Electronic Supplementary Material (ESI) for Chemical Science.

Enantiomerically Enriched Tetrahydropyridine Allyl Chlorides

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Supplementary Information

Experimental Details, Computational Details and Spectral Data

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General Information:

Procedures using oxygen/moisture-sensitive materials were performed with anhydrous solvents under an atmosphere of anhydrous argon in flame-dried flasks, using standard Schlenk techniques. Analytical thin-layer chromatography was performed on precoated aluminum-backed plates (Silica Gel 60 F254; Merck), and visualized using a combination of UV light (254 nm) and aqueous basic potassium permanganate ($KMnO_4$) stain and developed upon heating. Flash column chromatography was carried out using Apollo Scientific silica gel 60 (0.040 – 0.063 nm), Merck 60 Å silica gel, VWR (40-63 μm) silica gel and Sigma Aldrich silica gel. Pressure was applied at the column head via a flow of nitrogen with the solvent system used in parentheses.

Reactions at 0 ºC were performed using an ice-water bath, covered with cotton wool and aluminum foil if overnight stirring is needed. Other temperatures were obtained using a Julabo FT902 immersion cooler or the heating plate of the stirrer.

NMR spectra were recorded at room temperature on Bruker AVIII HD 400 or AVIII HD 500 spectrometers and calibrated to the solvent signal ($CDCl_3$ δ = 7.26 ppm for ^1H NMR, δ = 77.0 ppm for ^{13}C NMR, C_6D_6 δ = 7.16 ppm for ^1H NMR, δ = 128.0 ppm for ^{13}C NMR). Chemical shifts are reported in ppm from the residual solvent peak. Chemical shifts (δ) are given in ppm and coupling constants (J) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or b (broadened).

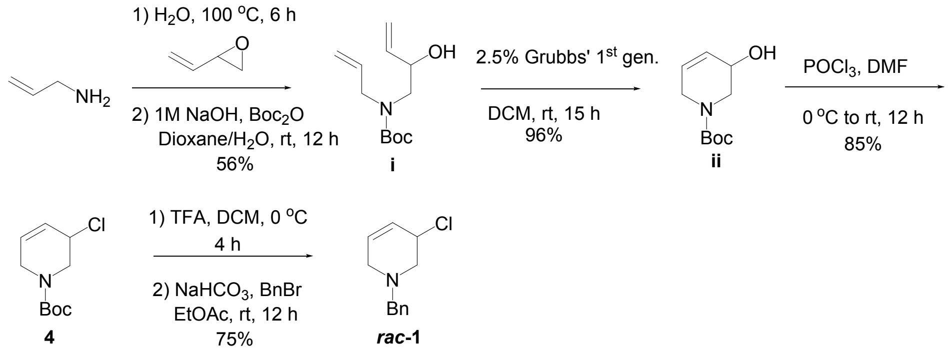
Chiral HPLC separations were achieved using an Agilent 1230 Infinity series normal phase HPLC unit and HP Chemstation software. Chiralpak® columns (250 × 4.6 mm), fitted with matching Chiralpak® Guard Cartridges (10 × 4 mm), were used as specified in the text. Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Honeywell); all eluent systems were isocratic. Chiral SFC (supercritical fluid chromatography) separations were conducted on a Waters Acquity UPC2 system using Waters Empower software. Chiralpak® columns (150 × 3 mm, particle size 3 μm) were used as specified in the text. Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Honeywell).

Low-resolution mass spectra were recorded using a Walters LCT premier XE. High resolution mass spectra (EI and ESI) were recorded using a Bruker MicroTOF spectrometer by the internal service at the University of Oxford. Infrared measurements (neat, thin film) were carried out using a Bruker Tensor 27 FT-IR with internal calibration in the range 600-4000 cm^{-1}. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 25°C in a 10 cm cell in the stated solvent; $[\alpha]_D$ values are given in 10^{-1} $deg.cm^2$ g^{-1} (concentration c given as g/100 mL).

Dry THF, $CHCl_3$, DMF, 1,4-dioxane, toluene, MTBE and CH_2Cl_2 were collected fresh from an mBraun SPS-5 solvent purification system having been passed through anhydrous alumina columns. All other dry solvents used were dried over 3 Å or 4 Å molecular sieves and stored under argon. All other solvents were used as purchased from Sigma Aldrich, Honeywell or Fisher Scientific. Unless stated otherwise, commercially available reagents were purchased from Sigma-Aldrich, Fisher Scientific, Apollo Scientific, Acros Organics, Strem Chemicals, Alfa Aesar or TCI UK and were used without purification. Petroleum ether refers to light petroleum boiling in the range 40-60 °C. Deuterated solvents were purchased from Sigma-Aldrich. Schwartz reagent was prepared according to the literature[1] from Cp_2ZrCl_2 purchased from Acros or Strem Chemicals. Phosphoramidite ligands were prepared according to literature.[2]

Synthesis of 1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (1):

Method A:



***N-tert*-butoxycarbonyl-5-chloro-3-piperidene (4):**

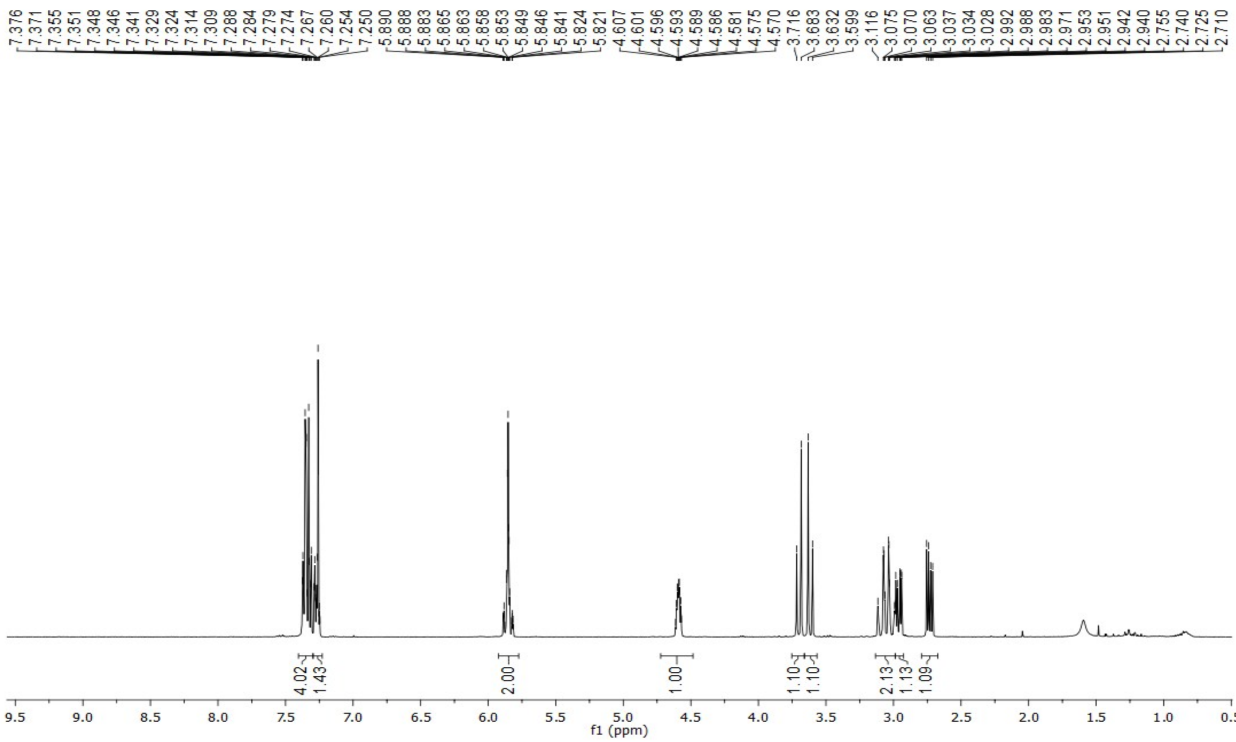
A stirred solution of *N-tert*-butoxycarbonyl-5-hydroxy-3-piperidene (**ii**, 8.1 g, 41 mmol) prepared according to literature,[3] in DMF (100 mL) was cooled to 0 ºC under argon atmosphere, and $POCl_3$ (8.8 mL, 94 mmol) was added dropwise over ~ 10 min. The reaction mixture was left to gradually warm to room temperature and stirring was continued overnight. H_2O (~ 40 mL) was carefully added at 0 °C, and the reaction mixture extracted with EtOAc. The organic phase was washed with brine, dried over $MgSO_4$, filtered, concentrated on rotary evaporator and purified by flash column chromatography on silica gel (pentane/EtOAc (10/1 to 9/1)) to give *N-tert*-butoxycarbonyl-5-chloro-3-piperidene (**iii**) in 85% yield (7.6 g, 35 mmol) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 1.48 (s, 9H), 3.55-4.15 (rotameric m, 4H), 4.51 (s, 1H), 5.80-5.92 (m, 2H). Spectral data is in agreement with literature.[4]

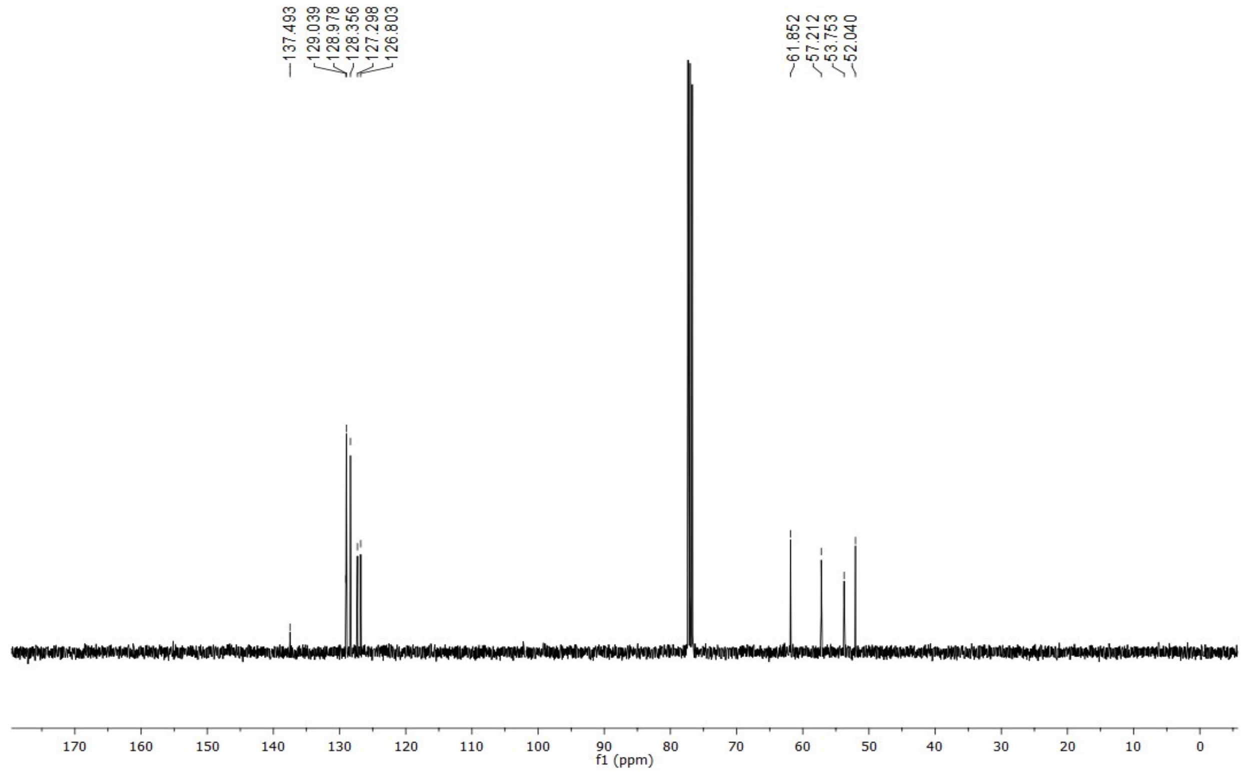
1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (1):

Trifluoroacetic acid (12 ml, 158 mmol) was added dropwise over 5 min to a stirred and cooled (0 ºC) flame dried flask containing *N-tert*-butoxycarbonyl-5-chloro-3- piperidene (**3**, 3.5 g, 16 mmol) in DCM (120 ml), and the reaction mixture was allowed to warm to room temperature. Upon completion (TLC control) the solvent was removed using a rotary evaporator, and this crude material was dissolved in EtOAc (10 ml).

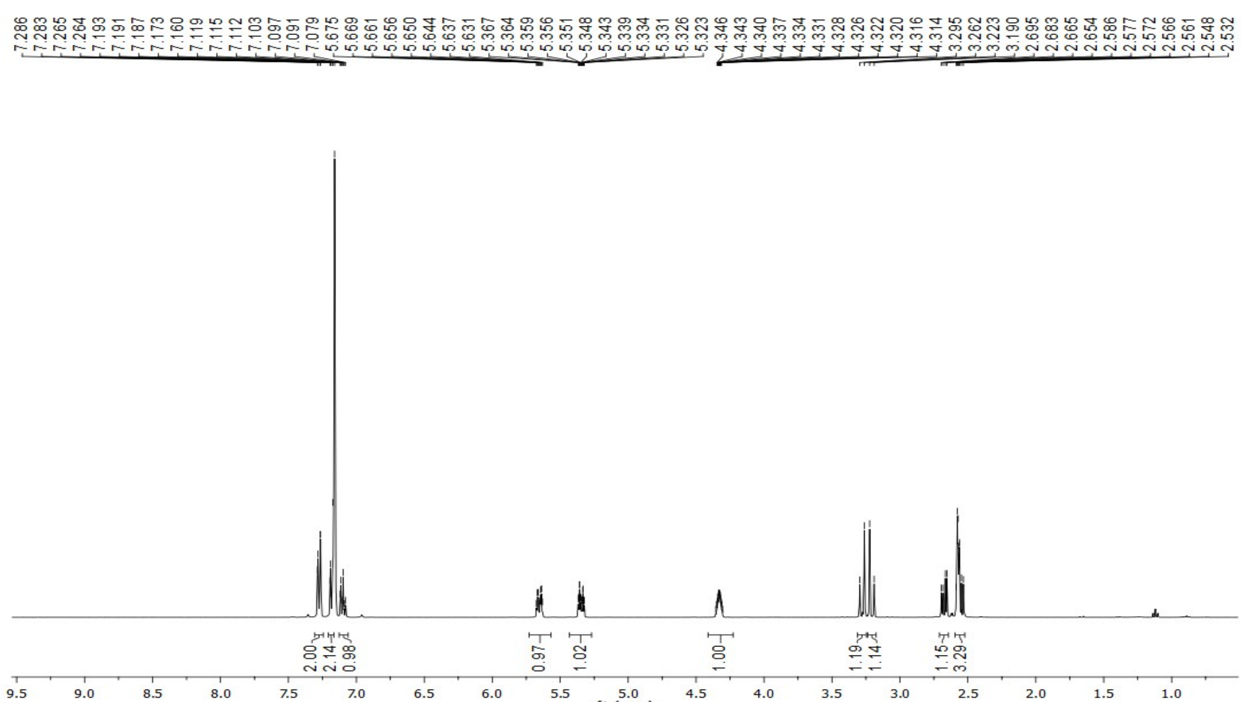
Benzyl bromide (2.0 ml, 17 mmol) and then EtOAc (25 ml) were added to a separate flame dried round bottom flask, which was then stirred and cooled to 0 ºC before the crude material prepared above was added dropwise over 5 minutes. $NaHCO_3$ (20 g, 238 mmol) then added in 3-4 portions at 0 ºC before the resulting suspension allowed to warm to room temperature and stirring was continued overnight. The reaction mixture was diluted with EtOAc and washed with H_2O (x2) then with brine, before the combined aqueous layers were extracted with EtOAc (x2). The combined organic phases were dried over $MgSO_4$, filtered, concentrated on rotary evaporator and purified by flash column chromatography on silica gel (hexanes or pentane/EtOAc (9/1)) to give 1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (**1**) in 75% yield (2.5 g, 12 mmol) as a colorless oil. *Note:* Lower yields were observed using this method on larger scales.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 2.73 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.96 (ddd, *J* = 12.0, 4.6, 0.8 Hz, 1H), 2.99-3.12 (m, 2H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.70 (d, *J* = 13.2 Hz, 1H), 4.57-4.61 (m, 1H), 5.82-5.89 (m, 2H), 7.25-7.29 (m, 1H), 7.31-7.38 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ: 52.0, 53.7, 57.2, 61.8, 126.8, 127.3, 128.3, 128.98, 129.04, 137.5; **^{1}H NMR** (400 MHz, C_6D_6, ppm) δ: 2.53-2.58 (m, 3H), 2.67 (dd, *J* = 12.0, 4.6 Hz, 1H), 3.21 (d, *J* = 13.2 Hz, 1H), 3.28 (d, *J* = 13.2 Hz, 1H), 4.30-4.35 (m, 1H), 5.35 (dtd, *J* = 9.8, 3.2, 1.2 Hz, 1H), 5.65 (bddd, *J* = 11.0, 5.2, 2.4 Hz, 1H), 7.08-7.12 (m, 1H), 7.16-7.19 (m, 2H), 7.26-7.28 (m, 2H); **IR** (ATR) ν (cm^{-1}) neat: 3030, 2802, 1493, 1453, 1144, 1071, 1026, 984, 911, 792, 731, 697; **HRMS** (ESI) *m/z* calcd for $C_{12}H_{15}NCl^+$ $[M+H]^+$ 208.08875, found 208.08884.

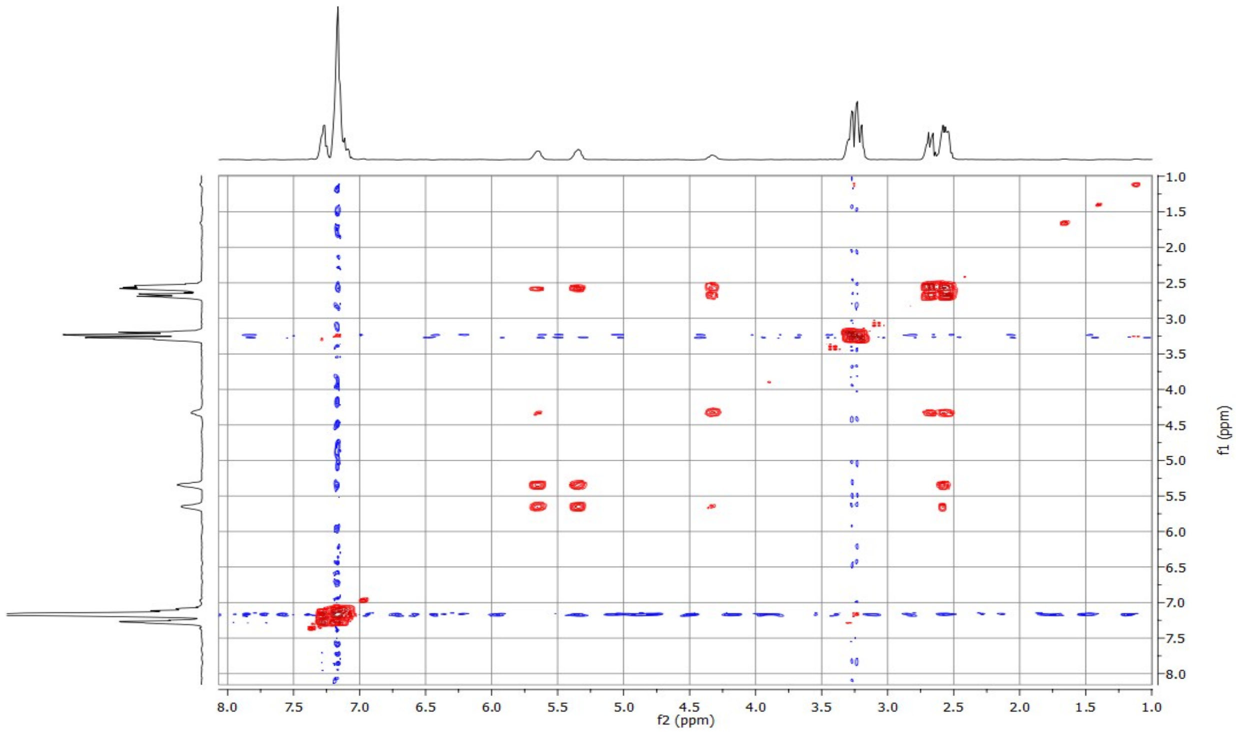




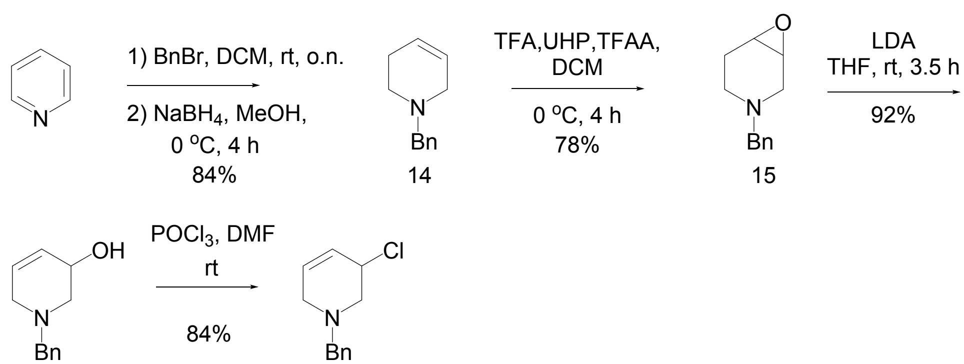
^{1}H-NMR of 1 in C_6D_6



COSY NMR of 1 in C_6D_6



Method B:



1-benzyl-1,2,3,6-tetrahydropyridine (14):

Pyridine (4 ml, 48 mmol) and DCM (12 ml) were added to a flame dried 100 ml-round-bottom flask, which was stirred and cooled 0 ºC before benzyl bromide (5.7 ml, 48 mmol) was added dropwise over ~5 min. The reaction mixture was allowed to stir and gradually warm to room temperature overnight before the solvent was removed. Et_2O (10 ml) was added, and then removed using a rotary evaporator to afford a pyridinium salt as an off-white solid which was used without further purification.

The benzylpyridinium bromide was dissolved in MeOH (240 ml), stirred and cooled to 0 ºC before $NaBH_4$ (2.2 g, 56 mmol) was added portionwise. Stirring at 0 ºC was continued for 4 hours before the reaction was quenched with H_2O and concentrated. EtOAc (100 ml) was added and the resulting solution was washed with brine, dried over $MgSO_4$, filtered, concentrated on rotary evaporator and purified by flash column chromatography on silica gel (hexanes/EtOAc/Et_3N (4/1/0.05)) to give 1-benzyl-1,2,3,6-tetrahydropyridine (**14**) in 84% yield (7.0 g, 40 mmol) as a viscous yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 2.14-2.18 (m, 2H), 2.56 (t, *J* = 5.6 Hz, 2H), 2.96-2.99 (m, 2H), 3.58 (s, 2H), 5.64-5.69 (m, 1H), 5.73-5.77 (m, 1H), 7.23-7.27 (m, 1H), 7.29-7.37 (m, 4H). Spectral data is in agreement with literature.[5]

1-benzyl-3,4-epoxypiperidine (15):

Urea hydrogen peroxide (UHP) (3.6 g, 38 mmol) and DCM (33 ml) were added in a dried flask and cooled 0 ºC. A solution of trifluoroacetic anhydride (TFAA) (5.4 ml, 38 mmol) in DCM (20 ml) was added dropwise over 30 min. The resultant suspension was stirred for 1 hour at 0 ºC. Meanwhile TFA (2.8 ml, 35 mmol) was added dropwise into a solution of 1-benzyl-1,2,3,6-tetrahydropyridine (**14**) (4.7 g, 27 mmol) in DCM (20 ml) at 0 ºC and stirred for 1 hour. Cold TFA/piperidine solution was added into UHP/TFAA solution dropwise and stirred for 4 hours at 0 ºC. After completion H_2O (50 ml) was added and biphasic solution was stirred for 15 minutes followed by addition of saturated Na_2SO_3 solution. Organic layer was separated and aqueous layer was neutralized by K_2CO_3 addition and washed with DCM (x3). The combined organic phases were washed with saturated $NaHCO_3$ (x3), dried over $MgSO_4$, filtered, concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes/acetone (7/1)) to give 1-benzyl-3,4-epoxypiperidine (**15**) in 78% yield (4.0 g, 21 mmol) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 1.94-2.08 (m, 2H), 2.20 (ddd, *J* = 11.4, 9.2, 4.2 Hz, 1H), 2.30-2.36 (m, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 3.03 (ddd, *J* = 13.6, 4.0, 1.2 Hz, 1H), 3.21-3.25 (m, 2H), 3.46 (s, 2H), 7.23-7.27 (m, 1H), 7.28-7.33 (m, 4H). Spectral data is in agreement with literature.[6]

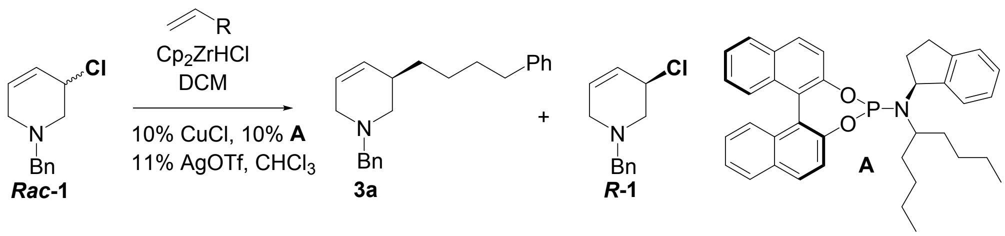
1-benzyl-1,2,3,6-tetrahydropyridin-3-ol (5):

THF (90 ml) and diisopropyl amine (4.3 ml, 30.4 mmol) were added in a flame dried 250 ml-round-bottom flask and cooled to 0 ºC. 2.5 M *n*-butyllithium solution (12 ml, 30.4 mmol) was added dropwise and the resultant solution was stirred at 0 ºC for 45 minutes. A solution of 1-benzyl-3,4-epoxypiperidine (**15**) (4.8 g, 25.4 mmol) in THF (40 ml) was added dropwise into the formed LDA solution, warmed up to room temperature and stirred for 3.5 hours. Reaction was quenched by addition of saturated NH_4Cl solution (40 ml) and extracted with DCM (x3). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, concentrated on rotary evaporator and purified by flash column chromatography on silica gel (hexanes/acetone (5/1)) to give 1-benzyl-1,2,3,6-tetrahydropyridin-3-ol (**5**) in 92% yield (4.4 g, 23.3 mmol) as a viscous yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 2.21 (bs, 1H (OH)), 2.51 (dd, *J* = 11.4, 3.2 Hz, 1H), 2.74-2.81 (m, 2H), 3.13 (dd, *J* = 17.0, 3.2 Hz, 1H), 3.61 (s, 2H), 4.05 (bd, *J* = 4.8 Hz, 1H), 5.82 (ddd, *J* = 10.0, 4.0, 2.4 Hz, 1H), 5.89-5.93 (m, 1H), 7.23-7.28 (m, 1H), 7.29-7.34 (m, 4H). Spectral data is in agreement with literature.[6]

1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (1):

A solution of 1-benzyl-1,2,3,6-tetrahydropyridin-3-ol (**5**) (2.8 g, 14.7 mmol) in DMF (60 mL) was cooled down to 0 ºC and under argon atmosphere $POCl_3$ (2.8 mL, 32.5 mmol) was added dropwise over ~5 min. The reaction mixture was left gradually warming up to room temperature and was stirred overnight. H_2O (30 ml) was carefully added at 0 ºC. The reaction solution was extracted with EtOAc. Aqueous layer was neutralized by K_2CO_3 and washed with EtOAc (x3). The combined organic phases were washed with brine (x2), dried over $MgSO_4$, filtered, concentrated and purified by flash column chromatography on silica gel (hexanes or pentane/EtOAc (9/1)) to give 1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (**1**) in 84% yield (2.6 g, 12.5 mmol) as a colorless oil.

Synthesis of 3a:



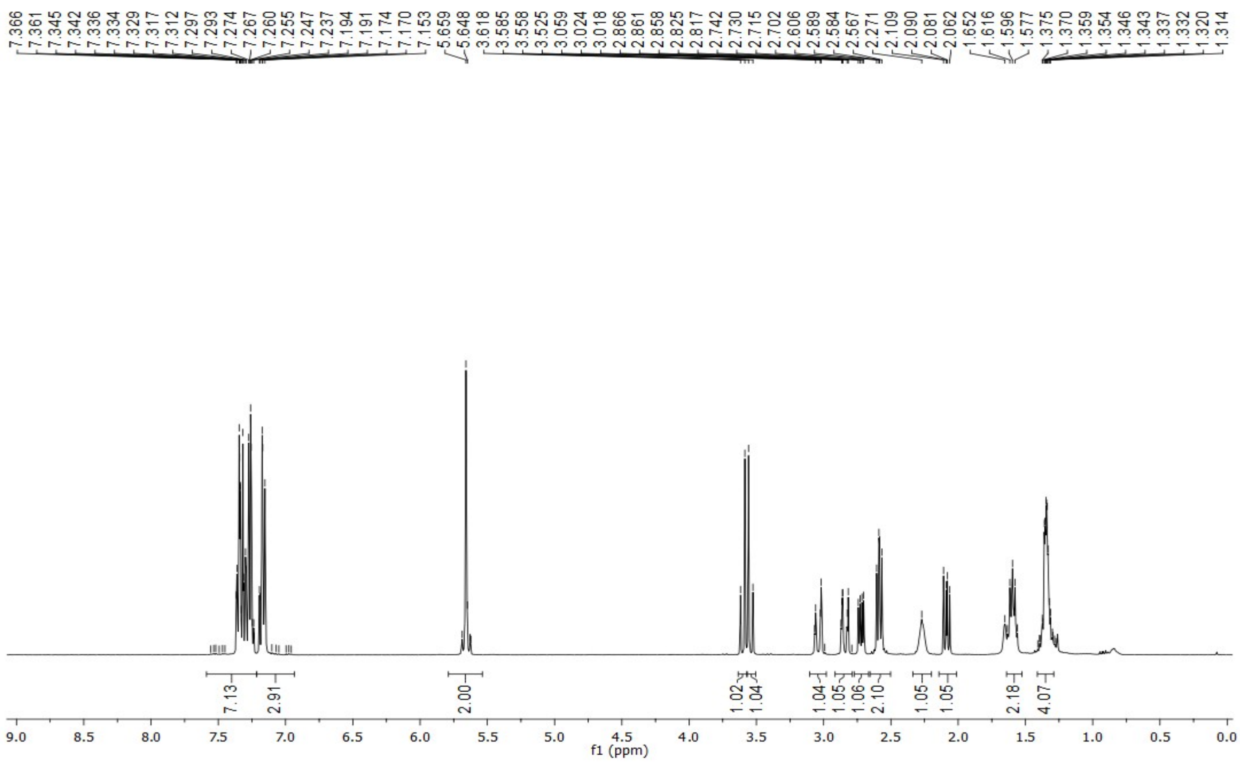
A round-bottom flask equipped with a stirbar was flame dried under vacuum and filled with Ar. The flask was charged with CuCl (4 mg, 0.04 mmol) and ligand **A** (23 mg, 0.04 mmol), flushed with argon, sealed with a septum and wrapped with aluminum foil. $CHCl_3$ (2 ml, freshly collected from SPS) was added and the resultant colorless solution was stirred at room temperature for 1 hour. Meanwhile a separate round-bottom flask containing a stirbar was flame dried under vacuum and filled with Ar. The second flask was charged with Cp_2ZrHCl (206 mg, 0.8 mmol), flushed with argon, sealed with septum and wrapped with aluminum foil. DCM (0.4 ml) and then 4-phenyl-1-butene (1 mmol) were added and the resultant suspension was stirred at room temperature until the mixture became completely clear. After 1 hour fine crystalline AgOTf (11.3 mg, 0.044 mmol) was quickly added to copper catalyst solution and stirred for 15 minutes until all the AgCl precipitated out. This suspension was injected into the solution containing alkylzirconocene using a syringe filter and the resultant black solution was then cooled to 0 ºC. After 5 minutes neat 1-benzyl-3 chloro-1,2,3,6-tetrahydropyridine (**1**) (83 mg, 0.4 mmol) was added with a syringe at once. The reaction was after 2.5 hours by pouring the reaction mixture into a separatory funnel containing Et_2O (10 ml). Material remaining in the flask was rinsed into the separatory funnel solution with EtOAc (2 ml x 2) and the resulting suspension was washed with saturated $NaHCO_3$ solution (5-7 ml x 3). The combined aqueous phases were extracted with EtOAc (5-7 ml x 2). The combined organic layers were dried over $MgSO_4$, filtered, concentrated. Flash column chromatography on silica gel (hexanes/EtOAc (15/1) + 0.5 % Et_3N) gave **3a** in 21% (58%) yield (26 mg, 0.08 mmol) as a yellow oil. Enantiomeric excess was 93% as determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:IPA 99:1; λ = 210 nm; major enantiomer t_R = 11.9 min; minor enantiomer t_R = 18.6 min]; $[D]^{25}_{589}$ = –30.5 (c 0.40 $CHCl_3$) for 93% ee; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 1.27-1.41 (m, 4H), 1.56-1.63 (m, 2H), 2.08 (dd, *J* = 11.2, 7.6 Hz, 1H), 2.27 (bs, 1H), 2.59 (dd, *J* = 8.8, 6.8 Hz, 2H), 2.72 (dd, *J* = 11.2, 5.0 Hz, 1H), 2.79-2.87 (m, 1H), 2.99-3.06 (m, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.60 (d, *J* = 13.2 Hz, 1H), 5.62-5.69 (m, 2H), 6.96-7.19 (m, 3H), 7.23-7.26 (m, 7H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ: 26.6, 31.7, 33.9, 35.89, 36.04, 53.1, 55.6, 62.8, 124.8, 125.6, 126.9, 128.2, 128.4, 129.0, 130.1, 138.5, 142.7; **IR**

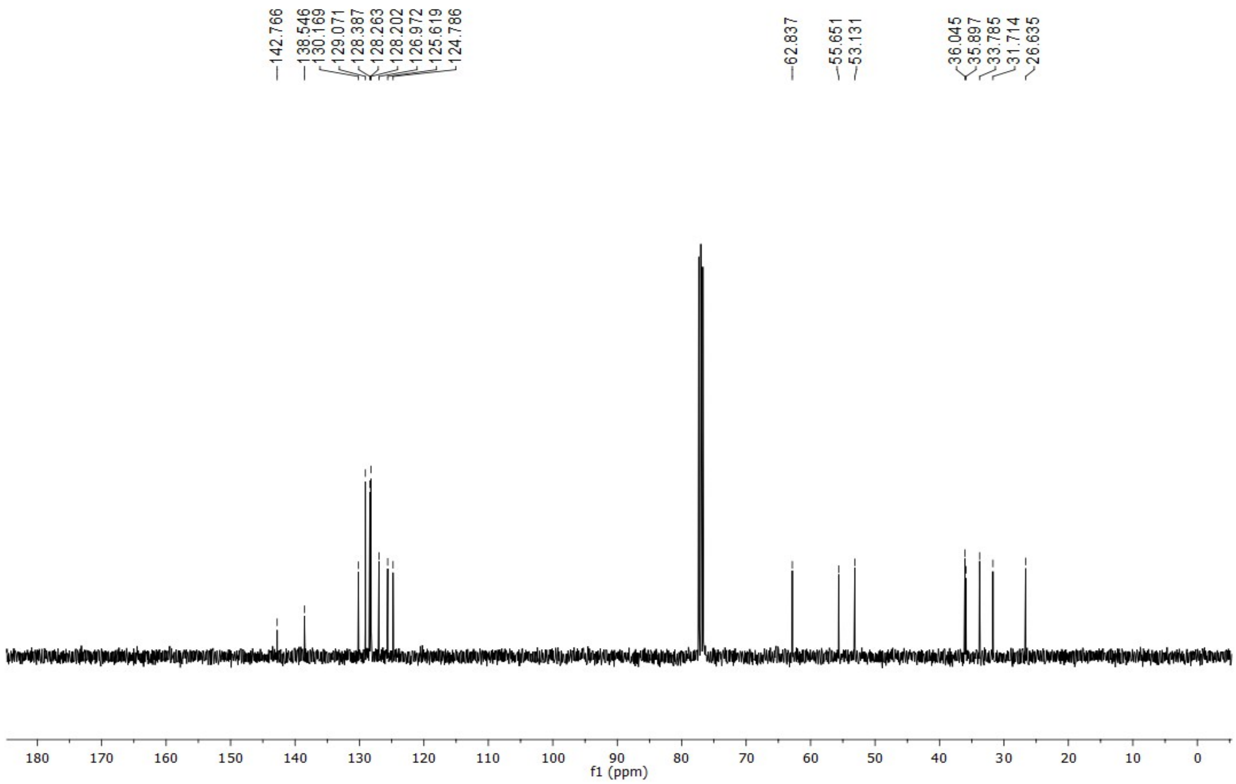
(ν_{max} /cm^{-1}): 695, 729, 908, 1026, 1133, 1360, 1454, 1494, 2855, 2926, 3026; **HRMS** (ESI) *m/z* calcd for $C_{22}H_{28}N^+$ $[M+H]^+$ 306.22163, found 306.22150.

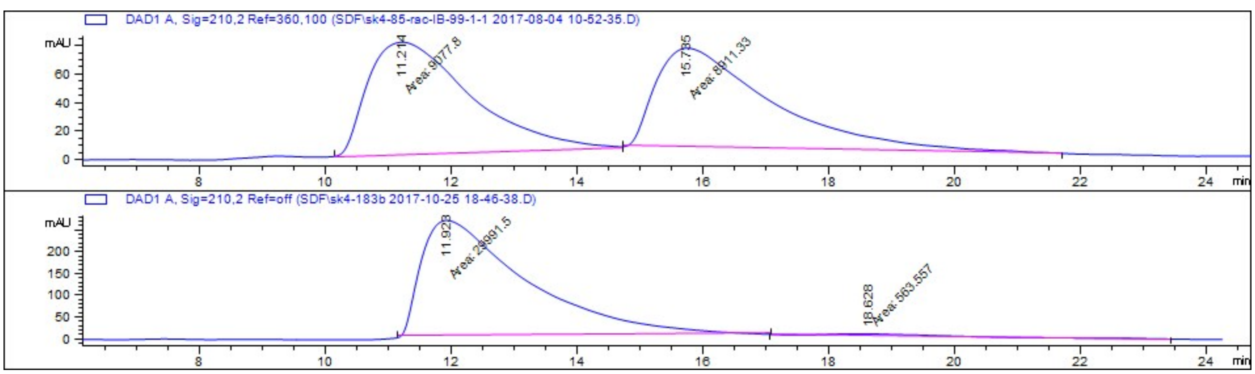
Yield in parenthesis calculated with respect to consumed starting material.

The reaction gave (*R*)-1-benzyl-3 chloro-1,2,3,6-tetrahydropyridine in 64% yield (53 mg, 0.26 mmol, ee = 25%). Enantiomeric excess of recovered ***R*-1** was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99.3:0.7; λ = 210 nm].

***Note*:** Solution heterogeneity was found to influence results. Ideally, Cu-catalysed reactions should be conducted in a round-bottom flask with an egg-shaped stirbar, magnetically stirred at ~350 rpm. Brand new septa were used to seal reaction flasks to prevent solvent evaporation.







General Procedure for Preparation of racemic products:

Racemic products were synthesized by above mentioned procedure using racemic (3,5-dioxo-4-phosphacyclohepta[2,1-a:3,4-a']dinaphthalen-4-yl)dimethylamine (MonoPhos®). Reactions were stirred at room temperature overnight.

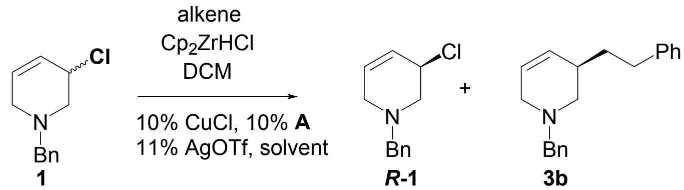
Kinetic Resolution of *rac*-1 in a Cu-catalysed asymmetric addition:

Experiment conditions are same as described for synthesis of **3a**.

Time (min)	Conversion[a] (%)	ee of 3a (%)	ee of *R*-1(%)
15	11	88	9
30	16	94	9
45	18	94	15
60	22	94	17
75	25	92	20
90	26	93	25
105	28	92	29
120	31	91	34
135	32	90	32
150	33	90	36
165	34	91	38
180	36	88	39
210	38	91	46
240	40	90	46
270	41	89	53
330	43	89	58
360	45	87	58
390	43	87	63
420	47	86	63
450	45	87	65
480	47	86	67
510	47	86	69
555	49	86	70
600	49	85	71
1320	52	78	81
1380	51	78	79
1440	52	78	81

[a]Conversion determined by ^{1}H-NMR

Optimization of resolution of 1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (1):

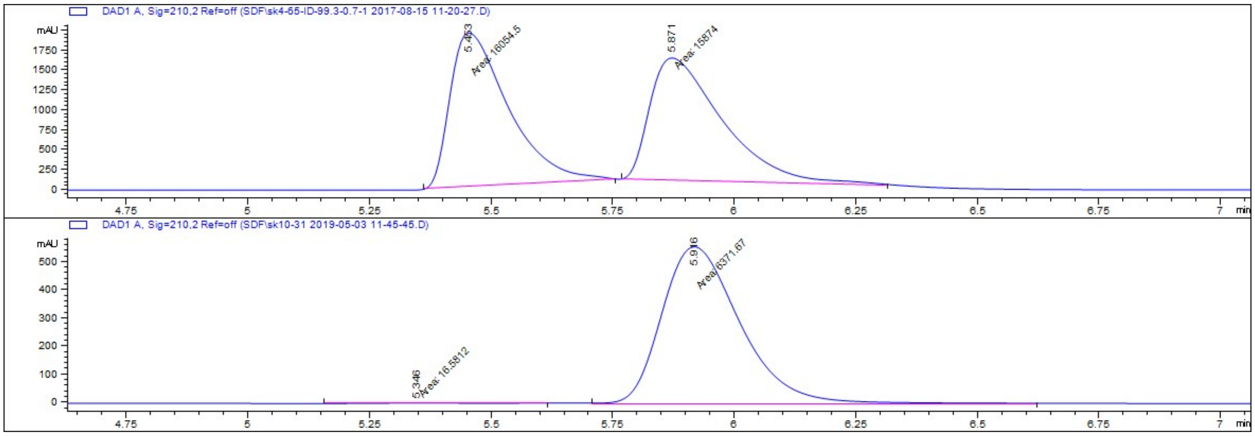


Entry	Alkene	Temp. (˚C)	Time	Solvent/Conc. (M)	Yield (%)	ee (%)
1	1-hexene	rt	40 min	$CHCl_3$/0.20	46	68
2	1-hexene	rt	2.5 h	$CHCl_3$/0.20	28	81
3	Styrene	0	4 h	$CHCl_3$/0.20	48	54
4	Styrene	0	18 h	$CHCl_3$/0.20	19	90
5	Styrene	0	18 h	$CHCl_3$/0.10	42	27
6	Styrene	0	18 h	Et_2O/0.10	69	2
7	Styrene	0	18 h	MTBE/0.10	65	3
8	Styrene	0	18 h	DCM/0.10	22	97
9	Styrene	–10	18 h	DCM/0.10	59	20
10[a]	Styrene	0	18 h	DCM/0.10	42	58
11	Styrene	0	18 h	DCM/0.075	33	98
12	Styrene	0	18 h	DCM/0.050	30	99

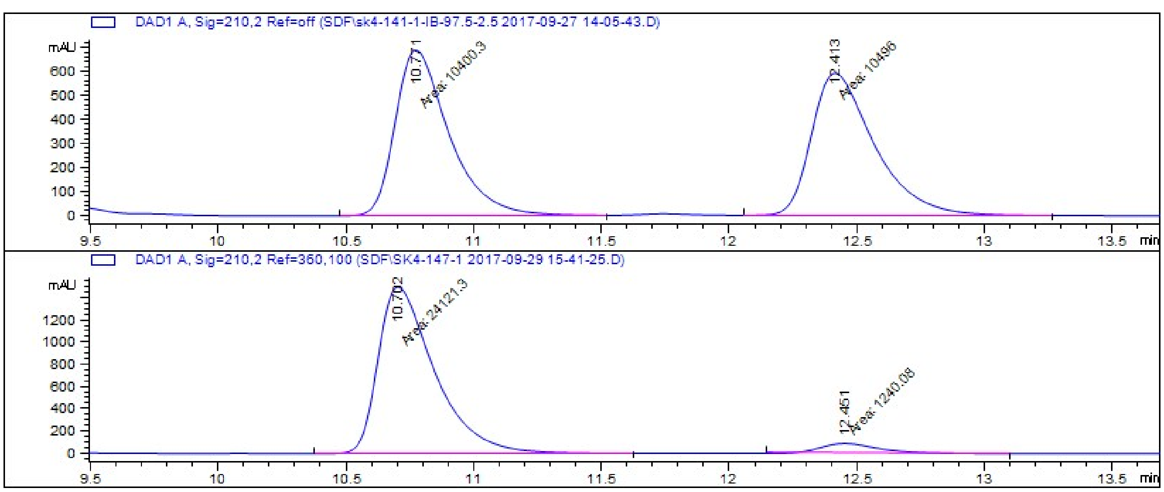
[a] 5% CuCl, 5% **A** and 5.5% AgOTf was used.

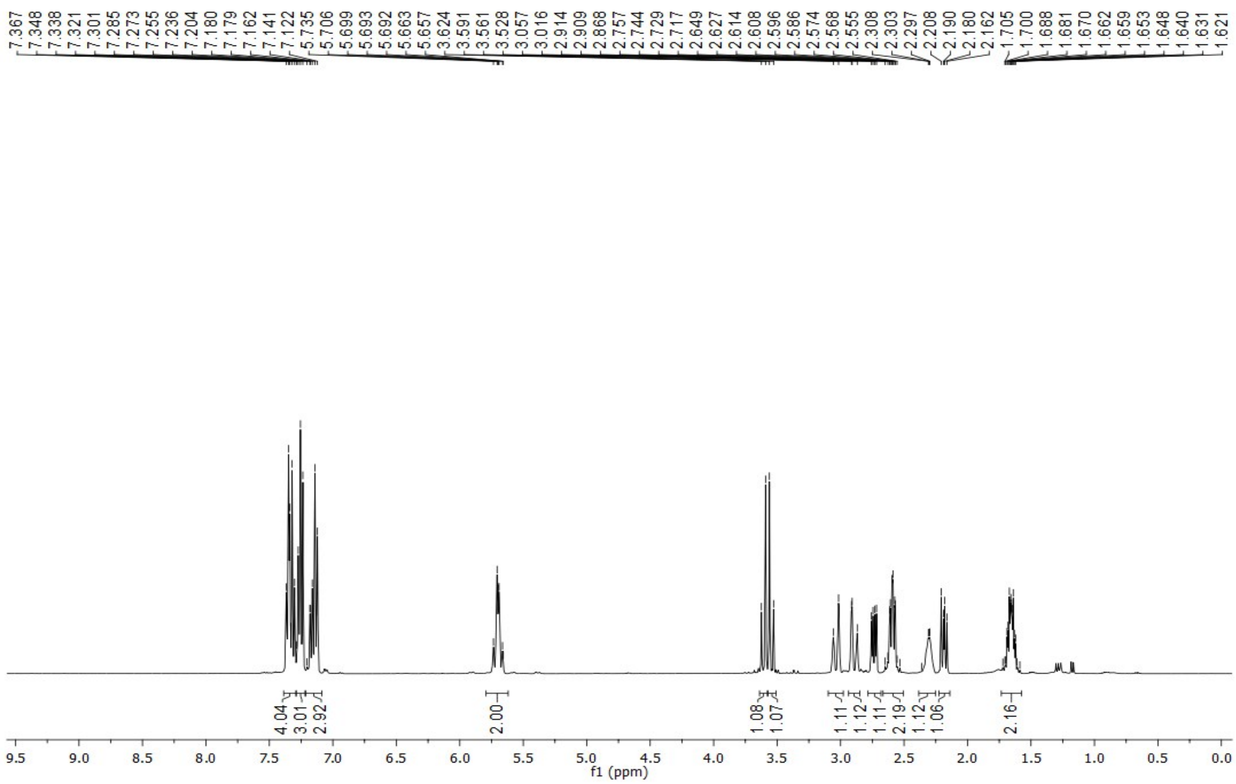
General Procedure for Resolution of 1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (1):

A round-bottom flask equipped with a stirbar was flame dried under vacuum and filled with Ar. The flask was charged with CuCl (4 mg, 0.04 mmol) and ligand **A** (23 mg, 0.04 mmol), flushed with argon, sealed with a septum and wrapped with aluminum foil. DCM (2 ml, freshly collected from SPS) was added and the resultant colorless solution was stirred at room temperature for 1 hour. Meanwhile a separate round-bottom flask containing a stirbar was flame dried under vacuum and filled with Ar upon cooling. The second flask was charged with Cp_2ZrHCl (206 mg, 0.8 mmol), flushed with argon, sealed with a septum and wrapped with aluminum foil. DCM (0.4 ml) and then styrene (0.12 ml, 1.0 mmol) were added and the resultant suspension was stirred at room temperature until the mixture became completely clear. After 1 hour fine crystalline Ag(OTf) (12 mg, 0.044 mmol) was quickly added to copper catalyst solution and stirred for 15 minutes until all the AgCl precipitated out. This suspension was injected into the solution containing alkylzirconocene using a syringe filter and the resultant black solution was cooled 0 ˚C and more DCM (5.6 ml) was added for dilution. After 5 minutes neat 1-benzyl-3 chloro-1,2,3,6-tetrahydropyridine (**1**) (83 mg, 0.4 mmol) was added with a syringe at once and solution was stirred for 18 hours at 0 ˚C. The reaction was stopped by pouring the reaction mixture into a seperatory funnel containing Et_2O (10 ml). Material remaining in the flask was rinsed into seperatory funnel with EtOAc (2 ml x2) and the resulting suspension was washed with saturated $NaHCO_3$ solution (5-7 ml x3). The combined aqueous phases were extracted with EtOAc (5-7 ml x2). The combined organic layers were dried over $MgSO_4$, filtered, concentrated on rotary evaporator and purified by flash column chromatography on silica gel (hexanes/EtOAc (19/1)) to give ***R*-1** in 30% yield (25 mg, 0.12 mmol) as a yellow oil. Enantiomeric excess of 99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99.3:0.7; λ = 210 nm, minor enantiomer t_R = 6.0 min, major enantiomer t_R = 6.6 min]; $[D]^{25}_{589}$ = +154.9 (c 1.00 $CHCl_3$) for 99% ee.



3b was obtained in 65% (93%) yield (72 mg, 0.26 mmol) as a yellow oil. Enantiomeric excess (for corresponding Cbz carbamate) of 88% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:IPA 97.5:2.5; λ = 210 nm; major enantiomer t_R = 10.7 min; minor enantiomer t_R = 12.4 min]; $[D]^{25}_{589}$ = –58.8 (c 0.40 $CHCl_3$) for 88% ee; $[D]^{25}_{589}$ = –49.7 (c 0.50 $CHCl_3$) for 88% ee for Cbz carbamate; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 1.59-1.72 (m, 2H), 2.18 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.30-2.36 (m, 1H), 2.53-2.65 (m, 2H), 2.74 (dd, *J* = 11.2, 5.0 Hz, 1H), 2.87-2.91 (m, 1H), 3.04 (bd, *J* = 16.4 Hz, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 5.67-5.73 (m, 2H), 7.12-7.20 (m, 3H), 7.23-7.28 (m, 3H), 7.30-7.37 (m, 4H). **^{1}H NMR** (400 MHz, C_6D_6, ppm) δ: 1.55-1.66 (m, 2H), 2.17 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.19-2.26 (m, 1H), 2.42 (d, *J* = 8.0 Hz, 1H), 2.44 (d, *J* = 8.0 Hz, 1H), 2.58 (dd, *J* = 10.4, 4.4 Hz, 1H), 2.78 (ddd, *J* = 16.2, 5.2, 2.6 Hz, 1H), 2.88 (ddd, *J* = 16.0, 4.8, 2.4 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 3.45 (d, *J* = 13.2 Hz, 1H), 5.54 (dtd, *J* = 9.8, 3.2, 2.0 Hz, 1H), 5.64 (bddd, *J* = 10.0, 5.0, 3.0 Hz, 1H), 7.02 (bd, *J* = 7.8 Hz, 2H), 7.05-7.14 (m, 3H), 7.16-7.22 (m, 3H), 7.37 (bd, *J* = 7.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 33.3, 35.74, 35.79, 53.2, 55.3, 62.8, 125.2, 125.7, 127.0, 128.2, 128.3, 128.4, 129.1, 129.7, 136.6, 142.5; **IR** (v_{max} /cm^{-1}): 695, 730, 998, 1028, 1140, 1453, 1493, 2749, 2793, 2858, 2922, 3026; **HRMS** (ESI) *m/z* calcd for $C_{20}H_{24}N^+$ $[M+H]^+$ 278.19033, found 278.19022.

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1.631
1.621
4.04
3.01
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2.00
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1.07
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1.12
1.11
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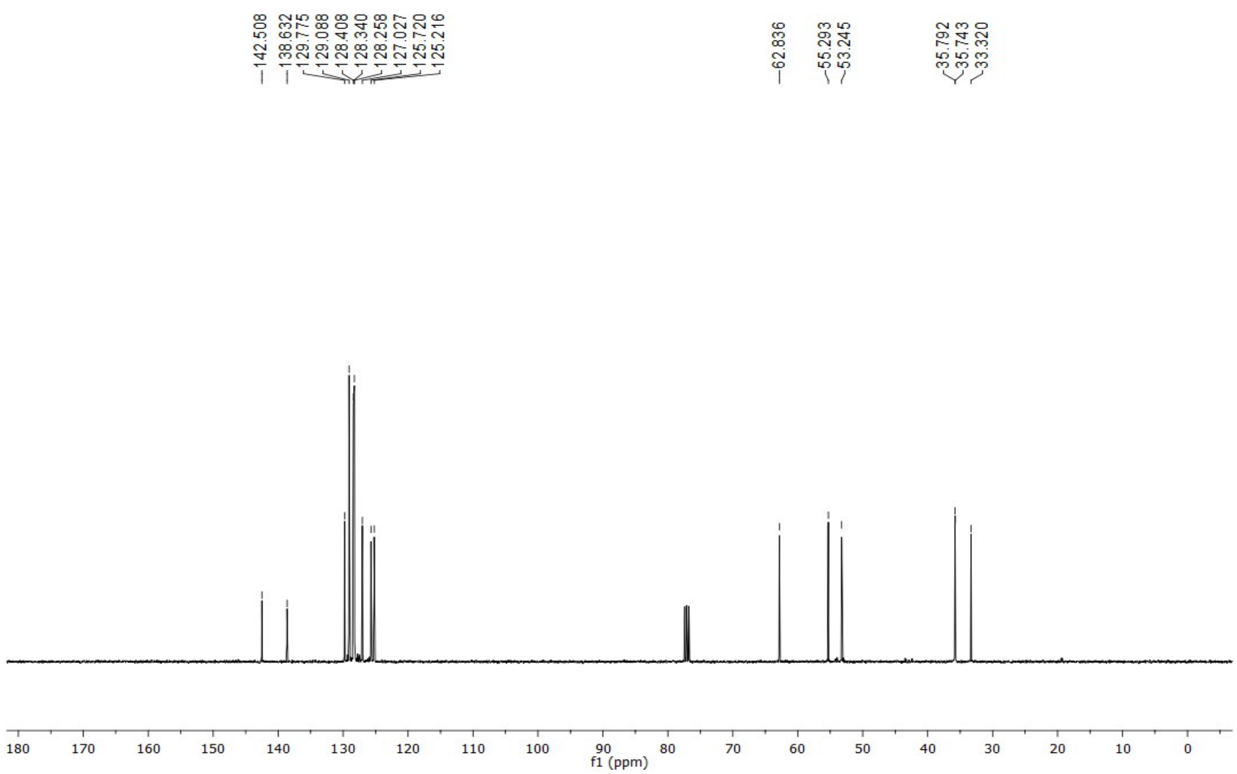
1.12
1.06
2.16
f1 (ppm)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125.216
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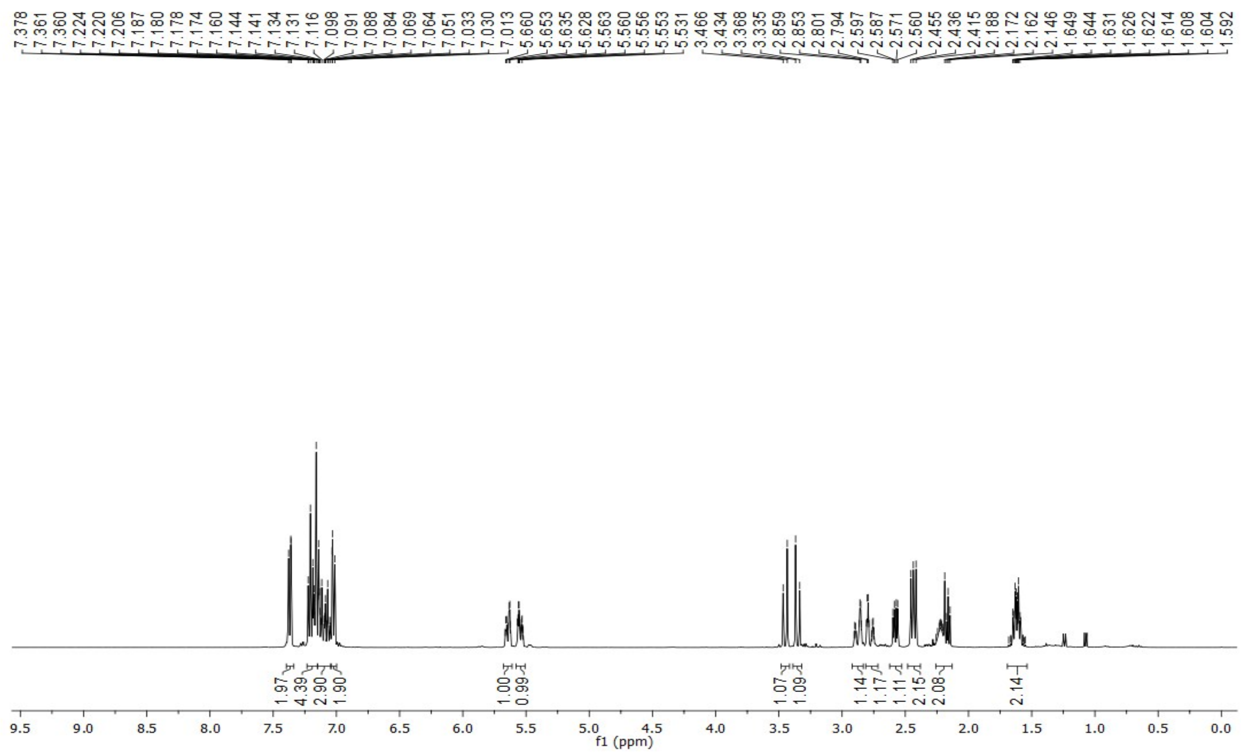
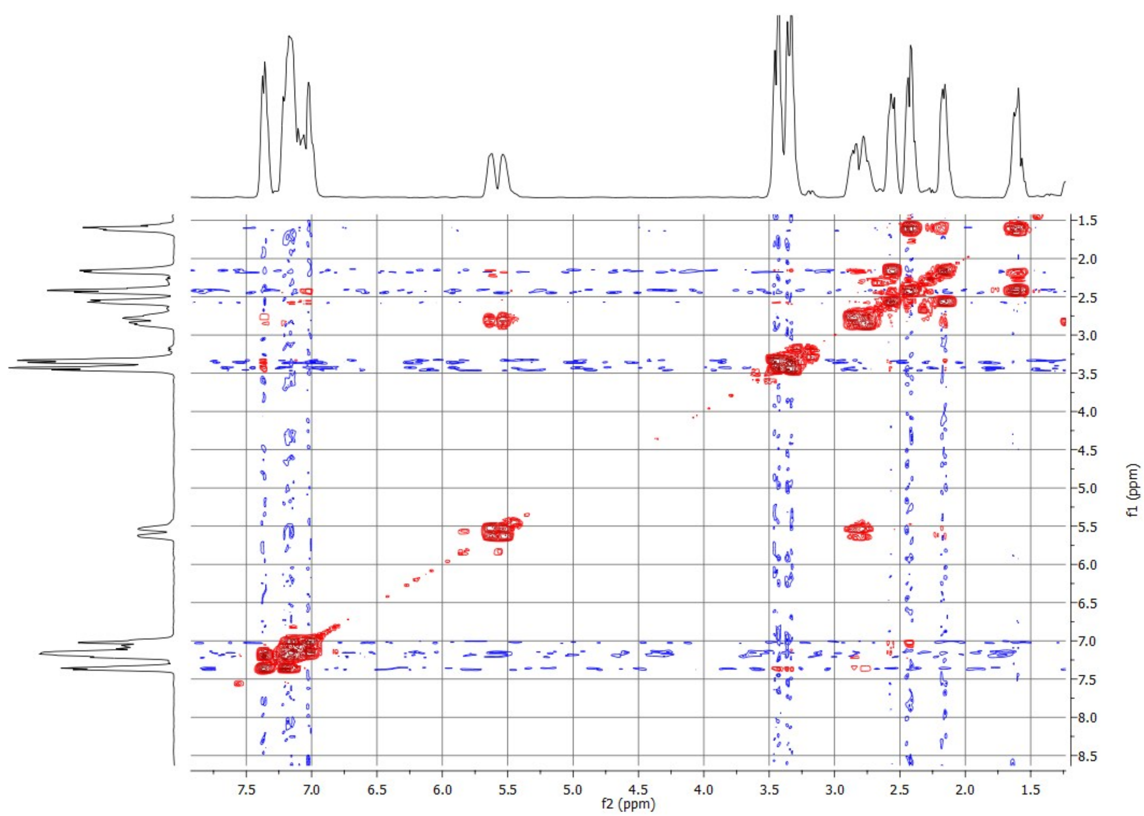
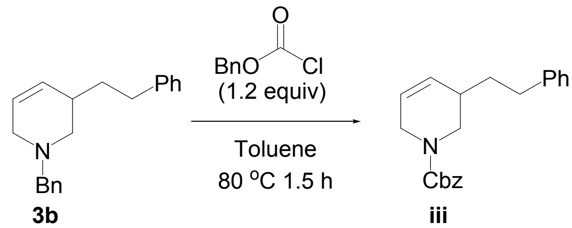
35.792
35.743
33.320
f1 (ppm)

[1]H-NMR and COSY-NMR of 3b in C_6D_6

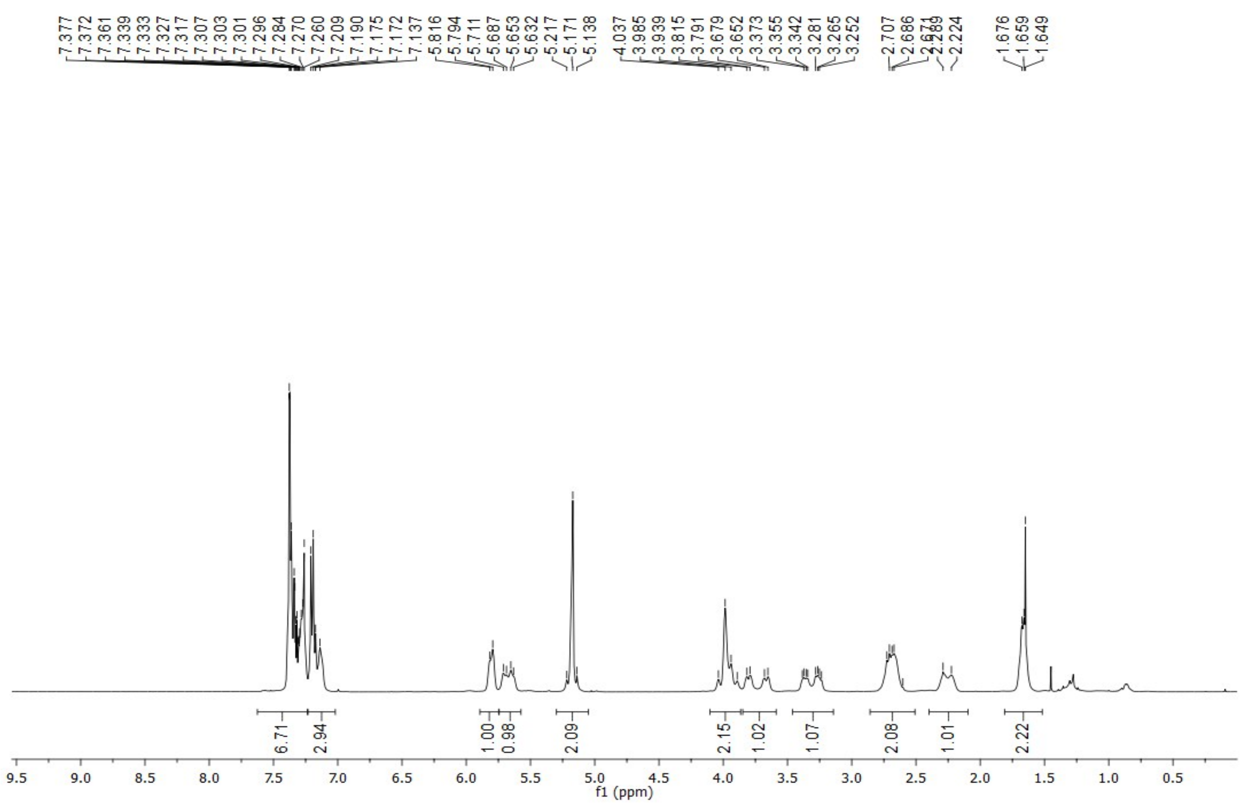


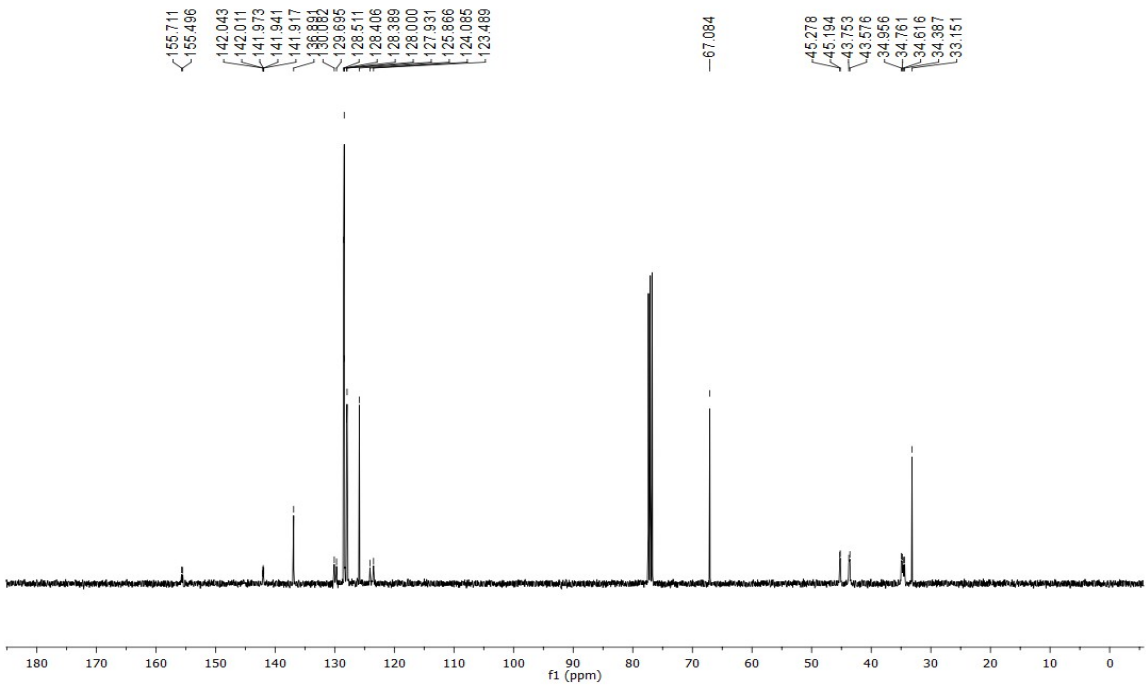


General Procedure for Synthesis of Cbz-carbamates for HPLC analysis:



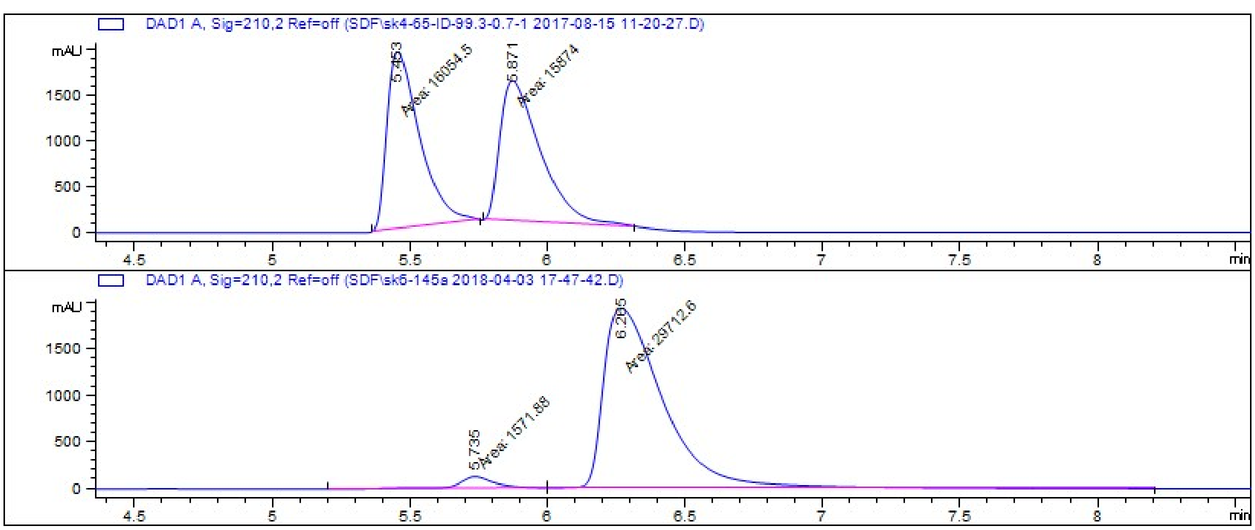
A literature procedure was followed.[7] Representative procedure; 1-benzyl-3-phenethyl-1,2,3,6-tetrahydropyridine (**3b**) (44 mg, 0.16 mmol), followed by benzyl chloroformate solution in toluene (0.5 M, 0.4 ml) was added to a vial charged with a stirbar. The vial was flushed with Ar, sealed with a cap, heated to 80 ºC and stirred at this temperature for 1.5 hours. The reaction solution was filtered through silica gel with 9/1 heaxane/EtOAc mixture to remove nonpolar impurities and unreacted benzyl chloroformate. Benzyl 3-phenethyl-3,6-dihydropyridine-1(2*H*)-carboxylate (**iii**) was obtained in 86% yield (42 mg, 0.14 mmol) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 1.65-1.67 (m, 2H), 2.22 and 2.29 (rotameric bs), 2.60-2.72 (m, 2H), 3.26 and 3.36 (rotameric dd, *J* = 12.0, 6.6 and 4.8 Hz, 1H), 3.66 and 3.80 (rotameric bd, *J* = 10.8 and 9.6 Hz, 1H), 3.89-4.03 (m, 2H), 5.14-5.21 (rotameric m, 2H), 5.63-5.71 (m, 1H), 5.80 (bd, *J* = 8.8 Hz, 1H), 7.10-7.21 (m, 3H), 7.26-7.37 (m, 7H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ: 33.1, 34.3 and 34.6 (rotameric), 34.7 and 34.9 (rotameric), 43.5 and 43.7 (rotameric), 45.19 and 45.27 (rotameric), 67.1, 123.5 and 124.1 (rotameric), 125.8, 127.9, 128.0, 128.39, 128.40, 128.5, 129.7 and 130.1 (rotameric), 136.9, 142.0 (m, rotameric), 155.5 and 155.7 (rotameric); **IR** (v_{max} /cm^{-1}): 695, 732, 1112, 1231, 1426, 1495, 1697, 2855, 2922, 3029; **HRMS** (ESI) *m/z* calcd for $C_{21}H_{23}O_2NNa^+$ $[M+Na]^+$ 344.16210, found 344.16202.



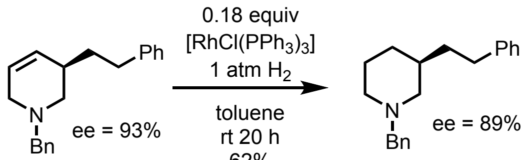


Procedure for resolution of 1 in larger scale:

The above procedure was followed using 831 mg (4.00 mmol) **1**, 1.2 ml (10.0 mmol) styrene, 40 mg (0.4 mmol) CuCl, 230 mg (0.4 mmol) ligand **A**, 120 mg (0.44 mmol) AgOTf and 2.0 g (8.0 mmol) Cp_2ZrHCl. The reaction was run in 80 ml DCM (20 ml of DCM was used for catalyst solution, 8 ml of DCM was used in hydrozirconation step and 52 ml of DCM was added for dilution) for 2 hours at 0 °C. Resolved ***R*-1** was obtained in 37% yield (309 mg, 1.5 mmol). Enantiomeric excess of 92% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99.3:0.7; λ = 210 nm, minor enantiomer t_R = 5.7 min major enantiomer t_R = 6.2 min].

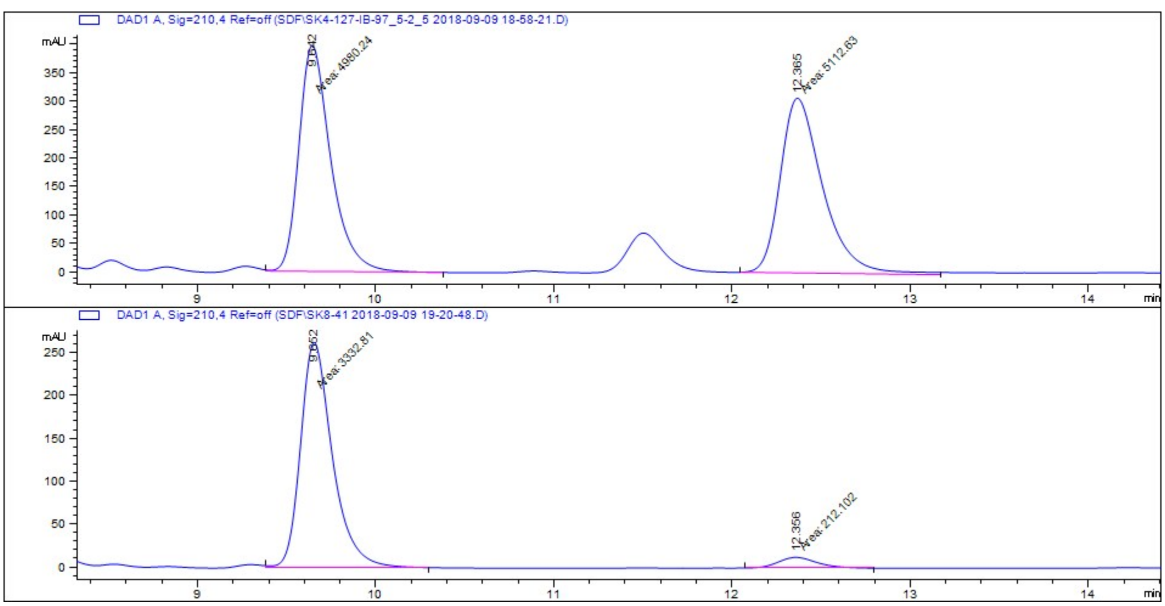


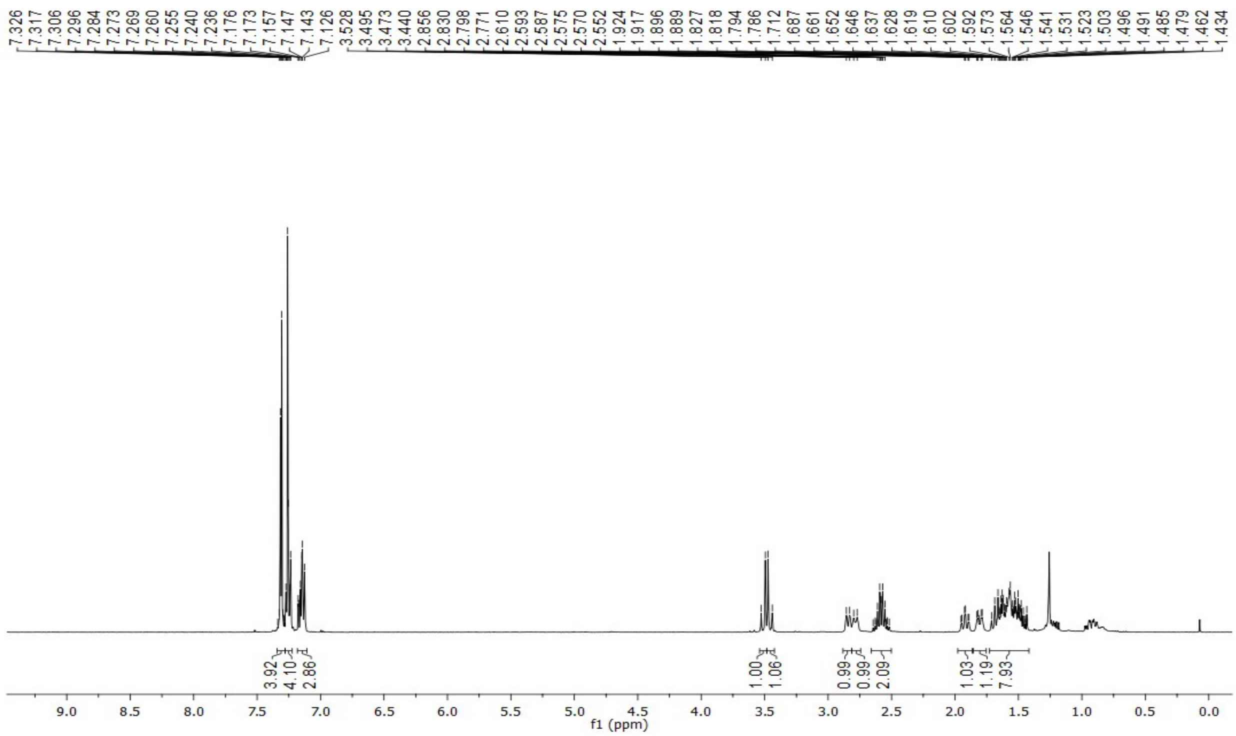
Synthesis of (*R*)-1-benzyl-3-phenethylpiperidine (3b-*H*)



3b **3b-*H***

A solution of (*R*)-1-benzyl-3-phenethyl-1,2,3,6-tetrahydropyridine (**3b**) (40 mg, 0.14 mmol), [$RhCl(PPh_3)_3$] (24 mg, 0.026 mmol) in toluene (2 mL) was first flushed with argon and after with H_2. The mixture was then stirred for 20 h at room temperature under H_2 atmosphere (1 atm). The resulting mixture was concentrated on rotary evaporator. Purification by column chromatography (pentane/EtOAc (9/1)) gave **3b-*H*** in 62% yield (25 mg, 0.09 mmol) as a colorless oil. Enantiomeric excess (for corresponding Cbz carbamate) of 89% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:IPA 97.5:2.5; λ = 210 nm; major enantiomer t_R = 9.6 min; minor enantiomer t_R = 12.3 min]; $[D]^{25}_{589}$ = –6.5 (c 1.0 $CHCl_3$) for 89% ee; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 1.43-1.71 (m, 7H), 1.78-1.82 (m, 1H), 1.92 (td, *J* = 11.2, 2.8 Hz, 1H), 2.52-2.64 (m, 2H), 2.78 (bd, *J* = 10.8 Hz, 1H), 2.84 (bd, *J* = 10.4 Hz, 1H), 3.46 (d, *J* = 13.2 Hz, 1H), 3.51 (d, *J* = 13.2 Hz, 1H), 7.12-7.17 (m, 3H), 7.23-7.27 (m, 3H), 7.28-7.33 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 25.3, 30.9, 33.2, 35.7, 36.4, 54.3, 60.2, 63.6, 125.6, 126.8, 128.1, 128.2, 128.3, 129.1, 142.7 (2C); **IR** (ν_{max} /cm^{-1}): 698, 739, 1029, 1075, 1107, 1157, 1452, 1494, 2337, 2361, 2794, 2852, 2927, 3026; **HRMS** (ESI) *m/z* calcd for $C_{20}H_{26}N^+$ $[M+H]^+$ 280.20598, found 280.20590. For Cbz carbamate **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 1.25-1.33 (m, 4H), 1.45-1.54 (m, 3H), 1.66 (bd, *J* = 9.2 Hz, 1H), 1.88 (bd, *J* = 13.6 Hz, 1H rotameric), 2.63 (bs, 1H rotameric), 2.86 (td, *J* = 11.6, 2.8 Hz, 1H), 3.48-3.53 (m, 1H), 4.00 (dt, *J* = 13.2, 4.0 Hz, 1H rotameric), 5.13 (bs, 2H), 7.16-7.19 (m, 3H), 7.24-7.28 (m, 2H), 7.29-7.37 (m, 5H).





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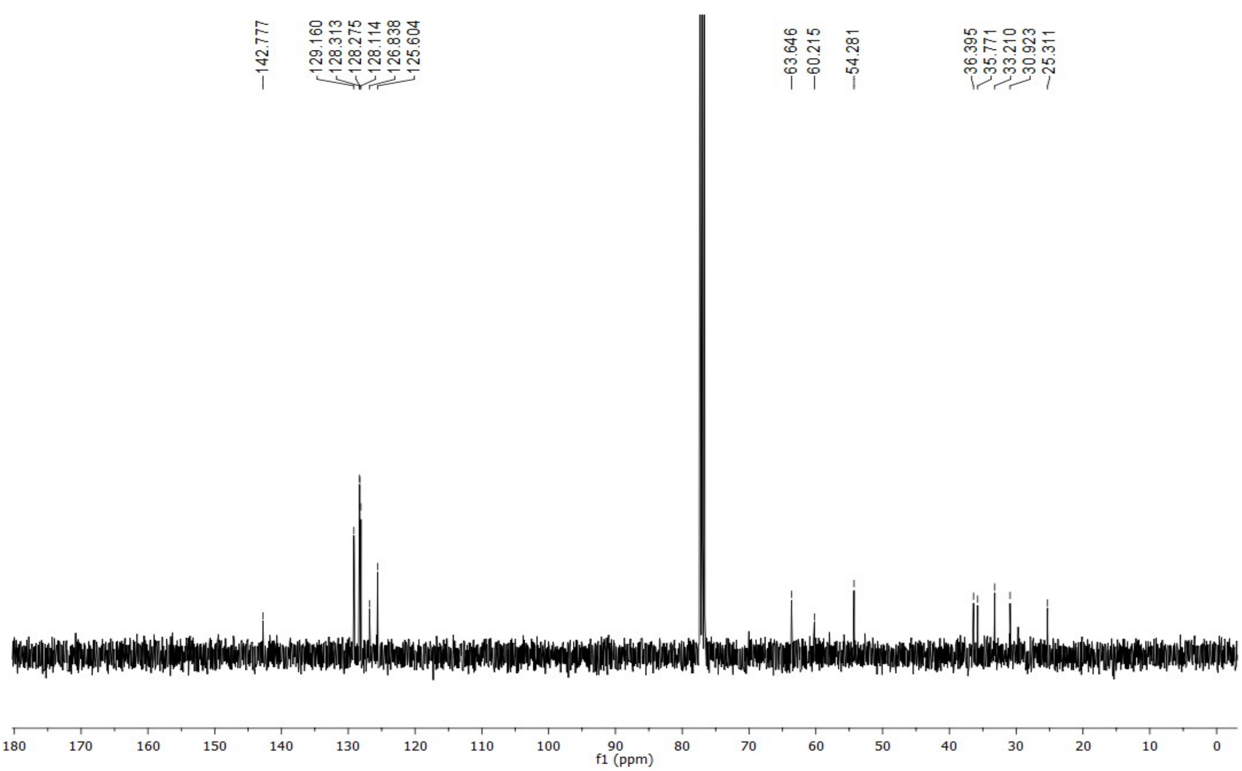

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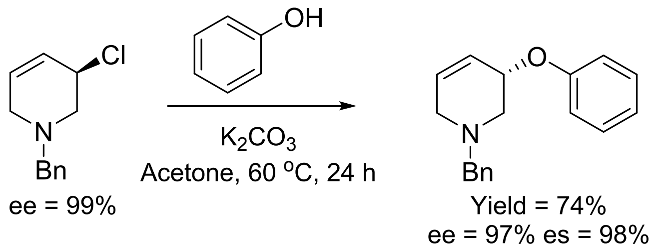
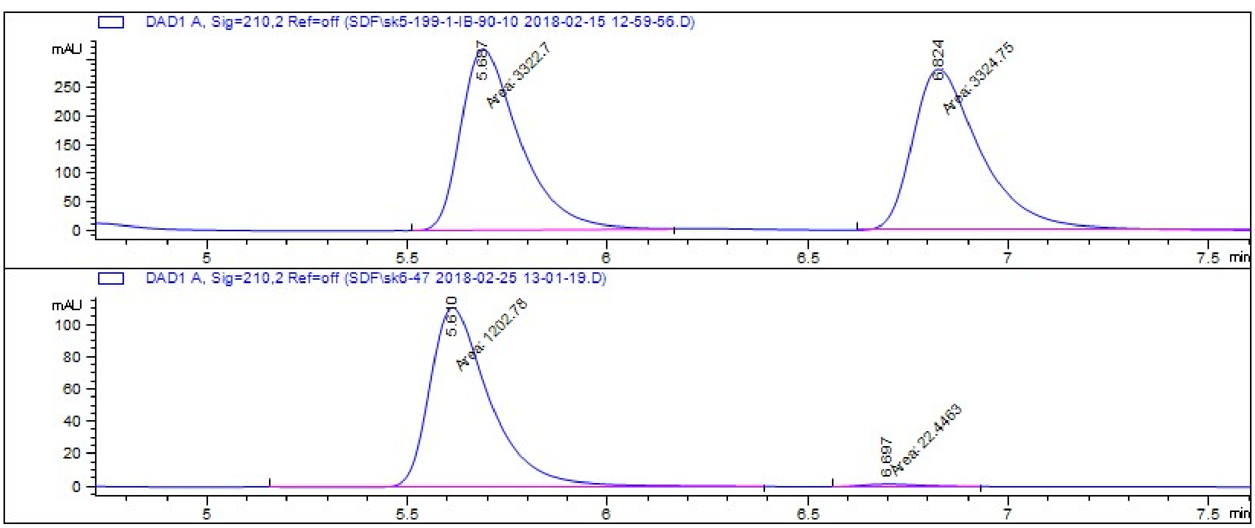
f1 (ppm)

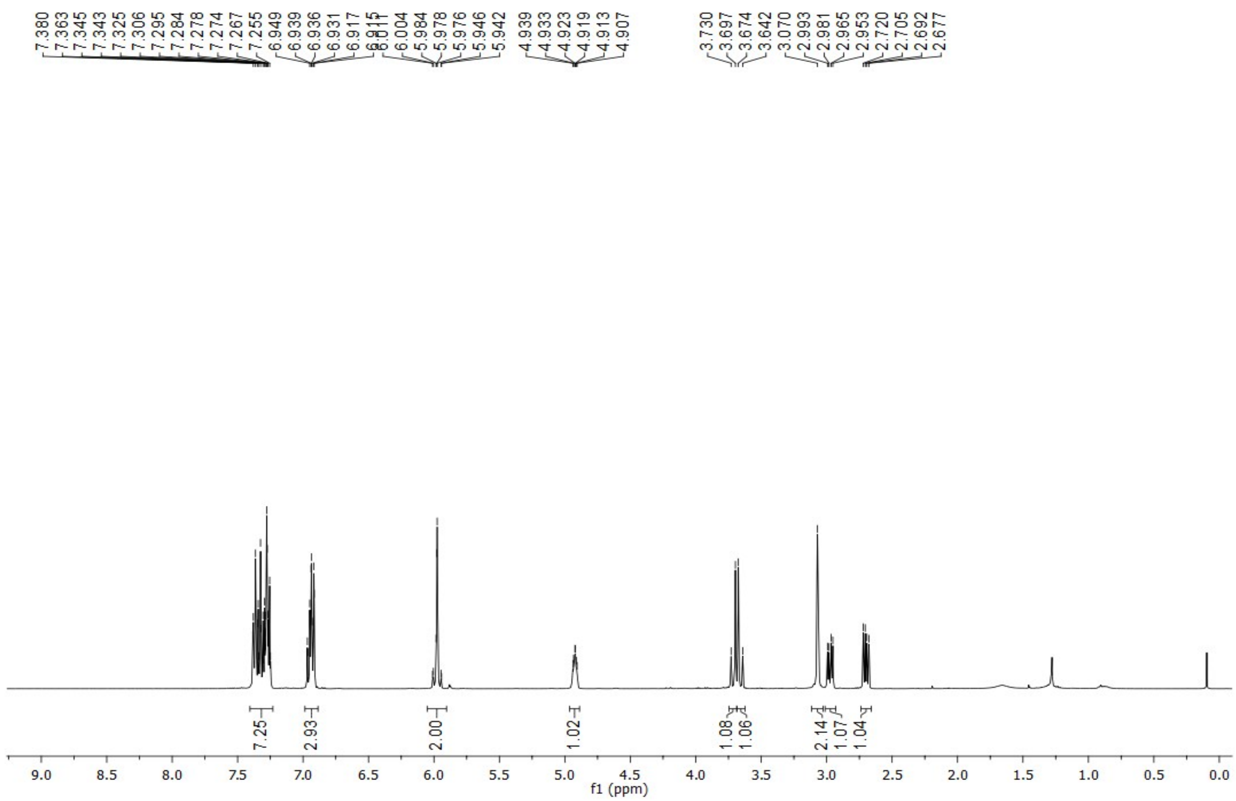
Nucleophilic substitution reactions with *R*-1:

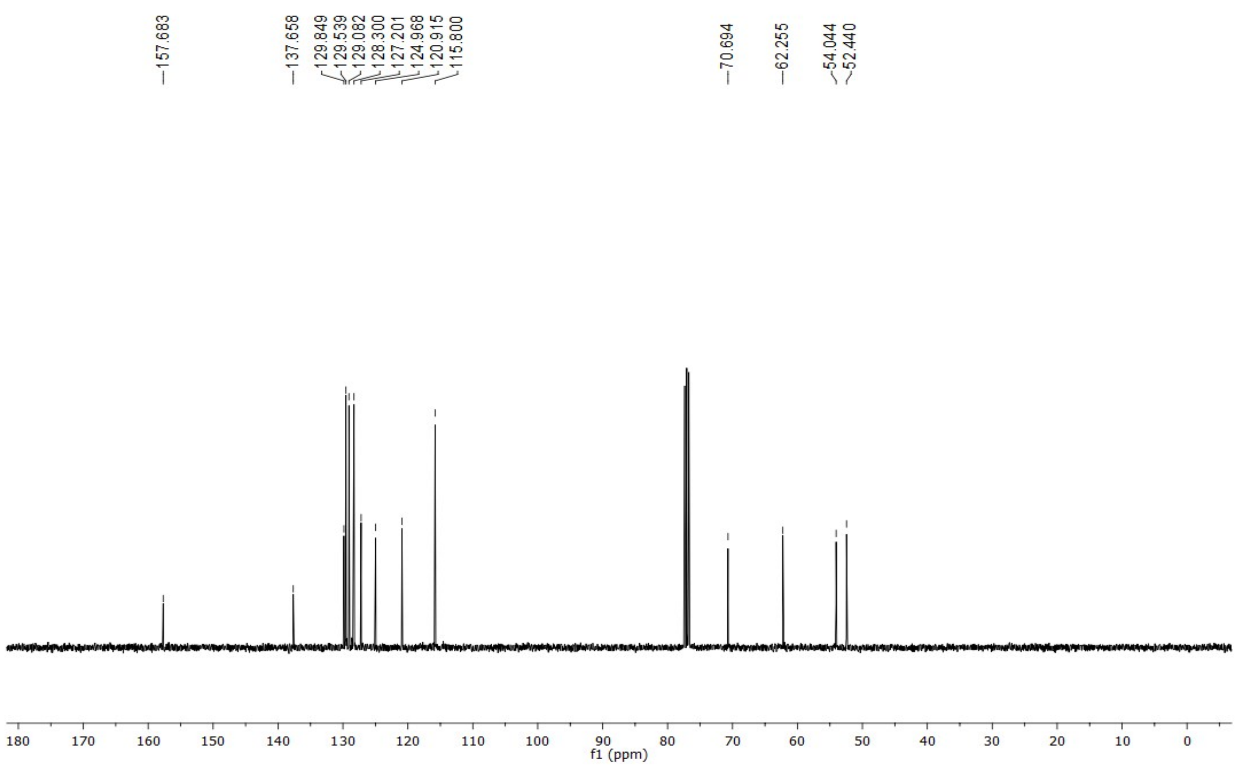
(*S*)-1-benzyl-3-phenoxy-1,2,3,6-tetrahydropyridine (6):



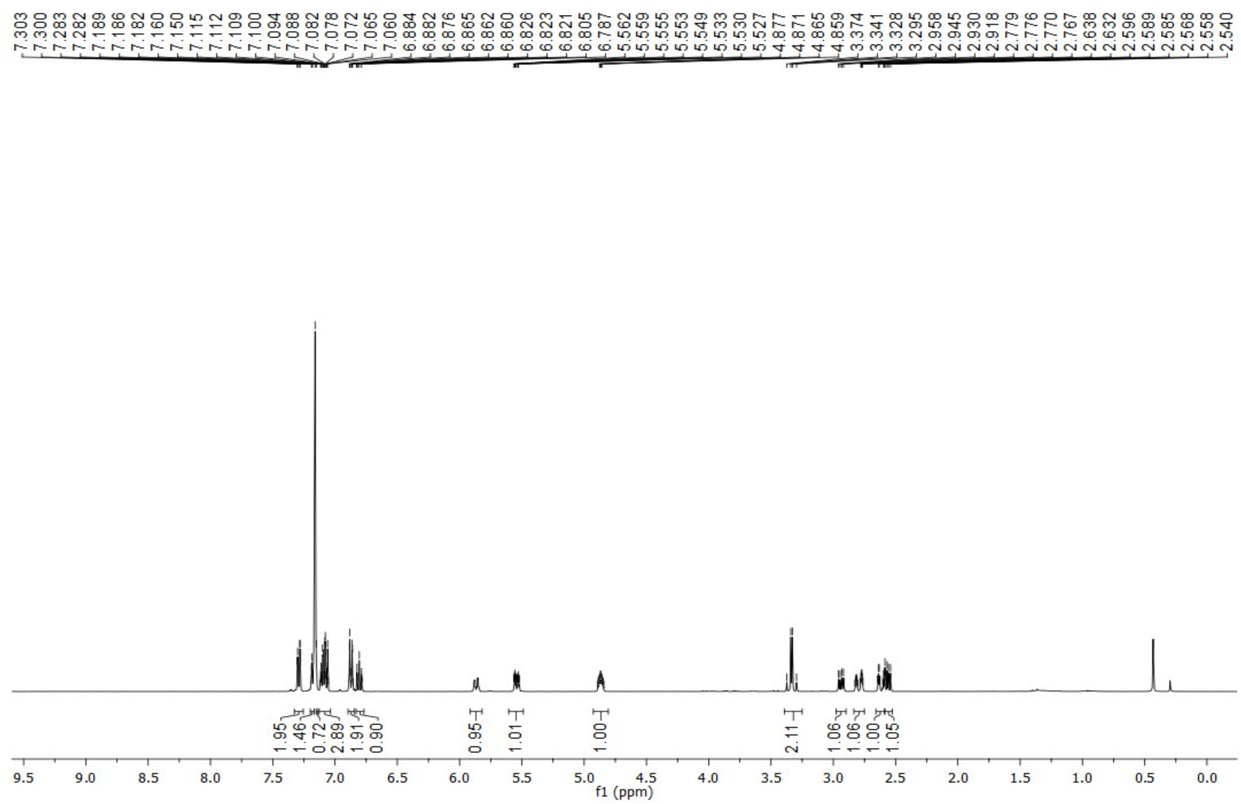
To a flame dried vial containing a stirbar was added phenol (21 mg, 0.22 mmol) and K_2CO_3 (111 mg, 0.80 mmol), and then a solution of (*R*)-1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (***R*-1**) (42 mg, 0.20 mmol) in acetone (1.5 ml). The vial was sealed with a cap and resulting suspension was stirred at 60 °C for 24 hours. Flash column chromatography on silica gel (hexanes/EtOAc (19/1 to 9/1)) gave **6** in 74% yield (39 mg, 0.15 mmol) as off-white solid. Enantiomeric excess of 97% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:IPA 90:10; λ = 210 nm; major enantiomer t_R = 5.6 min; minor enantiomer t_R = 6.7 min]; $[D]^{25}_{589}$ = +70.2 (c 0.85 $CHCl_3$) for 97% ee; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.70 (dd, *J* = 11.2, 6.0 Hz, 1H), 2.97 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.07 (bs, 2H), 3.66 (d, *J* = 12.8 Hz, 1H), 3.71 (d, *J* = 13.2 Hz, 1H), 4.91-4.94 (m, 1H), 5.94-6.01 (m, 2H), 6.91-6.97 (m, 3H), 7.25-7.38 (m, 7H); **^{1}H NMR (400 MHz, C_6D_6, ppm) δ:** 2.56 (dd, *J* = 10.8, 7.0 Hz, 1H), 2.61 (ddd, *J* = 16.8, 5.2, 2.8 Hz, 1H), 2.76-2.82 (m, 1H), 2.94 (bdd, *J* = 11.0, 5.0 Hz, 1H), 3.31 (d, *J* = 13.2 Hz, 1H), 3.36 (d, *J* = 13.2 Hz, 1H), 4.84-4.89 (m, 1H), 5.52-5.56 (m, 1H), 5.85-5.88 (m, 1H), 6.78-6.82 (m, 1H), 6.85-6.88 (m, 2H,), 7.05-7.12 (m, 3H), 7.15-7.19 (m, 2H), 7.28-7.30 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 52.4, 54.0, 62.2, 70.7, 115.8, 120.9, 124.9, 127.2, 128.3, 129.0, 129.5, 129.8, 137.6, 157.7; **IR** (ν_{max} /cm^{-1}): 692, 751, 773, 1032, 1238, 1490, 1591; **HRMS** (ESI) *m/z* calcd for $C_{18}H_{20}ON^+$ $[M+H]^+$ 266.15394, found 266.15396. Spectral data is in agreement with literature.[8]

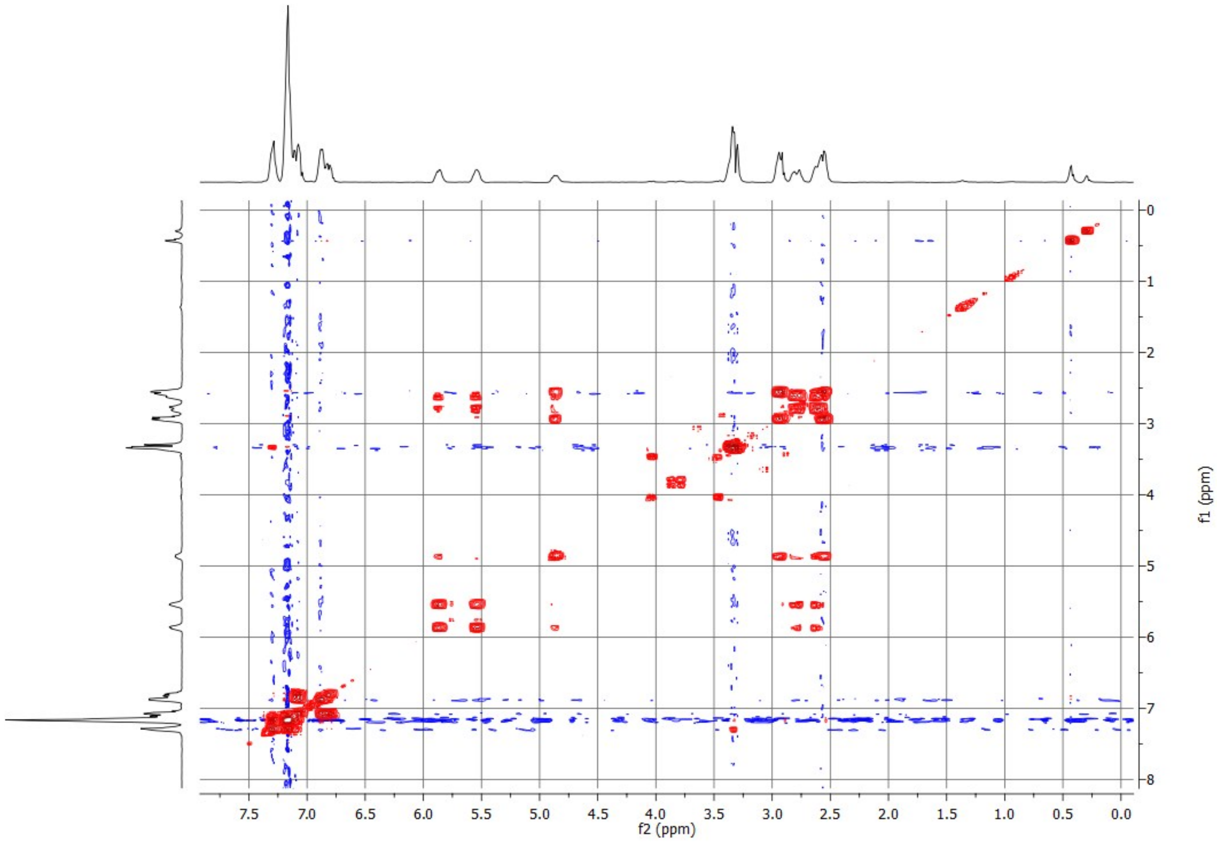




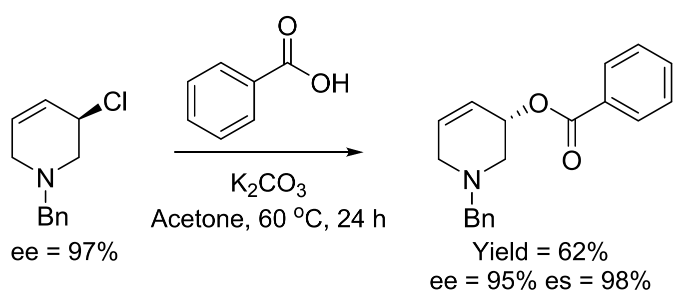


^{1}H-NMR and COSY-NMR of 6 in C_6D_6



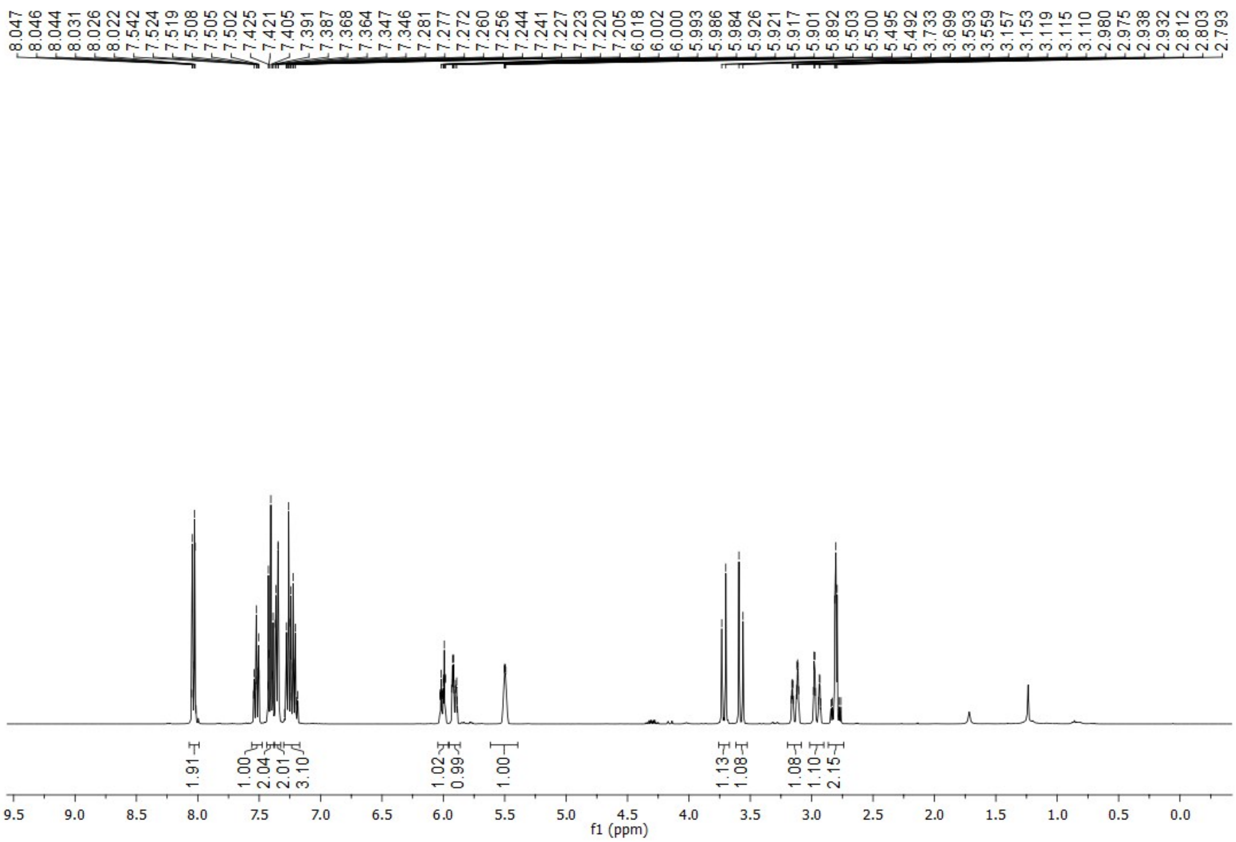


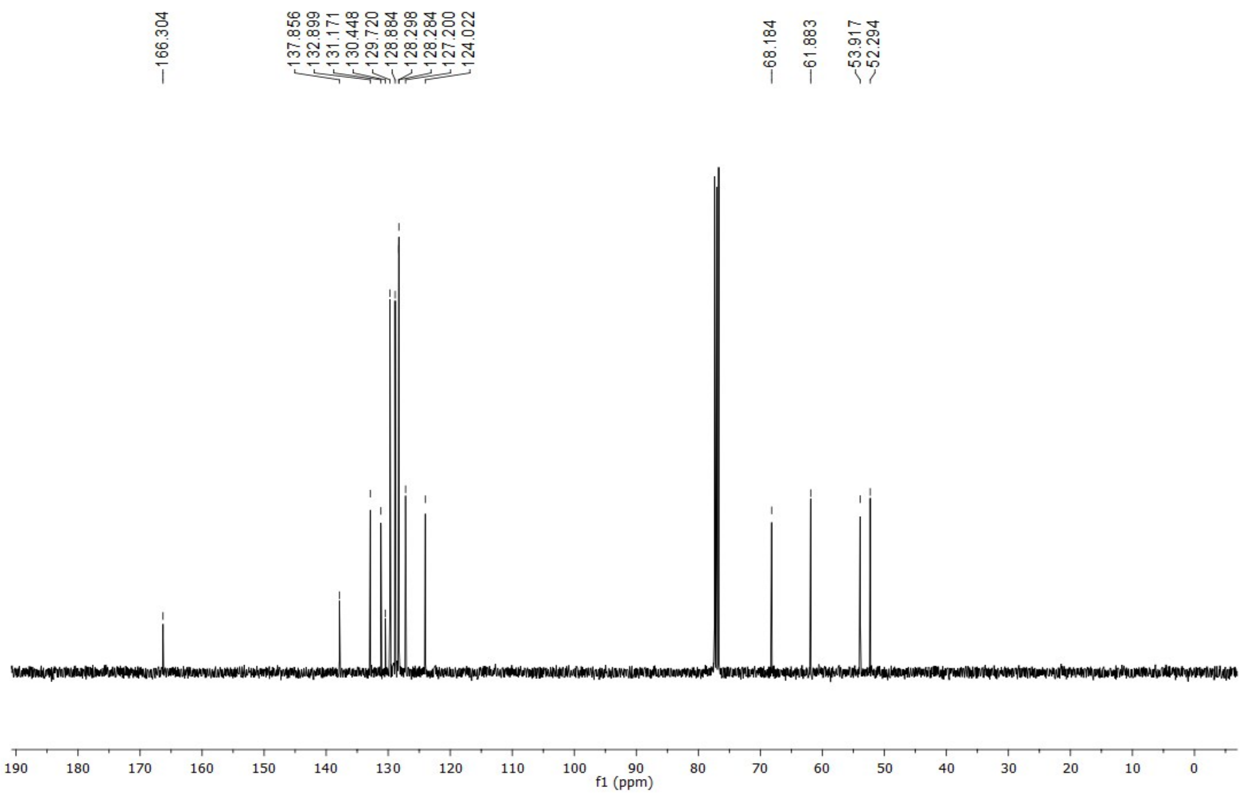
(S)-1-benzyl-1,2,3,6-tetrahydropyridin-3-yl benzoate (7):



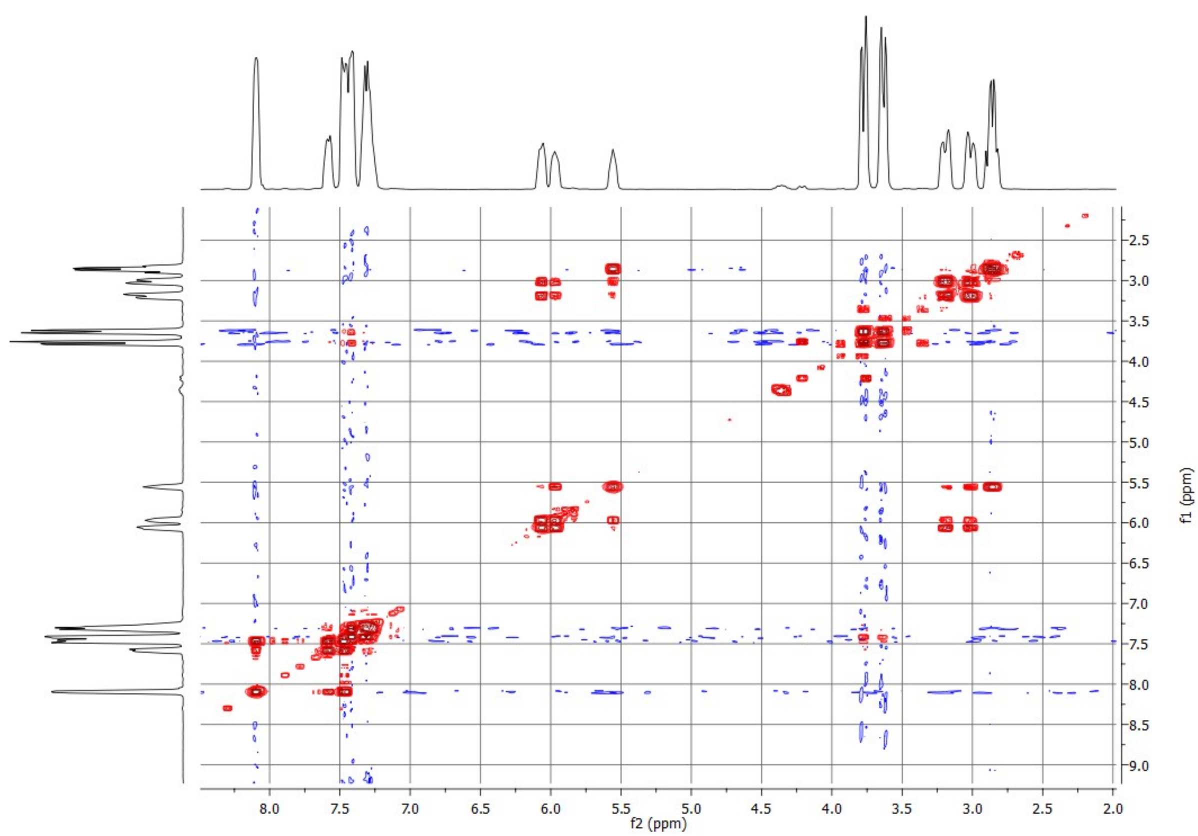
In a flame dried vial with a stirbar was added benzoic acid (32 mg, 0.26 mmol) and K_2CO_3 (100 mg, 0.72 mmol) followed by a solution of (R)-1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (***R*-1**) (50 mg, 0.24 mmol) in acetone (2.5 ml). The vial was sealed with a cap and resulting suspension was stirred at 60 °C for 24 hours. Flash column chromatography on silica gel (hexanes/EtOAc (19/1 to 9/1) + 0.5% Et_3N) gave **7** in 62% yield (43 mg, 0.15 mmol) as white solid. Enantiomeric excess of 95% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 90:10; λ = 210 nm; minor enantiomer t_R = 6.6 min; major enantiomer t_R = 7.7 min]; $[D]^{25}_{589}$ = +175.4 (c 0.83 $CHCl_3$) for 95% ee; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.76-2.84 (m, 2H), 2.96 (ddd, J = 16.8, 2.4, 2.0 Hz, 1H), 3.14 (ddt, J = 16.8, 3.2, 2.0 1H), 3.58 (d, J = 13.6 Hz, 1H), 3.72 (d, J = 13.6 Hz, 1H), 5.49-5.50 (bm, 1H), 5.91 (ddt, J = 10.0, 3.6, 2.0 Hz, 1H), 6.01 (dtd, J = 10.0, 3.2, 0.8 Hz, 1H), 7.18-7.29 (m, 3H), 7.34-7.37 (m, 2H), 7.38-7.43 (m, 2H), 7.50-7.54

(m, 1H), 8.01-8.05 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 52.3, 53.9, 61.9, 68.2, 124.0, 127.2, 128.28, 128.29, 128.8, 129.7, 130.4, 131.1, 132.9, 137.8, 166.3; **IR** ($ν_{max}$ /cm^{-1}): 705, 731, 1070, 1265, 1711; **HRMS** (ESI) *m/z* calcd for $C_{19}H_{20}O_2N^+$ [M+H]$^+$ 294.14886, found 294.14865.

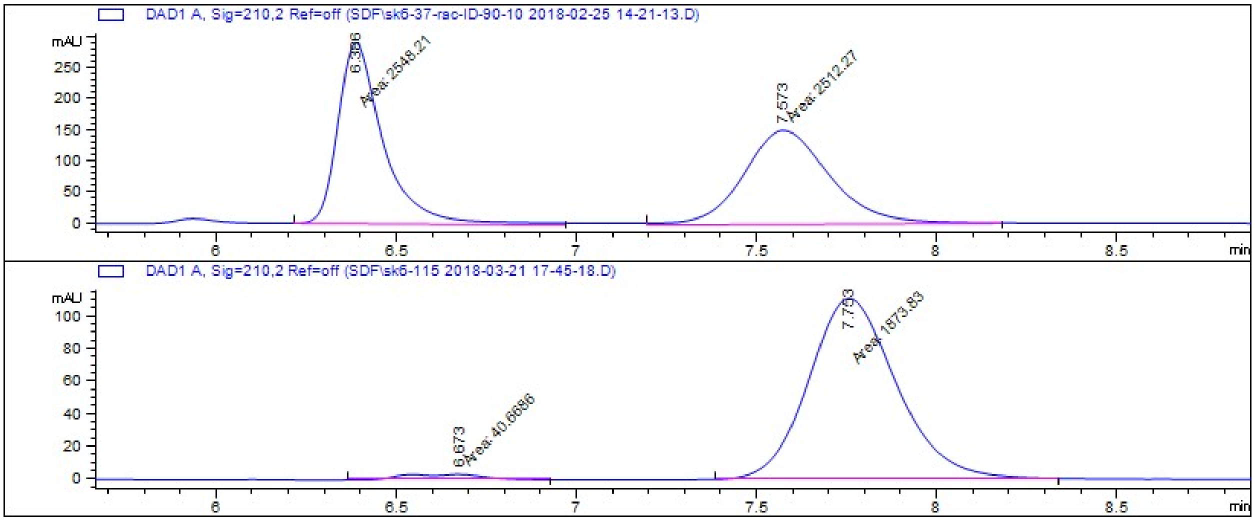




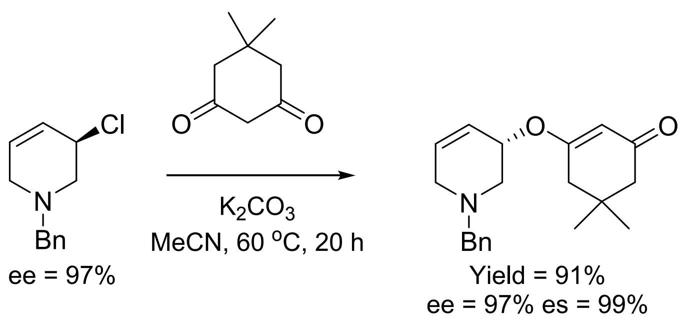
166.304
137.856
132.899
131.171
130.448
129.720
128.884
128.298
128.284
127.200
124.022
68.184
61.883
53.917
52.294
f1 (ppm)



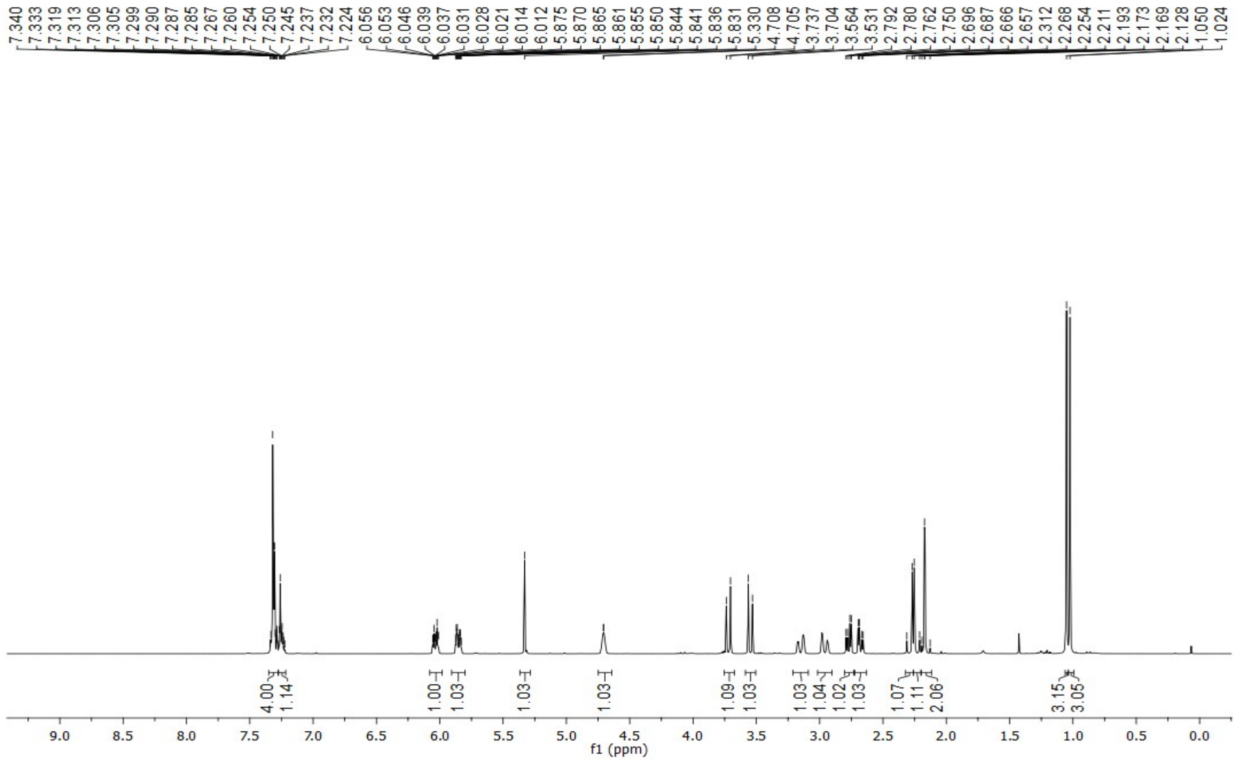
f2 (ppm)
f1 (ppm)

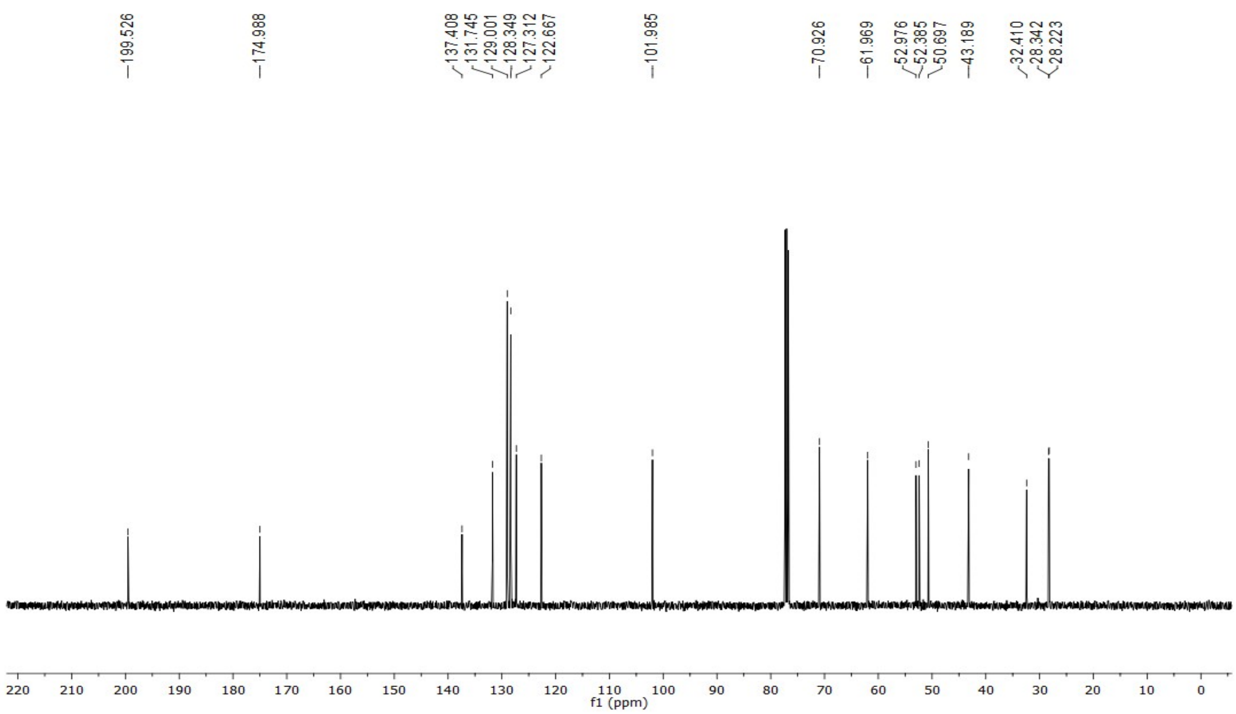


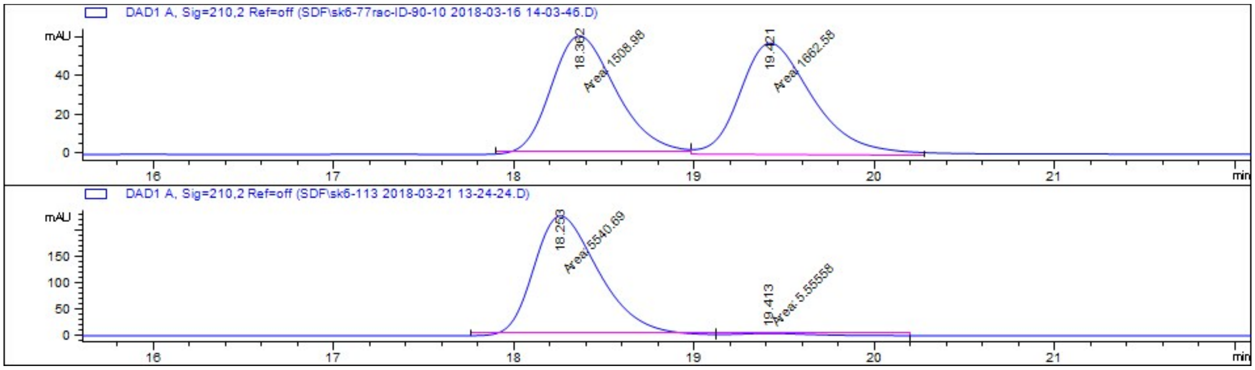
(*S*)-3-((1-benzyl-1,2,3,6-tetrahydropyridin-3-yl)oxy)-5,5-dimethylcyclohex-2-en-1-one (8):



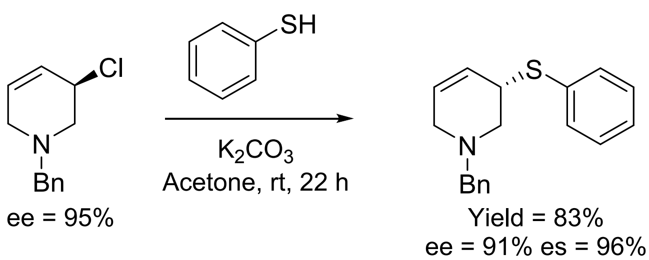
In a flame dried vial with a stirbar was added dimedone (67 mg, 0.48 mmol) and K_2CO_3 (116 mg, 0.84 mmol) followed by a solution of (*R*)-1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (***R*-1**) (50 mg, 0.24 mmol) in acetonitrile (2.5 ml). The vial was sealed with a cap and resulting suspension was stirred at 60 ˚C for 20 hours. Flash column chromatography on silica gel (hexanes/EtOAc (1/1)) gave **8** in 91% yield (68 mg, 0.22 mmol) as white solid. Enantiomeric excess of 97% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 90:10; λ = 210 nm; major enantiomer t_R = 18.2 min; minor enantiomer t_R = 19.4 min]; $[D]^{25}_{589}$ = +29.0 (c 0.84 $CHCl_3$) for 97% ee; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 1.02 (s, 3H), 1.05 (s, 3H), 2.15 (d, *J* = 18.0 Hz, 1H), 2.19 (d, *J* = 16.8 Hz, 1H), 2.23 (d, *J* = 17.2 Hz, 1H), 2.29 (d, *J* = 17.6 Hz, 1H), 2.68 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.77 (dd, *J* = 12.0, 4.8 Hz, 1H), 2.96 (bdd, *J* = 17.0, 1.8 Hz, 1H), 3.15 (bddt *J* = 16.8, 3.2, 1.6 Hz, 1H), 3.55 (d, *J* = 13.2 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 4.70 (bs, 1H), 5.33 (s, 1H), 5.85 (ddt, *J* = 10.0, 3.4, 2.2 Hz, 1H), 6.03 (dtd, *J* = 10.0, 3.2, 2.0 Hz, 1H), 7.22-7.27 (m, 1H), 7.28-7.34 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 28.22, 28.34, 32.4, 43.2, 50.7, 52.4, 52.9, 61.9, 70.9, 101.9, 122.6, 127.3, 128.3, 129.0, 131.7, 137.4, 174.9, 199.5; **IR** (ν_{max} /cm^{-1}): 729, 1042, 1144, 1219, 1378, 1589, 1638, 2965, 3749; **HRMS** (ESI) *m/z* calcd for $C_{26}H_{22}O_2N^+$ $[M+H]^+$ 312.19581, found 312.19556.



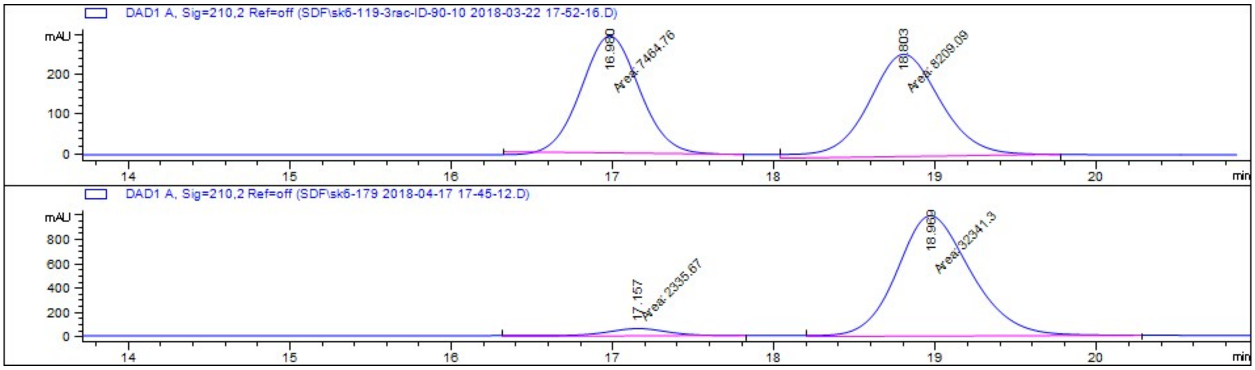




(*S*)-1-benzyl-3-(phenylthio)-1,2,3,6-tetrahydropyridine (9):



In a flame dried vial with a stirbar was added K_2CO_3 (166 mg, 1.2 mmol) and a solution of (*R*)-1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (***R*-1**) (50 mg, 0.24 mmol) in acetone (2.5 ml) followed by the addition of thiophenol (0.06 ml, 0.48 mmol). The vial was sealed with a cap and resulting suspension was stirred at room temperature for 22 hours. After completion, the reaction mixture was diluted with H_2O (4 ml) and extracted with Et_2O (x3). Combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes/EtOAc (19/1 to 9/1)) to give **9** in 83% yield (56 mg, 0.20 mmol) as a yellow oil. Enantiomeric excess (for corresponding Cbz carbamate) of 91% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 90:10; λ = 210 nm; minor enantiomer t_R = 17.1 min; major enantiomer t_R = 18.9 min]; $[D]^{25}_{589}$ = –45.8 (c 0.72 $CHCl_3$) for 91% ee; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.65 (dd, *J* = 11.6, 5.6 Hz, 1H), 2.81 (dd, *J* = 11.6, 4.4 Hz, 1H), 2.96-3.01 (m, 1H), 3.07 (ddd, *J* = 16.8, 4.8, 2.4 Hz, 1H), 3.52 (d, *J* = 13.2 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.83-3.87 (m, 1H), 5.78-5.82 (m, 1H), 5.83-5.87 (m, 1H), 7.17-7.38 (m, 10H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 44.7, 52.5, 54.7, 62.2, 125.8, 126.9, 127.1, 128.0, 128.2, 128.8, 129.1, 132.0, 135.1, 137.8; **IR** (v_{max} /cm^{-1}): 695, 736, 758, 1026, 1134, 2756, 3710; **HRMS** (ESI) *m/z* calcd for $C_{18}H_{20}SN^+$ $[M+H]^+$ 282.13110, found 282.13092. For corresponding Cbz carbamate; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 3.60-3.71 (m, 1H), 3.77 (bs, 2H), 3.86 and 3.91 (rotameric bs, 1H), 4.03 and 4.14 (rotameric bd, *J* = 19.0 Hz, 1H), 5.12-5.19 (rotameric m, 2H), 5.76 and 5.84 (rotameric bd, *J* = 10.0 Hz, 1H), 5.93 (bs, 1H), 7.10-7.36 (m, 9H), 7.54 (d, *J* = 6.4 Hz, 1H).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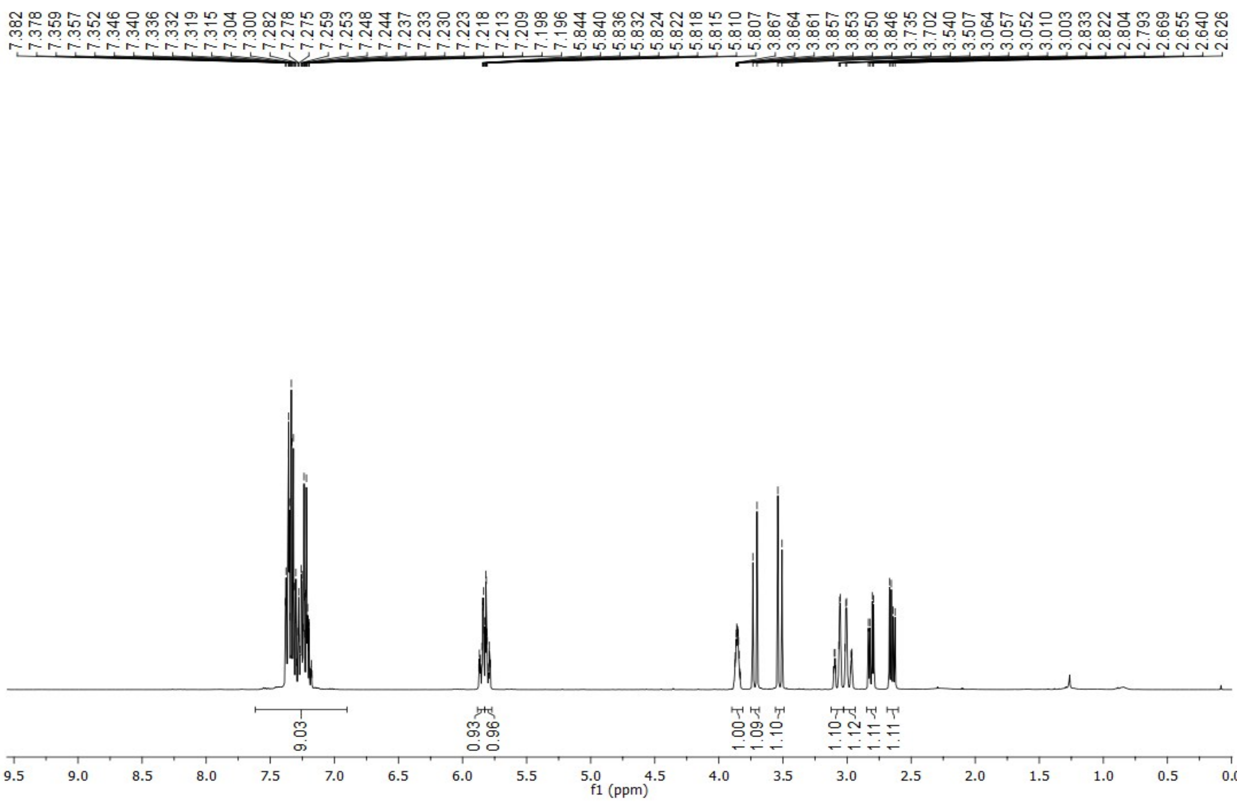
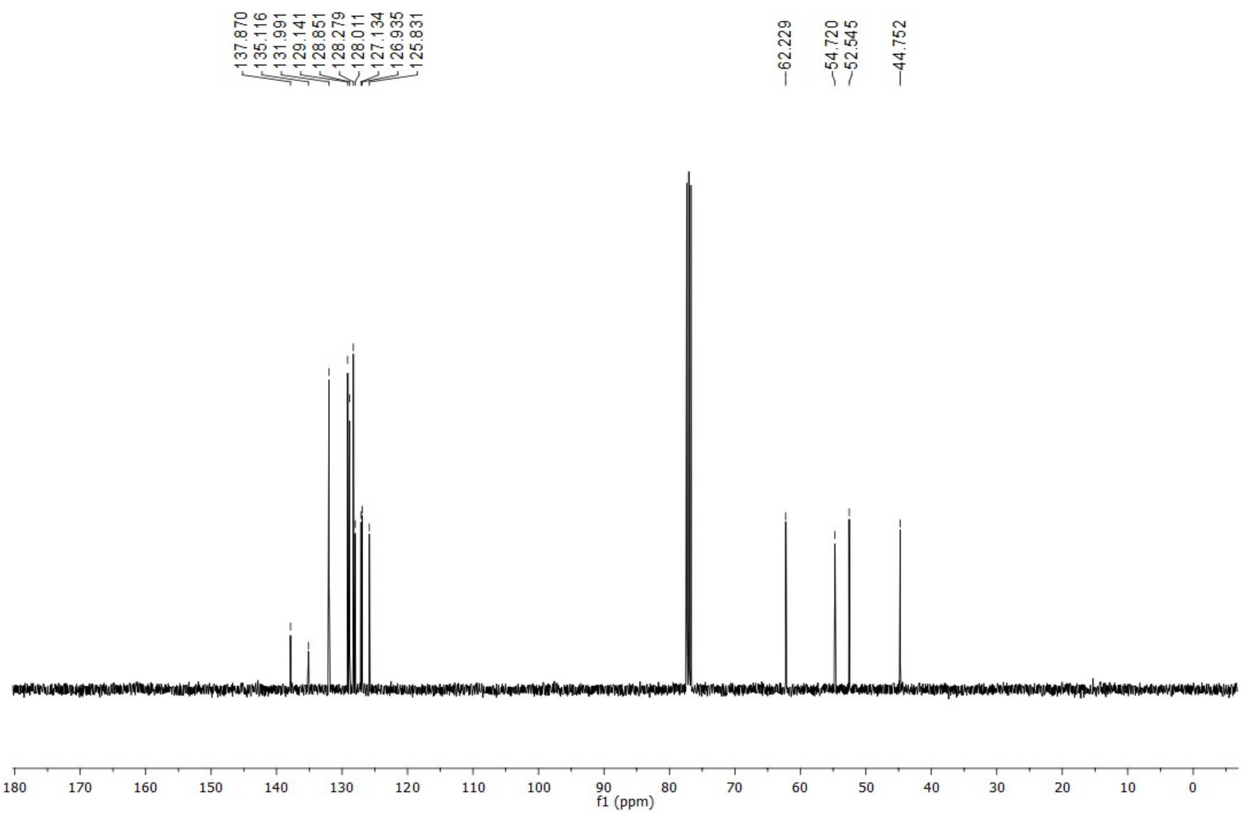
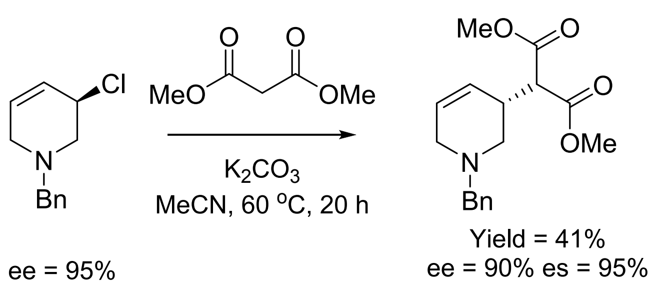
18.803
Area: 8209.09
DAD1 A, Sig=210,2 Ref=off (SDF\sk6-179 2018-04-17 17-45-12.D)
17.157
Area: 2335.67
18.969
Area: 32341.3
min

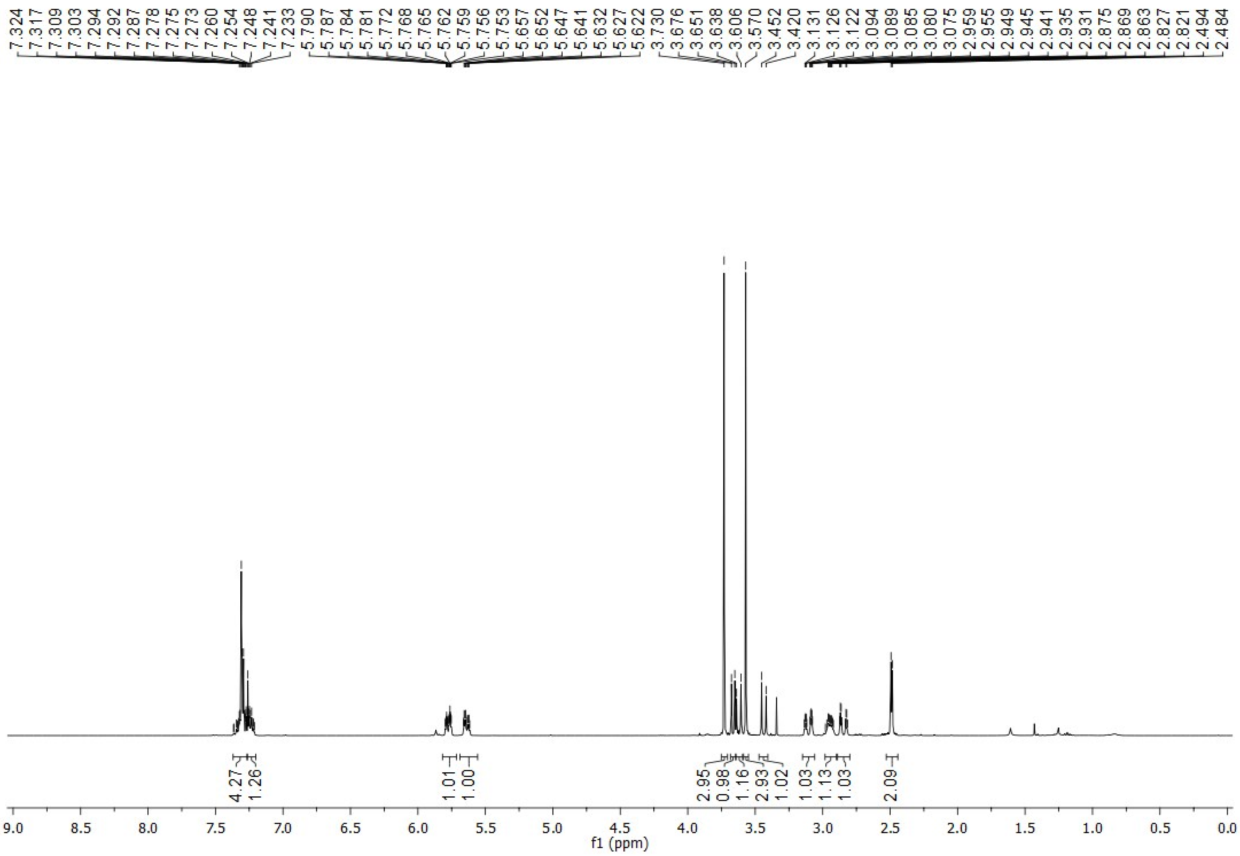

9.03
0.93
0.96
1.00
1.09
1.10
1.10
1.12
1.11
1.11
f1 (ppm)

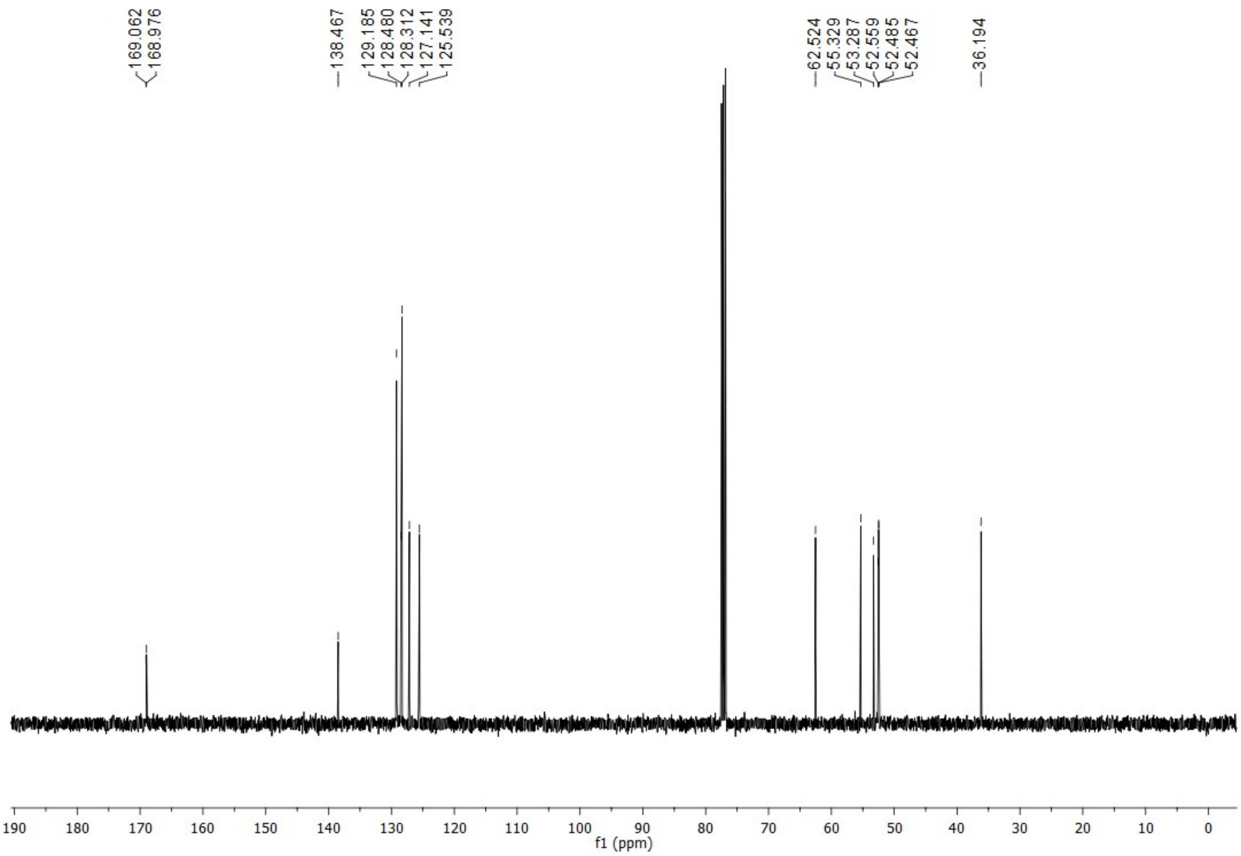


Dimethyl (*R*)-2-(1-benzyl-1,2,3,6-tetrahydropyridin-3-yl)malonate (10):

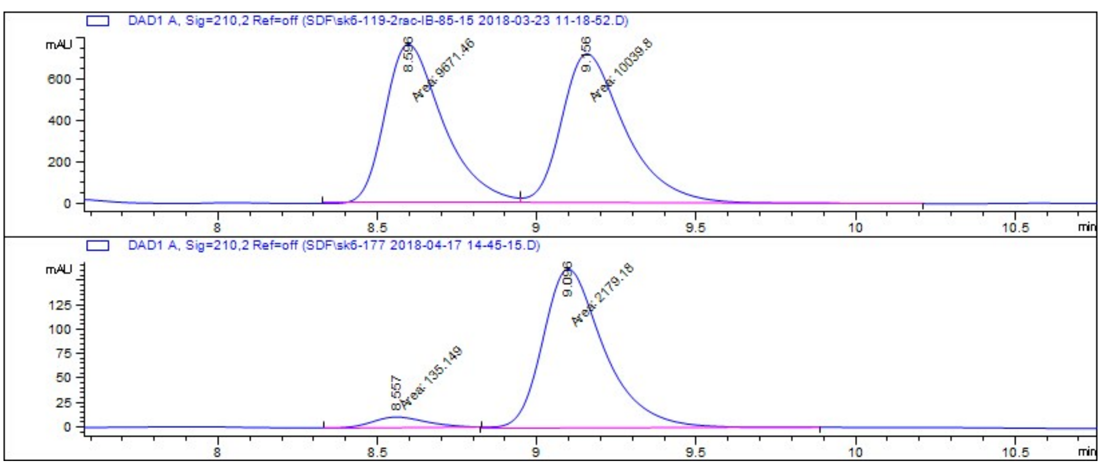


In a flame dried vial with a stirbar was added K_2CO_3 (166 mg, 1.2 mmol) and a solution of (*R*)-1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (***R*-1**) (50 mg, 0.24 mmol) in acetone (2.5 ml) followed by the addition of dimethyl malonate (0.05 ml, 0.36 mmol). The vial was sealed with a cap and resulting suspension was stirred at 60 ˚C for 24 hours. The reaction mixture was diluted with H_2O (4 ml) and extracted with EtOAc (x3). Combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated and purified by flash column chromatography on silica gel (hexanes/EtOAc (19/1)) to give **10** in 41% yield (30 mg, 0.10 mmol) as a yellow oil. Enantiomeric excess (for corresponding Cbz carbamate) of 90% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:IPA 85:15; λ = 210 nm; minor enantiomer t_R = 8.5 min; major enantiomer t_R = 9.1 min]; $[D]^{25}_{589}$ = +127.4 (c 0.27 $CHCl_3$) for 90% ee; $[D]^{25}_{589}$ = +84.9 (c 0.90 $CHCl_3$) for 91% ee for Cbz carbamate; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.49 (d, *J* = 4.0 Hz, 2H), 2.84 (ddd, *J* = 16.8, 4.8, 2.4 Hz, 1H), 2.90-2.98 (m, 1H), 3.11 (ddt, *J* = 16.4, 3.6, 2.0 Hz, 1H), 3.44 (d, *J* = 12.8 Hz, 1H), 3.57 (s, 3H), 3.62 (d, *J* = 12.8 Hz, 1H), 3.66 (d, *J* = 10.0 Hz, 1H), 3.73 (s, 3H), 5.64 (ddt, *J* = 10.0, 4.0, 2.0 Hz, 1H), 5.77 (dtd, *J* = 10.0, 2.4, 1.2 Hz, 1H), 7.21-7.26 (m, 1H), 7.27-7.36 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 36.2, 52.46, 52.48, 52.56, 53.3, 55.3, 62.5, 125.5, 127.1, 128.3, 128.5, 129.2, 138.4, 168.97, 169.06; **IR** (v_{max} /cm^{-1}): 700, 735, 1020, 1148, 1241, 1492, 1733, 2801, 2953, 3749; **HRMS** (ESI) *m/z* calcd for $C_{17}H_{22}O_4N^+$ $[M+H]^+$ 304.15433, found 304.15439. Spectral data is in agreement with literature.[8] For corresponding Cbz carbamate; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.99 and 3.03 (rotameric bs, 1H), 3.38 (bd, *J* = 9.2 Hz, 1H), 3.45-3.52 (rotameric m, 2H), 3.69-3.83 (rotameric m, 6H), 3.88-4.17 (rotameric m, 2H), 5.12 (bs, 2H), 5.67-5.83 (m, 2H), 7.30-7.37 (m, 5H). Spectral data is in agreement with literature.[9]





169.062
168.976
138.467
129.185
128.480
128.312
127.141
125.539
62.524
55.329
53.287
52.559
52.485
52.467
36.194
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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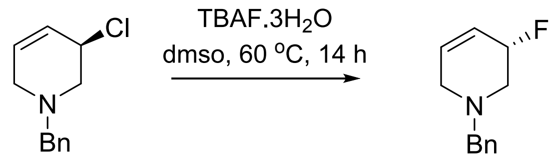
9.156
Area: 10039.8
DAD1 A, Sig=210,2 Ref=off (SDF\sk6-177 2018-04-17 14-45-15.D)
8.557
Area: 135.149
9.096
Area: 2179.18
min

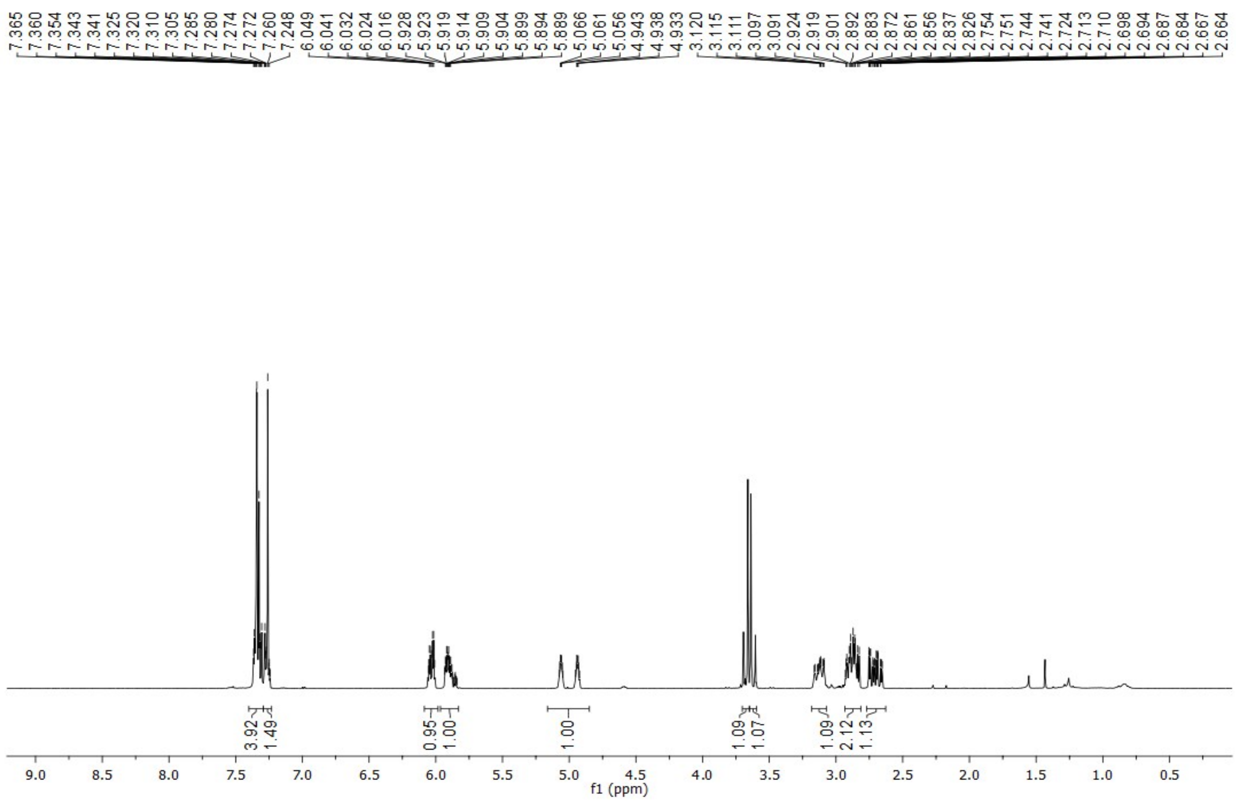
(*S*)-1-benzyl-3-fluoro-1,2,3,6-tetrahydropyridine (11):

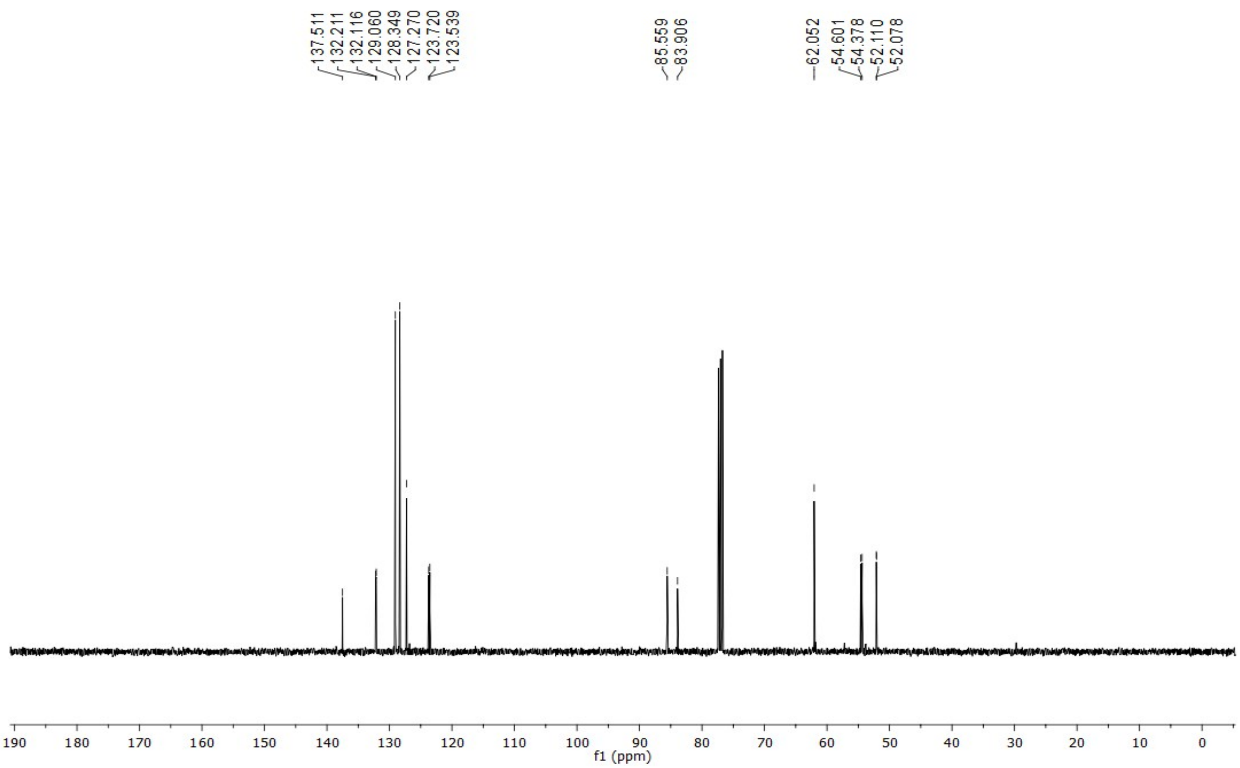


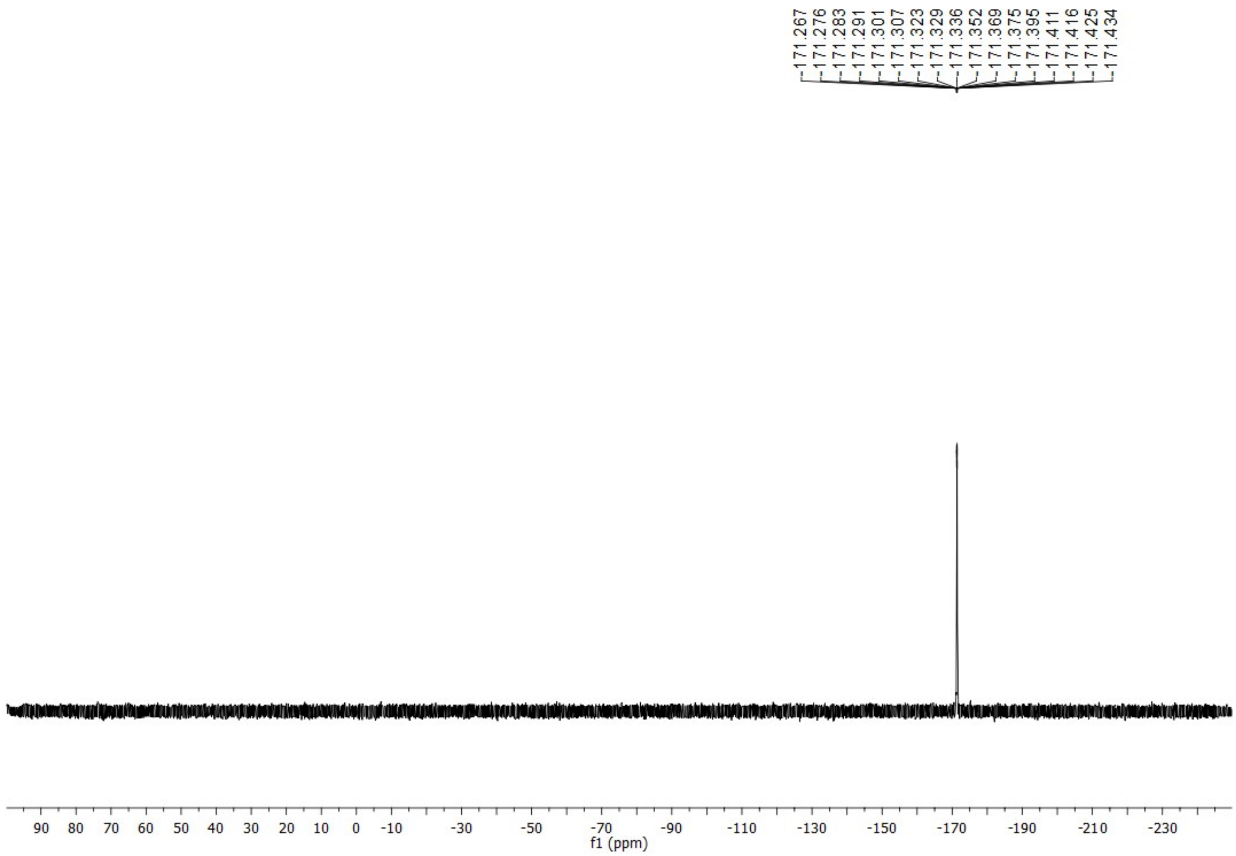
ee = 95%

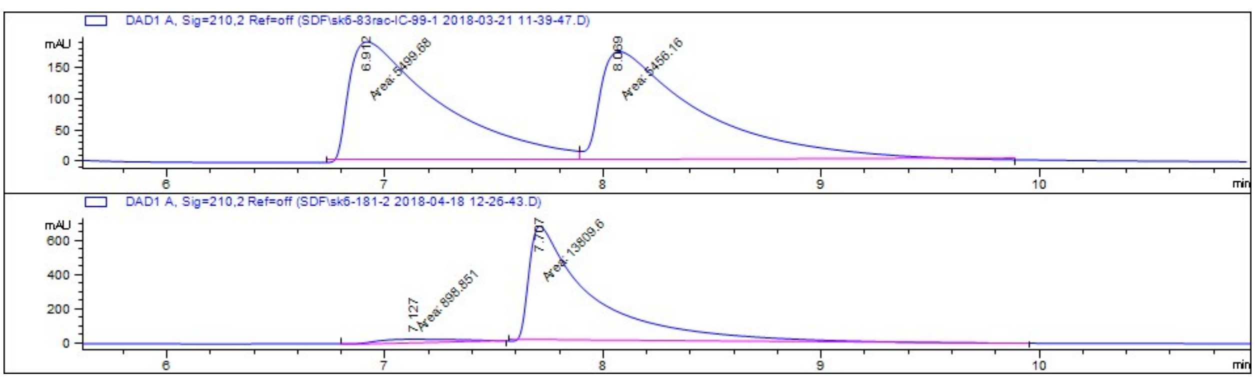
Yield = 47%
ee = 89% es = 94%

In a flame dried vial with a stirbar were added TBAF·3H_2O (152 mg, 0.48 mmol) and a solution of (*R*)-1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (***R*-1**) (50 mg, 0.24 mmol) in dmso (2.5 ml). The vial was sealed with a cap and resulting solution was stirred at 60 ˚C for 14 hours. The reaction mixture was diluted with H_2O (4 ml) and extracted with Et_2O (x3). Combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated and purified by flash column chromatography on silica gel (hexanes/EtOAc (19/1)) to give **11** in 47% yield (21 mg, 0.11 mmol) as a yellow oil. Enantiomeric excess of 89% was determined by HPLC [Chiralpak® IC; flow: 1.0 mL/min; hexane:IPA 99:1; λ = 210 nm; minor enantiomer t_R = 7.1 min; major enantiomer t_R = 7.7 min]; $[D]^{25}_{589}$ = +44.7 (c 0.27 $CHCl_3$) for 89% ee; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.70 (dddd, *J* = 22.4, 12.2, 4.0, 1.2 Hz, 1H), 2.82-2.93 (m, 2H), 3.09-3.16 (m, 1H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.68 (d, *J* = 13.2 Hz, 1H), 5.0 (dm, J_{HF} = 49.6 Hz, 1H), 5.84-5.93 (m, 1H), 6.03 (bddd, *J* = 10.0, 3.2, 2.8 Hz, 1H), 7.24-7.28 (m, 1H), 7.30-7.36 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 52.1 (d, ^4J = 3.23 Hz), 54.5 (d, ^2J = 22.5 Hz), 62.0, 84.7 (d, ^1J = 166.9 Hz), 123.6 (d, ^2J = 18.3 Hz), 127.2, 128.3, 129.0, 132.1 (d, ^3J = 9.6 Hz), 137.5; **^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ:** –171.35 (m); **IR** (v_{max} /cm^{-1}): 697, 736, 998, 1147, 1493, 2759, 2804, 2922; **HRMS** (ESI) *m/z* calcd for $C_{12}H_{15}FN^+$ $[M+H]^+$ 192.11830, found 192.11801.

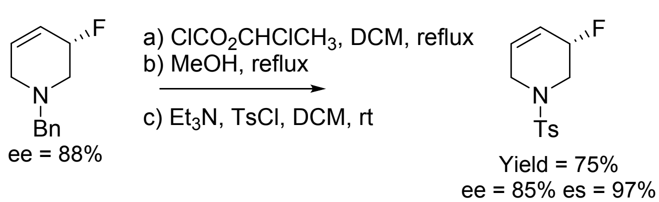

7.365
7.360
7.354
7.343
7.341
7.325
7.320
7.310
7.305
7.285
7.280
7.274
7.272
7.260
7.248
6.049
6.041
6.032
6.024
6.016
5.928
5.923
5.919
5.914
5.909
5.904
5.899
5.894
5.889
5.066
5.061
5.056
4.943
4.938
4.933
3.120
3.115
3.111
3.097
3.091
2.924
2.919
2.901
2.892
2.883
2.872
2.861
2.856
2.837
2.826
2.754
2.751
2.744
2.741
2.724
2.713
2.710
2.698
2.694
2.687
2.684
2.667
2.664
3.92
1.49
0.95
1.00
1.00
1.09
1.07
1.09
2.12
1.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


137.511
132.211
132.116
129.060
128.349
127.270
123.720
123.539
85.559
83.906
62.052
54.601
54.378
52.110
52.078
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

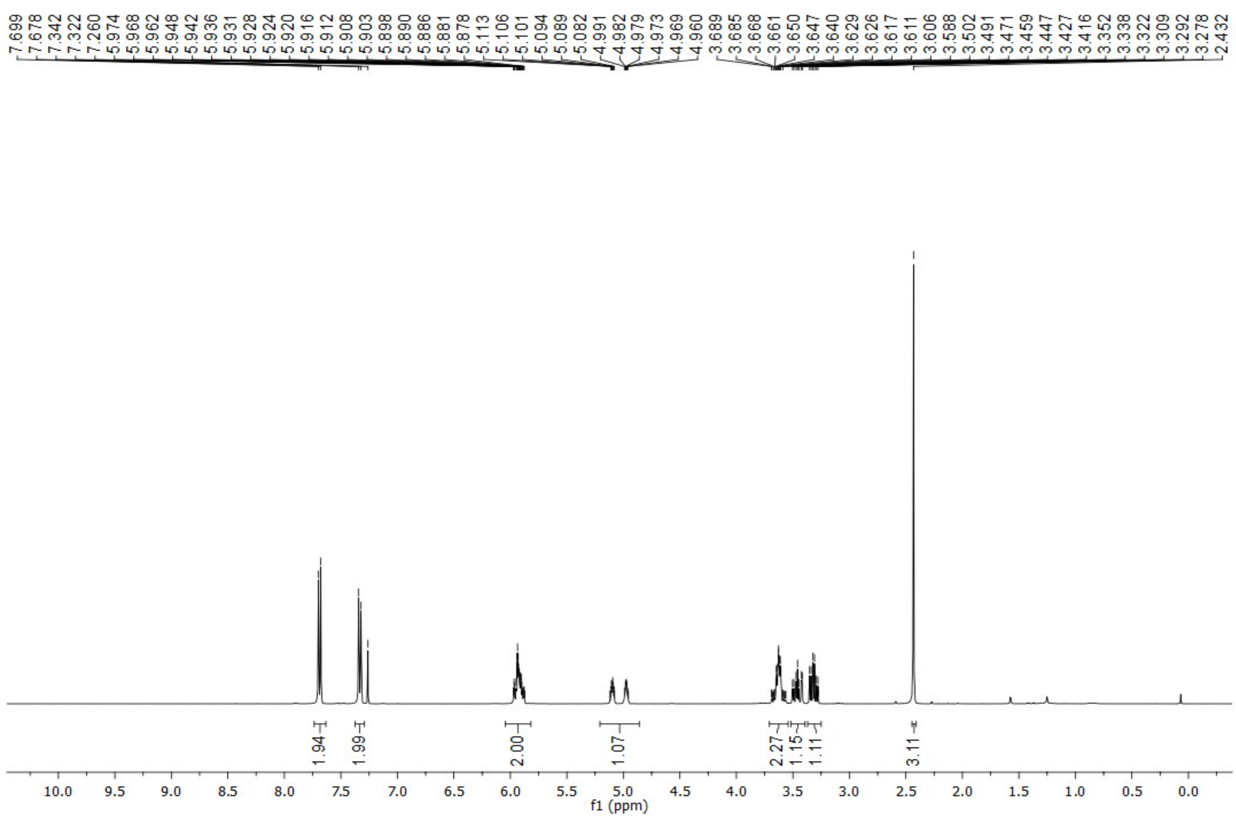


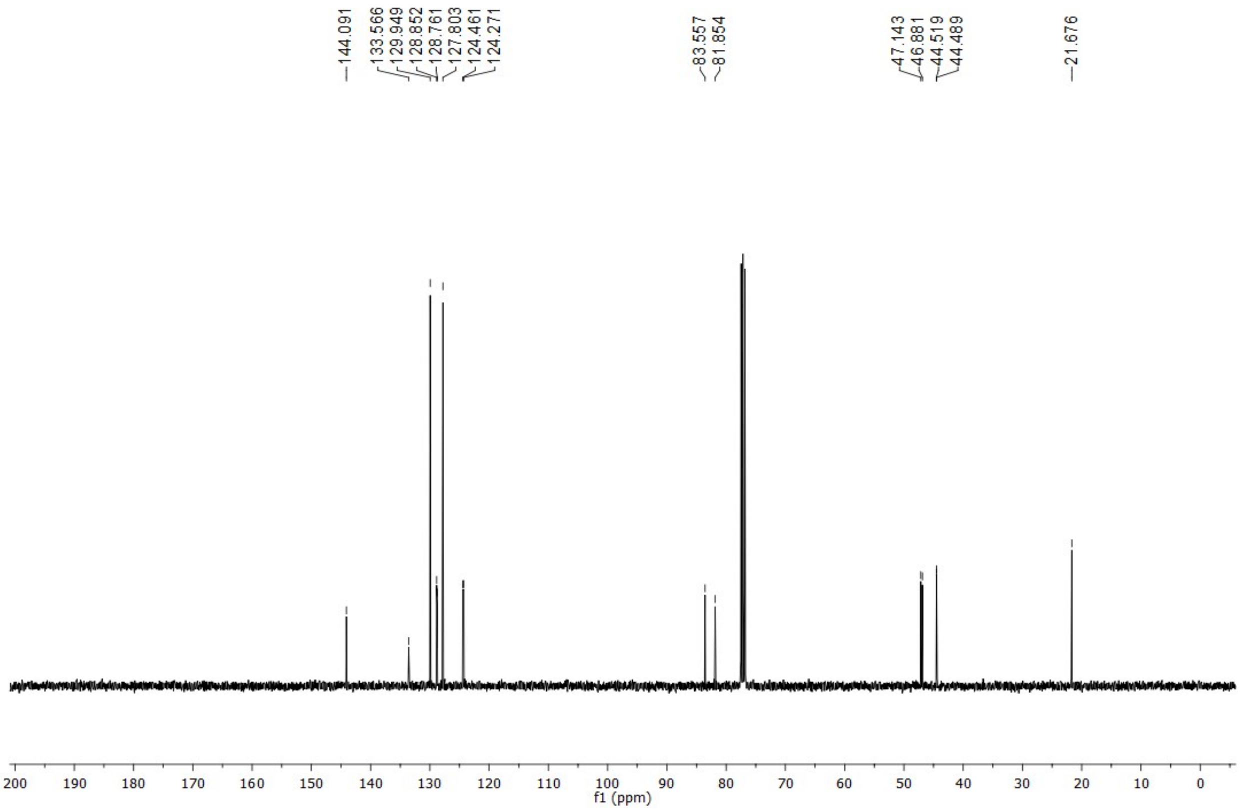


(*S*)-3-fluoro-1-tosyl-1,2,3,6-tetrahydropyridine (12):



11 (21 mg, 0.115 mmol), DCM (1.2 ml) and 1-chloroethyl chloroformate (0.015 ml, 0.15 mmol) were added to a flame dried round bottom flask and the resulting solution heated to reflux for 2 hours, before it was allowed to cool to room temperature and the solvent removed on a rotary evaporator. The residue was dissolved in MeOH (1.2 ml) and heated to reflux for 1 hour, before removing the solvent on rotary evaporator and adding dry DCM (1.0 ml). The solution was stirred and cooled to 0 ºC before Et_3N (0.04 ml, 0.3 mmol) was added followed by portion-wise addition of toluenesulfonyl chloride (22 mg, 0.115 mmol). The reaction mixture was then stirred at room temperature for 2 hours before being concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes/EtOAc (9/1 to 4/1)) to give **12** in 75% yield (22 mg, 0.09 mmol) as a white solid. Enantiomeric excess of 85% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 80:20; λ = 210 nm; minor enantiomer t_R = 20.6 min; major enantiomer t_R = 25.1 min]; $[D]^{25}_{589}$ = +10.8 (c 1.0 $CHCl_3$) for 85% ee, reported[10] $[D]^{23}_{589}$ = –29.7 (c 1.1 $CHCl_3$) for (*R*)-3-fluoro-1-tosyl-1,2,3,6-tetrahydropyridine with ee of 96%; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.43 (s, 3H), 3.32 (td, J = 12.0, 5.6 Hz, 1H), 3.46 (ddd, J = 17.2, 12.4, 4.6 Hz, 1H), 3.56-3.69 (m, 2H), 5.04 (dm, J_{HF} = 48.8 Hz, 1H), 5.87-5.97 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 21.7, 44.5 (d, ^4J = 3.03 Hz), 47.0 (d, ^2J = 26.5 Hz), 82.7 (d, ^1J = 172.0 Hz), 124.4 (d, ^2J = 19.2 Hz), 127.8, 128.8 (d, ^3J = 9.2 Hz), 129.9, 133.5, 144.1; **^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: -**175.01 (m). Spectral data is in agreement with literature.[10]




144.091
133.566
129.949
128.852
128.761
127.803
124.461
124.271
83.557
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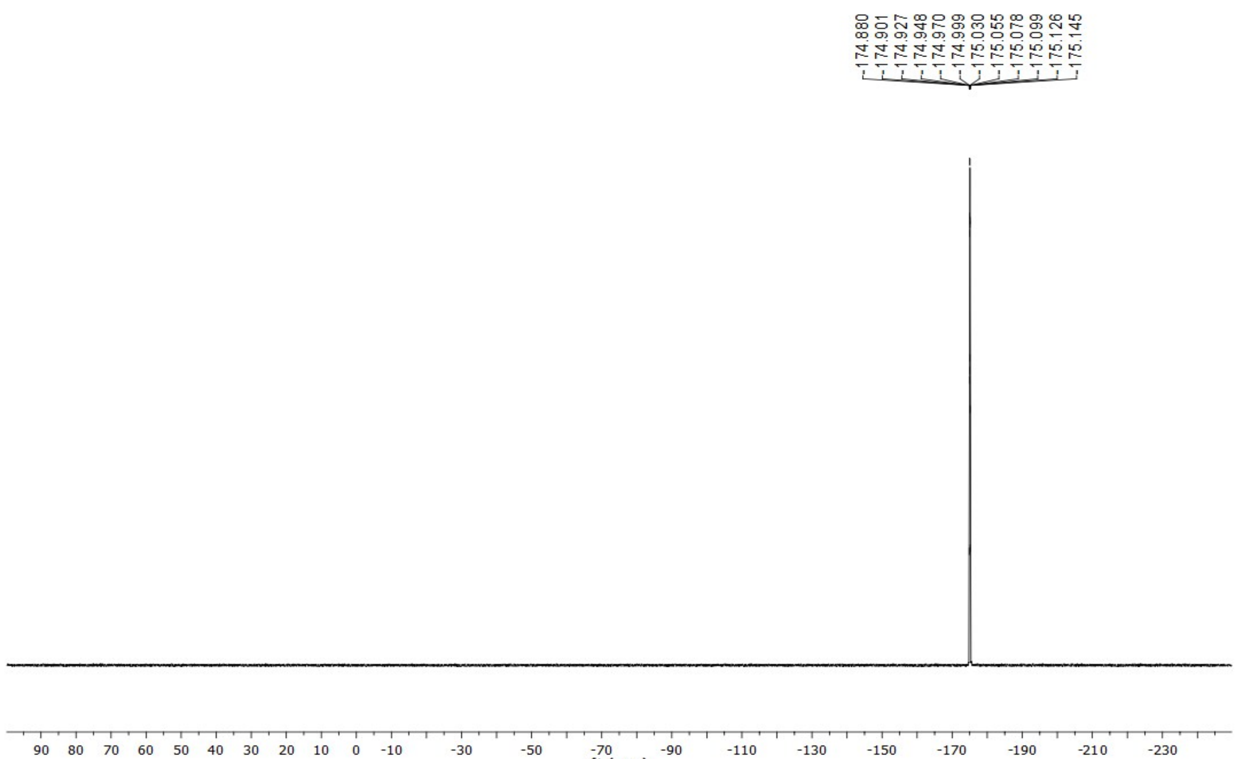
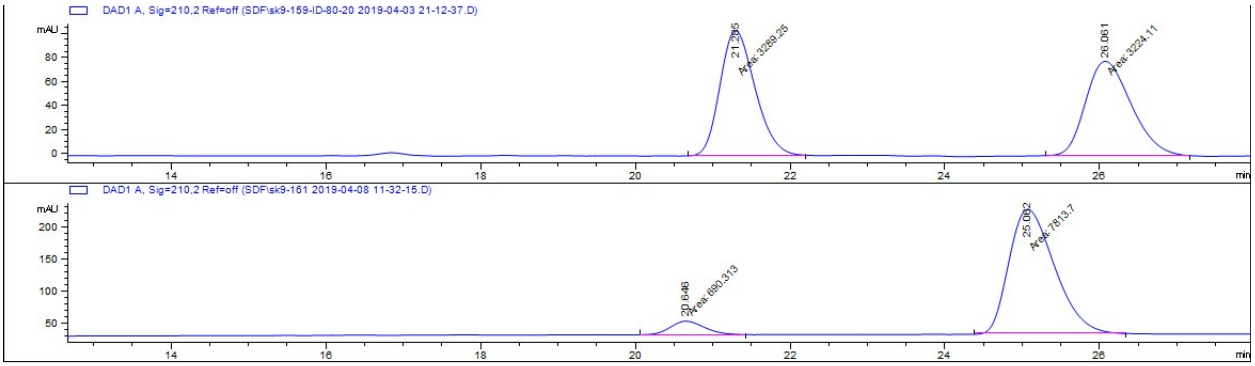
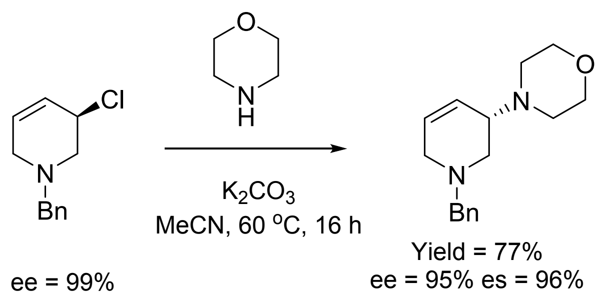
47.143
46.881
44.519
44.489
21.676
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

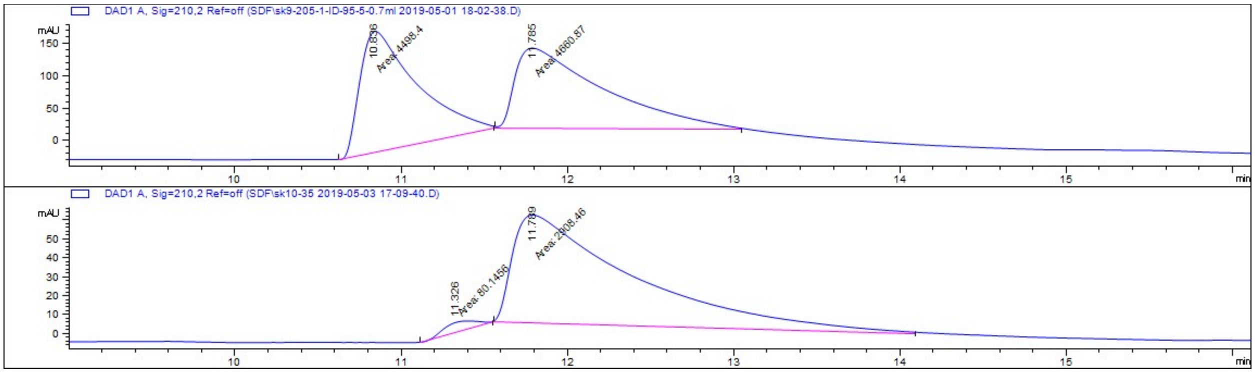

174.880
174.901
174.927
174.948
174.970
174.999
175.030
175.055
175.078
175.099
175.126
175.145
90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



(*S*)-4-(1-benzyl-1,2,3,6-tetrahydropyridin-3-yl)morpholine (13):



In a flame dried vial with a stirbar was added K_2CO_3 (88 mg, 0.63 mmol) and a solution of (*R*)-1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine (***R*-1**) (44 mg, 0.21 mmol) in MeCN (2.0 ml) followed by the addition of morpholine (0.03 ml, 0.30 mmol). The vial was sealed with a cap and resulting suspension was stirred at 60 ˚C for 16 hours. The solution was concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes/acetone (3/1 to 2/1)) to give **13** in 77% yield (42 mg, 0.16 mmol) as a yellow oil. Enantiomeric excess of 95% was determined by HPLC [Chiralpak® ID; flow: 0.7 mL/min; hexane:IPA 95:5; λ = 210 nm; minor enantiomer t_R = 11.3 min; major enantiomer t_R = 11.8 min]; $[D]^{25}_{589}$ = +49.3 (c 1.0 $CHCl_3$) for 95% ee; **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.57 (overlapping dd, *J* = 11.4, 6.2 Hz, 2H), 2.59 (overlapping dd, *J* = 9.6, 5.2 Hz, 1H), 2.65 (overlapping dd, *J* = 9.6, 5.2 Hz, 1H), 2.66 (overlapping dd, *J* = 11.2, 4.8 Hz, 2H), 2.91 (dd, *J* = 2.8, 2.4 Hz, 2H) 3.22-3.27 (m, 1H), 3.57 (s, 2H), 3.68 (ddd, *J* = 8.8, 3.2, 2.8 Hz, 4H), 5.77 (ddt, *J* = 8.2, 2.6, 2.0 Hz, 1H), 5.87 (dtd, *J* = 10.2, 3.2, 2.0 Hz, 1H), 7.23-7.27 (m, 1H), 7.28-7.32 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 49.9, 51.1, 52.7, 59.7, 62.8, 67.5, 125.7, 127.1, 128.2, 128.7, 129.0, 138.1; **IR** (ν_{max} /cm^{-1}): 698, 734, 1002, 1114, 1249, 1288, 1452, 1493, 1662, 2808, 2852, 2953; **HRMS** (ESI) *m/z* calcd for $C_{16}H_{23}ON_2^+$ [M+H]$^+$ 259.18049, found 259.18020.


DAD1 A, Sig=210,2 Ref=off (SDF\sk9-205-1-ID-95-5-0.7ml 2019-05-01 18-02-38.D)
10.836
Area: 4498.4
11.785
Area: 4660.87
DAD1 A, Sig=210,2 Ref=off (SDF\sk10-35 2019-05-03 17-09-40.D)
11.326
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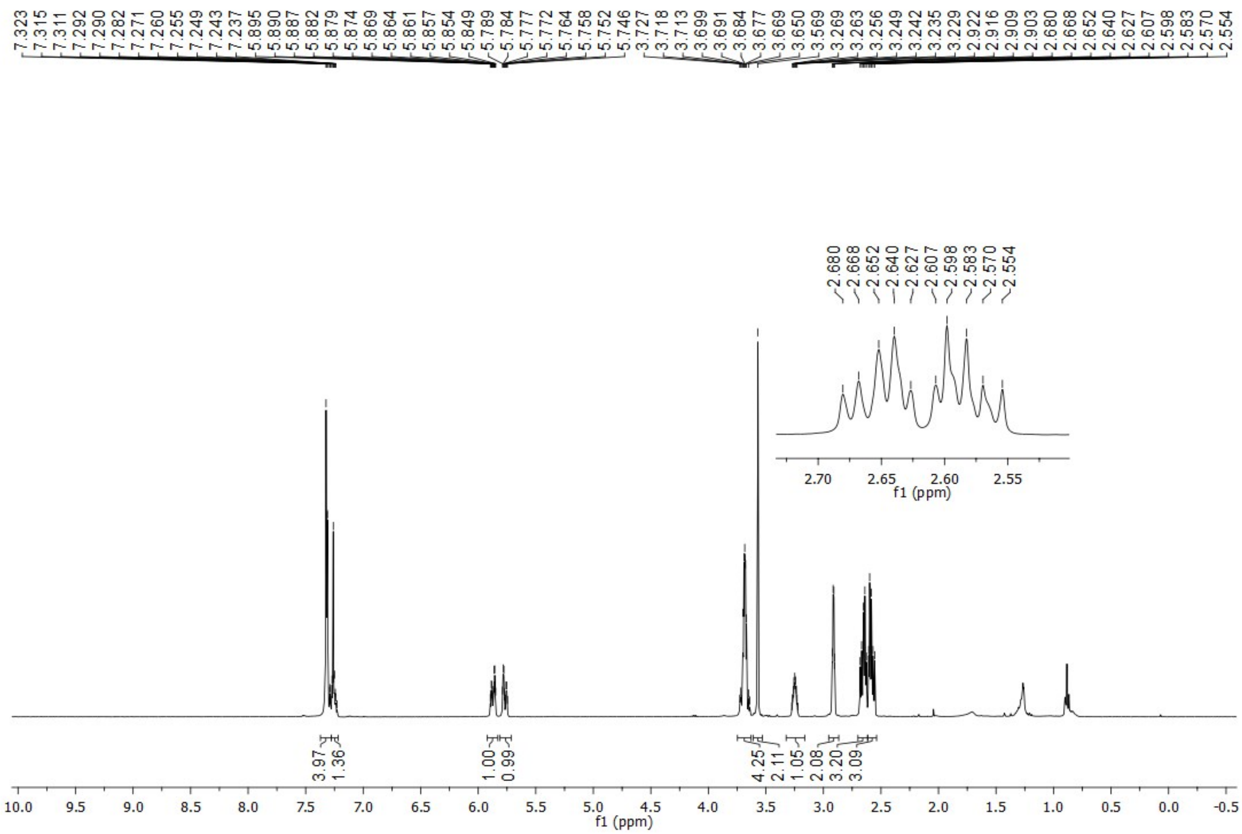
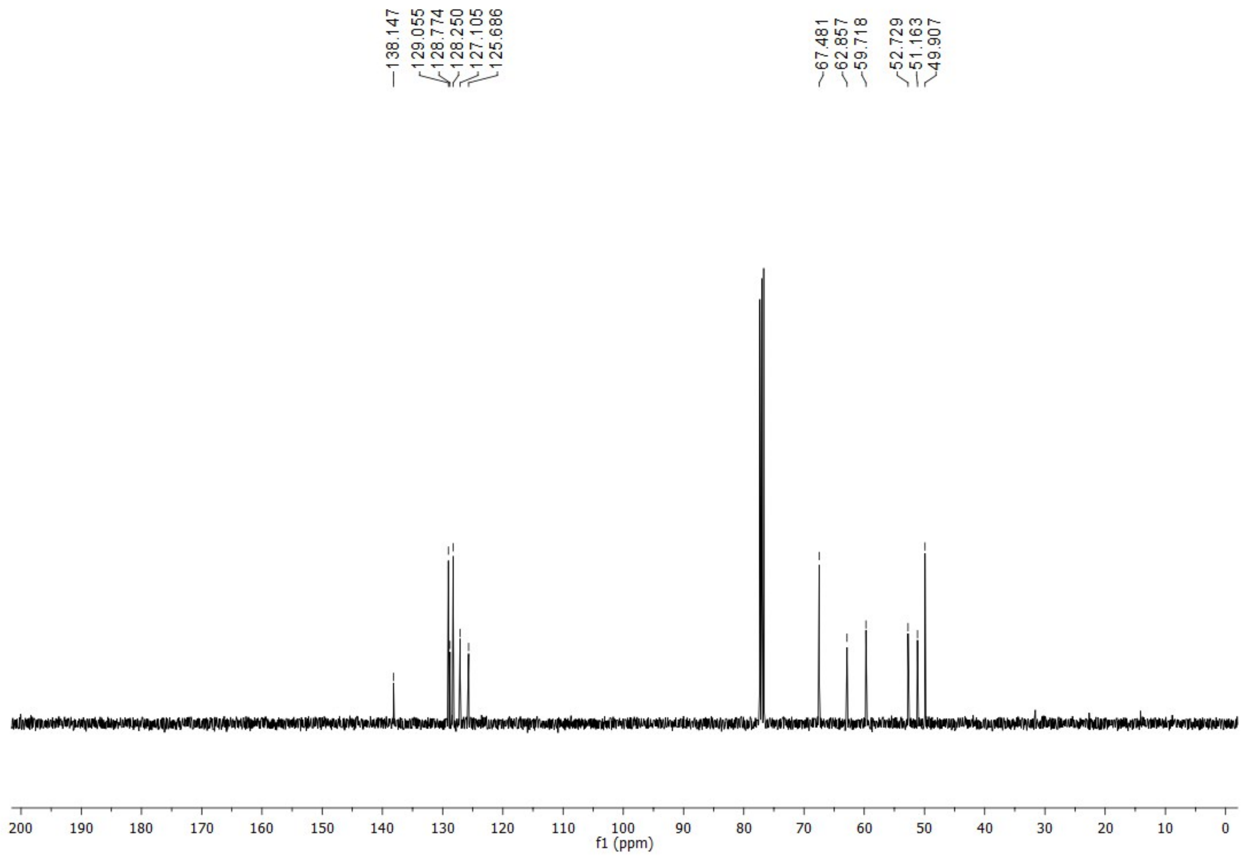
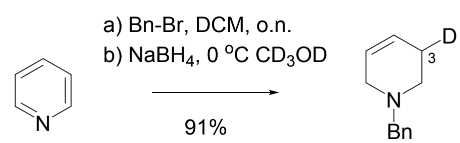
11.789
Area: 2908.46


f1 (ppm)



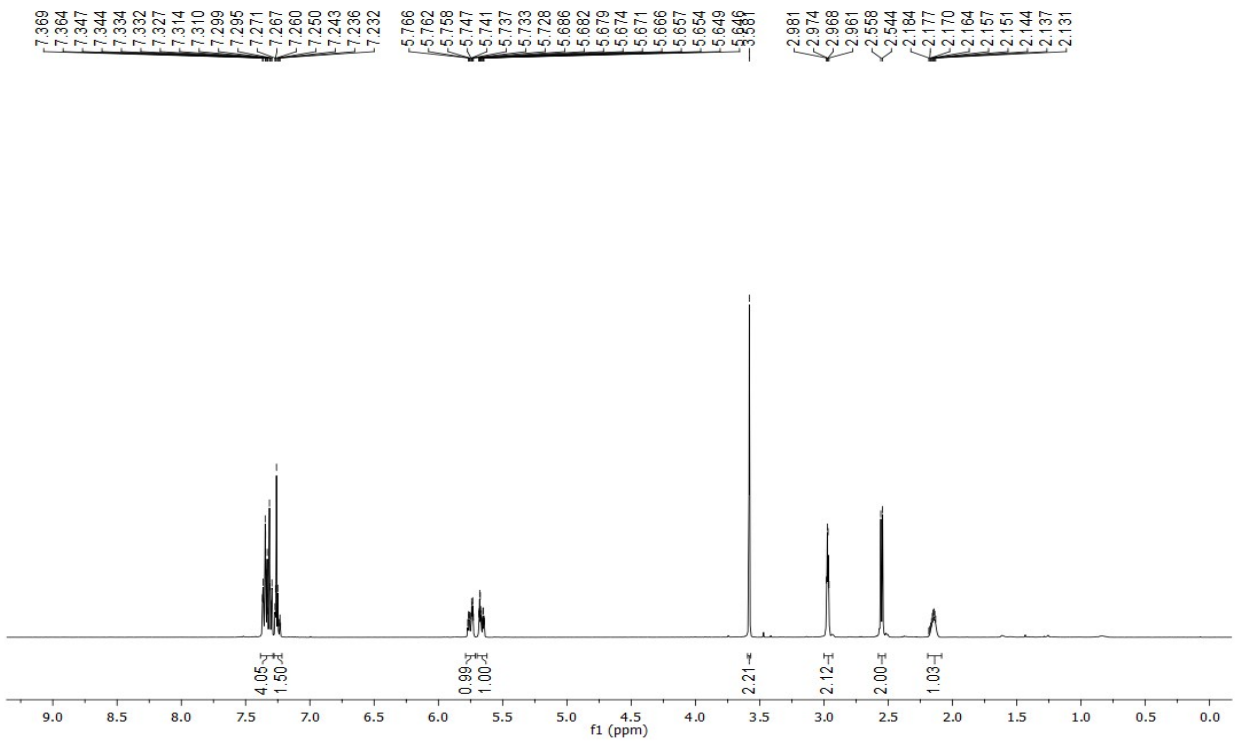
Preparation of 1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine-5-d (*rac*-1-d):

1-benzyl-1,2,3,6-tetrahydropyridine-3-*d* (14-d):



14-d

Benzylpyridinium bromide (2 g, 8 mmol) was dissolved in MeOH-d_4 (10 ml) and cooled to 0 ºC. $NaBH_4$ (360 mg, 9.5 mmol) was added portionwise and the reaction mixture was stirred at 0 ºC for 4 hours before being quenched with H_2O (~50 mL) and washed with EtOAc (x3). The combined organic material was washed with brine, dried over $MgSO_4$, filtered, concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes/EtOAc/Et_3N (4/1/0.05)) to give 1-benzyl-1,2,3,6-tetrahydropyridine-3-*d* (**14-d**) in 91% yield (1.27 g, 7.29 mmol) as a viscous yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ:** 2.13-2.18 (m, 1H, CD-3 H), 2.55 (d, *J* = 5.6 Hz, 2H, C-2 H), 2.97 (dd, *J* = 5.2, 2.8 Hz, 2H, C-6 H), 3.58 (s, 2H, benzylic), 5.66 (dtd, *J* = 10.0, 3.2, 2.0 Hz, 1H, vinylic), 5.75 (ddt, *J* = 10.0, 3.2, 2.2 Hz, 1H, vinylic), 7.23-7.27 (m, 1H, aromatic), 7.29-7.37 (m, 4H, aromatic); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 25.8 (t, CDH), 49.6, 52.8, 63.0, 125.2, 125.5, 127.0, 128.2, 129.2, 138.4; **HRMS** (ESI) *m/z* calcd for $C_{12}H_{15}DN^+$ $[M+H]^+$ 175.13400, found 175.13403.


7.369
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7.332
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7.314
7.310
7.299
7.295
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7.260
7.250
7.243
7.236
7.232
5.766
5.762
5.758
5.747
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5.733
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5.682
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5.671
5.666
5.657
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3.581
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2.974
2.968
2.961
2.558
2.544
2.184
2.177
2.170
2.164
2.157
2.151
2.144
2.137
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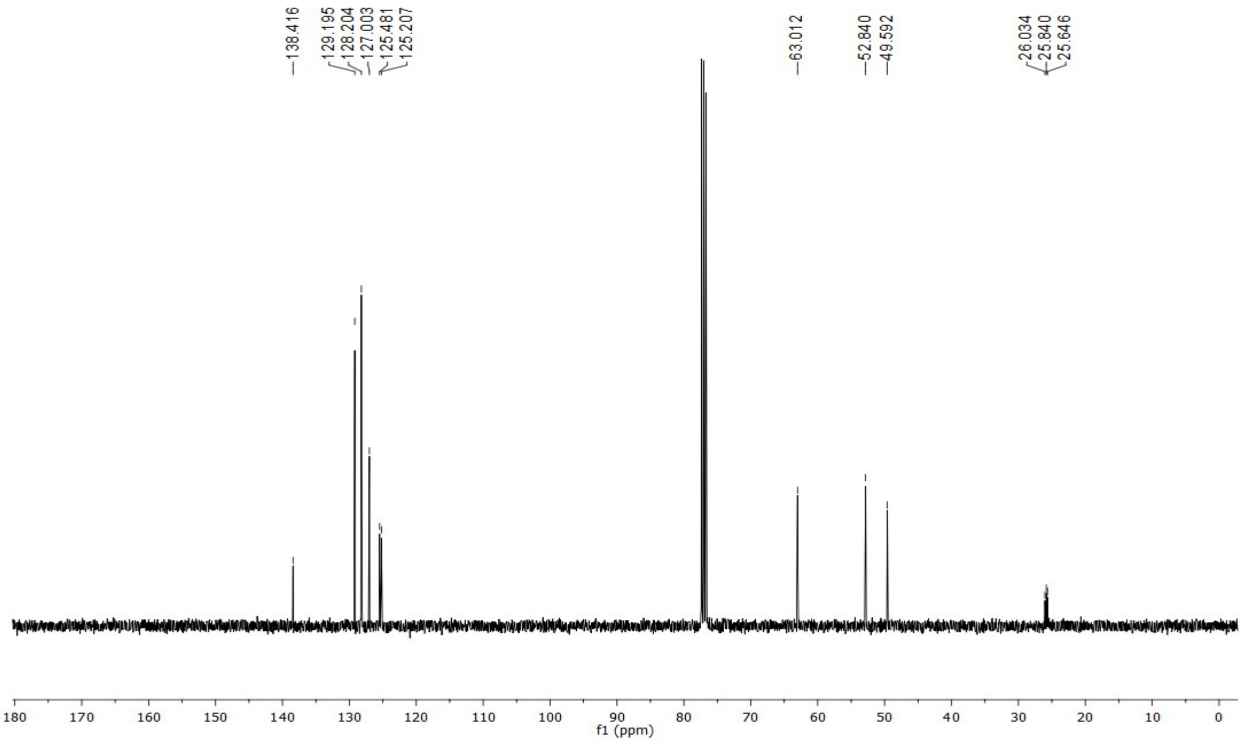
1.50
0.99
1.00
2.21
2.12
2.00
1.03
f1 (ppm)


138.416
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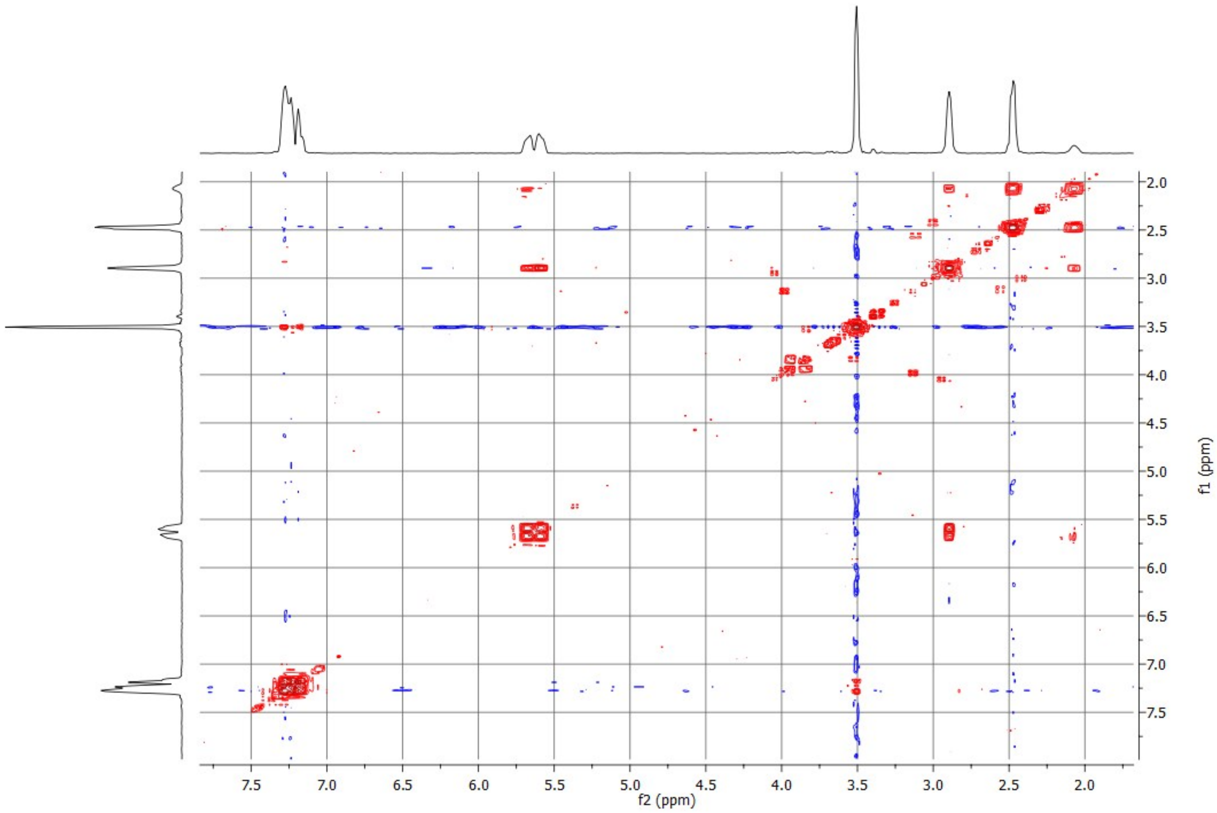
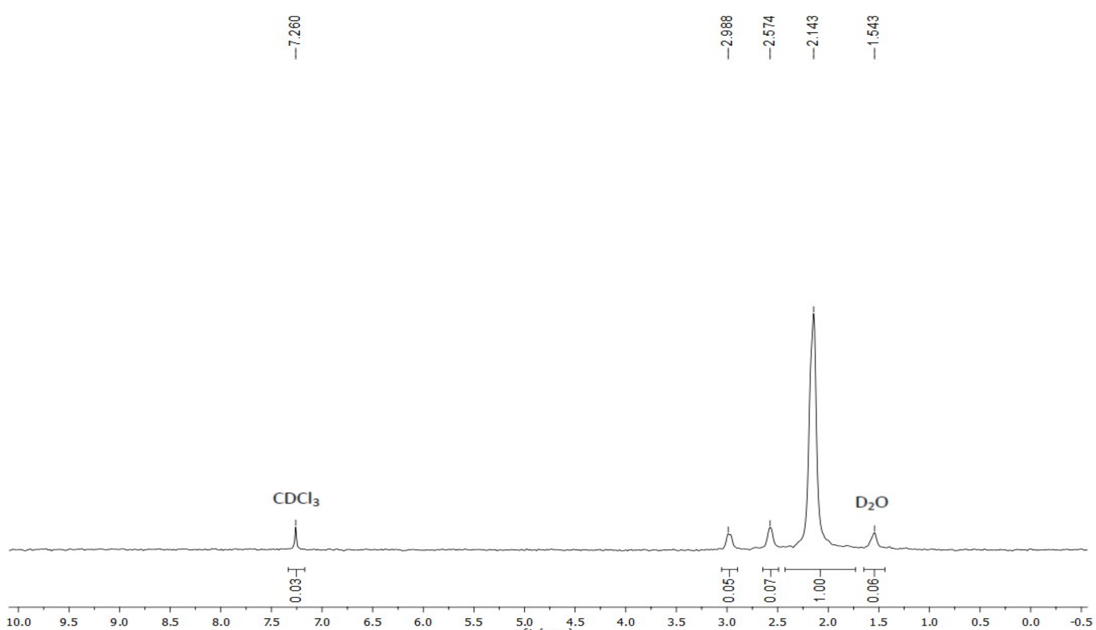
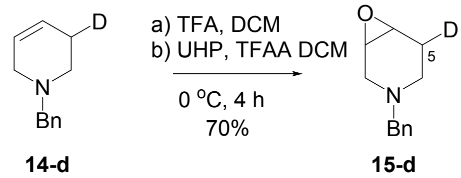
125.481
125.207
63.012
52.840
49.592
26.034
25.840
25.646
f1 (ppm)



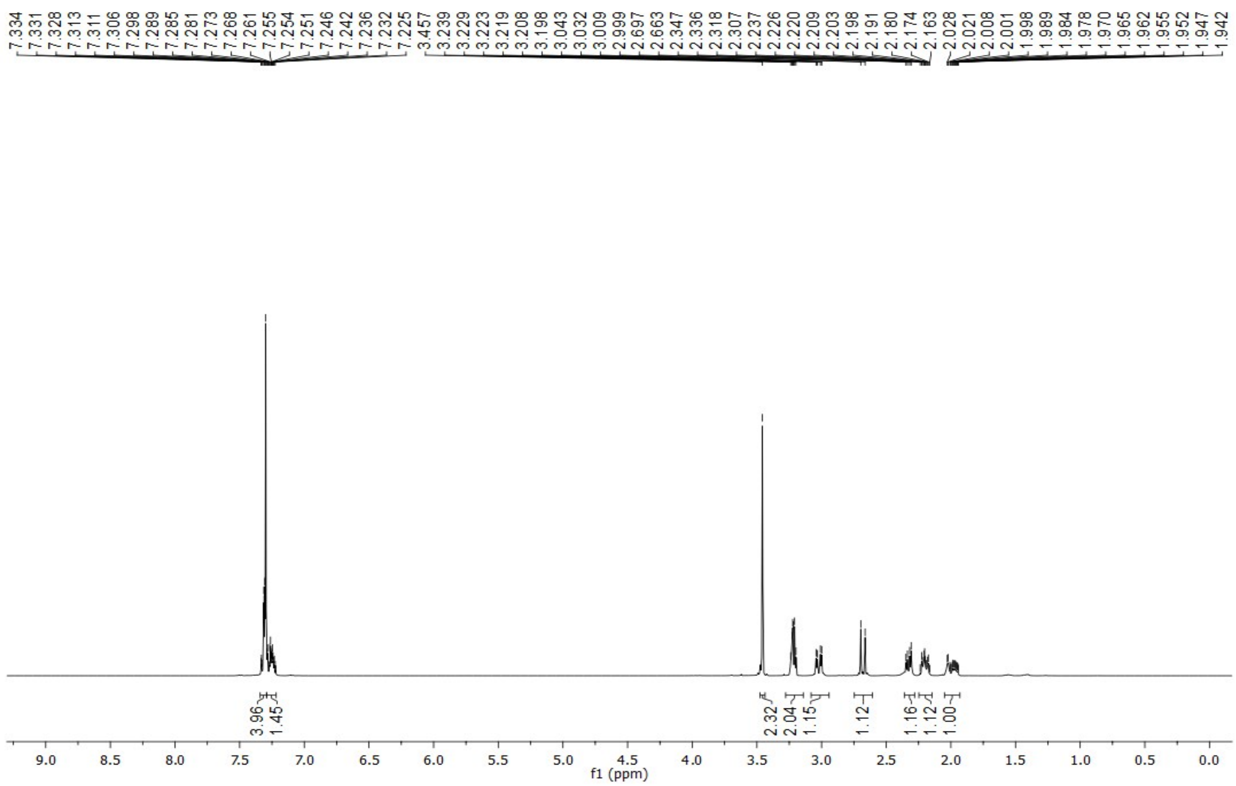
D-NMR of 14-d in $CHCl_3$



3-benzyl-7-oxa-3-azabicyclo[4.1.0]heptane-5-*d* (15-d):



Urea hydrogen peroxide (UHP) (2.7 g, 28 mmol) and DCM (24 ml) were added into a flame dried flask and cooled 0 ˚C. A solution of trifluoroacetic anhydride (TFAA) (3.9 ml, 28 mmol) in DCM (15 ml) was added dropwise over 30 minutes. The resulting suspension was stirred for 1 hour at 0 ˚C. Meanwhile TFA (2.2 ml, 27.5 mmol) was added dropwise into a solution of **14-d** (3.4 g, 19 mmol) in DCM (15 ml) at 0 ˚C and stirred for 1 hour. Cold TFA/piperidine solution was added into UHP/TFAA solution dropwise and stirred for 4 hours at 0 ˚C. After completion H_2O (40 ml) was added and biphasic solution was stirred for 15 minutes followed by addition of saturated Na_2SO_3 solution. Organic layer was separated and aqueous layer was neutralized by K_2CO_3 and washed with DCM (x3). The combined organic phases were washed with saturated $NaHCO_3$ (x3), dried over $MgSO_4$, filtered, concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes/acetone (7/1)) to give 1-benzyl-3,4-epoxypiperidine-5-*d* (**15-d**) in 70% yield (2.6 g, 13 mmol) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 1.94-2.03 (m, 1H, CD-5 H), 2.16-2.23 (m, 1H, C-6 H), 2.33 (dd, *J* = 11.6, 4.4 Hz, 1H, C-6 H), 2.68 (d, *J* = 13.6 Hz, 1H, C-2 H), 3.02 (bdd, *J* = 13.6, 4.2 Hz, 1H, C-2 H), 3.20-3.24 (m, 2H, C-3, C-4 H), 3.46 (s, 2H, benzylic), 7.22-7.29 (m, 1H, aromatic), 7.30-7.33 (m, 4H, aromatic); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 25.4 (t, CDH), 45.9 (m), 50.8 (m), 51.4 (d, *J* = 3.7 Hz), 52.5, 62.5, 127.2, 128.4, 129.2, 138.0; **HRMS** (ESI) *m/z* calcd for $C_{12}H_{15}DON^+$ $[M+H]^+$ 191.12892, found 191.12885.



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3.208
3.198
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3.032
3.009
2.999
2.697
2.663
2.347
2.336
2.318
2.307
2.237
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2.220
2.209
2.203
2.198
2.191
2.180
2.174
2.163
2.028
2.021
2.008
2.001
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1.947
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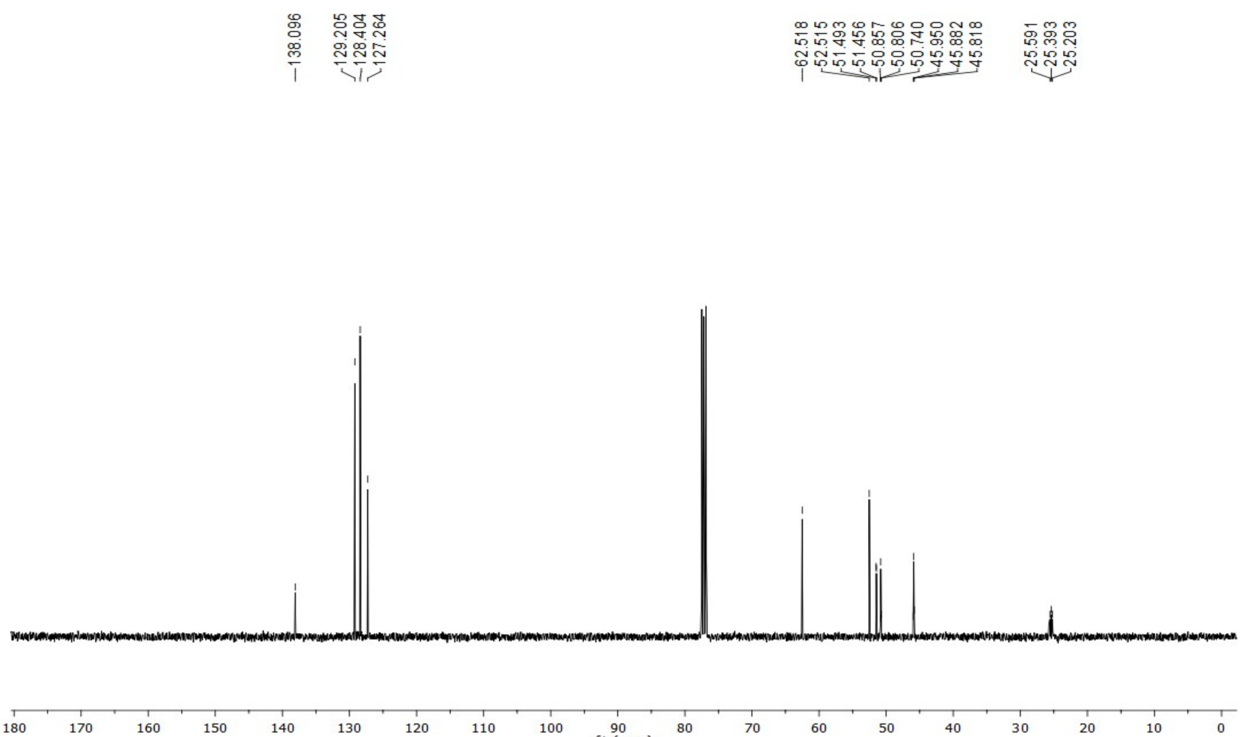
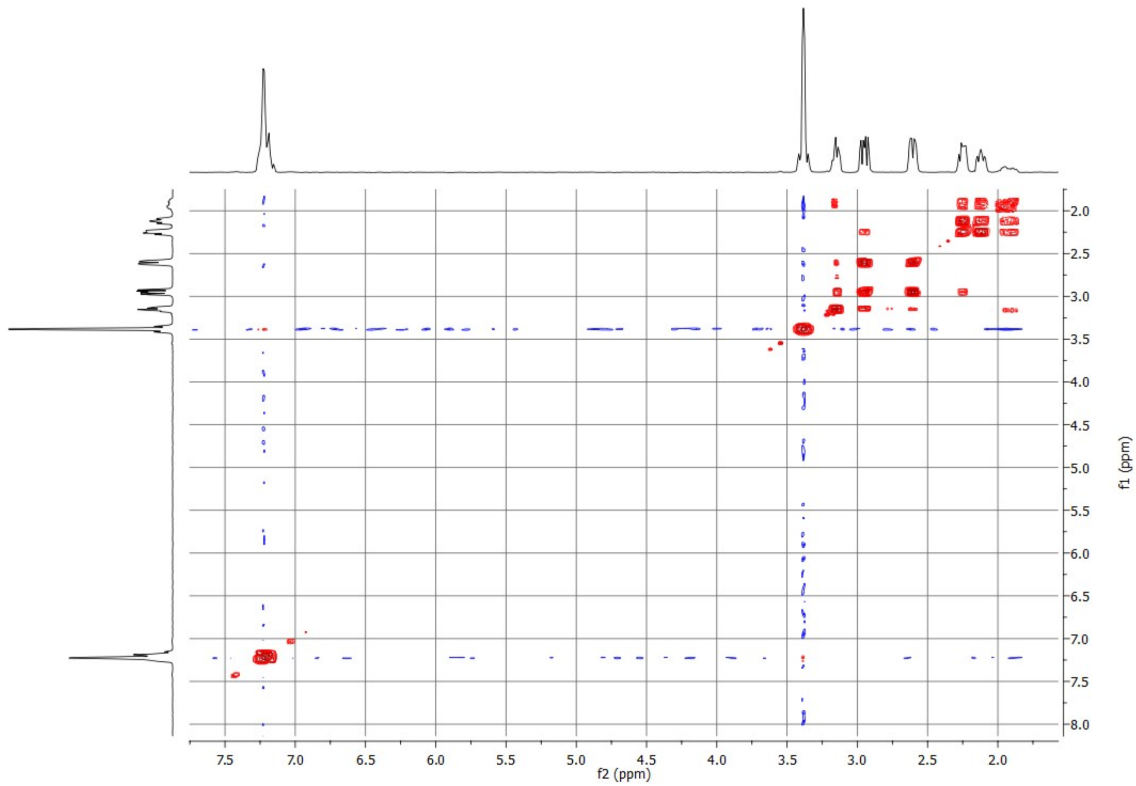
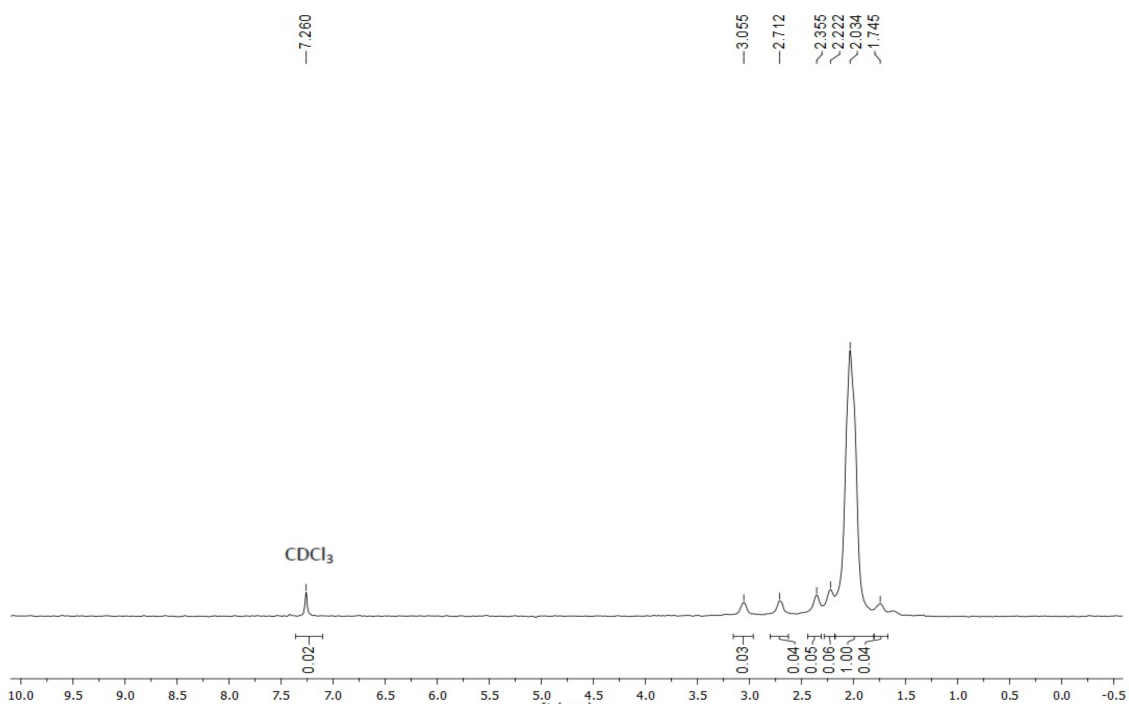
3.96
1.45
2.32
2.04
1.15
1.12
1.16
1.12
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



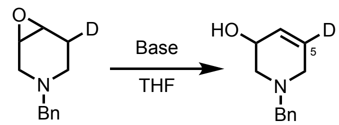
138.096
129.205
128.404
127.264
62.518
52.515
51.493
51.456
50.857
50.806
50.740
45.950
45.882
45.818
25.591
25.393
25.203
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



D-NMR of 15-d in $CHCl_3$



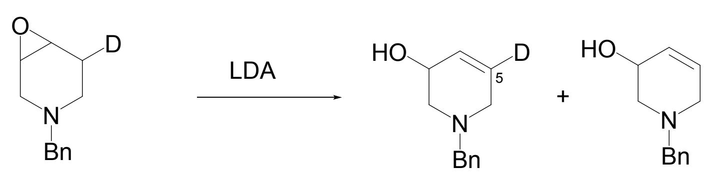
Optimization of 5-d Synthesis:



Entry	Base	Base Equiv.	Temp. (˚C)	Time (h)	Yield (%)	D% @5
1	LiHMDS	1	rt	13	-	-
2	LiHMDS	0.5	rt	13	-	-
3	NaHMDS	0.5	rt	13	-	-
4	LDA	0.5	rt	2	4	82
5	LDA	0.5	0	17	6	67
6	LDA	0.5	–78	17	-	-
7	LDA	0.5	–78 to –13	13	-	-
8	LDA	0.5	0	4	25	69
9	LDA	1.5	rt	2	54	68
10	LDA	0.5	rt	2	14	75
11[a]	LDA	0.5	rt	2	37	71
11[a]	LDA	0.5	rt	2	31	**75**
12[a,b]	LDA	0.5	rt	2	**53**	70

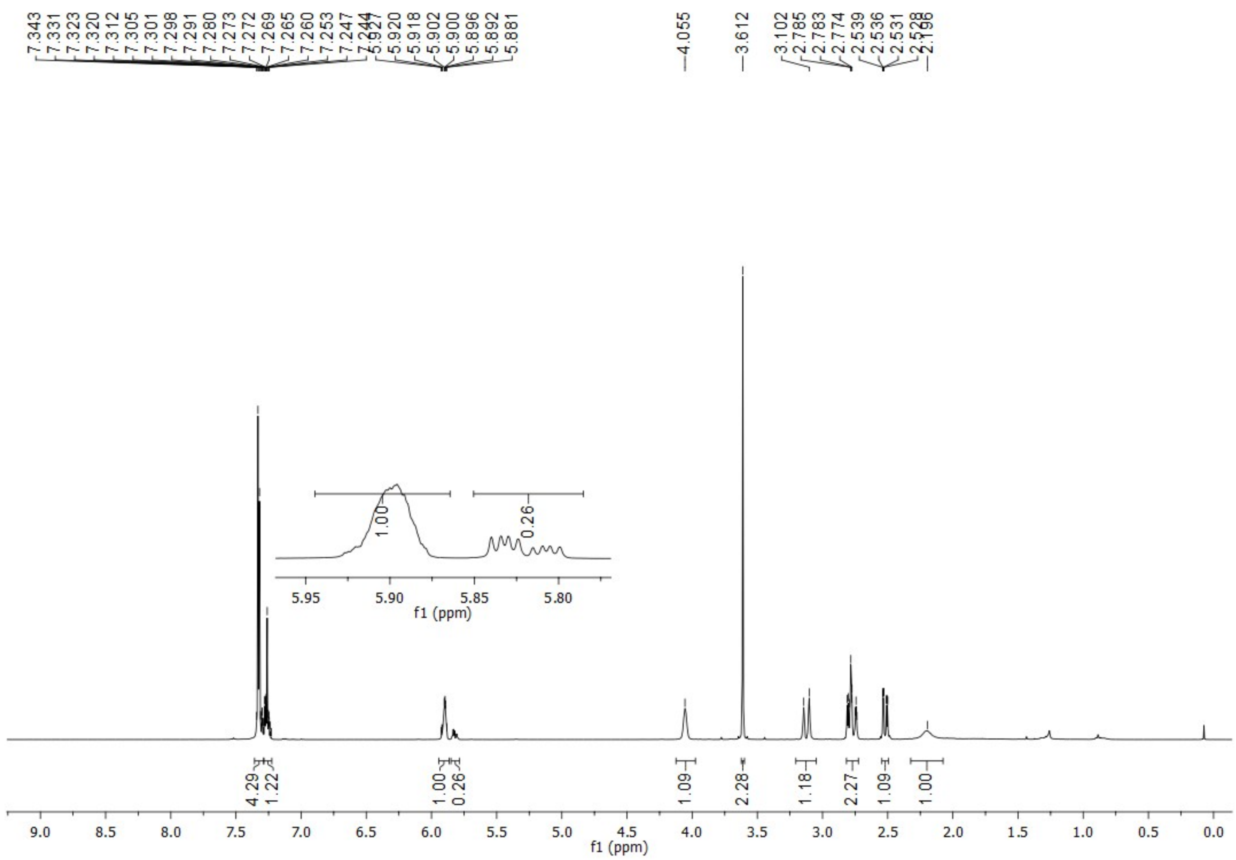
[a]4.5 mmol of 15-d was used. [b]Reaction concentration was 0.13M as opposed to 0.15M.

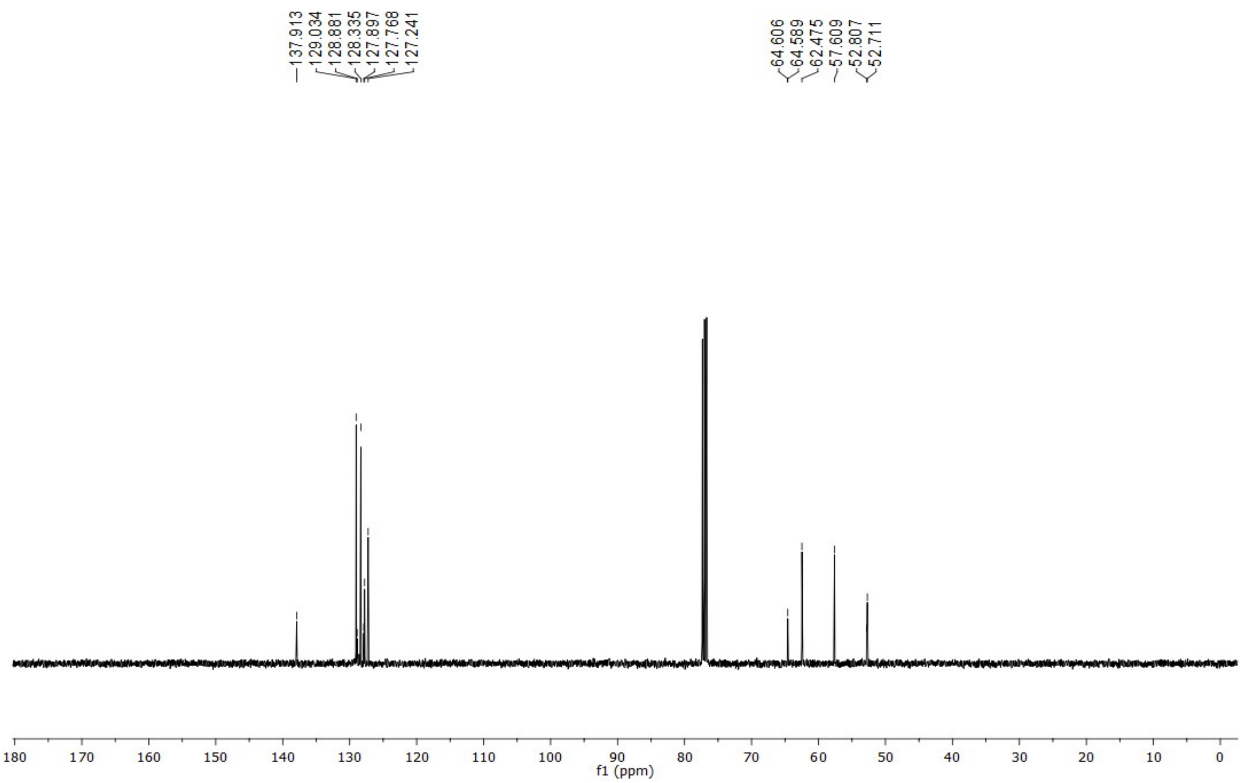
1-benzyl-1,2,3,6-tetrahydropyridin-5-*d*-3-ol (5-d):



THF (20 ml) and diisopropyl amine (0.3 ml, 2.2 mmol) were added to flame dried 100 ml-round-bottom flask under an argon atmosphere and stirred and cooled to 0 °C. 2.5 M *n*-butyllithium (0.9 ml, 2.2 mmol) was added dropwise and stirring was continued at 0 ºC for 20-30 minutes. A solution of 1-benzyl-3,4-epoxypiperidine-5-*d* (**15-d**) (850 mg, 4.5 mmol) in THF (10 ml) was added dropwise, and then the cooling bath was removed, and the reaction mixture stirred for 2 hours before being quenched by addition of saturated aq. NH_4Cl (20 ml) and extracted with DCM. The organic phase was washed with brine, dried over $MgSO_4$, filtered, concentrated on rotary evaporator and purified by flash column chromatography on silica gel (hexanes/acetone (5/1)) to give (**5-d**+**5**) in 31% yield (265 mg, 1.4 mmol, n_D/n_H = 2.85/1) as a viscous yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ:** 2.19 (bs, 1H (OH)), 2.52 (ddd, *J* = 11.4, 3.2, 1.0 Hz, 1H, C-2 H), 2.73-2.81 (m, 2H, C-2 H and C-6 H), 3.12 (d, *J* = 16.8 Hz, 1H, C-6 H), 3.61 (s, 2H, benzylic), 4.05 (bs, 1H, C-3 H), 5.88-5.93 (m, 1H, C-4 H), 7.23-7.29 (m, 1H), 7.29-7.34 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$, ppm) δ:**

52.7 (d, J = 9.7 Hz, C-6), 57.6, 62.5, 64.6 (d, J = 1.7 Hz, C-3), 127.2, 127.8 (d, J = 13.0 Hz, C-4), 128.3, 128.8 (m, CD-5), 129.0, 137.9; **HRMS** (ESI) *m/z* calcd for $C_{12}H_{15}DON^+$ [M+H]$^+$ 191.12892, found 191.12871.





137.913
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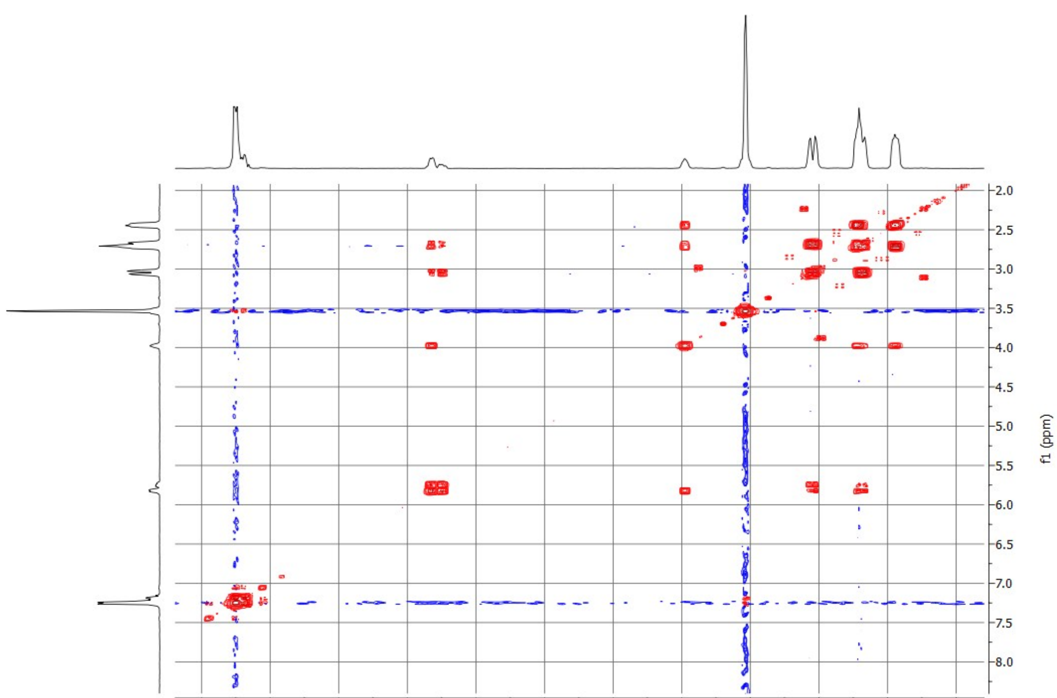
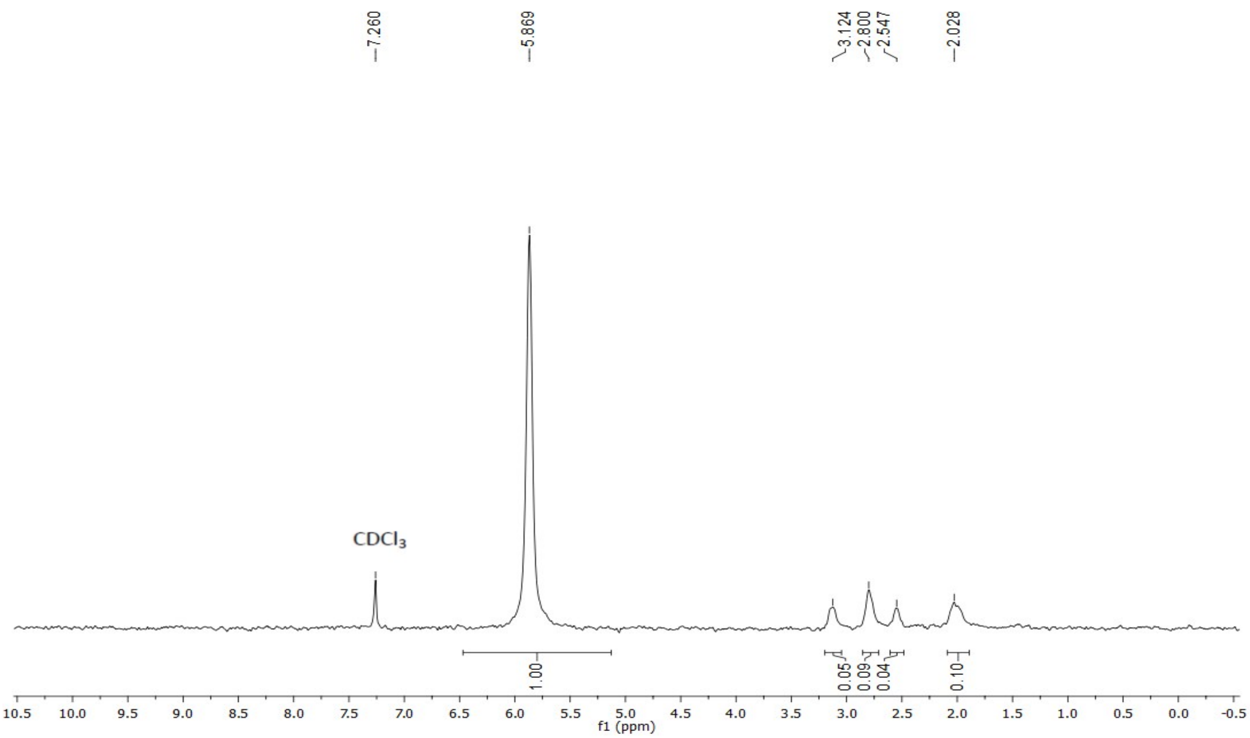
57.609
52.807
52.711
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

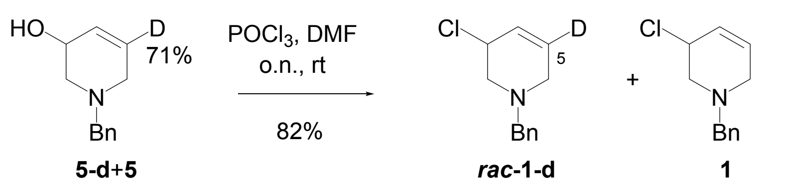


7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f2 (ppm)
f1 (ppm)

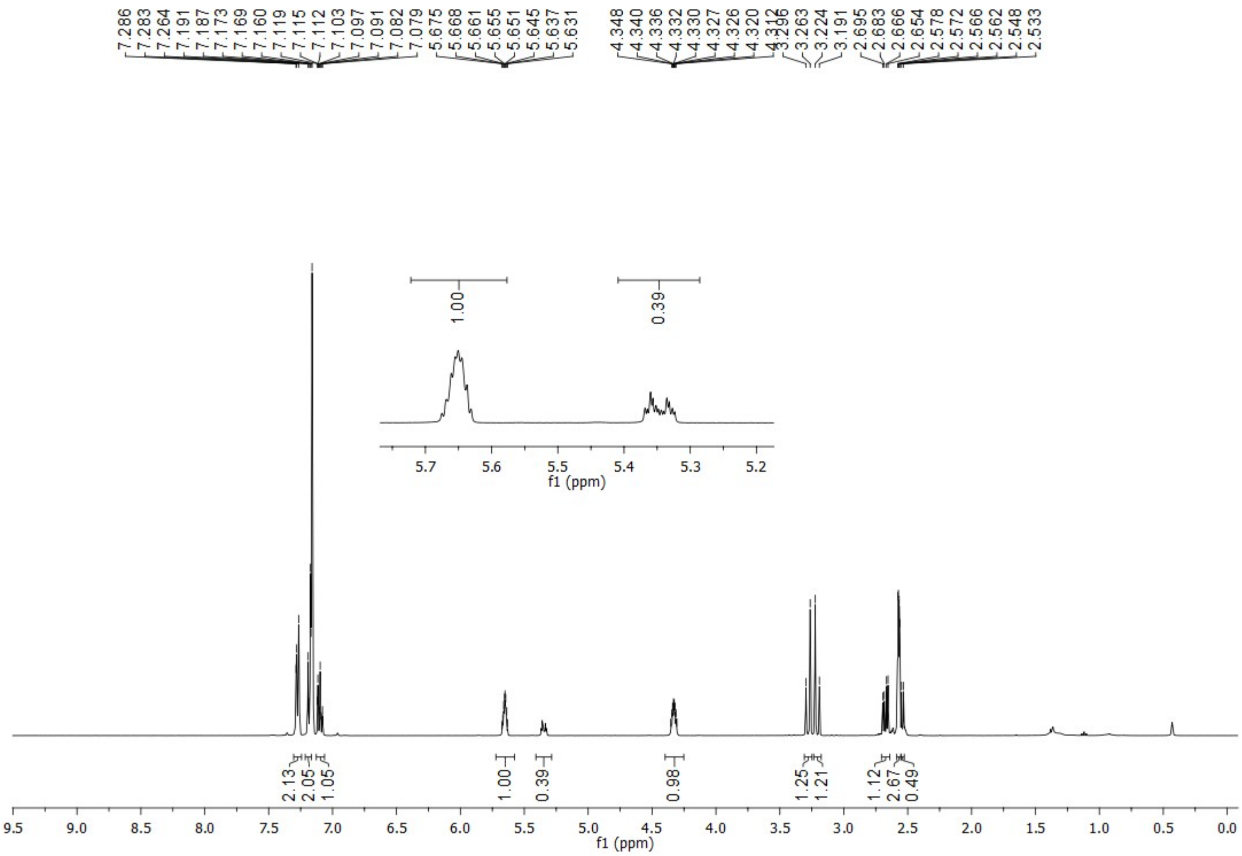
D-NMR of 5-d in $CHCl_3$



1-benzyl-3-chloro-1,2,3,6-tetrahydropyridine-5-*d* (*rac*-1-d):



$POCl_3$ (0.3 mL, 3.5 mmol) was added dropwise to a stirred and cooled (0 ºC) solution of (**5-d**+**5** n_D/n_H = 2.45/1) (312 mg, 1.6 mmol) in DMF (7 mL) under an argon atmosphere. The reaction mixture was left to gradually warm up to room temperature and stirring was continued overnight before H_2O was carefully added at 0 ºC. The reaction mixture was extracted with EtOAc. Aqueous material was neutralized by K_2CO_3 and washed with EtOAc (x3). The combined organic phases were washed with brine (x2), dried over $MgSO_4$, filtered, concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes or pentane/EtOAc (9/1)) to give (***rac*-1-d**+**1**) in 82% yield (280 mg, 1.3 mmol, n_D/n_H = 1.56/1) as a colorless oil. **^{1}H NMR** (400 MHz, C_6D_6, ppm) δ: 2.53-2.58 (m, 3H, C-2 H and C-6 H), 2.67 (dd, *J* = 11.6, 4.8 Hz, 1H, C-2 H), 3.21 (d, *J* = 13.2 Hz, 1H, benzylic), 3.28 (d, *J* = 13.2 Hz, 1H, benzylic), 4.30-4.35 (m, 1H, C-3 H), 5.63-5.67 (m, 1H, C-4 H), 7.08-7.12 (m, 1H, aromatic), 7.16-7.19 (m, 2H, aromatic), 7.26-7.28 (m, 2H, aromatic); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ: 52.0 (d, *J* = 9.3 Hz, C-6), 53.7 (C-3), 57.2, 61.8, 126.8, 126.7 (d, *J* = 12.5 Hz, C-4), 127.3, 128.3, 128.9, 129.14 (m, C-5), 137.5; **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}DONCl^+$ $[M+H]^+$ 209.09503, found 209.09515.



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5.668
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2.695
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2.666
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2.562
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0.39
f1 (ppm)
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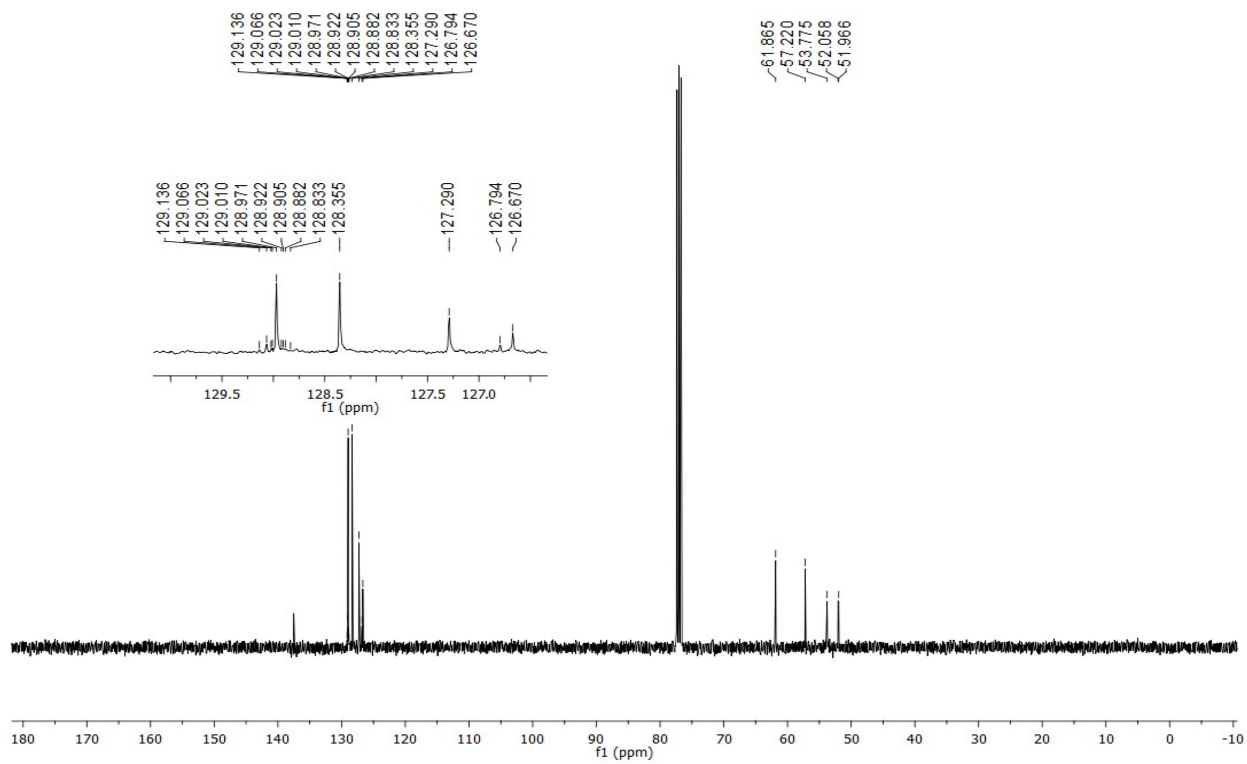
1.12
2.67
0.49
f1 (ppm)



129.136
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128.922
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126.794
126.670
61.865
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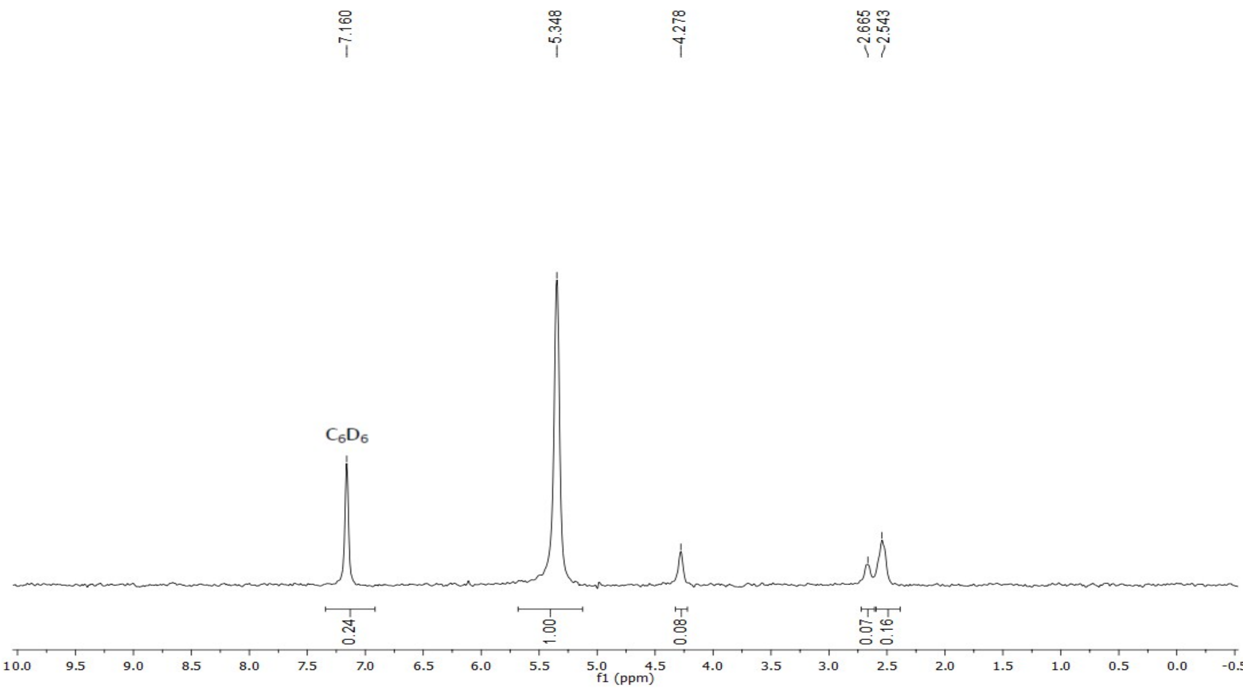
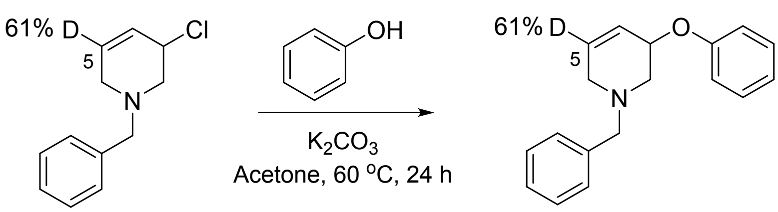
53.775
52.058
51.966
f1 (ppm)
f1 (ppm)

D-NMR of *rac*-1-d in C_6H_6

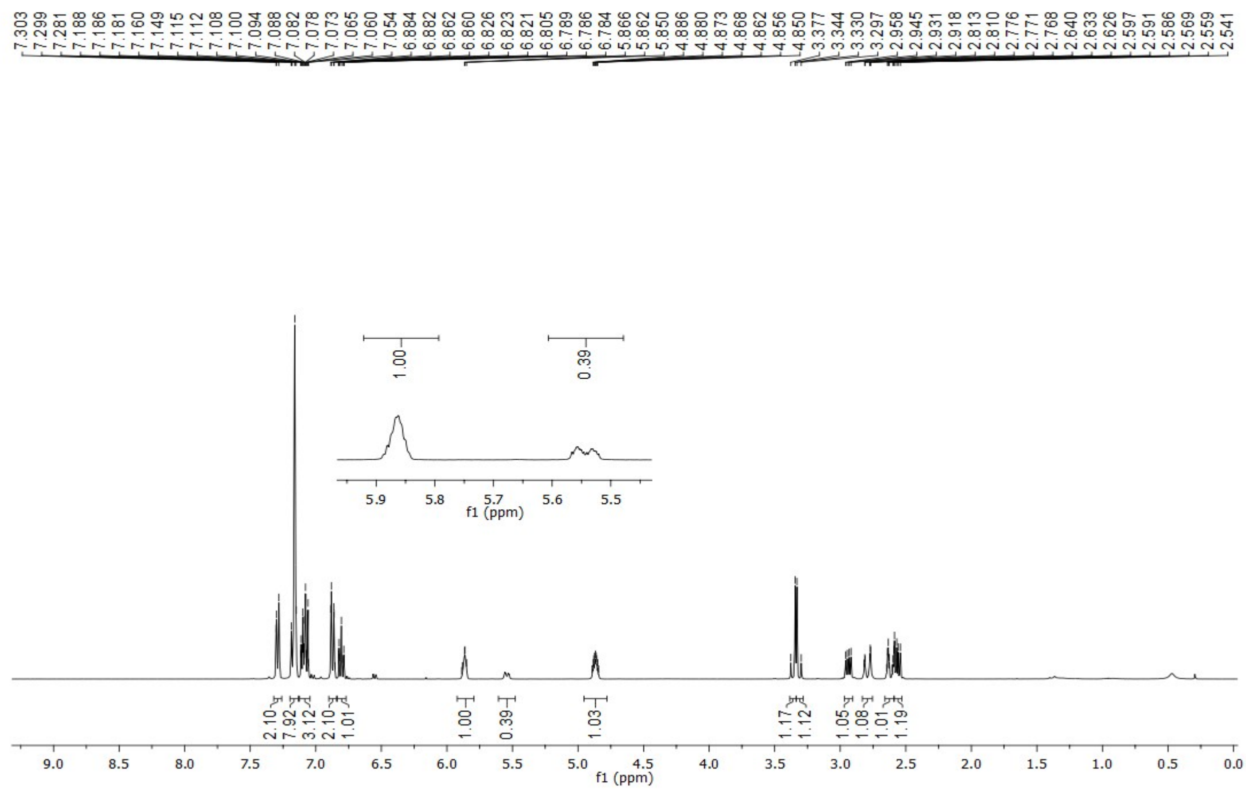


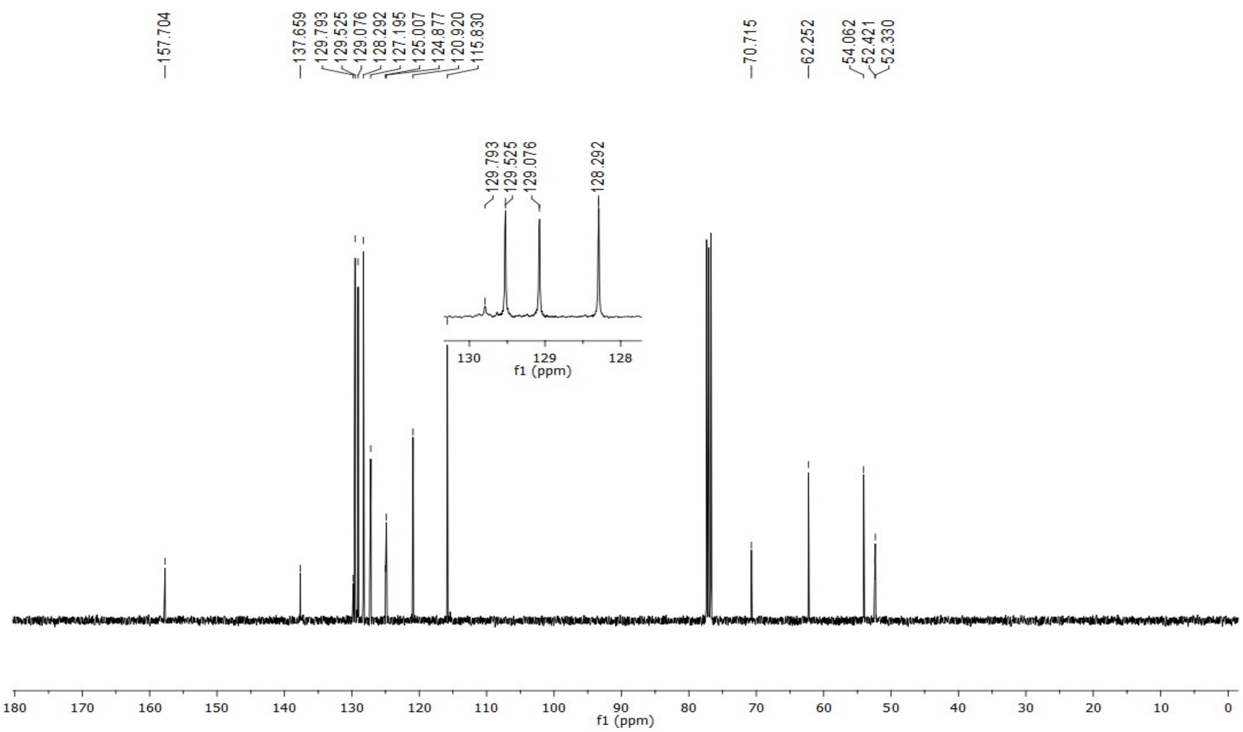
Nucleophilic substitution reactions with *rac*-1-d

1-benzyl-3-phenoxy-1,2,3,6-tetrahydropyridine-5-*d* (6-d):

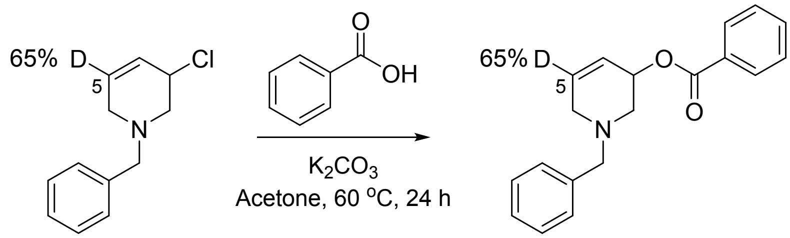


^{1}H NMR (400 MHz, C_6D_6, ppm) δ: 2.56 (dd, *J* = 10.8, 6.8 Hz, 1H, C-2 H), 2.58-2.64 (m, 1H, C-6 H), 2.76-2.82 (m, 1H, C-6 H), 2.94 (dd, *J* = 10.8, 5.2 Hz, 1H, C-2 H), 3.31 (d, *J* = 13.2 Hz, 1H, benzylic), 3.36 (d, *J* = 13.2 Hz, 1H, benzylic), 4.84-4.89 (m, 1H, C-3 H), 5.85-5.88 (m, 1H, C-4 H), 6.76-6.82 (m, 1H, aromatic), 6.85-6.88 (m, 2H, aromatic), 7.05-7.11 (m, 3H, aromatic), 7.15-7.19 (m, 2H, aromatic), 7.28-7.30 (m, 2H, aromatic); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 52.4 (d, *J* = 9.2 Hz, C-6), 54.0, 62.2, 70.7, 115.8, 120.9, 124.9 (d, *J* = 13.1 Hz, C-4), 127.2, 128.3, 129.0, 129.5, 129.8 (m, C(D)-5), 137.6, 157.7; **HRMS** (ESI) *m/z* calcd for $C_{18}H_{19}DON^+$ $[M+H]^+$ 267.16022, found 267.15994.

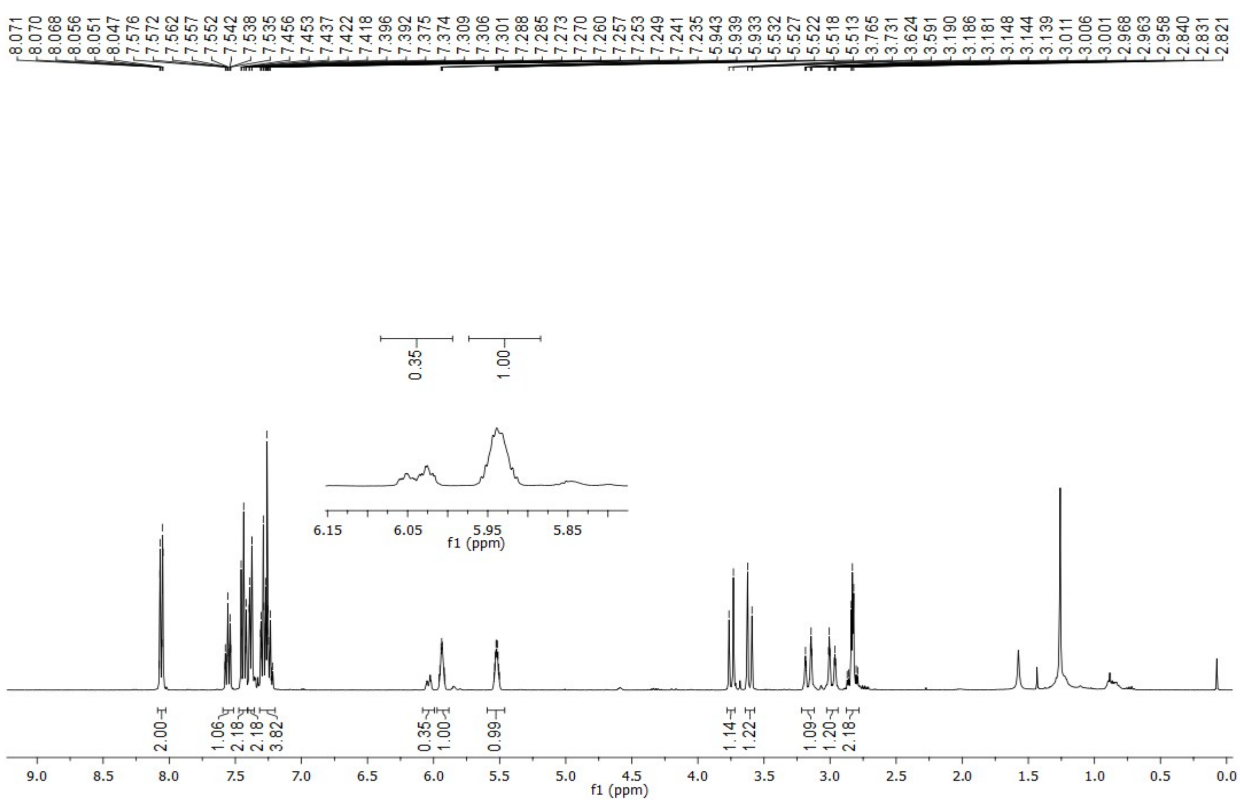

7.303
7.299
7.281
7.188
7.186
7.181
7.160
7.149
7.115
7.112
7.108
7.100
7.094
7.088
7.082
7.078
7.073
7.065
7.060
7.054
6.884
6.882
6.862
6.860
6.826
6.823
6.821
6.805
6.789
6.786
6.784
5.866
5.862
5.850
4.886
4.880
4.873
4.868
4.862
4.856
4.850
3.377
3.344
3.330
3.297
2.958
2.945
2.931
2.918
2.813
2.810
2.776
2.771
2.768
2.640
2.633
2.626
2.597
2.591
2.586
2.569
2.559
2.541
1.00
0.39
f1 (ppm)
2.10
7.92
3.12
2.10
1.01
1.00
0.39
1.03
1.17
1.12
1.05
1.08
1.01
1.19
f1 (ppm)

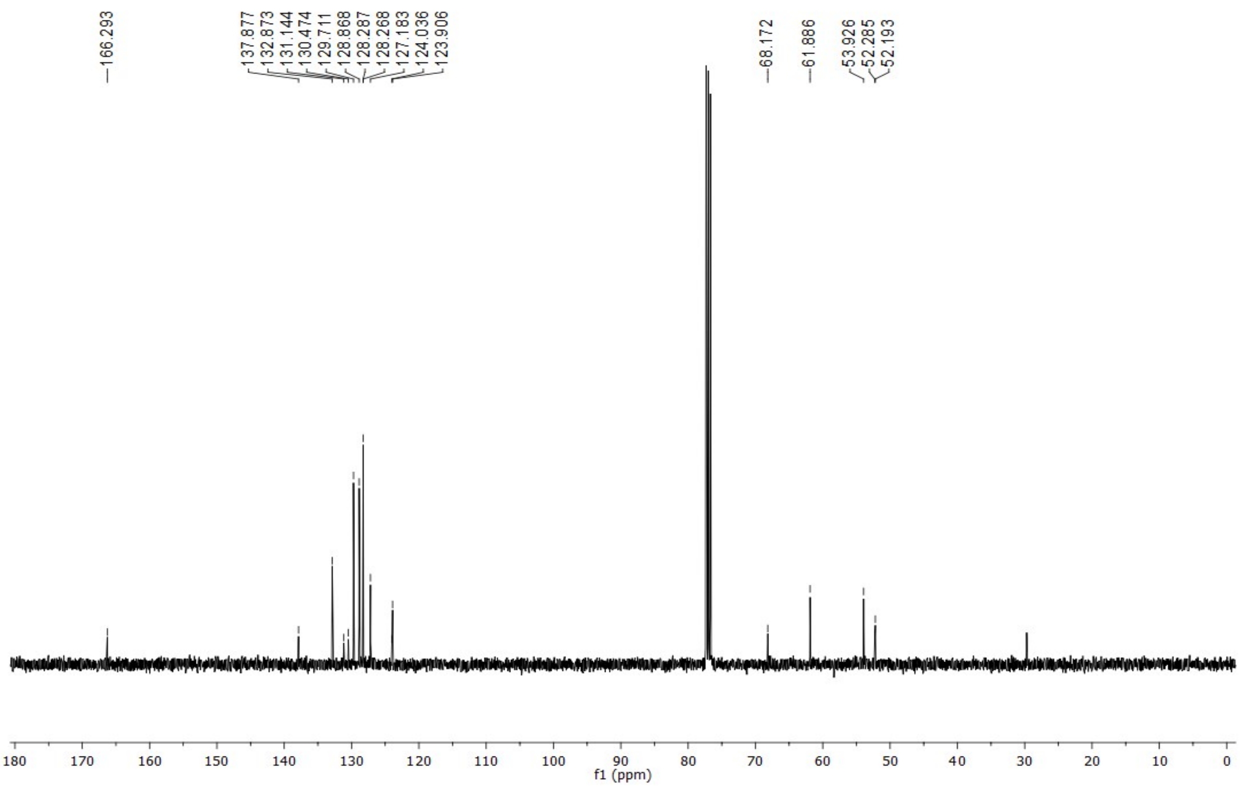

157.704
137.659
129.793
129.525
129.076
128.292
127.195
125.007
124.877
120.920
115.830
70.715
62.252
54.062
52.421
52.330
129.793
129.525
129.076
128.292
f1 (ppm)
f1 (ppm)

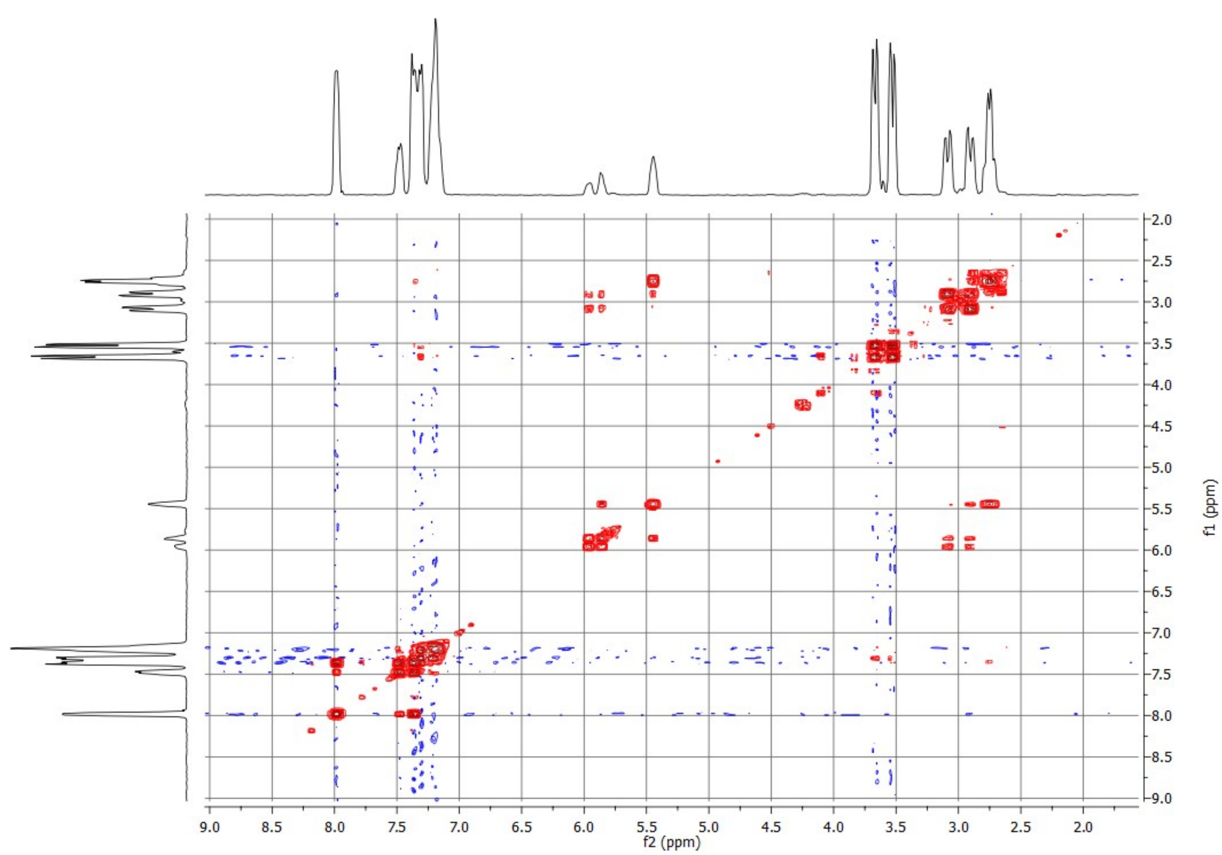
1-benzyl-1,2,3,6-tetrahydropyridin-3-yl benzoate-5-*d* (7-d):



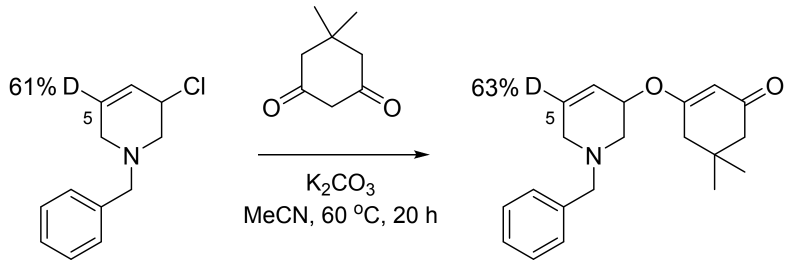
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 2.79-2.87 (m, 2H, C-2 H), 2.98 (bdt, *J* = 17.2, 2.0 Hz, 1H, C-6 H), 3.16 (bdt, *J* = 16.8, 2.0 1H, C-6 H), 3.61 (d, *J* = 13.2 Hz, 1H, benzylic), 3.72 (d, *J* = 13.2 Hz, 1H, benzylic), 5.50-5.54 (m, 1H, C-3 H), 5.91-5.96 (m, 1H, C-4 H), 7.20-7.31 (m, 3H), 7.37-7.39 (m, 2H), 7.42-7.45 (m, 2H), 7.53-7.58 (m, 1H), 8.04-8.07 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 52.2 (d, *J* = 9.3 Hz, C-6), 53.9, 61.9, 68.2, 123.9 (d, *J* = 13.1 Hz, C-4), 127.2, 128.27, 128.28, 128.8, 129.7, 130.4, 131.1 (m, C(D)-5), 132.8, 137.8, 166.3; **HRMS** (ESI) *m/z* calcd for $C_{19}H_{19}DO_2N^+$ $[M+H]^+$ 295.15513, found 295.15475.



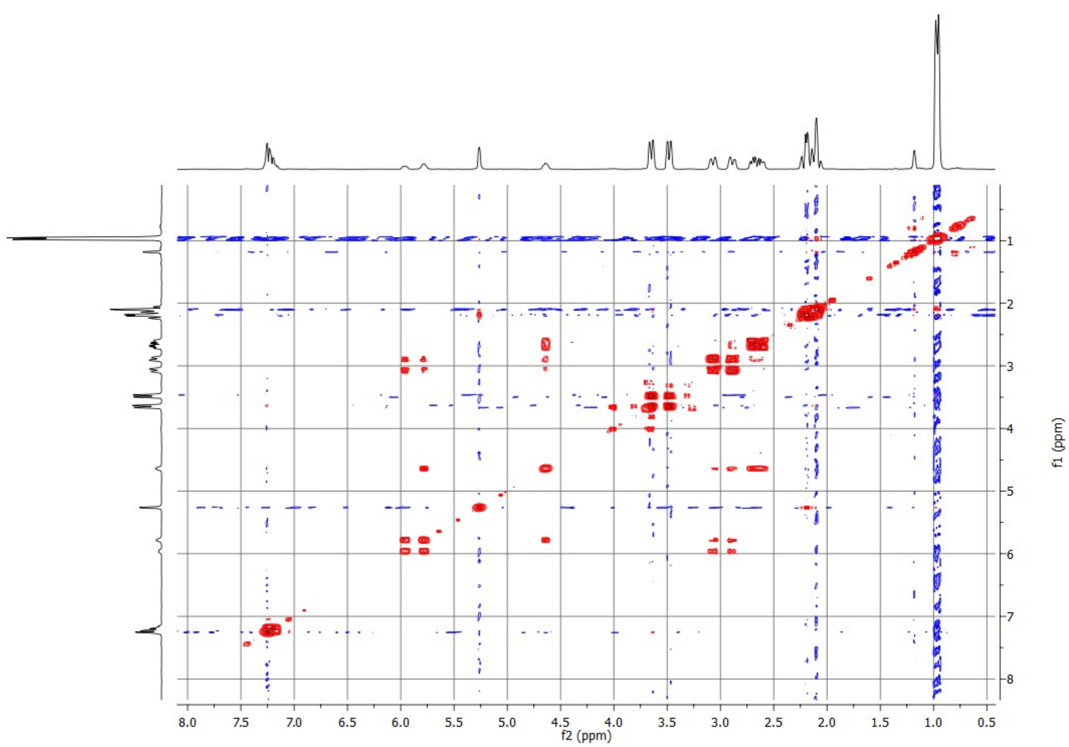

166.293
137.877
132.873
131.144
130.474
129.711
128.868
128.287
128.268
127.183
124.036
123.906
68.172
61.886
53.926
52.285
52.193
f1 (ppm)

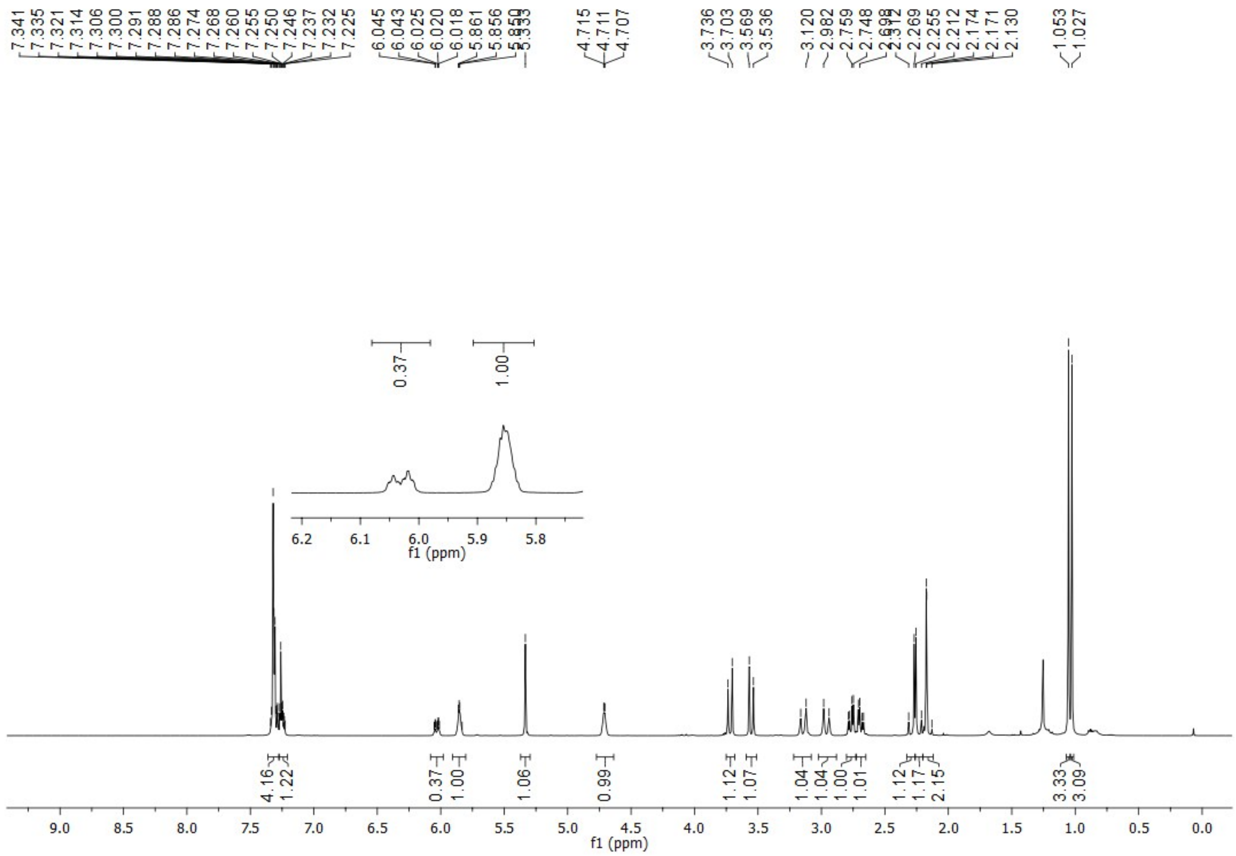

f2 (ppm)
f1 (ppm)

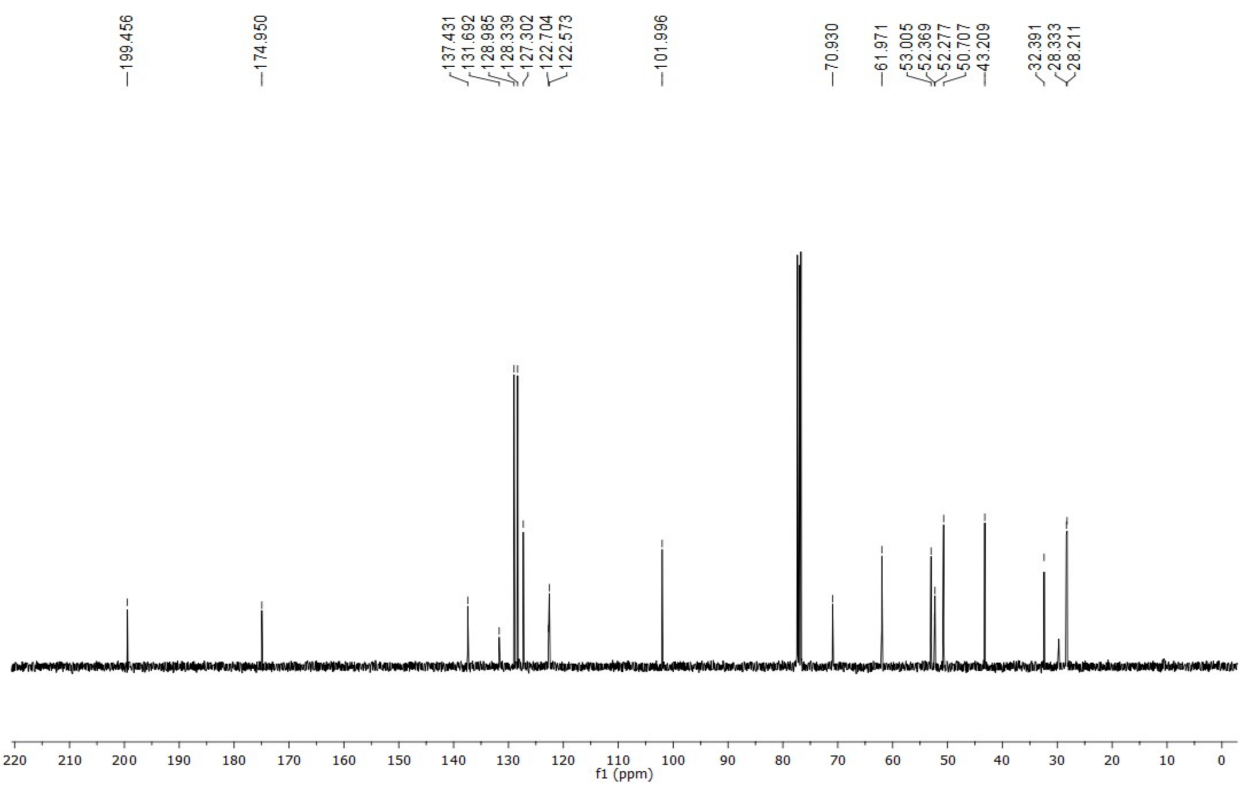
3-((1-benzyl-1,2,3,6-tetrahydropyridin-3-yl-5-*d*)oxy)-5,5-dimethylcyclohex-2-en-1-one (8-d):



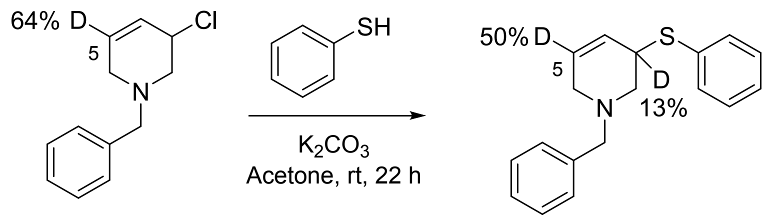
^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 1.02 (s, 3H), 1.05 (s, 3H), 2.15 (d, *J* = 17.6 Hz, 1H), 2.19 (d, *J* = 16.8 Hz, 1H), 2.23 (d, *J* = 17.2 Hz, 1H), 2.29 (d, *J* = 17.2 Hz, 1H), 2.69 (dd, *J* = 12.0, 4.4 Hz, 1H, C-2 H), 2.77 (dd, *J* = 12.0, 4.4 Hz, 1H, C-2 H), 2.96 (bd, *J* = 16.8 Hz, 1H, C-6 H), 3.14 (bd *J* = 17.2 Hz, 1H, C-6 H), 3.55 (d, *J* = 13.2 Hz, 1H, benzylic), 3.72 (d, *J* = 13.2 Hz, 1H, benzylic), 4.70-4.71 (m, 1H, C-3 H), 5.33 (s, 1H), 5.83-5.86 (m, 1H, C-4 H), 7.22-7.27 (m, 1H), 7.28-7.34 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$, ppm) δ:** 28.21, 28.33, 32.4, 43.2, 50.7, 52.3 (d, *J* = 9.6 Hz, C-6), 52.9, 61.9, 70.9, 101.9, 122.6 (d, *J* = 13.2 Hz, C-4), 127.3, 128.3, 128.9, 131.7 (m, C(D)-5), 137.4, 174.9, 199.4; **HRMS** (ESI) *m/z* calcd for $C_{20}H_{25}DO_2N^+$ $[M+H]^+$ 313.20208, found 313.20153.



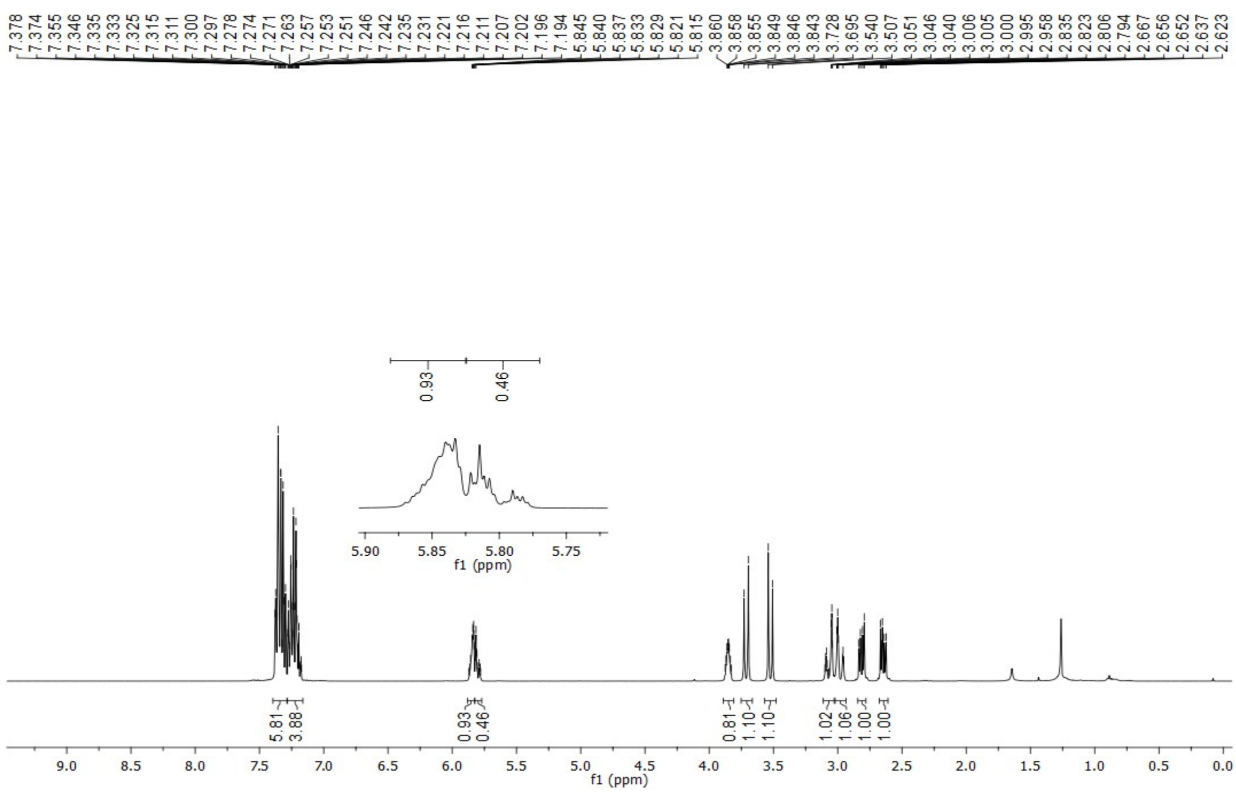


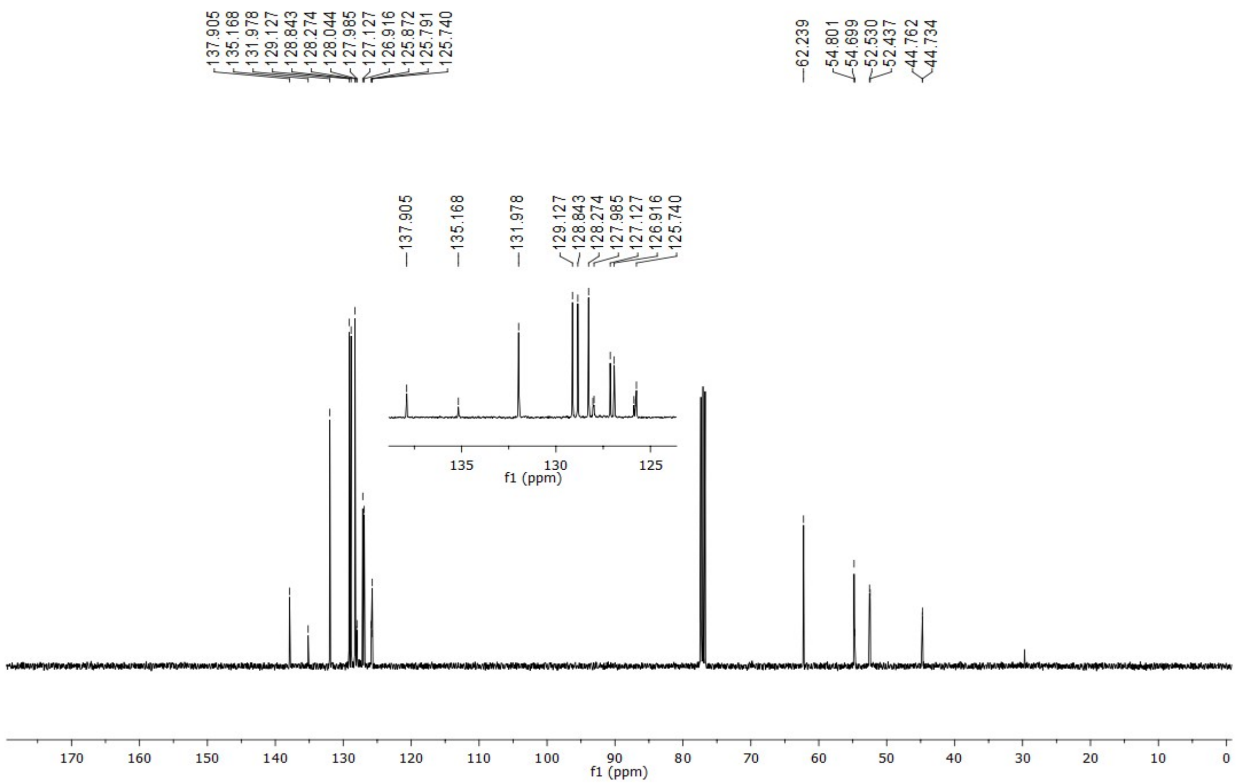


1-benzyl-3-(phenylthio)-1,2,3,6-tetrahydropyridine-5-*d* (9-d):

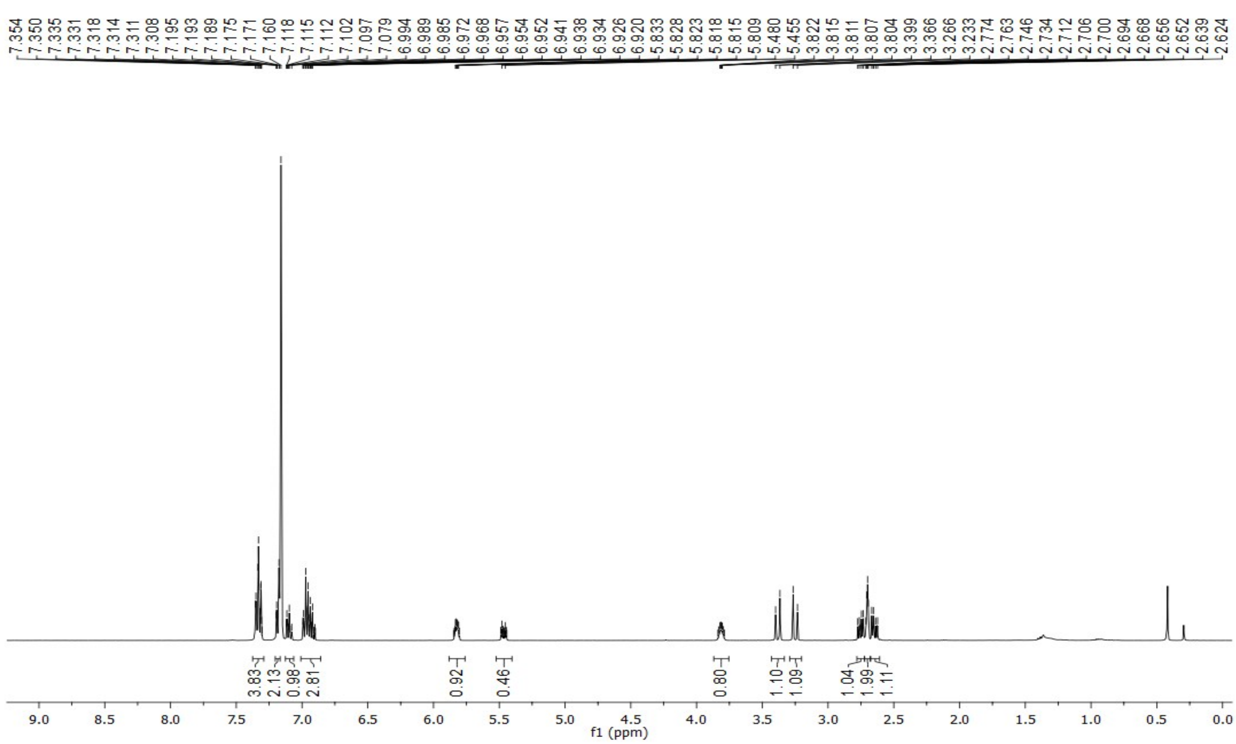


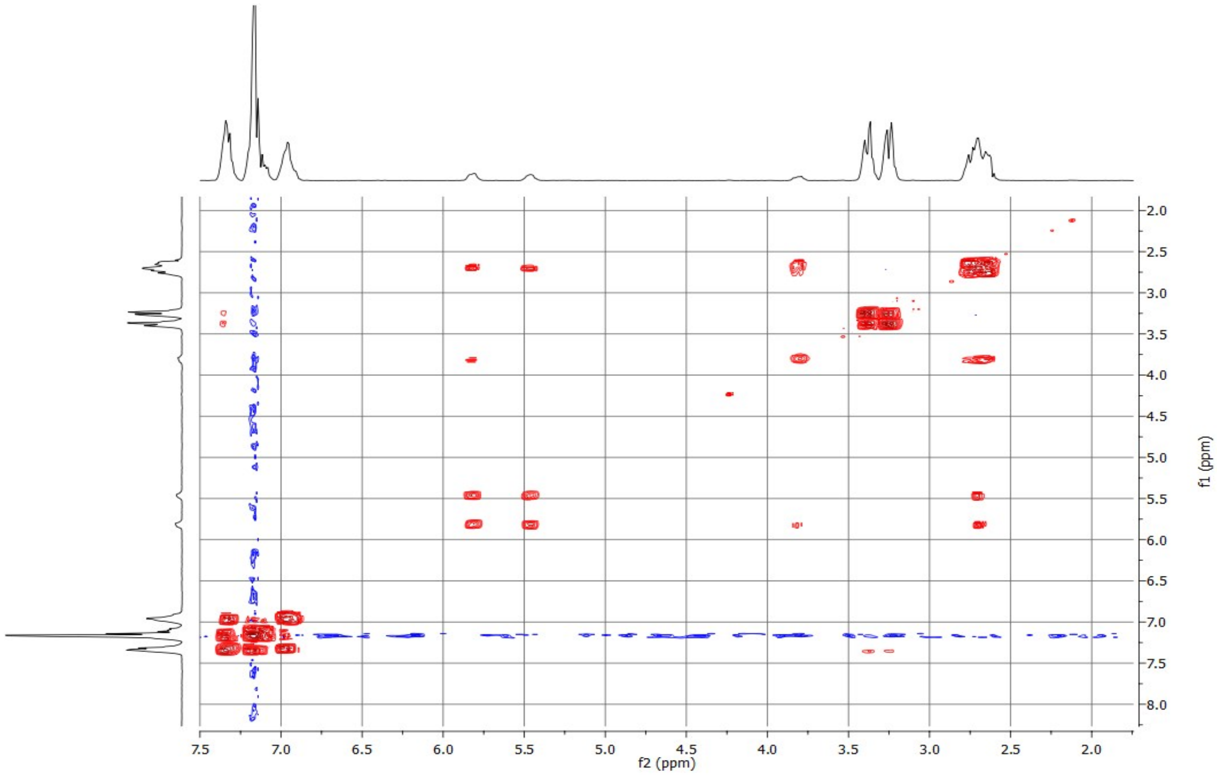
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 2.64 (dd, *J* = 11.8, 5.8 Hz, 1H, C-2 H), 2.81 (dd, *J* = 11.6, 4.8 Hz, 1H, C-2 H), 2.95-3.00 (m, 1H, C-6 H), 3.04-3.09 (m, 1H, C-2 H), 3.52 (d, *J* = 13.2 Hz, 1H, benzylic), 3.71 (d, *J* = 13.2 Hz, 1H, benzylic), 3.83-3.87 (m, 1H, C-3 H), 5.83-5.87 (m, 1H, C-4 H), 7.17-7.28 (m, 4H), 7.29-7.37 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 44.7 (d, *J* = 2.5 Hz, C-3), 52.5 (d, *J* = 9.4 Hz, C-6), 54.7 (d, *J* = 10.3 Hz, C-2), 62.2, 125.8 (m, C-4), 126.9, 127.1, 128.0 (d, *J* = 5.9 Hz, C(D)-5), 128.2, 128.8, 129.1, 131.9, 135.1, 137.9; **HRMS** (ESI) *m/z* calcd for $C_{18}H_{19}DNS^+$ $[M+H]^+$ 283.13737, found 283.13702.



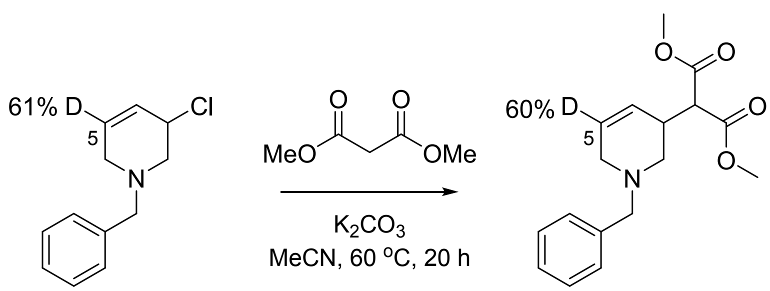


^{1}H-NMR and COSY-NMR of 9-d in C_6D_6

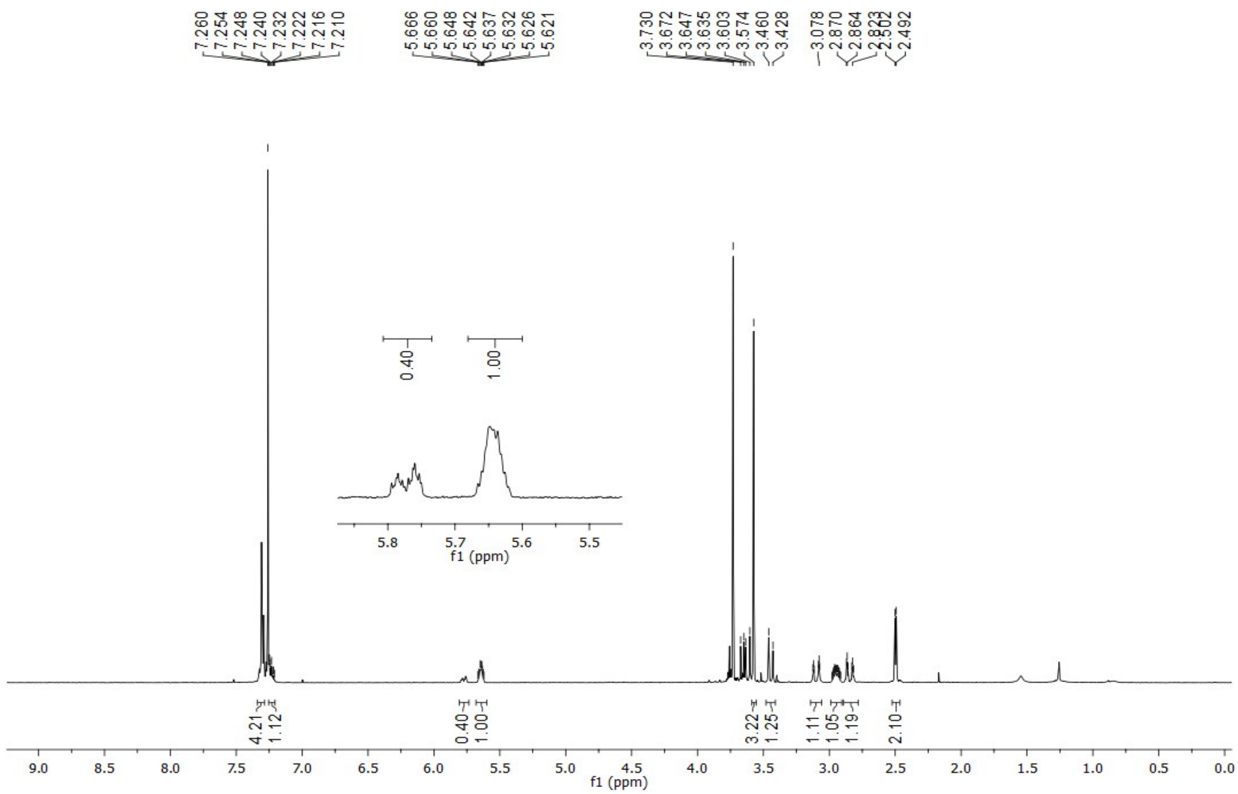


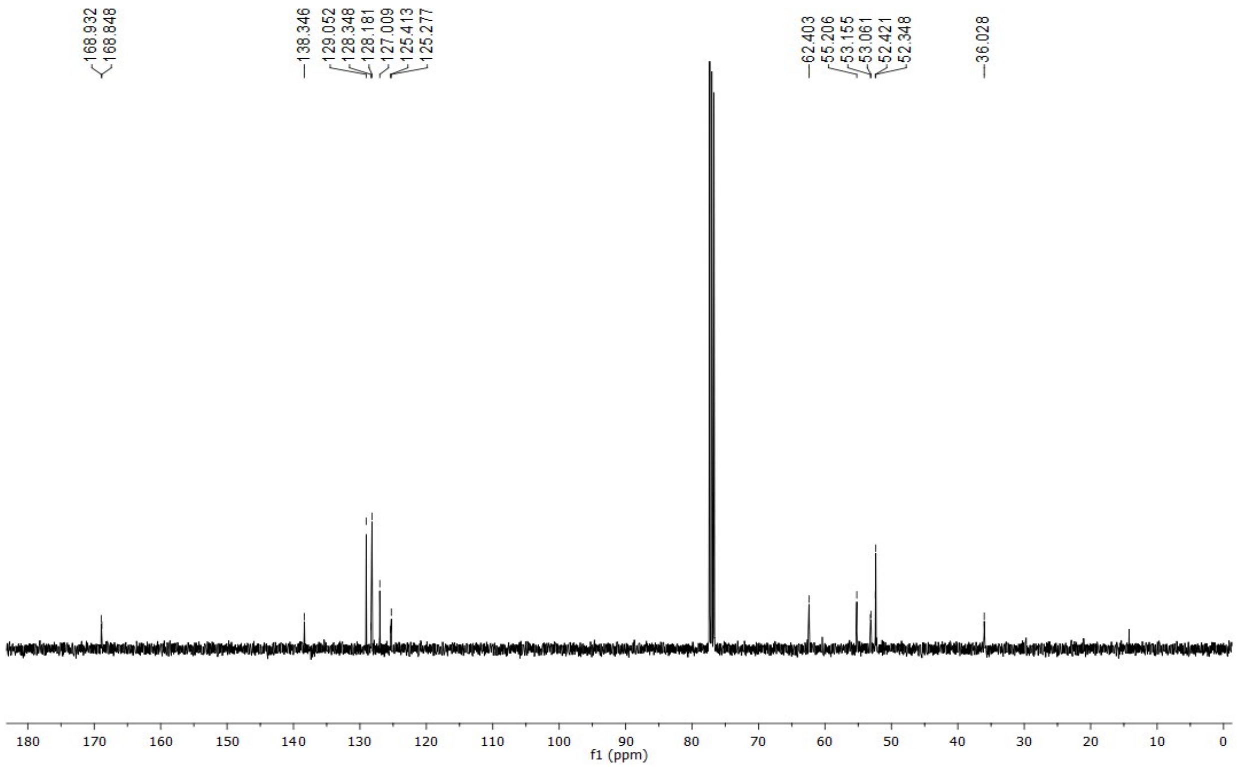


Dimethyl 2-(1-benzyl-1,2,3,6-tetrahydropyridin-3-yl-5-*d*)malonate (10-d):

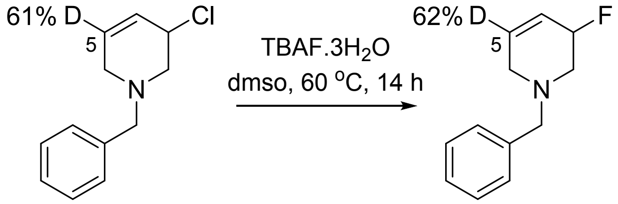


^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 2.50 (d, *J* = 4.0 Hz, 2H, C-2 H), 2.84 (dt, *J* = 16.4, 2.4 Hz, 1H, C-6 H), 2.91-2.98 (m, 1H, C-3 H), 3.10 (dt, *J* = 16.4, 1.8 Hz, 1H, C-6 H), 3.44 (d, *J* = 12.8 Hz, 1H, benzylic), 3.57 (s, 3H, CH_3), 3.62 (d, *J* = 12.8 Hz, 1H, benzylic), 3.66 (d, *J* = 10.0 Hz, 1H, $CH(CO_2CH_3)_2$), 3.73 (s, 3H, CH_3), 5.62-5.66 (m, 1H, C-4 H), 7.21-7.26 (m, 1H), 7.27-7.36 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 36.0, 52.3 (2C), 52.4, 53.1 (d, *J* = 9.5 Hz, C-6), 55.2, 62.4, 125.3 (d, *J* = 13.7 Hz, C-4), 127.0, 128.2, 128.3 (m, C(D)-5), 129.0, 138.3, 168.85, 169.93; **HRMS** (ESI) *m/z* calcd for $C_{17}H_{21}DO_4N^+$ $[M+H]^+$ 305.16061, found 305.16040.

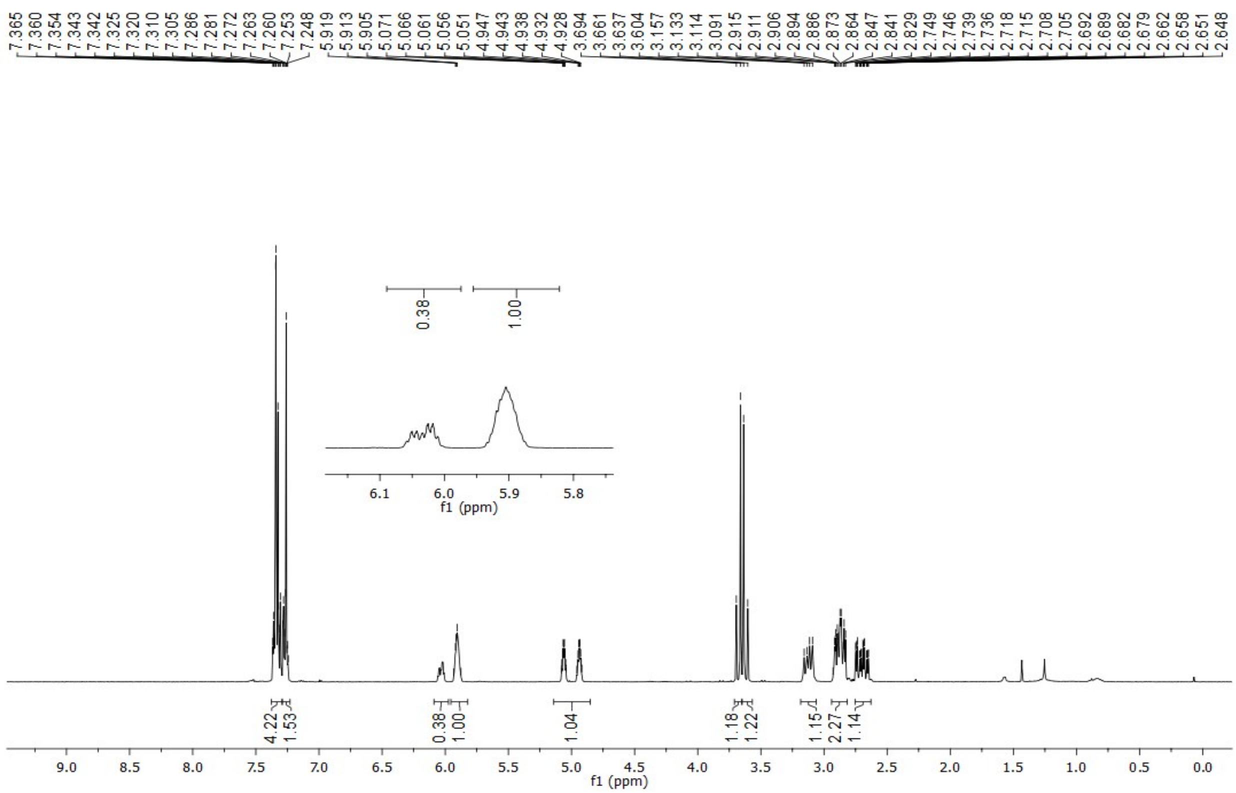

7.260
7.254
7.248
7.240
7.232
7.222
7.216
7.210
5.666
5.660
5.648
5.642
5.637
5.632
5.626
5.621
3.730
3.672
3.647
3.635
3.603
3.574
3.460
3.428
3.078
2.870
2.864
2.492
0.40
1.00
5.8
5.7
5.6
5.5
f1 (ppm)
4.21
1.12
0.40
1.00
3.22
1.25
1.11
1.05
1.19
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

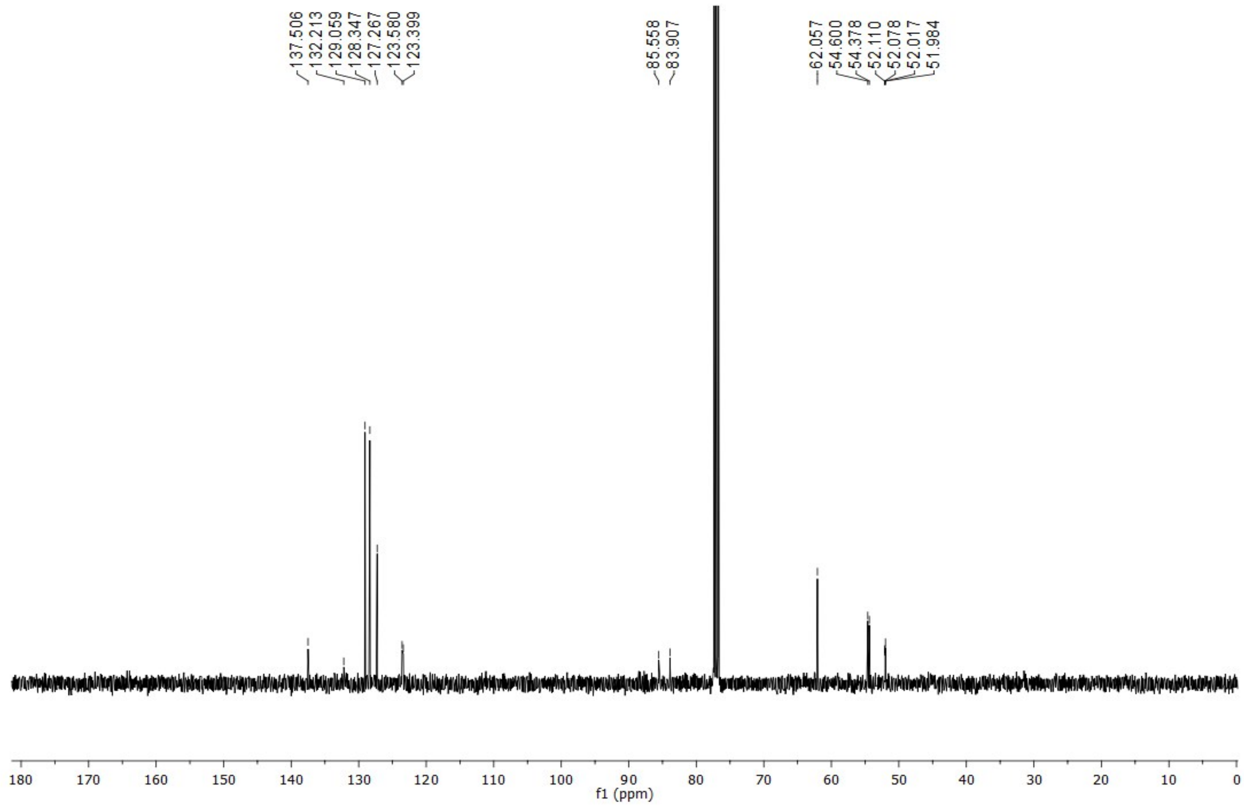

168.932
168.848
138.346
129.052
128.348
128.181
127.009
125.413
125.277
62.403
55.206
53.155
53.061
52.421
52.348
36.028
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1-benzyl-3-fluoro-1,2,3,6-tetrahydropyridine-5-*d* (11-d):

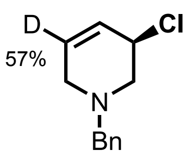


^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 2.70 (dddd, J = 22.8, 12.4, 4.0, 1.2 Hz, 1H, C-2 H), 2.83-2.93 (m, 2H, C-2 and C-6 H), 3.12 (bdd, J = 17.0, 9.4 Hz, 1H, C-6 H), 3.62 (d, J = 13.2 Hz, 1H, benzylic), 3.68 (d, J = 13.2 Hz, 1H, benzylic), 5.0 (dm, J_{HF} = 49.2 Hz, 1H, C-3 H), 5.87-5.93 (m, 1H, C-4 H), 7.24-7.28 (m, 1H), 7.30-7.36 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ:** 52.1 (dd, ^{4}J = 3.28, J = 9.4 Hz, C-6), 54.5 (d, ^{2}J = 22.4 Hz, C-2), 62.0, 84.7 (d, ^{1}J = 166.8 Hz, C-3), 123.5 (bd, ^{2}J = 18.3 Hz, C-4), 127.2, 128.3, 129.0, 132.2 (m, C(D)-5), 137.5; **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}DNF^{+}$ $[M+H]^{+}$ 193.12458, found 193.12462.



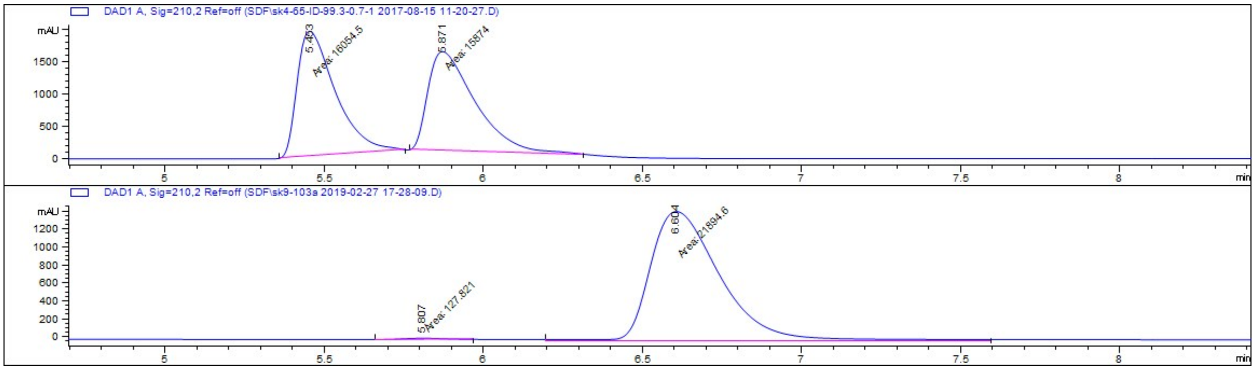


Synthesis of *R*-1-d:

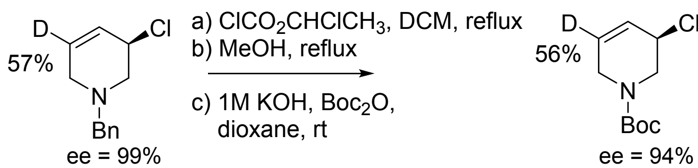


***R*-1-d**

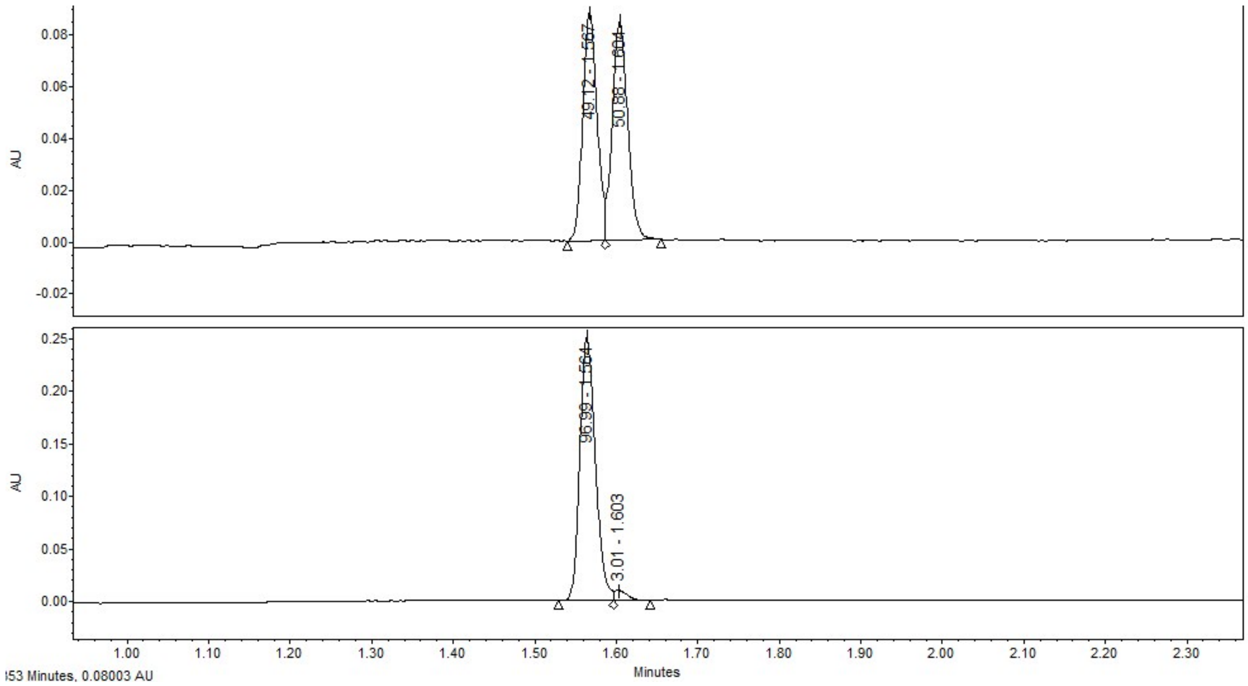
A round-bottom flask equipped with a stirbar was flame dried under vacuum and filled with Ar. The flask was charged with CuCl (15 mg, 0.15 mmol) and ligand **A** (88 mg, 0.15 mmol), flushed with argon, sealed with a septum and wrapped with aluminum foil. DCM (8 ml) was added and the resultant colorless solution was stirred at room temperature for 1 hour. Meanwhile a separate round-bottom flask containing a stirbar was flame dried under vacuum and filled with Ar. The second flask was charged with Cp_2ZrHCl (763 mg, 2.96 mmol), flushed with Ar and wrapped with aluminum foil. DCM (3.6 ml) and then styrene (0.45 ml, 3.75 mmol) were added and the resultant suspension was stirred at room temperature until the mixture became completely clear. After 1 hour fine crystalline Ag(OTf) (46 mg, 0.17 mmol) was quickly added to copper catalyst solution and stirred for 15 minutes until all the AgCl precipitated out. This suspension was injected into the solution containing alkylzirconocene using a syringe filter and the resultant black solution was cooled 0 ˚C and more DCM (19 ml) was added for dilution. After 5 minutes neat 1-benzyl-3 chloro-1,2,3,6-tetrahydropyridine (*rac*-**1-d** with 59% D saturation) (317 mg, 1.52 mmol) was added with a syringe at once and solution was stirred for 1.5 hours at 0 ˚C. The reaction was stopped by pouring the reaction mixture into a seperatory funnel containing Et_2O (30 ml). Material remaining in the flask was rinsed into the seperatory funnel solution with EtOAc (6 ml x2) and the resulting suspension was washed with saturated $NaHCO_3$ solution (15-20 ml x3). The combined aqueous phases were extracted with EtOAc (15-20 ml x2). The combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by flash column chromatography on silica gel (hexanes/EtOAc (19/1)) to give ***R*-1-d** in 27% yield (87 mg, 0.41 mmol) with 57% D saturation as a yellow oil. Enantiomeric excess of 99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99.3:0.7; λ = 210 nm, minor enantiomer t_R = 5.8 min, major enantiomer t_R = 6.6 min].



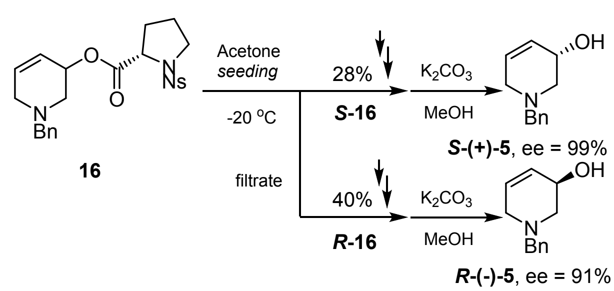
Synthesis of (*R*)-*N*-tert-butoxycarbonyl-5-chloro-3-piperidene-5-d (*R*-4-d):



***R*-1-d** (153 mg, 0.73 mmol), DCM (8 ml) and 1-chloroethyl chloroformate (0.10 ml, 1.0 mmol) were added in a dried round bottom flask and the resulting solution was heated to reflux for 2 hours, before it was allowed to cool to room temperature and the solvent removed on rotary evaporator. The residue was dissolved in MeOH (8 ml) and heated to reflux for 1 hour, Before removing the solvent on rotary evaporator and adding 1,4-dioxane (5.0 ml). The solution was stirred and cooled to 0 °C before1M KOH (3.5 ml) was added dropwise followed by addition of di-*tert*-butyl dicarbonate (235 mg, 1.10 mmol). The reaction solution was then stirred at room temperature overnight. Upon completion the reaction mixture was diluted with H_2O (10 ml) and extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, concentrated under vacuum and purified by flash column chromatography on silica gel (pentane/Et_2O (9/1)) to give ***R*-4-d** in 62% yield (100 mg, 0.46 mmol) as a colorless oil. Enantiomeric excess of 94% was determined on SFC by using a non-racemic chiral column (Chiralpak® IF; 1500 psi, 30°C; flow: 1.5 mL/min; from 1 % to 30 % MeOH in 5 min; λ = 215 nm; Rt = 1.59 min and 1.60 min).



Alternative method to prepare R- and S-1:



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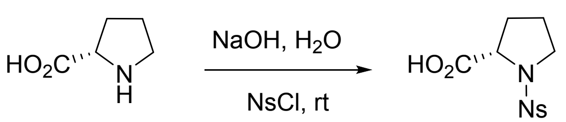
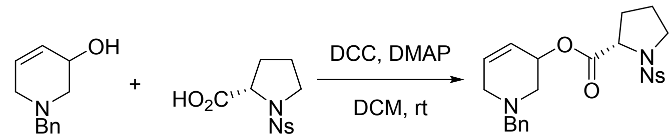
((4-nitrophenyl)sulfonyl)-L-proline (iv):



L-proline (1.84 g, 16.0 mmol), water (8ml) and NaOH (2M, 8 ml) were added to a round bottom flask and stirred until complete dissolution of acid. The solution was cooled to 0 ºC and then 4-nitrobenzenesulfonyl chloride (5.5 g, 24.0 mmol) was added portion-wise over 30 minutes and the resulting suspension was stirred at room temperature. Extra NaOH solution was added to reaction mixture to keep the reaction solution pH at 9-10. Once the pH was stable at 9-10 for at least 45 minutes, the reaction mixture was allowed to stir overnight, before diluted with H_2O ~15 mL and washed with Et_2O (10 ml x 3). The aqueous layer was acidified to pH 2 with 1M HCl solution and extracted with EtOAc (20 ml x 3). The combined EtOAc layers were dried over $MgSO_4$, filtered and the solvent was removed under vacuum to give **iv** in 86% yield (4.1 g, 13.76 mmol) as a yellow solid. $[D]^{25}_{589}$ = –73.5 (c 1.0 $CHCl_3$) for >99% ee; **^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ:** 1.62-1.71 (m, 1H), 1.77-1.92 (m, 2H), 1.95-2.02 (m, 1H), 3.24 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.38-3.44 (m, 1H), 4.21 (dd, *J* = 8.4, 4.0 Hz, 1H), 8.08-8.11 (m, 2H), 8.39-8.42 (m, 2H), 12.82 (bs, OH). Spectral data is in agreement with literature.[11]

1-benzyl-1,2,3,6-tetrahydropyridin-3-yl ((4-nitrophenyl)sulfonyl)-L-prolinate (16):



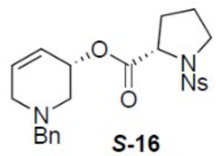
5 **iv** **16**

5 (2.4 g, 12.7 mmol), **iv** (5.8 g, 19.3 mmol), DMAP (168 mg, 1.3 mmol) and DCM (90 ml) were added to a dried round bottom flask. The resulting solution was cooled to 0 °C and DCC (3.8 g, 18.4 mmol) was added into this cooled solution portionwise. The resulting solution was warmed up to room temperature and stirred overnight. Upon completion, the reaction mixture was concentrated on a rotary evaporator and purified by flash column chromatography on silica gel (hexanes/EtOAc (3/1 to 2/1)) to give **16** in 98% yield (5.83 g, 12.4 mmol) as a yellow solid. **IR** (ν_{max} /cm^{-1}): 621, 641, 736, 855, 892, 1087, 1158, 1271, 1310, 1346, 1537, 1570, 1623, 1736, 2341, 2360, 2849, 2927, 3323; **HRMS** (ESI) *m/z* calcd for $C_{23}H_{26}O_6N_3S^+$ $[M+H]^+$ 472.15368, found 472.15304.

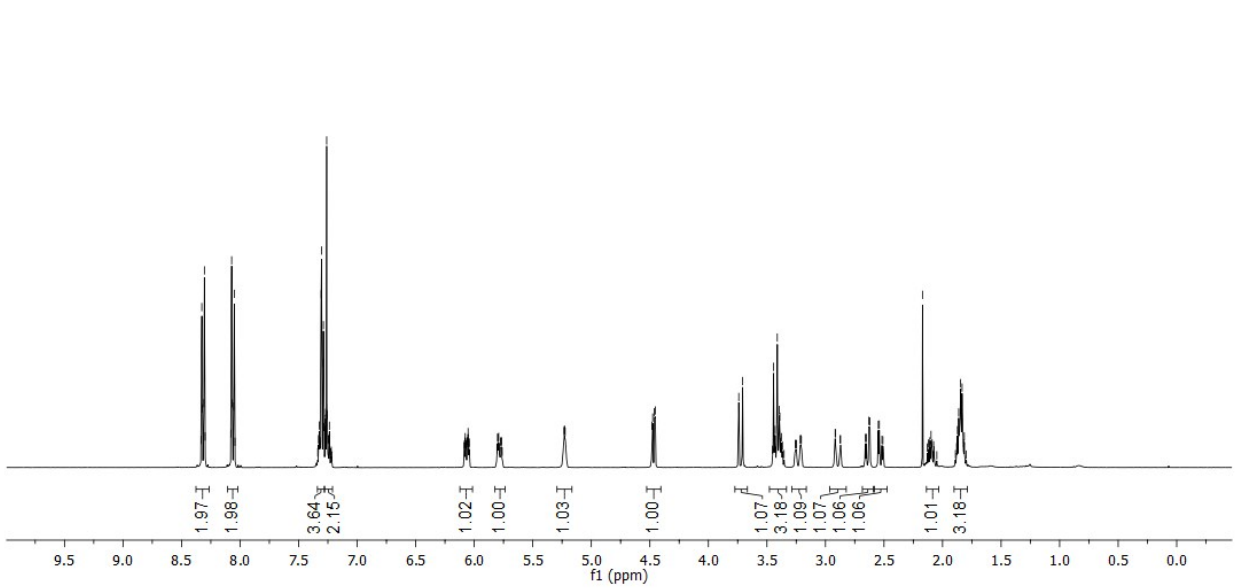
Diastereomeric crystallization of 16:

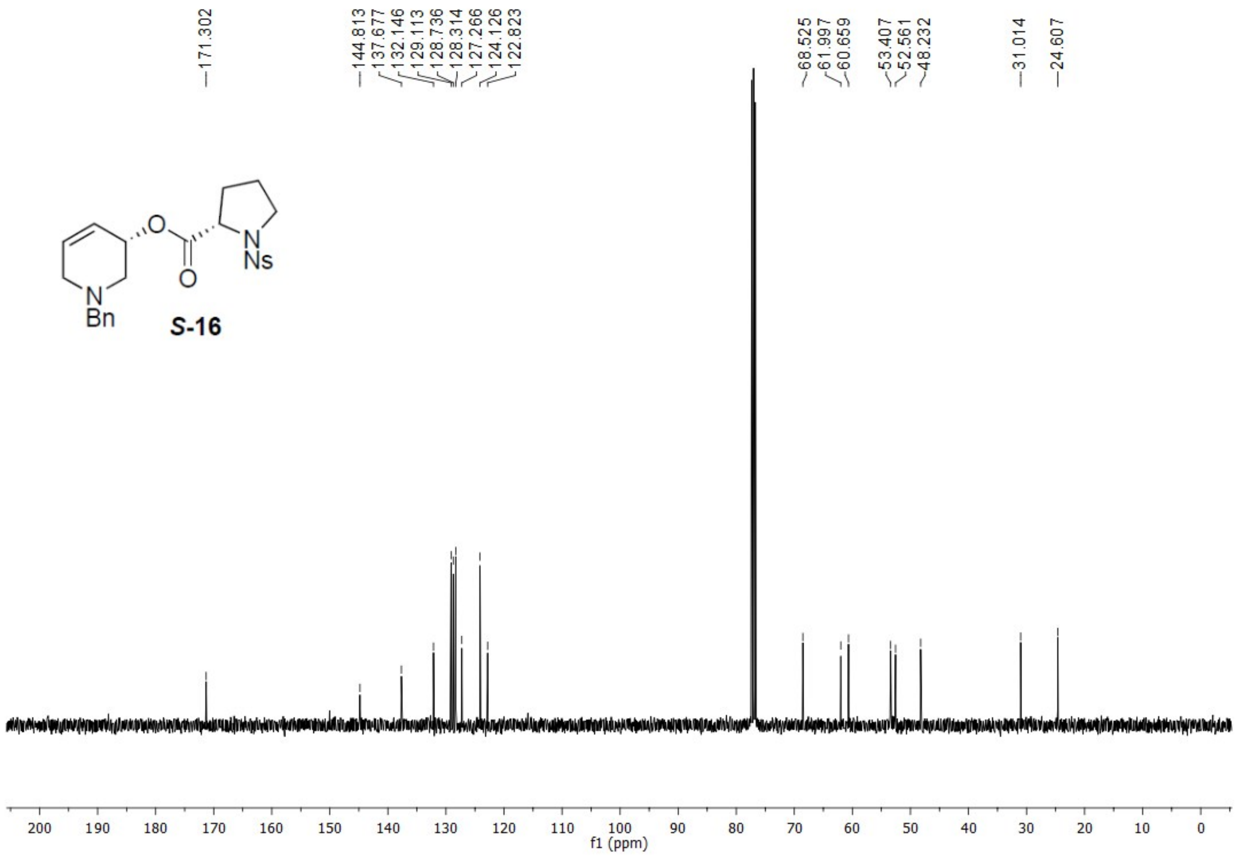
Flash column chromatography of the diastereomeric mixture of **16** on silica gel with 9/1 pentane/2-propanol was used to obtain small amounts of each diastereomer to use as seeds for crystallization. Crystallization worked most effectively in acetone (90 ml for 5.8 g of **16**) at –20 ºC (freezer). (*S*)-1-benzyl-1,2,3,6-tetrahydropyridin-3-yl ((4-nitrophenyl)sulfonyl)-L-prolinate (***S*-16**) was obtained in 28% yield (0.56 g, 1.2 mmol) with dr > 50/1 in 3 crops (24-48 h for each crystallization) as yellow crystals. (*R*)-1-benzyl-1,2,3,6-tetrahydropyridin-3-yl ((4-nitrophenyl)sulfonyl)-L-prolinate (***R*-16**) was obtained in 40% yield (0.81 g, 1.7 mmol) with 1/~25 dr in 3 crops (24-48 h for each crystallization) as white fine crystals. 30% (1.8 g, 3.8 mmol, dr = 1/1) of **16** is recovered. **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ for *S*-16:** 1.79-1.89 (m, 3H), 2.05-2.13 (m, 1H), 2.52 (dd, *J* = 12.0, 3.4 Hz, 1H), 2.64 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.86 (bdd, *J* = 16.8, 1.4 Hz, 1H), 3.23 (ddd, *J* = 16.8, 3.8, 2.0 Hz, 1H), 3.35-3.45 (m, 2H), 3.53 (d, *J* = 13.2 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 4.46 (dd, *J* = 8.8, 3.2 Hz, 1H), 5.22-5.23 (bm, 1H), 5.78 (ddt, *J* = 10.0, 4.0, 2.0 Hz, 1H), 6.06 (dtd, *J* = 10.0, 3.6, 1.0 Hz, 1H), 7.21-7.33 (m, 5H), 8.06 (dm, *J* = 9.2 Hz, 2H), 8.32 (dm, *J* = 8.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ *S*-16:** 24.6, 31.0, 48.2, 52.5, 53.4, 60.6, 61.9, 68.5, 122.8, 124.1, 127.2, 128.3, 128.7, 129.1, 132.1, 137.6, 144.8, 171.3. **^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ for *R*-16:** 1.86-2.05 (m, 3H), 2.13-2.22 (m, 1H), 2.69 (ddd, *J* = 15.6, 12.0, 4.0 Hz, 2H), 2.91 (ddt, *J* = 17.2, 2.4, 2.0 Hz, 1H), 3.15 (ddt, *J* = 16.8, 3.6, 2.0 Hz, 1H), 3.40-3.50 (m, 2H), 3.56 (d, *J* = 13.2 Hz, 1H), 3.71 (d, *J* = 13.2 Hz, 1H), 4.46 (dd, *J* = 8.4, 3.4 Hz, 1H), 5.26 (bs, 1H), 5.69 (ddt, *J* = 10.0, 4.0, 2.0 Hz, 1H), 6.00 (dtd, *J* = 10.0, 3.6, 1.0 Hz, 1H), 7.25-7.34 (m, 5H), 8.00 (dm, *J* = 9.2 Hz, 2H), 8.28 (dm, *J* = 8.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ *R*-16:** 24.6, 31.1, 48.3, 52.2, 53.6, 60.7, 62.0, 68.7, 122.8, 124.1, 127.3, 128.4, 128.7, 128.9, 131.9, 137.5, 144.8, 171.3.

^{1}H and ^{13}C NMRs of *S*-16



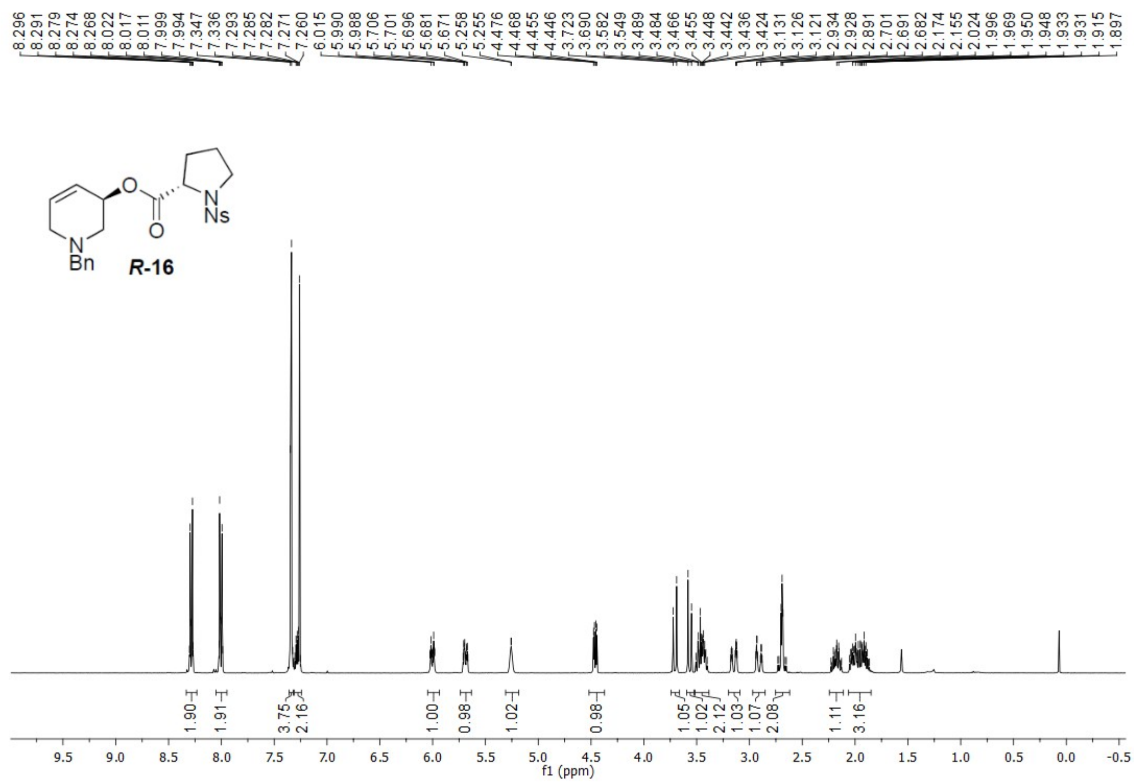
S-16

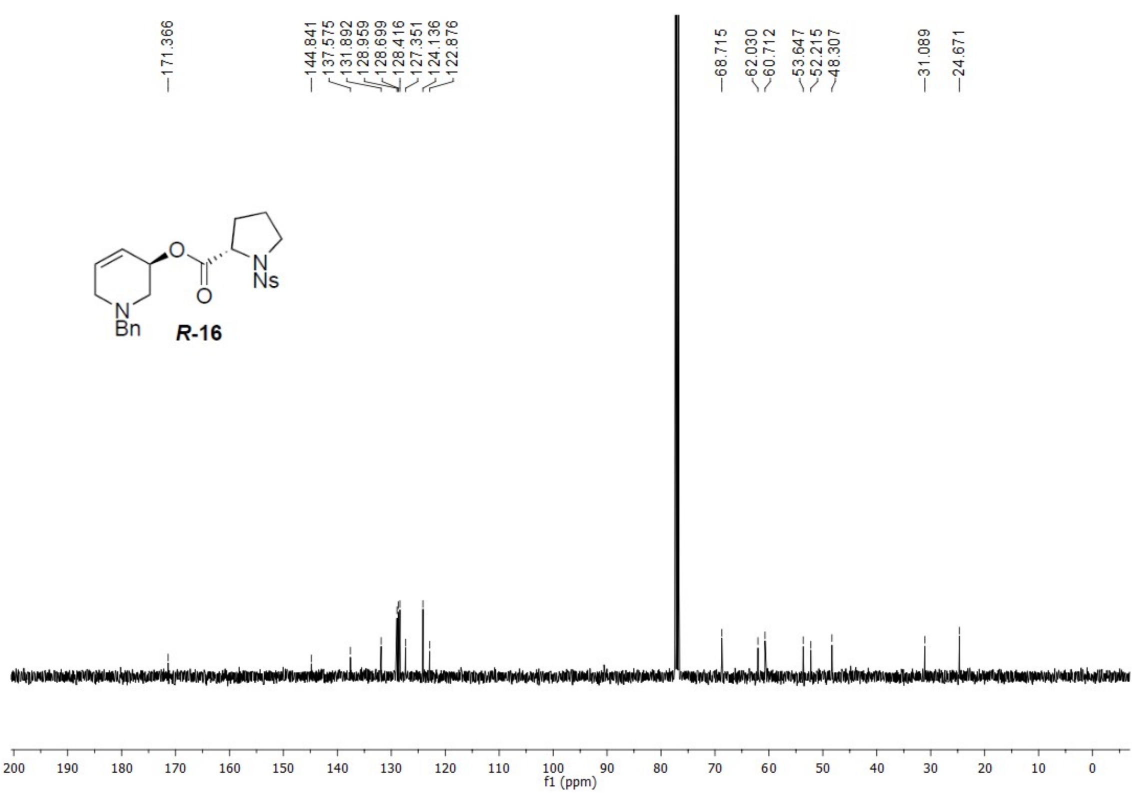




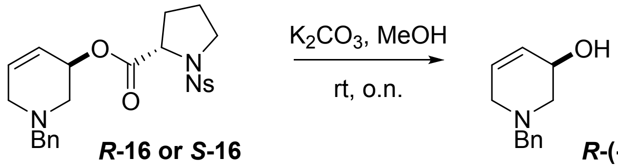
171.302
144.813
137.677
132.146
129.113
128.736
128.314
127.266
124.126
122.823
68.525
61.997
60.659
53.407
52.561
48.232
31.014
24.607
O
O
N
Ns
N
Bn
S-16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

[1]H and [13]C NMRs of *R*-16





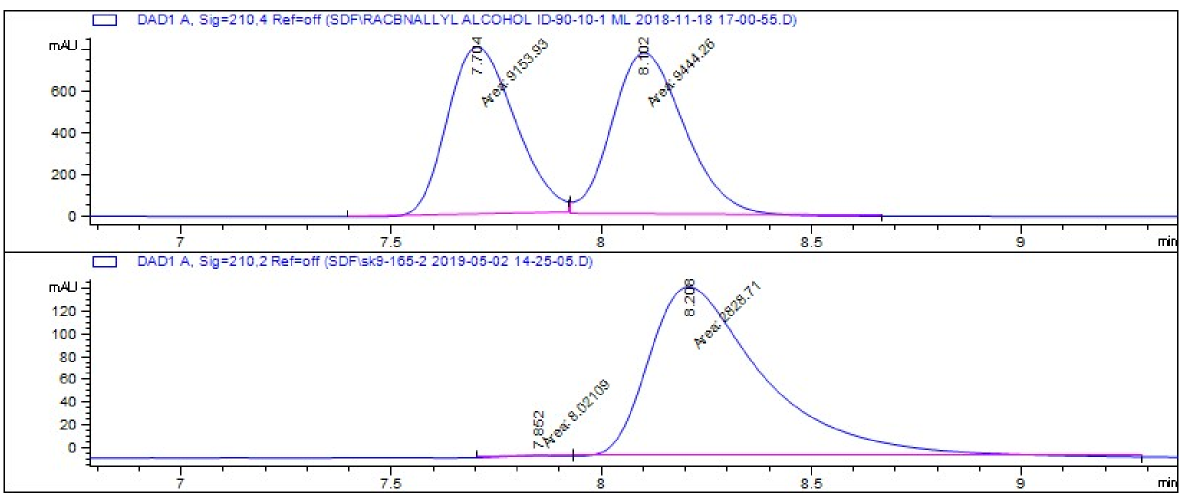
General Procedure for Hydrolysis of esters S- and R-16 to R-(-)- and S-(+)-5



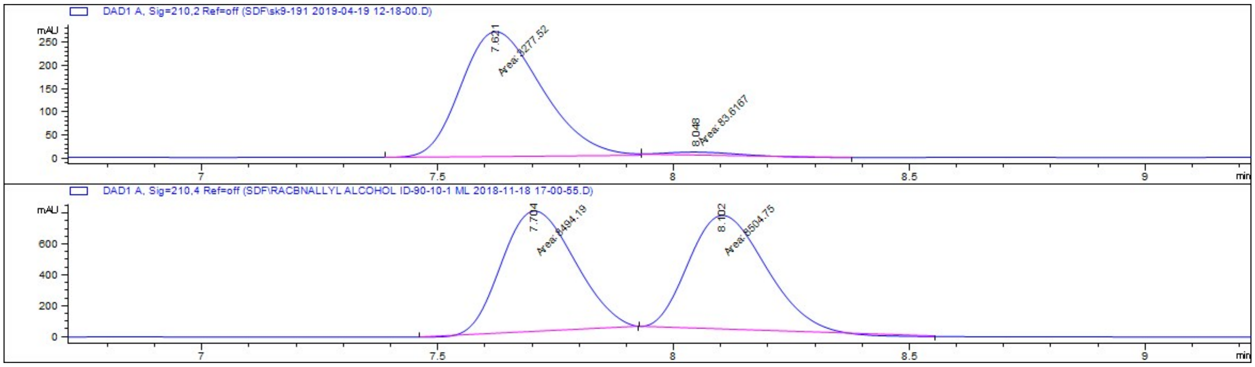
***R*-16 or *S*-16** ***R*-(-)-5 or *S*-(+)-5**

***S*-16** or ***R*-16** (1 equiv.), solid K_2CO_3 (5 equiv.) and MeOH (8 ml for 0.8 mmol of ester) were added to a dried flask and the resulting suspension was stirred at room temperature overnight. The reaction mixture was diluted with water (~15 ml for 0.8 mmol of ester) and the pH of solution was adjusted to 8-9 by addition of 1M HCl. This aqueous solution was washed with EtOAc (x3), the combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. Flash column chromatography on silica gel with 3/1 hexane/acetone afforded **S-** or **R-5** in 95-99% yield. For ***S*-(+)-5** enantiomeric excess of 99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 90:10; λ = 210 nm; minor enantiomer t_R = 7.8 min; major enantiomer t_R = 8.2 min]; $[D]^{25}_{589}$ = +80.8 (c 0.8 $CHCl_3$) for 99% ee; For ***R*-5** enantiomeric excess of –91% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 90:10; λ = 210 nm; minor enantiomer t_R = 8.0 min; major enantiomer t_R = 7.6 min]; $[D]^{25}_{589}$ = –64.3 (c 1.0 $CHCl_3$) for 91% ee.

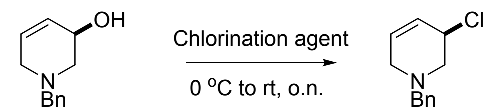
HPLC trace of *S*-(+)-5



HPLC trace of *R*-(-)-5



Stereospecific chlorination trials:



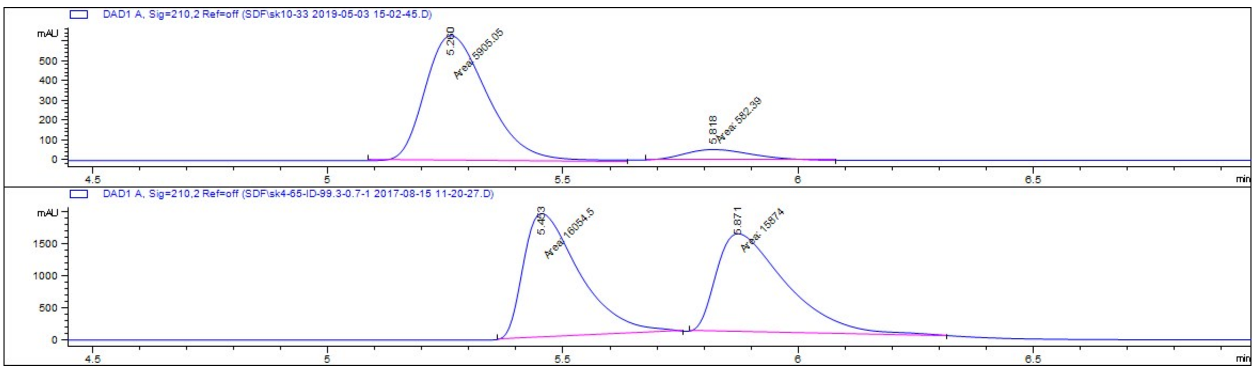
***R*-(-)-5 or *S*-(+)-5** ***R*-(+)-1 or *S*-(-)-1**

Entry[a]	Chlorination agent (equiv.)	Solvent	Add. or base (equiv.)	ee of *R*-(-)-5 or *S*-(+)-5 (%)	ee of *R*-(+)-1 or *S*-(-)-1 (%)
1	$POCl_3$ (2.2)	DMF	-	–71 (R)	64 (R)
2	$POCl_3$ (1.2)	DMF	-	–71 (R)	64 (R)
3	$POCl_3$ (1.2)	DMF	Et_3N (1.5)	–71 (R)	0
4[b]	$SOCl_2$ (2.2)	DCM	-	–71 (R)	-
5[b]	PCl_3 (2.2)	DCM	-	–71 (R)	-
6[b,c]	$POCl_3$ (2.2)	DMF	-	–71 (R)	-
7	$POCl_3$ (2.2)	DMF	LiCl (1)	–73 (R)	69 (R)
8[c]	$(COCl)_2$ (2.2)	DMF	-	–73 (R)	70 (R)
9[b]	MsCl (1.2)	DCM	-	–91 (R)	-
10[b]	MsCl (1.2)	DCM	LiCl (1)	–91 (R)	-
11[d,e]	MsCl (1.2)	DCM	Et_3N (1.5) + LiCl (1)	–91 (R)	–84[f] (S)
12[d,e]	MsCl (1.2)	DCM	Et_3N (1.5)	93 (S)	82 (R)
13[g]	$POCl_3$ (2.2)	DMF	LiCl (1)	–91 (R)	83 (R)
14[g]	$(COCl)_2$ (2.2)	DMF	-	–91 (R)	85[h] (R)
15[g]	$(COCl)_2$ (3.3)	DMF	3Å MS	–80 (R)	78 (R)
16	$(COCl)_2$ (3.3)	DMF	3Å MS	99 (S)	–82 (S)

[a]Reactions performed with 0.2 mmol **5**. [b]Trace amount of **1** formed. [c]Chlorination agent added first followed by addition of **5**. [d]Inversion of configuration. [e]Reaction performed at 0 °C. [f]Yield is 38%. [g]Reactions performed with 0.4 mmol **5**. [h]Yield is 44%.

Characterization of *S*-(-)-1:

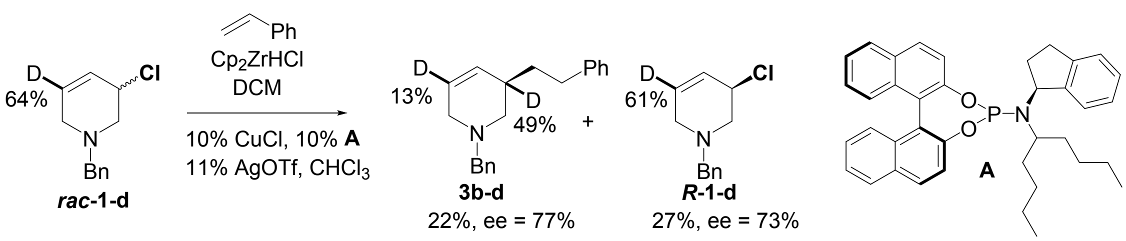
DMF (3ml) was added to a flame dried round bottom flask containing 3Å MS (~0.7 g), and the reaction flask was cooled to 0 ºC before oxalyl chloride (0.2 ml, 2.33 mmol) was added dropwise and resulting suspension was stirred at this temperature. After 20 minutes a solution of ***S*-(+)-5** (135 mg, 0.71 mmol) in DMF (2ml) was added dropwise and reaction mixture allowed to stir overnight and gradually warm to room temperature. H_2O was carefully added at 0 °C. The reaction solution was extracted with EtOAc. Aqueous layer was neutralized by K_2CO_3 and washed with EtOAc (x3). The combined organic phases were washed with brine (x2), dried over $MgSO_4$, filtered, concentrated under vacuum and purified by flash column chromatography on silica gel (hexanes or pentane/EtOAc (9/1)) to give ***S*-(-)-1** in 78% yield (115 mg, 0.55 mmol) as a colorless oil. Enantiomeric excess of 82% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 90:10; λ = 210 nm; minor enantiomer t_R = 5.8 min; major enantiomer t_R = 5.2 min]; $[D]^{25}_{589}$ = -129.9 (c 1.0 $CHCl_3$) for 82% ee.



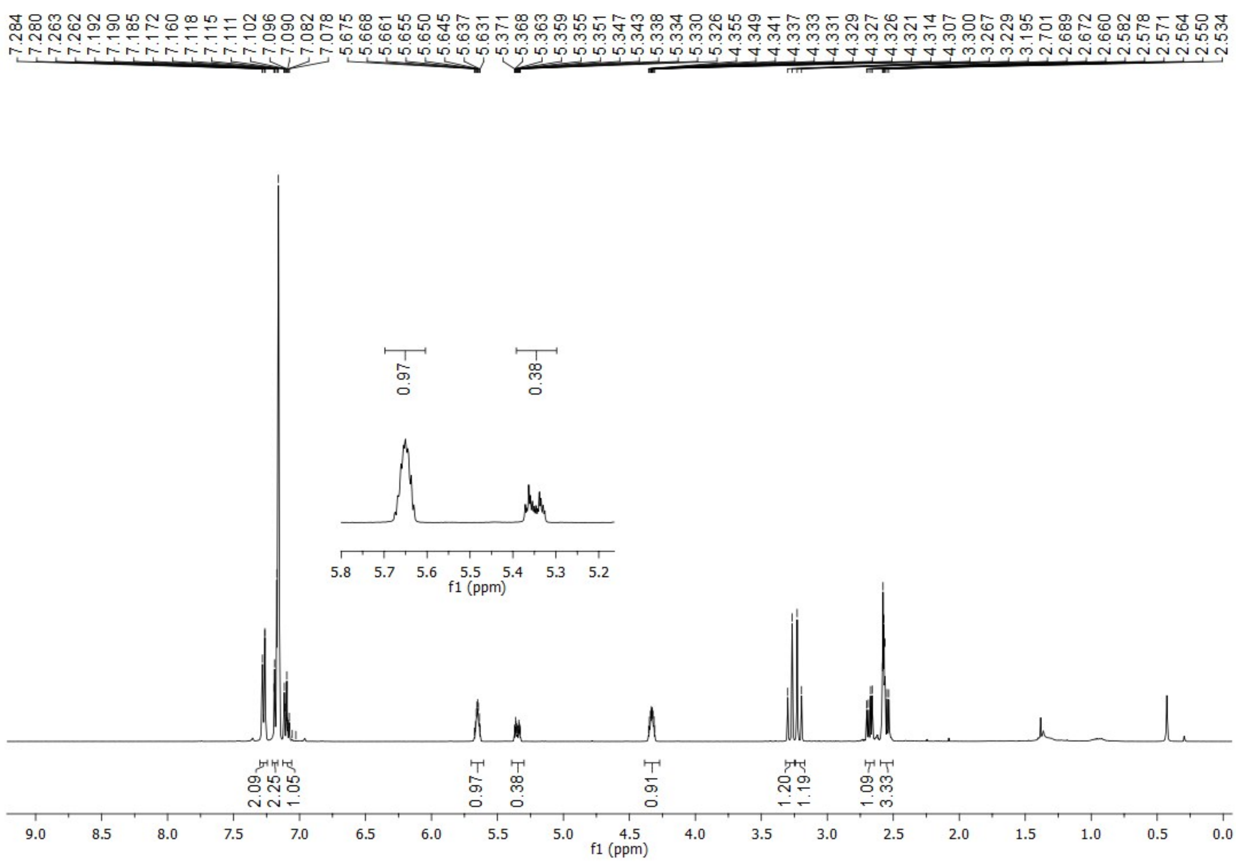
Determination of absolute configurations:

X-ray crystallographic analysis of allyl fluoride **12** was performed by the Doyle research group.[10] Our mechanistic studies with D-labelled allyl chloride (***rac*-1-d**) show that substitution reactions follow S_N2 pathways (inversion of configuration); therefore, assuming the change in protecting group does not affect the configuration of the allyl fluoride, the absolute stereochemistry of **1** can be assigned. This assignment is further supported by previous reports on malonate **10**.[8,9] The absolute configurations of Cu-catalysed 3-alkyl AAA products were assigned by comparing optical rotation of piperidine **3b-*H*** with reported data.[12] Absolute configurations of ***R*-(-)-5** and ***S*-(+)-5** were assigned according to literature.[13]

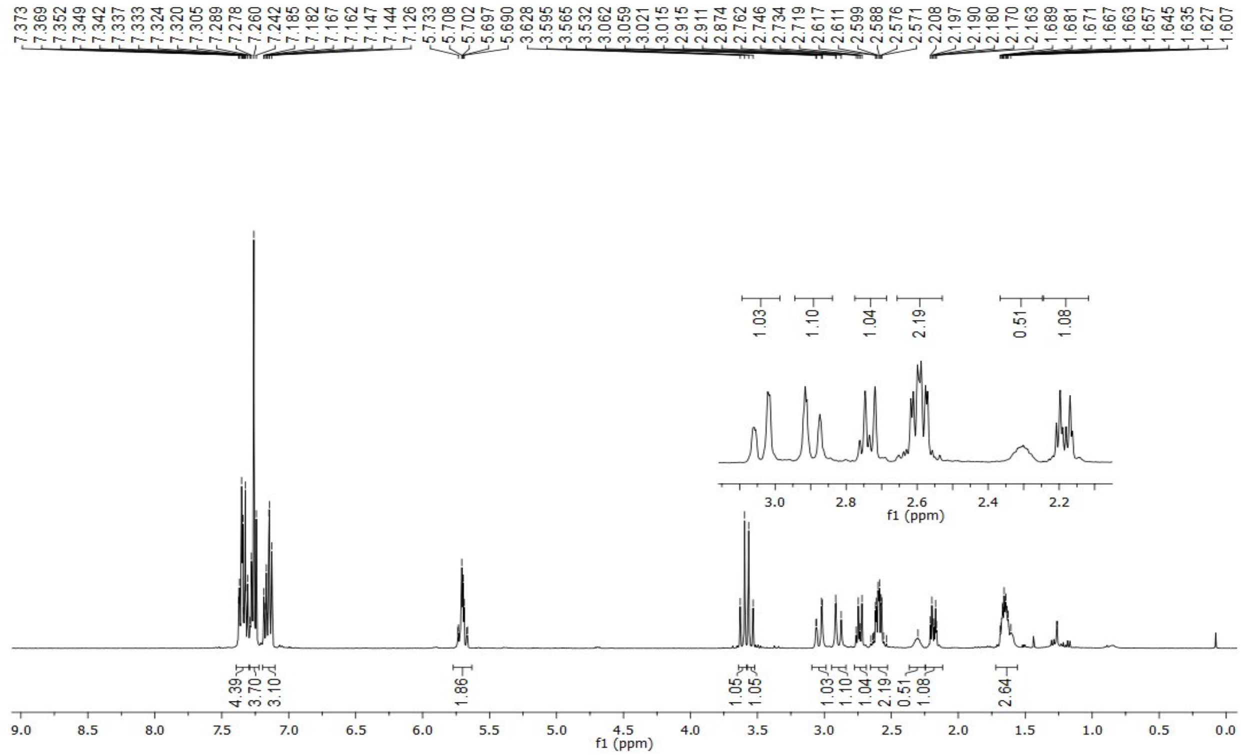
General Procedure for Cu-catalysed AAA performed with *rac*-1-d:



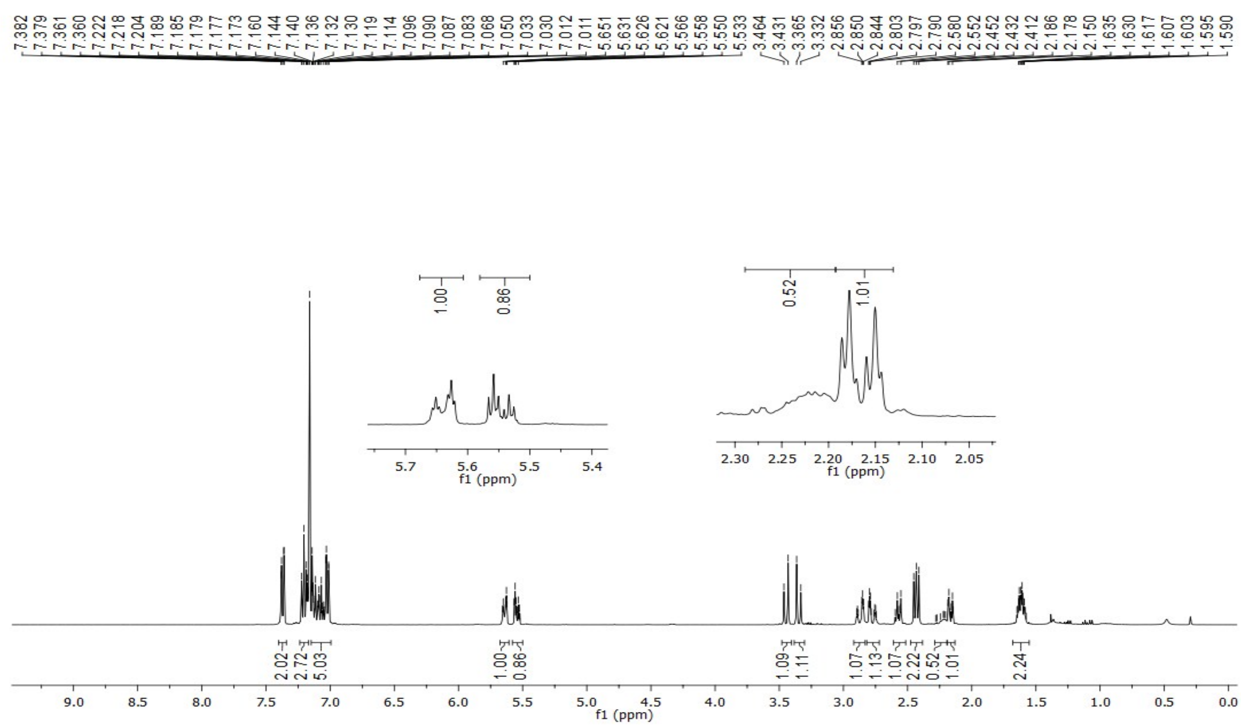
^{1}H-NMR of *R*-1-d in C_6D_6



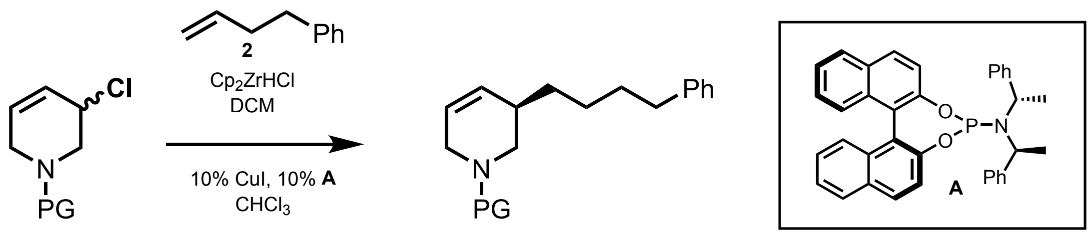
^{1}H-NMR of 3b-d in $CDCl_3$



1H-NMR of 3b-d in C_6D_6



Screening protecting groups:



Entry	PG	Temp.	Yield (%)	ee (%)
1	Boc	rt	15	9
2	Boc	reflux	24	0
3	Cbz	rt	28	5
4	Ts	rt	35	0
5	Ms	rt	42	7
6	Bn	rt	37	47

Computational Section

1. General Information

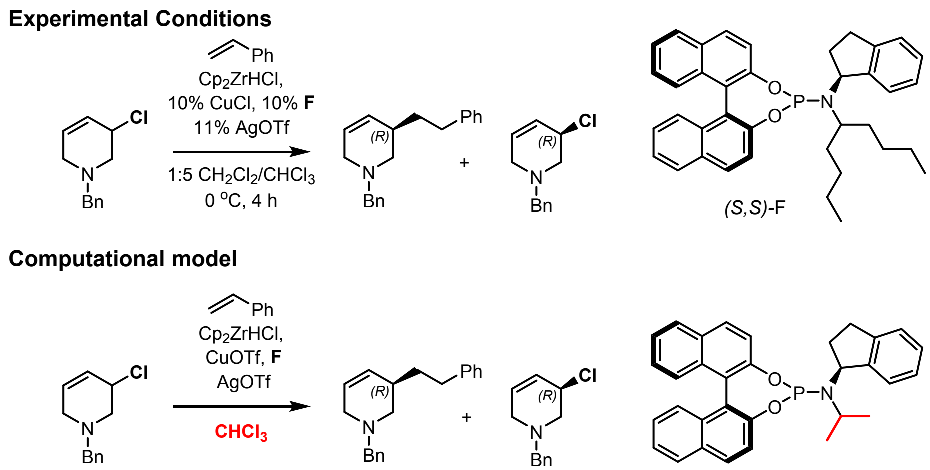
Density functional theory (DFT) geometry optimizations and frequency analyses were performed using the Gaussian 09, Revision D.01 software package.[14] Geometry optimisations were carried out with M062X functional used with ultrafine (99,590) integration grid and the 6-31G(d) basis set for C, H, N, O, P, Cl atoms and the LANL2DZ effective core potential/valence double zeta basis set for Cu.[15] Single point energy corrections were obtained at the M062X/def2-TZVPP level of theory with chloroform solvation described by an implicit Solvation Model based on Density (SMD),[16] then corrected using D3-dispersion energy as developed by Grimme.[17]

Vibrational frequencies were used to classify stationary points. Stationary points with all real frequencies were classified as minima, and those with a single imaginary frequency as a transition state (TS). All the TSs possesses a single imaginary harmonic vibrational frequency. Thermochemistry was evaluated at the solution standard state of 1 mol dm^{-3} and temperature of 298.15 K. Gas phase species were evaluated at standard pressure of 1 bar. Gibbs free energies were calculated using vibrational frequencies with GoodVibes[18] python script employing a quasi-harmonic approximation for entropy calculation with a free-rotor description below 100 cm^{-1}, as proposed by Grimme.[19]

3D molecular graphics were generated by Open source Pymol Version 1.8.6.0. wSterimol[20] and Mopac version 2016 for semi-empirical calculations[21] were used to realise conformational samplings on substituents when required. All energetic terms were reported in kcal/mol.

2. Density functional theory (DFT) calculations

In order to model the catalytic cycle involved in the kinetic resolution of ***rac*-1**, it was necessary to work on a simplified model (Scheme S1). Thus we decided to remove the alkyl chain on the ligand that would have required a significant effort in conformational sampling and would have complicated the optimisation convergence. To model the solvent, we also decided to only retain chloroform as the main solvent effect. We also kept the benzyl protecting group in our calculations even though it would require a conformational sampling of the TSs, because it was experimentally proven to be important.



Scheme S1. Simplified model used in the mechanism investigation of the catalytic cycle involved in the kinetic resolution of ***rac*-1**.

a) Substrate complexation

Benzyl protecting group proved to be experimentally important in order to obtain satisfactory results. We hypothesized that it might help the catalyst and the substrate together by forming a stable complex. We therefore explored the different complexation modes that the substrate could realise to gain insights about the role of the benzyl group (Figure S1). We found that the Nitrogen lone pair binding to the copper metal was leading to the lowest ground state but was not energetically favoured in both cases, which was not explaining the importance of the benzyl group.

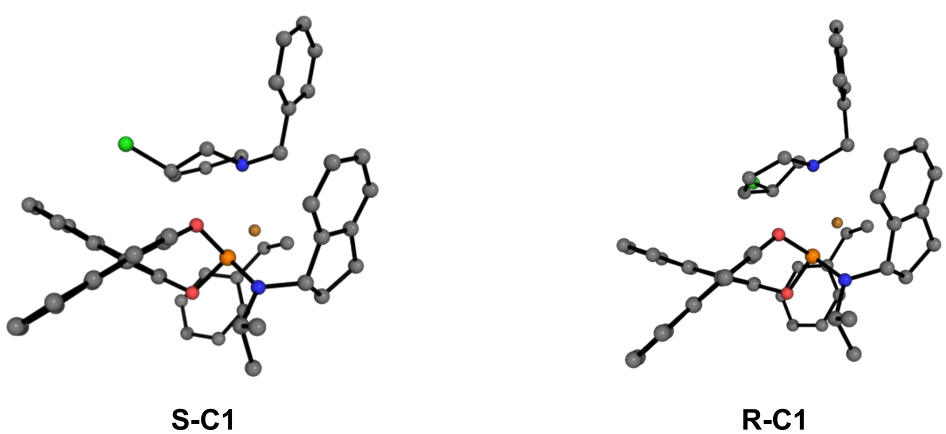
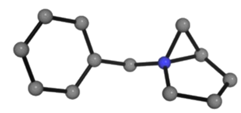


Figure S1. Geometries of key ground state complexes

b) Aziridinium formation

Aziridinium formation was also envisaged to explain the importance of the benzyl protecting group. In our hand, no transition states leading to the aziridinium could be obtained likely due to cyclic strain. We therefore calculated the energy of the aziridinium intermediate (Figure S2). Chloride had to be removed due to convergence difficulties and was treated at an infinite distance from the aziridium cation. The Gibbs energy of the resulting intermediate is high (37.8 kcal/mol), implying the associated TS would be found at higher energies and is therefore disfavoured.



Aziridinium

Figure S2. Geometry of aziridinium intermediate calculated from ***S*-1** substrate after intramolecular S_N2.

c) Mechanistic investigation

We considered both (*R*) and (*S*) substrates and we studied their pathway through *anti*-S_N2' (TS5), *syn*-oxidativeaddition (TS4), *anti*-oxidative addition (TS3), S_N2 (TS2) and *syn*-S_N2' (TS1) pathways (Figure S3).

Syn-oxidative addition covers both oxidative insertion and *syn*-S_N2'-oxidative addition. Both pathways were investigated, but in practice our geometries modelled to mimic an oxidative insertion or a *syn*-S_N2'-oxidative addition always converged (when they converged) toward the same type of transition states. The most favoured transition state among *syn*-oxidative additions was called S-TS4 and R-TS4 for each conformer.

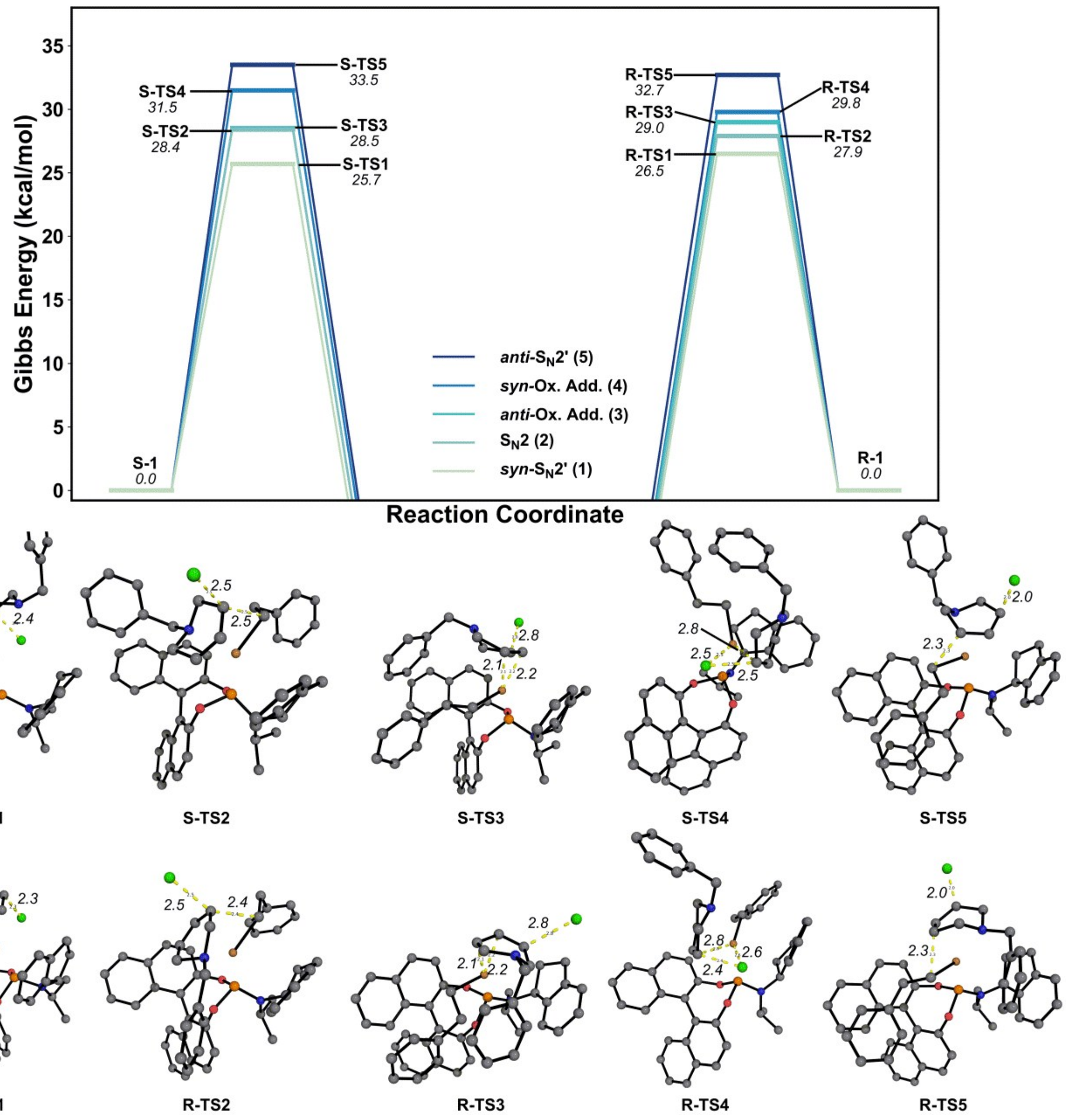


Figure S3. Gibbs free energy profile comparing *syn*-S_N2' (TS1), S_N2 (TS2), *anti*-oxidative addition (TS3), *syn*-oxidative insertion (TS4) and *anti*-S_N2' (TS5) pathways.

3. Cartesian coordinates

S-C1

Cu	-1.61007800	0.73139200	1.02998700
C	-2.82973600	1.78506500	2.30716200
H	-3.87435800	1.73696500	1.95194700
H	-2.86719500	1.35447800	3.31977500
C	-2.44873900	3.26908300	2.42118700
H	-3.13104700	3.82588100	3.08852100
H	-2.54094500	3.75974900	1.44158600
C	-1.04474000	3.52570400	2.92545100
C	-0.29525200	4.60611800	2.44747100
C	-0.46559100	2.71633000	3.91078300
C	0.97667400	4.88455000	2.94532400
H	-0.72268000	5.24070000	1.67364200
C	0.80521000	2.98894700	4.41334600
H	-1.02118300	1.86295300	4.28819000
C	1.53374500	4.07546400	3.93323600
H	1.53467400	5.73374900	2.55969500
H	1.23085700	2.34642600	5.17888500
H	2.52595100	4.28577100	4.31999900
O	0.68459900	-1.37649000	-0.56460500
P	0.14259000	-0.90758700	0.95065500
O	1.55952400	-0.25707800	1.52028600
C	3.06393700	-1.09322300	-0.62858300
C	1.94959500	-1.90314200	-0.73551500
C	2.09582800	0.73204600	0.71062400
C	2.86759800	0.35702200	-0.36975900
C	3.03791500	2.74244800	-0.95841300
C	3.34508300	1.38123400	-1.25108600
C	2.26849000	3.05993500	0.19156600
C	1.78893400	2.07495100	1.01302900
H	2.03700300	4.09972100	0.40630300
C	4.35712400	-1.70024900	-0.73718900
C	3.27430100	-3.85383500	-1.20927800
C	2.04388800	-3.27746600	-1.04913200
H	3.36102100	-4.90820800	-1.45666200
C	4.45790200	-3.08901600	-1.03889700
C	3.47678700	3.76084500	-1.84598800
C	4.05975600	1.09243100	-2.44583800
C	4.46512100	2.09921400	-3.28340900
H	5.00106700	1.85607800	-4.19538700
C	4.17711400	3.45118000	-2.98131500
H	4.50205900	4.23630900	-3.65632200
C	5.55704600	-0.96904500	-0.51747800
C	5.74093500	-3.68692100	-1.15037400
C	6.87929100	-2.95122200	-0.95124700
H	7.85529500	-3.41807400	-1.03548000
C	6.78130700	-1.57822300	-0.62203400
H	7.68475700	-1.00309800	-0.44595200
H	3.23641600	4.79334400	-1.60568100
H	4.26442100	0.05912500	-2.70311500
H	5.49164500	0.08202700	-0.25707100
H	5.79944300	-4.74513700	-1.39091300
H	1.12448200	-3.84142700	-1.16780800
H	1.17441700	2.29451300	1.88068600
N	0.09448400	-2.25873100	1.92338000
C	-1.85252300	-1.66201800	3.49570500
H	-1.47111100	-0.65315900	3.30684600
H	-1.59985600	-1.92370900	4.52672800
C	-2.28955300	-2.84001300	1.43227400
C	-3.50529900	-2.31424500	1.86255400
C	-4.63991700	-2.44389100	1.06366000
C	-4.53941400	-3.10321500	-0.16058500
C	-3.31591000	-3.62863900	-0.58670700
C	-2.17934400	-3.49609500	0.20906500
H	-5.59146600	-2.03030900	1.38744500
H	-5.41323700	-3.19511300	-0.79838100
H	-3.25299800	-4.13364800	-1.54589100
H	-1.21832100	-3.88926600	-0.11390400
C	1.30789600	-2.91180300	2.46319500
C	1.49850400	-2.56008000	3.93780900
C	1.29590200	-4.42279200	2.23270400
H	2.14971400	-2.49690200	1.90323200
H	0.67438200	-2.95484400	4.54345000
H	1.53733000	-1.47458300	4.06406900
H	0.55495600	-4.93176000	2.85784100

H	1.08791000	-4.65448100	1.18493700
C	-3.37633800	-1.68974100	3.23260100
H	-3.81101300	-0.68586800	3.26719600
H	-3.89953500	-2.30370300	3.97557800
C	-1.21127000	-2.64957600	2.48032500
H	-1.04484500	-3.61467400	2.97144900
H	2.27675600	-4.83652900	2.48623500
H	2.42937200	-2.99317800	4.31699100
C	-0.61896400	3.04633600	-1.69647000
C	-0.20886600	1.64845900	-2.04476800
C	-1.41275400	0.72937000	-2.22785100
C	-2.93988000	2.28907700	-1.20898200
C	-1.86715600	3.33354400	-1.33003100
H	-1.07891200	-0.31315700	-2.20667500
H	-3.52090200	2.45352200	-0.29325300
H	-3.63164600	2.37217900	-2.06663700
H	-1.87953300	0.92902700	-3.20563000
N	-2.35446700	0.94914100	-1.13072800
C	-3.37158500	-0.11197200	-1.02306300
H	-3.97682400	0.12252700	-0.13898700
H	-2.83192700	-1.04232400	-0.81266400
C	-4.26493700	-0.30975200	-2.22830800
C	-3.88784600	-1.18230700	-3.25340300
C	-5.48118900	0.36899700	-2.34057800
C	-4.69646900	-1.35973000	-4.37217400
H	-2.95435300	-1.73369800	-3.16310900
C	-6.29475200	0.19464800	-3.45745800
H	-5.79515700	1.03300500	-1.53791900
C	-5.90184900	-0.66863400	-4.47706600
H	-4.38923600	-2.04058200	-5.15998700
H	-7.23745900	0.72830200	-3.52896000
H	-6.53547400	-0.80783700	-5.34735300
H	0.47618600	1.23979100	-1.29742600
Cl	0.74744200	1.65359300	-3.58327100
H	-2.14994700	4.35731600	-1.09870300
H	0.14877300	3.81292500	-1.75579600

R-C1

Cu	-1.64331600	0.15759500	1.04235900
C	-2.88932600	1.03076500	2.42902600
H	-3.93595300	0.93517000	2.09232200
H	-2.86708600	0.50393800	3.39584500
C	-2.63174900	2.52384900	2.68729900
H	-3.34381300	2.94503000	3.41916500
H	-2.79733200	3.11011400	1.77069600
C	-1.24701900	2.86105600	3.19866100
C	-0.63444100	4.07295300	2.85766400
C	-0.56086400	2.00268400	4.06690700
C	0.60493100	4.43089000	3.38657700
H	-1.14469800	4.74675500	2.17195800
C	0.67775300	2.35572800	4.59904300
H	-1.00967200	1.05019500	4.33292000
C	1.26645200	3.57375900	4.26351900
H	1.05370900	5.38219200	3.11314700
H	1.18782900	1.67486900	5.27461500
H	2.23268800	3.84826200	4.67518100
O	0.90398400	-1.36129800	-0.85313400
P	0.35431900	-1.10826900	0.70703100
O	1.70305700	-0.36400700	1.31918100
C	3.23014100	-0.77821000	-0.94899100
C	2.21360400	-1.69904300	-1.11931600
C	2.13148400	0.76080100	0.63464000
C	2.89805600	0.59901000	-0.49931500
C	2.96512600	3.05690400	-0.68913000
C	3.29141500	1.77446600	-1.22052900
C	2.20593900	3.15052500	0.50793200
C	1.76941600	2.02342000	1.14965600
H	1.94023000	4.13071400	0.89405400
C	4.57999500	-1.21442400	-1.16803500
C	3.72914300	-3.40534300	-1.88307600
C	2.45113700	-3.00372300	-1.60926200
H	3.92379400	-4.40282700	-2.26720000
C	4.82427400	-2.53257600	-1.65087800
C	3.34840600	4.22356700	-1.40213400
C	3.95587200	1.71483300	-2.47631200
C	4.30184100	2.86136500	-3.14595800
H	4.80079600	2.79233700	-4.10743600
C	4.00582700	4.13293200	-2.60121200

H	4.28658700	5.03112300	-3.14156800
C	5.70096400	-0.38698100	-0.88168500
C	6.15956600	-2.95936000	-1.87541500
C	7.21704000	-2.12961900	-1.61115400
H	8.23448100	-2.46596400	-1.78225800
C	6.98007900	-0.83272900	-1.09755500
H	7.82018100	-0.18562200	-0.86625500
H	3.09107400	5.19202100	-0.98192800
H	4.17836300	0.74595900	-2.91042700
H	5.53416200	0.60496700	-0.47675300
H	6.32413700	-3.96457800	-2.25430800
H	1.59729000	-3.65437400	-1.76786600
H	1.16046900	2.06898400	2.04720100
N	0.48502300	-2.55170600	1.52837800
C	-1.41309500	-2.37905600	3.25968500
H	-1.18176800	-1.31203000	3.17690600
H	-1.03915200	-2.72690500	4.22626400
C	-1.87112400	-3.27718100	1.06823500
C	-3.10425900	-3.00159600	1.65669000
C	-4.27801300	-3.18038900	0.92738900
C	-4.19887100	-3.63444500	-0.38893300
C	-2.95772800	-3.89066800	-0.97924700
C	-1.78184300	-3.70780700	-0.25234500
H	-5.24400300	-2.96821600	1.37740000
H	-5.10724100	-3.76971500	-0.96836300
H	-2.91078500	-4.23687200	-2.00764900
H	-0.80912800	-3.90033200	-0.69907900
C	1.77994600	-3.13726900	1.93787600
C	2.00729500	-2.95397900	3.43753000
C	1.90596400	-4.60130500	1.51634100
H	2.54896700	-2.57024100	1.40700600
H	1.26152900	-3.51095600	4.01649700
H	1.93800900	-1.89536200	3.70269300
H	1.25778000	-5.25851200	2.10530000
H	1.65905600	-4.72401800	0.45858800
C	-2.93694300	-2.58679900	3.10071300
H	-3.49846800	-1.67684900	3.33321500
H	-3.30264300	-3.38116100	3.76280000
C	-0.74761200	-3.13548000	2.07726300
H	-0.47544900	-4.14487000	2.40724400
H	2.93633600	-4.93682300	1.66880700
H	2.99670700	-3.32546800	3.72193900
C	-0.25990700	2.21619300	-1.63760200
C	-0.36715600	1.04782700	-2.26791700
C	-1.58017800	0.17095200	-2.16682600
C	-2.67883000	2.02786500	-1.06725700
C	-1.35702500	2.72201500	-0.75041600
H	-1.27883000	-0.86993600	-1.99029600
H	-3.41865000	2.26354300	-0.29497200
H	-3.05336500	2.38310400	-2.04073200
H	-2.12278900	0.19706500	-3.12859400
N	-2.44444900	0.58368400	-1.05961700
C	-3.67741100	-0.21843200	-0.97964300
H	-4.20026700	0.09392500	-0.06873600
H	-3.35869500	-1.25582100	-0.83396600
C	-4.59718700	-0.13249900	-2.17845000
C	-4.51588600	-1.08317900	-3.19985500
C	-5.53239000	0.89946100	-2.29714400
C	-5.33802100	-1.00016100	-4.32037400
H	-3.80128600	-1.89839200	-3.10451100
C	-6.35578100	0.98819800	-3.41630400
H	-5.62119000	1.63374700	-1.49969100
C	-6.25848700	0.03908800	-4.43144000
H	-5.26304000	-1.74718900	-5.10468800
H	-7.07789000	1.79508700	-3.49326000
H	-6.90226400	0.10599900	-5.30283700
H	-1.09924100	2.59792600	0.30916100
H	0.63285100	2.82494000	-1.73287600
H	0.44784500	0.68952400	-2.89192900
Cl	-1.56248600	4.51028200	-0.95764200

Aziridinium

C	3.57458700	0.26758100	-0.16719800
C	2.66130700	-0.76053400	0.40955800
C	1.72287800	-1.40970700	-0.54609900
C	1.39663000	1.10986200	-0.49544100
C	2.87943500	1.27078200	-0.69775400
H	1.20384900	-2.31712000	-0.25695500

H	0.97207400	1.87476900	0.16202100
H	0.80457900	1.07867900	-1.41364000
H	1.87862700	-1.25290900	-1.60858800
N	1.28709100	-0.21285900	0.20311900
C	0.21213400	-0.35347500	1.24048400
H	0.42696900	0.39898900	2.00422800
H	0.33707100	-1.34671100	1.68113200
C	-1.14347600	-0.16484400	0.62108300
C	-1.75469000	-1.21637500	-0.06794900
C	-1.78636000	1.07201500	0.70648000
C	-2.98929900	-1.02650300	-0.67847000
H	-1.28070000	-2.19459700	-0.10793100
C	-3.02387100	1.26052100	0.09762900
H	-1.33132800	1.88423900	1.26913900
C	-3.62186600	0.21329100	-0.59842700
H	-3.46451100	-1.84766200	-1.20439100
H	-3.52384300	2.21999700	0.17571100
H	-4.58897100	0.35807500	-1.06831600
H	2.84972100	-1.22545500	1.37303300
H	3.29130500	2.12893100	-1.21442400
H	4.65106700	0.15510300	-0.15623400

S-TS1

Cu	1.26948100	0.02939600	0.22784100
C	1.73664500	-0.18428500	2.24847800
H	1.92528400	-1.26334100	2.25382200
H	2.60379000	0.32881700	2.67022200
C	0.47391800	0.17572100	3.03222400
H	0.59798800	-0.10788400	4.09050900
H	-0.38462400	-0.39094800	2.65521000
C	0.18192200	1.65588700	2.95053700
C	0.85620900	2.55399600	3.78300800
C	-0.69043400	2.17015700	1.98468800
C	0.67791800	3.92923800	3.64901300
H	1.53180900	2.16521700	4.54245200
C	-0.87975400	3.54493800	1.85212100
H	-1.23624100	1.48328300	1.33941400
C	-0.18960400	4.42855100	2.67984700
H	1.21100500	4.61060000	4.30577100
H	-1.57601000	3.92518600	1.10958400
H	-0.33682900	5.49933200	2.57774700
O	-1.88842900	-0.85014700	0.80855600
P	-0.76298200	-1.12364700	-0.41053500
O	-1.65835100	-0.54429200	-1.67346400
C	-3.91269600	-0.01711000	-0.15697400
C	-3.24585500	-0.95249400	0.61014600
C	-2.04139500	0.77974300	-1.55209300
C	-3.14253600	1.08886100	-0.78126100
C	-2.71348600	3.46592300	-1.28177700
C	-3.46052900	2.47332500	-0.58369000
C	-1.64143800	3.07155900	-2.12580600
C	-1.28862500	1.75453200	-2.24438900
H	-1.08663500	3.83886600	-2.65959100
C	-5.32187700	-0.18638300	-0.36605300
C	-5.27631400	-2.13694300	1.12591500
C	-3.92342000	-2.00240300	1.27203200
H	-5.80897900	-2.93377400	1.63741900
C	-6.00561200	-1.24779700	0.29406500
C	-3.02572200	4.83732100	-1.08538700
C	-4.46140400	2.90031800	0.33131700
C	-4.72299600	4.23422900	0.51679400
H	-5.48129900	4.53945700	1.23065600
C	-4.00782300	5.21713500	-0.20769300
H	-4.23121100	6.26836400	-0.05671700
C	-6.06821200	0.64912200	-1.24241200
C	-7.40201900	-1.41021700	0.09692600
C	-8.09690100	-0.57414300	-0.73660900
H	-9.16367500	-0.70813000	-0.88382600
C	-7.41503700	0.45968600	-1.42059600
H	-7.96270000	1.10615500	-2.09898900
H	-2.45415100	5.58116000	-1.63419100
H	-5.00815200	2.15492000	0.89888100
H	-5.55686900	1.43756000	-1.78337100
H	-7.90661100	-2.21993000	0.61735400
H	-3.34804800	-2.67163100	1.90283900
H	-0.45390500	1.41224000	-2.84860200
N	-0.79785100	-2.73966400	-0.78288300
C	1.69609900	-3.30844500	-1.12236800

H	1.87578600	-2.22925200	-1.16841300
H	1.71507200	-3.67962000	-2.15031200
C	0.74420900	-3.55555300	1.04875800
C	2.11329200	-3.80484300	1.17172100
C	2.69754000	-3.88245000	2.43013200
C	1.90015700	-3.69023200	3.56085500
C	0.53662400	-3.42653400	3.43182200
C	-0.05370900	-3.36349700	2.16822200
H	3.76192400	-4.07534700	2.53506700
H	2.34811200	-3.73194600	4.54889000
H	-0.06750600	-3.26148500	4.31863400
H	-1.11204700	-3.14574700	2.05585500
C	-1.87385400	-3.35015100	-1.59810400
C	-1.35261600	-3.68033800	-2.99496000
C	-2.50350400	-4.56011300	-0.90791900
H	-2.64951600	-2.58690000	-1.69378800
H	-0.57905500	-4.45594400	-2.94862800
H	-0.92084400	-2.78672400	-3.45445700
H	-1.82890600	-5.42173500	-0.87796400
H	-2.80025500	-4.31306600	0.11515400
C	2.73896600	-3.96389400	-0.19669100
H	3.72521800	-3.49710000	-0.27399000
H	2.86094700	-5.02971600	-0.43362800
C	0.34982200	-3.58062700	-0.41681900
H	0.04657000	-4.60809500	-0.65407700
H	-3.39784600	-4.86573900	-1.45952500
H	-2.16374700	-4.05433400	-3.62776900
C	1.94310500	2.03346400	-0.69310700
C	2.52167400	1.64643000	-1.90892900
C	3.90968100	1.06567100	-1.88989300
C	3.96214800	1.14099700	0.49146800
C	2.55505100	1.67833100	0.53980300
H	4.06258400	0.42781900	-2.76162500
H	4.18726700	0.55838500	1.38849200
H	4.66380100	2.00029500	0.46873000
H	4.62317300	1.91400300	-1.95579600
N	4.10825000	0.28895300	-0.67771400
C	5.33490700	-0.50585800	-0.68707900
H	5.32743700	-1.11728800	0.22324500
H	5.26728100	-1.18709000	-1.54325600
C	6.62194400	0.29344700	-0.76078200
C	7.18016700	0.63342700	-1.99586400
C	7.24872400	0.74575200	0.40339900
C	8.33141700	1.41312200	-2.06819800
H	6.70982900	0.27544800	-2.90912700
C	8.40000100	1.52587000	0.33730300
H	6.83312100	0.47497900	1.37172500
C	8.94277400	1.86275200	-0.90035600
H	8.75428500	1.66495800	-3.03583300
H	8.87662900	1.86585900	1.25153500
H	9.84211600	2.46810900	-0.95434500
H	2.26327400	2.23613400	1.42462500
H	1.02975000	2.62194700	-0.68469000
Cl	1.46163800	-0.27300600	-2.82244200
H	2.22973200	2.16631400	-2.81442800

S-TS2

Cu	-1.95109000	0.37057400	-0.42202100
C	-3.48426600	0.97911300	0.92888200
H	-4.42632000	1.52025800	0.85762100
H	-3.75968700	-0.08773400	0.92346100
C	-2.72806300	1.32471000	2.22628700
H	-2.99586000	2.33532500	2.55635600
H	-1.63809800	1.33780600	2.06402100
C	-3.03771900	0.33772800	3.32654200
C	-4.10661600	0.54001100	4.20394800
C	-2.30162800	-0.84686500	3.44043400
C	-4.43004600	-0.41125700	5.16713100
H	-4.68949700	1.45469800	4.12676100
C	-2.62428300	-1.80472400	4.39932000
H	-1.46867700	-1.02358000	2.76040600
C	-3.69079200	-1.58861900	5.26801700
H	-5.26090800	-0.23286100	5.84318000
H	-2.03805700	-2.71664000	4.47029700
H	-3.94250600	-2.32922500	6.02050400
O	0.82514900	-0.96711000	-1.27149100
P	-0.33926800	-1.35073100	-0.14975600
O	0.63662300	-1.53023200	1.18986000

C	2.98166300	-1.39396000	-0.33549600
C	2.03607400	-1.62930700	-1.31048600
C	1.54296900	-0.52646000	1.48503500
C	2.69531300	-0.40276300	0.73440500
C	3.26885100	1.57732600	2.09227200
C	3.56029400	0.71081600	0.99900300
C	2.13053600	1.32110600	2.90157200
C	1.26659700	0.30527700	2.59357800
H	1.93219100	1.97066800	3.74947500
C	4.19513000	-2.15968900	-0.37070400
C	3.43890400	-3.19750100	-2.46736100
C	2.26061700	-2.50721100	-2.39405300
H	3.63172600	-3.87181300	-3.29700000
C	4.42294300	-3.05809200	-1.45315800
C	4.10199600	2.70147900	2.33248300
C	4.67724700	1.01762300	0.17326800
C	5.45668600	2.11836200	0.42677100
H	6.29606300	2.34312000	-0.22379300
C	5.17161400	2.97040100	1.51970500
H	5.79218200	3.84143800	1.70189100
C	5.17364800	-2.08497000	0.65828900
C	5.62535000	-3.81166900	-1.49443000
C	6.55817900	-3.70246200	-0.49707700
H	7.47292900	-4.28478000	-0.53560100
C	6.32036700	-2.83522200	0.59511800
H	7.05128300	-2.76665300	1.39443900
H	3.86015400	3.35609200	3.16507600
H	4.89731600	0.38111300	-0.67701400
H	5.00018600	-1.43210000	1.50653600
H	5.78600100	-4.48364400	-2.33314700
H	1.48858000	-2.60066900	-3.15070600
H	0.37269400	0.11745200	3.17957800
N	-0.77060900	-2.94382800	-0.34116200
C	-3.15961000	-2.96723200	0.59278500
H	-2.80659000	-2.08625200	1.13906300
H	-3.20190100	-3.79372400	1.30666600
C	-2.81624700	-2.45567700	-1.72503200
C	-4.14027100	-2.13085100	-1.42590900
C	-4.92224100	-1.46255800	-2.36317300
C	-4.36489700	-1.13365000	-3.59954100
C	-3.03819500	-1.45810400	-3.89206700
C	-2.25138400	-2.12139400	-2.95112600
H	-5.95203800	-1.19972200	-2.13804500
H	-4.96341600	-0.60757000	-4.33691200
H	-2.61827500	-1.18629300	-4.85574400
H	-1.21294000	-2.36709500	-3.16188600
C	0.12259400	-4.07318600	0.00769500
C	-0.30692500	-4.72272700	1.32215300
C	0.21929900	-5.09194800	-1.12749000
H	1.11526100	-3.64006100	0.15403000
H	-1.28663700	-5.20290800	1.22121200
H	-0.36363900	-3.97129300	2.11504300
H	-0.70388000	-5.66874600	-1.24409600
H	0.44451000	-4.59799600	-2.07598200
C	-4.52157400	-2.65364600	-0.05872500
H	-5.11143600	-1.94082400	0.52558000
H	-5.12486100	-3.56435300	-0.16357300
C	-2.19247300	-3.23950500	-0.58552100
H	-2.23453100	-4.30355300	-0.84752900
H	1.02323000	-5.80194500	-0.91095000
H	0.41281500	-5.49238500	1.61723300
C	-2.71735800	1.64337300	-2.11280000
C	-3.00379400	2.50540500	-0.96621800
C	-1.83431300	3.21758500	-0.32245000
C	-0.30016900	2.16814000	-1.86825100
C	-1.44319000	1.44638200	-2.53468000
H	-2.02822000	3.37869800	0.74188000
H	0.61134700	1.56190700	-1.91231300
H	-0.10250800	3.12628400	-2.38011000
H	-1.71187300	4.19030300	-0.81498100
N	-0.64607100	2.36492200	-0.45433800
C	0.49310900	2.78042700	0.36616500
H	1.20604700	1.94933500	0.34732200
H	0.12767700	2.87580300	1.39577500
C	1.21198700	4.04418100	-0.05612200
C	0.67443900	5.31153200	0.18908300
C	2.44793000	3.95136400	-0.69916600
C	1.34915800	6.45819200	-0.21903900
H	-0.27520700	5.40290200	0.71024200
C	3.13164600	5.09632300	-1.09946900
H	2.88486100	2.96919900	-0.87078700

C	2.57946000	6.35266400	-0.86510900
H	0.91601400	7.43513600	-0.02917400
H	4.09542600	5.00530200	-1.59166800
H	3.10644900	7.24804700	-1.17974000
H	-4.01557100	2.76227500	-0.72355200
Cl	-3.59347200	4.33902400	-2.60765100
H	-1.24475700	0.84618600	-3.41674400
H	-3.55609600	1.17741700	-2.61775400

S-TS3

Cu	2.13840300	0.26935600	0.36632100
C	1.38134700	0.91381200	2.07780100
H	1.17015600	0.00596800	2.65164800
H	2.06814800	1.54183000	2.65392000
C	0.08697600	1.65068100	1.71007600
H	-0.42488500	1.15292300	0.87794300
H	0.32712900	2.65637700	1.35313100
C	-0.90954700	1.76461300	2.84035800
C	-2.17359700	1.18304000	2.72952000
C	-0.60165000	2.46912300	4.00767800
C	-3.11082600	1.30281700	3.75295500
H	-2.42898000	0.64230000	1.82102300
C	-1.53367900	2.59398500	5.03248800
H	0.37649700	2.93474300	4.10449500
C	-2.79406500	2.01030700	4.90893200
H	-4.08960200	0.84318000	3.64446700
H	-1.27920300	3.15049100	5.93061400
H	-3.52316400	2.10805700	5.70818600
O	-0.45829400	-1.38158700	0.94110700
P	0.77323900	-1.54944900	-0.13017800
O	-0.05682700	-1.76299200	-1.54103100
C	-2.53910500	-1.61106500	-0.23334600
C	-1.71213300	-1.94102700	0.81820000
C	-0.92954000	-0.75451900	-1.92236800
C	-2.12394700	-0.60527000	-1.24877500
C	-2.58028800	1.34359800	-2.69102400
C	-2.94645700	0.52175200	-1.58679600
C	-1.38861700	1.06253600	-3.40960700
C	-0.56001100	0.04589600	-3.02309000
H	-1.11255000	1.67964100	-4.26044300
C	-3.79248500	-2.31047100	-0.33809000
C	-3.33402400	-3.40061100	1.81560500
C	-2.10728500	-2.80414000	1.86296700
H	-3.65620600	-4.05824300	2.61804300
C	-4.19434500	-3.19251700	0.70567400
C	-3.40891000	2.44027100	-3.04712600
C	-4.11198900	0.86505200	-0.84896600
C	-4.88806800	1.93577900	-1.21384600
H	-5.77136500	2.18256500	-0.63260700
C	-4.54248900	2.72808400	-2.33288900
H	-5.16654000	3.57125200	-2.61209800
C	-4.64147100	-2.18816100	-1.47143500
C	-5.43843100	-3.86830800	0.61130100
C	-6.24566300	-3.70758400	-0.48376800
H	-7.19378000	-4.23217300	-0.54918900
C	-5.83114300	-2.86718900	-1.54081100
H	-6.45726200	-2.76206900	-2.42150400
H	-3.11965200	3.05395300	-3.89609900
H	-4.38497100	0.27501600	0.01904200
H	-4.33600200	-1.55737600	-2.29801700
H	-5.73371300	-4.52793800	1.42320100
H	-1.42212000	-2.95732200	2.68932000
H	0.36887900	-0.13865100	-3.55825600
N	1.41771800	-3.06076100	0.05705200
C	3.58487500	-2.96497400	-1.30448900
H	3.10672700	-2.10700100	-1.79209500
H	3.51769200	-3.80847300	-1.99529300
C	3.64502500	-2.35159600	1.00696500
C	4.87979600	-2.00236300	0.45753000
C	5.76406900	-1.20946800	1.17933800
C	5.39627600	-0.77193100	2.45360200
C	4.16518000	-1.13061900	3.00174600
C	3.28130700	-1.93281800	2.28053900
H	6.72411800	-0.92610000	0.75613100
H	6.07526800	-0.14443600	3.02363300
H	3.88549000	-0.77278100	3.98757700
H	2.31353600	-2.20330700	2.69391300
C	0.56911700	-4.26715000	-0.08680700

C	0.90909200	-5.06199600	-1.34752800
C	0.61894800	-5.12072900	1.17960300
H	-0.45581500	-3.90678800	-0.20337100
H	1.90357000	-5.51772100	-1.28431000
H	0.87220500	-4.41491600	-2.22825000
H	0.37390800	-4.51806500	2.05882600
H	-0.10678000	-5.93708200	1.10691800
C	5.03343200	-2.60214400	-0.92233400
H	5.50261500	-1.92582600	-1.64423400
H	5.66135000	-3.50158000	-0.87341200
C	2.87441200	-3.23449300	0.04505800
H	3.05072900	-4.27717100	0.33585600
H	1.60743900	-5.56813300	1.33317000
H	0.18331900	-5.87080400	-1.47993100
C	3.62529900	0.85023500	-1.00799500
C	2.55441800	0.92751300	-1.89646400
C	1.61104300	2.08800200	-1.75460300
C	2.97803400	3.08029200	0.01010500
C	3.58299300	1.70496900	0.13010900
H	1.20948700	2.29833000	-2.74722200
H	3.80215100	3.80774200	0.07048700
H	2.32896100	3.27629300	0.88025700
H	0.75111200	1.79299000	-1.11263800
N	2.31971000	3.25396800	-1.26844700
C	1.59163100	4.51080200	-1.40693900
H	2.29803900	5.32184600	-1.19058500
H	1.30732300	4.60355500	-2.46082900
C	0.37309900	4.63233900	-0.51119900
C	-0.83274000	4.02259600	-0.86813000
C	0.45881900	5.26166100	0.73380100
C	-1.91156200	4.00315500	0.01070500
H	-0.92517600	3.54334800	-1.83941500
C	-0.62136300	5.25457600	1.61353500
H	1.38569700	5.75564000	1.01873400
C	-1.80448200	4.61302900	1.25816200
H	-2.83004300	3.50102600	-0.27550800
H	-0.53371800	5.73391000	2.58409100
H	-2.63297600	4.57333300	1.95854900
H	4.31843900	1.56387200	0.91766600
H	4.34964800	0.04738400	-1.07396600
Cl	2.74167400	1.16646900	-4.64641000
H	2.35146000	0.14479600	-2.60965400

S-TS4

Cu	1.13391000	0.11917500	-0.47586300
C	2.90999700	0.02122000	0.52904300
H	3.64943900	-0.47818400	-0.10687300
H	3.29360900	1.01525900	0.79273500
C	2.59533800	-0.84249800	1.74982800
H	2.05830200	-1.74597900	1.42663600
H	1.91703500	-0.30747800	2.43171200
C	3.82285900	-1.27035800	2.53240400
C	4.15581000	-2.61878800	2.67542100
C	4.65807500	-0.31687400	3.12424700
C	5.28119900	-3.00927500	3.39996600
H	3.52073600	-3.37075500	2.21279900
C	5.78240400	-0.69830500	3.84905200
H	4.41577400	0.73818300	3.01384800
C	6.09753700	-2.04988200	3.99356100
H	5.51768000	-4.06449100	3.50355100
H	6.41287800	0.05789400	4.30810700
H	6.97164700	-2.35018100	4.56337200
O	-2.16480200	0.77324400	-0.90713000
P	-1.10553000	0.84605400	0.37613100
O	-1.90816100	-0.14271400	1.44059800
C	-4.18836900	-0.27640600	-0.15914000
C	-3.53170200	0.80049500	-0.72079800
C	-2.31341000	-1.39284600	1.00453900
C	-3.42625500	-1.50170100	0.20038700
C	-3.04887300	-3.93780100	0.16559800
C	-3.78329100	-2.80364700	-0.28442800
C	-1.95623200	-3.76033400	1.05443200
C	-1.57783600	-2.50962700	1.45211100
H	-1.39919200	-4.63324600	1.38156200
C	-5.59395600	-0.14357100	0.10369800
C	-5.56344700	2.06454400	-0.97274300
C	-4.21270500	1.95953500	-1.15726100
H	-6.09995600	2.94742500	-1.30907500

C	-6.28242400	1.03074800	-0.31789700
C	-3.40662100	-5.22913700	-0.30203200
C	-4.82724600	-3.00846000	-1.22732400
C	-5.14170700	-4.26880600	-1.66864600
H	-5.93764400	-4.40083500	-2.39485500
C	-4.43229800	-5.39693900	-1.19493000
H	-4.69328700	-6.38846000	-1.55068400
C	-6.32983000	-1.13264400	0.81367800
C	-7.67343000	1.15679000	-0.06262100
C	-8.35764000	0.17595800	0.60527600
H	-9.42002800	0.28271400	0.79925200
C	-7.67055100	-0.97565500	1.05658400
H	-8.20965900	-1.74116900	1.60561200
H	-2.83727000	-6.08285800	0.05547500
H	-5.37026600	-2.15075500	-1.60925900
H	-5.81383200	-2.01587400	1.17288300
H	-8.18188500	2.05514300	-0.40264500
H	-3.63660900	2.74043600	-1.64316000
H	-0.71512000	-2.33997700	2.08738800
N	-1.37506300	2.28032300	1.19202800
C	0.97047100	2.73078900	2.14961700
H	1.20241700	1.70396800	1.84704500
H	0.80047800	2.74271500	3.22939200
C	0.36059900	3.73674700	0.07017100
C	1.71251700	4.01914500	0.27770200
C	2.47022200	4.58535500	-0.74200100
C	1.85977300	4.85706700	-1.96939000
C	0.51193900	4.55608200	-2.17627000
C	-0.25002900	3.99086100	-1.15138100
H	3.52307700	4.80801200	-0.59106400
H	2.44220100	5.29248900	-2.77550400
H	0.05721100	4.75767300	-3.14103000
H	-1.29810800	3.74235200	-1.30034000
C	-2.60529200	2.54706500	1.97439400
C	-2.33252800	2.43733000	3.47379500
C	-3.23647300	3.88933400	1.60429900
H	-3.31337100	1.76051500	1.70442600
H	-1.62497800	3.20684600	3.80421500
H	-1.91803400	1.45380200	3.70973600
H	-2.64348600	4.73863500	1.95989000
H	-3.35675500	3.97685400	0.52158600
C	2.11454200	3.65760000	1.69171300
H	3.09707900	3.17966800	1.74802700
H	2.15542100	4.56316200	2.31152000
C	-0.26160400	3.21863000	1.35189700
H	-0.67802900	4.08827900	1.87548300
H	-4.22608300	3.96532100	2.06525400
H	-3.25951800	2.57400200	4.03936300
C	0.93506800	0.54505100	-2.71736700
C	1.23639700	-0.77683700	-3.07634400
C	2.68025900	-1.21392700	-2.97733600
C	3.39384800	1.06200300	-2.49558100
C	1.95881600	1.30643600	-2.13920200
H	2.86070600	-2.04795700	-3.66367200
H	3.73718500	1.94601300	-3.05743300
H	3.99833700	1.02427900	-1.57684500
H	2.86451100	-1.58241900	-1.95738200
N	3.55780900	-0.10627200	-3.35113700
C	4.96192300	-0.51022600	-3.48318000
H	5.50337100	0.33860000	-3.91919100
H	4.99702600	-1.33071200	-4.20932100
C	5.61679000	-0.92347500	-2.18020000
C	5.43450000	-2.20988300	-1.66243700
C	6.31498600	0.01204600	-1.41201400
C	5.89701600	-2.53631900	-0.39068200
H	4.91340000	-2.95757100	-2.25629900
C	6.78158600	-0.31123100	-0.14047700
H	6.47943000	1.01061100	-1.81281700
C	6.56133600	-1.58355100	0.37864300
H	5.72755100	-3.53091000	0.01063900
H	7.30479700	0.43306800	0.45230300
H	6.89266400	-1.83031200	1.38244100
H	0.53873000	-1.35744000	-3.66488300
Cl	0.39436600	-2.17480300	-1.20771900
H	1.73280800	2.29990600	-1.76719500
H	-0.08492100	0.91492800	-2.77367700

S-TS5

Cu	-1.35617100	0.26854300	0.38487600
C	-0.41466900	-1.27638200	1.67818500
H	-0.73251000	-2.26963600	2.00651800
H	0.26600300	-1.43306000	0.82821300
C	0.30392500	-0.50629700	2.78254900
H	-0.29460000	-0.54453600	3.70458600
H	0.37872200	0.55886000	2.51735700
C	1.69972400	-1.01657900	3.07693700
C	1.90759000	-2.32535500	3.52748700
C	2.81711300	-0.19802200	2.89808000
C	3.18799500	-2.79346500	3.80090900
H	1.05087400	-2.98067200	3.66692400
C	4.10577800	-0.66608200	3.15245500
H	2.66851500	0.82521200	2.56442400
C	4.29582500	-1.96668600	3.61072900
H	3.32477500	-3.81021100	4.15886600
H	4.95725500	-0.00921000	2.99466200
H	5.29620600	-2.33465600	3.81944500
O	1.65155600	1.27127500	0.30086000
P	0.35130500	1.36871300	-0.73381600
O	0.98517400	0.53436700	-2.02267400
C	3.37266500	-0.05561000	-0.71844300
C	2.96330900	1.09854200	-0.08300700
C	1.23648500	-0.79465200	-1.70903000
C	2.38184000	-1.12041500	-1.01702400
C	1.56786300	-3.44943400	-0.94733500
C	2.53659400	-2.47505600	-0.56913700
C	0.44779900	-3.05929700	-1.72905100
C	0.26748400	-1.75041500	-2.08409400
H	-0.27733800	-3.81490100	-2.02057500
C	4.75196000	-0.16631000	-1.09981900
C	5.20000200	1.98208000	0.00256100
C	3.87217700	2.11200300	0.30072100
H	5.91004600	2.74692800	0.30447700
C	5.67023700	0.85417700	-0.72032000
C	1.72017400	-4.78949800	-0.50666600
C	3.59104400	-2.86932600	0.29524700
C	3.69906900	-4.16910700	0.72023600
H	4.49914400	-4.44241000	1.40104800
C	2.76593200	-5.14647400	0.30426200
H	2.86949700	-6.17209400	0.64385800
C	5.24105500	-1.25258800	-1.87610500
C	7.03703400	0.73754500	-1.08494500
C	7.48110300	-0.33291400	-1.81564900
H	8.52728700	-0.41230000	-2.09270900
C	6.56603300	-1.33193800	-2.22246400
H	6.91539100	-2.16806800	-2.81985100
H	0.98048600	-5.52362400	-0.81495300
H	4.29169700	-2.12242200	0.65217900
H	4.54987400	-2.02121200	-2.20335000
H	7.72296100	1.52244800	-0.77750800
H	3.48811800	2.96358600	0.85296100
H	-0.59595800	-1.41612200	-2.65058900
N	0.34429100	2.89038000	-1.38671200
C	-2.13071600	3.37751400	-1.80558800
H	-2.24815300	2.28954200	-1.71717400
H	-2.15875100	3.64002900	-2.86675000
C	-1.20351200	3.90915600	0.32768600
C	-2.58163500	4.10125000	0.42155500
C	-3.18149700	4.26432700	1.66507100
C	-2.38331600	4.21852300	2.80925800
C	-1.00593100	4.01624400	2.70982200
C	-0.40221800	3.86529300	1.46121500
H	-4.25724700	4.39457700	1.75147800
H	-2.84249000	4.32344000	3.78720400
H	-0.40200900	3.96797400	3.61052600
H	0.66695900	3.68436700	1.37749700
C	1.45397600	3.39002200	-2.22631200
C	0.97874300	3.62466400	-3.65858100
C	2.11001400	4.63240900	-1.62473600
H	2.20096900	2.59068600	-2.24550900
H	0.21074500	4.40604600	-3.69381300
H	0.55989800	2.70349500	-4.07212400
H	1.45596100	5.50891700	-1.67680700
H	2.37489100	4.46218000	-0.57801100
C	-3.20976200	4.07820700	-0.95648800
H	-4.17597100	3.56420300	-0.98347800
H	-3.37985900	5.10180300	-1.31548600
C	-0.79894700	3.77182300	-1.12841300
H	-0.50470600	4.76297400	-1.49611500
H	3.02410200	4.87027300	-2.17702600

H	1.81247100	3.94766600	-4.28945500
C	-3.02172300	0.65465200	1.80201900
C	-4.11919200	0.95676700	0.90587700
C	-4.23196900	0.07625100	-0.34927400
C	-3.22847500	-1.65741700	0.98531800
C	-2.58330600	-0.69146800	1.95301700
H	-4.04939700	0.69087900	-1.24191500
H	-2.65128700	-2.58222000	0.91043800
H	-4.25747200	-1.90177600	1.30008300
H	-5.24367500	-0.34044600	-0.42650200
N	-3.21366700	-0.98077300	-0.32434800
C	-3.30021600	-1.88921000	-1.47212400
H	-2.43361800	-2.55706500	-1.40717700
H	-3.17975300	-1.27612700	-2.37480600
C	-4.57456700	-2.70213000	-1.57536500
C	-5.66922600	-2.22598800	-2.30120800
C	-4.68640700	-3.93499900	-0.92718500
C	-6.85319800	-2.95495300	-2.36757600
H	-5.58960700	-1.27418700	-2.82209500
C	-5.86779000	-4.66822400	-0.99004000
H	-3.83636700	-4.32679100	-0.37318600
C	-6.95496800	-4.17771300	-1.70918400
H	-7.69488200	-2.56933000	-2.93414300
H	-5.93857300	-5.62431300	-0.48088600
H	-7.87684100	-4.74833400	-1.75948900
H	-4.22232000	2.01240500	0.67803000
Cl	-5.87838100	0.75569000	1.84466500
H	-2.34111100	-1.06361300	2.94400100
H	-2.79849500	1.37862600	2.57896500

R-TS1

O	1.90610900	0.60167000	0.76881400
P	1.06556100	1.55721500	-0.32914100
O	1.47520600	0.74116300	-1.71473100
C	3.17731400	-1.02481600	-0.43362800
C	3.11697000	0.02690700	0.45899500
C	1.10508900	-0.59659300	-1.70060400
C	1.91563600	-1.50651300	-1.05259800
C	0.20368000	-3.22021200	-1.49825000
C	1.44327800	-2.85095300	-0.90181700
C	-0.54006000	-2.25331500	-2.22470000
C	-0.11796000	-0.95351100	-2.30936400
H	-1.47517300	-2.55697800	-2.68739600
C	4.45998900	-1.57735300	-0.75131400
C	5.48842100	-0.03253600	0.85838900
C	4.26415100	0.51759600	1.12363700
H	6.37766700	0.33077700	1.36611300
C	5.62051700	-1.07953400	-0.09126200
C	-0.29066900	-4.53922200	-1.31537000
C	2.12199700	-3.81069700	-0.10118100
C	1.60744900	-5.06922300	0.07332600
H	2.12523200	-5.77673000	0.71284200
C	0.39307700	-5.44533600	-0.54893600
H	-0.00064800	-6.44618800	-0.40181200
C	4.62575500	-2.59467900	-1.73101000
C	6.89076700	-1.63153400	-0.40333600
C	7.01595800	-2.62291400	-1.34062800
H	7.99167900	-3.03681200	-1.57386300
C	5.86790200	-3.10179900	-2.01553000
H	5.97290500	-3.87548800	-2.76952500
H	-1.23375500	-4.80747900	-1.78496500
H	3.03770900	-3.52429100	0.40453000
H	3.75285200	-2.96330800	-2.25897100
H	7.76424000	-1.24499500	0.11519600
H	4.13809300	1.31941400	1.84401700
H	-0.69864400	-0.17722600	-2.79765900
N	1.98495800	2.92927000	-0.55130600
C	0.41013800	4.88984000	-1.06695100
H	0.13492600	4.17689100	-1.84773100
H	0.85620700	5.76222900	-1.55199300
C	0.64181300	4.06361900	1.20055400
C	-0.61289600	4.66058400	1.11597300
C	-1.47059400	4.62782100	2.21645800
C	-1.06803600	3.97257300	3.37846600
C	0.18934300	3.36721700	3.45248700
C	1.05547600	3.41699300	2.36403900
H	-2.44614900	5.10632200	2.16938200
H	-1.73467900	3.93438400	4.23474300

H	0.48905900	2.85342200	4.36038100
H	2.02774700	2.93279300	2.40477600
C	3.21568600	2.94730800	-1.37002400
C	2.95061300	3.54226500	-2.75224900
C	4.36837400	3.65738500	-0.65941100
H	3.50261900	1.90055000	-1.50033900
H	2.67285800	4.59958000	-2.67519900
H	2.13885800	3.00251900	-3.24743700
H	4.24213600	4.74501700	-0.65172600
H	4.46674600	3.30715200	0.37200900
C	-0.84283600	5.27688300	-0.24308000
H	-1.75301600	4.88401500	-0.71247900
H	-0.95981100	6.36338700	-0.16125500
C	1.41874100	4.20993100	-0.09448100
H	2.27455400	4.86939500	0.08643500
H	5.30365000	3.44248500	-1.18493100
H	3.85008600	3.47585800	-3.37275000
Cu	-1.28207300	1.45868200	0.50456600
C	-1.03711100	0.06370200	2.02225600
H	-1.78344200	-0.03072300	2.81617300
H	-0.11720700	0.47808400	2.45189800
C	-0.77725100	-1.26071100	1.30934300
H	-1.71058100	-1.67137800	0.90532800
H	-0.13785800	-1.08553100	0.43981400
C	-0.10062800	-2.32742400	2.14692600
C	-0.68737700	-3.57706800	2.34638000
C	1.16805700	-2.09294200	2.69209400
C	-0.03141000	-4.57109800	3.07146400
H	-1.66440100	-3.77982600	1.91209800
C	1.82766100	-3.08166800	3.41365100
H	1.63725600	-1.12465900	2.53405300
C	1.22933800	-4.32696700	3.60704200
H	-0.50501900	-5.53885400	3.21145300
H	2.81446100	-2.88349300	3.82268000
H	1.74379000	-5.09957400	4.17072300
C	-3.39877300	2.50709600	0.28121800
C	-3.69766600	2.24409300	-1.06574900
C	-4.20187200	0.87384000	-1.42910000
C	-3.88646900	0.12073300	0.82322800
C	-3.28428200	1.44780800	1.20837800
H	-3.97210100	0.65208900	-2.47388400
H	-3.47176900	-0.68659100	1.43235300
H	-4.97589400	0.16092700	1.02785700
H	-5.30712500	0.90537500	-1.32511400
N	-3.60747200	-0.14650100	-0.58126100
C	-3.94683400	-1.50471400	-1.00532100
H	-3.32583800	-2.19635800	-0.42320900
H	-3.63799900	-1.59480500	-2.05325100
C	-5.40898500	-1.88237400	-0.86578000
C	-6.31453700	-1.63462100	-1.90089000
C	-5.88664000	-2.44879600	0.31903400
C	-7.66622600	-1.93487600	-1.75378700
H	-5.95251200	-1.21042100	-2.83506300
C	-7.23696400	-2.75103900	0.47205000
H	-5.18836100	-2.66188000	1.12601000
C	-8.13038800	-2.49204500	-0.56478500
H	-8.35575600	-1.73961500	-2.56926100
H	-7.59085900	-3.19389100	1.39788600
H	-9.18309700	-2.72991600	-0.44907800
H	-3.26138500	1.69250900	2.26598600
H	-3.20688300	3.52633400	0.59511000
Cl	-1.70851400	2.26196600	-2.23353800
H	-4.05717800	3.05737400	-1.68629700

R-TS2

O	-1.06945600	-0.02479200	1.00437800
P	0.02867400	-1.00280400	0.21501700
O	-0.96118800	-1.53010600	-1.01724400
C	-3.25152400	-0.38156000	0.11353200
C	-2.38310800	-0.40203700	1.18354300
C	-1.63934800	-0.56990400	-1.75212200
C	-2.74929300	0.05090500	-1.21628800
C	-2.88655600	1.41150200	-3.27239500
C	-3.36231100	1.11176400	-1.96318900
C	-1.80778800	0.66176000	-3.81103500
C	-1.18381100	-0.29876300	-3.06253600
H	-1.46763100	0.87842000	-4.81959600
C	-4.59452600	-0.84308600	0.32009400

C	-4.08273100	-1.15680100	2.70447300
C	-2.78863300	-0.77193100	2.48548600
H	-4.41280000	-1.43866700	3.70039200
C	-5.01018700	-1.21725100	1.63107300
C	-3.48770400	2.46454100	-4.01103900
C	-4.41033000	1.91011200	-1.42808500
C	-4.96368300	2.92739300	-2.16317900
H	-5.75550700	3.53181300	-1.73241700
C	-4.50632200	3.20569500	-3.47296700
H	-4.95455800	4.01406300	-4.04109900
C	-5.52698300	-0.98026000	-0.74477800
C	-6.34063200	-1.66590600	1.84125500
C	-7.22216800	-1.76542000	0.79746700
H	-8.23623600	-2.11228000	0.96701200
C	-6.80236800	-1.42772300	-0.51068000
H	-7.49597600	-1.52910100	-1.33923000
H	-3.11155400	2.67783000	-5.00762900
H	-4.76056300	1.71594300	-0.42011500
H	-5.21654400	-0.73519700	-1.75431400
H	-6.64182300	-1.93662100	2.84966500
H	-2.05446000	-0.73965500	3.28431800
H	-0.35475900	-0.87262300	-3.45984400
N	0.14625700	-2.41902300	1.07752900
C	2.48278900	-3.37043300	0.65341400
H	2.38027500	-2.82176700	-0.28822500
H	2.33256000	-4.42994800	0.43530700
C	2.21824000	-1.66209300	2.30371800
C	3.58812400	-1.82007000	2.08866600
C	4.48779600	-0.88719600	2.59245900
C	4.00075200	0.20295300	3.31394900
C	2.63093900	0.35142600	3.54028700
C	1.72859200	-0.58744100	3.03826100
H	5.55368300	-0.99625400	2.41168600
H	4.69298200	0.94235700	3.70578400
H	2.26018800	1.20301600	4.10311400
H	0.65972000	-0.46471900	3.20042600
C	-0.94438600	-3.42331300	1.11589700
C	-0.63199500	-4.61626500	0.21444000
C	-1.26622800	-3.87039300	2.54323900
H	-1.82872100	-2.92253800	0.71521600
H	0.21114600	-5.19445100	0.60769200
H	-0.38003600	-4.27607700	-0.79349800
H	-0.52594800	-4.57824600	2.92951000
H	-1.31918500	-3.01593000	3.22243900
C	3.85837600	-3.06343600	1.27328900
H	4.63162700	-2.91681500	0.51178400
H	4.19164000	-3.88019900	1.92675500
C	1.44952400	-2.79882700	1.65034900
H	1.22931700	-3.54583900	2.42289400
H	-2.23652900	-4.37597600	2.55227100
H	-1.49850200	-5.28297900	0.15986400
Cu	1.89476200	0.42952800	-0.30224900
C	3.91581600	0.03742500	-0.99359400
H	3.88525300	-0.73655800	-0.21097000
H	4.73156600	0.70987700	-0.71717400
C	4.18792500	-0.63168500	-2.34604300
H	3.93469100	0.04176700	-3.17891100
H	5.25912300	-0.84915900	-2.45957900
C	3.42680600	-1.92255900	-2.51501900
C	2.03833700	-1.90853400	-2.68467400
C	4.07013800	-3.16061400	-2.45721400
C	1.31103700	-3.09098400	-2.79453100
H	1.53316000	-0.94656100	-2.72379800
C	3.35038000	-4.35020700	-2.56622100
H	5.14960600	-3.19069100	-2.32866900
C	1.96880400	-4.31946700	-2.73534900
H	0.23179700	-3.05630600	-2.91709300
H	3.87156600	-5.30187400	-2.52095400
H	1.40634600	-5.24430900	-2.82115100
C	1.61498700	1.87328700	-2.19247100
C	2.97186300	2.12799400	-1.70751500
C	3.12813700	2.90943200	-0.42229400
C	0.74671000	3.19316600	-0.29165300
C	0.54738500	2.35584800	-1.52394300
H	4.00491100	2.55539600	0.12654000
H	-0.12275000	3.11702400	0.36333400
H	0.86702300	4.25387900	-0.58107600
H	3.26385300	3.97117900	-0.66536900
N	1.93935200	2.70974400	0.42976500
C	2.17276400	3.42760200	1.68683600
H	3.06088800	2.96973600	2.14343400

H	2.42938900	4.48018900	1.47314200
C	1.03998400	3.40018000	2.68564100
C	0.93698200	4.42520900	3.62792500
C	0.11844000	2.35427300	2.72567900
C	-0.05939800	4.39970700	4.60032200
H	1.64254200	5.25220800	3.59833700
C	-0.89060000	2.33553400	3.68444000
H	0.18549600	1.55868200	1.99262700
C	-0.97966900	3.35485200	4.62961400
H	-0.12409600	5.20373700	5.32681700
H	-1.61745600	1.52841400	3.68128900
H	-1.76631200	3.34126100	5.37742300
H	3.82357100	1.91468200	-2.32451400
Cl	3.08047800	4.10566000	-3.23506700
H	-0.45948600	2.22395000	-1.90937700
H	1.50096900	1.32915000	-3.12569700

R-TS3

O	0.97395400	-0.96304800	-0.79172600
P	0.04445800	-1.71339700	0.36127400
O	1.23388800	-2.09735900	1.45302500
C	3.26701600	-0.96163000	-0.08616000
C	2.30494200	-1.24154900	-1.03382000
C	1.89130100	-0.98783400	1.96676000
C	2.86629000	-0.36922800	1.21539100
C	2.97346000	1.37452500	2.95899800
C	3.38840400	0.88169000	1.68788000
C	2.03383800	0.63549900	3.72651400
C	1.47861600	-0.51323700	3.23125200
H	1.73659700	1.01560300	4.70000600
C	4.63197900	-1.28253200	-0.39131400
C	3.93253200	-1.98221400	-2.63998200
C	2.62706800	-1.73022200	-2.32059300
H	4.19640600	-2.34699400	-3.62857300
C	4.96242700	-1.78449600	-1.68272600
C	3.46278900	2.62695900	3.41348600
C	4.23159300	1.69813500	0.88775500
C	4.65878000	2.92012300	1.34127800
H	5.27591500	3.54188600	0.70078200
C	4.28748300	3.38514600	2.62446100
H	4.64296400	4.34943000	2.97291300
C	5.67635500	-1.14195000	0.56280800
C	6.31404500	-2.09108200	-1.98900300
C	7.30109800	-1.92754800	-1.05300900
H	8.33135500	-2.16742400	-1.29467600
C	6.97209300	-1.45567700	0.23938800
H	7.75307400	-1.34593600	0.98497200
H	3.15018000	2.98136900	4.39201200
H	4.50406200	1.36388600	-0.10688400
H	5.43735300	-0.79030600	1.56037800
H	6.54734700	-2.46586100	-2.98195000
H	1.82223600	-1.87171900	-3.03425400
H	0.73010800	-1.07857600	3.77862700
N	-0.33662800	-3.22533400	-0.16500100
C	-2.59002400	-3.81091300	0.92222600
H	-2.36420600	-2.99233500	1.61904300
H	-2.37232000	-4.75332200	1.43177500
C	-2.58719300	-2.65942100	-1.17080300
C	-3.91527900	-2.73964800	-0.74703800
C	-4.90445600	-2.00427800	-1.39191800
C	-4.53434100	-1.19409000	-2.46889800
C	-3.20214300	-1.10220400	-2.87822000
C	-2.20991300	-1.83960100	-2.22790900
H	-5.92529400	-2.02469200	-1.02074400
H	-5.29350900	-0.61117600	-2.98347300
H	-2.93556900	-0.45481700	-3.70892400
H	-1.16900100	-1.77191200	-2.53803900
C	0.71548500	-4.23757300	-0.42383500
C	0.60720300	-5.39022200	0.57123300
C	0.68997800	-4.71959500	-1.87391100
H	1.67150900	-3.73390500	-0.25311200
H	-0.34123900	-5.92536400	0.45077000
H	0.66933100	-5.01375000	1.59562000
H	0.66188800	-3.87275500	-2.56453300
H	1.59121400	-5.30439900	-2.08083100
C	-4.04530800	-3.69065100	0.42282100
H	-4.75999700	-3.32908200	1.17098500
H	-4.40639500	-4.66608900	0.07074400

C	-1.74138700	-3.61527400	-0.35312700
H	-1.70924700	-4.57121800	-0.89088500
H	-0.17319400	-5.36035200	-2.07937800
H	1.41808900	-6.10672200	0.40888400
Cu	-1.27478200	0.11073200	1.19247000
C	-0.07456500	1.74116100	0.92198700
H	0.90003800	1.29663400	1.12868700
H	-0.20597500	2.61745400	1.55883300
C	-0.23053900	2.07004600	-0.56422500
H	-0.38360500	1.16198600	-1.16203300
H	-1.10813000	2.70571600	-0.72230800
C	1.01647300	2.76424300	-1.06870500
C	1.92202400	2.09279100	-1.89296300
C	1.31882700	4.06995300	-0.66800600
C	3.10131900	2.70725200	-2.31107300
H	1.69013100	1.08194700	-2.21770700
C	2.49576000	4.68634900	-1.07978800
H	0.61674800	4.60334500	-0.03031500
C	3.39361200	4.00562800	-1.90272800
H	3.78979300	2.16763600	-2.95585200
H	2.71328700	5.70217000	-0.76274500
H	4.31028100	4.48874300	-2.22771300
C	-2.92725500	0.13151100	2.61285200
C	-3.67828900	-0.32985900	1.55000400
C	-3.95682000	0.61716200	0.41947600
C	-3.04190300	2.50084900	1.71226600
C	-2.31242100	1.42127000	2.47231000
H	-4.88507600	0.29525500	-0.05616400
H	-3.46641500	3.18946300	2.46106200
H	-2.32189900	3.09155700	1.12145200
H	-3.14380700	0.52194100	-0.34795500
N	-4.13335600	1.96307100	0.92640700
C	-4.70418000	2.91341600	-0.01924600
H	-5.03713200	3.78836500	0.55334000
H	-5.59658800	2.44495900	-0.44750700
C	-3.75103200	3.35517500	-1.11454600
C	-3.50379200	2.53129000	-2.21736500
C	-3.03780400	4.55265500	-1.00303300
C	-2.54870100	2.88257500	-3.16828200
H	-4.06248000	1.60424000	-2.32592100
C	-2.08298900	4.90986200	-1.95353200
H	-3.23485300	5.21035500	-0.15861600
C	-1.82956200	4.06909500	-3.03478500
H	-2.36476400	2.22995500	-4.01679200
H	-1.53157700	5.83923500	-1.84760500
H	-1.07555600	4.33717500	-3.76790900
H	-1.64030400	1.76349900	3.25331900
H	-2.68283500	-0.51425200	3.45192800
Cl	-6.39303800	-1.15397100	1.66795700
H	-4.03569300	-1.34550400	1.48743200

R-TS4

O	-1.94981400	-0.13500000	-1.37044600
P	-1.23319400	1.05489400	-0.44866500
O	-2.13652800	0.82164000	0.95738100
C	-3.63663300	-1.28116200	-0.09399600
C	-3.22189800	-0.63464800	-1.24209900
C	-1.97417800	-0.42361000	1.52301700
C	-2.67729500	-1.49890600	1.01844300
C	-1.48819700	-2.93467200	2.63939400
C	-2.39913400	-2.80350400	1.55105300
C	-0.84880400	-1.77860300	3.16026600
C	-1.06874200	-0.54891100	2.60223000
H	-0.16396700	-1.88976500	3.99688300
C	-5.00664000	-1.70621300	-0.01071700
C	-5.33926400	-0.99191200	-2.33532900
C	-4.05783300	-0.52191300	-2.38055000
H	-5.98425500	-0.91682300	-3.20637600
C	-5.85626100	-1.56959400	-1.14482700
C	-1.21149600	-4.22229100	3.16942600
C	-2.95807800	-3.98925000	0.99883500
C	-2.65957400	-5.22068000	1.52451300
H	-3.09331600	-6.11200900	1.08242300
C	-1.78656600	-5.34294400	2.63105500
H	-1.56527600	-6.32359100	3.03962900
C	-5.56684600	-2.23298400	1.18521700
C	-7.20642500	-1.99812900	-1.06443500
C	-7.71133000	-2.52135100	0.09731800

H	-8.74648100	-2.84259200	0.15066600
C	-6.88008000	-2.62772200	1.23629800
H	-7.28684300	-3.01990500	2.16306300
H	-0.52303700	-4.29931500	4.00672900
H	-3.61891800	-3.91264400	0.14285800
H	-4.94505900	-2.30930800	2.07051600
H	-7.83481200	-1.89371300	-1.94498000
H	-3.64084600	-0.06796500	-3.27264800
H	-0.57271500	0.34573200	2.96457300
N	-1.90647600	2.49245400	-0.94868100
C	-0.82036600	4.42309300	0.34300100
H	-0.57485900	3.65372800	1.08596300
H	-1.67408500	4.99201600	0.71747100
C	0.30298900	3.56478100	-1.57498300
C	1.15970800	4.48705900	-0.97053600
C	2.48958500	4.56912200	-1.36810700
C	2.95603100	3.69632400	-2.35278400
C	2.10029200	2.76297900	-2.94043600
C	0.75581000	2.70503000	-2.56779400
H	3.16016700	5.28152300	-0.89447700
H	3.99888400	3.73138600	-2.65339200
H	2.47413000	2.06374700	-3.68139600
H	0.09410000	1.97552100	-3.02929100
C	-3.36993200	2.63930900	-1.10105200
C	-3.96272500	3.65989600	-0.13095000
C	-3.73370300	2.95223800	-2.55210500
H	-3.80463500	1.67131500	-0.84144200
H	-3.63802300	4.67781100	-0.37059700
H	-3.66982600	3.42596700	0.89632100
H	-3.42291600	3.96366200	-2.83507700
H	-3.24753500	2.24490800	-3.22897100
C	0.42232000	5.29071500	0.07503800
H	1.01562700	5.47896700	0.97473300
H	0.12673000	6.26527300	-0.33759900
C	-1.09707700	3.71596800	-1.00643600
H	-1.64764000	4.40703000	-1.66100900
H	-4.81744400	2.88546400	-2.69126600
H	-5.05480500	3.63597500	-0.19755800
Cu	1.28283200	0.27938800	-0.54869600
C	2.42241500	1.47049800	0.65411400
H	2.46567500	2.28266200	-0.08175900
H	3.44294300	1.13091000	0.84667700
C	1.70397700	1.91548500	1.91667000
H	0.61428300	1.90554600	1.75707300
H	1.87827800	1.18742800	2.72473000
C	2.04852300	3.30318800	2.44050800
C	1.18434300	3.93653900	3.34122600
C	3.19457700	3.98859600	2.03374600
C	1.44939800	5.21632600	3.81781000
H	0.28187700	3.41756400	3.66108100
C	3.46718000	5.27116400	2.50852000
H	3.86789700	3.51735700	1.32381700
C	2.59531500	5.89181500	3.39907100
H	0.75970700	5.69045500	4.50992600
H	4.36290100	5.78854900	2.17652900
H	2.80398400	6.89311100	3.76293900
C	0.96544900	-1.95981000	-0.09381500
C	1.36515200	-2.43788700	-1.35368000
C	2.82720300	-2.68977600	-1.59700800
C	3.37759400	-1.63611000	0.49138800
C	1.92063200	-1.34770600	0.73787000
H	3.03933000	-2.66970500	-2.66843000
H	4.00612900	-0.86246800	0.93989200
H	3.61539000	-2.59110200	1.00714900
H	3.03110500	-3.71928100	-1.23006200
N	3.64600000	-1.69509600	-0.93162100
C	5.06336200	-1.78084700	-1.26846000
H	5.55485100	-0.91113000	-0.81687000
H	5.14198900	-1.67335400	-2.35630400
C	5.75503000	-3.05519600	-0.82192000
C	5.78006400	-4.18047400	-1.65027600
C	6.33636600	-3.14594200	0.44559100
C	6.36275600	-5.37009300	-1.22146300
H	5.34526200	-4.11792900	-2.64561900
C	6.92097800	-4.33260700	0.87994900
H	6.33817600	-2.27194700	1.09371600
C	6.93313700	-5.44874400	0.04671200
H	6.37708800	-6.23364200	-1.87929500
H	7.37254200	-4.38440300	1.86590000
H	7.39130300	-6.37397200	0.38175700
H	1.63650200	-1.08606100	1.75327300

H	-0.08538800	-1.97532200	0.17993800
Cl	1.09587300	-0.66910600	-2.90944900
H	0.66920600	-3.03674800	-1.92952000

R-TS5

O	0.86375900	1.02702300	0.56094700
P	-0.08777600	1.13607400	-0.79874400
O	1.09272400	0.98472700	-1.95720400
C	3.16947700	0.98952500	-0.09701700
C	2.13953100	1.55085400	0.63022400
C	1.88763000	-0.14644700	-1.87942900
C	2.90534000	-0.19854000	-0.95010900
C	3.33234300	-2.51405300	-1.68210600
C	3.62553300	-1.43033800	-0.80505800
C	2.33342700	-2.36102300	-2.67973500
C	1.60633300	-1.20515800	-2.76891600
H	2.12988500	-3.19085400	-3.35089600
C	4.46058400	1.61262900	-0.02934800
C	3.58163500	3.19100400	1.63581600
C	2.33975900	2.63019600	1.52010000
H	3.75244500	4.01632300	2.32133800
C	4.66446700	2.71342200	0.85193400
C	4.01972800	-3.74638500	-1.51999200
C	4.57403100	-1.63801900	0.23361000
C	5.20736100	-2.84530600	0.37438800
H	5.90422300	-2.99244200	1.19304600
C	4.93794100	-3.91071000	-0.51723300
H	5.44754200	-4.86080300	-0.39205500
C	5.54958100	1.19187700	-0.84137900
C	5.94392400	3.32447200	0.92330100
C	6.97828900	2.88335800	0.14096500
H	7.95200500	3.35871800	0.19988600
C	6.77103300	1.81022800	-0.75749000
H	7.58659900	1.47555800	-1.39056000
H	3.78826000	-4.56088600	-2.20115100
H	4.76418100	-0.84123400	0.94387100
H	5.40213400	0.37592000	-1.54001800
H	6.08220700	4.15629000	1.60884500
H	1.49456400	2.97663100	2.10598900
H	0.80830100	-1.07493400	-3.49193300
N	-0.44173700	2.73532700	-1.08416700
C	-2.81595600	2.49462300	-2.03766700
H	-2.63080100	1.41359400	-2.01678500
H	-2.69478000	2.83917500	-3.06815500
C	-2.55513300	3.09424700	0.26121300
C	-3.91954100	2.89591500	0.04576000
C	-4.79756900	2.86120600	1.12382300
C	-4.29035700	3.02379400	2.41342600
C	-2.92410500	3.21573100	2.62287300
C	-2.04224900	3.25073000	1.54266200
H	-5.86160500	2.70160700	0.96889700
H	-4.96168300	2.97634800	3.26489900
H	-2.54641500	3.32515700	3.63475100
H	-0.97427000	3.38829000	1.69182700
C	0.59267600	3.71641700	-1.49682900
C	0.42240500	4.08563500	-2.96955600
C	0.60898600	4.94342600	-0.58690400
H	1.55470100	3.21018000	-1.38829000
H	-0.53564900	4.58796400	-3.14677300
H	0.46602800	3.18552200	-3.58794100
H	-0.31553700	5.52610600	-0.65647200
H	0.75786800	4.65175900	0.45577900
C	-4.20504200	2.79299500	-1.43833600
H	-4.95430900	2.03361500	-1.68503500
H	-4.58750100	3.75141600	-1.81374600
C	-1.83425600	3.18940600	-1.06722500
H	-1.80098400	4.25066800	-1.34246900
H	1.43503200	5.59985500	-0.87691000
H	1.21784000	4.76786300	-3.28450500
Cu	-1.53945700	-0.69494800	-0.59450600
C	-0.79754900	-2.12455800	0.92803400
H	-1.33119100	-2.86024200	1.53535200
H	-0.71197700	-1.21329200	1.54093000
C	0.58598200	-2.60118500	0.50251900
H	0.51601800	-3.55879800	-0.03231700
H	0.99414000	-1.89067200	-0.22650000
C	1.60777300	-2.74492700	1.61092600
C	2.23363900	-3.96387900	1.87238000

C	1.98165400	-1.63106200	2.37386000
C	3.20483000	-4.07511700	2.86703600
H	1.96511400	-4.83552700	1.27997900
C	2.95272700	-1.73468500	3.36355500
H	1.50190600	-0.67488900	2.17817400
C	3.57035500	-2.96029300	3.61478200
H	3.67890500	-5.03492100	3.05289100
H	3.23266900	-0.85605400	3.93843300
H	4.32755700	-3.04366600	4.38877400
C	-1.90542700	-2.28668900	-2.13956800
C	-3.06667500	-1.78074200	-2.84989100
C	-4.14865800	-1.12408000	-1.97425200
C	-3.44419200	-2.64296400	-0.25832000
C	-2.06289600	-2.83354300	-0.83502400
H	-4.21642100	-0.05686300	-2.21647700
H	-3.44899000	-2.79650700	0.82103100
H	-4.16269800	-3.33917800	-0.72716900
H	-5.12928900	-1.57574800	-2.18058900
N	-3.80919900	-1.24324100	-0.55184000
C	-4.89827100	-0.74424700	0.28997900
H	-5.09935200	0.28796900	-0.02607900
H	-5.82062900	-1.32677600	0.11980700
C	-4.53364600	-0.77460700	1.75393500
C	-5.29333200	-1.50362300	2.66849200
C	-3.39905600	-0.09614800	2.20326800
C	-4.92660700	-1.55862000	4.01201500
H	-6.17347900	-2.04100400	2.32346900
C	-3.02392100	-0.15696000	3.54080000
H	-2.81172200	0.49000500	1.49818300
C	-3.78663300	-0.88995600	4.44885400
H	-5.52514200	-2.13241800	4.71268500
H	-2.13577100	0.37259700	3.87294000
H	-3.49172000	-0.94059300	5.49236400
H	-2.83015400	-1.18050800	-3.72508400
Cl	-4.00422300	-3.25682500	-3.80988000
H	-1.53040900	-3.74024000	-0.56733300
H	-1.04771500	-2.58722100	-2.73188800

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