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Supporting Information

Optimum Bifunctionality in 2-(2-pyridyl-2-ol)-1,10-phenanthroline Based Ruthenium Complex for Transfer Hydrogenation of Ketones and Nitriles: Impact of the Number of 2-Hydroxypyridine Fragments

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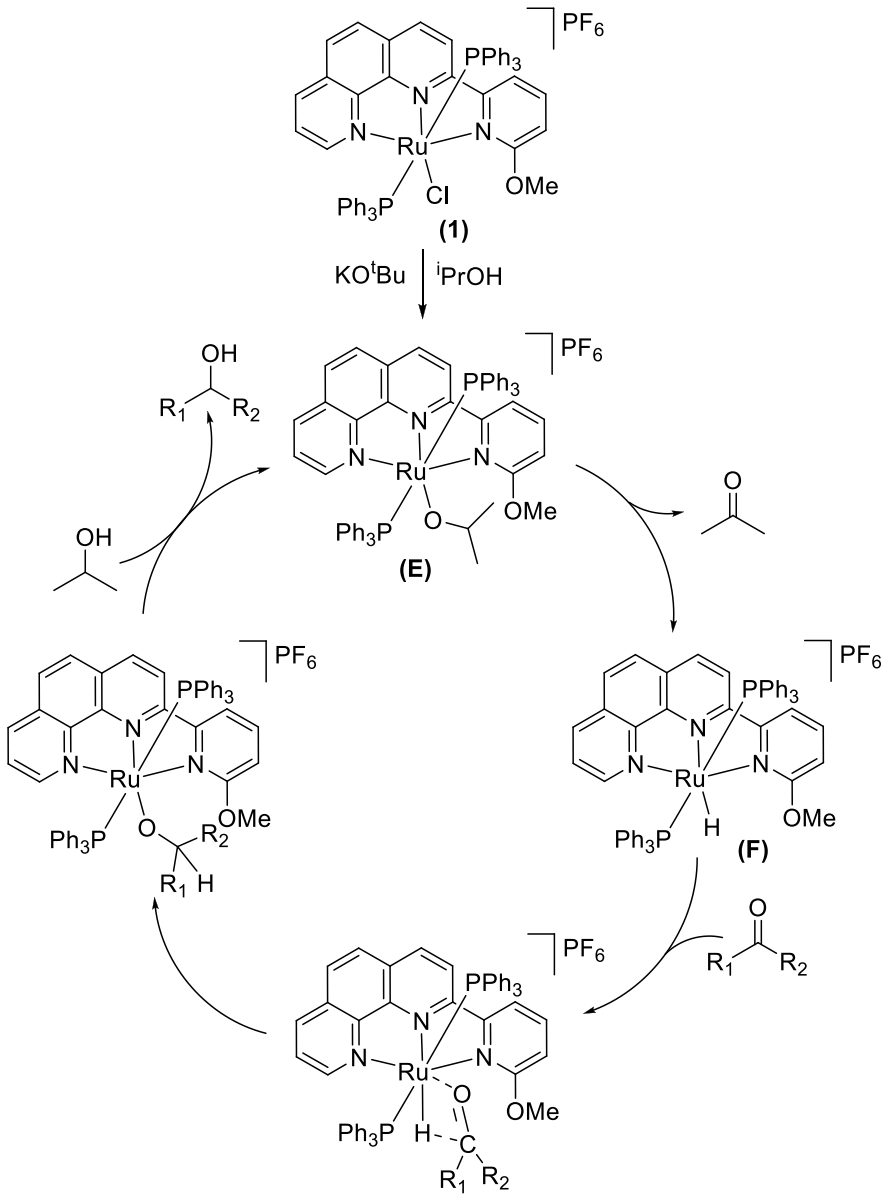
Contents

Text S1: Hg^0 poisoning experiment. Two identical TH experiments were conducted in parallel following the outlined procedure; one acted as a control reaction (with both acetophenone and benzonitrile). The reactions were monitored by GC to ensure reactions had proceeded past the initiation period (10 min for ketones and 1 h for nitrile). Inside the glovebox one drop of Hg^0 was added to one of the screw cap tube and vigorously agitated. Then the tubes were removed from the glovebox, heated for specified time in the oil bath and the progress of the reaction was monitored by GC (toluene was used as internal standred). Using catalyst **2** with acetophenone 95% conversion in 25 minutes at 80 °C and with benzonitrile 93% conversion in 12h at 120 °C was observed. Using catalyst **1** with acetophenone 90% conversion in 90 minutes at 80 °C and with benzonitrile 59% conversion in 12h at 120 °C was observed.

Scheme S1: Proposed mechanism for the transfer hydrogenation of ketones with 1/KO^{t}Bu.



Text S2: General Procedure for the ^{31}P-NMR studies. In a J-Young NMR tube 5 mg complex **1** or **2** was dissolved in 2:1 mixture of 2-propanol and DCM under argon atmosphere at RT. Then 0.050 M stock solution of NaO^{i}Pr (3 eq.) in 2-propanol was added at -20 $^{\circ}$C. After that ^{31}P-NMR spectrum was recorded at room temperature with specified time interval (10, 30, and 45 min.) for complex **2**. With complex **1** the solution was heated to 80 $^{\circ}$C for 15, 45 and 90 minutes interval and ^{31}P-NMR spectrum was recorded at room temperature.

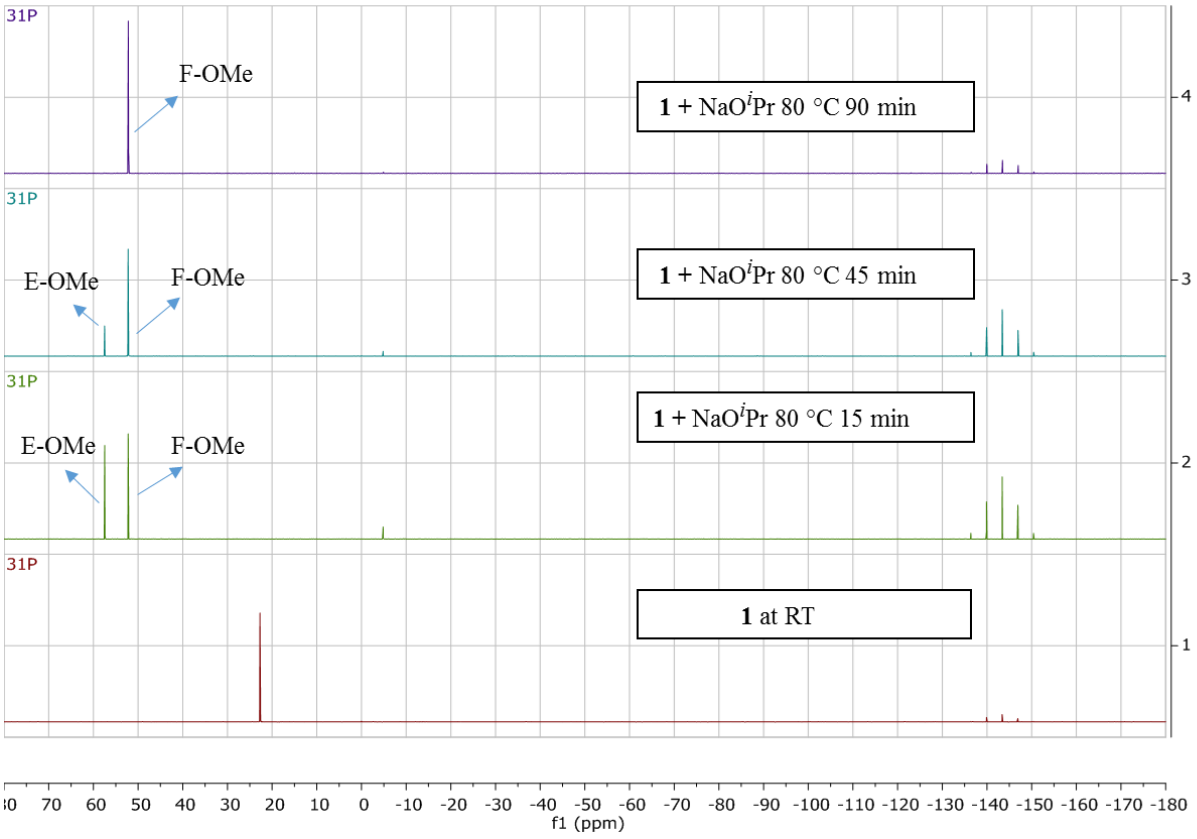
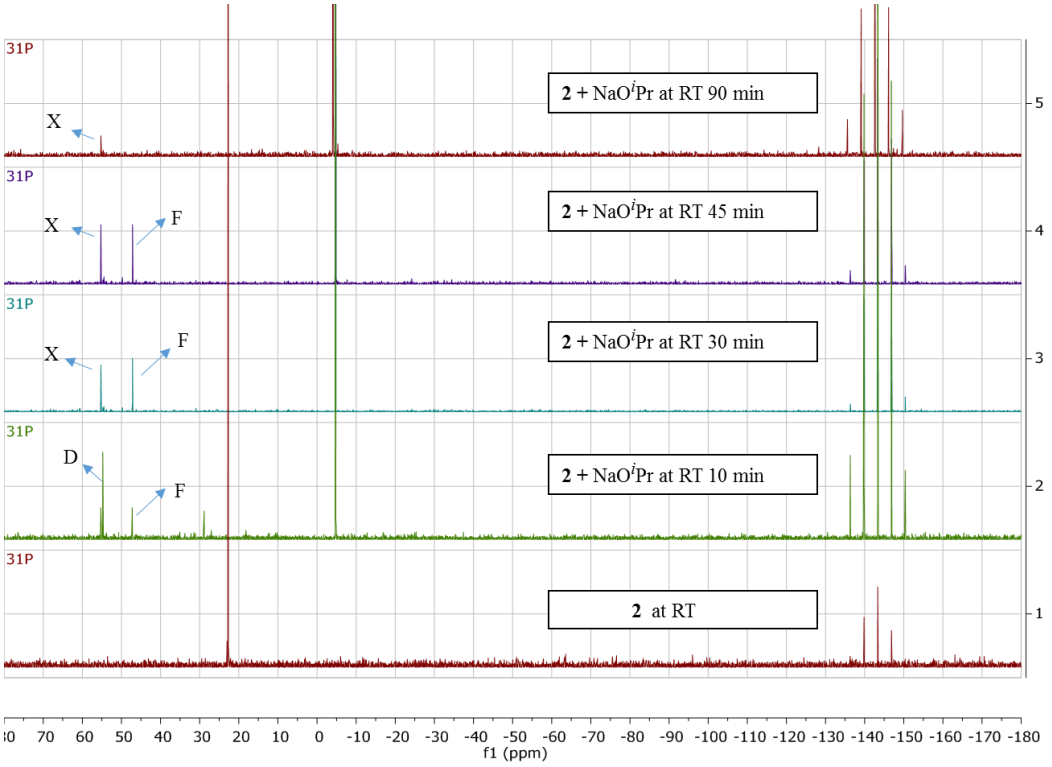
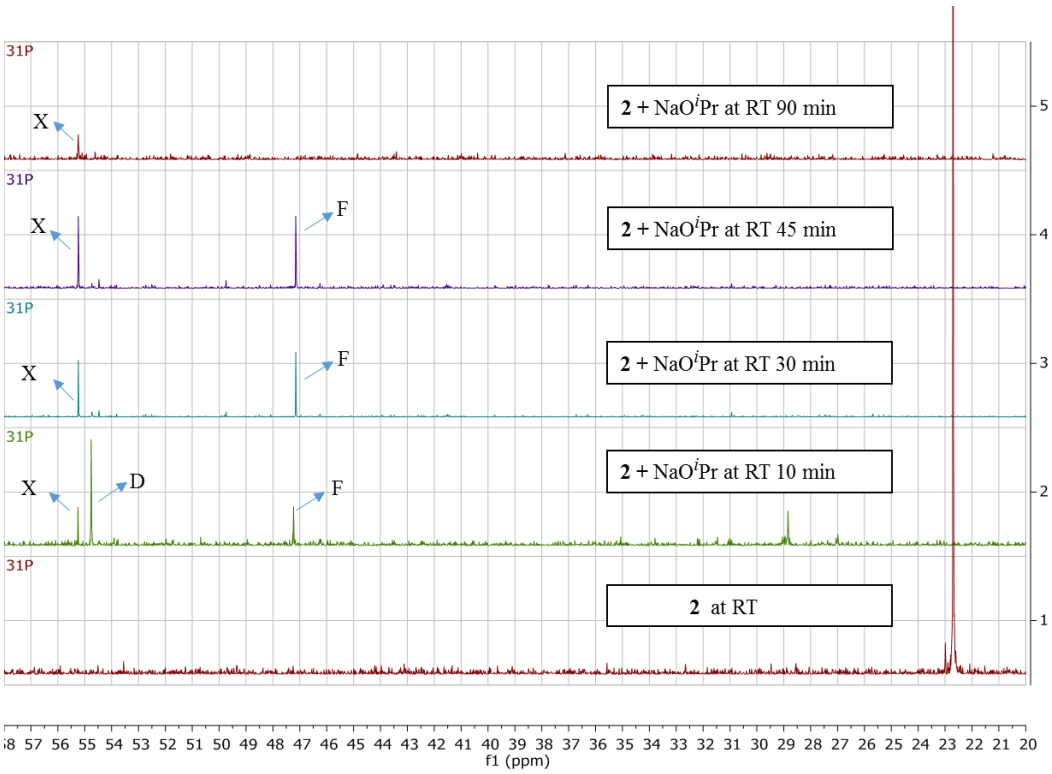


Figure S1 : ^{31}P-NMR studies of complex **1**.



X = Unidentified compound



X = Unidentified compound

Figure S2 : ^{31}P-NMR studies of complex **2**.

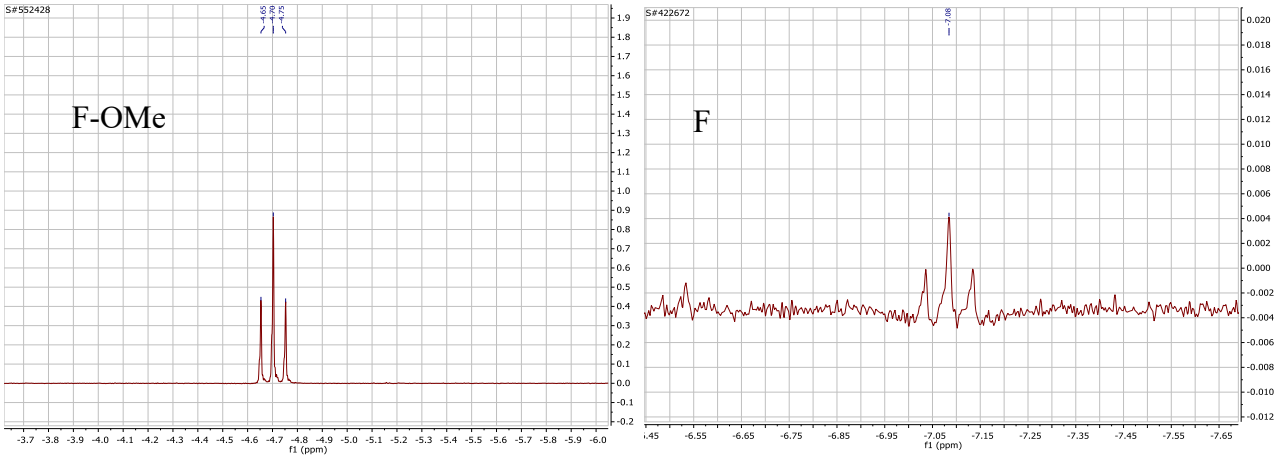


Figure S3 : Hydride Signals of **F-OMe** (from complex **1**) and **F** (from complex **2**).

Text S3: X-ray Crystallographic Studies. Single crystal of complex **1** was obtained from DCM-Et_2O mixture and for complex **2** from DCM-benzene mixture under slow evapouration. Single-crystal X-ray data of all the complexes were collected at 100 K by using a Bruker SMART APEX II CCD diffractometer and Bruker D8 Quest Single Crystal diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ =0.71073 Å). The frames were indexed, integrated and scaled using SMART and SAINT software package[1] and the data were corrected for absorption using the SADABS program.[2] The structures were solved and refined using WINGX and SHELX programs.[3] The crystallographic figures have been generated using Diamond 3 software10 (30% probability thermal ellipsoids).[4] The CCDC number of complexes **1** and **2** are CCDC 1453888 and CCDC 1453889.

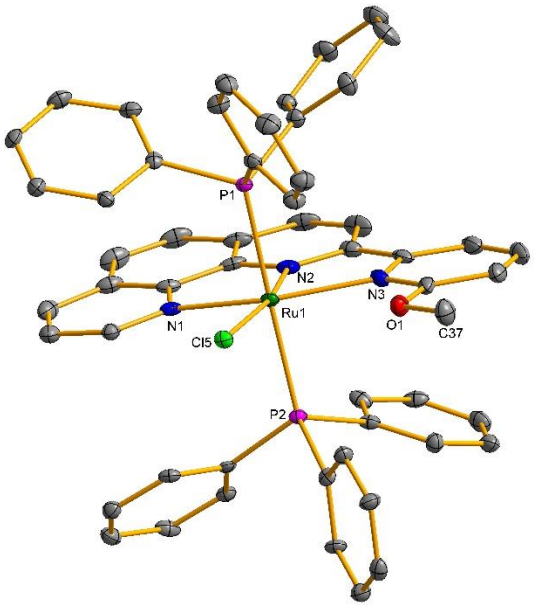


Figure S4: Solid state structure of **1** (30 % thermal ellipsoids; hydrogen atoms were omitted for clarity).

Table S1. Crystallographic Data and Refinement Parameters for **1**.

Identification code	Complex 1
Empirical formula	$C_{56}H_{47}N_3OF_6P_3Cl_5Ru$
Formula weight	1263.19
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	11.925(5)
b/Å	14.713(5)
c/Å	15.876(5)
α/°	101.331(5)
β/°	91.090(5)
γ/°	100.225(5)
Volume/Å^3	2683.6(17)
Z	2
ρ_{calc}g/cm^3	1.563

μ/mm^{-1}	0.696
F(000)	1280.0
Crystal size/mm^3	0.02 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71069)
2Θ range for data collection/°	8.158 to 50.046
Index ranges	-14 ≤ h ≤ 13, -13 ≤ k ≤ 17, -18 ≤ l ≤ 16
Reflections collected	13852
Independent reflections	9255 [R_{int} = 0.0303, R_{sigma} = 0.0625]
Data/restraints/parameters	9255/0/677
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0706, wR_2 = 0.1911
Final R indexes [all data]	R_1 = 0.0949, wR_2 = 0.2370
Largest diff. peak/hole / e Å^{-3}	2.15/-1.60

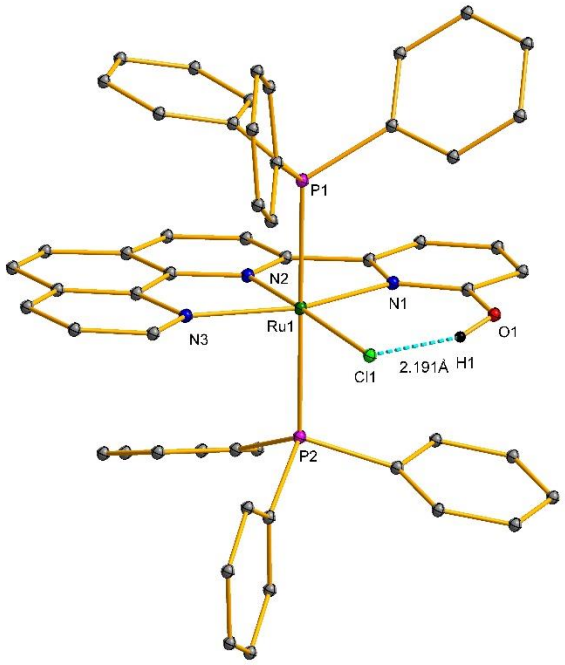


Figure S5: Solid state structures of **2** (30 % thermal ellipsoids; hydrogen atoms were omitted for clarity).

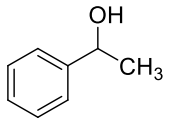
Table S2. Crystallographic Data and Refinement Parameters for **2**

Identification code	Complex 2
Empirical formula	$C_{62}H_{50}N_3OF_6P_3ClRu$
Formula weight	1196.48
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.058(5)
b/Å	23.924(5)
c/Å	22.914(5)
α/°	90

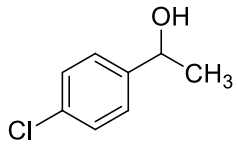
β/°	98.455(5)
γ/°	90
Volume/Å^3	5454(3)
Z	4
ρ_{calc}g/cm^3	1.457
μ/mm^{-1}	0.491
F(000)	2444.0
Crystal size/mm^3	0.02 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71069)
2Θ range for data collection/°	8.192 to 50.05
Index ranges	$-11 \leq h \leq 11$, $-28 \leq k \leq 28$, $-27 \leq l \leq 26$
Reflections collected	42994
Independent reflections	9570 [R_{int} = 0.0672, R_{sigma} = 0.0632]
Data/restraints/parameters	9570/0/653
Goodness-of-fit on F^2	1.112
Final R indexes [I>=2σ (I)]	R_1 = 0.0630, wR_2 = 0.1356
Final R indexes [all data]	R_1 = 0.0896, wR_2 = 0.1451
Largest diff. peak/hole / e Å^{-3}	1.48/-0.91

Text S4: General Procedure for the Catalytic Transfer Hydrogenation of Ketones. The stock solution was prepared by dissolving complex **2** in CH_3CN before use. Then, the catalyst solution (0.1 mol%) was taken into a 10 mL screw cap tube equipped with a magnetic stirrer bar and CH_3CN was removed in vacuum. Then the tube was charged with 0.83 mmol ketone, KO^{t}Bu (0.049 mmol) and 4 mL 2-propanol under argon atmosphere and heated at 80 ˚C for the specified time. After that the tube was cooled and 10 μL solution was syringe out for GC analysis (toluene was used as internal standard). Next, the reaction mixture was concentrated under reduced pressure and the corresponding alcohol was isolated by silica gel column chromatography using hexane and ethyl acetate as an eluent. Final product was confirmed by comparison with the authentic sample through NMR and GC-MS analysis.

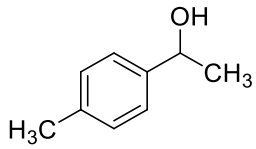
Characterization Data of Alcohol products.



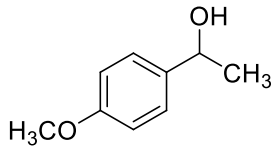
Obtained as a faint yellow liquid (90% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.25 (m, 5H), 4.88 (q, $J_{H,H}$ = 5.0 Hz, 1H), 2.63 (brs, 1H), 1.49 (d, $J_{H,H}$ = 5.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.90, 128.58, 127.54, 125.47, 70.47, 25.22.



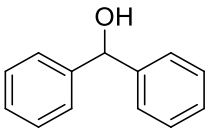
Obtained as a pale yellow liquid (90% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.27 (m, 4H), 4.86 (q, $J_{H,H}$ = 6.4 Hz, 1H), 2.35 (brs, 1H), 1.46 (d, $J_{H,H}$ = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.34, 133.09, 128.89, 126.88, 69.75, 23.31.



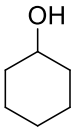
Obtained as a yellow liquid (87% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.15 (d, $J_{H,H}$ = 7.8 Hz, 2H), 4.85 (q, $J_{H,H}$ = 6.3, 1H), 2.34 (s, 3H), 1.47 (d, $J_{H,H}$ = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ =143.02, 137.18, 129.44, 125.47, 70.28, 25.18, 21.19.



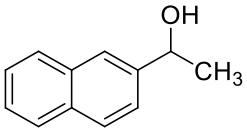
Obtained as a dense oil (76% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, $J_{H,H}$ = 10.0, 2H), 6.90 (d, $J_{H,H}$ = 8.2 Hz, 2H), 4.85 (q, $J_{H,H}$ = 6.4 Hz, 1H), 3.79 (s, 3H), 1.46 (d, $J_{H,H}$ = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.02, 138.18, 126.76, 113.91, 69.97, 55.36, 25.01.



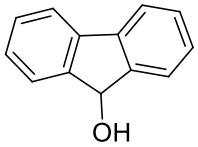
Obtained as a white crystalline solid (89% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (t, $J_{H,H}$ = 6.9 Hz, 4H), 7.30 (t, $J_{H,H}$ =1.4 Hz, 4H), 7.23 (t, $J_{H,H}$ = 7.32 Hz, 2H), 5.82 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.78, 128.46, 127.53, 126.52, 76.22.



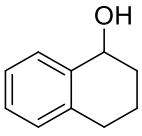
Obtained as a liquid (90% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.00 (quin, $J_{H,H}$ = 5.9 Hz, 1H), 1.88-1.71 (m, 4H), 1.28-1.16 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.26, 35.54, 25.52, 24.22.



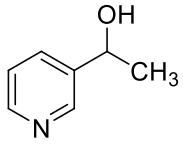
Obtained as a white crystalline solid (86% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.81 (m, 4H), 7.51-7.45 (m, 3H), 5.06 (q, $J_{H,H}$ =6.4 Hz, 1H), 1.57 (d, $J_{H,H}$ = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.29, 133.43, 133.03, 128.40, 128.04, 127.77, 126.23, 125.88, 123.92, 123.90, 70.61, 25.22.



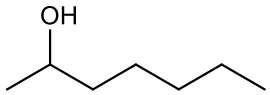
Obtained as a white solid (83% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65-7.62 (m, 4H), 7.38 (dd, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ =1.0Hz, 2H), 7.31 (dd, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 1.3 Hz, 2H), 5.58 (d, $J_{H,H}$ =8.72 Hz, 1H), 1.88 (d, $J_{H,H}$ =10.00 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.62, 139.95, 129.02, 127.76, 125.09, 119.92, 75.18.



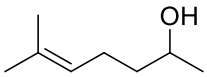
Obtained as a dense liquid (80% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.40 (m, 1H), 7.20-7.16 (m, 2H), 7.4-7.08 (m, 1H), 4.77 (q, $J_{H,H}$ = 9.6 Hz, 1H), 2.78-2.69 (m, 2H), 1.97-1.68 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.92, 137.20, 129.09, 128.76, 127.65, 126.25, 68.21, 32.36, 29.34, 18.92.



Obtained as a yellow liquid (42% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 8.17 (d, $J_{H,H}$ = 2.8 Hz, 1H), 7.62 (t, $J_{H,H}$ = 6.4 Hz, 1H), 7.11 (q, $J_{H,H}$ = 7.8 Hz, 1H), 4.76 (q, $J_{H,H}$ =6.6 Hz, 1H), 1.35 (d, $J_{H,H}$ = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.06, 147.09, 141.88, 133.64, 123.63, 67.56, 25.24.

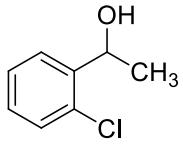


Obtained as a transparent liquid (82% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (m, 1H), 1.52 (bs, 1H), 1.39 (m, 3H), 1.28 (m, 5H), 1.16 (d, $J_{H,H}$ = 6.4 Hz, 3H), 0.86 (t, $J_{H,H}$ = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 68.21, 39.40, 31.92, 25.51, 23.51, 22.70, 14.08

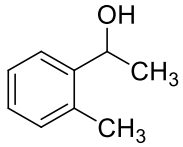


Obtained as a liquid (88% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.12(tt, $J_{H,H}$ = 1.4 Hz, 1H), 3.80 (sex, $J_{H,H}$ =6.4 Hz, 1H), 2.10-2.02 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.44-1.49 (m, 2H), 1.17 (d, $J_{H,H}$ =6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 129.55, 121.59, 65.46, 36.74, 23.22, 22.01, 20.98, 15.17.

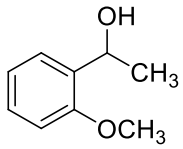
For all other alcohols ^{1}H NMR were taken from the crude reaction mixture after passing through silica gel (100-200 mesh) flash column.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ =1.4Hz, 1H), 7.32-7.25 (m, 2H), 7.18 (dd, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.8Hz, 1H), 5.27 (q, $J_{H,H}$ = 3.7 Hz, 1H), 1.47 (d, $J_{H,H}$ = 6.4 Hz, 3H).

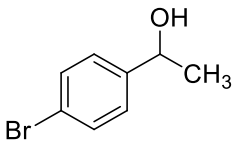


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, $J_{H,H}$ = 8.2 Hz,1H), 7.21 (d, $J_{H,H}$ = 6.4 Hz, 1H), 7.18-7.11 (m, 2H), 5.12 (t, $J_{H,H}$ = 6.4 Hz, 1H), 2.33 (s, 3H), 1.45 (d, $J_{H,H}$ = 6.4 Hz, 3H).

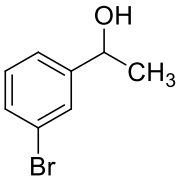


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, $J_{H,H}$ = 7.8Hz, $J_{H,H}$ = 1.8 Hz, 1H), 7.24 (dd, $J_{H,H}$ =

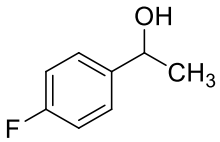
8.2 Hz, $J_{H,H}$ = 1.8 Hz, 1H), 6.95 (td, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ =1.0 Hz, 1H), 6.86 (d, $J_{H,H}$ = 8.2 Hz, 1H), 5.08 (q, $J_{H,H}$ = 5.0 Hz,1H), 3.86 (s, 3H), 1.50 (d, $J_{H,H}$ = 6.4 Hz, 3H).



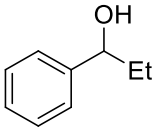
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, $J_{H,H}$ = 10.0, 2H), 6.90 (d, $J_{H,H}$ = 8.2 Hz, 2H), 4.85 (q, $J_{H,H}$ = 6.4 Hz, 1H), 2.57 (brs, 1H), 1.46 (d, $J_{H,H}$ = 6.4 Hz, 3H).



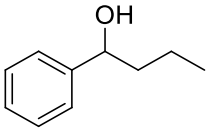
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, $J_{H,H}$ = 1.8Hz, 1H), 7.39 (dt, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.0 Hz, 1H), 7.25 (d, $J_{H,H}$ = 6.8 Hz, 1H), 7.20 (t, $J_{H,H}$ = 7.8 Hz, 1H), 4.85 (q, $J_{H,H}$ = 6.9 Hz, 1H), 1.47 (d, $J_{H,H}$ = 6.4 Hz, 3H).



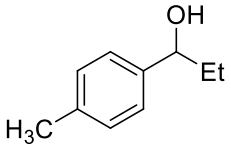
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 2H), 7.05-6.99 (m, 2H), 4.89 (q, $J_{H,H}$ = 6.4 Hz, 1H), 1.47 (d, $J_{H,H}$ = 6.4 Hz, 3H).



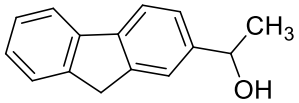
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.33 (m, 5H), 4.58 (t, $J_{H,H}$ = 12.8 Hz, 1H), 1.85-1.70 (m, 2H), 0.90 (t, $J_{H,H}$ = 14.6 Hz, 3H).



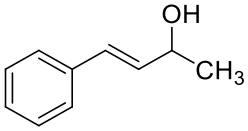
^{1}H NMR (400 MHz, $CDCl_3$,): δ = 7.34-7.25 (m, 5H), 4.67 (t, $J_{H,H}$ = 12.8 Hz, 1H), 1.75-1.64 (m, 2H), 1.26-1.35 (m, 2H), 0.90 (t, $J_{H,H}$ = 15.1 Hz, 3H).



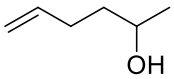
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.14 (d, $J_{H,H}$ = 7.8 Hz, 2H), 4.54 (t, $J_{H,H}$ = 13.2 Hz, 1H), 2.33 (s, 3H), 1.82-1.66 (m, 2H), 0.92-0.87 (m, 3H).



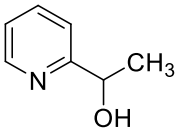
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (t, $J_{H,H}$ = 8.2 Hz, 2H), 7.54 (t, $J_{H,H}$ = 10.6 Hz, 2H), 7.38-7.34 (m, 2H), 7.29 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.0 Hz, 1H), 4.97 (q, $J_{H,H}$ =6.4 Hz, 1H), 3.89 (s, 2H), 1.54 (d, $J_{H,H}$ = 6.9 Hz, 3H).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.35 (m, 2H), 7.31-7.26 (m, 2H), 7.22-7.20 (m, 1H), 6.55 (d, $J_{H,H}$ = 16 Hz, 1H), 6.25 (dd, $J_{H,H}$ = 15.6 Hz, 1H), 4.50-4.45 (m, 1H), 1.35 (d, $J_{H,H}$ = 6.4 Hz, 3H).



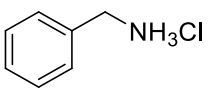
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81 (m, 1 H), 4.98 (m, 2 H), 3.80 (q, $J_{H,H}$ = 5.2 Hz, 1 H), 2.15 (m, 2 H), 1.57 (m, 2 H), 1.50 (s, 1 H), 1.20 (d, $J_{H,H}$ = 6.4 Hz, 3 H).



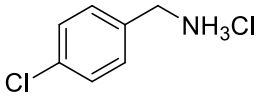
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, $J_{H,H}$ = 4.34 Hz 1H), 7.6 (m, 1H), 7.32 (d, $J_{H,H}$ = 7.4 Hz, 1H), 7.21-7.18 (m, 1H), 4.86 (q, $J_{H,H}$ =6.4 Hz, 1H), 1.31 (d, $J_{H,H}$ = 5.8 Hz, 3H).

Text S5: General Procedure for the Catalytic Transfer Hydrogenation of Nitriles. The stock solution was prepared by dissolving complex **2** in CH_3CN before use. Then, the catalyst solution (2 mol %) was taken into a 10 mL screw cap tube equipped with a magnetic stirrer bar and CH_3CN was removed in vacuum. Then the tube was charged with 0.485 mmol mmol nitrile, KO^{t}Bu (0.29 mmol) and 10 pieces of 3 Å molecular sieves and 3 mL 2-propanol under argon atmosphere and heated at 120 $^\circ$C for the specified time. After that the tube was cooled and 10 μL solution was syringe out for GC and GC-MS analysis (toluene was used as internal standard). The isolation of pure imine product by alumina and silica gel column chromatography using hexane and ethyl acetate as an eluent was unsuccessful as it produced some unidentified compounds. Thus, the imine was hydrolyzed by treating the resulting 2-propanol solution with 1 M HCl (1.5 mL) and was stirred for 1 hour. After removing volatile, the solid was washed with dichloromethane, ethyl acetate and diethyl ether and dried under vacuum. The corresponding ammonium salt $RCH_2NH_3^+Cl$ was obtained as a white crystalline solid and was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

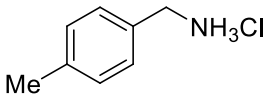
Characterization data of amine salts generated from final product imines.



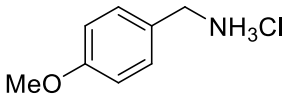
Obtained as a white crystalline solid (82% isolated yield). ^{1}H NMR (500 MHz, D_2O): δ = 7.39 (m, 5H), 4.10 (s, 2H). ^{13}C NMR (125 MHz, D_2O): δ = 132.68, 129.32, 128.92, 43.21.



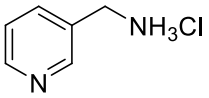
Obtained as a cream white solid (78% isolated yield). ^{1}H NMR (500 MHz, D_2O): δ = 7.39 (d, $J_{H,H}$ = 8.6 Hz, 2H), 7.33 (d, $J_{H,H}$ = 8.6 Hz, 2H), 4.08 (s, 2H). ^{13}C NMR (125 MHz, D_2O): δ = 134.61, 131.28, 130.54, 129.26, 42.53.



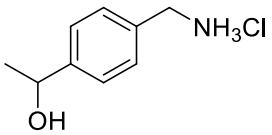
Obtained as a white solid (72% isolated yield). ^{1}H NMR (500 MHz, D_2O): δ = 7.25 (d, $J_{H,H}$ = 8.0 Hz, 2H), 7.21 (d, $J_{H,H}$ = 8.0 Hz, 2H), 4.04 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, D_2O): δ = 139.68, 129.82, 129.65, 128.94, 42.94, 20.33.



Obtained as a white crystalline solid (70% isolated yield). ^{1}H NMR (500 MHz, D_2O): δ = 7.32 (d, $J_{H,H}$ = 8.0 Hz, 2H), 6.95 (d, $J_{H,H}$ = 8.4 Hz, 2H), 4.04 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, D_2O): δ = 159.49, 130.67, 125.24, 114.66, 55.50, 42.68.

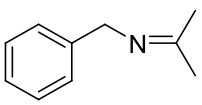


Obtained as a yellow solid (40% isolated yield). ^{1}H NMR (500 MHz, D_2O): δ = 8.89 (s, 1H), 8.80 (d, $J_{H,H}$ = 5.7 Hz, 1H), 8.68 (d, $J_{H,H}$ = 8.0 Hz, 1H), 8.10 (q, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 5.7 Hz), 4.42 (s, 2H). ^{13}C NMR (125 MHz, D_2O): δ = 147.84, 142.00, 141.75, 133.16, 128.05, 39.73.



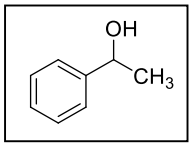
Obtained as a pale yellow solid (60% isolated yield). ^{1}H NMR (500 MHz, D_2O): δ = 7.38 (m, 4H), 4.85 (q, $J_{H,H}$ = 13.15 Hz, $J_{H,H}$ = 6.3 Hz, 1H), 4.10 (s, 2H), 1.38 (d, $J_{H,H}$ = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, D_2O): δ = 146.01, 131.86, 129.16, 126.40, 69.46, 42.87. 23.65.

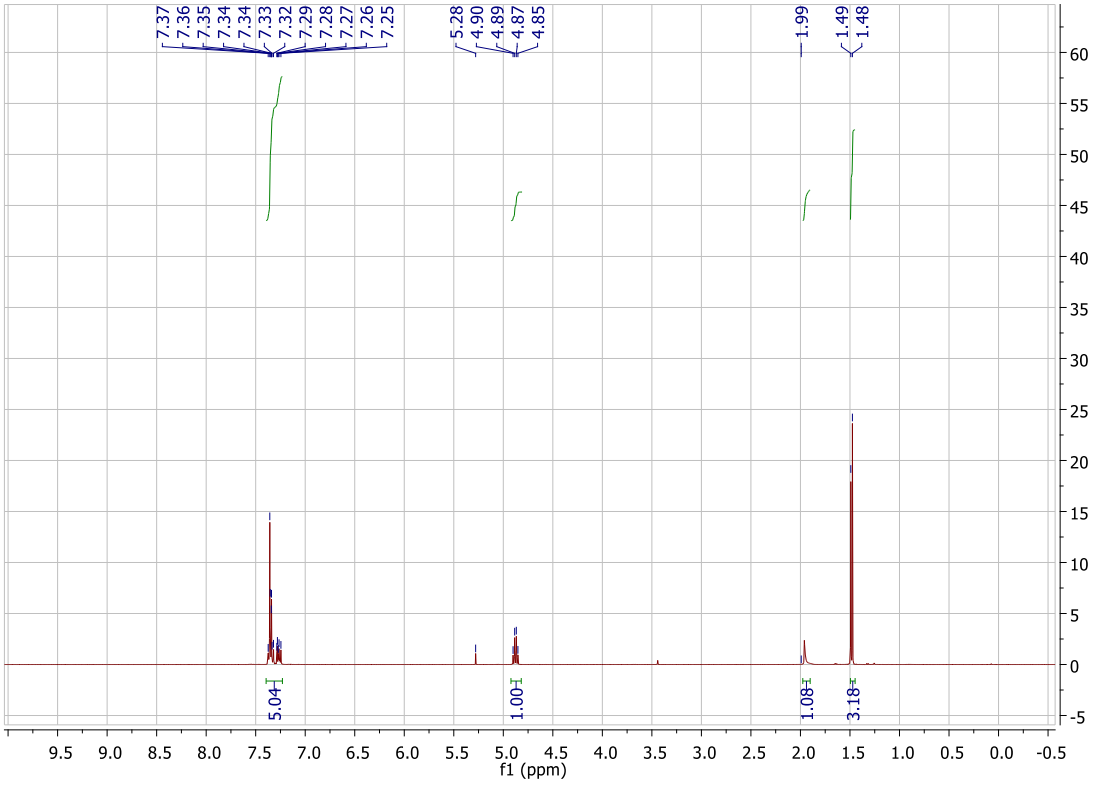
Isolation of pure imine product by alumina and silica gel column chromatography using hexane and ethyl acetate as an eluent was unsuccessful as it produced some unidentified compounds. To isolate the imine product from benzonitrile, the 2-propanol solution of imine and Ru complex was filtered through celite and submitted for ^{1}H NMR spectroscopy.

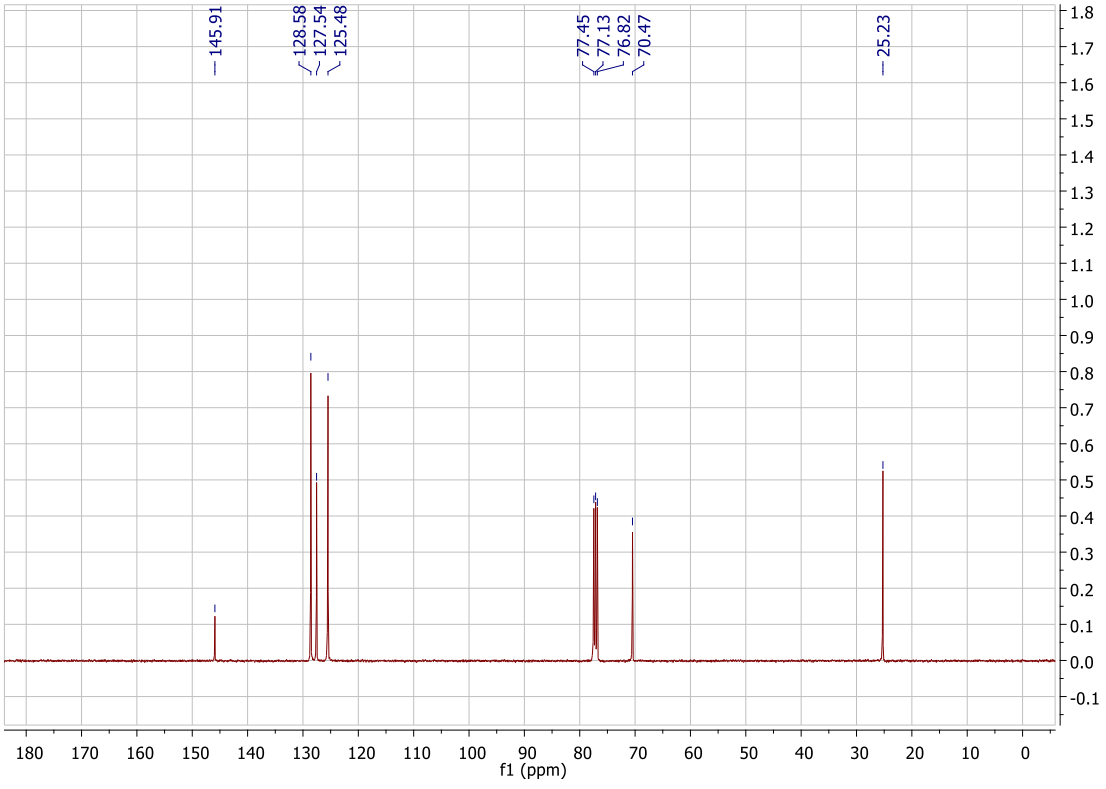


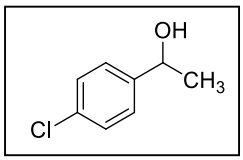
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.33 (m, 5H), 7), 4.45 (s, 2H), 2.08 (s, 3H), 1.93 (s, 3H). It also contained 2 mol % complex **2**.

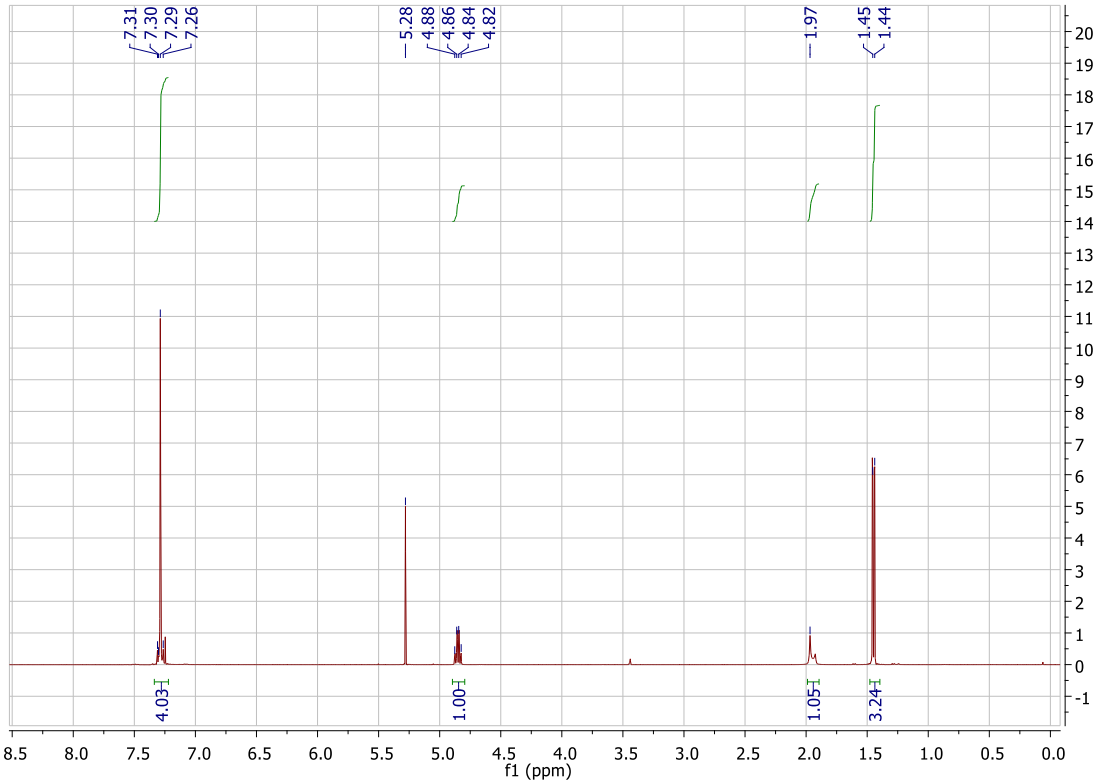
Copies of ^{1}H and ^{13}C NMR Spectra of Alcohols








OH
CH3
Cl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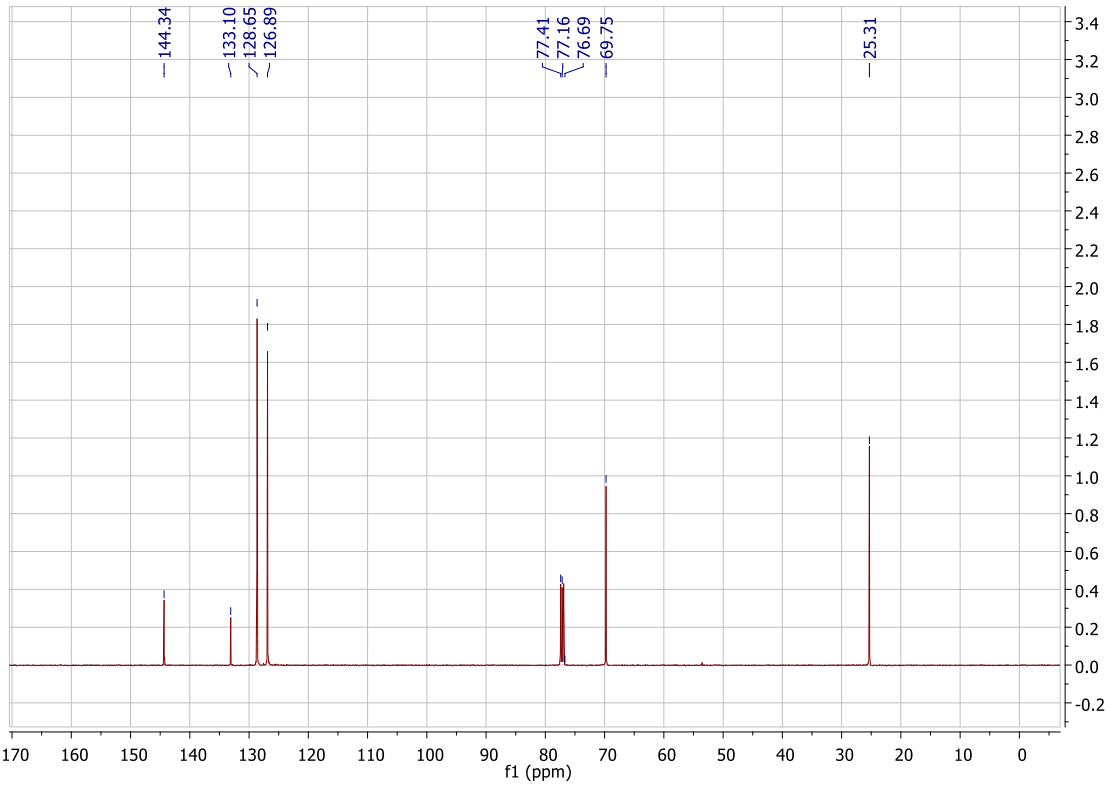
7.29
7.26
5.28
4.88
4.86
4.84
4.82
1.97
1.45
1.44
4.03
1.00
1.05
3.24
f1 (ppm)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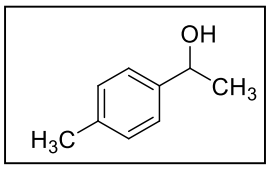
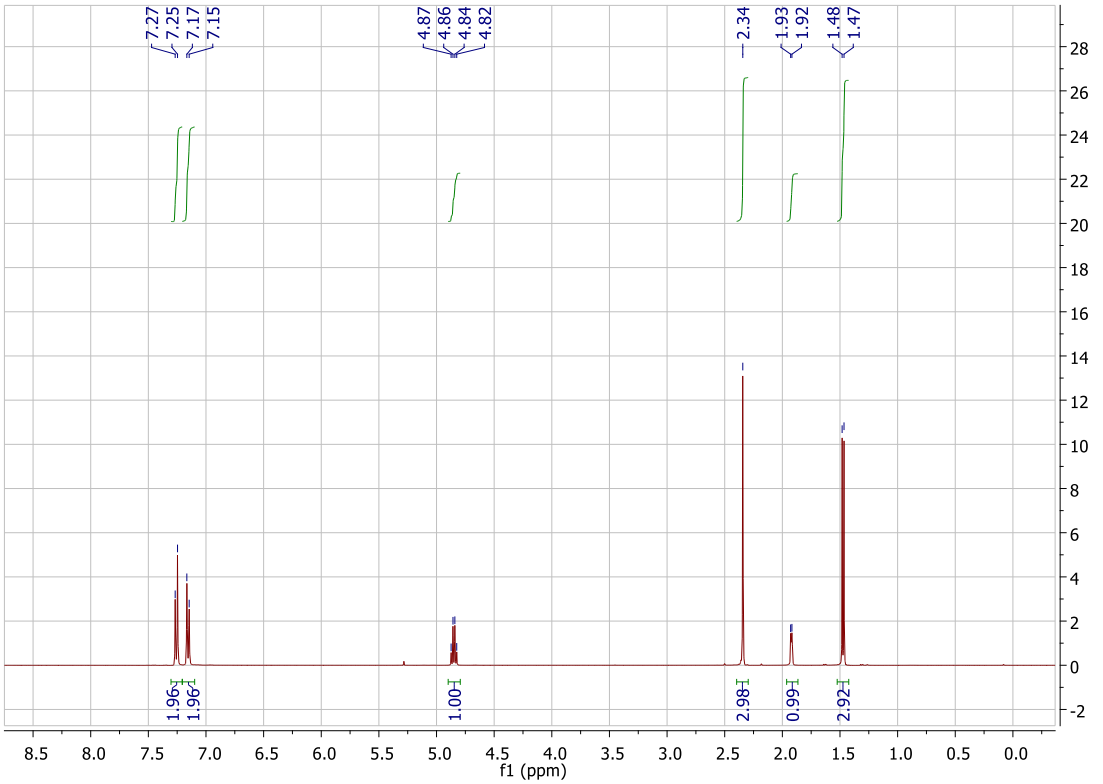
126.89
77.41
77.16
76.69
69.75
25.31
f1 (ppm)


OH
CH3
H3C


7.27
7.25
7.17
7.15
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4.86
4.84
4.82
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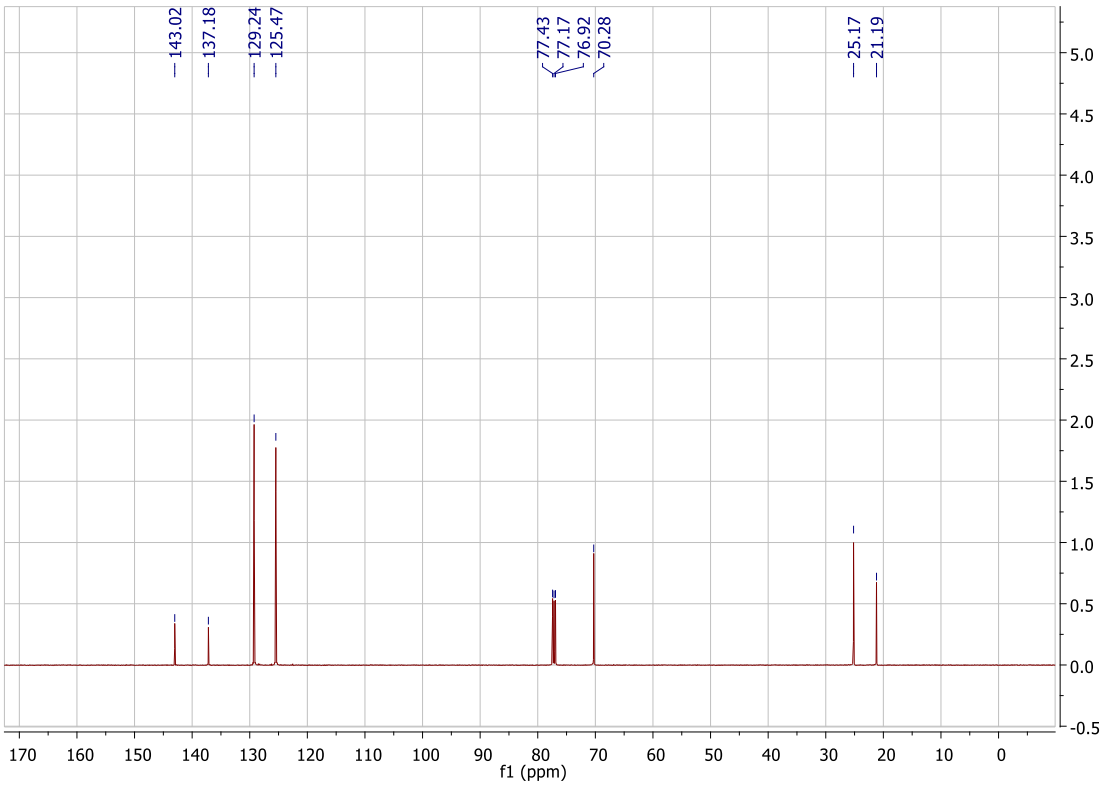
1.93
1.92
1.48
1.47
1.96
1.96
1.00
2.98
0.99
2.92
f1 (ppm)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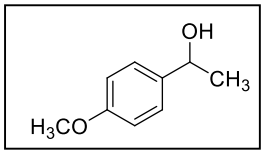
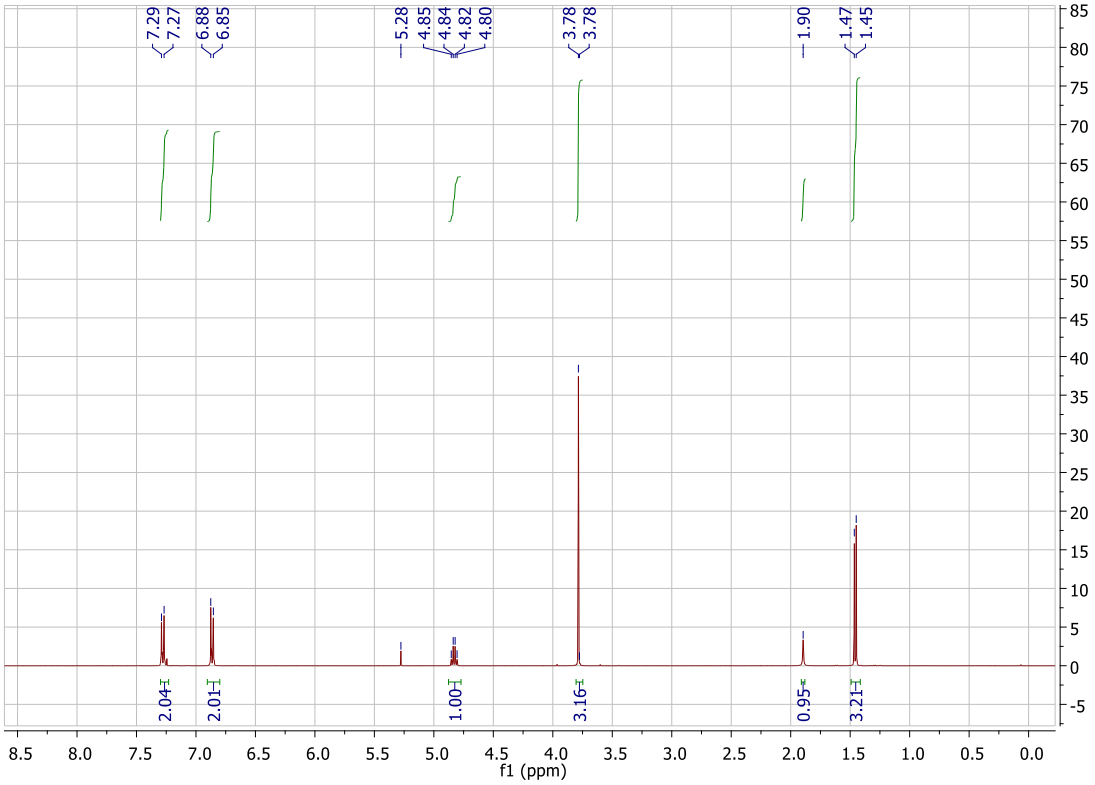
129.24
125.47
77.43
77.17
76.92
70.28
25.17
21.19
f1 (ppm)


OH
CH3
H3CO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4.85
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4.82
4.80
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3.78
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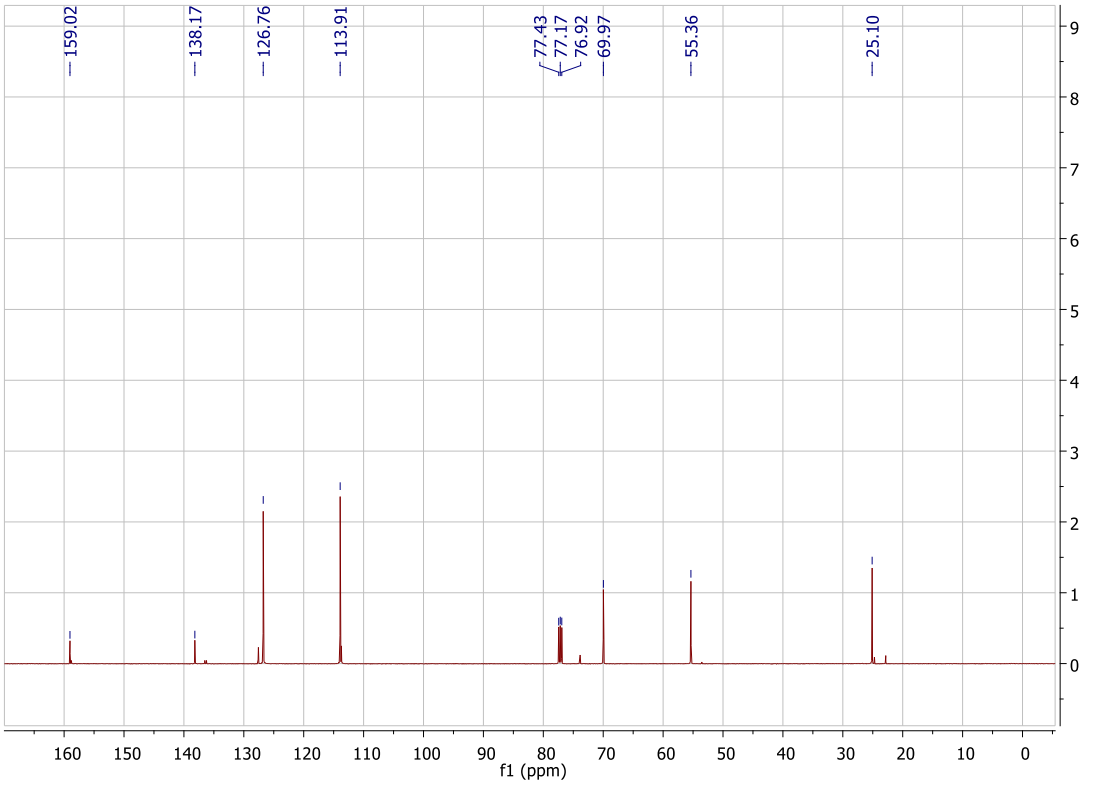
1.47
1.45
2.04
2.01
1.00
3.16
0.95
3.21
f1 (ppm)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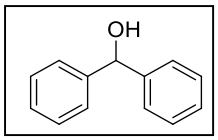
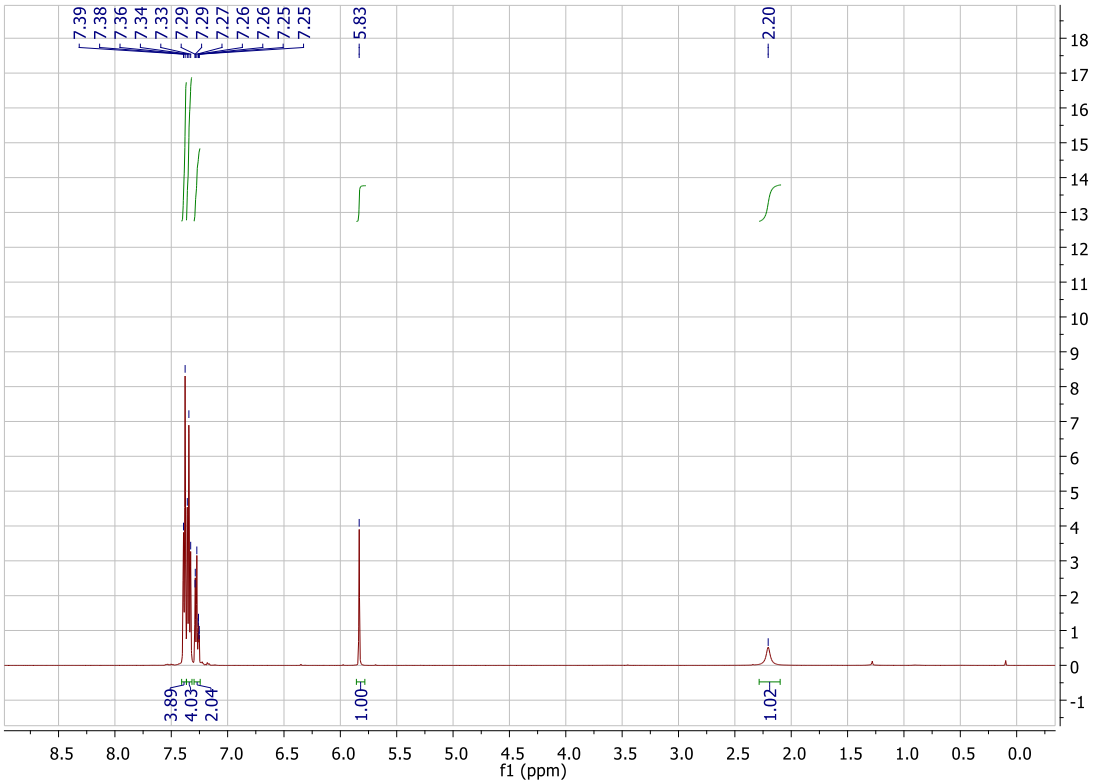

OH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7.29
7.27
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7.26
7.25
7.25
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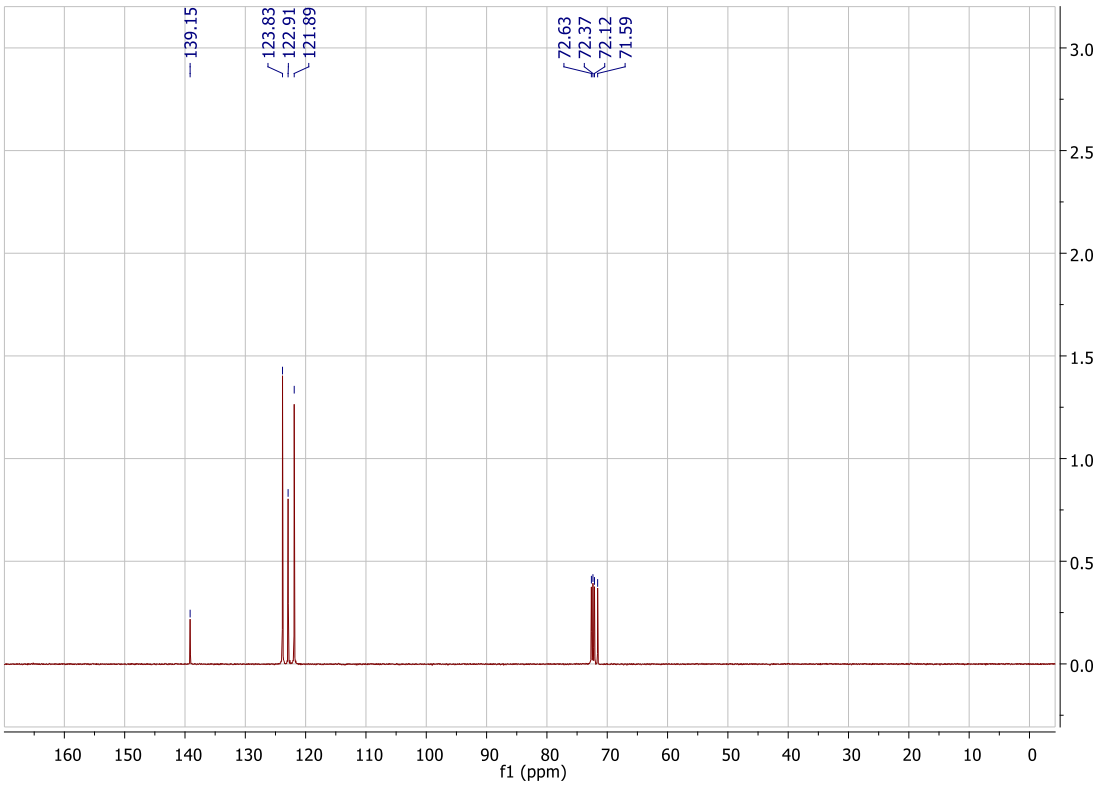
4.03
2.04
1.00
1.02
f1 (ppm)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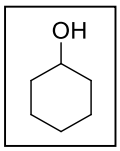
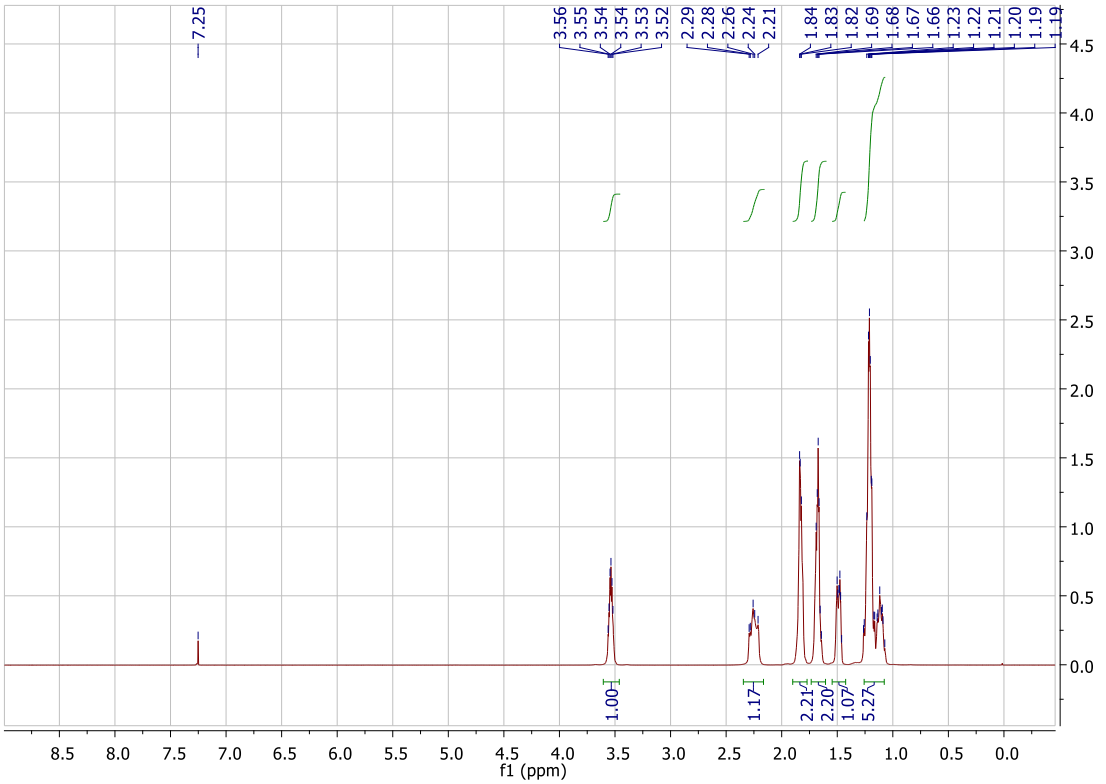
121.89
72.63
72.37
72.12
71.59
f1 (ppm)


OH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2.29
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2.24
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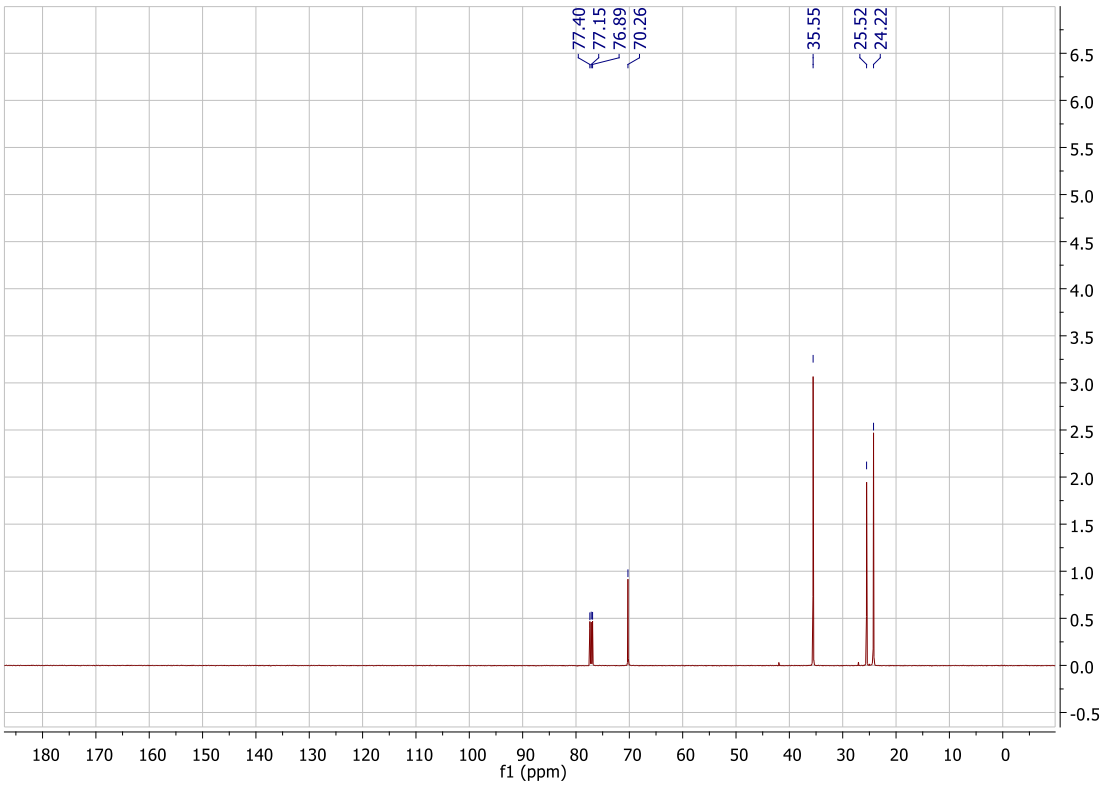
1.84
1.83
1.82
1.69
1.68
1.67
1.66
1.23
1.22
1.21
1.20
1.19
1.19
1.00
1.17
2.21
2.20
1.07
5.27
f1 (ppm)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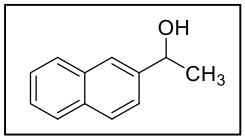
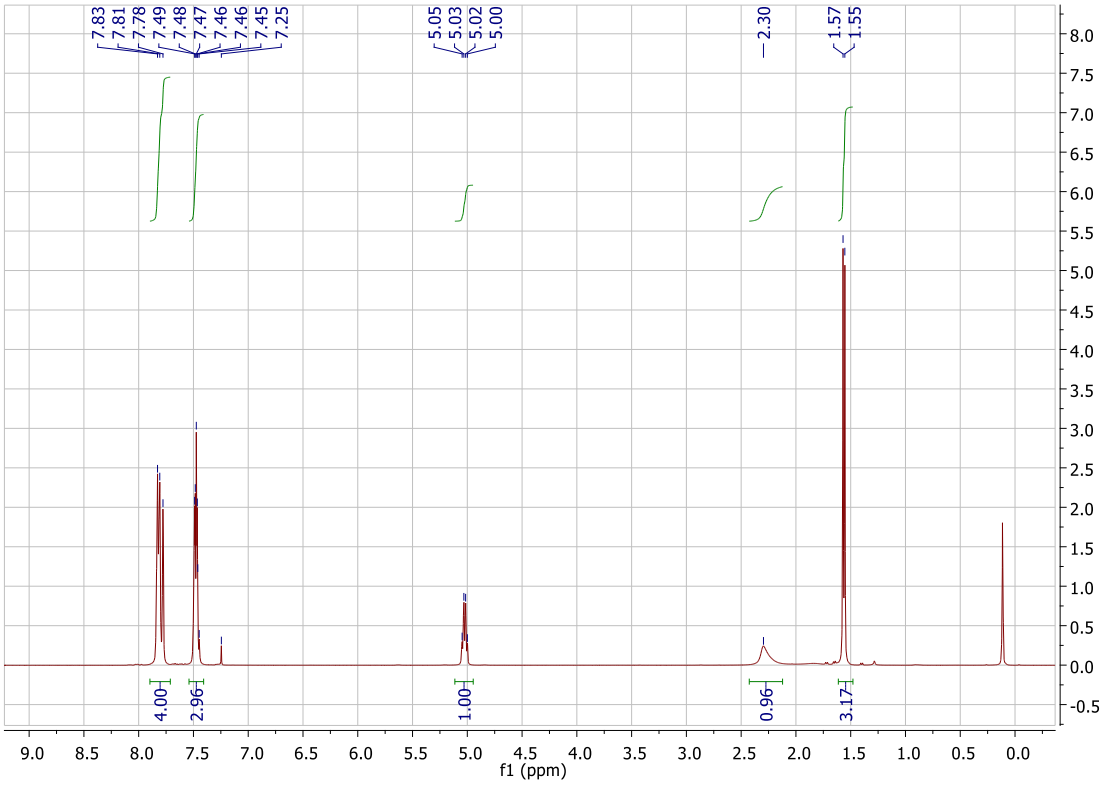
35.55
25.52
24.22
f1 (ppm)


OH
CH3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7.46
7.46
7.45
7.25
5.05
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2.30
1.57
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1.00
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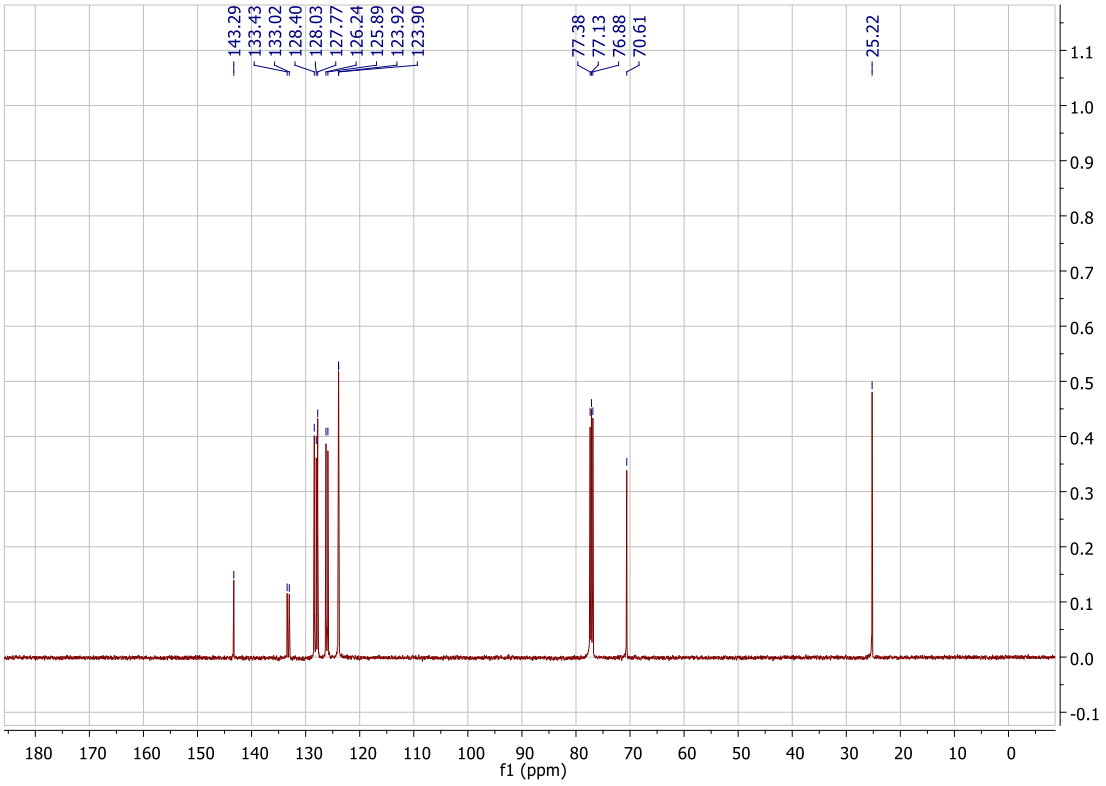
f1 (ppm)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128.03
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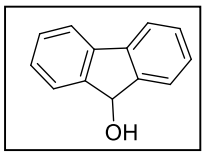
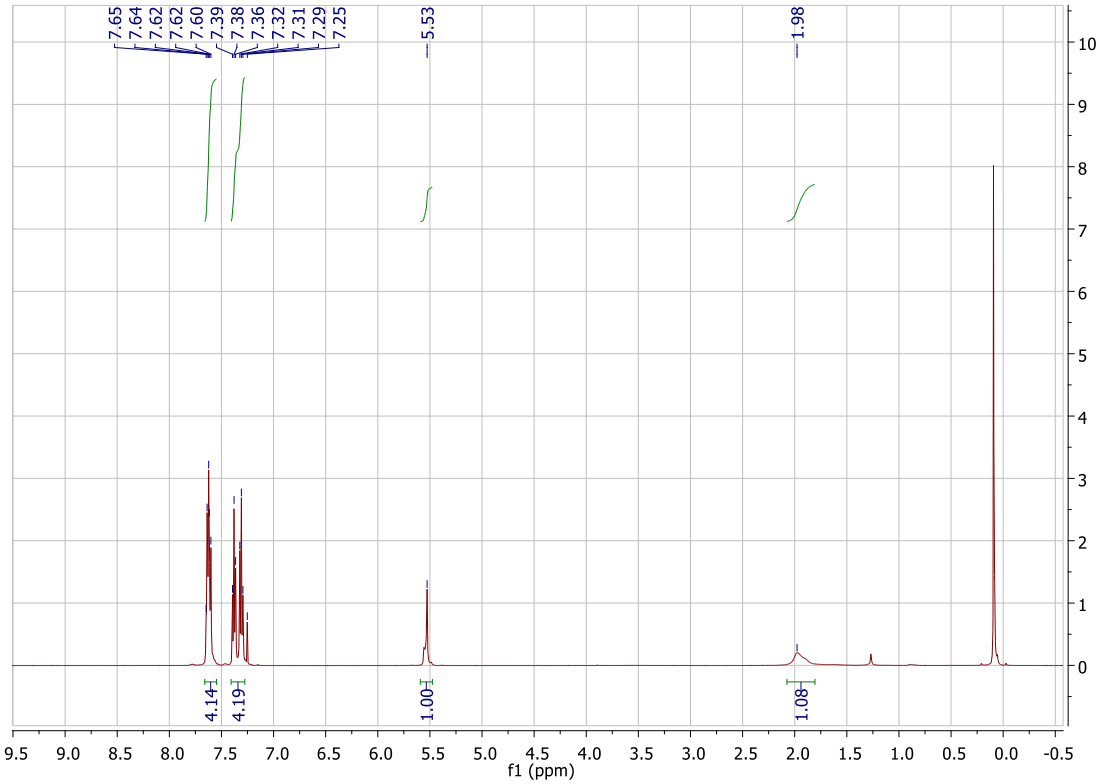
123.92
123.90
77.38
77.13
76.88
70.61
25.22
f1 (ppm)


OH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7.64
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7.62
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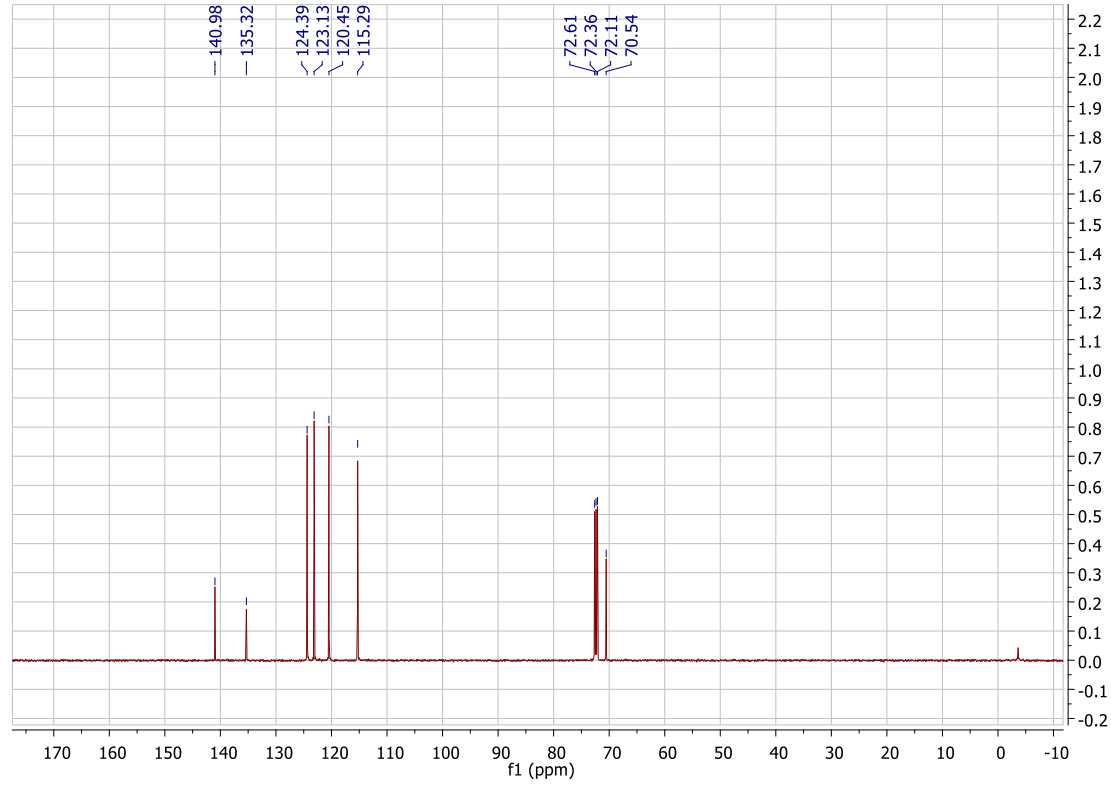
7.31
7.29
7.25
5.53
1.98
4.14
4.19
1.00
1.08
f1 (ppm)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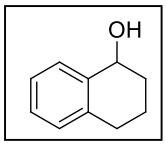
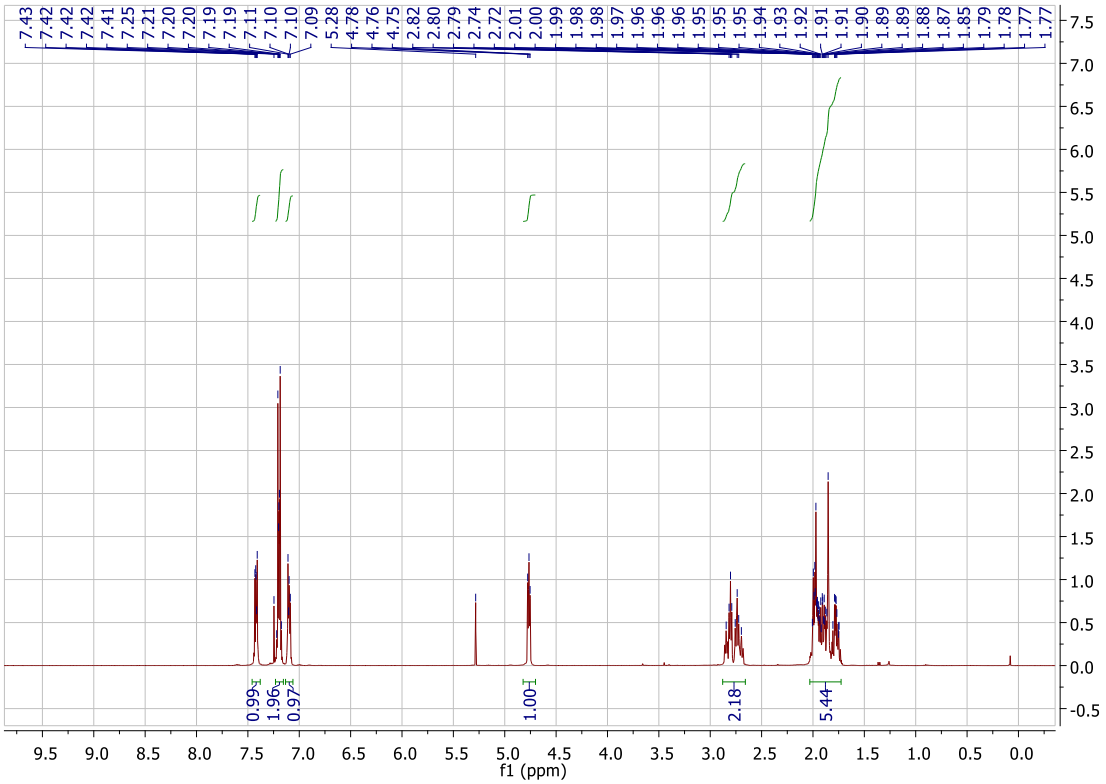
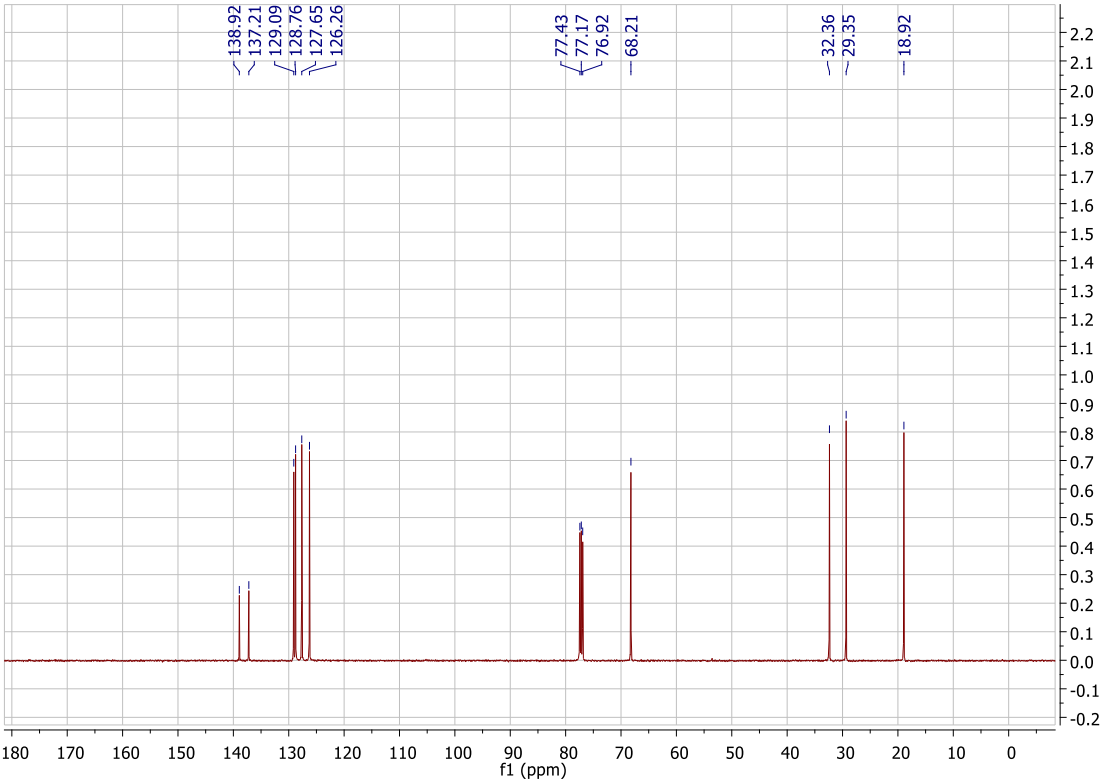
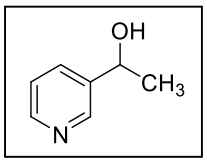
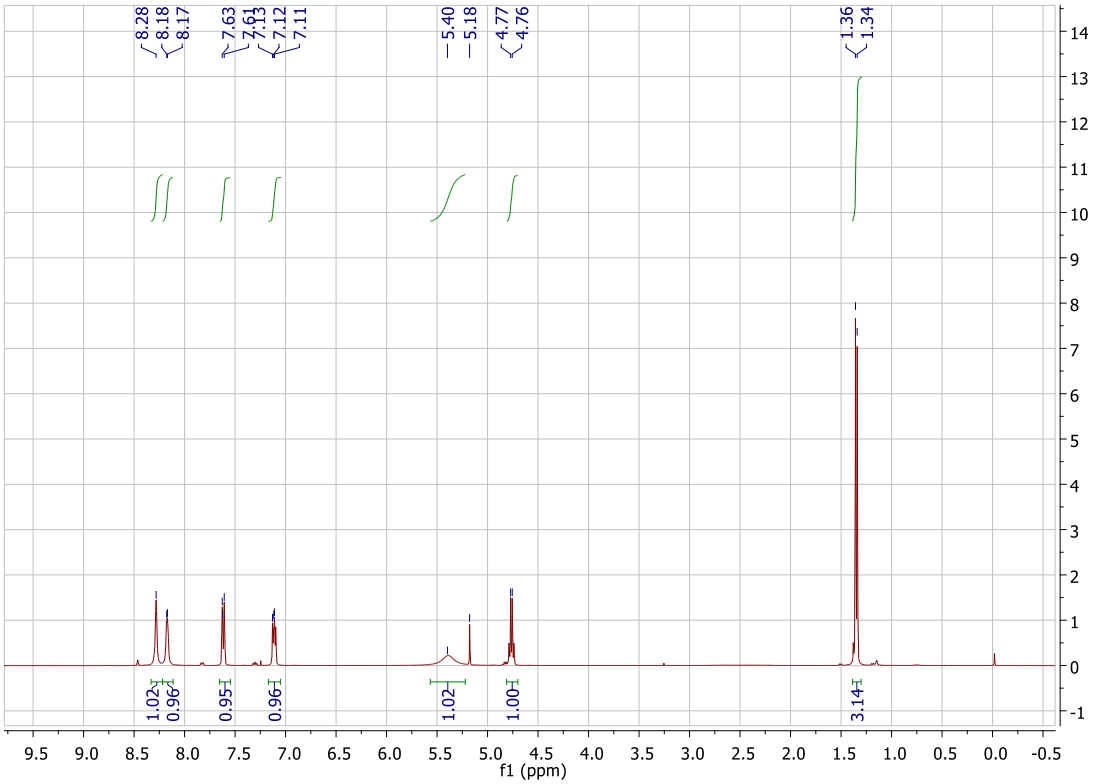
124.39
123.13
120.45
115.29
72.61
72.36
72.11
70.54
f1 (ppm)

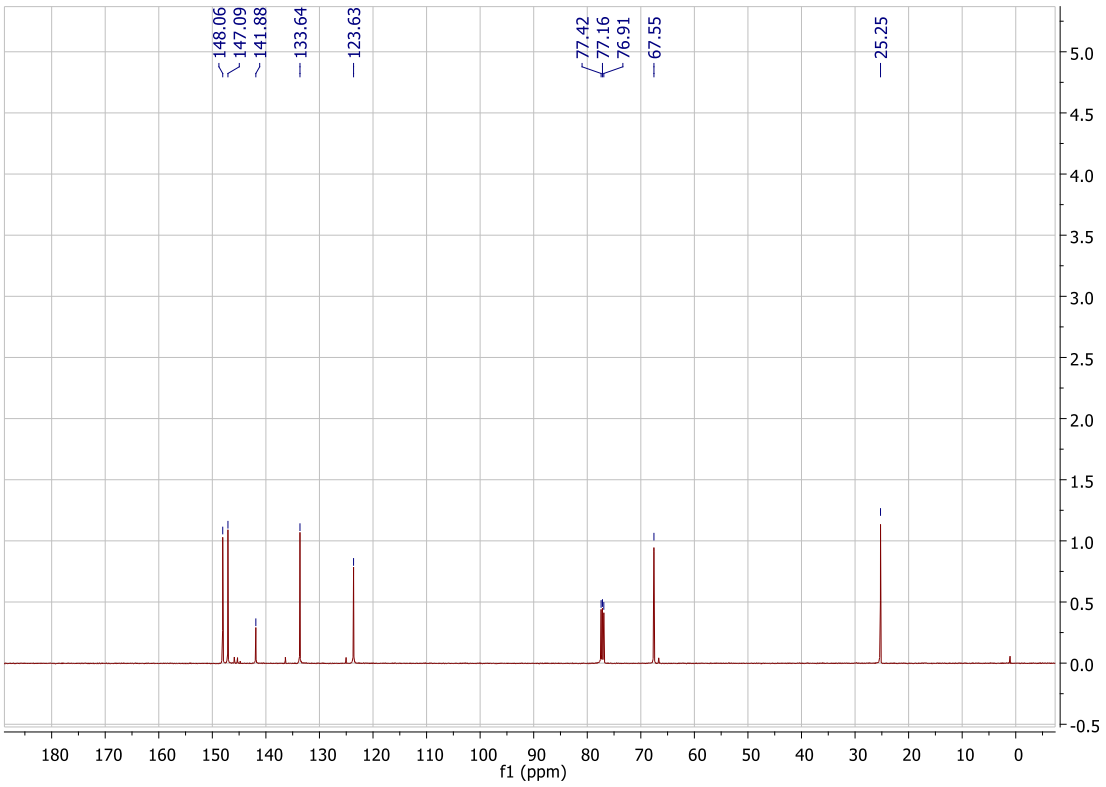

OH

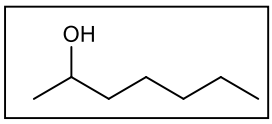

7.43 7.42 7.42 7.42 7.41 7.25 7.21 7.20 7.20 7.19 7.19 7.11 7.10 7.10 7.09 5.28 4.78 4.76 4.75 2.82 2.80 2.79 2.74 2.72 2.01 2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.96 1.95 1.95 1.95 1.94 1.93 1.92 1.91 1.91 1.90 1.89 1.89 1.88 1.87 1.85 1.79 1.78 1.77 1.77
0.99 1.96 0.97 1.00 2.18 5.44
f1 (ppm)

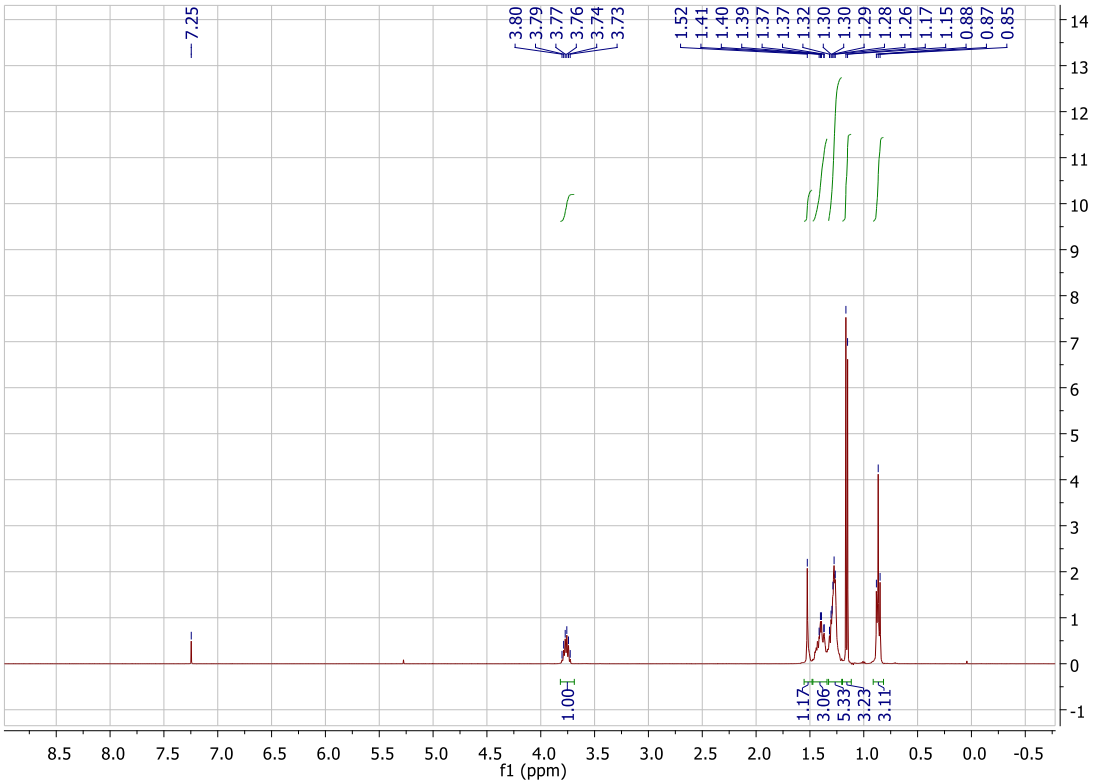

138.92 137.21 129.09 128.76 127.65 126.26 77.43 77.17 76.92 68.21 32.36 29.35 18.92
f1 (ppm)


OH
CH3
N


8.28
8.18
8.17
7.63
7.61
7.13
7.12
7.11
5.40
5.18
4.77
4.76
1.36
1.34
1.02
0.96
0.95
0.96
1.02
1.00
3.14
f1 (ppm)


148.06
147.09
141.88
133.64
123.63
77.42
77.16
76.91
67.55
25.25
f1 (ppm)


OH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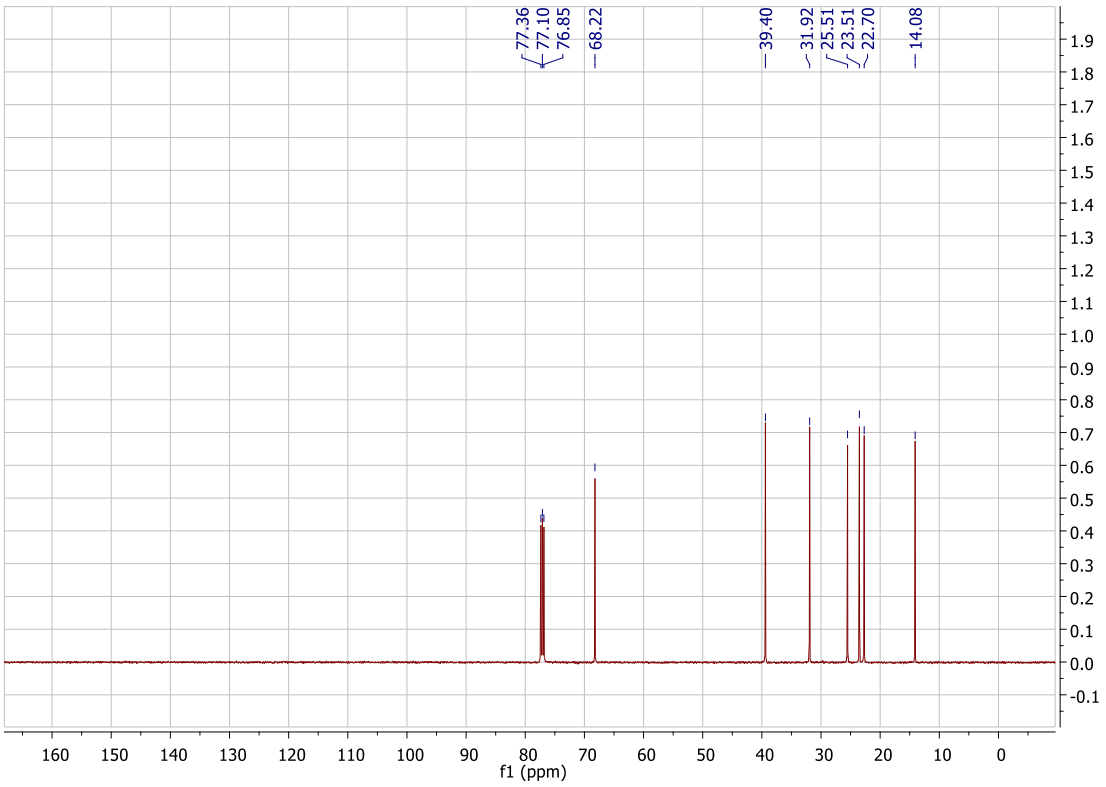
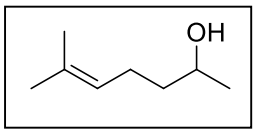
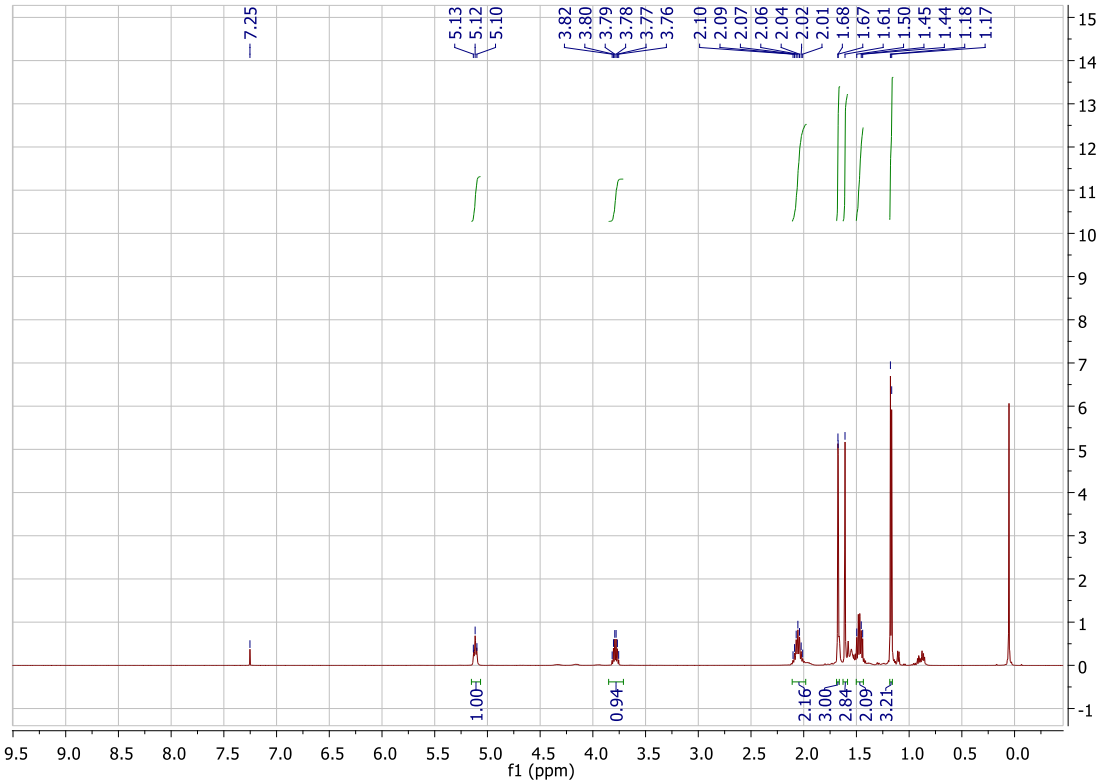
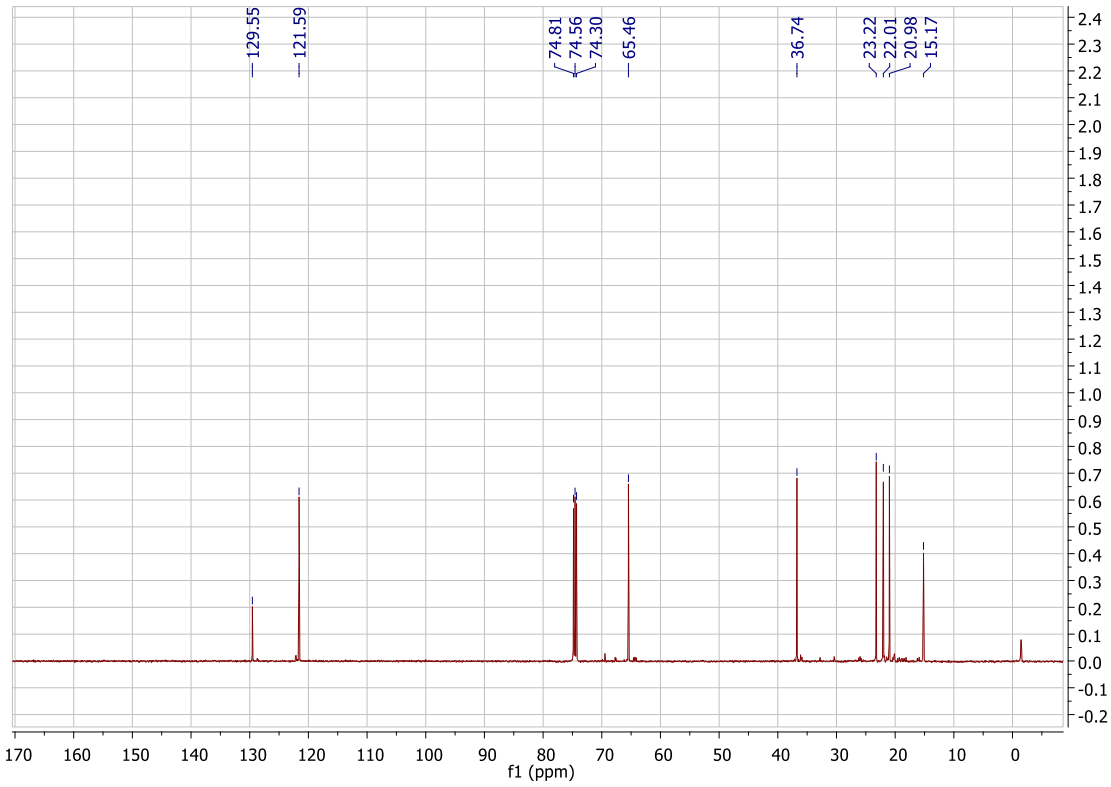
3.80
3.79
3.77
3.76
3.74
3.73
1.52
1.41
1.40
1.39
1.37
1.37
1.32
1.30
1.30
1.29
1.28
1.26
1.17
1.15
0.88
0.87
0.85
1.00
1.17
3.06
5.33
3.23
3.11
f1 (ppm)

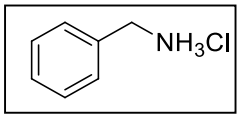

77.36
77.10
76.85
68.22
39.40
31.92
25.51
23.51
22.70
14.08
f1 (ppm)

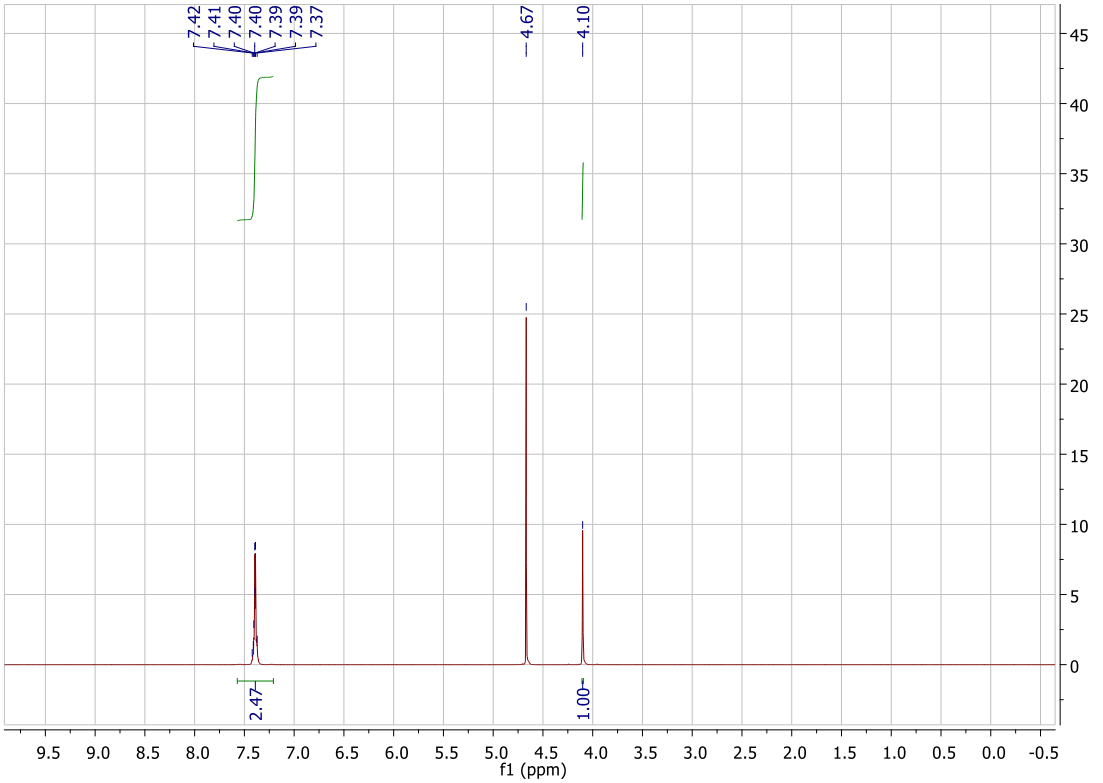

OH

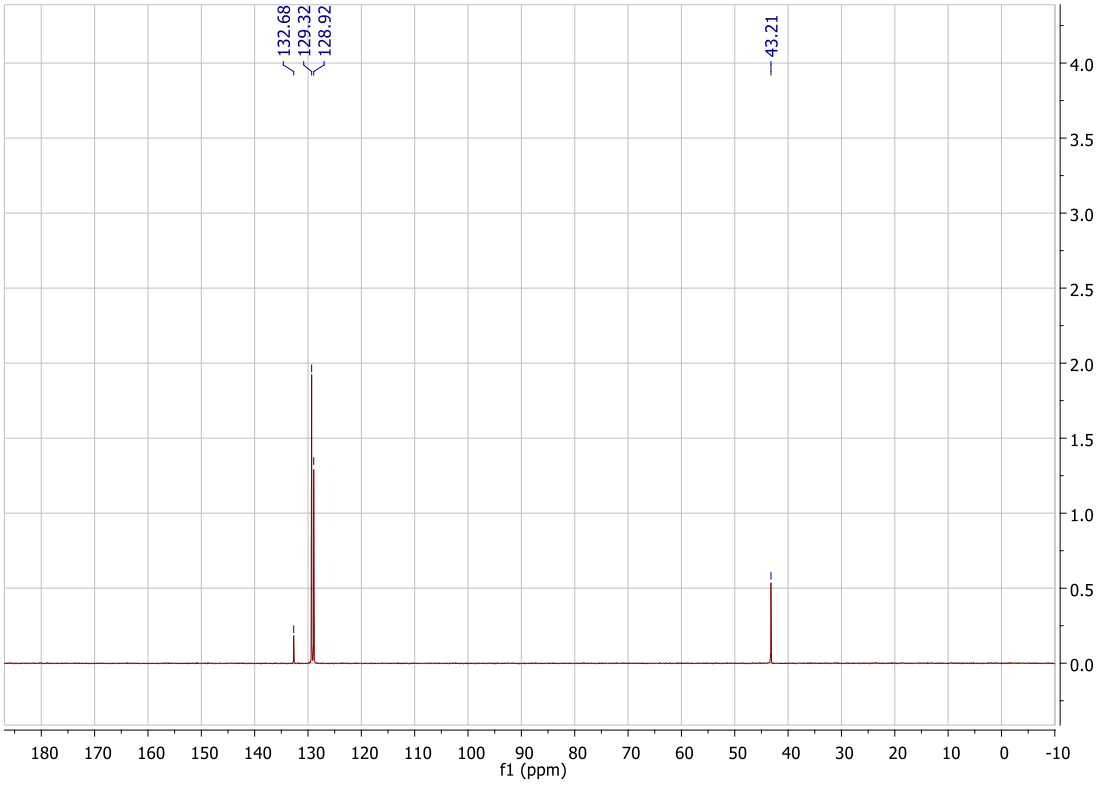

7.25
5.13
5.12
5.10
3.82
3.80
3.79
3.78
3.77
3.76
2.10
2.09
2.07
2.06
2.04
2.02
2.01
1.68
1.67
1.61
1.50
1.45
1.44
1.18
1.17
1.00
0.94
2.16
3.00
2.84
2.09
3.21
f1 (ppm)

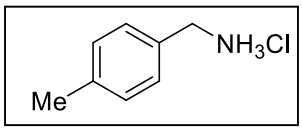

129.55
121.59
74.81
74.56
74.30
65.46
36.74
23.22
22.01
20.98
15.17
f1 (ppm)

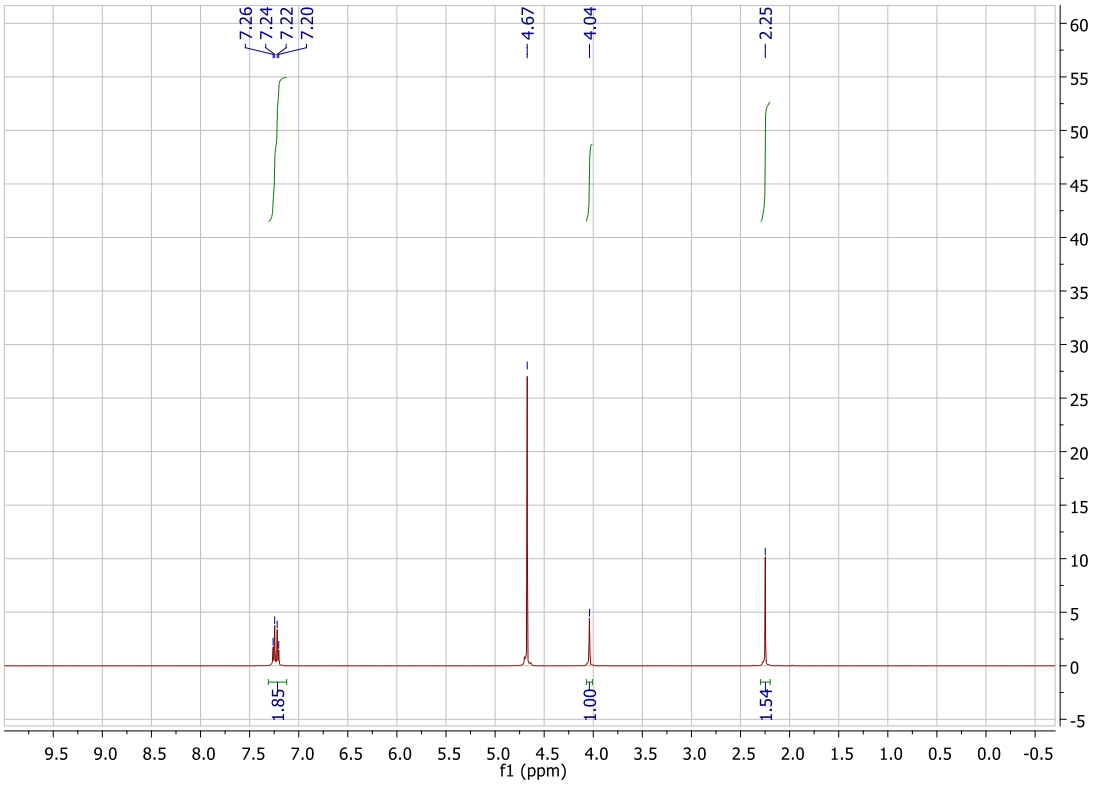
Copies of ^{1}H and ^{13}C NMR Spectra of Amine Salts.

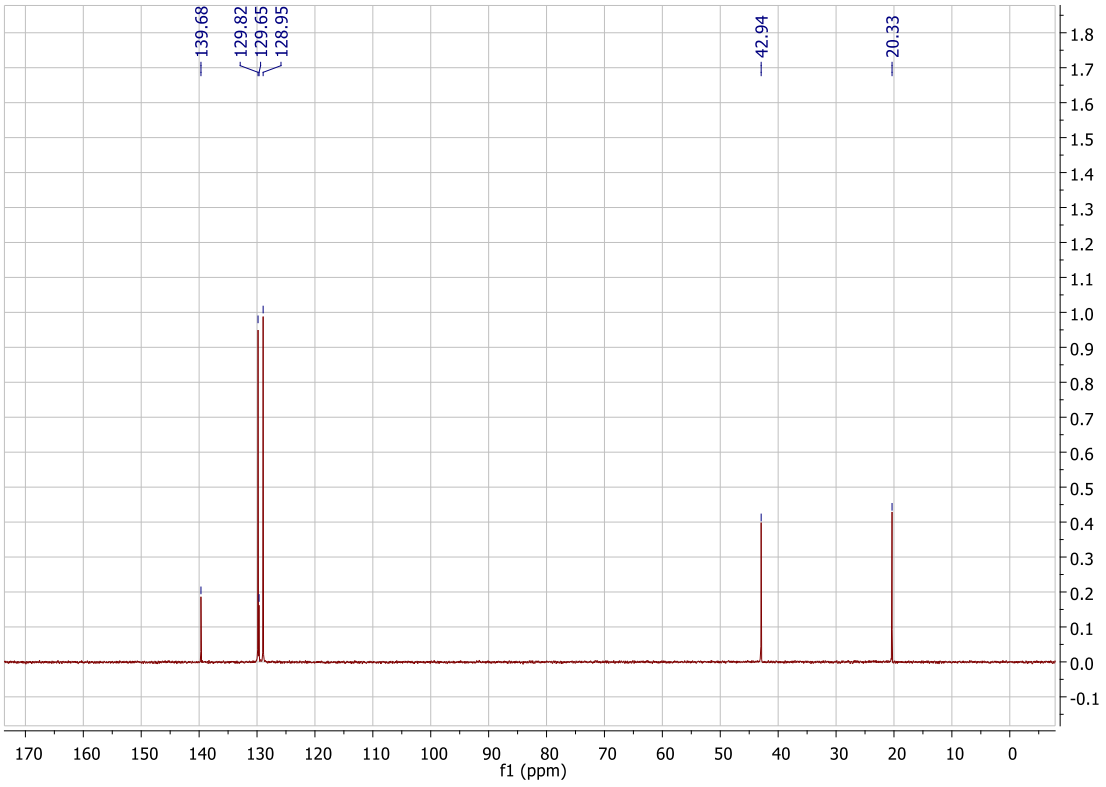


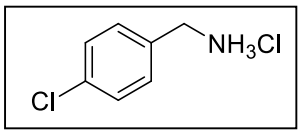


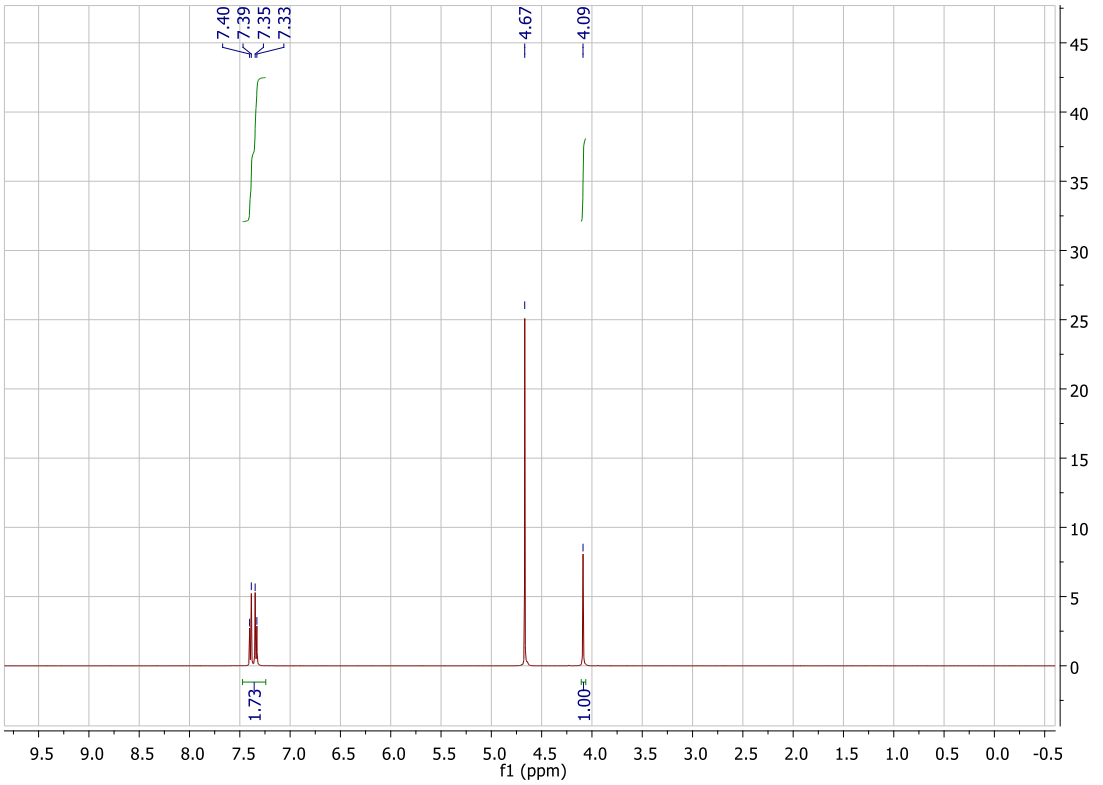


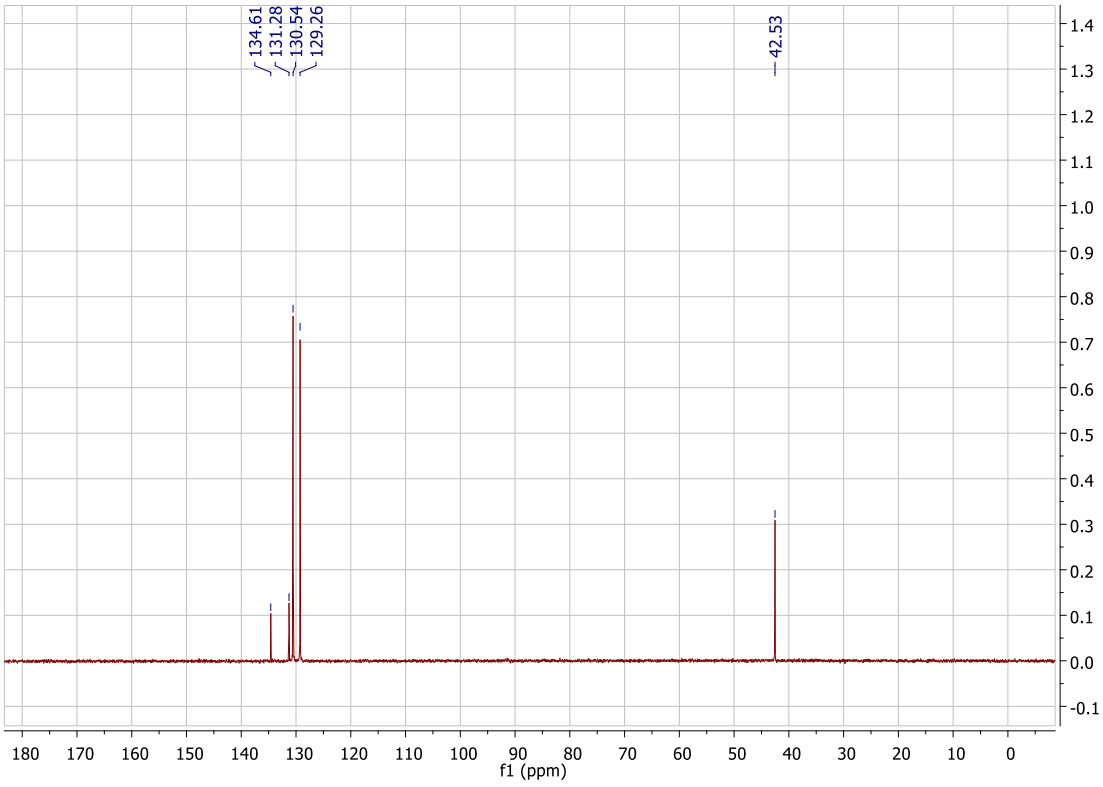

NH3Cl
Me

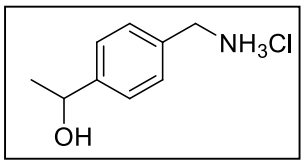

7.26
7.24
7.22
7.20
4.67
4.04
2.25
1.85
1.00
1.54
f1 (ppm)

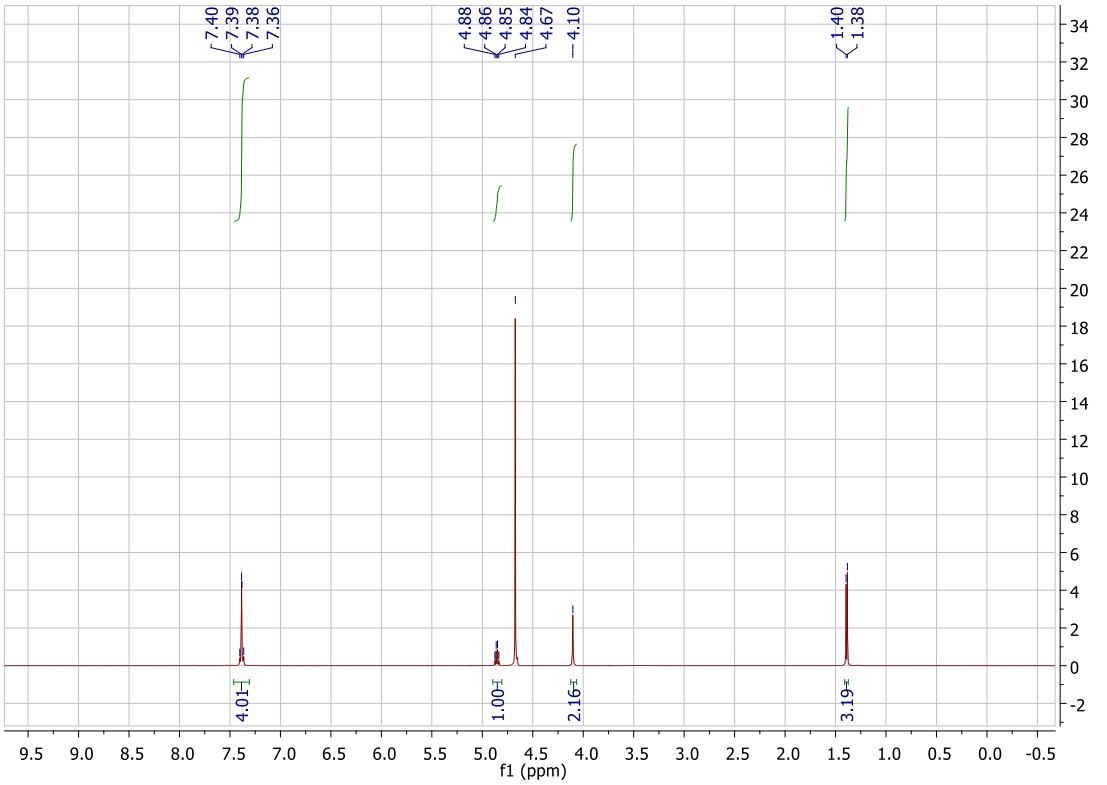

139.68
129.82
129.65
128.95
42.94
20.33
f1 (ppm)

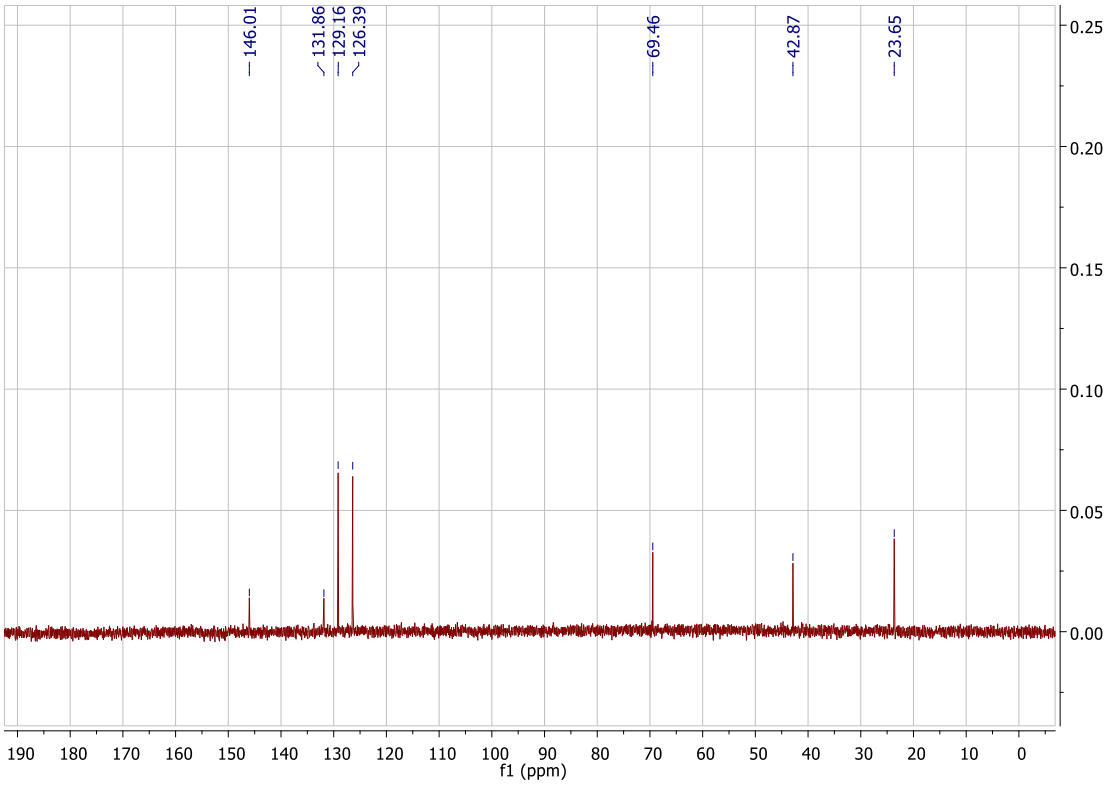

NH3Cl
Cl

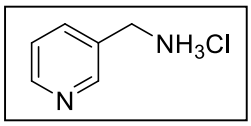

7.40
7.39
7.35
7.33
4.67
4.09
1.73
1.00
f1 (ppm)

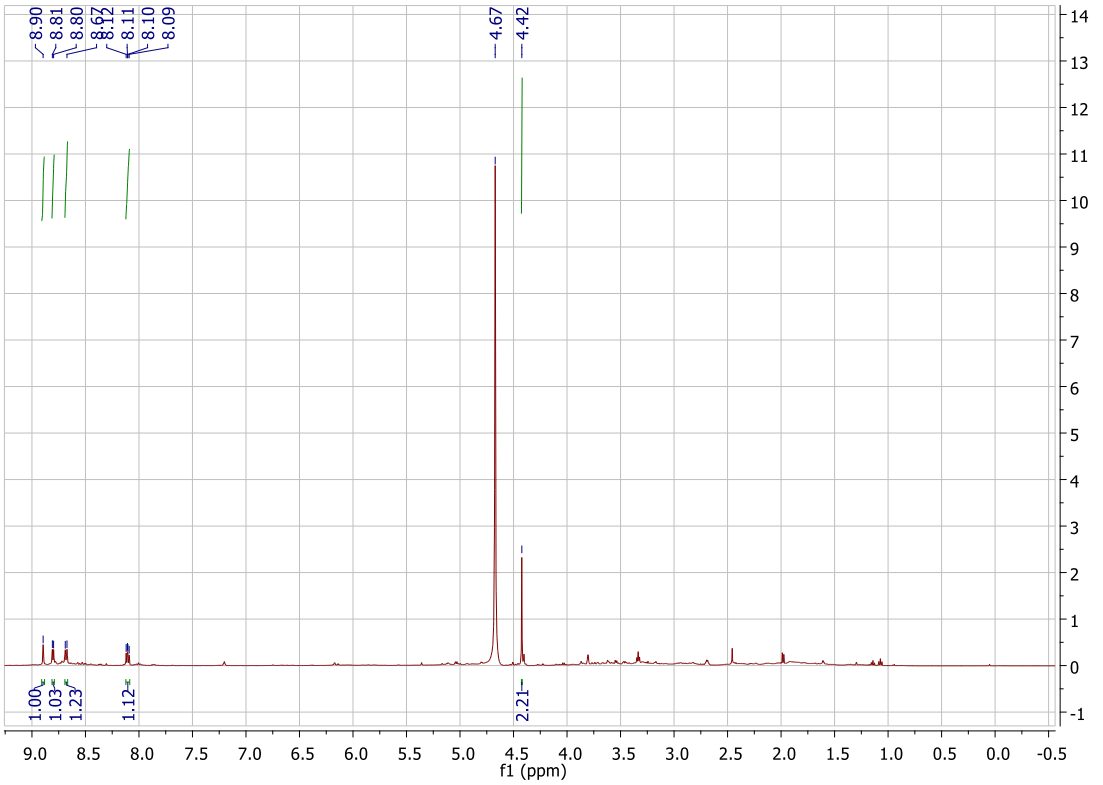

134.61
131.28
130.54
129.26
42.53
f1 (ppm)

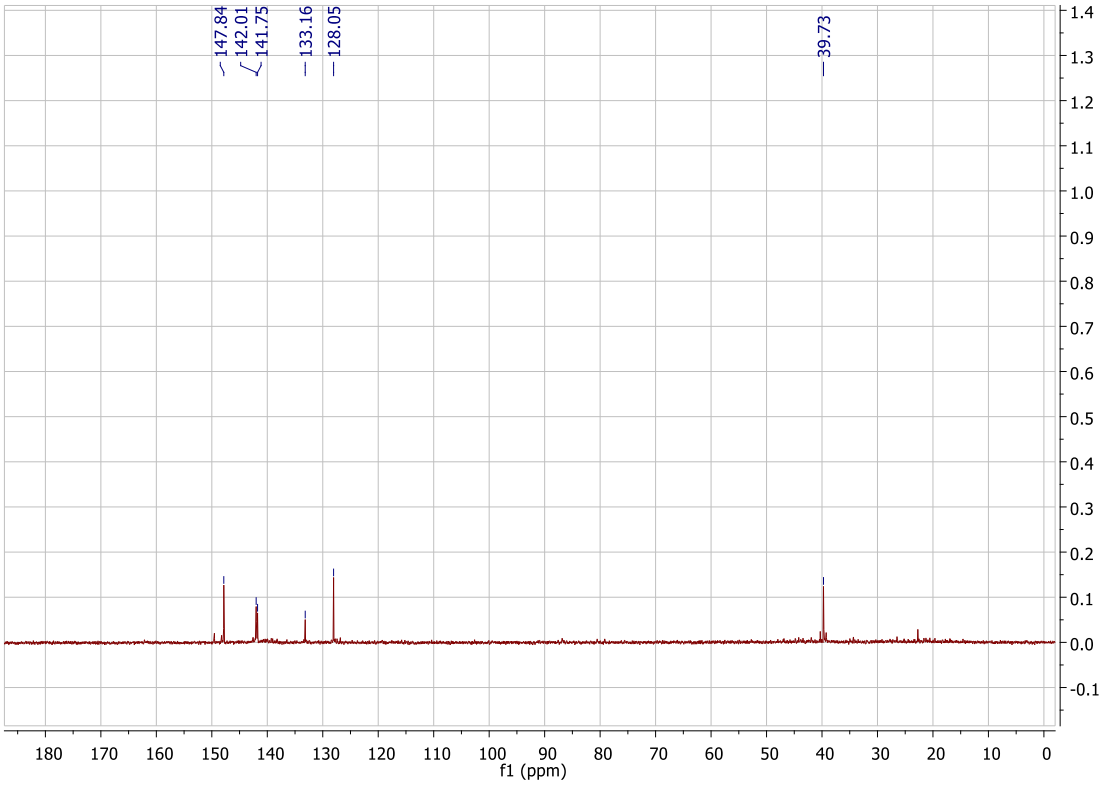

NH3Cl
OH


7.40
7.39
7.38
7.36
4.88
4.86
4.85
4.84
4.67
4.10
1.40
1.38
4.01
1.00
2.16
3.19
f1 (ppm)


146.01
131.86
129.16
126.39
69.46
42.87
23.65
f1 (ppm)


NH3Cl
N


8.90
8.81
8.80
8.12
8.11
8.10
8.09
4.67
4.42
1.00
1.03
1.23
1.12
2.21
f1 (ppm)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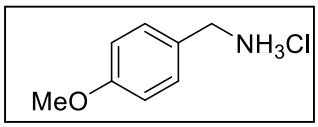
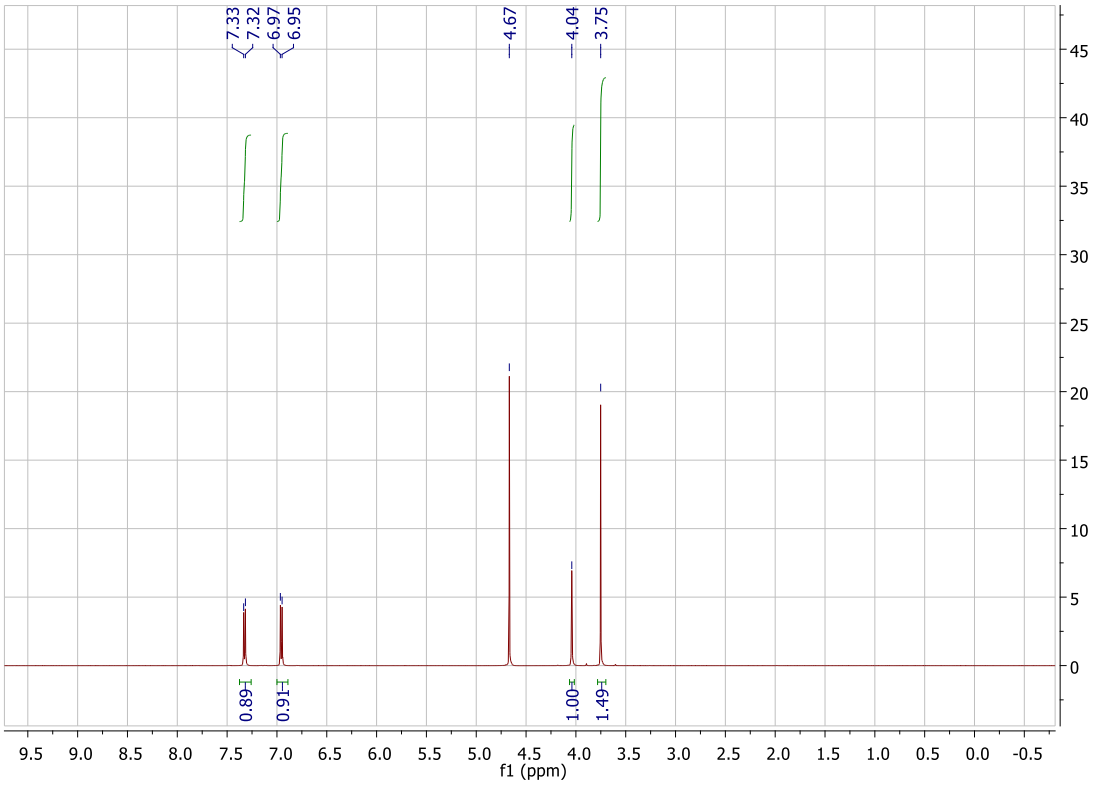
141.75
133.16
128.05
39.73
f1 (ppm)


NH3Cl
MeO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7.32
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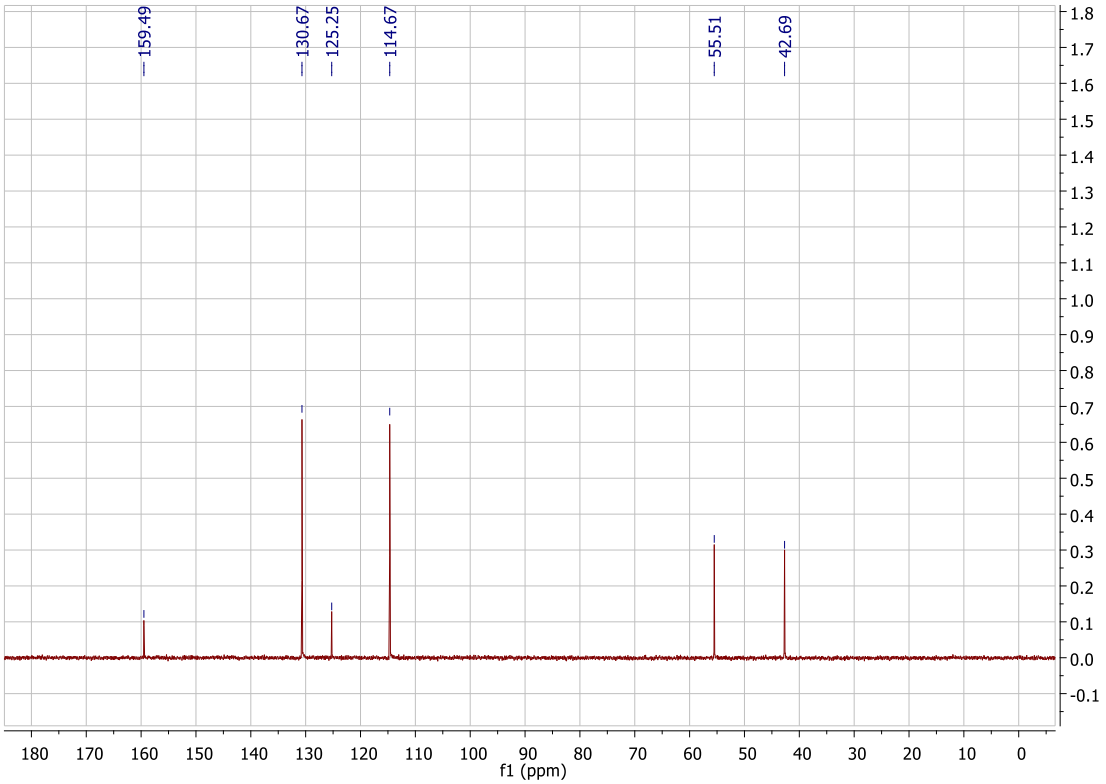
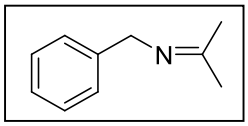
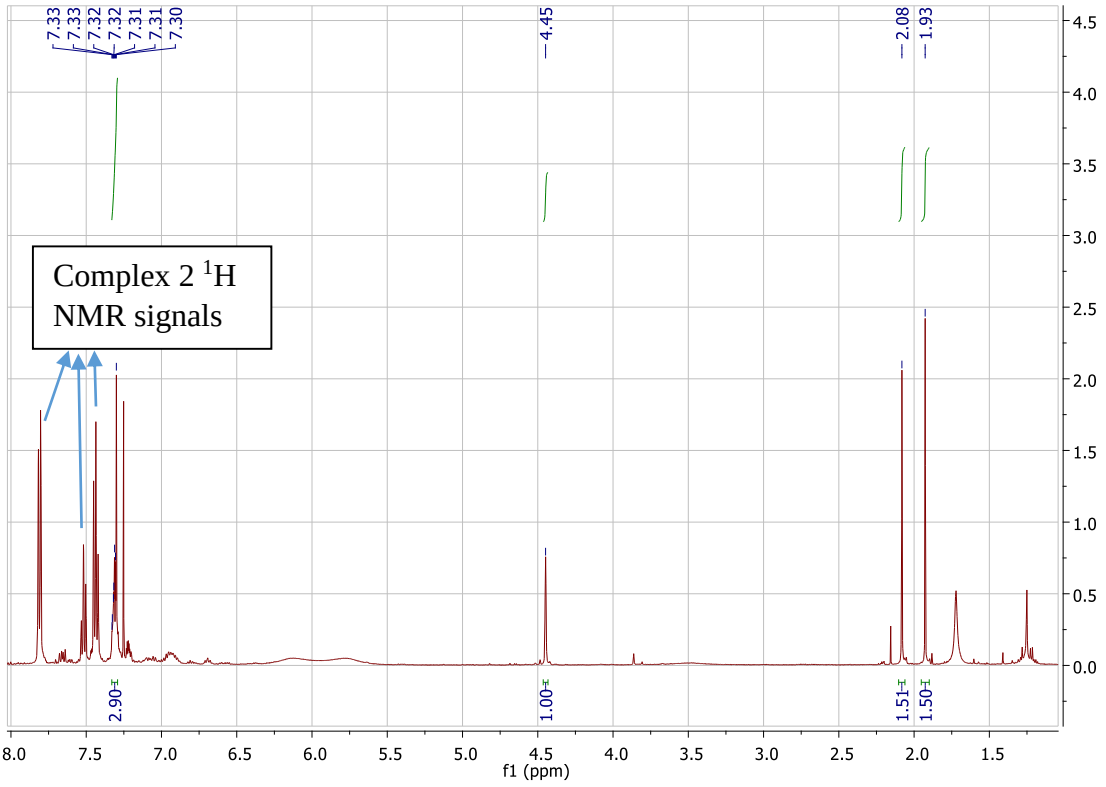
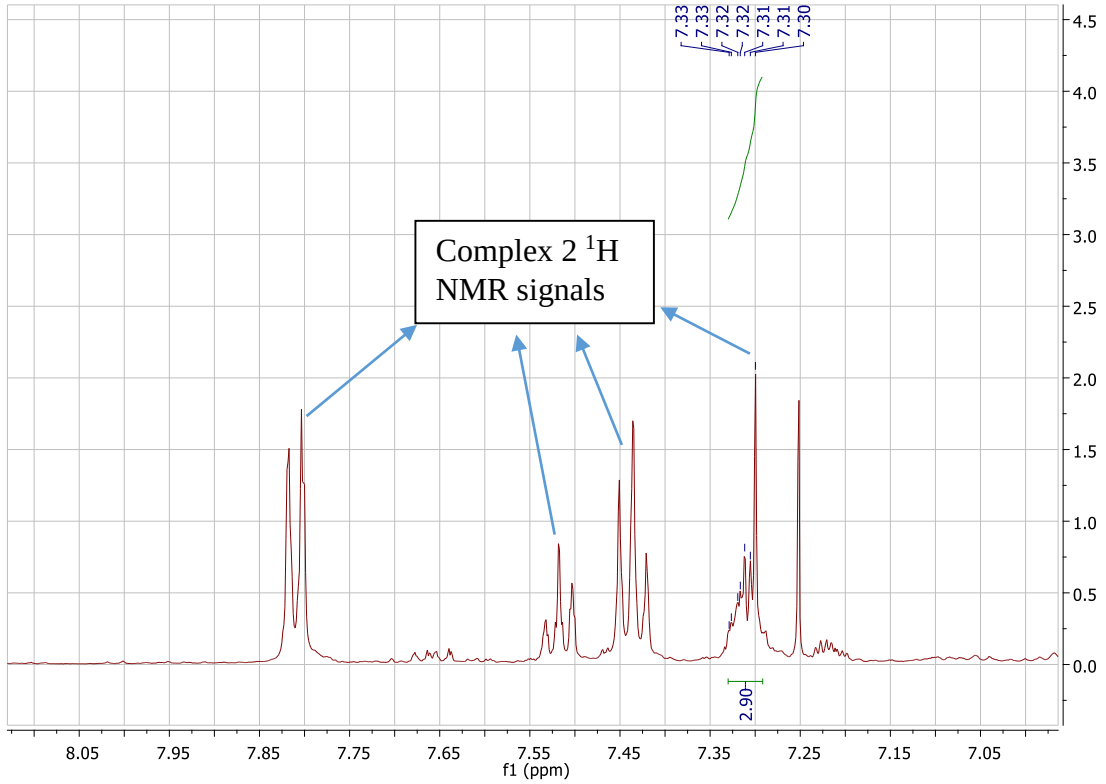
6.95
4.67
4.04
3.75
0.89
0.91
1.00
1.49
f1 (ppm)


159.49
130.67
125.25
114.67
55.51
42.69
f1 (ppm)




Complex 2 ^{1}H NMR signals
7.33
7.33
7.32
7.32
7.31
7.31
7.30
4.45
2.08
1.93
2.90
1.00
1.51
1.50
f1 (ppm)


Complex 2 ^{1}H NMR signals
7.33
7.33
7.32
7.32
7.31
7.31
7.30
2.90
f1 (ppm)

References.

(1) SAINT+ Software for CCD Difractometers, Bruker AXS, Madison, WI, **2000**.
(2) Sheldrick, G. M.; SADABS Program for Correction of Area Detector Data, University of Gottingen, Gottingen, Germany, **1999**.
(3) (a) SHELXTL Package v. 6.10, Bruker AXS, Madison, WI, 2000; (b) Sheldrick, G. M.; SHELXS-86 and SHELXL-97, University of Gottingen, Gottingen, Germany, **1997**.
(4) Bradenburg, K.; Diamond, version 3.1e; Crystal Impact GbR: Bonn, Germany, **2005**.