Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Bifunctional Ru (II) Complex Catalysed Carbon–Carbon Bond Formation: An Eco-friendly Hydrogen Borrowing Strategy

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Contents

Text S1: General Procedures and Materials. 3

Text S2: General Procedure for the Catalytic β-alkylation of alcohols. 3

Text S3: Determination of PPh_3 dependence in β-alkylation of alcohols. 3

Text S4 : Procedure for the control experiments. 3-4

Text S5: General Procedure for time dependent product distribution studies. 5

Text S6: Hg^0 poisoning experiment 5

Characterization data of product alcohols 5-11

Copies of ^1H and ^{13}C NMR spectra of product alcohols 12-43

References 44

Text S1: General Procedures and Materials: All reactions were carried out under an inert atmosphere using standard Schlenk-line techniques. Glasswares were flame-dried under vacuum prior to use. Solvents were dried according to literature methods, distilled under argon and deoxygenated prior to use. $RuCl_3.nH_2O$ (39% Ru) and $PdCl_2$ (60% Pd) were purchased from Arora Matthey, India. 2-bromo phenanthroline, 5-methoxy-2-tributylstannylpyridine, 5-methyl-2-tributylstannylpyridine, 2-tributylstannylpyridine were synthesized following the literature procedures.[70-74] Synthesis of complexes **1** and **2** were already reported from our group.[52] All the chemicals were purchased from Sigma-Aldrich, Alfa Aesar, SDFCL and Spectrochem. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded on JEOL 400 and 500 MHz spectrometers. Elemental analyses was performed on a Thermoquest EA1110 CHNS/O analyser. The crystallized compounds were powdered, washed several times with dry diethyl ether and dried under vacuum for at least 48 h prior to elemental analyses. ESI-MS were recorded on a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. All the GC analysis were done using Perkein Elmer Clarus 600 Gas Chromatograph and GC-MS were taken using Agilent 7890 A Gas Chromatograph equipped with Agilent 5890 triple-quadrupole mass system.

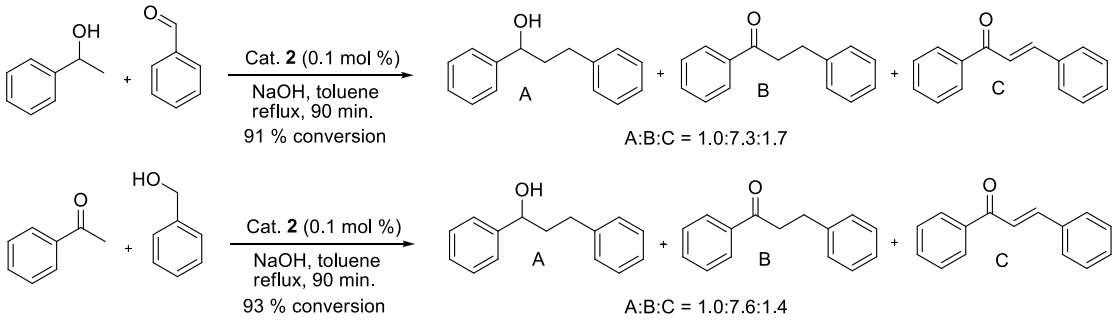
Text S2: General Procedure for the Catalytic β-Alkylation of Alcohols: The catalyst solution was prepared by dissolving complex **2** in CH_3CN (1 mL) in an argon filled glovebox. Then red catalyst solution (0.1 mol%) was taken into a Schlenk tube and solvent was removed under vacuum. After that secondary alcohol (0.654 mmol), primary alcohol (0.654 mmol), NaOH (0.327 mmol) and 3.0 ml toluene were added under an argon atmosphere. Then, the tube was dipped at oil bath (the red color immediately changed to purple) and heated for 90 minutes at 125 $^{\circ}$C (oil bath temperature). It was cooled to room temperature and 10 μL solution was syringed out for GC analysis (faint purple color). The reaction mixture was concentrated under reduced pressure and submitted crude for NMR to calculate the conversion and product selectivity. The final desired alcohol (**A**, major) and ketone (**B**, minor) products were isolated and purified by column chromatography (silica) using hexane-ethyl acetate as eluent.

For turnover number (TON) calculation a reaction of 1-phenylethanol with benzyl alcohol was setup with 0.002 mol% catalyst **2** and it was heated for 16 h at 125 $^{\circ}$C (oil bath temperature). This reaction furnished 63% conversion of 1-phenylethanol with 96:4 selectivity of **A**: **B**, which showed 31500 TON.

Text S3: Determination of PPh_3 Dependence in β-alkylation of Alcohols. The general procedure outlined above for the catalytic β-alkylation of alcohols was used with 1-phenylethanol as the substrate and varying amounts of 0.050 M stock solution of PPh_3 in toluene were added (0, 2, 4, 8 eq. of PPh_3 with respect of catalyst). The consumption of 1-phenylethanol during β-alkylation of alcohols was monitored by GC using acetonitrile as internal standard. The dependence of PPh_3 in β-alkylation of 1-phenylethanol was calculated by plotting the concentration of 1-phenylethanol as a function of equivalent of PPh_3 added at the end of 90 minutes reaction (Figure 4).

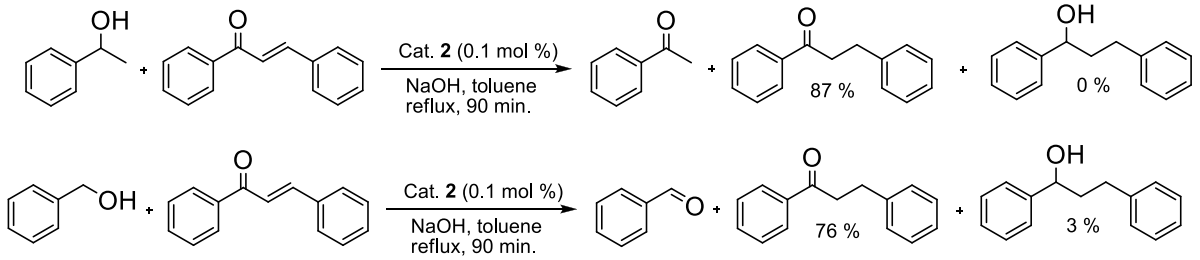
Text S4 : Procedure for the Control Experiments.

1.



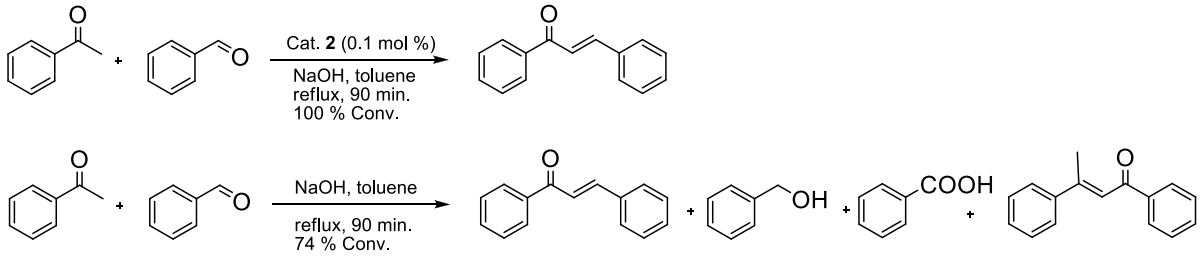
The catalyst solution was prepared by dissolving complex **2** in CH_3CN in argon filled glovebox. Then catalyst solution was taken into a Schlenk tube and solvent was removed under vacuum. After that 1-phenylethanol or acetophenone (0.654 mmol), benzaldehyde or benzyl alcohol (0.654 mmol), NaOH (0.327 mmol) and 3.0 ml toluene were added under argon atmosphere. Then the tube was heated for 90 minutes at 125 $^{\circ}$C (oil bath temparature). It was cooled to room temparature and 10 μL solution was syringe out for GC analysis. The reaction mixture was concentrated under reduced pressure and submitted crude for NMR and GC-MS analysis to calculate the conversion and product selectivity. The final compounds were purified by column chromatography using hexane-ethyl acetate as eluent for further confirmation of the product identity.

2.



The catalyst solution was prepared by dissolving complex **2** in CH_3CN in argon filled glovebox. Then catalyst solution was taken into a Schlenk tube and solvent was removed under vacuum. After that 1-phenylethanol or benzyl alcohol (0.654 mmol), chalcone (0.654 mmol), NaOH (0.327 mmol) and 3.0 ml toluene were added under argon atmosphere. Then the tube was heated for 90 minutes at 125 $^{\circ}$C (oil bath temparature). It was cooled to room temparature and 10 μL solution was syringe out for GC analysis. The reaction mixture was concentrated under reduced pressure and submitted crude for NMR and GC-MS analysis to calculate the conversion and product selectivity. The final compounds were purified by column chromatography using hexane-ethyl acetate as eluent for further confirmation of the product identity.

3.

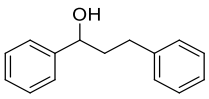


The catalyst solution was prepared by dissolving complex **2** in CH_3CN in argon filled glovebox. Then catalyst solution was taken into one Schlenk tube and solvent was removed under vacuum. After that acetophenone (0.654 mmol), benzaldehyde (0.654 mmol), NaOH (0.327 mmol) and 3.0 ml toluene were added under argon atmosphere in both of the Schlenk tubes. Then the tubes were heated for 90 minutes at 125 °C (oil bath temparature). It was cooled to room temparature and 10 μL solution was syringe out for GC analysis. The reaction mixture was concentrated under reduced pressure and submitted crude for NMR and GC-MS analysis to calculate the conversion and product selectivity. The final compounds were purified by column chromatography using hexane-ethyl acetate as eluent for further confirmation of the product identity.

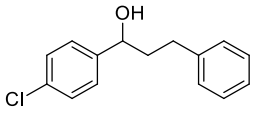
Text S5: General Procedure for Time Dependent Product Distribution Studies. The conversion and product selectivity of β-alkylation of alcohols at different time interval was determined by performing six identical reactions in six different schlenk tubes under standard reaction condition using 1-phenylethanol and benzyl alcohol as substrate. The reactions were monitored at different time intervals (15 mins, 30 mins, 45 mins, 60 mins, 75 mins and 90 mins). After that the conversion and product selectivity were determined by ^{1}H NMR. All this reactions were repeated triplicate and an average data were plotted % Mol vs time (Figure 3).

Text S6: Hg^0 Poisoning Experiment. Two identical TH experiments were conducted in parallel following the outlined procedure; one acted as a control reaction. The reactions were monitored by GC and ^{1}H NMR to ensure reactions had proceeded past the initiation period (10 mins). Under the argon condition one drop of Hg^0 was added to one of the schlenk tube and vigorously agitated whether the other keep in same argon condition. Then the tubes were removed from the argon flow, heated for remaining 80 mins. in the oil bath and the progress of the reaction was monitored by GC and ^{1}H NMR. The conversion with mercury was 95% where without mercury it was 99%.

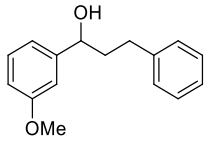
Characterization of Products.



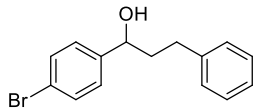
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.32 (m, 4H), 7.31-7.27 (m, 3H), 7.21-7.17 (m, 3H), 4.68 (dd, $J_{H,H}$ = 5.5, 5.0 Hz, 1H), 2.79-2.63 (m, 2H), 2.15-2.00 (m, 2H), 1.91 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.66, 141.88, 128.63, 128.55, 128.50, 127.75, 126.04, 125.96, 73.98, 40.56, 32.16.



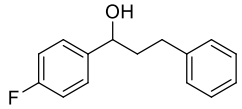
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.26 (m, 6H), 7.20-7.16 (m, 3H), 4.66 (dd, $J_{H,H}$ = 5.5, 5.4, Hz, 1H), 2.76-2.61 (m, 2H), 2.14-1.94 (m, 2H), 1.84 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.10, 141.57, 133.33, 128.73, 128.54, 128.51, 127.40, 126.06, 73.23, 40.58, 32.01.



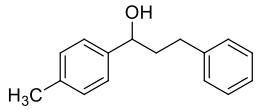
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.27 (m, 3H), 7.25-7.18 (m, 3H), 6.94-6.92 (m, 2H), 6.84-6.82 (d, $J_{H,H}$ = 8.0 Hz, 1H), 4.68 (dd, $J_{H,H}$ = 5.5, 5.4, Hz, 1H), 3.81 (s, 3H), 2.79-2.65 (m, 2H), 2.14-2.01 (m, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.90, 146.45, 141.89, 129.63, 128.55, 128.49, 125.96, 118.37, 113.17, 111.54, 73.88, 55.33, 40.56, 32.14.



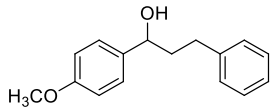
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.45 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.17 (m, 5H), 4.61 (dd, $J_{H,H}$= 5.5, 5.4, Hz, 1H), 2.75-2.61 (m, 2H), 2.19 (bs, 1H), 2.09-1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.63, 141.58, 131.68, 128.58, 128.54, 127.79, 126.10, 121.44, 73.24, 40.53, 32.00.



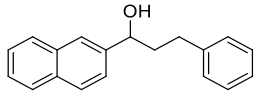
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.27 (m, 4H), 7.21-7.18 (m, 3H), 7.05-7.02 (m, 2H), 4.66 (dd, $J_{H,H}$= 5.5, 4.4 Hz, 1H), 2.76-2.62 (m, 2H), 2.15-1.96 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.28, 161.33, 141.68, 140.41, 140.38, 128.53, 128.52, 127.69, 127.63, 126.04, 115.49, 115.32, 73.29, 40.64, 32.09.



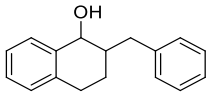
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.15 (m, 9H), 4.64 (dd, $J_{H,H}$ = 5.5, 5.4 Hz, 1H), 2.77-2.61(m, 2H), 2.35 (s, 3H), 2.16-1.98 (m, 2H), 1.81 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.94, 141.67, 137.43, 129.29, 128.54, 128.47, 126.00, 125.91, 73.82, 40.45, 32.19, 21.22.



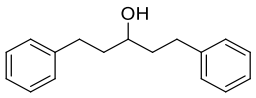
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.24 (m, 4H), 7.18-7.15 (m, 3H), 6.90-6.86 (m, 2H), 4.63 (t, $J_{H,H}$ = 7.3 Hz, 1H), 3.80 (s, 3H), 2.75-2.59 (m, 2H), 2.14-2.00 (m, 2H), 1.78 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.20, 141.91, 136.76, 128.52, 128.46, 127.29, 125.91, 113.97, 73.58, 55.38, 40.42, 32.21.



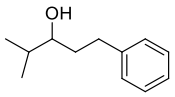
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.78 (m, 4H), 7.50-7.45 (m, 3H), 7.30-7.17 (m, 5H), 4.86 (dd, $J_{H,H}$= 5.5, 5.4 Hz, 1H), 2.81-2.66 (m, 2H), 2.26-2.11 (m, 2H), 1.88 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.97, 141.83, 133.37, 133.11, 128.56, 128.51, 128.49, 128.03, 127.79, 126.29, 125.98, 124.78, 124.14, 74.08, 40.42, 32.15.



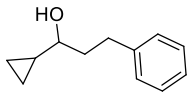
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.49 (m, 1H), 7.32-7.27 (m, 2H), 7.23-7.18 (m, 5H), 7.09-7.07 (m, 1H), 4.50 (d, $J_{H,H}$ = 8.0 Hz, 1H), 3.07 (dd, $J_{H,H}$ = 12 Hz, 4 Hz), 2.77-2.73 (m, 2H), 2.50 (dd, $J_{H,H}$ = 12 Hz, 4 Hz), 2.09-1.93 (m, 2H), 1.68 (bs, 1H), 1.54-1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.94, 141.67, 137.43, 129.29, 128.54, 128.47, 126.00, 125.91, 73.82, 40.45, 32.19, 21.22.



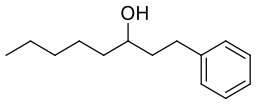
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.26 (m, 4H), 7.23-7.18 (m, 6H), 3.66 (m, 1H), 2.81-2.64 (m, 4H), 1.86-1.78 (m, 4H), 1.53 (bs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.57, 125.97, 125.94, 123.40, 68.40, 36.77, 29.59.



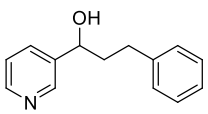
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.16 (m, 5H), 3.41-3.37 (m, 1H), 2.87-2.61 (m, 2H), 1.82-1.64 (m, 3H), 0.91 (d, $J_{H,H}$ = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.44, 128.53, 128.48, 125.87, 76.23, 36.04, 33.77, 32.56, 18.86, 17.25.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.19 (m, 5H), 2.95-2.72 (m, 3H), 2.14 (bs, 1H), 1.99-1.93 (m, 2H), 1.00-0.92 (m, 1H), 0.58-0.48 (m, 2H), 0.33-0.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =142.43, 128.53, 128.48, 125.83, 76.11, 38.90, 32.18, 18.08, 2.85, 2.75.

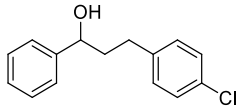


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.16 (m, 5H), 3.65-3.59 (m, 1H), 2.83-2.63 (m, 2H), 1.83-1.68 (m, 2H), 1.49-1.39 (m, 4H), 1.34-1.26 (m, 5H), 0.89 (t, $J_{H,H}$ = 10.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ =142.34, 128.50, 128.48, 125.87, 71.49, 39.18, 37.66, 32.18, 31.98, 25.38, 22.73, 14.13.

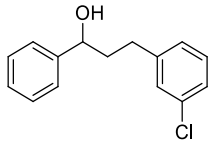


^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47-8.43 (m, 2H), 7.72-7.69 (m, 1H), 7.28-7.25 (m, 3H), 7.19-7.16 (m, 3H), 4.70 (dd, $J_{H,H}$ = 8.0 Hz, 8.0 Hz), 3.29 (bs, 1H), 2.77-2.64 (m, 2H), 2.13-

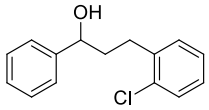
1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.45, 147.51, 141.40, 140.48, 134.11, 128.57, 128.50, 126.11, 123.78, 71.28, 40.55, 31.96.



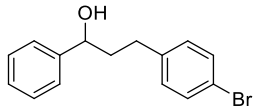
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.31 (m, 4H), 7.25-7.21 (m, 3H), 7.12-7.09 (m, 2H), 4.66 (t, $J_{H,H}$ = 5.9 Hz, 1H), 2.42 (m, 2H), 2.04 (m, 2H), 1.83 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.47, 140.30, 131.62, 129.89, 128.67, 128.55, 127.85, 125.97, 73.79, 40.39, 31.47.



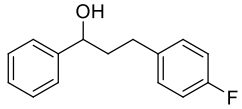
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.26 (m, 5H), 7.21-7.14 (m, 3H), 7.06-7.04 (m, 1H), 4.66 (dd, $J_{H,H}$ = 5.4, 5.4 Hz, 1H), 2.68 (m, 2H), 2.05 (m, 2H), 1.82 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =144.44, 143.94, 134.20, 129.70, 128.67, 127.85, 126.72, 126.14, 125.95, 73.78, 40.25, 31.80.



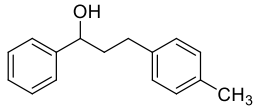
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.10 (m, 9H), 4.70 (dd, $J_{H,H}$ = 5.4, 5.3 Hz, 1H), 2.93-2.73 (m, 2H), 2.24 (bs, 1H), 2.14-1.99 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 139.6, 134.0, 130.5, 129.6, 128.6, 127.8, 127.5, 126.9, 126.0, 74.0, 38.8, 30.1



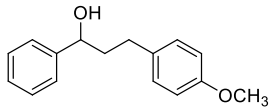
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.26 (m, 7H), 7.04 (d, $J_{H,H}$ = 8.2 Hz, 2H), 4.63 (dd, $J_{H,H}$ = 5.4, 5.4 Hz, 1H), 2.62 (m, 2H), 2.04 (m, 2H), 1.94 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.48, 140.85, 131.52, 130.32, 128.68, 127.85, 126.00, 125.49, 119.66, 73.77, 40.32, 31.53.



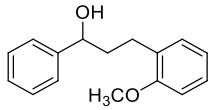
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.26 (m, 5H), 7.14-7.11 (m, 2H), 6.97-6.92 (m, 2H), 4.66 (t, $J_{H,H}$ = 6.4 Hz, 1H), 2.66 (m, 2H), 2.03 (m, 2H), 1.87 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.55, 137.45, 129.87, 128.64, 127.80, 125.98, 115.28, 115.07, 73.83, 40.65, 31.31.



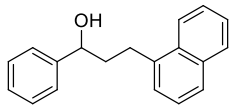
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.33 (m, 4H), 7.29-7.26 (m, 1H), 7.07-7.10 (m, 4H), 4.67 (dd, $J_{H,H}$ = 5.5, 5.5 Hz, 1H), 2.66 (m, 2H), 2.31 (s, 3H), 2.03 (m, 2H), 1.75 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =144.71, 138.75, 135.40, 129.19, 128.61, 128.43, 127.72, 126.05, 73.98, 40.66, 31.70, 21.19.



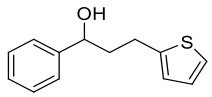
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.25 (m, 5H), 7.10 (d, $J_{H,H}$ = 8.2, 2H), 6.81 (d, $J_{H,H}$ = 8.2, 2H), 4.66 (dd, $J_{H,H}$ = 5.0, 5.0 Hz, 1H), 3.79 (s, 3H), 2.64 (m, 2H), 2.04 (m, 2H), 1.76 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =157.80, 144.75, 133.93, 129.44, 128.60, 127.69, 126.05, 113.92, 73.91, 55.35, 40.79, 31.23.



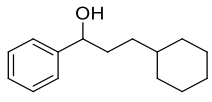
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.25 (m, 5H), 7.22-7.14 (m, 2H), 6.92-6.85 (m, 2H), 4.62 (dd, $J_{H,H}$ = 5.0, 4.5 Hz, 1H), 3.82 (s, 3H), 2.76 (m, 2H),2.29 (bs, 1H), 2.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =157.46, 144.74, 130.18, 128.88, 127.45, 125.70, 120.79, 110.41, 73.63, 55.43, 39.48, 26.54.



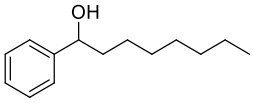
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01-7.98 (m, 1H), 7.87-7.85 (m, 1H), 7.72 (d, $J_{H,H}$ = 5.0 Hz), 7.51-7.46 (m, 2H), 7.42-7.34 (m, 6H), 7.32-7.29 (m, 1H), 4.81-4.78 (m, 1H), 3.29-3.09 (m, 2H), 2.30-2.14 (m, 2H), 2.04 (bs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ =144.64, 138.12, 134.03, 131.96, 128.88, 128.65, 127.80, 126.07, 125.91, 125.66, 125.57, 123.90, 74.29, 39.95, 29.22.



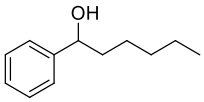
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.26 (m, 5H), 7.11 (dd, $J_{H,H}$ = 5.0, $J_{H,H}$ = 1.3, 1H), 6.91 (dd, $J_{H,H}$ = 5.0, $J_{H,H}$ = 3.6, 1H), 6.81-6.79 (m, 1H), 4.72 (dd, $J_{H,H}$ = 5.5, 5.5 Hz, 1H), 3.00-2.87 (m, 2H), 2.23-2.03 (m, 2H), 1.85 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.69, 144.43, 128.65, 128.60, 127.81, 126.85, 125.97, 124.40, 123.18, 73.61, 40.77, 26.30.



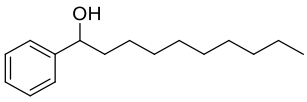
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 4H), 7.29-7.26 (m, 1H), 4.62 (t, $J_{H,H}$ = 6.4 Hz, 1H),1.83-1.74 (m, 2H), 1.36-1.09 (m, 10H), 0.89-0.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.03, 128.52, 128.50, 127.56, 125.98, 75.14, 37.73, 36.55, 33.55, 33.43, 33.36, 29.77, 26.73, 26.44.



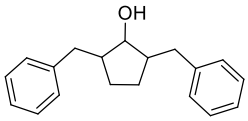
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.24 (m, 5H), 4.63 (dd, $J_{H,H}$ = 5.5, 5.4 Hz, 1H), 2.04 (bs, 1H), 1.83-1.66 (m, 2H), 1.32-1.27 (m, 10H), 0.90-0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.33, 123.72, 122.75, 121.24, 70.00, 34.46, 27.15, 24.84, 24.71, 24.56, 21.15, 17.91, 9.40.



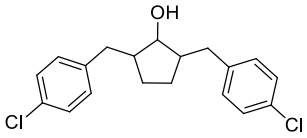
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 4H), 7.29-7.25 (m, 1H), 4.63 (dd, $J_{H,H}$ = 5.4, 5.4, Hz, 1H), 2.18 (bs, 1H), 1.83-1.66 (m, 2H), 1.44-1.38 (m, 1H), 1.32-1.29 (m, 5H), 0.90 (t, $J_{H,H}$ = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.10, 128.48, 127.51, 126.02, 74.74, 39.17, 31.84, 25.61, 22.68, 14.13.



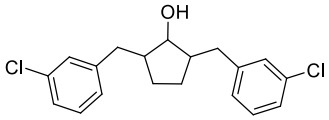
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.25 (m, 5H), 4.64 (dd, $J_{H,H}$ = 5.5, 5.4 Hz, 1H), 1.98 (bs, 1H), 1.83-1.67 (m, 2H), 1.42-1.22 (m, 14H), 0.90 (t, $J_{H,H}$ = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.33, 128.47, 127.43, 125.91, 74.70, 39.17, 31.93, 29.54, 29.32, 25.84, 22.78, 14.11.



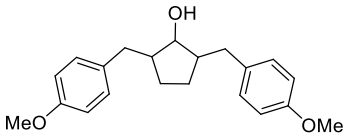
White solid (isolated yield 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.25 (m, 4H), 7.20-7.08 (m, 6H), 3.45 (t, $J_{H,H}$ = 7.6 Hz, 1H), 2.88 (dd, $J_{H,H}$ = 10 Hz, 5 Hz, 2H), 2.55 (dd, $J_{H,H}$ = 10 Hz, 5 Hz, 2H), 2.07-2.00 (m, 2H), 1.74-1.70 (m, 2H), 1.32-1.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.10, 128.92, 128.49, 126.03, 83.25, 48.75, 40.13, 27.21. ESI-MS: m/z = 284.2018 [100%, $(M+NH_4)^+$].



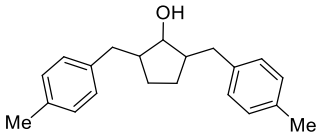
White solid (isolated yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.21 (m, 4H), 7.11-7.08 (m, 4H), 3.38 (t, $J_{H,H}$ = 8.0 Hz, 1H), 2.86 (dd, $J_{H,H}$ = 8 Hz, 4 Hz, 2H), 2.48 (dd, $J_{H,H}$ = 12 Hz, 8 Hz, 2H), 1.99-1.97 (m, 2H), 1.71-1.67 (m, 2H), 1.28-1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.41, 131.78, 130.24, 128.58, 83.03, 48.59, 39.27, 26.89. ESI-MS: m/z = 379.0862 [100%, $(M+HCO_2)^-$].



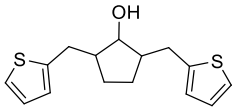
White solid (isolated yield 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.14 (m, 6H), 7.05 (d, $J_{H,H}$ = 8 Hz, 2H), 3.39 (t, $J_{H,H}$ = 8.0 Hz, 1H), 2.89 (dd, $J_{H,H}$ = 8 Hz, 4 Hz, 2H), 2.48 (dd, $J_{H,H}$ = 12 Hz, 8 Hz, 2H), 2.03-1.97 (m, 2H), 1.73-1.69 (m, 2H), 1.29-1.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.08, 134.23, 129.73, 129.01, 127.08, 126.27, 83.07, 48.50, 39.63, 26.90. ESI-MS: m/z = 379.0861 [100%, $(M+HCO_2)^-$].



White solid (isolated yield 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, $J_{H,H}$ = 12 Hz, 4H), 6.81 (d, $J_{H,H}$ = 12Hz, 4H), 3.77 (s, 6H), 3.40 (t, $J_{H,H}$ = 8.0 Hz, 1H), 2.80 (dd, $J_{H,H}$ = 8 Hz, 4 Hz, 2H), 2.49 (dd, $J_{H,H}$ = 12 Hz, 8 Hz, 2H), 2.01-1.95(m, 2H), 1.72-1.68 (m, 2H), 1.30-1.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.89, 133.11, 129.81, 113.89, 83.25, 55.32, 48.88, 39.16, 27.17. ESI-MS: m/z = 371.8608 [100%, $(M+HCO_2)^-$].

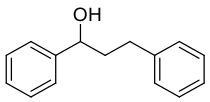


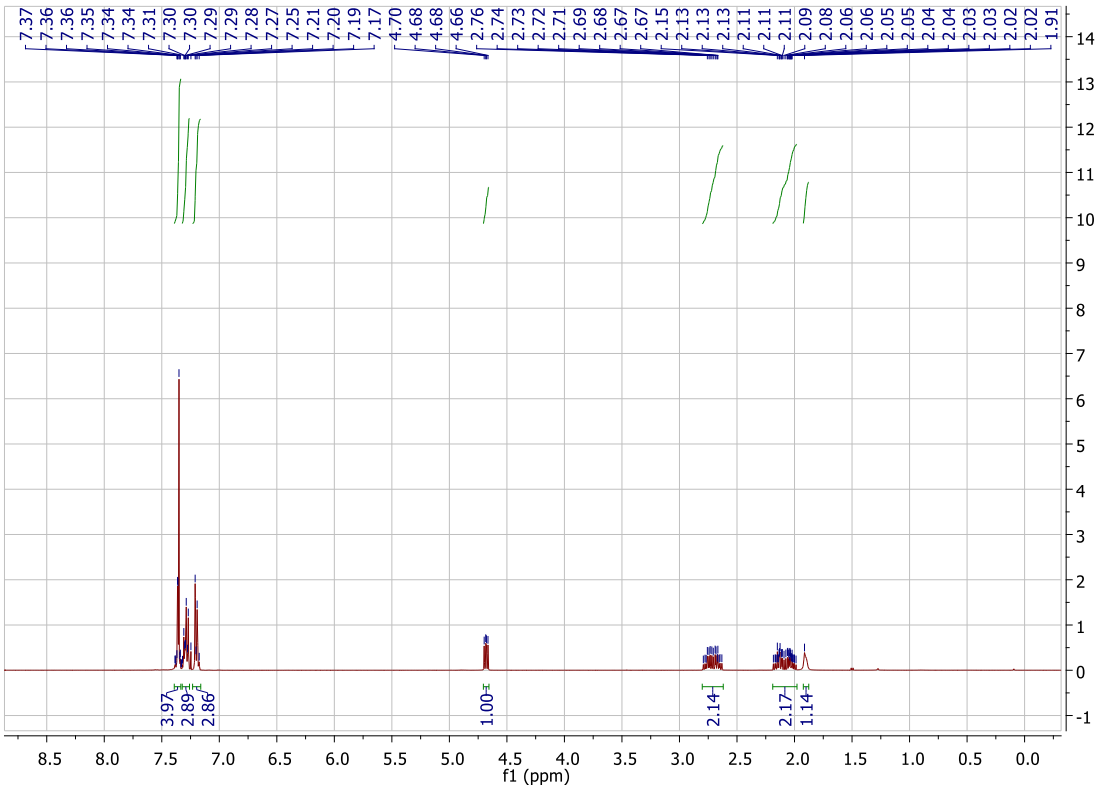
White solid (isolated yield 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11-7.04 (m, 8H), 3.42 (t, $J_{H,H}$ = 8.0 Hz, 1H), 2.82 (dd, $J_{H,H}$ = 8 Hz, 4 Hz, 2H), 2.51 (dd, $J_{H,H}$ = 8 Hz, 8 Hz, 2H), 2.30 (s, 6H), 2.02-1.97 (m, 2H), 1.73-1.58 (m, 2H), 1.30-1.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.98, 135.47, 129.19, 128.49, 83.35, 48.79, 39.69, 27.22, 21.10. ESI-MS: m/z = 312.2326 [100%, $(M+NH_4)^+$].

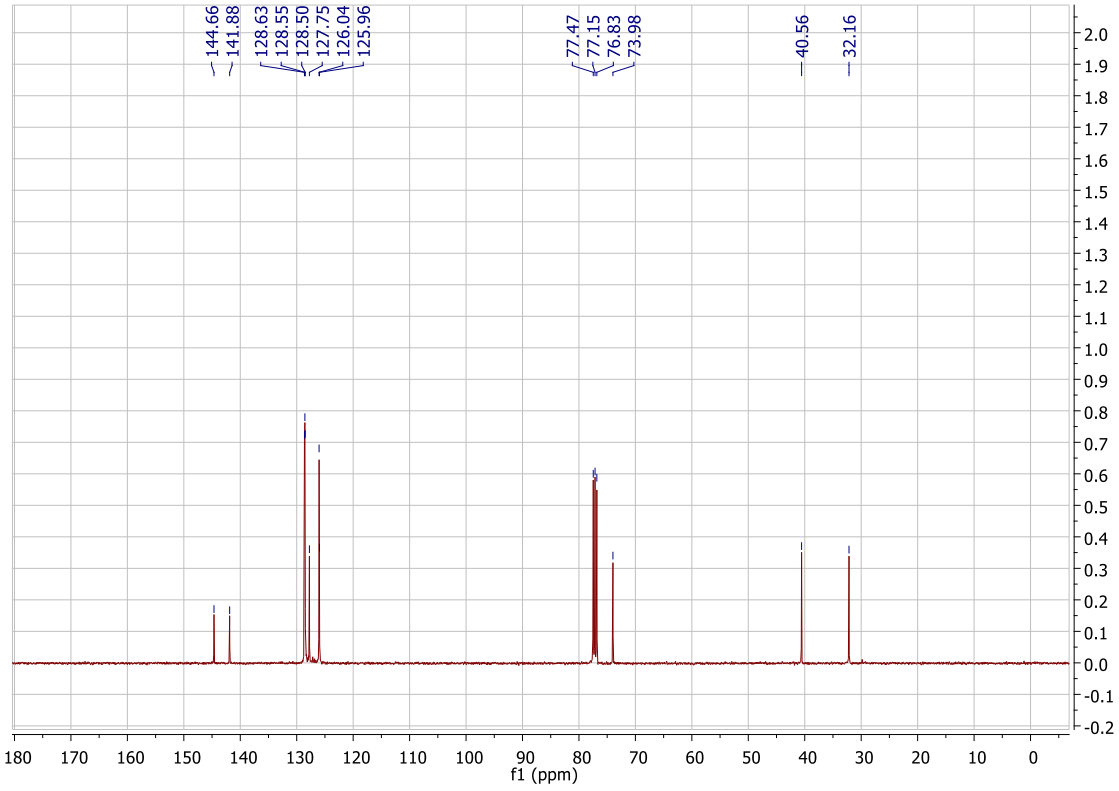


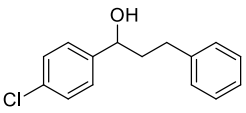
White solid (isolated yield 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, $J_{H,H}$ = 4 Hz, 2H), 6.91 (d, $J_{H,H}$ = 8 Hz, 2H), 6.80 (d, $J_{H,H}$ = 4 Hz, 2H), 3.45 (t, $J_{H,H}$ = 10.0 Hz, 1H), 3.08 (dd, $J_{H,H}$ = 12 Hz, 8 Hz, 2H), 2.78 (dd, $J_{H,H}$ = 8 Hz, 8 Hz, 2H), 2.10-2.04 (m, 2H), 1.88-1.84 (m, 2H), 1.37-1.29 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.58, 126.90, 124.96, 123.47, 83.04, 49.06, 33.90, 27.41.

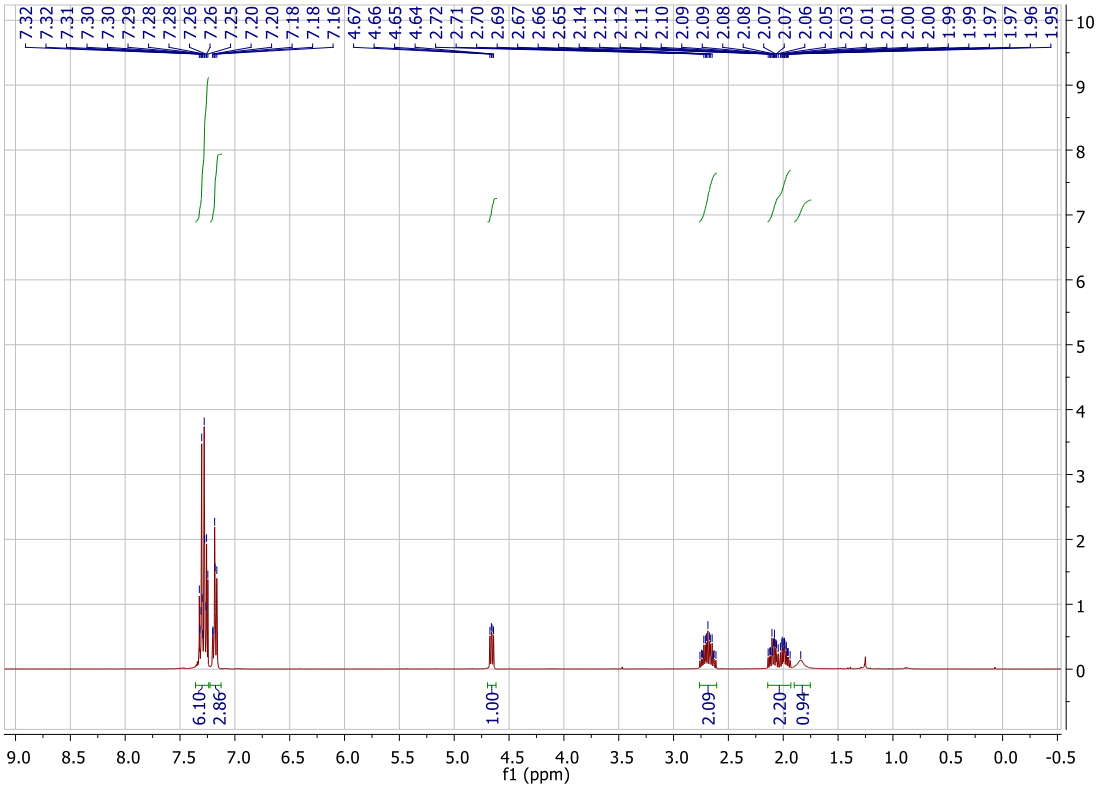
Copies of ^{1}H and ^{13}C NMR Spectra of Alcohols








OH
Cl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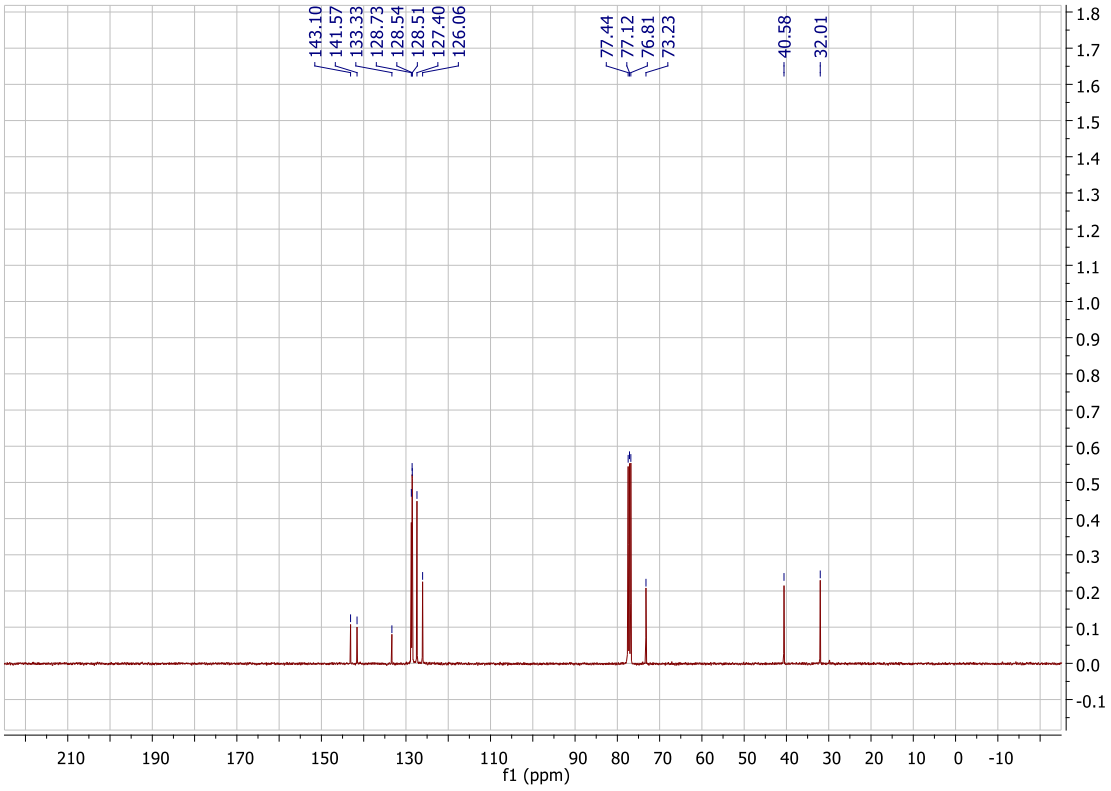
4.67 4.66 4.65 4.64 2.72 2.71 2.70 2.69 2.67 2.66 2.65 2.14 2.12 2.12 2.11 2.10 2.09 2.09 2.08 2.08 2.07 2.07 2.06 2.05 2.03 2.01 2.01 2.00 2.00 1.99 1.99 1.97 1.97 1.96 1.95
6.10 2.86 1.00 2.09 2.20 0.94
f1 (ppm)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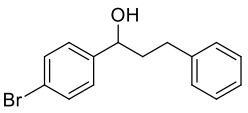
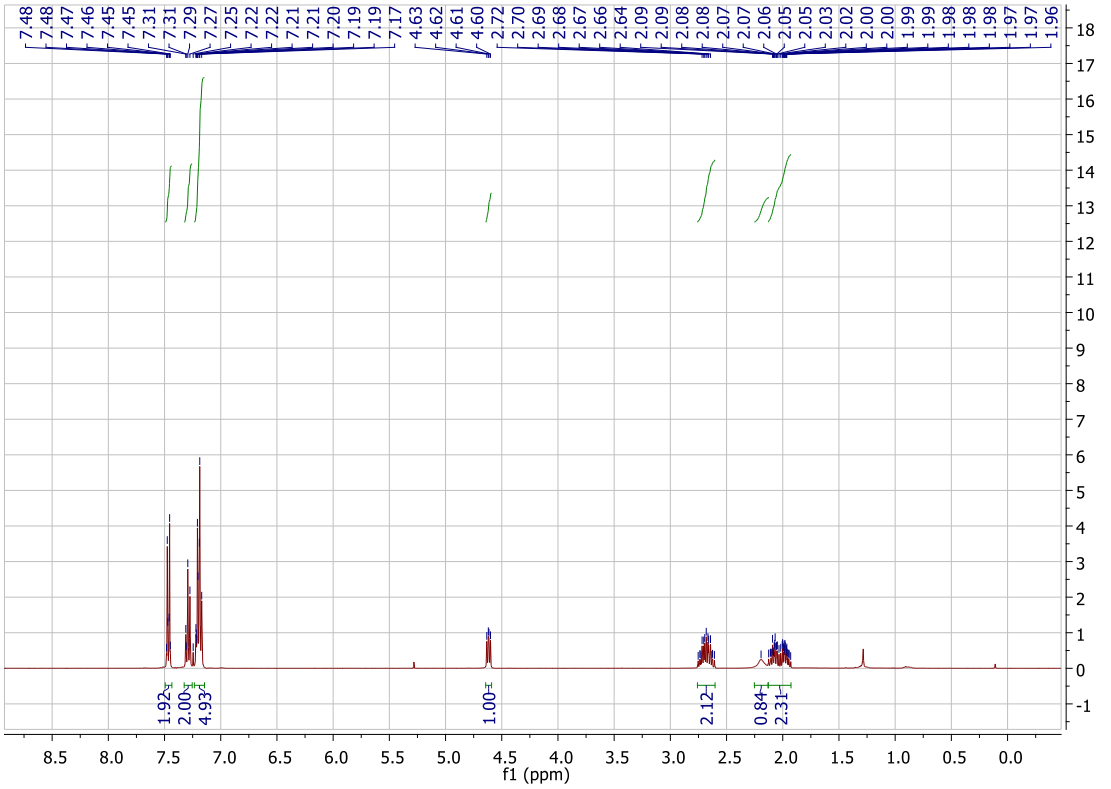
40.58 32.01
f1 (ppm)


OH
Br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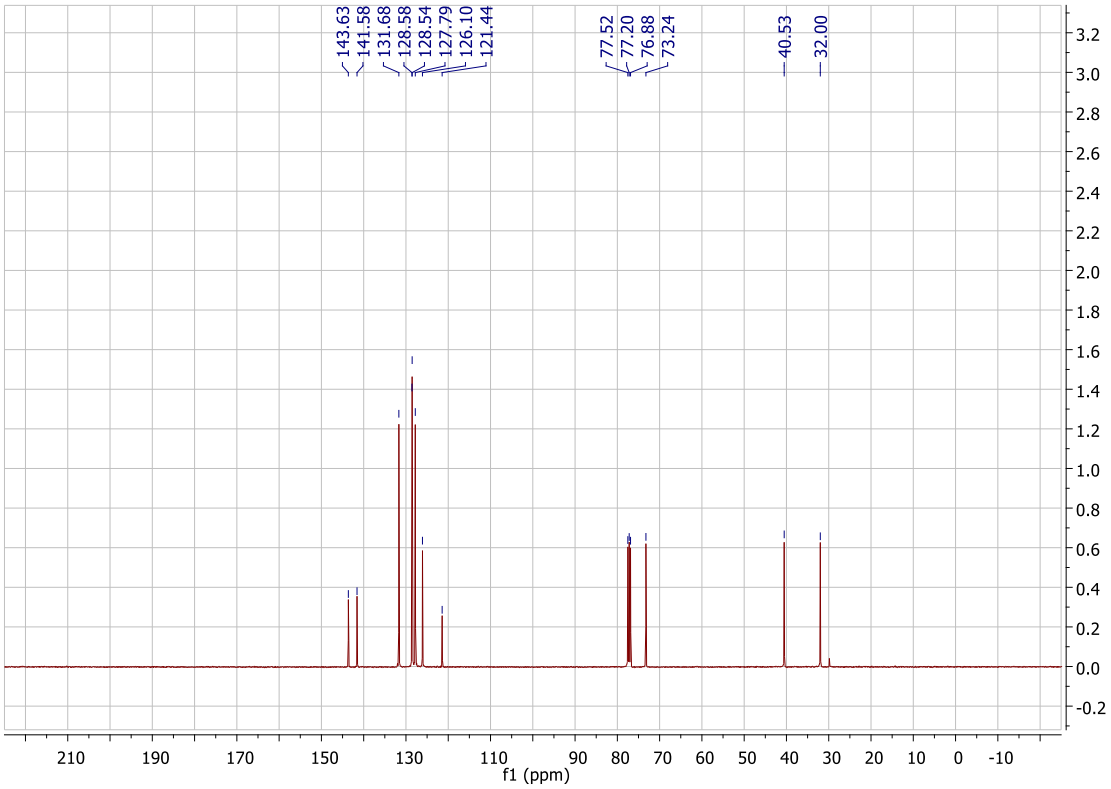
1.92 2.00 4.93 1.00 2.12 0.84 2.31
f1 (ppm)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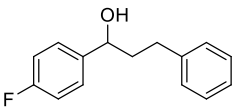
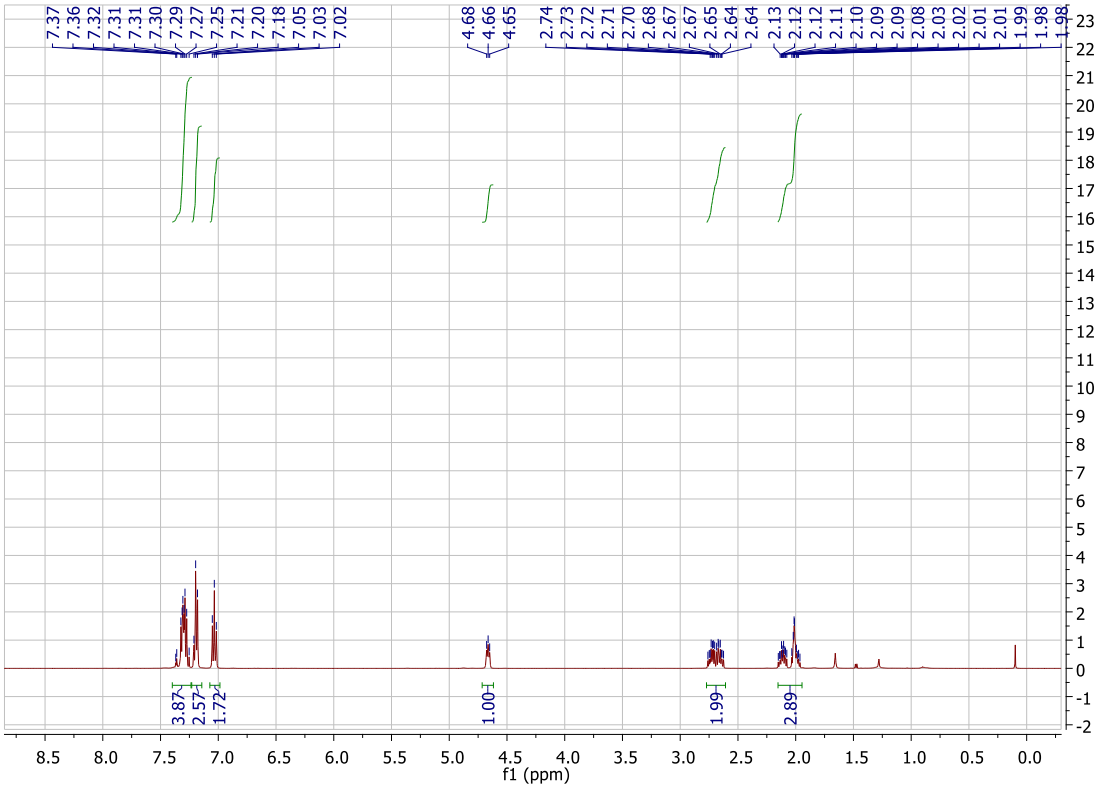
f1 (ppm)


OH
F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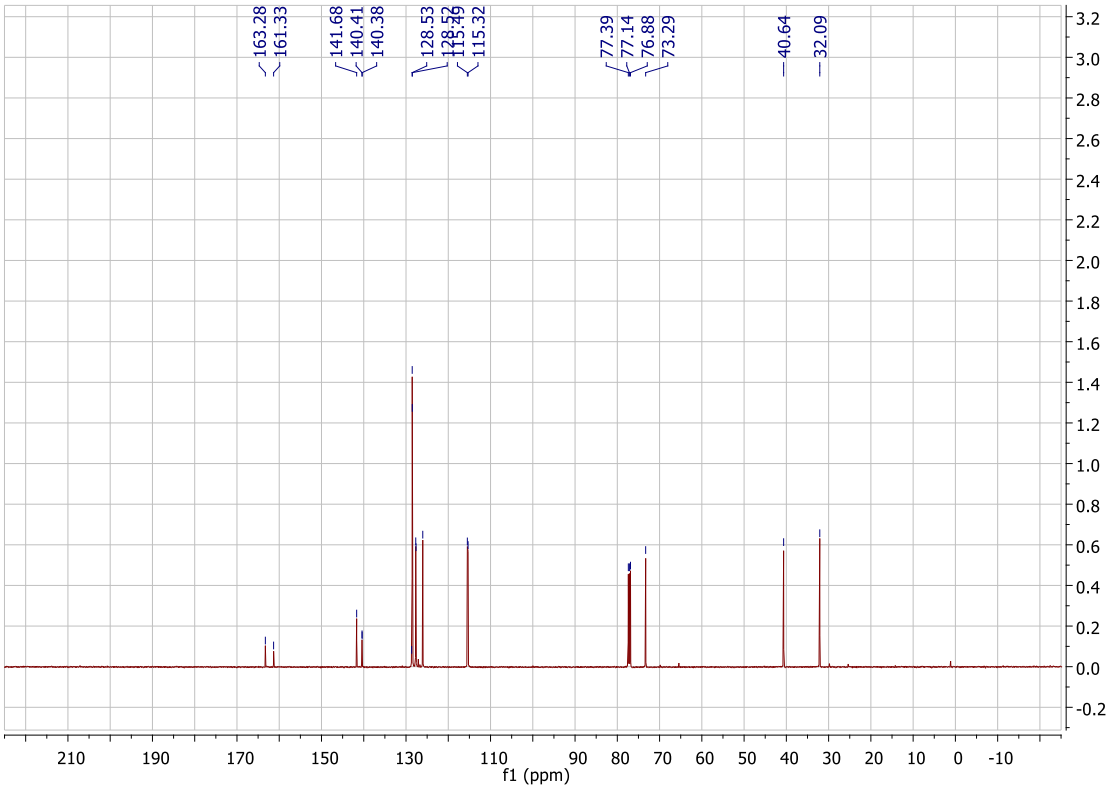
f1 (ppm)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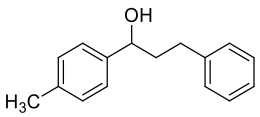
77.39
77.14
76.88
73.29
40.64
32.09
f1 (ppm)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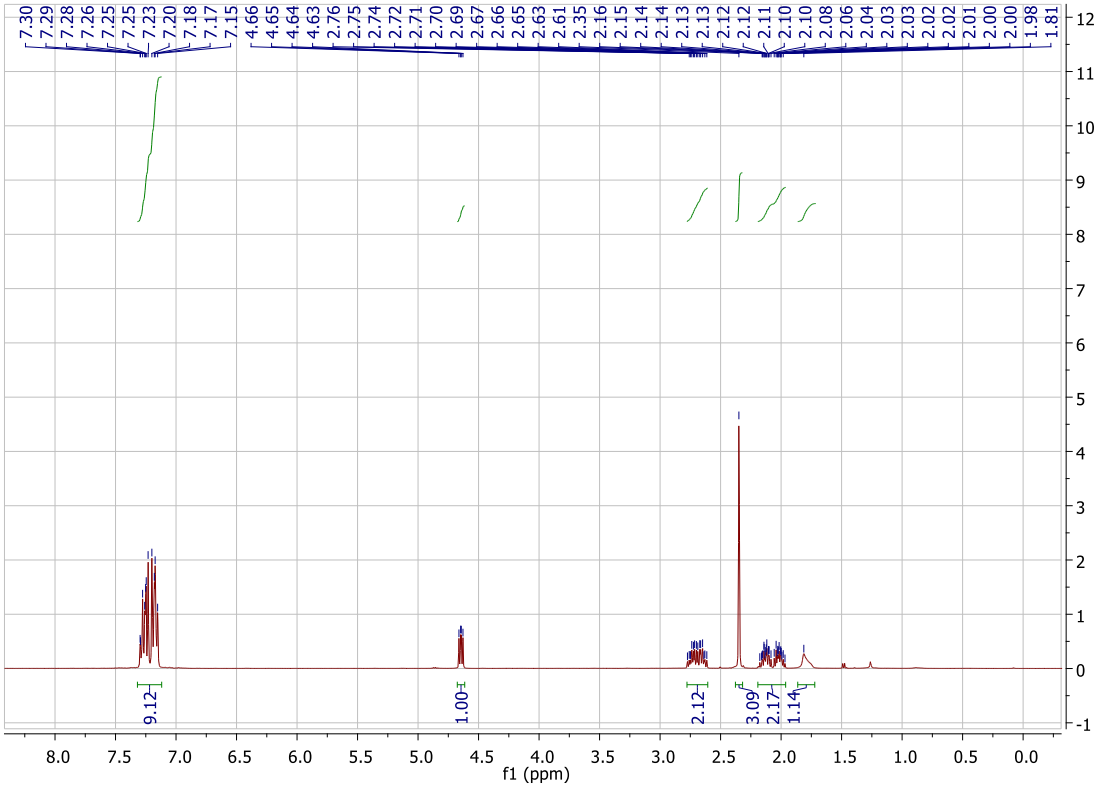
H3C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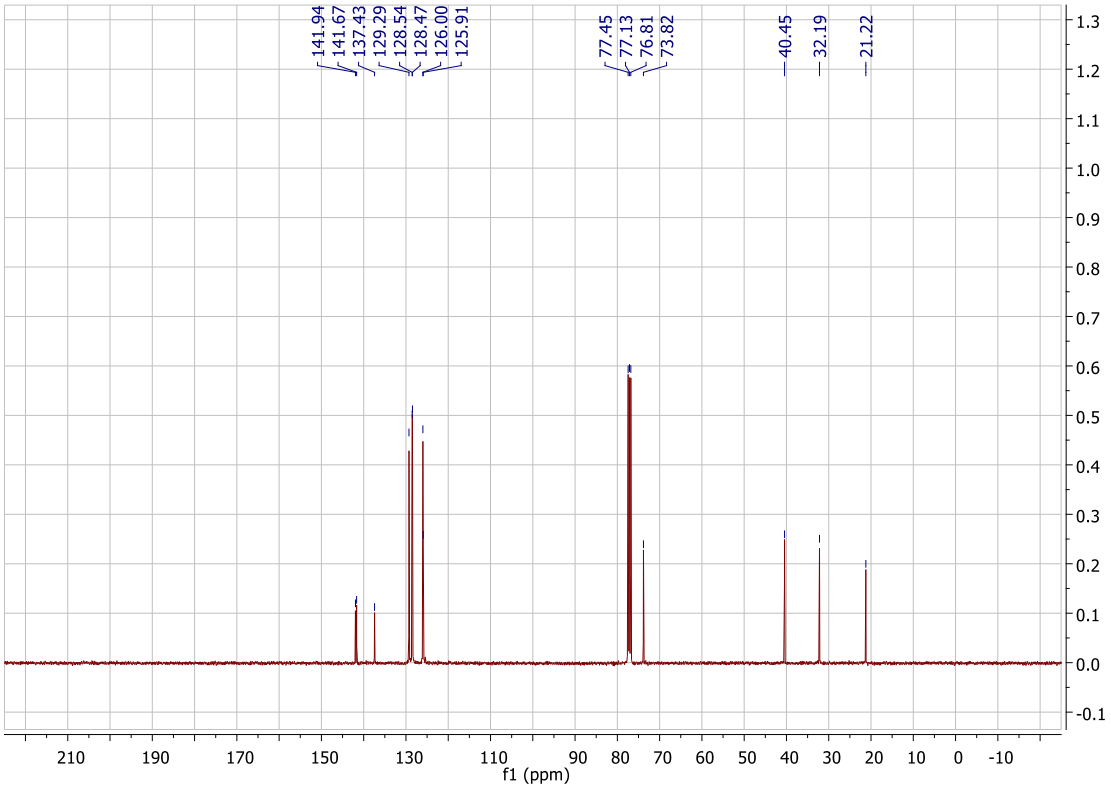
4.66 4.65 4.64 4.63 2.76 2.75 2.74 2.72 2.71 2.70 2.69 2.67 2.66 2.65 2.63 2.61 2.35 2.16 2.15 2.14 2.14 2.13 2.13 2.12 2.12 2.11 2.10 2.10 2.08 2.06 2.04 2.03 2.03 2.02 2.02 2.01 2.00 2.00 1.98 1.81
9.12
1.00
2.12
3.09
2.17
1.14
f1 (ppm)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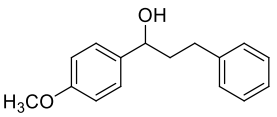
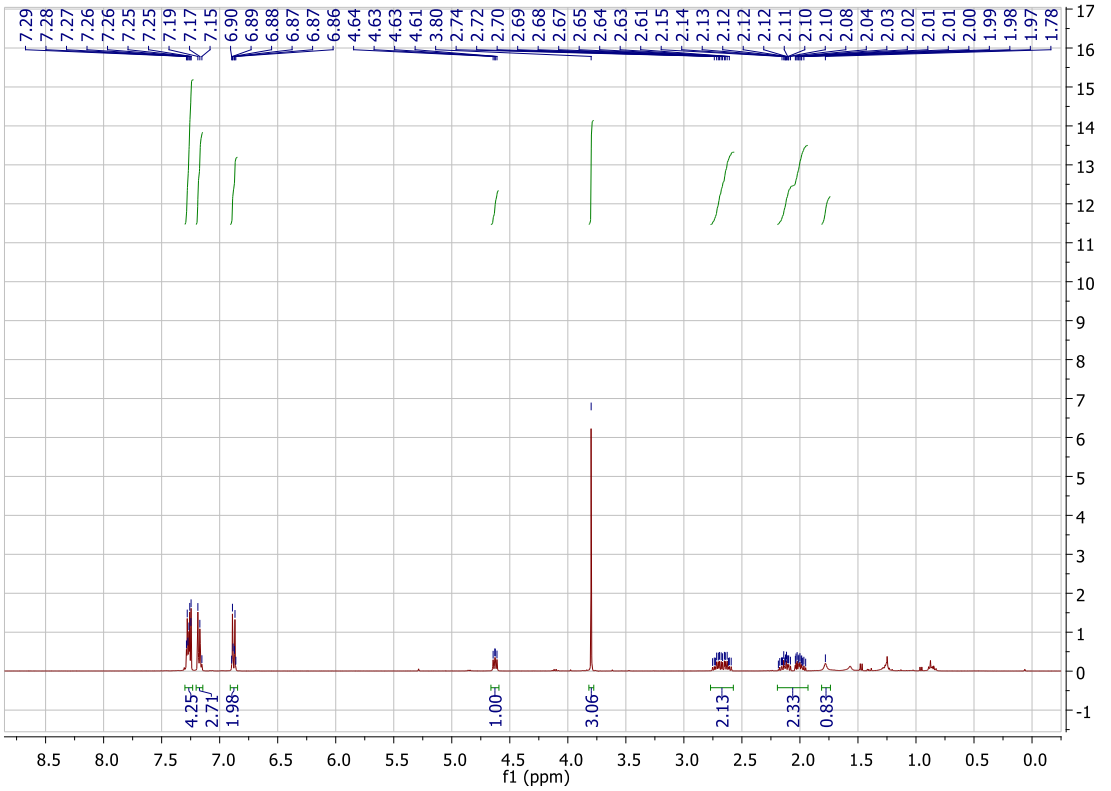
77.45 77.13 76.81 73.82
40.45 32.19 21.22
f1 (ppm)


OH
H3CO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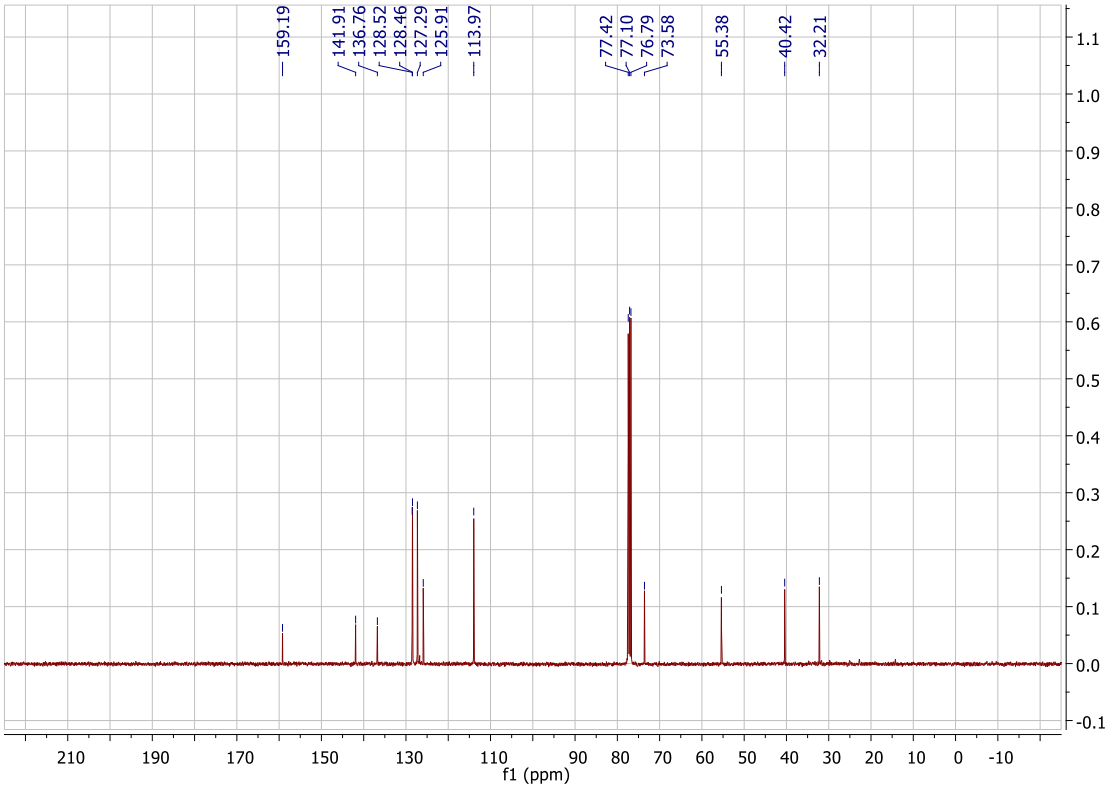
4.25 2.71 1.98 1.00 3.06 2.13 2.33 0.83
f1 (ppm)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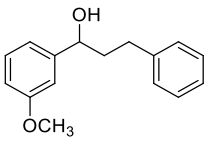
f1 (ppm)


OH
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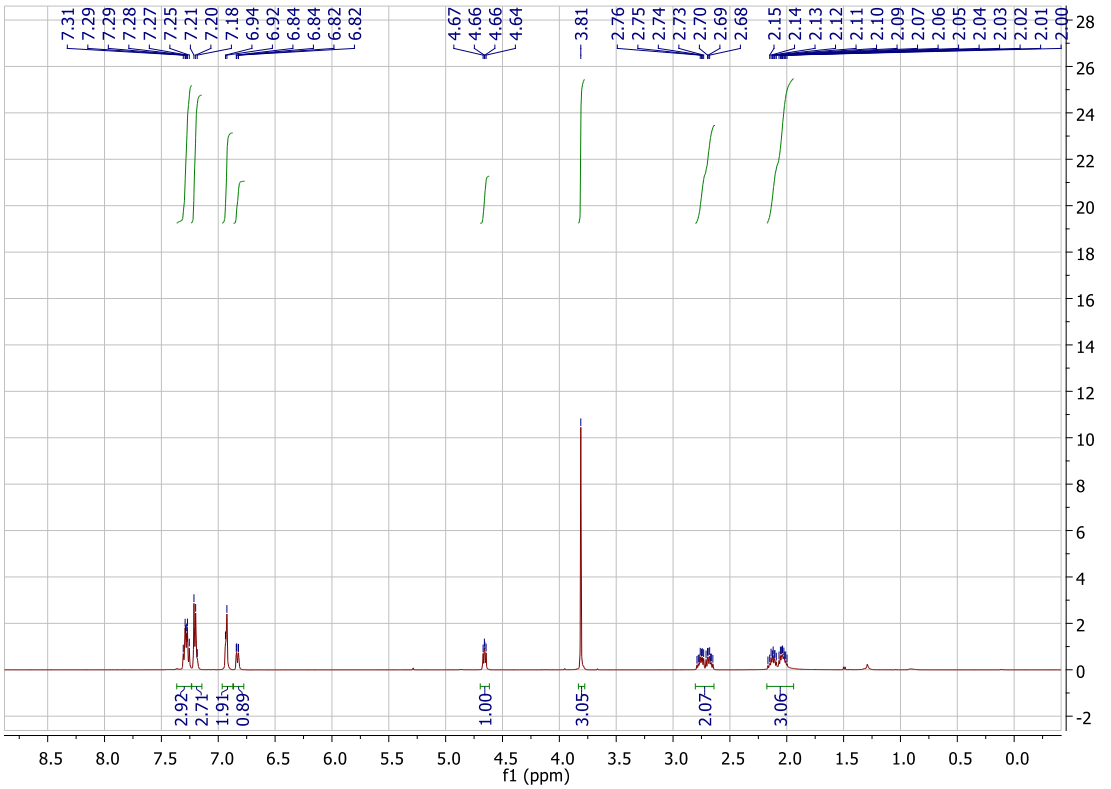
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4.66
4.64
3.81
2.76
2.75
2.74
2.73
2.70
2.69
2.68
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2.14
2.13
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2.09
2.07
2.06
2.05
2.04
2.03
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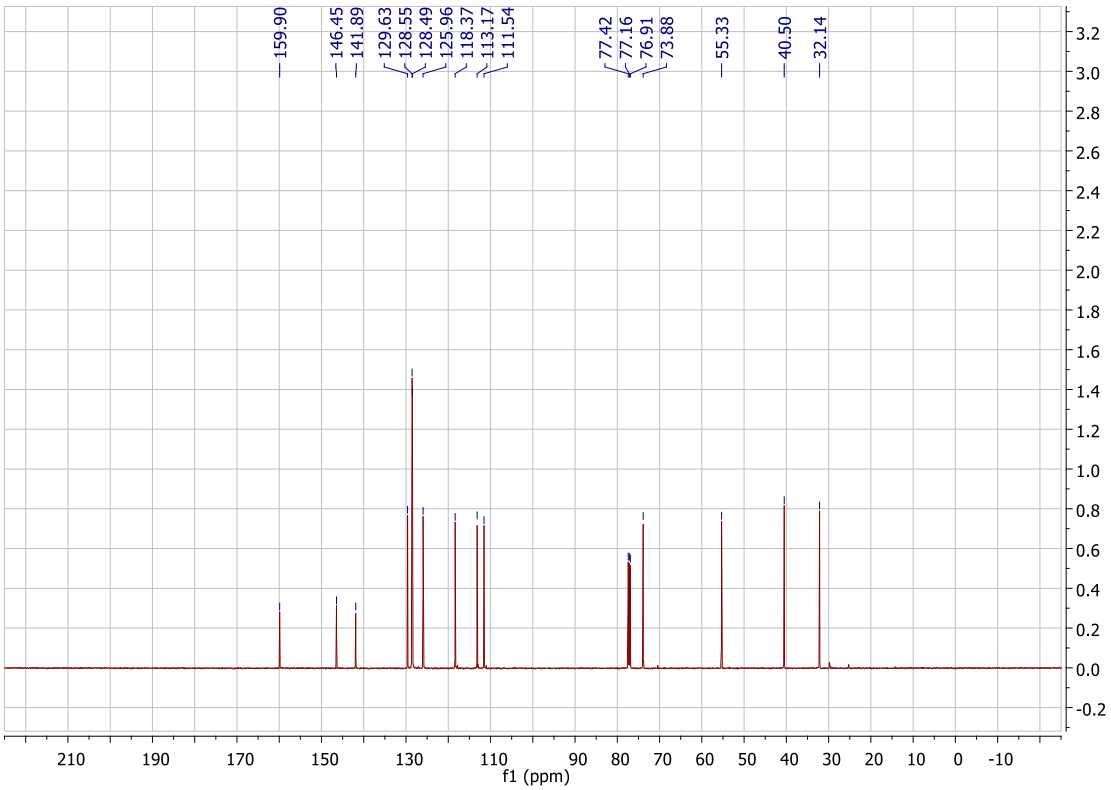
0.89
1.00
3.05
2.07
3.06
f1 (ppm)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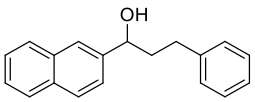
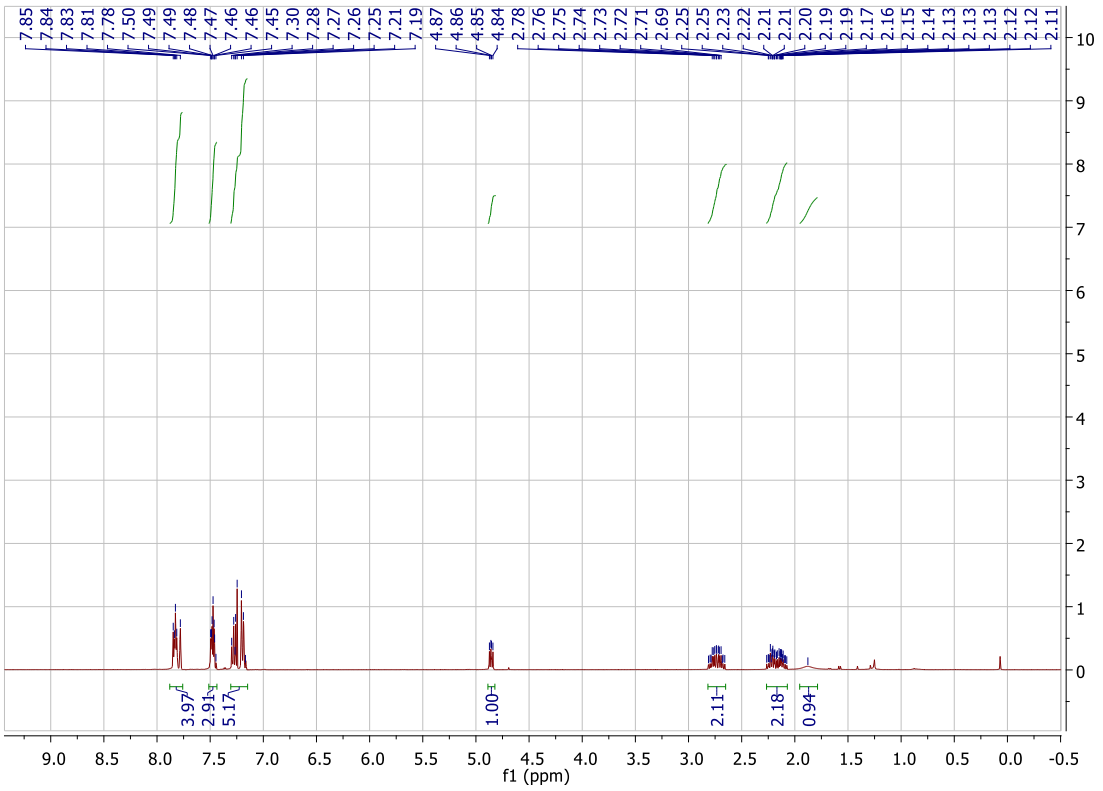
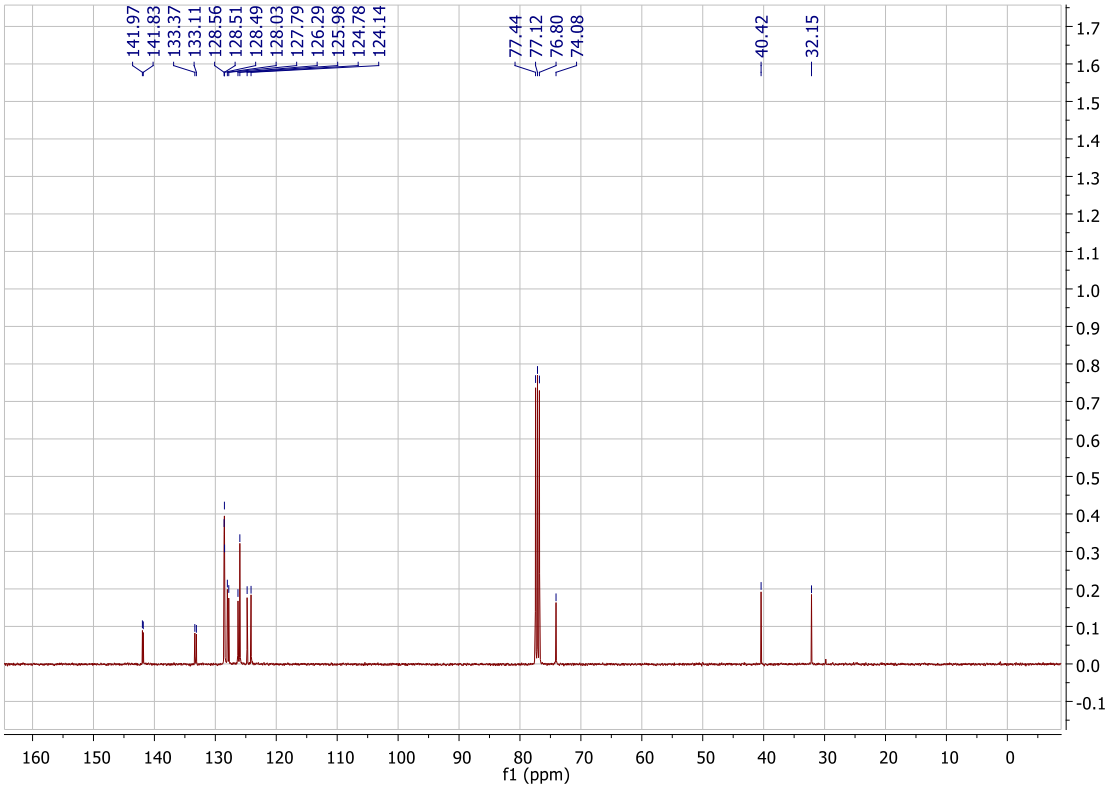
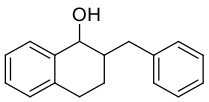
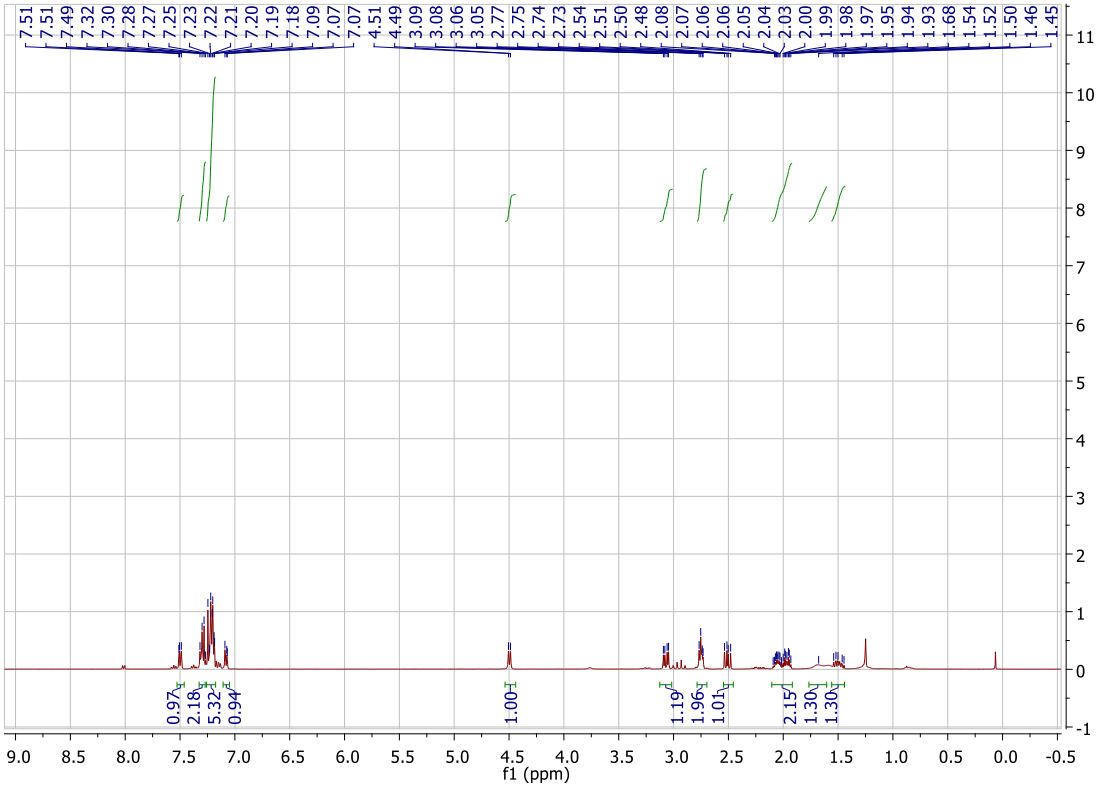
55.33
40.50
32.14
f1 (ppm)


OH


7.85 7.84 7.83 7.81 7.78 7.50 7.49 7.49 7.48 7.47 7.46 7.46 7.45 7.30 7.28 7.27 7.26 7.25 7.21 7.19 4.87 4.86 4.85 4.84 2.78 2.76 2.75 2.74 2.73 2.72 2.71 2.69 2.25 2.25 2.23 2.22 2.21 2.21 2.20 2.19 2.19 2.17 2.16 2.15 2.14 2.13 2.13 2.13 2.12 2.12 2.11
3.97 2.91 5.17 1.00 2.11 2.18 0.94
f1 (ppm)


141.97 141.83 133.37 133.11 128.56 128.51 128.49 128.03 127.79 126.29 125.98 124.78 124.14
77.44 77.12 76.80 74.08
40.42 32.15
f1 (ppm)


OH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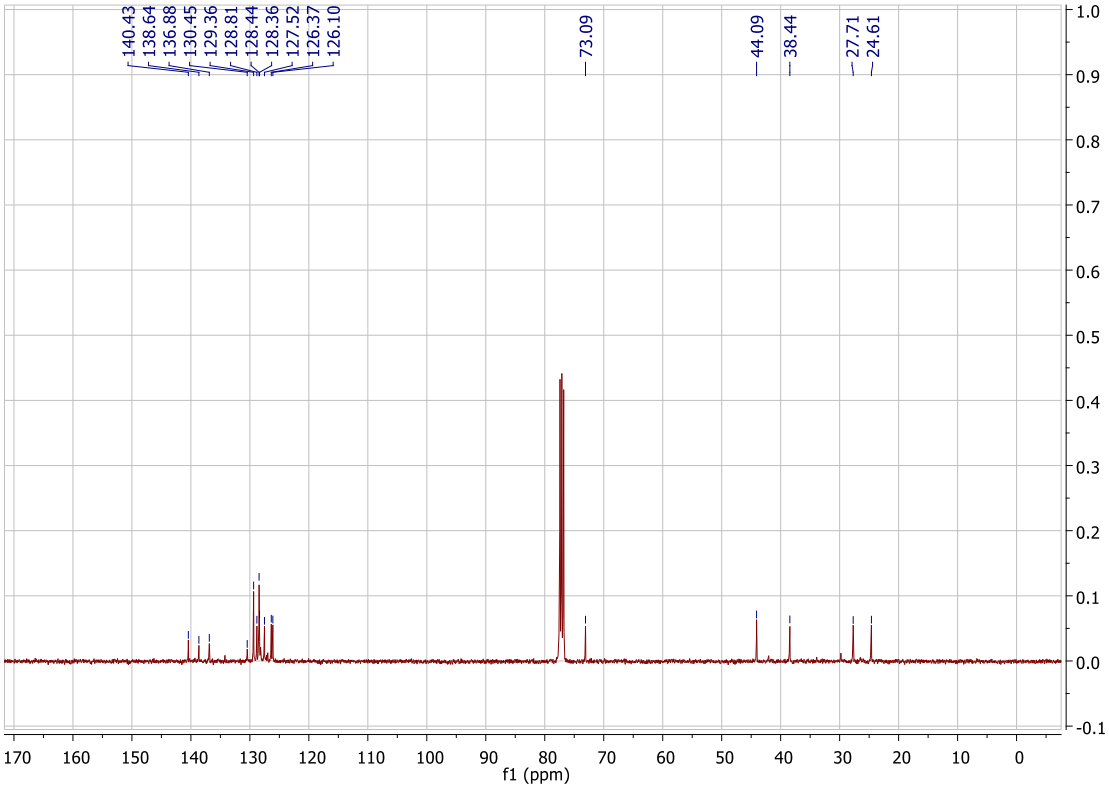
4.51 4.49 3.09 3.08 3.06 3.05 2.77 2.75 2.74 2.73 2.54 2.51 2.50 2.48 2.08 2.07 2.06 2.06 2.05 2.04 2.03 2.00 1.99 1.98 1.97 1.95 1.94 1.93 1.68 1.54 1.52 1.50 1.46 1.45
0.97 2.18 5.32 0.94 1.00 1.19 1.96 1.01 2.15 1.30 1.30
f1 (ppm)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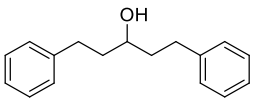
73.09
44.09 38.44 27.71 24.61
f1 (ppm)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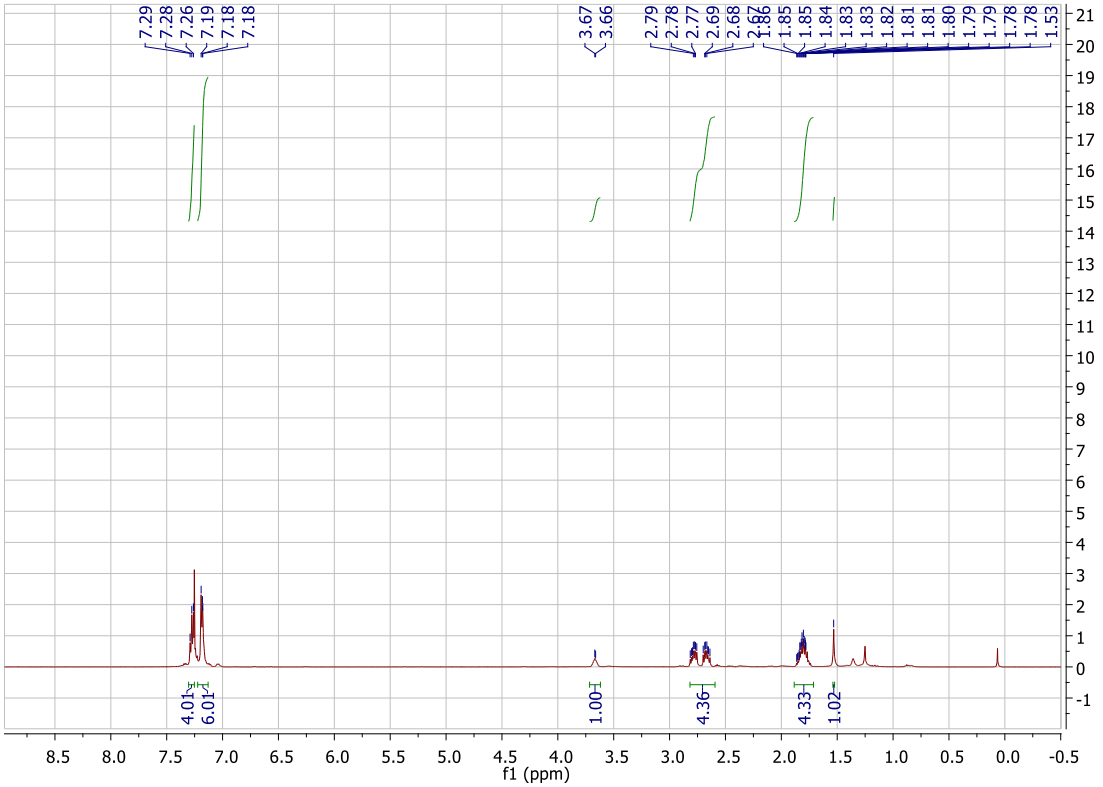
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1.84
1.83
1.83
1.82
1.81
1.81
1.80
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1.78
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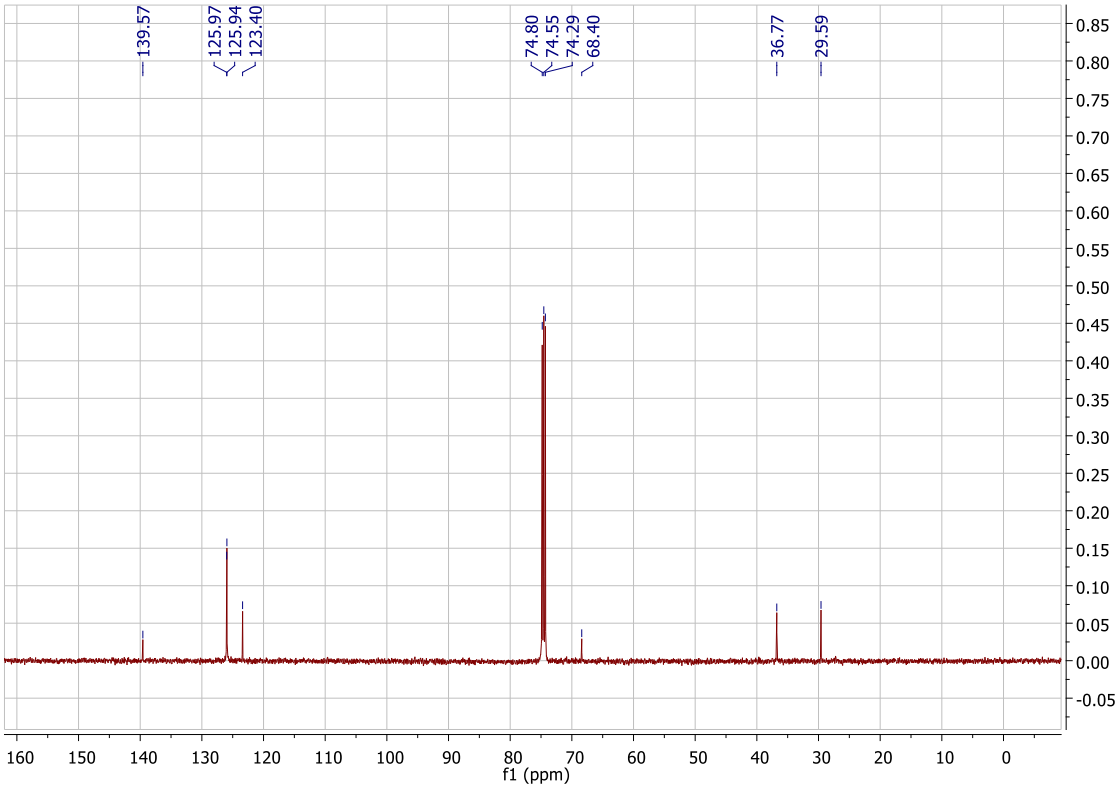
6.01
1.00
4.36
4.33
1.02
f1 (ppm)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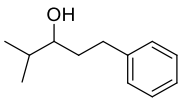
29.59
f1 (ppm)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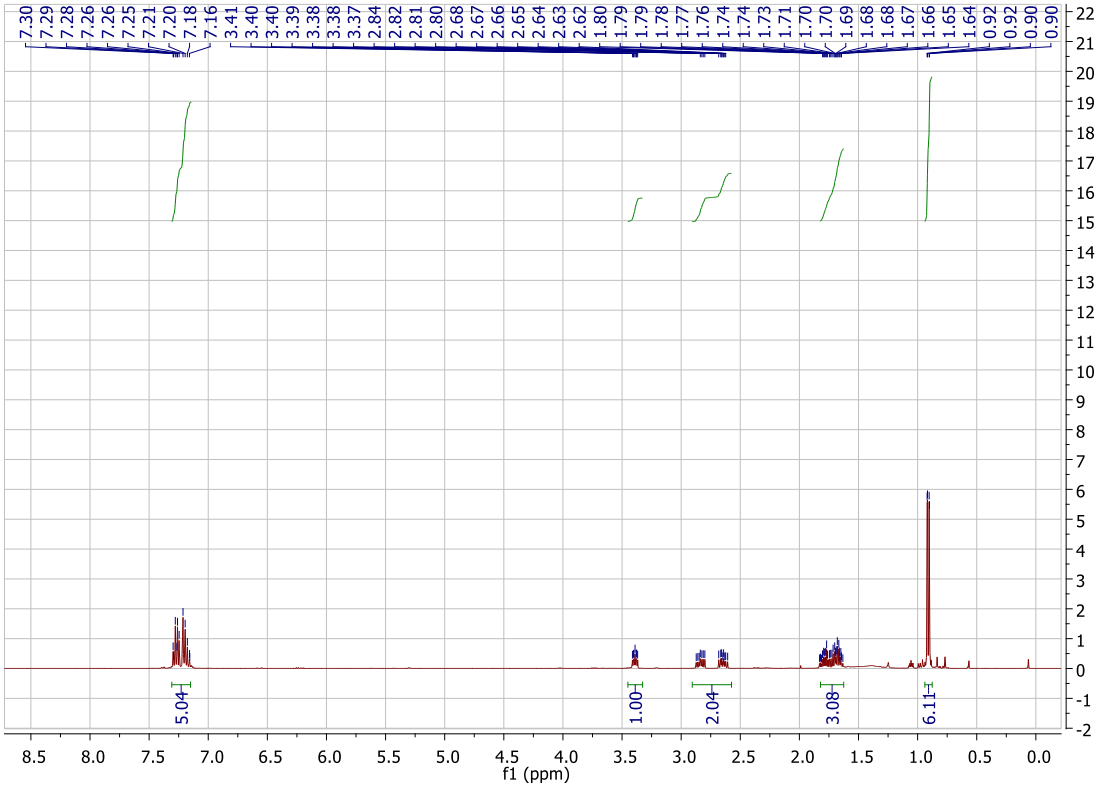
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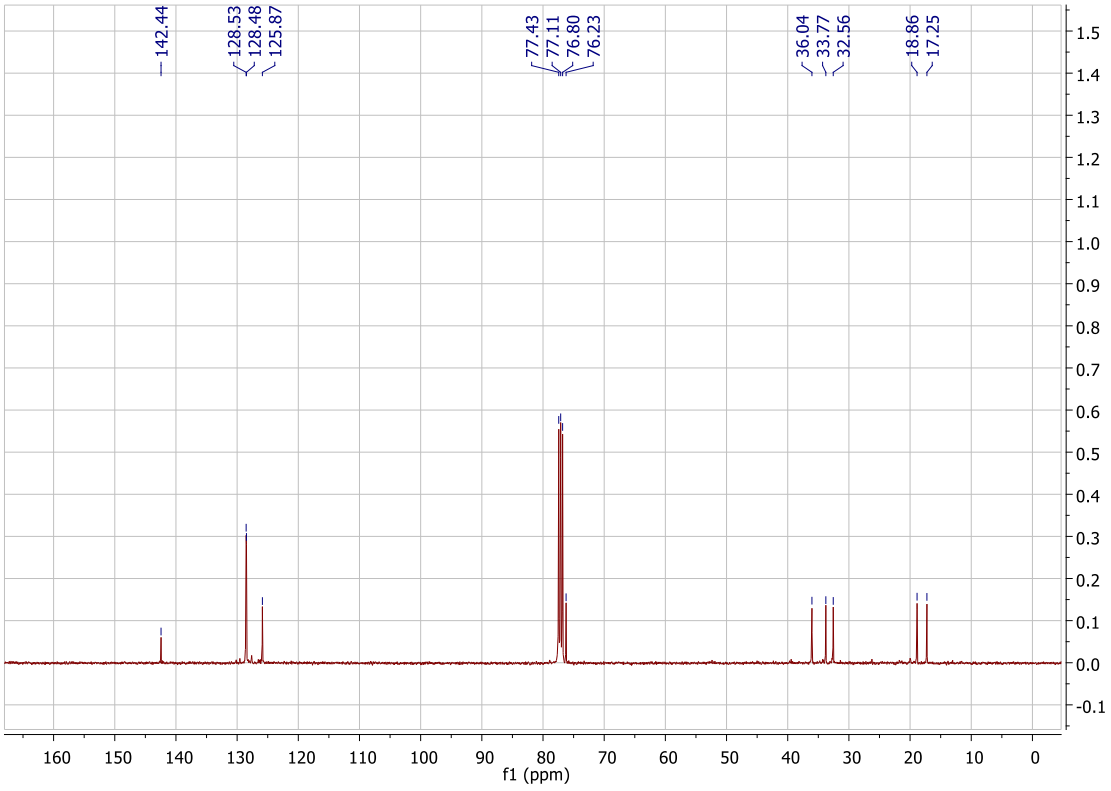
5.04 1.00 2.04 3.08 6.11
f1 (ppm)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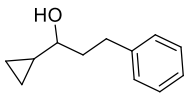
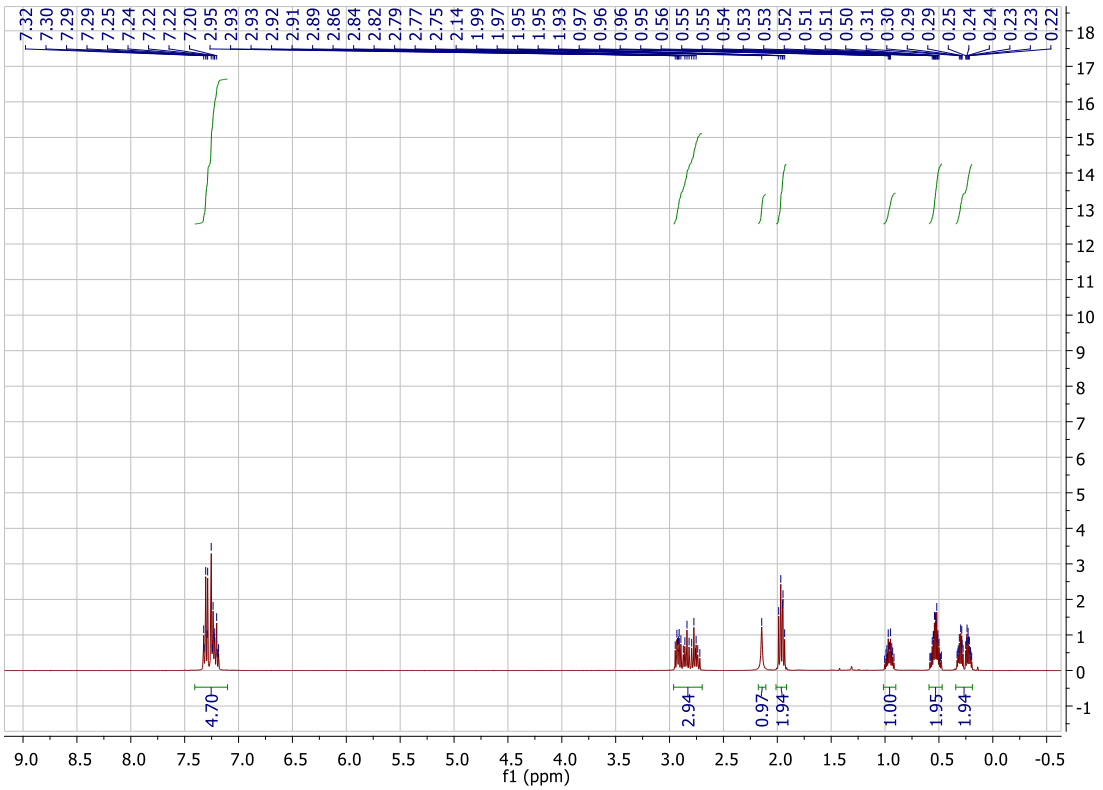
f1 (ppm)


HO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2.84
2.82
2.79
2.77
2.75
2.14
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1.97
1.95
1.95
1.93
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0.96
0.96
0.95
0.56
0.55
0.55
0.54
0.53
0.53
0.52
0.51
0.51
0.50
0.31
0.30
0.29
0.29
0.25
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1.00
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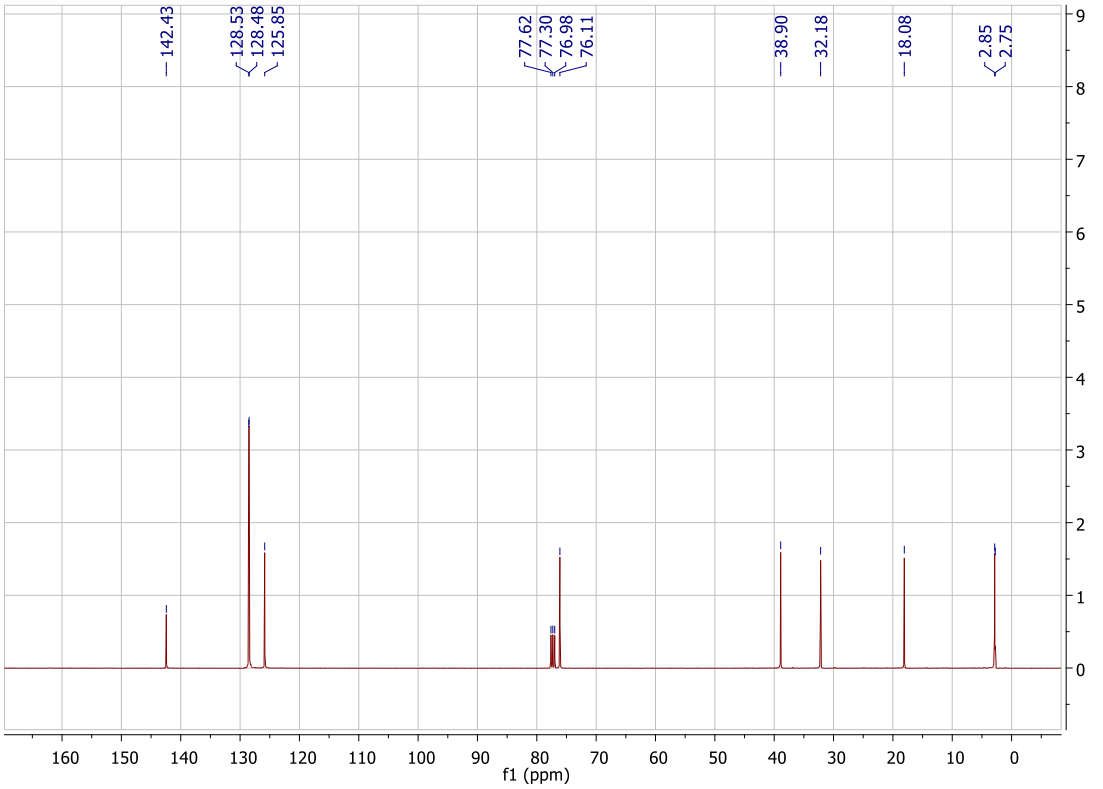
f1 (ppm)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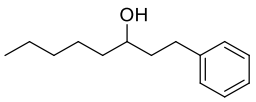
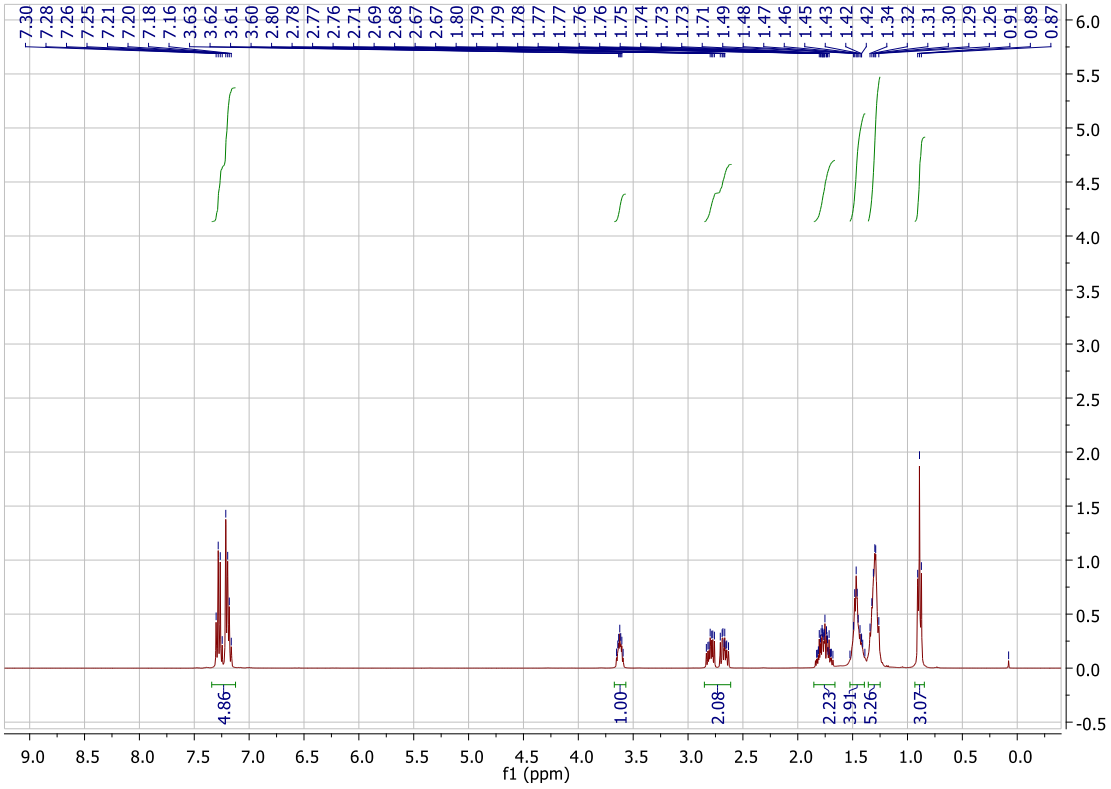
18.08
2.85
2.75
f1 (ppm)


OH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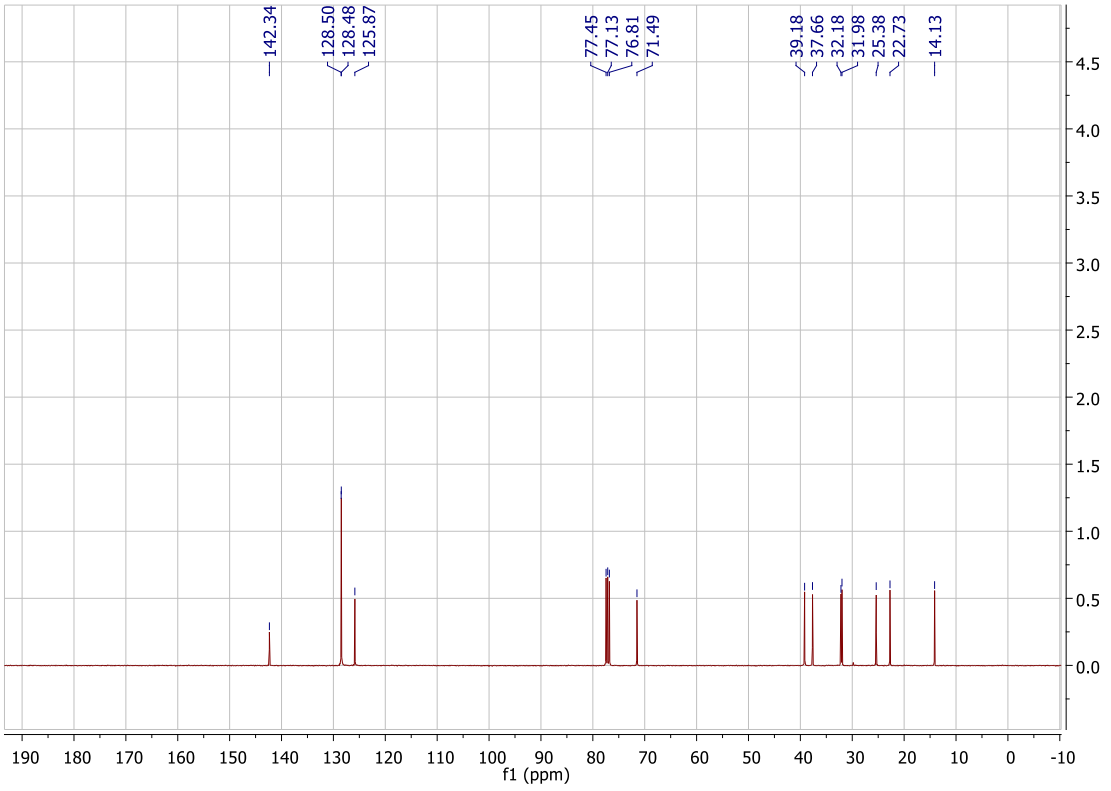
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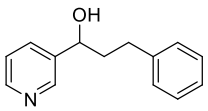
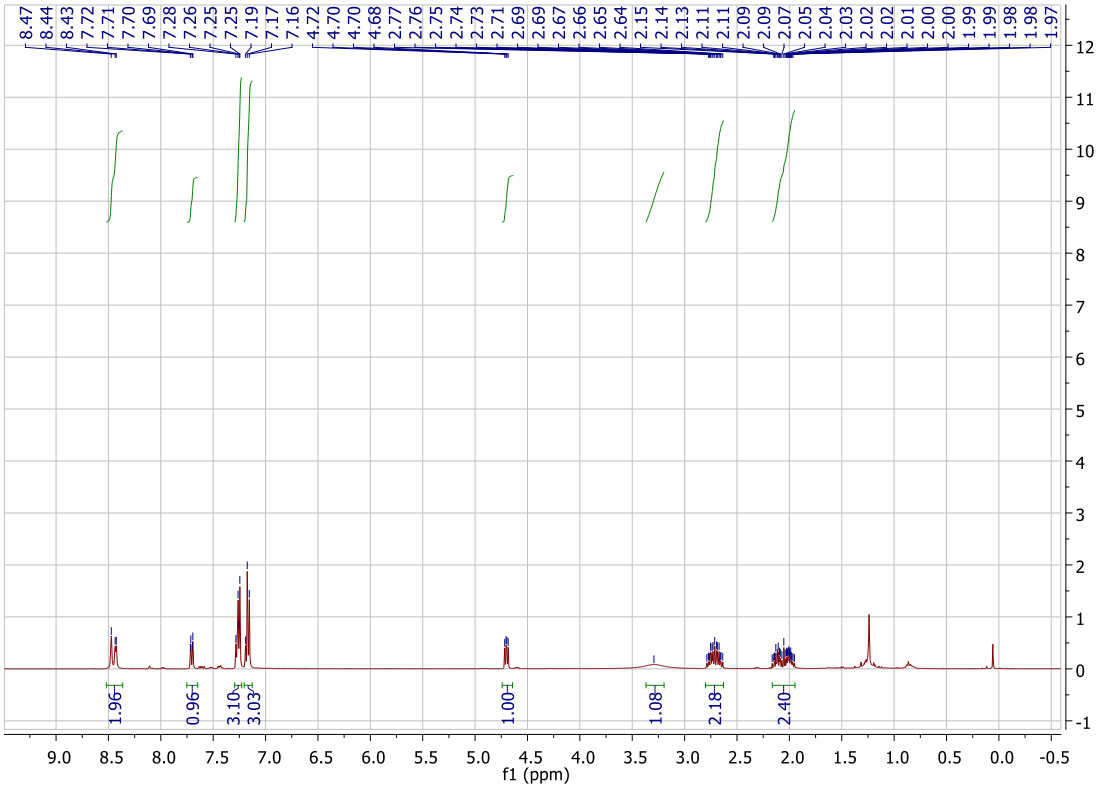
31.98
25.38
22.73
14.13
f1 (ppm)


OH
N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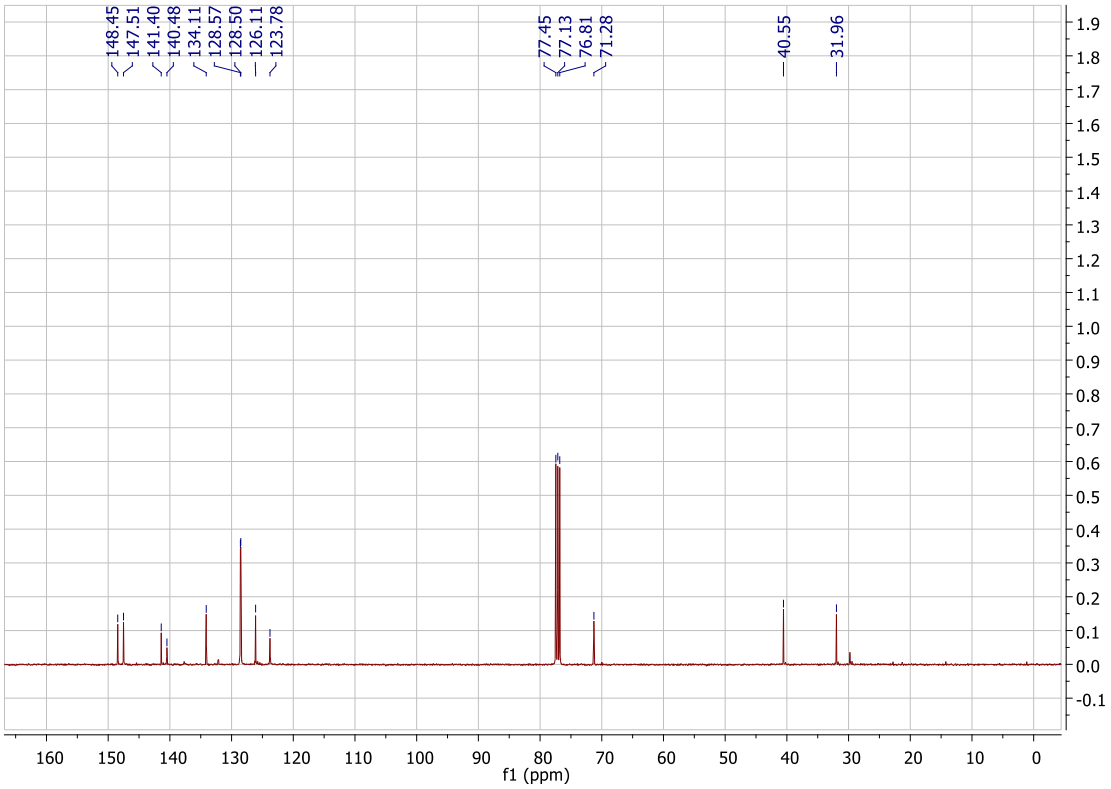
1.96 0.96 3.10 3.03 1.00 1.08 2.18 2.40
f1 (ppm)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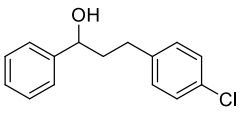
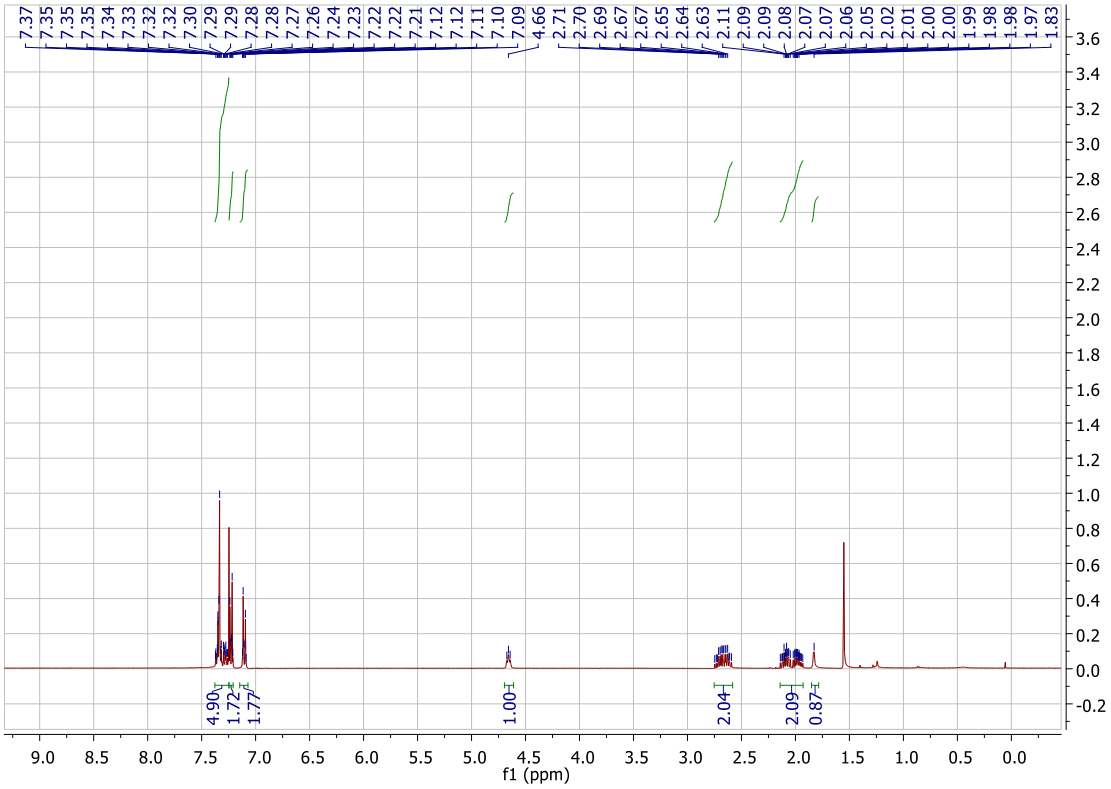
77.45 77.13 76.81 71.28
40.55 31.96
f1 (ppm)


OH
Cl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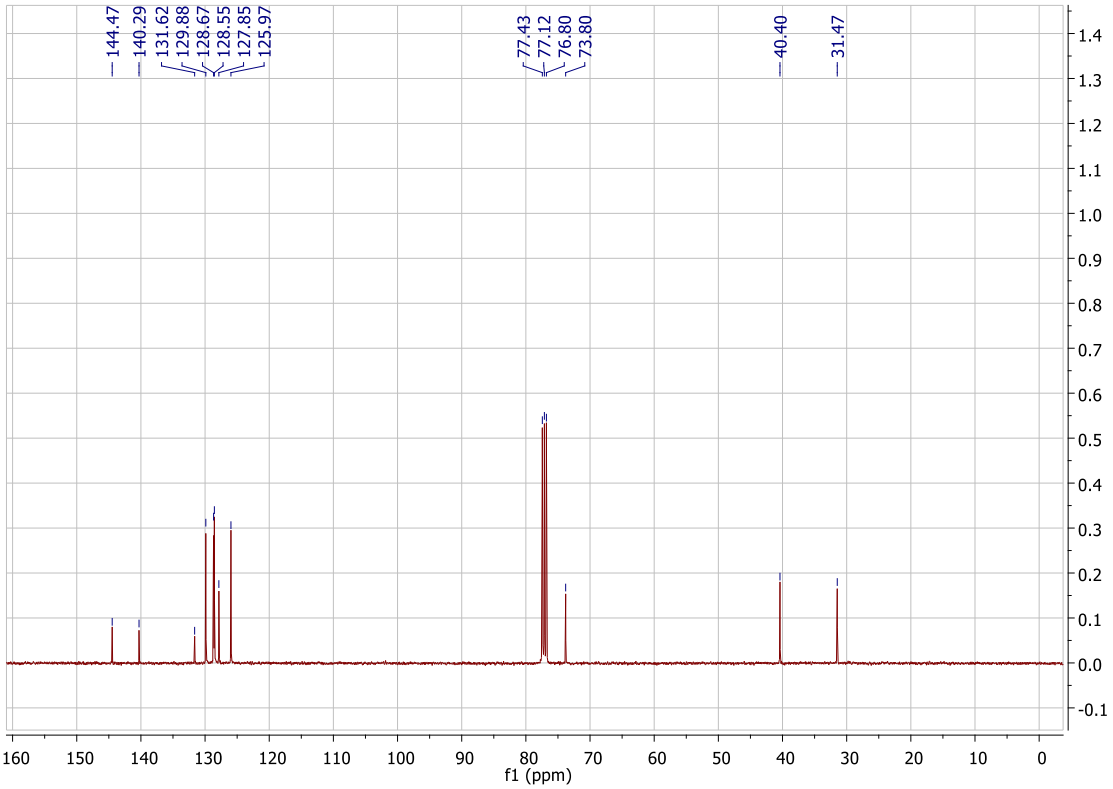
4.90 1.72 1.77 1.00 2.04 2.09 0.87
f1 (ppm)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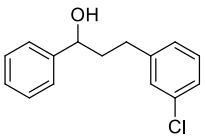
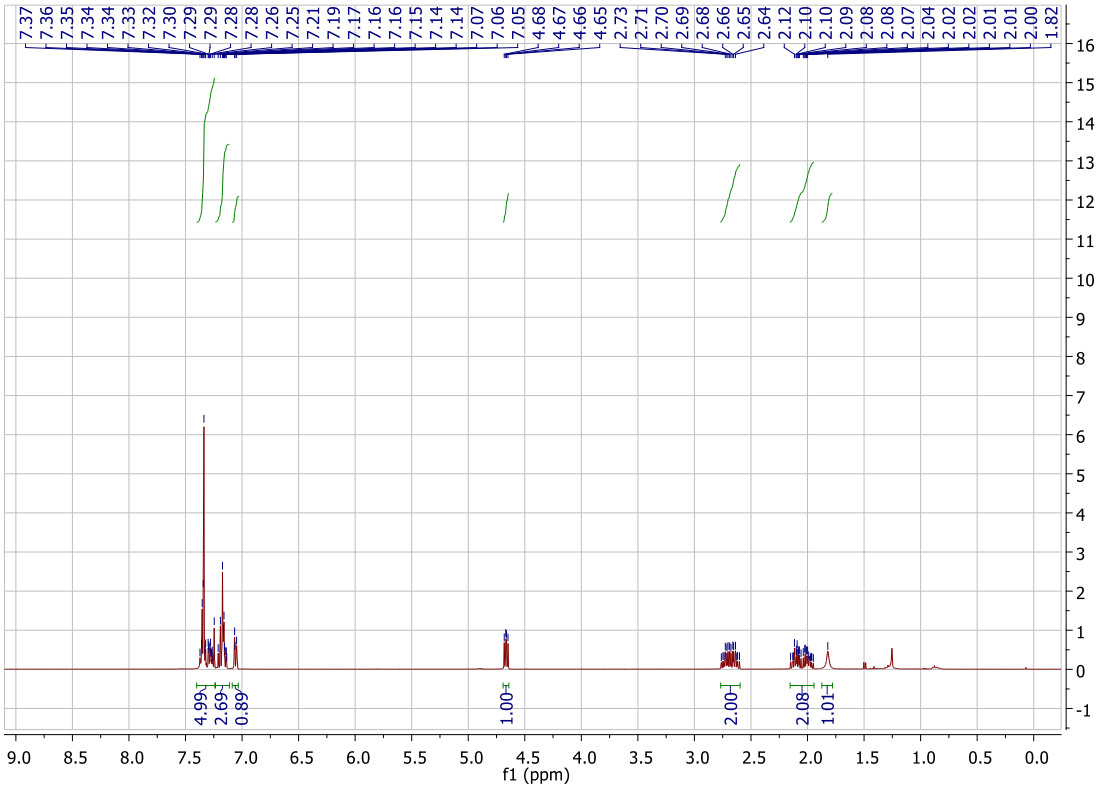
f1 (ppm)


OH
Cl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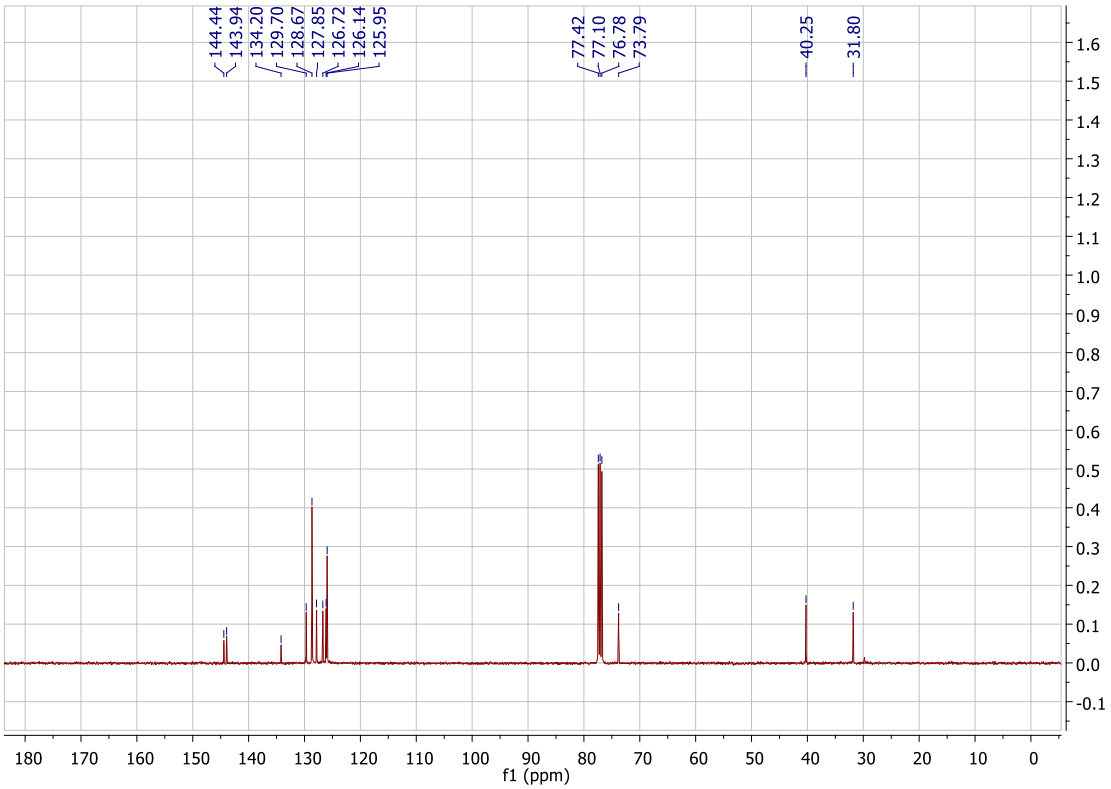
4.99 2.69 0.89 1.00 2.00 2.08 1.01
f1 (ppm)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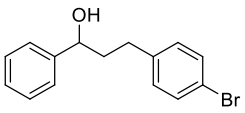
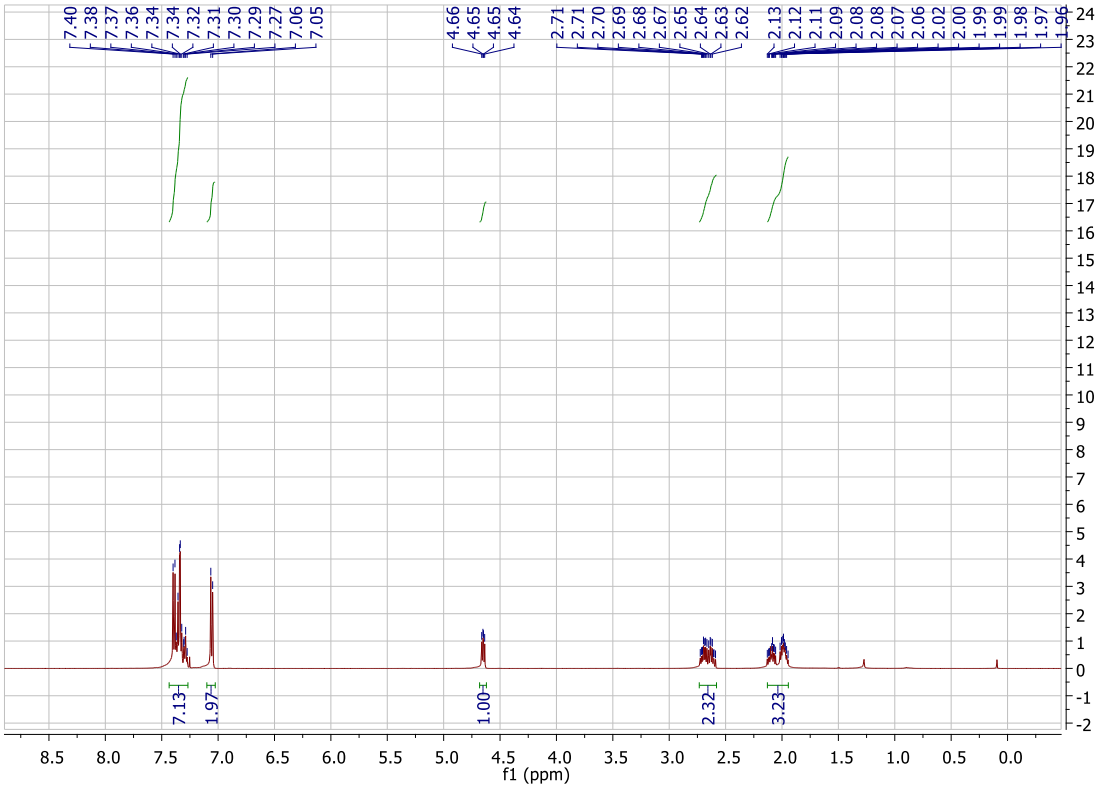
40.25 31.80
f1 (ppm)


OH
Br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4.65
4.64
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2.02
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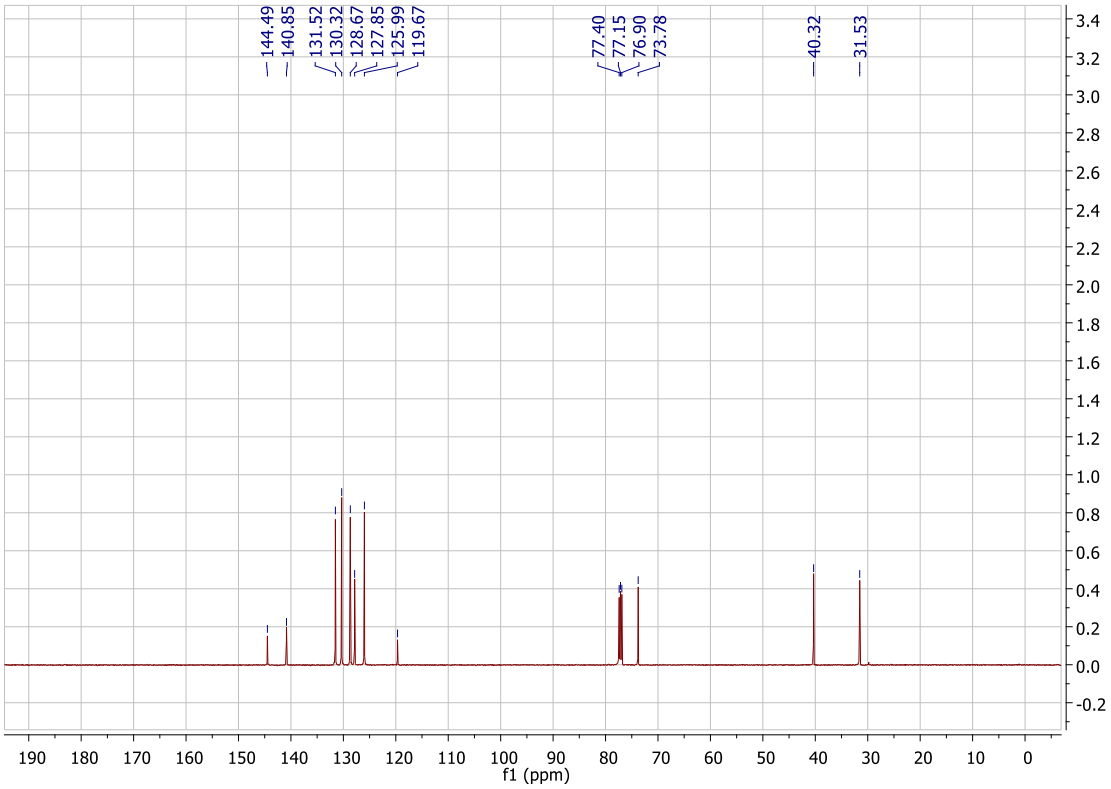
f1 (ppm)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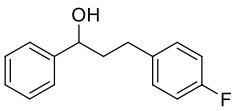
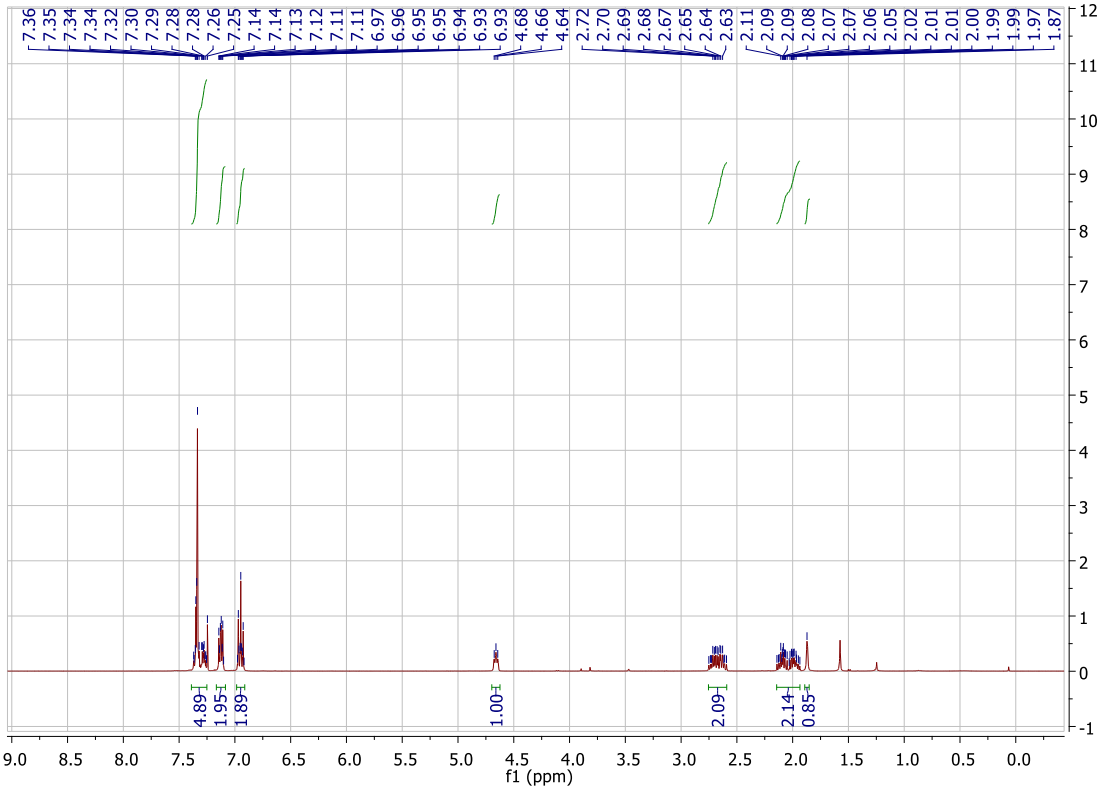
31.53
f1 (ppm)


OH
F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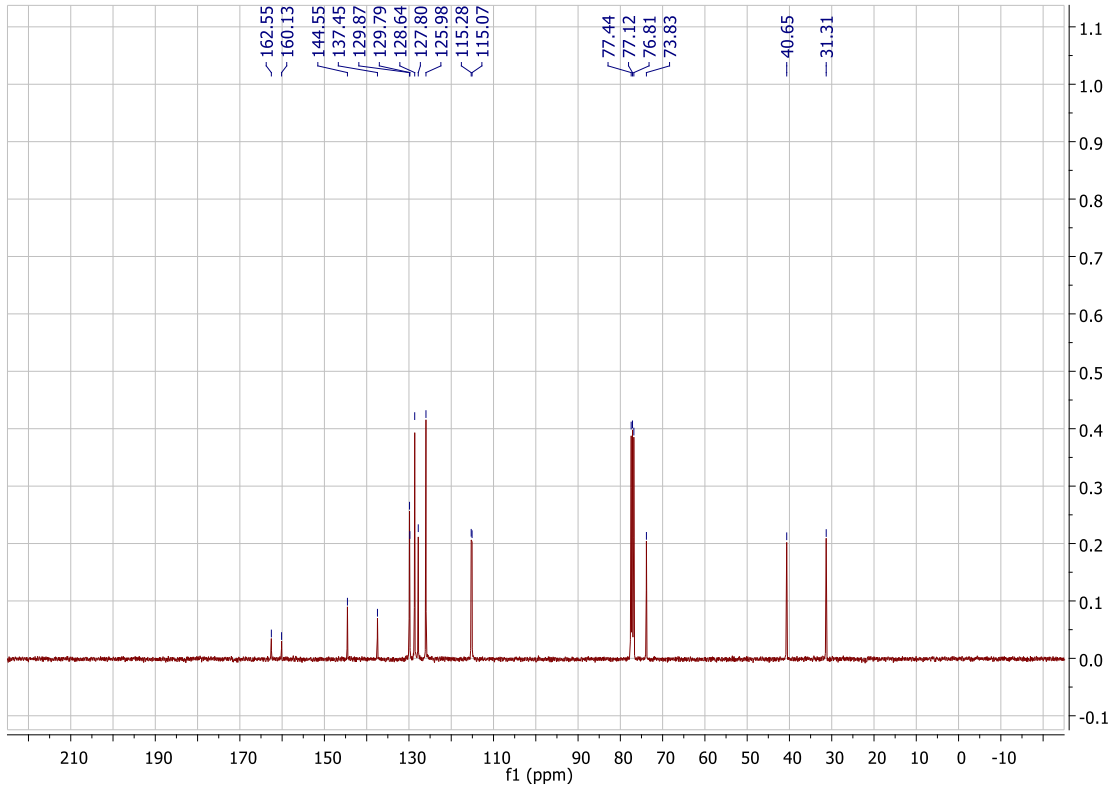
f1 (ppm)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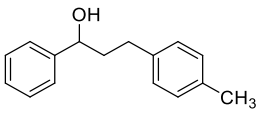
77.12
76.81
73.83
40.65
31.31
f1 (ppm)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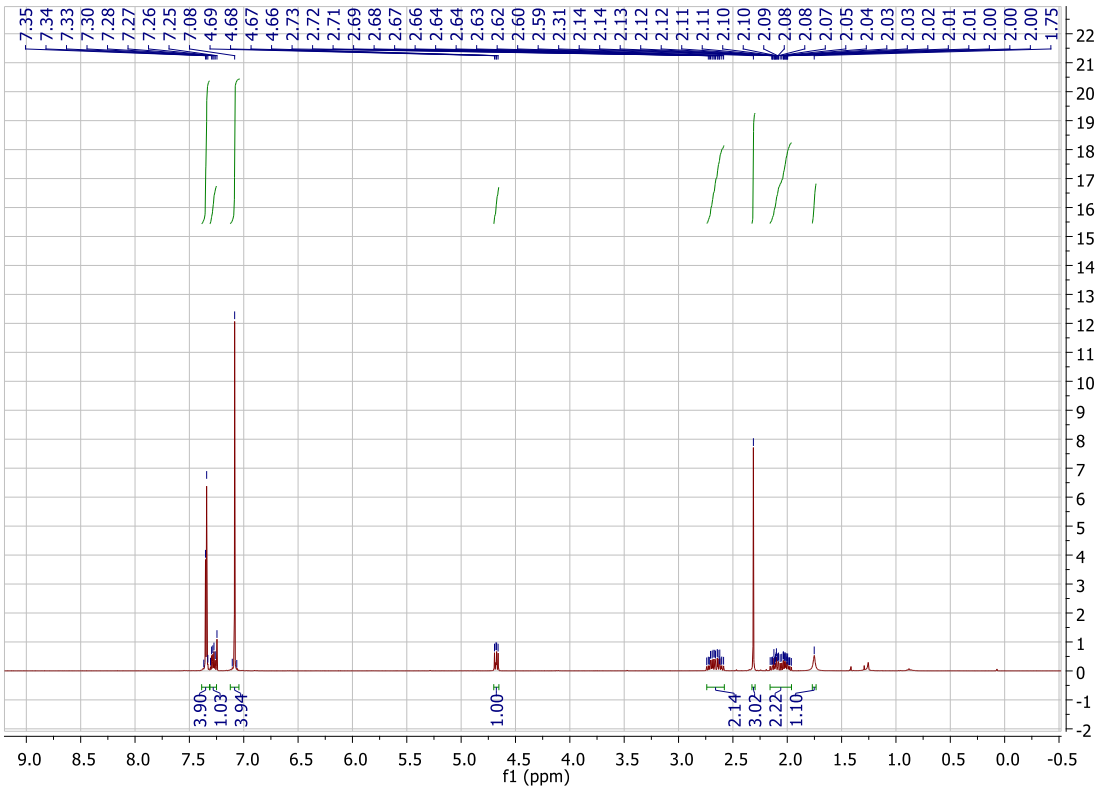
CH3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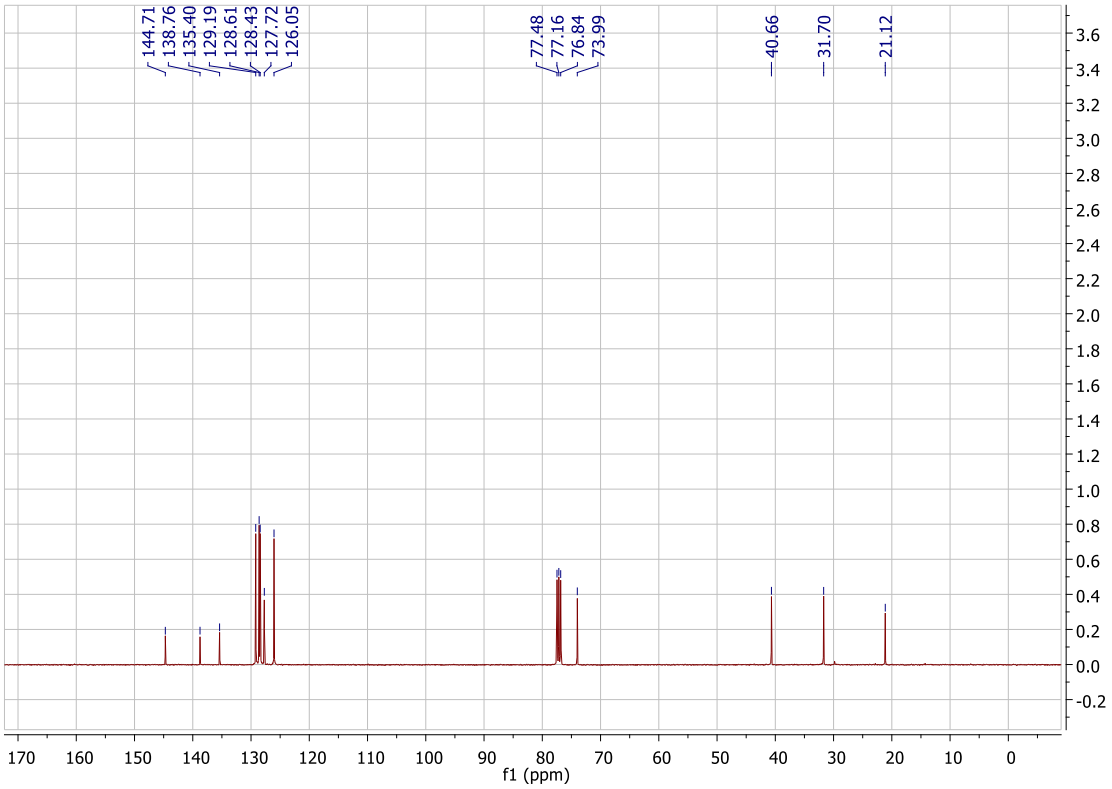
f1 (ppm)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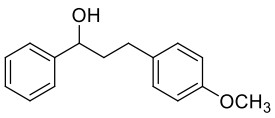
77.48 77.16 76.84 73.99
40.66 31.70 21.12
f1 (ppm)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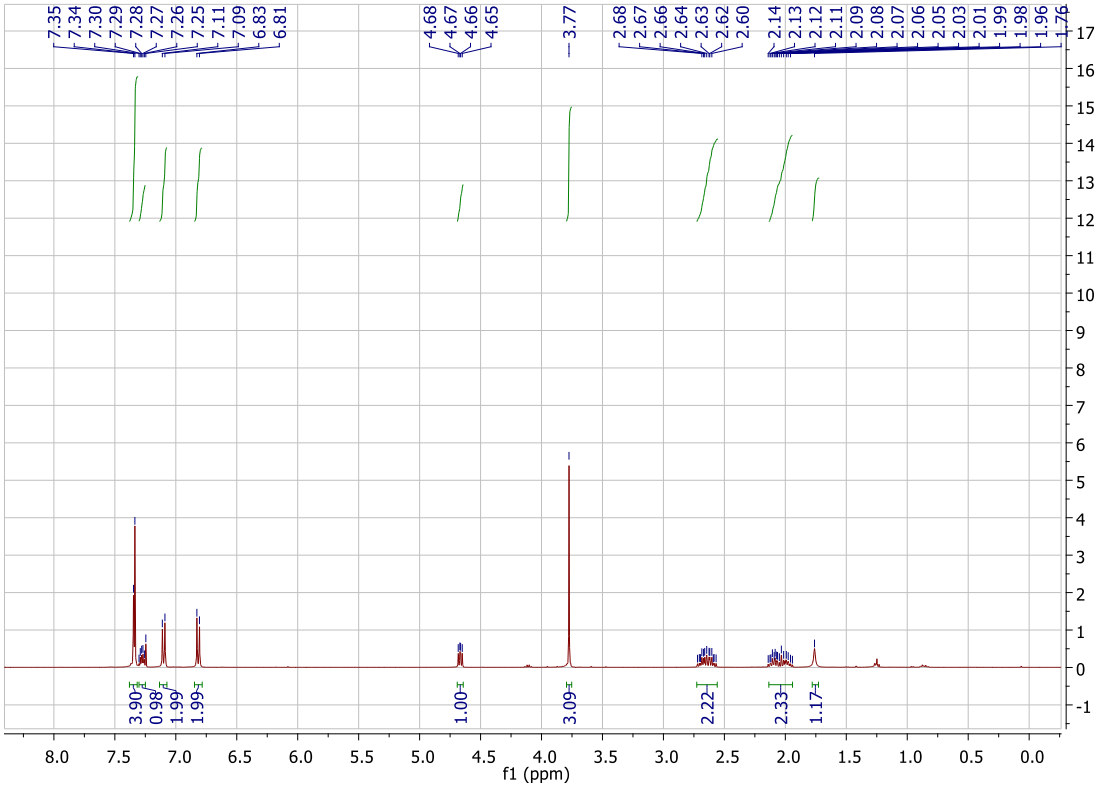
OCH3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2.09
2.08
2.07
2.06
2.05
2.03
2.01
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1.98
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1.99
1.00
3.09
2.22
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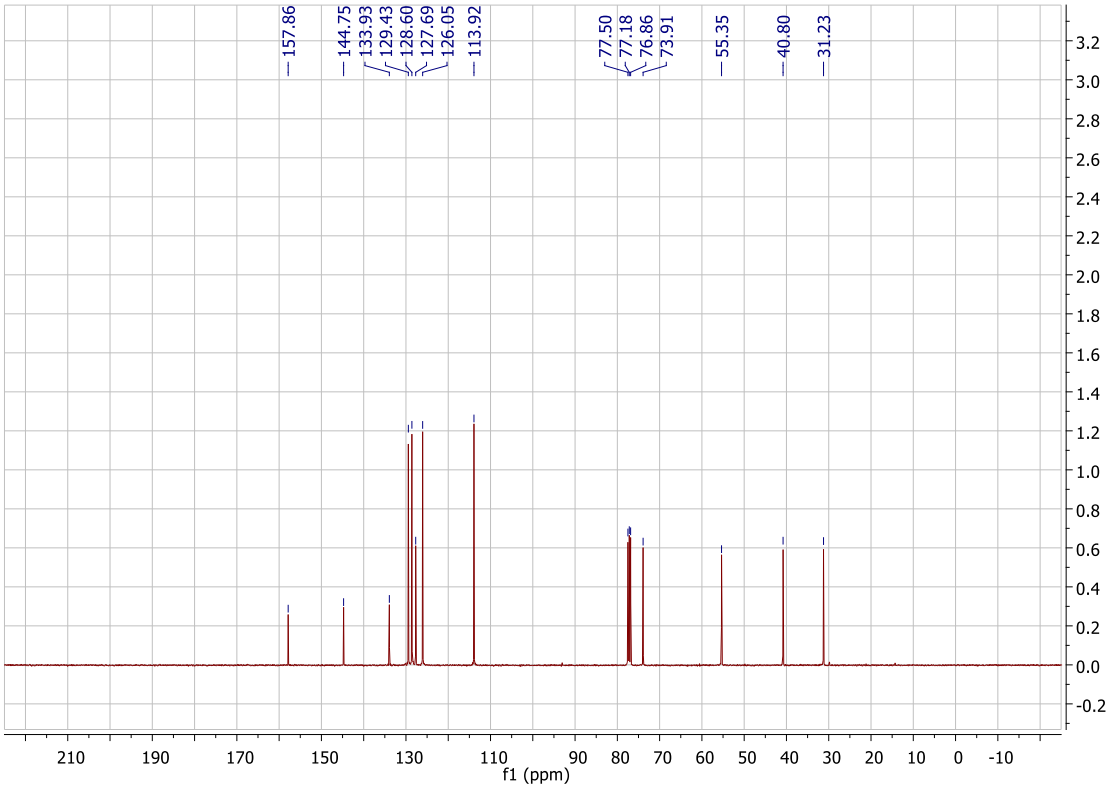
1.17
f1 (ppm)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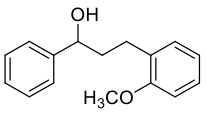
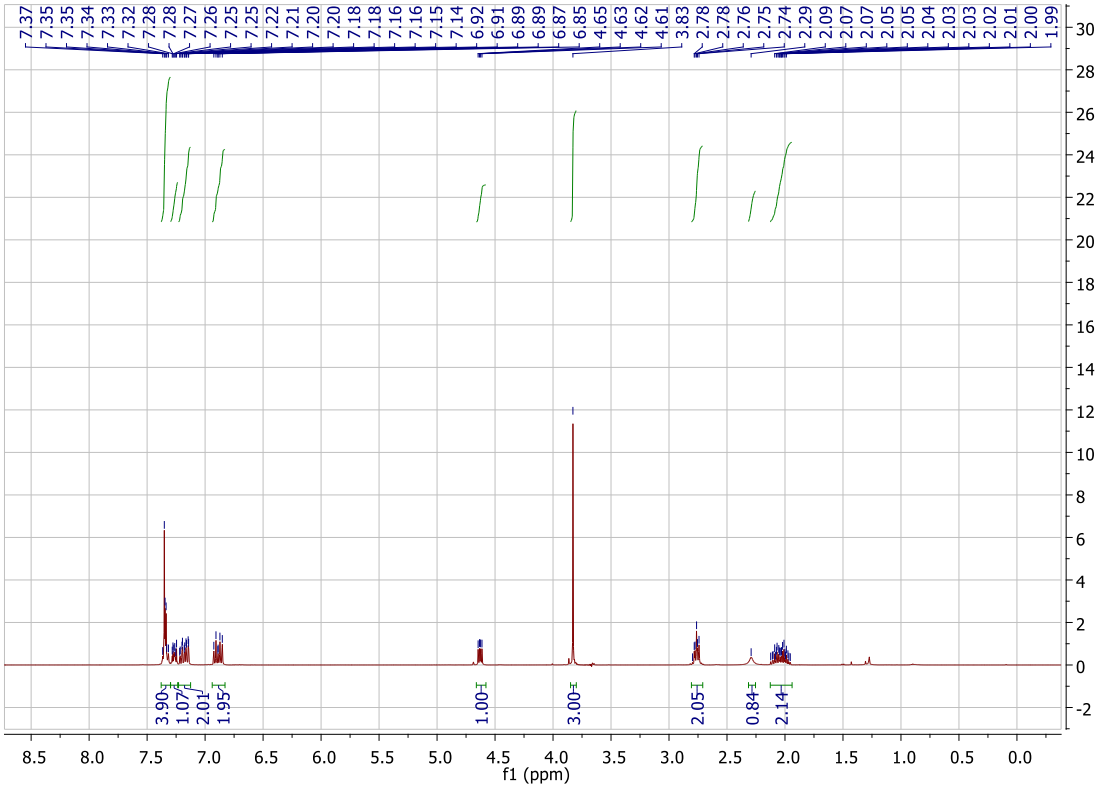
31.23
f1 (ppm)


OH
H3CO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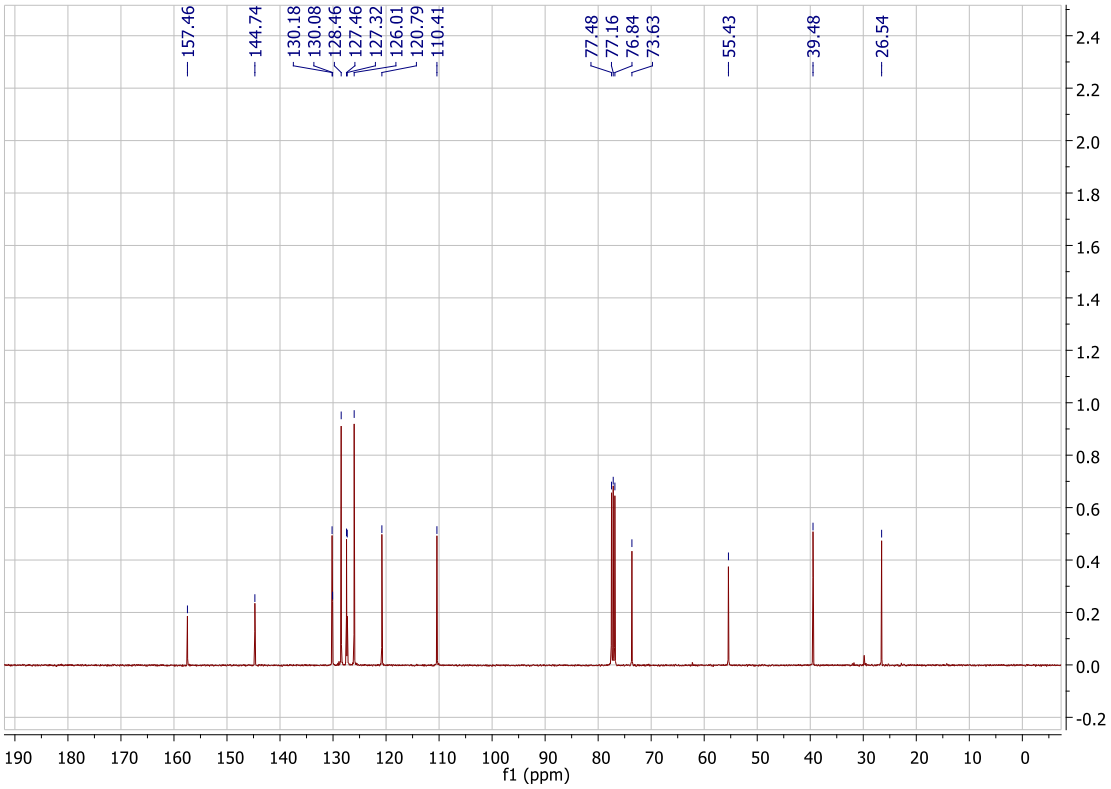
3.90 1.07 2.01 1.95 1.00 3.00 2.05 0.84 2.14
f1 (ppm)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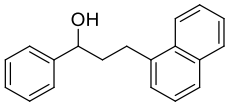
f1 (ppm)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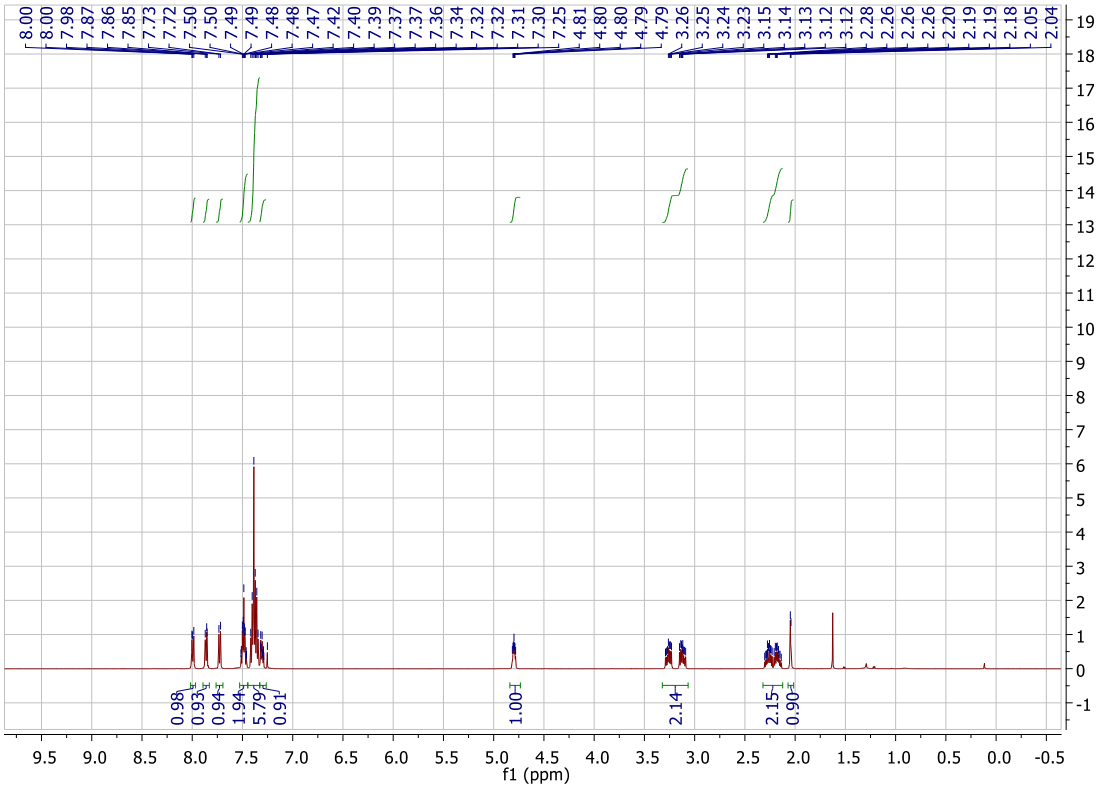
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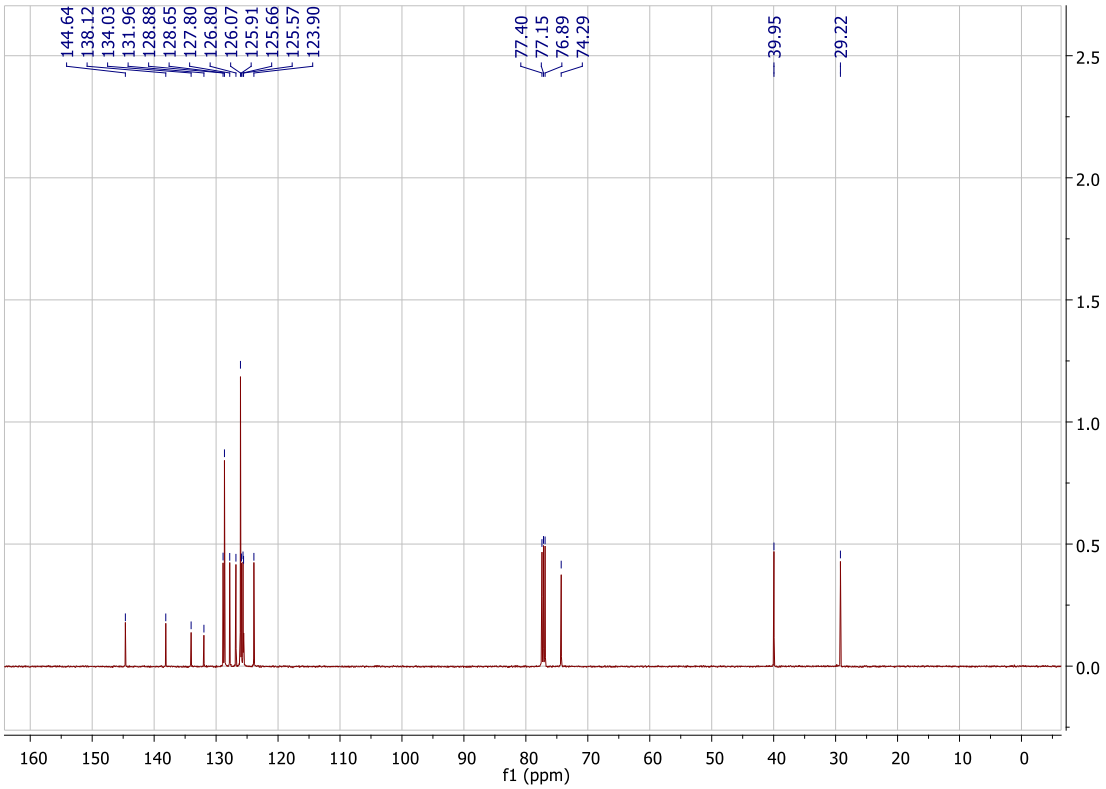
f1 (ppm)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74.29
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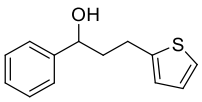
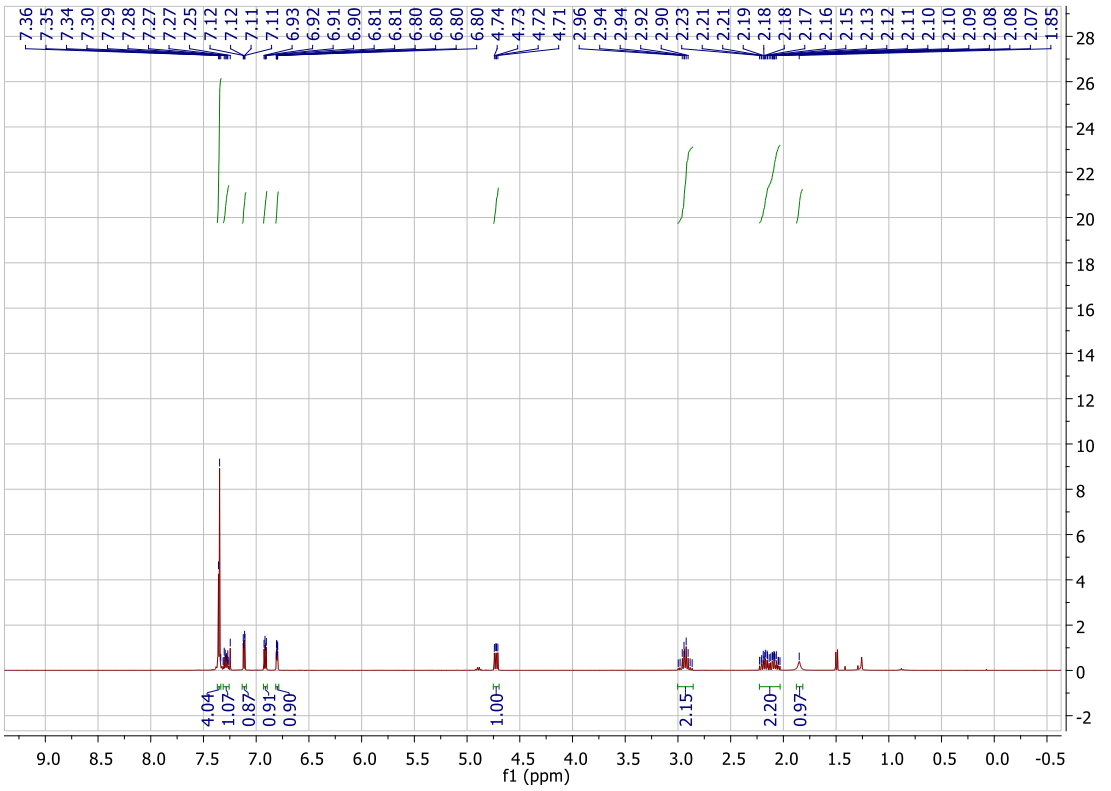
29.22
f1 (ppm)


OH
S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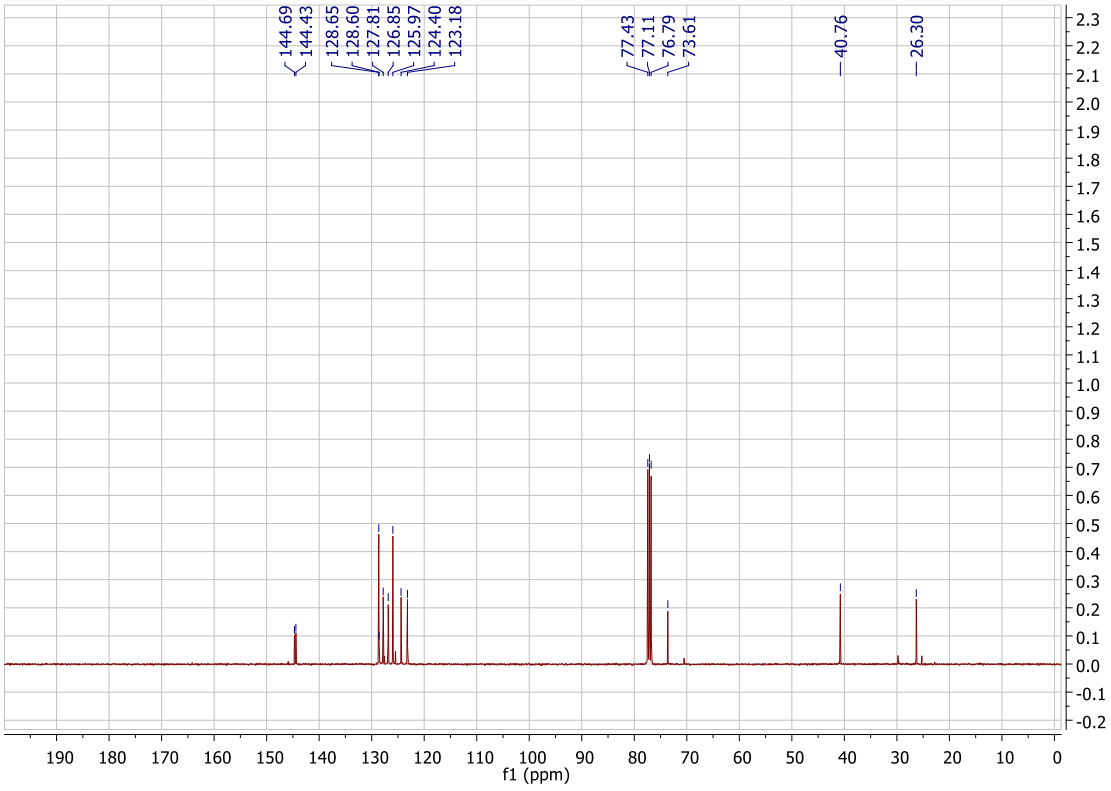
4.04 1.07 0.87 0.91 0.90 1.00 2.15 2.20 0.97
f1 (ppm)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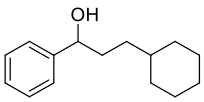
f1 (ppm)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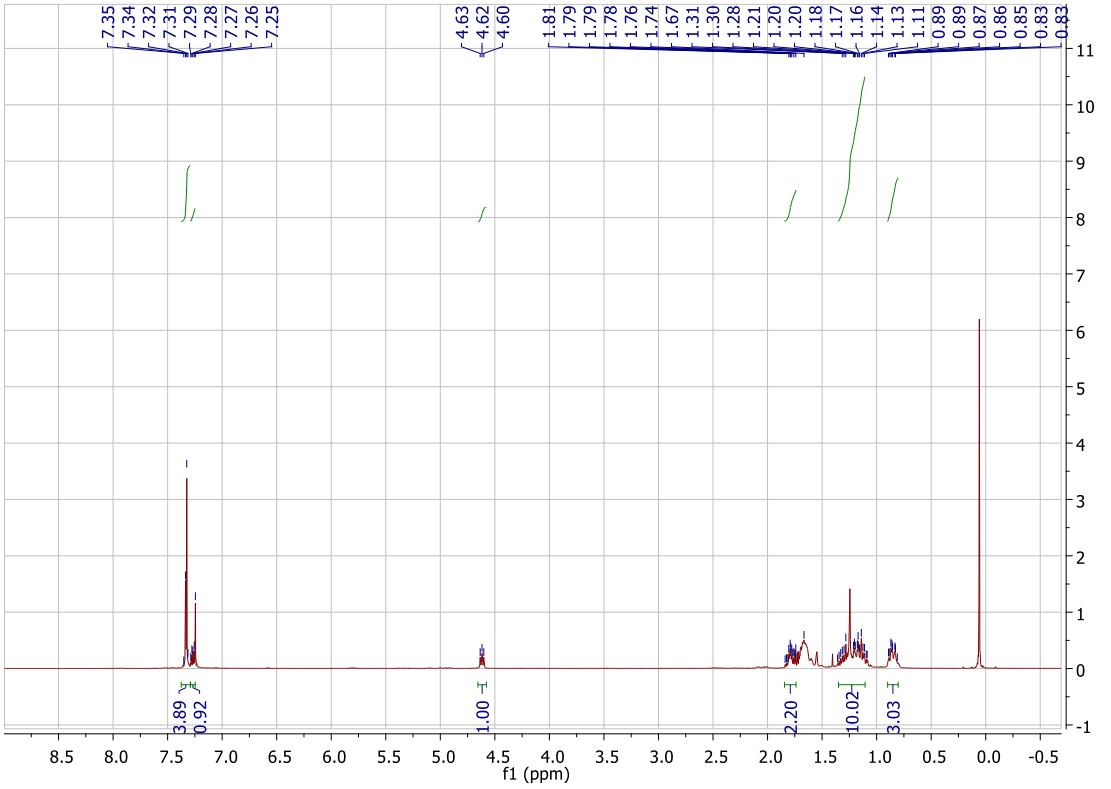
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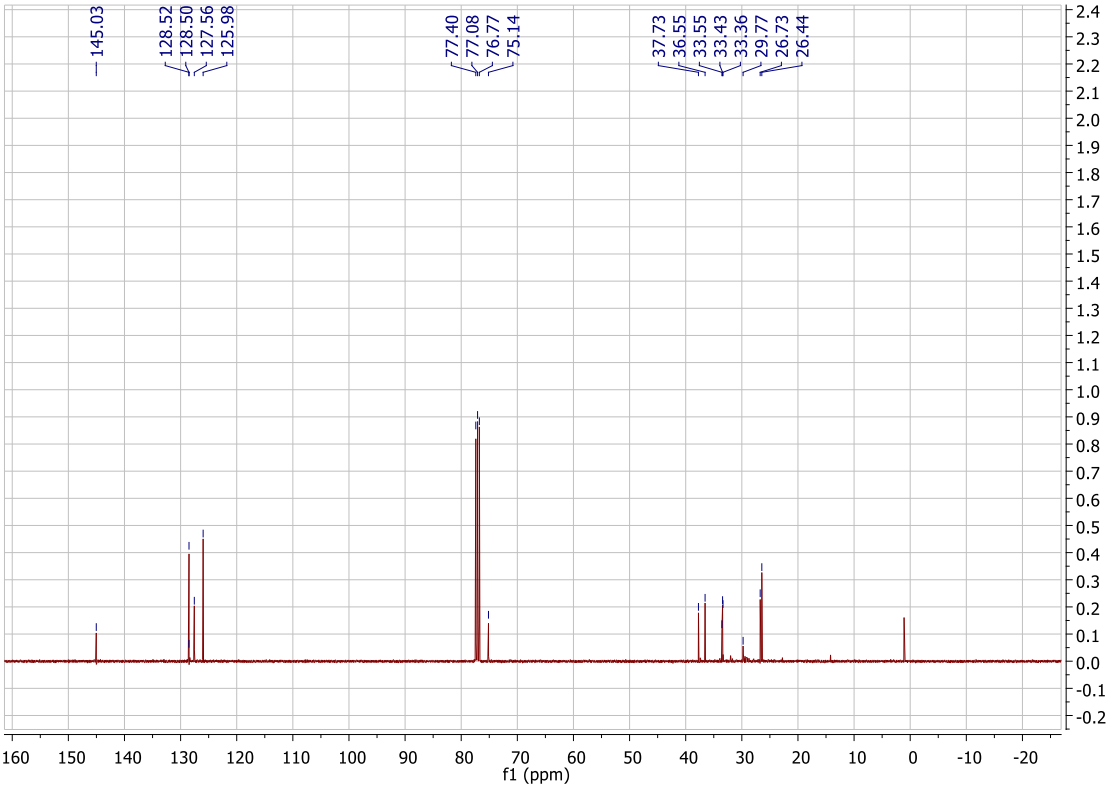
f1 (ppm)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33.36
29.77
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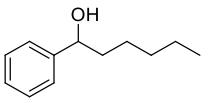
26.44
f1 (ppm)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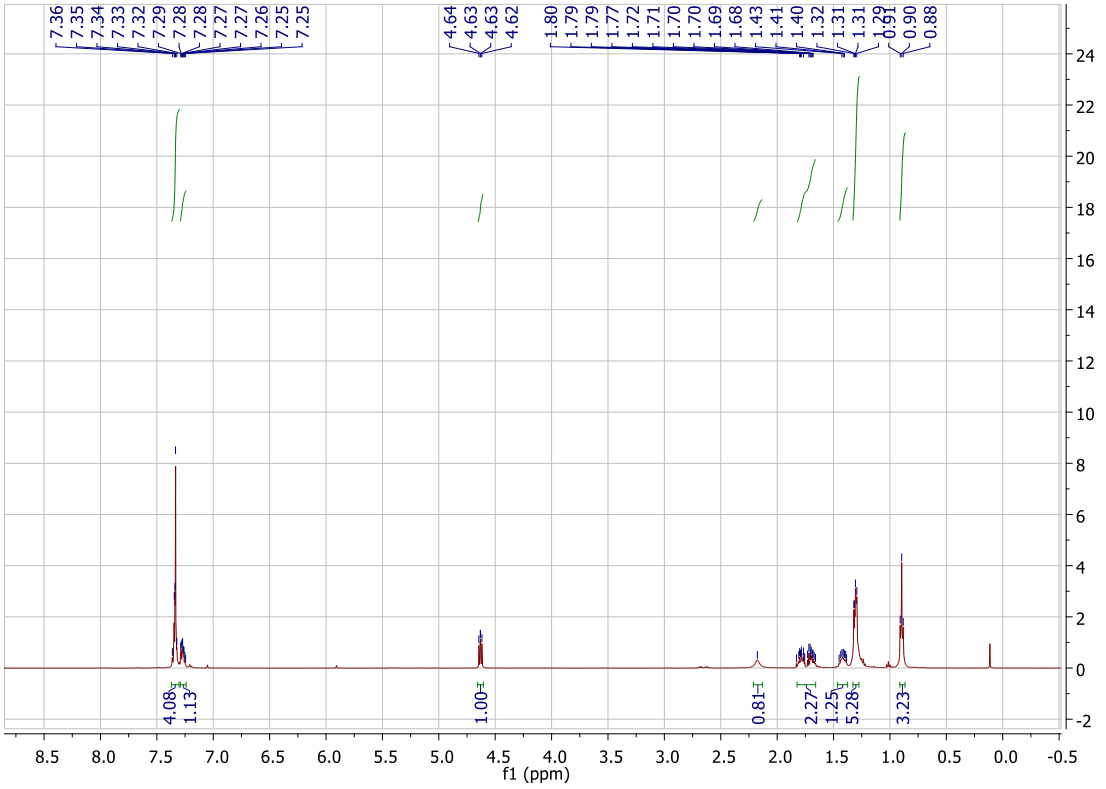
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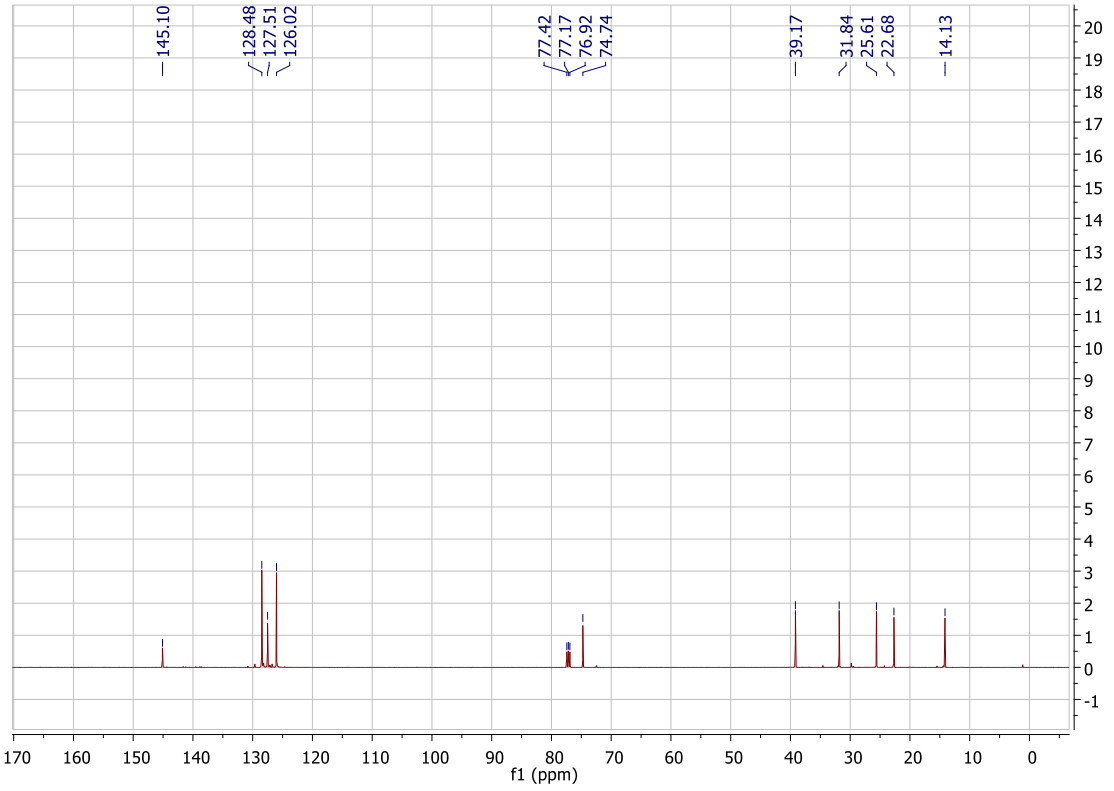
1.25
5.28
3.23
f1 (ppm)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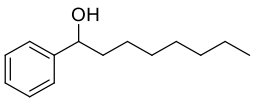
22.68
14.13
f1 (ppm)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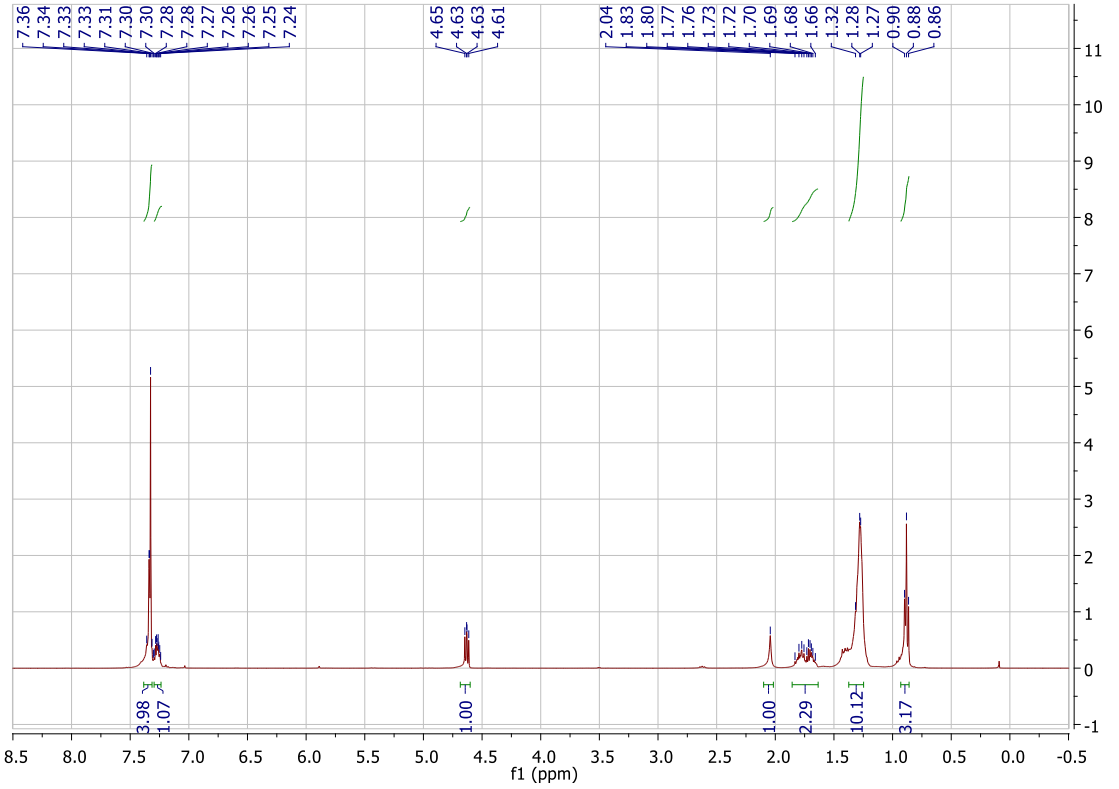
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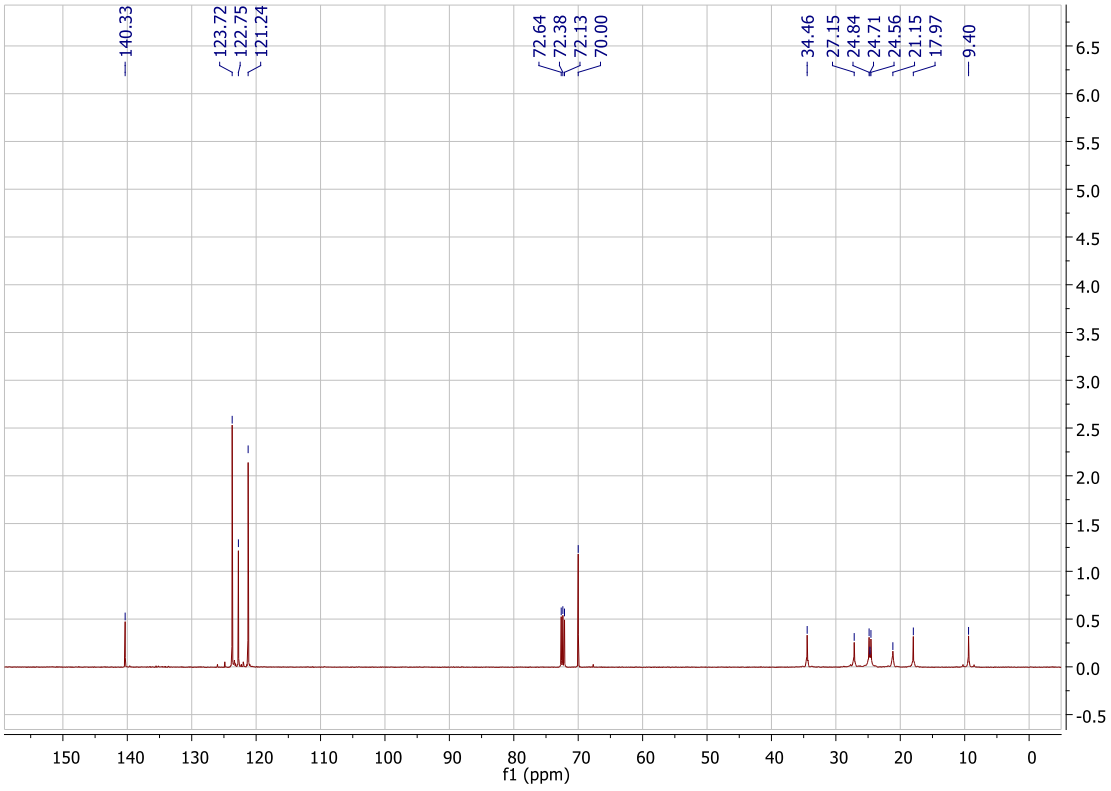
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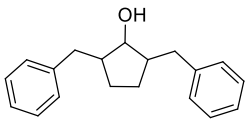
f1 (ppm)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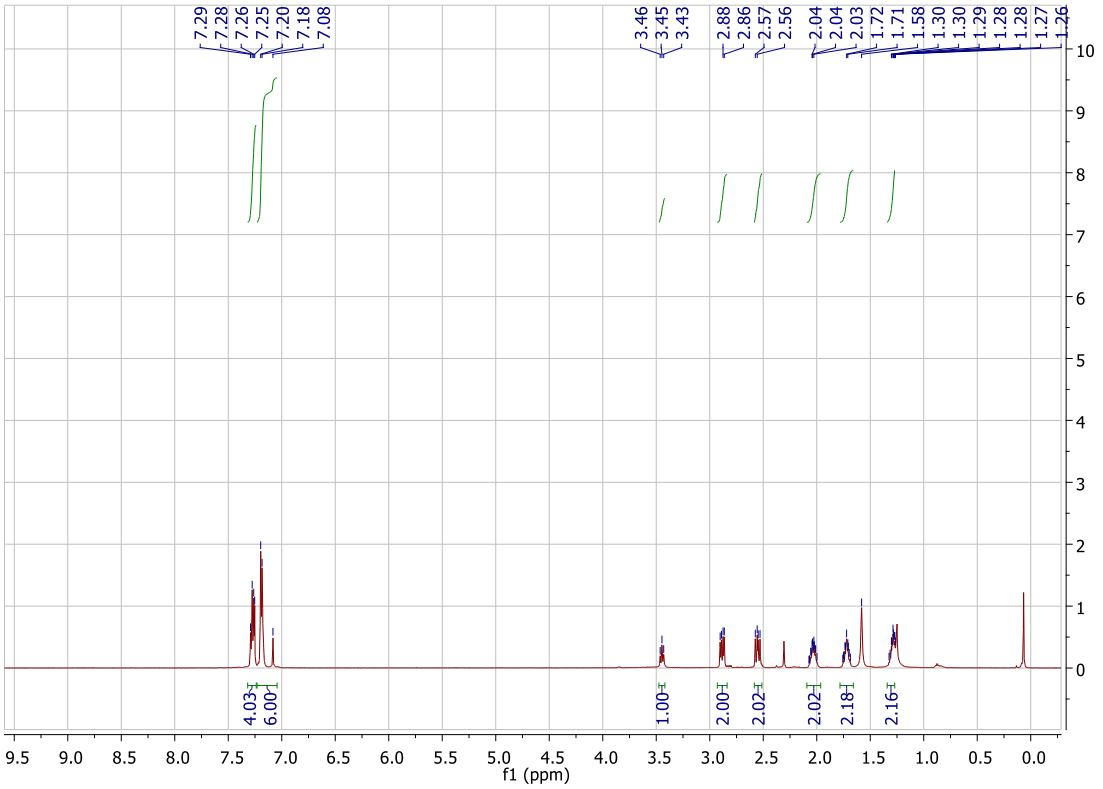
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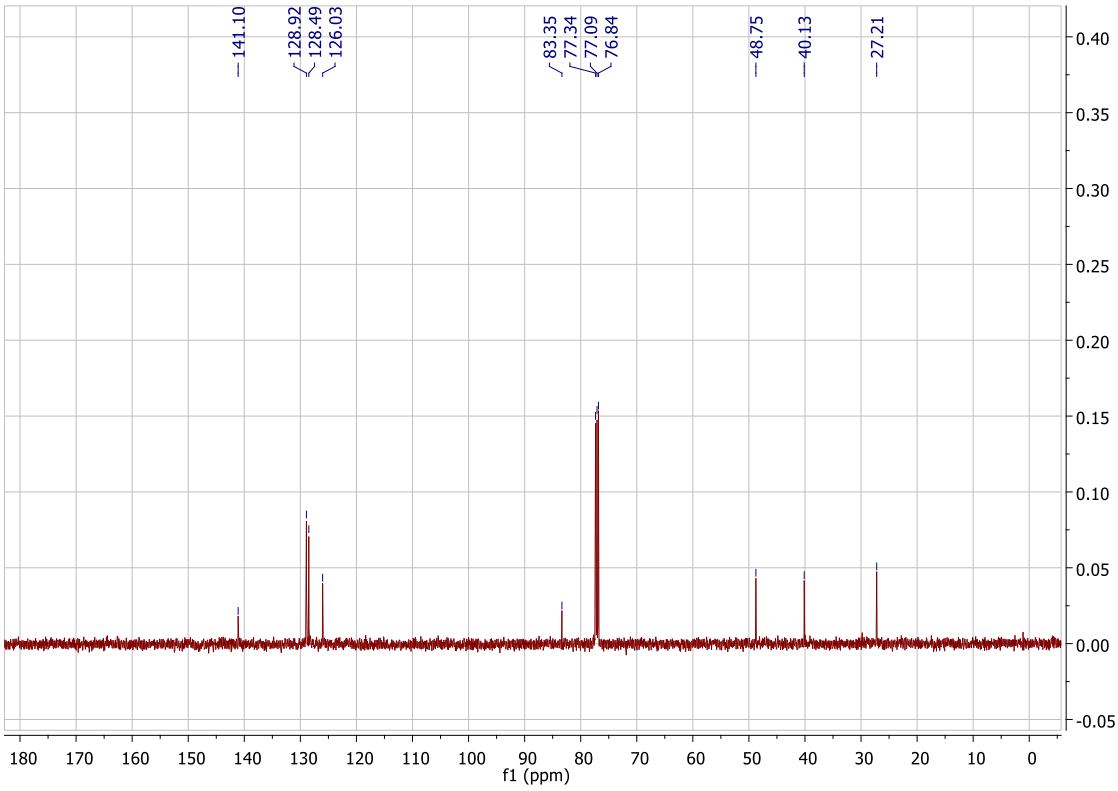
f1 (ppm)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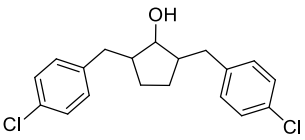
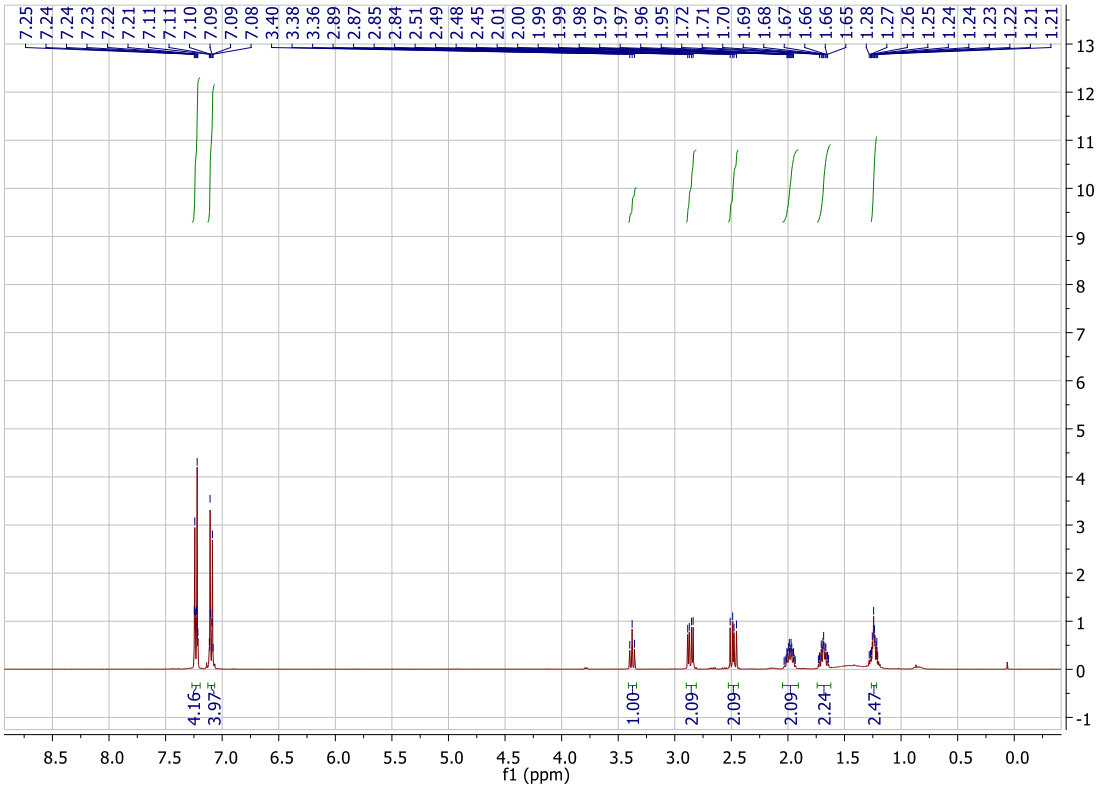
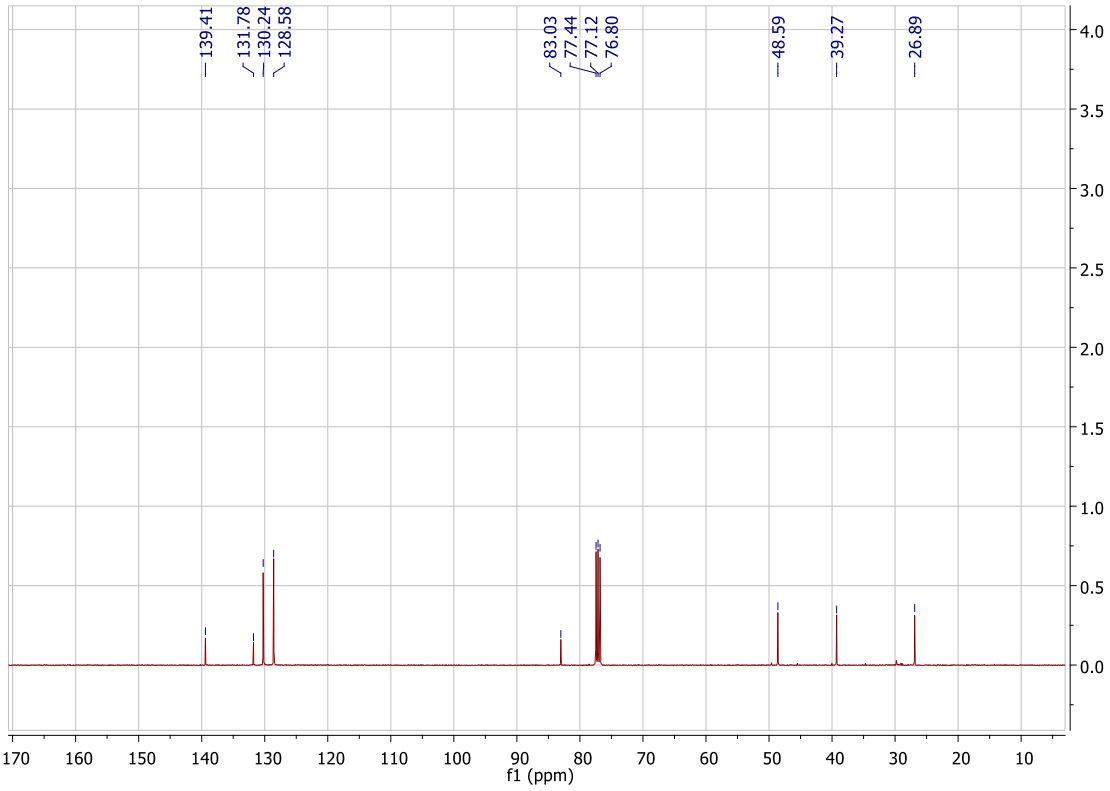
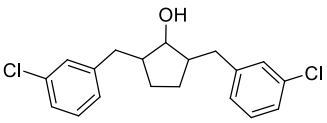
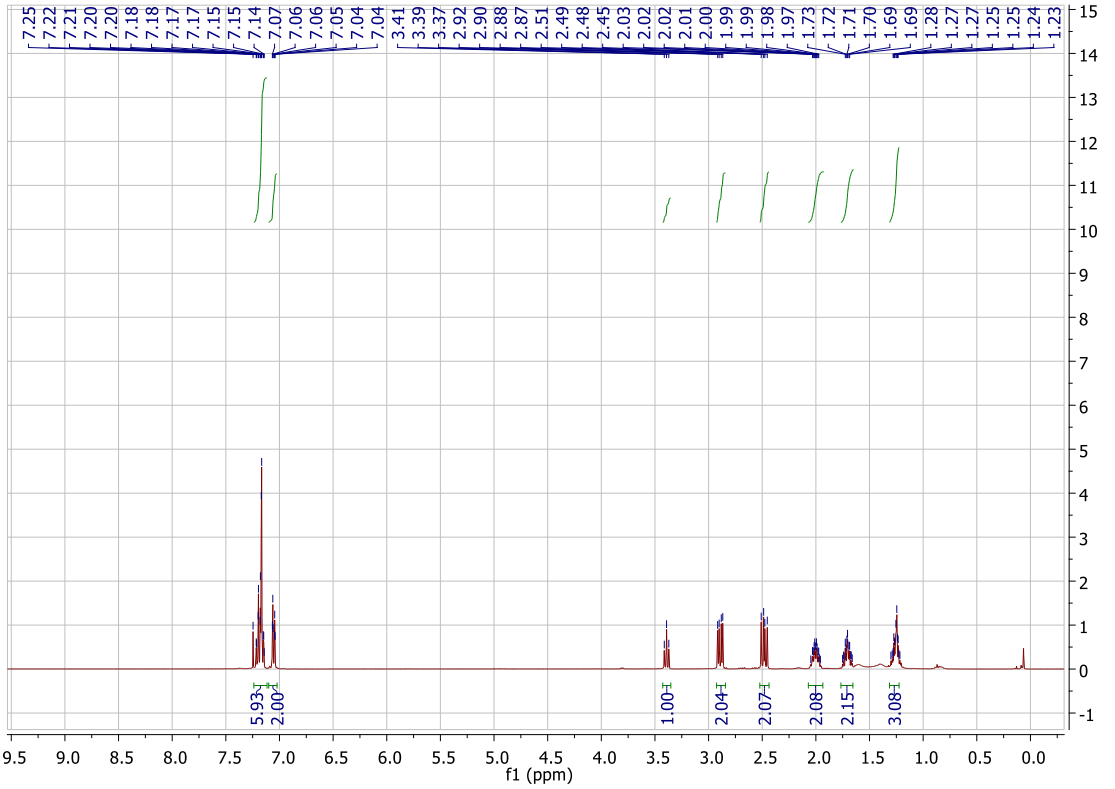
f1 (ppm)

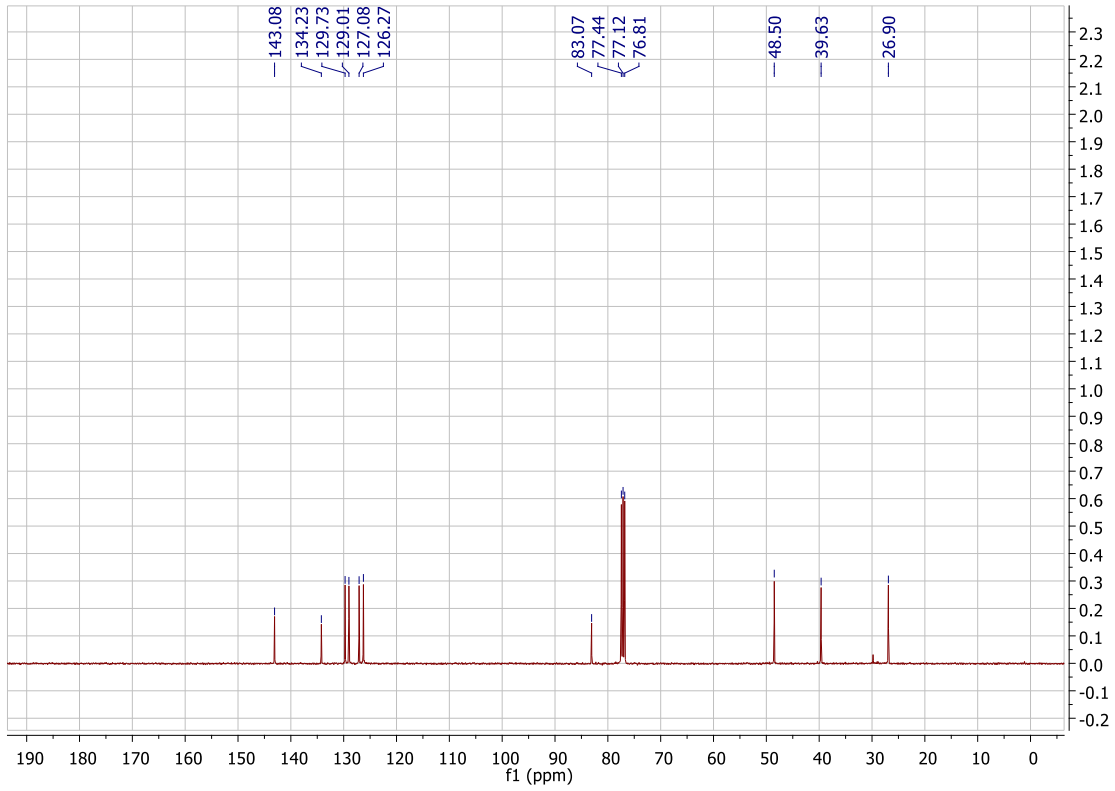

OH
Cl
Cl

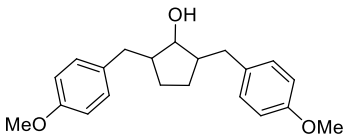

7.25 7.24 7.24 7.23 7.22 7.21 7.11 7.11 7.10 7.09 7.09 7.08 3.40 3.38 3.36 2.89 2.87 2.85 2.84 2.51 2.49 2.48 2.45 2.01 2.00 1.99 1.99 1.98 1.97 1.97 1.96 1.95 1.72 1.71 1.70 1.69 1.68 1.67 1.66 1.66 1.65 1.28 1.27 1.26 1.25 1.24 1.24 1.23 1.22 1.21 1.21
4.16
3.97
1.00
2.09
2.09
2.09
2.24
2.47
f1 (ppm)

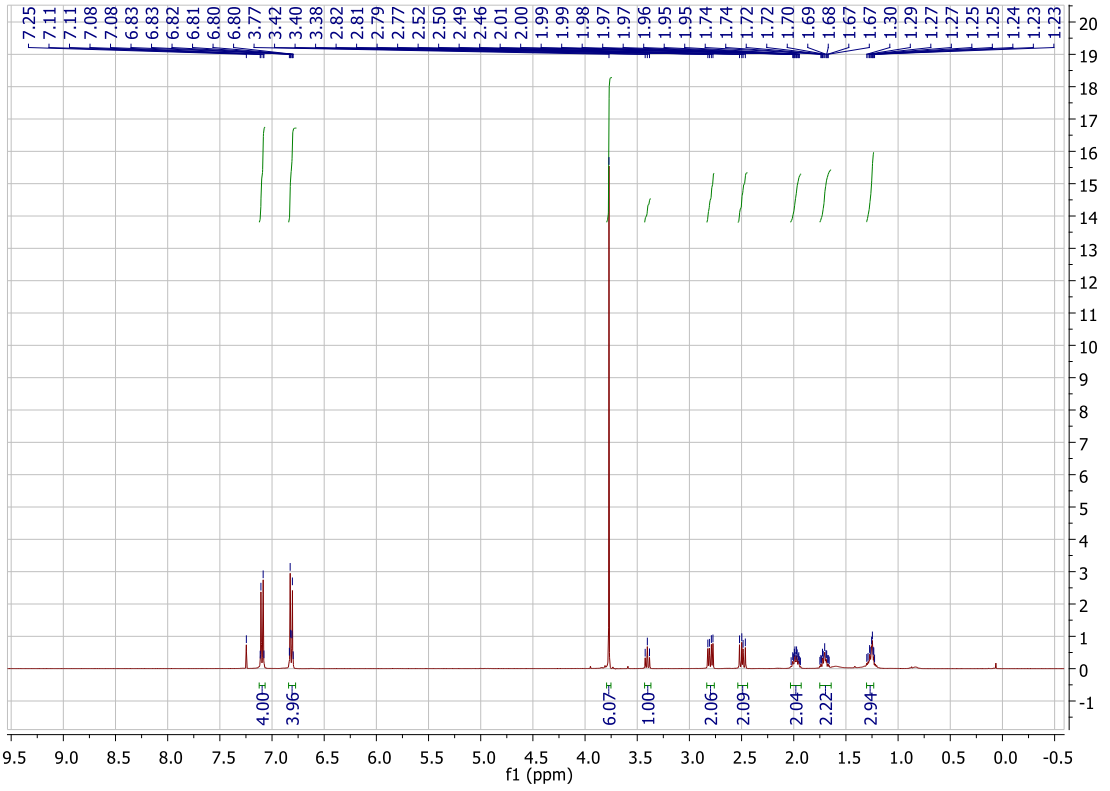

139.41
131.78
130.24
128.58
83.03
77.44
77.12
76.80
48.59
39.27
26.89
f1 (ppm)

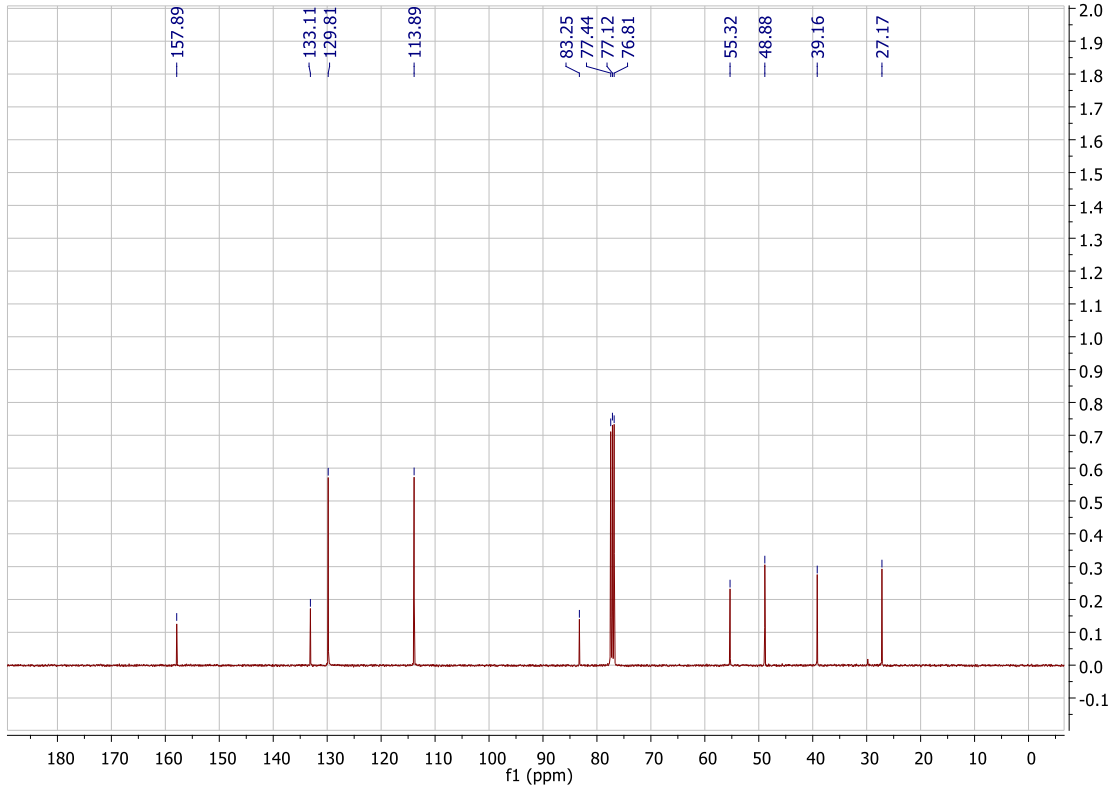

OH
Cl
Cl

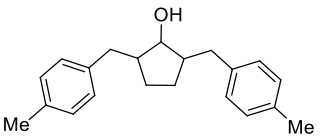

7.25 7.22 7.21 7.20 7.20 7.18 7.18 7.17 7.17 7.17 7.15 7.15 7.14 7.07 7.06 7.06 7.05 7.04 7.04
3.41 3.39 3.37 2.92 2.90 2.88 2.87 2.51 2.49 2.48 2.45 2.03 2.02 2.02 2.01 2.00 1.99 1.99 1.98 1.97 1.73 1.72 1.71 1.70 1.69 1.69 1.28 1.27 1.27 1.25 1.25 1.24 1.23
5.93 2.00 1.00 2.04 2.07 2.08 2.15 3.08
f1 (ppm)

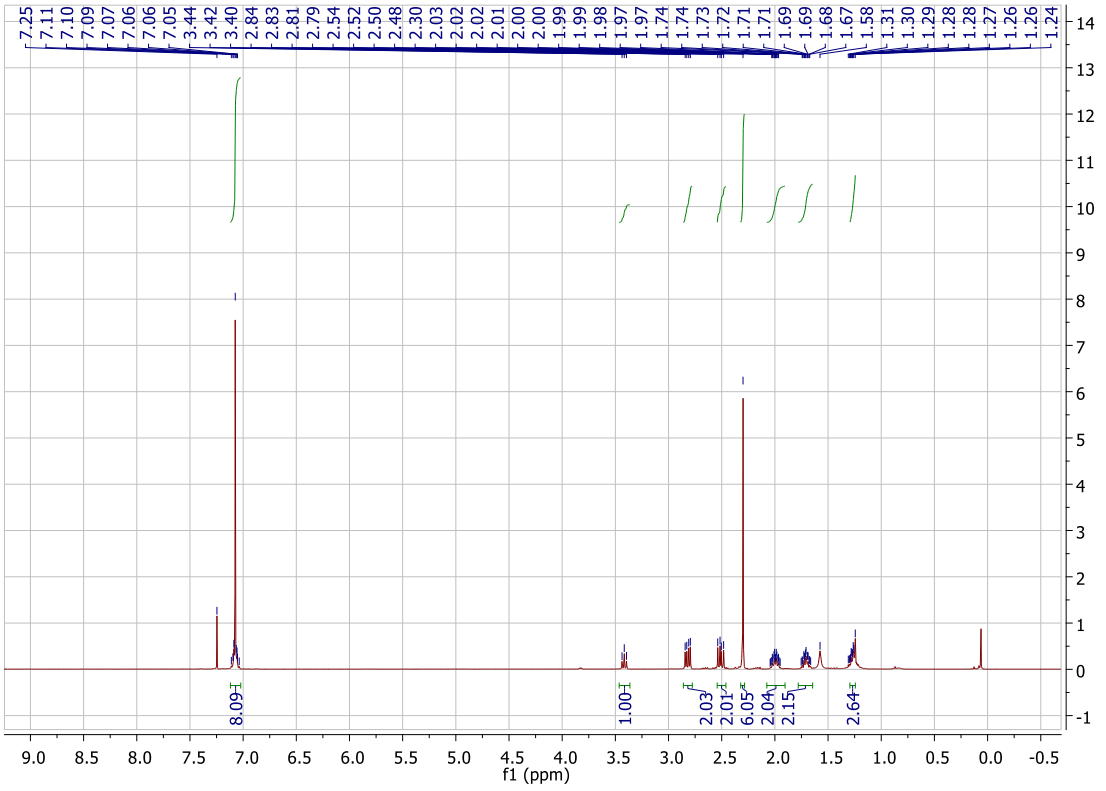

143.08 134.23 129.73 129.01 127.08 126.27
83.07 77.44 77.12 76.81
48.50 39.63 26.90
f1 (ppm)

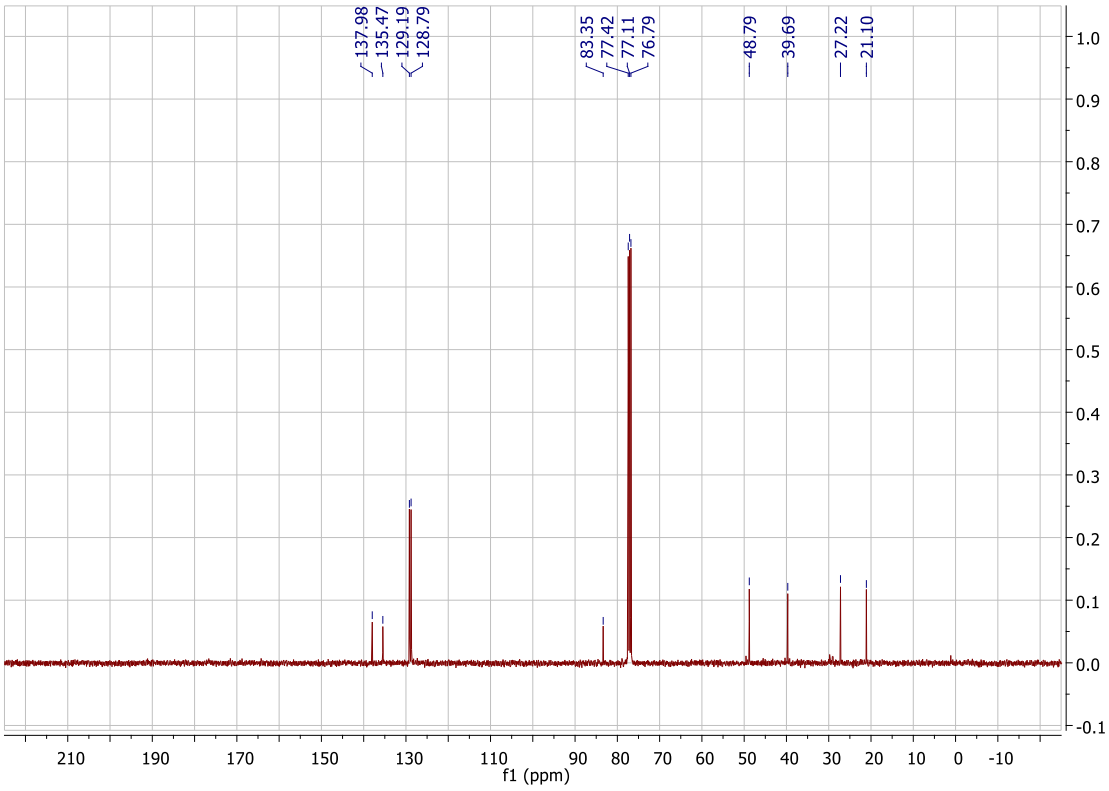

OH
MeO
OMe

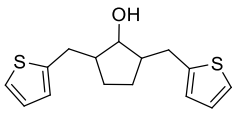

7.25 7.11 7.11 7.08 7.08 6.83 6.83 6.82 6.81 6.80 6.80 3.77 3.42 3.40 3.38 2.82 2.81 2.79 2.77 2.52 2.50 2.49 2.46 2.01 2.00 1.99 1.99 1.98 1.97 1.97 1.96 1.95 1.95 1.74 1.74 1.72 1.72 1.70 1.69 1.68 1.67 1.67 1.30 1.29 1.27 1.27 1.25 1.25 1.24 1.23 1.23
4.00 3.96 6.07 1.00 2.06 2.09 2.04 2.22 2.94
f1 (ppm)

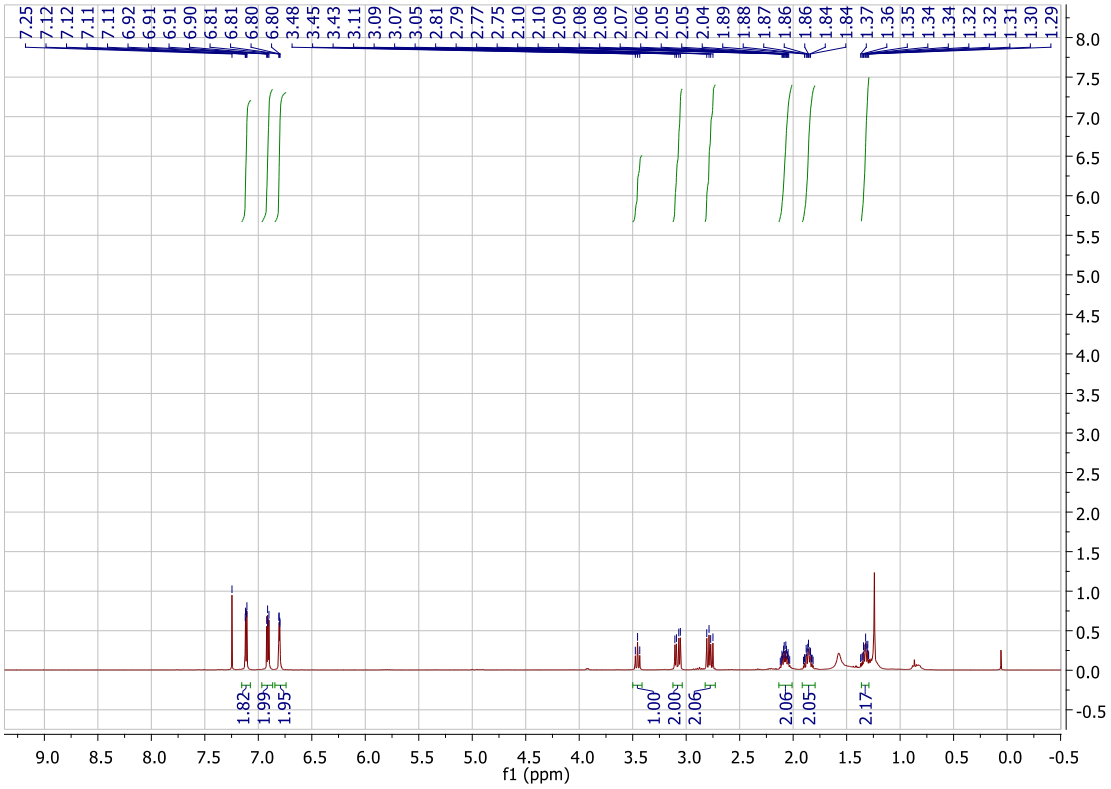

157.89 133.11 129.81 113.89 83.25 77.44 77.12 76.81 55.32 48.88 39.16 27.17
f1 (ppm)

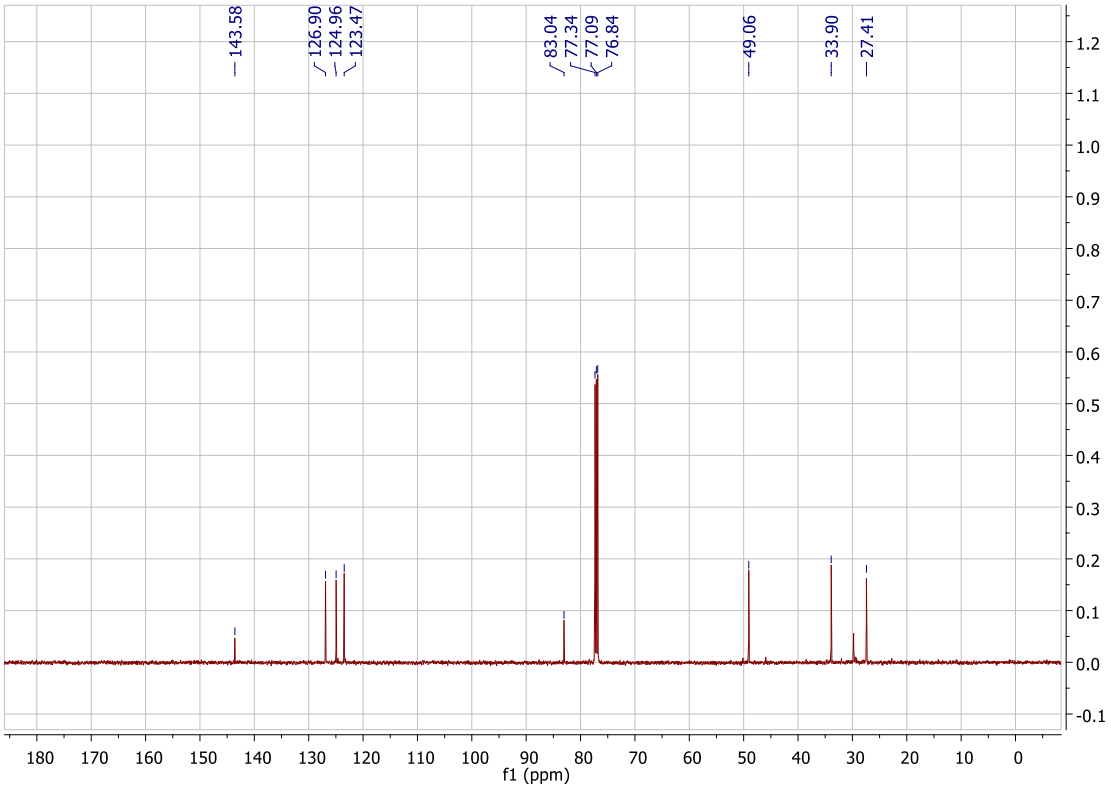

OH
Me
Me


7.25 7.11 7.10 7.09 7.07 7.06 7.06 7.05 3.44 3.42 3.40 2.84 2.83 2.81 2.79 2.54 2.52 2.50 2.48 2.30 2.03 2.02 2.02 2.01 2.00 2.00 1.99 1.99 1.98 1.97 1.97 1.74 1.74 1.73 1.72 1.71 1.71 1.69 1.69 1.68 1.67 1.58 1.31 1.30 1.29 1.28 1.28 1.27 1.26 1.26 1.24
8.09
1.00
2.03
2.01
6.05
2.04
2.15
2.64
f1 (ppm)


137.98
135.47
129.19
128.79
83.35
77.42
77.11
76.79
48.79
39.69
27.22
21.10
f1 (ppm)


OH
S
S


7.25 7.12 7.12 7.11 7.11 6.92 6.91 6.91 6.90 6.81 6.81 6.80 6.80 3.48 3.45 3.43 3.11 3.09 3.07 3.05 2.81 2.79 2.77 2.75 2.10 2.10 2.09 2.08 2.08 2.07 2.06 2.05 2.05 2.04 1.89 1.88 1.87 1.86 1.86 1.84 1.84 1.37 1.36 1.35 1.34 1.34 1.32 1.32 1.31 1.30 1.29
1.82 1.99 1.95 1.00 2.00 2.06 2.06 2.05 2.17
f1 (ppm)


143.58 126.90 124.96 123.47 83.04 77.34 77.09 76.84 49.06 33.90 27.41
f1 (ppm)

References.

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