

Supporting Information:

Hydroamination of Terminal Alkynes with Secondary Amines Catalyzed by Copper: Regioselective Access to Amines

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I. General considerations

All reactions were performed in oven-dried 45x14.75 mm Screw tubes under an atmosphere of argon. N-methyl-2-pyrrolidone (NMP) was distilled from P₂O₅ and stored over activated 3 Å molecular sieves under an argon atmosphere. CuCN stored in a dessicator cabinet and

weighed to air. All reagents (alkynes and amines) were purchased from either Sigma-Aldrich® or Alfa Aesar® or Acros Organic®. All reagents were weighed in the air.

¹H and ¹³C NMR spectra were recorded with a Bruker AC-400 MHz spectrometer in CDCl₃. For ¹H NMR (400 MHz), CHCl₃ and TMS served as internal standards ($\delta = 7.27$ and $\delta = 0$ ppm) and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (in Hz), and integration. For ¹³C NMR (100 MHz), CHCl₃ was used as internal standards ($\delta = 77.2$ ppm) and spectra were obtained with complete proton decoupling. Gas chromatography–mass spectra (GC-MS) were recorded on a Shimadzu QP2012-SE with a Zebron ZB-5MS (20m × 0,18mm), capillary apolar column (Stationary phase: 0.18 μ m film). GC-MS method: Initial temperature: 50 °C; Initial time: 2 min; Ramp: 2 °C/min until 50 °C then 10 °C/min; Final Temperature: 280 °C; Final time: 15 min. Melting points (mp) were carried out on a Büchi B-540 melting point apparatus, and are uncorrected. HRMS (Q-TOF) were performed on a JEOL JMS-DX300 spectrometer (3 keV, xenon) in a m-nitrobenzylalcohol matrix.

II. General procedure for hydroamination of alkynes with amines

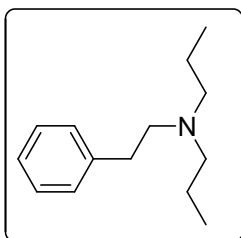
After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Screw tubes equipped with a magnetic stirring bar was charged with CuCN (0.15 mmol, 15 mol %) and the alkyne if a solid (1 mmol, 1 equiv). The tube was evacuated, back-filled with nitrogen. If a liquid, the alkyne was added under a stream of nitrogen by syringe at room temperature (1 mmol, 1 equiv) followed by the amine (5 mmol, 5 equiv) which can play, in the same time, the role of solvent or we can added the solvent NMP (1.0 mL, 1 M). The tube was sealed under a positive pressure of nitrogen, stirred and heated to 120°C. The mixture was stirred for 8 hours at 120°C. After allowing the reaction to cool to room temperature, 1,3,5-trimethoxybenzene (56.06 mg, 0.33 mmol, 0.33 equiv) was added as internal standard for calculating NMR yields of enamines.* The residue was concentrated under vacuum and then dissolved with CH₂Cl₂ (6 mL) and was transferred to 25 mL flask containing NaBH₃CN (2 mmol, 2equiv) then we added ACOH (2 mmol, 2 equiv). The suspension was then stirred at ambient temperature for 24 h. The reaction was quenched by the addition of 1M NaOH (aq) (4 mL). The phases were separated and the aqueous layer extracted with two further portions of CH₂Cl₂. The combined organic phases were dried over Na₂SO₄.

We release the starting amine (when they have high boiling point) with a treatment of solution of 1M HCl (aq).

* When NMP is the solvent of this reaction, the resulting mixture was diluted with ethyl acetate, washed 3 times with water and once with brine. The combined organic layers were dried over anhydrous MgSO_4 and ethyl acetate was evaporated under reduced pressure to remove the NMP. The residue was purified by simple washing with diethyl ether or by silica gel column chromatography.

III. Characterization of compounds 7a-7w

N-phenethyl-N-propylpropan-1-amine 7a



NMR Yield of corresponding enamine = 90 %

Yield (isolated) = 75 %

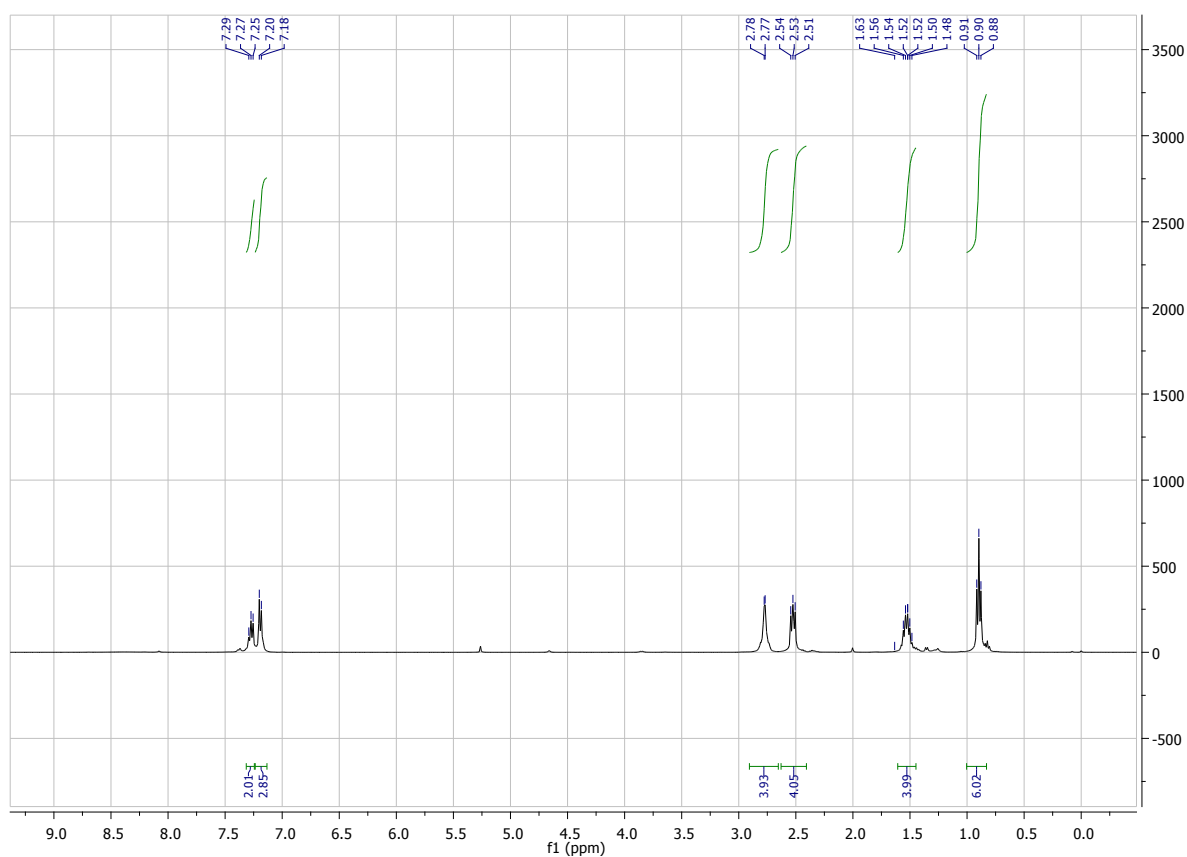
¹H NMR (400 MHz, CDCl₃): δ 0.88-0.91 (t, J = 7.3 Hz, 6H), 1.48-1.56 (m, 4H), 2.51-2.54 (t, J = 8 Hz, 4H), 2.77-2.78 (d, 4H), 7.18-7.20 (d, 3H), 7.25-7.29 (m, 2H).

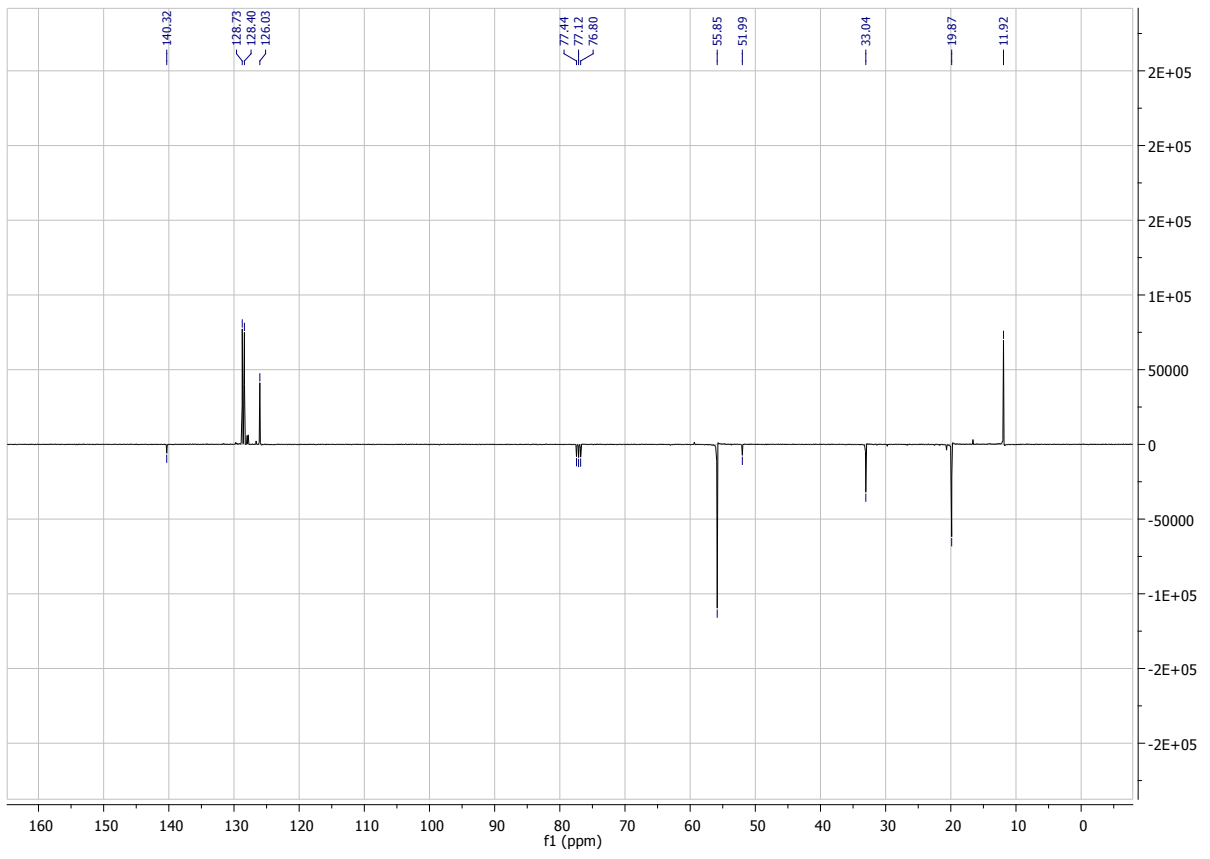
¹³C NMR (100 MHz, CDCl₃): δ 11.9, 19.8, 33.0, 51.9, 95.8, 126.0, 128.4, 128.7, 140.3.

GC/MS: rt = 08.12 min, M/Z = 205

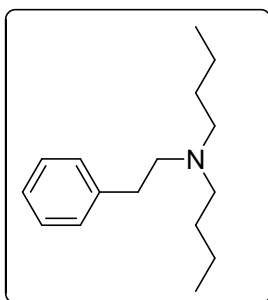
HRMS: 206.1909 (M+H). Theoretical: 206.1909

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 70:30.





N-butyl-*N*-phenethylbutan-1-amine **7b**



NMR Yield of corresponding enamine = 86 %

Yield (isolated) = 76 %

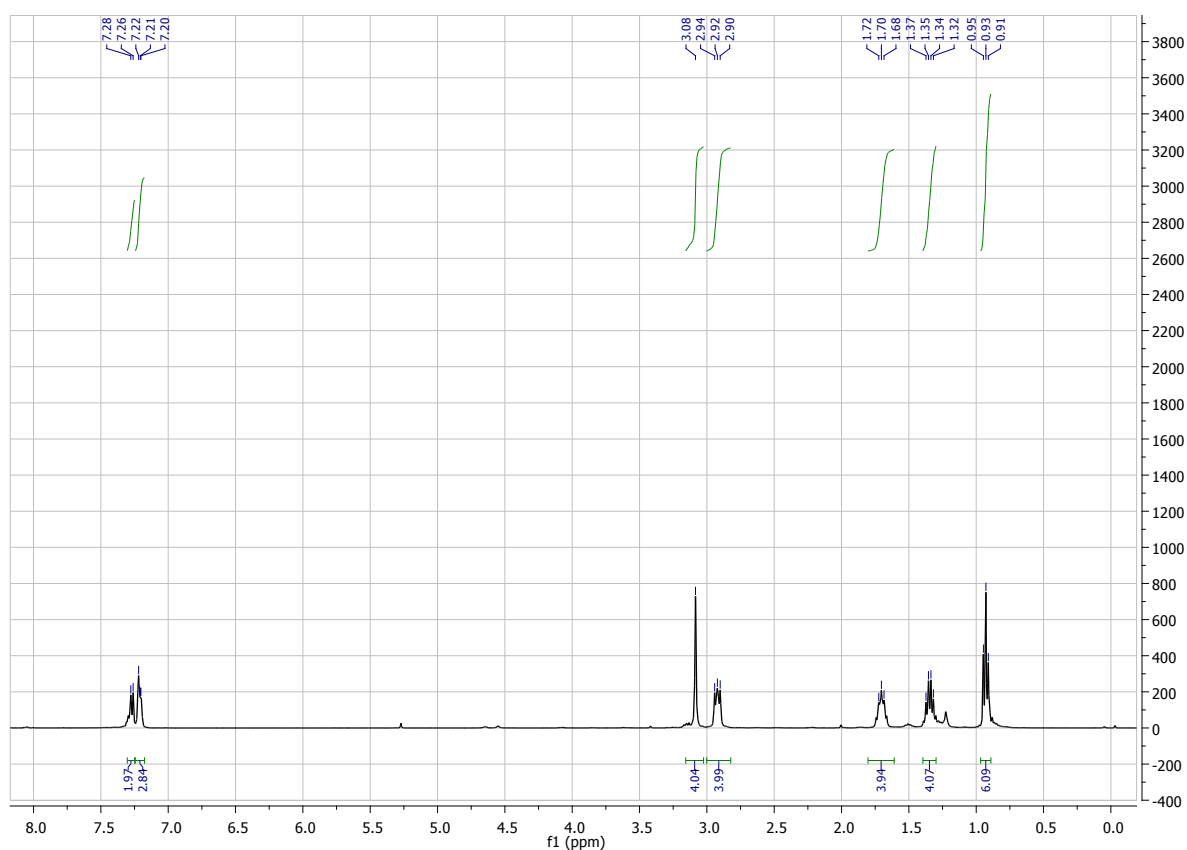
¹H NMR (400 MHz, CDCl₃): δ 0.91-0.95 (t, *J* = 7.3 Hz, 6H), 1.32-1.37 (dd, *J* = 7.3 Hz, 4H), 1.61-1.80 (m, 4H), 2.82-3.00 (t, 4H), 3.08 (s, 4H), 7.20-7.22 (m, 3H), 7.26-7.28 (d, *J* = 6.9 Hz, 2H).

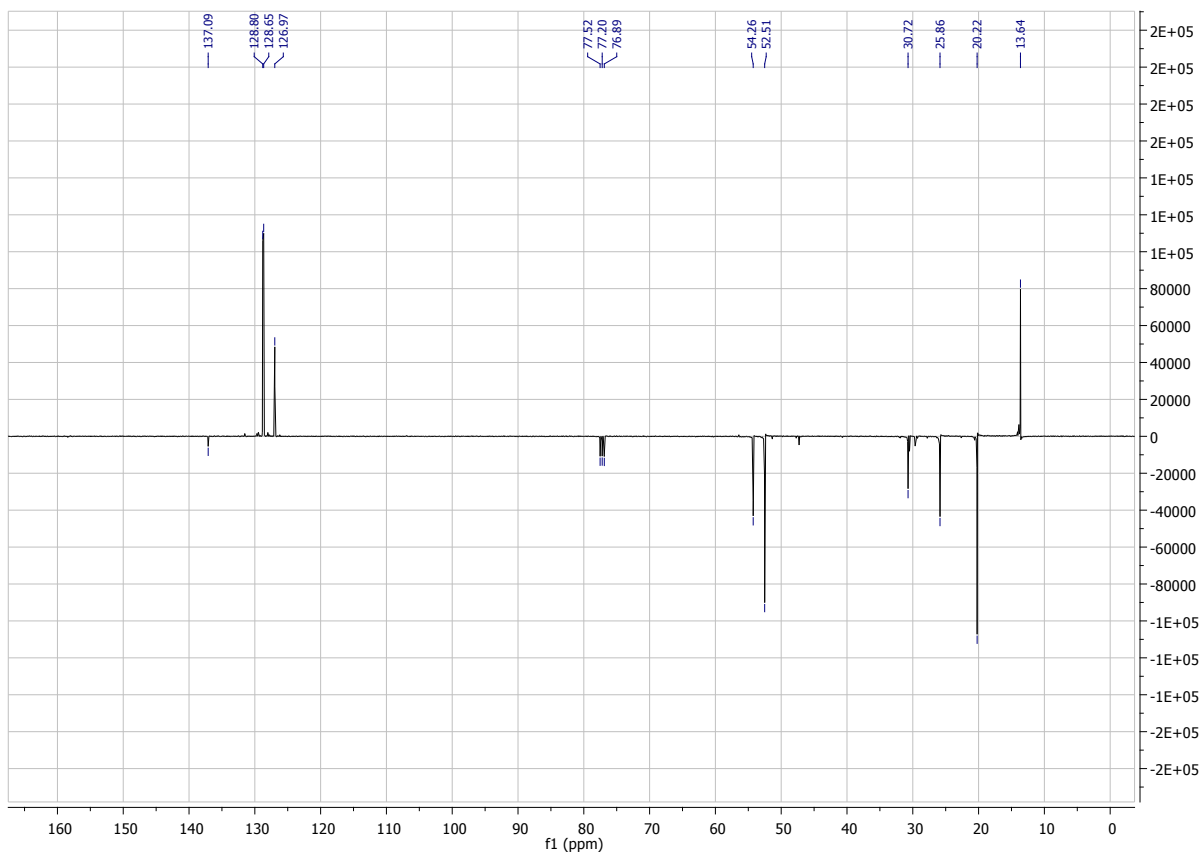
¹³C NMR (100 MHz, CDCl₃): δ 13.6, 20.2, 25.9, 30.7, 52.5, 54.3, 126.8, 128.7, 128.8, 137.1.

GC/MS: rt = 09.09 min, M/Z = 233

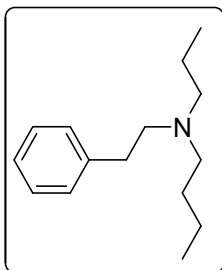
HRMS: 234.2223 (M+H). Theoretical: 234.2222

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 60:40.





N-phenethyl-*N*-propylbutan-1-amine 7c



NMR Yield of corresponding enamine = 75 %

Yield (isolated) = 80 %

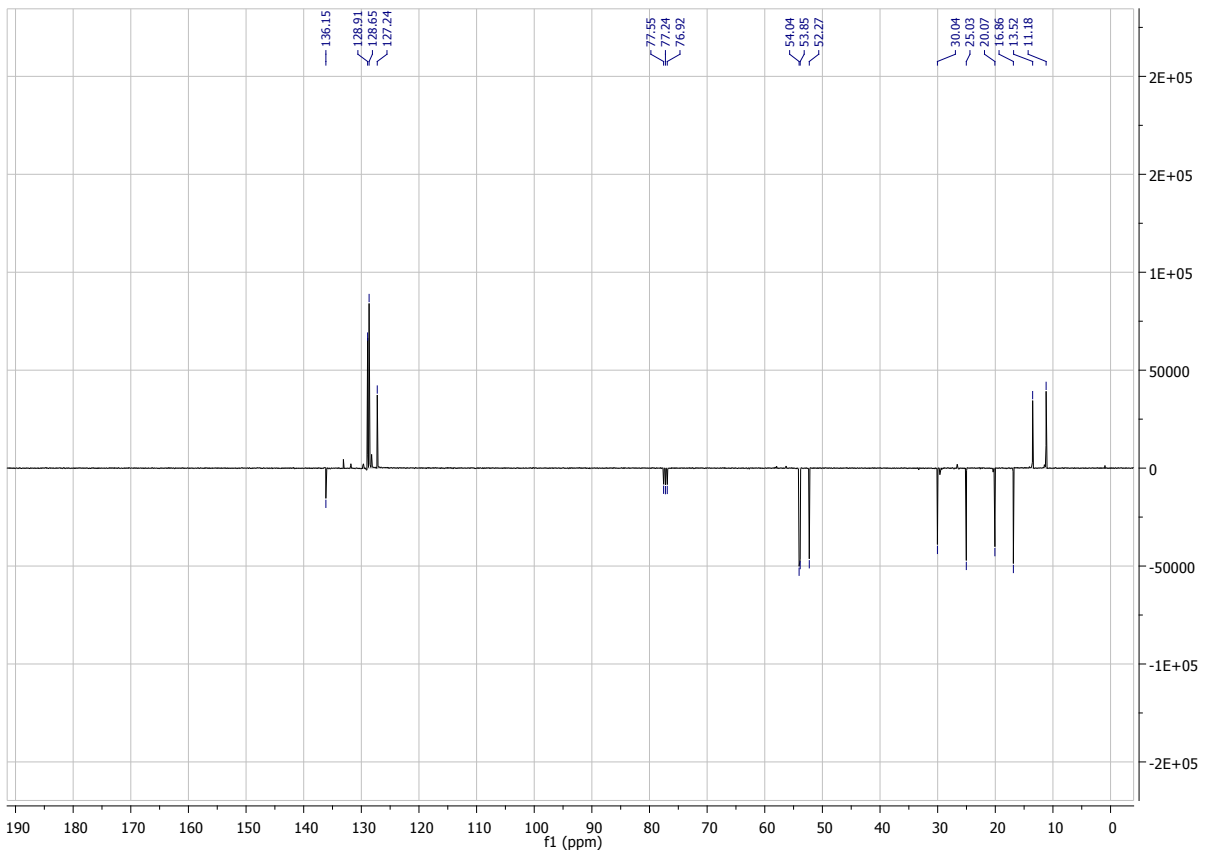
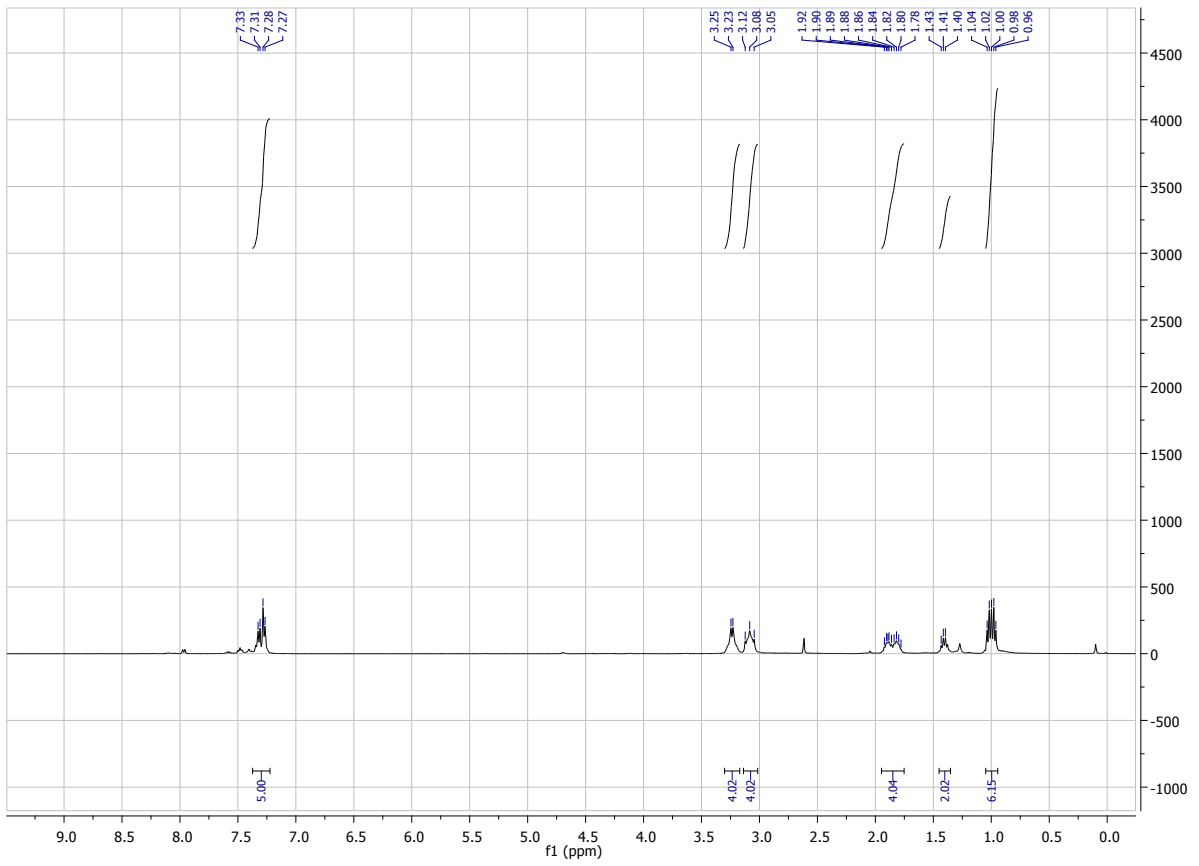
¹H NMR (400 MHz, CDCl₃): δ 0.94-1.05 (m, 6H), 1.35-1.45 (m, 2H), 1.75-1.95 (m, 4H), 3.05-3.12 (t, *J* = 15.5 Hz, 4H), 3.23-3.25 (d, *J* = 6.7 Hz, 4H), 7.27-7.33 (dd, *J*¹ = 7.02 Hz, *J*² = 17.1 Hz, 5H).

¹³C NMR (100 MHz, CDCl₃): δ 11.2, 13.5, 16.86, 20.1, 25.0, 30.0, 52.3, 53.9, 54.0, 127.2, 128.7, 128.9, 136.2.

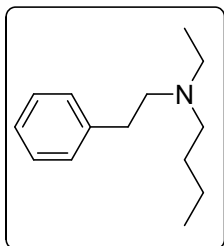
GC/MS: rt = 08.61 min, M/Z = 219

HRMS: 220.2067 (M+H). Theoretical: 220.2065

Purification: Washing with diethyl ether.



N-ethyl-*N*-phenethylbutan-1-amine 7d



NMR Yield of corresponding enamine = 84 %

Yield (isolated) = 68 %

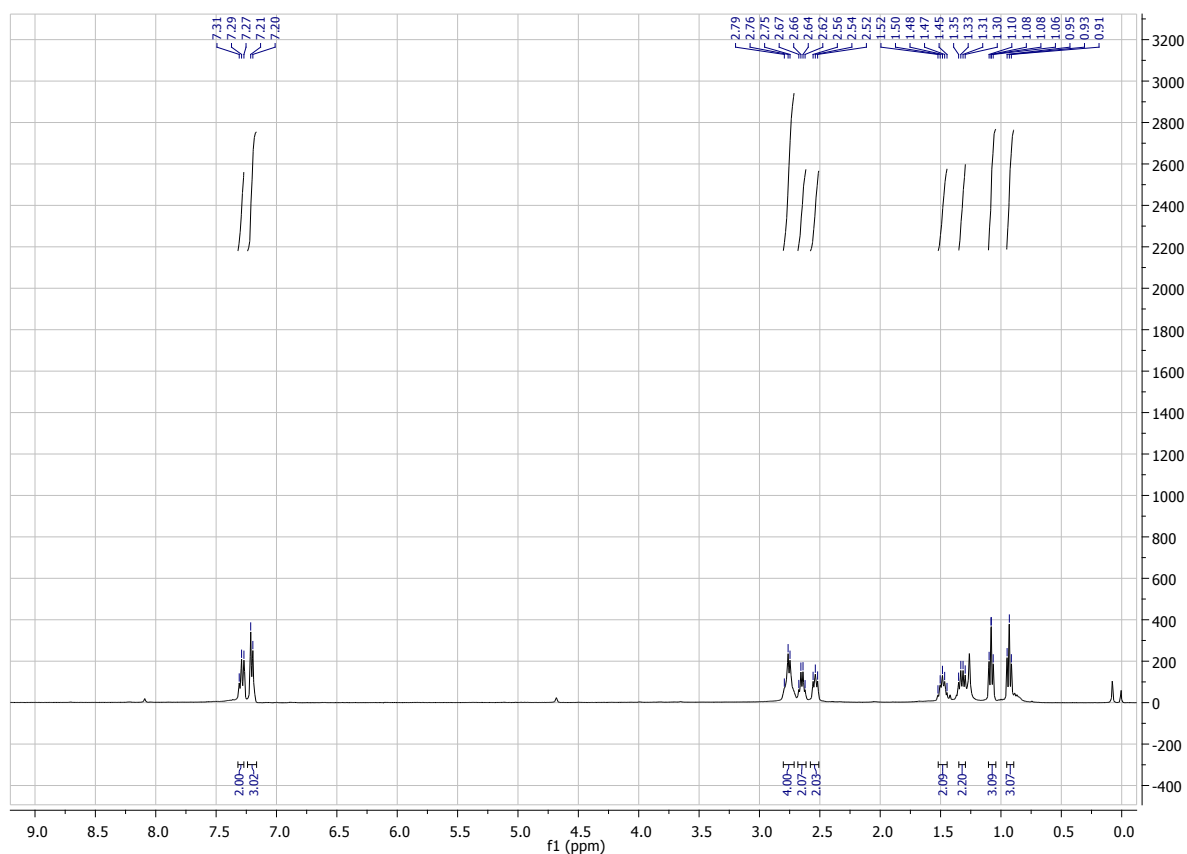
¹H NMR (400 MHz, CDCl₃): δ 0.91-0.95 (t, *J* = 7.1 Hz, 3H), 1.06-1.10 (t, *J* = 7.1 Hz, 3H), 1.30-1.35 (m, 2H), 2.52-2.56 (m, 2H), 2.62-2.67 (dd, *J'* = 6.9 Hz, *J* = 13.9 Hz, 2H), 2.75-2.79 (t, *J* = 9.4 Hz, 4H), 7.20-7.21 (d, *J* = 7.1 Hz, 3H), 7.27-2.31 (d, *J* = 7.8 Hz, 2H).

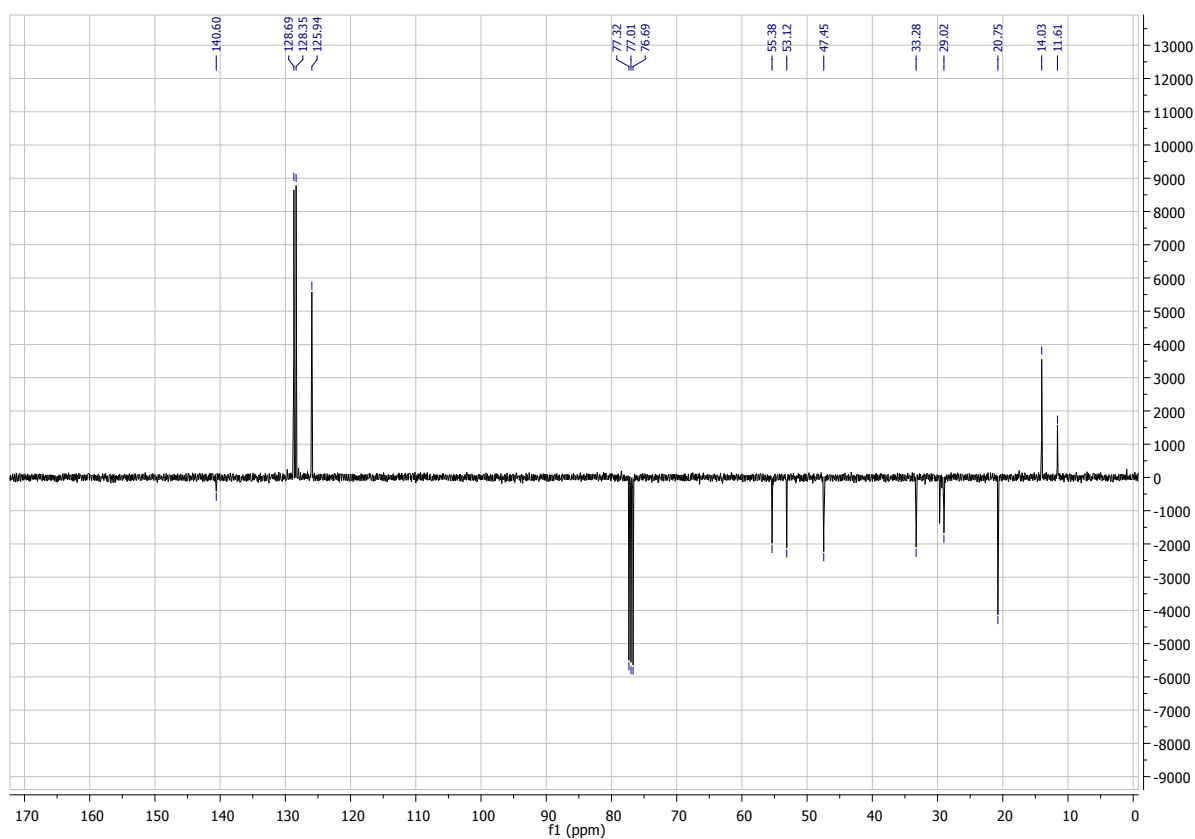
¹³C NMR (100 MHz, CDCl₃): δ 11.6, 14.0, 20.8, 29.0, 33.3, 47.5, 53.1, 55.4, 125.8, 128.7, 140.6.

GC/MS: rt = 08.16 min, M/Z = 205

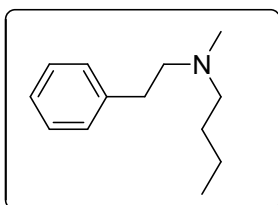
HRMS: 206.1836 (M+H). Theoretical: 206.1834

Purification: Washing with diethyl ether.





N-methyl-*N*-phenethylbutan-1-amine 7e



NMR Yield of corresponding enamine = 70 %

Yield (isolated) = 64 %

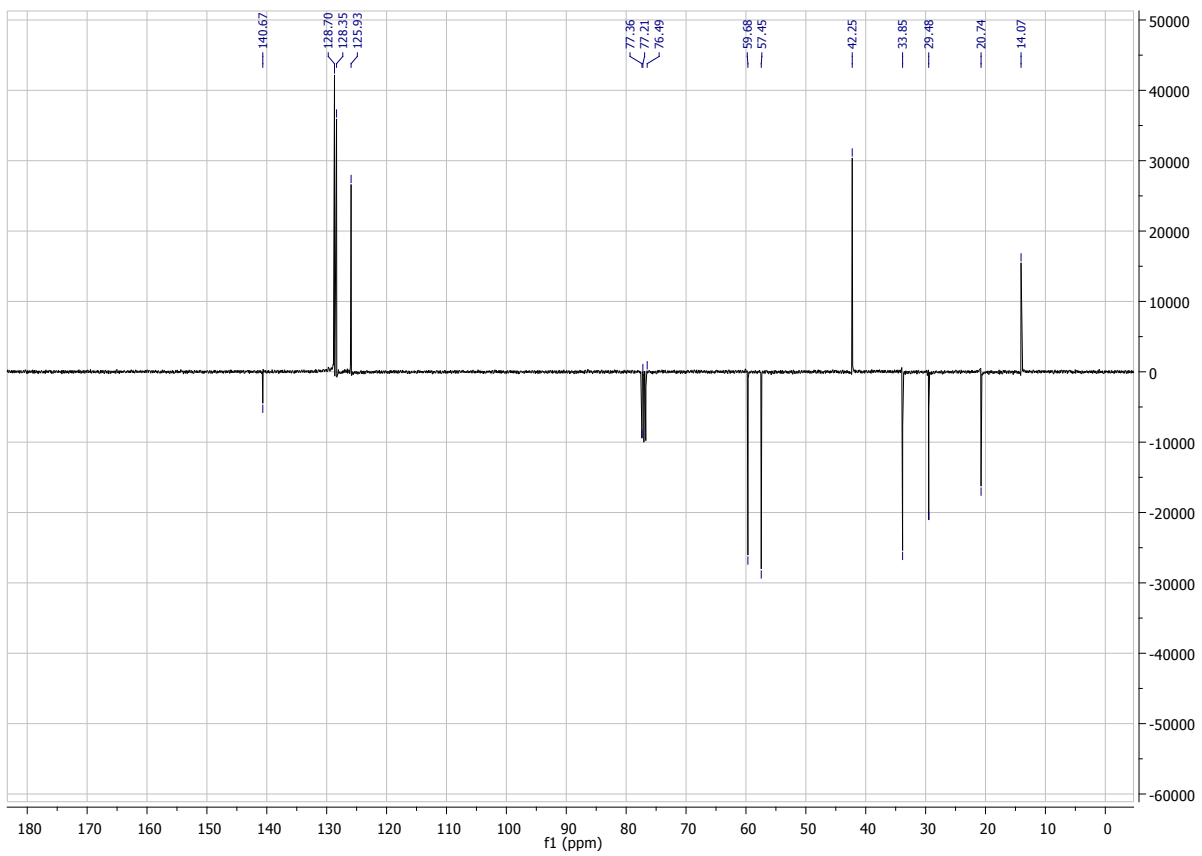
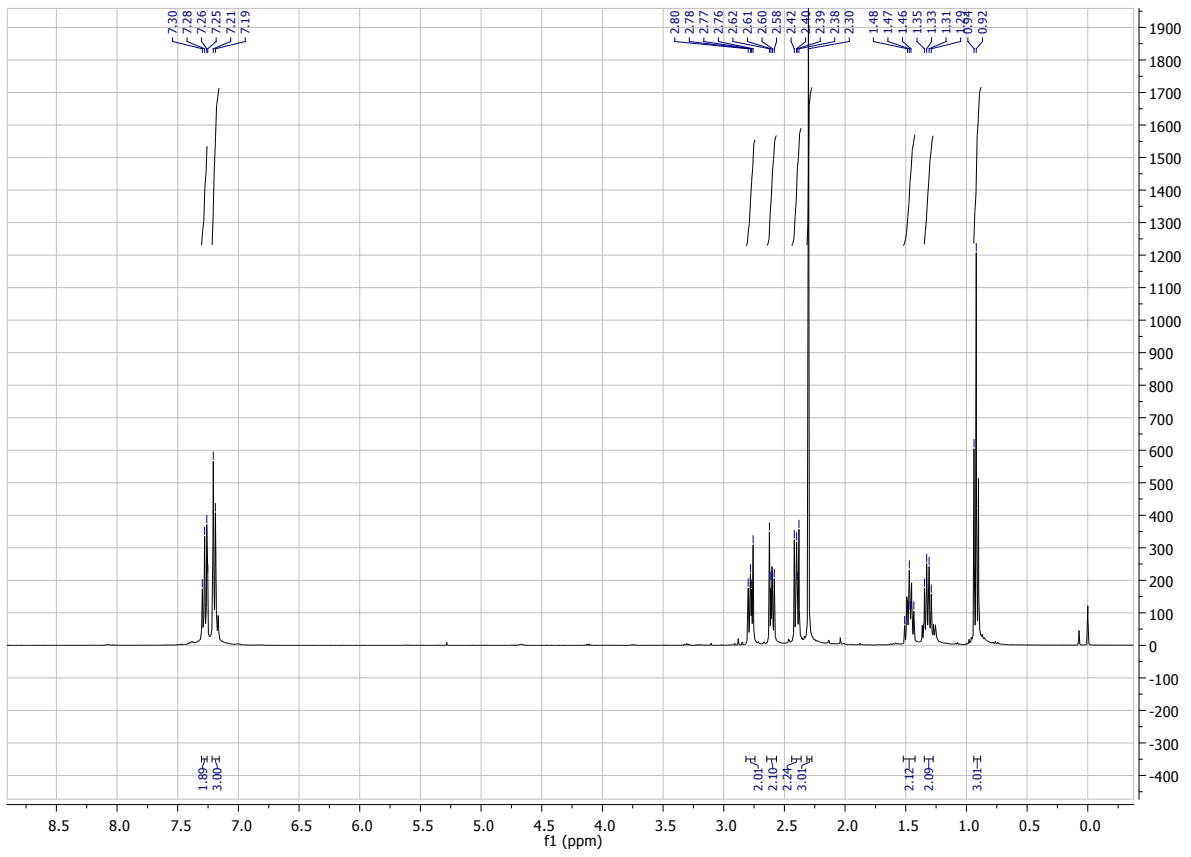
¹H NMR (400 MHz, CDCl₃): δ 0.88-0.94 (t, *J* = 7.3 Hz, 3H), 1.29-1.36 (m, 2H), 1.43-1.51 (m, 2H), 2.30 (s, 3H), 2.36-2.42 (dd, *J*¹ = 6.6 Hz, *J*² = 8.7 Hz, 2H), 2.58-2.62 (dd, *J*¹ = 5.3 Hz, *J*² = 10.7 Hz, 2H), 2.75-2.80 (dd, *J*¹ = 6.2 Hz, *J*² = 10 Hz, 2H), 7.19-7.22 (d, *J* = 7.1 Hz, 3H), 7.26-7.30 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 14.1, 20.7, 29.5, 33.8, 42.3, 57.4, 59.7, 125.9, 128.3, 128.7, 140.7.

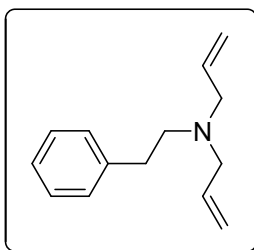
GC/MS: rt = 07.79 min, *M/Z* = 191

HRMS: 192.1756 (*M*+*H*). Theoretical: 192.1752

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 70:30.



N-allyl-*N*-phenethylprop-2-en-1-amine 7f



mp: 129°C-130°C

NMR Yield of corresponding enamine = 70 %

Yield (isolated) = 70 %

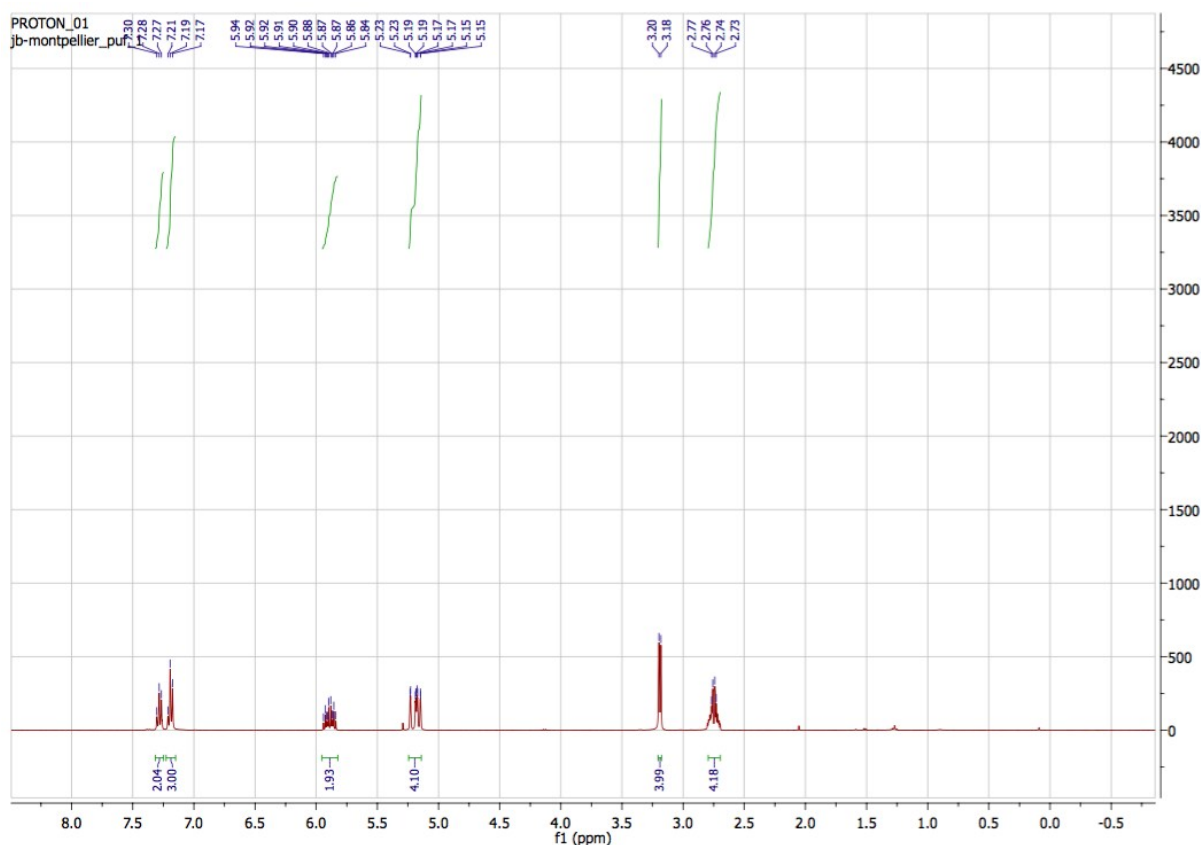
¹H NMR (400 MHz, CDCl₃): δ 2.73-2.77 (m, 4H), 3.18-3.2 (d, *J* = 6.5 Hz, 4H), 5.15-5.23 (ddd, *J* = 13.7 Hz, *J* = 11.1 Hz, *J* = 1.2 Hz, 4H), 5.84-5.94 (ddt, *J* = 16.7 Hz, *J* = 10.1 Hz, *J* = 6.5 Hz, 2H), 7.17-7.21 (t, *J* = 7.2 Hz, 3H), 7.27-7.30 (m, 2H).

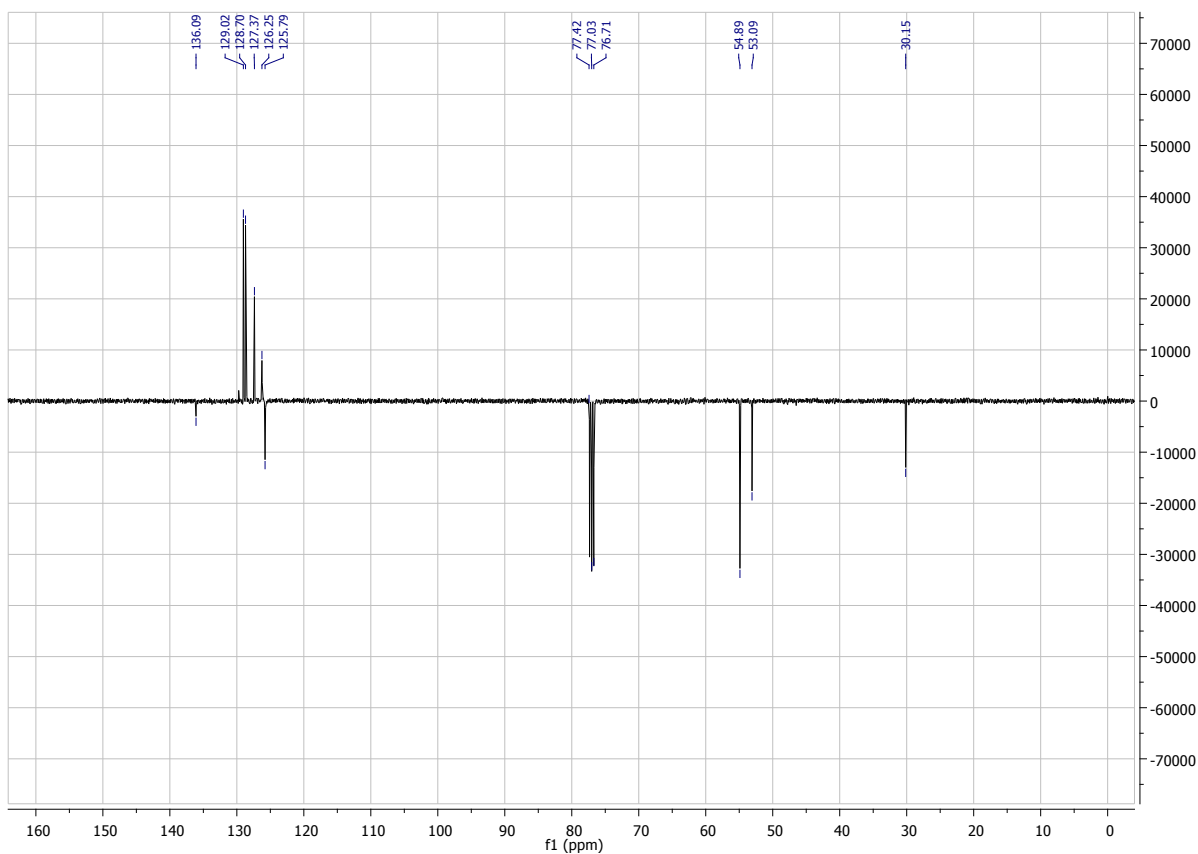
¹³C NMR (100 MHz, CDCl₃): δ 30.2, 53.1, 54.9, 125.8, 126.3, 127.4, 128.7, 129.0, 136.1.

GC/MS: rt = 08.04 min, M/Z = 201

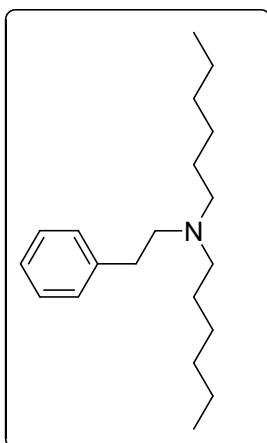
HRMS: 202.1597 (M+H). Theoretical: 202.1596

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 65:35.





***N*-hexyl-*N*-phenethylhexan-1-amine 7g**



NMR Yield of corresponding enamine = 83 %

Yield (isolated) = 70 %

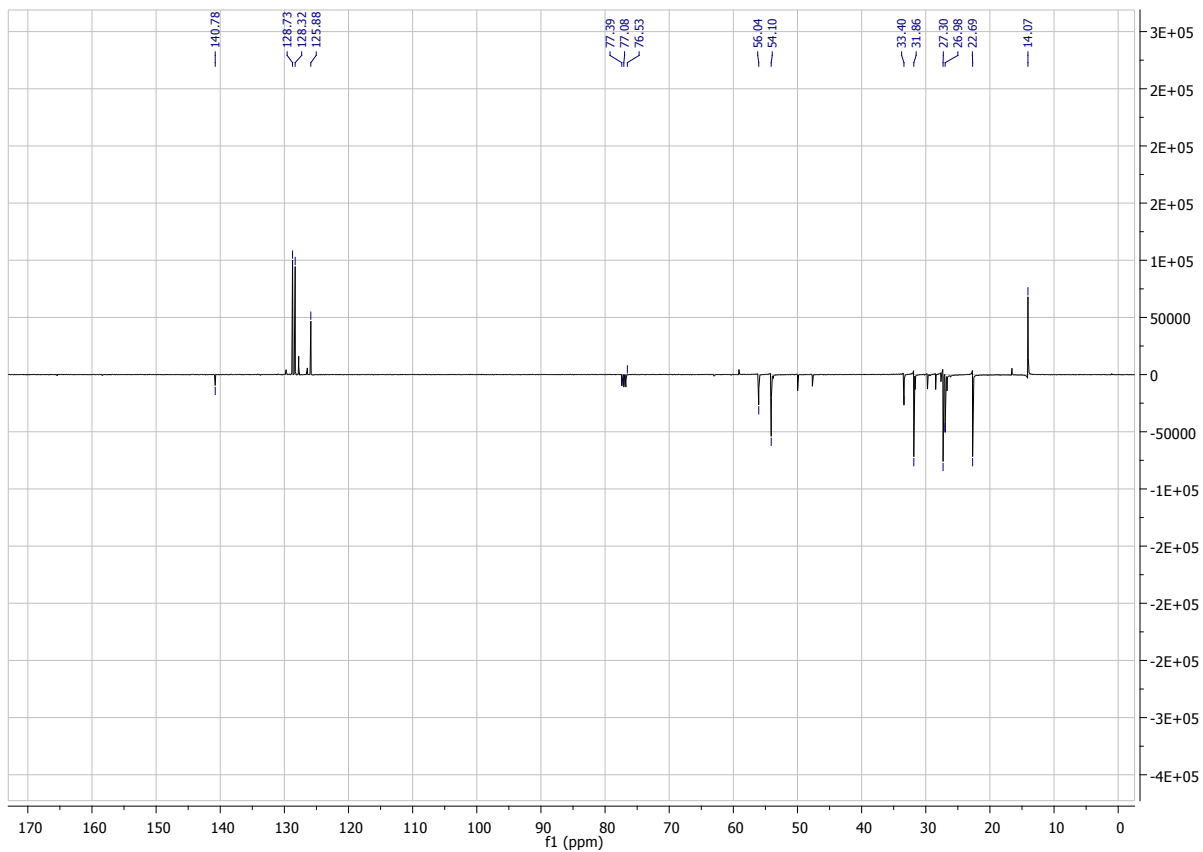
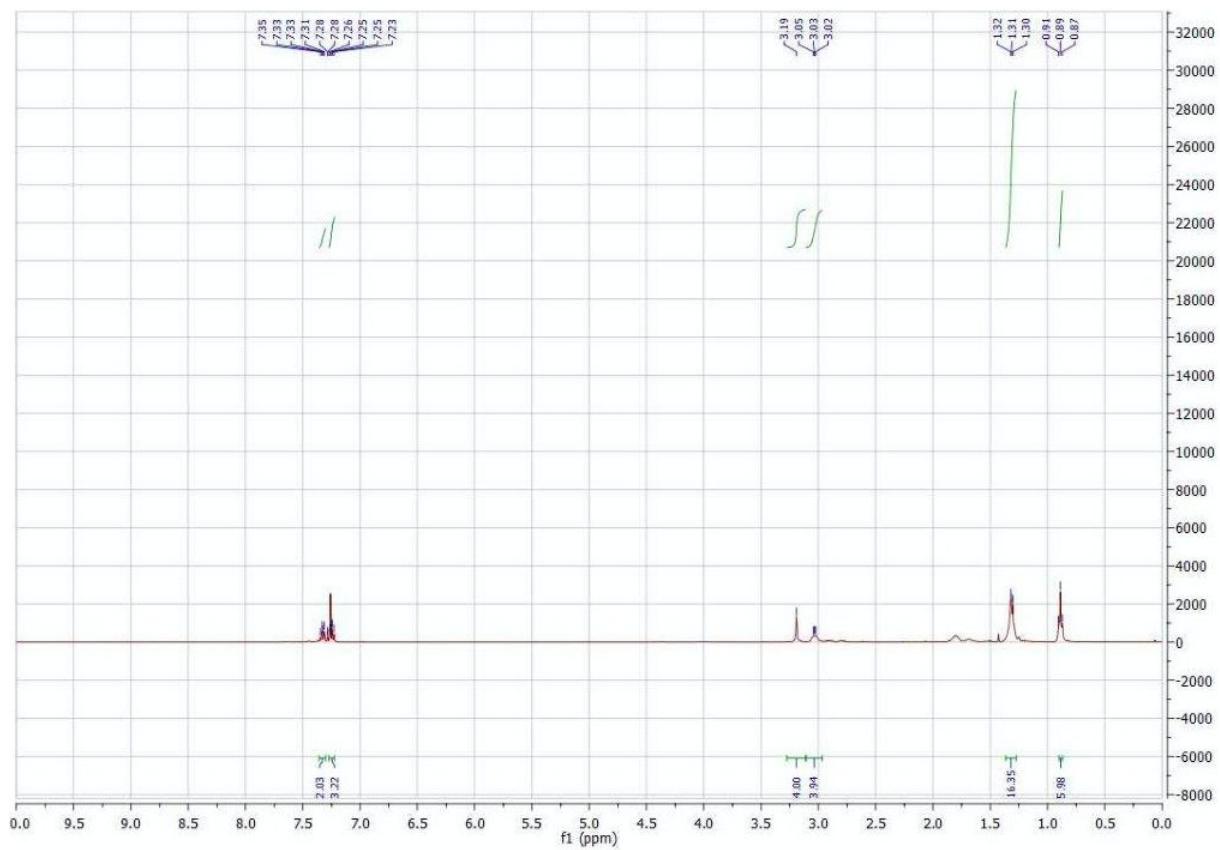
¹H NMR (400 MHz, CDCl₃): δ 0.87-0.91 (t, *J* = 6.6 Hz, 6H), 1.30-1.32 (m, 16H), 2.97-3.11 (m, 4H), 3.19 (s, 4H), 7.23-7.28 (dd, *J* = 7.9, 6.4 Hz, 3H), 7.31-7.35 (dd, *J* = 6.4, 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 15.0, 22.7, 27, 27.3, 33.4, 54.1, 56, 125.9, 128.3, 128.7, 140.8.

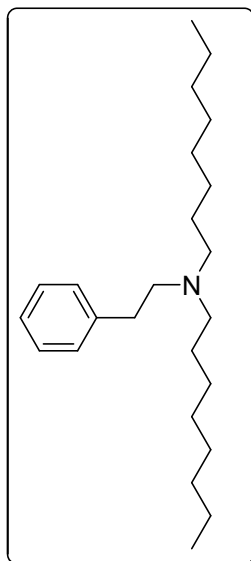
GC/MS: rt = 10.87 min, M/Z = 289

HRMS: 290.2849 (M+H). Theoretical: 290.2848

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 50:50.



N-octyl-*N*-phenethyloctan-1-amine 7h



mp: 133°C-135°C

NMR Yield of corresponding enamine = 81 %

Yield (isolated) = 76 %

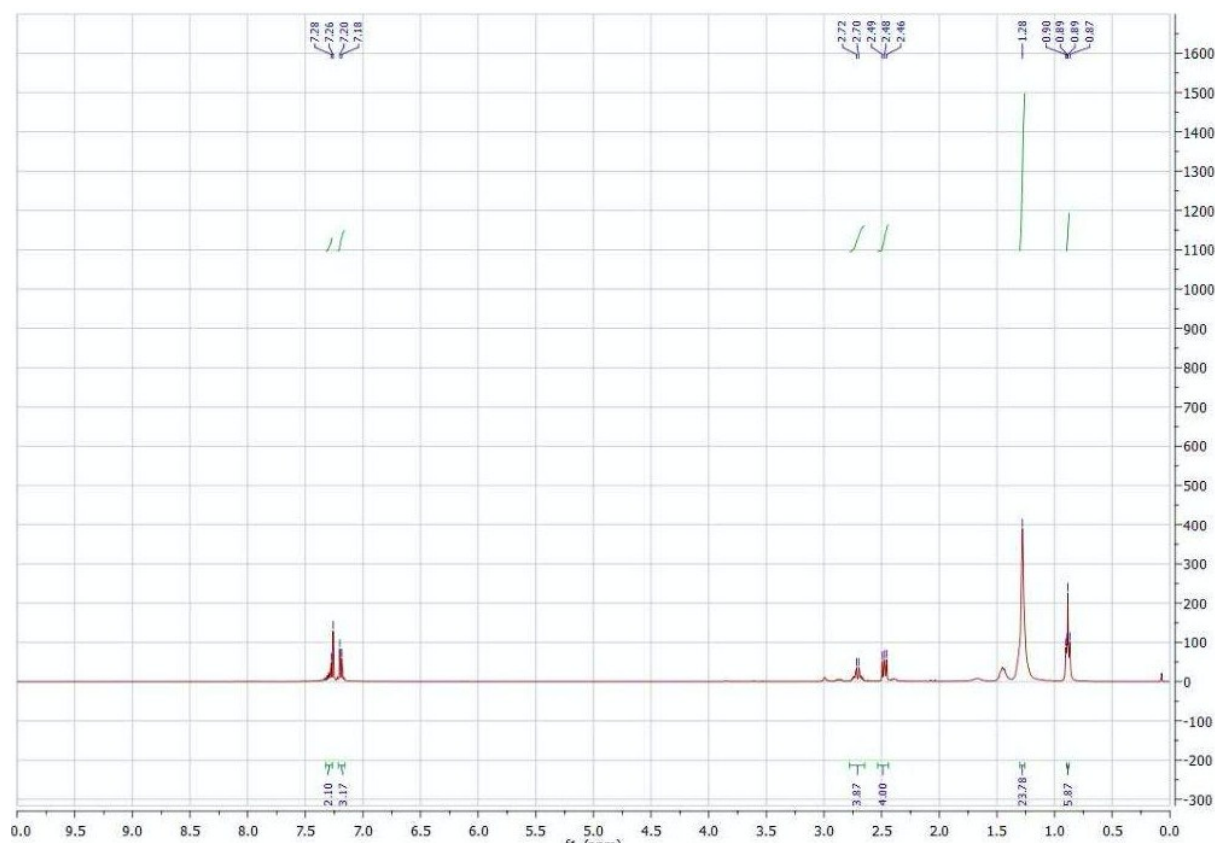
¹H NMR (400 MHz, CDCl₃): δ 0.87-0.90 (t, *J* = 6.8 Hz, 6H), 1.28 (m, 24H), 2.46-2.49 (m, 4H), 2.66-2.72 (d, *J* = 7.3 Hz, 4H), 7.18-7.20 (d, *J* = 7.2 Hz, 3H), 7.26-7.28 (d, *J* = 8.2 Hz, 2H).

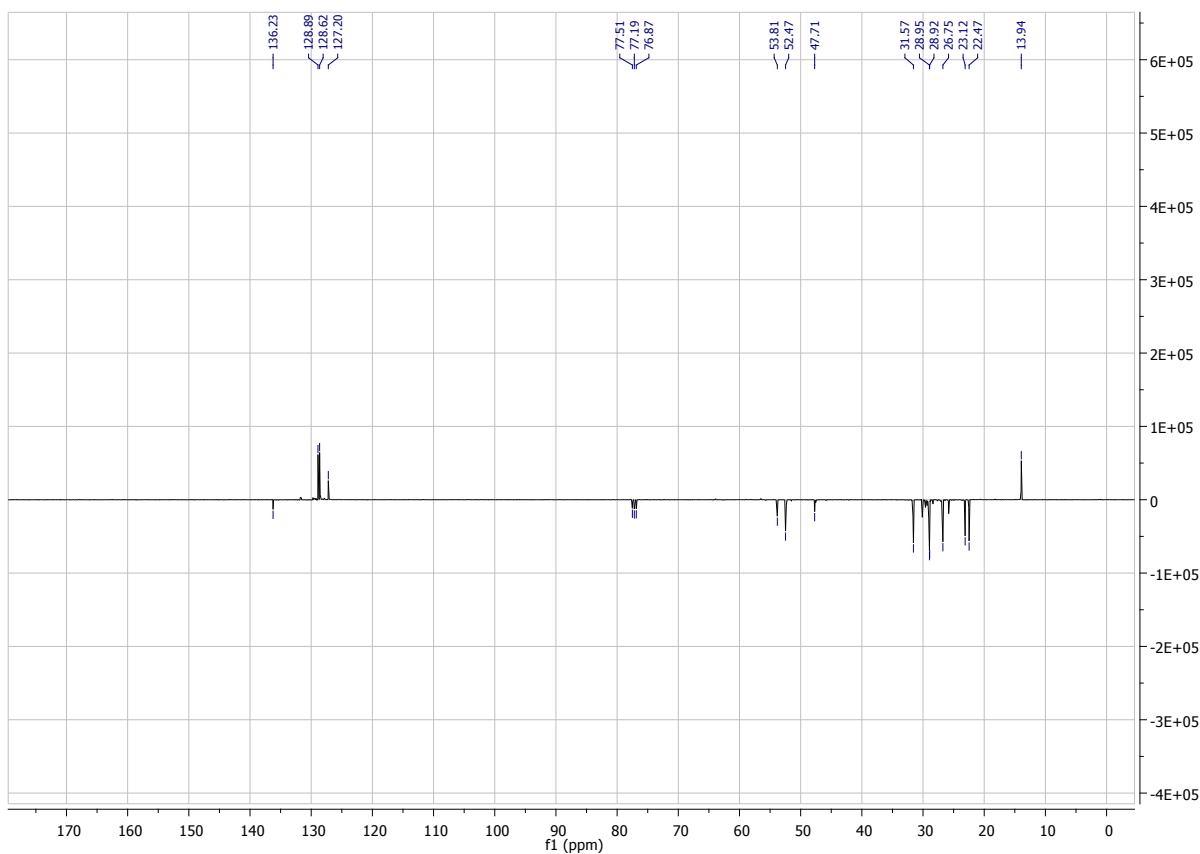
¹³C NMR (100 MHz, CDCl₃): δ 13.9, 22.5, 23.1, 26.8, 28.9, 29.0, 31.6, 47.7, 52.5, 53.8, 127.2, 128.6, 128.4, 128.8, 136.2.

GC/MS: rt = 12.48 min, M/Z = 345

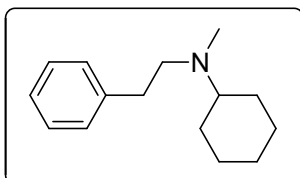
HRMS: 346.3474 (M+H). Theoretical: 346.3474

Purification: Washing with diethyl ether.





N-methyl-*N*-phenethylcyclohexanamine **7i**



mp: 164°C-165°C

NMR Yield of corresponding enamine = 84 %

Yield (isolated) = 77 %

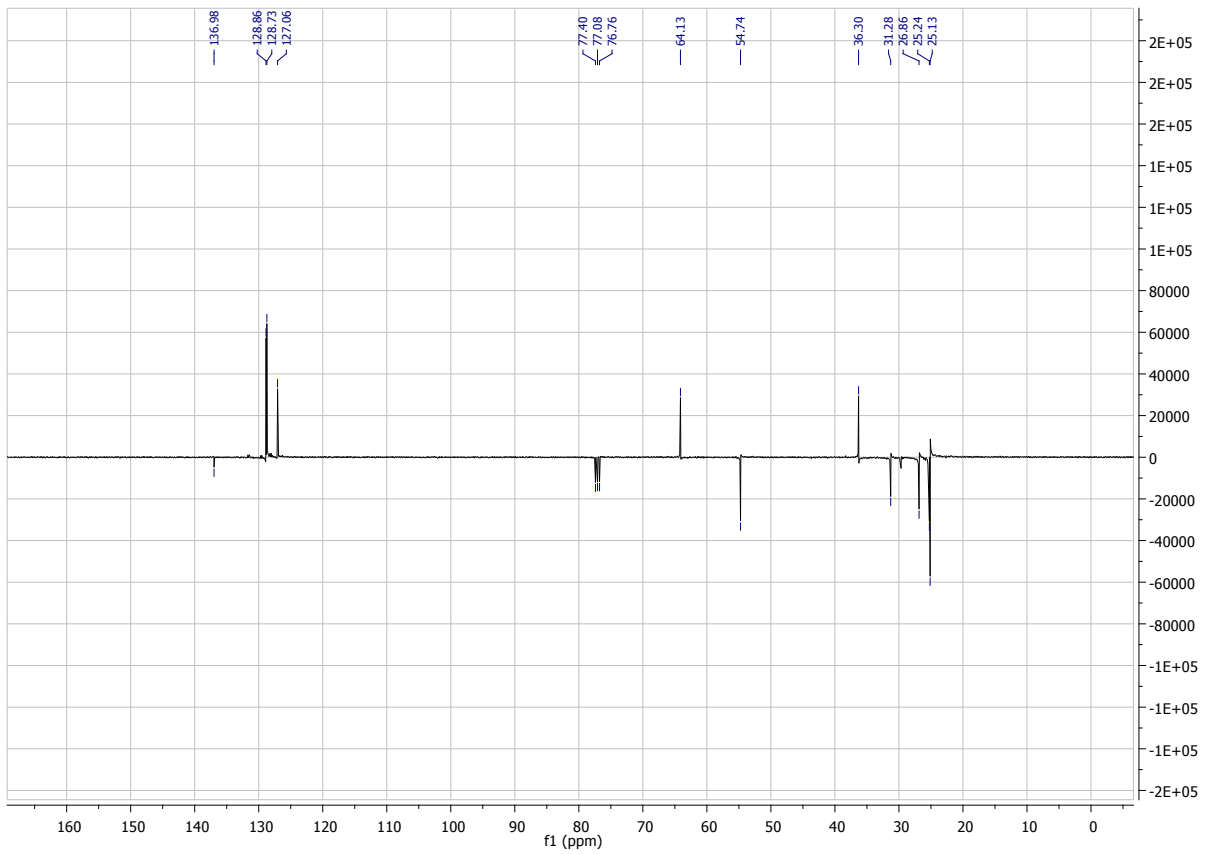
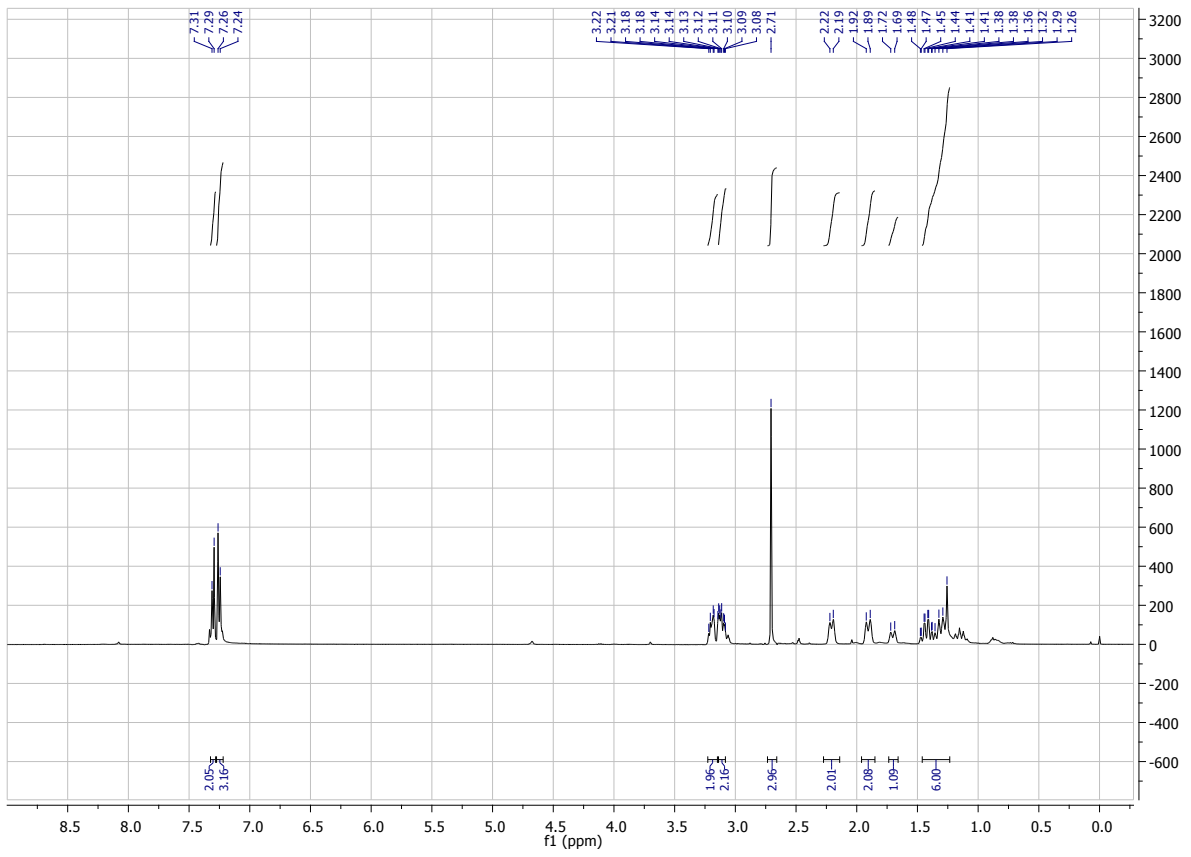
¹H NMR (400 MHz, CDCl₃): δ 1.23-1.46 (m, 6H), 1.69-1.72 (d, *J* = 13 Hz, 1H), 1.89-1.92 (d, *J* = 13.1 Hz, 2H), 2.19-2.22 (d, *J* = 11.2 Hz, 2H), 3.09-3.13 (m, 2H), 3.17-3.22 (m, 2H), 7.24-7.26 (d, *J* = 7.2 Hz, 3H), 7.29-7.31 (d, *J* = 7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 25.1, 25.2, 26.9, 31.3, 36.3, 54.7, 64.1, 127.0, 128.7, 128.9, 137.0.

GC/MS: rt = 09.5 min, *M/Z* = 217

HRMS: 218.1909 (M+H). Theoretical: 218.1909

Purification: Washing with diethyl ether.



N,N-diethyl-2-phenylethanamine 7j



NMR Yield of corresponding enamine = 80 %

Yield (isolated) = 74 %

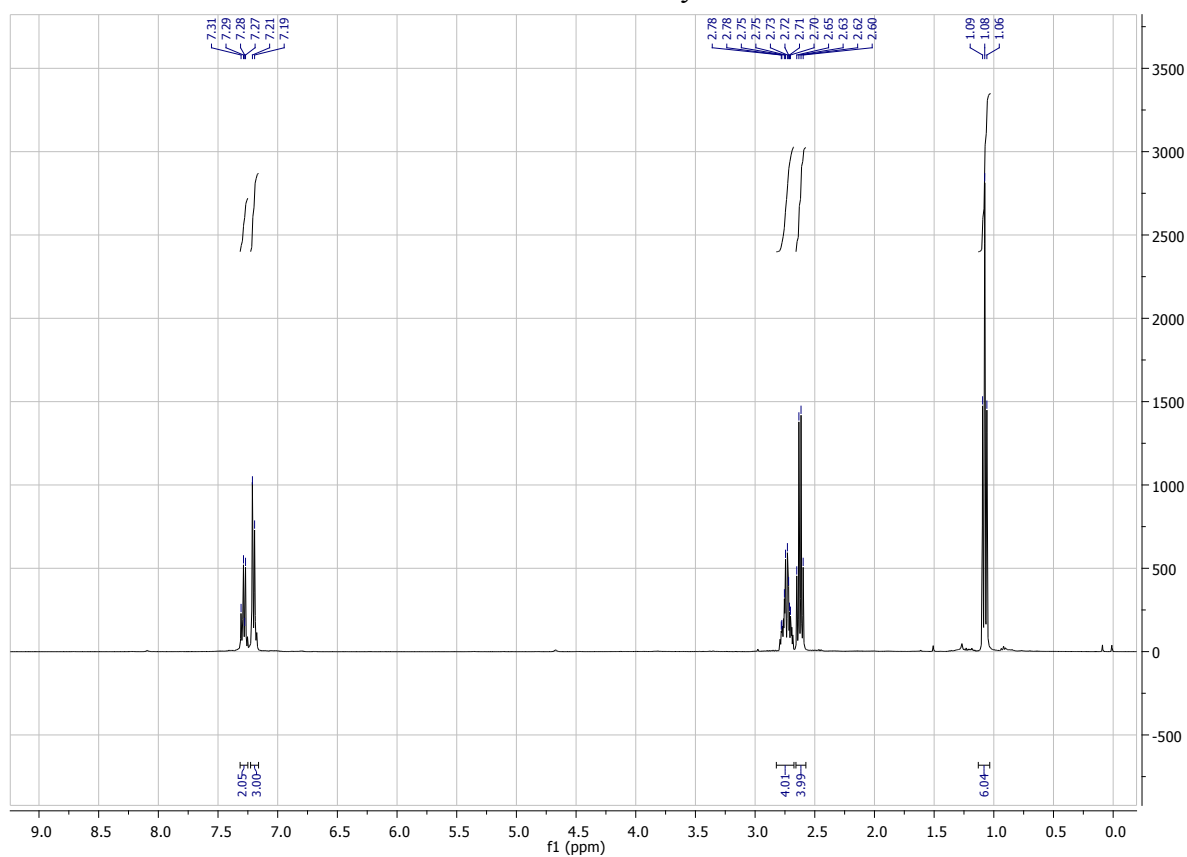
¹H NMR (400 MHz, CDCl₃): δ 1.06-1.09 (t, *J* = 7.2 Hz, 6H), 2.60-2.70 (q, *J* = 7.2 Hz, 4H), 2.72-2.87 (m, 4H), 7.19-7.21 (d, *J* = 7.2 Hz, 3H), 7.29-7.31 (m, 2H).

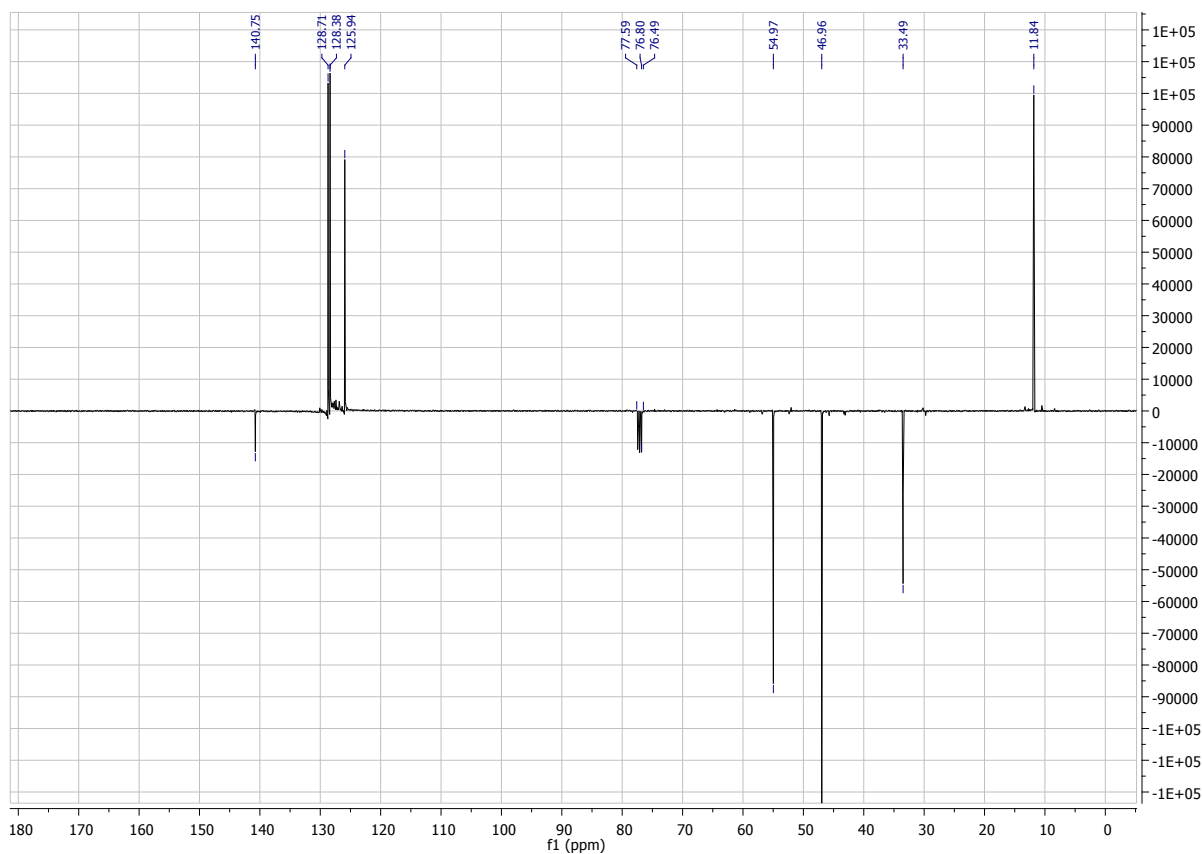
¹³C NMR (100 MHz, CDCl₃): δ 11.8, 33.5, 47.0, 55.0, 125.9, 128.7, 140.8.

GC/MS: rt = 08.47 min, *M/Z* = 177

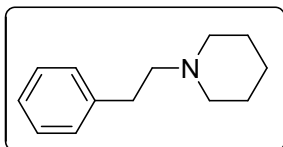
HRMS: 178.1598 (*M*+*H*). Theoretical: 178.1596

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 60:40.





1-phenethylpiperidine **7k**



NMR Yield of corresponding enamine = 90 %

Yield (isolated) = 86 %

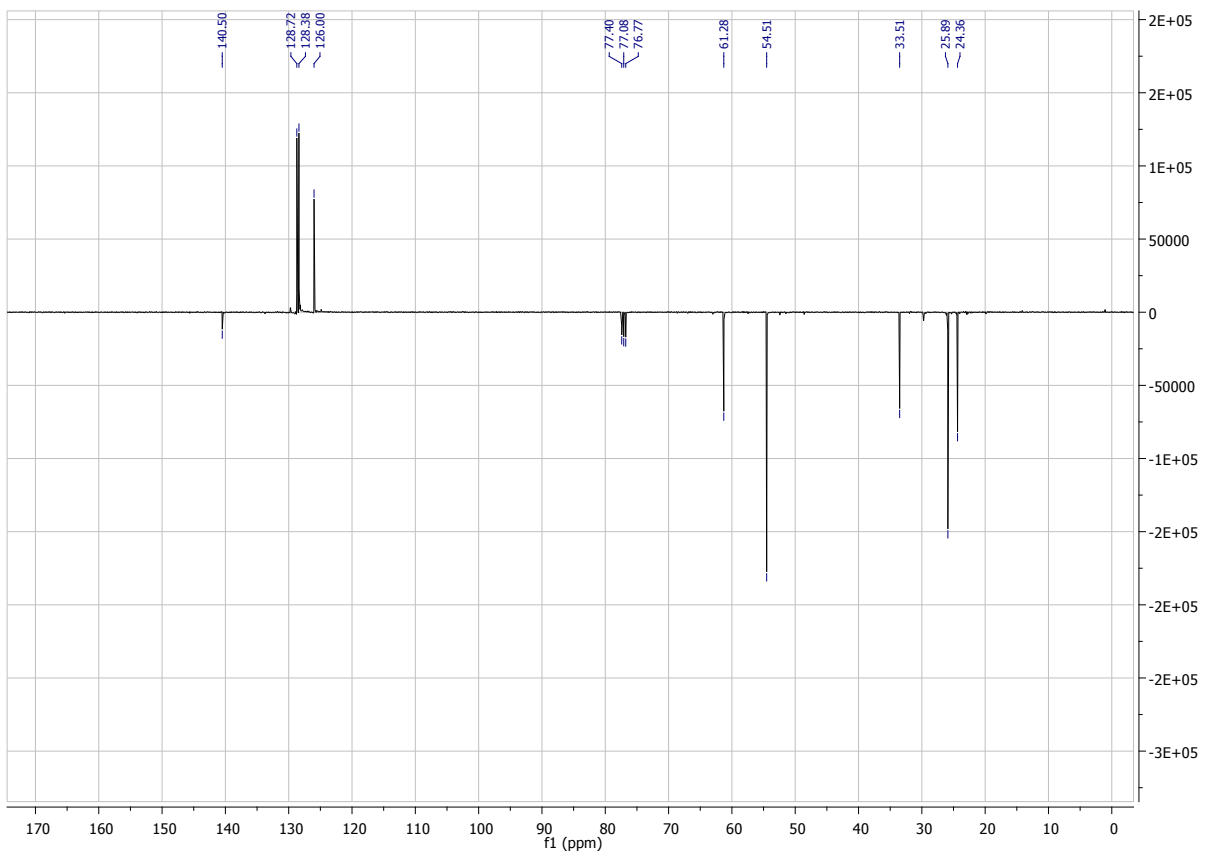
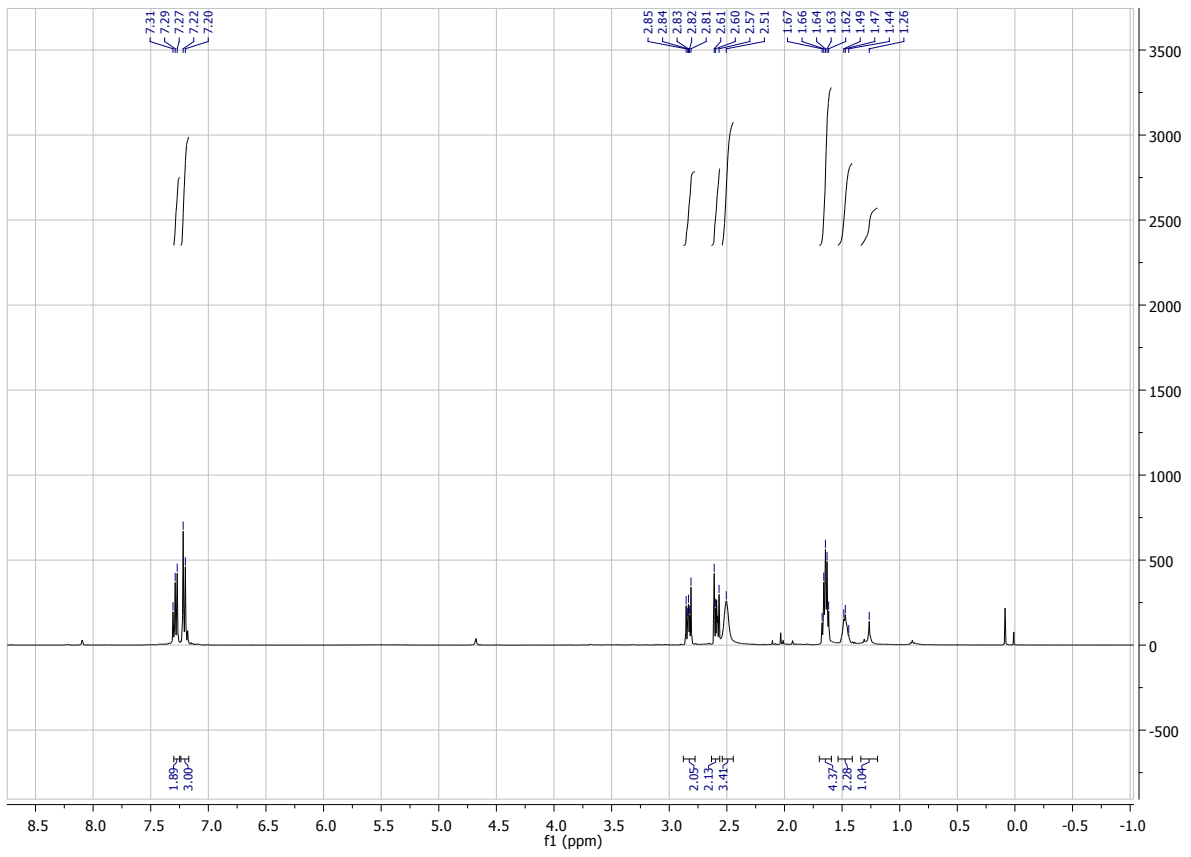
¹H NMR (400 MHz, CDCl₃): δ 1.26 (s, 1H), 1.44-1.49 (t, *J* = 8.6 Hz, 2H), 1.62-1.67 (dt, *J*¹ = 5.6 Hz, *J*² = 11.1 Hz, 4H), 2.51 (s, 3H), 2.56-2.63 (m, 2H), 2.78-2.88 (m, 2H), 7.2-7.22 (d, *J* = 7.7 Hz, 3H), 7.29-7.33 (d, *J* = 7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 24.4, 26.9, 33.5, 54.5, 61.3, 126.0, 128.4, 128.7, 140.5.

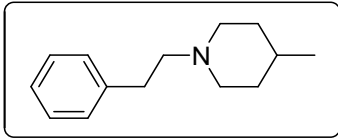
GC/MS: rt = 08.35 min, M/Z = 189

HRMS: 190.1598 (M+H). Theoretical: 190.1596

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 80:20.



4-methyl-1-phenethylpiperidine 71



NMR Yield of corresponding enamine = 82 %

Yield (isolated) = 80 %

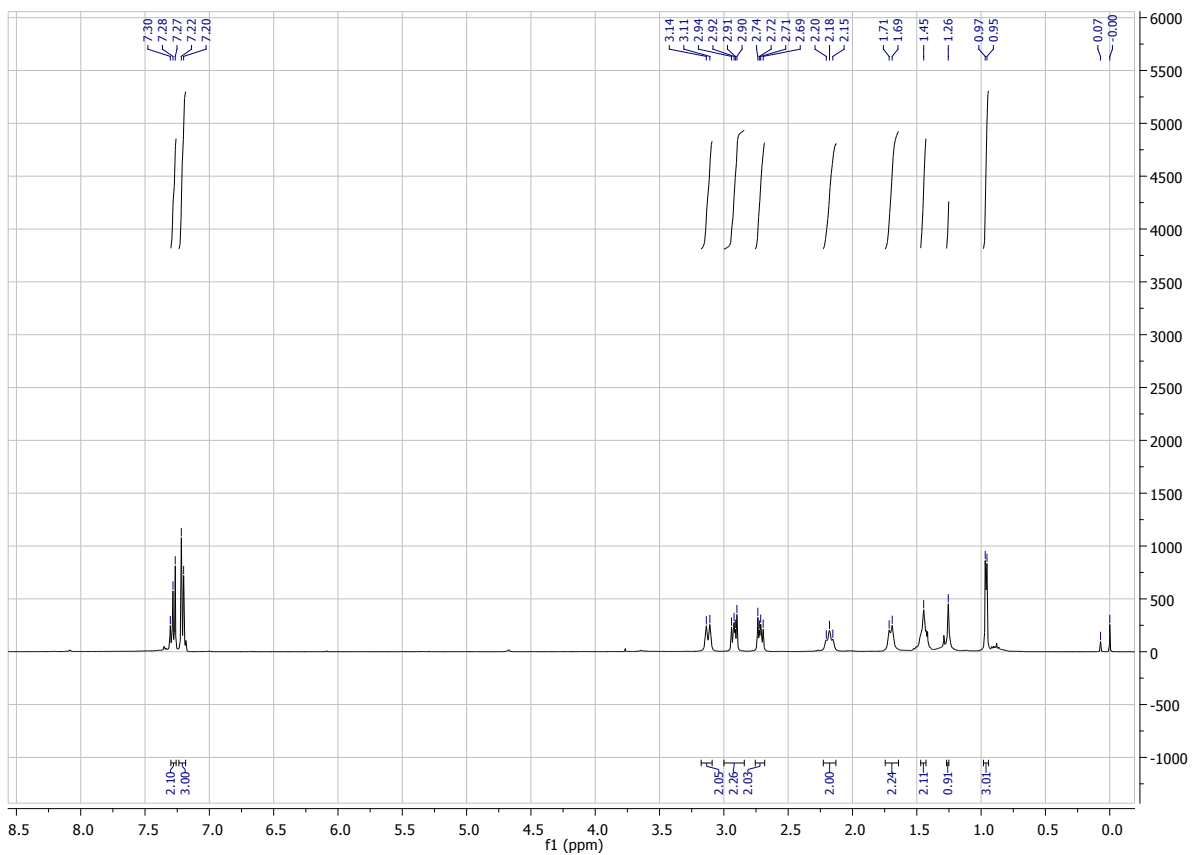
^1H NMR (400 MHz, CDCl_3): δ 0.95-0.97 (d, $J = 5.4$ Hz, 3H), 1.26 (s, 1H), 1.45 (s, 2H), 1.69-1.71 (d, $J = 9.5$ Hz, 2H), 2.15-2.2 (t, $J = 10.2$ Hz, 2H), 2.89-2.74 (dd, $J^1 = 6.3$ Hz, $J^2 = 10.4$ Hz, 2H), 2.90-7.94 (dd, $J^1 = 6.3$ Hz, $J^2 = 10.4$ Hz, 2H), 3.11-3.14 (d, $J = 10.9$ Hz, 2H), 7.20-7.22 (d, $J = 7.2$ Hz, 3H), 7.28-7.3 (t, $J = 7.2$ Hz, 2H).

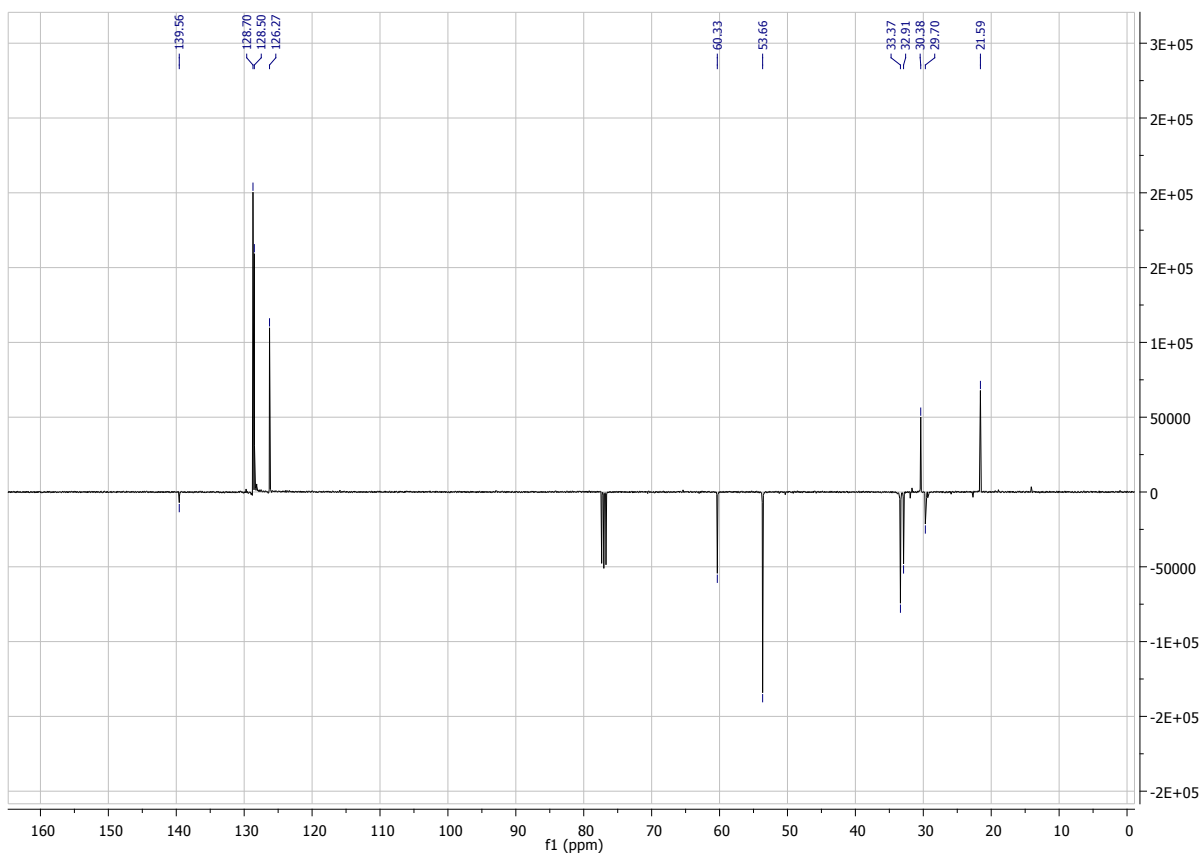
^{13}C NMR (100 MHz, CDCl_3): δ 22.0, 29.7, 30.4, 32.9, 33.4, 53.6, 60.3, 126.3, 128.5, 128.7, 139.6.

GC/MS: rt = 08.32 min, M/Z = 203

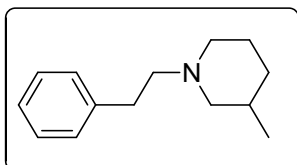
HRMS: 204.1753 (M+H). Theoretical: 204.1752

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 75:25.





3-methyl-1-phenethylpiperidine 7m



mp: 128°C-130°C

NMR Yield of corresponding enamine = 78 %

Yield (isolated) = 74 %

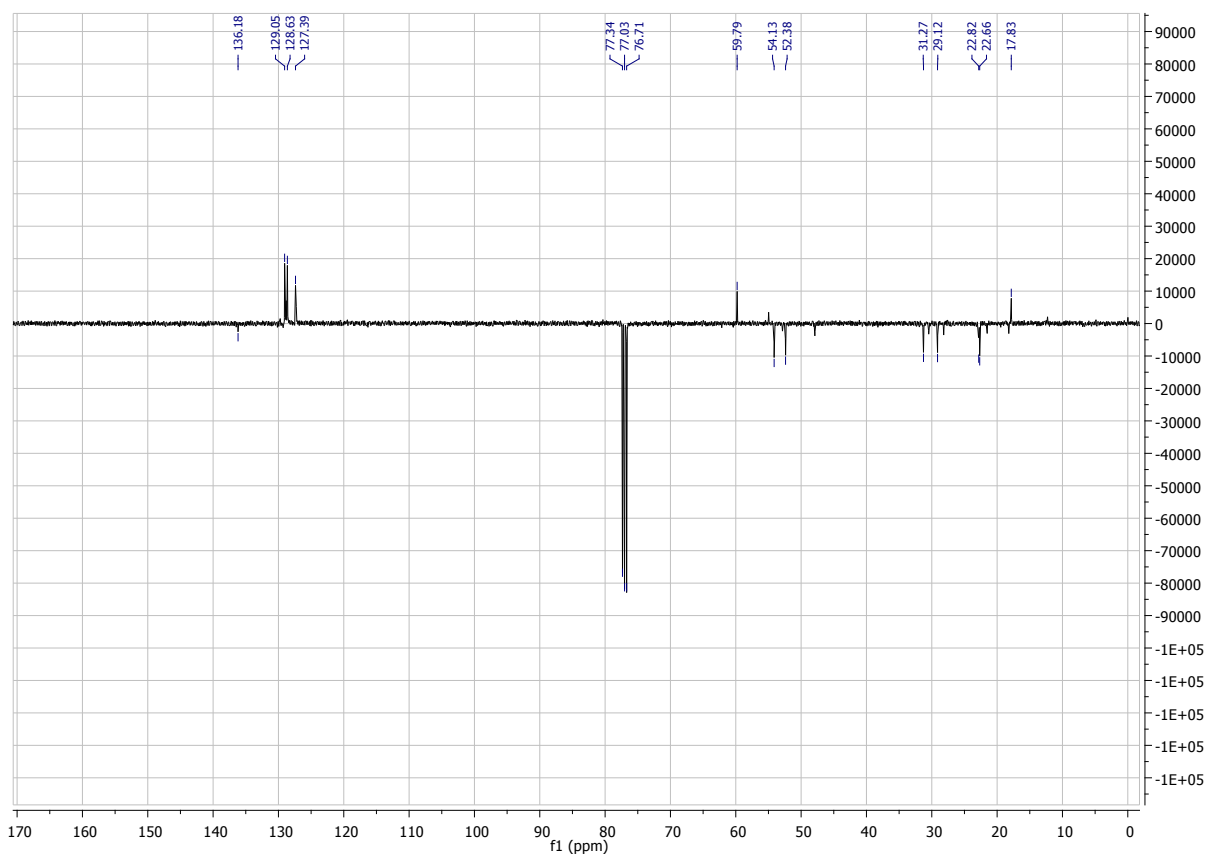
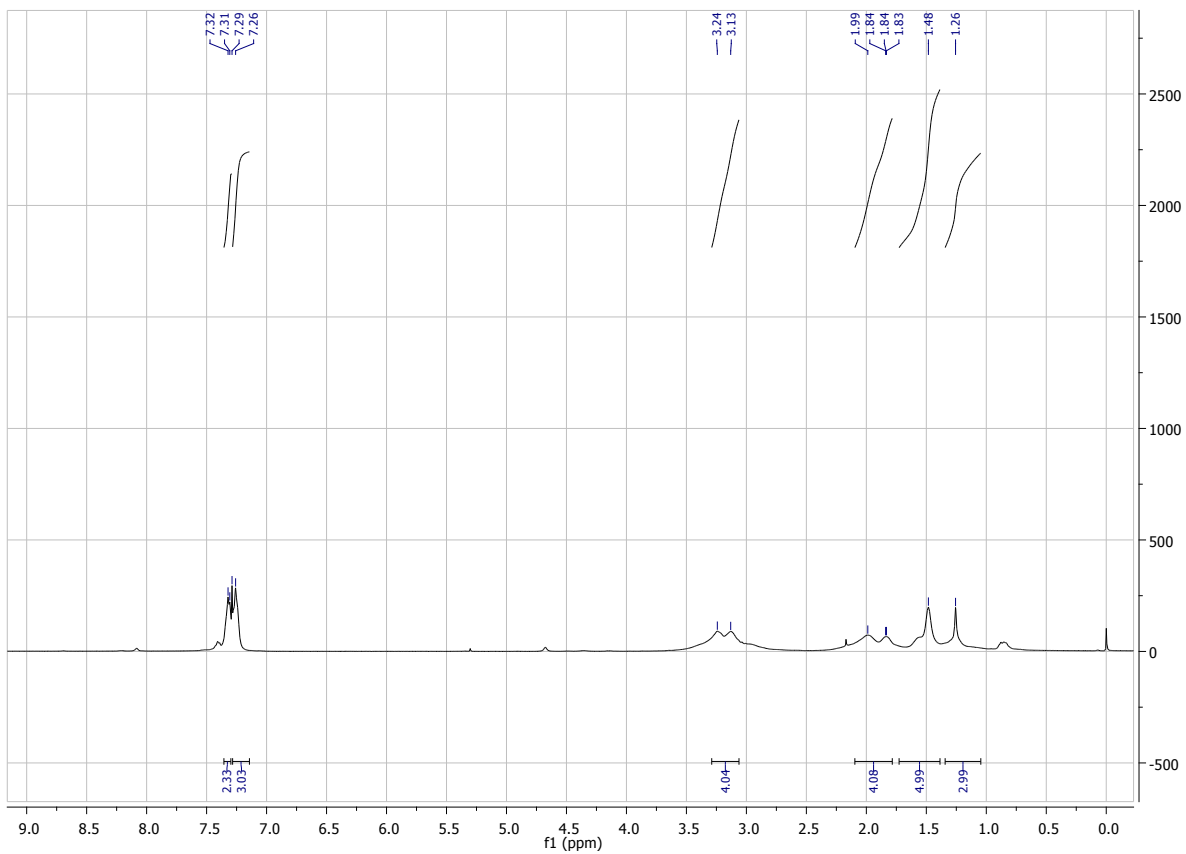
¹H NMR (400 MHz, CDCl₃): δ 1.26 (s, 3H), 1.48 (s, 5H), 1.84-1.98(m, 4H), 3.13-3.24 (m, 4H), 7.26 (s, 3H), 7.31-7.32 (d, *J* = 5.9 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 17.8, 22.6, 22.9, 31.3, 52.4, 54.1, 99.8, 127.4, 128.6, 129.0, 136.2.

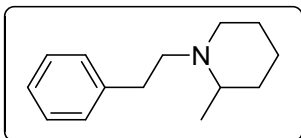
GC/MS: rt = 09.07 min, M/Z = 203

HRMS: 204.1160 (M+H). Theoretical: 204.1158

Purification Washing with diethyl ether.



2-methyl-1-phenethylpiperidine 7n



mp: 145°C-155°C

NMR Yield of corresponding enamine = 80 %

Yield (isolated) = 76 %

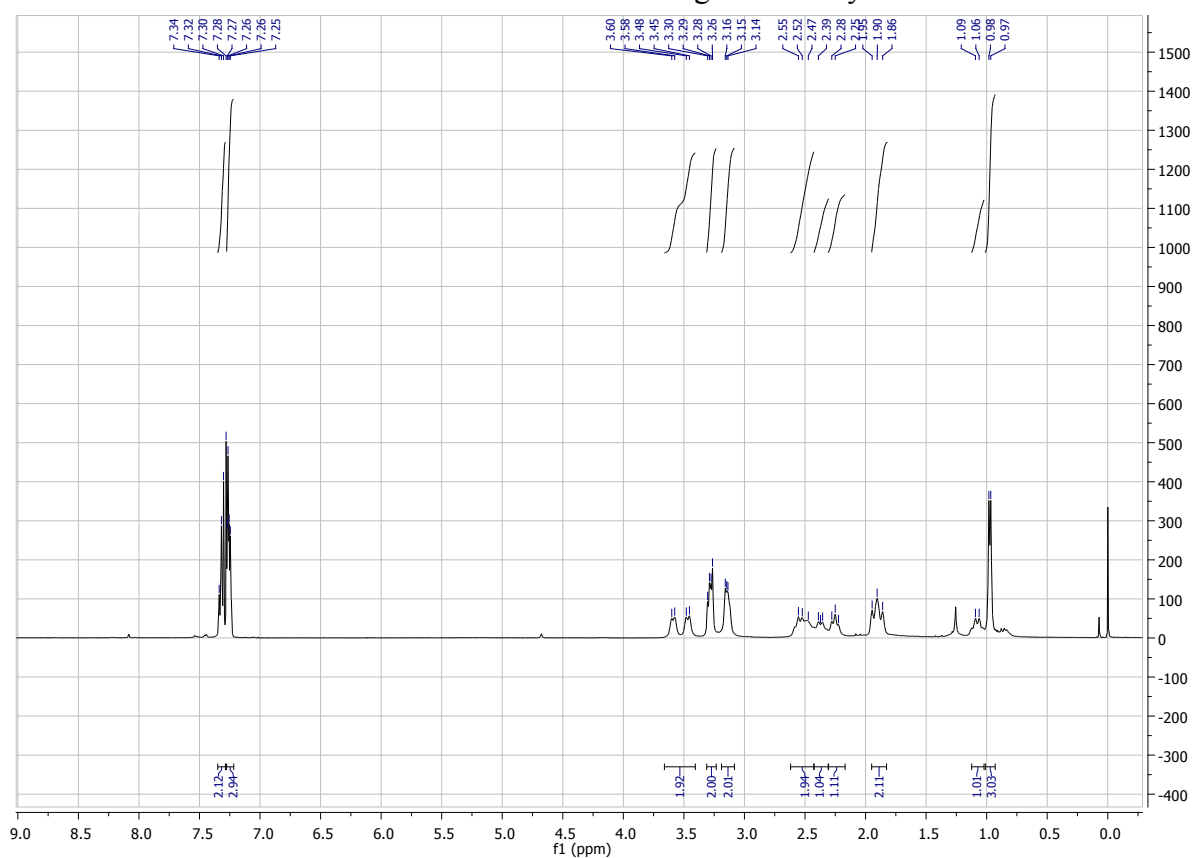
¹H NMR (400 MHz, CDCl₃): δ 0.97-0.98 (d, *J* = 6.2 Hz, 3H), 1.06-1.09 (d, *J* = 12.2 Hz, 1H), 1.86-1.95 (m, 2H), 2.22-2.28 (t, *J* = 11.1 Hz, 1H), 2.31-2.43 (m, 1H), 2.45-2.62 (m, 2H), 3.08-3.19 (m, 2H), 3.26-3.3 (dd, *J*¹ = 5.4 Hz, *J*² = 10.8 Hz, 2H), 3.46-3.6 (dd, *J*¹ = 9.9 Hz, *J*² = 48.5 Hz, 2H), 7.25-7.27 (m, 3H), 7.3-7.34 (m, 2H).

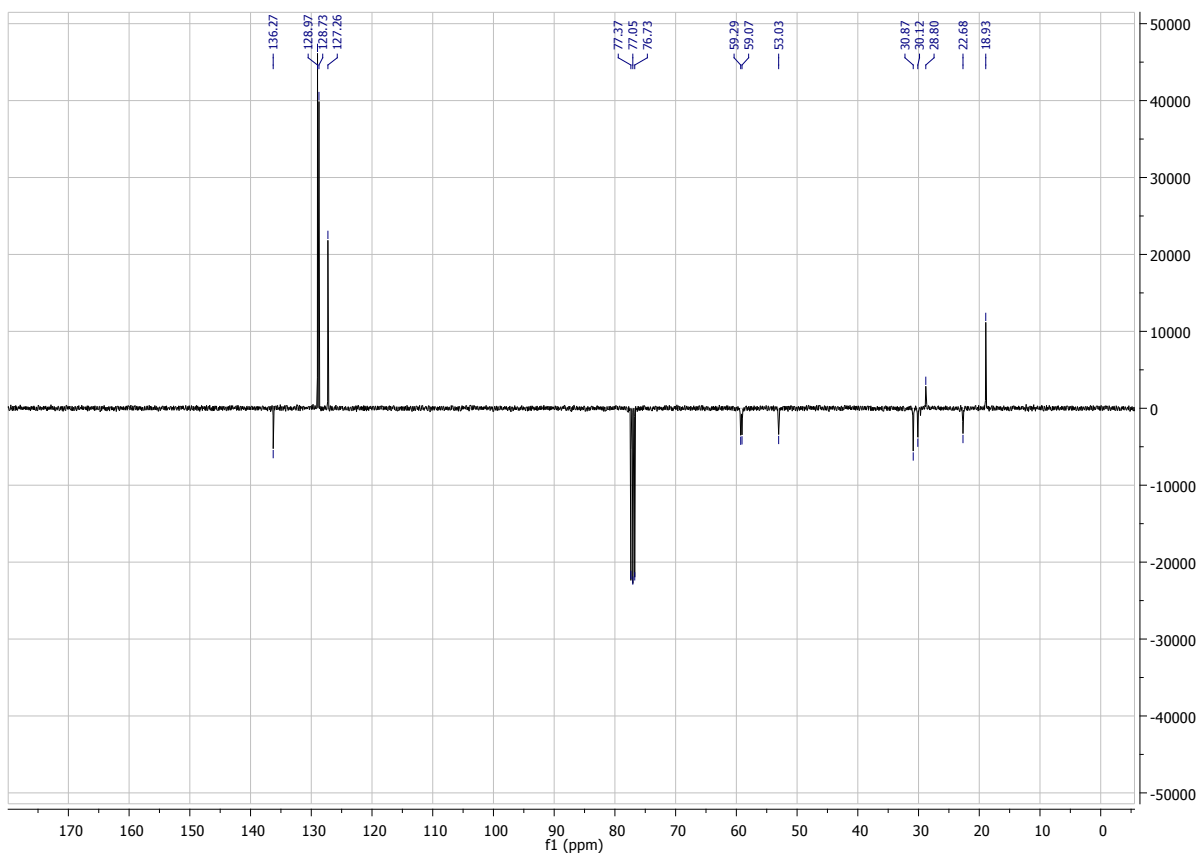
¹³C NMR (100 MHz, CDCl₃): δ 18.9, 22.7, 28.8, 30.1, 30.9, 53.0, 59.0, 127.9, 128.7, 129.0, 136.3.

GC/MS: rt = 08.66 min, M/Z = 203

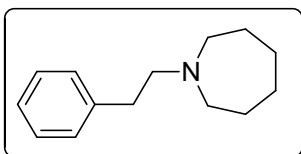
HRMS: 204.1754 (M+H). Theoretical: 204.1752

Purification: Washing with diethyl ether.





1-phenethylazepane 7o



mp: 148°C-150°C

NMR Yield of corresponding enamine = 83 %

Yield (isolated) = 76 %

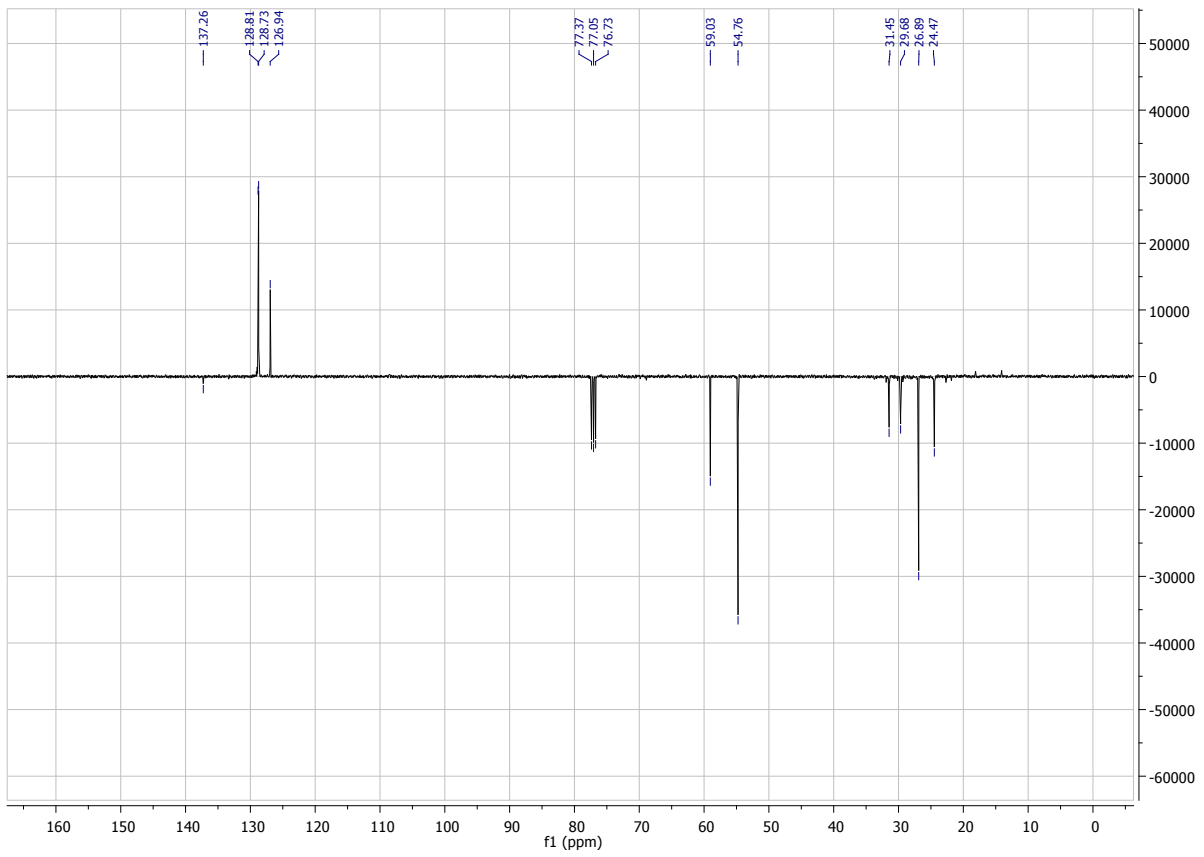
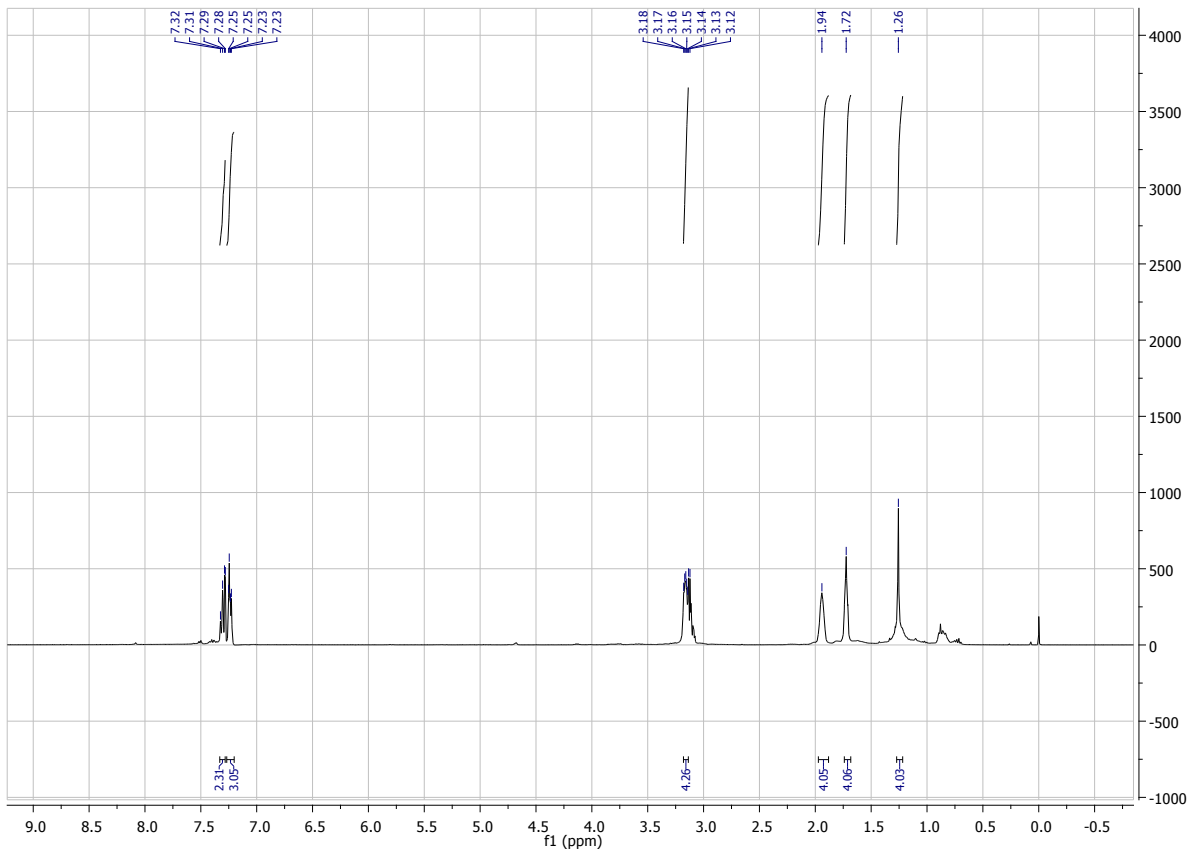
¹H NMR (400 MHz, CDCl₃): δ 1.26 (s, 4H), 1.72 (s, 4H), 2.94 (s, 4H), 3.12-3.18 (m, 4H), 7.23-7.25 (m, 3H), 7.29-7.32 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 24.5, 26.8, 29.4, 31.5, 54.8, 99.0, 126.9, 128.7, 128.8, 137.3.

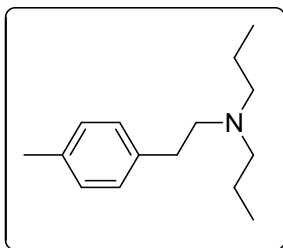
GC/MS: rt = 08.67 min, M/Z = 203.17

HRMS: 204.1753 (M+H). Theoretical: 204.1752

Purification: Washing with diethyl ether.



N-(4-methylphenethyl)-*N*-propylpropan-1-amine 7p



NMR Yield of corresponding enamine = 67 %

Yield (isolated) = 60 %

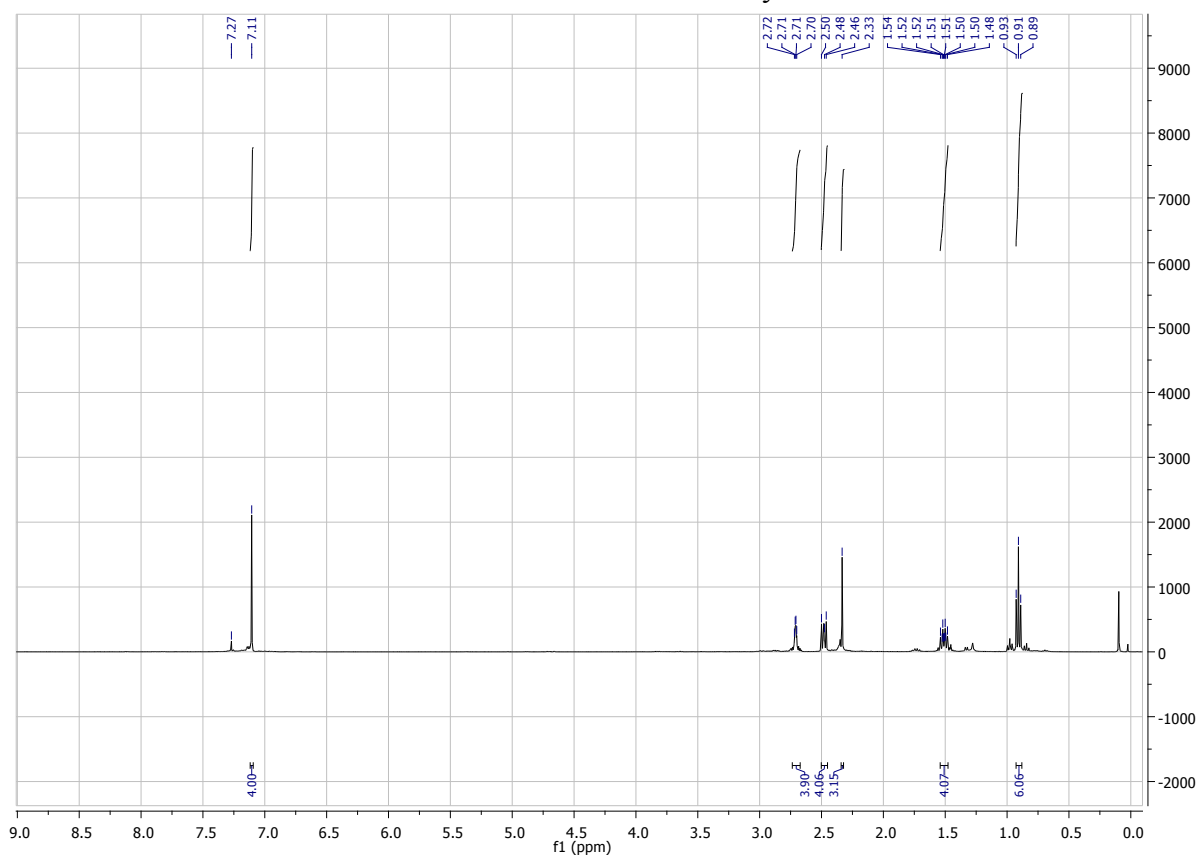
¹H NMR (400 MHz, CDCl₃): δ 0.80-0.93 (t, *J* = 7.4 Hz, 6H), 1.64-1.54 (m, 4H), 2.33 (s, 3H), 2.46-2.50 (m, 4H), 2.67-7.30 (m, 4H), 7.11 (s, 4H).

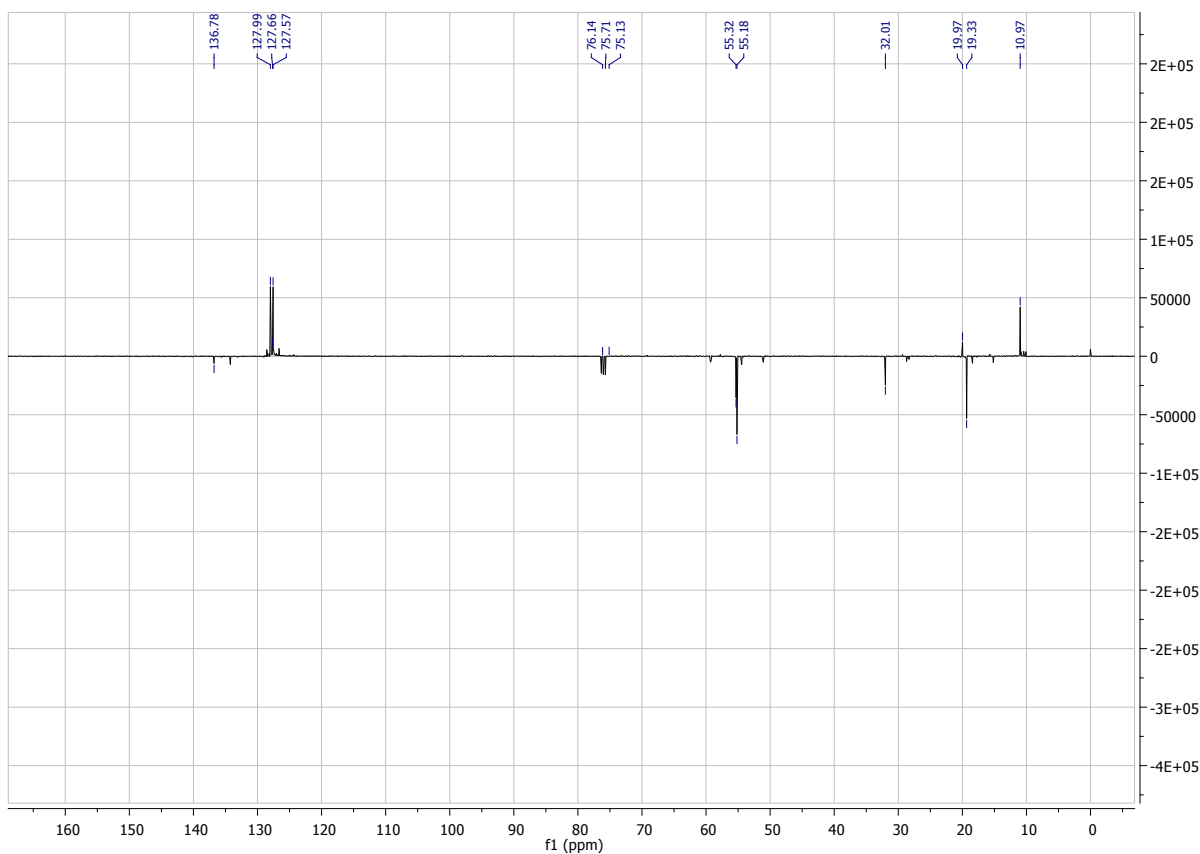
¹³C NMR (100 MHz, CDCl₃): δ 11.0, 19.3, 20.0, 32.0, 55.2, 55.3, 127.6, 128.0, 136.8.

GC/MS: rt = 08.65 min, *M/Z* = 219.20

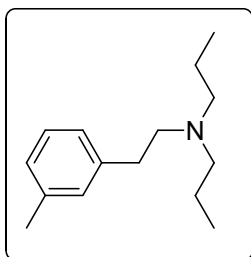
HRMS: 220.2066 (*M+H*). Theoretical: 220.2065

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 70:30.





N-(3-methylphenethyl)-*N*-propylpropan-1-amine **7q**



NMR Yield of corresponding enamine = 82 %

Yield (isolated) = 78 %

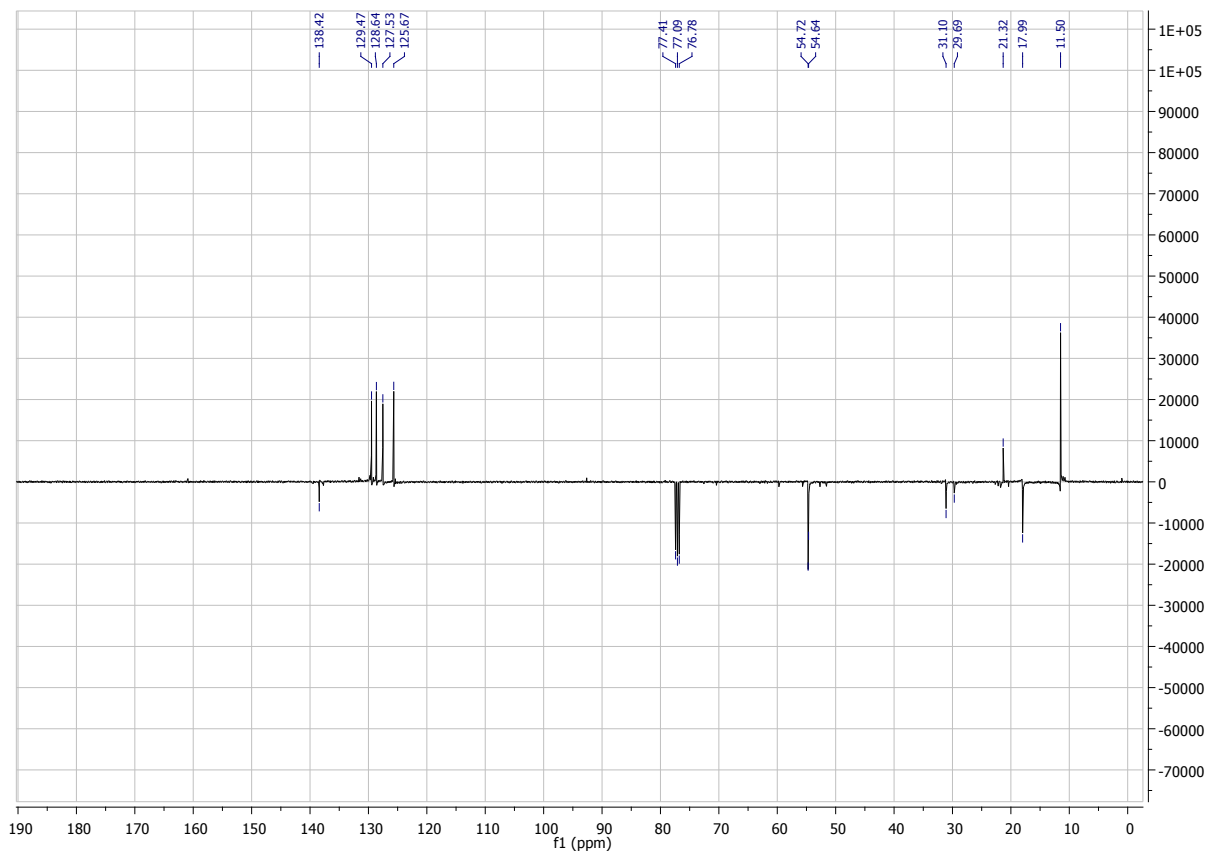
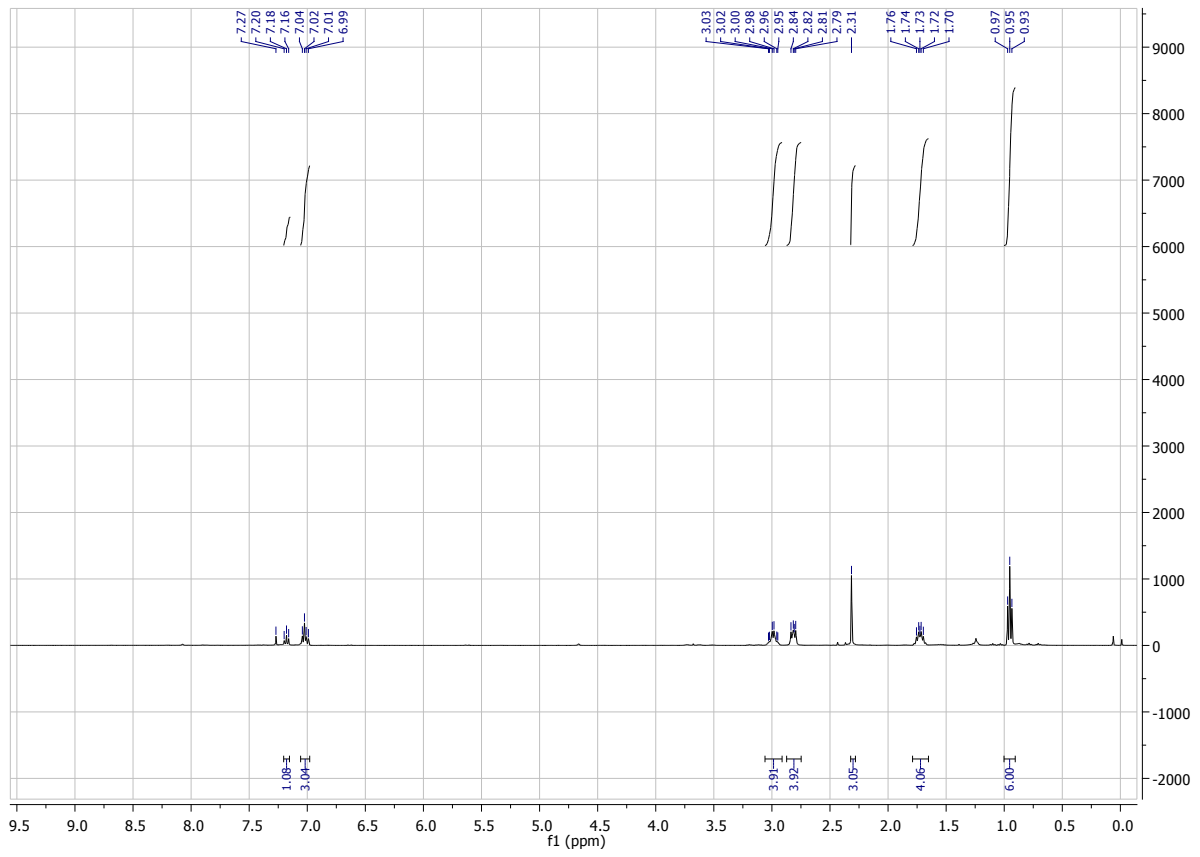
¹H NMR (400 MHz, CDCl₃): δ 0.93-0.97 (t, *J* = 7.4 Hz, 6H), 1.70-1.76 (m, 4H), 2.31(s, 3H), 2.79-2.84 (m, 4H), 2.95-3.03 (m, 3H), 6.99-7.04 (m, 3H), 7.16-7.20 (t, *J* = 7.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 11.5, 18.0, 21.3, 29.7, 31.1, 54.6, 54.7, 125.6, 127.5, 128.6, 129.5, 138.4.

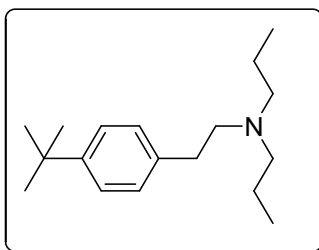
GC/MS: rt = 08.6 min, M/Z = 219.2

HRMS: 220.2066 (M+H). Theoretical: 220.2065

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 60:40.



N-(4-(*tert*-butyl)phenethyl)-*N*-propylpropan-1-amine **7r**



NMR Yield of corresponding enamine = 73 %

Yield (isolated) = 70 %

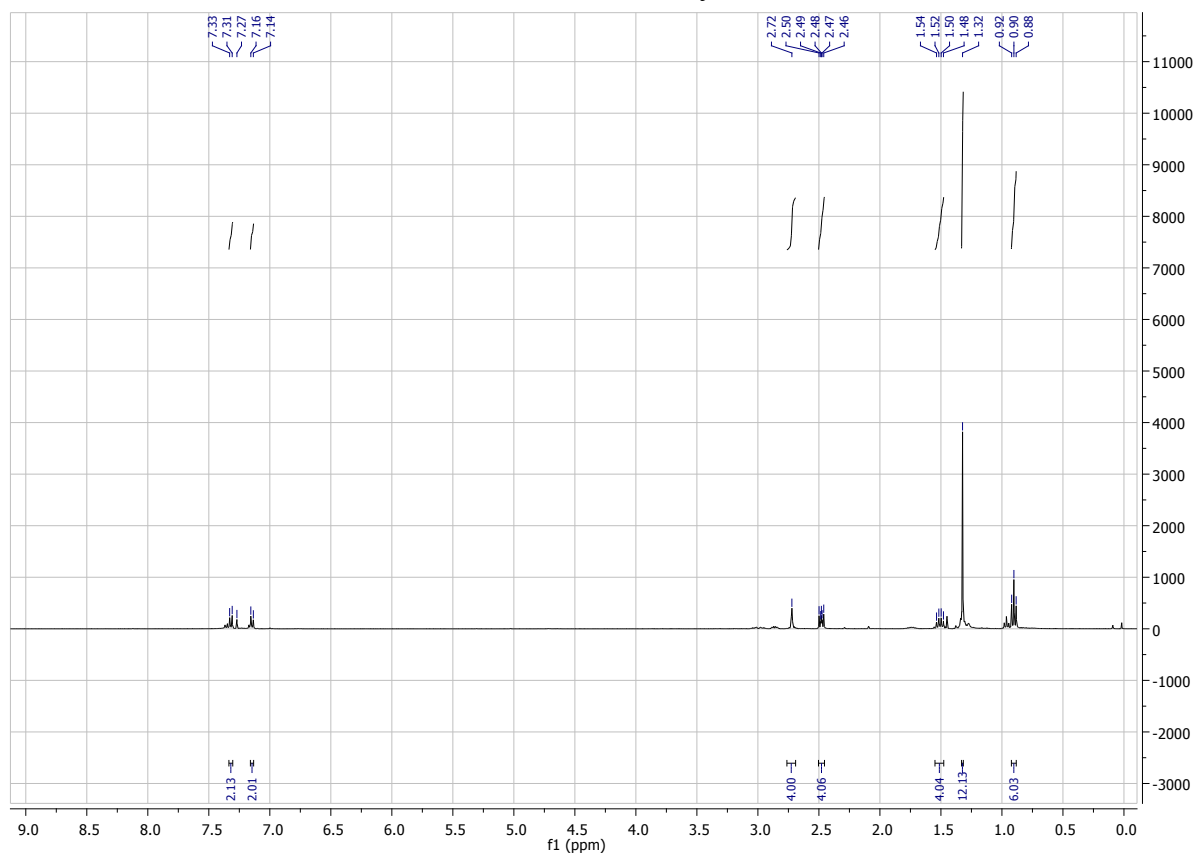
¹H NMR (400 MHz, CDCl₃): δ 0.88-0.92 (t, *J* = 7.4 Hz, 6H), 1.32 (s, 12H), 1.48-1.54 (m, 4H), 2.45-2.5 (m, 4H), 2.72 (s, 4H), 7.14-7.16 (d, *J* = 8.3 Hz, 2H), 7.31-7.33 (d, *J* = 8.3 Hz, 2H).

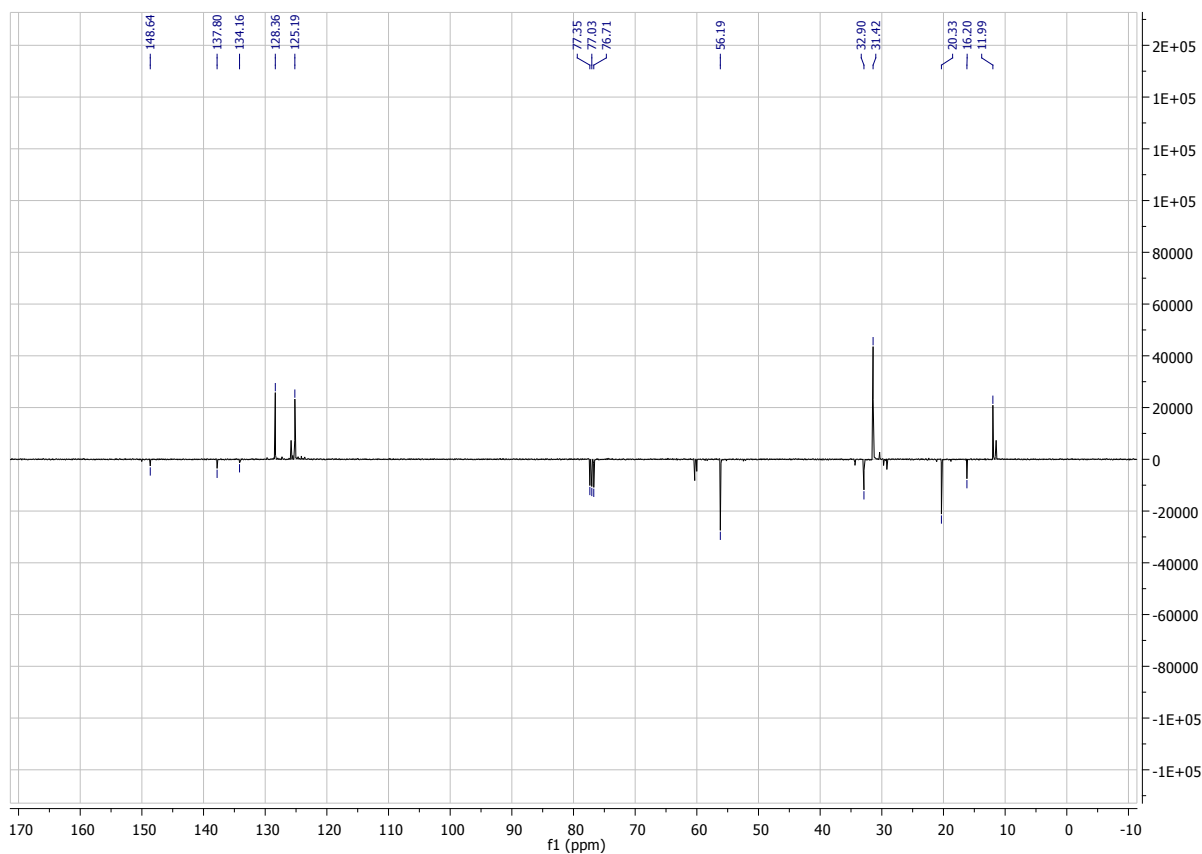
¹³C NMR (100 MHz, CDCl₃): δ 12.0, 16.2, 20.3, 31.4, 32.9, 56.2, 125.2, 128.4, 134.2, 137.8, 148.6.

GC/MS: rt = 09.78 min, M/Z = 261.25

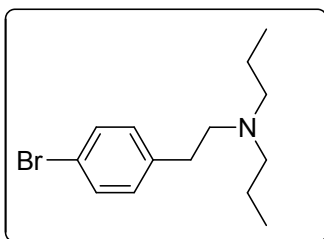
HRMS: 262.2539 (M+H). Theoretical: 262.2535

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 60:40.





N-(4-bromophenethyl)-*N*-propylpropan-1-amine 7s



NMR Yield of corresponding enamine = 96 %

Yield (isolated) = 90 %

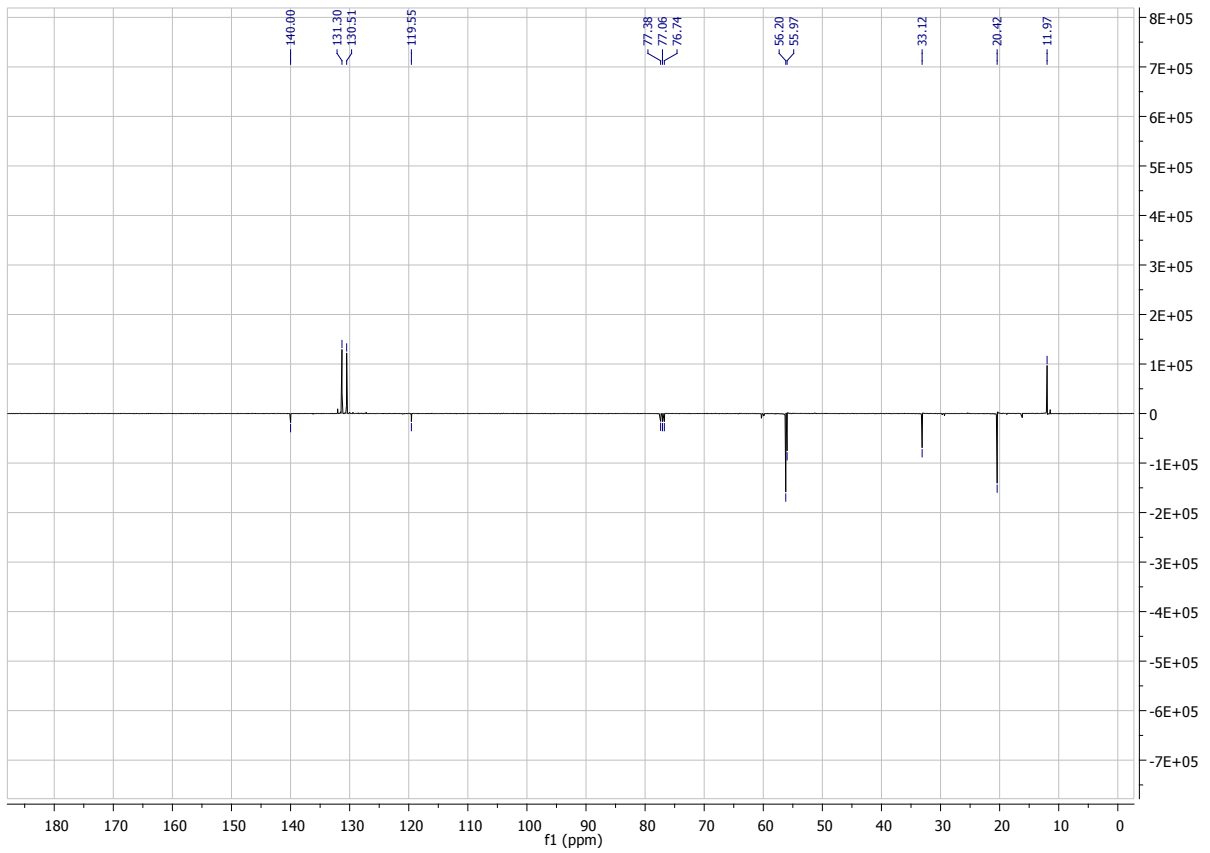
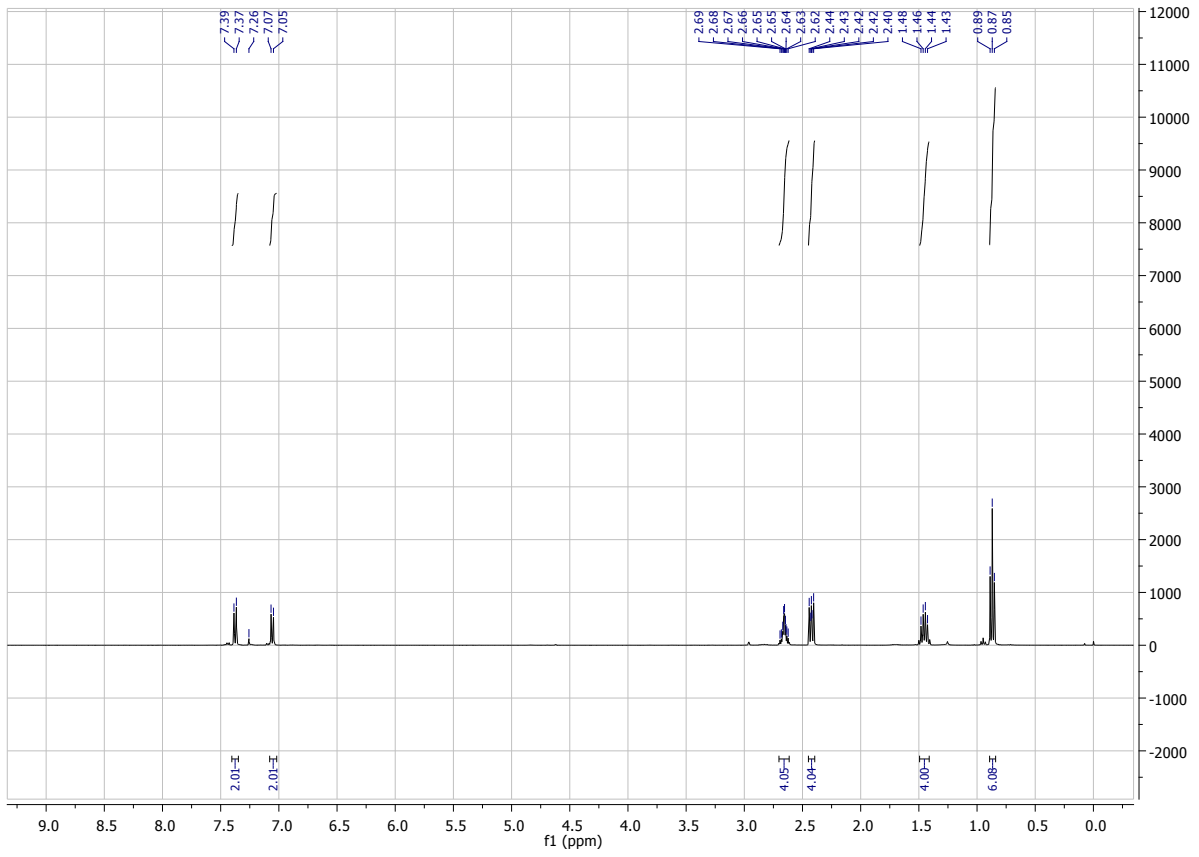
¹H NMR (400 MHz, CDCl₃): δ 0.85-0.89 (t, *J* = 7.4 Hz, 6H), 1.43-1.48 (m, 4H), 2.40-2.44 (m, 4H), 2.62-2.69 (m, 4H), 7.05-7.07 (d, *J* = 8.4 Hz, 2H), 7.37-7.39 (d, *J* = 8.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 12.0, 20.4, 33.1, 56.0, 56.2, 119.5, 130.5, 131.3, 140.0.

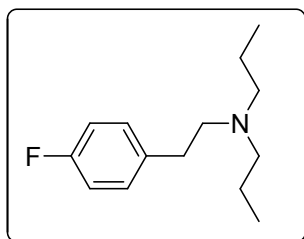
GC/MS: rt = 09.72 min, *M/Z* = 283.09

HRMS: 284.1020 (*M*+*H*). Theoretical: 284.1014

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 85:25.



N-(4-fluorophenethyl)-*N*-propylpropan-1-amine 7t



NMR Yield of corresponding enamine = 79 %

Yield (isolated) = 73 %

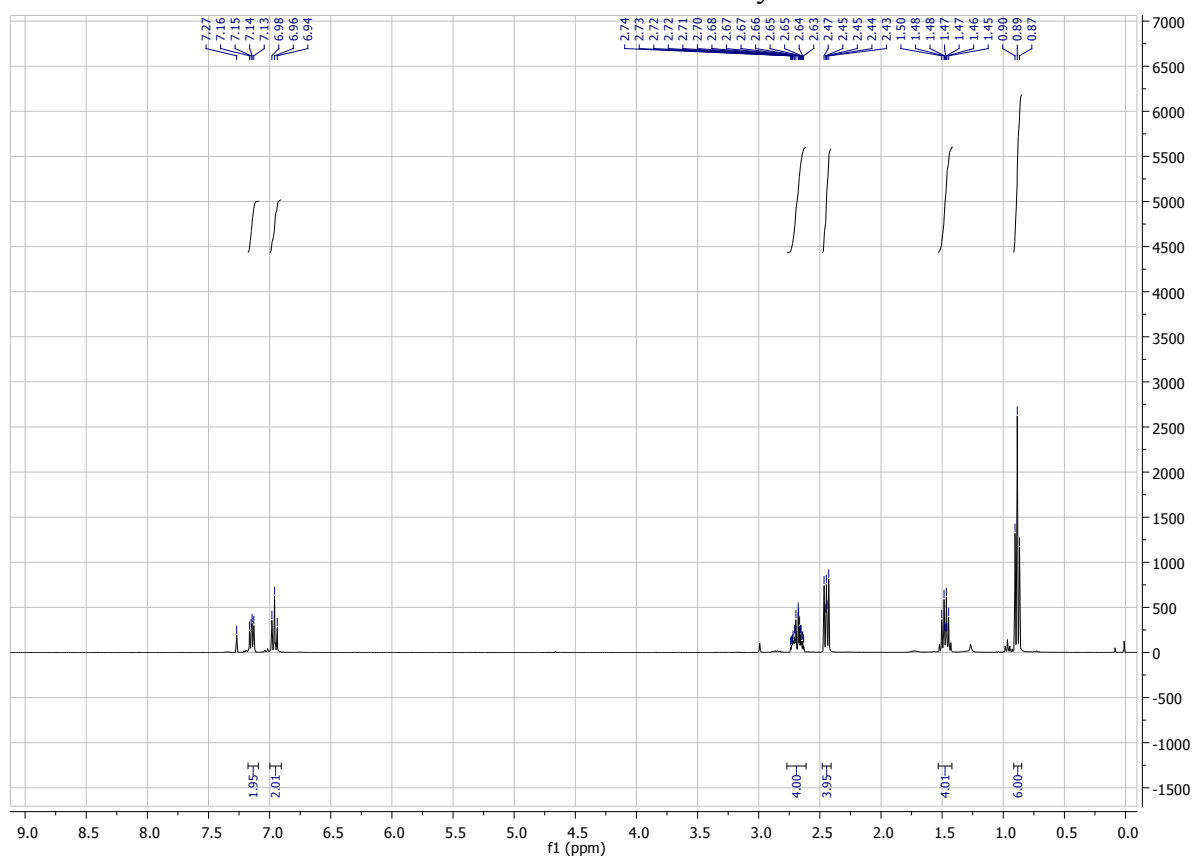
¹H NMR (400 MHz, CDCl₃): δ 0.87-0.90 (t, *J* = 7.4 Hz, 6H), 1.45-1.50 (m, 4H), 2.41-2.48 (m, 4H), 2.61-2.77 (m, 4H), 6.94-6.98 (t, *J* = 8.8 Hz, 2H), 7.13-7.15 (dd, *J*¹ = 5.5 Hz, *J*² = 8.6 Hz, 2H).

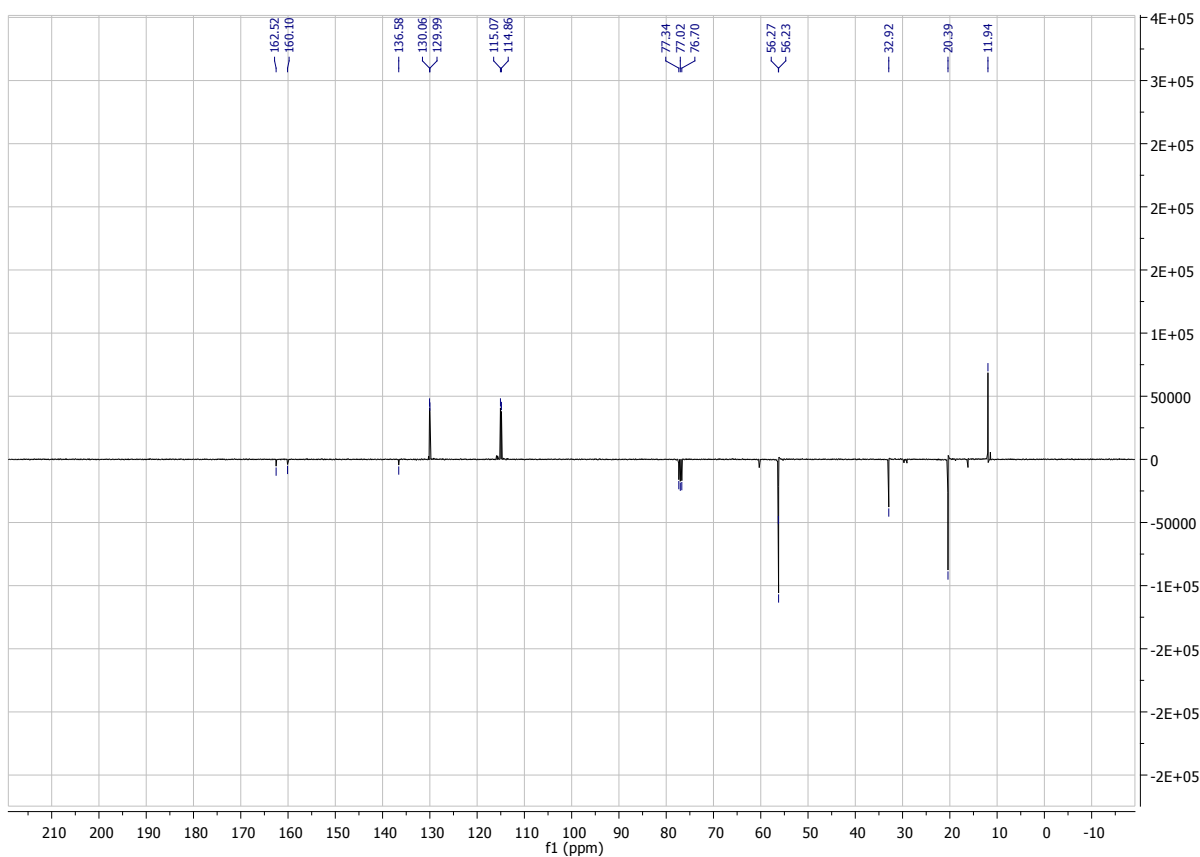
¹³C NMR (100 MHz, CDCl₃): δ 11.9, 20.4, 32.9, 56.2, 56.3, 114.8-115.1 (d, *J*_{C-F} = 84 Hz), 129.9-130.1 (d, *J*_{C-F} = 7.9 Hz), 160.1, 162.5.

GC/MS: rt = 08.14 min, *M/Z* = 223

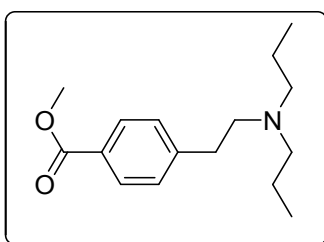
HRMS: 224.1816 (M+H). Theoretical: 224.1815

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 70:30.





Methyl 4-(2-(dipropylamino) ethyl)benzoate 7u



NMR Yield of corresponding enamine = 91 %

Yield (isolated) = 85 %

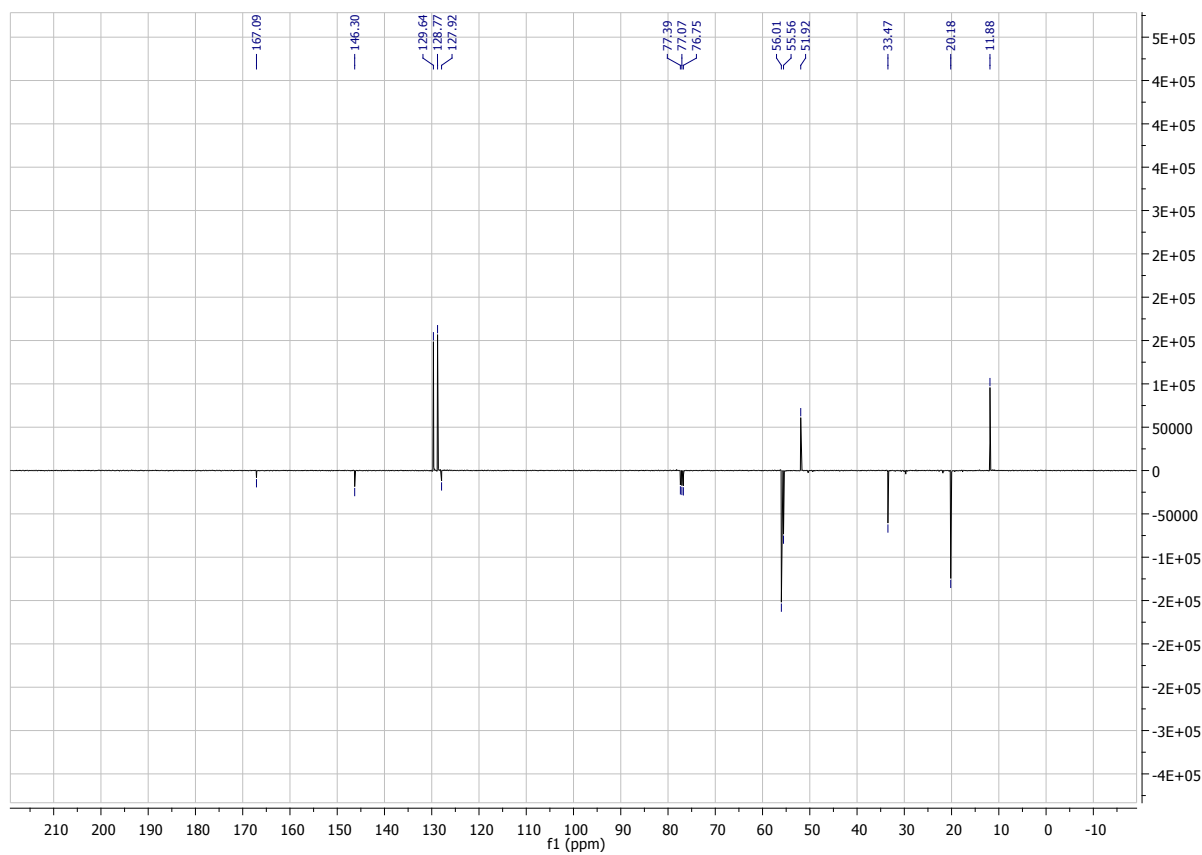
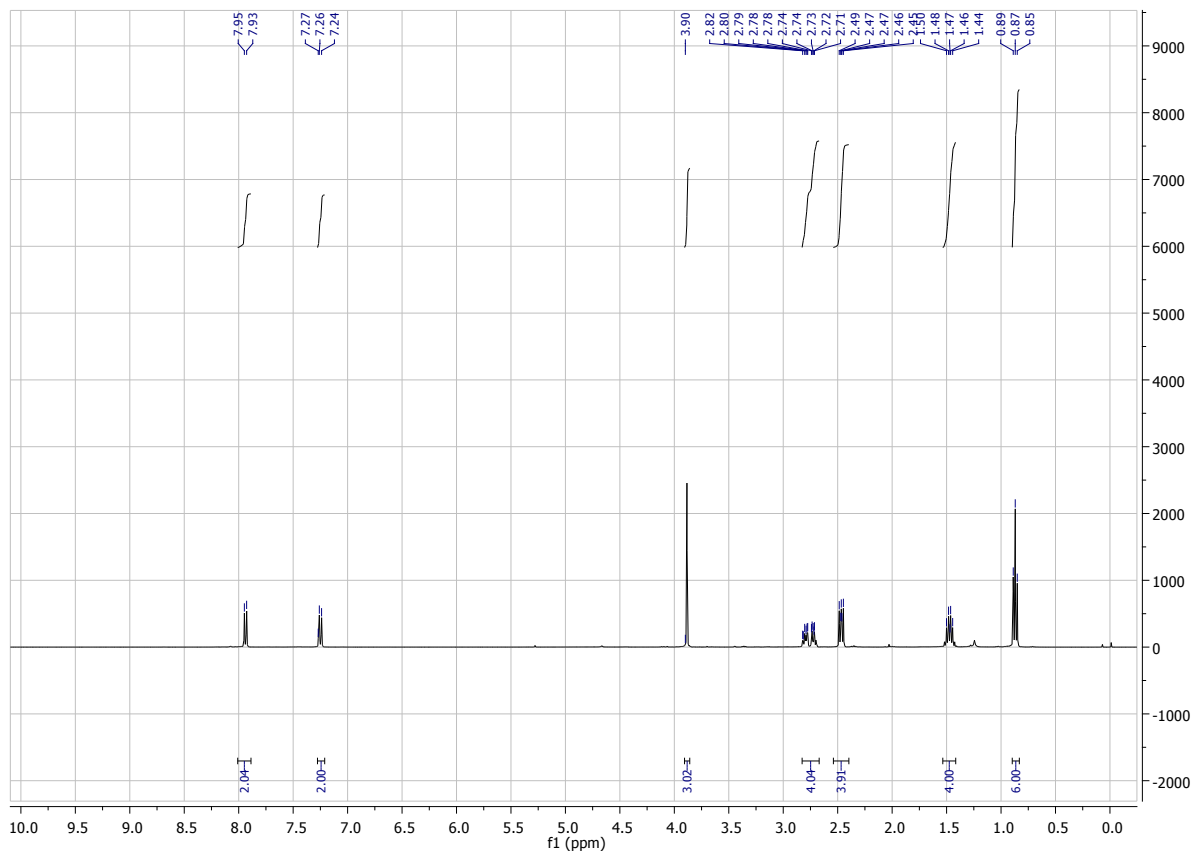
¹H NMR (400 MHz, CDCl₃): δ 0.85-0.88 (t, *J* = 7.4 Hz, 6H), 1.44-1.5 (m, 4H), 2.44-2.48 (m, 4H), 2.67-2.83 (m, 4H), 3.88 (s, 3H), 7.24-7.26 (d, *J* = 8 Hz, 2H), 7.93-7.95 (d, *J* = 8.3 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 11.9, 20.2, 33.5, 51.9, 55.6, 56.0, 127.9, 128.7, 129.6, 146.3, 167.1.

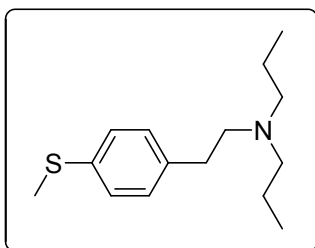
GC/MS: rt = 10.48 min, M/Z = 263.19

HRMS: 264.1964 (M+H). Theoretical: 264.1964

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 80:20.



N-(4-methylthio)phenethyl)-*N*-propylpropan-1-amine 7v



NMR Yield of corresponding enamine = 69 %

Yield (isolated) = 60 %

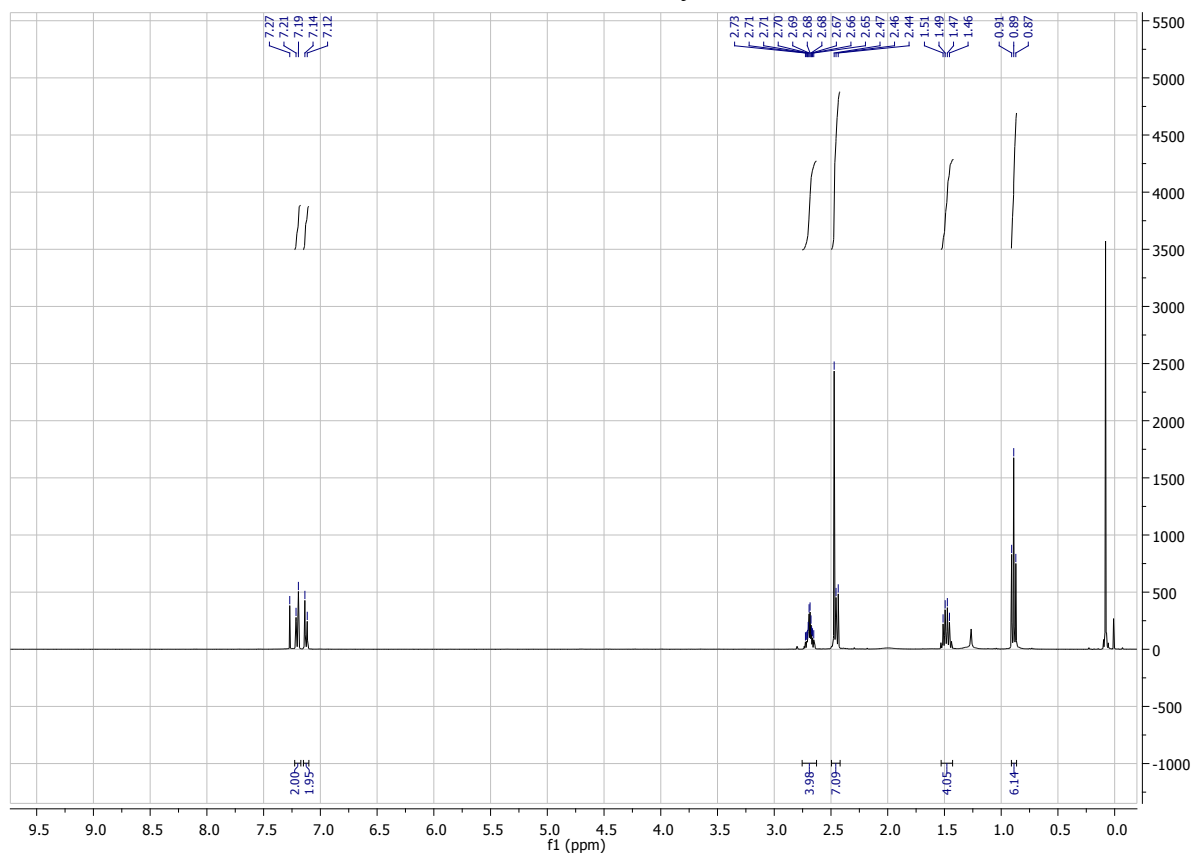
¹H NMR (400 MHz, CDCl₃): δ 0.87-0.91 (t, *J* = 7.4 Hz, 6H), 1.48-1.51 (m, 4H), 2.42-2.5 (m, 7H), 2.63-2.75 (m, 4H), 7.12-7.14 (d, *J* = 8.3 Hz, 2H), 7.19-7.21 (d, *J* = 8.3 Hz, 2H).

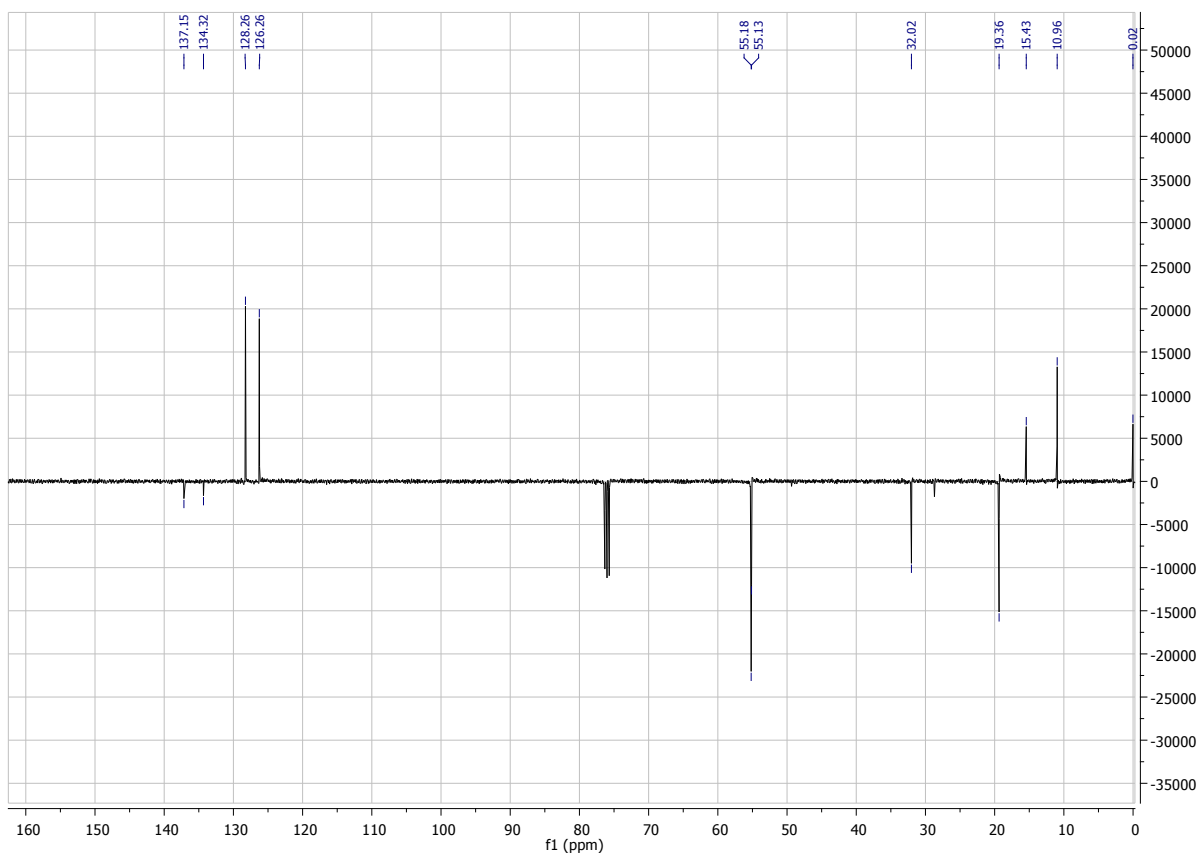
¹³C NMR (100 MHz, CDCl₃): δ 12.0, 15.4, 19.4, 32.0, 55.1, 55.2, 126.3, 128.3, 134.3, 137.1.

GC/MS: rt = 10.4 min, M/Z = 251

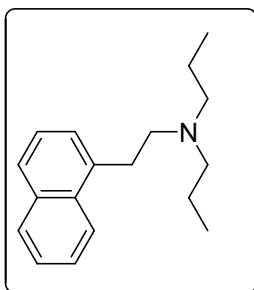
HRMS: 252.1787 (M+H). Theoretical: 252.1786

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 60:40.





N-(2-(naphthalene-1-yl)ethyl)-*N*-propylpropan-1-amine 7w



NMR Yield of corresponding enamine = 84 %

Yield (isolated) = 80 %

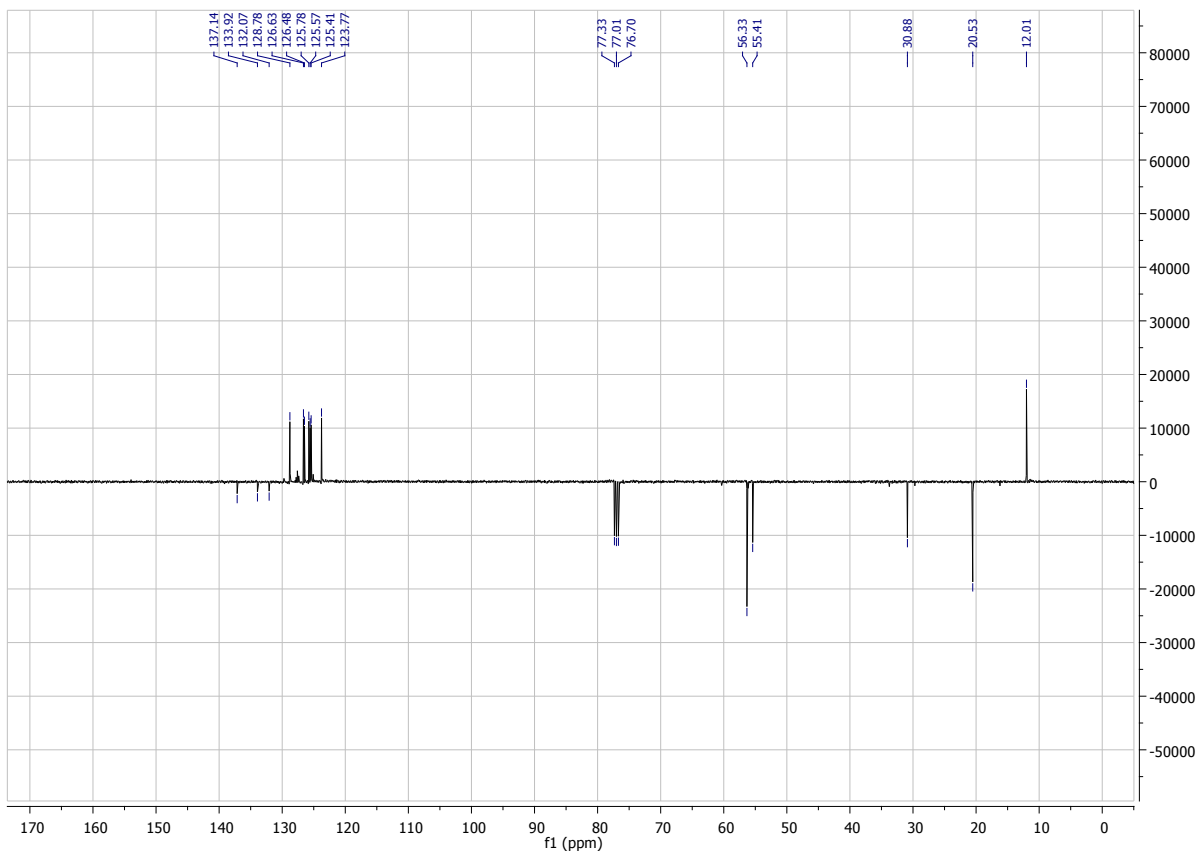
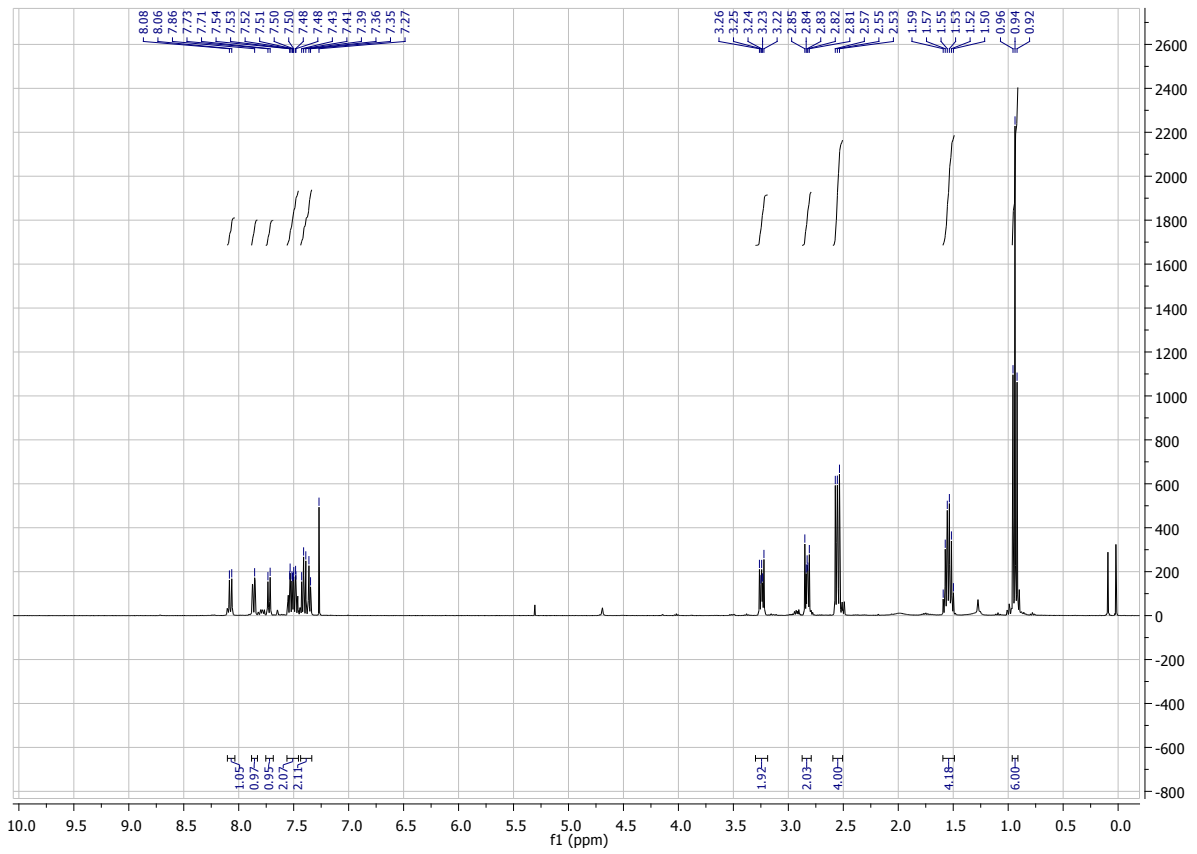
¹H NMR (400 MHz, CDCl₃): δ 0.92-0.96 (t, *J* = 7.4 Hz, 6H), 1.49-1.59 (m, 4H), 2.51-2.59 (m, 4H), 2.79-2.87 (m, 4H), 3.19-3.3 (m, 4H), 7.34-7.44 (m, 2H), 7.48-7.54 (m, 2H), 7.71-7.73 (d, *J* = 8.1 Hz, 1H), 7.85-7.87 (d, *J* = 7.3 Hz, 1H), 8.06-8.08 (d, *J* = 8.5 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 12.0, 20.5, 30.9, 55.4, 56.3, 123.7, 125.4, 125.6, 125.8, 126.5, 126.6, 128.8, 132, 133.9, 137.1.

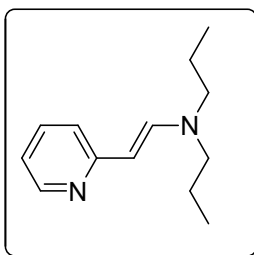
GC/MS: rt = 10.85 min, M/Z = 255

HRMS: 256.2067 (M+H). Theoretical: 256.2065

Purification: by silica gel column chromatography, eluent: Pentane/ ethyl acetate 70:30.



(E)-N-propyl-N-(2-(pyridin-2-yl) vinyl)propan-1-amine 3x



NMR Yield of corresponding enamine = 100 %

Yield (isolated) = 98 %

¹H NMR (400 MHz, CDCl₃): δ 0.89-0.92 (t, *J* = 7.4 Hz, 6H), 1.56-1.65 (m, 4H), 3.09-3.12 (dd, *J* = 8.2Hz, 2*J* = 6.9Hz, 4H), 5.13-5.16 (d, *J* = 13.4 Hz, 1H), 6.71-6.74 (ddd, *J* = 7.3 Hz, *J* = 4.9 Hz, *J* = 1.1Hz, 1H), 6.84-6.86 (dt, *J* = 8.1 Hz, *J* = 1Hz, 1H), 7.35-7.39 (ddd, *J* = 8 Hz, *J* = 7.3 Hz, *J* = 1.9, 1H), 7.43-7.47 (d, *J* = 13.4 Hz, 1H), 8.27-8.29 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 11.3, 21.2, 53.7, 94.2, 116.9, 118.6, 135.9, 142.4, 148.6, 159.

GC/MS: rt = 09.7 min, M/Z = 204

HRMS: 205.1704 (M+H). Theoretical: 205.1705

