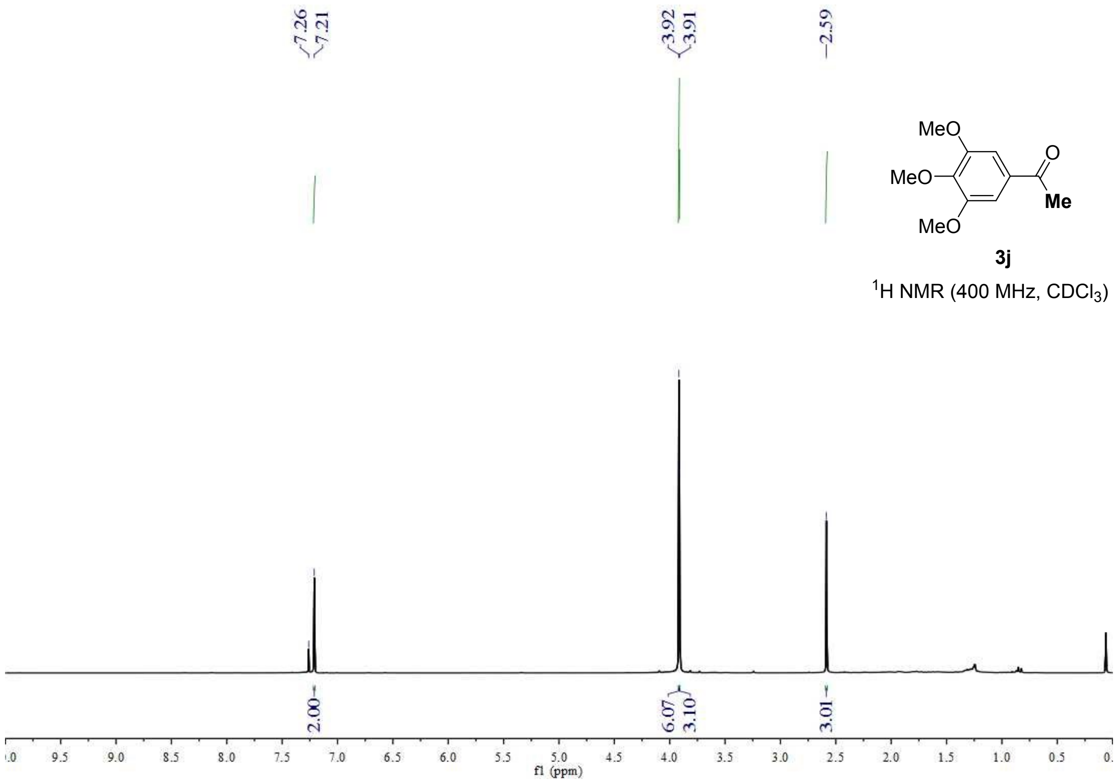
3i

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



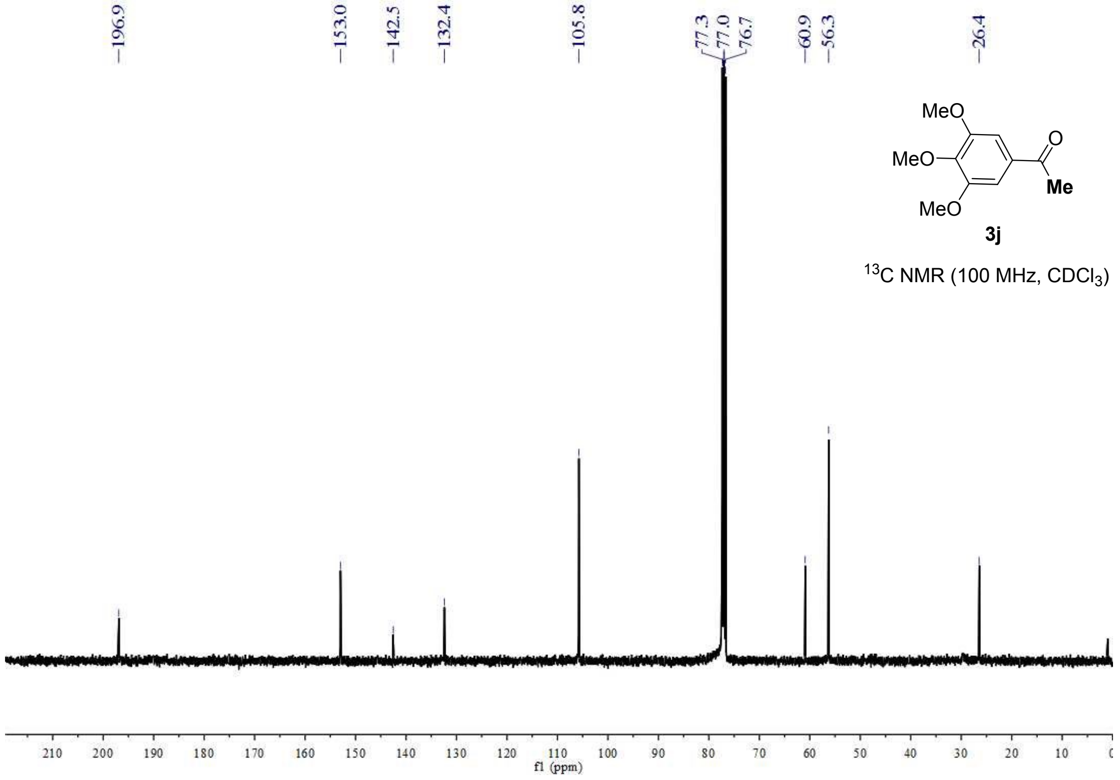
3i

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



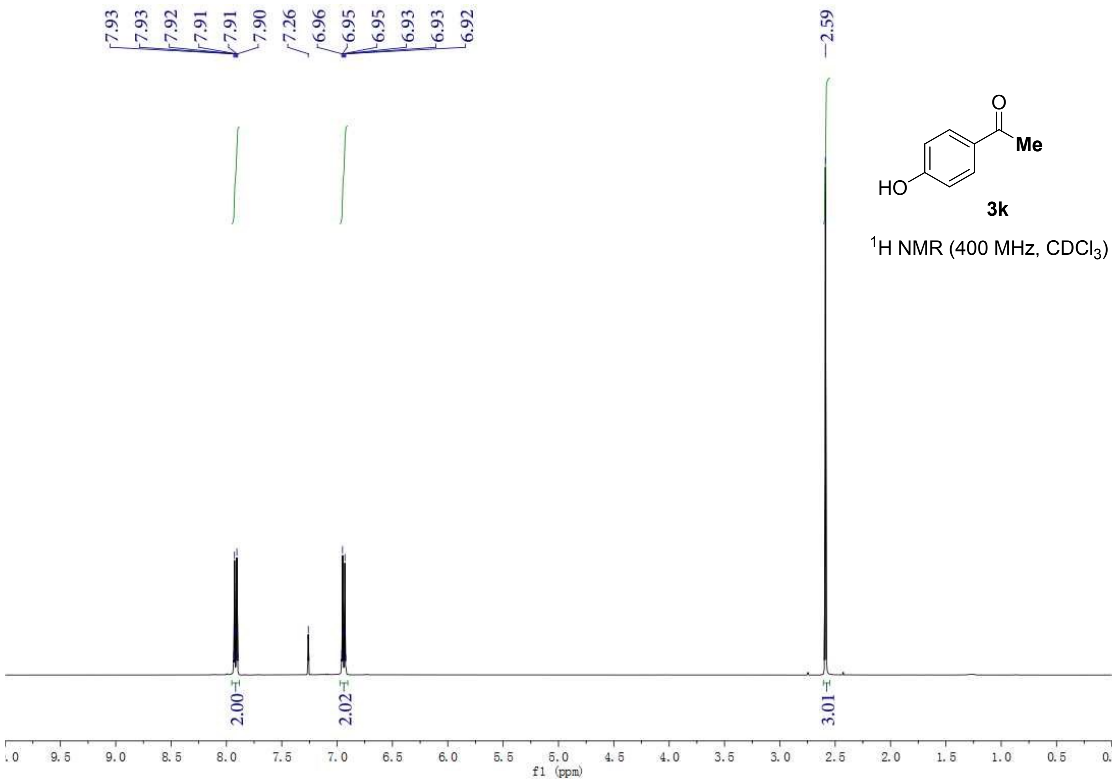
3j

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



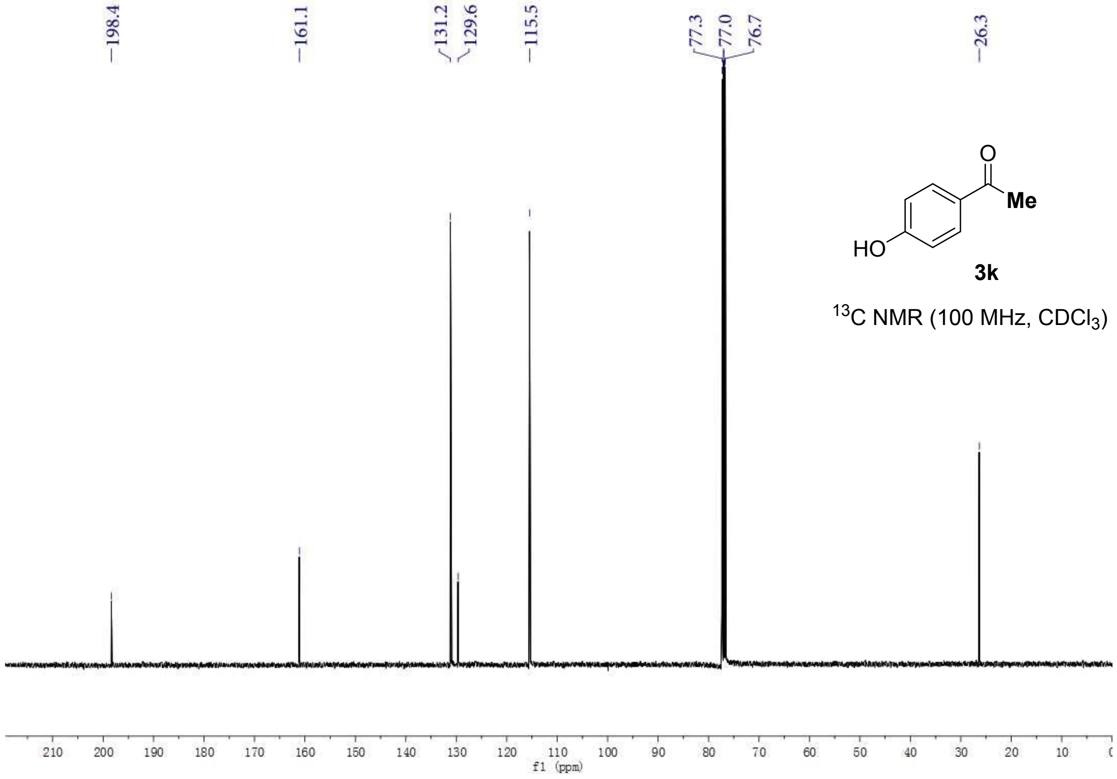
3j

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



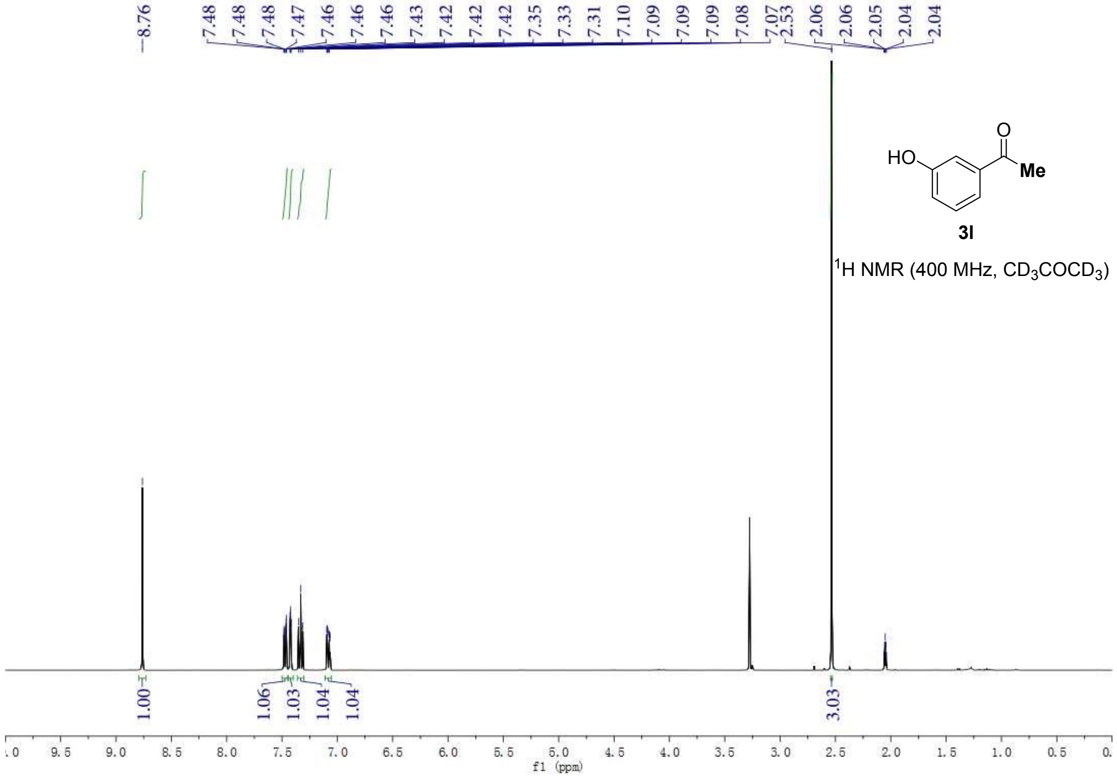
3k

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



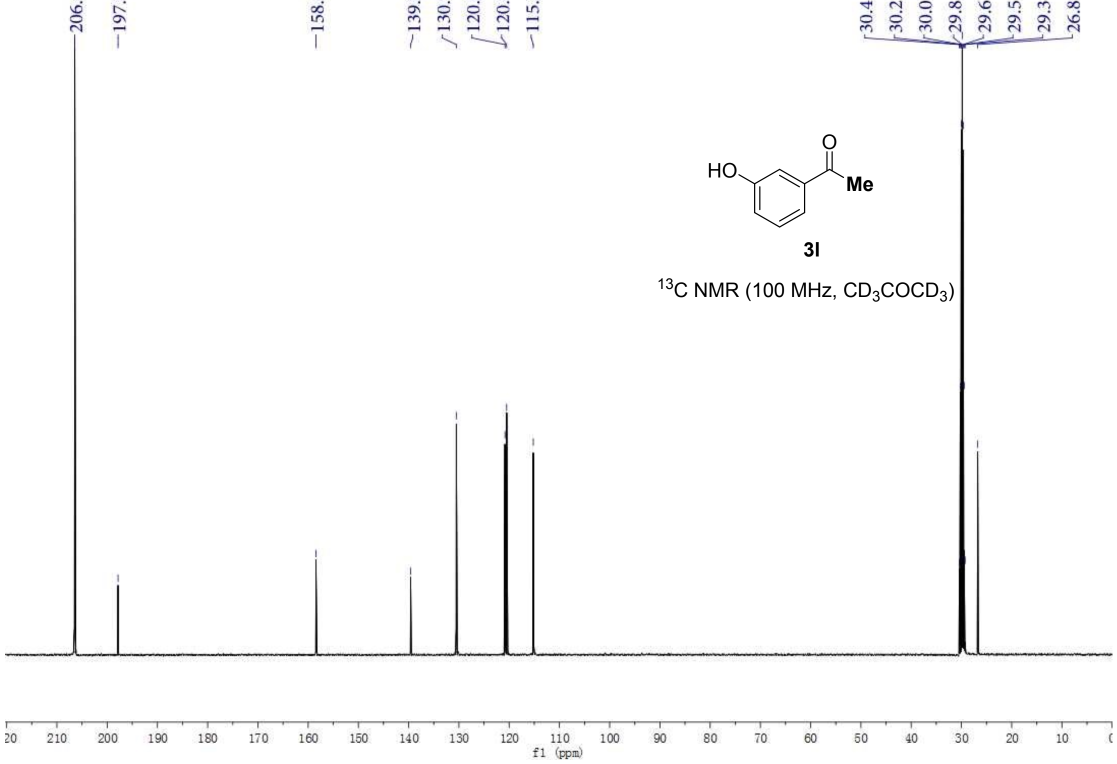
3k

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



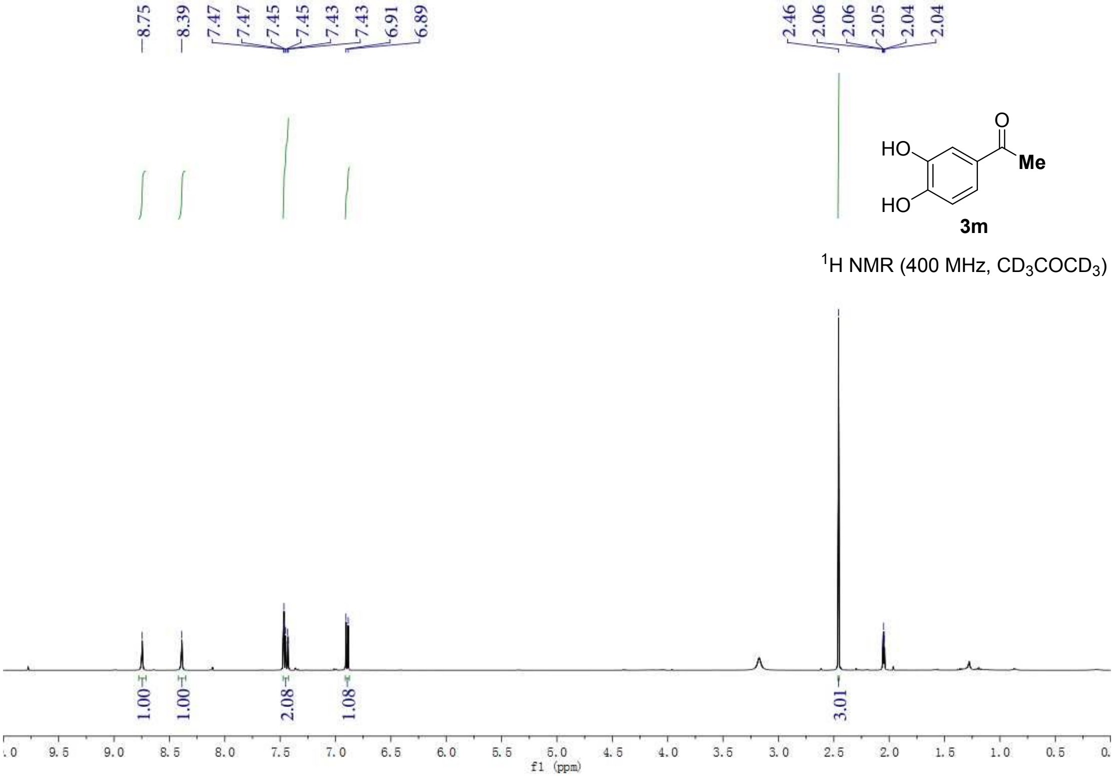
3l

^{1}H NMR (400 MHz, CD_3COCD_3)



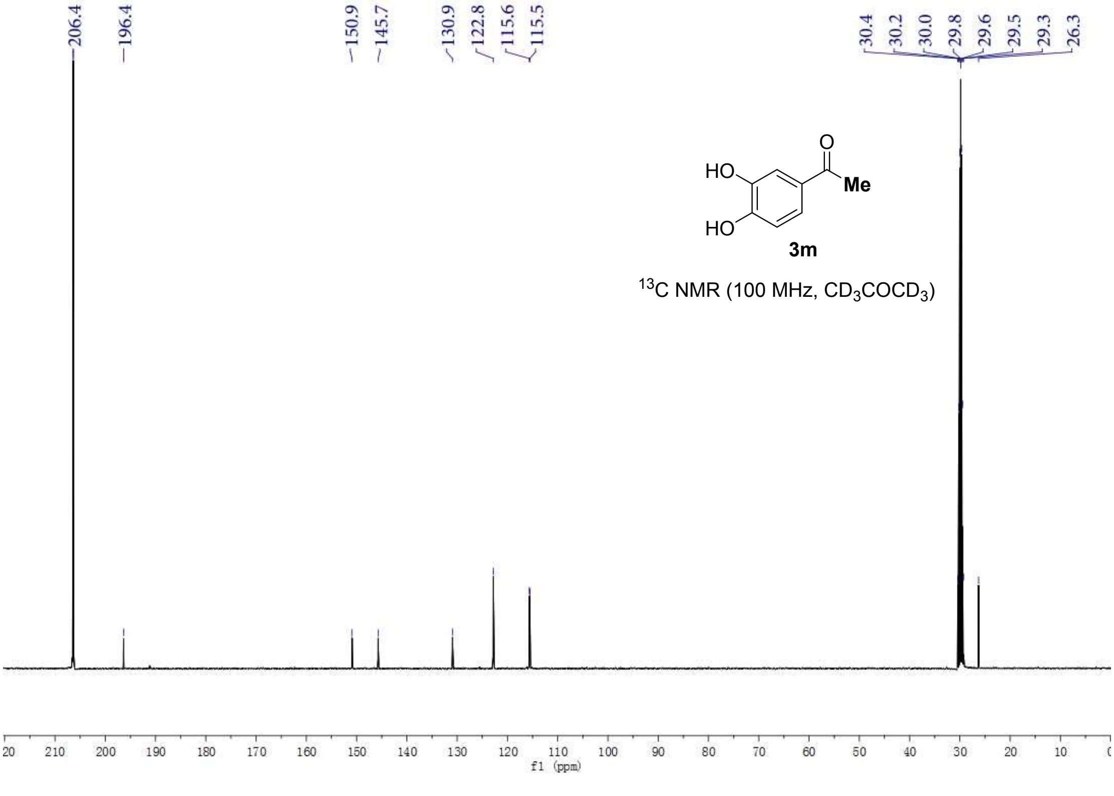
3l

^{13}C NMR (100 MHz, CD_3COCD_3)



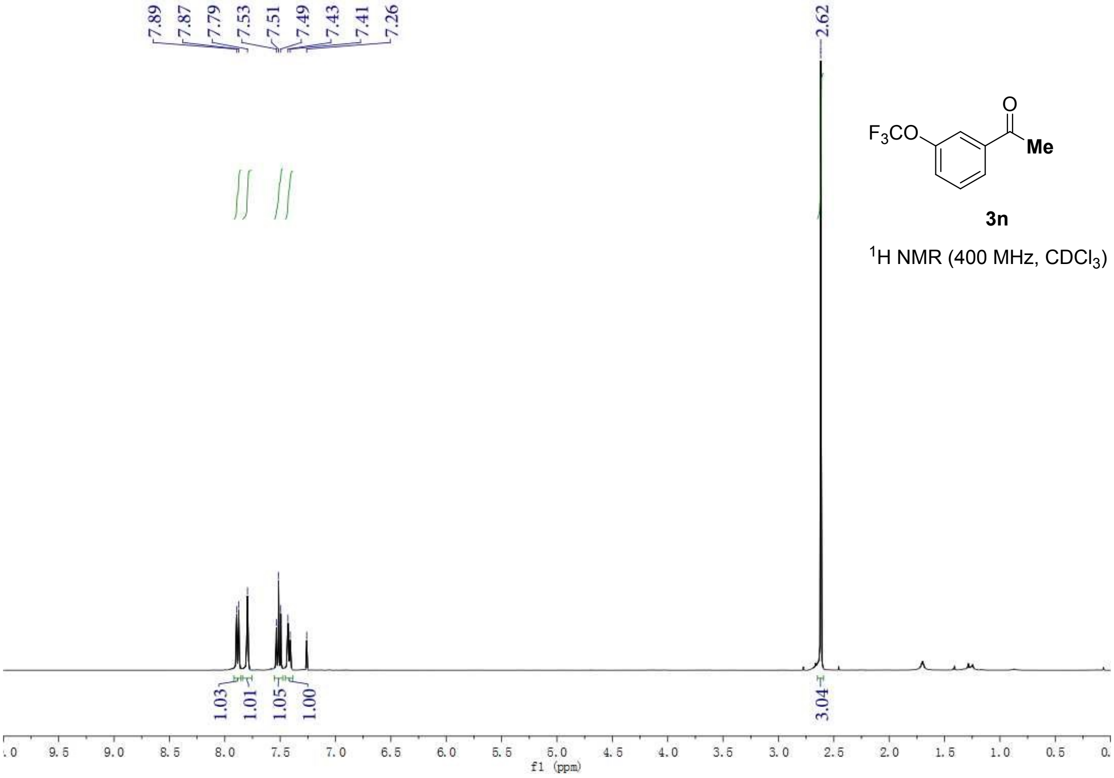
3m

^{1}H NMR (400 MHz, CD_3COCD_3)



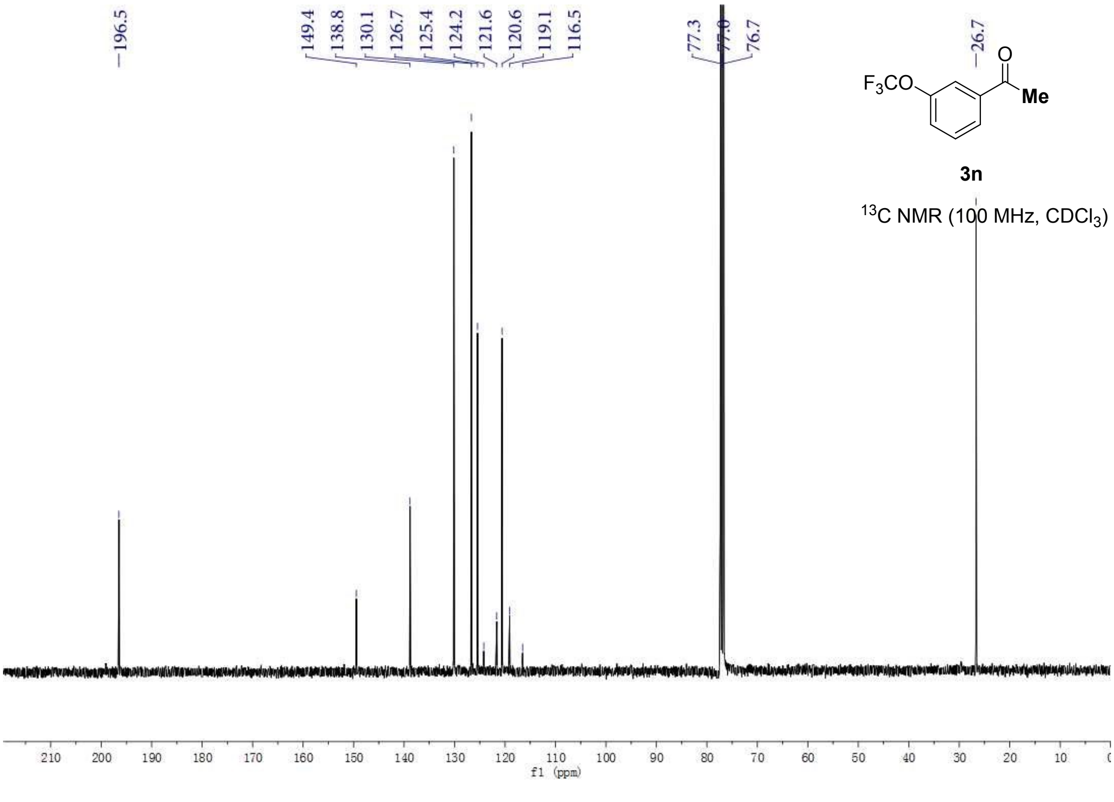
3m

^{13}C NMR (100 MHz, CD_3COCD_3)



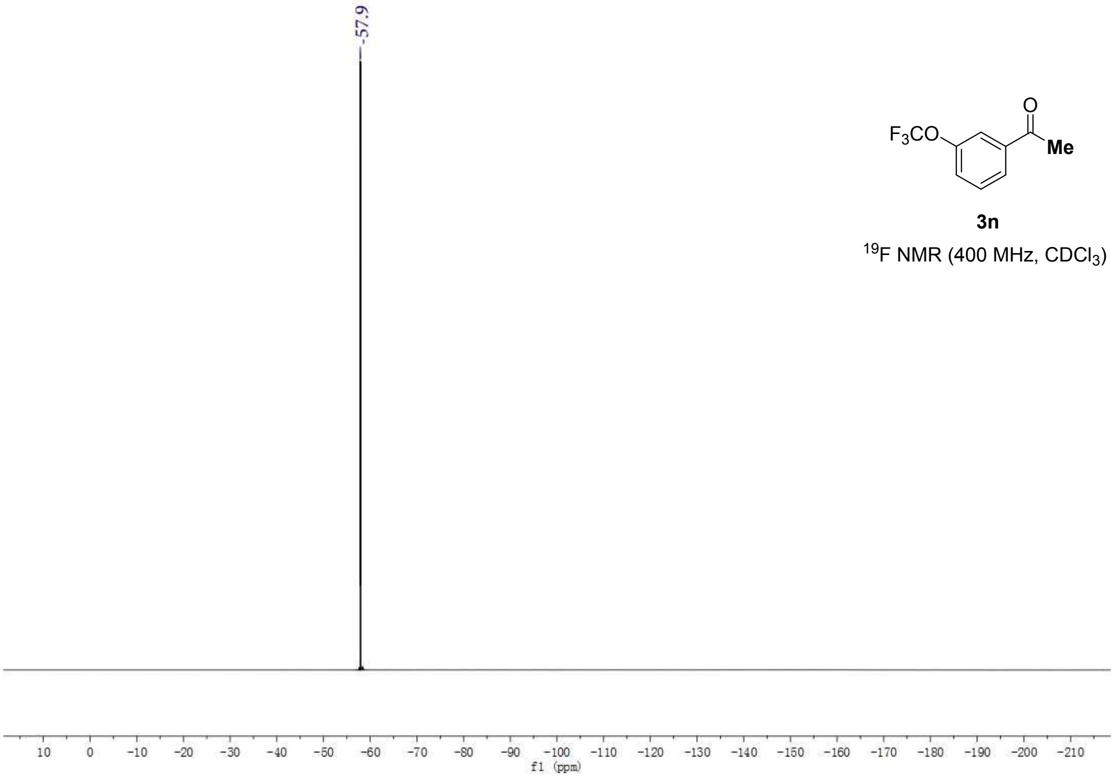
3n

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



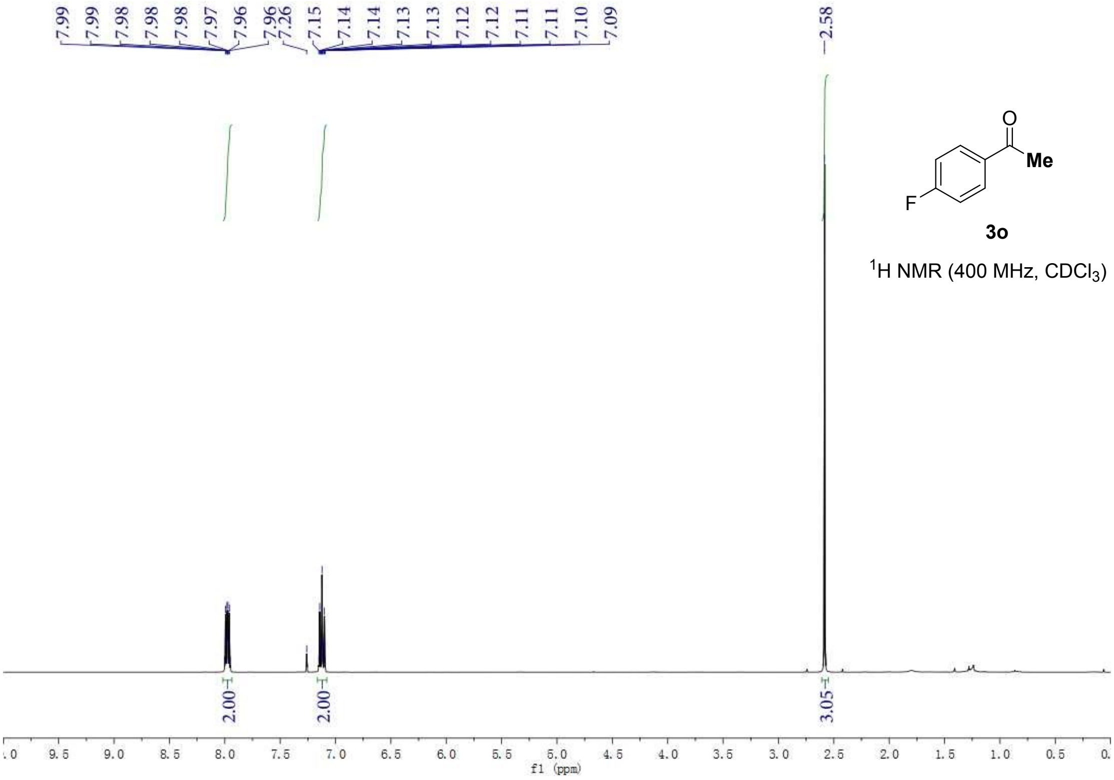
3n

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



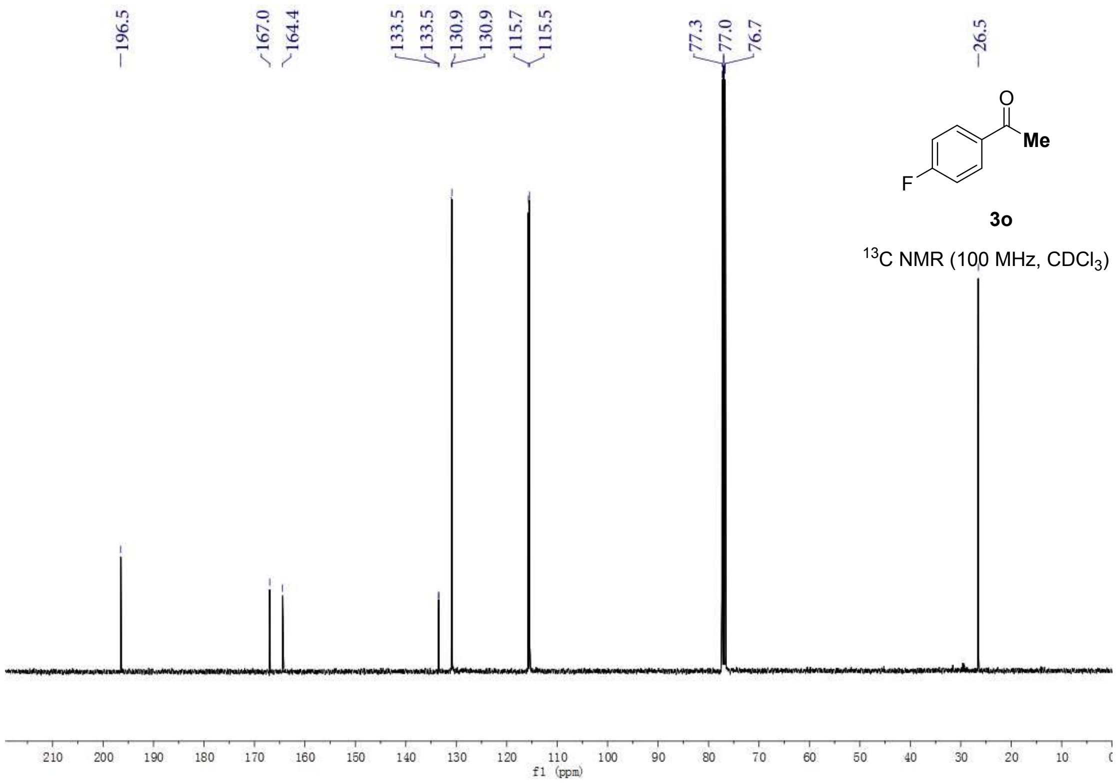
3n

^{19}F NMR (400 MHz, $CDCl_3$)

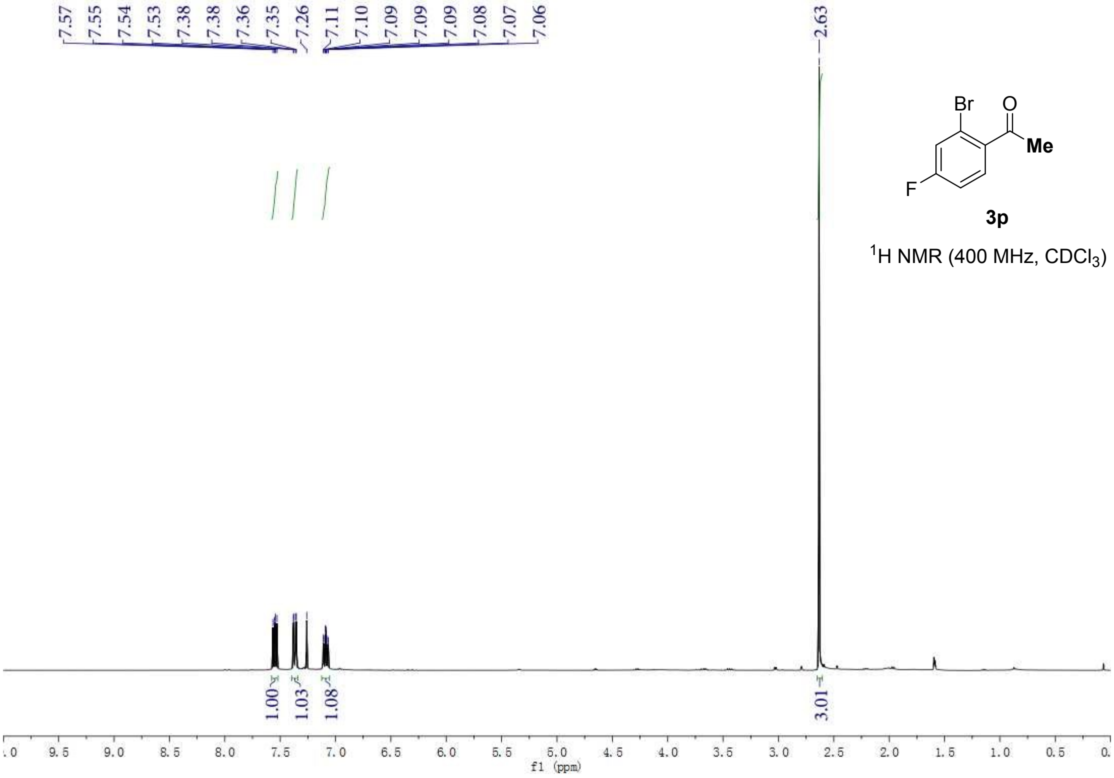


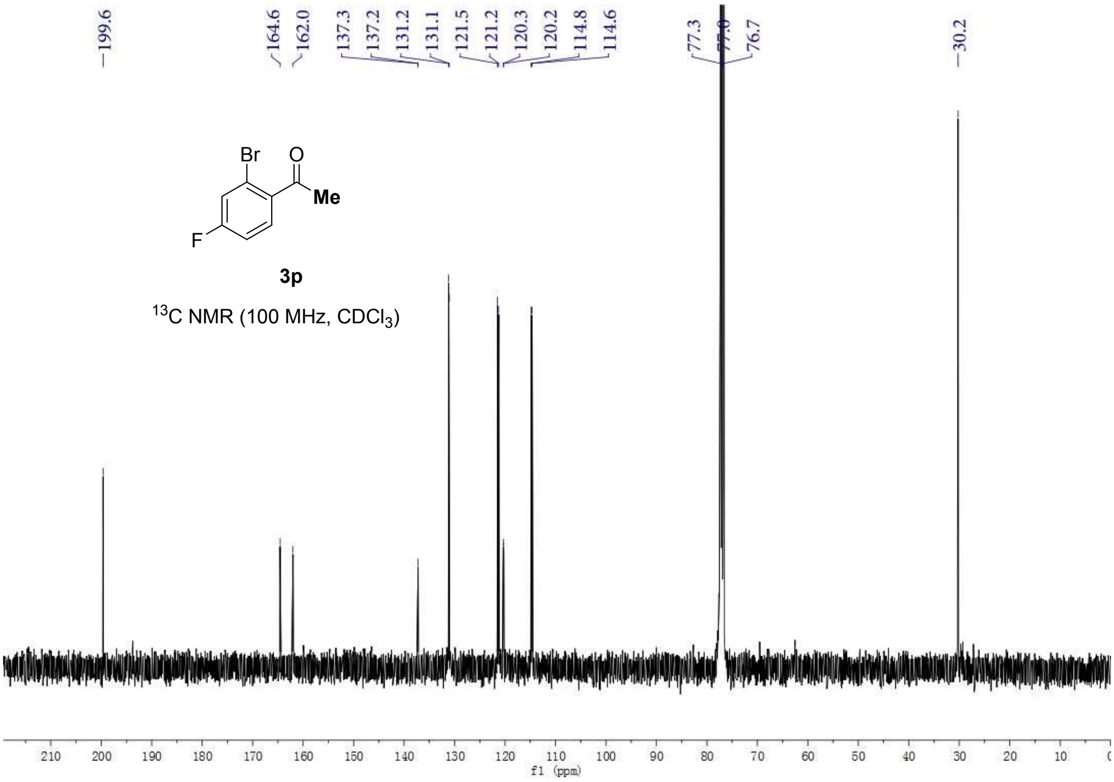
3o

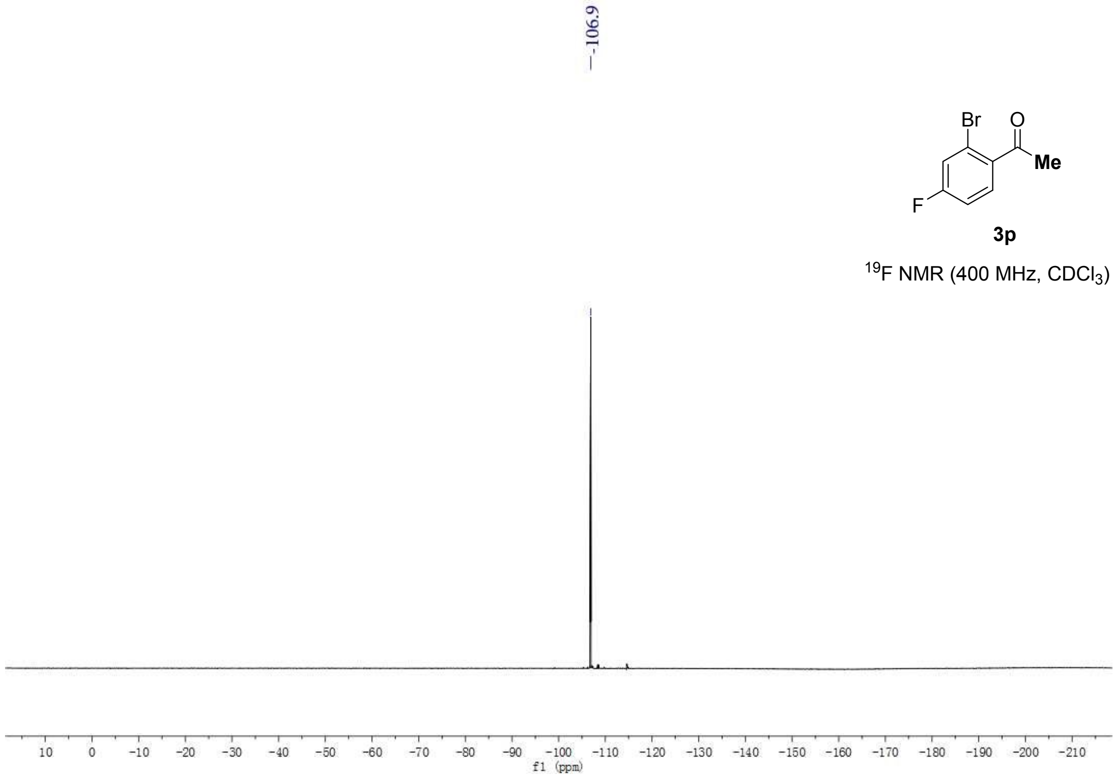
^{1}H NMR (400 MHz, $CDCl_3$)


196.5
167.0
164.4
133.5
133.5
130.9
130.9
115.7
115.5
77.3
77.0
76.7
26.5
O
Me
F
3o
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-105.3
O
Me
F
3o
^{19}F NMR (400 MHz, CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

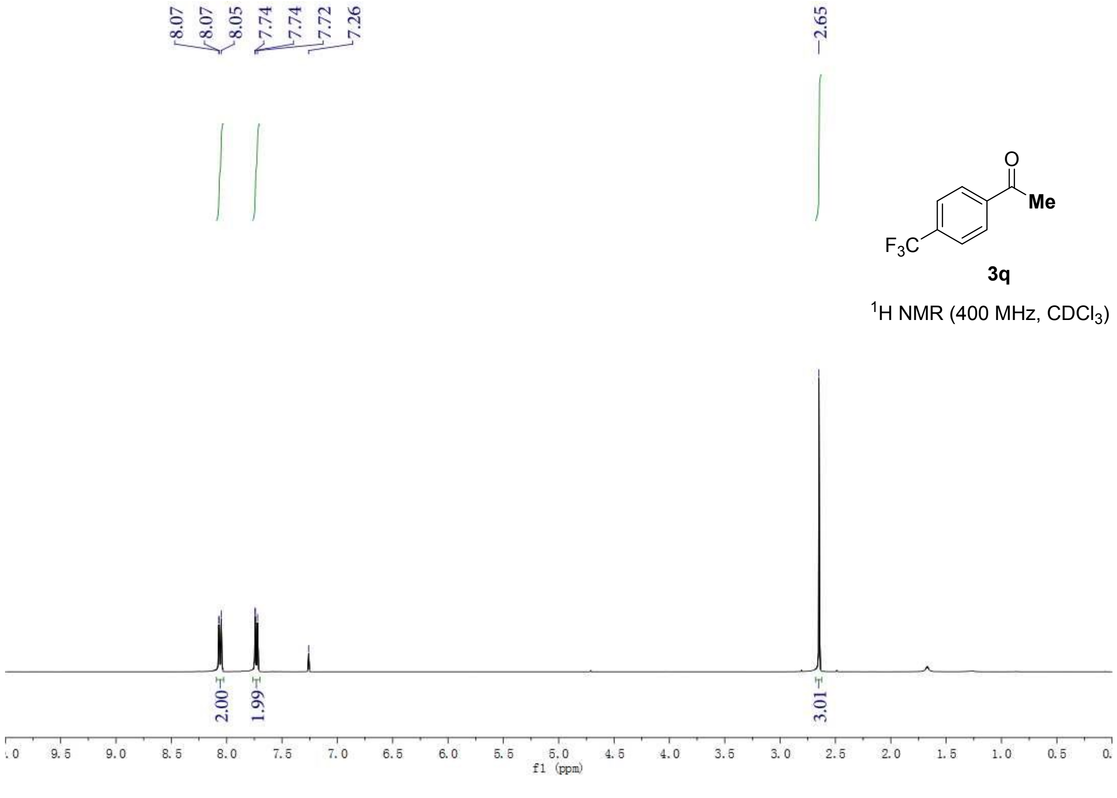

7.57
7.55
7.54
7.53
7.38
7.38
7.36
7.35
7.26
7.11
7.10
7.09
7.09
7.09
7.08
7.07
7.06
2.63
Br
O
Me
F
3p
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.03
1.08
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


199.6
164.6
162.0
137.3
137.2
131.2
131.1
121.5
121.2
120.3
120.2
114.8
114.6
77.3
77.0
76.7
30.2
Br
O
Me
F
3p
^{13}C NMR (100 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



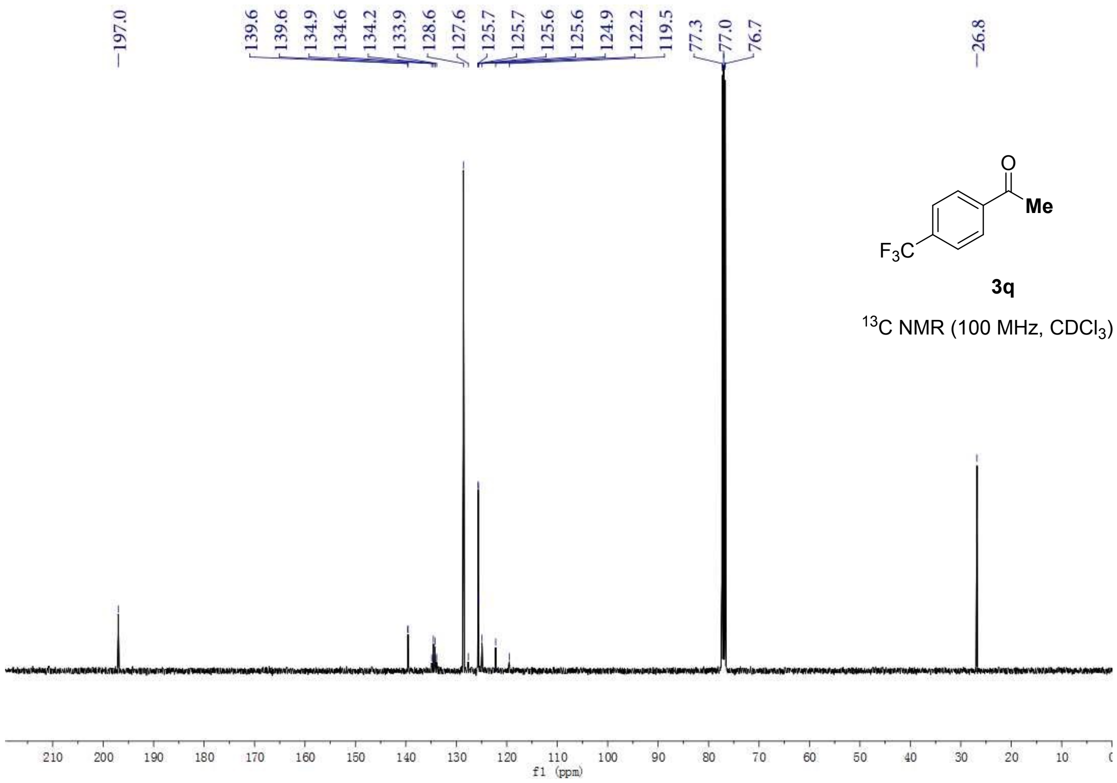
3p

^{19}F NMR (400 MHz, $CDCl_3$)



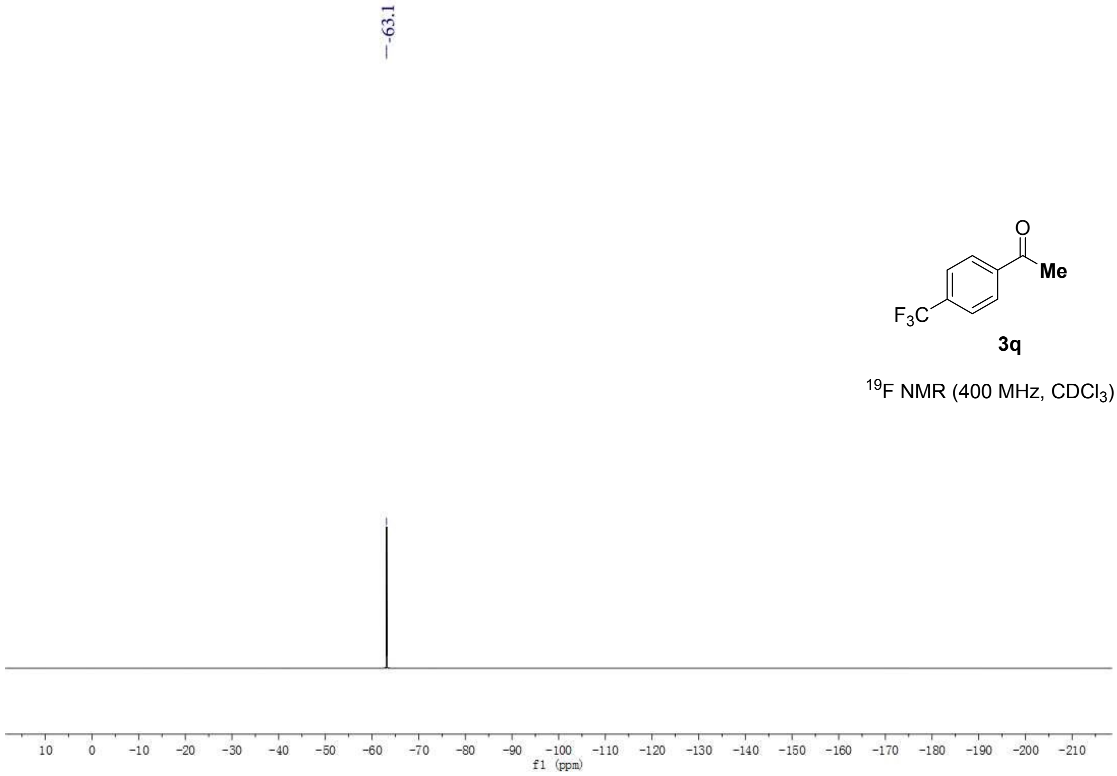
3q

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



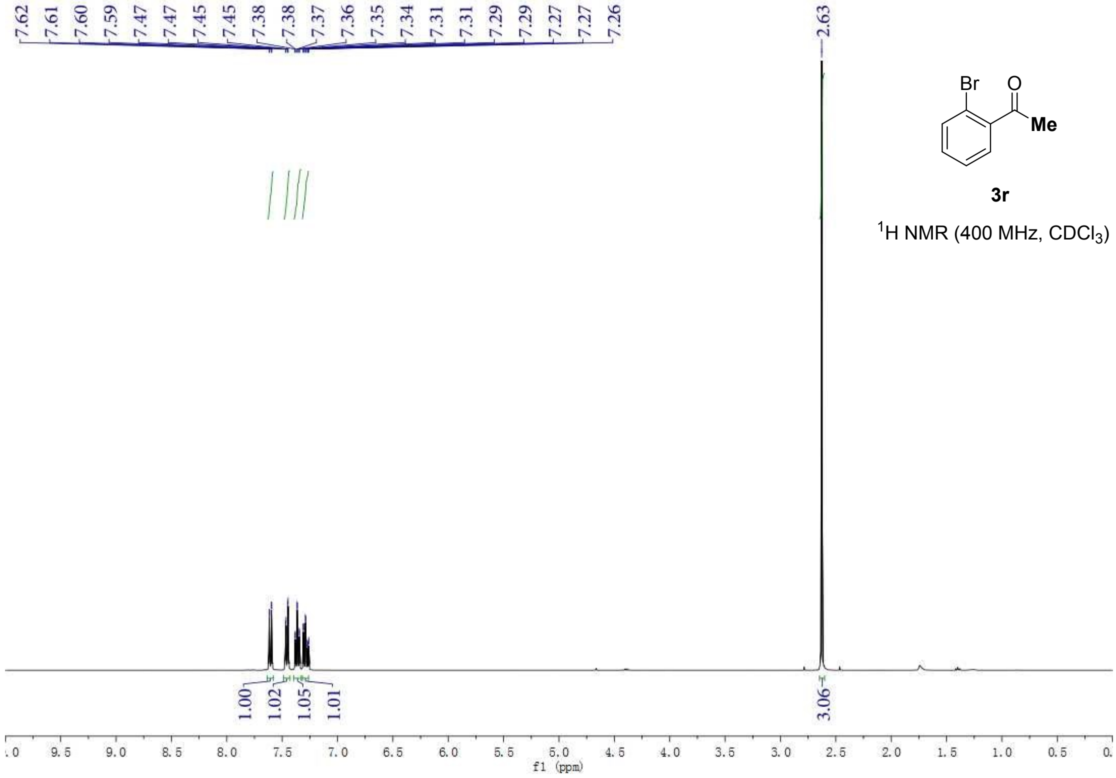
3q

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



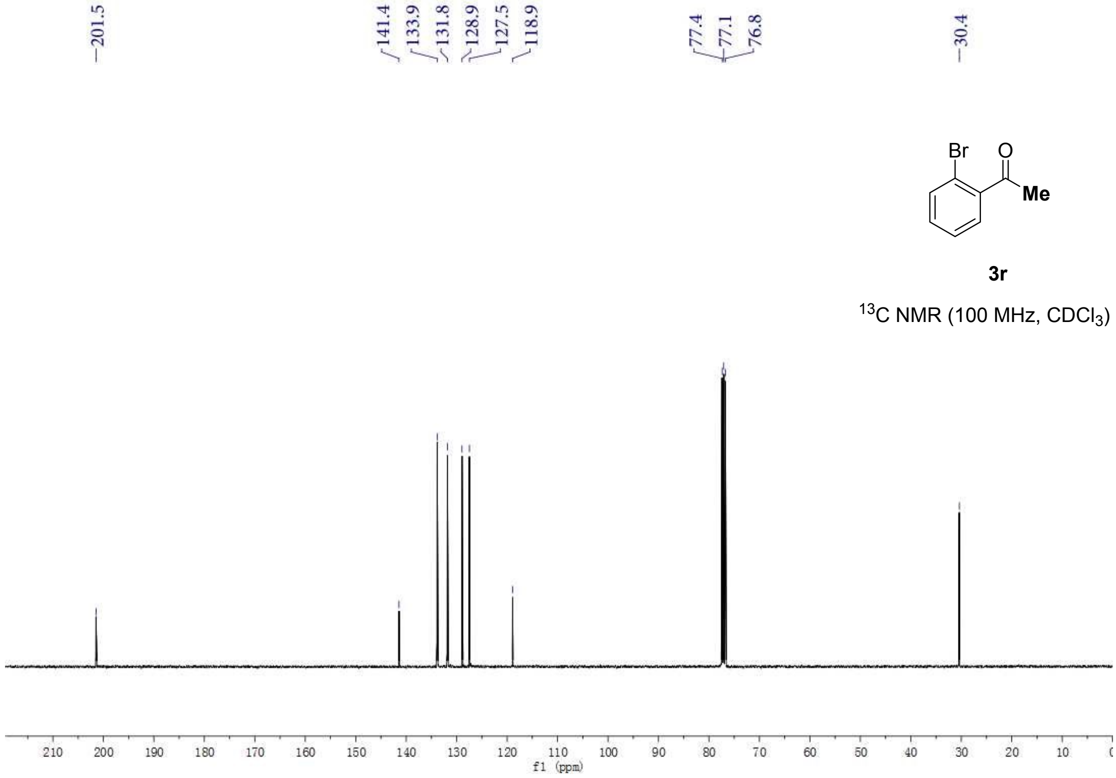
3q

^{19}F NMR (400 MHz, CDCl$_3$)



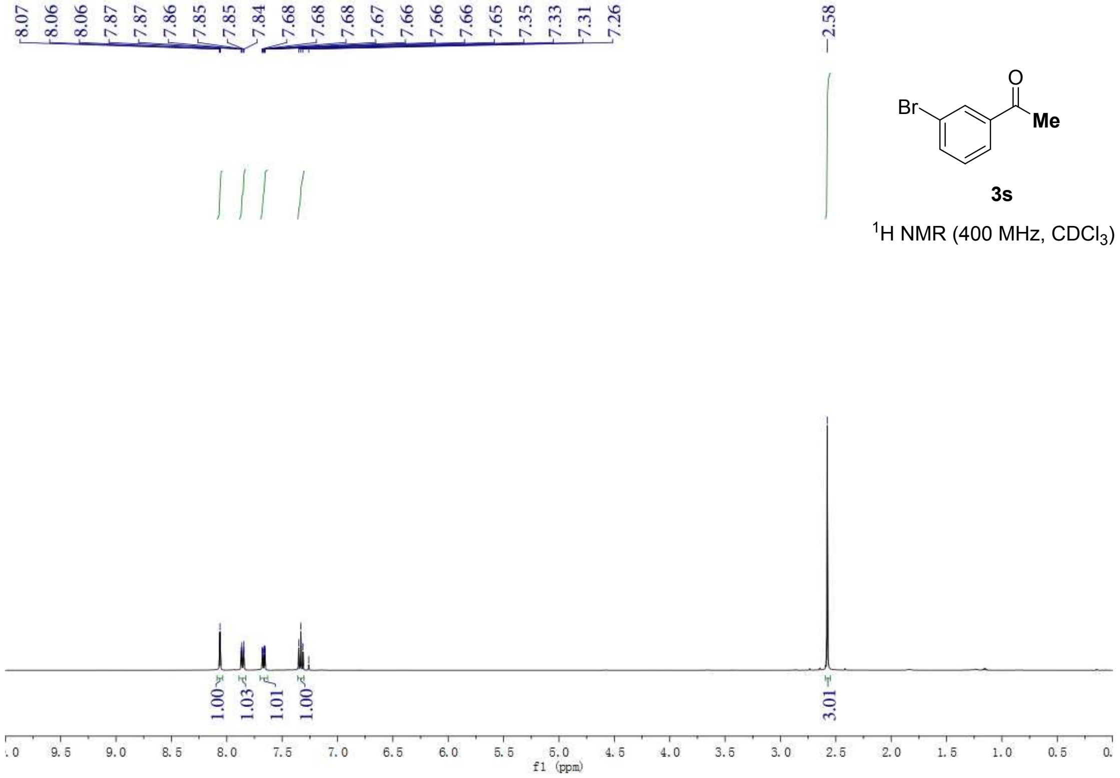
3r

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



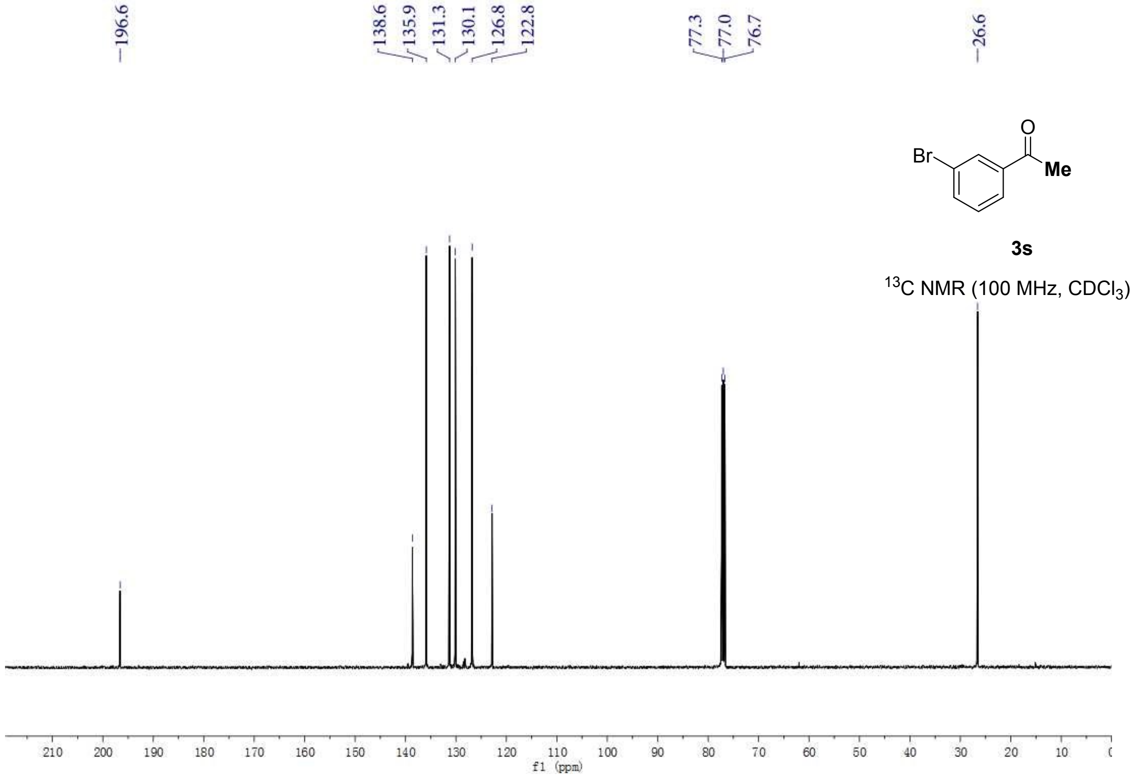
3r

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



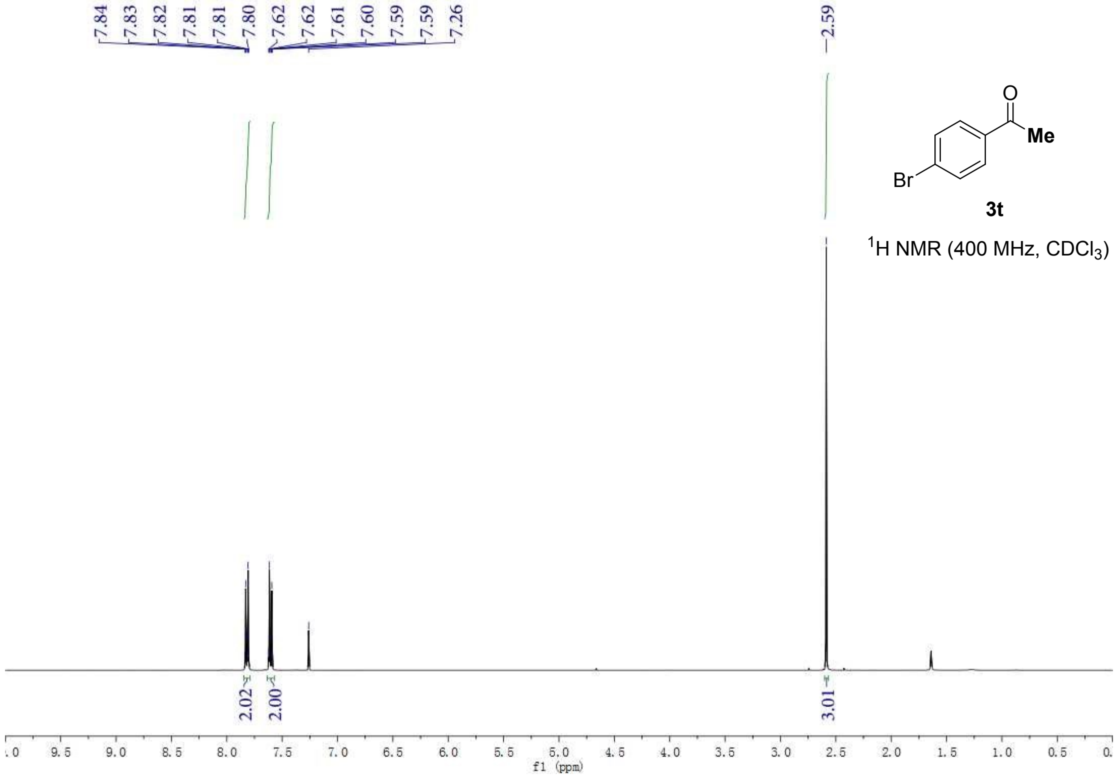
3s

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



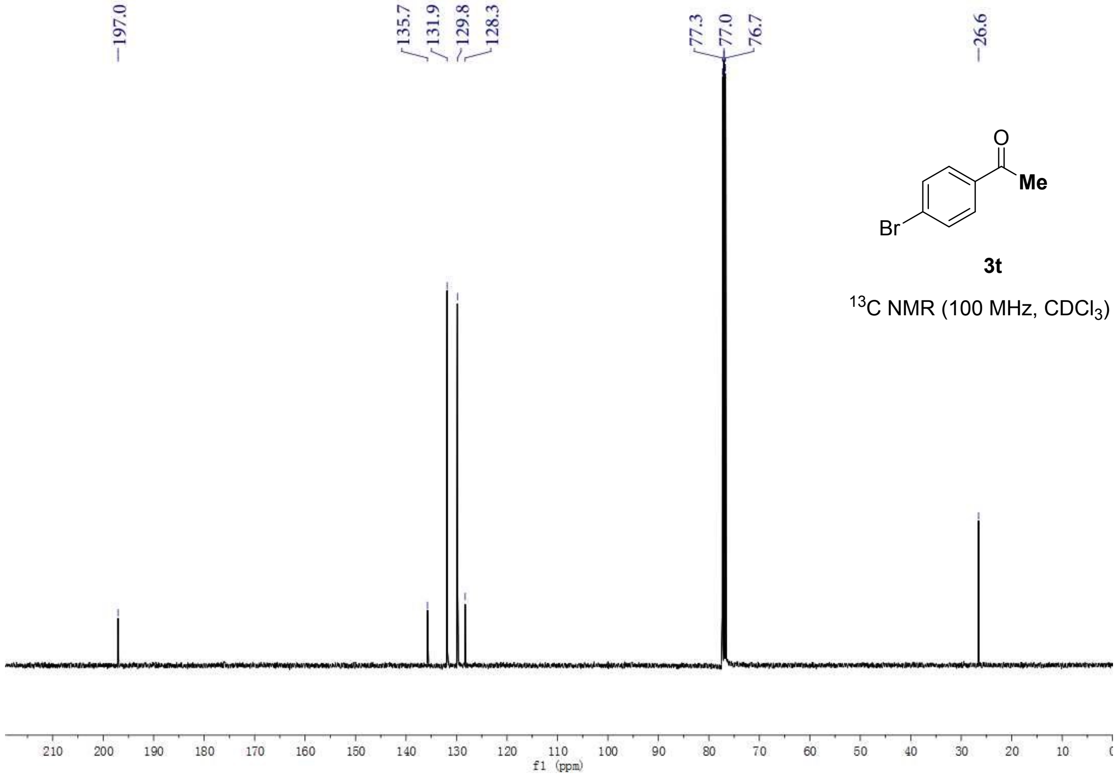
3s

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



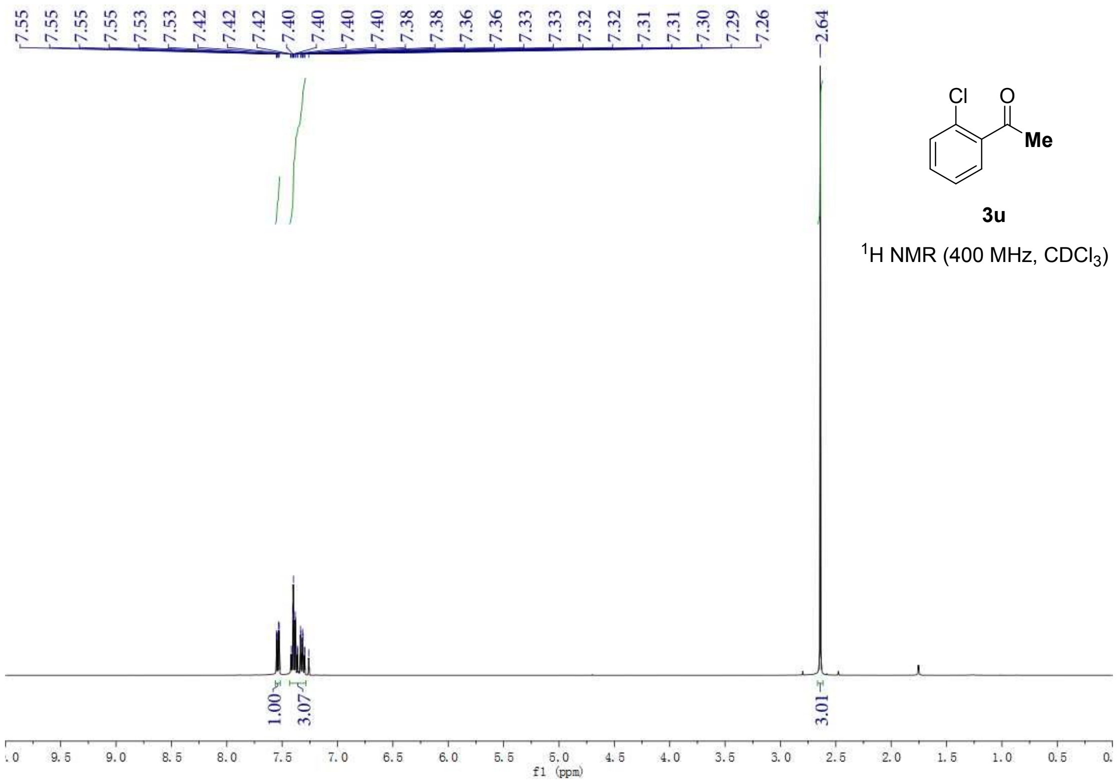
3t

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



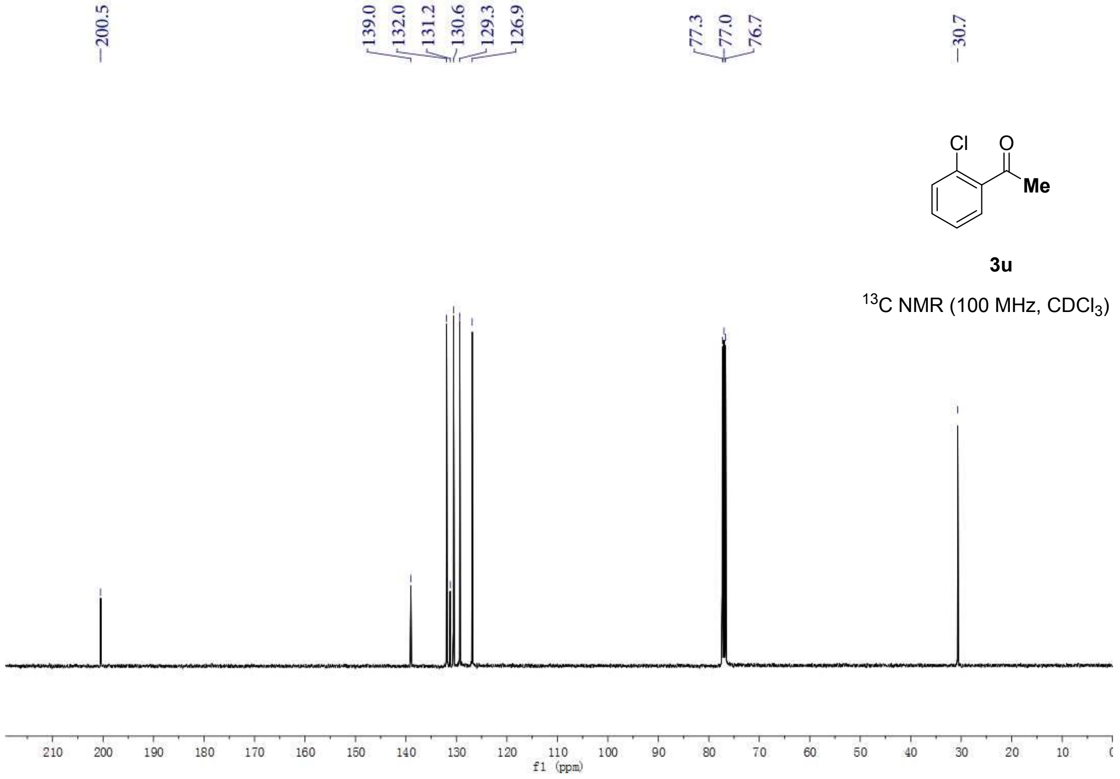
3t

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



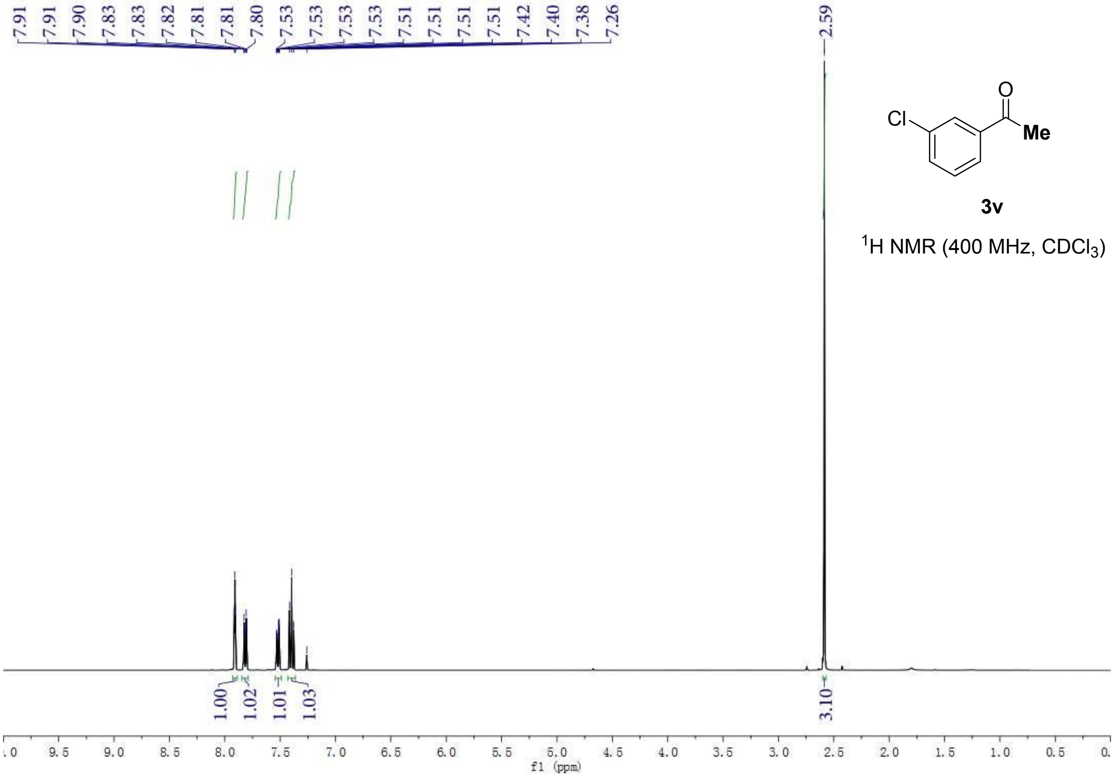
3u

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



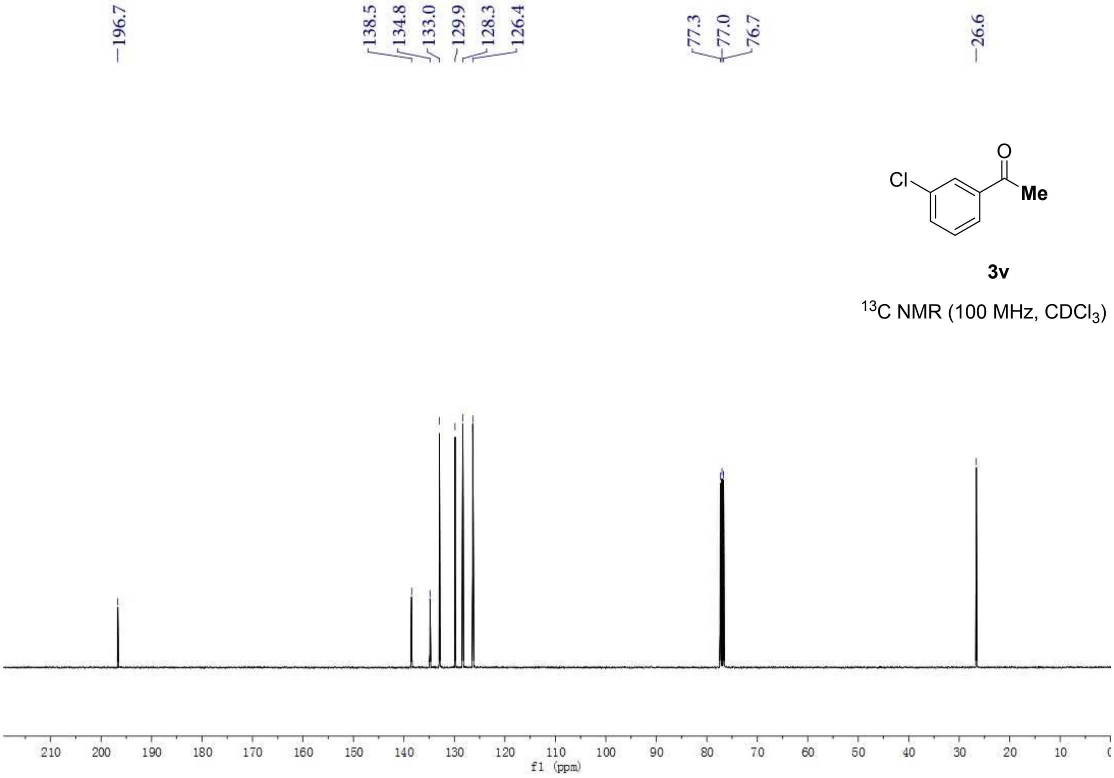
3u

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



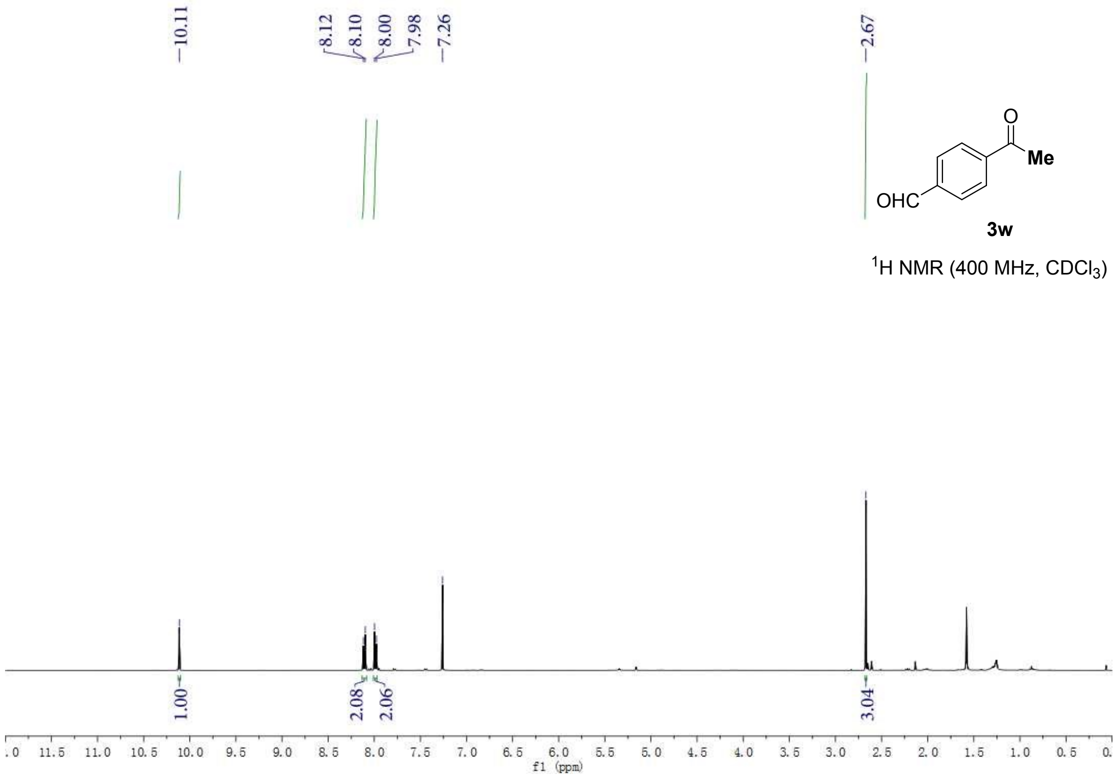
3v

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



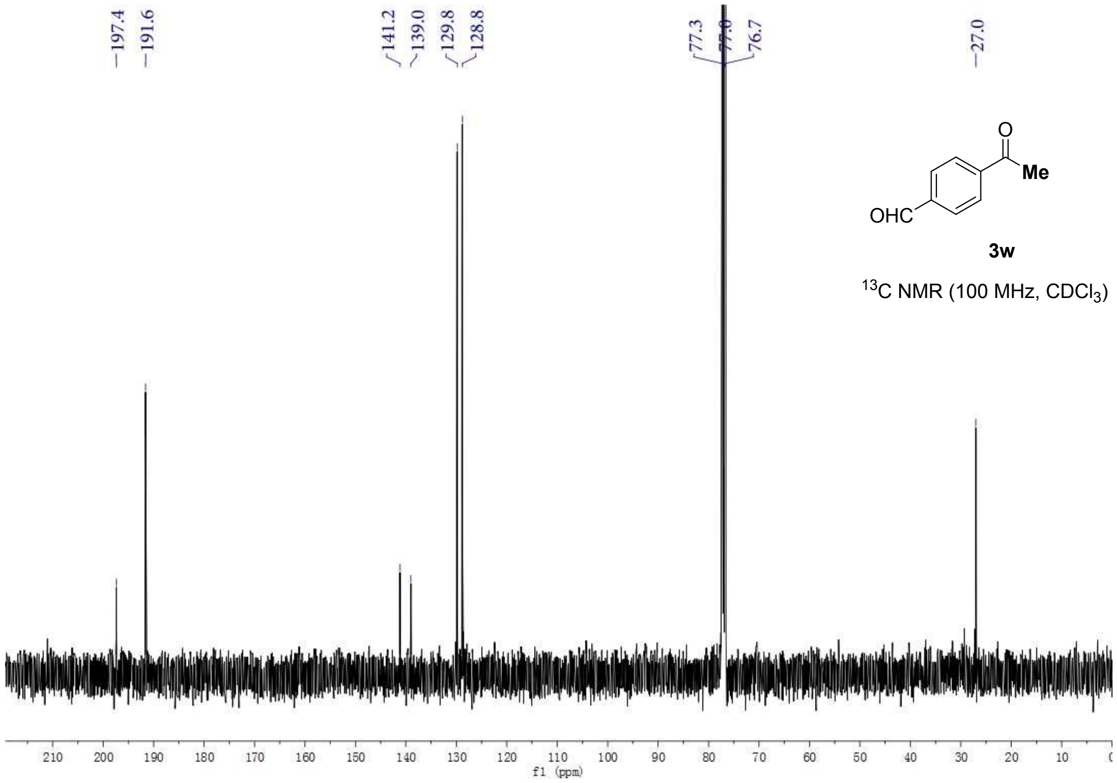
3v

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



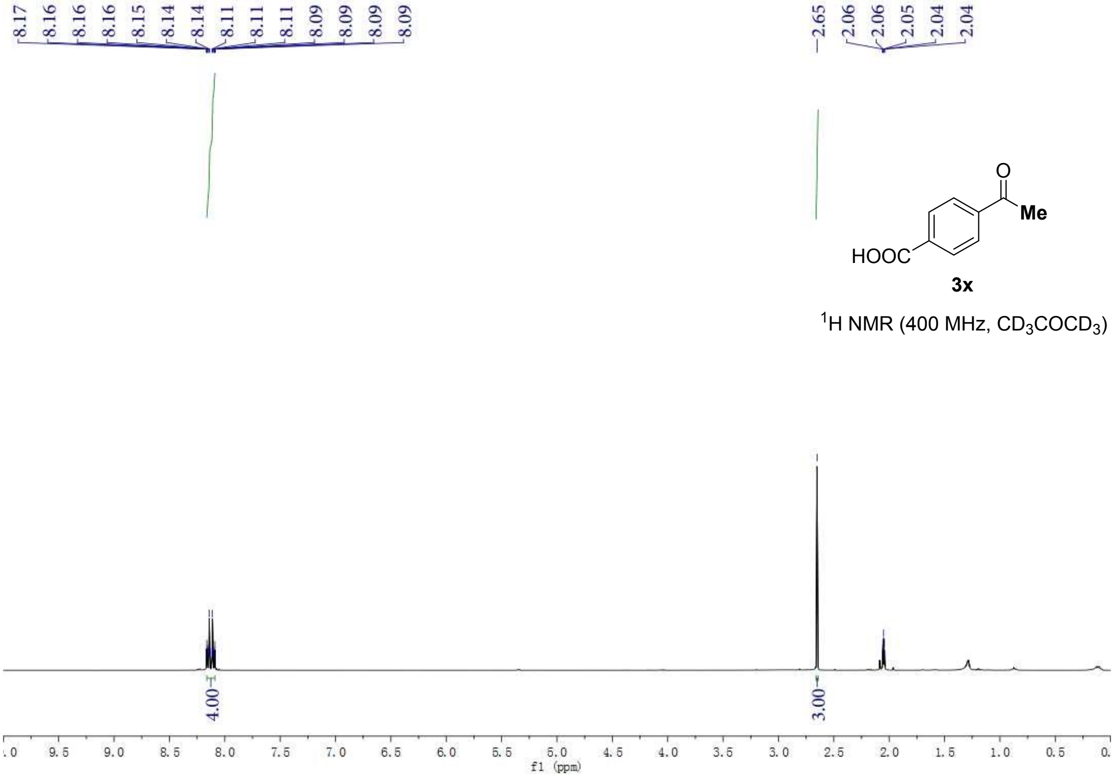
3w

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



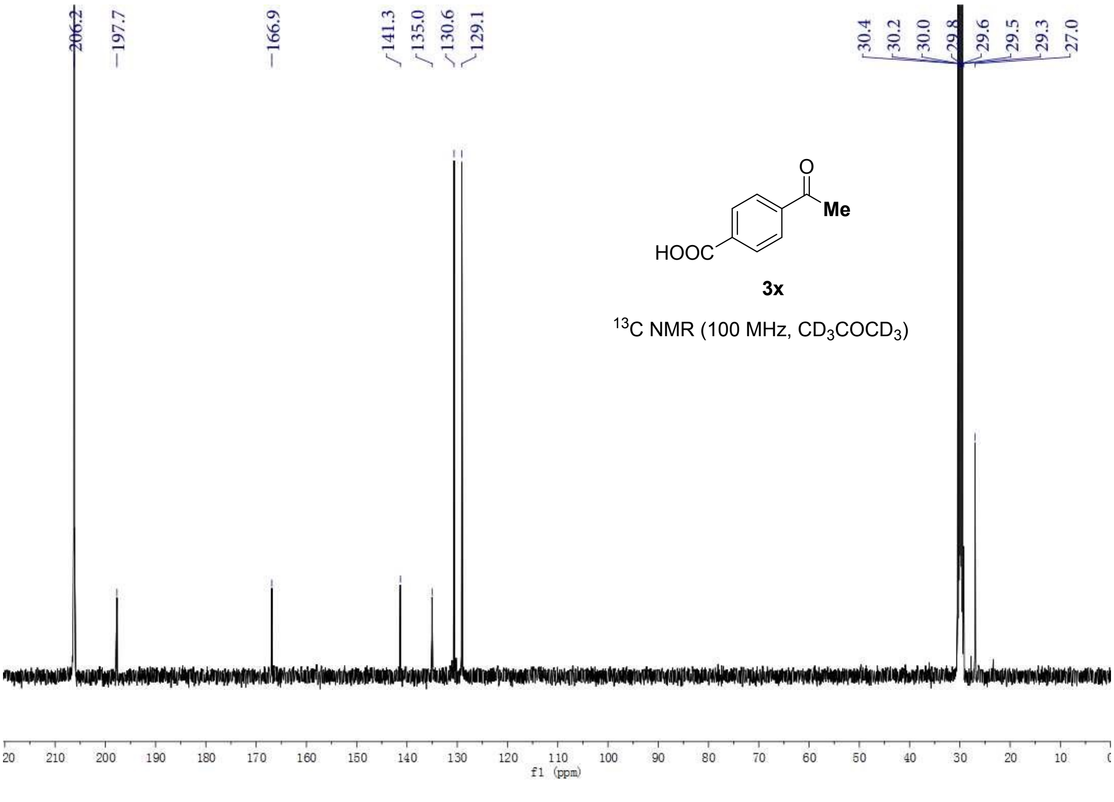
3w

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



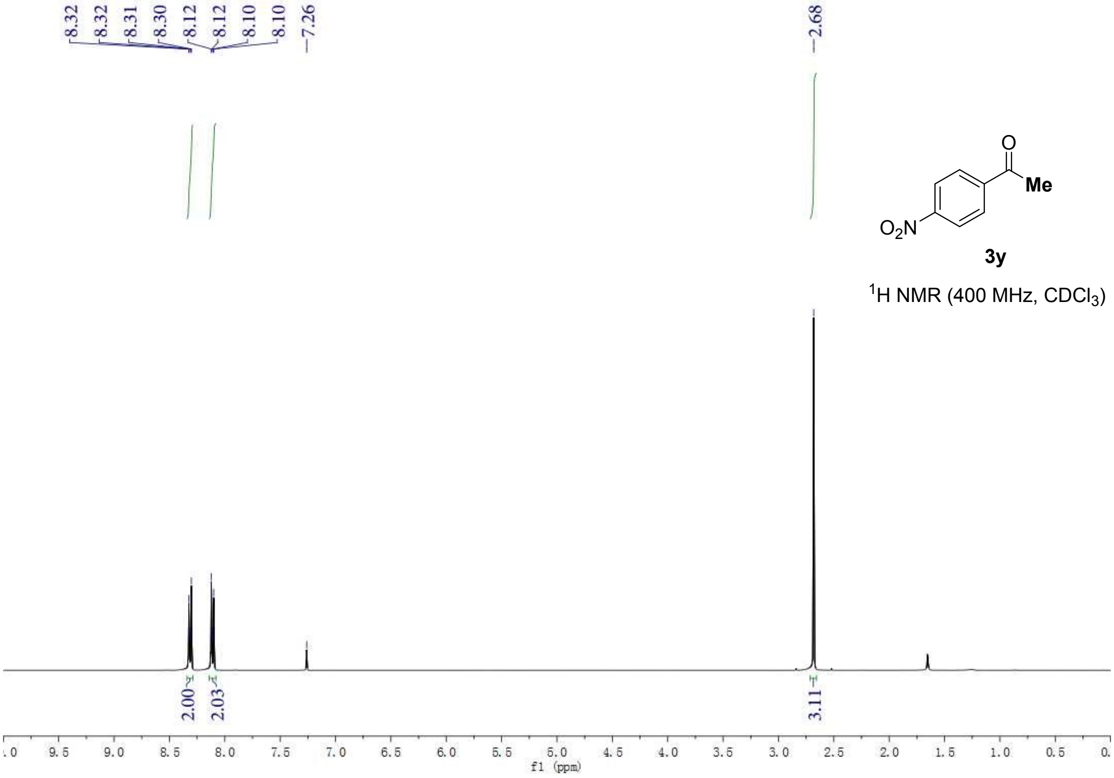
3x

^{1}H NMR (400 MHz, CD_3COCD_3)



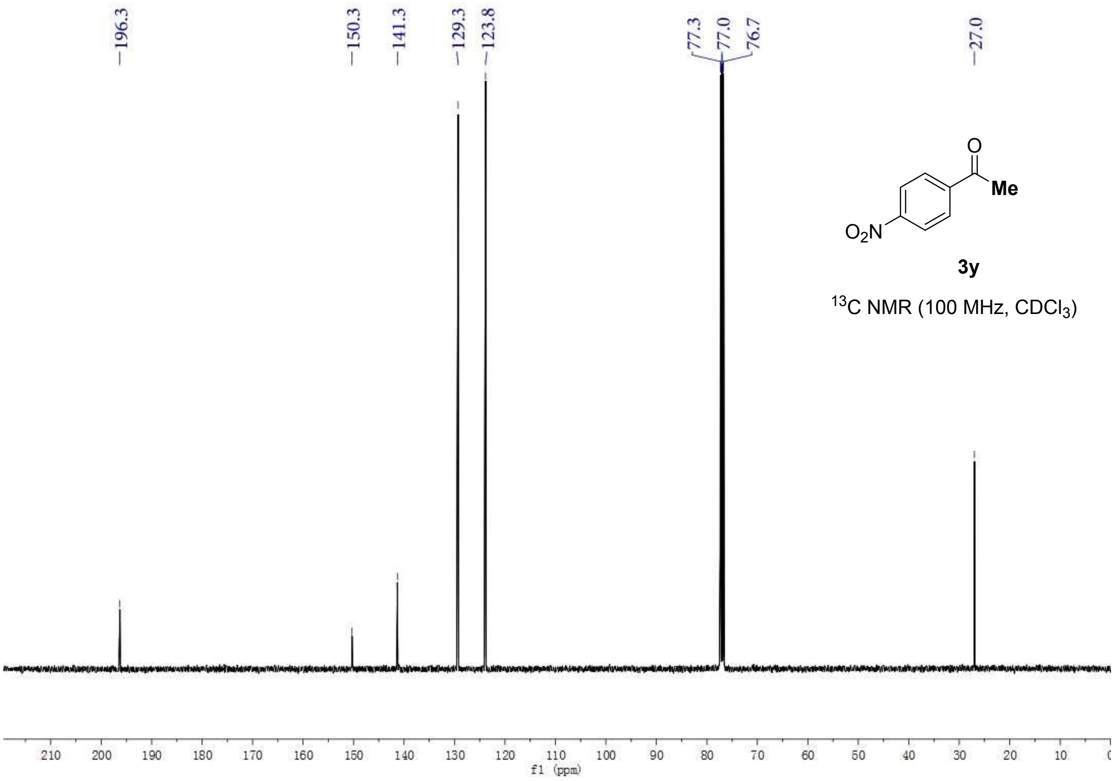
3x

^{13}C NMR (100 MHz, CD_3COCD_3)



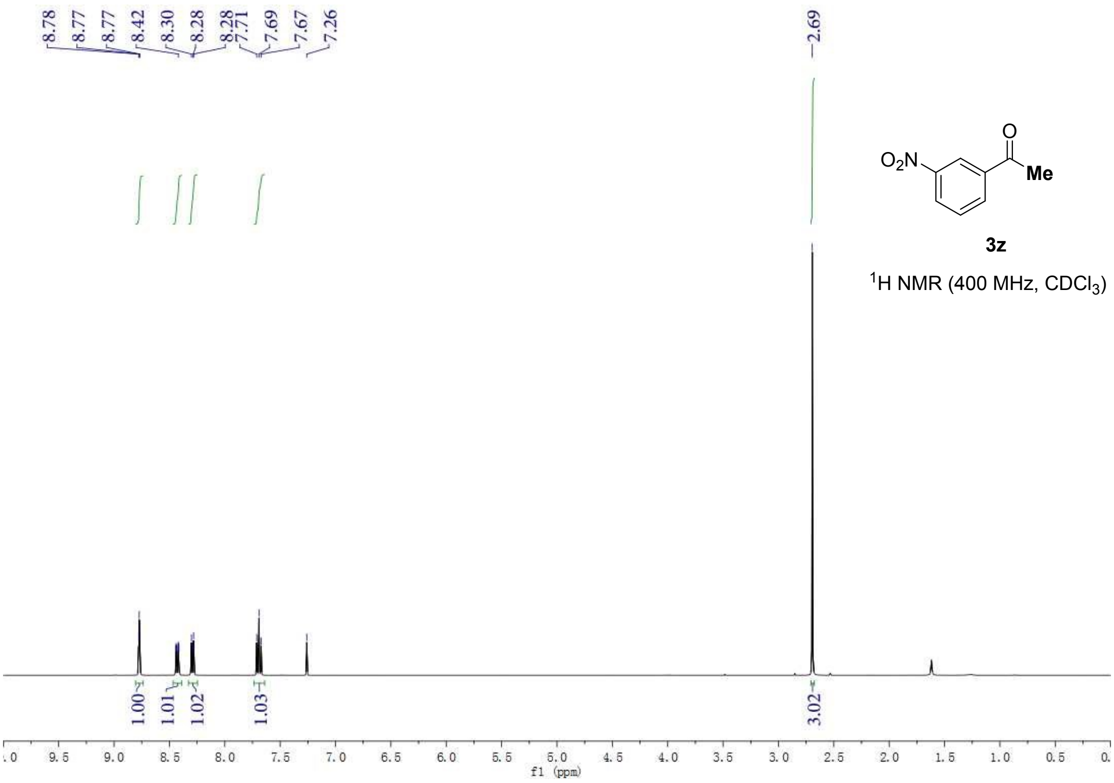
3y

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



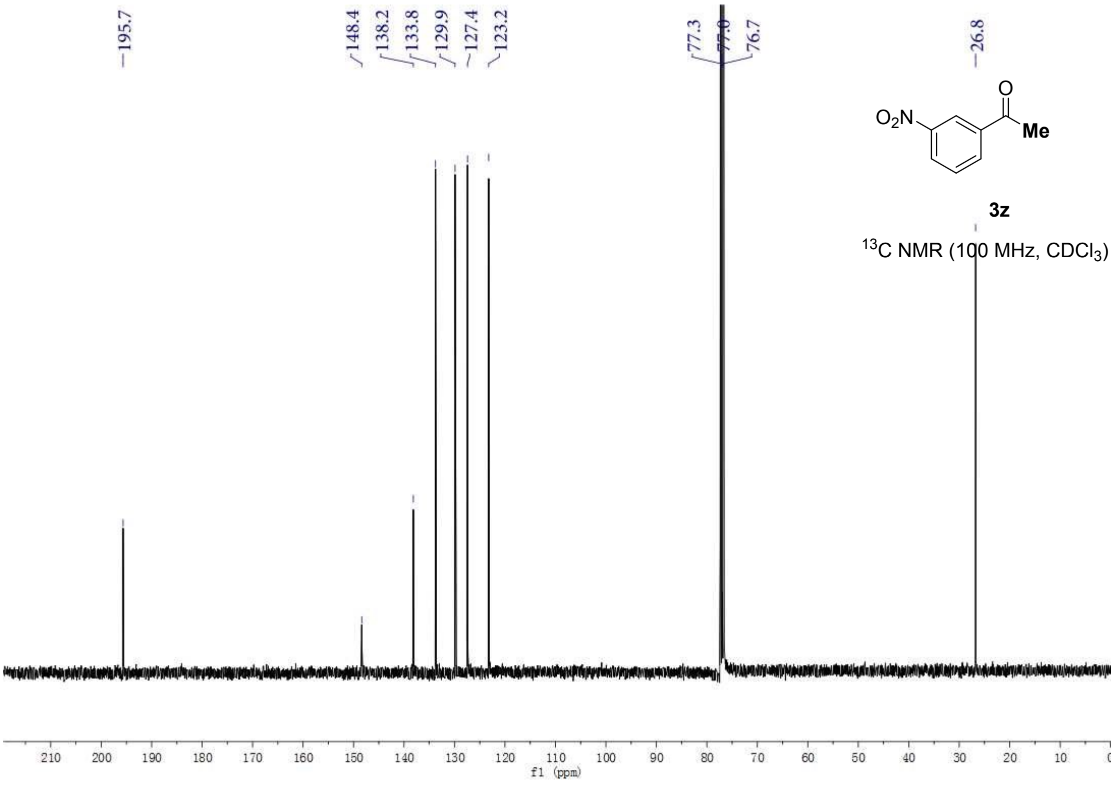
3y

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



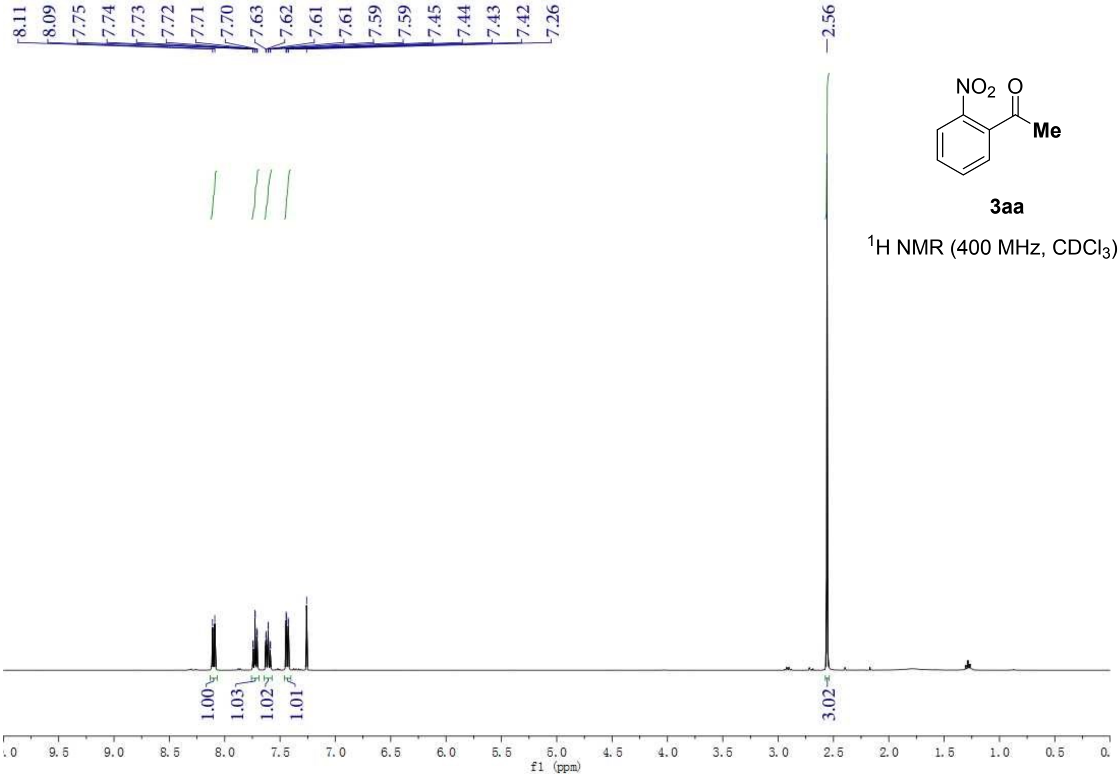
3z

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



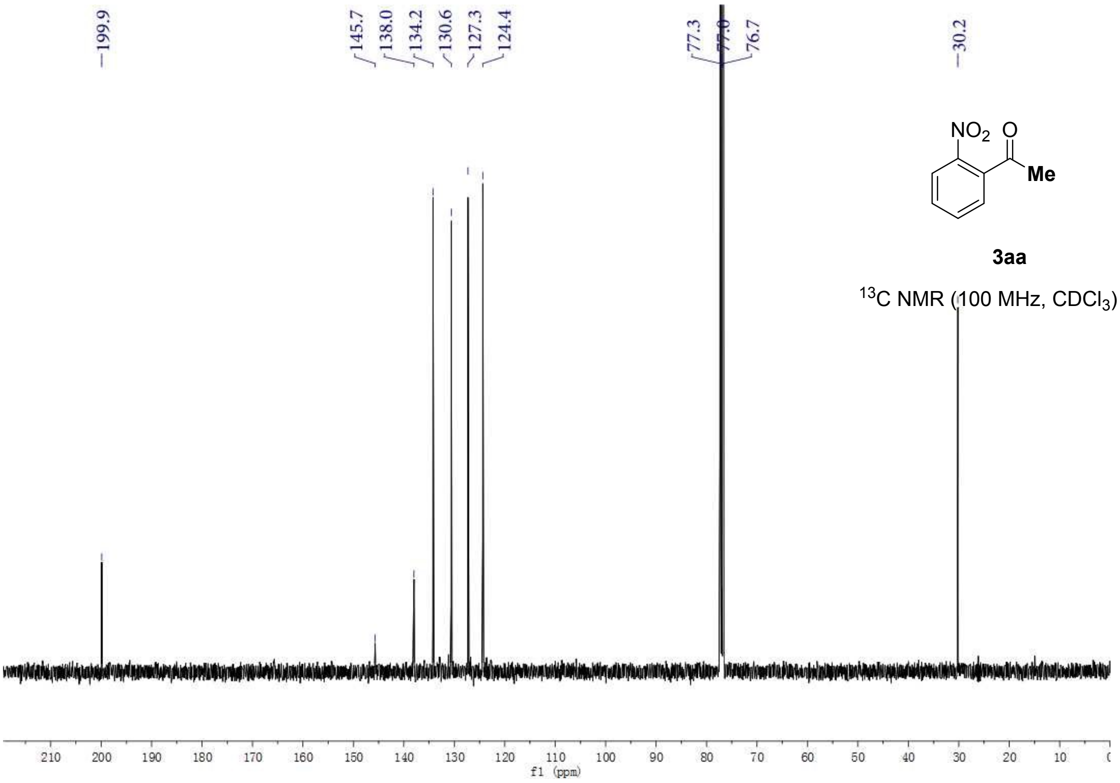
3z

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



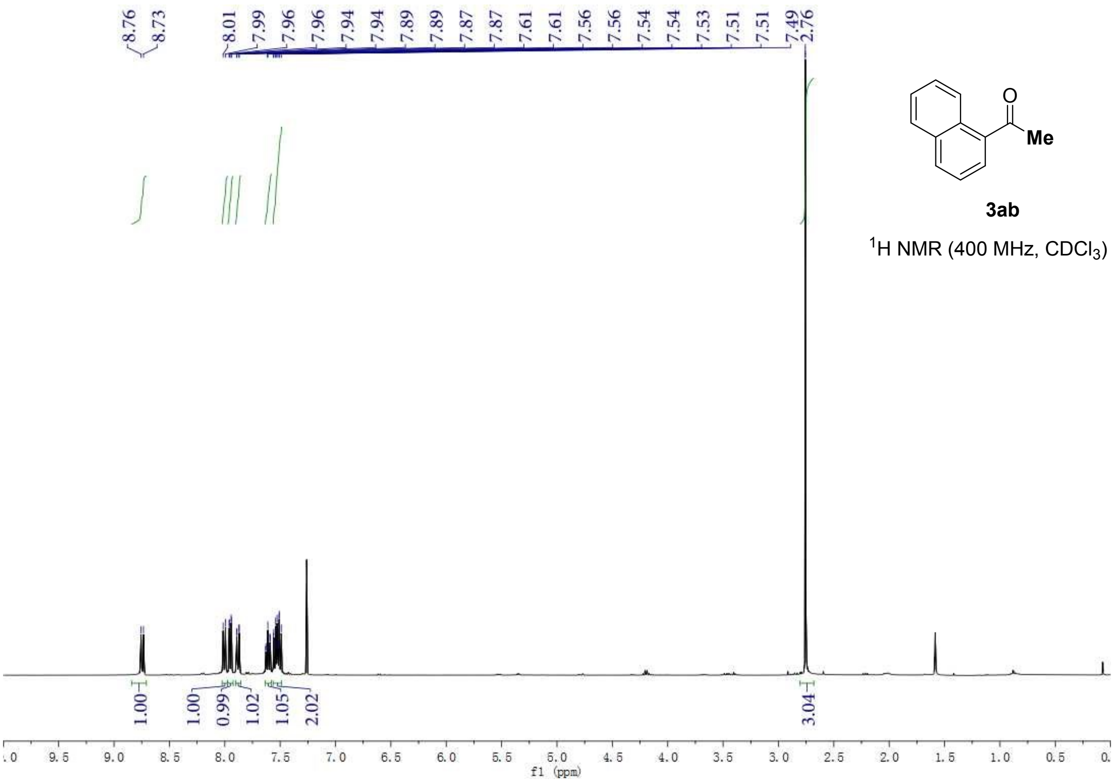
3aa

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



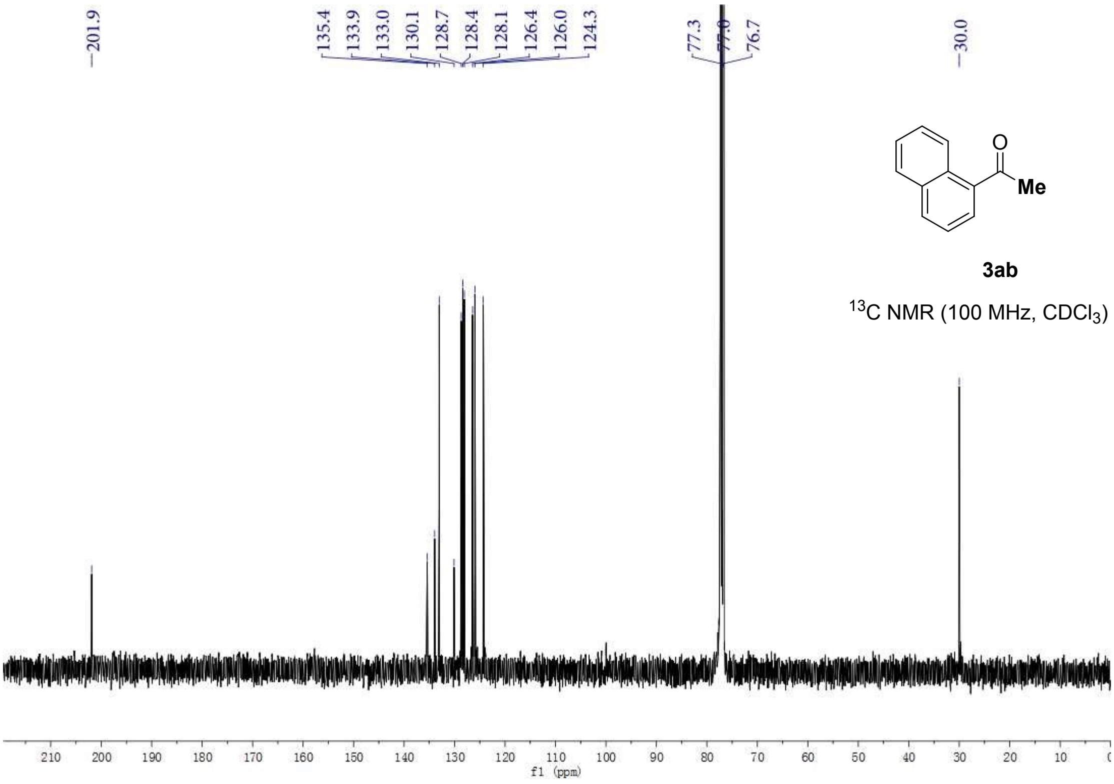
3aa

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



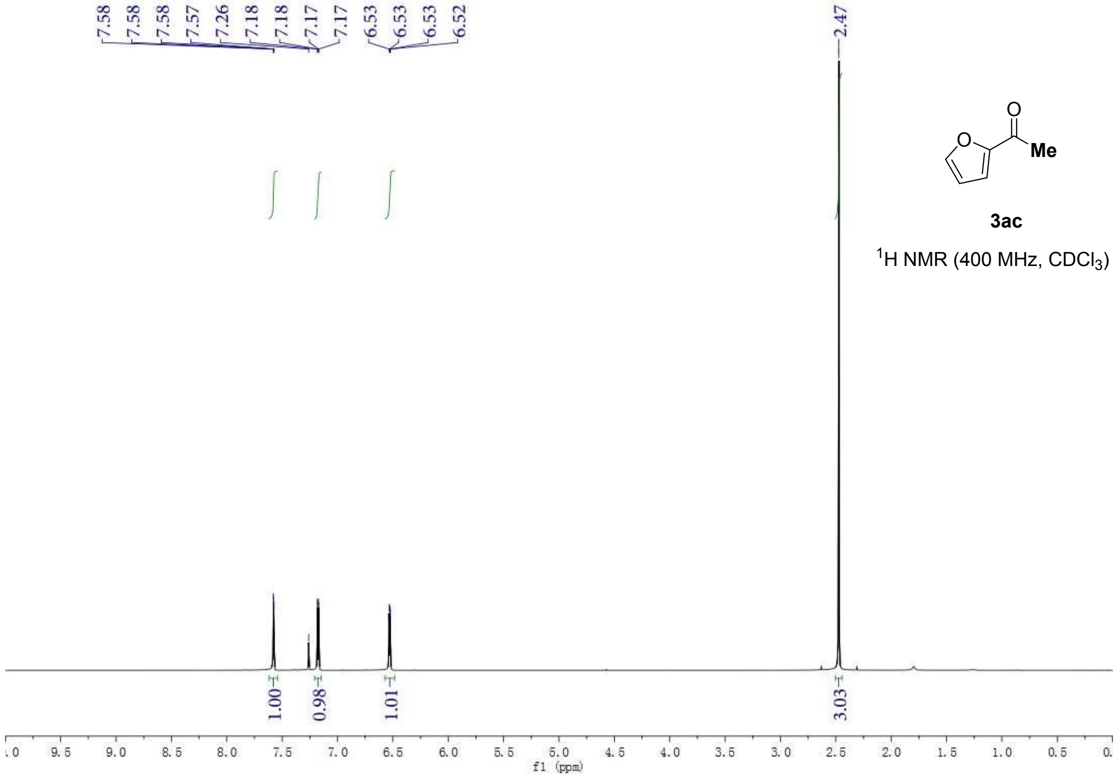
3ab

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



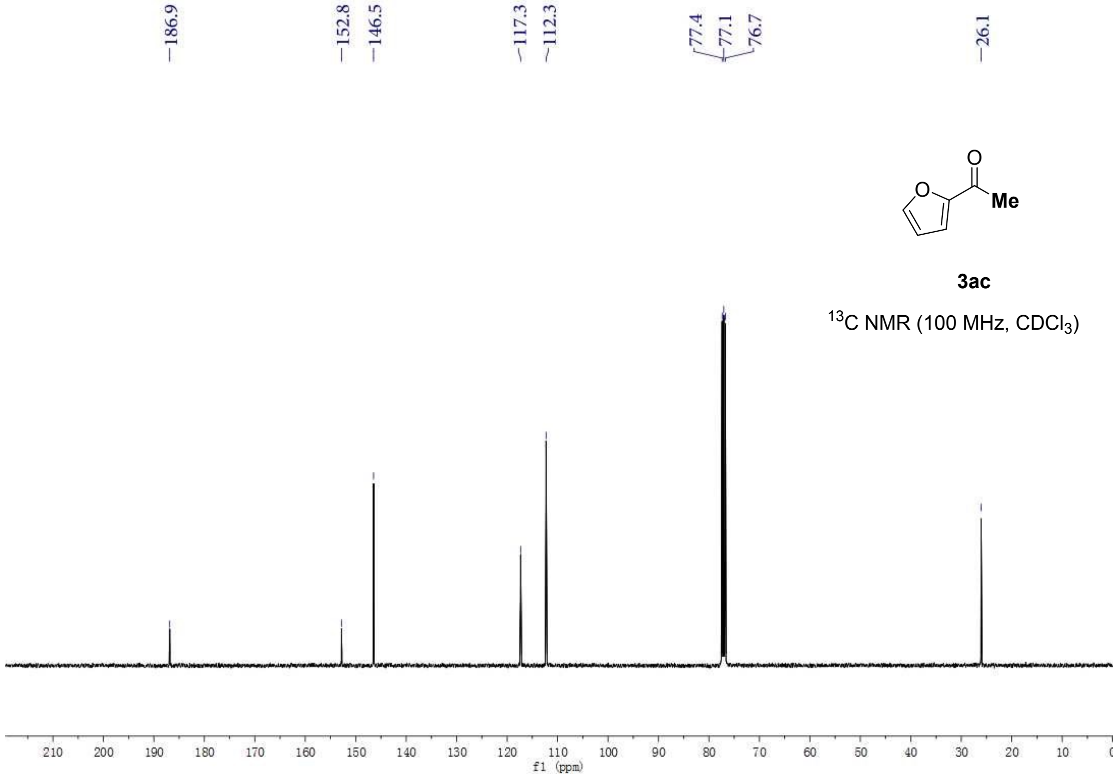
3ab

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



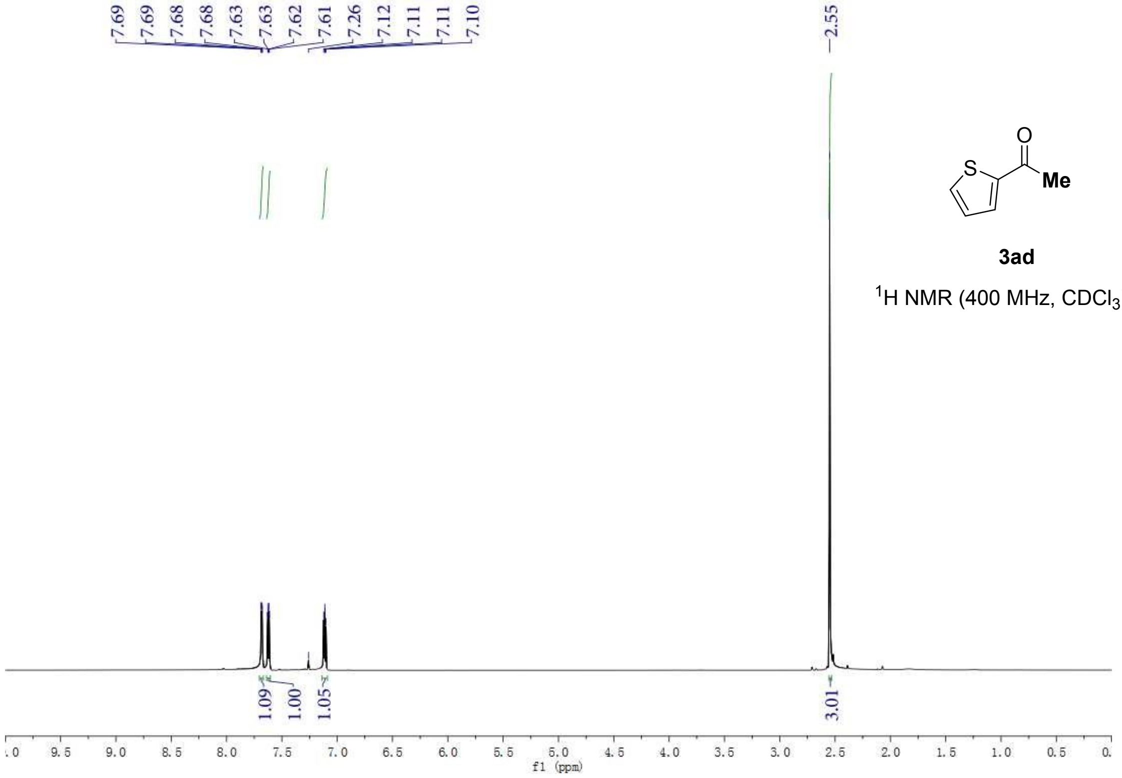
3ac

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



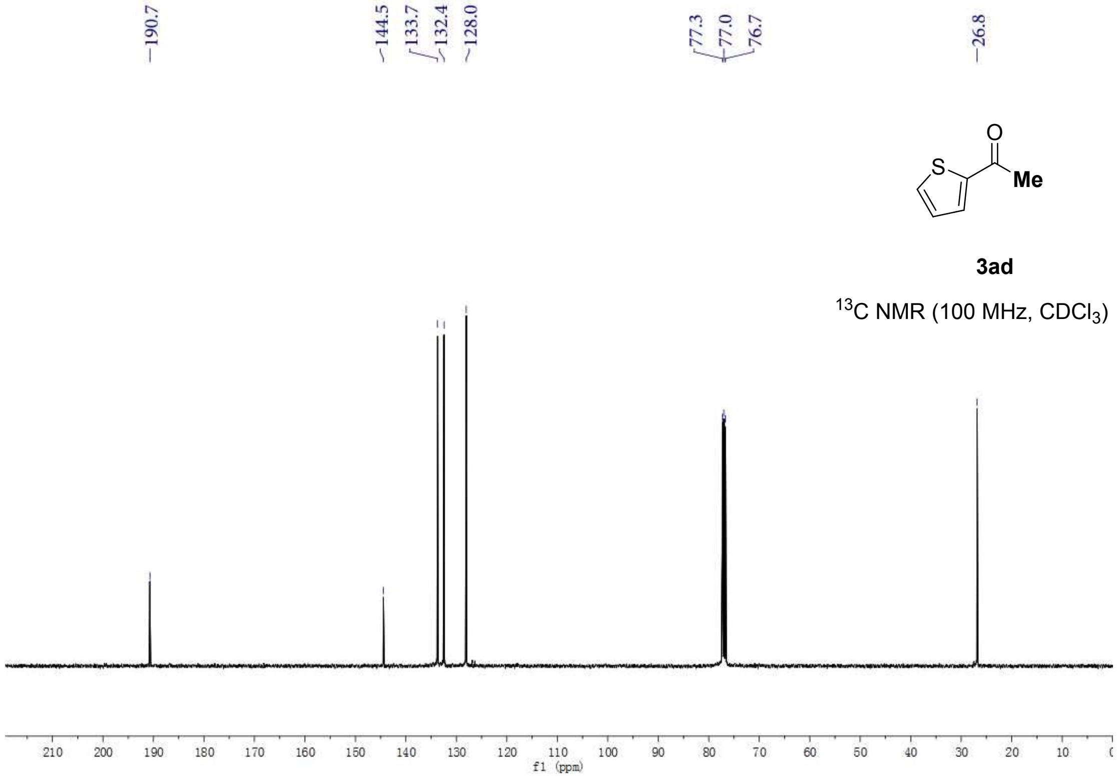
3ac

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



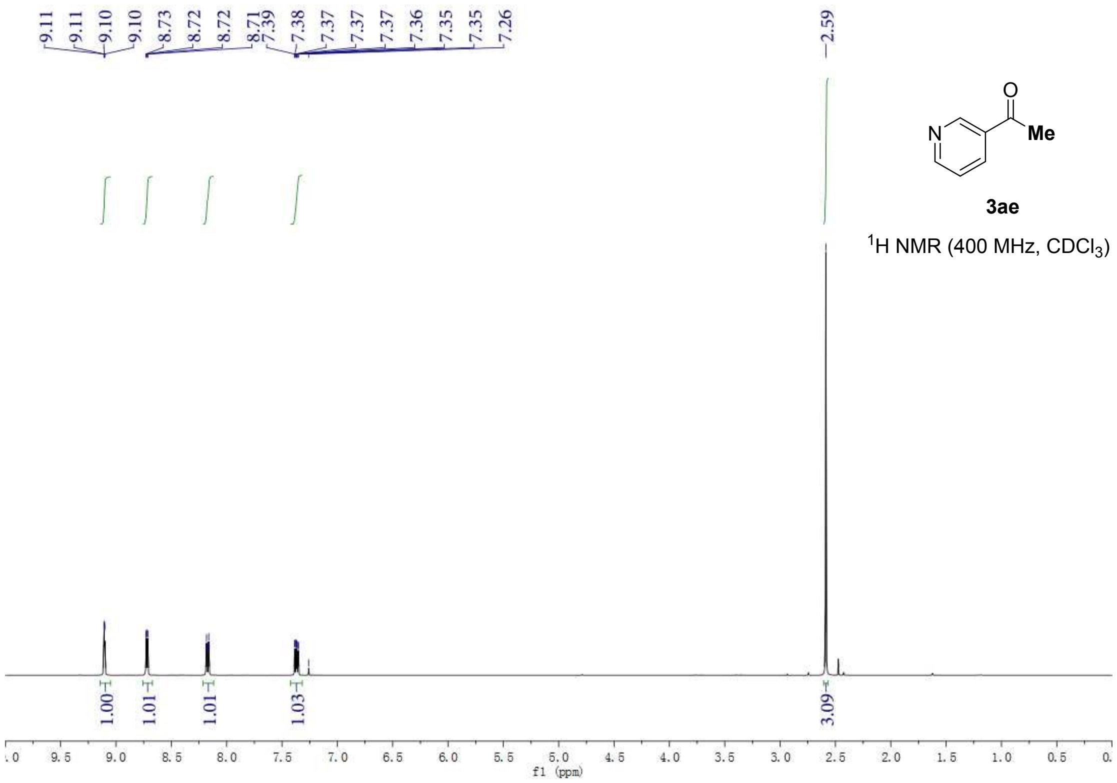
3ad

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



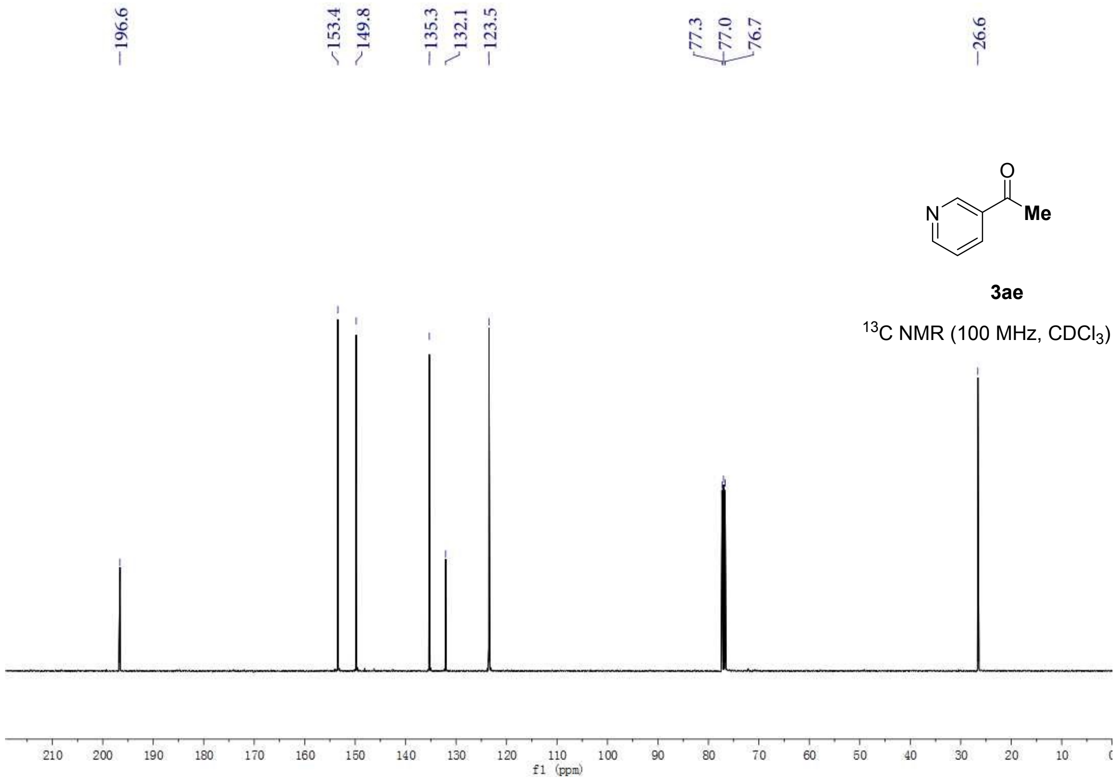
3ad

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



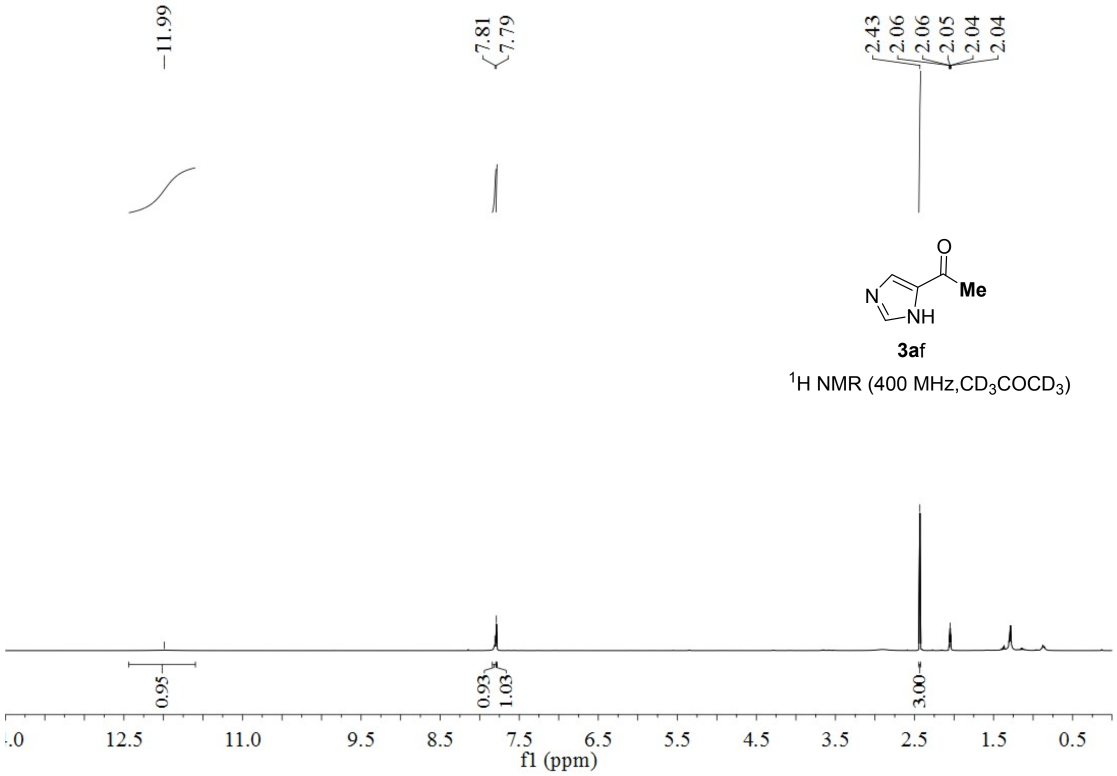
3ae

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



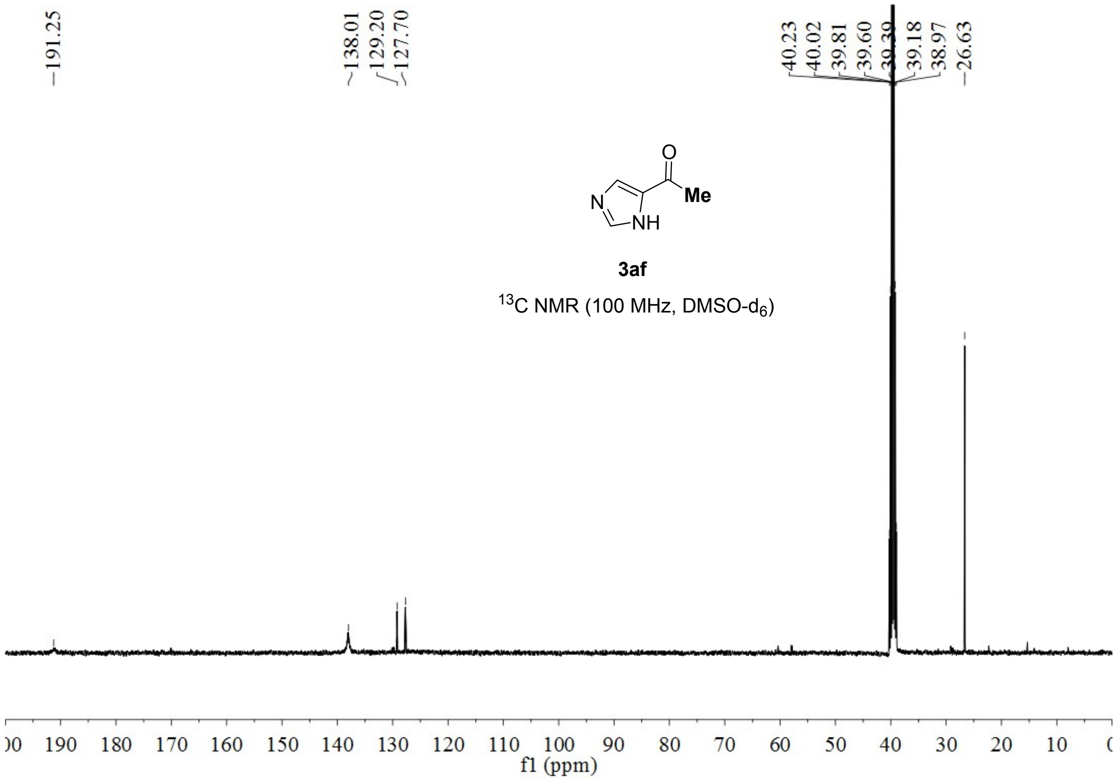
3ae

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



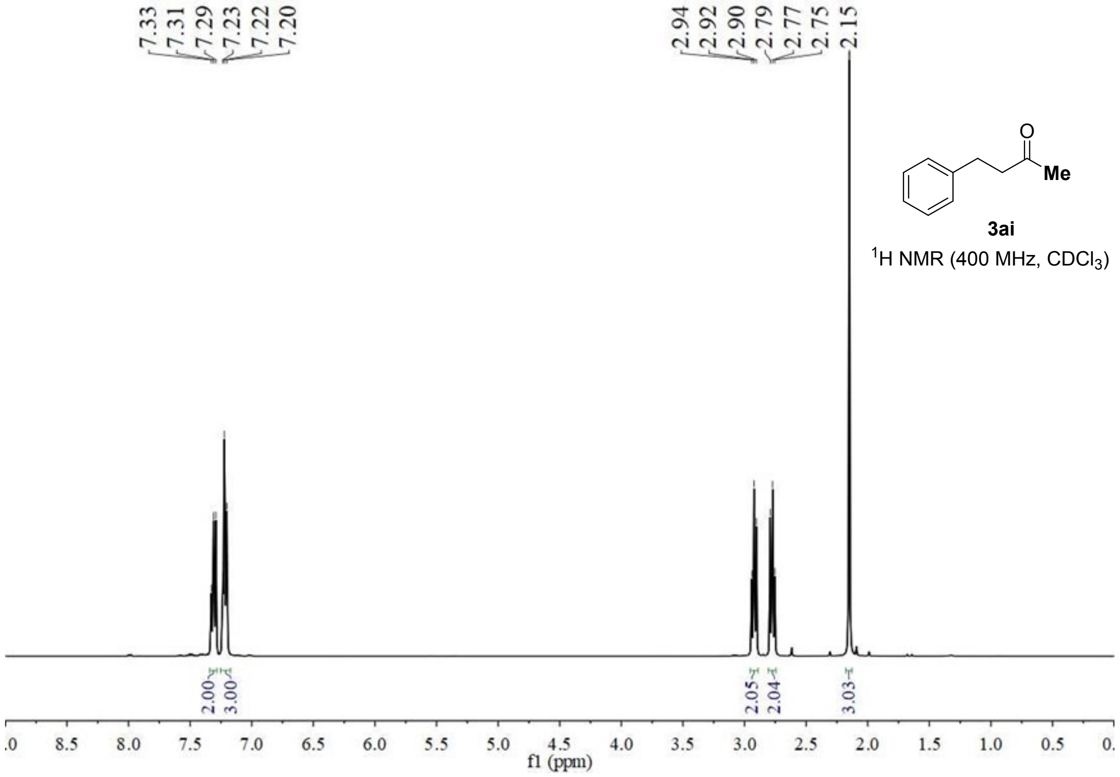
3af

^{1}H NMR (400 MHz,CD_3COCD_3)



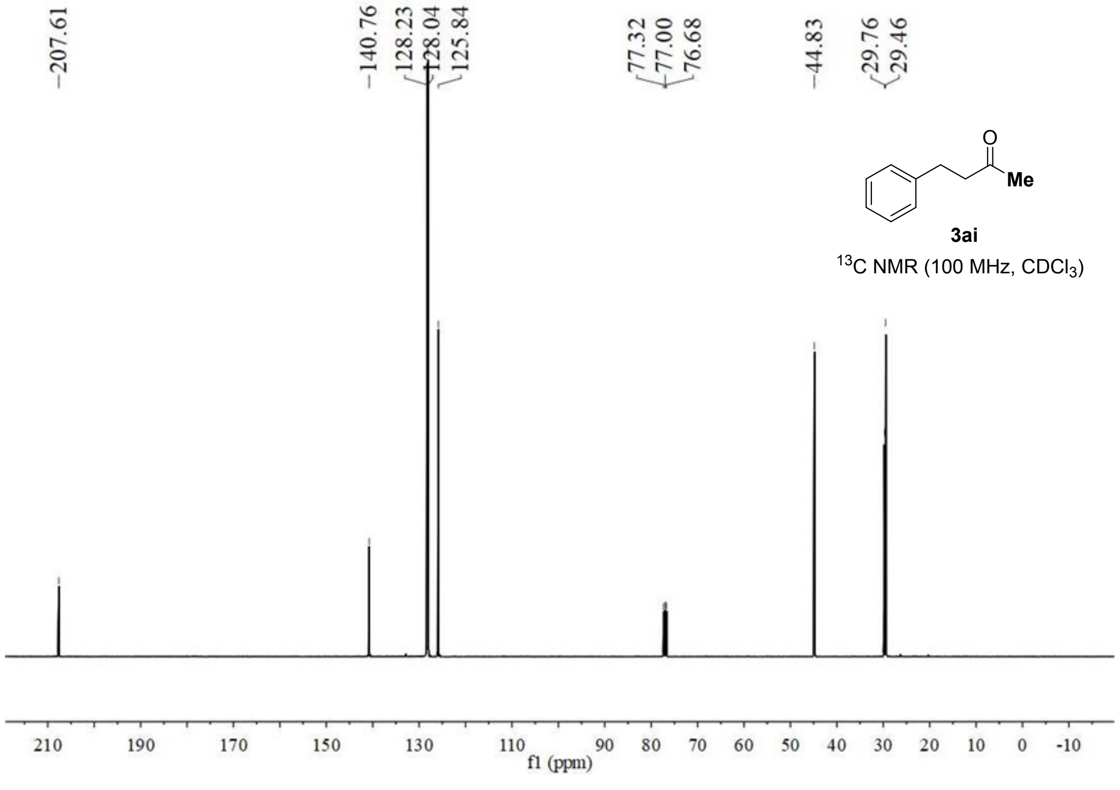
3af

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



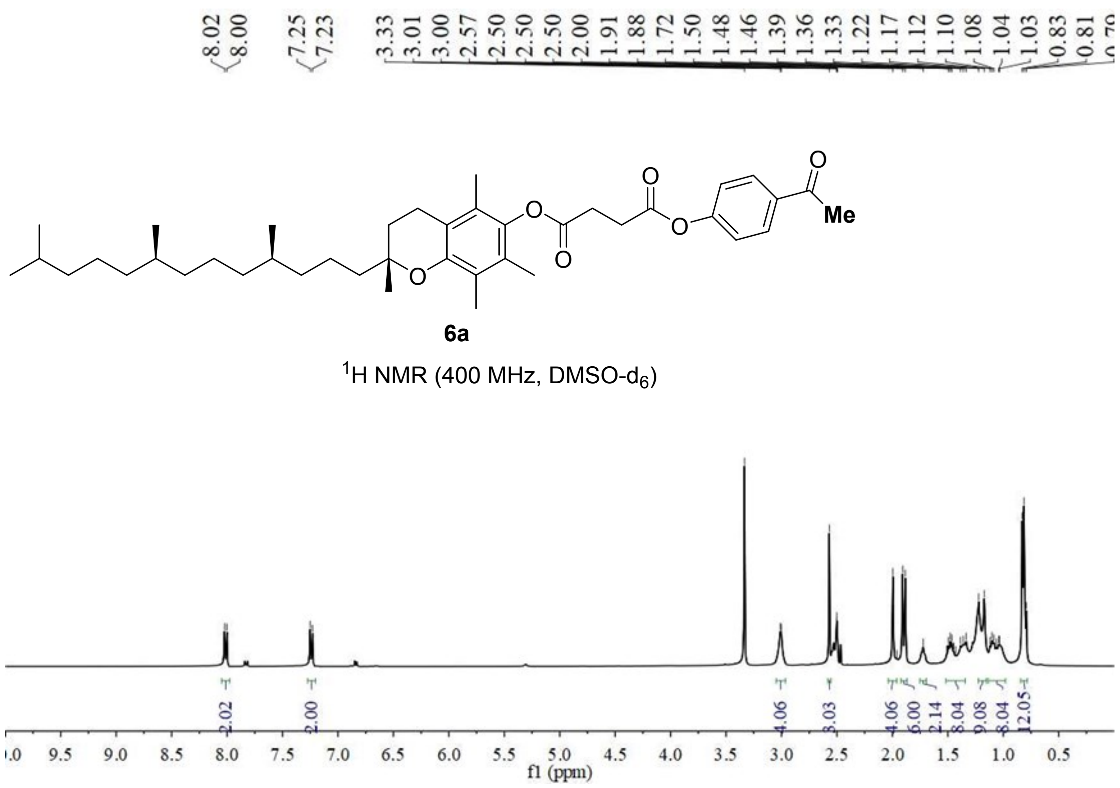
3ai

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



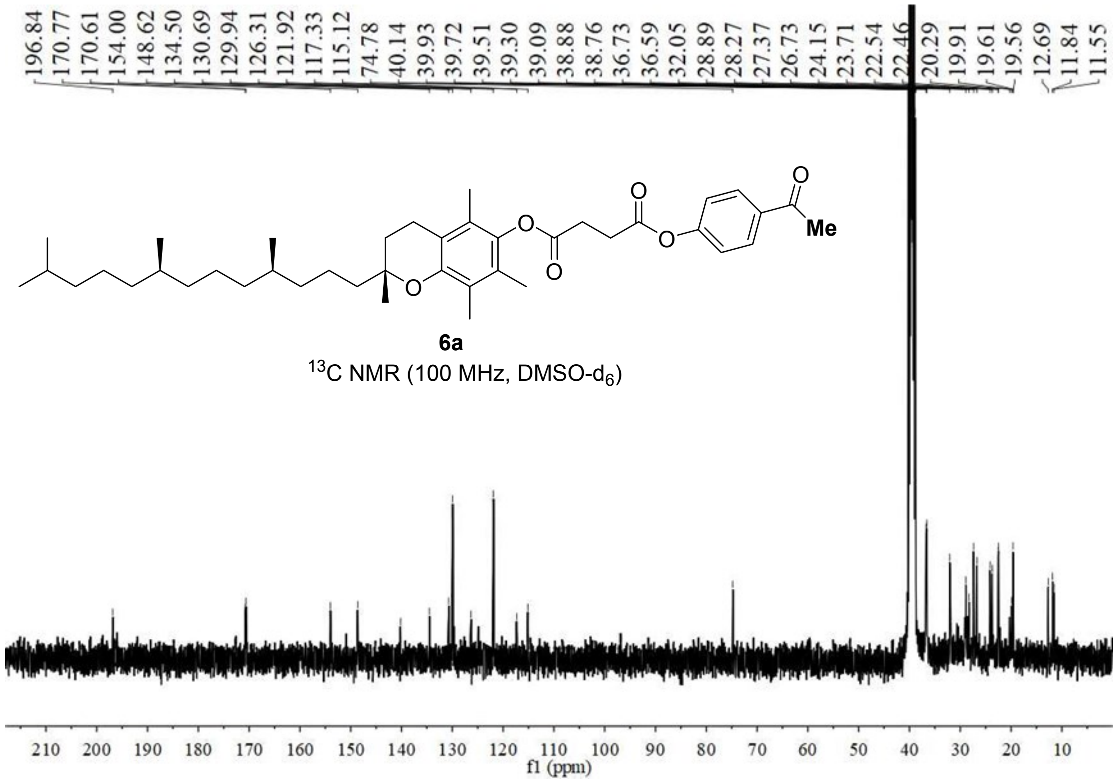
3ai

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



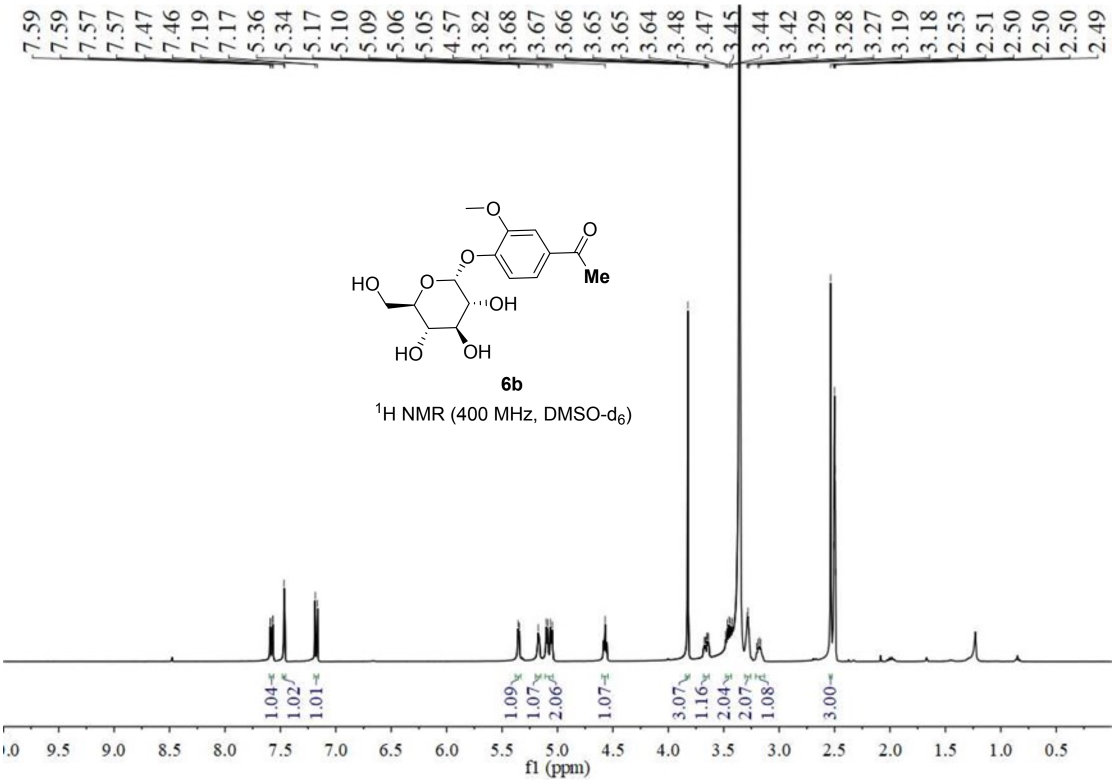
6a

^{1}H NMR (400 MHz, DMSO-d$_6$)



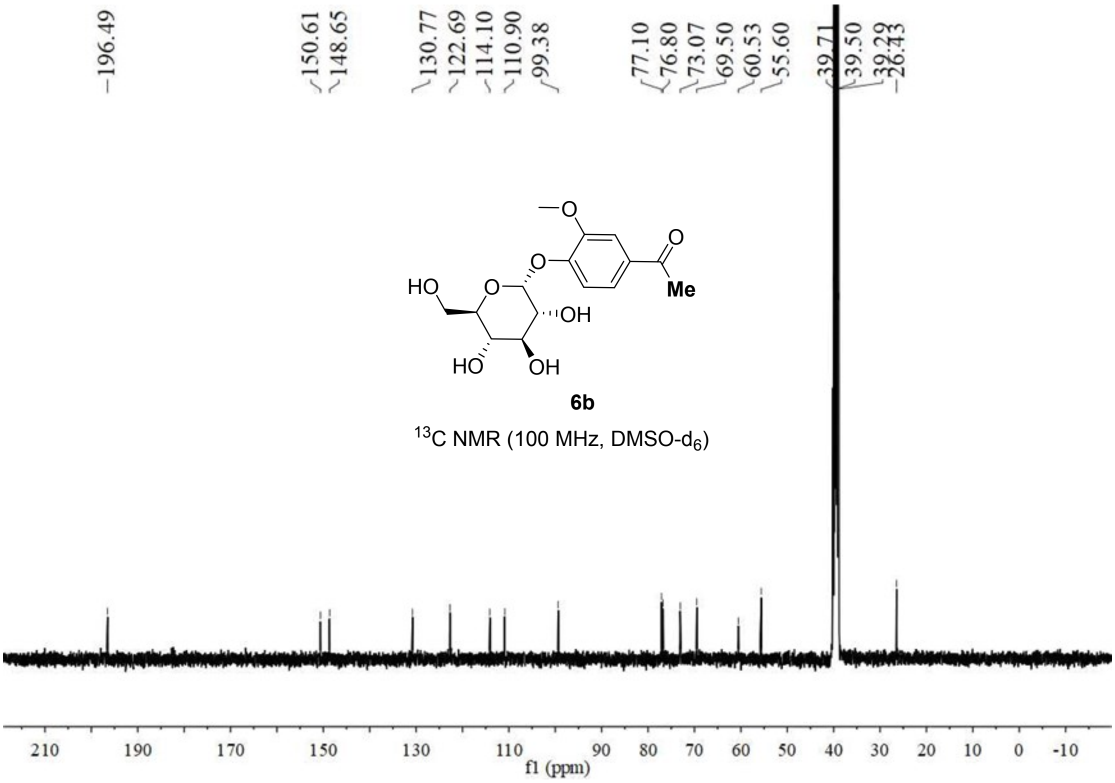
6a

^{13}C NMR (100 MHz, DMSO-d$_6$)



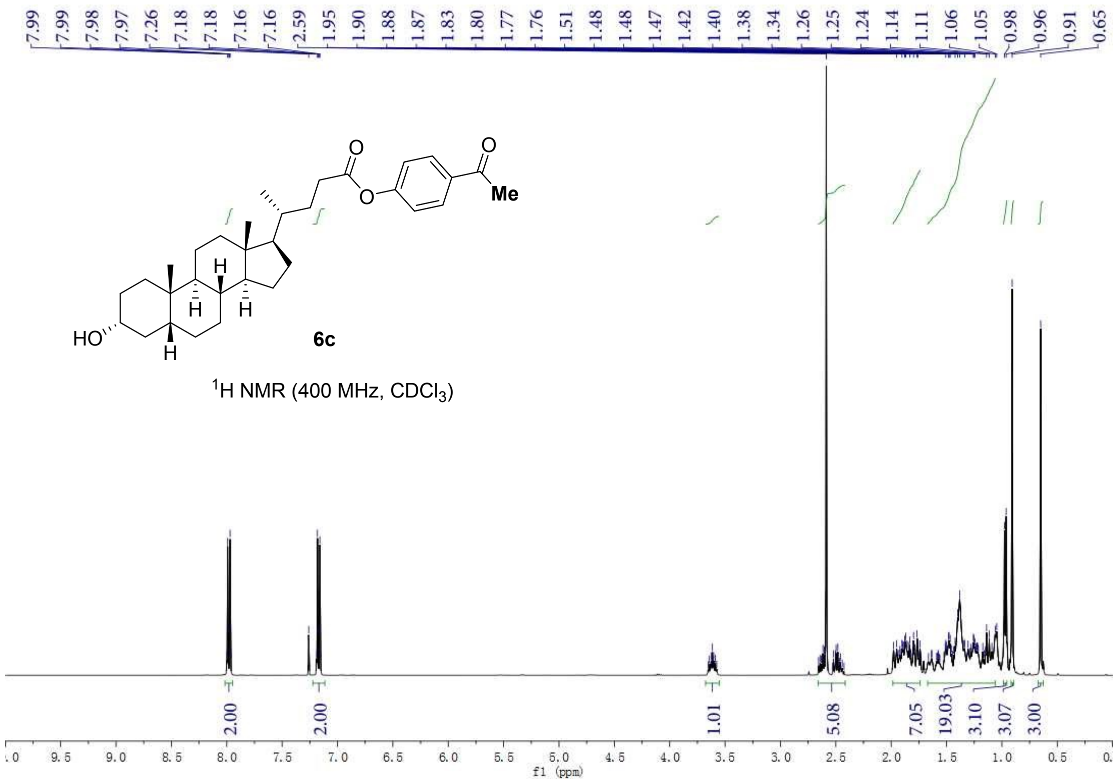
6b

^{1}H NMR (400 MHz, DMSO-d$_6$)



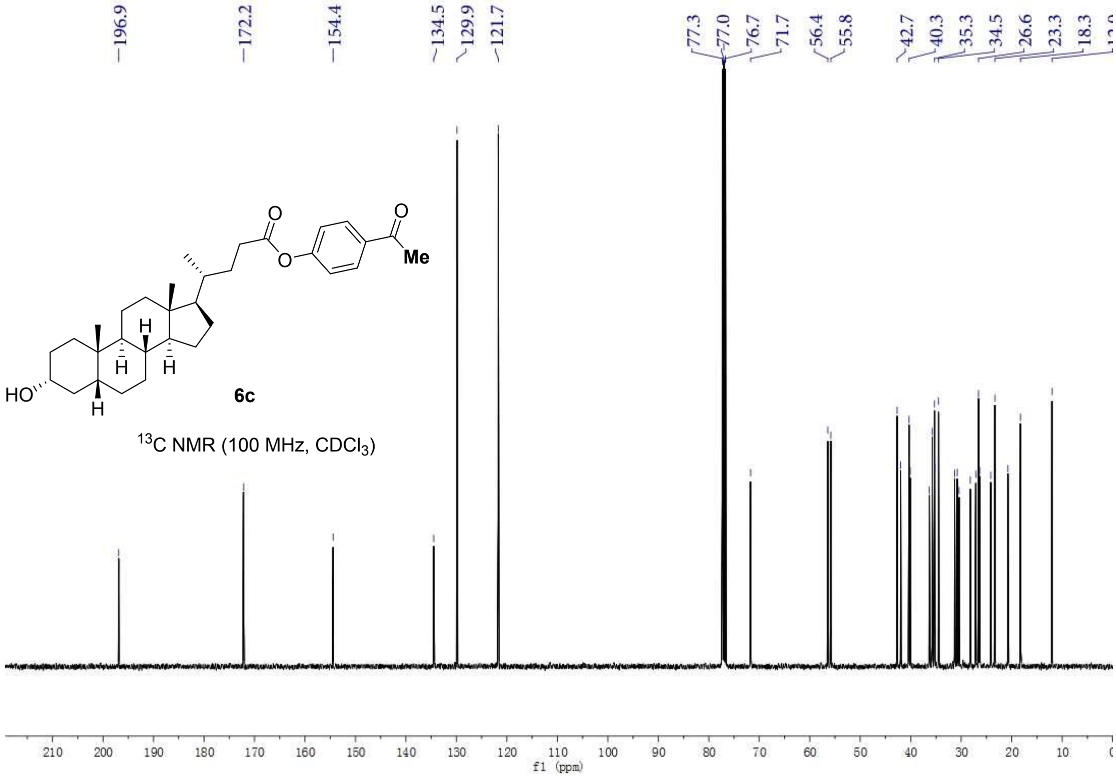
6b

^{13}C NMR (100 MHz, DMSO-d$_6$)



6c

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



6c

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