Supporting information for

Synthesis of unsaturated secondary amines by direct reductive amination of aliphatic aldehydes with nitroarenes over Au/Al_2O_3 catalyst in a continuous flow mode

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1. Characterization of Au/Al_2O_3 catalyst samples

1.1. XRD data

XRD patterns of the as-prepared and regenerated Au/γ-Al_2O_3 catalysts were recorded on a Shimadzu XRD-7000 diffractometer using CuK_α radiation (λ = 0.15418 nm) and Ni filter on the reflected beam. The data were collected for 50 s per step with a 0.1° step size in the 2Θ range between 30° and 90°. XRD data are presented in Figure S3. The volume-averaged crystallite sizes (D) of the face centred cubic structure of Au particles were determined from the value of the integral breadths of the (111), diffraction peak, using the Scherrer equation [*B.D. Cullity, Elements of X-ray Diffraction, 2nd ed., Addison-Wesley Publishing Company, Reading, Massachusetts, USA, 1978.*] after subtraction of contribution of the γ-Al_2O_3 support. According to XRD data the volume-averaged crystallite sizes of the gold nanoparticles for as-prepared Au/Al_2O_3 catalyst is about 3.5 nm. The regenerated Au/Al_2O_3 catalyst has the same mean diameter of the gold nanoparticles as the as-prepared catalyst (Figure S1).

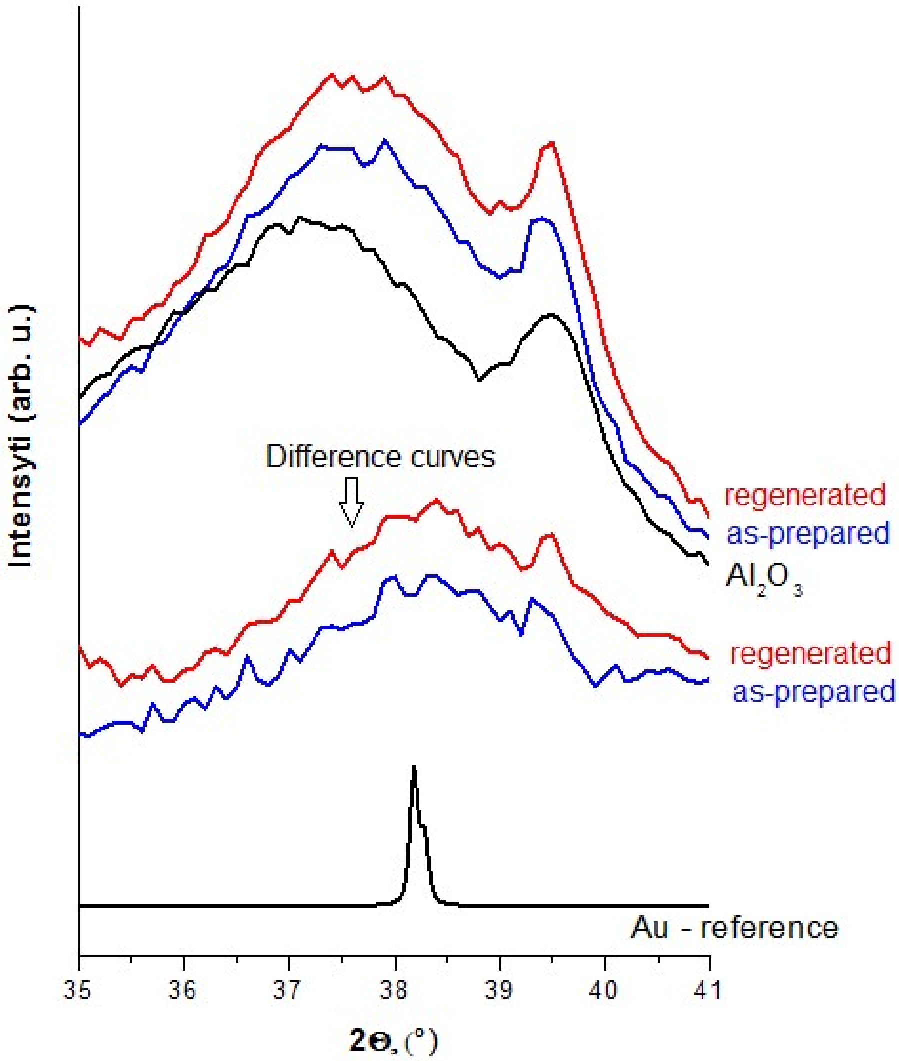


Figure S1. Fragments of X-ray diffraction patterns for as-prepared and regenerated Au/Al_2O_3 catalyst.

1.2. TG–DSC–MS data for the regenerated Au/Al$_2$O$_3$ catalyst

The simultaneous TG–DSC–MS measurement of the as-prepared, spent and regenerated catalysts was performed in an apparatus consisting of a STA 449 F1 Jupiter thermal analyzer and a QMS 403D Aëolos quadrupole mass spectrometer (NETZSCH, Germany). The spectrometer was connected online to a thermal analyzer (STA) instrument by a quartz capillary heated to 280 °C. The QMS was operated with an electron impact ionizer with the energy of 70 eV. The ion currents of the selected mass/charge (m/z) numbers were monitored in multiple ion detection (MID) mode with the collection time of 1 s for each channel. The measurements were made in a "synthetic air" flow (80 % vol. Ar and 20 % vol. O$_2$) in the temperature range of 30–800 °C using the heating rate of 10 °C min^{-1} the gas flow rate of 25 mL min^{-1} and open Al$_2$O$_3$ crucibles. The sample weight is 25 mg. The treatment of experiment results was performed using standard software Proteus Analysis [*NETZSCH Proteus Thermal Analysis v. 6.1.0 – NETZSCH-Gerätebau GmbH Selb/Bayern, Germany, 2013*]. TG, DTG, DSC and MS curves of the regenerated Au/Al$_2$O$_3$ catalyst are shown in Figure S2.

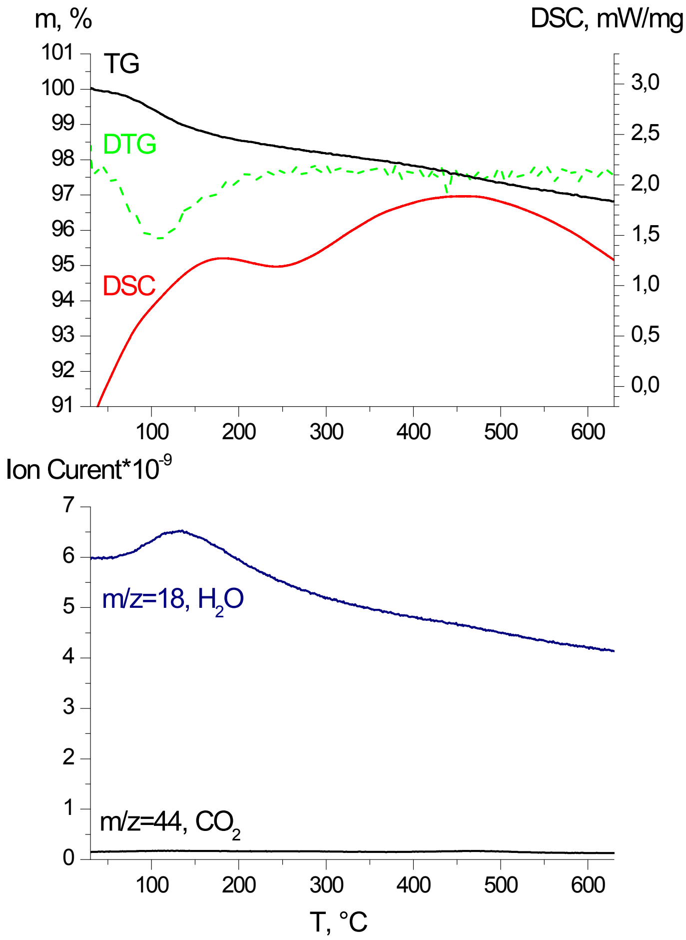
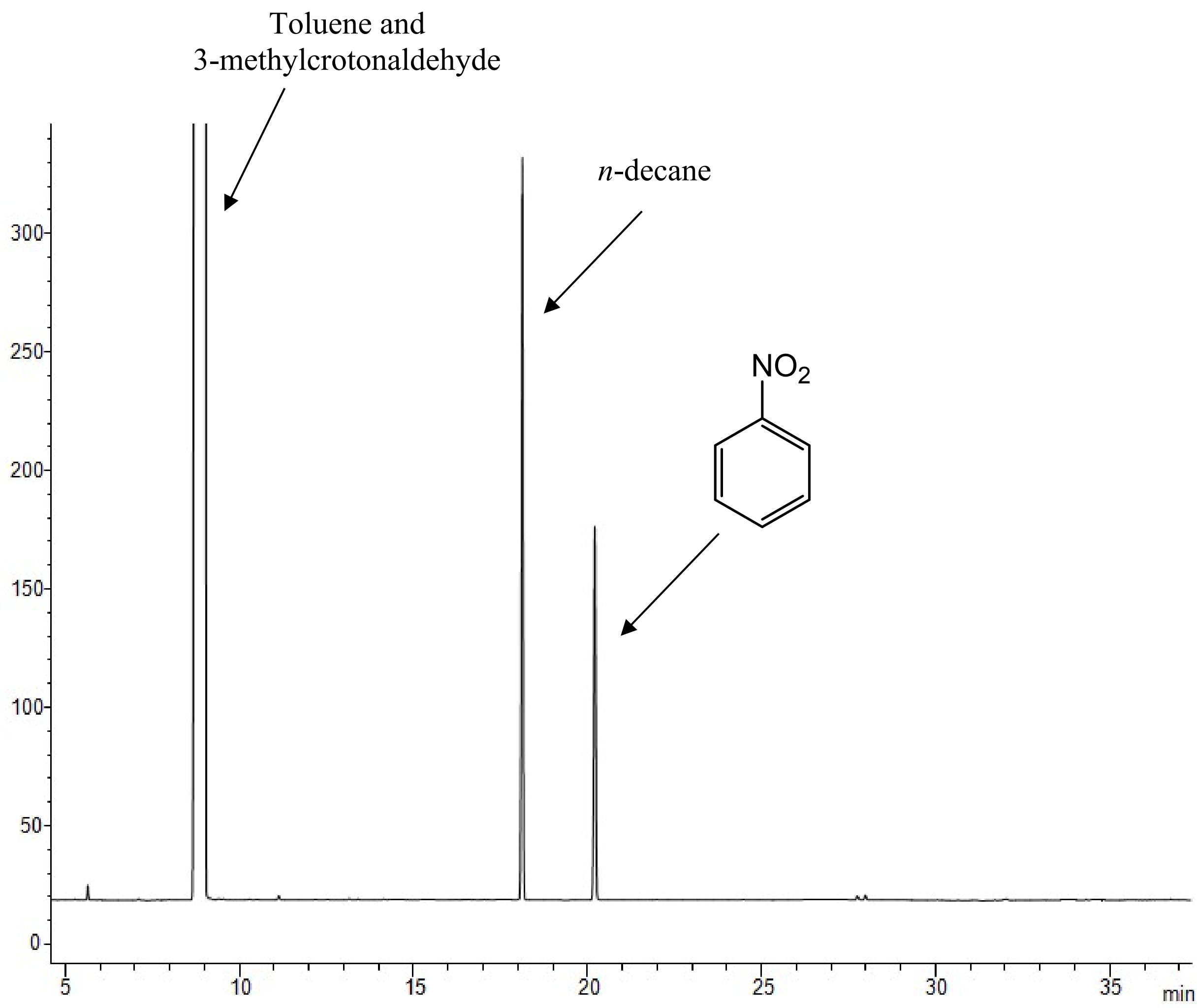


Figure S2. TG–DSC–MS data for the regenerated Au/Al$_2$O$_3$ catalyst.

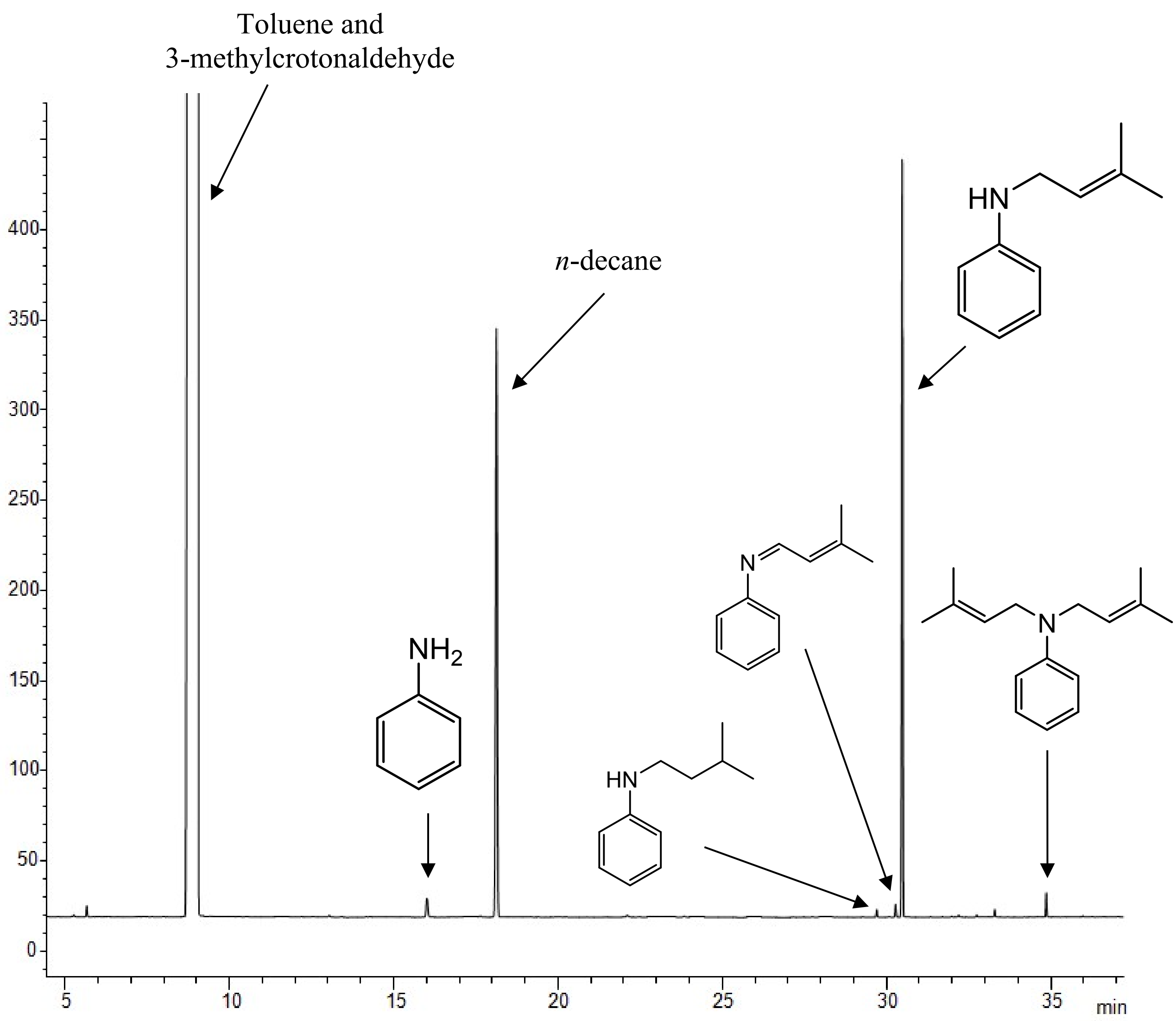
2. GC chromatograms

GC analysis was carried out using Agilent 6890N equipped with HP 5-MS column (60.0 m × 320 µm × 0.25 µm) and the flame ionization detector.

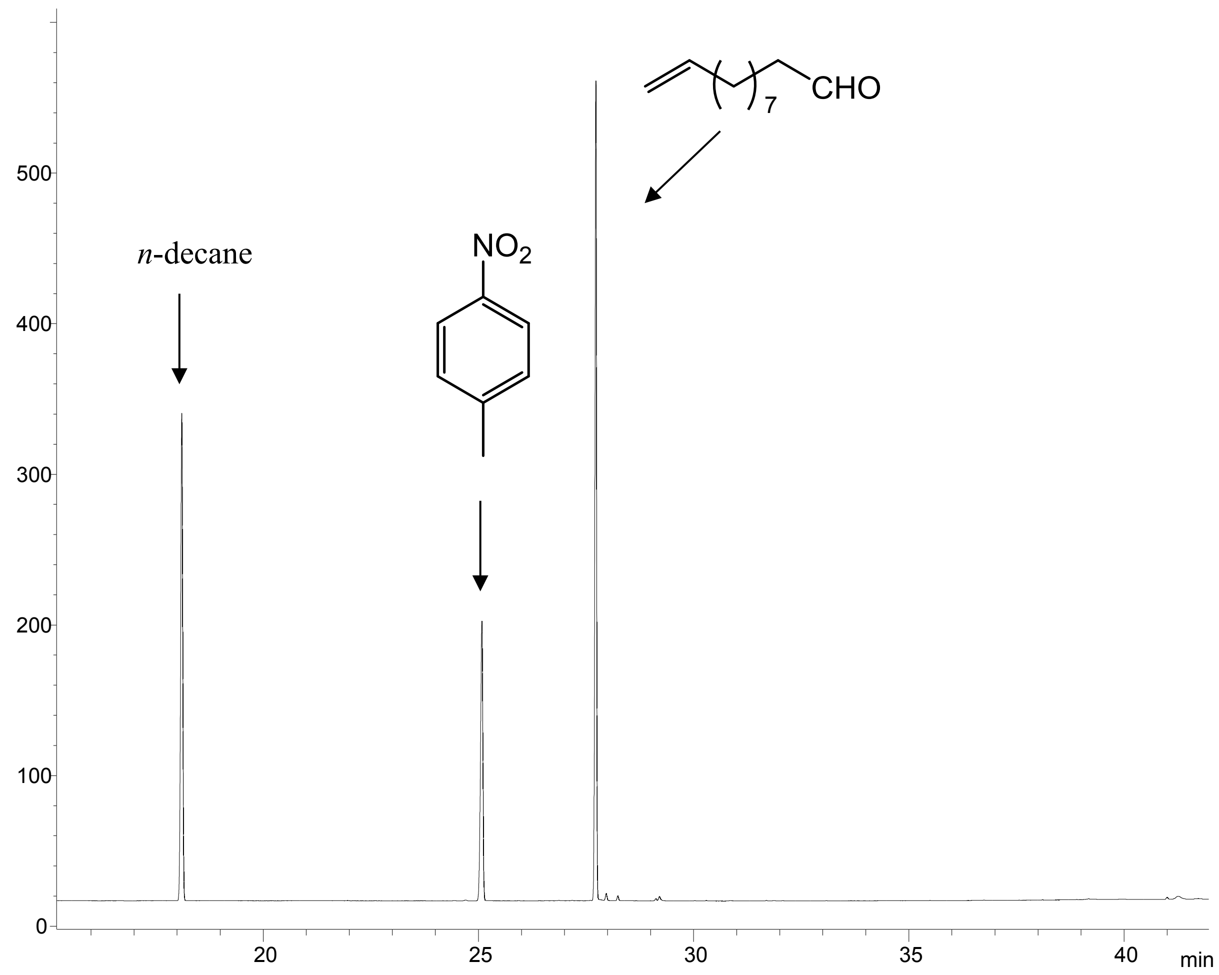
GC chromatogram for Table 1 Entry 1: before reaction.



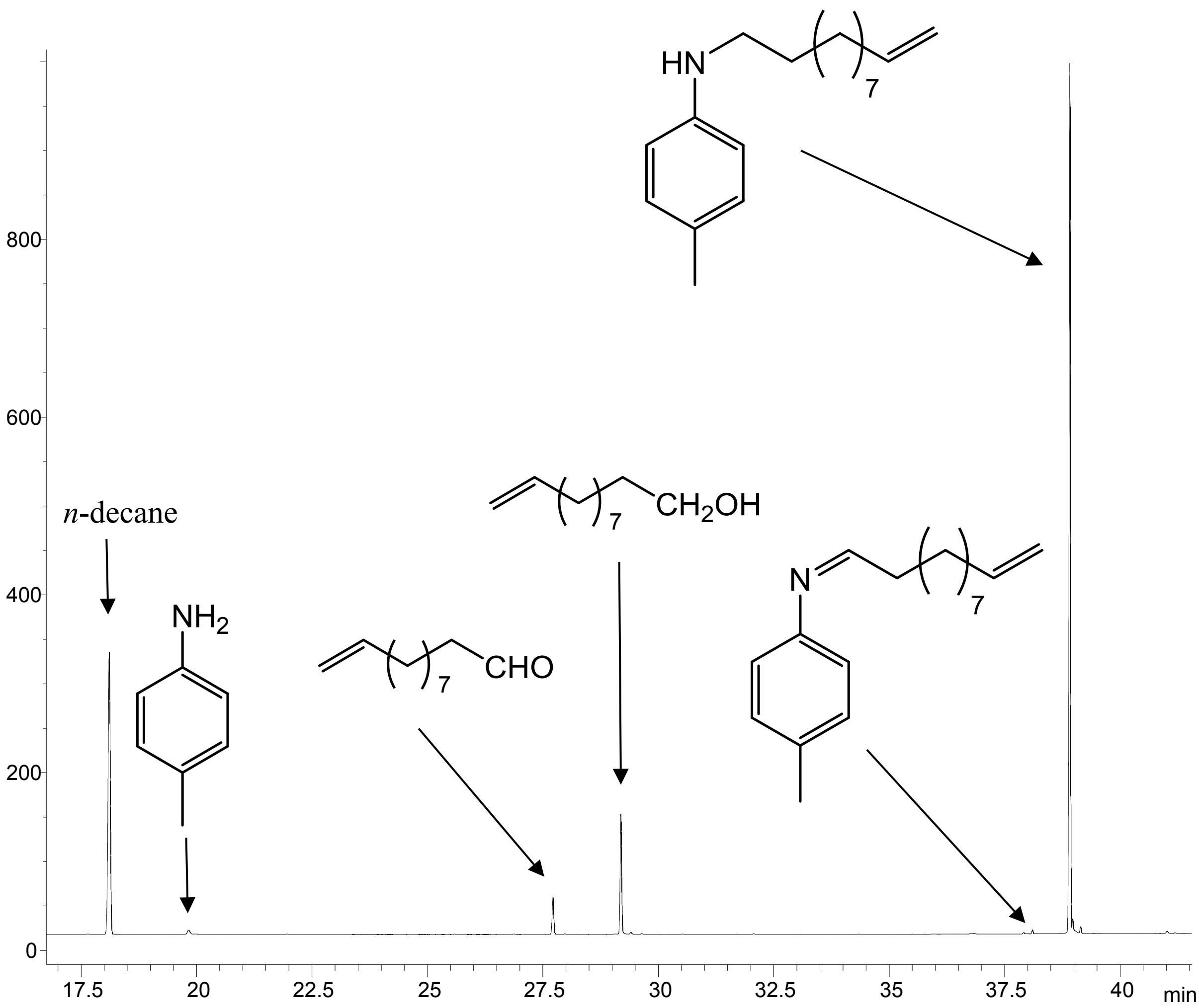
GC chromatogram for Table 1 Entry 1: after reaction.



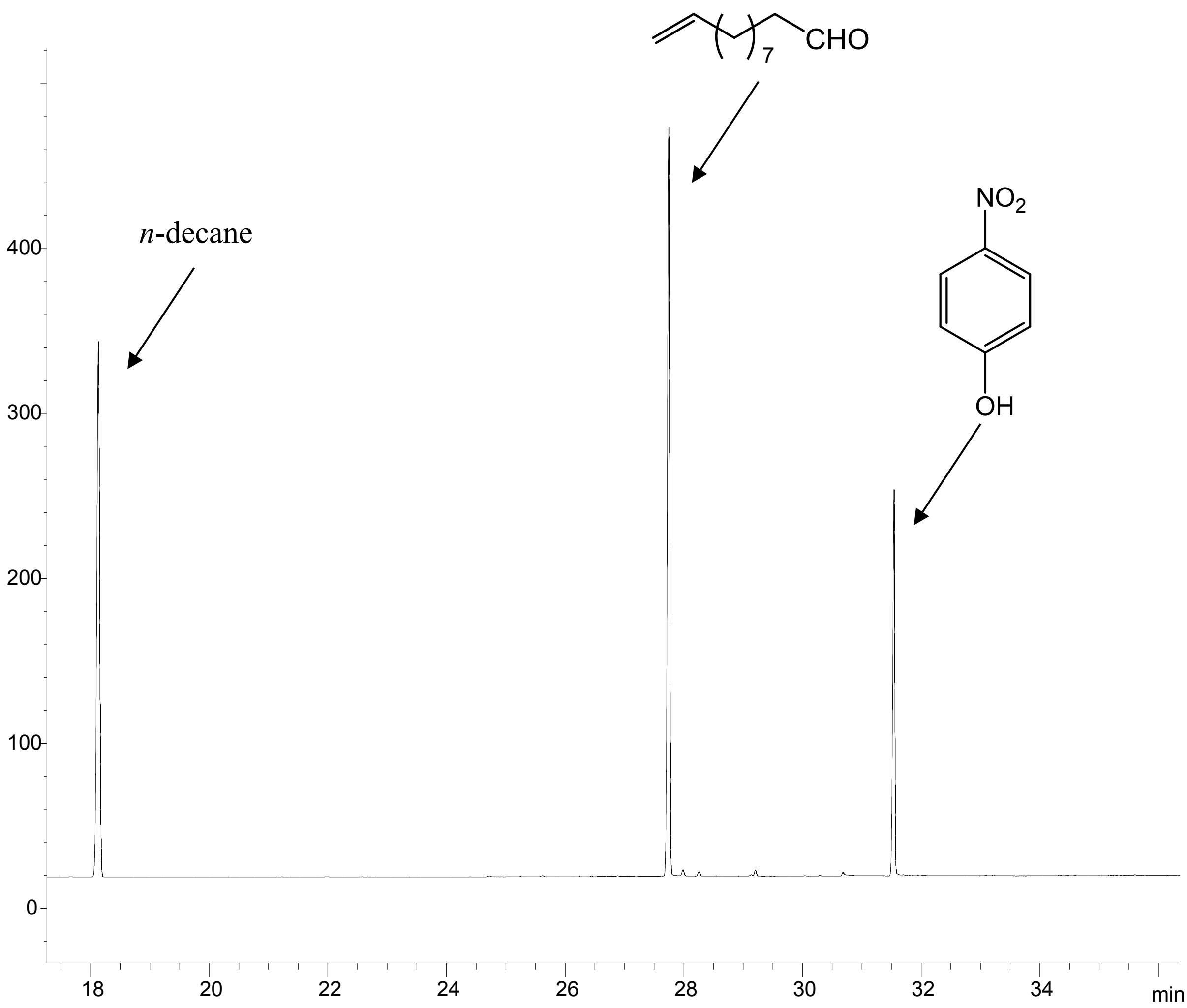
GC chromatogram for Table 1 Entry 7: before reaction.



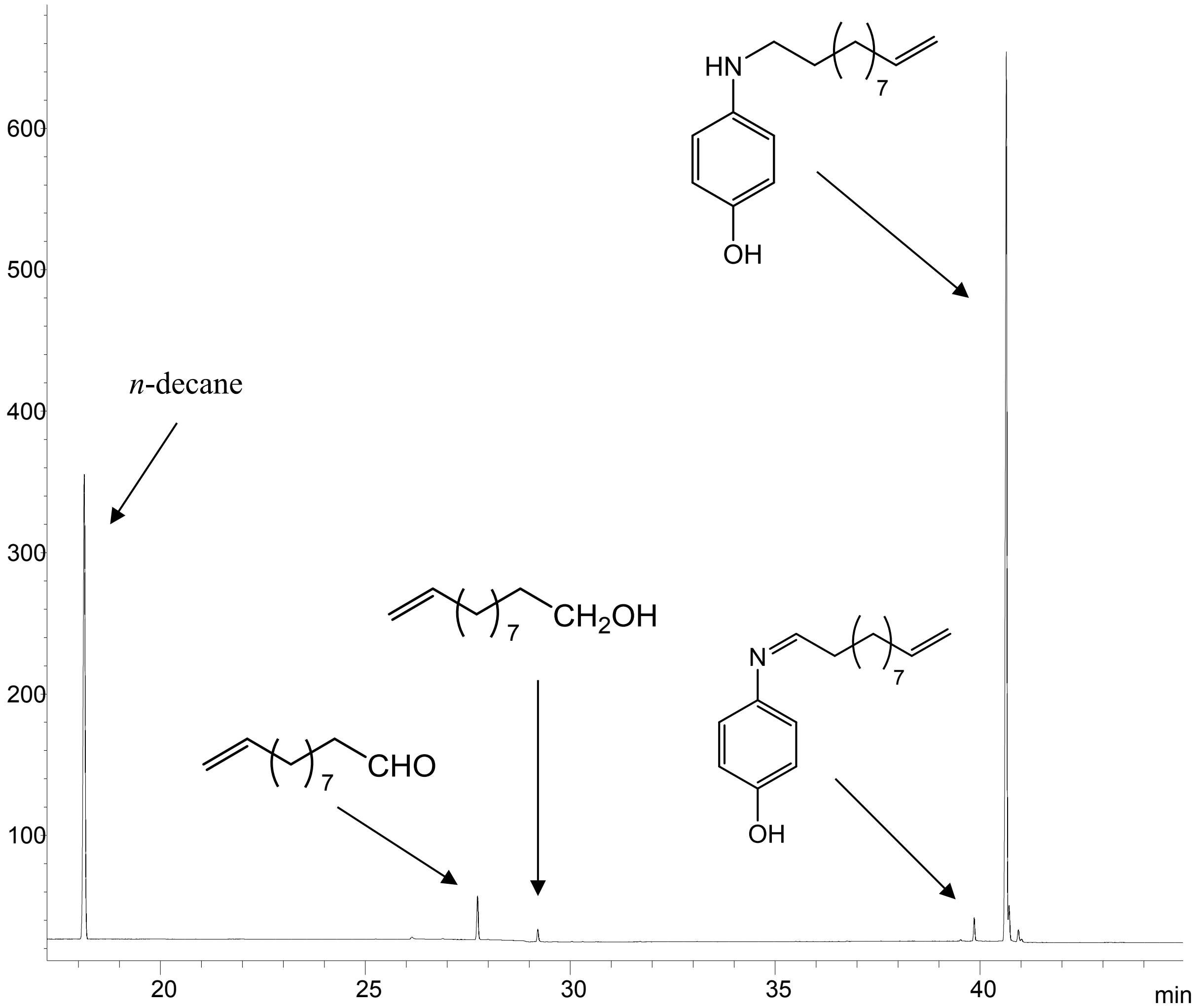
GC chromatogram for Table 1 Entry 7: after reaction.



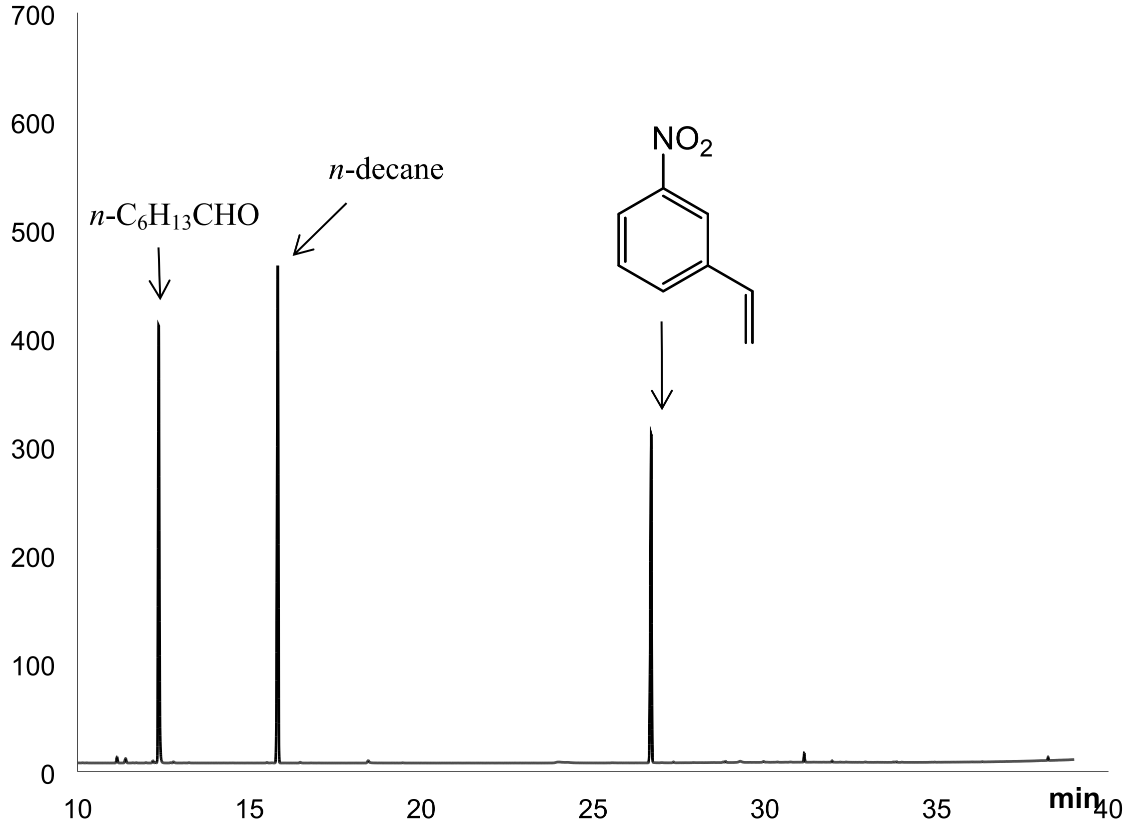
GC chromatogram for Table 2 Entry 5: before reaction.



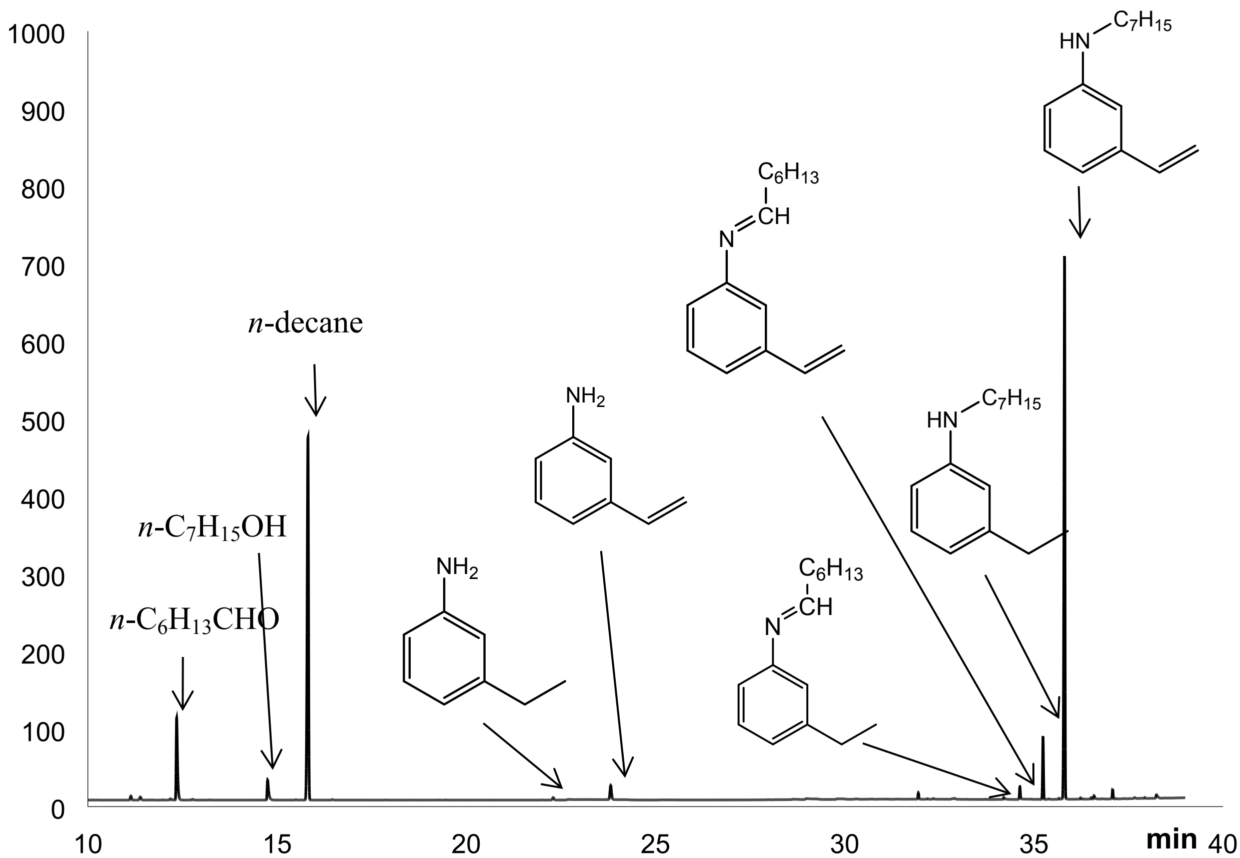
GC chromatogram for Table 2 Entry 5: after reaction.



GC chromatogram for Table 3 Entry 4: before reaction.

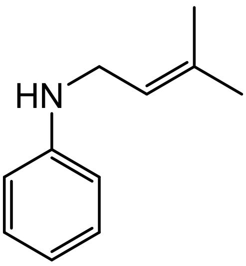


GC chromatogram for Table 3 Entry 4: after reaction.

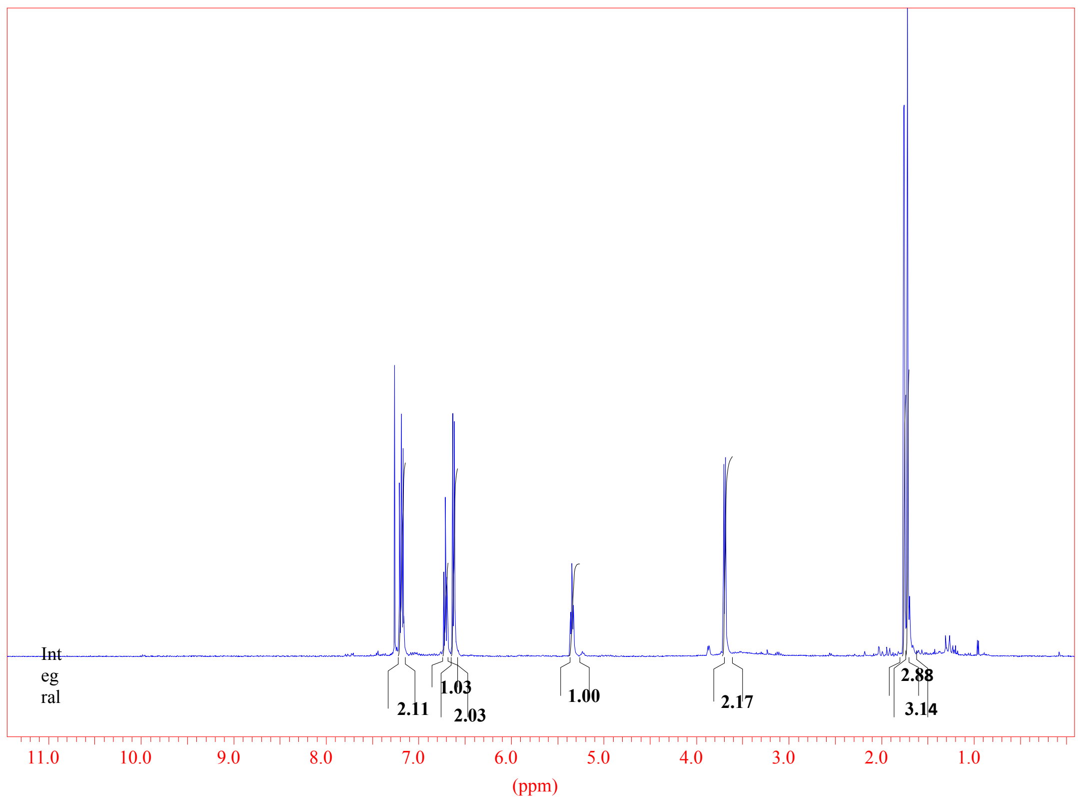


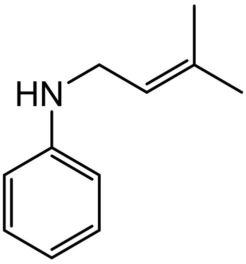
3. NMR data

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz on a Bruker AV400 spectrometer. The chemical shifts are reported relative to tetramethylsilane. The resonance of the residual protons of the solvent was used as internal standard for ^{1}H (δ 7.26 $CDCl_3$). The resonance of deuterium solvent was used as internal standard for ^{13}C (δ 77.0 $CDCl_3$). ^{1}H assignment abbreviations are the following: singlet (s), doublet (d), triplet (t), broad singlet (brs), doublet of doublets (dd) and multiplet (m).

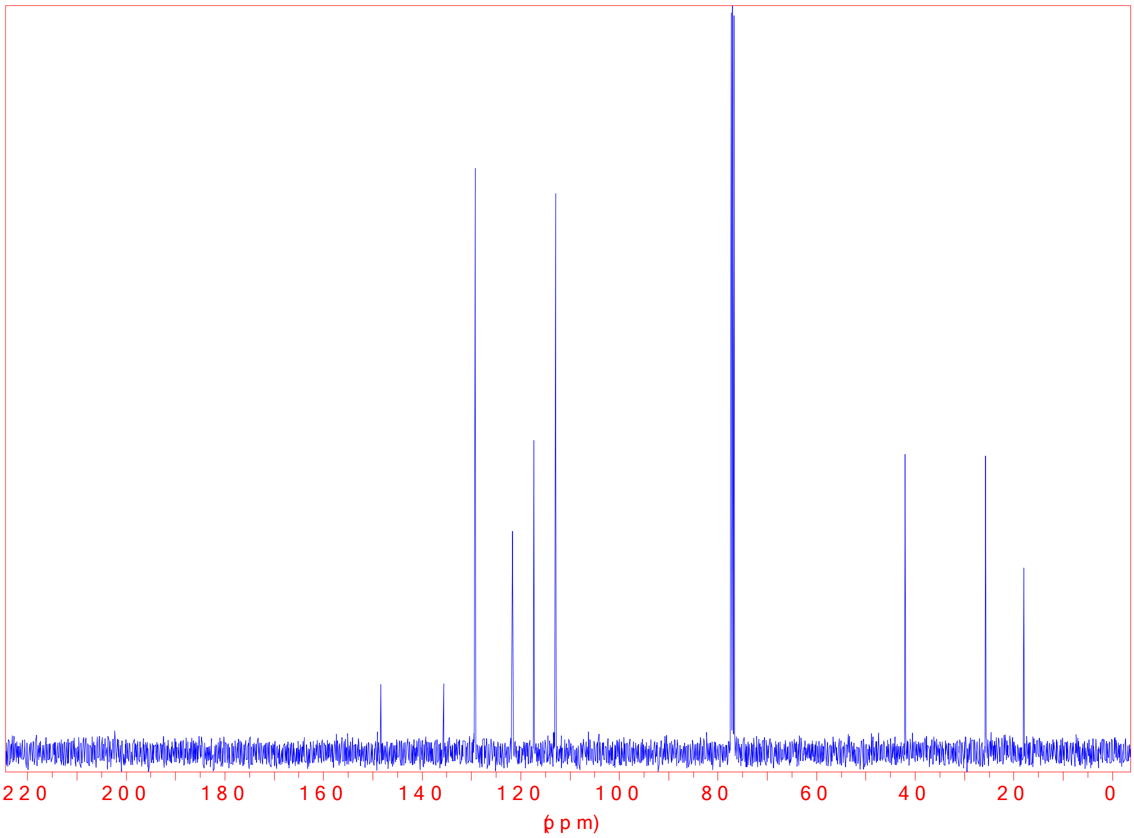


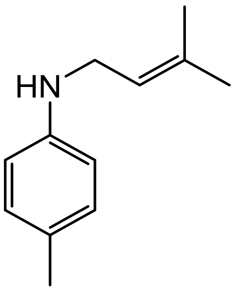
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70-1.73 (s, 3H), 1.74-1.77 (d, 3H), 3.64-3.72 (d, 2H), 5.27-5.38 (m, 1H), 6.58-6.65 (dd, 2H), 6.68-6.74 (m, 1H), 7.15-7.22 (m, 2H).



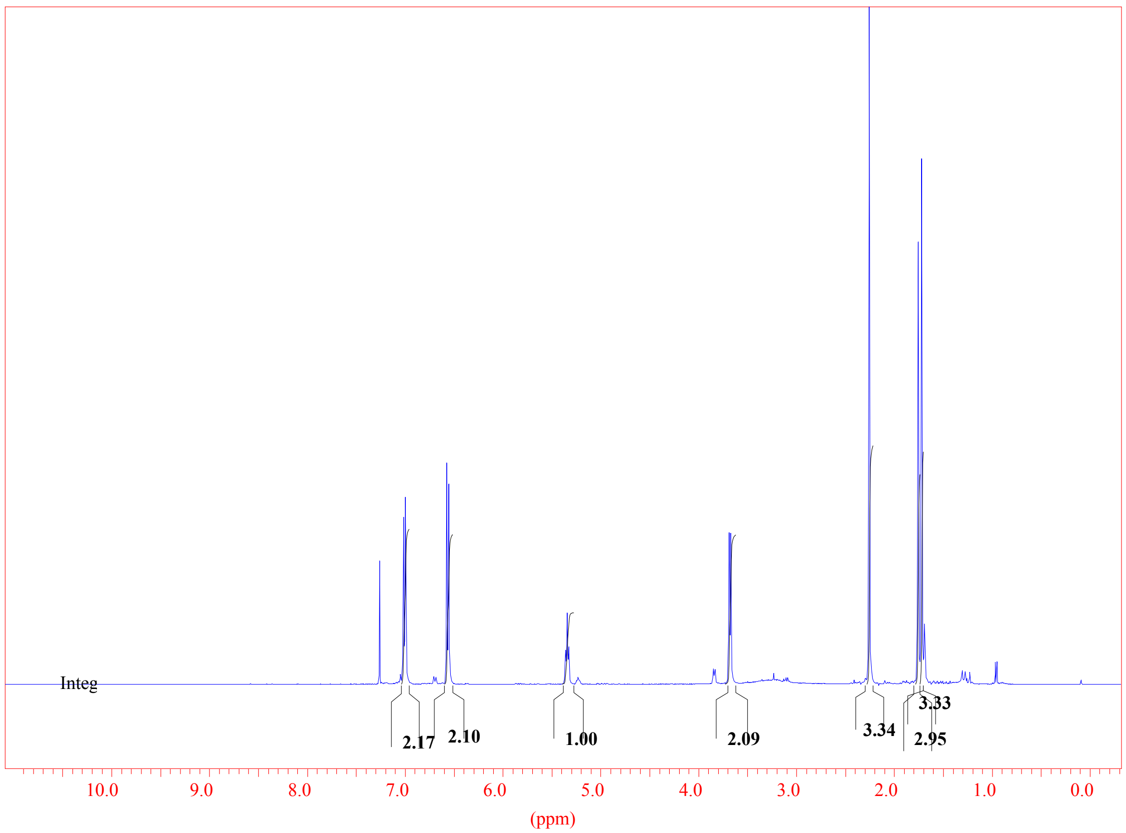


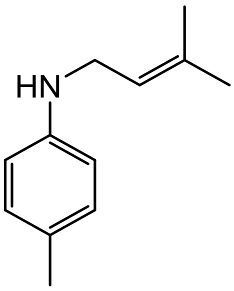
^{13}C NMR (100 MHz, $CDCl_3$): δ 18.0, 25.7, 42.0, 112.9, 117.3, 121.6, 129.2, 135.6, 148.5.



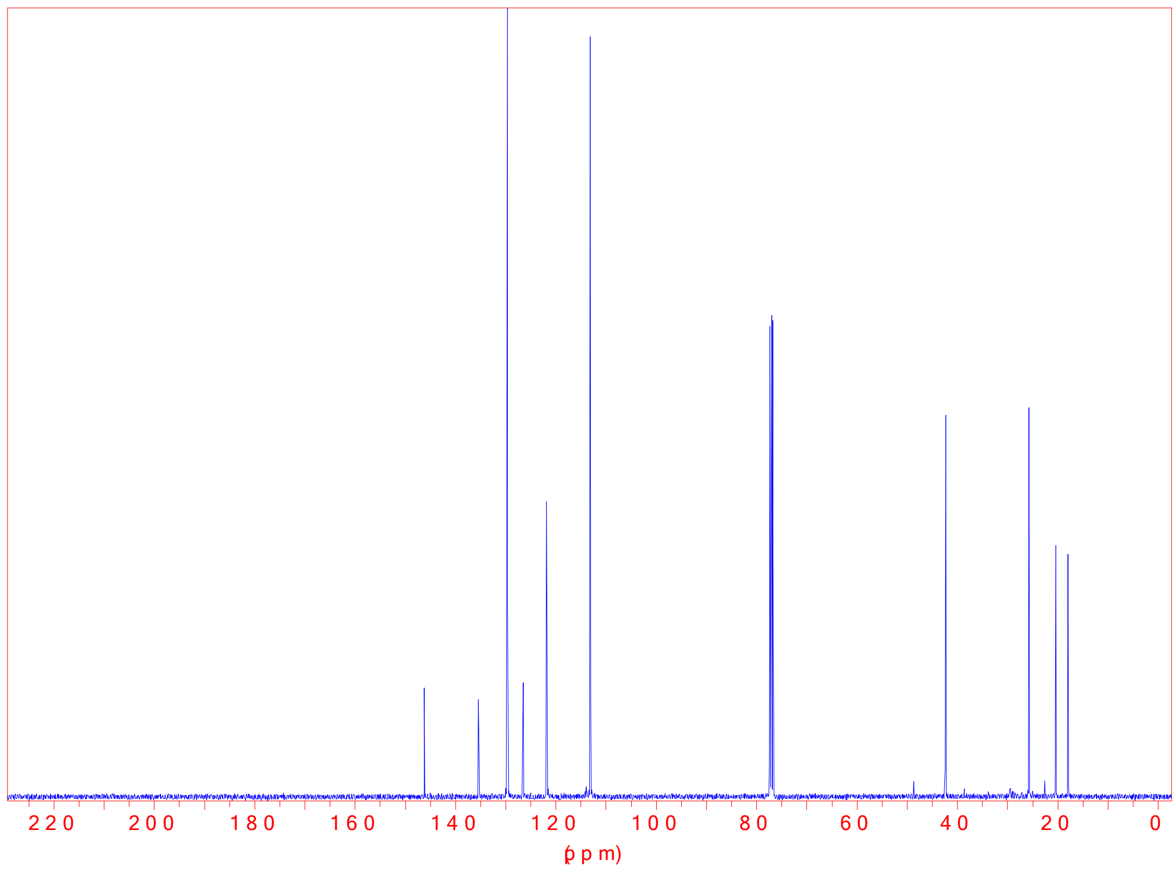


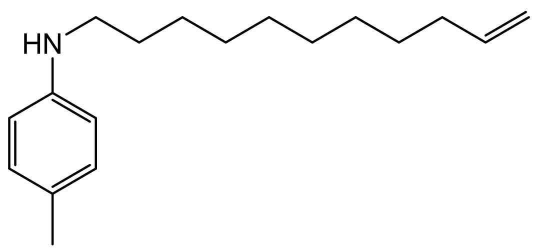
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70-1.74 (s, 3H), 1.74-1.77 (d, 3H), 2.21-2.28 (s, 3H), 3.63-3.72 (d, 2H), 5.30-5.39 (m, 1H), 6.52-6.59 (d, 2H), 6.97-7.04 (d, 2H).



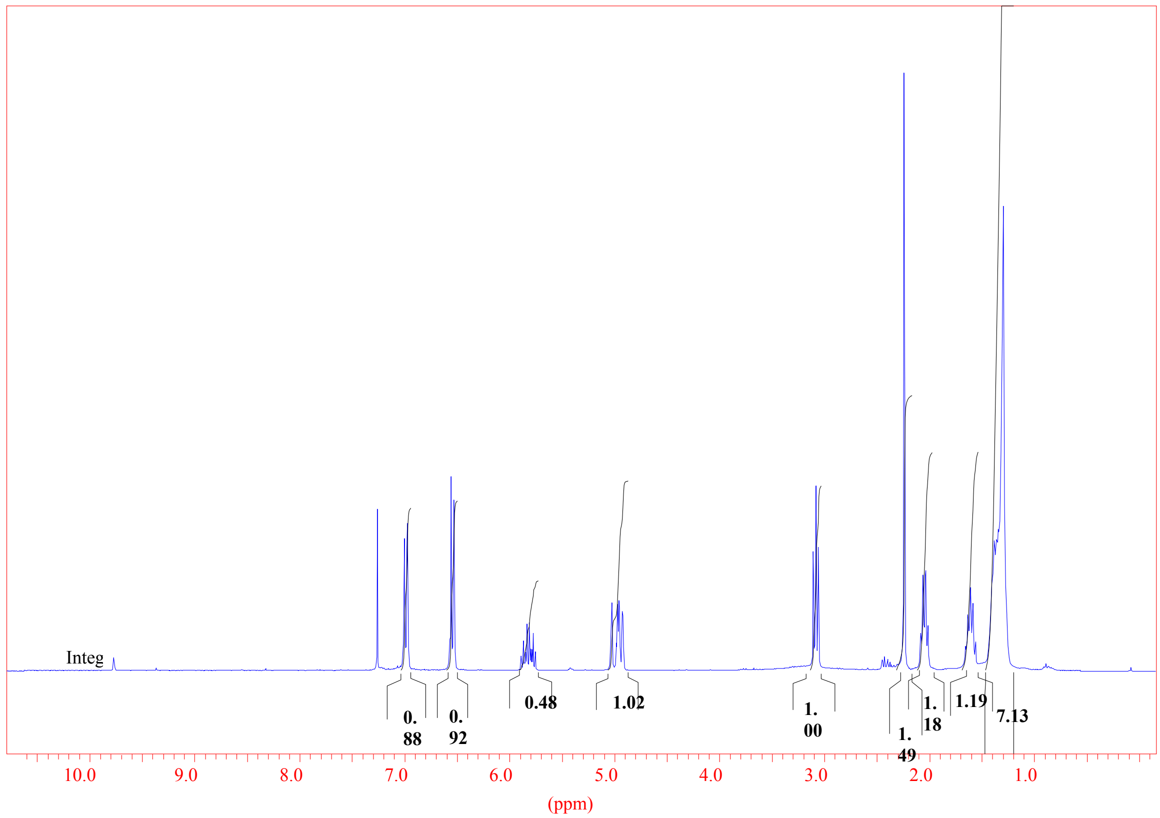


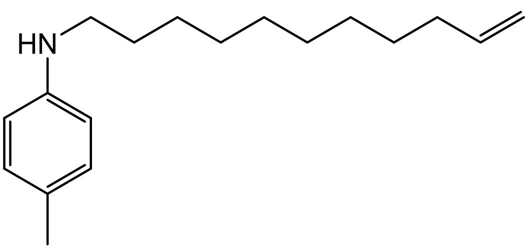
^{13}C NMR (100 MHz, $CDCl_3$): δ 18.0, 20.4, 25.7, 42.3, 113.1, 121.8, 126.5, 129.7, 135.4, 146.1.



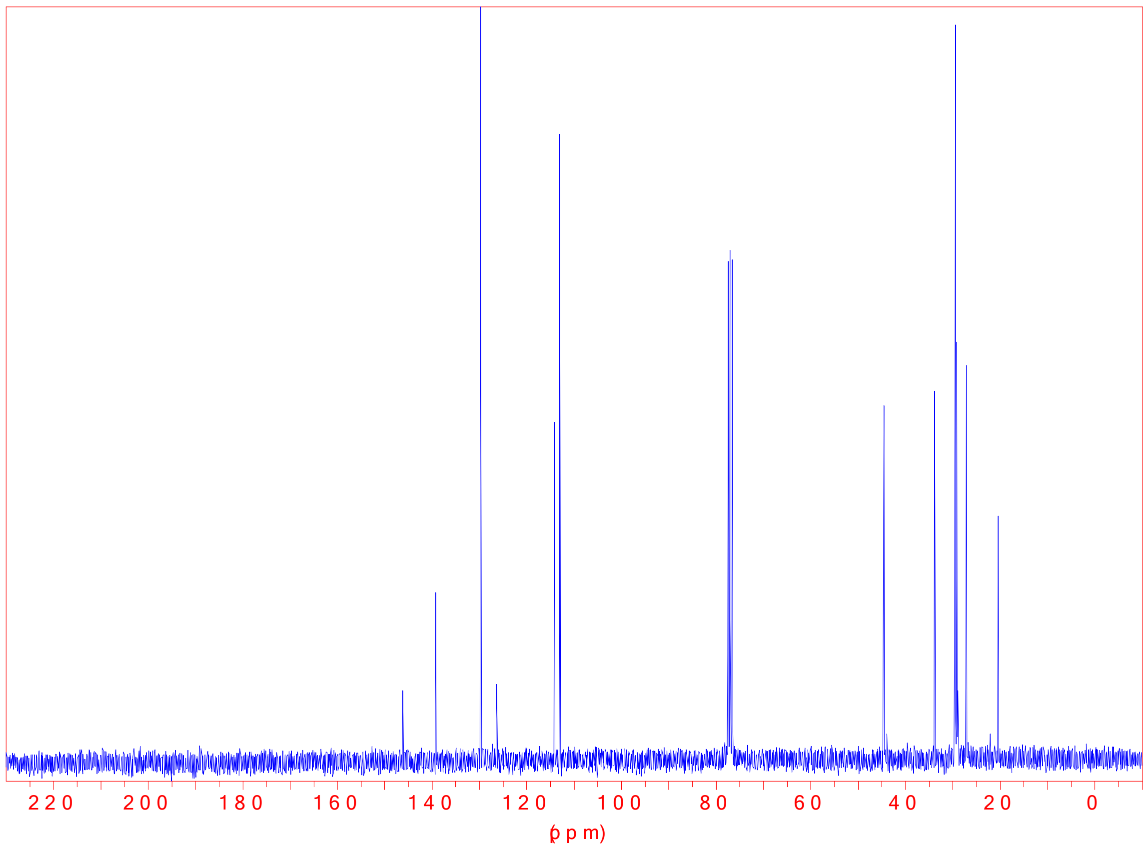


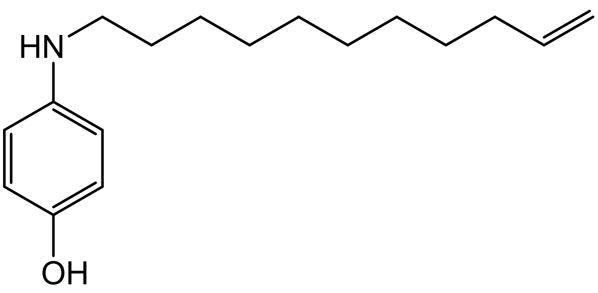
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23-1.46 (m, 12H), 1.54-1.68 (m, 2H), 1.99-2.11 (m, 2H), 2.22-2.28 (s, 3H), 3.04-3.13 (t, 2H), 4.89 -5.06 (m, 2H), 5.74-5.91 (m, 1H), 6.50-6.59 (d, 2H), 6.94-7.03 (d, 2H).



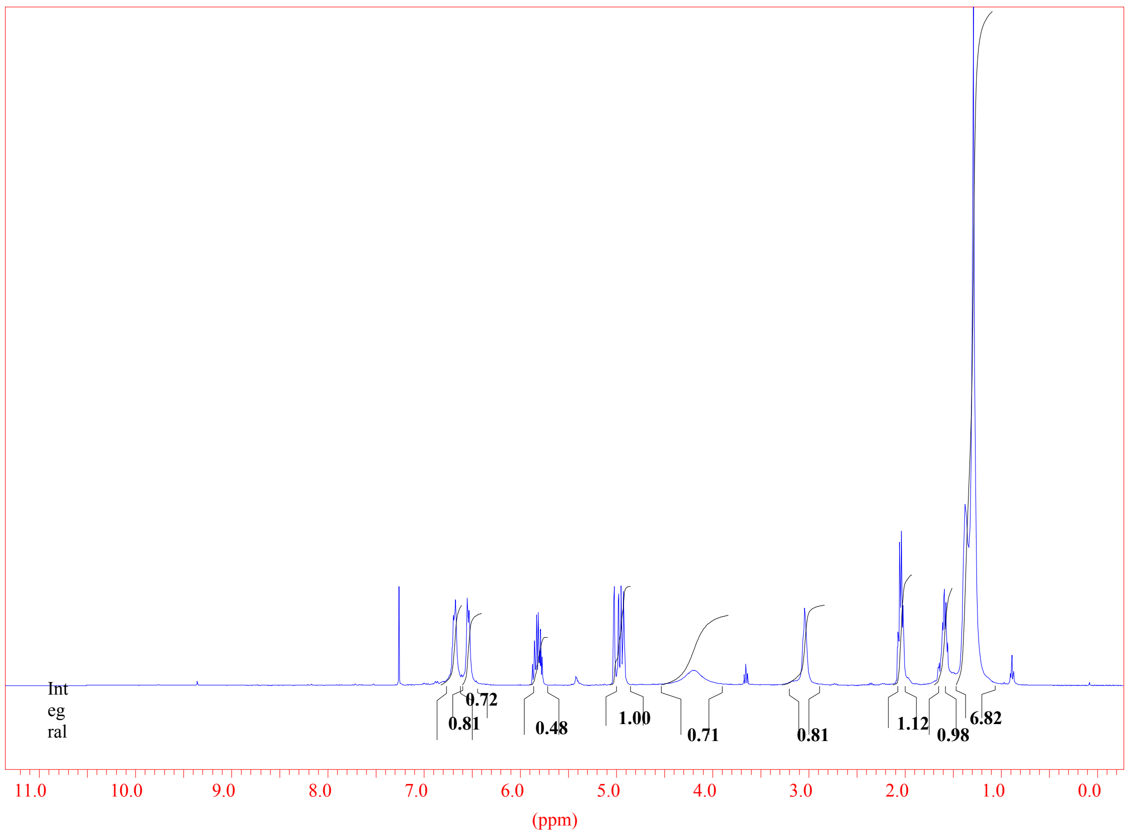


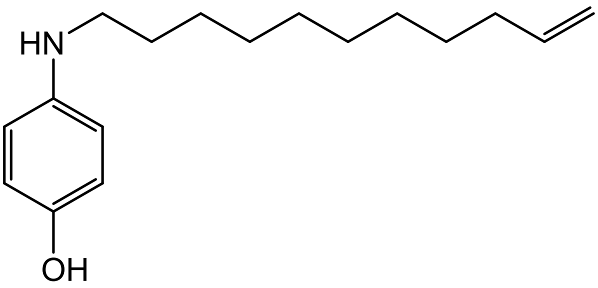
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 27.2, 28.9, 29.1, 29.4, 29.5, 29.6, 33.8, 44.5, 113.0, 114.1, 126.4, 129.7, 139.3, 146.2.



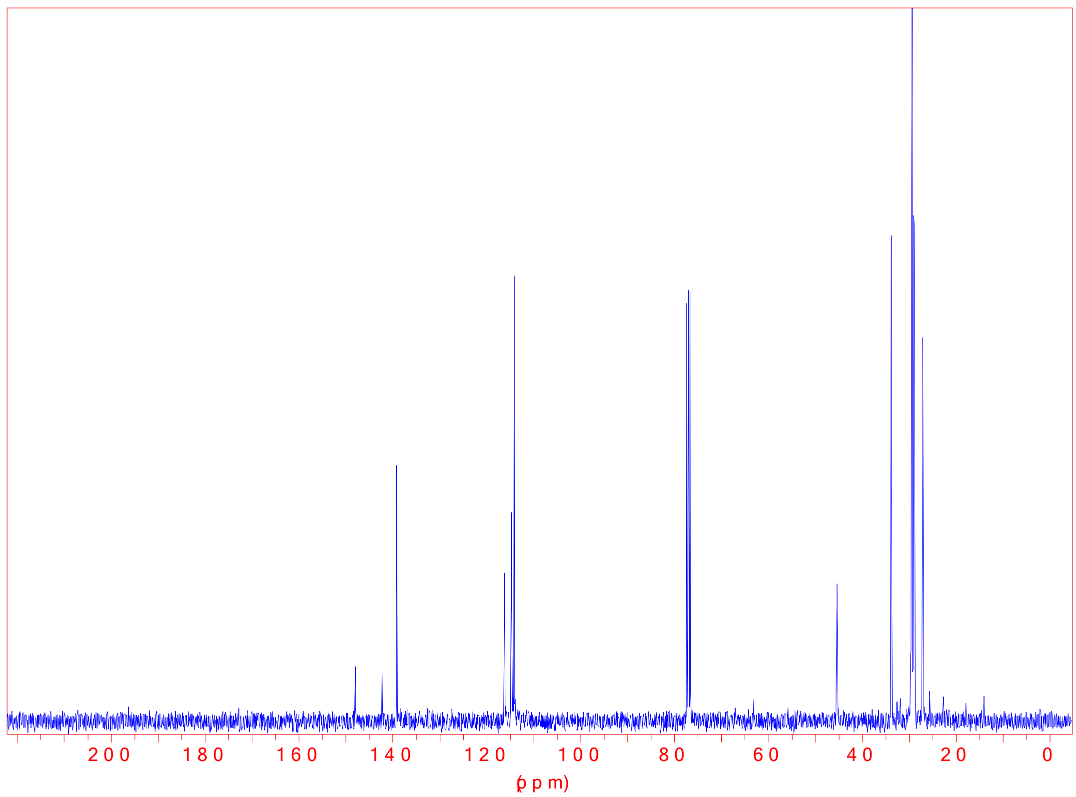


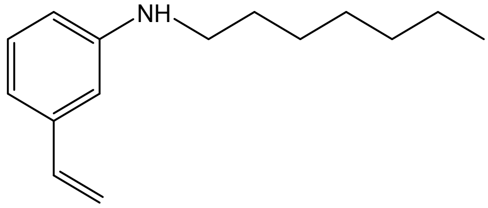
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01-1.48 (m, 12H), 1.51-1.69 (m, 2H), 1.92-2.13 (m, 2H), 2.95-3.19 (t, 2H), 3.90-4.51 (brs, 1H), 4.88 -5.05 (m, 2H), 5.71-5.90 (m, 1H), 6.41-6.60 (d, 2H), 6.62-6.83 (d, 2H).



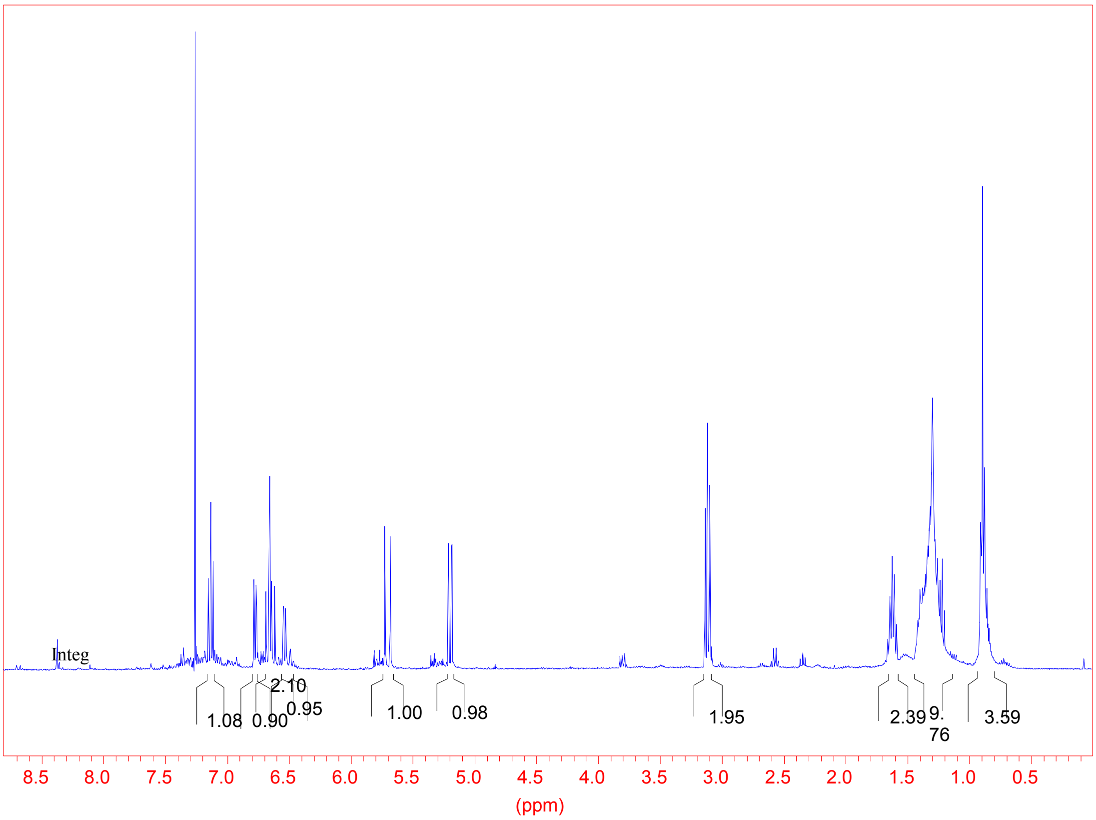


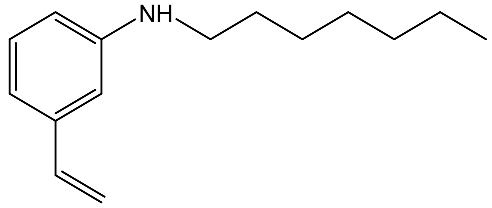
^{13}C NMR (100 MHz, $CDCl_3$): δ 27.2, 28.9, 29.1, 29.4, 29.5, 29.6, 33.8, 45.4, 114.1, 114.7, 116.2, 139.2, 142.3, 148.0.





^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80-0.95 (m, 3H), 1.17-1.44 (m, 8H), 1.58-1.67 (m, 2H), 3.07-3.15 (t, 2H), 5.17-5.22 (dd, 1H), 5.67-5.74 (dd, 1H), 6.51-6.56 (m, 1H), 6.61-6.69 (m, 2H), 6.76-6.80 (m, 1H), 7.11-7.16 (t, 1H).





^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 27.1, 29.1, 29.5, 31.8, 44.2, 110.5, 112.6, 113.4, 115.6, 129.3, 137.3, 138.5, 148.5.