Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Halogen–bonded Iodonium Ion Catalysis: A Route to α–Hydroxy Ketone via Domino Oxidations of Secondary Alcohol and Aliphatic C–H Bond with High Selectivity and Control

Somraj Guha, Imran Kazi, Pranamita Mukherjee and Govindasamy Sekar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai,

Tamilnadu-600 036, India

gsekar@iitm.ac.in

Table of contents

1. General methods

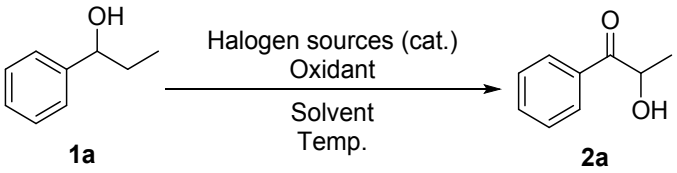
Commercially available chemicals were purchased from Alfa Aesar or Sigma-Aldrich and used as received. All the starting materials were synthesized according to the reported procedures. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized by UV lamp for reaction monitoring. Silica gel for column chromatography (particle size 100–200 mesh) was purchased from SRL India. ^{1}H, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz instrument. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane (δ 0.00), chloroform (7.26 ppm) or DMSO (2.50 ppm). ^{1}H NMR splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), (quint) quintate etc. ^{13}C NMR spectral values were reported relative to $CDCl_3$ (77.16 ppm) and DMSO-d_6 (39.52 ppm).^{19}F NMR spectra (470 MHz) were recorded using hexafluorobenzene (C_6F_6) as an internal standard (δ -164.9 ppm). FTIR spectra were recorded on a JASCO spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were recorded on a Q-Tof Micro mass spectrometer for all compounds.

2. Optimization of the domino reaction for the synthesis of *α*-hydroxy ketone 2a

The 1-phenyl propanol **1a** (1mmol) was used as model substrate with iodine (20 mol%) and IBX (1.2 equiv) in DMSO (1 mL) at 60 ^{o}C (Table 1, entry 1). This reaction gave 60% yield of **2a**, the domino oxidation product was obtained with this new 'redox catalytic system'. To check the effect of other halonium ions on the domino oxidation and *α*-hydroxylation reaction, NBS and NCS were screened. NBS yielded 40% of the product while the reaction failed when NCS was used as the reagent (entries 2 and 3). Catalytic amount of TBAI also failed to yield any product which is probably due to its inability in forming iodonium ions (entry 4). When the oxidizing agents other than IBX were employed, a decrease in yield was observed (entries 5-7). The screening of solvents revealed that the presence of DMSO is indispensible for the reaction to proceed (entries 8-12). A mixture of 2 mL of DMSO and 1 mL of 1,4-dioxane was found to be the best solvent system for the reaction (65% yield, entry 12). The yield increased to 70% when the temperature was increased to 80 ^{o}C (entry 13). Further increase in temperature to 100 ^{o}C was found to be counter-productive (entry 14). The lowering of the reaction temperature to the room temperature shut down the reaction completely (entry 15). Finally, the ratio of iodine and IBX equivalences were screened and the highest yield of 82% was obtained at 80 ^{o}C with 30 mol% of iodine and 3 equiv. of IBX. Interestingly, when less electrophilic molecular iodine and other halogen(I)

precursor such as NIS and NBS were employed in stoichiometric amount the product did not form (entries 17–19).

Table 1. Screening of reaction condition[a]



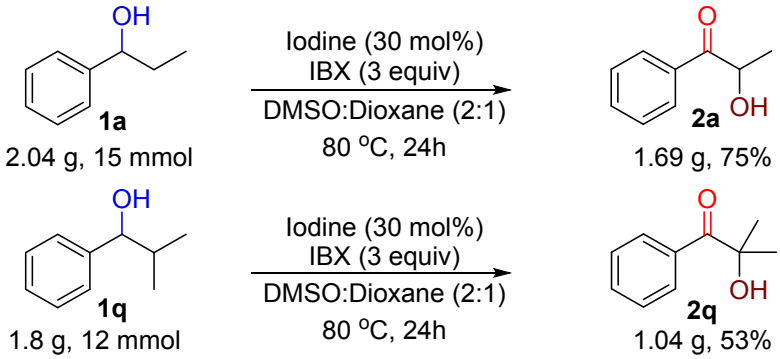
1a **2a**

Entry	Catalyst	Oxidant	Solvent	Temp (°C)	Yield (%)[b]
1	I_2	IBX	DMSO	60	60
2	NBS	IBX	DMSO	60	40
3	NCS	IBX	DMSO	60	-
4	TBAI	IBX	DMSO	60	-
5	I_2	TBHP	DMSO	60	42[c]
6	I_2	Oxone	DMSO	60	26
7	I_2	$PhI(OAc)_2$	DMSO	60	30
8	I_2	IBX	toluene	60	-
9	I_2	IBX	CH_3CN	60	-
10	I_2	IBX	DMSO:Water	60	38[d]
11	I_2	IBX	DMSO:Tolune	60	43[d]
12	I_2	IBX	DMSO:Dioxane	60	65[e]
13	I_2	IBX	DMSO:Dioxane	80	70[e]
14	I_2	IBX	DMSO:Dioxane	100	40[e]
15	I_2	IBX	DMSO:Dioxane	rt	-[e]
16	I_2	IBX	DMSO:Dioxane	80	82[e,f]
17	I_2	-	DMSO:Dioxane	80	-[g]
18	NIS	-	DMSO:Dioxane	80	-[g]
19	NBS	-	DMSO:Dioxane	80	-[g]

[a]Reaction condition: All the reactions were carried out using **1a** (1 mmol) with 20 mol% catalyst and 1.2 equivalents of oxidant in 1 mL solvent, unless otherwise mentioned. [b]Isolated yield. [c]5.0–6.0 M in decane. [d]2 mL solvent was used in 1:1 ratio. [e]2 mL of DMSO was taken with 1 mL 1,4-dioxane. [f]30 mol% iodine was used with 3 equiv of IBX. [g]1.2 Equivalents of I_2 NBS and NIS were used.

3. Scale-up reactions

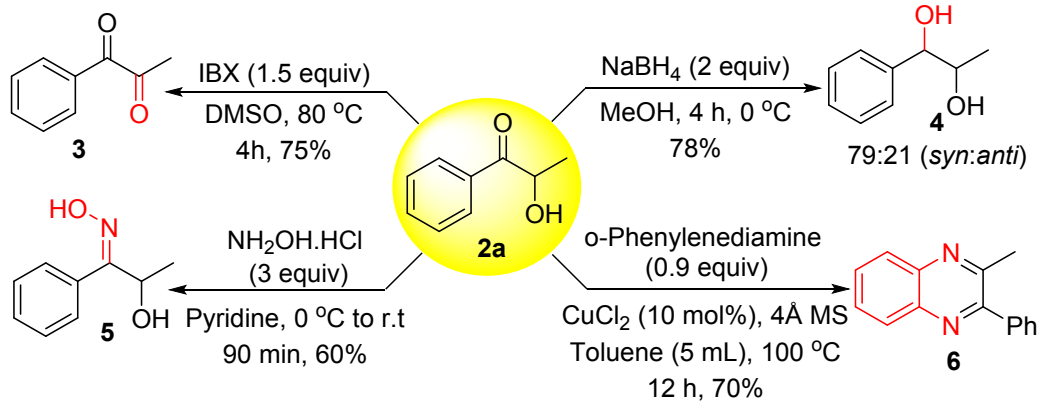
The consistency of the reaction in large scale synthesis was examined by treating 2.04 g (15 mmol) of **1a** and 1.8 g (12 mmol) of **1q** under the standard reaction conditions. These two reactions proceeded in a smooth manner to provide 75% of **2a** and 53% of **2q** which showed very less deviation from the laboratory scale synthesis (Scheme 1).



Scheme 1. Gram scale synthesis

4. Synthetic transformation of the *α*-hydroxy ketone 2a

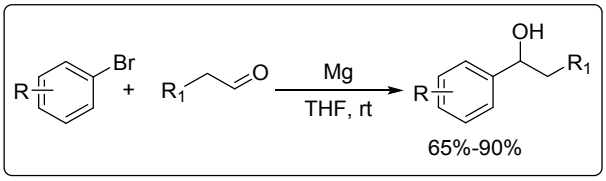
The synthetic application of *α*-hydroxy ketone **2a** was shown by its conversion to diketo compound **3**, diol **4** and *α*–hydroxy imine **5** by means of oxidation with 1.5 equiv of IBX reduction with $NaBH_4$, and imination with hydroxylamine respectively. All these derivatives find their use as important precursors and ligands in organic synthesis.[1] We have also established the importance of our medhodology by synthesising an important hetecyclic compound quinoxalines **6** from the *α*-hydroxy ketone **2a** (Scheme 2).[1b]



Scheme 2. Follow-up chemistry with *α*-hydroxy ketone **2a**

5. General procedure for synthesis of secondary alcohols[2]

A dried round-bottom flask containing stir bar was charged with magnesium (1.2 equiv.), small piece of iodine and the solvent THF under nitrogen atmosphere. To the solution, aryl bromides (1.0 equiv) was dropped slowly and stirred for 30 min. After the formation of the Grignard reagent is completed, the reaction mixture is cooled to 0 °C, then 1.5 equiv of corresponding aldehydes was added. The resulting mixture was stirred for 1-2 h. After the completion of the reaction, the reaction mixture was washed with saturated NH_4Cl solution and extracted with ethyl acetate for several times. The combined organic layer was washed with saturated NaCl and dried over anhydrous Na_2SO_4. The organic layer was then concentrated under vacuum, and the crude residue was purified by silica gel column chromatography (hexanes/ ethyl acetate) to afford the secondary alcohols (Scheme 3).



Scheme 3: Synthesis of benzylic secondary alcohols

6. UV-vis experiment establishing the formation of DMSO-coordinated iodonium ions

a) A mixture of 0.25 mmol iodine and 50 µL DMSO was stirred at 80 °C for 1h and the UV-vis spectra of the reaction mixture were recorded in $CHCl_3$. The emergence of three peaks was observed near 520 nm, 360 nm and 295 nm (Figure 1, spectrum A).[3] These peaks are corresponds to iodine in $CHCl_3$, I_3^- and $[(DMSO)_nI^+]$. An enhancement of the band near 295 nm was observed when the experiment was carried out in $CHCl_3$ with a well stirred mixture of 0.25 mmol of I_2 and 0.25 mmol of IBX in DMSO at 80 °C for 1h (Figure 1, spectrum B).

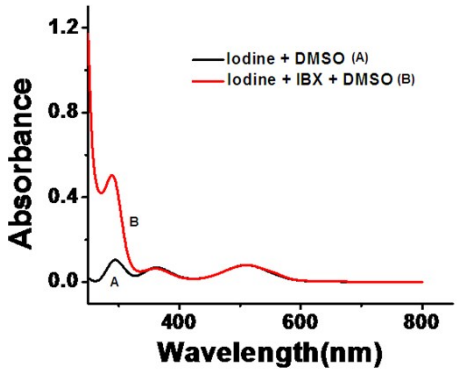


Figure 1. UV-vis experiment establishing the formation of DMSO-coordinated iodonium ions at 80 °C

b) A mixture of 0.25 mmol iodine and 50 µL DMSO was stirred at rt for 1h and the UV-vis spectra of the reaction mixture were recorded in $CHCl_3$. The emergence of two peaks was observed near 520 nm, and 295 nm (Figure 2, spectrum A).

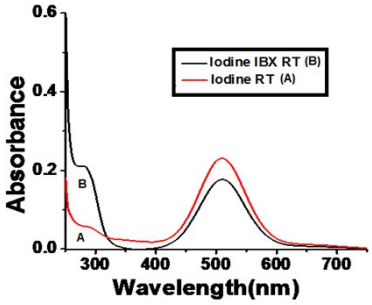


Figure 2. UV-vis experiment establishing the formation of DMSO-coordinated iodonium ions at rt.

These peaks are corresponds to iodine in $CHCl_3$ and $[(DMSO)_nI^+]$. This time the extinction co-efficient of the band corresponds to $[(DMSO)_nI^+]$ is less and the absorption band correspond to $[I_3]^-$ (formed via the association of I_2 and I^-) is not visible. This is probably due to the less dissociation of iodine to I^+ and I^- in DMSO at rt. An enhancement of the band near 295 nm was observed when the experiment was carried out in $CHCl_3$ with a well stirred mixture of 0.25 mmol of I_2 and 0.25 mmol of IBX in DMSO at rt for 1h (Figure 2, spectrum B). A consequent decrease of the absorption maxima of the band near 520 nm has been observed too.

c) IBX is insoluble in $CHCl_3$. In DMSO it shows the λ_{max} around 265 nm (Figure 3).

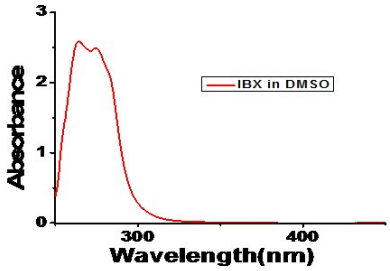


Figure 3. UV-vis spectrum of IBX in DMSO

7. IR experiment to support the formation of stabilized DMSO-coordinated iodonium ions

To conduct this experiment, 0.25 mmol iodine and 0.25 mmol IBX in 50 µL DMSO, 0.25 mmol IBX in 50 µL DMSO, 0.25 mmol iodine in 50 µL DMSO were taken separately and stirred at 80 ^oC in three different reaction tube for 1h. The IR spectra of those reaction mixtures were recorded (Spectra A, B, C respectively in Figure 4). The spectra of DMSO and 2-iodobenzoic acid were

recorded separately (Spectra D and E respectively). Emergence of a new band at 1139.72 cm^{-1} was observed.

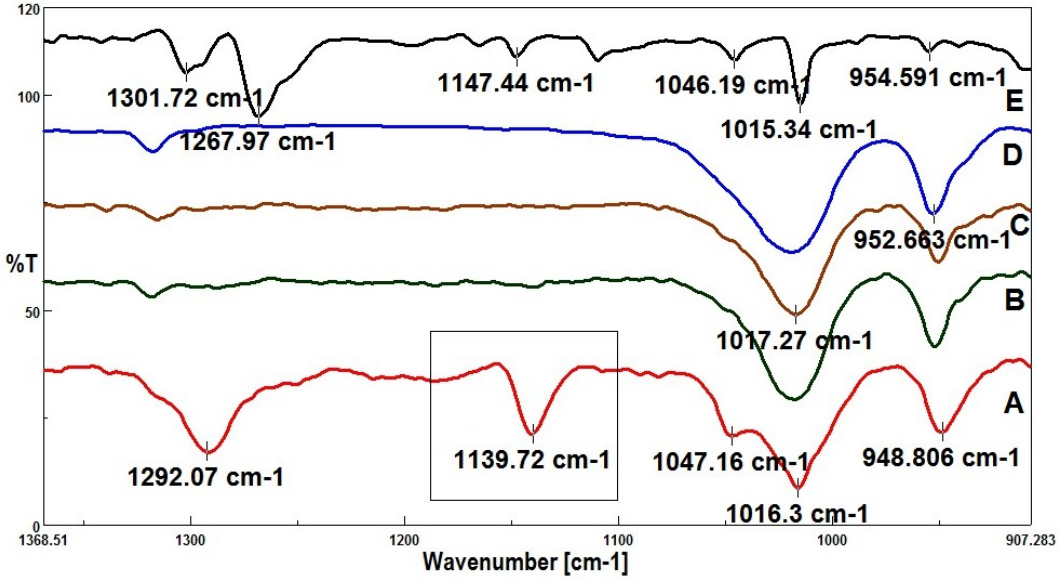
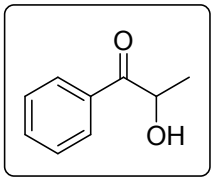


Figure 4. IR experiment showing the shift of S–O stretching frequency of DMSO

8. General procedure to synthesize α-hydroxy ketones from benzylic secondary alcohols through domino reaction

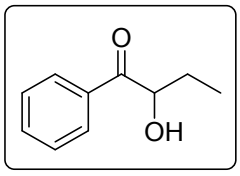
A reaction tube equipped with a magnetic stir bar, was charged with alcohols (1 mmol), iodine (30 mol %), DMSO (2mL) and 1,4-dioxane (1 mL). The reaction mixture was stir for 5 min at rt. Then 3 equiv. IBX was added and the reaction was kept at 80 ^{o}C. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with 15 mL of ethyl acetate and washed with dilute $NaHCO_3$ solution (2 times) followed by saturated $Na_2S_2O_3$ one time. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate = 10:1) to give corresponding pure product.

9. Spectroscopic data for *α*-hydroxyketone derivatives

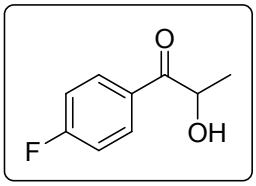


2-Hydroxy-1-phenylpropan-1-one (2a): 123.15 mg, 82% yield; pale yellow liquid; R_f = 0.25 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 700, 971, 1129, 1450, 1598, 1687, 2982, 3467; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (d, *J* = 7 Hz, 3H), 3.79 (d, *J* = 6 Hz, 1H), 5.13–5.20 (m, 1H), 7.50 (t, *J* = 8 Hz, 2H), 7.60–7.64 (m, 1H),

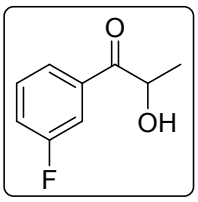
7.91–7.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 69.5, 128.8, 129.0, 133.5, 134.1, 202.5; GC-MS (m/z): $[M]^+$ 150.18



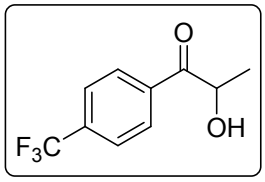
2-Hydroxy-1-phenylbutan-1-one (2b): 116.58 mg, 71% yield; pale yellow liquid; R_f = 0.16 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 963, 1246, 1449, 1598, 1681, 2968, 3479; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.57–1.65 (m, 1H), 1.90–2.01 (m, 1H), 3.71 (d, *J* = 6.4 Hz, 1H), 5.03–5.08 (m ,1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.59–7.64 (m, 1H), 7.89–7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 29.0, 74.1, 128.6, 129.0, 134.0, 134.1, 202.3; HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_{12}O_2$: 187.0735; found: 187.0714



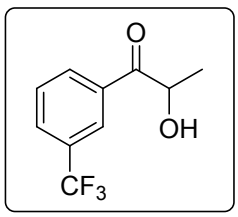
1-(4-Fluorophenyl)-2-hydroxypropan-1-one (2c): 136.22 mg, 81% yield; yellow liquid; R_f = 0.19 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 846, 973, 1131, 1507, 1598, 1685, 2983, 3462; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (d, *J* = 7.2 Hz, 3H), 3.71–3.75 (m, 1H), 5.01–5.16 (m, 1H), 7.15–7.21 (m, 2H), 7.94–7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 69.3, 116.2, 116.4, 131.5, 131.6, 167.6, 200.9; ^{19}F NMR ($CDCl_3$ 470 MHz) δ -106.30; HRMS (m/z) $[M + H]^+$calcd for $C_9H_9O_2$: 191.0484; found: 191.0510.



1-(3-Fluorophenyl)-2-hydroxypropan-1-one (2d): 105.95 mg, 63% yield; yellow liquid; R_f = 0.32 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}):1271, 1443, 1588, 1692, 2983, 3448; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (d, *J* = 6.8 Hz, 3H), 3.70 (d, *J* = 6.4 Hz, 1H), 5.11 (quint, *J* = 6.8 Hz, 1H), 7.32 (tdd, J_1 = 0.8 Hz, J_2 = 2.4 Hz, J_3 = 8.4 Hz, 1H), 7.49 (td, J_1 = 5.6 Hz, J_2 = 8.4 Hz, 1H), 7.59–7.65 (m, 1H), 7.69 (dt, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 69.7, 115.6 (d, *J* = 22.4 Hz), 121.2 (d, *J* = 21.3 Hz), 124.5 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 7.5 Hz), 135.5 (d, *J* = 6.2 Hz), 163.0 (d, *J* = 247.3 Hz), 201.4; ^{19}F NMR ($CDCl_3$ 470 MHz) δ -114.10; HRMS (m/z) $[M + Na]^+$calcd for $C_9H_9O_2FNa$: 191.0484; found: 191.0485.

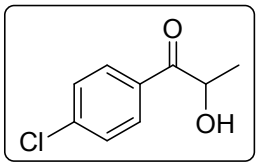


2-Hydroxy-1-(4-(trifluoromethyl)phenyl)propan-1-one (2e): 141.82 mg, 65% yield; yellow liquid; R_f = 0.20 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}):1131, 1327, 1412, 1689, 3448; ^{1}H NMR (400 MHz, $CDCl_3$) δ1.45 (d, *J* = 6.8 Hz, 3H), 3.68 (d, *J* = 6.4 Hz, 1H), 5.17 (quint, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 69.8, 123.5 (q, *J* = 293.4 Hz), 126.1 (q, *J* = 3.6 Hz), 129.1, 135.3 (q, *J* = 32.7, Hz), 136.4, 201.7; ^{19}F NMR ($CDCl_3$ 470 MHz) δ -66.47 (s, 3F); HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_{10}O_2F_3$: 219.0633; found: 219.0652.

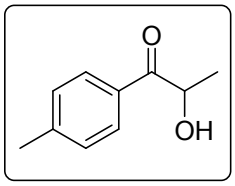


2-Hydroxy-1-(3-(trifluoromethyl)phenyl)propan-1-one (2f): 130.90 mg, 60% yield; yellow liquid; R_f = 0.24 (hexane/ethyl acetate = 5.7:1); FTIR (neat) ν (cm^{-1}):

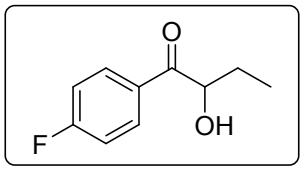
694, 1074, 1129, 1331, 1614, 1695, 2986, 3458; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (d, *J* = 7.2 Hz, 3H), 3.66 (d, *J* = 6.4 Hz, 1H), 5.14–5.21 (m, 1H), 7.66 (t, *J* = 8 Hz, 1H), 7.88 (d, *J* = 8 Hz, 1H), 8.10 (d, *J* = 8 Hz, 1H), 8.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 69.7, 123.6 (q, *J* = 278.4 Hz), 125.6 (q, *J* = 3.7 Hz), 129.7,130.5 (q, *J* = 3.5 Hz), 131.9, 132.0, 134.2, 201.3; ^{19}F NMR ($CDCl_3$ 470 MHz) δ -66.05 (s, 3F); HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_9O_2F_3$: 241.0452; found: 241.0476.



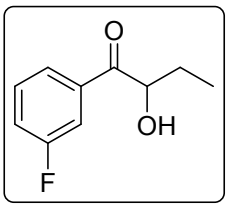
1-(4-Chlorophenyl)-2-hydroxypropan-1-one (2g): 105.23 mg, 57% yield; yellow liquid; R_f = 0.23 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 839, 972, 1132, 1489, 1591, 1685, 2981, 3458; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.8 Hz, 3H), 3.70 (s, 1H), 5.08–5.15 (m, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 69.4, 129.4, 130.2, 131.8, 140.7, 201.3; HRMS (m/z) $[M + H]^+$calcd for $C_9H_9O_2Cl$: 207.0189; found: 207.0205.



2-Hydroxy-1-(p-tolyl)propan-1-one (2h): 114.94 mg, 70%; yellow liquid; R_f = 0.16 (hexane/ethyl acetate = 19:1); FTIR (neat) ν (cm^{-1}): 971, 1131, 1456, 1609, 1680, 2854, 2926, 3480; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.8 Hz, 3H), 2.43 (s, 3H), 3.82 (d, *J* = 4.8 Hz, 1H), 5.08–5.18 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.6, 69.3, 128.9, 129.7, 130.9, 145.2, 202.1; HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_{12}O_2$: 187.0735; found: 187.0742.

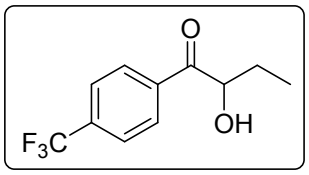


1-(4-Fluorophenyl)-2-hydroxybutan-1-one (2i): 138.45 mg, 76% yield; yellow liquid; R_f = 0.29 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 670, 967, 1239, 1507, 1602, 1683, 2973, 3473; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.54–1.65 (m, 1H), 1.88–1.99 (m, 1H), 3.66 (d, *J* = 6.8 Hz, 1H), 4.99–5.04 (m, 1H), 7.14–7.20 (m, 2H), 7.93–7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 29.0, 74.0, 116.3 (d, *J* = 21.8 Hz), 130.3 (d, *J* = 3.3 Hz), 131.3 (d, *J* = 9.4 Hz), 166.3(d, *J* = 254.8 Hz), 200.6;^{19}F NMR ($CDCl_3$ 470 MHz) δ -106.43 (s,1F); HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_{11}O_2F$: 205.0641; found: 205.0668

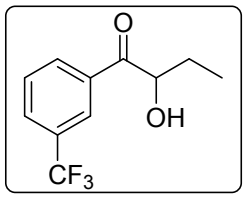


1-(3-Fluorophenyl)-2-hydroxybutan-1-one (2j): 107.45 mg, 59% yield; pale yellow liquid; R_f = 0.26 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}):1122, 1260, 1448, 1588, 1686, 2968, 3448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.55–1.62 (m,1H), 1.90–2.00 (m, 1H), 3.62 (d, *J* = 6.5 Hz, 1H), 5.01 (sex, *J* = 4.0 Hz, 1H), 7.32 (tdd, J_1 = 1.0 Hz, J_2 = 2.5 Hz, J_3 = 8.5 Hz, 1H), 7.49 (td, J_1 = 5.5 Hz, J_2 = 8.0 Hz, 1H), 7.61 (dt,J_1 = 2.5 Hz, J_2 = 9.0 Hz, 1H), 7.68(d, *J* = 8.0 Hz, 1H);^{13}C NMR (125 MHz, $CDCl_3$) δ 8.9,

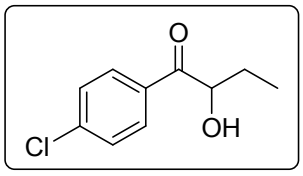
28.9, 74.3, 115.4 (d, J = 22.4 Hz), 121.2 (d, J = 21.3 Hz), 124.4 (d, J = 3.1 Hz), 130.7 (d, J = 7.8 Hz), 135.9 (d, J = 6.3 4Hz), 162.9 (d, J = 247.5 Hz), 201.2; ^{19}F NMR ($CDCl_3$ 470 MHz) δ -114.1 ; HRMS (m/z) $[M + Na]^+$calcd for $C_{10}H_{11}O_2FNa$: 205.0641; found: 205.0665



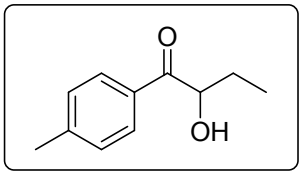
2-Hydroxy-1-(4-(trifluoromethyl)phenyl)butan-1-one (2k): 118.42 mg, 51% yield; pale yellow liquid; R_f = 0.24 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 1133, 1327, 1460, 1687, 2925, 3448; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 1.55–1.64 (m, 1H), 1.88–2.01 (m, 1H), 3.60 (d, J = 6.4 Hz, 1H), 5.07 (sex, J = 4.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 28.7, 74.5, 123.5 (q, J = 217.2 Hz), 126.1 (q, J = 3.6 Hz), 129.0, 135.5, 136.8, 201.5; ^{19}F NMR ($CDCl_3$ 470 MHz) δ -66.50 (s,3F); HRMS (m/z) $[M + H]^+$calcd for $C_{11}H_{12}O_2F_3$: 233.0789; found: 233.0772



2-Hydroxy-1-(3-(trifluoromethyl)phenyl)butan-1-one (2l): 130.03 mg, 56% yield; pale yellow liquid; R_f = 0.33 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 695, 982, 1074, 1131, 1333, 1458, 1613, 1689, 2974, 3470; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J = 7.5 Hz, 3H), 1.60–1.63 (m, 1H), 1.92–1.98 (m, 1H), 3.59 (d, J = 6.5 Hz, 1H), 5.05–5.09 (m, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8 Hz, 1H), 8.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.9, 28.8, 74.3, 123.6 (q, J = 271.13 Hz), 125.5 (q, J = 3.63 Hz), 129.7, 130.4 (q, J = 3.38 Hz), 131.7, 132.0 134.6, 201.1; ^{19}F NMR ($CDCl_3$ 470 MHz) δ -66.02 (s,3F); HRMS (m/z) $[M + H]^+$calcd for $C_{11}H_{11}O_2F_3$: 255.0609; found: 255.0612.

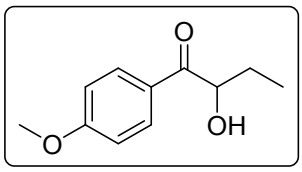


1-(4-Chlorophenyl)-2-hydroxybutan-1-one (2m): 145.01 mg, 73% yield; yellow liquid; R_f = 0.33 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 737, 977, 1133, 1247, 1460, 1592, 1683, 2970, 3477; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 3H), 1.55–1.63 (m, 1H), 1.89–1.98 (m, 1H), 3.64 (d, J = 6.5 Hz, 1H), 4.99–5.03 (m, 1H), 7.46–7.49 (m, 2H), 7.84–7.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.0, 28.9, 74.1, 29.4, 130.0, 132.2, 140.6, 201.1; HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_{11}O_2Cl$: 221.0345; found: 221.0318.

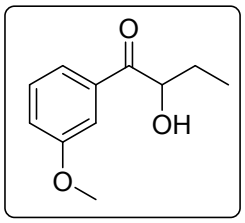


2-Hydroxy-1-(p-tolyl)butan-1-one (2n): 139.02 mg, 78% yield; pale yellow liquid; R_f = 0.35 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 964, 1133, 1460, 1606, 1677, 2968, 3474; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 3H), 1.56–1.65 (m, 1H), 1.90–1.98 (m, 1H), 2.42 (s, 3H), 3.74 (d, J = 6.5 Hz, 1H), 5.00–5.05 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz,

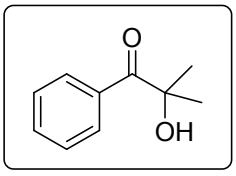
$CDCl_3$) δ 8.9, 21.9, 29.1, 73.9, 128.7, 129.7, 131.3, 145.1, 201.7; HRMS (m/z) $[M + H]^+$calcd for $C_{11}H_{14}O_2$: 201.0891; found: 201.0918.



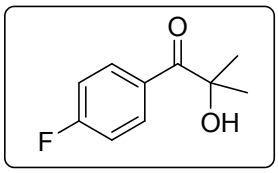
2-Hydroxy-1-(4-methoxyphenyl)butan-1-one (2o): 134.96 mg, 70% yield; pale yellow liquid; R_f = 0.27 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 974, 1176, 1260, 1510, 1601, 1671, 2967, 3465; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.55–1.63 (m, 1H), 1.89–1.99 (m, 1H), 3.76 (d, *J* = 6.8 Hz, 1H), 3.88 (s, 3H), 4.97–5.02 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.91 d,(*J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 29.2, 55.5, 73.5, 114.1, 126.5, 130.9, 164.2, 200.3; HRMS (m/z) $[M + H]^+$calcd for $C_{11}H_{14}O_3$: 217.0841; found: 217.0852.



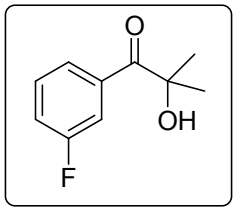
2-Hydroxy-1-(3-methoxyphenyl)butan-1-one (2p): 91.9 mg, 51% yield; pale yellow liquid; R_f = 0.34 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 1266, 1461, 1598, 1685, 2964, 3467; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.61–1.66 (m, 1H), 1.90–2.00 (m, 1H), 3.68 (s, 1H), 3.87 (s, 3H), 5.02–5.04 (m, 1H), 7.13–7.18 (m, 1H), 7.37–7.43 (m, 1H), 7.44–7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 29.1, 55.6, 74.2, 113.1, 120.3, 121.1, 130.0, 135.2, 160.1, 202.1; HRMS (m/z) $[M + Na]^+$calcd for $C_{11}H_{14}O_3Na$: 217.0841; found: 217.0840.



2-Hydroxy-2-methyl-1-phenylpropan-1-one (2q): 90.31 mg, 55% yield; pale yellow liquid; R_f = 0.39 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 716, 958, 1171, 1447, 1599, 1672, 2980, 3444; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 6H), 4.09 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.54–7.59 (m, 1H), 7.99–8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 76.4, 128.6, 129.8, 133.1, 134.0, 204.9;HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_{12}O_2Na$: 187.0735; found: 187.0763

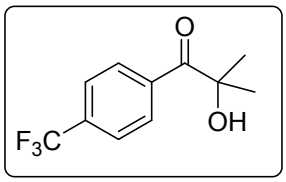


1-(4-Fluorophenyl)-2-hydroxy-2-methylpropan-1-one (2r): 111.14 mg, 61% yield; colourless liquid; R_f = 0.36 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 1155, 1506, 1598, 1674, 2984; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 6H), 3.97 (s, 1H), 7.12 (t, *J* = 8.4 Hz, 2H), 8.07–8.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 76.6, 115.7 (d, *J* = 21.6 Hz), 130.1 (d, *J* = 3.3 Hz), (d, *J* = 21.6 Hz), 132.8 (d, *J* = 9.2 Hz), 165.6 (d, *J* = 253.9 Hz), 202.9;^{19}F NMR ($CDCl_3$ 470 MHz) δ -107.98 (s, F)HRMS (m/z) $[M + H]^+$calcd for $C_{10}H_{11}O_2FNa$: 205.0641; found: 205.0661

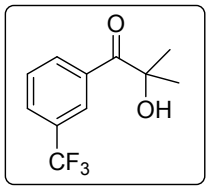


1-(3-Fluorophenyl)-2-hydroxy-2-methylpropan-1-one (2s): 129.36 mg, 71% yield; pale yellow liquid; R_f = 0.19 (hexane/ethyl acetate = 19:1); FTIR (neat) ν (cm^{-}

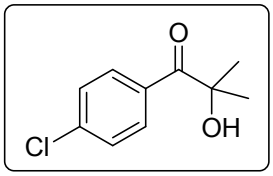
[1]): 1269, 1484, 1586, 1680, 2983, 3450; [1]H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 6H), 3.87 (s, 1H), 7.23–7.31 (m, 1H), 7.41–7.49 (m, 1H), 7.73 (d, *J* = 9.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H); [13]C NMR (100 MHz, $CDCl_3$) δ 28.4, 76.8, 116.8 (d, *J* = 22.8 Hz), 120.1 (d, *J* = 21.2 Hz), 125.5 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 7.6 Hz), 136.0 (d, *J* = 6.3 Hz),162.6 (d, *J* = 246.1 Hz), 203.6 ; [19]F NMR ($CDCl_3$ 470 MHz) δ -114.68 (s, F);HRMS (m/z) $[M + K]^+$calcd for $C_{10}H_{11}OFK$: 205.0431; found: 205.0404



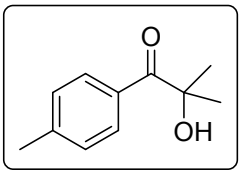
2-Hydroxy-2-methyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (2t): 153.30 mg, 66% yield; pale yellow liquid; R_f = 0.33 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 1328, 1466, 1685, 2985, 3449; [1]H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 6H), 3.57 (s, 1H), 7.72(d, *J* = 8.4 Hz, 2H), 8.09–8.15 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ28.3, 76.8, 123.7 (q, *J* = 271.1Hz), 125.5 (q, *J* = 3.6 Hz), 130.0, 134.2 (q, *J* = 33.0 Hz), 137.4, 204.2; [19]F NMR ($CDCl_3$ 470 MHz) δ -66.39 (s,3F); HRMS (m/z) $[M + H]^+$calcd for $C_{11}H_{12}O_2F_3$: 233.0789; found: 233.0798



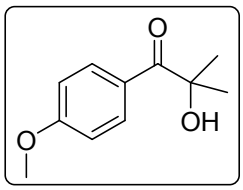
2-Hydroxy-2-methyl-1-(3-(trifluoromethyl)phenyl)propan-1-one (2u): 153.25 mg, 66% yield; colourless liquid; R_f = 0.30 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 1131, 1333, 1611, 1684, 2985, 3449; [1]H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 6H), 3.58 (s, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H) ; [13]C NMR (100 MHz, $CDCl_3$) δ 28.4, 76.8, 125.3 (q, *J* = 271.0 Hz), 126.8 (q, *J* = 3.7 Hz), 129.2, 129.4 (q, *J* = 3.5 Hz), 131.2 (q, *J* = 32.7 Hz), 133.0, 134.9, 203.5 ;[19]F NMR ($CDCl_3$ 470 MHz) δ -66.04 (s,3F)HRMS (m/z) $[M + Na]^+$calcd for $C_{11}H_{11}O_2F_3Na$: 255.0609; found: 255.0603



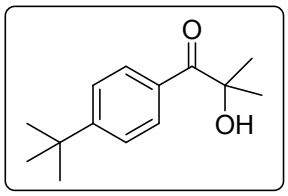
1-(4-Chlorophenyl)-2-hydroxy-2-methylpropan-1-one (2v): 131.10 mg, 66% yield; colourless liquid; R_f = 0.34 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 740, 1266, 1489, 1589, 1673, 3055, 3473; [1]H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 6H), 3.82 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 28.5, 76.7, 128.9, 131.4, 132.2, 139.6, 203.5; HRMS (m/z) $[M + Na]^+$calcd for $C_{10}H_{11}O_2NaCl$: 221.0345; found: 221.0356



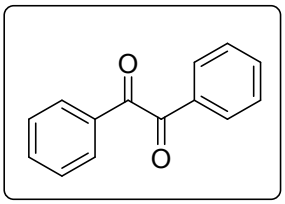
2-Hydroxy-2-methyl-1-(p-tolyl)propan-1-one (2w): 106.94 mg, 60% yield; pale yellow liquid; R_f = 0.39 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 959, 1170, 1460, 1608, 1672, 2980, 3445; [1]H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 6H), 2.41 (s, 3H), 4.21 (s, 1H), 7.26 (d, *J* = 8 Hz, 2H), 7.93 (d, *J* = 8 Hz, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 21.7, 28.7, 76.2, 129.3, 130.1, 131.0, 144.1, 204.2; HRMS (m/z) $[M + H]^+$calcd for $C_{11}H_{15}O_2$: 179.1072; found: 179.1065



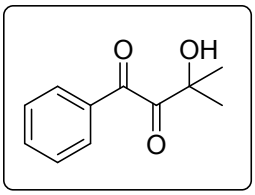
2-Hydroxy-1-(4-methoxyphenyl)-2-methylpropan-1-one (2x): 135.96 mg, 70% yield; colourless liquid; R_f = 0.21 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 959, 1164, 1258, 1507, 1603, 1666, 2977, 3444; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 6H), 3.88 (s, 3H), 4.27 (s, 1H), 6.94 (d, *J* = 7.2 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 55.6, 75.9, 113.8, 126.0, 132.5, 163.6, 202.7; HRMS (m/z) $[M + Na]^+$calcd for $C_{11}H_{14}O_3Na$: 217.0841; found: 217.0866



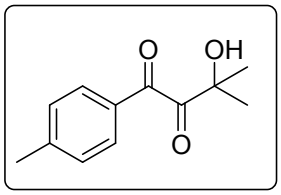
1-(4-(Tert-butyl)phenyl)-2-hydroxy-2-methylpropan-1-one (2y): 107.95 mg, 49% yield; colourless liquid; R_f = 0.19 (hexane/ethyl acetate = 19:1); FTIR (neat) ν (cm^{-1}): 1173, 1561, 1604, 1669, 2967, 3450; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 1.63 (s, 6H), 4.26 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.6, 31.1, 35.2, 76.2, 125.5, 129.9, 130.8, 156.9, 204.1; HRMS (m/z) $[M + Na]^+$calcd for $C_{14}H_{20}O_2Na$: 243.1361; found: 243.1332



Benzil (2z): 210.23 mg, 70% yield; yellow solid; R_f = 0.48 (hexane/ethyl acetate = 19:1);mp 92–94 °C [96–97, lit];[4] FTIR (neat) ν (cm^{-1}): 1212, 1449, 1596, 1671, 3063; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.52 (t, *J* = 8.0 Hz, 4H), 7.60–7.69 (m, 2H), 7.96–8.00 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.2, 130.0, 133.1, 135.0, 194.7;



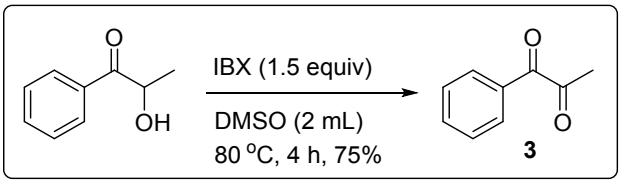
3-Hydroxy-3-methyl-1-phenylbutane-1,2-dione (2aa): 80.73 mg, 42% yield; yellow liquid; R_f = 0.20 (hexane/ethyl acetate = 19:1); FTIR (neat) ν (cm^{-1}): 1180, 1451, 1597, 1676, 1719, 2981, 3512; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (s, 6H), 3.01–3.15 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.66 (td, J_1 = 0.4 Hz, J_2 = 7.2 Hz,1H), 7.85–7.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 76.7, 129.1, 129.9, 132.6, 135.1, 195.1, 207.5; HRMS (m/z) $[M + Na]^+$calcd for $C_{11}H_{14}O_2Na$: 201.0891; found: 201.0882



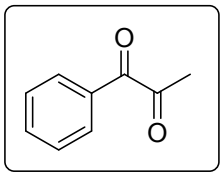
3-Hydroxy-3-methyl-1-(p-tolyl)butane-1,2-dione (2ab): 88.68 mg, 43% yield; brown liquid; R_f = 0.27 (hexane/ethyl acetate = 9:1); FTIR (neat) ν (cm^{-1}): 1180, 1542, 1605, 1672, 1718; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 6H), 2.44 (s, 3H),3.05–3.13 (m, 1H), 7.29–7.33 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 26.9, 76.7, 129.9, 130.0, 130.2, 146.5, 194.6, 207.6; HRMS (m/z) $[M + Na]^+$calcd for $C_{12}H_{14}O_3Na$: 229.0841; found: 229.0840

10. General procedure to synthesize 1-phenylpropane-1,2-dione (3) from *α*-hydroxyketone

To a round-bottom flask containing magnetic stir bar, *α*-hydroxyketone **2a** (1 mmol) and 3 mL of methanol was added. The IBX (1.5 equiv) was added and the reaction mixture was allowed to stir at 80 ^{o}C temperature for 4 h. After completion, the reaction mixture was diluted with 15 mL of ethyl acetate and washed with dilute $NaHCO_3$ solution (2 times) followed by saturated $Na_2S_2O_3$ one time. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate = 15:1) to give corresponding pure product (Scheme 4).



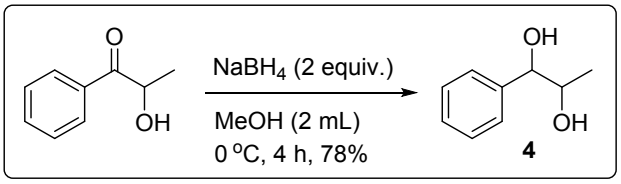
Scheme 4: Synthesis of 1-phenylpropane-1,2-dione



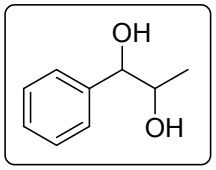
1-Phenylpropane-1,2-dione (3): 111.12 mg, 75% yield; Yellow liquid ; R_f = 0.46 (hexane/ethyl acetate = 19:1); FT IR (neat) ν (cm^{-1}): 1165, 1450, 1673, 1714, 2930; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 129.0, 130.5, 131.9, 134.7, 191.5, 200.7 ; HRMS (m/z) $[M + H]^+$ calcd for $C_9H_9O_2$: 149.0603; found: 149.0609

11. General procedure to synthesize1-phenylpropane-1,2-diol (4) from *α*-hydroxyketone[5]

To a round bottom flask containing magnetic stir bar, *α*-hydroxyketone **2a** (1 mmol) and 3 mL of methanol was added. The $NaBH_4$ (2 equiv) was added in portion wise and the reaction mixture was allowed to stir at room temperature for 4 h. After completion, the reaction mixture was washed with NH_4Cl solution and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was contains the 79 : 21 mixture of *syn* and *anti* alcohols (Scheme 5).



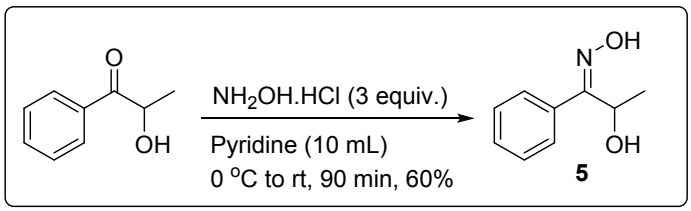
Scheme 5: Synthesis of 1-phenylpropane



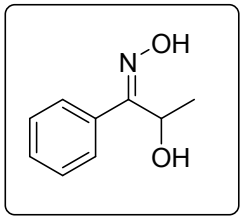
1-Phenylpropane-1,2-diol (4)[4]: 78.72 : 21.28 (*syn:anti*); 118. 71 mg, 78% yield; white semi-liquid; R_f = 0.23 (hexane/ethyl acetate = 7:3); FTIR (neat) ν (cm^{-1}):1130, 1201, 1453, 1494, 1640, 2980, 3386, 3397; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 1.07 (d, *J* = 6.4 Hz, 3H), 3.95–4.03 (m, 1H), 2.19 (s, 1H), 2.73 (s, 1H), 4.66 (d, *J* = 4.4 Hz, 1H), 7.32–7.37 (m, 5H); (minor) δ 1.04 (d, *J* = 6.4 Hz, 0.81H), 3.80–3.88 (m, 0.24H), 1.85 (s, 0.37H), 2.98 (s, 0.21H), 4.34 (d, *J* = 7.2 Hz, 0.23H), 7.27–7.32 (m, 1.44); ^{13}C NMR (100 MHz, $CDCl_3$) (major)δ 17.3, 71.4, 77.6, 126.8, 127.9, 128.5, 140.5; (minor) δ 18.9, 72.3, 79.6, 126.9, 128.2, 128.6, 14.2; HRMS (m/z) $[M + H]^+$ calcd for $C_9H_{12}O_2Na$: 175.0735 ; found: 175.0741

12. General procedure to synthesize *α*-hydroxy imine (5) from *α*-hydroxyketone[6]

To a solution of *α*-hydroxyketone in 5 mL of pyridine, a solution of hydroxylamine hydrochloride was added under cooling in an ice bath. The reaction mixture was stirred for 90 minutes at room temperature and the reaction mixture was concentrated in vacuo. The residue was extracted with ethylacetate and the extract was washed with 10% citric acid and water. The organic layer was dried over Na_2SO_4 and was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate = 5:1) to give corresponding pure product (Scheme 6).



Scheme 6: Synthesis of α-hydroxy imine

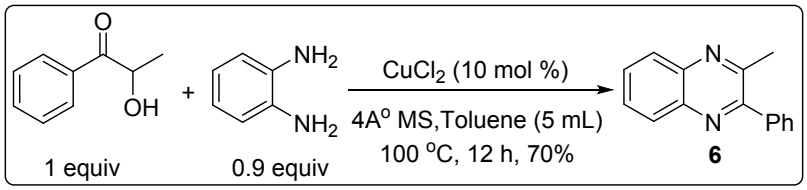


(Z)-2-Hydroxy-1-phenylpropan-1-one oxime (5)[5]: 99.11 mg, 60% yield; Yellow liquid; R_f = 0.22 (hexane/ethyl acetate = 4:1); FT IR (neat) ν (cm^{-1}): 1076, 1300, 1447, 2363, 3212; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (d, *J* = 6.8 Hz, 3H), 5.16 (d, *J* = 4.4 Hz, 1H), 5.29–5.37 (m, 1H), 7.31–7.36 (m, 3H), 7.63–7.68 (m, 2H),

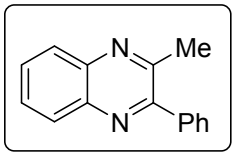
11.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 61.2, 127.7, 127.9, 128.1, 134.6, 161.1; HRMS (m/z) $[M + H]^+$ calcd for $C_9H_{12}NO_2$: 166.0868; found: 166.0853

13. General procedure to synthesize 2-methyl-3-phenylquinoxaline (6) from *α*-hydroxyketone[7]

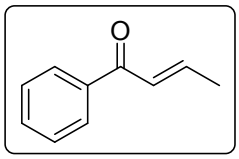
To a round-bottom flask containing magnetic stir bar *o*-phenylenediamine (0.5 mmol), 2-hydroxyacetophenone (0.55 mmol), $CuCl_2$ (0.05 mmol), MS 4Å (0.3 g) and dry toluene (5 mL) were added. The whole system was flushed with O_2 from a balloon. The reaction mixture was stirred at 100 °C for 10 h. After the completion, the reaction mixture was filtered through a filter paper and then washed with ethyl acetate and dried under vacuo. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate = 5:1) to give corresponding pure product (Scheme 7).



Scheme 7: Synthesis of 2-methyl-3-phenylquinoxaline



2-Methyl-3-phenylquinoxaline (6): 154.19 mg, 70% yield; light yellow solid; mp 55-57 °C [54-56 °C, lit.];[8] R_f = 0.23 (hexane/ethyl acetate = 19:1); FT IR (neat) ν (cm^{-1}): 1343, 1558, 1652, 2925; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 7.47–7.56 (m, 3H), 7.63–7.68 (m, 2H), 7.69–7.77 (m, 2H), 8.04–8.08 (m, 1H), 8.10–8.14 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 128.4, 128.7, 129.0, 129.1, 129.4, 129.9, 139.2, 141.1, 141.3, 152.7, 155.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{15}H_{13}N_2$: 221.1079 ; found: 221.1050



(E)-1-phenylbut-2-en-1-one (7): 80.4045 mg, 55% yield; pale Yellow liquid; R_f = 0.38 (hexane/ethyl acetate = 49:1); FTIR (neat) ν (cm^{-1}): 1219, 1297, 1449, 1578, 1625, 1672, 2925; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 3H), 6.88–6.94 (m, 1H), 7.02–7.13 (m, 1H), 7.43–7.49 (m, 2H), 7.52–7.58 (m, 1H), 7.90–7.95 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 127.6, 128.6, 132.7, 138.0, 145.2, 190.9; HRMS (m/z) $[M + Na]^+$ calcd for $C_{10}H_{10}ONa$: 169.0629 ; found: 169.0627

References

[1]. a) K. Harada, S. Shiono, *Bull. Chem. Soc. Jpn.,* 1984, **57**, 1040; b) C. S. Cho, W. X. Ren, *J. Organomet. Chem*., 2009, **694**, 3215.

[2]. a) H. Zong, H. Huang, J. Liu, G. Bian, L. Song, *J. Org. Chem.,* 2012, **77**, 4645; b) H. G. Richey Jr., *Grignard Reagents: New Developments*, John Wiley & Sons Inc., New York, 2000.

[3]. a) R. S. Mulliken, *J. Am. Chem. Soc*., 1950, **72**, 600; b) N. M. Ghobrial, *Asian. J. Chem.,* 1992, **4**, 597; c) P. Klaeboe, *Acta Chem. Scand.,* **1964,** *18*, 27; d) Z. Kebede, S. –E. Lindquist, *Sol. Energy Mater. Sol. Cells,* 1999, **57**, 259; e) W. F. Forbes, M. B. Sheratte, *Can. J. Chem.* 1955, **33**, 1829.

[4]. R. K. Sodhi, S. Paul, *Catal. Lett*. 2011, **141**, 608.

[5]. M. Takeshita, T. Sato, *Chem. Pharm. Bull*. 1989, **37**, 1085.

[6]. K. Harada, S. Shiono, *Bull. Chem. Soc. Jpn*. 1984, **57**, 1040.

[7]. C. K. Cho, W. X. Ren, *J. Organomet. Chem*. 2009, **694**, 3215.

[8]. H. R. Darabi, S. Mohandessi, K. Aghapoor, F. Mohsenzadeh, *Catal. Commun.* 2007, 8, 389.

14. Copies of ^{1}H and ^{13}C-NMR spectra of all compounds and mass spectra of reaction mixture:

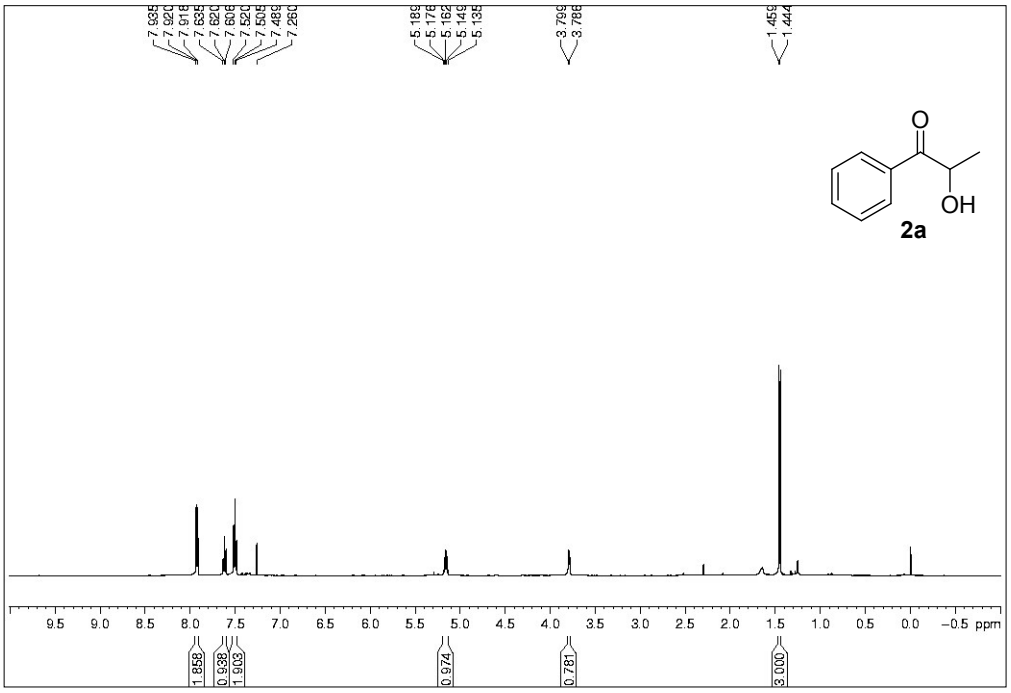


Figure 5: ^{1}H NMR spectrum of **2a** (500 MHz, $CDCl_3$)

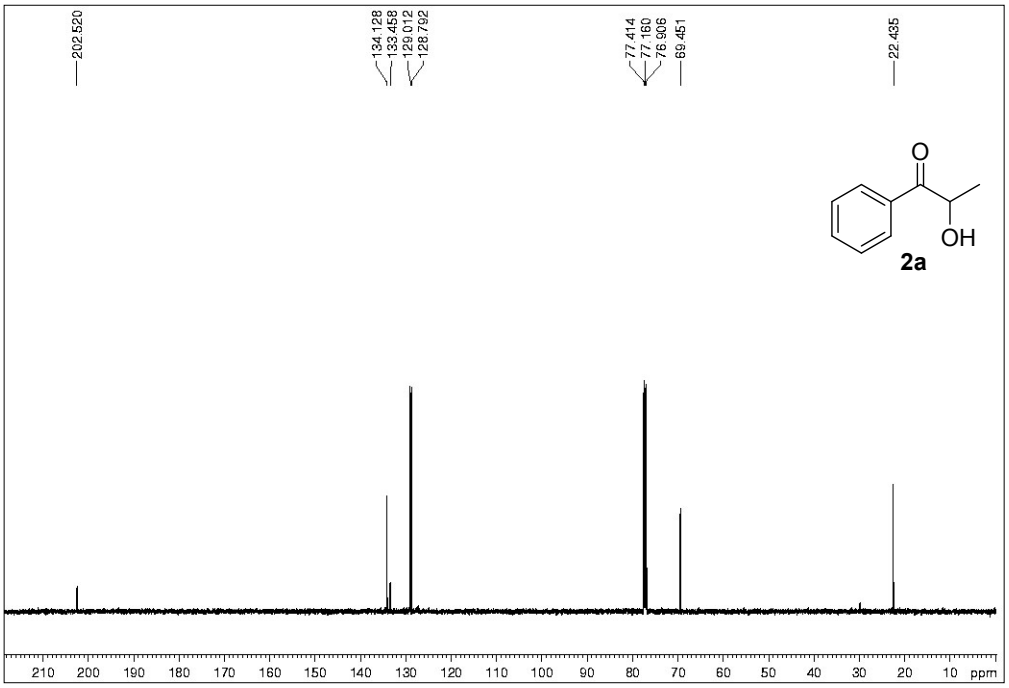


Figure 6: ^{13}C NMR spectrum of **2a** (125 MHz, $CDCl_3$)

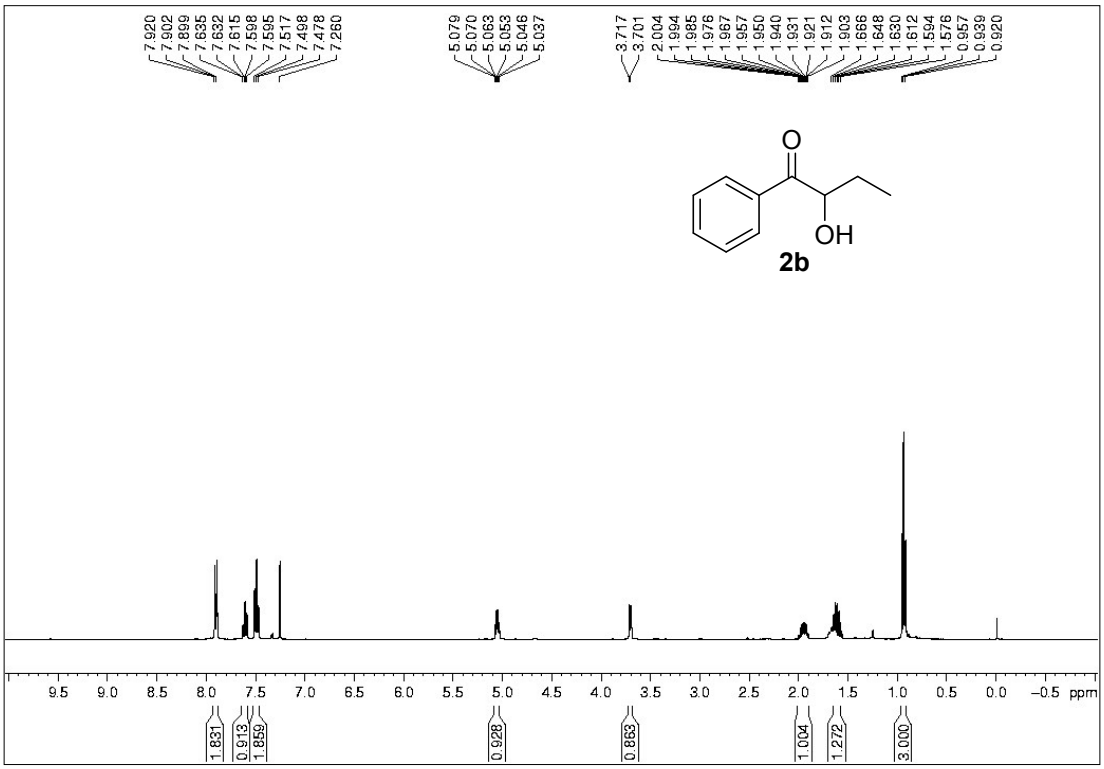


Figure 7: ^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)

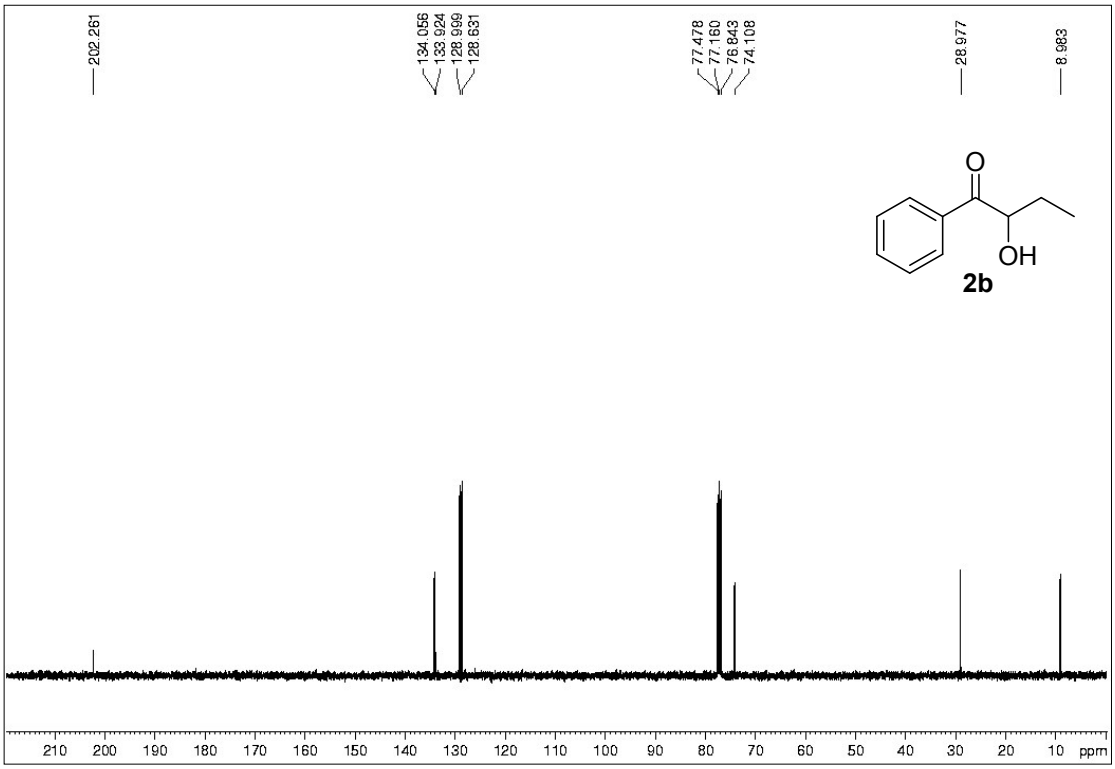


Figure 8: ^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$)

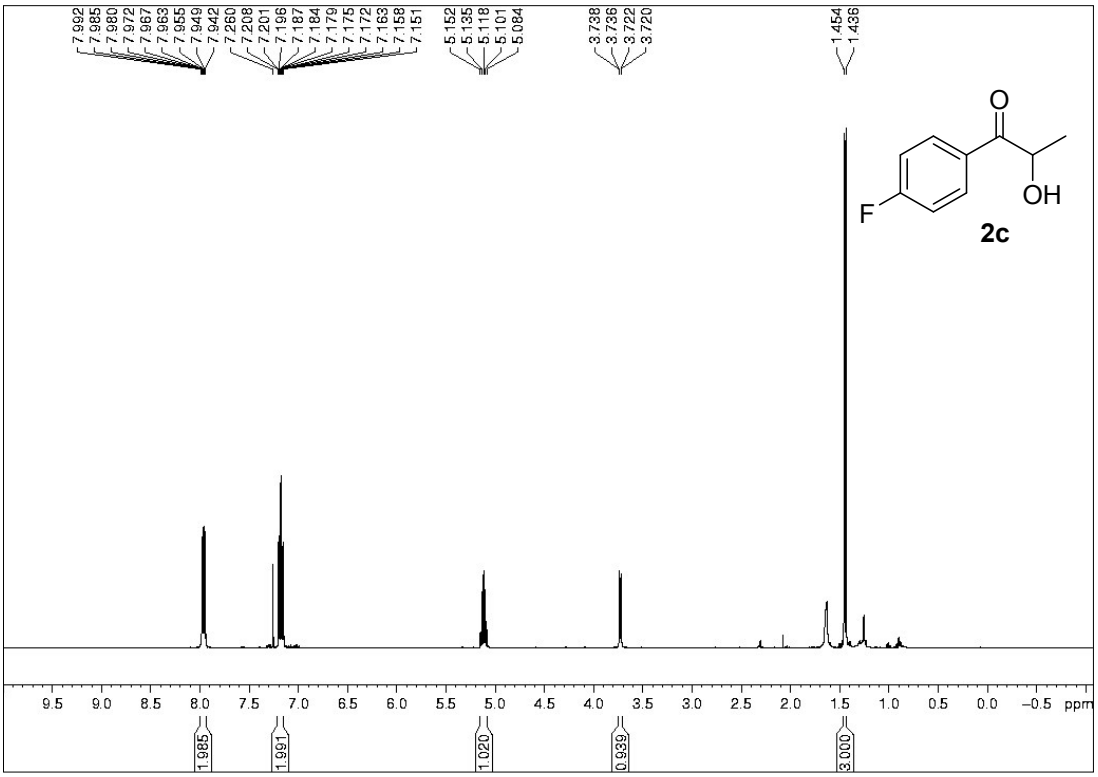


Figure 9: ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$)

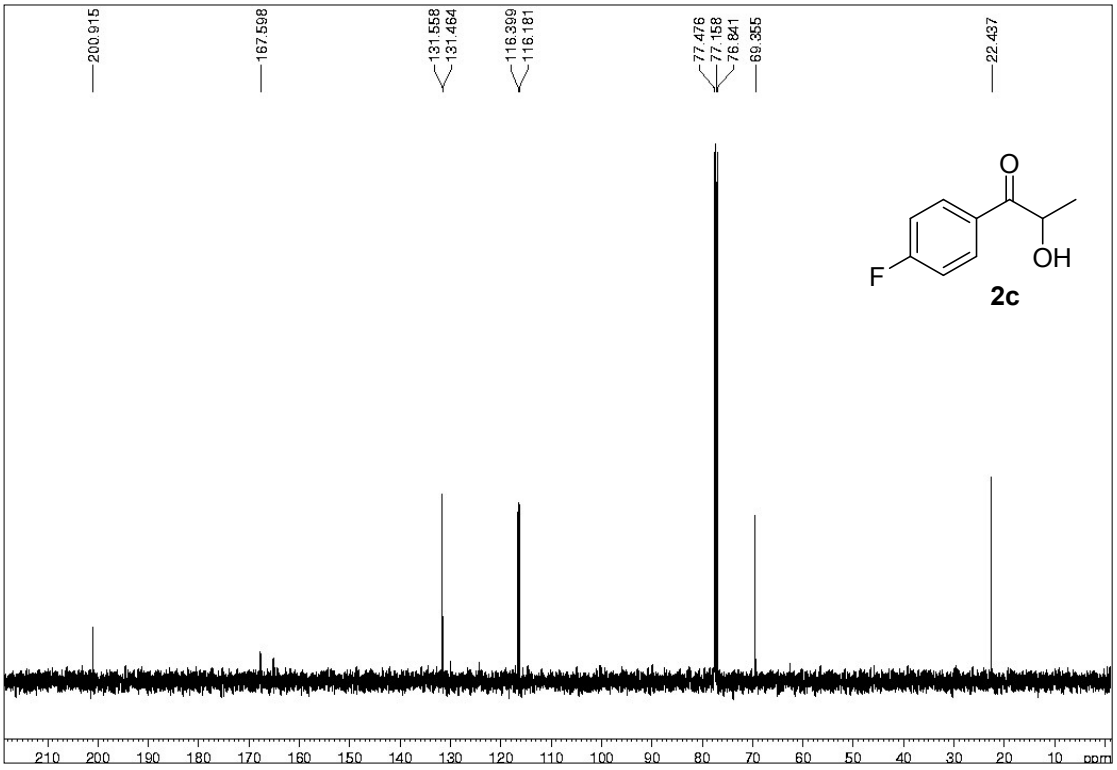


Figure 10: ^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)

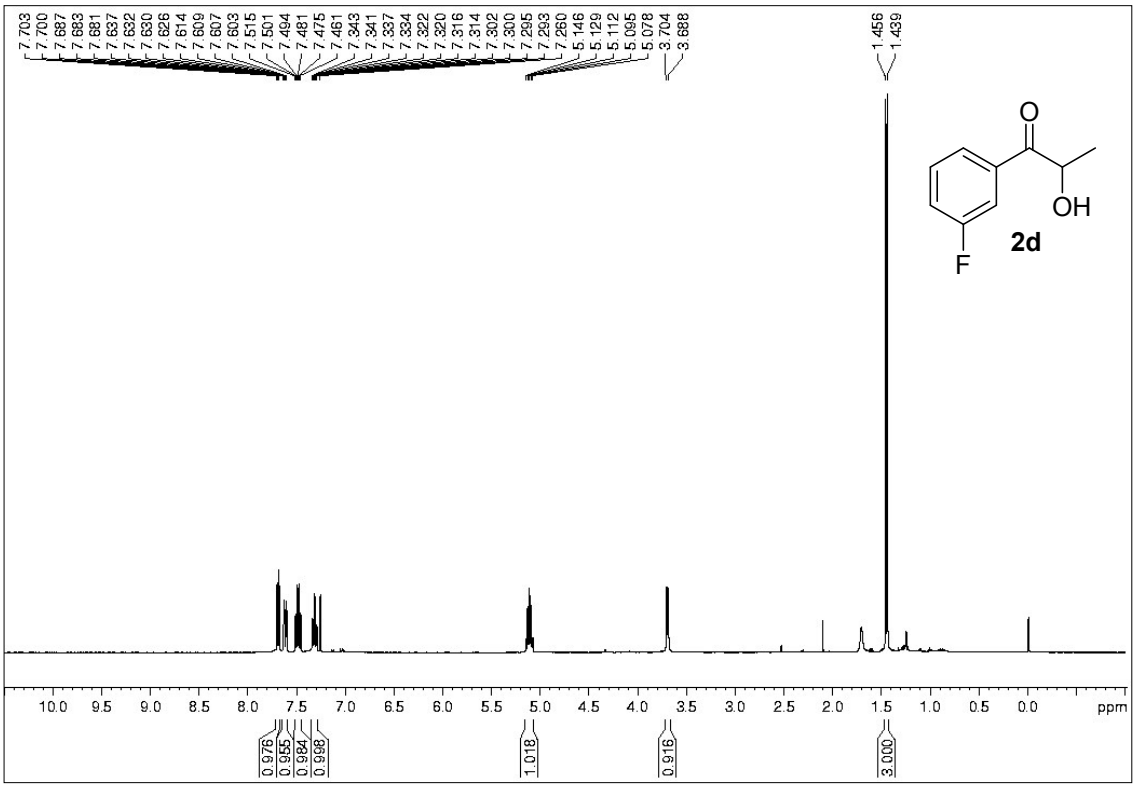


Figure 11: ^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$)

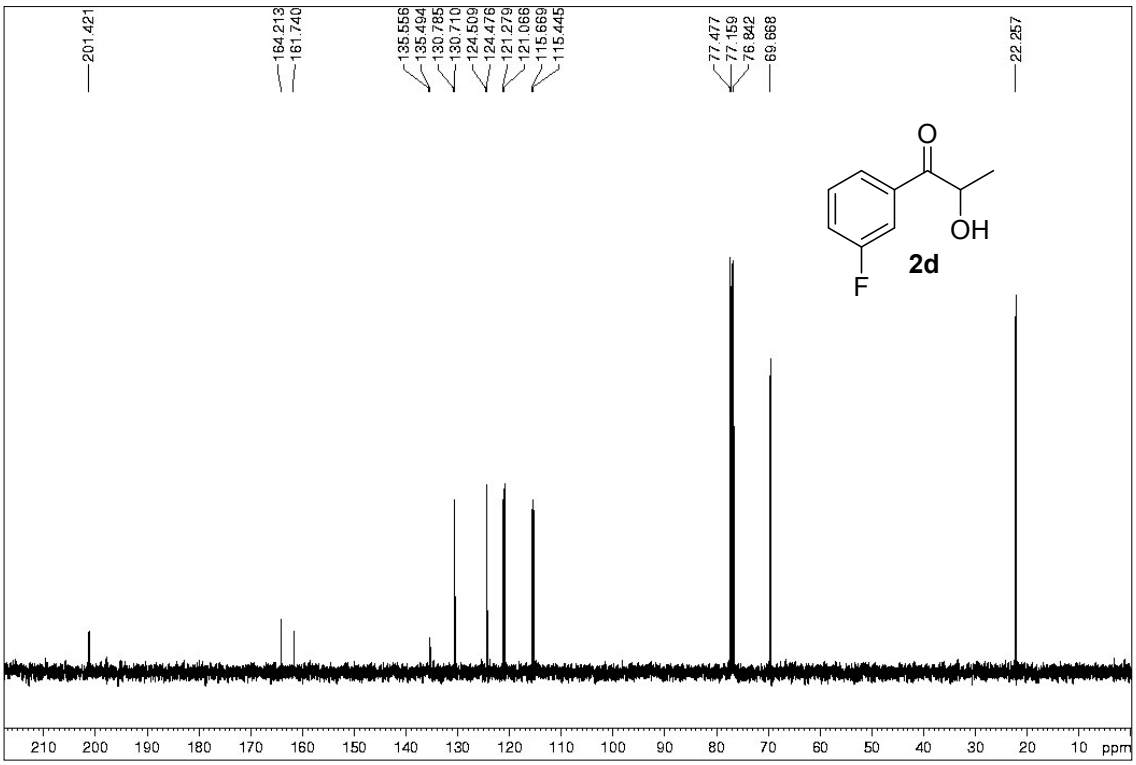


Figure 12: ^{13}C NMR spectrum of **2d** (100 MHz, $CDCl_3$)

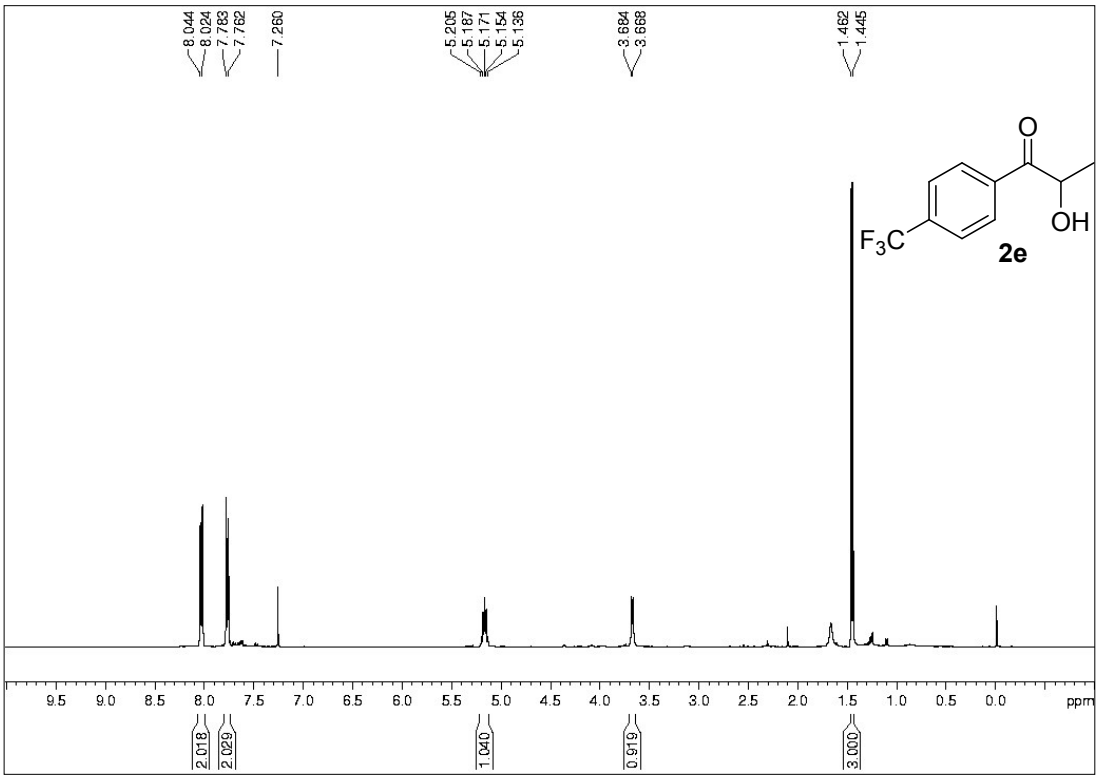


Figure 13: ^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$)

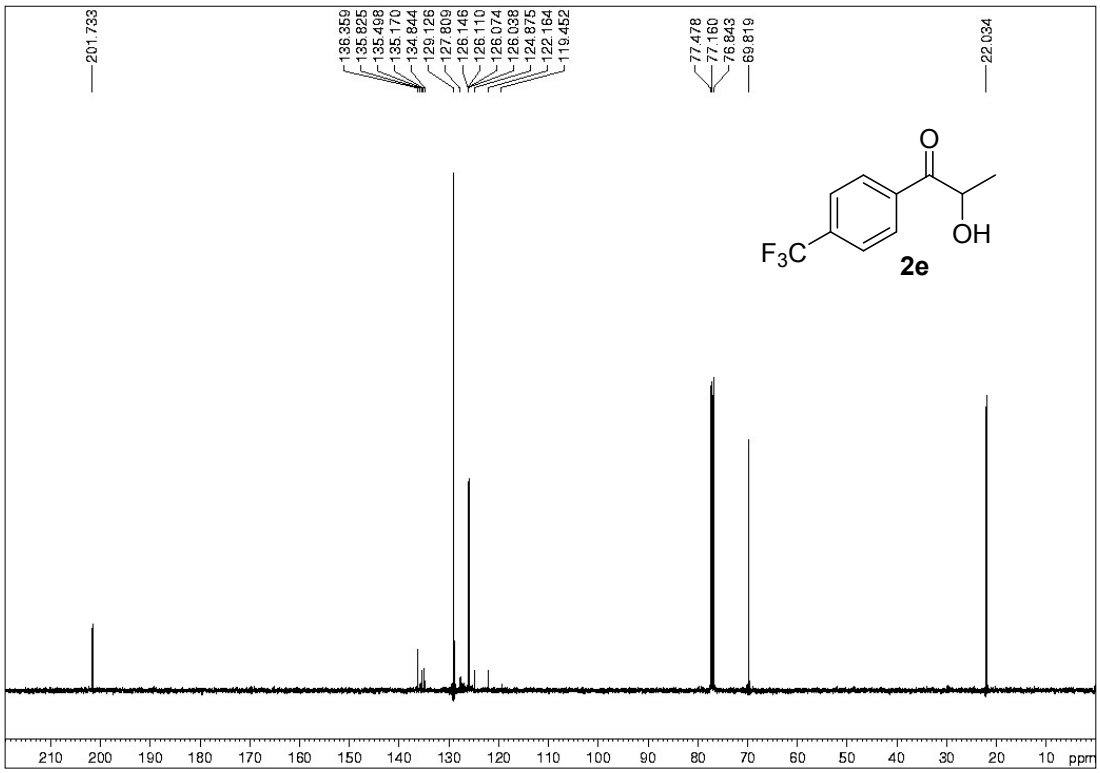


Figure 14: ^{13}C NMR spectrum of **2e** (100 MHz, $CDCl_3$)

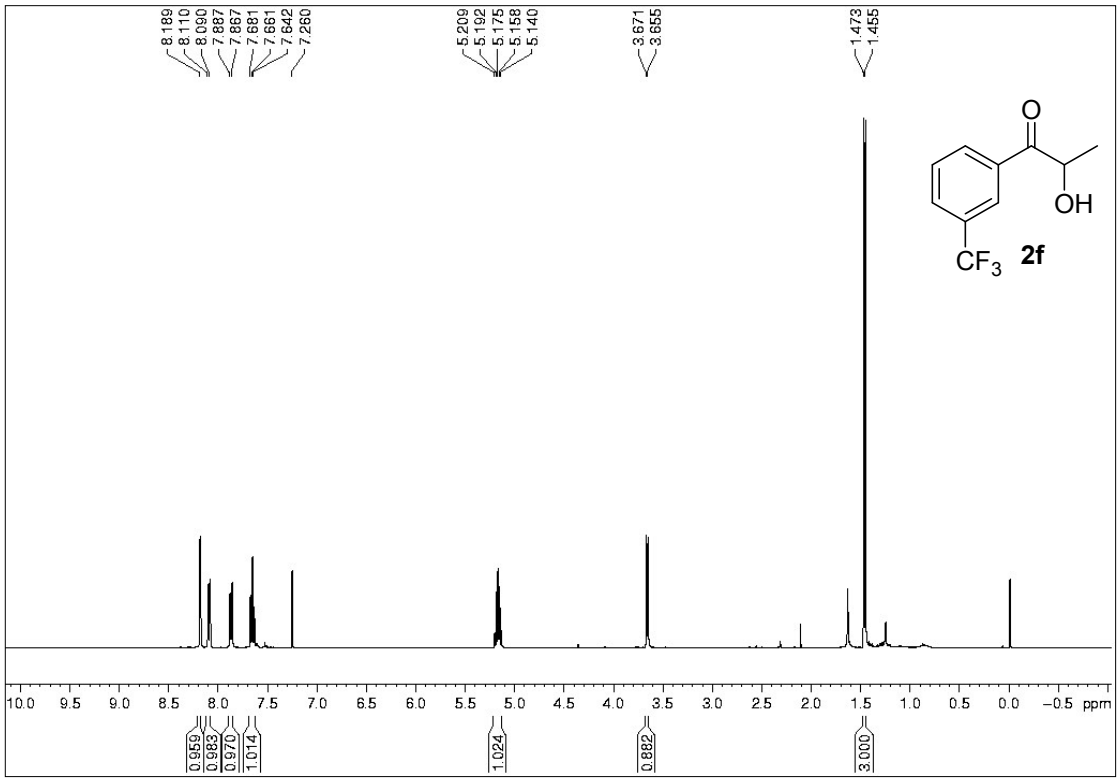


Figure 15: ^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$)

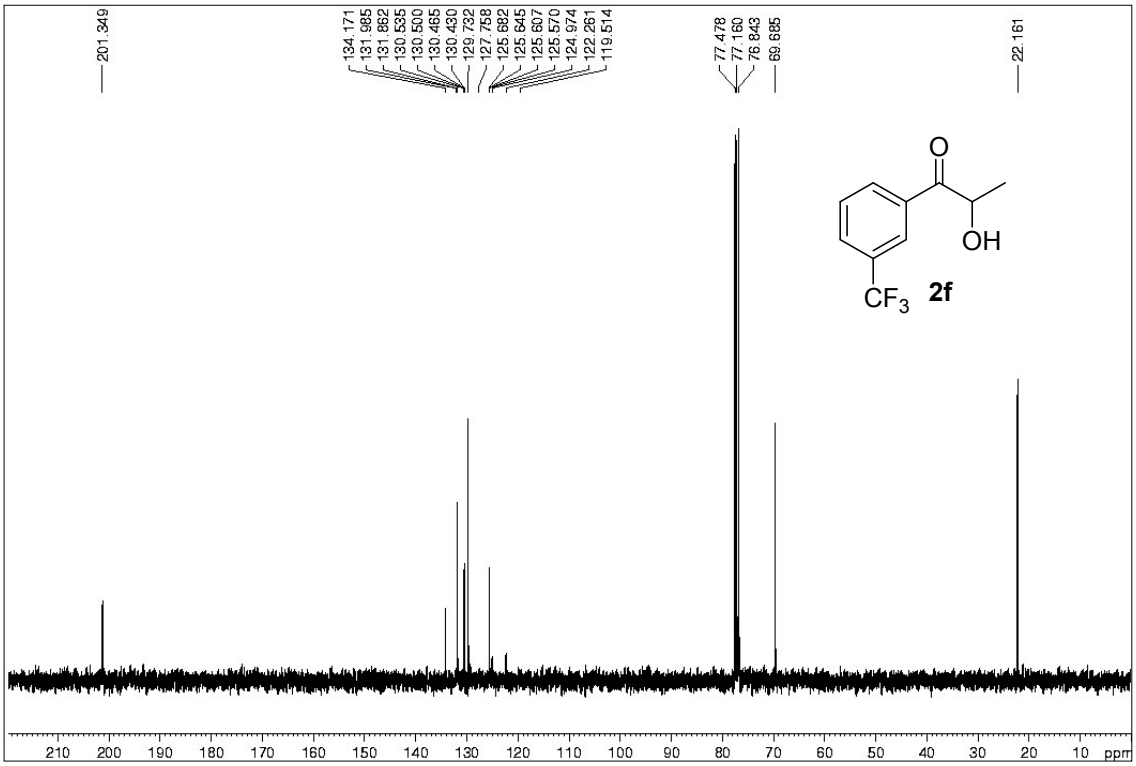


Figure 16: ^{13}C NMR spectrum of **2f** (100 MHz, $CDCl_3$)

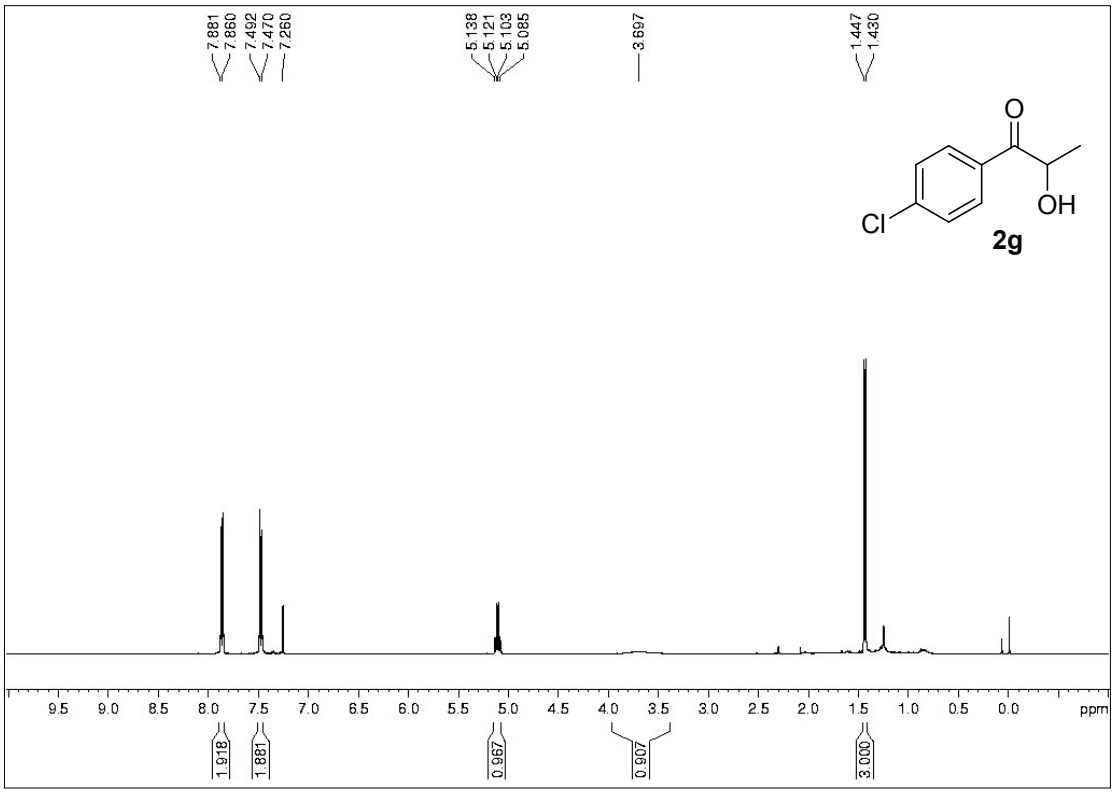


Figure 17: ^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)

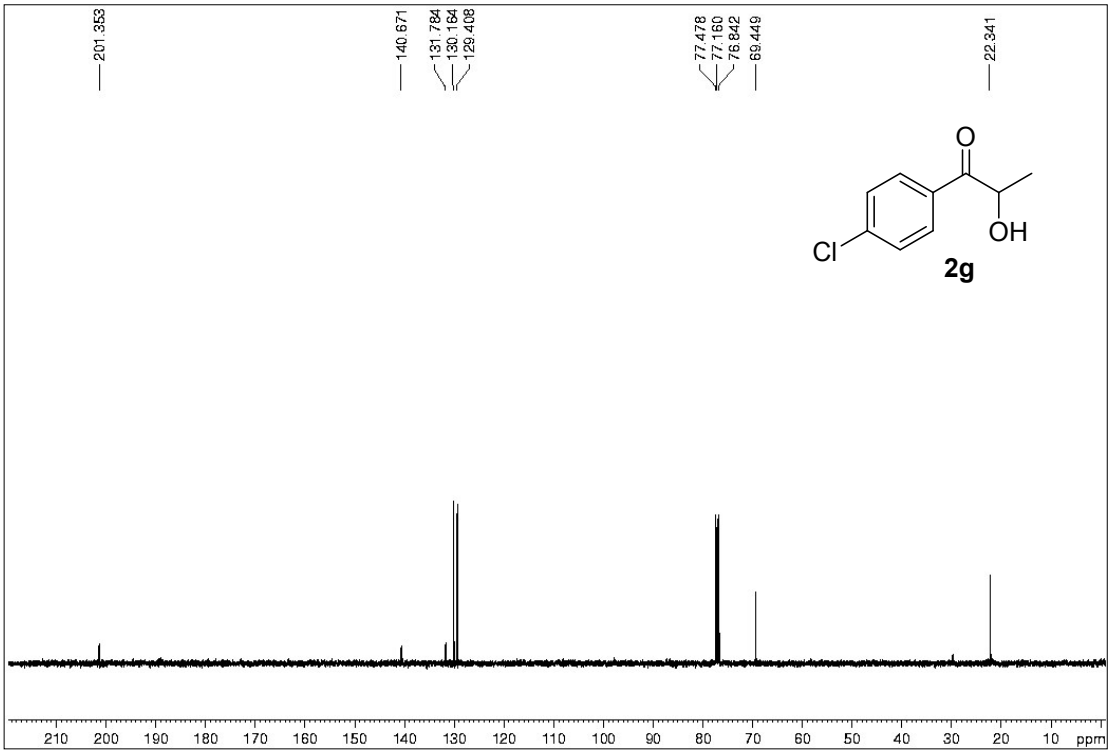


Figure 18: ^{13}C NMR spectrum of **2g** (100 MHz, $CDCl_3$)

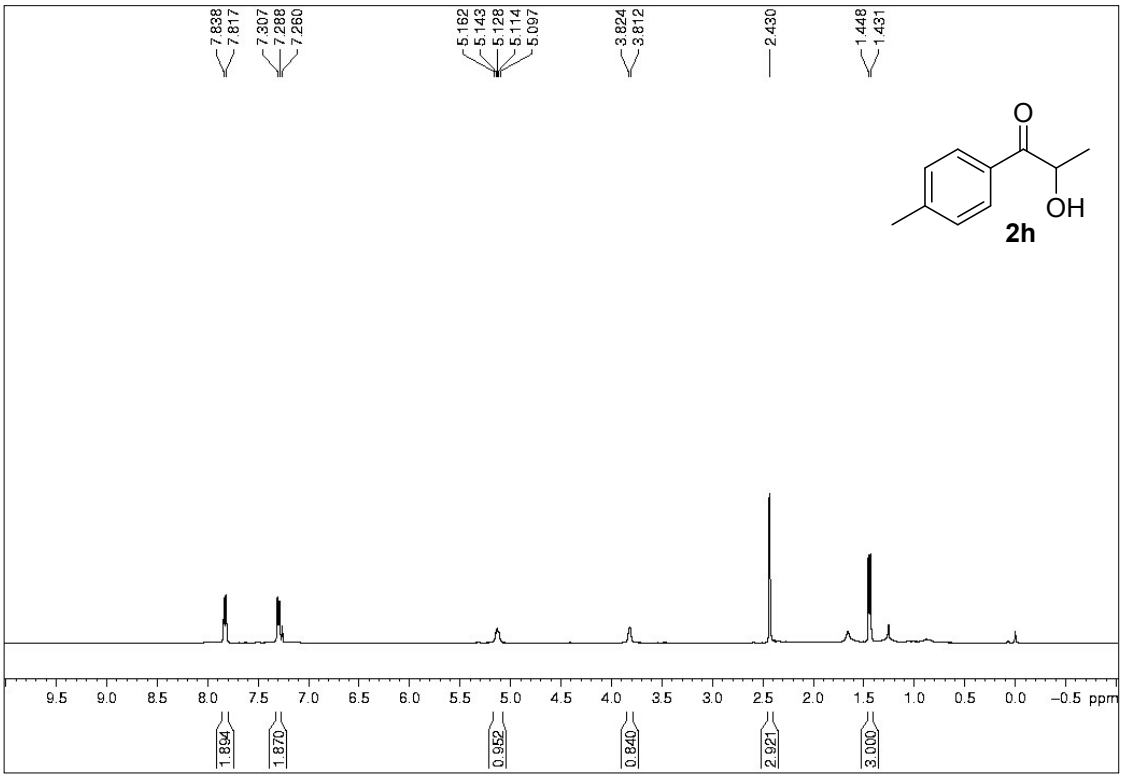


Figure 19: ^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$)

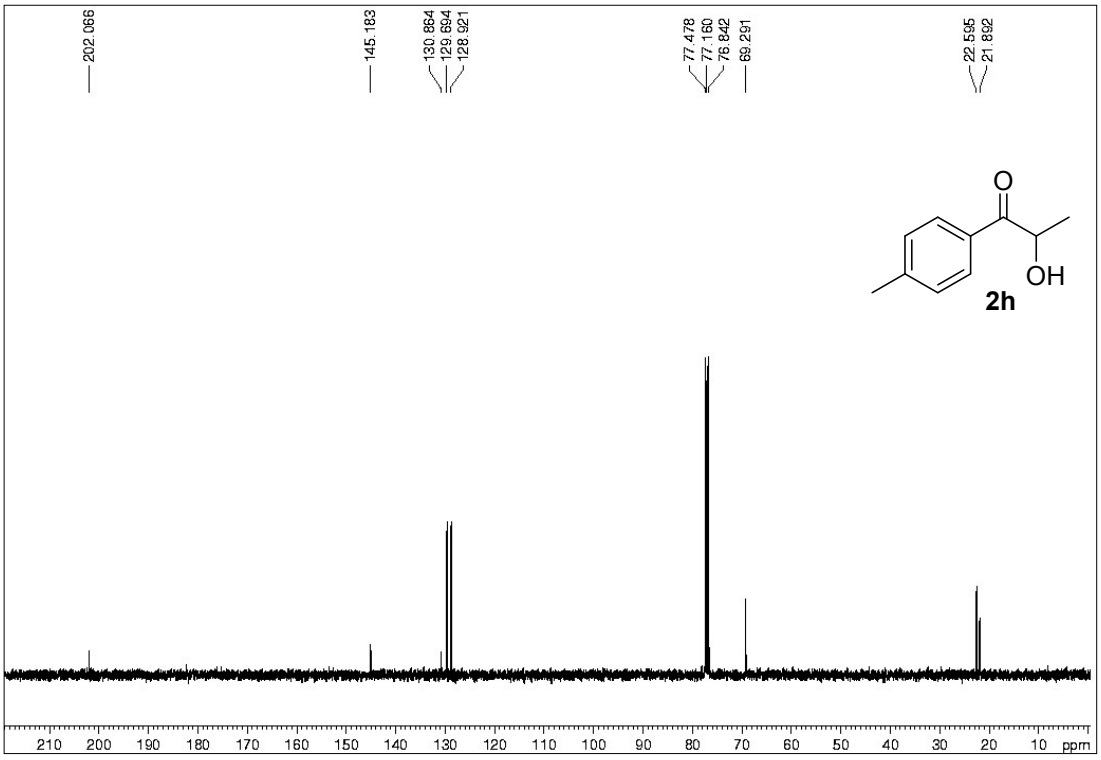


Figure 20: ^{13}C NMR spectrum of **2h** (100 MHz, $CDCl_3$)

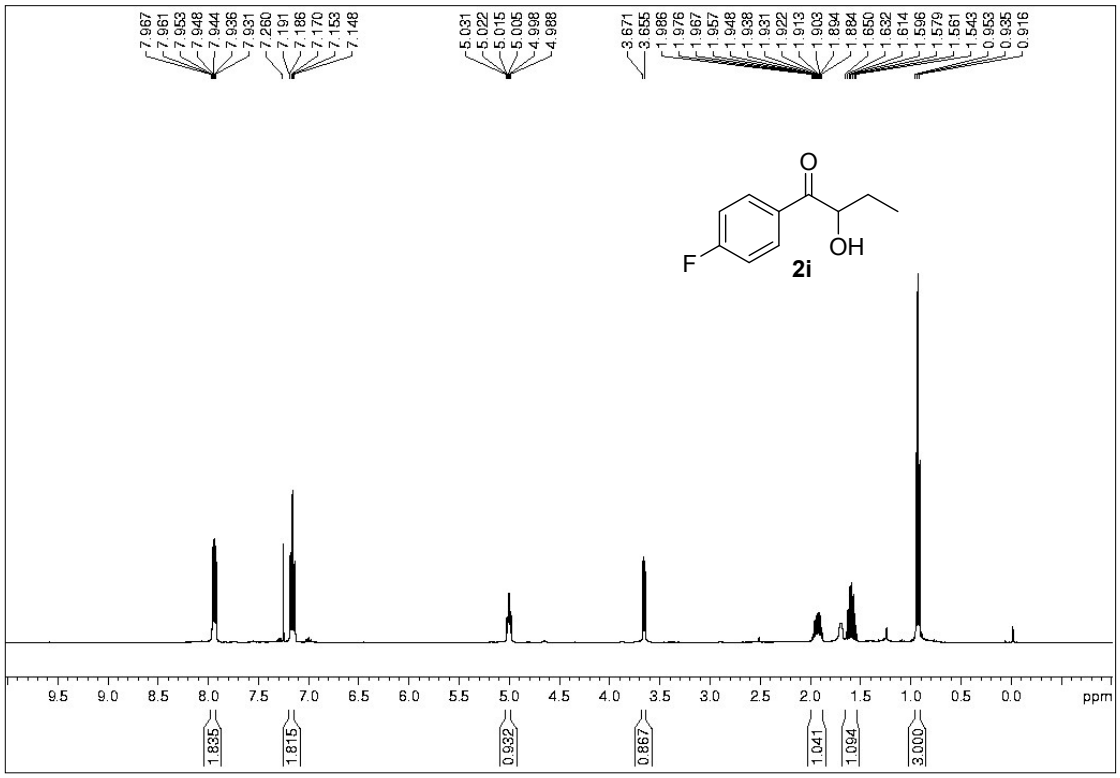


Figure 21: ^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$)

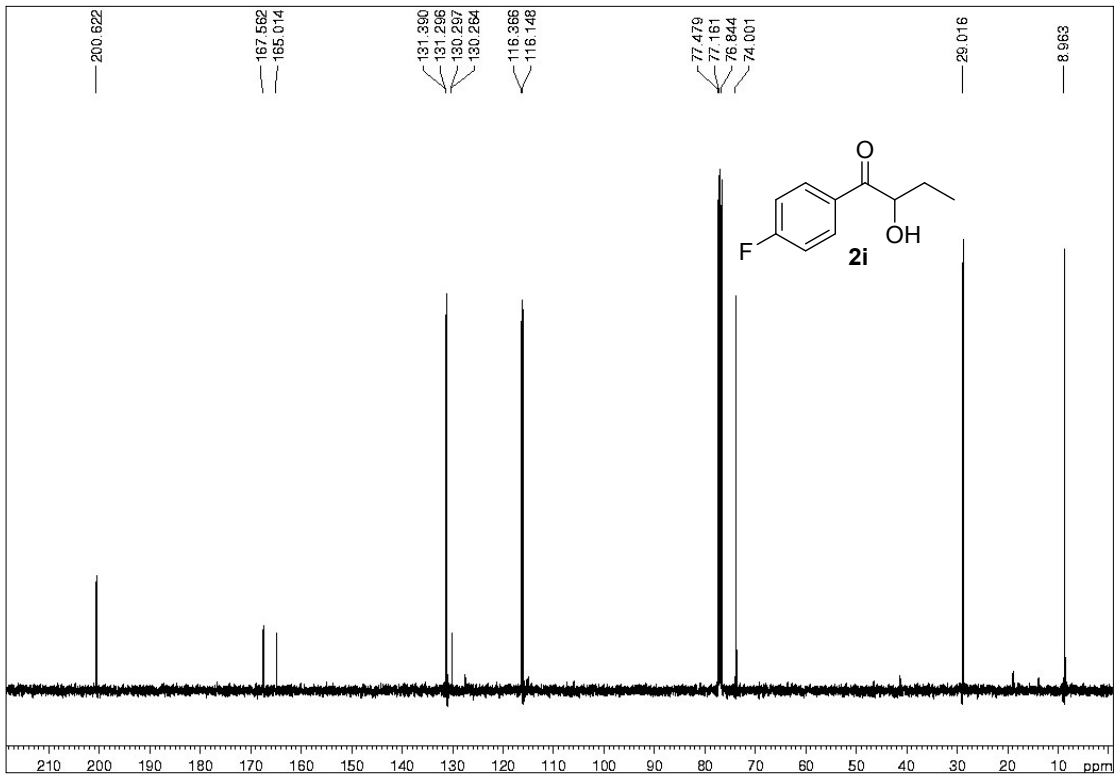


Figure 22: ^{13}C NMR spectrum of **2i** (100 MHz, $CDCl_3$)

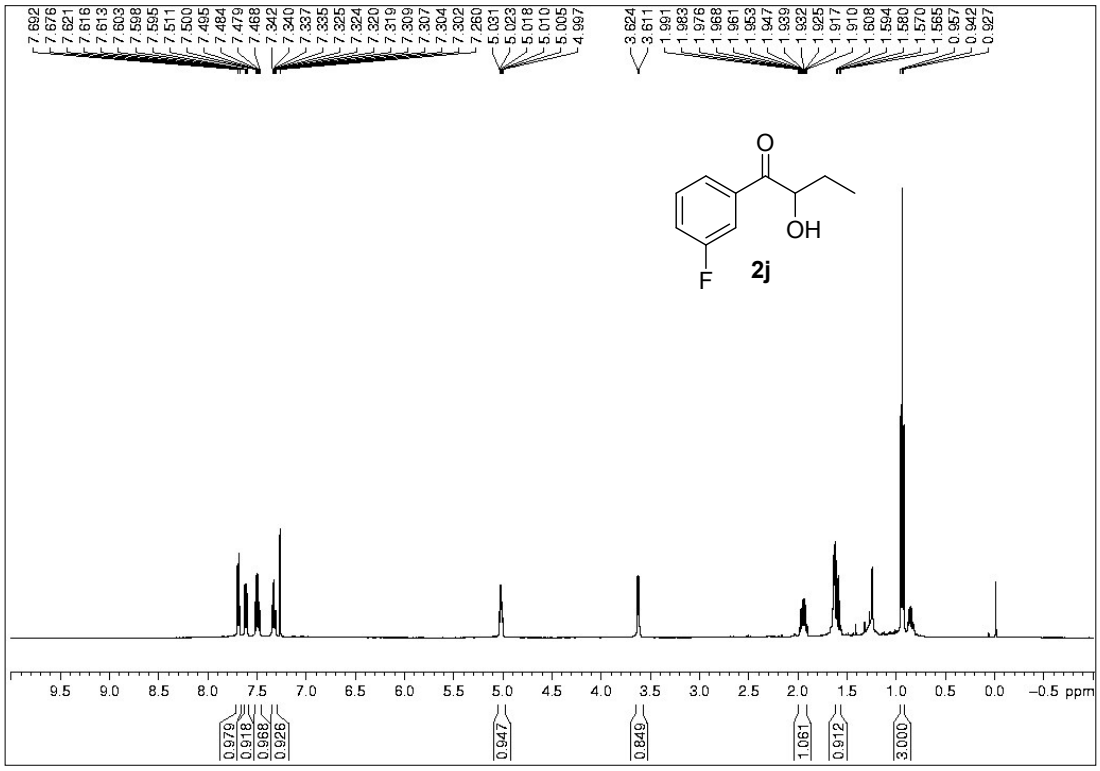


Figure 23: ^{1}H NMR spectrum of **2j** (500 MHz, $CDCl_3$)

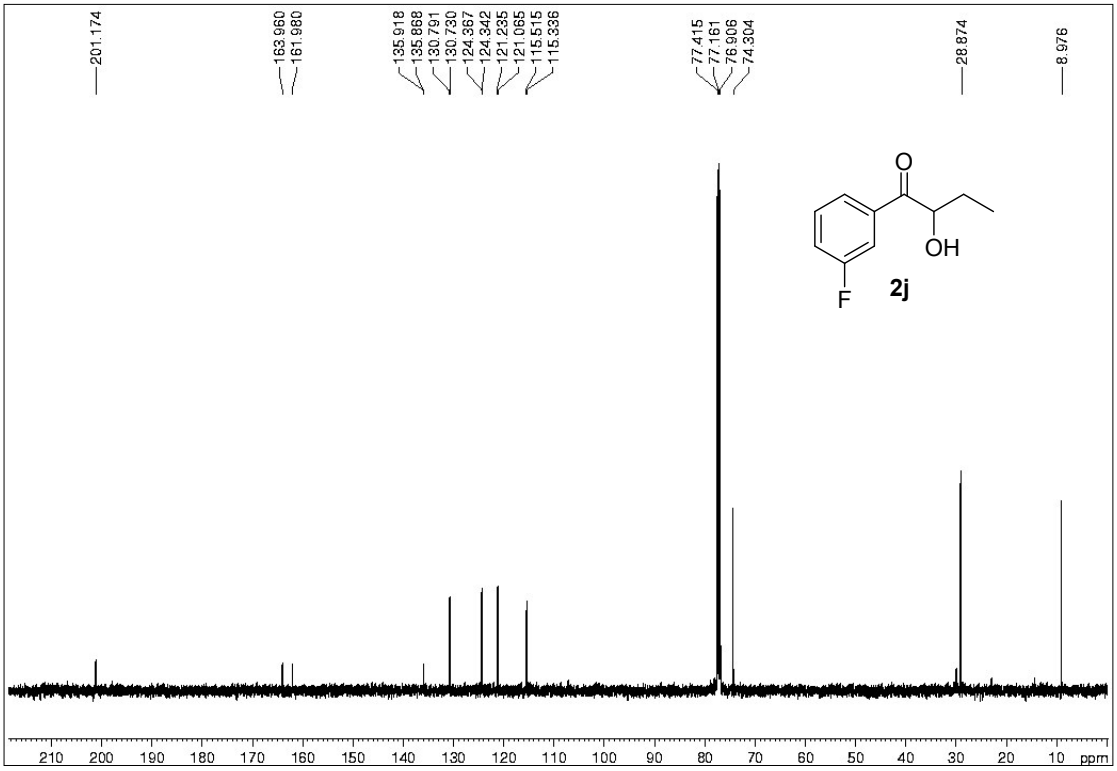


Figure 24: ^{13}C NMR spectrum of **2j** (125 MHz, $CDCl_3$)

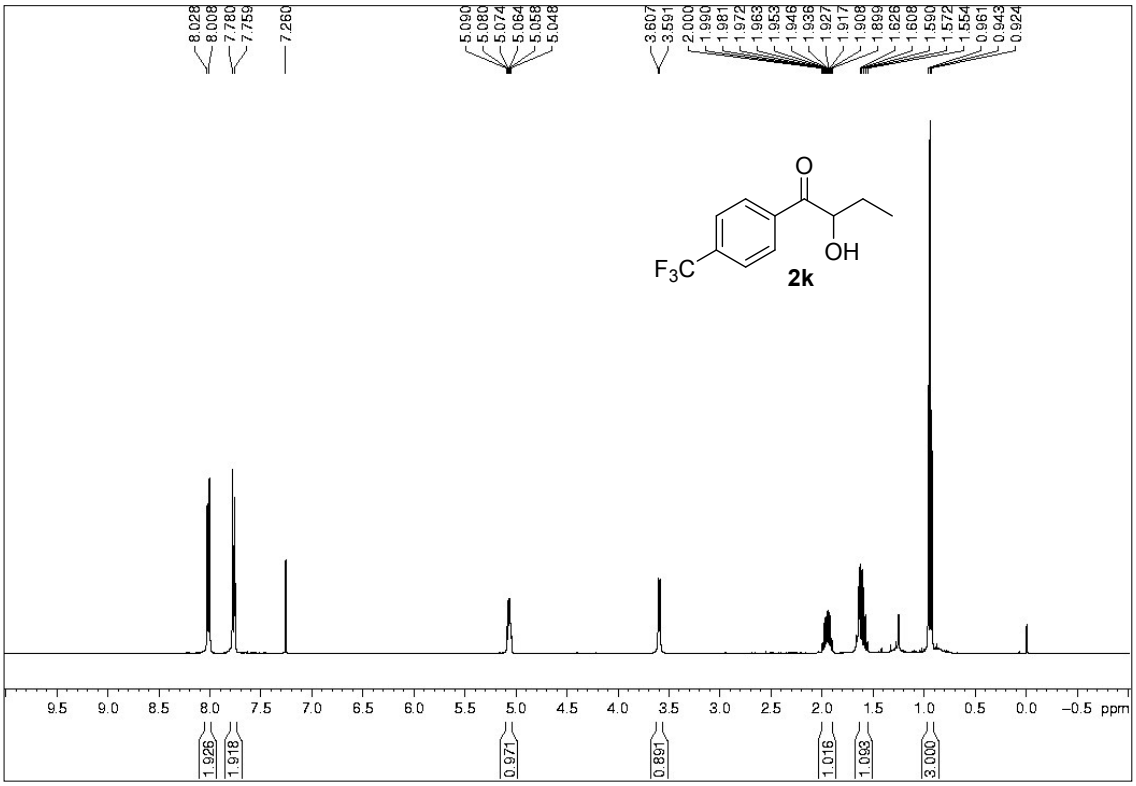


Figure 25: ^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$)

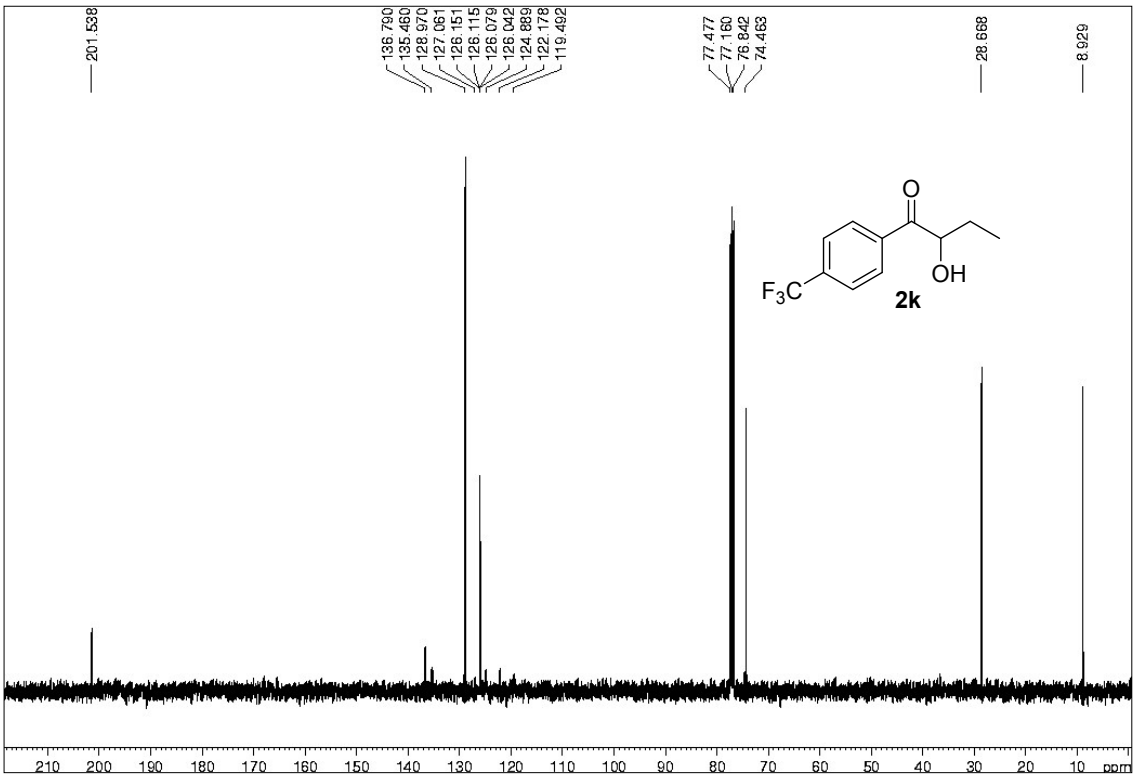


Figure 26: ^{13}C NMR spectrum of **2k** (100 MHz, $CDCl_3$)

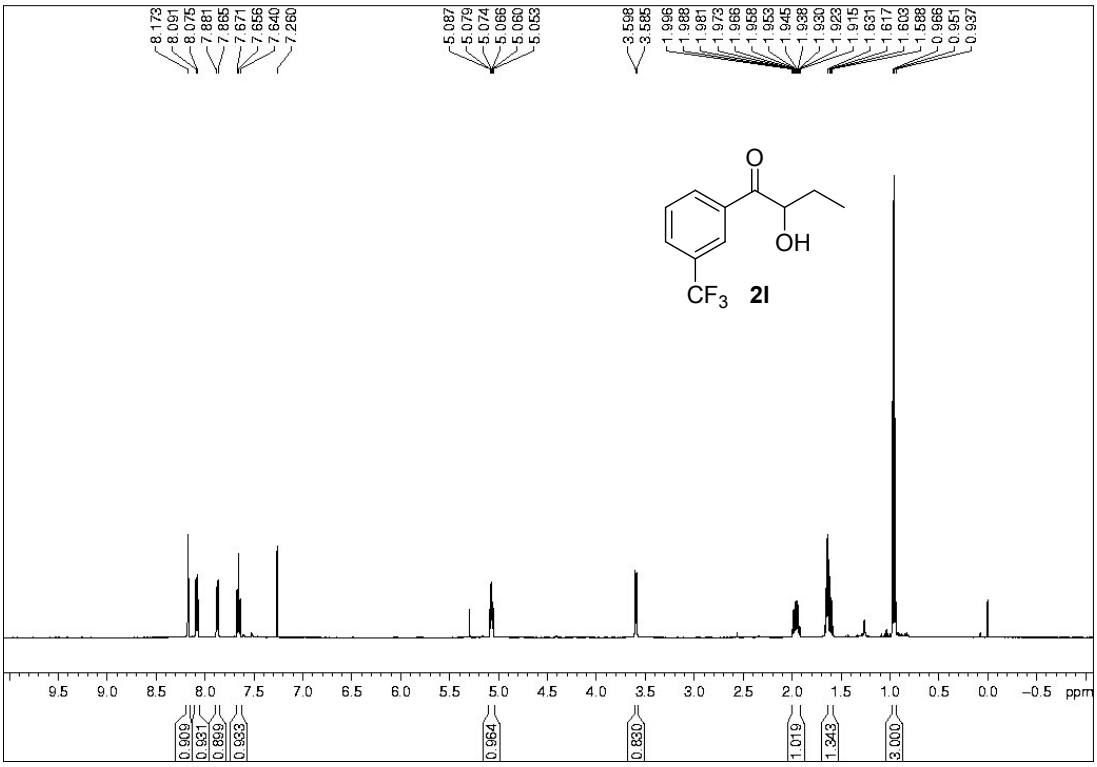


Figure 27: ^{1}H NMR spectrum of **2l** (500 MHz, $CDCl_3$)

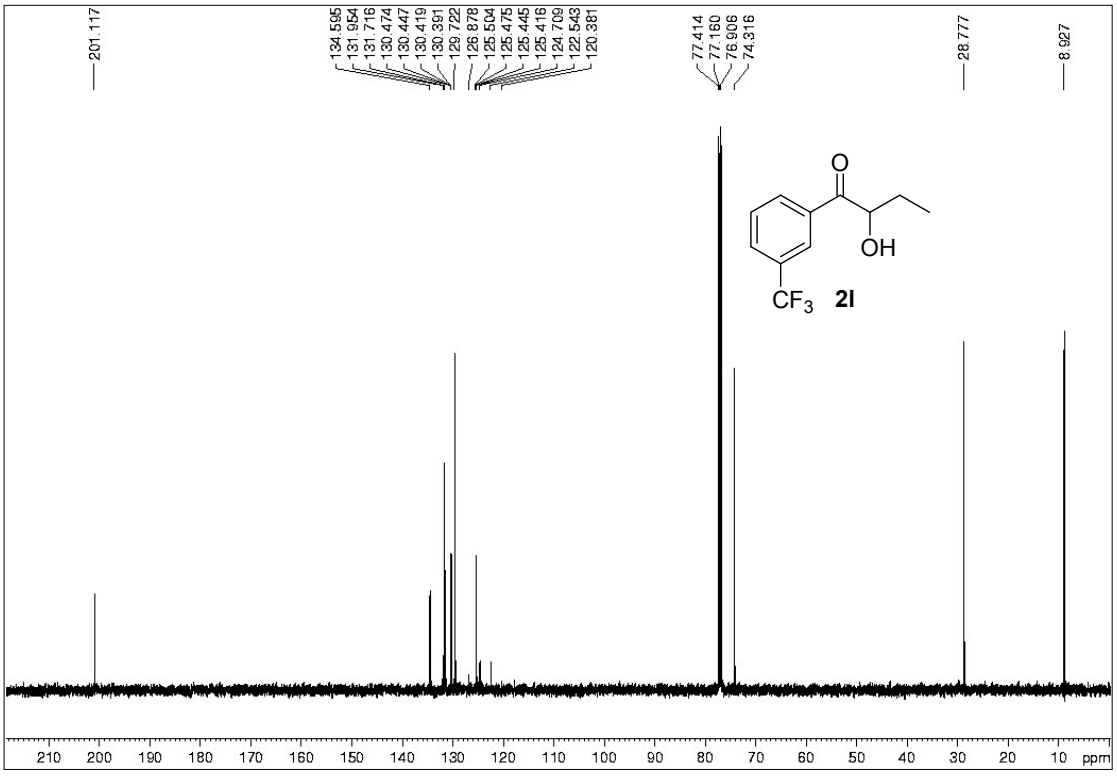


Figure 28: ^{13}C NMR spectrum of **2l** (125 MHz, $CDCl_3$)

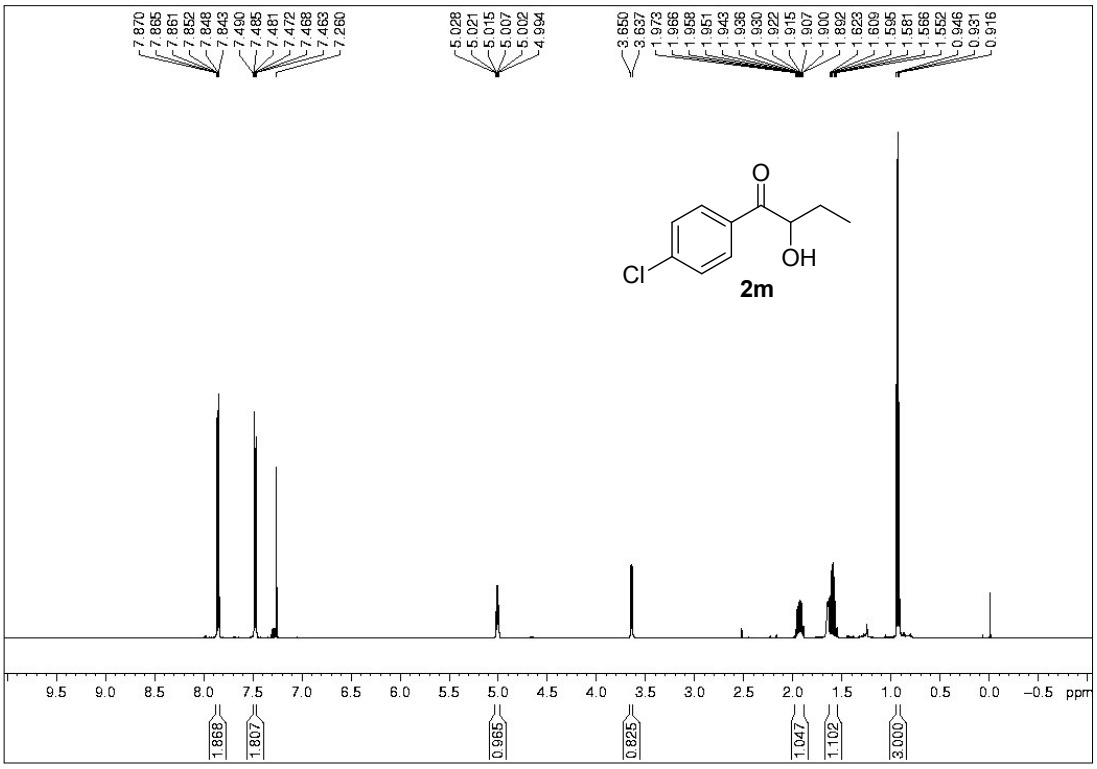


Figure 29: ^{1}H NMR spectrum of **2m** (500 MHz, $CDCl_3$)

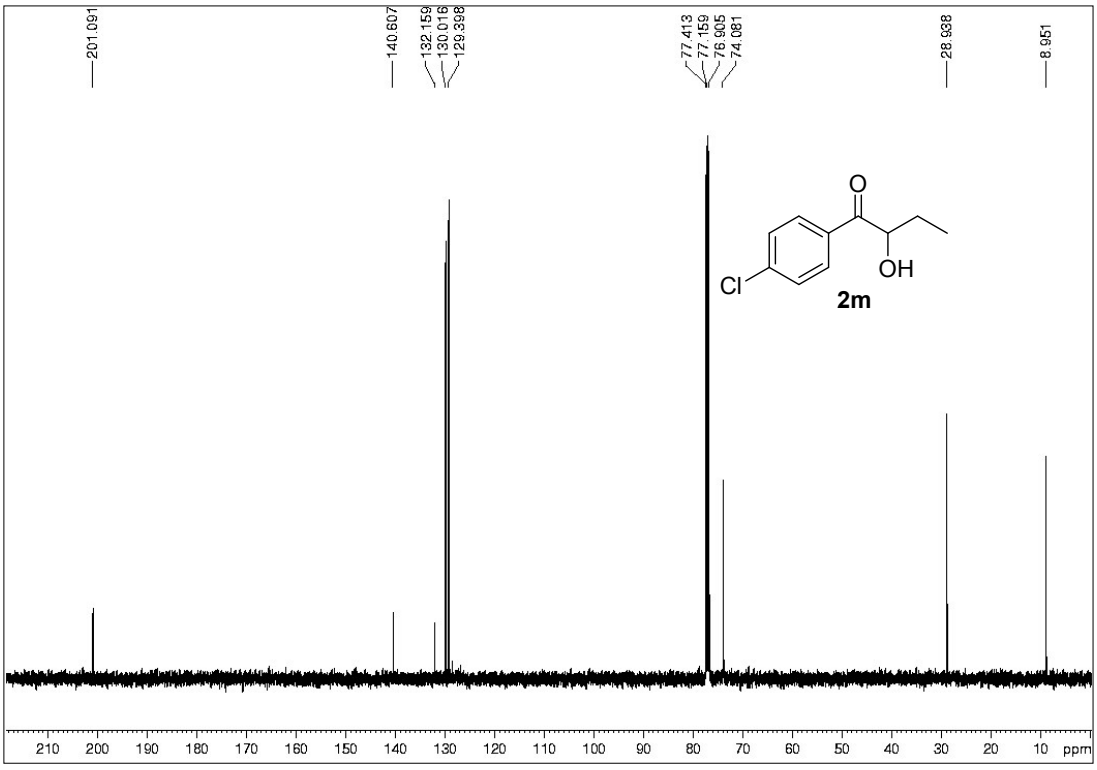


Figure 30: ^{13}C NMR spectrum of **2m** (125 MHz, $CDCl_3$)

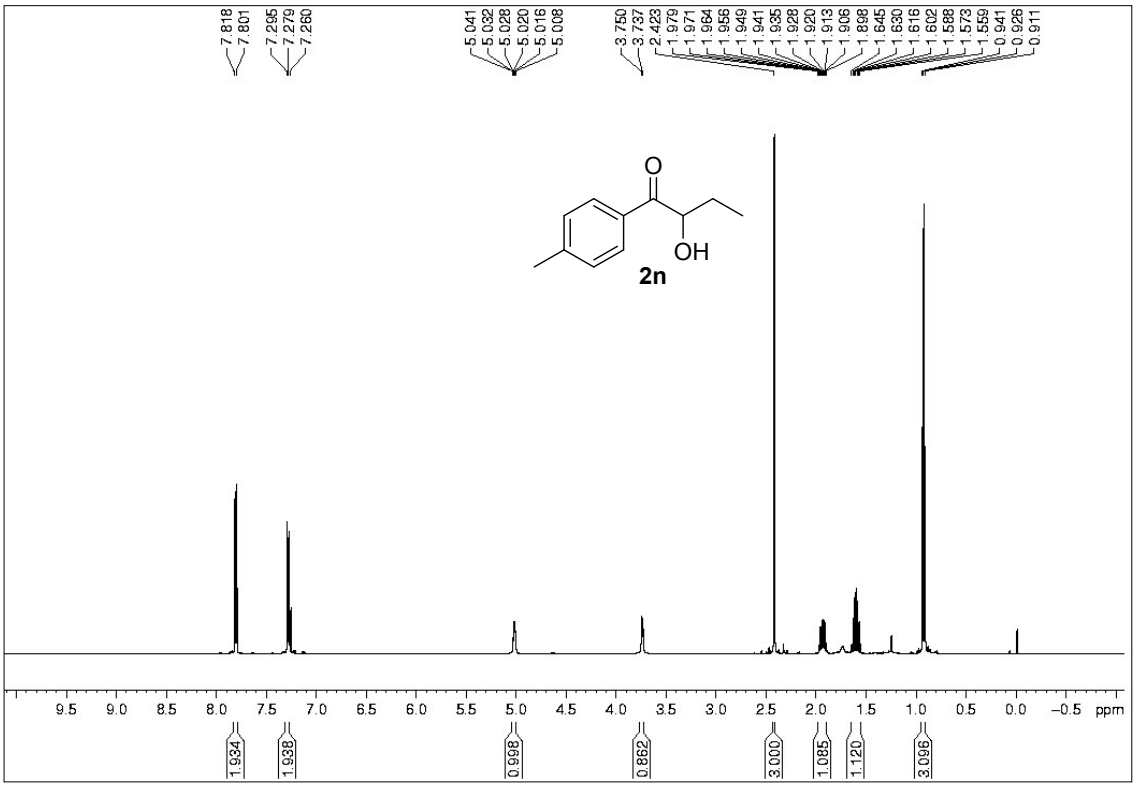


Figure 31: ^{1}H NMR spectrum of **2n** (500 MHz, $CDCl_3$)

Figure 32: ^{13}C NMR spectrum of **2n** (125 MHz, $CDCl_3$)

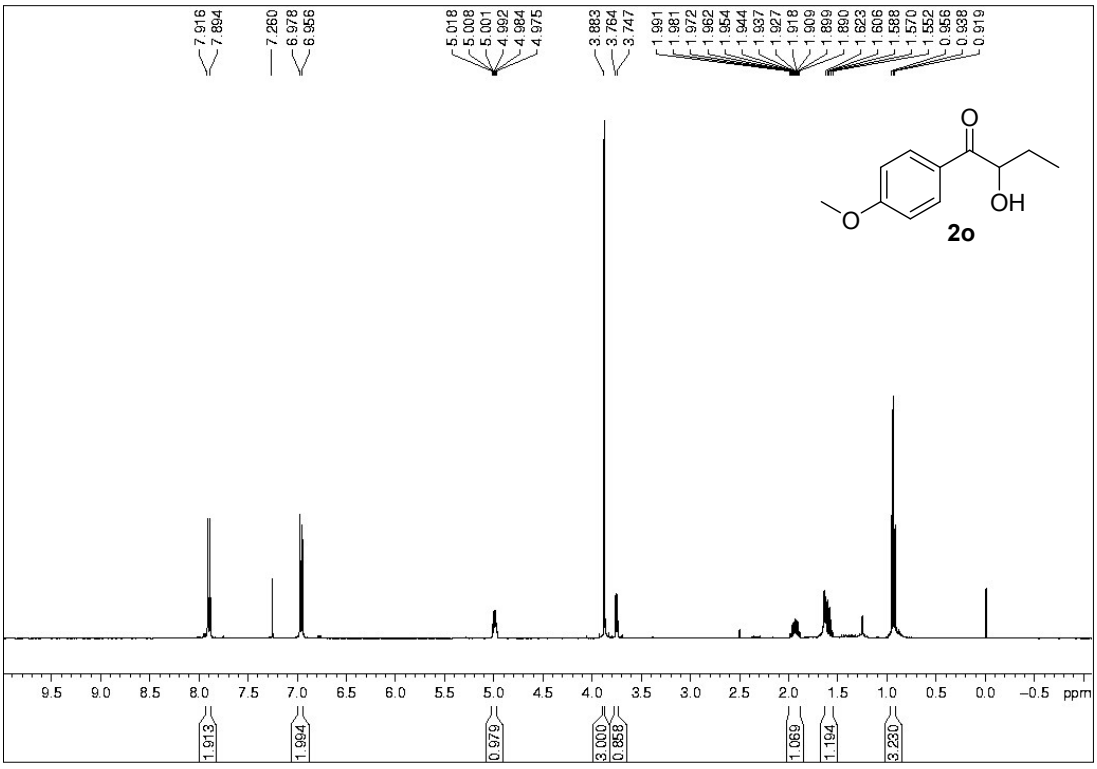


Figure 33: ^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$)

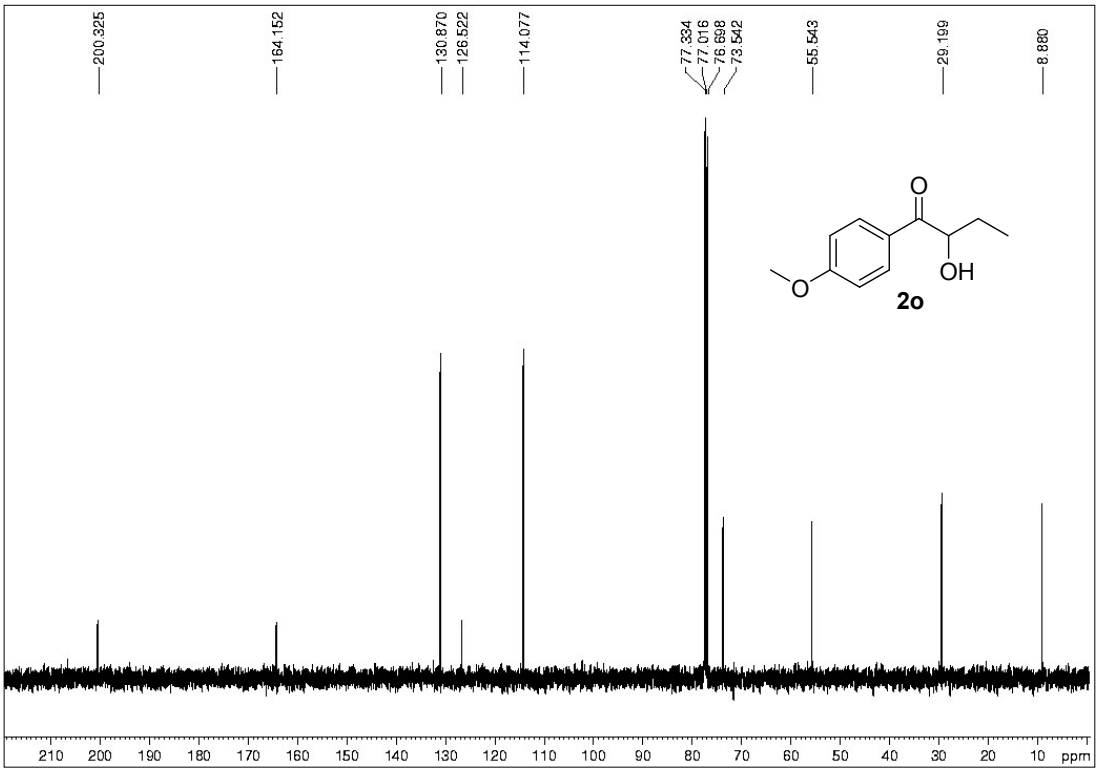


Figure 34: ^{13}C NMR spectrum of **2o** (100 MHz, $CDCl_3$)

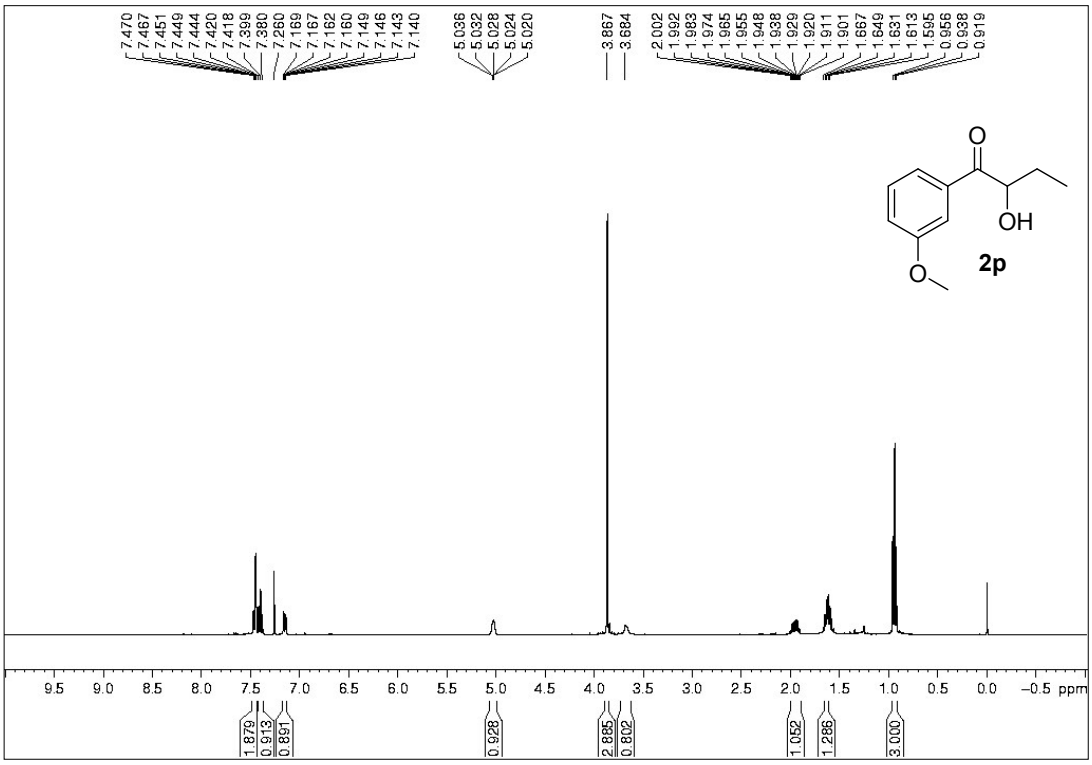


Figure 35: ^{1}H NMR spectrum of **2p** (400 MHz, $CDCl_3$)

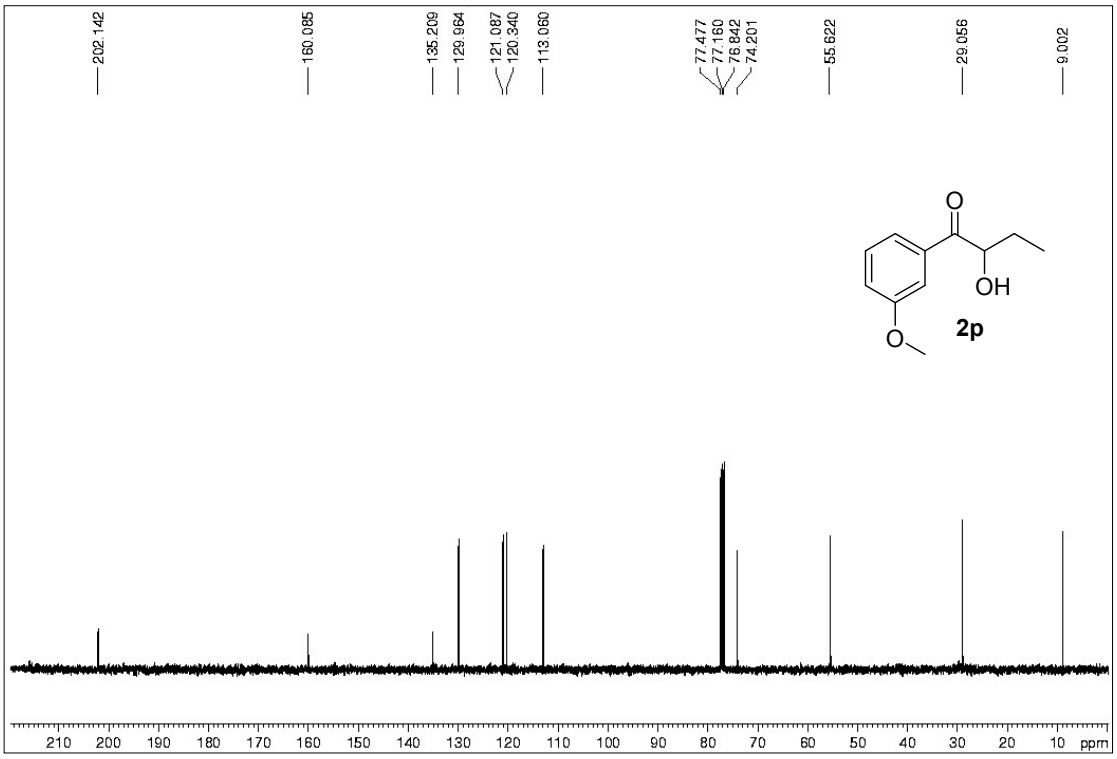


Figure 36: ^{13}C NMR spectrum of **2p** (100 MHz, $CDCl_3$)

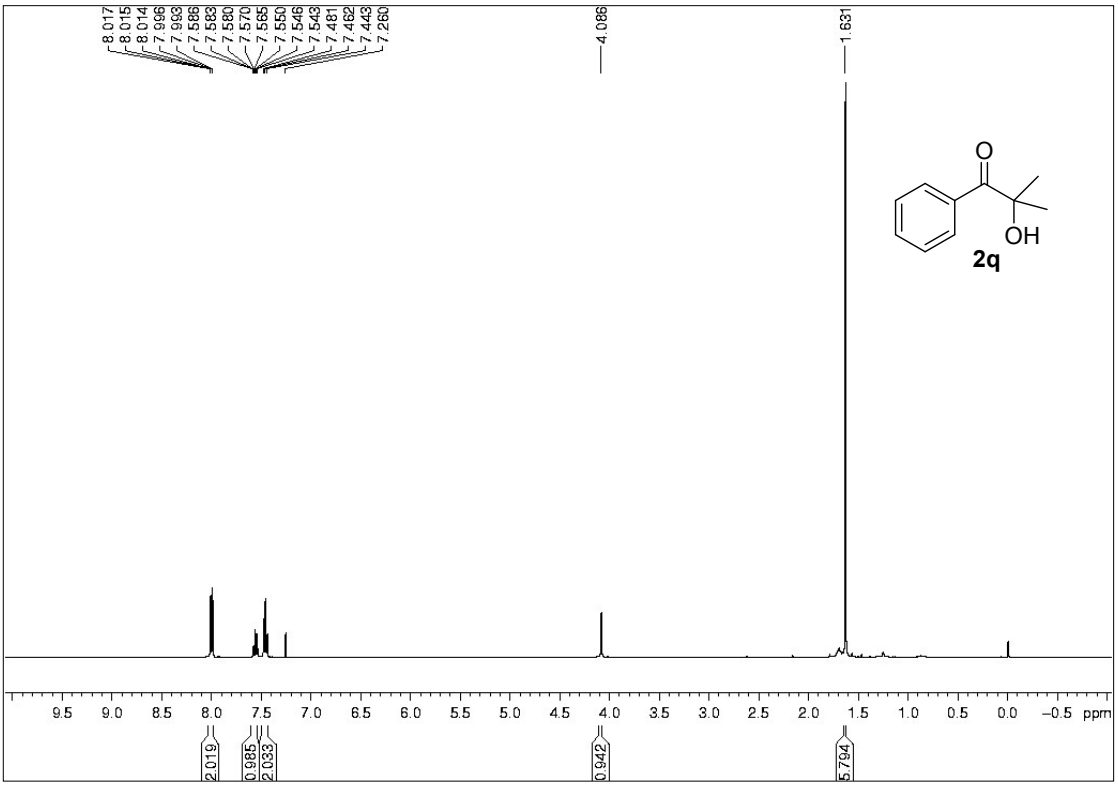


Figure 37: ^{1}H NMR spectrum of **2q** (400 MHz, $CDCl_3$)

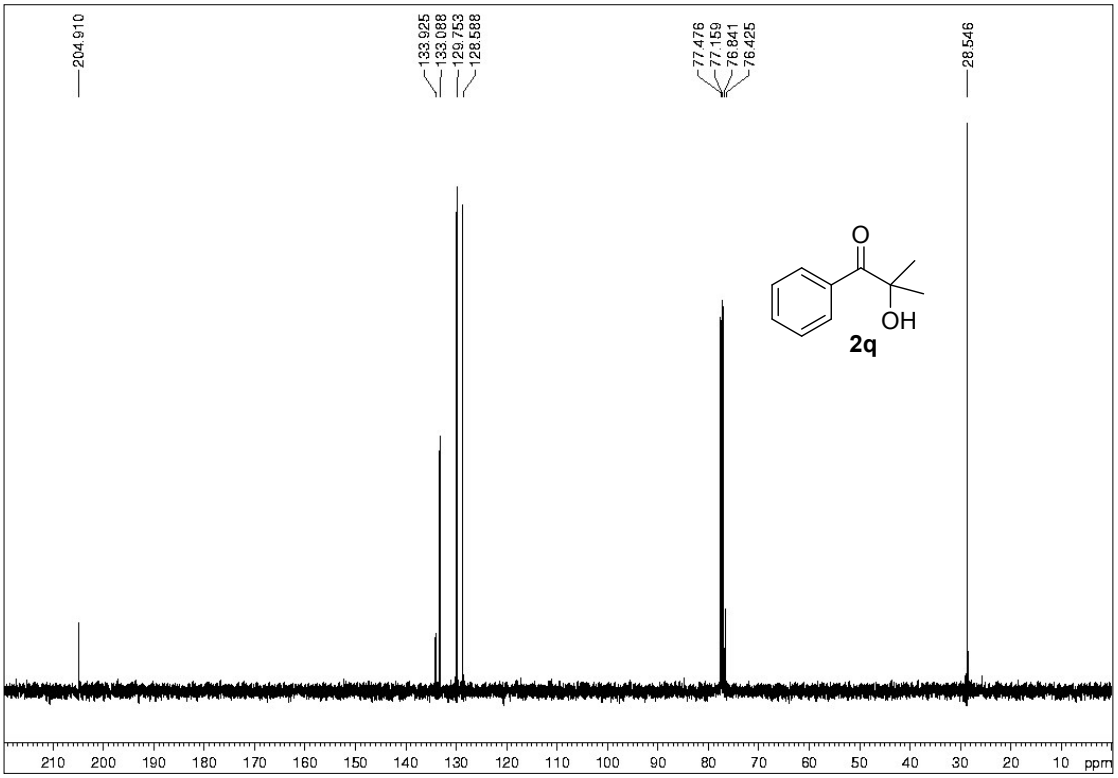


Figure 38: ^{13}C NMR spectrum of **2q** (100 MHz, $CDCl_3$)

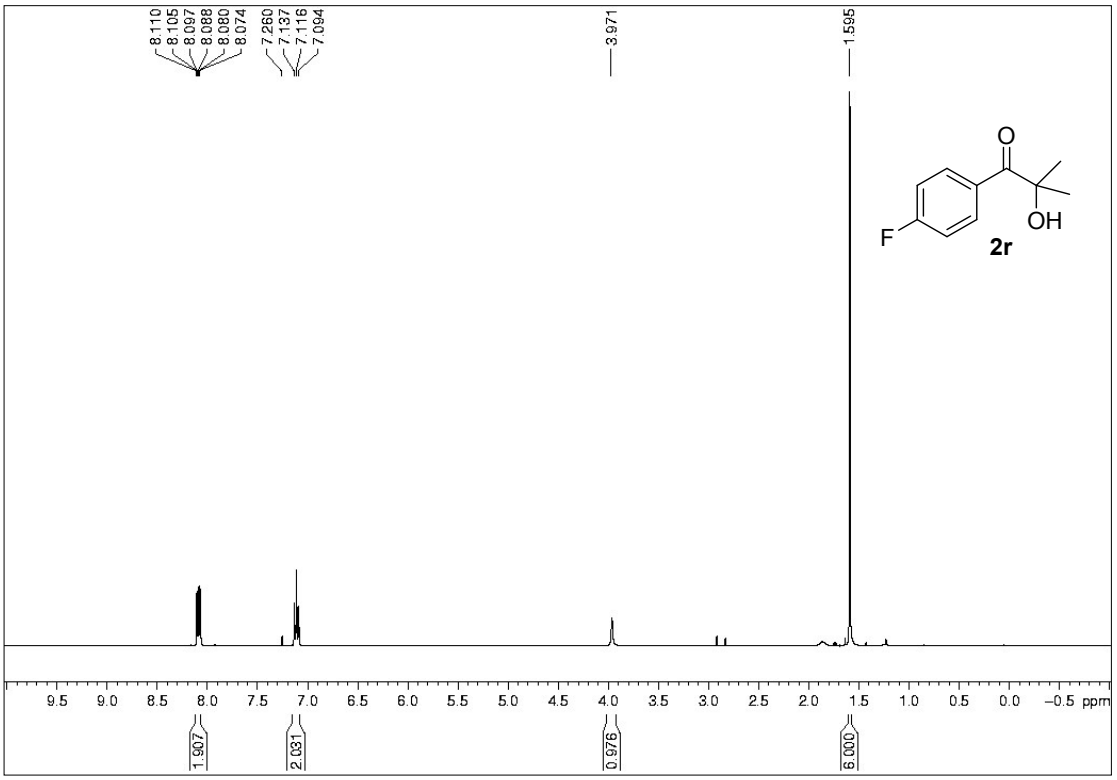


Figure 39: ^{1}H NMR spectrum of **2r** (400 MHz, $CDCl_3$)

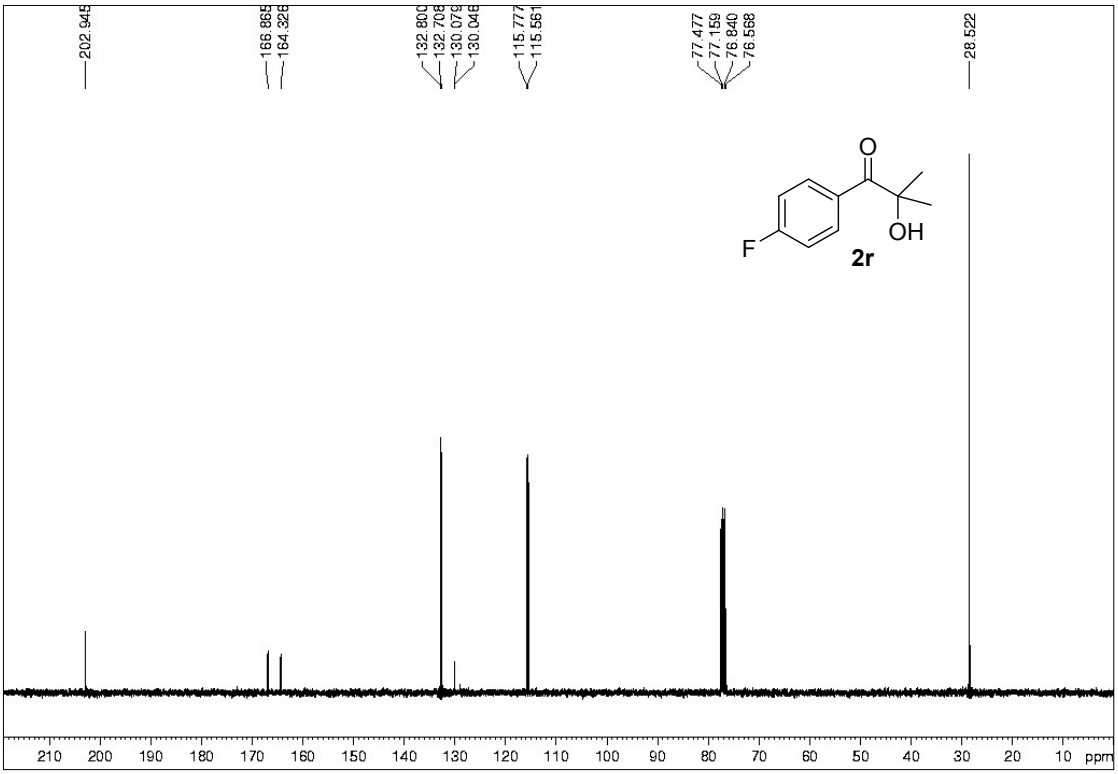


Figure 40: ^{13}C NMR spectrum of **2r** (100 MHz, $CDCl_3$)

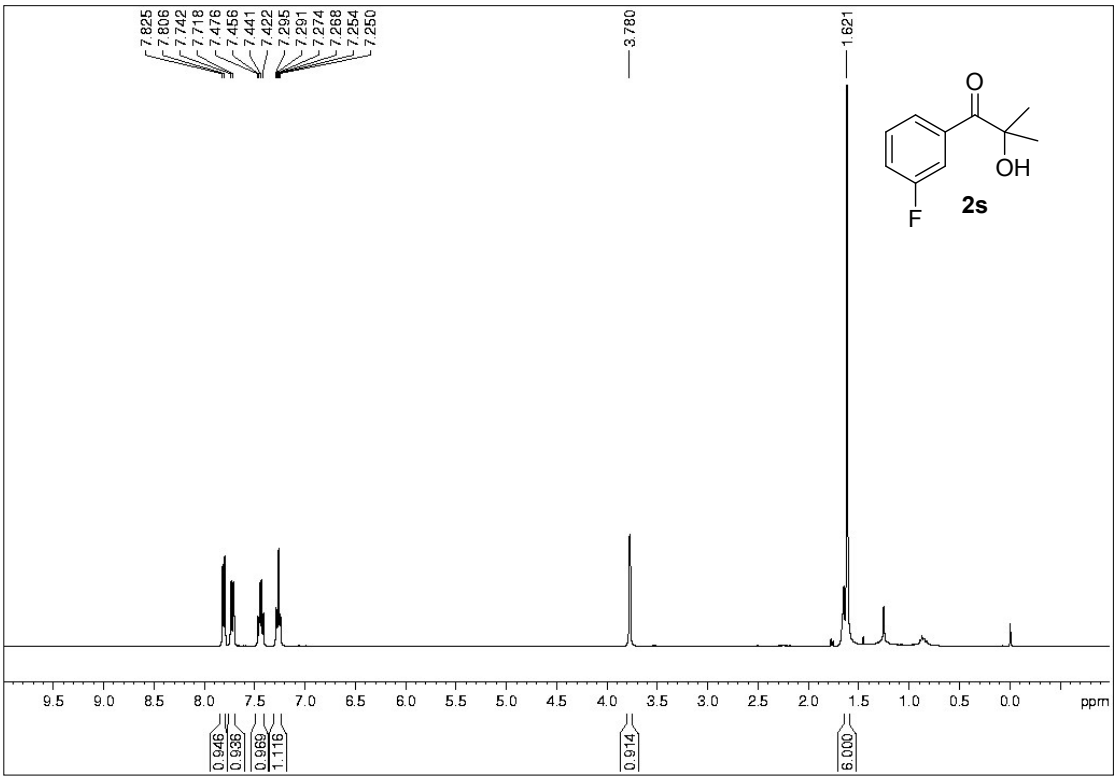


Figure 41: ^{1}H NMR spectrum of **2s** (400 MHz, $CDCl_3$)

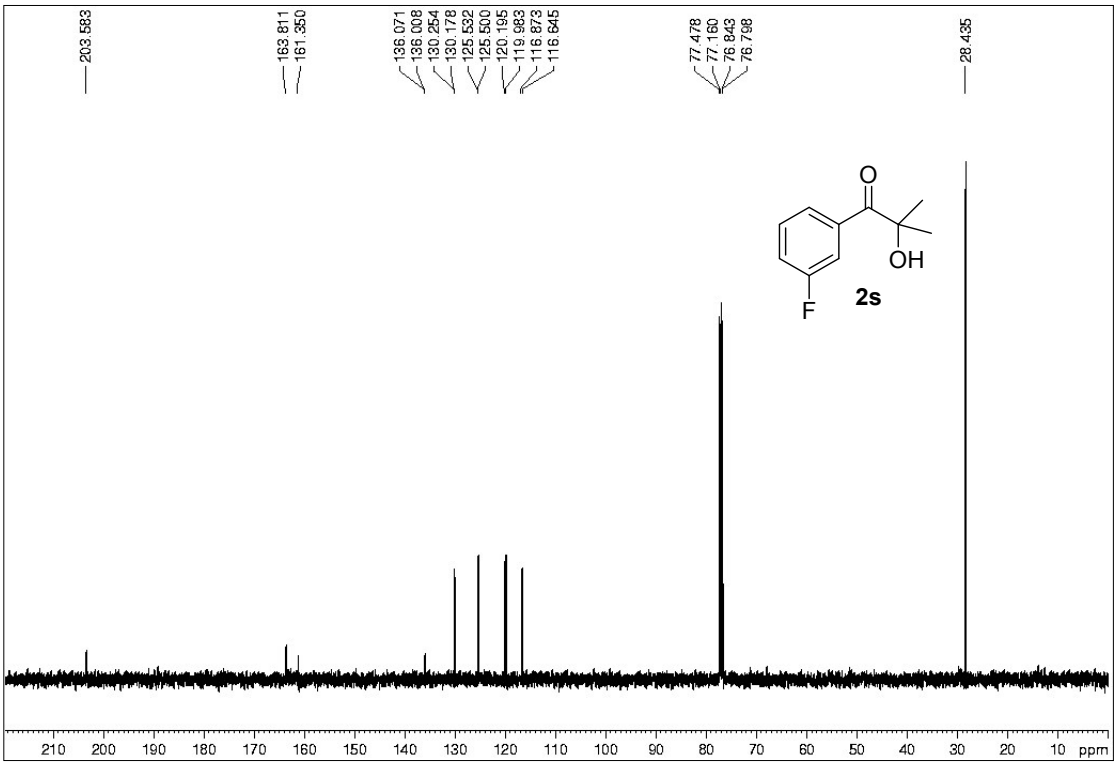


Figure 42: ^{13}C NMR spectrum of **2s** (100 MHz, $CDCl_3$)

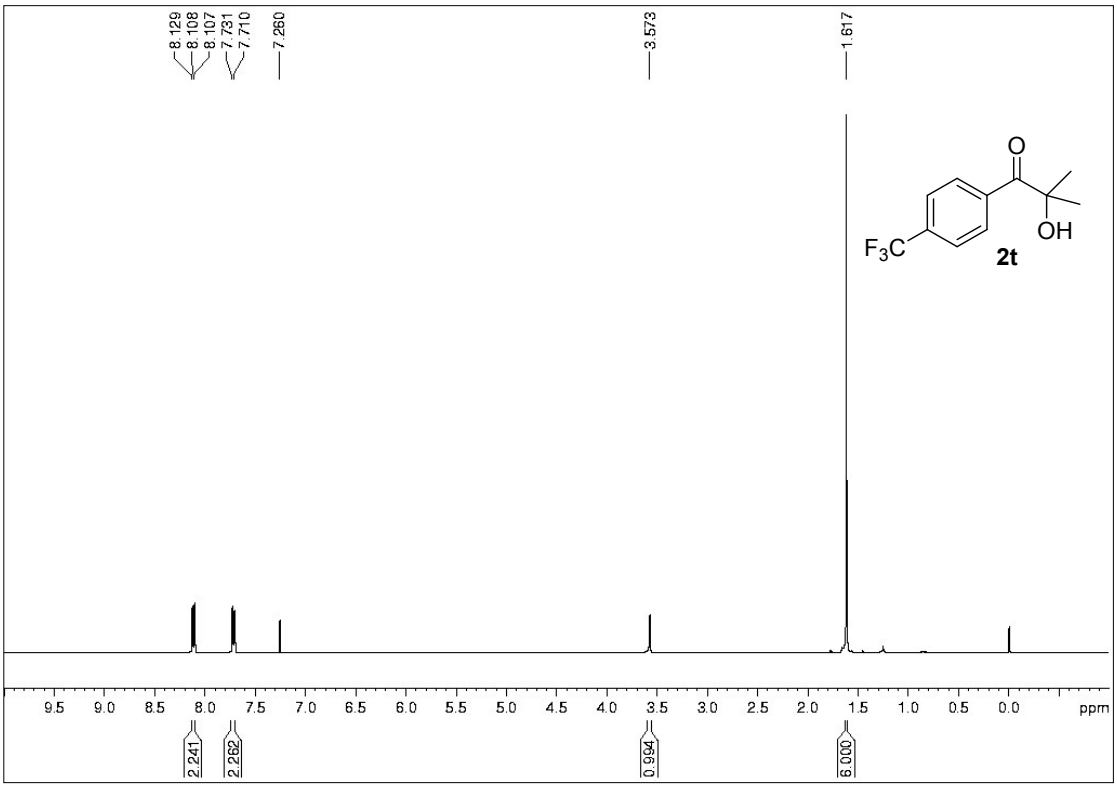


Figure 43: ^{1}H NMR spectrum of **2t** (400 MHz, $CDCl_3$)

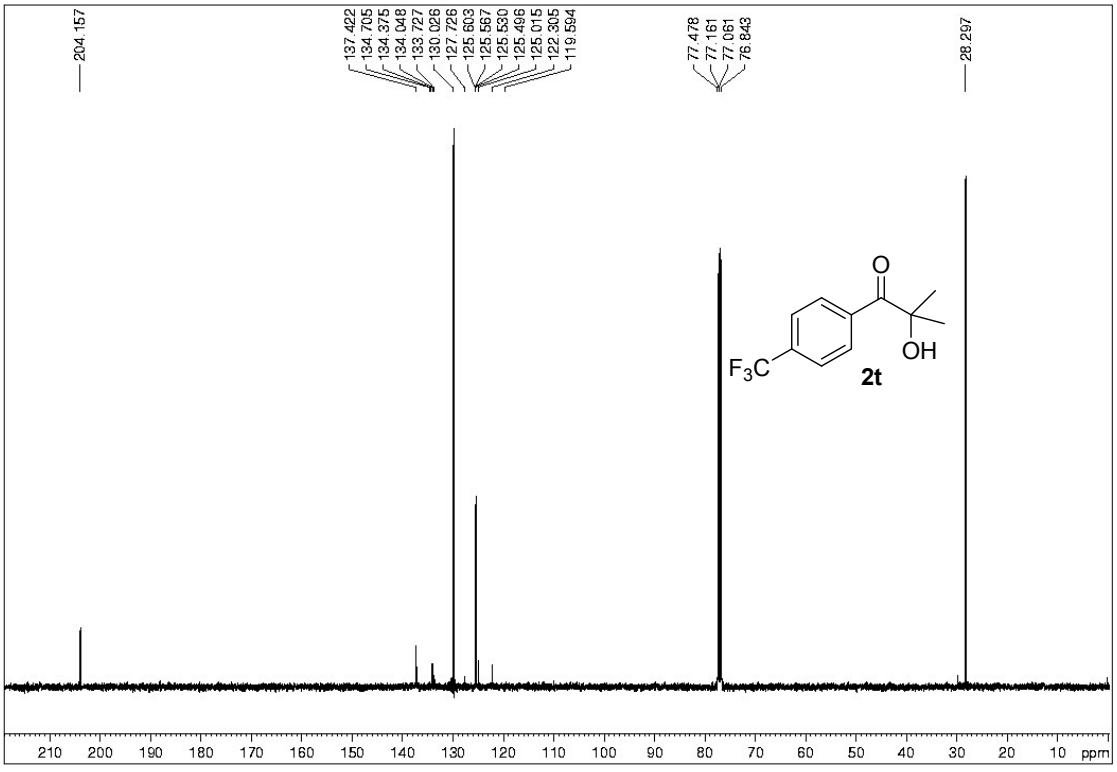


Figure 44: ^{13}C NMR spectrum of **2t** (100 MHz, $CDCl_3$)

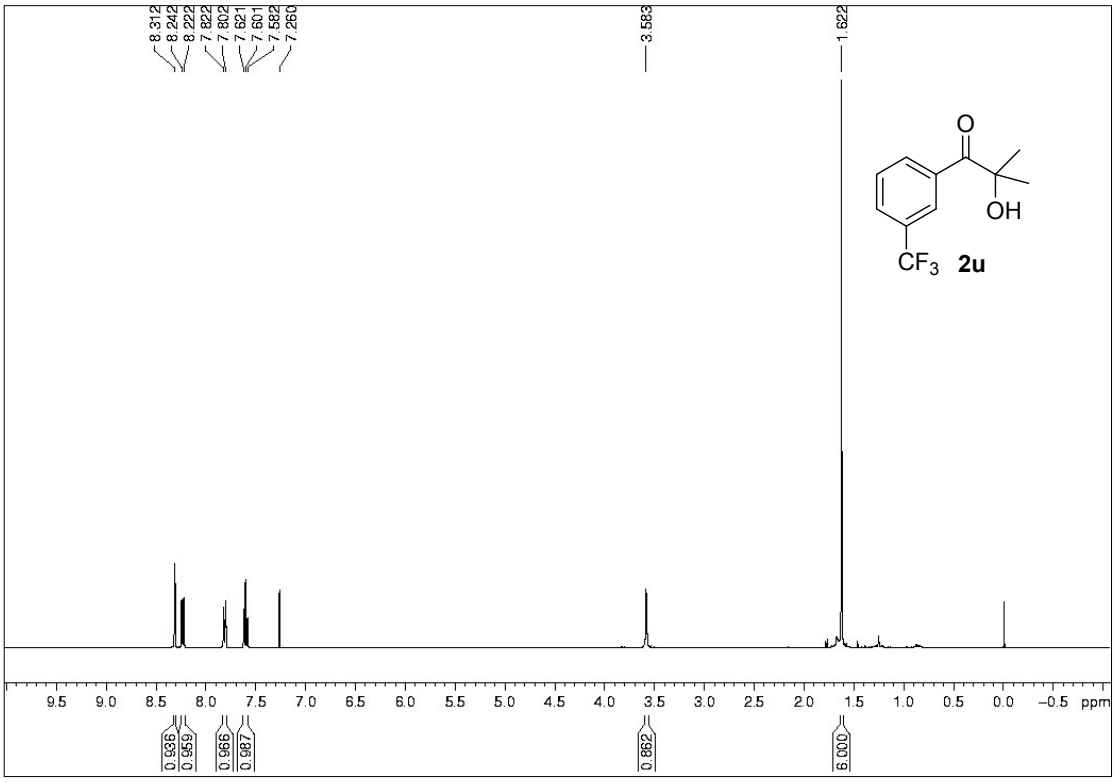


Figure 45: ^{1}H NMR spectrum of **2u** (400 MHz, $CDCl_3$)

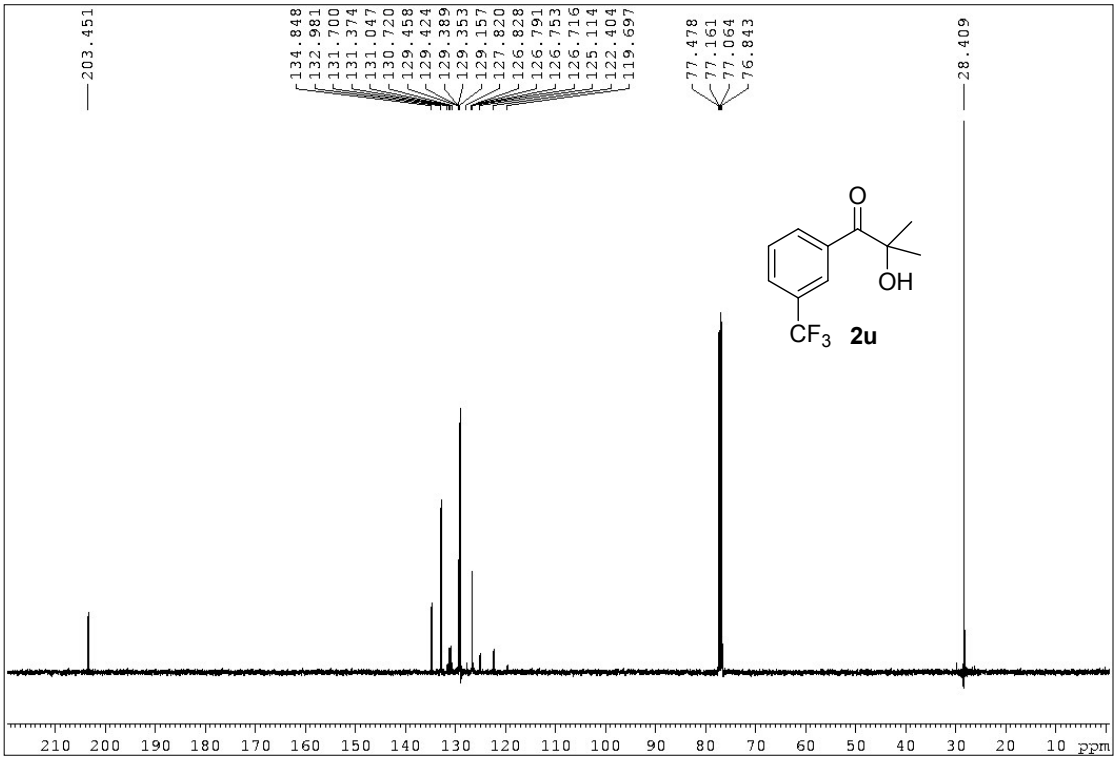


Figure 46: ^{13}C NMR spectrum of **2u** (100 MHz, $CDCl_3$)

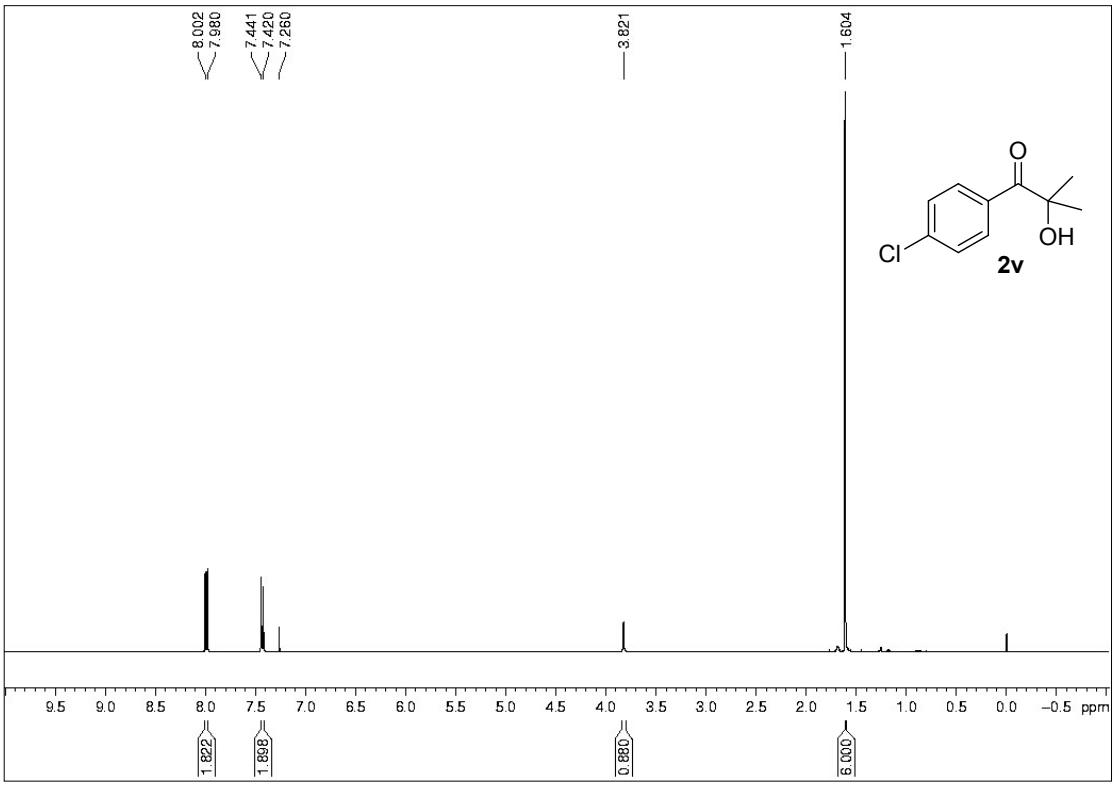


Figure 47: ^{1}H NMR spectrum of **2v** (400 MHz, $CDCl_3$)

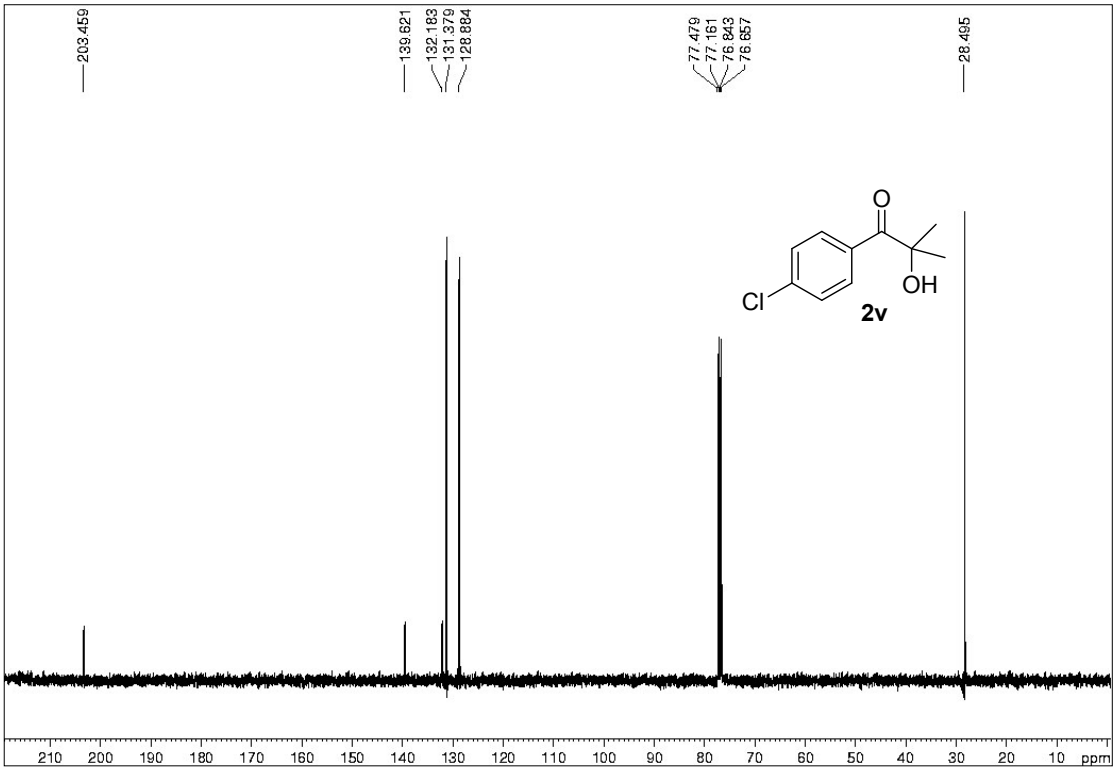


Figure 48: ^{13}C NMR spectrum of **2v** (100 MHz, $CDCl_3$)

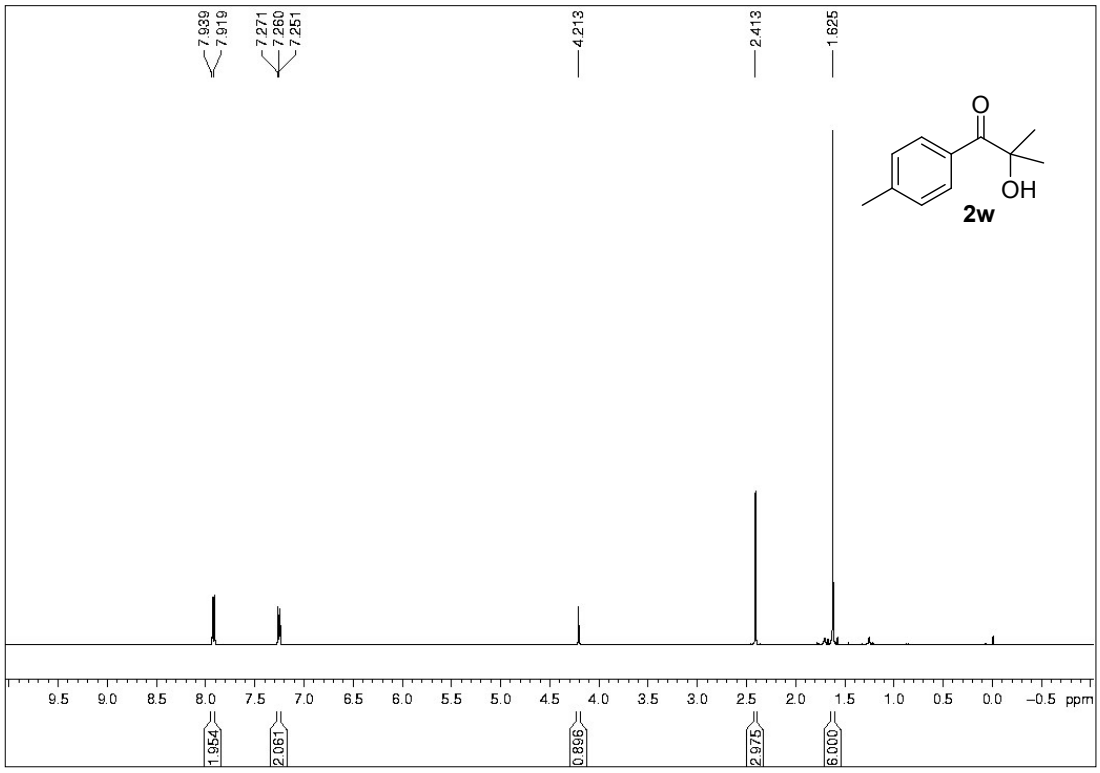


Figure 49: ^{1}H NMR spectrum of **2w** (400 MHz, $CDCl_3$)

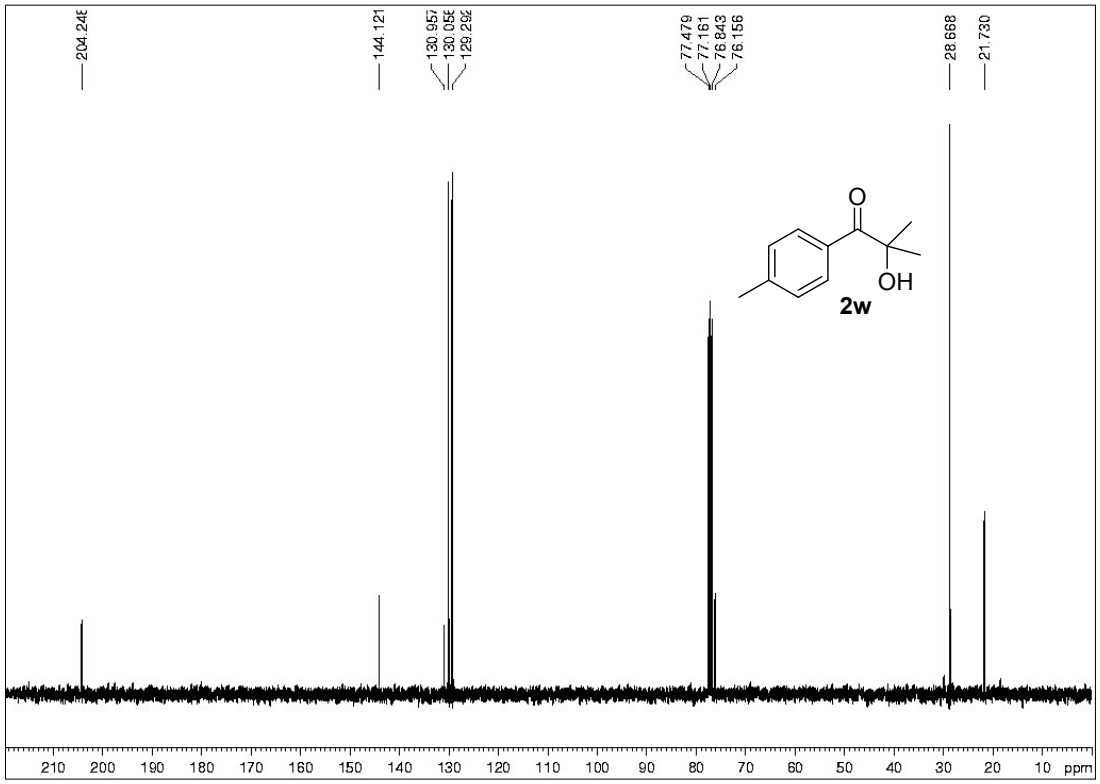


Figure 50: ^{13}C NMR spectrum of **2w** (100 MHz, $CDCl_3$)

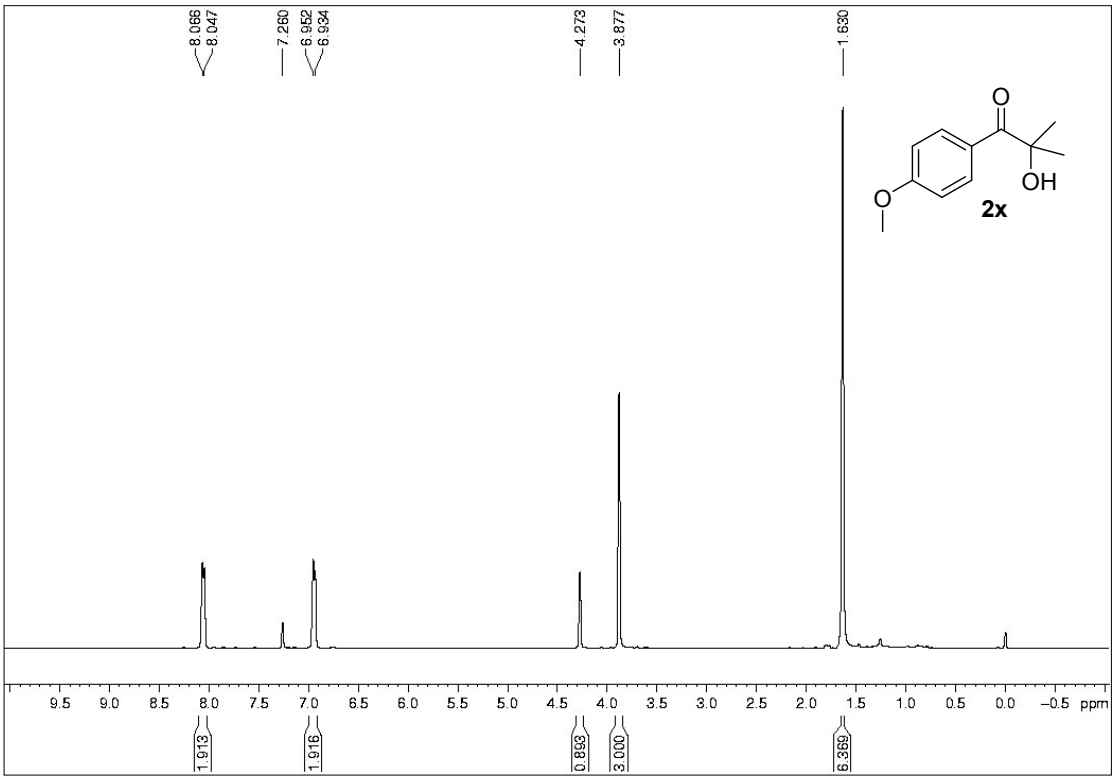


Figure 51: ^{1}H NMR spectrum of **2x** (400 MHz, $CDCl_3$)

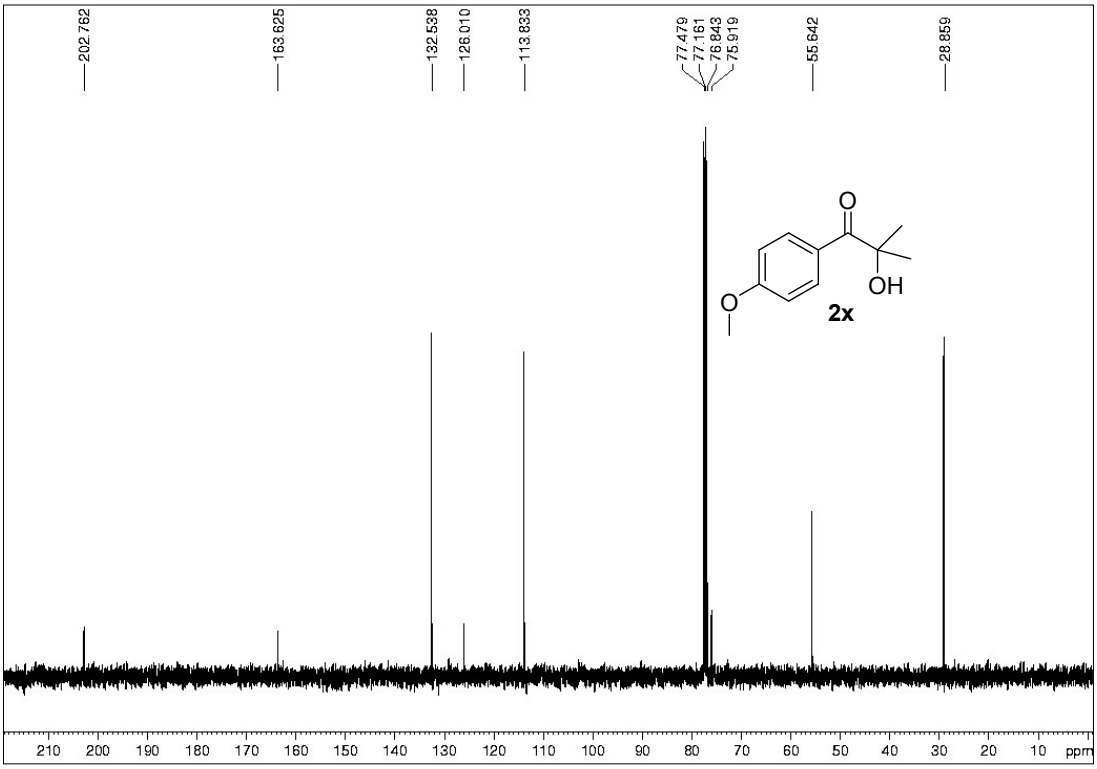


Figure 52: ^{13}C NMR spectrum of **2x** (100 MHz, $CDCl_3$)

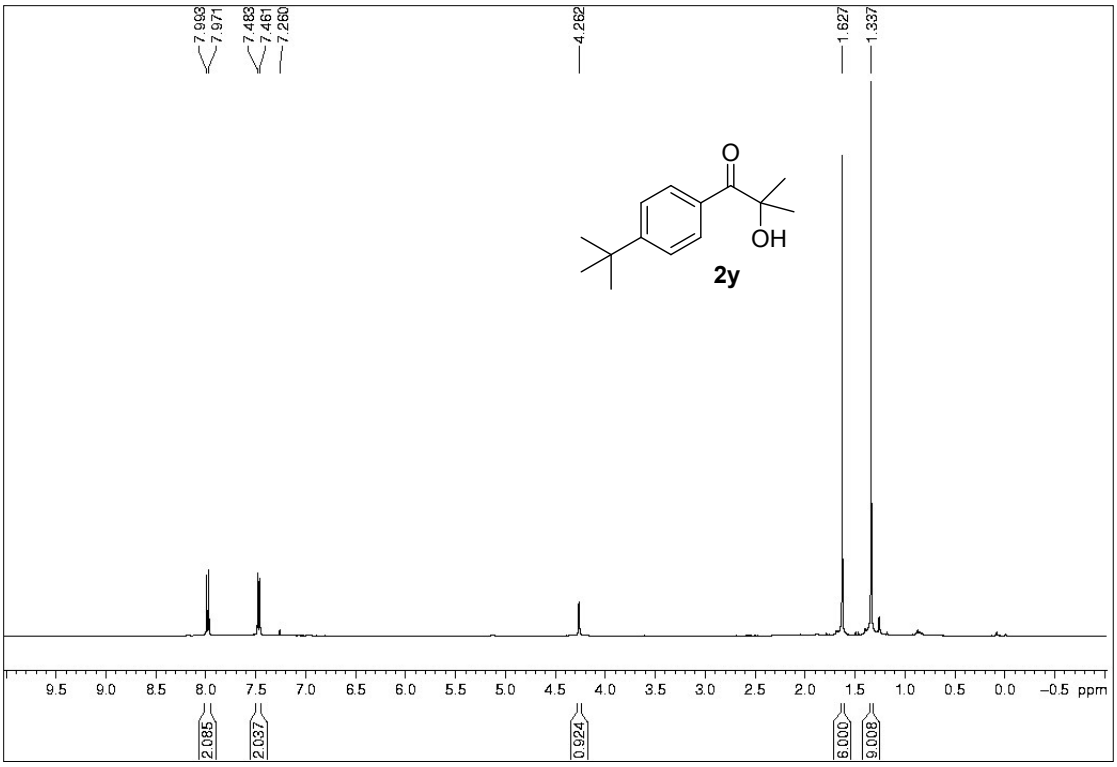


Figure 53: ^{1}H NMR spectrum of **2y** (400 MHz, $CDCl_3$)

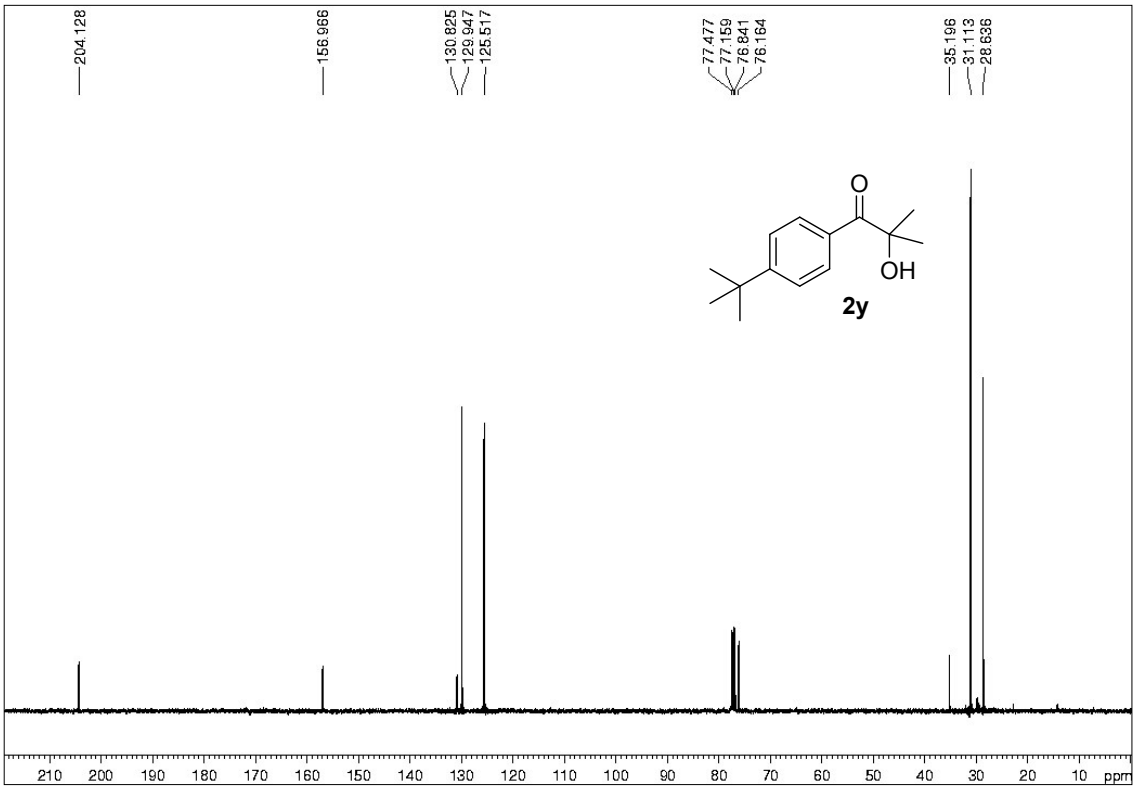


Figure 54: ^{13}C NMR spectrum of **2y** (100 MHz, $CDCl_3$)

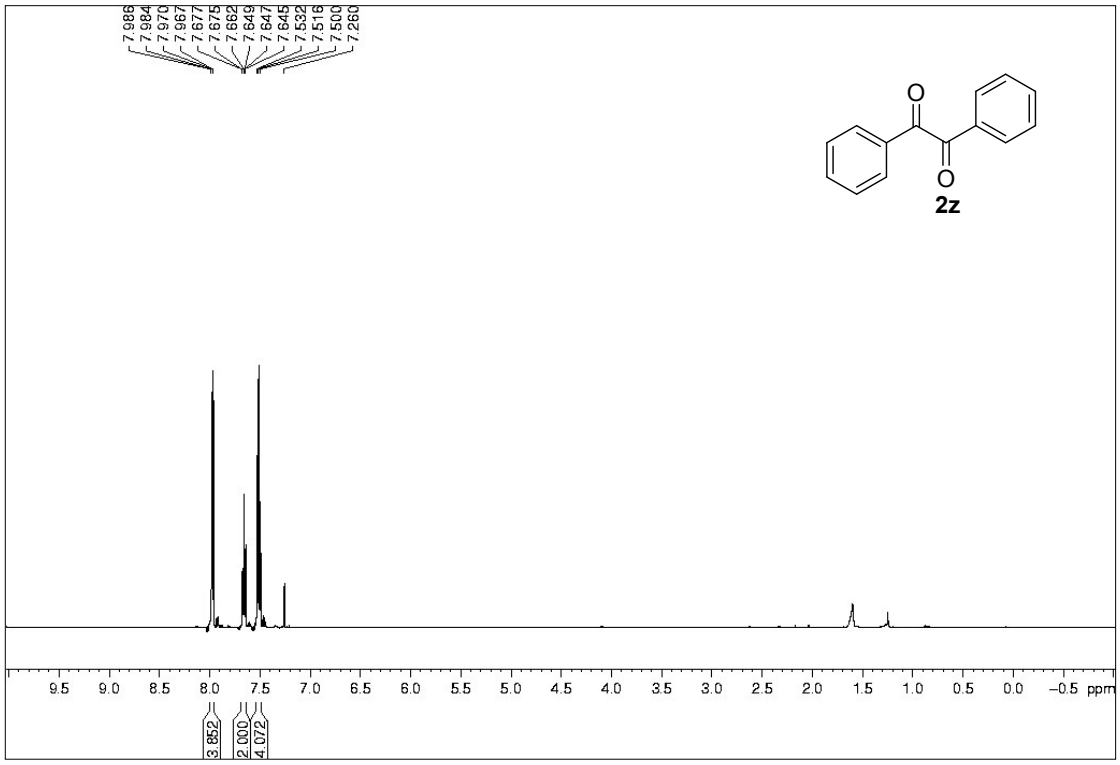


Figure 55: ^{1}H NMR spectrum of **2z** (500 MHz, $CDCl_3$)

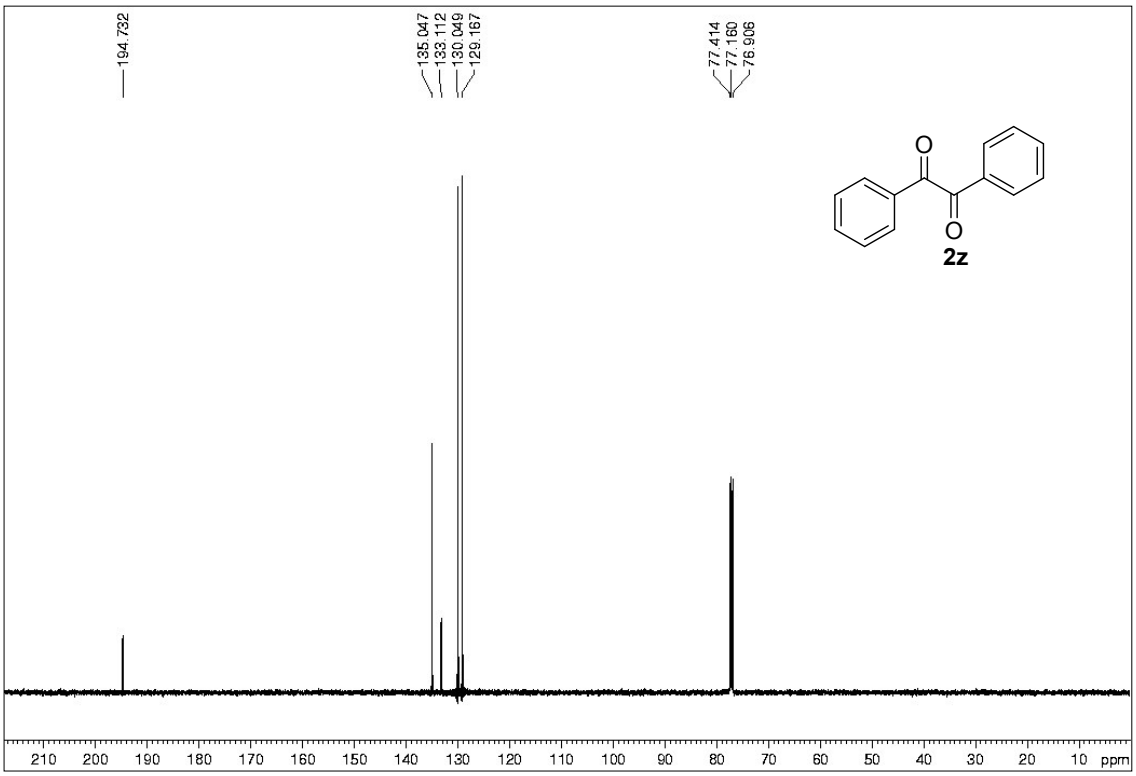


Figure 56: ^{13}C NMR spectrum of **2z** (125 MHz, $CDCl_3$)

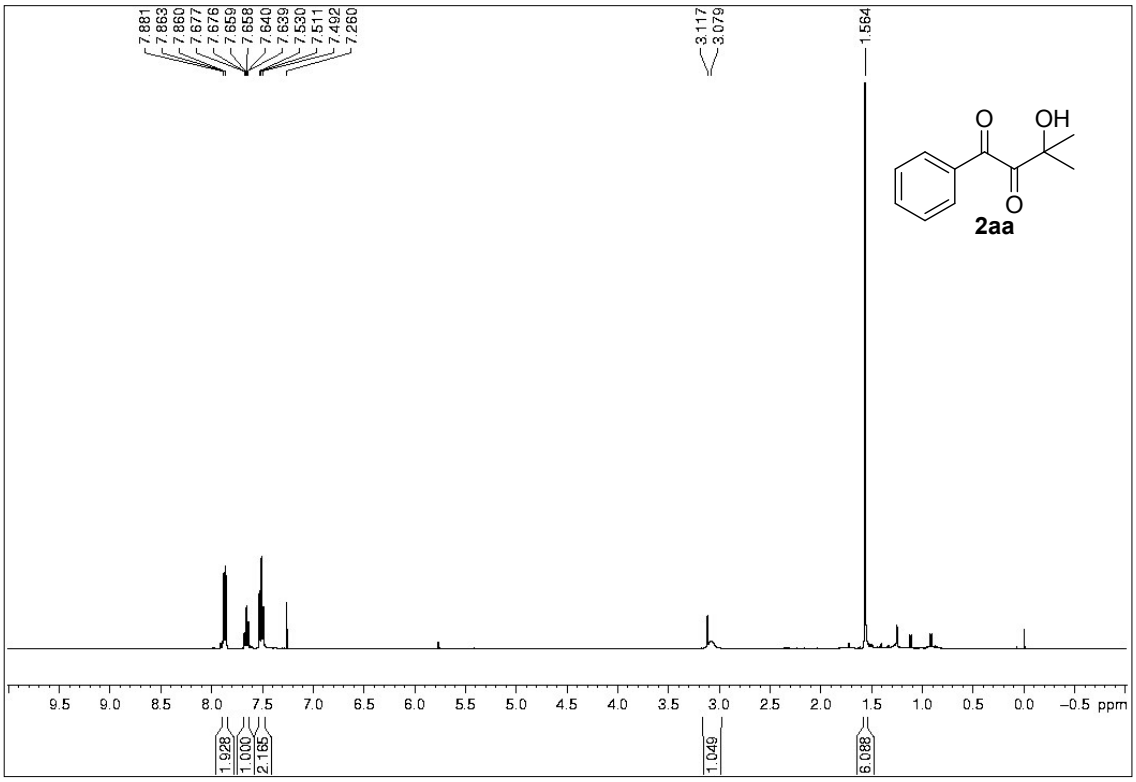


Figure 57: ^{1}H NMR spectrum of **2aa** (400 MHz, $CDCl_3$)

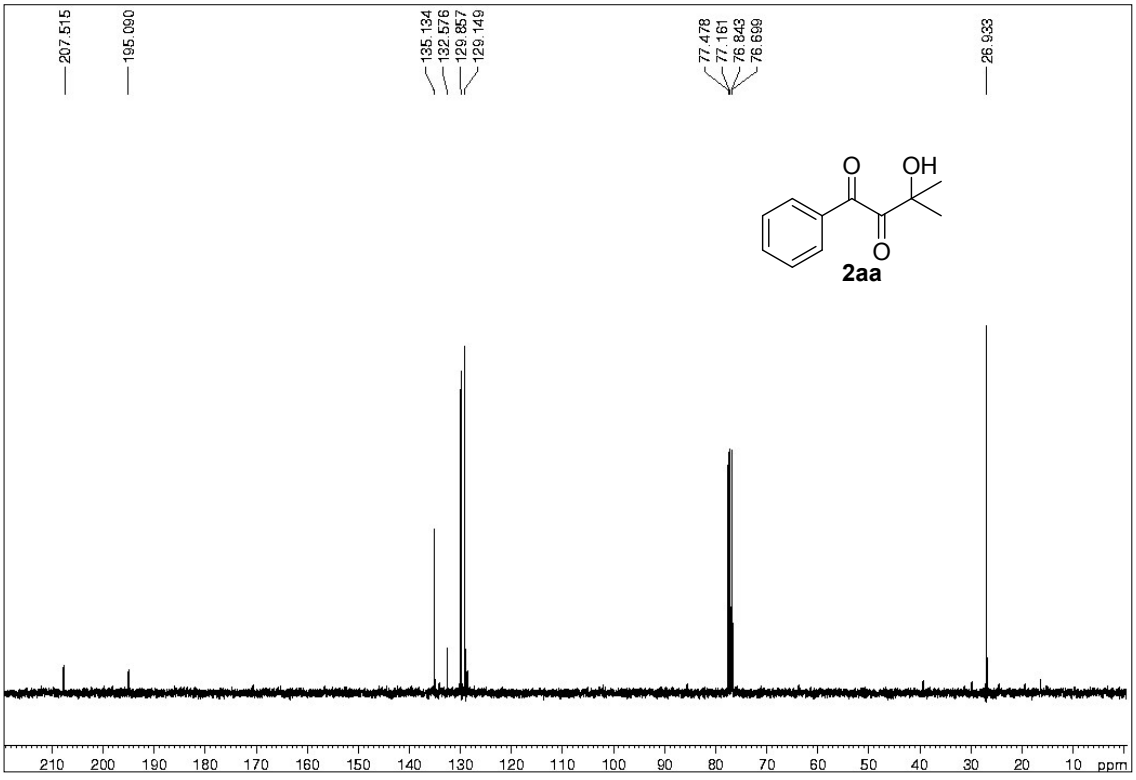


Figure 58: ^{13}C NMR spectrum of **2aa** (100 MHz, $CDCl_3$)

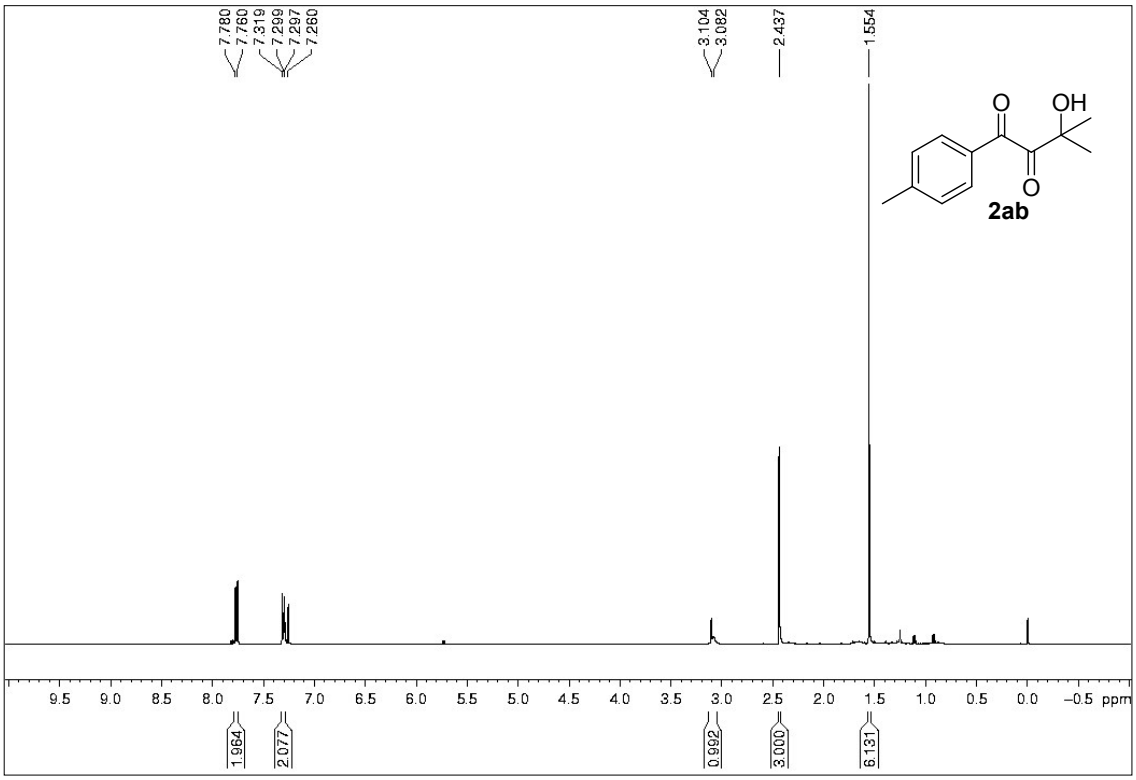


Figure 59: ^{1}H NMR spectrum of **2ab** (400 MHz, $CDCl_3$)

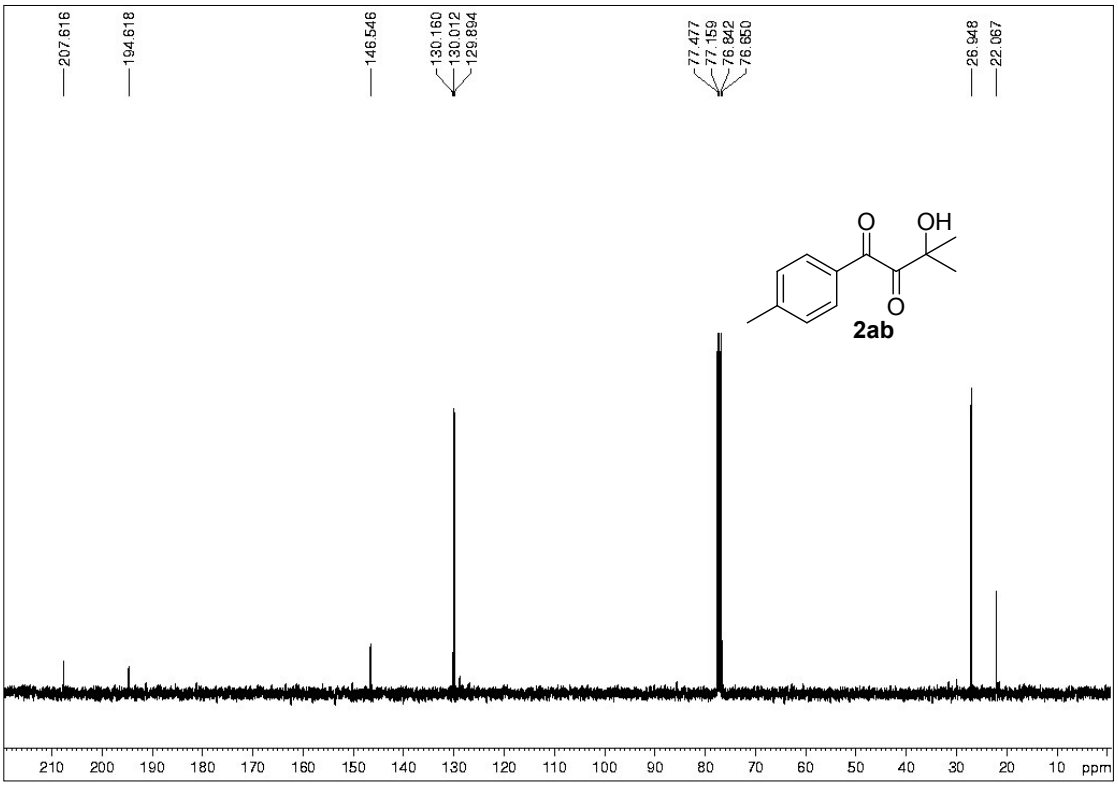


Figure 60: ^{13}C NMR spectrum of **2ab** (100 MHz, $CDCl_3$)

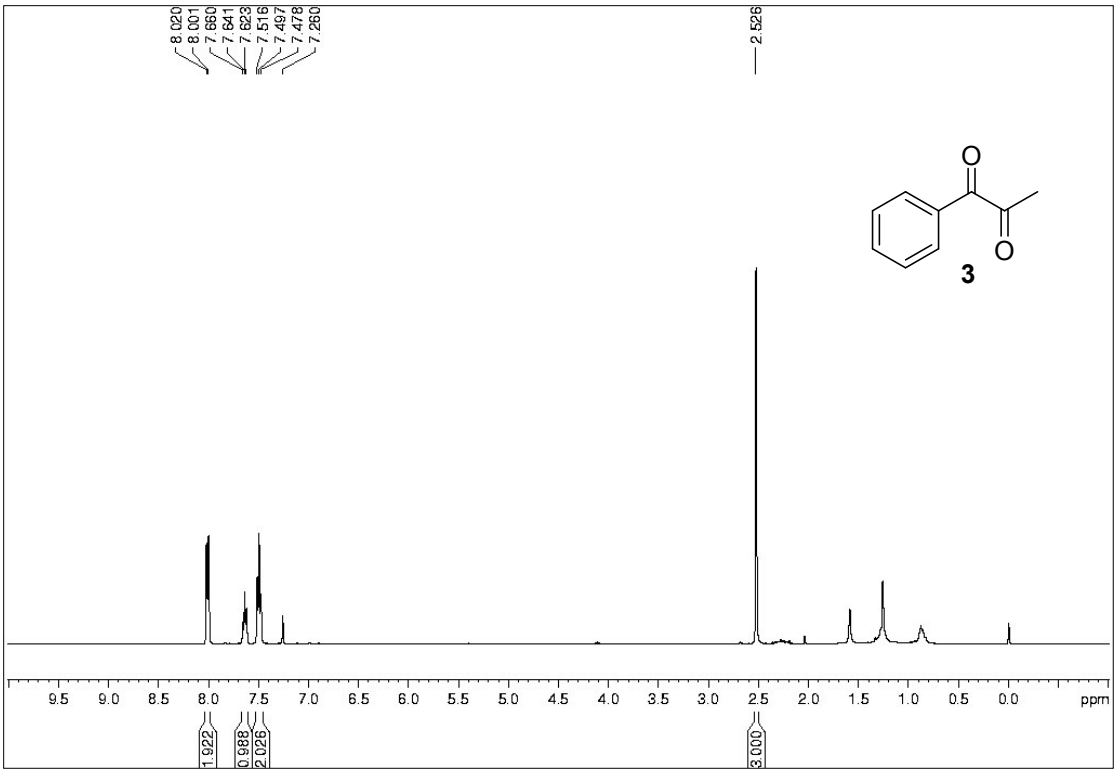


Figure 61: ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$)

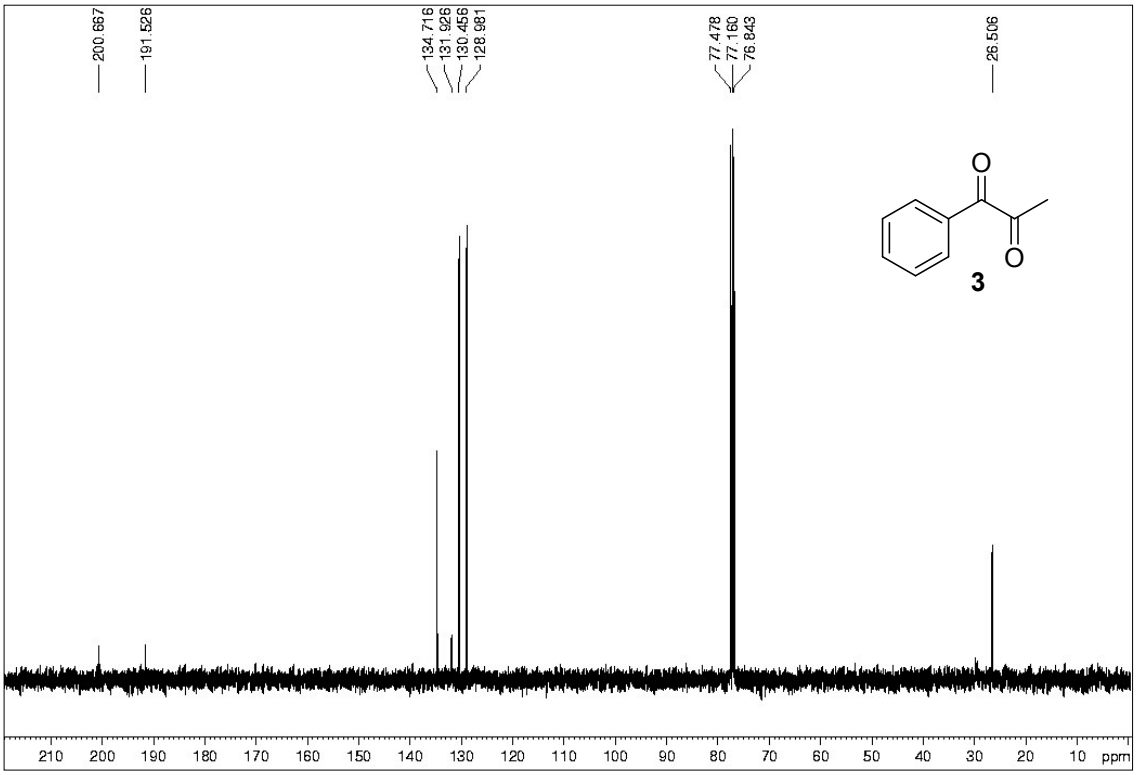


Figure 62: ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$)

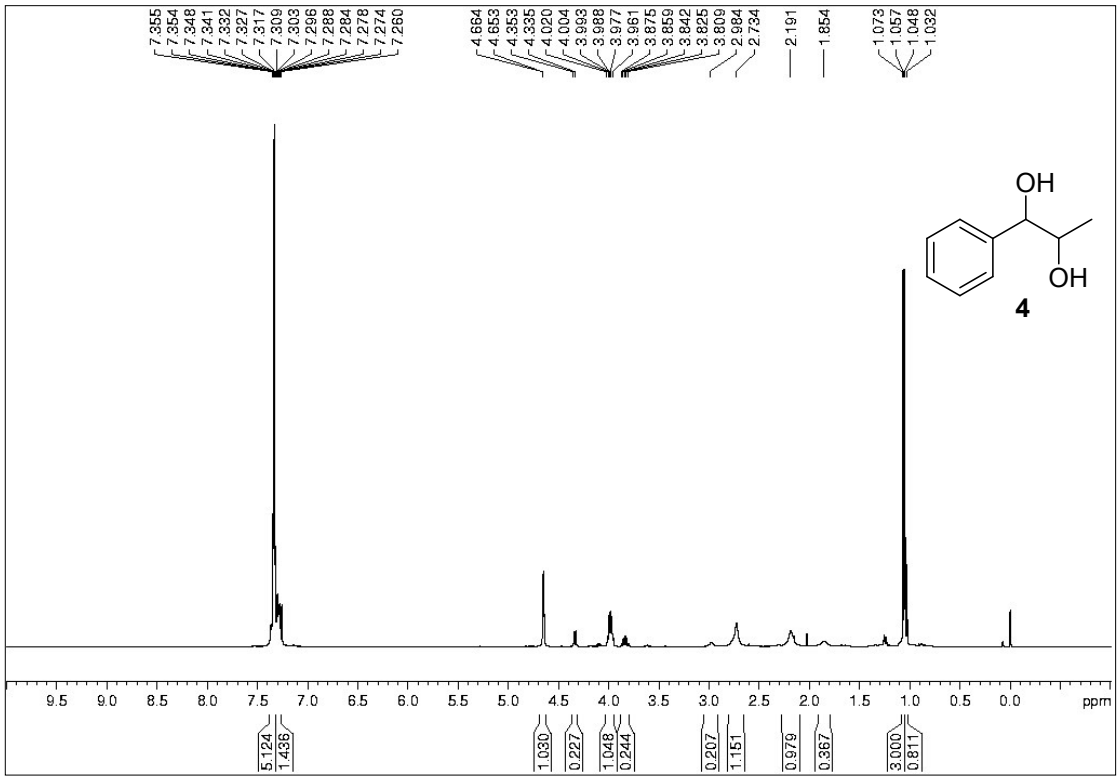


Figure 65: ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)

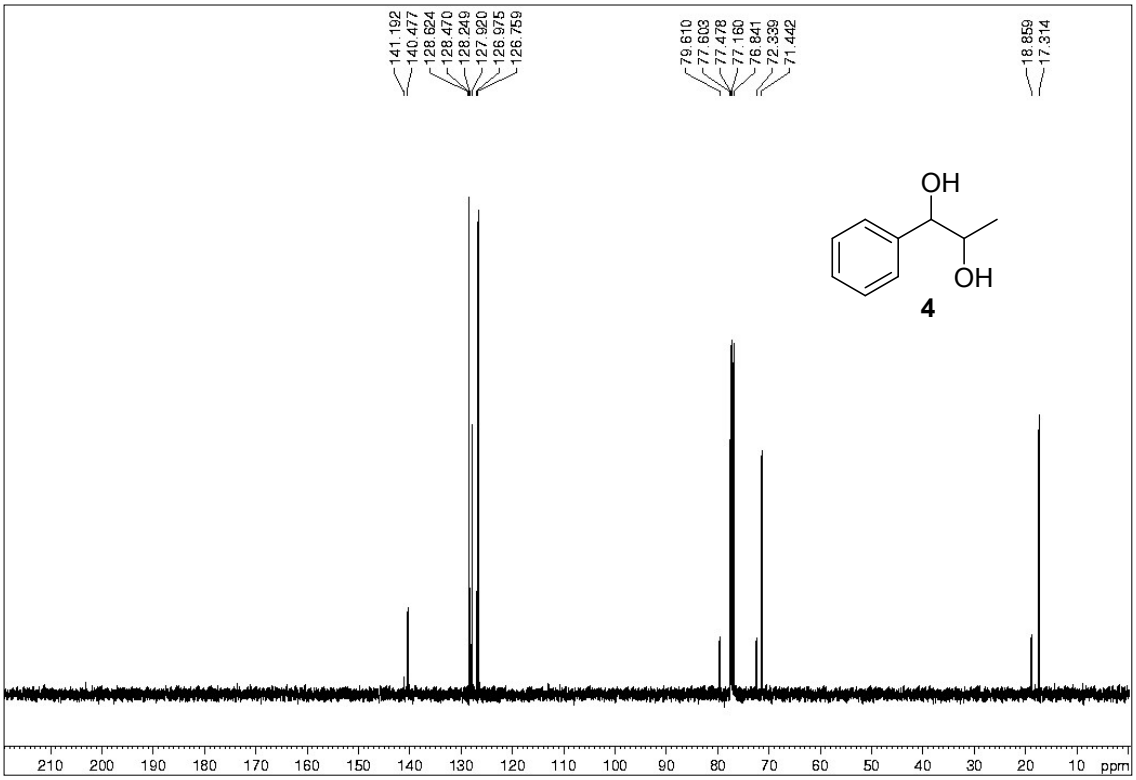


Figure 66: ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$)

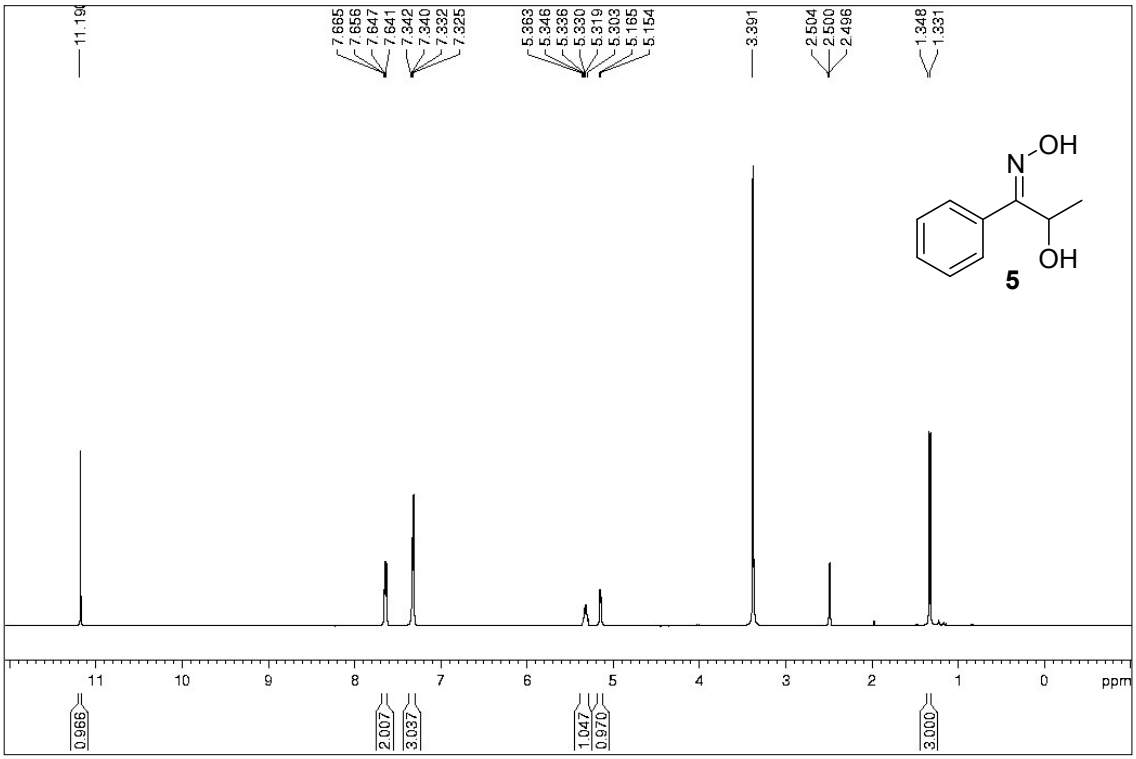


Figure 67: ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)

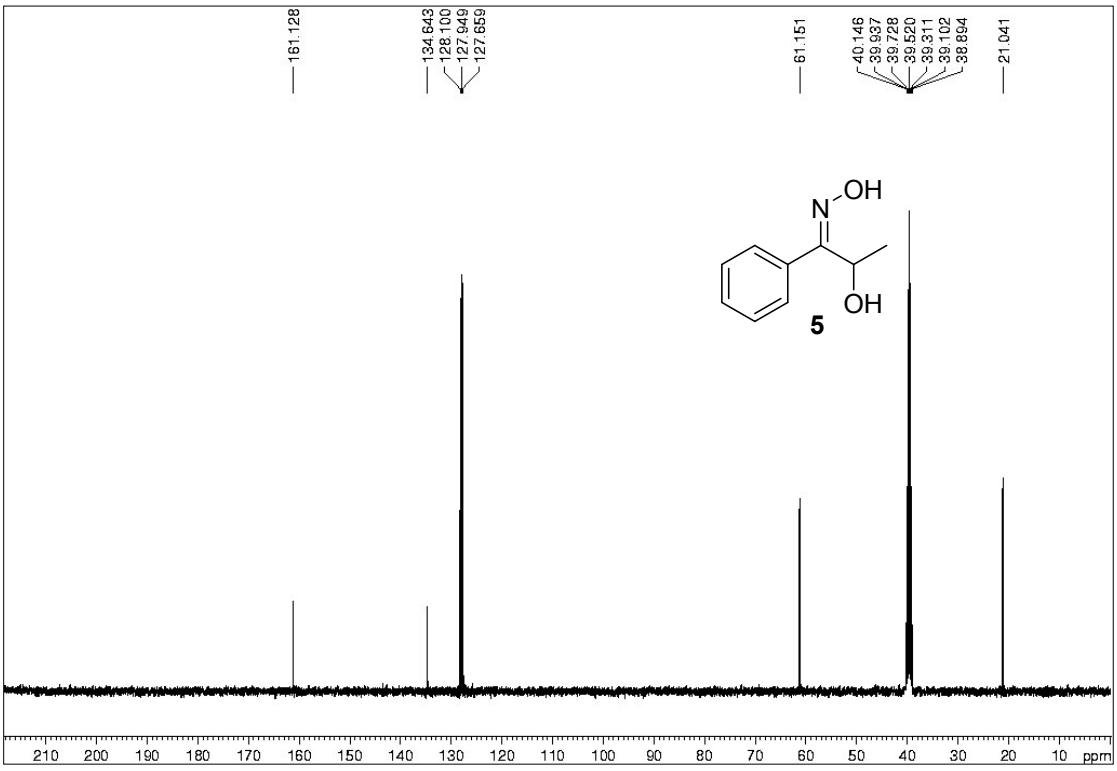


Figure 68: ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$)

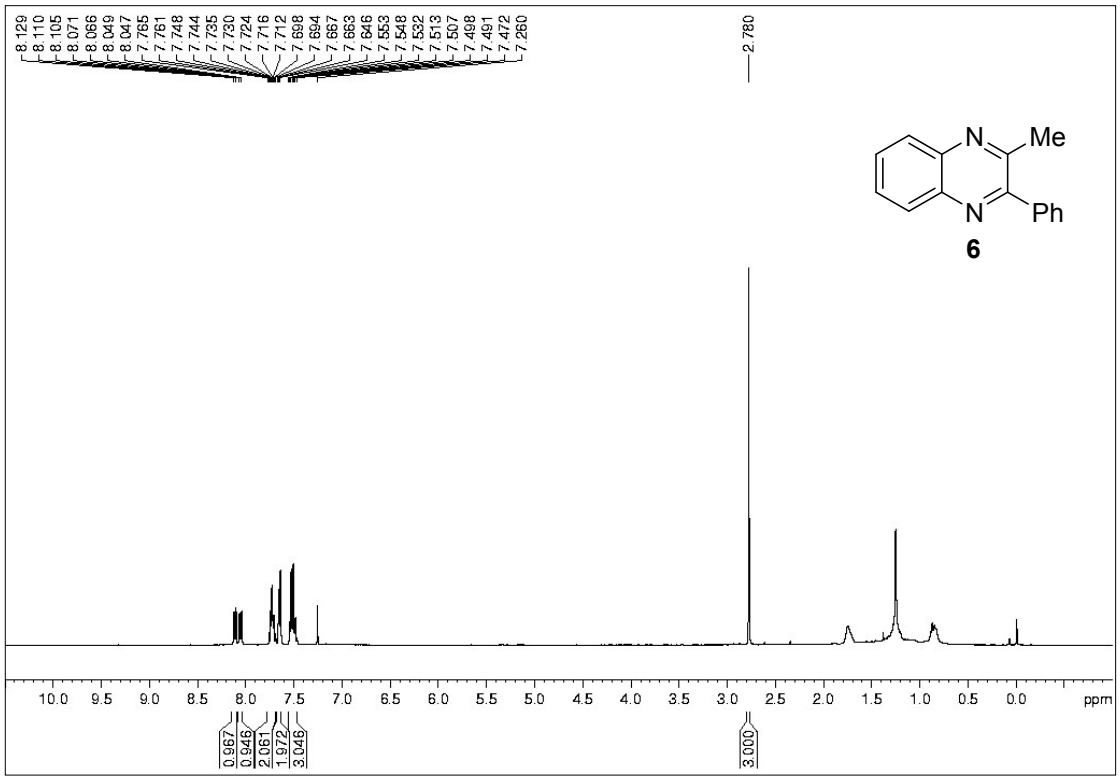


Figure 69: ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)

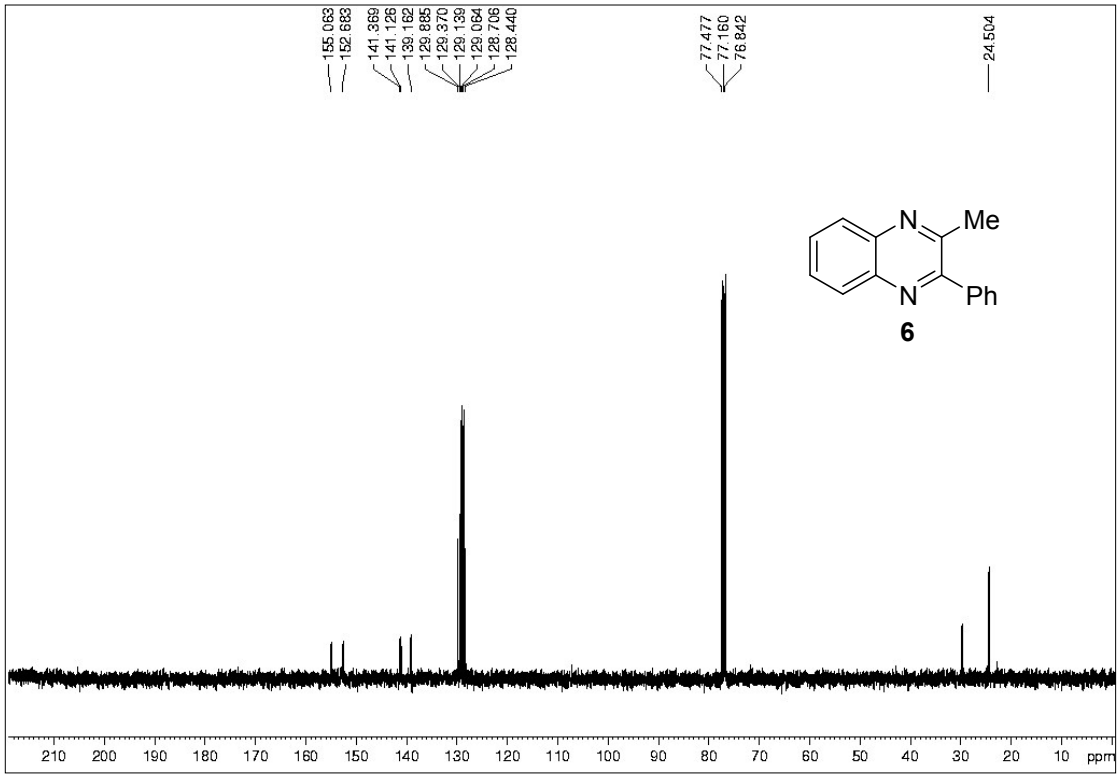


Figure 70: ^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$)

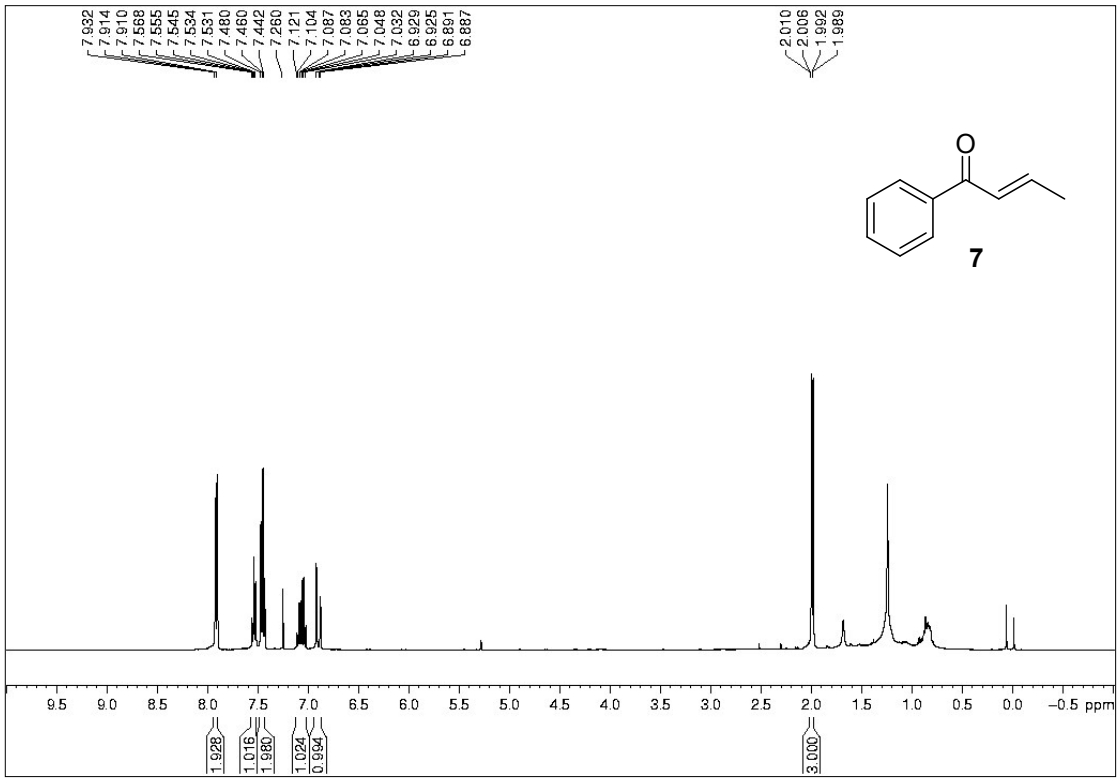


Figure 63: ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)

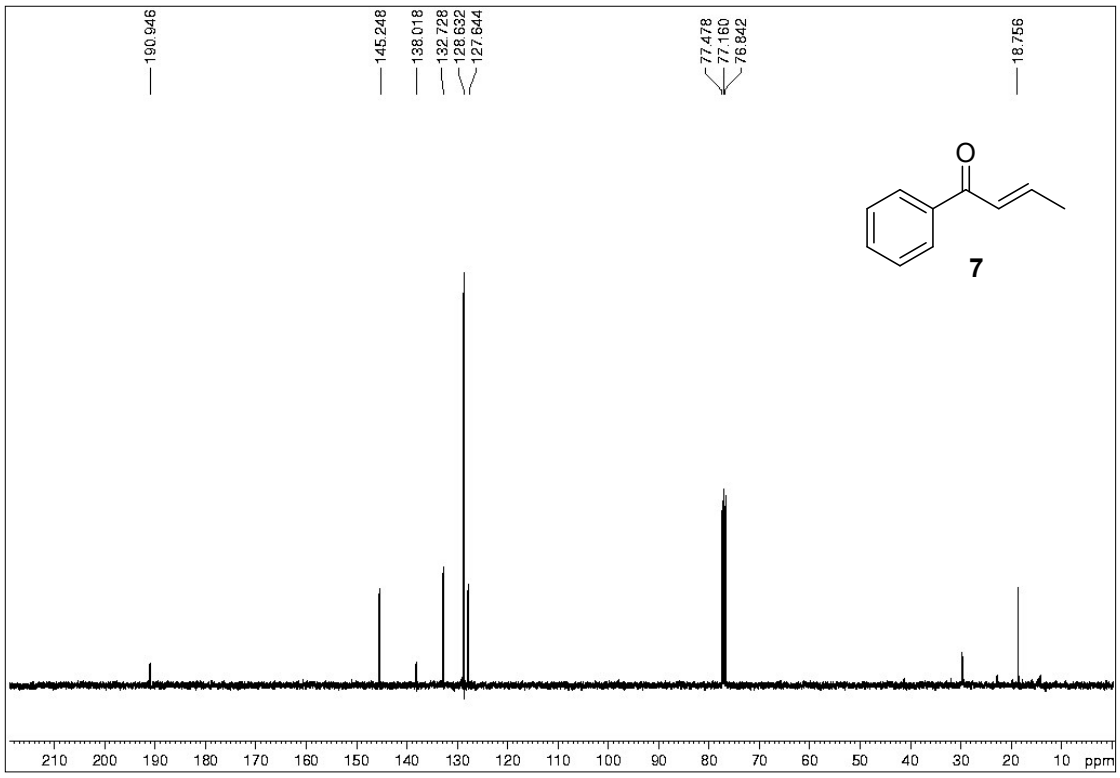


Figure 64: ^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$)

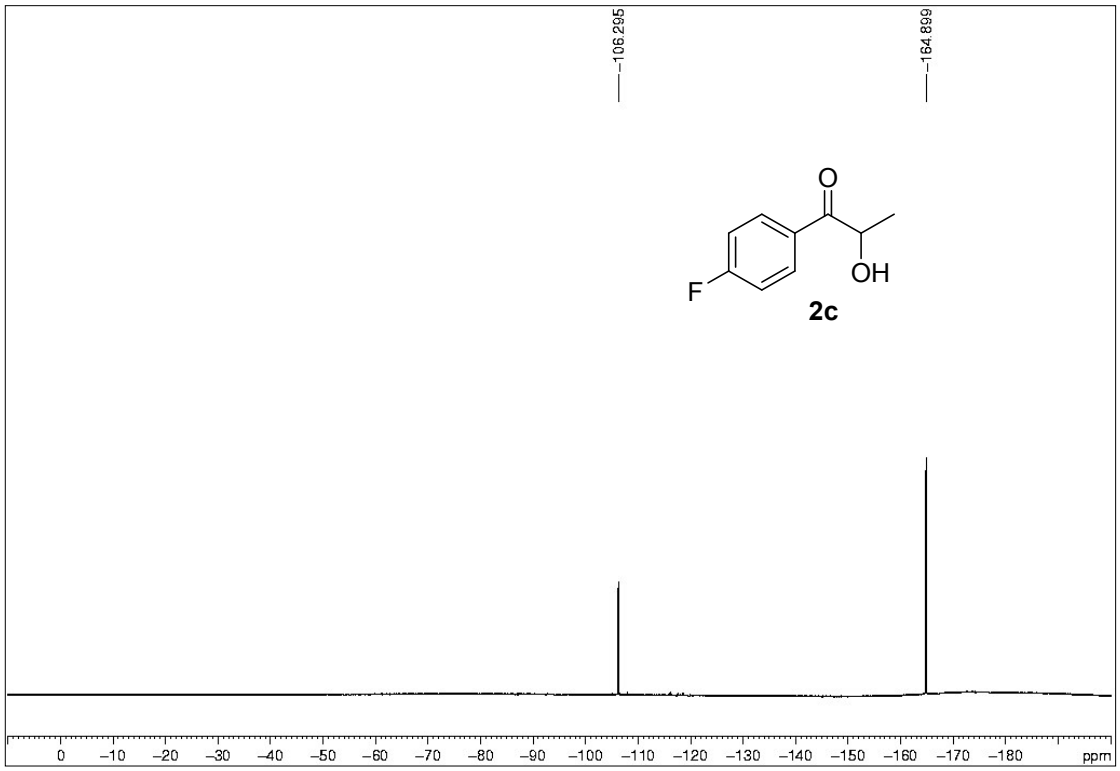


Figure 71: ^{19}F NMR spectrum of **2c** (470 MHz, $CDCl_3$)

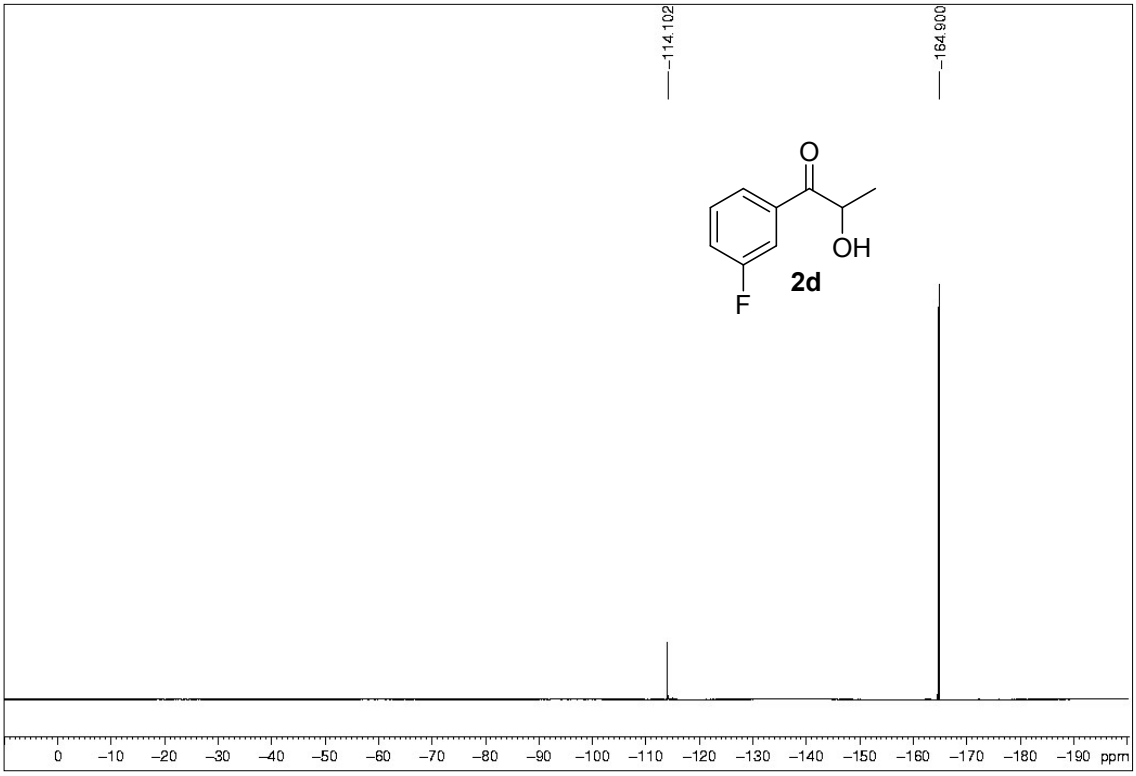


Figure 72: ^{19}F NMR spectrum of **2d** (470 MHz, $CDCl_3$)

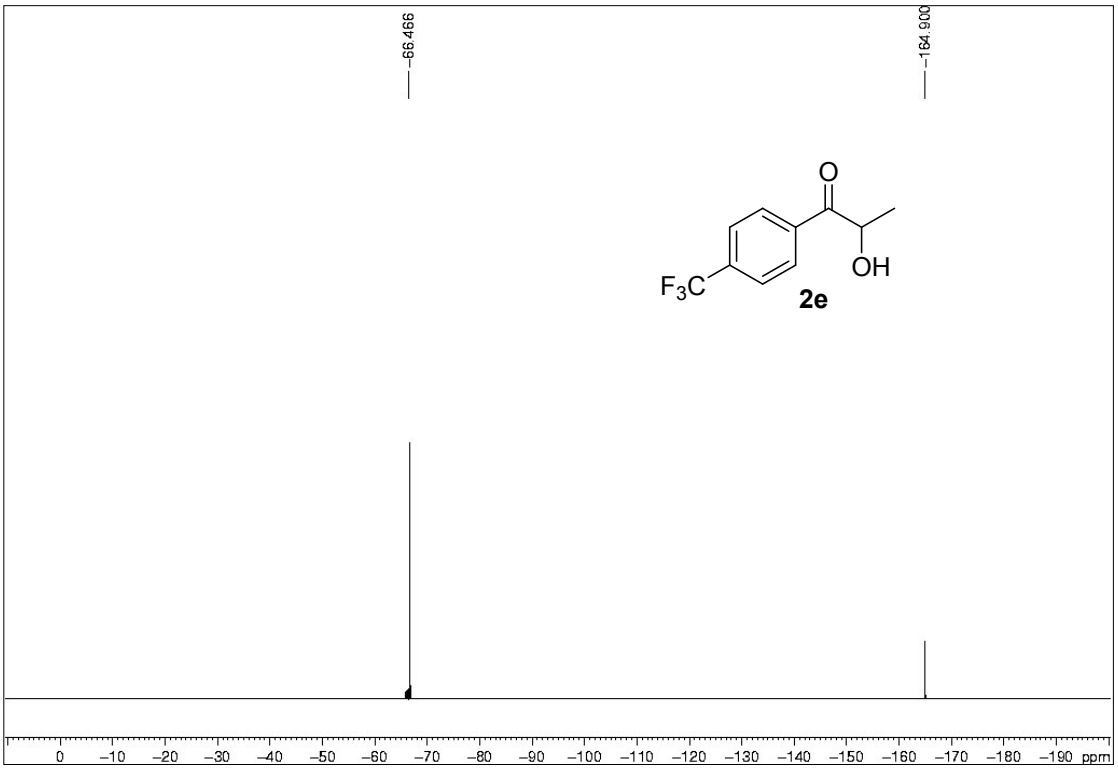


Figure 73: ^{19}F NMR spectrum of **2e** (470 MHz, $CDCl_3$)

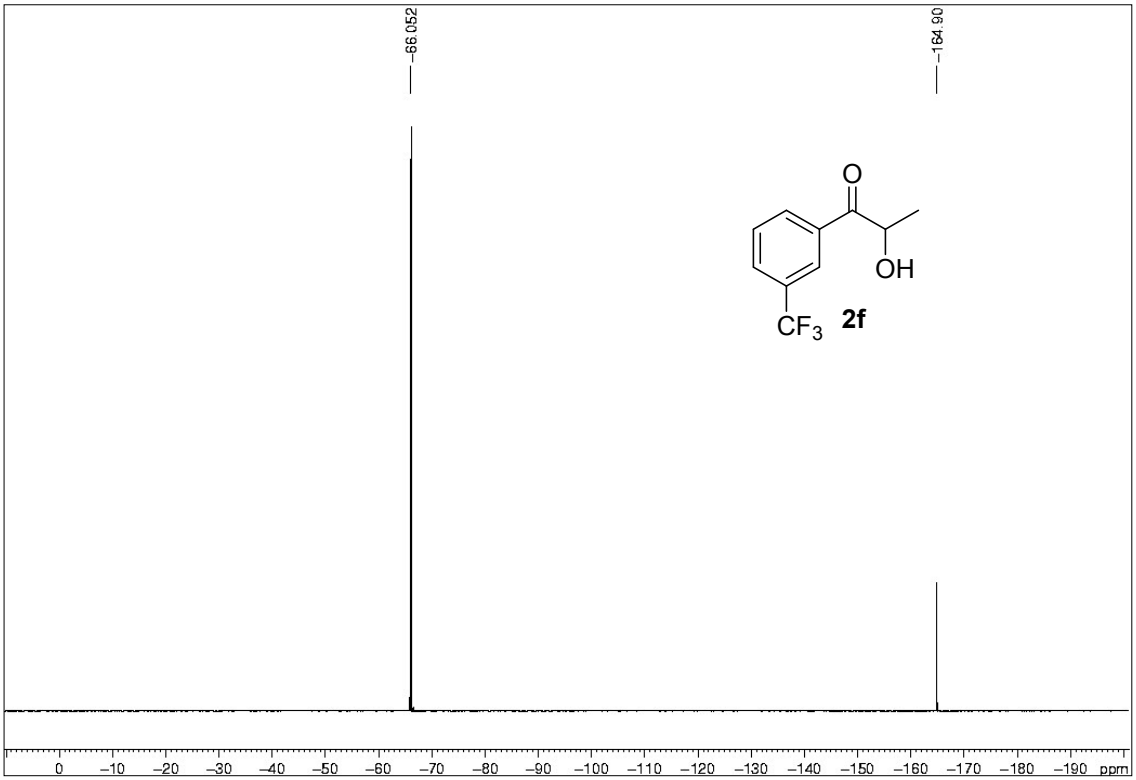


Figure 74: ^{19}F NMR spectrum of **2f** (470 MHz, $CDCl_3$)

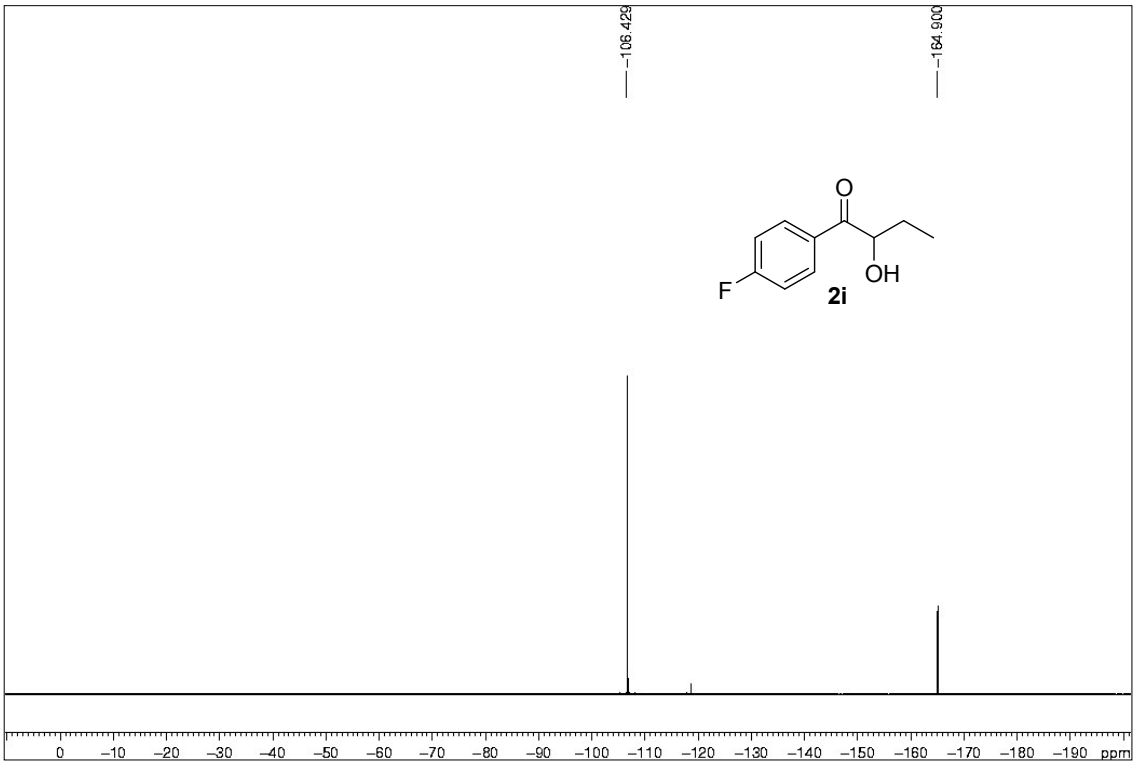


Figure 75: ^{19}F NMR spectrum of **2i** (470 MHz, $CDCl_3$)

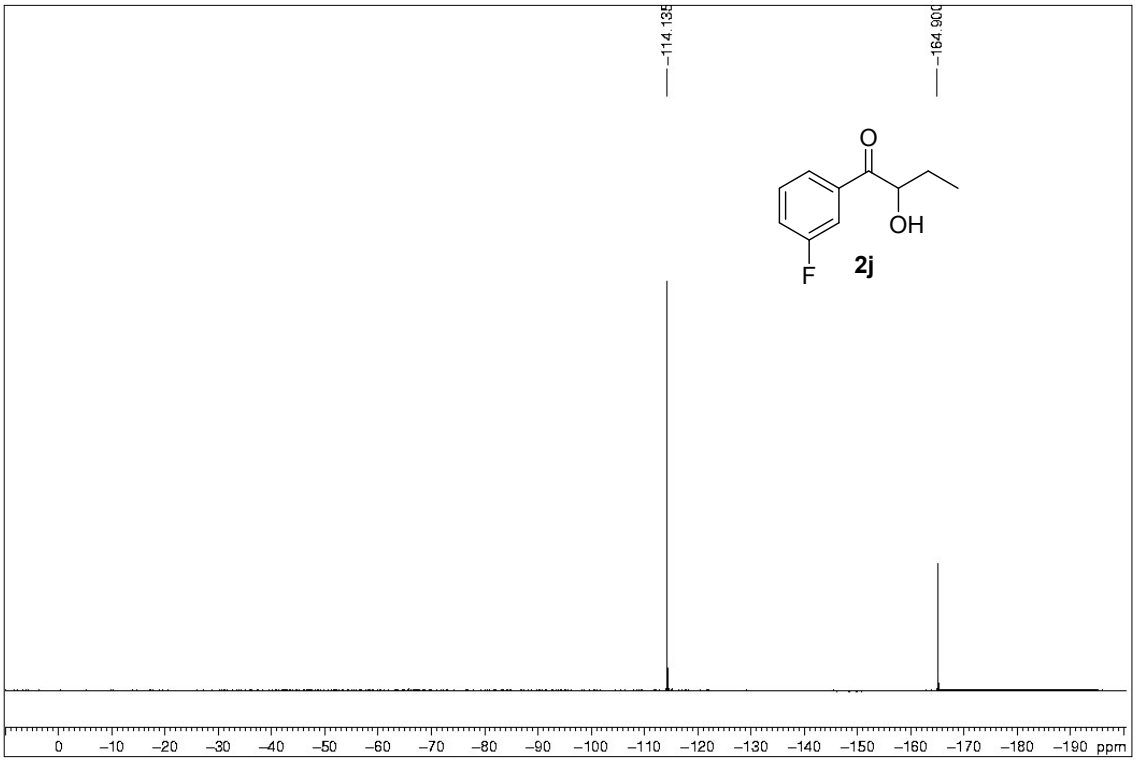


Figure 76: ^{19}F NMR spectrum of **2j** (470 MHz, $CDCl_3$)

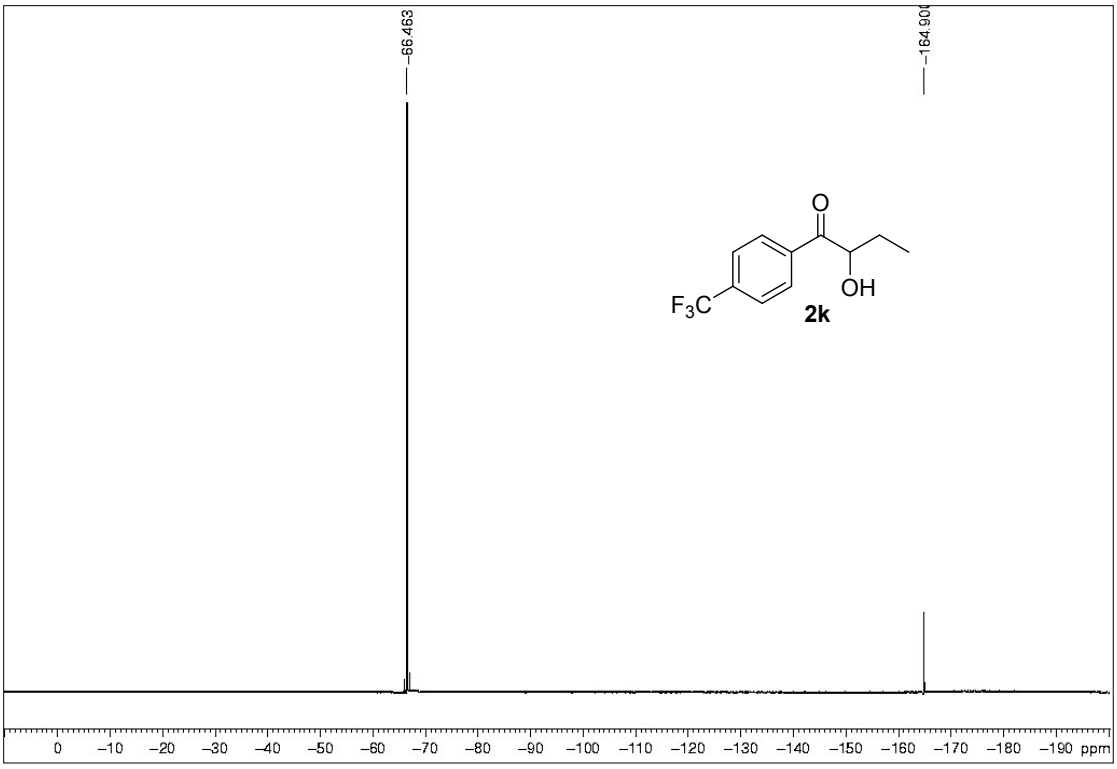


Figure 77: ^{19}F NMR spectrum of **2k** (470 MHz, $CDCl_3$)

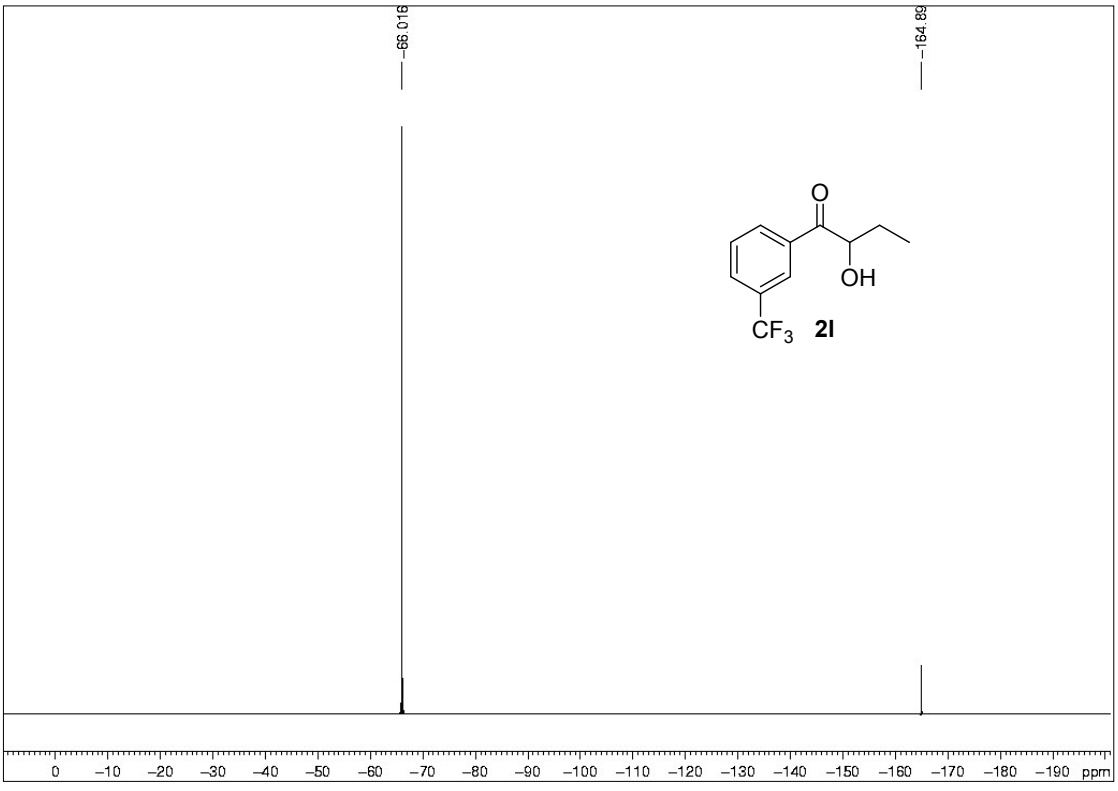


Figure 78: ^{19}F NMR spectrum of **2l** (470 MHz, $CDCl_3$)

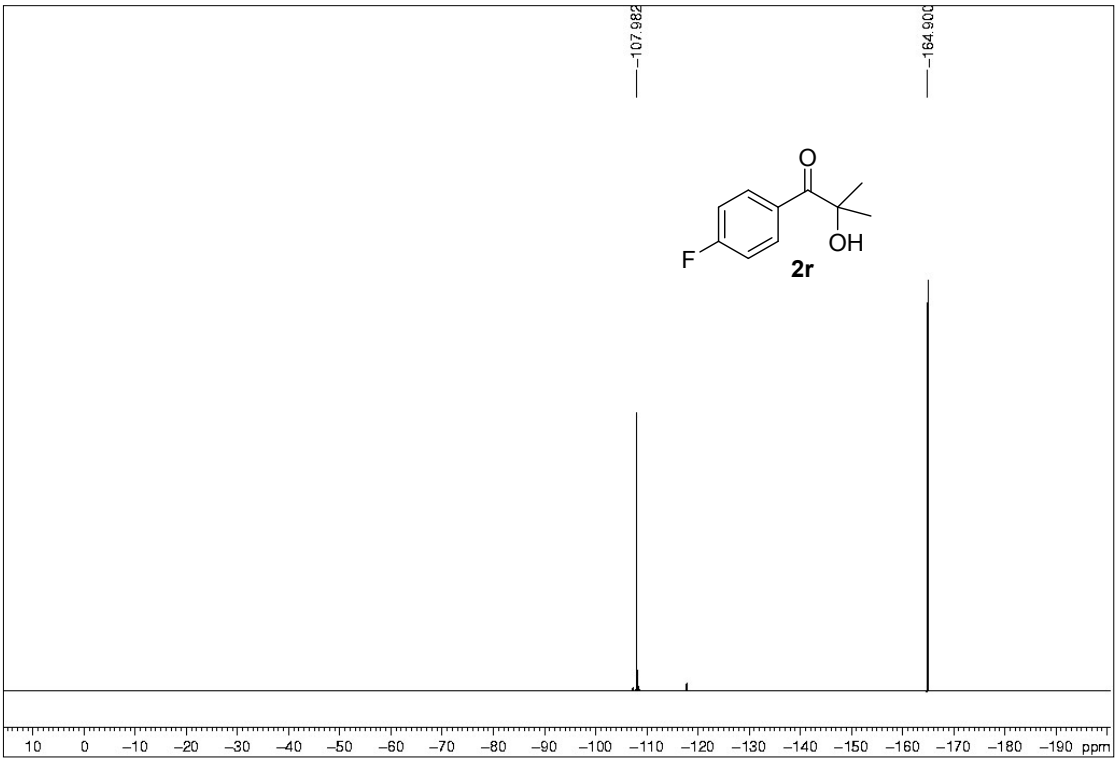


Figure 79: ^{19}F NMR spectrum of **2r** (470 MHz, $CDCl_3$)

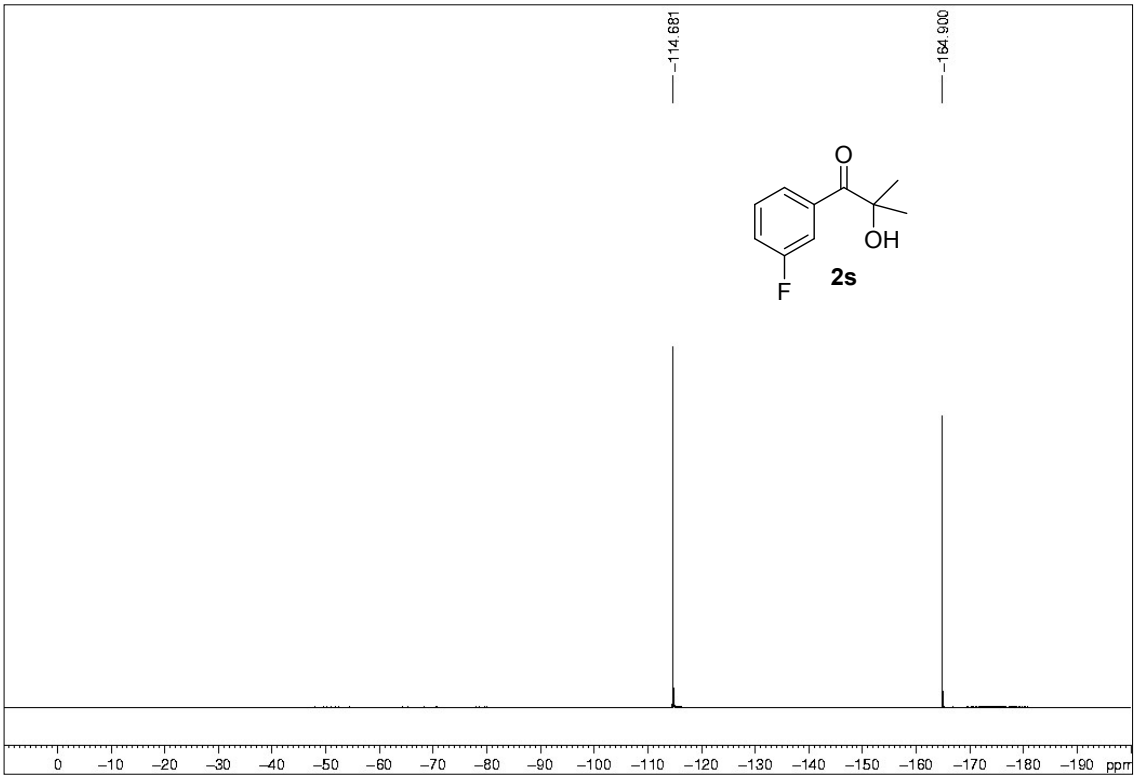


Figure 80: ^{19}F NMR spectrum of **2s** (470 MHz, $CDCl_3$)

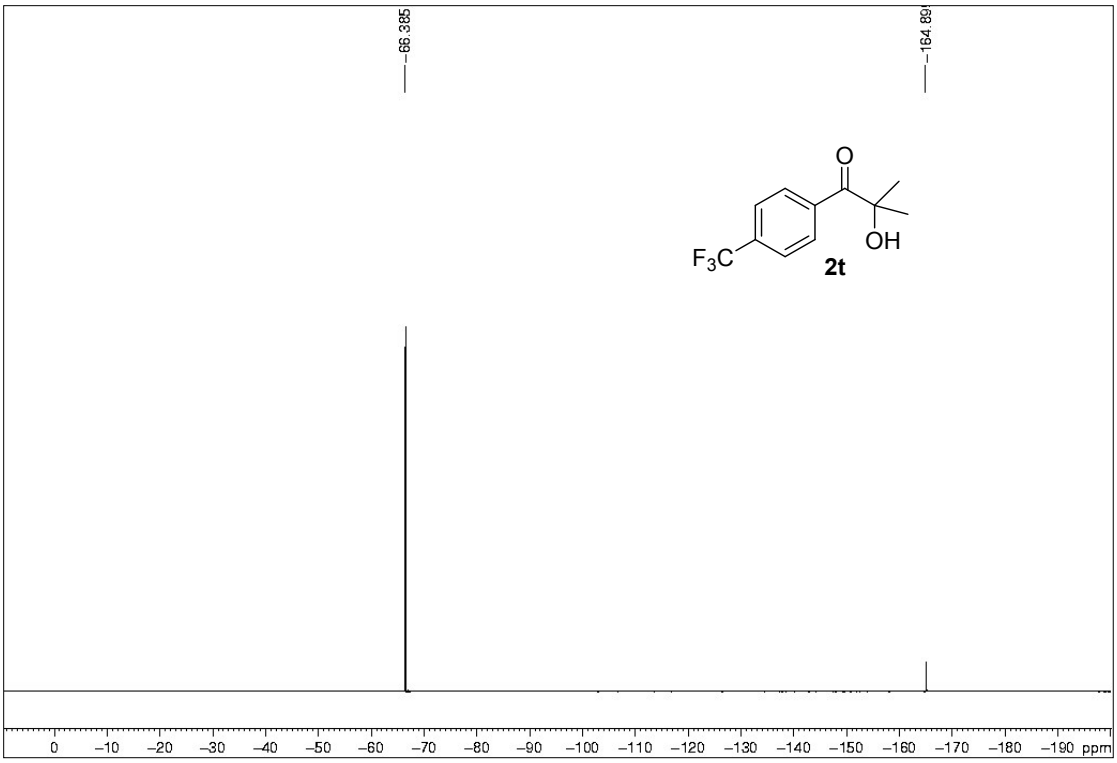


Figure 81: ^{19}F NMR spectrum of **2t** (470 MHz, $CDCl_3$)

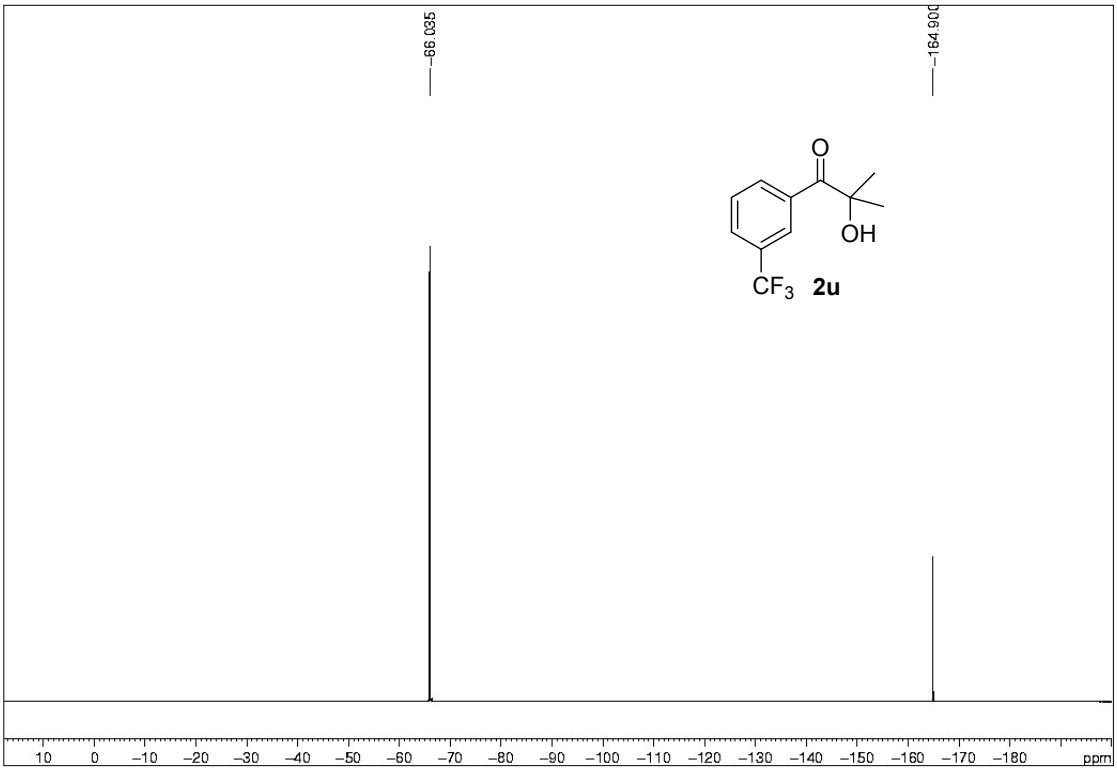


Figure 82: ^{19}F NMR spectrum of **2u** (470 MHz, $CDCl_3$)

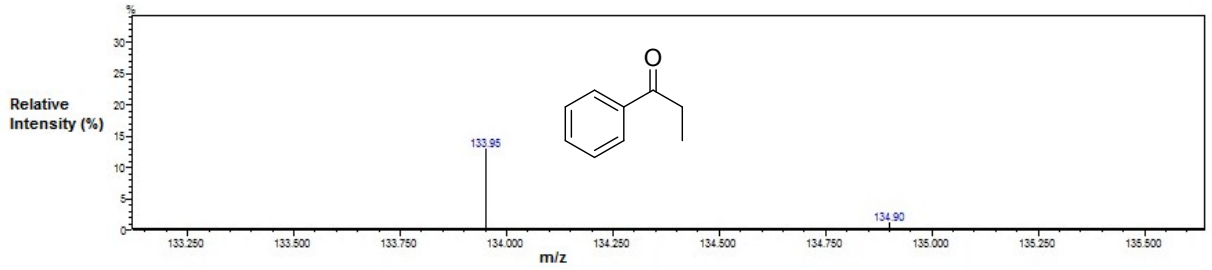


Figure 83: Mass spectra of reaction mixture showing propiophenone intermediate