

# Supporting Information

## Electrooxidative $\alpha$ -hydroxymethylation of ketones with dimethylformamide as the carbon source

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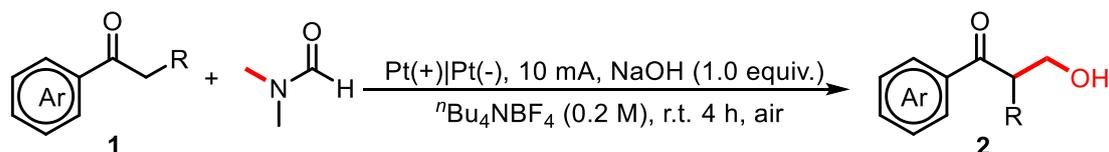
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## 1. General Information

Chemicals were received from commercial sources without further purification or prepared by literature methods. Melting points are uncorrected and recorded on Digital Melting Point Apparatus WRS-1B.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a 400 MHz Bruker spectrometer, using  $\text{CDCl}_3$  as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts were reported in units (ppm) by assigning the residual protonated solvent of  $\text{CDCl}_3$  resonance in the  $^1\text{H}$  spectrum as 7.26 ppm and  $\text{CDCl}_3$  resonance in the  $^{13}\text{C}$  spectrum as 77.0 ppm. All coupling constants ( $J$  values) were reported in Hertz (Hz). Chemical shifts of common trace  $^1\text{H}$  NMR impurities (ppm):  $\text{H}_2\text{O}$ : 1.56,  $\text{CHCl}_3$ : 7.26. High-resolution mass spectrometry (HRMS) was performed with a TOF MS instrument with an ESI source. Column chromatography was performed using EM silica gel 60 (300–400 mesh). Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm). Electrolysis experiments were performed using a MESTEK power supply (DP3005B). Cyclic voltammograms were obtained on a CHI 760E potentiostat.

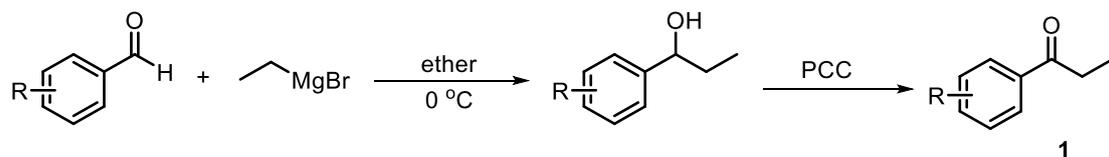
## 2. Experimental Section

### 2.1 General procedure for the synthesis of 2



An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with substrate (0.1 mmol),  $t\text{Bu}_4\text{NBF}_4$  (1.0 mmol, 0.2 M), NaOH (0.1 mmol, 1.0 equiv.). The flask was equipped with a platinum plate anode (10 mm x 10 mm x 0.1 mm) and a platinum plate cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (5.0 mL) using a constant current of 10 mA for 4 hours. The reaction mixture was extracted with EtOAc (15 mL  $\times$  3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products.

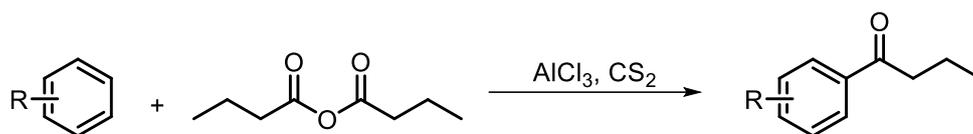
### 2.2 General procedure for the synthesis of ketones 1c, 1d, 1e, 1o



A flask was evacuated and filled with nitrogen. After ether (10 mL) and aldehyde (5.0 mmol) were added, the mixture was kept at 0 °C in the ice bath. EtMgBr (6 mmol, 1.2 equiv.) was added dropwise. After completion of the EtMgBr addition, the mixture was further stirred at 0 °C until complete consumption of the substrate (monitored by TLC), and water (30 mL) was added. After usual aqueous workup, the crude products were subjected to column chromatography on silica gel (hexane/EtOAc) to give pure 1-arylpropanol.

Pyridinium chlorochromate (7.5 mmol, 1.5 equiv.) was added to a solution of alcohol (5 mmol) in DCM (10 mL) and the resulting mixture was stirred under nitrogen at r.t. for 1-2 hours. The reaction was then diluted with ether (100 mL) and filtered through a silica pad. The filtrate was concentrated under vacuum to give the crude product. The crude product was subjected to column chromatography on silica gel (hexane/EtOAc) to give pure ketone 1c, 1d, 1e, 1o.

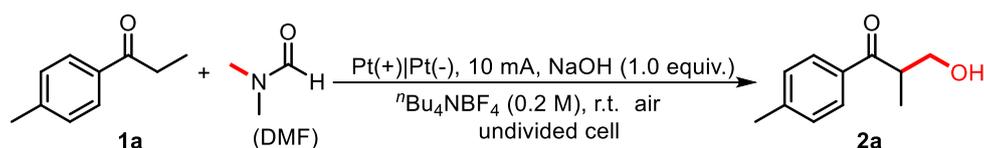
### 2.3 General procedure for the synthesis of ketones **1r**, **1s**, **1t**



After substituted benzene (2.5 mmol),  $\text{AlCl}_3$  (5.6 mmol) and  $\text{CS}_2$  (10 mL) were added, the mixture is heated on a steam bath until gentle refluxing starts, and then butyric anhydride (2.0 mmol) is added slowly. The time of addition is about one hour. Gentle refluxing should be continued throughout the time of addition of the anhydride and for one hour afterward. Then, the mixture was concentrated under vacuum to give the crude product. The crude product was subjected to column chromatography on silica gel (hexane/EtOAc) to give pure ketone **1r**, **1s**, **1t**.

### 2.4 Optimization of reaction conditions

Table S1. the 10 equivalents of DMF in different solvents



entr	solvents	time	yield <sup>b</sup>
1	CH <sub>3</sub> CN	4 h	16%
2	MeOH	4 h	12%
3	DMSO	4 h	18%
4	DMSO	8 h	21%
5	anhydrous DMF	4	9%

<sup>a</sup>Standard conditions: **1a** (0.1 mmol), Pt(+)|Pt(-), 10 mA, NaOH (1.0 equiv.), <sup>t</sup>Bu<sub>4</sub>NBF<sub>4</sub> (0.2 M), DMF (10 equiv.) and solvent (5 mL), in an undivided cell, rt, 4 h, in air. <sup>b</sup>Yield of the isolated product **2a**.

### 3. ON/OFF experiment

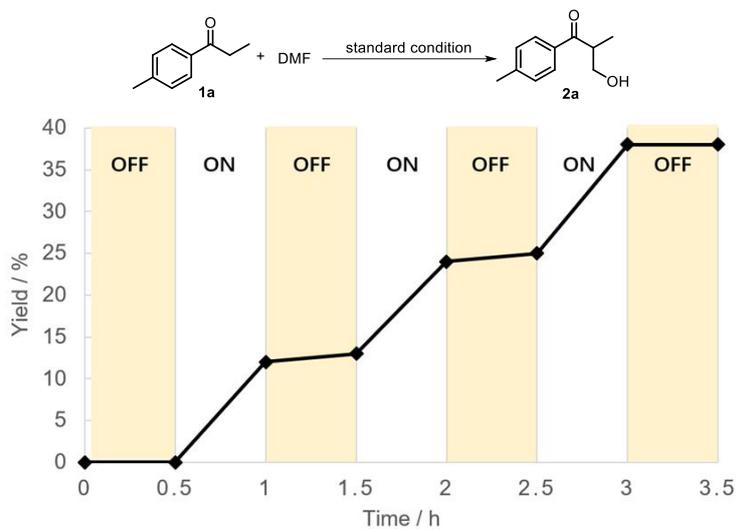


Figure S1. On/Off experiment. Reaction conditions: 1 (0.10 mmol), Pt(+)|Pt(-), 10 mA, NaOH (1.0 equiv.),  $n\text{Bu}_4\text{NBF}_4$  (0.2 M), and DMF (5 mL), in an undivided cell, rt, in air, GC yields (Internal standard: Dodecane).

#### 4. Cyclic voltammetry studies

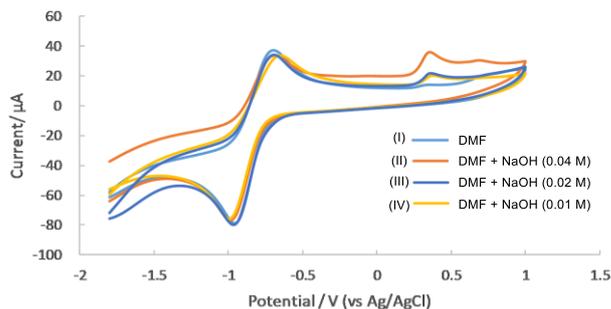


Figure S2. The cyclic voltammograms were recorded in an electrolyte of  $n\text{Bu}_4\text{NBF}_4$  (0.1 M) in DMF using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s. (I) DMF,  $n\text{Bu}_4\text{NBF}_4$  (0.2 M), and 100  $\text{mV}\cdot\text{s}^{-1}$  (II) DMF,  $n\text{Bu}_4\text{NBF}_4$  (0.2 M), NaOH (0.04 M), and 100  $\text{mV}\cdot\text{s}^{-1}$  (III) DMF,  $n\text{Bu}_4\text{NBF}_4$  (0.2 M), NaOH (0.02 M), and 100  $\text{mV}\cdot\text{s}^{-1}$  (IV) DMF,  $n\text{Bu}_4\text{NBF}_4$  (0.2 M), NaOH (0.01 M), and 100  $\text{mV}\cdot\text{s}^{-1}$

As the Figure S2 shown, In the presence of  $n\text{Bu}_4\text{NBF}_4$  electrolyte, DMF has two oxidation peaks at  $-0.69$  V and  $0.33$  V, and has one reduction peak at  $-0.98$  V. After the addition of NaOH, the intensity of the second anode peak was significantly increased. Meanwhile, the higher concentration of NaOH, the intensity of the second anode peak was more significantly increased, indicating that NaOH promotes the stepwise oxidation of DMF to form the iminium cation.

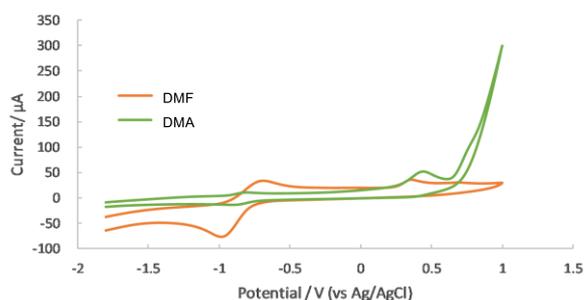
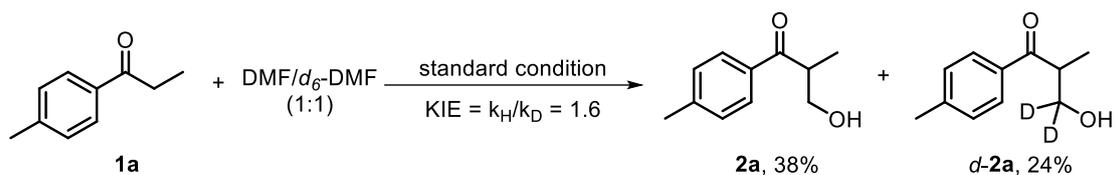


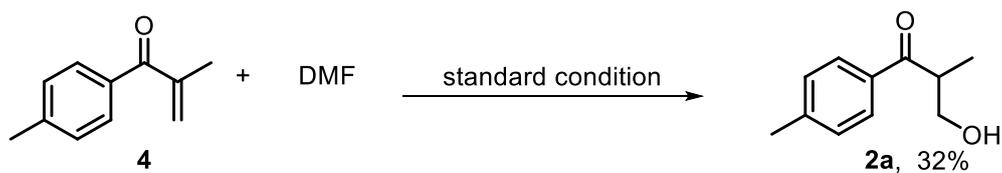
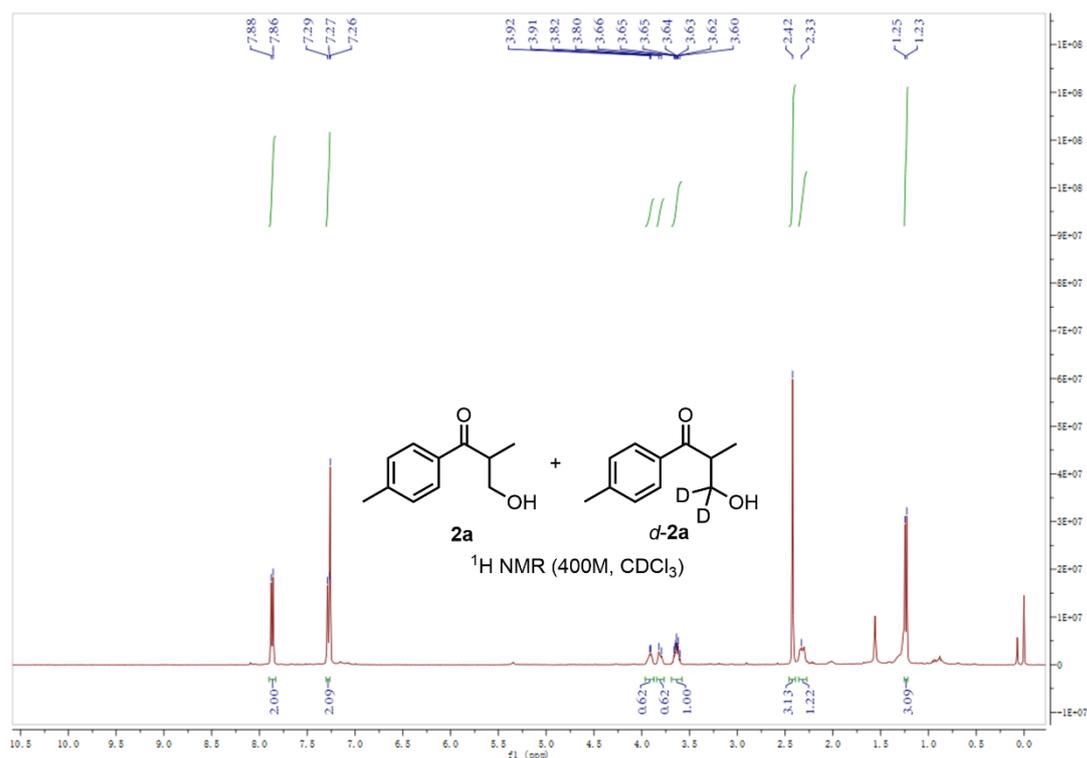
Figure S3: CV studies: (I) DMF,  $n\text{Bu}_4\text{NBF}_4$  (0.2 M), NaOH (0.04 M), and 100  $\text{mV}\cdot\text{s}^{-1}$  (II) DMA,  $n\text{Bu}_4\text{NBF}_4$  (0.2 M), NaOH (0.04 M), and 100  $\text{mV}\cdot\text{s}^{-1}$

In the presence of  $n\text{Bu}_4\text{NBF}_4$  electrolyte, DMF has two oxidation peaks at  $-0.69$  V and  $0.33$  V, and DMA has two oxidation peaks at  $-0.80$  V and  $0.44$  V. The intensity of DMA first anode peak is weaker than DMF's, which possible led DMA to afford a lower yield than DMF.

## 5. Control experiments

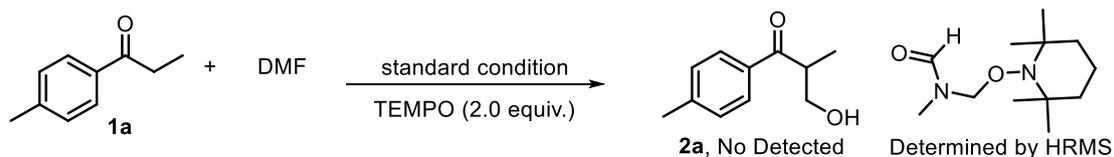


An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **1a** (0.1 mmol),  $n\text{Bu}_4\text{NBF}_4$  (1.0 mmol, 0.2 M), NaOH (0.1 mmol, 1.0 equiv.). The flask was equipped with a platinum plate anode (10 mm x 10 mm x 0.1 mm) and a platinum plate cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (2.5 mL) and  $d_6$ -DMF (2.5 mL) using a constant current of 10 mA for 4 hours. The reaction mixture was extracted with EtOAc (15 mL  $\times$  3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **2a** and  $d_2$ -**2a**.



An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged

with **4** (0.1 mmol),  ${}^n\text{Bu}_4\text{NBF}_4$  (1.0 mmol, 0.2 M), NaOH (0.1 mmol, 1.0 equiv.). The flask was equipped with a platinum plate anode (10 mm x 10 mm x 0.1 mm) and a platinum plate cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (5.0 mL) using a constant current of 10 mA. The reaction mixture was extracted with EtOAc (15 mL  $\times$  3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product **2a**.



An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **1a** (0.1 mmol),  ${}^n\text{Bu}_4\text{NBF}_4$  (1.0 mmol, 0.2 M), NaOH (0.1 mmol, 1.0 equiv.), TEMPO (2.0 equiv.). The flask was equipped with a platinum plate anode (10 mm x 10 mm x 0.1 mm) and a platinum plate cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (5.0 mL) using a constant current of 10 mA for 4 hours. The product **2a** was not detected and the TEMPO-DMF adduct was detected by HRMS analysis

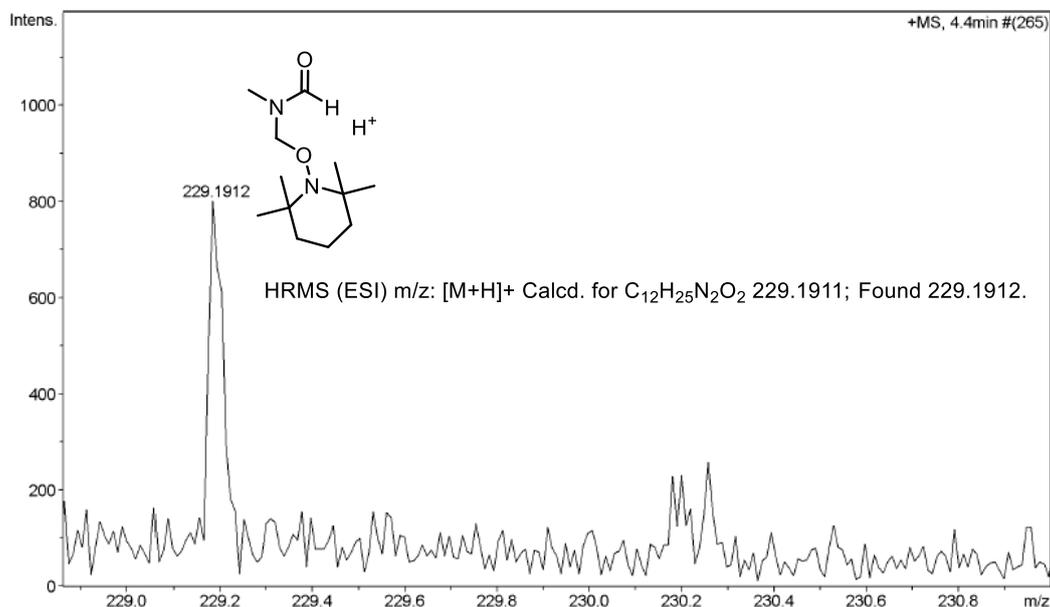
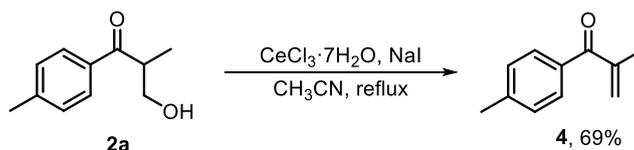
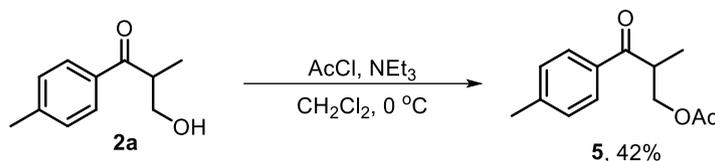


Figure S4. HRMS analysis of TEMPO-DMF adduct

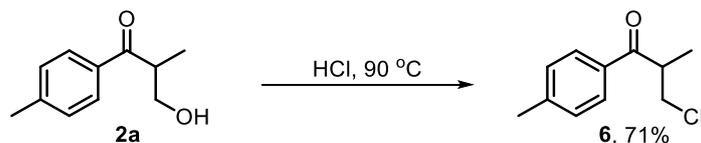
## 6. Transformations of **2a**.



Prepared following a literature procedure.<sup>1</sup> To a stirred suspension of **2a** (0.2 mmol) and cerium(III) chloride heptahydrate (0.11 g, 0.3 mmol) in acetonitrile (2 mL) was added sodium iodide (0.04 g, 0.3 mmol), and the resulting mixture was stirred for 10 h at reflux. The reaction mixture was diluted with ether and treated with 0.5 N HCl (4 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3\*25 mL). The combined organic layers were washed twice with an aqueous saturated NaHCO<sub>3</sub> solution and a saturated NaCl solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The extracts were then concentrated under reduced pressure, and the residue was chromatographed on a silica gel column (hexanes-ethyl acetate) to give enone **4**.

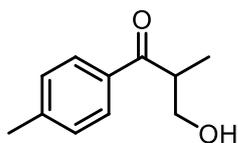


To a stirred solution of **2a** (0.2 mmol) in dichloromethane (2 mL) were added triethylamine (0.4 mmol) and acetylchloride (0.3 mmol, 1.5 equiv.) dropwise under 0 °C. Then the mixture was stirred at room temperature for 1 h, quenched with H<sub>2</sub>O and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL). The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and purified by column chromatography (petroleum ether/ethyl acetate) to afford compound **5**.



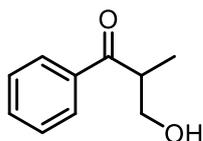
Prepared following a literature procedure.<sup>2</sup> A suspension of **2a** (0.2 mmol) in concentrated hydrochloric acid (0.5 mL) is stirred at 90 °C for 0.5 hours. After cooling, the reaction mixture was diluted with ether. The organic layer was separated, and the aqueous layer was extracted with ether (3\*25 mL). The combined organic layers were washed twice with an aqueous saturated NaHCO<sub>3</sub> solution and a saturated NaCl solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The extracts were then concentrated under reduced pressure, and the residue was chromatographed on a silica gel column (hexanes-ethyl acetate) to give product **6**.

## 7. Analytical data for products



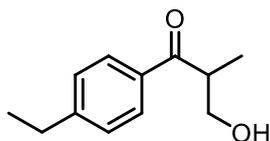
### 3-hydroxy-2-methyl-1-(p-tolyl)propan-1-one (2a)<sup>3</sup>

Yellow liquid (15.2 mg, 85%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.92 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 6.8 Hz, 1H), 3.78 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.69-3.62 (m, 1H), 2.65 (brs, 1H), 2.41 (s, 3H), 1.22 (d, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.1, 144.2, 133.5, 129.3, 128.5, 64.6, 42.7, 21.6, 14.6.



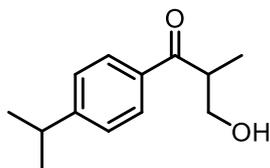
### 3-hydroxy-2-methyl-1-phenylpropan-1-one (2b)<sup>3</sup>

Yellow liquid (11.7 mg, 71%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.56-7.60 (m, 1H), 7.46-7.50 (m, 2H), 3.94-3.92 (m, 1H), 3.82-3.79 (m, 1H), 3.71-3.63 (m, 1H), 2.38 (brs, 1H), 1.24 (d, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.4, 136.1, 133.3, 128.7, 128.4, 64.5, 42.9, 14.6.



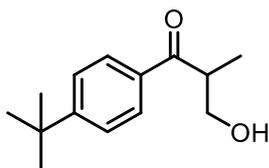
### 1-(4-ethylphenyl)-3-hydroxy-2-methylpropan-1-one (2c)<sup>3</sup>

Red liquid (13.9 mg, 72%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 3.92 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H), 3.82-3.79 (m, 1H), 3.69-3.63 (m, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.41 (brs, 1H), 1.29-1.23 (m, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.1, 150.4, 133.8, 128.7, 128.2, 64.6, 42.7, 28.9, 15.1, 14.7.



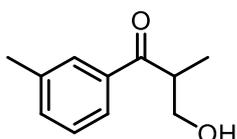
### 3-hydroxy-1-(4-isopropylphenyl)-2-methylpropan-1-one (2d)

Red solid (13.4 mg, 65%), m.p. 52-55 °C. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.91(d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.93 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 6.8 Hz, 1H), 3.78 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.68-3.63 (m, 1H), 3.01-2.94 (m, 1H), 2.43 (brs, 1H), 1.28 (d, *J* = 7.2 Hz, 6H), 1.24 (d, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.1, 154.9, 133.8, 128.7, 126.8, 64.6, 42.7, 34.2, 23.6, 14.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>13</sub>H<sub>19</sub>O<sub>2</sub> 207.1380; Found 207.1383.



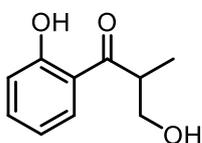
**1-(4-(tert-butyl)phenyl)-3-hydroxy-2-methylpropan-1-one (2e)**

Red liquid (17.8 mg, 81%).  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.91(d,  $J = 6.8$  Hz, 2H), 7.49 (d,  $J = 7.2$  Hz, 2H), 3.92-3.90 (m, 1H), 3.81-3.78 (m, 1H), 3.68-3.63 (m, 1H), 2.41 (brs, 1H), 1.35 (s, 9H), 1.24 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ )  $\delta$  204.1, 157.2, 133.4, 128.4, 125.7, 64.6, 42.7, 35.1, 31.0, 14.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{14}\text{H}_{21}\text{O}_2$  221.1537; Found 221.1540.



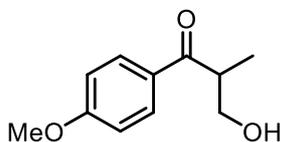
**3-hydroxy-2-methyl-1-(m-tolyl)propan-1-one (2f)<sup>3</sup>**

Yellow liquid (13.9 mg, 78%).  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.75 (m, 2H), 7.41-7.35 (m, 2H), 3.92 (dd,  $J_1 = 10.8$  Hz,  $J_2 = 7.2$  Hz, 1H), 3.81 (dd,  $J_1 = 10.8$  Hz,  $J_2 = 3.6$  Hz, 1H), 3.69-3.64 (m, 1H), 2.42 (s, 3H), 2.37 (brs, 1H), 1.24 (d,  $J = 7.6$  Hz, 3H).  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ )  $\delta$  204.7, 138.5, 136.1, 134.1, 128.9, 128.6, 125.6, 64.6, 42.9, 21.4, 14.6.



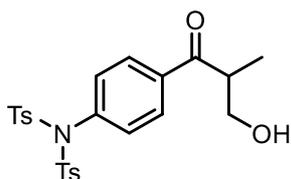
**3-hydroxy-1-(2-hydroxyphenyl)-2-methylpropan-1-one (2g)<sup>4</sup>**

Yellow liquid (8.8 mg, 49%).  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ )  $\delta$  12.3 (s, 1H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.51-7.47 (m, 1H), 7.00 (d,  $J = 8.0$  Hz, 1H), 6.94-6.90 (m, 1H), 3.99-3.94 (m, 1H), 3.82-3.79 (m, 1H), 3.75-3.71 (m, 1H), 2.17 (s, 1H), 1.29 (d,  $J = 4.0$  Hz, 3H).  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ )  $\delta$  210.0, 163.2, 136.7, 130.1, 119.0, 118.8, 118.6, 64.4, 42.6, 15.0.



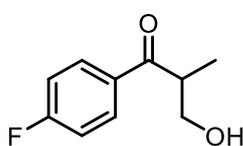
**3-hydroxy-1-(4-methoxyphenyl)-2-methylpropan-1-one (2h)<sup>3</sup>**

Yellow liquid (17.9 mg, 92%).  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.8$  Hz, 2H), 6.96 (d,  $J = 8.8$  Hz, 2H), 3.92 (dd,  $J_1 = 11.2$  Hz,  $J_2 = 7.2$  Hz, 1H), 3.88 (s, 3H), 3.80 (dd,  $J_1 = 11.2$  Hz,  $J_2 = 4.0$  Hz, 1H), 3.65-3.59 (m, 1H), 2.50 (brs, 1H), 1.24 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ )  $\delta$  203.0, 163.7, 130.8, 129.0, 113.9, 64.7, 55.5, 42.4, 14.8.



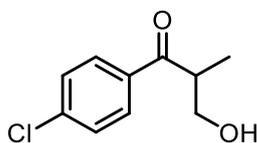
**N-(4-(3-hydroxy-2-methylpropanoyl)phenyl)-4-methyl-N-tosylbenzenesulfonamide (2i)**

Yellow liquid (13.1 mg, 27%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.95-7.93 (m, 2H), 7.82-7.79 (m, 4H), 7.36-7.34 (m, 4H), 7.16-7.14 (m, 2H), 3.95 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 7.2 Hz, 1H), 3.79 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.67-3.62 (m, 1H), 2.48 (s, 6H), 1.24 (d, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.3, 145.4, 138.7, 137.2, 136.4, 132.0, 129.8, 129.2, 128.6, 64.6, 43.3, 21.8, 14.5. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>24</sub>H<sub>26</sub>NO<sub>6</sub>S<sub>2</sub> 488.1197; Found 488.1198.



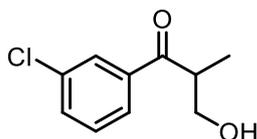
**1-(4-fluorophenyl)-3-hydroxy-2-methylpropan-1-one (2j)<sup>3</sup>**

Yellow liquid (9.7 mg, 53%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.02-7.98 (m, 2H), 7.17-7.13 (m, 2H), 3.93 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 3.79 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.68-3.53 (m, 1H), 2.47 (s, 1H), 1.23 (d, *J* = 8.0 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 202.7, 165.9 (d, *J* = 263 Hz), 132.5, 131.1 (d, *J* = 10.0 Hz), 115.8 (d, *J* = 20.0 Hz), 64.5, 42.8, 14.5. <sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>) δ -104.7.



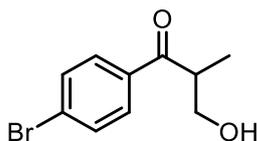
**1-(4-chlorophenyl)-3-hydroxy-2-methylpropan-1-one (2k)<sup>3</sup>**

Red liquid (13.7 mg, 69%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 3.93 (dd, *J*<sub>1</sub> = 10.4 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 3.80 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H), 3.66-3.58 (m, 1H), 2.29 (brs, 1H), 1.22 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.1, 139.8, 134.4, 129.8, 129.0, 64.5, 43.0, 14.5.



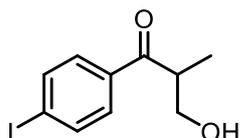
**1-(3-chlorophenyl)-3-hydroxy-2-methylpropan-1-one (2l)<sup>3</sup>**

Red liquid (12.5 mg, 63%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.93 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.45-7.41 (m, 1H), 3.94-3.92 (m, 1H), 3.82-3.79 (m, 1H), 3.66-3.58 (m, 1H), 2.20 (s, 1H), 1.23 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.0, 137.7, 135.1, 133.2, 130.0, 128.5, 126.5, 64.5, 43.2, 14.4.



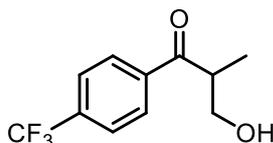
**1-(4-bromophenyl)-3-hydroxy-2-methylpropan-1-one (2m)<sup>3</sup>**

Yellow liquid (20.9 mg, 86%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 3.93 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 7.2 Hz, 1H), 3.89 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H), 3.66-3.57 (m, 1H), 2.35 (brs, 1H), 1.22 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.3, 134.8, 132.0, 129.9, 128.5, 64.5, 42.9, 14.5.



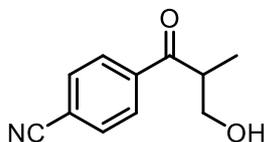
**3-hydroxy-1-(4-iodophenyl)-2-methylpropan-1-one (2n)**

Yellow liquid (10.5 mg, 36%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 3.93-3.91 (m, 1H), 3.81-3.78 (m, 1H), 3.64-3.56 (m, 1H), 2.23 (s, 1H), 1.22 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.6, 138.1, 135.4, 129.8, 101.4, 64.5, 42.9, 14.5. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>10</sub>H<sub>12</sub>IO<sub>2</sub> 290.9877; Found 290.9875.



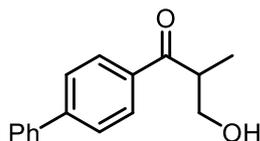
**3-hydroxy-2-methyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (2o)**

Yellow liquid (14.4 mg, 62%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 3.97 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 7.2 Hz, 1H), 3.82 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.70-3.64 (m, 1H), 2.33 (brs, 1H), 1.23 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.4, 138.9, 134.5 (q, *J* = 33.0 Hz), 128.7, 125.8 (q, *J* = 3.0 Hz), 123.5 (q, *J* = 271.0 Hz), 64.4, 43.4, 14.3. <sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>) δ -63.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>11</sub>H<sub>12</sub>F<sub>3</sub>O<sub>2</sub> 233.0784; Found 233.0786.



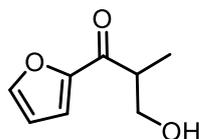
**3-Hydroxy-2-methyl-1-(thiophen-2-yl)propan-1-one (2p)**

Yellow oil (7.2 mg, 38%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 3.95 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H), 3.80 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.69-3.64 (m, 1H), 2.33 (s, 1H), 1.22 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 202.9, 139.3, 132.5, 128.8, 117.8, 116.4, 64.3, 43.4, 14.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>11</sub>H<sub>12</sub>NO<sub>2</sub> 190.0863; Found 190.0860.



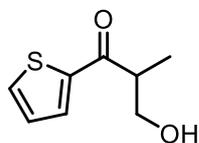
**1-([1,1'-biphenyl]-4-yl)-3-hydroxy-2-methylpropan-1-one (2q)**

Red solid (13.0 mg, 54%), 60-63 °C. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.06-8.04 (m, 2H), 7.72-7.70 (m, 2H), 7.64-7.63 (m, 2H), 7.50-7.46 (m, 2H), 7.43-7.41 (m, 1H), 3.98-3.94 (m, 1H), 3.85-3.83 (m, 1H), 3.72-3.70 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.0, 146.1, 139.8, 134.7, 129.0, 129.0, 128.3, 127.4, 127.3, 64.6, 42.9, 14.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> 241.1224; Found 241.1228.



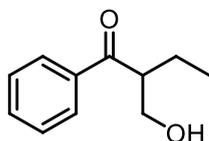
**1-(furan-2-yl)-3-hydroxy-2-methylpropan-1-one (2r)**

Red liquid (7.1 mg, 46%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 0.8 Hz, 1H), 7.26 (d, *J* = 4.0 Hz, 1H), 6.56 (dd, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 0.8 Hz, 1H), 3.90 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H), 3.77 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.50-3.45 (m, 1H), 2.44 (brs, 1H), 1.24 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 192.8, 152.2, 146.7, 118.0, 112.3, 64.3, 43.7, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>8</sub>H<sub>11</sub>O<sub>3</sub> 155.0703; Found 155.0705.



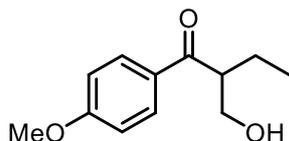
**4-(3-hydroxy-2-methylpropanoyl)benzonitrile (2s)<sup>3</sup>**

Yellow oil (10.5 mg, 62%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.88-7.77 (m, 1H), 7.68-7.66 (m, 1H), 7.16-7.14 (m, 1H), 3.91 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 7.2 Hz, 1H), 3.78 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 4.4 Hz, 1H), 3.55-3.50 (m, 1H), 2.50 (s, 1H), 1.28 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 196.9, 143.6, 134.2, 132.4, 128.2, 64.6, 44.6, 14.8.



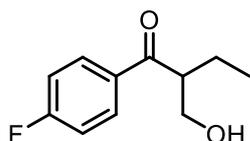
**2-(hydroxymethyl)-1-phenylbutan-1-one (2t)<sup>3</sup>**

Red liquid (12.1 mg, 68%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.61-7.57 (m, 1H), 7.51-7.47 (m, 2H), 3.99-3.97 (m, 1H), 3.87-3.85 (m, 1H), 3.58-3.53 (m, 1H), 2.30 (s, 1H), 1.84-1.75 (m, 1H), 1.72-1.65 (m, 1H), 0.97 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.6, 136.8, 133.3, 128.7, 128.3, 62.6, 49.5, 22.3, 11.8.



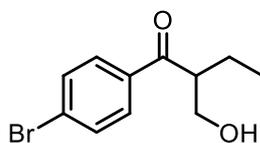
**2-(hydroxymethyl)-1-(4-methoxyphenyl)butan-1-one (2u)**

Yellow liquid (9.6 mg, 46%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.95 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 6.8 Hz, 1H), 3.88 (s, 3H), 3.83 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H), 3.51-3.45 (m, 1H), 1.82-1.63 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.1, 163.7, 130.7, 129.9, 113.9, 62.7, 55.5, 49.0, 22.5, 11.9. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>12</sub>H<sub>17</sub>O<sub>3</sub> 209.1173; Found 209.1174.



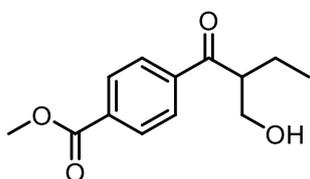
**1-(4-fluorophenyl)-2-(hydroxymethyl)butan-1-one (2v)<sup>3</sup>**

Colourless liquid (12.2 mg, 62%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.04-8.01 (m, 2H), 7.20-7.16 (m, 2H), 4.00 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 3.87 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.57-3.51 (m, 1H), 2.38 (s, 1H), 1.85-1.74 (m, 1H), 1.73-1.63 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 202.9, 165.9 (d, *J* = 254 Hz), 133.3, 131.1 (d, *J* = 10.0 Hz), 115.8 (d, *J* = 20.0 Hz), 62.6, 49.5, 22.4, 11.8. <sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>) δ -104.8.



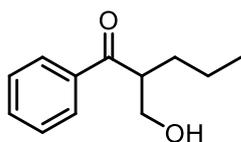
**1-(4-bromophenyl)-2-(hydroxymethyl)butan-1-one (2w)**

Yellow liquid (14.4 mg, 56%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 4.00-3.94 (m, 1H), 3.85-3.83 (m, 1H), 3.52-3.46 (m, 1H), 2.14 (s, 1H), 1.79-1.72 (m, 1H), 1.69-1.60 (m, 1H), 0.95 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.4, 135.7, 132.0, 129.9, 128.5, 62.6, 49.6, 22.3, 11.8. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>11</sub>H<sub>14</sub>BrO<sub>2</sub> 257.0172, 259.0152; Found 257.0176, 259.0156.



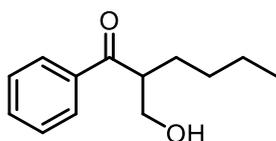
**methyl 4-(2-(hydroxymethyl)butanoyl)benzoate (2x)**

Red oil (11.3 mg, 48%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 4.00 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 7.2 Hz, 1H), 3.98 (s, 3H), 3.86 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.59-3.54 (m, 1H), 2.29 (s, 1H), 1.80-1.73 (m, 1H), 1.72-1.63 (m, 1H), 0.96 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.1, 166.2, 140.2, 134.0, 129.9, 128.2, 62.6, 52.5, 50.1, 22.2, 11.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub> 237.1122; Found 237.1120.



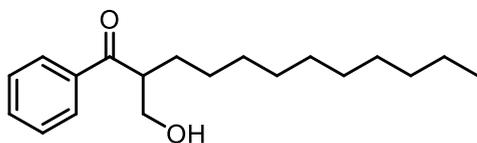
**2-(hydroxymethyl)-1-phenylpentan-1-one (2y)<sup>3</sup>**

Yellow liquid (12.7 mg, 66%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 6.0 Hz, 2H), 7.58-7.57 (m, 1H), 7.50-7.48 (m, 2H), 3.98-3.93 (m, 1H), 3.86-3.82 (m, 1H), 3.64-3.62 (m, 1H), 2.35 (brs, 1H), 1.70-1.59 (m, 2H), 1.40-1.32 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.7, 136.8, 133.3, 128.7, 128.3, 62.9, 47.9, 31.3, 20.6, 14.1.



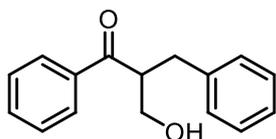
**2-(hydroxymethyl)-1-phenylhexan-1-one (2z)<sup>5</sup>**

Yellow liquid (11.1 mg, 54%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 6.8 Hz, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 3.96 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 6.8 Hz, 1H), 3.84 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H), 3.64-3.59 (m, 1H), 2.42 (brs, 1H), 1.74-1.62 (m, 1H), 1.63-1.62 (m, 1H), 1.36-1.31 (m, 4H), 0.86 (t, *J* = 5.6 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.7, 136.8, 133.2, 128.7, 128.3, 63.0, 48.1, 29.5, 28.9, 22.7, 13.8.



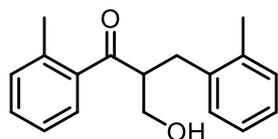
**2-(hydroxymethyl)-1-phenyl-dodecan-1-one (2aa)**

Colorless liquid (14.5 mg, 50%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.60-7.57 (m, 1H), 7.50-7.46 (m, 2H), 3.96 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 6.8 Hz, 1H), 3.85 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H), 3.63-3.57 (m, 1H), 2.30 (brs, 1H), 1.74-1.60 (m, 4H), 1.25-1.23 (m, 14H), 0.87 (t, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 204.7, 136.8, 133.3, 128.7, 128.3, 62.9, 48.1, 31.9, 29.7, 29.5, 29.5, 29.3, 29.3, 29.2, 27.4, 22.7, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>19</sub>H<sub>31</sub>O<sub>2</sub> 291.2319; Found 291.2322.



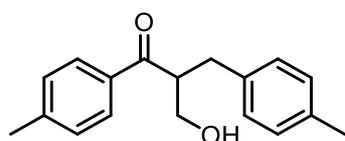
**2-benzyl-3-hydroxy-1-phenylpropan-1-one (2ab)<sup>5</sup>**

Yellow liquid (13.7 mg, 57%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.94-7.91 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.29-7.25 (m, 2H), 7.23-7.19 (m, 3H), 3.86-3.83 (m, 3H), 3.08-3.03 (m, 1H), 2.96-2.91 (m, 1H), 2.36 (brs, 1H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.9, 138.8, 136.5, 133.4, 129.0, 128.7, 128.5, 128.4, 126.5, 62.4, 49.9, 34.9.



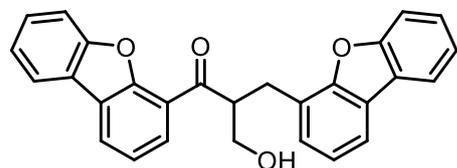
**3-hydroxy-2-(2-methylbenzyl)-1-(o-tolyl)propan-1-one (2ac)**

Yellow liquid (14.0 mg, 52%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.37-7.33 (m, 1H), 7.24-7.19 (m, 2H), 7.13-7.08 (m, 4H), 3.88-3.80 (m, 2H), 3.71-3.65 (m, 1H), 3.00 (dd, *J*<sub>1</sub> = 13.6 Hz, *J*<sub>2</sub> = 6.0 Hz, 1H), 2.87 (dd, *J*<sub>1</sub> = 14.0 Hz, *J*<sub>2</sub> = 8.8 Hz, 1H), 2.43 (s, 3H), 2.28 (s, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 208.1, 138.2, 138.0, 137.0, 136.1, 131.8, 131.3, 130.5, 129.8, 127.9, 126.6, 126.0, 125.6, 62.5, 51.8, 31.6, 20.7, 19.4. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>18</sub>H<sub>21</sub>O<sub>2</sub> 269.1537; Found 269.1541.



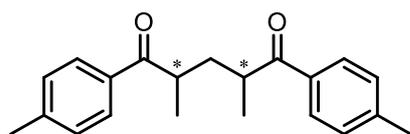
**3-hydroxy-2-(4-methylbenzyl)-1-(p-tolyl)propan-1-one (2ad)**

Yellow liquid (9.1 mg, 34%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 6.8 Hz, 2H), 7.12-7.07 (m, 4H), 3.85-3.76 (m, 3H), 3.01 (dd, *J*<sub>1</sub> = 14.0 Hz, *J*<sub>2</sub> = 5.2 Hz, 1H), 2.89 (dd, *J*<sub>1</sub> = 13.6 Hz, *J*<sub>2</sub> = 8.8 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 203.6, 144.3, 136.0, 135.7, 133.9, 129.4, 129.2, 128.9, 128.6, 62.3, 49.7, 34.5, 21.6, 21.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>18</sub>H<sub>21</sub>O<sub>2</sub> 269.1537; Found 269.1539.



**1,3-bis(dibenzo[b,d]furan-4-yl)-2-(hydroxymethyl)propan-1-one (2ae)**

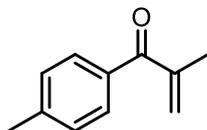
Red solid (16.8 mg, 40%), 71-75 °C. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.42-7.29 (m, 8H), 7.22-7.18 (m, 1H), 4.73-4.67 (m, 1H), 4.10-4.04 (m, 2H), 3.52 (dd, *J*<sub>1</sub> = 14.0 Hz, *J*<sub>2</sub> = 6.0 Hz, 1H), 3.42 (dd, *J*<sub>1</sub> = 14.0 Hz, *J*<sub>2</sub> = 8.8 Hz, 1H), 2.49 (s, 1H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 202.1, 156.0, 155.9, 154.8, 154.2, 128.3, 128.1, 127.8, 127.0, 125.8, 125.6, 124.4, 123.9, 123.4, 123.1, 122.8, 122.7, 122.3, 120.7, 120.6, 118.9, 111.9, 111.6, 62.5, 51.8, 28.9. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>28</sub>H<sub>21</sub>O<sub>4</sub> 421.1435; Found 421.1433.



**2,4-dimethyl-1,5-di-p-tolylpentane-1,5-dione (3a)<sup>6</sup>**

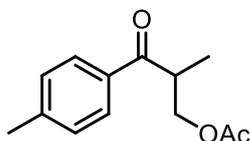
Yellow liquid (2.5 mg, 16%), an inseparable mixture of two diastereomers, diastereomeric ratio: 1.25:1. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.4 Hz, 4H), 7.67 (d, *J* = 8.0 Hz, 3H), 7.29 (d, *J*

= 8.0 Hz, 4H), 7.11 (d,  $J = 8.0$  Hz, 3H), 3.61-3.56 (m, 2H), 3.49-3.42 (m, 2H), 2.44-2.39 (m, 7H), 2.34 (s, 5H), 1.98 (t,  $J = 7.2$  Hz, 2H), 1.50-1.43 (m, 1H), 1.19 (d,  $J = 6.8$  Hz, 5H), 1.15 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  204.0, 203.4, 143.8, 143.6, 133.9, 133.7, 129.4, 129.1, 128.5, 128.2, 38.4, 37.9, 37.4, 37.1, 21.6, 21.5, 18.7, 17.6.



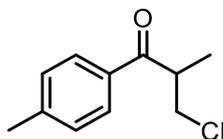
**2-methyl-1-(p-tolyl)prop-2-en-1-one (4)<sup>7</sup>**

Yellow liquid (22.1 mg, 69%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 8.0$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 5.85 (s, 1H), 5.58 (s, 1H), 2.40 (s, 3H), 2.06 (s, 3H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  198.1, 143.8, 142.7, 134.8, 129.6, 128.8, 126.0, 21.5, 18.8.



**2-methyl-3-oxo-3-(p-tolyl)propyl acetate (5)<sup>8</sup>**

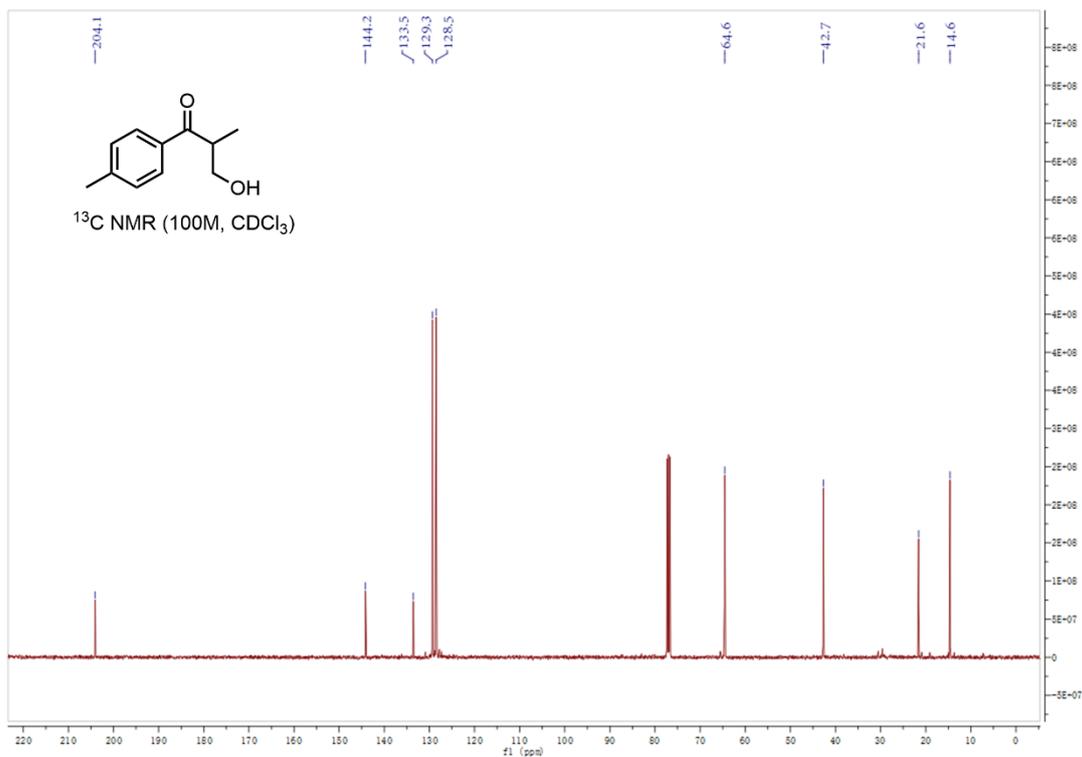
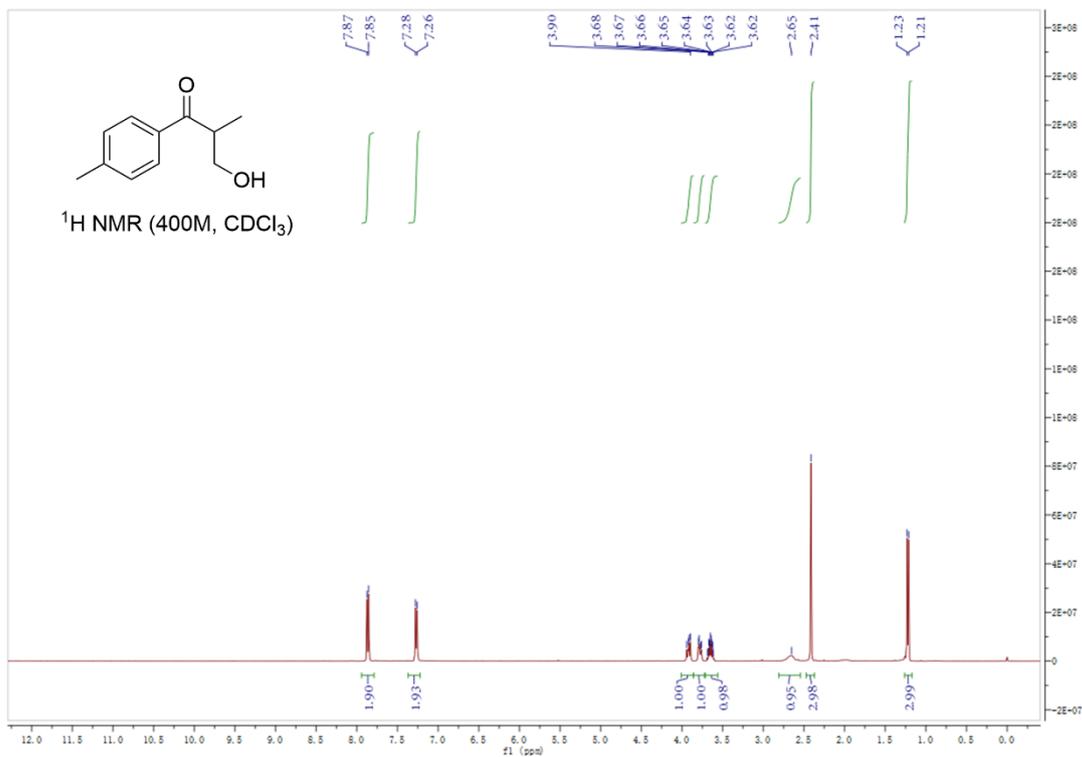
Yellow liquid (18.5 mg, 42%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 4.42 (dd,  $J_1 = 10.8$  Hz,  $J_2 = 8.0$  Hz, 1H), 4.18 (dd,  $J_1 = 10.8$  Hz,  $J_2 = 5.6$  Hz, 1H), 3.87-3.78 (m, 1H), 2.42 (s, 3H), 1.98 (s, 3H), 1.22 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  200.9, 170.9, 144.1, 133.7, 129.4, 128.5, 66.0, 39.8, 21.6, 20.8, 14.7.



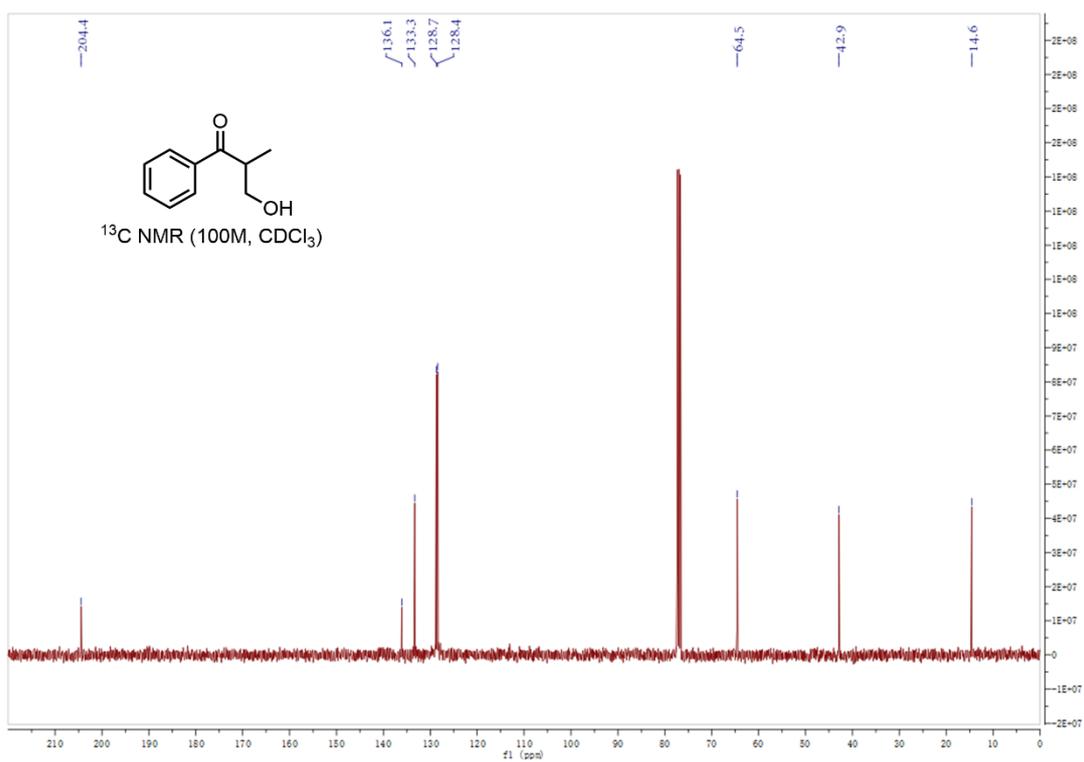
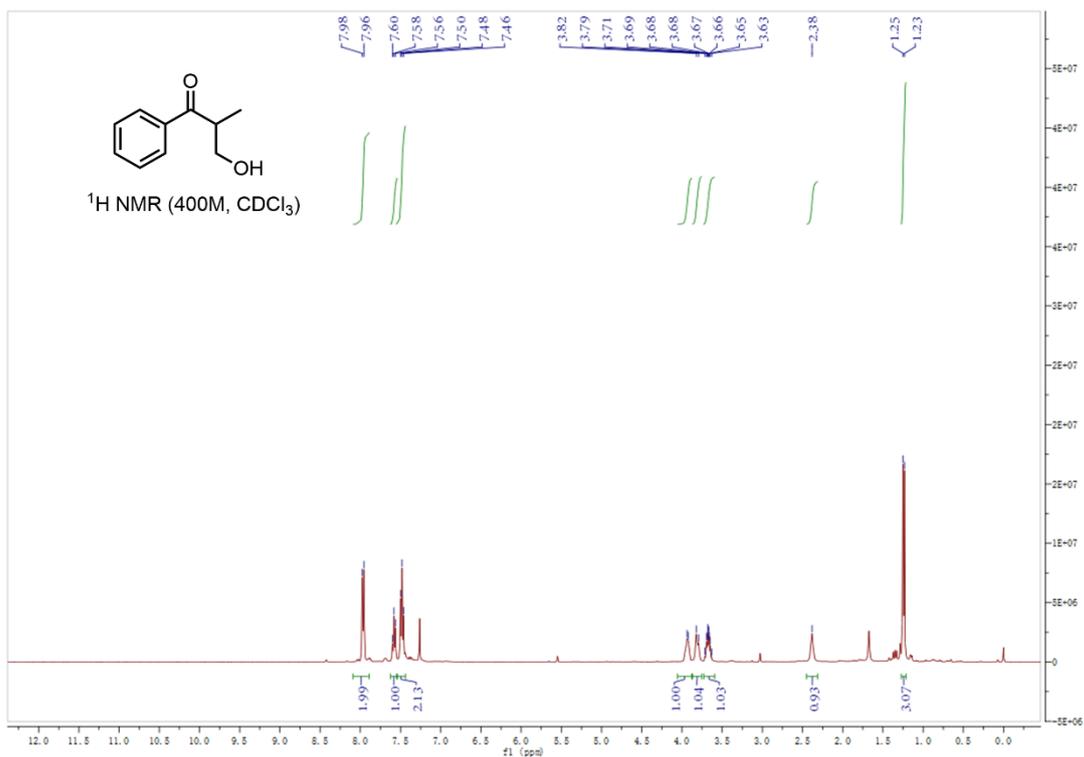
**3-chloro-2-methyl-1-(p-tolyl)propan-1-one (6)**

Yellow liquid (27.8 mg, 71%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 3.93 (dd,  $J_1 = 10.4$  Hz,  $J_2 = 7.2$  Hz, 1H), 3.82 (dd,  $J_1 = 14.0$  Hz,  $J_2 = 7.2$  Hz, 1H), 3.59-3.55 (m, 1H), 2.41 (s, 3H), 1.30 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  200.7, 144.3, 133.3, 129.4, 128.4, 45.9, 43.4, 21.6, 16.5. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{11}\text{H}_{14}\text{ClO}$  197.0728; Found 197.0725.

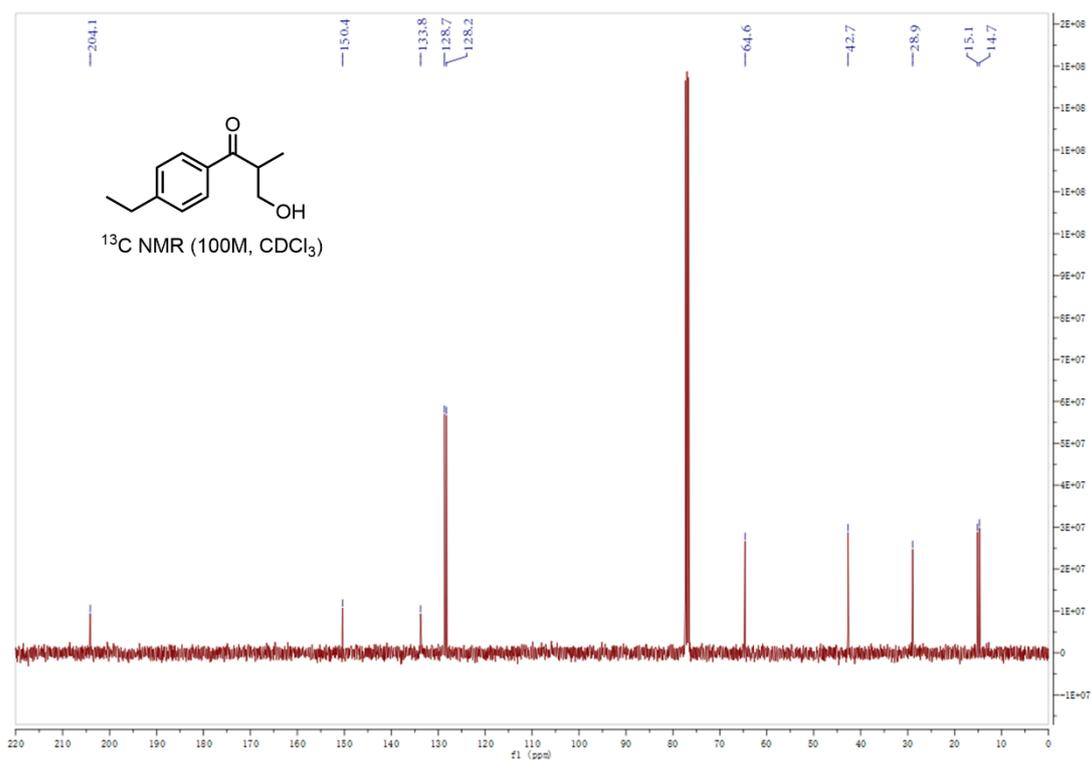
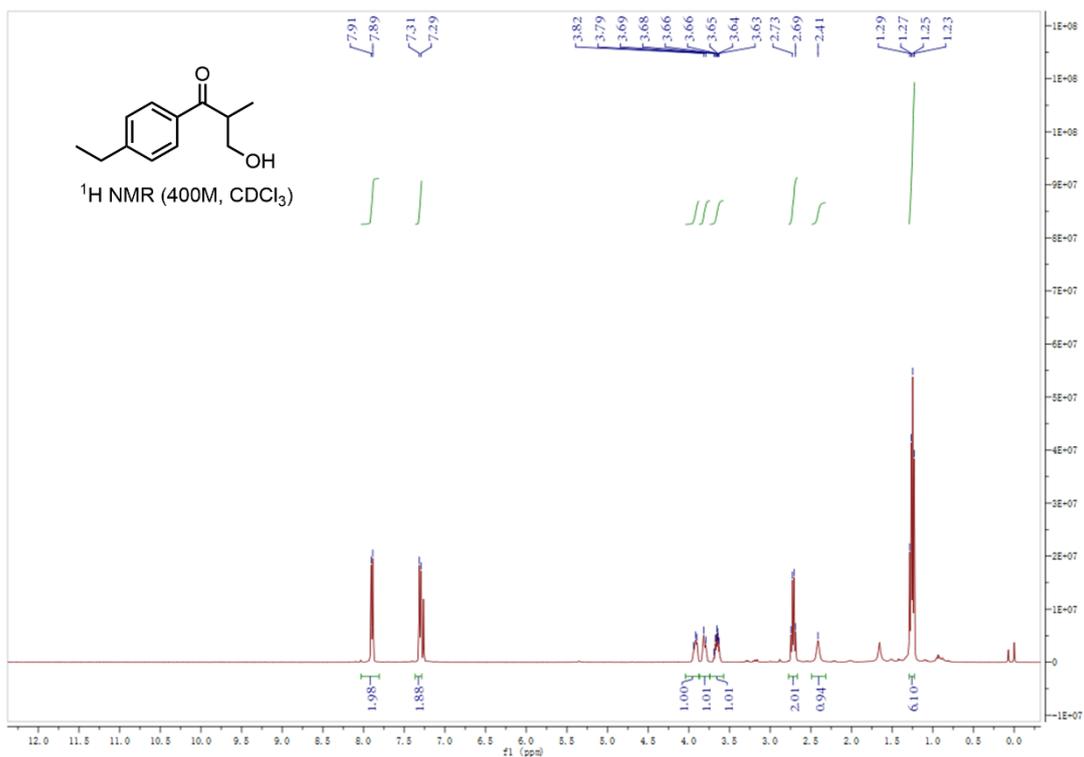
## 8. NMR spectra for products



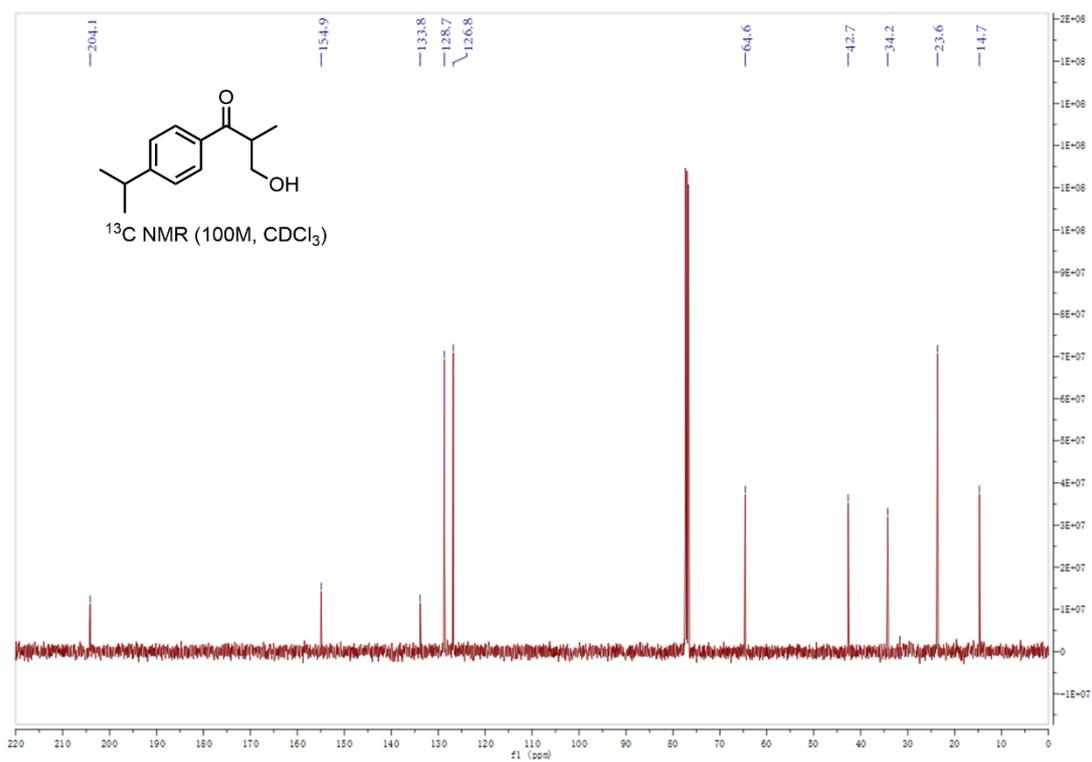
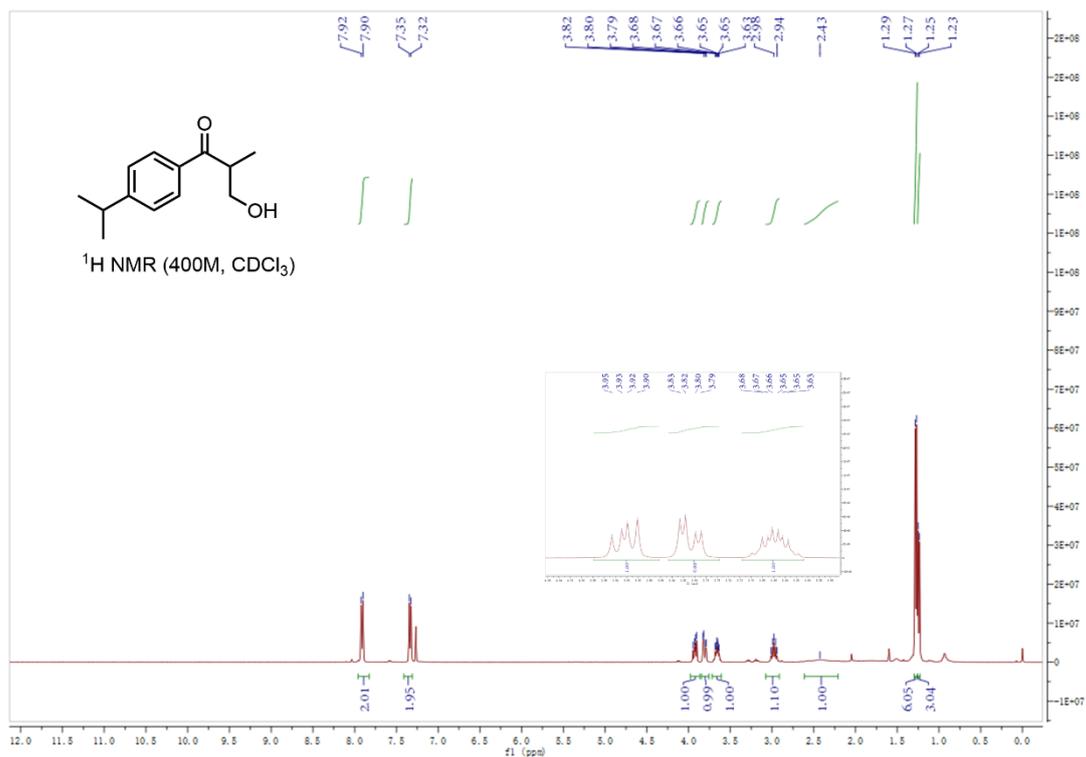
$^1\text{H NMR}$  of **2a** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C NMR}$  of **2a** (100 MHz,  $\text{CDCl}_3$ )



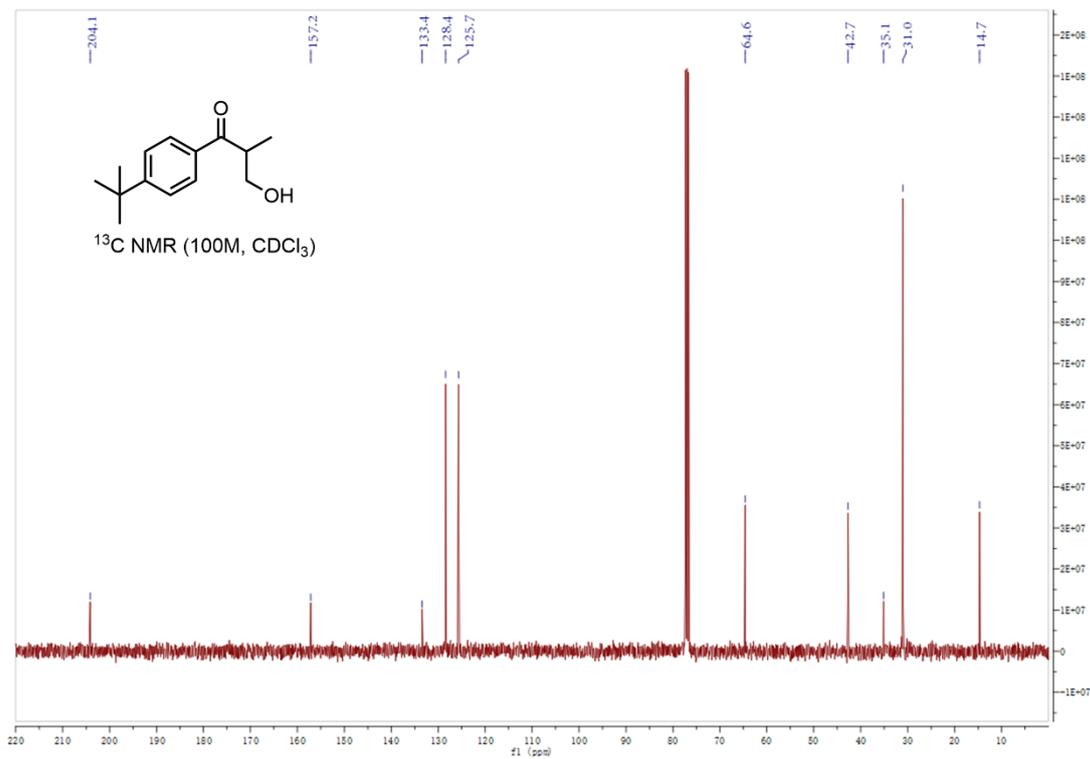
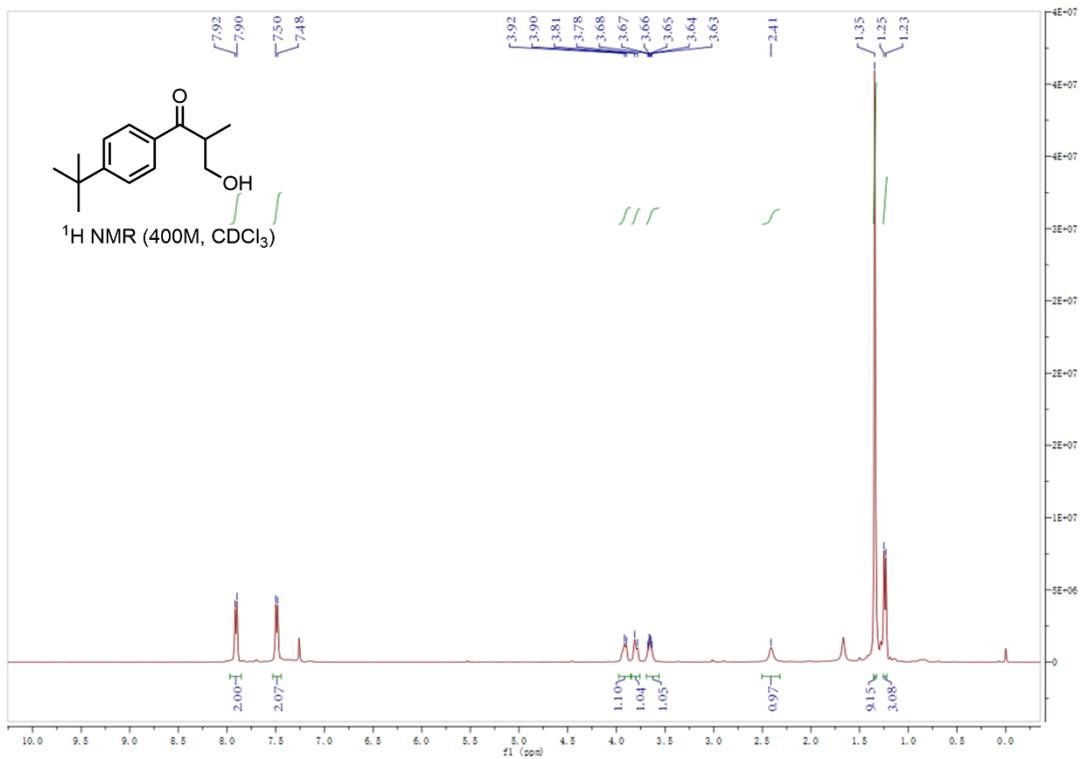
<sup>1</sup>H NMR of **2b** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2b** (100 MHz, CDCl<sub>3</sub>)



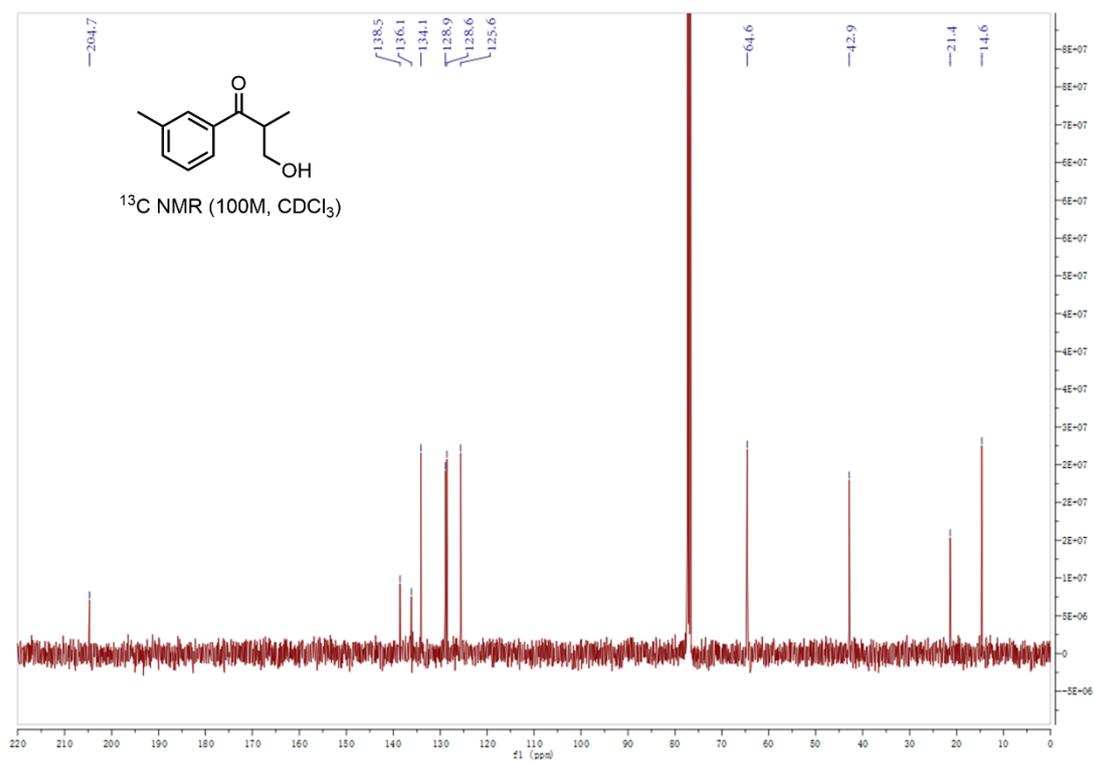
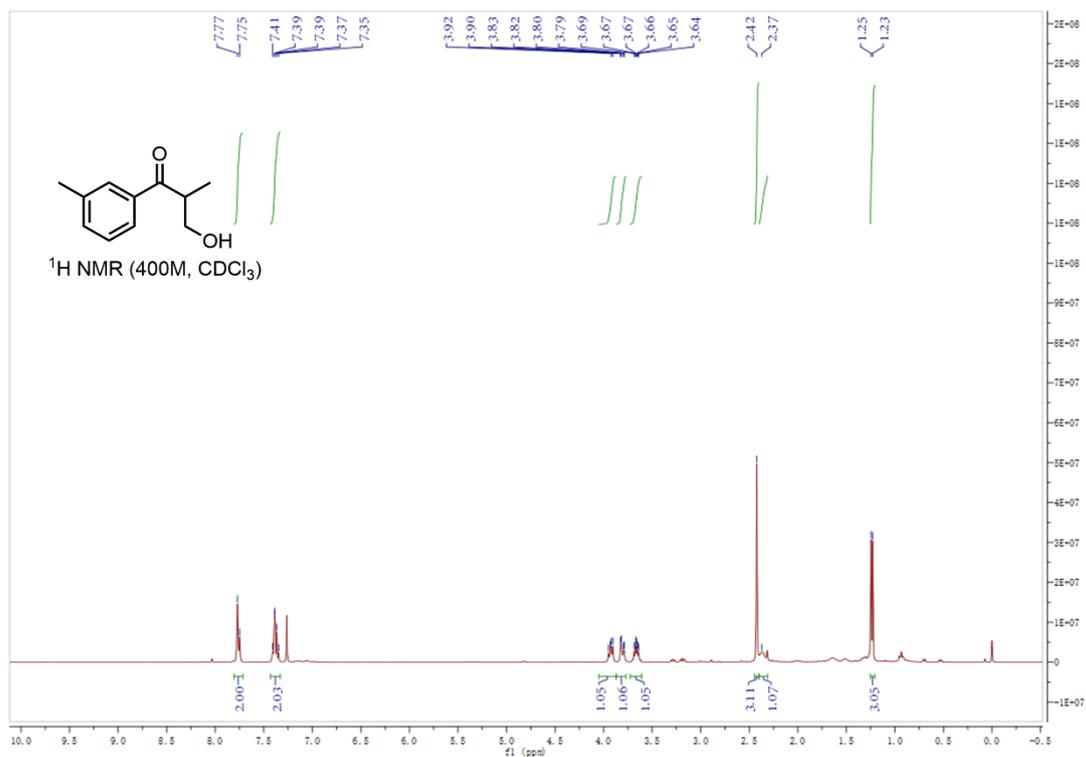
<sup>1</sup>H NMR of **2c** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2c** (100 MHz, CDCl<sub>3</sub>)



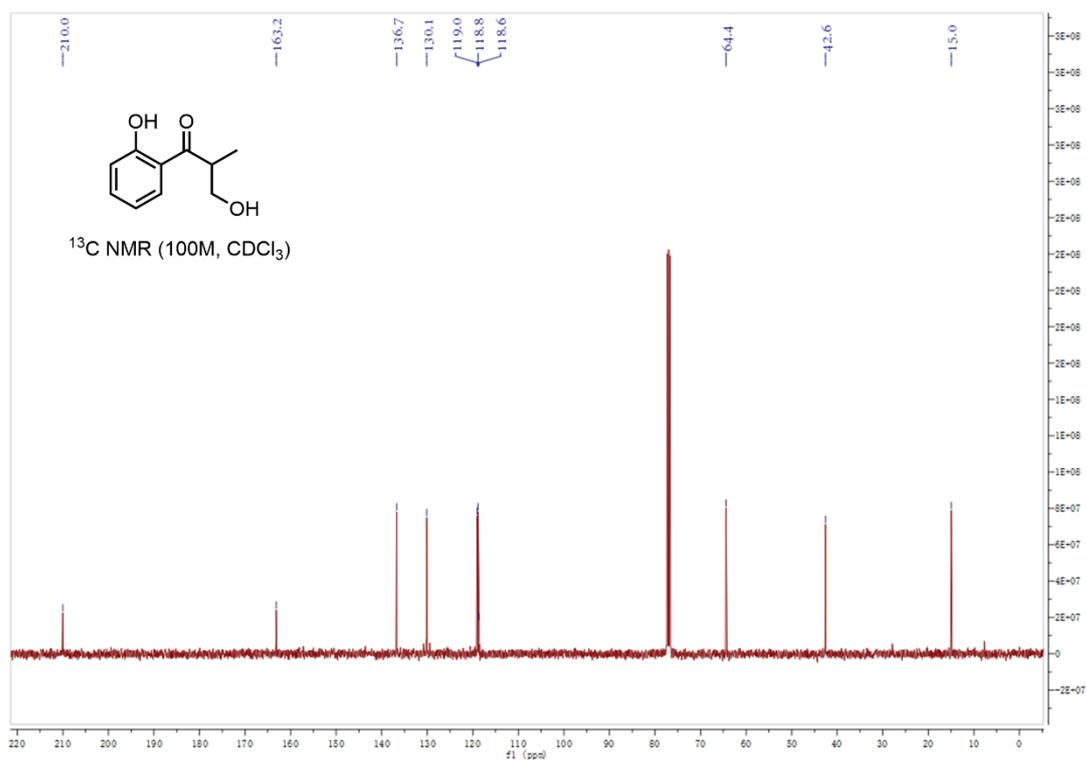
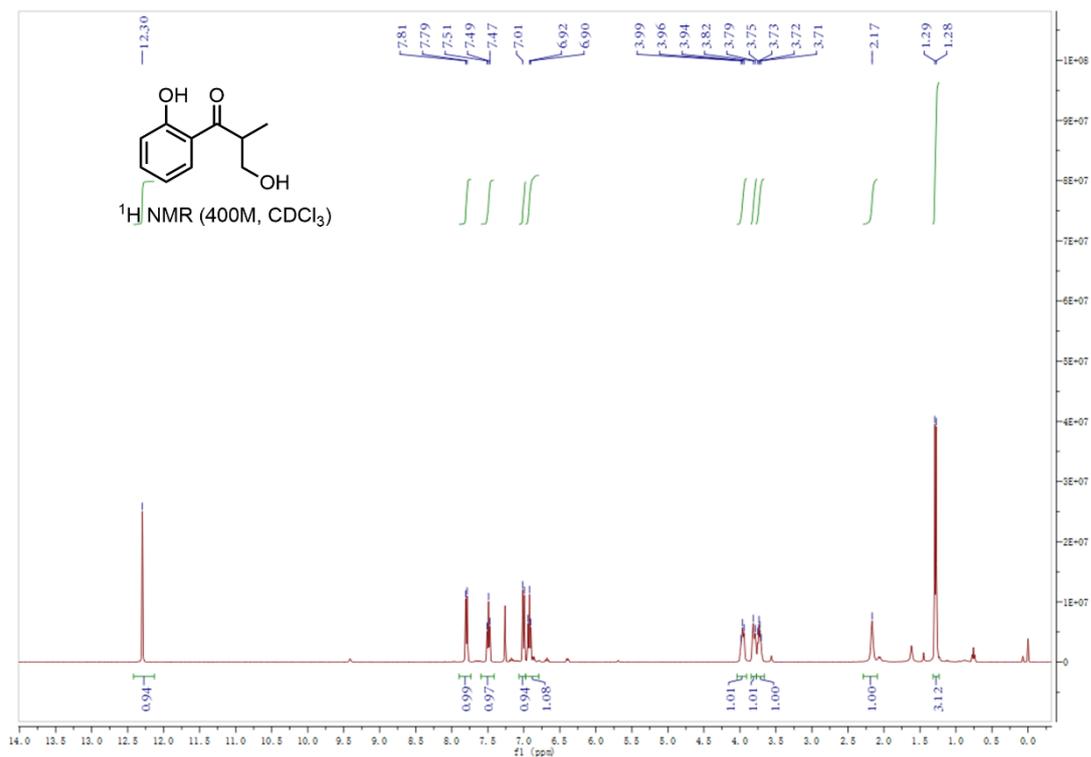
<sup>1</sup>H NMR of **2d** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2d** (100 MHz, CDCl<sub>3</sub>)



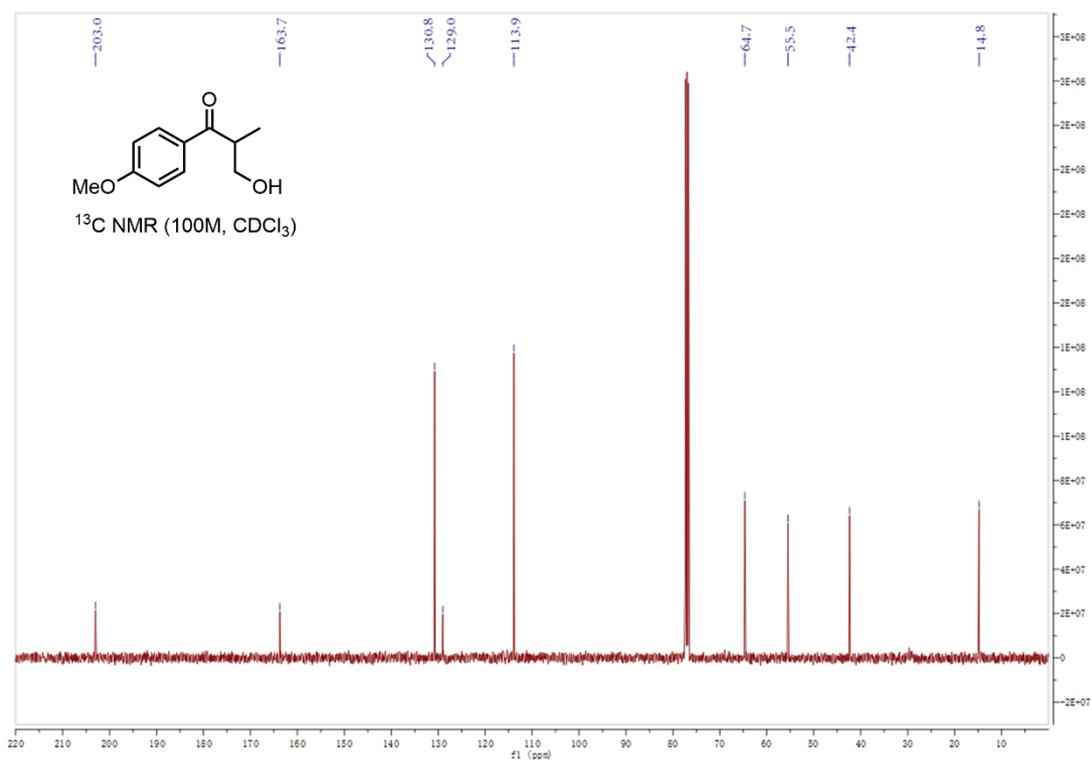
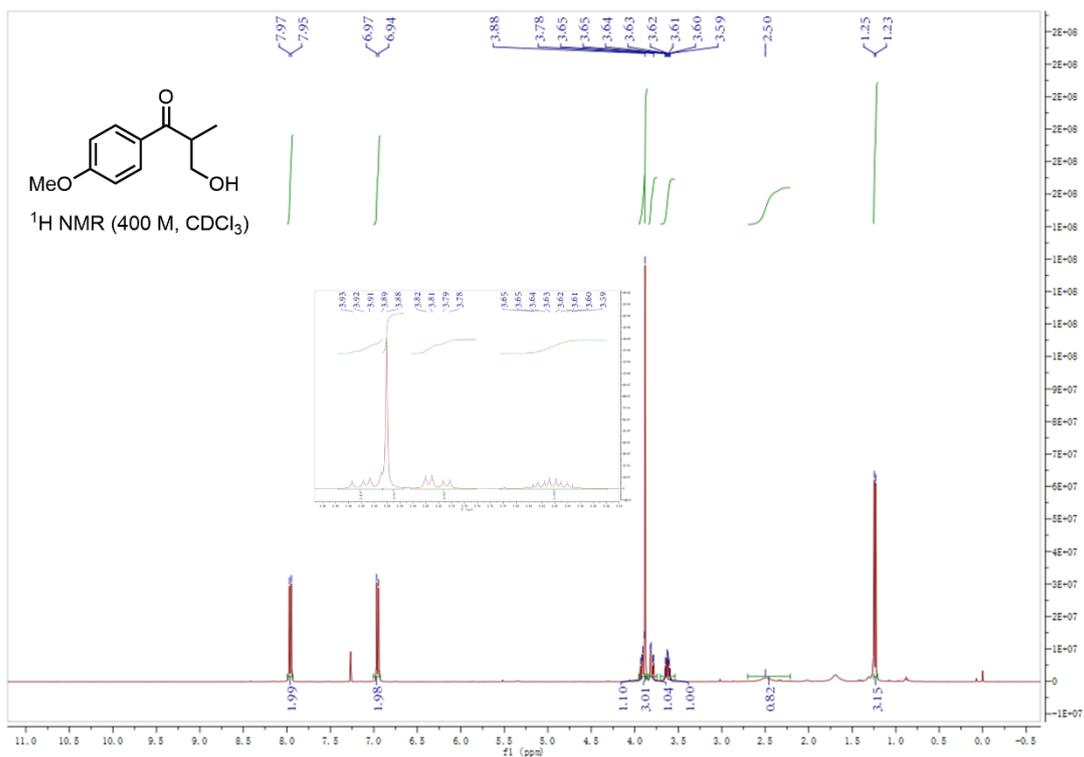
<sup>1</sup>H NMR of **2e** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2e** (100 MHz, CDCl<sub>3</sub>)



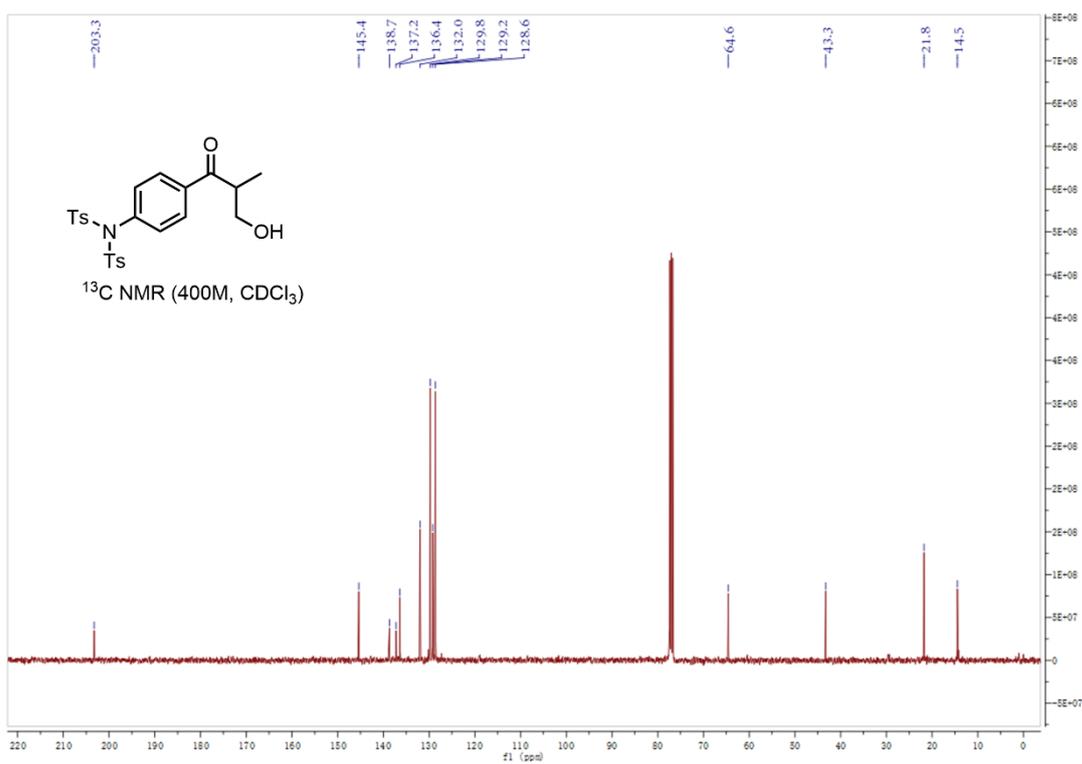
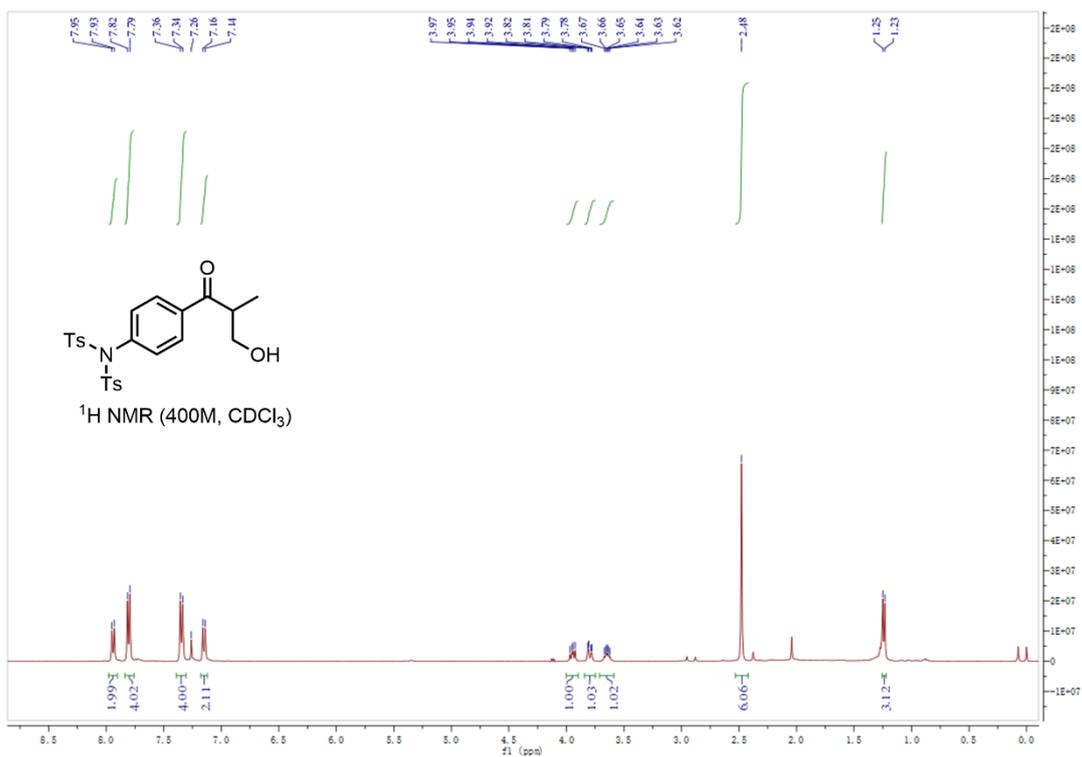
<sup>1</sup>H NMR of **2f** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2f** (100 MHz, CDCl<sub>3</sub>)



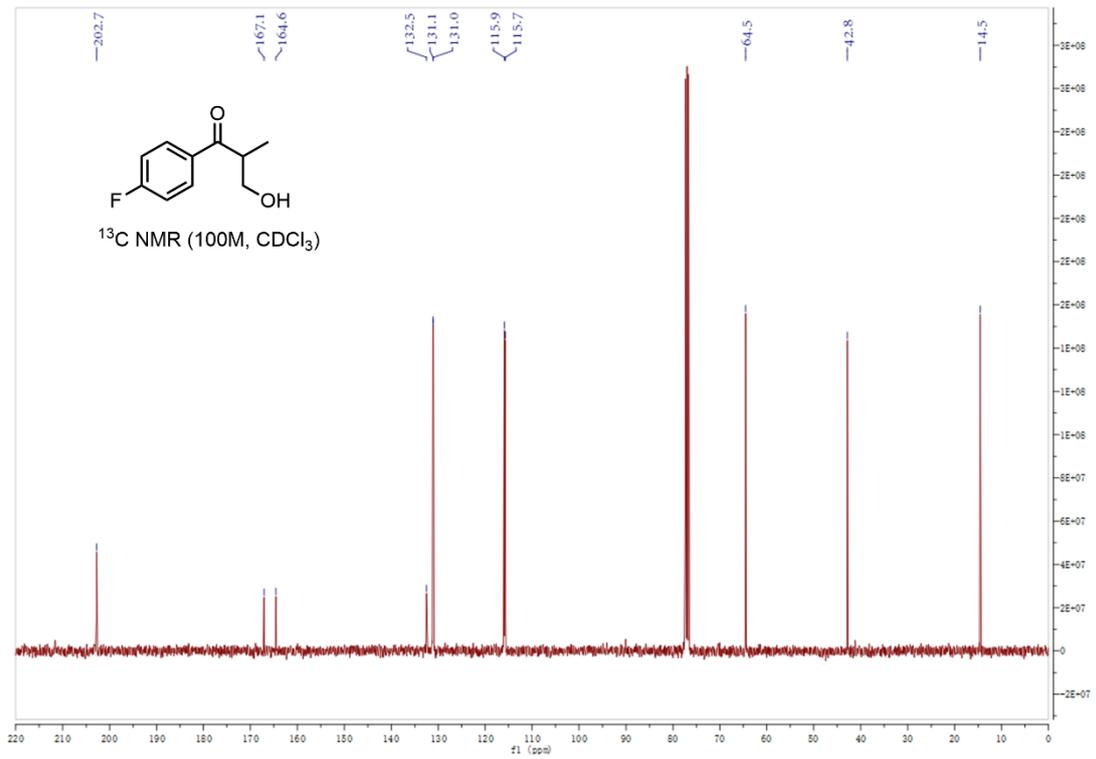
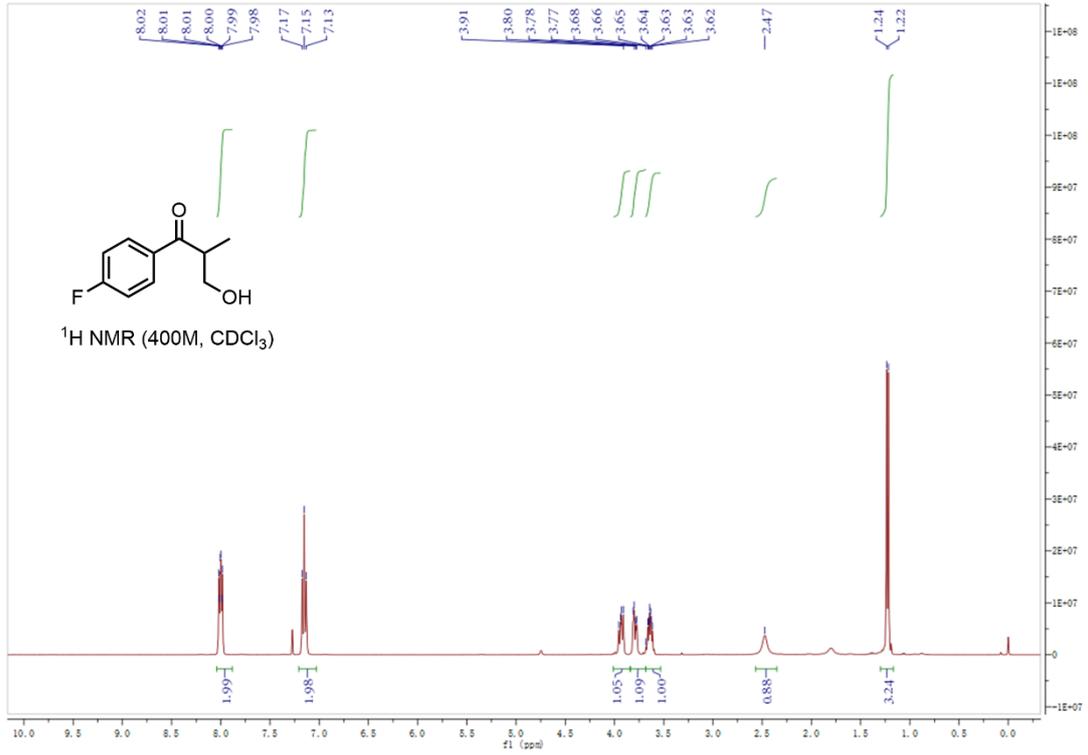
**<sup>1</sup>H NMR of **2g** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2g** (100 MHz, CDCl<sub>3</sub>)**

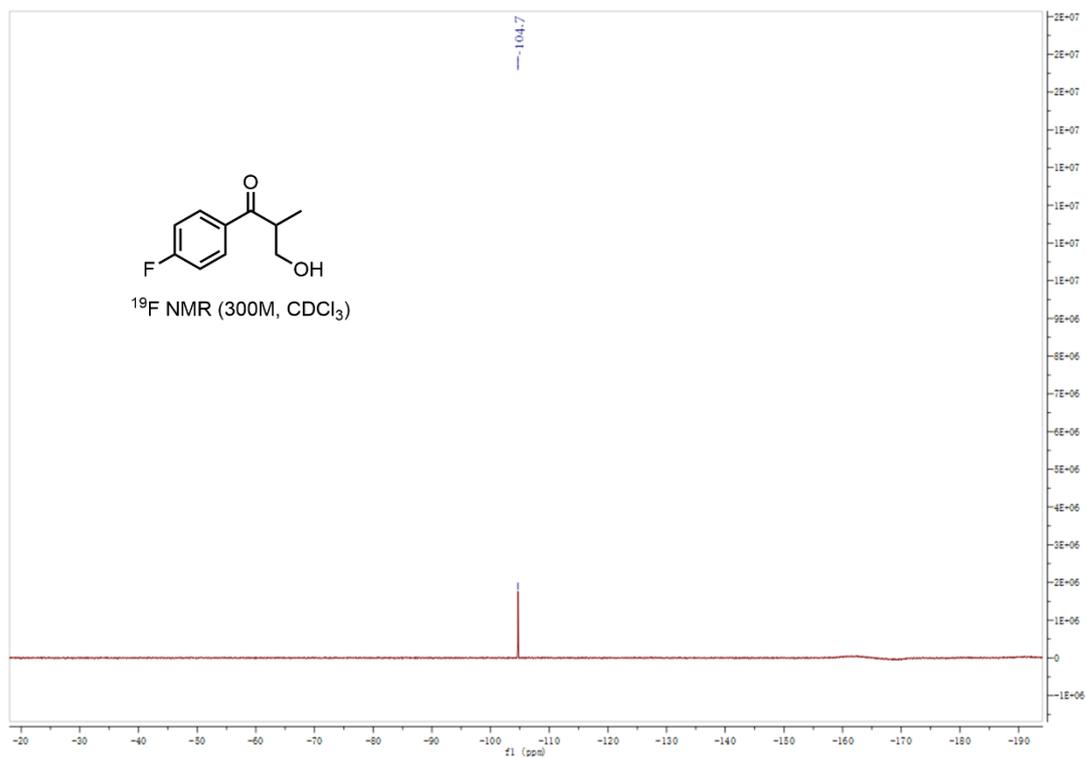


<sup>1</sup>H NMR of **2h** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2h** (100 MHz, CDCl<sub>3</sub>)

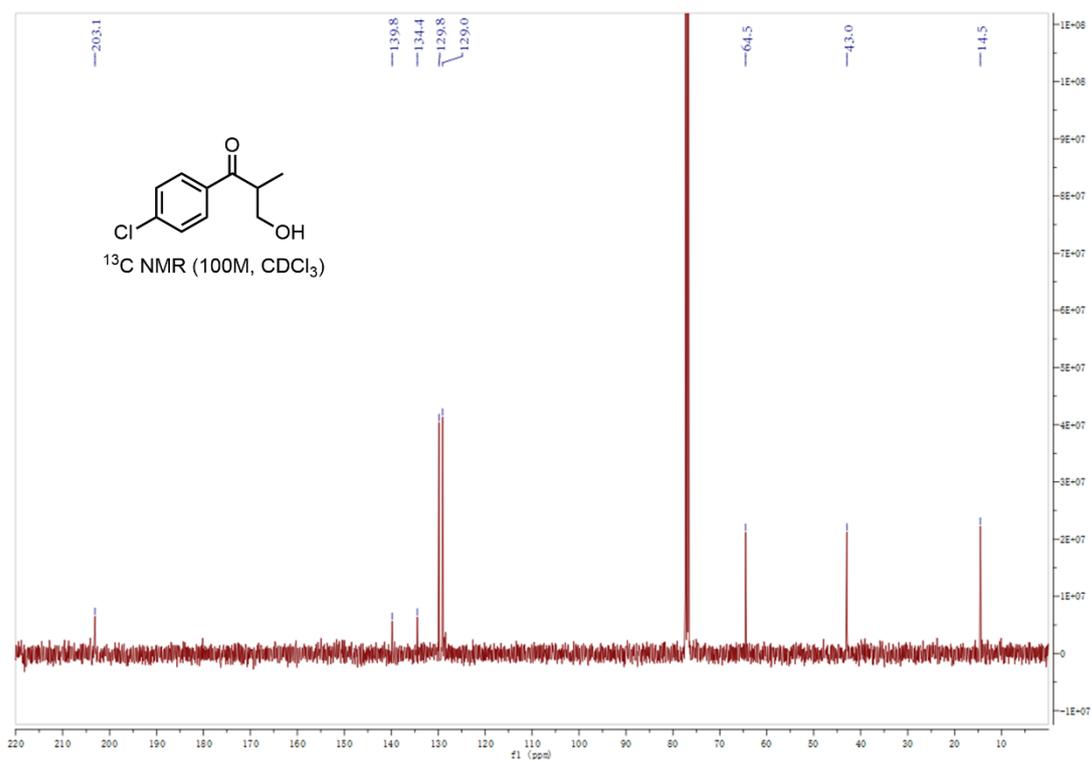
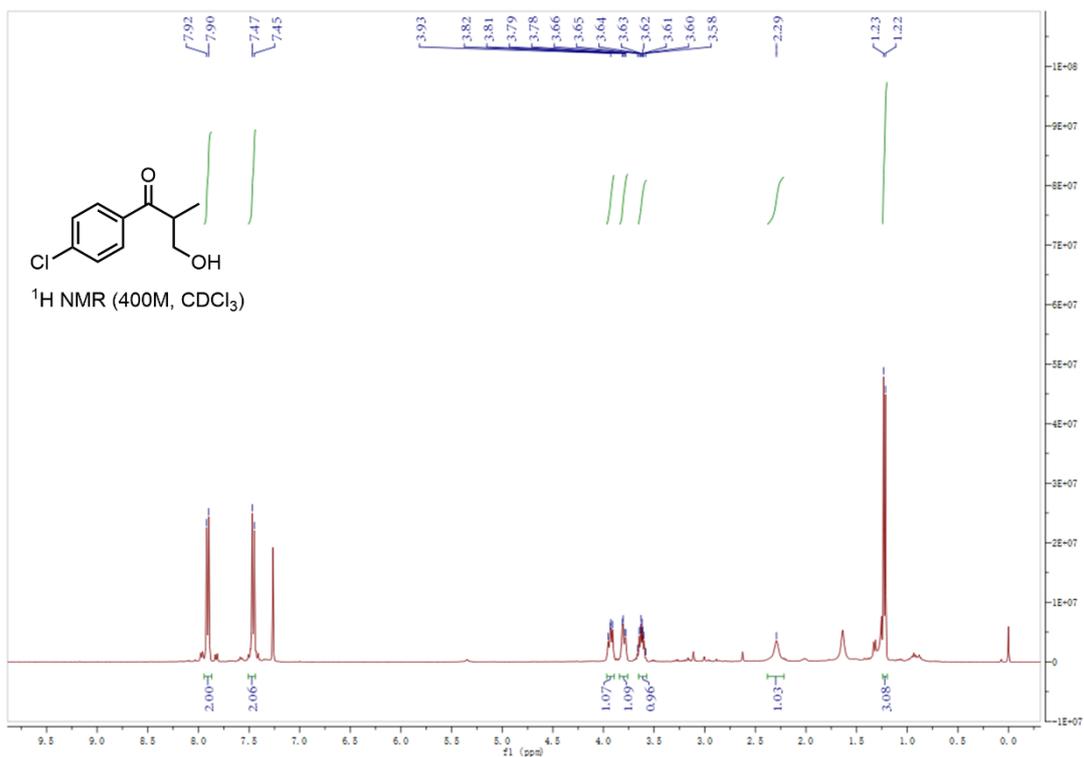


<sup>1</sup>H NMR of **2i** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2i** (100 MHz, CDCl<sub>3</sub>)

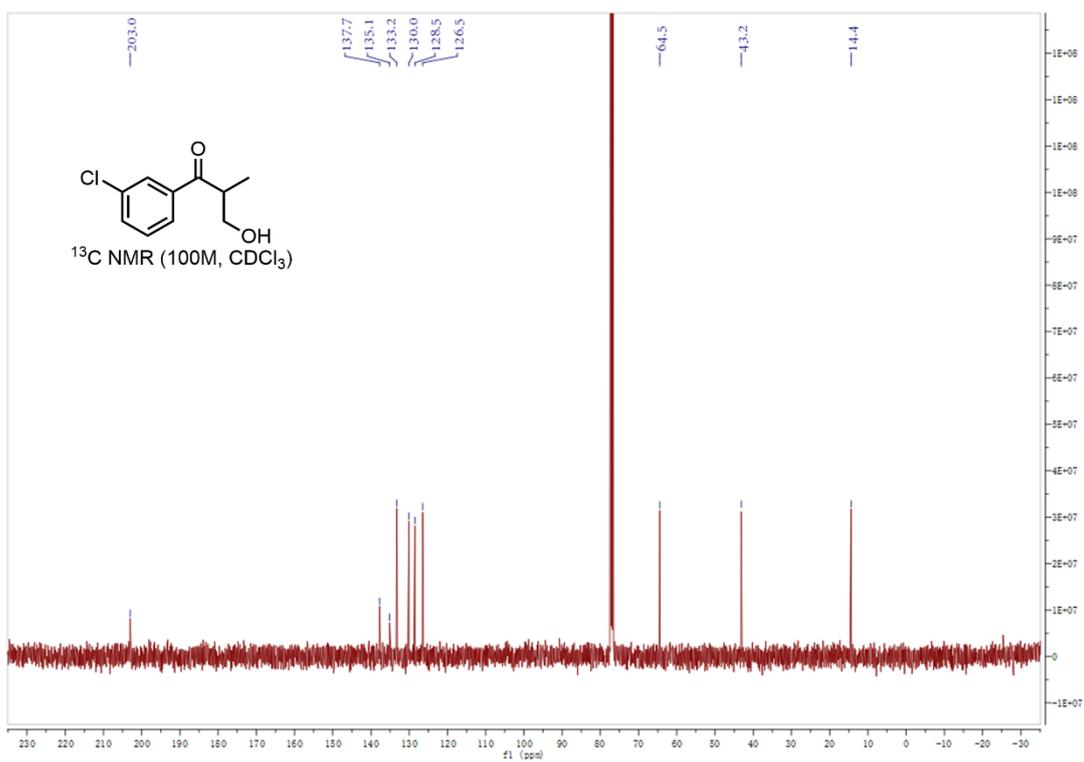
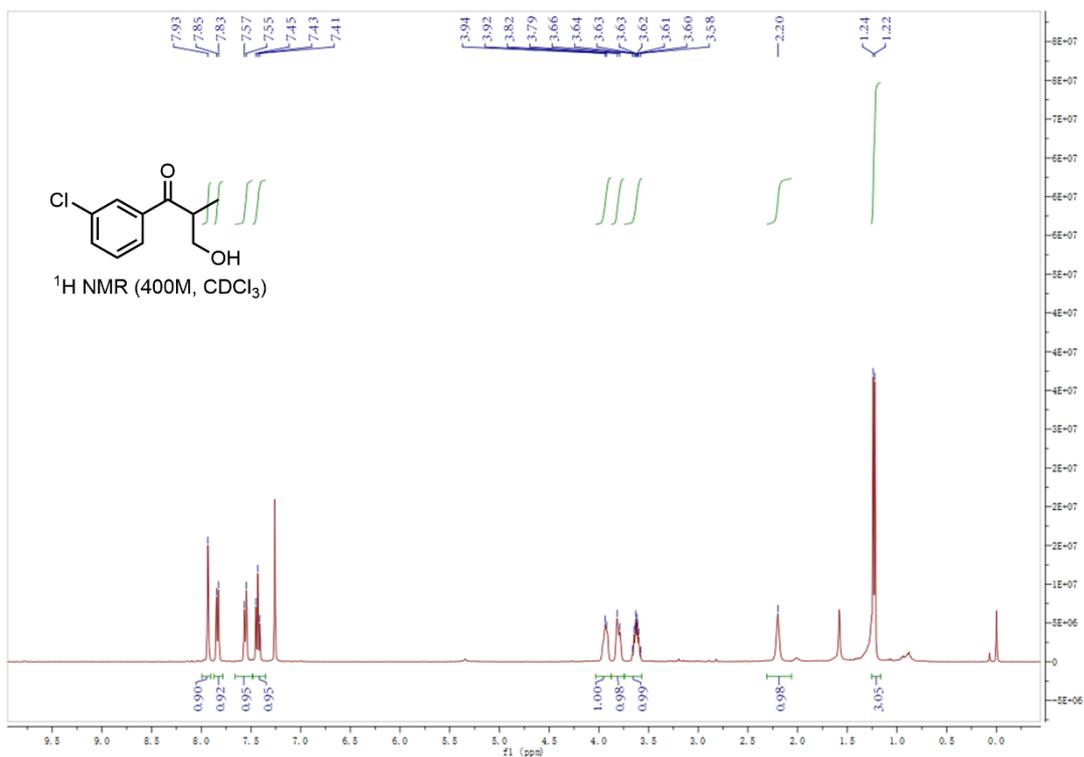




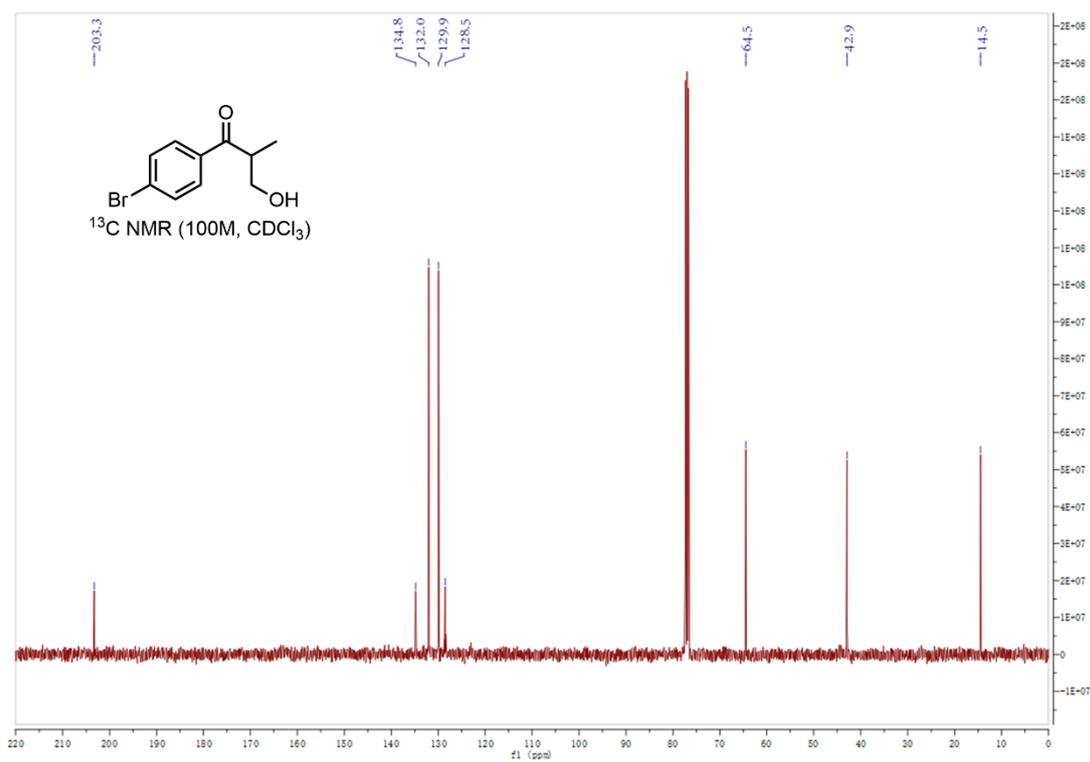
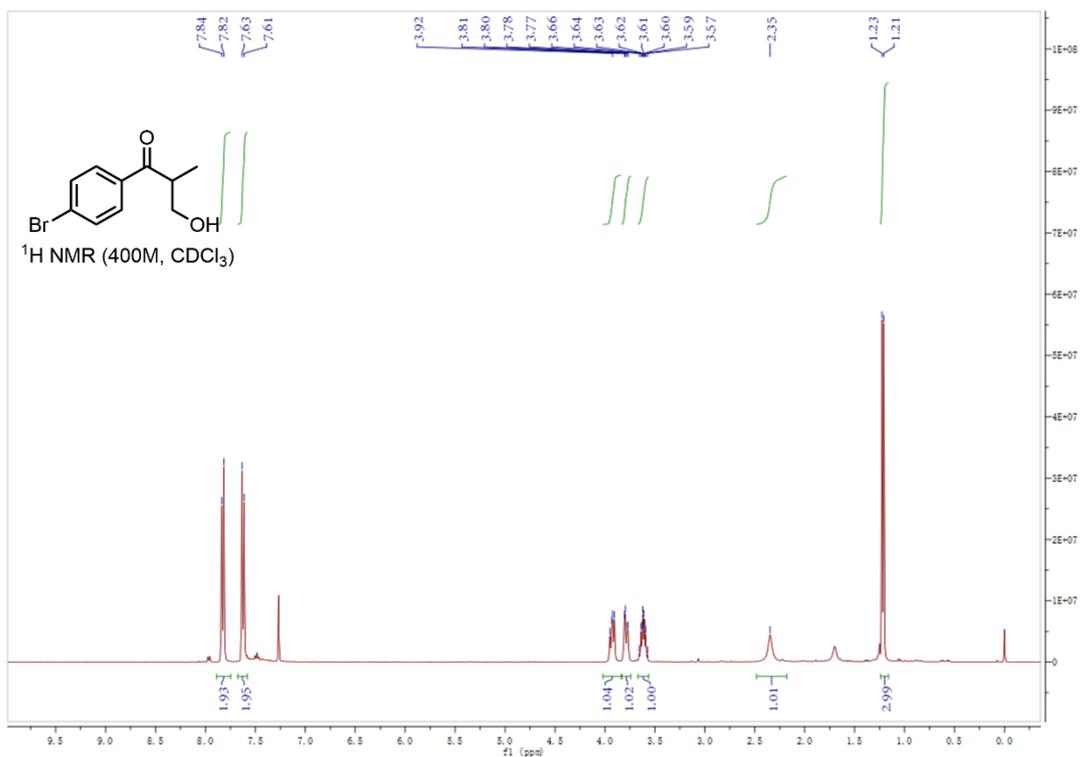
$^1\text{H}$  NMR of **2j** (400 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  NMR of **2j** (100 MHz,  $\text{CDCl}_3$ ) and  $^{19}\text{F}$  NMR of **2j** (300 MHz,  $\text{CDCl}_3$ )



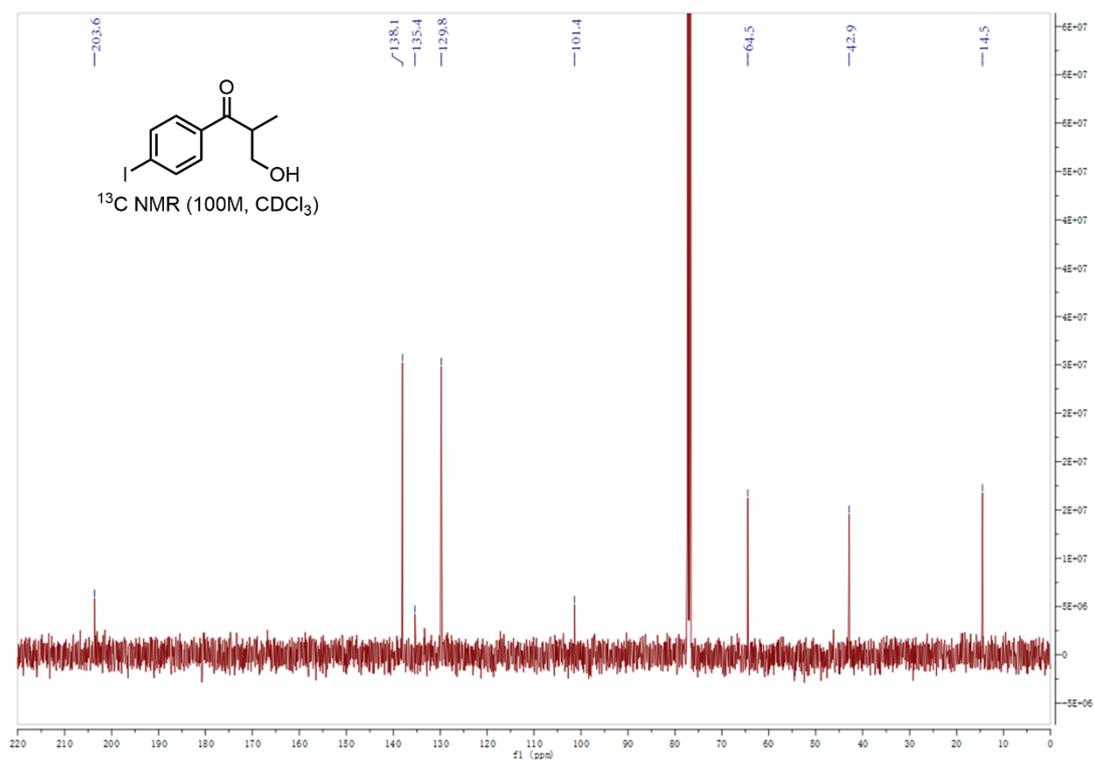
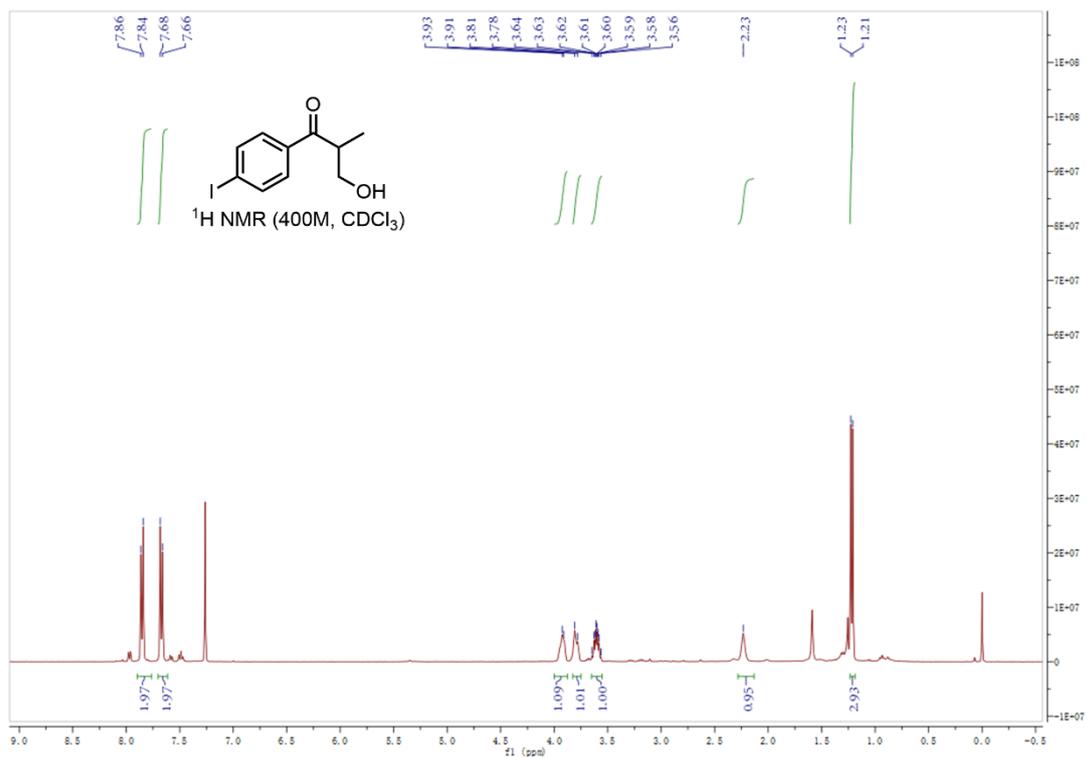
<sup>1</sup>H NMR of **2k** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2k** (100 MHz, CDCl<sub>3</sub>)



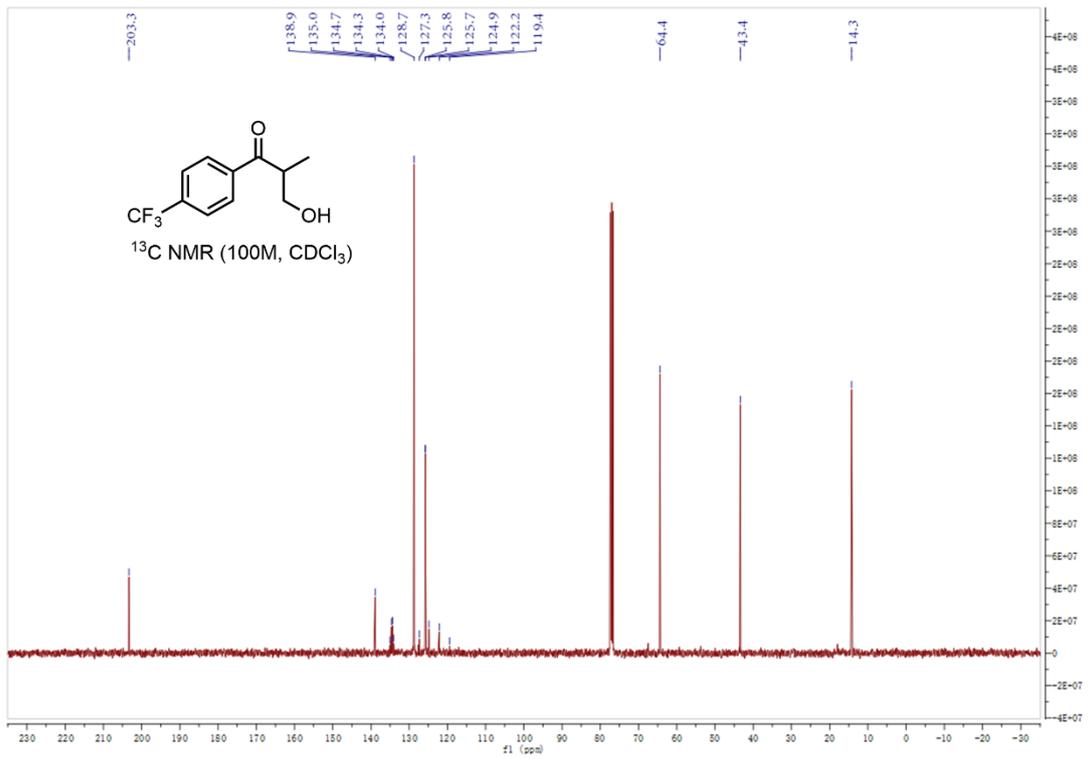
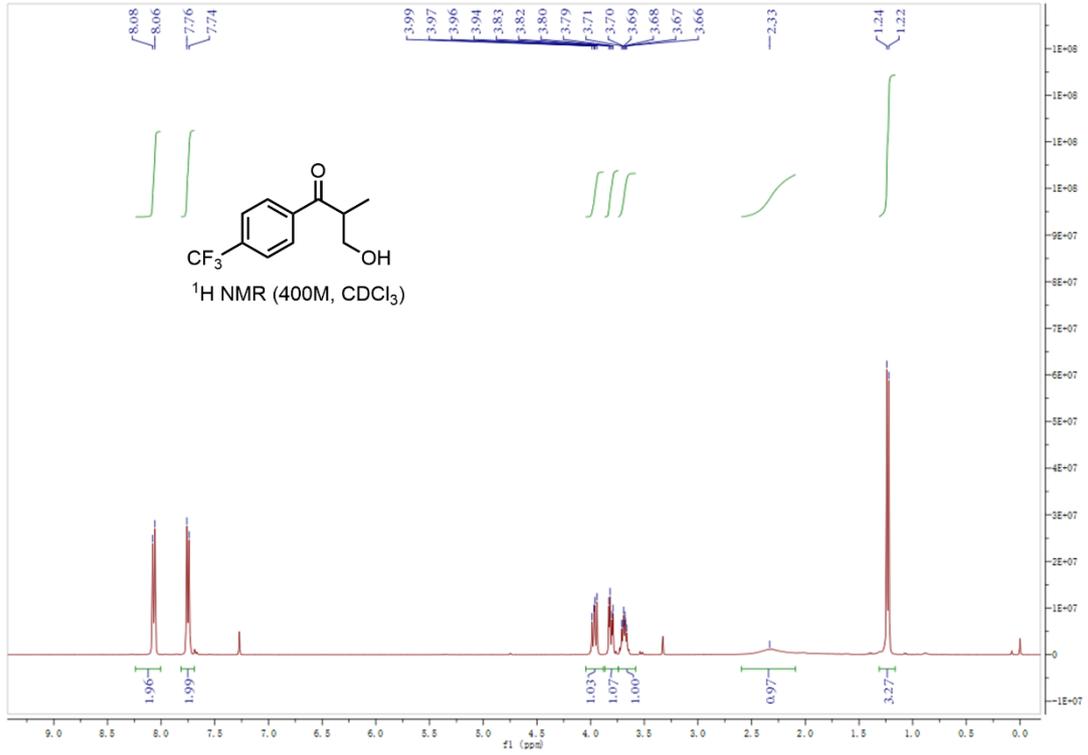
<sup>1</sup>H NMR of **21** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **21** (100 MHz, CDCl<sub>3</sub>)

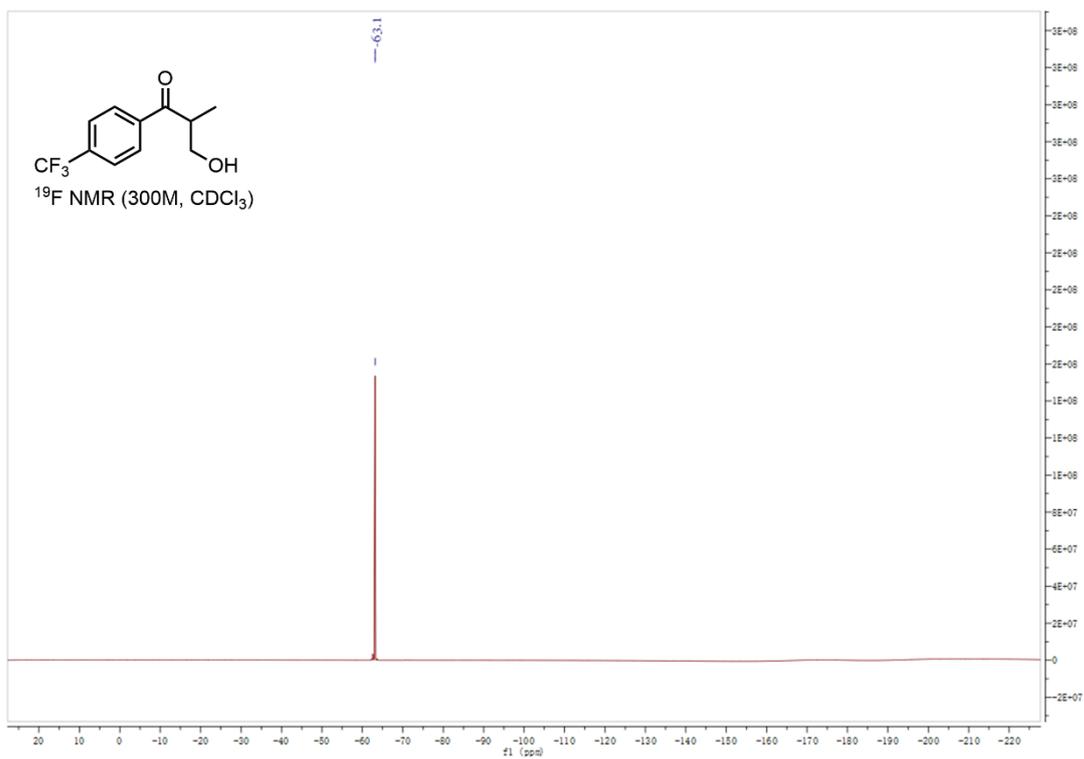


<sup>1</sup>H NMR of **2m** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2m** (100 MHz, CDCl<sub>3</sub>)

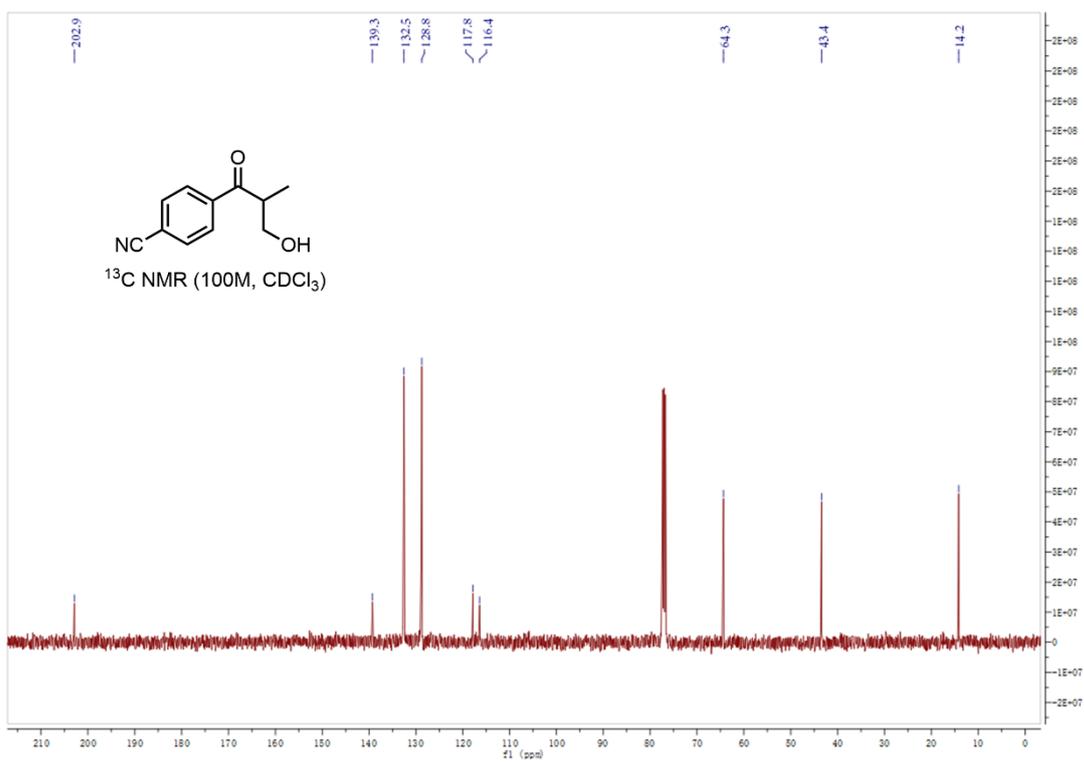
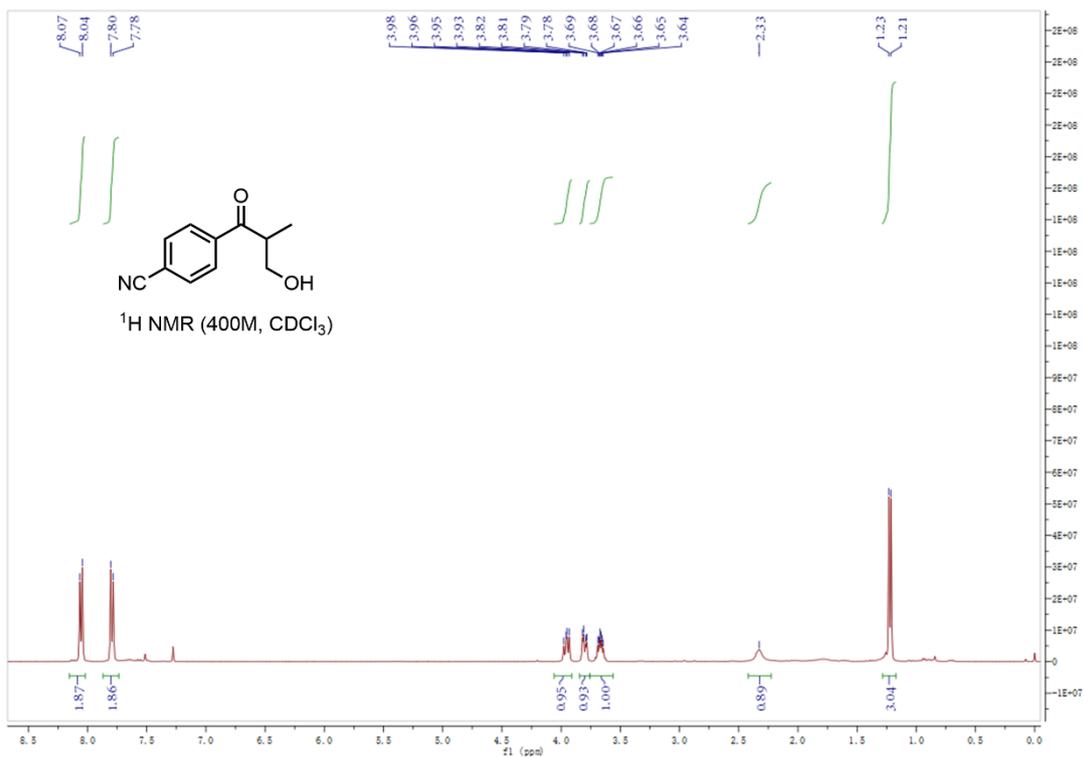


<sup>1</sup>H NMR of **2n** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2n** (100 MHz, CDCl<sub>3</sub>)

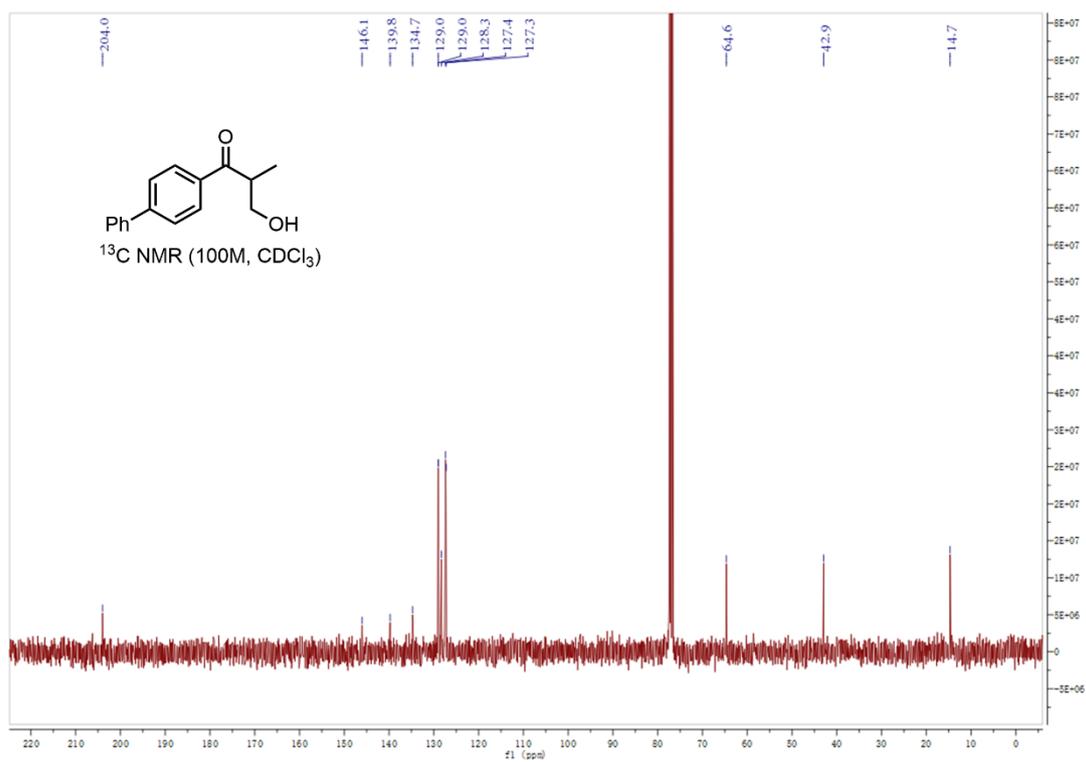
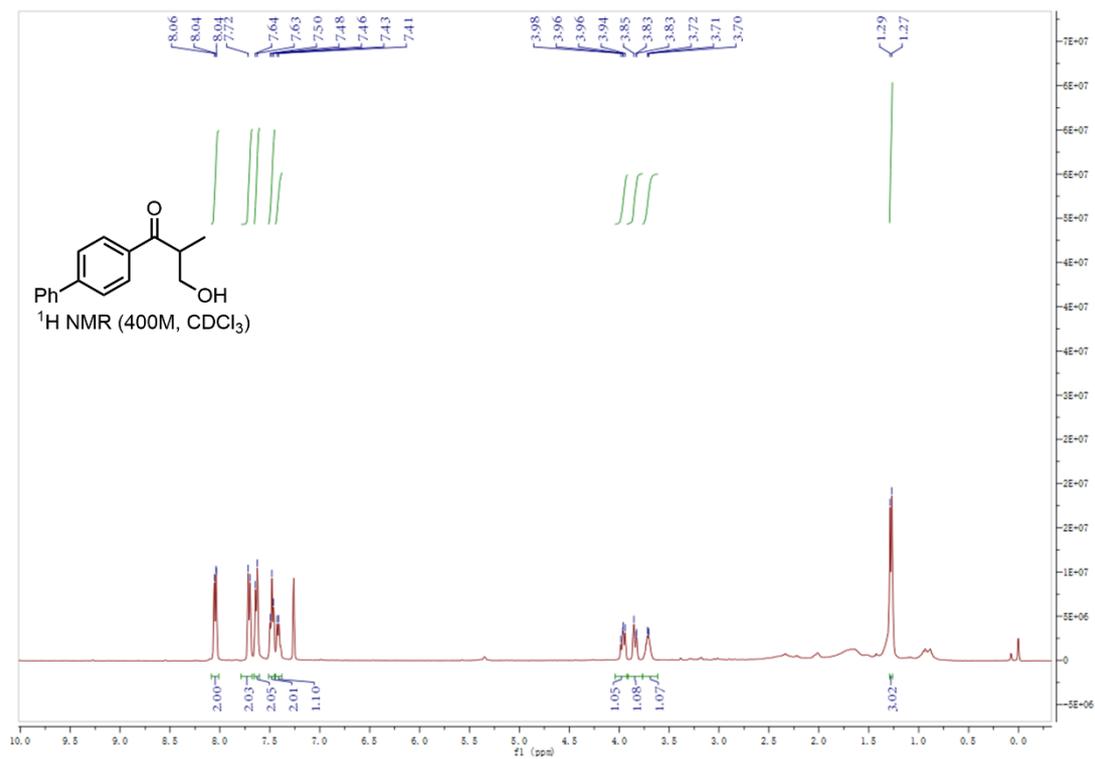




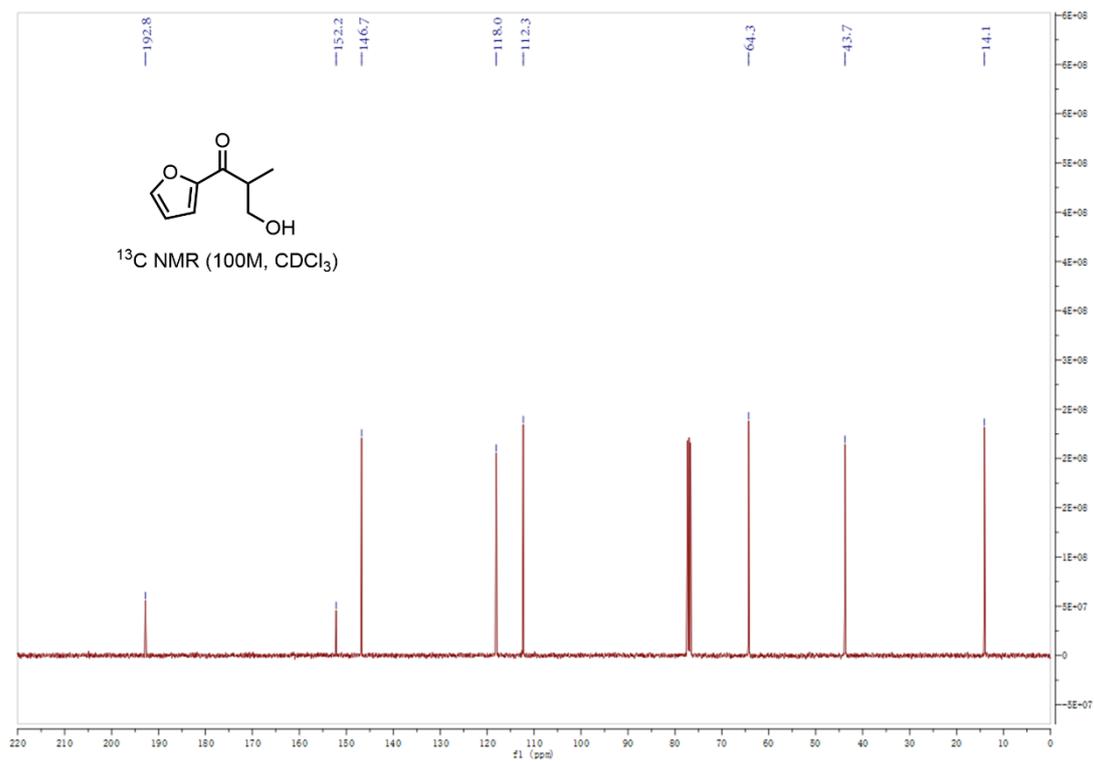
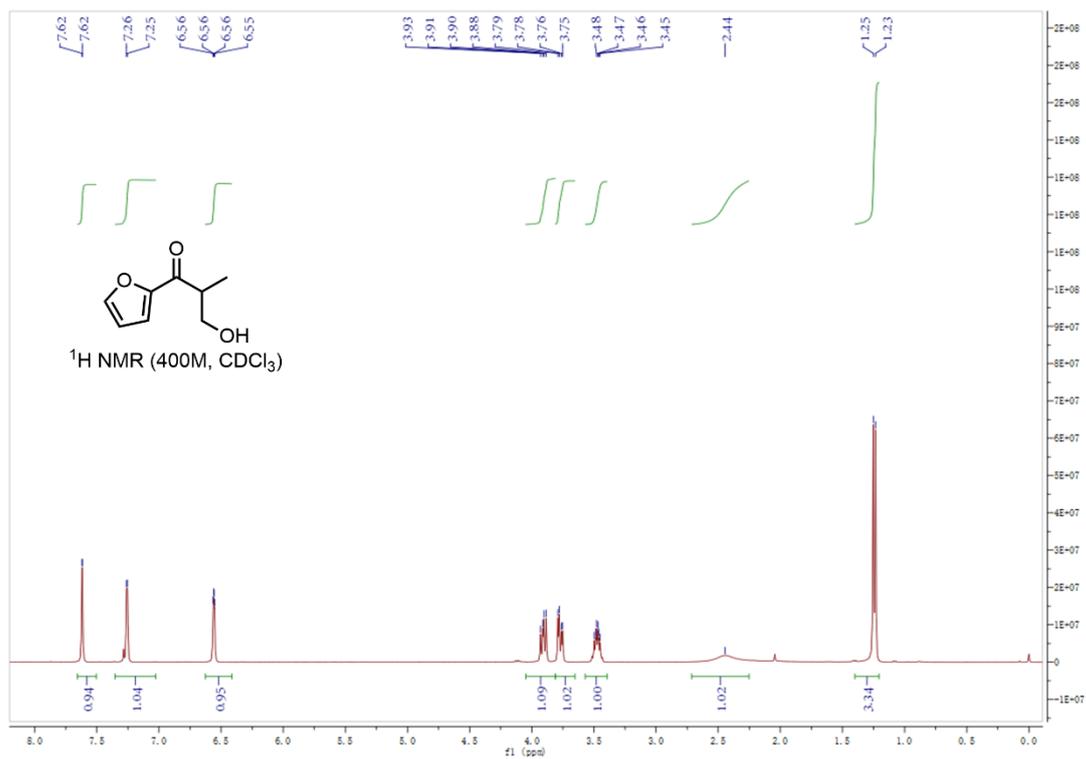
<sup>1</sup>H NMR of **2o** (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR of **2o** (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F NMR of **2o** (300 MHz, CDCl<sub>3</sub>)



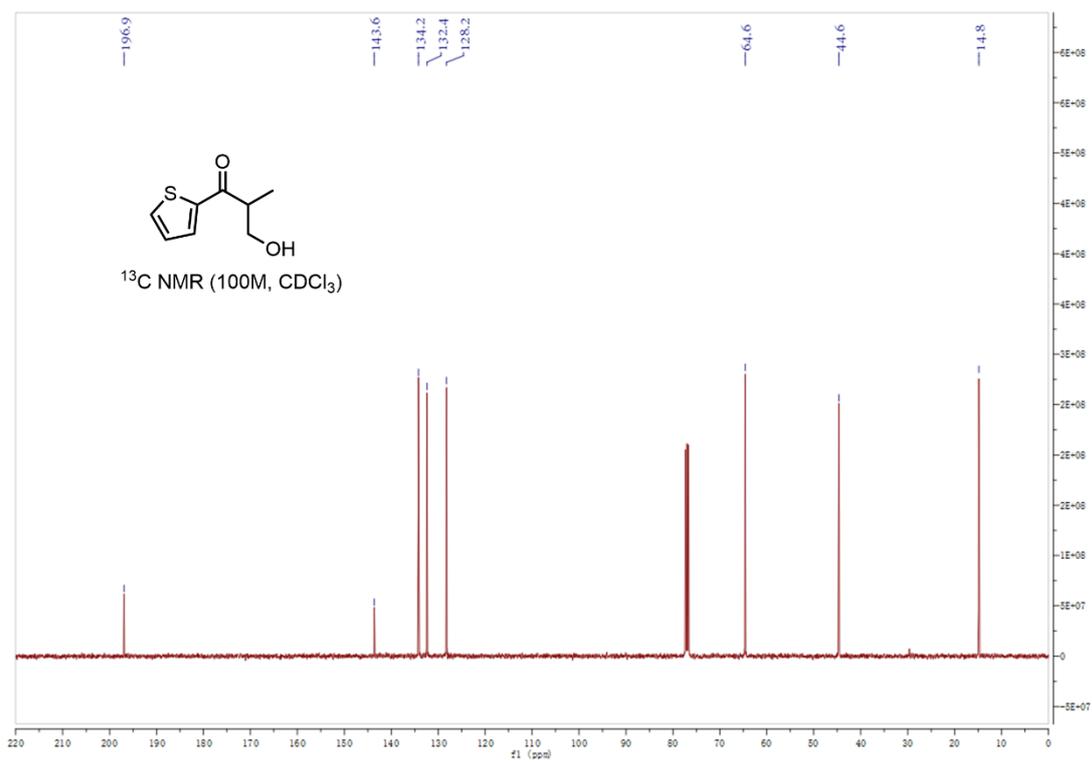
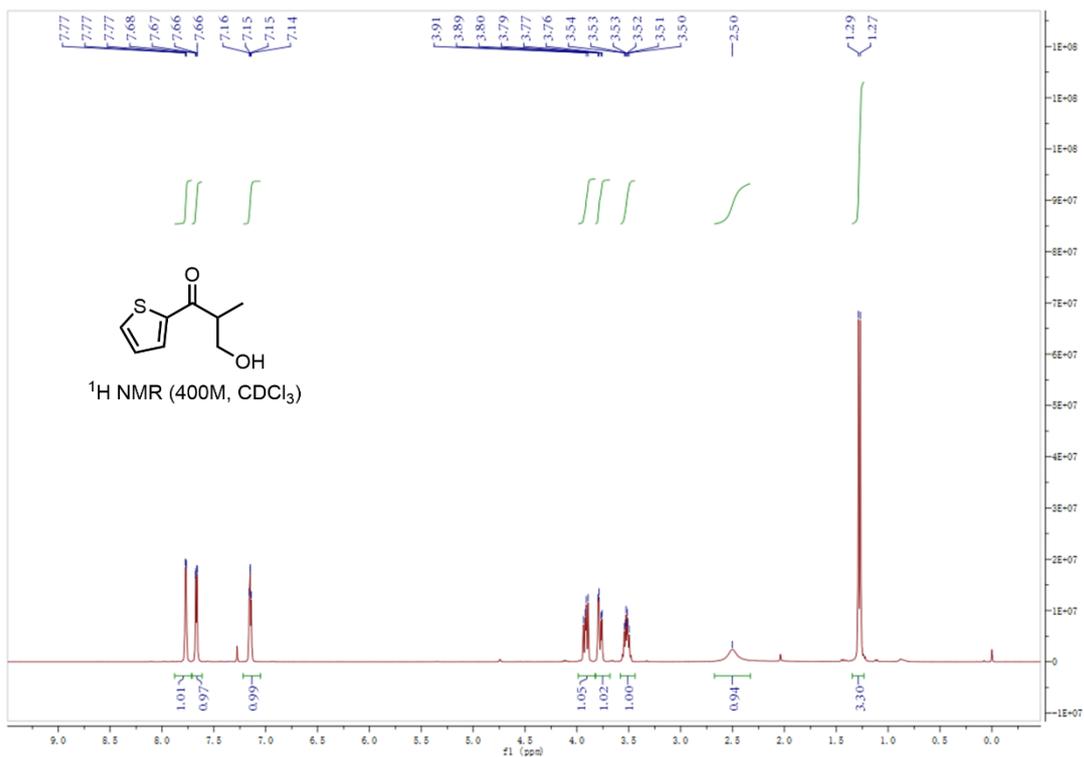
$^1\text{H NMR}$  of **2p** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C NMR}$  of **2p** (100 MHz,  $\text{CDCl}_3$ )



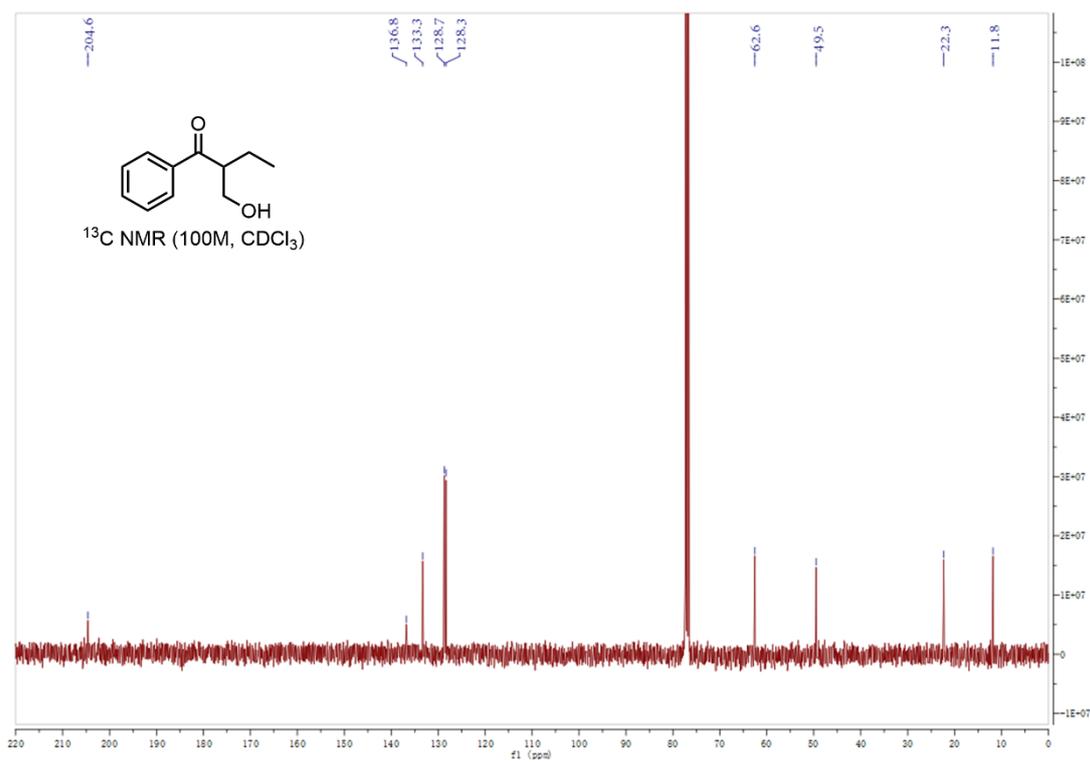
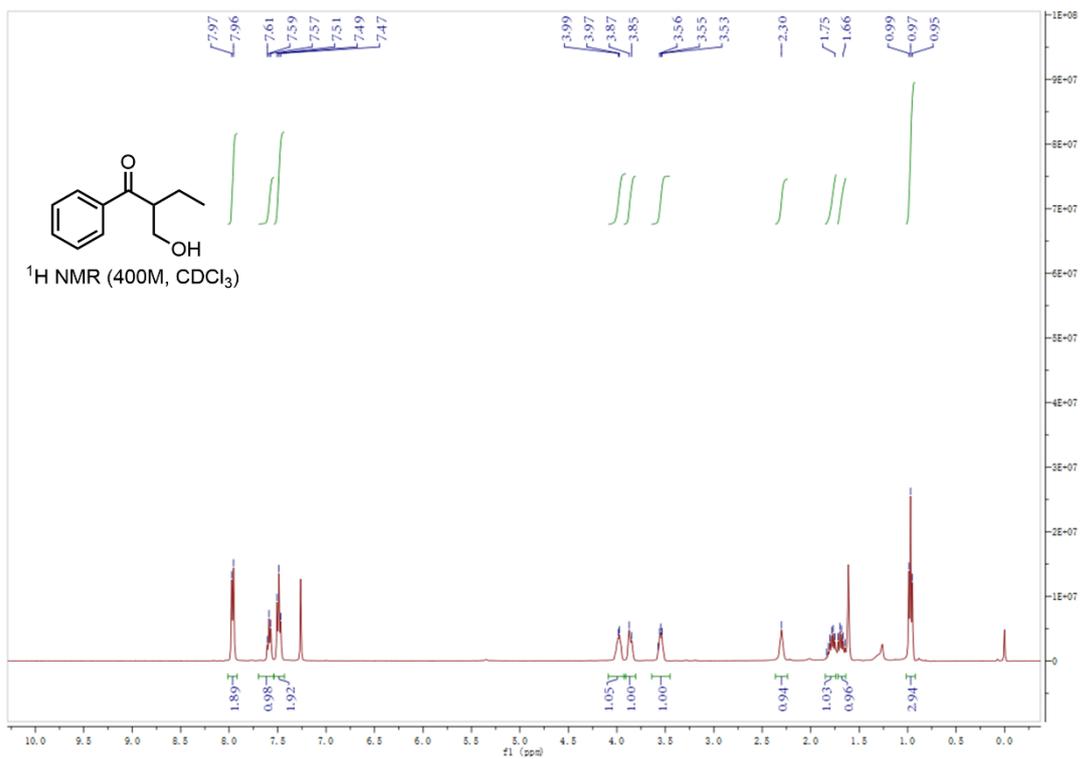
<sup>1</sup>H NMR of **2q** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2q** (100 MHz, CDCl<sub>3</sub>)



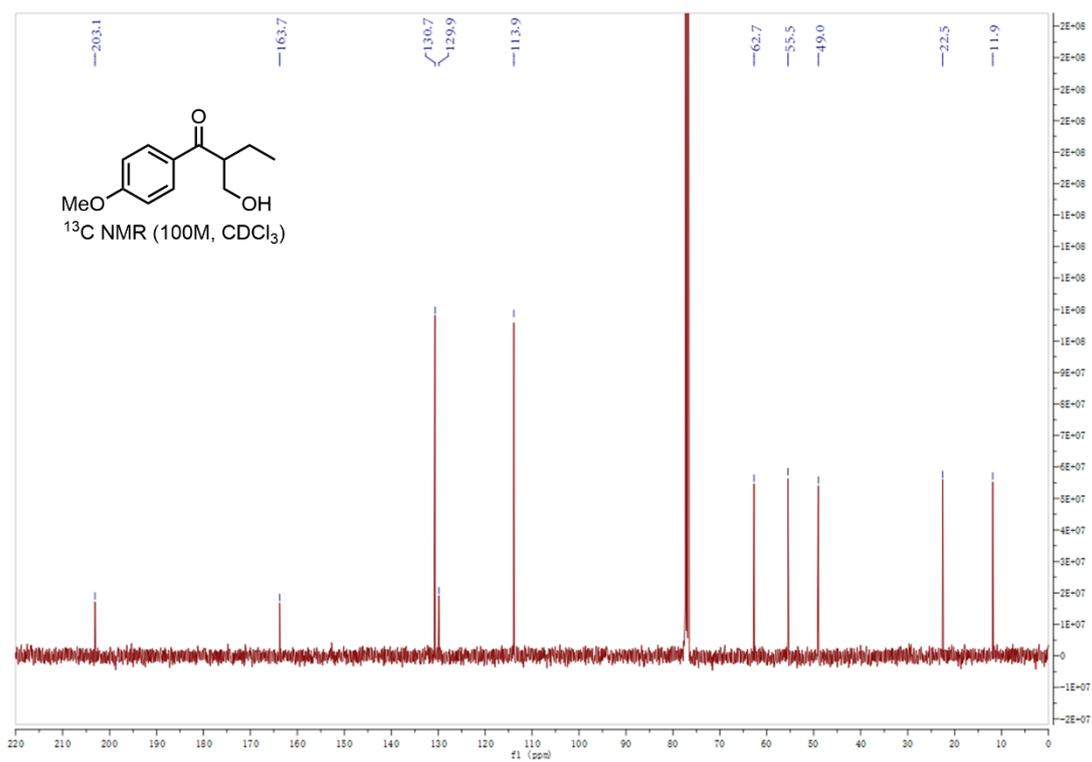
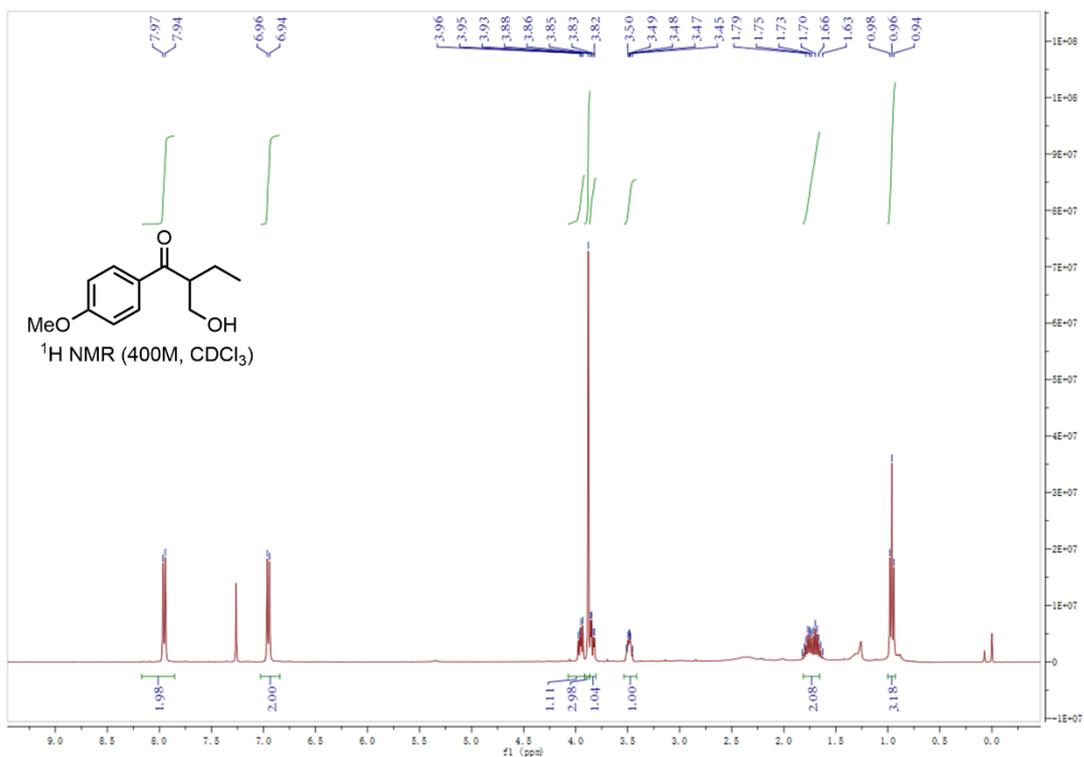
<sup>1</sup>H NMR of **2r** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2r** (100 MHz, CDCl<sub>3</sub>)



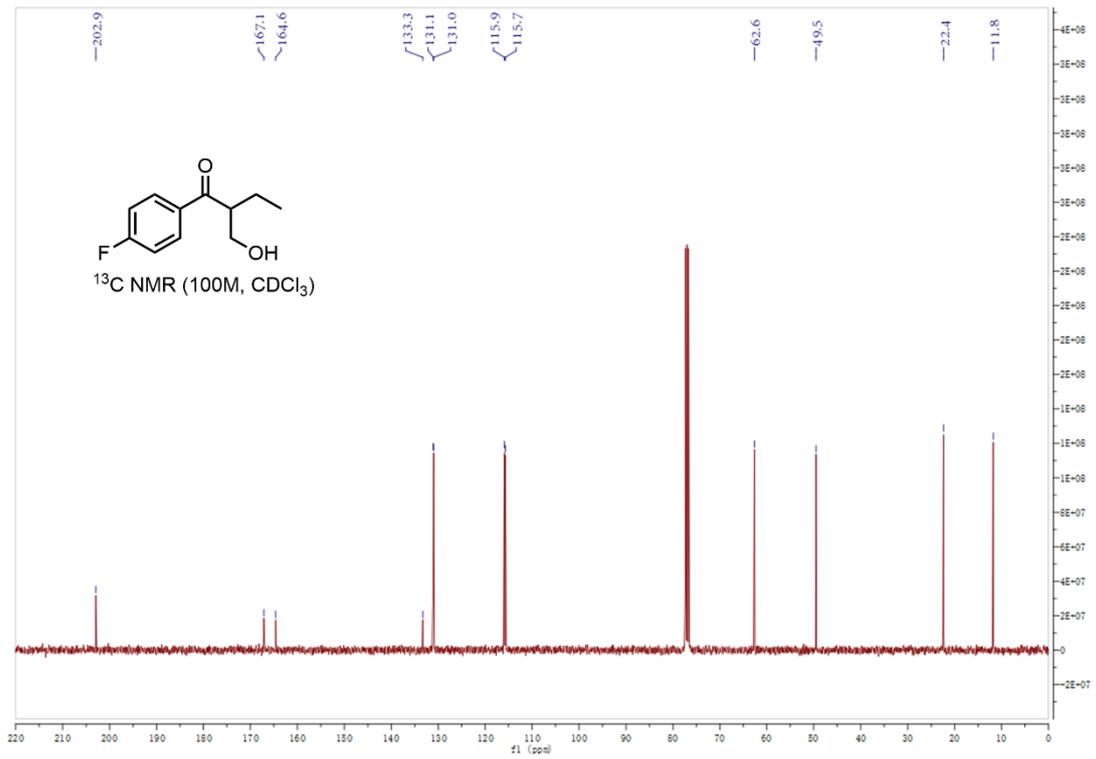
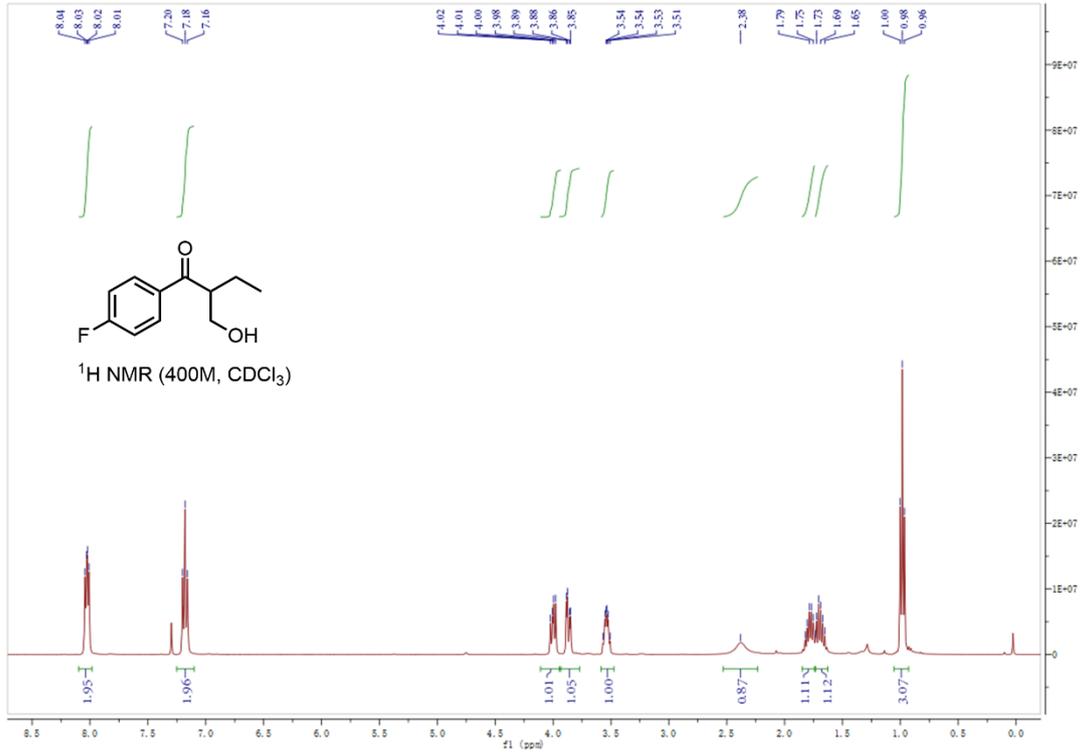
<sup>1</sup>H NMR of **2s** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2s** (100 MHz, CDCl<sub>3</sub>)

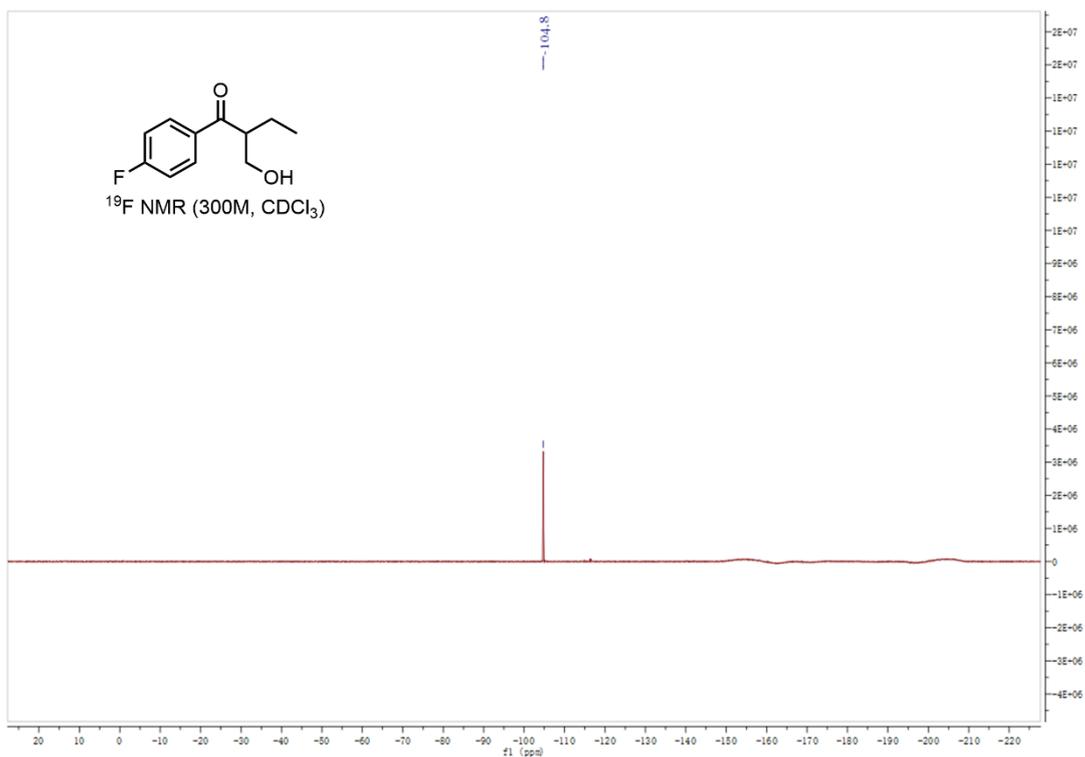


<sup>1</sup>H NMR of **2t** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2t** (100 MHz, CDCl<sub>3</sub>)

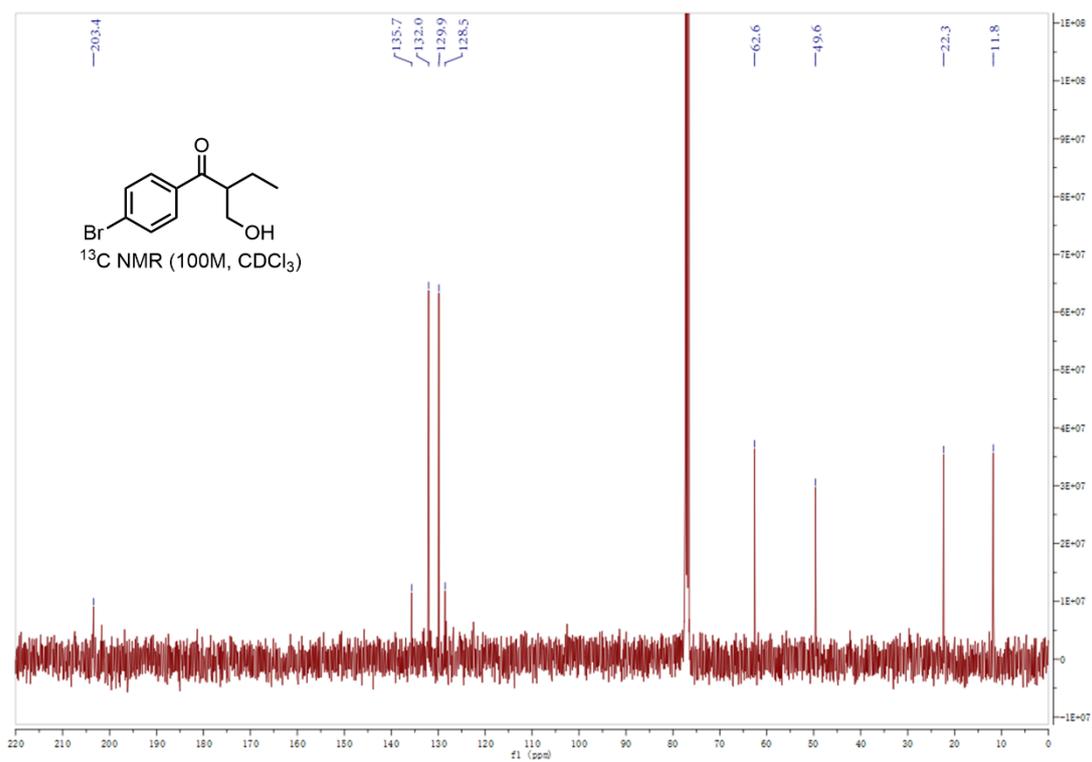
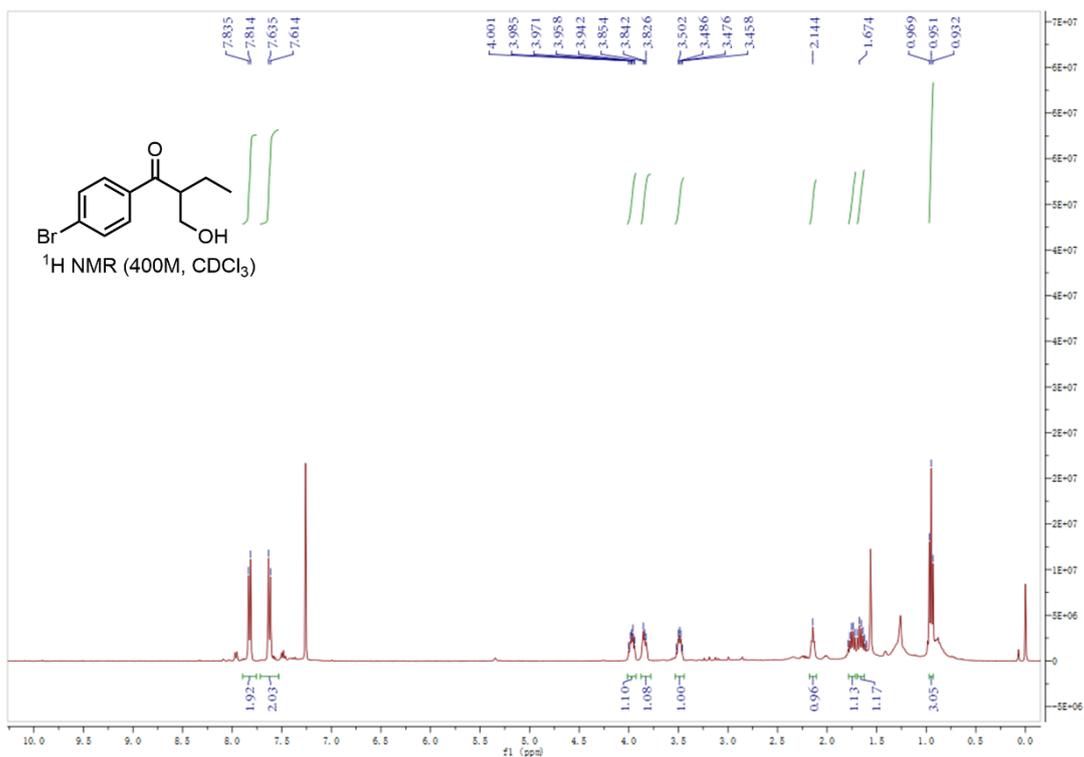


<sup>1</sup>H NMR of **2u** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2u** (100 MHz, CDCl<sub>3</sub>)

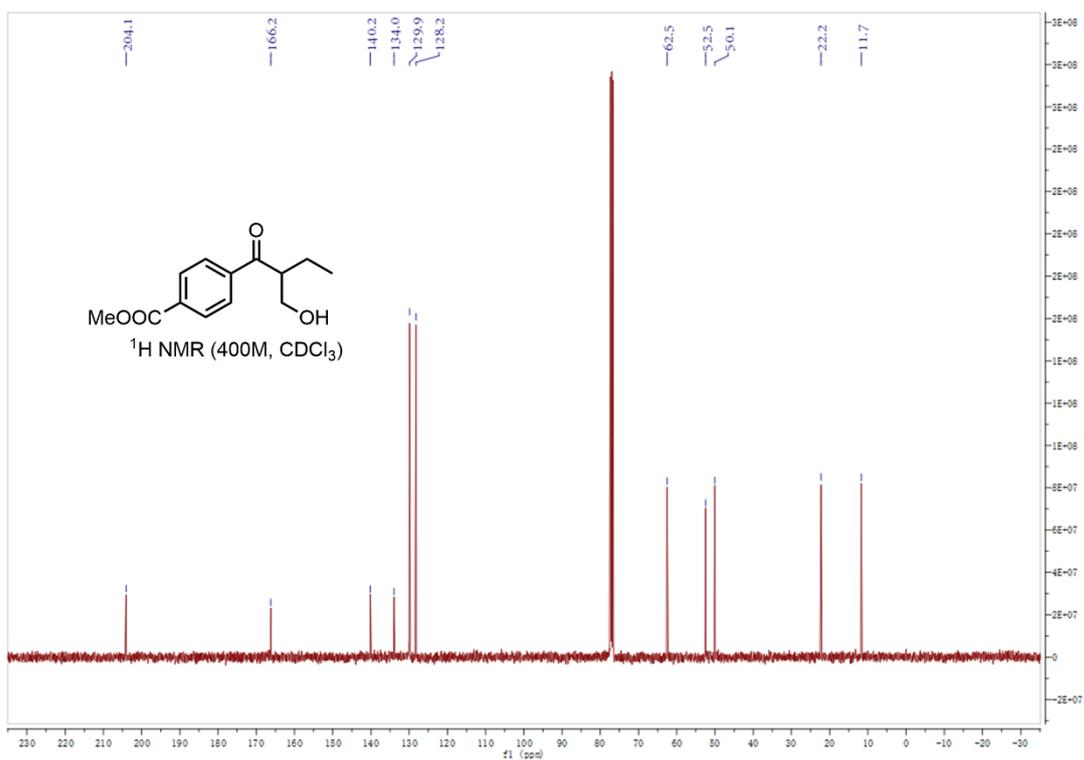
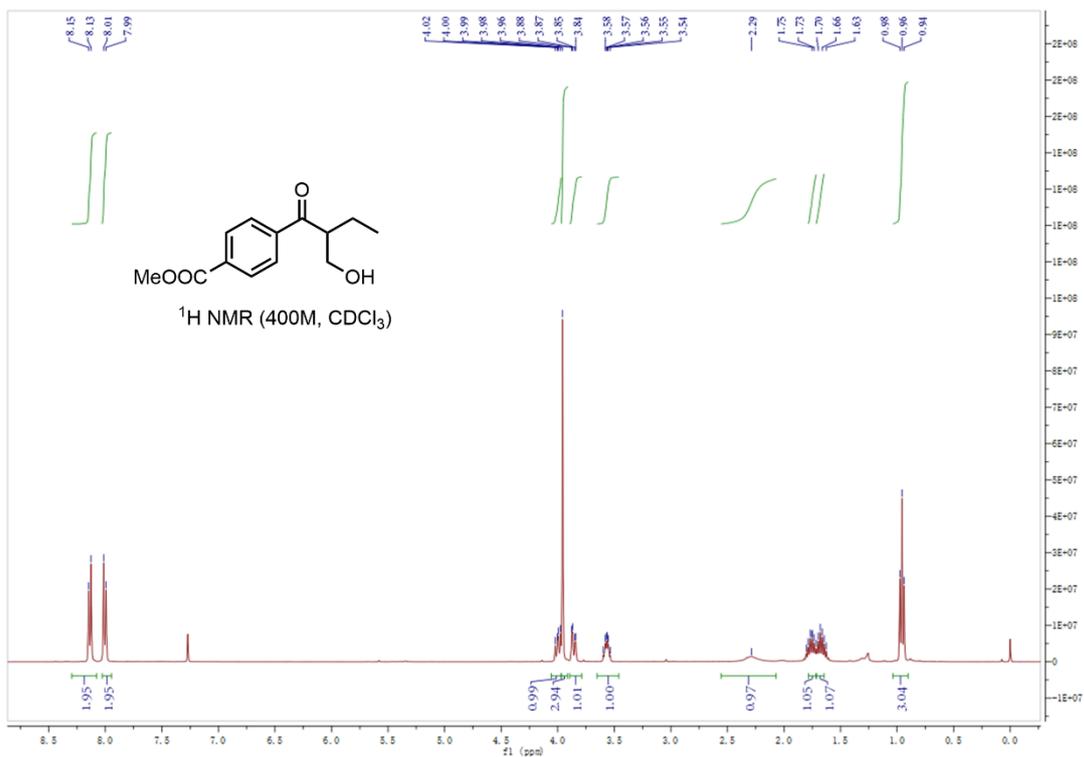




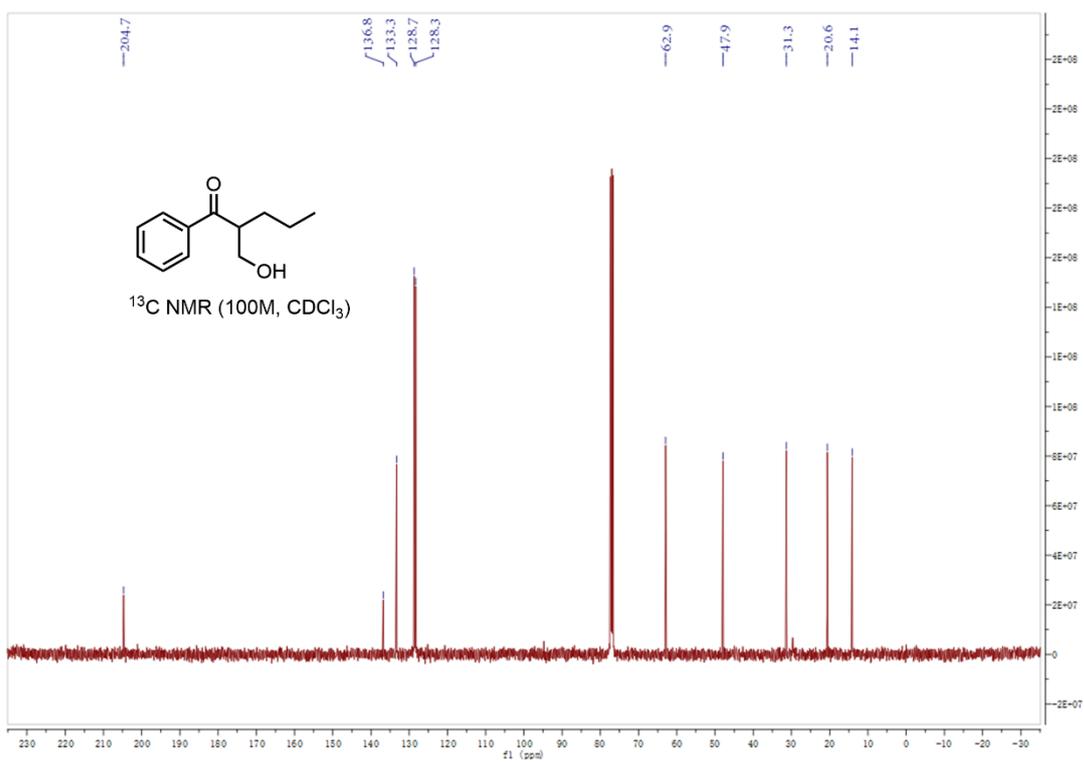
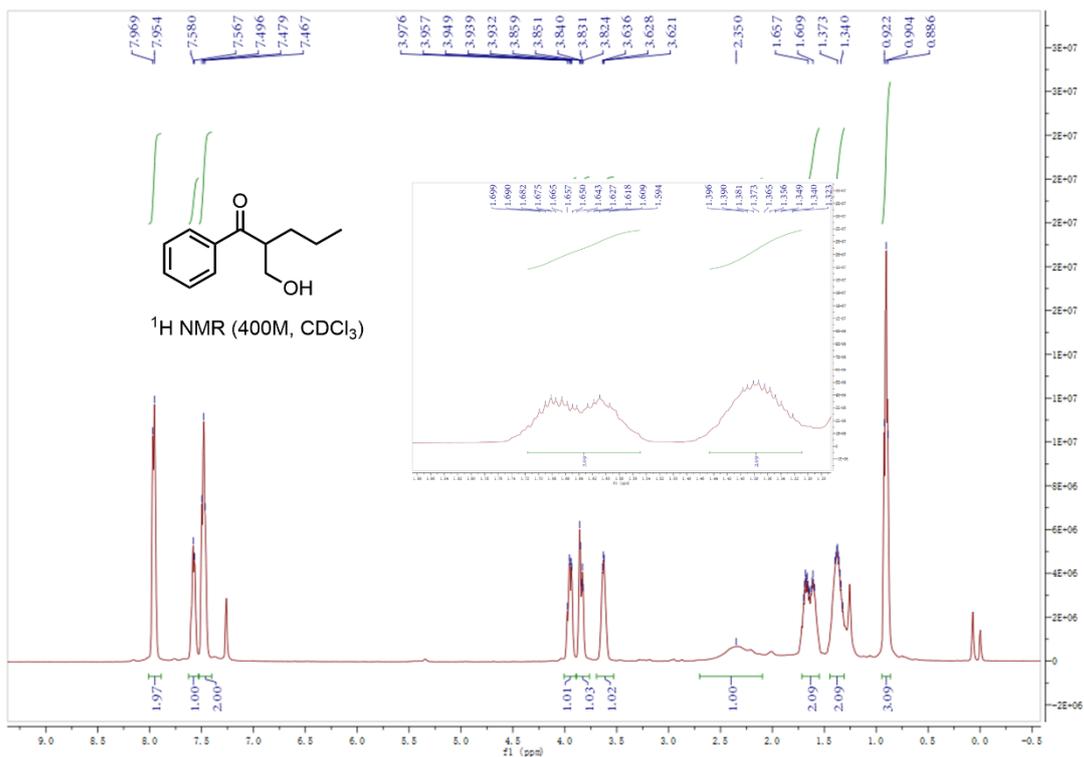
$^1\text{H}$  NMR of **2v** (400 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  NMR of **2v** (100 MHz,  $\text{CDCl}_3$ ) and  $^{19}\text{F}$  NMR of **2v** (300 MHz,  $\text{CDCl}_3$ )



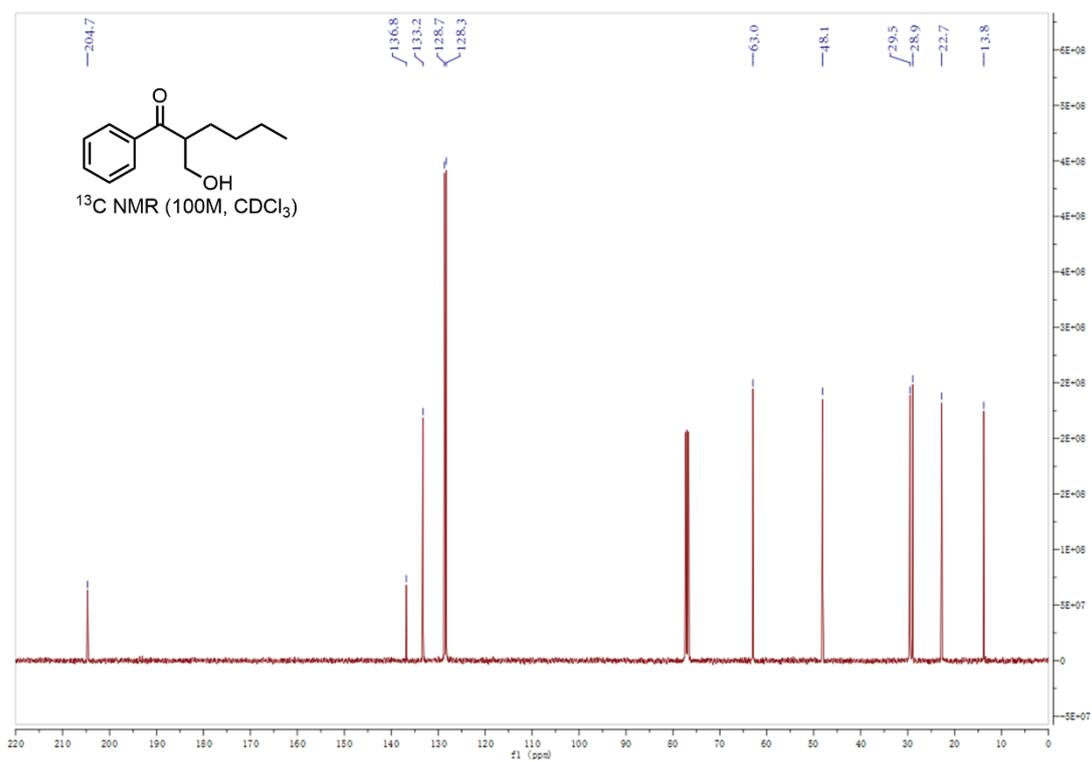
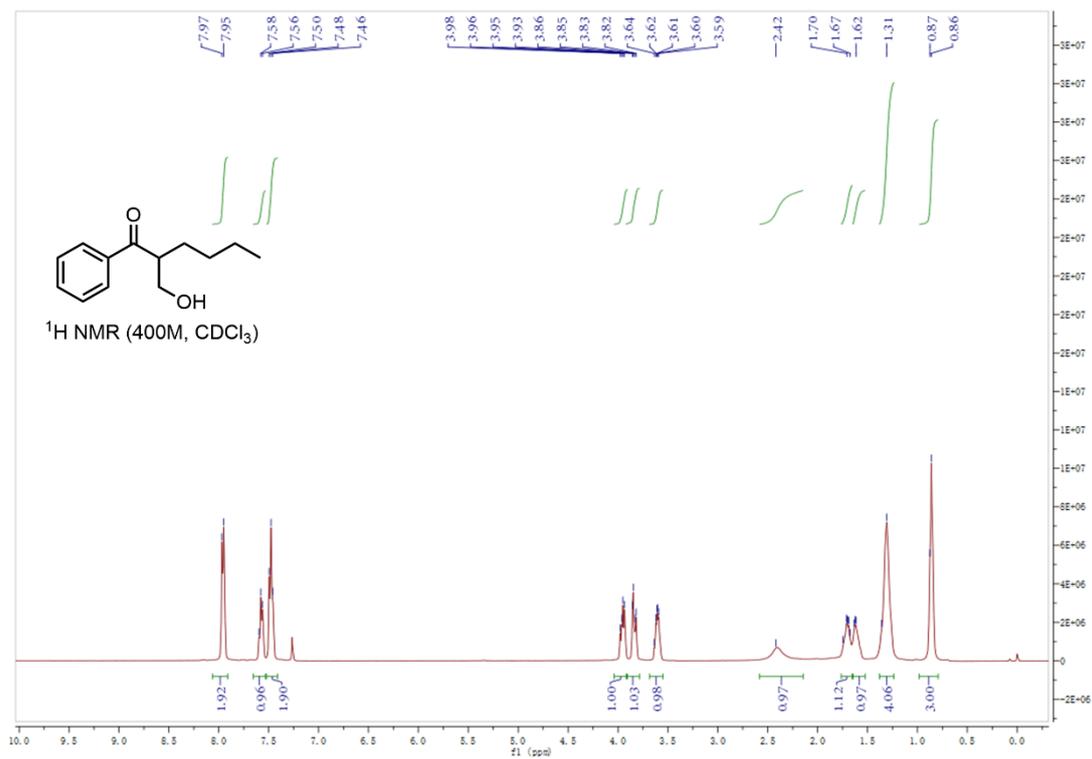
<sup>1</sup>H NMR of **2w** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2w** (100 MHz, CDCl<sub>3</sub>)



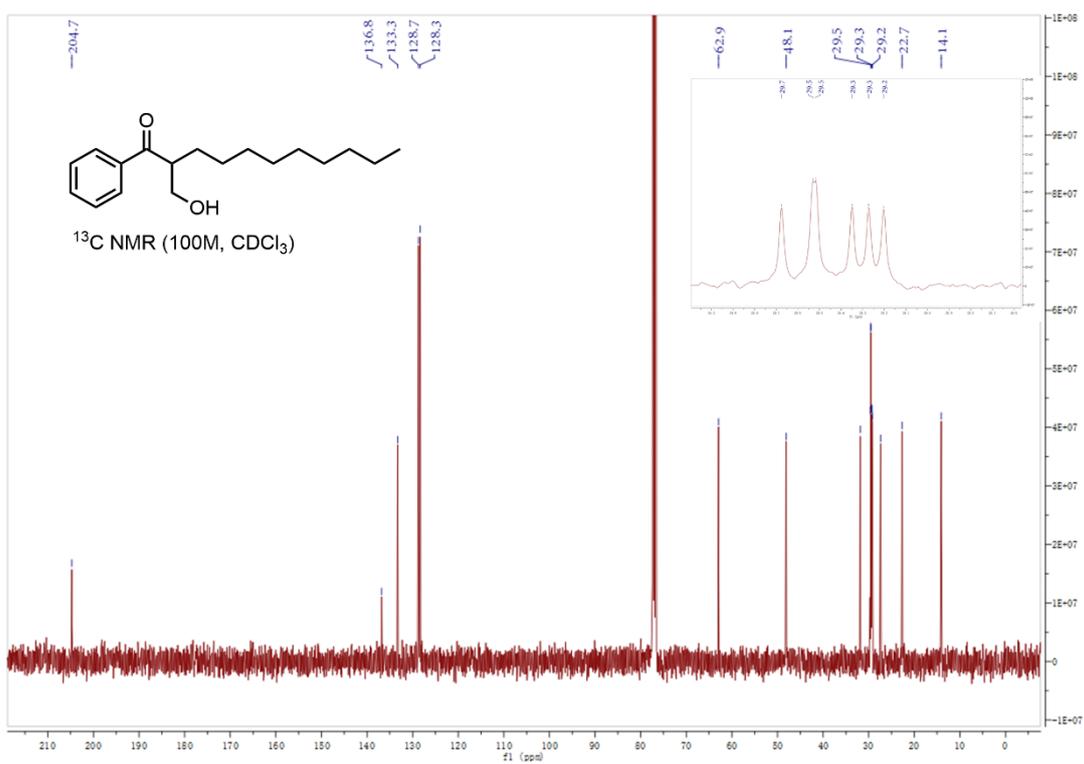
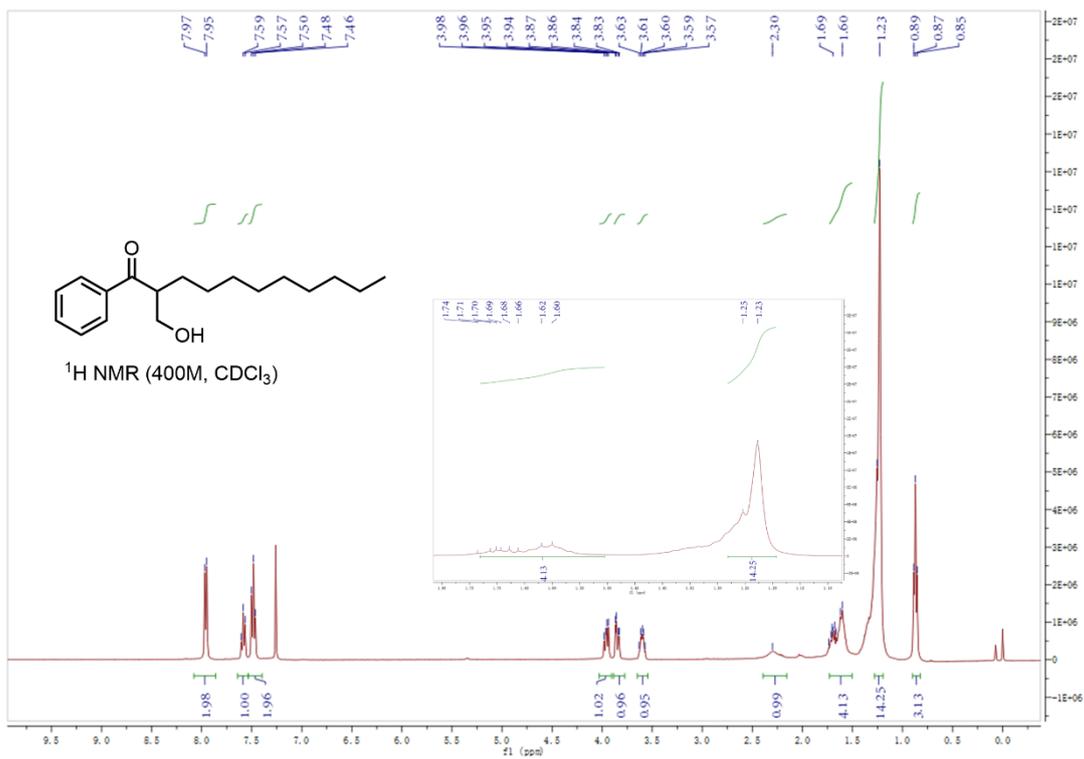
$^1\text{H NMR}$  of **2x** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C NMR}$  of **2x** (100 MHz,  $\text{CDCl}_3$ )



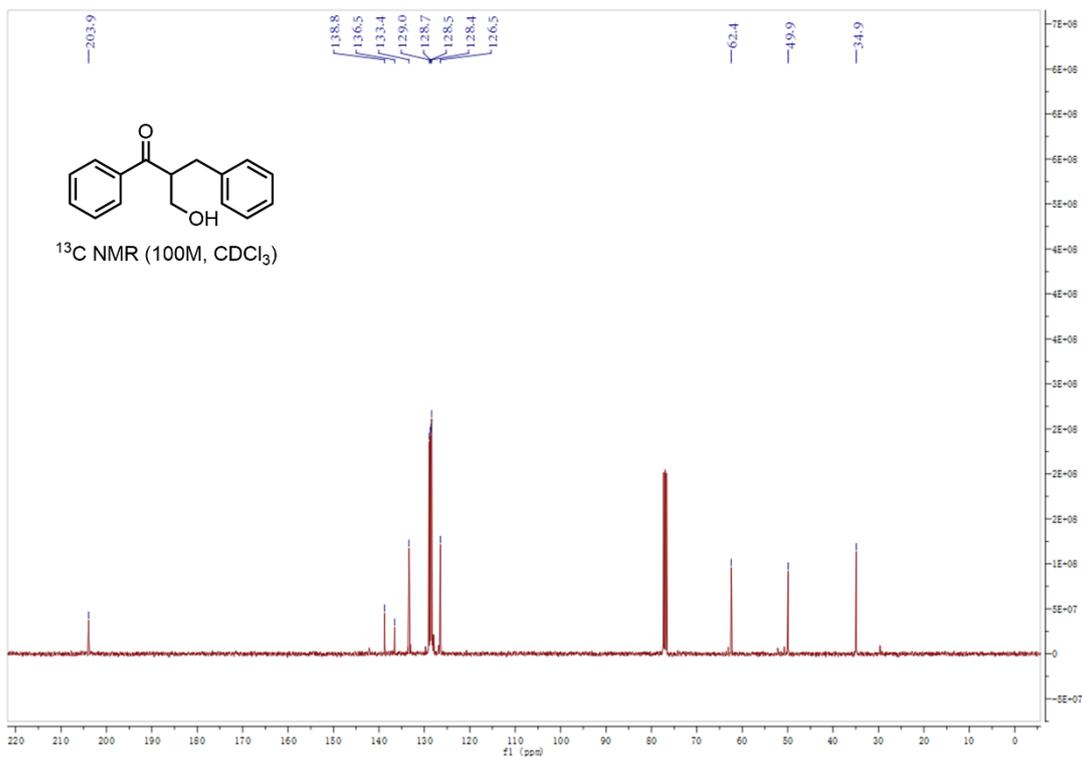
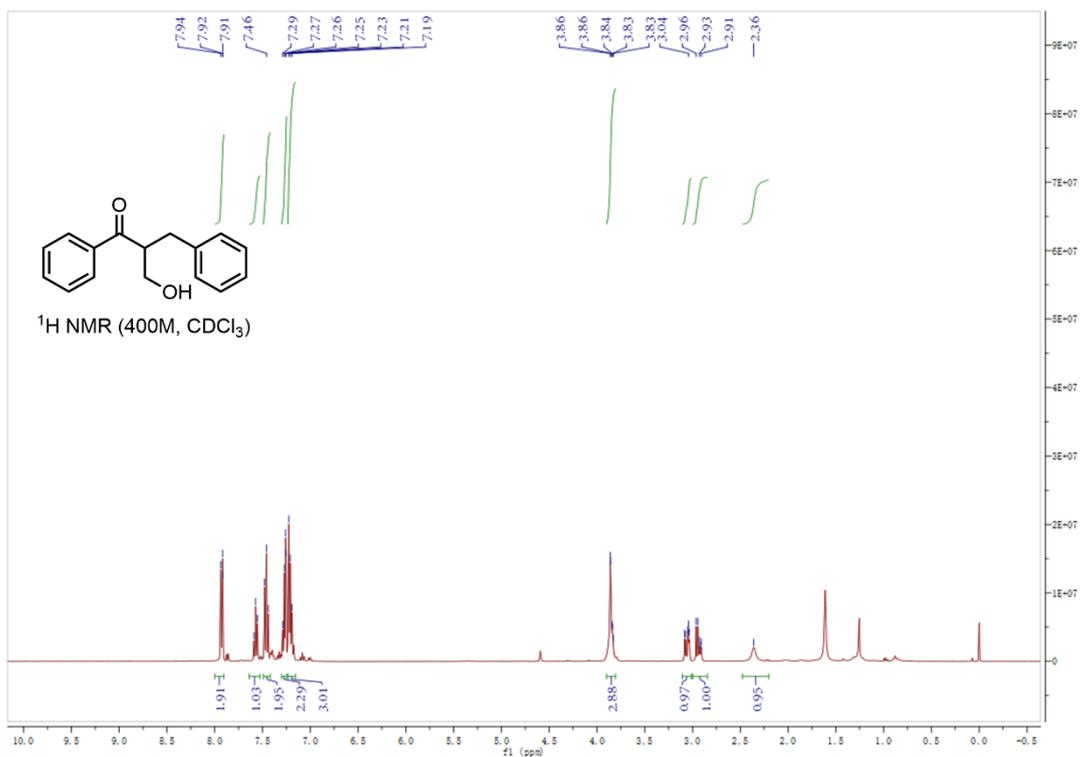
$^1\text{H NMR}$  of **2y** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C NMR}$  of **2y** (100 MHz,  $\text{CDCl}_3$ )



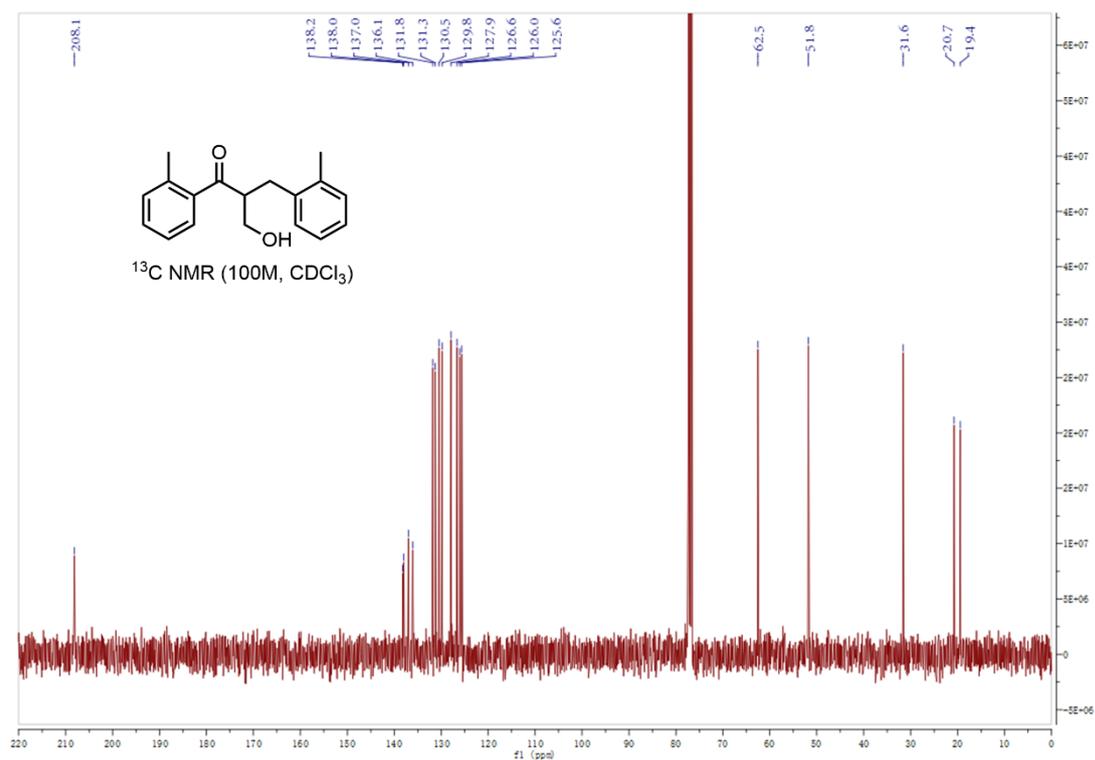
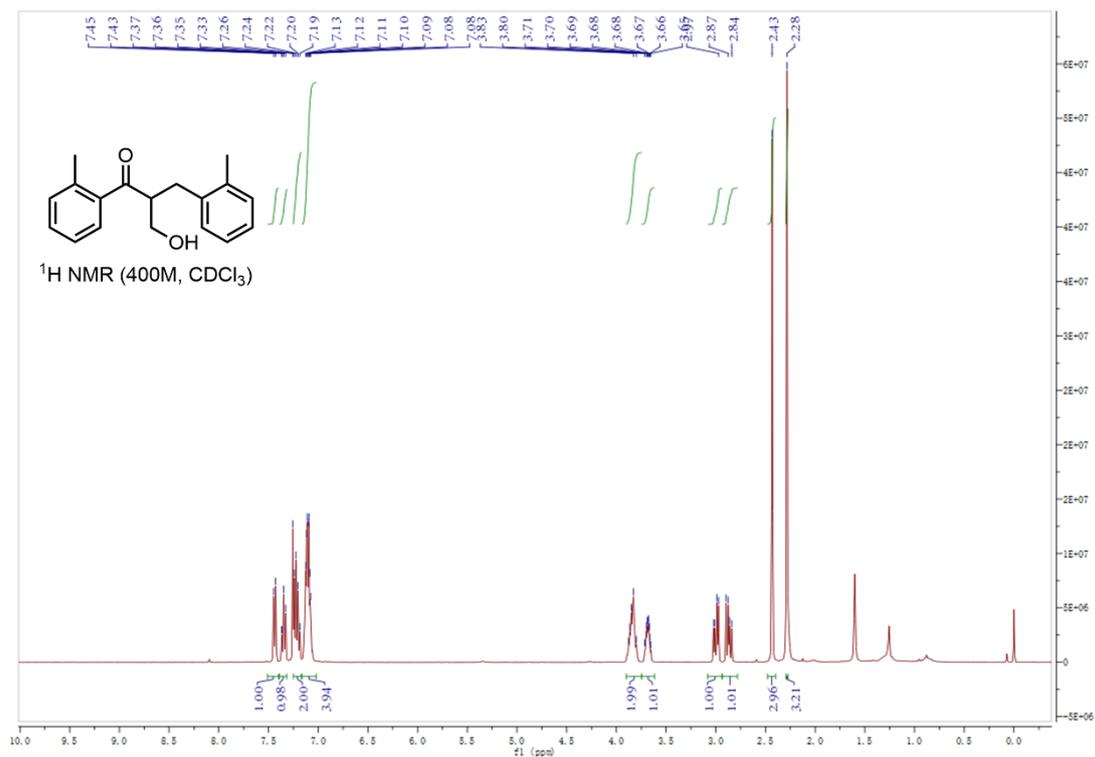
$^1\text{H NMR}$  of **2z** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C NMR}$  of **2z** (100 MHz,  $\text{CDCl}_3$ )



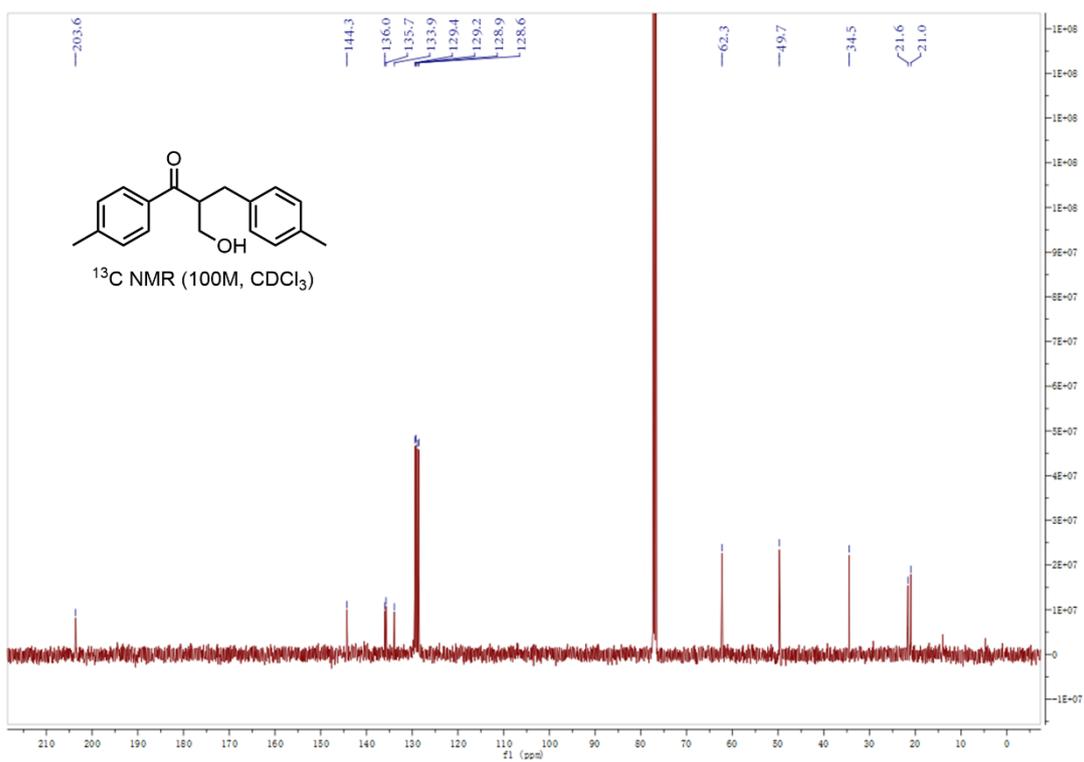
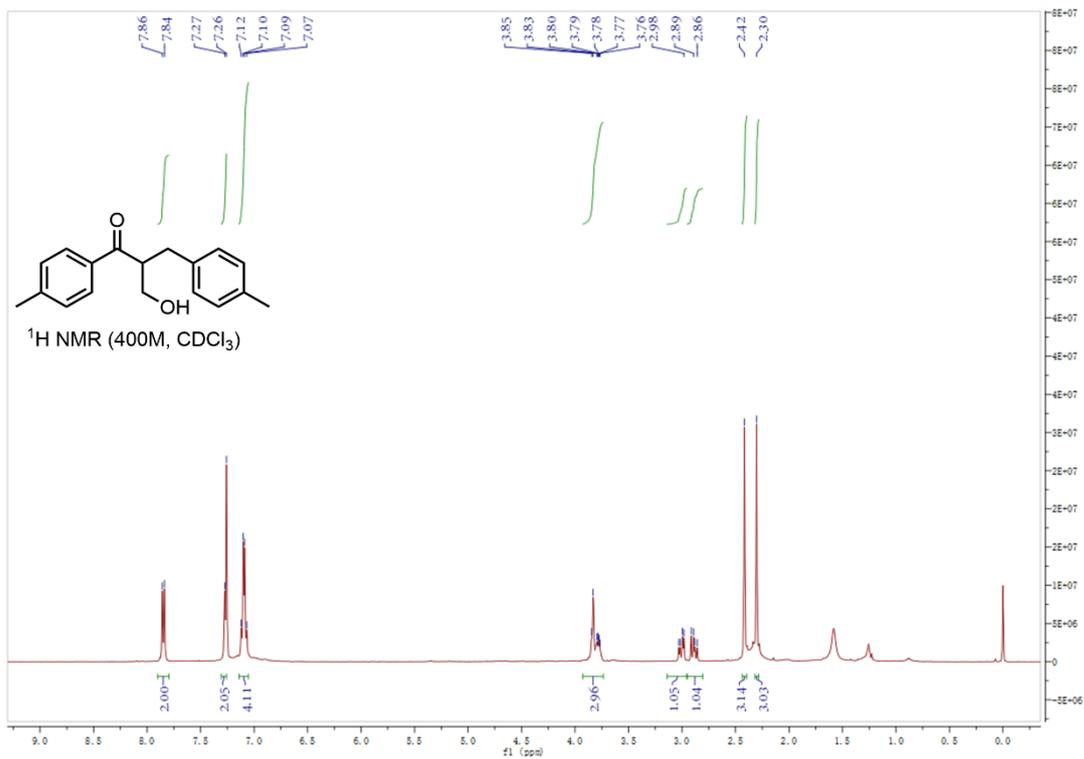
$^1\text{H NMR}$  of **2aa** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C NMR}$  of **2aa** (100 MHz,  $\text{CDCl}_3$ )



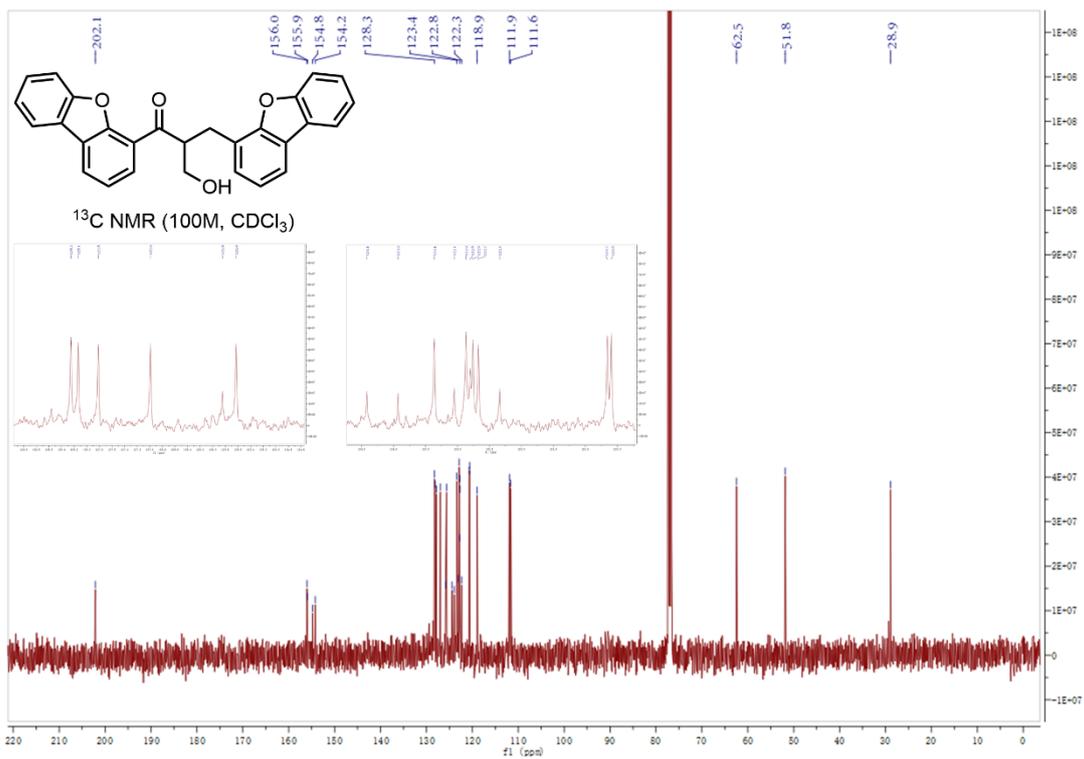
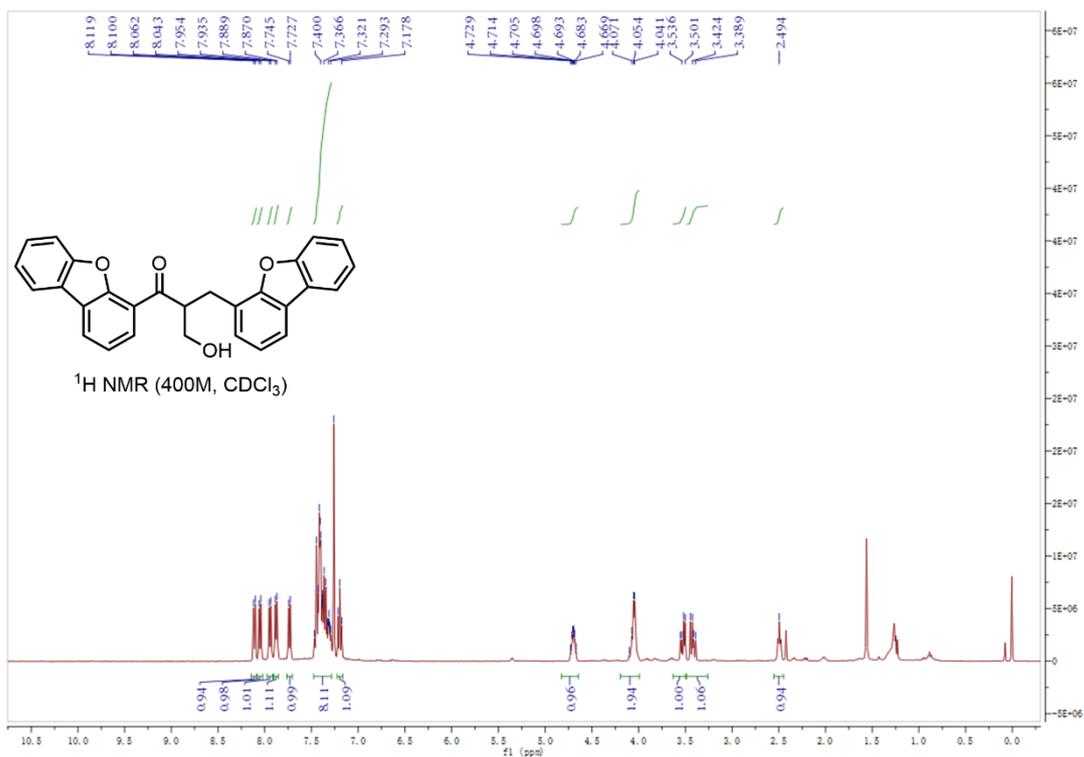
<sup>1</sup>H NMR of **2ab** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2ab** (100 MHz, CDCl<sub>3</sub>)



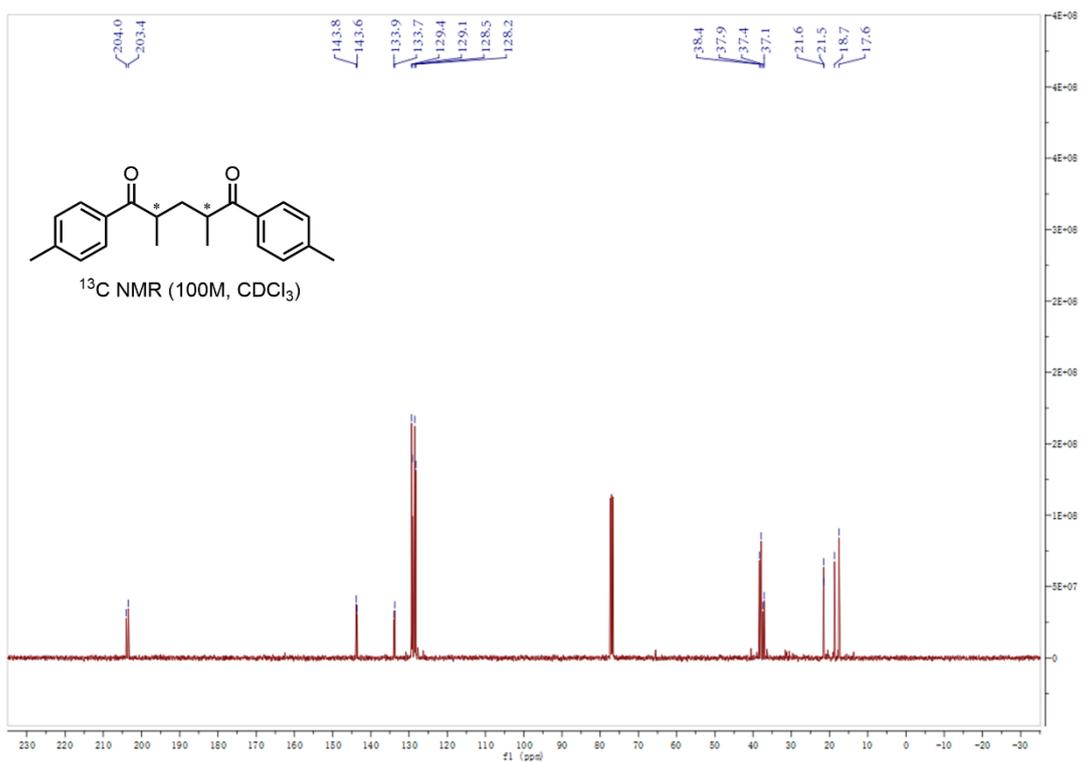
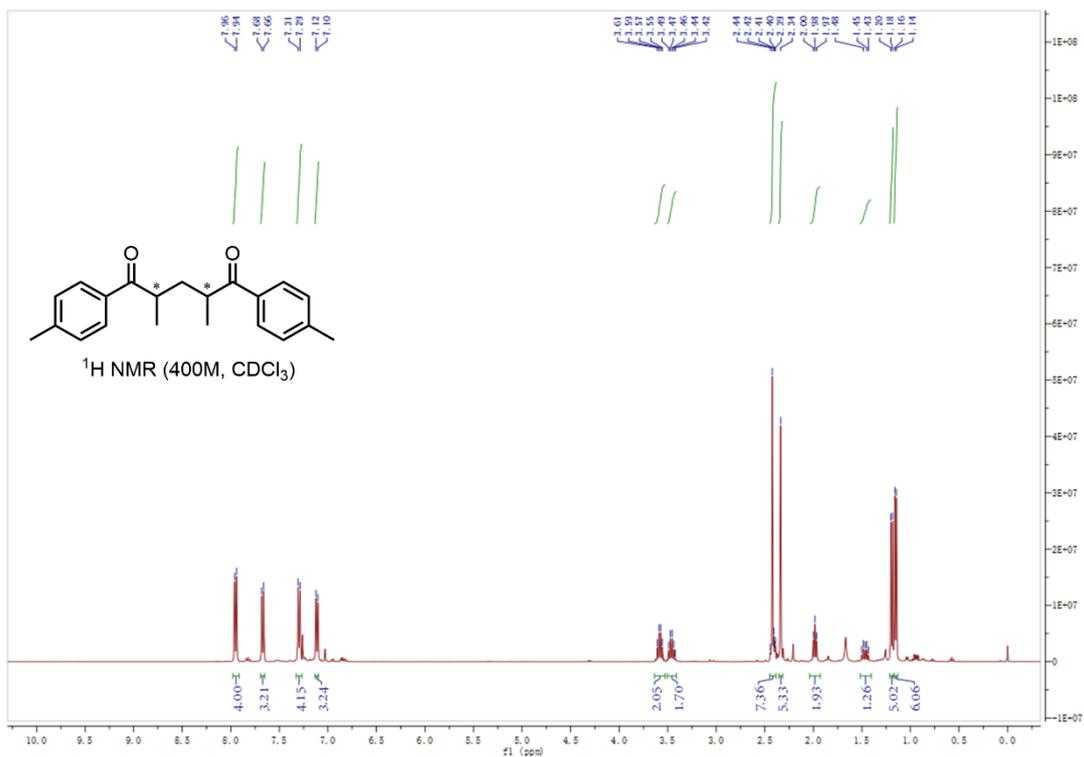
<sup>1</sup>H NMR of **2ac** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2ac** (100 MHz, CDCl<sub>3</sub>)



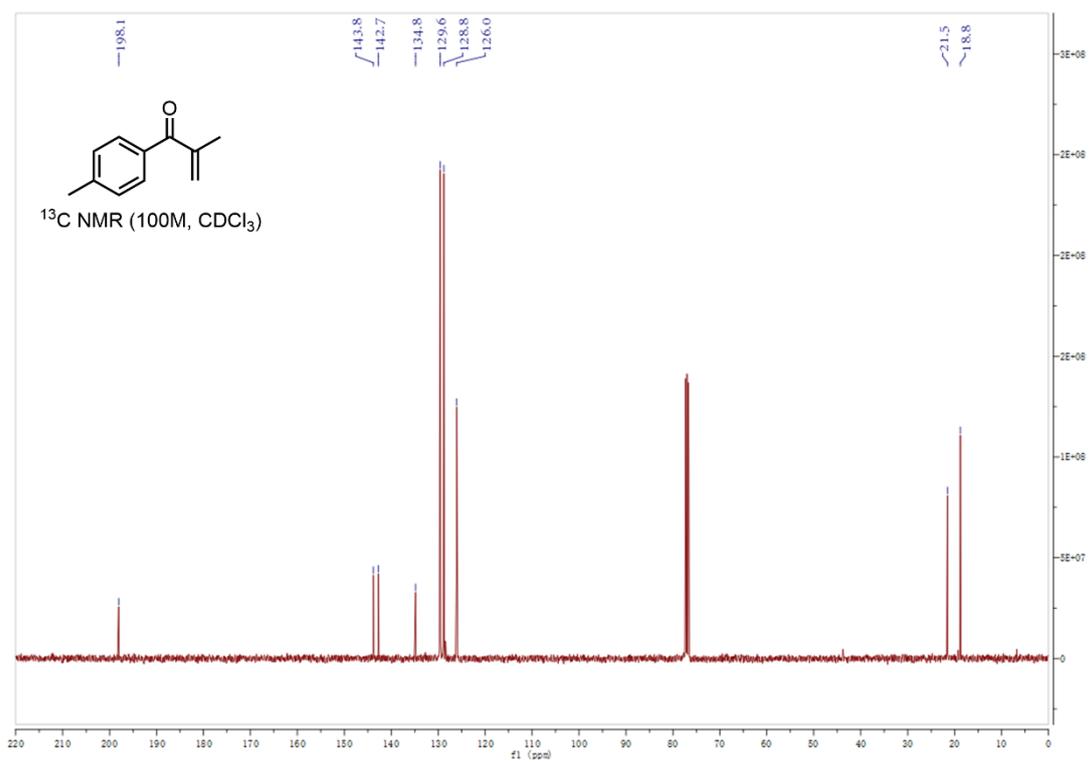
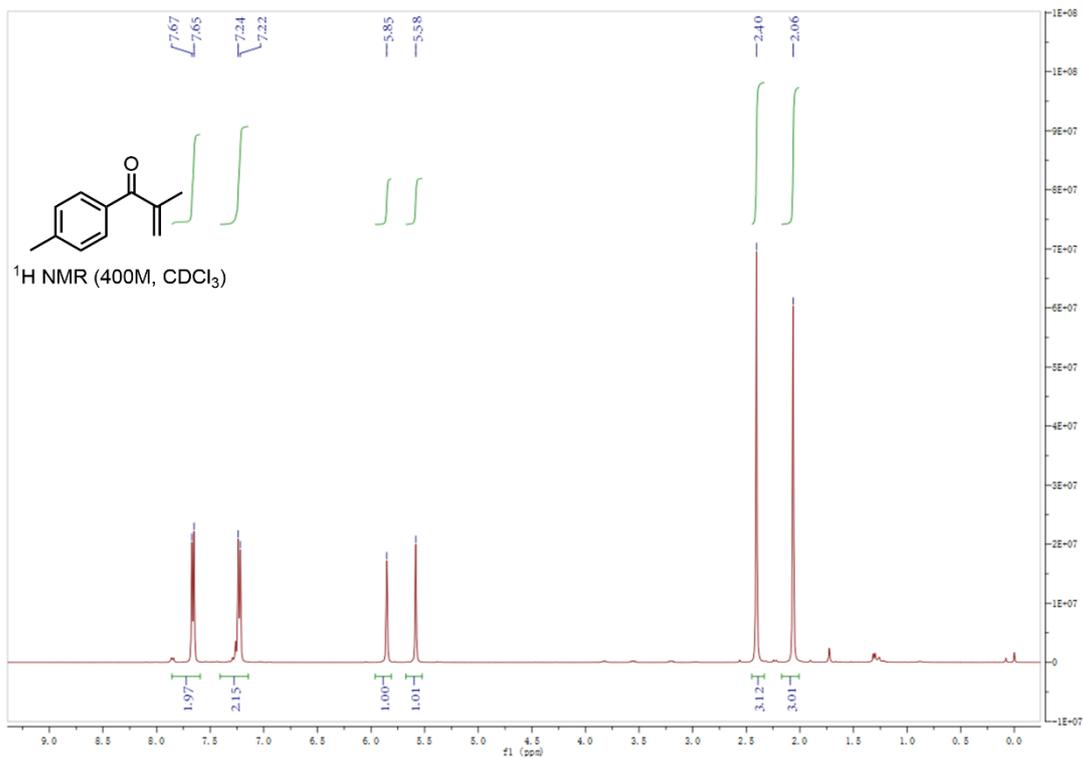
<sup>1</sup>H NMR of **2ad** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2ad** (100 MHz, CDCl<sub>3</sub>)



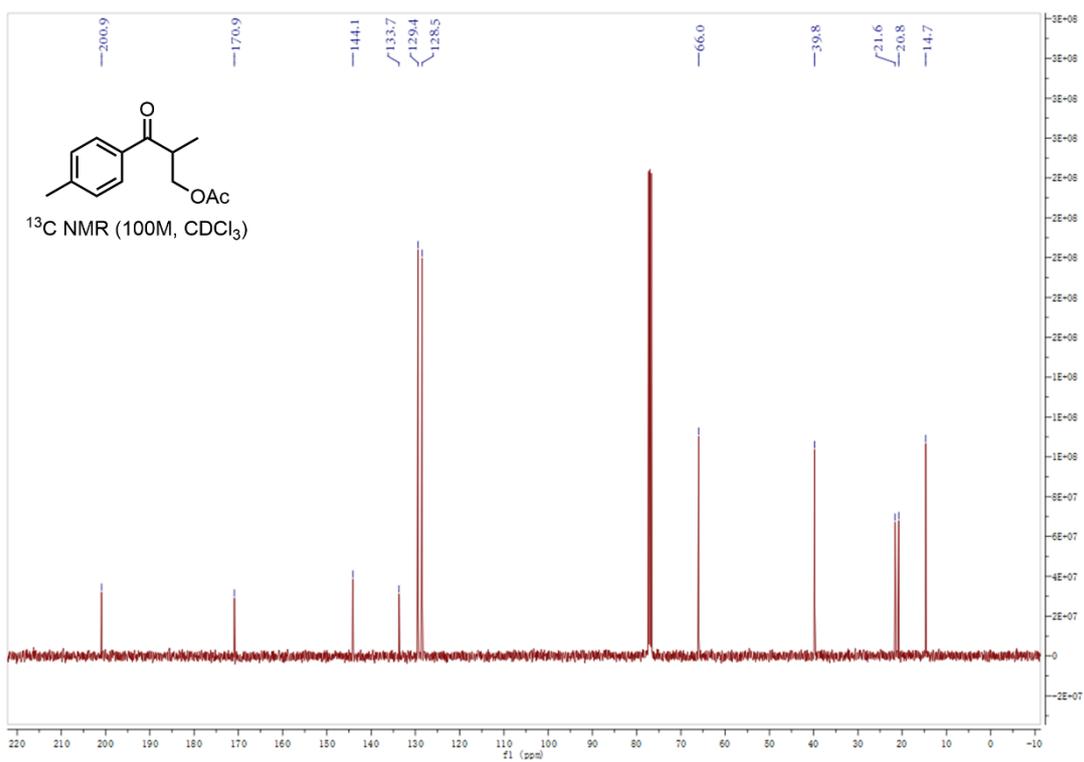
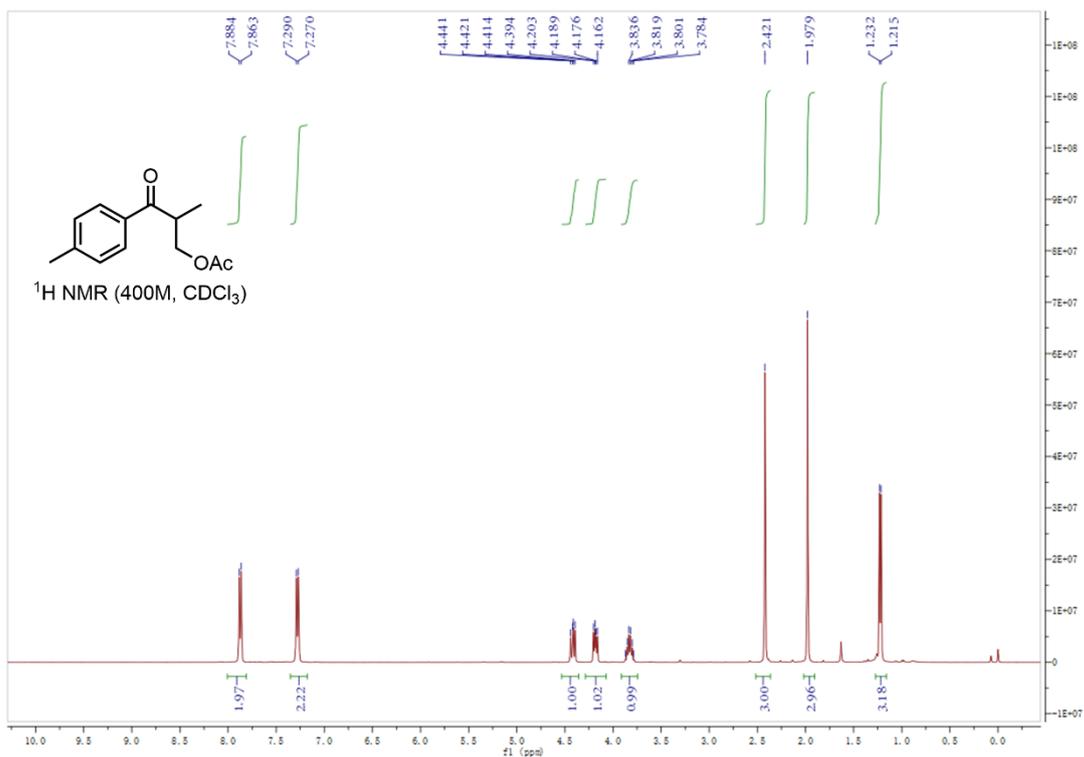
<sup>1</sup>H NMR of **2ae** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **2ae** (100 MHz, CDCl<sub>3</sub>)



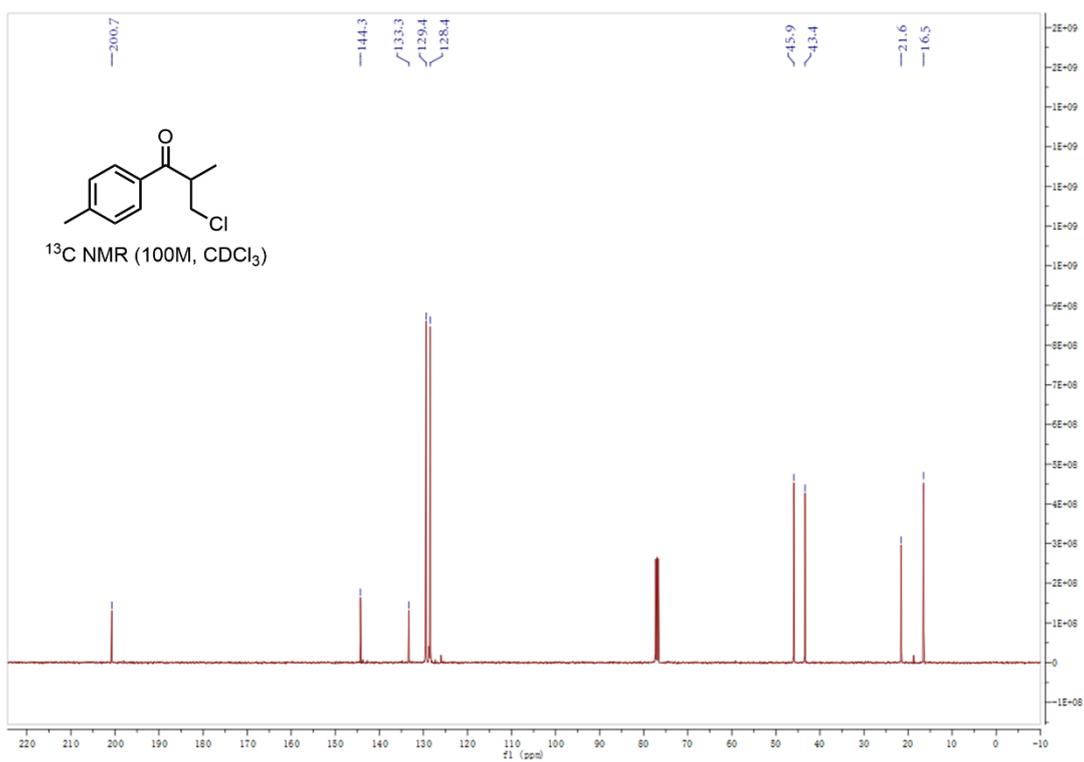
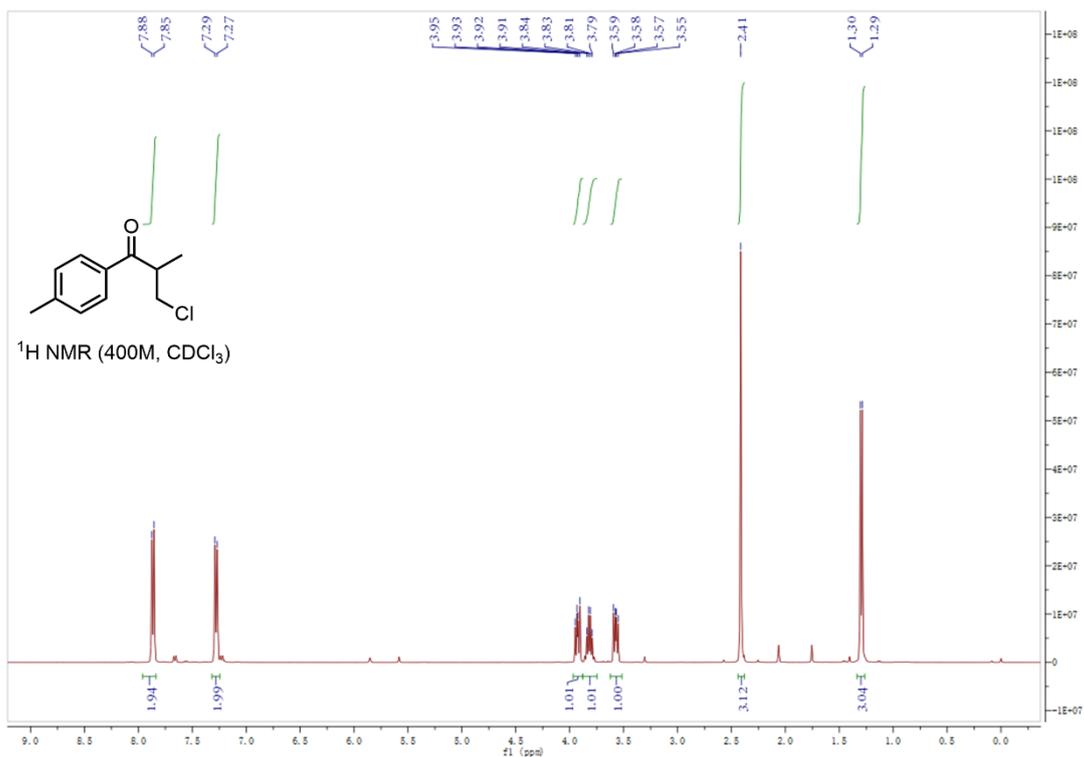
<sup>1</sup>H NMR of **3a** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3a** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **4** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **4** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **5** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **5** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **6** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **6** (100 MHz, CDCl<sub>3</sub>)

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