Supporting Information

for

Controlling the Selectivity and Efficiency of the Hydrogen Borrowing Reaction by Switching Between Rhodium and Iridium Catalysts

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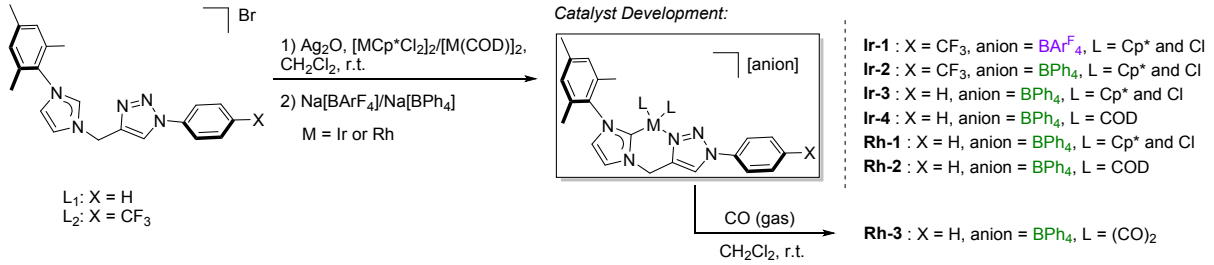
S1.1 General considerations

Unless otherwise specified, all manipulations were performed under inert atmosphere using standard Schlenk techniques or vacuum techniques[1] in a nitrogen or argon-filled Braun glovebox. All reagents were purchased from Aldrich Chemical Company Inc. or Alfa Aesar Inc. and used as received unless otherwise noted. $RhCl_3 \cdot xH_2O$ and $IrCl_3 \cdot xH_2O$ were purchased from Precious Metals Online PMO P/L. For all the air-sensitive and moisture-sensitive manipulations and preparations, acetonitrile, dichloromethane, tetrahydrofuran and pentane were dispensed from a LC Technology solvent purification system and stored under nitrogen or argon atmospheres in glass ampoules fitted with Young's Teflon valve. The bulk compressed gases argon (> 99.999%) and carbon monoxide (> 99.5%) were obtained from Air Liquide and used as received. Nitrogen gas for Schlenk line operation comes from in-house liquid nitrogen boil-off.

The Ir and Rh complexes studied in this work were synthesized using literature procedures.[2-4] ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker Jones 400, Ripley 500 and DMX 600 spectrometers operating at 400, 500 and 600 MHz (^{1}H) respectively and 101, 126 and 150 MHz (^{13}C) respectively. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were referenced internally to residual solvent resonances. Unless otherwise stated, spectra were recorded at 298 K and chemical shifts (d), with uncertainties ± 0.01 Hz for 1H and ± 0.05 Hz for ^{13}C, are quoted in parts per million, ppm. Multiplicity is abbreviated as: s, Singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; t, triplet; q, quartet; dq, doublet of quartets; td, triplet of doublets; m, multiplet; br, broad. Deuterated solvents were purchased from Cambridge Stable Isotopes and used as received. Air sensitive NMR samples were prepared in an inert gas glovebox or by vacuum transfer of deuterated solvents into NMR tubes fitted with a Young's Teflon valve.

S1.2 Synthesis

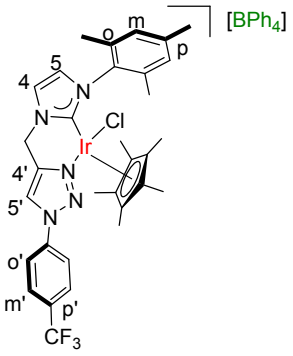
S1.2.1 General synthetic routes of the catalysts



Scheme S1 Synthetic routes of the metal complexes. COD = 1,5-cyclooctadiene.

Ligand $\mathbf{L_1}$ and $\mathbf{L_2}$, complexes **Ir-1**, **Rh-2** and **Rh-3** were reported in literature.[4]

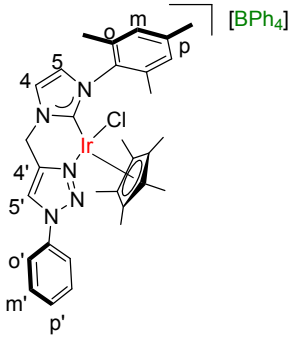
S1.2.2 Synthesis of **Ir-2**



Ligand $\mathbf{L_2}$ (111.1 mg, 0.225 mmol) was dissolved in CH_2Cl_2 (20 mL) followed by adding Ag_2O (91.4 mg, 0.390 mmol). The reaction mixture was stirred at room temperature overnight. The solid was removed filtering through Celite and washed thoroughly with CH_2Cl_2. The solvent was removed under reduced pressure and re-dissolved with CH_2Cl_2 (20 mL). $[IrCp^*Cl_2]_2$ (90.0 mg, 0.187 mmol) was added into the mixture prior to the addition of $Na[BPh_4]$ (77.0 mg, 0.225 mmol) and the mixture was stirred for 3 hours under N_2. The solvent was concentrated *in vacuo* to *ca*. 2 mL and pentane (25 mL) was added. Yellow precipitate forms in solution with vigorous stirring. The solid was dried *in vacuo* to afford the product as a yellow solid. (200.0 mg, 80%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.81 (d, $^3J_{Ho'\text{-}Hm'}$ = 8.5 Hz, 2H, *o*'-C**H** of Ph), 7.62 (d, $^3J_{Ho'\text{-}Hm'}$ = 8.4 Hz, 2H, *m*'-C**H** of Ph), 7.43 (br s, 8H, *o*-C**H** of BPh_4), 6.97 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 8H, *o*-C**H** of BPh_4 overlapped with Im-**H**4), 6.94 (s, 1H, *m*-C**H** of Mes), 6.93 (s, 1H, *m*-C**H** of Mes), 6.80 – 6.79 (m, 5H, *p*-C**H** of BPh_4 overlapped with Im-**H**5), 6.69 (s, 1H, Tz-**H**5'), 4.55 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_2$), 4.19 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_2$), 2.32 (s, 3H, *p*-C**H**$_3$ of Mes), 2.10 (s, 3H, *o*-C**H**$_3$ of Mes), 1.96 (s, 3H, *o*-C**H**$_3$ of Mes), 1.43 (s, 15H, C**H**$_3$ of Cp*) ppm. ^{13}C{^{1}H} NMR (101 MHz, Methylene Chloride-d_2) δ 164.7 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C**$_q$ of BPh_4), 152.9 (Im-**C**2), 141.8 (Tz-**C**4'), 140.5 (*p*-**C**CH$_3$ of Mes), 139.4 (*o*-**C**CH$_3$ of Mes), 138.8 (*ipso*-**C**$_q$ of $ArCF_3$), 136.7 (br s, *o*-**C**H of BPh_4), 135.8 (*ipso*-**C**$_q$ of Mes), 135.2 (*o*-**C**CH$_3$ of Mes), 132.7 (q, $^2J_{C\text{-}F}$ = 33.3 Hz, *p*'-**C**CF$_3$ of $ArCF_3$), 130.1 (*m*-**C**H of Mes), 128.8 (*m*-**C**H of Mes), 128.1 (q, $^3J_{C\text{-}F}$ = 3.44 Hz, *m*'-**C**H of $ArCF_3$), 126.8, (br s, *m*-**C**H of

BPh_4), 126.2 (Im-**C**5), 124.3 (q, $^1J_{C\text{-}F}$ = 272.0 Hz, Ar**C**F_3), 124.0 (Im-**C**4), 123.0 (*p*-**C**H of BPh_4), 122.5 (Tz-**C**5'), 121.9 (*o*'-**C**H of ArCF_3), 92.3 (**C**q of Cp*), 45.6 (**C**H_2), 21.6 (*p*-**C**H_3 of Mes), 20.5 (*o*-**C**H_3 of Mes), 19.8 (*o*-**C**H_3 of Mes), 10.0 (**C**H_3 of Cp*) ppm. HRMS (ESI^+, MeOH) calculated for $[C_{32}H_{35}ClF_3IrN_5]^+ = [M\text{-}BPh_4]^+$ = 774.2162; found $[C_{32}H_{35}ClF_3IrN_5]^+ = [M\text{-}BPh_4]^+$ = 774.2150. Elemental analysis calculated for $C_{56}H_{56}BClF_3IrN_5$: C, 61.51; H, 5.07; N, 6.40%; found C, 61.30; H, 5.62; N, 5.22% (deviations likely due to moisture).

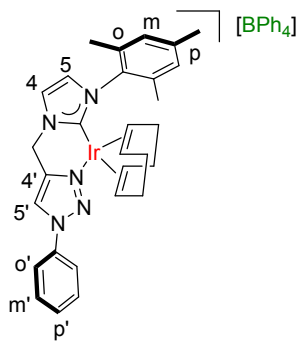
S1.2.3 Synthesis of Ir-3



Ligand **L_1** (126.9 mg, 0.300 mmol) was dissolved in CH_2Cl_2 (20 mL) followed by adding Ag_2O (121.3 mg, 0.523 mmol). The reaction mixture was stirred at room temperature overnight. The solid was removed filtering through Celite and washed thoroughly with CH_2Cl_2. The solvent was removed under reduced pressure and re-dissolved with CH_2Cl_2 (20 mL). $[IrCp^*Cl_2]_2$ (118.6 mg, 0.149 mmol) was added into the mixture prior to the addition of Na[BPh_4] (102.6 mg, 0.300 mmol) and the mixture was stirred for 3 hours under N_2. The solvent was concentrated *in vacuo* to *ca*. 2 mL and pentane (25 mL) was added. Yellow precipitate forms in solution with vigorous stirring. The solid was dried *in vacuo* to afford the product as a yellow solid. (230.8 mg, 75%). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.58 – 7.53 (m, 5H, *o*'-, *m*'- and *p*'-CH of Ph), 7.43 – 7.37 (br s, 8H, *o*-C**H** of BPh_4), 6.99 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 9H, *m*-C**H** of BPh_4 overlapped with Tz-**H**5), 6.93 – 6.94 (m, 3H, Im-**H**5 overlapped with *m*-C**H** of Mes), 6.92 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, 1H, Im-**H**5), 6.85 – 6.82 (t, 4H, $^3J_{H\text{-}H}$ = 7.3 Hz, 4H, *p*-C**H** of BPh_4), 6.79 (d, $^3J_{H4\text{-}H5}$ = 2.0, 1H, Im-**H**4), 4.55 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_2$), 4.20 (d, $^2J_{H\text{-}H}$ = 15.8 Hz, 1H, C**H**$_2$), 2.32 (s, 3H, *p*-C**H**$_3$ of Mes), 2.10 (s, 3H, *o*-C**H**$_3$ of Mes), 1.96 (s, 3H, *o*-C**H**$_3$ of Mes), 1.43 (s, 15H, C**H**$_3$ of Cp*) ppm. ^{13}C{^{1}H} NMR (126 MHz, Methylene Chloride-d_2) δ 164.8 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C**$_q$ of BPh_4), 152.9 (Im-**C**2), 141.4 (Tz-**C**4'), 140.5 (*p*-**C**CH_3 of Mes), 139.4 (*o*-**C**CH_3 of Mes), 136.8 (br s, *o*-**C**H of BPh_4), 136.6 (*ipso*-**C**$_q$ of Ph), 135.8 (*ipso*-**C**q of Mes), 135.3 (*o*-**C**CH_3 of Mes), 131.2 (*p*'-**C**H of Ph), 130.8 (*o*'-**C**H of Ph), 130.1 (*m*-**C**H of Mes), 128.8 (*m*-**C**H of Mes), 126.7 (br s, *m*-**C**H of BPh_4), 126.1 (Im-**C**4), 124.0 (Im-**C**5), 122.9 (*p*-**C**H of BPh_4), 122.4 (Tz-**C**5'), 121.6 (*m*'-**C**H of Ph), 92.2 (**C**q of Cp*), 45.6 (**C**H_2), 21.6 (*p*-**C**H_3 of Mes), 20.5 (*o*-**C**H_3 of Mes), 19.8 (*o*-**C**H_3 of Mes), 10.0 (**C**H_3 of Cp*) ppm. HRMS (ESI^+, MeOH) calculated for $[C_{31}H_{36}ClIrN_5]^+ = [M\text{-}BPh_4]^+$ = 706.2888;

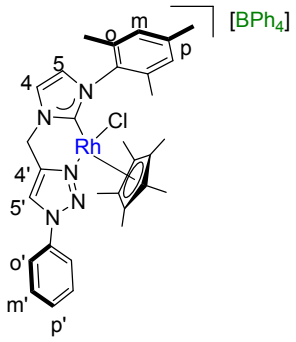
found $[C_{31}H_{36}ClIrN_5]^+$ = $[M\text{-}BPh_4]^+$ = 706.2876. Elemental analysis calculated for $C_{53}H_{54}BIrN_5$: C, 64.41; H, 5.50; N, 6.83%; found C, 64.39; H, 5.62; N, 6.99%.

S1.2.4 Synthesis of Ir-4



Ligand $\mathbf{L_1}$ (159.2 mg, 0.374 mmol) was dissolved in CH_2Cl_2 (20 mL) followed by adding Ag_2O (72.4 mg, 0.312 mmol). The reaction mixture was stirred at room temperature overnight. The solid was removed filtering through Celite and washed thoroughly with CH_2Cl_2. The solvent was removed under reduced pressure and re-dissolved with CH_2Cl_2 (20 mL). $[Ir(COD)Cl]_2$ (125.1 mg, 0.187 mmol) was added into the mixture prior to the addition of $Na[BPh_4]$ (127.6 mg, 0.373 mmol) and the mixture was stirred for 3 hours under N_2. The solvent was concentrated *in vacuo* to *ca*. 2 mL and pentane (25 mL) was added. Yellow precipitate forms in solution with vigorous stirring. The solid was dried *in vacuo* to afford the product as a red-pink solid. (230.1 mg, 64%) ^{1}H NMR (600 MHz, Methylene Chloride-d_2): δ 7.55 (m, 3H, *o*'- and *p*'-C**H** of Ph), 7.50 (m, 2**H**, *m*'-C**H** of Ph), 7.42 (m, 8H, *o*-C**H** of BPh_4), 7.02 (s, 2H, m-C**H** of Mes), 6.99 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 8H, *m*-C**H** of BPh_4), 6.93 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, 1H, Im-**H**5), 6.90 (s, 1H, Tz-**H**5'), 6.83 (d,$^3J_{H4\text{-}H5}$ = 2.0 Hz, 1H, Im-**H**4), 6.82 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 4H, *p*-C**H** of BPh_4), 4.65 (m, 2H, =C**H** of COD), 4.59 (s, 2H, C$\mathbf{H}_2$), 3.45 (m, 2H, =C**H** of COD), 2.36 (s, 3H, *p*-C$\mathbf{H}_3$ of Mes), 2.10 (m, 2H, C$\mathbf{H}_2$ of COD), 2.07 (s, 6H, *o*-C$\mathbf{H}_3$ of Mes), 1.83 (m, 6H, C$\mathbf{H}_2$ of COD) ppm. ^{13}C NMR (150 MHz, Methylene Chloride-d_2): *δ* 172.5 (Im-**C**2), 164.5 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, ipso-**C**q of BPh_4), 140.3 (*p*-**C**CH_3 of Mes), 139.1 (Cq, Tz-**C**4'), 136.3 (br s, *o*-**C**H of BPh_4), 136.1 (ipso-**C**q of Ph), 135.7 (*o*-**C**CH_3 of Mes), 135.6 (ipso-**C**q of Mes), 130.7 (*p*'-**C**H of Ph), 130.4 (*o*'-**C**H of Ph), 129.5 (*m*-**C**H of Mes), 126.3 (br s, *m*-**C**H of BPh_4), 123.5 (Im-**C**4), 122.4 (Tz-**C**5'), 122.4 (*p*-**C**H of BPh_4), 121.9 (Im-**C**5), 121.1 (*m*'-**C**H of Ph), 84.0 (2C, =**C**H of COD), 66.2 (2C, =**C**H of COD), 44.9 (**C**H_2), 33.5 (2C, -**C**H_2 of COD), 29.8 (2C, -**C**H_2 of COD), 21.2 (*p*-**C**H_3 of Mes), 18.7 (*o*-**C**H_3 of Mes) ppm. HRMS (ESI^+, MeOH) calculated for $[C_{29}H_{33}IrN_5]^+$ = $[M\text{-}BPh_4]^+$ = 644.2360, found $[C_{29}H_{33}IrN_5]^+$ = $[M\text{-}BPh_4]^+$ = 644.2371). Elemental analysis calculated for $C_{53}H_{54}BIrN_5$: C, 66.10; H, 5.55; N, 7.27%; found C, 66.36; H, 5.35; N, 7.03%.

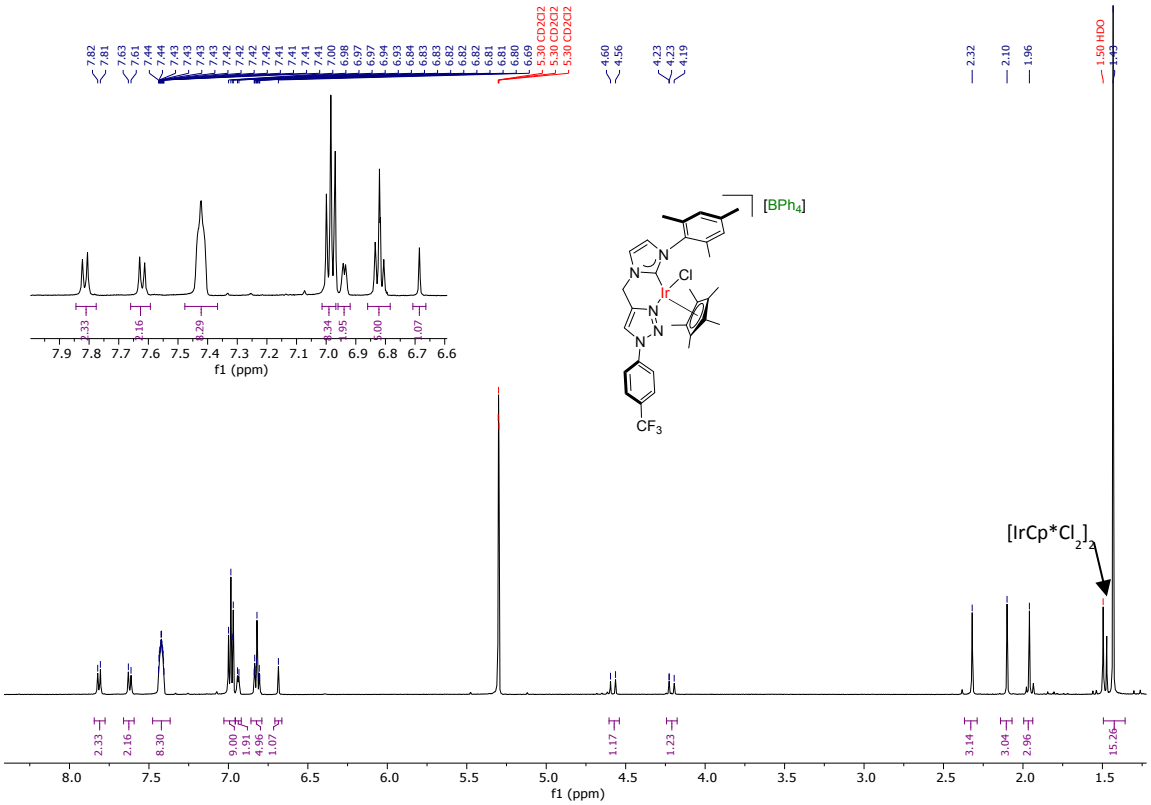
S1.2.5 Synthesis of Rh-1



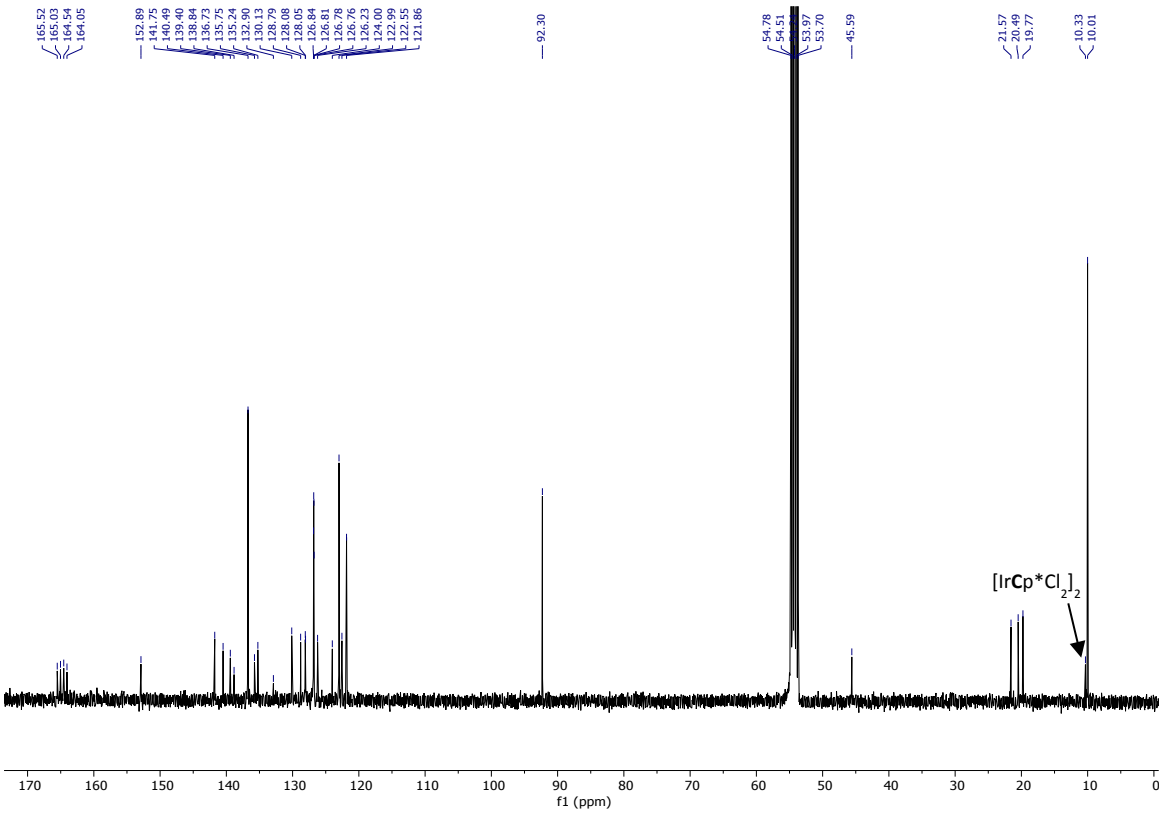
Ligand **L$_1$** (126.9 mg, 0.300 mmol) was dissolved in CH_2Cl_2 (20 mL) followed by adding Ag_2O (121.3 mg, 0.523 mmol). The reaction mixture was stirred at room temperature overnight. The solid was removed filtering through Celite and washed thoroughly with CH_2Cl_2. The solvent was removed under reduced pressure and re-dissolved with CH_2Cl_2 (20 mL). $[RhCp^*Cl_2]_2$ (86.7 mg, 0.149 mmol) was added into the mixture prior to the addition of $Na[BPh_4]$ (102.6 mg, 0.300 mmol) and the mixture was stirred for 3 hours under N_2. The solvent was concentrated *in vacuo* to *ca*. 2 mL and pentane (25 mL) was added. Yellow precipitate forms in solution with vigorous stirring. The solid was dried *in vacuo* to afford the product as a yellow solid. (232.9 mg, 83%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.63 – 7.52 (m, 5H, *o*'-, *m*'- and *p*'-CH of Ph), 7.39 (br s, 8H, *o*-C**H** of BPh_4), 7.26 (s, 1H, Tz-**H**5), 7.04 (d, $^3J_{H4\text{-}H5}$ = 1.9 Hz, 1H, Im-**H**5), 6.99 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 8H, *m*-C**H** of BPh_4), 6.95 (s, 2H, *m*-C**H** of Mes), 6.88 – 6.80 (m, 5H, *p*-C**H** of BPh_4 overlapped with Im-**H**4), 4.86 (d, $^2J_{H\text{-}H}$ = 15.8 Hz, 1H, C**H**$_2$), 4.40 (d, $^2J_{H\text{-}H}$ = 15.7 Hz, 1H, C**H**$_2$), 2.33 (s, 3H, *p*-C**H**$_3$ of Mes), 2.13 (s, 3H, *o*-C**H**$_3$ of Mes), 1.94 (s, 3H, *o*-C**H**$_3$ of Mes), 1.41 (s, 15H, C**H**$_3$ of Cp*).ppm. ^{13}C{^{1}H} NMR (126 MHz, Methylene Chloride-d_2) δ 169.2 (d, $^1J_{Rh\text{-}C}$ = 54.1 Hz, Im-**C**2) 164.7 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C**$_q$ of BPh_4), 142.2 (C$_q$, Tz-**C**4'), 140.5 (*p*-**C**CH_3 of Mes), 139.3 (*o*-**C**CH_3 of Mes), 136.8 (s, *o*-**C**H of BPh_4 overlapped with *ipso*-**C**$_q$ of Ph), 136.0 (ipso-**C**$_q$ of Mes), 135.3 (*o*-**C**CH_3 of Mes), 131.1 (*p'*-**C**H of Ph), 130.8 (*o'*-**C**H of ph), 130.2 (*m*-**C**CH_3 of Mes), 128.9 (*m*-**C**CH_3 of Mes), 126.7 (br s, *m*-**C**H of BPh_4), 126.4 (Im-**C**4), 125.0 (Im-**C**5), 122.9 (*p*-**C**H of BPh_4), 122.8 (Tz-**C**5'), 121.6 (*o'*-**C**H of Ph), 99.3 (d, $^2J_{Rh\text{-}C}$ = 6.9 Hz, **C**$_q$ of Cp*), 45.4 (**C**H_2), 21.6 (*p*-**C**H_3 of Mes), 20.4 (*o*-**C**H_3 of Mes), 19.6 (*o*-**C**H_3 of Mes), 10.2 (**C**H_3 of Cp*) ppm. HRMS (ESI$^+$, MeOH) calculated for $[C_{31}H_{36}N_5Rh]^+$ = $[M\text{-}BPh_4]^+$ = 616.1714; found $[C_{31}H_{36}N_5Rh]^+$ = $[M\text{-}BPh_4]^+$ = 616.1735. Elemental analysis calculated for $C_{53}H_{54}BIrN_5$: C, 70.56; H, 6.03; N, 7.48%; found C, 69.20; H, 6.24; N, 7.85%. (deviations likely due to moisture).

S1.2.6 NMR spectra of Ir and Rh complexes

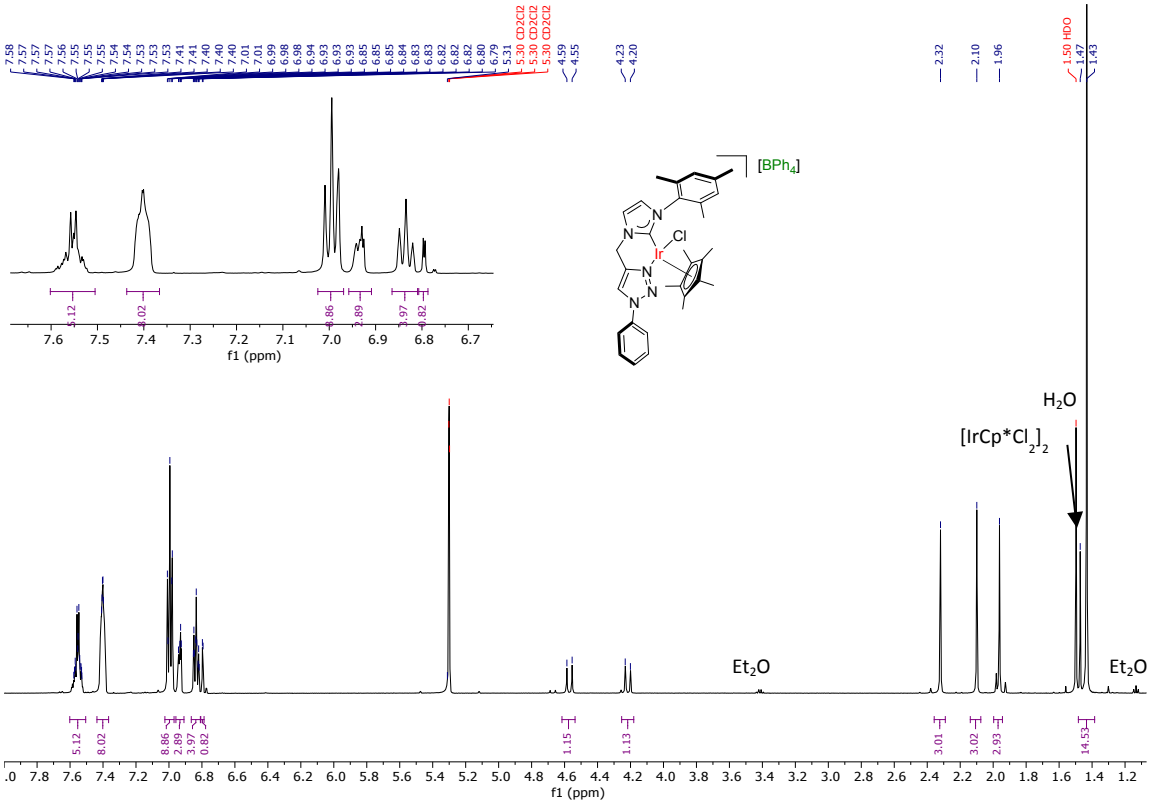
Ir-2 ^{1}H NMR (400 MHz, Methylene Chloride-d_2)



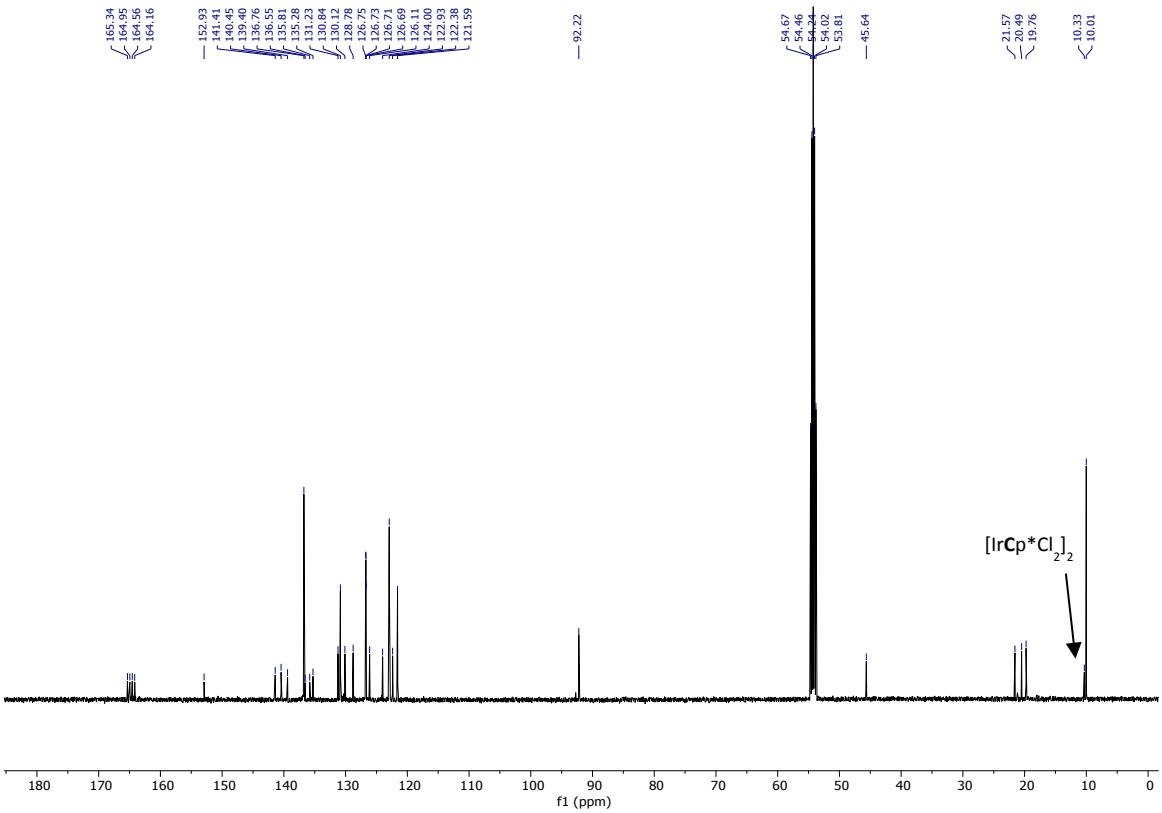
Ir-2 ^{13}C{^{1}H} NMR (101 MHz, Methylene Chloride-d_2)



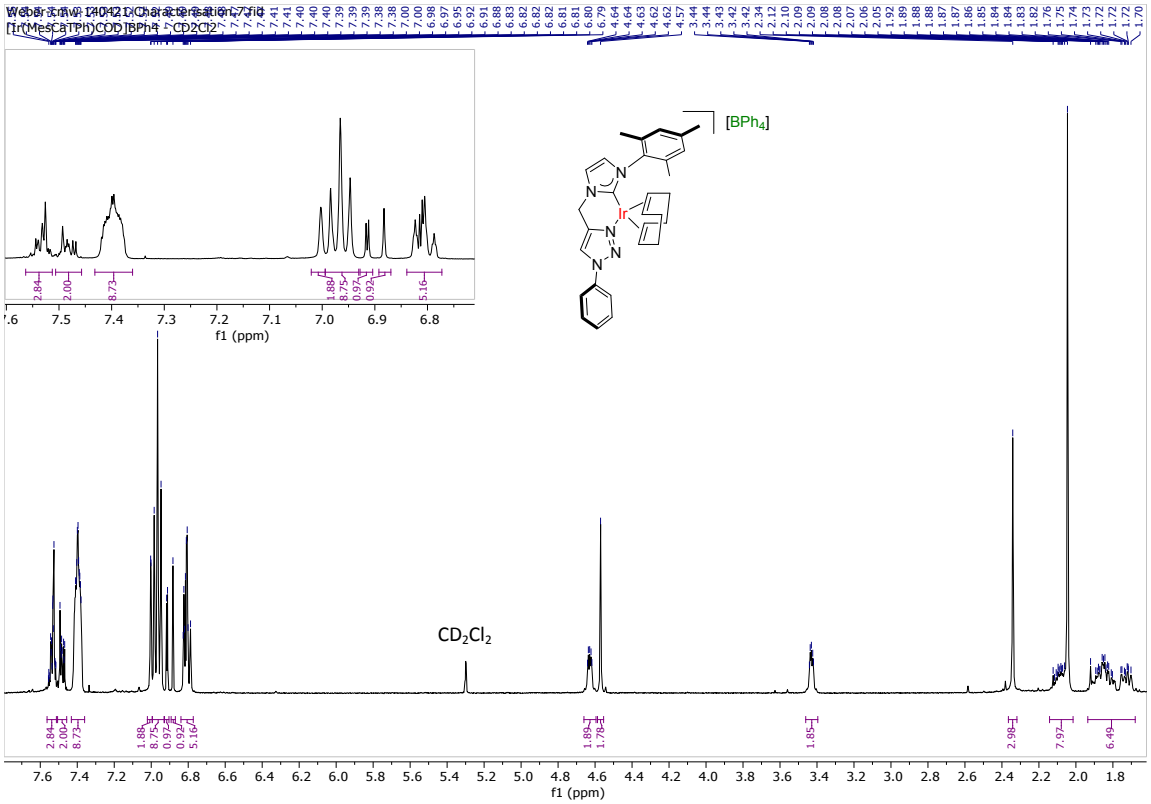
Ir-3 ^{1}H NMR (500 MHz, Methylene Chloride-d_2)



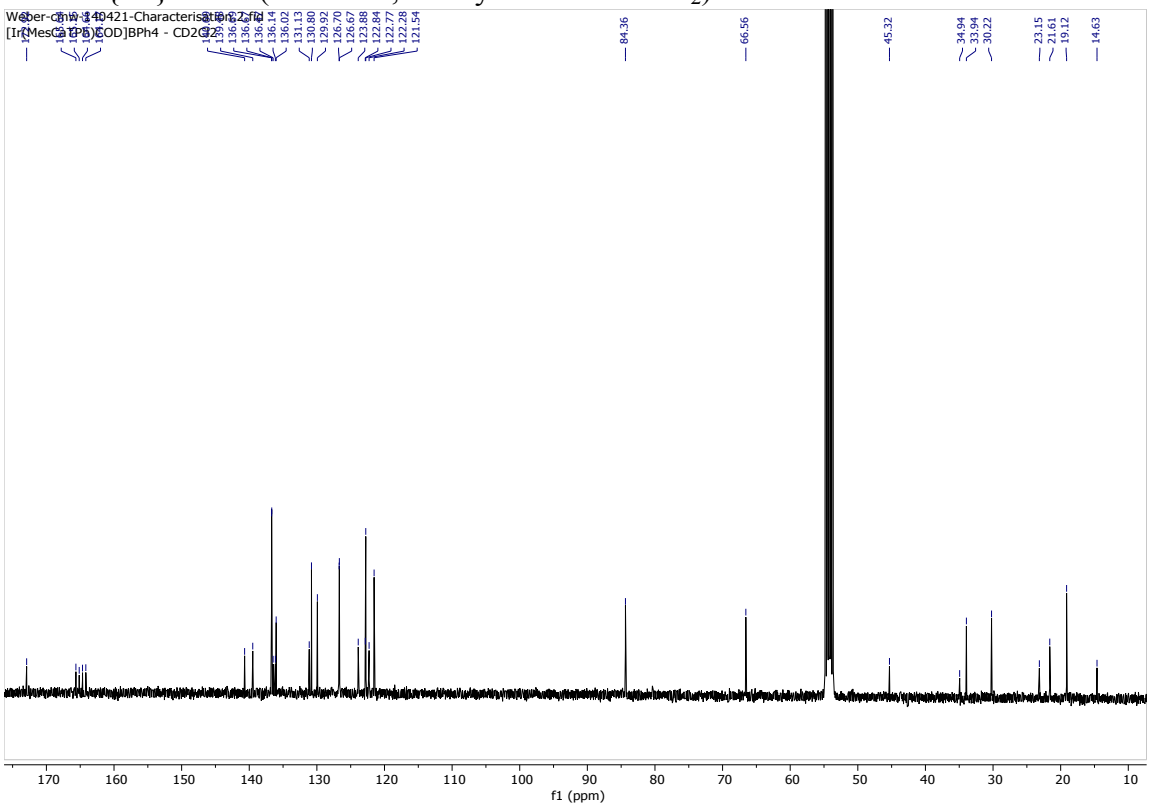
Ir-3 ^{13}C{^{1}H} NMR (126 MHz, Methylene Chloride-d_2)



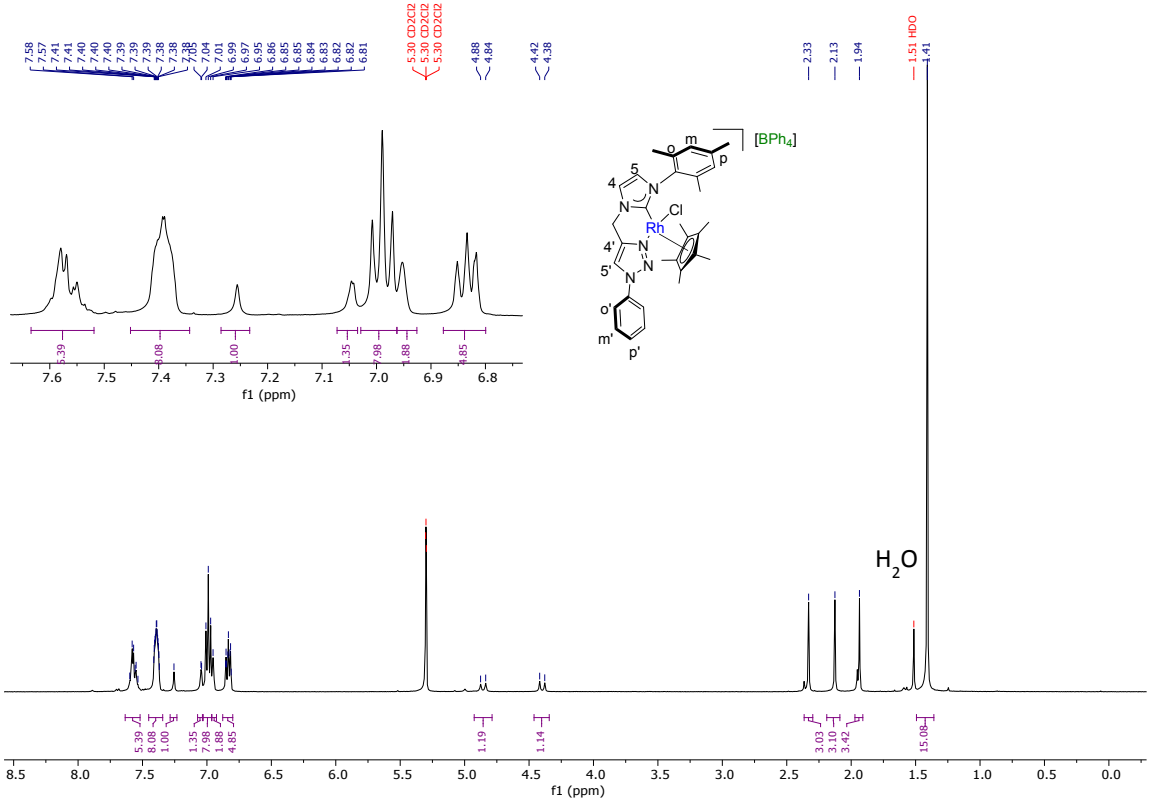
Ir-4 ^{1}H NMR (600 MHz, Methylene Chloride-d_2)



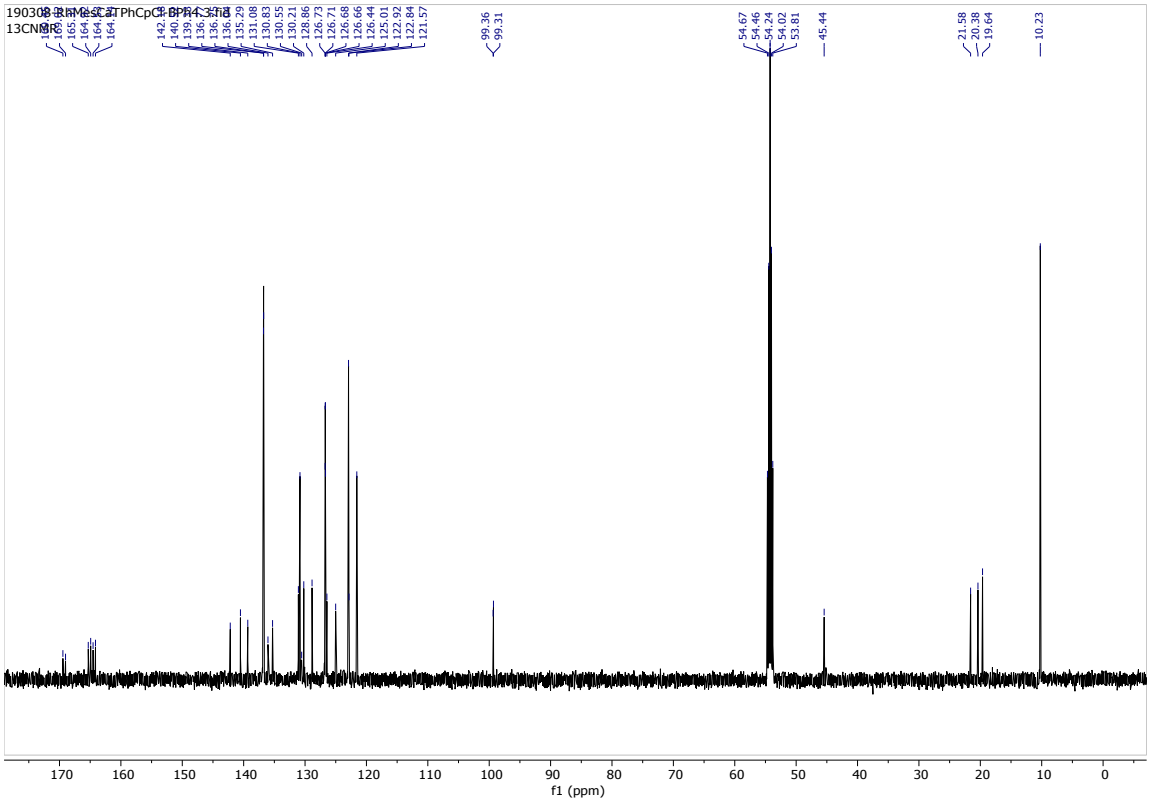
Ir-4 ^{13}C{^{1}H} NMR (150 MHz, Methylene Chloride-d_2)



Rh-1 ^{1}H NMR (500 MHz, Methylene Chloride-d_2)



Rh-1 ^{13}C{^{1}H} NMR (126 MHz, Methylene Chloride-d_2)



S1.2.1 Synthesis of the deuterated substrates

The two deuterated versions of the alcohol substrates **2a**: $C_6H_5CH_2OD$ (**2a-O*d*$_1$**)[5] and $C_6H_5CD_2OH$ (**2a-C*d*$_2$**)[6] were synthesised according to the literature.

S1.3 General catalysis procedure

S1.3.1 General catalysis procedure for the alkylation of ketone with primary alcohols to deliver mono-alkylated ketones

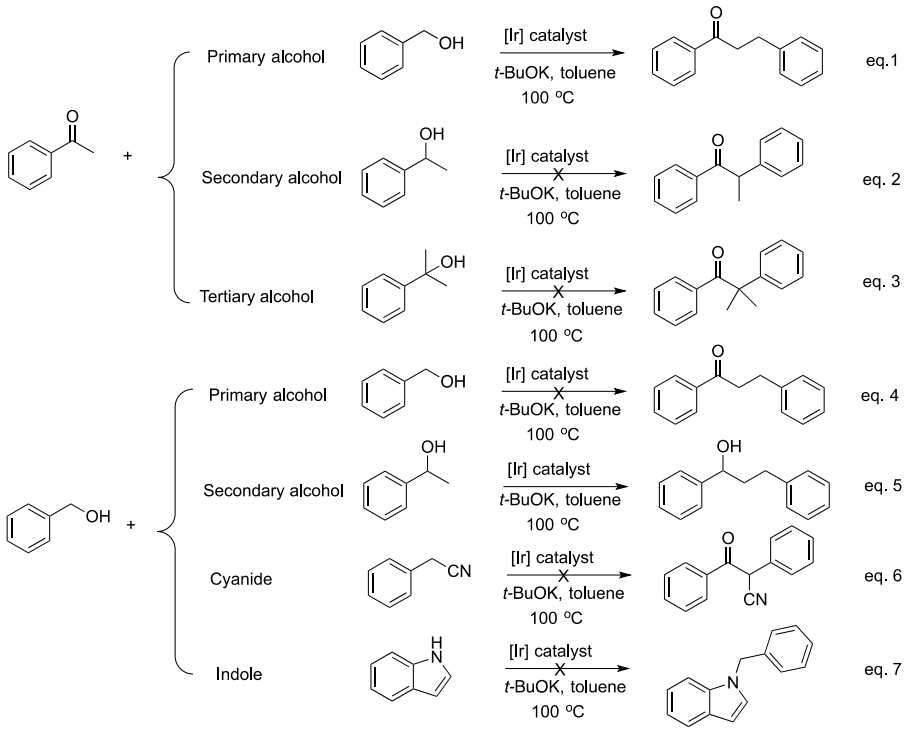
All the reactions were operated in air. The methyl ketone (**1a** – **1q**) (0.5 mmol), primary alcohol (**2a** – **2o**) (0.5 mmol), **Ir-3** (0.005 mmol, 1.0 mol%), KO^{t}Bu (0.1 mmol, 0.25 mmol or 0.40 mmol, 0.2 equiv., 0.5 equiv. or 0.8 equiv.) were weighed into a 4 mL glass vial fitted with a close-top melamine cap with PTFE liner and a stirrer bar. Toluene (1.0 mL) was then added to the mixture. The reaction mixture was stirred at room temperature for five minutes until a homogeneous mixture is observed before placing in an oil bath at 100 °C. After 6 hours, the reaction mixture was taken out of the oil bath and immediately cooled in the fridge before the work-up. The insoluble particles (mainly base) were filtered through 3 pipettes blocked with a cotton roll and were washed thoroughly with Et_2O. The crude products were combined and isolated by column chromatography using ethyl acetate/n-hexane (10:1, v/v) as eluent to afford the corresponding desired products.

S1.3.2 General catalysis procedure for the alkylation of ketone with primary alcohols to deliver mono-alkylated alcohols

All the reactions were operated in air. The methyl ketones (0.5 mmol), primary alcohols (1.0 mmol), **Rh-2** complex (0.005 mmol, 1 mol%), KOH (1.0 mmol, 2.0 equiv. in respect of ketone) were weighed into a 4 mL glass vial fitted with a close-top melamine cap with PTFE liner and a stirrer bar. Toluene (1.0 mL) was then added to the mixture. The reaction mixture was stirred at room temperature for five minutes until a homogeneous mixture is observed before placing in an oil bath at 120 °C. After 6 hours, the reaction mixture was taken out of the oil bath and immediately cooled in the fridge before the work-up. The insoluble particles (mainly base) was filtered through 3 pipettes blocked with a cotton roll and was washed thoroughly with Et_2O. The crude products were combined and isolated by column chromatography using ethyl acetate/n-hexane (3:1, v/v) as eluent to afford the corresponding desired products.

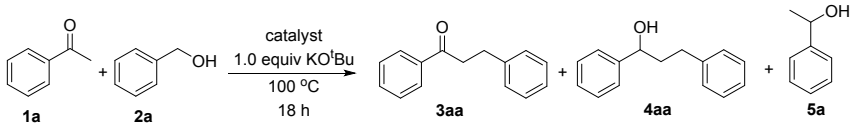
S1.4 Attempts at catalysing other HB reactions

The following benchmark reactions were conducted under our catalytic conditions in order to test the applicability in other types of HB reactions. However, we only found the reactions between acetophenone and benzylalcohol (eq. 1), benzylalcohol and 1-phenylethanol (eq. 5) were successful.

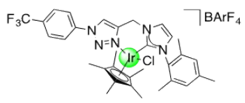


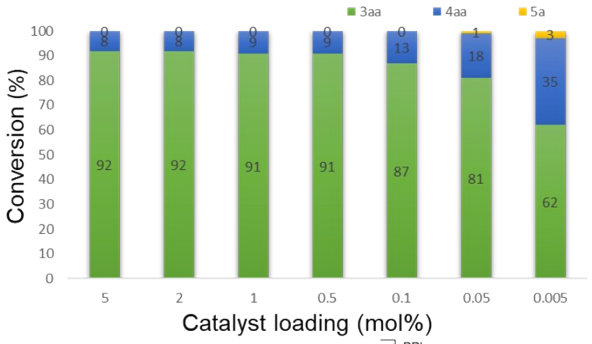
Scheme S2. Attempts at catalysing other HB reactions.

S1.5 Extended data of optimising the reaction conditions

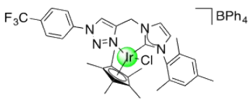


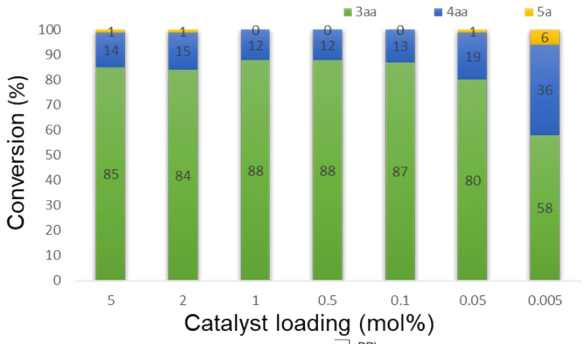
a)



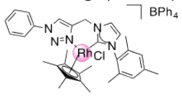


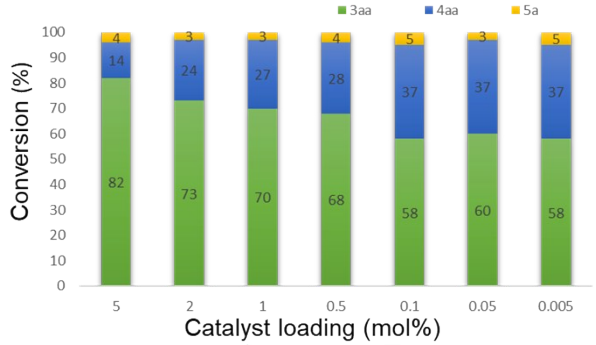
b)



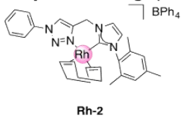


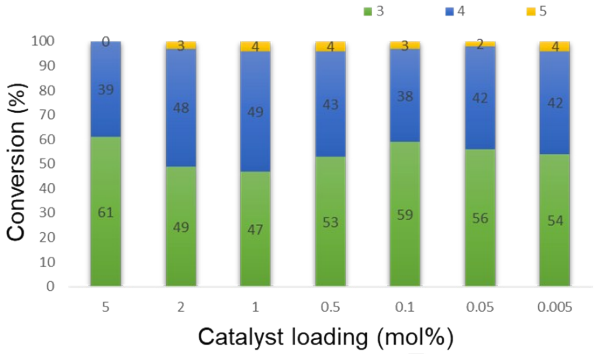
e)



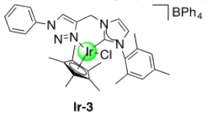


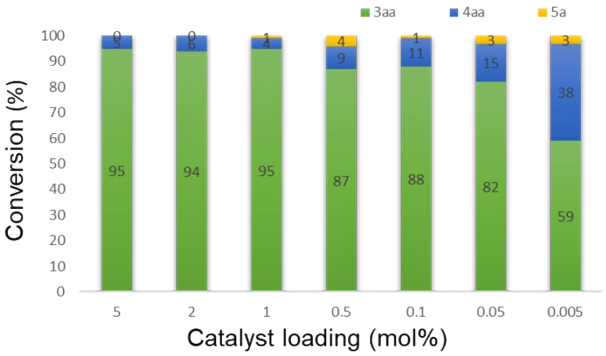
f)



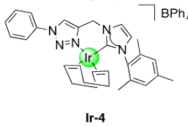


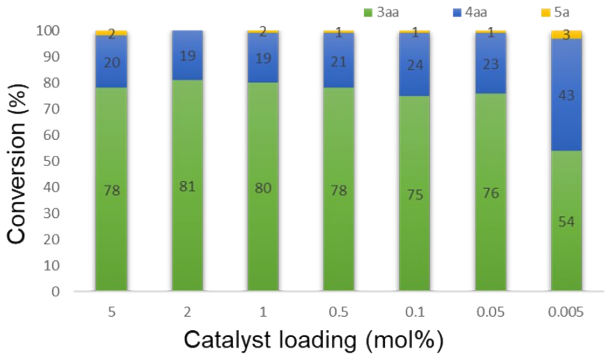
c)





d)





g)

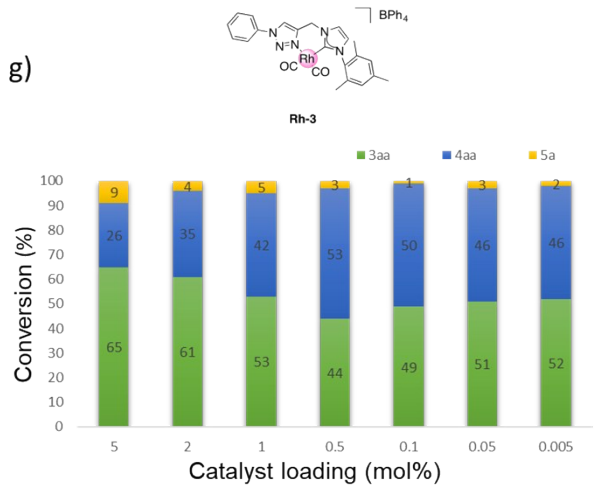


Figure S1. Catalyst (**Ir-1** – **Ir-4**; **Rh-1** – **Rh-3,** a – g) screening from the loading of 5 mol% to 0.005 mol% in the presence of 1.0 equiv. of KO^{t}Bu reacted in toluene-d_8 at 100 °C for 18 h. Conversions were measured by ^{1}H NMR spectral analysis.

entry	catalyst					base	temp (°C)	conversion (%)[a]			
	name	anion	X group	co-ligand(s)	mol%	(equiv)		**2a**	**3aa**	**4aa**	**5a**
1	**Ir-1**	$BArF_4$	CF_3	Cp*Cl	0.5	KO^{t}Bu (1.0)	60	48	22	30	-
2		$BArF_4$	CF_3	Cp*Cl	1	KO^{t}Bu (1.0)	60	33	30	37	-
3		$BArF_4$	CF_3	Cp*Cl	0.5	KO^{t}Bu (1.0)	100	0	91	9	-
4		$BArF_4$	CF_3	Cp*Cl	1	KO^{t}Bu (1.0)	100	0	91	9	-
5	**Ir-2**	BPh_4	CF_3	Cp*Cl	0.5	KO^{t}Bu (1.0)	100	0	85	14	1
6		BPh_4	CF_3	Cp*Cl	1	KO^{t}Bu (1.0)	100	0	85	13	2
7	**Ir-3**	BPh_4	H	Cp*Cl	0.5	KO^{t}Bu (1.0)	100	0	87	9	4
8		BPh_4	H	Cp*Cl	1	KO^{t}Bu (1.0)	100	0	95	4	1
9		BPh_4	H	Cp*Cl	1	KO^{t}Bu (0.8)	100	0	**99**	**1**	-
10		BPh_4	H	Cp*Cl	1	KO^{t}Bu (0.5)	100	0	94	4	2
11		BPh_4	H	Cp*Cl	1	KOH (1.0)	100	0	94	3	3
12		BPh_4	H	Cp*Cl	1	Cs_2CO_3 (1.0)	100	49	33	6	2
13		BPh_4	H	Cp*Cl	1	K_2CO_3 (1.0)	100	100	-	-	-
14		BPh_4	H	Cp*Cl	1	Na_2CO_3 (1.0)	100	100	-	-	-
15		BPh_4	H	Cp*Cl	1	NaOH (1.0)	100	5	80	12	3
16		BPh_4	H	Cp*Cl	1	NaOEt (1.0)	100	0	79	21	-
17	**Ir-4**	BPh_4	H	COD	1	KO^{t}Bu (1.0)	100	0	80	19	1

Table S1. [a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv) and **2a** (0.2 mmol, 1.0 equiv) in 0.5 mL toluene-d_8 reacted for 18 hours. Conversions were measured by ^{1}H NMR spectral analysis.

entry	catalyst	temp. (°C)	base (equiv)	**2a** (equiv)	conversion (%)[a]		
					3aa	**4aa**	**5aa**
1			KOH (1.0)	2.0	9	85	6
2			KOH (2.0)	2.0	6	89	5
3		100	KOH (3.0)	2.0	6	90	4
4			KOH (4.0)	2.0	7	91	2
5			KOH (5.0)	2.0	4	93	2
6		60		2.0	trace	trace	trace
7	**Rh-2**	80	KOH (2.0)	2.0	7	78	15
8		100		2.0	6	89	5
9		120		2.0	**8**	**92**	**-**
10		100	KO^{t}Bu (2.0)	2.0	8	78	-
11		120	KOH (2.0)	1.2	36	60	4
12		120	KOH (2.0)	1.5	18	80	2
13		120	KOH (2.0)	1.8	12	88	-

Table S2. [a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv) and **2a** (0.24 – 0.40 mmol, from 1.2 – 2.0 equiv.) in 0.5 mL toluene-d_8 reacted for 18 hours. Conversions were measured by ^{1}H NMR spectral analysis.

S1.6 Kinetic study

S1.6.1 Time course profile of the formation of ketone product **3aa** using the catalyst **Ir-1**

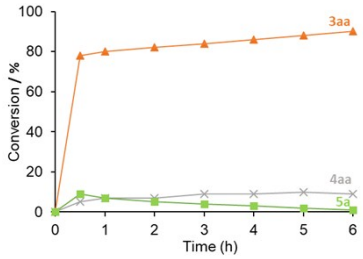


Figure S3. Time course profile of coupling benzylalcohol and acetophenone. Conditions: acetophenone **1a** (0.2 mmol), benzylalcohol **2a** (0.2 mmol), **Ir-1** (1.0 mol %), KO^{t}Bu (0.8 equiv), toluene-d_8 (0.5 mL), 100 °C, under air. Conversions were measured by ^{1}H NMR spectral analysis.

S1.6.2 Time course profile of the formation of alcohol product 4aa using the catalyst Rh-2

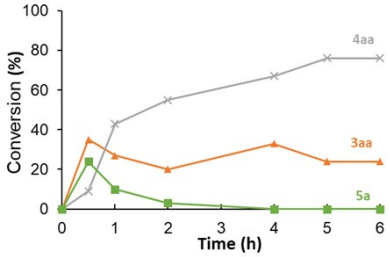
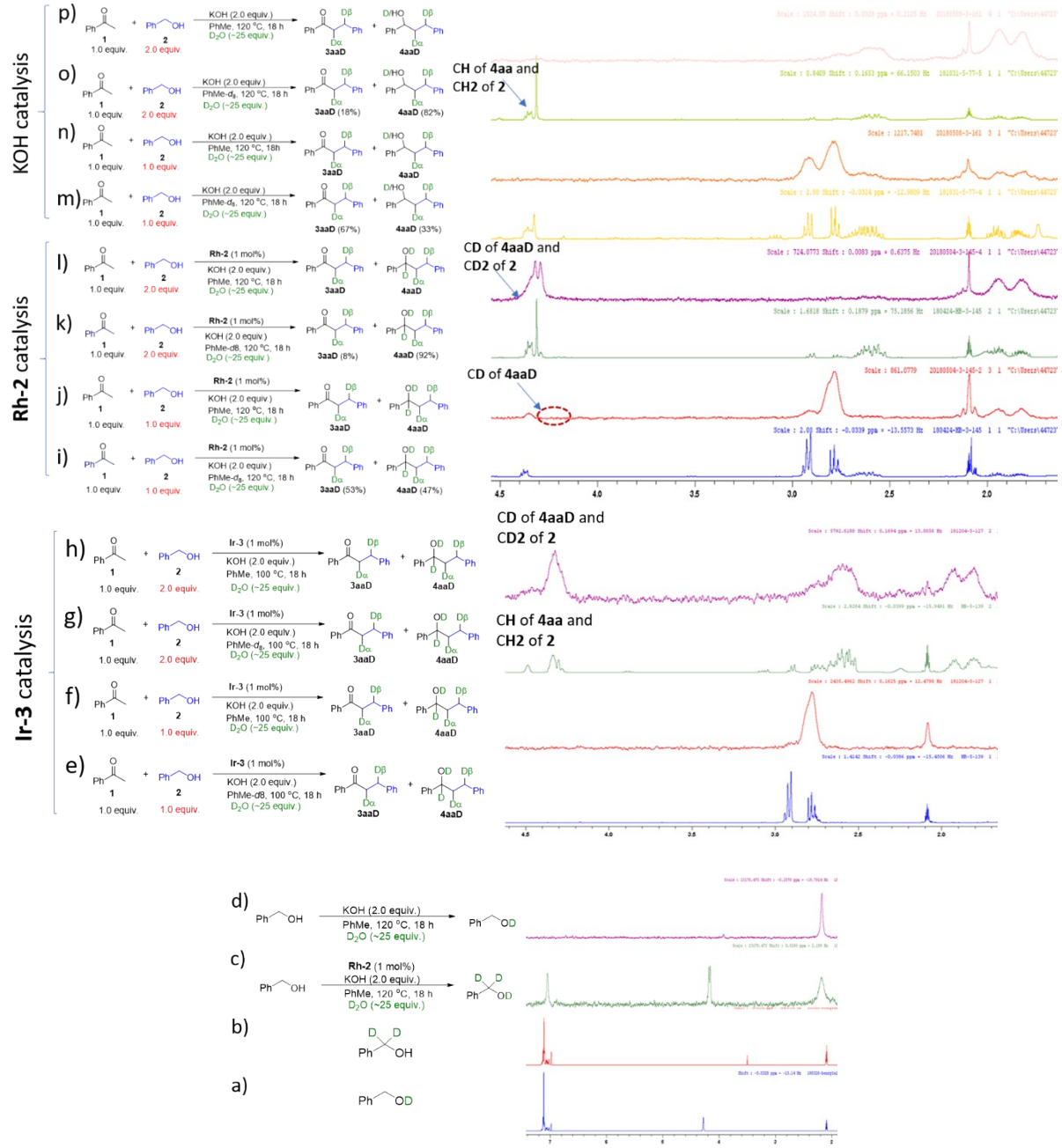


Figure S4. Time course profile of coupling benzylalcohol and acetophenone. Conditions: acetophenone **1a** (0.2 mmol), benzylalcohol **2a** (0.4 mmol), **Rh-2** (1.0 mol %), KOH (2.0 equiv.), toluene-d_8 (0.5 mL), 120 °C, under air. Conversions were measured by ^{1}H NMR spectral analysis.

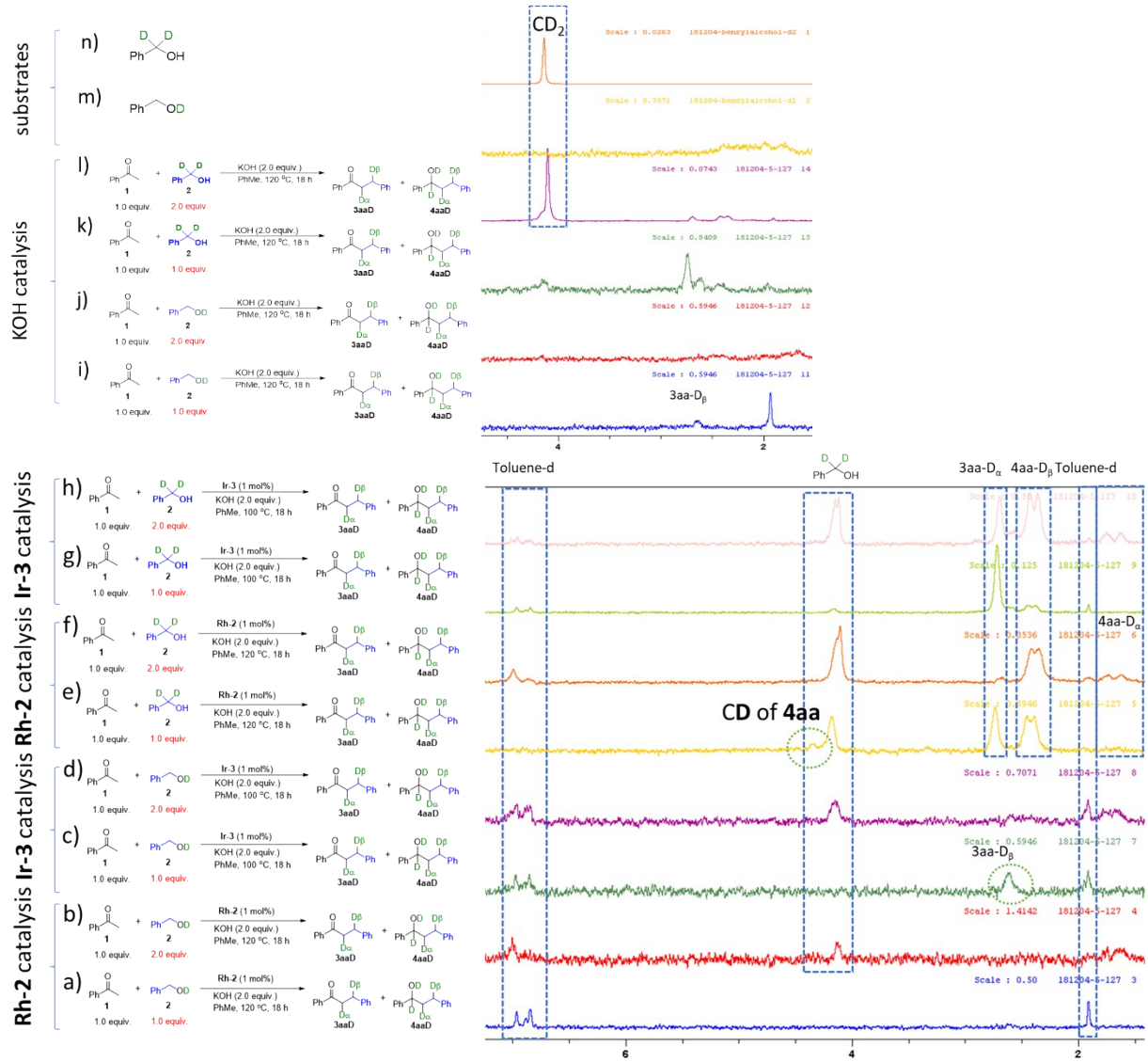
S1.7 Mechanistic investigations

S1.7.1 D_2O addition experiments



Scheme S5. Selected region of ^1H (400 MHz, PhMe-d_8, 298 K) and ^2H (77 MHz, toluene, 298 K) NMR spectra. Compare **Rh-2** and **Ir-3** catalysts and KOH promoted reactions, additional D_2O was added to the system to observe H/D scrambling. **a) - b)** The ^1H NMR spectra of two version of deuterated benzyl alcohols in toluene-d_8. **c) - d)** The ^2H NMR spectra for comparing the reactions using base KOH and **Rh-2** catalyst in the presence of 1.0 equivalent of benzyl alcohol and additional D_2O. **e) - p)** The ^1H and ^2H spectra NMR for comparing the reaction conditions.

S1.7.2 Deuterium labelling experiments

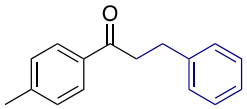


Scheme S6. Selected region of ^{2}H (77 MHz, toluene, 298 K) NMR spectra. Comparisons amongst **Rh-2**, **Ir-3** catalysts and KOH only promoted reactions, benzyl alcohol **2a-O*d*$_1$** and benzyl alcohol **2a-C*d*$_2$** are used as the deuterated substrates, respectively. Substrate ratio of **1** and **2** at 1:1 and 1:2 were examined, reaction conditions from **a)** to **l)** are depicted in the scheme. In some cases, H/D scrambling was observed in toluene.

S1.8 ^{1}H, $^{13}C\{^{1}H\}$ NMR data of catalysis products

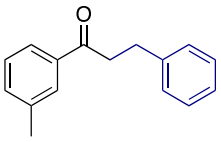
S1.8.1 Ketone scope for the alkylated ketones

3ba 3-phenyl-1-(*p*-tolyl)propan-1-one



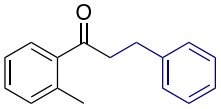
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.78 (m, 1H), 7.33 – 7.13 (m, 4H), 3.33 – 3.18 (m, 1H), 3.04 (dd, *J* = 8.6, 6.8 Hz, 1H), 2.37 (s, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 198.9, 143.9, 141.5, 134.5, 129.3, 128.6, 128.5, 128.2, 126.2, 40.4, 30.3, 21.7 ppm.

3ca 3-phenyl-1-(m-tolyl)propan-1-one



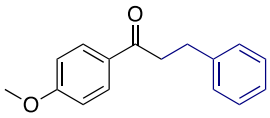
^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.73 (m, 2H), 7.44 – 7.17 (m, 8H), 3.36 – 3.23 (m, 2H), 3.07 (dd, *J* = 8.6, 6.9 Hz, 2H), 2.41 (d, *J* = 0.7 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 199.6, 141.5, 138.5, 137.0, 134.0, 128.7, 128.7, 128.6, 128.6, 126.2, 125.38, 40.7, 30.3, 21.5 ppm.

3da 3-phenyl-1-(o-tolyl)propan-1-one



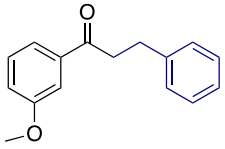
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.27 – 7.14 (m, 6H), 3.28 – 3.20 (m, 2H), 3.06 (dd, *J* = 8.4, 6.9 Hz, 2H), 2.48 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 203.5, 141.3, 138.2, 138.0, 132.1, 131.4, 128.6, 128.5, 128.5, 126.2, 125.8, 43.3, 30.5, 21.4 ppm.

3ea 1-(4-methoxyphenyl)-3-phenylpropan-1-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 2H), 7.34 – 7.18 (m, 5H), 6.96 – 6.88 (m, 2H), 3.87 (s, 3H), 3.30 – 3.22 (m, 2H), 3.06 (dd, *J* = 8.7, 6.8 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 198.0, 163.6, 141.6, 130.3 (d, *J* = 34.1 Hz), 128.6 (d, *J* = 8.0 Hz), 126.2, 113.9, 55.6, 40.3, 30.5 ppm.

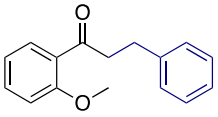
3fa 1-(3-methoxyphenyl)-3-phenylpropan-1-one



^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 (ddd, J = 7.7, 1.6, 1.0 Hz, 1H), 7.50 (dd, J = 2.7, 1.5 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.24 – 7.19 (m, 1H), 7.11 (ddd, J = 8.2, 2.7, 1.0 Hz, 1H), 3.85 (s, 3H), 3.34 – 3.26 (m, 2H), 3.08 (dd, J = 8.5, 6.9 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz,

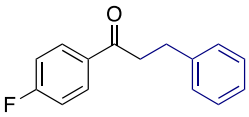
Chloroform-*d*) δ 199.2, 160.0, 141.4, 138.3, 129.7, 128.7, 128.6, 126.3, 120.8, 119.7, 112.4, 55.6, 40.7, 30.3 ppm.

3ga 1-(2-methoxyphenyl)-3-phenylpropan-1-one



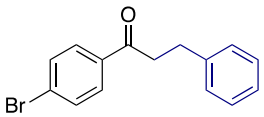
^{1}H NMR (400 MHz, Chloroform-d) δ 7.60 (dd, J = 7.7, 1.8 Hz, 1H), 7.36 (ddd, J = 8.4, 7.3, 1.9 Hz, 1H), 7.23 – 7.02 (m, 6H), 6.90 (td, J = 7.5, 1.0 Hz, 1H), 6.86 (dd, J = 8.4, 1.0 Hz, 1H), 3.78 (s, 3H), 3.25 – 3.18 (m, 2H), 2.94 (dd, J = 8.6, 7.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 201.8, 158.6, 141.8, 133.5, 130.5, 129.2, 128.6, 128.5, 128.4, 128.3, 126.0, 120.8, 111.6, 55.6, 45.5, 30.6 ppm.

3ha 1-(4-fluorophenyl)-3-phenylpropan-1-one



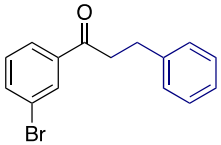
^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 – 7.94 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 – 7.18 (m, 2H), 7.16 – 7.07 (m, 2H), 3.32 – 3.23 (m, 2H), 3.07 (dd, J = 8.5, 6.9 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 197.8, 141.3, 130.8, 130.7, 128.7, 128.6, 126.3, 115.9, 115.7, 40.5, 30.2 ppm.

3ia 1-(4-bromophenyl)-3-phenylpropan-1-one



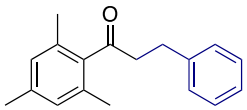
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.78 (m, 2H), 7.64 – 7.54 (m, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 3.34 – 3.19 (m, 2H), 3.06 (dd, *J* = 8.4, 6.9 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 198.3, 141.2, 135.7, 132.1, 129.7, 128.7, 128.5, 128.4, 126.4, 40.6, 30.2 ppm.

3ja 1-(3-bromophenyl)-3-phenylpropan-1-one



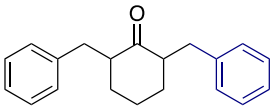
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (t, *J* = 1.8 Hz, 1H), 7.87 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1H), 7.68 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.40 – 7.17 (m, 7H), 3.31 – 3.24 (m, 2H), 3.07 (dd, *J* = 8.4, 6.9 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 197.9, 141.1, 138.7, 136.1, 131.3, 130.4, 128.7, 128.6, 126.7, 126.4, 123.1, 40.7, 30.1 ppm.

3ka 1-mesityl-3-phenylpropan-1-one



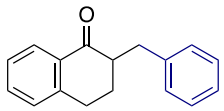
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.17 (m, 5H), 6.83 (q, *J* = 0.7 Hz, 2H), 3.12 – 2.98 (m, 4H), 2.28 (s, 3H), 2.12 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 209.8, 141.1, 139.6, 138.5, 132.7, 128.6, 128.6, 126.3, 46.5, 29.6, 21.2, 19.2 ppm.

3ma 2,6-dibenzylcyclohexan-1-one



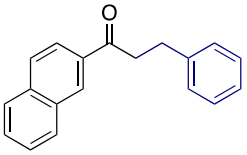
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.23 (m, 4H), 7.23 – 7.13 (m, 6H), 3.24 (dd, *J* = 13.9, 4.8 Hz, 2H), 2.58 (dddd, *J* = 13.4, 10.0, 4.3, 1.2 Hz, 2H), 2.44 (dd, *J* = 13.9, 8.6 Hz, 2H), 2.13 – 2.00 (m, 2H), 1.84 – 1.71 (m, 1H), 1.69 – 1.48 (m, 2H), 1.35 (qd, *J* = 13.1, 3.8 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 211.8, 139.56, 128.1, 127.3, 124.9, 51.9, 34.5, 33.8, 24.3 ppm.

3na 2-benzyl-3,4-dihydronaphthalen-1(2*H*)-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 (ddt, *J* = 7.8, 6.8, 1.1 Hz, 3H), 7.20 (ddt, *J* = 7.6, 5.6, 2.4 Hz, 4H), 3.46 (dt, *J* = 14.0, 4.3 Hz, 1H), 3.00 – 2.81 (m, 2H), 2.72 (ddt, *J* = 11.4, 9.6, 4.2 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.08 (dq, *J* = 13.4, 4.5 Hz, 1H), 1.76 (dddd, *J* = 13.4, 11.6, 10.0, 5.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.5, 144.2, 140.2, 133.4, 132.6, 129.4, 128.8, 128.5, 127.7, 126.7, 126.3, 49.6, 35.8, 35.7, 28.8, 28.7, 27.8, 27.7 ppm.

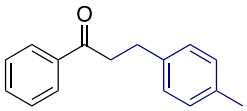
3oa 1-(naphthalen-2-yl)-3-phenylpropan-1-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (ddt, *J* = 8.6, 1.5, 0.8 Hz, 1H), 7.98 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.82 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.64 – 7.51 (m, 2H), 7.47 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.34 – 7.18 (m, 6H), 3.43 – 3.36 (m, 2H), 3.15 (dd, *J* = 8.4, 7.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 203.7, 141.3, 136.1, 134.1, 132.7, 130.3, 128.7, 128.6, 128.6, 128.0, 127.5, 126.6, 126.3, 125.9, 124.5, 44.0, 30.7 ppm.

S1.8.2 Alcohol scope for the alkylated ketones

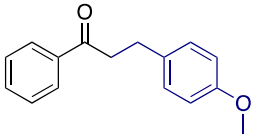
3ab 1-phenyl-3-(*p*-tolyl)propan-1-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.91 (m, 1H), 7.59 – 7.53 (m, 1H), 7.49 – 7.42 (m, 1H), 6.77 – 6.67 (m, 1H), 5.92 (s, 1H), 3.31 – 3.21 (m, 1H), 3.03 – 2.95 (m, 1H) ppm.

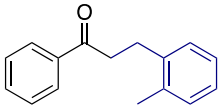
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.3, 147.8, 146.0, 137.0, 135.2, 133.2, 128.8, 128.2, 121.3, 109.1, 108.4, 101.0, 40.8, 30.0 ppm.

3ac 3-(4-methoxyphenyl)-1-phenylpropan-1-one



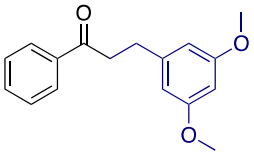
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 7.22 – 7.14 (m, 2H), 6.89 – 6.81 (m, 2H), 3.79 (s, 3H), 3.31 – 3.24 (m, 2H), 3.02 (dd, *J* = 8.4, 6.9 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.5, 158.1, 137.0, 133.4, 133.2, 129.5, 128.7, 128.2, 114.1, 55.4, 40.8, 29.4 ppm.

3ad 1-phenyl-3-(*o*-tolyl)propan-1-one



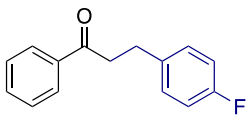
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 2H), 7.62 – 7.53 (m, 1H), 7.52 – 7.43 (m, 2H), 7.26 – 7.10 (m, 4H), 3.31 – 3.23 (m, 2H), 3.07 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.37 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.5, 139.5, 137.0, 136.1, 133.2, 130.5, 128.9, 128.7, 128.2, 126.4, 126.3, 39.2, 27.6, 19.5 ppm.

3ae 3-(3,5-dimethoxyphenyl)-1-phenylpropan-1-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.60 – 7.52 (m, 1H), 7.50 – 7.41 (m, 2H), 6.42 (d, *J* = 2.2 Hz, 2H), 6.33 (t, *J* = 2.3 Hz, 1H), 3.78 (s, 6H), 3.34 – 3.25 (m, 2H), 3.02 (dd, *J* = 8.5, 6.9 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.3, 161.0, 143.8, 137.0, 133.2, 128.7, 128.2, 106.6, 98.2, 55.4, 40.4, 30.6 ppm.

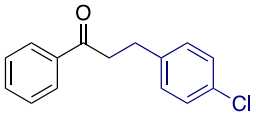
3af 3-(4-fluorophenyl)-1-phenylpropan-1-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.91 (m, 1H), 7.61 – 7.51 (m, 1H), 7.50 – 7.42 (m, 1H), 7.24 – 7.17 (m, 1H), 7.02 – 6.93 (m, 1H), 3.33 – 3.24 (m, 1H), 3.05 (t, *J* = 7.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101

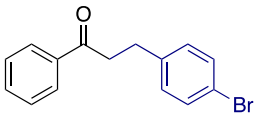
MHz, Chloroform-*d*) δ 199.2, 162.8, 137.0, 137.0, 137.0, 133.3, 130.0, 129.9, 128.8, 128.2, 115.5, 115.3, 40.6, 29.4 ppm.P

3ag 3-(4-chlorophenyl)-1-phenylpropan-1-one



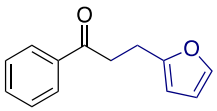
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.91 (m, 1H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 1H), 7.29 – 7.23 (m, 1H), 7.21 – 7.16 (m, 1H), 3.33 – 3.24 (m, 1H), 3.05 (t, *J* = 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.0, 139.9, 136.9, 133.3, 132.0, 130.0, 128.8, 128.7, 128.2, 40.3, 29.5 ppm.

3ah 3-(4-bromophenyl)-1-phenylpropan-1-one



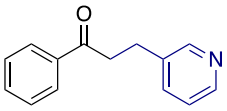
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.38 (m, 2H), 7.17 – 7.10 (m, 2H), 3.33 – 3.23 (m, 2H), 3.03 (t, *J* = 7.5 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 198.9, 140.4, 136.9, 133.3, 131.7, 130.4, 128.8, 128.1, 120.0, 40.2, 29.6 ppm.

3aj 3-(furan-2-yl)-1-phenylpropan-1-one



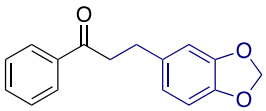
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.94 (m, 2H), 7.61 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 7.31 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.29 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.08 – 6.03 (m, 1H), 3.39 – 3.31 (m, 2H), 3.15 – 3.05 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 198.7, 154.8, 141.1, 136.8, 133.2, 128.6, 128.1, 110.3, 105.3, 37.00, 22.5 ppm.

3ak 1-phenyl-3-(pyridin-3-yl)propan-1-one



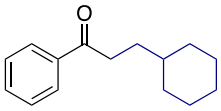
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.45 (d, *J* = 4.7 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.57 (ddt, *J* = 12.9, 6.9, 1.7 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.21 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.31 (dd, *J* = 7.8, 7.0 Hz, 2H), 3.08 (t, *J* = 7.4 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 198.6, 150.1, 147.8, 136.8, 136.2, 133.4, 128.8, 128.1, 123.5, 39.9, 27.2 ppm.

3al 3-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylpropan-1-one



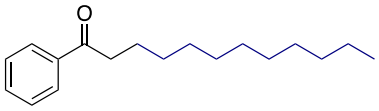
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 2H), 7.60 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 6.77 – 6.67 (m, 3H), 5.92 (s, 2H), 3.34 – 3.18 (m, 2H), 3.07 – 2.93 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.3, 147.8, 146.0, 137.0, 135.2, 133.2, 128.7, 128.1, 121.3, 109.0, 108.4, 100.9, 40.8, 30.0 ppm.

3an 3-cyclohexyl-1-phenylpropan-1-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 2H), 7.59 – 7.51 (m, 1H), 7.51 – 7.40 (m, 2H), 3.02 – 2.93 (m, 2H), 1.74 (dddd, *J* = 18.2, 11.5, 3.3, 1.5 Hz, 4H), 1.68 – 1.60 (m, 3H), 1.37 – 1.09 (m, 5H), 1.01 – 0.88 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 201.1, 137.2, 133.0, 128.7, 128.2, 37.6, 36.3, 33.4, 31.9, 26.7, 26.4 ppm.

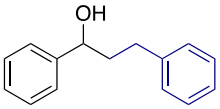
3ao 1-phenyldodecan-1-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.92 (m, 2H), 7.59 – 7.52 (m, 1H), 7.46 (dd, *J* = 8.3, 6.8 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.74 (q, *J* = 7.3 Hz, 2H), 1.46 – 1.12 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 200.8, 137.3, 133.0, 128.7, 128.2, 38.8, 32.1, 29.8, 29.7, 29.6, 29.5, 29.5, 24.5, 22.8, 14.3 ppm.

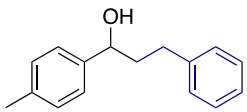
S1.8.3 Scope for the alkylated alcohols

4a 1,3-diphenylpropan-1-ol



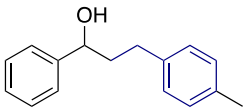
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 4.3 Hz, 4H), 7.33 – 7.26 (m, 3H), 7.23 – 7.16 (m, 3H), 4.70 (dd, *J* = 7.8, 5.3 Hz, 1H), 2.85 – 2.61 (m, 2H), 2.23 – 1.97 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 144.7, 141.9, 128.7, 128.6, 128.5, 127.8, 126.1, 126.0, 74.0, 40.6, 32.2 ppm.

4b 3-phenyl-1-(p-tolyl)propan-1-ol



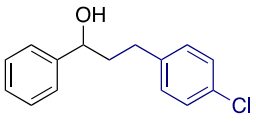
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.23 (m, 4H), 7.19 (dd, *J* = 11.0, 7.6 Hz, 5H), 4.66 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.81 – 2.60 (m, 2H), 2.36 (s, 3H), 2.22 – 1.96 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 142.0, 141.1, 137.5, 129.3, 128.6, 128.5, 126.0, 126.0, 73.9, 40.5, 32.2, 21.3 ppm.

4d 1-(4-bromophenyl)-3-phenylpropan-1-ol



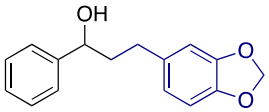
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.27 (m, 1H), 7.10 (s, 4H), 4.69 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.79 – 2.58 (m, 2H), 2.33 (s, 3H), 2.19 – 1.97 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 144.7, 138.8, 135.4, 129.2, 128.6, 128.4, 127.8, 126.1, 74.0, 40.7, 31.7, 21.1 ppm.

4e 3-(4-chlorophenyl)-1-phenylpropan-1-ol



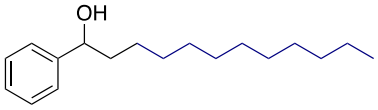
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (dtd, *J* = 7.2, 6.3, 1.4 Hz, 4H), 7.32 – 7.27 (m, 1H), 7.27 – 7.18 (m, 2H), 7.15 – 7.09 (m, 2H), 4.66 (dd, *J* = 7.9, 5.3 Hz, 1H), 2.68 (qdd, *J* = 14.0, 9.5, 6.2 Hz, 2H), 2.18 – 1.93 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 144.5, 140.4, 131.7, 129.9, 128.7, 128.6, 127.9, 126.0, 73.8, 40.4, 31.5 ppm.

4f 3-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylpropan-1-ol



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 6.68 – 6.52 (m, 3H), 5.82 (s, 2H), 4.58 (dd, *J* = 7.9, 5.3 Hz, 1H), 2.64 – 2.46 (m, 2H), 2.07 – 1.84 (m, 2H), 1.81 (s, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 147.7, 145.7, 144.7, 135.7, 128.6, 127.8, 126.03, 121.3, 109.0, 108.3, 100.9, 73.8, 40.8, 31.9 ppm.

4g 1-phenyldodecan-1-ol

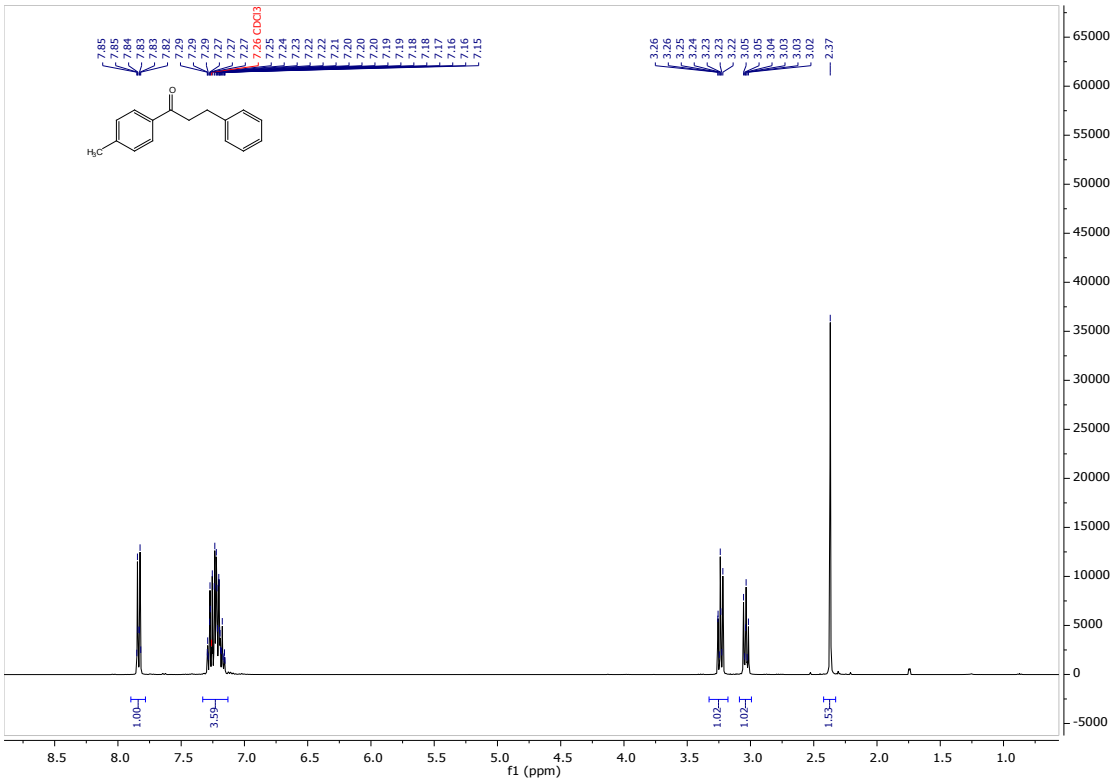


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 4.3 Hz, 4H), 7.24 – 7.17 (m, 1H), 4.59 (dd, *J* = 7.5, 5.8 Hz, 1H), 1.83 – 1.54 (m, 3H), 1.44 – 1.29 (m, 1H), 1.19 (d, *J* = 10.7 Hz, 18H), 0.89 – 0.73 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 145.1, 128.6, 127.6, 126.0, 74.9, 39.3, 32.1, 29.8, 29.8, 29.73, 29.7, 29.7, 29.5, 26.00, 22.8, 14.3 ppm.

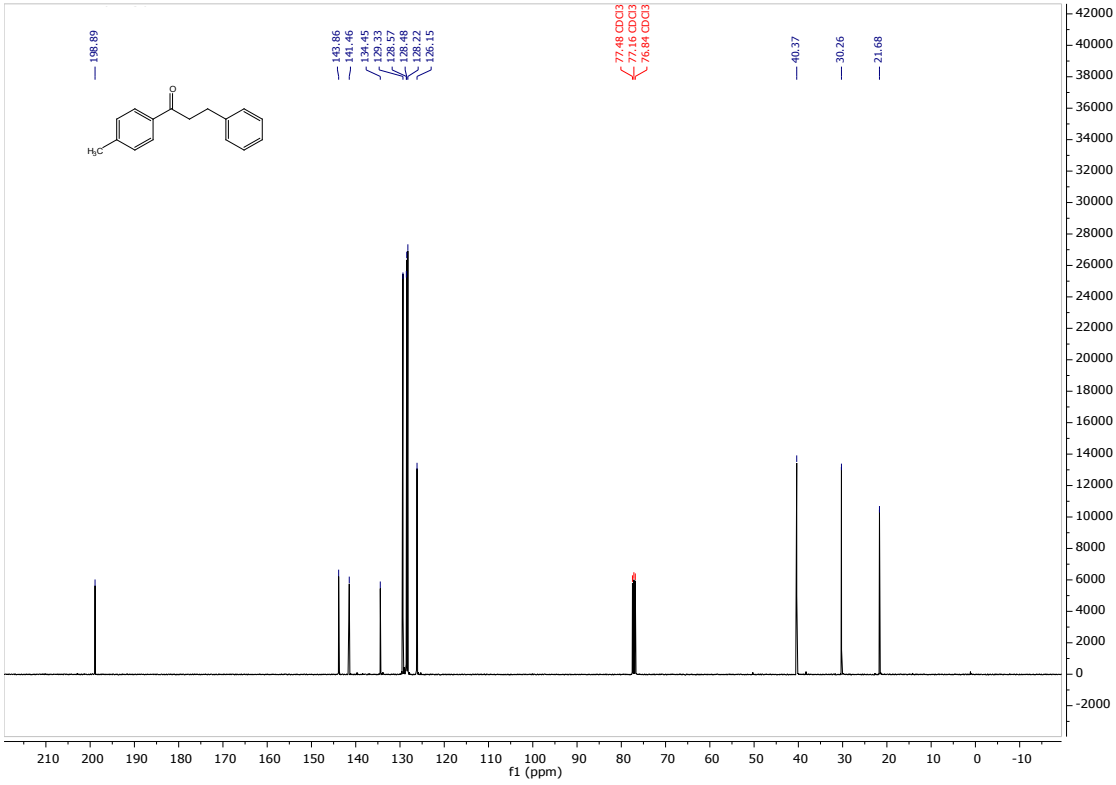
S1.9 ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of catalysis products

S1.9.1 Ketone scope for the alkylated ketones

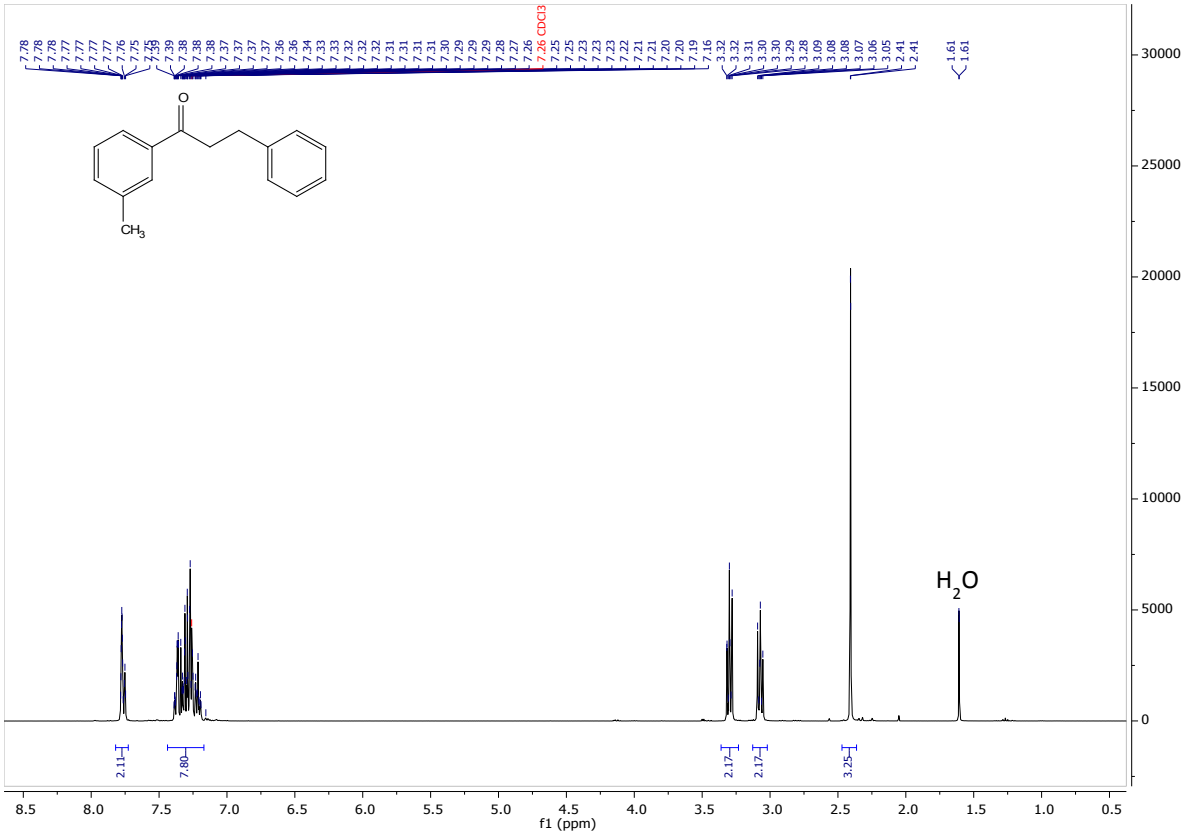
3ba ^{1}H NMR (400 MHz, Chloroform-*d*)



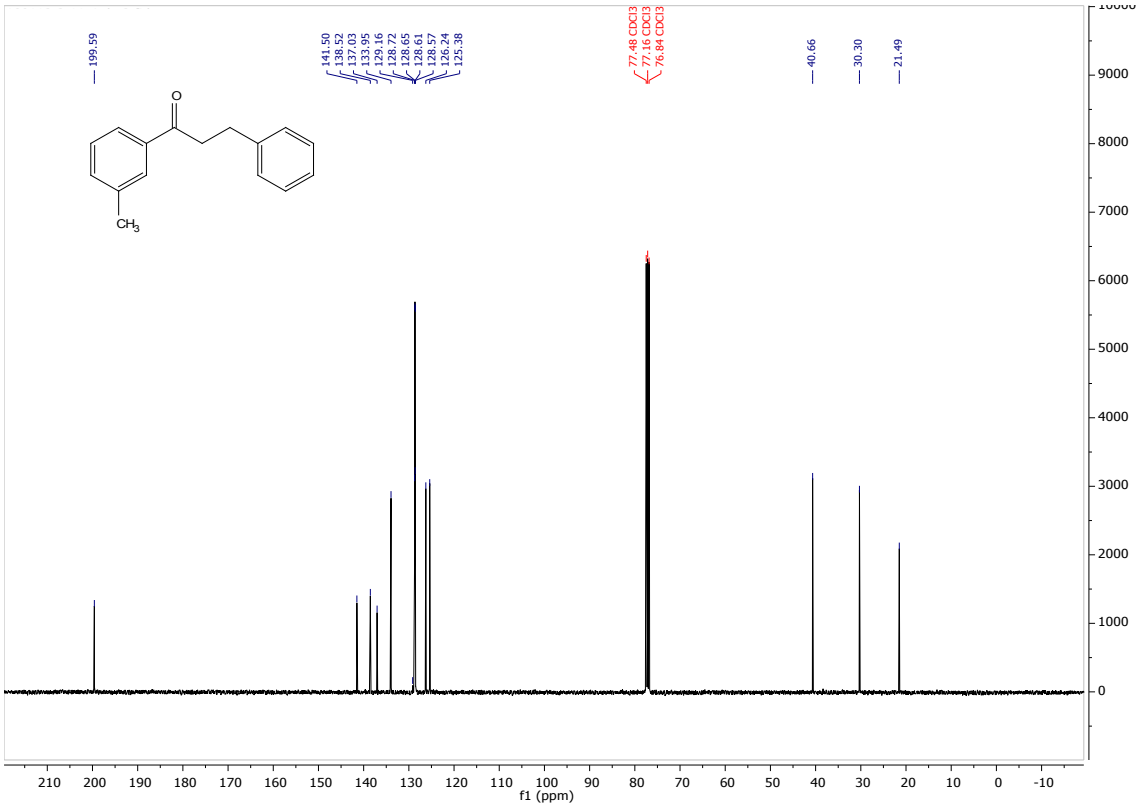
3ba $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)



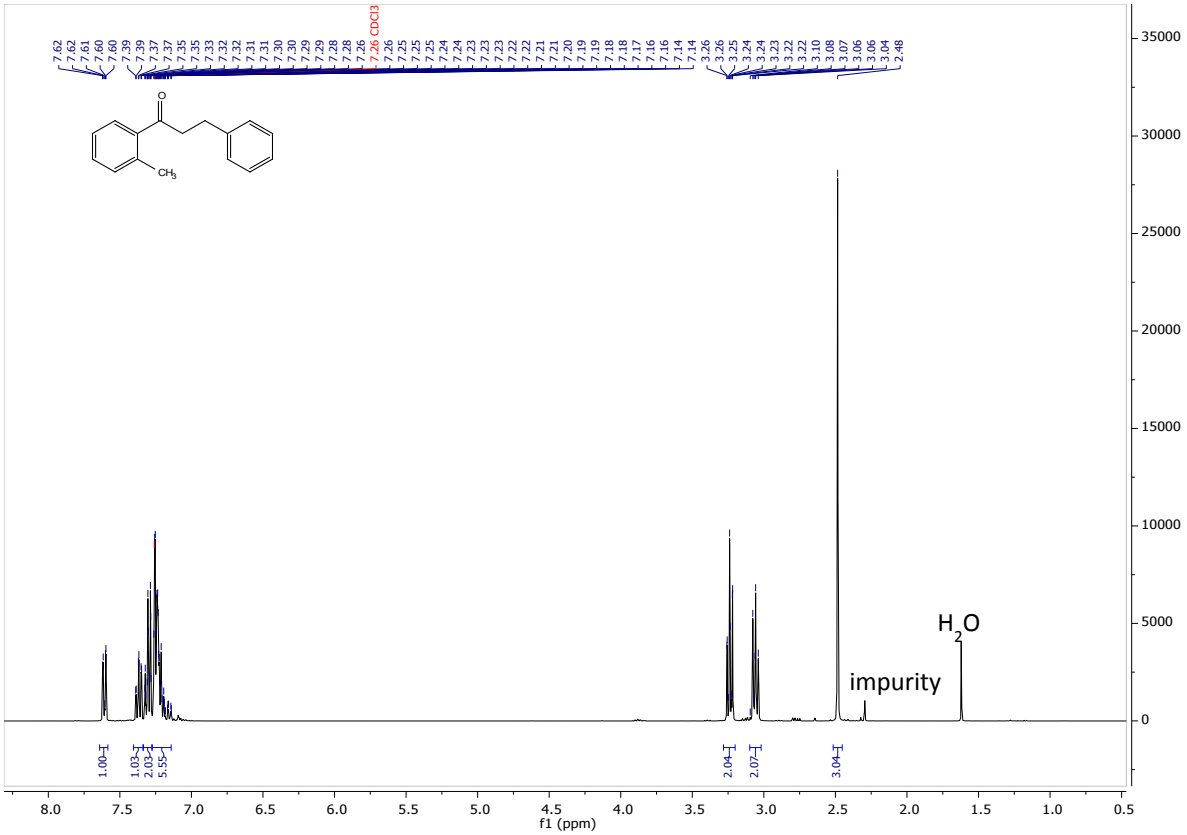
3ca ^{1}H NMR (400 MHz, Chloroform-*d*)



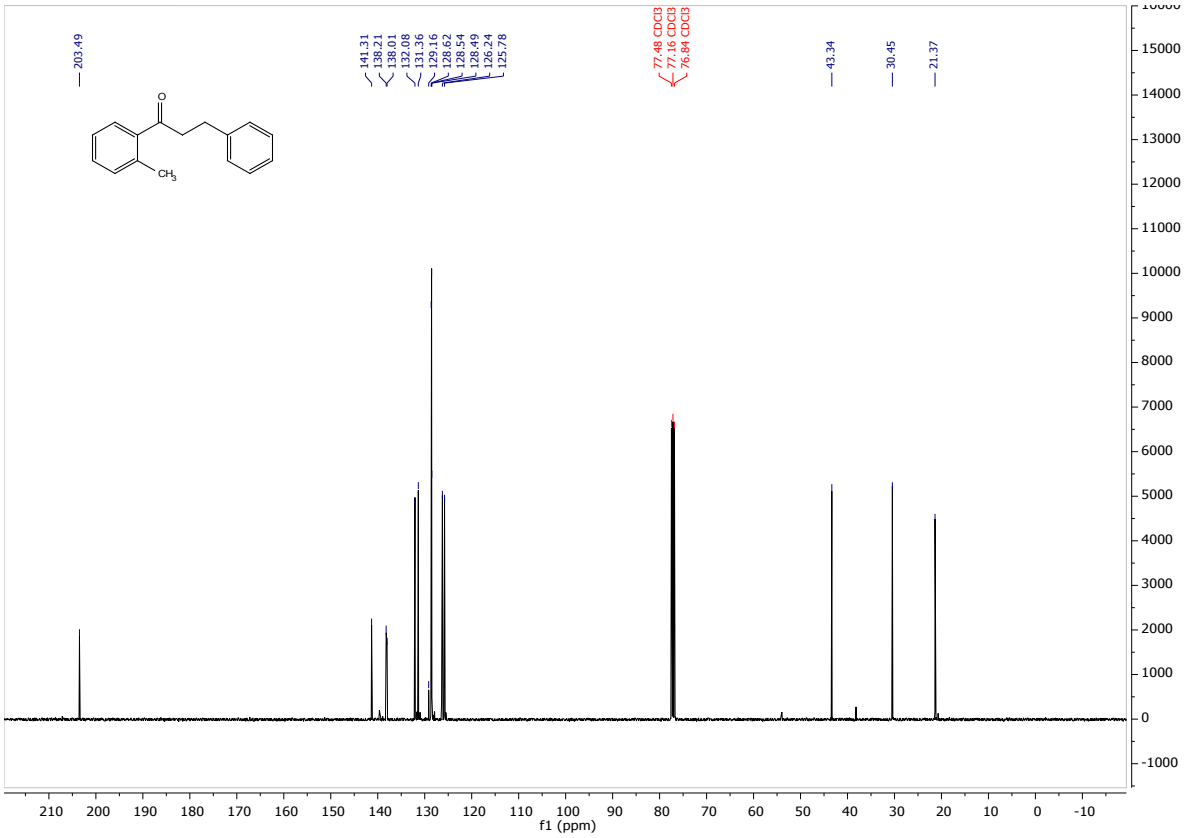
3ca ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



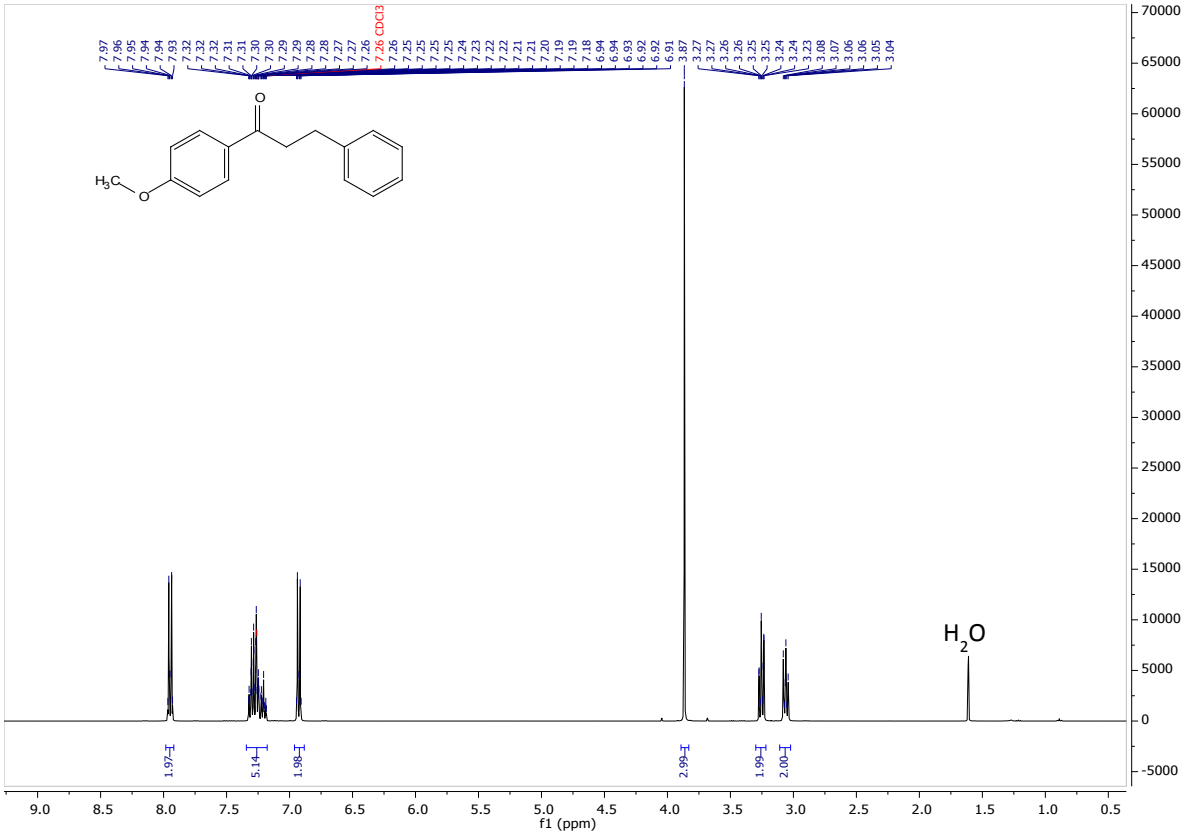
3da ^{1}H NMR (400 MHz, Chloroform-*d*)



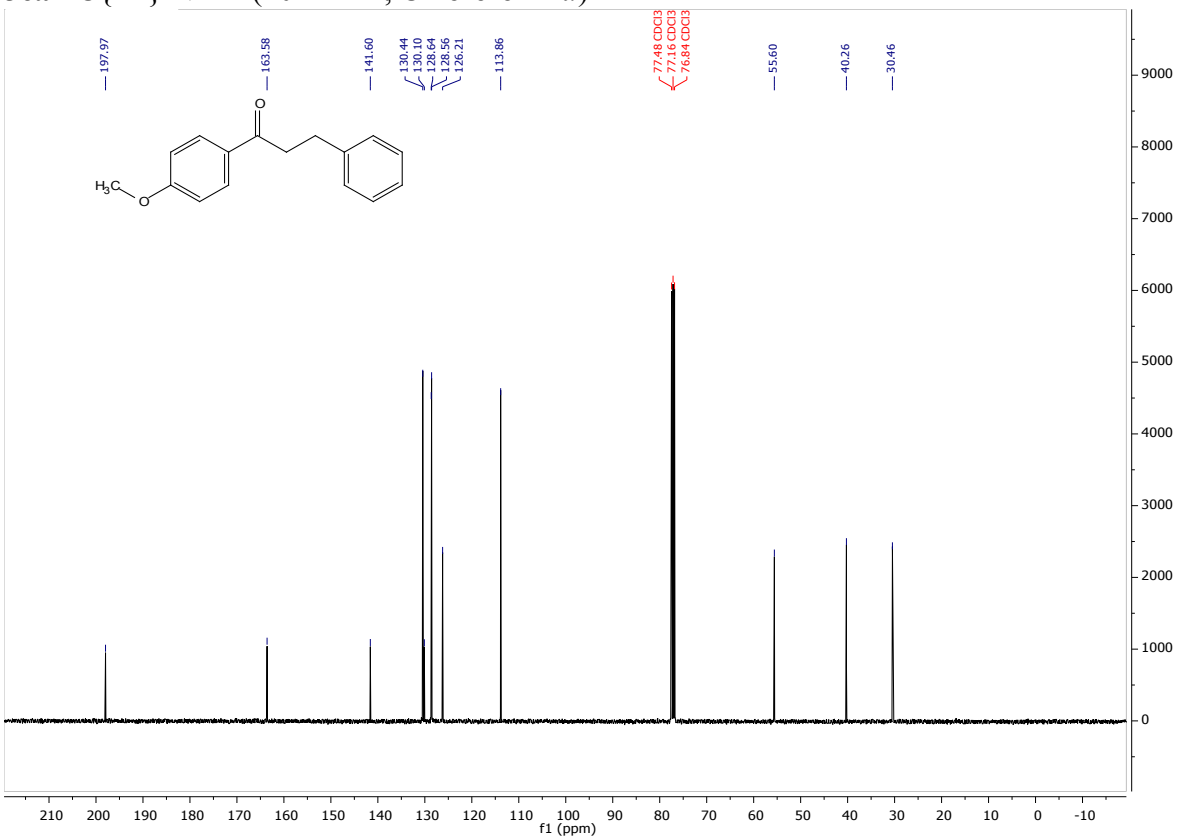
3da $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)



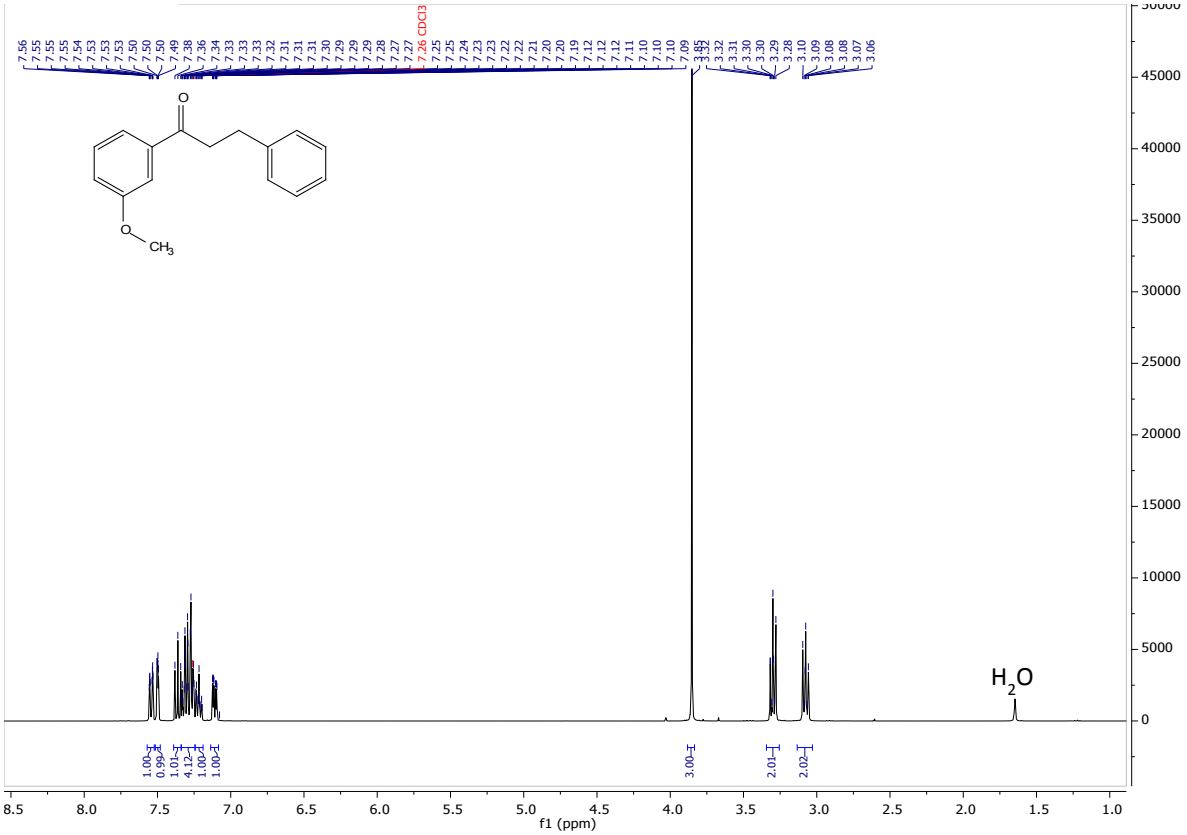
3ea ^{1}H NMR (400 MHz, Chloroform-*d*)



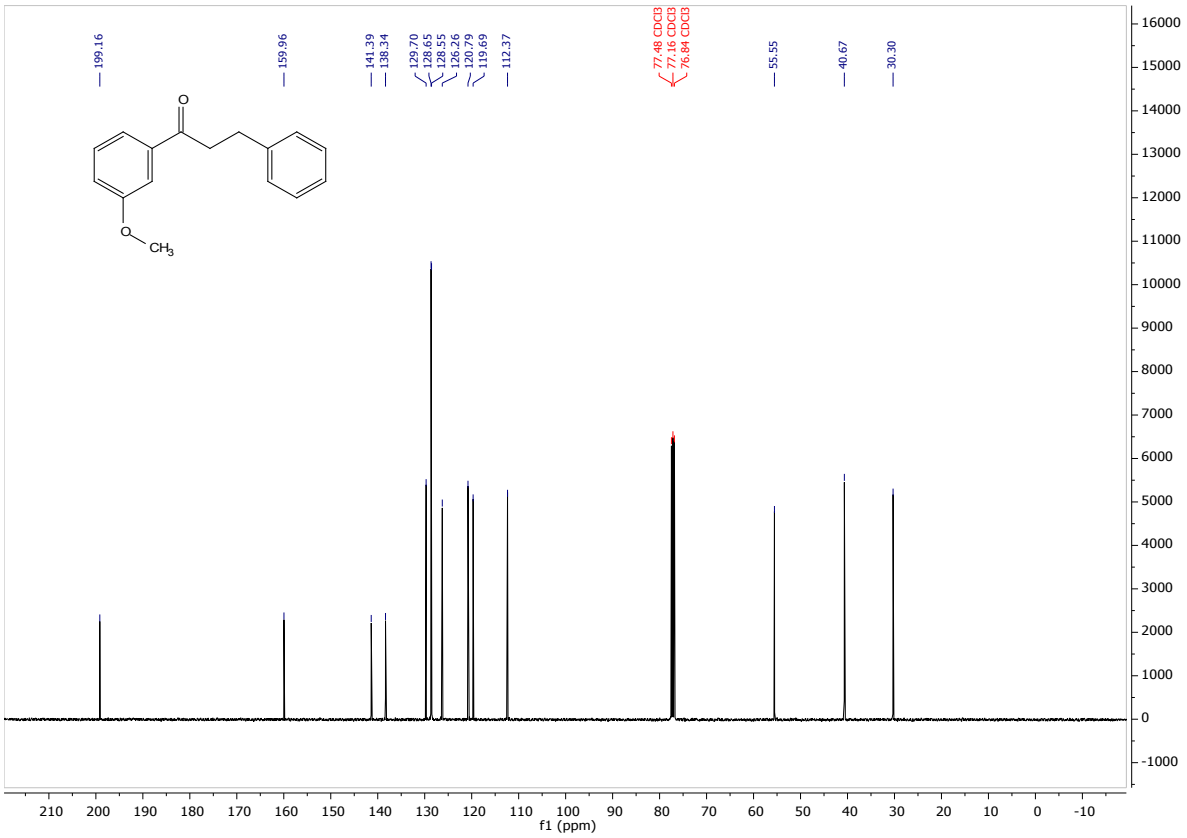
3ea ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



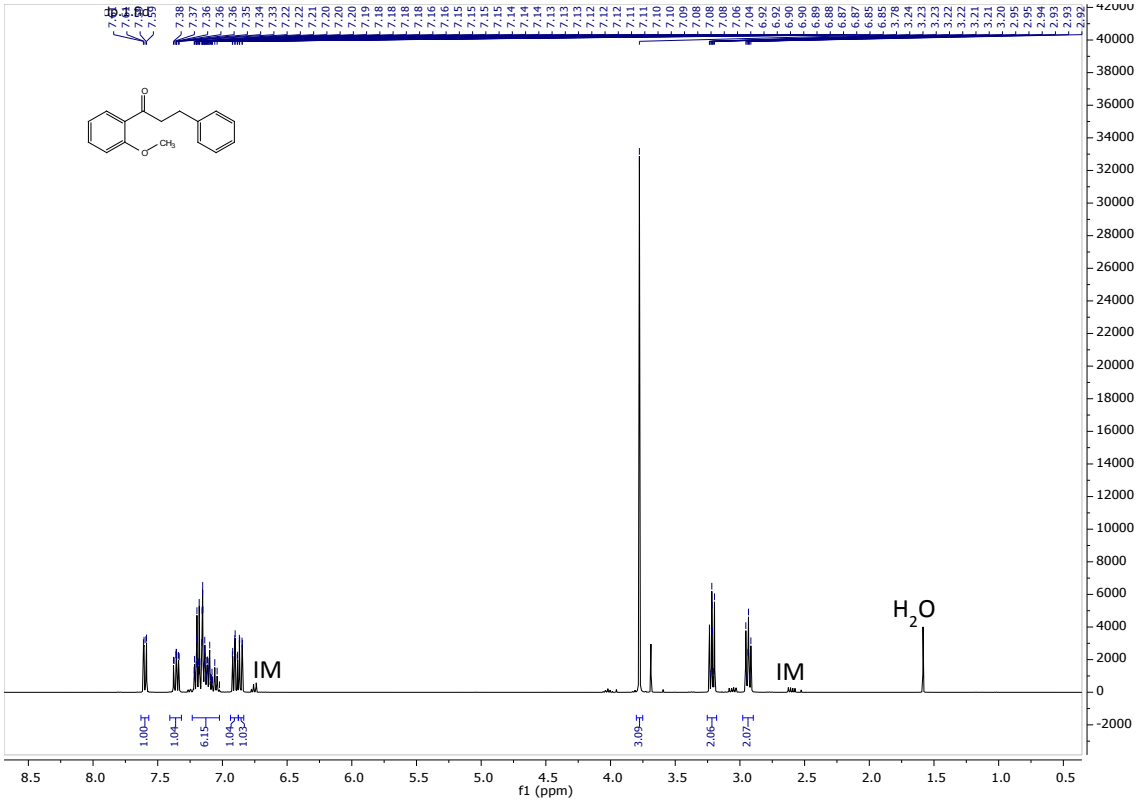
3fa ^{1}H NMR (400 MHz, Chloroform-*d*)



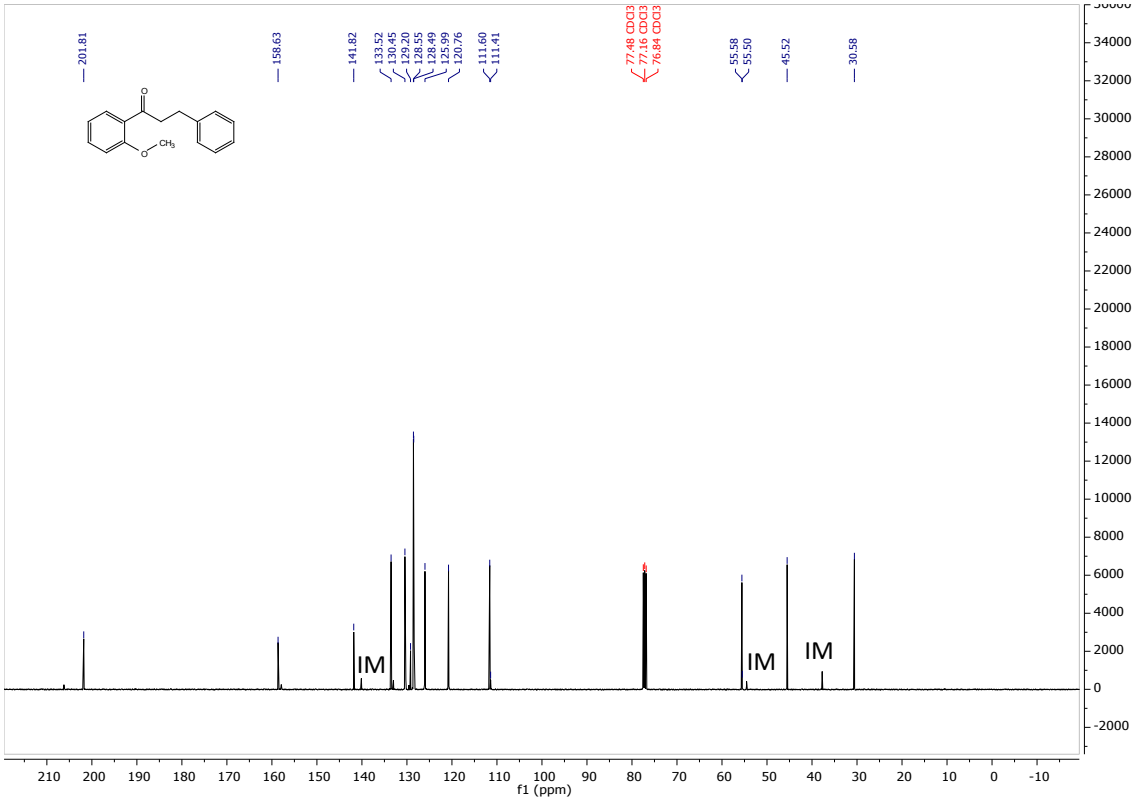
3fa $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)



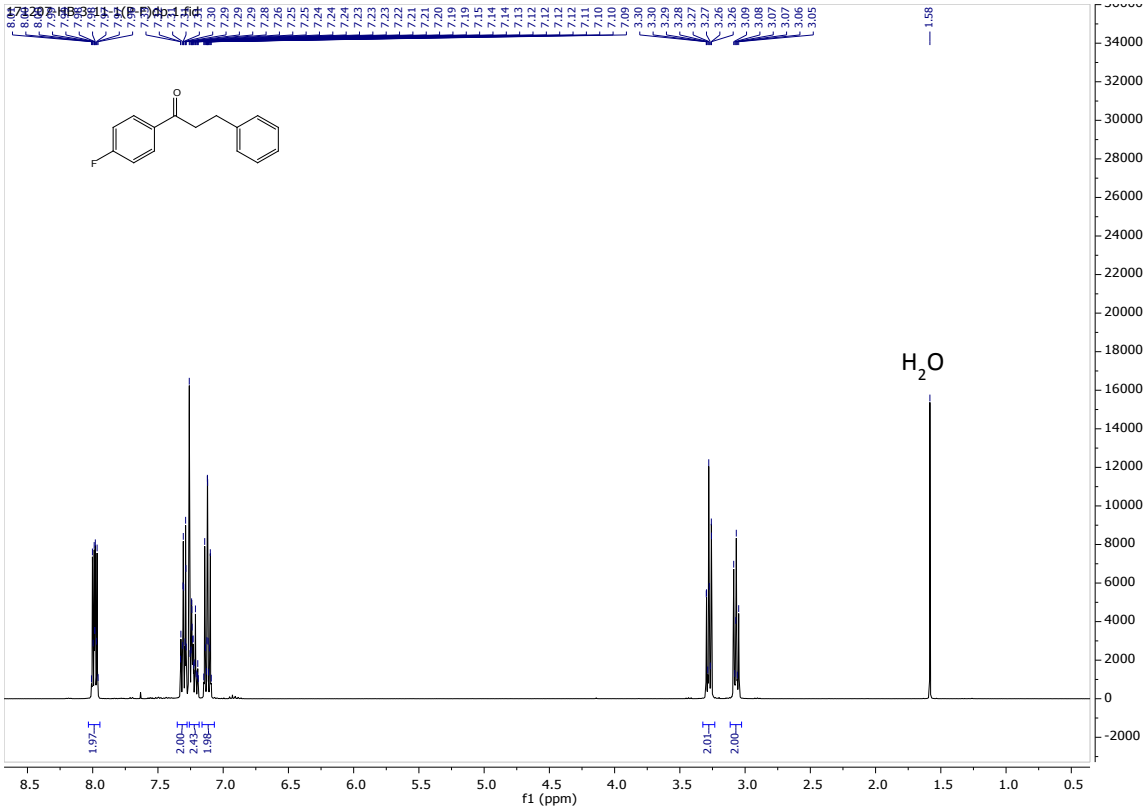
3ga ^{1}H NMR (400 MHz, Chloroform-*d*)



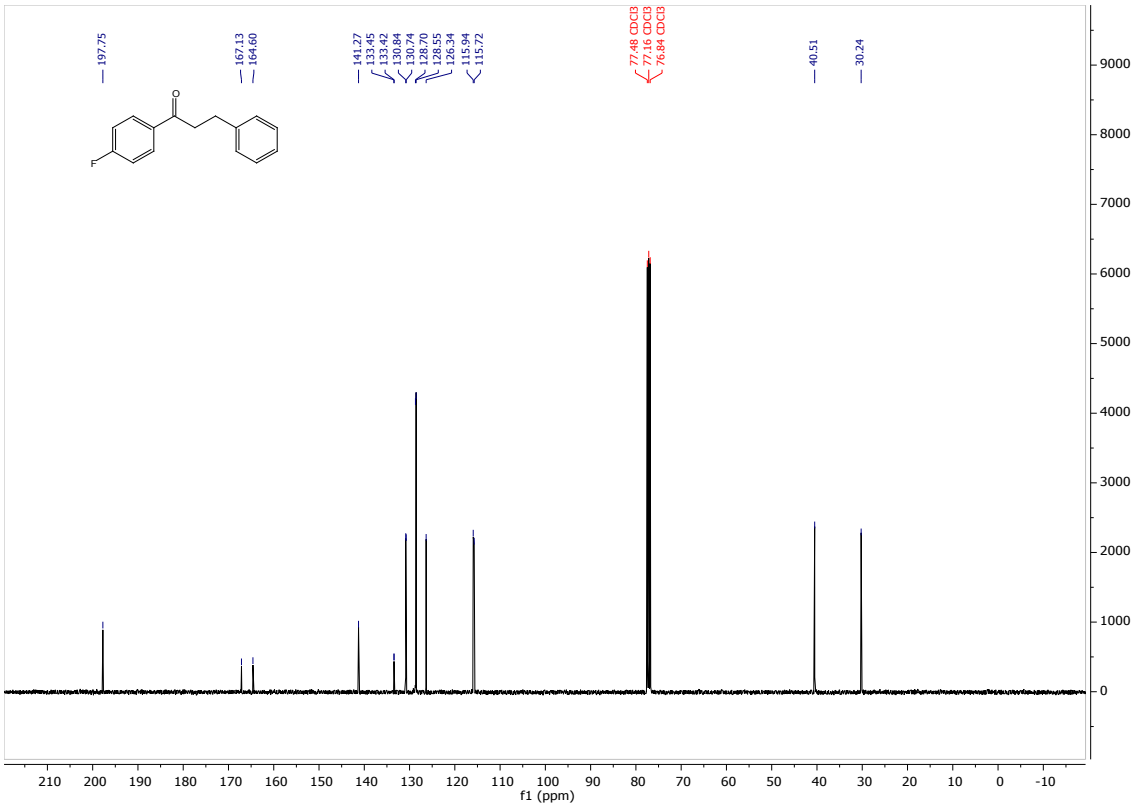
3ga ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



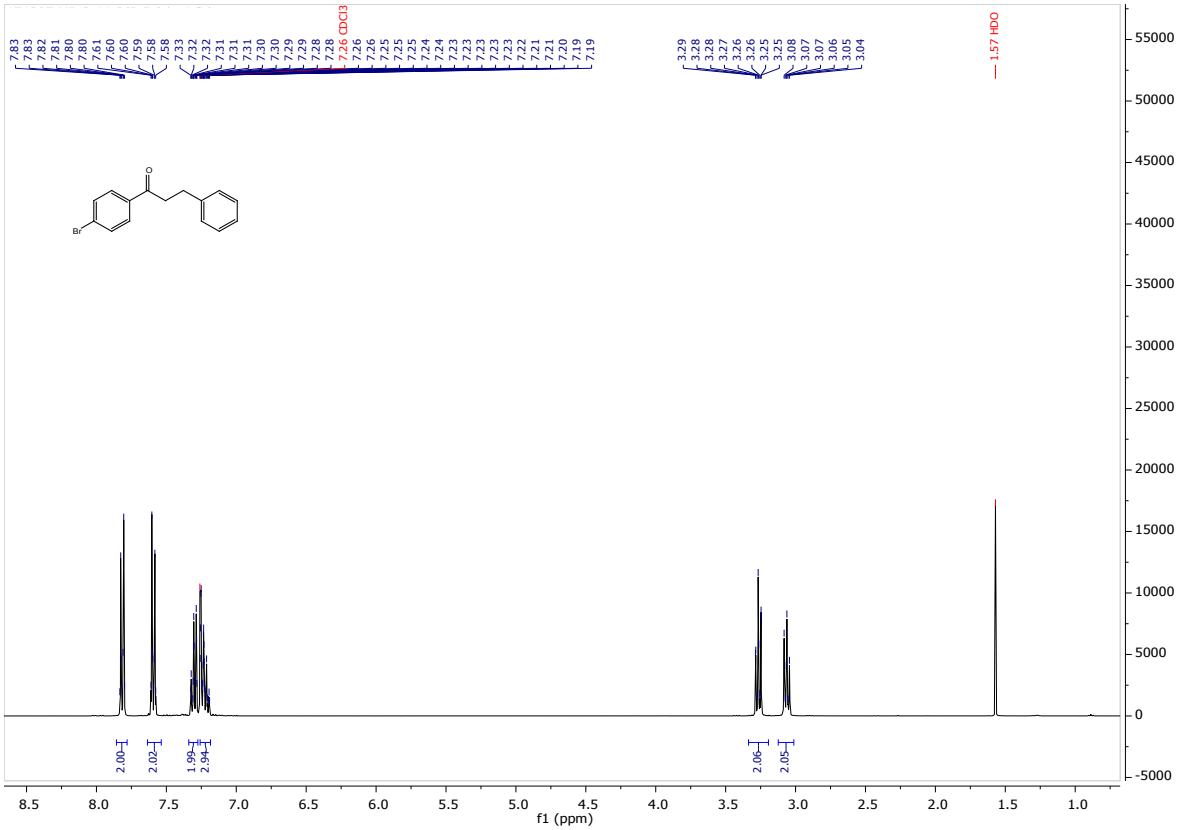
3ha ^{1}H NMR (400 MHz, Chloroform-*d*)



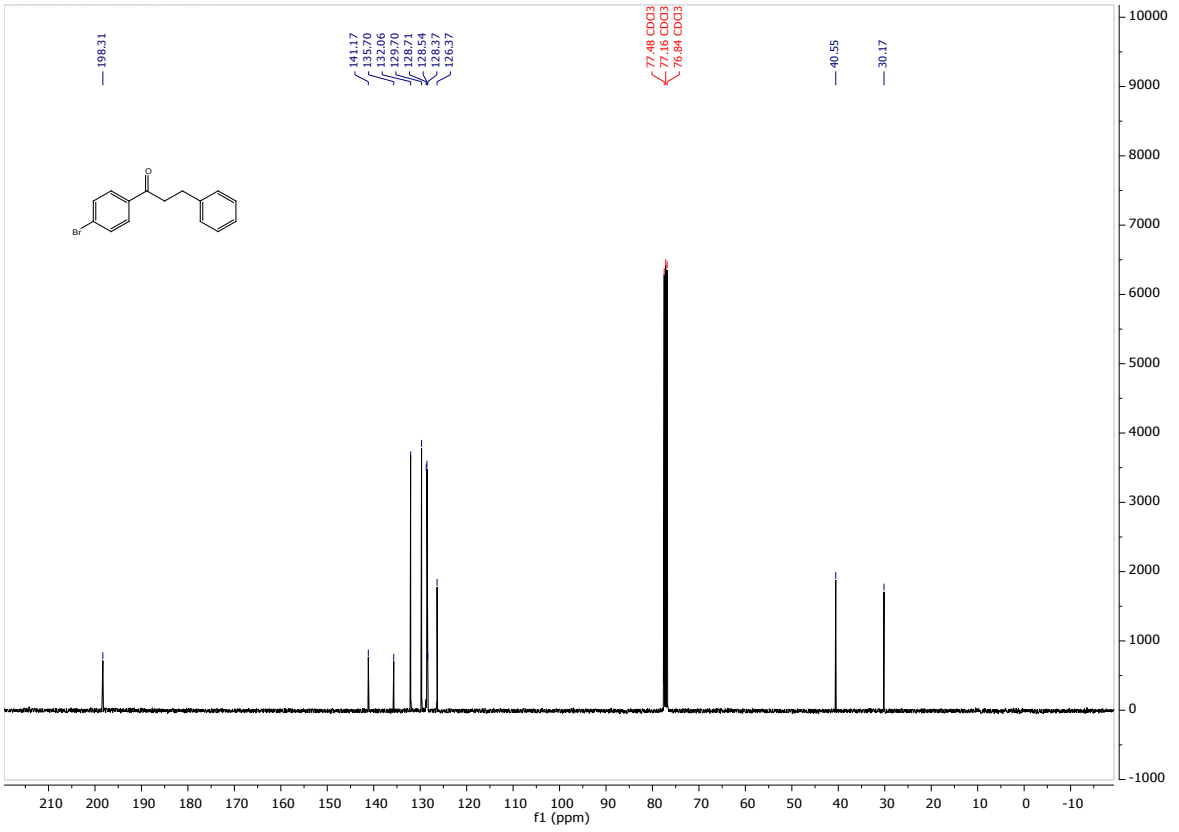
3ha ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



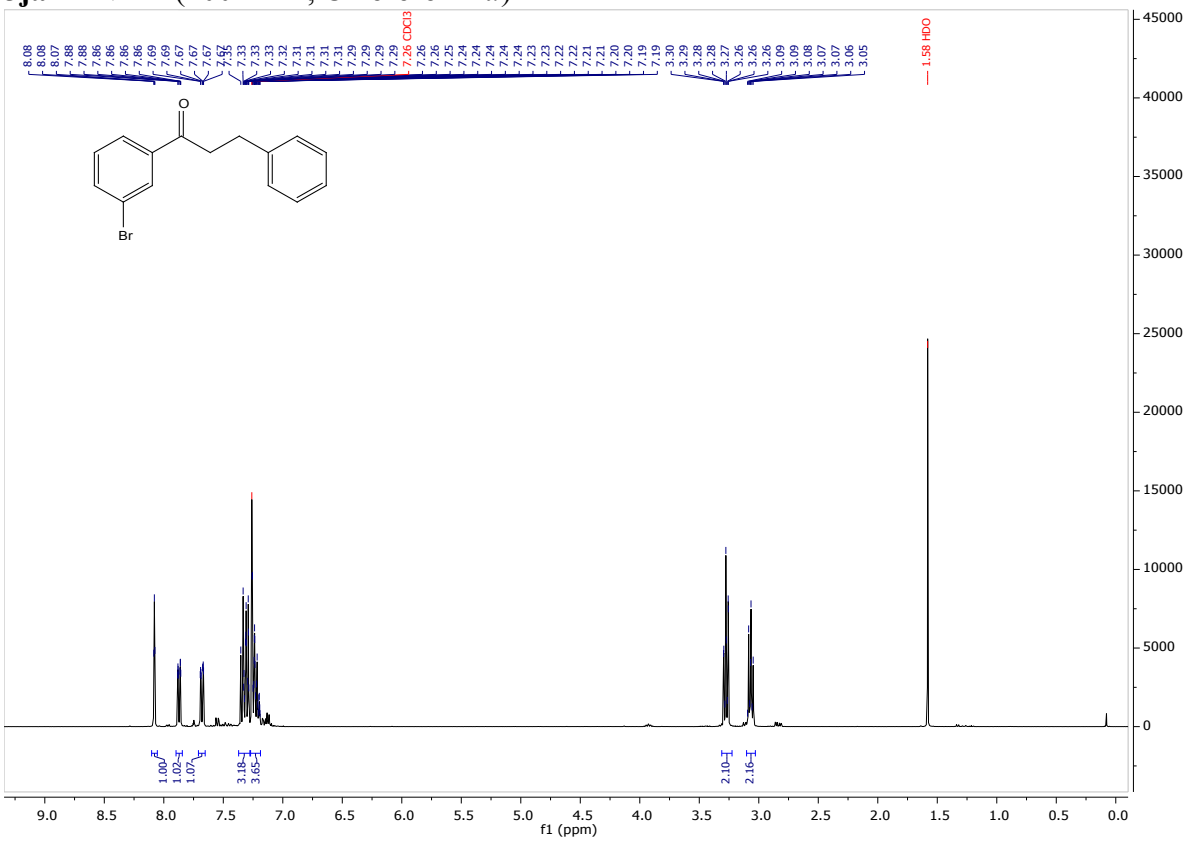
3ia ^{1}H NMR (400 MHz, Chloroform-*d*)



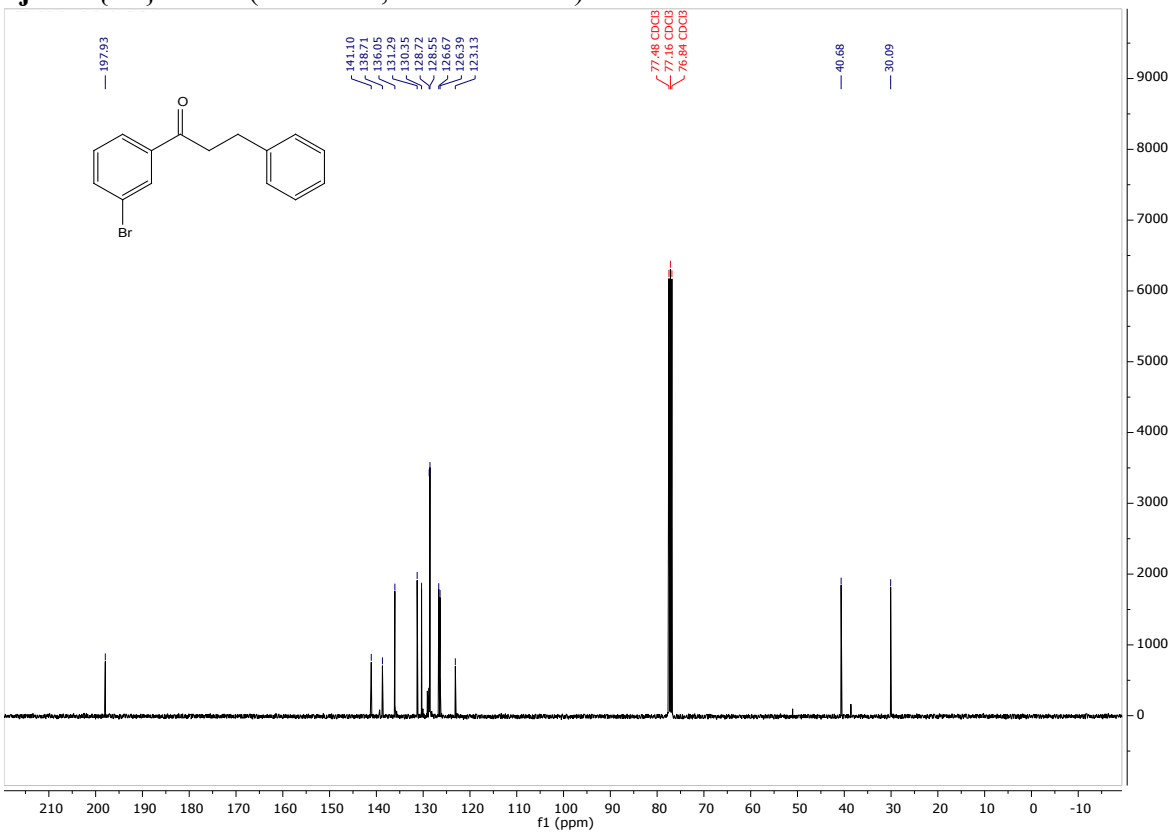
3ia ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



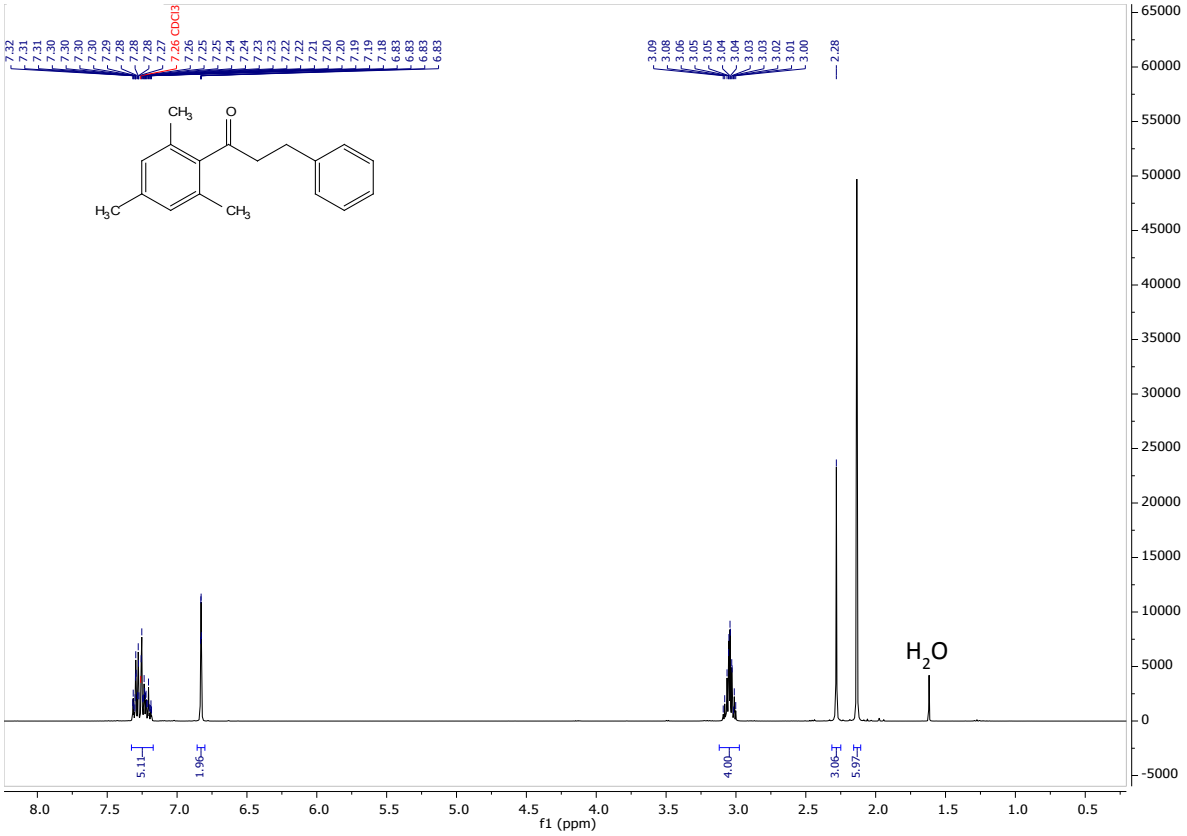
3ja ^{1}H NMR (400 MHz, Chloroform-*d*)



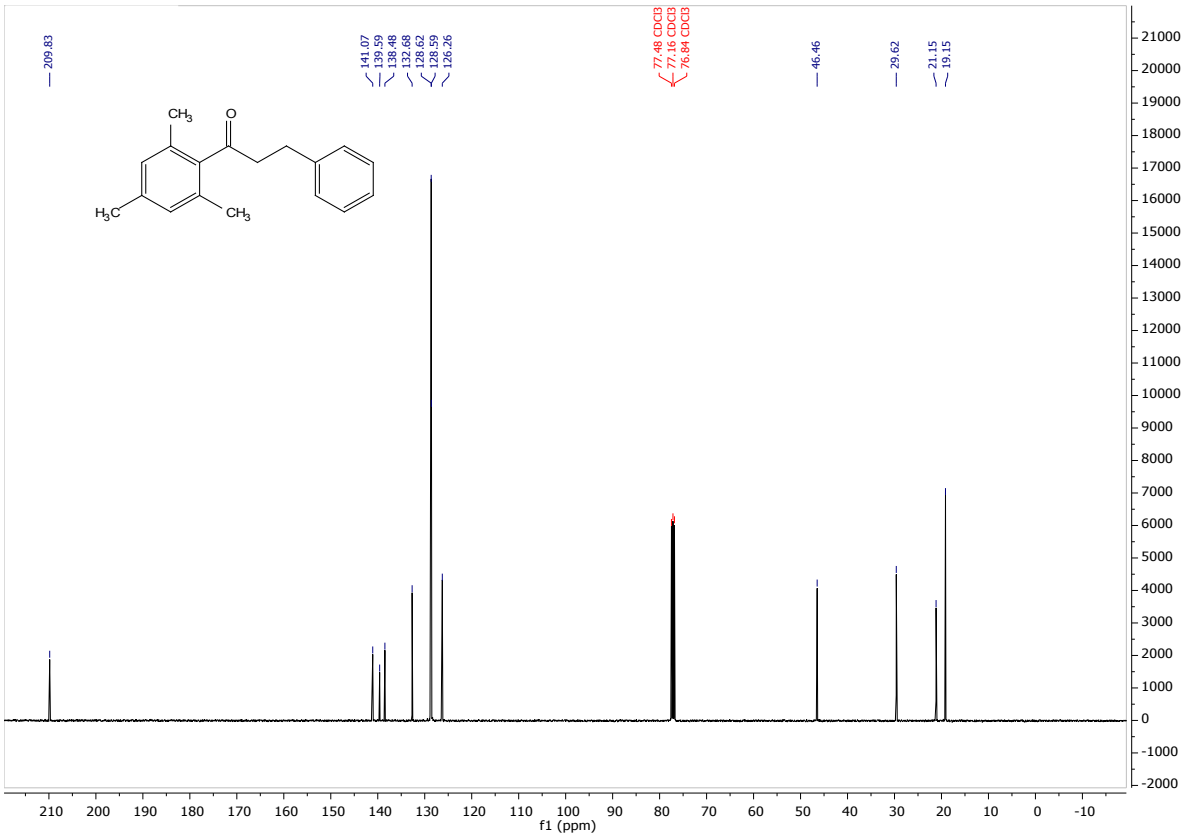
3ja ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



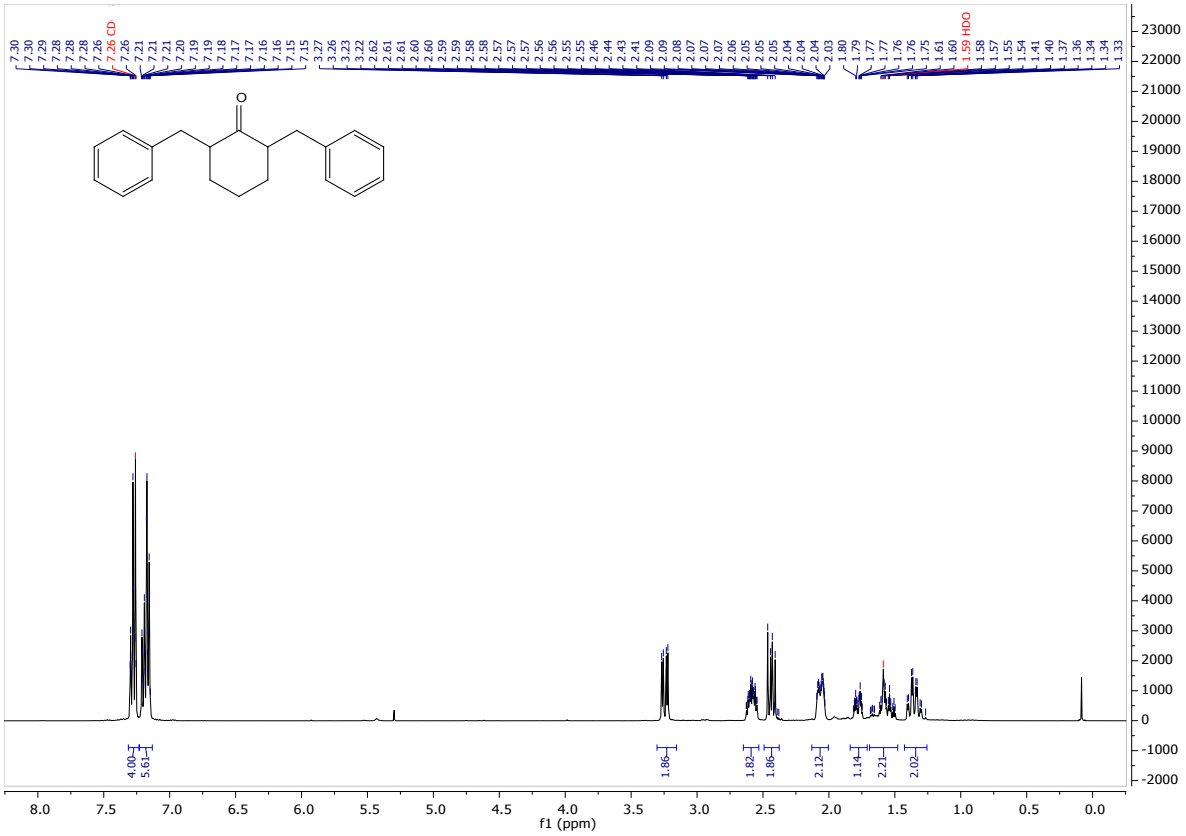
3ka ^{1}H NMR (400 MHz, Chloroform-*d*)



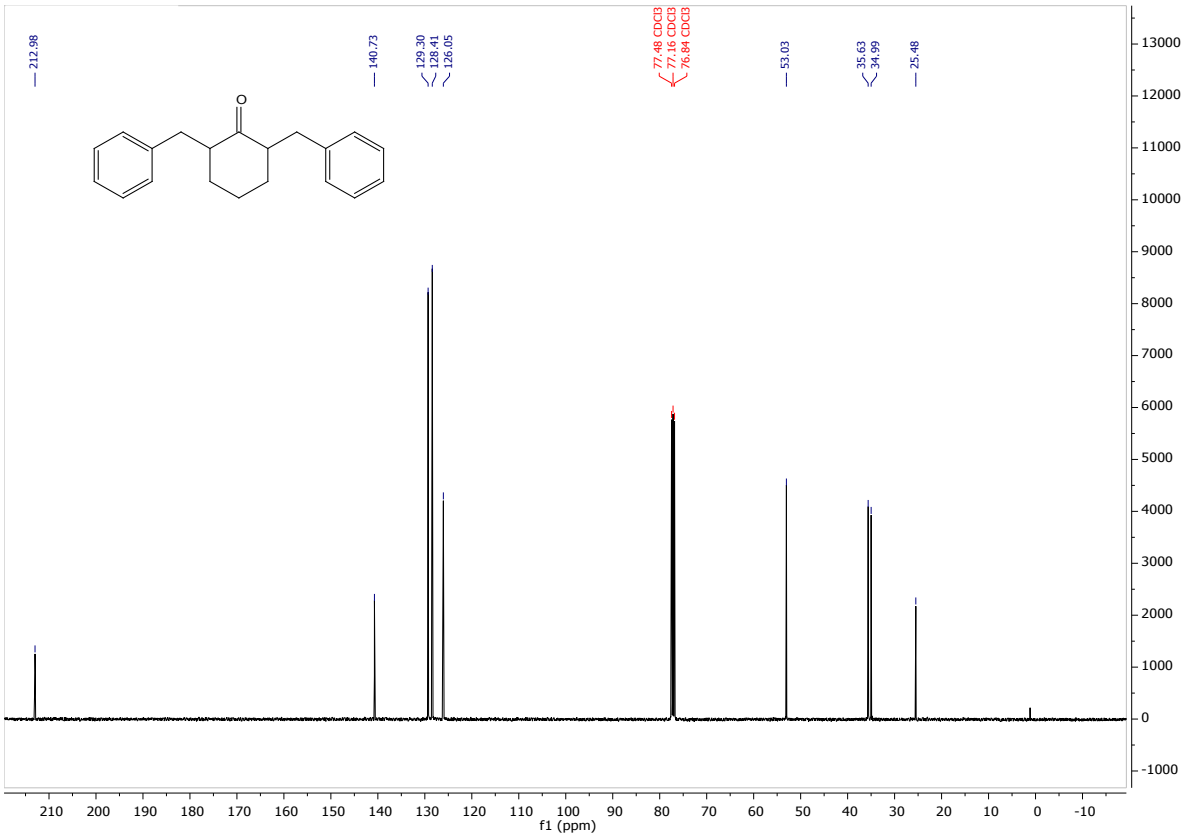
3ka ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



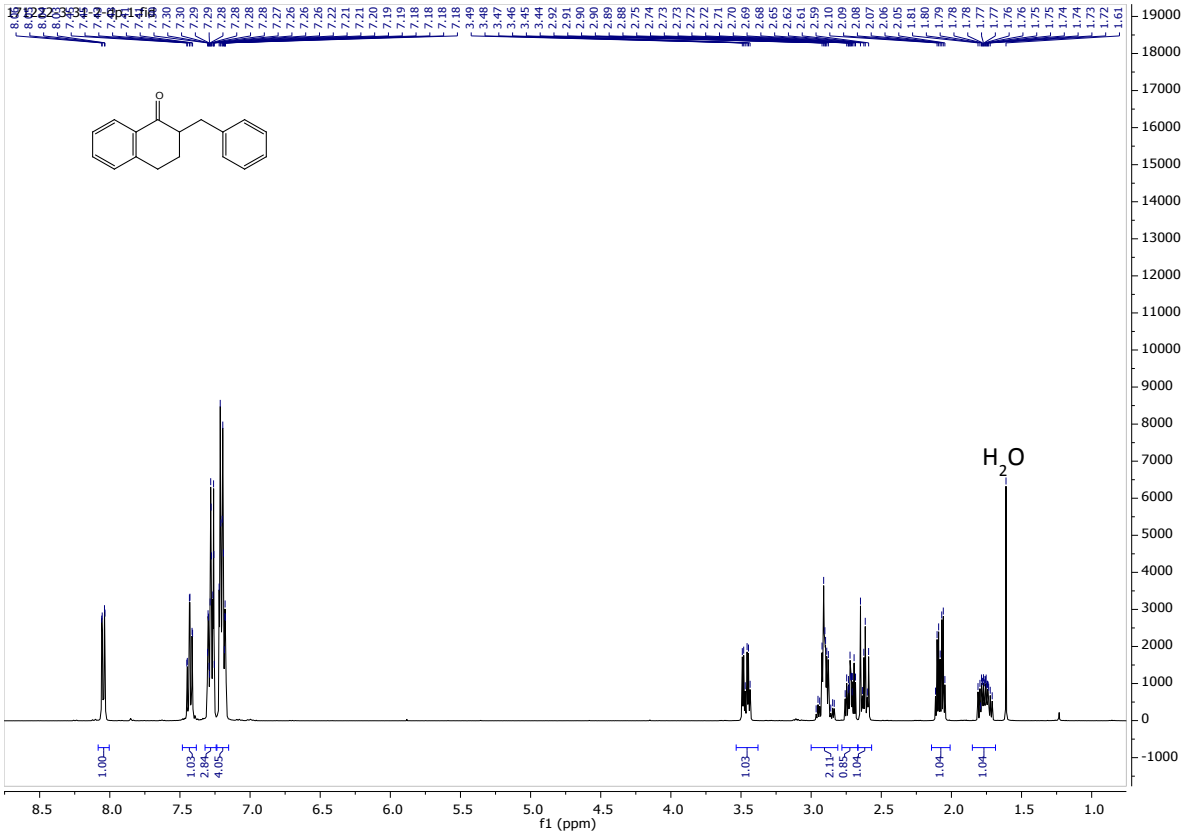
3ma ^{1}H NMR (400 MHz, Chloroform-*d*)



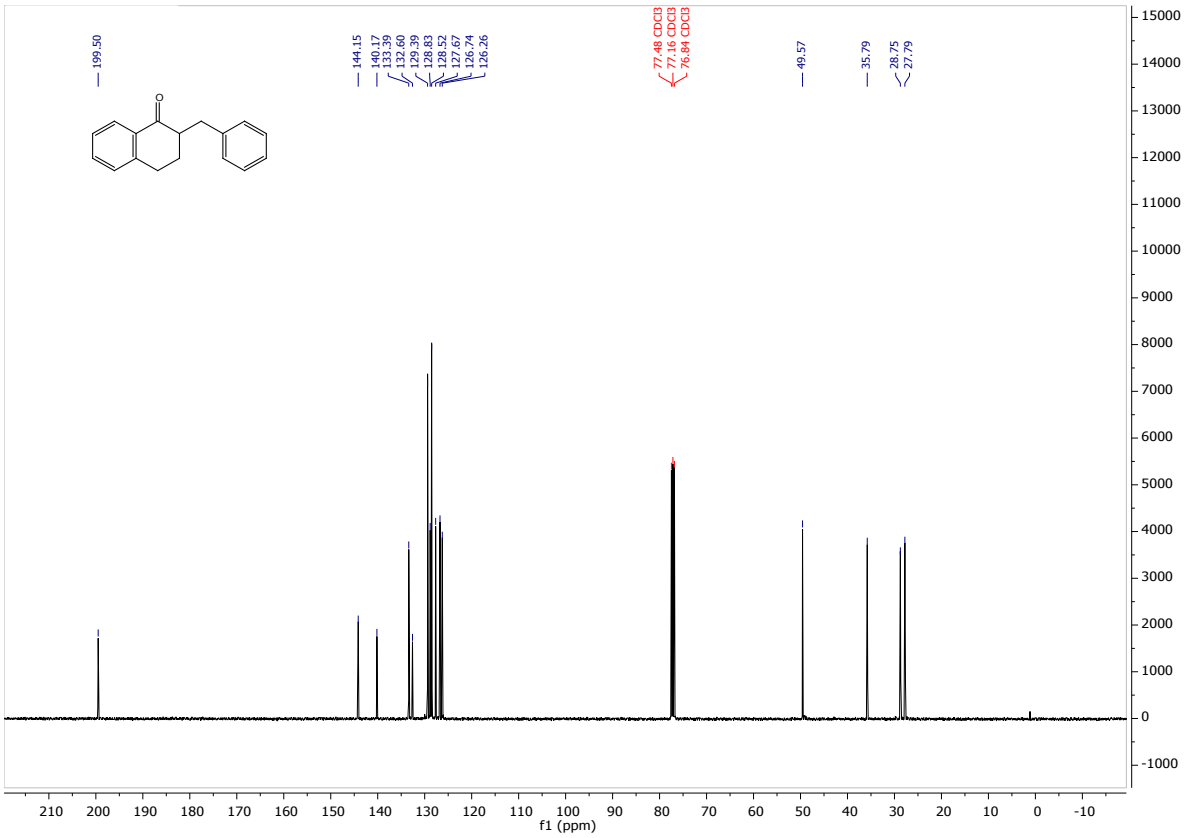
3ma ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



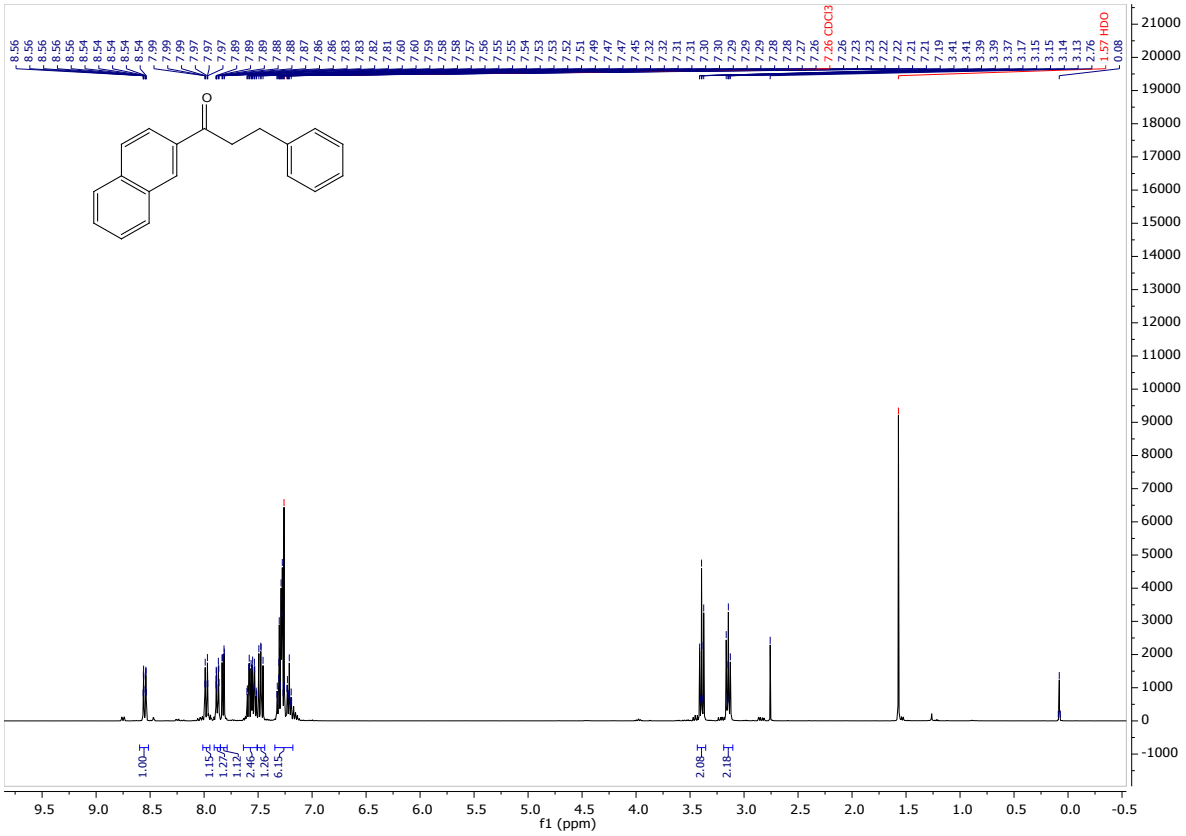
3na ^{1}H NMR (400 MHz, Chloroform-*d*)



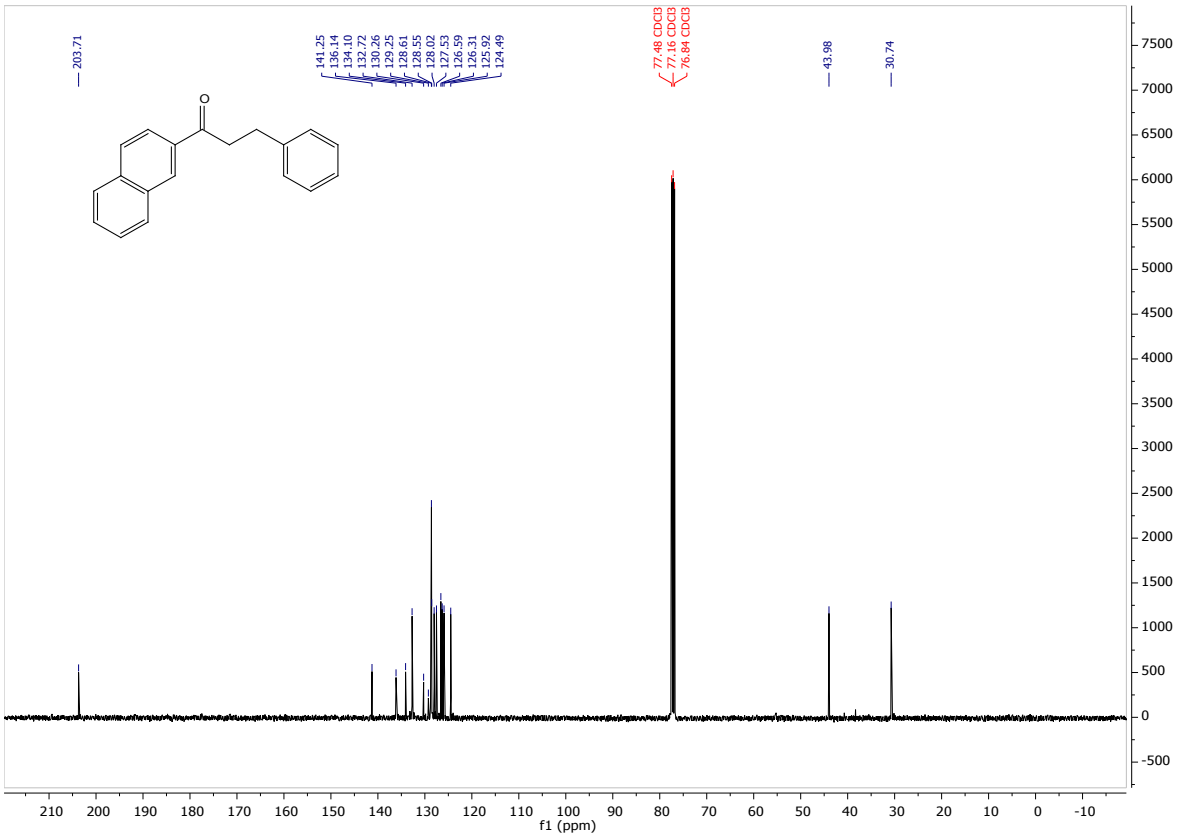
3na ^{13}C{^{1}H} NMR (400 MHz, Chloroform-*d*)



3oa ^{1}H NMR (400 MHz, Chloroform-*d*)

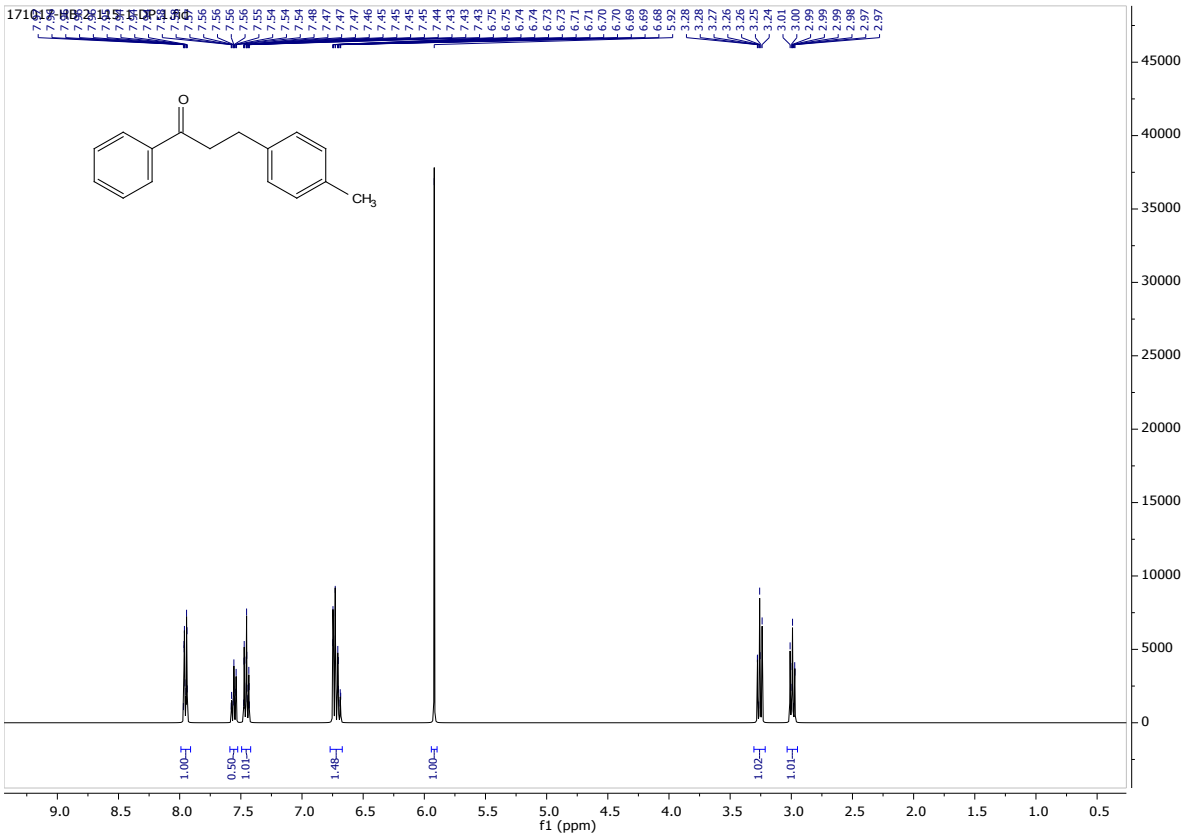


3oa ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

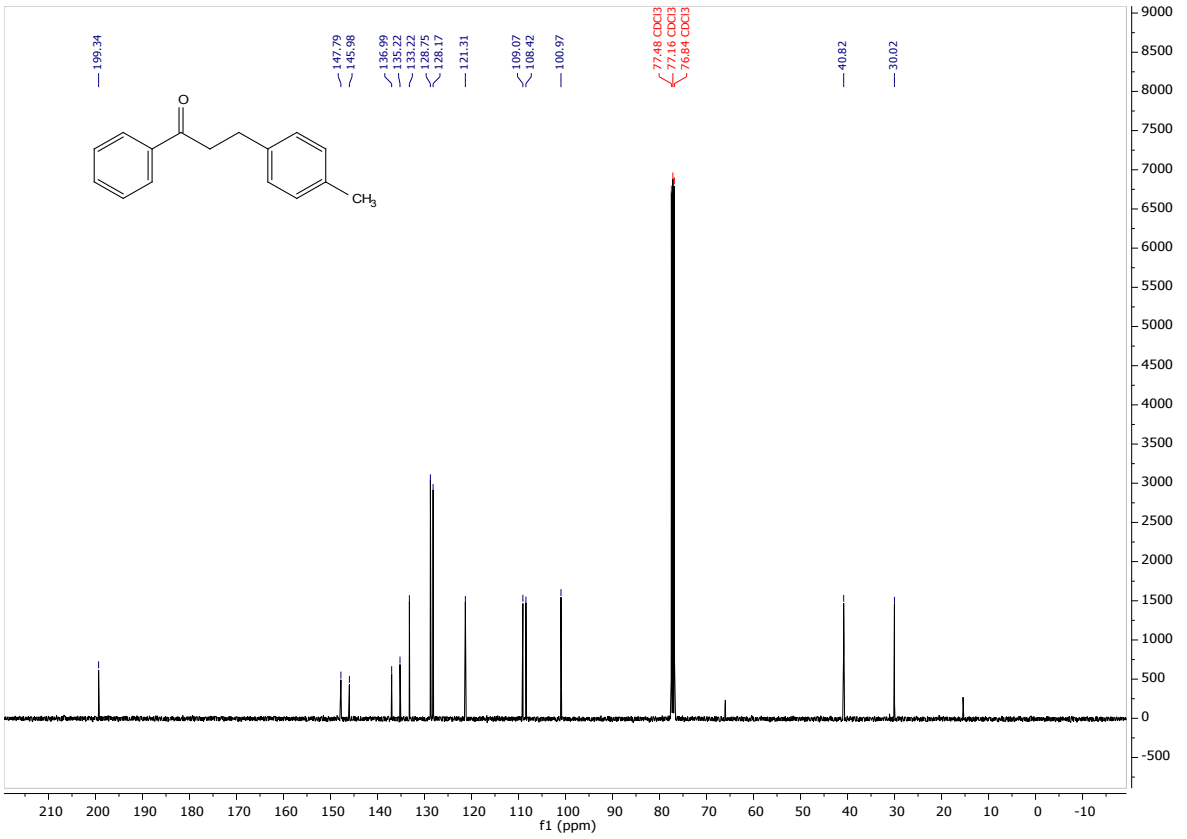


S1.9.2 Alcohol scope for the alkylated ketones

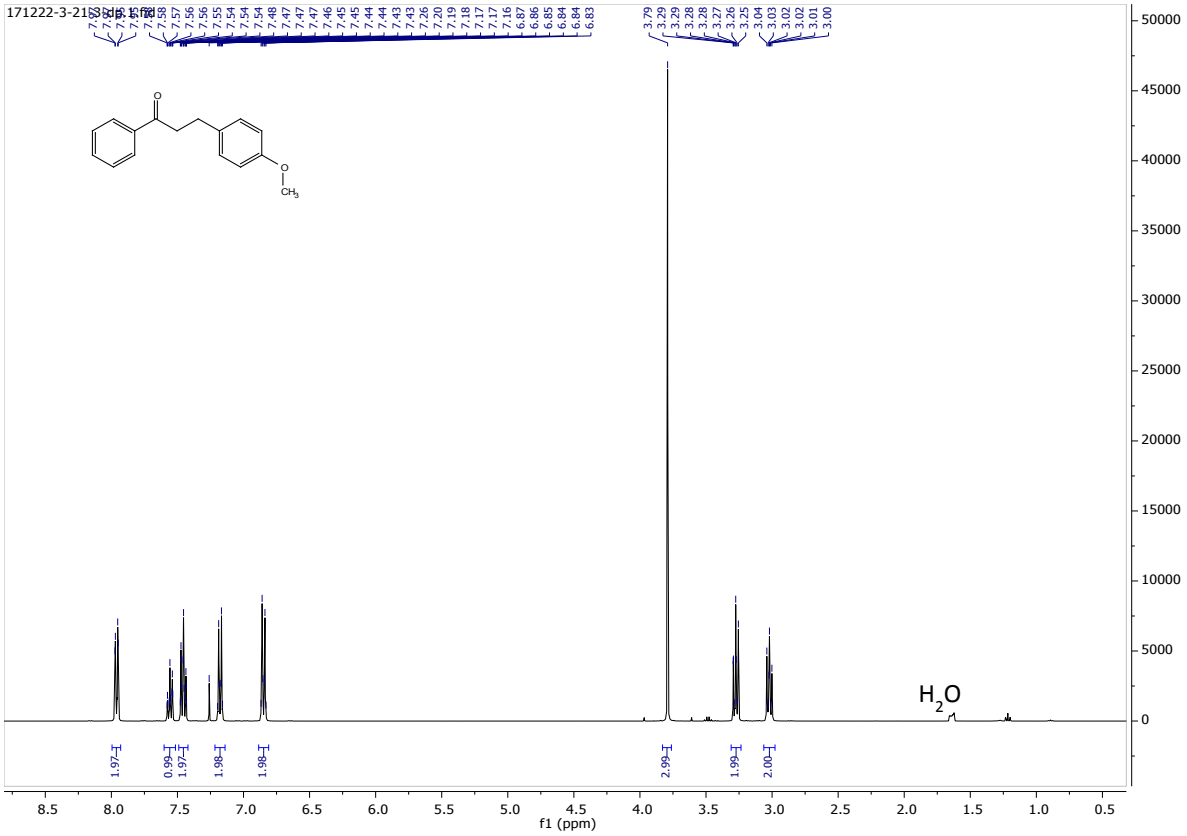
3ab ^{1}H NMR (400 MHz, Chloroform-*d*)



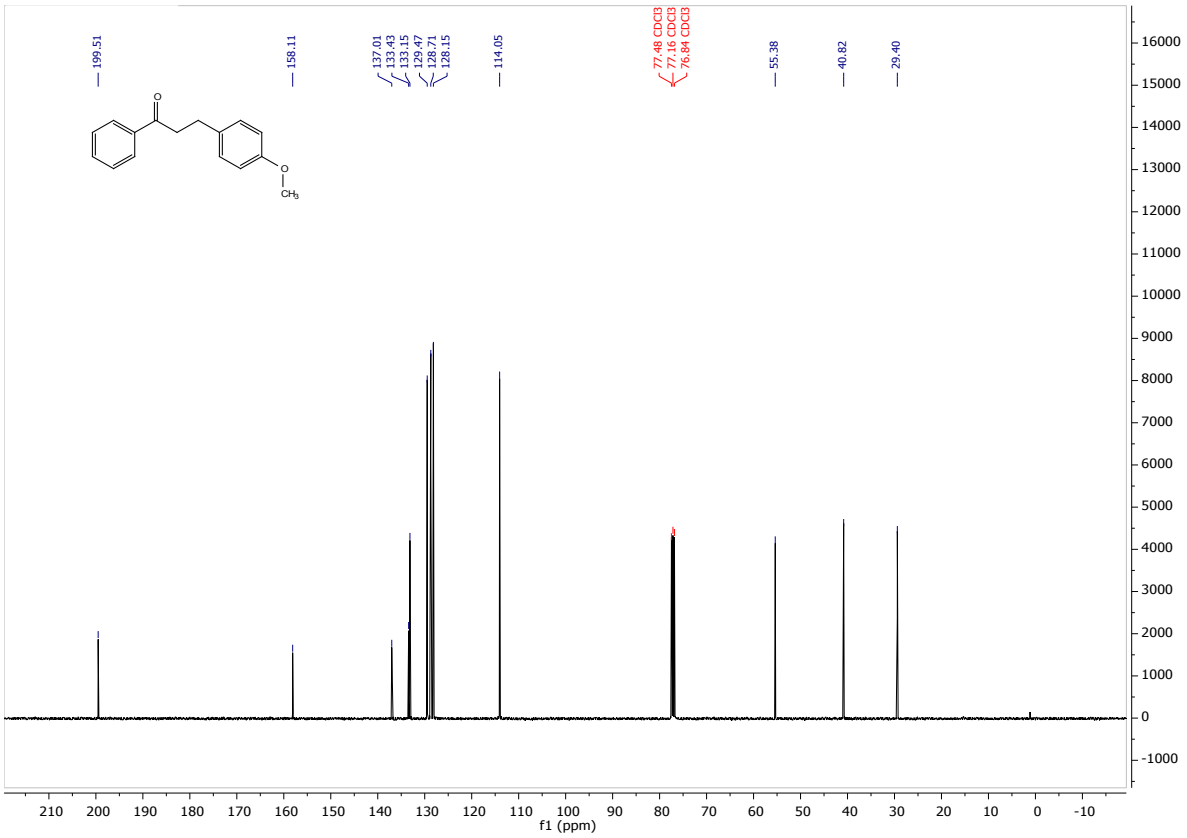
3ab ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



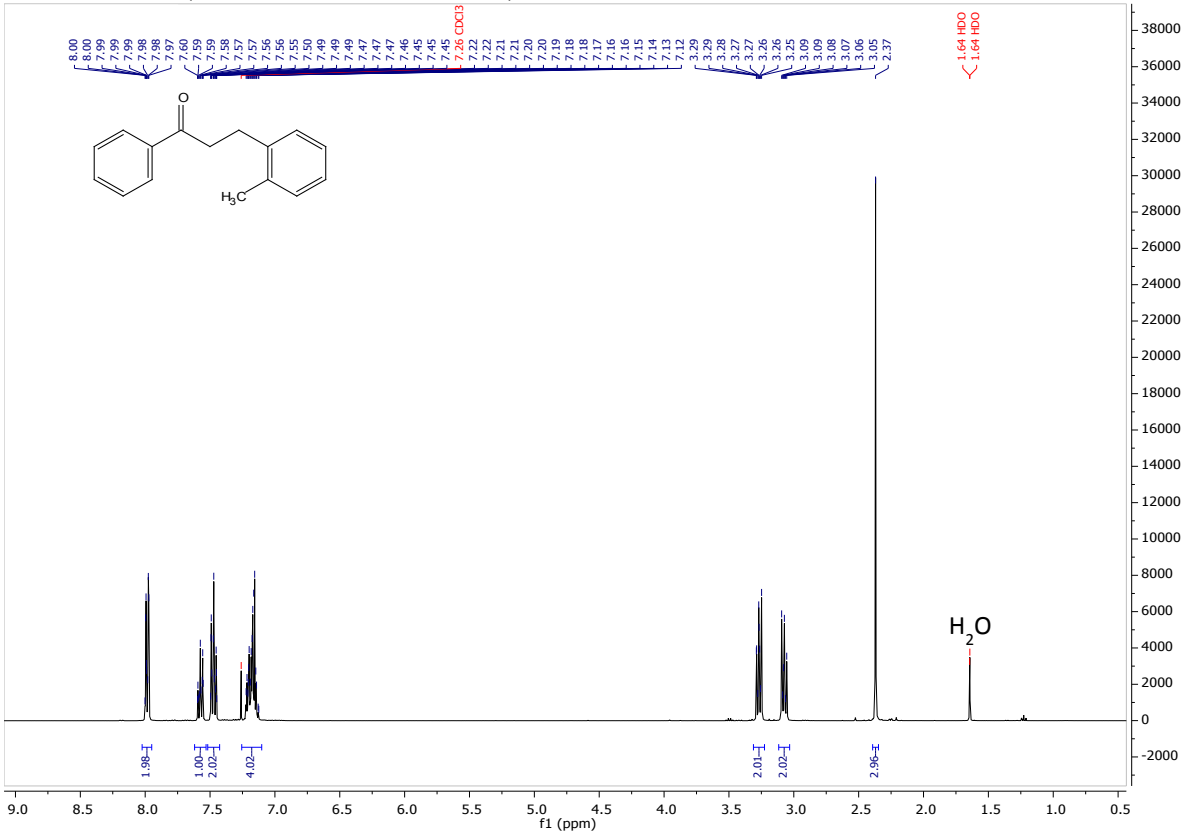
3ac ^{1}H NMR (400 MHz, Chloroform-*d*)



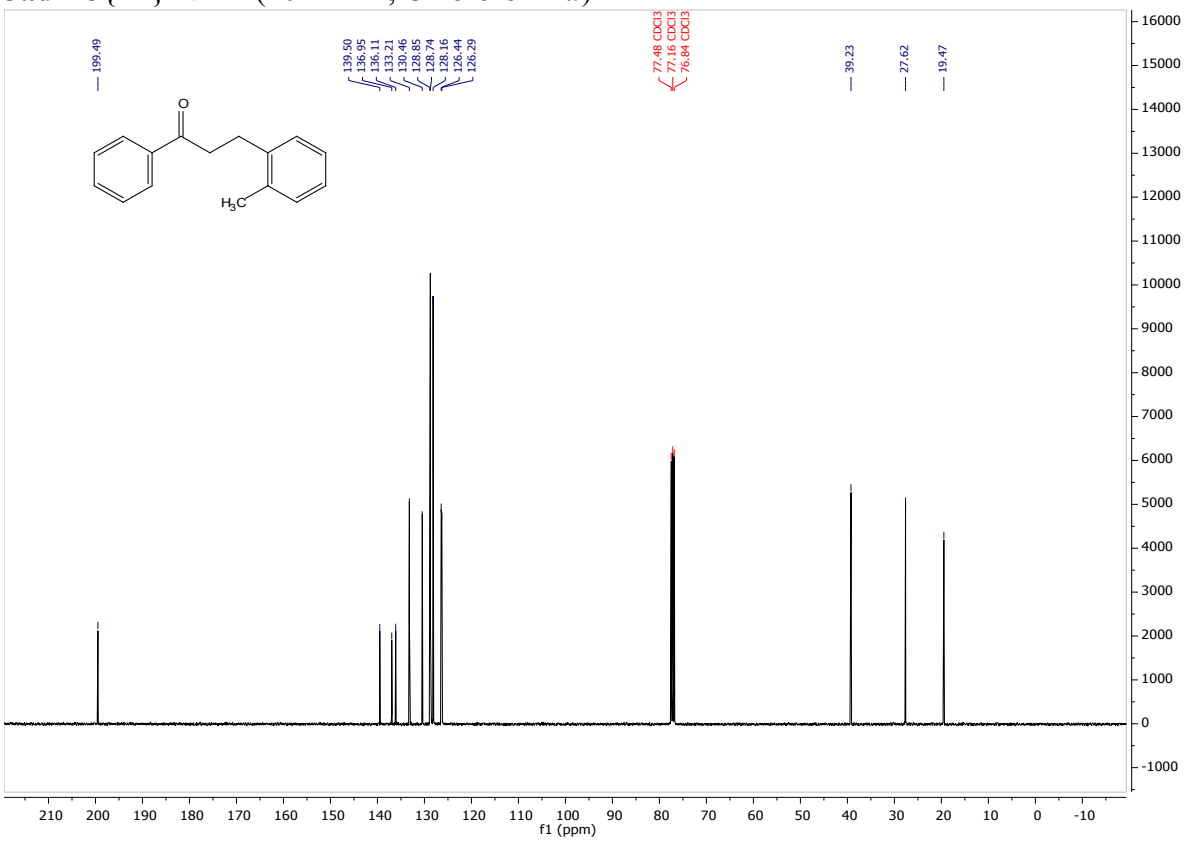
3ac ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



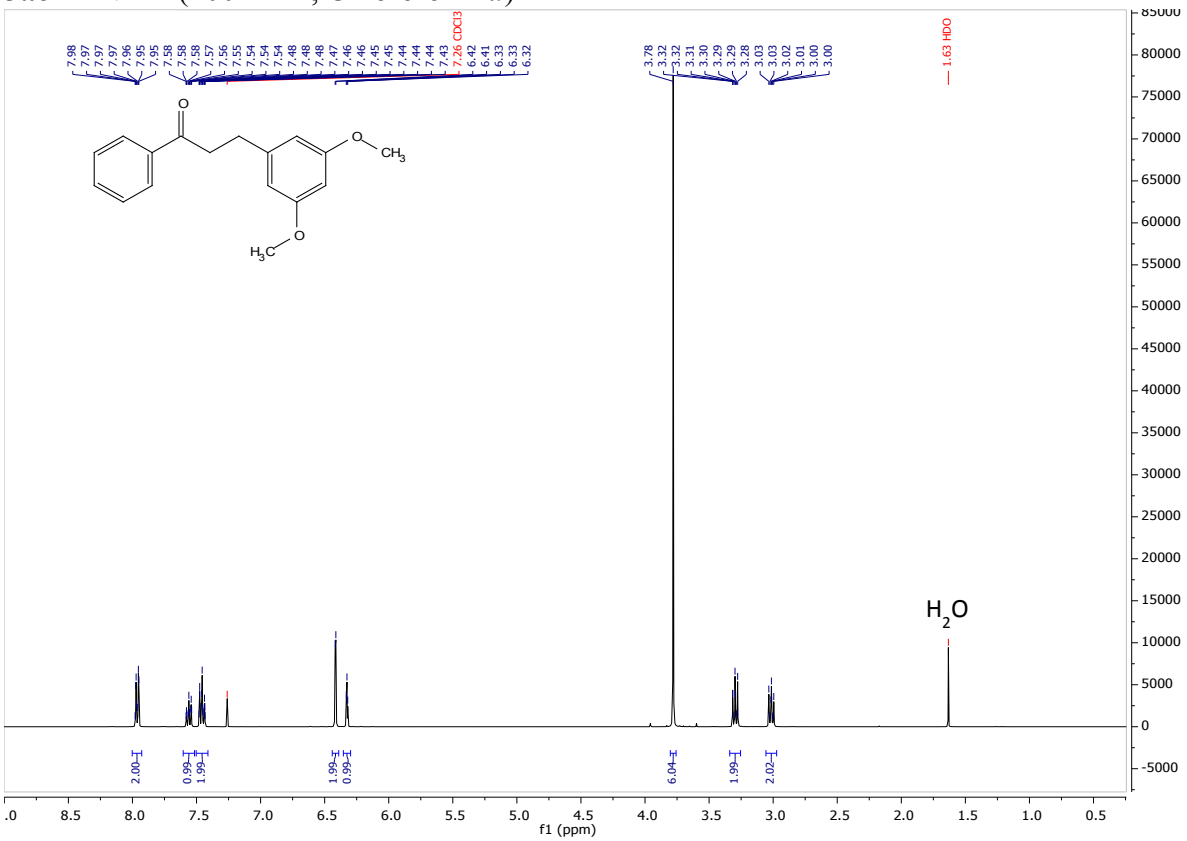
3ad ^{1}H NMR (400 MHz, Chloroform-*d*)



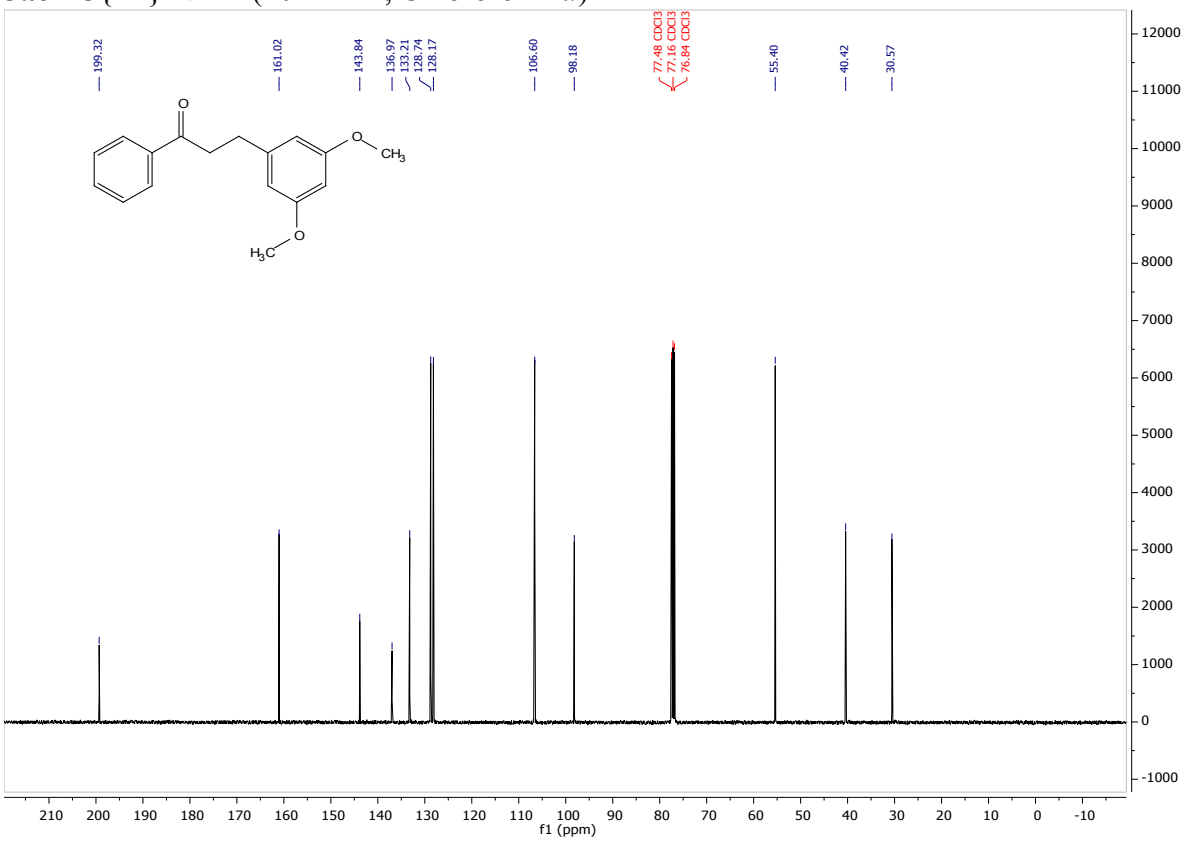
3ad ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



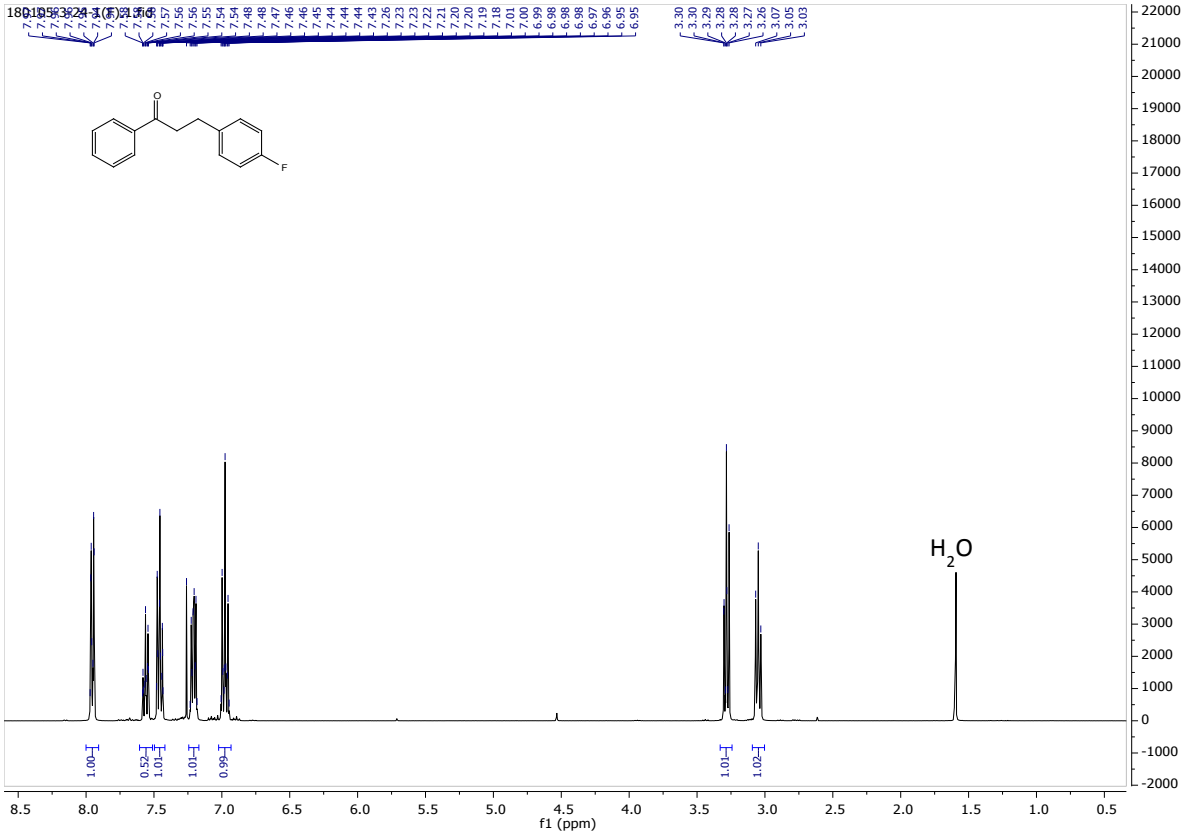
3ae ^{1}H NMR (400 MHz, Chloroform-*d*)



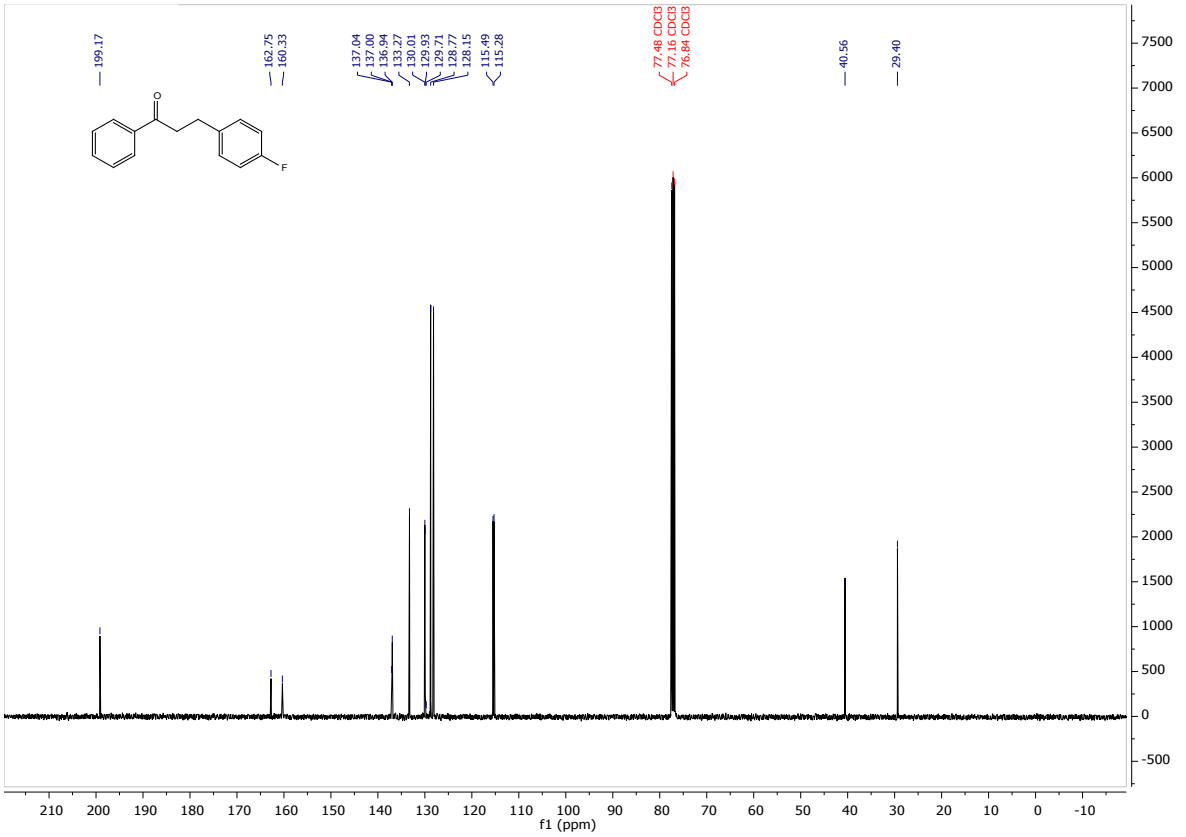
3ae ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



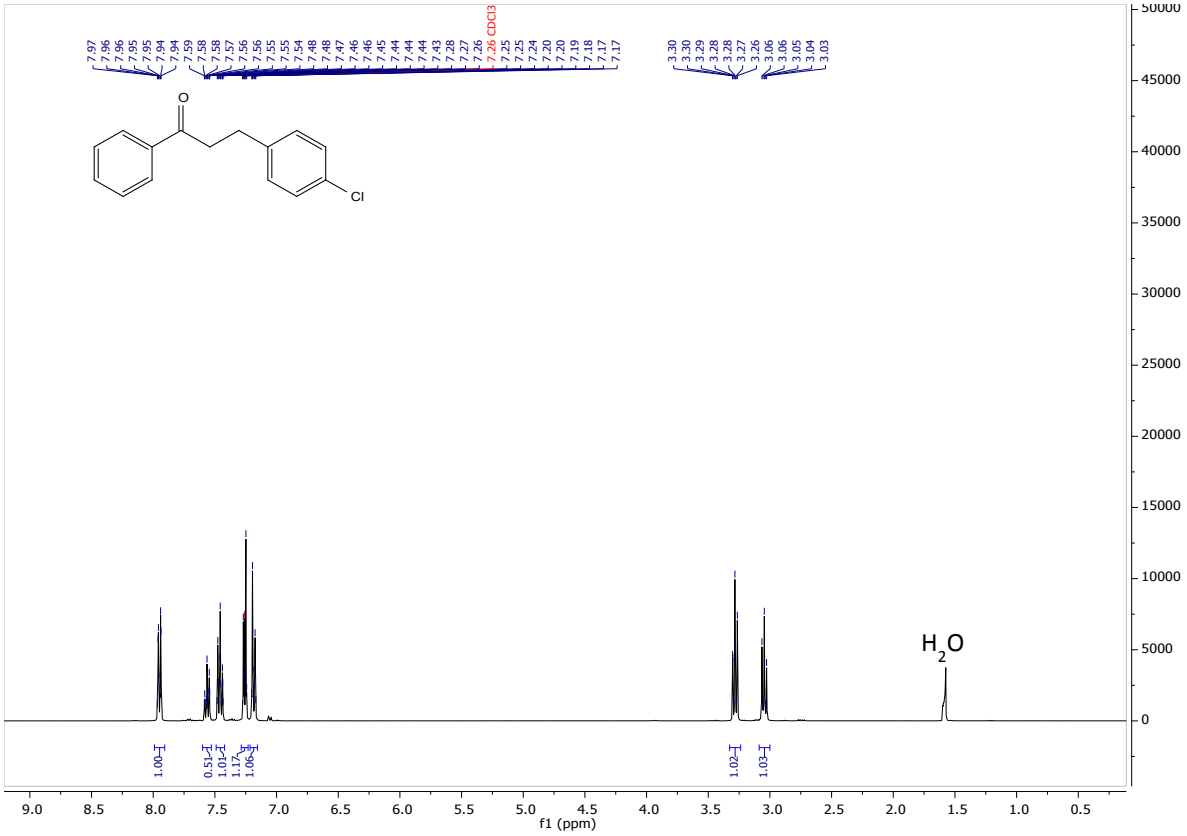
3af ^{1}H NMR (400 MHz, Chloroform-*d*)



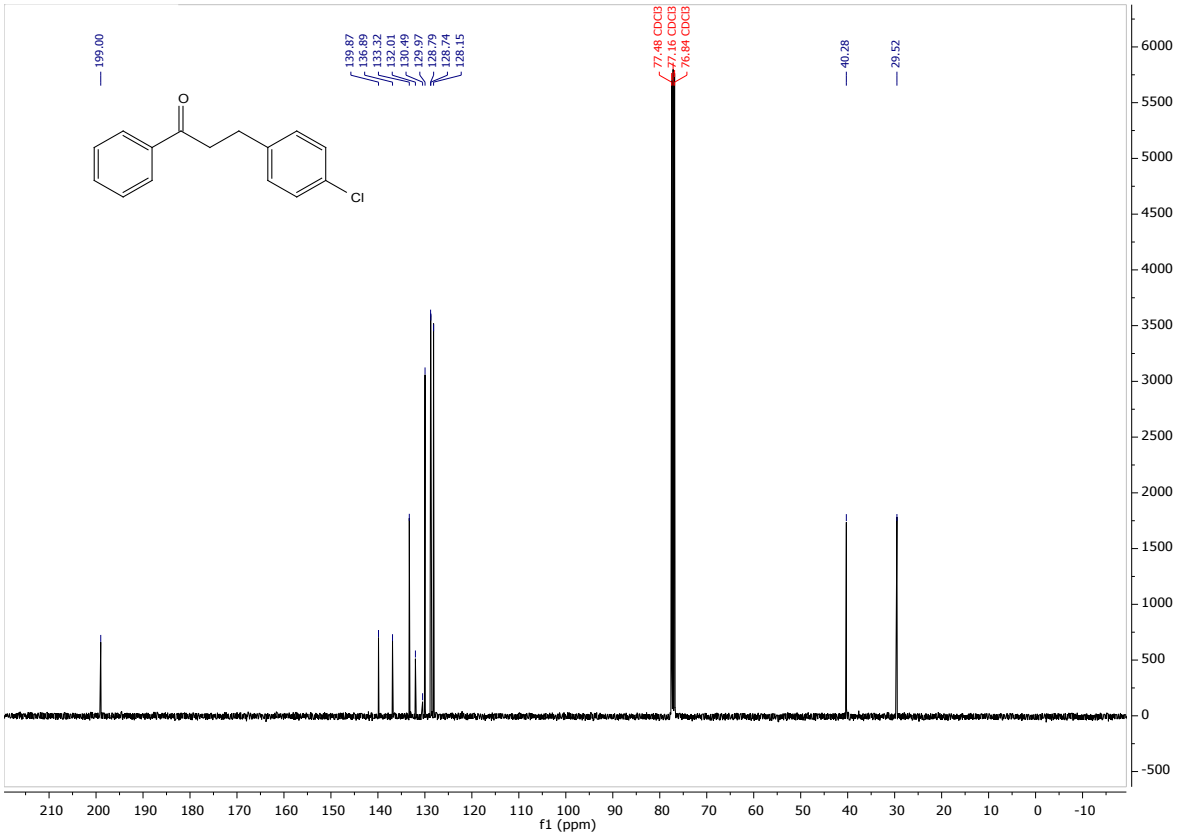
3af ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



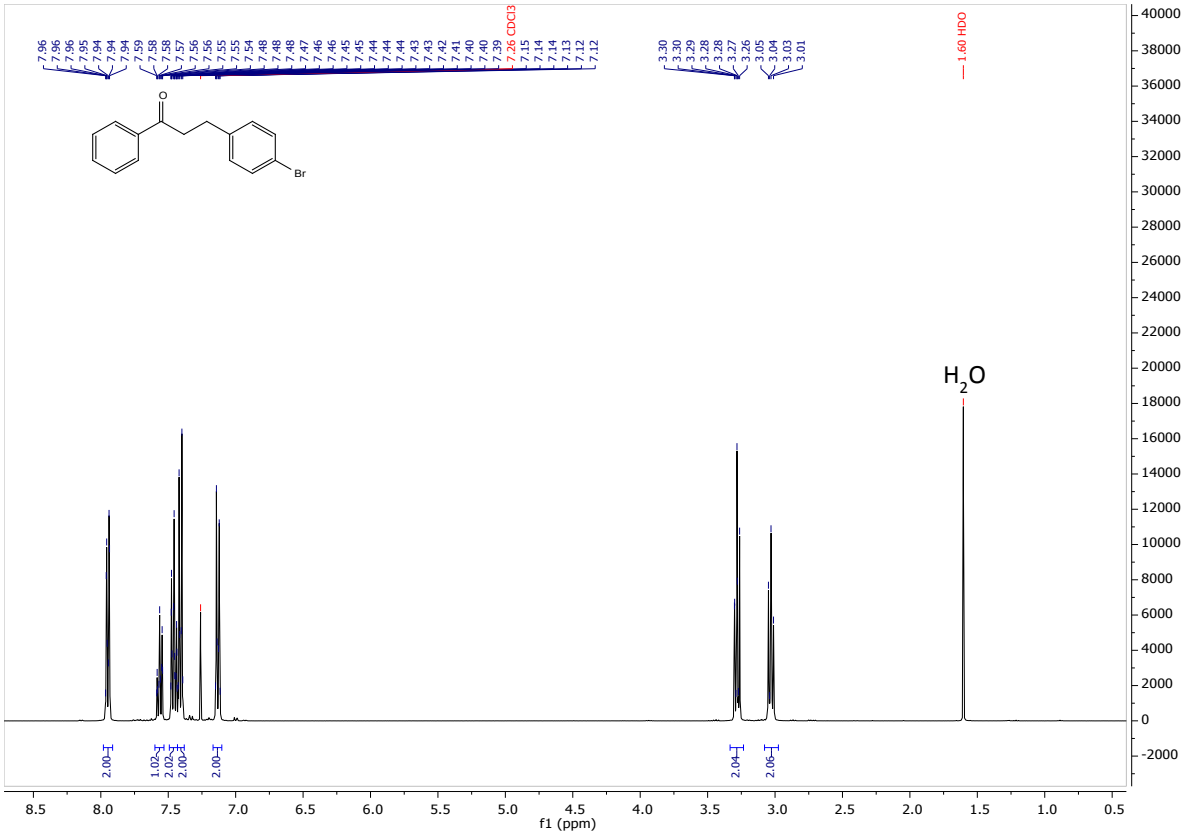
3ag ^{1}H NMR (400 MHz, Chloroform-*d*)



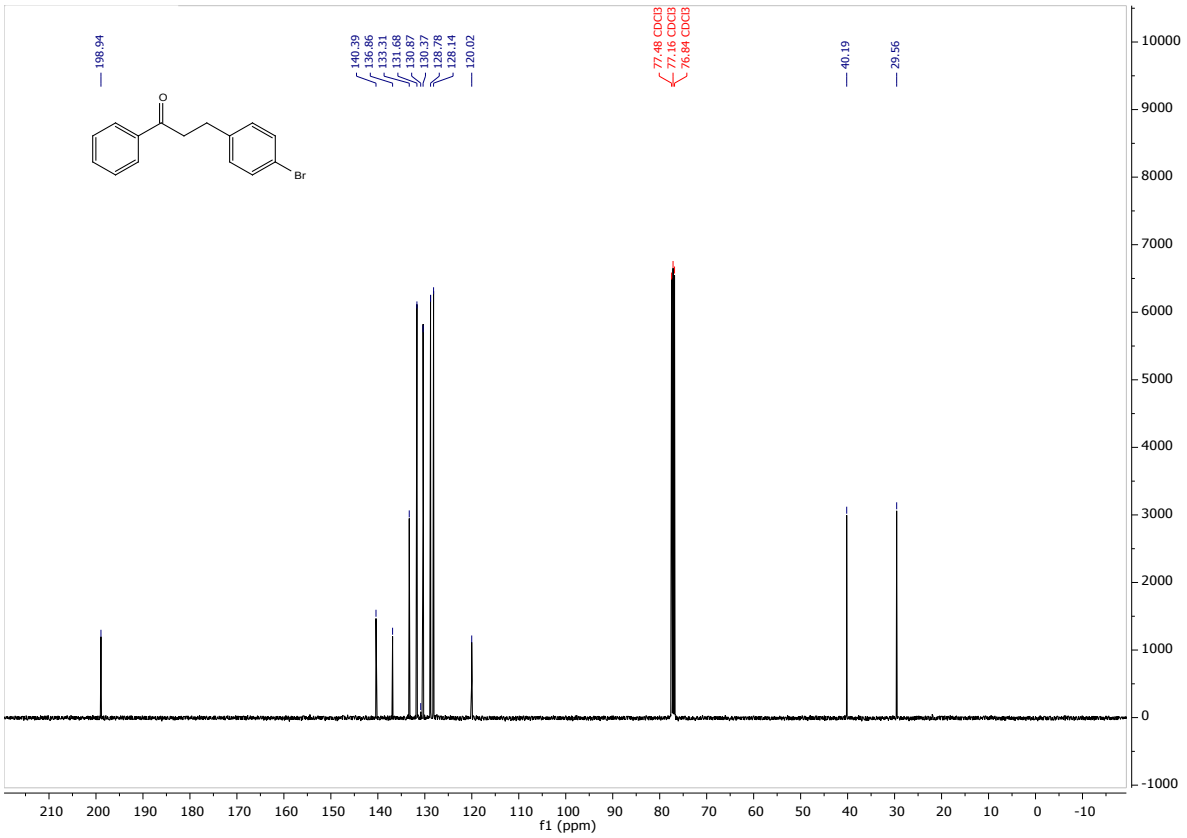
3ag ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



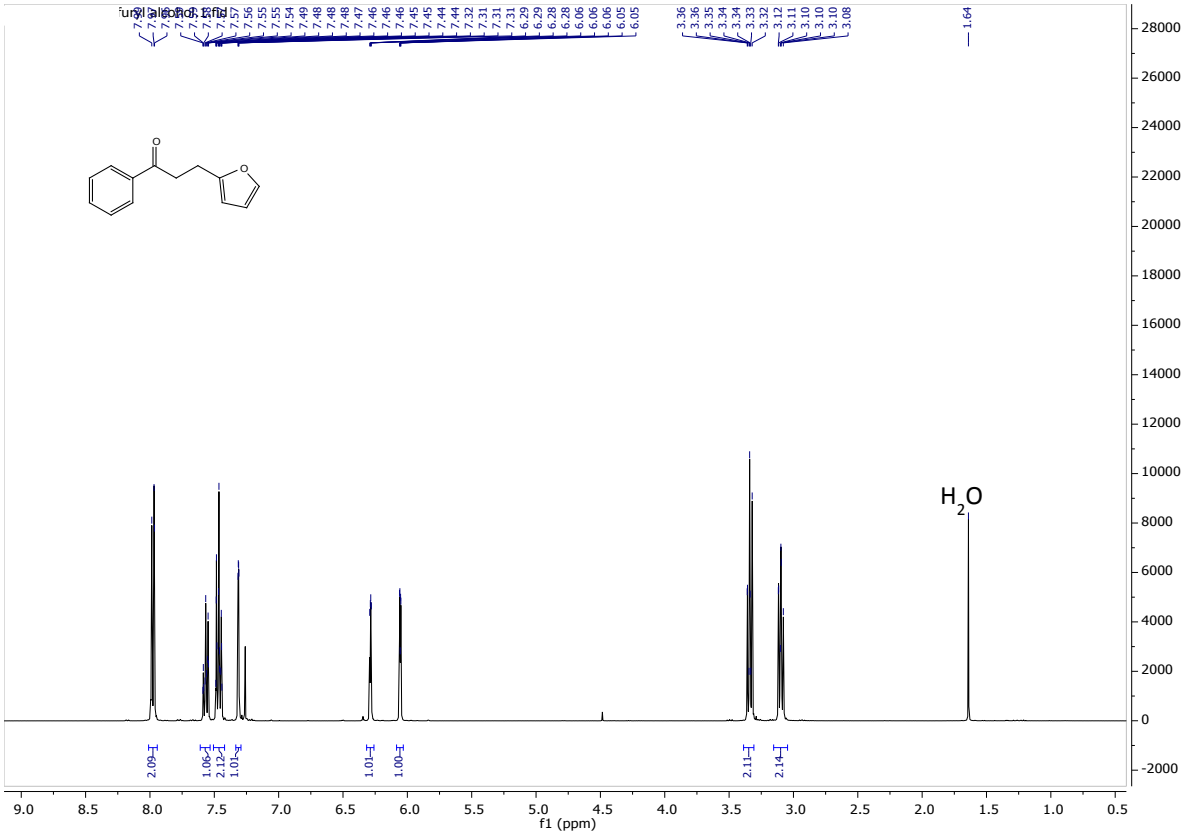
3ah ^{1}H NMR (400 MHz, Chloroform-*d*)



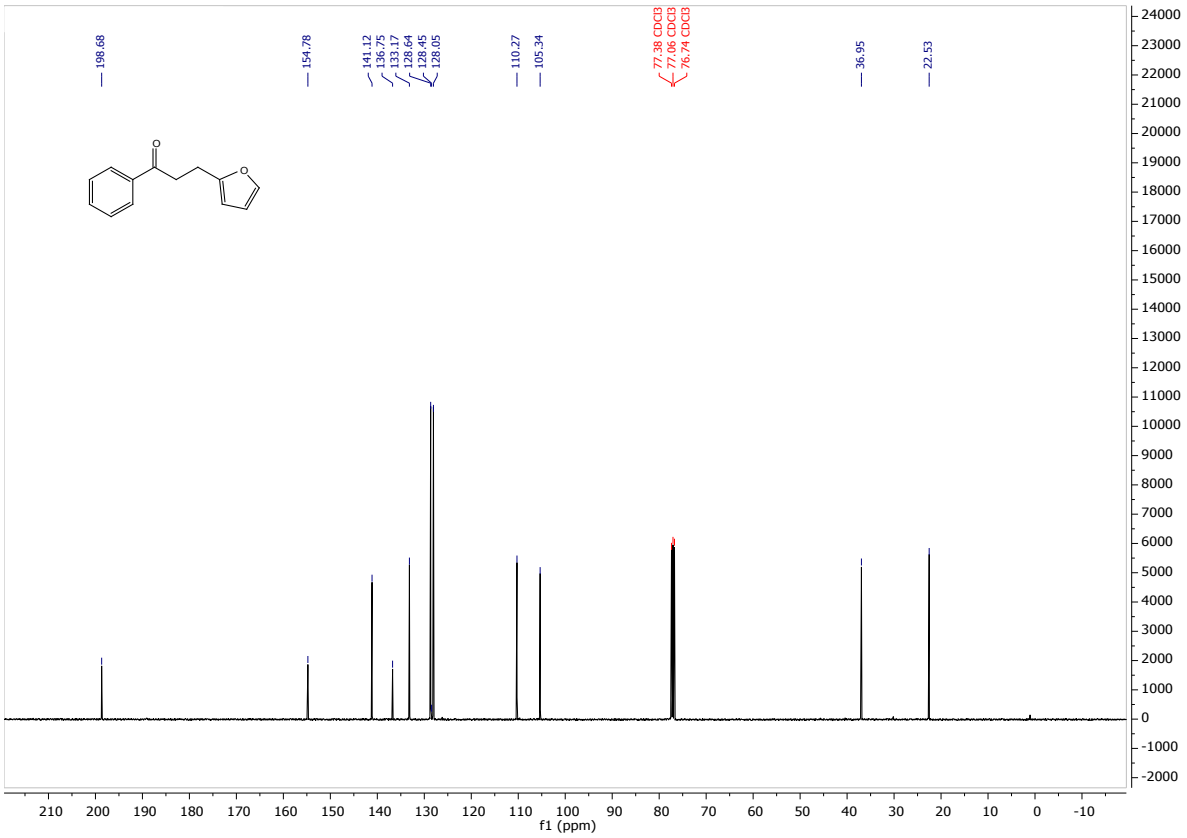
3ah ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



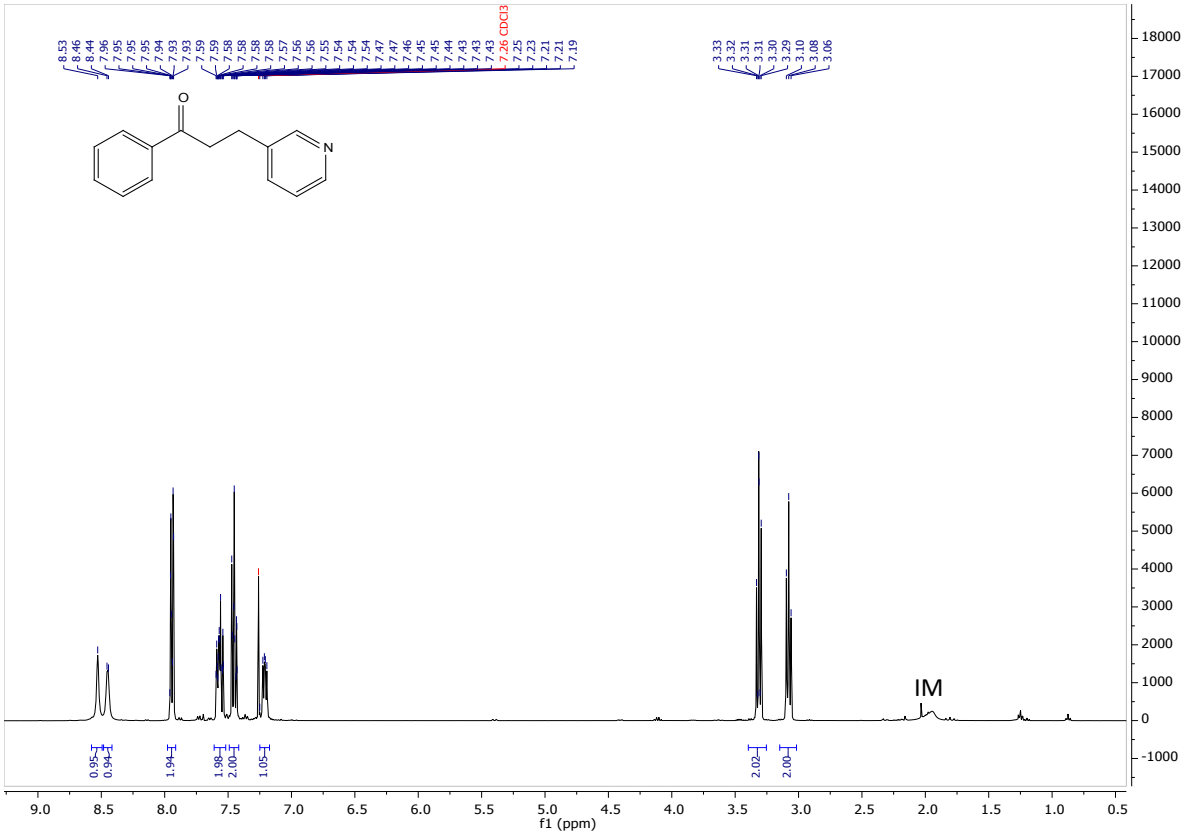
3aj ^{1}H NMR (400 MHz, Chloroform-*d*)



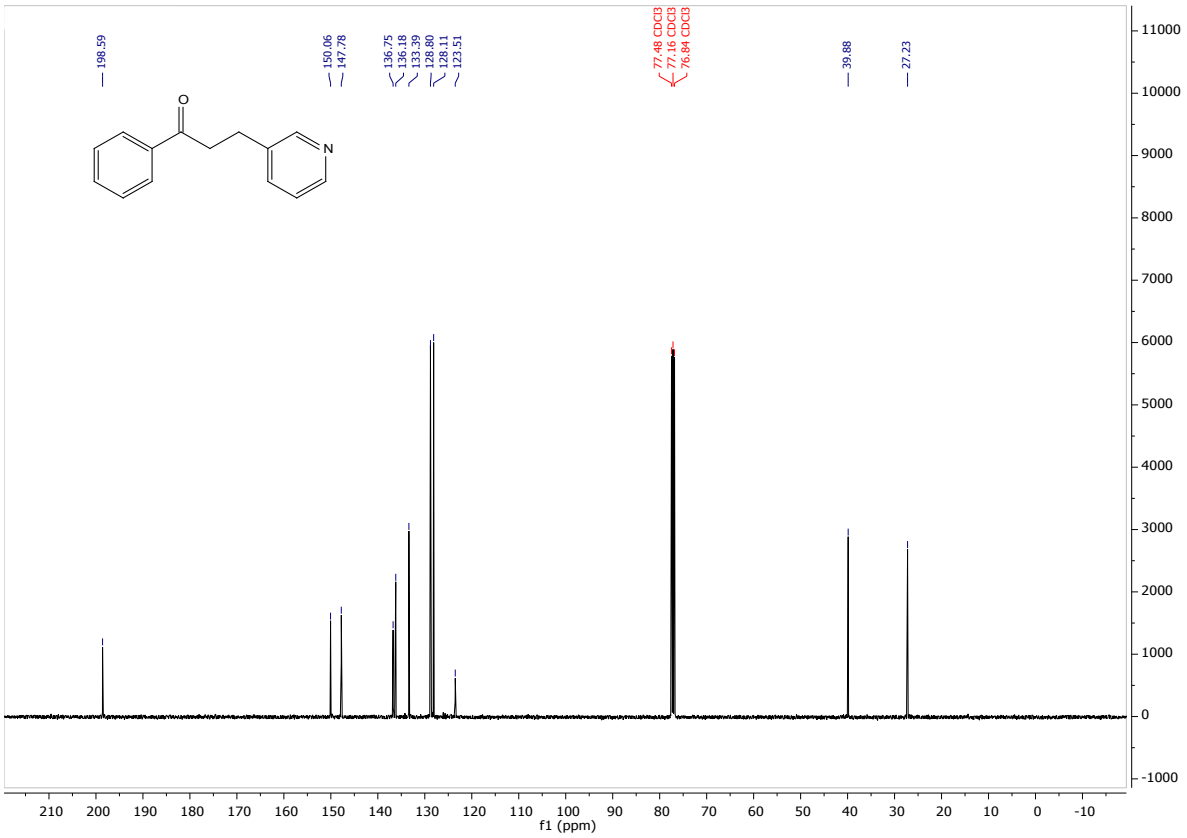
3aj ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



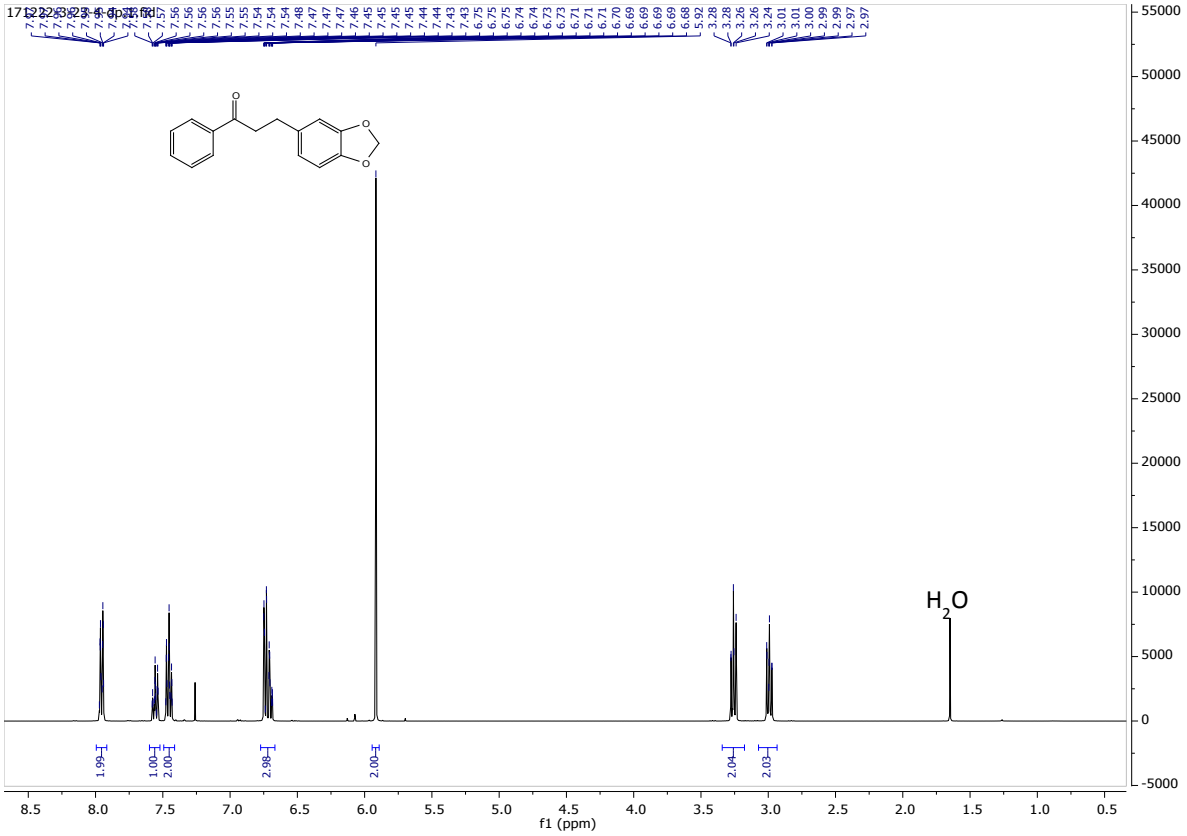
3ak ^{1}H NMR (400 MHz, Chloroform-*d*)



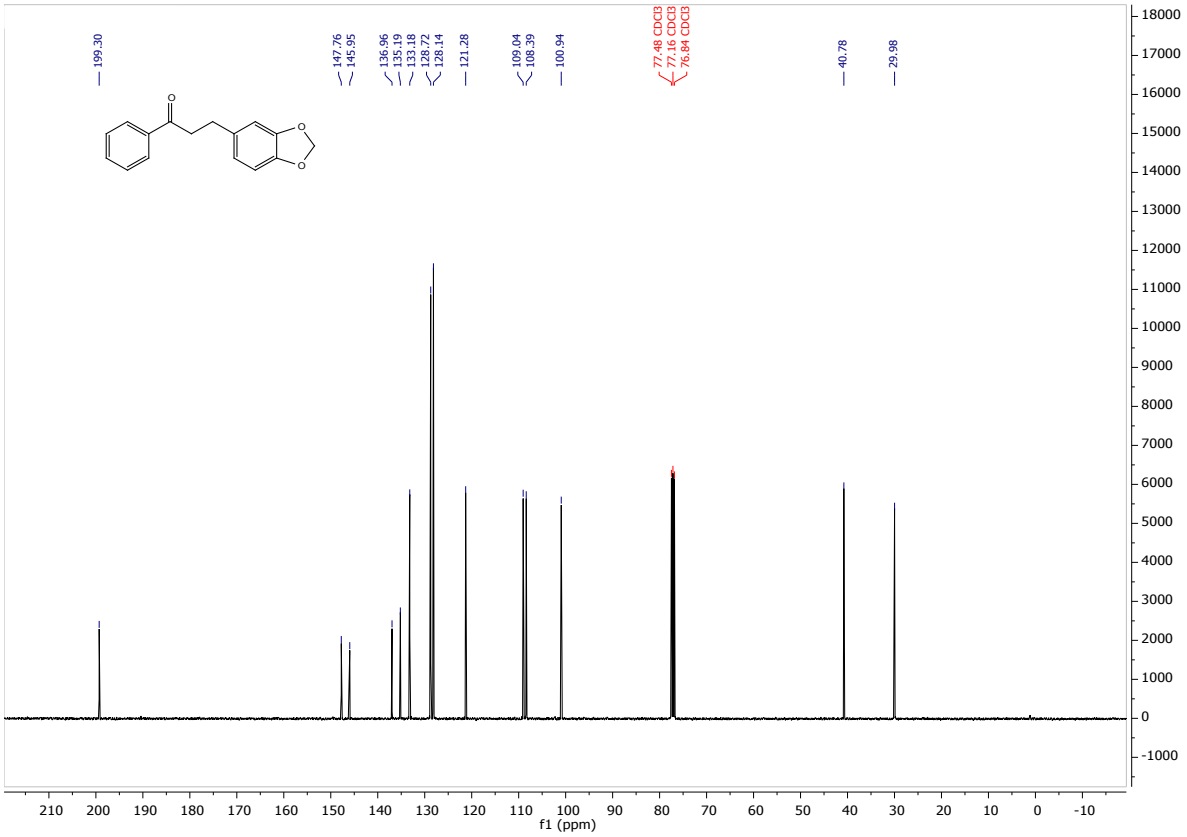
3ak ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



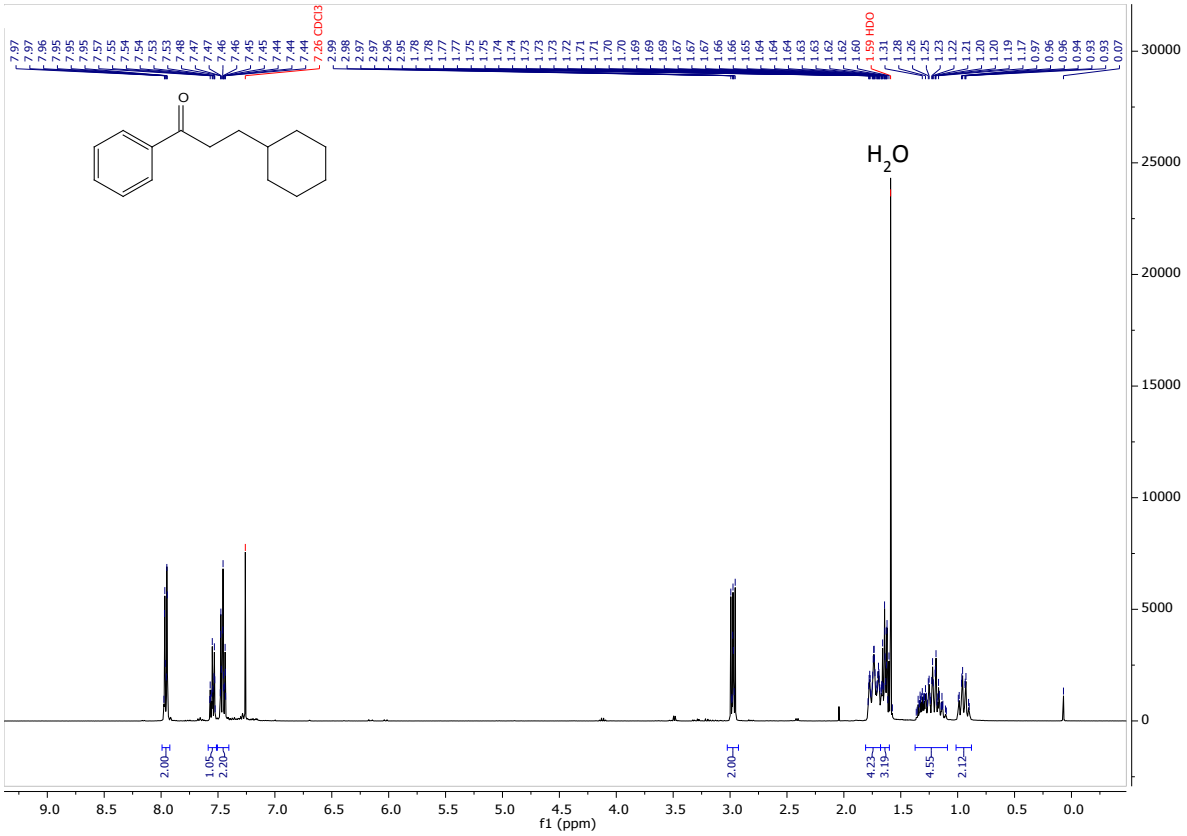
3al ^{1}H NMR (400 MHz, Chloroform-*d*)



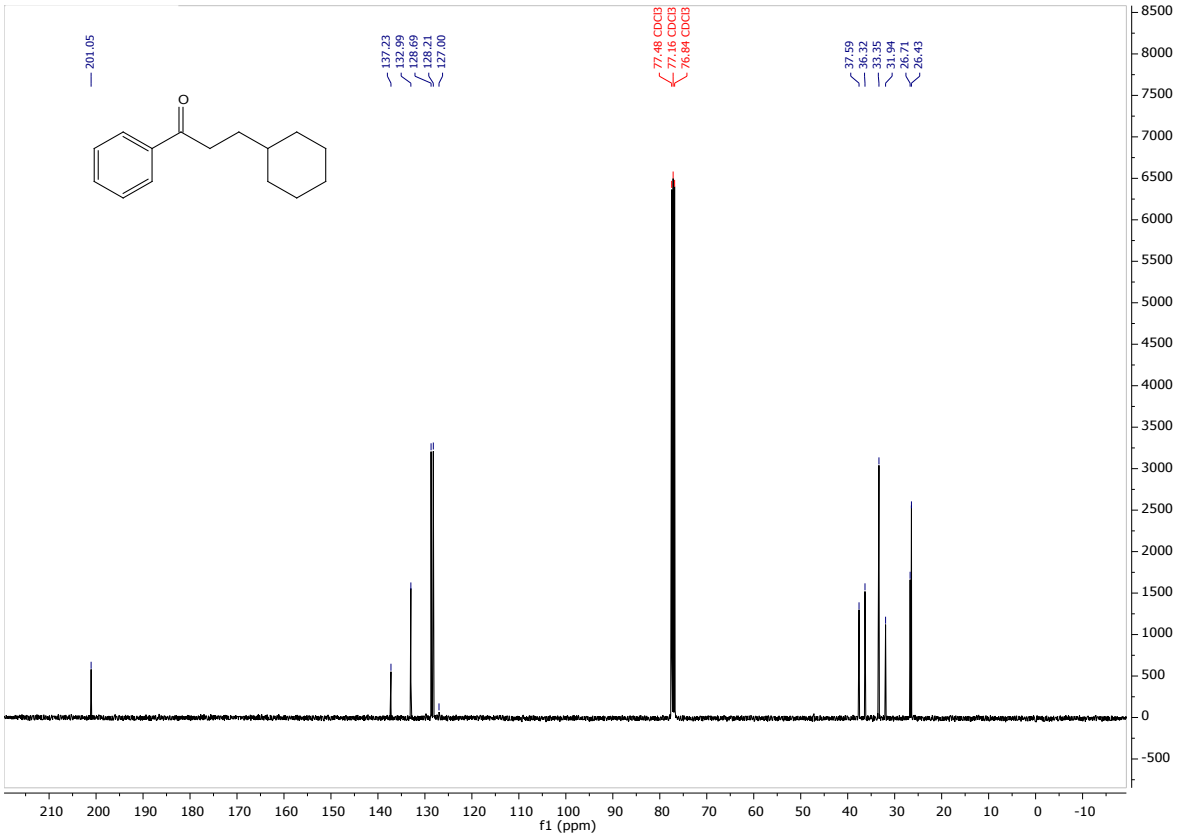
3al ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



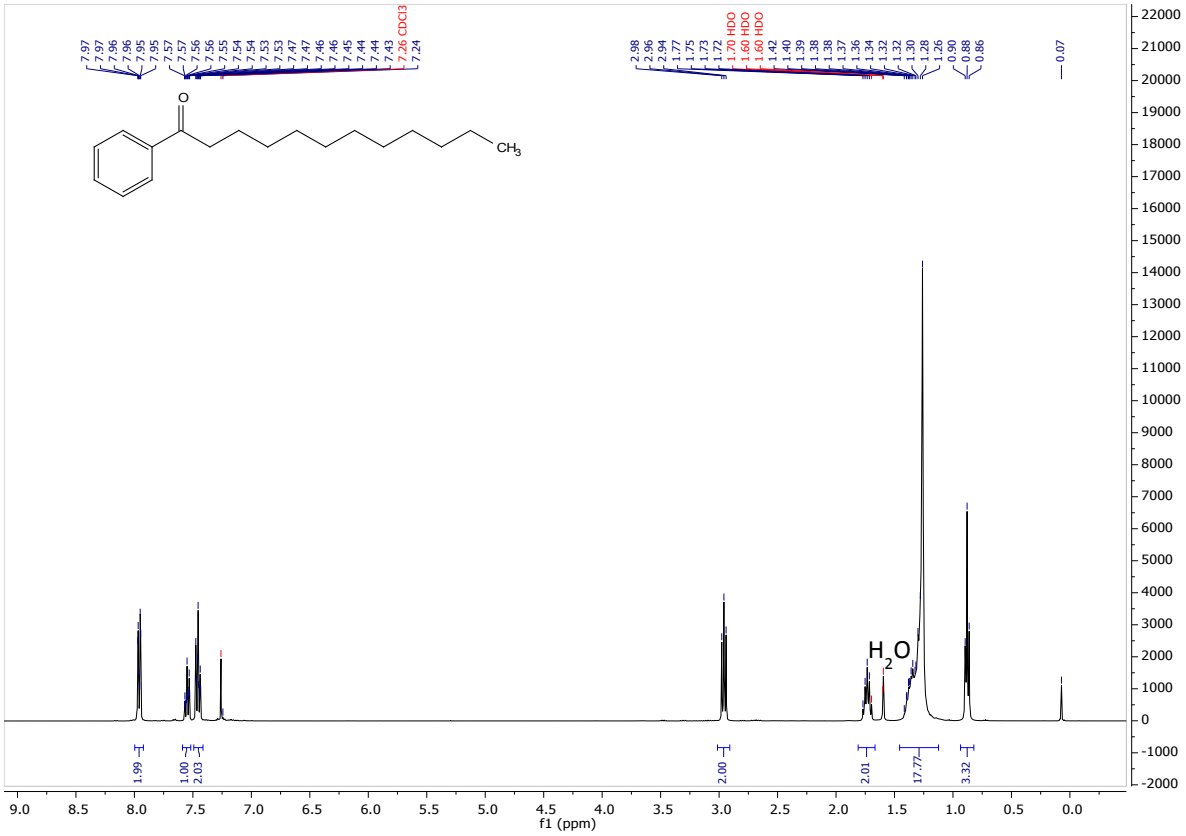
3an ^{1}H NMR (400 MHz, Chloroform-*d*)



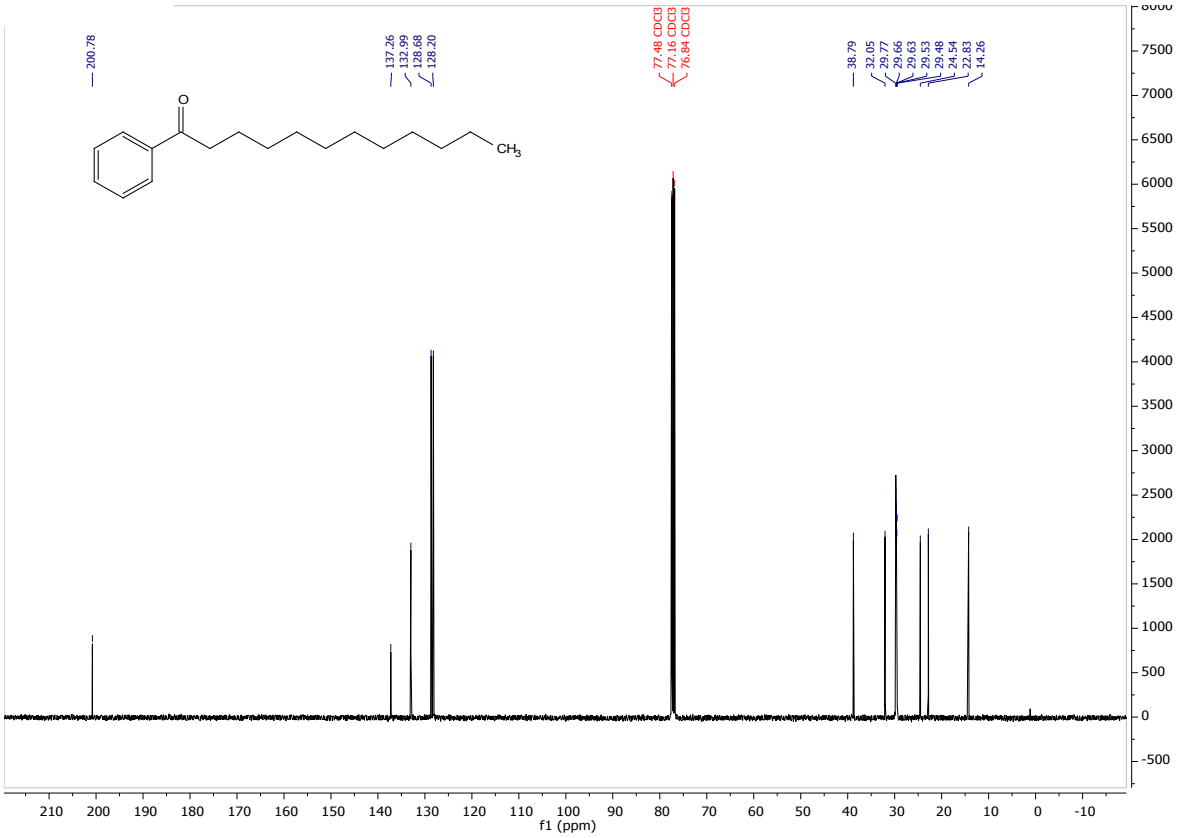
3an ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



3ao ^{1}H NMR (400 MHz, Chloroform-*d*)

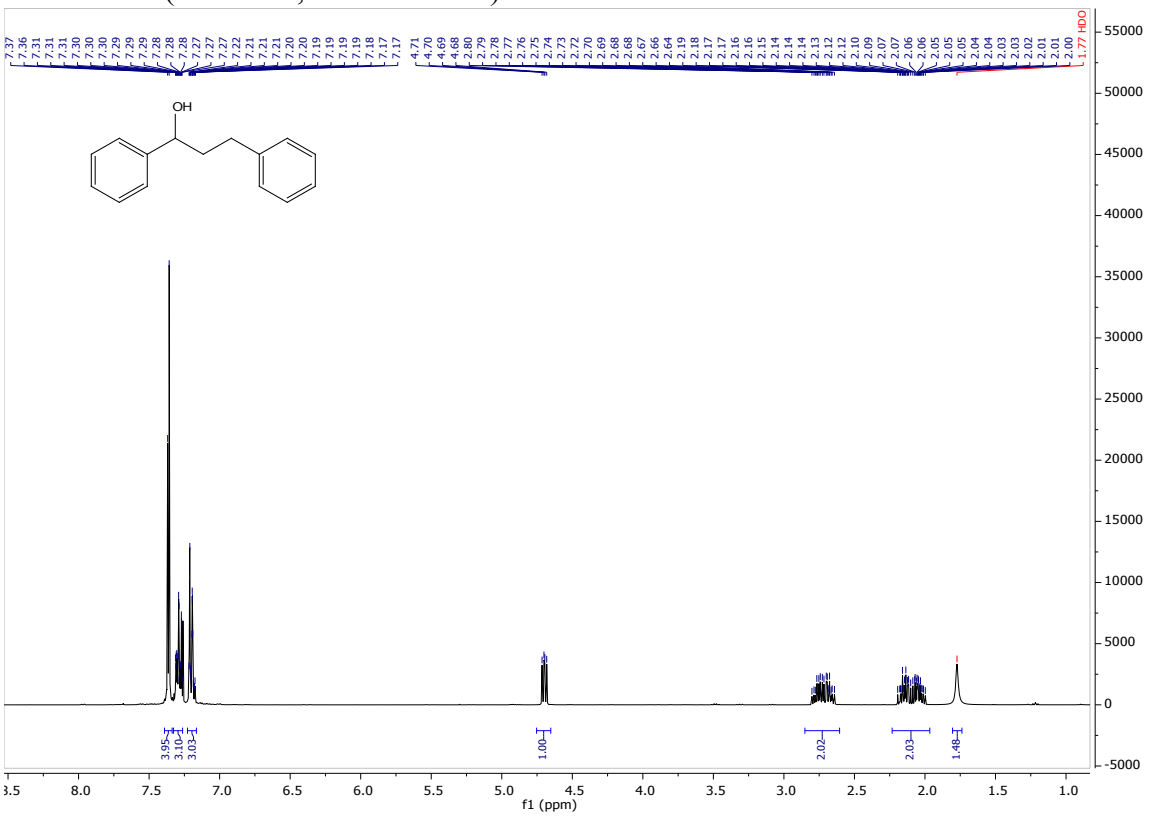


3ao ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

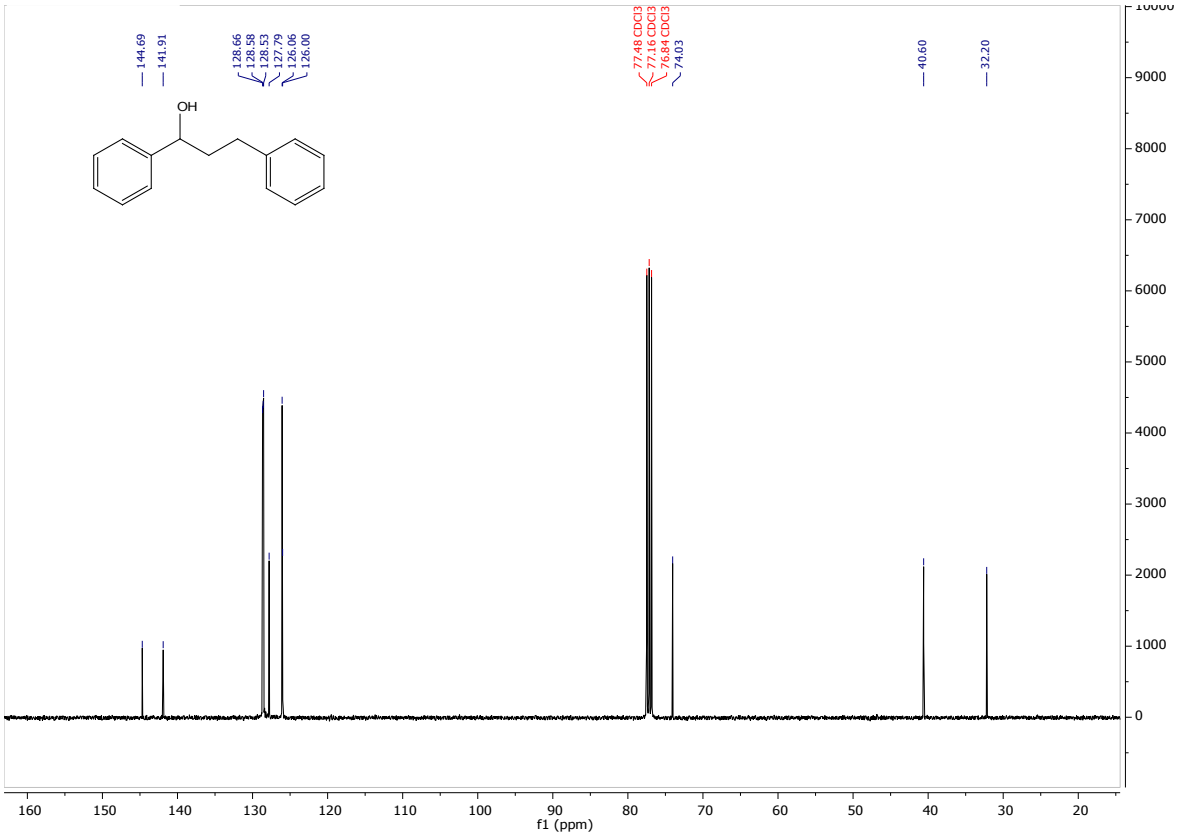


S1.9.3 Scope for the alkylated alcohols

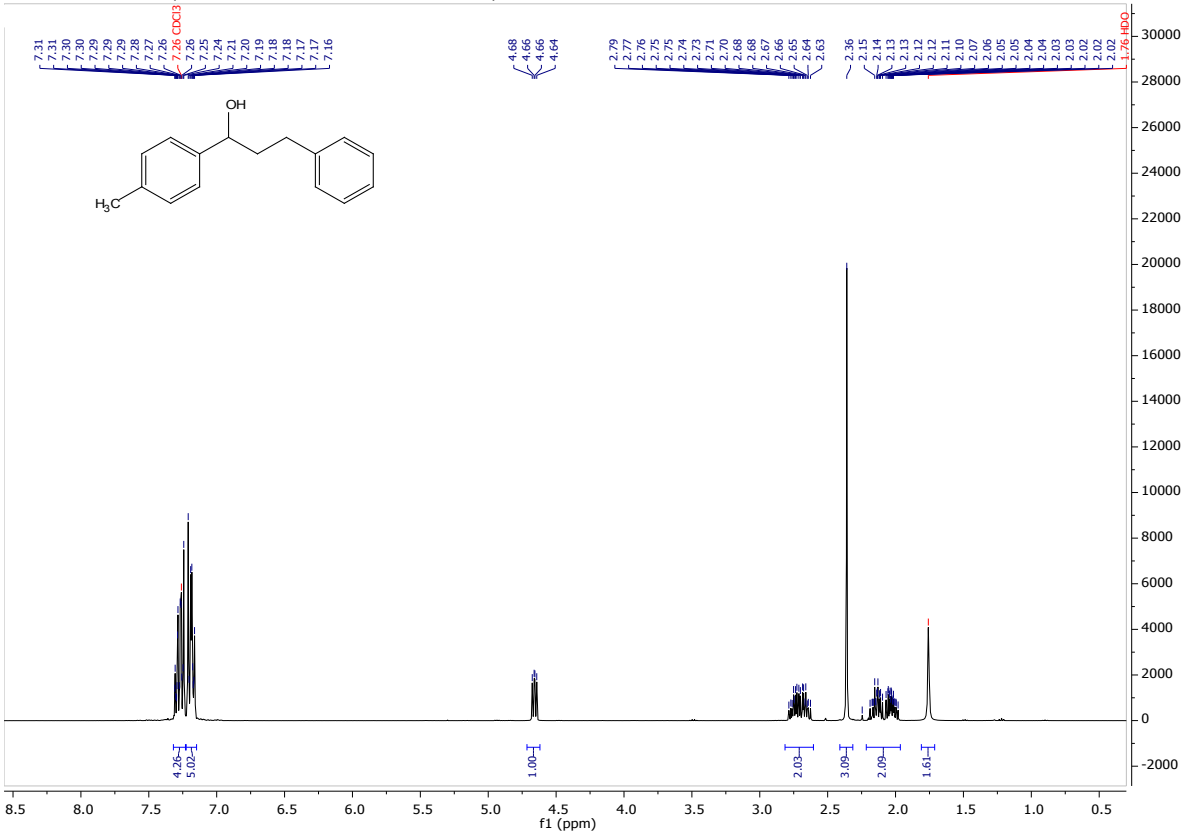
4a ^{1}H NMR (400 MHz, Chloroform-*d*)



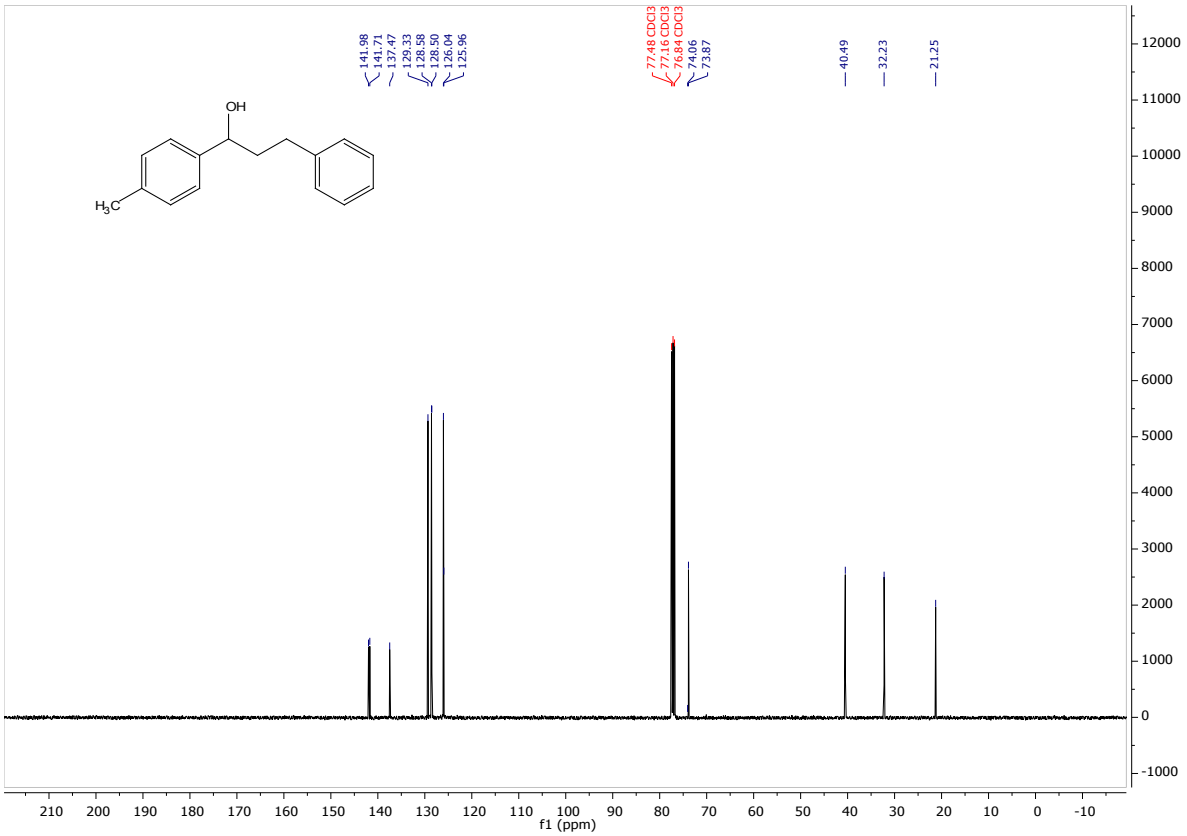
4a ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



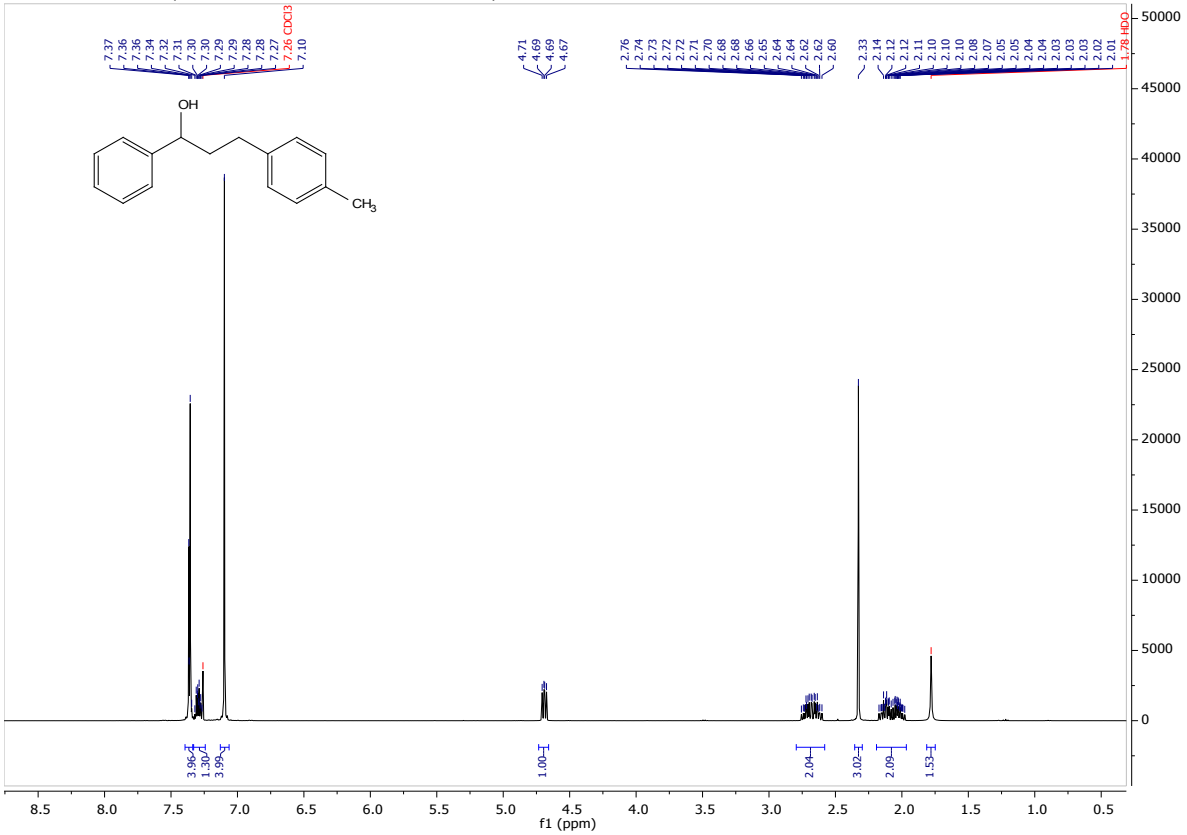
4b ^{1}H NMR (400 MHz, Chloroform-*d*)



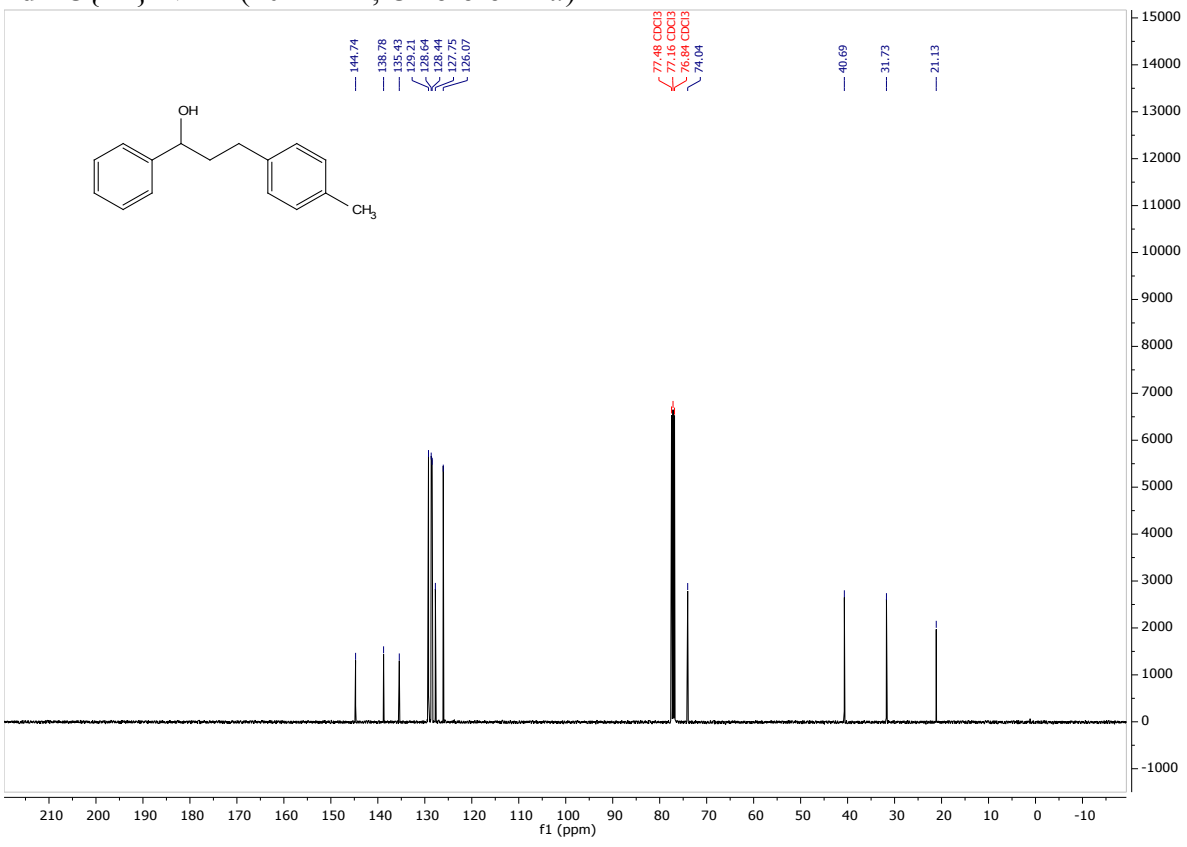
4b ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



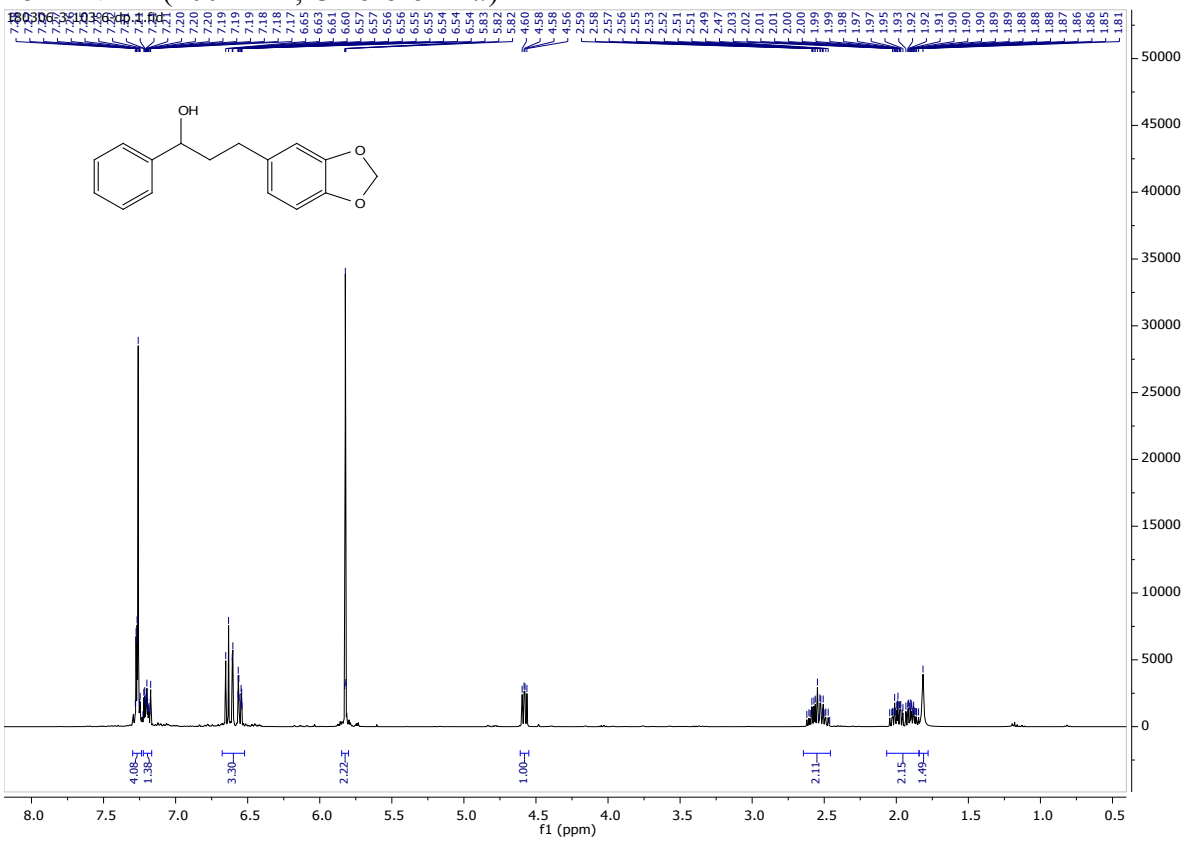
4d ^{1}H NMR (400 MHz, Chloroform-*d*)



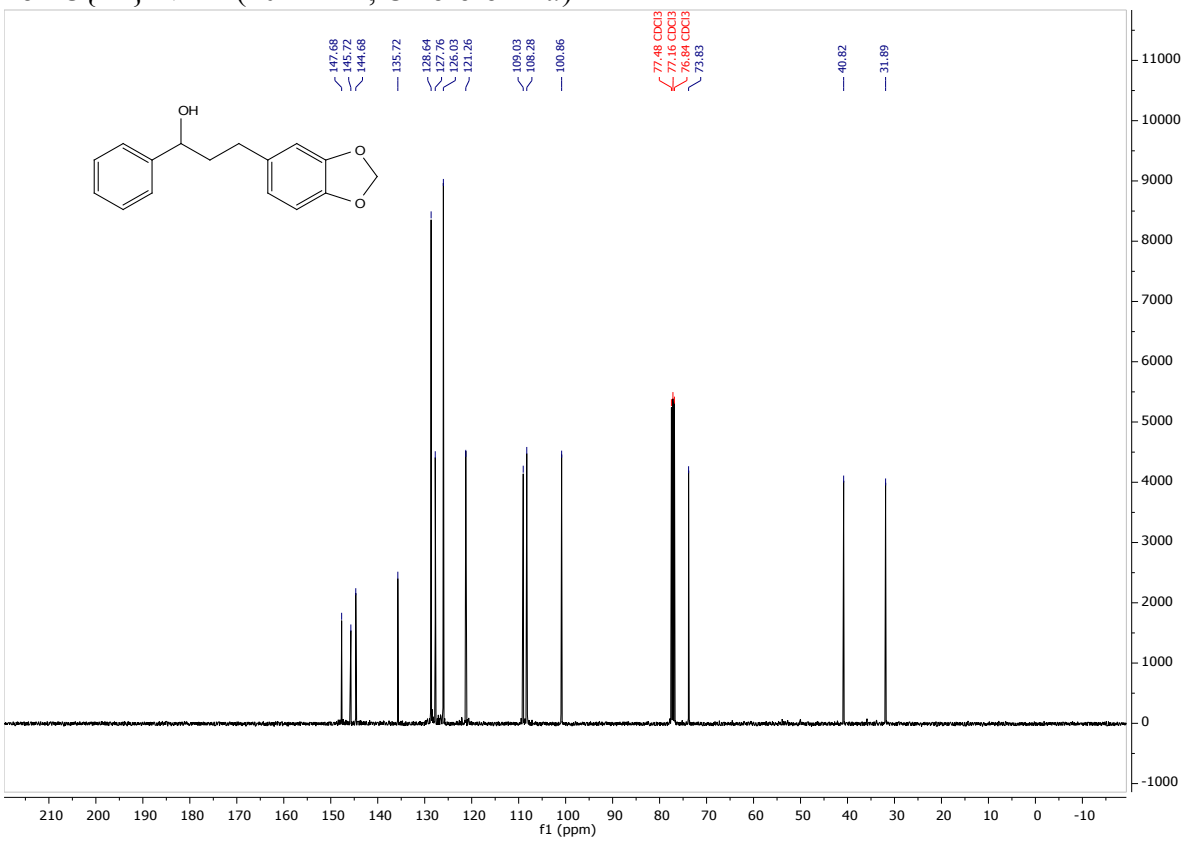
4d ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



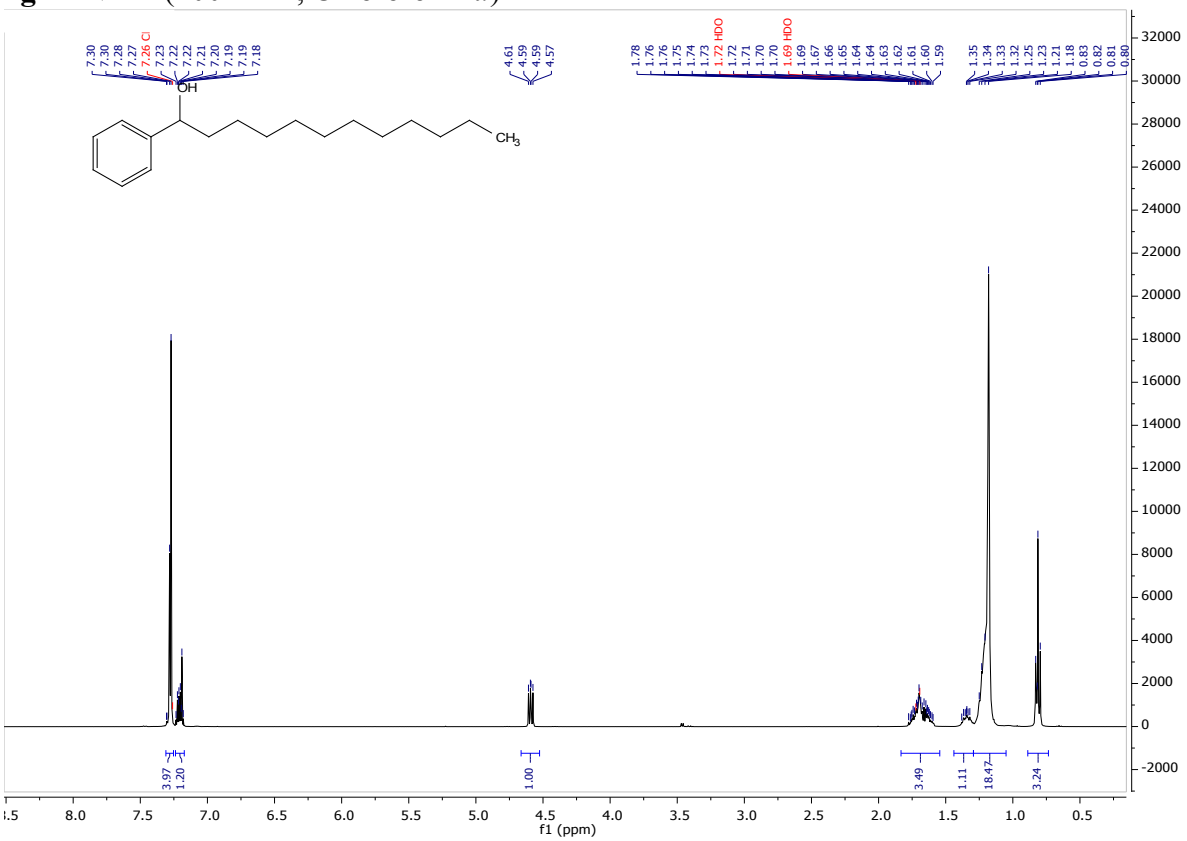
4e ^{1}H NMR (400 MHz, Chloroform-*d*)



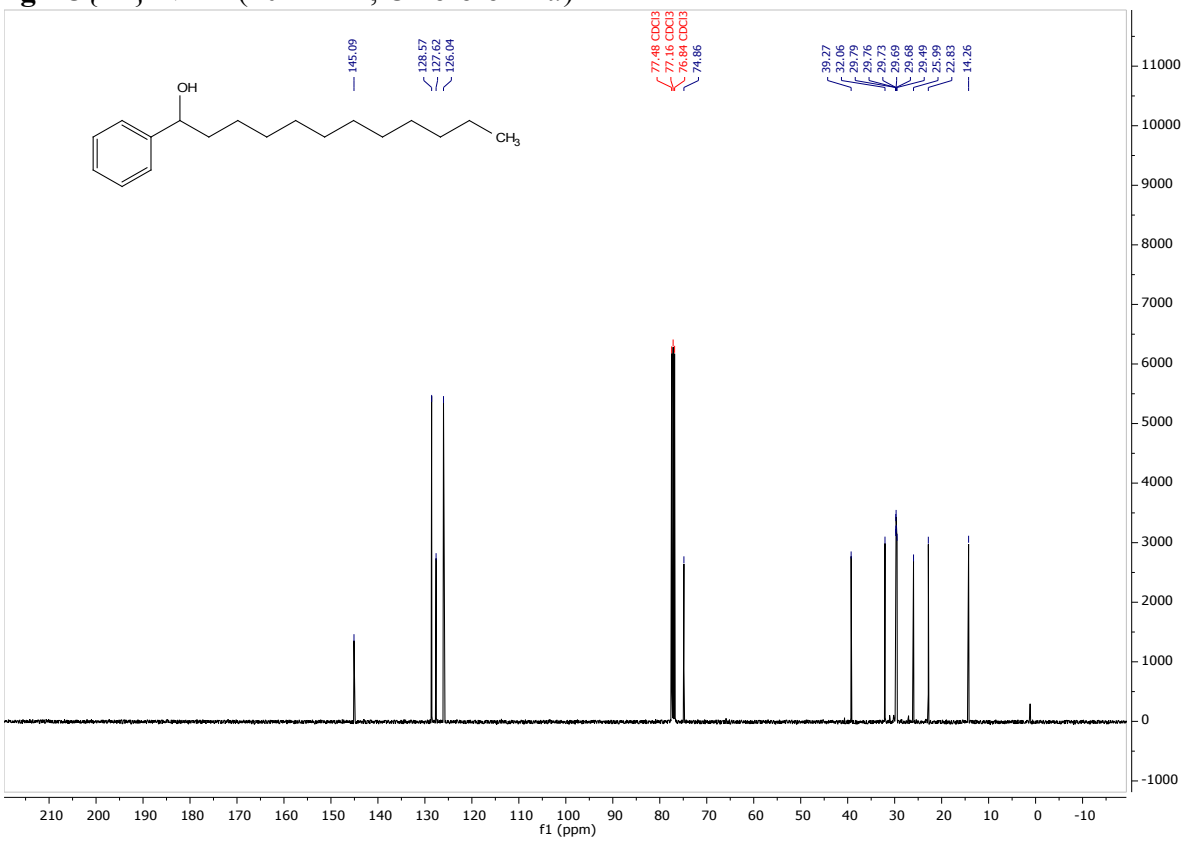
4e ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



4g ^{1}H NMR (400 MHz, Chloroform-*d*)



4g ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



S1.10 References

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