Supporting Information for:

Direct, Catalytic α-Alkylation of *N*-Heterocycles by Hydroaminoalkylation: Substrate Effects for Regiodivergent Product Formation

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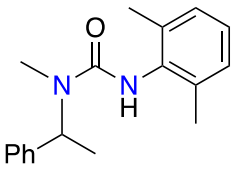
S1. Materials and Instrumentation

All reactions were performed under a N_2 atmosphere using Schlenk or glovebox techniques, unless otherwise stated. $TaCl_5$ (Strem), $Ta(NMe_2)_5$ (Strem), (chloromethyl)trimethylsilane (Aldrich), *N,N*-diphenylamine (Alfa), *N*-isopropylaniline (Combi-Blocks), triphosgene (Oakwood), 2,6-dimethylaniline (Aldrich), 2,6-diisopropylaniline (Alfa), *N*-methyl-1-phenylethan-1-amine (CombiBlocks), *N*-methyl-1,1-diphenylmethanamine (CombiBlocks), *N*-methylpropan-2-amine (CombiBlocks), 2,4,6-trimethylaniline (Aldrich), 4-bromo-2,6-dimethylaniline (Aldrich), and 4-chloro-2,6-dimethylaniline (Aldrich) were used as received. All amines and alkenes were commercially available, dried over CaH_2 and distilled and degassed prior to use in catalytic experiments. $[Ta(NMe_2)_3Cl_2]_2$,[1] $Ta(CH_2CMe_3)_3Cl_2$,[2] and $Ta(CH_2SiMe_3)_3Cl_2$[3] were synthesized according to literature protocols. The proteo-ligands and their corresponding ligand salts **L1-L3**[4], **L4**[5], **L5**[6], $TaMe_3Cl_2$,[7] can be prepared as previously described. All glassware was dried in a 180 °C oven overnight before use. Toluene, and hexanes were dried over activated alumina columns and stored over activated molecular sieves (4 Å). d_8-Toluene was dried over sieves, sparged, and freeze/pump/thawed prior to use. Experiments conducted on an NMR tube scale were performed in J. Young NMR tubes (8" x 5 mm) sealed with screw-type Teflon caps.

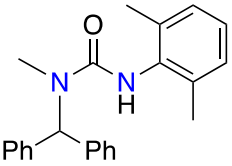
^1H and ^{13}C NMR spectra were recorded on Bruker 300 MHz and 400 MHz Avance spectrometers at ambient temperature. Chemical shifts (δ) are given relative to the corresponding residual protio solvent and are reported in parts per million (ppm). Coupling constants *J* are given in Hertz (Hz). The following abbreviations are used to indicate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Assignment of the signals was carried out using 1D (^1H, $^{13}C\{^1H\}$) and 2D (COSY, HSQC and HMBC) NMR experiments. High resolution mass-spectra (HRMS) were measured by the mass spectrometry services at University of British Columbia, UBC on a Kratos MS-50 spectrometer using a Bruker maXis Ultra-High Resolution tandem TOF (UHR-Qq-TOF) mass spectrometer using a positive electrospray ionization source. Fragment signals are given in mass per charge number (*m/z*). GC/MS analyses were conducted on an Agilent 7890B GC with an Agilent 5977 inert CI mass detector, utilizing methane as the ionization gas. **Note that the peak at 6.294 represents residual internal standard in any cases where this is present.** Single-crystal X-ray structure determination was performed on a APEX II diffractometer at the Department of Chemistry, University of British Columbia, by Pargol Daneshmand.

S2. Ligand Syntheses and Characterization

General procedure for the synthesis of urea based proteoligands: Prepared following a modified literature procedure[1] in which a chosen primary amine (1 equiv.) was dissolved in dichloromethane and the solution was cooled to 0 °C. Triphosgene (0.35 equiv.) was added in portions as a solid. The solution was stirred for five minutes after which *N*,*N*-diisopropylethylamine DIPEA (2 equiv.) was added and the cold bath removed. The solution was stirred for 1 hour and then the appropriate amine (1 equiv.) and a second portion of DIPEA (1 equiv.) was added. The solution was stirred for an additional hour, and then diluted with 1M HCl. The organic phase was washed three times with 1M HCl dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to give the crude product. Product was then recrystallized using ethyl acetate, all ligand yields reported are recrystallized yields.



Synthesis of 3-(2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea (L4-H): Prepared following the general procedure outlined above: 2,6-dimethylaniline (2.25 g, 18.5 mmol), triphosgene (1.81 g, 6.10 mmol), DIPEA (7.2 g, 55.5 mmol), *N*-methyl-1-phenylethan-1-amine (2.5 g, 18.5 mmol). Recrystallization from a concentrated ethyl acetate solution provided the desired compound as a white solid (3.48 g, 66.9 %). All characterization data matched a previous report from our group.[6]



Synthesis of 1-benzhydryl-3-(2,6-dimethylphenyl)-1-methylurea (L5-H): Prepared following the general procedure outlined above: 2,6-dimethylaniline (307 mg, 2.53 mmol), triphosgene (250.2 mg, 0.843 mmol), DIPEA (981 mg, 7.59 mmol), *N*-methyl-1,1-diphenylmethanamine (500 mg, 2.53 mmol). Recrystallization from a concentrated ethyl acetate solution provided the desired compound as a white solid (750 mg, 86 %): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.41-7.27 (overlapping m, 10H, *o,m,p*-C_6H_5), 7.04 (s, 3H, *m,p*-C_6H_5), 6.70 (s, 1H, NHC*H*), 5.78 (br s, 1H, N*H*), 2.88 (s, 3H, CH_3), 2.16 (s, 6H, 2,6-(CH_3)$_2$$C_6H_3$) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 156.57 (*C*=O), 139.66, 135.47, 135.30, 128.80, 128.77, 128.25, 127.80, 126.49, 63.30, 32.05, 28.48 ppm. HRMS (ESI): *m/z* calcd for $C_{23}H_{25}N_2O$ [M+H$^+$]: 345.1967 Found: 345.1964. Anal. Calcd. for $C_{23}H_{25}N_2O$: C, 80.20; H, 7.02; N, 8.13; Found: C, 80.50; H, 7.12; N, 8.18.

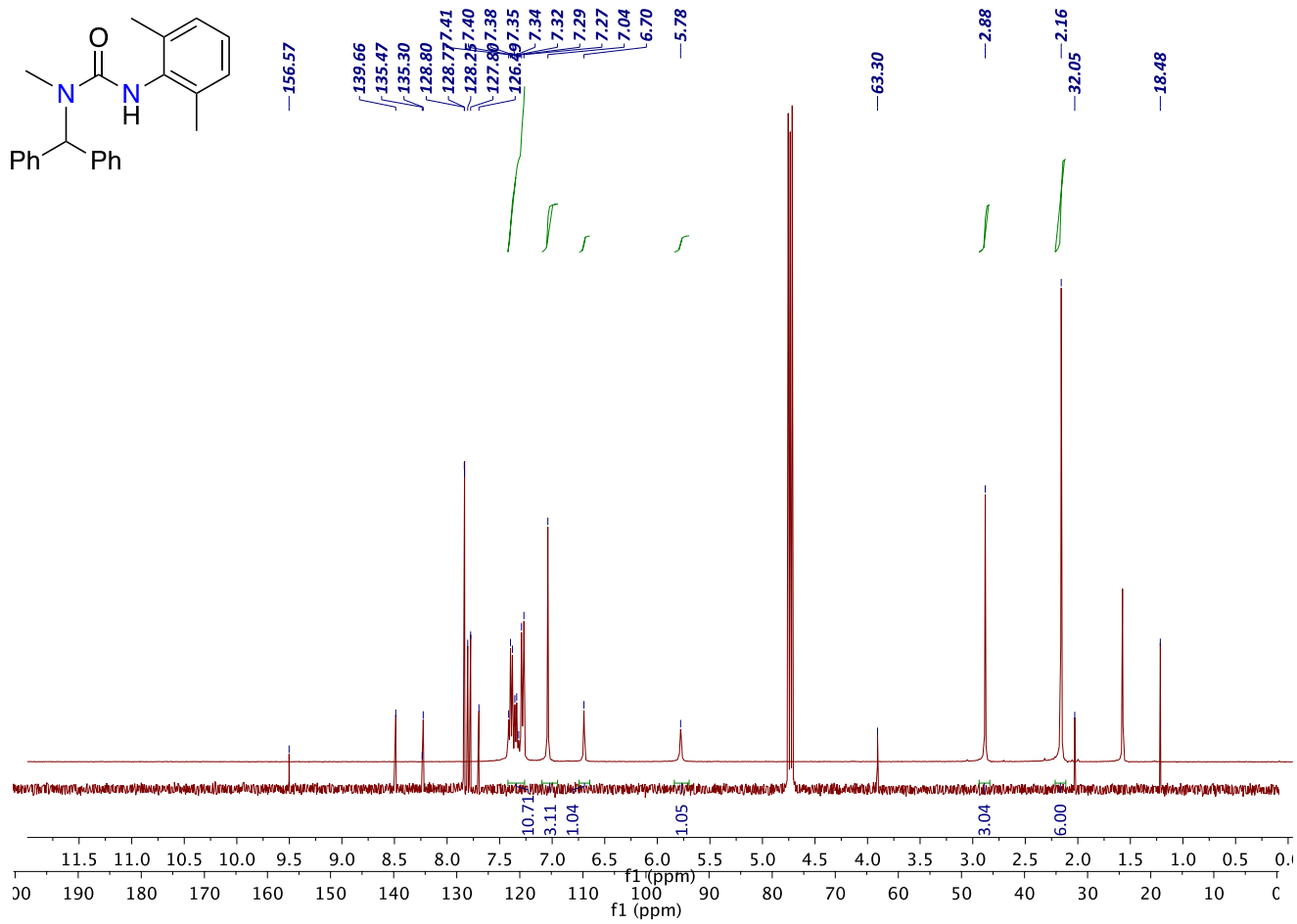


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1-benzhydryl-3-(2,6-dimethylphenyl)-1-methylurea.

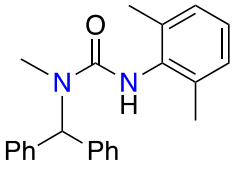
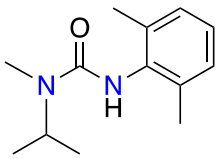


Figure S2. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1-benzhydryl-3-(2,6-dimethylphenyl)-1-methylurea.



Synthesis of 3-(2,6-dimethylphenyl)-1-isopropyl-1-phenylurea (L6-H): Prepared following the general procedure outlined above: 2,6-dimethylaniline (1.5 g, 20.5 mmol), triphosgene (2.02 g, 7.41 mmol), DIPEA (7.95 g, 61.5 mmol), *N*-isopropylaniline (2.5 g, 20.5 mmol). Recrystallization from a concentrated ethyl acetate solution provided the desired compound as a white solid (3.20 g, 65 %*)*: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.05 (s, 3H, *o,m,p*-C_6H_5), 5.69 (br s, 1H, N*H*), 4.56-4.49 (m, 1H, C*H*$(CH_3)_2$), 2.86 (s, 3H, CH_3), 2.24 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 1.17 (d, $J_{H\text{-}H}$ = 1.7 Hz, 6H, CH$(CH_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 156.00 (*C*=O), 135.70, 135.57, 128.20, 126.40, 45.89, 27.45, 20.21, 18.56 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{21}N_2O$ [M+H$^+$]: 221.1654. Found: 221.1656. Anal. Calcd. for $C_{13}H_{21}N_2O$: C, 70.87; H, 9.15; N, 12.72; Found: C, 70.89; H, 9.14; N, 12.63.

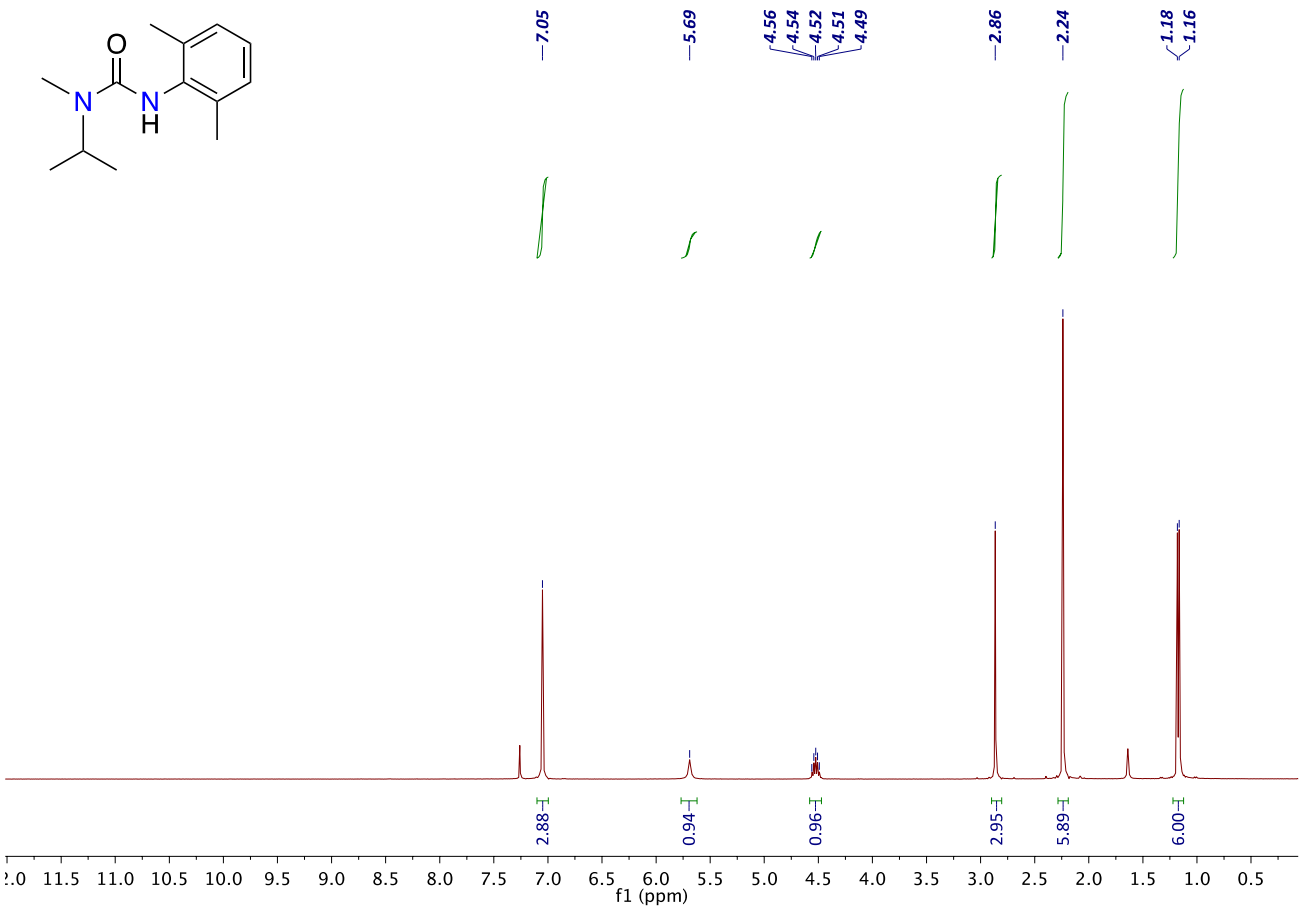


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-(2,6-dimethylphenyl)-1-isopropyl-1-phenylurea.

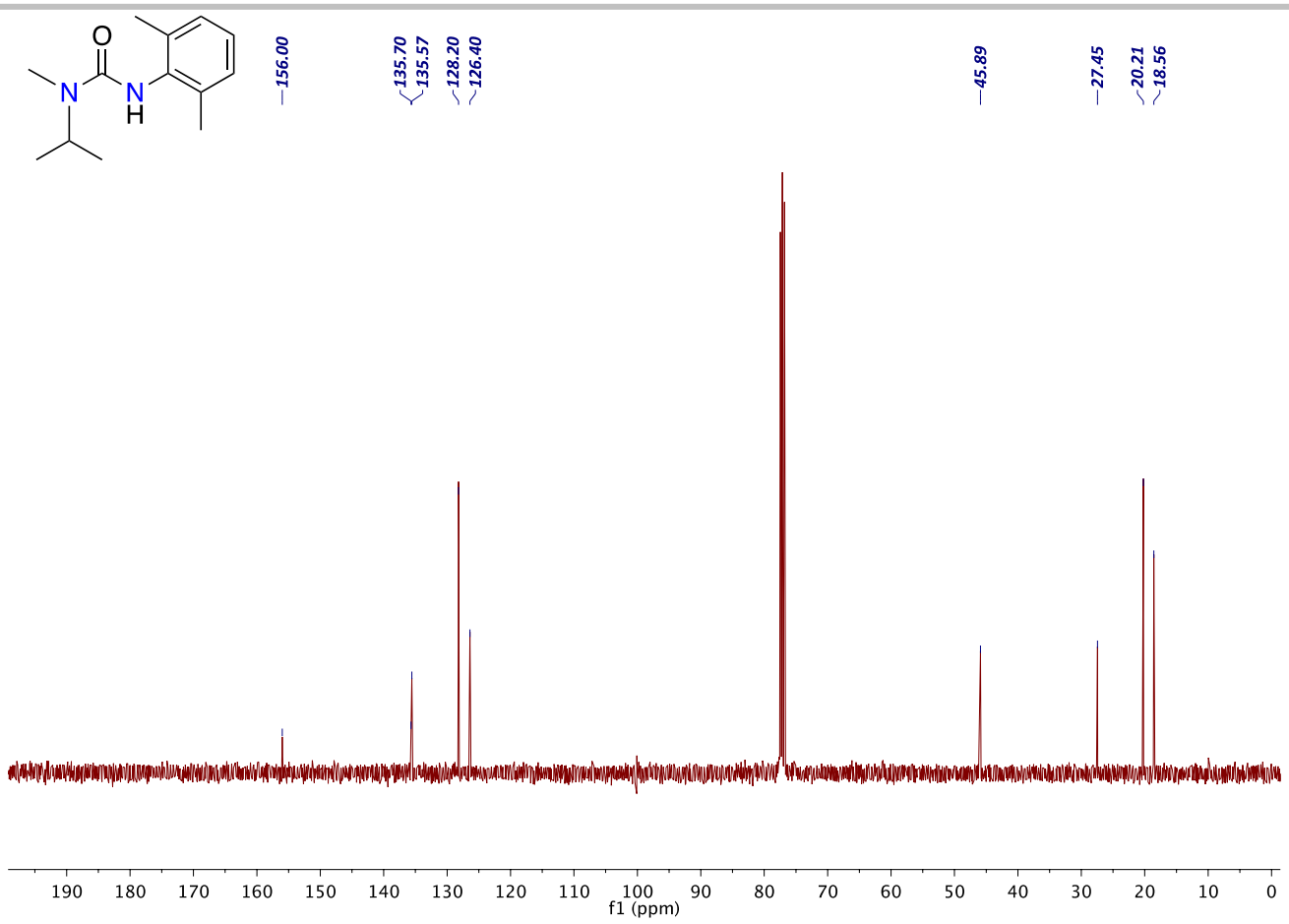
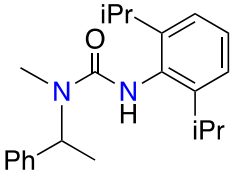


Figure S4. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 3-(2,6-dimethylphenyl)-1-isopropyl-1-phenylurea.



Synthesis of 3-(2,6-diisopropylphenyl)-1-methyl-1-(1-phenylethyl)urea (L7-H): Prepared following the general procedure outlined above: 2,6-dimethylaniline (1.32 g, 7.40 mmol), triphosgene (724 mg, 2.44 mmol), DIPEA (2.87 g, 22.2 mmol), *N*-methyl-1,1-diphenylmethanamine (1.0 g, 7.40 mmol). Recrystallization from a concentrated ethyl acetate solution provided the desired compound as a white solid (1.81 g, 72.3 %): ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.51-7.50 (overlapping m, 4H), 7.45-7.39 (overlapping m, 2H), 7.37-7.35 (m, 1H), 7.28 (m, 1H), 5.78-5.72 (overlapping m, 2H), 3.22-3.12 (m, 2H, C*H*$(CH_3)_2$), 3.00 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.31 (s, 12H, CH(C*H*$_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 157.22 (*C*=O), 146.52, 142.12, 132.80, 128.73, 127.63, 127.41, 126.95, 123.36, 52.99, 29.82, 28.79, 23.81 ppm. HRMS (ESI): *m/z* calcd for $C_{22}H_{31}N_2O$ [M+H$^+$]: 339.2437. Found: 339.2444. Anal. Calcd. for $C_{22}H_{31}N_2O$: C, 78.06; H, 8.73; N, 8.28; Found: C, 78.18; H, 8.96; N, 8.31.

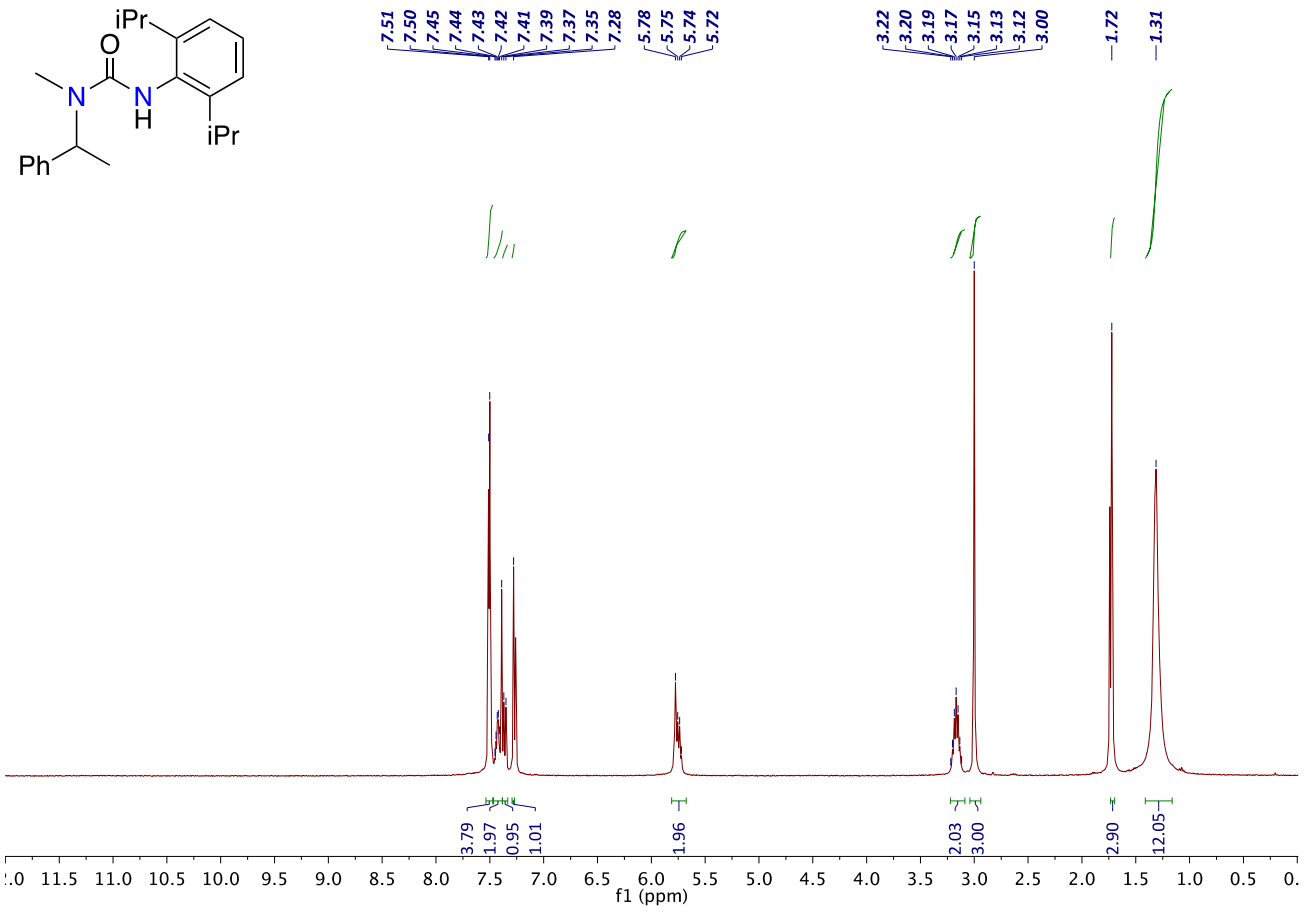


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-(2,6-diisopropylphenyl)-1-methyl-1-(1-phenylethyl)urea.

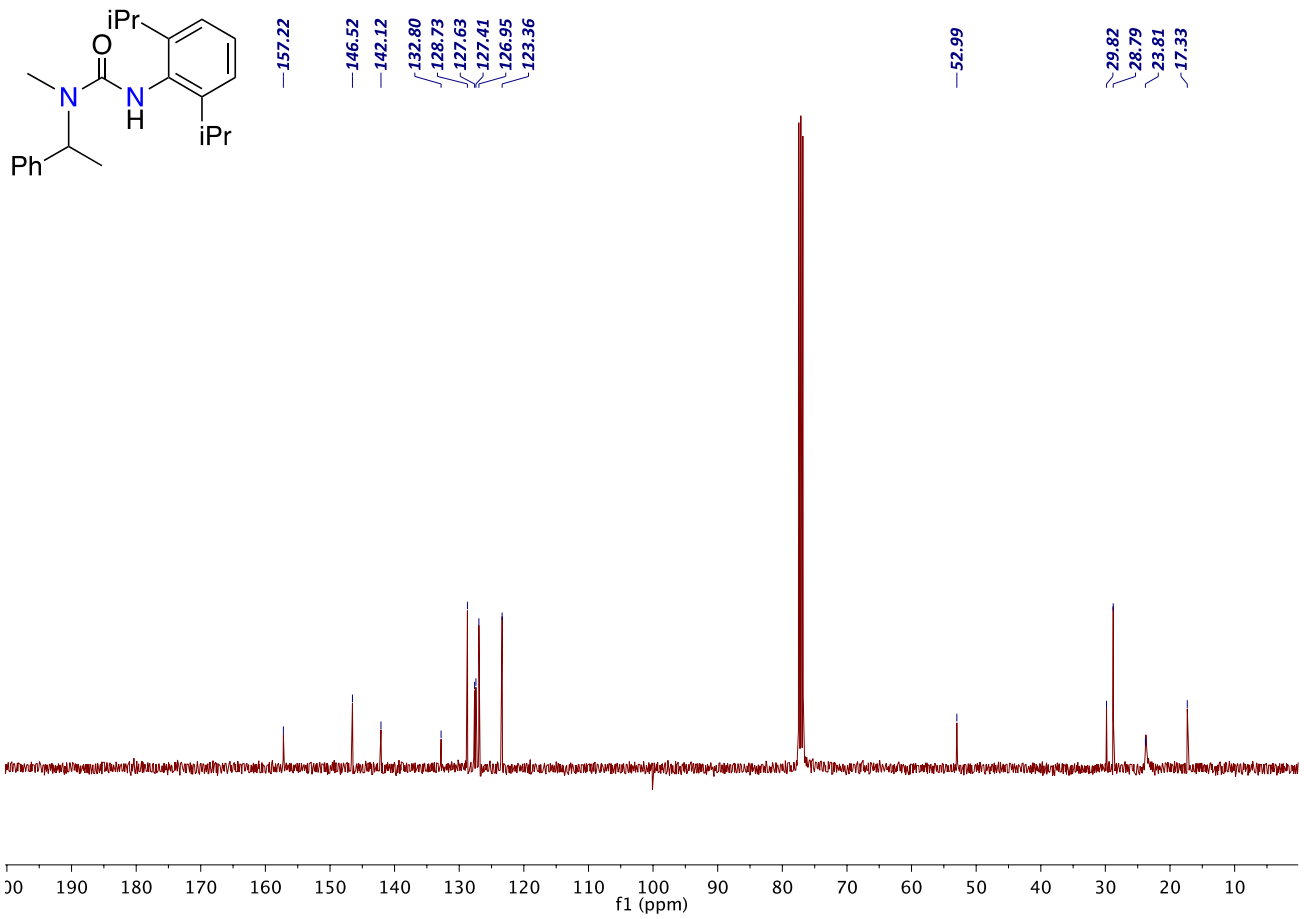
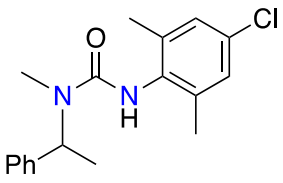


Figure S6. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 3-(2,6-diisopropylphenyl)-1-methyl-1-(1-phenylethyl)urea.



Synthesis of 3-(4-chloro-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea (L8-H): Prepared following the general procedure outlined above: 4-chloro-2,6-dimethylaniline (2.50 g, 15.8 mmol), triphosgene (1.30 g, 5.26 mmol), DIPEA (12.3 mL, 68.0 mmol), *N*-methyl-1-phenylethan-1-amine (2.34 g, 15.8 mmol). Recrystallization from a concentrated ethyl acetate solution provided the desired compound as a white solid (0.94 g, 38 %): ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.36 (m, 4H, o,m-C_6H_5), 7.31 (m, 1H, p-CH_3), 7.03 (s, 2H, CH), 5.84 (br s, 1H, NH), 5.56 (m, 1H, $CH(CH_3Ph)$), 2.84 (s, 3H, CH_3), 2.14 (s, 6H, 2,6-$(CH_3)2C_6H_3$), 1.60 (d, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 156.12 (C=O), 141.69, 137.36, 134.23, 131.59, 128.87, 128.01, 127.58, 126.95, 53.23, 29.92, 18.48, 17.29 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{21}ClN_2O$ [M+H+]: 317.1419. Found: 317.1421.

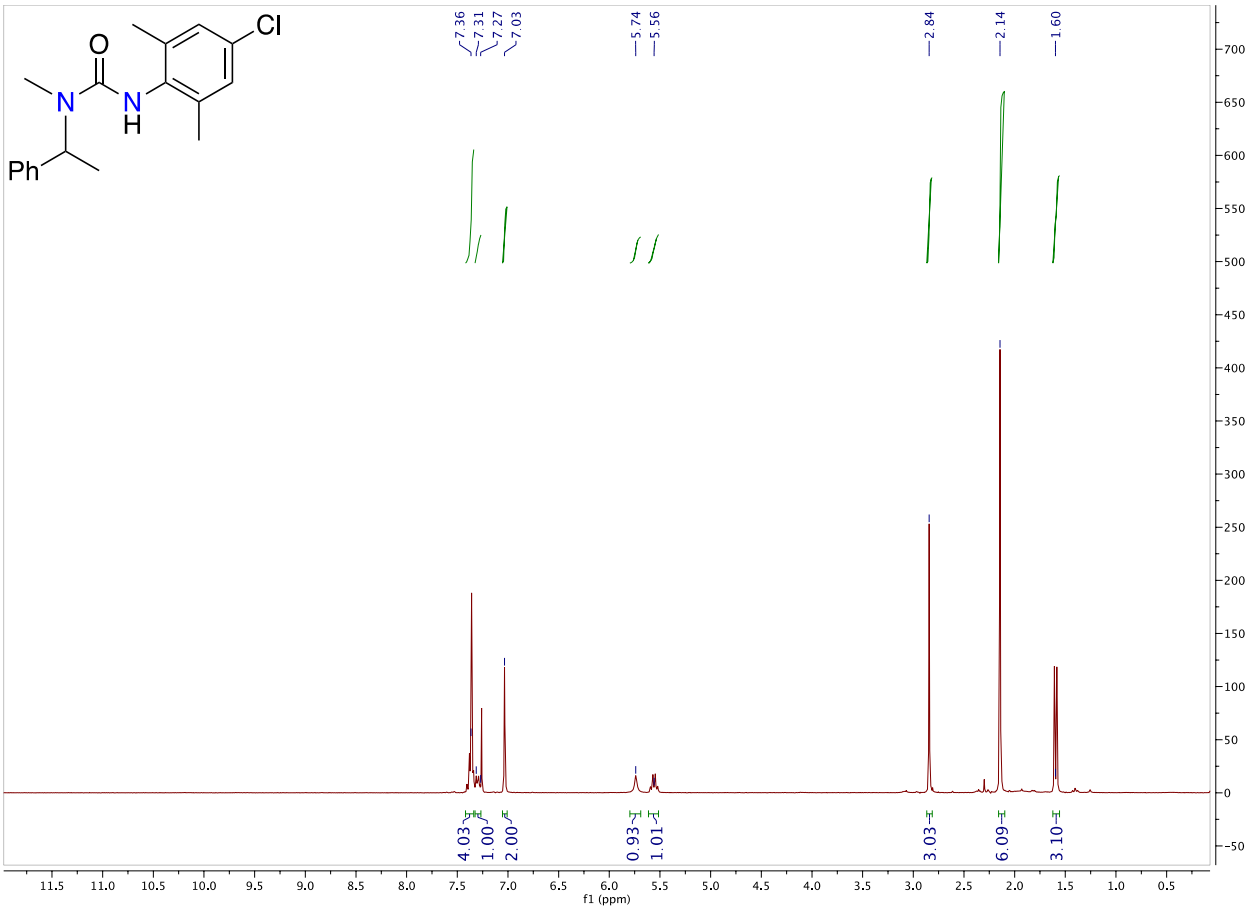


Figure S7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-(4-chloro-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea.

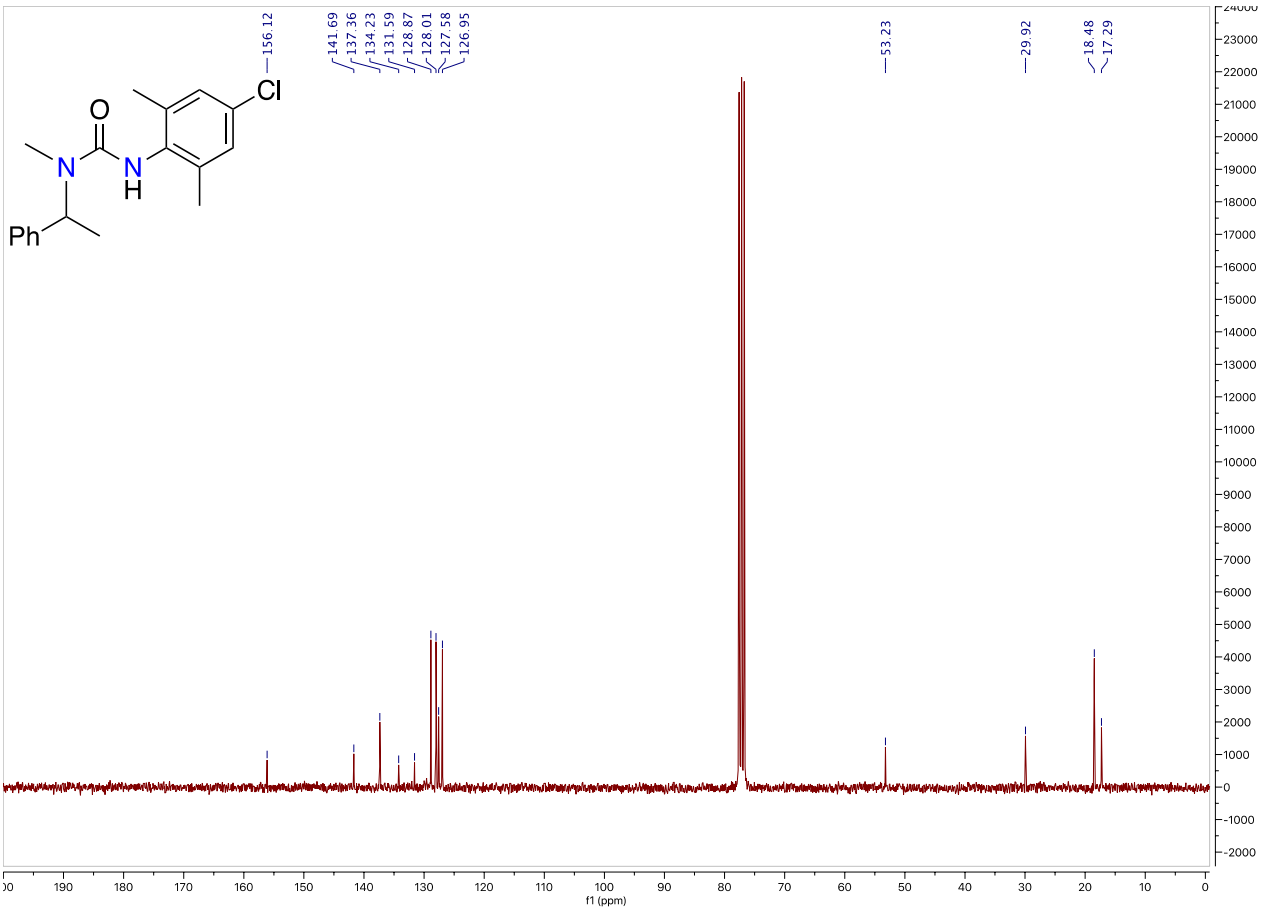
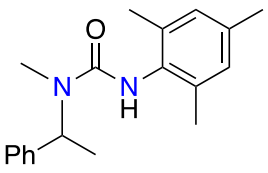


Figure S8: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of of 3-(4-chloro-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea.



Synthesis of 3-mesityl-1-methyl-1-(1-phenylethyl)urea (L9-H): Prepared following the general procedure outlined above: 2,4,6-trimethylaniline (2.28 g, 15.8 mmol), triphosgene (1.39 g, 7.40 mmol), DIPEA (12.3 mL, 68.0 mmol), *N*-methyl-1-phenylethan-1-amine (2.5 g, 15.8 mmol). Recrystallization from a concentrated ethyl acetate solution provided the desired compound as a white solid (4.53 g, 91 %): ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.37 (m, 4H, o,m-C_6H_5), 7.30 (m, 1H, p-C_6H_5), 6.86 (S, 2H), 5.72 (br s, 1H, NH), 5.59 (m, 1H, $CH(CH_3)_2$), 2.81 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 1.59 (d, $J_{H\text{-}H}$ = 1.6 Hz, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 156.57 (C=O), 141.92, 136.01, 135.36, 132.89, 128.90, 128.72, 127.36, 126.97, 52,90, 29.68, 20.98, 18.42, 17.13 ppm. HRMS (ESI): m/z calcd for $C_{19}H_{24}N_2O$ [M+H+]: 297.1967. Found: 297.1963.

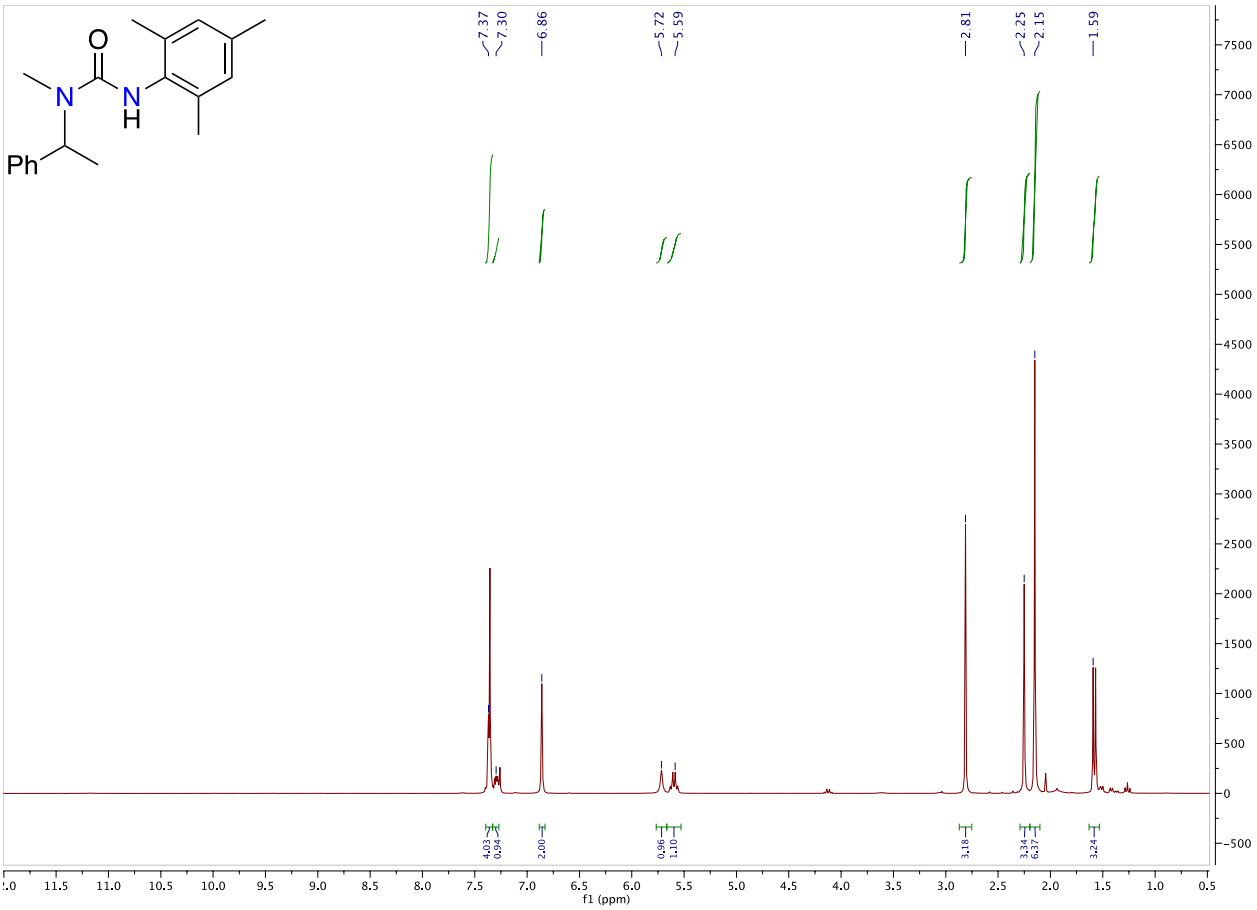


Figure S9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-mesityl-1-methyl-1-(1-phenylethyl)urea.

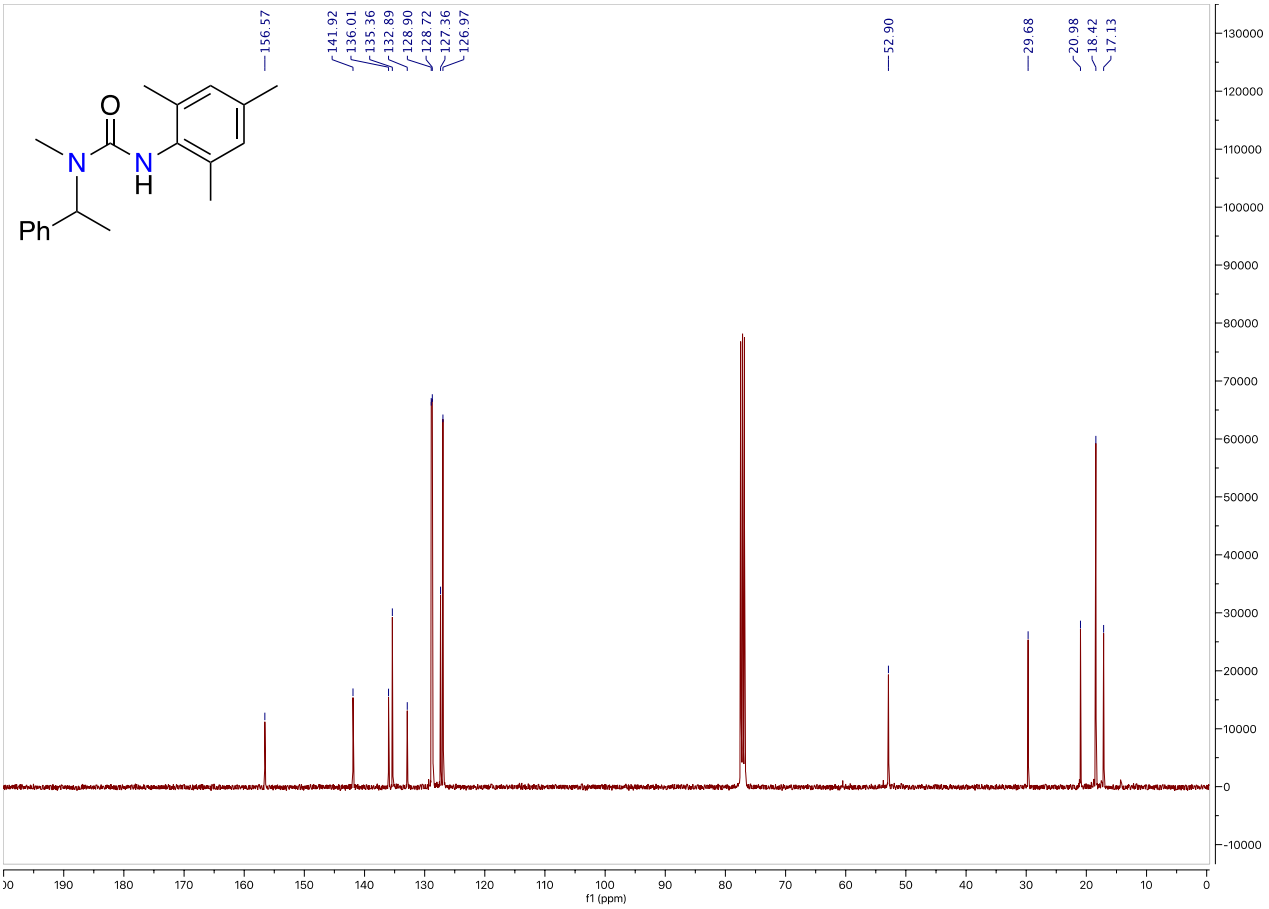
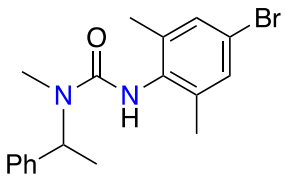


Figure S10: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 3-mesityl-1-methyl-1-(1-phenylethyl)urea.



Synthesis of 3-(4-bromo-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea (L10-H): Prepared following the general procedure outlined above: 4-bromo-2,6-dimethylaniline (2.34 g, 11.7 mmol), triphosgene (0.96 g, 3.89 mmol), DIPEA (9.15 mL, 52.5 mmol), *N*-methyl-1-phenylethan-1-amine (1.58 g, 11.7 mmol). Recrystallization from a concentrated ethyl acetate solution provided the desired compound as a white solid (2.36 g, 56 %): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.37 (m, 4H, o,m-C_6H_5), 7.30 (m, 1H, p-C_6H_5), 6.86 (s, 2H, *m*-CH), 5.72 (broad s, 1H, NH), 5.99 (m, 1H, $CH(CH_3Ph)$), 2.81 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 1.59 (d, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 156.57 (C=O), 141.92, 136.01, 135.36, 132.89, 128.90, 128.72, 127.36, 126.97, 52.90, 29.68, 20.98, 18.42, 17.13 ppm. Anal. Calcd. for $C_{18}H_{21}BrN_2O$: C, 59.84; H, 5.86; N, 7.75; Found: C, 59.91; H, 5.89; N, 7.73.

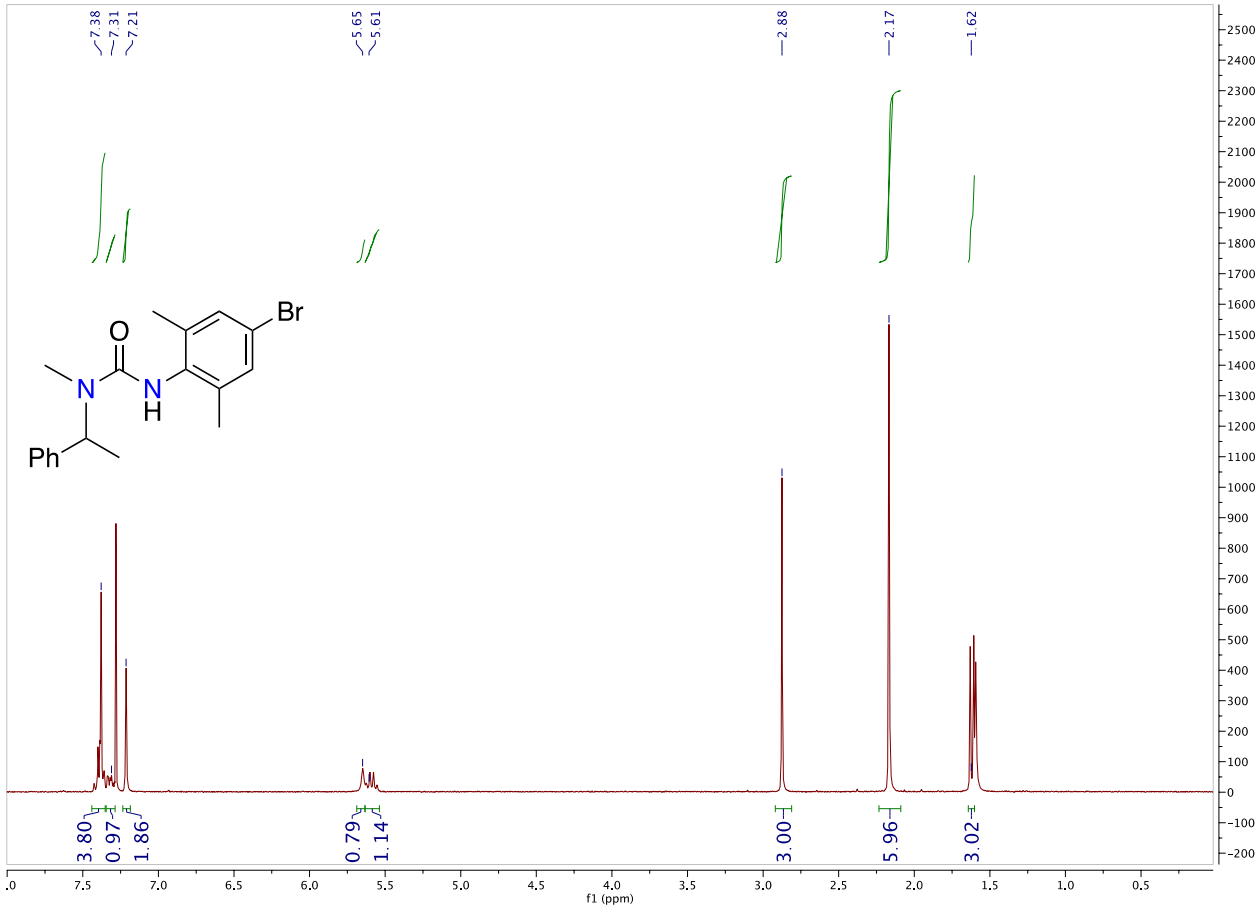


Figure S11: 1H NMR spectrum (400 MHz, CDCl3, 298 K) of 3-(4-bromo-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea.

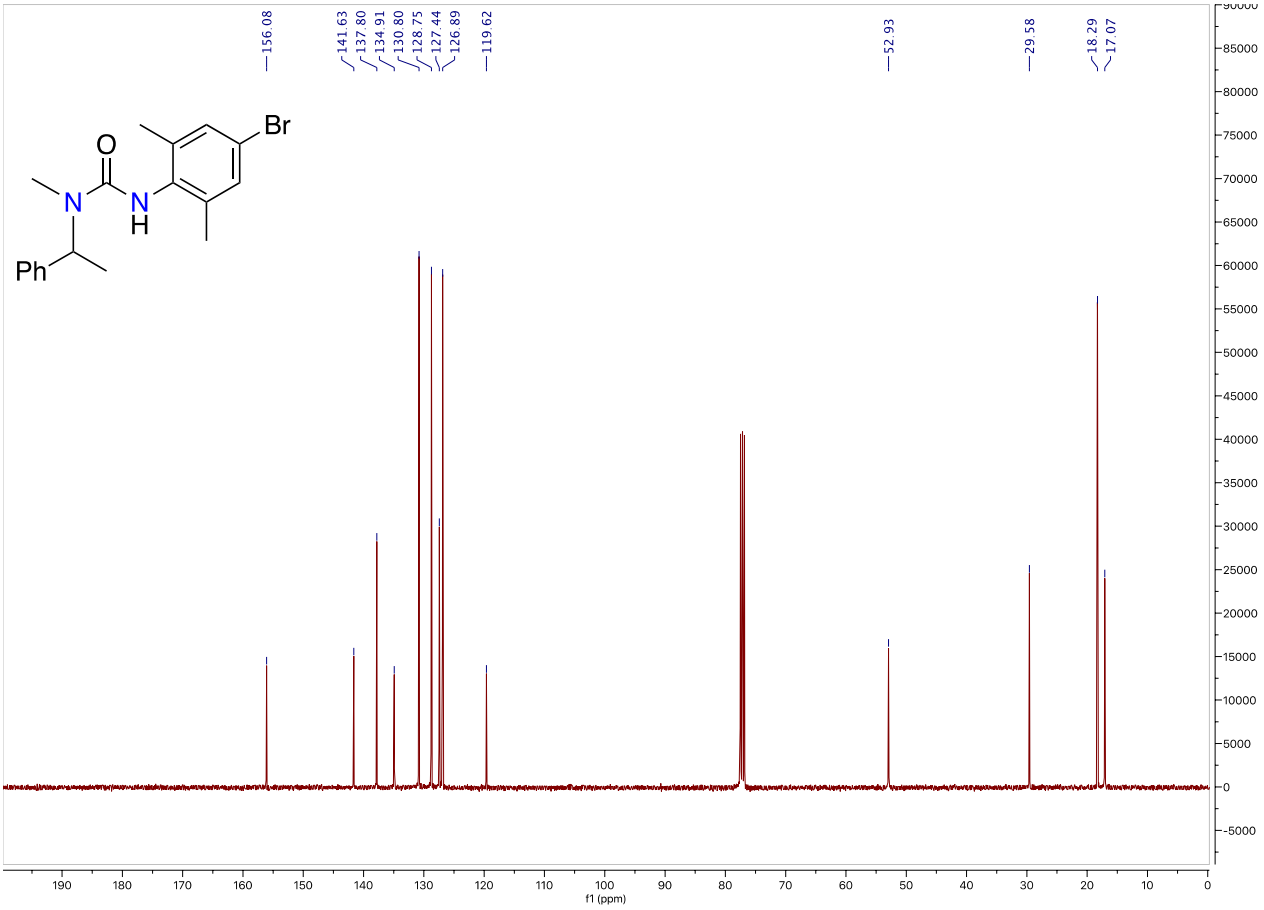


Figure S12: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 3-(4-bromo-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea.

General procedure for the synthesis of all ureate ligand salts: $NaN(SiMe_3)_2$ (1 equiv.) was added in portions to a suspension of the corresponding proteoligand (1 equiv.) in hexanes (~10 mL) and stirred overnight at room temperature. The volatiles were then removed at low pressure and the resulting solid was thoroughly washed with hexanes (3 x 5 mL) and dried to give the sodium salt in quantitative yield as a colorless powder. The resulting ligand salts were used directly without further purification and were stored in a glovebox. NMR characterization was precluded due to poor solubility in common NMR solvents (*e.g.* d_6-benzene or d_8-toluene).

Synthesis of sodium (2,6-dimethylphenyl)(diphenylcarbamoyl)amide (L5): Prepared following the general procedure outlined above: 3-(2,6-dimethylphenyl)-1,1-diphenylurea (0.68 g, 2.17 mmol), $NaN(SiMe_3)_2$ (0.40 g, 2.17 mmol).

Synthesis of sodium (2,6-dimethylphenyl)(isopropyl(phenyl)carbamoyl)amide (L6): Prepared following the general procedure outlined above: 3-(2,6-dimethylphenyl)-1-isopropyl-1-phenylurea (1.81 g, 2.64 mmol), $NaN(SiMe_3)_2$ (0.48 g, 2.64 mmol).

Synthesis of sodium (2,6-diisopropylphenyl)(methyl(1-phenylethyl)carbamoyl)amide (L7): Prepared following the general procedure outlined above: 3-(2,6-diisopropylphenyl)-1-methyl-1-(1-phenylethyl)urea (0.74 g, 5.35 mmol), $NaN(SiMe_3)_2$ (0.98 g, 5.35 mmol).

Synthesis of sodium (4-chloro-2,6-dimethylphenyl)(methyl(1-phenylethyl)carbamoyl)amide (L8): Prepared following the general procedure outlined above: 3-(4-chloro-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea (0.94 g, 6.00 mmol), $NaN(SiMe_3)_2$ (1.10 g, 6.00 mmol).

Synthesis of sodium mesityl(methyl(1-phenylethyl)carbamoyl)amide (L9): Prepared following the general procedure outlined above: 3-mesityl-1-methyl-1-(1-phenylethyl)urea (4.53 g, 14.37 mmol), $NaN(SiMe_3)_2$ (2.64 g, 14.37 mmol).

Synthesis of sodium (4-bromo-2,6-dimethylphenyl)(methyl(1-phenylethyl)carbamoyl)amide (L10): Prepared following the general procedure outlined above: 3-(4-bromo-2,6-dimethylphenyl)-1-methyl-1-(1-phenylethyl)urea (2.36 g, 6.55 mmol), $NaN(SiMe_3)_2$ (1.20 g, 6.55 mmol).

S3. Obtaining and Characterizing an Isolated Precatalyst

Mono(*N*-(2,6-dimethylphenyl)-*N*-methyl-*N*-(1-phenylethyl)carbamoylamidate)-tris(methylenetrimethylsilane)chlorotantalum (1): In a glovebox, to a stirring suspension of $Ta(CH_2SiMe_3)_3Cl_2$ (0.169 g, 0.33 mmol) in toluene (~3 mL) in a 20 mL vial, a suspension of sodium (2,6-dimethylphenyl)(methyl(1-phenylethyl)carbamoyl)amide (**L4**, 0.100 g, 0.33 mmol) in toluene (~3 mL) was added dropwise over 5 minutes. The mixture was stirred at ambient temperature for one hour, filtered through Celite™, and concentrated *in vacuo* overnight. The resulting crude residue was dissolved in minimal hexanes (~2 mL), storage at -35 °C overnight produced a yellow precipitate. The supernatant was decanted and the white crystals (0.0813 g, 31%) were obtained and dried *in vacuo* overnight. A sample from these crystals was used for single crystal X-ray structure analysis: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.18 (m, 3H), 7.05 (m, 2H), 6.84 (m, 3H), 6.05 (m, 1H), 2.22 (s, 3H), 2.17 (s, 3H), 2.13 (m, 4H), 1.72 (s, 3H), 1.45 (m, 6H), 1.22 (m, 3H), 0.38 (s, 27H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 164.71, 142.01, 139.17, 135.23, 135.05, 126.82, 93.17, 86.58, 52.71, 35.02, 32.06, 28.16, 23.12, 15.74, 2.96 ppm.

Table S1: List of crystallographic parameters for mono(N-(2,6-dimethylphenyl)-N-methyl-N-(1-phenylethyl)carbamoylamidate)-tris(methylenetrimethylsilane)chlorotantalum

Identification code	ls806 - AAU10Na
Empirical formula	$C_{30}H_{54}ClN_2OSi_3Ta$
Formula weight	759.42
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.6561(8)
b/Å	16.2013(10)
c/Å	17.5797(11)
α/°	90
β/°	90.103(2)
γ/°	90
Volume/Å^3	3604.6(4)
Z	4
ρ_{calc}g/cm^3	1.399
μ/mm^{-1}	3.247
F(000)	1552.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	3.418 to 59.178
Index ranges	-17 ≤ h ≤ 9, -22 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	28395
Independent reflections	10122 [R_{int} = 0.0546, R_{sigma} = 0.0685]
Data/restraints/parameters	10122/0/361
Goodness-of-fit on F^2	0.981
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = 0.0612
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.0673
Largest diff. peak/hole / e $Å^{-3}$	0.89/-0.78

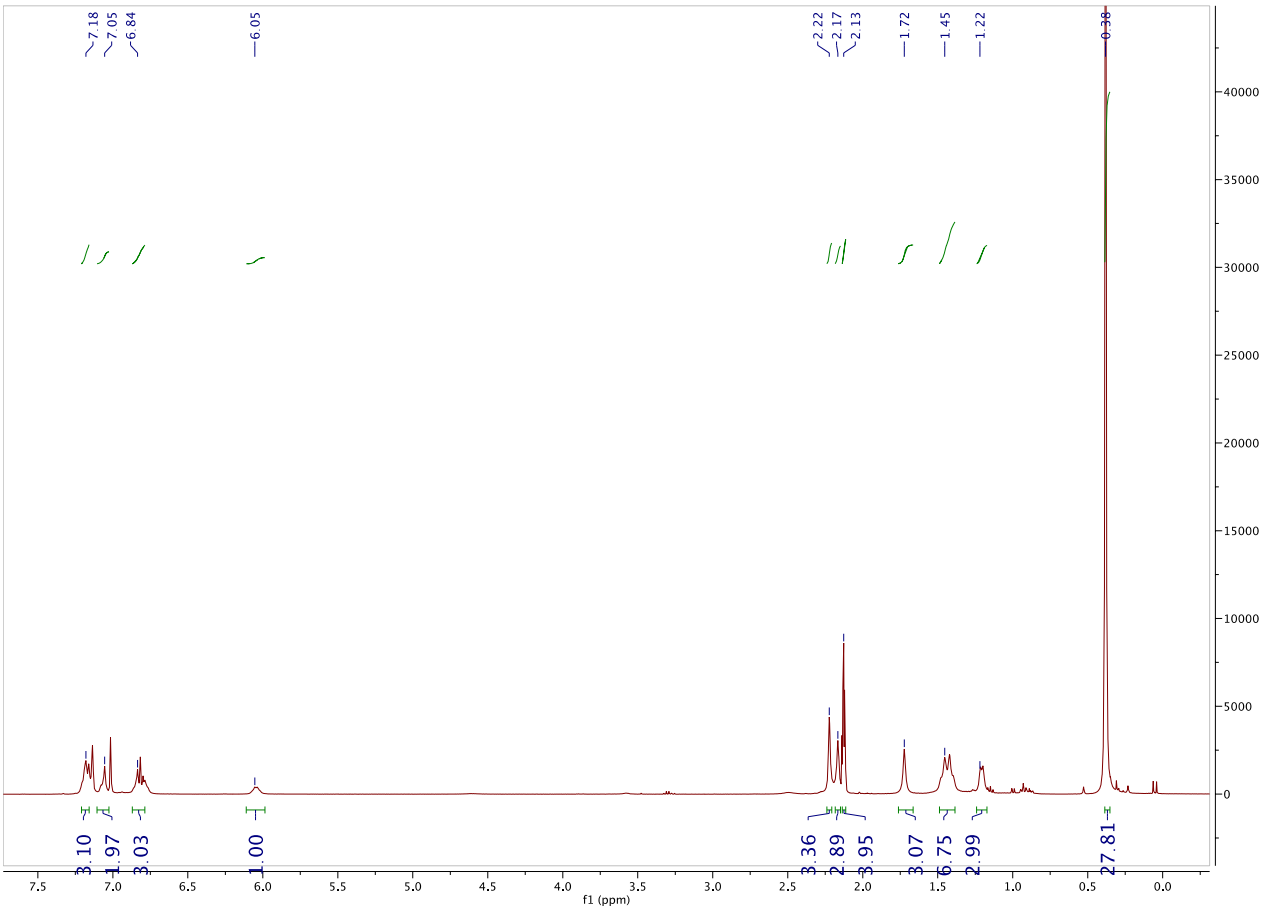


Figure S13: ^{1}H NMR spectrum (400 MHz, Tol-d_8, 298 K) for mono(*N*-(2,6-dimethylphenyl)-*N*-methyl-*N*-(1-phenylethyl)carbamoylamidate)-tris(methylenetrimethylsilane)chlorotantalum

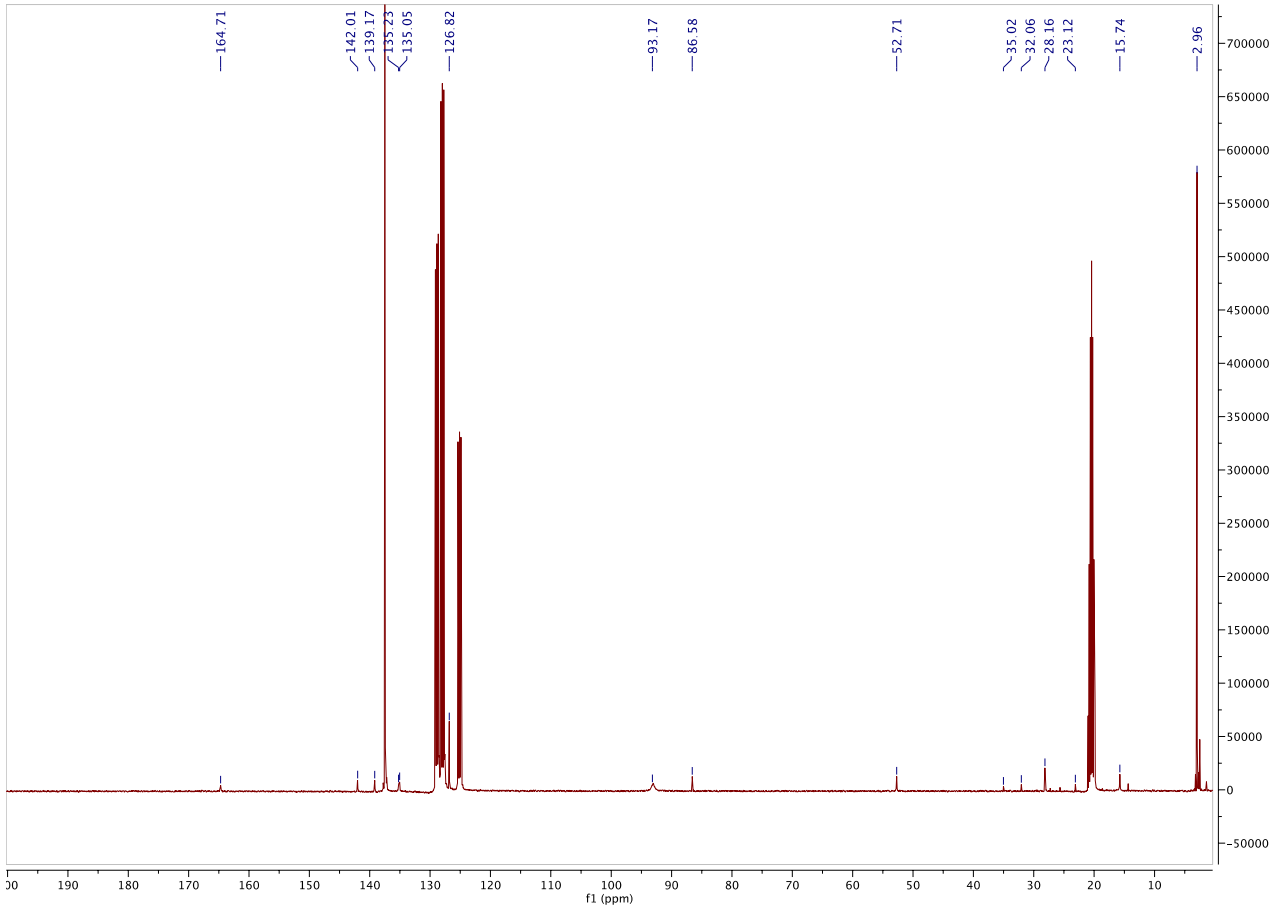


Figure S14: ^{13}C NMR spectrum (101 MHz, Tol-d_8, 298 K) for mono(*N*-(2,6-dimethylphenyl)-*N*-methyl-*N*-(1-phenylethyl)carbamoylamidate)-tris(methylenetrimethylsilane)chlorotantalum

S4. General Procedures for Ligand Screening Reactions

General procedure for ligand screening reactions:

Unless otherwise stated, $Ta(CH_2SiMe_3)_3Cl_2$ (0.005 mmol, 26.0 mg) was weighed into a vial, followed by addition of the ligand salt (0.005 mmol). Toluene-d_8 (300 mg) was added and the resultant mixture was left for 15 minutes. Piperidine (85 mg, 1 mmol), followed by 1-octene (112 mg, 1 mmol) were then added by mass with a micropipette. The reaction vial was rinsed with 300 mg of toluene-d_8 and transferred into a J. Young NMR tube. An initial ^{1}H NMR spectrum was recorded and the sample was added to a pre-heated oil bath at 150 °C for 20 hours. All conversion values were determined by ^{1}H NMR spectroscopy by integrating the product peak at 2.96 ppm (1H) relative to one of the alkene starting material peaks. After quenching, product ratios were assessed by GC-MS

S5. General Procedures for Qualitative and Quantitative Catalysis using L4

General procedure for qualitative catalytic experiments:

Unless otherwise stated, $Ta(CH_2SiMe_3)_3Cl_2$ (0.005 mmol, 26.0 mg) was weighed into a vial, followed by addition of **L4** (0.005 mmol, 15.2 mg). Toluene-d_8 (300 mg) was added and the resultant mixture was left for 15 minutes. Amine (1 mmol), followed by alkene (1 mmol) were then added by mass with a micropipette. The reaction vial was rinsed with 300 mg of toluene-d_8 and transferred into a J. Young NMR tube. An initial ^{1}H NMR spectrum was recorded and the sample was added to a pre-heated oil bath at 150 °C for 20 hours. All conversion values were determined by ^{1}H NMR spectroscopy by integrating the product peak at 2.96 ppm (^{1}H) relative to one of the alkene peaks. After quenching the reaction, rinsing the NMR tube with dichloromethane, and removal of all reaction solvent, the resulting amine was purified *via* a silica-filtration and fractions were dried *in vacuo* overnight to afford the desired product. These qualitative experiments served to identify reactions that afford both branched and linear products, as was evident from both the GC-MS analysis and the corresponding complex alkyl region in crude ^{1}H NMR spectra after reaction. GC-MS would clearly show two different reaction products, and the presence of two notably different spin systems by 2D NMR would indicate regioisomers from diastereomers. In cases that generate branched product only, there would be a clear methyl product doublet in the ^{1}H NMR spectrum, as highlighted in Figure S16. If you are observing a branched reaction product and a small amount of its corresponding diastereomer, there is often a smaller, but observable second methyl group doublet from the minor diastereomer. An assumption used

in this step is that the GS-MS response factors with a CI ionization source are similar for all isomers.

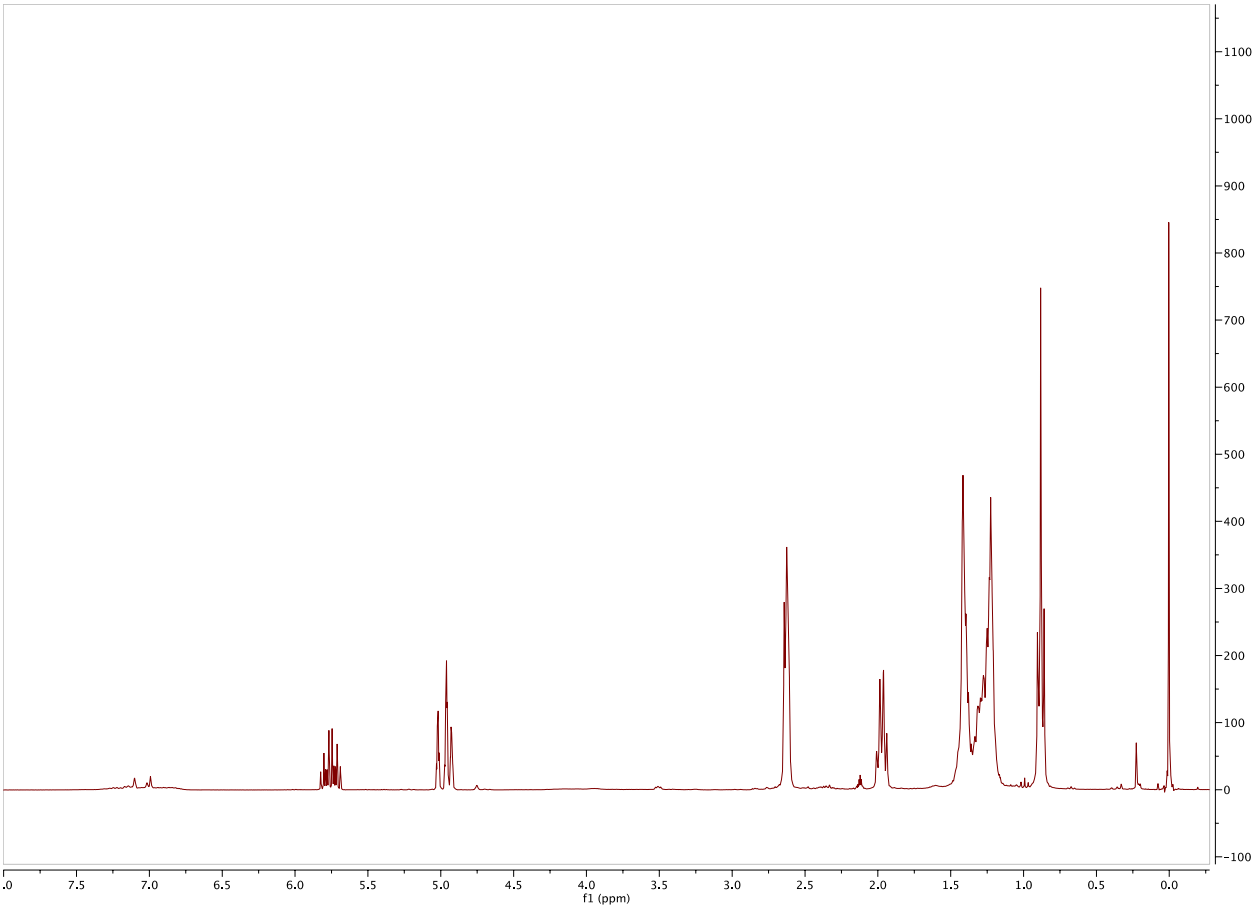


Figure S15: ^{1}H NMR spectrum (400 MHz, Tol-d_8, 298 K) for the crude reaction mixture between piperidine and 1-octene before heating.

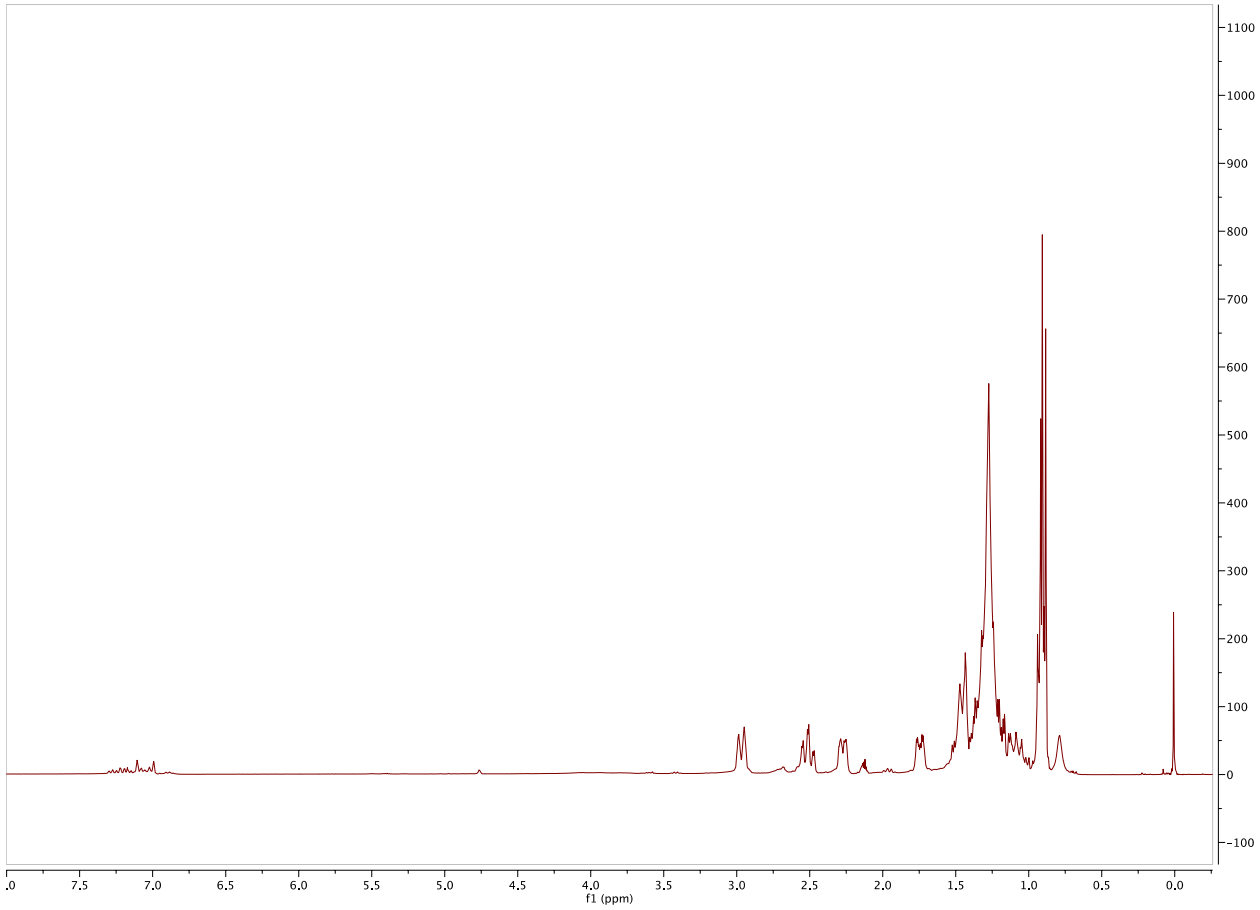


Figure S16: ^{1}H NMR spectrum (400 MHz, Tol-d_8, 298 K) for the crude reaction mixture between piperidine and 1-octene after heating.

General Procedures for Quantitative Catalytic Experiments:

Quantitative Catalytic Experimental Procedure for Predominantly Branched Products ***(2-10)***

Unless otherwise stated, $Ta(CH_2SiMe_3)_3Cl_2$ (0.005 mmol, 26.0 mg) was weighed into a vial, followed by addition of **L4** (0.005 mmol, 15.2 mg). A 0.0011 mmol/g stock solution of 1,3,5-trimethoxybenzene in d8-toluene was prepared by weighing out 1.85g solid internal standard and dissolving it in 10g d8-toluene. To each reaction 300 mg of that solution was added as an internal standard (0.33 eq). The resultant mixture was left for 15 minutes. Piperidine (1 mmol), followed by alkene (1 mmol) were then added by mass with a micropipette via small drops over an analytical balance. This mixture was then transferred into a J. Young NMR tube. The reaction vial was rinsed with and additional 300 mg of toluene-d_8 via micropipette over an analytical balance and transferred into the J. Young NMR tube. An initial ^{1}H NMR spectrum was recorded and the sample was added to a pre-heated oil bath at 150 °C for 20 hours. All NMR yield values for reactions that generate predominantly BRANCHED product were determined by ^{1}H NMR spectroscopy by integrating the product peak at 2.96 ppm (1H) relative to the internal standard peak for the three methyl groups at 3.40 ppm (integrated to 3H instead of 9H due to 0.33 equivalents relative to amine being used). **Note that for all quantitative NMR reactions, D1 values were determined to be and set as 200 s.** After quenching the reaction, the NMR tube was rinsed with dichloromethane into a 20 mL scintillation vial. All reaction solvent was removed, the resulting amine was purified by silica gel chromatography using 5: 4.5: 0.5 hexanes: ethylacetate: triethylamine as eluant. The resulting fractions were dried *in vacuo* overnight to afford the desired

product. Regioisomer and diastereomer product ratios were determined by GC-MS of the crude reaction mixture prior to chromatographic separation.

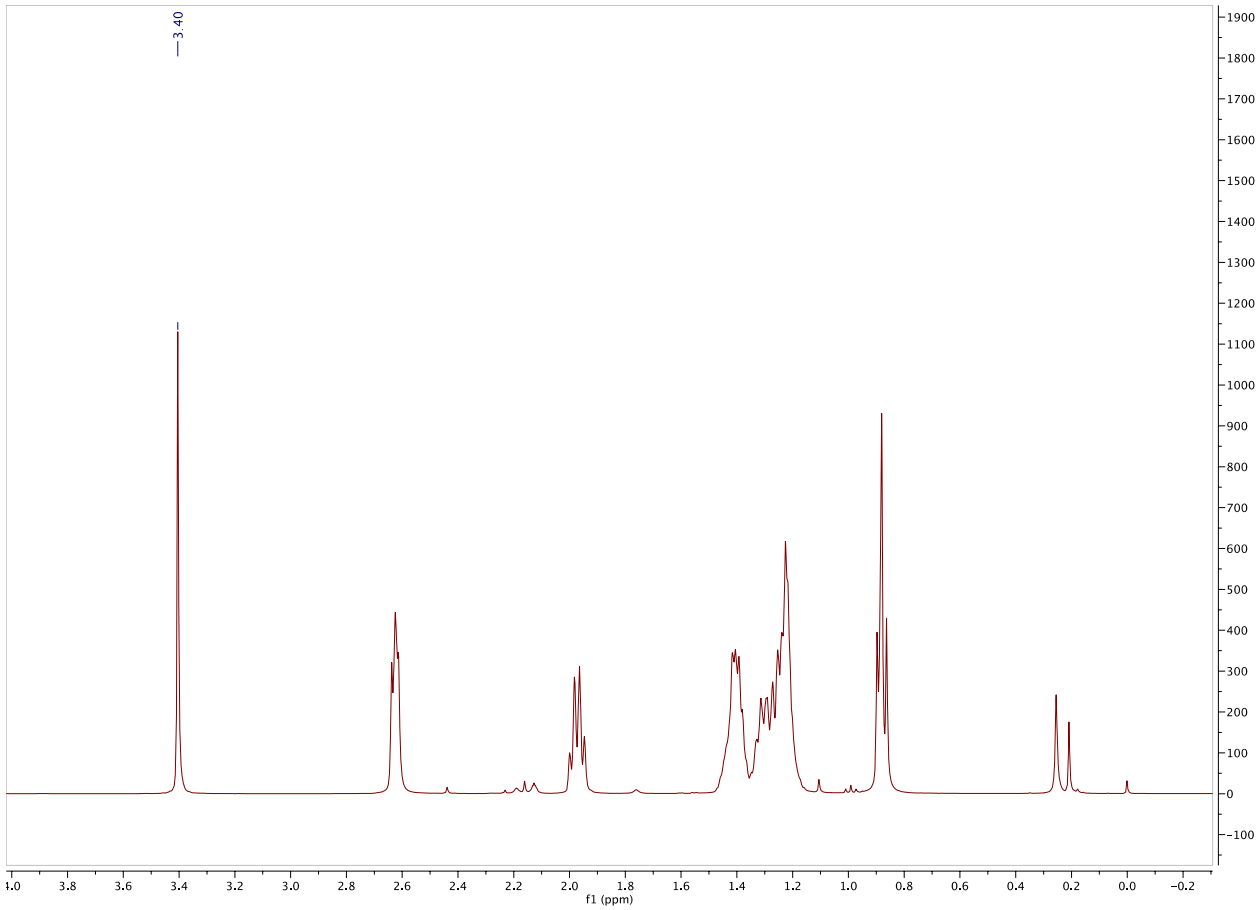


Figure S17: ^{1}H NMR spectrum (400 MHz, Tol-d_8, 298 K) for the crude reaction mixture between piperidine and 1-octene with 1,3,5-trimethoxybenzene as an internal standard (0.33 eq.) before heating. This image is specifically zoomed in on the product region of the NMR spectrum.

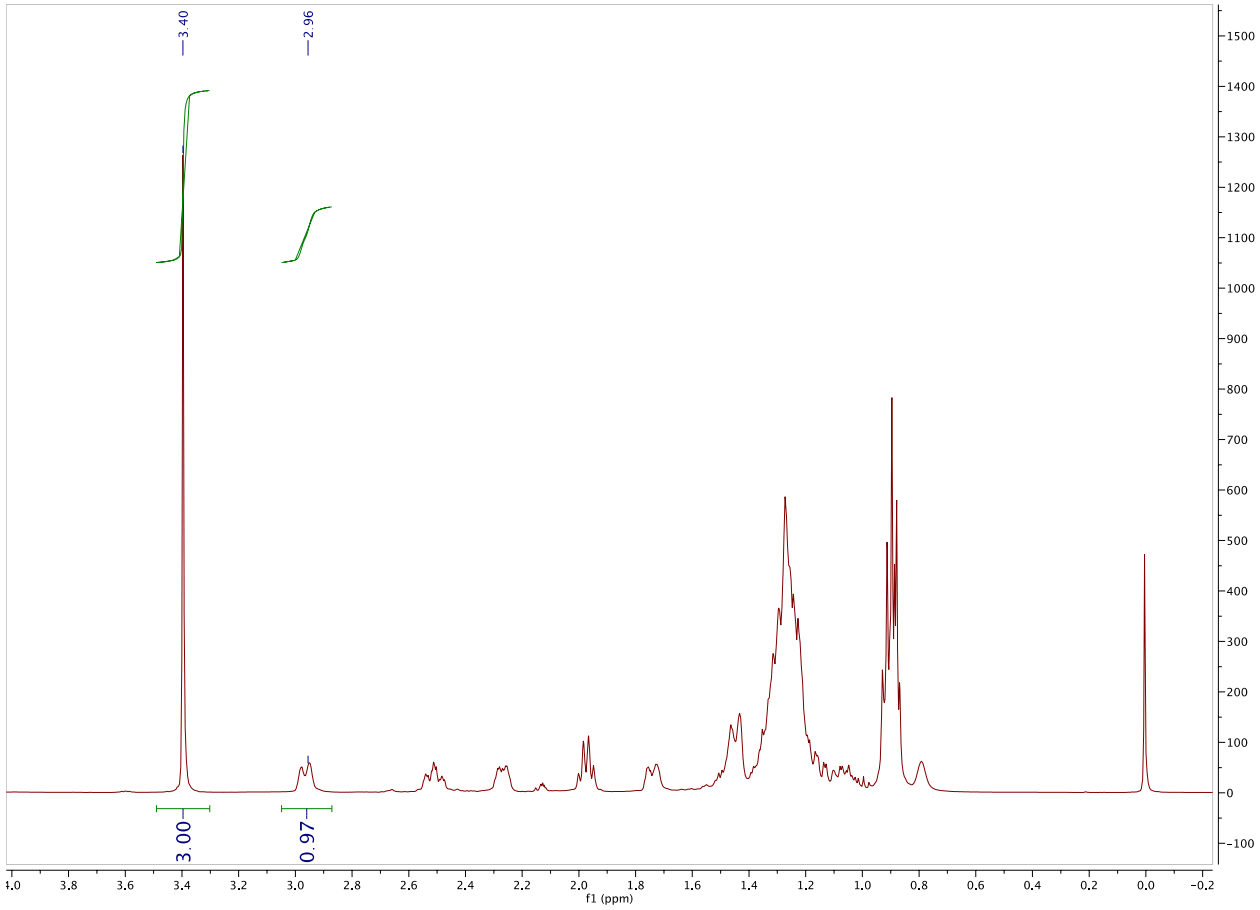


Figure S18: ^{1}H NMR spectrum (400 MHz, Tol-d_8, 298 K) for the crude reaction mixture between piperidine and 1-octene with 1,3,5-trimethoxybenzene as an internal standard (0.33 eq.) after heating. This image is specifically zoomed in on the product region of the NMR spectrum.

Note: This crude reaction GC-MS spectrum is a representative example of how we determined d.r ratios for all amine products presented.

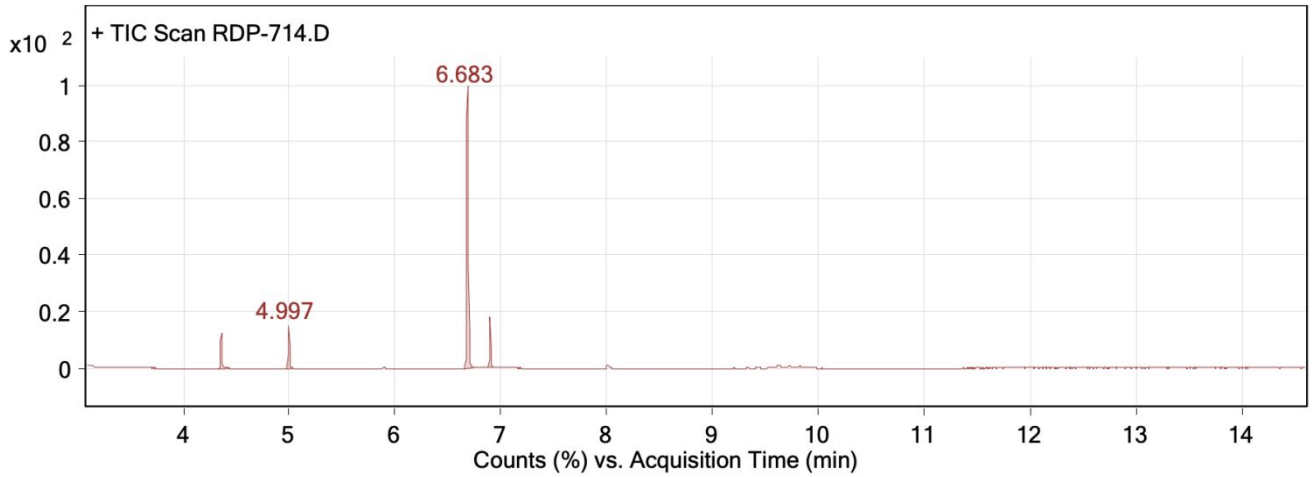
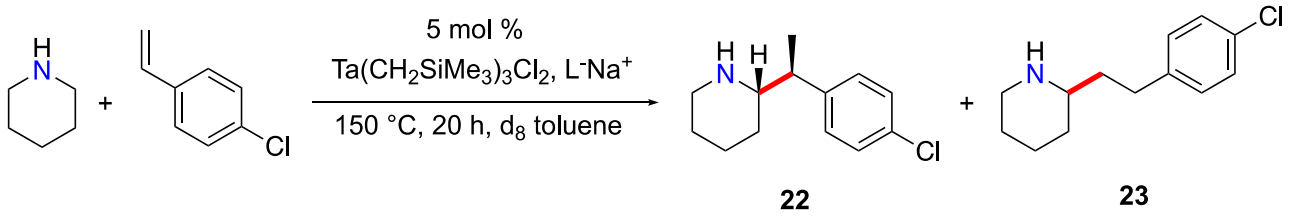


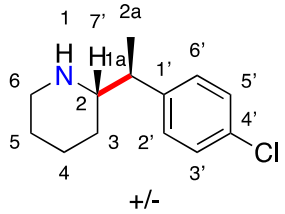
Figure S19: GC-MS for crude reaction mixture between piperidine and 1-octene.

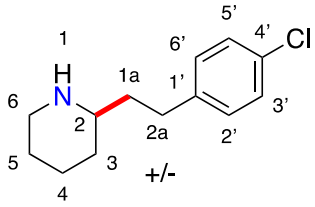
*Quantitative Catalytic Experimental Procedure for Branched and Linear Regioisomer Products (***14-33**)

Unless otherwise stated, $Ta(CH_2SiMe_3)_3Cl_2$ (0.005 mmol, 26.0 mg) was weighed into a vial, followed by addition of the ligand salt **L4** (0.005 mmol, 15.2 mg). A 0.0011 mmol/g stock solution of 1,3,5-trimethoxybenzene in d8-toluene was prepared by weighing out 1.85g solid internal standard and dissolving it in 10g d8-toluene. To each reaction 300 mg of that solution was added as an internal standard (0.33 eq). The resultant mixture was left for 15 minutes. Piperidine (1 mmol), followed by alkene (1 mmol) were then added by mass with a micropipette via small drops over an analytical balance. This mixture was then transferred into a J. Young NMR tube. The reaction vial was rinsed with and additional 300 mg of toluene-d_8 via micropipette over an analytical balance and transferred into the J. Young NMR tube. An initial ^{1}H NMR spectrum was recorded and the sample was added to a pre-heated oil bath at 150 °C for 20 hours. In determining the NMR yield values for reactions that generate mixtures of branched and linearly products the peak at 2.87 ppm could be used to assess the combined yield of both regioisomers. Due to numerous overlapping peaks in a crude ^{1}H NMR spectrum, new 2D NMR data was required for crude reaction mixtures in toluene. This data was used to assess where CH proton peaks for each isomer were so that they could be accurately integrated. COSY, and HMBC NMR spectra were required of the NMR tube reaction to assess these complicated NMR yields in samples that contained significant mixtures of two products. The sample T20 ^{1}H, COSY and HMBC NMR spectra below represent an example of how we solved this problem in the selected illustrative example below:



22 **23**





Synthesis of 2-(1-(4-chlorophenyl)ethyl)piperidine and 2-(4-chlorophenethyl)piperidine (22 and 23): Prepared following the general procedure outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), 4-chlorostyrene (138.59 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 54 % for 2-(1-(4-chlorophenyl)ethyl)piperidine and 46 % for 2-(4-chlorophenethyl)piperidine by NMR (1,3,5-trimethoxybenzene as a standard). The regioisomers could be separated by column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine). This reaction was scaleable up to 25 mmol. Yields from chromatography were 35 % for branched (**22**) and 22 % for linear (**23**).

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.25 (m, 2H, 3' and 5'), 7.11 (m, 2H, 2' and 6'), 3.11 (m, 1H, ½ of 6), 2.65 (m, 1H, 1a), 2.59 (m, 1H, ½ of 6), 2.52 (m, 1H, 2), 1.85 (broad s, 1H, NH), 1.71 (m, 1H, ½ of 4), 1.57 (m, 1H, ½ of 5), 1.41 (m, 1H, ½ of 3), 1.33 (m, 1H, ½ of 5), 1.26 (d, J = 1.31, 3H, 2a), 1.22 (m, 1H, ½ of 4), 1.03 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 143.42, 131.88, 129.17, 128.43, 62.38, 47.38, 45.06, 30.63, 26.25, 24.81, 17.35 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NCl$ [M+H$^+$]: 224.1206 Found: 224.1201.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.22 (m, 2H, 3' and 5'), 7.10 (m, 2H, 2' and 6'), 3.14 (m, 1H, ½ of 6), 2.66 (m, 2H, 2a), 2.64 (m, 1H, ½ of 6), 2.53 (m, 1H, 2), 2.45, (broad s, 1H, NH), 1.82 (m, 1H, ½ of 4), 1.74 (m, 2H, 1a), 1.69 (m, 1H, ½ of 3), 1.61 (m, 1H, ½ of 5), 1.48 (m, 1H, ½ of 5), 1.34 (m, 1H, ½ of 4), 1,22 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 140.87, 131.55, 129.77, 128.55, 56.42, 47.22, 39.11, 32.95, 31.71, 26.66, 24.86 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NCl$ [M+H$^+$]: 224.1206 Found: 224.1207.

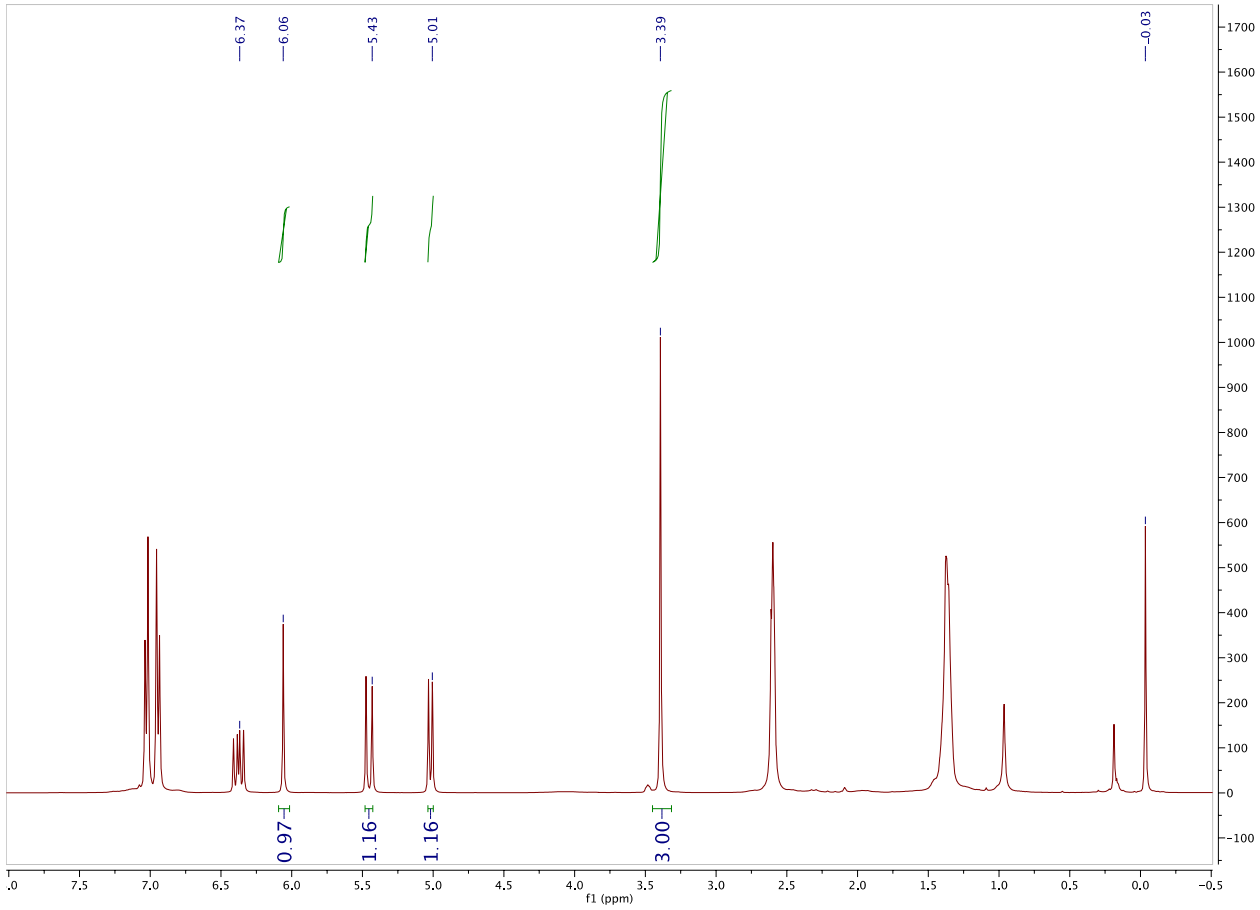


Figure S20: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) before the reaction mixture was heated. Peaks at 6.06 and 3.39 ppm represent the 1,3,5-trimethoxybenzene as an internal standard. The peak at 0.03 ppm represents $SiMe_4$ that is released upon catalyst activation. Peaks at 5.43 and 5.01 represent alkene protons.

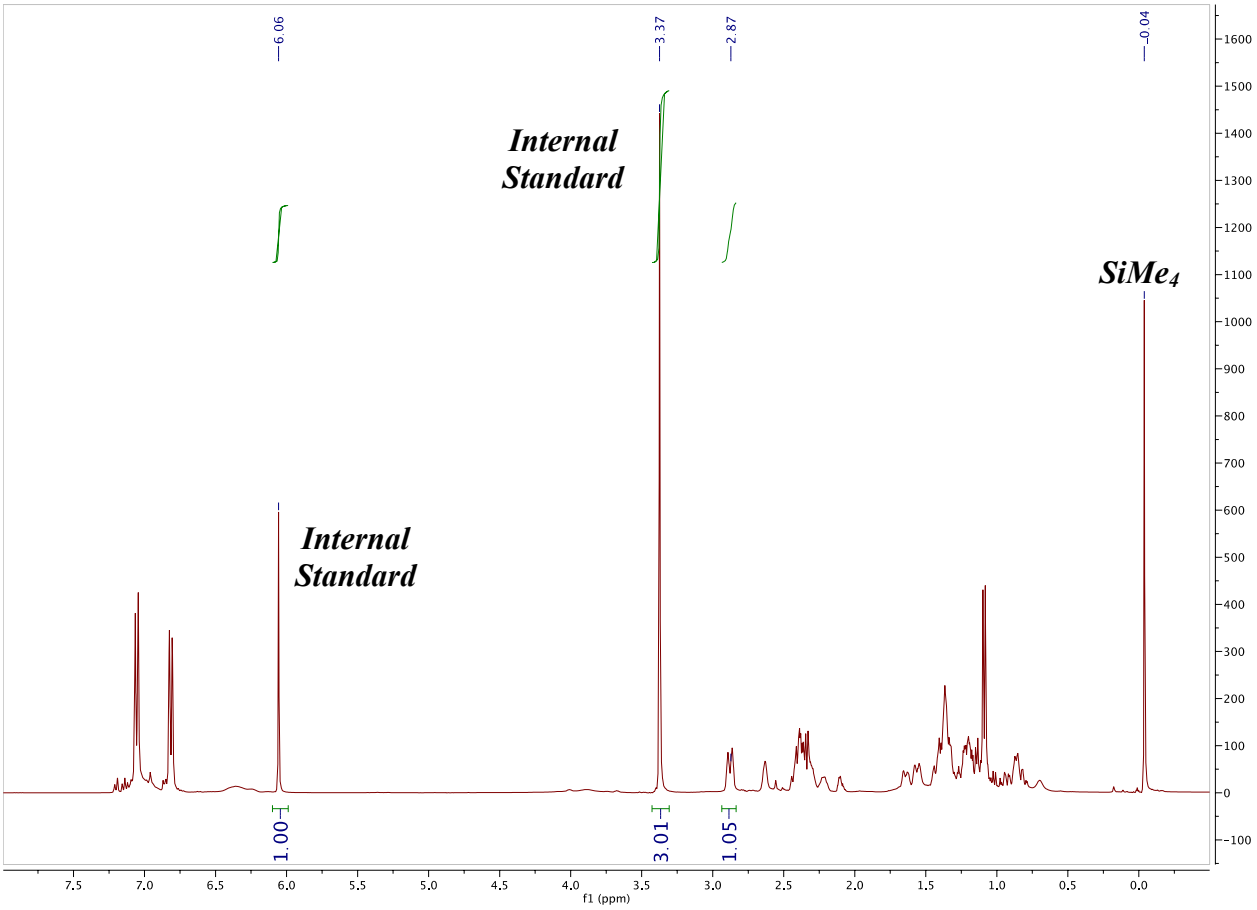


Figure S21: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) upon completion of the reaction of piperidine with 4-chlorostyrene. Peaks at 6.06 and 3.37 ppm represent the 1,3,5-trimethoxybenzene as an internal standard. Integration of the peak at 2.87 ppm represents the combined yield of products. The peak at 0.04 ppm is tetramethylsilane from alkyl ligands being protonated off the Ta precatalyst during reaction.

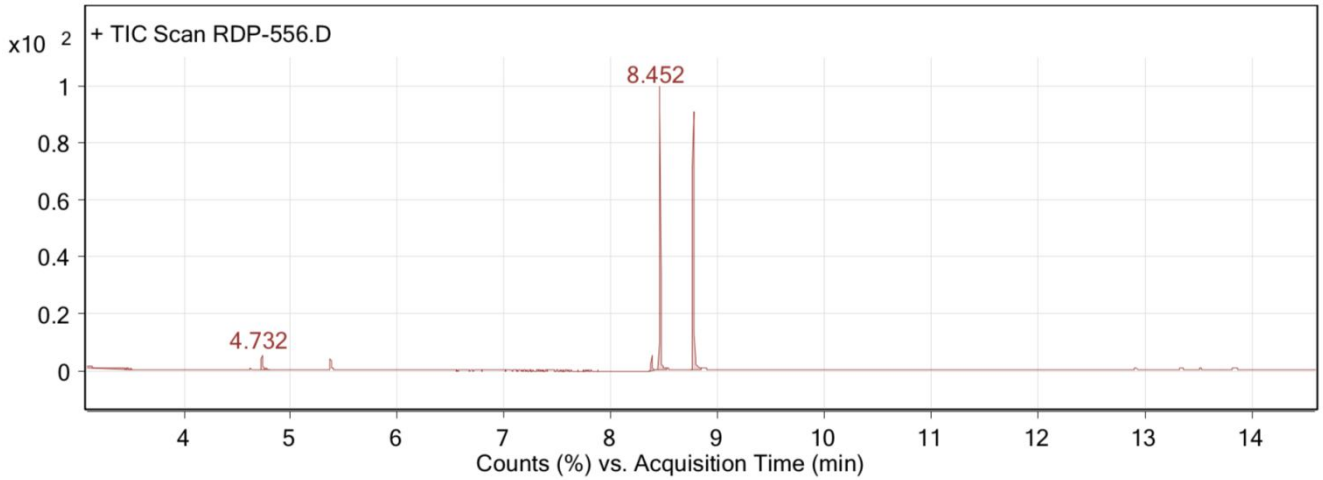


Figure S22: GC-MS for the crude reaction mixture between piperidine and 4-chlorostyrene.

Figure S23: COSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the completed reaction of piperidine with 4-chlorostyrene. The linear and branched products are overlapping in the 2.87-2.90 ppm peak.

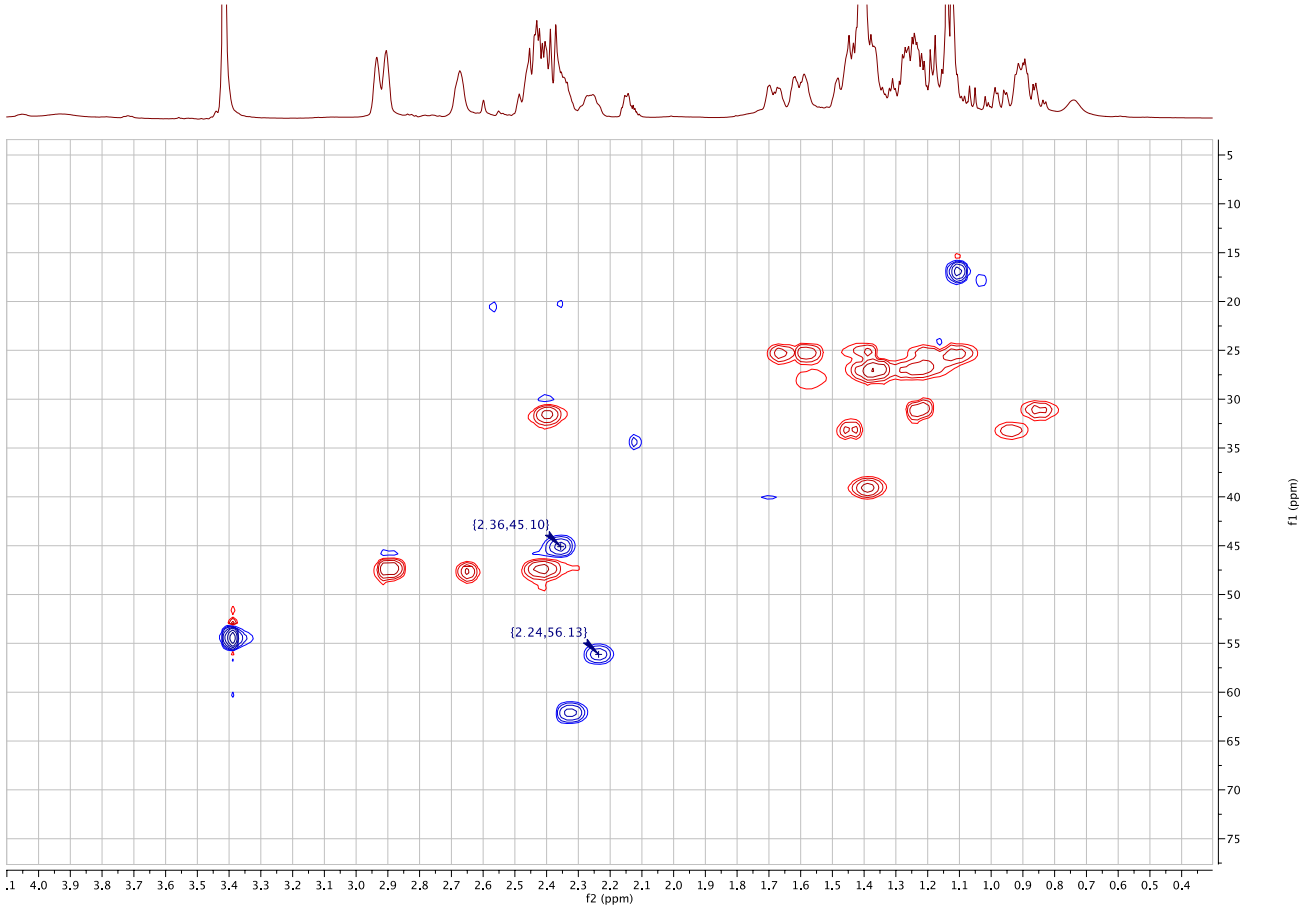


Figure S24: T20 HSQC NMR spectrum (400 MHz/ 100 MHz, $CDCl_3$, 298 K) of the reaction of piperidine with 4-chlorostyrene that has been zoomed in on the aliphatic region of the reaction.

We were able to analyze these spectra to assess that the peak at 2.36 ppm is the CH proton from the branched product and the peak at 2.24 ppm is the CH peak from the linear product. These peaks could then be integrated in the original proton spectrum to give NMR yields for each of these products, respectively. These NMR yields were then verified by using relative GC-MS areas for these peaks and integrations were consistent, within error, across all styrene products. See below for an integrated proton NMR spectrum of the crude reaction mixture.

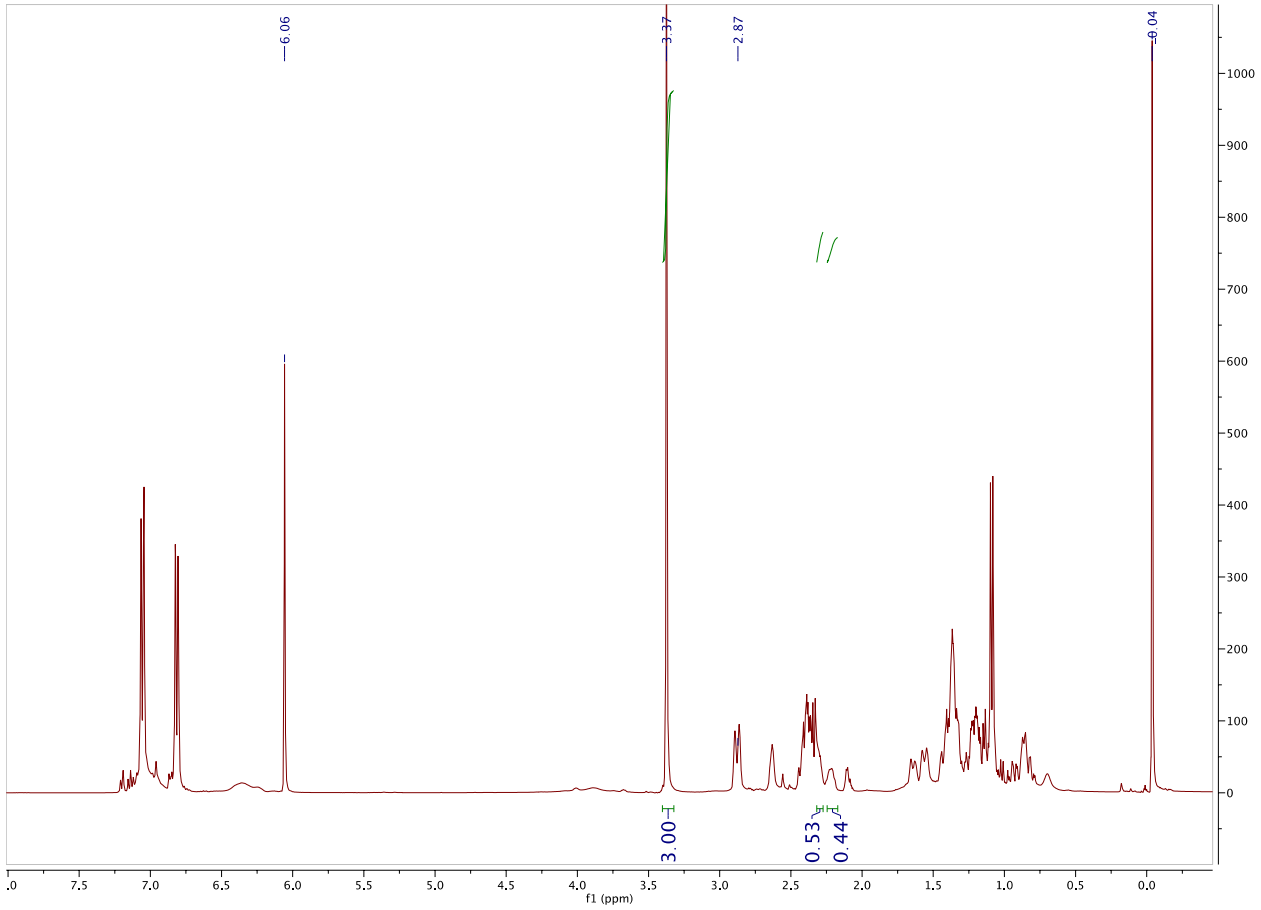


Figure S25: T20 ^{1}H NMR spectrum (400 MHz/ 100 MHz, $CDCl_3$, 298 K) of the reaction of piperidine with 4-chlorostyrene. In this spectrum, diagnostic CH protons from branched and linear regioisomers have been integrated.

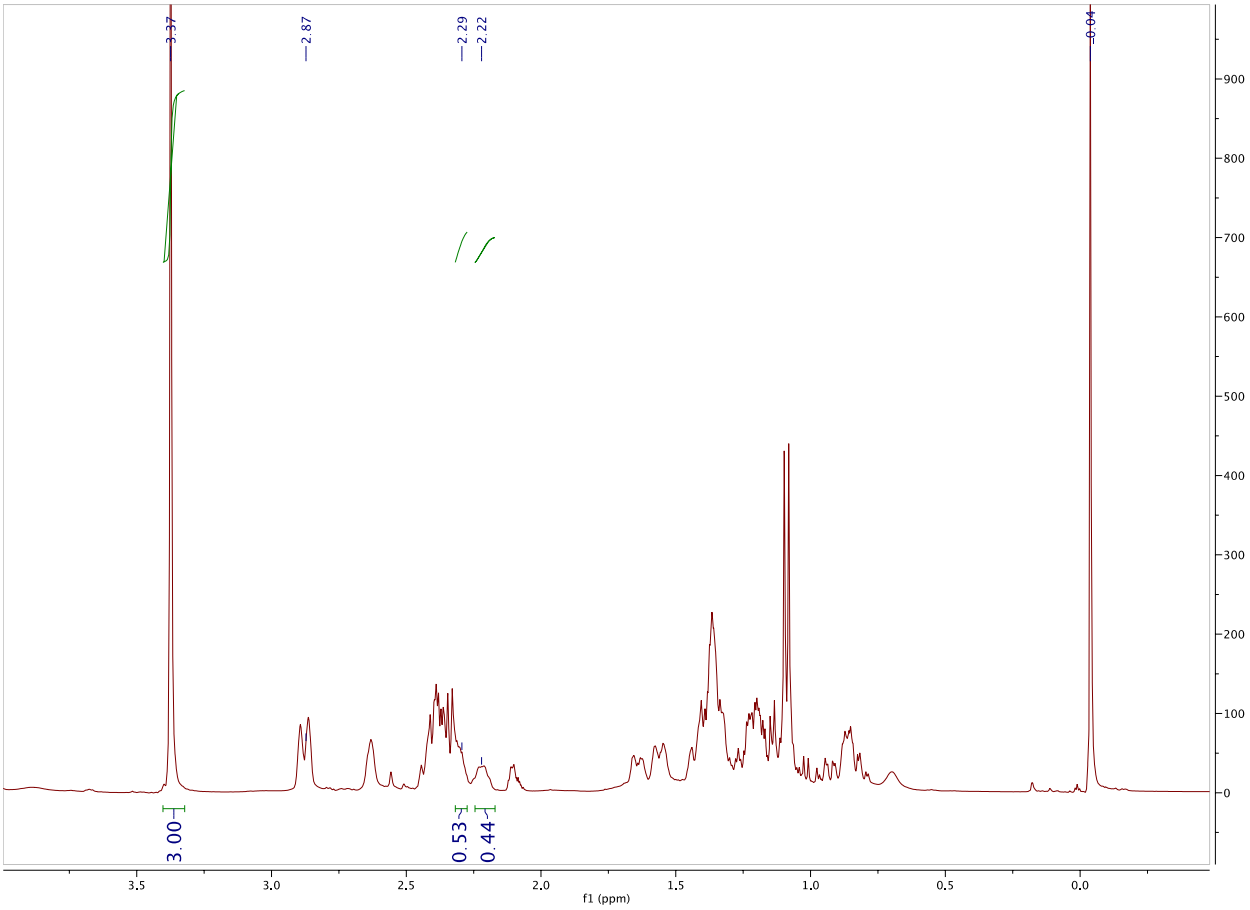


Figure S26: T20 ^{1}H NMR spectrum (400 MHz/ 100 MHz, $CDCl_3$, 298 K) of the reaction of piperidine with 4-chlorostyrene. In this spectrum, data has been zoomed to the alkyl region.

The peak at 3.37 ppm represents the methyl groups of the 1,3,5-trimethoxybenzene internal standard. This has been integrated to 3 protons instead of 9 because 0.33 equivalents of this internal standard relative to either substrate were consistently used in all reactions. The integrations of 0.53 and 0.44 protons reflect branched and linear NMR yields, respectively.

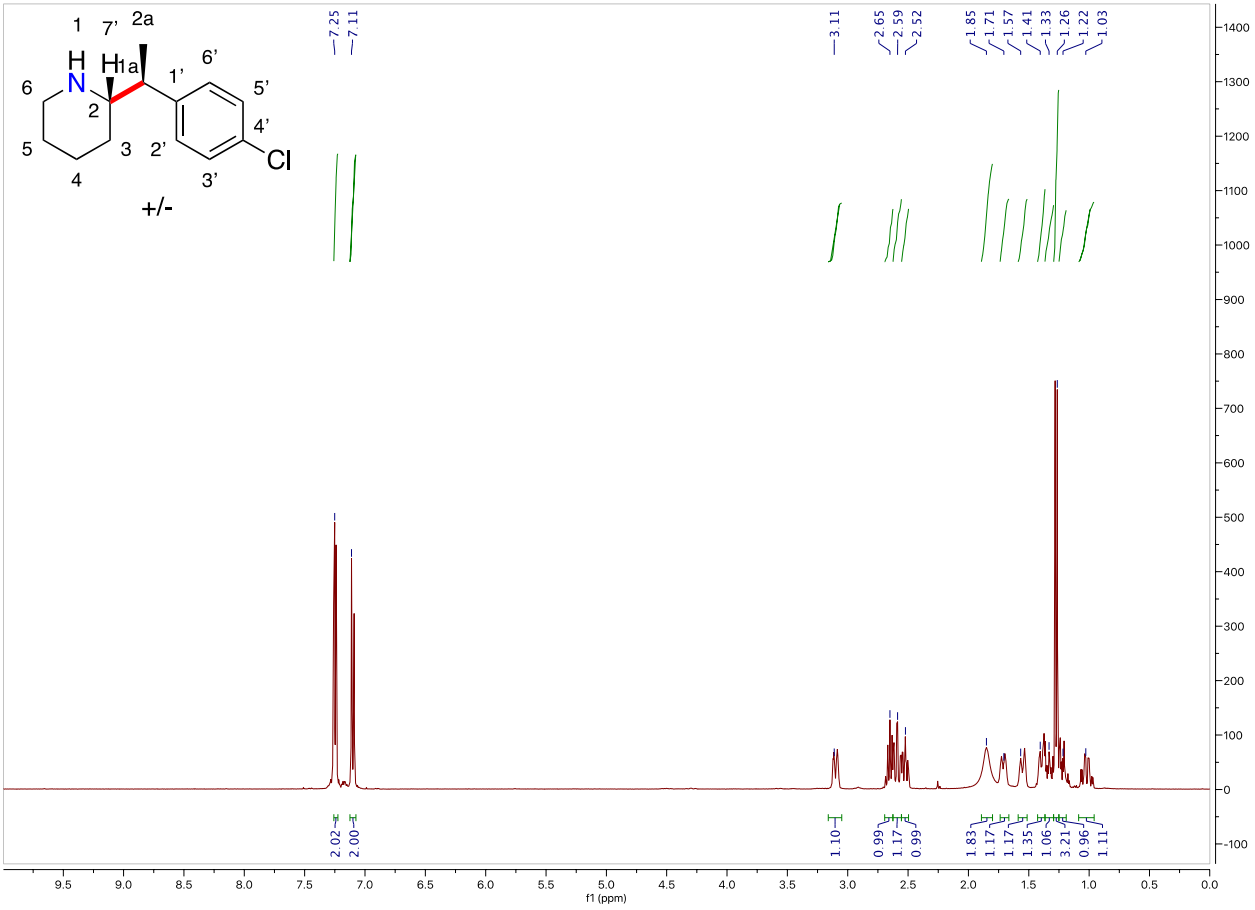


Figure S27: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of purified 2-(1-(4-chlorophenyl)ethyl)piperidine.

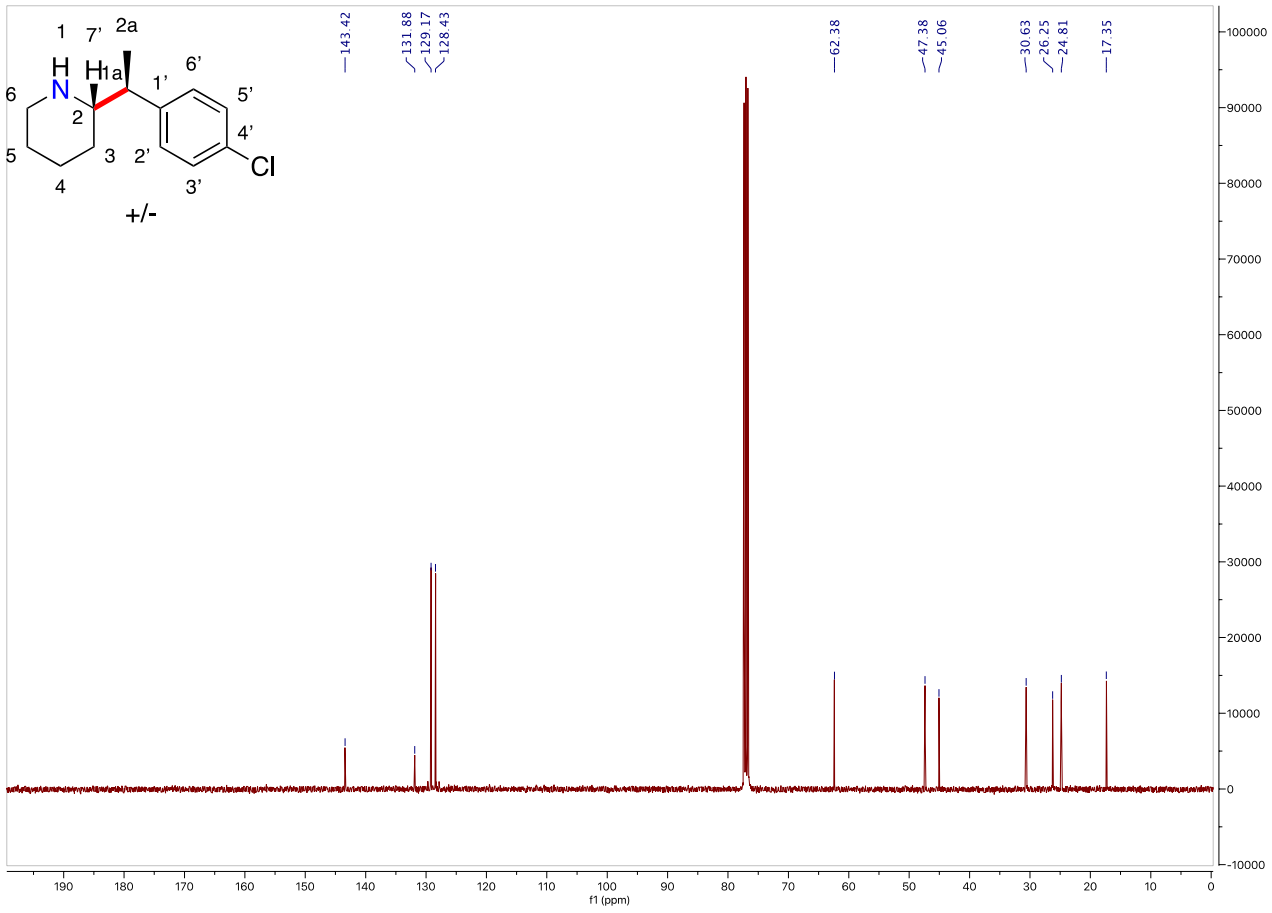


Figure S28: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of purified 2-(1-(4-chlorophenyl)ethyl)piperidine.

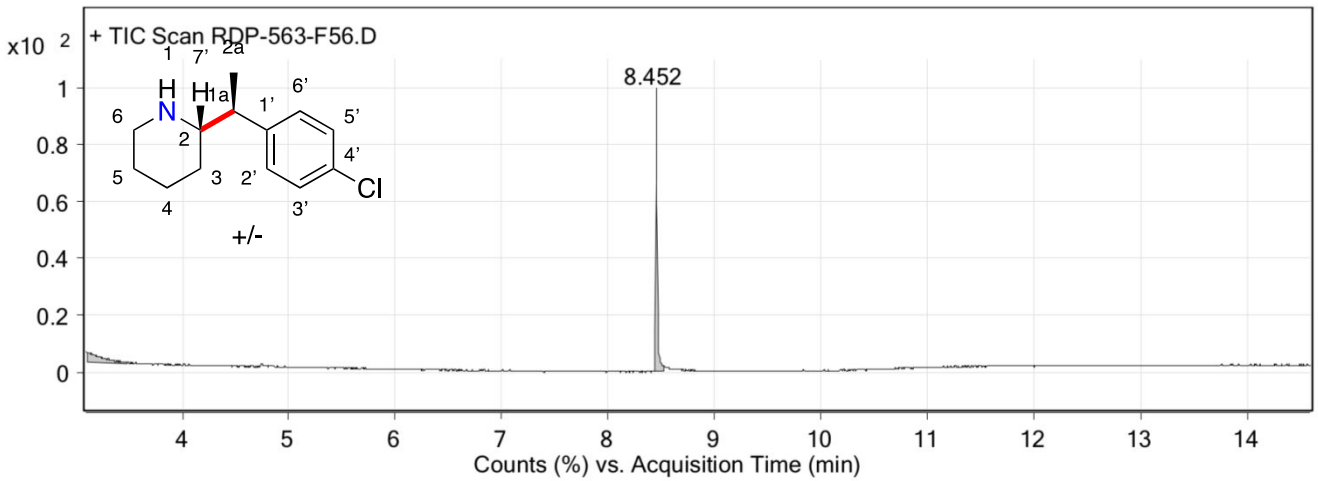


Figure S29: GC-MS report of purified 2-(1-(4-chlorophenyl)ethyl)piperidine.

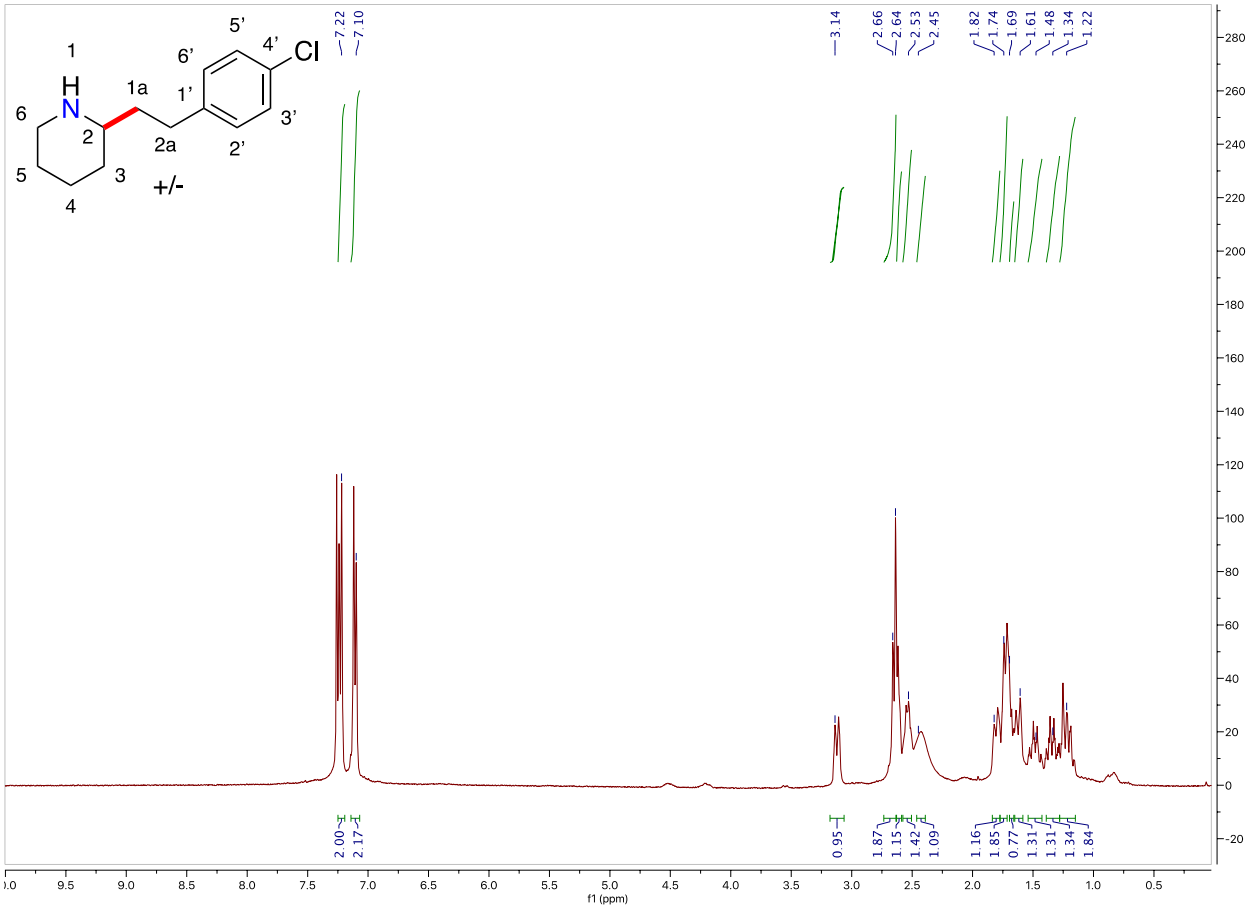


Figure S30: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of purified 2-(4-chlorophenethyl)piperidine.

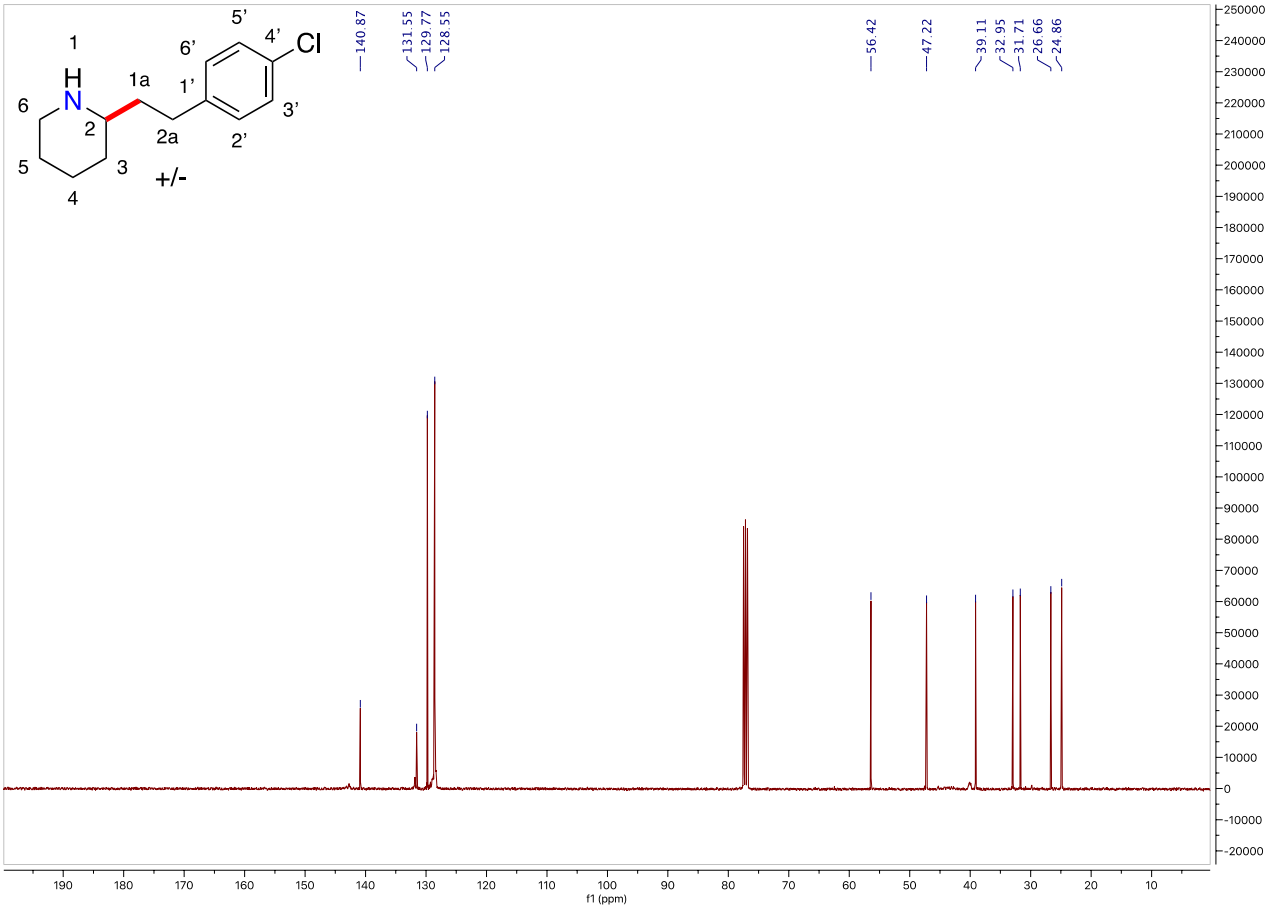


Figure S31: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of purified 2-(4-chlorophenethyl)piperidine.

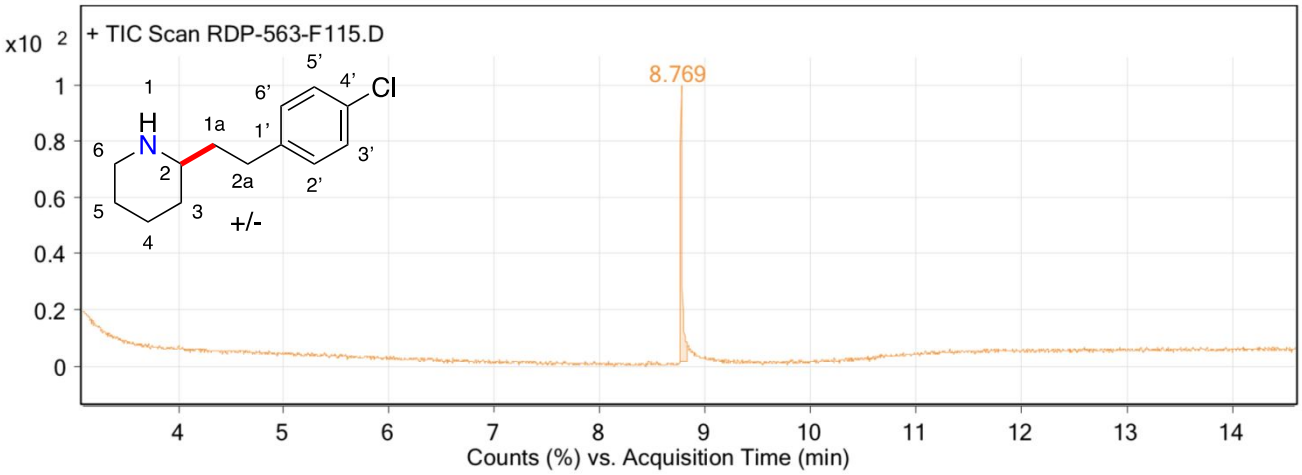
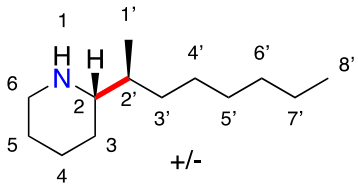


Figure S32: GC-MS report of 2-(4-chlorophenethyl)piperidine.

S6. Synthesis and Characterization of Amine Scope Products



Synthesis of 2-(octan-2-yl)piperidine (2): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), 1-octene (122.12 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 99 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine). Chemical shifts for the title compound match those reported in the literature.[8]

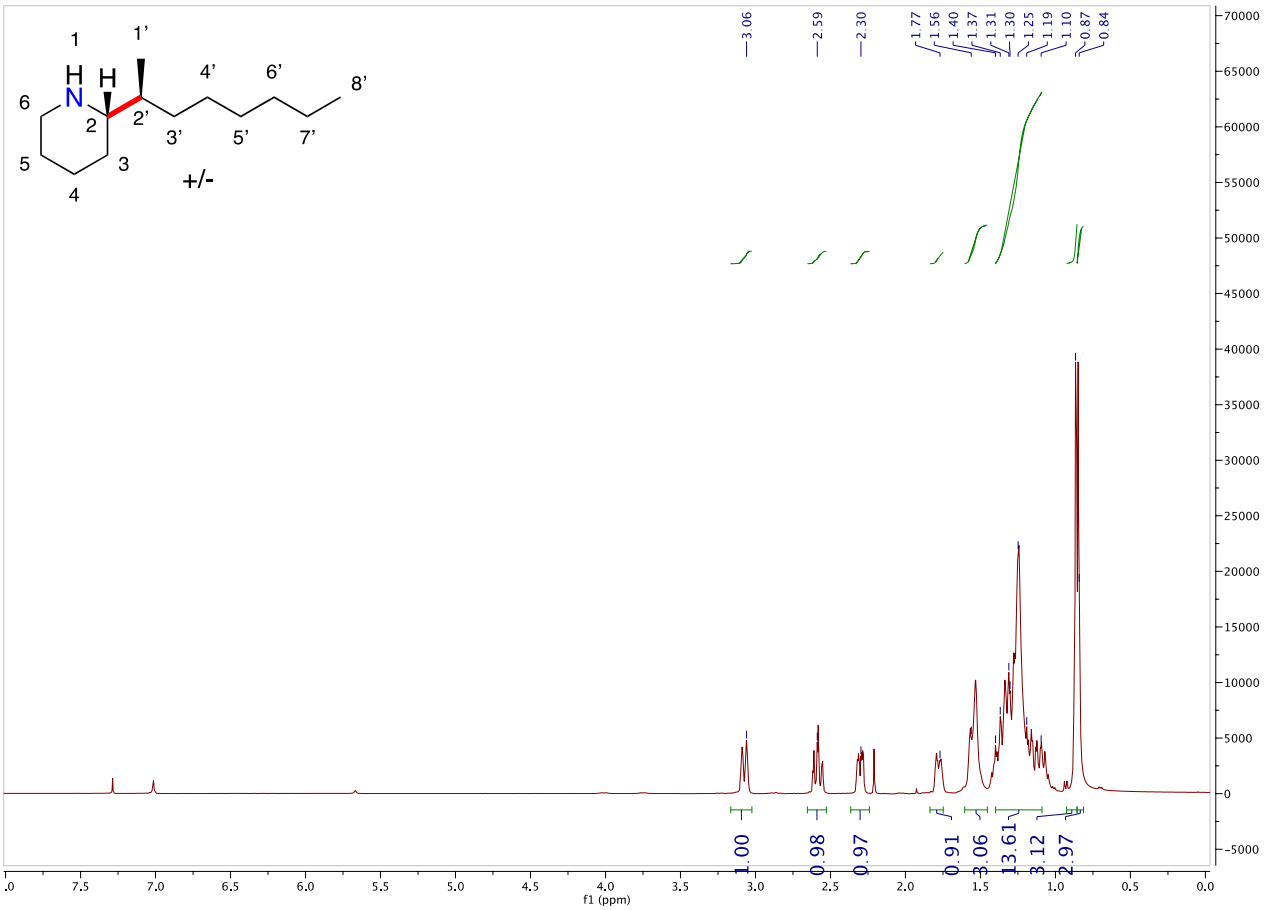


Figure S33: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(octan-2-yl)piperidine.

Note: This crude reaction GC-MS spectrum is a representative example of how we determined d.r ratios for all amine products presented.

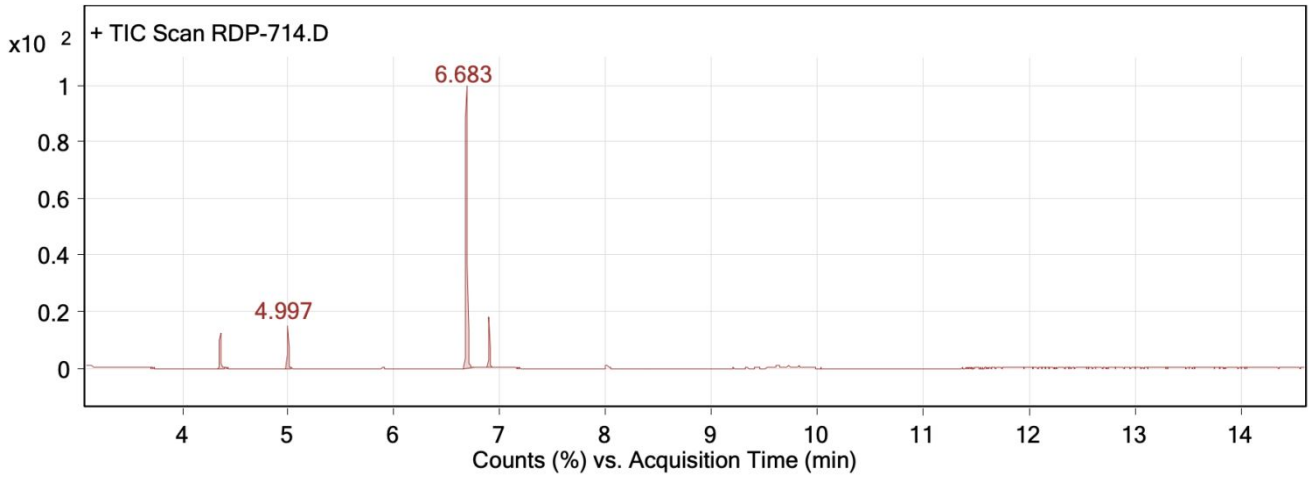


Figure S34: GC-MS for crude reaction mixture between piperidine and 1-octene.

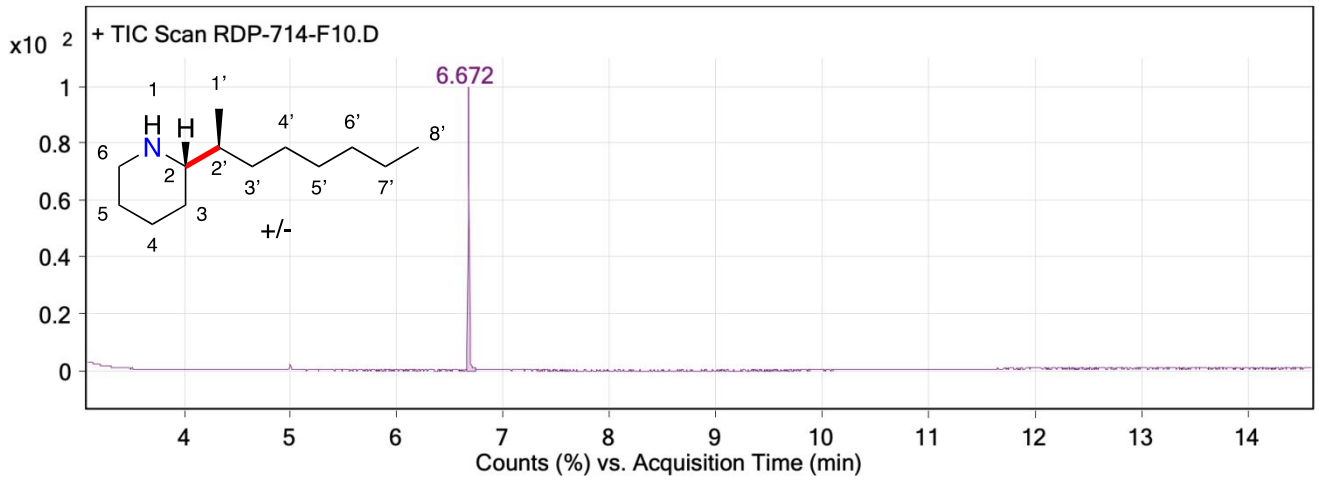
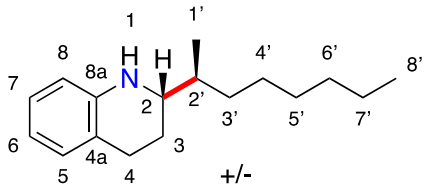


Figure S35: GC-MS report of 2-(octan-2-yl)piperidine.



Synthesis of 2-(octan-2-yl)-1,2,3,4-tetrahydroquinoline (3): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, 1,2,3,4-tetrahydroquinoline (133.19 mg, 1.0 mmol), 1-octene (122.12 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 65 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine). The chemical shifts for the title compound match those reported in the literature.[9]

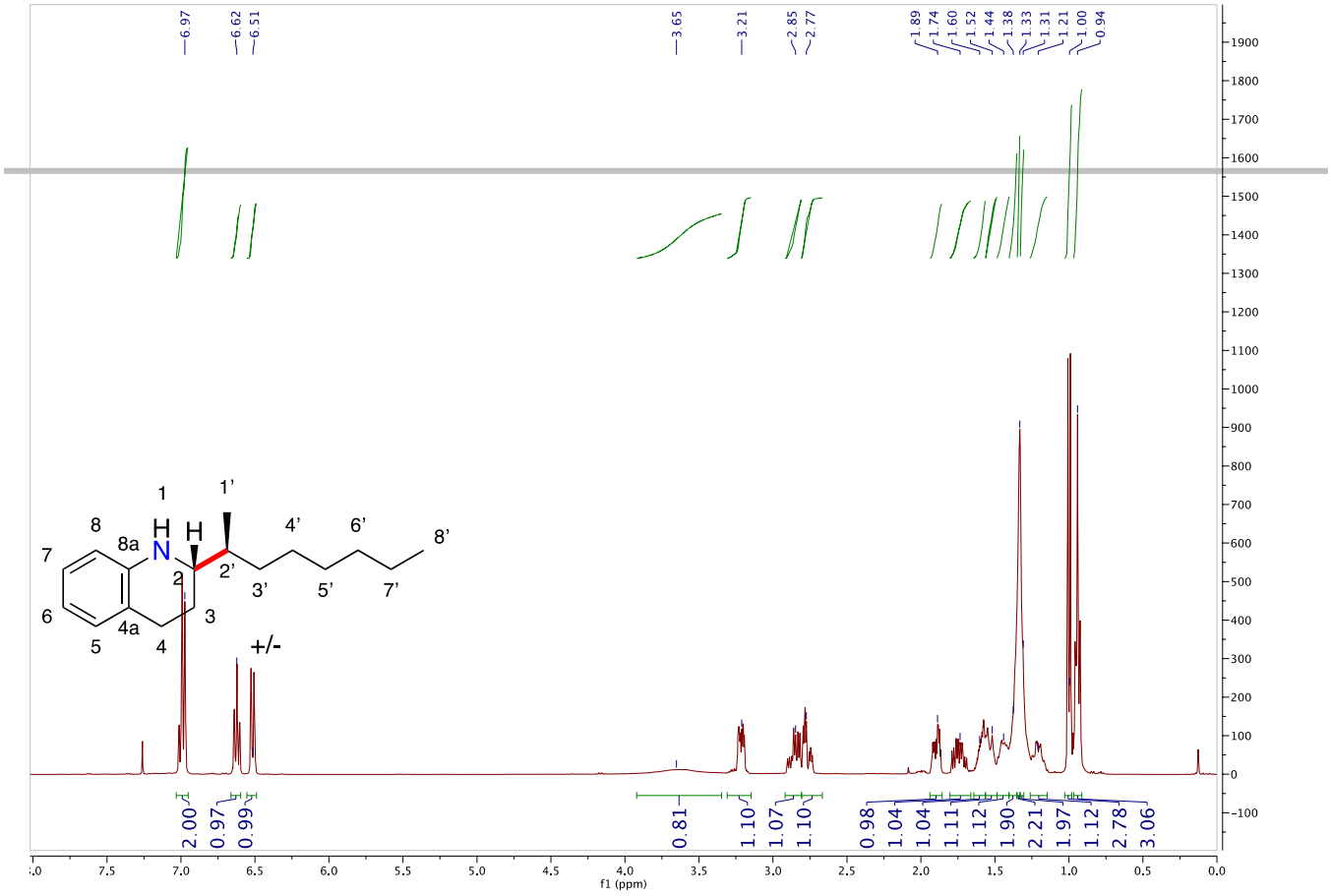


Figure S36: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(octan-2-yl)-1,2,3,4-tetrahydroquinoline.

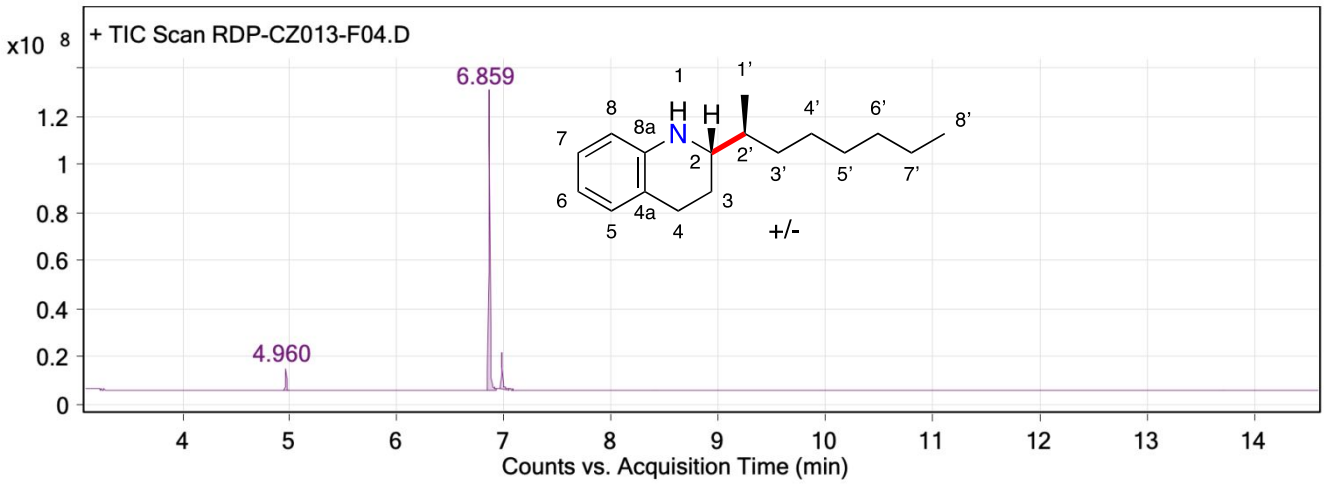
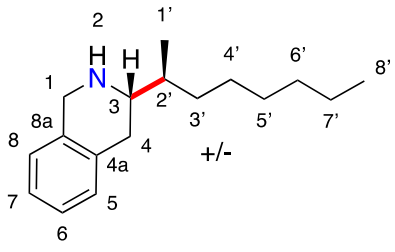
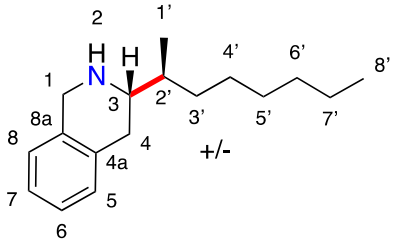


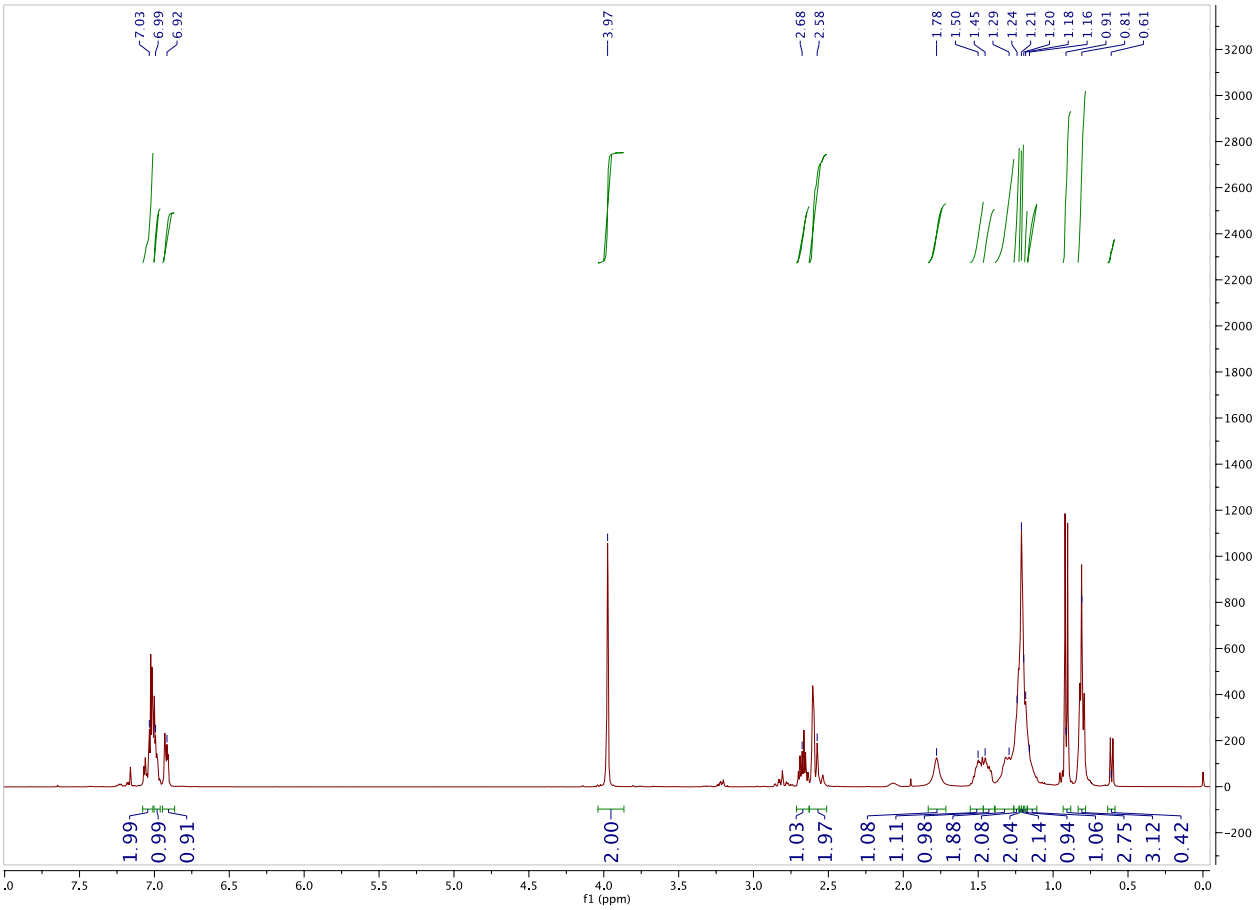
Figure S37: GC-MS report of 2-(octan-2-yl)-1,2,3,4-tetrahydroquinoline.



Synthesis of 3-(octan-2-yl)-1,2,3,4-tetrahydroisoquinoline (4): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, 1,2,3,4-tetrahydroisoquinoline (133.19 mg, 1.0 mmol), 1-octene (112.22 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 99 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): 7.03 (m, 2H, **6** and **7**), 6.99 (m, 1H, **5**), 6.92 (m, 1H, **8**), 3.97 (s, 2H, **1**),



2.68, (m, 1H, **3**), 2.58 (m, 2H, **4**), 1.78 (broad s, 1H, NH), 1.50 (m, 1H, **2'**), 1.45 (m, 1H, ½ of **3'**), 1.29 (m, 2H, **4'/5'/6'/7'**), 1.24 (m, 2H, **4'/5'/6'/7'**), 1.21 (m, 2H, **4'/5'/6'/7'**), 1.20 (m, 2H, **4'/5'/6'/7'**), 1.18 (m, 1H, ½ of **3'**), 1.16 (m, 1H, ½ of **3**), 0.91 (d, J = 0.91, 3H, **1'**), 0.81 (t, 3H, **8'**), 0.61 (d, J = 0.61, 0.42H, **1' of minor regiosiomer**) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 133.83 (minor), 136.49 (minor), 135.91, 135.40, 129.46, 129.16 (minor), 126.07, 126.00, 125.95 (minor), 125.69, 125.65 (minor), 125.56 (minor), 59.55 (minor), 58.28, 49.22, 43.04 (minor), 37.88, 37.71 (minor), 34.53 (minor), 32.94, 32.38, 32.00, 30.61 (minor), 29.73, 27.97 (minor), 27.43, 22.77, 15.58, 14.20, 13.46 ppm. HRMS (ESI): *m/z*



calcd for $C_{17}H_{27}N$ [M+H$^+$]: 246.2221 Found: 246.2220.

Figure S38: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-(octan-2-yl)-1,2,3,4-tetrahydroisoquinoline.

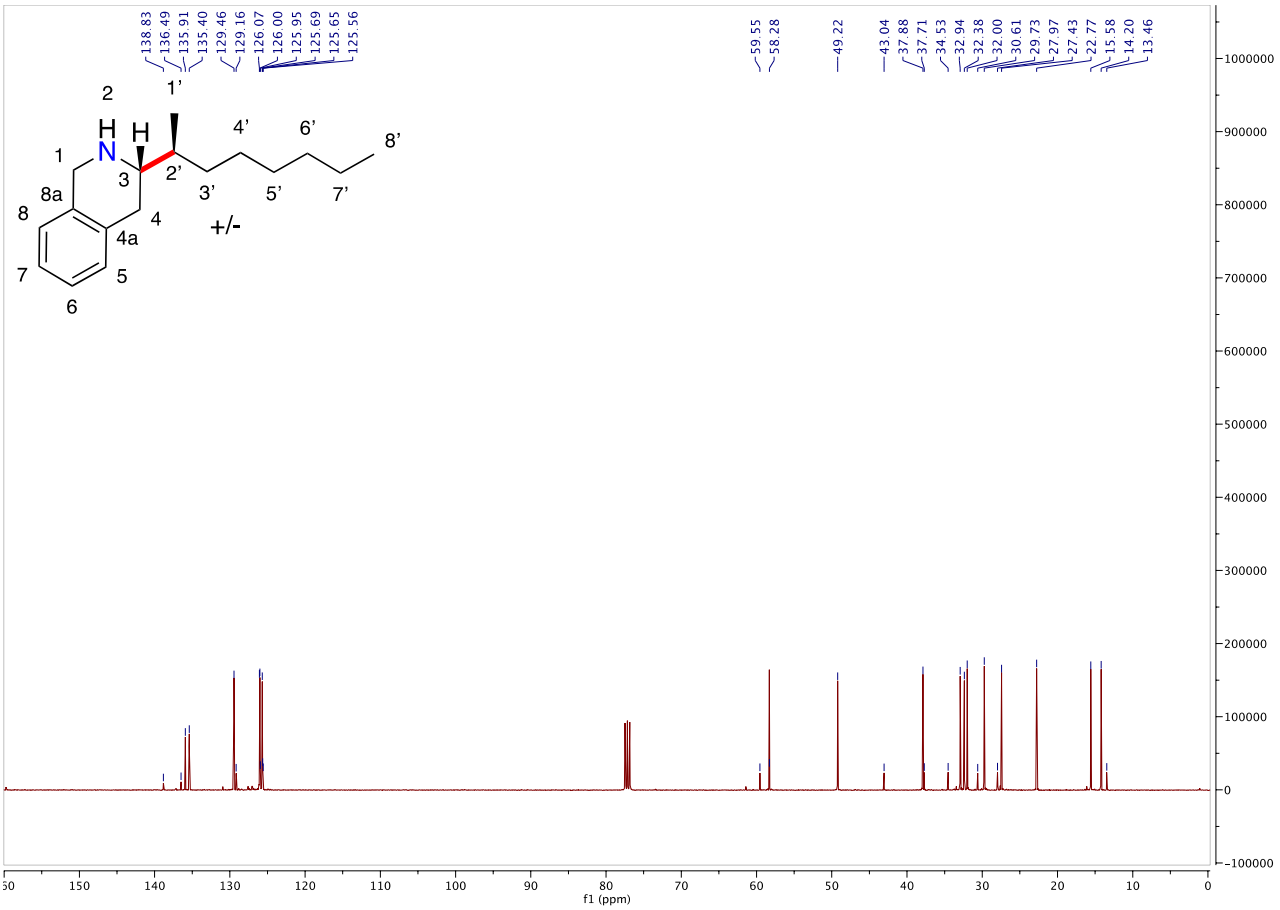


Figure S39: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 3-(octan-2-yl)-1,2,3,4-tetrahydroisoquinoline.

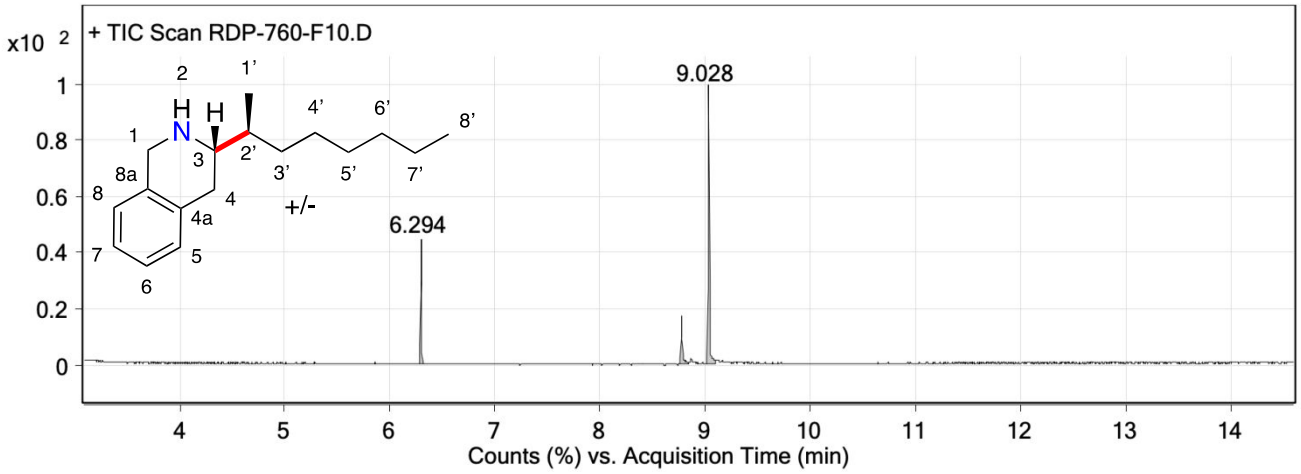
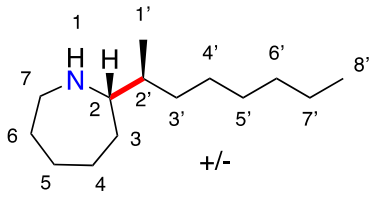


Figure S40: GC-MS report of 3-(octan-2-yl)-1,2,3,4-tetrahydroisoquinoline. Note that the peak at 6.294 represents residual internal standard.



Synthesis of 2-(octan-2-yl)azepane (5): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg Ligand, azepane (99.17 mg, 1.0 mmol), 1-octene (112.22 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 91 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 3.00 (m, 1H, ½ of 7), 2.64 (m, 1H, ½ of 7), 2.47 (m, 1H, 2), 1.69 (m, 1H, ½ of 3/4), 1.63 (m, 1H, ½ of 3/4), 1.60 (m, 2H, 6/5), 1.57 (m, 1H, ½ of 3/4), 1.46 (m, 2H, 6/5), 1.42 (m, 1H, 2'), 1.38 (m, 1H, ½ of 3'/4'), 1.35 (m, 1H, ½ of 3/4), 1.27 (m, 1H, ½ of 3/4), 1.26 (m, 2H, 5'/6'/7'), 1.24 (m, 2H, 5'/6'/7'), 1.20 (m, 2H, 5'/6'/7'), 1.14 (m, 1H, ½ of 3'/4'), 1.09 (m, 1H, ½ of 3'/4'), 0.85 (overlapping t, 3H, 8'), 0.81 (overlapping d, 3H, 1') ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 63.17, 55.33, 48.70, 39.59, 33.82, 33,59, 32.01, 31.33, 29.77, 27.74, 26.97, 22.76, 15.36, 14.16 ppm. HRMS (ESI): *m/z* calcd for $C_{14}H_{29}N$ [M+H$^+$]: 212.2378 Found: 212.2372.

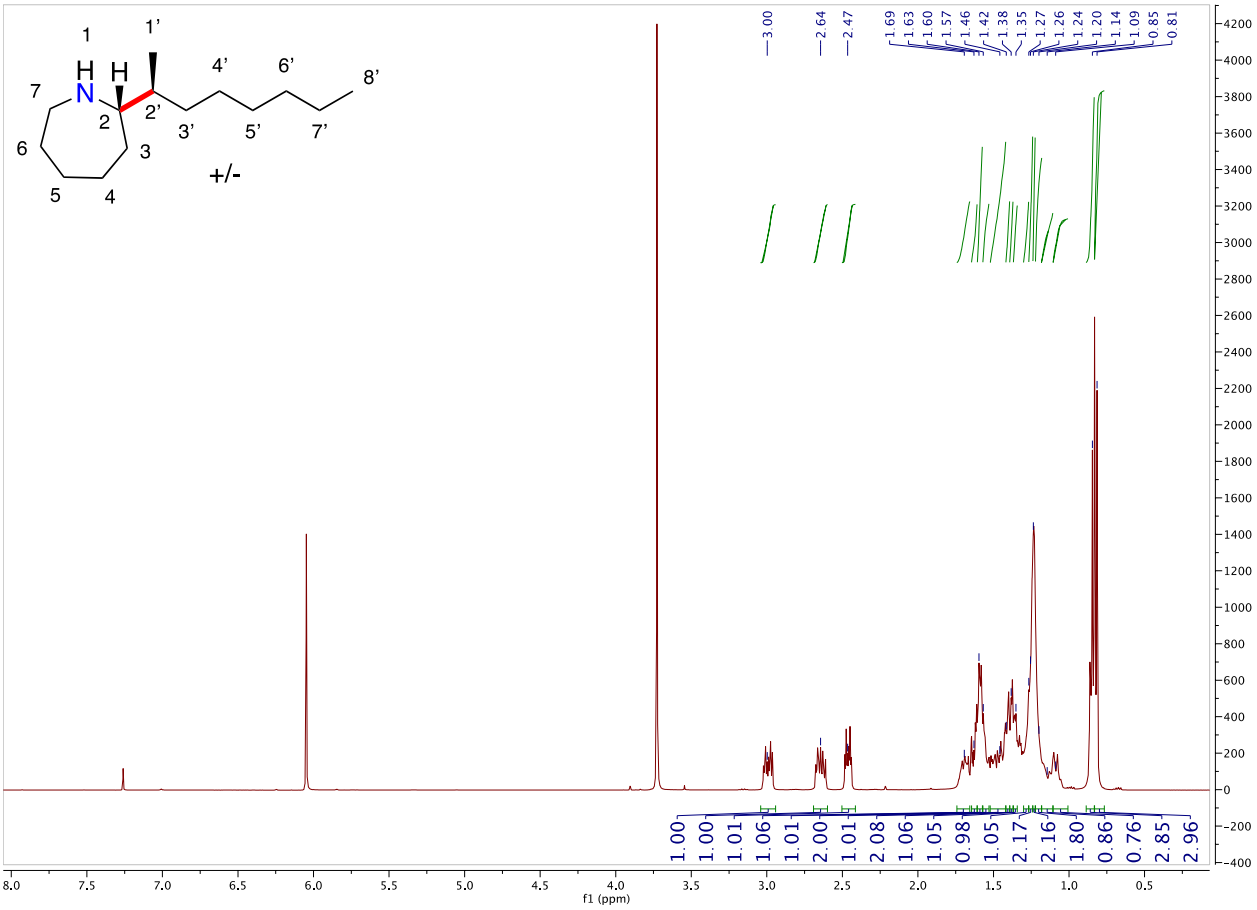


Figure S41: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(octan-2-yl)azepane.

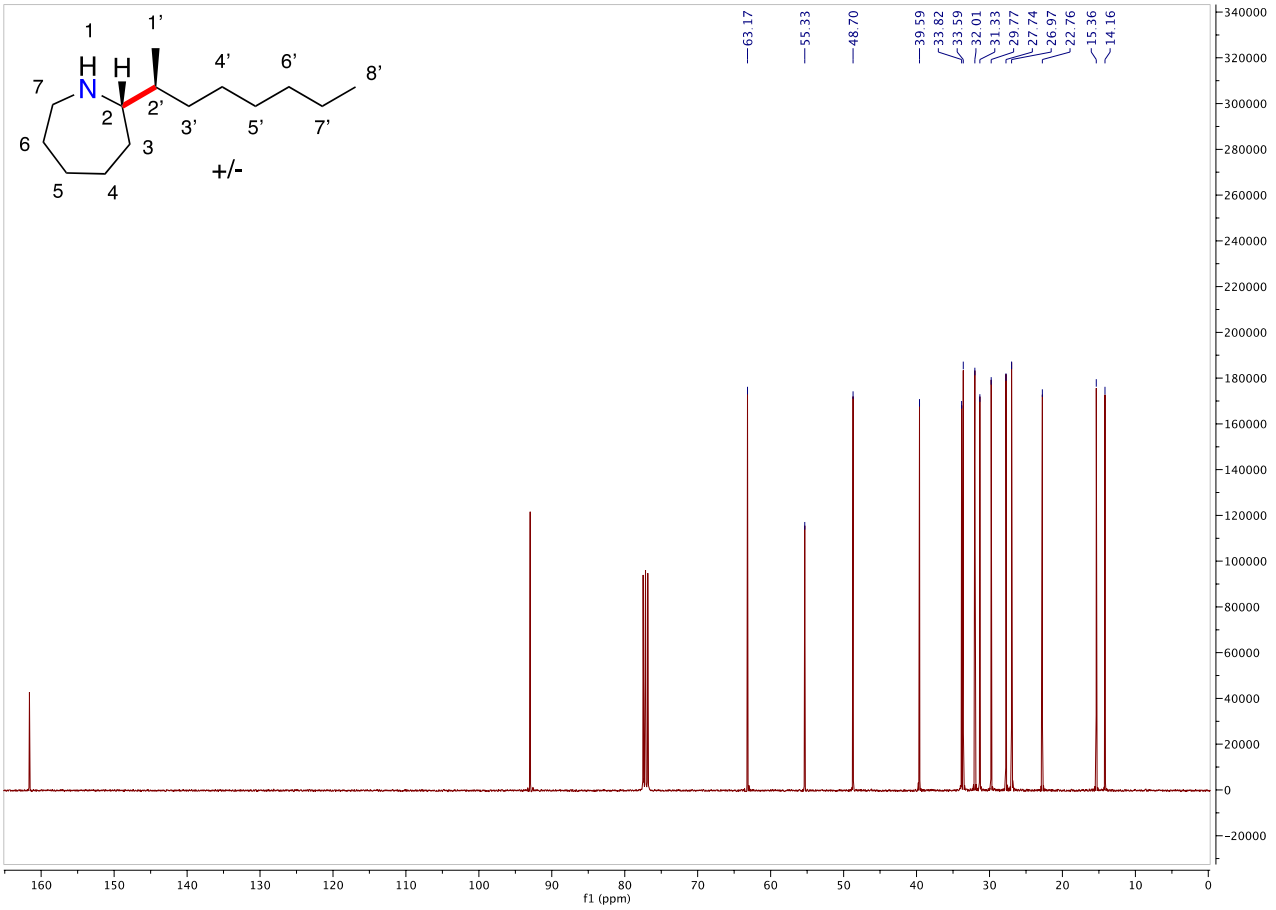


Figure S42: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(octan-2-yl)azepane.

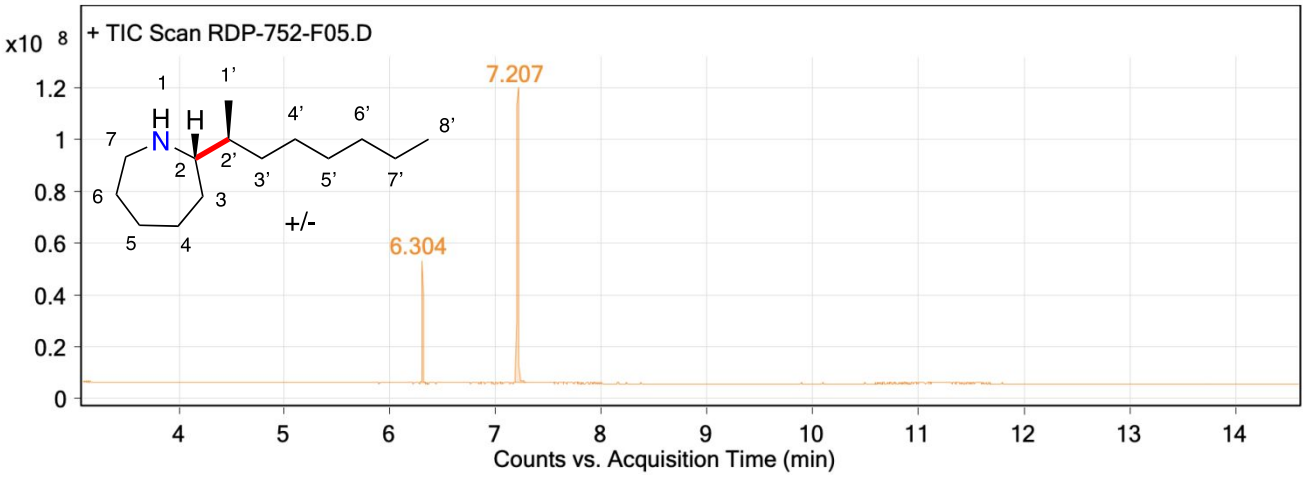
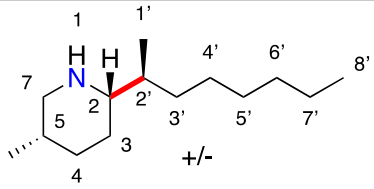


Figure S43: GC-MS report of 2-(octan-2-yl)azepane. Note that the peak at 6.304 min represents residual internal standard.



Synthesis of 4-methyl-2-(octan-2-yl)piperidine (6): Prepared following the general procedure for predominantly branched product formation: : 26.0 mg Ta, 15.2 Ligand, 3-methylpiperidine (99.17 mg, 1.0 mmol), 1-octene (112.22 mg, 1.0 mmol). The reaction was subsequently concentrated and the combined yield was determined to be 86 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification by column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine) yields an inseparable mixture of diastereomers (8:1) as determined by GC-MS. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 3.03 (m, 1H, ½ of 7), 2.33 (minor diastereomer) and 2.26 (m, 1H, 2), 2.21 (m, 1H, ½ of 7), 1.89 (broad s, 1H, NH), 1.78 (m, 1H, ½ of 4), 1.59 (m, 1H, ½ of 3), 1.46 (m, 1H, 5), 1.41 (m, 1H, ½ of 3'/4'), 1.37 (m, 1H, 2'), 1.32 (m, 1H, ½ of 4'/3'), 1.28 (m, 2H, 5'/6'/7'), 1.26 (m, 2H, 5'/6'/7'), 1.25 (m, 2H, 5'/6'/7'), 1.23 (m, 1H, ½ of 3), 1.20, (m, 1H, ½ of 3'/4'), 1.08 (m, 1H, ½ of 3'/4'), 0.98 (m, 1H, ½ of 4), 0.87 (overlapping d, 3H, 1'), 0.86 (overlapping t, 3H, 8'), 0.81 (d, J = 0.81, 3H, 6) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 61.41 (major) and 61.41 (minor), 54.43 (major), 54.30 (minor), 37.23 (major), 33.17 (major), 32.33 (major), 31.31 (major), 31.04 (major), 29.46 (minor), 28.76 (major), 28.73 (minor), 27.38 (minor), 26.58 (major), 26.51 (minor), 23.59 (major), 21.80 (major), 18.64 (major), 16.32 (minor), 14.75 (minor), 14.68 (major), 13.22 (major). HRMS (ESI): *m/z* calcd for $C_{14}H_{29}N$ [M+H$^+$]: 212.2378 Found: 212.2381.

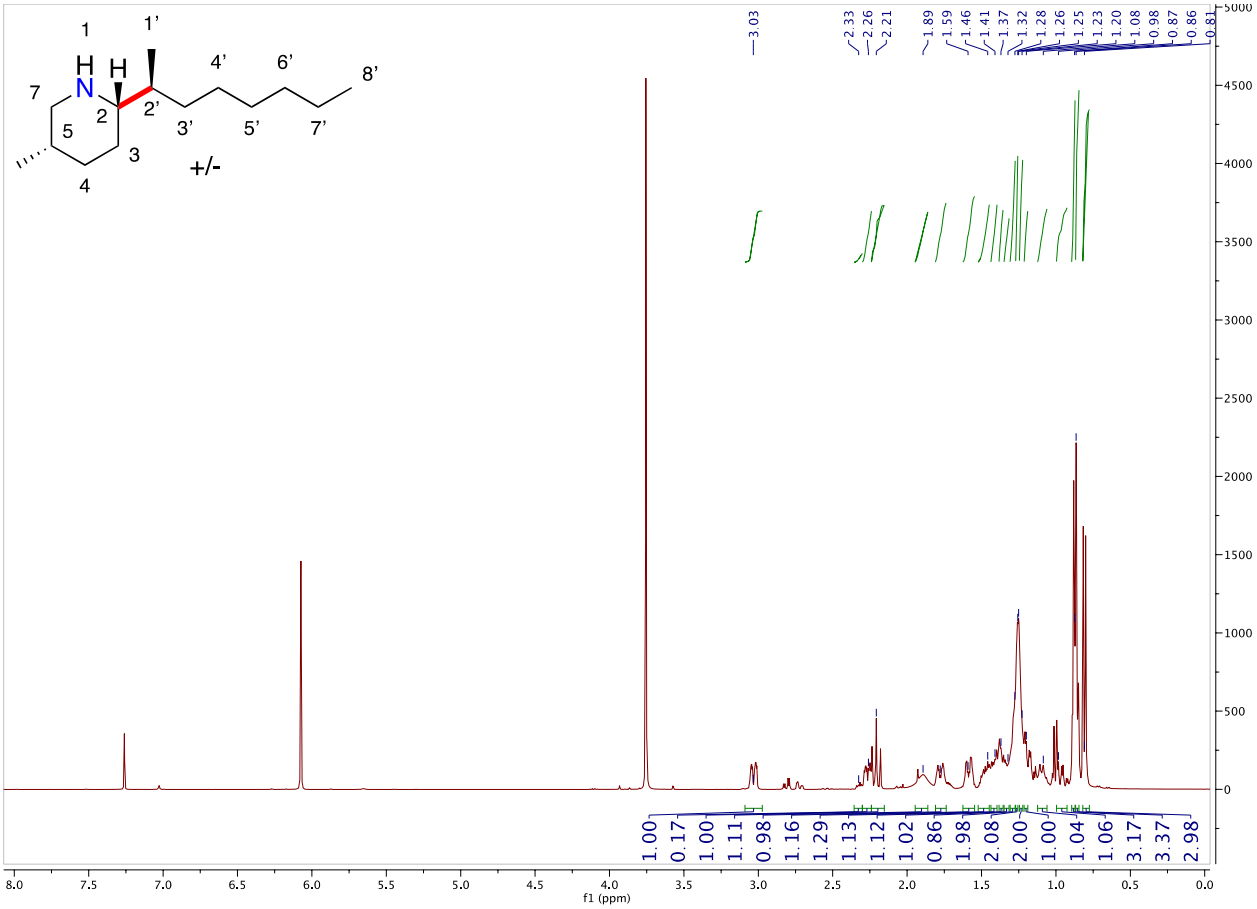


Figure S44: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of both diastereomers of 4-methyl-2-(octan-2-yl)piperidine (1:10). Note that peaks at 3.7 and 6.1 ppm represent residual 1,3,5-trimethoxybenzene internal standard.

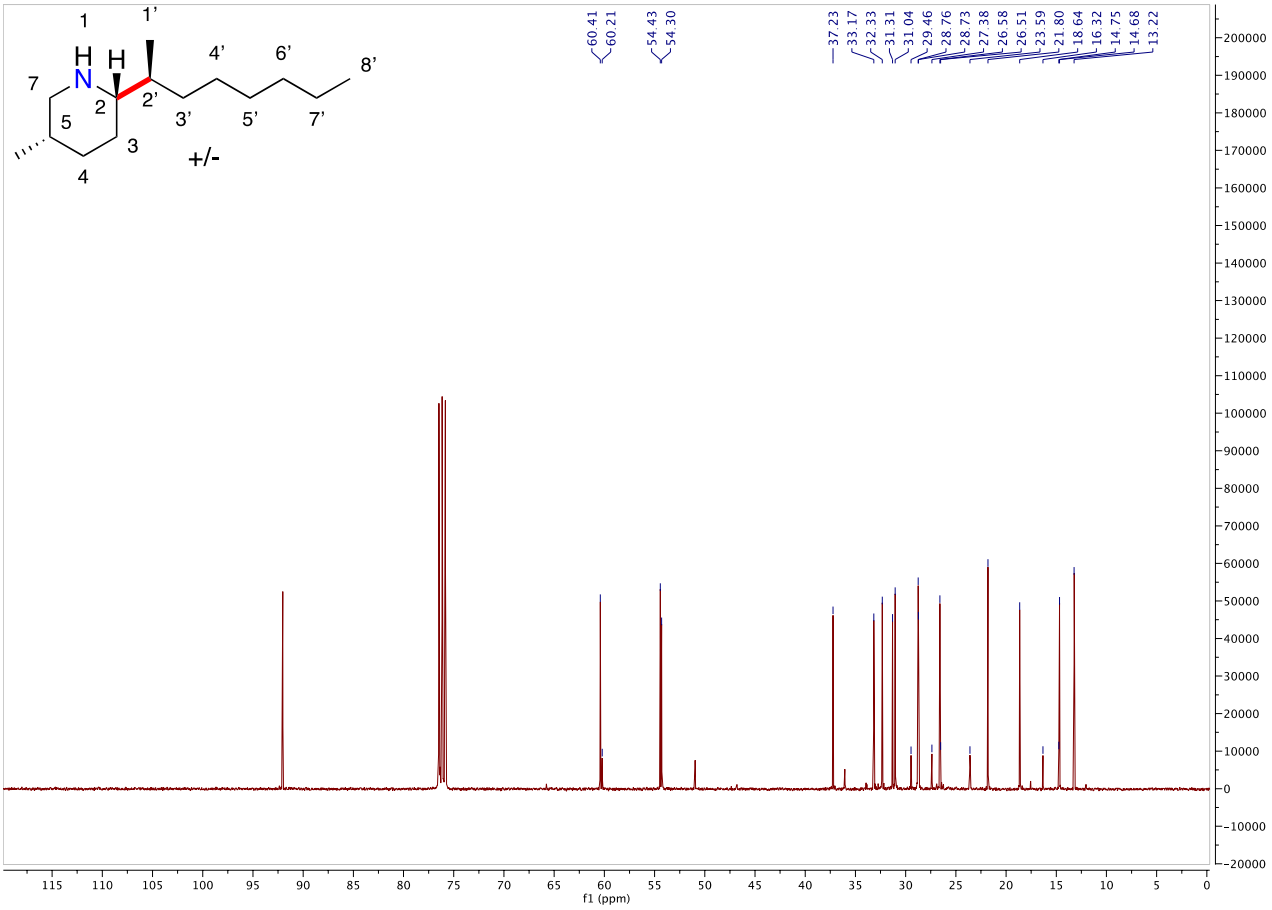


Figure S45: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.

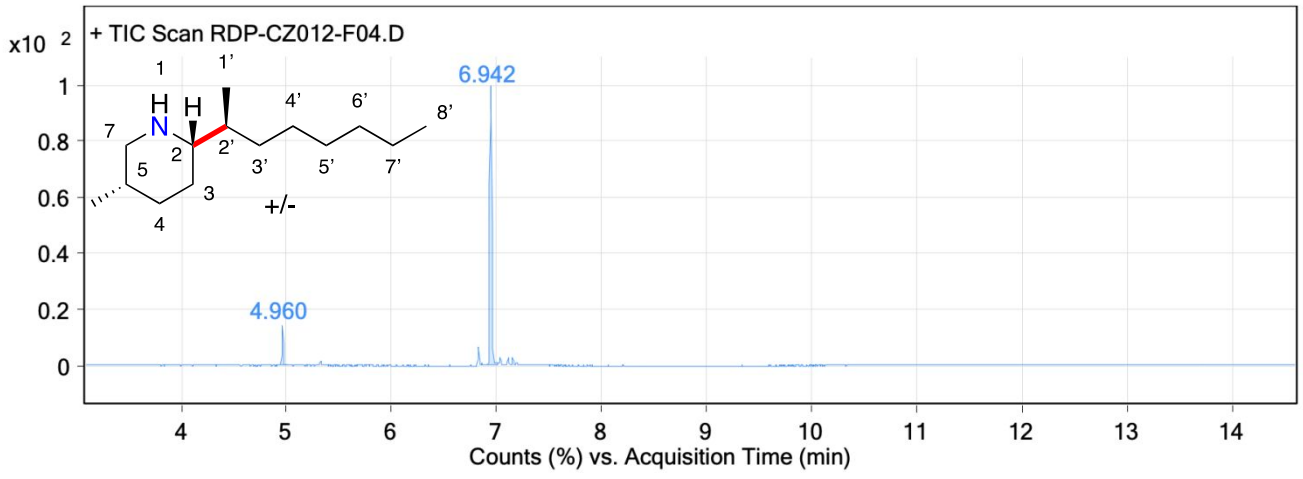


Figure S46: GC-MS report of 4-methyl-2-(octan-2-yl)piperidine.

Synthesis of 4-methyl-2-(octan-2-yl)piperidine (7): Prepared following the general procedure for predominantly branched product formation: 26.0 Ta, 15.2 ligand **L4**, 4-methylpiperidine (99.17 mg, 1.0 mmol), 1-octene

(250.2 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 84 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 3.09 (m, 1H, ½ of 7), 2.59 (m, 1H, ½ of 7), 2.33 (m, 1H, 2), 1.99 (broad s, 1H, NH), 1.59 (m, 1H, ½ of 6), 1.55 (m, 1H, ½ of 3), 1.44 (m, 1H, 4), 1.42 (m, 1H, ½ of 3'), 1.36 (m, 1H, 2'), 1.30 (m, 1H, ½ of 4'), 1.28 (m, 2H, 5'/6'/7'), 1.26 (m, 2H, 5'/6'/7'), 1.25 (m, 2H, 5'/6'/7'), 1.17 (m, 1H, ½ of 4'), 1.08 (m, 1H, ½ of 3'), 1.01 (m, 1H, ½ of 6), 0.90 (d, J = 0.90, 3H, 5), 0.88 (overlapping d, 3H, 1'), 0.87 (overlapping t, 3H, 8'), 0.80 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 61.52, 55.44, 47.29, 38.52, 38.38, 35.37, 33.26, 32.05, 31.85, 29.77, 27.62, 22.81, 15.62, 14.22 ppm. HRMS (ESI): *m/z* calcd for $C_{14}H_{29}N$ [M^+]: 212.2299 Found: 212.2310.

Note: The 1D/2D NMR spectroscopy data for this compound is a representative example of how we were able to were able to assign all proton and carbon signals conclusively in products with 1-octene as a coupling partner as well as assign relative stereochemistry for all compounds.

For NOESY experiments: The 1D NOESY experiment illustrated irradiated the peak at 2.59 ppm (1/2 of **7**) selectively. This data suggests that this proton interacts spatially with the other peak on the same methylene (3.09 (m, 1H, ½ of 7)), as well as the CH at 2.33 ppm (m, 1H, 2). Other important interactions in the 1D NOESY include the coupling of the proton at 1.59 ppm (m, 1H, ½ of 6) with the CH at 1.44 ppm (m, 1H, 4). This interaction with 4 is key, because it shows that the methyl group **5** is facing into the page as illustrated in the major diastereomer above. 2D NOESY data shown below was used to further corroborate this analysis and rule out the other possible orientation.

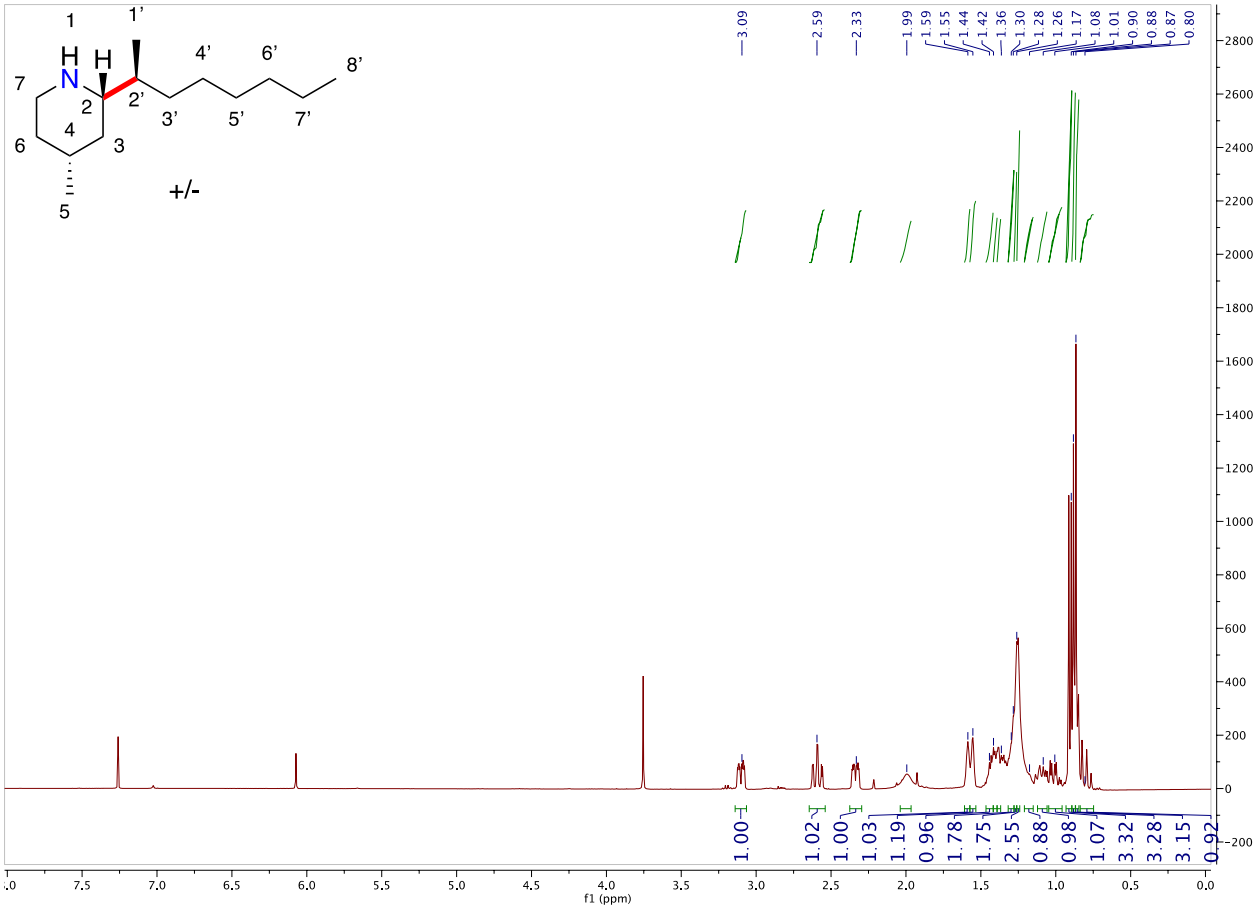


Figure S47: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.

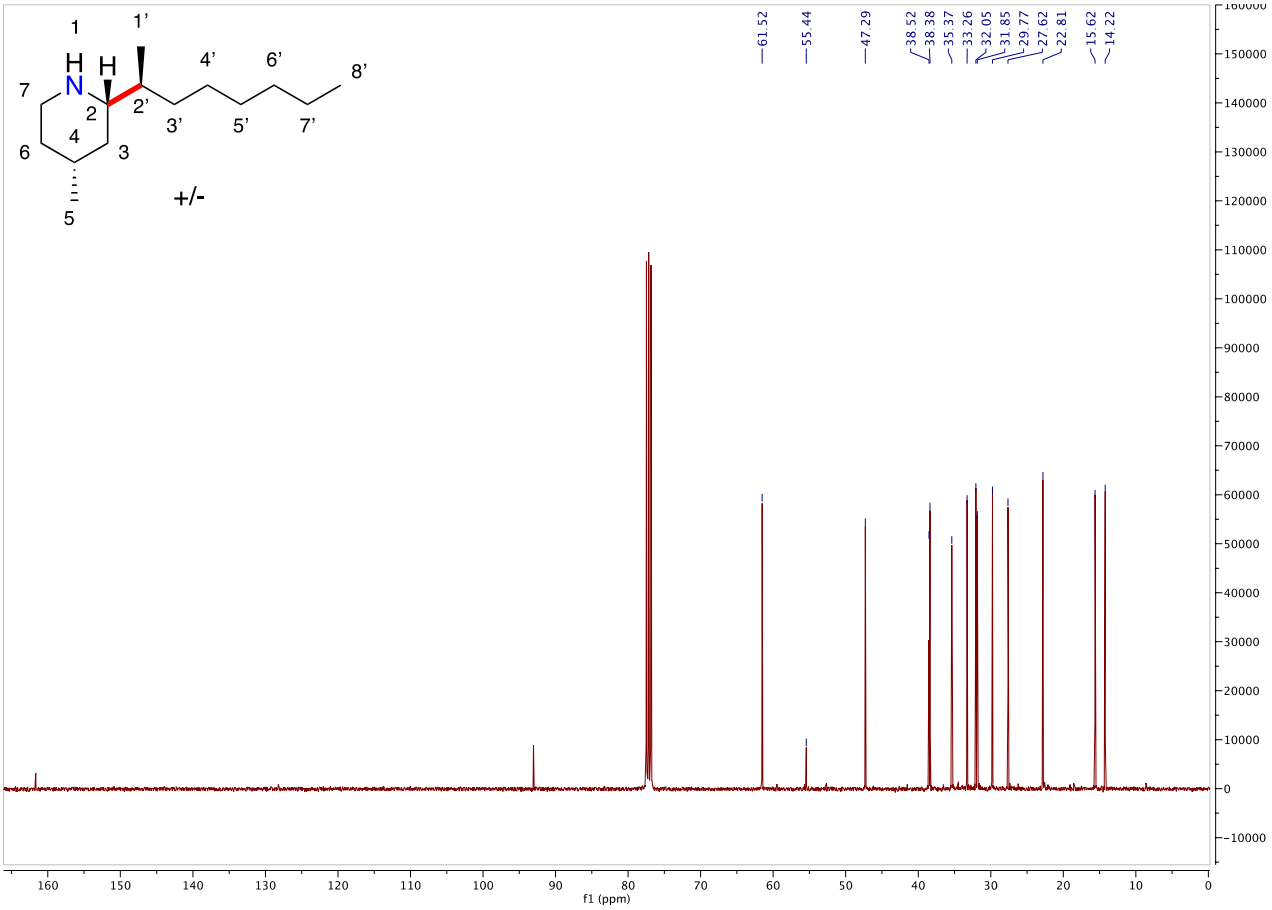


Figure S48: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.

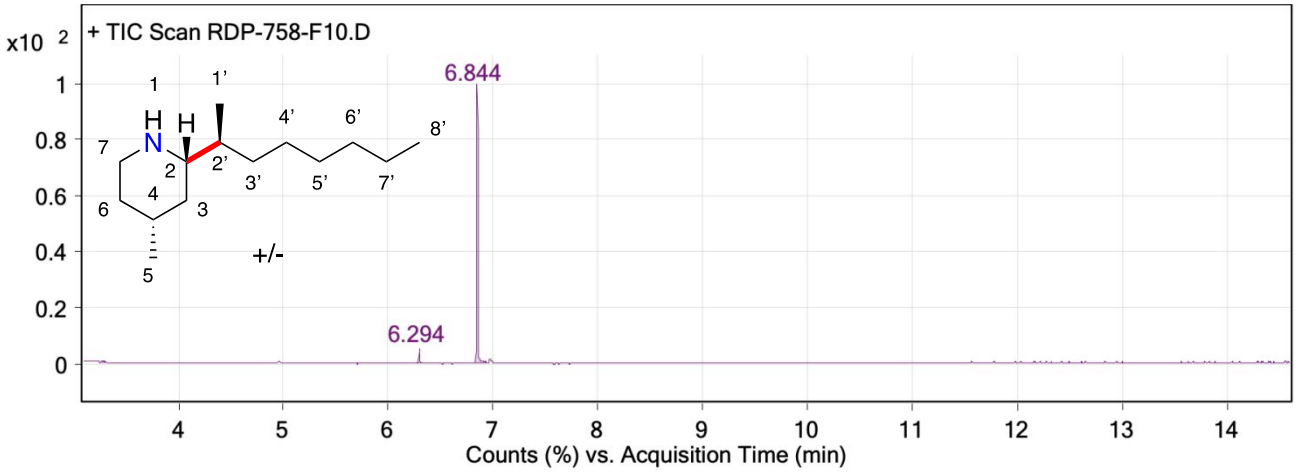


Figure S49: GC-MS report of 4-methyl-2-(octan-2-yl)piperidine.

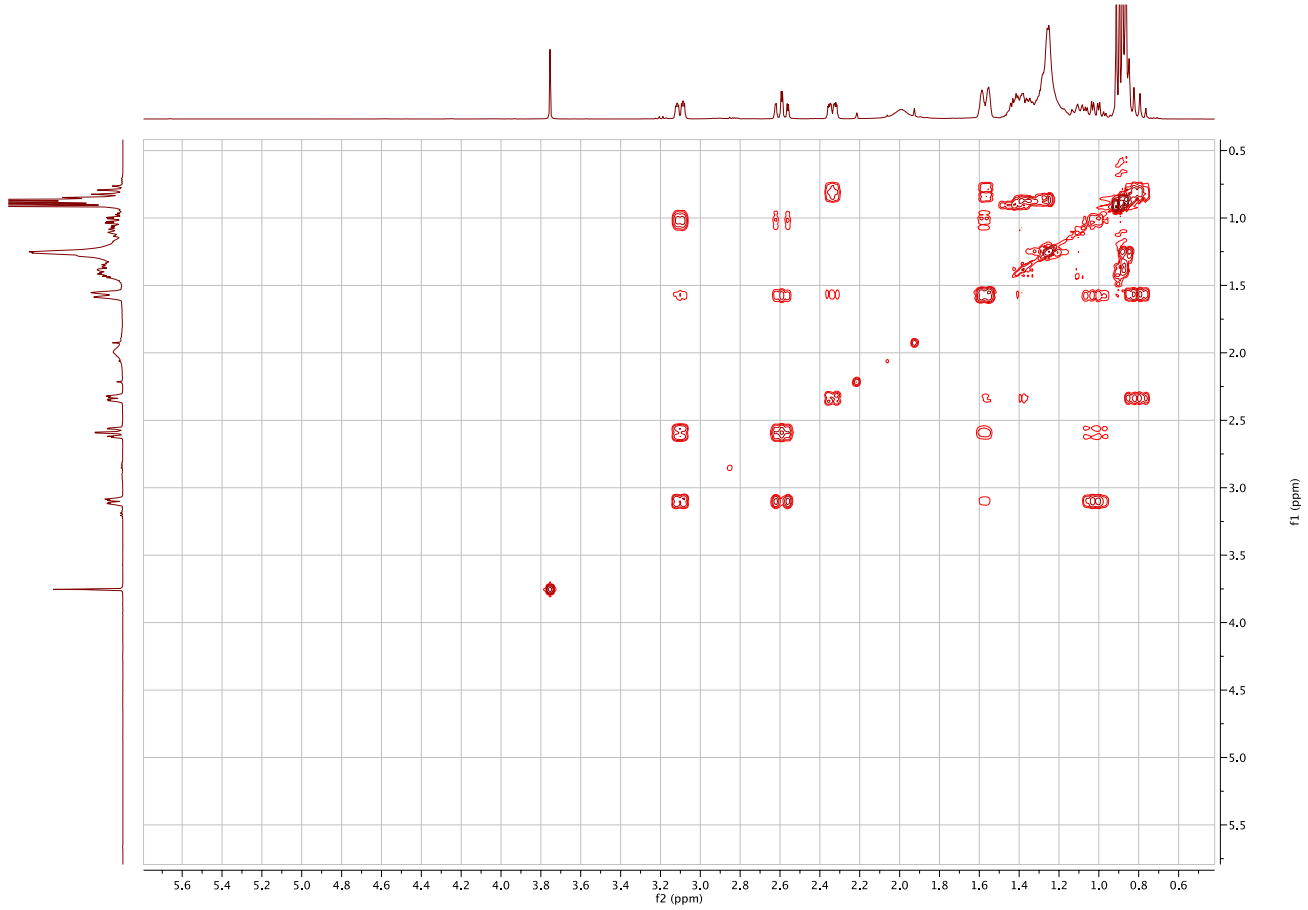


Figure S50: COSY spectrum (400 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.

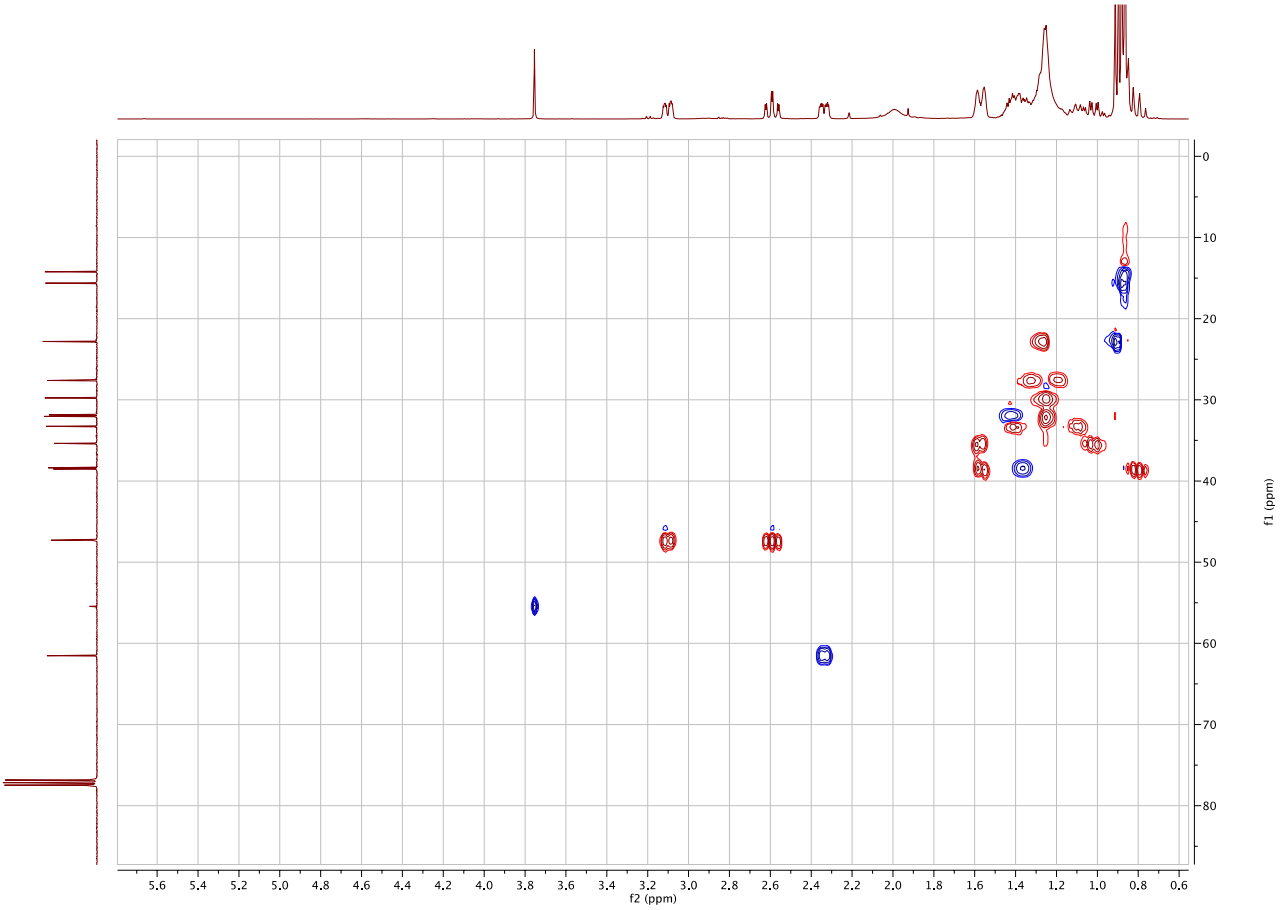


Figure S51: HSQC spectrum (400 and 101 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.

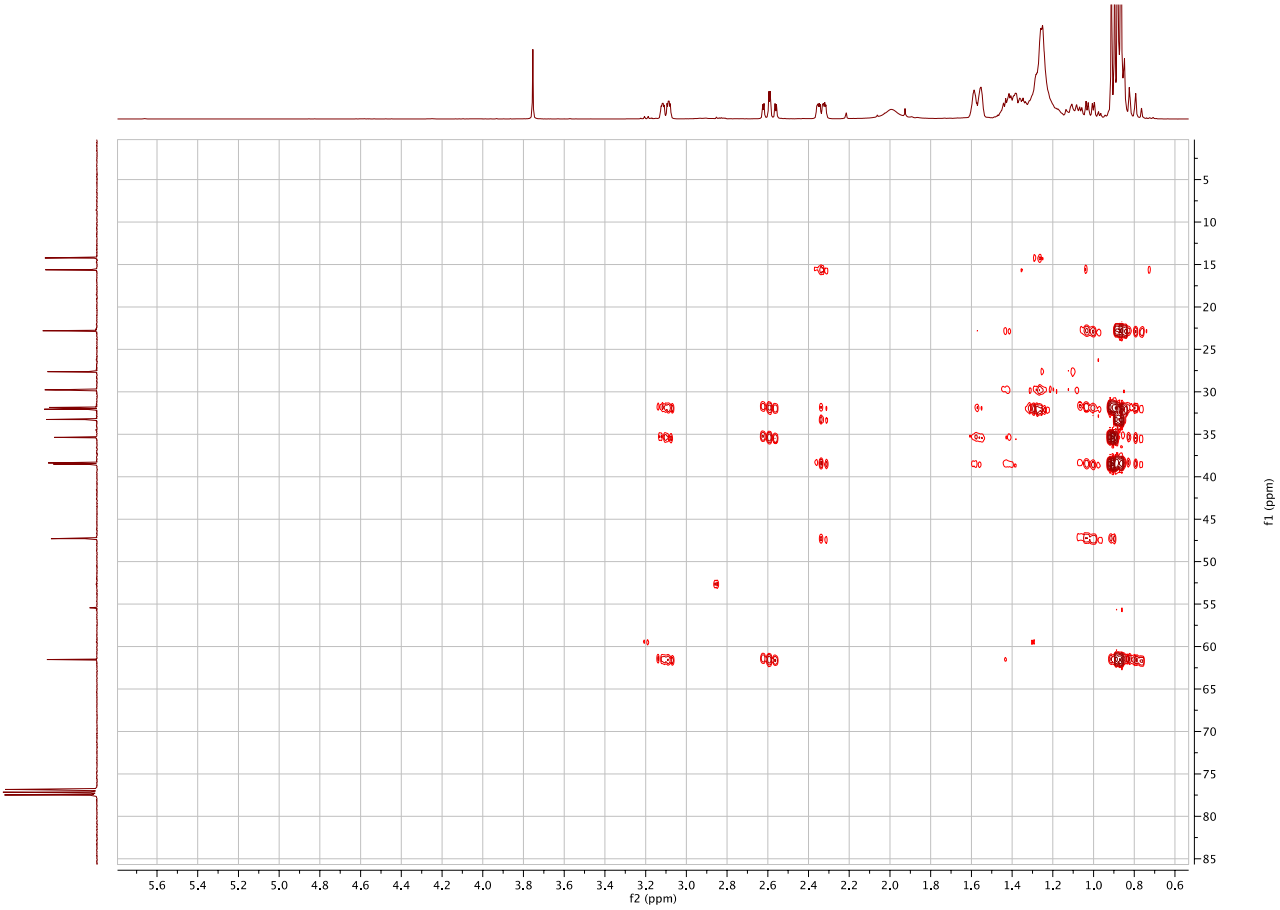


Figure S52: HMBC spectrum (400 and 101 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.

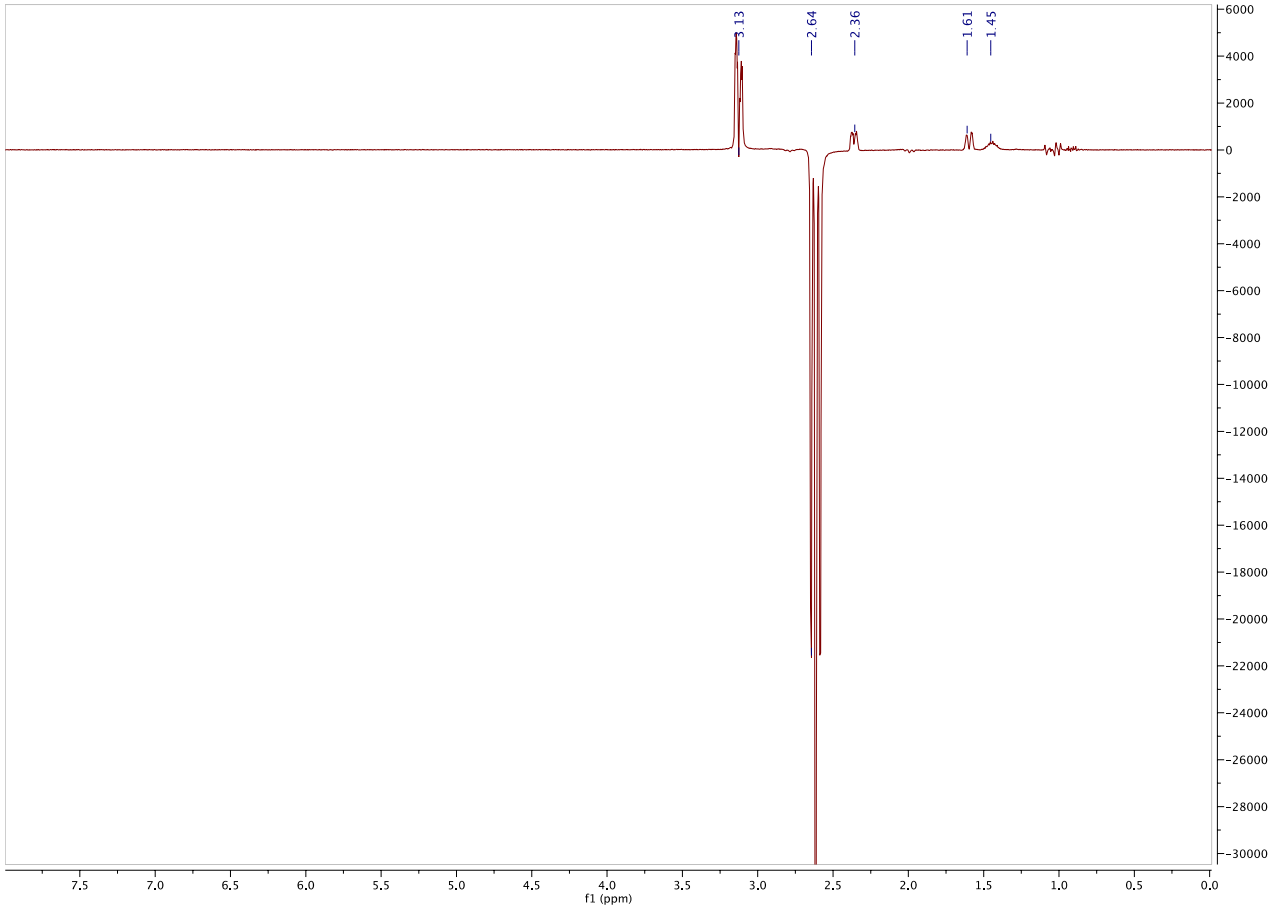


Figure S53: 1D NOE spectrum (400 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.

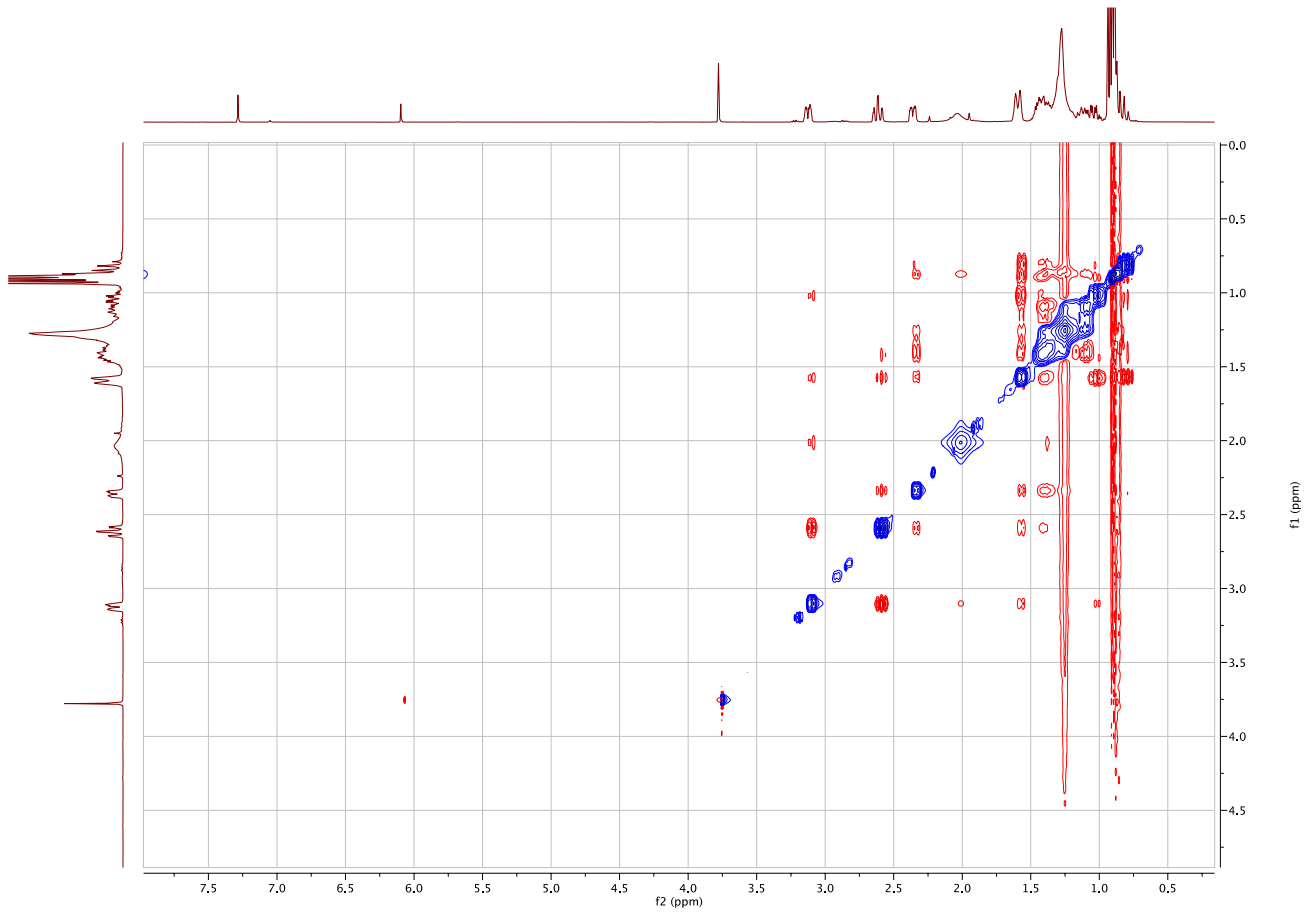
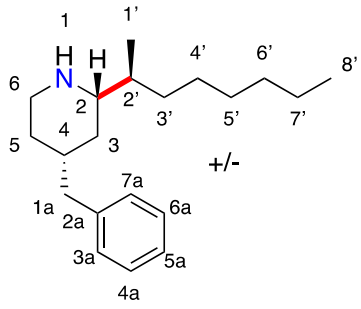


Figure S54: 2D NOESY spectrum (400 MHz, $CDCl_3$, 298 K) of 4-methyl-2-(octan-2-yl)piperidine.



Synthesis of 4-benzyl-2-(octan-2-yl)piperidine (8): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, 4-benzylpiperazine (175.3 mg, 1.0 mmol), 1-octene (112.22 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 84 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.31 (m, 2H, 4a and 6a), 7.23 (m, 1H, 5a), 7.18 (m, 2H, 3a and 7a), 3.58 (broad s, 1H, NH), 3.30 (m, 1H, ½ of 6), 2.68 (m, 1H, ½ of 6), 2.60 (m, 1H, 4), 2.55 (m, 1H, 2), 1.75 (m, 1H, ½ of 3), 1.71 (m, 1H, ½ of 5/3'), 1.67 (m, 1H, ½ of 5/3'), 1.61 (m, 1H, ½ 5/3'), 1.51 (m, 1H, 2'), 1.37 (m, 1H, ½ 5/3') 1.33 (m, 2H, 1a), 1.30 (m, 2H, 4'/5'/6'/7'), 1.29 (m, 2H, 4'/5'/6'/7'), 1.26 (m, 2H, 4'/5'/6'/7'), 1.23 (m, 2H, 4'/5'/6'/7'), 1.17 (m, 1H, ½ of 3), 0.98 (d, J = 0.98, 3H, 1'), 0.91 (t, 3H, 8') ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ ppm. HRMS (ESI): *m/z* calcd for $C_{20}H_{33}N$ [M+H$^+$]: 288.2691 Found: 288.2692.

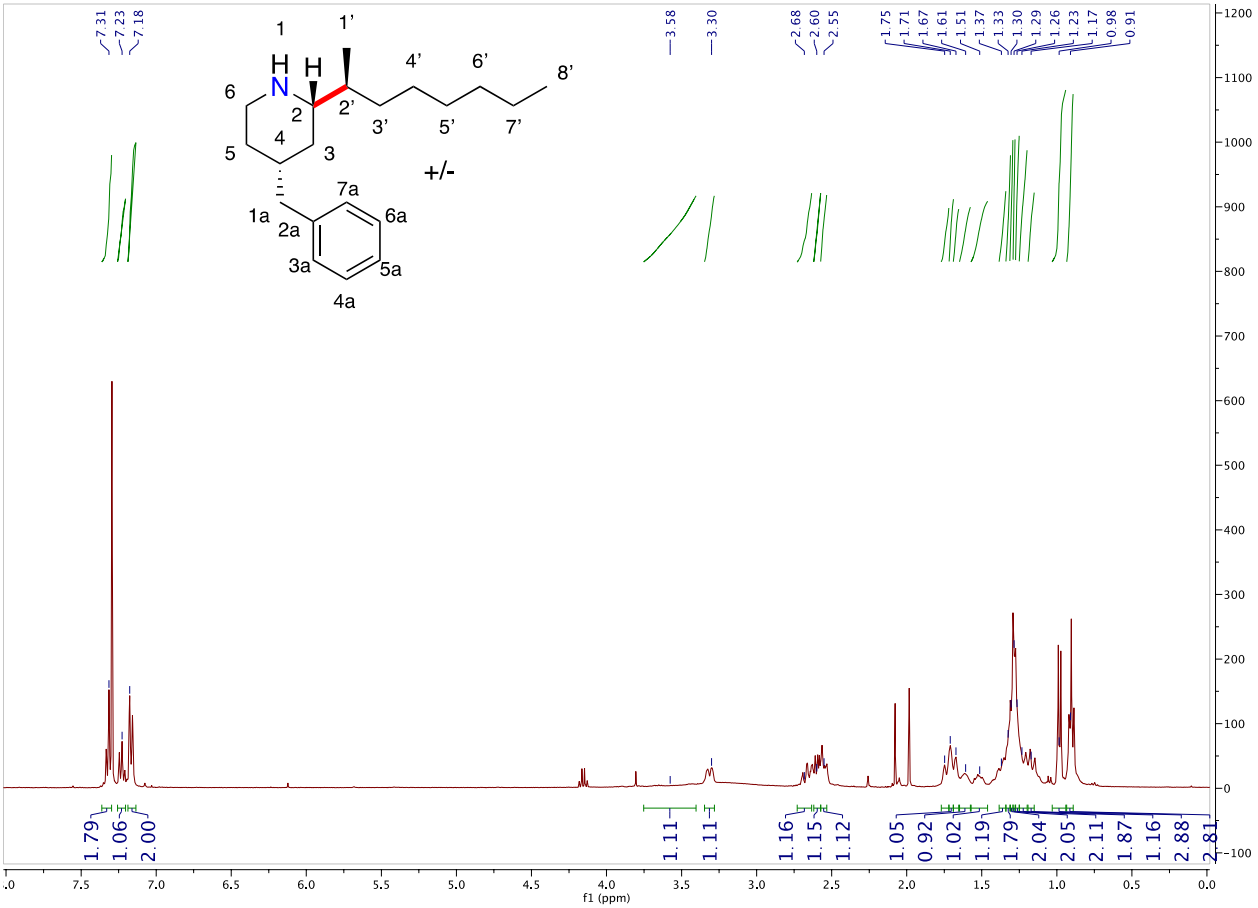


Figure S55: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 4-benzyl-2-(octan-2-yl)piperidine.

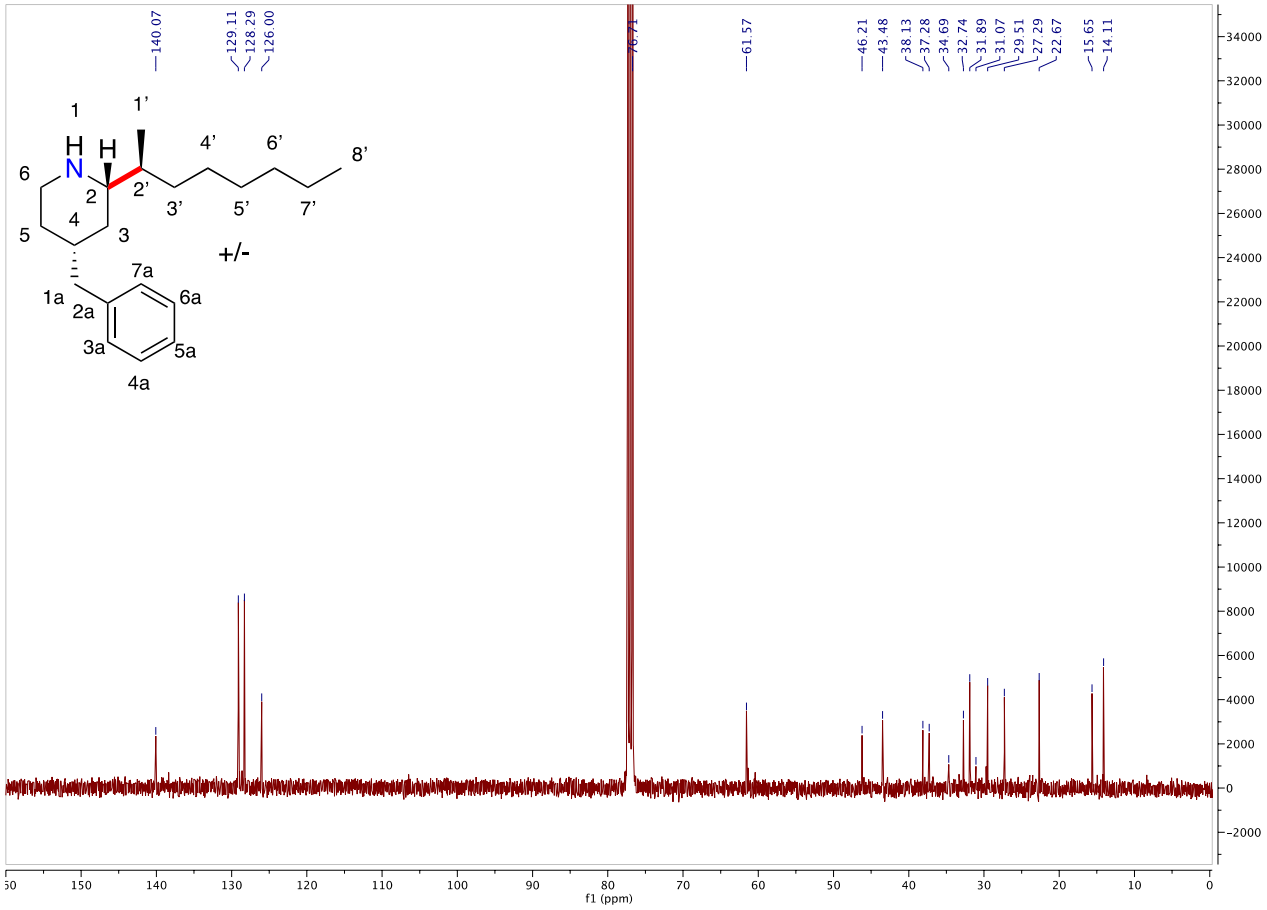


Figure S56: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 4-benzyl-2-(octan-2-yl)piperidine.

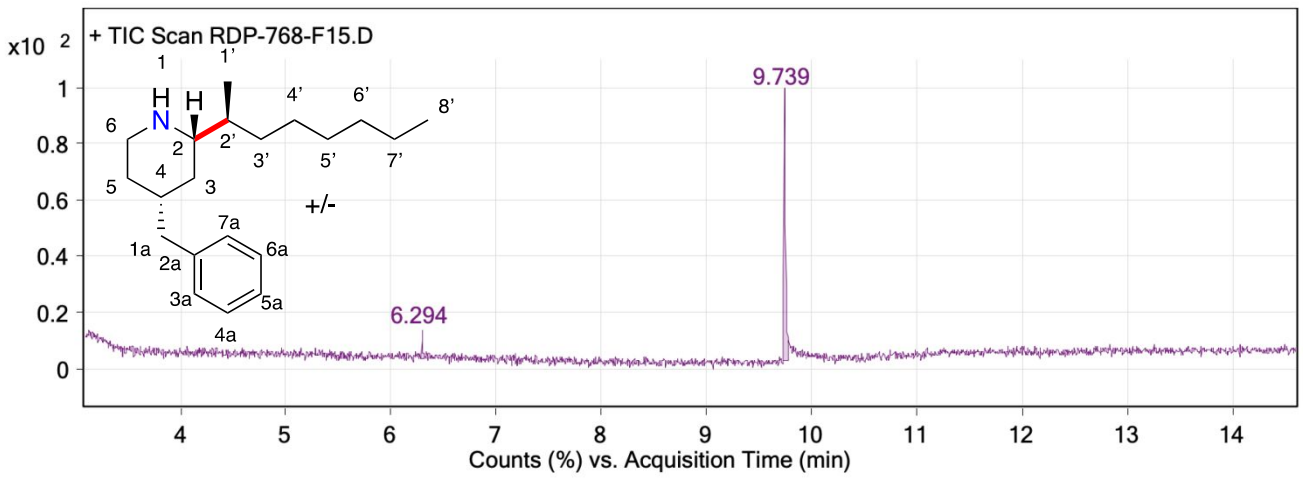


Figure S57: GC-MS report of 4-benzyl-2-(octan-2-yl)piperidine.

Synthesis of 2-(octan-2-yl)-4-phenylpiperidine (9): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, 4-phenylpiperidine (307 mg, 1.0 mmol), 1-

octene (250.2 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 99 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.31 (m, 2H, 3a and 5a), 7.24 (m 2H, 2a and 6a), 7.20 (m, 1H, 4a), 3.26 (m 1H, ½ of 6), 2.79 (m, 1H, ½ of 6), 2.61 (m, 1H, 4), 2.53 (m, 1H, 2), 1.90 (broad s, 1H, NH), 1.83 (m, 1H, ½ of 3), 1.80 (m, 1H, ½ of 5), 1.64 (m, 1H, ½ of 5), 1.49 (m, 1H, ½ of 4'), 1.44 (m 1H, 2'), 1.39 (m, 1H, ½ of 3), 1.32 (m, 1H, ½ of 3'), 1.28 (m, 2H, 5'/6'/7'), 1.26 (m, 2H, 5'/6'/7'), 1.24 (m, 2H, 5'/6'/7'), 1.21 (m, 1H, ½ of 3'), 1.14 (m, 1H, ½ of 4'), 0.92 (d, J = 0.93, 3H, 1'), 0.88 (overlapping t, 3H, 8') ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 146.99, 128.56, 127.00, 126.23, 61.89, 47.51, 43.56, 38.46, 37.68, 34.12, 33.23, 32.03, 29.76, 27.62, 22.80, 15.67, 14.23 ppm. HRMS (ESI): *m/z* calcd for $C_{19}H_{31}N$ [M^+]: 273.2456 Found: 273.2464.

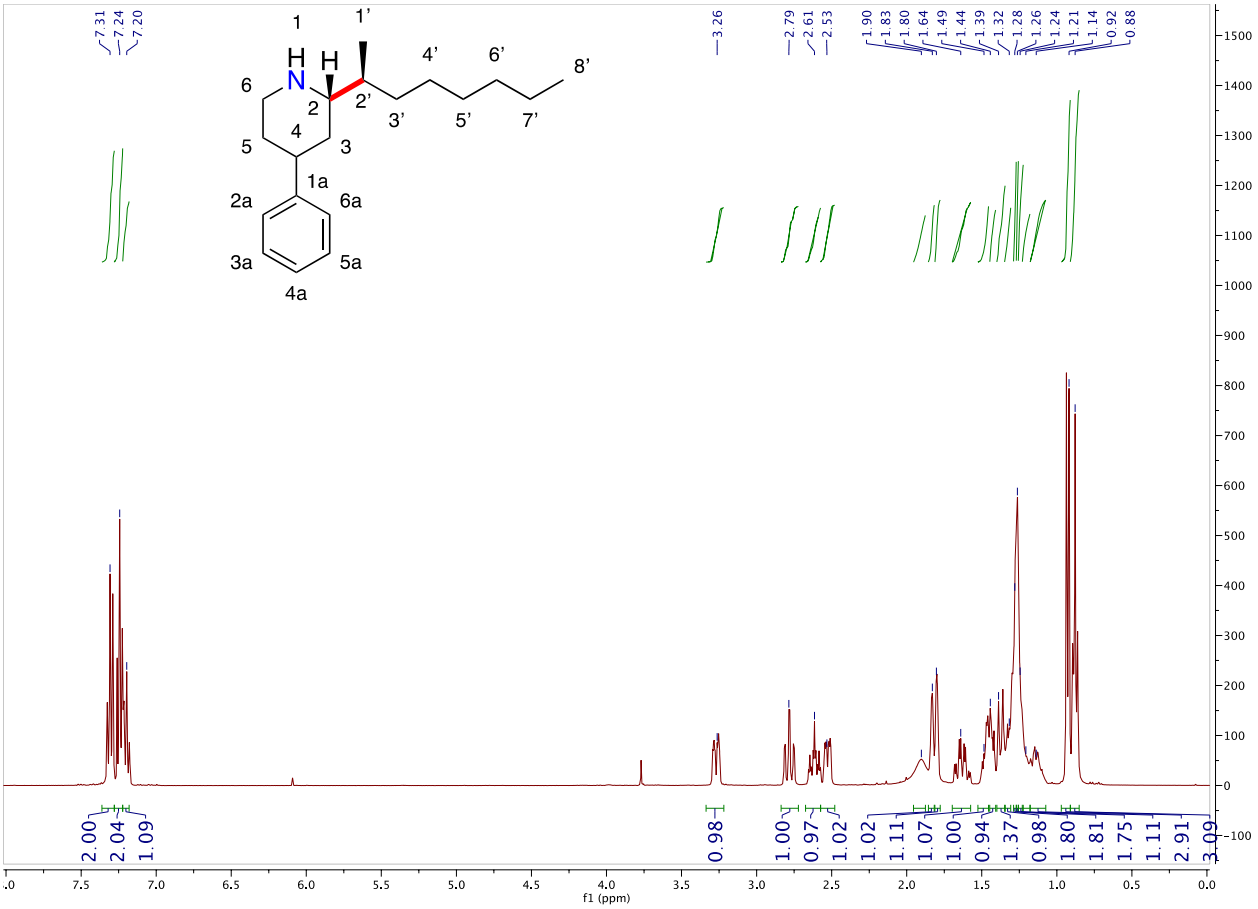


Figure S58: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(octan-2-yl)-4-phenylpiperidine.

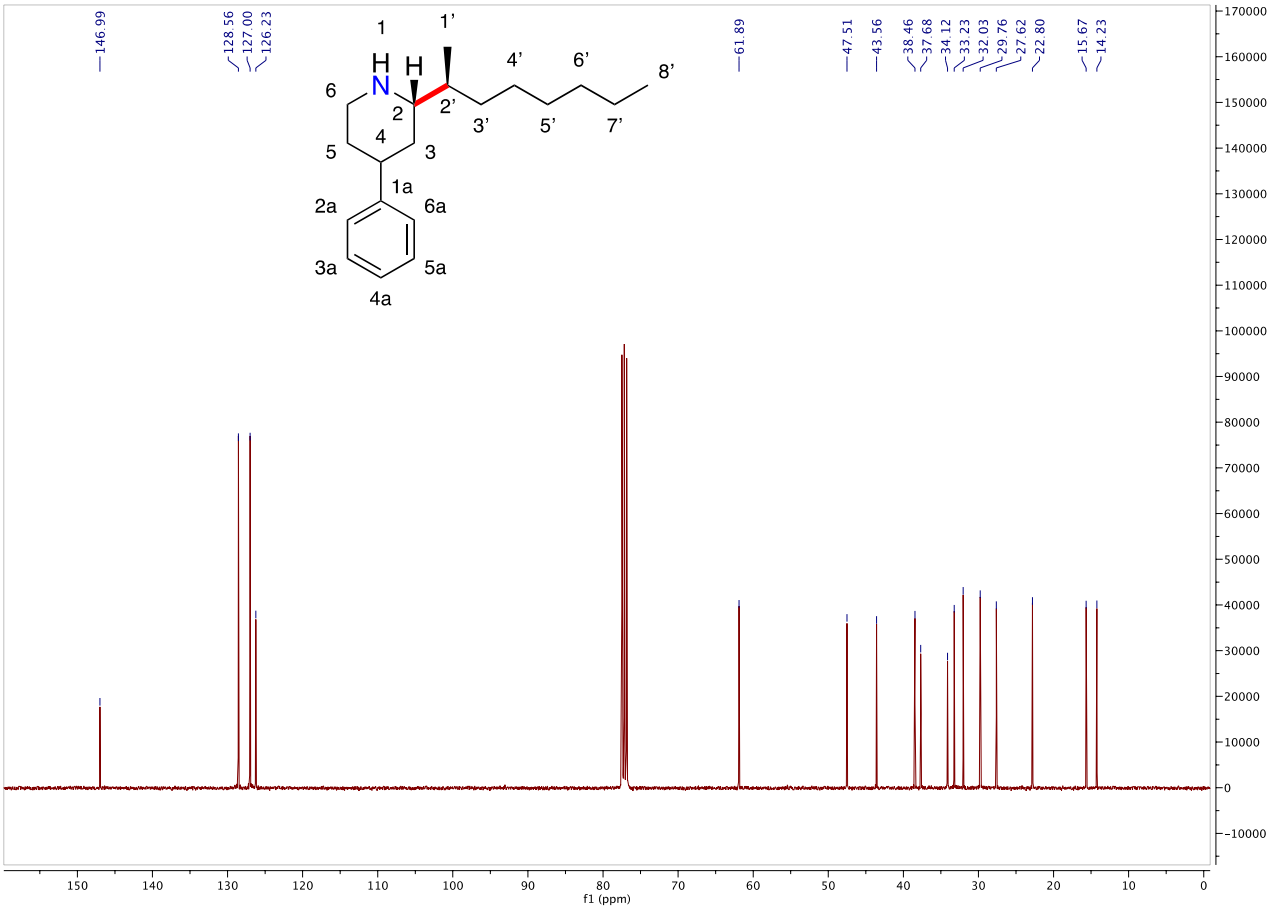


Figure S59: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(octan-2-yl)-4-phenylpiperidine.

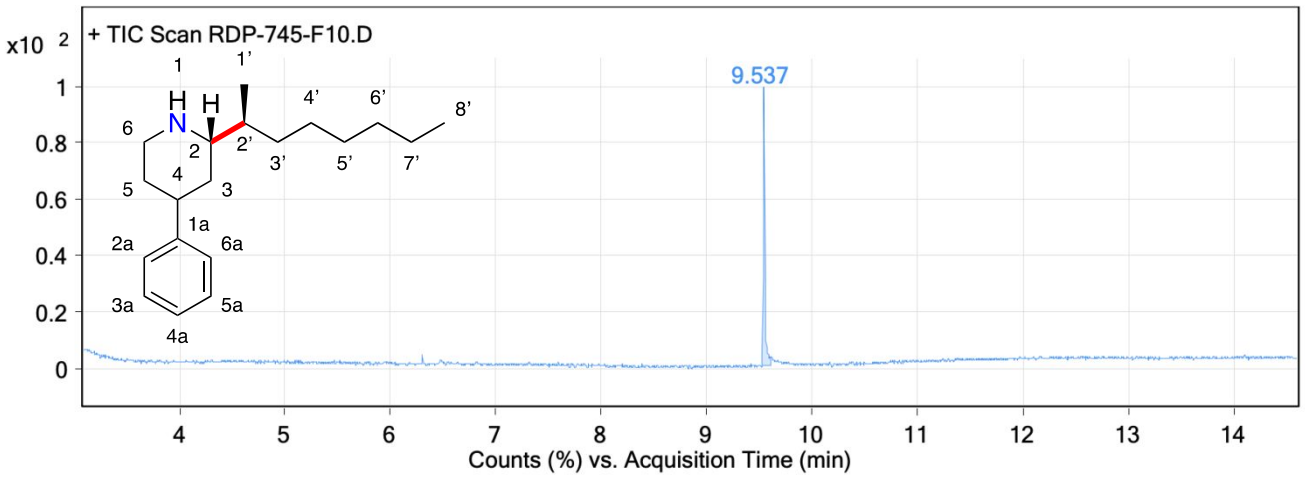
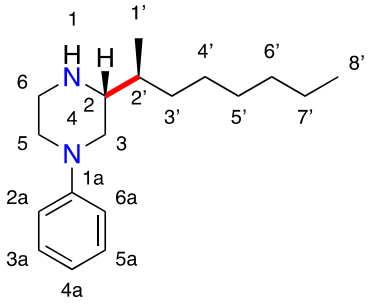


Figure S60: GC-MS report of 2-(octan-2-yl)-4-phenylpiperidine.



Synthesis of 3-(octan-2-yl)-1-phenylpiperazine (10): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 ligand **L4**, 4-phenylpiperazine (162.24 mg, 1.0 mmol), 1-octene (112.22 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 48 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine). The chemical shifts for the title compound match those reported in the literature.[8]

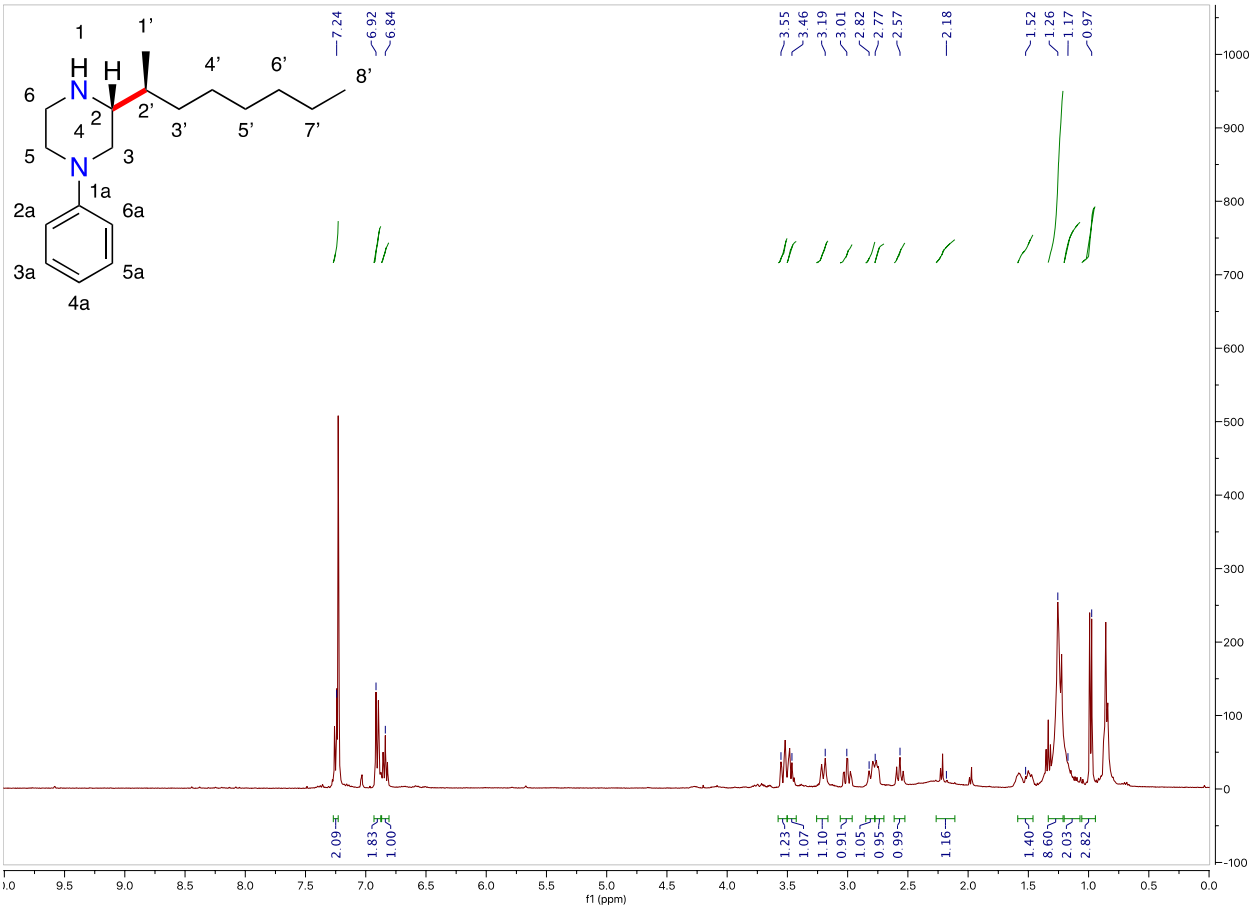


Figure S61: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-(octan-2-yl)-1-phenylpiperazine.

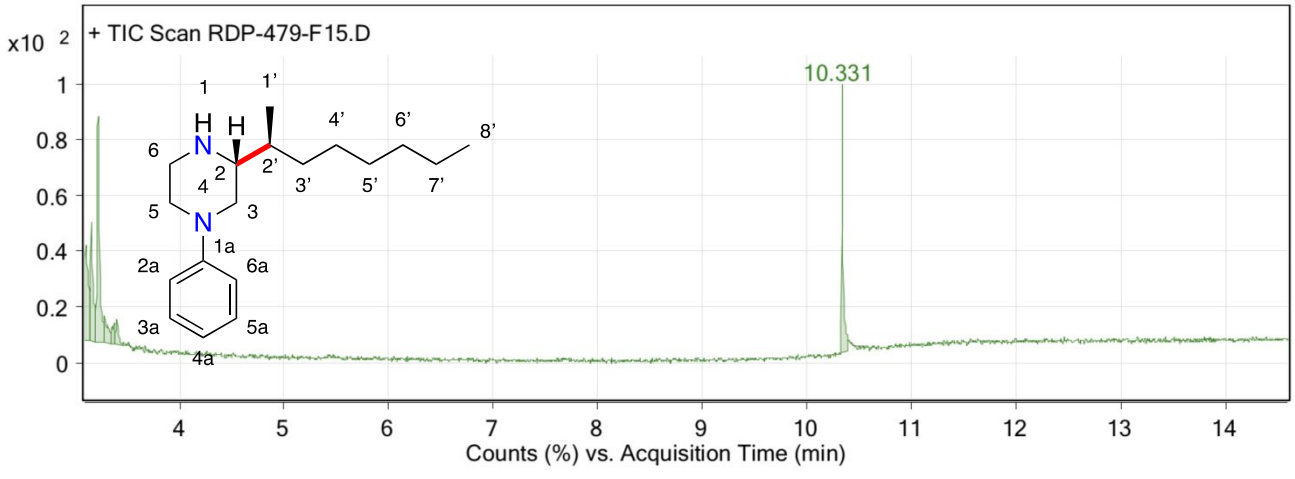
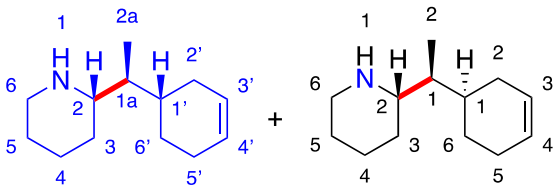


Figure S62: GC-MS report of 3-(octan-2-yl)-1-phenylpiperazine.

S7. Synthesis and Characterization of Alkene Scope Products



Synthesis of 2-(1-(cyclohex-3-en-1-yl)ethyl)piperidine (11): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), vinylcyclohexene (108.18 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 99 % (2.7:1 major-minor) by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine) yields a mixture of diastereomers (2.7:1) that could only be separated in small amounts, see below.: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 5.63 (m, 2H, 3’ and 4’ and 3’ and 4’), 3.09 (m, 1H, ½ of 6 and 6), 2.57 (m, 1H, ½ of 6 and 6), 2.47 (m, 1H, 2 and 2), 2.03 (m, 1.08H, 5’), 1.96 (m, 1H, ½ of 5’), 1.89 (m, 1H, ½ of 2’ and 2’), 1.81 (m, 0.95H, ½ of 5’), 1.75 (m, 1H, ½ of 4 and 4), 1.69 (m, 1H, ½ of 2’ and 2’), 1.63 (m, 1H, ½ of 1’ and 1’), 1.60 (m, 1H, ½ of 6’ and 6’), 1.57 (m, 1H, ½ of 3 and 3), 1.54 (m, 1H, ½ of 5 and 5), 1.39 (m, 1H, ½ of 4 and 4), 1.34 (m, 1H, ½ of 6’ and 6’), 1.28 (m, 1H, ½ of 5 and 5),

1.23 (m, 1H, 1a and 1a), 1.17 (m, 1H, ½ of 3 and 3), 0.86 (d, J = 0.95, 3H, 2a), 0.84 (d, 0.57H, 2a), ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 127.15 (major and minor), 127.05 (major and minor), 126. 91 (major and minor), 58.98 (major and minor), 47.70 (major), 47.67 (minor), 43.17 (major), 42.71 (minor), 35.26 (minor), 35.11 (minor), 31.19 (minor), 31.12 (major), 30.73 (major and minor), 27.81 (major), 27.69 (minor), 26.80 (minor), 26.76 (major), 26.11 (major), 25.96 (minor), 25.46 (minor), 25.39 (major), 11.61 (minor), 11.19 (major) ppm. HRMS (ESI): *m/z* calcd for major: $C_{13}H_{23}N$ [M^+]: 193.1830 Found: 193.1834 and minor: $C_{13}H_{23}N$ [$M+H^+$]: 193.1830 Found:193.1832.

Note: With these diastereomers, we obtained enough sample for each pure diastereomer to get a clean GC-MS sample for each. However, NMR peaks are reported for the mixture.

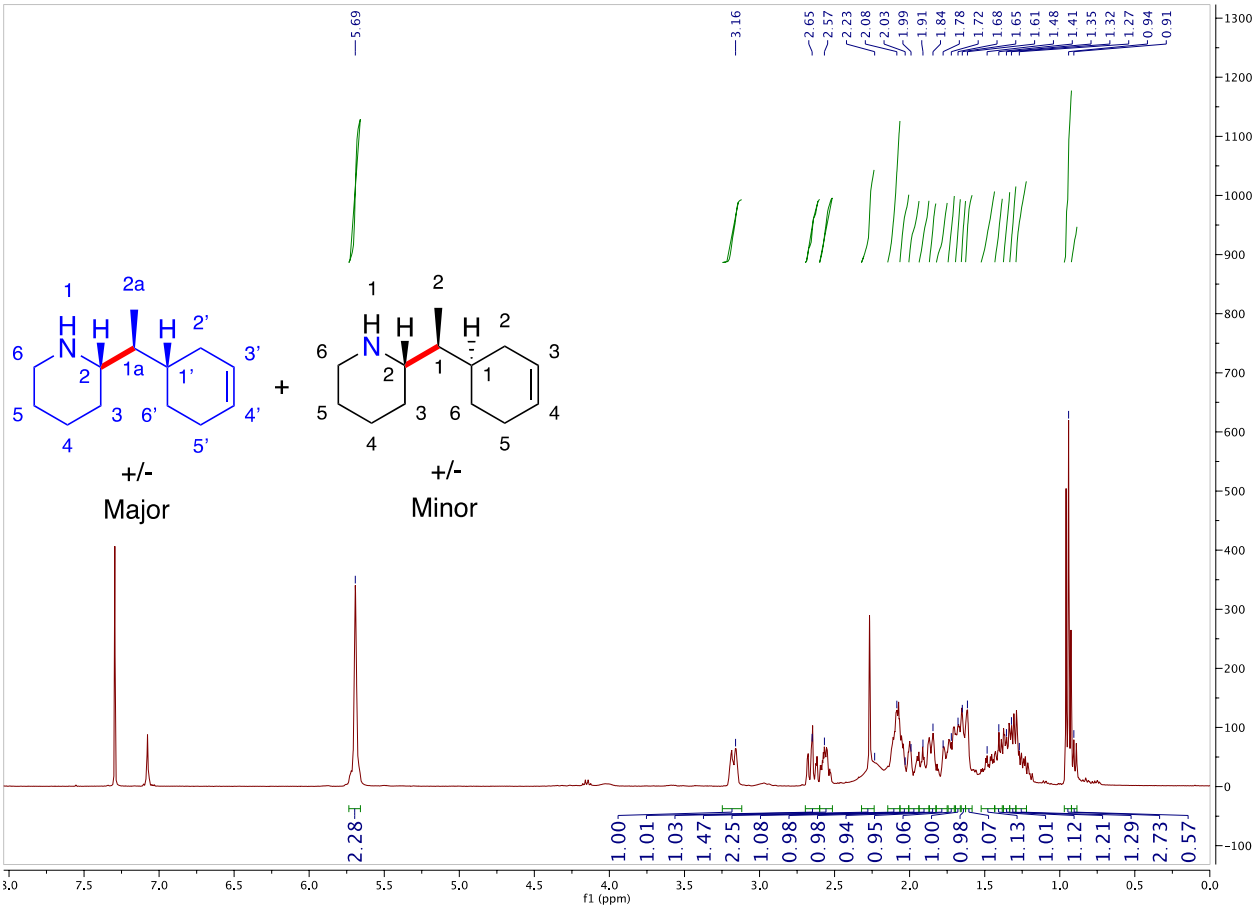


Figure S63: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(cyclohex-3-en-1-yl)ethyl)piperidine.

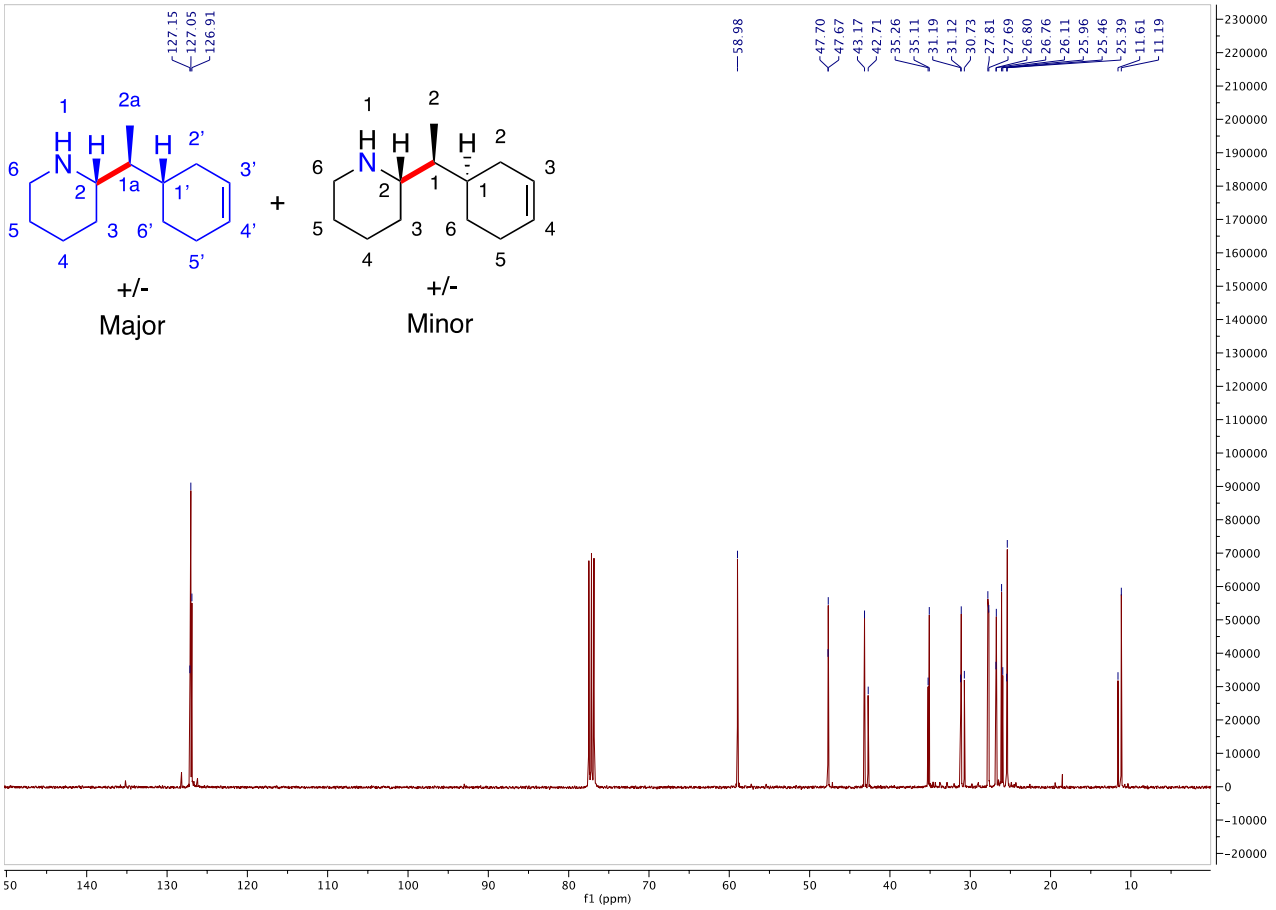


Figure S64: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of both diastereomers of 2-(1-(cyclohex-3-en-1-yl)ethyl)piperidine.

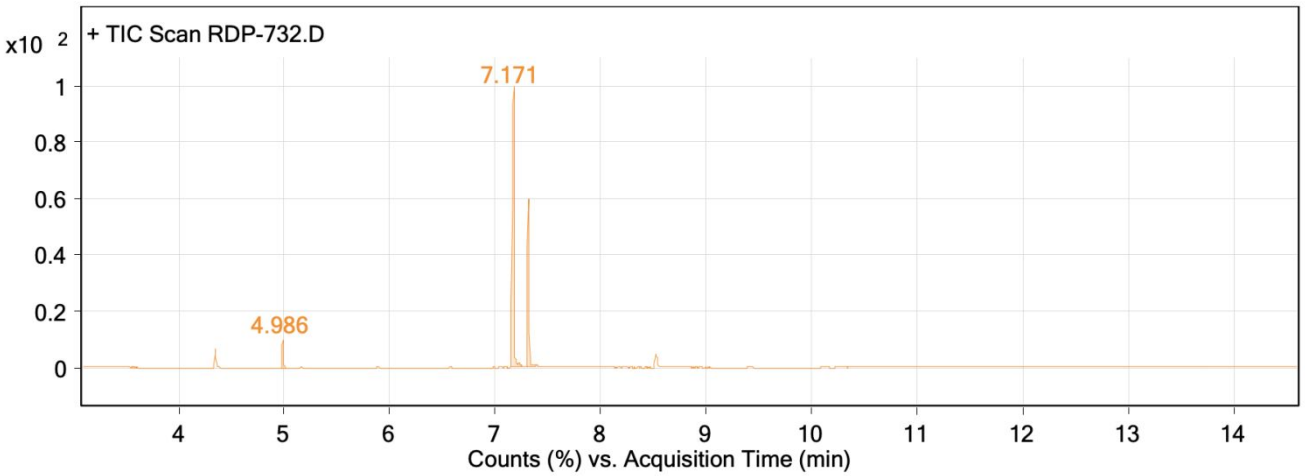


Figure S65: GC-MS for crude reaction mixture between piperidine and vinylcyclohexene.

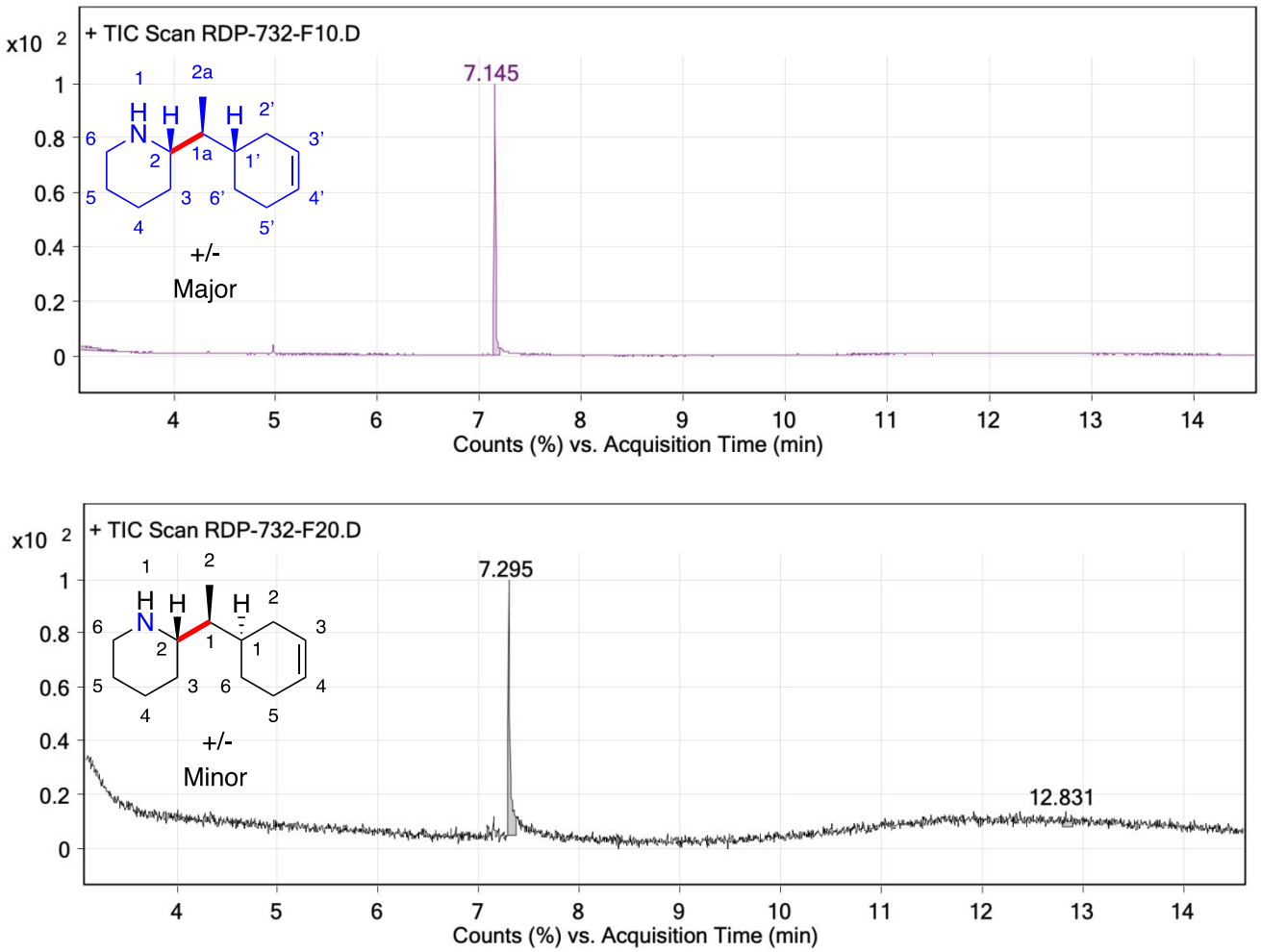
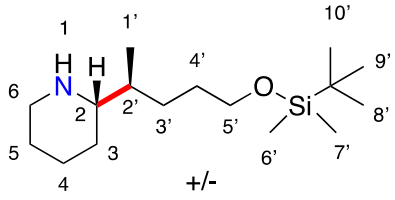


Figure S66: GC-MS reports for the two diastereomers of 2-(1-(cyclohex-3-en-1-yl)ethyl)piperidine.



Synthesis of 2-(5-((tert-butyldimethylsilyl)oxy)pentan-2-yl)piperidine (12): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), tert-butyldimethyl(pent-4-en-1-yloxy)silane (200.4 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 93 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 3.57 (m, 2H, 5'), 3.09 (m, 1H, ½ of 6), 2.59 (m, 1H, ½ of 6), 2.33 (m, 1H, 2), 2.17 (broad s, 1H, NH), 1.78 (m, 1H, ½ of 4), 1.60 (m, 1H, ½ of 3'), 1.57 (m, 1H, ½ of 4'), 1.55 (m, 1H, ½ of 5), 1.47 (m, 1H, ½ of 4'), 1.42 (m, 1H, ½ of 3), 1.38 (m, 1H, 2'), 1.34 (m 1H, ½ of 5), 1.29 (m, 1H, ½ of 4), 1.17 (m, 1H, ½ of 3'), 1.12 (m, 1H, ½ of 3), 0.89 (overlapping d, 3H, 1'), 0.87 (s, 9H, 8' and 9' and 10'), 0.03 (s, 6H, 6' and 7') ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 63.65, 61.64, 47.68, 38.21, 30.83, 29.77, 29.24, 26.70, 26.10, 25.27, 18.47, 15.62, -5.13 ppm. HRMS (ESI): *m/z* calcd for $C_{16}H_{35}NOSi$ [M+H$^+$]: 285.2488 Found: 285.2492.

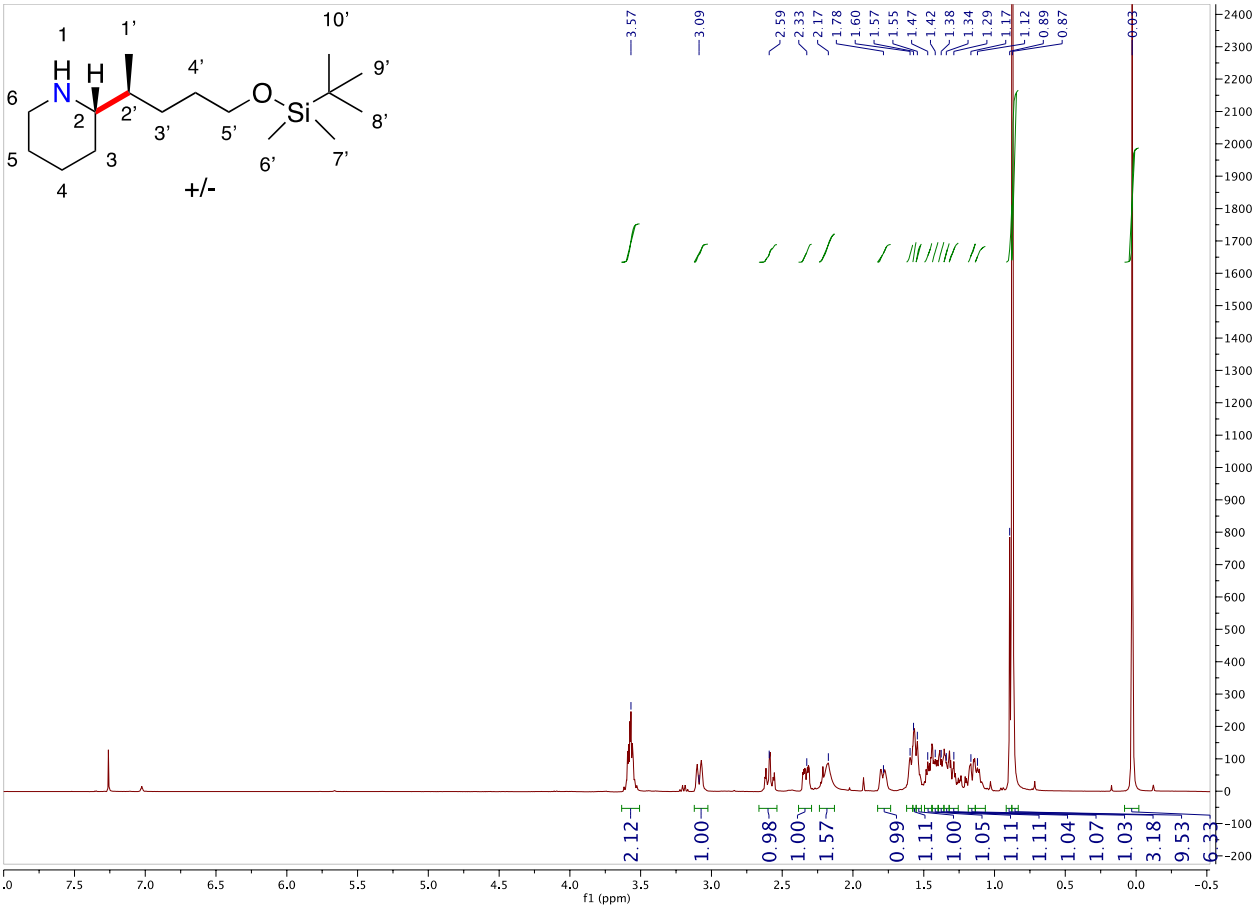


Figure S67: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(5-((tert-butyldimethylsilyl)oxy)pentan-2-yl)piperidine.

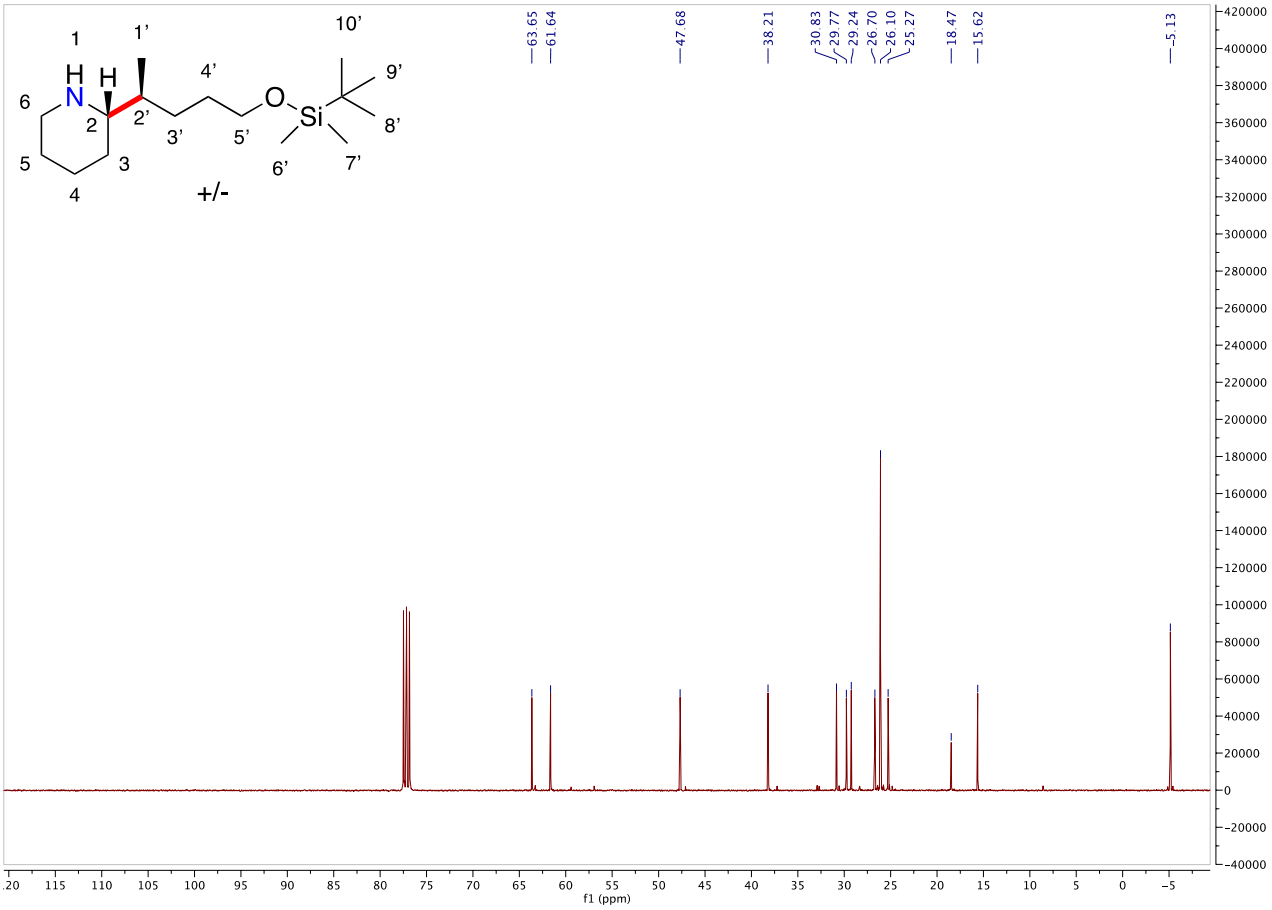


Figure S68: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(5-((tert-butyldimethylsilyl)oxy)pentan-2-yl)piperidine.

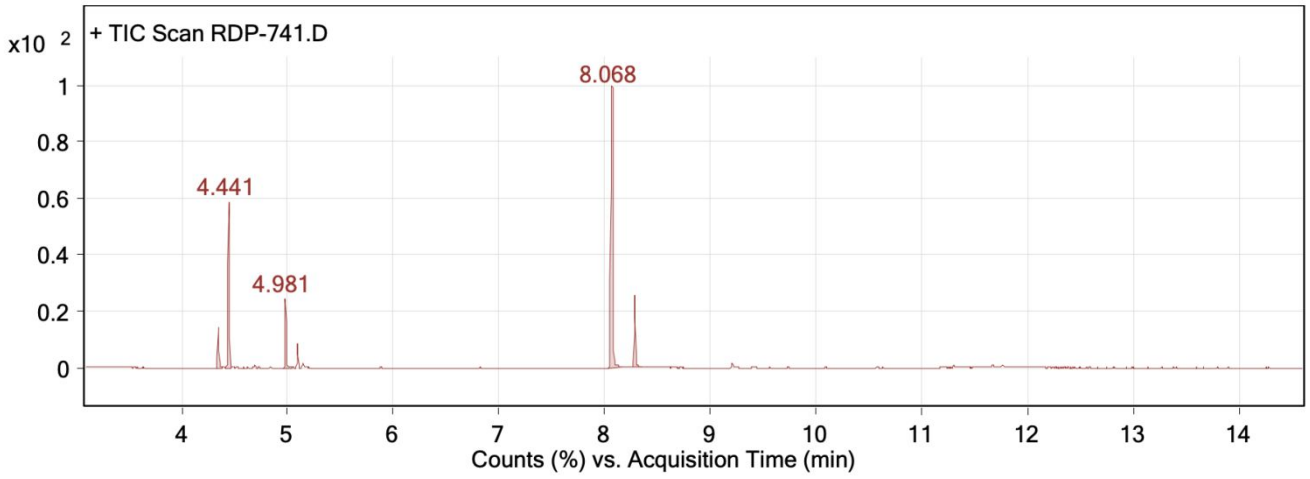


Figure S69: GC-MS for crude reaction mixture between piperidine and tert-butyldimethyl(pent-4-en-1-yloxy)silane.

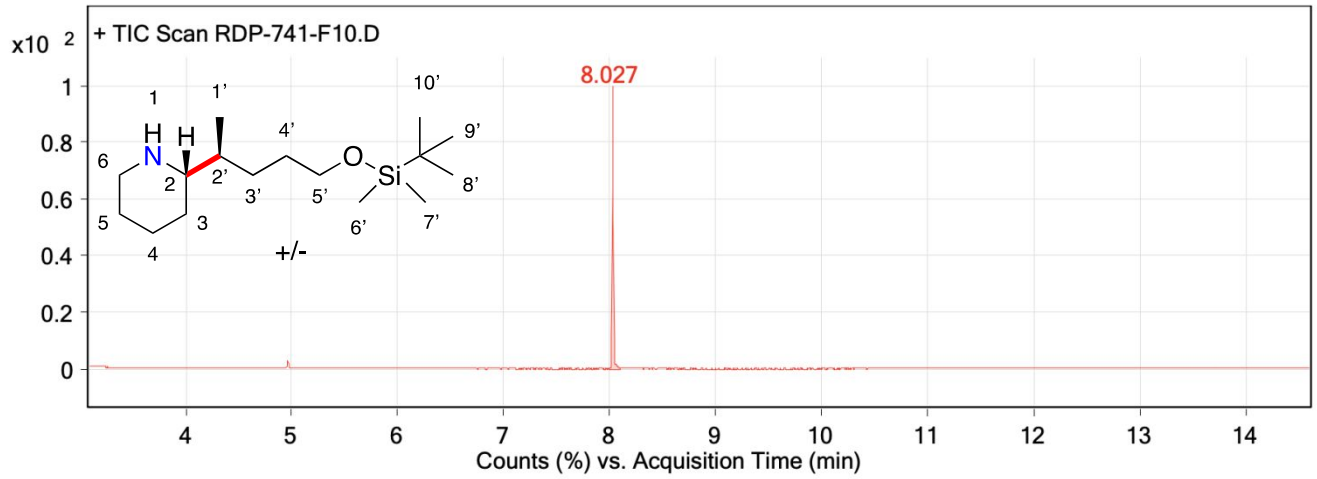
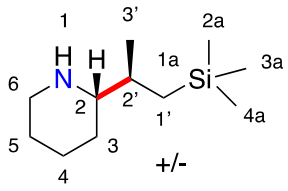


Figure S70: GC-MS report of 2-(5-((tert-butyldimethylsilyl)oxy)pentan-2-yl)piperidine.



Synthesis of 2-(1-(trimethylsilyl)propan-2-yl)piperidine (13): Prepared following the general procedure for predominantly branched product formation: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), allyltrimethylsilane (114.26 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 99 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 3.12 (m 1H, ½ of 6), 2.60 (m, 1H, ½ of 6), 2.25 (m, 1H, 2), 1.95 (broad s, 1H, NH), 1.81 (m, 1H, ½ of 4), 1.60 (m, 1H, ½ of 3), 1.57 (m, 1H, ½ of 2), 1.54 (m, 1H, 2'), 1.40 (m, 1H, ½ of 5), 1.29 (m, 1H, ½ of 4), 1.15 (m, 1H, ½ of 3), 0.90 (d, J = 0.90, 3H, 3'), 0.71 (m, 1H, ½ of 1'), 0.36 (m, 1H, ½ of 1'), 0.00, (s, 9H, 2a and 3a and 4a) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 64.74, 48.32, 35.46, 29.65, 27.25, 25.84, 21.22, 19.10, 0.00 ppm. HRMS (ESI): *m/z* calcd for $C_{11}H_{26}N_1Si_1$ [M+H$^+$]: 200.1835 Found: 200.1835.

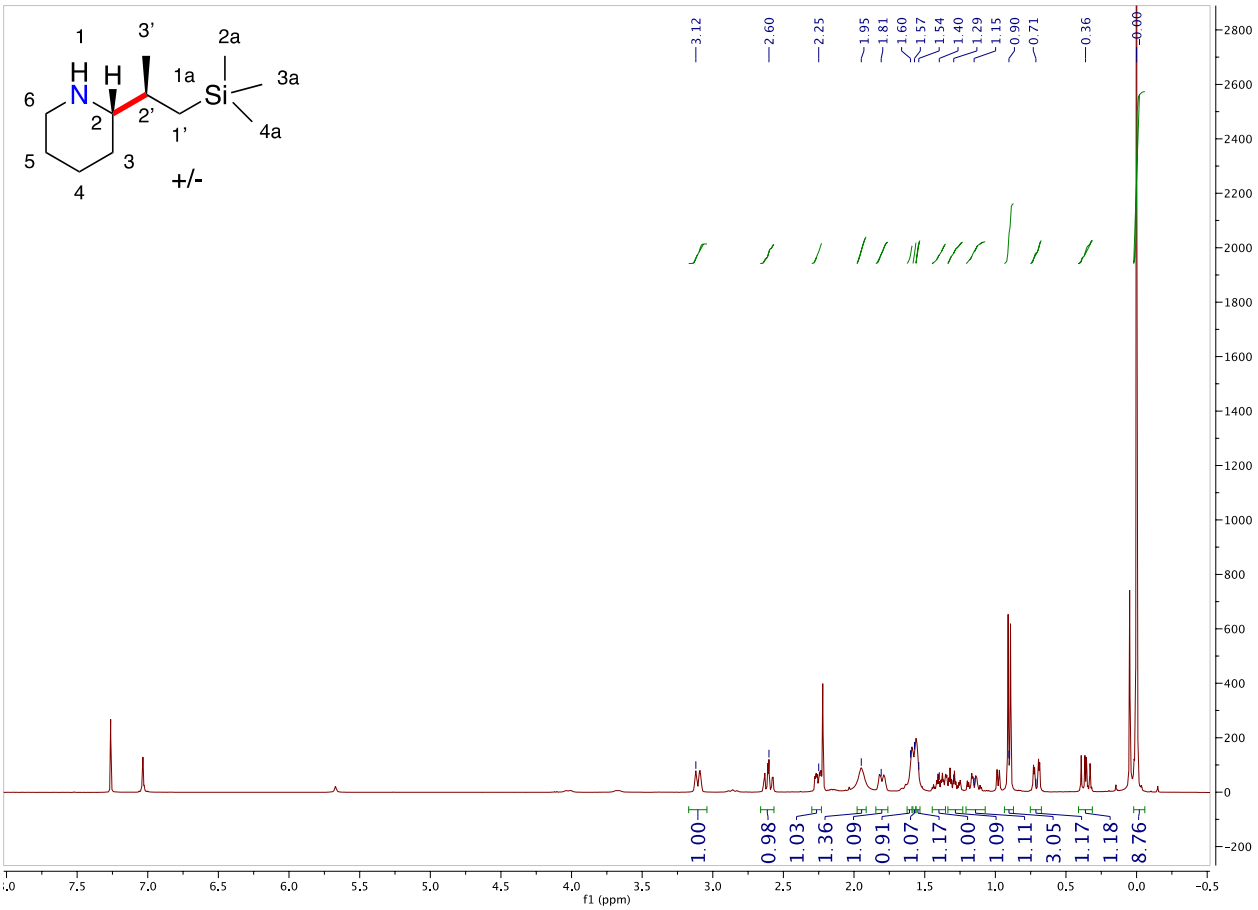


Figure S71: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(trimethylsilyl)propan-2-yl)piperidine.

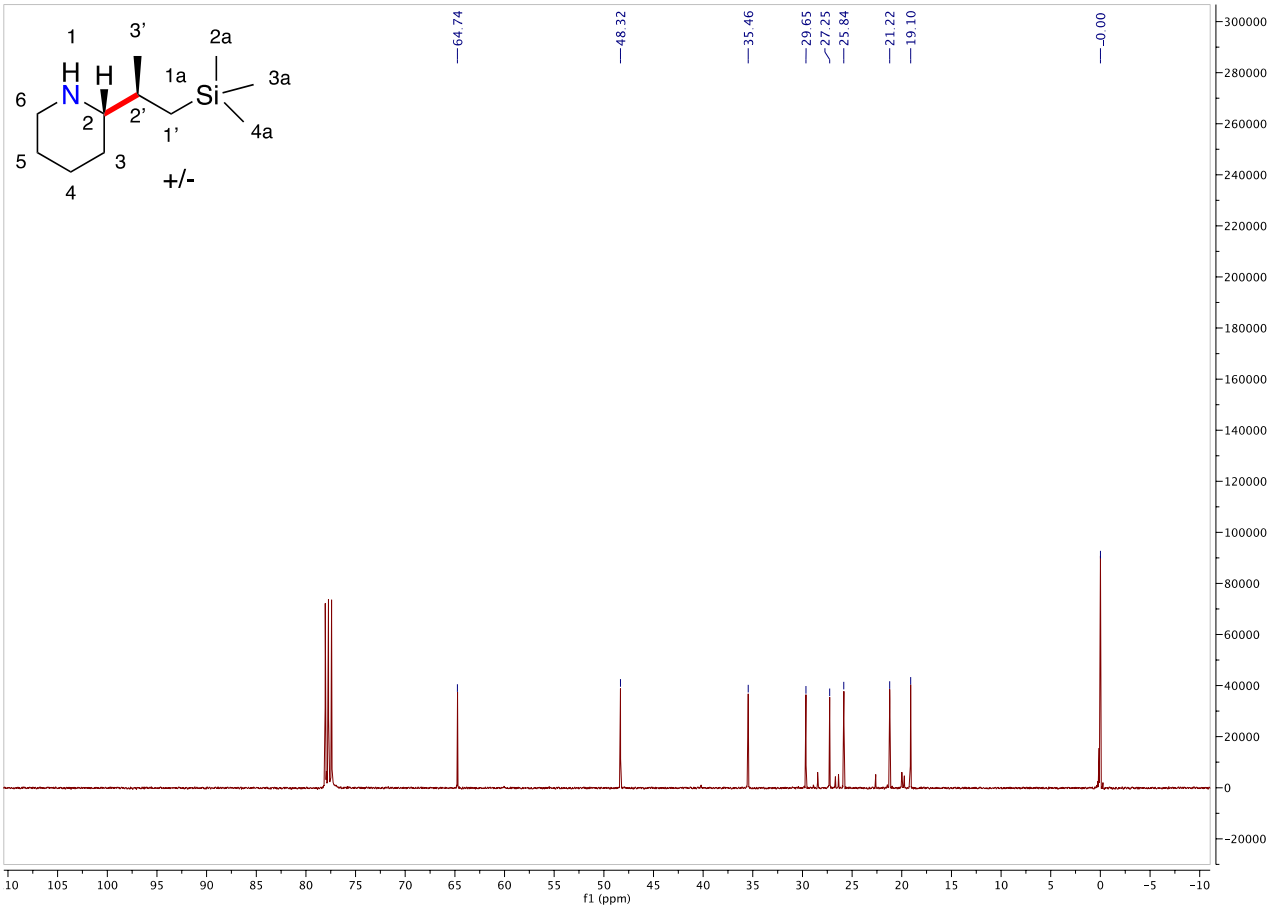


Figure S72: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(1-(trimethylsilyl)propan-2-yl)piperidine.

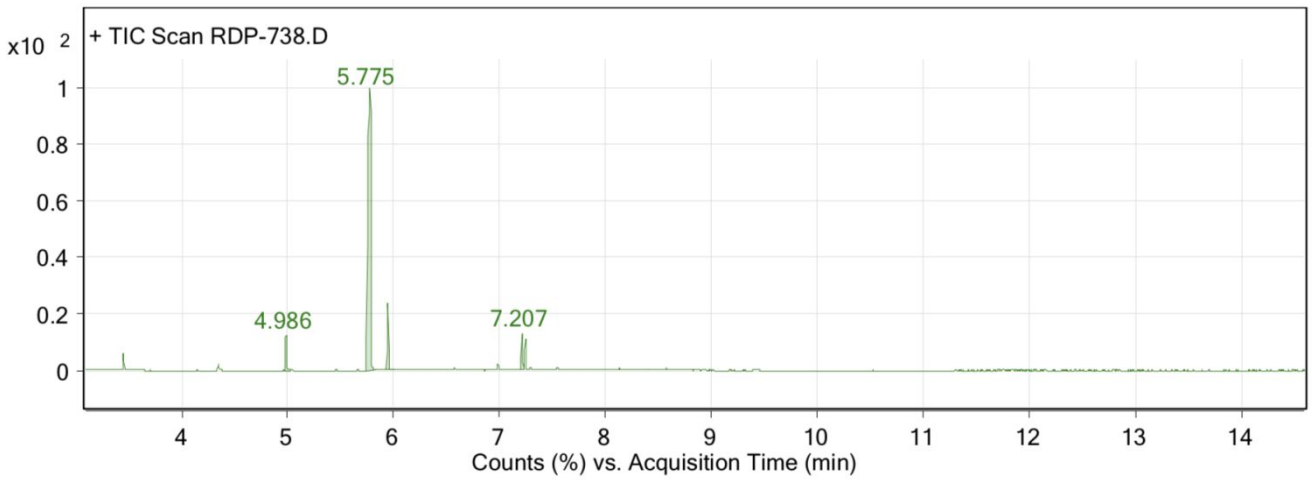


Figure S73: GC-MS for the crude reaction between piperidine and allyltrimethylsilane.

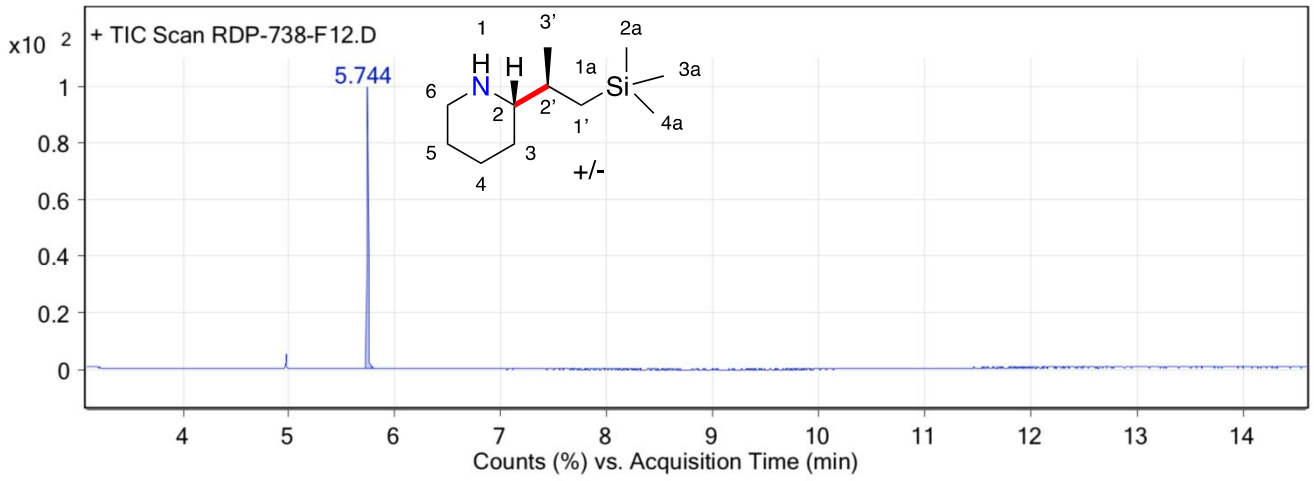
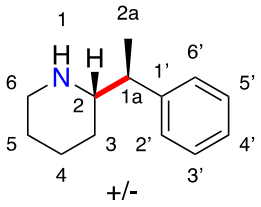


Figure S74: GC-MS report of 2-(1-(trimethylsilyl)propan-2-yl)piperidine.

NOTE: For all reactions that generate significant amounts of both regioisomers, both products could be isolated from a single reaction as indicated in main text. Yields indicated represents yields by quantitative NMR studies and are yields for a single regioisomer.



Synthesis of 2-(1-phenylethyl)piperidine (14 and 15): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), styrene (104.15 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 60 % for 2-(1-phenylethyl)piperidine and 40 % for 2-phenethylpiperidine by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regiosiomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.22 (m, 2H, 3' and 5'), 7.16 (m, 2H, 2' and 6'), 7.12 (m, 1H, 4'), 3.07 (m, 1H, ½ of 6), 2.63 (m, 1H, 1a), 2.52 (m, 1H, ½ of 6), 2.52 (m, 1H, 2), 1.92 (broad s, 1H, NH), 1.68 (m, 1H, ½ of 4), 1.52 (m, 1H, ½ of 5), 1.39 (m, 1H, ½ of 3), 1.30 (m, 1H, ½ of 5), 1.25 (d, J = 1.26, 3H, 2a), 1.19 (m, 1H, ½ of 4), 1.00 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 145.12, 128.43, 127.98, 126.34, 62.61, 47.53, 45.72, 30.85, 26.43, 25.01, 17.42 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{20}N$ [M+H$^+$]: 190.1596 Found: 190.1594.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.23 (m, 2H, 3' and 5'), 7.16 (m, 2H, 2' and 6'), 7.14 (m, 1H, 4'), 3.07 (m, 1H, ½ of 6), 2.66 (m, 2H, 2a), 2.59 (m, 1H, ½ of 6), 2.50 (m, 1H, 2), 2.19 (broad s, 1H, NH), 1.76 (m, 1H, ½ of 4), 1.70 (m, 2H, 1a), 1.64 (m, ½ of 3), 1.55 (m, 1H, ½ of 5), 1.41 (m, 1H, ½ of 5), 1.31 (m, 1H, ½ of 4), 1.14 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 142.37, 128.51, 128.47, 125.90, 56.61, 47.14, 39.04, 32.77, 32.38, 26.48, 24.81 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{20}N$ [M+H$^+$]: 190.1596 Found: 190.1592.

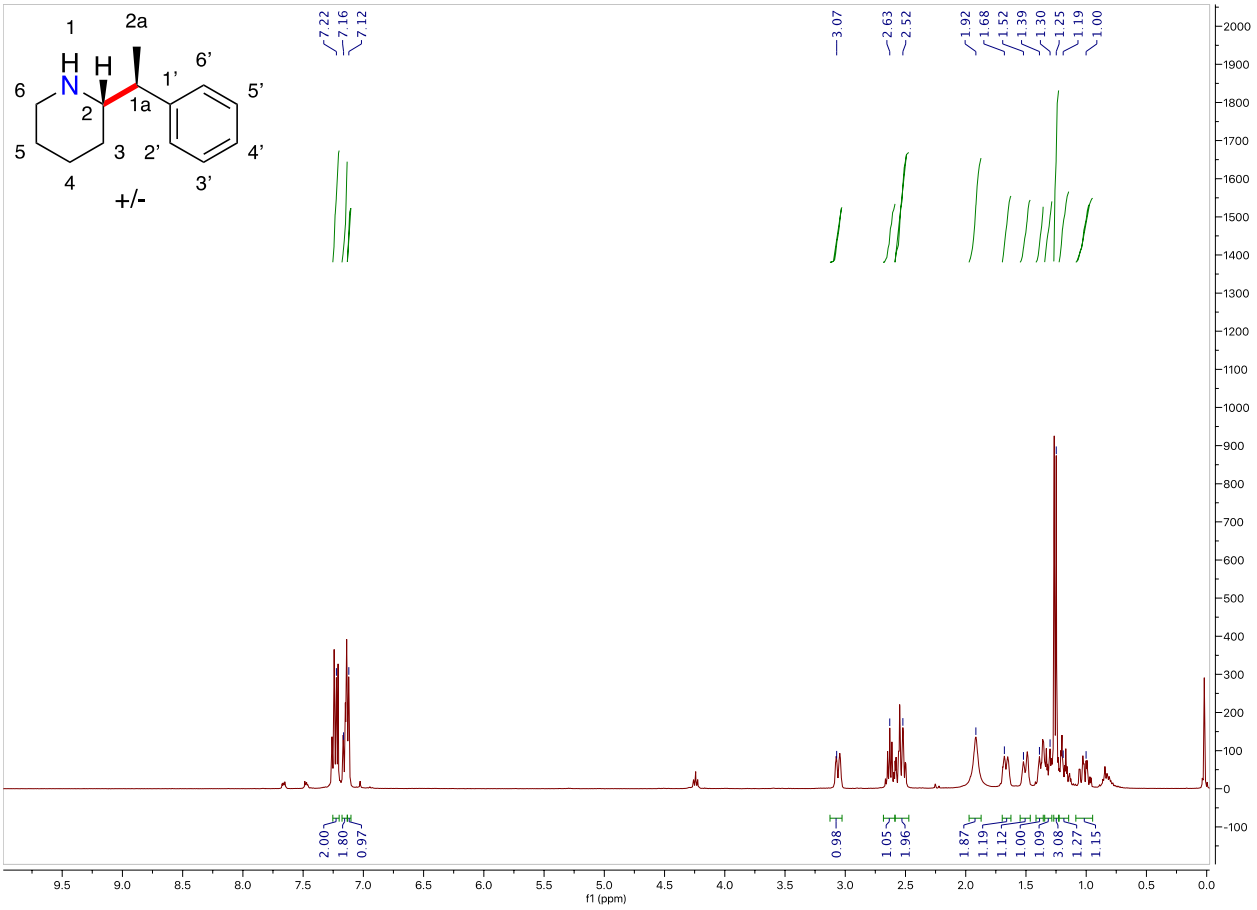


Figure S75: ^{1}H NMR spectrum of 2-(1-phenylethyl)piperidine.

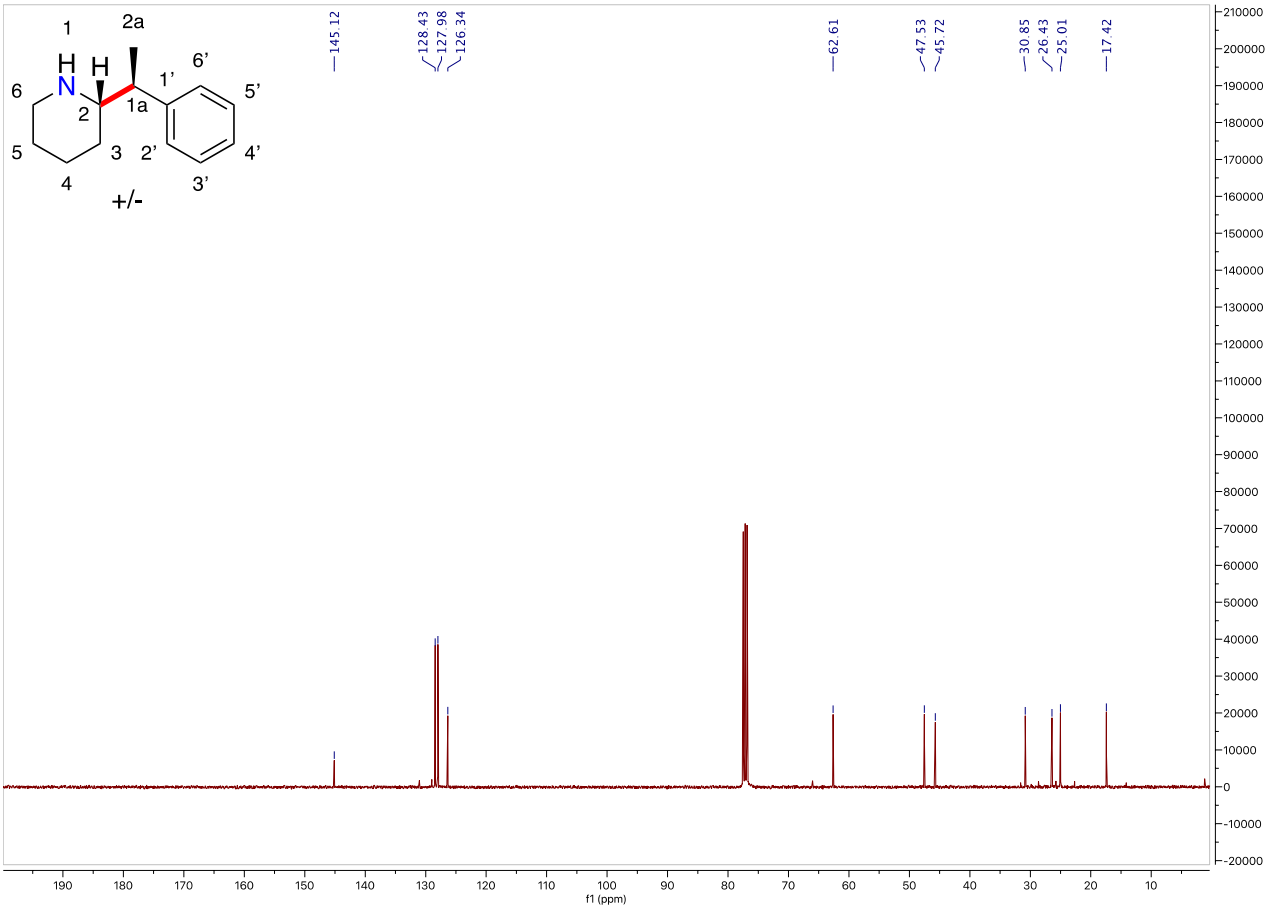


Figure S76: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(1-phenylethyl)piperidine.

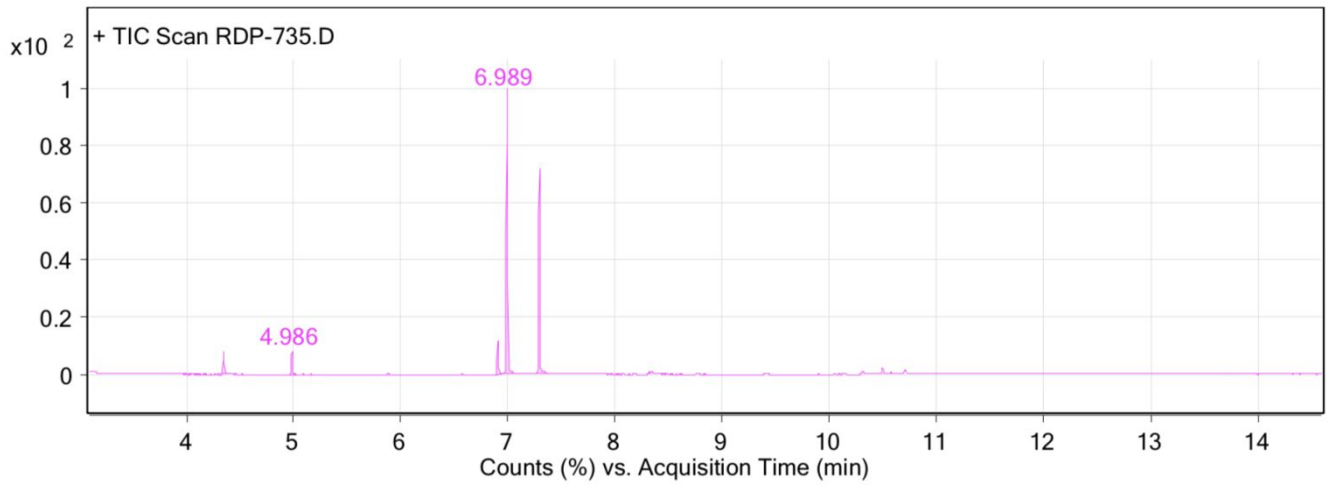


Figure S77: GC-MS for the crude reaction mixture between piperidine and styrene.

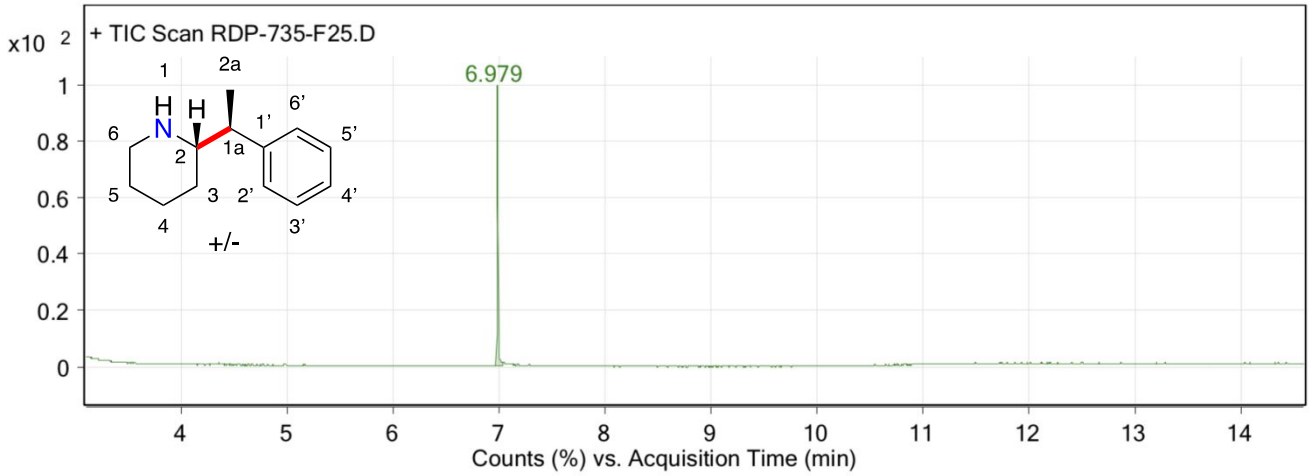


Figure S78: GC-MS report of 2-(1-phenylethyl)piperidine.

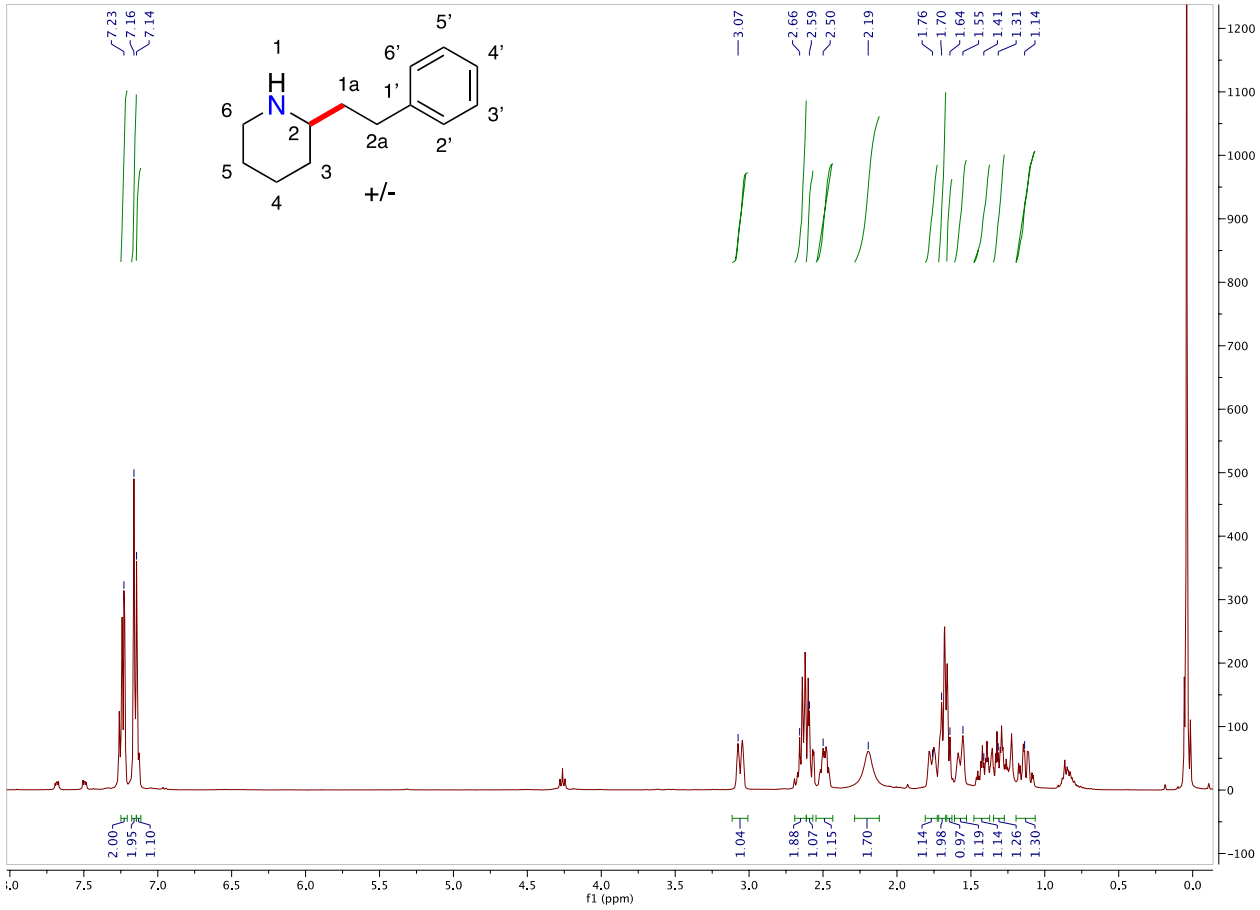


Figure S79: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-phenethylpiperidine.

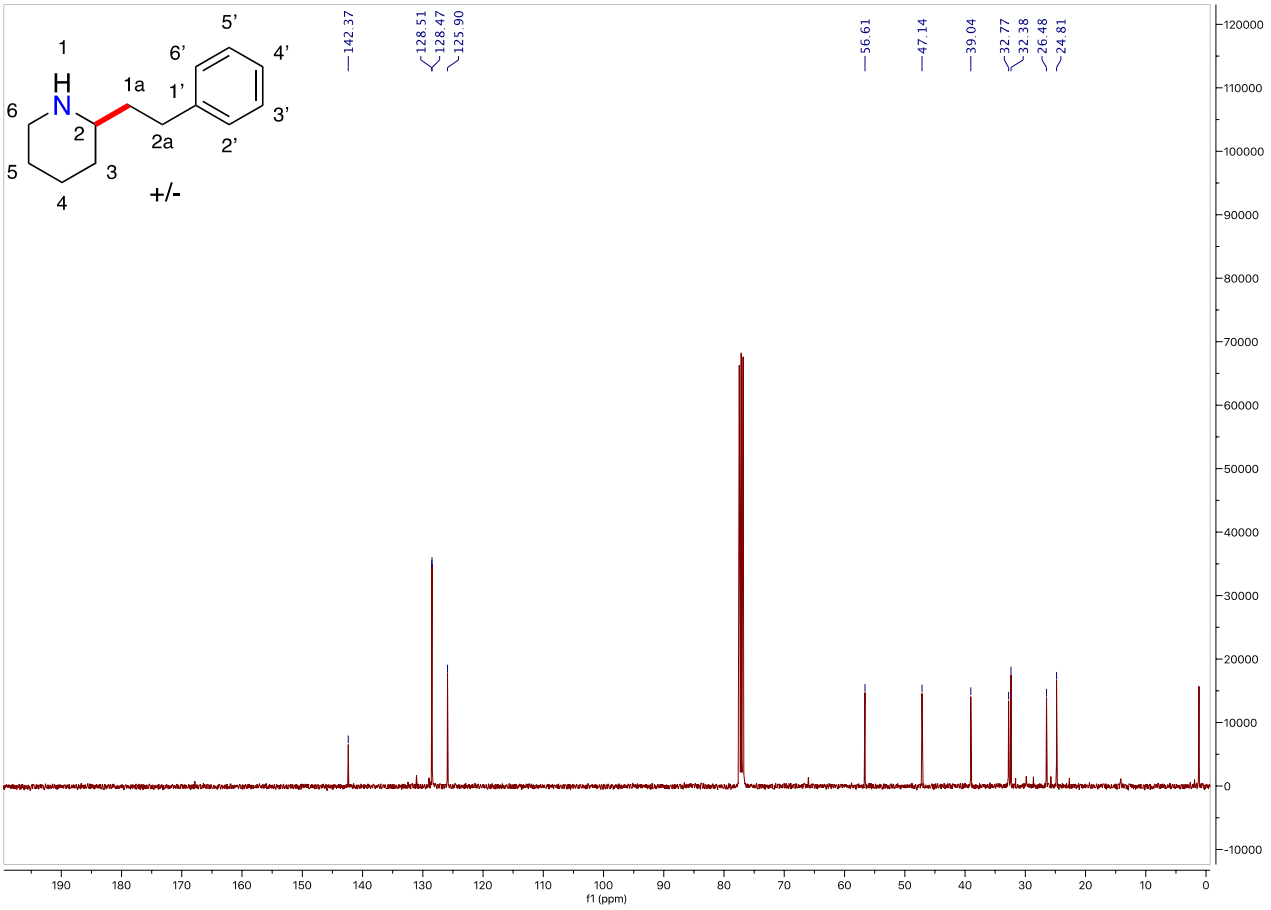


Figure S80: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-phenethylpiperidine.

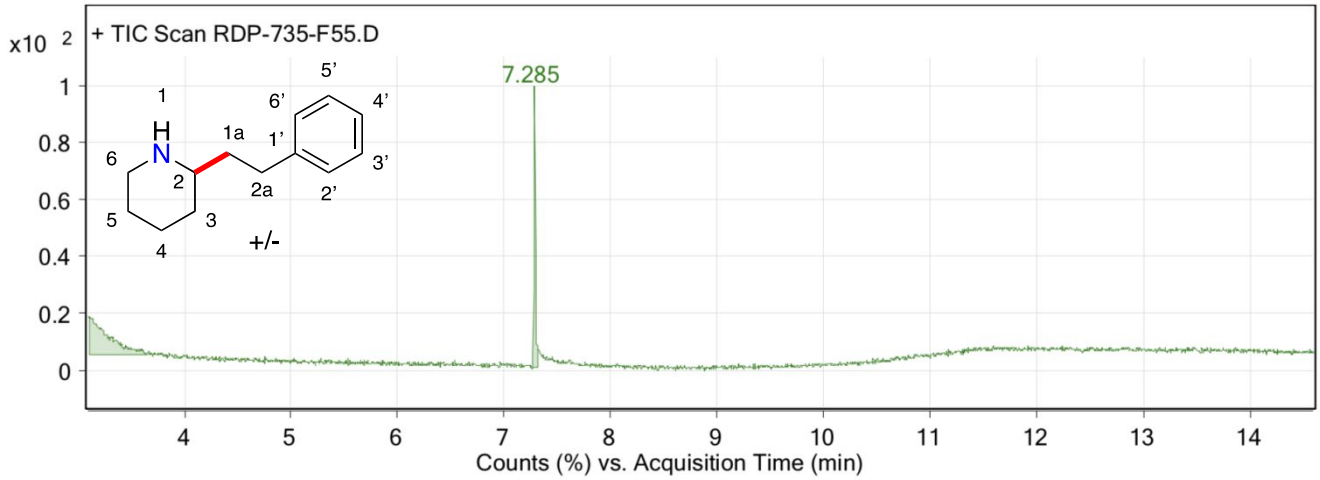
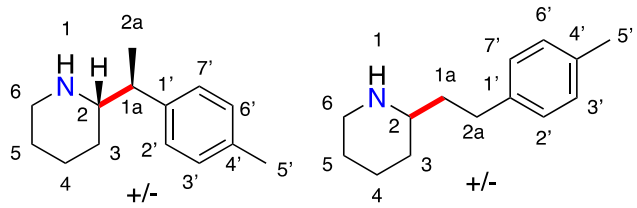


Figure S81: GC-MS report (101 MHz, $CDCl_3$, 298 K) of 2-phenethylpiperidine.



Synthesis of 2-(1-(p-tolyl)ethyl)piperidine and 2-(4-methylphenethyl)piperidine (16 and 17): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 Ta, 15.2 Ligand, piperidine (85.15 mg, 1.0 mmol), 4-methylstyrene (118.18 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 67 % for 2-(1-(p-tolyl)ethyl)piperidine and 29 % for 2-(4-methylphenethyl)piperidine by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.10 (m, 2H, 3' and 6'), 7.08 (m, 2H, 2' and 7'), 3.12 (m, 1H, ½ of 6), 2.65 (m, 1H, 1a), 2.62 (m, 1H, ½ of 6), 2.54 (m, 1H, 2), 2.32 (s, 3H, 5'), 1.95 (broad s, 1H, NH), 1.72 (m, 1H, ½ of 4), 1.56 (m, 1H, ½ of 5), 1.45 (m, 1H, ½ of 3), 1.36 (m, 1H, ½ of 5), 1.29 (d, J = 1.28, 3H, 2a), 1.24 (m, 1H, ½ of 4), 1.06 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 142.07, 135. 79, 129.11, 127.84, 62.64, 47.54, 45.26, 30.83, 26.46, 25.04, 21.13, 17.43 ppm. HRMS (ESI): *m/z* calcd for $C_{14}H_{22}N$ [M+H$^+$]: 204.1752 Found: 204.1748.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.08 (m, 4H, 2' and 3' and 6' and 7'), 3.09 (m, 1H, ½ of 6), 2.65 (m, 1H, ½ of 6), 2.59 (m, 2H, 2a), 2.52 (m, 1H, 2), 2.31 (s, 3H, 5'), 1.96 (broad s, 1H, NH), 1.81 (m, 1H, ½ of 4), 1.73 (m, 1H, ½ of 3), 1.68 (m, 2H, 1a), 1.58 (m, 1H, ½ of 5), 1.45 (m, 1H, ½ of 5), 1.35 (m, 1H, ½ of 4), 1.14 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 139.29, 135.33, 129.19, 128.34, 56.60, 47.17, 39.22, 32.82, 31.92, 26.53, 24.84, 21.12 ppm. HRMS (ESI): *m/z* calcd for $C_{14}H_{22}N$ [M+H$^+$]: 204.1752 Found: 204.1755.

Note: The 1D/2D NMR spectroscopy data for the branched regioisomer below is a representative example of how we were able to were able to assign all proton and carbon signals conclusively in products with styrenes as coupling partners.

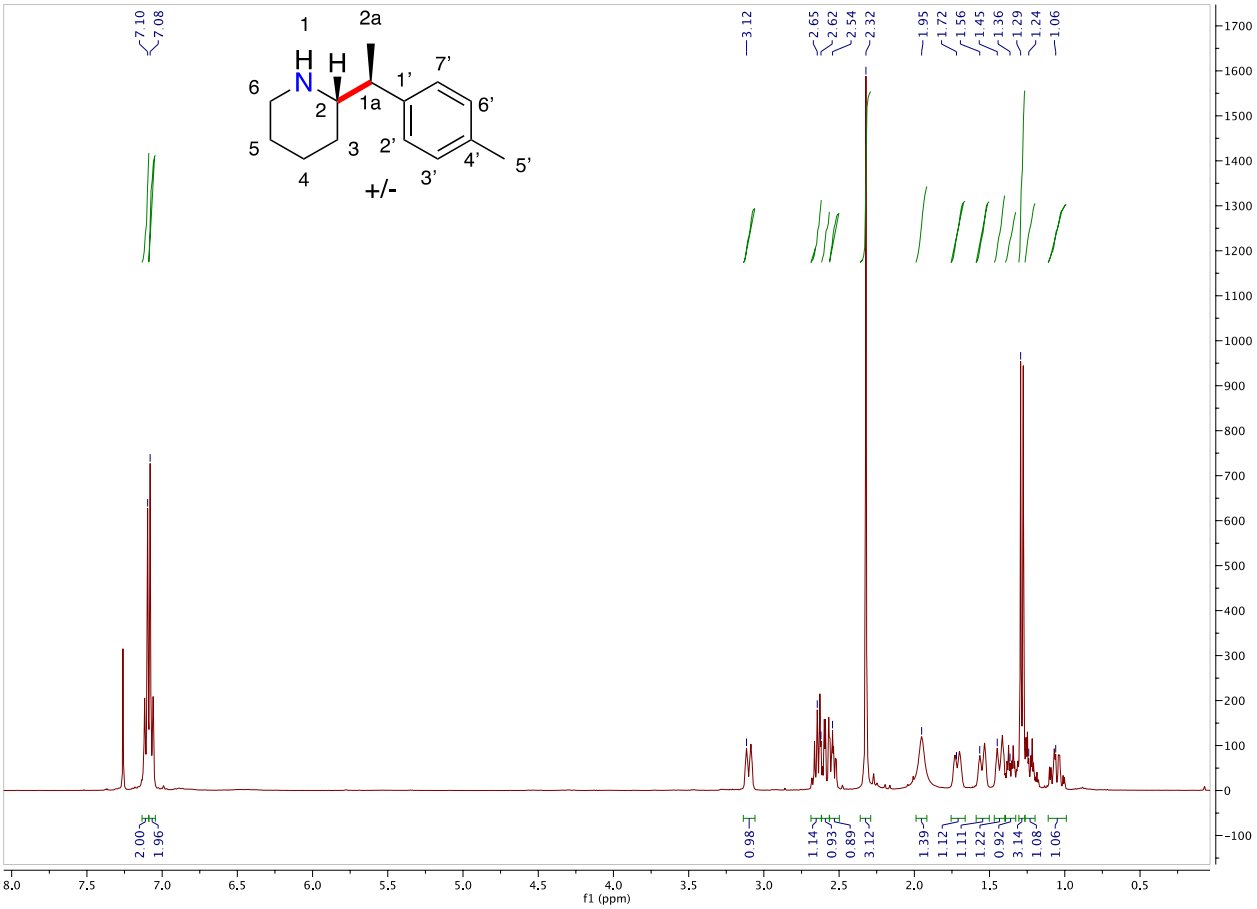


Figure S82: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(p-tolyl)ethyl)piperidine.

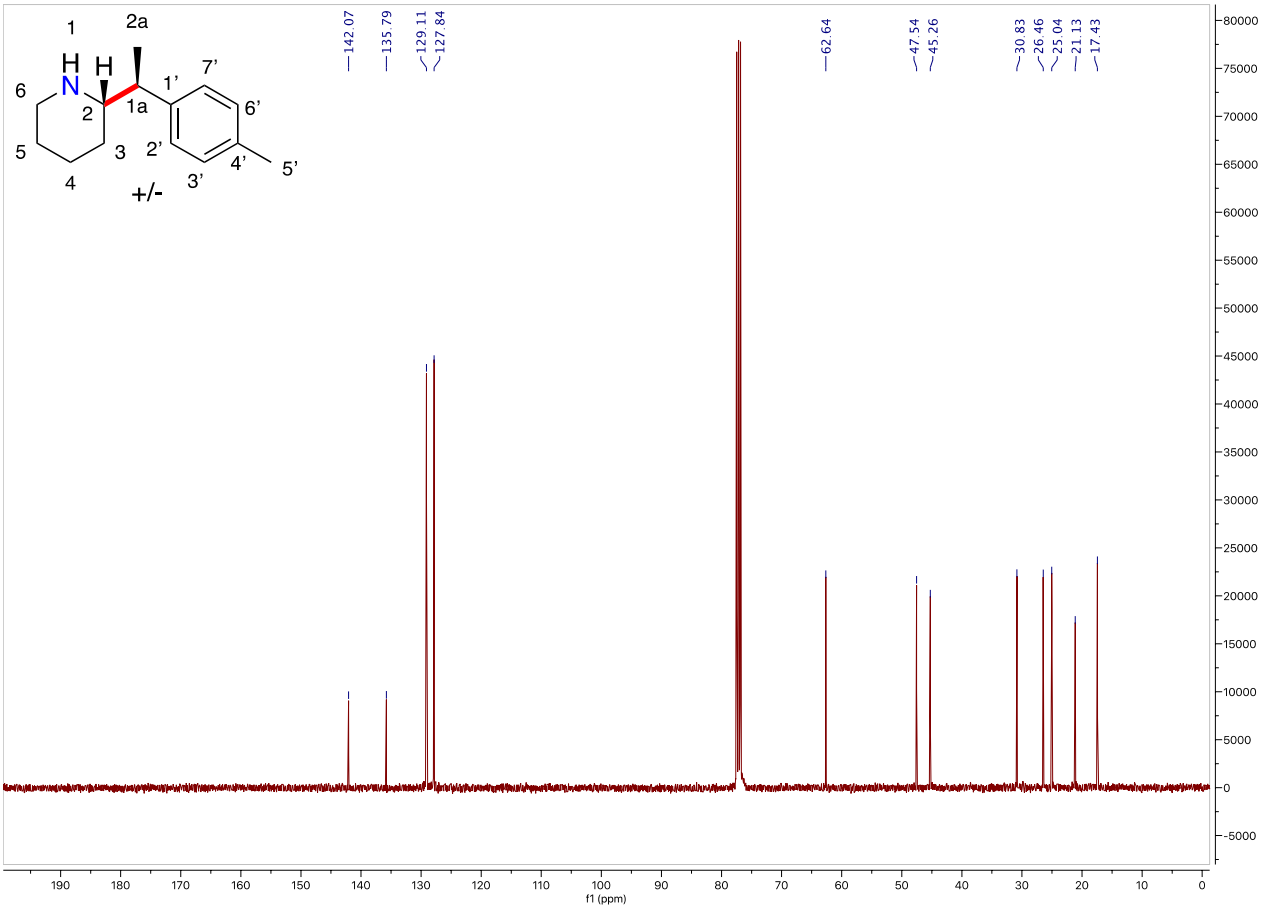


Figure S83: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(1-(p-tolyl)ethyl)piperidine.

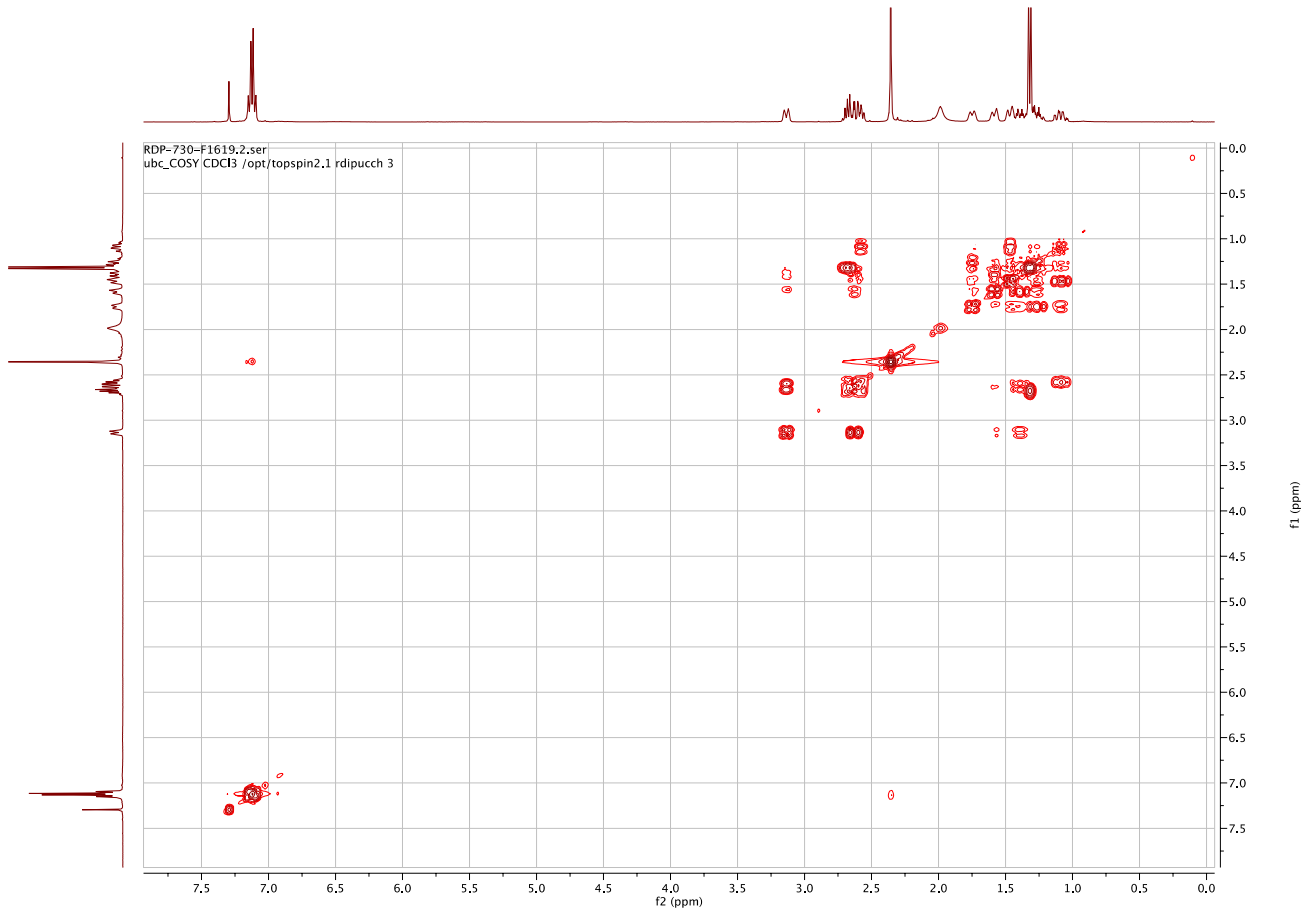


Figure S84: COSY spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(p-tolyl)ethyl)piperidine.

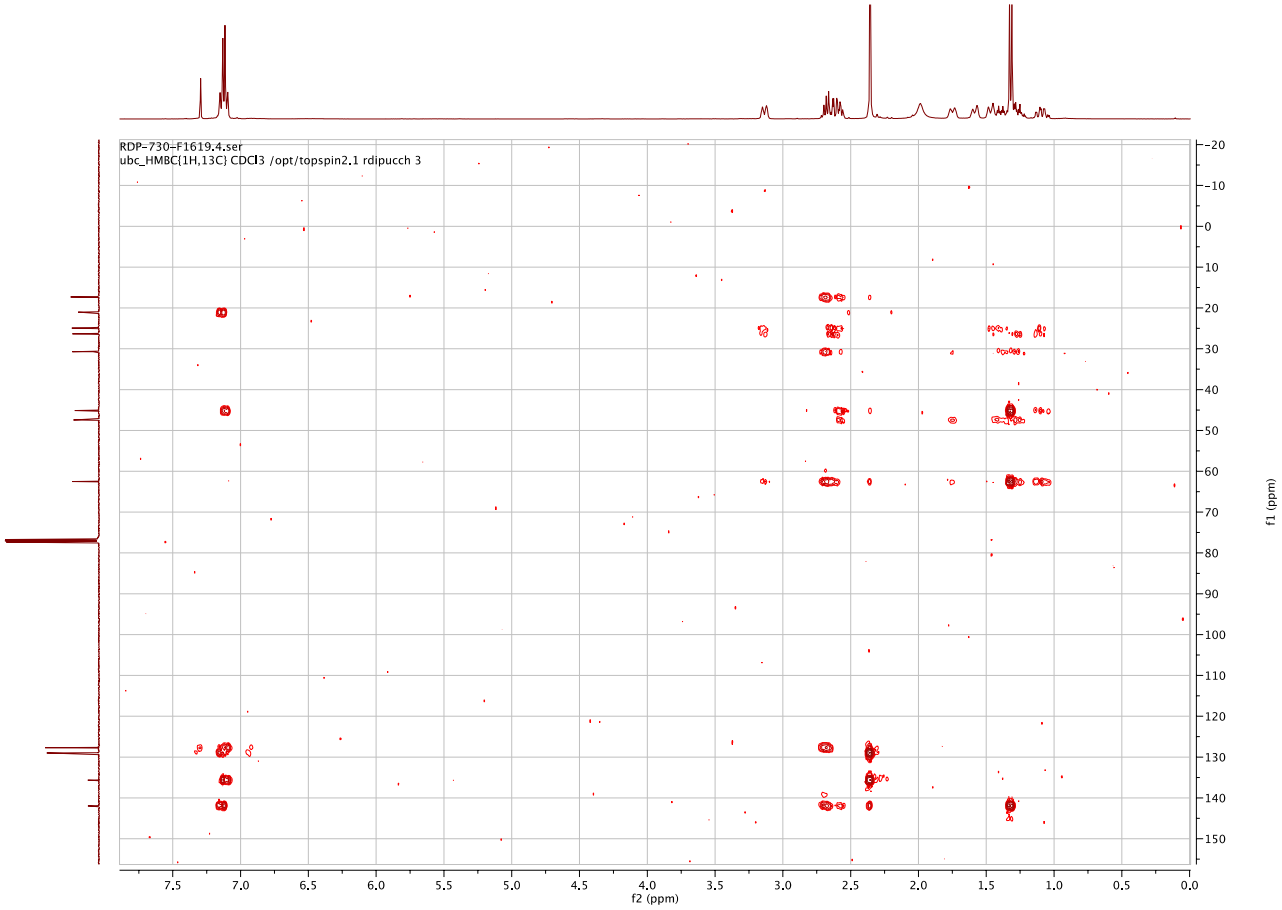


Figure S85: HMBC spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(p-tolyl)ethyl)piperidine.

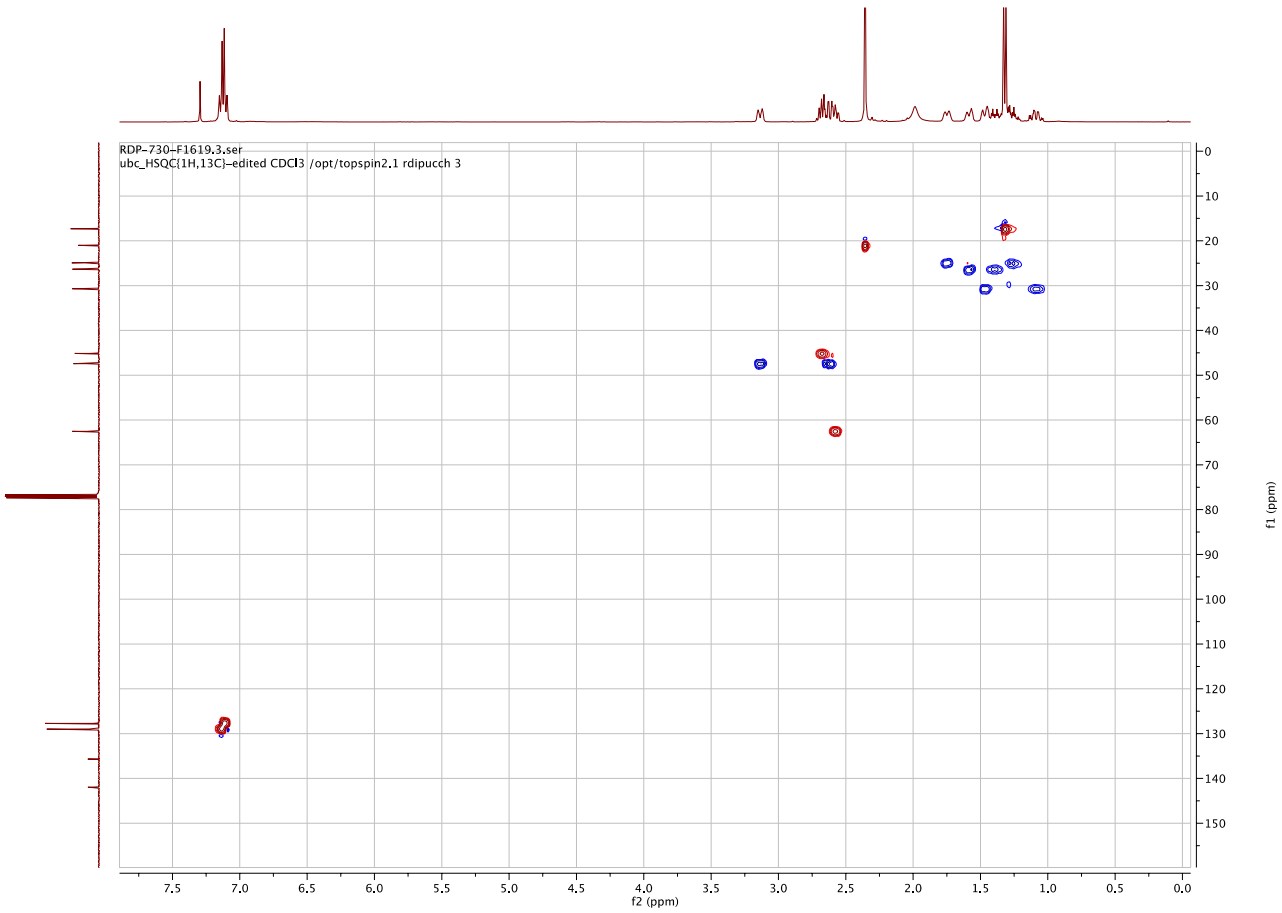


Figure S86: HSQC spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(p-tolyl)ethyl)piperidine.

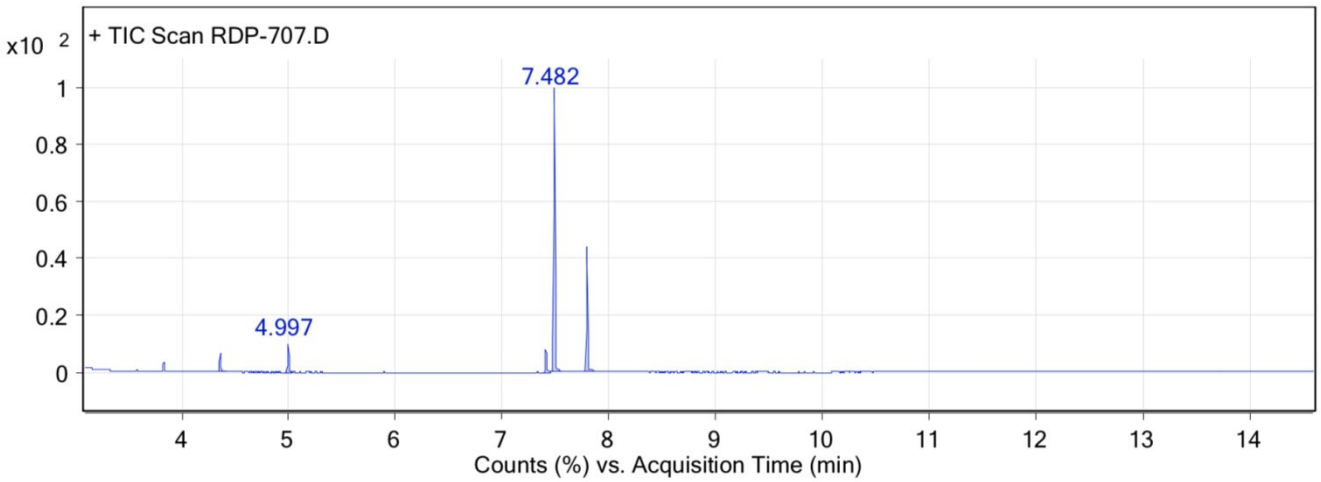


Figure S87: GC-MS for crude reaction mixture between piperidine and 4-methylstyrene.

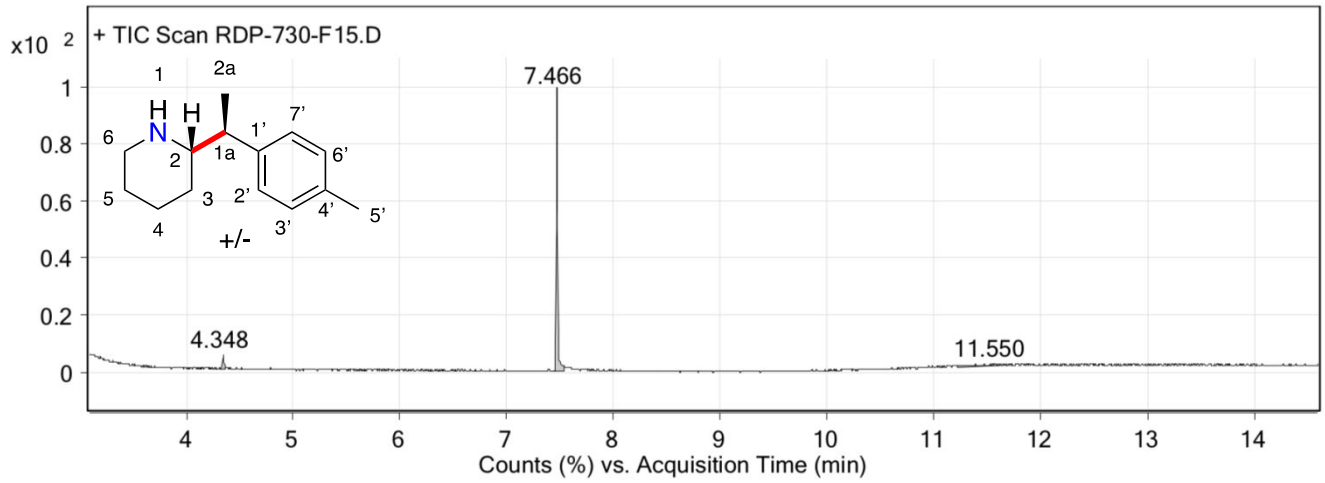


Figure S88: GC-MS report of 2-(1-(p-tolyl)ethyl)piperidine.

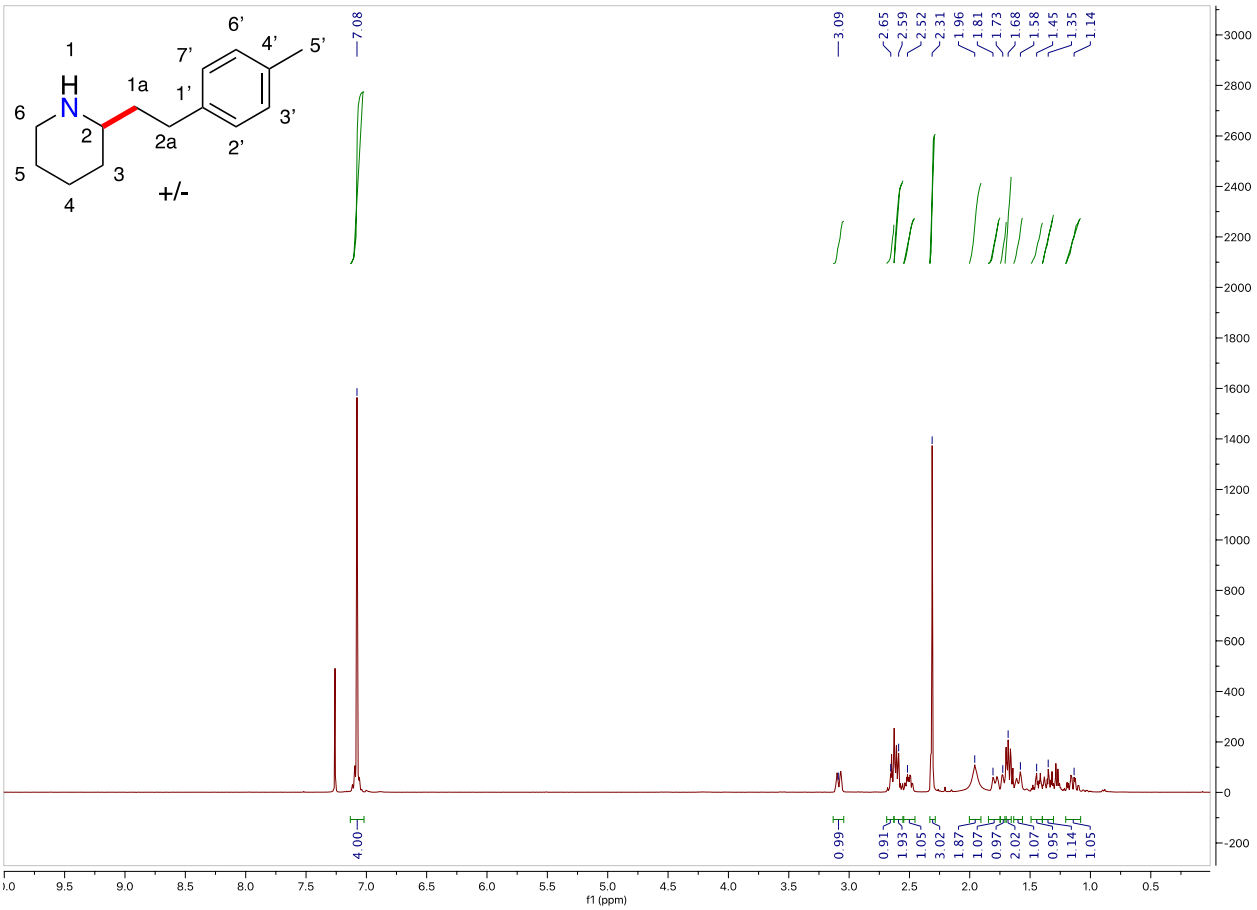


Figure S89: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(4-methylphenethyl)piperidine.

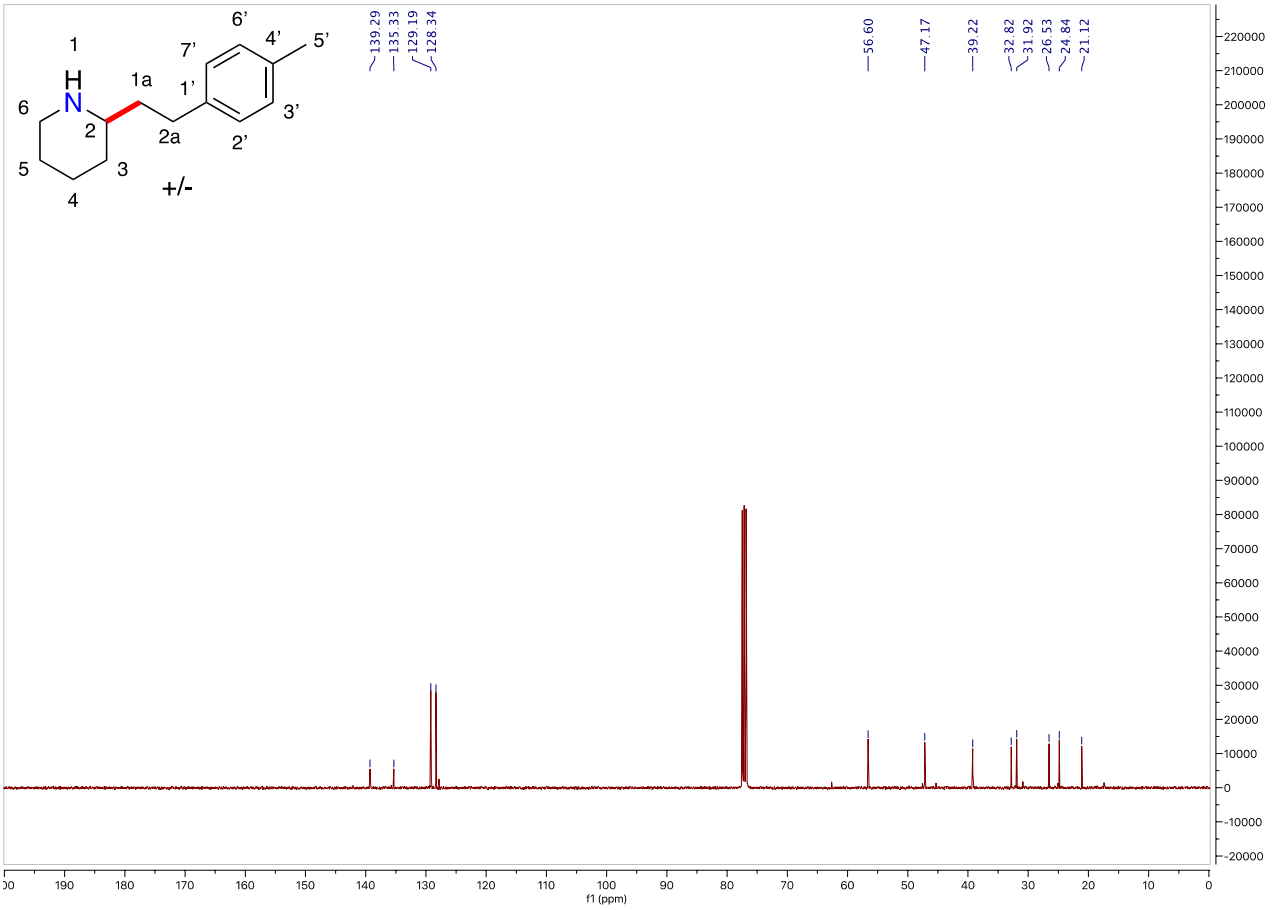


Figure S90: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(4-methylphenethyl)piperidine.

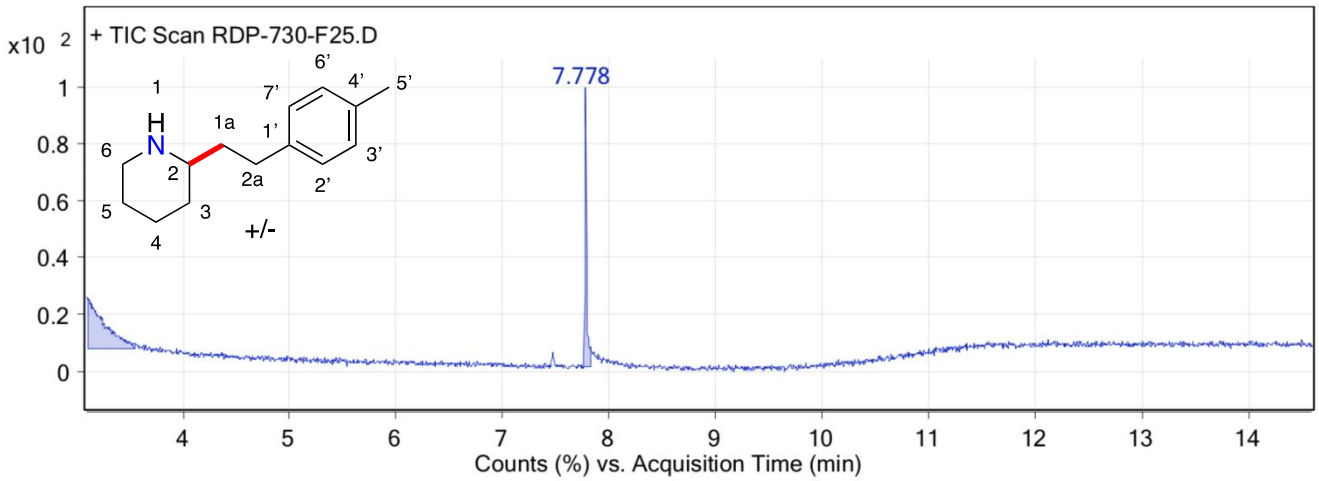
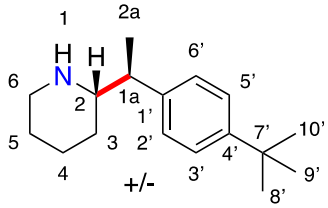
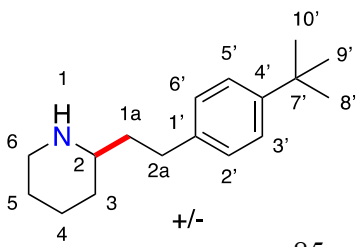
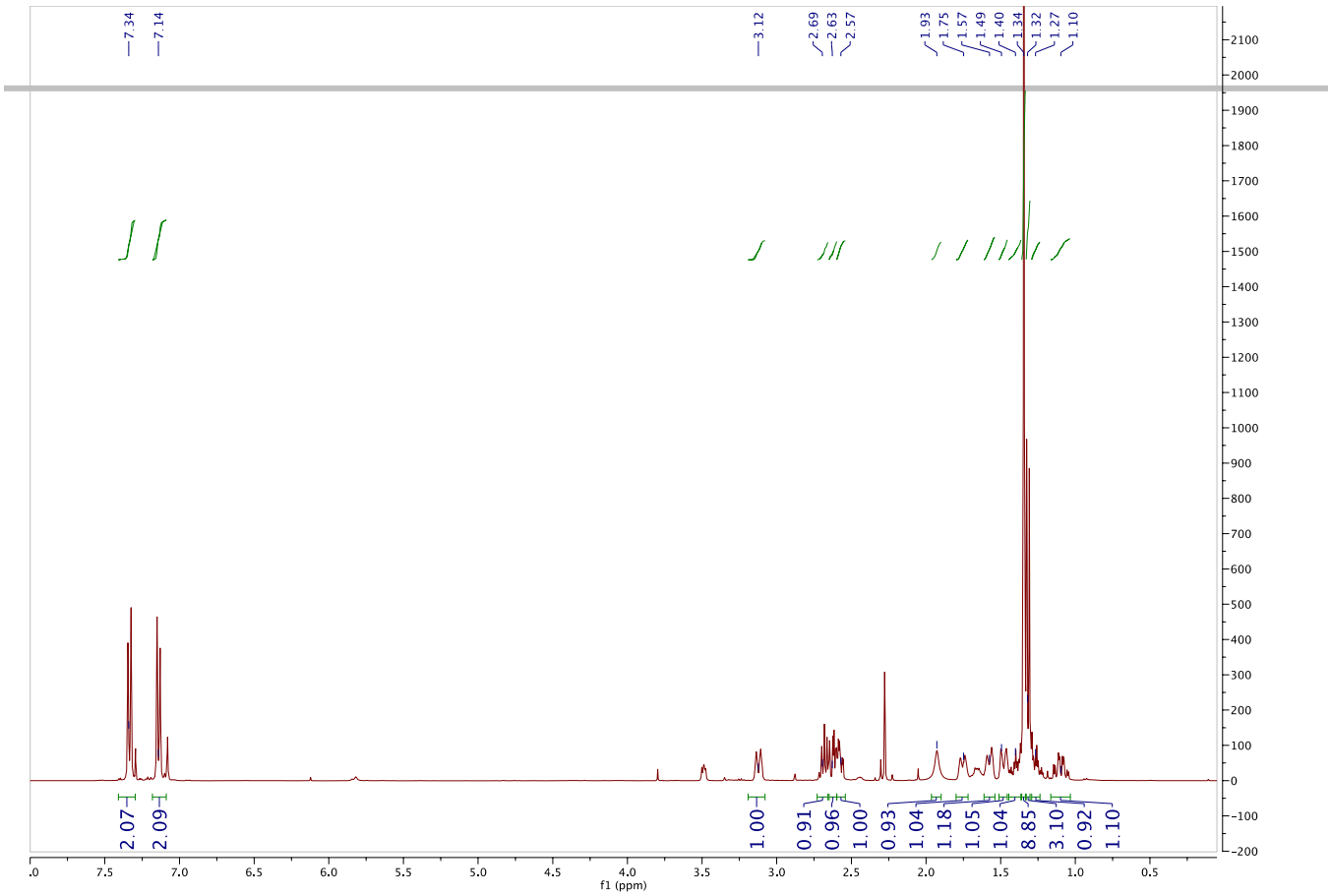


Figure S91: GC-MS report (101 MHz, $CDCl_3$, 298 K) of 2-(4-methylphenethyl)piperidine.

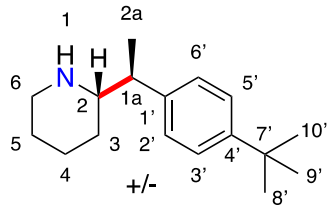




Synthesis of 2-(1-(4-(tert-butyl)phenyl)ethyl)piperidine and 2-(4-(tert-butyl)phenethyl)piperidine (18 and 19): Prepared following the general procedure



for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), para-t-butylstyrene (160.13 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 65 % for 2-(1-(4-(tert-butyl)phenyl)ethyl)piperidine and 34 % for 2-(4-butyl)phenethyl)piperidine by NMR (1,3, 5-(tert-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):



Branched product: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.34 (m, 2H, 3' and 5'), 7.14 (m, 2H, 2' and 6'), 3.12 (m, 1H, ½ of 6), 2.69 (m, 1H, 1a), 2.63 (m, 1H, ½ of 6), 2.57 (m, 1H, 2), 1.93 (broad s, 1H, NH), 1.75 (m, 1H, ½ of 4), 1.57 (m, 1H, ½ of 5), 1.49 (m, 1H, ½ of 3), 1.40 (m, 1H, ½ of 5), 1.34 (s, 9H, 8' and 9' and 10'), 1.32 (d, J = 1.32, 3H, 2a), 1.27 (m, 1H, ½ of 4), 1.10 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 148.86, 141.88, 127.44, 125.11, 47.47, 45.03, 34.37, 31.44, 30.79, 26.46, 25.02, 17.00 ppm. HRMS (ESI): *m/z* calcd for $C_{17}H_{27}N$ [M+H$^+$]: 245.2143 Found: 245.2147.

Linear Product: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.33 (m, 2H, 3' and 5'), 7.15 (m, 2H, 2' and 6'), 3.12 (m, 1H, ½ of 6), 2.70 (m, 1H, ½ of 6), 2.64 (m, 2H, 2a), 2.56 (m, 1H, 2), 2.26 (broad s, 1H, NH), 1.82 (m, 1H, ½ of 4), 1.77 (m, 1H, ½ of 3), 1.70 (m, 2H, 1a), 1.63 (m, 1H, ½ of 5), 1.48 (m, 1H, ½ of 5), 1.41 (m, 1H, ½ of 4), 1.34 (s, 9H, 8' and 9' and 10'), 1.18 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 148.55, 139.22, 127.97, 125.26, 56.56, 47.05, 39.01, 34.36, 32.75, 31.72, 31.42, 26.46, 24.76 ppm. HRMS (ESI): *m/z* calcd for $C_{17}H_{27}N$ [M+H$^+$]: 245.2143 Found: 245.2148.

Figure S92: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(4-(tert-butyl)phenyl)ethyl)piperidine.

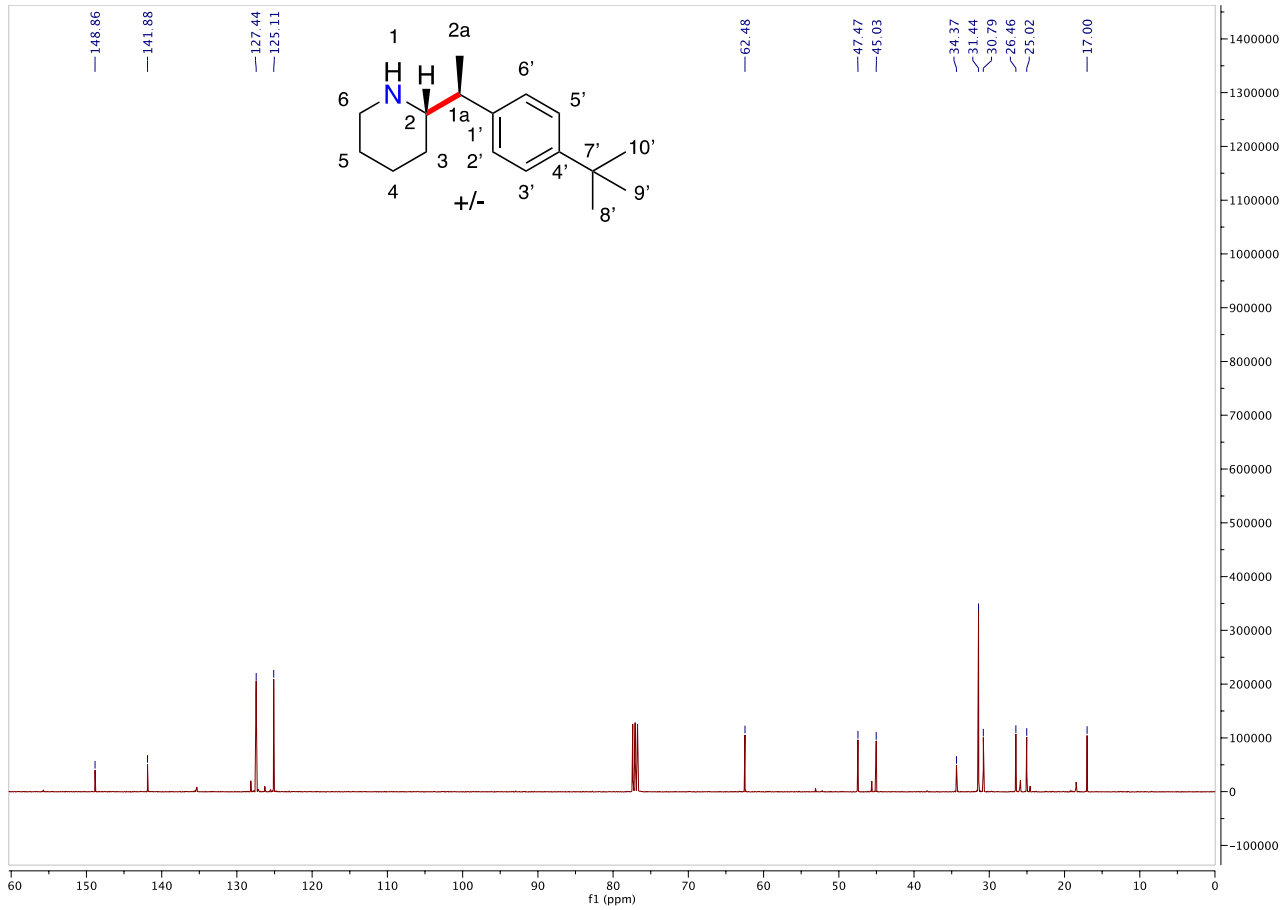


Figure S93: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(4-(tert-butyl)phenyl)ethyl)piperidine.

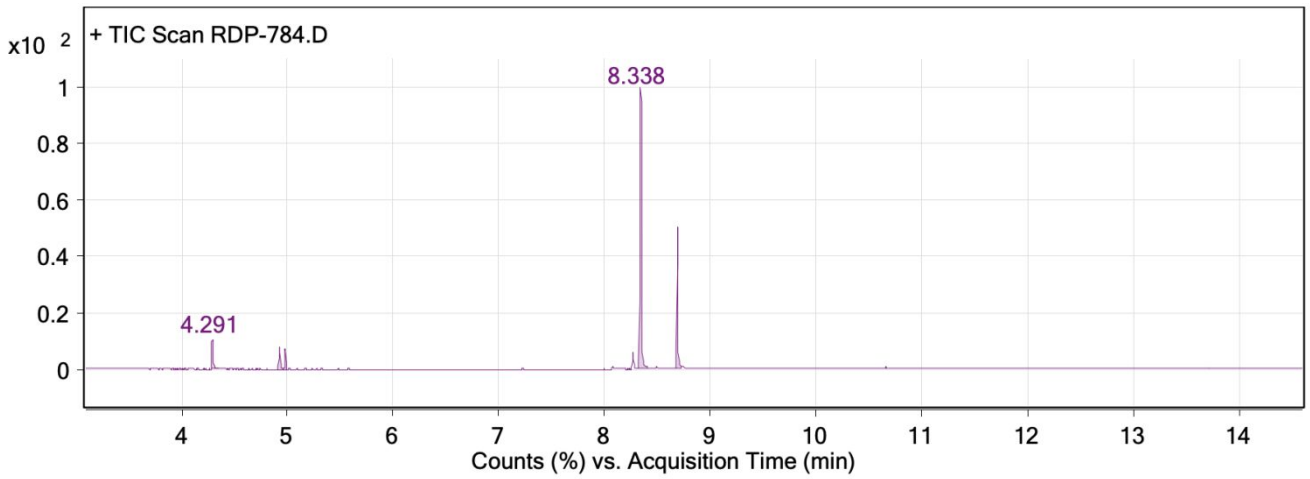


Figure S94: GC-MS report for the crude reaction mixture between piperidine and para-t-butylstyrene.

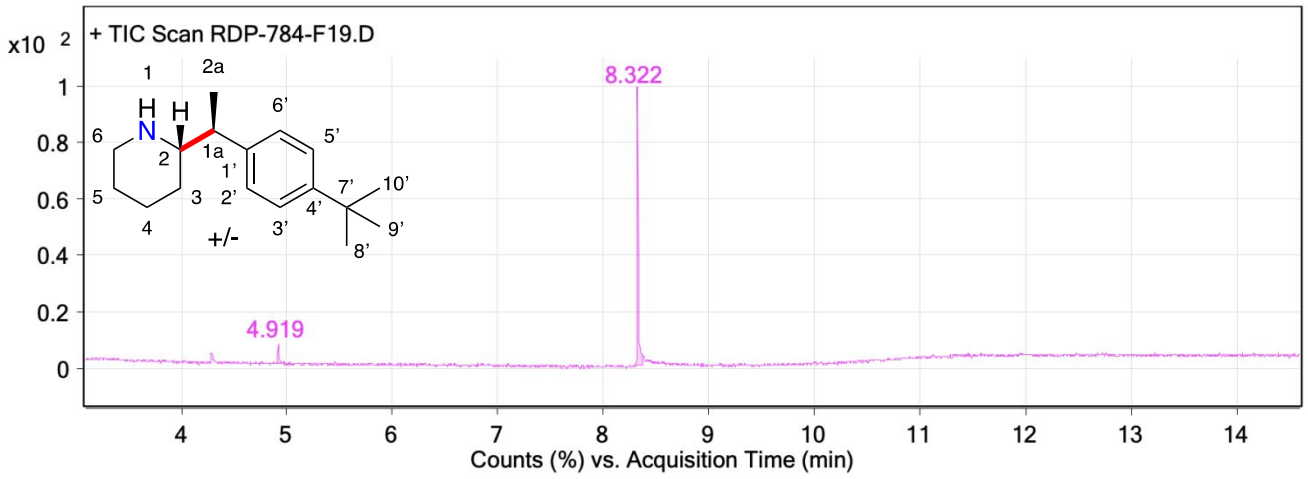


Figure S95: GC-MS report for 2-(1-(4-(tert-butyl)phenyl)ethyl)piperidine.

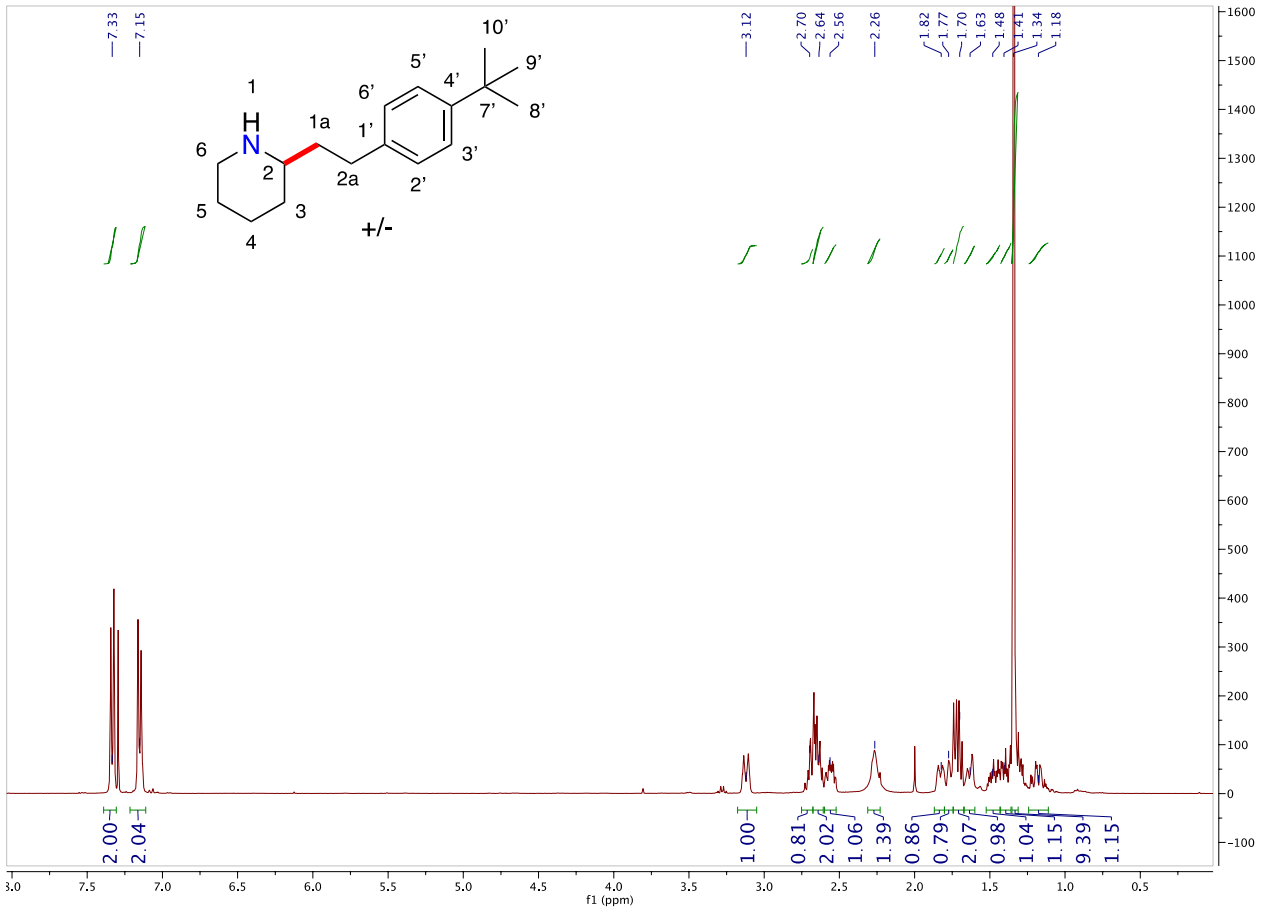


Figure S96: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(4-(tert-butyl)phenethyl)piperidine.

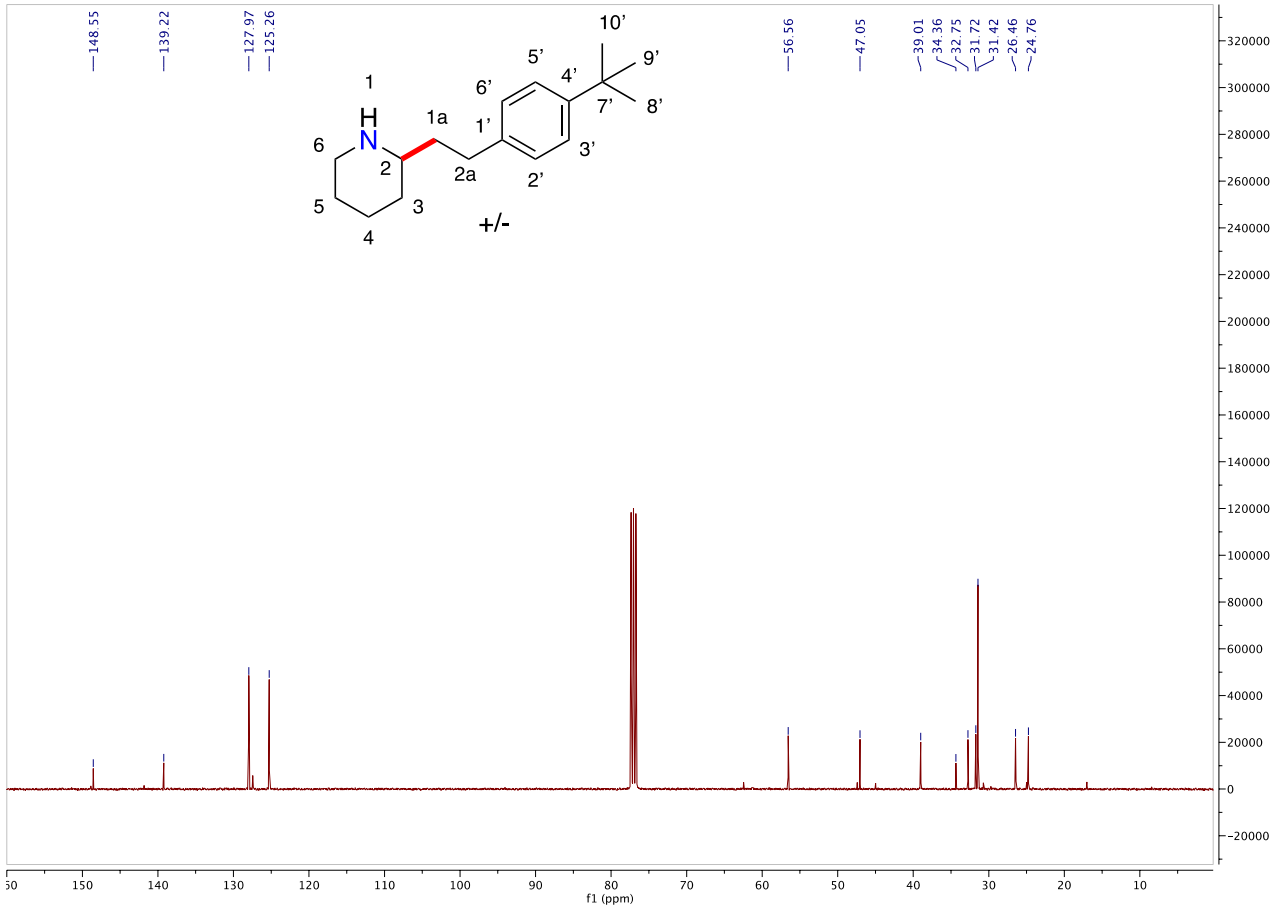


Figure S97: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(4-(tert-butyl)phenethyl)piperidine.

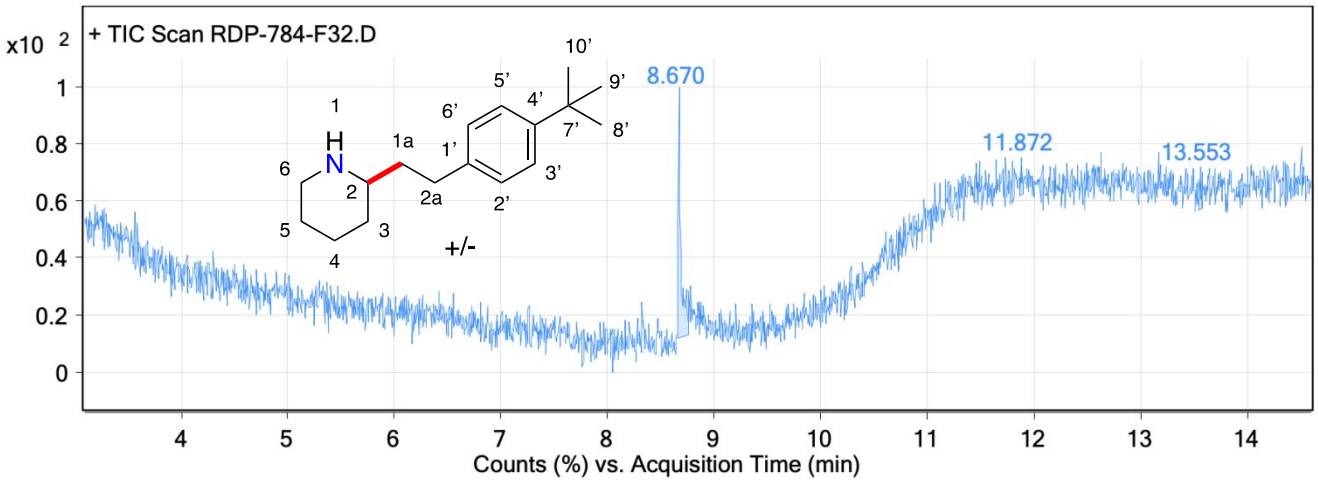
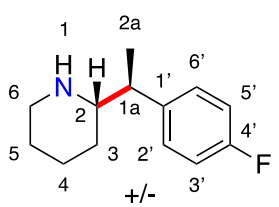
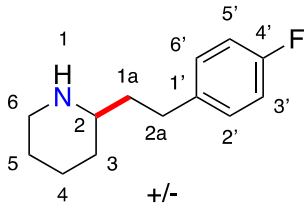


Figure S98: GC-MS report for 2-(4-(tert-butyl)phenethyl)piperidine.





Synthesis of 2-(1-(4-fluorophenyl)ethyl)piperidine and 2-(4-fluorophenethyl)piperidine) (20 and 21): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), para-fluorostyrene (122.05 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 60 % for 2-(1-(4-fluorophenyl)ethyl)piperidine and 39 % for 2-(4-fluorophenethyl)piperidine by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.12 (m, 2H, 3' and 5'), 6.96 (m, 2H, 2' and 6'), 3.09 (m, 1H, ½ of 6), 2.64 (m, 1H, 1a), 2.58 (m, 1H, ½ of 6), 2.50 (m, 1H, 2), 1.74 (broad s, 1H, NH), 1.70 (m, 1H, ½ of 4), 1.55 (m, 1H, ½ of 5), 1.37 (m, 1H, ½ of 4), 1.32 (m, 1H, ½ of 5), 1.25 (d, J = 1.26, 3H, 2a), 1.21 (m, 1H, ½ of 4), 1.02 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 162.70-160-27 (d, J = 242.97), 140.79, 129.24-129.17 (d, J = 7.546), 115.20-114.99 (J = 20.8689), 62.60, 47.54, 45.06, 30.83, 26.54, 25.03, 17.51 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}FN$ [M+H$^+$]: 207.1423 Found: 207.1427.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.13 (m, 2H, 3' and 5'), 6.95 (m, 2H, 2' and 6'), 3.07 (m, 1H, ½ of 6), 2.66 (m, 2H, 1a), 2.58 (m, 1H, ½ of 6), 2.49 (m, 1H, 2), 2.08 (broad s, 1H, NH), 1.79 (m, 1H, ½ of 4), 1,71 (m, 2H, 2a), 1.64 (m, 1H, ½ of 3), 1.58 (m, 1H, ½ of 5), 1.42 (m, 1H, ½ of 5), 1.34 (m, 1H, ½ of 4), 1.12 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 161.56-160.14 (d, J = 243.074), 138.03-138.00 (d, J = 3.382), 129.77-129.69 (q, J = 7.762), 115.32-115.11 (q, J = 21.148), 56.46, 47.19, 39.31, 32.92, 31.58, 26.62, 24.87 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}FN$ [M+H$^+$]: 207.1423 Found: 207.1427.

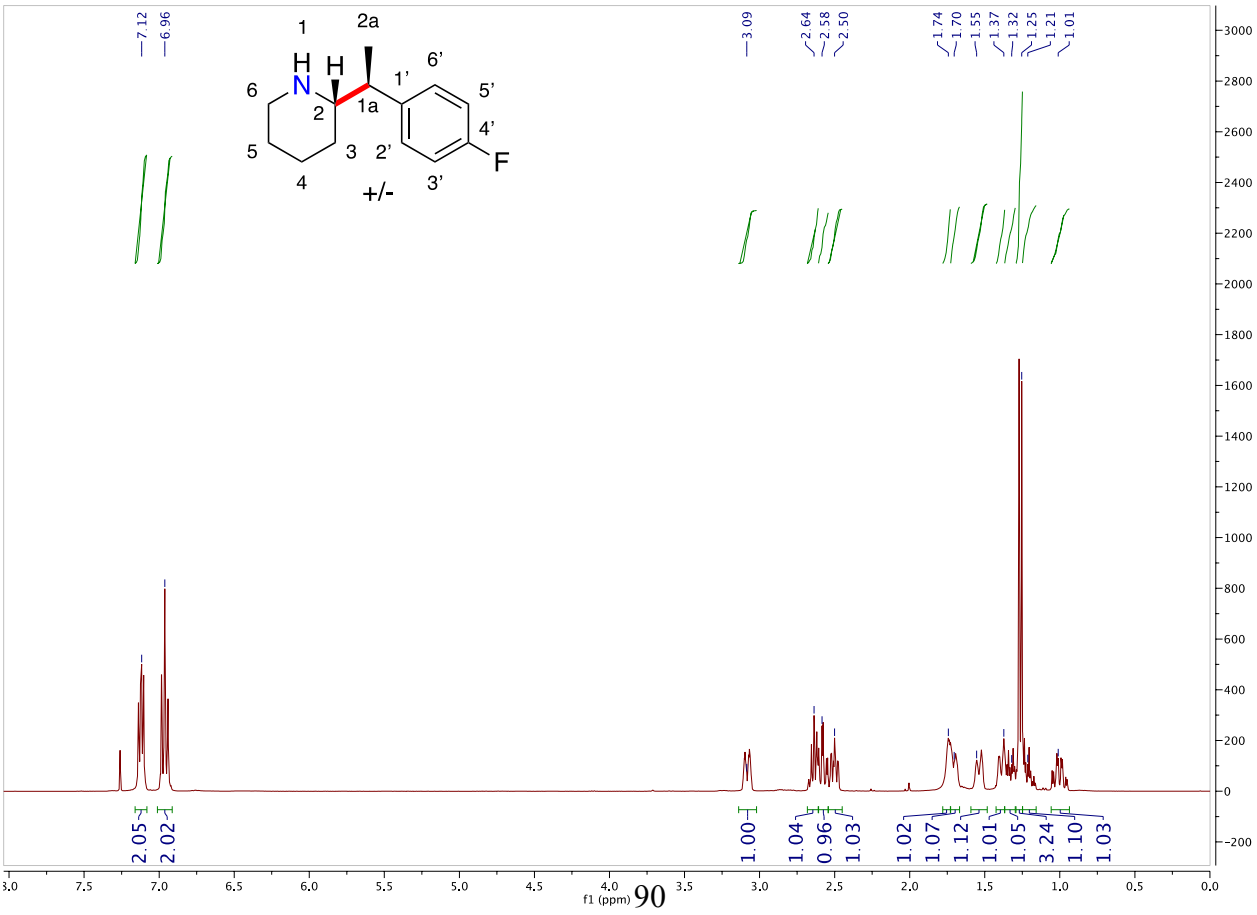


Figure S99: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(4-fluorophenyl)ethyl)piperidine.

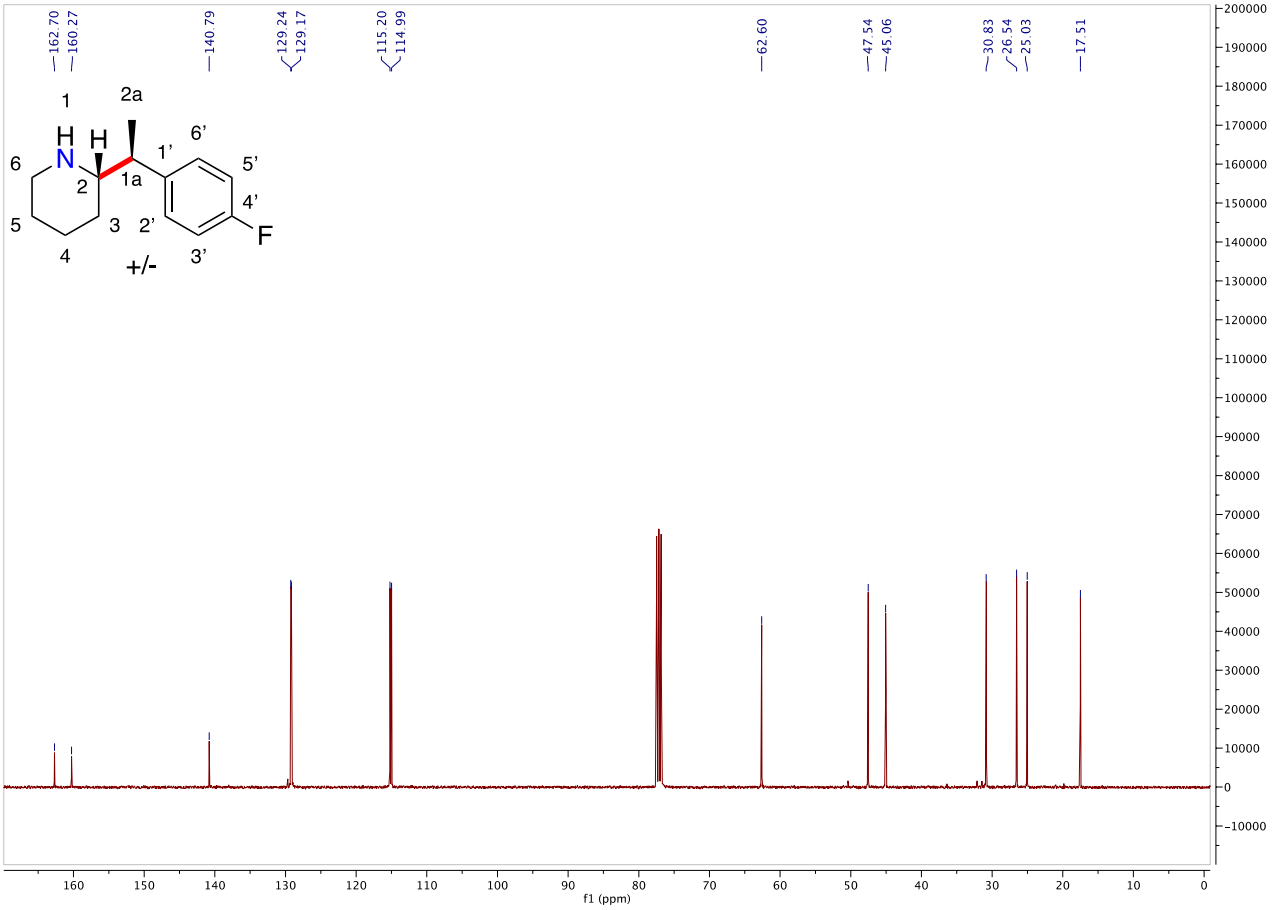


Figure S100: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(4-fluorophenyl)ethyl)piperidine.

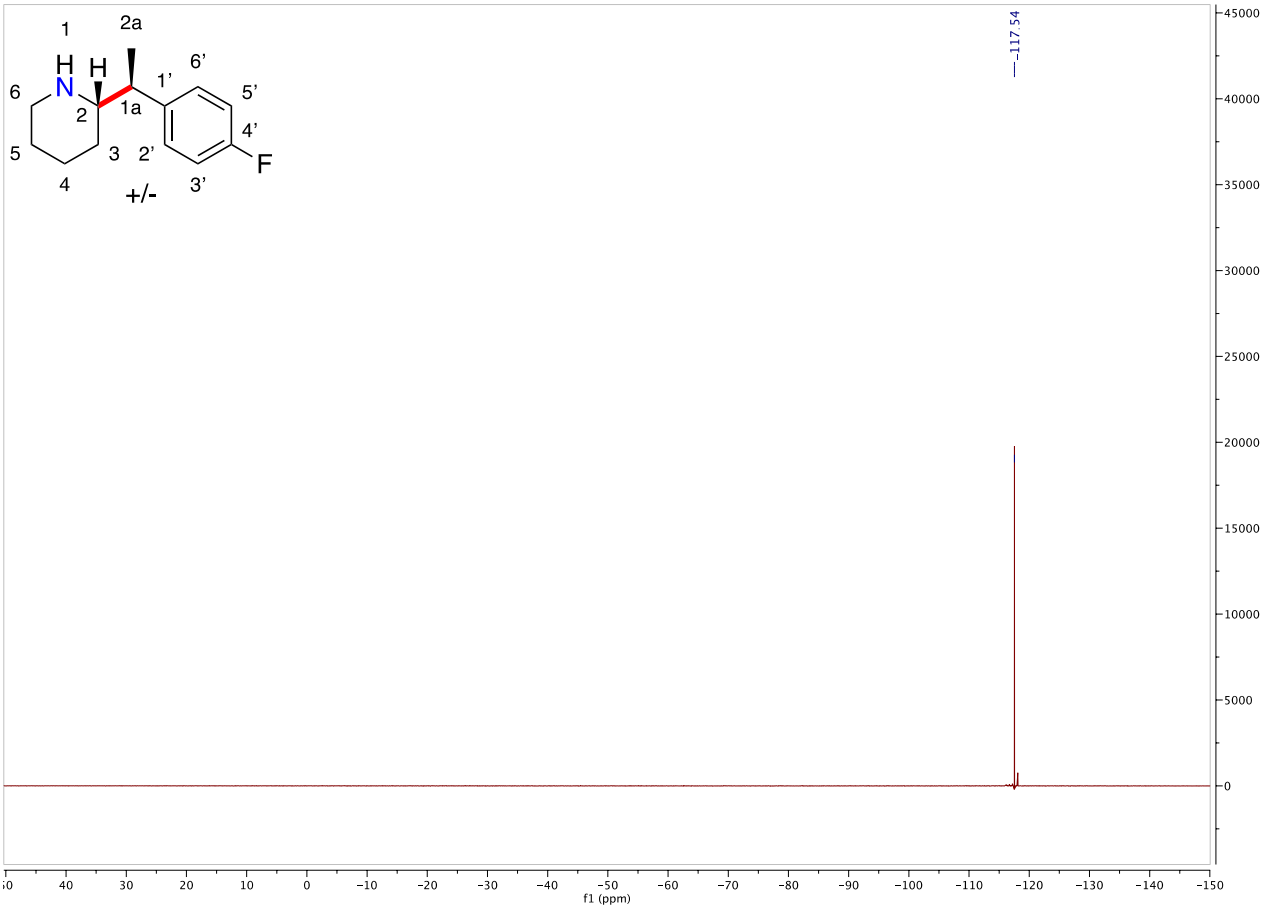


Figure S101: ^{19}F NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(4-fluorophenyl)ethyl)piperidine

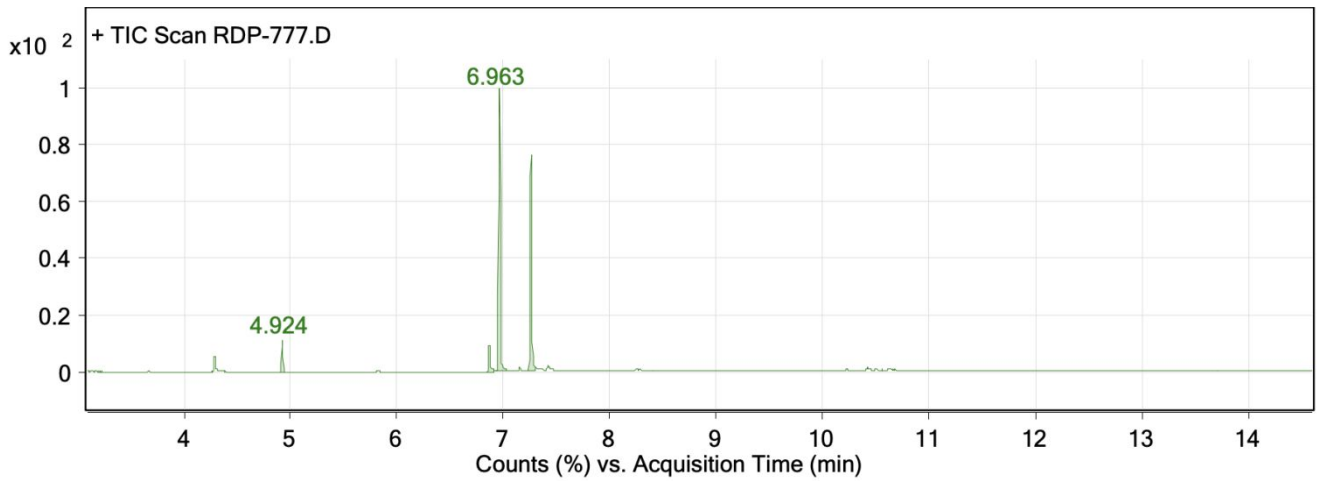


Figure S102: GC-MS for crude reaction mixture between piperidine and para-fluorostyrene.

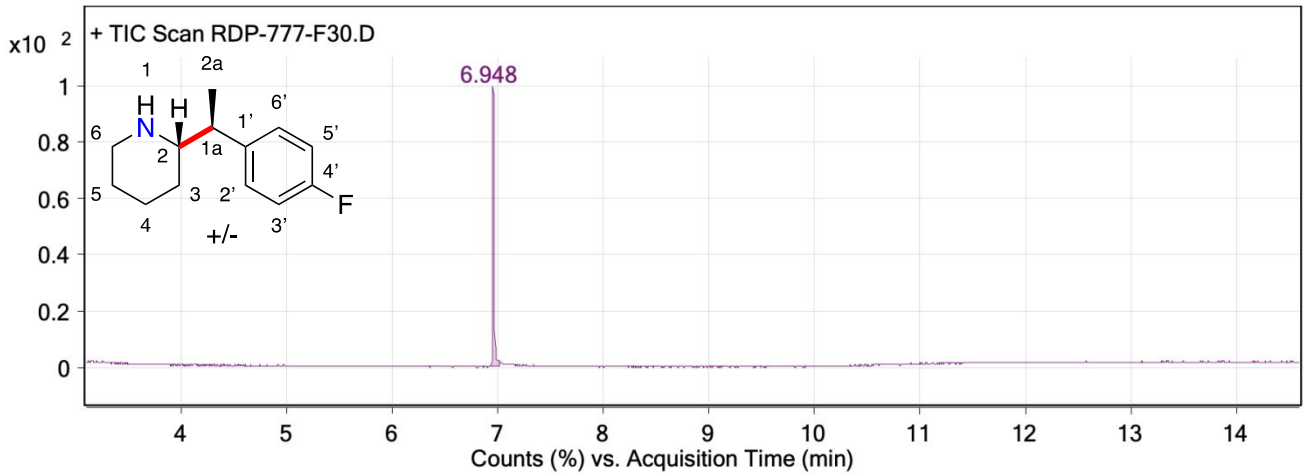


Figure S103: GC-MS report for 2-(1-(4-fluorophenyl)ethyl)piperidine.

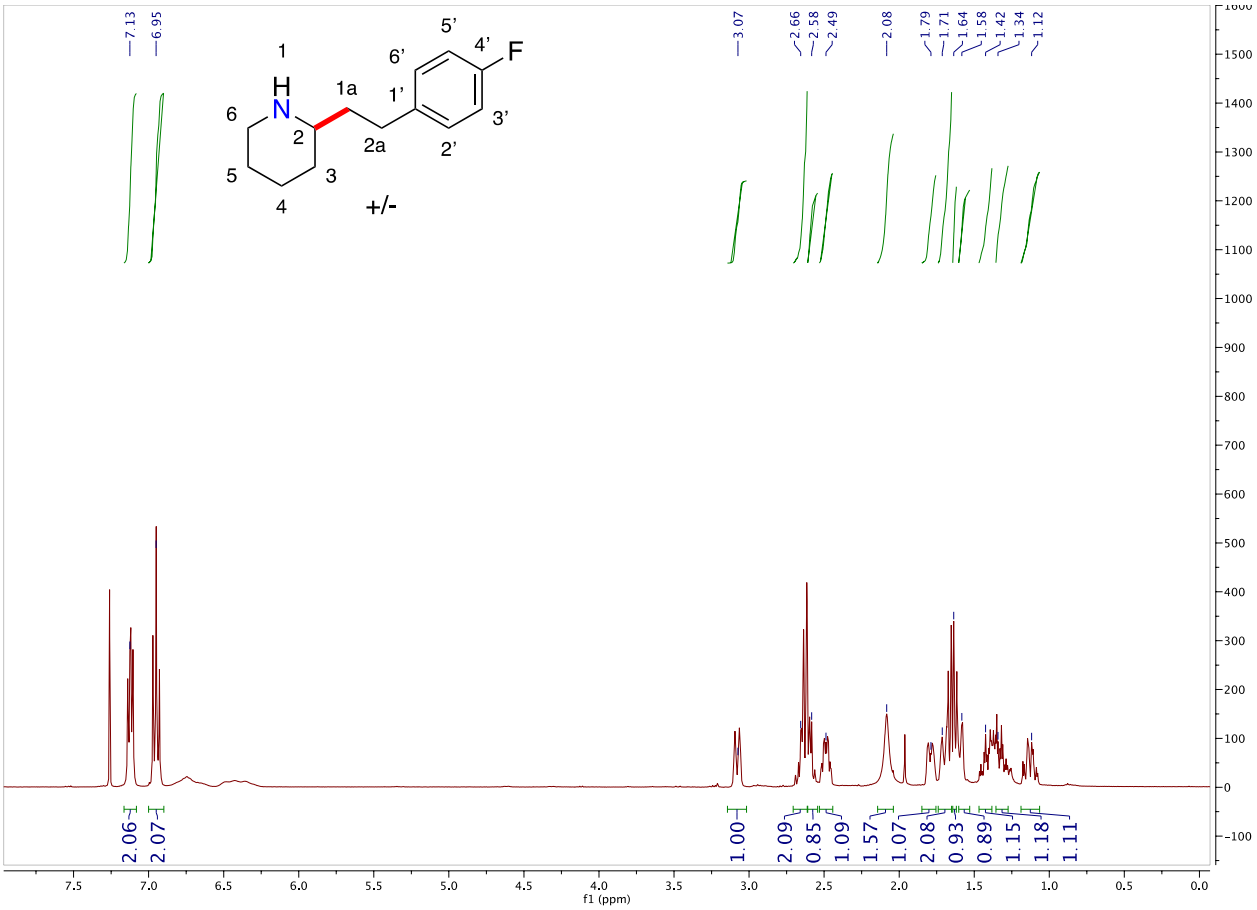


Figure S104: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(4-fluorophenethyl)piperidine.

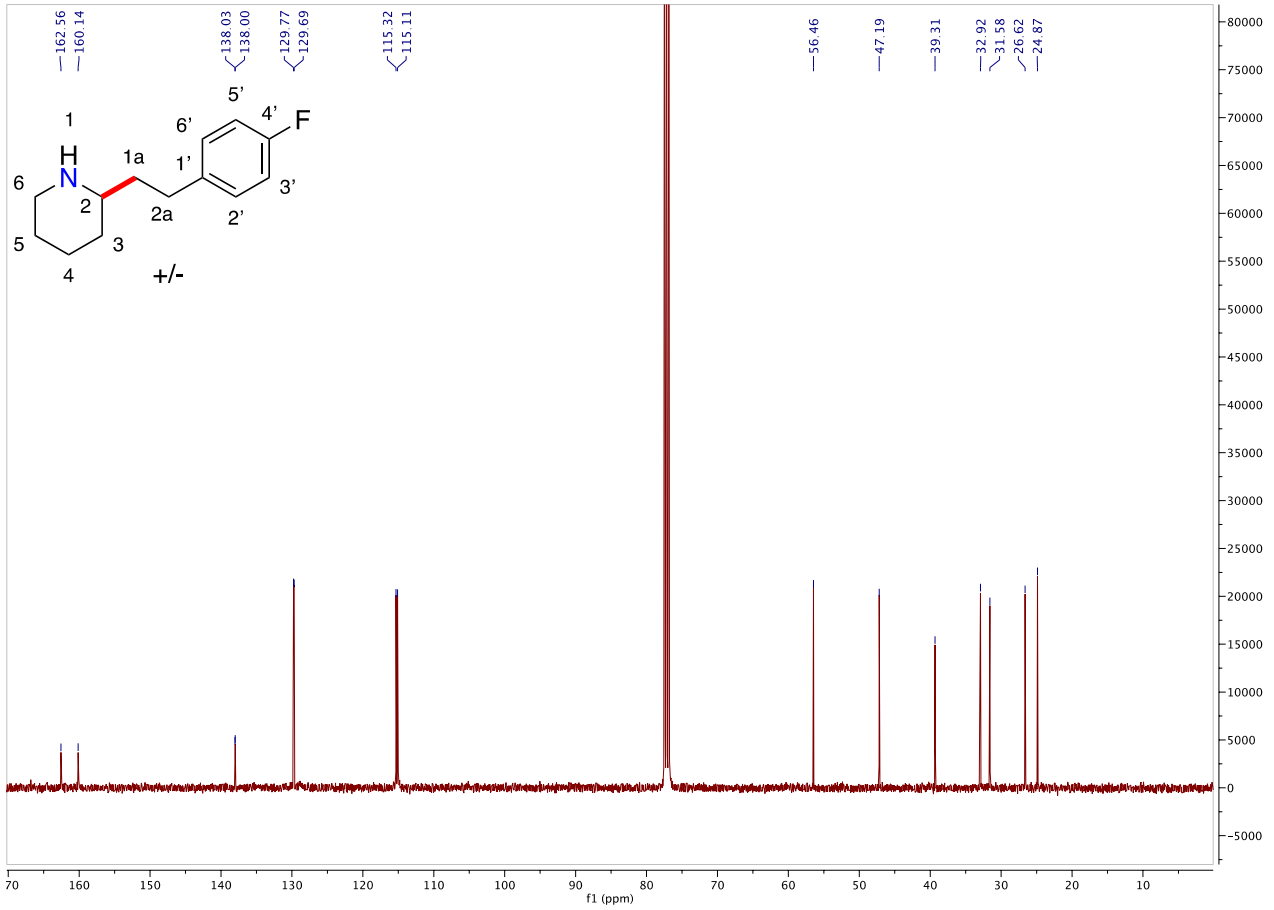


Figure S105: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(4-fluorophenethyl)piperidine.

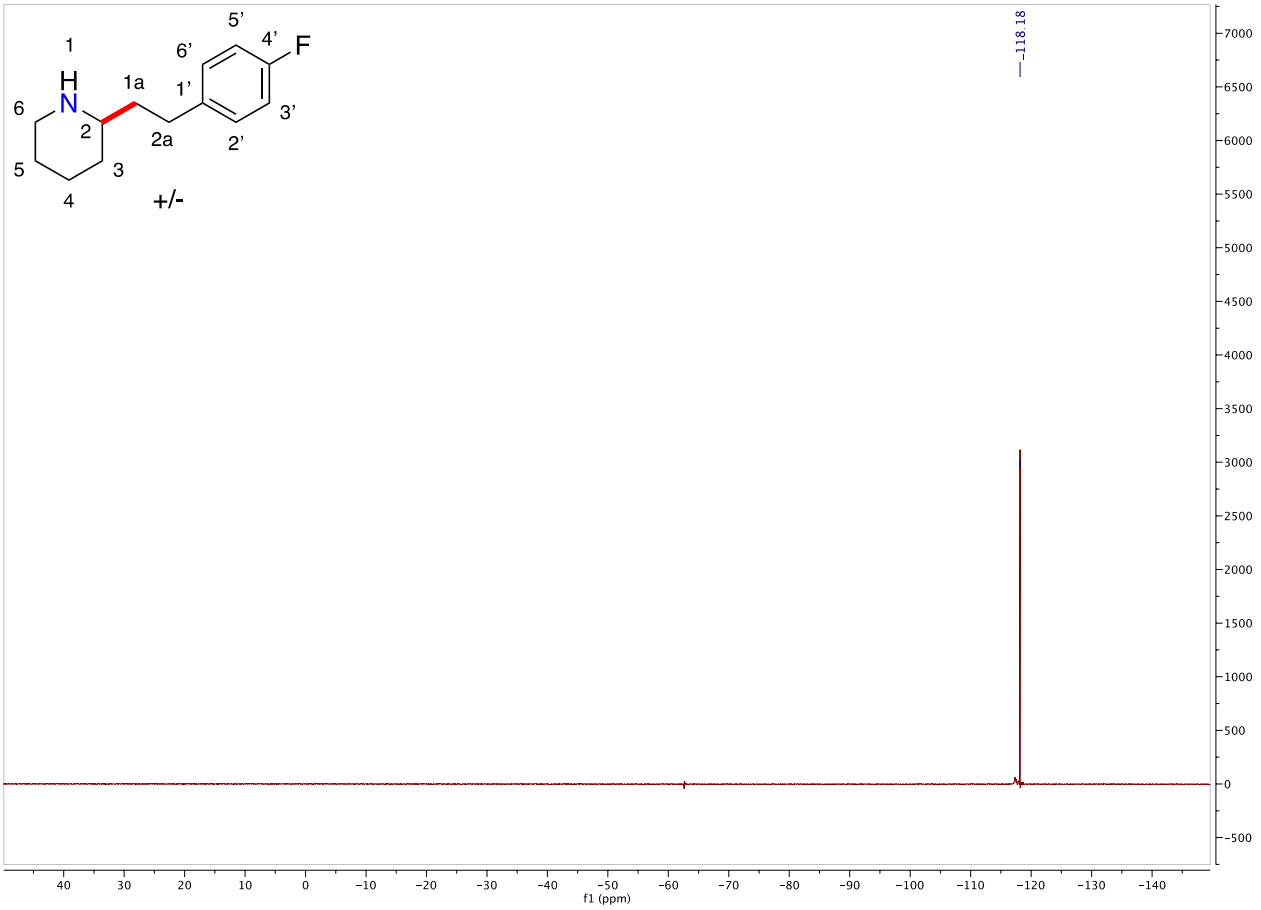


Figure S106: ^{19}F NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(4-fluorophenethyl)piperidine.

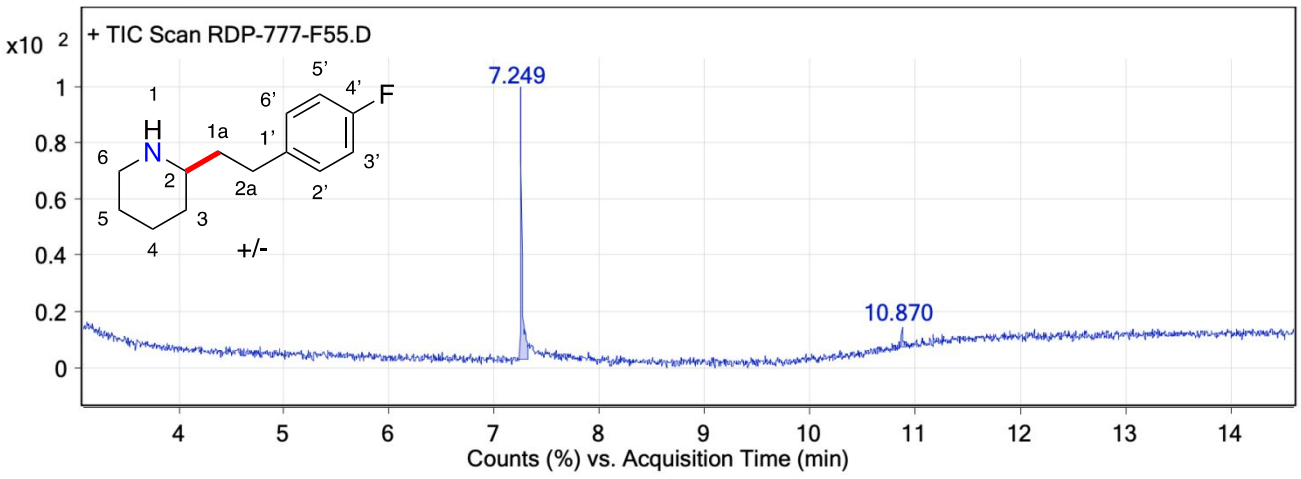
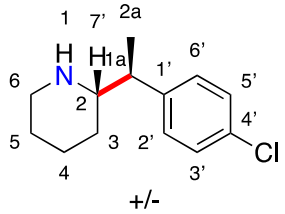
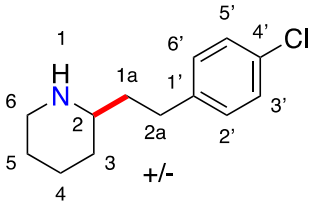


Figure S107: GC-MS report for 2-(4-fluorophenethyl)piperidine.





Synthesis of 2-(1-(4-chlorophenyl)ethyl)piperidine and 2-(4-chlorophenethyl)piperidine (22 and 23): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), 4-chlorostyrene (138.59 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 54 % for 2-(1-(4-chlorophenyl)ethyl)piperidine and 46 % for 2-(4-chlorophenethyl)piperidine by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.25 (m, 2H, 3' and 5'), 7.11 (m, 2H, 2' and 6'), 3.11 (m, 1H, ½ of 6), 2.65 (m, 1H, 1a), 2.59 (m, 1H, ½ of 6), 2.52 (m, 1H, 2), 1.85 (broad s, 1H, NH), 1.71 (m, 1H, ½ of 4), 1.57 (m, 1H, ½ of 5), 1.41 (m, 1H, ½ of 3), 1.33 (m, 1H, ½ of 5), 1.26 (d, J = 1.31, 3H, 2a), 1.22 (m, 1H, ½ of 4), 1.03 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 143.42, 131.88, 129.17, 128.43, 62.38, 47.38, 45.06, 30.63, 26.25, 24.81, 17.35 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NCl$ [M+H$^+$]: 224.1206 Found: 224.1201.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.22 (m, 2H, 3' and 5'), 7.10 (m, 2H, 2' and 6'), 3.14 (m, 1H, ½ of 6), 2.66 (m, 2H, 2a), 2.64 (m, 1H, ½ of 6), 2.53 (m, 1H, 2), 2.45, (broad s, 1H, NH), 1.82 (m, 1H, ½ of 4), 1.74 (m, 2H, 1a), 1.69 (m, 1H, ½ of 3), 1.61 (m, 1H, ½ of 5), 1.48 (m, 1H, ½ of 5), 1.34 (m, 1H, ½ of 4), 1,22 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 140.87, 131.55, 129.77, 128.55, 56.42, 47.22, 39.11, 32.95, 31.71, 26.66, 24.86 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NCl$ [M+H$^+$]: 224.1206 Found: 224.1207.

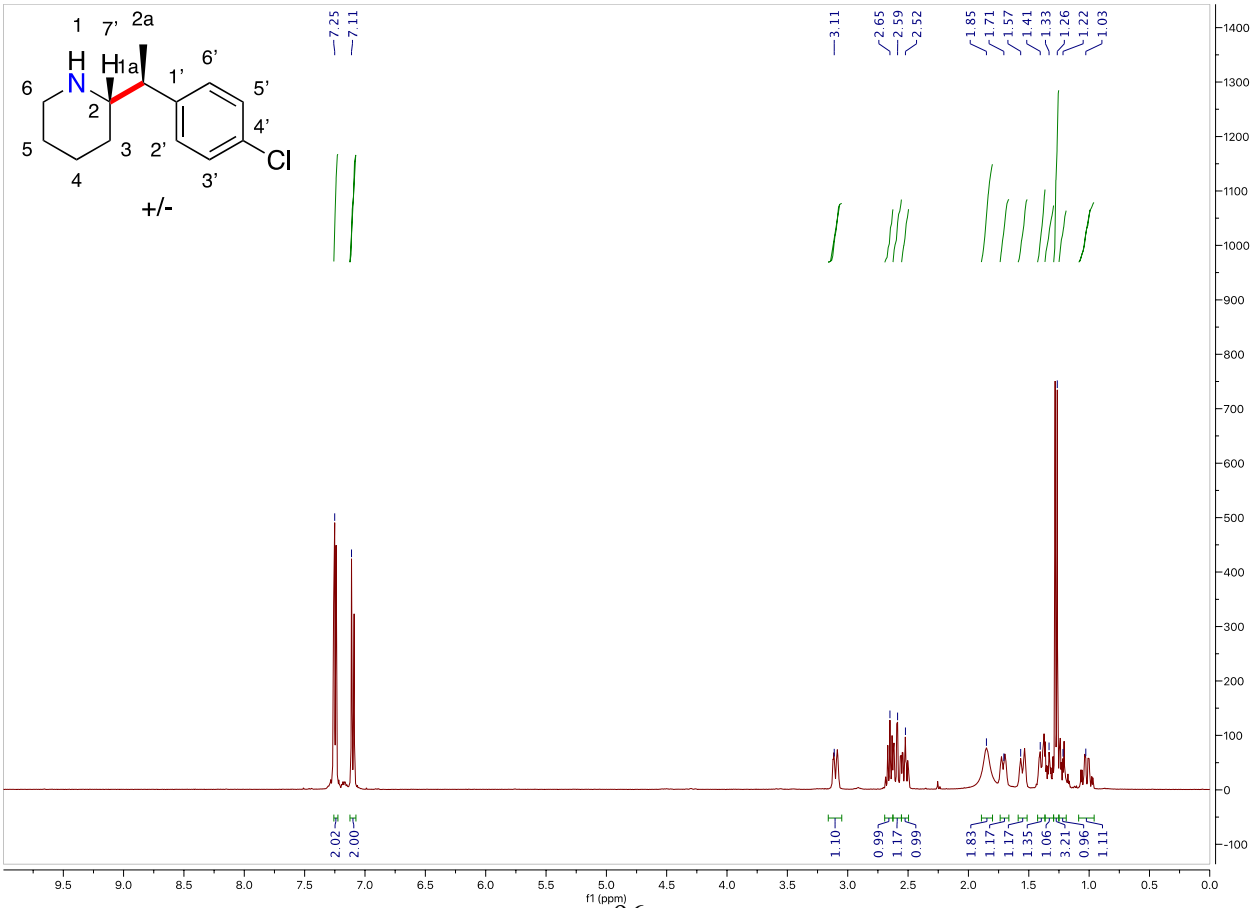


Figure S108: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(4-chlorophenyl)ethyl)piperidine.

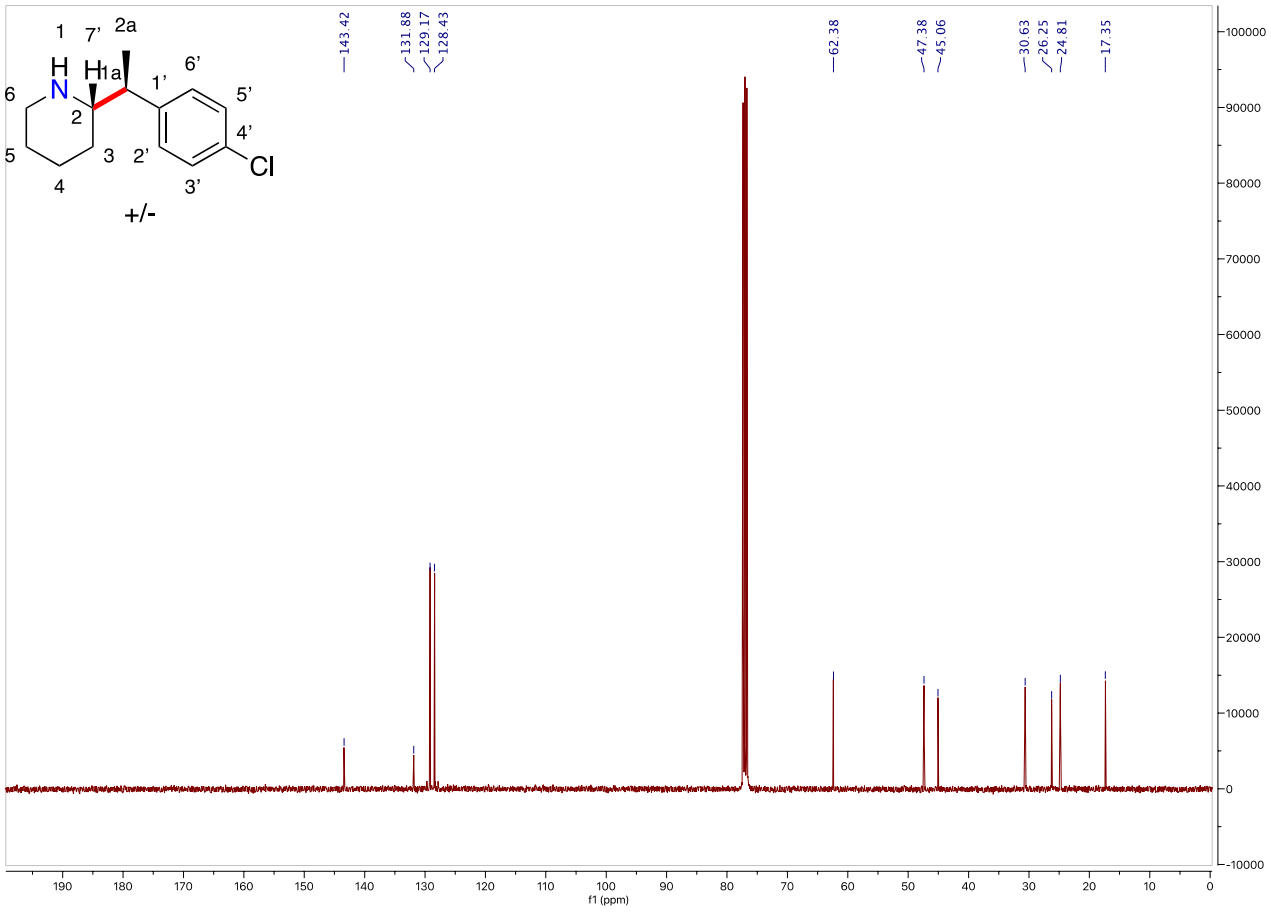


Figure S109: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(1-(4-chlorophenyl)ethyl)piperidine.

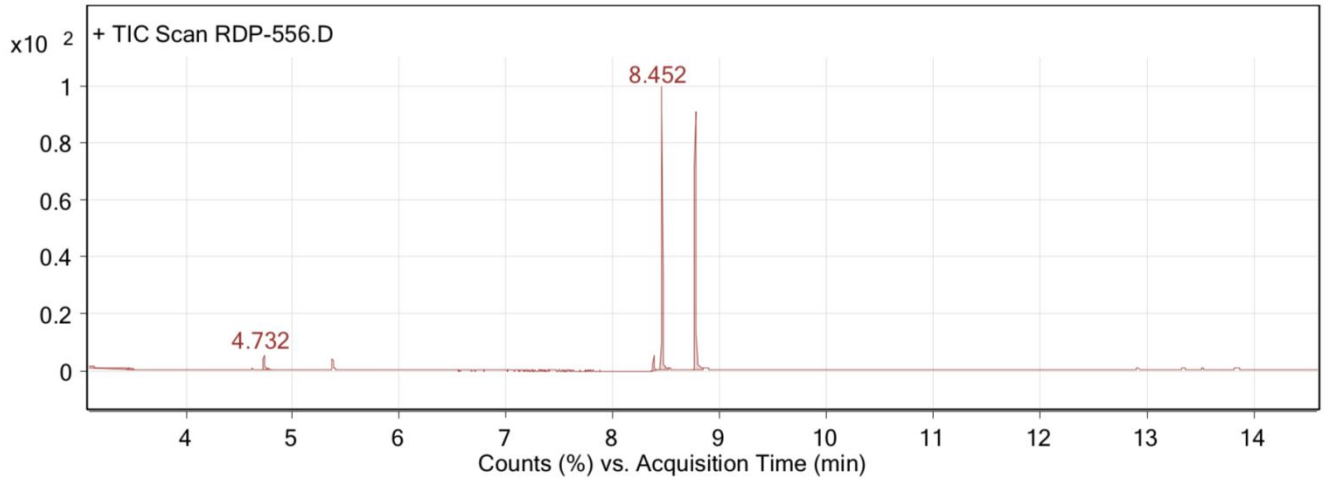


Figure S110: GC-MS for the crude reaction mixture between piperidine and 4-chlorostyrene.

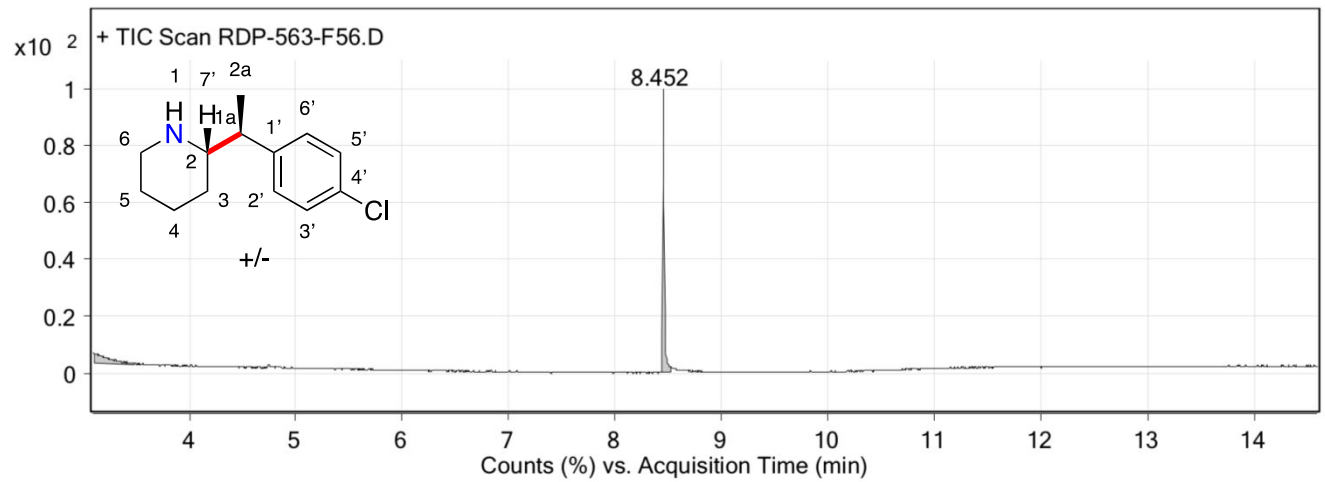


Figure S111: GC-MS report of 2-(1-(4-chlorophenyl)ethyl)piperidine.

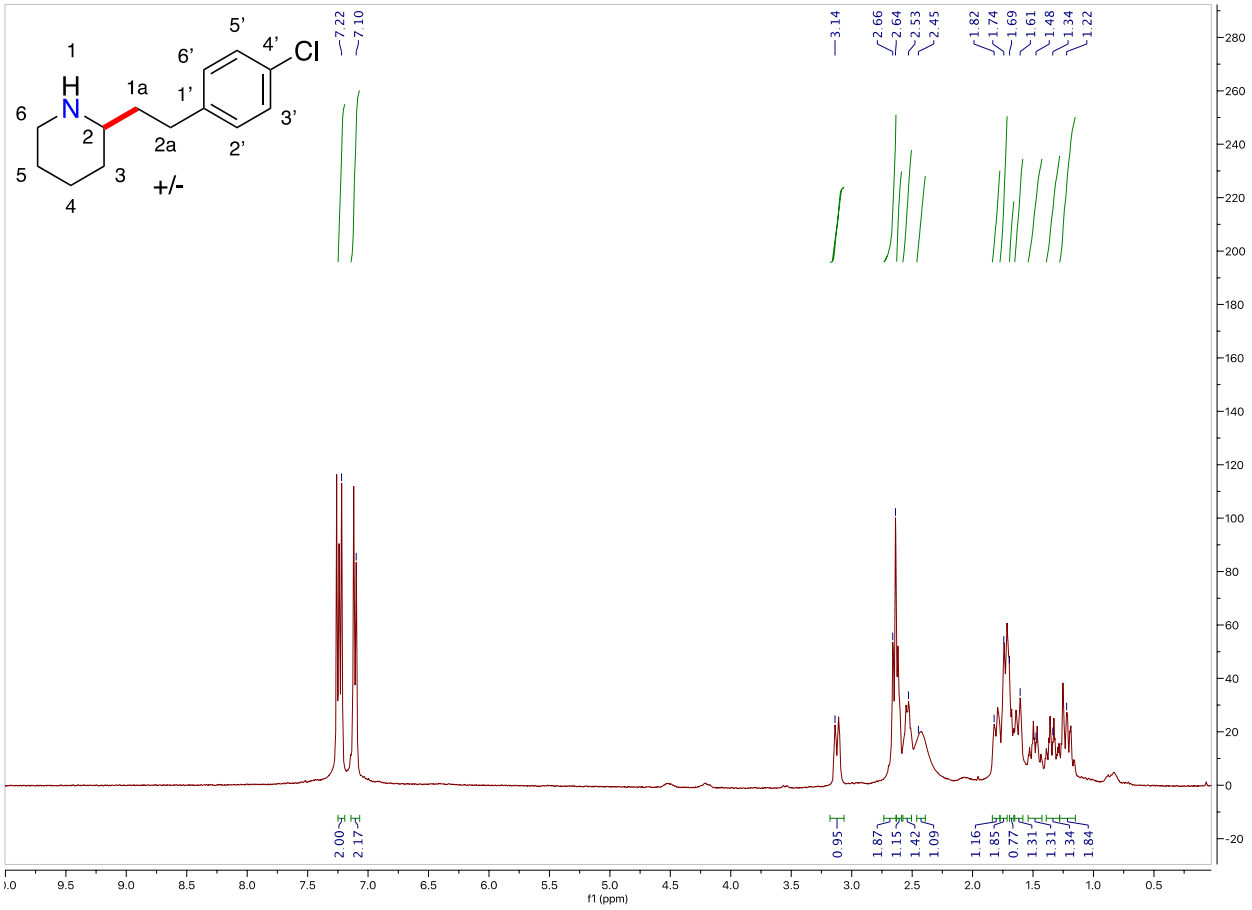


Figure S112: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(4-chlorophenethyl)piperidine.

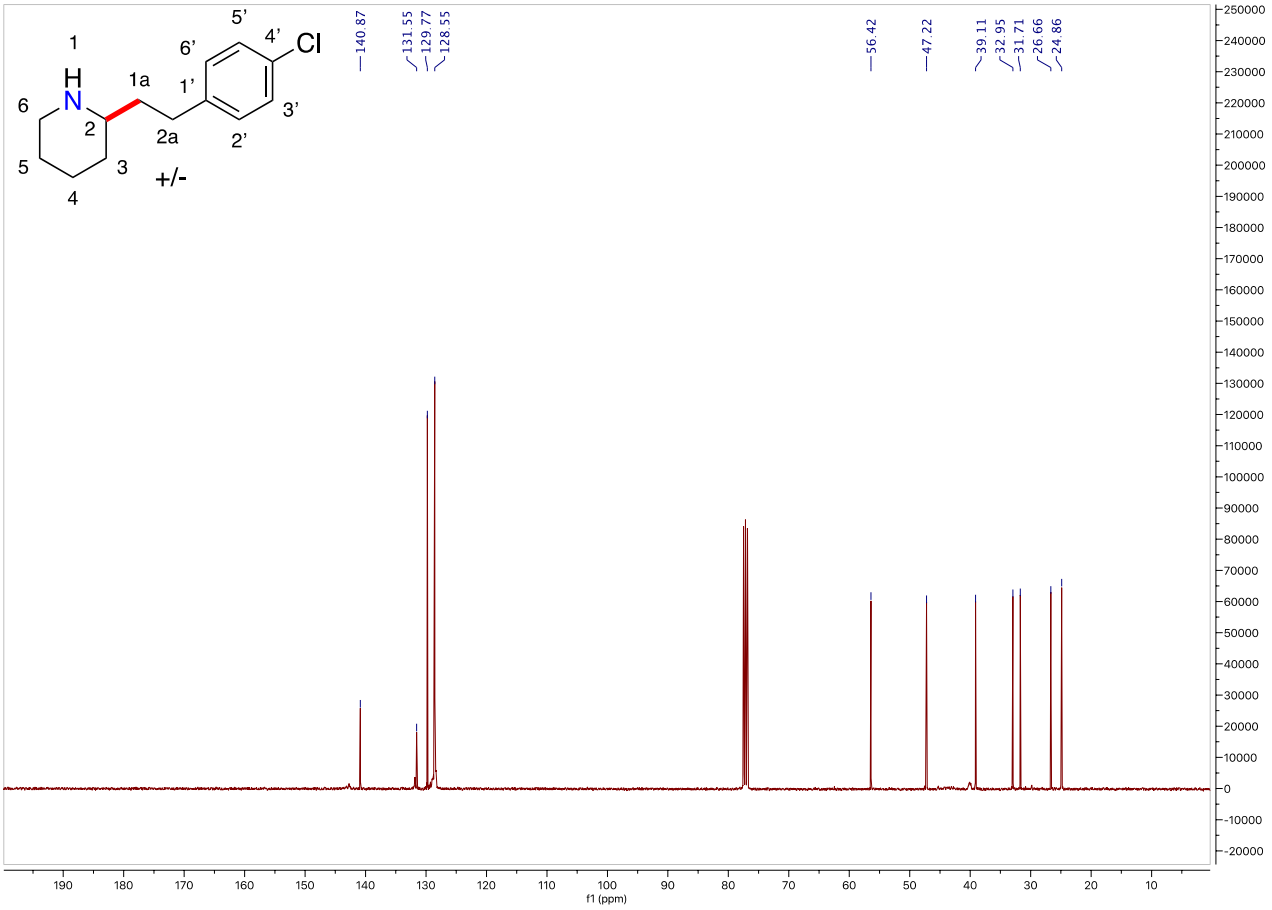


Figure S113: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(4-chlorophenethyl)piperidine.

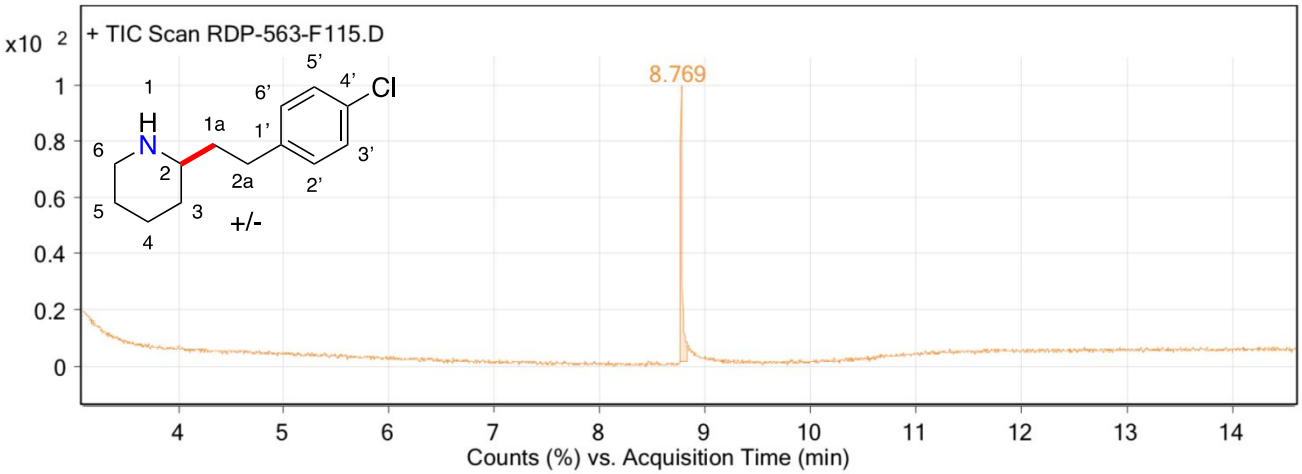
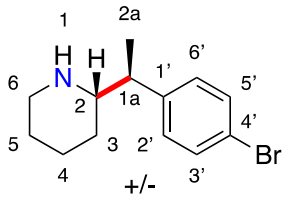
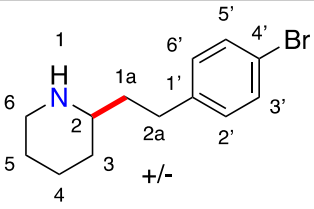


Figure S114: GC-MS report of 2-(4-chlorophenethyl)piperidine.





Synthesis of 2-(1-(4-bromophenyl)ethyl)piperidine and 2-(2-(4-bromophenethyl)piperidine (24 and 25): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), para-bromostyrene (181.9 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 58 % for 2-(1-(4-bromophenyl)ethyl)piperidine and 42 % for 2-(4-bromophenethyl)piperidine by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.40 (m, 2H, 3' and 5'), 7.07 (m, 2H, 2' and 6'), 3.11 (m, 1H, ½ of 6), 2.65 (m, 1H, 1a), 2.59 (m, 1H, ½ of 6), 2.52 (m, 1H, 2), 1.81 (broad s, 1H, NH), 1.71 (m, 1H, ½ of 4), 1.54 (m, 1H, ½ of 5), 1.39 (m, 1H, ½ of 3), 1.34 (m, 1H, ½ of 5), 1.26 (d, J = 1.27, 3H, 2a), 1.22 (m, 1H, ½ of 4), 1.02 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 144.17, 131.47, 129.71, 120.00, 62.41, 47.53, 45.32, 30.84, 26.51, 25.00, 17.32 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}BrN$ [M+H$^+$]: 267.0623 Found: 267.0626.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39 (m, 2H, 3' and 5'), 7.04 (m, 2H, 2' and 6'), 3.11 (m, 1H, ½ of 6) 2.82 (broad s 1H, NH), 2.65 (m, 1H, ½ of 6), 2.60 (m, 2H, 2a), 2.52 (m, 1H, 2), 1.79 (m, 1H, ½ of 4), 1.73 (m, 1H, ½ of 3), 1.67 (m, 2H, 1a), 1.61 (m, 1H, ½ of 5), 1.45 (m, 1H, ½ of 5), 1.36 (m, 1H, ½ of 4), 1.18 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 141.22, 131.56, 130.23, 119.65, 56.34, 46.88, 38.58, 32.46, 31.70, 26.30, 24.64 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}BrN$ [M+H$^+$]: 267.0623 Found: 267.0625.

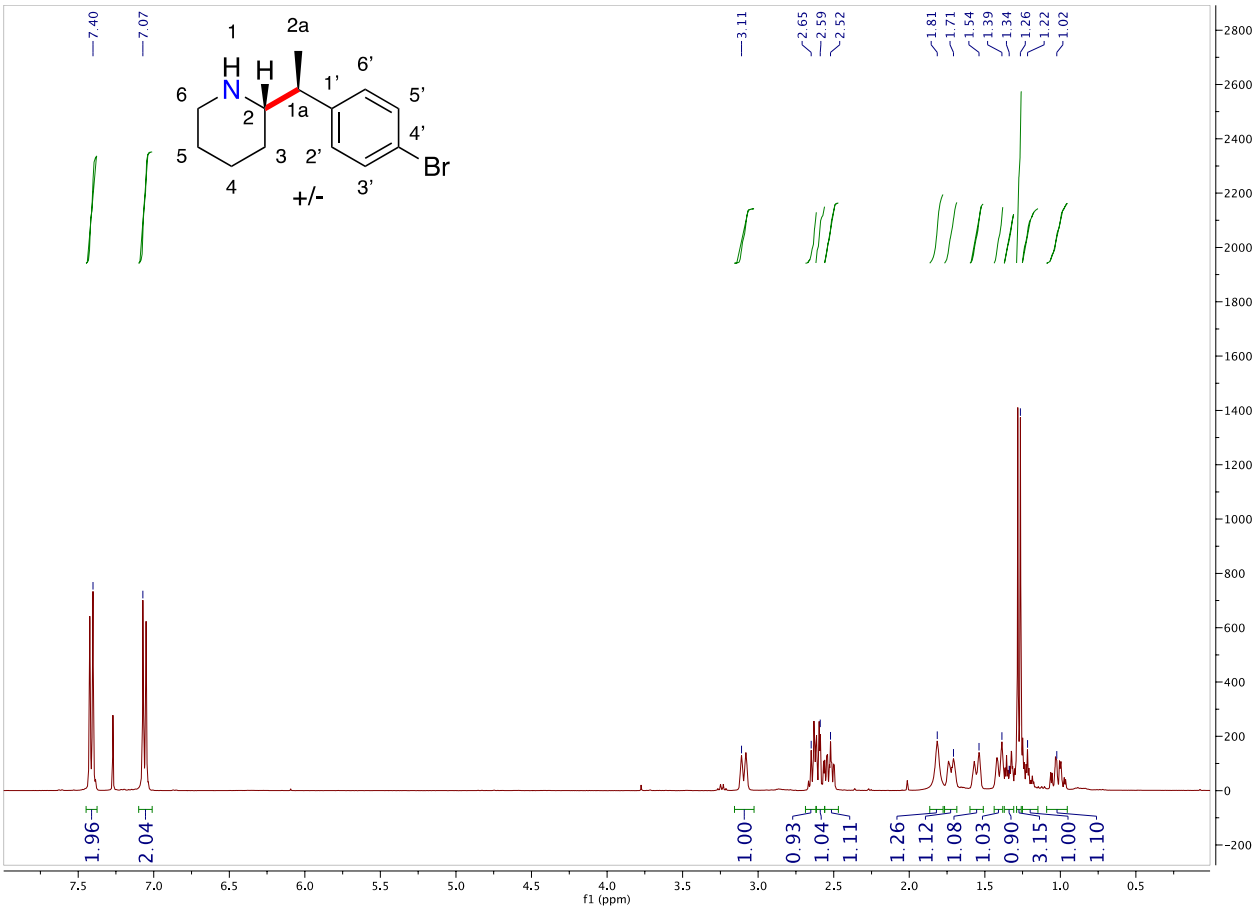


Figure S115: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(4-bromophenyl)ethyl)piperidine.

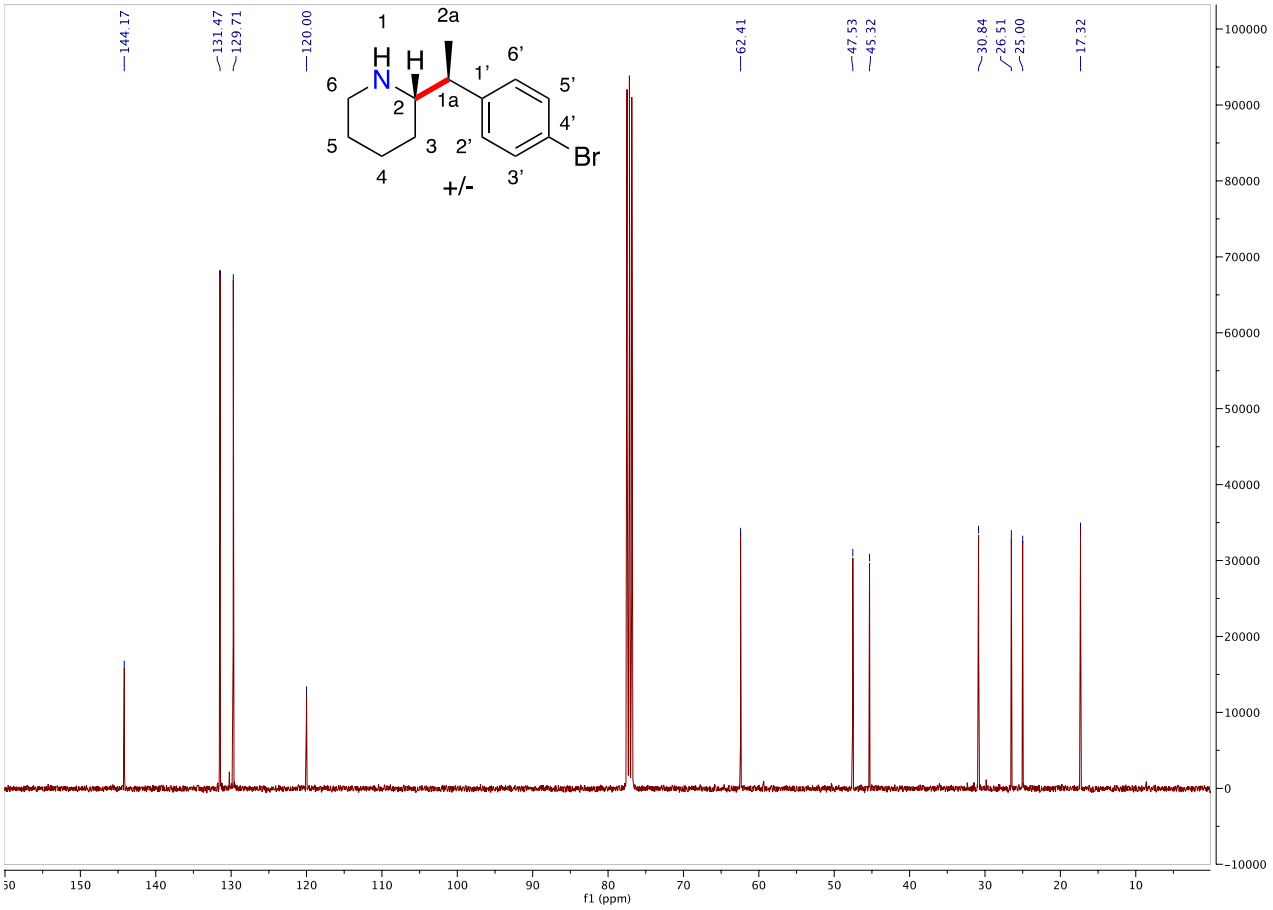


Figure S116: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(4-bromophenyl)ethyl)piperidine.

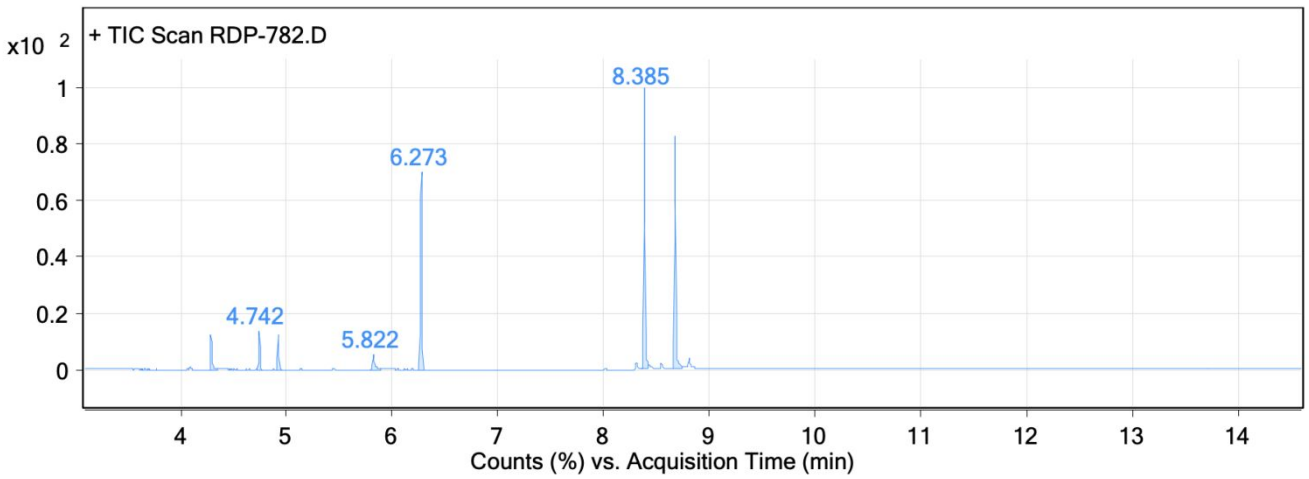


Figure S117: GC-MS for the crude reaction mixture between piperidine and para-bromostyrene.

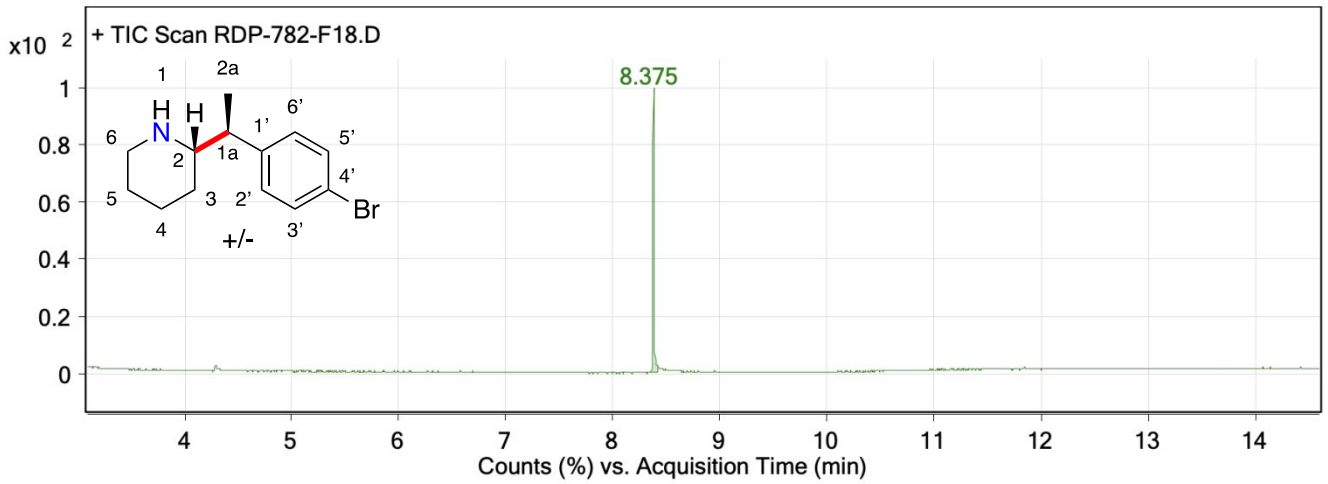


Figure S118: GC-MS report for 2-(1-(4-bromophenyl)ethyl)piperidine.

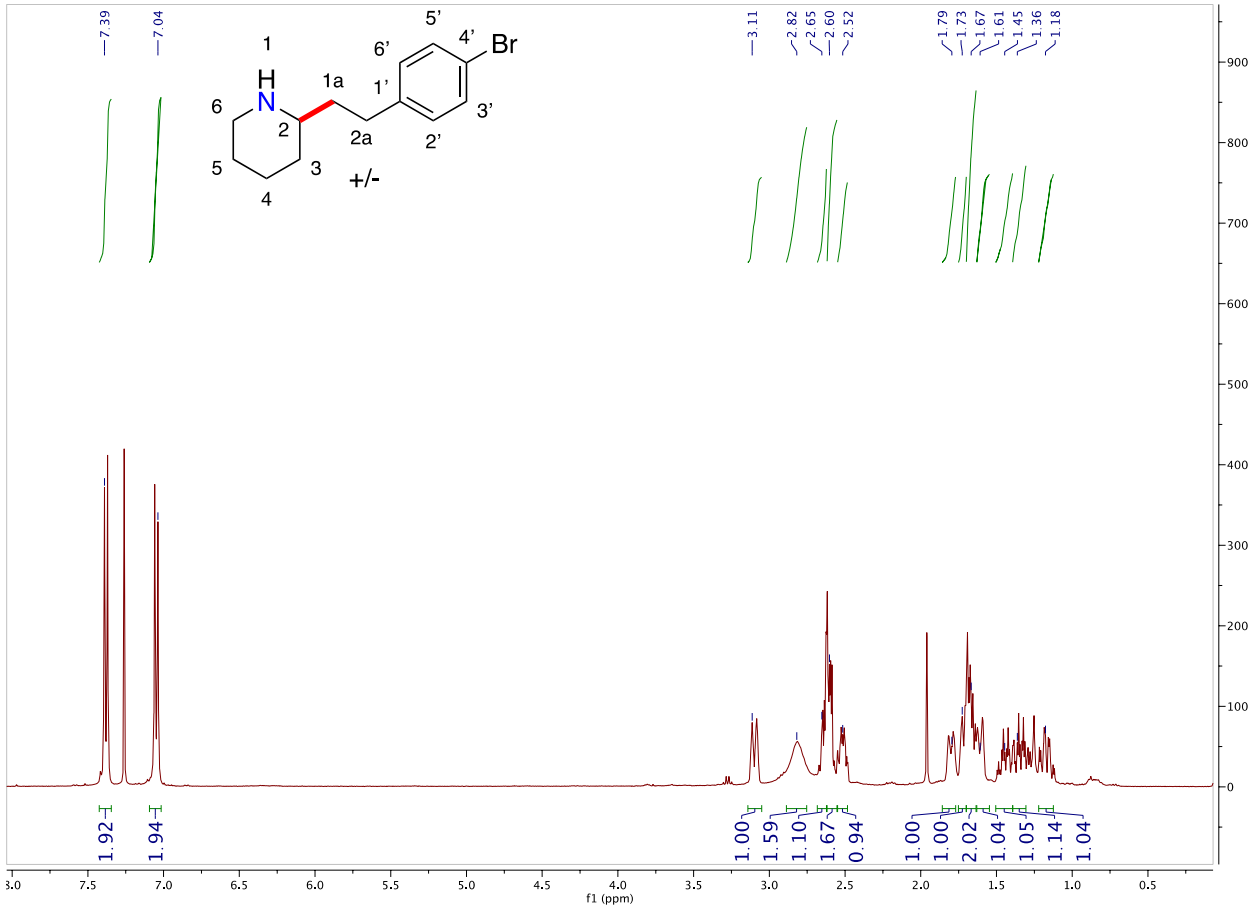


Figure S119: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(4-bromophenethyl)piperidine.

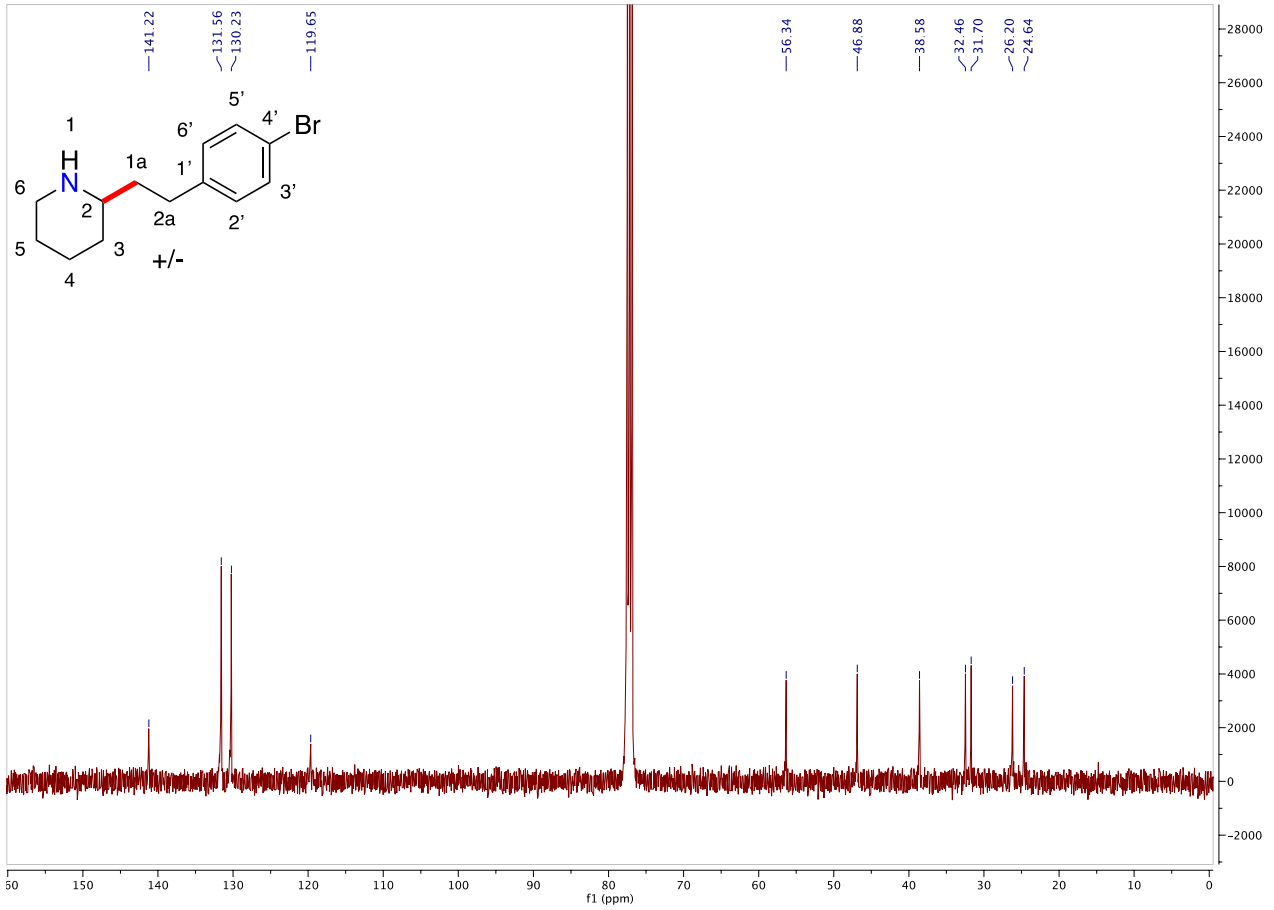


Figure S120: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(4-bromophenethyl)piperidine.

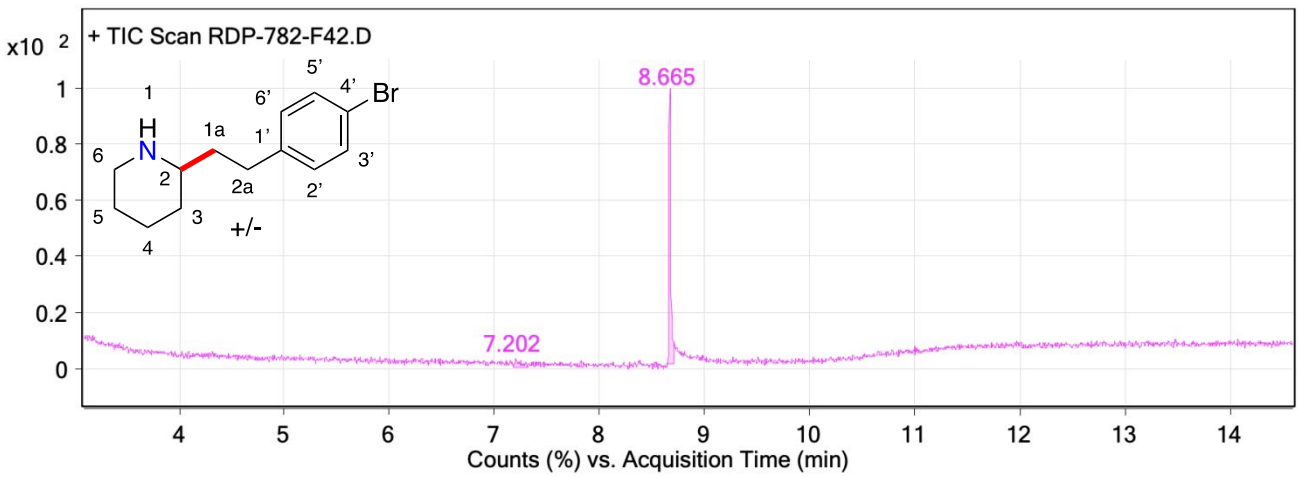
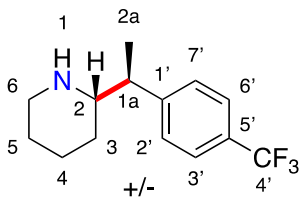
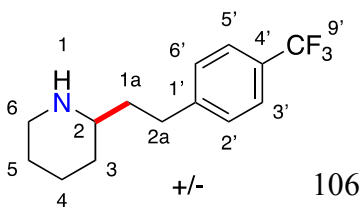


Figure S121: GC-MS report for 2-(4-bromophenethyl)piperidine.





Synthesis of 2-(1-(4-(trifluoromethyl)phenyl)ethyl)piperidine and

2-(4-(trifluoromethyl)phenethyl)piperidine (26 and 27): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), para-trifluoromethylstyrene (172.05 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 37 % for 2-(1-(4-(trifluoromethyl)phenyl)ethyl)piperidine and 55 % for 2-(4-(trifluoromethyl)phenethyl)piperidine by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.53 (m, 2H, 3' and 6'), 7.28 (m, 2H, 2' and 7'), 3.12 (m, 1H, ½ of 6), 2.74 (m, 1H, 1a), 2.61 (overlapping dt, 1H, ½ of 6), 2.57 (m, 1H, 2), 2.02 (broad s, 1H, NH), 1.70 (m, 1H, ½ of 4), 1.56 (m, 1H, ½ of 5), 1.38 (m, 1H, ½ of 3), 1.34 (m, 1H, ½ of 5), 1.31 (d, J = 1.31, 3H, 2a), 1.22 (m, 1H, ½ of 4), 1.02 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 149.24 , 128.76 (q, J = 32), 128.54, 128.29 (q, J = 271.26), 125.36, 63.33, 47.45, 45.73, 30.78, 26.32, 25.88, 17.42 ppm. HRMS (ESI): *m/z* calcd for $C_{14}H_{18}F_3N$ [M+H$^+$]: 257.2391 Found: 257.1395.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.53 (m, 2H, 2' and 3'), 7.29 (m, 2H, 3' and 5'), 3.09 (m, 1H, ½ of 6), 2.72 (m, 2H, 2a), 2.62 (m, 1H, ½ of 6), 2.50 (m, 1H, 2), 2.00 (broad s, 1H, NH), 1.80 (m, 1H, ½ of 4), 1.72 (m, 1H, ½ of 3), 1.68 (m, 2H, 1a), 1.60 (m, 1H, ½ of 5), 1.41 (m, 1H, ½ of 5), 1.35 (m, 1H, ½ of 4), 1.14 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 146.63, 128.75 (q, J = 32.42), 125.84 (q, J = 4.063), 125.44 (q, J = 272.85), 56.43, 47.20, 38.93, 32.95, 32.24, 25.66, 24.85 ppm. HRMS (ESI): *m/z* calcd for $C_{14}H_{18}F_3N$ [M+H$^+$]: 257.2391 Found: 257.1394.

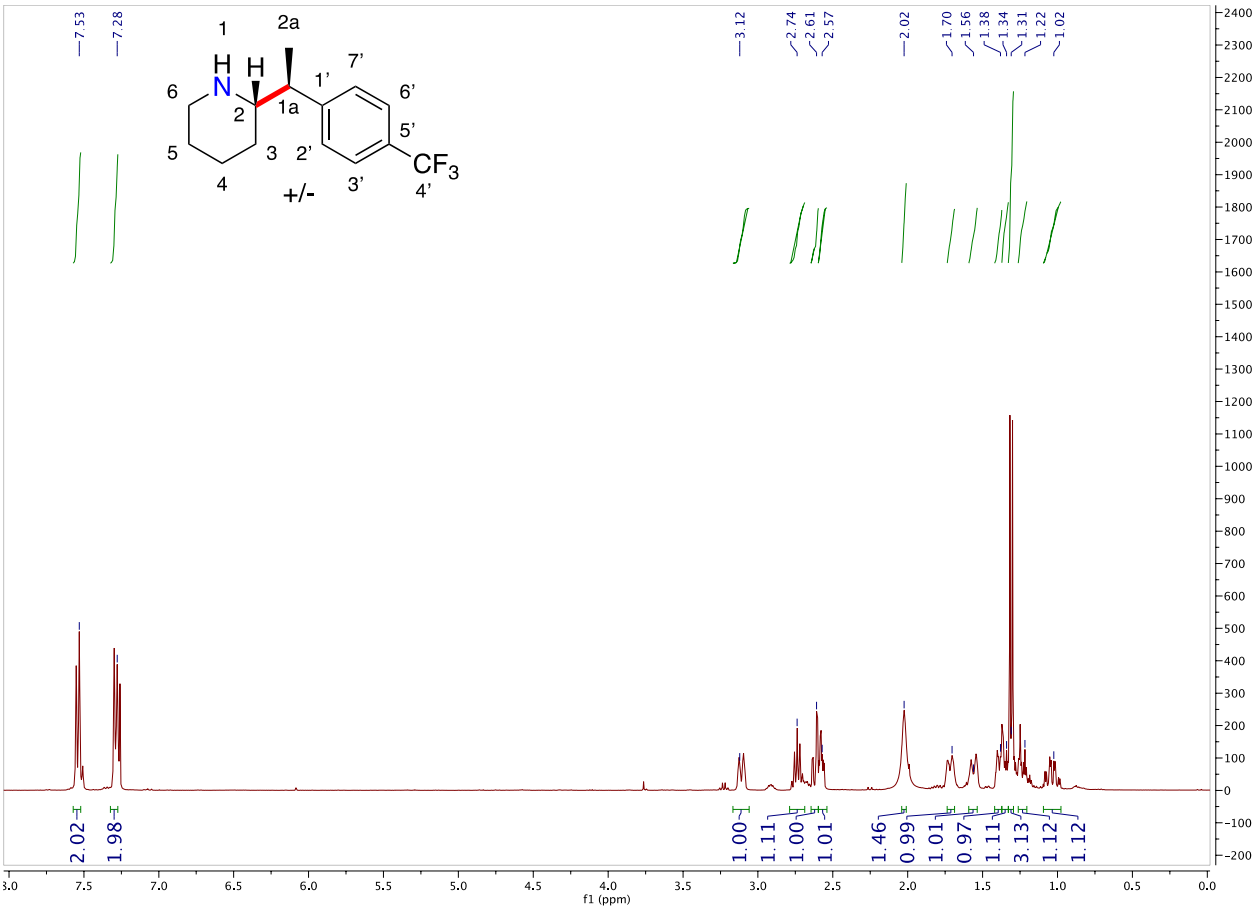


Figure S122: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(4-(trifluoromethyl)phenyl)ethyl)piperidine.

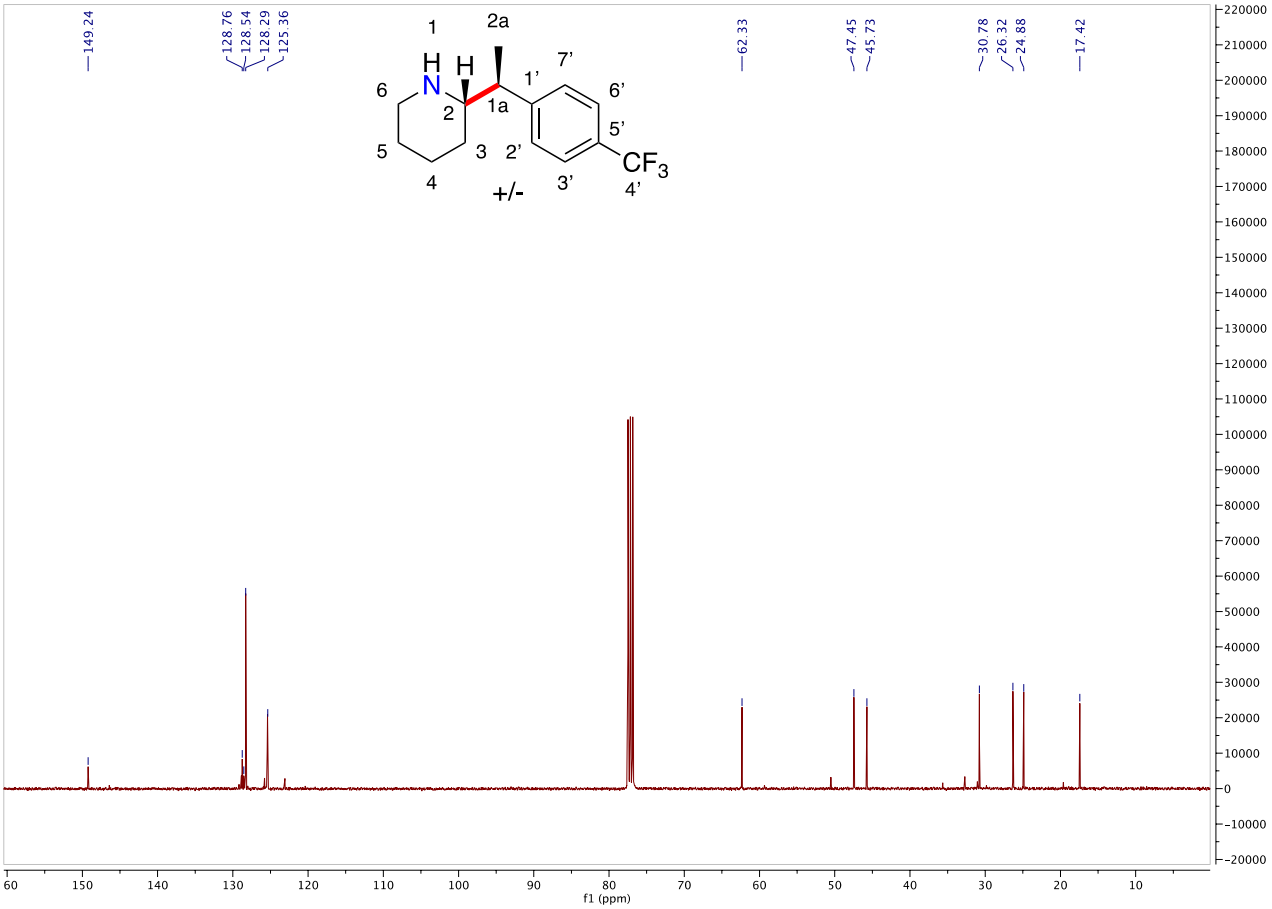


Figure S123: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(4-(trifluoromethyl)phenyl)ethyl)piperidine.

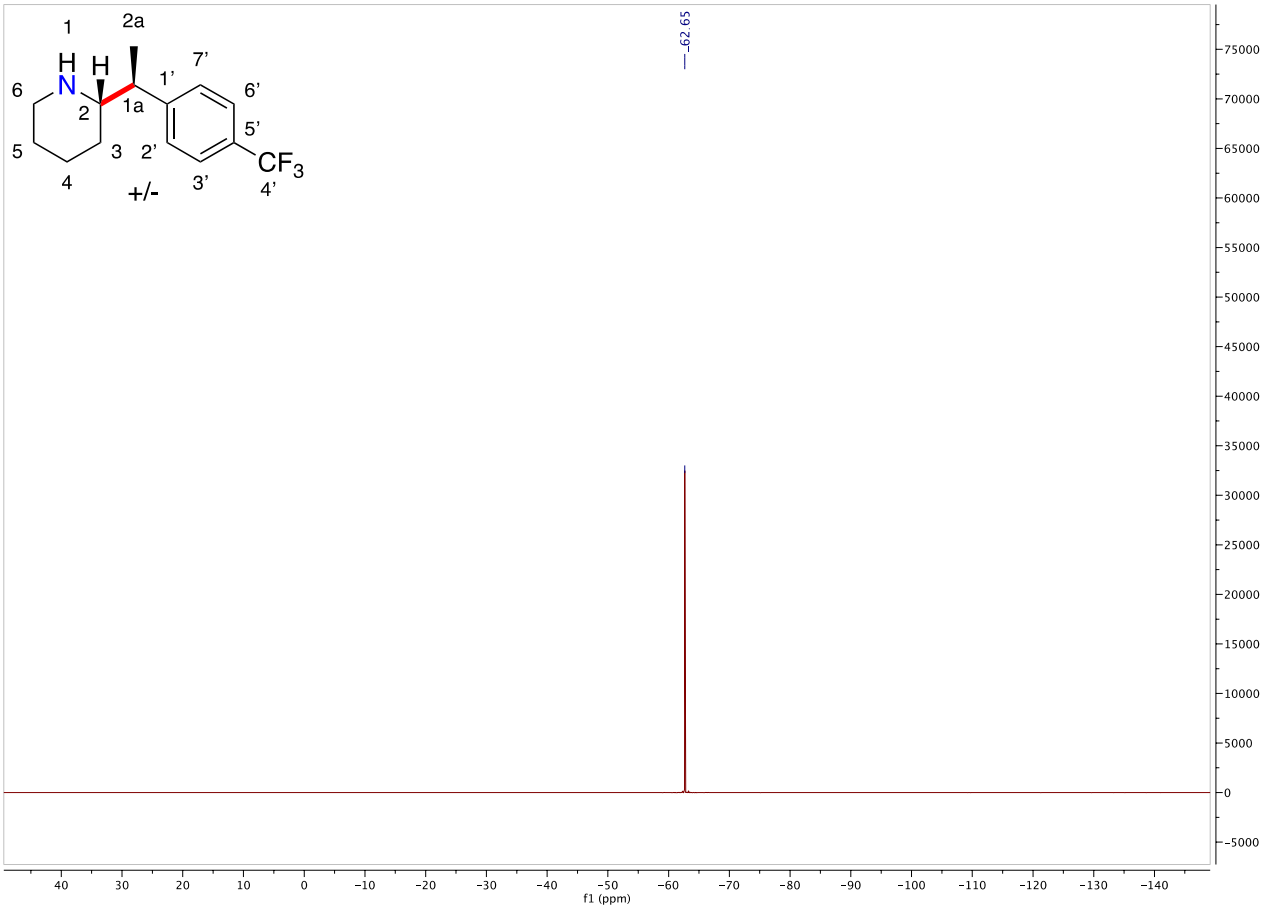


Figure S124: ^{19}F NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(4-(trifluoromethyl)phenyl)ethyl)piperidine.

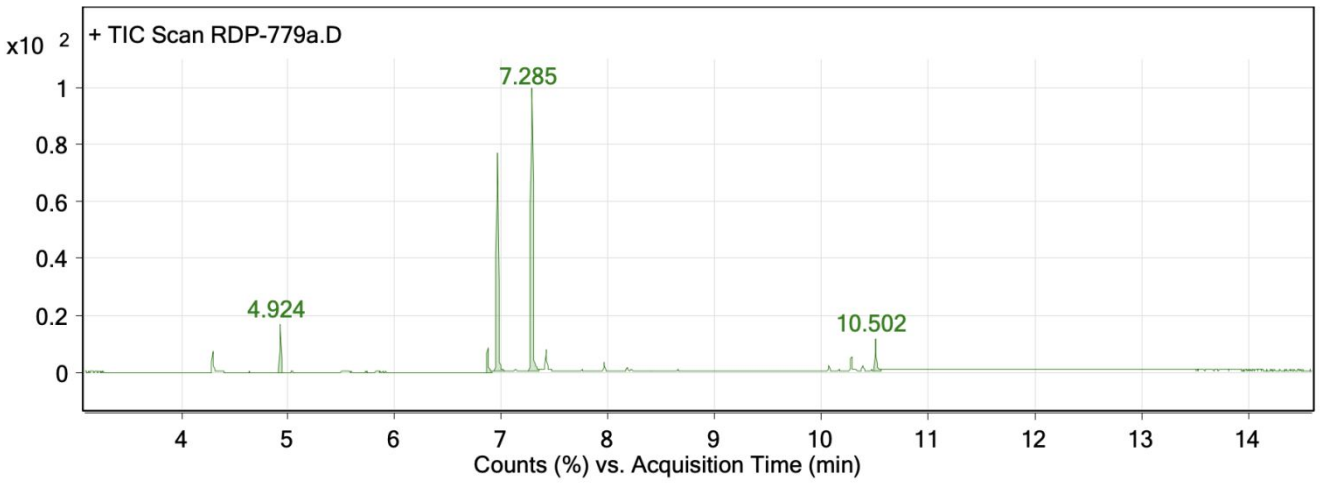


Figure S125: GC-MS for the crude reaction mixture between piperidine and para-trifluoromethylstyrene.

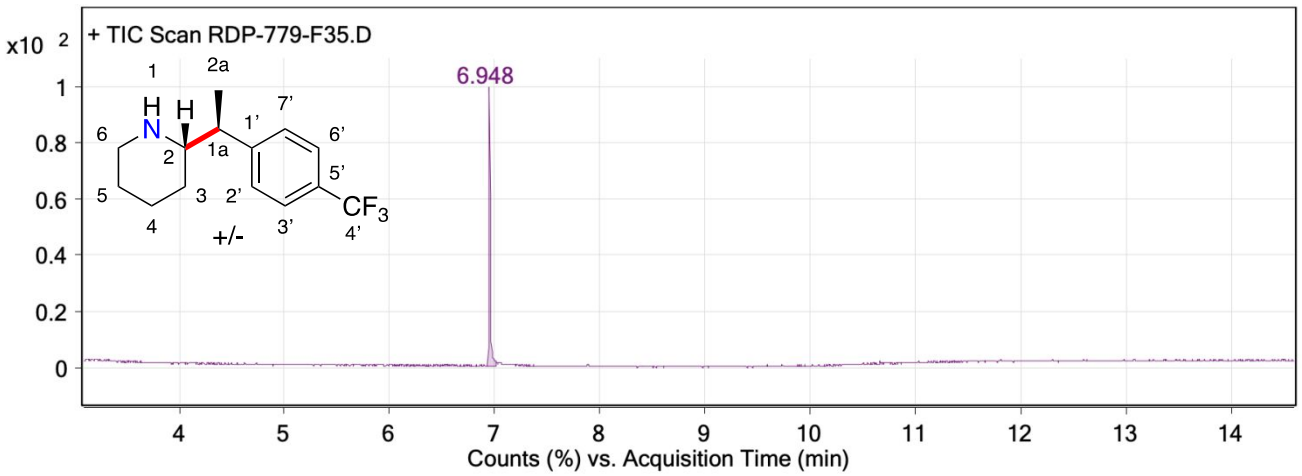


Figure S126: GC-MS report for 2-(1-(4-(trifluoromethyl)phenyl)ethyl)piperidine.

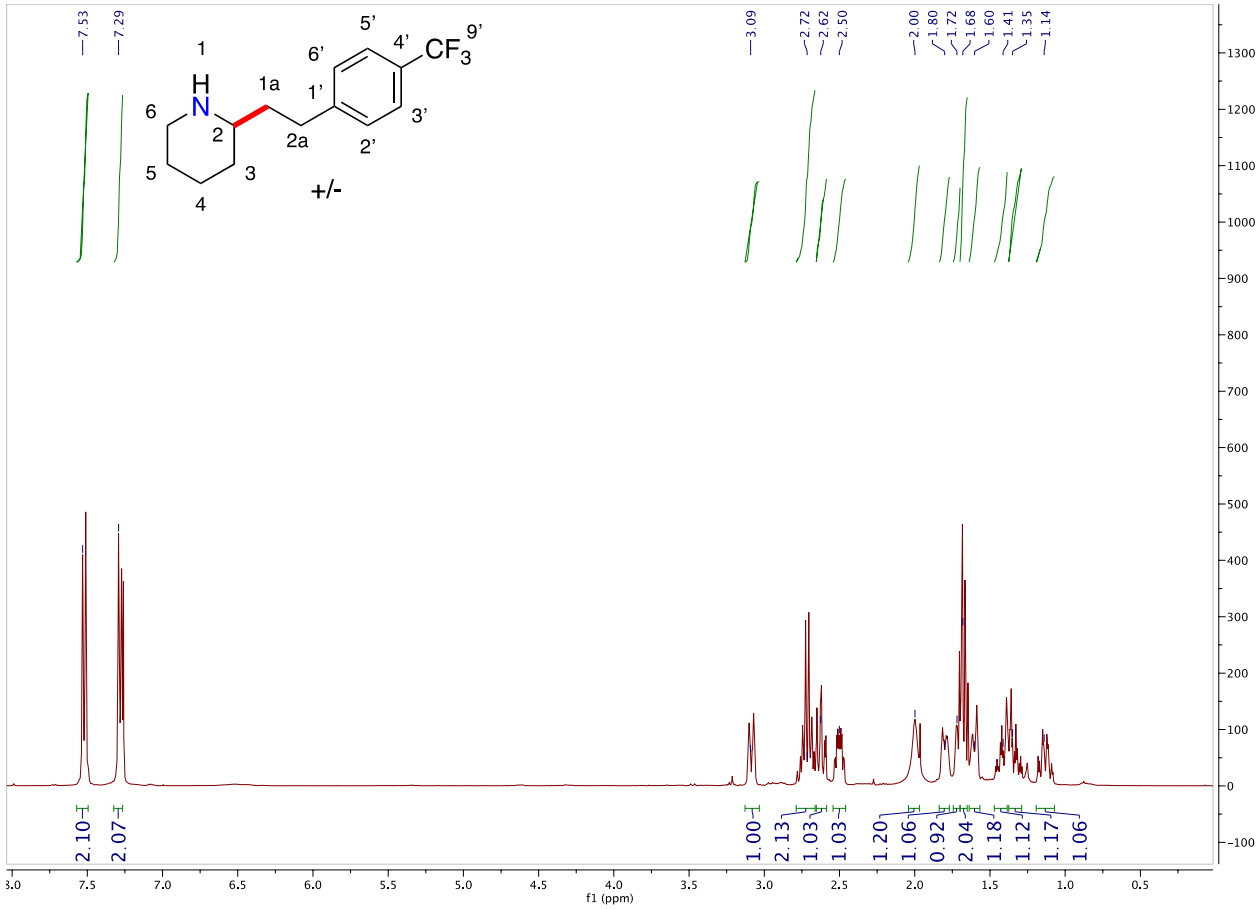


Figure S127: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(4-(trifluoromethyl)phenethyl)piperidine.

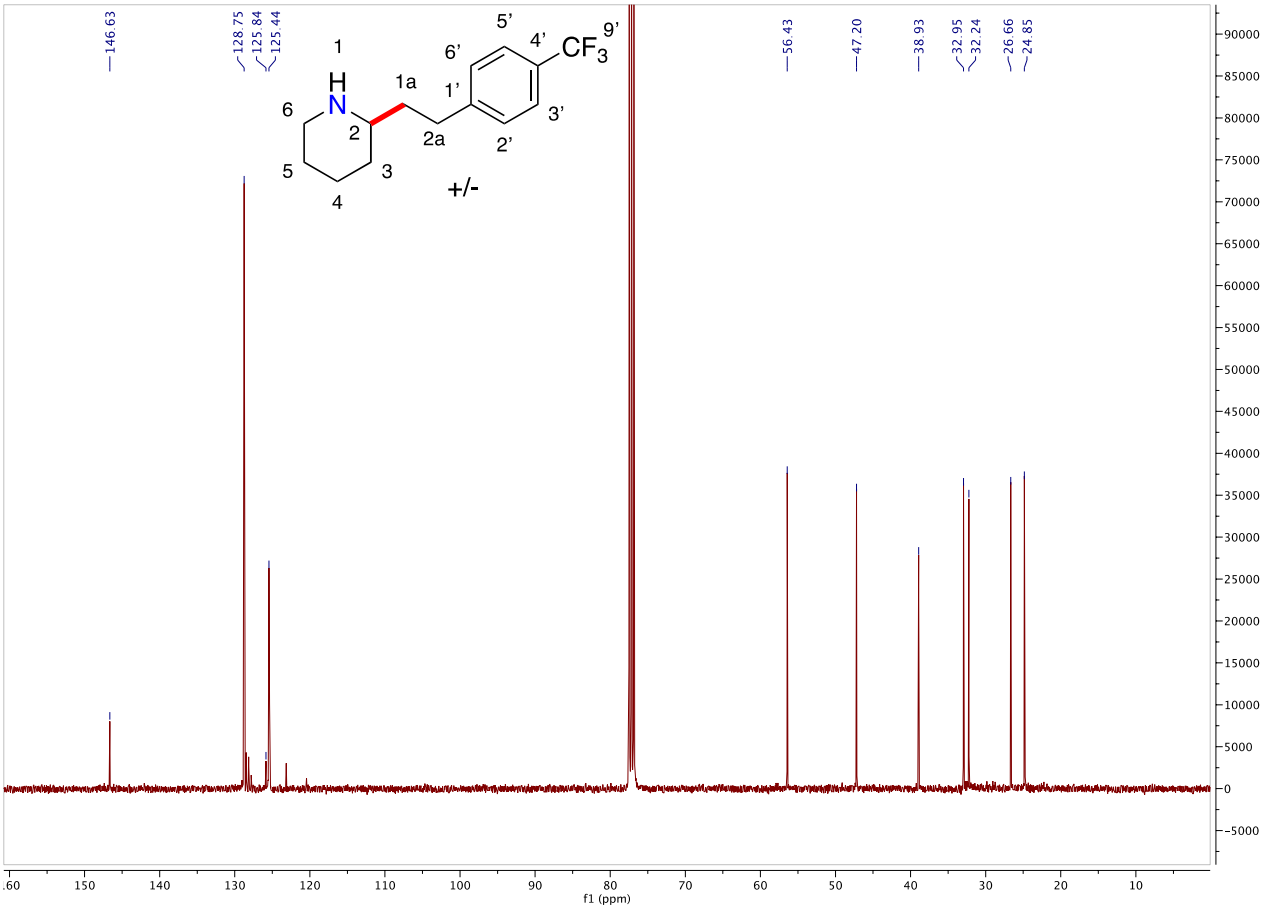


Figure S128: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(4-(trifluoromethyl)phenethyl)piperidine.

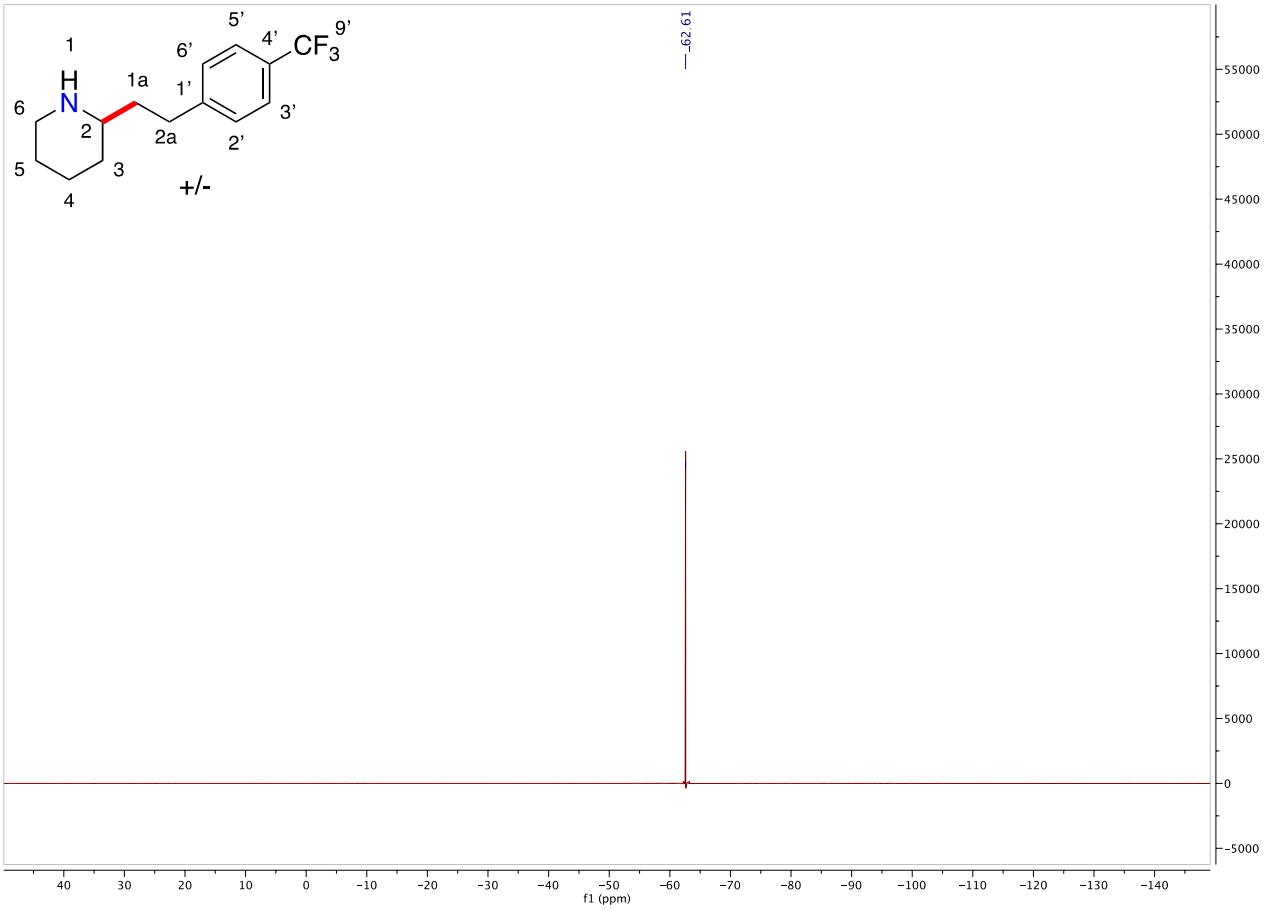


Figure S129: ^{19}F NMR spectrum (400 MHz, $CDCl_3$, 298 K) 2-(4-(trifluoromethyl)phenethyl)piperidine.

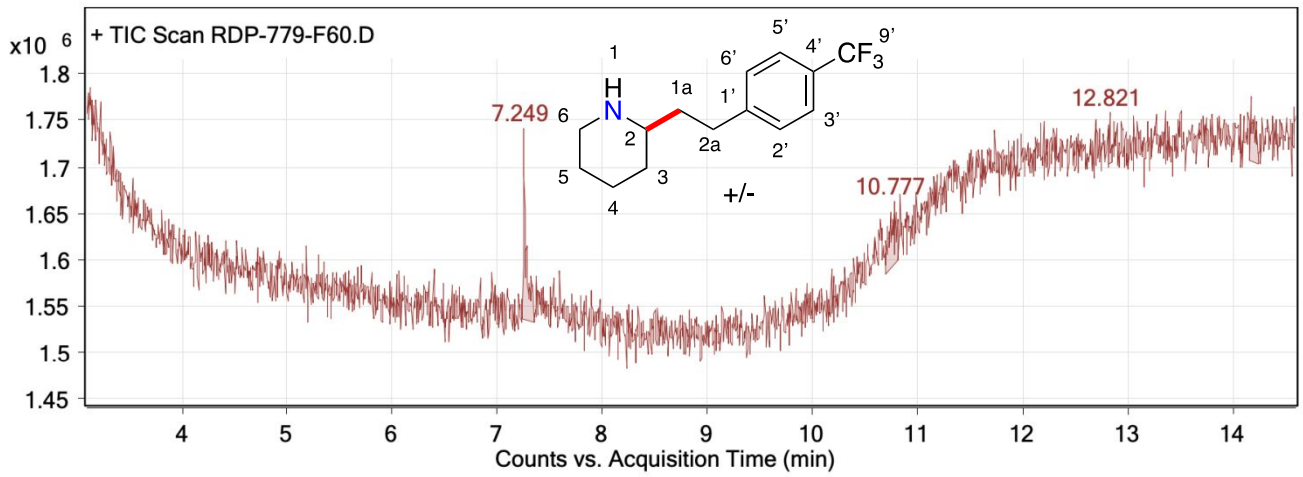
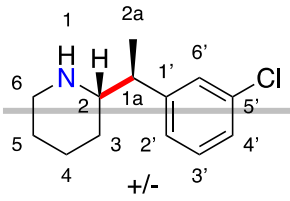
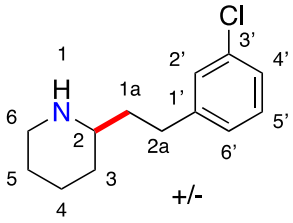


Figure S130: GC-MS report for 2-(4-(trifluoromethyl)phenethyl)piperidine.





Synthesis of 2-(1-(3-chlorophenyl)ethyl)piperidine and 2-(3-chlorophenethyl)piperidine (28 and 29): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), meta-chlorostyrene (138.59 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 45 % for 2-(1-(3-chlorophenyl)ethyl)piperidine and 53 % for 2-(3-chlorophenethyl)piperidine by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.23 (m, 1H, 3'), 7.18 (m, 1H, 4'), 7.16 (m, 1H, 6'), 7.05, (m, 1H, 2'), 3.09 (m, 1H, ½ of 6), 2.63 (m, 1H, 1a), 2.59 (m, 1H, ½ of 6), 2.53 (m, 1H, 2), 2.00 (broad s, 1H, NH), 1.72 (m, 1H, ½ of 4), 1.54 (m, 1H, ½ of 5), 1.41 (m, 1H, ½ of 3), 1.34 (m, 1H, ½ of 5), 1.27 (d, J = 1.28, 3H, 2a), 1.23 (m, 1H, ½ of 4), 1.02 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 147.20, 134.12, 129.55, 127.90, 126.41, 126.13, 62.24, 47.37, 45.54, 30.76, 26.30, 24.83, 17.27 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}ClN$ [M+H$^+$]: 223.1128 Found: 223.1135.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.19 (m, 1H, 4'), 7.17 (m, 1H, 2'/6'), 7.16 (m, 1H, 2'/6'), 7.05 (m, 1H, 5'), 3.12 (m, 1H, ½ of 6), 2.65 (m, 2H, 2a), 2.63 (m, 1H, ½ of 6), 2.54 (m, 1H, 2), 1.81 (m, 1H, ½ of 4), 1.73 (m, 1H, ½ of 3), 1.71 (m, 2H, 1a), 1.60 (m, 1H, ½ of 5), 1.47 (m, 1H, ½ of 5), 1.35, (m, 1H, ½ of 4), 1.20 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 144.13, 134.13, 129.65, 128.48, 126.54, 126.04, 56.31, 46.73, 38.25, 32.21, 31.82, 25.95, 24.44 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}ClN$ [M+H$^+$]: 223.1128 Found: 223.1137.

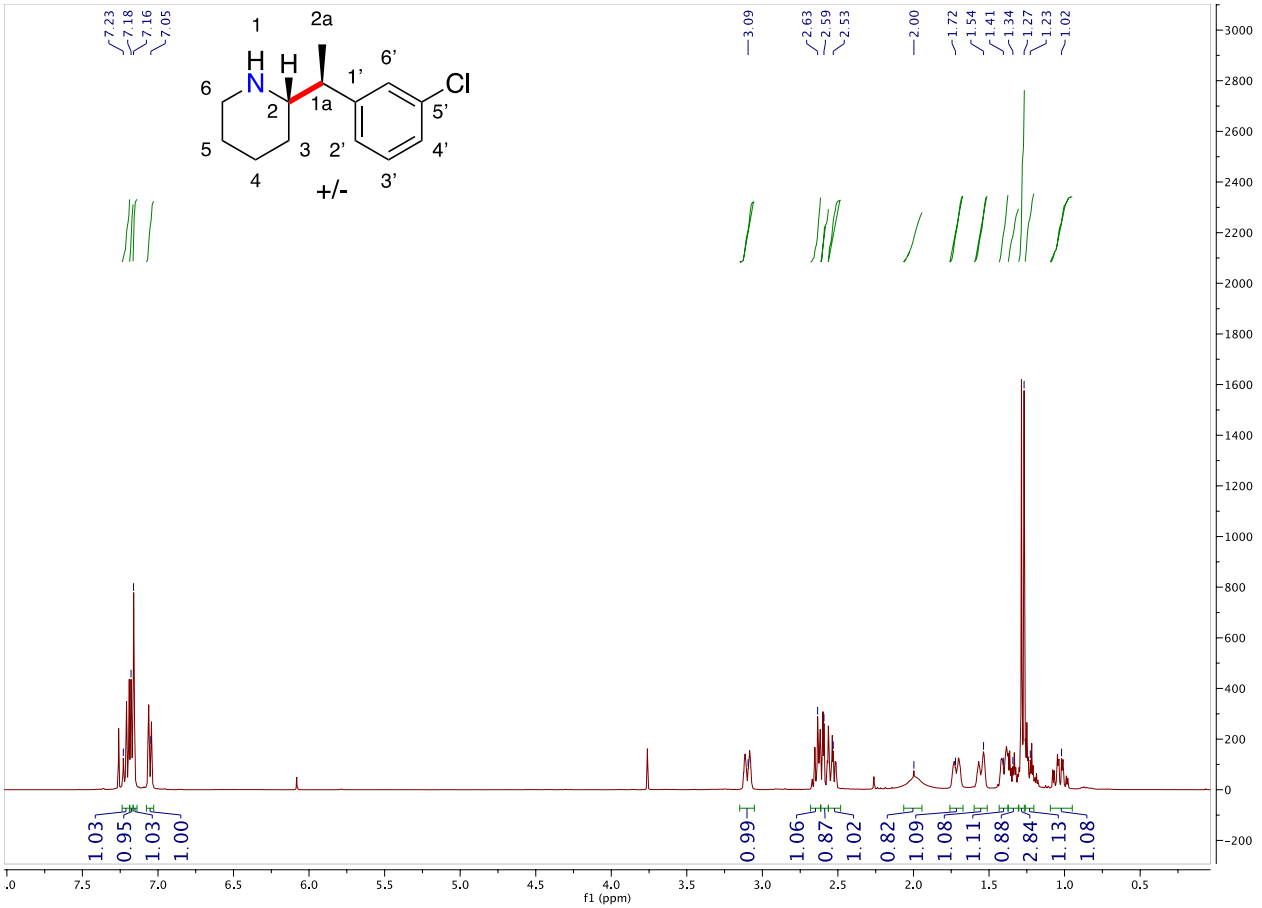


Figure S131: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(3-chlorophenyl)ethyl)piperidine.

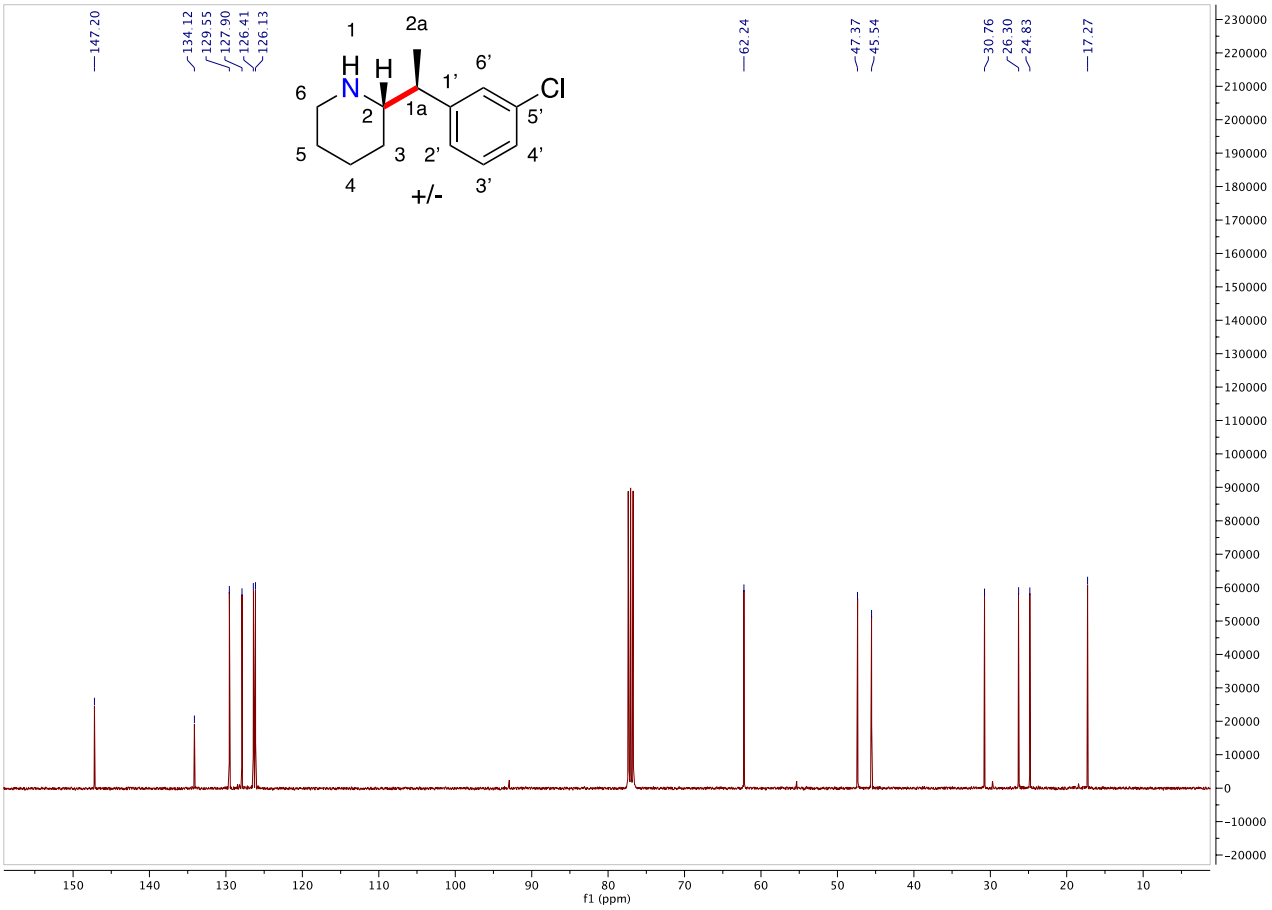


Figure S132: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(1-(3-chlorophenyl)ethyl)piperidine.

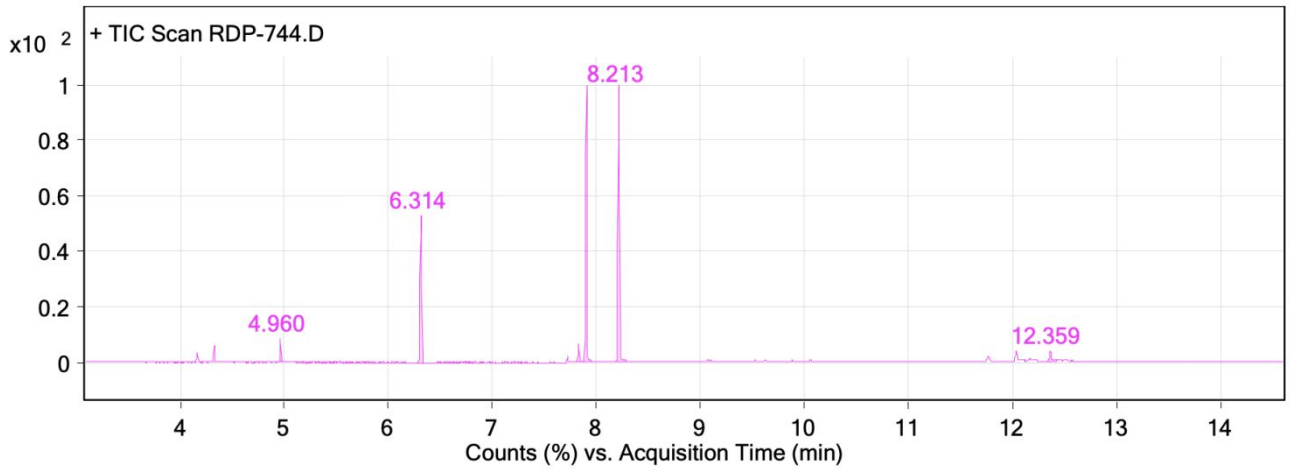


Figure S133: GC-MS for the crude reaction mixture between piperidine and meta-chlorostyrene.

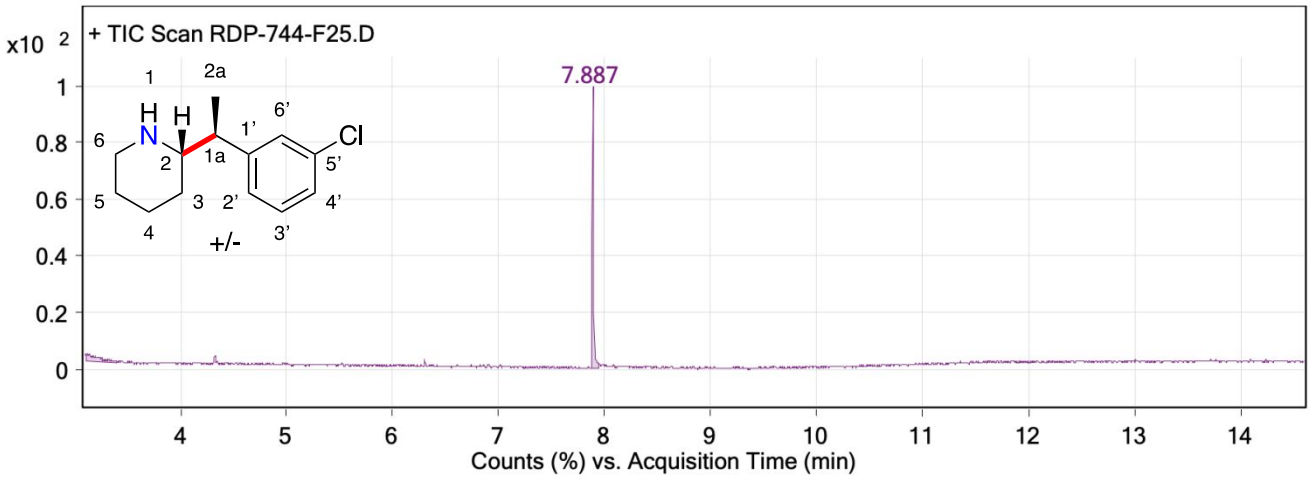


Figure S134: GC-MS report for 2-(1-(3-chlorophenyl)ethyl)piperidine.

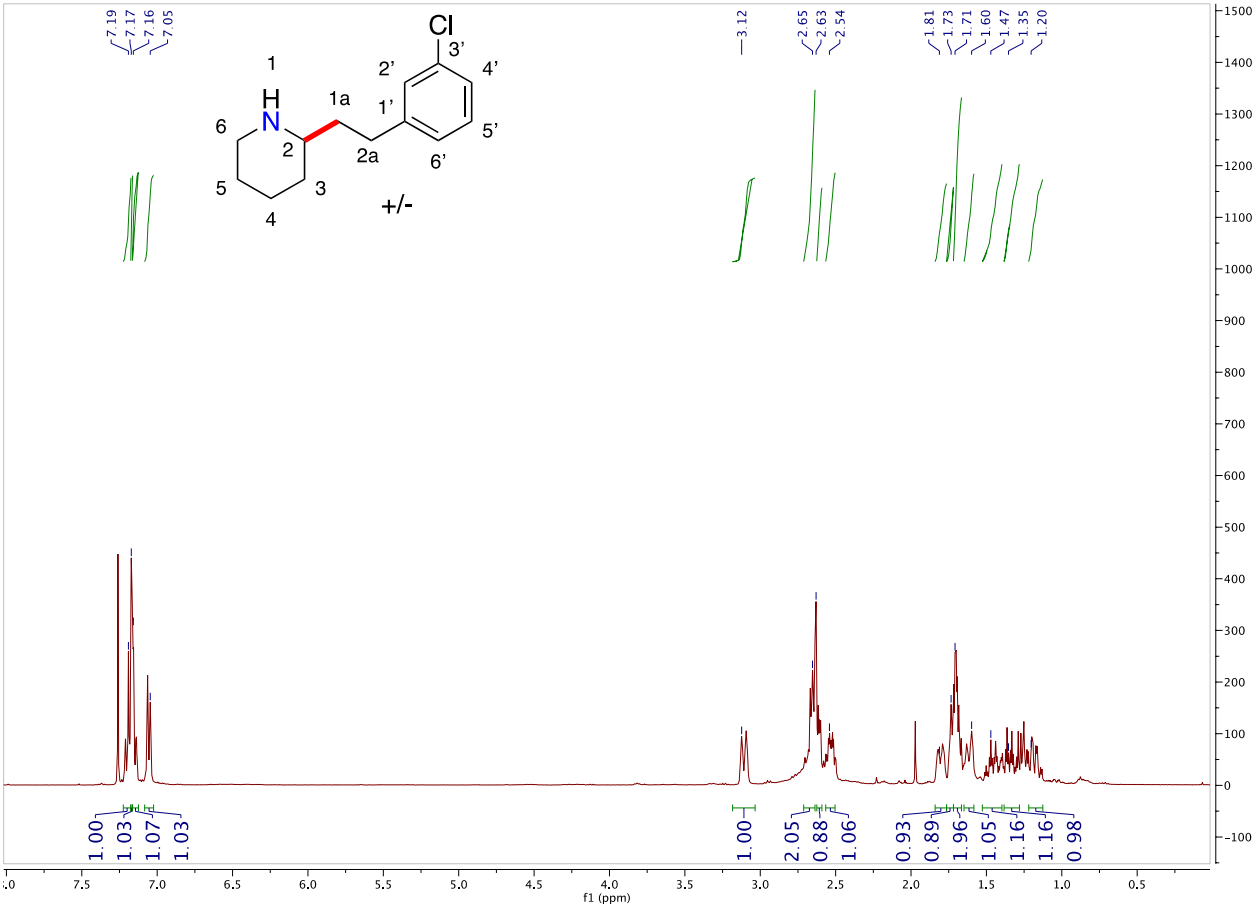


Figure S135: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(3-chlorophenethyl)piperidine.

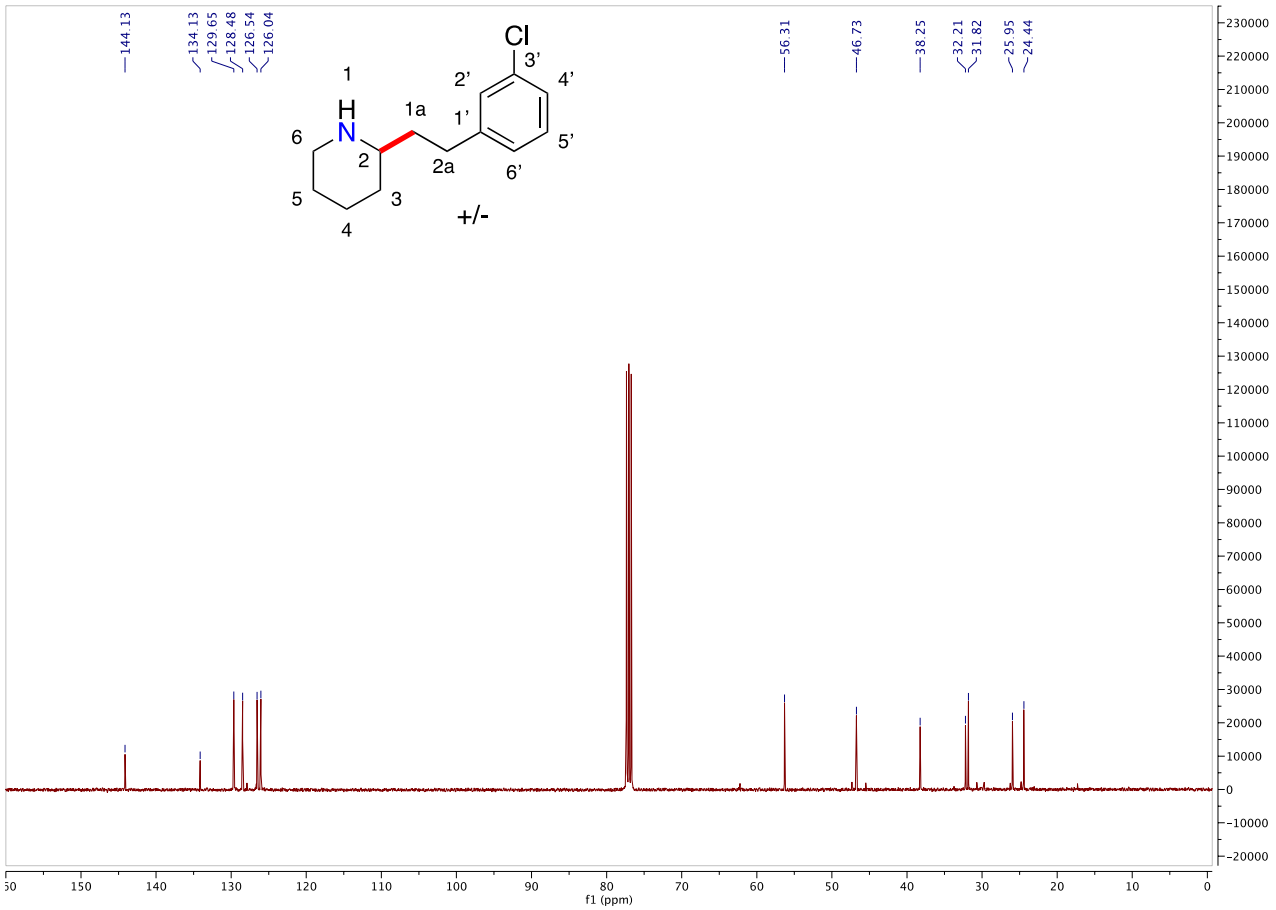


Figure S136: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) 2-(3-chlorophenethyl)piperidine.

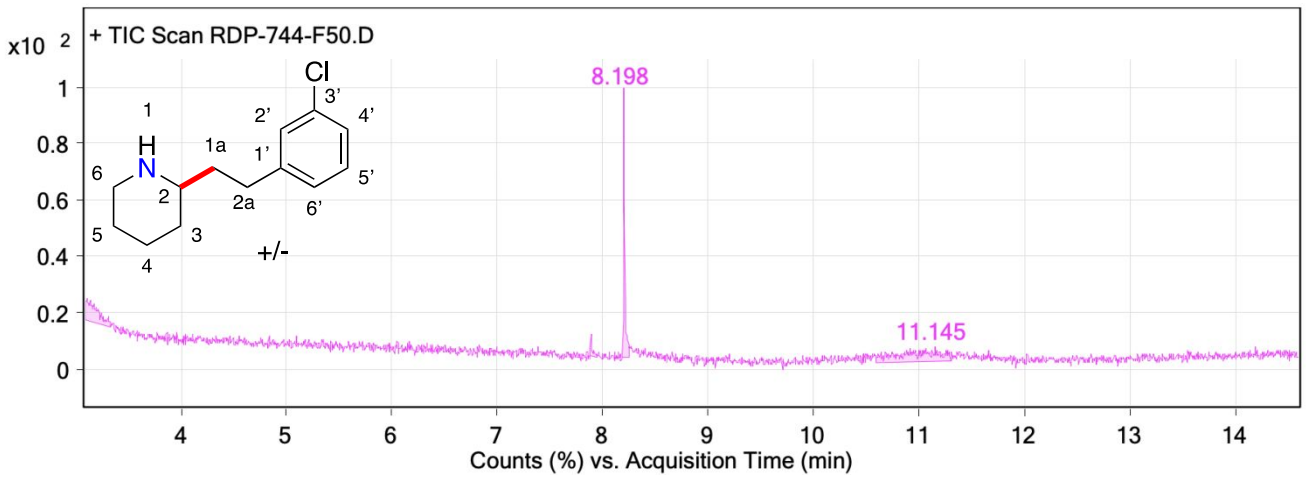
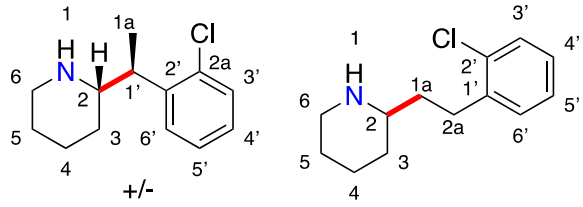


Figure S137: GC-MS report for 2-(3-chlorophenethyl)piperidine.



Synthesis of 2-(1-(2-chlorophenyl)ethyl)piperidine and 2-(1-(2-chlorophenyl)ethyl)piperidine (30 and 31): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), 2-chlorostyrene (138.59 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 51 % for 2-(1-(2-chlorophenyl)ethyl)piperidine and 49 % for)ethyl)piperidine and 2 by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.57 (m, 1H, 3'), 7.47 (m, 1H, 5'/6'), 7.43 (m, 1H, 5'/6'), 7.33 (m, 1H, 4'), 3.52 (m, 1H, 1'), 3.33 (m, 1H, ½ of 6), 2.86 (m, 1H, 2), 2.80 (m, 1H, ½ of 6), 2.00 (broad s, 1H, NH), 1.92 (m, 1H, ½ of 4), 1.75 (m, 1H, ½ of 5), 1.64 (m, 1H, ½ of 5), 1.57 (m, 1H, ½ of 3), 1.48 (d, J = 1.49, 3H, 1a), 1.45 (m, 1H. ½ of 4), 1.38 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NCl$ [M+H$^+$]: 224.1206 Found: 224.1208.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.33 (m, 1H, 3'), 7.21 (m, 1H, 6'), 7.14 (m, 2H, 4' and 5'), 3.12 (m, 1H, ½ of 6), 2.77 (m, 2H, 2a), 2.65 (m, 1H, ½ of 6), 2.55 (m, 1H, 2), 2.11 (broad s, 1H, NH), 1.82 (m, 1H, ½ of 4), 1.76 (m, 1H, ½ of 3), 1.69 (m, 2H, 1a), 1.62 (m, 1H, ½ of 5), 1.47 (m, 1H, ½ of 5), 1.38 (m, 1H, ½ of 4), 1.18 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 140.01, 134.01, 130.39, 129.61, 127.41, 126.95, 56.74, 47.19, 37.39, 32.77, 30.15, 26.51, 24.83 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NCl$ [M+H$^+$]: 224.1206 Found: 224.1208.

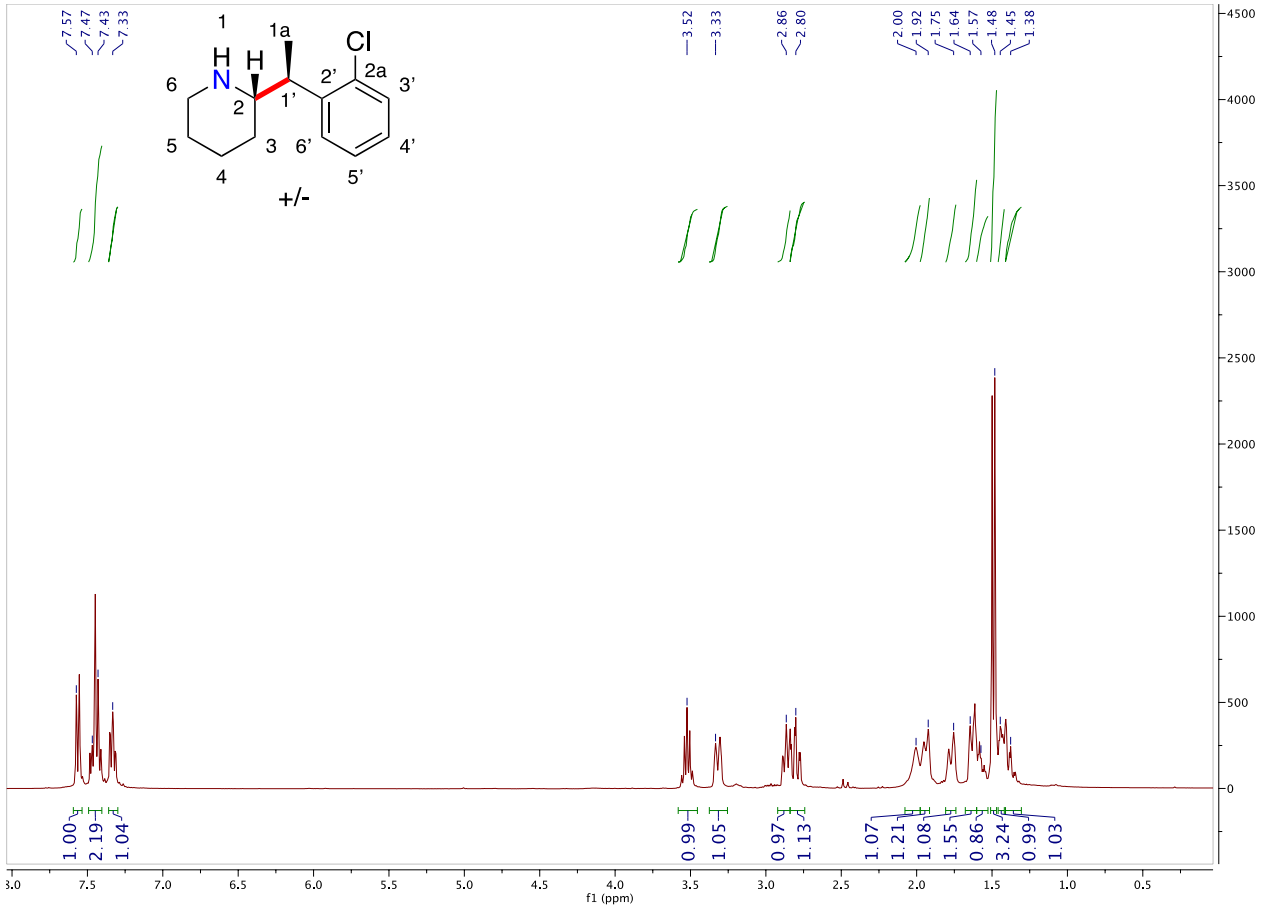


Figure S138: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(2-chlorophenyl)ethyl)piperidine.

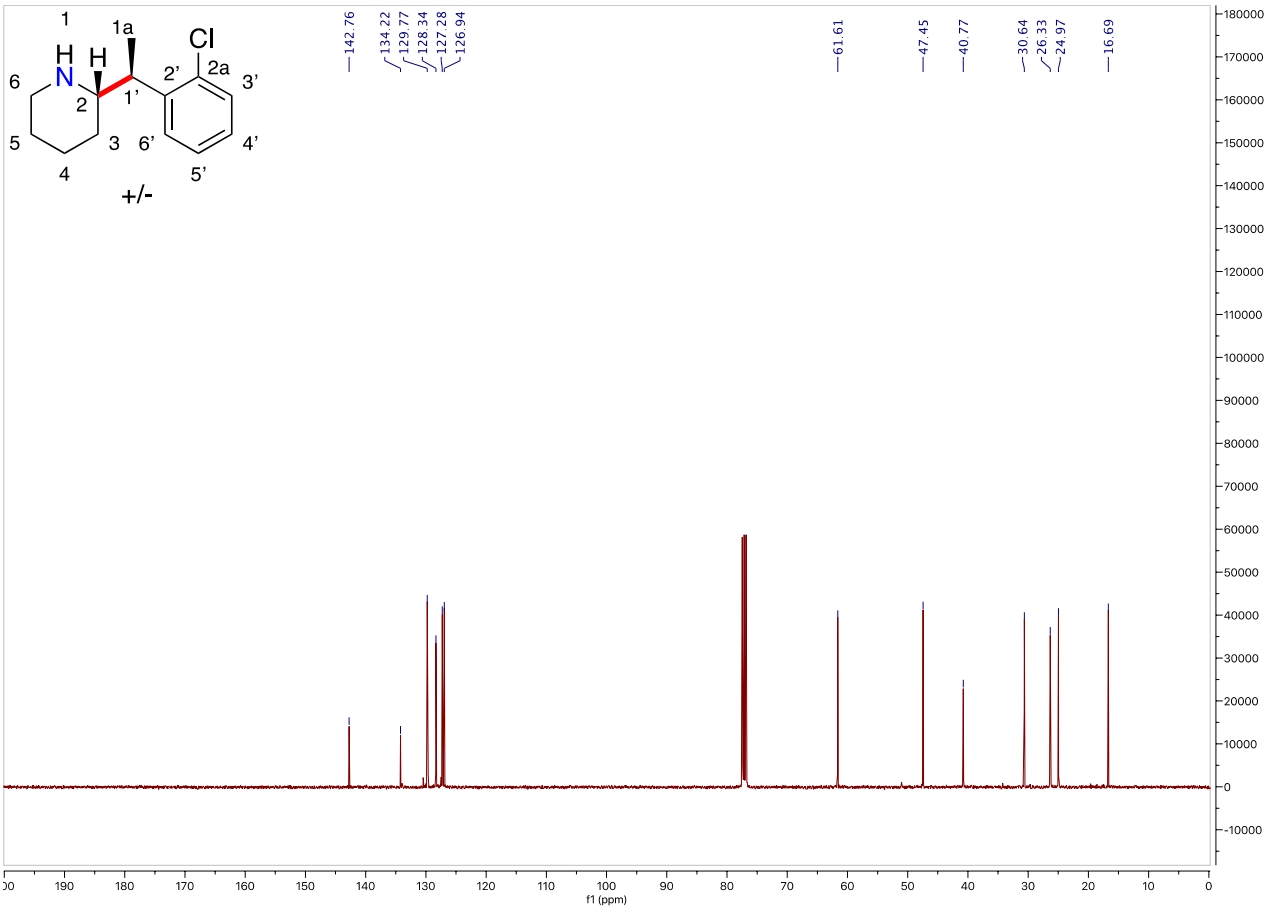


Figure S139: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(1-(2-chlorophenyl)ethyl)piperidine.

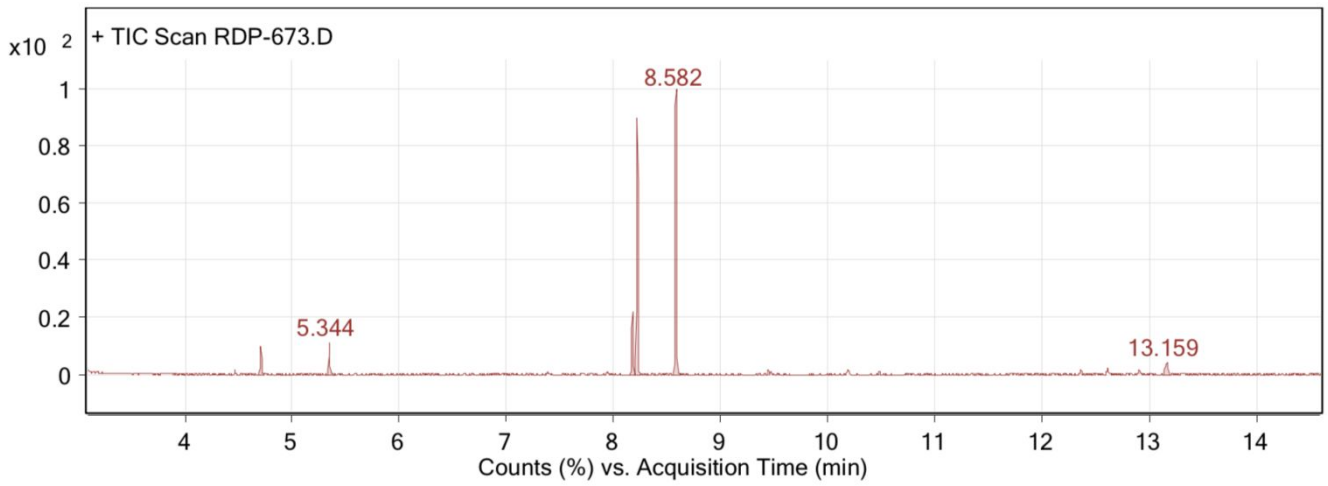


Figure S140: GC-MS for the crude reaction between 2-chlorostyrene and piperidine.

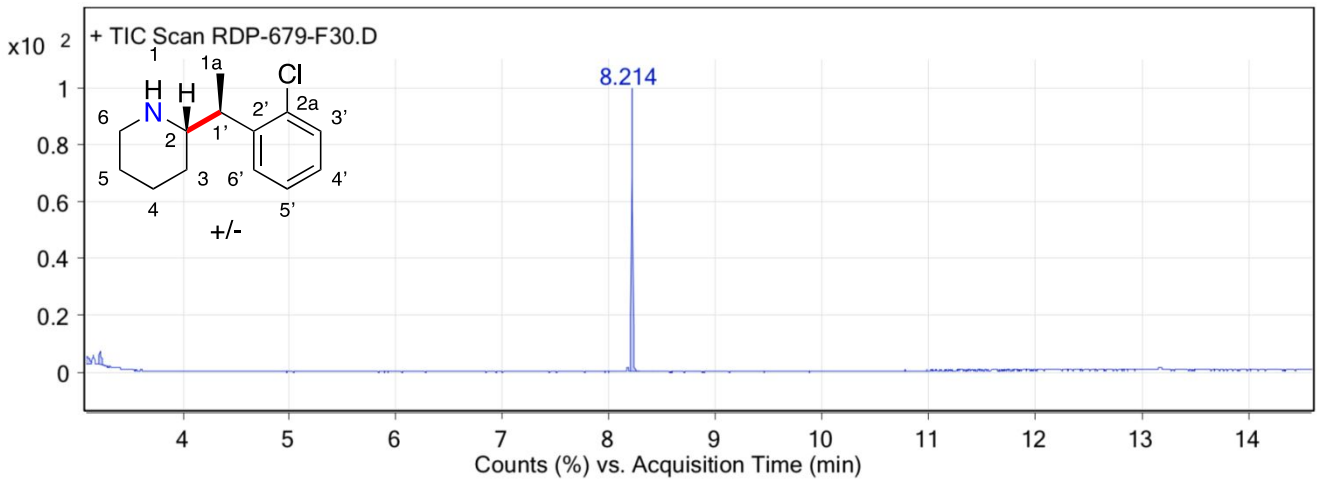


Figure S141: GC-MS report of 2-(1-(2-chlorophenyl)ethyl)piperidine.

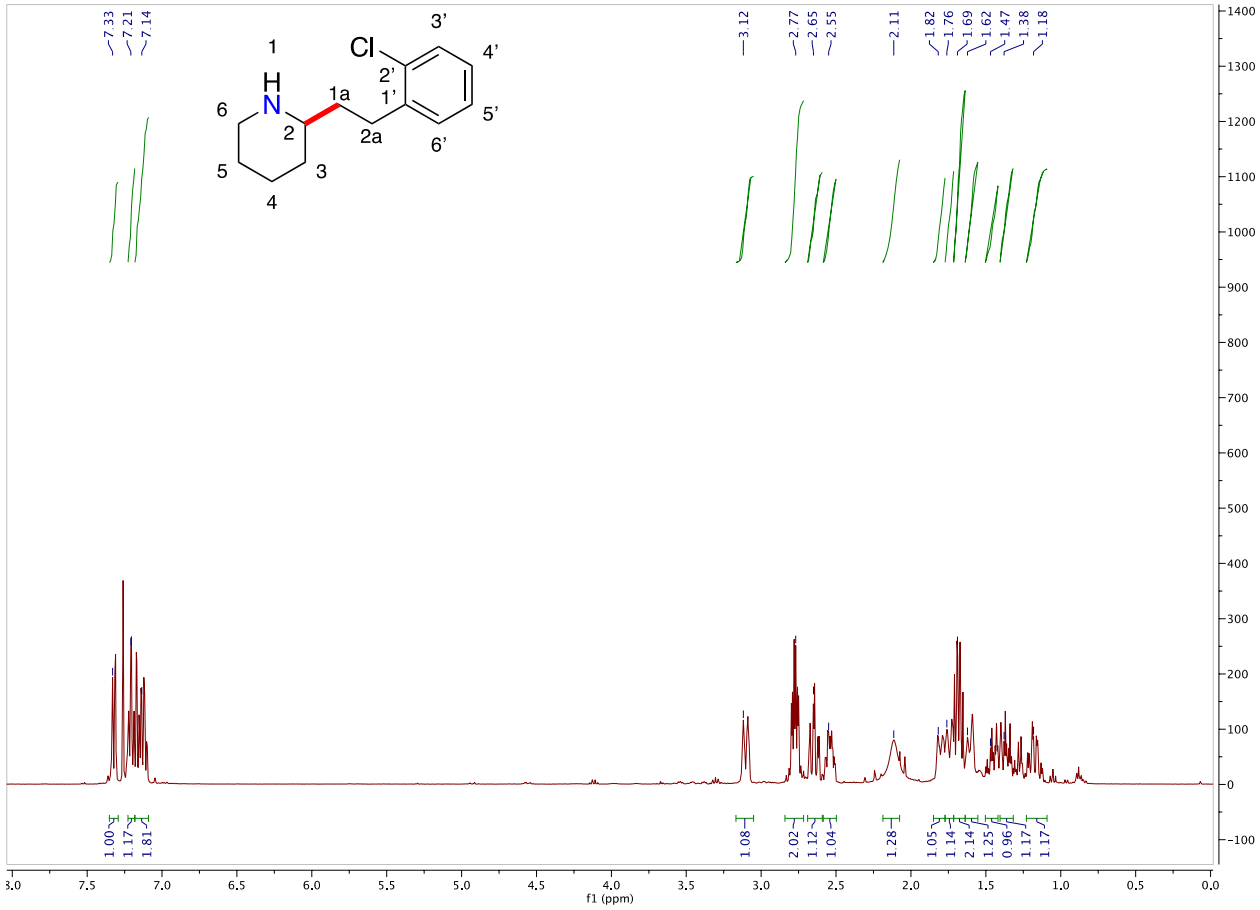


Figure S142: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(2-chlorophenyl)ethyl)piperidine.

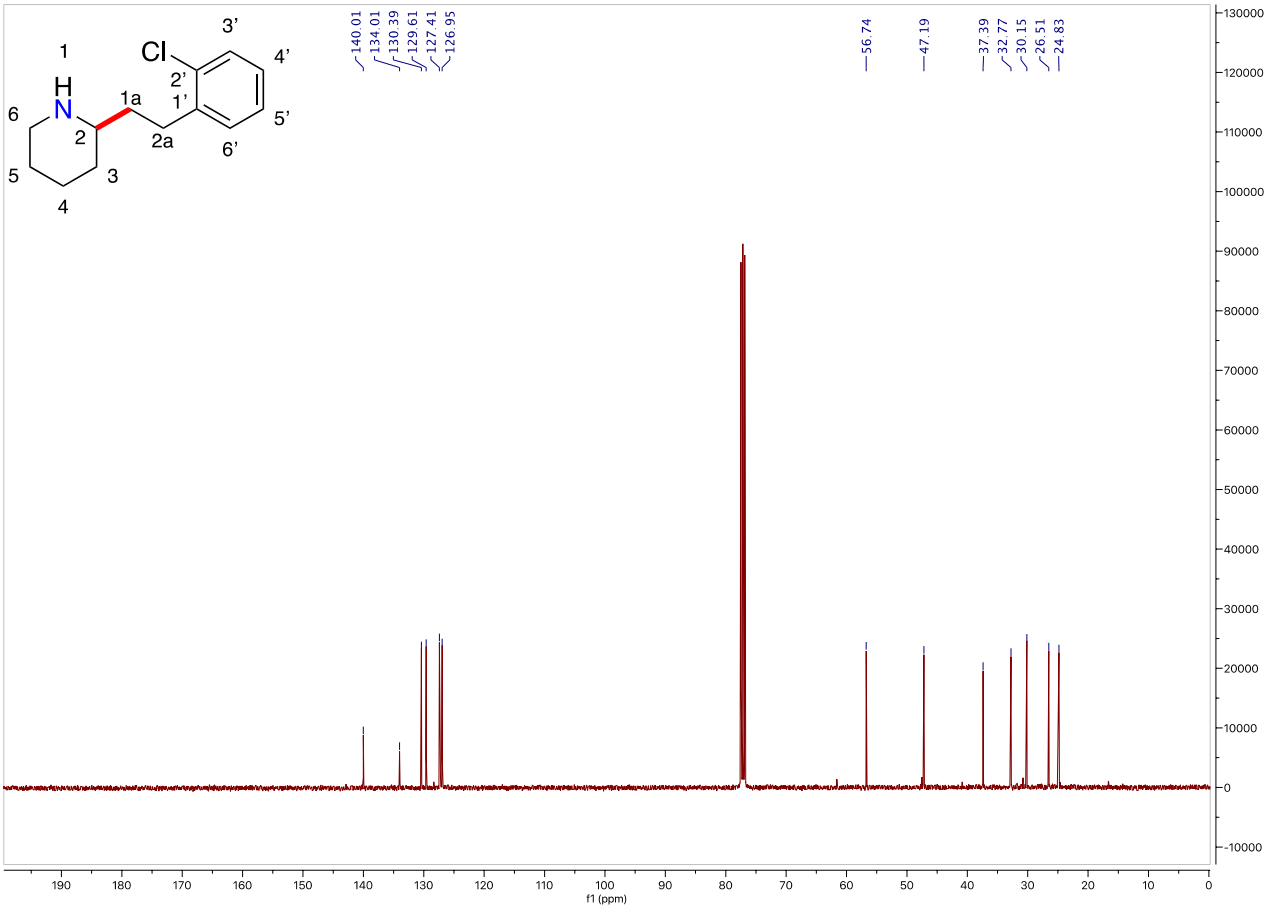


Figure S143: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(1-(2-chlorophenyl)ethyl)piperidine.

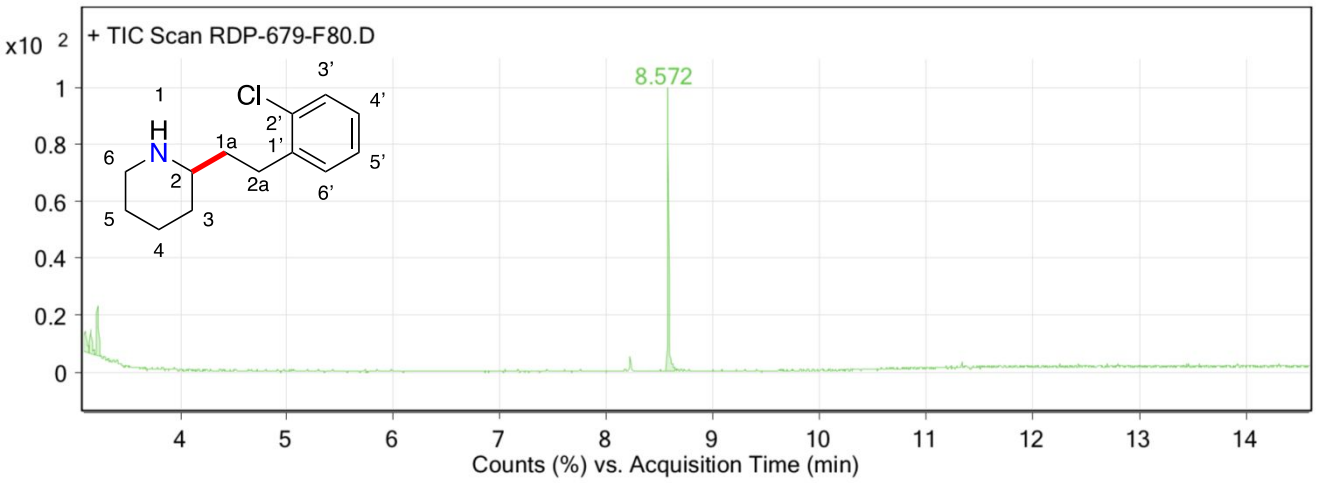
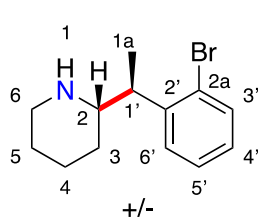
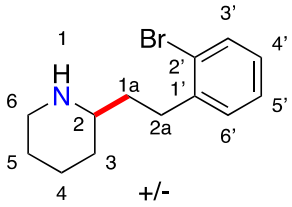


Figure S144: GC-MS report of 2-(1-(2-chlorophenyl)ethyl)piperidine.





Synthesis of 2-(1-(2-bromophenyl)ethyl)piperidine and 2-(2-bromophenethyl)piperidine (32 and 33): Prepared following the general procedure outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), 2-bromostyrene (181.9 mg, 1.0 mmol). The reaction was subsequently concentrated. Yield of the reaction mixture could not be determined due to issues with this styrene polymerization during reaction. The unwanted polymerization resulted in broadened signals that could not be carefully integrated in the NMR spectrum. This could not be adequately improved with filtration. Total reaction NMR yield was 99 %. Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine):

Branched Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.56 (m, 1H, 3'), 7.27 (m, 1H, 5'), 7.23 (m, 1H, 6'), 7.05 (m, 1H, 4'), 3.29 (m, 1H, 1a), 3.11 (m, 1H, ½ of 6), 2.67 (m, 1H, 2), 2.60 (m, 1H, ½ of 6), 1.95 (broad s, 1H, NH), 1.74 (m, 1H, ½ of 4), 1.55 (m, 1H, ½ of 5), 1.44 (m, 1H, ½ of 3), 1.38 (m, 1H, ½ of 5), 1.28 (d, J = 1.27, 3H, 2a), 1.25 (m, 1H, ½ of 3), 1.22 (m, 1H, ½ of 4) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 144.51, 133.15, 128.36, 127.65, 127.61, 125.29, 61.70, 47.50, 43.46, 30.70, 26.38, 25.02, 16.84 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NBr$ [M+H$^+$]: 268.0701 Found: 268.0704.

Linear Regioisomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.49 (m, 1H, 3'), 7.19 (m, 2H, 5' and 6'), 7.02 (m, 1H, 4'), 3.08 (m, 1H, ½ of 6), 2.77 (m, 2H, 2a), 2.64 (m, 1H, ½ of 6), 2.54 (m, 1H, 2), 2.28 (broad s, 1H, NH), 1.80 (m, 1H, ½ of 4), 1.71 (m, 1H, ½ of 3), 1.66 (m, 1H, 1a), 1.57 (m, 1H, ½ of 5), 1.44 (m, 1H, ½ of 5), 1.35 (m, 1H, ½ of 4), 1.16 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 141.71, 132.86, 130.31, 127.60, 127.56, 124.48, 56.66, 47.17, 37.57, 32.79, 32.70, 26.53, 24.82 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NBr$ [M+H$^+$]: 268.0701 Found: 268.0704.

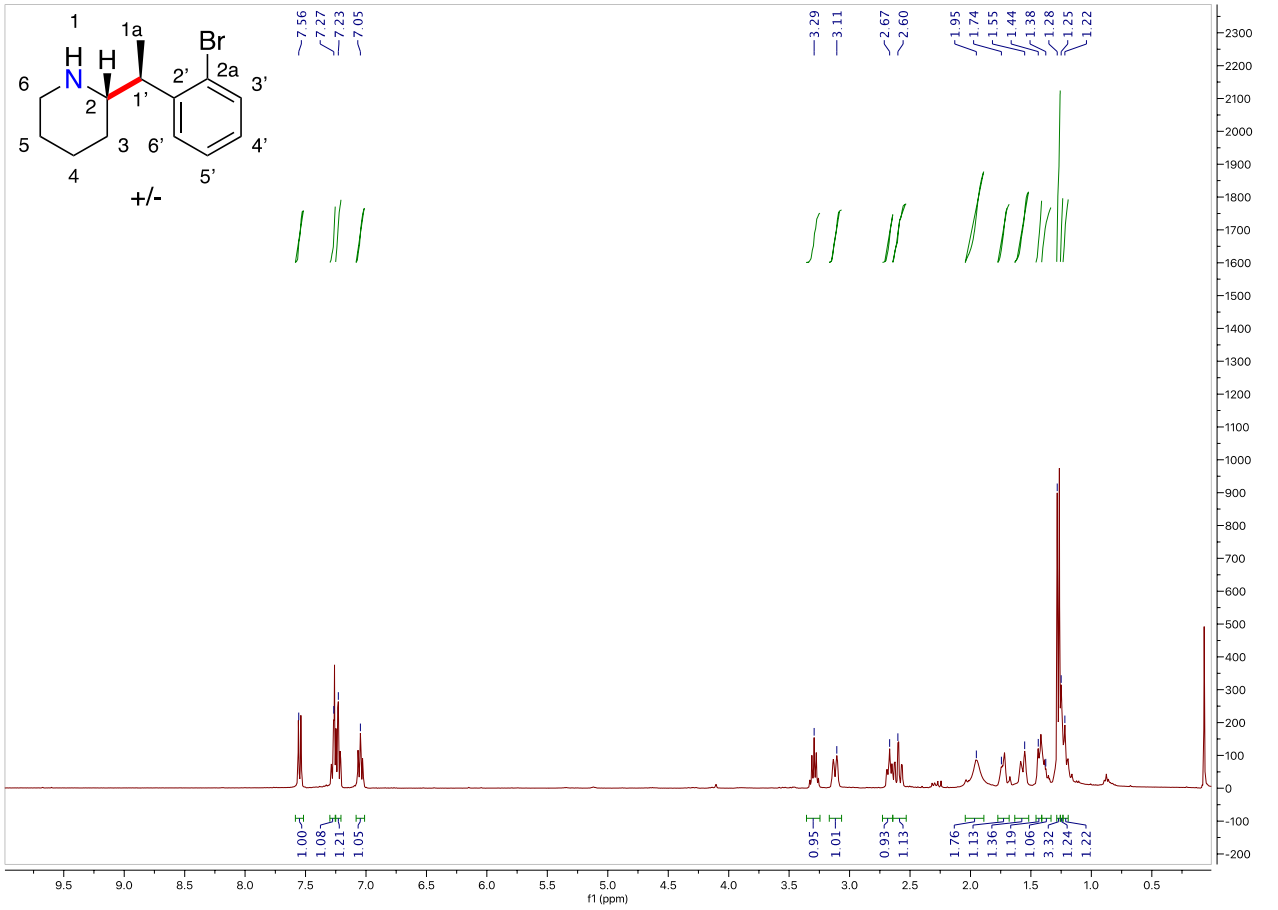


Figure S145: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(1-(2-bromophenyl)ethyl)piperidine.

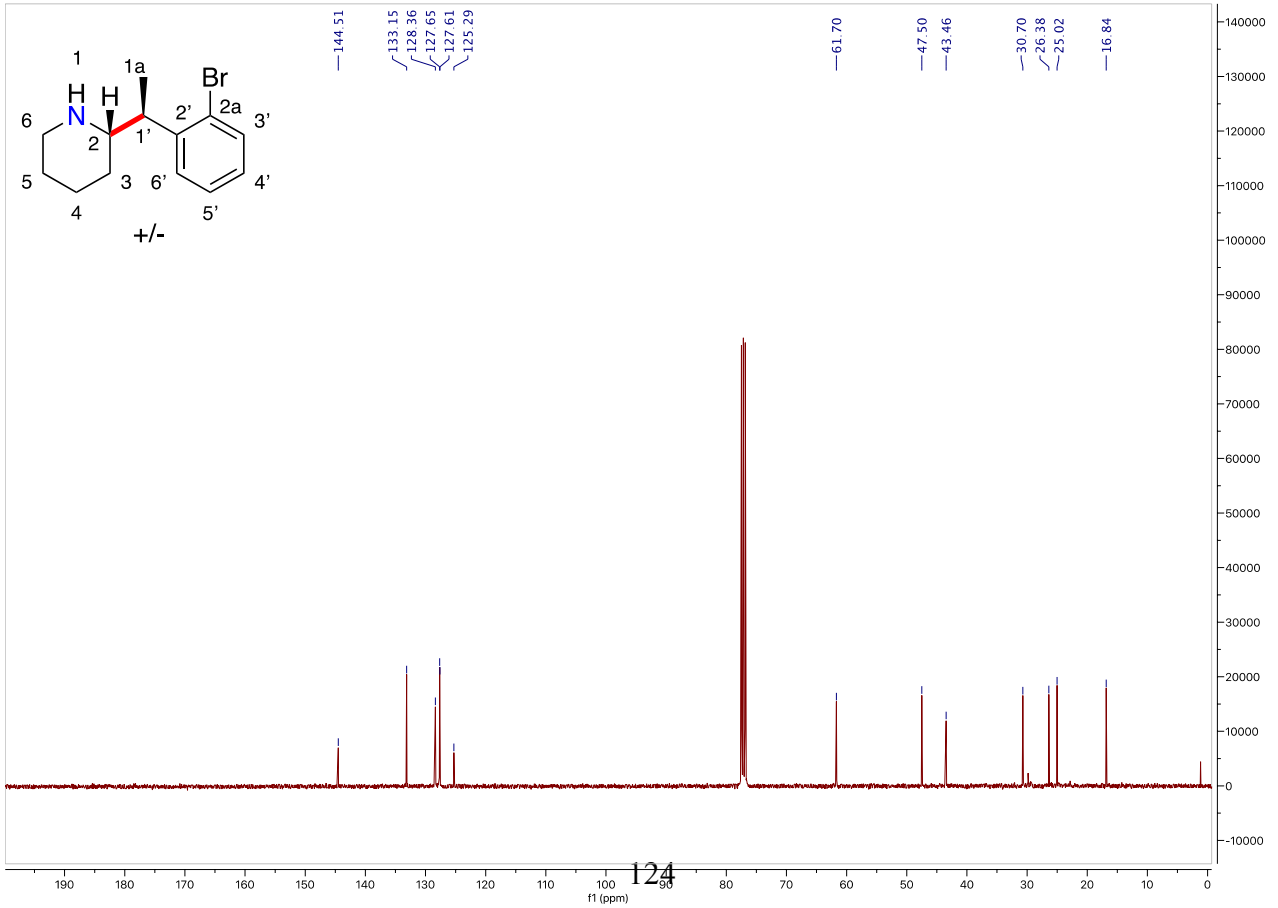


Figure S146: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(1-(2-bromophenyl)ethyl)piperidine.

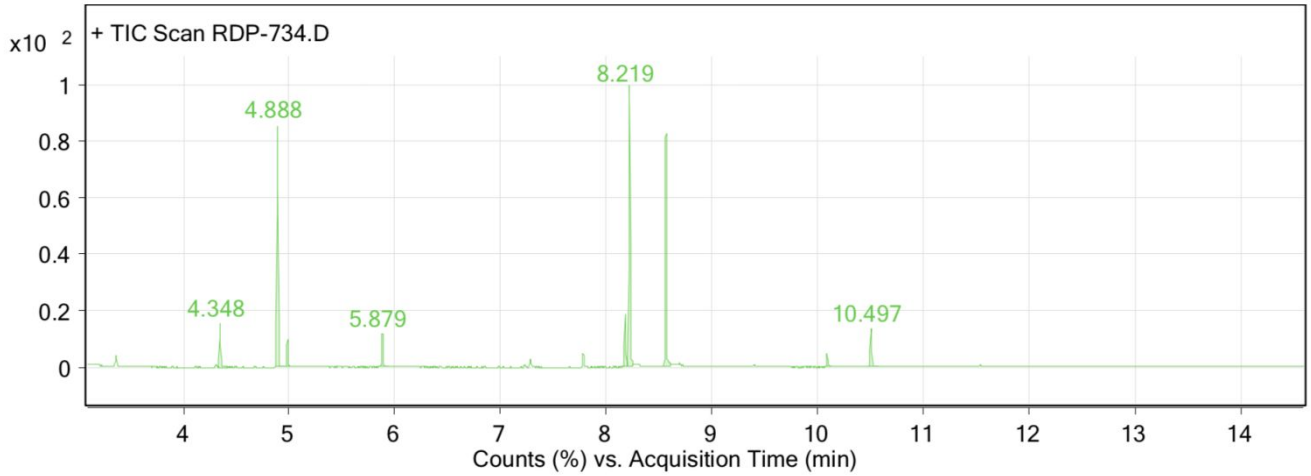


Figure S147: GC-MS for the crude reaction mixture between piperidine and 2-bromostyrene.

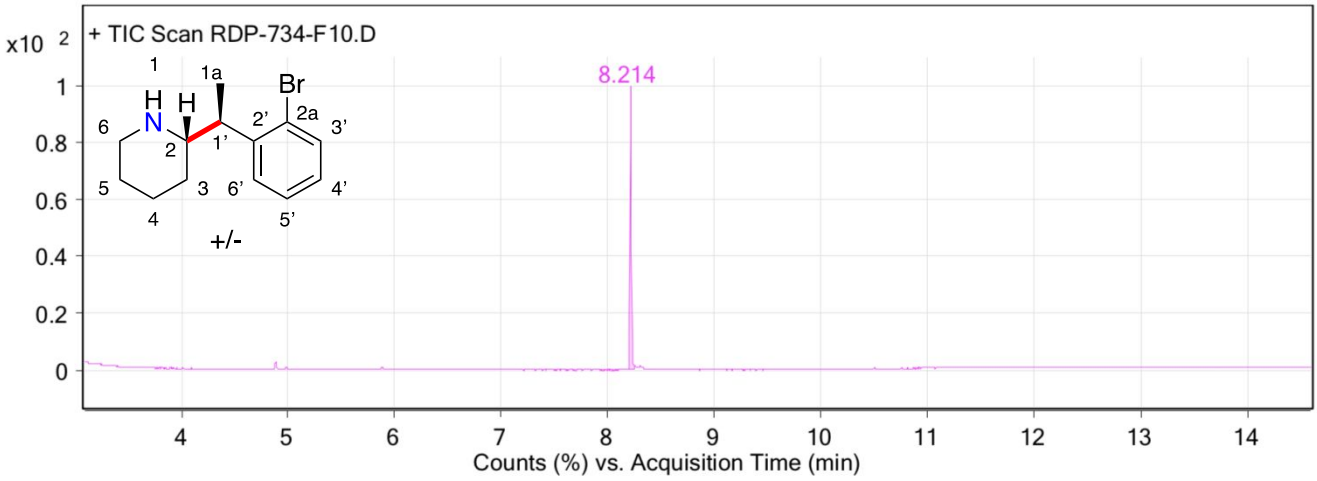


Figure S148: GC-MS spectrum of 2-(1-(2-bromophenyl)ethyl)piperidine.

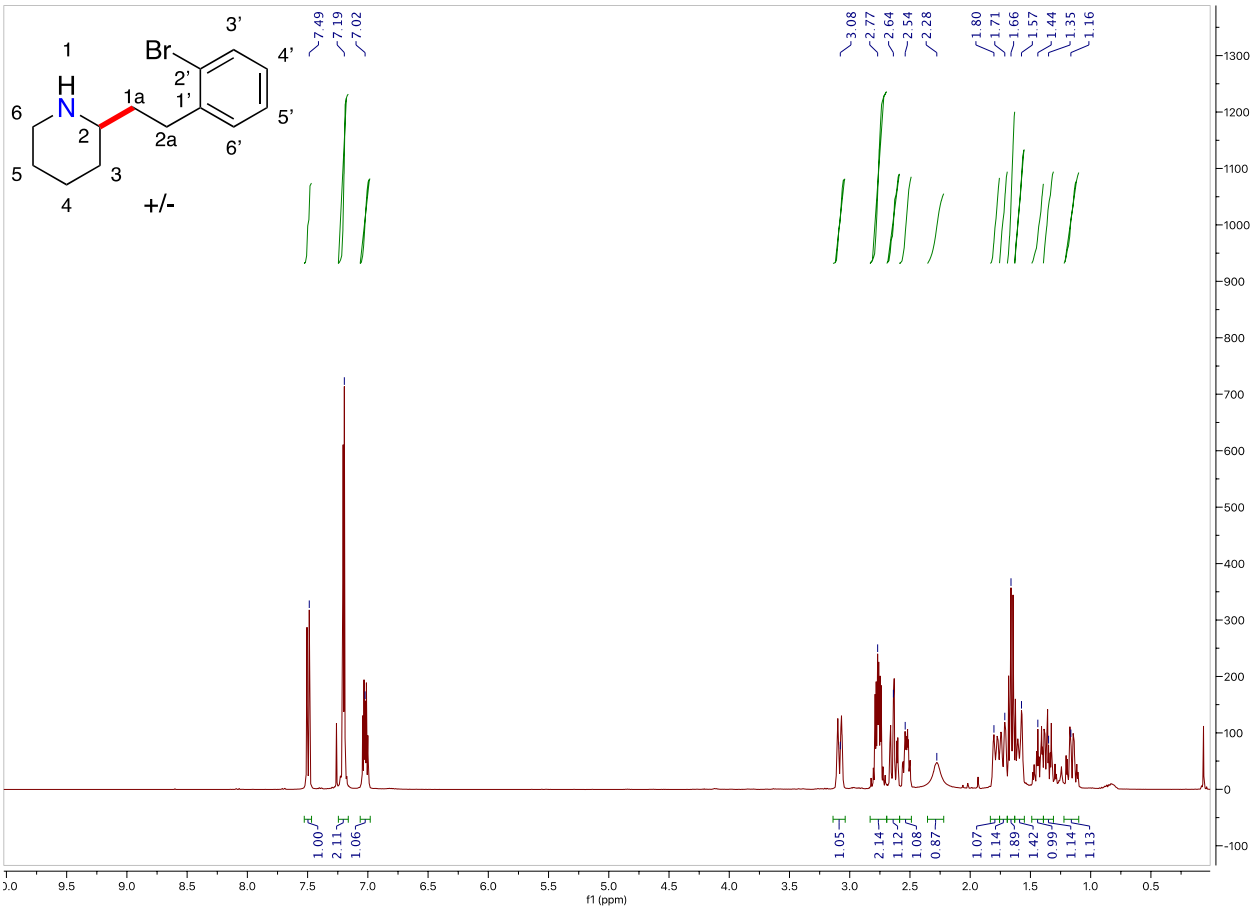


Figure S149: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(2-bromophenethyl)piperidine.

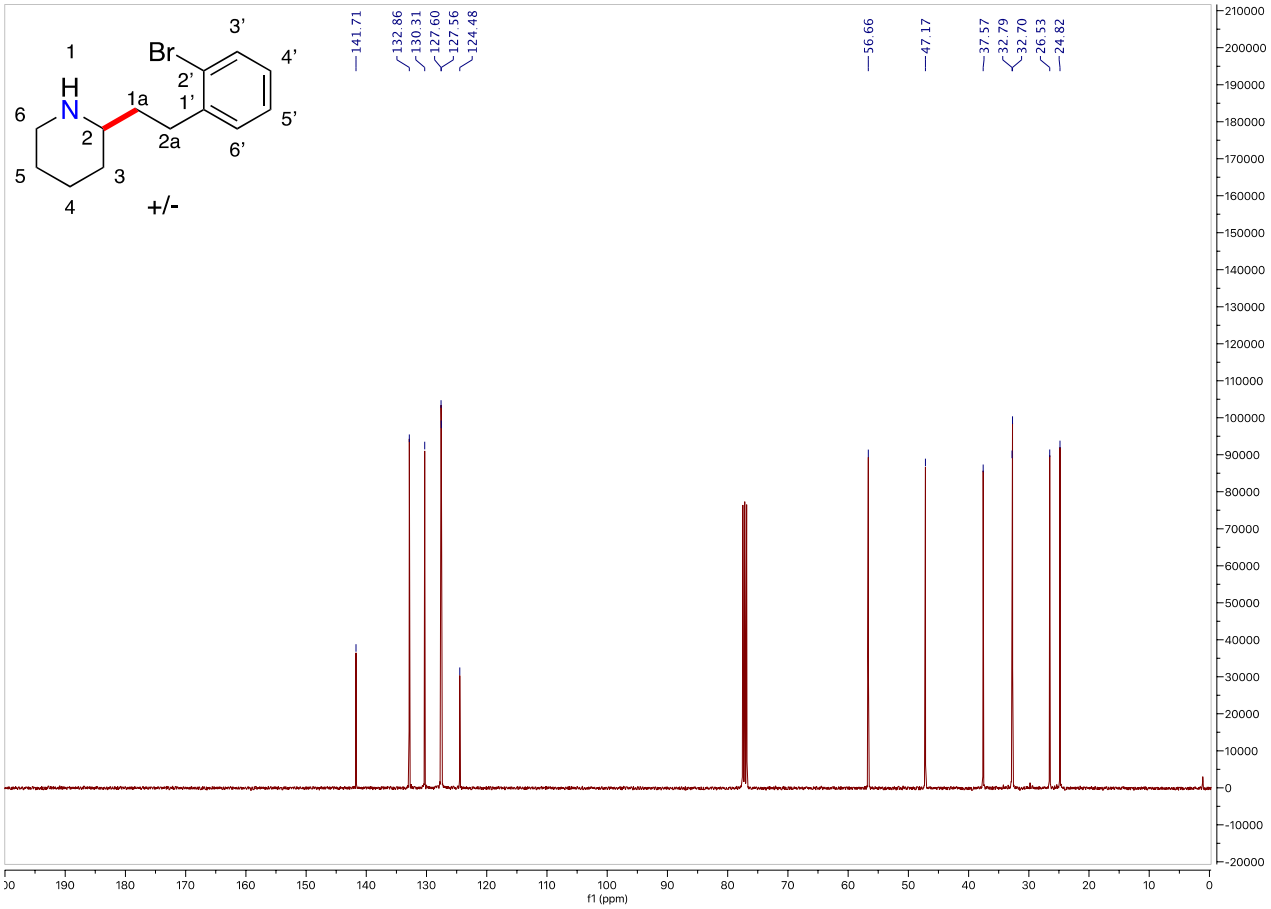


Figure S150: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(2-bromophenethyl)piperidine.

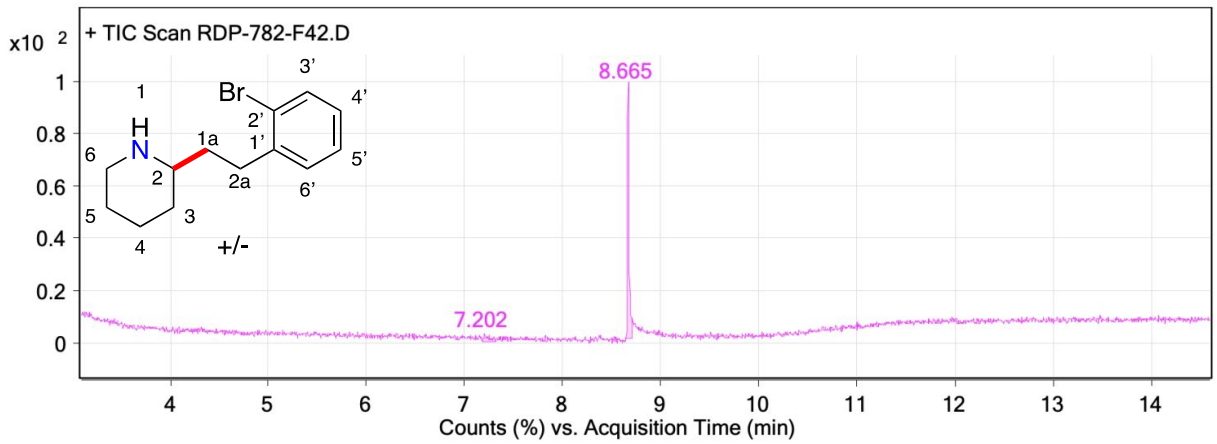
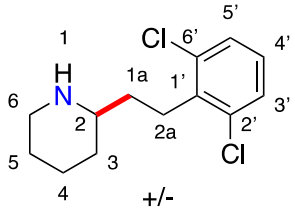


Figure S151: GC-MS report (101 MHz, $CDCl_3$, 298 K) of 2-(2-bromophenethyl)piperidine.



Synthesis of 2-(2,6-dichlorophenethyl)piperidine (34): Prepared following the general procedure for branched and linear product mixtures outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), 2,6-dichlorostyrene (173.04 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 45 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography

(7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.28 (m, 2H, 3' and 5'), 7.07 (m, 1H, 4'), 3.19 (m, 1H, ½ of 6), 2.98 (m, 2H, 2a), 2.73 (m, 1H, ½ of 6), 2.66 (m, 1H, 2), 2.22 (broad s, 1H, NH), 1.85 (m, 1H, ½ of 4), 1.83 (m, 1H, ½ of 3), 1.73 (m, 2H, 1a), 1.66 (m, 1H, ½ of 5), 1.56 (m, 1H, ½ of 5), 1.43 (m, 1H, ½ of 4), 1.34 (m, 1H, ½ of 3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 138.08, 135.38, 128.31, 127.73, 57.00, 46.78, 34.78, 31.95, 28.00, 25.82, 24.46 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}NCl_2$ [M+H$^+$]: 258.0815 Found: 258.0816.

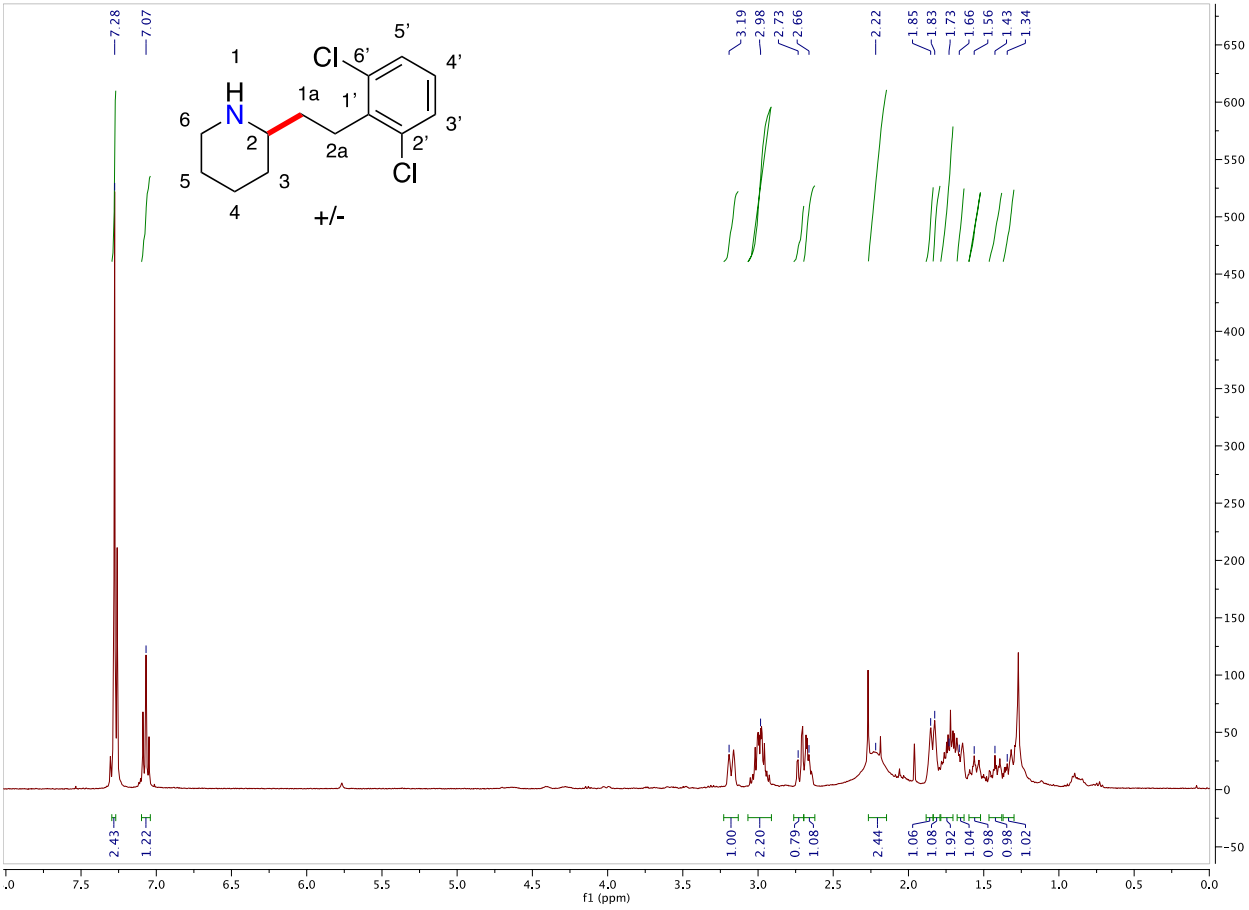


Figure S152: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-(2,6-dichlorophenethyl)piperidine.

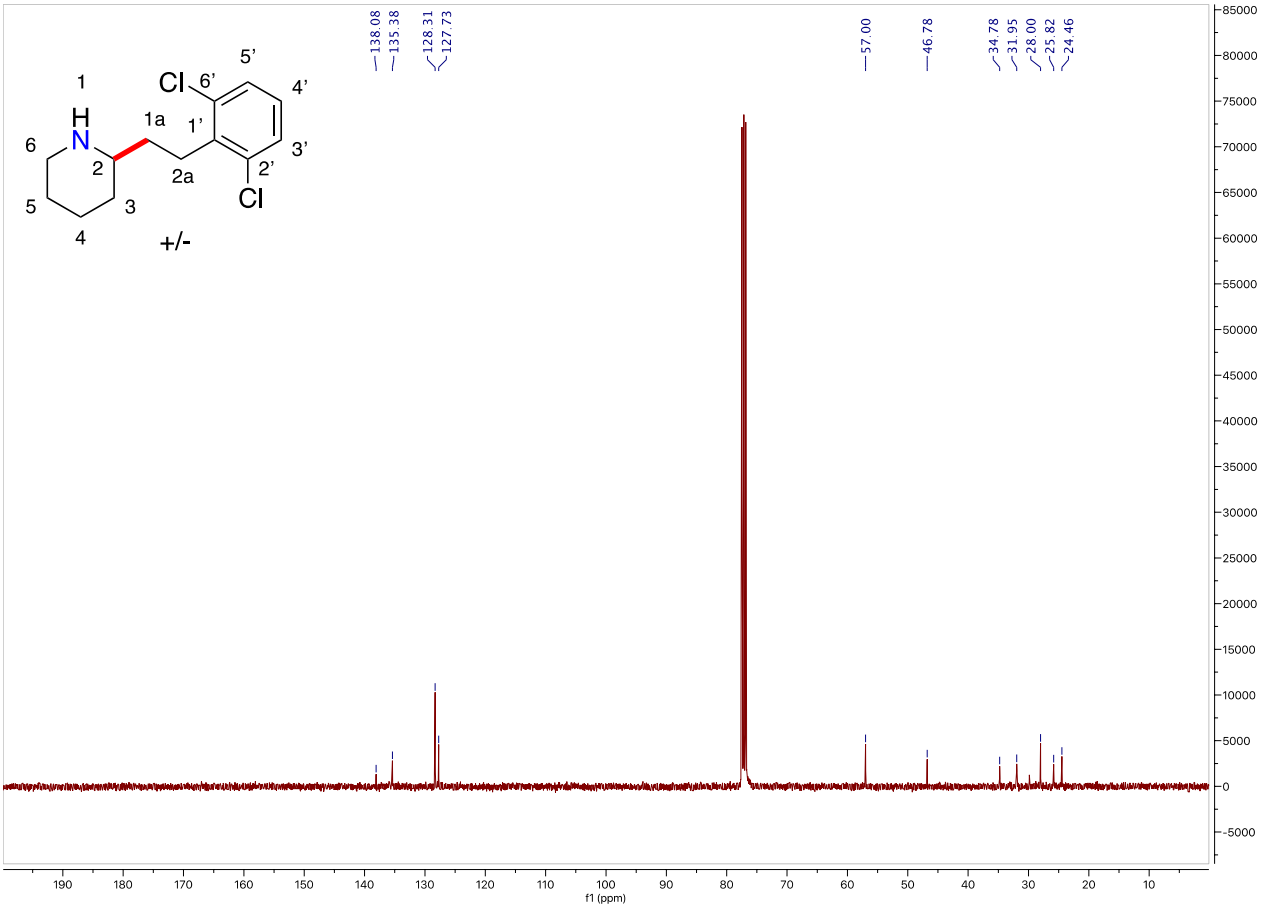


Figure S153: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(2,6-dichlorophenethyl)piperidine.

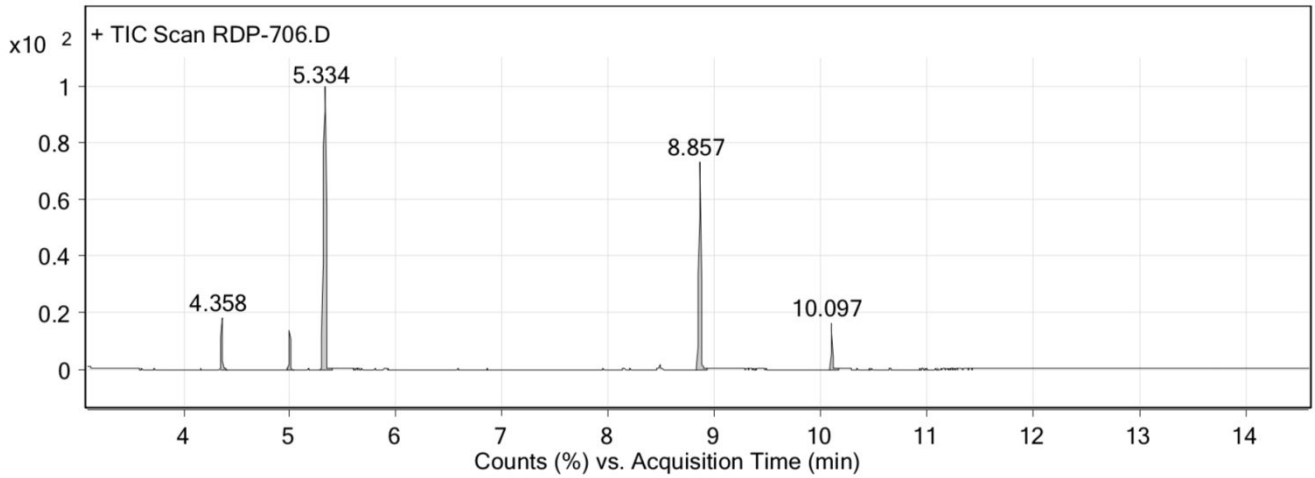


Figure 154: GC-MS for the crude reaction mixture between piperidine and 2-chlorosrtyrene.

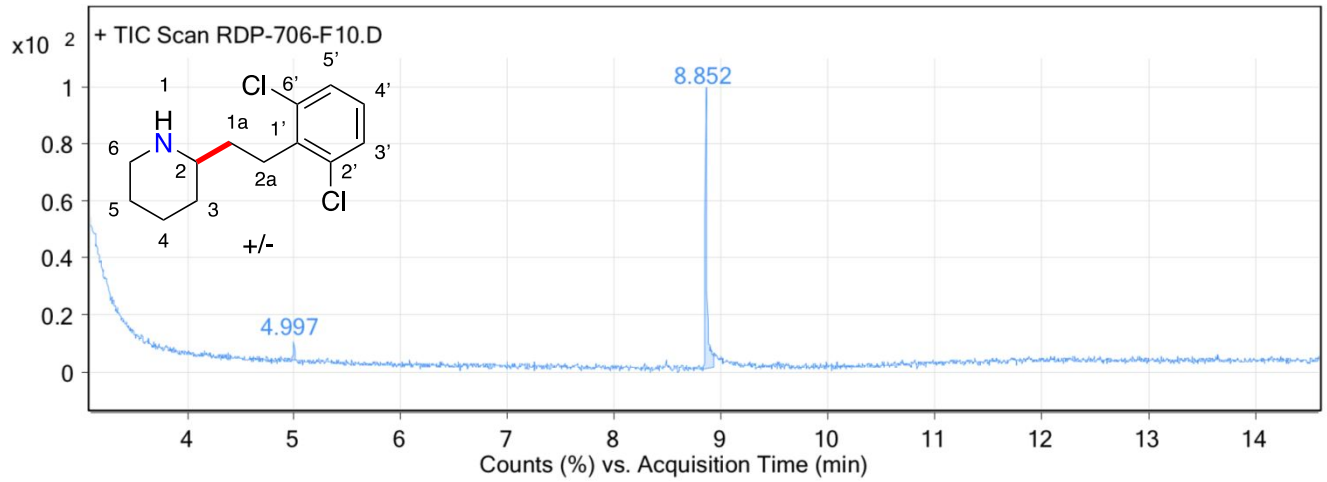
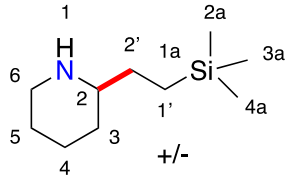


Figure S155: GC-MS report of 2-(2,6-dichlorophenethyl)piperidine.



Synthesis of 2-(2-(trimethylsilyl)ethyl)piperidine (35): Prepared following the general procedure outlined above: 26.0 mg Ta, 15.2 mg ligand **L4**, piperidine (85.15 mg, 1.0 mmol), vinyltrimethylsilane (100.24 mg, 1.0 mmol). The reaction was subsequently concentrated and the yield was determined to be 68 % by NMR (1,3,5-trimethoxybenzene as a standard). Purification via column chromatography (7:2.5:0.5 hexanes : ethyl acetate : triethyl amine): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 3.09 (m, 1H, ½ of 6), 2.61 (m, 1H, ½ of 6), 2.33 (m, 1H, 2), 1.83 (broad s, 1H, NH), 1.79 (m, 1H, ½ of 4), 1.69 (m, 1H, ½ of 5), 1.57 (m, 1H, ½ of 5), 1.41 (m, 2H, 2'), 1.32 (m, 2H, 1'), 1.04 (m, 1H, ½ of 3), 0.52 (m, 1H, ½ of 4), 0.43 (m, 1H, ½ of 3), 0.03 (s, 9H, 2a and 3a and 4a) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 47.40, 32.74, 31.61, 26.78, 25.07, 12.65, -1.67 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}NCl_2$ [M+H$^+$]: 258.0815 Found: 258.0816.

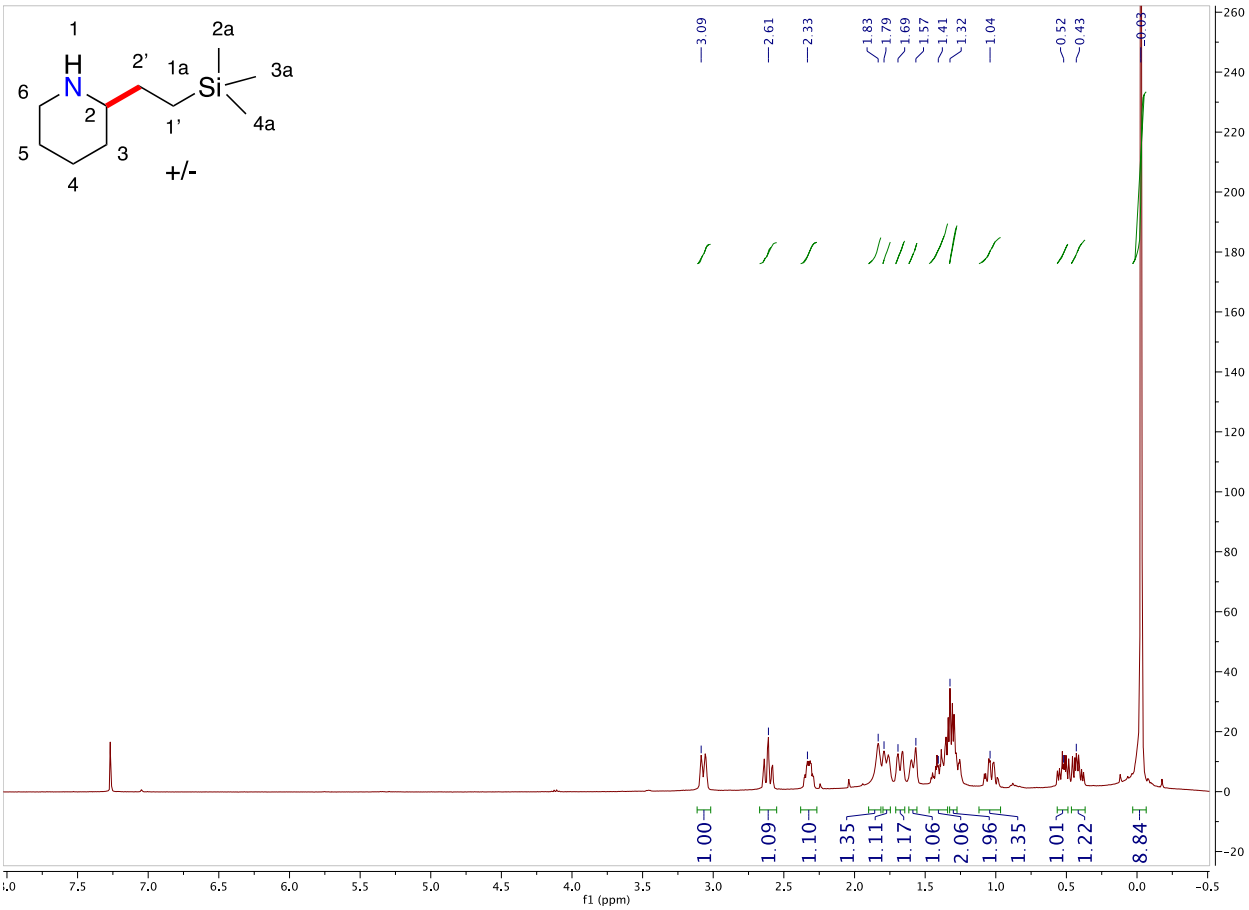


Figure S156: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) 2-(2-(trimethylsilyl)ethyl)piperidine.

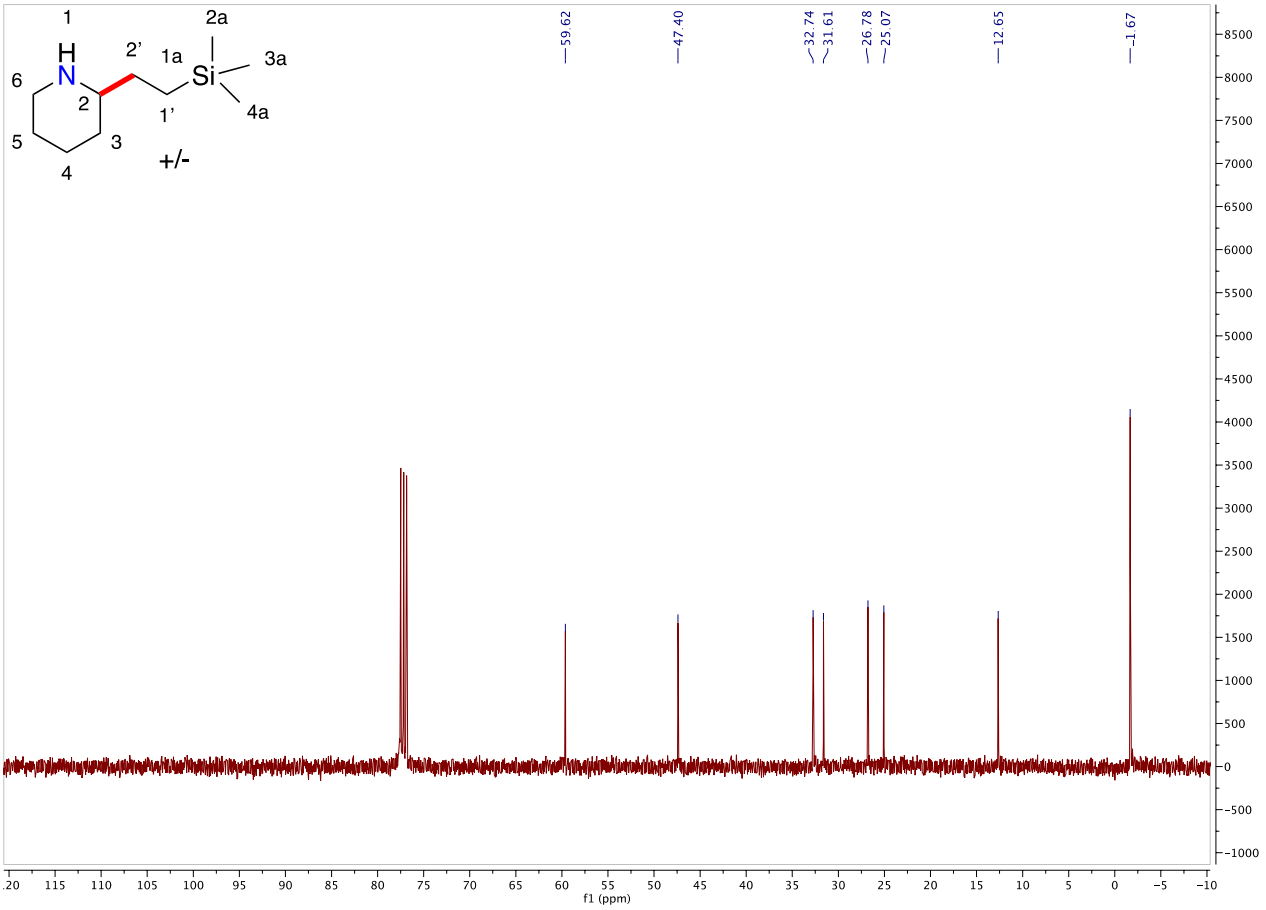


Figure S157: ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-(2-(trimethylsilyl)ethyl)piperidine.

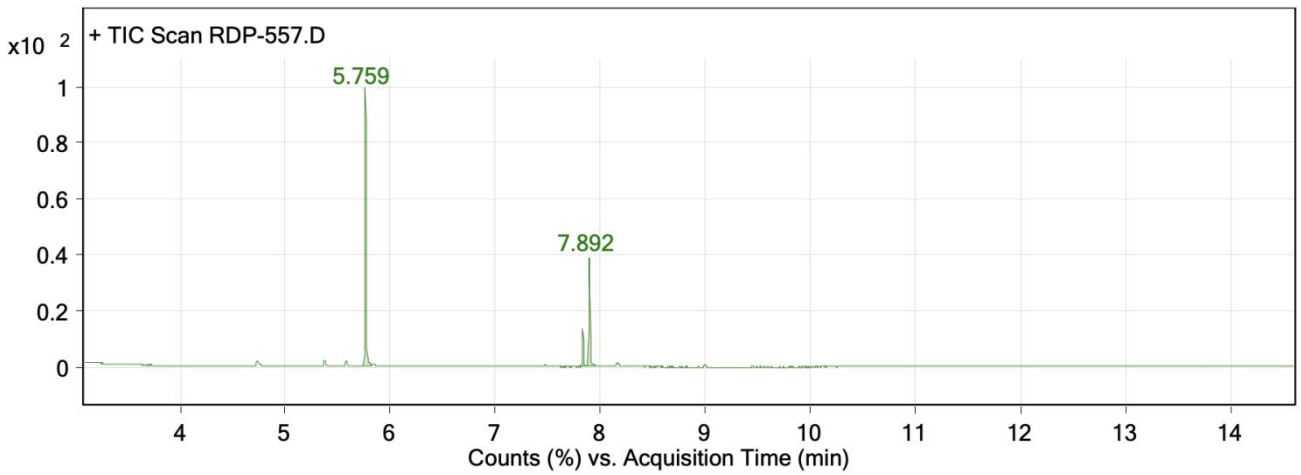


Figure S158: GC-MS for the crude reaction mixture between piperidine and trimethylvinylsilane.

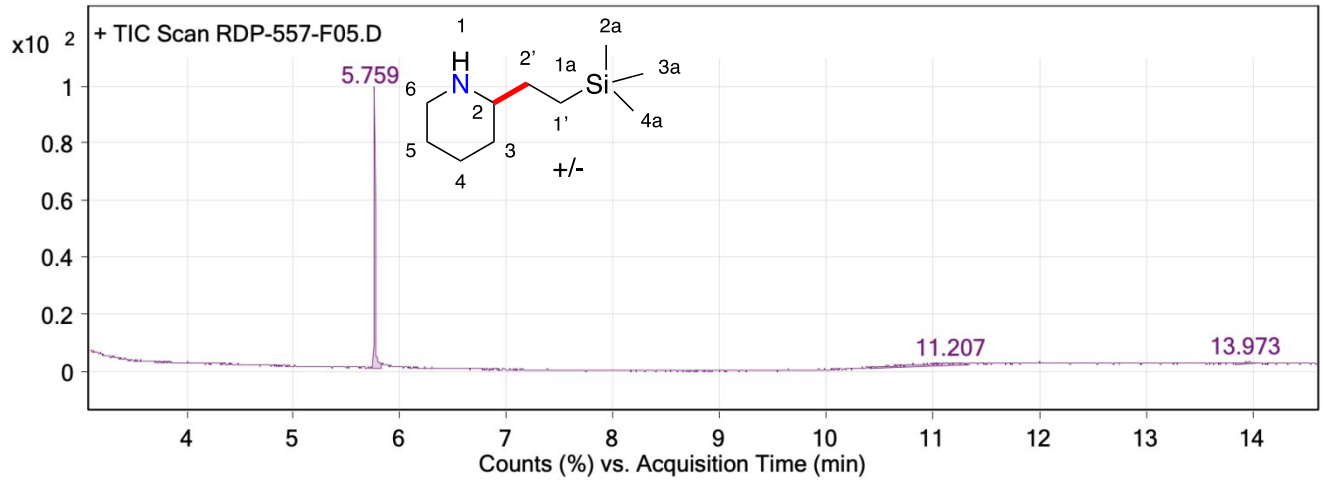
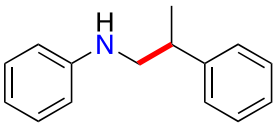


Figure S159: GC-MS report of 2-(2-(trimethylsilyl)ethyl)piperidine.



Synthesis of *N*-(2-phenylpropyl)aniline: Prepared following the general procedure outlined above: 12.8 mg Ta, 7.6 mg ligand **L4**, *N*-methylaniline (53.58 mg, 0.5 mmol), styrene (52.08 mg, 0.5 mmol). Both GC peaks below have molecular ion masses that match the target products. These branched and linear regioisomers have been previously published and published NMR spectroscopic and GC-MS data have been compared.[10]

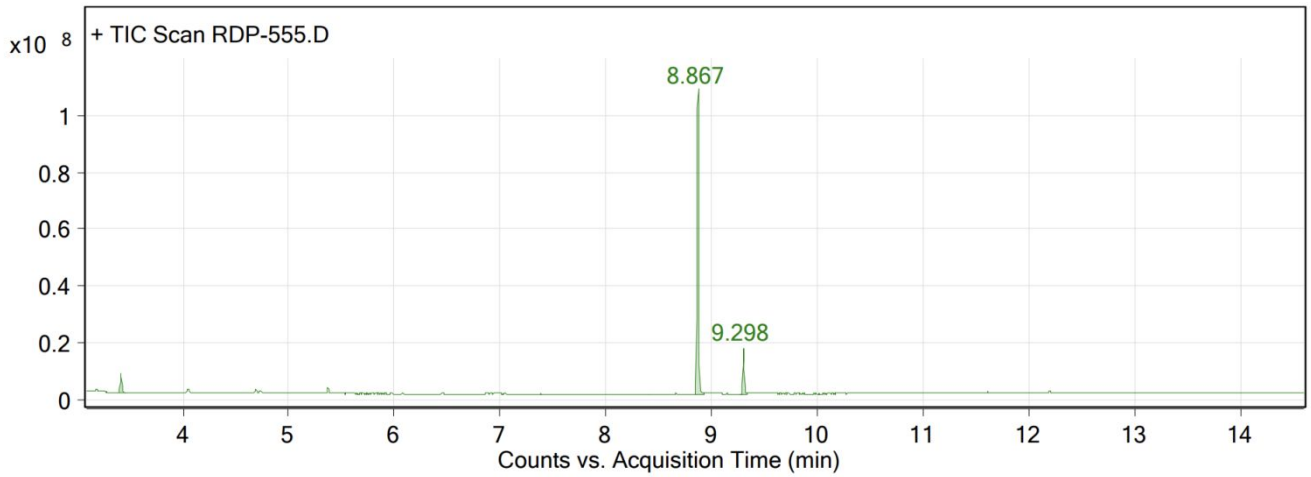


Figure S160: GC-MS report for the crude reaction mixture between *N*-methylaniline and styrene. Here, the peak at 8.867 minutes represents branched regioisomer and the peak at 9.928 minutes represents the linear regioisomer.

S8. References

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