**Supporting Information for**

# Enantioselective Catalytic Dearomative Addition of Grignard Reagents to 4-Methoxypyridinium Ions

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## 1. General experimental information

All reactions were carried out with anhydrous solvents (*vide infra*), under a nitrogen atmosphere using oven-dried glassware and standard Schlenk techniques. Reactions were monitored by $^{1}H$ NMR. Purification of the products was performed by column chromatography using Merck 60 Å 230-400 mesh silica gel. Components were visualized by UV and $KMnO_4$ or $I_2$ staining of thin layer chromatography (TLC) plates. NMR data was collected on a Varian MercuryPlus ($^{1}H$ at 300 MHz; $^{31}P$ at 121 MHz) equipped with a 300 Autosw probe, a Varian MercuryPlus ($^{1}H$ at 400 MHz; $^{13}C$ at 101 MHz; $^{31}P$ at 162 MHz ) equipped with a 400 Autosw probe, a Varian 400MR ($^{1}H$ at 400 MHz; $^{13}C$ at 101 MHz; $^{31}P$ at 162 MHz ) equipped with a OneNMR probe and a Bruker NEO ($^{1}H$ at 600 MHz; $^{13}C$ at 151 MHz; $^{31}P$ at 243 MHz; NOESY at 600 MHz) equipped with a SmartProbe BBFO. Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak ($CDCl_3$, $^{1}H$: 7.26 ppm; $^{13}C$: 77.16 ppm). Coupling constants are reported in Hertz (Hz). Multiplicity is reported with the usual abbreviations (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quadruplet, m: multiplet). Exact mass spectra were recorded on a LTQ Orbitrap XL apparatus with ESI ionization. Enantiomeric excess (ee) was determined by chiral HPLC analysis using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector. The optical rotation of compound **7** was determined by a SCHMIDT HAENSCH polartronic MH8.

## 2. Chemicals

Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Solvents not required to be dry were purchased as technical grade and used as received. Dry solvents were freshly collected from a dry solvent purification system prior to use. Inert atmosphere experiments were performed with standard Schlenk techniques using dried ($P_2O_5$) nitrogen gas. Grignard reagents were purchased from Sigma-Aldrich (EtMgBr (3.0 M in $Et_2O$); *i*BuMgBr, *n*PentMgBr, *i*PentMgBr, *n*HexMgBr, (2.0 M in $Et_2O$)). All other Grignard reagents 4-ClBuMgBr (1.2 M in $Et_2O$), but-3-en-1-ylMgBr (1.8 M in $Et_2O$), phenethylMgBr (1.9 M in $Et_2O$) and hept-6-en-1-ylMgBr (1.7 M in $Et_2O$) were prepared from the corresponding alkyl bromides and Mg activated with $I_2$ in $Et_2O$. All Grignard reagents were titrated by $^{1}H$ NMR before use. Chiral ligands **L1-L8** were purchased and used without prior purification ((*R*,*R*)-**L1** was purchased from Strem Chemicals, (*R*)-**L2**, (*R*)-**L5** and (*R*)-**L6** from TCI Chemicals, (*R*,*S*)-**L3** and (*R*,*S*)-**L4** from Solvias and (*S*,*S*,*S*)-**L7**

and (*R,R*)-**L8** from Merck). Ligands **L9** and **L10** were prepared according to literature procedures (detailed procedure are shown in section 8). Substrates **3a** and **3g** were purchased from Merck and **3b-f**, **3h** were prepared following literature procedures (detailed procedures are shown in section 5).[i] All reported compounds were characterized by $^{1}H$ and $^{13}C$ NMR and compared with literature data. All new compounds were fully characterized by $^{1}H$ and $^{13}C$ NMR and HRMS techniques.

## 3. Determination of absolute configuration

The absolute configuration was determined by comparison of the obtained optical rotation and HPLC data for compound **7** with the reported data for the same compound:

Obtained data: >99% ee, chiral OD column, *i*PrOH 1-25% in hexane, 60 min, 1.0 mL/min, 30 $^{o}C$, single enantiomer (-)-enantiomer $R_t$ = 29.18 min, (HPLC spectra are shown in section 7); $[\alpha]_D^{20}$ = -182.1 (*c* 1.0, $CHCl_3$), *S*-configuration.

Reported data (Niphakis, M. J.; Turunen, B. J.; Georg, G. I. *J. Org. Chem*. **2010**, *75*, 6793-6805):[ii] 44% ee, chiral OD column, *i*PrOH 1-25% in hexane, 60 min, 1.0 mL/min, 30 $^{o}C$, (-)-enantiomer $R_t$ =36.3 min, (+)-enantiomer $R_t$ =39.6 min; $[\alpha]_D^{22}$ = -95.0 (*c* 0.924, $CHCl_3$), *S*-configuration.

The absolute configurations of other compounds were assigned by analogy.

## 4. General computational details and considerations

The Density Functional Theory (DFT) in the Kohn-Sham formulation[iii] was used to optimize all the stationary points reported in this manuscript. Due to the excessive computational cost associated with the mechanistic exploration of this study the PCM($CH_2Cl_2$)[iv]-B3LYP[v,vi]-D3/def2tzvpp[vii]//PCM($CH_2Cl_2$)-B3LYP-GD3/def2svp computational level was used for the study of the reaction mechanism. Calculations were performed at normal conditions of temperature and pressure and not 210K because while the entropic correction does not alter the reactivity description significantly (please see H and G values below) this choice of temperature allows us to confirm that the reaction can reach enantioselectivity at room temperature.

IRC[iv] calculations were conducted to ensure the connectivity of the transition states with the proposed reactants and products. The stability of the wavefunction was analyzed for all the

presented stationary points.[v] When the studied stationary points possessed conformational freedom, conformational analysis was performed manually. In this sense it must be pointed that only the most stable conformers are reported for the sake of clarity.

The visualization of the reported structures was performed using MOLDEN.[vi] The representation of the structures here presented were generated using CYLView.[vii]

The Grignard reagents used in this work are synthesized in $Et_2O$, in this sense, it has been already proposed that ethereal solvents can strongly coordinate magnesium and thus be present in the first coordination sphere of the metallic center, even in high dilution conditions.[viii] In line with this, we have calculated the ergonicity of the solvation of EtMgBr with one and two solvent molecules, obtaining that the latter is the most exergonic process (-4.32 kcal/mol). Therefore we have considered the Grignard reagent in the form of $EtMgBr \cdot 2Et_2O$ for these simulations.

## 5. Synthesis of 4-methoxypyridine derivatives: general procedures and product characterization

## General procedures

**Method 1** (used for compounds **3b**, **3c** and **3d**):[ia]

To a flame-dried two-necked flask, substrate 2-chloro-4-methoxypyridine (5.0 mmol, 1.0 equiv.), $Fe(acac)_3$ (0.25 mmol, 5 mol%), THF (35 mL), and NMP (*N*-Methyl-2-pyrrolidone) (3.0 mL) were added under nitrogen, forming a red solution. Then, a solution of the corresponding Grignard reagent (1.3 equiv.) was added via syringe, causing an immediate color change from red to dark brown. The resulting mixture was stirred for 10 min. Then, the reaction was diluted with $Et_2O$. After that, the crude was purified by flash chromatography.

**Method 2** (used for compounds **3e** and **3h**):[ib]

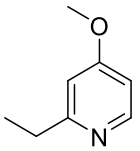
To a dried Schlenk tube, sodium methoxide (35 mL, 1 M in MeOH) was added. Then, the substrate (4-chloroquinoline or 3-methyl-4-chloropyridine) (0.53 mmol, 1.0 equiv.) was added and the resulting mixture was heated to reflux for 24 h. The solvent was removed under reduced pressure, and the resulting residue purified by flash chromatography to obtain the pure products**.**

**Method 3** (used for compound **3f**):[ic]

To a flame-dried two-necked flask, $Pd(PPh_3)_4$ (1 mol%), $K_2CO_3$ (2.0 equiv.) and EtOH (5 mL) were added under nitrogen. Then, a solution of the phenyl boronic acid (1.5 equiv.) in EtOH (5 mL) was added to the reaction vessel followed by the addition of the 2-bromo-4-methoxypyridine (5.0 mmol, 1.0 equiv.). The reaction mixture was heated up to 100 °C and kept in reflux for 15 h. Then, the mixture was cooled to room temperature and aqueous NaOH (1 M) was added. Later, the mixture was extracted with EtOAc (3x10 mL), the combined organic extracts were washed with brine, dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by flash chromatography.

## Characterization of products

### 2-Ethyl-4-methoxypyridine (3b)



**3b**

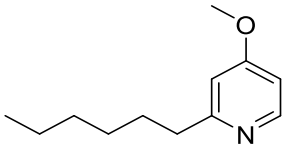
The product **3b** was synthesized following **Method 1** using EtMgBr and obtained after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) as a colorless oil in 76% yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 5.7 Hz, 1H, C*H*$_{Ar}$), 6.47 (s, 1H, C*H*$_{Ar}$), 6.42 (d, *J* = 5.7 Hz, 1H, C*H*$_{Ar}$), 3.60 (s, 3H, OC*H*$_3$), 2.57 (q, *J* = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 1.09 (t, *J* = 7.7 Hz, 3H, CH$_2$C*H*$_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.81, 164.87, 150.07, 107.52, 106.88, 54.60, 31.21, 13.54.

HRMS (ESI+, m/Z): calcd for $C_8H_{11}NO$ $[M+H]^+$: 138.0913, found: 138.0912.

### 2-Hexyl-4-methoxypyridine (3c)



**3c**

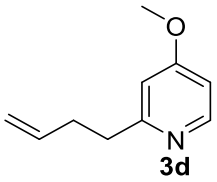
The product **3c** was synthesized following **Method 1** using *n*HexMgBr and obtained after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) as a colorless oil in 11% yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 5.7 Hz, 1H, C*H*$_{Ar}$), 6.68-6.50 (m, 2H, C*H*$_{Ar}$), 3.79 (s, 3H, OC*H*$_3$), 2.70 (t, *J* = 7.8 Hz, 2H, C*H*$_2$), 1.75-1.57 (m, 2H, C*H*$_2$), 1.40-1.20 (m, 6H, C*H*$_2$), 0.85 (t, *J* = 6.4 Hz, 3H, C*H*$_3$CH$_2$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.05, 164.29, 150.44, 108.53, 107.22, 55.03, 38.67, 31.80, 29.89, 29.18, 22.66, 14.16.

HRMS (ESI+, m/Z): calcd for $C_8H_{11}NO$ $[M+H]^+$: 194.1539, found: 194.1540.

**2-(But-3-en-1-yl)-4-methoxypyridine (3d)**



**3d**

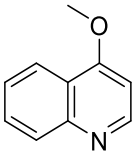
The product **3d** was synthesized following **Method 1** using but-3-en-1-ylMgBr and obtained after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) as a colorless oil in 27% yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 5.6 Hz, 1H, C*H*$_{Ar}$), 6.69-6.56 (m, 2H, C*H*$_{Ar}$), 5.90-5.78 (m, 1H, $CH_2$=C*H*), 5.07-4.90 (m, 2H, C*H*$_2$=CH), 3.80 (s, 3H, OC*H*$_3$), 2.81 (t, *J* = 7.7 Hz, 2H, $CH_2$=CHC$H_2$C*H*$_2$), 2.49-2.41 (m, 2H, $CH_2$=CHC*H*$_2$C$H_2$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.06, 163.15, 150.49, 137.85, 115.15, 108.77, 107.39, 55.06, 37.88, 33.74.

HRMS (ESI+, m/Z): calcd for $C_{10}H_{13}NO$ $[M+H]^+$: 164.1069, found: 164.1068.

**4-Methoxyquinoline (3e)** [ib]



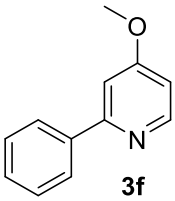
**3e**

The product **3e** was synthesized following **Method 2** starting from 4-chloro-quinoline and obtained after column chromatography ($SiO_2$, pentane:$Et_2O$ 2:1) as a white solid in 89% yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.2 Hz, 1H, C*H*$_{Ar}$), 8.12 (d, *J* = 7.7 Hz, 1H, C*H*$_{Ar}$), 7.99 (d, *J* = 8.5 Hz, 1H, C*H*$_{Ar}$), 7.67-7.59 (m, 1H, C*H*$_{Ar}$), 7.46-7.38 (m, 1H, C*H*$_{Ar}$), 6.65-6.56 (m, 1H,C*H*$_{Ar}$), 3.89 (s, 3H, OC*H*$_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.16, 151.33, 149.10, 129.65, 128.82, 125.52, 121.76, 121.33, 99.98, 55.56.

**4-Methoxy-2-phenylpyridine (3f)**




**3f**

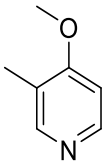
The product **3f** was synthesized following **Method 3** and obtained after column chromatography ($SiO_2$, pentane:$Et_2O$ 5:1) as a white solid in 82% yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.7 Hz, 1H, C*H*$_{Ar}$), 7.99-7.93 (m, 2H, C*H*$_{Ar}$), 7.50-7.38 (m, 3H, C*H*$_{Ar}$), 7.23 (d, *J* = 2.4 Hz, 1H, C*H*$_{Ar}$), 6.78 (dd, *J* = 5.7, 2.4 Hz, 1H, C*H*$_{Ar}$), 3.90 (s, 3H, OC*H*$_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.56, 159.34, 150.98, 139.52, 129.15, 128.81, 127.10, 108.25, 107.02, 55.31.

HRMS (ESI+, m/Z): calcd for $C_{12}H_{11}NO$ $[M+H]^+$: 186.0913, found: 186.0914.

**4-Methoxy-3-methylpyridine (3h)**




**3h**

The product **3h** was synthesized following **Method 2** starting from 4-chloro-3-methylpyridine hydrochloride and obtained after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) as a colorless oil in 82% yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 5.6 Hz, 1H, C*H*$_{Ar}$), 8.22 (s, 1H, C*H*$_{Ar}$), 6.70 (d, *J* = 5.7 Hz, 1H, C*H*$_{Ar}$), 3.85 (s, 3H, OC*H*$_3$), 2.15 (s, 3H, Ar-C*H*$_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.85, 150,92, 149.45, 122.25, 105.53, 55.16, 13.11.

HRMS (ESI+, m/Z): calcd for $C_7H_9NO$ $[M+H]^+$: 124.0756, found: 124.0755.

## 6. Racemic and catalytic asymmetric additions of Grignard reagents to pyridinium salts: general procedures and product characterization

### General procedures

**General procedure for the preparation of racemic products:** In a flame-dried Schlenk tube equipped with a septum and a magnetic stirring bar, the corresponding substrate (0.2 mmol, 1.0 equiv.) was added to anhydrous THF (2 mL). After stirring for 5 min at room temperature (18-25 $^{o}$C), chloroformate reagent (2.0 equiv.) was added dropwise (this addition is accompanied by the formation of a white solid) and after stirring for another 10 min at room temperature, the reaction was transferred to -78 $^{o}$C followed by the addition of the corresponding Grignard reagent (2.0 equiv.). The reaction was stirred at -78 $^{o}$C overnight (**very important to ensure good stirring**). After that, the reaction was quenched by 1.0 M HCl solution. The reaction mixture was extracted with $Et_2O$ (3x3 mL) and the combined organic phases were dried over $MgSO_4$, filtered and solvents were evaporated under reduced pressure. The crude was used to find a method for separation of enantiomers via HPLC without further purification.

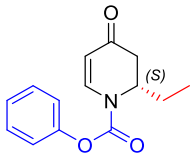
**Cu-catalyzed asymmetric addition of Grignard reagents to 4-methoxypyridine:** In a flame-dried Schlenk tube equipped with a septum and a magnetic stirring bar, $CuBr{\cdot}SMe_2$ (5 mol%), and the ligand **L1** (*R*,*R*)-Ph-BPE (6 mol%) were dissolved in toluene (2 mL) and stirred under nitrogen atmosphere for 20 min. Then, the 4-methoxypyridine (0.2 mmol, 1.0 equiv.) was added at once. After stirring for 5 min at room temperature (18-25 $^{o}$C), benzyl chloroformate (2.0 equiv.) was added dropwise (a white solid was formed immediately). After vigorous stirring for 10 min at room temperature (**important to ensure good stirring**), the reaction vessel was transferred to -78 $^{o}$C and the corresponding Grignard reagent (2.0 equiv.) was added in 10 min. The reaction was stirred at -78 $^{o}$C overnight (**important to ensure good stirring, insufficient stirring could result in the decrease of both conversion and enantioselectivity**). After that, the reaction was quenched with saturated aqueous $NH_4Cl$ (or 1.0 M HCl solution). The reaction mixture was extracted with $CH_2Cl_2$ (3×3 mL). The combined organic phases were dried over $MgSO_4$, filtered and solvents were evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel.

**Cu-catalyzed asymmetric addition of Grignard reagents to 2 or 3-substituted 4-methoxypyridines:** In a flame-dried Schlenk tube equipped with a septum and a magnetic

stirring bar, CuBr·$SMe_2$ (5 mol%), and the ligand **L1** (*R*,*R*)-Ph-BPE (6 mol%) were dissolved in $CH_2Cl_2$ (2 mL) and stirred under nitrogen atmosphere for 20 min. The corresponding substrate **3** (0.2 mmol, 1.0 equiv.) was added at once. After stirring for 5 min at room temperature (18-25 $^oC$), methyl chloroformate (2.0 equiv.) was added dropwise. After stirring for 10 min at room temperature, everything was dissolved and the reaction was transferred to -78 $^oC$ followed by the addition of the corresponding Grignard reagent (2.0 equiv.) in 10 min. The reaction was stirred at -78 $^oC$ overnight (**important to ensure good stirring, insufficient stirring could result in decrease of both conversion and enantioselectivity**). After that, the reaction was quenched with 1.0 M HCl solution (important to use acid to quench the solution). The reaction mixture was extracted with $CH_2Cl_2$ (3×3 mL). The combined organic phases were dried over $MgSO_4$, filtered and solvents were evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel.

## Characterization of chiral conjugate addition products

### Phenyl (*S*)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2a)



**2a**

The reaction was performed with 0.2 mmol **1a**, CuBr·$SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), phenyl chloroformate (50 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 $^oC$. Product **2a** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 2:1) [Colorless oil, 85% yield, 94% ee, (*S*)-configuration].

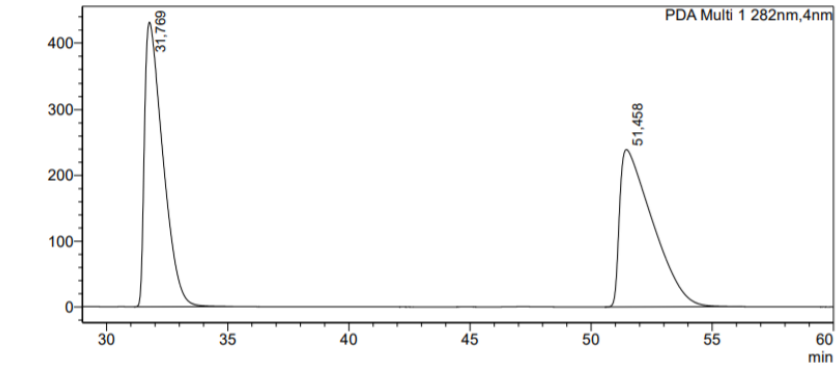
$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H, CH=C*H*N), 7.43 (t, *J* = 7.8 Hz, 2H, C$H_{Ar}$), 7.27 (t, *J* = 7.4 Hz 1H, C$H_{Ar}$), 7.18 (d, *J* = 8.2 Hz, 2H, C$H_{Ar}$), 5.43 (d, *J* = 8.1 Hz, 1H, COC*H*=CH), 4.71-4.63 (m, 1H, C*H*$CH_2CH_3$), 2.92 (dd, *J* = 16.6, 6.5 Hz, 1H, COC$H_2$), 2.56 (d, *J* = 16.7 Hz, 1H, COC$H_2$), 1.92-1.66 (m, 2H, C$H_2$$CH_3$), 1.00 (t, *J* = 7.0 Hz, 3H, C$H_3$).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 193.02, 151.46, 150.53, 141.22, 129.68, 126.40, 121.31, 108.16, 55.20, 39.54, 23.87, 10.38.

HRMS (ESI+, m/Z): calcd for $C_{14}H_{15}NO_3$ $[M+H]^+$: 246.1124, found: 246.1126.

HPLC analysis: Chiracel-ASH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 $^oC$, detection at 282 nm. Retention time (min): 29.5 (minor) and 47.0 (major).

**<Chromatogram>**

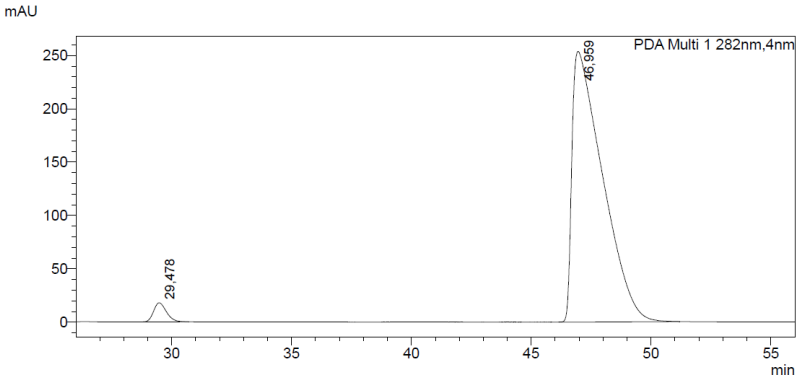



**<Peak Table>**

PDA Ch1 282nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 31,769 | 22789935 | 431404 | 50,085 | | | |
| 2 | 51,458 | 22712474 | 239432 | 49,915 | | | |
| Total | | 45502409 | 670836 | | | | |

**<Chromatogram>**

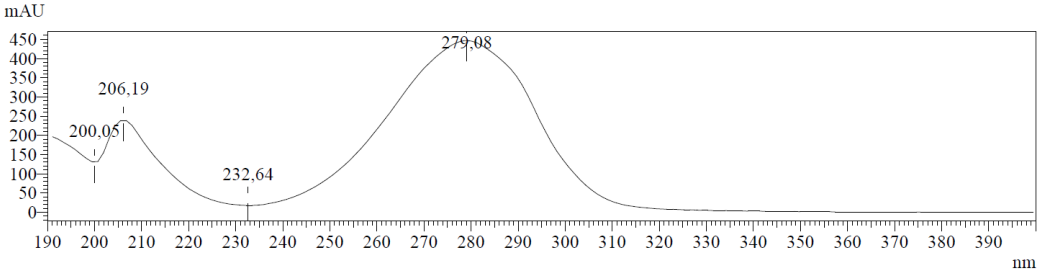


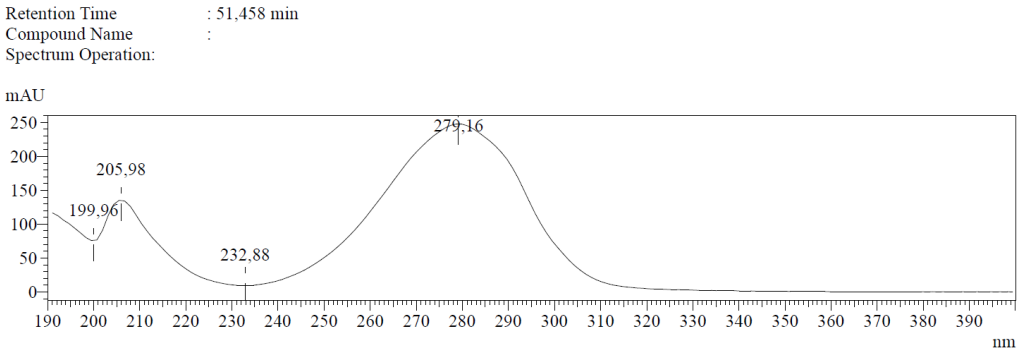

**<Peak Table>**

PDA Ch1 282nm

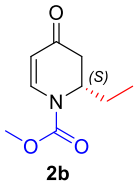
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 29,478 | 667331 | 17929 | 2,877 | | | |
| 2 | 46,959 | 22531259 | 253721 | 97,123 | | | |
| Total | | 23198590 | 271650 | | | | |

Retention Time : 31,769 min
Compound Name :
Spectrum Operation:






**Methyl (*S*)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2b)**




**2b**

The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), methyl chloroformate (30 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2b** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) [Colorless oil, 91% yield, 81% ee, (*S*)-configuration].

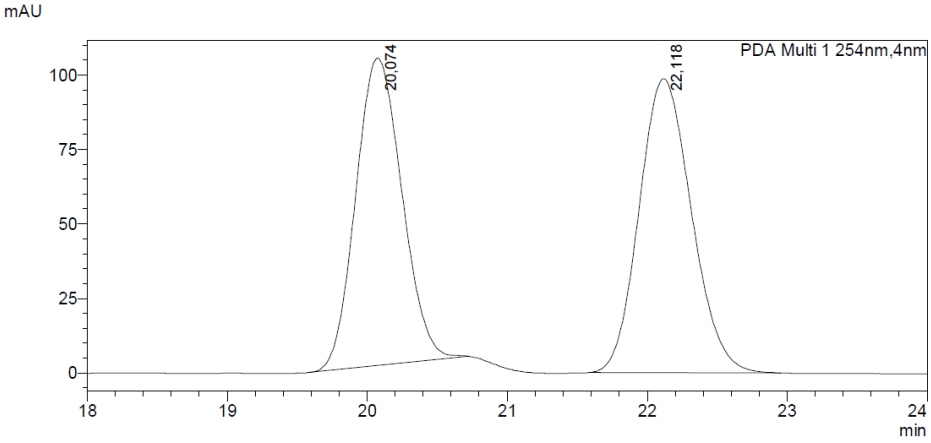
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 5.5 Hz , 1H, CH=C*H*N), 5.29 (d, *J* = 7.2 Hz, 1H, COC*H*=CH), 4.50-4.40 (br s, 1H, C*H*$CH_2CH_3$), 3.84 (s, 3H, O$CH_3$), 2.77 (dd, *J* = 16.5, 6.6 Hz, 1H, COC$H_2$), 2.46 (d, *J* = 16.6 Hz, 1H, COC$H_2$), 1.76-1.55 (m, 2H, C$H_2$$CH_3$), 0.88 (t, *J* = 7.5 Hz, 3H, $CH_2$C$H_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.26, 153.45, 141.72, 107.22, 54.81, 54.19, 39.39, 23.68, 10.29.

HRMS (ESI+, m/Z): calcd for $C_9H_{13}NO_3$ $[M+H]^+$: 184.0968, found: 184.0967.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 254 nm. Retention time (min): 19.8 (minor) and 21.6 (major).

**<Chromatogram>**

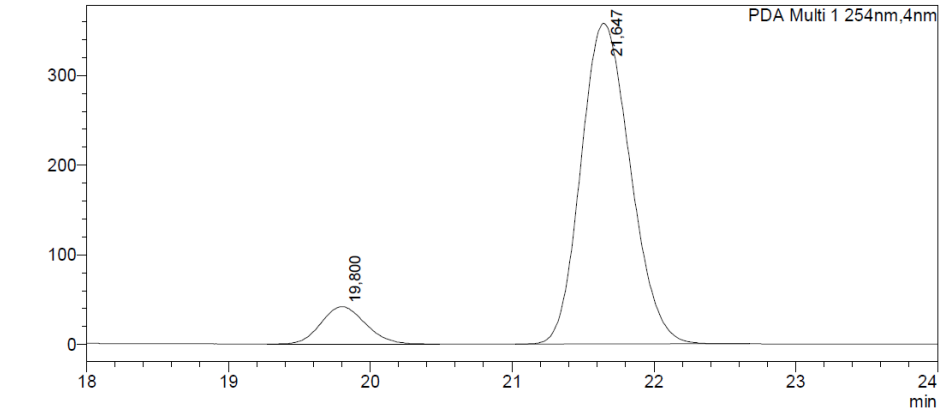



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 20,074 | 2367933 | 103185 | 47,978 | | M | |
| 2 | 22,118 | 2567536 | 98650 | 52,022 | | M | |
| Total | | 4935469 | 201835 | | | | |

**<Chromatogram>**

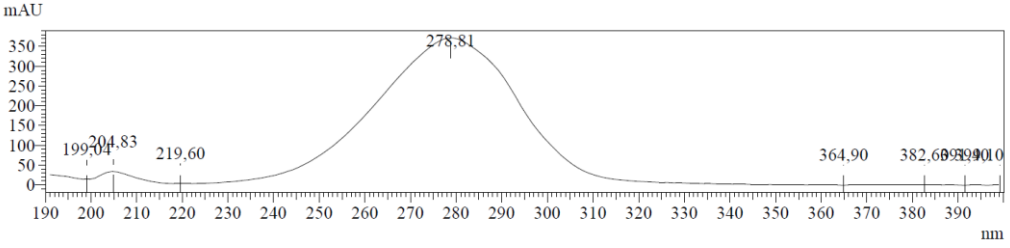


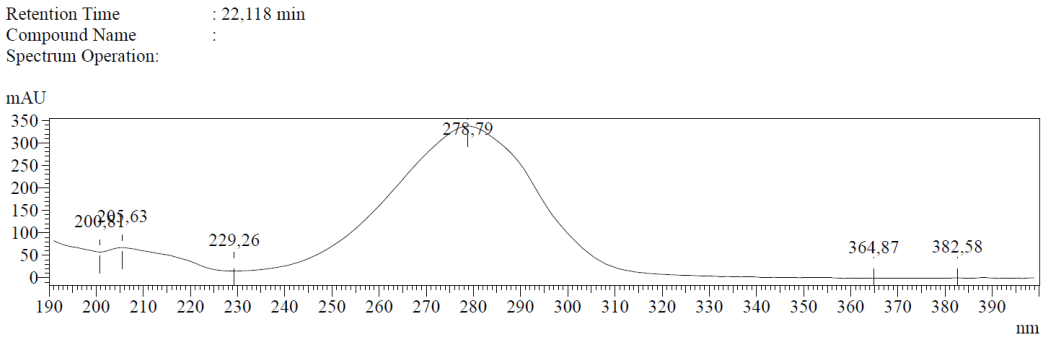

**<Peak Table>**

PDA Ch1 254nm

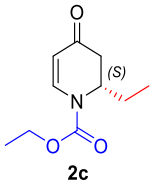
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 19,800 | 904426 | 41616 | 9,440 | | | |
| 2 | 21,647 | 8675970 | 358014 | 90,560 | | | |
| Total | | 9580396 | 399630 | | | | |

Retention Time : 20,074 min
Compound Name :
Spectrum Operation:






**Ethyl (*S*)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2c)**




**2c**

The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), ethyl chloroformate (38 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2c** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) [Colorless oil, 88% yield, 98% ee, (*S*)-configuration].

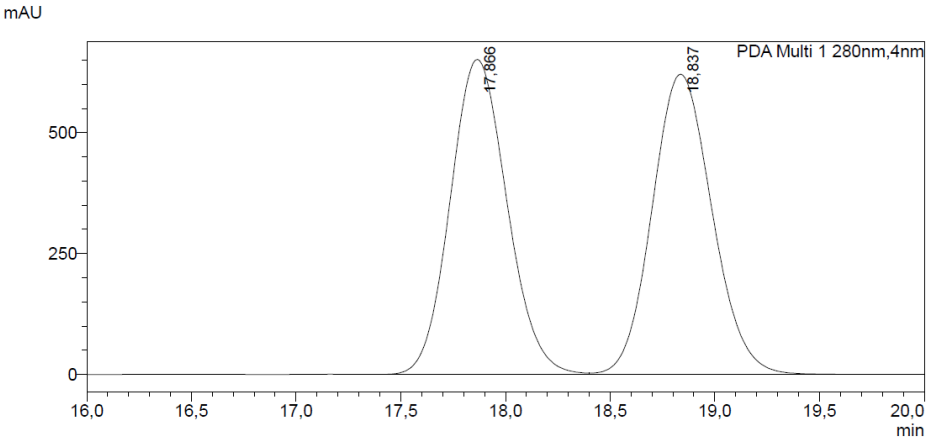
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 1H, CH=C*H*N), 5.29 (d, *J* = 8.2 Hz, 1H, COC*H*=CH), 4.45-4.44 (m, 1H, C*H*$CH_2CH_3$), 4.36-4.22 (m, 2H, OC*H*$_2CH_3$), 2.78 (dd, *J* = 16.6, 6.6 Hz, 1H, COC*H*$_2$), 2.46 (d, *J* = 16.6 Hz, 1H, COC*H*$_2$), 1.75-1.55 (m, 2H, C*H*$_2CH_3$), 1.32 (t, *J* = 7.1 Hz, 3H, $OCH_2$C*H*$_3$), 0.89 (t, *J* = 7.5 Hz, 3H, $CH_2$C*H*$_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.28, 141.82, 106.96, 63.48, 54.62, 39.44, 30.42, 23.69, 14.46, 10.34.

HRMS (ESI+, m/Z): calcd for $C_{10}H_{15}NO_3$ $[M+H]^+$: 198.1124, found: 198.1124.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 17.3 (minor) and 18.3 (major).

**<Chromatogram>**

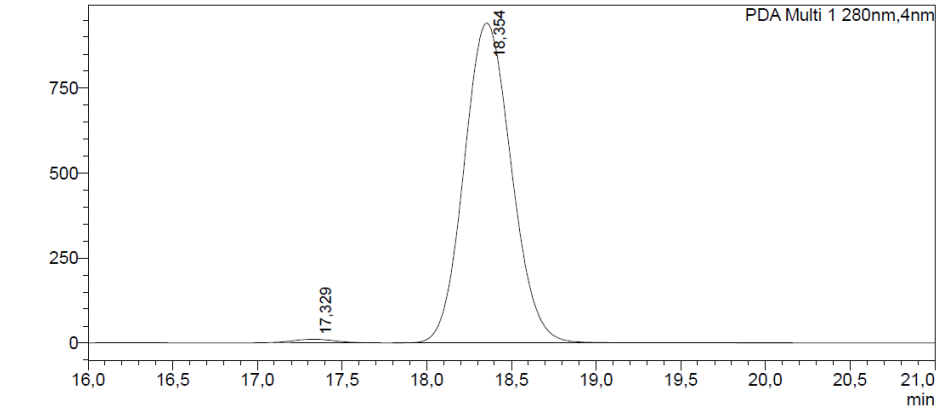



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,866 | 12296615 | 651741 | 49,880 | | | |
| 2 | 18,837 | 12355956 | 621362 | 50,120 | | V | |
| Total | | 24652572 | 1273103 | | | | |

**<Chromatogram>**

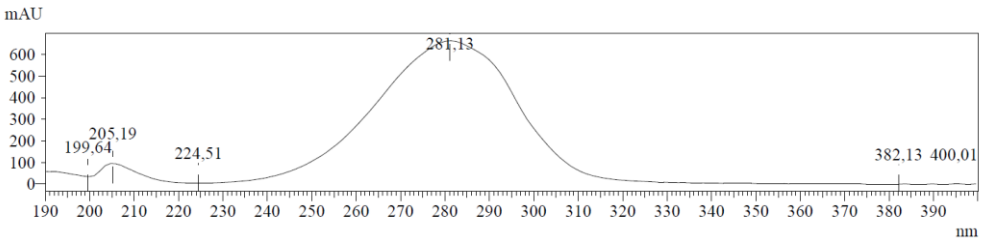


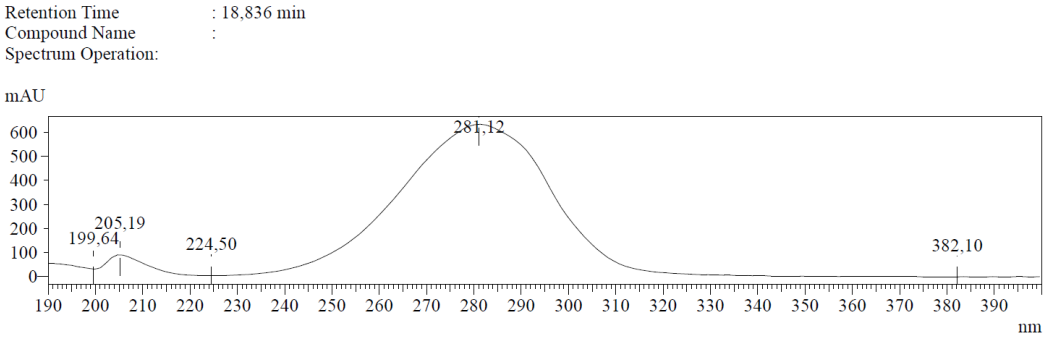

**<Peak Table>**

PDA Ch1 280nm

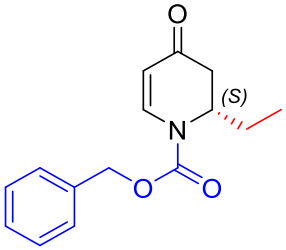
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,329 | 155237 | 9867 | 0,842 | | M | |
| 2 | 18,354 | 18272820 | 941038 | 99,158 | | M | |
| Total | | 18428056 | 950905 | | | | |

Retention Time : 17,865 min
Compound Name :
Spectrum Operation:






**Benzyl (*S*) 2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2d)**[ix]




**2d**

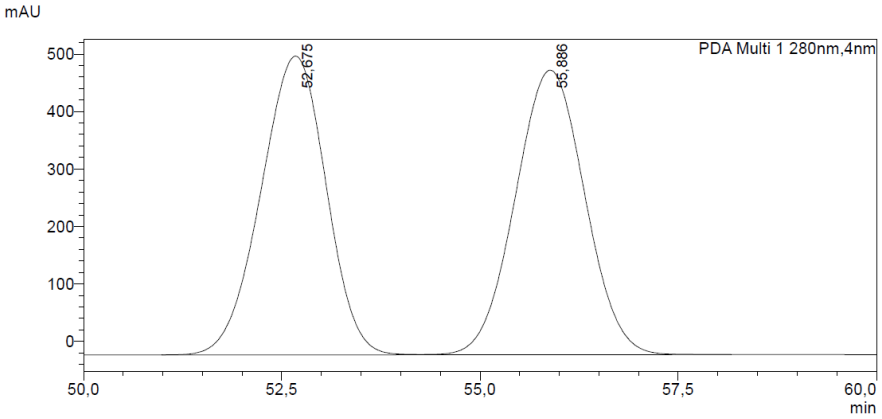
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2d** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) [Colorless oil, 96% yield, >99% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.16 Hz, 1H, CH=C*H*N), 7.38 (s, 5H, C$H_{Ar}$), 5.30 (d, *J* = 8.40 Hz, 1H, COC*H*=CH), 5.25 (s, 2H, C$H_2$Bn), 4.58-4.45 (m, 1H, C*H*$CH_2CH_3$), 2.78 (dd, *J* = 16.6, 6.6 Hz, 1H, COC$H_2$), 2.46 (d, *J* = 16.7 Hz, 1H, COC$H_2$), 1.77-1.56 (m, 2H, C$H_2CH_3$), 0.88 (t, *J* = 7.5 Hz, 3H, C$H_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.27, 152.71, 141.66, 135.12, 128.90, 128.87, 128.55, 107.30, 69.12, 54.82, 39.41, 23.75, 10.33.

HPLC analysis: Chiracel-ODH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): not found (minor) and 58.1 (major).

**<Chromatogram>**

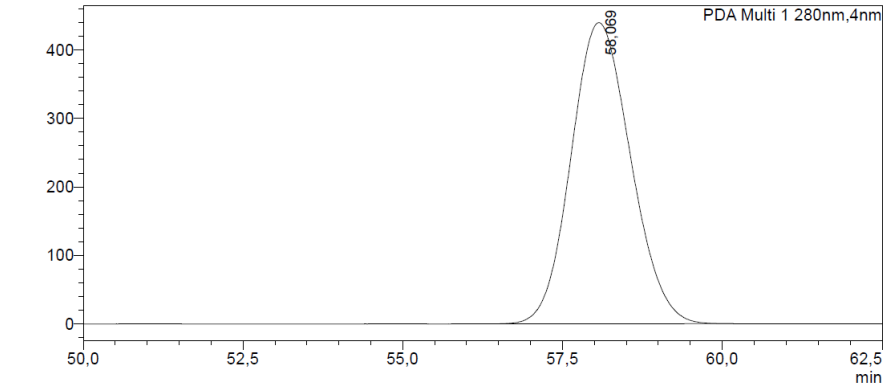



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 52,675 | 29741478 | 519984 | 49,630 | | | |
| 2 | 55,886 | 30185500 | 495234 | 50,370 | | V | |
| Total | | 59926978 | 1015218 | | | | |

**<Chromatogram>**

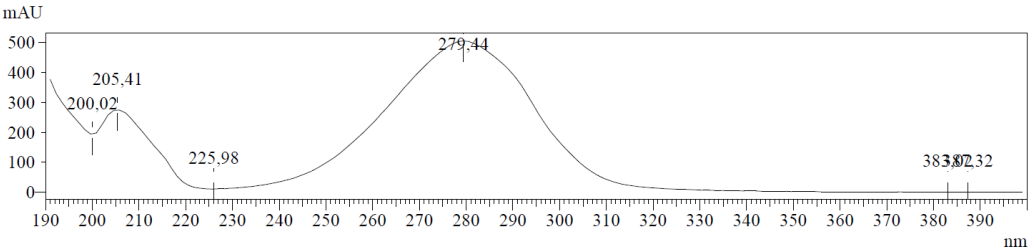


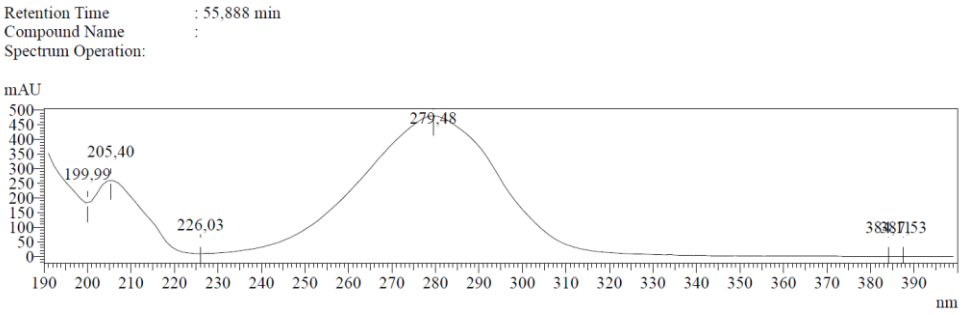

**<Peak Table>**

PDA Ch1 280nm

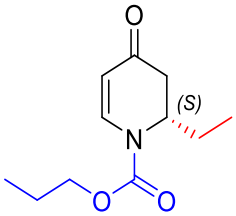
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 58,069 | 28532115 | 439821 | 0,000 | | M | |
| Total | | 28532115 | 439821 | | | | |

Retention Time : 52,674 min
Compound Name :
Spectrum Operation:






**Propyl (*S*)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2e)**




**2e**

The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), propyl chloroformate (45 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2e** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) [Colorless oil, 92% yield, 90% ee, (*S*)-configuration].

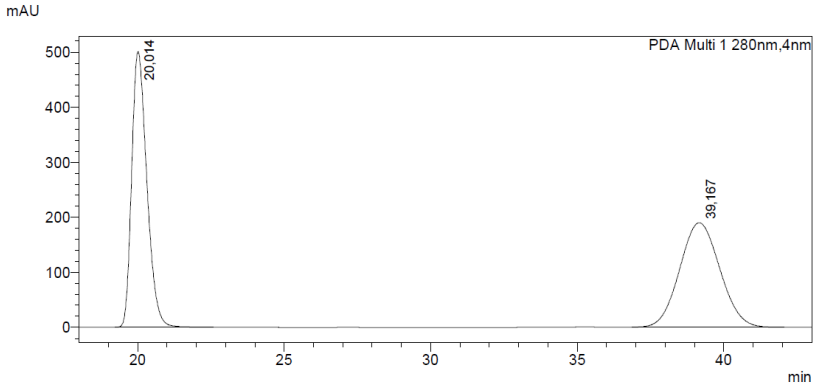
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.0 Hz, 1H, CH=C*H*N), 5.31 (d, *J* = 8.7 Hz, 1H, COC*H*=CH), 4.56-4.44 (m, 1H, C*H*$CH_2CH_3$), 4.20 (t, *J* = 6.7 Hz, 2H, OC*H*$_2CH_2CH_3$), 2.80 (dd, *J* = 16.6, 6.6 Hz, 1H, COC*H*$_2$), 2.40 (d, *J* = 16.6 Hz, 1H, COC*H*$_2$), 1.79-1.59 (m, 4H, C*H*$_2CH_3$ and $OCH_2CH_2CH_3$), 0.99 (t, *J* = 7.4 Hz, 3H, $OCH_2CH_2CH_3$), 0.91 (t, *J* = 7.5 Hz, 3H, $CH_2CH_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.18, 152.86, 141.79, 106.90, 68.94, 54.58, 39.33, 23.63, 22.10, 10.37, 10.24.

HRMS (ESI+, m/Z): calcd for $C_{11}H_{17}NO_3$ $[M+H]^+$: 212.1281, found: 212.1280.

HPLC analysis: Chiracel-OBH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 19.5 (minor) and 37.4 (major).

**<Chromatogram>**

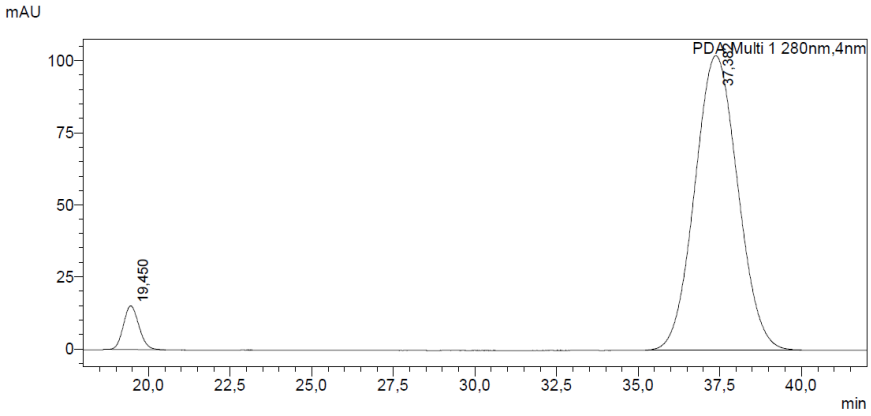



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 20,014 | 18020054 | 500747 | 49,867 | | | |
| 2 | 39,167 | 18116137 | 189886 | 50,133 | | | |
| Total | | 36136190 | 690633 | | | | |

**<Chromatogram>**

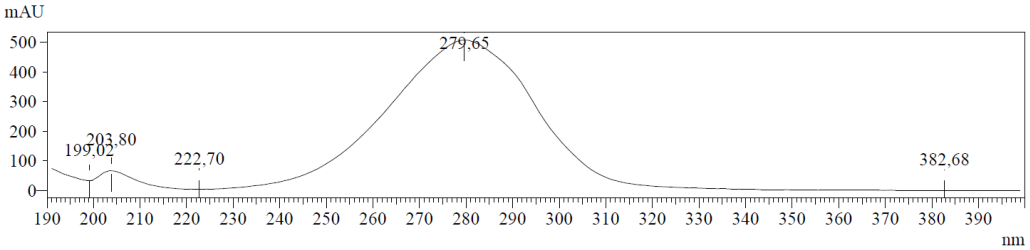


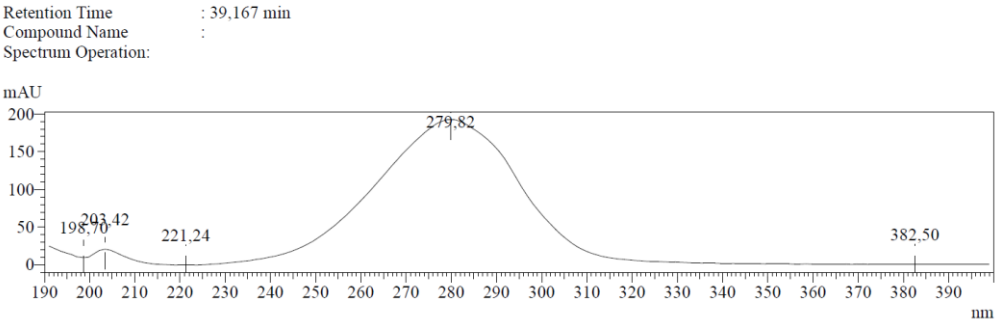

**<Peak Table>**

PDA Ch1 280nm

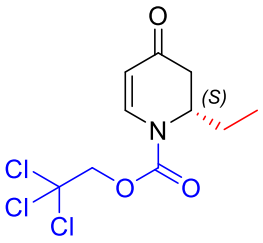
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 19,450 | 503286 | 15197 | 5,098 | | | |
| 2 | 37,382 | 9369826 | 102253 | 94,902 | | | |
| Total | | 9873112 | 117449 | | | | |

Retention Time : 20,014 min
Compound Name :
Spectrum Operation:






**2,2,2-trichloroethyl (*S*)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2g)**




**2g**

The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), 2,2,2-trichloroethyl chloroformate (55 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 $^oC$. Product **2g** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 1:1) [Colorless oil, 86% yield, 90% ee, (*S*)-configuration].

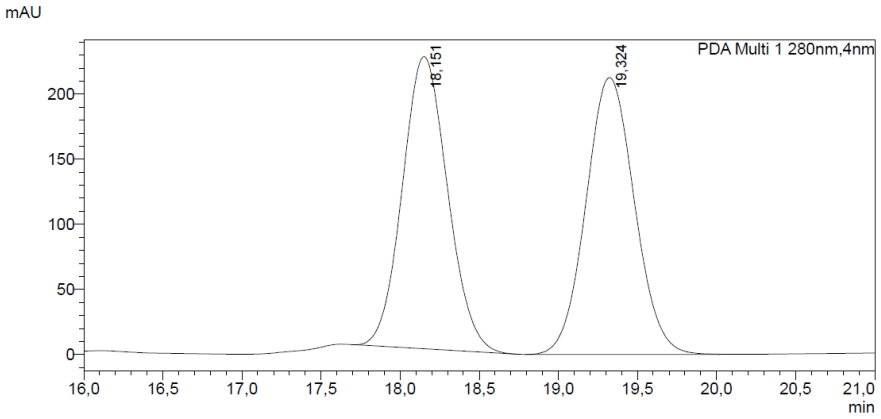
$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1H, CH=C*H*N), 5.41 (d, *J* = 7.2 Hz, 1H, COC*H*=CH), 4.87 (br s, 2H, $CCl_3CH_2$), 4.61-4.51 (m, 1H, $CHCH_2CH_3$), 2.84 (dd, *J* = 16.8, 6.6 Hz, 1H, $COCH_2$), 2.53 (d, *J* = 16.7 Hz, 1H, $COCH_2$), 1.83-1.65 (m, 2H, $CH_2CH_3$), 0.93 (t, *J* = 7.5 Hz, 3H, $CH_2CH_3$).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 192.90, 151.11, ($CCl_3$; 141.35, 140.29), 108.74, 94.61, 75.96, 55.39, 39.43, 23.90, 10.34.

HRMS (ESI+, m/Z): calcd for $C_{10}H_{12}Cl_3NO_3$ $[M+H]^+$: 299.9955, found: 299.9958.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 $^oC$, detection at 280 nm. Retention time (min): 17.9 (major) and 18.9 (minor).

**<Chromatogram>**

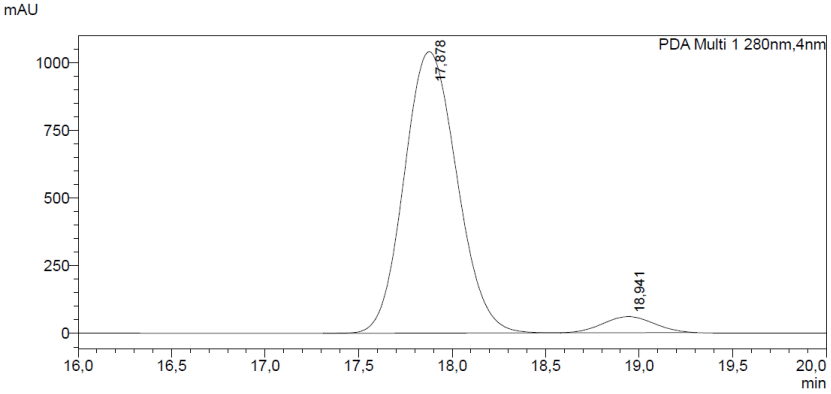



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18,151 | 4463614 | 224405 | 49,585 | | | |
| 2 | 19,324 | 4538340 | 212618 | 50,415 | | | |
| Total | | 9001955 | 437022 | | | | |

**<Chromatogram>**

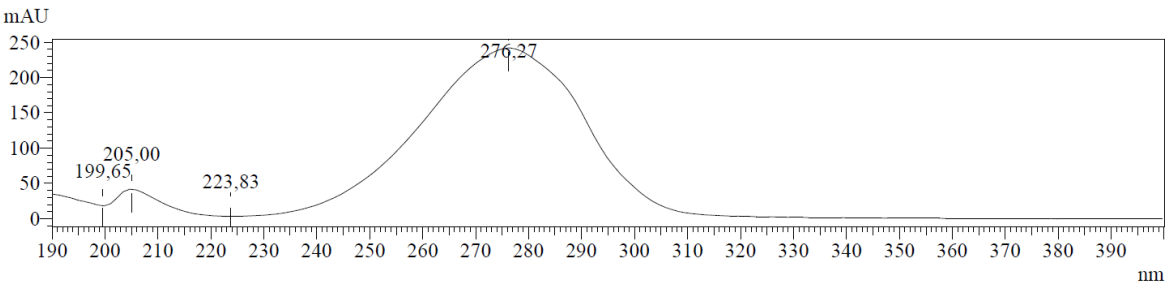



**<Peak Table>**

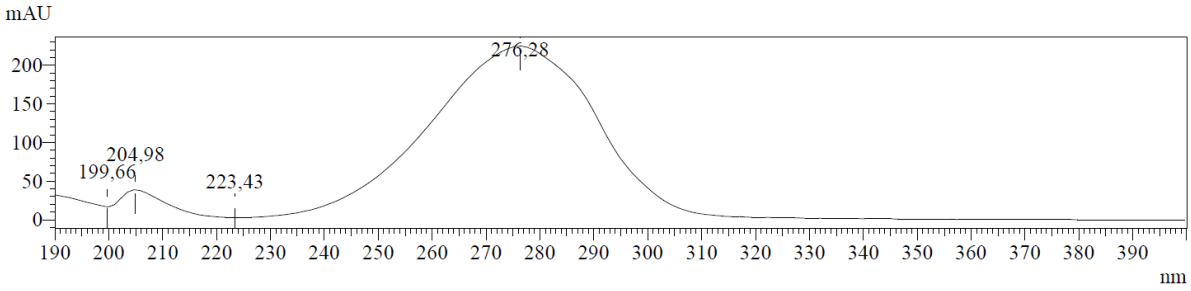
PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,878 | 20403932 | 1040609 | 94,781 | | M | |
| 2 | 18,941 | 1123547 | 59197 | 5,219 | | M | |
| Total | | 21527479 | 1099806 | | | | |

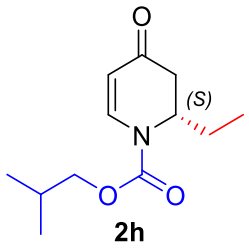
Retention Time : 18,150 min
Compound Name :
Spectrum Operation:



Retention Time : 19,324 min
Compound Name :
Spectrum Operation:




**Isobutyl (*S*)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2h)**




**2h**

The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), isobutyl chloroformate (52 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2h** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 4:1) [Colorless oil, 82% yield, 90% ee, (*S*)-configuration].

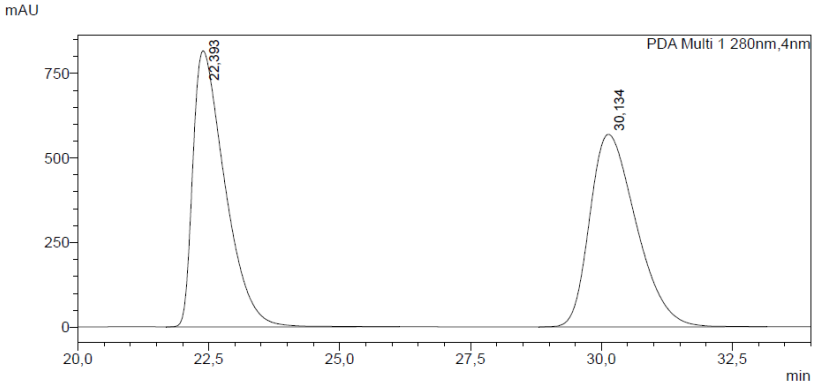
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.8 Hz, 1H, CH=C*H*N), 5.31 (d, *J* = 8.5 Hz, 1H, COC*H*=CH), 4.54-4.41 (m, 1H, C*H*$CH_2CH_3$), 4.02 (d, *J* = 6.6 Hz, 2H, $COOCH_2$), 2.80 (dd, *J* = 16.7, 6.6 Hz, 1H, $COCH_2$), 2.48 (d, *J* = 16.6 Hz, 1H, $COCH_2$), 2.08-1.93 (m, 1H, $COOCH_2CH(CH_3)_2$), 1.71-1.63 (m, 2H, $CH_2CH_3$), 0.98 (d, *J* = 6.7 Hz, 6H, 2x$CH_3$), 0.91 (t, *J* = 7.5 Hz, 3H, $CH_2CH_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.23, 152.84, 141.77, 106.89, 73.36, 54.62, 39.24, 27.87, 23.62, 19.05, 10.24

HRMS (ESI+, m/Z): calcd for $C_{12}H_{19}NO_3$ $[M+H]^+$: 226.1437, found: 226.1438.

HPLC analysis: Chiracel-OBH, *n*heptane/*i*PrOH 95:5, 0.5 ml/min, 40 °C, detection at 280 nm. Retention time (min): 23.1 (minor) and 29.1 (major).

**<Chromatogram>**

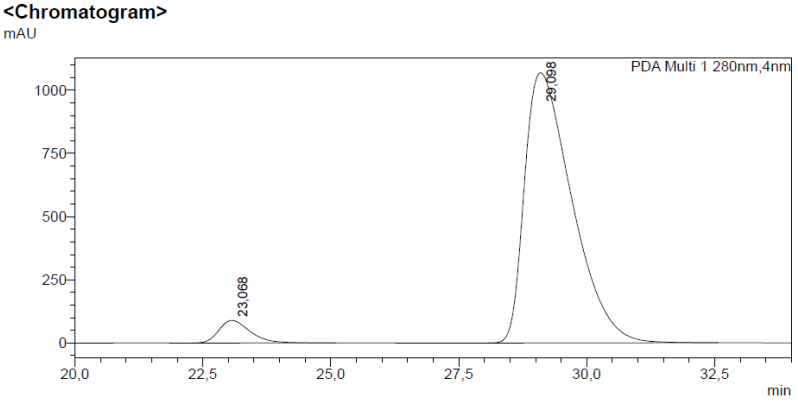



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 22,393 | 34765785 | 816213 | 49,763 | | | |
| 2 | 30,134 | 35097259 | 569332 | 50,237 | | | |
| Total | | 69863044 | 1385545 | | | | |

**<Chromatogram>**

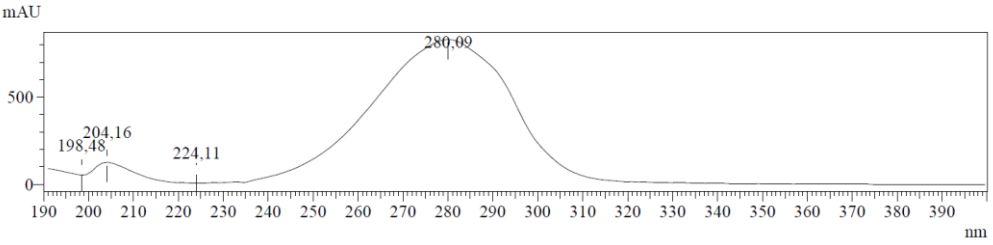


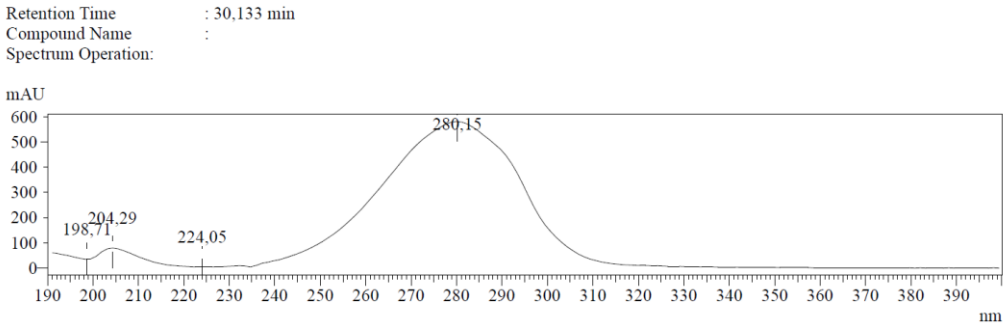

**<Peak Table>**

PDA Ch1 280nm

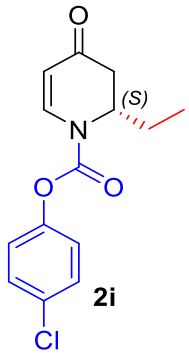
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 23,068 | 3787786 | 89151 | 5,219 | | | |
| 2 | 29,098 | 68795989 | 1068427 | 94,781 | | | |
| Total | | 72583774 | 1157579 | | | | |

Retention Time : 22,393 min
Compound Name :
Spectrum Operation:






**4-Chlorophenyl (*S*)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2i)**




The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), 4-chlorophenyl chloroformate (56 µL, 0.4 mmol), EtMgBr (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2i** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 1:1) [Colorless oil, 98% yield, 98% ee, (*S*)-configuration].

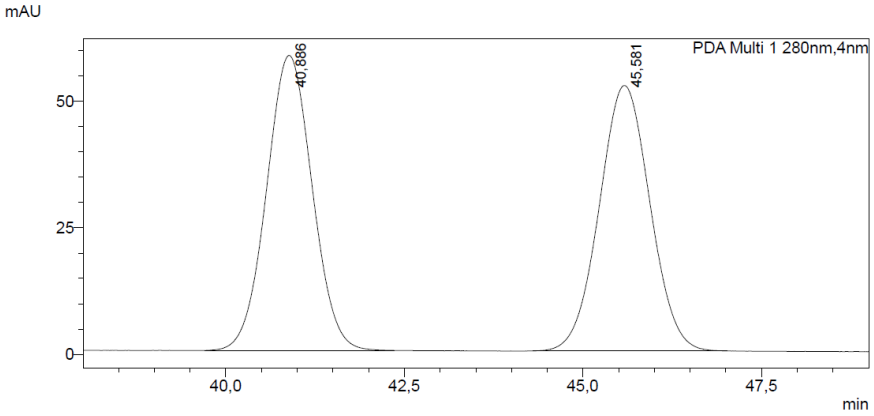
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.4, 1.3 Hz, 1H, C$H_{Ar}$), 7.42-7.34 (m, 2H, C$H_{Ar}$+CH=C$\underline{H}$N*), 7.13-7.07 (m, 2H, C$H_{Ar}$ +CH=C$\underline{H}$N*), 5.42 (d, *J* = 7.7 Hz, 1H, COC$\underline{H}$=CH), 4.70-4.55 (m, 1H, C$\underline{H}$$CH_2CH_3$), 2.89 (dd, *J* = 16.6, 6.4 Hz, 1H, COC$\underline{H_2}$), 2.54 (d, *J* = 16.6 Hz, 1H, COC$\underline{H_2}$), 1.93-1.63 (m, 2H, C$\underline{H_2}$$CH_3$), 0.97 (t, *J* = 7.2 Hz, 3H, $CH_2$C$\underline{H_3}$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.96, 151.12, 149.04, 140.85, 131.95, 129.81, 122.78, 108.50, 55.39, 39.61, 23.95, 10.45.

HRMS (ESI+, m/Z): calcd for $C_{14}H_{14}ClNO_3$ $[M+H]^+$: 280.0735, found: 280.0735.

HPLC analysis: Chiracel-ODH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 40.2 (minor) and 44.7 (major).

**<Chromatogram>**

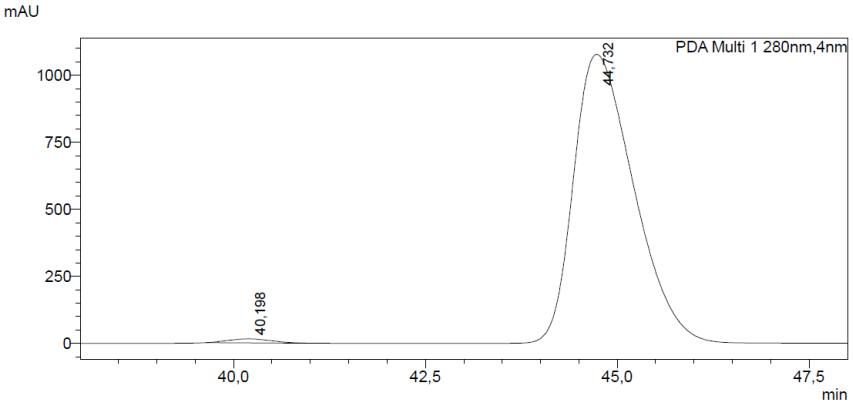



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 40,886 | 2594148 | 58217 | 50,043 | | | |
| 2 | 45,581 | 2589655 | 52375 | 49,957 | | | |
| Total | | 5183804 | 110593 | | | | |

**<Chromatogram>**

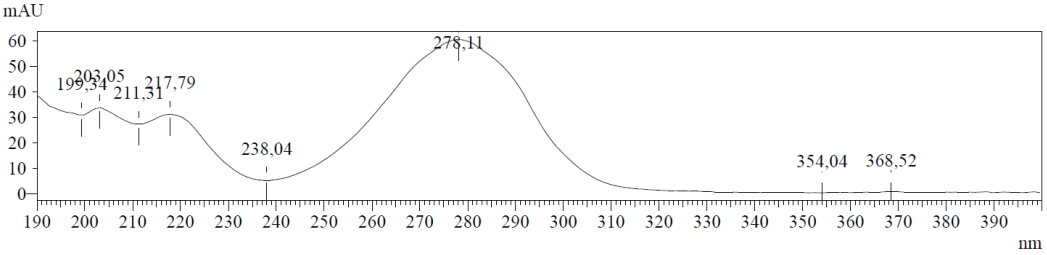


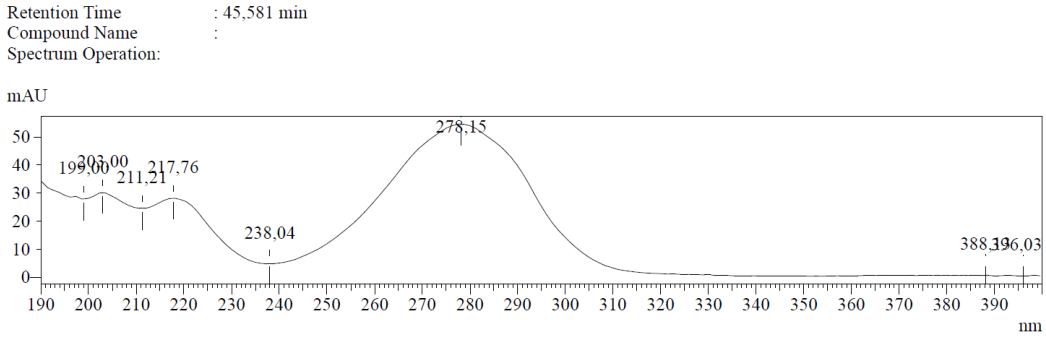

**<Peak Table>**

PDA Ch1 280nm

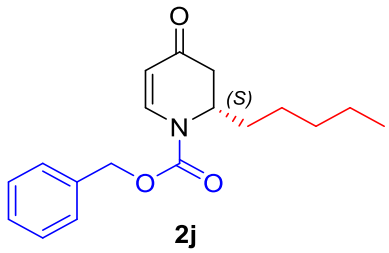
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 40,198 | 576056 | 14808 | 0,966 | | M | |
| 2 | 44,732 | 59027882 | 1077859 | 99,034 | | M | |
| Total | | 59603938 | 1092666 | | | | |

Retention Time : 40,886 min
Compound Name :
Spectrum Operation:






**Benzyl (*S*)-4-oxo-2-pentyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2j)** [ix]




**2j**

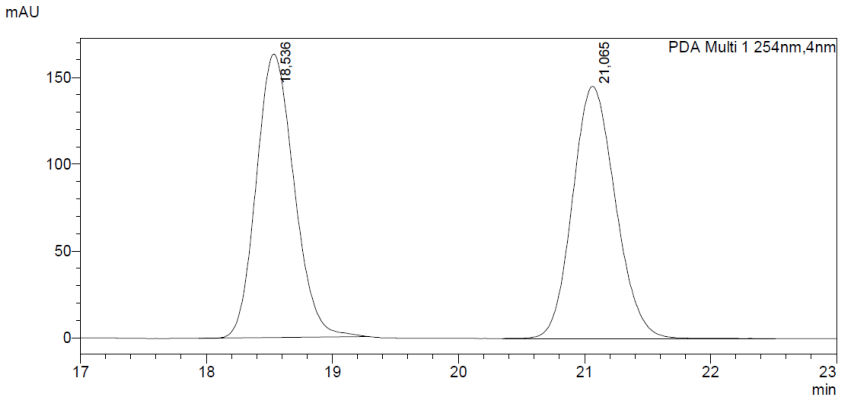
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), *n*PentMgBr (0.4 mmol, 2.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2j** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 4:1) [Colorless oil, 92% yield, 98% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.7 Hz, 1H, CH=C*H*N), 7.38 (s, 5H, C$H_{Ar}$), 5.34-5.28 (m, 1H, COC*H*=CH), 5.26 (d, 2H, *J* = 4.9 Hz, C$H_2$Bn), 4.57 (d, *J* = 5.5 Hz, 1H, C*H*$(CH_2)_4CH_3$), 2.78 (dd, *J* = 16.7, 6.5 Hz, 1H, COC$H_2$), 2.44 (d, *J* = 16.5 Hz, 1H, COC$H_2$), 1.67-1.55 (m, 2H, C$H_2(CH_2)_3CH_3$), 1.29-1.10 (m, 6H, $CH_2$(C$H_2$)$_3CH_3$), 0.84 (t, *J* = 6.6 Hz, 3H, C$H_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.33, 152.68, 141.68, 135.12, 128.91, 128.86, 128.59, 107.26, 69.12, 53.56, 39.75, 31.52, 30.54, 25.42, 22.52, 14.04.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 254 nm. Retention time (min): 17.6 (minor) and 20.3 (major).

**<Chromatogram>**

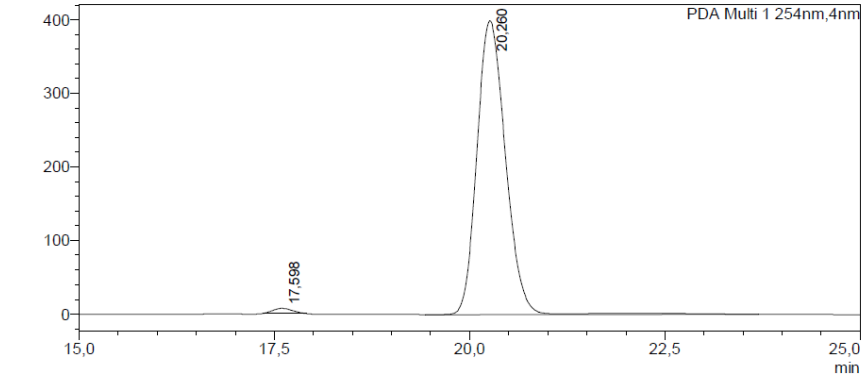



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18,536 | 3413164 | 163264 | 49,842 | | M | |
| 2 | 21,065 | 3434735 | 145128 | 50,158 | | M | |
| Total | | 6847899 | 308392 | | | | |

**<Chromatogram>**

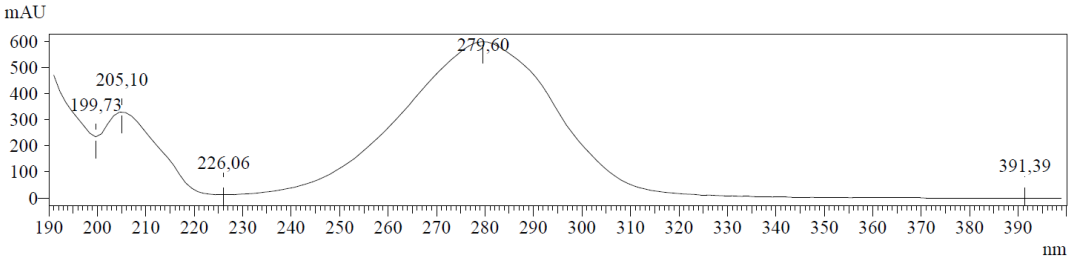


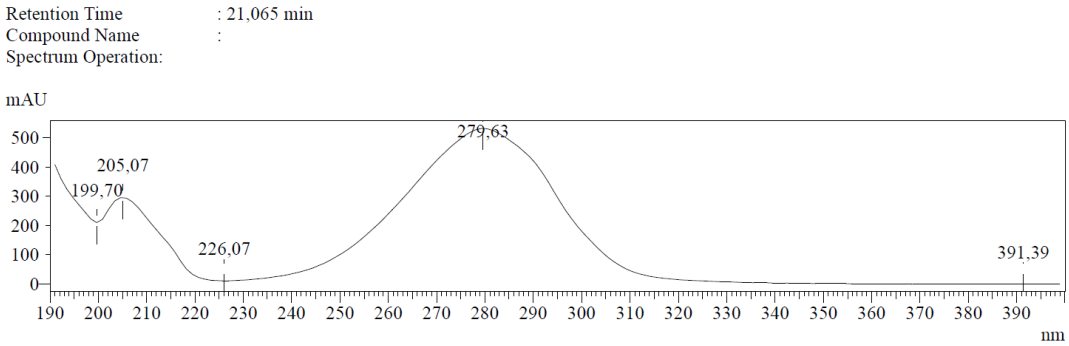

**<Peak Table>**

PDA Ch1 254nm

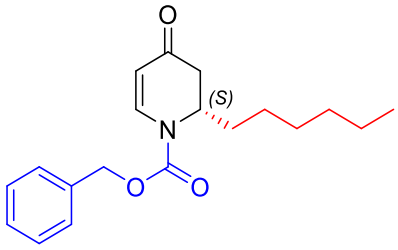
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,598 | 121591 | 6947 | 1,177 | | M | |
| 2 | 20,260 | 10212904 | 398969 | 98,823 | | M | |
| Total | | 10334495 | 405916 | | | | |

Retention Time : 18,536 min
Compound Name :
Spectrum Operation:






**Benzyl (S)-2-hexyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2k)** [ix]




**2k**

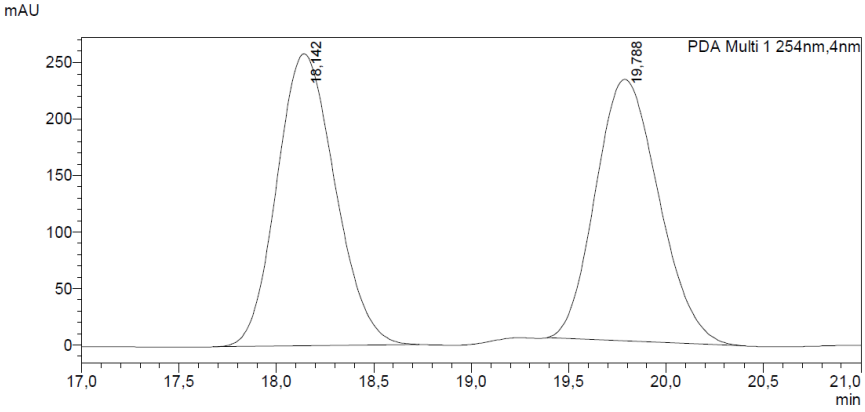
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), *n*HexMgBr (0.4 mmol, 2.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2k** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 4:1) [Colorless oil, 95% yield, 98% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.7 Hz, 1H, CH=C*H*N), 7.38 (s, 5H, C$H_{Ar}$), 5.35-5.29 (m, 1H, COC*H*=CH), 5.24 (d, *J* = 4.9 Hz, 2H, C$H_2$Bn), 4.64-4.50 (m, 1H, C*H*$(CH_2)_5CH_3$), 2.79 (dd, *J* = 16.5, 6.6 Hz, 1H, COC$H_2$), 2.44 (d, *J* = 16.6 Hz, 1H, COC$H_2$), 1.67-1.55 (m, 2H, C$H_2(CH_2)_4CH_3$), 1.30-1.10 (m, 8H, $CH_2$(C$H_2)_4CH_3$), 0.85 (t, *J* = 6.8 Hz, 3H, C$H_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.28, 152.71, 141.68, 135.15, 128.92, 128.88, 128.60, 107.32, 69.13, 53.61, 39.82, 31.72, 30.66, 29.08, 25.77, 22.64, 14.15.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 254 nm. Retention time (min): 16.3 (minor) and 18.6 (major).

**<Chromatogram>**

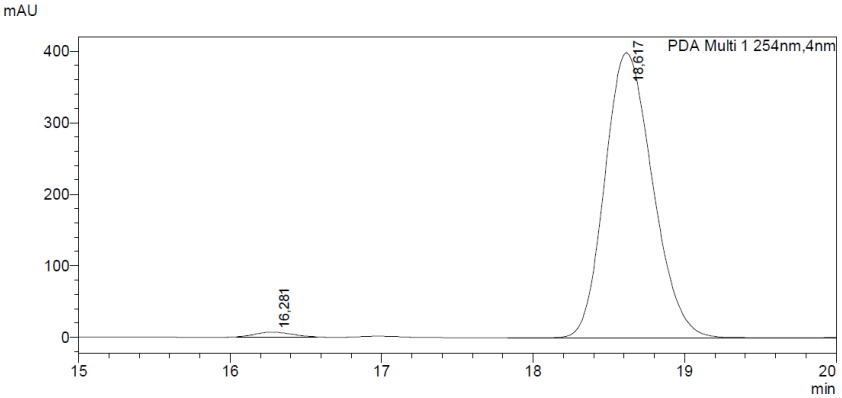



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18,142 | 5379457 | 258409 | 50,653 | | M | |
| 2 | 19,788 | 5240793 | 231690 | 49,347 | | M | |
| Total | | 10620250 | 490098 | | | | |

**<Chromatogram>**

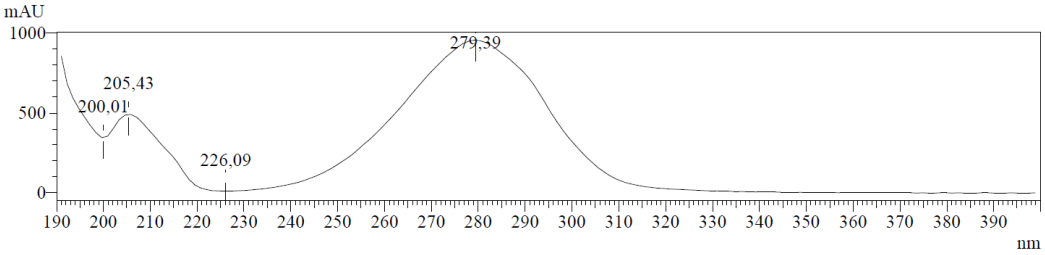


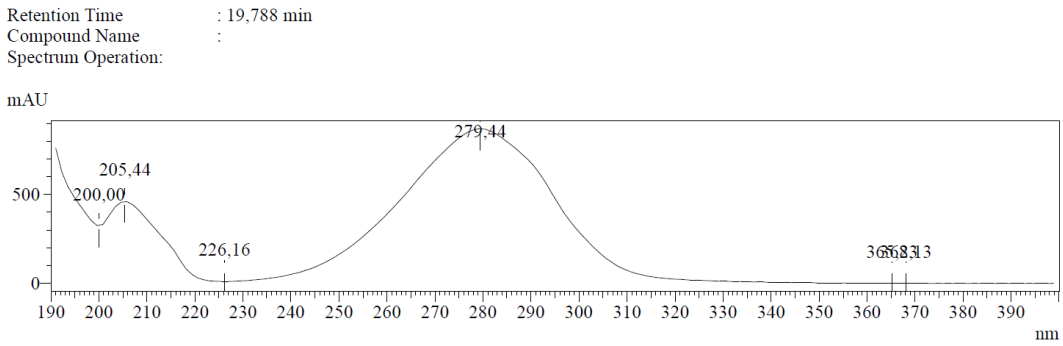

**<Peak Table>**

PDA Ch1 254nm

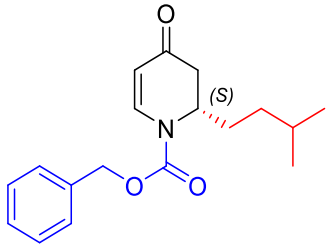
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 16,281 | 106682 | 6542 | 1,206 | | M | |
| 2 | 18,617 | 8737377 | 398085 | 98,794 | | M | |
| Total | | 8844060 | 404626 | | | | |

Retention Time : 18,142 min
Compound Name :
Spectrum Operation:






**Benzyl (*S*)-2-isopentyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2l)** [ix]




**2l**

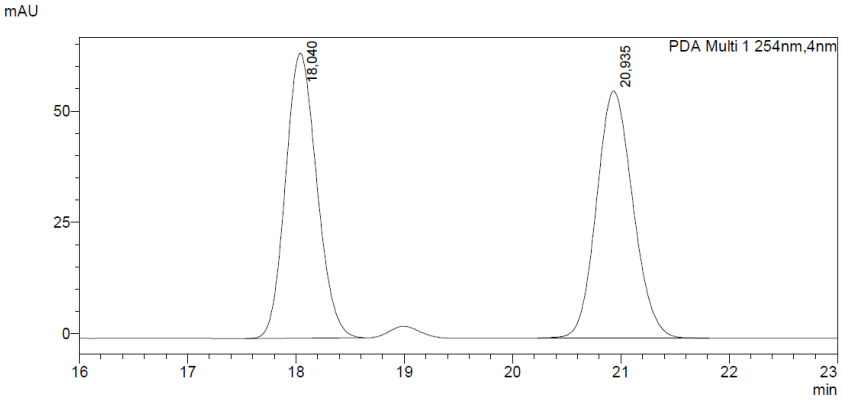
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), *i*PentMgBr (0.4 mmol, 2.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2l** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 4:1) [Colorless oil, 90% yield, 99% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.9 Hz, 1H, CH=C*H*N), 7.41-7.35 (m, 5H, C$H_{Ar}$), 5.34-5.20 (m, 3H, C$H_2$Bn, COC*H*=CH), 4.62-4.47 (m, 1H, C*H*$(CH_2)_2CH(CH_3)_2$), 2.79 (dd, *J* = 16.6, 6.6 Hz, 1H, COC$H_2$), 2.45 (d, *J* = 16.5 Hz, 1H, COC$H_2$), 1.71-1.54 (m, 2H, CHC$H_2CH_2CH(CH_3)_2$), 1.52-1.40 (m, 1H, $CHCH_2CH_2CH(CH_3)_2$), 1.27-1.01 (m, 2H, $CHCH_2CH_2CH(CH_3)_2$), 0.83 (m, 6H, C$H_3$).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 193.35, 152.67, 141.70, 135.12, 128.94, 128.89, 128.64, 107.32, 69.15, 53.83, 39.78, 34.77, 28.43, 27.94, 22.69, 22.36.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 254 nm. Retention time (min): 17.1 (minor) and 19.8 (major).

**<Chromatogram>**

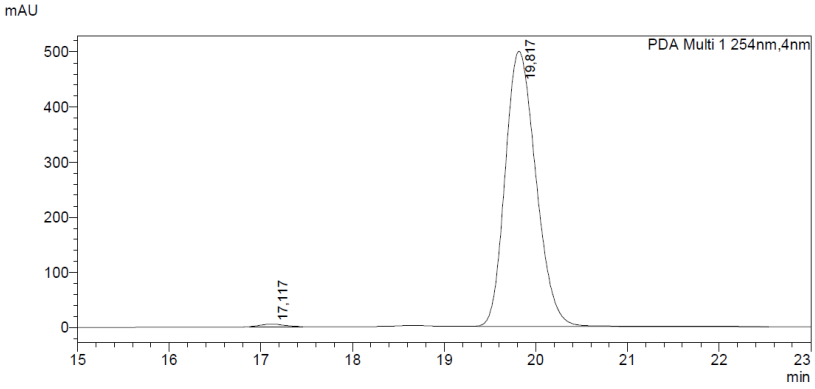



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18,040 | 1287476 | 63945 | 49,833 | | M | |
| 2 | 20,935 | 1296089 | 55430 | 50,167 | | M | |
| Total | | 2583565 | 119375 | | | | |

**<Chromatogram>**

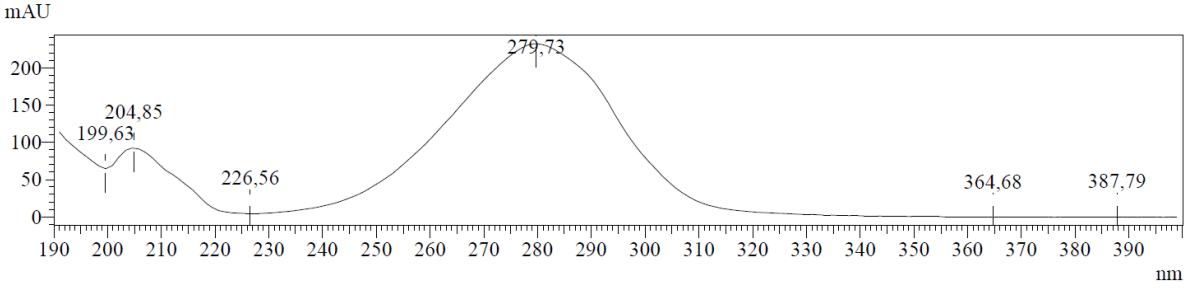



**<Peak Table>**

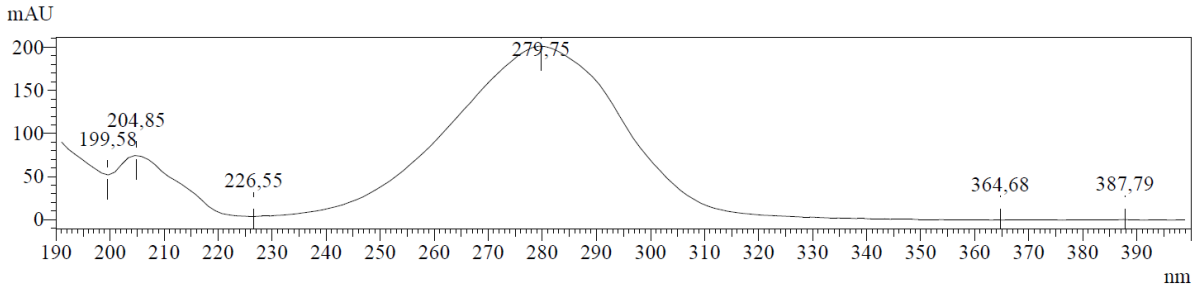
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,117 | 78446 | 4528 | 0,669 | | M | |
| 2 | 19,817 | 11655420 | 498783 | 99,331 | | M | |
| Total | | 11733867 | 503310 | | | | |

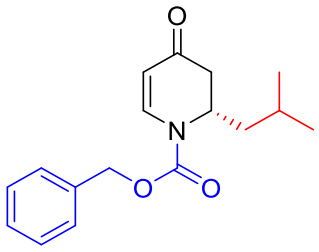
Retention Time : 18,040 min
Compound Name :
Spectrum Operation:



Retention Time : 20,935 min
Compound Name :
Spectrum Operation:




**Benzyl (*S*)-2-isobutyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2m)** [ix]




**2m**

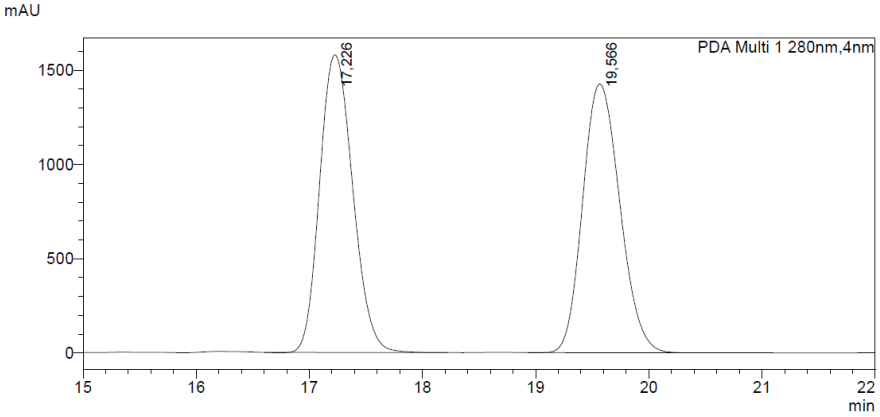
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), *i*BuMgBr (0.4 mmol, 2.0 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2m** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 4:1) [Colorless oil, 81% yield, 80% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (br s, 1H, CH=C*H*N), 7.39 (s, 5H, C$H_{Ar}$), 5.38-5.15 (m, 3H, C$H_2$Bn, COC*H*=CH), 4.65 (br s, 1H, C*H*$CH_2CH(CH_3)_2$), 2.78 (dd, *J* = 16.6, 6.3 Hz, 1H, COC$H_2$), 2.42 (d, *J* = 16.4 Hz, 1H, COC$H_2$), 1.63-1.35I (m, 3H, $CHCH_2CH(CH_3)_2$), 1.00-0.72 (m, 6H, C$H_3$).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 193.22, 152.67, 141.70, 135.02, 128.92, 128.83, 128.67, 107.19, 69.14, 51.87, 39.64, 39.08, 24.51, 23.37, 21.67.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 17.1 (minor) and 18.4 (major).

**<Chromatogram>**

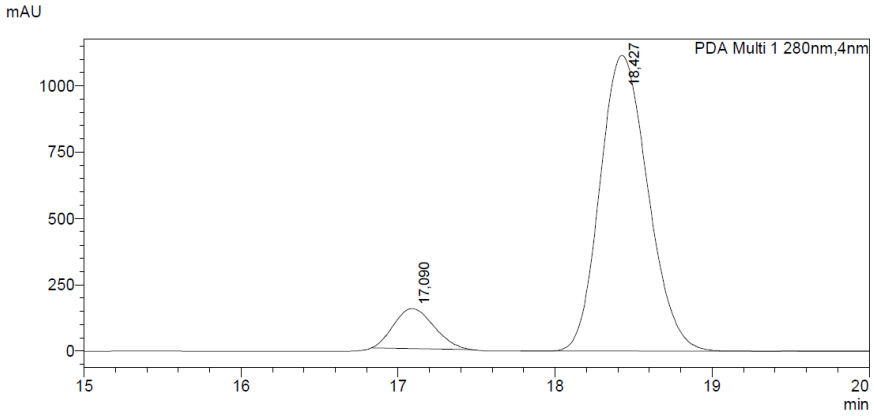



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,226 | 32145047 | 1579535 | 49,639 | | | |
| 2 | 19,566 | 32613200 | 1425620 | 50,361 | | | |
| Total | | 64758247 | 3005154 | | | | |

**<Chromatogram>**

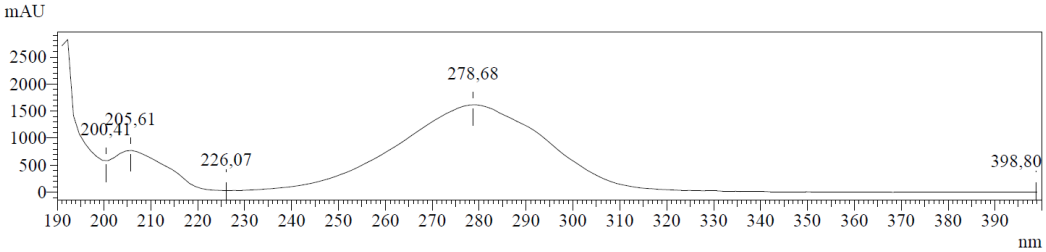


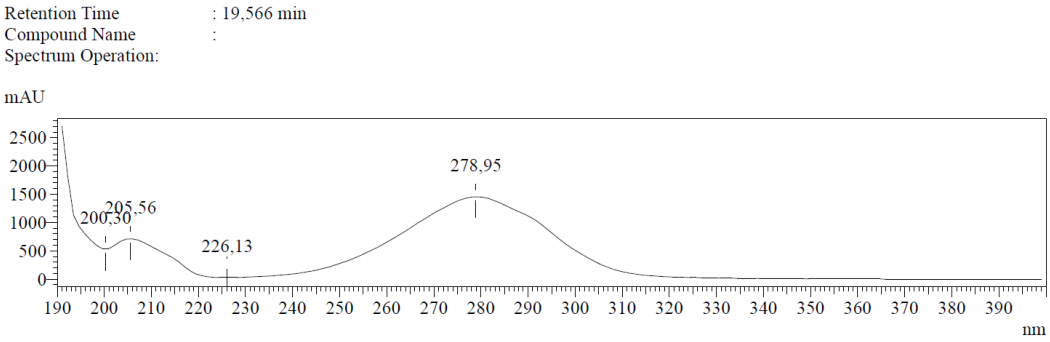

**<Peak Table>**

PDA Ch1 280nm

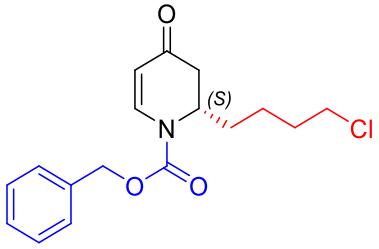
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,090 | 2686778 | 150905 | 10,189 | | M | |
| 2 | 18,427 | 23682842 | 1114635 | 89,811 | | M | |
| Total | | 26369620 | 1265540 | | | | |

Retention Time : 17,226 min
Compound Name :
Spectrum Operation:






**Benzyl (*S*)-2-(4-chlorobutyl)-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2n)** [ix]




**2n**

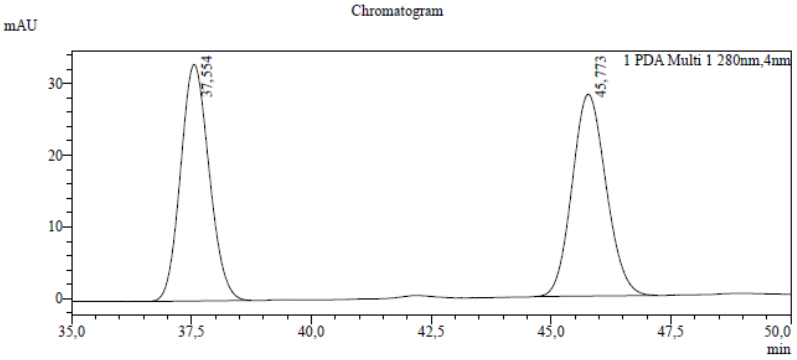
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), 4-ClBuMgBr (0.4 mmol, 1.2 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2n** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 2:1) [Colorless oil, 58% yield, 98% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.9 Hz, 1H, CH=C*H*N), 7.39 (s, 5H, C$H_{Ar}$), 5.40-5.19 (m, 3H, C$H_2$Bn, COC*H*=CH), 4.60 (br s, 1H, C*H*$(CH_2)_4$Cl), 3.45 (t, *J* = 5.8 Hz, 2H, C$H_2$Cl), 2.82 (dd, *J* = 16.5, 6.5 Hz, 1H, COC$H_2$), 2.44 (d, *J* = 16.5 Hz, 1H, COC$H_2$), 1.79-1.59 (m, 4H, $(CH_2)_3CH_2Cl$), 1.50-1.32 (m, 2H, $(CH_2)_3CH_2Cl$).

$^{13}$C NMR (101 MHz, CDCl3) δ 192.80, 141.35, 134.88, 128.85, 128.77, 128.55, 120.28, 107.27, 69.11, 53.12, 44.46, 39.77, 32.02, 29.81, 23.01.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 34.7 (minor) and 42.5 (major).

**<Chromatogram>**

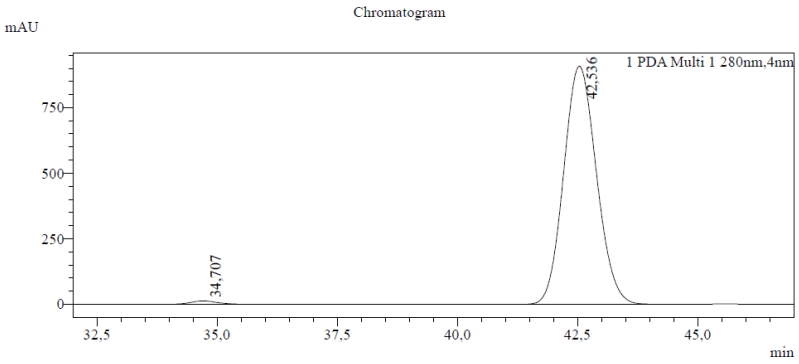



Peak Table

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Area% | Height | Conc. | Unit | Mark |
|---|---|---|---|---|---|---|---|
| 1 | 37,554 | 1368263 | 49,648 | 32954 | 0,000 | | |
| 2 | 45,773 | 1387658 | 50,352 | 28112 | 0,000 | | |
| Total | | 2755922 | 100,000 | 61066 | | | |

**<Chromatogram>**

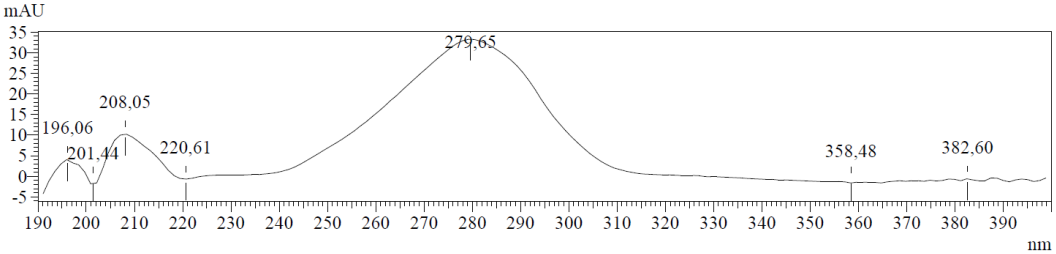


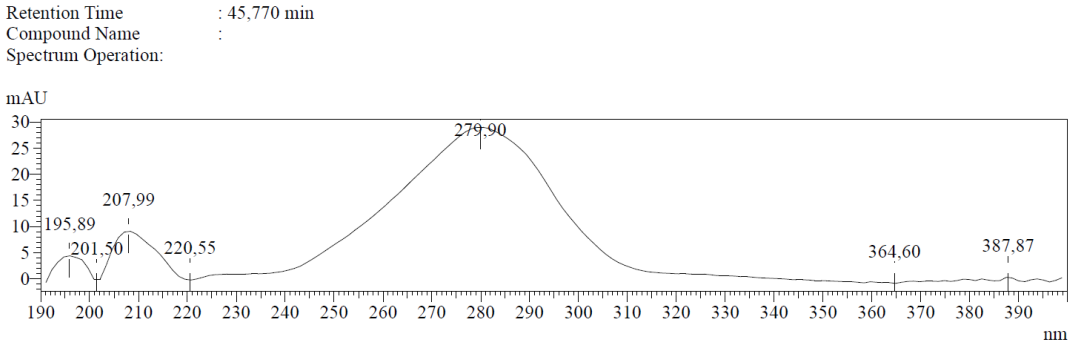

Peak Table

PDA Ch1 280nm

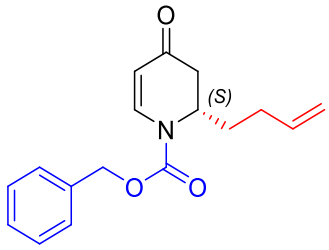
| Peak# | Ret. Time | Area | Area% | Height | Conc. | Unit | Mark |
|---|---|---|---|---|---|---|---|
| 1 | 34,707 | 490716 | 1,126 | 12700 | 0,000 | | |
| 2 | 42,536 | 43070852 | 98,874 | 908099 | 0,000 | | |
| Total | | 43561568 | 100,000 | 920799 | | | |

Retention Time : 37,551 min
Compound Name :
Spectrum Operation:






**Benzyl (*S*)-2-(but-3-en-1-yl)-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2o)** [ix]




**2o**

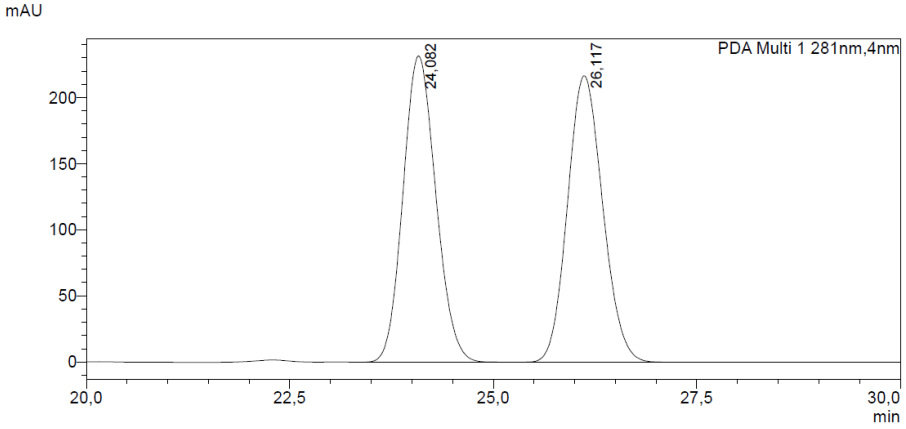
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), but-3-en-1-ylMgBr, (0.4 mmol, 1.8 M in $Et_2O$), in 2 mL of toluene at -78 °C. Product **2o** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 1:1) [Colorless oil, 94% yield, 98% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (br s, 1H, CH=C*H*N), 7.39 (s, 5H, C$H_{Ar}$), 5.71 (br s, 1H, C*H*=$CH_2$), 5.36-5.20 (m, 3H, C$H_2$Bn, COC*H*=CH), 5.05-4.90 (m, 2H, CH=C$H_2$), 4.62 (br s, 1H, C*H*$(CH_2)_2$), 2.80 (dd, *J* = 16.7, 6.4 Hz, 1H, COC$H_2$), 2.46 (d, *J* = 16.5 Hz, 1H, COC$H_2$), 2.20-2.05 (m, 1H, C$H_2$CH=$CH_2$), 2.05-1.87 (m, 1H, C$H_2$CH=$CH_2$), 1.81-1.65 (m, 2H, CHC$H_2$$CH_2$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.15, 152.58, 141.72, 136.92, 135.03, 128.96, 128.88, 128.63, 115.71, 107.31, 69.21, 53.01, 39.57, 29.80, 29.57.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 281 nm. Retention time (min): 24.9 (minor) and 26.6 (major).

**<Chromatogram>**

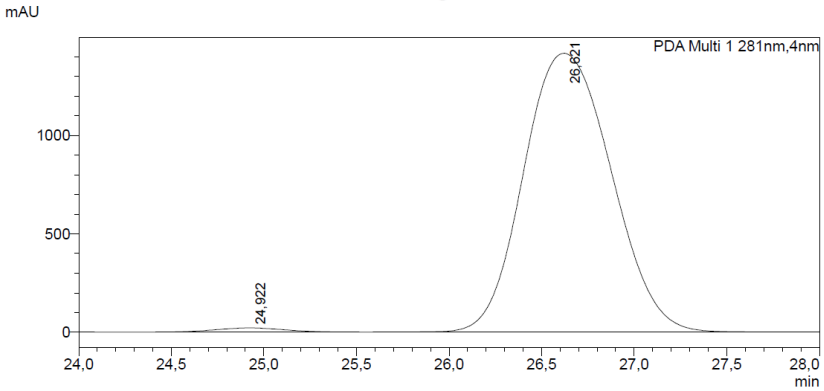



**<Peak Table>**

PDA Ch1 281nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 24,082 | 6515976 | 231691 | 49,961 | | | |
| 2 | 26,117 | 6526156 | 216725 | 50,039 | | | |
| Total | | 13042132 | 448415 | | | | |

**Chromatogram**

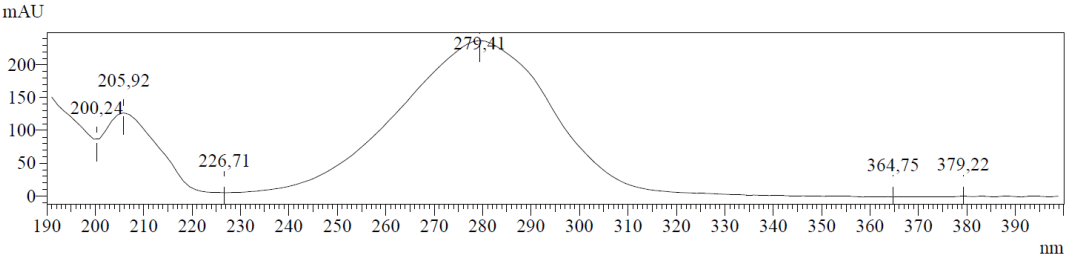


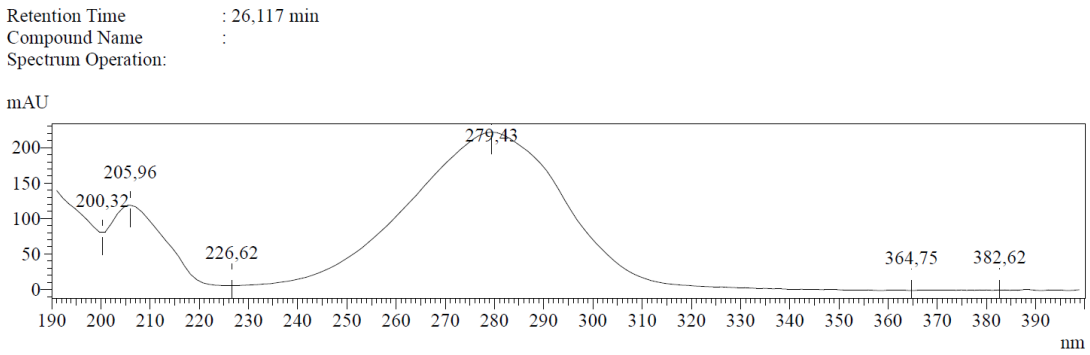

**Peak Table**

PDA Ch1 281nm

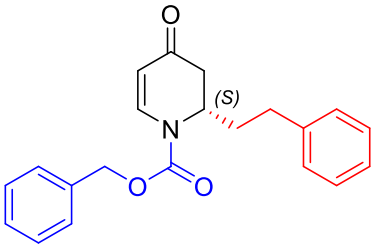
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 24,922 | 518307 | 20553 | 1,100 |
| 2 | 26,621 | 46599595 | 1416331 | 98,900 |
| Total | | 47117902 | 1436884 | 100,000 |

Retention Time : 24,082 min
Compound Name :
Spectrum Operation:






**Benzyl (*S*)-4-oxo-2-phenethyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2p)** [ix]




**2p**

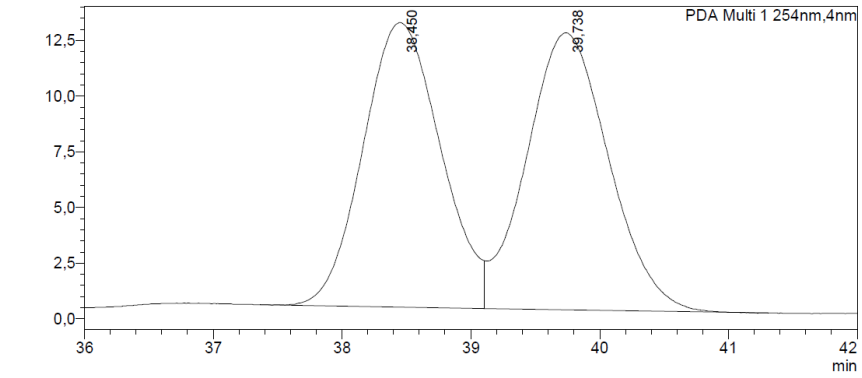
The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), phenethylMgBr, (0.4 mmol, 1.9 M in $Et_2O$), in 2 mL of toluene at -78 $^oC$. Product **2p** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 1:1) [Colorless oil, 82% yield, 99% ee, (*S*)-configuration].

$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.76 (br s, 1H, CH=C*H*N), 7.43-7.31 (m, 5H, C$H_{Ar}$), 7.28-7.20 (m, 2H, C$H_{Ar}$), 7.20-7.14 (m, 1H, C$H_{Ar}$), 7.14-7.05 (m, 2H, C$H_{Ar}$), 5.34 (d, *J* = 7.8 Hz, 1H, COC*H*=CH), 5.28-5.18 (m, 2H, C$H_2$Bn), 4.65 (br s, 1H, C*H*$(CH_2)_2$), 2.82 (dd, *J* = 16.6, 6.6 Hz, 1H, COC$H_2$), 2.76-2.64 (m, 1H, COC$H_2$), 2.53 (d, *J* = 16.6 Hz, 2H, $CH_2$C*H*$_2$Ph), 2.07-1.90 (m, 2H, C*H*$_2CH_2$Ph).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 192.96, 152.60, 141.76, 140.44, 135.01, 128.95, 128.89, 128.65, 128.59, 128.28, 126.29, 107.37, 69.19, 53.15, 39.62, 31.88, 31.85.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 $^{o}$C, detection at 254 nm. Retention time (min): 38.6 (minor) and 40.0 (major).

**<Chromatogram>**

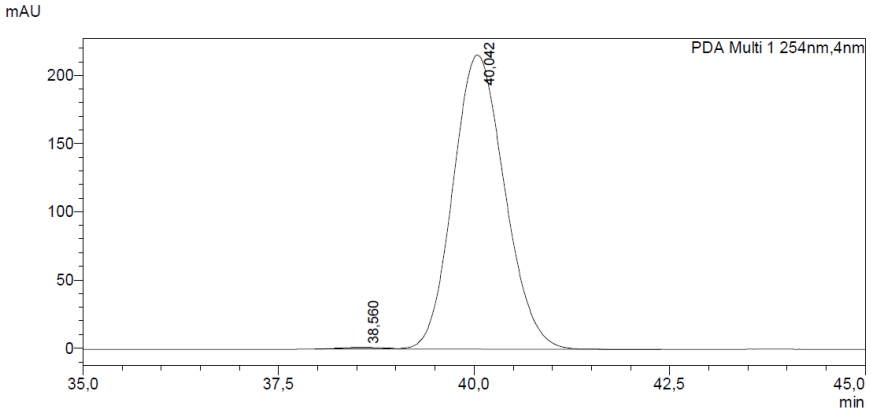



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 38,450 | 536144 | 12777 | 49,235 | | M | |
| 2 | 39,738 | 552808 | 12437 | 50,765 | | V M | |
| Total | | 1088952 | 25214 | | | | |

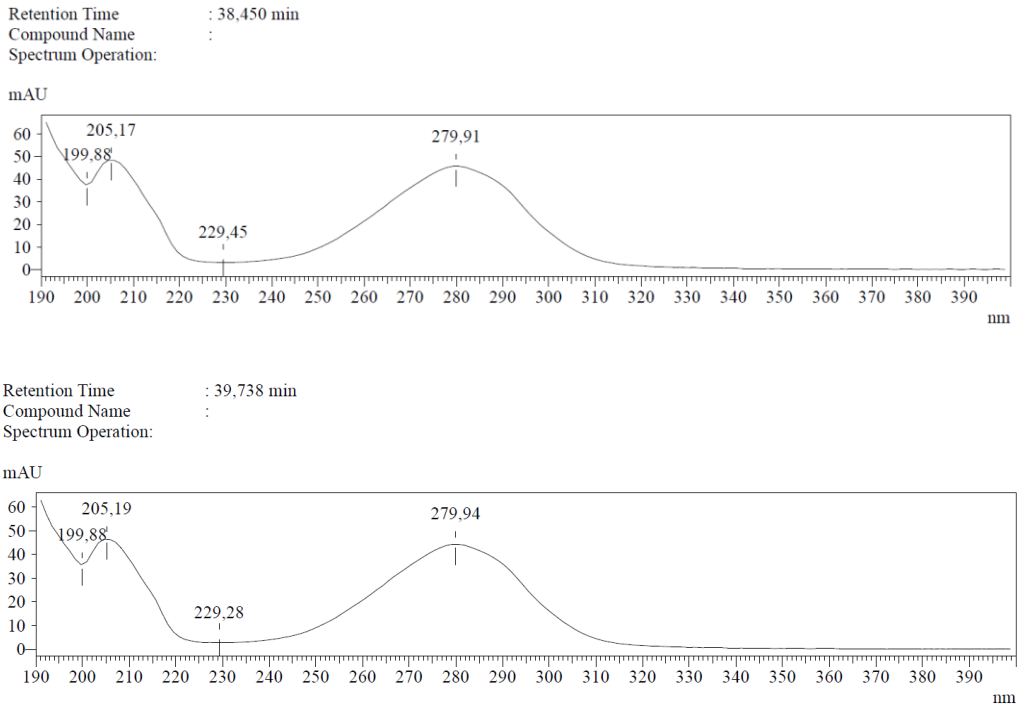
**<Chromatogram>**



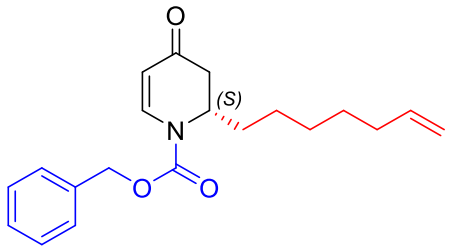

**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 38,560 | 46539 | 1319 | 0,469 | | M | |
| 2 | 40,042 | 9879965 | 215553 | 99,531 | | V M | |
| Total | | 9926504 | 216872 | | | | |




**Benzyl (*S*)-2-(hept-6-en-1-yl)-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (2q)**




**2q**

The reaction was performed with 0.2 mmol **1a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), benzyl chloroformate (57 µL, 0.4 mmol), hept-6-en-1-ylMgBr, (0.4 mmol, 1.7 M in $Et_2O$), in 2 mL of toluene at -78 $^oC$. Product **2q** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 1:1) [Colorless oil, 82% yield, >99% ee, (*S*)-configuration].

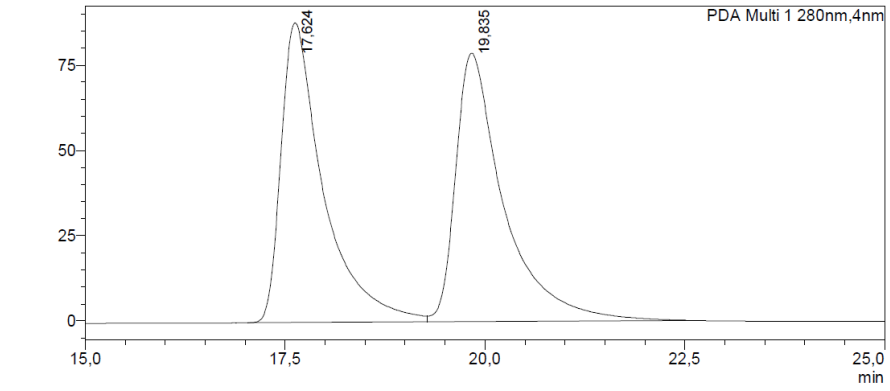
$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.6 Hz, 1H, CH=C*H*N), 7.43-7.32 (m, 5H, $CH_{Ar}$), 5.85-5.69 (m, 1H, C*H*=$CH_2$), 5.35-5.21 (m, 3H, $CH_2$Bn, COC*H*=CH), 5.02-4.88 (m, 2H, CH=C$H_2$), 4.64-4.50 (m, 1H, C*H*$CH_2CH_2$), 2.79 (dd, *J* = 16.6, 6.6 Hz, 1H, COC$H_2$), 2.44 (d, *J* = 16.5 Hz, 1H, COC$H_2$), 2.03-1.92 (m, 2H, $CH_2$CH=$CH_2$), 1.69-1.55 (m, 2H, CHC$H_2CH_2$), 1.39-1.12 (m, 6H, $(CH_2)_3CH_2$CH=$CH_2$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.21, 152.66, 141.61, 138.87, 135.09, 128.90, 128.85, 128.58, 114.51, 107.26, 69.10, 53.50, 39.77, 33.66, 30.54, 28.81, 28.69, 25.60.

HRMS (ESI+, m/Z): calcd for $C_{20}H_{25}NO_3$ $[M+Na]^+$: 350.1726, found: 350.1728.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 $^oC$, detection at 280 nm. Retention time (min): 18.9 (major) and 21.7 (minor).

**<Chromatogram>**

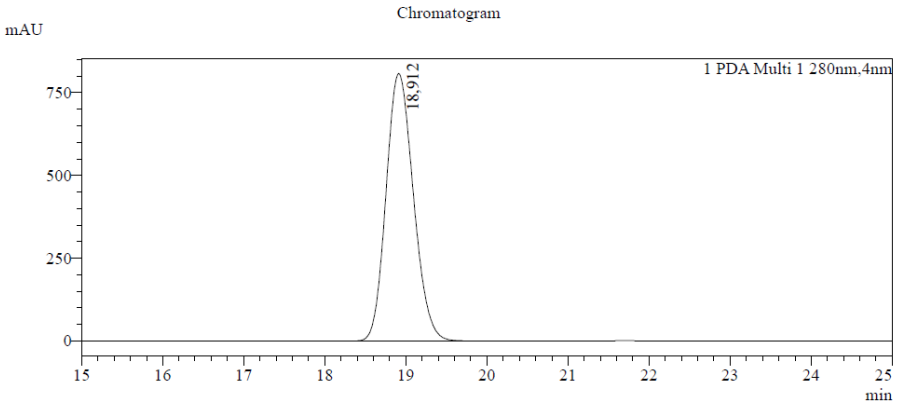



**<Peak Table>**

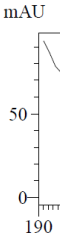
PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,624 | 3238639 | 87862 | 49,498 | | | |
| 2 | 19,835 | 3304333 | 78737 | 50,502 | | V | |
| Total | | 6542972 | 166599 | | | | |

**<Chromatogram>**



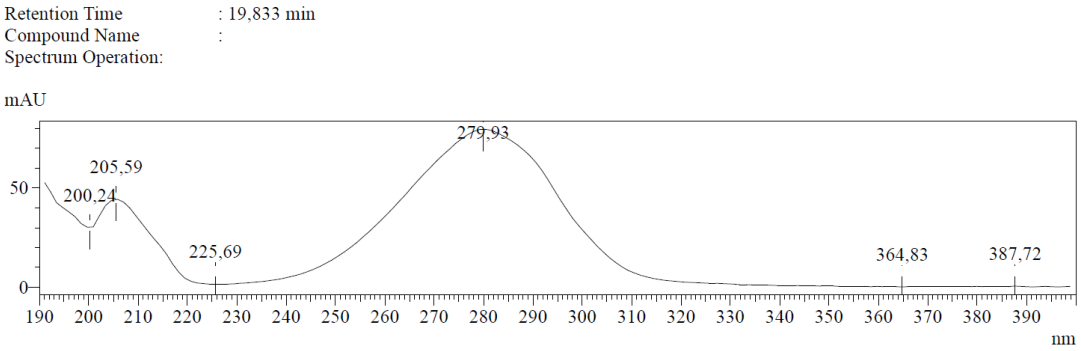

Retenti
Compo
Spectru



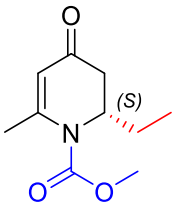

Peak Table

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Area% | Height | Conc. | Unit | Mark |
|---|---|---|---|---|---|---|---|
| 1 | 18,912 | 18975904 | 100,000 | 808259 | 0,000 | | |
| Total | | 18975904 | 100,000 | 808259 | | | |




**Methyl (*S*)-2-ethyl-6-methyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (4a)**




**4a**

The reaction was performed with 0.2 mmol **3a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), methyl chloroformate (30 µL, 0.4 mmol), EtMgBr, (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of $CH_2Cl_2$ at -78 °C. Product **4a** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 1:1) [Colorless oil, 66% yield, 98% ee, (*S*)-configuration].

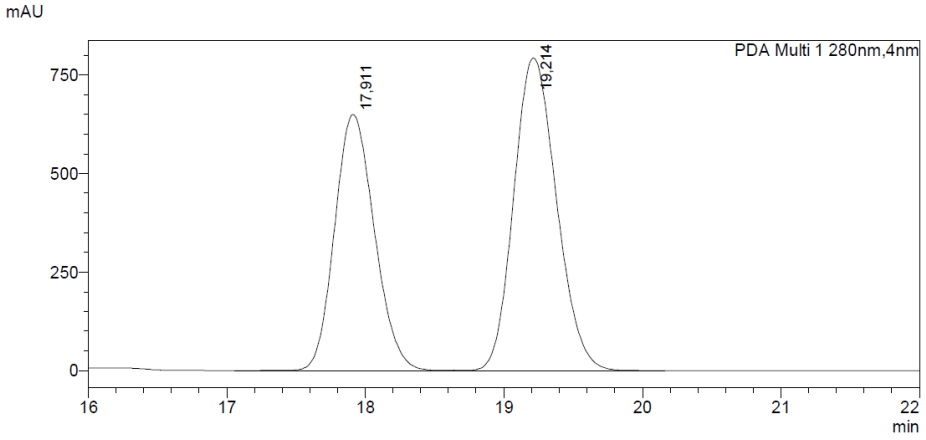
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H, COC*H*), 4.67-4.59 (m, 1H, C*H*$CH_2$), 3.82 (s, 3H, O$CH_3$), 2.73 (dd, *J* = 17.1, 6.0 Hz, 1H, COC$H_2$), 2.36 (d, *J* = 17.1 Hz, 1H, COC$H_2$), 2.31 (s, 3H, CH=C-C$H_3$), 1.83-1.65 (m, 1H, C$H_2$$CH_3$), 1.64-1.52 (m, 1H, C$H_2$$CH_3$), 0.89 (t, *J* = 7.4 Hz, 3H, $CH_2CH_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.51, 154.69, 154.34, 112.66, 57.50, 53.65, 40.48, 23.93, 23.33, 10.75.

HRMS (ESI+, m/Z): calcd for $C_{10}H_{15}NO_3$ $[M+H]^+$: 198.1124, found: 198.1122.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 18.1 (major) and 19.5 (minor).

**<Chromatogram>**

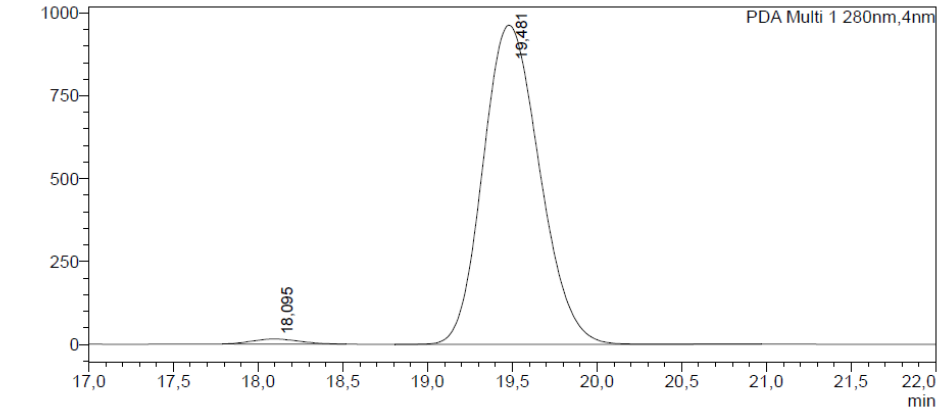



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,911 | 12990969 | 650280 | 43,281 | | | |
| 2 | 19,214 | 17024590 | 793124 | 56,719 | | V | |
| Total | | 30015559 | 1443404 | | | | |

**<Chromatogram>**

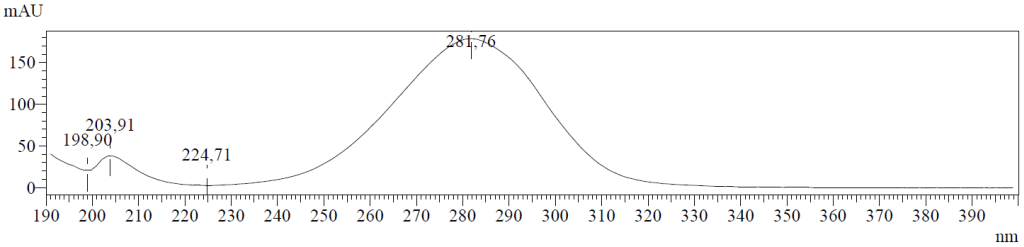


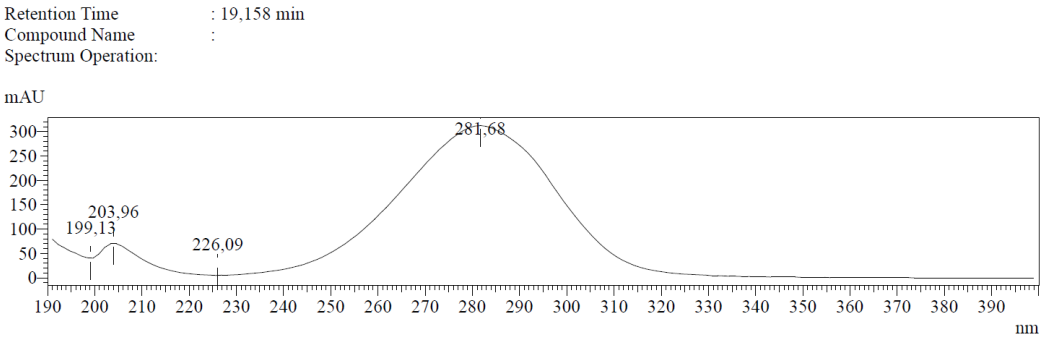

**<Peak Table>**

PDA Ch1 280nm

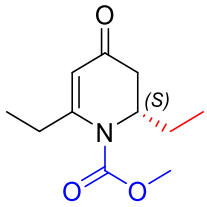
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18,095 | 300290 | 15281 | 1,327 | | | |
| 2 | 19,481 | 22337141 | 962948 | 98,673 | | M | |
| Total | | 22637431 | 978229 | | | | |

Retention Time : 17,857 min
Compound Name :
Spectrum Operation:






**Methyl (*S*)-2,6-diethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (4b)**




**4b**

The reaction was performed with 0.2 mmol **3b**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (6 mg, 0.012 mmol, 6 mol%), methyl chloroformate (30 µL, 0.4 mmol), EtMgBr, (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of $CH_2Cl_2$ at -78 °C. Product **4b** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 2:1) [Colorless oil, 51% yield, 91% ee, (*S*)-configuration].

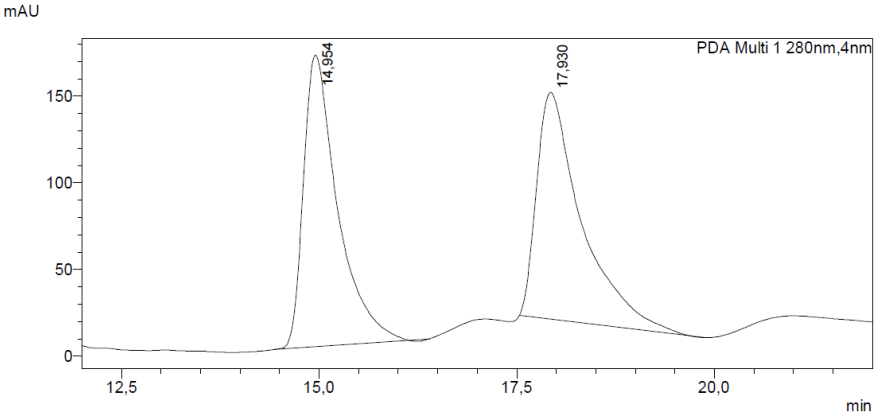
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.45 (s, 1H, COC*H*), 4.70-4.61 (m, 1H, C*H*$CH_2$), 3.83 (s, 3H, $OCH_3$), 2.99-2.86 (m, 1H, CH=CC*H*$_2$$CH_3$), 2.78 (dd, J = 17.1, 6.0 Hz, 1H, COC*H*$_2$), 2.58-2.45 (m, 1H, CH=CC*H*$_2$$CH_3$), 2.36 (dt , *J* = 17.1 and 1.4 Hz , 1H, $COCH_2$), 1.85-1.70 (m, 1H, CHC*H*$_2$$CH_3$), 1.60-1.49 (m, 2+1H, CHC*H*$_2$$CH_3$ + $H_2O$), 1.10 (t, *J* = 7.4 Hz, 3H, $CH=CCH_2CH_3$), 0.92 (t, *J* = 7.4 Hz, 3H, $CHCH_2CH_3$).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 194.05, 160.02, 154.27, 112.08, 57.82, 53.66, 41.03, 29.17, 23.38, 12.70, 10.79.

HRMS (ESI+, m/Z): calcd for C11H17NO3 [M+H]+: 212.1281, found: 212.1281.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 17.3 (minor) and 21.2 (major).

**<Chromatogram>**

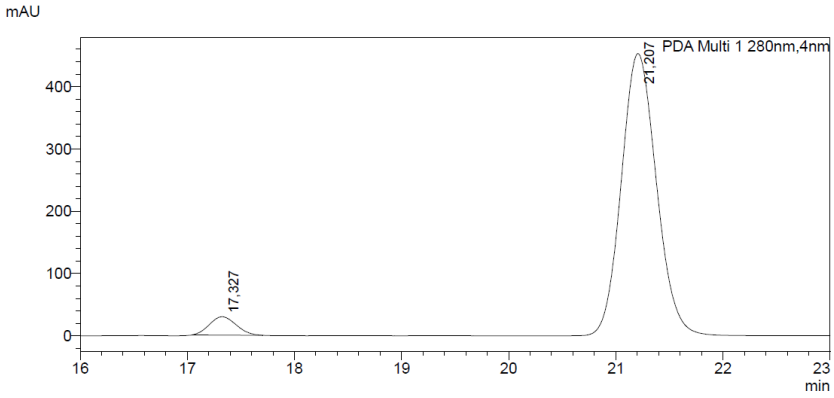



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14,954 | 5061267 | 168244 | 49,528 | | M | |
| 2 | 17,930 | 5157779 | 130861 | 50,472 | | M | |
| Total | | 10219046 | 299104 | | | | |

**<Chromatogram>**

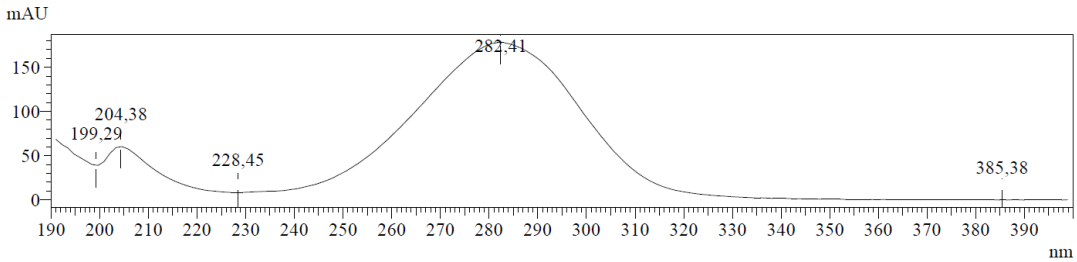


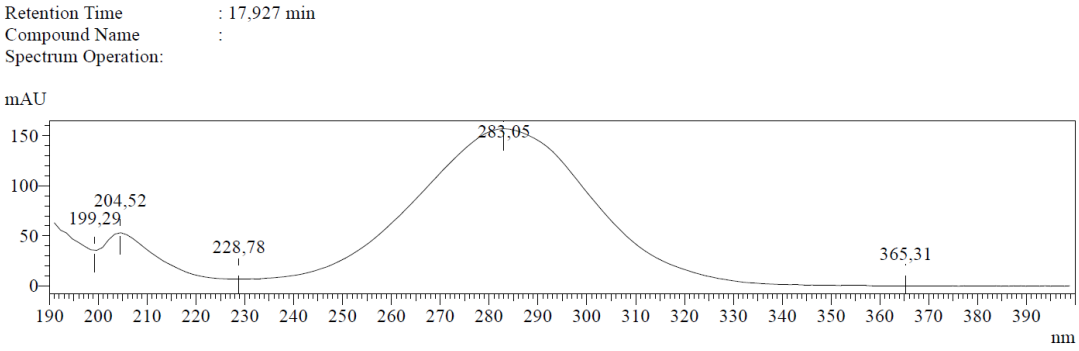

**<Peak Table>**

PDA Ch1 280nm

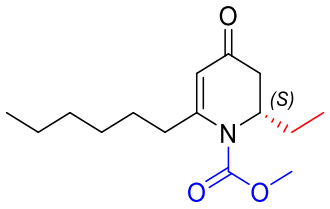
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,327 | 511457 | 29498 | 4,717 | | M | |
| 2 | 21,207 | 10332462 | 453432 | 95,283 | | M | |
| Total | | 10843919 | 482930 | | | | |

Retention Time : 14,953 min
Compound Name :
Spectrum Operation:






**Methyl (*S*)-2-ethyl-6-hexyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (4c)**




**4c**

The reaction was performed with 0.2 mmol **3c**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), methyl chloroformate (30 µL, 0.4 mmol), EtMgBr, (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of $CH_2Cl_2$ at -78 °C. Product **4c** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 5:1) [Colorless oil, 56% yield, 80% ee, (*S*)-configuration].

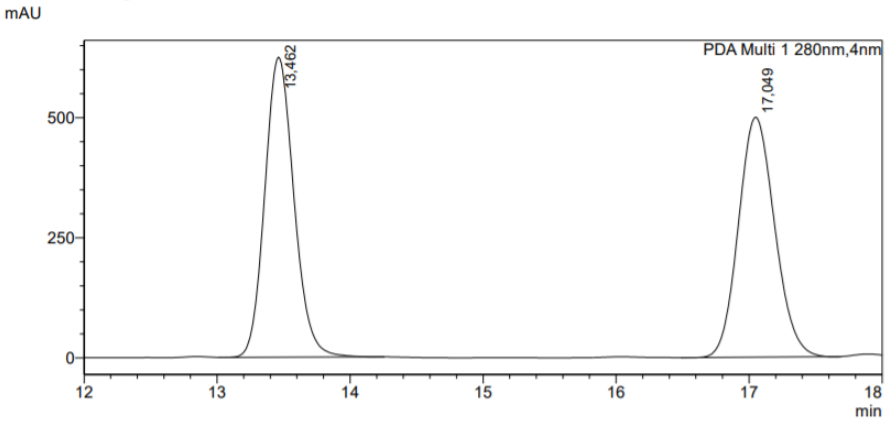
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.41 (s, 1H, COC*H*), 4.67-4.59 (m, 1H, C*H*$CH_2$), 3.82 (s, 3H, O$CH_3$), 3.08-2.97 (m, 1H, C$H_2$C=CH), 2.77 (dd, *J* = 17.3, 6.0 Hz, 1H, COC$H_2$), 2.39-2.29 (m, 2H, C$H_2$C=CH, COC$H_2$), 1.83-1.70 (m, 1H, C$H_2$$CH_3$), 1.62-1.49 (m, 1H, C$H_2$$CH_3$), 1.48-1.38 (m, 2H, C$H_2$), 1.36-1.22 (m, 6H, C$H_2$), 0.94-0.82 (m, 6H, 2xC$H_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.90, 158.79, 154.31, 112.70, 57.92, 53.65, 40.99, 36.05, 31.64, 29.09, 28.23, 23.45, 22.67, 14.15, 10.84.

HRMS (ESI+, m/Z): calcd for $C_{15}H_{25}NO_3$ $[M+H]^+$: 268.1907, found: 268.1909.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 13.4 (minor) and 17.0 (major).

**<Chromatogram>**

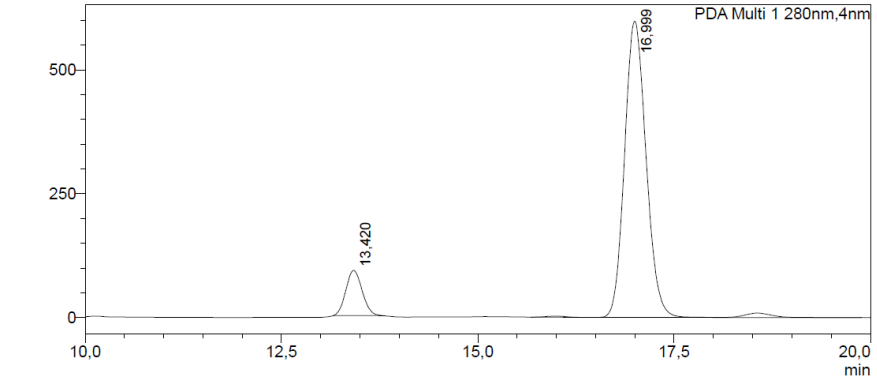



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13,462 | 9539752 | 624625 | 50,165 | | | |
| 2 | 17,049 | 9477140 | 499270 | 49,835 | | | |
| Total | | 19016892 | 1123895 | | | | |

**<Chromatogram>**

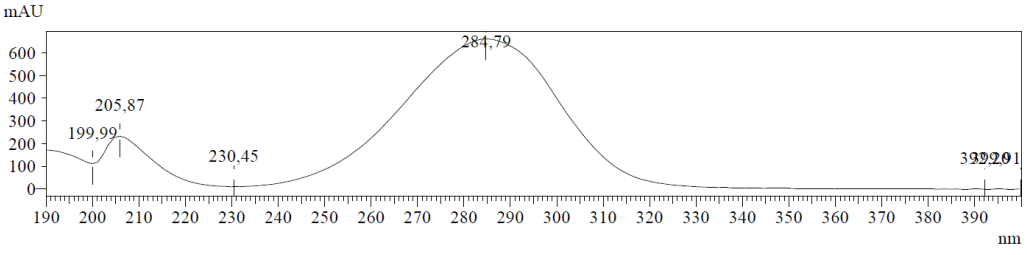


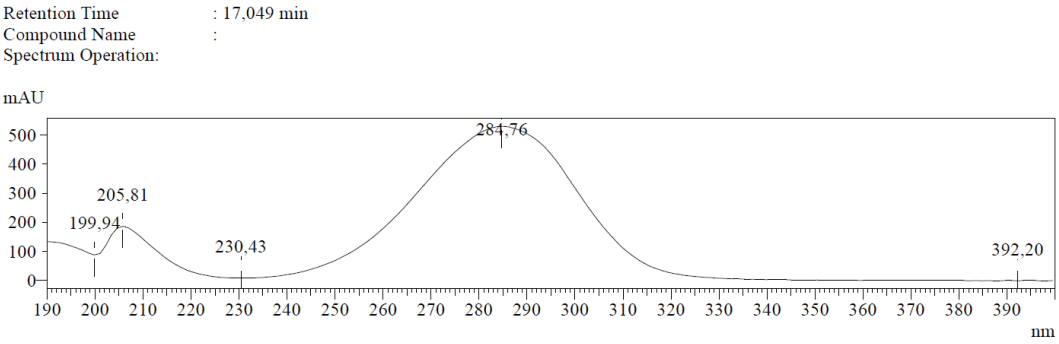

**<Peak Table>**

PDA Ch1 280nm

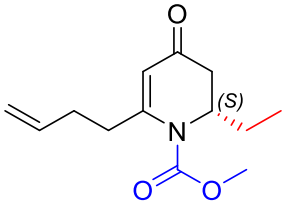
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13,420 | 1313291 | 91120 | 10,195 | | M | |
| 2 | 16,999 | 11568428 | 596939 | 89,805 | | M | |
| Total | | 12881720 | 688059 | | | | |

Retention Time : 13,462 min
Compound Name :
Spectrum Operation:






**Methyl (*S*)-6-(but-3-en-1-yl)-2-ethyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (4d)**




**4d**

The reaction was performed with 0.2 mmol **3d**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), methyl chloroformate (30 µL, 0.4 mmol), EtMgBr, (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of $CH_2Cl_2$ at -78 °C. Product **4d** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 5:1) [Colorless oil, 55% yield, 90% ee, (*S*)-configuration].

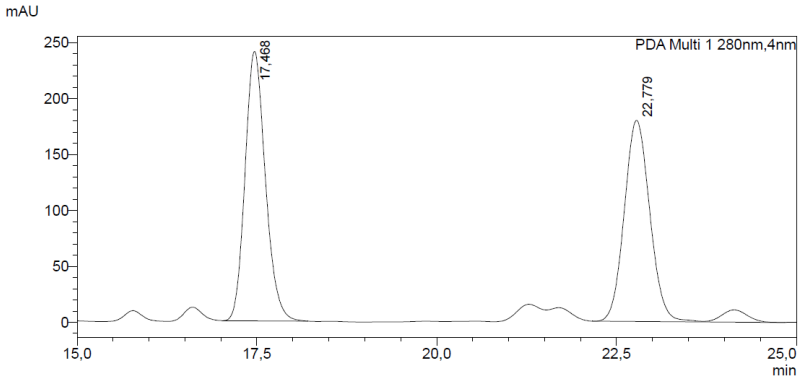
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.86-5.72 (m, 1H, C*H*=$CH_2$), 5.43 (s, 1H, COC*H*), 5.10-4.98 (m, 2H, CH=C*H*$_2$), 4.70-4.60 (m, 1H, C*H*$CH_2CH_3$), 3.83 (s, 3H, OC*H*$_3$), 3.20-3.05 (m, 1H, $CH_2$C*H*$_2$), 2.78 (dd, *J* = 17.1, 6.0 Hz, 1H, COC*H*$_2$), 2.54-2.43 (m, 1H, $CH_2$C*H*$_2$), 2.37 (d, *J* = 17.1 Hz, 1H, COC*H*$_2$), 2.31-2.16 (m, 2H, C*H*$_2$$CH_2$), 1.84-1.71 (m, 1H, C*H*$_2$$CH_3$), 1.70-1.46 (m, 1H, C*H*$_2$$CH_3$), 0.91 (t, *J* = 7.6 Hz, 3H, C*H*$_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.79, 157.68, 154.26, 136.80, 115.97, 113.00, 57.97, 53.73, 40.93, 35.35, 32.22, 23.50, 10.90.

HRMS (ESI+, m/Z): calcd for $C_{13}H_{19}NO_3$ $[M+H]^+$: 238.1437, found: 238.1435.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 17.6 (minor) and 22.8 (major).

**<Chromatogram>**

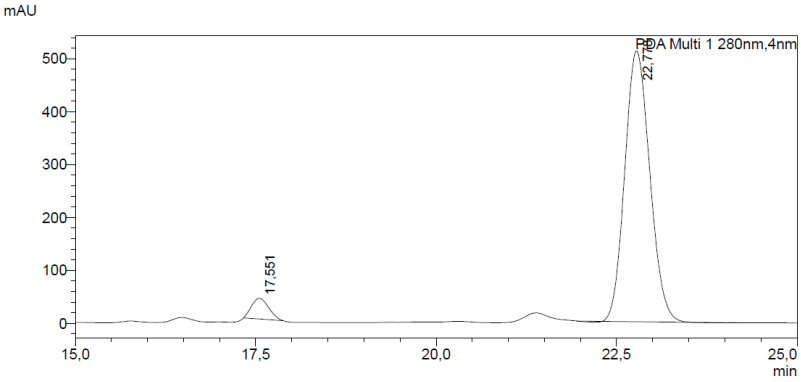



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,468 | 4740319 | 240712 | 50,169 | | M | |
| 2 | 22,779 | 4708298 | 179665 | 49,831 | | M | |
| Total | | 9448617 | 420378 | | | | |

**<Chromatogram>**

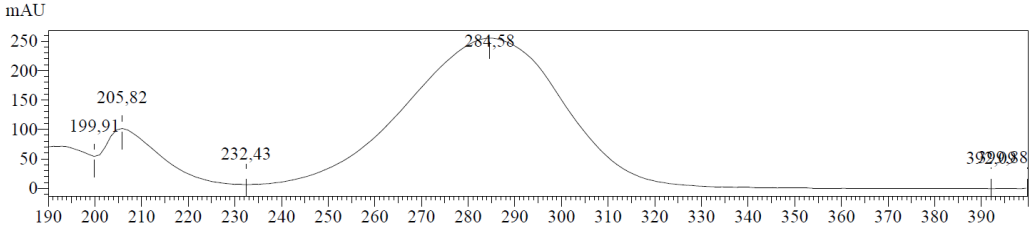


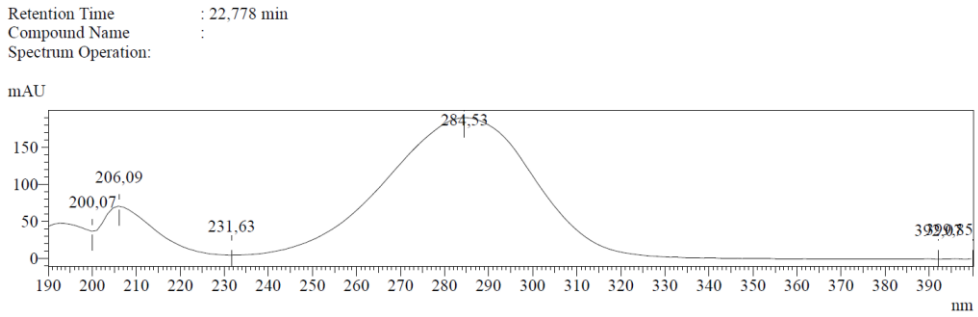

**<Peak Table>**

PDA Ch1 280nm

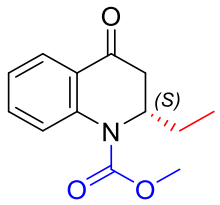
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17,551 | 642366 | 38719 | 4,957 | | M | |
| 2 | 22,778 | 12315446 | 511114 | 95,043 | | M | |
| Total | | 12957812 | 549833 | | | | |

Retention Time : 17,468 min
Compound Name :
Spectrum Operation:






**Methyl (*S*)-2-ethyl-4-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (4e)**




**4e**

The reaction was performed with 0.2 mmol **3e**, $CuBr{\cdot}SMe_2$ (0.02 mmol, 10 mol%), ligand (*R*,*R*)-**L1** (0.024 mmol, 12 mol%), methyl chloroformate (30 µL, 0.4 mmol), EtMgBr, (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of $CH_2Cl_2$ at -78 °C. Product **4e** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 2:1) [Colorless oil, 75% yield, 97% ee, (*S*)-configuration].

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.8, 1.6 Hz, 1H, C$H_{Ar}$), 7.74 (d, *J* = 8.3 Hz, 1H, C$H_{Ar}$), 7.56-7.05 (m, 1H, C$H_{Ar}$), 7.20-7.13 (m, 1H, C$H_{Ar}$), 4.92-4.83 (m, 1H, C$\underline{H}$C$H_2$C$H_3$), 3.85 (s, 3H, OC$H_3$), 3.04 (dd, *J* = 17.6, 5.8 Hz, 1H, COC$H_2$), 2.65 (dd, *J* = 17.6, 1.7 Hz, 1H, COC$\underline{H_2}$), 1.67-1.43 (m, 2H, C$\underline{H_2}$C$H_3$), 0.88 (t, *J* = 7.4 Hz, 3H, C$H_2$C$\underline{H_3}$).

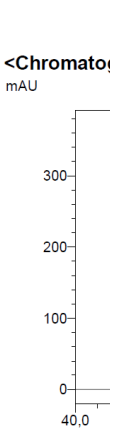
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.59, 155.01, 141.04, 134.51, 126.92, 125.10, 124.83, 124.28, 55.53, 53.50, 43.20, 24.74, 10.80.

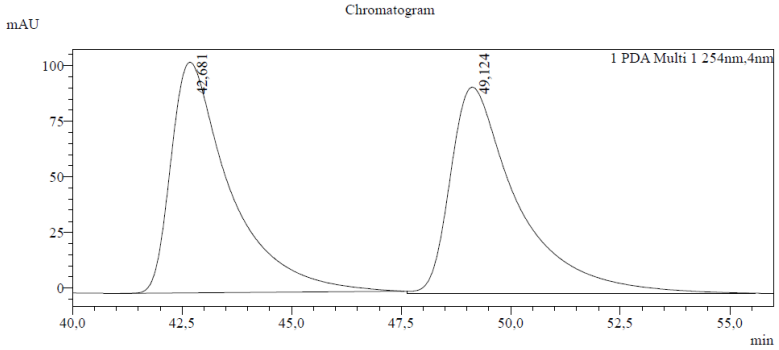
HRMS (ESI+, m/Z): calcd for $C_{13}H_{15}NO_3$ $[M+H]^+$: 234.1124, found: 234.1122.

HPLC analysis: Chiracel-OBH, *n*heptane/*i*PrOH 99:1, 0.5 mL/min, 40 °C, detection at 254 nm. Retention time (min): 45.4 (major) and 53.2 (minor).*

*It is observed that in this case the major peak has a shorter retention time than the minor peak, which is in contrast with all the other compounds.

**<Chromatogram>**



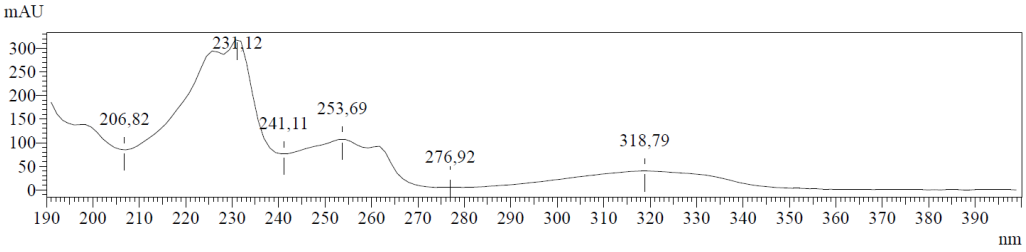



Peak Table

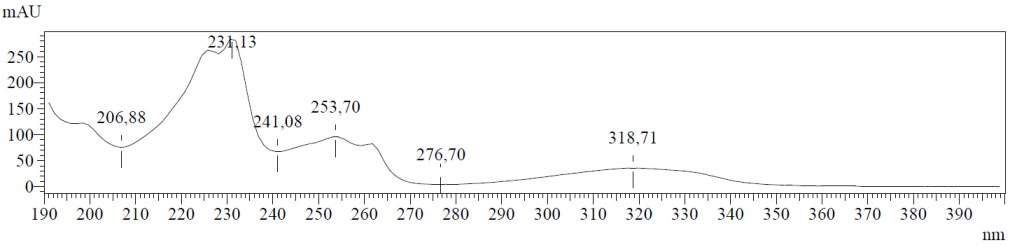
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% | Height | Conc. | Unit | Mark |
|---|---|---|---|---|---|---|---|
| 1 | 42,681 | 9759703 | 49,609 | 103747 | 0,000 | | M |
| 2 | 49,124 | 9913378 | 50,391 | 92713 | 0,000 | | |
| Total | | 19673081 | 100,000 | 196461 | | | |

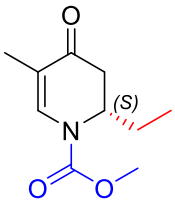
Retention Time : 42,681 min
Compound Name :
Spectrum Operation:




Retention Time : 49,123 min
Compound Name :
Spectrum Operation:




## Methyl (*S*)-2-ethyl-5-methyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (4h)




**4h**

The reaction was performed with 0.2 mmol **3h**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), methyl chloroformate (30 µL, 0.4 mmol), EtMgBr, (0.4 mmol, 3.0 M in $Et_2O$), in 2 mL of $CH_2Cl_2$ at -78 °C. Product **4h** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 3:1) [Colorless oil, 62% yield, 82% ee, (*S*)-configuration].

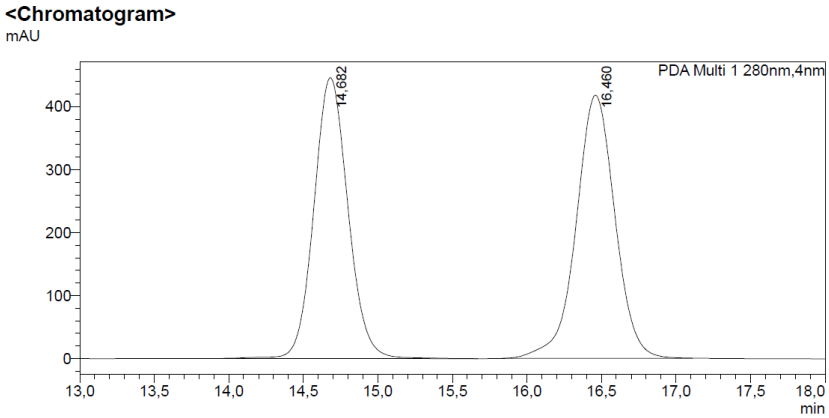
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H, CC*H*N), 4.46 (br s, 1H, C*H*$CH_2$), 3.84 (s, 3H, O$CH_3$), 2.77 (dd, *J* = 16.6, 6.6 Hz, 1H, CO$CH_2$), 2.49 (dd, *J* = 17.9 and 1.30 Hz, 1H, CO$CH_2$), 1.74 (s, 3H, $CH_3$C), 1.69-1.56 (m, 2H, C$H_2$$CH_3$), 0.89 (t, *J* = 7.5 Hz, 3H, $CH_2$C$H_3$).

$^{13}$C NMR (151 MHz, $CDCl_3$)* δ 193.57, 153.38, 138.17, 114.51, 54.83, 53.94, 39.48, 23.80, 12.94, 10.34.

*Impurity was distinguished from product by comparison with compound **2b**

HRMS (ESI+, m/Z): calcd for $C_{10}H_{15}NO_3$ $[M+H]^+$: 198.1124, found: 198.1126.

HPLC analysis: Chiracel-ODH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 280 nm. Retention time (min): 14.7 (minor) and 16.5 (major).

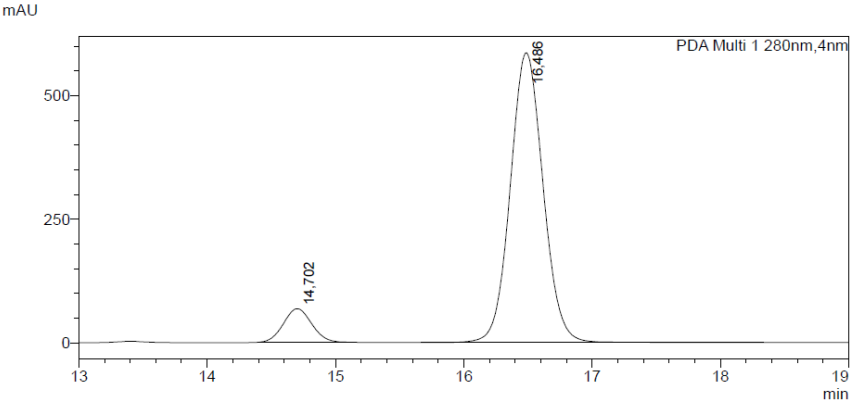



**<Peak Table>**

PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14,682 | 7096165 | 445886 | 48,343 | | | |
| 2 | 16,460 | 7582643 | 417993 | 51,657 | | M | |
| Total | | 14678808 | 863879 | | | | |

<Chromatogram>

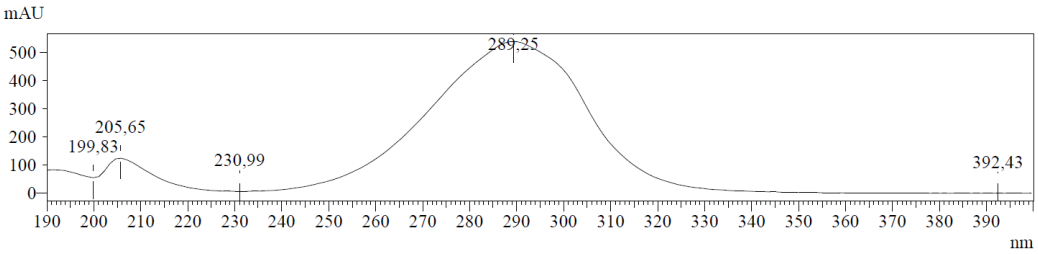



<Peak Table>

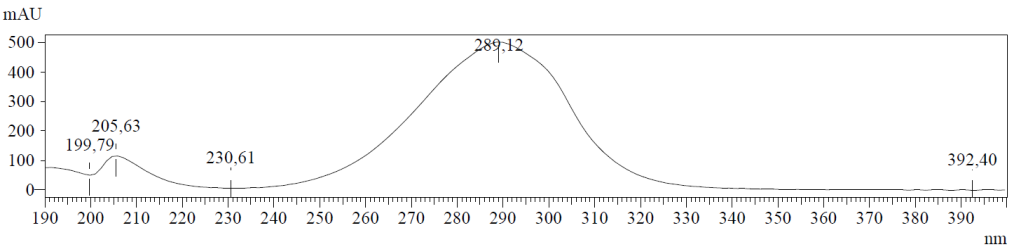
PDA Ch1 280nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14,702 | 1041419 | 67932 | 9,077 | | M | |
| 2 | 16,486 | 10432356 | 586204 | 90,923 | | M | |
| Total | | 11473775 | 654136 | | | | |

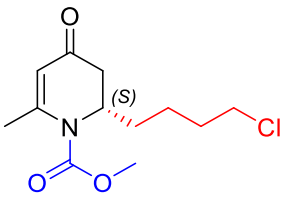
Retention Time : 14,682 min
Compound Name :
Spectrum Operation:




Retention Time : 16,461 min
Compound Name :
Spectrum Operation:




## Methyl (*S*)-2-(4-chlorobutyl)-6-methyl-4-oxo-3,4-dihydropyridine-1(2*H*)-carboxylate (4i)




**4i**

The reaction was performed with 0.2 mmol **3a**, $CuBr{\cdot}SMe_2$ (0.01 mmol, 5 mol%), ligand (*R*,*R*)-**L1** (0.012 mmol, 6 mol%), methyl chloroformate (30 µL, 0.4 mmol), 4-ClBuMgBr, (0.4 mmol, 1.2 M in $Et_2O$), in 2 mL of $CH_2Cl_2$ at -78 °C. Product **4i** was obtained as a colorless oil after column chromatography ($SiO_2$, pentane:$Et_2O$ 1:1) [Colorless oil, 52% yield, 99% ee, (*S*)-configuration].

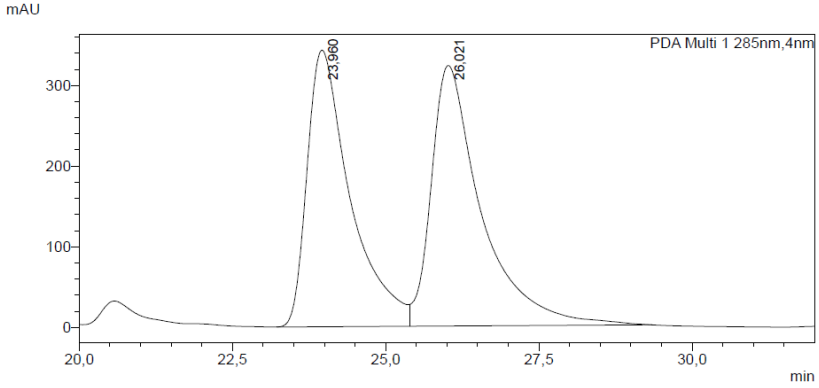
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.21 (s, 1H, COC*H*=CCH$_3$N), 4.64-4.55 (m, 1H, C*H*CH$_2$), 3.69 (s, 3H, OC*H*$_3$), 3.38 (t, *J* = 6.5 Hz, 2H, C*H*$_2$Cl), 2.65 (dd, *J* = 17.0, 6.0 Hz, 1H, COC*H*$_2$), 2.22 (br s, 1H, COC*H*$_2$), 2.18 (br s, 3H, C*H*$_3$C), 1.73-1.56 (m, 3H, C*H*$_2$C*H*$_2$), 1.47-1.23 (m, 3H, C*H*$_2$C*H*$_2$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.82, 154.25, 153.83, 112.20, 55.51, 53.38, 44.40, 40.47, 31.82, 29.11, 23.54, 23.12.

HRMS (ESI+, m/Z): calcd for $C_{12}H_{18}ClNO_3$ $[M+H]^+$: 260.1048, found: 260.1044.

HPLC analysis: Chiracel-ADH, *n*heptane/*i*PrOH 95:5, 0.5 mL/min, 40 °C, detection at 285 nm. Retention time (min): 28.9 (minor) and 31.2 (major).

<Chromatogram>

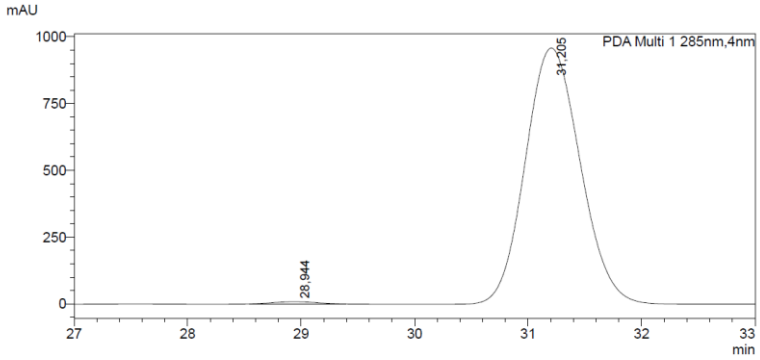



<Peak Table>

PDA Ch1 285nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 23,960 | 16808265 | 343084 | 47,813 | | | |
| 2 | 26,021 | 18345927 | 323195 | 52,187 | | V | |
| Total | | 35154192 | 666279 | | | | |

**<Chromatogram>**

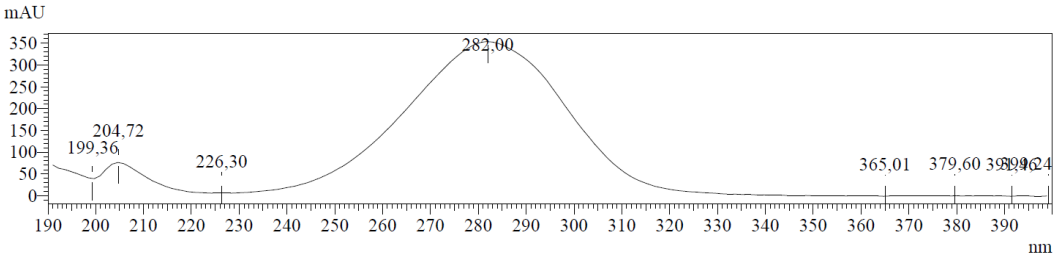



**<Peak Table>**

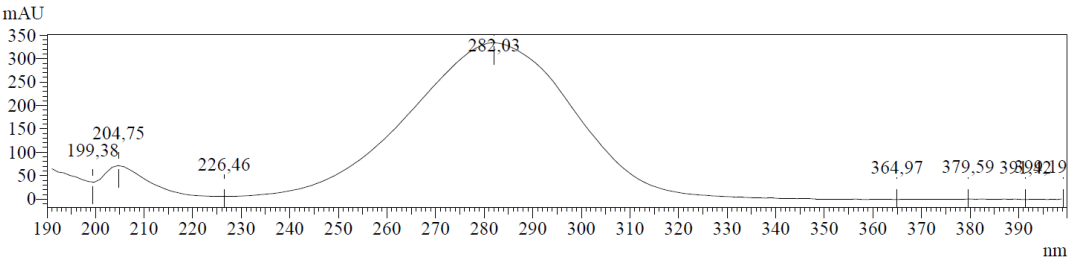
PDA Ch1 285nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 28,944 | 223715 | 8487 | 0,688 | | M | |
| 2 | 31,205 | 32308949 | 958268 | 99,312 | | M | |
| Total | | 32532664 | 966755 | | | | |

Retention Time : 23,960 min
Compound Name :
Spectrum Operation:

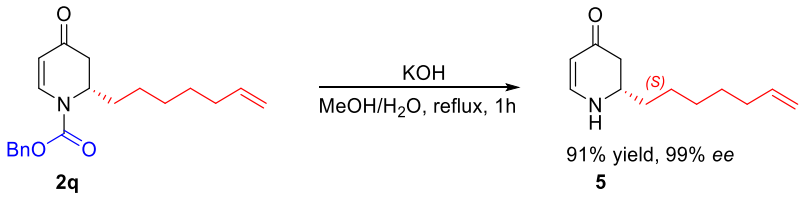



Retention Time : 26,021 min
Compound Name :
Spectrum Operation:



## 7. Transformations of chiral addition products: synthesis of compounds 5, 6 and 7

### Synthesis of (*S*)-2-(hept-6-en-1-yl)-2,3-dihydropyridin-4(1*H*)-one (5)

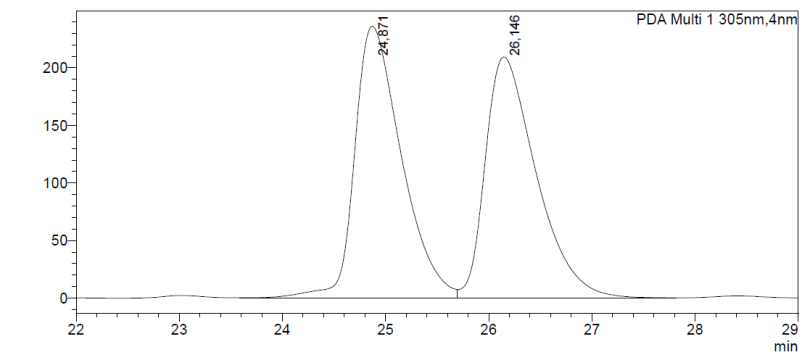



KOH (1 mL; 40% aqueous) was added to a solution of **2q** (0.2 mmol; 99% ee) in MeOH (1 mL) and the mixture was refluxed for 1 h. After cooling to room temperature, the reaction mixture was extracted with $Et_2O$ (3×3 mL) and the organic layer was washed with brine, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. Compound **5** was obtained as a yellow oil and characterized without further purification. (35 mg, 91% yield, >99% ee, (*S*)-configuration).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.19-7.12 (m, 1H, CH=C*H*NH), 5.92 (br s, 1H, N*H*), 5.82-5.65 (m, 1H, C*H*=$CH_2$), 4.99-4.85 (m, 3H, CH=C*H*$_2$, C*H*=CHNH), 3.66-3.54 (m, 1H, C*H*$CH_2$), 2.43-2.30 (m, 2H, COC*H*$_2$), 2.05-1.94 (m, 2H, C*H*$_2$CH=$CH_2$), 1.70-1.48 (m, 2H, CHC*H*$_2$$CH_2$), 1.40-1.24 (m, 6H, $CH_2$(C*H*$_2$)$_3$$CH_2$).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.26, 151.84, 138.77, 114.51, 98.23, 53.21, 41.91, 34.00, 33.63, 28.88, 28.71, 25.21.

HPLC analysis: Chiracel-ODH, *n*heptane/*i*PrOH 90:10, 0.5 mL/min, 40 $^o$C, detection at 305 nm. Retention time (min): 25.06 (minor) and 25.62 (major).

**<Chromatogram>**

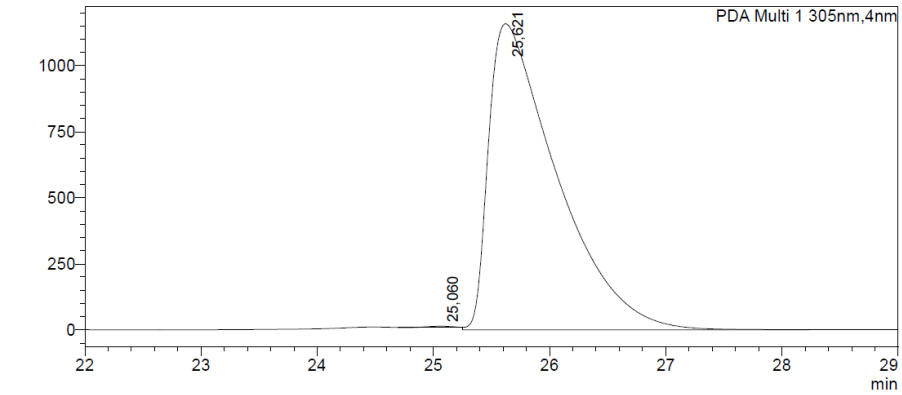



**<Peak Table>**

PDA Ch1 305nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 24,871 | 7481604 | 236462 | 50,838 | | | |
| 2 | 26,146 | 7234955 | 209771 | 49,162 | | V | |
| Total | | 14716558 | 446233 | | | | |

**<Chromatogram>**

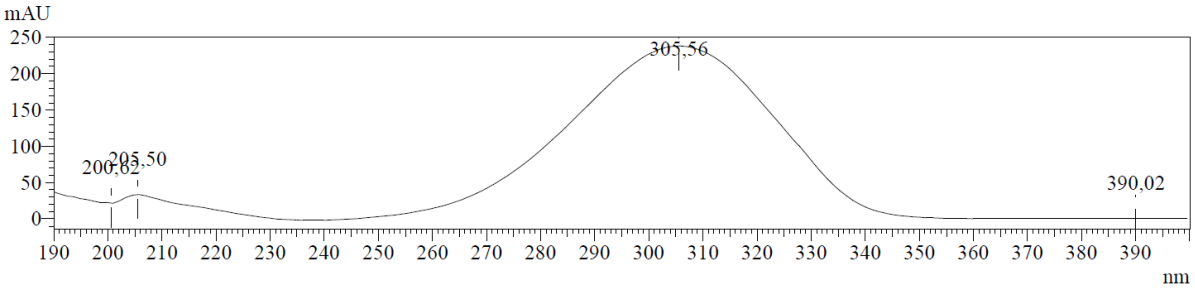



**<Peak Table>**

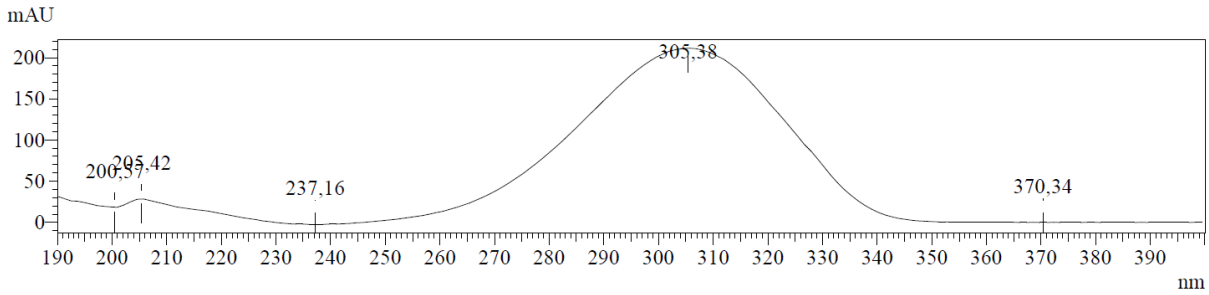
PDA Ch1 305nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 25,060 | 64659 | 4935 | 0,136 | | | |
| 2 | 25,621 | 47321081 | 1158197 | 99,864 | | | |
| Total | | 47385740 | 1163131 | | | | |

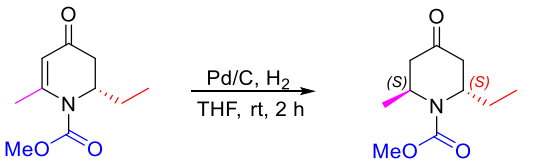
Retention Time : 24,876 min
Compound Name :
Spectrum Operation:



Retention Time : 26,143 min
Compound Name :
Spectrum Operation:




**Synthesis of methyl (2*S*,6*S*)-2-ethyl-6-methyl-4-oxopiperidine-1-carboxylate (6)** [x]




92% yield; trans product

**4a** **6**

In a flame-dried Schlenk tube equipped with a septum and a magnetic stirring bar, substrate **4a** (0.2 mmol), Pd/C (10 mol%) and THF (2 mL) were added under hydrogen atmosphere (balloon). The reaction mixture was stirred at room temperature for 2 h. After that, the reaction mixture was filtered (to remove Pd/C) using 0.2 mm filter membrane and the solvent was removed by rotary evaporator. The crude was purified by flash chromatography on silica gel ($Et_2O$:Pentane= 1:1) obtaining **6** as a single product with 92% yield.

In order to determine the absolute configuration of product **6**, a NOESY experiment was carried out (Figure S1 and Figure S2). We observe that there is no NOE correlation between $H_1$ and $H_6$, revealing a transperiplanar disposition of these two hydrogens and consequently we can state that **6** possesses a *trans* substitution pattern.

$^1$H NMR (400 MHz, $CDCl_3$) δ 4.79-4.68 (m, 1H, $CH_3CH$), 4.59-4.45 (m, 1H, $CHCH_2$), 3.71 (s, 3H, $OCH_3$), 2.63-2.59 (m, 2H, $COCH_2$), 2.37-2.29 (m, 2H, $COCH_2$), 1.69-1.48 (m, 2H, $CH_2CH_3$), 1.25 (d, *J* = 7.0 Hz, 3H, $CH_3CH$), 0.90 (t, *J* = 7.4 Hz, 3H, $CH_2CH_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.19, 156.36, 54.59, 52.95, 48.78, 45.56, 43.40, 29.81, 22.70, 11.38.

HRMS (ESI+, m/Z): calcd for $C_{10}H_{17}NO_3$ $[M+H]^+$: 200.1281, found: 200.1276.

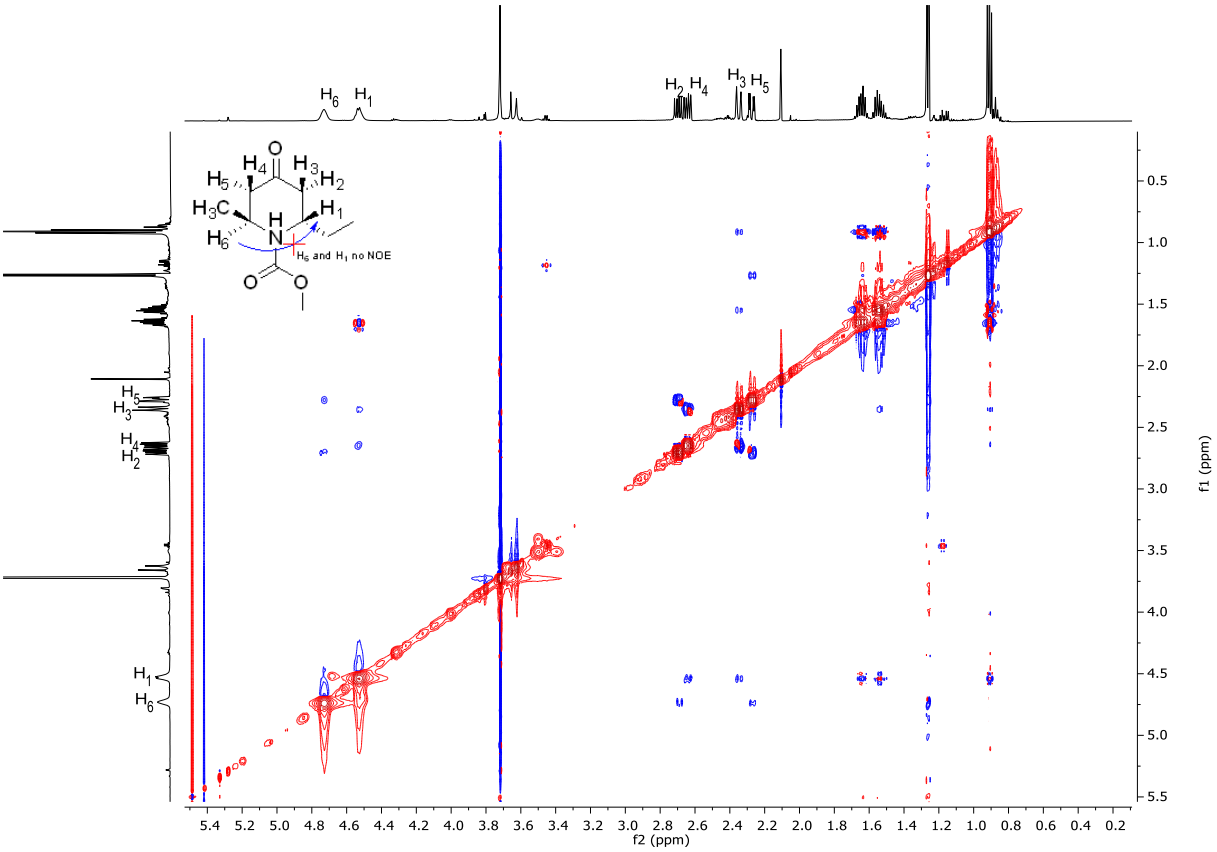



**Figure S1. Noesy spectra of compound 6.**

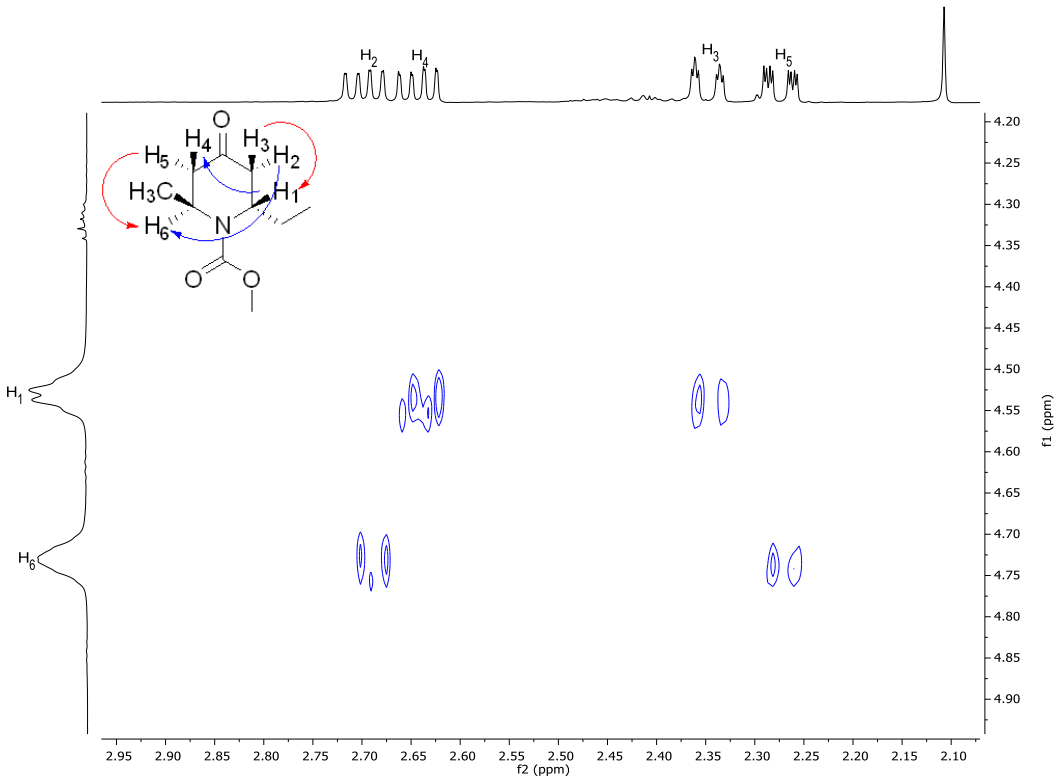
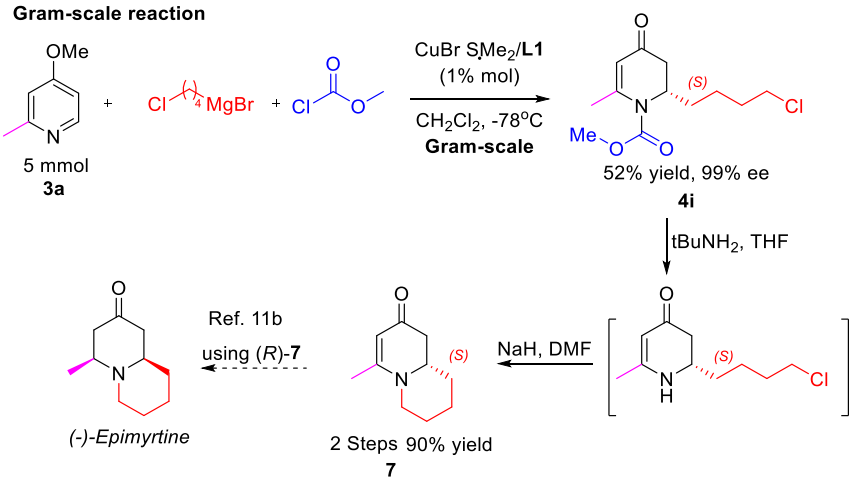



**Figure S2. Noesy spectra of compound 6 (enlarged Figure S1).**

**Synthesis of (*S*)-4-met**

**hyl-1,6,7,8,9,9a-hexahydro-2*H*-quinolizin-2-one (7).**




In a flame-dried Schlenk tube, equipped with a septum and a magnetic stirring bar, $CuBr{\cdot}SMe_2$ (0.05 mmol, 1 mol%), and the ligand **L1** (*R*,*R*)-Ph-BPE (0.05 mmol, 1 mol%) were dissolved in $CH_2Cl_2$ (50 mL) and stirred under nitrogen atmosphere for 20 min. Then, 4-methoxy-2-methylpyridine **3a** (5 mmol, 1.0 equiv.) was added at once. After stirring for 5 min at room temperature (18-25 $^oC$), methyl chloroformate (10 mmol, 2.0 equiv.) was added dropwise (the color of the solution changed from colorless to red). The mixture was stirred for 10 min at room temperature, and then the reaction was transferred to -78 $^oC$ and 4-ClBuMgBr (10 mmol, 2.0 equiv., 1.2 M in $Et_2O$) was added by syringe pump for 2 h. The reaction was stirred overnight at -78 $^oC$. After that, the reaction was quenched with 1.0 M HCl solution (50 mL). The reaction mixture was extracted with $CH_2Cl_2$ (3×50 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvents were evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel ($Et_2O$:Pentane= 1:1) to give the product **4i** with 52% yield and 99% ee.

In a flame-dried Schlenk tube equipped with septum and magnetic stirring bar, substrate **4i** (260 mg, 1.0 mmol) was dissolved in 10 mL MeOH. Then, *t*$BuNH_2$ (30 mmol, 3.2 mL) was added to the solution. The solution refluxed at 100 $^oC$ for 6 h, after which it was cooled down and the MeOH and *t*$BuNH_2$ were evaporated using reduced pressure. The crude was used in the next step without purification.[xia]

To a DMF (anhydrous, 5 mL) solution of the crude (202 mg, 1.0 mmol), sodium hydride (80 mg, 60% in oil, 2.0 equiv.) was added at 0 $^oC$. The reaction was stirred at 0 $^oC$ for 2 h. Then, it was quenched with saturated aqueous $NH_4Cl$ solution. The mixture was extracted with EtOAc

(3x10 mL) and the combined organic layers were washed with brine and dried over $Na_2SO_4$. After concentration, the crude was purified by column chromatography on silica gel ($Et_2O$/MeOH=20:1) to afford the product **7** with 90% yield in two steps (>99% ee, (*S*)-configuration).[xi]

$^1$H NMR (400 MHz, $CDCl_3$) δ 4.96 (s, 1H, COC*H*), 3.75 (d, *J* = 13.1 Hz, 1H, COC$H_2$), 3.38-3.27 (m, 1H, NC*H*), 2.83-2.71 (m, 1H, NC$H_2$), 2.48 (dd, *J* = 16.5, 5.8 Hz, 1H, COC$H_2$), 2.26 (dd, *J* = 16.4, 10.6 Hz, 1H, COC$H_2$), 1.95 (s, 3H, C$H_3$), 1.84-1.41 (m, 6H, $NCH_2(C\underline{H_2})_3$).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 191.39, 163.06, 101.86, 58.64, 48.12, 42.93, 31.47, 25.81, 23.74, 21.27.

$[\alpha]_D^{20}$ = -182.1 (*c* 1.0, $CHCl_3$), *S*-configuration.

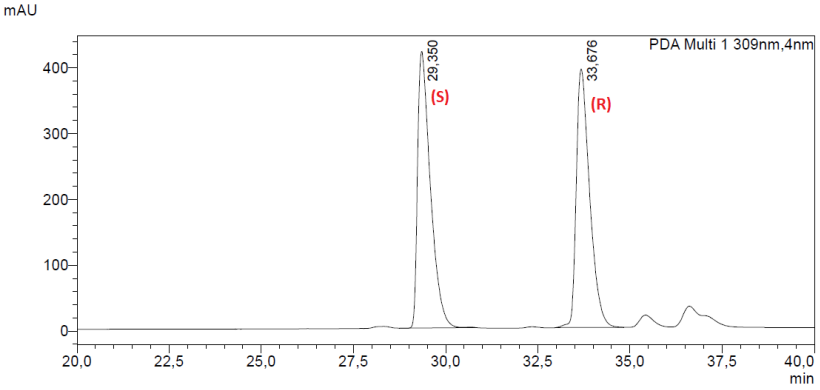
HRMS (ESI+, m/Z): calcd for $C_{10}H_{15}NO$ $[M+H]^+$: 166.1226, found: 166.1226.

HPLC analysis: Chiracel-ODH, *i*-PrOH 1-25% in hexane, 1.0 mL/min, 30 °C, detection at 309 nm. Retention time (min): 29.18 min (major).

The NMR, HPLC, rotation data are in accordance with data described in reference 15b and 2.

Reference ii shows the reported data for **7** (44% ee, chiral OD column, *i*PrOH 1-25% in hexane, 60 min, 1.0 mL/min, 30 °C, (-)-Enantiomer $R_t$=36.3 min, (+)-Enantiomer $R_t$=39.6 min; $[\alpha]_D^{22}$ = -95.0 (*c* 0.924, $CHCl_3$), *S*-configuration).

**<Chromatogram>**

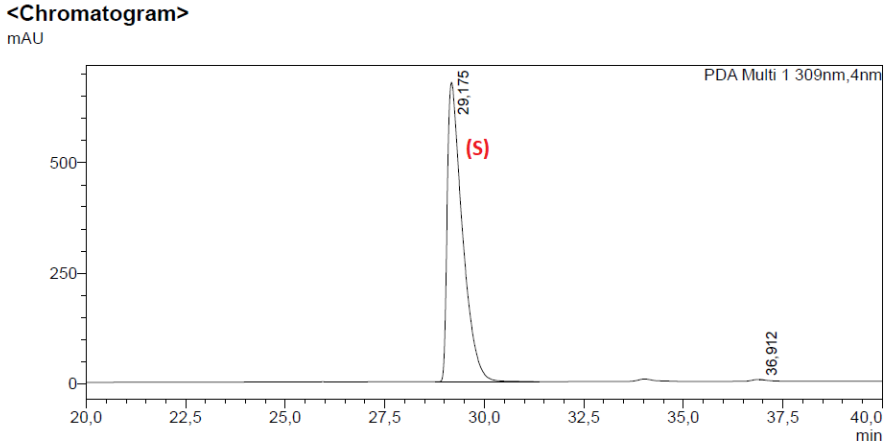



**<Peak Table>**

PDA Ch1 309nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 29,350 | 10159764 | 420002 | 50,598 | | | |
| 2 | 33,676 | 9919656 | 392536 | 49,402 | | | |
| Total | | 20079420 | 812538 | | | | |

**<Chromatogram>**



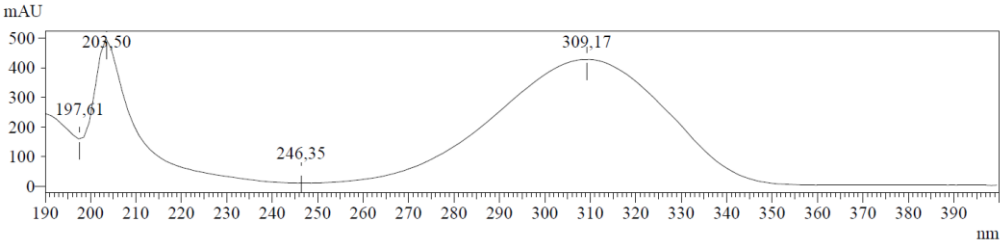

**<Peak Table>**

PDA Ch1 309nm

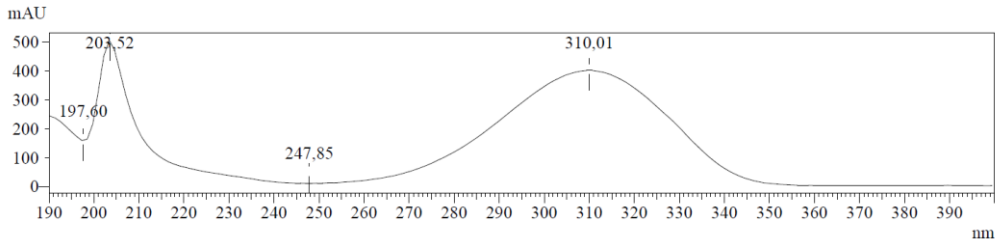
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 29,175 | 17880279 | 676634 | 100,000 | | | |
| 2 | 36,912 | 63 | 42 | 0,000 | | M | |
| Total | | 17880342 | 676676 | | | | |

UV Spectrum

Peak# : 1
Retention Time : 29,350 min
Compound Name :
Spectrum Operation:



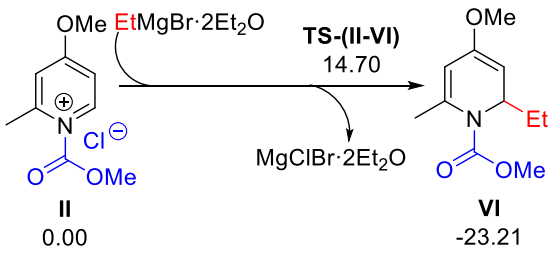

Peak# : 2
Retention Time : 33,676 min
Compound Name :
Spectrum Operation:



## 8. Computational and mechanistic studies

Our first step in the mechanistic elucidation of the copper catalyzed addition of Grignard reagents to 4-methoxy-pyridine was the computational study of the blank reaction, *i.e.* the addition of the Grignard reagent to the 4-methoxypyridinium salt. The formation of this salt results in sufficient activation of the pyridine to make the background addition reaction competitive at the working temperature (Figure S3).

**Figure S3. Computational study on the direct addition of EtMgBr to II** [a]




[a]Calculations were performed at the PCM($CH_2Cl_2$)/B3LYP-D3/def2tzvpp//B3LYP-D3/def2svpp computational level using the Gaussian 09 program. The thermochemistry was obtained at 1 atm and 298 K.

**Table S1. Summary of the energies for the calculated stationary points in the study of the Grignard addition to 4-methoxy-1-(methoxycarbonyl)- pyridin-1-ium** [a]

| ID | Im Freqs | Stable | SCF(B3LYP-D3/def2svpp) | SCF(B3LYP-D3/def2TZVPP) | SCF+ZPV | H[b] | G[c] |
|---|---|---|---|---|---|---|---|
| **II + EtMgBr·2Et2O** | - | Yes | -4410.409693 | -4412.380383 | -4409.821645 | -4409.820701 | -4409.933039 |
| **TS-(II-VI)** | -344.7579 | Yes | -4410.386911 | -4412.353641 | -4409.835756 | -4409.797853 | -4409.906230 |
| **VI** | - | Yes | -4410.470632 | -4412.438507 | -4409.915376 | -4409.878603 | -4409.984231 |

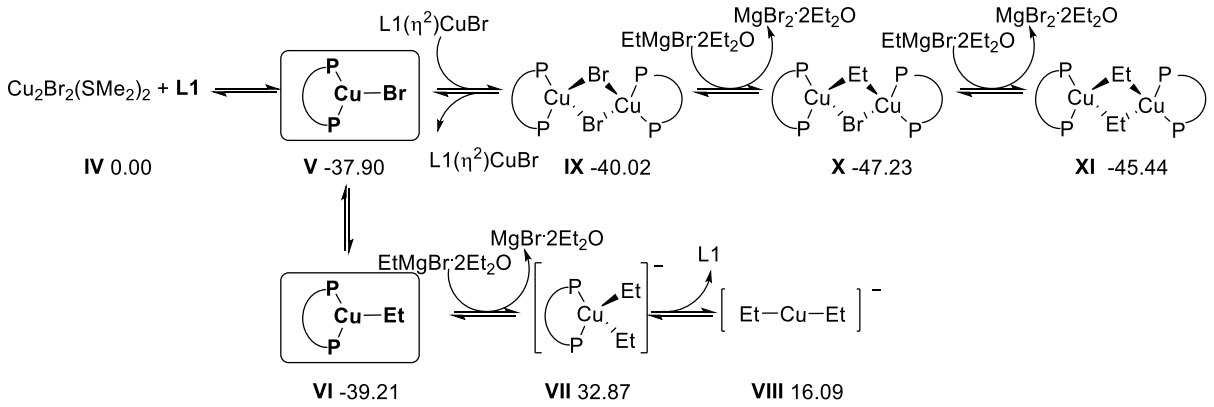
[a]Energies are expressed in a.u. and the imaginary frequencies in $cm^{-1}$. [b]H represents enthalpies. [c]G represents Gibbs free energies.

### Mechanistic exploration:

It has been argued that the copper salt might form aggregates in solution.[xii] Accordingly, prior to the computational mechanistic study we have performed an analysis of the energetics of all the potential copper complexes that can be formed in solution when (*R*,*R*)-Ph-BPE is explored as ligand (Figure S4). We have found that, in line with the experimental evidence, CuBr in the presence of the ligand (**L1**) will form **V**. Then, **V** can further evolve towards the formation of the dimeric species **IX** (-40.02 kcal/mol). The exergonicity found for the formation of **IX** is in line with previous literature.[xiii] Species **IX** can further evolve towards **X** and **XI** via transmetallation with the Grignard reagent. We have found that once **IX** and **XI** interact with the pyridine, the dimeric structure is broken by losing one of the monomers. Moreover, the

degree of dilution in which the catalyst (copper source) is present in the reaction medium led us to explore the direct transmetallation of **V** to form species **VI**, another species that is feasible at the reaction conditions (ratio substrate : copper : Grignard = 1:0.06:2). We next explored further transmetallation of copper species **VI** to form organocuprates **VII** and **VIII.** Note that species **VIII** is not chiral. We have found that, in our system those species are unlikely to be present since their relative energies with respect to **VI** are rather high.

**Figure S4. Computational study on the copper speciation in solution** [a]




[a]Calculations were performed at the PCM($CH_2Cl_2$)/B3LYP-D3/def2tzvpp//B3LYP-D3/def2svpp computational level using the Gaussian 09 program. The thermochemistry was obtained at 1 atm and 298 K. The structure of the ligand **L1** has been represented by an arc for simplicity.

## Summary of electronic energies on the study of the copper speciation in solution

**Table S2. Summary of the energies for the calculated stationary points in the study on the speciation of copper in solution** [a]

| ID | Im Freqs | Stable | SCF (B3LYP-D3/def2svpp) | SCF (B3LYP-D3/def2tzvpp) | SCF+ZPV | H[b] | G[c] |
|---|---|---|---|---|---|---|---|
| **$Cu_2Br_2(SMe_2)_2$** | - | Yes | -9384.324825 | -9385.935919 | -9384.169294 | -9384.14848 | -9384.22525 |
| **L1** | - | Yes | -1998.909269 | -2000.647372 | -1998.299323 | -1998.266684 | -1998.365894 |
| **L1CuBr (V)** | - | Yes | -6213.255009 | -6215.554873 | -6212.642326 | -6212.605982 | -6212.714326 |
| **$L1_2Cu_2Br_2$ (IX)** | - | Yes | -12426.56932 | -12431.1428 | -12425.34169 | -12425.26827 | -12425.45606 |
| **$MgBr_2{\cdot}2Et_2O$** | - | Yes | -5814.999674 | -5816.274358 | -5814.71919 | -5814.698459 | -5814.769621 |
| **$L1_2Cu_2BrEt$ (X)** | - | Yes | -9931.766098 | -9936.127839 | -9930.475325 | -9930.400655 | -9930.588384 |
| **$L1_2Cu_2Et_2$ (XI)** | - | Yes | -7436.944424 | -7441.096295 | -7435.59001 | -7435.513938 | -7435.704066 |
| **L1CuEt (VI)** | - | Yes | -3718.446528 | -3720.529988 | -3717.771692 | -3717.733522 | -3717.842954 |
| **$L1CuEt_2$ (VII)** | - | Yes | -3797.646442 | -3799.836452 | -3796.909616 | -3796.868121 | -3796.982869 |
| **$CuEt_2$ (VIII)** | - | Yes | -1798.730783 | -1799.189085 | -1798.605638 | -1798.596297 | -1798.639048 |

[a]Energies are expressed in a.u. and the imaginary frequencies in $cm^{-1}$. [b]H represents enthalpies. [c]G represents Gibbs free energies.

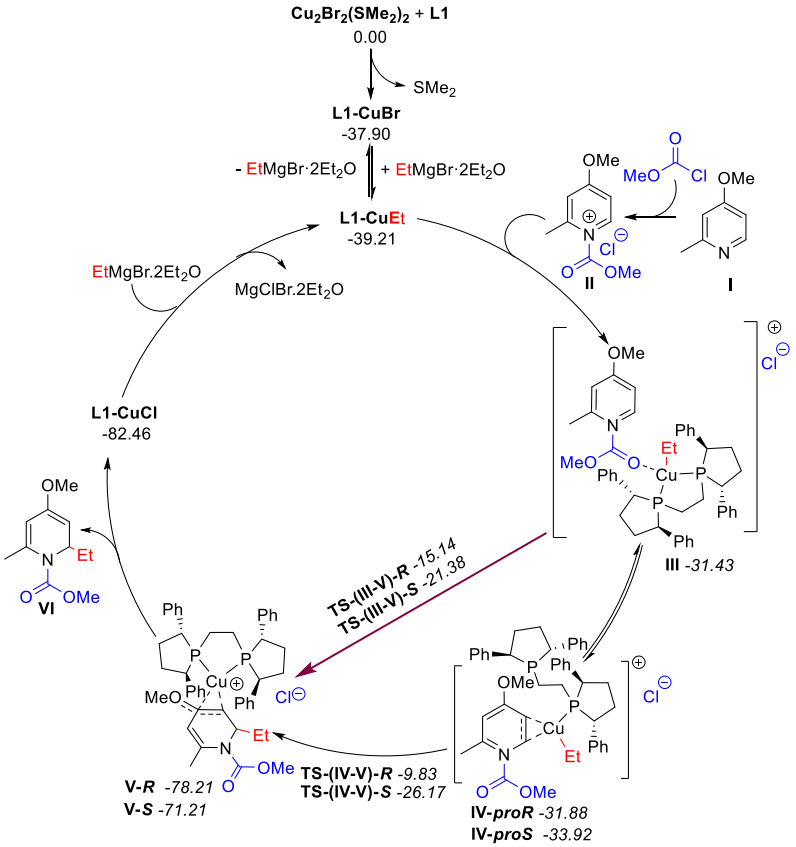
Once we had identified the potential species present in the reaction medium (**V**, **VI**), we decided to study the relative stability of the complexes that can be formed between these species (**V** and **VI**) and the pyridine substrate (**II**) and how they can evolve. All our attempts to locate the complex between **V** and **II** led to the two independent species. Therefore this path was disregarded and we moved towards the study of the copper catalyzed asymmetric conjugate addition of EtMgBr·2$Et_2O$ to **II**, as described in the main text.

**Study of the potential competitive mechanisms that could account for the Cu-catalyzed asymmetric addition of EtMgBr to II**

It is proposed in the main text that after the formation of complex **L1-CuBr** and the subsequent transmetallation upon addition of EtMgBr leading to **L1-CuEt**, the resulting organocopper species **L1-CuEt** can coordinate intermediate **II** at C-5-C-6 or at the carbonyl moiety rendering **III**. Once **III** is formed, it can evolve as described in the main text, but it can also evolve via the direct addition of the *Et* moiety to position C-6. The delivery of the *Et* group at C-6 can take place from the top or bottom face of the substrate yielding **V-*R*** or **V-*S*** through **TS-(III-V)-*R*** or **TS-(III-V)-*S***, respectively. The relative energies for these two transition states -15.14 and -21.38 imply an energy barrier of 16.29 and 10.05 kcal/mol, respectively. These energies are higher than the proposed path for the evolution of **III** to **V** via **IV**, rendering it non-competitive at the working conditions.

It is quite remarkable that the evolution of **III** showcases an energetically more plausible route for the erosion of the enantioselectivities than that found for the evolution of **IV**. Notice, that while in both cases the formation of the (*S*)-enantiomer of the product is the most favorable reaction, a comparison of **TS-(IV-V)-*R*** and **TS-(III-V)-*R*** reveals that the latter is energetically preferred over the former thus providing a potential competitive path for erosion of the enantioselectivity in other similar substrates.

**Scheme S1. Mechanistic proposal** [a]




[a]Calculations were performed at the PCM($CH_2Cl_2$)[xii] /B3LYP-D3/def2tzvpp //B3LYP-D3/def2svpp computational level using the Gaussian 09 program. The thermochemistry was obtained at 1 atm and 298.15 K. The following color code was selected: the pyridinium species is represented with black color, the protecting group with blue, the **L1** ligand is depicted in black and the ethyl group is depicted in red.

## Summary of electronic energies on the mechanistic study for the copper catalyzed asymmetric conjugated addition of Grignard reagents to II

## Table S3. Summary of the energies for the calculated stationary points in the study of the copper catalyzed formation of 4-methoxy-1-(methoxycarbonyl)- pyridin-1-ium derivatives [a]

| ID | ImFreqs | Stable | SCF (B3LYP-D3/def2svpp) | SCF (B3LYP-D3/def2tzvpp) | SCF+ZPV | H[b] | G[c] |
|---|---|---|---|---|---|---|---|
| **$Cu_2Br_2(SMe_2)_2$** | - | Yes | -9384.324825 | -9385.935919 | -9384.169294 | -9384.14848 | -9384.22525 |
| **L1** | - | Yes | -1998.909269 | -2000.647372 | -1998.299323 | -1998.266684 | -1998.365894 |
| **L1-CuBr** | - | Yes | -6213.255009 | -6215.554873 | -6212.642326 | -6212.605982 | -6212.714326 |
| **EtMgBr·$2Et_2O$** | - | Yes | -3320.18153 | -3321.244234 | -3319.840154 | -3319.81692 | -3319.893004 |
| **L1-CuEt** | - | Yes | -3718.446528 | -3720.529988 | -3717.771692 | -3717.733522 | -3717.842954 |
| **I-Me or I** | - | Yes | -401.8343139 | -402.3068089 | -401.685694 | -401.676318 | -401.719096 |
| **II** | - | Yes | -1090.216132 | -1091.12968 | -1090.010715 | -1089.994841 | -1090.054319 |

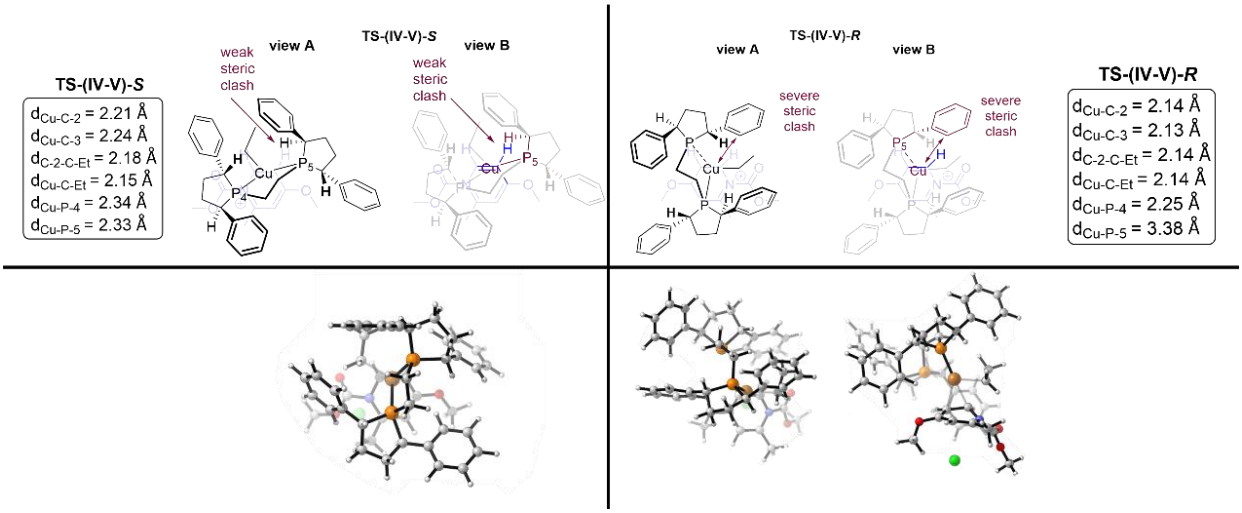
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **III** | - | Yes | -4808.693416 | -4811.672091 | -4807.810859 | -4807.756562 | -4807.900899 |
| **TS-(III-V)-*R*** | -302.8928 | Yes | -4808.67207352 | -4811.64845695 | -4807.789841 | -4807.736305 | -4807.877555 |
| **TS-(III-V)-*S*** | -303.8981 | Yes | -4808.683916 | -4811.657402 | -4807.802787 | -4807.748864 | -4807.891503 |
| **IV-*proR*** | - | Yes | -4808.684876 | -4808.684876 | -4807.801704 | -4807.747354 | -4807.893186 |
| **IV-*proS*** | - | Yes | -4808.689249 | -4811.673587 | -4807.806223 | -4807.751852 | -4807.898738 |
| **TS-(IV-V)-*R*** | -277.338 | Yes | -4808.660443 | -4811.64202470 | -4807.777387 | -4807.723762 | -4807.858054 |
| **TS-(IV-V)-*S*** | -307.3739 | Yes | -4808.68559752 | -4811.66717922 | -4807.801732 | -4807.748757 | -4807.888312 |
| **V-*R*** | - | Yes | -4808.773907 | -4811.747402 | -4807.887715 | -4807.8341 | -4807.977 |
| **V-*S*** | - | Yes | -4808.73435 | -4811.712202 | -4807.847826 | -4807.794134 | -4807.936993 |
| **L1-CuCl** | - | Yes | -4099.443134 | -4101.592252 | -4098.830402 | -4098.794191 | -4098.901438 |
| **MgClBr·2Et$_2$O** | - | Yes | -3701.199418 | -3702.317915 | -3700.919234 | -3700.898354 | -3700.97004 |

[a]Energies are expressed in a.u. and the imaginary frequencies in $cm^{-1}$. [b]H represents enthalpies. [c]G represents Gibbs free energies.

## Unraveling the origin of the enantioselectivity using molecular modelling

To understand the difference in energy between **TS-(IV-V)-*R*** and **TS-(IV-V)-*S*** we have performed a detailed structural analysis of the transition states (Figure S5). In **TS-(IV-V)-*R*** (Figure S5-right) one of the Cu-P bonds (Cu-P-5) is significantly elongated with respect to the other (Cu-P-4) so that the substrate can be accommodated (view A and Scheme 5 in the Manuscript). The reason behind the necessary decoordination of the phosphorous atom resides in the clash between one of the phenyl rings of the ligand and the substrate (view B). In the **TS-(IV-V)-*S*** (Figure S5-left) the phenyl group is no longer occupying the same position, in this structure a hydrogen is now close to the substrate (view B), thus reducing significantly the steric interaction between the substrate and the substituents in the ligand. It could be argued at this point that there is not a phenyl group in that same region of the molecule, it is only reoriented towards the carbonyl unit and thus still a clash in between groups could be present. However, this is not the case since the ligand orients the phenyl group in the space in such a way that it remains far from the carbonyl moiety due to the structural constriction imposed by the conformation of the five membered ring in which this group resides (Figure S5-left, view A).

**Figure S5. Chemdraw and 3D representation of the TS-(IV-V).**[a]




[a]Top-left: representation of **TS-(IV-V)-*S***. In view A the complete superposition of the organocopper species and the catalyst is colored while in view B only the relevant groups are represented in color. Bottom-left: 3D representation of the **TS-(IV-V)-*S***. Top-right: representation of **TS-(IV-V)-*R***. In view A the complete superposition of the organocopper species and the catalyst is presented while in view B only the relevant groups are represented in color. Bottom-right: 3D representation of the **TS-(IV-V)-*R***, in this case two different perspectives of the transition state are depicted in order to ensure a comprehensive visualization of the structure.

## Study of the influence of the structure of the chiral ligand on the outcome of Cu(I)-catalyzed asymmetric addition of EtMgBr to II (or 1a)

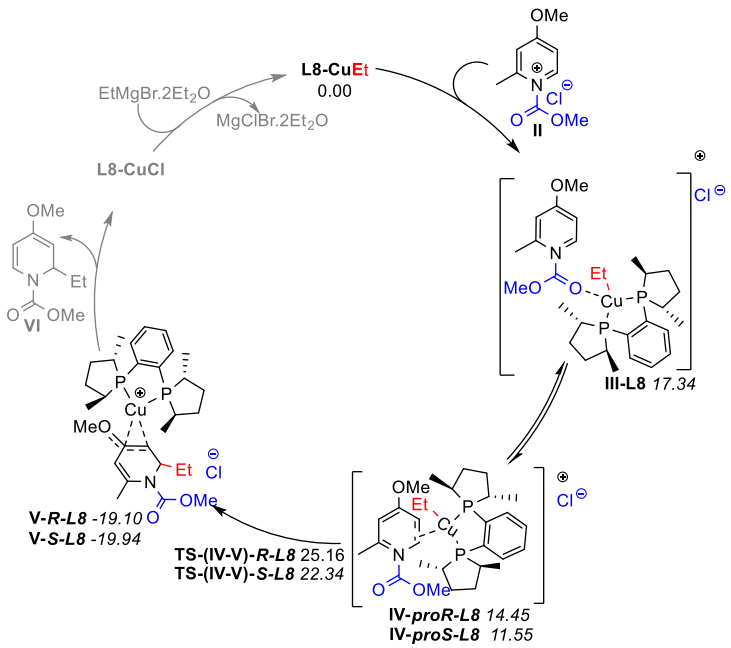
At this point, we decided to evaluate the influence of the rigidity of the ligand (binding angle) and the mono- and bidentate nature of the phosphine on the reaction outcome.

Starting with the analysis of the influence of the mono- and bidentate nature of the ligands, we explored the reaction using with **1a** as substrate, EtMgBr as the Grignard reagent and **L7** as a monodentate ligand, under the optimal reaction conditions. No substrate conversion was observed indicating that the bidentate nature of the ligand is important for the reaction outcome. Then, we moved to study the effect of the rigidity of the ligand on the reaction outcome. With this purpose, an alternative bidentate ligand featuring structural rigidity, namely (*R*,*R*)-Me-DuPhos (**L8**) was tested in the copper catalyzed transformation of **1a** once again without any substrate conversion detected.

To get deeper understanding of the influence of the binding angle and the ligand rigidity on the reaction outcome, we recomputed the mechanism described in Scheme S1 using **L8**, more specifically we recomputed the mechanism until the stereodetermining step. We found that enantiodiscrimination in principle can be achieved with **L8**, but the difference in energy

betweenthe paths leading to the *R* and *S* enantiomers of the product is much less than that obtained in the case of flexible bidentate ligand **L1** (compare Scheme S1 and Scheme S2). The structural rigidity of **L8** impedes the release of one of the phosphine armsand as a consequence worse enantiodiscrimination. Note that for both **IV** and **TS-(IV-V)** the differences between the two diastereomeric complexes are not severe (2.9 and 2.8 kcal/mol, respectively). These results are in line with previous reports by our group, where we showed that **L8** can induce enantiodiscrimination but to a considerably lower extent.[xiii] Nonetheless, for the presented protocol, the energies of the complexes **IV** and also the subsequent transition states are quite high, explaining the unfruitful attempts to make this reaction work with substrate **1a** experimentally, and emphasizing the relevance of a bidentate ligand in this protocol.

**Scheme S2. Computational study of the influence of using Me-DuPhos (L8) on the enantiodetermining step of the copper catalyzed asymmetric Grignard addition to II** [a]




[a]Calculations were performed at the PCM($CH_2Cl_2$)/B3LYP-D3/def2tzvpp //B3LYP-D3/def2svpp computational level using the Gaussian 09 program.The thermochemistry was obtained at 1 atm and 298.15 K. The pyridinium species and ligand **L8** are depicted in black, the protecting group in blue and the ethyl group in red.

**Table S4. Energy report of those structures depicted at Figure S6** [a]

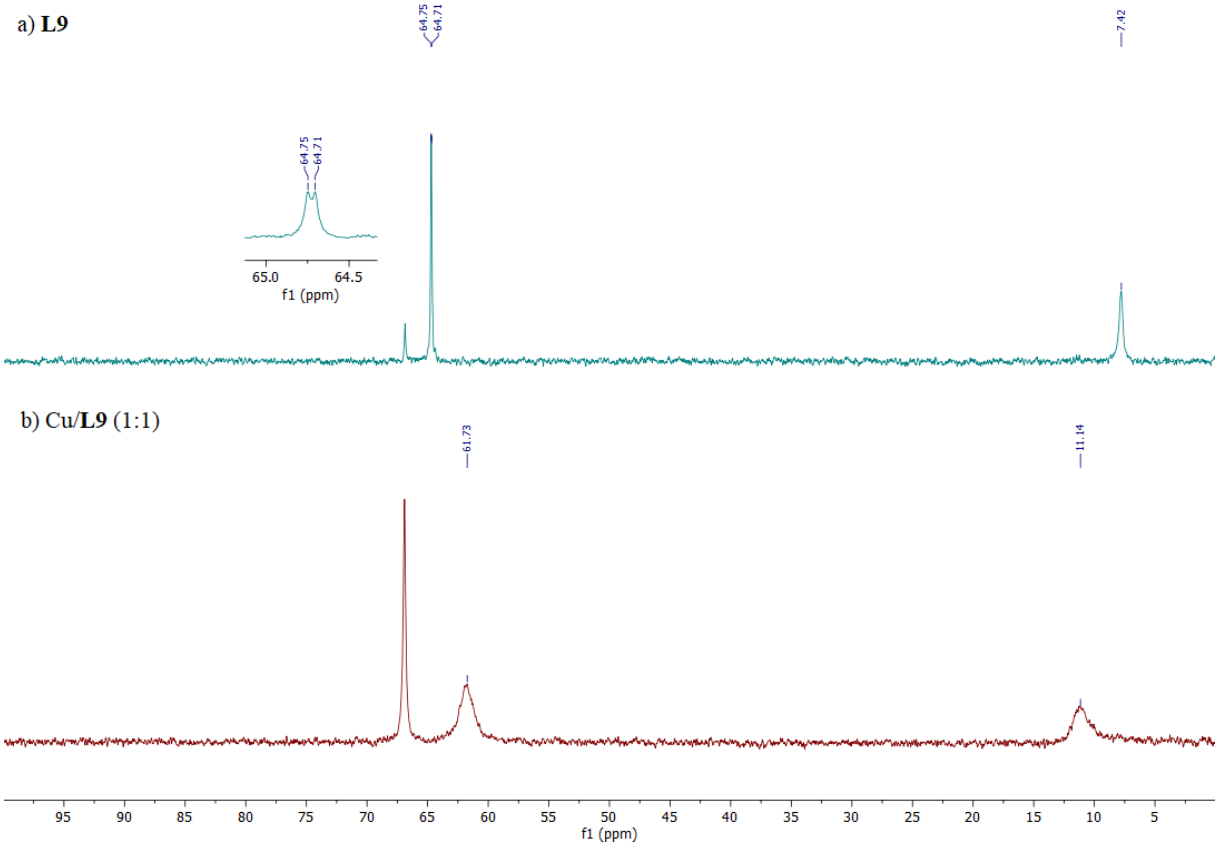
| ID | Im Freqs | Stable | SCF(B3LYP-D3/def2svpp) | SCF(B3LYP-D3/def2tzvpp) | SCF+ZPV | H[b] | G[c] |
|---|---|---|---|---|---|---|---|
| **L8-CuEt** | | Yes | -3104.33768 | -3105.753011 | -3103.853395 | -3103.82485 | -3103.912174 |
| **II** | - | Yes | -1090.217377 | -1091.129978 | -1090.011914 | -1089.996222 | -1090.054305 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **III-L8** | - | Yes | -4194.566997 | -4196.883391 | -4193.87386 | -4193.829654 | -4193.950376 |
| **IV-*proR*-L8** | - | Yes | -4194.575448 | -4196.890029 | -4193.881732 | -4193.837716 | -4193.956801 |
| **IV-*proS*-L8** | - | Yes | -4194.583108 | -4196.893765 | -4193.890305 | -4193.846137 | -4193.965353 |
| **TS-(IV-V)-*R*-L8** | -264.675 | Yes | -4194.571793 | -4196.875239 | -4193.877786 | -4193.834762 | -4193.950871 |
| **TS-(IV-V)-*S*-L8** | -320.895 | Yes | -4194.562669 | -4196.877836 | -4193.86917 | -4193.825934 | -4193.943639 |
| **V-*R*-L8** | - | Yes | -4194.633877 | -4196.944535 | -4193.937619 | -4193.893867 | -4194.014198 |
| **V-*S*-L8** | - | Yes | -4194.629771 | -4196.943085 | -4193.934661 | -4193.890907 | -4194.012875 |

[a]Energies are expressed in a.u. and the imaginary frequencies in $cm^{-1}$. [b]H represents enthalpies. [c]G represents Gibbs free energies.

To study the role of the flexible linkage in the ligand structure bearing labile phosphinoxide group on the reaction outcome, we explored monooxidized biphosphine ligands. These bidentate ligand are expected to have one labile coordinating group (phosphine oxide moiety), that would in principle allow to reproduce the coordination and decoordination pattern found for **L1** (Scheme S1). We started by exploring the Me-DuPhos(O) ligand (**L9**). Initially, we studied its complexation with copper ($CuBr{\cdot}SMe_2$), using NMR spectroscopy (Figure S6) to confirm that changing one phosphine moiety to a phosphine oxide would not alter its bidentate character. $^{31}$P NMR studies, using $CD_2Cl_2$ as a solvent, revealed that the binding of **L9** to copper is bidentate. This bidentate coordination is revealed by the shift of the $^{31}$ P NMR signals from 7.4 and 64.7 ppm a to 11.1 and 61.7 ppm accompanied by a broadening of the signals, respectively (compare Figure S6a and b). Then, we tested this ligand in the copper catalyzed reaction with **1a** as substrate, and we found no conversion to the product. This result emphasizes once again the importance of a flexible ligand for the reaction.

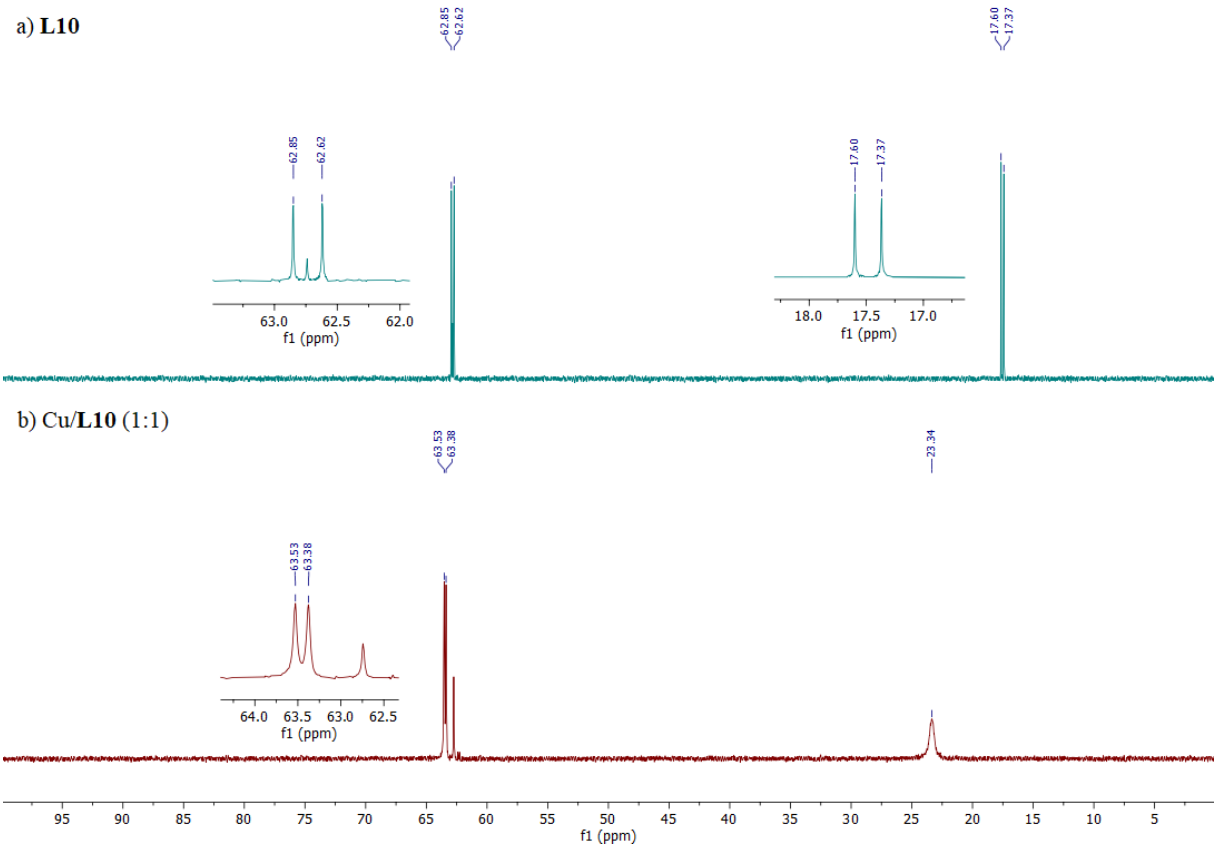
**Figure S6. $^{31}$P NMR of *(R,R)*-Me-DuPhos(O) L9 (a) and its complexation with CuBr·SMe$_2$ (b) in $CD_2Cl_2$ [a]**




[a] a) *To prepare the NMR sample 0.012 mmol of **L9** were dissolved in 0.6 mL of $CD_2Cl_2$. b) To prepare the NMR sample 0.012 mmol of **L9** and 0.012 mmol of the copper source were dissolved in 0.6 mL of $CD_2Cl_2$.*

Finally we synthesized Ph-BPE(O) (**L10**) and tested in the model reaction. We were expecting that **L10** and **L1** would show analogous results or even that **L10** would outperform **L1**, due to the presence of a more labile group in the ligand structure. Following the same protocol as with**L9**) we studied the complexation of **L10** with copper (CuBr·SMe$_2$) using $^{31}$P NMR spectroscopy. Surprisingly $^{31}$P NMR studies, using $CD_2Cl_2$ as a solvent, showed that in contrast to **L9**, **L10** coordinates to copper as a monodentate ligand. Note that only the doublet at 17.5 ppm – corresponding to the phosphine moiety- shifts notoriously to a broad signal at 23.3 ppm when the copper source is added to the NMR tube (Figure S7a and b). Therefore this experiment cannot provide us with the expected insight, however it does provide information about the behavior of the reaction when other monodentate ligands, structurally similar to **L1** are tested. When we tested **L10** in the copper catalyzed addition of EtMgBr to **1a**, we found that the reaction does not evolve to products, emphasizing once again the fact that bidentate ligands are crucial for this reaction to be successful.

**Figure S7. $^{31}$P NMR of (*R,R)*-Ph-BPE(O) L10 (a) and its complexation with $CuBr \cdot SMe_2$ (b) in $CD_2Cl_2$ [a]**




[a] a) *To prepare the NMR samples 0.07 mmol of **L10** was dissolved in 0.6 mL of $CD_2Cl_2$. b) To prepare the NMR samples 0.07 mmol of **L10** and 0.07 mmol of the copper source were dissolved in 0.6 mL of $CD_2Cl_2$.*

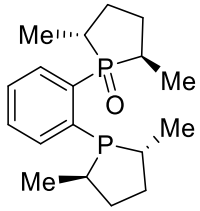
## General procedure for the synthesis of the tested biphosphine oxide ligands and characterization

### General procedure for the synthesis of biphosphine monoxides[xiv]

To a flame-dried round bottom flask the corresponding biphosphine ligand (1.0 equiv.) was added under inert conditions. The ligand was dissolved in dry THF (0.1 M) and the solution was cooled to 0 $^{o}$C before $BH_3 \cdot DMS$ (1.1 equiv., 1.0 M in THF) was added dropwise. After 45 minutes, $H_2O_2$ (12 equiv., 30 wt% in $H_2O$) was added slowly and the mixture was allowed to warm to room temperature and stir for another 45 minutes. The mixture was quenched with a saturated $Na_2S_2O_3$ solution (5 mL), extracted with EtOAc (3x5 mL), dried over $Na_2SO_4$ and the solvent was removed under reduced pressure. The crude product together with DABCO (1.5 equiv.) were placed in a flame-dried round bottom flask under an inert atmosphere.

Anhydrous toluene was added (0.1 M) and the solution was heated to 50 $^{o}$C for 12 hours. The solvent was removed under reduced pressure and the product was obtained after column chromatography (EtOAc:MeOH, 20:1).

**(*2R,5R*)-1-(2-((*2R,5R*)-2,5-dimethylphospholan-1-yl)phenyl)-2,5-dimethylphospholane 1-oxide (L9)[xiv] ***




**L9**

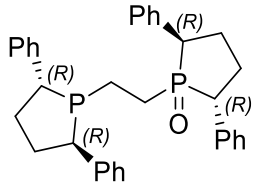
The reaction was performed following the **general procedure for the synthesis of phosphine monoxides** with 0.5 mmol (*R,R*)-Me-DuPhos. The product **L9** was obtained as a white solid after column chromatography ($SiO_2$, EtOAc:MeOH, 20:1) with 34% yield.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H, C$H_{Ar}$), 7.62 (t, *J* = 9.5 Hz, 1H, C$H_{Ar}$), 7.49 (t, *J* = 7.5 Hz, 1H, C$H_{Ar}$), 7.41 (t, *J* = 7.5 Hz, 1H, C$H_{Ar}$), 2.72 – 2.44 (m, 4H), 2.44 – 2.26 (m, 1H), 2.26 – 2.04 (m, 3H), 1.93 – 1.62 (m, 2H), 1.62 – 1.37 (m, 2H), 1.37 – 1.20 (m, 6H, 2x C$H_3$), 0.91 (dd, *J* = 17.7, 7.4 Hz, 3H, C$H_3$), 0.82 (dd, *J* = 9.5, 7.1 Hz, 3H, C$H_3$).
$^{31}$P NMR (121 MHz, $CD_2Cl_2$) δ 64.73 (d, *J* = 5.42 Hz), 7.39.

HRMS (ESI+, m/Z): calcd. for $C_{18}H_{28}OP_2$ $[M+H]^+$: 323.1699, found: 323.1691.

** Due to difficulties for obtaining a clear $^{13}$C NMR, as acknowledged previously in literature,[xiv] we characterized **L9** using $^{1}$H NMR, $^{31}$P NMR and HRMS.*

**(2*R*,5*R*)-1-(2-((2*R*,5*R*)-2,5-diphenylphospholan-1-yl)ethyl)-2,5-diphenylphospholane 1-oxide (L10)**



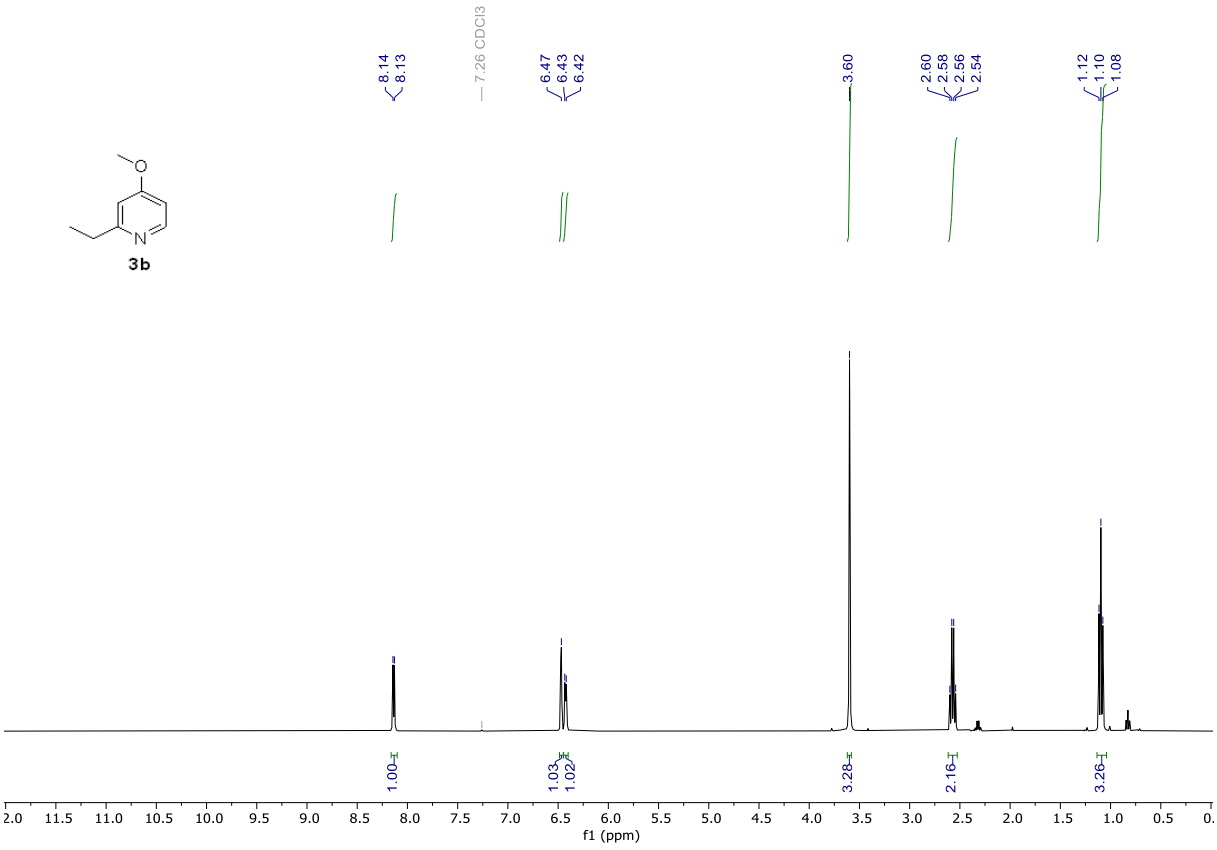

**L10**

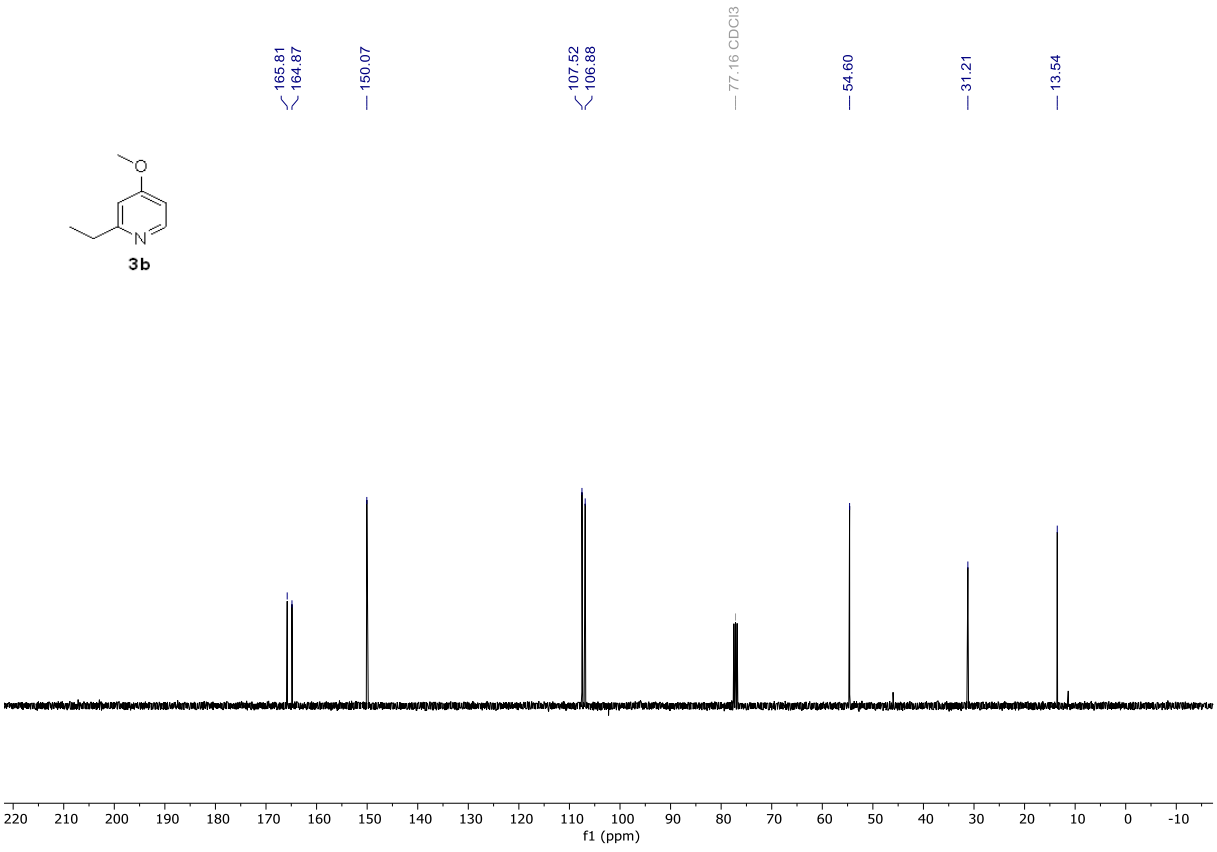
The reaction was performed following the **general procedure for the synthesis of phosphine monoxides** with 0.07 mmol (*R*,*R*)-Ph-BPE. The product was obtained as a white solid after column chromatography ($SiO_2$, EtOAc:MeOH, 20:1) with 38% yield.

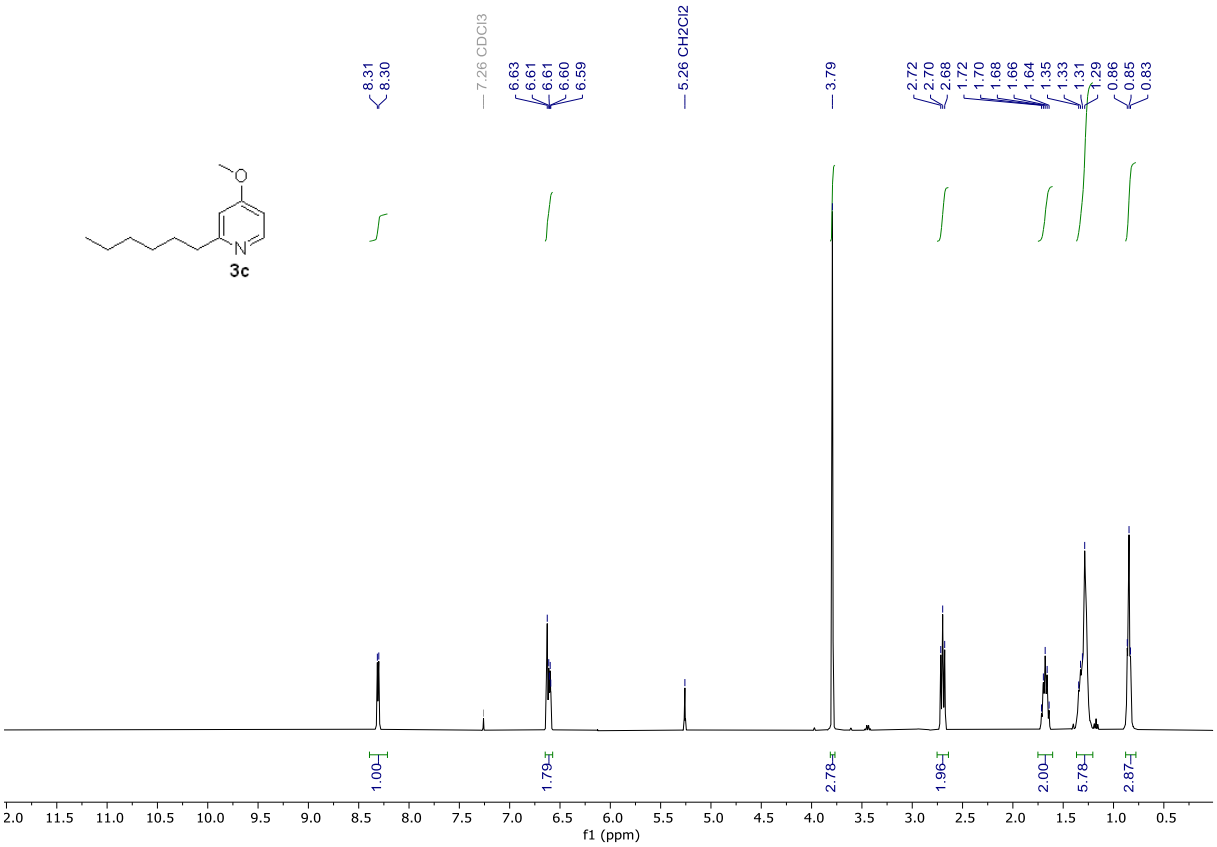
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.03 (m, 20H, C$H_{Ar}$), 3.62 – 3.43 (m, 2H, P(O)C$\underline{H}$), 2.81 – 2.71 (m, 2H, PC$\underline{H}$), 2.51 – 2.16 (m, 4H, P(O)CHC$\underline{H_2}$), 1.90 – 1.68 (m, 4H, PCHC$\underline{H_2}$), 0.99 – 0.59 (m, 4H, P(O)C$\underline{H_2}$C$\underline{H_2}$P).
$^{31}$P NMR (162 MHz, $CDCl_3$) δ 61.33 (d, *J* = 37.0 Hz), 16.08 (d, *J* = 37.8 Hz).

HRMS (ESI+, m/Z): calcd for $C_{34}H_{36}OP_2$ $[M+H]^+$: 523.2325, found: 523.2306.
** Due to difficulties for obtaining a clear $^{13}$C NMR, we characterized **L10** using $^1$H NMR, $^{31}$P NMR and HRMS.*

# 9. NMR spectra

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8.30
7.26 CDCl3
6.63
6.61
6.61
6.60
6.59
5.26 CH2Cl2
3.79
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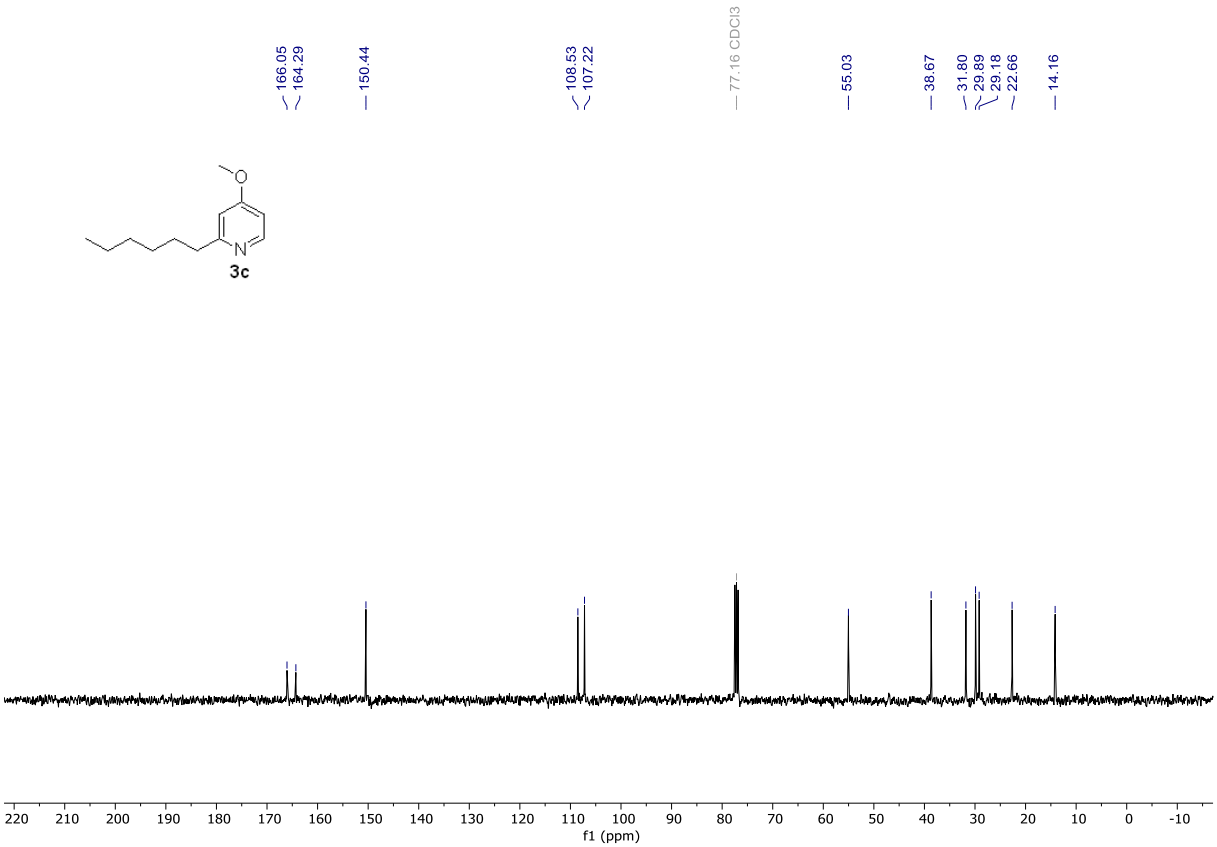
2.70
2.68
1.72
1.70
1.68
1.66
1.64
1.35
1.33
1.31
1.29
0.86
0.85
0.83
3c
1.00
1.79
2.78
1.96
2.00
5.78
2.87
f1 (ppm)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164.29
150.44
108.53
107.22
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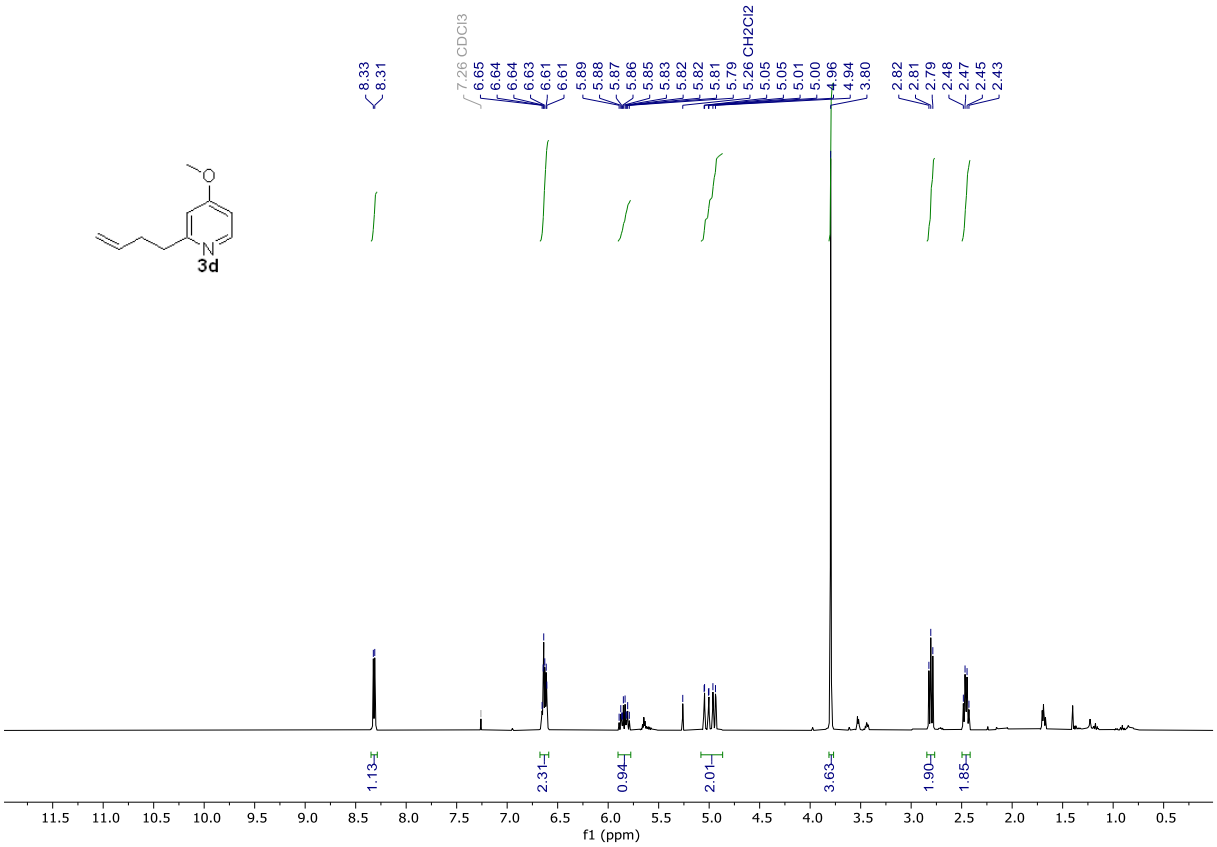
55.03
38.67
31.80
29.89
29.18
22.66
14.16
3c
f1 (ppm)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8.31
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6.64
6.64
6.63
6.61
6.61
5.89
5.88
5.87
5.86
5.85
5.83
5.82
5.82
5.81
5.79
5.26 CH2Cl2
5.05
5.05
5.01
5.00
4.96
4.94
3.80
2.82
2.81
2.79
2.48
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3d
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2.31
0.94
2.01
3.63
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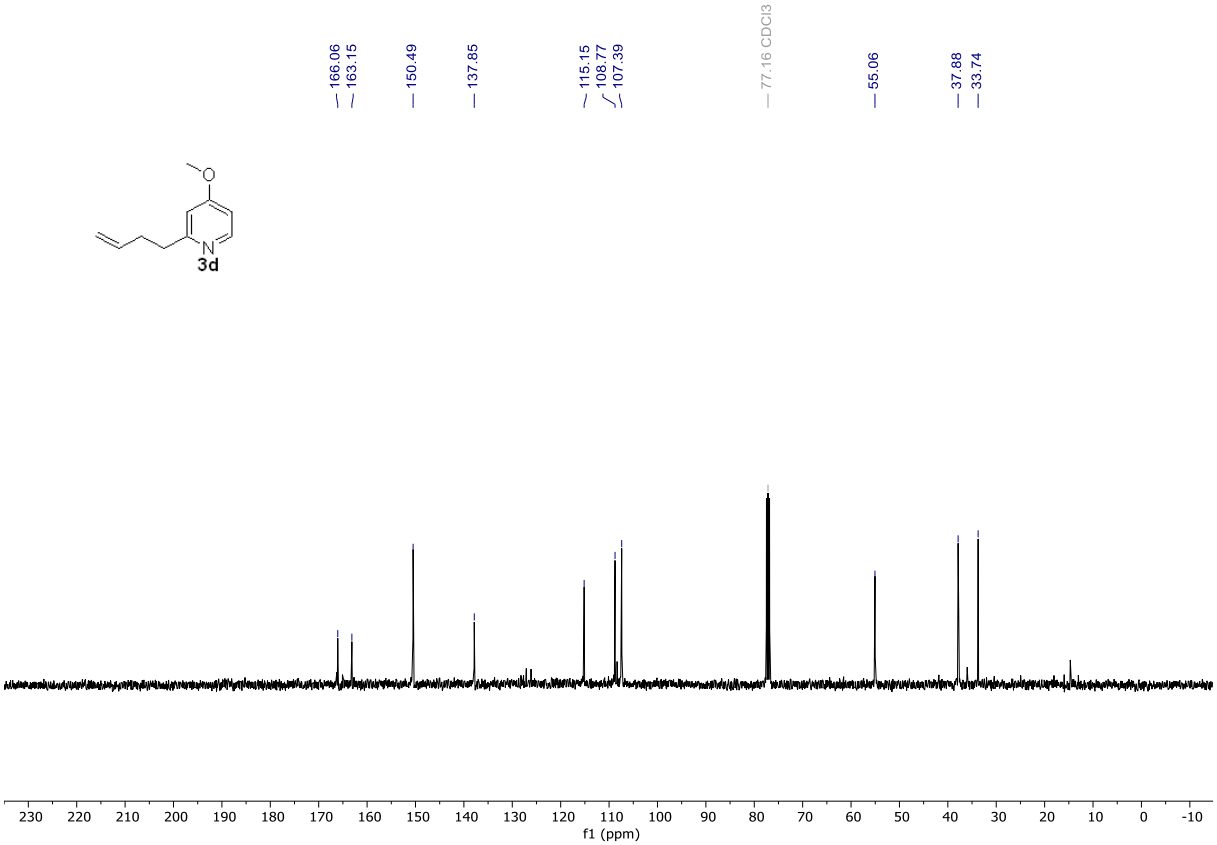
1.85
f1 (ppm)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163.15
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77.16 CDCl3
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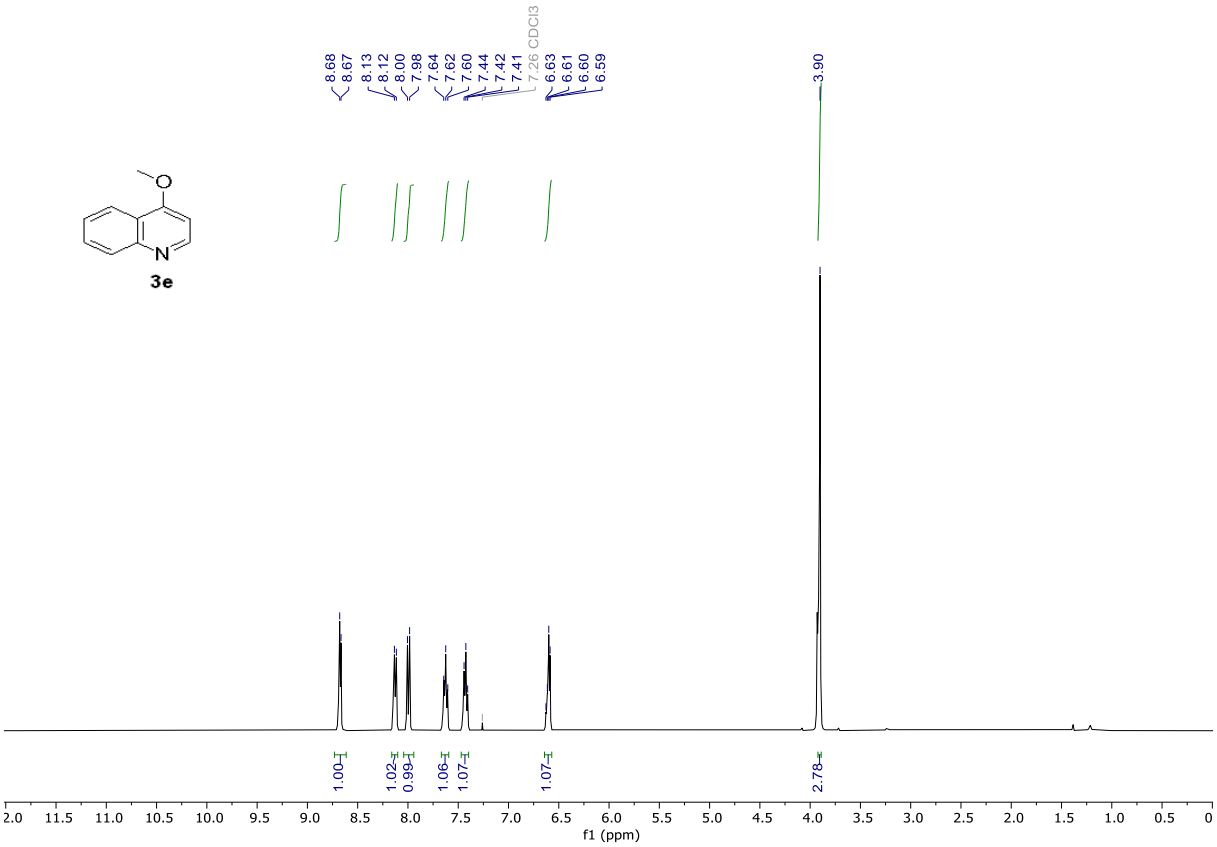
3d
f1 (ppm)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7.62
7.60
7.44
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7.41
7.26 CDCl3
6.63
6.61
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6.59
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1.02
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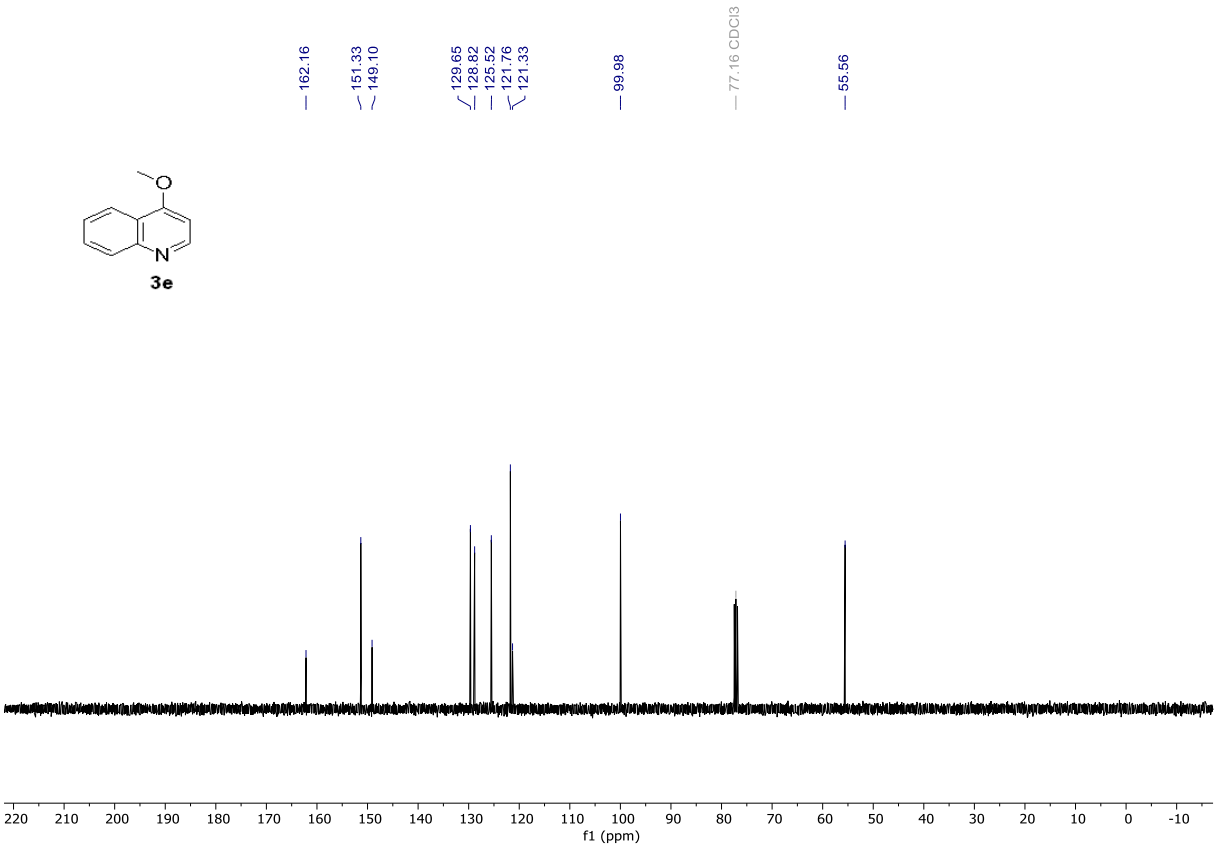
1.07
1.07
2.78
f1 (ppm)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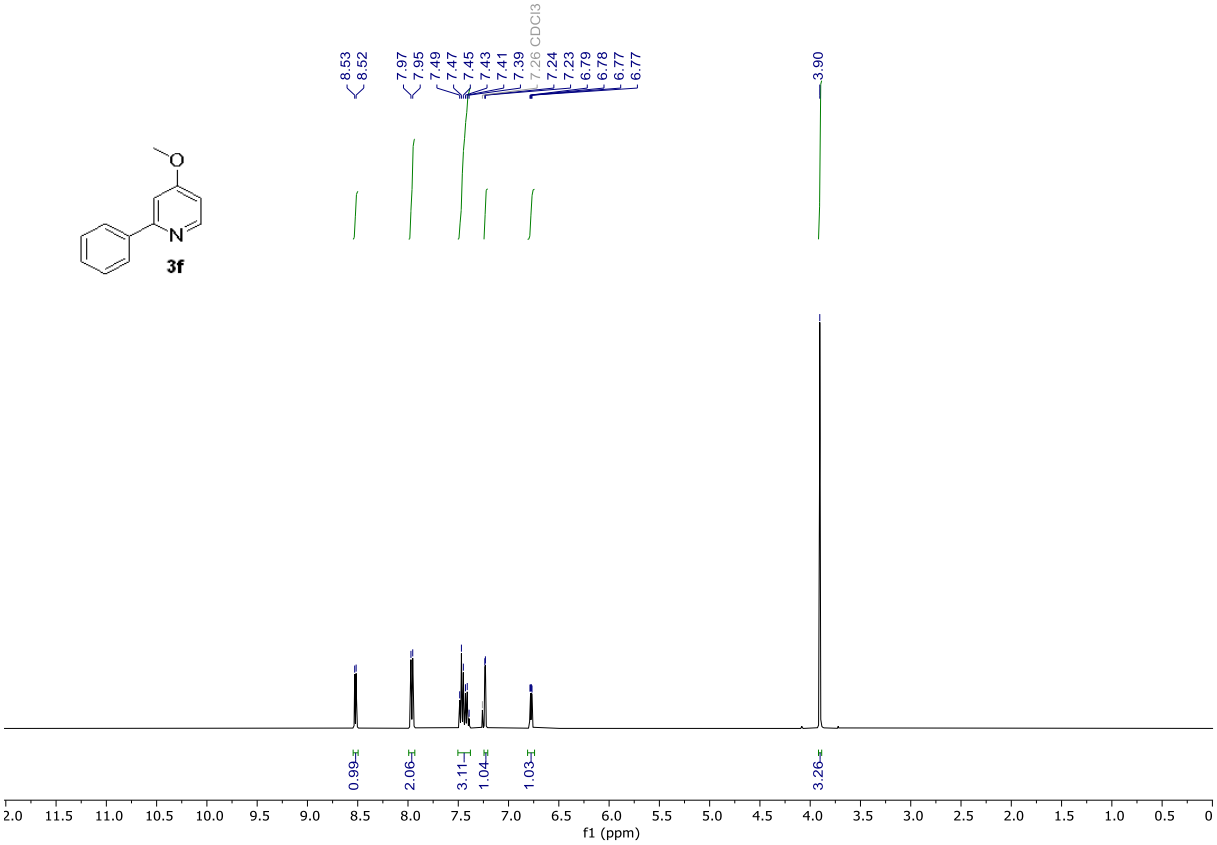
125.52
121.76
121.33
99.98
77.16 CDCl3
55.56
3e
f1 (ppm)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7.39
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7.23
6.79
6.78
6.77
6.77
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N
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0.99
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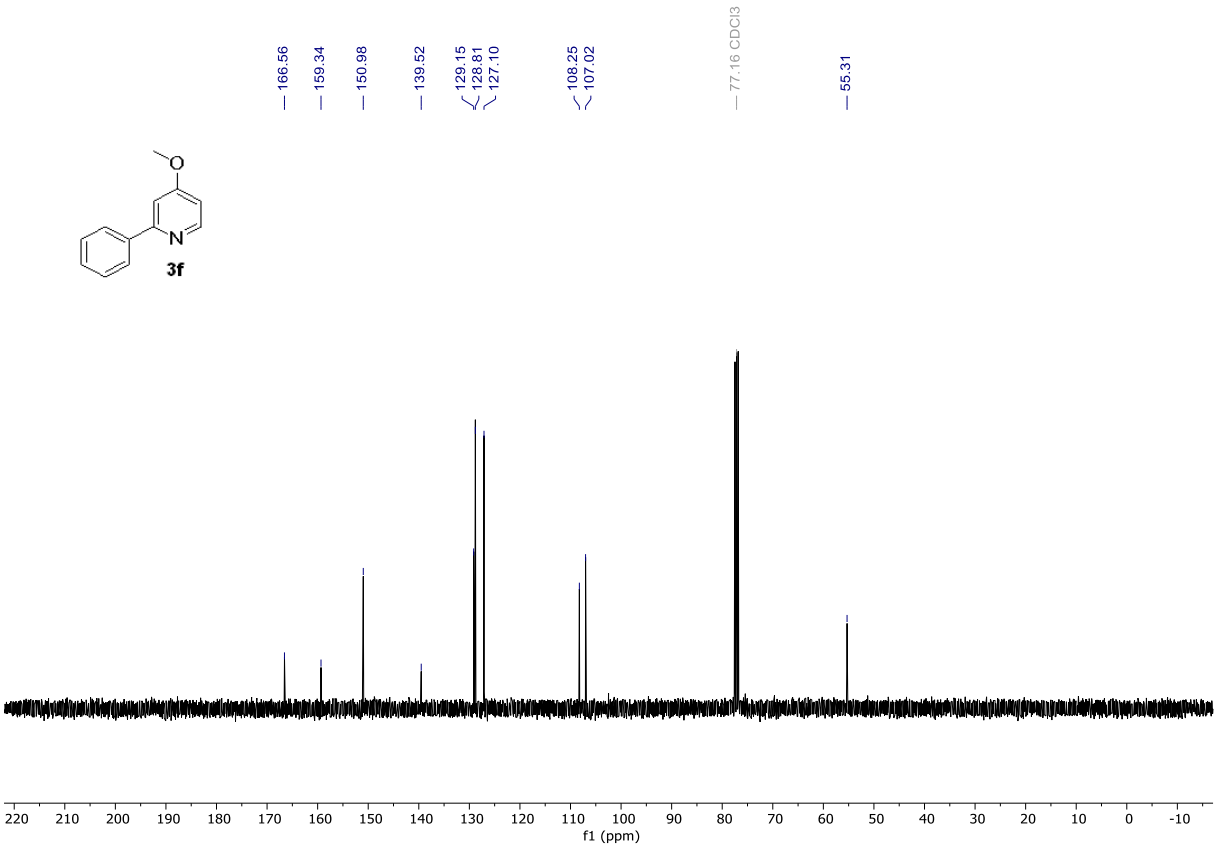
1.03
3.26
f1 (ppm)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128.81
127.10
108.25
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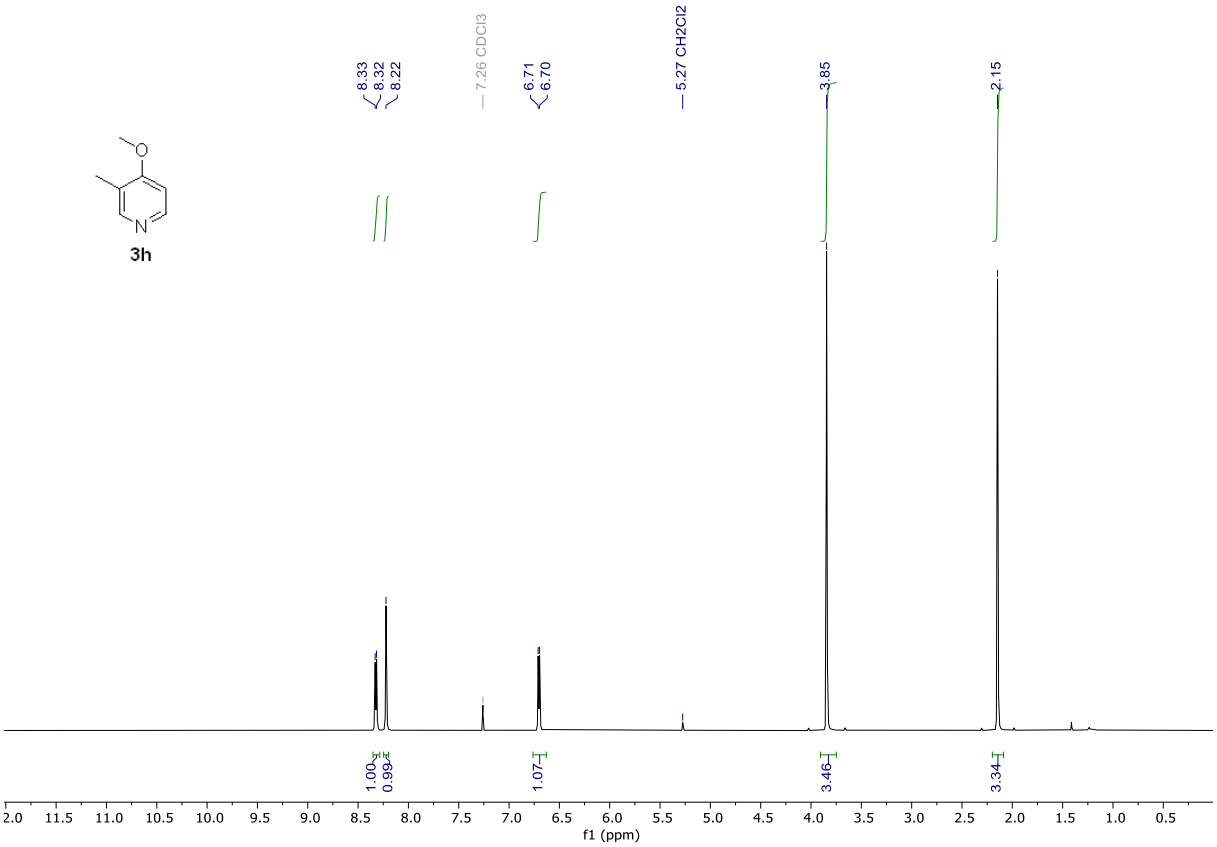
77.16 CDCl3
55.31
O
N
3f
f1 (ppm)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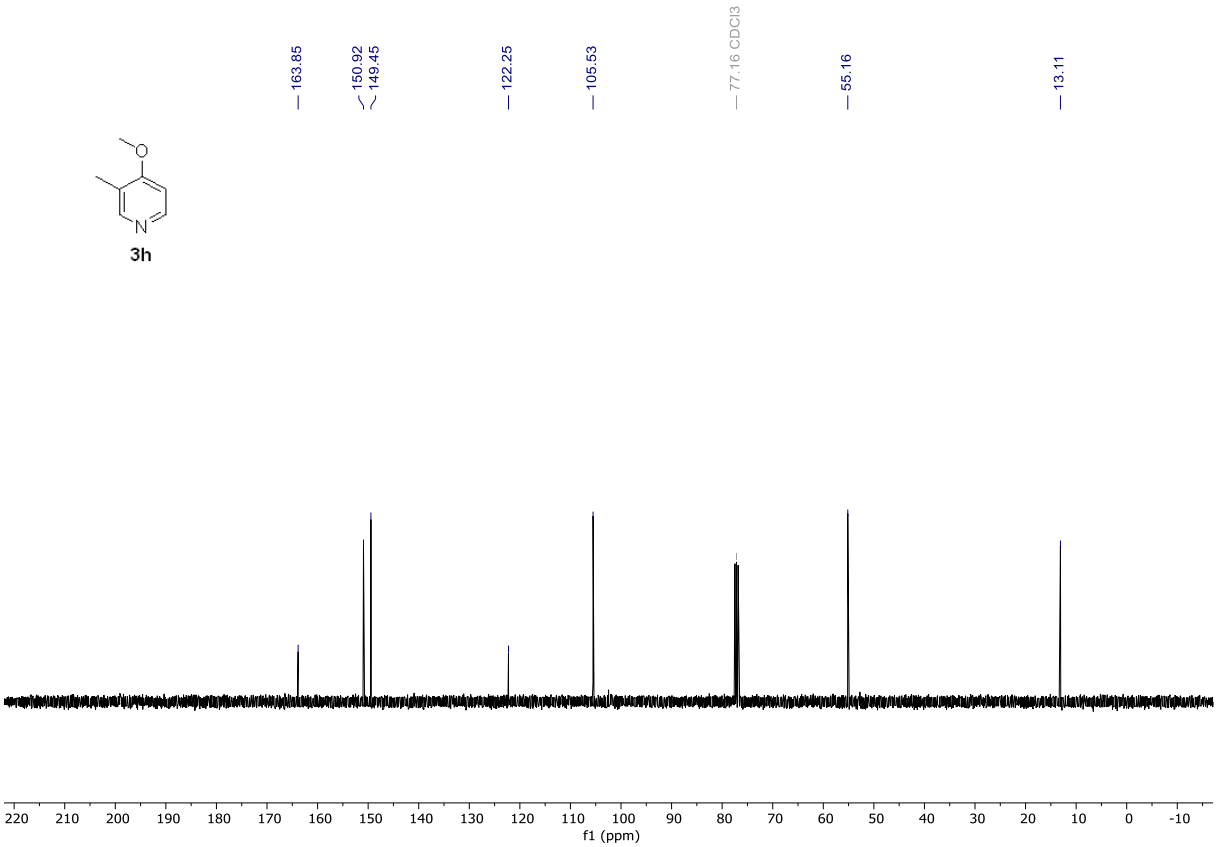
3.34
f1 (ppm)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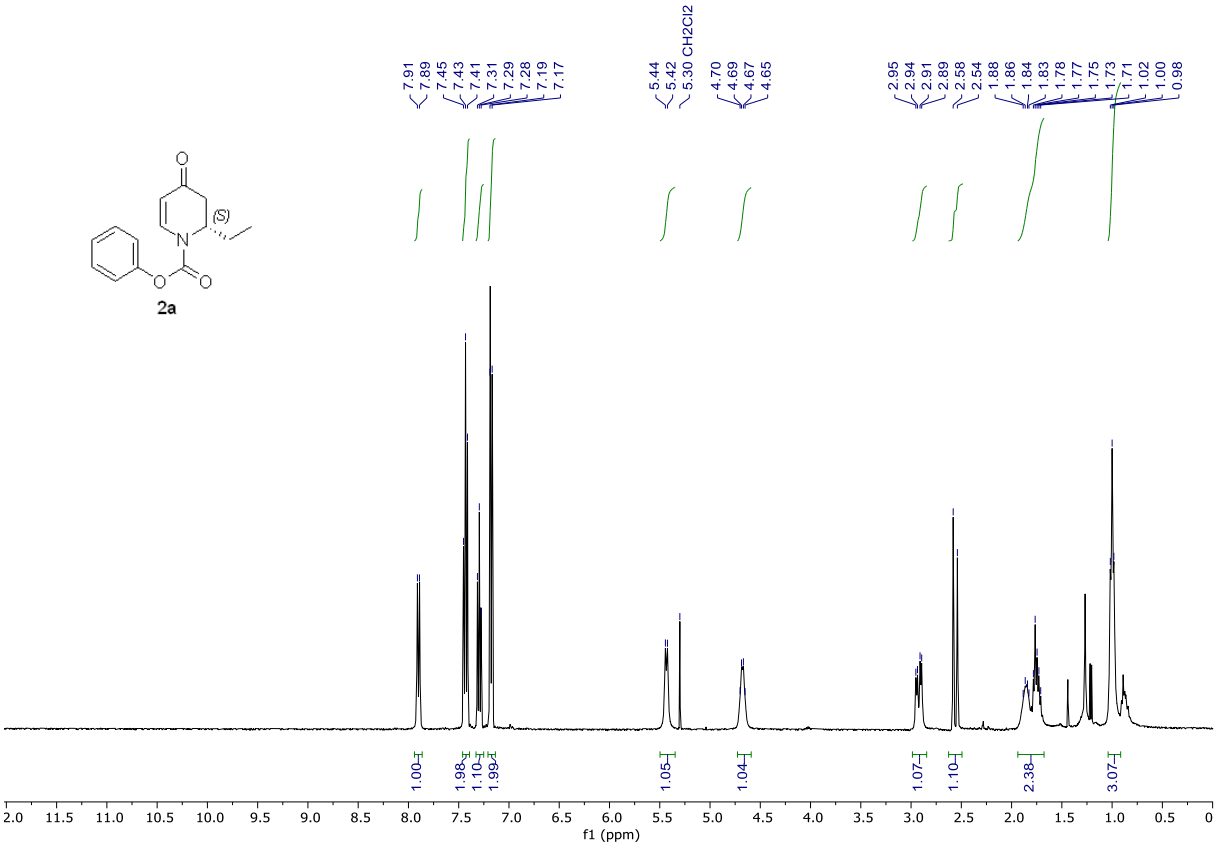
13.11
3h
f1 (ppm)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7.28
7.19
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5.42
5.30 CH2Cl2
4.70
4.69
4.67
4.65
2.95
2.94
2.91
2.89
2.58
2.54
1.88
1.86
1.84
1.83
1.78
1.77
1.75
1.73
1.71
1.02
1.00
0.98
1.00
1.98
1.10
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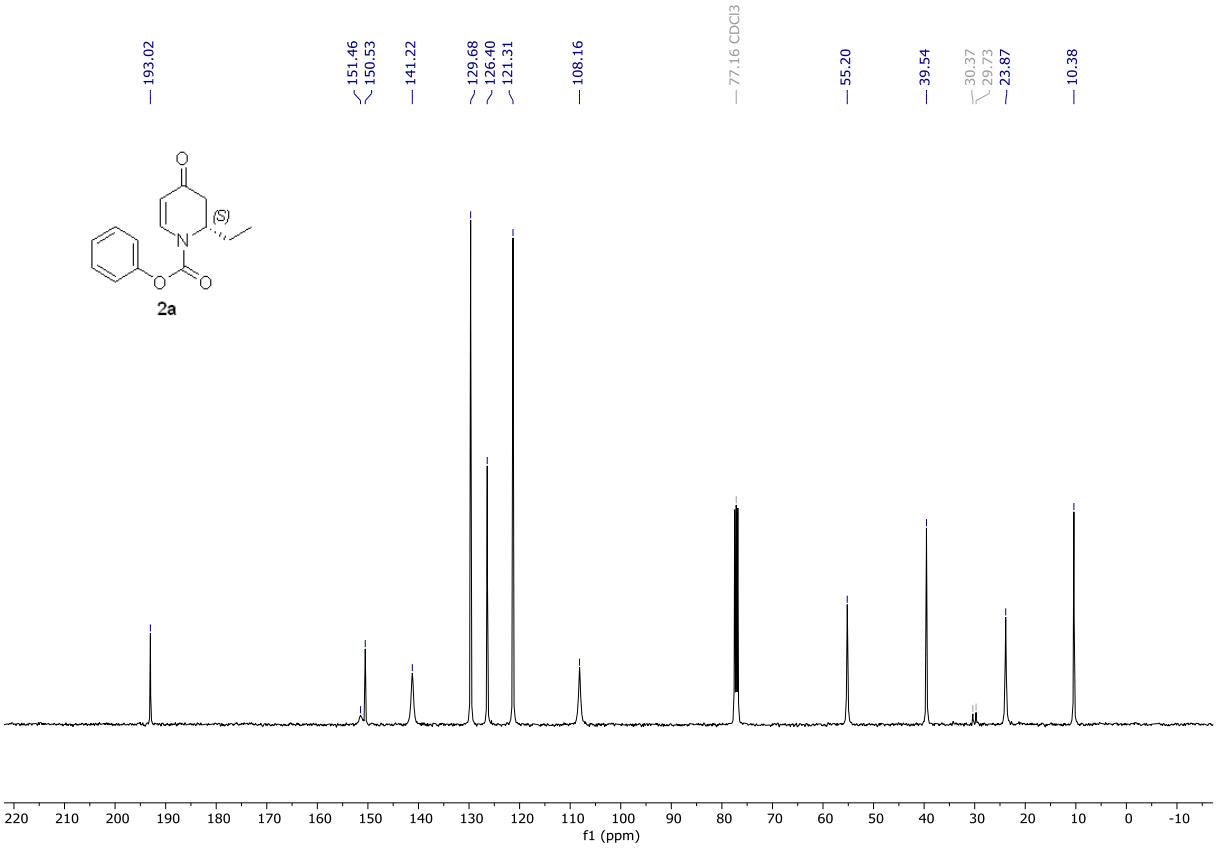
1.05
1.04
1.07
1.10
2.38
3.07
f1 (ppm)
(S)
2a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121.31
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55.20
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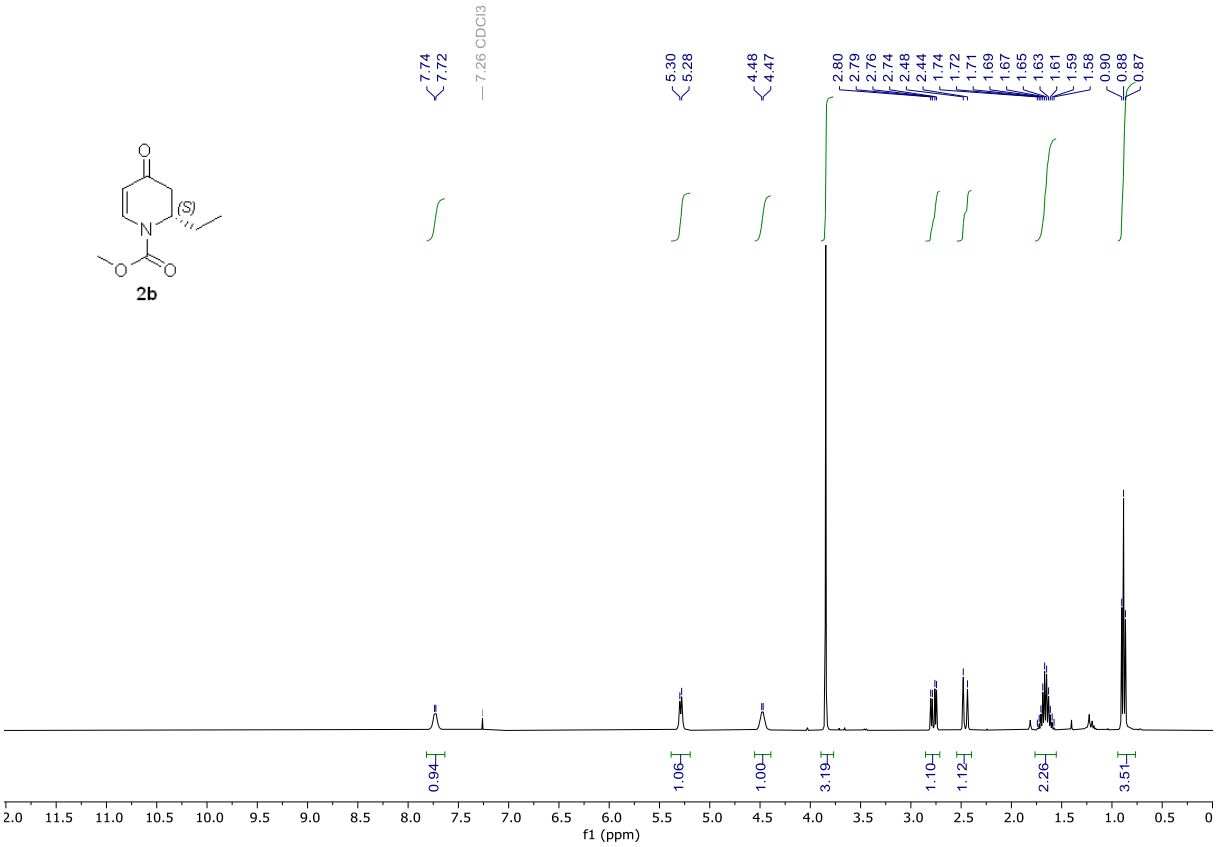
30.37
29.73
23.87
10.38
f1 (ppm)
(S)
2a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2.76
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2.48
2.44
1.74
1.72
1.71
1.69
1.67
1.65
1.63
1.61
1.59
1.58
0.90
0.88
0.87
(S)
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1.12
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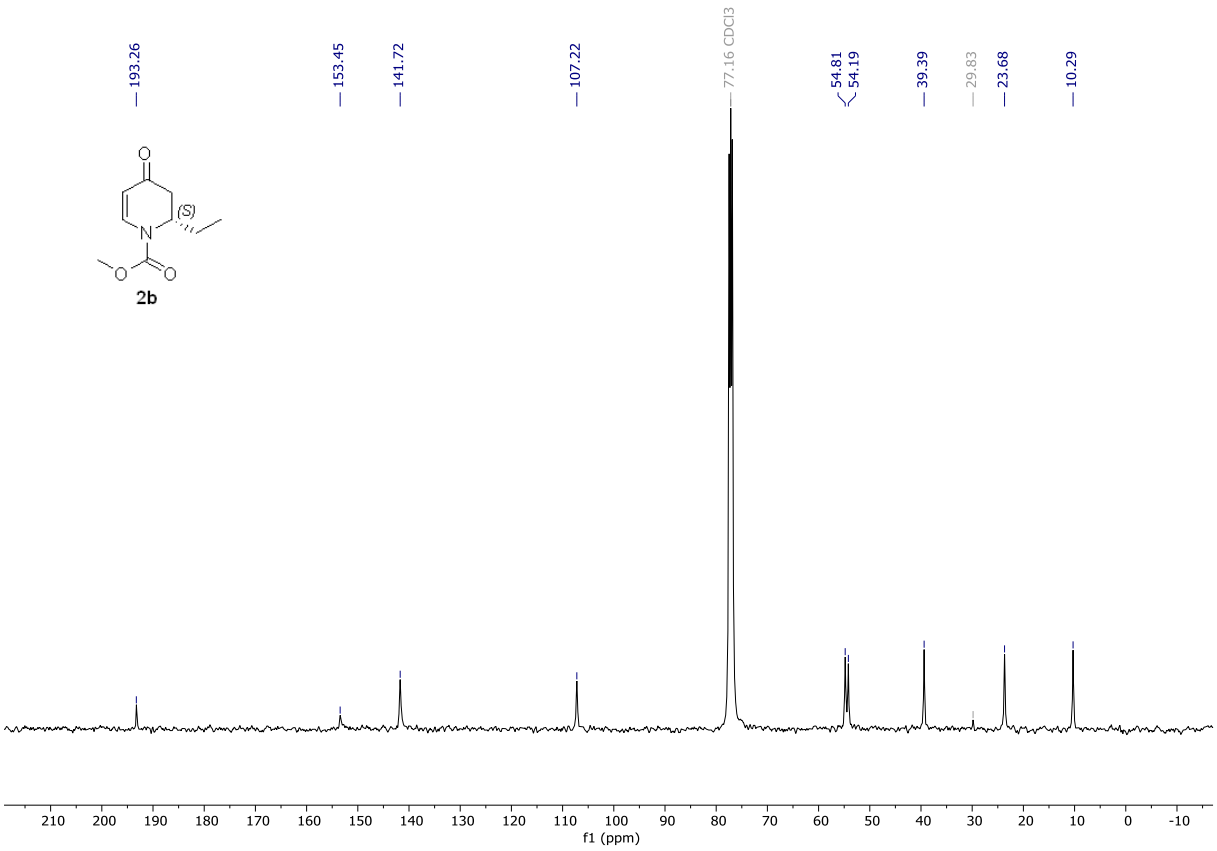
3.51
f1 (ppm)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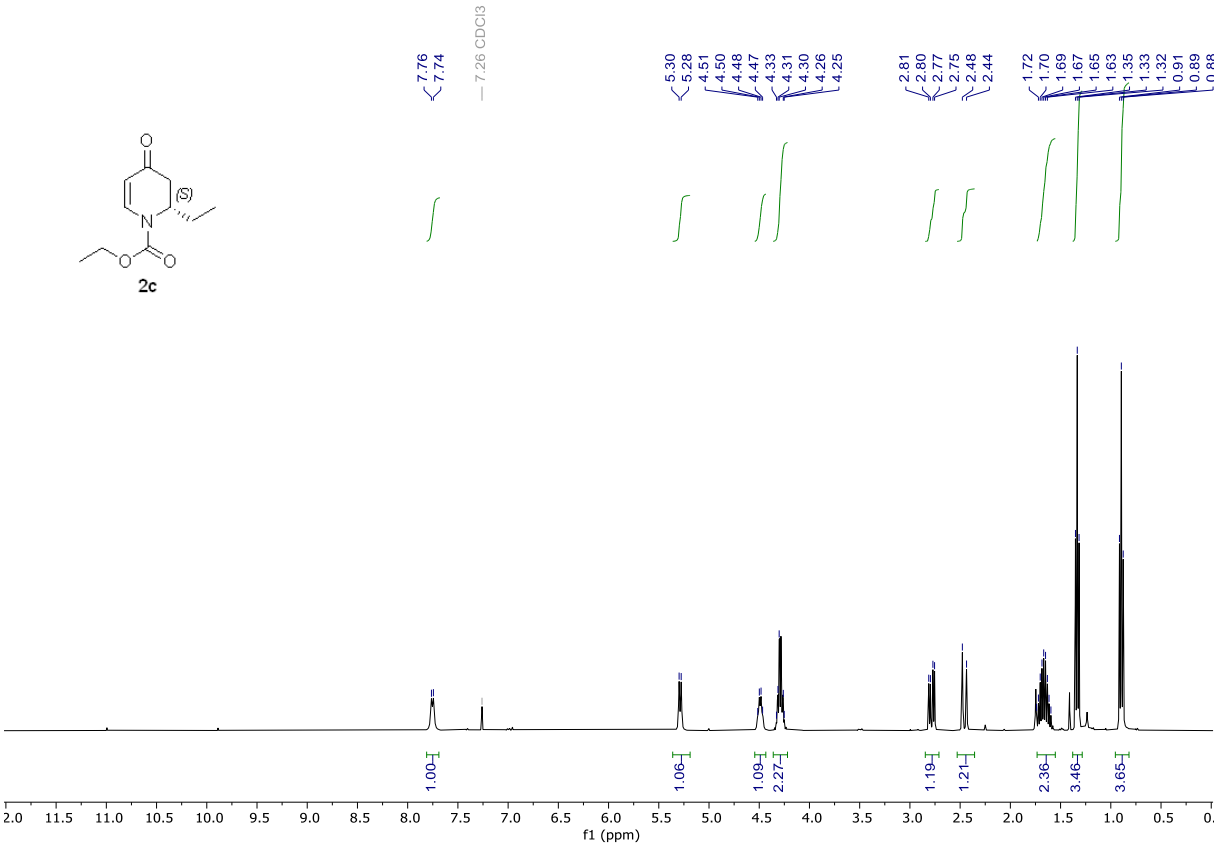
O
O
2b
f1 (ppm)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4.30
4.26
4.25
2.81
2.80
2.77
2.75
2.48
2.44
1.72
1.70
1.69
1.67
1.65
1.63
1.35
1.33
1.32
0.91
0.89
(S)
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2.27
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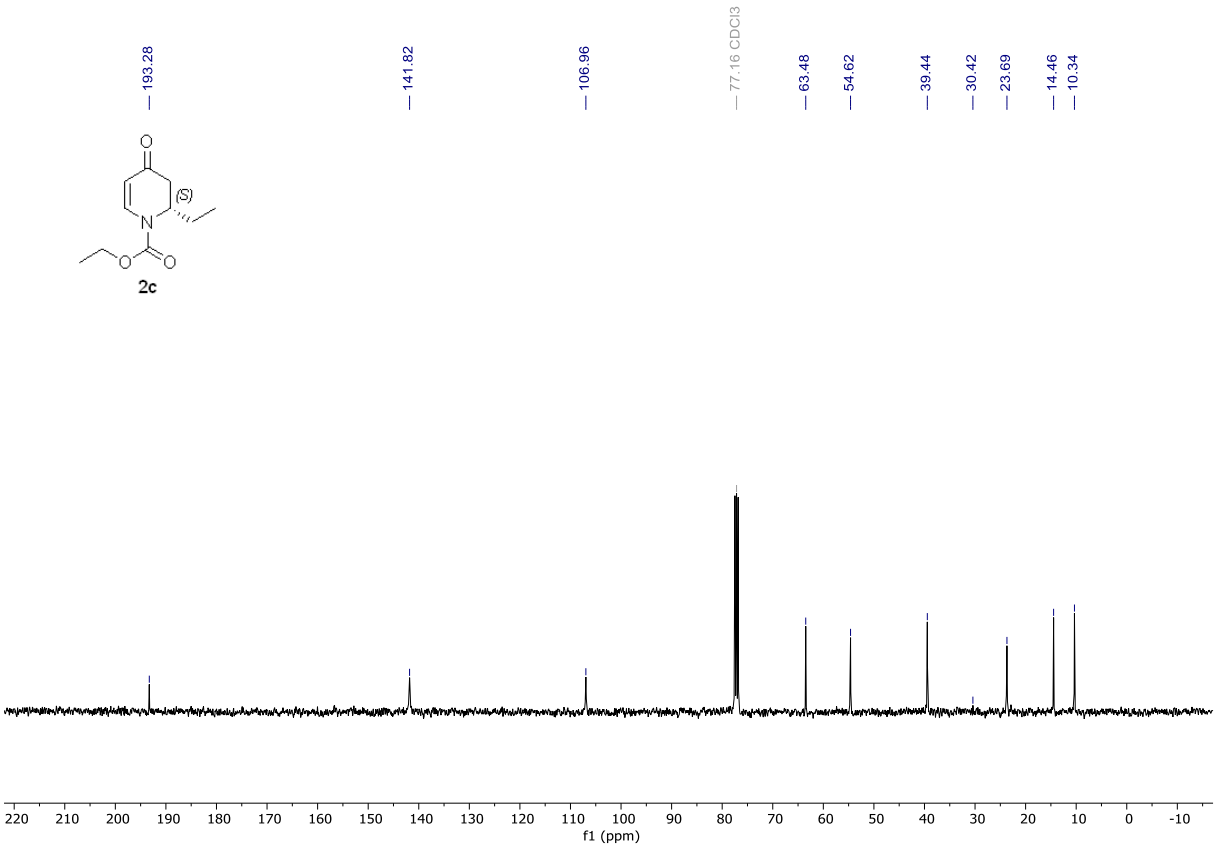
3.65
f1 (ppm)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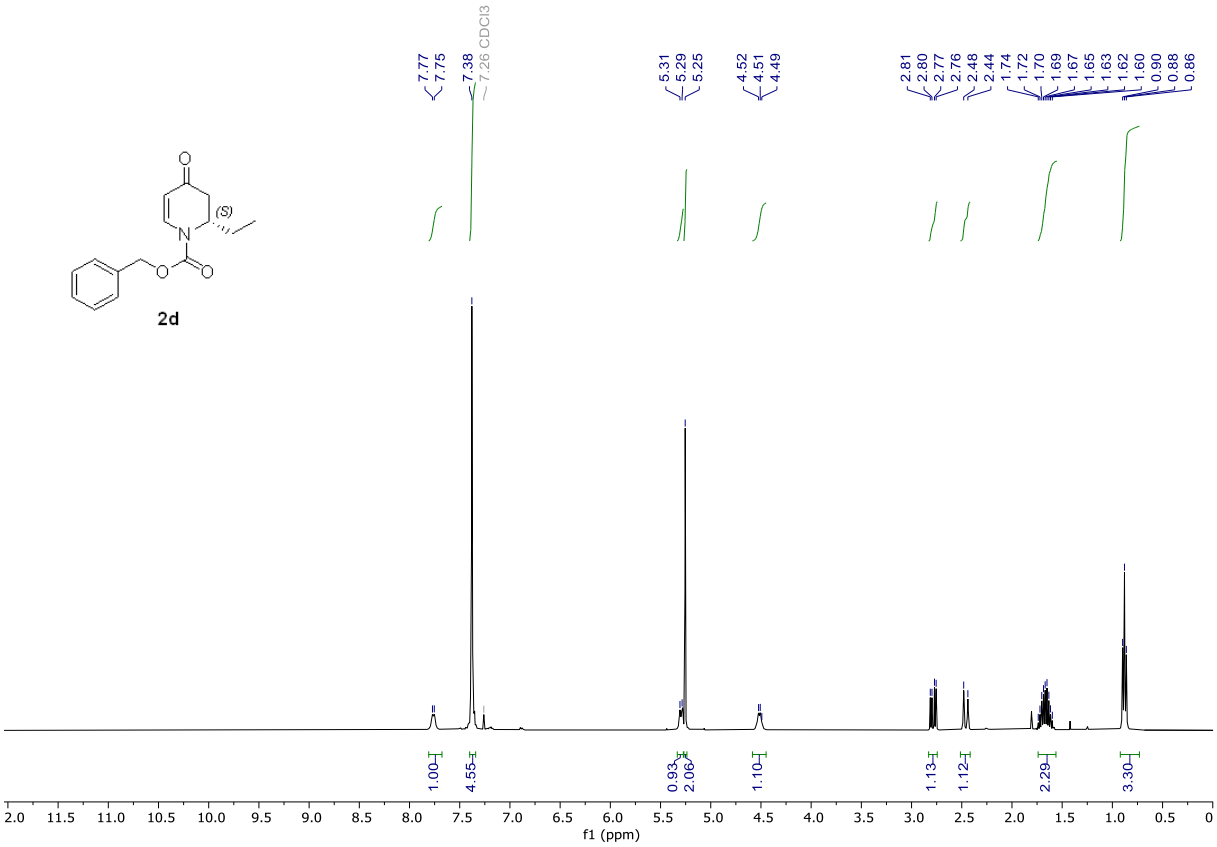
23.69
14.46
10.34
(S)
2c
f1 (ppm)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7.26 CDCl3
5.31
5.29
5.25
4.52
4.51
4.49
2.81
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2.77
2.76
2.48
2.44
1.74
1.72
1.70
1.69
1.67
1.65
1.63
1.62
1.60
0.90
0.88
0.86
(S)
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1.12
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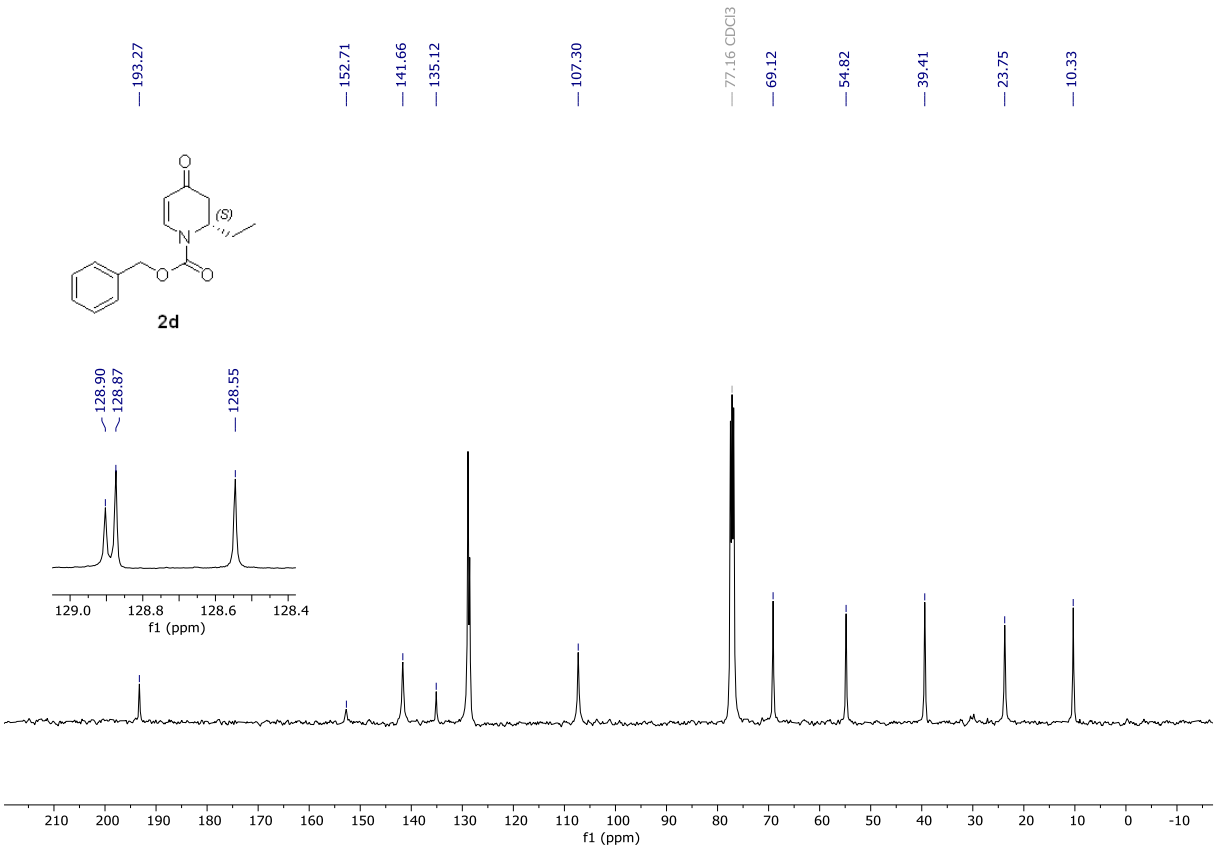
3.30
f1 (ppm)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(S)
2d
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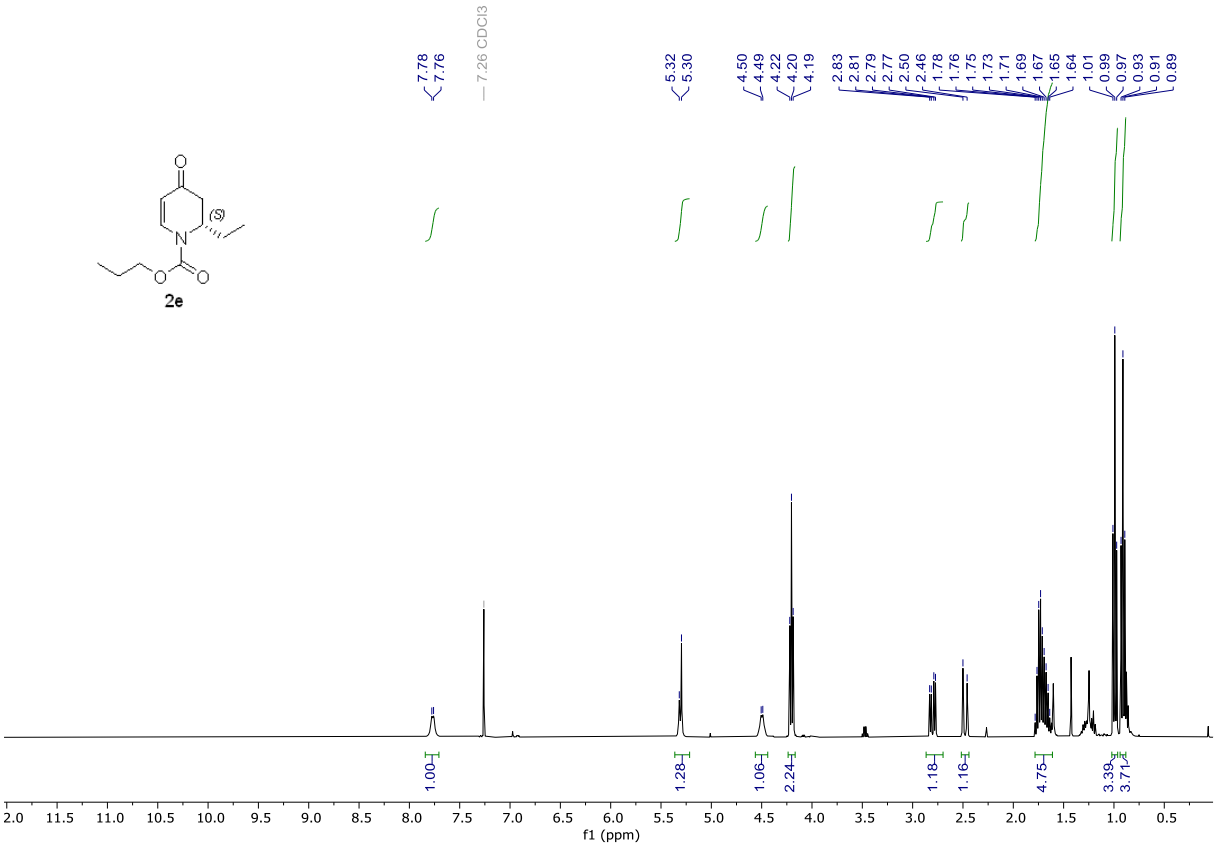
128.55
f1 (ppm)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1.75
1.73
1.71
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1.64
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0.97
0.93
0.91
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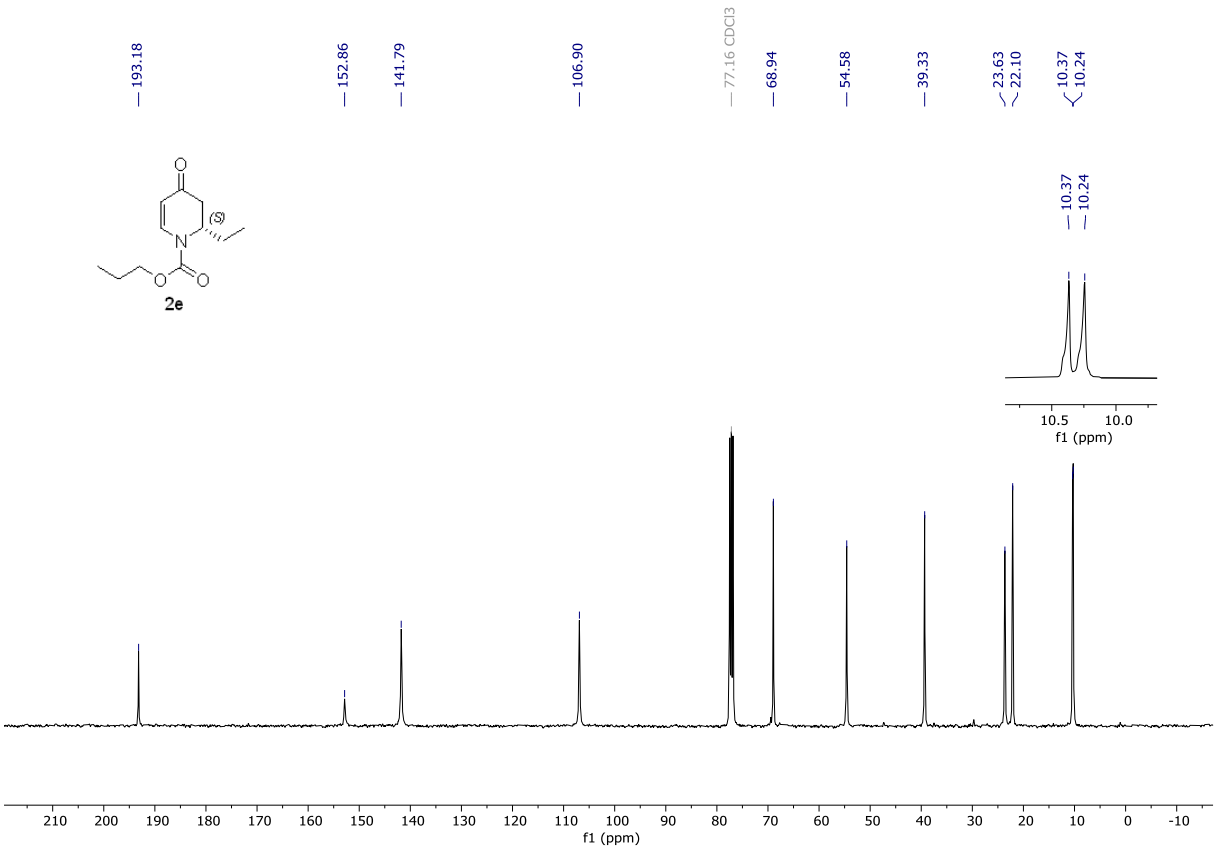
f1 (ppm)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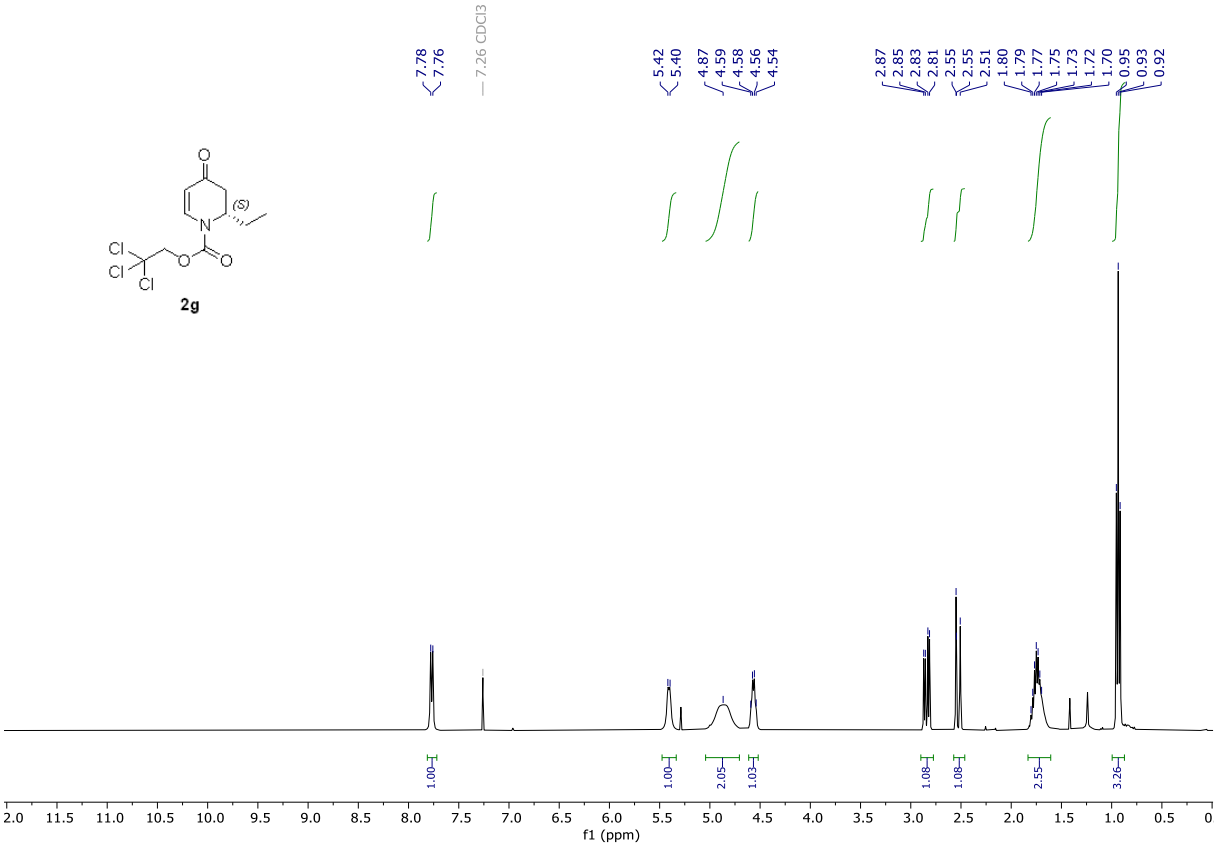
2e
f1 (ppm)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2.83
2.81
2.55
2.55
2.51
1.80
1.79
1.77
1.75
1.73
1.72
1.70
0.95
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0.92
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1.08
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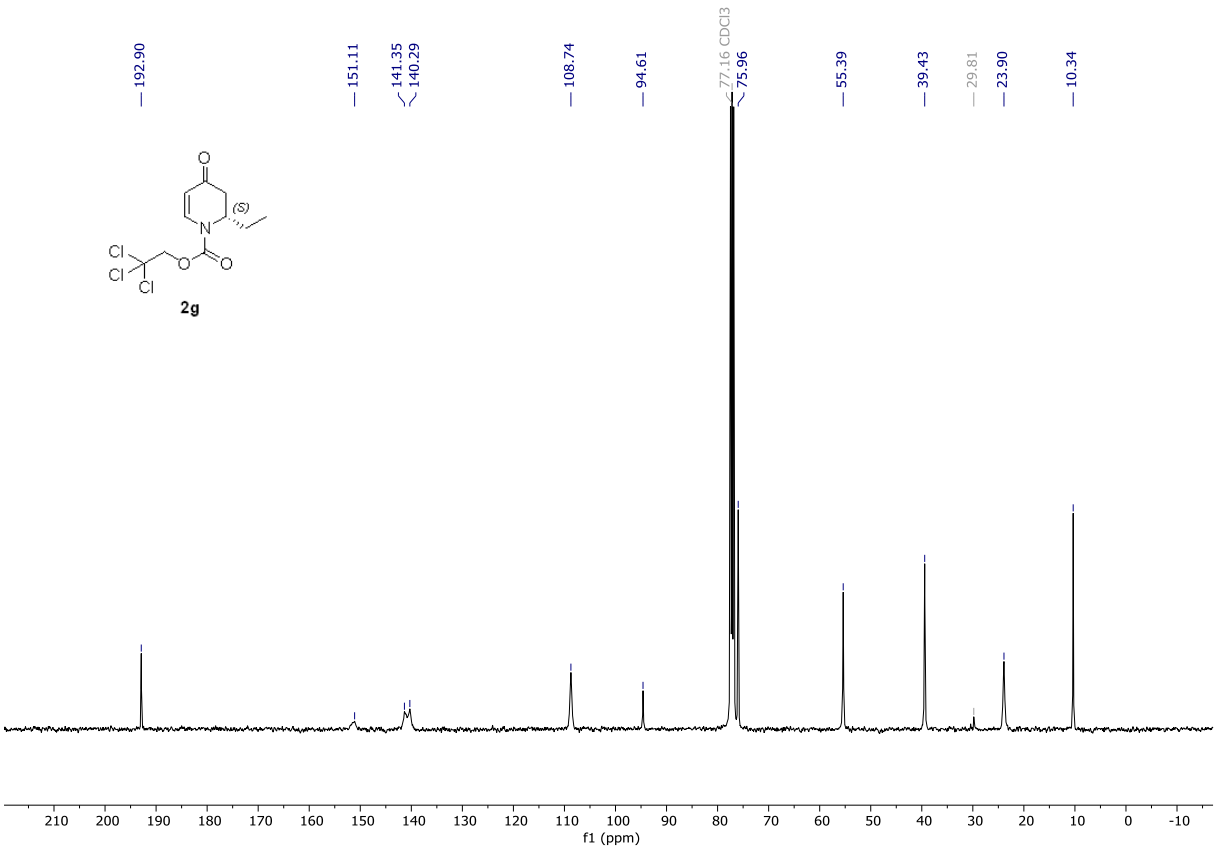
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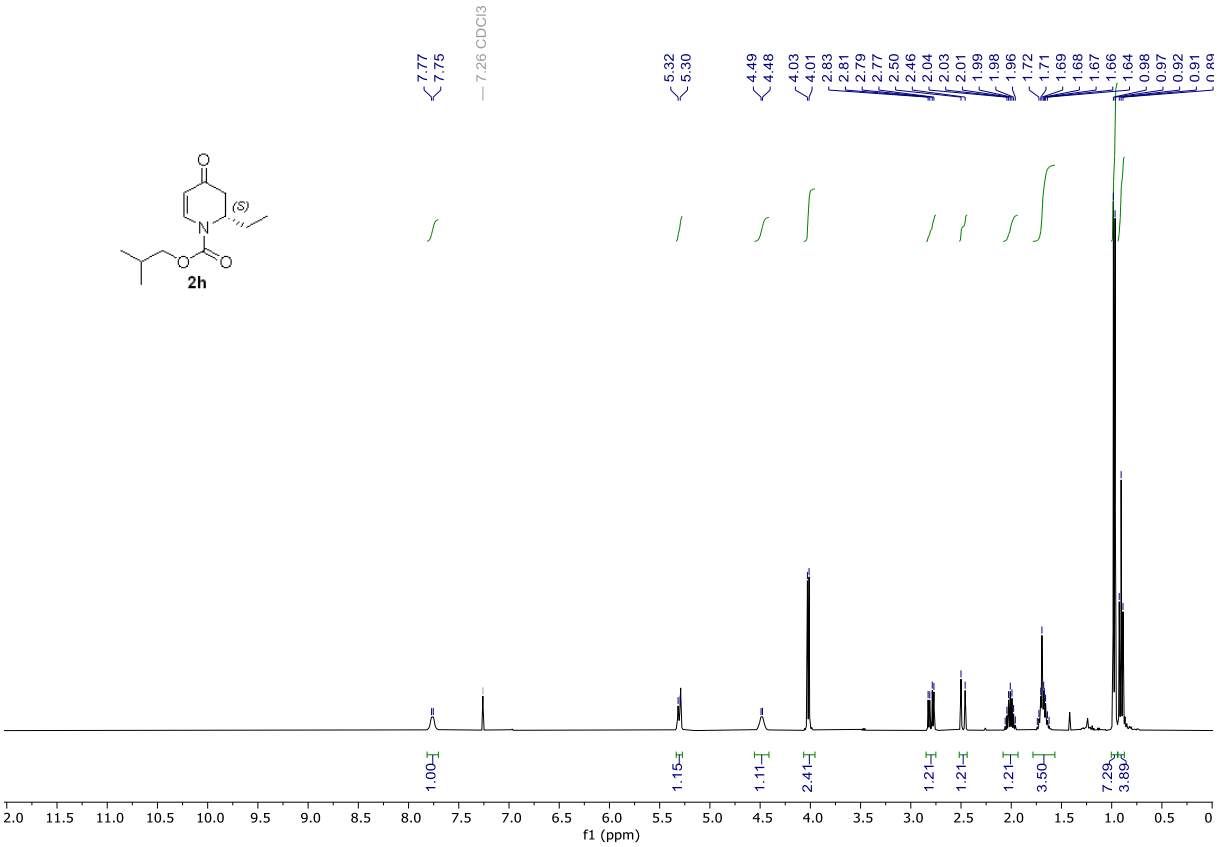
2g
f1 (ppm)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2.77
2.50
2.46
2.04
2.03
2.01
1.99
1.98
1.96
1.72
1.71
1.69
1.68
1.67
1.66
1.64
0.98
0.97
0.92
0.91
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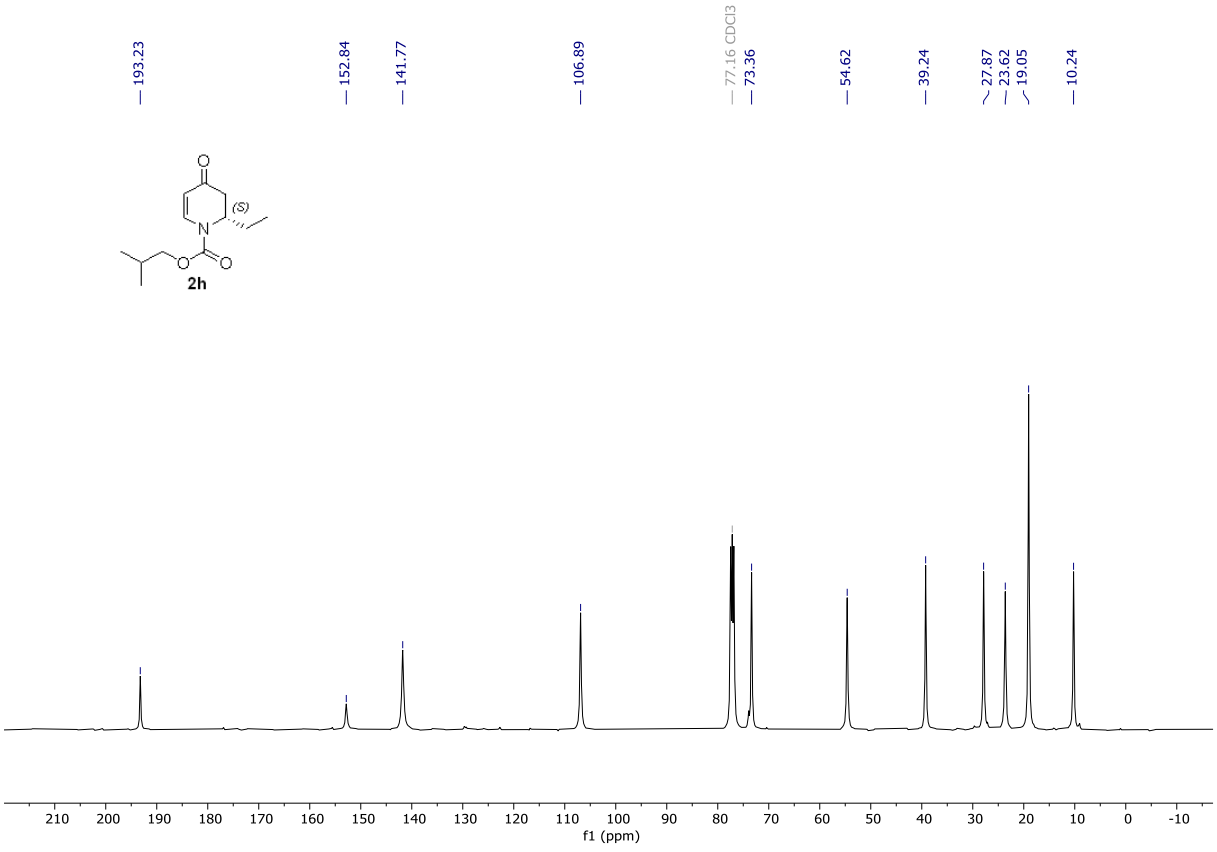
f1 (ppm)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23.62
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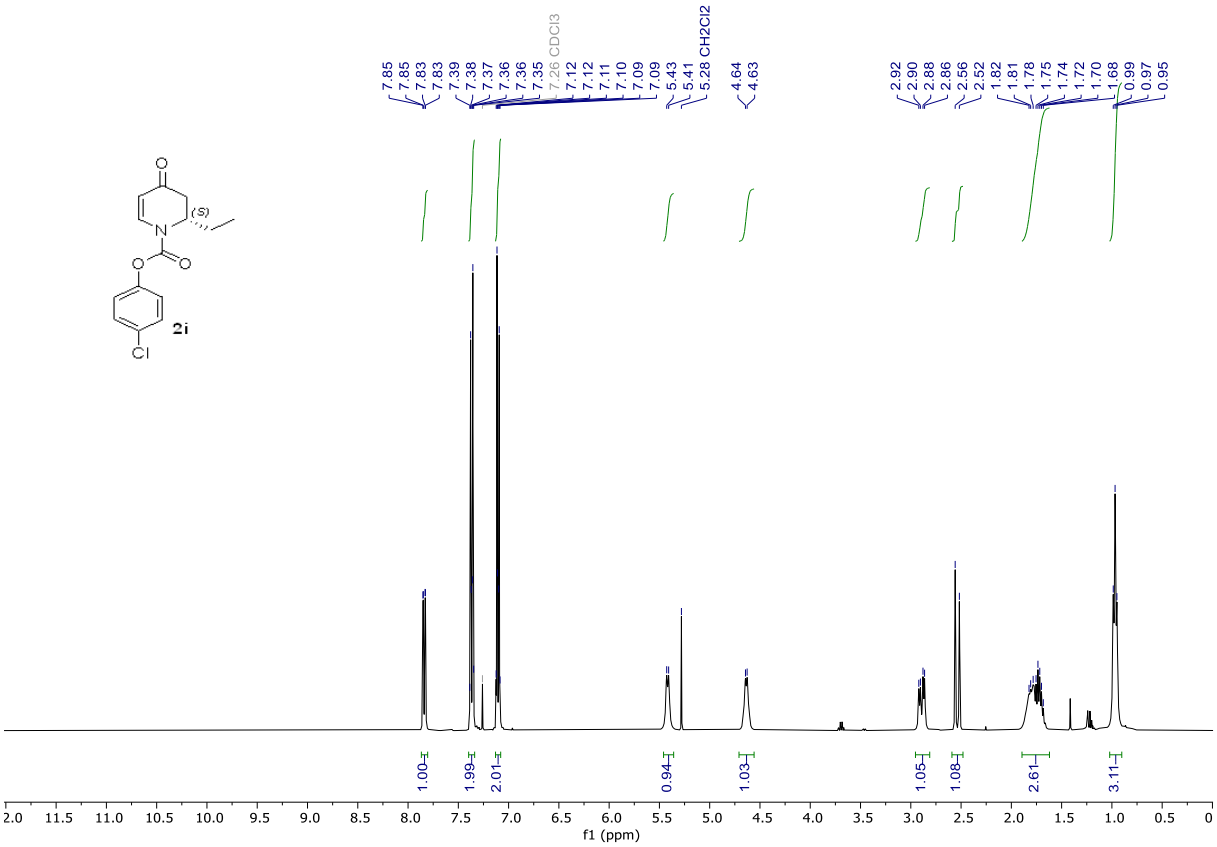
2h
f1 (ppm)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7.12
7.12
7.11
7.10
7.09
7.09
5.43
5.41
5.28 CH2Cl2
4.64
4.63
2.92
2.90
2.88
2.86
2.56
2.52
1.82
1.81
1.78
1.75
1.74
1.72
1.70
1.68
0.99
0.97
0.95
(S)
2i
Cl
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0.94
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1.08
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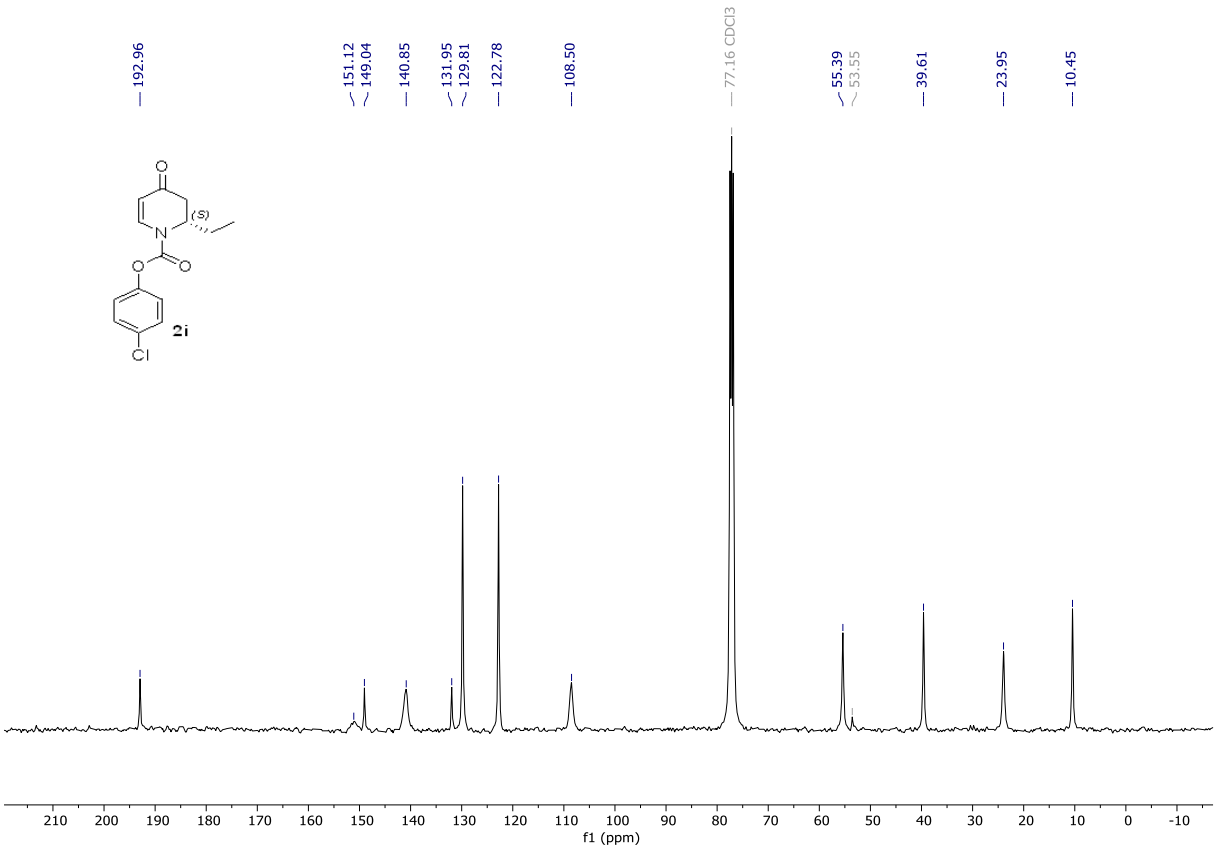
f1 (ppm)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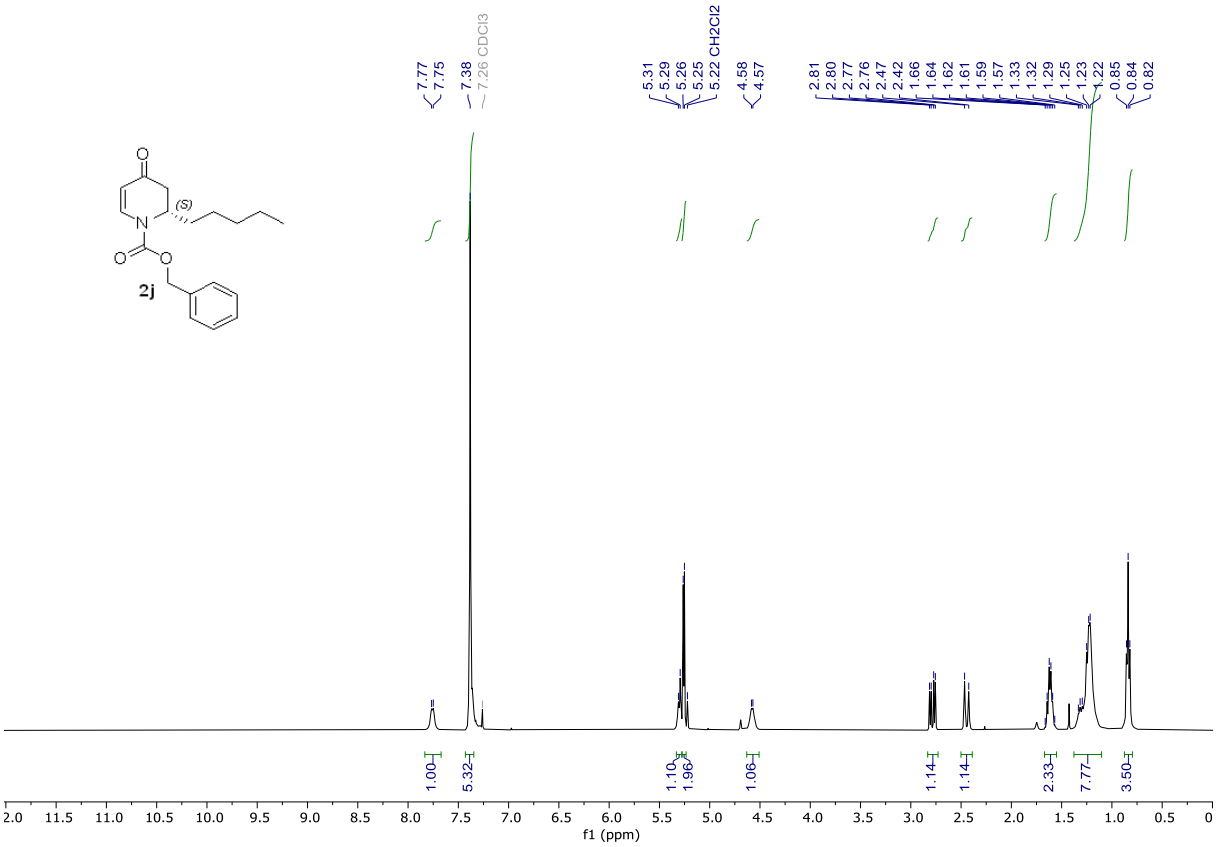
10.45
(S)
2i
Cl
f1 (ppm)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5.22 CH2Cl2
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1.64
1.62
1.61
1.59
1.57
1.33
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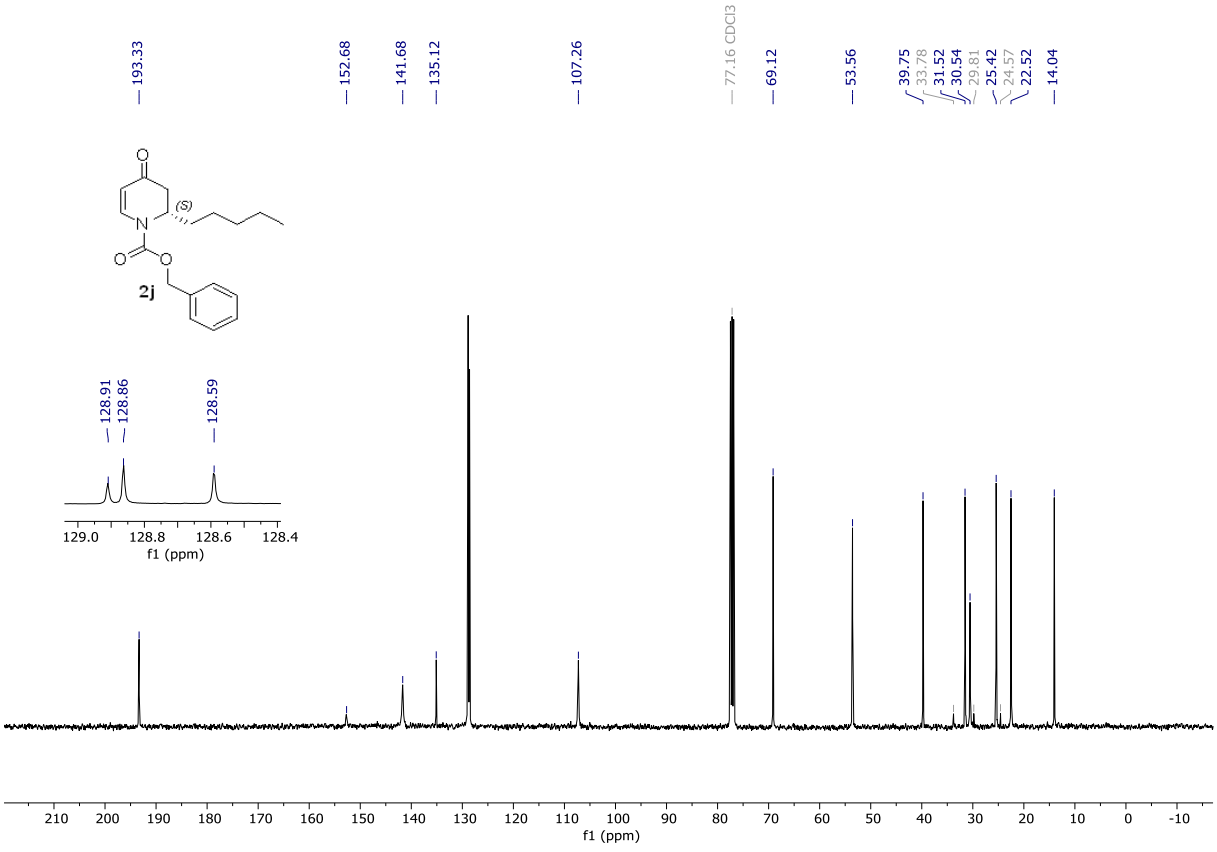
f1 (ppm)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107.26
77.16 CDCl3
69.12
53.56
39.75
33.78
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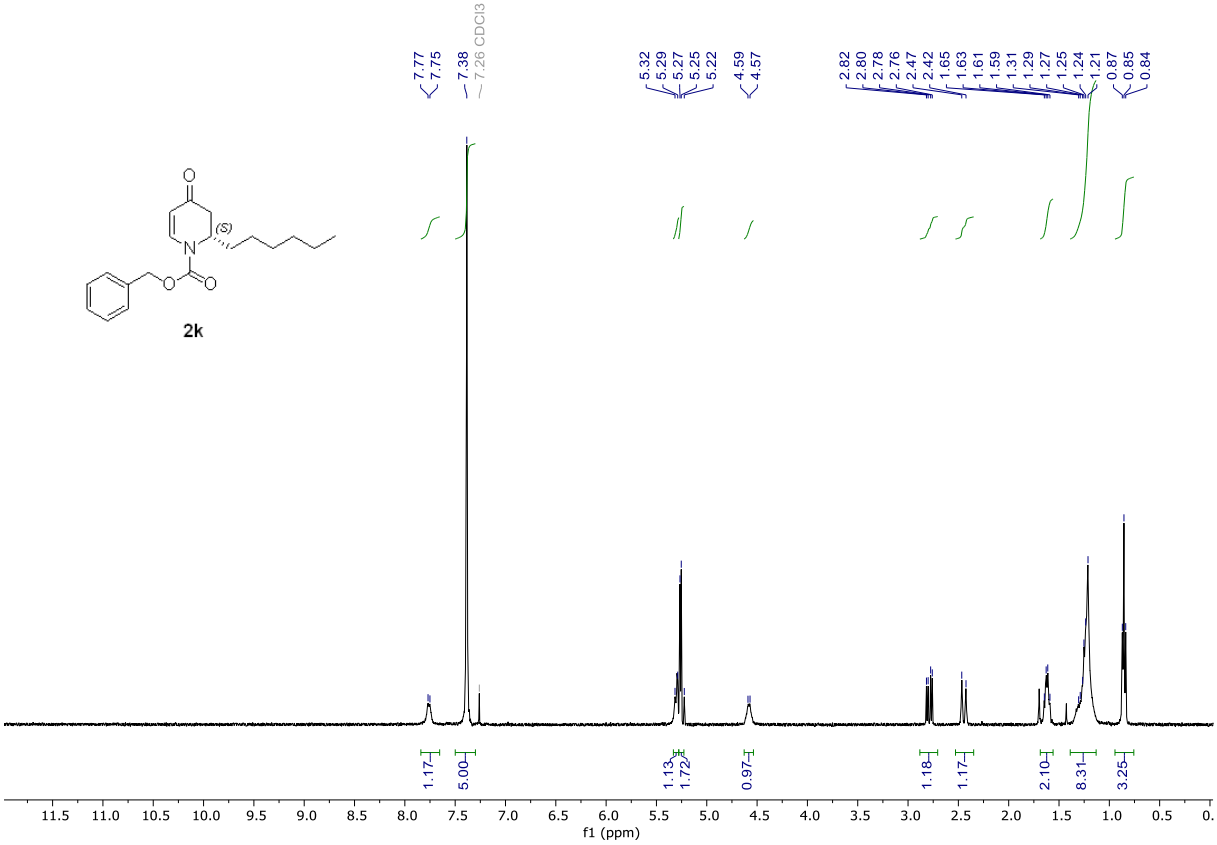
30.54
29.81
25.42
24.57
22.52
14.04
2j
128.91
128.86
128.59
f1 (ppm)


7.77
7.75
7.38
7.26 CDCl3
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4.59
4.57
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2.80
2.78
2.76
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2.42
1.65
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1.61
1.59
1.31
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1.25
1.24
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0.84
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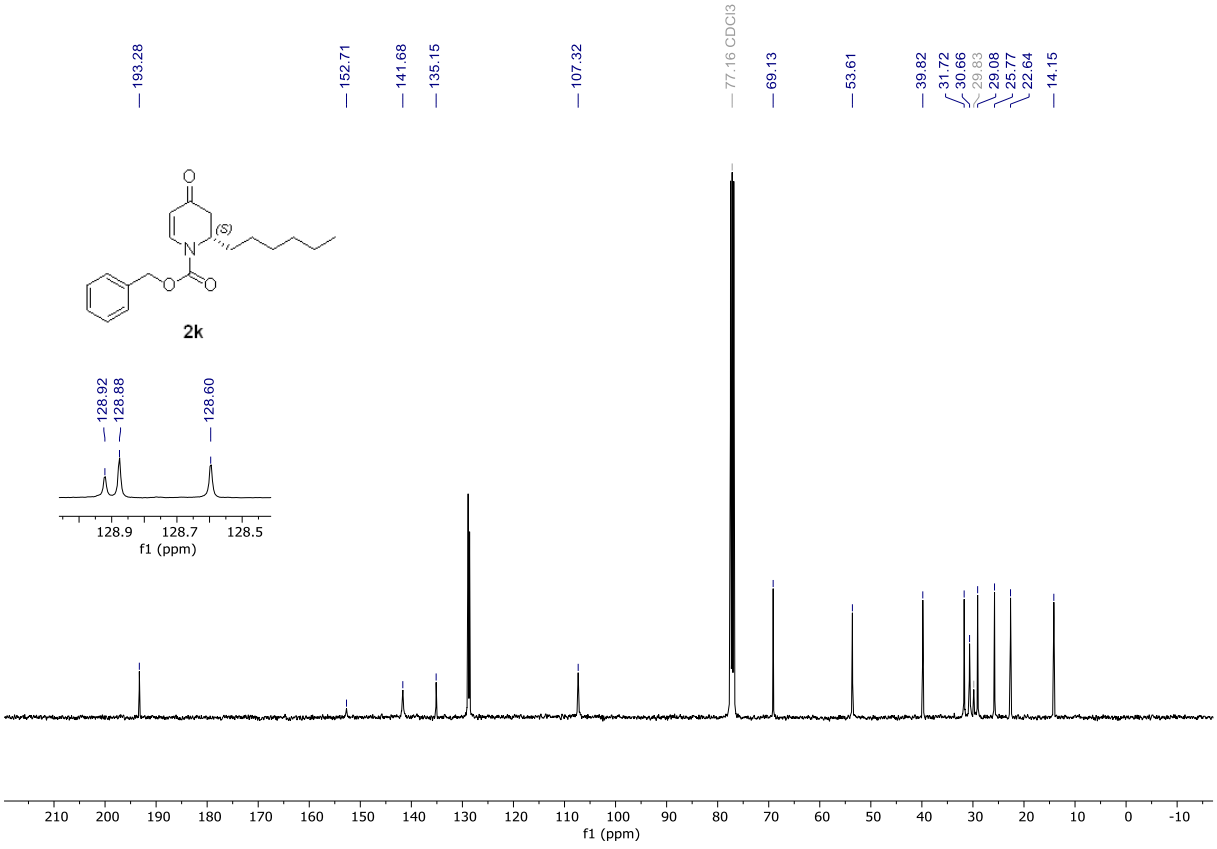
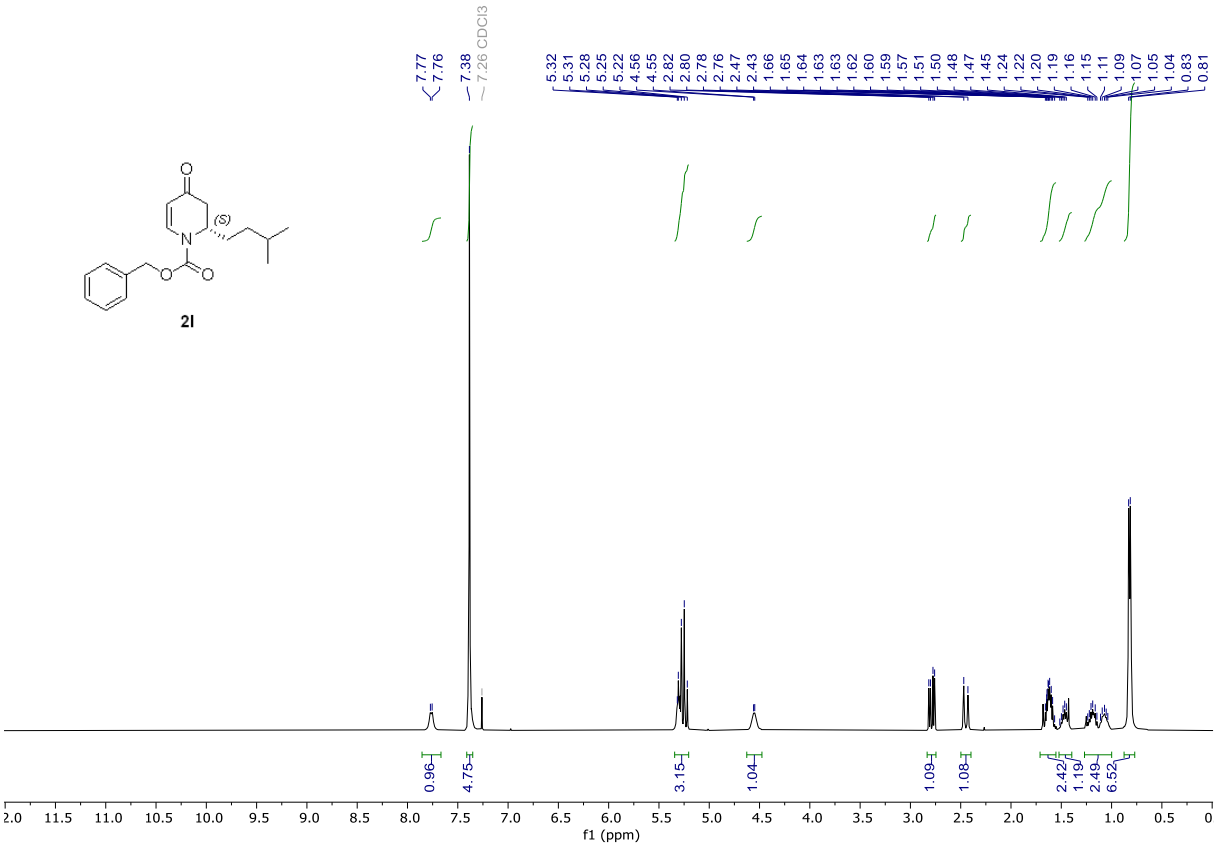
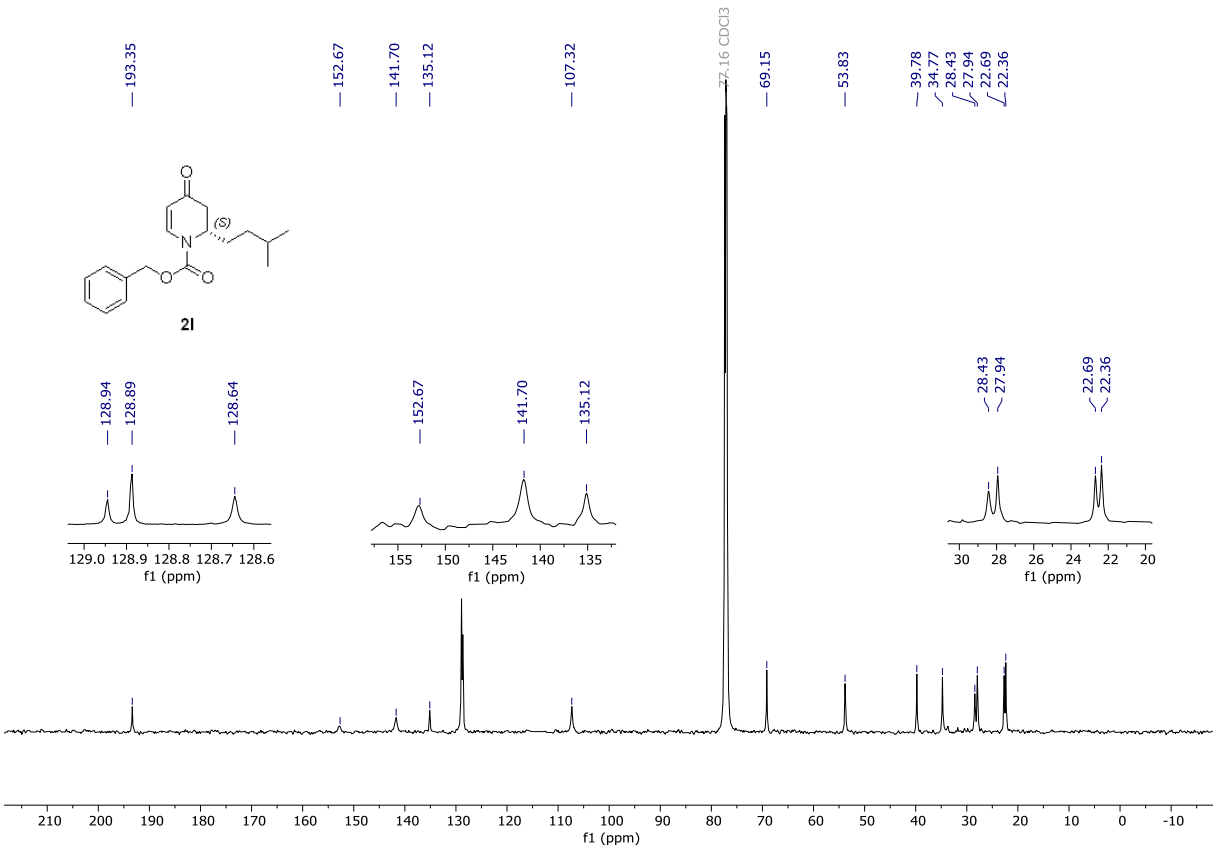
1.13
1.72
0.97
1.18
1.17
2.10
8.31
3.25
f1 (ppm)


193.28
152.71
141.68
135.15
107.32
77.16 CDCl3
69.13
53.61
39.82
31.72
30.66
29.83
29.08
25.77
22.64
14.15
2k
128.92
128.88
128.60
f1 (ppm)


7.77
7.76
7.38
7.26 CDCl3
5.32
5.31
5.28
5.25
5.22
4.56
4.55
2.82
2.80
2.78
2.76
2.47
2.43
1.66
1.65
1.64
1.63
1.63
1.62
1.60
1.59
1.57
1.51
1.50
1.48
1.47
1.45
1.24
1.22
1.20
1.19
1.16
1.15
1.11
1.09
1.07
1.05
1.04
0.83
0.81
(S)
N
O
O
O
2l
0.96
4.75
3.15
1.04
1.09
1.08
2.42
1.19
2.49
6.52
f1 (ppm)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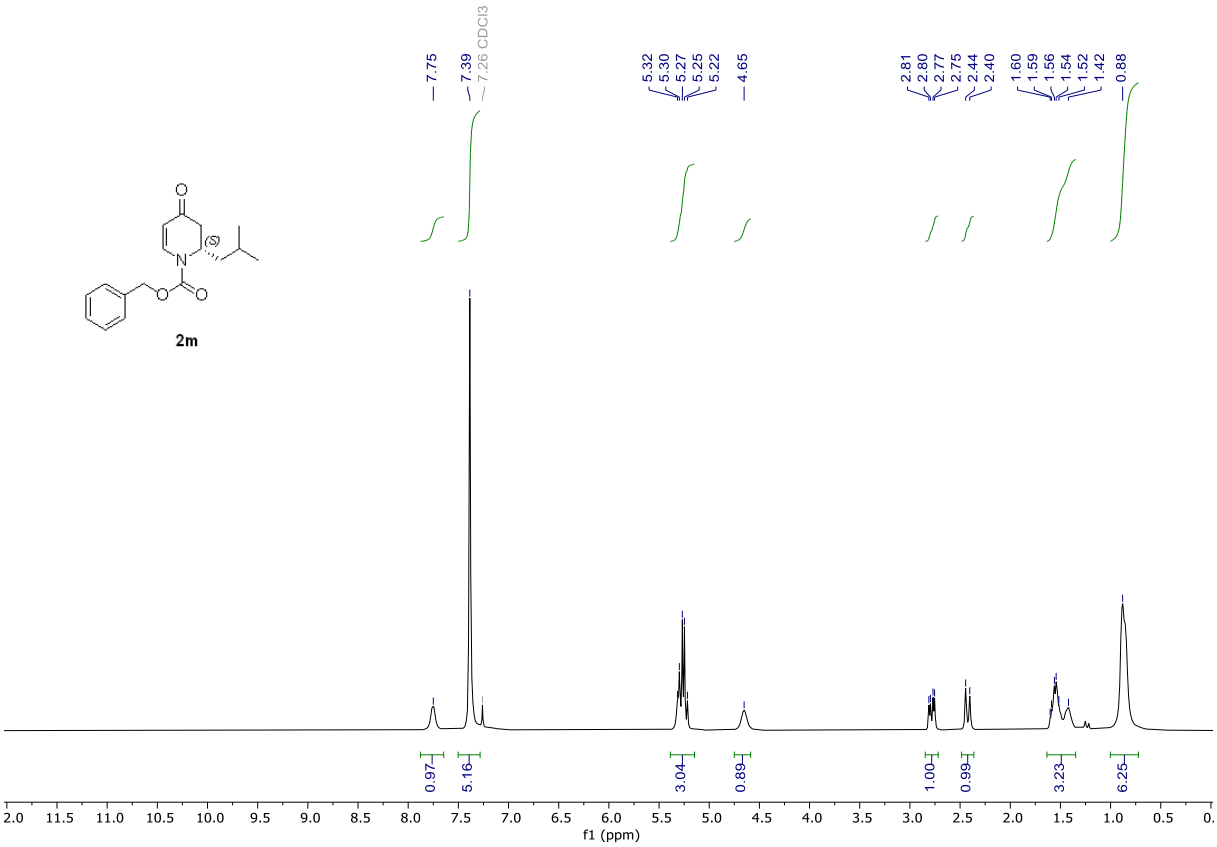
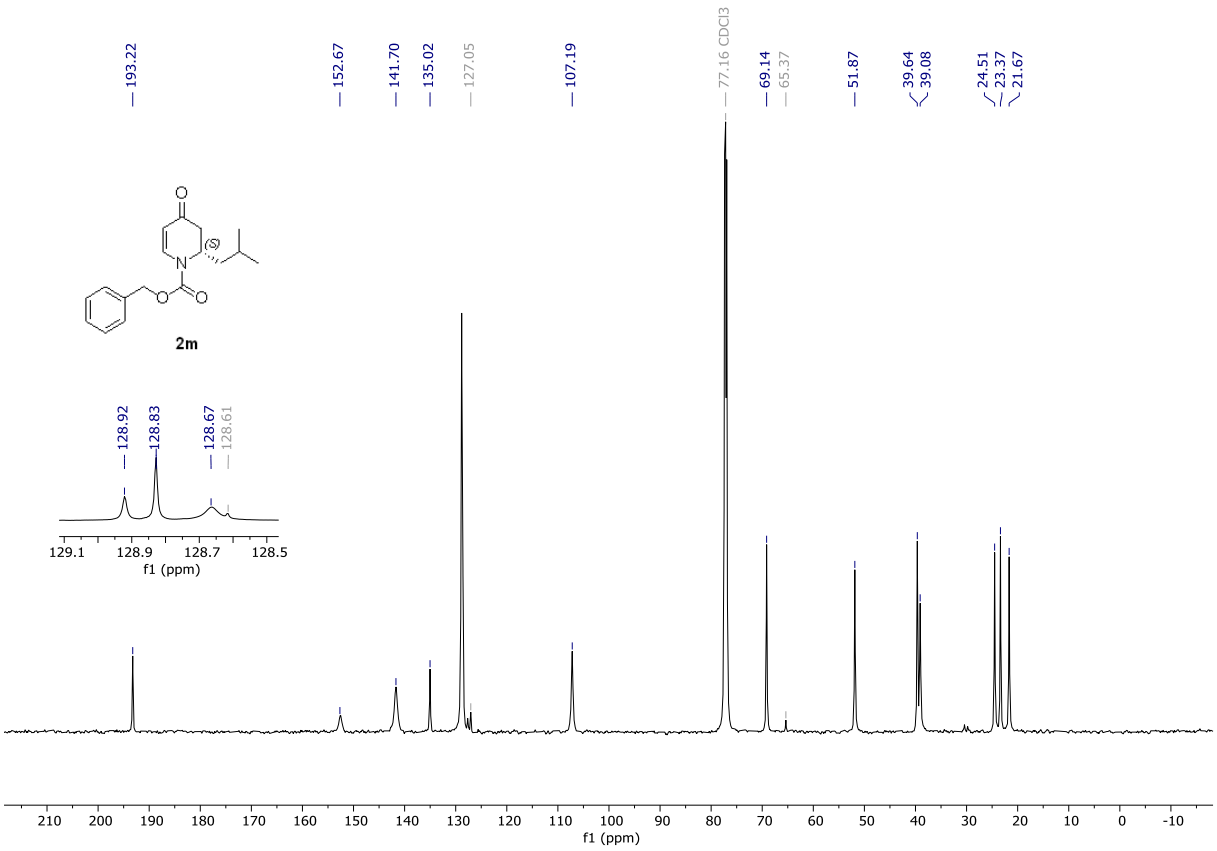
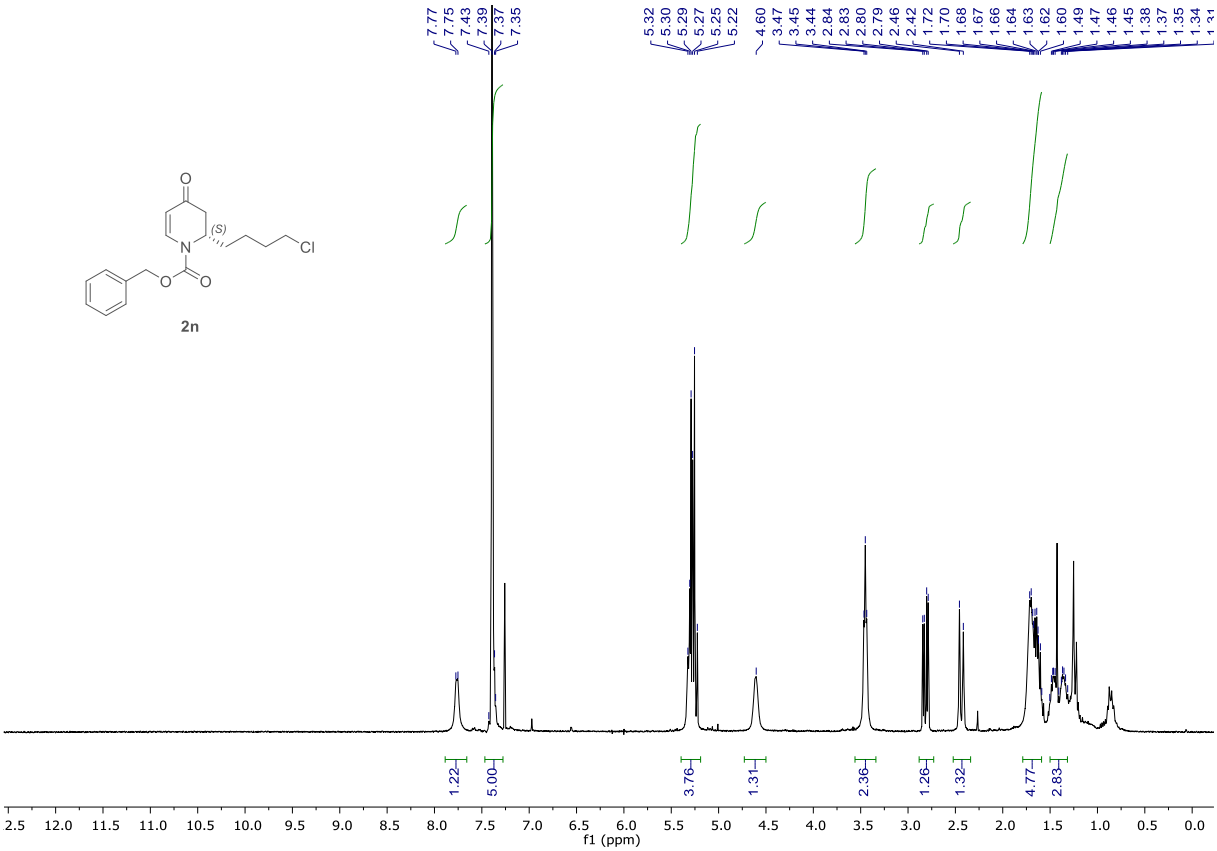
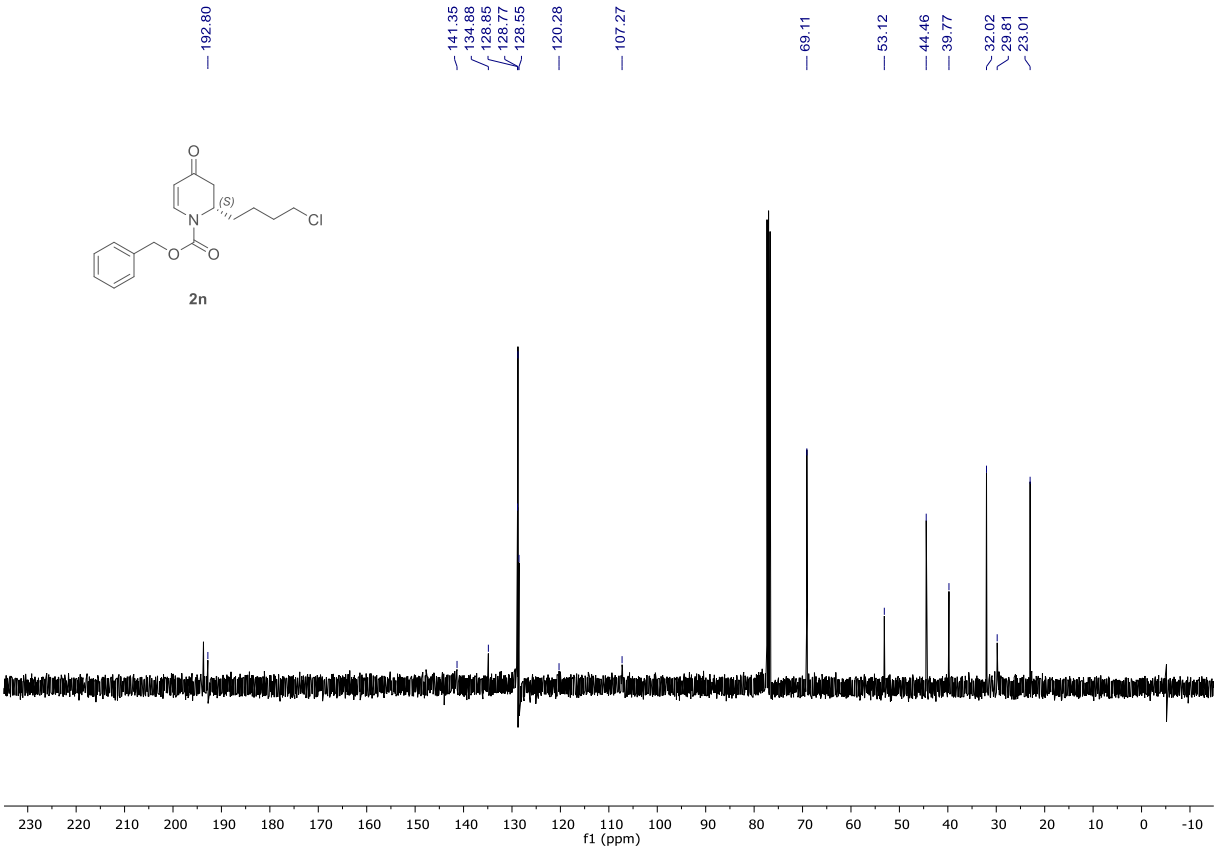
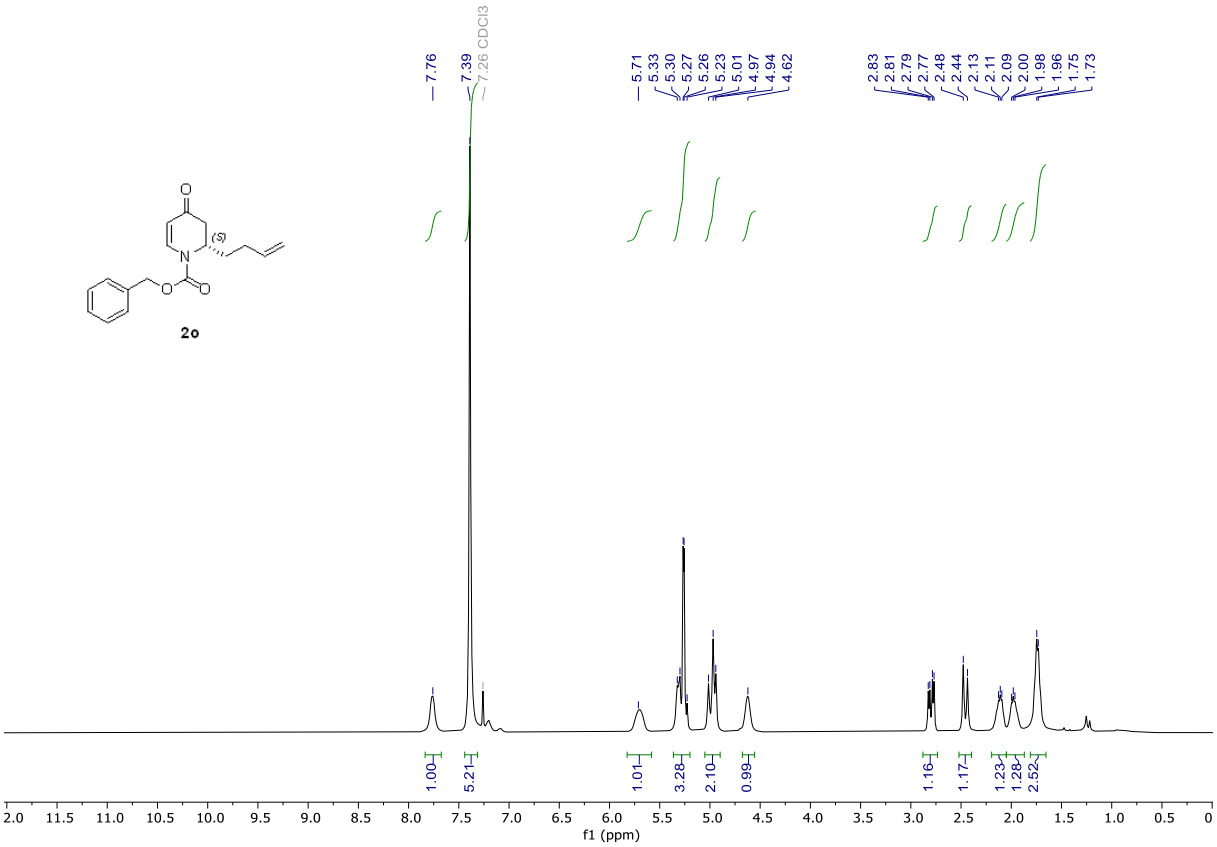
152.67
141.70
135.12
107.32
77.16 CDCl3
69.15
53.83
39.78
34.77
28.43
27.94
22.69
22.36
(S)
N
O
O
O
2l
128.94
128.89
128.64
152.67
141.70
135.12
28.43
27.94
22.69
22.36
f1 (ppm)

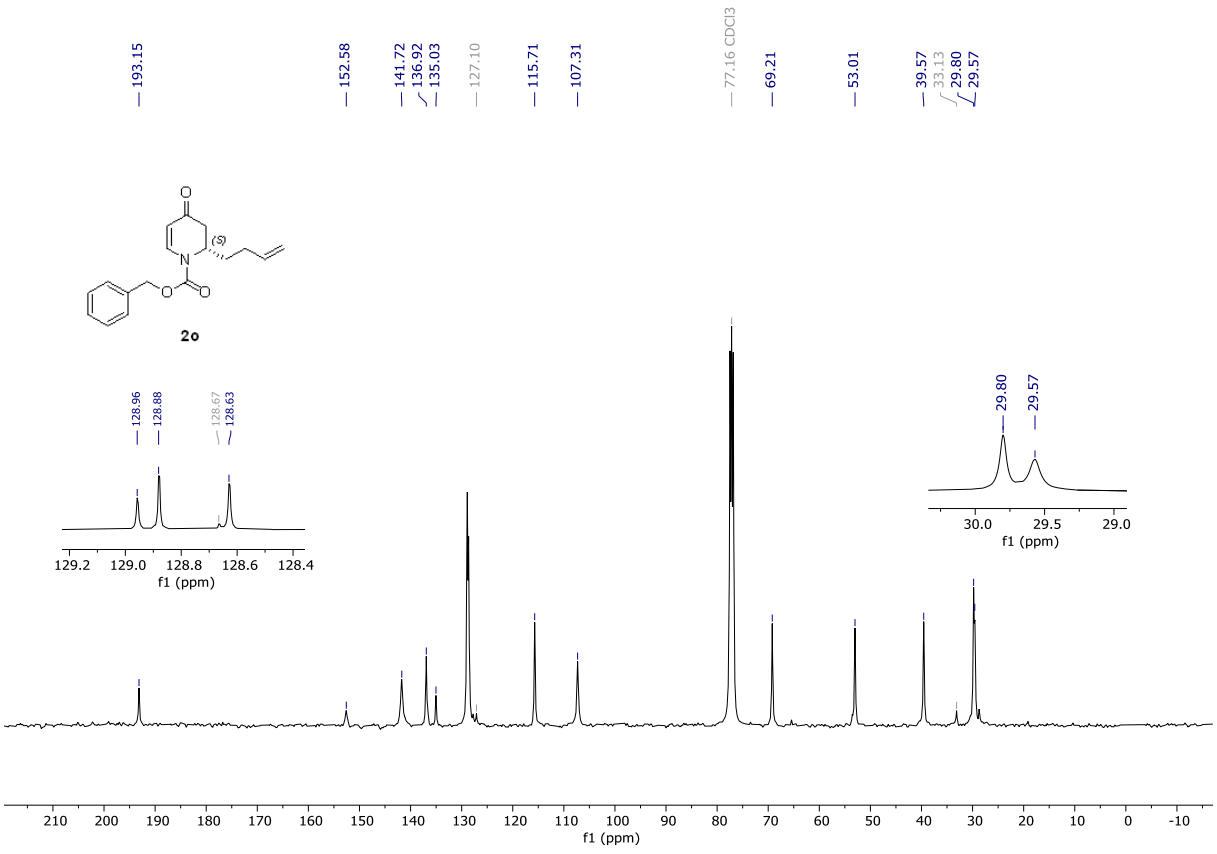

7.75
7.39
7.26 CDCl3
5.32
5.30
5.27
5.25
5.22
4.65
2.81
2.80
2.77
2.75
2.44
2.40
1.60
1.59
1.56
1.54
1.52
1.42
0.88
2m
0.97
5.16
3.04
0.89
1.00
0.99
3.23
6.25
f1 (ppm)

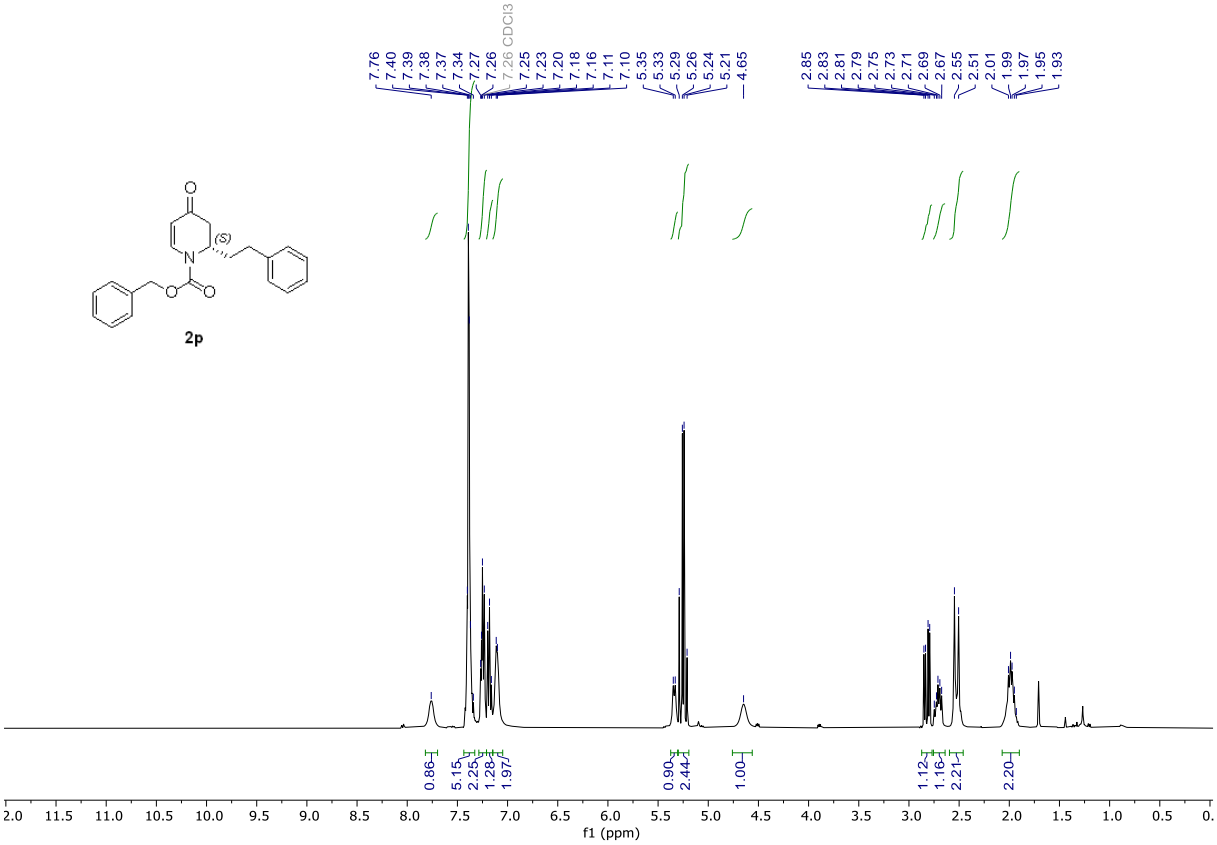

193.22
152.67
141.70
135.02
127.05
107.19
77.16 CDCl3
69.14
65.37
51.87
39.64
39.08
24.51
23.37
21.67
2m
128.92
128.83
128.67
128.61
f1 (ppm)

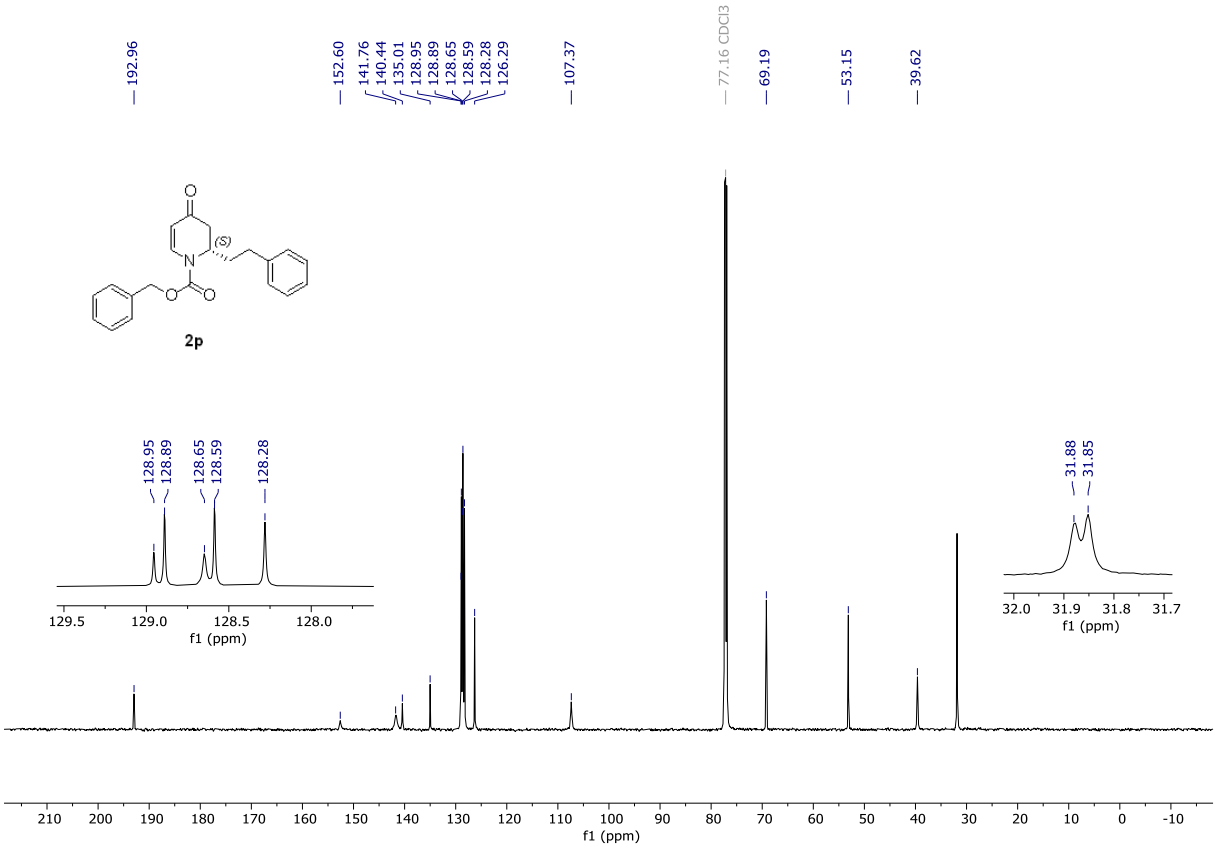

7.77
7.75
7.43
7.39
7.37
7.35
5.32
5.30
5.29
5.27
5.25
5.22
4.60
3.47
3.45
3.44
2.84
2.83
2.80
2.79
2.46
2.42
1.72
1.70
1.68
1.67
1.66
1.64
1.63
1.62
1.60
1.49
1.47
1.46
1.45
1.38
1.37
1.35
1.34
O
(S)
N
Cl
O
O
2n
1.22
5.00
3.76
1.31
2.36
1.26
1.32
4.77
2.83
f1 (ppm)

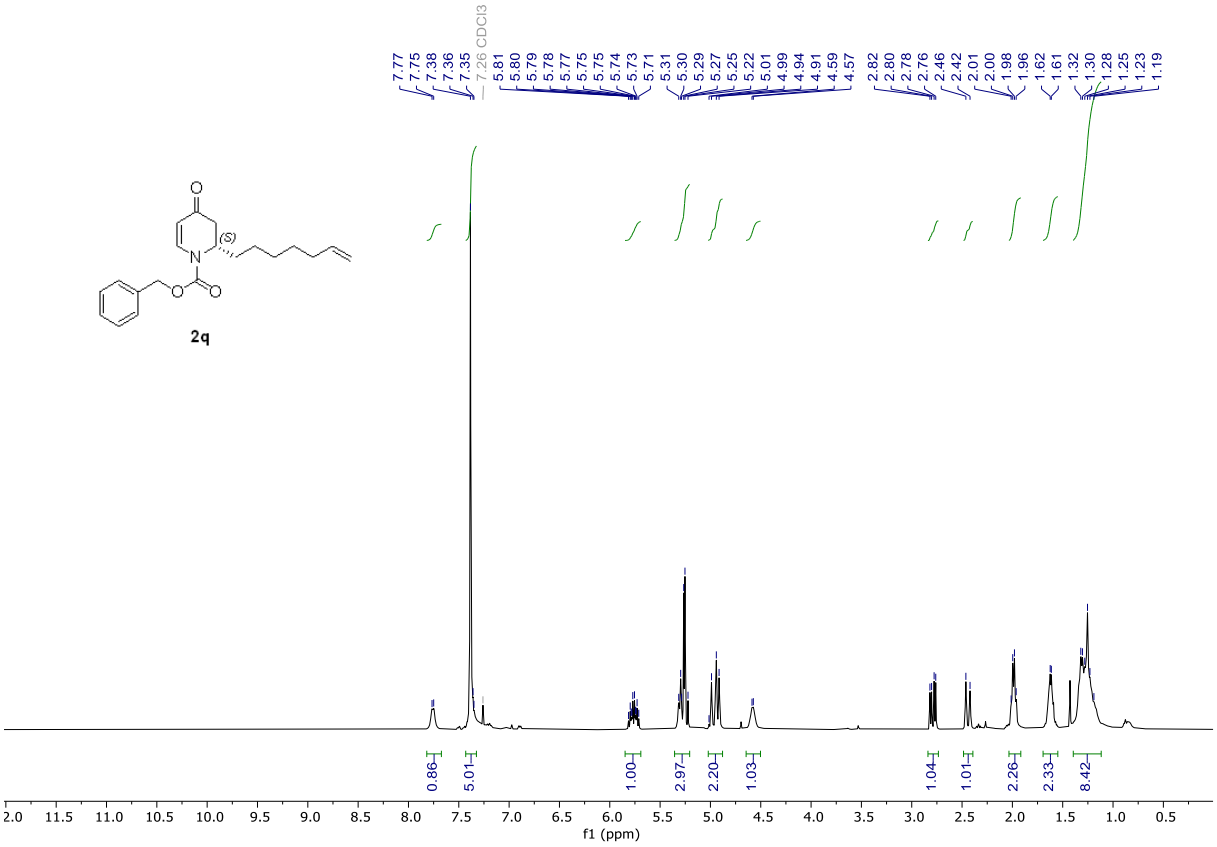

192.80
141.35
134.88
128.85
128.77
128.55
120.28
107.27
69.11
53.12
44.46
39.77
32.02
29.81
23.01
O
(S)
N
Cl
O
O
2n
f1 (ppm)

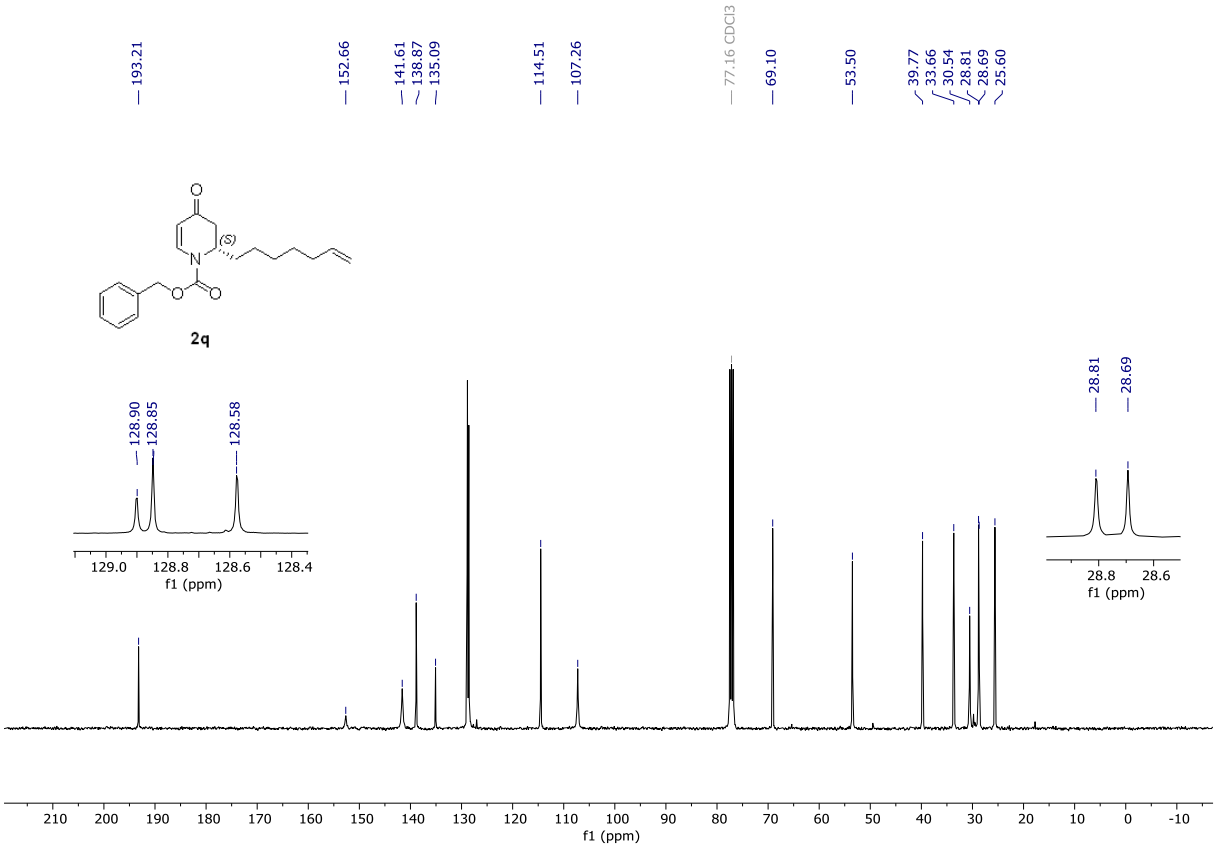

7.76
7.39
7.26 CDCl3
5.71
5.33
5.30
5.27
5.26
5.23
5.01
4.97
4.94
4.62
2.83
2.81
2.79
2.77
2.48
2.44
2.13
2.11
2.09
2.00
1.98
1.96
1.75
1.73
2o
1.00
5.21
1.01
3.28
2.10
0.99
1.16
1.17
1.23
1.28
2.52
f1 (ppm)

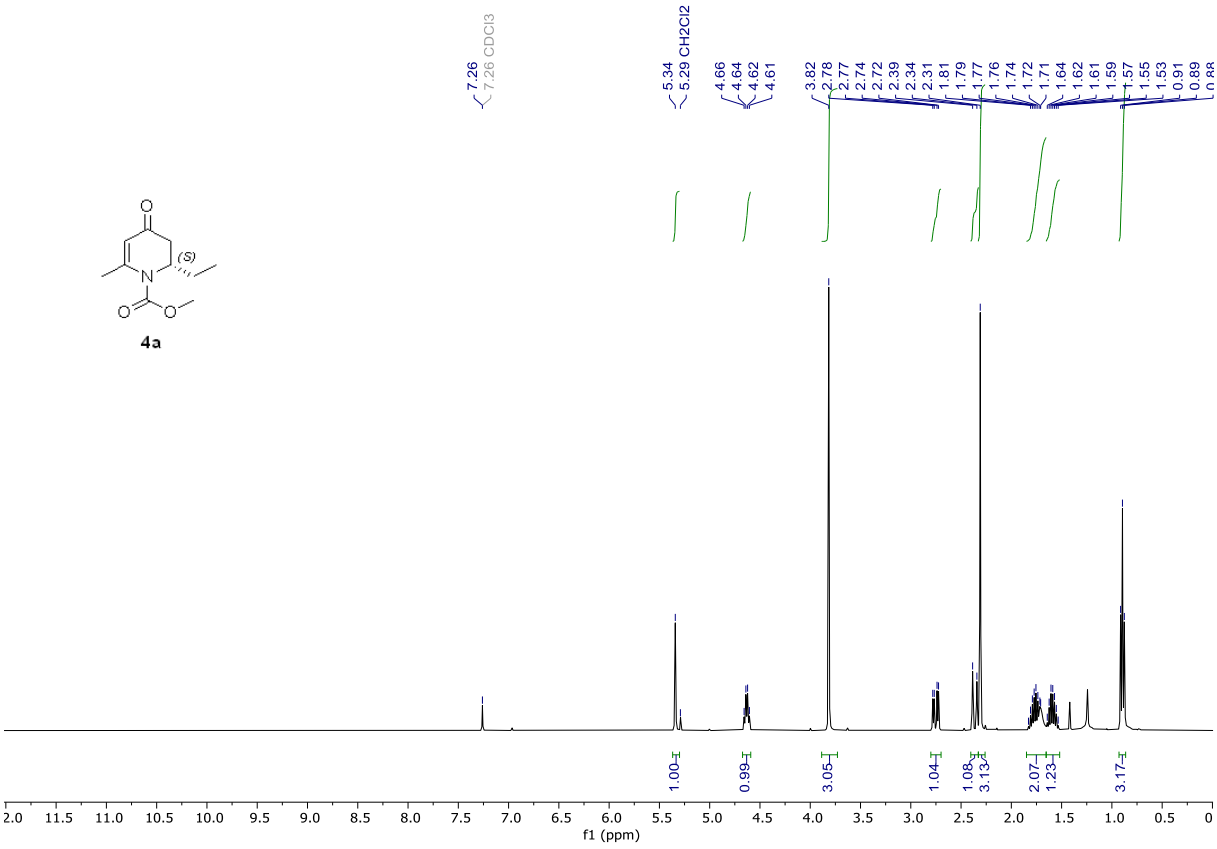

193.15
152.58
141.72
136.92
135.03
127.10
115.71
107.31
77.16 CDCl3
69.21
53.01
39.57
33.13
29.80
29.57
2o
128.96
128.88
128.67
128.63
29.80
29.57
f1 (ppm)
f1 (ppm)


7.76
7.40
7.39
7.38
7.37
7.34
7.27
7.26
7.26 CDCl3
7.25
7.23
7.20
7.18
7.16
7.11
7.10
5.35
5.33
5.29
5.26
5.24
5.21
4.65
2.85
2.83
2.81
2.79
2.75
2.73
2.71
2.69
2.67
2.55
2.51
2.01
1.99
1.97
1.95
1.93
(S)
2p
0.86
5.15
2.25
1.28
1.97
0.90
2.44
1.00
1.12
1.16
2.21
2.20
f1 (ppm)


192.96
152.60
141.76
140.44
135.01
128.95
128.89
128.65
128.59
128.28
126.29
107.37
77.16 CDCl3
69.19
53.15
39.62
(S)
2p
128.95
128.89
128.65
128.59
128.28
129.5
129.0
128.5
128.0
f1 (ppm)
31.88
31.85
32.0
31.9
31.8
31.7
f1 (ppm)
f1 (ppm)

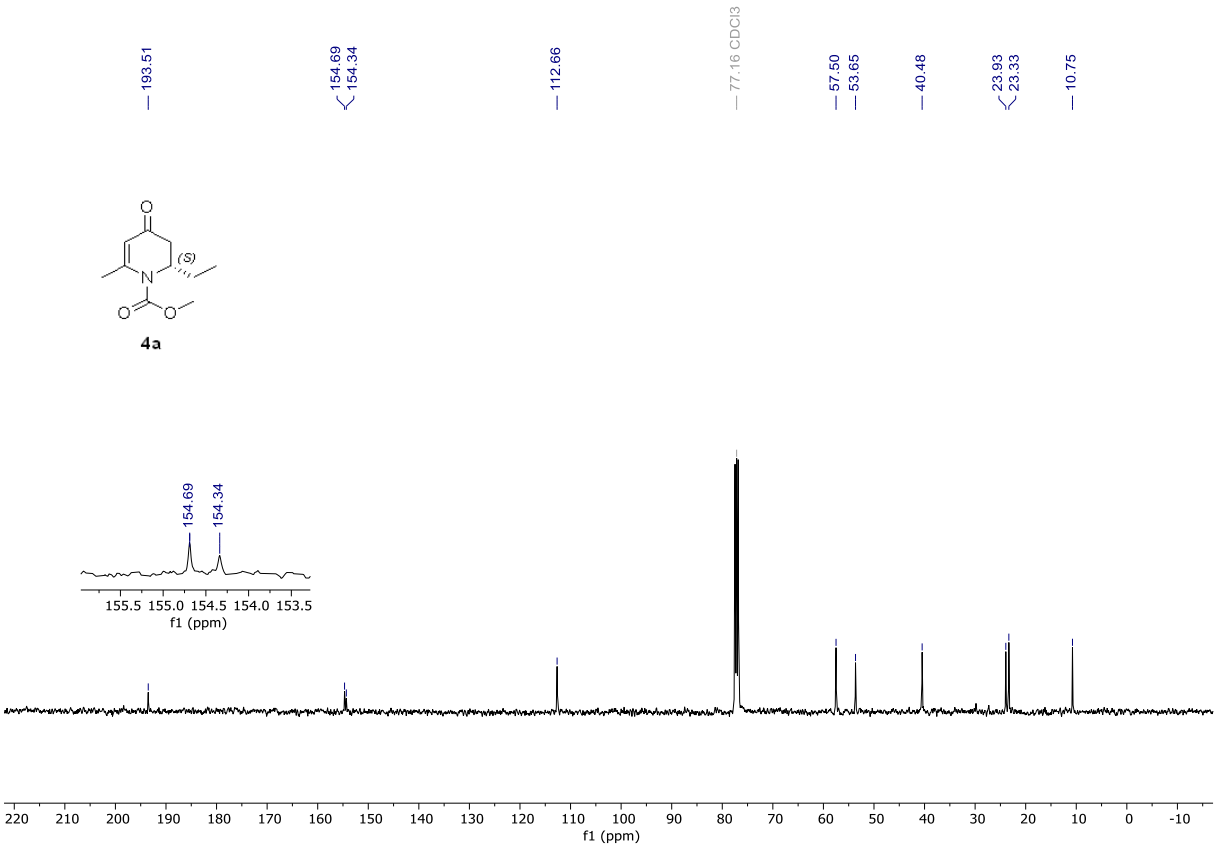

7.77
7.75
7.38
7.36
7.35
7.26 CDCl3
5.81
5.80
5.79
5.78
5.77
5.75
5.75
5.74
5.73
5.71
5.31
5.30
5.29
5.27
5.25
5.22
5.01
4.99
4.94
4.91
4.59
4.57
2.82
2.80
2.78
2.76
2.46
2.42
2.01
2.00
1.98
1.96
1.62
1.61
1.32
1.30
1.28
1.25
1.23
1.19
(S)
2q
0.86
5.01
1.00
2.97
2.20
1.03
1.04
1.01
2.26
2.33
8.42
f1 (ppm)


193.21
152.66
141.61
138.87
135.09
114.51
107.26
77.16 CDCl3
69.10
53.50
39.77
33.66
30.54
28.81
28.69
25.60
(S)
2q
128.90
128.85
128.58
129.0
128.8
128.6
128.4
f1 (ppm)
28.81
28.69
28.8
28.6
f1 (ppm)
f1 (ppm)


7.26
7.26 CDCl3
5.34
5.29 CH2Cl2
4.66
4.64
4.62
4.61
3.82
2.78
2.77
2.74
2.72
2.39
2.34
2.31
1.81
1.79
1.77
1.76
1.74
1.72
1.71
1.64
1.62
1.61
1.59
1.57
1.55
1.53
0.91
0.89
1.00
0.99
3.05
1.04
1.08
3.13
2.07
1.23
3.17
f1 (ppm)

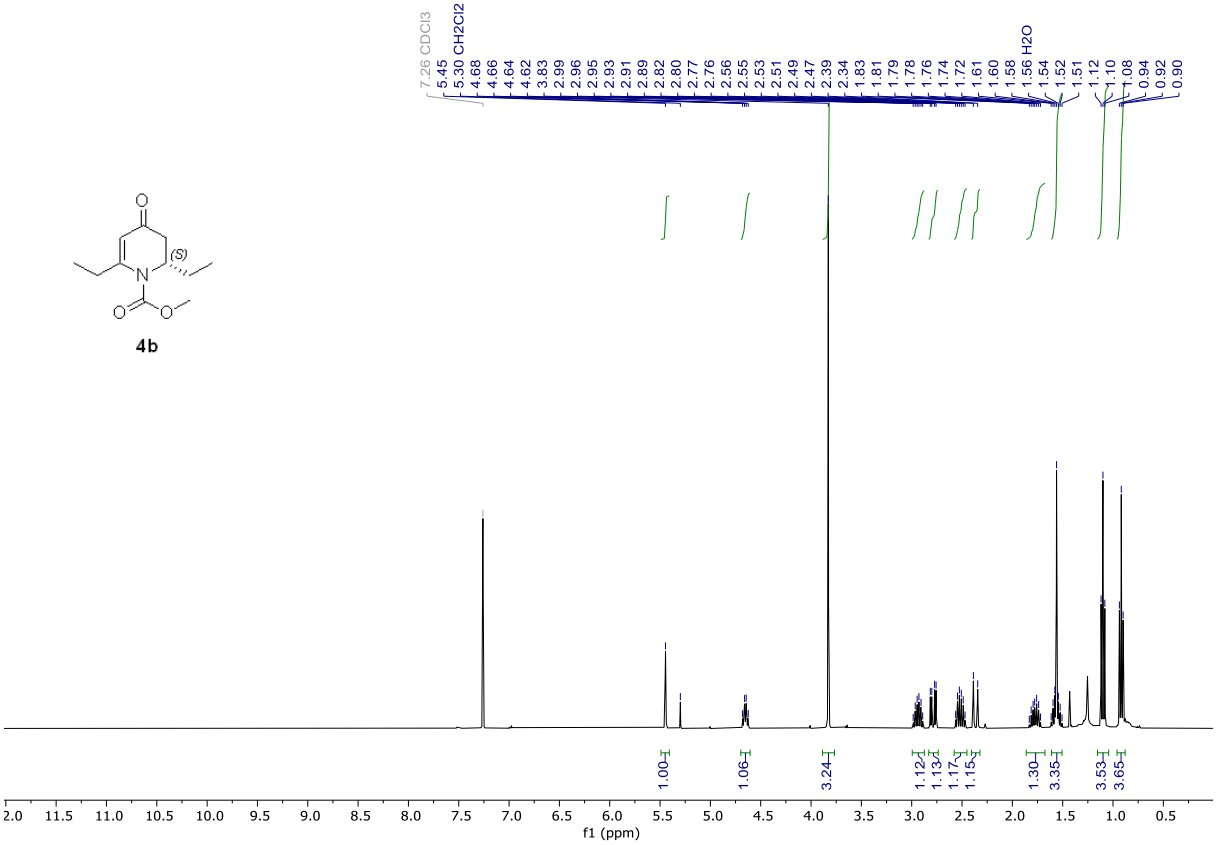


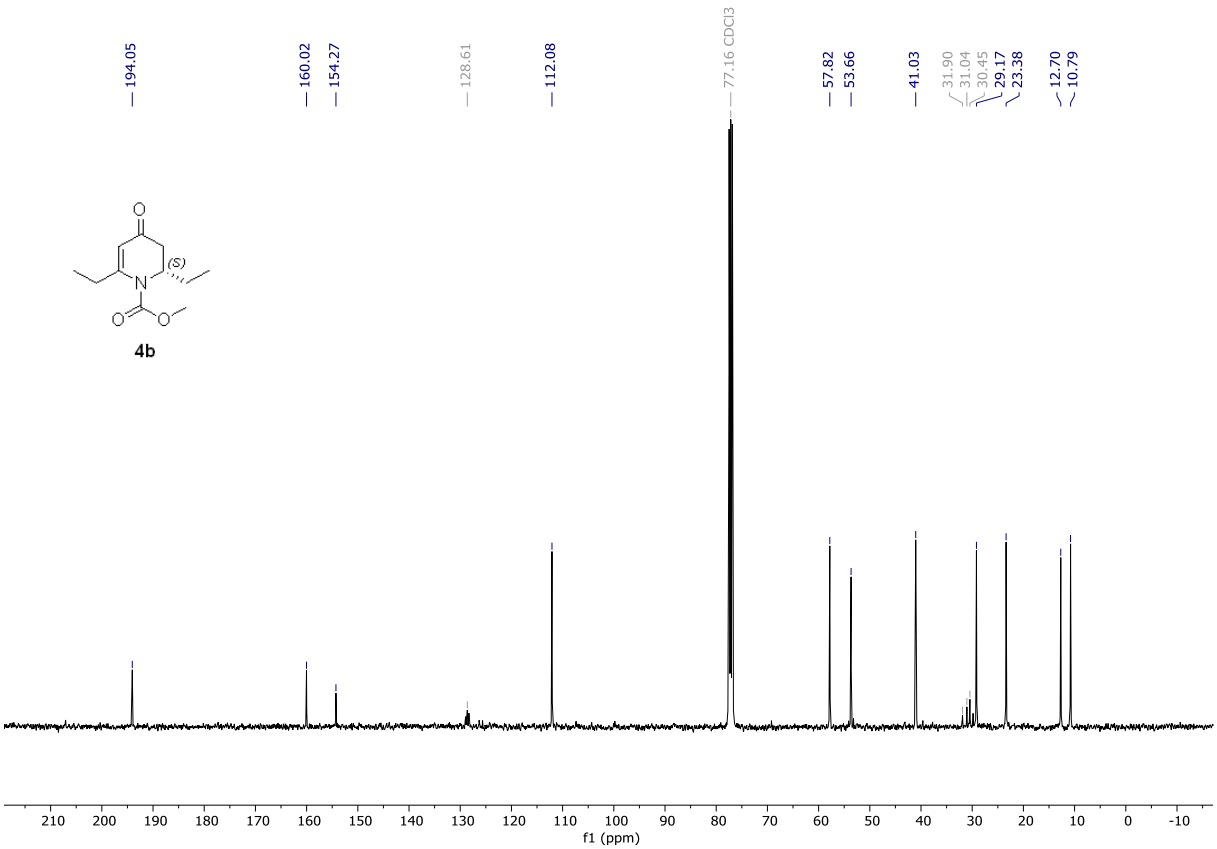
4a

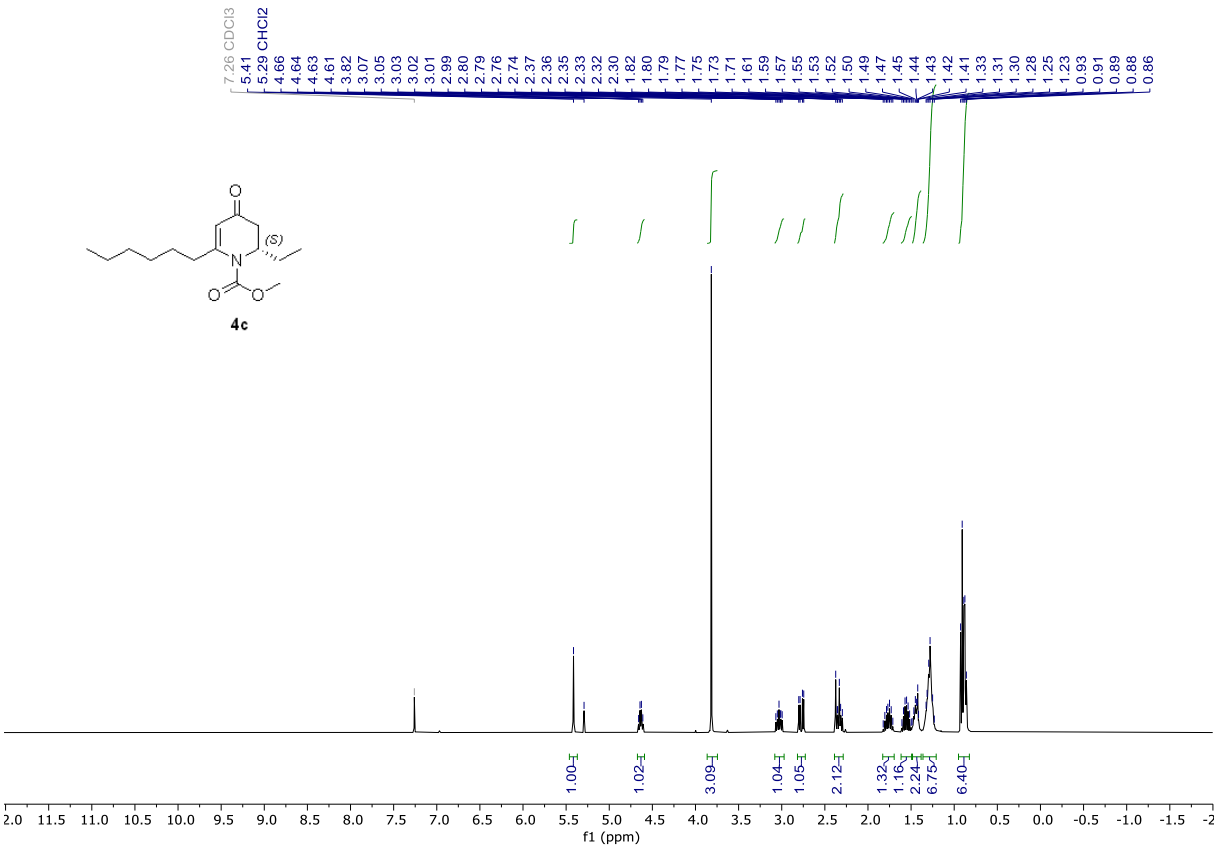

193.51
154.69
154.34
112.66
77.16 CDCl3
57.50
53.65
40.48
23.93
23.33
10.75
154.69
154.34
155.5 155.0 154.5 154.0 153.5
f1 (ppm)
f1 (ppm)

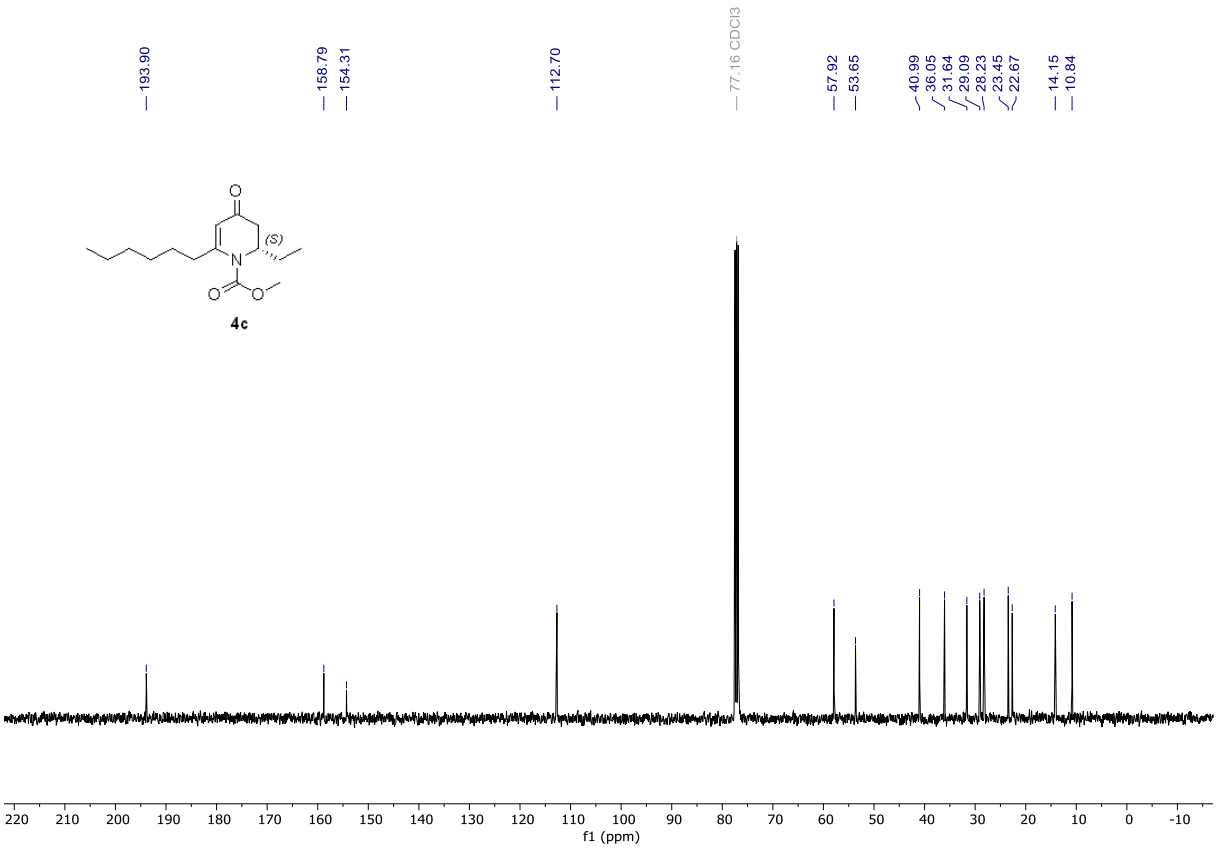


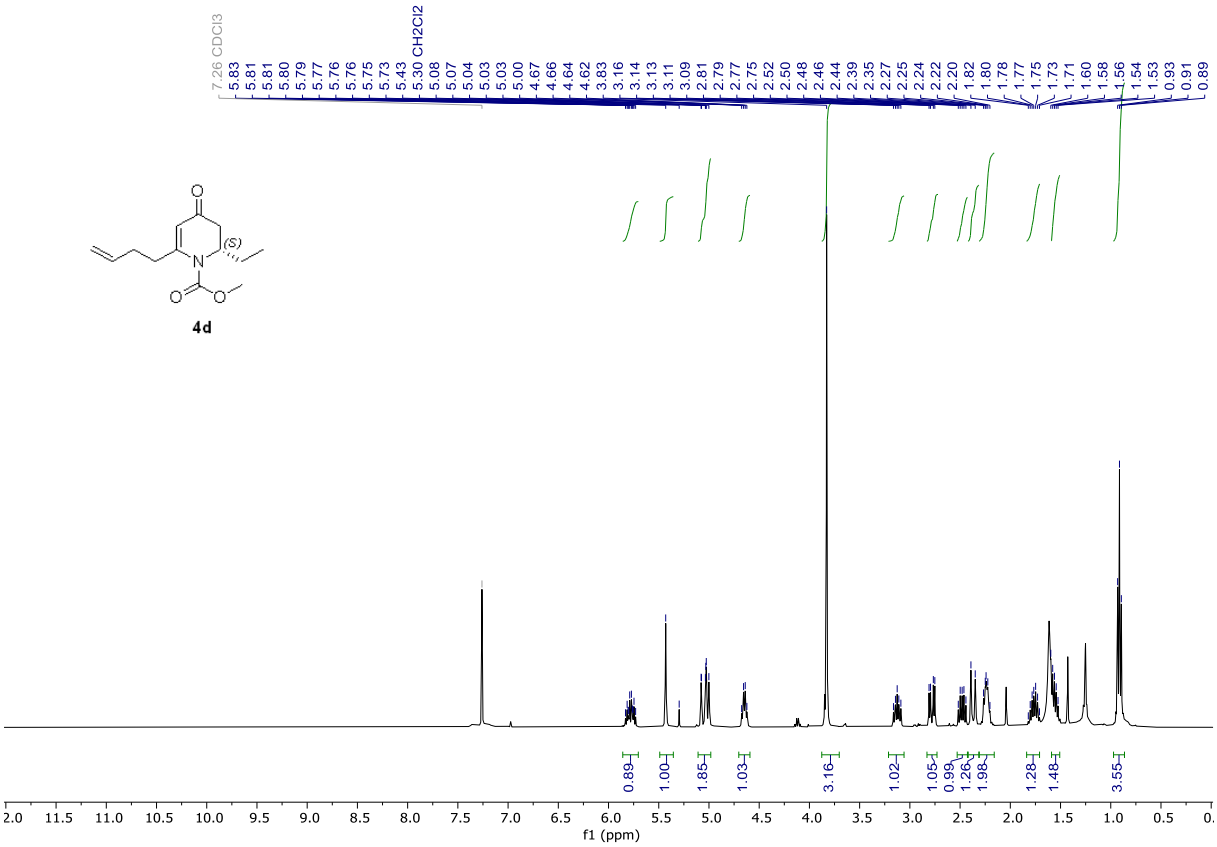
4a


7.26 CDCl3
5.45
5.30 CH2Cl2
4.68
4.66
4.64
4.62
3.83
2.99
2.96
2.95
2.93
2.91
2.89
2.82
2.80
2.77
2.76
2.56
2.55
2.53
2.51
2.49
2.47
2.39
2.34
1.83
1.81
1.79
1.78
1.76
1.74
1.72
1.61
1.60
1.58
1.56 H2O
1.54
1.52
1.51
1.12
1.10
1.08
0.94
0.92
0.90
4b
1.00
1.06
3.24
1.12
1.13
1.17
1.15
1.30
3.35
3.53
3.65
f1 (ppm)

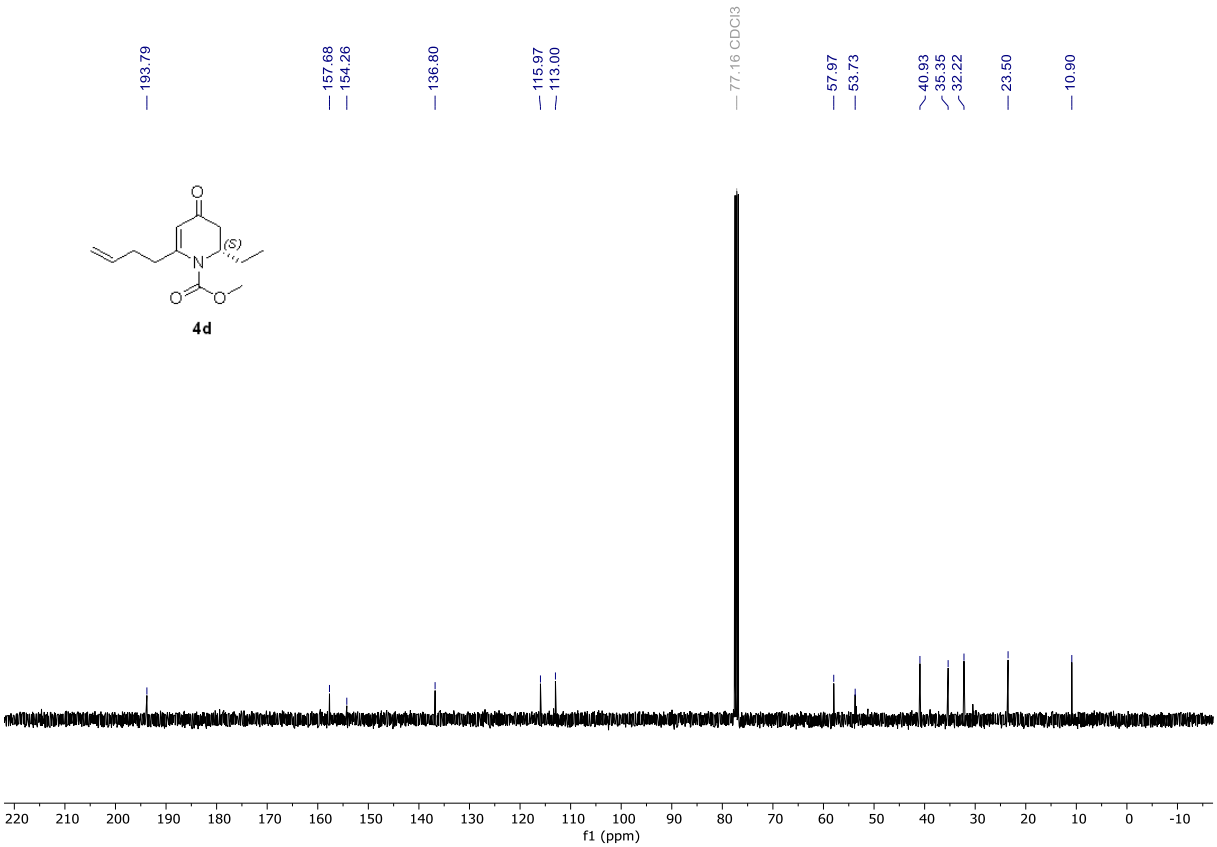

194.05
160.02
154.27
128.61
112.08
77.16 CDCl3
57.82
53.66
41.03
31.90
31.04
30.45
29.17
23.38
12.70
10.79
4b
f1 (ppm)


7.26 CDCl3
5.41
5.29 CHCl2
4.66
4.64
4.63
4.61
3.82
3.07
3.05
3.03
3.02
3.01
2.99
2.80
2.79
2.76
2.74
2.37
2.36
2.35
2.33
2.32
2.30
1.82
1.80
1.79
1.77
1.75
1.73
1.71
1.61
1.59
1.57
1.55
1.53
1.52
1.50
1.49
1.47
1.45
1.44
1.43
1.42
1.41
1.33
1.31
1.30
1.28
1.25
1.23
0.93
0.91
0.89
0.88
0.86
(S)
4c
1.00
1.02
3.09
1.04
1.05
2.12
1.32
1.16
2.24
6.75
6.40
f1 (ppm)

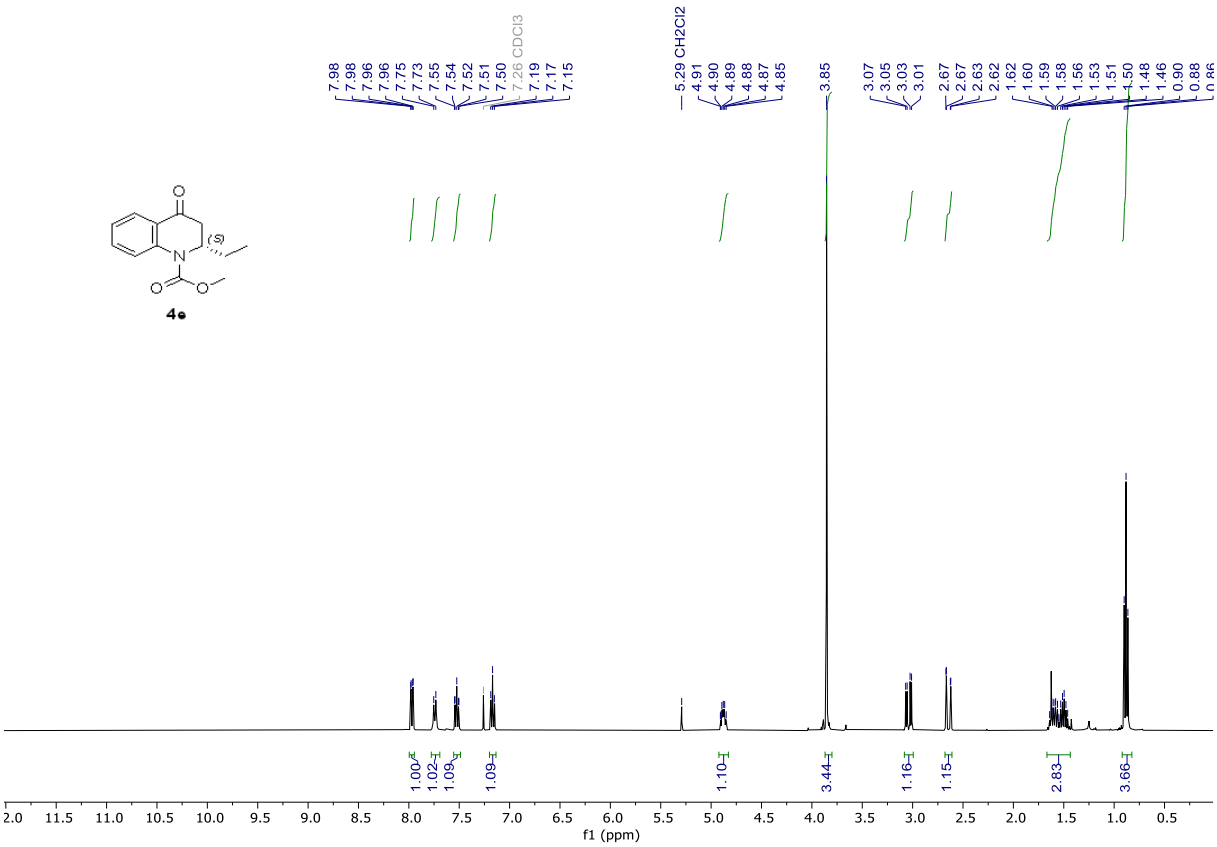

193.90
158.79
154.31
112.70
77.16 CDCl3
57.92
53.65
40.99
36.05
31.64
29.09
28.23
23.45
22.67
14.15
10.84
(S)
4c
f1 (ppm)

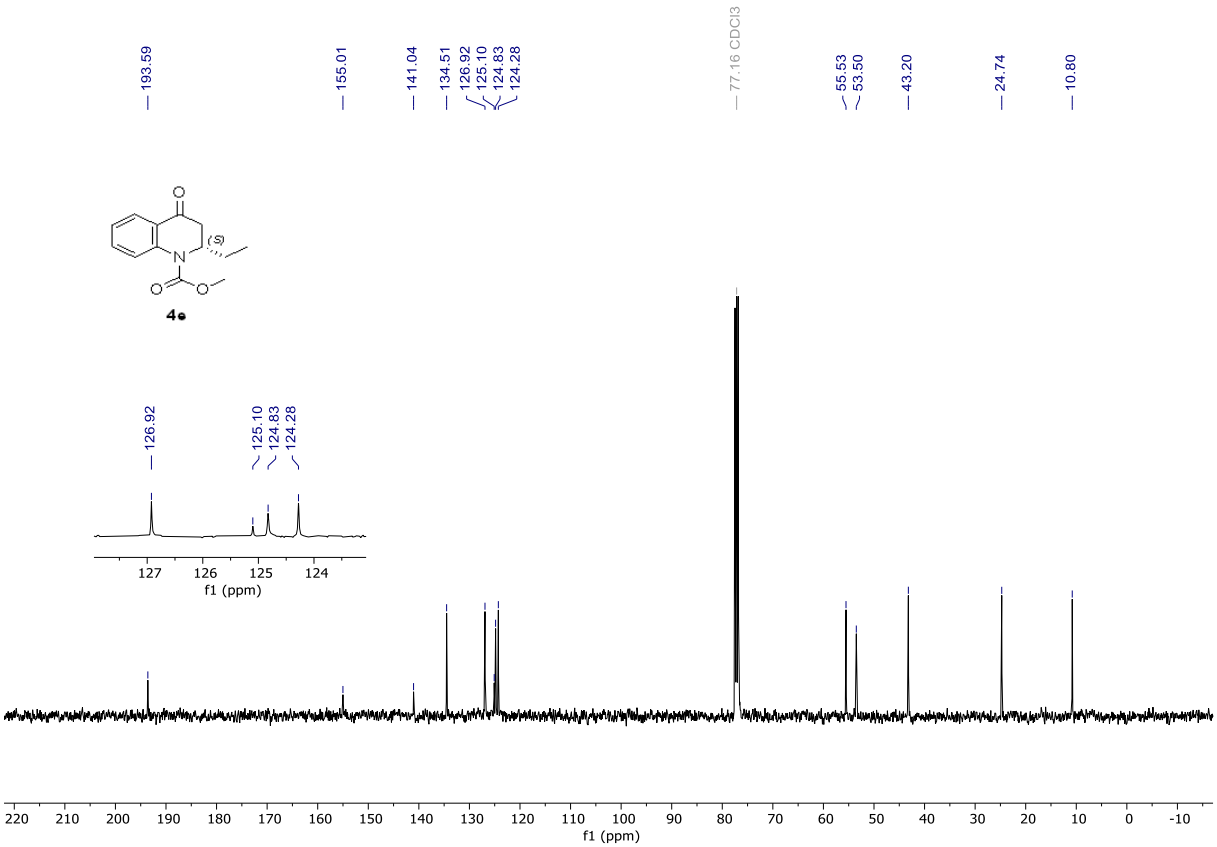

7.26 CDCl3
5.30 CH2Cl2
0.89
1.00
1.85
1.03
3.16
1.02
1.05
0.99
1.26
1.98
1.28
1.48
3.55
f1 (ppm)

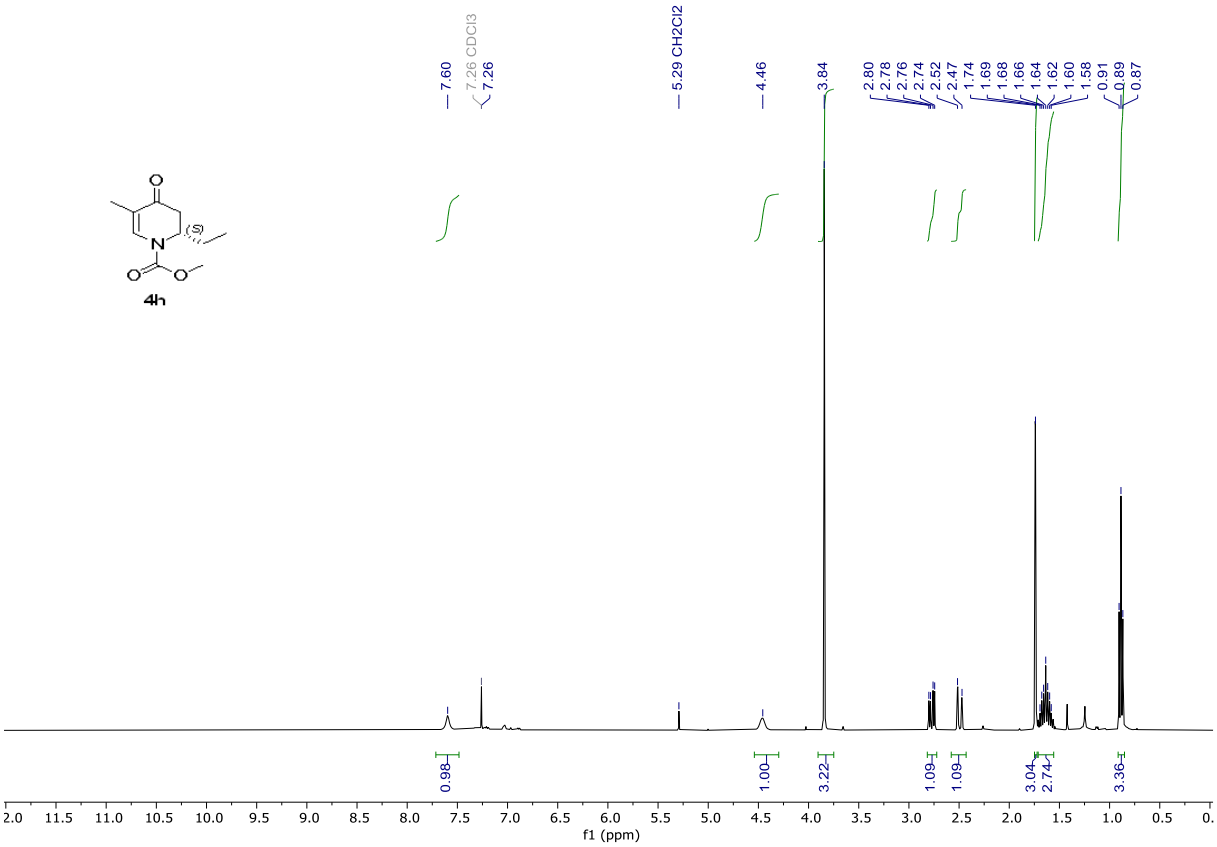
4d

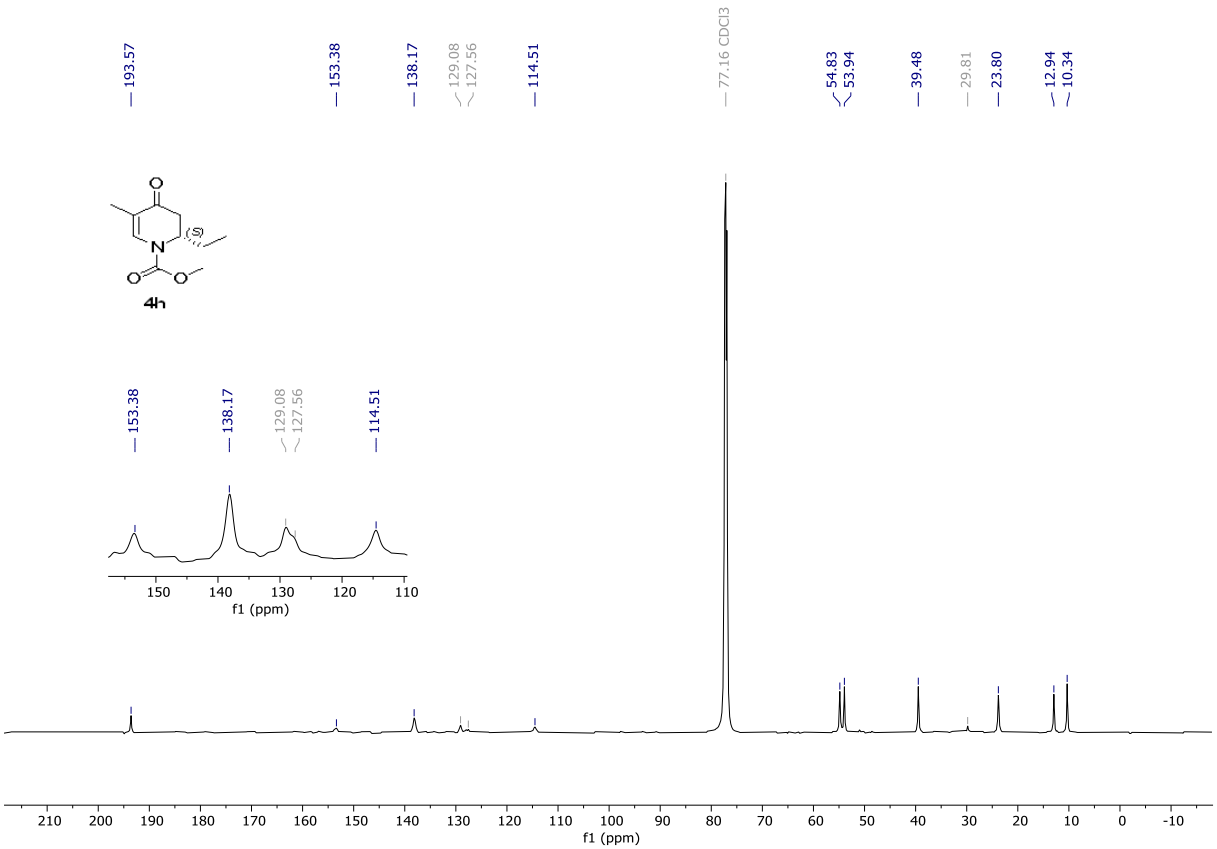

193.79
157.68
154.26
136.80
115.97
113.00
77.16 CDCl3
57.97
53.73
40.93
35.35
32.22
23.50
10.90
f1 (ppm)

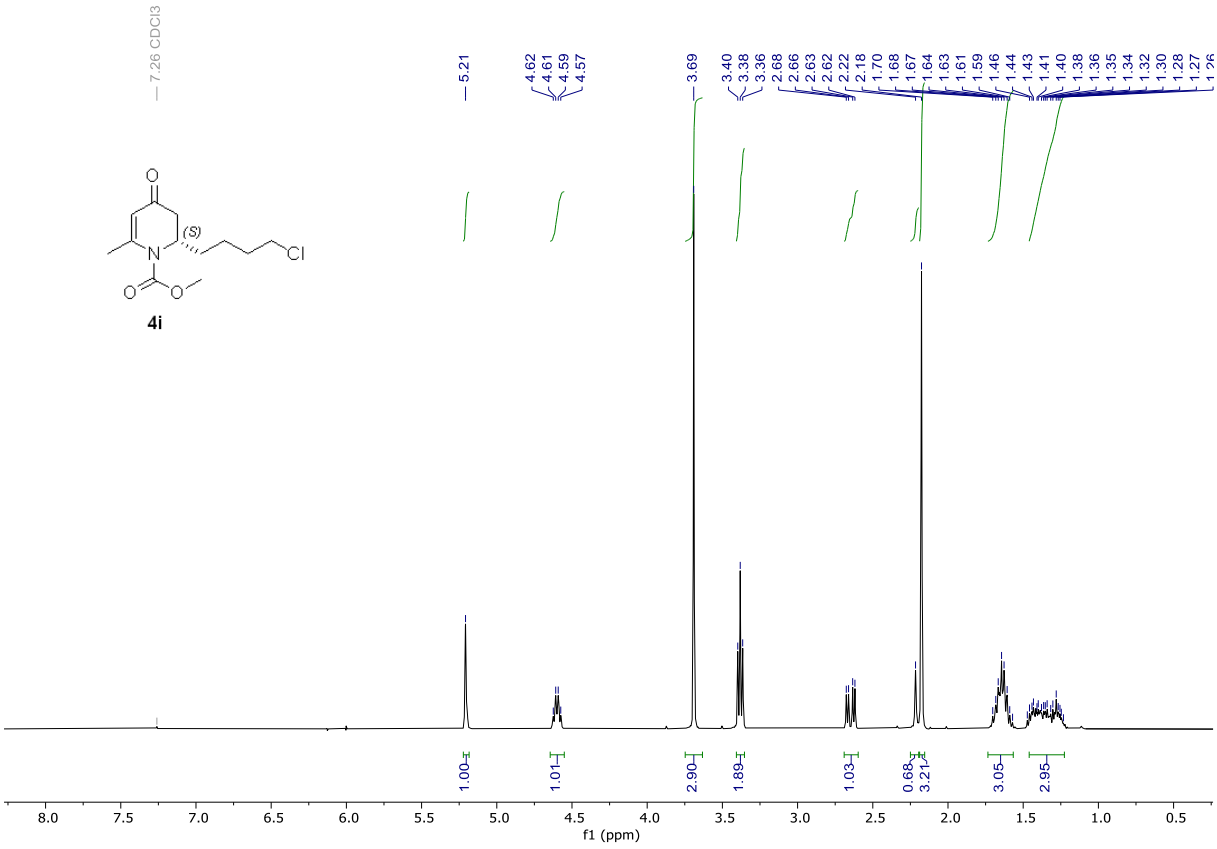
4d

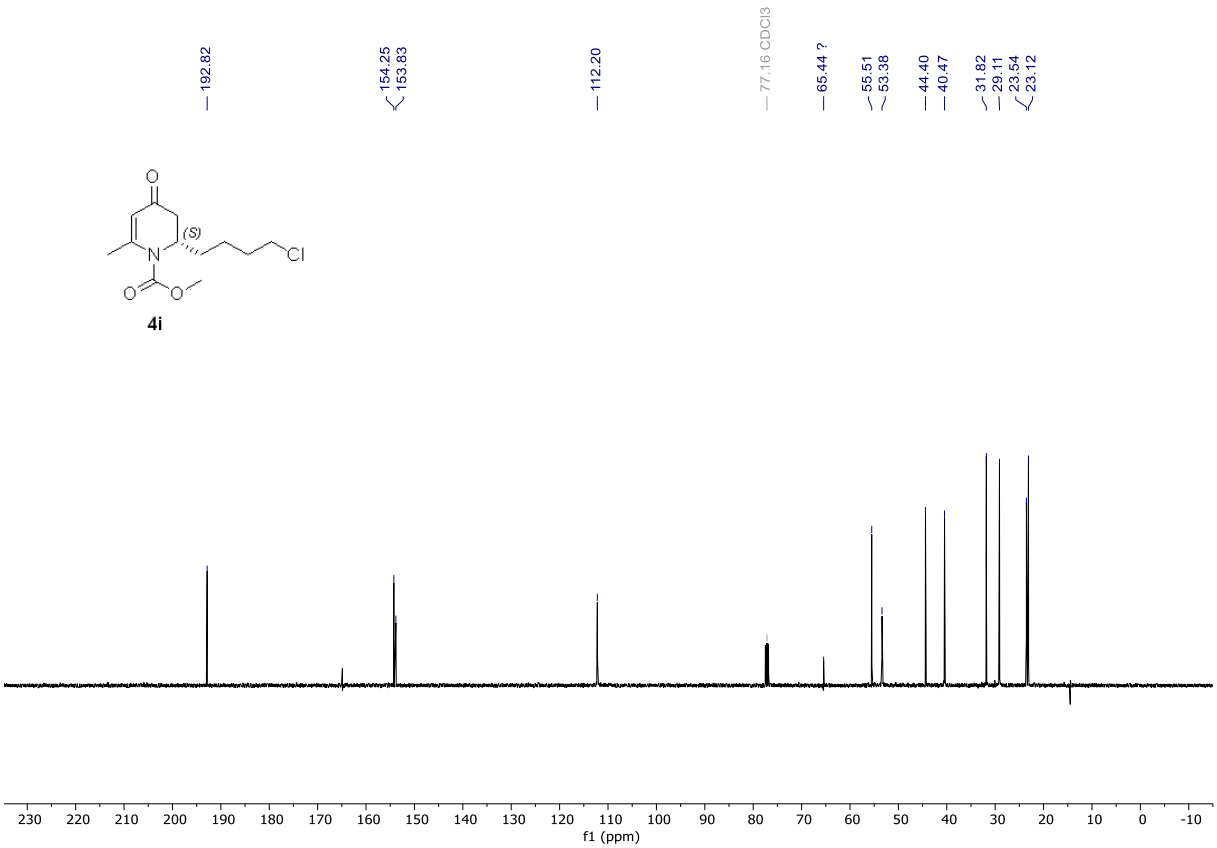

7.98
7.98
7.96
7.96
7.75
7.73
7.55
7.54
7.52
7.51
7.50
7.26 CDCl3
7.19
7.17
7.15
5.29 CH2Cl2
4.91
4.90
4.89
4.88
4.87
4.85
3.85
3.07
3.05
3.03
3.01
2.67
2.67
2.63
2.62
1.62
1.60
1.59
1.58
1.56
1.53
1.51
1.50
1.48
1.46
0.90
0.88
1.00
1.02
1.09
1.09
1.10
3.44
1.16
1.15
2.83
3.66
f1 (ppm)
4e

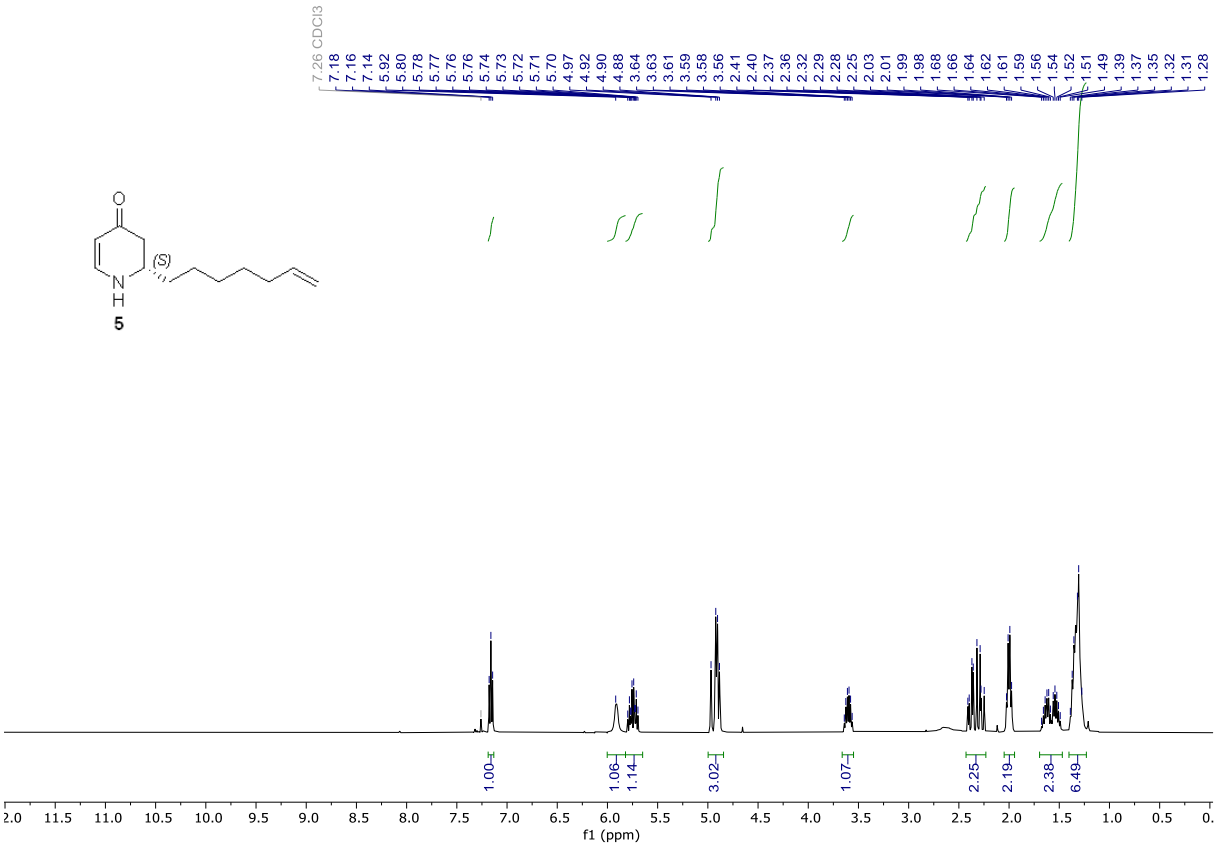

193.59
155.01
141.04
134.51
126.92
125.10
124.83
124.28
77.16 CDCl3
55.53
53.50
43.20
24.74
10.80
126.92
125.10
124.83
124.28
f1 (ppm)
f1 (ppm)
4e

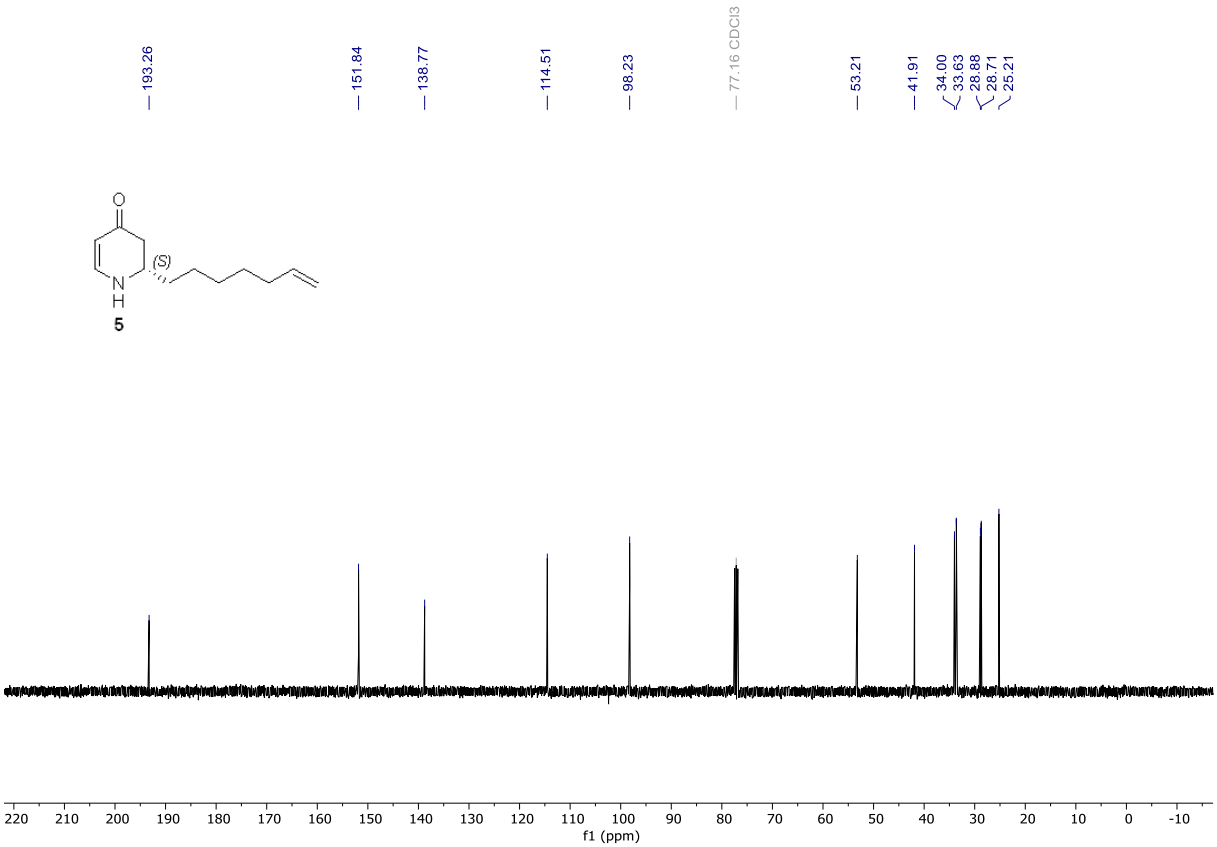

7.60
7.26 CDCl3
7.26
5.29 CH2Cl2
4.46
3.84
2.80
2.78
2.76
2.74
2.52
2.47
1.74
1.69
1.68
1.66
1.64
1.62
1.60
1.58
0.91
0.89
0.87
4h
0.98
1.00
3.22
1.09
1.09
3.04
2.74
3.36
f1 (ppm)

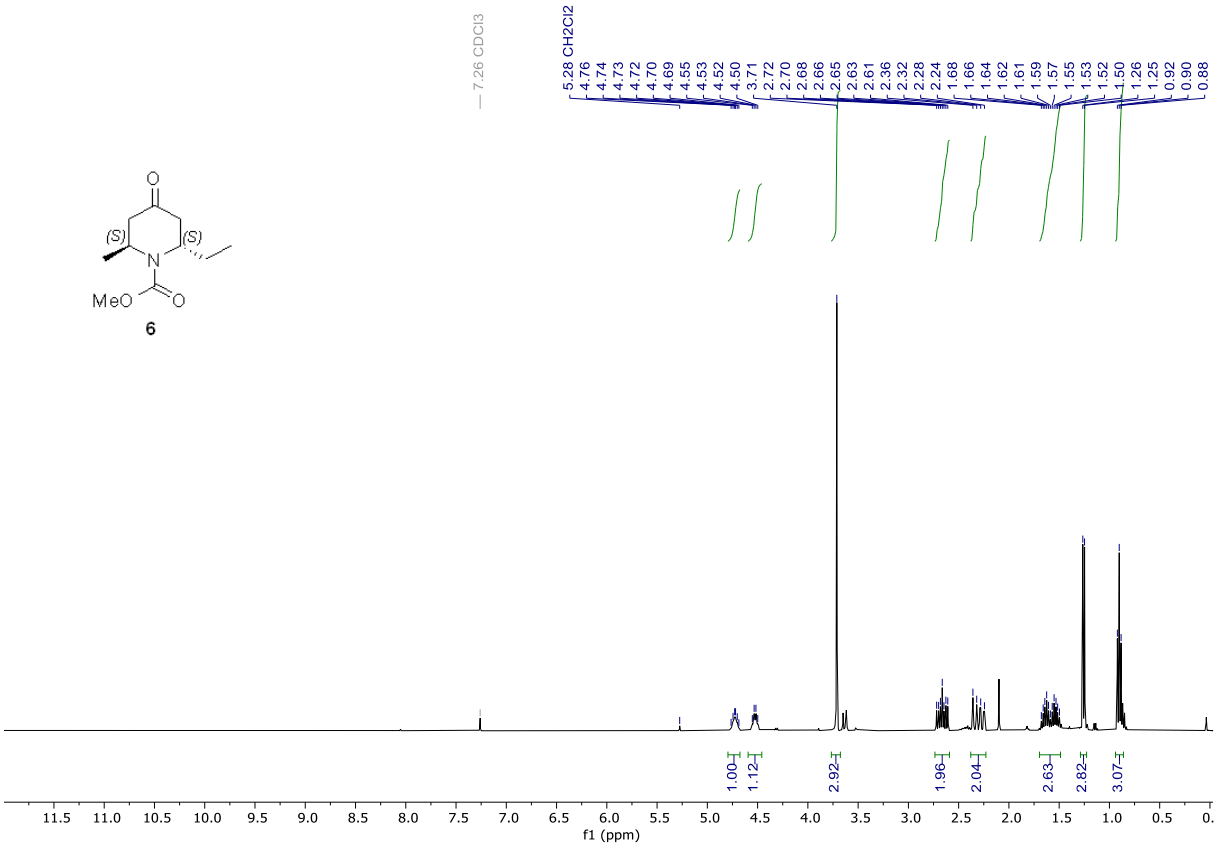

193.57
153.38
138.17
129.08
127.56
114.51
77.16 CDCl3
54.83
53.94
39.48
29.81
23.80
12.94
10.34
4h
153.38
138.17
129.08
127.56
114.51
f1 (ppm)
f1 (ppm)

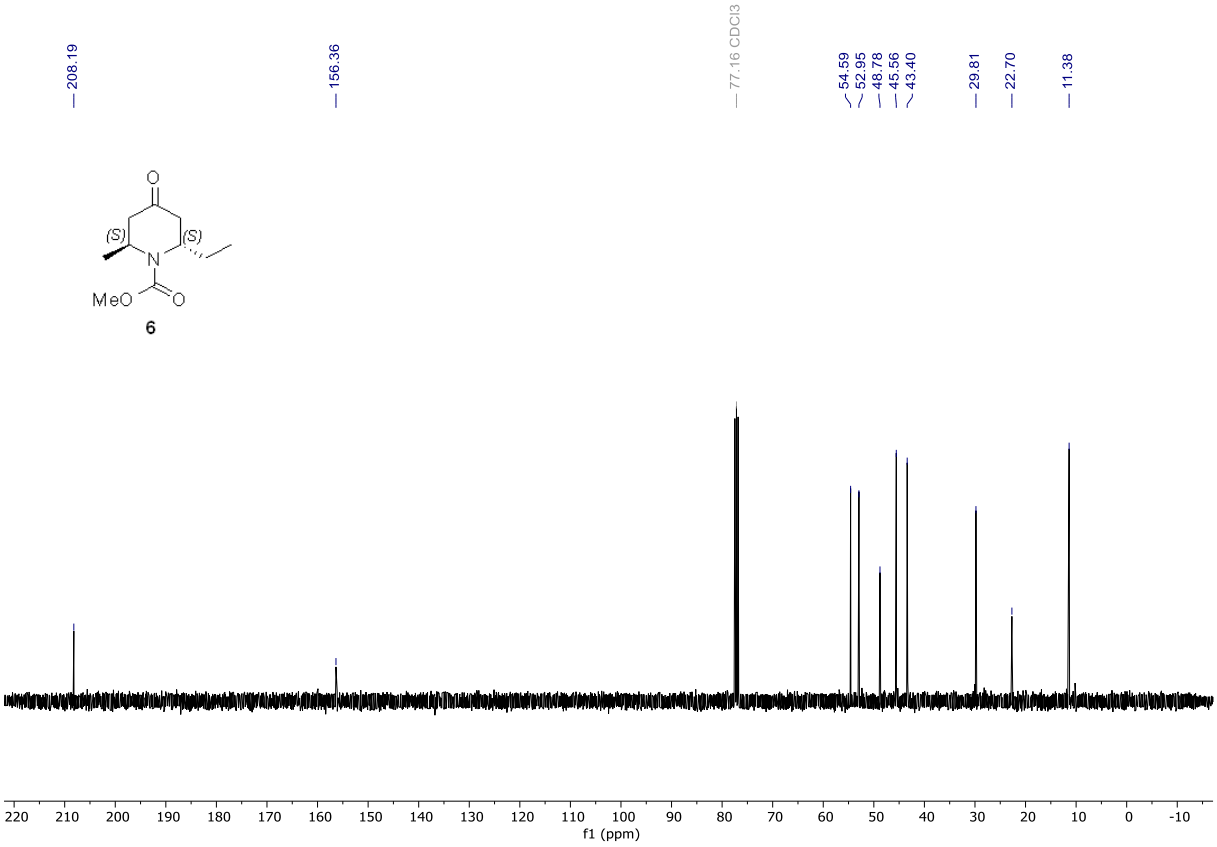

7.26 CDCl3
5.21
4.62
4.61
4.59
4.57
3.69
3.40
3.38
3.36
2.68
2.66
2.63
2.62
2.22
2.18
1.70
1.68
1.67
1.64
1.63
1.61
1.59
1.46
1.44
1.43
1.41
1.40
1.38
1.36
1.35
1.34
1.32
1.30
1.28
1.27
1.26
(S)
N
Cl
O
O
O
4i
1.00
1.01
2.90
1.89
1.03
0.68
3.21
3.05
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

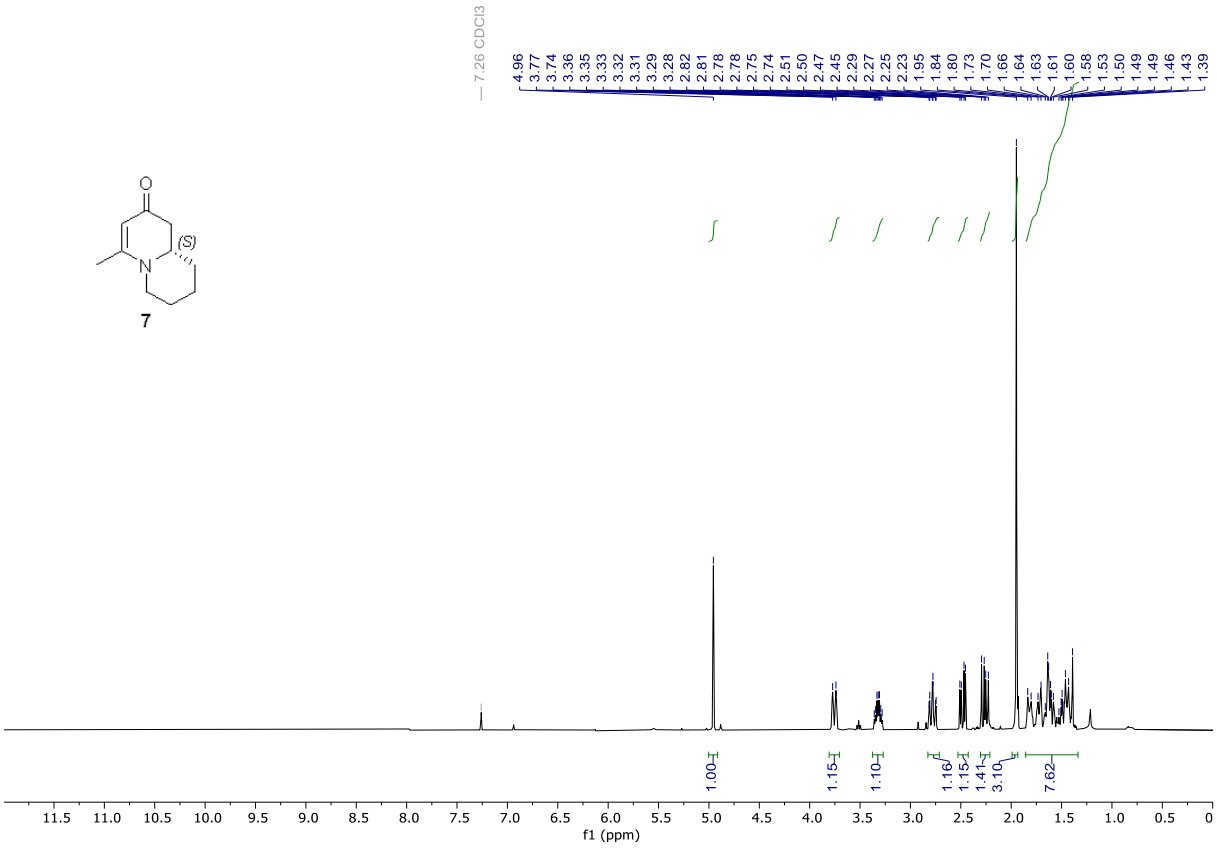

192.82
154.25
153.83
112.20
77.16 CDCl3
65.44 ?
55.51
53.38
44.40
40.47
31.82
29.11
23.54
23.12
(S)
N
Cl
O
O
O
4i
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

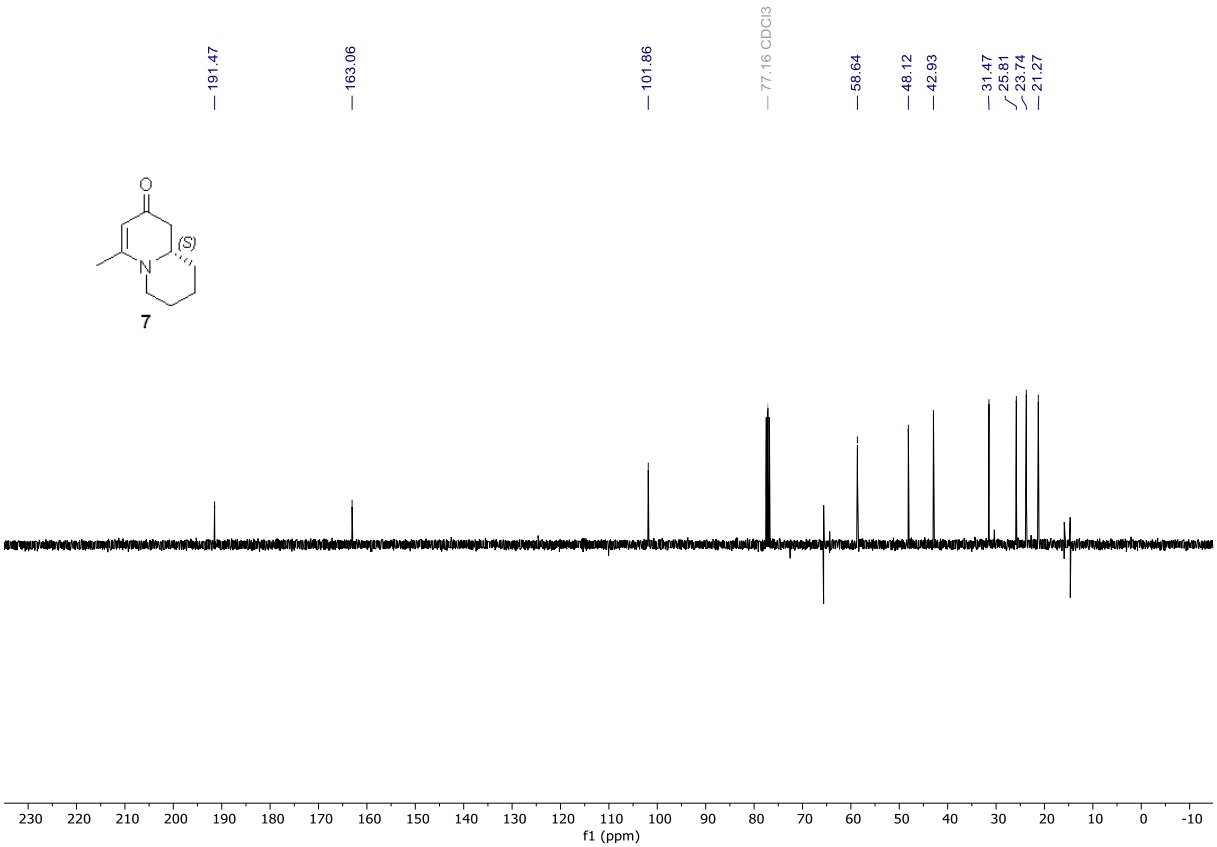

7.26 CDCl3
7.18
7.16
7.14
5.92
5.80
5.78
5.77
5.76
5.76
5.74
5.73
5.72
5.71
5.70
4.97
4.92
4.90
4.88
3.64
3.63
3.61
3.59
3.58
3.56
2.41
2.40
2.37
2.36
2.32
2.29
2.28
2.25
2.03
2.01
1.99
1.98
1.68
1.66
1.64
1.62
1.61
1.59
1.56
1.54
1.52
1.51
1.49
1.39
1.37
1.35
1.32
1.31
1.28
O
(S)
N
H
5
1.00
1.06
1.14
3.02
1.07
2.25
2.19
2.38
6.49
f1 (ppm)

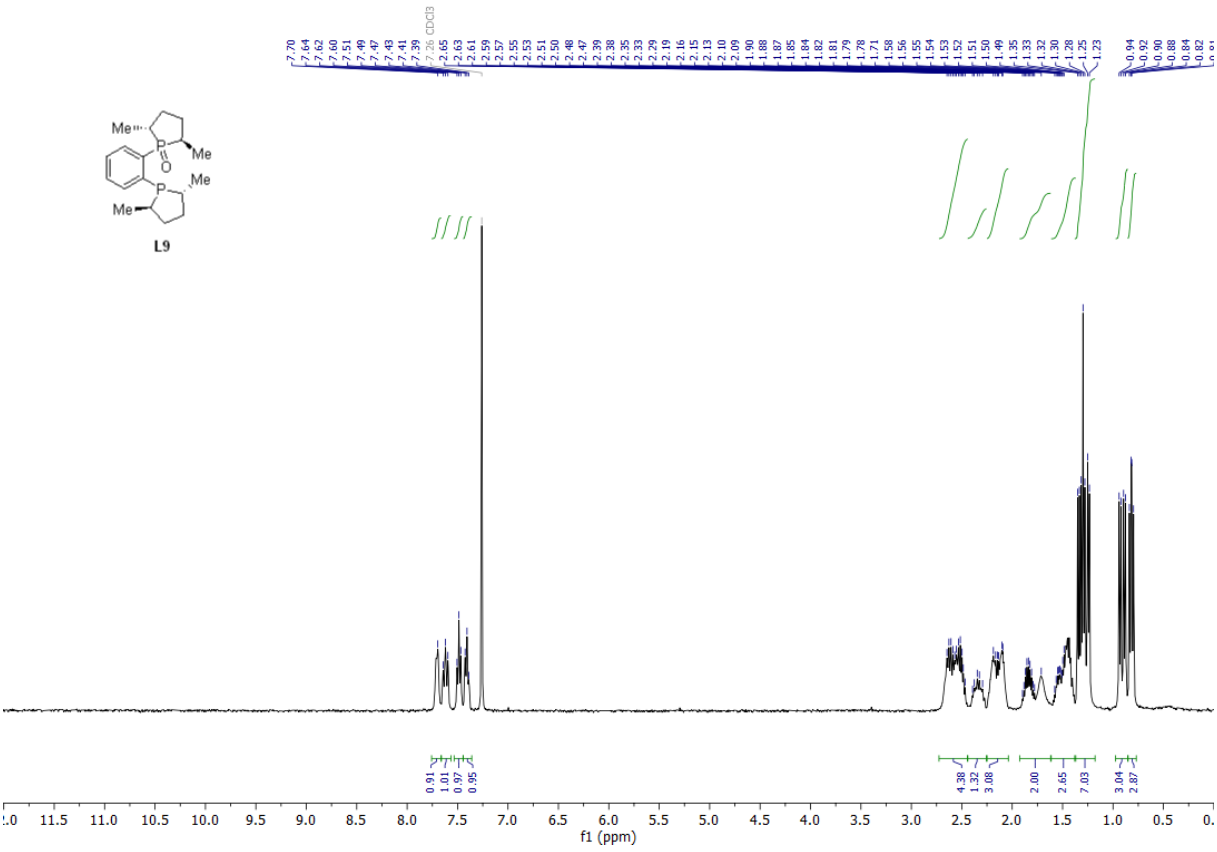

193.26
151.84
138.77
114.51
98.23
77.16 CDCl3
53.21
41.91
34.00
33.63
28.88
28.71
25.21
O
(S)
N
H
5
f1 (ppm)

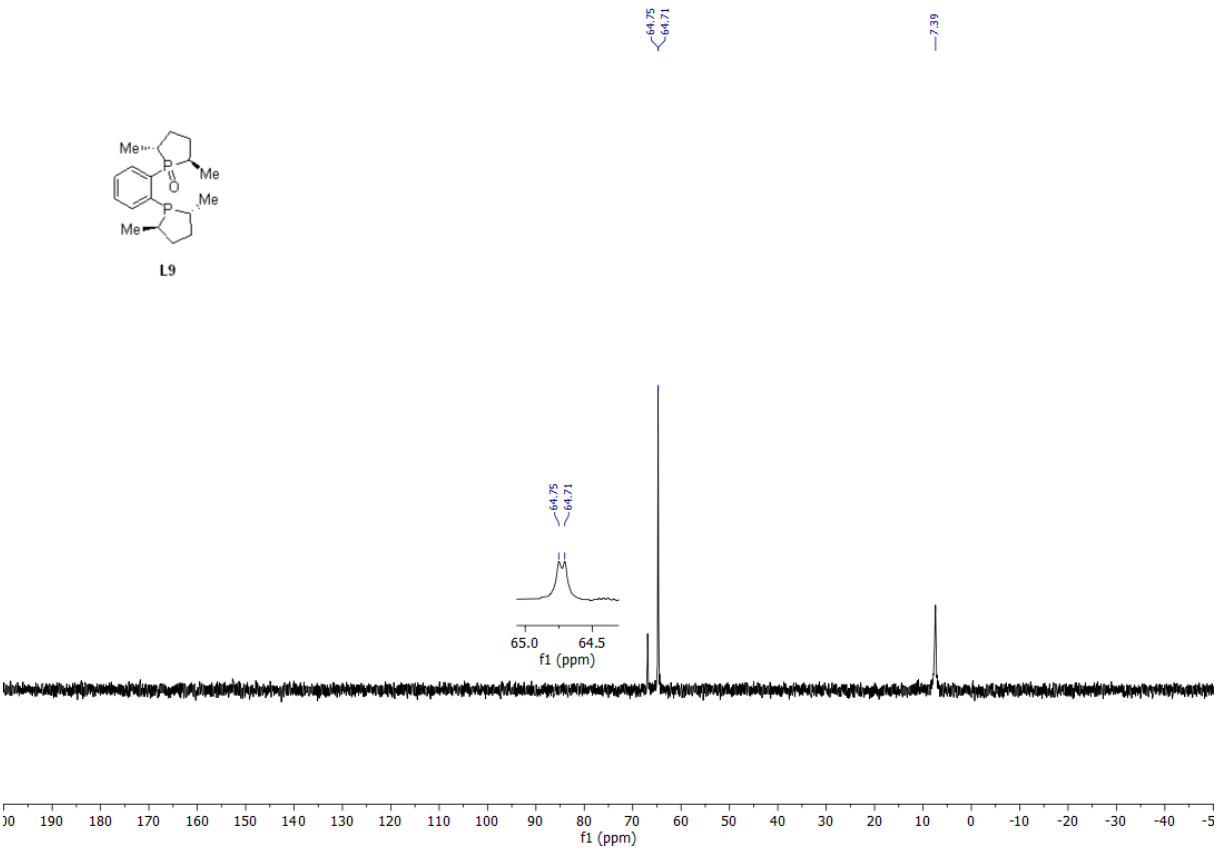

7.26 CDCl3
5.28 CH2Cl2
4.76
4.74
4.73
4.72
4.70
4.69
4.55
4.53
4.52
4.50
3.71
2.72
2.70
2.68
2.66
2.65
2.63
2.61
2.36
2.32
2.28
2.24
1.68
1.66
1.64
1.62
1.61
1.59
1.57
1.55
1.53
1.52
1.50
1.26
1.25
0.92
0.90
0.88
(S)
(S)
N
MeO
O
O
6
1.00
1.12
2.92
1.96
2.04
2.63
2.82
3.07
f1 (ppm)

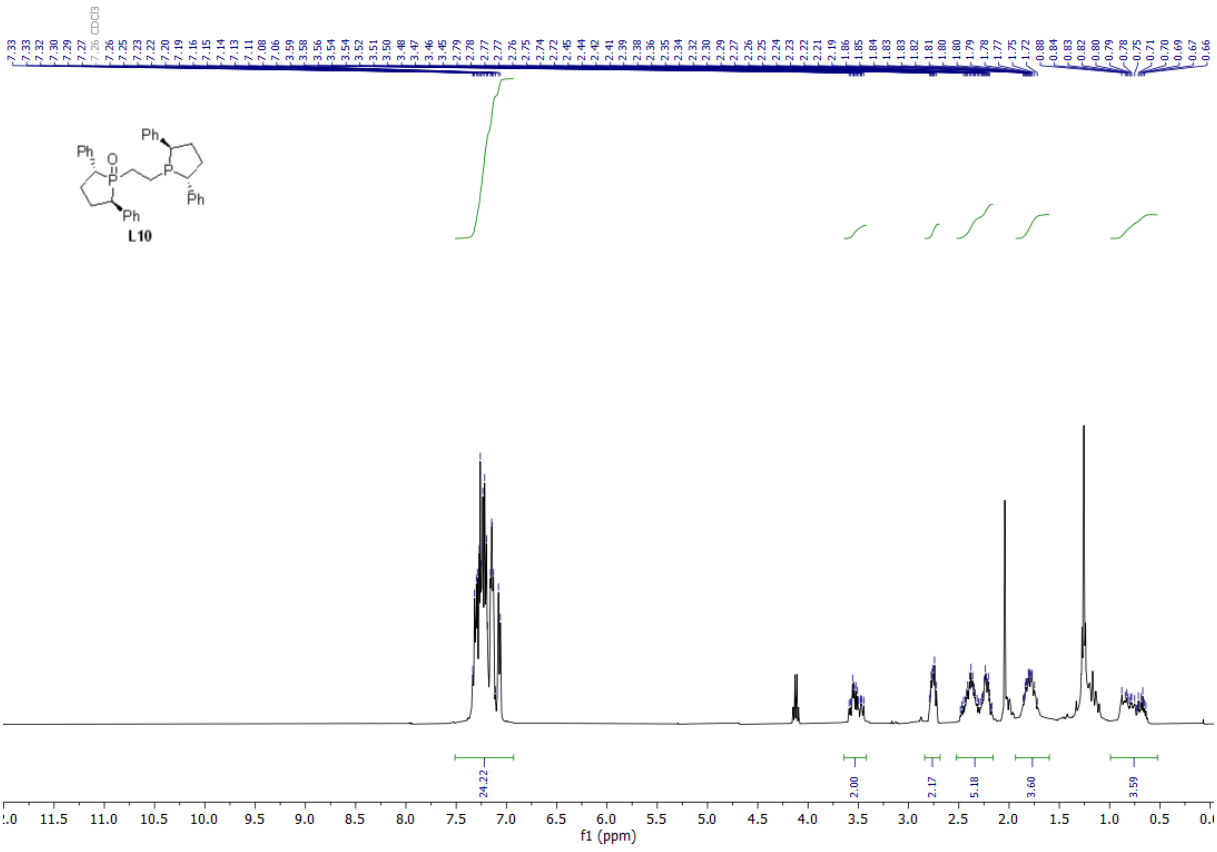

208.19
156.36
77.16 CDCl3
54.59
52.95
48.78
45.56
43.40
29.81
22.70
11.38
(S)
(S)
N
MeO
O
O
6
f1 (ppm)

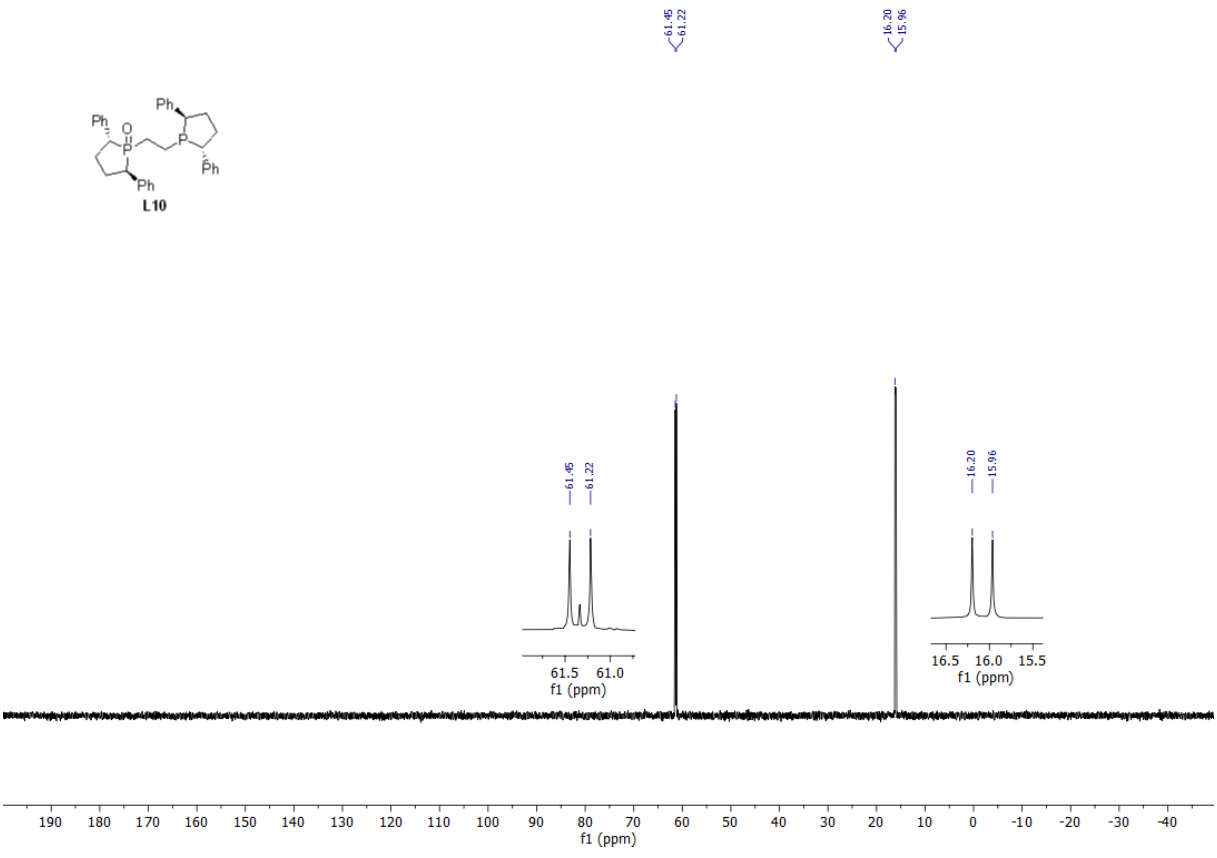

7.26 CDCl3
4.96
3.77
3.74
3.36
3.35
3.33
3.32
3.31
3.29
3.28
2.82
2.81
2.78
2.78
2.75
2.74
2.51
2.50
2.47
2.45
2.29
2.27
2.25
2.23
1.95
1.84
1.80
1.73
1.70
1.66
1.64
1.63
1.61
1.60
1.58
1.53
1.50
1.49
1.49
1.46
1.43
1.39
O
(S)
N
7
1.00
1.15
1.10
1.16
1.15
1.41
3.10
7.62
11.5 11.0 10.5 10.0 9.5 9.0 8.5 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
f1 (ppm)


191.47
163.06
101.86
77.16 CDCl3
58.64
48.12
42.93
31.47
25.81
23.74
21.27
O
(S)
N
7
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
L9
f1 (ppm)


Me
Me
Me
Me
L9
64.75
64.71
f1 (ppm)


L10
24.22
2.00
2.17
5.18
3.60
3.59
f1 (ppm)


61.45
61.22
16.20
15.96
L10
61.5 61.0
16.5 16.0 15.5
f1 (ppm)

# 9. Cartesian coordinates

**$Cu_2Br_2(SMe_2)_2$**

| | | | |
|---|---|---|---|
| Cu | -1.199139 | -0.105440 | -0.285010 |
| Br | 0.447988 | -1.894709 | -0.175796 |
| Br | -0.486227 | 2.249157 | -0.062850 |
| Cu | 1.221200 | 0.534911 | 0.038366 |
| S | -3.449474 | -0.536069 | -0.375572 |
| S | 3.519215 | 0.495138 | 0.247569 |
| C | -4.097355 | 0.757458 | 0.738414 |
| H | -5.173713 | 0.602713 | 0.918867 |
| H | -3.538446 | 0.753624 | 1.687746 |
| H | -3.931816 | 1.718798 | 0.227663 |
| C | -3.567935 | -2.010333 | 0.695645 |
| H | -3.052364 | -1.825862 | 1.651632 |
| H | -4.624313 | -2.274181 | 0.867952 |
| H | -3.055582 | -2.825347 | 0.160959 |
| C | 3.931153 | -0.548284 | -1.194691 |
| H | 3.804397 | 0.078548 | -2.091583 |
| H | 4.977417 | -0.887994 | -1.122364 |
| H | 3.237587 | -1.403445 | -1.238906 |
| C | 3.695499 | -0.739068 | 1.582879 |
| H | 4.743496 | -1.076112 | 1.642323 |
| H | 3.411899 | -0.239285 | 2.522646 |
| H | 3.016039 | -1.585536 | 1.392919 |

**L1**

| | | | |
|---|---|---|---|
| C | -0.160076 | -0.749123 | 0.876140 |
| H | -0.741031 | -1.031149 | -0.018416 |
| H | -0.781091 | -1.016531 | 1.749029 |
| C | 0.160095 | 0.749050 | 0.876033 |
| H | 0.781213 | 1.016578 | 1.748813 |
| H | 0.740928 | 1.030989 | -0.018628 |
| C | 2.072929 | -1.512054 | -0.801045 |

| | | | |
|---|---|---|---|
| C | 0.744373 | -3.566351 | 0.579742 |
| C | 1.604899 | -2.723124 | -1.637376 |
| H | 1.581269 | -0.601426 | -1.177727 |
| C | 1.464359 | -3.956793 | -0.731276 |
| H | 1.126274 | -4.193769 | 1.401167 |
| H | 0.626452 | -2.476563 | -2.081691 |
| H | 2.286848 | -2.919927 | -2.483273 |
| H | 0.938772 | -4.782103 | -1.243935 |
| H | 2.468476 | -4.337475 | -0.474842 |
| C | -2.072979 | 1.512003 | -0.801046 |
| C | -0.744322 | 3.566240 | 0.579742 |
| C | -1.604766 | 2.722986 | -1.637385 |
| H | -1.581464 | 0.601286 | -1.177710 |
| C | -1.464224 | 3.956682 | -0.731323 |
| H | -1.126256 | 4.193676 | 1.401136 |
| H | -0.626290 | 2.476334 | -2.081582 |
| H | -2.286590 | 2.919798 | -2.483381 |
| H | -0.938572 | 4.781948 | -1.243985 |
| H | -2.468337 | 4.337418 | -0.474954 |
| P | 1.397332 | -1.789422 | 0.974148 |
| P | -1.397314 | 1.789323 | 0.974138 |
| C | -3.562487 | 1.225657 | -0.761292 |
| C | -3.992192 | -0.074911 | -0.432406 |
| C | -4.544301 | 2.198902 | -1.008367 |
| C | -5.349492 | -0.393151 | -0.354986 |
| H | -3.250355 | -0.855076 | -0.231096 |
| C | -5.907582 | 1.883991 | -0.930951 |
| H | -4.255205 | 3.220547 | -1.267964 |
| C | -6.318033 | 0.587980 | -0.604240 |
| H | -5.649389 | -1.414817 | -0.099963 |
| H | -6.652362 | 2.661546 | -1.129422 |
| H | -7.383092 | 0.343104 | -0.544826 |
| C | 0.765926 | 3.673138 | 0.596838 |
| C | 1.427621 | 3.783293 | 1.835796 |
| C | 1.559174 | 3.616476 | -0.562688 |
| C | 2.821793 | 3.818010 | 1.917448 |

| | | | |
|---|---|---|---|
| H | 0.833611 | 3.833060 | 2.754883 |
| C | 2.956839 | 3.655585 | -0.486366 |
| H | 1.092917 | 3.538809 | -1.546976 |
| C | 3.596624 | 3.750285 | 0.752972 |
| H | 3.306097 | 3.899681 | 2.895673 |
| H | 3.548146 | 3.602785 | -1.405860 |
| H | 4.689067 | 3.775185 | 0.812102 |
| C | -0.765874 | -3.673281 | 0.596747 |
| C | -1.427644 | -3.783369 | 1.835670 |
| C | -1.559046 | -3.616734 | -0.562836 |
| C | -2.821821 | -3.818089 | 1.917240 |
| H | -0.833690 | -3.833065 | 2.754797 |
| C | -2.956715 | -3.655829 | -0.486597 |
| H | -1.092719 | -3.539172 | -1.547099 |
| C | -3.596577 | -3.750428 | 0.752709 |
| H | -3.306186 | -3.899694 | 2.895440 |
| H | -3.547970 | -3.603101 | -1.406126 |
| H | -4.689025 | -3.775306 | 0.811768 |
| C | 3.562400 | -1.225516 | -0.761328 |
| C | 3.991992 | 0.075221 | -0.432990 |
| C | 4.544310 | -2.198796 | -1.007918 |
| C | 5.349264 | 0.393608 | -0.355640 |
| H | 3.250097 | 0.855414 | -0.232023 |
| C | 5.907558 | -1.883744 | -0.930573 |
| H | 4.255298 | -3.220582 | -1.267063 |
| C | 6.317894 | -0.587552 | -0.604414 |
| H | 5.649043 | 1.415413 | -0.101037 |
| H | 6.652410 | -2.661330 | -1.128658 |
| H | 7.382932 | -0.342570 | -0.545053 |

**L1-CuBr**

| | | | |
|---|---|---|---|
| Cu | 0.220621 | 0.032117 | 1.243161 |
| C | 0.244897 | -0.056691 | -2.048363 |
| H | 0.539230 | 0.381161 | -3.016869 |
| H | 0.378895 | -1.147918 | -2.144519 |

| | | | |
|---|---|---|---|
| C | -1.222445 | 0.285031 | -1.727430 |
| H | -1.381149 | 1.377677 | -1.735298 |
| H | -1.897995 | -0.137613 | -2.490571 |
| C | 1.623971 | 2.336118 | -1.137476 |
| C | 3.139087 | -0.009830 | -1.201230 |
| C | 2.754548 | 2.299619 | -2.185352 |
| H | 0.680850 | 2.662123 | -1.609008 |
| C | 3.818752 | 1.275336 | -1.750858 |
| H | 3.621307 | -0.300332 | -0.255555 |
| H | 2.320982 | 1.995700 | -3.154201 |
| H | 3.193985 | 3.299103 | -2.346690 |
| H | 4.505844 | 1.036883 | -2.579774 |
| H | 4.436536 | 1.706261 | -0.946616 |
| C | -2.048463 | -2.158129 | -0.312911 |
| C | -3.495569 | 0.189861 | 0.271695 |
| C | -3.590783 | -2.270649 | -0.349556 |
| H | -1.635069 | -2.404789 | -1.304367 |
| C | -4.227838 | -1.155936 | 0.501809 |
| H | -3.475830 | 0.755779 | 1.215882 |
| H | -3.918140 | -2.170135 | -1.397532 |
| H | -3.923468 | -3.267526 | -0.012567 |
| H | -5.306322 | -1.054702 | 0.290791 |
| H | -4.141329 | -1.414174 | 1.570755 |
| P | 1.388702 | 0.517457 | -0.678192 |
| P | -1.687827 | -0.320407 | -0.020501 |
| C | -1.297533 | -2.980652 | 0.717618 |
| C | 0.048827 | -3.305414 | 0.467842 |
| C | -1.854798 | -3.367854 | 1.945517 |
| C | 0.817048 | -3.984827 | 1.415516 |
| H | 0.506638 | -3.017812 | -0.484183 |
| C | -1.088909 | -4.053431 | 2.896265 |
| H | -2.895534 | -3.129819 | 2.178572 |
| C | 0.250051 | -4.362674 | 2.638201 |
| H | 1.863258 | -4.221306 | 1.196547 |
| H | -1.543981 | -4.340442 | 3.849315 |
| H | 0.849233 | -4.890821 | 3.385945 |

| | | | |
|---|---|---|---|
| C | -4.026477 | 1.109852 | -0.805802 |
| C | -3.755308 | 2.488606 | -0.713521 |
| C | -4.736375 | 0.650161 | -1.927548 |
| C | -4.171127 | 3.376891 | -1.708687 |
| H | -3.204245 | 2.869144 | 0.153814 |
| C | -5.158863 | 1.538013 | -2.924096 |
| H | -4.969793 | -0.411507 | -2.035244 |
| C | -4.875772 | 2.903863 | -2.822413 |
| H | -3.947859 | 4.443981 | -1.611413 |
| H | -5.713475 | 1.155472 | -3.786712 |
| H | -5.205218 | 3.596312 | -3.603045 |
| C | 3.101672 | -1.229041 | -2.094816 |
| C | 3.059038 | -2.507159 | -1.508500 |
| C | 3.028810 | -1.138242 | -3.495056 |
| C | 2.933562 | -3.657886 | -2.292221 |
| H | 3.116371 | -2.597888 | -0.418720 |
| C | 2.911559 | -2.288353 | -4.283197 |
| H | 3.054598 | -0.160294 | -3.983791 |
| C | 2.857412 | -3.552868 | -3.686067 |
| H | 2.896707 | -4.640015 | -1.810493 |
| H | 2.857133 | -2.193500 | -5.372243 |
| H | 2.760572 | -4.451190 | -4.303294 |
| C | 1.834497 | 3.180909 | 0.109631 |
| C | 0.773015 | 3.297741 | 1.028556 |
| C | 3.035203 | 3.843092 | 0.405271 |
| C | 0.908245 | 4.034475 | 2.205406 |
| H | -0.176681 | 2.790567 | 0.822548 |
| C | 3.174856 | 4.588069 | 1.584527 |
| H | 3.881939 | 3.790567 | -0.282417 |
| C | 2.116048 | 4.684223 | 2.490815 |
| H | 0.070072 | 4.093737 | 2.906251 |
| H | 4.123724 | 5.092403 | 1.792769 |
| H | 2.229220 | 5.259173 | 3.414951 |
| Br | 0.635795 | -0.121565 | 3.546123 |

**EtMgBr·2($Et_2O$)**

| | | | |
|---|---|---|---|
| C | 1.612756 | 0.643570 | 2.261893 |
| H | 1.400422 | 0.002463 | 3.145844 |
| H | 2.589630 | 0.272646 | 1.878413 |
| C | 1.778851 | 2.101148 | 2.732178 |
| H | 2.567851 | 2.251243 | 3.503045 |
| H | 2.034729 | 2.777135 | 1.890987 |
| H | 0.838143 | 2.496894 | 3.163560 |
| Mg | 0.116652 | 0.321632 | 0.755580 |
| Br | -2.240637 | 1.191963 | 0.472938 |
| O | 1.015676 | 0.640204 | -1.103090 |
| O | -0.182589 | -1.694263 | 0.262796 |
| C | 2.290313 | 1.309435 | -1.196660 |
| H | 2.276434 | 1.980121 | -2.072533 |
| H | 2.364889 | 1.933881 | -0.293470 |
| C | 0.390126 | 0.269401 | -2.348606 |
| H | 1.165117 | -0.122300 | -3.030812 |
| H | -0.285187 | -0.560899 | -2.092789 |
| C | 3.443552 | 0.321446 | -1.265778 |
| H | 3.356872 | -0.342922 | -2.143264 |
| H | 4.399588 | 0.868680 | -1.346216 |
| H | 3.474462 | -0.298698 | -0.353969 |
| C | -0.379572 | 1.423492 | -2.969563 |
| H | -0.860682 | 1.086603 | -3.905282 |
| H | -1.160751 | 1.771166 | -2.272873 |
| H | 0.284568 | 2.270440 | -3.215468 |
| C | 0.943485 | -2.517194 | -0.101960 |
| H | 0.590184 | -3.334271 | -0.754334 |
| H | 1.600414 | -1.869277 | -0.701609 |
| C | -1.439753 | -2.381403 | 0.444341 |
| H | -1.239201 | -3.374146 | 0.883324 |
| H | -2.002101 | -1.786851 | 1.179651 |
| C | 1.670156 | -3.044193 | 1.124680 |
| H | 1.012344 | -3.686762 | 1.735644 |
| H | 2.545218 | -3.643183 | 0.815529 |

| | | | |
|---|---|---|---|
| H | 2.018779 | -2.203617 | 1.749107 |
| C | -2.207723 | -2.479562 | -0.862620 |
| H | -2.446946 | -1.467671 | -1.230615 |
| H | -1.626638 | -3.015695 | -1.633618 |
| H | -3.153509 | -3.027635 | -0.703109 |

**L1-CuEt**

| | | | |
|---|---|---|---|
| Cu | 0.125696 | 1.237373 | 1.417845 |
| C | 0.328304 | -0.881121 | -1.300129 |
| H | 0.677505 | -1.056962 | -2.332139 |
| H | 0.433243 | -1.833538 | -0.752692 |
| C | -1.139701 | -0.415306 | -1.286800 |
| H | -1.285489 | 0.437571 | -1.974102 |
| H | -1.813356 | -1.217320 | -1.632899 |
| C | 1.609246 | 1.720738 | -1.739234 |
| C | 3.200694 | -0.279669 | -0.562157 |
| C | 3.018814 | 1.512481 | -2.337503 |
| H | 0.846103 | 1.526009 | -2.510365 |
| C | 3.942483 | 0.866728 | -1.288513 |
| H | 3.556065 | -0.339182 | 0.478833 |
| H | 2.926965 | 0.845469 | -3.210279 |
| H | 3.440184 | 2.461147 | -2.713037 |
| H | 4.882022 | 0.505484 | -1.741784 |
| H | 4.227928 | 1.621772 | -0.535712 |
| C | -2.107077 | -1.430002 | 1.300547 |
| C | -3.440907 | 0.701865 | 0.360242 |
| C | -3.187838 | -0.964646 | 2.312465 |
| H | -2.589240 | -2.057172 | 0.532158 |
| C | -3.909182 | 0.318526 | 1.790227 |
| H | -3.442826 | 1.797607 | 0.248906 |
| H | -3.899579 | -1.790159 | 2.484418 |
| H | -2.715951 | -0.753661 | 3.285303 |
| H | -5.005626 | 0.203419 | 1.805972 |
| H | -3.672319 | 1.161011 | 2.459539 |
| P | 1.411435 | 0.364845 | -0.418651 |

| | | | |
|---|---|---|---|
| P | -1.636091 | 0.158931 | 0.421458 |
| C | -0.931856 | -2.193495 | 1.868725 |
| C | -0.616073 | -3.473501 | 1.384785 |
| C | -0.105564 | -1.634812 | 2.862134 |
| C | 0.489247 | -4.178594 | 1.875801 |
| H | -1.242914 | -3.923954 | 0.608050 |
| C | 1.004920 | -2.331067 | 3.346442 |
| H | -0.320973 | -0.633601 | 3.248268 |
| C | 1.306199 | -3.608854 | 2.857379 |
| H | 0.714243 | -5.175062 | 1.483385 |
| H | 1.639822 | -1.869210 | 4.108983 |
| H | 2.176668 | -4.153804 | 3.235273 |
| C | -4.206293 | 0.097714 | -0.794155 |
| C | -4.200266 | 0.754633 | -2.039718 |
| C | -4.894609 | -1.124660 | -0.696879 |
| C | -4.844848 | 0.206715 | -3.151213 |
| H | -3.677673 | 1.712792 | -2.136218 |
| C | -5.540996 | -1.677263 | -1.809228 |
| H | -4.939818 | -1.656674 | 0.256556 |
| C | -5.516806 | -1.017298 | -3.041833 |
| H | -4.825752 | 0.739615 | -4.107129 |
| H | -6.070373 | -2.629807 | -1.706847 |
| H | -6.023369 | -1.449269 | -3.910295 |
| C | 3.290425 | -1.667506 | -1.158153 |
| C | 3.009569 | -2.772572 | -0.331775 |
| C | 3.597284 | -1.914957 | -2.506761 |
| C | 3.025860 | -4.075582 | -0.833225 |
| H | 2.755786 | -2.606375 | 0.720013 |
| C | 3.619902 | -3.221123 | -3.011696 |
| H | 3.827931 | -1.088167 | -3.182124 |
| C | 3.331416 | -4.307732 | -2.180053 |
| H | 2.796823 | -4.912725 | -0.166562 |
| H | 3.865028 | -3.386670 | -4.065679 |
| H | 3.346726 | -5.327496 | -2.576895 |
| C | 1.299875 | 3.069666 | -1.115674 |
| C | -0.046168 | 3.459676 | -0.978611 |

| | | | |
|---|---|---|---|
| C | 2.288038 | 3.923180 | -0.601275 |
| C | -0.394501 | 4.653724 | -0.343963 |
| H | -0.837252 | 2.811969 | -1.371650 |
| C | 1.943403 | 5.123379 | 0.032741 |
| H | 3.344338 | 3.656520 | -0.683886 |
| C | 0.602040 | 5.493590 | 0.167303 |
| H | -1.449501 | 4.928561 | -0.247231 |
| H | 2.733250 | 5.769465 | 0.428656 |
| H | 0.333818 | 6.428587 | 0.668469 |
| C | 0.936130 | 2.207924 | 2.963598 |
| H | 0.455437 | 1.959481 | 3.935584 |
| H | 0.816248 | 3.308083 | 2.855265 |
| C | 2.438050 | 1.878271 | 3.049889 |
| H | 2.978660 | 2.375362 | 3.889666 |
| H | 2.605543 | 0.788259 | 3.165673 |
| H | 2.961068 | 2.167894 | 2.116549 |

**I**

| | | | |
|---|---|---|---|
| C | -1.625689 | -0.272228 | -0.000004 |
| C | -0.406212 | -0.952284 | -0.000002 |
| C | 0.797478 | -0.224105 | 0.000001 |
| C | 0.721142 | 1.177260 | 0.000003 |
| C | -0.553710 | 1.756244 | 0.000001 |
| N | -1.698296 | 1.074729 | -0.000003 |
| C | -2.938848 | -1.015581 | 0.000002 |
| H | -0.362460 | -2.044129 | -0.000003 |
| H | 1.606897 | 1.813752 | 0.000004 |
| H | -0.637562 | 2.851472 | 0.000001 |
| O | 1.938434 | -0.938895 | 0.000001 |
| C | 3.185348 | -0.260678 | -0.000001 |
| H | 3.960040 | -1.041950 | -0.000003 |
| H | 3.302033 | 0.368741 | -0.902153 |
| H | 3.302036 | 0.368740 | 0.902152 |
| H | -3.535081 | -0.735820 | -0.887586 |
| H | -2.797290 | -2.108695 | -0.000005 |

| | | | |
|---|---|---|---|
| H | -3.535058 | -0.735830 | 0.887610 |

**II**

| | | | |
|---|---|---|---|
| C | 1.132169 | 0.122939 | 0.161824 |
| C | -0.087357 | -0.533269 | 0.173825 |
| C | -1.194650 | 1.588314 | -0.000214 |
| C | -0.007350 | 2.261967 | -0.022292 |
| H | -2.153233 | 2.100419 | -0.054700 |
| H | 0.011382 | 3.350220 | -0.097001 |
| Cl | 3.591542 | -2.039492 | -0.340489 |
| O | 2.323062 | 2.212701 | 0.021845 |
| C | 3.591769 | 1.542193 | 0.154669 |
| H | 3.681650 | 1.113451 | 1.166792 |
| H | 3.698962 | 0.726452 | -0.579397 |
| H | 4.350046 | 2.322155 | 0.001029 |
| H | 2.039391 | -0.509862 | 0.172231 |
| C | -0.115572 | -2.032952 | 0.219161 |
| H | 0.911075 | -2.399838 | 0.050074 |
| H | -0.481010 | -2.388072 | 1.196686 |
| H | -0.791347 | -2.449022 | -0.545987 |
| C | -2.561012 | -0.416996 | 0.171591 |
| N | -1.249745 | 0.217210 | 0.101864 |
| O | -3.443351 | 0.306356 | -0.487432 |
| C | -4.810136 | -0.154628 | -0.454603 |
| H | -4.874504 | -1.159105 | -0.901364 |
| H | -5.171367 | -0.183124 | 0.585746 |
| H | -5.377848 | 0.574649 | -1.046877 |
| O | -2.761371 | -1.440185 | 0.759387 |
| C | 1.202487 | 1.526032 | 0.058978 |

**III**

| | | | |
|---|---|---|---|
| Cu | -0.128540 | -0.650644 | -0.374849 |
| C | -2.738794 | -0.672540 | 1.766665 |
| H | -3.214911 | -1.191269 | 2.615629 |
| H | -2.968688 | 0.403758 | 1.873901 |
| C | -3.272090 | -1.214096 | 0.432135 |

| | | | |
|---|---|---|---|
| H | -3.063281 | -2.295209 | 0.351233 |
| H | -4.367402 | -1.091858 | 0.364316 |
| C | -0.558034 | -2.451698 | 2.700054 |
| C | -0.481944 | 0.092871 | 3.447490 |
| C | -1.131697 | -2.279541 | 4.126149 |
| H | -1.105713 | -3.229162 | 2.142113 |
| C | -1.085941 | -0.785732 | 4.569773 |
| H | 0.619322 | 0.007943 | 3.509069 |
| H | -2.175738 | -2.630547 | 4.127396 |
| H | -0.598003 | -2.930939 | 4.837489 |
| H | -2.107136 | -0.434621 | 4.793094 |
| H | -0.504476 | -0.662462 | 5.499720 |
| C | -3.572829 | 1.070897 | -1.395542 |
| C | -3.029181 | -1.406496 | -2.499159 |
| C | -4.104837 | 0.782158 | -2.822025 |
| H | -4.417281 | 0.965053 | -0.694016 |
| C | -4.336725 | -0.727258 | -2.935581 |
| H | -2.265214 | -1.204867 | -3.271606 |
| H | -5.023740 | 1.363785 | -3.013221 |
| H | -3.356039 | 1.104390 | -3.568548 |
| H | -5.165647 | -1.016671 | -2.264488 |
| H | -4.624583 | -1.028047 | -3.959070 |
| P | -0.872046 | -0.801431 | 1.837765 |
| P | -2.409307 | -0.391074 | -1.014670 |
| C | -2.983612 | 2.452413 | -1.226259 |
| C | -3.640183 | 3.404629 | -0.427485 |
| C | -1.810085 | 2.841021 | -1.894857 |
| C | -3.151571 | 4.710719 | -0.313412 |
| H | -4.551038 | 3.118849 | 0.109908 |
| C | -1.317741 | 4.144696 | -1.786747 |
| H | -1.252192 | 2.120432 | -2.501118 |
| C | -1.990909 | 5.086302 | -0.998770 |
| H | -3.678168 | 5.434136 | 0.317517 |
| H | -0.394429 | 4.396754 | -2.316965 |
| H | -1.605166 | 6.107175 | -0.909656 |
| C | -3.040799 | -2.894294 | -2.228867 |

| | | | |
|---|---|---|---|
| C | -1.824879 | -3.542244 | -1.932598 |
| C | -4.218151 | -3.658253 | -2.217718 |
| C | -1.790079 | -4.903034 | -1.622142 |
| H | -0.902764 | -2.955697 | -1.908606 |
| C | -4.184128 | -5.026649 | -1.914913 |
| H | -5.179355 | -3.192975 | -2.449004 |
| C | -2.972857 | -5.654992 | -1.611831 |
| H | -0.832333 | -5.378155 | -1.385432 |
| H | -5.115563 | -5.602072 | -1.915926 |
| H | -2.948735 | -6.722406 | -1.370805 |
| C | -0.824727 | 1.570084 | 3.467106 |
| C | -1.257390 | 2.214198 | 4.639254 |
| C | -0.665069 | 2.349185 | 2.305856 |
| C | -1.514441 | 3.591300 | 4.649530 |
| H | -1.387439 | 1.645906 | 5.563687 |
| C | -0.915804 | 3.723232 | 2.313796 |
| H | -0.351341 | 1.877605 | 1.372503 |
| C | -1.342879 | 4.352733 | 3.488776 |
| H | -1.849769 | 4.069739 | 5.575509 |
| H | -0.787714 | 4.292186 | 1.389371 |
| H | -1.546353 | 5.428210 | 3.497720 |
| C | 0.930240 | -2.740596 | 2.601562 |
| C | 1.453275 | -3.212043 | 1.382072 |
| C | 1.828236 | -2.488177 | 3.652203 |
| C | 2.822830 | -3.426477 | 1.218565 |
| H | 0.775692 | -3.383866 | 0.542637 |
| C | 3.203494 | -2.706242 | 3.493507 |
| H | 1.465261 | -2.111980 | 4.612071 |
| C | 3.706399 | -3.176790 | 2.276943 |
| H | 3.201925 | -3.779303 | 0.254864 |
| H | 3.881805 | -2.504824 | 4.328600 |
| H | 4.780521 | -3.347380 | 2.152102 |
| C | 1.213649 | -1.519396 | -1.611648 |
| H | 1.109275 | -2.625557 | -1.647455 |
| H | 2.248006 | -1.366180 | -1.242496 |
| C | 1.093862 | -0.964504 | -3.040128 |

| | | | |
|---|---|---|---|
| H | 1.857576 | -1.350840 | -3.755961 |
| H | 0.104329 | -1.205504 | -3.478485 |
| H | 1.174733 | 0.139239 | -3.066637 |
| C | 3.492736 | 0.455551 | 0.270178 |
| C | 3.612234 | 1.097258 | -2.030455 |
| C | 4.543829 | -0.414368 | 0.071099 |
| C | 4.650827 | 0.222257 | -2.265869 |
| C | 5.138516 | -0.561661 | -1.200056 |
| H | 4.893689 | -1.035691 | 0.895172 |
| H | 5.055142 | 0.158563 | -3.275361 |
| O | 6.116931 | -1.447763 | -1.293481 |
| C | 6.754820 | -1.689698 | -2.550995 |
| H | 7.251585 | -0.775364 | -2.919480 |
| H | 7.506179 | -2.468123 | -2.359682 |
| H | 6.024382 | -2.051430 | -3.295351 |
| C | 2.761591 | 0.553057 | 1.570287 |
| H | 2.613458 | 1.597652 | 1.892085 |
| H | 1.768323 | 0.088844 | 1.435130 |
| H | 3.297649 | 0.000178 | 2.354074 |
| C | 1.889980 | 2.107017 | -0.568390 |
| N | 3.061684 | 1.212426 | -0.795743 |
| O | 0.793379 | 1.635490 | -0.492671 |
| O | 2.179347 | 3.345983 | -0.264062 |
| C | 3.416353 | 3.989426 | -0.632765 |
| H | 4.285083 | 3.409348 | -0.280323 |
| H | 3.416536 | 4.107014 | -1.728602 |
| H | 3.391261 | 4.966244 | -0.131441 |
| Cl | 1.748509 | 3.226923 | -3.569830 |
| H | 3.159798 | 1.746552 | -2.802693 |

**TS-(III-V)-*R***

| | | | |
|---|---|---|---|
| Cu | 0.150913 | 0.290515 | -0.429009 |
| C | 1.931191 | 0.412267 | 2.346884 |
| H | 2.068621 | 0.743153 | 3.390063 |
| H | 2.291271 | -0.630195 | 2.288503 |
| C | 2.720954 | 1.319057 | 1.388677 |

| | | | |
|---|---|---|---|
| H | 2.373834 | 2.362117 | 1.487759 |
| H | 3.795580 | 1.316432 | 1.641175 |
| C | -0.596856 | 1.874776 | 2.756208 |
| C | -0.619980 | -0.761411 | 3.193603 |
| C | -0.498752 | 1.558451 | 4.269207 |
| H | 0.039259 | 2.736161 | 2.493914 |
| C | -0.534265 | 0.023379 | 4.530118 |
| H | -1.683959 | -0.801207 | 2.892896 |
| H | 0.447727 | 1.972722 | 4.651443 |
| H | -1.299968 | 2.080191 | 4.817998 |
| H | 0.376131 | -0.286859 | 5.069389 |
| H | -1.385581 | -0.247195 | 5.177372 |
| C | 3.928251 | -0.265247 | -0.828008 |
| C | 3.096657 | 2.311207 | -1.422841 |
| C | 4.539271 | 0.409596 | -2.078391 |
| H | 4.644498 | -0.145417 | 0.002666 |
| C | 4.532441 | 1.921838 | -1.830309 |
| H | 2.466819 | 2.268549 | -2.326819 |
| H | 5.556119 | 0.021982 | -2.263970 |
| H | 3.932796 | 0.169621 | -2.970664 |
| H | 5.246482 | 2.155061 | -1.021591 |
| H | 4.852078 | 2.490535 | -2.721426 |
| P | 0.115801 | 0.365034 | 1.887692 |
| P | 2.449630 | 0.837315 | -0.400256 |
| C | 3.592614 | -1.731845 | -0.974064 |
| C | 4.158108 | -2.677027 | -0.100476 |
| C | 2.711260 | -2.187111 | -1.968635 |
| C | 3.864228 | -4.039534 | -0.226032 |
| H | 4.839013 | -2.340645 | 0.689124 |
| C | 2.415221 | -3.545711 | -2.098743 |
| H | 2.201084 | -1.487870 | -2.637587 |
| C | 2.994009 | -4.478729 | -1.230964 |
| H | 4.313656 | -4.757892 | 0.467249 |
| H | 1.698354 | -3.841436 | -2.869918 |
| H | 2.757749 | -5.543571 | -1.327116 |
| C | 2.872987 | 3.650431 | -0.760822 |

| | | | |
|---|---|---|---|
| C | 1.656246 | 4.328799 | -0.961951 |
| C | 3.806428 | 4.221813 | 0.121993 |
| C | 1.373251 | 5.524968 | -0.295588 |
| H | 0.915319 | 3.908127 | -1.646988 |
| C | 3.531204 | 5.423637 | 0.783574 |
| H | 4.759081 | 3.720865 | 0.312215 |
| C | 2.311247 | 6.079001 | 0.583246 |
| H | 0.416144 | 6.027234 | -0.468277 |
| H | 4.275910 | 5.847086 | 1.464966 |
| H | 2.094677 | 7.016039 | 1.105339 |
| C | -0.096540 | -2.187245 | 3.225985 |
| C | -0.225563 | -2.968939 | 4.388816 |
| C | 0.485710 | -2.784307 | 2.093482 |
| C | 0.206349 | -4.299656 | 4.413715 |
| H | -0.676534 | -2.541874 | 5.288477 |
| C | 0.916724 | -4.114684 | 2.113593 |
| H | 0.604865 | -2.212925 | 1.171236 |
| C | 0.778628 | -4.880052 | 3.275691 |
| H | 0.092688 | -4.886405 | 5.330959 |
| H | 1.366934 | -4.538912 | 1.211381 |
| H | 1.116689 | -5.920766 | 3.296987 |
| C | -1.990840 | 2.125011 | 2.209597 |
| C | -2.142067 | 2.874327 | 1.029116 |
| C | -3.145889 | 1.588907 | 2.804616 |
| C | -3.399484 | 3.074381 | 0.456181 |
| H | -1.255549 | 3.295846 | 0.546251 |
| C | -4.408463 | 1.788979 | 2.232555 |
| H | -3.072364 | 1.005189 | 3.726056 |
| C | -4.541297 | 2.529980 | 1.055090 |
| H | -3.486744 | 3.652249 | -0.469054 |
| H | -5.292211 | 1.355874 | 2.711666 |
| H | -5.523283 | 2.666989 | 0.594665 |
| C | -0.833647 | 1.570340 | -1.874822 |
| H | -0.142610 | 2.086982 | -1.161506 |
| H | -1.793296 | 2.081805 | -1.726448 |
| C | -0.273307 | 1.734564 | -3.282601 |

| | | | |
|---|---|---|---|
| H | -0.975491 | 1.382142 | -4.061630 |
| H | -0.025705 | 2.787069 | -3.540365 |
| H | 0.648629 | 1.138754 | -3.410682 |
| C | -3.239820 | -1.372159 | -0.422652 |
| C | -2.136366 | -0.345098 | -2.332163 |
| C | -4.279809 | -0.500061 | -0.557922 |
| C | -3.323197 | 0.396856 | -2.600637 |
| C | -4.367489 | 0.357987 | -1.704244 |
| H | -5.064536 | -0.455352 | 0.196500 |
| H | -3.321520 | 1.055681 | -3.468212 |
| O | -5.501193 | 1.074083 | -1.786001 |
| C | -5.644615 | 2.019068 | -2.836180 |
| H | -5.633140 | 1.523218 | -3.824396 |
| H | -6.618751 | 2.505748 | -2.681836 |
| H | -4.841242 | 2.778401 | -2.797620 |
| C | -3.111356 | -2.317226 | 0.738859 |
| H | -3.311589 | -3.362271 | 0.446223 |
| H | -2.097653 | -2.290142 | 1.171264 |
| H | -3.830288 | -2.036434 | 1.522748 |
| C | -1.126516 | -2.263976 | -1.249451 |
| N | -2.252889 | -1.379793 | -1.408542 |
| O | -0.055740 | -1.824783 | -0.899529 |
| O | -1.367235 | -3.551331 | -1.332039 |
| C | -2.394981 | -4.062547 | -2.208454 |
| H | -3.390332 | -3.682480 | -1.926795 |
| H | -2.129819 | -3.769078 | -3.237603 |
| H | -2.361538 | -5.153313 | -2.081795 |
| Cl | -0.247095 | -2.296741 | -4.250397 |
| H | -1.423327 | -0.582683 | -3.126503 |

**TS-(III-V)-*S***

| | | | |
|---|---|---|---|
| Cu | 0.247451 | 0.240007 | -0.127671 |
| C | 1.550665 | -2.555305 | 1.033289 |
| H | 2.069936 | -3.108874 | 1.834841 |
| H | 0.801557 | -3.242225 | 0.600082 |
| C | 2.547749 | -2.093491 | -0.039714 |

| | | | |
|---|---|---|---|
| H | 3.280211 | -1.387596 | 0.390169 |
| H | 3.118379 | -2.948983 | -0.441192 |
| C | 1.806902 | -0.441302 | 3.045090 |
| C | -0.540633 | -1.881439 | 2.997037 |
| C | 1.170140 | -0.825778 | 4.407866 |
| H | 2.739299 | -1.015595 | 2.915660 |
| C | 0.358839 | -2.117042 | 4.223706 |
| H | -1.227221 | -1.047642 | 3.231404 |
| H | 1.950266 | -0.929153 | 5.182153 |
| H | 0.488431 | -0.023784 | 4.737707 |
| H | 1.039438 | -2.974920 | 4.072850 |
| H | -0.251552 | -2.341763 | 5.117047 |
| C | 1.060858 | -2.619580 | -2.502830 |
| C | 3.044647 | -0.698691 | -2.595672 |
| C | 1.945213 | -2.561011 | -3.777340 |
| H | 1.312355 | -3.535706 | -1.943621 |
| C | 3.315844 | -1.980573 | -3.405728 |
| H | 2.556277 | 0.028545 | -3.268593 |
| H | 2.029519 | -3.563349 | -4.231648 |
| H | 1.474933 | -1.908296 | -4.532471 |
| H | 3.882477 | -2.712430 | -2.803565 |
| H | 3.922934 | -1.760927 | -4.302278 |
| P | 0.606012 | -1.098442 | 1.730729 |
| P | 1.653559 | -1.183100 | -1.406812 |
| C | -0.435468 | -2.591689 | -2.724410 |
| C | -1.269066 | -3.491177 | -2.041404 |
| C | -1.036614 | -1.641570 | -3.568762 |
| C | -2.657758 | -3.454567 | -2.202515 |
| H | -0.828957 | -4.225642 | -1.358171 |
| C | -2.422666 | -1.609759 | -3.741914 |
| H | -0.418159 | -0.905949 | -4.092872 |
| C | -3.241464 | -2.516158 | -3.057908 |
| H | -3.281625 | -4.160020 | -1.647277 |
| H | -2.866760 | -0.873139 | -4.418725 |
| H | -4.327822 | -2.484044 | -3.185788 |
| C | 4.201294 | -0.004725 | -1.916362 |

| | | | |
|---|---|---|---|
| C | 4.193411 | 1.397006 | -1.794327 |
| C | 5.270482 | -0.712027 | -1.338492 |
| C | 5.207671 | 2.069581 | -1.107526 |
| H | 3.375044 | 1.968580 | -2.241713 |
| C | 6.289501 | -0.041621 | -0.652722 |
| H | 5.310500 | -1.801520 | -1.413265 |
| C | 6.260866 | 1.351988 | -0.529549 |
| H | 5.171322 | 3.159699 | -1.021003 |
| H | 7.110569 | -0.614868 | -0.210763 |
| H | 7.055149 | 1.875362 | 0.011505 |
| C | -1.362026 | -3.016702 | 2.440788 |
| C | -0.928277 | -4.353610 | 2.450598 |
| C | -2.597752 | -2.718786 | 1.835132 |
| C | -1.703469 | -5.363713 | 1.867559 |
| H | 0.027957 | -4.615060 | 2.912290 |
| C | -3.370797 | -3.724965 | 1.252608 |
| H | -2.941931 | -1.680760 | 1.830970 |
| C | -2.927029 | -5.053347 | 1.263237 |
| H | -1.347695 | -6.399071 | 1.886758 |
| H | -4.322811 | -3.465943 | 0.778705 |
| H | -3.530993 | -5.842360 | 0.803645 |
| C | 2.109242 | 1.024470 | 2.829953 |
| C | 3.368884 | 1.426240 | 2.357662 |
| C | 1.121851 | 2.009849 | 3.023934 |
| C | 3.650241 | 2.773923 | 2.103999 |
| H | 4.142237 | 0.672859 | 2.171416 |
| C | 1.407164 | 3.356704 | 2.785234 |
| H | 0.108953 | 1.724630 | 3.330591 |
| C | 2.671572 | 3.747290 | 2.325858 |
| H | 4.637423 | 3.057046 | 1.726961 |
| H | 0.630262 | 4.109347 | 2.953856 |
| H | 2.887132 | 4.802762 | 2.132073 |
| C | 0.668451 | 2.235675 | -0.733839 |
| H | 1.648596 | 1.721279 | -0.606389 |
| H | 0.765206 | 3.146533 | -0.132221 |
| C | 0.402520 | 2.516927 | -2.205465 |

| | | | |
|---|---|---|---|
| H | -0.486242 | 3.157165 | -2.342200 |
| H | 1.247813 | 3.036904 | -2.708066 |
| H | 0.221538 | 1.580174 | -2.766822 |
| C | -3.132931 | 2.505397 | -1.562825 |
| C | -1.499897 | 2.275844 | 0.249874 |
| C | -3.012121 | 3.864201 | -1.516193 |
| C | -1.515758 | 3.694855 | 0.387724 |
| C | -2.239057 | 4.485967 | -0.470916 |
| H | -3.476210 | 4.454416 | -2.304738 |
| H | -0.919693 | 4.153935 | 1.176649 |
| O | -2.187506 | 5.819852 | -0.296289 |
| C | -3.000915 | 6.678666 | -1.082523 |
| H | -4.071947 | 6.420280 | -0.989695 |
| H | -2.838538 | 7.693671 | -0.690355 |
| H | -2.705797 | 6.653655 | -2.147998 |
| C | -3.822756 | 1.793516 | -2.692405 |
| H | -3.115663 | 1.101382 | -3.182701 |
| H | -4.685254 | 1.191090 | -2.366123 |
| H | -4.173795 | 2.523669 | -3.436615 |
| C | -2.757549 | 0.339993 | -0.457193 |
| N | -2.501817 | 1.740875 | -0.578692 |
| O | -1.854585 | -0.462529 | -0.502159 |
| O | -4.018556 | -0.033654 | -0.331248 |
| C | -4.976178 | 0.799530 | 0.366938 |
| H | -4.542418 | 1.097668 | 1.336405 |
| H | -5.257516 | 1.678785 | -0.234964 |
| H | -5.854931 | 0.155941 | 0.511968 |
| Cl | -2.606559 | 0.913788 | 2.998786 |
| H | -1.335401 | 1.683315 | 1.151536 |

**IV-*proR***

| | | | |
|---|---|---|---|
| Cu | 1.886953 | 1.828572 | -0.177691 |
| C | -1.720801 | -0.754064 | -0.152607 |
| H | -1.579138 | -1.172348 | 0.857496 |
| H | -0.891689 | -1.123741 | -0.773543 |

| | | | |
|---|---|---|---|
| C | -1.753847 | 0.777904 | -0.125953 |
| H | -1.861017 | 1.190780 | -1.142892 |
| H | -2.627949 | 1.142101 | 0.441173 |
| C | -4.449131 | -1.144814 | 0.609738 |
| C | -3.206725 | -3.281073 | -0.698695 |
| C | -4.293910 | -2.441485 | 1.427998 |
| H | -4.024130 | -0.302984 | 1.180818 |
| C | -4.164590 | -3.635212 | 0.470390 |
| H | -3.627645 | -3.681639 | -1.634110 |
| H | -3.378965 | -2.356027 | 2.040031 |
| H | -5.126842 | -2.579053 | 2.140061 |
| H | -3.826626 | -4.543369 | 0.999026 |
| H | -5.154653 | -3.871388 | 0.045567 |
| C | -0.341842 | 0.969962 | 2.429247 |
| C | -0.873477 | 3.321116 | 1.064607 |
| C | -0.399543 | 2.277179 | 3.254490 |
| H | -1.326539 | 0.482205 | 2.521569 |
| C | -1.359332 | 3.224950 | 2.523540 |
| H | 0.051420 | 3.920558 | 1.053371 |
| H | -0.730022 | 2.062426 | 4.285264 |
| H | 0.605509 | 2.731082 | 3.321055 |
| H | -2.379536 | 2.805872 | 2.573134 |
| H | -1.394929 | 4.224595 | 2.990546 |
| P | -3.318741 | -1.372727 | -0.919319 |
| P | -0.262127 | 1.573442 | 0.636888 |
| C | 0.723790 | -0.029346 | 2.815631 |
| C | 0.369567 | -1.335512 | 3.189133 |
| C | 2.088033 | 0.313577 | 2.804980 |
| C | 1.347093 | -2.273281 | 3.543031 |
| H | -0.686178 | -1.625159 | 3.209054 |
| C | 3.067274 | -0.620603 | 3.150252 |
| H | 2.390412 | 1.320583 | 2.510691 |
| C | 2.699662 | -1.919735 | 3.523132 |
| H | 1.047033 | -3.283776 | 3.837115 |
| H | 4.122818 | -0.337978 | 3.105608 |
| H | 3.465737 | -2.654119 | 3.789446 |

| | | | |
|---|---|---|---|
| C | -1.803273 | 3.852293 | -0.001102 |
| C | -1.250167 | 4.309945 | -1.212745 |
| C | -3.202127 | 3.821228 | 0.119319 |
| C | -2.066889 | 4.708869 | -2.273845 |
| H | -0.160225 | 4.342681 | -1.323427 |
| C | -4.023517 | 4.221740 | -0.941873 |
| H | -3.669118 | 3.474935 | 1.044526 |
| C | -3.460969 | 4.662302 | -2.143788 |
| H | -1.613545 | 5.058695 | -3.206573 |
| H | -5.111327 | 4.184579 | -0.824808 |
| H | -4.103409 | 4.971446 | -2.973772 |
| C | -1.788725 | -3.799669 | -0.596185 |
| C | -1.096833 | -4.155461 | -1.769296 |
| C | -1.116814 | -3.941824 | 0.631367 |
| C | 0.205530 | -4.660289 | -1.719874 |
| H | -1.595580 | -4.046681 | -2.738138 |
| C | 0.188273 | -4.442557 | 0.685718 |
| H | -1.615108 | -3.669190 | 1.565044 |
| C | 0.852477 | -4.814646 | -0.488040 |
| H | 0.716225 | -4.938048 | -2.647040 |
| H | 0.688874 | -4.540514 | 1.653079 |
| H | 1.867603 | -5.220072 | -0.444436 |
| C | -5.850411 | -0.728107 | 0.198189 |
| C | -6.045147 | 0.582172 | -0.284188 |
| C | -6.968179 | -1.574164 | 0.266688 |
| C | -7.305230 | 1.030195 | -0.683355 |
| H | -5.188841 | 1.263287 | -0.350078 |
| C | -8.235358 | -1.129452 | -0.135777 |
| H | -6.867131 | -2.595017 | 0.642142 |
| C | -8.411196 | 0.172125 | -0.612600 |
| H | -7.424708 | 2.054701 | -1.050828 |
| H | -9.090006 | -1.810549 | -0.071872 |
| H | -9.401087 | 0.518156 | -0.925717 |
| C | 2.918728 | 3.266831 | 0.778041 |
| H | 2.309518 | 3.538956 | 1.665087 |
| H | 2.876274 | 4.148300 | 0.102742 |

| | | | |
|---|---|---|---|
| C | 4.364401 | 3.016494 | 1.211970 |
| H | 4.773613 | 3.833532 | 1.844367 |
| H | 4.467522 | 2.082871 | 1.797090 |
| H | 5.039534 | 2.918942 | 0.345133 |
| C | 3.388307 | -1.306358 | -0.587839 |
| C | 3.469314 | 0.966580 | -1.406634 |
| C | 2.160315 | -1.461708 | -1.201356 |
| C | 2.264900 | 0.788014 | -2.110181 |
| C | 1.591851 | -0.444385 | -1.999310 |
| H | 1.627795 | -2.407442 | -1.107134 |
| H | 1.947529 | 1.569651 | -2.802253 |
| O | 0.450970 | -0.733406 | -2.608679 |
| C | -0.191594 | 0.234535 | -3.441060 |
| H | 0.414674 | 0.434002 | -4.341384 |
| H | -1.155180 | -0.209785 | -3.725886 |
| H | -0.365277 | 1.173272 | -2.887258 |
| C | 4.017988 | -2.453547 | 0.131934 |
| H | 4.205816 | -2.213977 | 1.186773 |
| H | 3.353699 | -3.327180 | 0.065468 |
| H | 4.988846 | -2.666821 | -0.360057 |
| C | 5.380621 | 0.096679 | -0.160989 |
| N | 4.053386 | -0.098595 | -0.724459 |
| O | 5.732338 | -0.410361 | 0.868528 |
| O | 6.039890 | 0.994026 | -0.869074 |
| C | 7.430354 | 1.149104 | -0.550149 |
| H | 7.787292 | 1.978192 | -1.176348 |
| H | 7.557003 | 1.384185 | 0.518871 |
| H | 7.936534 | 0.205770 | -0.812394 |
| Cl | 6.561010 | -1.898953 | -2.131326 |
| H | 4.136946 | 1.792481 | -1.636054 |

**IV-*proS***

| | | | |
|---|---|---|---|
| Cu | 2.168742 | -0.249299 | 0.804700 |
| C | -1.736361 | -0.318931 | -0.065749 |
| H | -1.955697 | -1.214750 | 0.539383 |

| | | | |
|---|---|---|---|
| H | -0.907211 | -0.586733 | -0.733059 |
| C | -1.306354 | 0.856140 | 0.816534 |
| H | -1.018264 | 1.724923 | 0.204220 |
| H | -2.103828 | 1.184183 | 1.507603 |
| C | -4.591924 | -0.398334 | 0.036263 |
| C | -3.347123 | -1.548147 | -2.190505 |
| C | -4.737420 | -1.925243 | -0.113251 |
| H | -4.211276 | -0.155127 | 1.044013 |
| C | -4.563133 | -2.300491 | -1.593777 |
| H | -3.591553 | -1.213963 | -3.211144 |
| H | -3.949857 | -2.412689 | 0.487498 |
| H | -5.698953 | -2.288922 | 0.290505 |
| H | -4.462630 | -3.391667 | -1.726306 |
| H | -5.464548 | -2.000896 | -2.153855 |
| C | -0.607730 | -0.806112 | 3.091827 |
| C | 0.540664 | 1.706733 | 3.019829 |
| C | -0.184825 | -0.172046 | 4.439423 |
| H | -1.694792 | -0.654248 | 2.984356 |
| C | -0.282054 | 1.354214 | 4.272277 |
| H | 1.605544 | 1.544314 | 3.259727 |
| H | -0.828059 | -0.543431 | 5.255567 |
| H | 0.854029 | -0.457325 | 4.685880 |
| H | -1.341726 | 1.637739 | 4.142326 |
| H | 0.094548 | 1.892863 | 5.159353 |
| P | -3.189723 | 0.088139 | -1.171136 |
| P | 0.172428 | 0.323091 | 1.793286 |
| C | -0.308379 | -2.269893 | 2.874872 |
| C | -1.341887 | -3.168093 | 2.563812 |
| C | 1.009791 | -2.756231 | 2.916680 |
| C | -1.069475 | -4.513965 | 2.293133 |
| H | -2.375604 | -2.808448 | 2.522790 |
| C | 1.286186 | -4.099488 | 2.648416 |
| H | 1.829978 | -2.067711 | 3.136086 |
| C | 0.247001 | -4.984413 | 2.332454 |
| H | -1.890046 | -5.194029 | 2.044308 |
| H | 2.320383 | -4.456265 | 2.679249 |

| | | | |
|---|---|---|---|
| H | 0.464205 | -6.034662 | 2.115195 |
| C | 0.403919 | 3.050614 | 2.345614 |
| C | 1.416465 | 3.456242 | 1.454094 |
| C | -0.731674 | 3.864307 | 2.478201 |
| C | 1.293635 | 4.631477 | 0.709955 |
| H | 2.304803 | 2.826298 | 1.331186 |
| C | -0.854360 | 5.046930 | 1.737707 |
| H | -1.536511 | 3.578580 | 3.160369 |
| C | 0.152939 | 5.433267 | 0.847609 |
| H | 2.091921 | 4.923656 | 0.020514 |
| H | -1.747698 | 5.667908 | 1.857055 |
| H | 0.052774 | 6.355076 | 0.266683 |
| C | -2.038364 | -2.305912 | -2.264239 |
| C | -1.066200 | -1.912713 | -3.202954 |
| C | -1.707572 | -3.342496 | -1.372890 |
| C | 0.186545 | -2.529932 | -3.258321 |
| H | -1.265434 | -1.077310 | -3.881782 |
| C | -0.454096 | -3.963260 | -1.420550 |
| H | -2.421557 | -3.665998 | -0.611475 |
| C | 0.497753 | -3.563662 | -2.365812 |
| H | 0.925177 | -2.144543 | -3.967223 |
| H | -0.219810 | -4.752559 | -0.699439 |
| H | 1.481970 | -4.042067 | -2.394809 |
| C | -5.835916 | 0.445515 | -0.188325 |
| C | -5.793702 | 1.811911 | 0.154716 |
| C | -7.034676 | -0.057465 | -0.718945 |
| C | -6.900306 | 2.643178 | -0.026454 |
| H | -4.869646 | 2.228572 | 0.570883 |
| C | -8.147887 | 0.773693 | -0.905873 |
| H | -7.121142 | -1.111796 | -0.989995 |
| C | -8.087570 | 2.126519 | -0.562598 |
| H | -6.837385 | 3.699975 | 0.252376 |
| H | -9.068880 | 0.353472 | -1.322573 |
| H | -8.957116 | 2.774779 | -0.708747 |
| C | 3.773032 | -0.367247 | 2.008355 |
| H | 3.446783 | -0.111818 | 3.038418 |

| | | | |
|---|---|---|---|
| H | 4.468135 | 0.443341 | 1.701353 |
| C | 4.519030 | -1.706388 | 2.025056 |
| H | 5.395018 | -1.710078 | 2.709600 |
| H | 3.864823 | -2.538055 | 2.345681 |
| H | 4.895375 | -1.977986 | 1.023262 |
| C | 3.729474 | 1.878118 | -1.540180 |
| C | 3.199735 | -0.431545 | -1.038003 |
| C | 2.395388 | 2.107938 | -1.793168 |
| C | 1.850245 | -0.224340 | -1.358319 |
| H | 3.616554 | -1.436233 | -1.019446 |
| C | 1.431981 | 1.067122 | -1.763479 |
| H | 2.097259 | 3.115748 | -2.071553 |
| H | 1.185899 | -1.074336 | -1.515468 |
| O | 0.145961 | 1.247136 | -1.962701 |
| C | -0.338128 | 2.425334 | -2.616089 |
| H | 0.155256 | 2.495092 | -3.600470 |
| H | -1.419826 | 2.266738 | -2.727707 |
| H | -0.158507 | 3.320172 | -1.994944 |
| C | 4.705969 | 3.014461 | -1.642974 |
| H | 5.530377 | 2.777198 | -2.334555 |
| H | 4.179377 | 3.907750 | -2.010153 |
| H | 5.162920 | 3.236743 | -0.666229 |
| C | 5.526067 | 0.290891 | -0.972928 |
| N | 4.150741 | 0.593592 | -1.229665 |
| O | 6.354469 | 1.105235 | -0.659971 |
| O | 5.751663 | -1.006219 | -1.132536 |
| C | 7.076990 | -1.468365 | -0.824469 |
| H | 7.059597 | -2.550764 | -1.007961 |
| H | 7.811997 | -0.972872 | -1.478303 |
| H | 7.314006 | -1.256997 | 0.230576 |
| Cl | 1.714628 | 0.528627 | -4.668227 |

**TS-(IV-V)-*R***

| | | | |
|---|---|---|---|
| Cu | -0.707506 | 0.858477 | -0.528899 |
| C | 2.828581 | 0.124686 | 1.135703 |

| | | | |
|---|---|---|---|
| H | 3.412413 | 0.145285 | 2.072641 |
| H | 3.505627 | -0.265798 | 0.356797 |
| C | 2.391289 | 1.554105 | 0.774113 |
| H | 1.781608 | 2.004575 | 1.575972 |
| H | 3.279974 | 2.195883 | 0.656051 |
| C | 0.859234 | -0.824039 | 3.051007 |
| C | 2.291454 | -2.758392 | 1.644847 |
| C | 1.768058 | -1.752934 | 3.892904 |
| H | 1.063640 | 0.229146 | 3.307983 |
| C | 1.934540 | -3.067458 | 3.120350 |
| H | 1.800681 | -3.493323 | 0.986974 |
| H | 2.747883 | -1.264102 | 4.036389 |
| H | 1.341069 | -1.920963 | 4.897634 |
| H | 2.687985 | -3.727330 | 3.584131 |
| H | 0.978337 | -3.617514 | 3.147695 |
| C | 2.604650 | 1.090920 | -2.117802 |
| C | 1.366681 | 3.447122 | -1.386030 |
| C | 2.345451 | 2.111365 | -3.251692 |
| H | 3.593191 | 1.339046 | -1.689729 |
| C | 2.327288 | 3.497660 | -2.597458 |
| H | 0.338384 | 3.554403 | -1.766790 |
| H | 3.128229 | 2.029503 | -4.025063 |
| H | 1.377759 | 1.889665 | -3.740284 |
| H | 3.350623 | 3.746645 | -2.270767 |
| H | 2.011023 | 4.287074 | -3.300365 |
| P | 1.403813 | -1.089480 | 1.251464 |
| P | 1.391116 | 1.635924 | -0.791055 |
| C | 2.649016 | -0.356058 | -2.566468 |
| C | 3.858656 | -0.847855 | -3.090941 |
| C | 1.540427 | -1.214350 | -2.540407 |
| C | 3.954485 | -2.151808 | -3.583343 |
| H | 4.740057 | -0.197972 | -3.111090 |
| C | 1.635121 | -2.525819 | -3.020007 |
| H | 0.591730 | -0.869636 | -2.128144 |
| C | 2.840686 | -2.999392 | -3.546529 |
| H | 4.906291 | -2.510813 | -3.987177 |

| | | | |
|---|---|---|---|
| H | 0.753716 | -3.169097 | -2.968711 |
| H | 2.916019 | -4.025590 | -3.919016 |
| C | 1.564207 | 4.465693 | -0.285501 |
| C | 0.442673 | 5.028204 | 0.349456 |
| C | 2.839932 | 4.846900 | 0.167779 |
| C | 0.585224 | 5.932251 | 1.406170 |
| H | -0.560841 | 4.751807 | 0.012106 |
| C | 2.987165 | 5.754054 | 1.222112 |
| H | 3.737315 | 4.434923 | -0.301783 |
| C | 1.860814 | 6.298927 | 1.848695 |
| H | -0.305722 | 6.352533 | 1.882780 |
| H | 3.990881 | 6.035367 | 1.555542 |
| H | 1.976963 | 7.007394 | 2.674464 |
| C | 3.762608 | -2.740546 | 1.288624 |
| C | 4.145009 | -2.935804 | -0.051871 |
| C | 4.774389 | -2.487825 | 2.231470 |
| C | 5.486998 | -2.881871 | -0.436814 |
| H | 3.377111 | -3.117070 | -0.810546 |
| C | 6.120004 | -2.435582 | 1.849308 |
| H | 4.522388 | -2.329324 | 3.282519 |
| C | 6.484221 | -2.631231 | 0.513189 |
| H | 5.750177 | -3.034361 | -1.487393 |
| H | 6.887668 | -2.239895 | 2.604881 |
| H | 7.536331 | -2.590093 | 0.214551 |
| C | -0.624587 | -1.077672 | 3.264903 |
| C | -1.321283 | -0.328463 | 4.229761 |
| C | -1.348534 | -2.031560 | 2.529253 |
| C | -2.695743 | -0.499967 | 4.424567 |
| H | -0.780868 | 0.419949 | 4.819265 |
| C | -2.729295 | -2.190343 | 2.696520 |
| H | -0.838379 | -2.638530 | 1.775361 |
| C | -3.407537 | -1.417673 | 3.644259 |
| H | -3.217837 | 0.110681 | 5.168183 |
| H | -3.284529 | -2.860421 | 2.031543 |
| H | -4.491774 | -1.509558 | 3.749220 |
| C | -2.101274 | 2.146770 | 0.457380 |

| | | | |
|---|---|---|---|
| H | -3.186854 | 2.226479 | 0.558909 |
| H | -1.807275 | 2.875003 | -0.324259 |
| C | -1.424277 | 2.377545 | 1.799490 |
| H | -1.819601 | 3.291433 | 2.286879 |
| H | -1.611800 | 1.532981 | 2.483630 |
| H | -0.333004 | 2.505362 | 1.715555 |
| C | -3.045449 | -0.330420 | -2.754711 |
| C | -1.880163 | -0.916714 | -0.702169 |
| C | -3.969256 | 0.402009 | -2.074244 |
| C | -2.661363 | 0.137278 | -0.030873 |
| H | -1.321466 | -1.639933 | -0.111198 |
| H | -2.808968 | -0.062976 | 1.029693 |
| N | -3.912458 | 0.406645 | -0.671419 |
| C | -5.042639 | 0.311851 | 0.162331 |
| O | -4.965591 | 0.322926 | 1.369850 |
| O | -6.174608 | 0.237346 | -0.530424 |
| C | -7.310628 | -0.278023 | 0.173349 |
| H | -7.491468 | 0.288221 | 1.101168 |
| H | -8.161751 | -0.173035 | -0.514716 |
| H | -7.118613 | -1.341088 | 0.395913 |
| C | -5.009201 | 1.221127 | -2.789386 |
| H | -5.942149 | 0.649863 | -2.919775 |
| H | -5.256387 | 2.134374 | -2.224546 |
| H | -4.632168 | 1.503593 | -3.786115 |
| H | -3.045609 | -0.321102 | -3.845243 |
| C | -2.132055 | -1.176923 | -2.026789 |
| O | -1.533398 | -2.228680 | -2.607506 |
| C | -2.301179 | -3.002091 | -3.537740 |
| H | -2.461210 | -2.460907 | -4.487340 |
| H | -1.707950 | -3.906929 | -3.738476 |
| H | -3.266406 | -3.270407 | -3.072488 |
| Cl | -4.748772 | -2.876536 | -0.533971 |

**TS-(IV-V)-*S***

| | | | |
|---|---|---|---|
| Cu | -0.022563 | -0.233024 | -0.545633 |

| | | | |
|---|---|---|---|
| C | -2.663600 | -0.766378 | 1.274749 |
| H | -3.726691 | -0.642548 | 1.539737 |
| H | -2.451915 | -1.849069 | 1.297655 |
| C | -1.765943 | -0.011096 | 2.267093 |
| H | -2.026231 | 1.060754 | 2.280329 |
| H | -1.918719 | -0.387903 | 3.293031 |
| C | -3.358092 | 1.378971 | -0.558825 |
| C | -3.551978 | -1.221685 | -1.546430 |
| C | -4.795085 | 0.880733 | -0.866461 |
| H | -3.330281 | 1.835777 | 0.443616 |
| C | -4.710322 | -0.249505 | -1.903845 |
| H | -2.988809 | -1.464543 | -2.460170 |
| H | -5.251784 | 0.507904 | 0.067778 |
| H | -5.428852 | 1.710708 | -1.223720 |
| H | -5.667943 | -0.788470 | -1.994002 |
| H | -4.506840 | 0.189362 | -2.894337 |
| C | 0.661737 | -1.615043 | 2.792386 |
| C | 0.894881 | 1.139930 | 2.905178 |
| C | 1.745838 | -1.028772 | 3.723966 |
| H | -0.195430 | -1.910793 | 3.419553 |
| C | 1.267119 | 0.354919 | 4.176487 |
| H | 1.829793 | 1.357280 | 2.357956 |
| H | 1.926792 | -1.705852 | 4.576296 |
| H | 2.704240 | -0.921374 | 3.187564 |
| H | 0.383087 | 0.248210 | 4.831387 |
| H | 2.043697 | 0.883011 | 4.756687 |
| P | -2.346056 | -0.201116 | -0.477823 |
| P | 0.039843 | -0.124701 | 1.789815 |
| C | 1.043614 | -2.796980 | 1.931071 |
| C | 0.094360 | -3.800673 | 1.669262 |
| C | 2.308400 | -2.909335 | 1.331261 |
| C | 0.399081 | -4.884846 | 0.840518 |
| H | -0.902915 | -3.731585 | 2.116989 |
| C | 2.620391 | -3.998382 | 0.512289 |
| H | 3.064882 | -2.137119 | 1.479798 |
| C | 1.668187 | -4.991416 | 0.261330 |

| | | | |
|---|---|---|---|
| H | -0.359472 | -5.649862 | 0.650473 |
| H | 3.611300 | -4.058806 | 0.053765 |
| H | 1.911037 | -5.838822 | -0.386705 |
| C | 0.140480 | 2.442452 | 3.068786 |
| C | -0.356128 | 3.115848 | 1.935221 |
| C | -0.077378 | 3.023094 | 4.328423 |
| C | -1.034703 | 4.330501 | 2.054983 |
| H | -0.227289 | 2.676921 | 0.942320 |
| C | -0.760451 | 4.240319 | 4.451492 |
| H | 0.292881 | 2.533329 | 5.231838 |
| C | -1.240256 | 4.901038 | 3.317210 |
| H | -1.401977 | 4.830735 | 1.154480 |
| H | -0.914193 | 4.673135 | 5.444982 |
| H | -1.772056 | 5.852384 | 3.414019 |
| C | -3.907746 | -2.529324 | -0.871324 |
| C | -3.031734 | -3.623628 | -0.993469 |
| C | -5.045469 | -2.676839 | -0.060732 |
| C | -3.282047 | -4.825654 | -0.325933 |
| H | -2.136345 | -3.529793 | -1.615914 |
| C | -5.299484 | -3.879812 | 0.607598 |
| H | -5.744442 | -1.845322 | 0.063134 |
| C | -4.418158 | -4.958994 | 0.480988 |
| H | -2.587929 | -5.663469 | -0.441760 |
| H | -6.192688 | -3.971387 | 1.233442 |
| H | -4.616774 | -5.898946 | 1.004695 |
| C | -2.819436 | 2.390761 | -1.551787 |
| C | -2.319716 | 2.024680 | -2.813415 |
| C | -2.832639 | 3.754844 | -1.216950 |
| C | -1.847532 | 2.989403 | -3.708598 |
| H | -2.269734 | 0.970552 | -3.102245 |
| C | -2.358140 | 4.723163 | -2.106927 |
| H | -3.220204 | 4.061106 | -0.240174 |
| C | -1.861418 | 4.342950 | -3.357702 |
| H | -1.454296 | 2.677672 | -4.681145 |
| H | -2.371093 | 5.778738 | -1.817361 |
| H | -1.480930 | 5.096723 | -4.053648 |

| | | | |
|---|---|---|---|
| C | 0.675642 | -1.974784 | -1.594766 |
| H | 0.046925 | -2.389568 | -0.782760 |
| H | 1.644753 | -2.470236 | -1.498415 |
| C | 0.048850 | -2.192780 | -2.958413 |
| H | -0.110730 | -3.270503 | -3.162458 |
| H | -0.929129 | -1.689274 | -3.047708 |
| H | 0.688473 | -1.809081 | -3.775584 |
| C | 3.207752 | 0.964384 | -0.135335 |
| C | 1.764972 | -0.106486 | -1.830846 |
| C | 2.417464 | 2.081811 | -0.178858 |
| C | 1.040318 | 1.150329 | -1.950095 |
| H | 1.966602 | -0.581932 | -2.785876 |
| C | 1.356240 | 2.216116 | -1.138532 |
| H | 2.627087 | 2.890194 | 0.518519 |
| H | 0.345192 | 1.288726 | -2.778476 |
| O | 0.668309 | 3.357198 | -1.304443 |
| C | 1.200933 | 4.597398 | -0.851150 |
| H | 2.220925 | 4.757102 | -1.243908 |
| H | 0.524480 | 5.369120 | -1.246571 |
| H | 1.209883 | 4.659184 | 0.250597 |
| C | 4.348881 | 0.918462 | 0.838381 |
| H | 5.294977 | 0.883332 | 0.267429 |
| H | 4.326778 | 1.830522 | 1.455392 |
| H | 4.300521 | 0.036878 | 1.495363 |
| C | 3.881215 | -1.120164 | -1.356212 |
| N | 2.950306 | -0.093862 | -1.019567 |
| O | 3.815630 | -1.722117 | -2.401897 |
| O | 4.695308 | -1.426437 | -0.356221 |
| C | 5.845893 | -2.214455 | -0.692024 |
| H | 6.343385 | -2.432062 | 0.263739 |
| H | 5.542600 | -3.147974 | -1.192803 |
| H | 6.488582 | -1.604062 | -1.348225 |
| Cl | 6.131731 | 0.932552 | -2.161055 |

**V-*R***

| | | | |
|---|---|---|---|
| Cu | 0.107554 | -0.178535 | -0.135292 |
| C | 2.568666 | 1.847924 | 0.604225 |
| H | 3.108997 | 2.506465 | 1.305956 |
| H | 3.330372 | 1.312031 | 0.010677 |
| C | 1.650491 | 2.676464 | -0.311274 |
| H | 0.882224 | 3.206725 | 0.278660 |
| H | 2.228080 | 3.443298 | -0.855303 |
| C | 0.860281 | 1.581690 | 2.955199 |
| C | 2.794598 | -0.356247 | 2.618135 |
| C | 1.522289 | 0.992515 | 4.227262 |
| H | 1.257110 | 2.599228 | 2.802214 |
| C | 2.943780 | 0.543756 | 3.860990 |
| H | 2.185301 | -1.229800 | 2.917579 |
| H | 1.513138 | 1.738276 | 5.041227 |
| H | 0.954601 | 0.111316 | 4.568285 |
| H | 3.585833 | 1.420388 | 3.654146 |
| H | 3.415926 | -0.019390 | 4.685808 |
| C | 2.090793 | 1.242359 | -2.815483 |
| C | -0.242586 | 2.724001 | -2.619839 |
| C | 1.534554 | 1.881627 | -4.112652 |
| H | 2.959231 | 1.837507 | -2.488731 |
| C | 0.750345 | 3.140647 | -3.723823 |
| H | -0.991061 | 2.053785 | -3.077370 |
| H | 2.358858 | 2.103629 | -4.811834 |
| H | 0.858572 | 1.174980 | -4.625221 |
| H | 1.446513 | 3.913251 | -3.352919 |
| H | 0.213529 | 3.574779 | -4.585556 |
| P | 1.575164 | 0.560015 | 1.527363 |
| P | 0.753340 | 1.561093 | -1.511148 |
| C | 2.511420 | -0.206705 | -2.905291 |
| C | 3.776209 | -0.607062 | -2.442973 |
| C | 1.650540 | -1.189152 | -3.424971 |
| C | 4.179982 | -1.944196 | -2.517961 |
| H | 4.457904 | 0.136165 | -2.016053 |
| C | 2.054246 | -2.523542 | -3.510858 |
| H | 0.644132 | -0.914303 | -3.755961 |

| | | | |
|---|---|---|---|
| C | 3.322773 | -2.906268 | -3.061051 |
| H | 5.165426 | -2.230695 | -2.141462 |
| H | 1.364884 | -3.272063 | -3.910404 |
| H | 3.635424 | -3.953297 | -3.120008 |
| C | -0.975836 | 3.802002 | -1.857719 |
| C | -2.303540 | 3.577753 | -1.455191 |
| C | -0.362802 | 5.008779 | -1.477148 |
| C | -2.996501 | 4.516720 | -0.687086 |
| H | -2.797764 | 2.647779 | -1.747974 |
| C | -1.053896 | 5.953000 | -0.710206 |
| H | 0.668040 | 5.219179 | -1.773045 |
| C | -2.372148 | 5.710028 | -0.307566 |
| H | -4.027478 | 4.313006 | -0.382024 |
| H | -0.556387 | 6.885184 | -0.425028 |
| H | -2.909860 | 6.447500 | 0.295994 |
| C | 4.034798 | -0.850015 | 1.919753 |
| C | 5.126989 | -0.014243 | 1.625950 |
| C | 4.103135 | -2.198130 | 1.521427 |
| C | 6.245343 | -0.506747 | 0.944279 |
| H | 5.107402 | 1.035486 | 1.931315 |
| C | 5.218427 | -2.692790 | 0.839723 |
| H | 3.267995 | -2.861852 | 1.765592 |
| C | 6.294570 | -1.847619 | 0.545382 |
| H | 7.084465 | 0.161492 | 0.725786 |
| H | 5.246419 | -3.744182 | 0.536813 |
| H | 7.168606 | -2.231974 | 0.010412 |
| C | -0.650646 | 1.657390 | 2.952644 |
| C | -1.294384 | 2.848603 | 2.577575 |
| C | -1.443107 | 0.545936 | 3.297340 |
| C | -2.690698 | 2.944414 | 2.573248 |
| H | -0.697006 | 3.719086 | 2.284342 |
| C | -2.837638 | 0.646222 | 3.304248 |
| H | -0.969074 | -0.414791 | 3.530707 |
| C | -3.467986 | 1.845776 | 2.951157 |
| H | -3.166348 | 3.881585 | 2.270084 |
| H | -3.439542 | -0.228133 | 3.571829 |

| | | | |
|---|---|---|---|
| H | -4.559752 | 1.916672 | 2.952166 |
| C | -2.830316 | 0.173279 | -0.176087 |
| H | -2.400778 | 0.281662 | -1.188954 |
| H | -2.231052 | 0.807464 | 0.503037 |
| C | -4.284138 | 0.653578 | -0.165405 |
| H | -4.340381 | 1.742614 | -0.330350 |
| H | -4.876084 | 0.158464 | -0.955273 |
| H | -4.761763 | 0.432976 | 0.802300 |
| C | -1.873826 | -2.548348 | -2.058362 |
| C | -1.229371 | -1.834622 | 0.203311 |
| C | -3.204513 | -2.480897 | -1.784789 |
| C | -2.659630 | -1.286658 | 0.287774 |
| H | -0.742216 | -2.119633 | 1.151749 |
| H | -2.974395 | -1.345152 | 1.335115 |
| N | -3.584550 | -2.167273 | -0.465390 |
| C | -4.715248 | -2.625467 | 0.189712 |
| O | -5.063836 | -2.245974 | 1.289926 |
| O | -5.378402 | -3.552231 | -0.518148 |
| C | -6.592001 | -4.040830 | 0.058537 |
| H | -7.307311 | -3.216800 | 0.218857 |
| H | -6.996528 | -4.762643 | -0.665349 |
| H | -6.391294 | -4.536277 | 1.022700 |
| C | -4.241274 | -2.671561 | -2.860169 |
| H | -4.672283 | -3.684819 | -2.831845 |
| H | -5.073996 | -1.958764 | -2.736951 |
| H | -3.778147 | -2.516900 | -3.848087 |
| H | -1.522858 | -2.764948 | -3.068997 |
| C | -0.910258 | -2.495258 | -0.971224 |
| O | 0.188170 | -3.220652 | -1.207485 |
| C | 1.256389 | -3.212448 | -0.263174 |
| H | 0.914571 | -3.479933 | 0.751768 |
| H | 1.998022 | -3.932505 | -0.635390 |
| H | 1.721261 | -2.209208 | -0.231568 |
| Cl | 0.292273 | -2.666189 | 3.296162 |

**V-*S***

| | | | |
|---|---|---|---|
| Cu | -0.363825 | 0.211679 | 0.526872 |
| C | 2.946262 | -0.984022 | 0.225501 |
| H | 1.886081 | -1.248726 | 0.062876 |
| H | 3.294072 | -1.619688 | 1.056376 |
| C | 3.076497 | 0.507719 | 0.598284 |
| H | 3.924471 | 0.691180 | 1.278909 |
| H | 3.227807 | 1.146365 | -0.288637 |
| C | 2.802620 | -0.593324 | -2.631963 |
| C | 3.156980 | -3.113434 | -1.845076 |
| C | 2.908525 | -1.542790 | -3.856595 |
| H | 1.773556 | -0.647281 | -2.240097 |
| C | 3.229404 | -2.993717 | -3.388558 |
| H | 3.859066 | -3.889986 | -1.501091 |
| H | 1.966200 | -1.495507 | -4.429635 |
| H | 3.697746 | -1.186911 | -4.538589 |
| H | 2.555632 | -3.730735 | -3.856986 |
| H | 4.251127 | -3.260136 | -3.706862 |
| C | 1.634229 | 2.983807 | 1.517555 |
| C | 1.624540 | 0.790676 | 3.199406 |
| C | 1.671707 | 3.243100 | 3.050486 |
| H | 2.612705 | 3.251233 | 1.085920 |
| C | 2.339457 | 2.043502 | 3.734684 |
| H | 0.573805 | 0.829043 | 3.535134 |
| H | 2.194848 | 4.190502 | 3.262478 |
| H | 0.639462 | 3.351722 | 3.428355 |
| H | 3.414326 | 2.022139 | 3.481960 |
| H | 2.264236 | 2.100216 | 4.834627 |
| P | 3.893415 | -1.425888 | -1.321267 |
| P | 1.498977 | 1.109100 | 1.347437 |
| C | 0.543600 | 3.719952 | 0.769433 |
| C | 0.861316 | 4.676933 | -0.204709 |
| C | -0.814788 | 3.448647 | 1.018166 |
| C | -0.145859 | 5.333751 | -0.922927 |
| H | 1.911307 | 4.902445 | -0.413682 |

| | | | |
|---|---|---|---|
| C | -1.823071 | 4.094801 | 0.300154 |
| H | -1.095840 | 2.705655 | 1.771251 |
| C | -1.491252 | 5.041104 | -0.677705 |
| H | 0.125964 | 6.072727 | -1.683106 |
| H | -2.869867 | 3.847332 | 0.500422 |
| H | -2.278322 | 5.546103 | -1.245586 |
| C | 2.174733 | -0.580852 | 3.504865 |
| C | 1.314652 | -1.691838 | 3.419231 |
| C | 3.530415 | -0.801686 | 3.794825 |
| C | 1.798585 | -2.986793 | 3.615751 |
| H | 0.257492 | -1.536904 | 3.177425 |
| C | 4.017231 | -2.100797 | 3.983999 |
| H | 4.222438 | 0.040449 | 3.872641 |
| C | 3.154621 | -3.198002 | 3.893733 |
| H | 1.113140 | -3.835668 | 3.548102 |
| H | 5.078090 | -2.252919 | 4.205568 |
| H | 3.535304 | -4.212979 | 4.042553 |
| C | 1.790443 | -3.427588 | -1.274927 |
| C | 1.693745 | -4.070653 | -0.026086 |
| C | 0.590421 | -3.086742 | -1.928855 |
| C | 0.452454 | -4.369729 | 0.543593 |
| H | 2.610690 | -4.338961 | 0.509686 |
| C | -0.652965 | -3.380262 | -1.358011 |
| H | 0.614055 | -2.598112 | -2.905302 |
| C | -0.730408 | -4.025914 | -0.120541 |
| H | 0.410917 | -4.881710 | 1.509691 |
| H | -1.586902 | -3.118673 | -1.863962 |
| H | -1.719985 | -4.244868 | 0.291354 |
| C | 3.111557 | 0.856361 | -2.921921 |
| C | 2.146011 | 1.849809 | -2.684747 |
| C | 4.359966 | 1.255545 | -3.434875 |
| C | 2.405717 | 3.194701 | -2.973010 |
| H | 1.178193 | 1.566501 | -2.259333 |
| C | 4.627151 | 2.598286 | -3.714953 |
| H | 5.135893 | 0.503720 | -3.610593 |
| C | 3.647602 | 3.574924 | -3.491276 |

| | | | |
|---|---|---|---|
| H | 1.629901 | 3.942645 | -2.790729 |
| H | 5.606272 | 2.884672 | -4.112088 |
| H | 3.853534 | 4.625605 | -3.717974 |
| C | -2.427125 | 0.778979 | -1.722974 |
| H | -2.046573 | 1.649376 | -1.154251 |
| H | -3.209079 | 1.158331 | -2.403326 |
| C | -1.313920 | 0.144518 | -2.559446 |
| H | -0.843858 | 0.884699 | -3.228379 |
| H | -0.512056 | -0.290116 | -1.931791 |
| H | -1.711488 | -0.679943 | -3.177810 |
| C | -4.524032 | 1.080298 | 0.754457 |
| C | -3.082579 | -0.233285 | -0.765402 |
| C | -3.529059 | 1.074951 | 1.706086 |
| C | -2.259452 | -0.624228 | 0.463002 |
| H | -3.274347 | -1.171446 | -1.298987 |
| C | -2.549637 | 0.027447 | 1.666054 |
| H | -3.604849 | 1.761168 | 2.547865 |
| H | -1.992322 | -1.687775 | 0.543233 |
| O | -1.954633 | -0.427895 | 2.787203 |
| C | -2.223945 | 0.164931 | 4.055275 |
| H | -3.297750 | 0.106378 | 4.303838 |
| H | -1.642605 | -0.417901 | 4.784044 |
| H | -1.888630 | 1.217168 | 4.081715 |
| C | -5.718356 | 1.981206 | 0.911311 |
| H | -6.587652 | 1.413055 | 1.278110 |
| H | -5.487252 | 2.783325 | 1.629996 |
| H | -6.007002 | 2.429532 | -0.054003 |
| C | -5.564065 | -0.211379 | -1.021669 |
| N | -4.423831 | 0.254783 | -0.344458 |
| O | -6.676478 | -0.244743 | -0.546480 |
| O | -5.253816 | -0.566595 | -2.268656 |
| C | -6.179511 | -1.424878 | -2.945123 |
| H | -5.836394 | -1.470711 | -3.988869 |
| H | -6.124151 | -2.421865 | -2.476343 |
| H | -7.201893 | -1.017130 | -2.892949 |
| Cl | -4.257103 | -3.398077 | -0.671609 |

**L1-CuCl**

| | | | |
|---|---|---|---|
| Cu | 0.224086 | 0.078341 | 1.460395 |
| C | 0.303657 | -0.129349 | -1.838518 |
| H | 0.623166 | 0.278032 | -2.812235 |
| H | 0.426414 | -1.224259 | -1.902705 |
| C | -1.165767 | 0.236237 | -1.558991 |
| H | -1.316077 | 1.328469 | -1.620333 |
| H | -1.831136 | -0.217229 | -2.313231 |
| C | 1.680540 | 2.275375 | -0.947420 |
| C | 3.181961 | -0.078905 | -0.953695 |
| C | 2.817443 | 2.212903 | -1.986616 |
| H | 0.742878 | 2.603067 | -1.428889 |
| C | 3.872555 | 1.191334 | -1.524380 |
| H | 3.652896 | -0.350241 | 0.003296 |
| H | 2.389295 | 1.893271 | -2.952830 |
| H | 3.263971 | 3.206626 | -2.163757 |
| H | 4.563729 | 0.932555 | -2.343756 |
| H | 4.487711 | 1.634771 | -0.725047 |
| C | -2.001899 | -2.138536 | -0.029298 |
| C | -3.490456 | 0.220623 | 0.377029 |
| C | -3.541652 | -2.278825 | -0.075591 |
| H | -1.572183 | -2.437615 | -0.999069 |
| C | -4.207817 | -1.117188 | 0.686582 |
| H | -3.502793 | 0.852954 | 1.278235 |
| H | -3.857074 | -2.259961 | -1.131740 |
| H | -3.862752 | -3.254290 | 0.328708 |
| H | -5.283788 | -1.046203 | 0.451483 |
| H | -4.136743 | -1.300640 | 1.772090 |
| P | 1.426340 | 0.464706 | -0.459901 |
| P | -1.667625 | -0.281881 | 0.166004 |
| C | -1.251076 | -2.881165 | 1.060191 |
| C | 0.100959 | -3.207267 | 0.845023 |
| C | -1.811996 | -3.176844 | 2.311837 |
| C | 0.871245 | -3.797446 | 1.849402 |

| | | | |
|---|---|---|---|
| H | 0.561798 | -2.988926 | -0.123721 |
| C | -1.044417 | -3.773547 | 3.319128 |
| H | -2.857026 | -2.933473 | 2.518693 |
| C | 0.300867 | -4.082415 | 3.095304 |
| H | 1.922062 | -4.036697 | 1.656924 |
| H | -1.502366 | -3.989158 | 4.289475 |
| H | 0.902078 | -4.539262 | 3.887097 |
| C | -4.011632 | 1.051252 | -0.775234 |
| C | -3.771338 | 2.438886 | -0.774466 |
| C | -4.685575 | 0.499281 | -1.877623 |
| C | -4.181728 | 3.246076 | -1.838626 |
| H | -3.249254 | 2.891509 | 0.075868 |
| C | -5.102284 | 1.305631 | -2.943380 |
| H | -4.895148 | -0.572021 | -1.915669 |
| C | -4.849765 | 2.681168 | -2.931862 |
| H | -3.983016 | 4.322088 | -1.811555 |
| H | -5.628337 | 0.851408 | -3.788961 |
| H | -5.174757 | 3.309958 | -3.766373 |
| C | 3.152694 | -1.316069 | -1.822303 |
| C | 3.107824 | -2.582554 | -1.211548 |
| C | 3.092417 | -1.253400 | -3.224791 |
| C | 2.992044 | -3.748933 | -1.973389 |
| H | 3.157762 | -2.651483 | -0.119858 |
| C | 2.984626 | -2.419003 | -3.991093 |
| H | 3.120937 | -0.285250 | -3.732501 |
| C | 2.927953 | -3.671649 | -3.369641 |
| H | 2.954130 | -4.721514 | -1.472834 |
| H | 2.939921 | -2.345723 | -5.082250 |
| H | 2.838892 | -4.582218 | -3.969872 |
| C | 1.894508 | 3.135785 | 0.288899 |
| C | 0.833666 | 3.269754 | 1.205996 |
| C | 3.099810 | 3.792073 | 0.579838 |
| C | 0.975013 | 4.010076 | 2.379545 |
| H | -0.120578 | 2.770969 | 1.001521 |
| C | 3.244720 | 4.544426 | 1.753758 |
| H | 3.946414 | 3.728659 | -0.107020 |

| | | | |
|---|---|---|---|
| C | 2.187572 | 4.652337 | 2.660855 |
| H | 0.138054 | 4.075895 | 3.081192 |
| H | 4.196940 | 5.044081 | 1.958025 |
| H | 2.305911 | 5.230992 | 3.582054 |
| Cl | 0.572400 | 0.065051 | 3.639236 |

**VI**

| | | | |
|---|---|---|---|
| C | 4.059566 | -0.089374 | 0.001866 |
| C | 3.155620 | -0.764875 | -0.740264 |
| C | 1.731925 | 1.265691 | -0.759200 |
| C | 2.560460 | 1.781369 | 0.392329 |
| H | 2.267498 | 2.706042 | 0.894523 |
| Cl | 7.132692 | -1.607540 | -0.130879 |
| O | 4.507050 | 1.623140 | 1.695704 |
| C | 5.377564 | 0.731071 | 2.391362 |
| H | 5.877833 | 1.339342 | 3.161626 |
| H | 4.801857 | -0.075947 | 2.885586 |
| H | 6.133852 | 0.270203 | 1.728918 |
| H | 5.098767 | -0.453013 | 0.002561 |
| C | 3.526647 | -1.959634 | -1.575558 |
| H | 4.624594 | -2.065729 | -1.561115 |
| H | 3.083159 | -2.894185 | -1.195992 |
| H | 3.178733 | -1.829833 | -2.617759 |
| C | 0.695622 | -0.948016 | -0.801050 |
| N | 1.822324 | -0.217335 | -0.799362 |
| O | 0.870139 | -2.252686 | -0.679559 |
| C | -0.261297 | -3.128585 | -0.791506 |
| H | -0.854137 | -2.887184 | -1.687833 |
| H | 0.157301 | -4.140928 | -0.866199 |
| H | -0.896831 | -3.051413 | 0.106679 |
| O | -0.447859 | -0.437561 | -0.887809 |
| C | 3.693635 | 1.124993 | 0.731482 |
| H | 0.679083 | 1.498991 | -0.565545 |
| C | 2.110833 | 1.851717 | -2.136850 |
| H | 1.475802 | 1.365587 | -2.901457 |

| | | | |
|---|---|---|---|
| C | 1.945811 | 3.370352 | -2.208560 |
| H | 2.592099 | 3.880055 | -1.472739 |
| H | 2.216575 | 3.743688 | -3.211239 |
| H | 0.901342 | 3.672913 | -2.009732 |
| H | 3.156876 | 1.575069 | -2.358559 |
| Mg | -2.324430 | -0.343757 | -0.308630 |
| Br | -4.270654 | -1.591682 | -1.181324 |
| O | -2.876344 | 1.611919 | -0.539960 |
| O | -2.006132 | -0.913673 | 1.646823 |
| C | -1.964949 | 2.575960 | -1.121714 |
| H | -1.087877 | 1.996855 | -1.445225 |
| H | -2.433237 | 2.995079 | -2.028719 |
| C | -1.583957 | 3.654689 | -0.123727 |
| H | -0.890586 | 4.373457 | -0.593816 |
| H | -2.471236 | 4.213448 | 0.220671 |
| H | -1.085699 | 3.213880 | 0.756823 |
| C | -4.277075 | 2.016252 | -0.516986 |
| H | -4.804095 | 1.391035 | -1.255500 |
| H | -4.325878 | 3.066201 | -0.844052 |
| C | -4.877302 | 1.859683 | 0.866563 |
| H | -4.289982 | 2.416195 | 1.616849 |
| H | -5.907257 | 2.257909 | 0.860161 |
| H | -4.934589 | 0.799625 | 1.165460 |
| C | -0.717832 | -0.825724 | 2.309423 |
| H | -0.774268 | -1.405834 | 3.243756 |
| H | 0.011687 | -1.332740 | 1.659802 |
| C | -0.317990 | 0.614013 | 2.573894 |
| H | -1.044524 | 1.113383 | 3.235721 |
| H | 0.676956 | 0.640733 | 3.050657 |
| H | -0.250234 | 1.186076 | 1.634085 |
| C | -3.096520 | -1.443083 | 2.446849 |
| H | -3.925446 | -1.580986 | 1.736196 |
| H | -2.794765 | -2.441260 | 2.810485 |
| C | -3.490220 | -0.524938 | 3.590776 |
| H | -2.687096 | -0.430807 | 4.341318 |
| H | -3.743218 | 0.481482 | 3.218612 |

| | | | |
|---|---|---|---|
| H | -4.377117 | -0.942387 | 4.098995 |

**$MgClBr(Et_2O)_2$**

| | | | |
|---|---|---|---|
| Mg | 0.263503 | 0.304856 | -0.723759 |
| Cl | 1.119000 | -0.664186 | -2.637133 |
| O | 1.197789 | -0.699833 | 0.820377 |
| O | -1.651712 | -0.462440 | -0.618322 |
| C | 2.247103 | -1.657606 | 0.542060 |
| H | 2.282724 | -2.386347 | 1.369126 |
| H | 1.931155 | -2.181944 | -0.371596 |
| C | 1.021313 | -0.337211 | 2.208905 |
| H | 2.015269 | -0.271661 | 2.683829 |
| H | 0.589913 | 0.675377 | 2.193468 |
| C | 3.582488 | -0.965600 | 0.330642 |
| H | 3.892393 | -0.398199 | 1.225337 |
| H | 4.362591 | -1.716114 | 0.111466 |
| H | 3.514917 | -0.272080 | -0.524996 |
| C | 0.114554 | -1.317047 | 2.933706 |
| H | -0.005681 | -1.002420 | 3.985438 |
| H | -0.880531 | -1.345712 | 2.460563 |
| H | 0.530574 | -2.339529 | 2.928616 |
| C | -2.801573 | 0.338573 | -0.265078 |
| H | -2.405707 | 1.356030 | -0.128221 |
| H | -3.491741 | 0.349234 | -1.128039 |
| C | -1.914189 | -1.794382 | -1.131916 |
| H | -2.981367 | -1.855271 | -1.402612 |
| H | -1.314969 | -1.886703 | -2.050963 |
| C | -3.493396 | -0.144795 | 0.997962 |
| H | -2.791400 | -0.149653 | 1.849424 |
| H | -4.327405 | 0.537339 | 1.240453 |
| H | -3.910945 | -1.159199 | 0.877947 |
| C | -1.526126 | -2.865161 | -0.127161 |
| H | -0.461917 | -2.769161 | 0.144480 |
| H | -2.125968 | -2.794304 | 0.795073 |
| H | -1.682506 | -3.863666 | -0.572660 |

| | | | |
|---|---|---|---|
| Br | 0.152169 | 2.653270 | 0.093688 |

**TS-(II-VI)**

| | | | |
|---|---|---|---|
| C | 3.546283 | 0.605774 | 0.106612 |
| C | 3.345625 | -0.694069 | -0.256224 |
| C | 1.075240 | -0.524664 | 0.566366 |
| C | 1.387371 | 0.718398 | 1.183663 |
| H | 0.637679 | 1.236981 | 1.780430 |
| Cl | 2.442955 | 3.115742 | -1.834102 |
| O | 2.871217 | 2.469784 | 1.539000 |
| C | 4.064905 | 3.189954 | 1.226889 |
| H | 4.963635 | 2.602898 | 1.491328 |
| H | 4.055103 | 3.454367 | 0.154826 |
| H | 4.032171 | 4.098576 | 1.846491 |
| H | 4.421509 | 1.121750 | -0.279567 |
| C | 4.325336 | -1.401887 | -1.152107 |
| H | 4.990736 | -0.654105 | -1.610588 |
| H | 4.941021 | -2.130530 | -0.601478 |
| H | 3.806871 | -1.952140 | -1.954264 |
| C | 1.908006 | -2.720708 | 0.198286 |
| N | 2.156282 | -1.329568 | 0.165887 |
| O | 3.000510 | -3.441712 | -0.005758 |
| C | 2.828422 | -4.867074 | -0.038160 |
| H | 2.440133 | -5.226451 | 0.928273 |
| H | 2.129756 | -5.148052 | -0.842850 |
| H | 3.827771 | -5.279525 | -0.232205 |
| O | 0.809507 | -3.177404 | 0.420733 |
| C | 2.607190 | 1.308594 | 0.943559 |
| H | 0.287307 | -1.130800 | 1.010275 |
| C | 0.367816 | -0.126473 | -1.552363 |
| H | 1.276673 | 0.488075 | -1.612692 |
| C | 0.450754 | -1.371832 | -2.423360 |
| H | 0.705245 | -1.106575 | -3.469656 |
| H | 1.243397 | -2.063133 | -2.089749 |
| H | -0.500011 | -1.931951 | -2.445223 |

| | | | |
|---|---|---|---|
| H | -0.392518 | 0.566437 | -1.990521 |
| Mg | -1.545669 | -0.002792 | -0.347445 |
| Br | -3.326987 | -0.872359 | -1.818545 |
| O | -1.809697 | 2.030524 | -0.151156 |
| O | -2.143928 | -0.562565 | 1.551178 |
| C | -0.696411 | 2.917718 | -0.473980 |
| H | 0.194502 | 2.289445 | -0.589581 |
| H | -0.894275 | 3.374075 | -1.458392 |
| C | -0.444002 | 3.957973 | 0.599448 |
| H | 0.464296 | 4.512439 | 0.308004 |
| H | -1.278210 | 4.671611 | 0.714672 |
| H | -0.252209 | 3.477242 | 1.574808 |
| C | -3.126497 | 2.588959 | -0.397313 |
| H | -3.414282 | 2.325182 | -1.429462 |
| H | -3.052322 | 3.684712 | -0.319984 |
| C | -4.124856 | 2.050543 | 0.608474 |
| H | -3.836448 | 2.329227 | 1.635527 |
| H | -5.121215 | 2.474978 | 0.395230 |
| H | -4.203983 | 0.952730 | 0.540422 |
| C | -3.003917 | -1.730429 | 1.714930 |
| H | -3.496572 | -1.649568 | 2.696826 |
| H | -3.772828 | -1.655425 | 0.930946 |
| C | -2.212590 | -3.015707 | 1.583413 |
| H | -1.435473 | -3.093896 | 2.361439 |
| H | -2.897882 | -3.877007 | 1.676612 |
| H | -1.712484 | -3.072241 | 0.603292 |
| C | -1.975426 | 0.261899 | 2.729998 |
| H | -1.559090 | 1.212436 | 2.364583 |
| H | -2.976555 | 0.483088 | 3.138277 |
| C | -1.077837 | -0.382706 | 3.771866 |
| H | -1.510327 | -1.323028 | 4.153499 |
| H | -0.077660 | -0.598056 | 3.359850 |
| H | -0.958420 | 0.307082 | 4.625597 |

**$L1_2Cu_2Br_2$**

| | | | |
|---|---|---|---|
| Cu | 1.590639 | -0.520803 | 0.070896 |
| C | 4.100180 | 1.415491 | 1.021771 |
| H | 5.029223 | 1.358179 | 1.614758 |
| H | 4.218611 | 2.267768 | 0.332649 |
| C | 2.891252 | 1.641965 | 1.948256 |
| H | 2.808218 | 0.829742 | 2.688301 |
| H | 2.994537 | 2.593157 | 2.499183 |
| C | 5.083268 | -1.323893 | 0.775049 |
| C | 4.974559 | 0.121823 | -1.573366 |
| C | 6.458418 | -0.879466 | 0.213962 |
| H | 5.035909 | -1.164674 | 1.864219 |
| C | 6.295270 | -0.650287 | -1.296455 |
| H | 4.410782 | -0.393766 | -2.367329 |
| H | 6.768195 | 0.058647 | 0.710088 |
| H | 7.237324 | -1.632122 | 0.430047 |
| H | 7.166942 | -0.127630 | -1.723682 |
| H | 6.238763 | -1.629872 | -1.799611 |
| C | 1.347538 | 3.352123 | 0.192318 |
| C | -0.095143 | 2.038415 | 2.213266 |
| C | 0.474393 | 4.209065 | 1.144320 |
| H | 2.397491 | 3.685937 | 0.257799 |
| C | -0.686638 | 3.328611 | 1.619078 |
| H | -0.805001 | 1.204957 | 2.087853 |
| H | 1.086969 | 4.531835 | 2.003281 |
| H | 0.104196 | 5.119187 | 0.647604 |
| H | -1.347129 | 3.844941 | 2.332991 |
| H | -1.314354 | 3.072566 | 0.749070 |
| P | 3.881386 | -0.127524 | -0.024704 |
| P | 1.293476 | 1.620809 | 0.980720 |
| C | 0.945441 | 3.472231 | -1.274851 |
| C | 0.597586 | 2.381777 | -2.079640 |
| C | 0.975158 | 4.745570 | -1.874347 |
| C | 0.291244 | 2.547272 | -3.435437 |
| H | 0.583658 | 1.378367 | -1.659432 |

| | | | |
|---|---|---|---|
| C | 0.646065 | 4.923220 | -3.219621 |
| H | 1.267079 | 5.616409 | -1.279049 |
| C | 0.302688 | 3.819545 | -4.012305 |
| H | 0.050446 | 1.665633 | -4.036541 |
| H | 0.672245 | 5.926495 | -3.656509 |
| H | 0.054905 | 3.952549 | -5.069832 |
| C | 0.310813 | 2.096270 | 3.676875 |
| C | 0.637592 | 0.900050 | 4.343550 |
| C | 0.346602 | 3.289507 | 4.418769 |
| C | 0.988932 | 0.893736 | 5.694829 |
| H | 0.639888 | -0.040839 | 3.784694 |
| C | 0.699929 | 3.287016 | 5.774592 |
| H | 0.088472 | 4.242683 | 3.953617 |
| C | 1.023314 | 2.090630 | 6.420685 |
| H | 1.237788 | -0.054832 | 6.181261 |
| H | 0.717489 | 4.232083 | 6.326878 |
| H | 1.297520 | 2.089980 | 7.480260 |
| C | 5.075510 | 1.575113 | -1.969990 |
| C | 4.042236 | 2.144181 | -2.734773 |
| C | 6.122417 | 2.409343 | -1.541007 |
| C | 4.050673 | 3.501998 | -3.064033 |
| H | 3.207417 | 1.517084 | -3.062444 |
| C | 6.136549 | 3.768896 | -1.871915 |
| H | 6.932500 | 2.001690 | -0.929340 |
| C | 5.100146 | 4.321871 | -2.633446 |
| H | 3.225947 | 3.917340 | -3.648811 |
| H | 6.961902 | 4.400293 | -1.527542 |
| H | 5.109285 | 5.386319 | -2.887853 |
| C | 4.784571 | -2.783639 | 0.483118 |
| C | 4.157020 | -3.212667 | -0.697650 |
| C | 5.206345 | -3.761473 | 1.400338 |
| C | 3.978467 | -4.574319 | -0.964860 |
| H | 3.769402 | -2.484153 | -1.415064 |
| C | 5.016612 | -5.122752 | 1.145697 |
| H | 5.687033 | -3.447694 | 2.333071 |
| C | 4.405518 | -5.536287 | -0.044136 |

| | | | |
|---|---|---|---|
| H | 3.492191 | -4.880111 | -1.896168 |
| H | 5.345555 | -5.864056 | 1.880981 |
| H | 4.256629 | -6.601110 | -0.248428 |
| Br | 0.555033 | -1.341856 | -2.067080 |
| Br | 1.528228 | -1.946685 | 2.147162 |
| Cu | -1.018429 | -0.473498 | -0.400127 |
| P | -2.406195 | -1.560514 | 1.072873 |
| P | -2.918203 | 0.621345 | -1.441603 |
| C | -4.052564 | -0.762910 | 0.718094 |
| C | -2.845405 | -3.389001 | 0.828290 |
| C | -2.201891 | -1.646658 | 2.953580 |
| C | -4.182284 | -0.614182 | -0.809117 |
| C | -4.039619 | 2.173494 | -1.531270 |
| C | -2.822709 | 0.371519 | -3.329026 |
| H | -4.876435 | -1.367554 | 1.133450 |
| H | -4.081986 | 0.216836 | 1.227304 |
| C | -2.934693 | -3.977694 | 2.267786 |
| H | -3.849475 | -3.399031 | 0.376097 |
| C | -1.920141 | -4.142989 | -0.102949 |
| C | -2.051175 | -3.162717 | 3.227608 |
| H | -1.235000 | -1.160123 | 3.148662 |
| C | -3.282009 | -0.895706 | 3.703456 |
| H | -3.994190 | -1.580155 | -1.307055 |
| H | -5.200836 | -0.304606 | -1.098414 |
| C | -4.388384 | 2.324848 | -3.037483 |
| H | -4.946368 | 1.878391 | -0.983330 |
| C | -3.525942 | 3.426301 | -0.857987 |
| C | -3.263865 | 1.735015 | -3.902670 |
| H | -1.748643 | 0.215163 | -3.513923 |
| C | -3.551680 | -0.860927 | -3.825351 |
| H | -3.986639 | -3.945432 | 2.596446 |
| H | -2.636933 | -5.039899 | 2.265918 |
| C | -0.527712 | -4.122644 | 0.064216 |
| C | -2.455812 | -4.915601 | -1.146997 |
| H | -2.282199 | -3.392325 | 4.282585 |
| H | -0.991900 | -3.423588 | 3.062057 |

| | | | |
|---|---|---|---|
| C | -3.087849 | 0.466007 | 4.001217 |
| C | -4.501762 | -1.481793 | 4.084667 |
| H | -5.330314 | 1.785955 | -3.231634 |
| H | -4.570944 | 3.383657 | -3.288888 |
| C | -4.057725 | 3.796836 | 0.390545 |
| C | -2.582212 | 4.278617 | -1.456066 |
| H | -3.569773 | 1.641683 | -4.959077 |
| H | -2.395848 | 2.414980 | -3.886601 |
| C | -2.934454 | -2.119409 | -3.683414 |
| C | -4.832258 | -0.816219 | -4.402494 |
| C | 0.306181 | -4.859469 | -0.778815 |
| H | -0.071644 | -3.496066 | 0.833991 |
| C | -1.623353 | -5.659143 | -1.991703 |
| H | -3.539230 | -4.932940 | -1.305795 |
| C | -4.077071 | 1.221026 | 4.637367 |
| H | -2.140094 | 0.941750 | 3.741795 |
| C | -5.493250 | -0.731577 | 4.727206 |
| H | -4.691385 | -2.537637 | 3.881822 |
| C | -3.680596 | 4.989598 | 1.014099 |
| H | -4.788555 | 3.142667 | 0.878415 |
| C | -2.214259 | 5.478786 | -0.840799 |
| H | -2.120862 | 4.012113 | -2.409972 |
| C | -3.573247 | -3.287673 | -4.106185 |
| H | -1.944063 | -2.183921 | -3.220986 |
| C | -5.474631 | -1.986474 | -4.825113 |
| H | -5.345782 | 0.137865 | -4.537627 |
| C | -0.236047 | -5.635193 | -1.808975 |
| H | 1.387622 | -4.804797 | -0.632727 |
| H | -2.062138 | -6.257007 | -2.797399 |
| C | -5.290201 | 0.625376 | 5.000969 |
| H | -3.892061 | 2.277519 | 4.855895 |
| H | -6.432781 | -1.214487 | 5.014089 |
| C | -2.763042 | 5.843038 | 0.393181 |
| H | -4.110181 | 5.254261 | 1.985432 |
| H | -1.481419 | 6.125566 | -1.329974 |
| C | -4.849157 | -3.228376 | -4.679400 |

| | | | |
|---|---|---|---|
| H | -3.066831 | -4.248313 | -3.982178 |
| H | -6.471057 | -1.921823 | -5.273887 |
| H | 0.418221 | -6.209389 | -2.473009 |
| H | -6.067841 | 1.211332 | 5.500524 |
| H | -2.467582 | 6.781055 | 0.873116 |
| H | -5.350327 | -4.142993 | -5.011227 |

**$MgBr_2(Et_2O)_2$**

| | | | |
|---|---|---|---|
| Mg | 0.219837 | 0.274765 | -0.436485 |
| Br | 2.401177 | -0.652142 | -1.207000 |
| O | 0.306432 | 0.129824 | 1.620109 |
| O | -1.164052 | -1.174980 | -0.907896 |
| C | 1.549649 | -0.176877 | 2.299713 |
| H | 1.311087 | -0.572434 | 3.300471 |
| H | 2.014255 | -0.981210 | 1.710584 |
| C | -0.760491 | 0.641669 | 2.453816 |
| H | -0.335929 | 1.382165 | 3.153453 |
| H | -1.431539 | 1.181407 | 1.766991 |
| C | 2.460910 | 1.036393 | 2.372051 |
| H | 1.982486 | 1.872088 | 2.911512 |
| H | 3.390958 | 0.770277 | 2.905119 |
| H | 2.729032 | 1.374797 | 1.356612 |
| C | -1.494885 | -0.469351 | 3.185433 |
| H | -2.322811 | -0.036809 | 3.774259 |
| H | -1.915399 | -1.194086 | 2.469380 |
| H | -0.832765 | -1.012915 | 3.881224 |
| C | -2.508478 | -0.850370 | -1.333171 |
| H | -2.504031 | 0.240115 | -1.478474 |
| H | -2.682811 | -1.328639 | -2.313554 |
| C | -0.787223 | -2.575149 | -0.943217 |
| H | -1.532283 | -3.115704 | -1.550497 |
| H | 0.182381 | -2.615013 | -1.463942 |
| C | -3.561734 | -1.255191 | -0.316563 |
| H | -3.369672 | -0.771511 | 0.656562 |
| H | -4.555804 | -0.932219 | -0.673168 |

| | | | |
|---|---|---|---|
| H | -3.594252 | -2.348154 | -0.168366 |
| C | -0.670300 | -3.160994 | 0.453415 |
| H | 0.064571 | -2.595543 | 1.050625 |
| H | -1.636584 | -3.142481 | 0.983904 |
| H | -0.327954 | -4.208905 | 0.385122 |
| Br | -0.851882 | 2.479515 | -0.854330 |

**$L1_2Cu_2BrEt$**

| | | | |
|---|---|---|---|
| Cu | -1.443142 | 0.397520 | 0.036559 |
| C | -3.940376 | -1.633754 | 1.004724 |
| H | -4.858102 | -1.601114 | 1.616624 |
| H | -4.076230 | -2.452925 | 0.279726 |
| C | -2.717942 | -1.921493 | 1.893860 |
| H | -2.644235 | -1.182737 | 2.707126 |
| H | -2.793327 | -2.926791 | 2.344544 |
| C | -4.942471 | 1.112266 | 0.881356 |
| C | -4.934585 | -0.288033 | -1.493216 |
| C | -6.337834 | 0.643649 | 0.396785 |
| H | -4.820238 | 0.945239 | 1.962377 |
| C | -6.262011 | 0.433025 | -1.123103 |
| H | -4.436983 | 0.269622 | -2.302455 |
| H | -6.599302 | -0.305291 | 0.899561 |
| H | -7.118968 | 1.376536 | 0.666778 |
| H | -7.140795 | -0.116296 | -1.499303 |
| H | -6.274609 | 1.417790 | -1.618856 |
| C | -1.115904 | -3.394503 | -0.033823 |
| C | 0.290748 | -2.189935 | 2.077526 |
| C | -0.136064 | -4.273054 | 0.789353 |
| H | -2.134420 | -3.812327 | 0.047438 |
| C | 0.964566 | -3.354815 | 1.332515 |
| H | 0.926114 | -1.293909 | 2.030949 |
| H | -0.687177 | -4.742775 | 1.621228 |
| H | 0.292057 | -5.085625 | 0.181707 |
| H | 1.685304 | -3.889783 | 1.971270 |
| H | 1.542396 | -2.954735 | 0.482109 |

| | | | |
|---|---|---|---|
| P | -3.754627 | -0.048485 | 0.005827 |
| P | -1.143977 | -1.744196 | 0.912962 |
| C | -0.782619 | -3.366711 | -1.525042 |
| C | -0.499409 | -2.209783 | -2.262844 |
| C | -0.795053 | -4.594966 | -2.214610 |
| C | -0.234961 | -2.278148 | -3.637226 |
| H | -0.488543 | -1.236819 | -1.768142 |
| C | -0.512179 | -4.671871 | -3.579001 |
| H | -1.036992 | -5.513534 | -1.670531 |
| C | -0.229501 | -3.506102 | -4.302517 |
| H | -0.034162 | -1.357877 | -4.192480 |
| H | -0.525711 | -5.643409 | -4.083060 |
| H | -0.014392 | -3.555638 | -5.374275 |
| C | -0.060732 | -2.436205 | 3.534753 |
| C | -0.414121 | -1.341210 | 4.346182 |
| C | -0.019278 | -3.707487 | 4.133782 |
| C | -0.719367 | -1.508265 | 5.698764 |
| H | -0.481758 | -0.344512 | 3.899266 |
| C | -0.325735 | -3.878475 | 5.490084 |
| H | 0.266153 | -4.587327 | 3.554205 |
| C | -0.678356 | -2.781096 | 6.280818 |
| H | -0.993311 | -0.634980 | 6.299636 |
| H | -0.282948 | -4.880810 | 5.928528 |
| H | -0.916710 | -2.915654 | 7.340642 |
| C | -5.019915 | -1.727516 | -1.939973 |
| C | -4.023313 | -2.239598 | -2.789420 |
| C | -6.018124 | -2.606600 | -1.483954 |
| C | -4.020164 | -3.583251 | -3.173486 |
| H | -3.225655 | -1.579349 | -3.143501 |
| C | -6.020479 | -3.951851 | -1.868351 |
| H | -6.797261 | -2.245533 | -0.806462 |
| C | -5.020701 | -4.447235 | -2.713849 |
| H | -3.224306 | -3.952738 | -3.825249 |
| H | -6.807460 | -4.617742 | -1.499898 |
| H | -5.020648 | -5.500603 | -3.011011 |
| C | -4.703170 | 2.582887 | 0.589257 |

| | | | |
|---|---|---|---|
| C | -4.220900 | 3.048524 | -0.645658 |
| C | -5.055827 | 3.537074 | 1.559357 |
| C | -4.123252 | 4.417683 | -0.913989 |
| H | -3.896695 | 2.341475 | -1.413203 |
| C | -4.953979 | 4.906811 | 1.299521 |
| H | -5.416058 | 3.196917 | 2.535671 |
| C | -4.495784 | 5.354316 | 0.054330 |
| H | -3.741351 | 4.749345 | -1.884038 |
| H | -5.231807 | 5.628474 | 2.074393 |
| H | -4.412484 | 6.425880 | -0.152147 |
| C | -0.694678 | 1.756973 | -1.422970 |
| Br | -1.669150 | 1.554870 | 2.466289 |
| Cu | 0.881916 | 0.688911 | -0.456606 |
| P | 2.330678 | 1.586504 | 1.111738 |
| P | 2.768963 | -0.039607 | -1.741680 |
| C | 4.019461 | 1.198026 | 0.413739 |
| C | 2.466325 | 3.472437 | 1.321014 |
| C | 2.364337 | 1.178985 | 2.963269 |
| C | 3.930206 | 1.297455 | -1.120008 |
| C | 4.067457 | -1.439432 | -1.869221 |
| C | 2.634213 | 0.243310 | -3.623285 |
| H | 4.784954 | 1.880743 | 0.820598 |
| H | 4.301750 | 0.178354 | 0.728802 |
| C | 2.628026 | 3.699158 | 2.848109 |
| H | 3.400415 | 3.755379 | 0.811136 |
| C | 1.338878 | 4.208483 | 0.629784 |
| C | 2.014740 | 2.526664 | 3.635510 |
| H | 1.520336 | 0.489709 | 3.113100 |
| C | 3.633991 | 0.471257 | 3.384467 |
| H | 3.524228 | 2.275386 | -1.430323 |
| H | 4.923083 | 1.199336 | -1.591145 |
| C | 4.496908 | -1.442426 | -3.362689 |
| H | 4.910258 | -1.075457 | -1.263180 |
| C | 3.695590 | -2.792008 | -1.304098 |
| C | 3.332706 | -0.982659 | -4.254019 |
| H | 1.555360 | 0.193674 | -3.828686 |

| | | | |
|---|---|---|---|
| C | 3.110028 | 1.617307 | -4.042236 |
| H | 3.704849 | 3.778729 | 3.072663 |
| H | 2.171143 | 4.657101 | 3.150250 |
| C | 0.084121 | 4.385487 | 1.231597 |
| C | 1.526155 | 4.697541 | -0.675036 |
| H | 2.338621 | 2.534901 | 4.690956 |
| H | 0.914978 | 2.613818 | 3.633427 |
| C | 3.750450 | -0.914101 | 3.155736 |
| C | 4.734453 | 1.137493 | 3.948764 |
| H | 5.350264 | -0.753775 | -3.480577 |
| H | 4.854780 | -2.442914 | -3.660467 |
| C | 4.309498 | -3.222816 | -0.113595 |
| C | 2.816283 | -3.675668 | -1.953079 |
| H | 3.673353 | -0.759595 | -5.280001 |
| H | 2.592000 | -1.796113 | -4.338459 |
| C | 2.217670 | 2.702379 | -3.954980 |
| C | 4.423719 | 1.875857 | -4.469281 |
| C | -0.954914 | 5.022879 | 0.549627 |
| H | -0.109866 | 3.984569 | 2.226456 |
| C | 0.493254 | 5.349609 | -1.355182 |
| H | 2.492722 | 4.561259 | -1.172613 |
| C | 4.923484 | -1.606271 | 3.465073 |
| H | 2.911346 | -1.459515 | 2.715679 |
| C | 5.910497 | 0.446317 | 4.265739 |
| H | 4.684230 | 2.209988 | 4.149046 |
| C | 4.077421 | -4.501658 | 0.400565 |
| H | 4.987511 | -2.546339 | 0.417898 |
| C | 2.591223 | -4.959312 | -1.446584 |
| H | 2.292266 | -3.368396 | -2.860731 |
| C | 2.624829 | 4.000555 | -4.273522 |
| H | 1.190061 | 2.527134 | -3.624660 |
| C | 4.833732 | 3.174817 | -4.790883 |
| H | 5.145780 | 1.060902 | -4.555962 |
| C | -0.754422 | 5.513024 | -0.744434 |
| H | -1.936773 | 5.105966 | 1.022293 |
| H | 0.663329 | 5.726360 | -2.368553 |

| | | | |
|---|---|---|---|
| C | 6.014085 | -0.926965 | 4.021852 |
| H | 4.981997 | -2.682266 | 3.272223 |
| H | 6.752287 | 0.989938 | 4.706329 |
| C | 3.223691 | -5.381268 | -0.272345 |
| H | 4.568191 | -4.810464 | 1.329188 |
| H | 1.903121 | -5.626004 | -1.972676 |
| C | 3.938367 | 4.244921 | -4.690736 |
| H | 1.908852 | 4.824444 | -4.199992 |
| H | 5.862475 | 3.348997 | -5.121760 |
| H | -1.571842 | 6.007061 | -1.277746 |
| H | 6.935015 | -1.464704 | 4.267129 |
| H | 3.039641 | -6.384695 | 0.123478 |
| H | 4.259811 | 5.260609 | -4.940580 |
| H | 0.261893 | 2.314056 | -1.572951 |
| C | -1.258547 | 1.409058 | -2.807544 |
| H | -1.313947 | 2.540042 | -0.948962 |
| H | -1.393006 | 2.298123 | -3.460732 |
| H | -0.600638 | 0.707429 | -3.349255 |
| H | -2.240629 | 0.907468 | -2.733413 |

**$L1_2Cu_2Et_2$**

| | | | |
|---|---|---|---|
| Cu | -1.145428 | 0.146785 | 0.361774 |
| C | -4.414164 | 1.002846 | 0.219185 |
| H | -5.184061 | 1.647200 | 0.679217 |
| H | -4.704559 | 0.869401 | -0.835536 |
| C | -4.343459 | -0.360980 | 0.921660 |
| H | -4.104393 | -0.240496 | 1.992708 |
| H | -5.314736 | -0.881717 | 0.865107 |
| C | -2.986389 | 3.074710 | 1.650159 |
| C | -2.849041 | 3.182205 | -1.131503 |
| C | -3.640263 | 4.307914 | 0.975752 |
| H | -3.695433 | 2.613327 | 2.357078 |
| C | -2.949146 | 4.530500 | -0.377134 |
| H | -1.876887 | 3.113812 | -1.640680 |
| H | -4.715711 | 4.104712 | 0.823746 |

| | | | |
|---|---|---|---|
| H | -3.567402 | 5.199732 | 1.623162 |
| H | -3.467952 | 5.293833 | -0.981786 |
| H | -1.930378 | 4.914877 | -0.202160 |
| C | -3.831038 | -2.095680 | -1.345393 |
| C | -3.023560 | -3.029967 | 1.139131 |
| C | -4.615631 | -3.320289 | -0.811769 |
| H | -4.536283 | -1.332223 | -1.711716 |
| C | -3.747173 | -4.053403 | 0.222860 |
| H | -1.966198 | -3.314901 | 1.235226 |
| H | -5.545739 | -2.961298 | -0.335132 |
| H | -4.917365 | -3.991586 | -1.635939 |
| H | -4.345153 | -4.767409 | 0.814150 |
| H | -2.985993 | -4.655103 | -0.299092 |
| P | -2.735505 | 1.842662 | 0.238438 |
| P | -2.964230 | -1.384763 | 0.175525 |
| C | -2.855363 | -2.407407 | -2.462344 |
| C | -1.668016 | -3.131915 | -2.249855 |
| C | -3.132297 | -1.965171 | -3.767018 |
| C | -0.808734 | -3.424573 | -3.311876 |
| H | -1.379780 | -3.453726 | -1.245812 |
| C | -2.261437 | -2.235176 | -4.828286 |
| H | -4.044753 | -1.389541 | -3.951034 |
| C | -1.095447 | -2.975207 | -4.605374 |
| H | 0.098237 | -4.003556 | -3.121244 |
| H | -2.497470 | -1.866941 | -5.831857 |
| H | -0.410178 | -3.193276 | -5.430214 |
| C | -3.569245 | -2.850165 | 2.536864 |
| C | -2.701234 | -2.436073 | 3.563674 |
| C | -4.929403 | -3.019103 | 2.848638 |
| C | -3.174273 | -2.193964 | 4.856512 |
| H | -1.642406 | -2.290131 | 3.336505 |
| C | -5.405739 | -2.783335 | 4.143138 |
| H | -5.634631 | -3.330789 | 2.073055 |
| C | -4.531422 | -2.366952 | 5.153660 |
| H | -2.476758 | -1.866765 | 5.634179 |
| H | -6.469582 | -2.922345 | 4.361164 |

| | | | |
|---|---|---|---|
| H | -4.905215 | -2.179110 | 6.165044 |
| C | -3.927201 | 2.879813 | -2.149480 |
| C | -3.682301 | 1.913463 | -3.144410 |
| C | -5.198111 | 3.478486 | -2.113737 |
| C | -4.666046 | 1.566335 | -4.074118 |
| H | -2.711022 | 1.414704 | -3.179091 |
| C | -6.186685 | 3.130563 | -3.042045 |
| H | -5.434074 | 4.225832 | -1.352390 |
| C | -5.926830 | 2.173691 | -4.028374 |
| H | -4.442771 | 0.819753 | -4.842451 |
| H | -7.167771 | 3.613595 | -2.991014 |
| H | -6.698938 | 1.903616 | -4.755352 |
| C | -1.716733 | 3.407818 | 2.403795 |
| C | -0.478972 | 3.569030 | 1.760791 |
| C | -1.768821 | 3.589808 | 3.796626 |
| C | 0.662043 | 3.917887 | 2.487492 |
| H | -0.376941 | 3.386943 | 0.687984 |
| C | -0.625376 | 3.924526 | 4.528596 |
| H | -2.722778 | 3.455685 | 4.317994 |
| C | 0.598917 | 4.094929 | 3.872507 |
| H | 1.603409 | 4.046652 | 1.954060 |
| H | -0.691424 | 4.048810 | 5.614260 |
| H | 1.499920 | 4.355437 | 4.436890 |
| Cu | 1.095846 | 0.456737 | -0.549946 |
| P | 3.090357 | 1.322758 | 0.194469 |
| P | 2.527999 | -1.978277 | -0.544820 |
| C | 4.445710 | 0.184135 | -0.408436 |
| C | 3.803509 | 2.980172 | -0.403821 |
| C | 3.530902 | 1.675850 | 2.035320 |
| C | 4.223777 | -1.300685 | -0.100903 |
| C | 2.824686 | -3.749661 | 0.115051 |
| C | 2.721450 | -2.513513 | -2.381424 |
| H | 4.481160 | 0.349935 | -1.497138 |
| H | 5.421579 | 0.496550 | -0.003832 |
| C | 4.900177 | 3.289347 | 0.631470 |
| H | 4.250458 | 2.770685 | -1.391770 |

| | | | |
|---|---|---|---|
| C | 2.739484 | 4.054680 | -0.598061 |
| C | 4.329269 | 3.010690 | 2.032484 |
| H | 2.552142 | 1.826320 | 2.516133 |
| C | 4.209156 | 0.504602 | 2.712816 |
| H | 5.023748 | -1.890186 | -0.579612 |
| H | 4.309002 | -1.473216 | 0.983982 |
| C | 3.574051 | -4.483568 | -1.018039 |
| H | 3.496515 | -3.626916 | 0.979764 |
| C | 1.554146 | -4.391866 | 0.635674 |
| C | 3.037466 | -4.032045 | -2.387256 |
| H | 1.718308 | -2.349205 | -2.801225 |
| C | 3.673442 | -1.611874 | -3.129789 |
| H | 5.767501 | 2.635678 | 0.439405 |
| H | 5.279237 | 4.321641 | 0.544111 |
| C | 2.800552 | 5.318415 | 0.012511 |
| C | 1.656627 | 3.796121 | -1.459123 |
| H | 5.125608 | 2.998674 | 2.794781 |
| H | 3.648487 | 3.829580 | 2.315395 |
| C | 3.435611 | -0.470466 | 3.368785 |
| C | 5.602629 | 0.316303 | 2.667675 |
| H | 4.645554 | -4.227675 | -0.944117 |
| H | 3.506168 | -5.580616 | -0.901971 |
| C | 1.158365 | -4.127881 | 1.961605 |
| C | 0.747409 | -5.251955 | -0.128255 |
| H | 3.745974 | -4.289643 | -3.192762 |
| H | 2.110430 | -4.580421 | -2.620680 |
| C | 3.183599 | -0.415475 | -3.684459 |
| C | 5.051136 | -1.871268 | -3.232847 |
| C | 1.809499 | 6.281924 | -0.215255 |
| H | 3.621728 | 5.571671 | 0.685851 |
| C | 0.673414 | 4.757686 | -1.698580 |
| H | 1.578373 | 2.816081 | -1.932092 |
| C | 4.023495 | -1.614354 | 3.916380 |
| H | 2.354194 | -0.340160 | 3.433035 |
| C | 6.195332 | -0.826098 | 3.216215 |
| H | 6.242983 | 1.060900 | 2.187525 |

| | | | |
|---|---|---|---|
| C | 0.014918 | -4.712333 | 2.508972 |
| H | 1.762294 | -3.448651 | 2.571986 |
| C | -0.405148 | -5.834997 | 0.414203 |
| H | 1.016138 | -5.488720 | -1.159290 |
| C | 4.038896 | 0.506453 | -4.292679 |
| H | 2.117104 | -0.201335 | -3.611461 |
| C | 5.912221 | -0.951286 | -3.842787 |
| H | 5.467912 | -2.795379 | -2.822296 |
| C | 0.739984 | 6.007444 | -1.070921 |
| H | 1.878424 | 7.252929 | 0.285013 |
| H | -0.151020 | 4.530017 | -2.380286 |
| C | 5.407895 | -1.804477 | 3.833324 |
| H | 3.393888 | -2.360448 | 4.411796 |
| H | 7.280919 | -0.952609 | 3.156129 |
| C | -0.774299 | -5.573344 | 1.736289 |
| H | -0.269082 | -4.487955 | 3.541420 |
| H | -1.015238 | -6.499669 | -0.205431 |
| C | 5.413022 | 0.246102 | -4.368028 |
| H | 3.628797 | 1.433863 | -4.705514 |
| H | 6.982778 | -1.171892 | -3.903215 |
| H | -0.036203 | 6.757979 | -1.248453 |
| H | 5.870636 | -2.701902 | 4.255214 |
| H | -1.679291 | -6.020599 | 2.157995 |
| H | 6.088806 | 0.966907 | -4.838617 |
| C | -0.151743 | 0.236136 | -2.146670 |
| H | 0.149232 | -0.743609 | -2.566518 |
| H | -1.231856 | 0.081359 | -1.941379 |
| C | -0.063371 | 1.297923 | -3.253019 |
| H | -0.474398 | 2.267641 | -2.921900 |
| H | 0.976991 | 1.504309 | -3.566290 |
| H | -0.618379 | 1.018639 | -4.176777 |
| C | 0.076936 | -0.464704 | 1.873814 |
| H | -0.108727 | -1.556603 | 1.931513 |
| H | 1.172138 | -0.397574 | 1.752363 |
| C | -0.302427 | 0.205529 | 3.201925 |
| H | 0.003585 | 1.265529 | 3.215266 |

| | | | |
|---|---|---|---|
| H | -1.395599 | 0.201352 | 3.371490 |
| H | 0.153604 | -0.275042 | 4.101323 |

**L1-CuEt$_2$**

| | | | |
|---|---|---|---|
| Cu | -0.464752 | 0.274120 | -1.512975 |
| C | -0.131472 | -0.314777 | 1.858453 |
| H | -0.669936 | -0.227224 | 2.819541 |
| H | 0.571483 | -1.157734 | 1.970869 |
| C | 0.638967 | 0.974153 | 1.548385 |
| H | -0.046091 | 1.837263 | 1.503324 |
| H | 1.377533 | 1.185225 | 2.342261 |
| C | -2.895144 | 0.000509 | 1.100290 |
| C | -1.870959 | -2.554125 | 0.889216 |
| C | -3.414589 | -1.009732 | 2.149765 |
| H | -2.632810 | 0.955743 | 1.586491 |
| C | -3.266894 | -2.413149 | 1.545614 |
| H | -1.974217 | -3.030709 | -0.097618 |
| H | -2.811163 | -0.924559 | 3.071579 |
| H | -4.462383 | -0.796536 | 2.431782 |
| H | -3.448869 | -3.202190 | 2.296614 |
| H | -4.036329 | -2.539014 | 0.764100 |
| C | 3.071125 | -0.072230 | 0.380017 |
| C | 2.374960 | 2.571961 | -0.241766 |
| C | 4.052927 | 1.018471 | 0.831581 |
| H | 2.777546 | -0.704857 | 1.235497 |
| C | 3.879313 | 2.239203 | -0.087448 |
| H | 2.179596 | 2.916530 | -1.268548 |
| H | 3.814574 | 1.296303 | 1.872014 |
| H | 5.100881 | 0.666751 | 0.843024 |
| H | 4.445057 | 3.112928 | 0.283064 |
| H | 4.287305 | 1.998412 | -1.084151 |
| P | -1.283352 | -0.744829 | 0.437615 |
| P | 1.455599 | 0.869615 | -0.139851 |
| C | 3.536194 | -0.995064 | -0.728793 |
| C | 2.725900 | -2.096236 | -1.071439 |

| | | | |
|---|---|---|---|
| C | 4.728395 | -0.817243 | -1.450599 |
| C | 3.089771 | -2.984647 | -2.084045 |
| H | 1.782673 | -2.241559 | -0.539638 |
| C | 5.098438 | -1.705029 | -2.470626 |
| H | 5.393649 | 0.019058 | -1.223784 |
| C | 4.282934 | -2.793315 | -2.793429 |
| H | 2.431758 | -3.824953 | -2.327771 |
| H | 6.033774 | -1.538847 | -3.015442 |
| H | 4.570760 | -3.484523 | -3.592037 |
| C | 1.840621 | 3.630913 | 0.698517 |
| C | 0.790057 | 4.468492 | 0.278389 |
| C | 2.336401 | 3.815740 | 2.002991 |
| C | 0.245641 | 5.436754 | 1.126813 |
| H | 0.390936 | 4.353777 | -0.731237 |
| C | 1.796691 | 4.785484 | 2.855312 |
| H | 3.157401 | 3.196815 | 2.371045 |
| C | 0.743381 | 5.599486 | 2.425024 |
| H | -0.573129 | 6.069171 | 0.768229 |
| H | 2.204731 | 4.903003 | 3.864701 |
| H | 0.318707 | 6.356245 | 3.092281 |
| C | -0.823361 | -3.312927 | 1.655737 |
| C | 0.212139 | -3.959485 | 0.952825 |
| C | -0.775757 | -3.341649 | 3.062353 |
| C | 1.264581 | -4.590147 | 1.622768 |
| H | 0.188730 | -3.959076 | -0.141289 |
| C | 0.269102 | -3.981333 | 3.736949 |
| H | -1.556745 | -2.844845 | 3.644477 |
| C | 1.300359 | -4.603527 | 3.022163 |
| H | 2.060791 | -5.072369 | 1.046380 |
| H | 0.281244 | -3.987064 | 4.831943 |
| H | 2.121925 | -5.096609 | 3.551166 |
| C | -3.929831 | 0.280009 | 0.024024 |
| C | -4.935054 | 1.231018 | 0.270351 |
| C | -3.952512 | -0.400178 | -1.204419 |
| C | -5.931623 | 1.496509 | -0.674570 |
| H | -4.930140 | 1.778833 | 1.219391 |

| | | | |
|---|---|---|---|
| C | -4.947480 | -0.141600 | -2.152984 |
| H | -3.153261 | -1.105155 | -1.448019 |
| C | -5.942012 | 0.807871 | -1.893574 |
| H | -6.698617 | 2.248382 | -0.460975 |
| H | -4.934121 | -0.677352 | -3.107632 |
| H | -6.716523 | 1.015266 | -2.639080 |
| C | -0.399770 | -0.945477 | -3.201950 |
| H | 0.572328 | -0.890618 | -3.745287 |
| H | -1.147883 | -0.580987 | -3.945934 |
| C | -0.697920 | -2.429300 | -2.932633 |
| H | -0.708333 | -3.096718 | -3.832566 |
| H | 0.043686 | -2.865993 | -2.234391 |
| H | -1.684492 | -2.564015 | -2.442623 |
| C | -1.374775 | 2.148035 | -1.516276 |
| C | -0.853593 | 3.004449 | -2.677061 |
| H | -2.463685 | 1.985145 | -1.653902 |
| H | -1.283492 | 2.720603 | -0.568451 |
| H | -1.291861 | 4.032472 | -2.754707 |
| H | 0.245565 | 3.144937 | -2.628961 |
| H | -1.045361 | 2.512064 | -3.651460 |

**$CuEt_2$**

| | | | |
|---|---|---|---|
| Cu | 0.000002 | -0.000005 | -0.076694 |
| C | -1.862765 | 0.686864 | -0.070416 |
| H | -2.110147 | 1.194897 | -1.032634 |
| H | -1.994674 | 1.485240 | 0.697935 |
| C | -2.924541 | -0.402164 | 0.183838 |
| H | -3.978782 | -0.034634 | 0.191486 |
| H | -2.878452 | -1.201518 | -0.582800 |
| H | -2.763109 | -0.907460 | 1.157321 |
| C | 1.862768 | -0.686873 | -0.070354 |
| C | 2.924532 | 0.402184 | 0.183828 |
| H | 1.994682 | -1.485190 | 0.698057 |
| H | 2.110165 | -1.194971 | -1.032534 |
| H | 3.978777 | 0.034666 | 0.191511 |

| | | | |
|---|---|---|---|
| H | 2.878442 | 1.201481 | -0.582870 |
| H | 2.763087 | 0.907553 | 1.157272 |

**L8-CuEt**

| | | | |
|---|---|---|---|
| Cu | 0.150245 | -1.768627 | 0.112052 |
| C | 2.871498 | 0.410494 | 1.281772 |
| C | 2.624263 | 0.541461 | -1.465491 |
| C | 4.053075 | 1.032692 | 0.513163 |
| C | 4.053473 | 0.425341 | -0.895479 |
| H | 3.928807 | 2.130484 | 0.450739 |
| H | 5.006493 | 0.849712 | 1.042033 |
| H | 4.781405 | 0.919026 | -1.564267 |
| H | 4.340638 | -0.642406 | -0.837245 |
| C | -2.696774 | -0.341959 | -1.521300 |
| C | -3.148082 | -0.425208 | 1.206311 |
| C | -4.138421 | -0.062542 | -1.058018 |
| C | -4.334841 | -0.781206 | 0.282603 |
| H | -4.288710 | 1.026430 | -0.932992 |
| H | -4.867865 | -0.399605 | -1.817369 |
| H | -5.294509 | -0.517472 | 0.762213 |
| H | -4.349948 | -1.874944 | 0.112655 |
| P | 1.498725 | 0.156515 | 0.002182 |
| P | -1.651938 | -0.336514 | 0.058093 |
| C | 0.749913 | -3.669115 | 0.228105 |
| H | 0.292060 | -4.293346 | -0.571700 |
| H | 0.406888 | -4.142167 | 1.175395 |
| C | 2.282096 | -3.796532 | 0.138145 |
| H | 2.667027 | -4.841627 | 0.200321 |
| H | 2.667661 | -3.374416 | -0.811534 |
| H | 2.782936 | -3.226198 | 0.946045 |
| C | 0.375379 | 1.630819 | 0.120822 |
| C | 0.863223 | 2.951067 | 0.143757 |
| H | 1.938294 | 3.137650 | 0.074717 |
| C | -1.022941 | 1.410428 | 0.194029 |
| C | -1.883519 | 2.518631 | 0.306731 |

| | | | |
|---|---|---|---|
| H | -2.965451 | 2.372102 | 0.360458 |
| C | -1.383243 | 3.821732 | 0.341154 |
| H | -2.071610 | 4.667963 | 0.427327 |
| C | -0.003281 | 4.039823 | 0.255086 |
| H | 0.397765 | 5.057689 | 0.275585 |
| C | -2.934694 | -1.409889 | 2.358170 |
| H | -3.852339 | -1.497759 | 2.969567 |
| H | -2.675296 | -2.413451 | 1.974795 |
| H | -2.113800 | -1.084273 | 3.021833 |
| C | -2.186005 | 0.542648 | -2.656808 |
| H | -1.145311 | 0.289662 | -2.929475 |
| H | -2.813627 | 0.407257 | -3.556892 |
| H | -2.213603 | 1.611029 | -2.380393 |
| C | 2.346389 | -0.360400 | -2.669120 |
| H | 2.455583 | -1.426141 | -2.397025 |
| H | 1.320505 | -0.215566 | -3.053423 |
| H | 3.050829 | -0.140001 | -3.492857 |
| C | 2.476099 | 1.116781 | 2.577283 |
| H | 3.326231 | 1.114931 | 3.284422 |
| H | 2.187010 | 2.166730 | 2.400004 |
| H | 1.626474 | 0.611100 | 3.070343 |
| H | -3.309117 | 0.584156 | 1.621562 |
| H | 2.441468 | 1.593341 | -1.747526 |
| H | -2.639707 | -1.397273 | -1.844711 |
| H | 3.142272 | -0.632858 | 1.528266 |

**III-L8**

| | | | |
|---|---|---|---|
| Cu | 0.762733 | 0.525987 | 1.225484 |
| C | 1.057369 | -2.545496 | 2.263230 |
| C | -0.951823 | -3.336627 | 0.559423 |
| C | 0.678822 | -4.030889 | 2.334404 |
| C | -0.777315 | -4.140340 | 1.871016 |
| H | 1.342901 | -4.620408 | 1.674277 |
| H | 0.814588 | -4.425543 | 3.358954 |
| H | -1.097994 | -5.188941 | 1.733837 |

| | | | |
|---|---|---|---|
| H | -1.433355 | -3.704306 | 2.648643 |
| C | 1.999941 | 1.467272 | -1.958656 |
| C | 4.077189 | 1.030498 | -0.143966 |
| C | 3.170675 | 2.481336 | -1.968827 |
| C | 4.438465 | 1.789389 | -1.441520 |
| H | 3.326243 | 2.875160 | -2.990683 |
| H | 2.910548 | 3.336280 | -1.319435 |
| H | 4.827192 | 1.084563 | -2.199800 |
| H | 5.244528 | 2.521732 | -1.251248 |
| P | 0.307494 | -1.906276 | 0.638793 |
| P | 2.319198 | 0.401330 | -0.421791 |
| C | -0.022536 | 0.862516 | 3.031517 |
| H | 0.092868 | 1.927101 | 3.327613 |
| H | 0.546254 | 0.289221 | 3.795769 |
| C | -1.503054 | 0.468076 | 3.123512 |
| H | -1.965708 | 0.616932 | 4.126249 |
| H | -1.654967 | -0.597923 | 2.859289 |
| C | -2.857777 | 0.399583 | -1.424879 |
| C | -4.298006 | 1.488653 | 0.145725 |
| C | -3.944300 | -0.342097 | -1.847999 |
| C | -5.387432 | 0.755307 | -0.246161 |
| C | -5.225689 | -0.196979 | -1.279426 |
| H | -3.812702 | -1.075468 | -2.644302 |
| H | -6.340242 | 0.929343 | 0.252616 |
| O | -6.180108 | -0.969192 | -1.755623 |
| C | -7.512298 | -0.899613 | -1.230266 |
| H | -7.938513 | 0.105943 | -1.386350 |
| H | -8.092250 | -1.641519 | -1.795479 |
| H | -7.519372 | -1.157821 | -0.157482 |
| C | -1.511053 | 0.171725 | -2.035694 |
| H | -1.076798 | 1.102140 | -2.431537 |
| H | -0.807856 | -0.212225 | -1.275350 |
| H | -1.605357 | -0.559961 | -2.851024 |
| C | -1.956667 | 2.163205 | 0.086463 |
| N | -3.057498 | 1.330386 | -0.414227 |
| O | -0.806089 | 1.888897 | -0.115292 |

| | | | |
|---|---|---|---|
| O | -2.432998 | 3.183903 | 0.753365 |
| C | -1.475003 | 4.031363 | 1.449185 |
| H | -2.051516 | 4.916971 | 1.747746 |
| H | -1.108582 | 3.483874 | 2.330703 |
| H | -0.620831 | 4.293349 | 0.799480 |
| Cl | 1.758138 | 4.894065 | 0.415569 |
| H | -4.366898 | 2.234740 | 0.933950 |
| C | 1.646103 | -2.363358 | -0.579453 |
| C | 1.845800 | -3.677979 | -1.041233 |
| H | 1.178299 | -4.481888 | -0.724029 |
| C | 2.900901 | -4.000973 | -1.898342 |
| H | 3.029099 | -5.033425 | -2.238080 |
| C | 2.542743 | -1.349850 | -1.010137 |
| C | 3.611917 | -1.696234 | -1.856398 |
| H | 4.322470 | -0.932168 | -2.178502 |
| C | 3.795246 | -3.006518 | -2.302583 |
| H | 4.633522 | -3.246696 | -2.963496 |
| C | 1.831995 | 0.707700 | -3.278595 |
| H | 2.777638 | 0.251889 | -3.617277 |
| H | 1.085028 | -0.101507 | -3.205022 |
| H | 1.498616 | 1.408539 | -4.066362 |
| C | 4.136696 | 1.918862 | 1.107165 |
| H | 3.514549 | 2.825333 | 0.991676 |
| H | 5.180941 | 2.235052 | 1.292641 |
| C | -2.381821 | -2.828910 | 0.352624 |
| H | -3.103059 | -3.666011 | 0.410300 |
| H | -2.662058 | -2.087754 | 1.124236 |
| H | -2.504463 | -2.350562 | -0.633435 |
| C | 2.538017 | -2.236849 | 2.468982 |
| H | 3.165774 | -2.731035 | 1.706391 |
| H | 2.721481 | -1.148699 | 2.417603 |
| H | 2.866281 | -2.590726 | 3.464045 |
| H | 1.060350 | 1.992766 | -1.725702 |
| H | 4.732235 | 0.154971 | 0.001734 |
| H | 0.479775 | -1.995775 | 3.028009 |
| H | -0.687873 | -3.974719 | -0.298624 |

| | | | |
|---|---|---|---|
| H | -2.129792 | 1.048466 | 2.416623 |
| H | 3.774433 | 1.373973 | 1.997438 |

**IV-*proR*-L8**

| | | | |
|---|---|---|---|
| Cu | -0.569573 | -0.820353 | -0.384897 |
| C | 2.564057 | -2.594477 | -1.726042 |
| C | 2.906395 | 0.062952 | -1.611854 |
| C | 4.019738 | -2.165422 | -2.077902 |
| C | 4.255848 | -0.677554 | -1.704747 |
| H | 4.743962 | -2.812580 | -1.552186 |
| H | 4.191294 | -2.331211 | -3.155530 |
| H | 4.766389 | -0.615217 | -0.728538 |
| H | 4.917650 | -0.177353 | -2.434192 |
| C | 1.039068 | 2.316215 | 1.261753 |
| C | -0.762925 | 0.952572 | 2.902331 |
| C | 0.062560 | 3.165959 | 2.105176 |
| C | -0.314901 | 2.358794 | 3.360284 |
| H | 0.519471 | 4.137793 | 2.364237 |
| H | -0.850939 | 3.390575 | 1.522648 |
| H | 0.564084 | 2.279807 | 4.024468 |
| H | -1.111541 | 2.857246 | 3.942064 |
| P | 1.774940 | -1.180448 | -0.773074 |
| P | 0.289557 | 0.574835 | 1.380844 |
| C | -1.403116 | -2.405420 | 0.572167 |
| H | -2.367640 | -2.097180 | 1.021605 |
| H | -0.699360 | -2.566392 | 1.413451 |
| C | -1.572104 | -3.693546 | -0.228562 |
| H | -1.899960 | -4.549564 | 0.401408 |
| H | -2.323842 | -3.588747 | -1.030574 |
| H | -0.624505 | -3.997329 | -0.708652 |
| C | -2.592982 | 2.061443 | -1.053781 |
| C | -1.327644 | 0.301499 | -2.163791 |
| C | -3.567960 | 1.161131 | -0.674104 |
| C | -2.243207 | -0.636907 | -1.640064 |
| H | -0.600570 | 0.005526 | -2.919423 |

| | | | |
|---|---|---|---|
| H | -2.369667 | -1.612169 | -2.107564 |
| N | -3.404388 | -0.176270 | -0.971458 |
| C | -4.317186 | -1.224368 | -0.609976 |
| O | -4.450835 | -2.213179 | -1.281634 |
| O | -4.914858 | -0.981754 | 0.542571 |
| C | -5.843071 | -1.977928 | 1.008739 |
| H | -6.260402 | -1.575623 | 1.941201 |
| H | -6.636048 | -2.138901 | 0.261448 |
| H | -5.308814 | -2.923257 | 1.195146 |
| C | -4.812388 | 1.660002 | 0.005812 |
| H | -5.720644 | 1.240590 | -0.456174 |
| H | -4.826266 | 1.376468 | 1.069713 |
| H | -4.850821 | 2.756545 | -0.070037 |
| H | -2.753277 | 3.112302 | -0.822172 |
| C | -1.452902 | 1.656668 | -1.803843 |
| O | -0.530138 | 2.483906 | -2.246324 |
| C | -0.531224 | 3.881437 | -1.917414 |
| H | -0.713387 | 4.027016 | -0.840044 |
| H | 0.491165 | 4.223003 | -2.141388 |
| H | -1.301501 | 4.403371 | -2.511897 |
| Cl | 2.922133 | 3.773482 | -1.535900 |
| C | -2.255089 | 0.903031 | 2.546710 |
| H | -2.516280 | 1.693885 | 1.823506 |
| H | -2.538867 | -0.063673 | 2.098066 |
| H | -2.869443 | 1.061413 | 3.452029 |
| C | 2.489974 | 2.446864 | 1.736443 |
| H | 3.151476 | 1.733399 | 1.220153 |
| H | 2.850130 | 3.456001 | 1.474903 |
| H | 2.595880 | 2.283195 | 2.823253 |
| C | 2.413234 | -4.010521 | -1.165332 |
| H | 1.353381 | -4.264825 | -0.996602 |
| H | 2.824621 | -4.743242 | -1.883485 |
| H | 2.947279 | -4.146073 | -0.210654 |
| C | 2.359174 | 0.498025 | -2.976544 |
| H | 1.400705 | 1.025959 | -2.864780 |
| H | 3.060339 | 1.224582 | -3.420993 |

| | | | |
|---|---|---|---|
| H | 2.231609 | -0.348459 | -3.677467 |
| H | 2.991770 | 0.973838 | -0.996469 |
| H | 1.964143 | -2.553906 | -2.653689 |
| H | -0.561956 | 0.190191 | 3.671814 |
| H | 1.028228 | 2.617066 | 0.201920 |
| C | 1.690613 | -0.486760 | 1.951133 |
| C | 2.403345 | -1.228373 | 0.971171 |
| C | 3.528457 | -1.971673 | 1.372261 |
| H | 4.109137 | -2.531793 | 0.638809 |
| C | 2.110316 | -0.532572 | 3.290792 |
| H | 1.581024 | 0.044138 | 4.053773 |
| C | 3.215904 | -1.295347 | 3.674130 |
| H | 3.524750 | -1.319230 | 4.723525 |
| C | 3.931429 | -2.010702 | 2.709621 |
| H | 4.808024 | -2.599957 | 2.995007 |

**TS-(IV-V)-*R*-L8**

| | | | |
|---|---|---|---|
| Cu | 0.193566 | -0.649696 | -0.406874 |
| C | -2.834315 | -1.645028 | -1.984450 |
| C | -3.026937 | -2.348420 | 0.671784 |
| C | -4.130311 | -2.382406 | -1.610110 |
| C | -3.836914 | -3.198224 | -0.343041 |
| H | -4.941157 | -1.653761 | -1.432648 |
| H | -4.469707 | -3.031454 | -2.438955 |
| H | -4.760043 | -3.586138 | 0.123384 |
| H | -3.229432 | -4.079086 | -0.624860 |
| C | 0.345416 | 2.785608 | 1.210122 |
| C | 0.212566 | 2.874277 | -1.568563 |
| C | 1.243828 | 3.816680 | 0.488342 |
| C | 0.577290 | 4.188379 | -0.843632 |
| H | 1.405517 | 4.703901 | 1.126876 |
| H | 2.238931 | 3.387673 | 0.287335 |
| H | -0.332517 | 4.783651 | -0.648229 |
| H | 1.236955 | 4.818300 | -1.468481 |
| P | -2.080402 | -1.074885 | -0.343253 |

| | | | |
|---|---|---|---|
| P | -0.289624 | 1.664550 | -0.188688 |
| C | 1.020819 | -1.280672 | -2.279888 |
| H | 1.935494 | -0.848140 | -2.699327 |
| H | 0.177640 | -0.614994 | -2.544157 |
| C | 0.761170 | -2.698182 | -2.754828 |
| H | 1.653459 | -3.343062 | -2.652614 |
| H | -0.058936 | -3.173462 | -2.187674 |
| H | 0.477344 | -2.716575 | -3.825868 |
| C | 2.349714 | -0.396493 | 2.083307 |
| C | 1.473483 | -2.227786 | 0.756650 |
| C | 3.133926 | 0.041315 | 1.061811 |
| C | 2.135173 | -1.667203 | -0.414217 |
| H | 0.950358 | -3.179450 | 0.658625 |
| H | 2.513793 | -2.425329 | -1.091453 |
| N | 3.183376 | -0.721001 | -0.132524 |
| C | 4.254356 | -0.737263 | -1.037382 |
| O | 4.227010 | -1.344091 | -2.086828 |
| O | 5.307482 | -0.044044 | -0.606007 |
| C | 6.430796 | 0.026454 | -1.492366 |
| H | 7.174235 | 0.651085 | -0.977860 |
| H | 6.836627 | -0.980881 | -1.680167 |
| H | 6.137892 | 0.485541 | -2.450901 |
| C | 3.884554 | 1.341768 | 1.175008 |
| H | 4.939044 | 1.182467 | 1.450929 |
| H | 3.880696 | 1.892943 | 0.222230 |
| H | 3.411928 | 1.964964 | 1.949751 |
| H | 2.262339 | 0.220375 | 2.975649 |
| C | 1.612985 | -1.641928 | 1.991099 |
| O | 1.124911 | -2.283791 | 3.054962 |
| C | 1.183030 | -1.692586 | 4.350882 |
| H | 0.559408 | -0.782639 | 4.367805 |
| H | 0.762544 | -2.443139 | 5.037200 |
| H | 2.227095 | -1.478191 | 4.645455 |
| Cl | -1.237653 | 0.073731 | 2.743511 |
| C | 1.381215 | 2.316697 | -2.393605 |
| H | 2.243883 | 2.046695 | -1.757136 |

| | | | |
|---|---|---|---|
| H | 1.089537 | 1.409724 | -2.946097 |
| H | 1.725619 | 3.067338 | -3.129170 |
| C | -0.699488 | 3.447712 | 2.114130 |
| H | -1.400822 | 2.694943 | 2.505394 |
| H | -0.179830 | 3.916597 | 2.971515 |
| H | -1.262270 | 4.243246 | 1.598535 |
| C | -2.979270 | -0.568775 | -3.059587 |
| H | -2.013989 | -0.075350 | -3.275114 |
| H | -3.345285 | -1.015654 | -4.002590 |
| H | -3.695983 | 0.212558 | -2.752464 |
| C | -2.105723 | -3.194060 | 1.555387 |
| H | -1.537532 | -2.553738 | 2.248775 |
| H | -2.702797 | -3.921798 | 2.137646 |
| H | -1.389033 | -3.768455 | 0.939180 |
| H | -3.703159 | -1.771146 | 1.323154 |
| H | -2.109655 | -2.398301 | -2.343556 |
| H | -0.653942 | 3.018801 | -2.235019 |
| H | 0.937289 | 2.101566 | 1.836672 |
| C | -2.144869 | 1.750172 | -0.198923 |
| C | -2.911621 | 0.562444 | -0.096893 |
| C | -4.305996 | 0.662876 | 0.043858 |
| H | -4.912129 | -0.237263 | 0.164912 |
| C | -2.814247 | 2.984611 | -0.262174 |
| H | -2.246054 | 3.907664 | -0.390038 |
| C | -4.204858 | 3.067905 | -0.155484 |
| H | -4.698314 | 4.043514 | -0.201048 |
| C | -4.952003 | 1.901897 | 0.028214 |
| H | -6.039411 | 1.951040 | 0.141122 |

**V-*R*-L8**

| | | | |
|---|---|---|---|
| Cu | -0.194161 | -0.145306 | 0.248235 |
| C | -1.883415 | -2.541893 | -1.602889 |
| C | -3.066035 | -2.557877 | 0.936508 |
| C | -1.961027 | -3.903582 | -0.873975 |
| C | -3.154917 | -3.856103 | 0.093758 |

| | | | |
|---|---|---|---|
| H | -2.058487 | -4.726026 | -1.606032 |
| H | -1.030820 | -4.072114 | -0.298888 |
| H | -4.101753 | -3.866658 | -0.476245 |
| H | -3.167758 | -4.742326 | 0.752462 |
| C | -1.494757 | 2.659928 | 1.654008 |
| C | -0.905473 | 3.423581 | -0.973274 |
| C | -0.794575 | 4.023530 | 1.449418 |
| C | -1.158594 | 4.551970 | 0.053292 |
| H | -1.084423 | 4.732348 | 2.245376 |
| H | 0.300628 | 3.893732 | 1.521347 |
| H | -2.223583 | 4.846002 | 0.036918 |
| H | -0.575941 | 5.454634 | -0.203890 |
| P | -2.117600 | -1.342708 | -0.160618 |
| P | -1.317430 | 1.830941 | -0.045888 |
| C | 1.864496 | -0.506473 | -1.782990 |
| H | 1.433567 | 0.506180 | -1.675296 |
| H | 1.021194 | -1.219477 | -1.844156 |
| C | 2.683433 | -0.578599 | -3.072951 |
| H | 2.044150 | -0.371564 | -3.949472 |
| H | 3.499828 | 0.164698 | -3.068958 |
| H | 3.139381 | -1.575165 | -3.199184 |
| C | 2.617776 | 1.484155 | 1.069206 |
| C | 1.798253 | -0.813242 | 0.776159 |
| C | 3.624285 | 1.318634 | 0.174354 |
| C | 2.644785 | -0.848513 | -0.499346 |
| H | 1.506574 | -1.797508 | 1.186097 |
| H | 3.030295 | -1.871179 | -0.596686 |
| N | 3.832766 | 0.026641 | -0.357175 |
| C | 5.065023 | -0.512429 | -0.687327 |
| O | 5.212264 | -1.585486 | -1.236592 |
| O | 6.085413 | 0.275489 | -0.313825 |
| C | 7.395046 | -0.174732 | -0.667892 |
| H | 7.486169 | -0.290648 | -1.760930 |
| H | 8.084948 | 0.601652 | -0.307299 |
| H | 7.617861 | -1.139857 | -0.183706 |
| C | 4.451909 | 2.483339 | -0.303720 |

| | | | |
|---|---|---|---|
| H | 5.417481 | 2.542801 | 0.222758 |
| H | 4.671071 | 2.391249 | -1.380792 |
| H | 3.900560 | 3.421890 | -0.130543 |
| H | 2.401408 | 2.466560 | 1.492547 |
| C | 1.861913 | 0.333224 | 1.542211 |
| O | 1.360512 | 0.491530 | 2.783928 |
| C | 0.666372 | -0.603467 | 3.378174 |
| H | 1.280632 | -1.520176 | 3.385634 |
| H | 0.417821 | -0.291197 | 4.402689 |
| H | -0.260262 | -0.821944 | 2.816776 |
| Cl | 1.034481 | -4.021991 | 1.534637 |
| C | -2.834408 | -2.414971 | -2.795796 |
| H | -3.872826 | -2.682362 | -2.539739 |
| H | -2.842976 | -1.391566 | -3.209002 |
| H | -2.504435 | -3.102739 | -3.595990 |
| C | -2.383114 | -2.750699 | 2.296013 |
| H | -2.330415 | -1.796476 | 2.851053 |
| H | -2.972307 | -3.459223 | 2.908109 |
| H | -1.358719 | -3.152333 | 2.185773 |
| H | -4.070018 | -2.134319 | 1.101972 |
| H | -0.855876 | -2.368815 | -1.962932 |
| C | 0.537926 | 3.390052 | -1.495564 |
| H | 0.677100 | 2.582103 | -2.234222 |
| H | 0.784755 | 4.347991 | -1.988550 |
| H | 1.268116 | 3.223153 | -0.684946 |
| C | -2.922626 | 2.771725 | 2.194200 |
| H | -3.411589 | 1.784128 | 2.255041 |
| H | -2.898783 | 3.203919 | 3.211362 |
| H | -3.557914 | 3.419722 | 1.567060 |
| H | -1.587116 | 3.511067 | -1.834550 |
| H | -0.903628 | 2.036420 | 2.344587 |
| C | -3.012502 | 1.329018 | -0.599139 |
| C | -3.363694 | -0.046420 | -0.625671 |
| C | -3.972613 | 2.287658 | -0.971441 |
| H | -3.720856 | 3.351158 | -0.959864 |
| C | -5.262504 | 1.910700 | -1.349514 |

| | | | |
|---|---|---|---|
| H | -5.991761 | 2.674906 | -1.634021 |
| C | -4.675793 | -0.405549 | -0.986143 |
| H | -4.974109 | -1.456694 | -0.985365 |
| C | -5.618744 | 0.558293 | -1.347330 |
| H | -6.630677 | 0.251981 | -1.628286 |

**IV-*proS*-L8**

| | | | |
|---|---|---|---|
| Cu | 0.195330 | -0.540564 | -0.945077 |
| C | 3.075090 | -1.837398 | 0.977910 |
| C | 3.658657 | -1.515616 | -1.702206 |
| C | 4.452503 | -2.348764 | 0.523767 |
| C | 4.334752 | -2.696338 | -0.964897 |
| H | 5.216144 | -1.563645 | 0.678824 |
| H | 4.765936 | -3.221283 | 1.125811 |
| H | 5.314011 | -2.929214 | -1.419438 |
| H | 3.705052 | -3.599933 | -1.076835 |
| C | -0.605758 | 2.890807 | -0.544494 |
| C | -0.172085 | 2.268414 | 2.105438 |
| C | -1.112222 | 3.903121 | 0.501462 |
| C | -1.405080 | 3.136215 | 1.794388 |
| H | -0.337330 | 4.670349 | 0.689778 |
| H | -2.004163 | 4.436819 | 0.125872 |
| H | -1.629877 | 3.810006 | 2.640772 |
| H | -2.291306 | 2.490908 | 1.646977 |
| P | 2.447814 | -0.779186 | -0.455139 |
| P | 0.308247 | 1.528546 | 0.418435 |
| C | -0.205875 | 0.102531 | -2.838360 |
| H | 0.741300 | 0.606581 | -3.118716 |
| H | -0.990388 | 0.881343 | -2.803617 |
| C | -0.567422 | -0.943198 | -3.890264 |
| H | -0.615239 | -0.523014 | -4.918861 |
| H | 0.161744 | -1.774186 | -3.920334 |
| H | -1.563623 | -1.386023 | -3.702517 |
| C | -2.709327 | -0.981934 | 1.269166 |
| C | -1.635453 | -1.651713 | -0.799548 |

| | | | |
|---|---|---|---|
| C | -1.794927 | -1.754719 | 1.970694 |
| C | -0.733645 | -2.461063 | -0.091819 |
| H | -1.883616 | -1.840872 | -1.840248 |
| C | -0.767552 | -2.466963 | 1.314307 |
| H | -1.898001 | -1.799438 | 3.052137 |
| H | -0.093996 | -3.168924 | -0.622129 |
| O | 0.149166 | -3.201440 | 1.935021 |
| C | 0.189420 | -3.264366 | 3.361633 |
| H | -0.721588 | -3.744552 | 3.758998 |
| H | 1.068228 | -3.876410 | 3.607485 |
| H | 0.308081 | -2.256478 | 3.795214 |
| C | -3.803066 | -0.280717 | 2.010291 |
| H | -4.773033 | -0.489306 | 1.508180 |
| H | -3.820712 | -0.640553 | 3.050319 |
| H | -3.653022 | 0.809594 | 2.014052 |
| C | -3.413942 | -0.075808 | -0.972797 |
| N | -2.609358 | -0.916643 | -0.102673 |
| O | -3.545895 | -0.332608 | -2.137137 |
| O | -3.761330 | 1.038954 | -0.359498 |
| C | -4.727832 | 1.863475 | -1.034200 |
| H | -4.836153 | 2.759593 | -0.407833 |
| H | -4.363772 | 2.131276 | -2.038852 |
| H | -5.669085 | 1.291455 | -1.089340 |
| Cl | -6.191124 | -1.226016 | -0.216823 |
| C | 0.130388 | 3.517061 | -1.727473 |
| H | -0.548315 | 4.206173 | -2.263897 |
| H | 1.008774 | 4.099070 | -1.401013 |
| H | 0.472391 | 2.754697 | -2.445025 |
| C | -0.374473 | 1.261788 | 3.235097 |
| H | -1.222072 | 0.590639 | 3.028051 |
| H | 0.521919 | 0.637243 | 3.394277 |
| H | -0.586157 | 1.791537 | 4.182309 |
| C | 3.041360 | -1.169015 | 2.349273 |
| H | 3.719781 | -0.298978 | 2.393368 |
| H | 2.025270 | -0.818885 | 2.601354 |
| H | 3.353529 | -1.886221 | 3.130344 |

| | | | |
|---|---|---|---|
| C | 2.973954 | -1.916512 | -3.010093 |
| H | 2.157194 | -2.637326 | -2.824905 |
| H | 2.536077 | -1.044266 | -3.523623 |
| H | 3.701606 | -2.392024 | -3.693717 |
| H | 0.654760 | 2.942026 | 2.387778 |
| H | -1.477992 | 2.336021 | -0.932985 |
| H | 2.372817 | -2.689373 | 0.989421 |
| H | 4.416367 | -0.746062 | -1.922630 |
| C | 3.056631 | 0.930701 | -0.076761 |
| C | 4.425263 | 1.255992 | -0.125600 |
| H | 5.162447 | 0.499422 | -0.404023 |
| C | 4.877941 | 2.540944 | 0.179400 |
| H | 5.947324 | 2.767292 | 0.132971 |
| C | 2.123645 | 1.930280 | 0.302850 |
| C | 2.600094 | 3.219876 | 0.606897 |
| H | 1.899287 | 4.006123 | 0.898520 |
| C | 3.959506 | 3.529906 | 0.544534 |
| H | 4.299722 | 4.542345 | 0.781549 |

**TS-(IV-V)-*S*-L8**

| | | | |
|---|---|---|---|
| Cu | 0.214805 | -0.513692 | -0.508972 |
| C | 2.963190 | -2.049039 | 1.045393 |
| C | 3.461845 | -2.026313 | -1.675245 |
| C | 4.218150 | -2.809438 | 0.583867 |
| C | 3.976595 | -3.242709 | -0.867820 |
| H | 5.102977 | -2.148051 | 0.647473 |
| H | 4.418022 | -3.674522 | 1.242078 |
| H | 4.884444 | -3.662536 | -1.335622 |
| H | 3.208207 | -4.038889 | -0.884266 |
| C | -0.131511 | 2.949214 | -0.797054 |
| C | 0.376523 | 2.589088 | 1.893104 |
| C | -0.413201 | 4.147587 | 0.129275 |
| C | -0.732674 | 3.592069 | 1.521384 |
| H | 0.476867 | 4.802752 | 0.181422 |
| H | -1.239135 | 4.762522 | -0.270962 |

| | | | |
|---|---|---|---|
| H | -0.802521 | 4.388324 | 2.283762 |
| H | -1.711199 | 3.074897 | 1.503603 |
| P | 2.441113 | -1.023655 | -0.447493 |
| P | 0.687601 | 1.629410 | 0.290041 |
| C | -0.839805 | -0.254171 | -2.404896 |
| H | 0.144166 | 0.250742 | -2.469148 |
| H | -1.608427 | 0.530433 | -2.418124 |
| C | -0.976405 | -1.240551 | -3.549560 |
| H | -0.686719 | -0.781251 | -4.515579 |
| H | -0.324876 | -2.120574 | -3.402049 |
| H | -2.016261 | -1.595105 | -3.656537 |
| C | -2.797706 | -0.321712 | 1.189664 |
| C | -1.802068 | -1.390088 | -0.804184 |
| C | -1.926590 | -1.014086 | 1.989039 |
| C | -1.011509 | -2.222581 | 0.089738 |
| H | -2.216621 | -1.921002 | -1.655467 |
| C | -1.025064 | -1.995012 | 1.450999 |
| H | -1.962715 | -0.832366 | 3.059853 |
| H | -0.490220 | -3.092455 | -0.315181 |
| O | -0.239913 | -2.770117 | 2.218781 |
| C | -0.209184 | -2.596513 | 3.630618 |
| H | -1.190999 | -2.818503 | 4.085505 |
| H | 0.536287 | -3.313309 | 4.004551 |
| H | 0.105329 | -1.572820 | 3.901686 |
| C | -3.771185 | 0.630913 | 1.817729 |
| H | -4.801093 | 0.310457 | 1.565955 |
| H | -3.632755 | 0.613592 | 2.910086 |
| H | -3.627559 | 1.659362 | 1.451923 |
| C | -3.767264 | -0.066005 | -1.112997 |
| N | -2.784594 | -0.543185 | -0.192522 |
| O | -3.984498 | -0.629785 | -2.157929 |
| O | -4.258343 | 1.112297 | -0.761294 |
| C | -5.432935 | 1.548325 | -1.461872 |
| H | -5.645414 | 2.557856 | -1.081743 |
| H | -5.246729 | 1.574107 | -2.547859 |
| H | -6.249409 | 0.848944 | -1.215103 |

| | | | |
|---|---|---|---|
| Cl | -6.304391 | -1.289198 | 0.399769 |
| C | 0.576808 | 3.291336 | -2.106482 |
| H | -0.032233 | 4.010649 | -2.684115 |
| H | 1.564427 | 3.749878 | -1.928913 |
| H | 0.725142 | 2.397442 | -2.736767 |
| C | 0.071823 | 1.732331 | 3.118660 |
| H | -0.858050 | 1.159990 | 2.979697 |
| H | 0.886124 | 1.017500 | 3.330725 |
| H | -0.050316 | 2.375958 | 4.009141 |
| C | 3.100506 | -1.272913 | 2.352236 |
| H | 3.906164 | -0.520005 | 2.294937 |
| H | 2.161934 | -0.750313 | 2.606697 |
| H | 3.335302 | -1.964148 | 3.182019 |
| C | 2.660507 | -2.404611 | -2.923024 |
| H | 1.766637 | -2.996208 | -2.655085 |
| H | 2.319522 | -1.511732 | -3.475856 |
| H | 3.278935 | -3.014464 | -3.607182 |
| H | 1.302794 | 3.157277 | 2.083196 |
| H | -1.099553 | 2.473528 | -1.039122 |
| H | 2.131655 | -2.768175 | 1.156599 |
| H | 4.319097 | -1.404264 | -1.980414 |
| C | 2.525850 | 1.767137 | 0.046403 |
| C | 3.295781 | 0.611630 | -0.250824 |
| C | 3.180816 | 3.005433 | 0.181040 |
| H | 2.605240 | 3.908068 | 0.401930 |
| C | 4.691553 | 0.737161 | -0.376977 |
| H | 5.306633 | -0.140890 | -0.588079 |
| C | 4.565056 | 3.115253 | 0.037222 |
| H | 5.048457 | 4.090951 | 0.141991 |
| C | 5.324724 | 1.973742 | -0.236149 |
| H | 6.411482 | 2.043727 | -0.340274 |

**V-*S*-L8**

| | | | |
|---|---|---|---|
| Cu | 0.161822 | 0.601981 | 0.066941 |
| C | 2.911221 | 2.212089 | -0.747354 |

| | | | |
|---|---|---|---|
| H | 3.979817 | 2.405557 | -0.555145 |
| H | 2.769464 | 2.266379 | -1.842295 |
| C | 2.034630 | 3.264753 | -0.039388 |
| H | 2.261671 | 3.279691 | 1.042687 |
| H | 2.248092 | 4.274845 | -0.426365 |
| C | 3.377875 | -0.028678 | 1.271586 |
| C | 3.449356 | -0.658587 | -1.379551 |
| C | -0.433003 | 3.494125 | -1.812539 |
| C | -0.671513 | 4.187324 | 0.880063 |
| C | -1.731923 | 4.218330 | -1.390630 |
| C | -1.413302 | 5.073589 | -0.152597 |
| H | -2.128544 | 4.827163 | -2.222518 |
| H | -2.509502 | 3.472250 | -1.139848 |
| H | -0.772294 | 5.922821 | -0.445936 |
| H | -2.330173 | 5.502905 | 0.288356 |
| P | 2.444784 | 0.468301 | -0.282428 |
| P | 0.208607 | 2.878110 | -0.150723 |
| C | -2.408866 | -0.193949 | -1.504521 |
| H | -2.441006 | 0.786686 | -0.989521 |
| H | -3.399943 | -0.345863 | -1.968599 |
| C | -1.338732 | -0.193844 | -2.599670 |
| H | -1.591004 | 0.535353 | -3.389829 |
| H | -0.338884 | 0.077049 | -2.207730 |
| H | -1.222850 | -1.198777 | -3.038231 |
| C | -3.462176 | -0.474387 | 1.528615 |
| C | -2.226410 | -1.307862 | -0.453971 |
| C | -2.288256 | -0.066935 | 2.086838 |
| C | -0.961379 | -1.236835 | 0.392048 |
| H | -2.166206 | -2.266635 | -0.981402 |
| C | -1.031425 | -0.641031 | 1.631503 |
| H | -2.314314 | 0.656696 | 2.899478 |
| H | -0.174614 | -1.956392 | 0.134683 |
| O | 0.051770 | -0.734042 | 2.453484 |
| C | 0.073070 | -0.040211 | 3.691930 |
| H | -0.734335 | -0.380546 | 4.364723 |
| H | 1.046522 | -0.270962 | 4.149591 |

| | | | |
|---|---|---|---|
| H | -0.002796 | 1.053003 | 3.542548 |
| C | -4.779235 | 0.041098 | 2.045711 |
| H | -5.311869 | -0.725543 | 2.628998 |
| H | -4.603690 | 0.920898 | 2.685644 |
| H | -5.444543 | 0.327916 | 1.213616 |
| C | -4.496620 | -2.180682 | 0.132113 |
| N | -3.425267 | -1.350093 | 0.431202 |
| O | -5.459184 | -2.374435 | 0.846139 |
| O | -4.342055 | -2.756154 | -1.071864 |
| C | -5.345659 | -3.696143 | -1.458373 |
| H | -6.332593 | -3.207858 | -1.520641 |
| H | -5.039068 | -4.069054 | -2.445887 |
| H | -5.400083 | -4.527747 | -0.735954 |
| Cl | 0.069816 | -3.547894 | -1.980331 |
| C | 4.634000 | 0.794470 | 1.595528 |
| H | 5.138019 | 0.368767 | 2.482018 |
| H | 5.357883 | 0.779205 | 0.761771 |
| H | 4.384478 | 1.846462 | 1.822096 |
| C | 2.764677 | -1.020228 | -2.699914 |
| H | 1.870328 | -1.646019 | -2.525627 |
| H | 2.469448 | -0.108688 | -3.251353 |
| H | 3.456970 | -1.584809 | -3.350687 |
| C | 0.524270 | 4.389486 | -2.607014 |
| H | 1.454702 | 3.861467 | -2.876145 |
| H | 0.037507 | 4.703076 | -3.548532 |
| H | 0.802206 | 5.304098 | -2.055419 |
| C | -1.614489 | 3.534506 | 1.898866 |
| H | -2.375436 | 2.905127 | 1.403523 |
| H | -1.061671 | 2.886697 | 2.600990 |
| H | -2.137961 | 4.308833 | 2.488693 |
| H | -0.669601 | 2.604588 | -2.417156 |
| H | 4.403007 | -0.134565 | -1.591378 |
| H | 2.677193 | 0.023757 | 2.120368 |
| H | 0.091977 | 4.772930 | 1.419419 |
| C | 3.687768 | -1.483044 | 0.945196 |
| C | 3.928662 | -2.463993 | 1.912499 |

| | | | |
|---|---|---|---|
| H | 3.890582 | -2.202596 | 2.975096 |
| C | 4.200011 | -3.779228 | 1.517969 |
| H | 4.380825 | -4.550055 | 2.273577 |
| C | 3.722070 | -1.814238 | -0.424995 |
| C | 3.967424 | -3.135597 | -0.813065 |
| H | 3.950694 | -3.410533 | -1.870543 |
| C | 4.214759 | -4.113077 | 0.157943 |
| H | 4.402849 | -5.146600 | -0.148970 |

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