Copper-Catalyzed Asymmetric 1,4-Addition of Alkenyl Alanes to *N*-Substituted-2-3-dehydro-4-piperidones

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SUPPORTING INFORMATION

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General. ^{1}H (400 MHz or 300 MHz) and ^{13}C (100 MHz or 75 MHz) NMR spectra were recorded in $CDCl_3$ and chemical shifts are given in ppm relative to residual $CHCl_3$. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), brs (broad singlet). Coupling constants are reported in Hertz (Hz). Mass spectra (MS) were obtained by ESI and High-resolution mass spectra HRMS by Electrospray Ionisation (ESI).Conversion was followed by GC-MS Hewlett Packard (EI mode) HP6890-5973 with OPTIMA delta (3 / 0.25 μm / 30m / 0.25 mm) as stationary phase or by TLC (Thin layer chromatography). were recorded on a Perkin-Elmer 241 polarimeter at 20°C in a 10 cm cell in $CHCl_3$; $[\alpha]_D$ values are given in 10^{-1} $deg \cdot cm^{2}$ g^{-1} (concentration c given as g/100 ml). Enantiomeric excesses determined by Chiral-GC or by Chiral-SFC measurement on a Berger SFC with the stated column. Gradient programs are described as follows: initial methanol concentration (%) - initial time (min) – percent gradient of methanol (% / min) - final methanol concentration (%); retention times (RT) are given in min. Flash chromatographies were performed using silica gel 32-63 μm, 60 Å and a pentane-diethylether mixture as eluent. All solvents were dried on alumina columns if not indicated otherwise. The racemates were prepared using racemic 1,1-diphenyl-*N*,*N*-bis(1-phenylethyl)phosphinamine as ligand (11 mol%) and Copper(II)naphtenate (10 mol%); the catalysis was carried out as described (*vide infra*).

- **Reagents for the synthesis of substrates and alkynes**

K(iPrO)$_3$BH was purchased from ACROS (ACROSEAL, 1.0M solution in THF) and used as received (CAS: 42278-67-1)
4-Methoxypyridine was purchased from ACROS (99%) and used as received.
Di-tert-butyl dicarbonate was purchased from ACROS (99%) and used as received.
Benzyl chloroformate was purchased from ACROS (97%) and used as received.
3-butyn-1-ol was purchased from ACROS (97%) and used as received.
Hexachloroacetone was purchased from ACROS (99%) and used as received.
Triphenylphosphine was purchased from ACROS (99%) and used as received.
***β*-Bromostyrene (**mixture of cis/trans isomers) was purchased from ACROS (97%) and used as received.
***p*-Methoxycinnamic acid** was purchased from ACROS (99%) and used as received.
4-fluorobenzaldehyde was purchased from ACROS (98%) and used as received.
trans-Cinnamaldehyde was purchased from ACROS (99%) and used as received.
Triphenylphosphine was purchased from ACROS (99%) and used as received.
Carbon tetrabromide was purchased from ACROS (98%) and used as received.
Dimethylphosphite was puchased from Sigma-Aldrich (98%) and used as received.
Trimethylsilylacetylene was purchased from Sigma-Aldrich (98%) and used as received
Bis(triphenylphosphine)palladium(II)chloride was purchased from ACROS (98%) and used as received (CAS: 13965-03-2).

- **Ligands**

L1 was prepared according to a published protocol.[1]
L2 was prepared according to a published protocol.[1]
L3 was prepared according to a published protocol.[2]
L4 was prepared according to a published protocol.[2]
(*R*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (R-BINAP) was purchased from TCI (98%) and used as received.
Josiphos Ligand (SL-J001-1) was received as a gift from SOLVIAS and used as received (CAS: 162291-02-3)

- **Reagents used for Catalysis**

Me$_3$Al was purchased from Sigma-Aldrich (2.0 M in heptane) and used as received.
Et$_3$Al was purchased from Sigma-Aldrich (1.0 M in hexane) and used as received.
DIBAL-H was purchased from ACROS (ACROSEAL, 1.0M solution in heptane) and used as received.
1-Pentyne was purchased from ACROS (99%) and used as received.
1-Hexyne was purchased from ACROS (98%) and used as received.
1-Heptyne was purchased from ACROS (99%) and used as received.
Cyclohexylacetylene was purchased from ACROS (98%) and used as received.
3,3-Dimethyl-1-butyne was purchased from ACROS (98%) and used as received.
***tert*-Butyl propargyl** was purchased from ACROS (98%) and used as received.
5-Chloro-1-pentyne was purchased from ACROS (98%) and used as received.
Phenylacetylene was purchased from ACROS (98%) and used as received.
1-Ethynyl-4-fluorobenzene was purchased from ACROS (98%) and used as received.
1-ethynyl-4-methoxybenzene was purchased from ACROS (97%) and used as received.
***tert*-Butyllithium** was purchased from ACROS (ACROSEAL, 1.6M solution in pentane) and used as received.

Dimethylaluminium chloride was purchased from Sigma Aldrich (1.0M solution in hexane) and used as received.

2-Bromopropene was purchased from Sigma Aldrich (99%) and used as received.

***trans*-1-Bromo-1-propene** was purchased from Sigma Aldrich (99%) and used as received.

Bromobenzene was purchased from ACROS (99%) and used as received.

***n*-Butyllithium** was purchased from ACROS (1.6M solution in hexane) and used as received.

Vinylmagnesium bromide solution was purchased from Sigma Aldrich ((1.0M solution in THF) and used as received.

Copper(II)naphtenate, 77% in mineral spirits (8% Cu) was purchased from Strem (CAS: 1338-02-9) and used as a solution in pentane (3.2 g of the fir green viscous oil was dissolved in pentane (50 mL)).

$Cu(CH_3CN)_4BF_4$] KUBAS salt [$Cu(CH_3CN)_4BF_4$] was purchased from ACROS (CAS: 15418-29-8) and used as received.

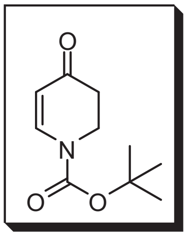
Dichlorobis(triphenylphosphine)nickel(II) was purchased from Fluka (98%) and used as received. (CAS: 14264-16-5).

1,3-Bis(diphenylphosphino)propane nickel(II) chloride was purchased from ACROS (99%) and used as received. (CAS: 15629-92-2)

H_2O_2 solution (0.6 M) 1 mL of H_2O_2 solution (30%), purchased from ACROS, was diluted with 14 mL of distilled water.

■ Preparation of substrates

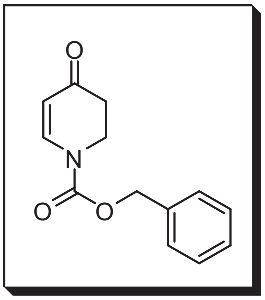
1-*t*-Butoxycarbonyl-2,3-dehydro-4-piperidone[3]



4-Methoxypyridine (1.02 mL, 1.10 g, 10.0 mmol) and Boc_2O (2.35 mL, 2.40 g, 11.0 mmol) were dissolved in THF (10 mL) and cooled to –15 °C. K(*i*-PrO)$_3$BH (12 mL, 12 mmol, 1.0 M in THF) was added to this solution and the resulting mixture was stirred for 1 h at –15 °C. To the resulting slush was then added 10% aq. citric acid (20 mL) was added at r.t. and the stirring continued for 5 min. The solution was diluted with Et_2O (10 mL), phases were separated and the aqueous phase extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried over $NaSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography (Pentane/Et_2O = 1.5:1) to give the product as a white solid (3.5 mmol, 691 mg, 35%). The analytical data was in accord with the literature.[3]

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.80 (brs, 1H), 5.28 (d, *J* = 7.9 Hz, 1H), 3.96 (t, *J* = 7.4 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 2H), 1.48 (s, 9H).

1-Benzyloxycarbonyl-2,3-dehydro-4-piperidone[3]

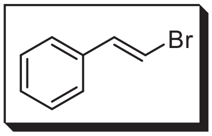


4-Methoxypyridine (1.01 mL, 0.09 g, 10.0 mmol) was dissolved in THF (10 mL) and cooled to -15 °C. K(*i*-PrO)$_3$BH (12 mL, 12 mmol, 1.0 M in THF) was added to this solution followed by neat benzyl chloroformate (1.56 mL, 1.88 g, 11.0 mmol). The resulting mixture was stirred for 1 h at –15 °C. Then the slurry was poured into 1 M aq. HCl (30 mL) and stirred for 2 min. The solution was diluted with CH_2Cl_2 (30 mL), phases were separated and the aqueous phase extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were dried over $NaSO_4$, concentrated under reduced pressure and dried under high vacuum (5 mbar) for 30 min to obtain a crop of yellow oily crystals. These were triturated with pentane/ether = 2:1 (15 mL) to afford the pure product as white crystals (1.55 g, 67%).

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ =7.85 (brs, 1H), 7.42-7.36 (m, 5H), 5.35 (brs, 1H), 5.26 (s, 1H), 4.05 (t, *J* = 7.3 Hz, 1H), 2.56 (t, *J* = 7.3 Hz, 1H). The analytical data was in accord with the literature.[3]

■ Preparation of alkenyl bromides

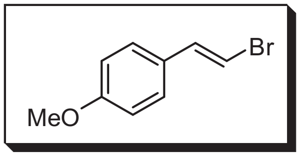
(*E*)-(2-bromovinyl)benzene



NaOH (6.80 g, 170 mmol, 0.85 equiv.) and a E/Z mixture of β-Bromostyrene (36.4 g, 25.6 mL, 200 mmol, 1.0 equiv.) were dissolved in Isopropanol (200 mL, technical grade) and heated at reflux for 2h. Then the reaction mixture was slowly cooled to room temperature and diluted with H_2O (100 mL) and pentane (100 mL). The organic phase was extracted with water (2 x 50 mL), dried over Na_2SO_4 and the solvent was removed *in vacuo* affording the crude compound as a brown oil. Distillation (69°C, 5 mbar) afforded the pure product as a pale yellow oil (25.5 g, 140 mmol, 70%).

^{1}H-NMR (400.133 MHz, $CDCl_3$): δ = 6.78 (d, *J* = 13.9 Hz, 1H), 7.12 (d, *J* = 13.9 Hz, 1H), 7.28-7.41 (m, 5H, Ar-H). The analytical data was in accord with the literature.[4]

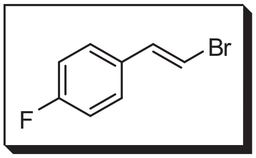
Synthesis of (E)-1-(2-bromovinyl)-4-methoxybenzene[5]



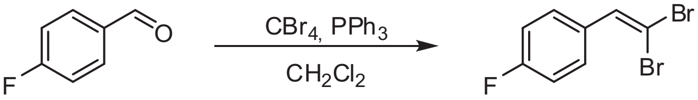
Triethylamine (308 μl, 224 mg, 2.24 mmol) was added to a solution of the α, β-unsaturated aromatic carboxylic acid (8.00 g, 44. 8 mmol, 1.0 eq.) in dichloromethane (150 mL, technical grade). After the mixture was stirred for 5 min at room temperature, NBS (9.54 g, 53.6 mmol, 1.2 eq.) was added. After 20 min no more gas evolution was observed. Then dichloromethane was evaporated under reduced pressure and the remaining slush was purified by flash chromatography (SiO_2, CH_2Cl_2) to afford the product as white crystals (8.13 g, 38.2 mmol, 85%).

^{1}H-NMR (400.133 MHz, $CDCl_3$):
δ = 7.24 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 14.0 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 13.9 Hz, 1H), 3.81 (s, 3H).The analytical data was in accord with the literature.[6]

(E)-1-(2-bromovinyl)-4-fluorobenzene

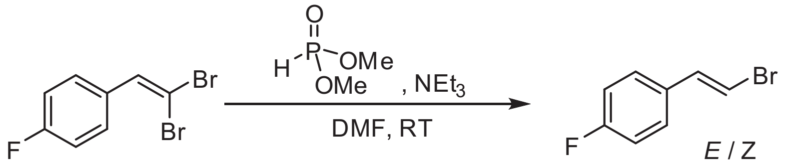


1st step:



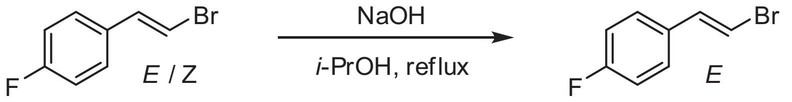
To a solution of the aldehyde (9.93 g, 80.0 mmol, 1.0 eq.) and CBr_4 (27.8 g, 84.0 mmol, 1.05 eq.) in CH_2Cl_2 (100 mL, technical grade) was added at 0°C triphenylphosphine (44.0 g, 168 mmol, 2.1 eq.) in small portions whereupon the solution turned from yellow to black. The reaction mixture was stirred for 1 h at r.t., then about half of the volume of dichlormethane was removed under reduced pressure and pentane (100 mL) was added which led to a white precipitate (PPh_3=O). After filtration and evaporation of the solvent, the residue was dissolved in pentane (50 mL) which led to further precipitation of PPh_3=O. Filtration and evaporation of the solvent afforded the crude dibromide as a yellow slurry (Purity > 90% determined by GC-MS).

2nd step.



To a solution of the crude dibromide (< 50.0 mmol, 1.0 eq.) and NEt_3 (25.3 g, 34.6 mL, 250 mmol, 1.0 eq.) in DMF (40 mL) was added dimethylphosphonate (22.0 g, 18.5 mL, 200.0 mmol, 4.0 eq.). The solution was stirred over night at room temperature, then water (60 mL) was added and the mixture was extracted with pentane (2 × 100 mL). The combined organic phases were washed with an aqueous solution of HCl (1M, 75 mL) dried over Na_2SO_4 and the solvent was evaporated in vacuo (Due to the pungent stench of the mixture the evaporation is best done in a special hood) to yield the crude vinyl bromide as a yellow viscous oil (*E* / *Z* = 92: 8; determined by GC-MS).

3rd step:

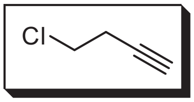


The crude product (< 80.0 mmol, 1.0 eq.) from the previous step was dissolved in isopropanol (100 mL), solid NaOH (2.72 g, 68.0 mmol, 0.85 eq.) was added and the mixture was heated at reflux for 1.5 hours (details are mentioned for each product). The reaction was cooled to room temperature and then extracted with pentane (2 × 100 mL). The combined organic phases were washed an aqueous solution of HCl (1M, 75 mL), dried over Na_2SO_4 and the solvent was removed in under reduced pressure and then under under high vacuum (5 mbar) at room temperature. The crude yellow oil crystallized in the freezer (–40 °C). Trituration with cold pentane afforded the product as white crystals (3.5 g, 17.4 mmol, 22%)[a] which melt slightly above room temperature (Mp = 27°C). The crystals were stored in the freezer (–40°C) until use.

[a] After 2 crops, not optimized.

^{1}H-NMR (400.133 MHz, $CDCl_3$): δ = 7.30 – 7.23 (m, 2H), 7.10 – 6.98 (m, 3H), 6.69 (dd, *J* = 14.0, 3.7 Hz, 1H).The analytical data was in accord with the literature.[7]

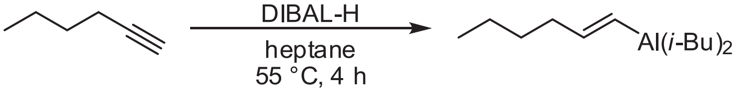
4-chlorobut-1-yne



To a solution of 3-butyn-1-ol (1.40 g, 1.52 ml, 20 mmol, 1.0 equiv.) in hexachloroacetone (6.10 mL, 10.6 g, 40 mmol, 2.0 equiv.) was added PPh_3 (5.51 g, 21 mmol, 1.05 equiv.) in portions over 3 min at 15°C (water bath). The solution warmed to room temperature and stirred for another 2h. On the round bottom flask the stopcock was replaced by a distillation apparatus and the reaction mixture was gently heated with a heat gun (82°C, atmospheric pressure) to afford the pure compound as a colorless liquid (1.56 g, 18 mmol, 90% yield).

^{1}H-NMR (400.133 MHz, $CDCl_3$): δ = 3.61 (t, *J* = 7.1 Hz, 2H), 2.66 (td, *J* = 7.1, 2.6 Hz, 2H), 2.08 (t, *J* = 2.6 Hz, 1H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 80.3, 70.5, 42.0, 22.9. The analytical data was in accord with the literature.[8]

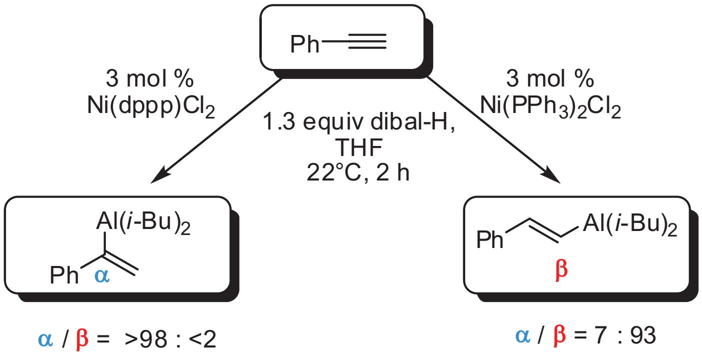
■ Representative procedure for the preparation of vinylaluminum reagents by hydroalumination[9]



To a flame-dried round bottom flask equipped with a stir bar was added hex-1-yne (463 µl, 328 mg, 4.0 mmol, 1.0 eq.) followed by dropwise addition of DIBAL-H (4.0 mL, 4.0 mmol, 1.0 eq., 1.0 M solution in heptane) at 22°C under an atmosphere of nitrogen. The clear solution was allowed to warm to 55 °C and stir for 4 h and was used without purification. In the case of 3,3-dimethylbut-1-yne the reaction mixture was not heated but stirred at 22°C for 4 h. Unfunctionalized alkenyl alanes, when stored in a tightly sealed schlenk tube under nitrogen, can be used for several weeks affording the same results as freshly prepared solutions.

■ Procedure for the preparation of vinylaluminum reagents via Nickel catalyzed hydroalumination[10]

The protocol described by Hoveyda and co-worker was exactly followed with the exception that a solution of DIBAL-H in heptane (ACROS, 1.0 M in heptane) was used instead of DIBAL-H neat. For a hydroalumination on a 1.0 mmol scale, 1.0 mmol of DIBAL-H was used and 1.0 mL of THF was added as a solvent.



■ Representative procedure for the preparation of vinylaluminum reagents by transmetalation from the corresponding lithium organyl

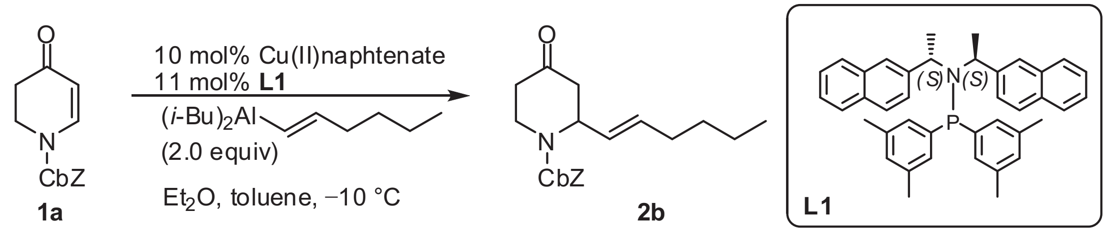
To a solution of (*E*)-(2-bromovinyl)benzene (387 μL, 549 mg, 3.0 mmol, 1.0 eq.) in Et_2O (3.0 mL)[a] was added under inert atmosphere a fresh solution of *t*-BuLi (3.2 mL, 6.0 mmol, 1.9 M in pentane, 2.0 eq.) at –78°C. The reaction was stirred for 30 min at this temperature. Then a fresh solution of Me_2AlCl (3.0 mL, 3.0 mmol, 1.0 M in hexanes, 1.0 eq.) was added and the reaction mixture was stirred for 1 h maintaining the temperature at –78°C. Now the cooling bath was removed and the reaction vessel was immediately submerged in a water bath. The alane was stirred over 5 h at room temperature.[b] The alane solution (1.9 mL, 0.6 mmol, 2.0 equiv) was taken out with a syringe and slowly added to the metal complex.

[a] In the case of (E)-1-(2-bromovinyl)-4-methoxybenzene the quantity of ether was doubled (6.0 mL) due to problems in solubility of the bromide at low temperatures.

[b] In the case of the styrylalanes this mostly results in a clear solution with a paste of salts on the bottom of the flask. In the case of vinyl alanes bearing an alkyl substituent a suspension is obtained and the flask is let to stand for about 15 min for the salts to settle before use of the supernatant alane solution. In the case of isopropenylalane the solution was stirred overnight instead of 5 h.

■ Representative general procedure for Cu- phosphine amine-catalyzed ACA of vinyl aluminums to *N*-substituted-2,3-dehydro-4-piperidones

Synthesis of (*E*)-benzyl 2-(hex-1-enyl)-4-oxopiperidine-1-carboxylate



A flame-dried Schlenk tube was charged with Copper(II)naphtenate solution in pentane (0.39 mL, 0.06 mmol Cu(II), 10 mol%) and a solution of **L1** (19 mg, 0.033 mmol, 11 mol%) in ether (1.0 mL). This mixture was stirred under an atmosphere of argon for 1 h at 22°C and the in situ formed complex was cooled to –10°C and (*E*)-hex-1-enyldiisobutylaluminum (0.67 mL, 2.0 eq., 0.9 M solution in heptane),[a] Me_3Al (0.15 mL, 0.3 mol, 1.0 equiv) and a solution of **1a** (69 mg, 0.3 mmol, 1.0 eq.) in toluene (1.0 mL) were added through a syringe, sequentially. The solution was allowed to stir at –10 °C o.n. (approximately 14 h) after which the reaction was quenched with methanol (0.1 mL) at –10°C. Then the reaction was let warm to 22°C and aq. 1 M HCl (3 mL) was added; the aqueous layer was extracted with Et_2O (3 × 6 mL) and the combined organic phases were vigorously shaken with an aqueous solution of H_2O_2 (0.1 mL, 0.6 M solution, described *vide supra*).[b] The extracts were dried over Na_2SO_4 and the solvents were removed *in vacuo* to yield the crude product as a green viscous oil. Purification by silica gel chromatography (pentane : ether = 1.5:1) afforded 84 mg of **2b** as a colourless viscous oil (47 mg, 0.15 mmol, 50% yield).[c]

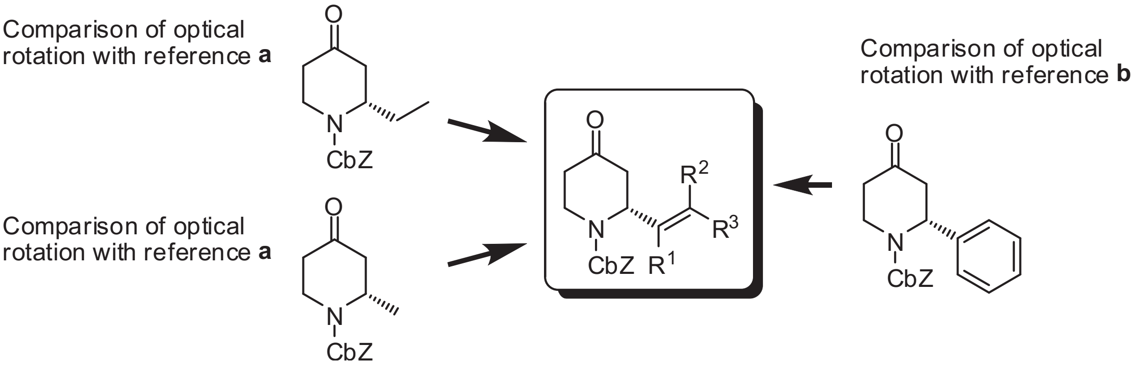
[a] In the case of addition of the vinyl aluminum reagent generated in situ by nickel catalyzed hydroalumination (described, *vide supra*), 1.3 mL (2.0 eq., for 0.3 mmol of substrate) of the freshly prepared black alane solution in THF was added.

[b] This was done to oxidize remaining phosphine amine ligand.

[c] The column was usually done in a less polar solvent mixture because the green residue was solubilized in acetone (0.2 mL) which then as co-solvents rendered the original solvent mixture more polar.

■ Assignment of absolute configuration

The absolute configuration has been assigned by assumption that the ligand will always direct the attack of the nucleophile from the same side. Comparison of the optical rotation (*vide infra*) of the methyl **2r**, ethyl **2s** and phenyl **2q** product with the ones reported in the literature consistently showed that the attack took place from the back side. Therefore, we propose also for the vinyl group an attack from the back side leading to an adduct bearing a stereogenic center with (*R*)-configuration when the (*S*,*S*)-ligand **L1** is used.

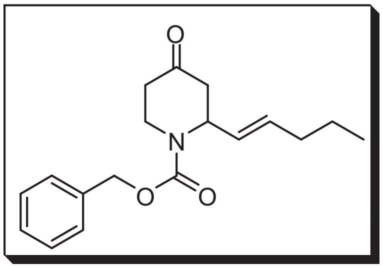


[a] R. Sebesta, M. G. Pizzuti, A. J. Boersma, A. J. Minnaard, B. L. Feringa, *Chem. Commun.* **2005**, 1711–1713.

[b] R. Shintani, N. Tokunaga, H. Doi, T. Hayashi, *J. Am. Chem. Soc.* **2004**, *126*, 6240–6241.

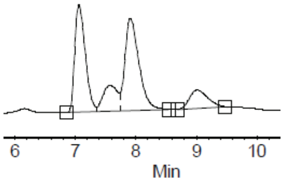
■ Analytical data for all products

(*E*)-benzyl 4-oxo-2-(pent-1-enyl)piperidine-1-carboxylate (2a)

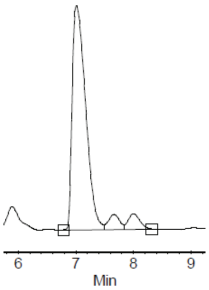


According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R_f = 0.44 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (52 mg, 0.17 mmol, 57% yield). Enantiomeric excess was determined by SFC (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 6.86 min (maj.), t_{R2} = 7.74 min (min.)). [α_D] /20°C = + 28.5 ($CHCl_3$, c = 0.30, ee = 89% (*R*))

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.43 – 7.28 (m, 5H), 5.61 – 5.53 (m, 1H), 5.38 (dd, *J* = 15.7, 4.7 Hz, 1H), 5.19 (d, *J* = 2.0 Hz, 2H), 5.24 – 5.14 (m, 1H), 4.22 (s, 1H), 3.37 (ddd, *J* = 13.5, 11.0, 4.1 Hz, 1H), 2.68 (dd, *J* = 15.0, 6.7 Hz, 1H), 2.56 (d, *J* = 15.0 Hz, 1H), 2.44 (dd, *J* = 10.8, 6.6 Hz, 1H), 2.34 (d, *J* = 15.3 Hz, 1H), 1.99 (dd, *J* = 14.3, 7.0 Hz, 2H), 1.34 (dt, *J* = 14.6, 7.3 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100.61 MHz, CDCl$_3$):** δ = 207.4, 155.3, 136.4, 134.4, 128.6, 128.3, 128.0, 127.7, 67.7, 53.0, 44.2, 40.5, 39.1, 34.4, 22.2, 13.6. **HRMS ESI:** $[M+H]^+$, calcd for $C_{18}H_{23}NO_3$: 302.1750; found 302.1750.

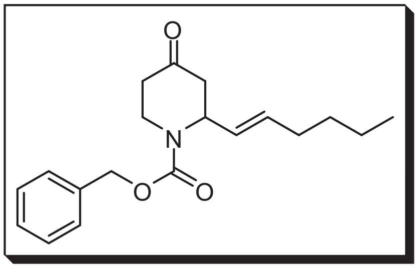


Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	6.86	7.06	7.35	0.00	36.13	372.3	74.8	36.128
4	UNKNOWN	7.74	7.91	8.54	0.00	40.99	319.8	84.9	40.987



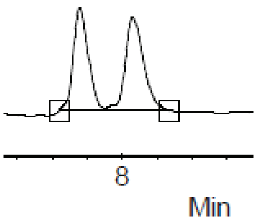
Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	6.78	7.01	7.49	0.00	94.28	1101.0	296.3	94.285
2	UNKNOWN	7.84	8.00	8.32	0.00	5.72	77.3	18.0	5.715

(*E*)-benzyl 2-(hex-1-enyl)-4-oxopiperidine-1-carboxylate (2b)

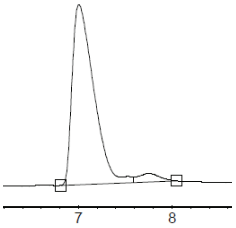


According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R$_f$ = 0.43 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (47 mg, 0.15 mmol, 50% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 7.51 min (maj.), t_{R2} = 7.83 min (min.)). [α_D] /20°C = + 26.4 (CHCl$_3$, c = 0.63, ee = 91% (*R*)).

^{1}H-NMR (400.13 MHz, CDCl$_3$): δ = 7.40-7.32 (m, 5H), 5.61-5.51 (m, 1H), 5.37 (dd, *J* = 15.7, 4.4 Hz, 1H), 5.24 – 5.12 (m, 3H), 4.23 (brs , 1H), 3.41 – 3.29 (m, 1H), 2.67 (dd, *J* = 15.0, 6.6 Hz, 1H), 2.56 (d, *J* = 14.9 Hz, 1H),2.51-2.40 (m, 1H), 2.34 (d, *J* = 15.2 Hz, 1H), 2.01 (dd, *J* = 13.2, 6.5 Hz, 2H), 1.35-1.20 (m, 4H), 0.87 (t, *J* = 6.6 Hz, 3H). **^{13}C-NMR (100.61 MHz, CDCl$_3$):** δ = 207.5, 155.3, 136.4, 134.6, 128.6, 128.3, 128.0, 127.5, 67.7, 53.0, 44.2, 40.5, 39.1, 32.1, 31.2, 22.2, 13.9.**HRMS ESI:** $[M+H]^+$, calcd for $C_{19}H_{25}NO_3$: 316.1907; found 316.19.06.

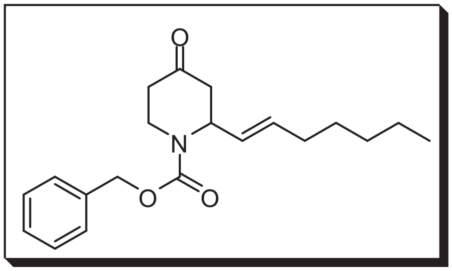


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.27	7.51	7.83	0.00	47.60	266.4	53.7	47.596
2	UNKNOWN	7.83	8.12	8.55	0.00	52.40	241.2	59.1	52.404



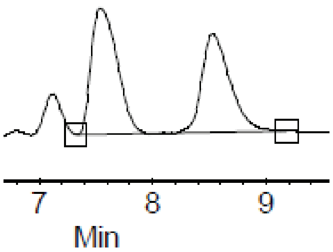
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.81	7.00	7.59	0.00	95.45	920.4	246.2	95.448
2	UNKNOWN	7.59	7.75	8.05	0.00	4.55	43.8	11.7	4.552

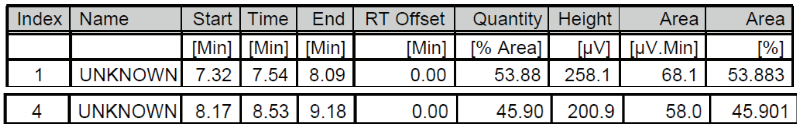
(E)-benzyl 2-(hept-1-enyl)-4-oxopiperidine-1-carboxylate (2c)



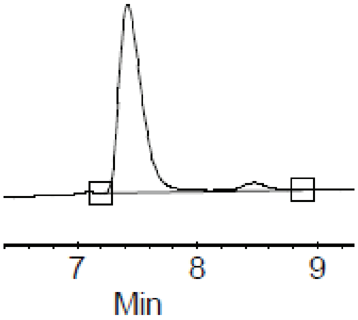
According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R_f = 0.47 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (62 mg, 0.19 mmol, 63% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 9.54 min (maj.), t_{R2} = 8.53 min (min.) $[\alpha_D]$ /20°C = + 9.1 ($CHCl_3$, c = 0.83, ee = 90% (*R*)).

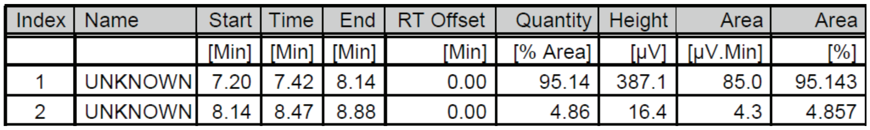
^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.46 – 7.34 (m, 5H), 5.68 – 5.58 (m, 1H), 5.42 (dd, *J* = 15.7, 3.8 Hz, 1H), 5.29 – 5.19 (m, 3H), 4.27 (brs, 1H), 3.47 – 3.36 (m, 1H), 2.72 (dd, *J* = 15.0, 6.7 Hz, 1H), 2.61 (d, *J* = 14.9 Hz, 1H), 2.57 – 2.44 (m, 1H), 2.39 (d, *J* = 15.4 Hz, 1H), 2.05 (dd, *J* = 13.7, 6.8 Hz, 2H), 1.44 – 1.20 (m, 6H), 0.92 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.4, 155.3, 136.4, 134.7, 128.6, 128.2, 128.0, 127.5, 67.6, 53.0, 44.2, 40.5, 39.1, 32.3, 31.4, 28.7, 22.5, 14.1. **HRMS ESI:** $[M+H]^+$, calcd for $C_{20}H_{27}NO_3$: 330.2063; found 330.2064.





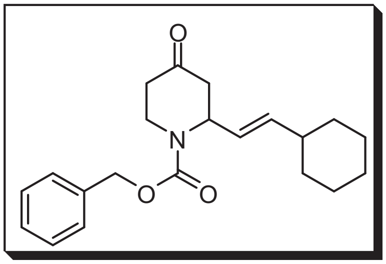
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.32	7.54	8.09	0.00	53.88	258.1	68.1	53.883
4	UNKNOWN	8.17	8.53	9.18	0.00	45.90	200.9	58.0	45.901



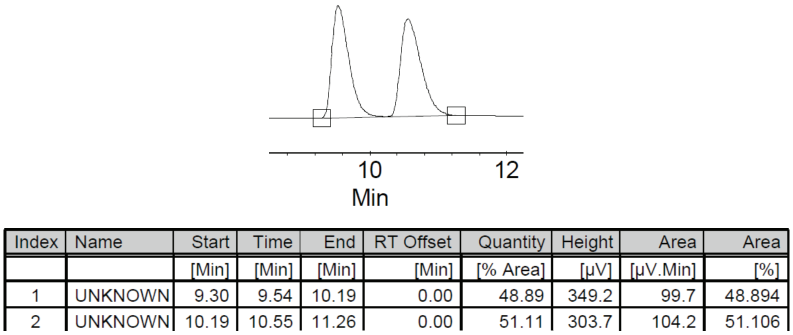


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.20	7.42	8.14	0.00	95.14	387.1	85.0	95.143
2	UNKNOWN	8.14	8.47	8.88	0.00	4.86	16.4	4.3	4.857

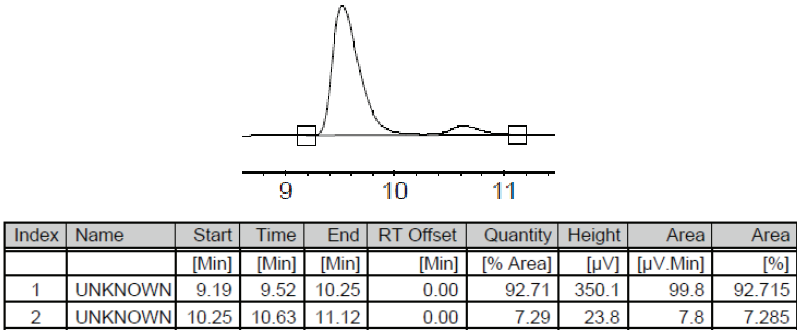
(*E*)-benzyl 2-(2-cyclohexylvinyl)-4-oxopiperidine-1-carboxylate (2d)



According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R_f = 0.46 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (55 mg, 0.16 mmol, 54% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 9.54 min (maj.), t_{R2} = 10.55 min (min.) $[\alpha_D]$ /20°C = + 20.4 ($CHCl_3$, c = 0.48, ee = 86% (*R*)).
^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.40 – 7.29 (m, 5H), 5.52 (dd, *J* = 15.8, 5.9 Hz, 1H), 5.32 (ddd, *J* = 15.8, 4.7, 1.0 Hz, 1H), 5.24 – 5.13 (m, 3H), 4.22 (dd, *J* = 7.1, 4.0 Hz, 1H), 3.37 (ddd, *J* = 13.6, 11.0, 4.2 Hz, 1H), 2.67 (dd, *J* = 15.0, 6.7 Hz, 1H), 2.55 (d, *J* = 15.0 Hz, 1H), 2.43 (dd, *J* = 10.8, 6.6 Hz, 1H), 2.34 (d, *J* = 15.4 Hz, 1H), 1.92 (dd, *J* = 6.7, 3.4 Hz, 1H), 1.60 – 1.74 (m, 5H), 1.31 – 0.94 (m, 5H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.4, 155.3, 140.2, 136.5, 128.6, 128.2, 128.0, 125.0, 67.6, 53.0, 44.3, 40.5, 39.0, 32.8, 32.7, 26.1, 25.9. **HRMS ESI:** $[M+H]^+$, calcd for $C_{21}H_{27}NO_3$: 342.2063; found 342.2058.

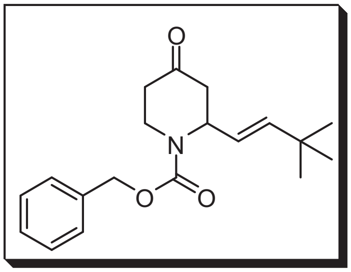


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.30	9.54	10.19	0.00	48.89	349.2	99.7	48.894
2	UNKNOWN	10.19	10.55	11.26	0.00	51.11	303.7	104.2	51.106



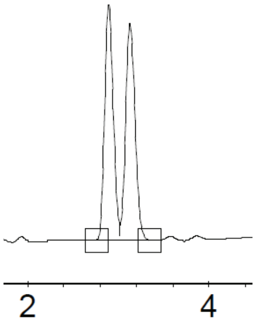
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.19	9.52	10.25	0.00	92.71	350.1	99.8	92.715
2	UNKNOWN	10.25	10.63	11.12	0.00	7.29	23.8	7.8	7.285

(*E*)-benzyl 2-(3,3-dimethylbut-1-enyl)-4-oxopiperidine-1-carboxylate (2e)

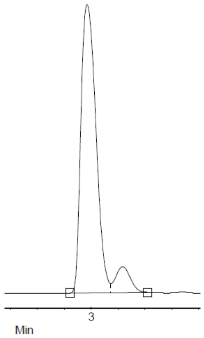


According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R_f = 0.43 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give yellow stains. The product was isolated as a viscous oil (57 mg, 0.18 mmol, 60% yield). Enantiomeric excess was determined by SFC. (ChiralCEL OJ-H: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 2.89 min (maj.), t_{R2} = 3.13 min (min.) [α_D] /20°C = + 19.5 ($CHCl_3$, c = 0.66, ee = 84% (*R*)).

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.40-7.27 (m, 5H), 5.59 (d, *J* = 15.2 Hz, 1H), 5.31-5.10 (m, 2 H) 5.19 (d, *J* = 5.8 Hz, 2H), 4.27-4.18 (m, 1H), 3.40 – 3.30 (m, 1H), 2.68 (dd, *J* = 15.1, 6.7 Hz, 1H), 2.56 (d, *J* = 15.0 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.34 (d, *J* = 15.3 Hz, 1H), 0.96 (s, 9H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.4, 155.3, 145.2, 136.4, 128.6, 128.3, 128.0, 122.4, 67.6, 52.9, 44.3, 40.5, 39.0, 33.2, 29.4. **HRMS ESI:** $[M+H]^+$, calcd for $C_{19}H_{25}NO_3$: 316.1907; found 316.1903.

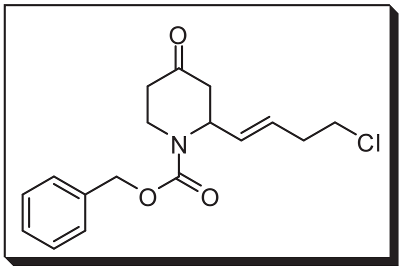


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.76	2.89	3.02	0.00	49.64	604.8	66.7	49.640
2	UNKNOWN	3.02	3.13	3.35	0.00	50.36	557.6	67.7	50.360



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.84	2.97	3.15	0.00	91.79	1693.7	218.3	91.792
2	UNKNOWN	3.15	3.23	3.42	0.00	8.21	151.9	19.5	8.208

(E)-benzyl 2-(5-chloropent-1-enyl)-4-oxopiperidine-1-carboxylate (2f)



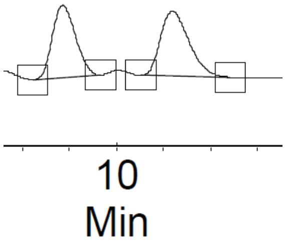
According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R_f = 0.30 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (74 mg, 0.23 mmol, 77% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 9.54 min (maj.), t_{R2} = 10.47 min (min.)). [α_D] /20°C = –37.9 ($CHCl_3$, c = 0.61, ee = 96% (*R*)).

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.30-7.40 (m, 5H), 5.56 – 5.50 (m, 2H), 5.27 – 5.11 (m, 3H), 4.27 – 4.20 (m, 1H), 3.49 (dd, *J* = 6.5, 5.2 Hz, 2H), 3.40 (ddd, *J* = 13.7, 10.9, 4.2 Hz, 1H), 2.70 (dd, *J* = 15.1, 6.8 Hz, 1H), 2.57 (d, *J* = 15.0 Hz, 1H), 2.52 – 2.41 (m, 3H), 2.36 (d, *J* = 15.5 Hz, 1H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** 207.11, 155.3, 136.3, 131.2, 129.7, 128.6, 128.3, 128.1, 67.8, 52.8, 44.0, 43.6, 40.5, 39.2, 35.3.[b]

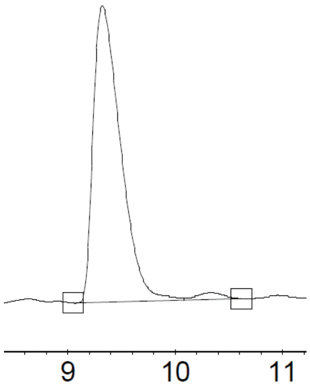
HRMS ESI: $[M+H]^+$, calcd for $C_{17}H_{20}ClNO_3$ 322.1204; found 322.1206.

[a] The complex has been prepared adding THF (0.2 mL) this was done in order to suppress Me and *i*-Bu transfer. Moreover, 3.0 equivalents of vinylalane have been added instead of 2.0 equivalents. The ligand loading was increased to 22 mol% as well as the amount of Cu(II)-naphtenante (20 mol%).

[b] The configuration of the double bond is supposed to be *E*, as hydroalumination of 5-chloropent-1-yne after quenching with iodine afforded exclusively the *E*-isomer.[11]

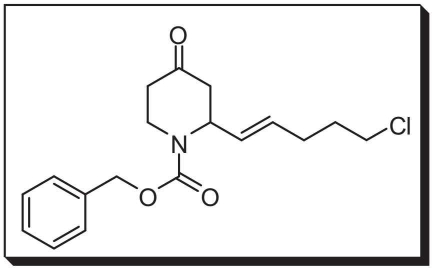


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.28	9.54	9.86	0.00	47.55	111.3	25.4	47.553
2	UNKNOWN	10.21	10.47	10.97	0.00	52.45	99.7	28.0	52.447



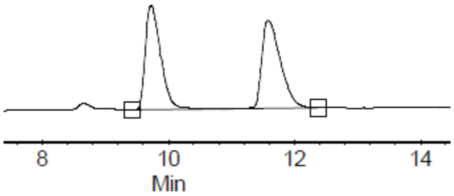
Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
	[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
UNKNOWN	9.04	9.32	10.08	0.00	97.84	607.7	179.3	97.837
UNKNOWN	10.08	10.32	10.61	0.00	2.16	13.5	4.0	2.163

(E)-benzyl 2-(5-chloropent-1-enyl)-4-oxopiperidine-1-carboxylate (2g)

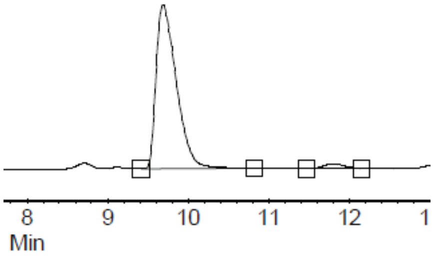


According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.29 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (59 mg, 0.18 mmol, 59% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 9.73 min (maj.), t_{R2} = 11.58 min (min.)). [α_D] /20°C = + 31.3 ($CHCl_3$, c = 0.67, ee = 95% (*R*)).

^{1}H-NMR (400.13 MHz, CDCl$_3$): δ = 7.40-7.31 (m, 5H), 5.58-5.49 (m, 1H), 5.44 (dd, *J* = 16.1, 3.9 Hz, 1H), 5.25 – 5.08 (m, 1H), 5.18 (d, *J* = 3.8 Hz, 2H), 4.23 (brs, 1H), 3.46 (t, *J* = 6.4 Hz, 2H), 3.36 (ddd, *J* = 13.7, 11.1, 4.1 Hz, 1H), 2.69 (dd, *J* = 15.0, 6.8 Hz, 1H), 2.55 (d, *J* = 14.9 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.34 (d, *J* = 15.4 Hz, 1H), 2.17 (dd, *J* = 13.7, 6.7 Hz, 2H), 1.84 – 1.75 (m, 2H). **^{13}C-NMR (100.61 MHz, CDCl$_3$):** δ =207.3, 155.2, 136.4, 132.4, 129.2, 128.6, 128.3, 128.1, 67.7, 53.0, 44.2, 44.11, 40.5, 39.2, 31.6, 29.4. **HRMS ESI:** [M+H]$^+$, calcd for $C_{18}H_{22}ClNO_3$: 336.1360; found 336.1358.

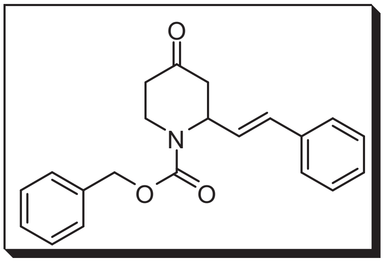


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.43	9.73	10.87	0.00	49.47	379.4	106.5	49.465
2	UNKNOWN	10.87	11.58	12.37	0.00	50.53	319.0	108.8	50.535



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.42	9.69	10.82	0.00	97.26	547.4	158.6	97.261
2	UNKNOWN	11.46	11.79	12.15	0.00	2.74	15.5	4.5	2.739

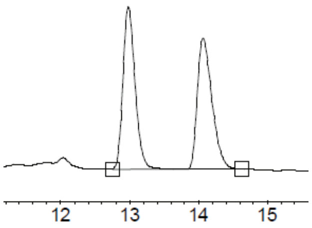
(*E*)-benzyl 4-oxo-2-styrylpiperidine-1-carboxylate (2h)

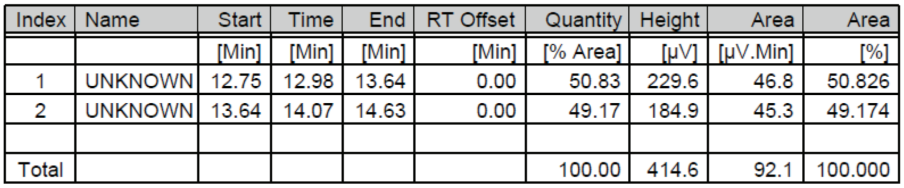


According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1.5; R_f = 0.32 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give red stains. The product was isolated as a viscous oil (80 mg, 0.24 mmol, 80% yield). Enantiomeric excess was determined by SFC. (Chiralcel OD-H: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 12.98 min (min.), t_{R2} = 14.07 min (maj.)). [α_D] /20°C = = + 52.9 (CHCl$_3$, c = 0.63, ee = 97% (*R*)).

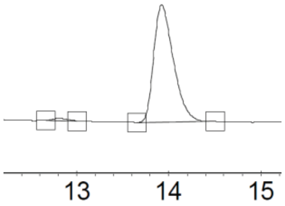
^{1}H-NMR (400.13 MHz, CDCl$_3$): δ = 7.58 – 7.09 (m, 11H), 6.47 (d, *J* = 16.1 Hz, 1H), 6.10 (d, *J* = 4.9 Hz, 1H), 5.40 (s, 1H), 5.27-5.18 (m, 2H), 4.28 (s, 1H), 3.46 (ddd, *J* = 13.6, 4.1, 2.0 Hz, 1H), 2.80 (dd, *J* = 15.1, 6.7 Hz, 1H), 2.70 (d, *J* = 15.0 Hz, 1H), 2.52 (dd, *J* = 19.8, 12.8 Hz, 1H), 2.40 (d, *J* = 15.6 Hz, 1H). **^{13}C-NMR (100.61 MHz, CDCl$_3$):** δ = 207.1, 155.3, 136.3, 136.0, 132.9, 128.7, 128.3, 128.2, 128.2, 127.1, 126.6, 67.9, 53.3, 44.2, 40.5, 39.4. Spectroscopic data are in accordance with the literature.[12]

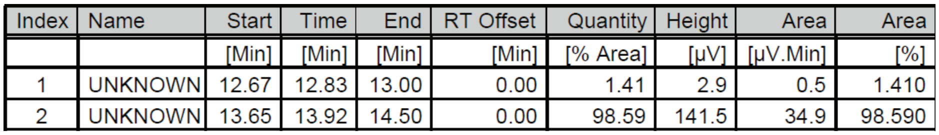
[a] (*E*)-dimethyl(styryl)aluminum was prepared according to the general procedure (*vide supra*) from the corresponding bromide.[13] Same level of enantioselectivity was obtained when (*E*)-diisobutyl(styryl)aluminum was used instead. However, in this case lower yields (37% yield, 97% ee) were observed) (*E*)-diisobutyl(styryl)aluminum was prepared by Ni-catalyzed hydroalumination according to a literature procedure.[10]





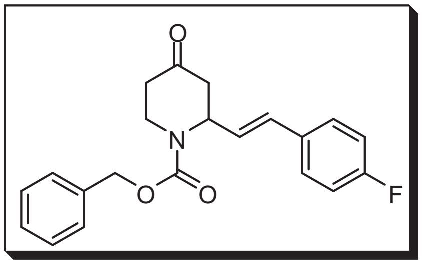
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	12.75	12.98	13.64	0.00	50.83	229.6	46.8	50.826
2	UNKNOWN	13.64	14.07	14.63	0.00	49.17	184.9	45.3	49.174
Total						100.00	414.6	92.1	100.000





Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	12.67	12.83	13.00	0.00	1.41	2.9	0.5	1.410
2	UNKNOWN	13.65	13.92	14.50	0.00	98.59	141.5	34.9	98.590

(*E*)-benzyl 2-(4-fluorostyryl)-4-oxopiperidine-1-carboxylate (2i)

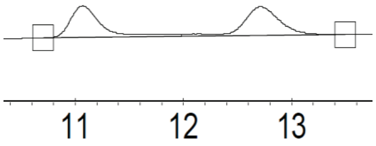


According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.37 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give red stains. The product was isolated as a viscous oil (80 mg, 0.23 mmol, 75% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 11.07 min (maj.), t_{R2} = 12.71 min (min.)). $[\alpha_D]$ /20°C = +48.6 ($CHCl_3$, c = 0.58, ee = 96% (*R*)).

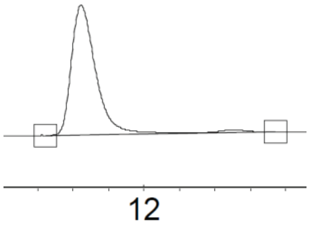
^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.42 – 7.20 (m, 7H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 16.1 Hz, 1H), 6.03 (dd, *J* = 16.2, 4.9 Hz, 1H), 5.38 (brs, 1H), 5.28 – 5.15 (m, 2H), 4.29 (brs, 1H), 3.50

– 3.38 (m, 1H), 2.80 (dd, *J* = 15.1, 6.8 Hz, 1H), 2.68 (d, *J* = 14.9 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.43 – 2.36 (m, 1H). **^{13}C-NMR (100.61 MHz, CDCl$_3$):** δ = 207.0, 162.6 (d, *J* = 248 Hz), 155.3, 136.3, 132.1 (d, *J* = 3 Hz), 131.7, 128.3 (d, *J* = 16 Hz), 128.2, 128.2, 128.1, 126.9 (d, *J* = 2 Hz) , 115.7, 115.5, 67.9, 53.3, 44.1, 40.5, 39.4. **HRMS ESI:** [M+H]$^+$, calcd for $C_{21}H_{21}NO_3$: 354.1499; found 354.1490.

[a] (*E*)-dimethyl(4-fluorostyryl)aluminum was prepared according to the general procedure (*vide supra*) from the corresponding bromide. Same level of enantioselectivity was obtained when (*E*)-diisobutyl(4-fluorostyryl)aluminum was used instead. However, in this case lower yields were observed (35% yield, 95% ee). (*E*)-diisobutyl(styryl)aluminum was prepared by Ni-catalyzed hydroalumination according to a literature procedure.[10]

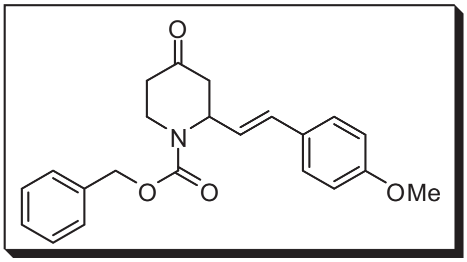


Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	10.70	11.07	11.98	0.00	48.08	40.6	13.3	48.083
2	UNKNOWN	11.98	12.71	13.50	0.00	51.92	36.9	14.4	51.917



Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	UNKNOWN	10.89	11.29	12.48	0.00	97.75	239.1	75.8	97.747
2	UNKNOWN	12.48	13.00	13.48	0.00	2.25	4.7	1.7	2.253

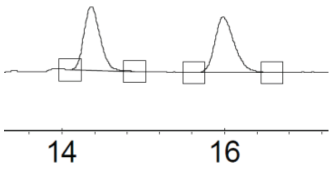
(*E*)-benzyl 2-(4-methoxystyryl)-4-oxopiperidine-1-carboxylate (2j)



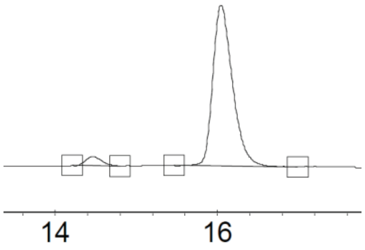
According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R$_f$ = 0.37 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give blue stains. The product was isolated as a yellow gum (41 mg, 0.11 mmol, 37% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t$_{R1}$ = 14.36 min (min.), t$_{R2}$ = 15.98 min (maj.)). [α_D] /20°C = +64.2 (CHCl$_3$, c = 0.16, ee = 91% (*R*))

^{1}H-NMR (400.13 MHz, CDCl$_3$): δ = 7.44 – 7.31 (m, 5H), 7.29 – 7.24 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.41 (d, *J* = 16.2 Hz, 1H), 5.98 (dd, *J* = 16.1, 4.9 Hz, 1H), 5.38 (brs, 1H), 5.26 – 5.17 (m, 1H), 4.27 (s, 1H), 3.81 (s, 3H), 3.51 – 3.39 (m, 1H), 2.78 (dd, *J* = 15.0, 6.6 Hz, 1H), 2.69 (d, *J* = 14.9 Hz, 1H), 2.58 – 2.46 (m, 1H), 2.39 (d, *J* = 15.4 Hz, 1H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.2, 159.6, 155.3, 136.3, 132.3, 128.7, 128.7, 128.3, 128.1, 27.8, 124.8, 114.1, 67.8, 55.4, 53.3, 44.3, 40.6, 39.3. **HRMS ESI:** $[M+H]^+$, calcd for $C_{21}H_{21}NO_3$: 366.1699; found 366.1691.

[a] (*E*)-dimethyl(4-methoxy-styryl)aluminum was prepared according to the general procedure (*vide supra*) from the corresponding bromide. For the creation of the complex a mixture of Et_2O (1.0 mL) and THF (0.2 mL) was used to suppress methyl and *i*-Bu transfer. When (*E*)-diisobutyl(4-methoxy-styryl)aluminum was used lower yield (31%) and ee (53%) were observed). (*E*)-diisobutyl(4-methoxy-styryl)aluminum was prepared by Ni-catalyzed hydroalumination according to a literature procedure.[10] The ligand loading was increased to 22 mol% as well as the amount of Cu(II)-naphtenante (20 mol%).

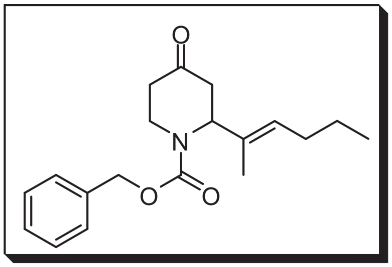


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	14.10	14.36	14.89	0.00	48.85	112.6	25.7	48.846
2	UNKNOWN	15.62	15.98	16.59	0.00	51.15	97.7	27.0	51.154



Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
	[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
UNKNOWN	14.22	14.47	14.80	0.00	4.51	9.8	2.3	4.509
UNKNOWN	15.46	16.05	16.99	0.00	95.49	173.9	48.5	95.491

(*E*)-benzyl 2-(hex-2-en-2-yl)-4-oxopiperidine-1-carboxylate (2k)

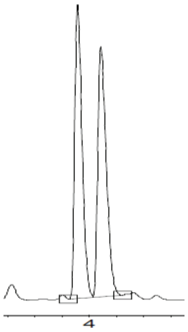


According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.37 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (49 mg, 0.16 mmol, 52% yield). Enantiomeric excess was determined by SFC. (ChiralCEL OJ-H: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 3.82 min (min.), t_{R2} = 4.17 min (maj.)). $[\alpha_D]$ /20°C = +34.0 ($CHCl_3$, c = 0.58, ee = 86% (*R*)).

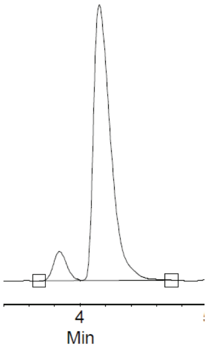
■ NMR-spectra were recorded at 55°C.

^{1}H-NMR (400.13 MHz, CDCl$_3$): δ = 7.39-7.29 (m, 5H), 5.26 – 5.17 (m, 2H), 5.12 br(s, 1H), 5.03 (s, 1H), 4.91 (s, 1H), 4.32 – 4.16 (m, 1H), 3.26 – 3.14 (m, 1H), 2.72 (d, *J* = 15.3 Hz, 1H), 2.62 (dd, *J* = 15.4, 6.7 Hz, 1H), 2.47-2.25 (m, 2H), 2.03 – 1.90 (m, 2H), 1.53 – 1.18 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100.61 MHz, CDCl$_3$):** δ = 206.5, 155.5, 147.5, 136.5, 128.5, 128.2, 128.0, 113.2, 67.7, 55.0, 43.3, 40.4, 38.7, 33.1, 29.9, 22.3, 13.6. **HRMS ESI:** [M+H]$^+$, calcd for $C_{19}H_{25}NO_3$: 316.1907; found 316.1904.

[a] Hex-1-en-2-yldiisobutylaluminum has been prepared according to a published protocol.[10]

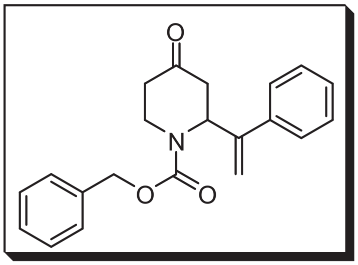


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.69	3.82	4.05	0.00	50.38	1195.0	150.0	50.378
2	UNKNOWN	4.05	4.17	4.49	0.00	49.62	1017.1	147.7	49.622



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.68	3.84	4.00	0.00	7.64	116.7	14.1	7.644
2	UNKNOWN	4.00	4.15	4.72	0.00	92.36	1096.4	170.3	92.356

Benzyl 4-oxo-2-(1-phenylvinyl)piperidine-1-carboxylate (2l)



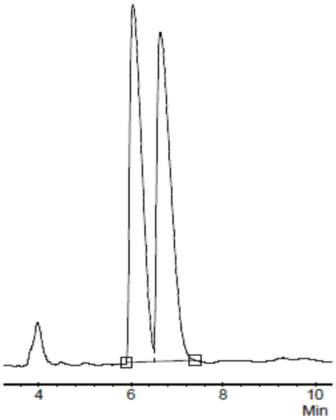
According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R_f = 0.43 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give yellow stains. The product was isolated as a viscous oil (66 mg, 0.20 mmol, 65% yield). Enantiomeric excess was determined by SFC. (Chiralcel AS-H: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 6.04 min (min.), t_{R2} =

6.64 min (maj.)). [α_D] /20°C = +16.0 ($CHCl_3$, c = 0.55, ee = 80% (*R*)).

■ NMR-spectra were recorded at 55°C.

^{1}H-NMR (400.13 MHz, $CDCl_3$): 7.39 – 7.18 (m, 10H), 5.70 (brs, 1H), 5.41 (brs, 1H), 5.21 (d, *J* = 1.8 Hz, 1H), 5.16 (s, 2H), 4.18 – 4.10 (m, 1H), 3.33 – 3.23 (m, 1H), 2.79 (dd, *J* = 15.4, 2.8 Hz, 1H), 2.72 (dd, *J* = 15.5, 6.5 Hz, 1H), 2.50 – 2.36 (m, 2H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** 206.2, 155.2, 139.3, 136.5, 128.5, 128.3, 128.1, 128.0, 127.9, 126.8, 116.1, 84.1, 67.7, 54.5, 43.4, 40.4, 38.9. **HRMS ESI:** $[M+H]^+$, calcd for $C_{21}H_{21}NO_3$: 336.1594; found 336.1602.

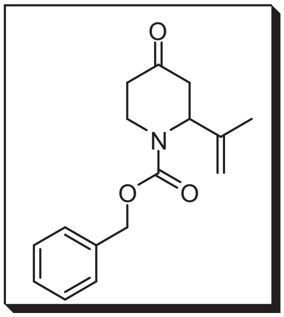
[a] Diisobutyl(1-phenylvinyl)aluminum has been prepared according to a published protocol.[10]



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.90	6.04	6.49	0.00	48.84	1888.1	570.2	48.835
2	UNKNOWN	6.49	6.64	7.39	0.00	51.16	1737.5	597.4	51.165
Total						100.00	3625.6	1167.6	100.000

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.51	6.67	6.99	0.00	9.87	182.1	33.6	9.875
2	UNKNOWN	6.99	7.20	7.87	0.00	90.13	1074.8	307.0	90.125

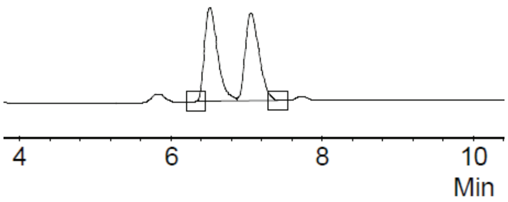
Benzyl 4-oxo-2-(prop-1-en-2-yl)piperidine-1-carboxylate (2m)



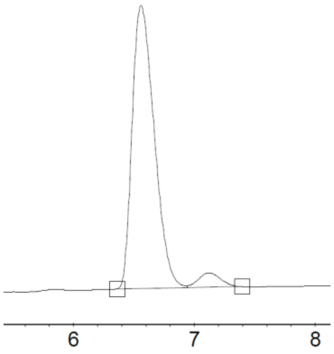
According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.37 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as viscous oil (68 mg, 0.25 mmol, 83% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 6.51 min (maj.), t_{R2} = 7.05 min (min.)). $[\alpha_D]$ /20°C = + 53.3 ($CHCl_3$, c = 0.74, ee = 90% (*R*)).

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.39-7.32 (m, 5H), 5.20 (d, *J* = 3.7 Hz, 2H), 5.14-5.04 (s, 1H), 5.03 (s, 1H), 4.85 (s, 1H), 4.27 (brs, 1H), 3.16 (ddd, *J* = 13.7, 11.5, 4.1 Hz, 1H), 2.75 (d, *J* = 15.3 Hz, 1H), 2.63 (dd, *J* = 15.3, 6.6 Hz, 1H), 2.51-2.38 (brs, 1H), 2.34 (d, *J* = 15.4 Hz, 1H), 1.68 (s, 3H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.1, 155.5, 142.9, 136.4, 128.6, 128.3, 128.0, 114.9, 67.8, 55.9, 43.2, 40.5, 38.6, 20.3. **HRMS ESI:** $[M+H]^+$, calcd for$C_{16}H_{19}NO_3$: 274.1437; found 274.1440.

[a] Dimethyl(prop-1-en-2-yl)aluminum has been prepared according to a published protocol.[13] However, for the generation of the alane Et_2O has been used instead of MTBE.

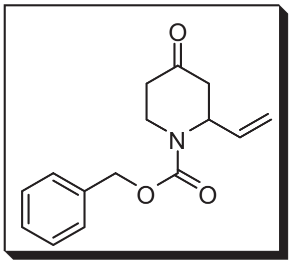


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.33	6.51	6.86	0.00	50.28	278.7	56.1	50.281
2	UNKNOWN	6.86	7.05	7.42	0.00	49.72	260.2	55.5	49.719
Total						100.00	538.9	111.5	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.36	6.56	6.94	0.00	95.06	417.0	88.2	95.057
2	UNKNOWN	6.94	7.12	7.39	0.00	4.94	21.5	4.6	4.943

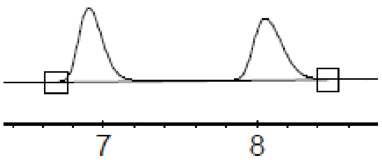
Benzyl 4-oxo-2-vinylpiperidine-1-carboxylate (2n)

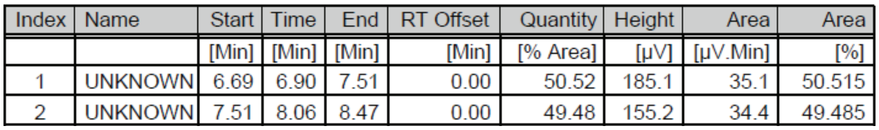


According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1.5:1; R_f = 0.48 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (29 mg, 0.11 mmol, 37% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 6.90 min (maj.), t_{R2} = 8.06 min (min.)). $[\alpha_D]$ /20°C = + 7.3 ($CHCl_3$, c = 0.36, ee = 63% (*R*)).

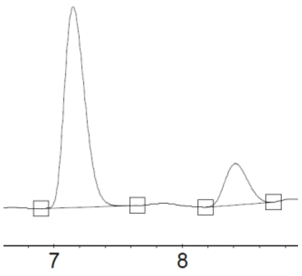
^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.40 – 7.31 (m, 5H), 5.77 (ddd, *J* = 17.4, 10.6, 4.2 Hz, 1H), 5.28 – 5.24 (m, 1H), 5.23 – 5.12 (m, 4H), 4.24 (d, *J* = 12.6 Hz, 1H), 3.39 (ddd, *J* = 13.7, 10.8, 4.2 Hz, 1H), 2.70 (dd, *J* = 15.2, 6.8 Hz, 1H), 2.61 (d, *J* = 15.0 Hz, 1H), 2.53 – 2.41 (m, 1H), 2.35 (dt, *J* = 15.5, 3.2 Hz, 1H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.0, 155.3, 136.3, 136.1, 128.6, 128.3, 128.1, 118.0, 67.8, 53.4, 43.4, 40.4, 39.2. Spectroscopic data are in accordance with the literature.[14]

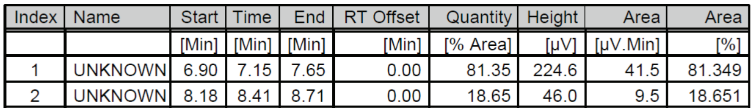
[a] Preparation of the vinyl aluminum reagent:
To a solution of vinyl grignard (2.0 mL, 2.0 mmol, 1.0 equiv., 1.0 M solution in THF) in ether (2.0 mL) was added Me_2AlCl (2.0 mL, 2.0 mmol, 1.0 equiv., 1.0 M solution in heptane) at 0°C. After 10 min the solution was warmed to room temperature and stirred for another 2 h. Then the white suspension was diluted with pentane (2.0 mL) and stirring was stopped. From the supernatant solution 2.4 mL (0.6 mmol) was taken and added to the preformed catalyst. All the following steps have been done according to the general protocol.





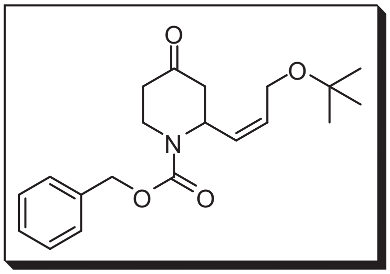
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.69	6.90	7.51	0.00	50.52	185.1	35.1	50.515
2	UNKNOWN	7.51	8.06	8.47	0.00	49.48	155.2	34.4	49.485





Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.90	7.15	7.65	0.00	81.35	224.6	41.5	81.349
2	UNKNOWN	8.18	8.41	8.71	0.00	18.65	46.0	9.5	18.651

(Z)-benzyl 2-(3-tert-butoxyprop-1-enyl)-4-oxopiperidine-1-carboxylate



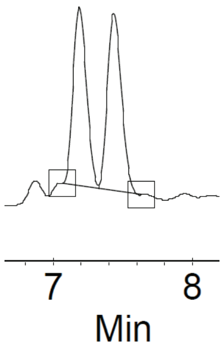
According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.37 (Pentane / Ether

= 1:2)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as a viscous oil (47 mg, 0.14 mmol, 45% yield). Enantiomeric excess was determined by SFC. (ChiralPAK OD-H: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 7.19 min (min.), t_{R2} = 7.43 min (maj.)). $[\alpha_D]$ /20°C = +1.7 ($CHCl_3$, c = 0.23, ee = 49% (*R*)).

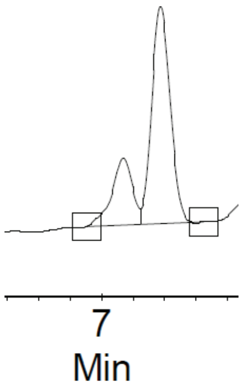
■ NMR-spectra were recorded at 55°C.

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.46 – 7.34 (m, 5H), 7.77 – 7.70 (m, 1H), 5.55 – 5.42 (m, 2H), 5.22 (d, *J* = 1.7 Hz, 2H), 4.39 – 4.29 (m, 1H), 4.11 – 4.01 (m, 1H), 3.93 (brs, 1H), 4.11 – 4.01 (m, 1H), 2.75 (dd, *J* = 14.7, 6.2 Hz, 1H), 2.67 – 2.50 (m, 1H), 2.44 (d, *J* = 15.6 Hz, 1H), 1.19 (s, 1H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.2, 154.8, 136.3, 128.7, 128.6, 128.3, 128.2, 127.7, 73.4, 67.8, 58.0, 49.8, 46.0, 40.7, 39.2, 27.5. **HRMS ESI:** $[M+H]^+$, calcd for $C_{20}H_{27}NO_4$: 346.2012; found 346.2010.

[a] The complex has been prepared with KUBAS salt $Cu(CH_3CN)_4BF_4$ = 20 mol%) and ligand **L1** **(**22 mol%) in THF (1.0 mL). When the reaction was carried out under standard conditions Cu(II)-naphtenate (20 mol%), LX (22 mol%) in ether (1.0 mL) the enantioselectivity dropped to 14% ee.

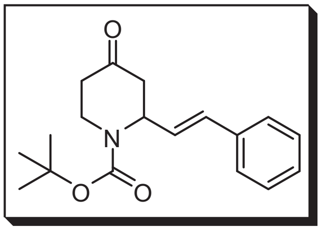


Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
	[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
UNKNOWN	7.06	7.19	7.32	0.00	48.89	290.1	32.4	48.893
UNKNOWN	7.32	7.43	7.63	0.00	51.11	287.7	33.8	51.107



Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
	[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
UNKNOWN	6.91	7.14	7.25	0.00	25.64	97.1	14.8	25.645
UNKNOWN	7.25	7.38	7.65	0.00	74.36	313.3	42.8	74.355

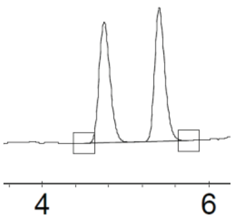
(*E*)-tert-butyl 4-oxo-2-styrylpiperidine-1-carboxylate (2p)



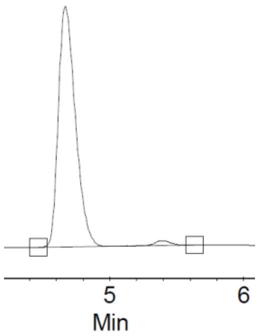
According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 2:1; R_f = 0.58 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give quickly fading blue stains. The product was isolated as a viscous oil (45 mg, 0.15 mmol, 50% yield). Enantiomeric excess was determined by SFC. (ChiralCEL OJ-H: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 4.74 min (min.), t_{R2} = 5.41 min (maj.)). [α_D] /20°C = +57.0 ($CHCl_3$, c = 0.96, ee = 97% (*R*)).

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.37 – 7.21 (m, 5H), 6.47 (d, *J* = 16.1 Hz, 1H), 6.11 (dd, *J* = 16.2, 4.9 Hz, 1H), 5.30 (brs, 1H), 4.20 (brs, 1H), 3.44 – 3.32 (m, 1H), 2.78 (dd, *J* = 15.1, 6.8 Hz, 1H), 2.68 (d, *J* = 14.9 Hz, 1H), 2.59 – 2.45 (m, 1H), 2.42 – 2.33 (m, 1H), 1.51 (s, 9H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.7, 154.7, 136.1, 132.4, 128.7, 128.1, 127.7, 126.5, 80.8, 53.0, 44.2, 40.6, 39.1, 28.5. **HRMS** ESI-MSHR**:** $[M+Na]^+$, calcd for $NaC_{18}H_{23}NO_3$: 324.1570; found 324.1569.

[a] (*E*)-dimethyl(styryl)aluminum was prepared according to the general procedure (*vide supra*) from the corresponding bromide.[13] Same level of enantioselectivity was observed when (*E*)-diisobutyl(styryl)aluminum was used instead. However, in this case lower yields (44% yield, 95% ee). (*E*)-diisobutyl(styryl)aluminum was prepared by Ni-catalyzed hydroalumination according to a literature procedure.[10] In both cases still traces of substrate were observed by TLC indicating that the conversion was less than 100%.

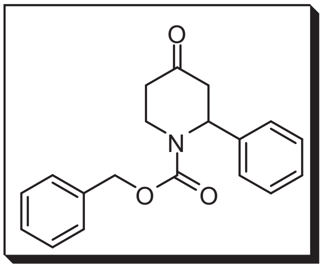


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.50	4.74	5.14	0.00	49.20	255.9	39.0	49.196
2	UNKNOWN	5.14	5.41	5.76	0.00	50.80	284.8	40.3	50.804



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.46	4.67	5.12	0.00	98.26	611.1	90.0	98.256
2	UNKNOWN	5.12	5.39	5.63	0.00	1.74	13.0	1.6	1.744

Benzyl 4-oxo-2-phenylpiperidine-1-carboxylate. (2q)

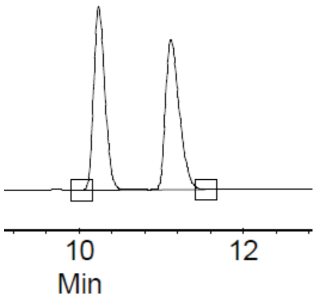


According to general procedure.[a] The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1.5; R_f = 0.36 (Pentane / Ether = 1:2)). Product was revealed with anisaldehyde to give red stains. The product was isolated as colorless solid (60 mg, 0.20 mmol, 65% yield). Enantiomeric excess was determined by SFC. (ChiralPAK OD-H: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 10.23 min (min.), t_{R2} = 11.11 min (maj.)). [α_D] /20°C = +46.9 ($CHCl_3$, c = 0.62, ee = 92% (*R*)). [Lit. +74.3 ($CHCl_3$, c = 1.00, ee = >99.5% (*R*))][15].

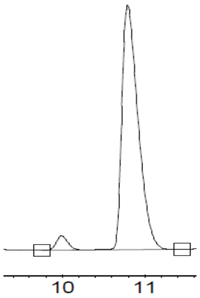
^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.40-7.22 (m, 5H), 5.84 (brs, 1H), 5.25 (d, *J* = 12.3 Hz, 1H), 5.20 (d, *J* = 12.6 Hz, 1H), 4.30 (s, 1H), 3.20 (t, *J* = 11.1 Hz, 1H), 2.99 (d, *J* = 13.8 Hz, 1H), 2.86 (dd, *J* = 15.5, 6.9 Hz, 1H), 2.60 – 2.45 (m, 1H), 2.37 (d, *J* = 15.9 Hz, 1H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.3, 155.5, 139.7, 136.3, 128.9, 128.6, 128.3, 128.1, 127.8, 126.8, 67.9, 54.7, 44.2, 40.6, 39.0. Spectroscopic data are in accordance with the literature.[15]

[a] Synthesis of dimethyl(phenyl)aluminum

To a solution of bromobenzene (211 µl, 314 mg, 2.0 mmol) in ether (2.0 mL) was added *n*-BuLi (1.25 mL, 2.0 mmol, 1.6 M solution in hexane) and the reaction mixture was stirred for 3 h at 0°C. Then Me_2AlCl (2.0 mL, 2.0 mmol, 1.0 M solution in heptane) was added to the solution of phenyllithium and stirred for another 30 min. Then the reaction was let warm to room temperature and stirred for another 2 h at room temperature. 1.62 mL (= 0.6 mmol, 2.0 equiv) of this solution (0.37 M) was added to the corresponding catalyzed reaction as described for the general protocol.

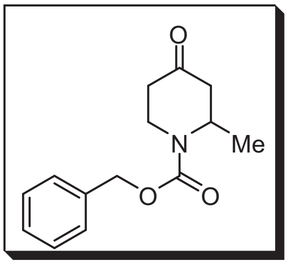


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	10.03	10.23	10.74	0.00	49.83	452.4	71.7	49.831
2	UNKNOWN	10.74	11.11	11.54	0.00	50.17	370.5	72.2	50.169



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.76	9.99	10.40	0.00	3.91	43.6	6.9	3.908
2	UNKNOWN	10.40	10.79	11.45	0.00	96.09	752.9	170.3	96.092

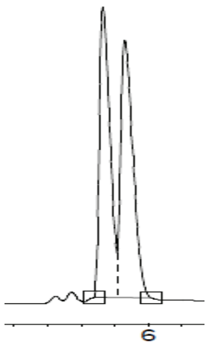
Benzyl 2-methyl-4-oxopiperidine-1-carboxylate (2r)



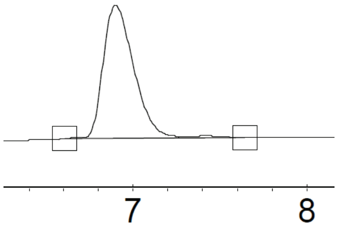
According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.33 (Pentane / Ether = 1:1)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as colorless solid (47 mg, 0.19 mmol, 64% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 6.85 min (maj.), t_{R2} = 7.34 min (min.)). [α_D] /20°C = + 6.3 ($CHCl_3$, c = 0.56, ee = >97% (*S*)). [Lit. –6.5 ($CHCl_3$, c = 0.37, ee = 96% (*R*))][3].

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.39-7.31 (m, 5H), 5.17 (s, 2H), 4.79 (brs, 1H), 4.31 (brs, 1H), 3.38 (ddd, *J* = 13.9, 11.4, 4.0 Hz, 1H), 2.68 (dd, *J* = 14.5, 6.7 Hz, 1H), 2.54-2.44 (m, 1H), 2.35 (d, *J* = 15.5 Hz, 1H), 2.26 (d, *J* = 14.4 Hz, 1H), 1.19 (t, *J* = 9.1 Hz, 3H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.8, 155.1, 136.4, 128.6, 128.3, 128.1, 67.6, 48.3, 46.6, 40.6, 38.6, 19.0. Spectroscopic data are in accordance with the literature.[3]

[a] Me_3Al (0.3 mL, 0.6 mmol, 2.0 equiv., 2.0 M in heptane) was used.

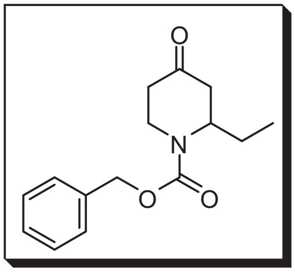


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.36	5.47	5.63	0.00	49.39	1312.0	192.0	49.390
2	UNKNOWN	5.63	5.72	6.04	0.00	50.61	1164.3	196.8	50.610



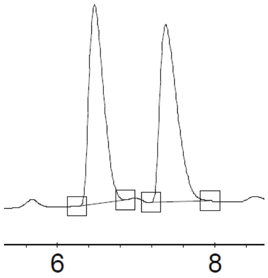
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.61	6.90	7.26	0.00	98.40	289.5	58.6	98.404
2	UNKNOWN	7.26	7.41	7.64	0.00	1.60	4.0	1.0	1.596

Benzyl 2-ethyl-4-oxopiperidine-1-carboxylate (2s)

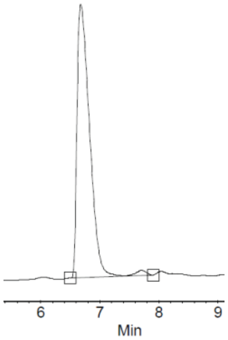


According to general procedure. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.38 (Pentane / Ether = 1:1)). Product was revealed with anisaldehyde to give brown stains. The product was isolated as colorless solid (36 mg, 0.14 mmol, 46% yield). Enantiomeric excess was determined by SFC. (ChiralPAK AD: 2 mL/min., 200 bar, MeOH, 5%, 2 minutes – 2%/min. – 25% – 30 °C) t_{R1} = 6.47 min (maj.), t_{R2} = 7.37 min (min.)). $[\alpha_D]$ /20°C = + 8.7 ($CHCl_3$, c = 0.47, ee = 97% (S)). [Lit. –2.3 ($CHCl_3$, c = 0.53, ee = 94% (*R*))][3].

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ = 7.41 – 7.30 (m, 5H), 5.25-5.13 (m, 2H), 4.58 (brs, 1H), 4.40 (brs, 1H), 3.20 (dd, *J* = 18.4, 7.0 Hz, 1H), 2.64 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.47 (brs, 1H),2.53 – 2.40 (brs, 1H), 2.32 (d, *J* = 14.3 Hz, 1H), 1.62 – 1.42 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 207.7, 156.0, 136.5, 128.6, 128.2, 128.0, 67.6, 53.8, 45.28, 40.6, 38.4, 25.4, 10.2. Spectroscopic data are in accordance with the literature.[3]



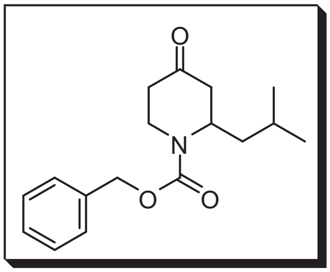
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.25	6.47	6.86	0.00	49.07	502.7	109.0	49.074
2	UNKNOWN	7.18	7.37	7.93	0.00	50.93	448.5	113.1	50.926



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.50	6.67	7.41	0.00	98.46	1195.8	292.8	98.461
2	UNKNOWN	7.41	7.70	7.90	0.00	1.54	21.6	4.6	1.539

Benzyl 2-isobutyl-4-oxopiperidine-1-carboxylate (2t)

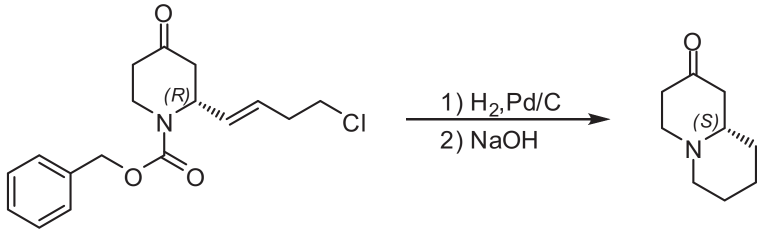
This compound was synthesized in order to confirm that the side product in some cases was really i-Bu transfer (Verified by same retention time (GC-MS) and mass pattern).



Instead of an aluminum organyl *i*-BuMgBr was added (0.6 mL, 2.0 equiv., 1.0 M solution in Et_2O). All the other steps were done according to the general protocol. The crude mixture was purified by flash-chromatography on silica gel (Solvent mixture: Pentane / Ether = 1:1; R_f = 0.39 (Pentane / Ether = 1:1)). Product was revealed with anisaldehyde to give brown stains.

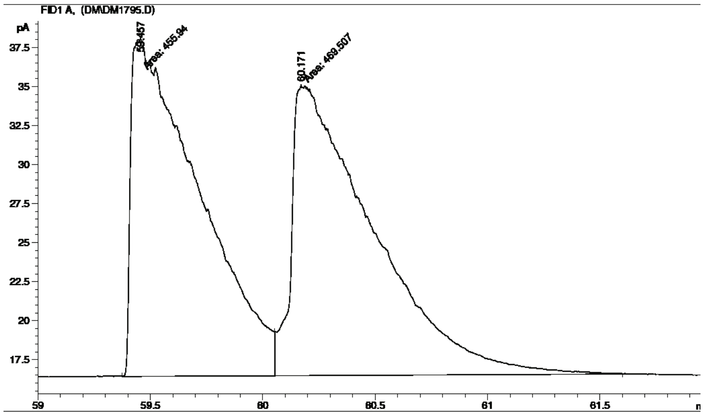
^{1}H-NMR (400.13 MHz, CDCl$_3$): δ = ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.28 – 5.13 (m, 2H), 4.73 (t, *J* = 13.1 Hz, 1H), 4.39 (dd, *J* = 13.5, 7.0 Hz, 1H), 3.29 – 3.18 (m, 1H), 2.63 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.53 – 2.39 (m, 1H), 2.36 – 2.22 (m, 2H), 1.61 – 1.41 (m, 2H), 1.32 – 1.15 (m, 1H), 0.90 (dd, *J* = 6.0, 4.4 Hz, 6H). **^{13}C-NMR (100.61 MHz, CDCl$_3$):** δ = 210.0, 136.6, 128.5, 128.1, 128.0, 67.6, 50.9, 45.7, 41.5, 40.6, 38.6, 24.7, 22.6, 22.1. **HRMS ESI:** $[M+H]^+$, calcd for $C_{17}H_{23}NO_3$: 290.175; found 290.1747.

Hexahydro-1H-quinolizin-2(6H)-one (3a)



A solution of adduct **2f** (120 mg, 0.37 mmol) in MeOH (3 mL) was hydrogenated at atmospheric pressure and at 25 °C, using 10% palladium-charcoal (20 mg). After stirring for 12 h, the reaction mixture was filtered through Celite, and the solvent was evaporated under reduced pressure. The residual oil was diluted with Et_2O (2.0 mL) and aqueous solution of NaOH (0.3 M, 2.0 mL) was added and the mixture was shaken vigorously for 2 min. Then the organic phase was separated and the aqueous phase extracted with Et_2O (2 x 3.0 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Purification by silica gel chromatography [Solvent mixture: Ether / MeOH / aq. NH_4OH = 20:1:0.2; R_f = 0.25 (same mixture) stained with $KMnO_4$] to afford the hexahydro-1H-quinolizin-2(6H)-one as a colourless oil (34 mg, 0.22 mmol, 60%). Enantiomeric excess was measured by chiral GC (CP-Chirasil-DEX-CB, 60-0-1-170-0-5, 30 cm/s; t_{R1} = 59.46 min (R), t_{R2} = 60.17 min (S)). [α_D] /20°C = −37.4 ($CHCl_3$, c = 0.27, ee = 95% (R))

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ =^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 – 3.03 (m, 1H), 2.97 (d, *J* = 11.4 Hz, 1H), 2.73 – 2.59 (m, 1H), 2.40 – 2.23 (m, 4H), 2.11 – 2.00 (m, 2H), 1.76 – 1.59 (m, 4H), 1.42 – 1.15 (m, 2H). **^{13}C-NMR (100.61 MHz, $CDCl_3$):** δ = 208.9, 61.9, 55.5, 55.4, 48.4, 41.5, 33.8, 25.6, 23.4. Spectroscopic data are in accordance with the literature.[16]



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----|-------|----|-------|----------|----------|--------|
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   2  60.171 FM     0.4198  469.50726   18.63979 50.73302
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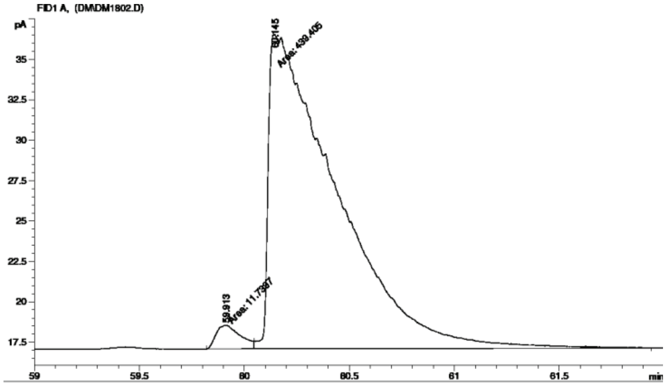

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References

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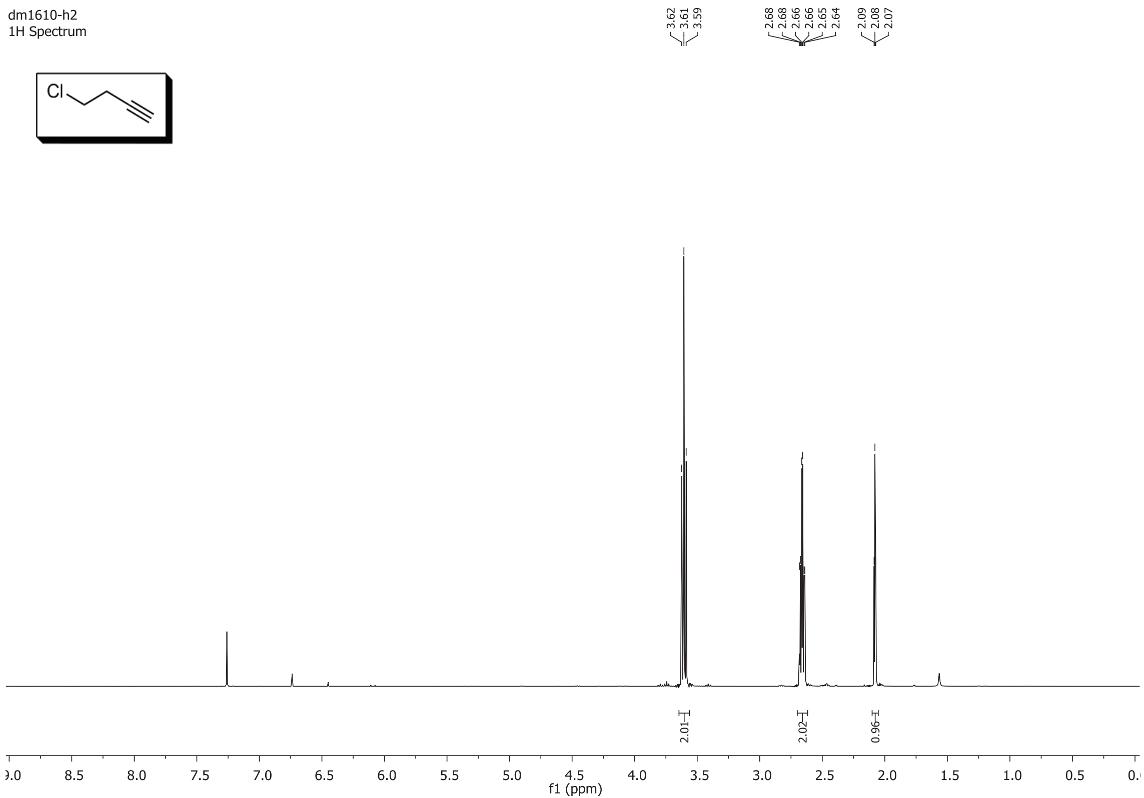
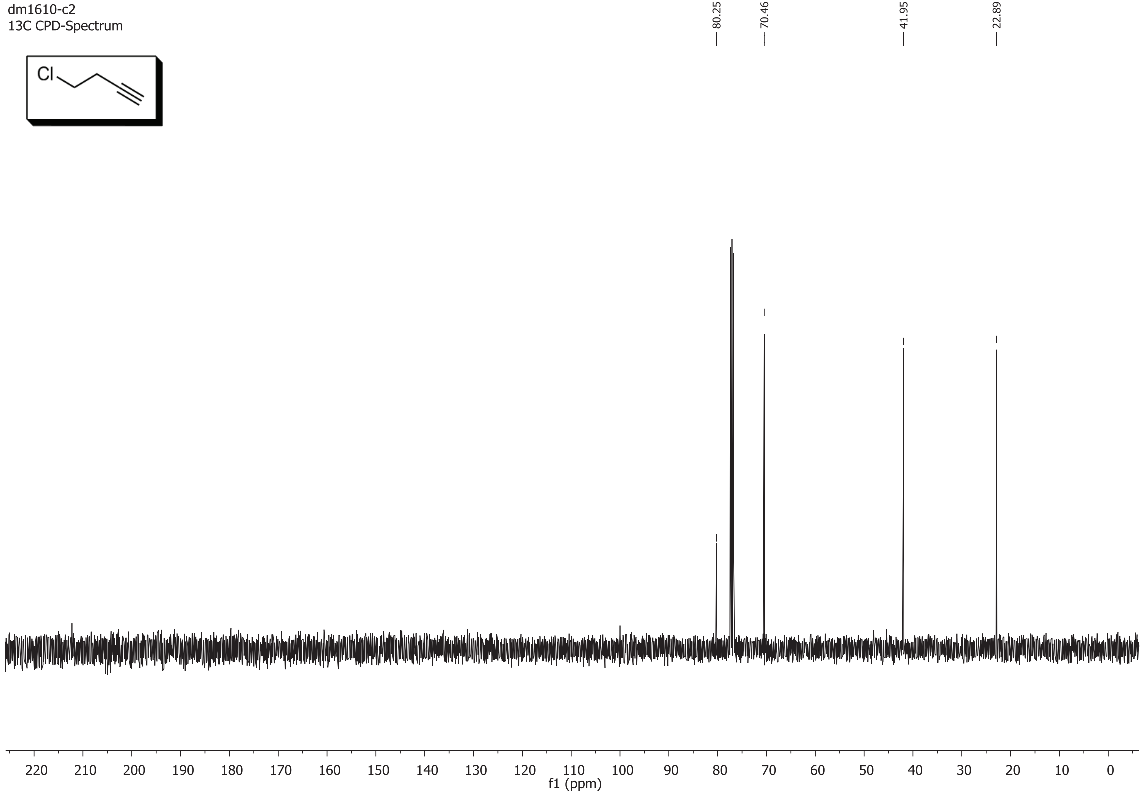
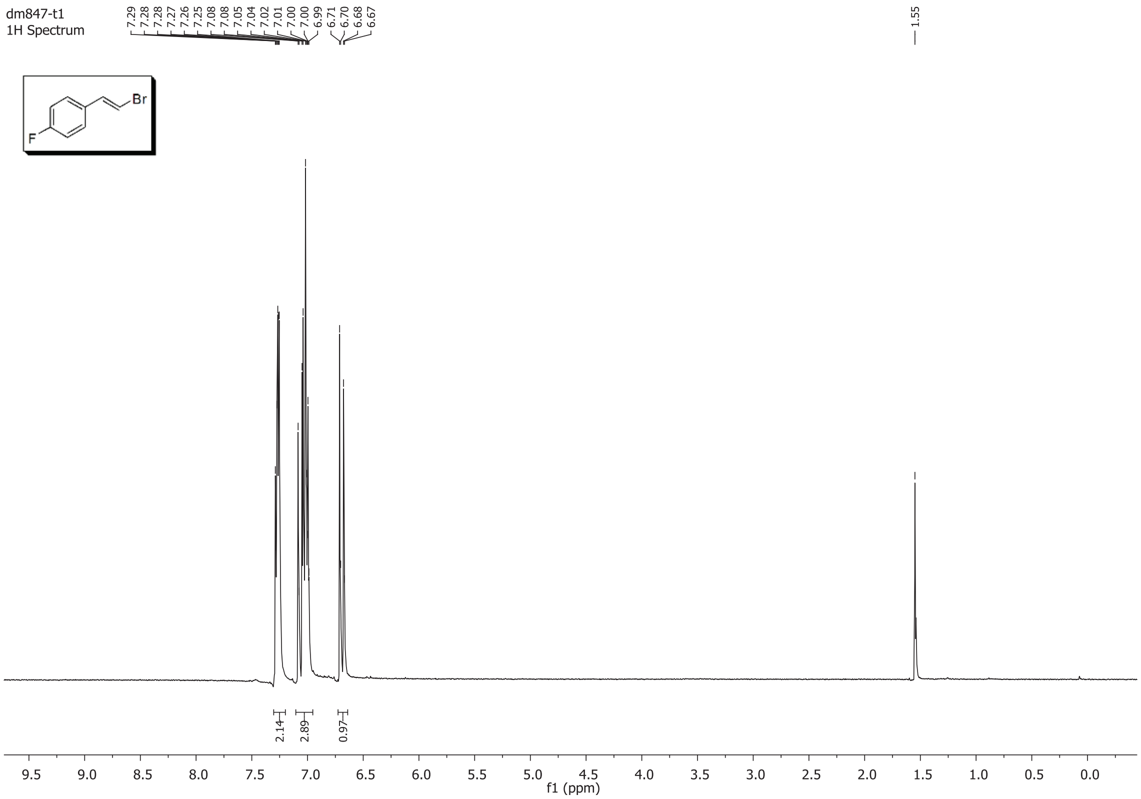
■ ^{1}H and ^{13}C-NMR spectra of all compounds



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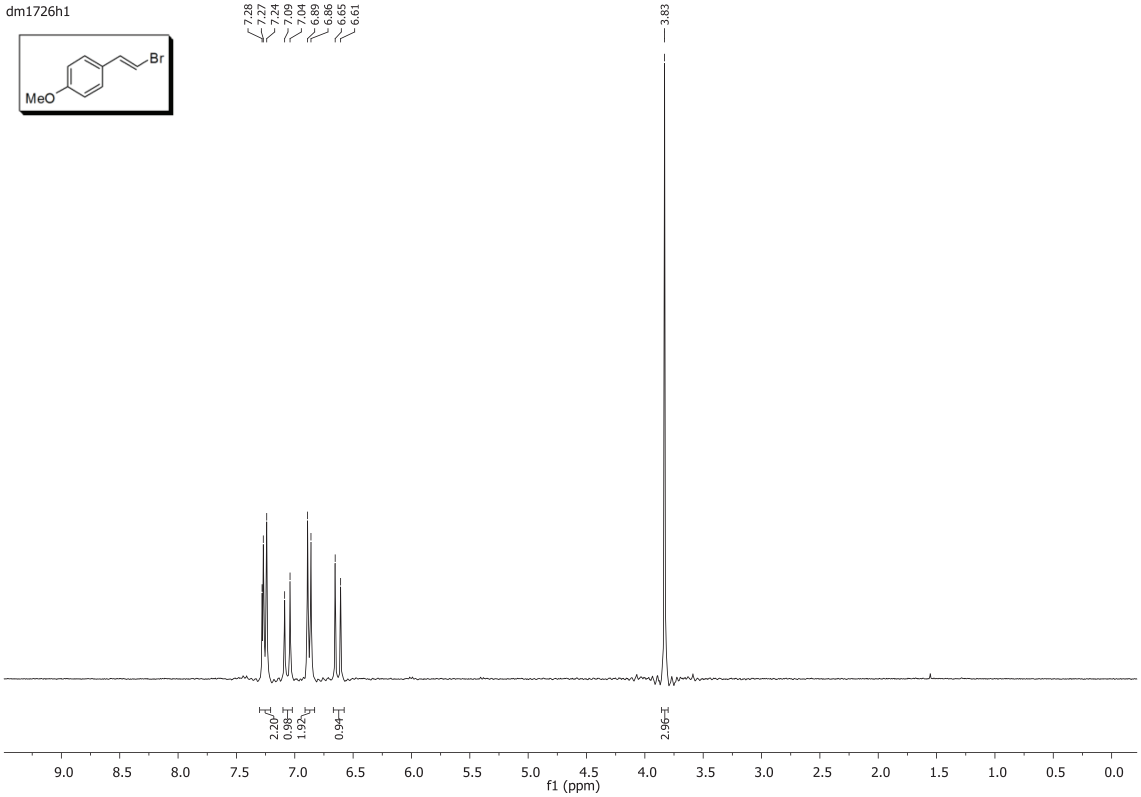
7.28
7.28
7.27
7.26
7.25
7.08
7.08
7.05
7.04
7.02
7.01
7.00
7.00
6.99
6.71
6.70
6.68
6.67
1.55
F
Br
2.14
2.89
0.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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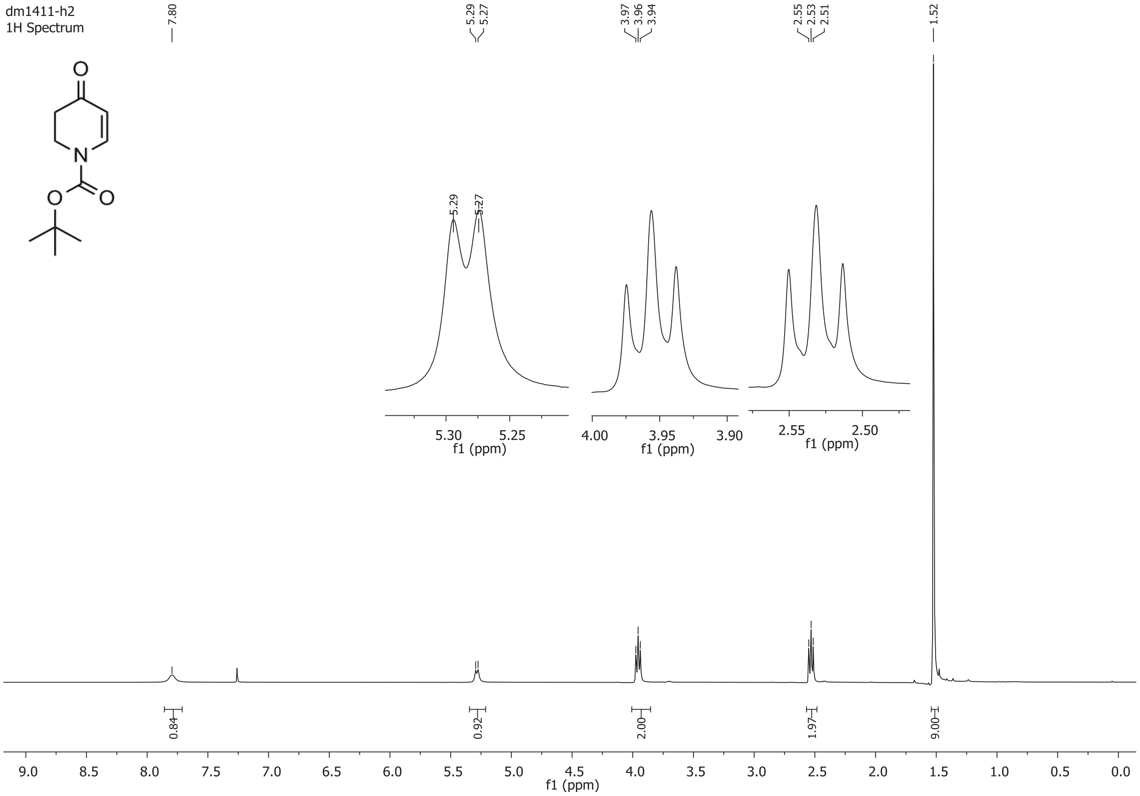
7.27
7.24
7.09
7.04
6.89
6.86
6.65
6.61
3.83
MeO
Br
2.20
0.98
1.92
0.94
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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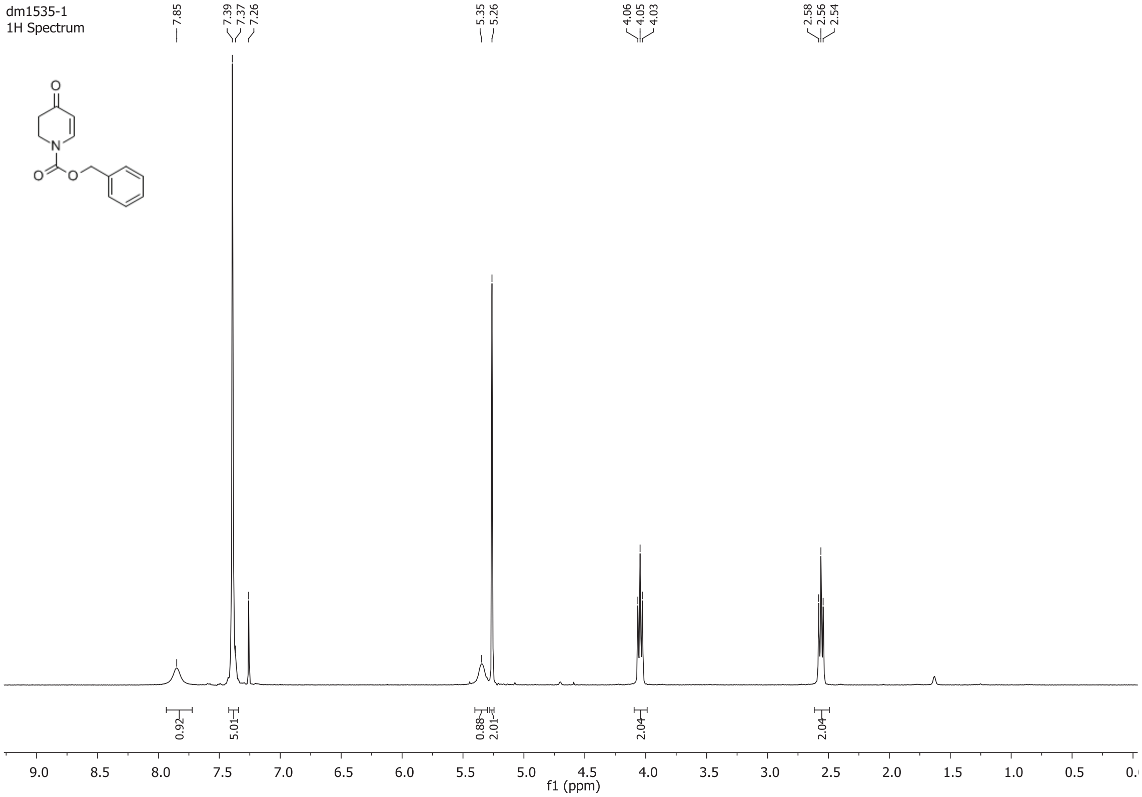
5.27
3.97
3.96
3.94
2.55
2.53
2.51
1.52
5.30
5.25
4.00
3.95
3.90
2.55
2.50
f1 (ppm)
0.84
0.92
2.00
1.97
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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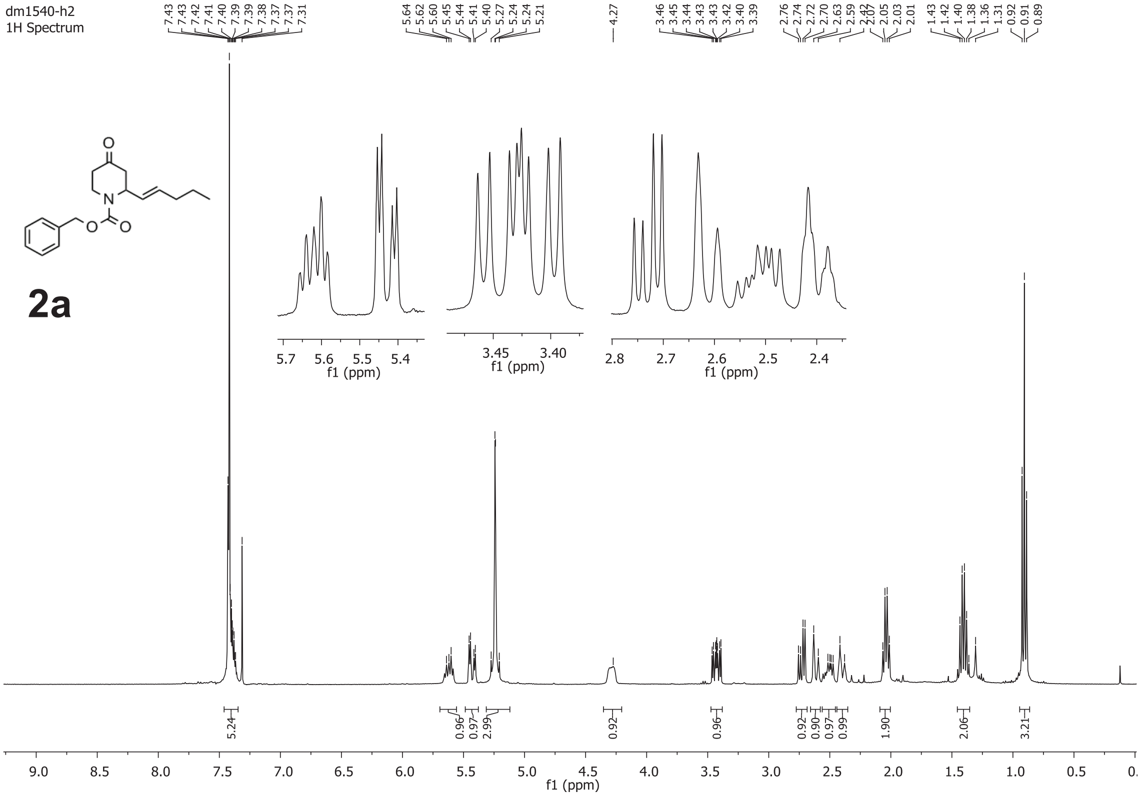
7.37
7.26
5.35
5.26
4.06
4.05
4.03
2.58
2.56
2.54
0.92
5.01
0.88
2.01
2.04
2.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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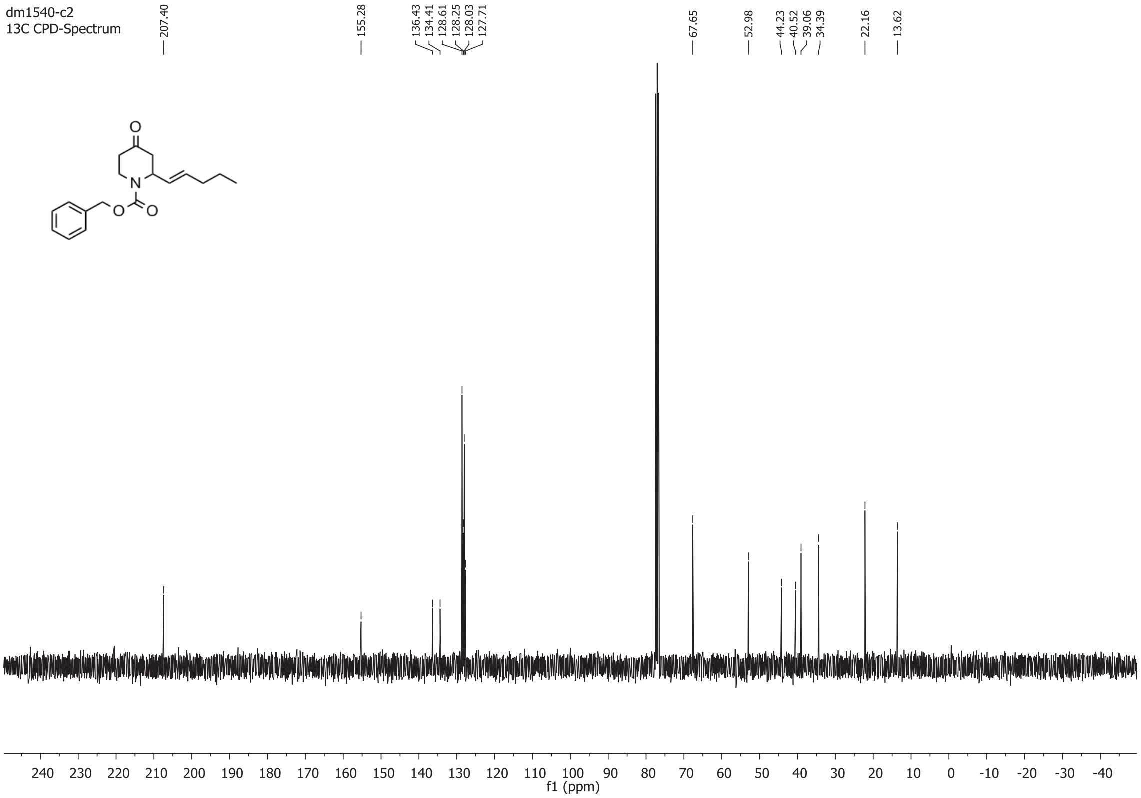
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.31
5.64
5.62
5.60
5.45
5.44
5.41
5.40
5.27
5.24
5.24
5.21
4.27
3.46
3.45
3.44
3.43
3.43
3.42
3.40
3.39
2.76
2.74
2.72
2.70
2.63
2.59
2.42
2.07
2.05
2.03
2.01
1.43
1.42
1.40
1.38
1.36
1.31
0.92
0.91
0.89
O
N
O
O
5.7 5.6 5.5 5.4
f1 (ppm)
3.45 3.40
f1 (ppm)
2.8 2.7 2.6 2.5 2.4
f1 (ppm)
5.24
0.96
0.97
2.99
0.92
0.96
0.92
0.90
0.97
0.99
1.90
2.06
3.21
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)

2a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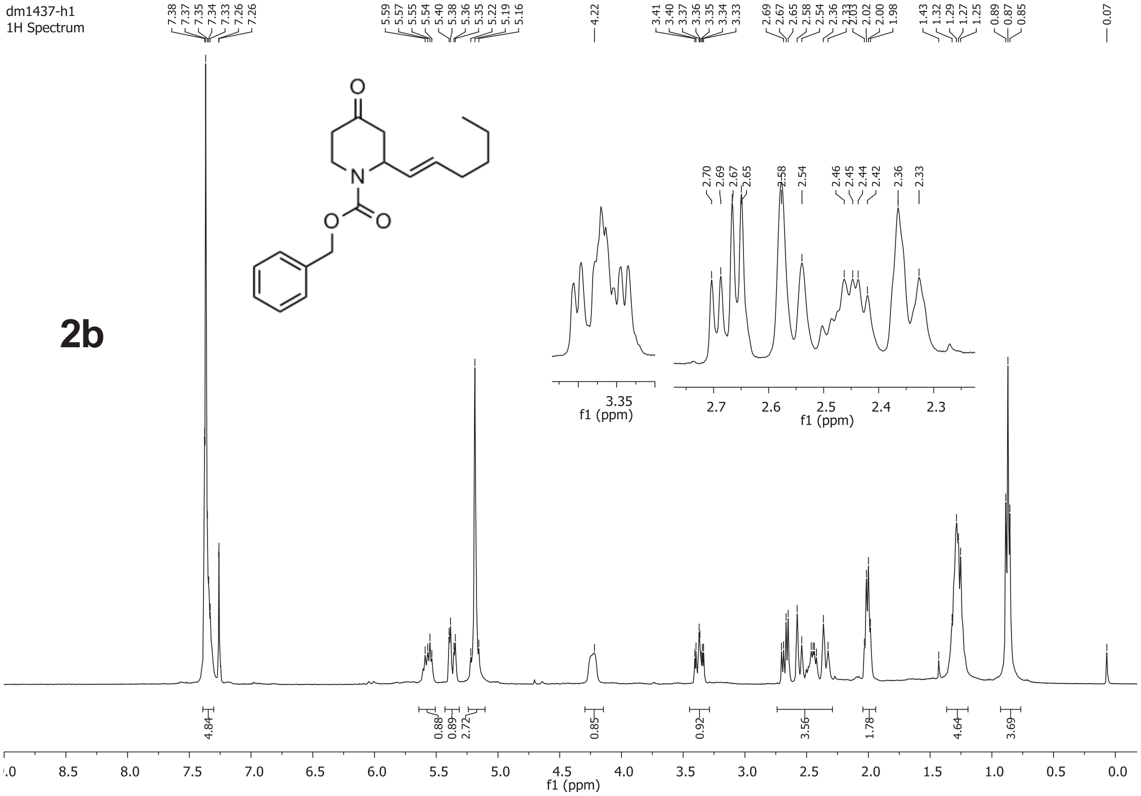
128.25
128.03
127.71
67.65
52.98
44.23
40.52
39.06
34.39
22.16
13.62
O
N
O
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

2b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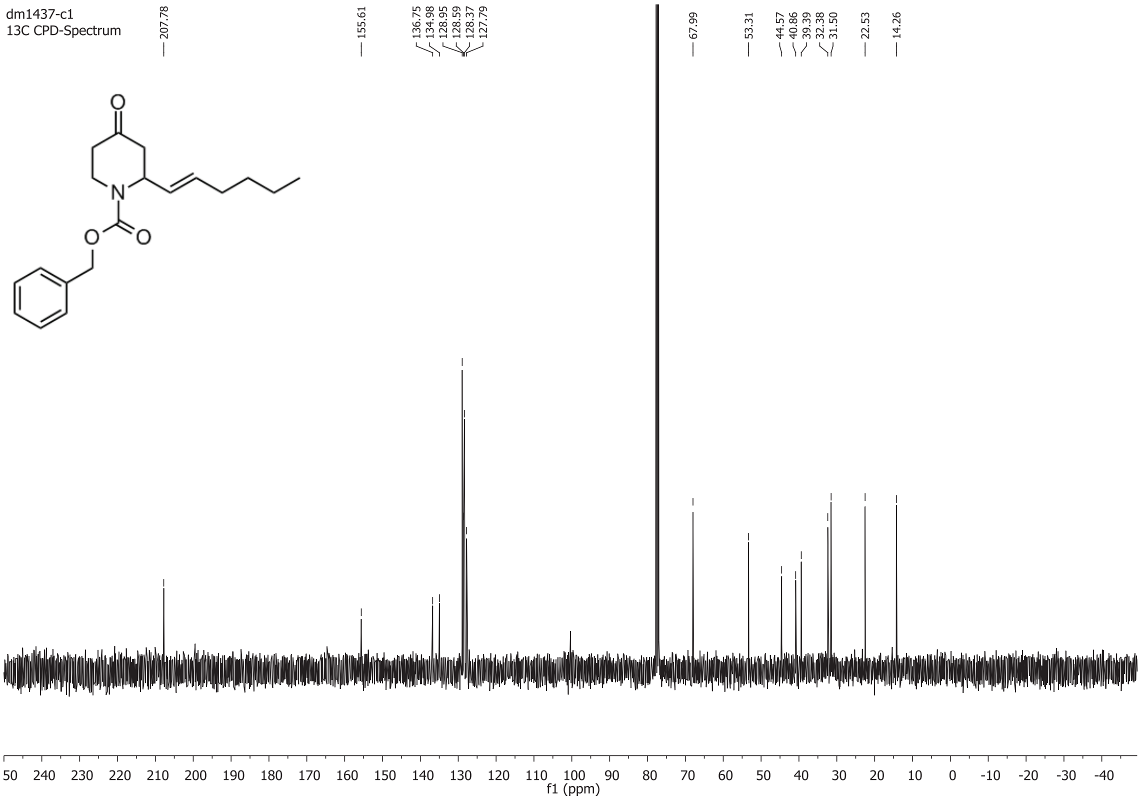
4.22
3.41 3.40 3.37 3.36 3.35 3.34 3.33
2.69 2.67 2.65 2.58 2.54 2.36 2.33 2.03 2.02 2.00 1.98
1.43 1.32 1.29 1.27 1.25
0.89 0.87 0.85
0.07
O
N
O
O
2.70 2.69 2.67 2.65 2.58 2.54 2.46 2.45 2.44 2.42 2.36 2.33
3.35
f1 (ppm)
2.7 2.6 2.5 2.4 2.3
f1 (ppm)
4.84
0.88 0.89 2.72
0.85
0.92
3.56
1.78
4.64
3.69
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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22.53
14.26
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O
O
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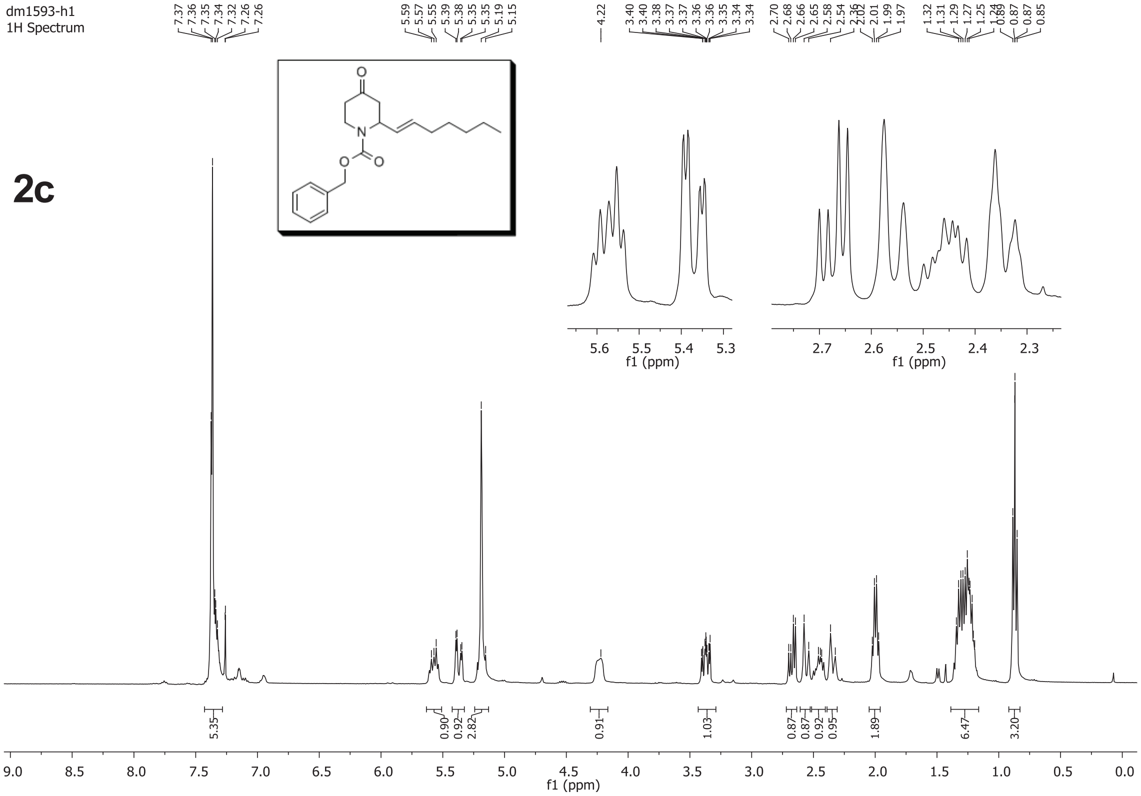
f1 (ppm)

2c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7.35
7.34
7.32
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7.26
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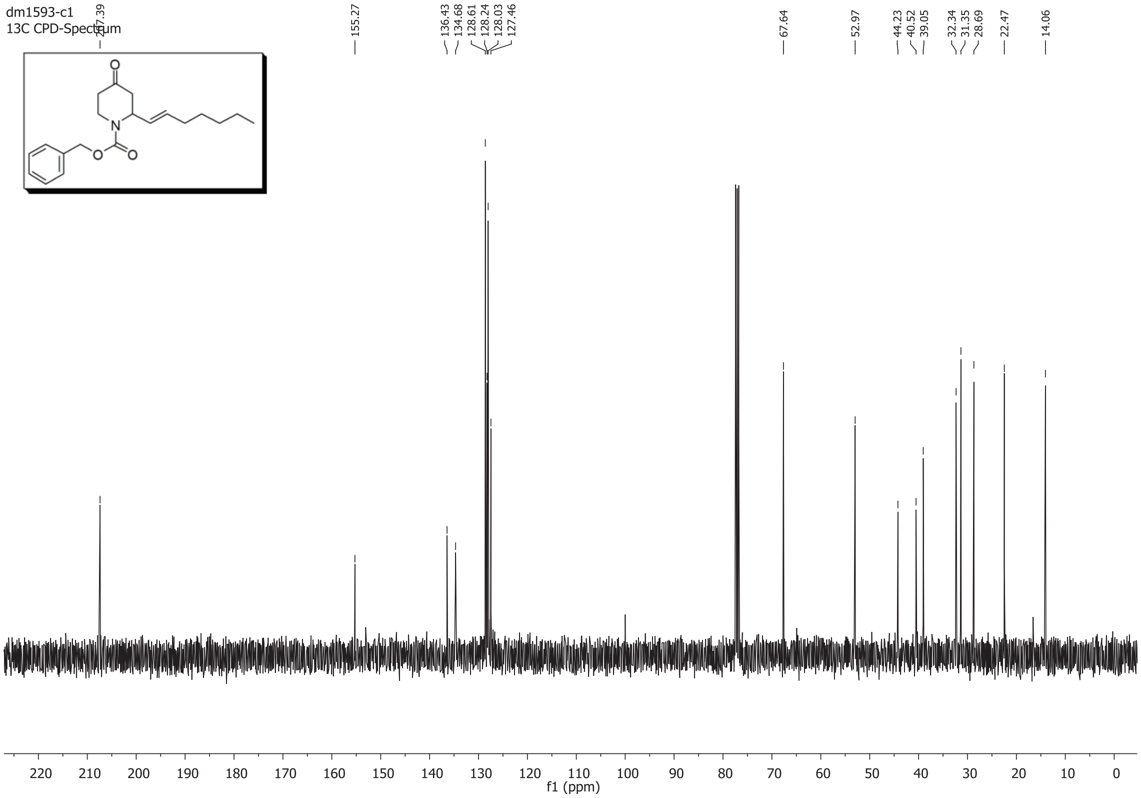
5.57
5.55
5.39
5.38
5.35
5.35
5.19
5.15
4.22
3.40
3.40
3.38
3.37
3.37
3.36
3.36
3.35
3.34
3.34
2.70
2.68
2.66
2.65
2.58
2.54
2.36
2.02
2.01
1.99
1.97
1.32
1.31
1.29
1.27
1.25
1.24
0.89
0.87
0.87
0.85
O
N
O
O
5.6
5.5
5.4
5.3
f1 (ppm)
2.7
2.6
2.5
2.4
2.3
f1 (ppm)
5.35
0.90
0.92
2.82
0.91
1.03
0.87
0.87
0.92
0.95
1.89
6.47
3.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.61
128.24
128.03
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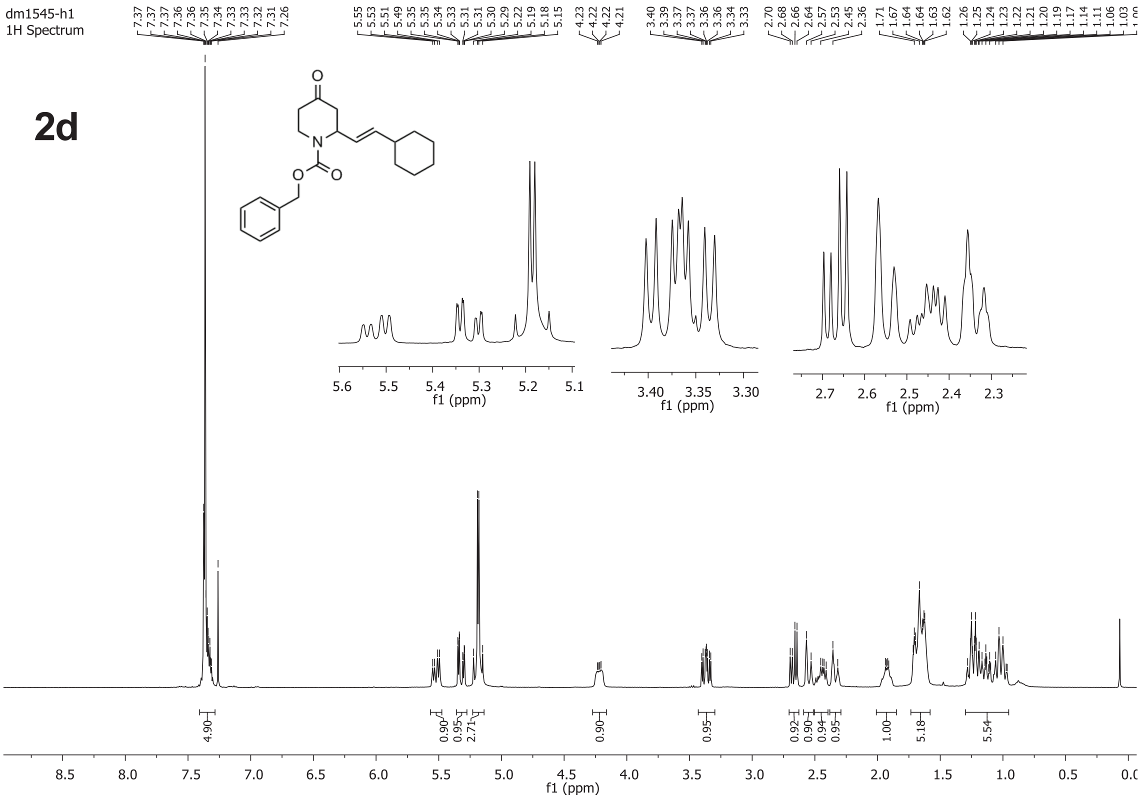
67.64
52.97
44.23
40.52
39.05
32.34
31.35
28.69
22.47
14.06
O
N
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2d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4.23 4.22 4.22 4.21
3.40 3.39 3.37 3.37 3.36 3.36 3.34 3.33
2.70 2.68 2.66 2.64 2.57 2.53 2.45 2.36
1.71 1.67 1.64 1.64 1.63 1.62
1.26 1.25 1.24 1.23 1.22 1.21 1.20 1.19 1.17 1.14 1.11 1.06 1.03
O
N
O
O
4.90
0.90 0.95 2.71
0.90
0.95
0.92 0.90 0.94 0.95
1.00
5.18
5.54
5.6 5.5 5.4 5.3 5.2 5.1
3.40 3.35 3.30
2.7 2.6 2.5 2.4 2.3
f1 (ppm)
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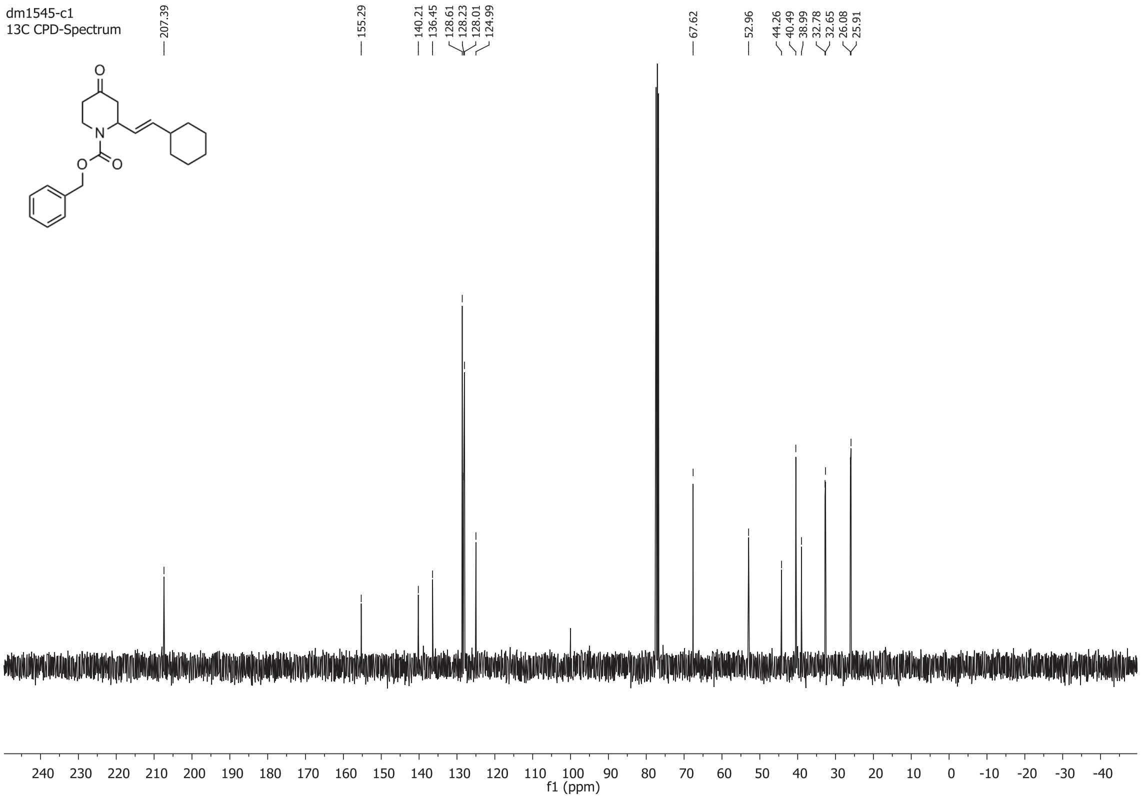
f1 (ppm)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67.62
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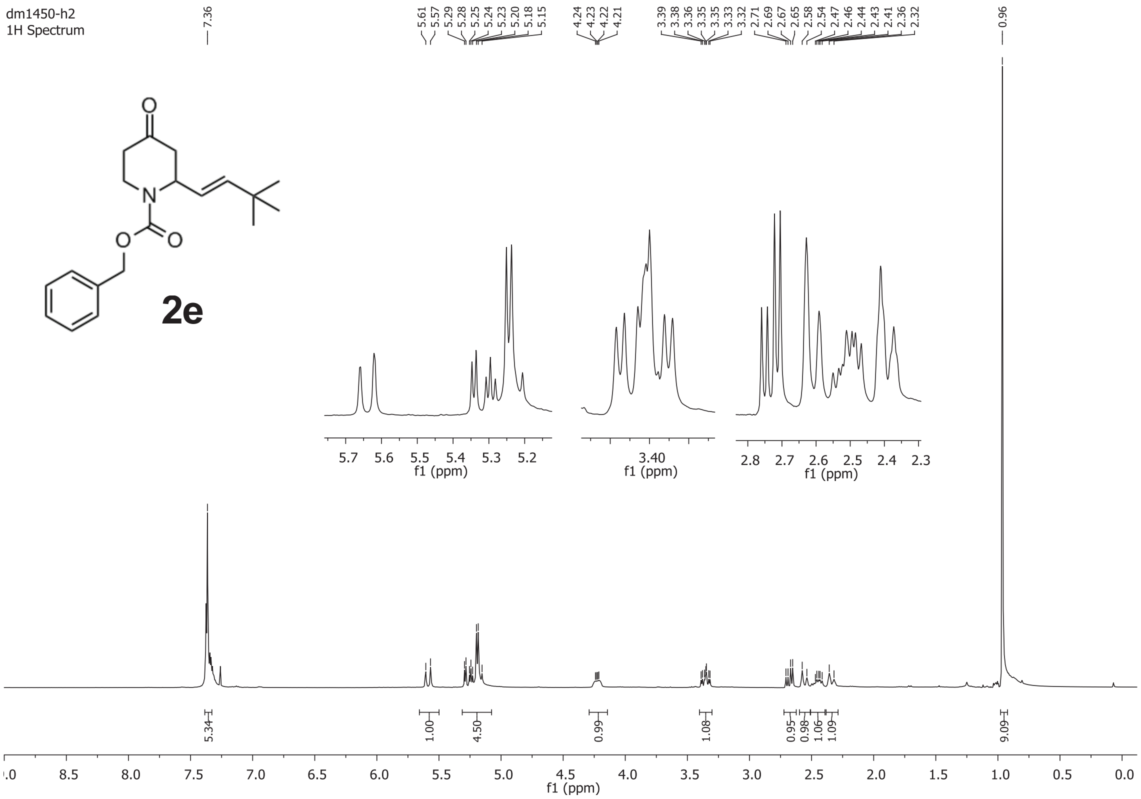
44.26 40.49 38.99 32.78 32.65 26.08 25.91
O
N
O
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


2e
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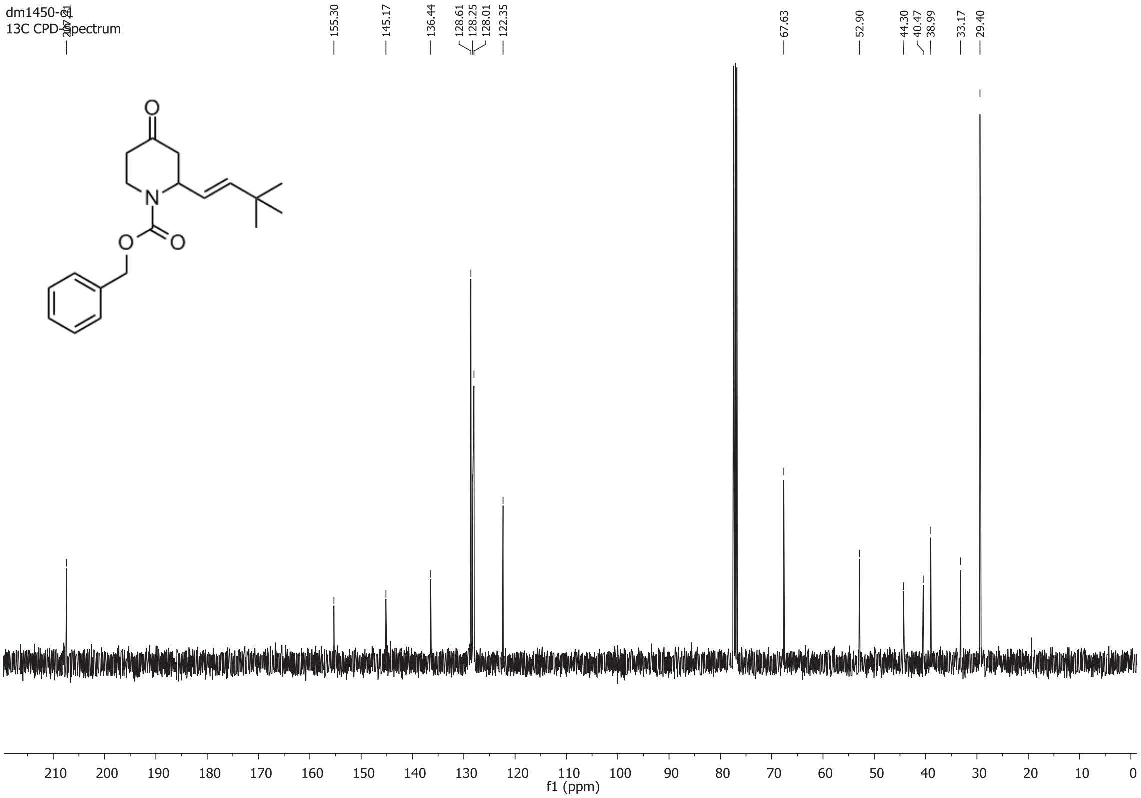
5.28
5.25
5.24
5.23
5.20
5.18
5.15
4.24
4.23
4.22
4.21
3.39
3.38
3.36
3.35
3.35
3.33
3.32
2.71
2.69
2.67
2.65
2.58
2.54
2.47
2.46
2.44
2.43
2.41
2.36
2.32
0.96
5.34
1.00
4.50
0.99
1.08
0.95
0.98
1.06
1.09
9.09
f1 (ppm)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145.17
136.44
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128.25
128.01
122.35
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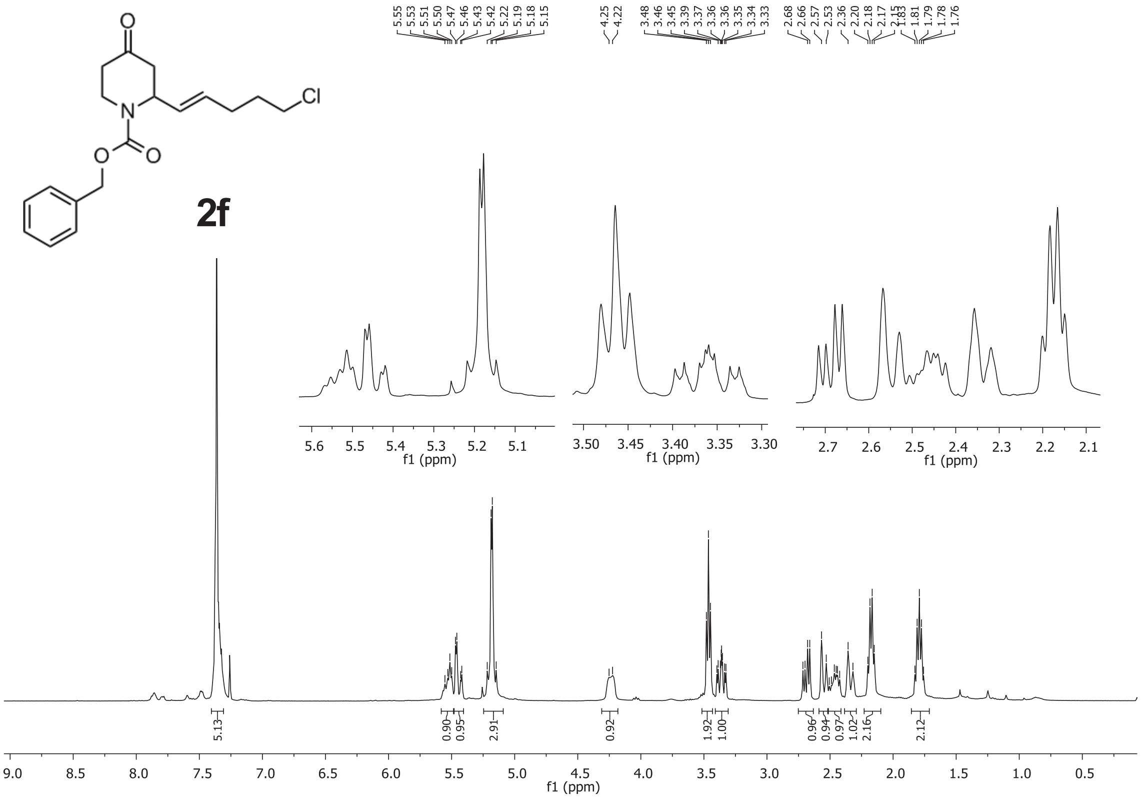
52.90
44.30
40.47
38.99
33.17
29.40
f1 (ppm)


2f
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O
O
Cl
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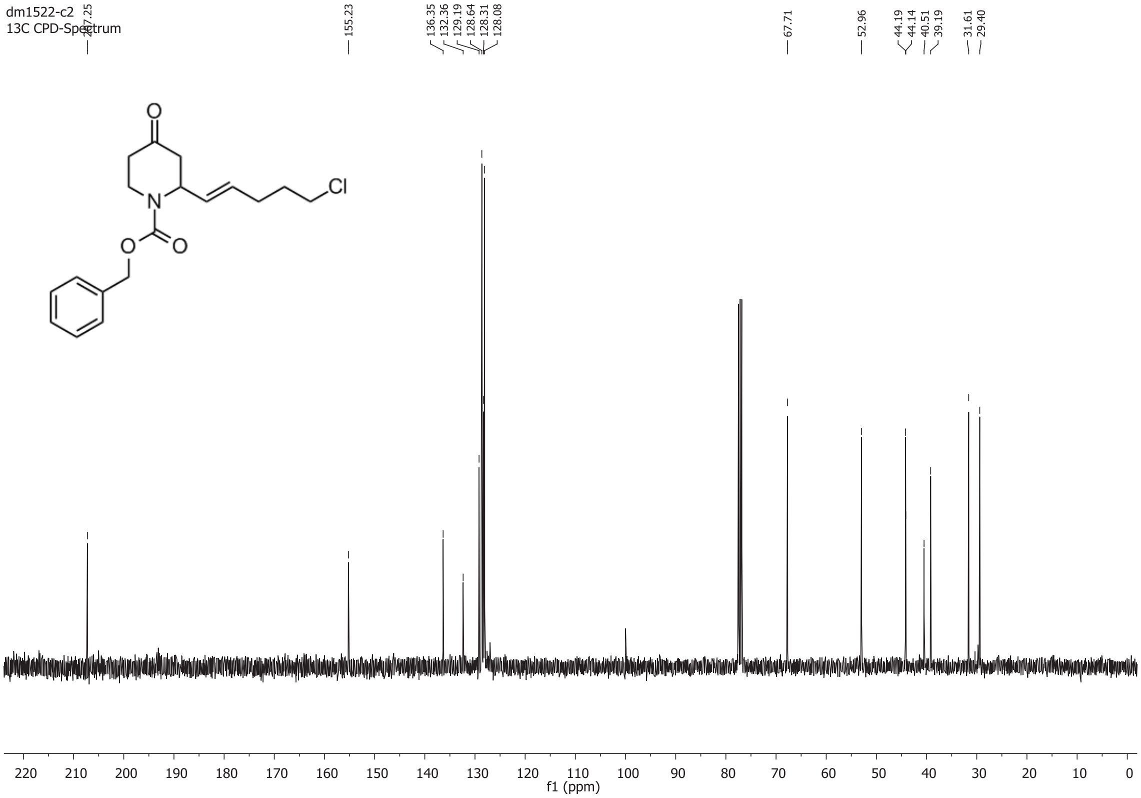
5.22
5.19
5.18
5.15
4.25
4.22
3.48
3.46
3.45
3.39
3.37
3.36
3.36
3.35
3.34
3.33
2.68
2.66
2.57
2.53
2.36
2.20
2.18
2.17
2.15
1.83
1.81
1.79
1.78
1.76
5.6 5.5 5.4 5.3 5.2 5.1
f1 (ppm)
3.50 3.45 3.40 3.35 3.30
f1 (ppm)
2.7 2.6 2.5 2.4 2.3 2.2 2.1
f1 (ppm)
5.13
0.90
0.95
2.91
0.92
1.92
1.00
0.96
0.94
0.97
1.02
2.16
2.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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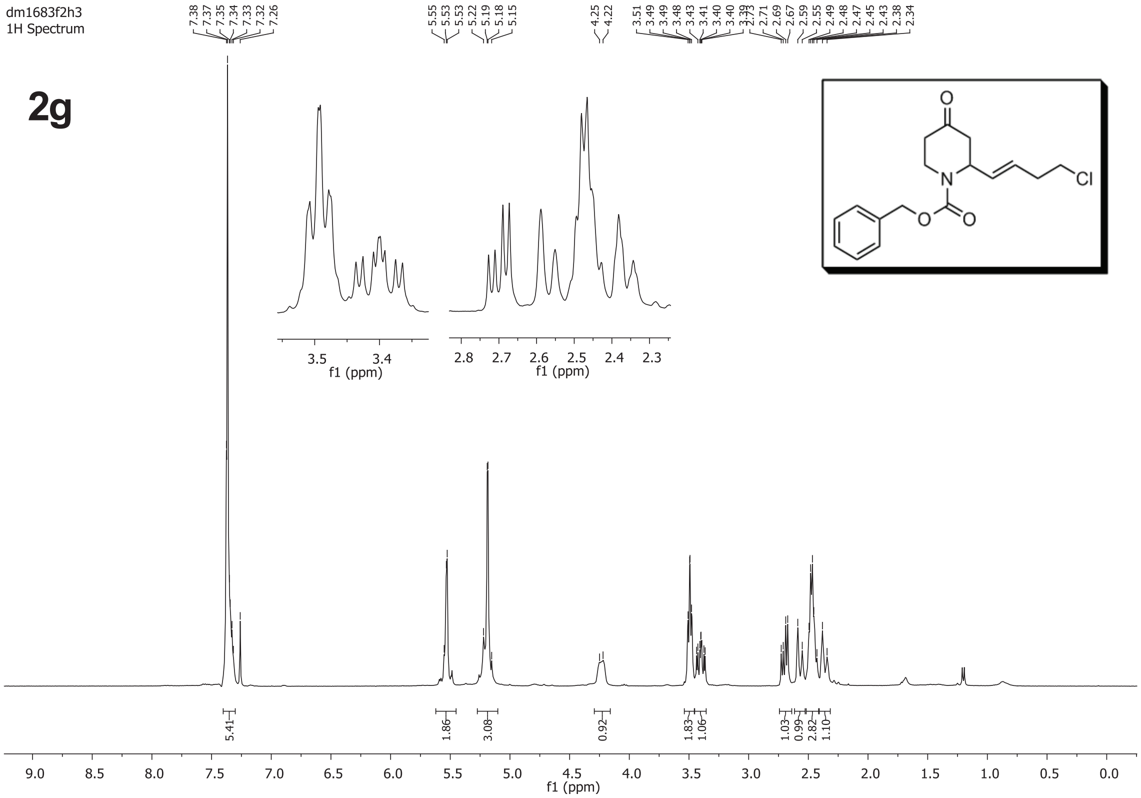
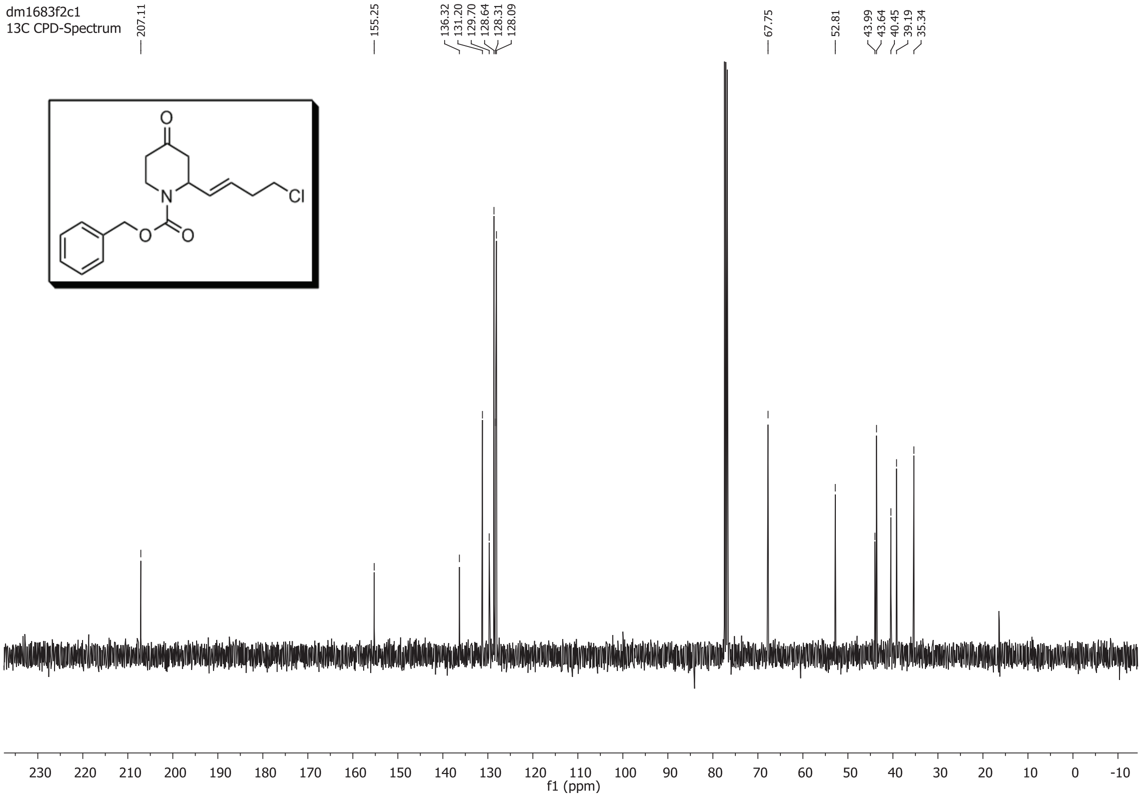
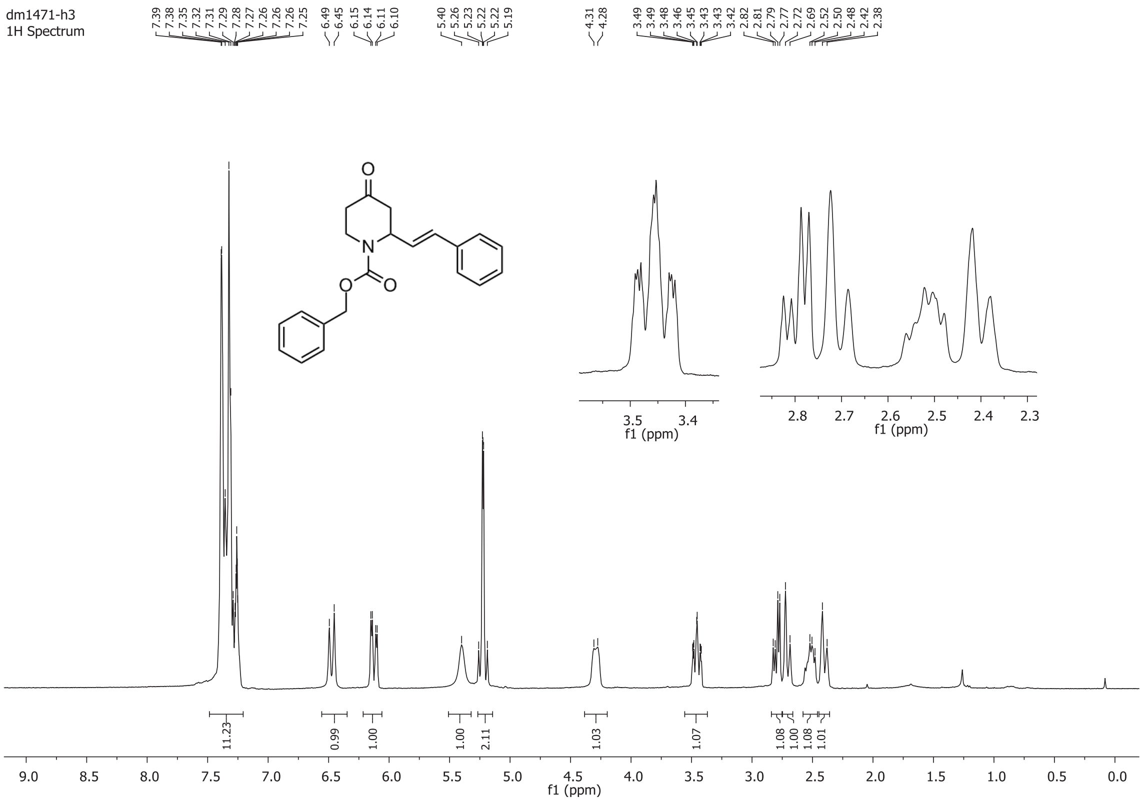
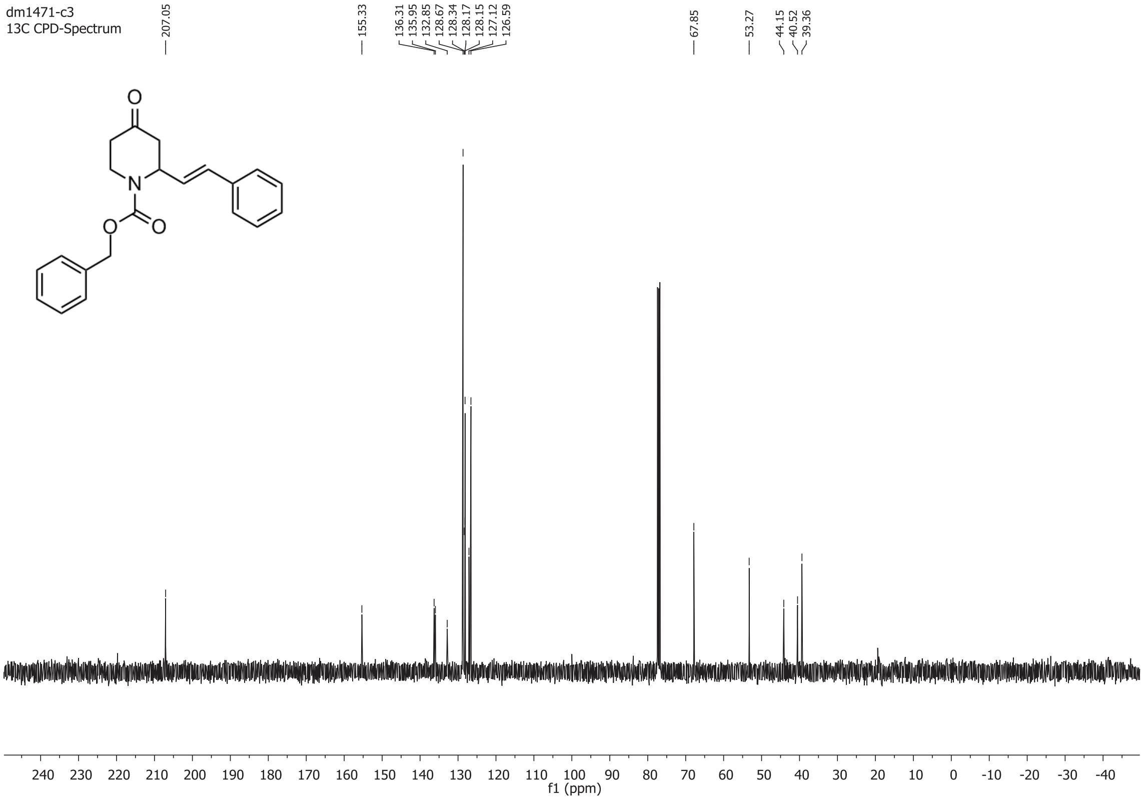
128.08
67.71
52.96
44.19
44.14
40.51
39.19
31.61
29.40
O
N
O
O
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

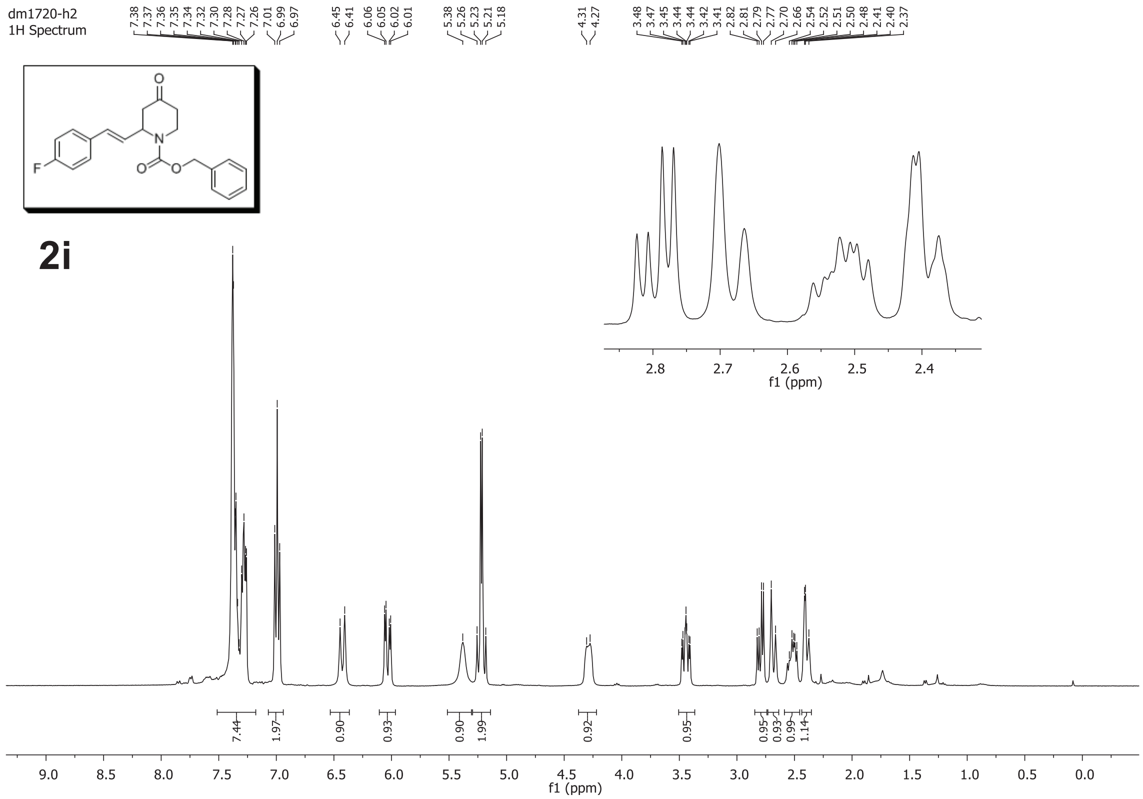
2g


dm1683f2h3
1H Spectrum
7.38
7.37
7.35
7.34
7.33
7.32
7.26
5.55
5.53
5.53
5.22
5.19
5.18
5.15
4.25
4.22
3.51
3.49
3.49
3.48
3.43
3.41
3.40
3.40
3.39
2.73
2.71
2.69
2.67
2.59
2.55
2.49
2.48
2.47
2.45
2.43
2.38
2.34
O
N
O
O
Cl
3.5
3.4
f1 (ppm)
2.8
2.7
2.6
2.5
2.4
2.3
f1 (ppm)
5.41
1.86
3.08
0.92
1.83
1.06
1.03
0.99
2.82
1.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

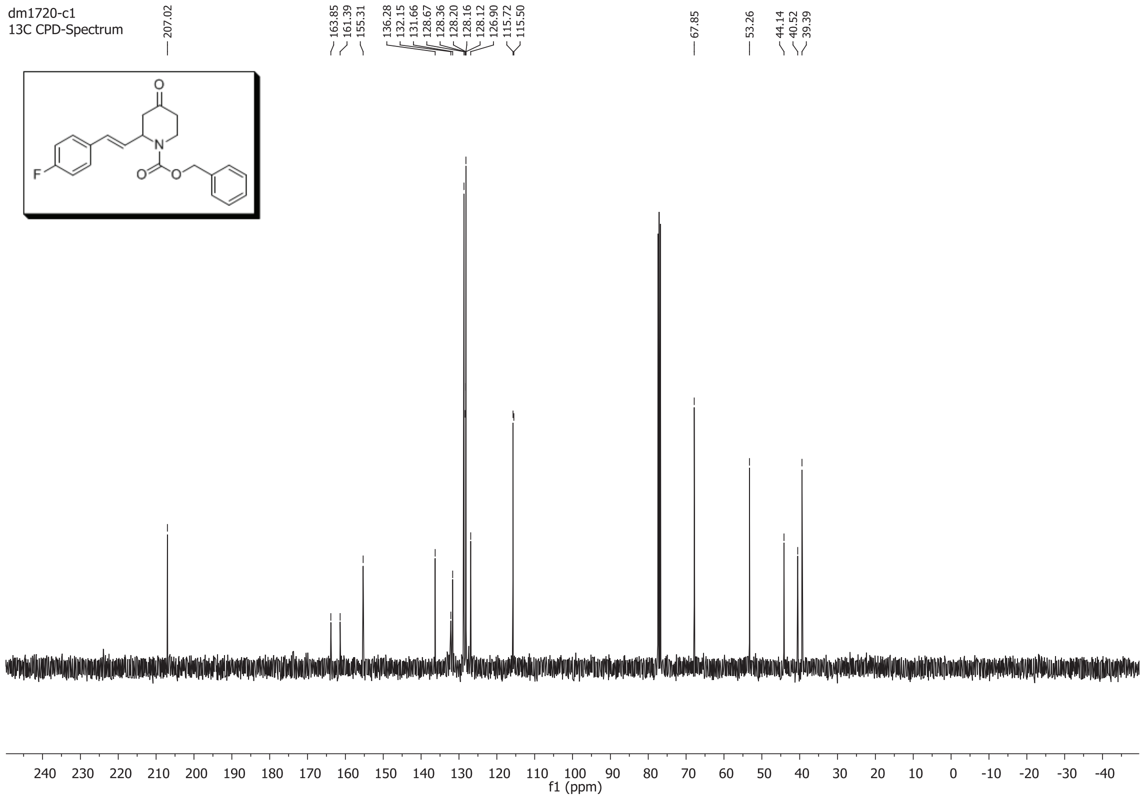

dm1683f2c1
13C CPD-Spectrum
207.11
155.25
136.32
131.20
129.70
128.64
128.31
128.09
67.75
52.81
43.99
43.64
40.45
39.19
35.34
O
N
O
O
Cl
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

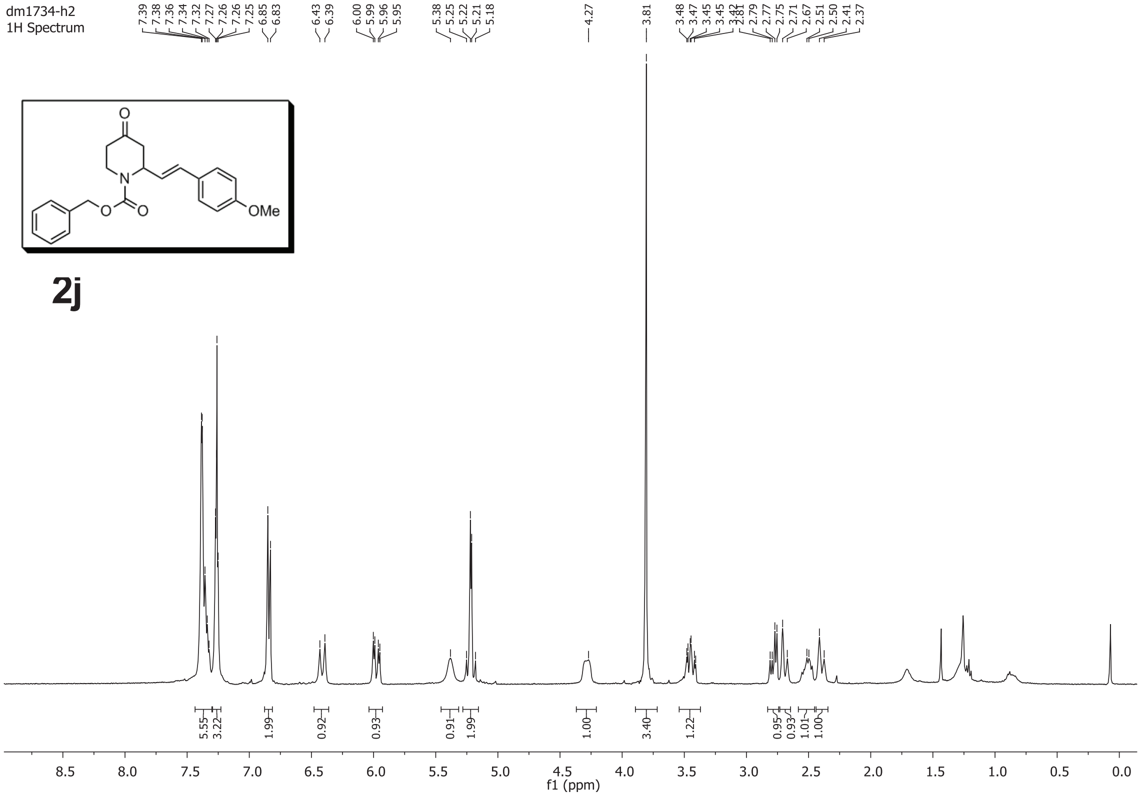

dm1471-h3
1H Spectrum
7.39 7.38 7.35 7.32 7.31 7.29 7.28 7.27 7.26 7.26 7.26 7.25
6.49 6.45 6.15 6.14 6.11 6.10
5.40 5.26 5.23 5.22 5.22 5.19
4.31 4.28
3.49 3.49 3.48 3.46 3.45 3.43 3.43 3.42 2.82 2.81 2.79 2.77 2.72 2.69 2.52 2.50 2.48 2.42 2.38
O
N
O
O
3.5 3.4
f1 (ppm)
2.8 2.7 2.6 2.5 2.4 2.3
f1 (ppm)
11.23
0.99
1.00
1.00
2.11
1.03
1.07
1.08
1.00
1.08
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

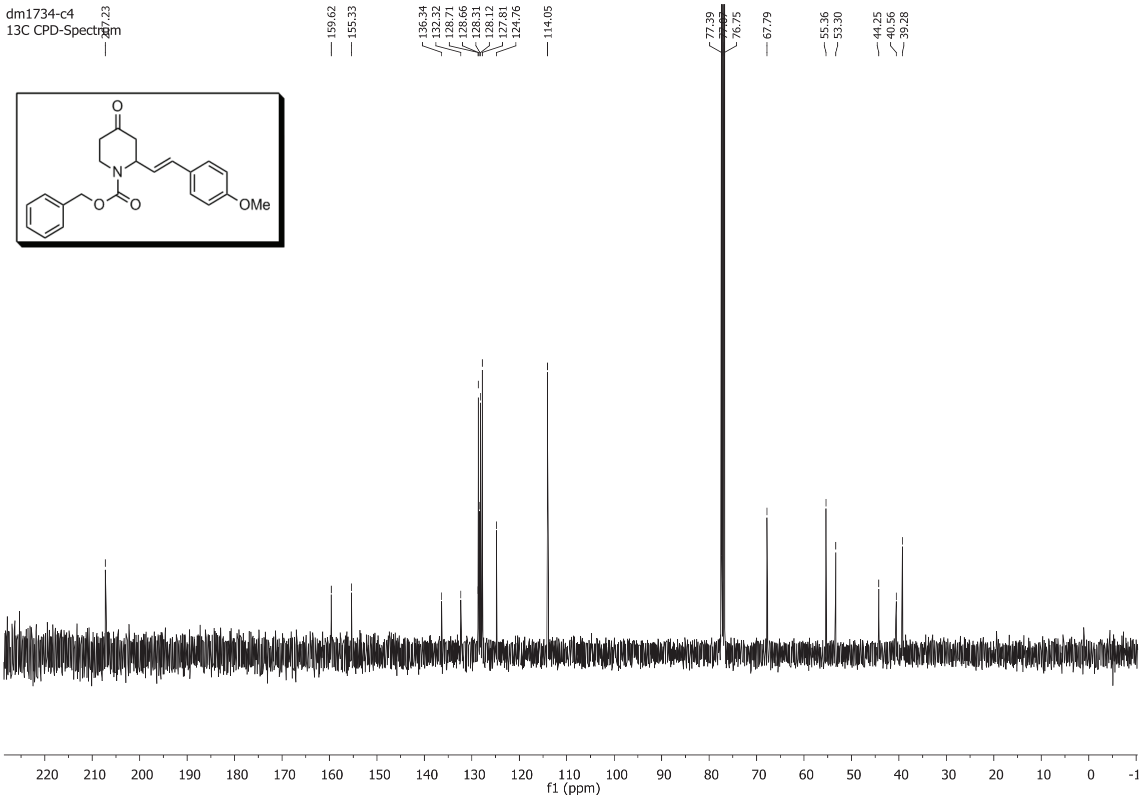

dm1471-c3
13C CPD-Spectrum
207.05
155.33
136.31 135.95 132.85 128.67 128.34 128.17 128.15 127.12 126.59
67.85
53.27
44.15 40.52 39.36
O
N
O
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


dm1720-h2
1H Spectrum
7.38 7.37 7.36 7.35 7.34 7.32 7.30 7.28 7.27 7.26 7.01 6.99 6.97
6.45 6.41 6.06 6.05 6.02 6.01
5.38 5.26 5.23 5.21 5.18
4.31 4.27
3.48 3.47 3.45 3.44 3.44 3.42 3.41 2.82 2.81 2.79 2.77 2.70 2.66 2.54 2.52 2.51 2.50 2.48 2.41 2.40 2.37
O
N
F
O
O
7.44
1.97
0.90
0.93
0.90
1.99
0.92
0.95
0.95
0.93
0.99
1.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
2.8 2.7 2.6 2.5 2.4
f1 (ppm)

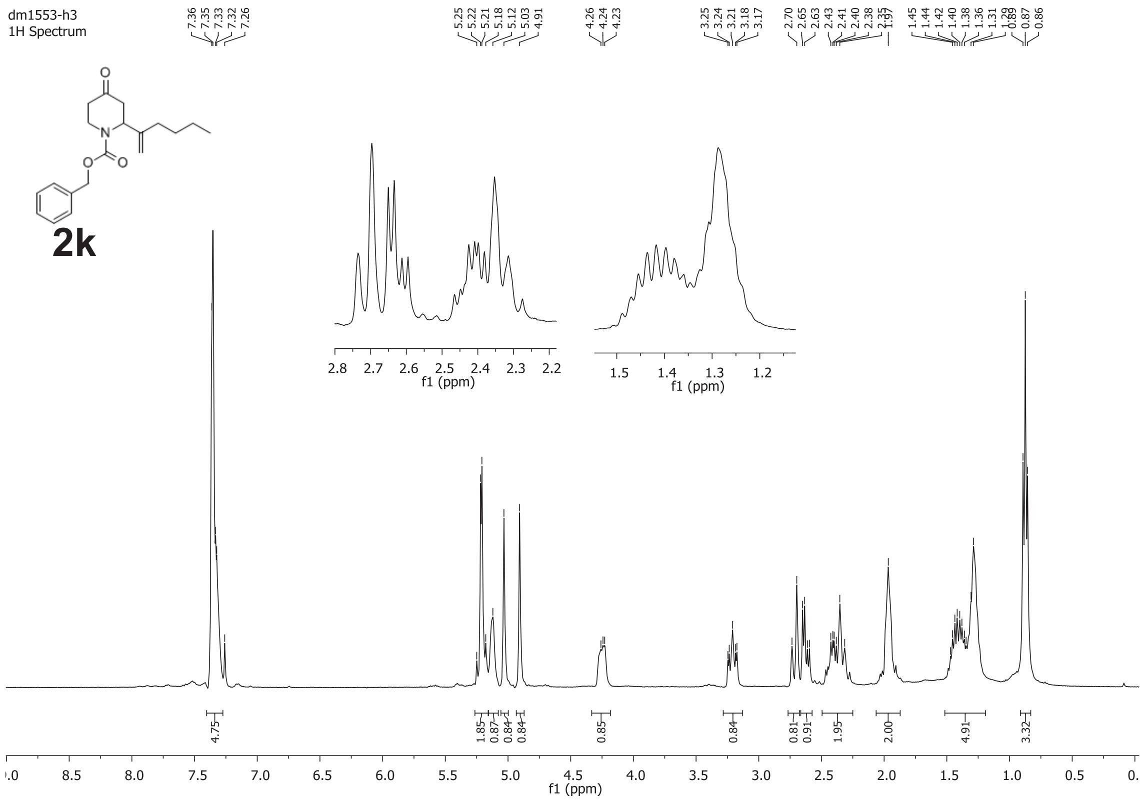
2i


dm1720-c1
13C CPD-Spectrum
207.02
163.85 161.39 155.31
136.28 132.15 131.66 128.67 128.36 128.20 128.16 128.12 126.90 115.72 115.50
67.85
53.26
44.14 40.52 39.39
O
N
F
O
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

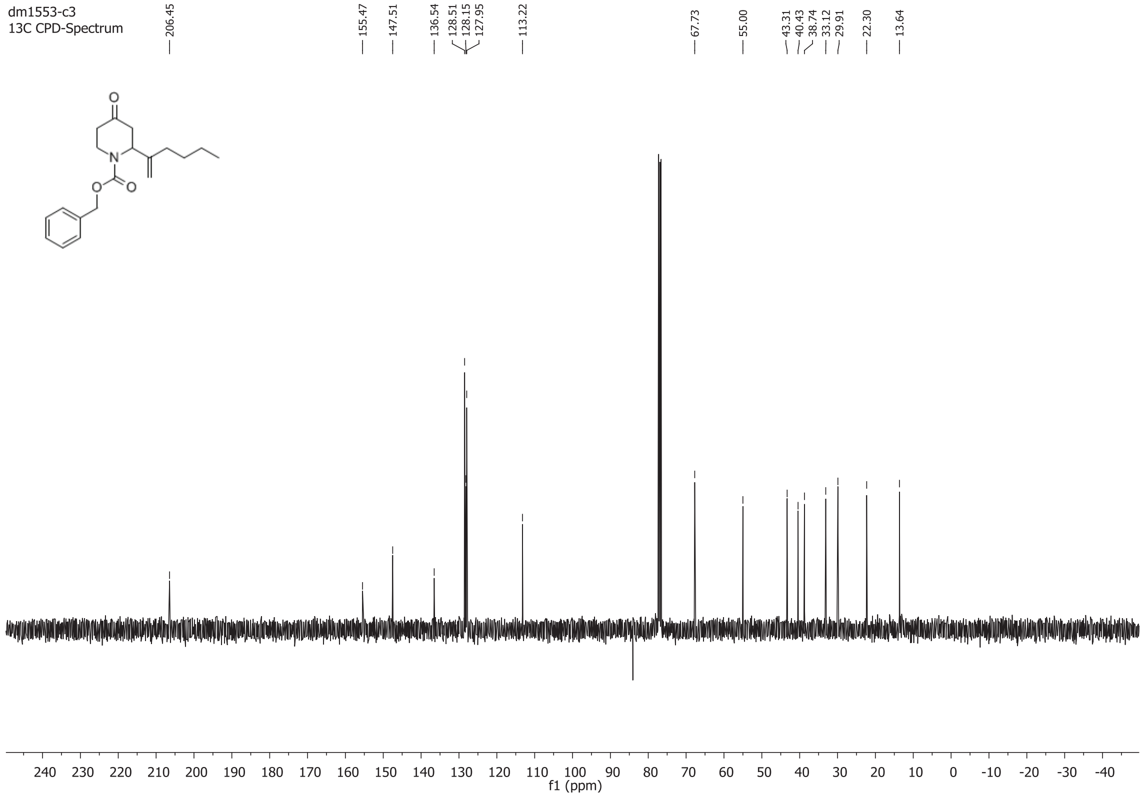

dm1734-h2
1H Spectrum
7.39
7.38
7.36
7.34
7.32
7.27
7.26
7.26
7.25
6.85
6.83
6.43
6.39
6.00
5.99
5.96
5.95
5.38
5.25
5.22
5.21
5.18
4.27
3.81
3.48
3.47
3.45
3.45
3.42
2.81
2.79
2.77
2.75
2.71
2.67
2.51
2.50
2.41
2.37
O
N
O
O
OMe
2j
5.55
3.22
1.99
0.92
0.93
0.91
1.99
1.00
3.40
1.22
0.95
0.93
1.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


dm1734-c4
13C CPD-Spectrum
207.23
159.62
155.33
136.34
132.32
128.71
128.66
128.31
128.12
127.81
124.76
114.05
77.39
77.07
76.75
67.79
55.36
53.30
44.25
40.56
39.28
O
N
O
O
OMe
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

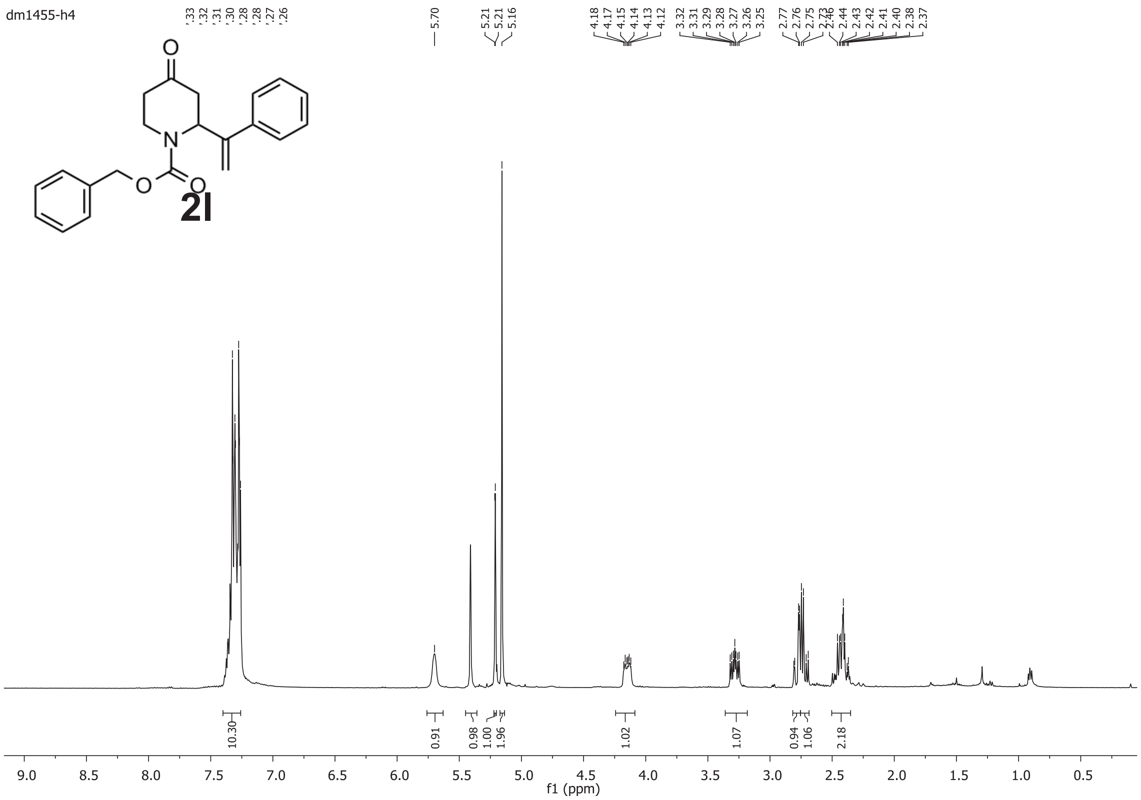
- NMR-spectra were recorded at 55°C.

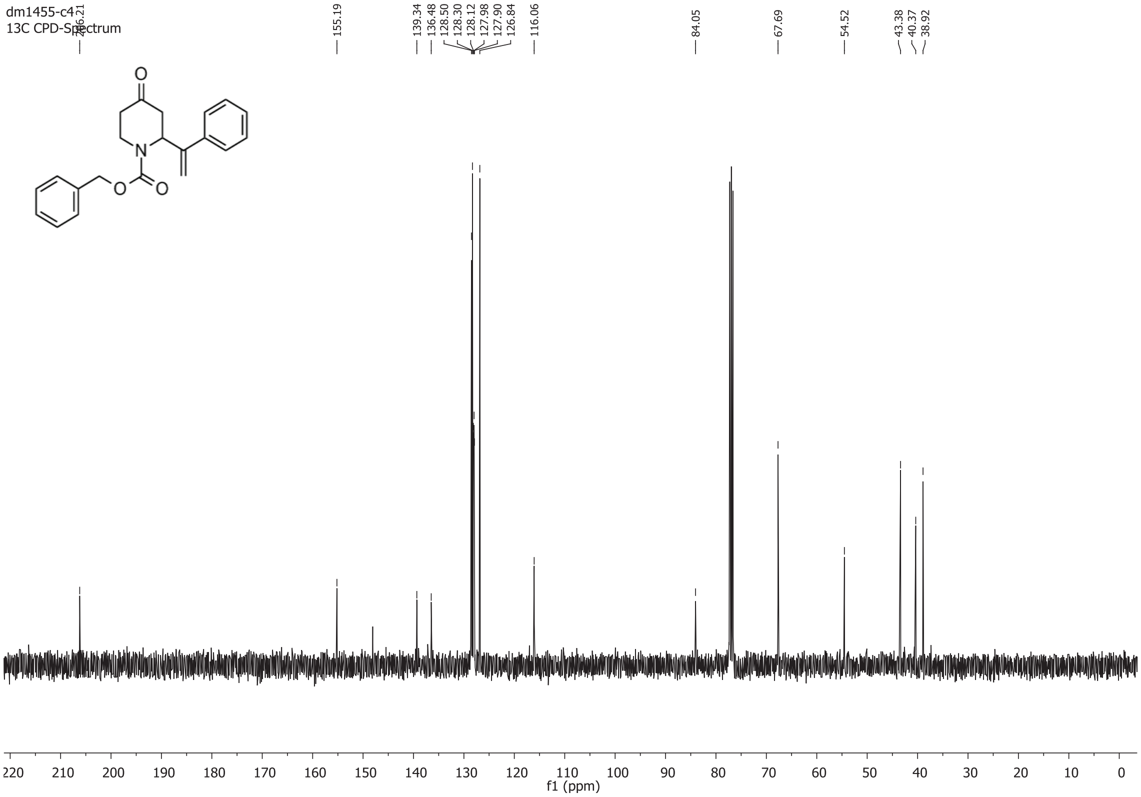


2k

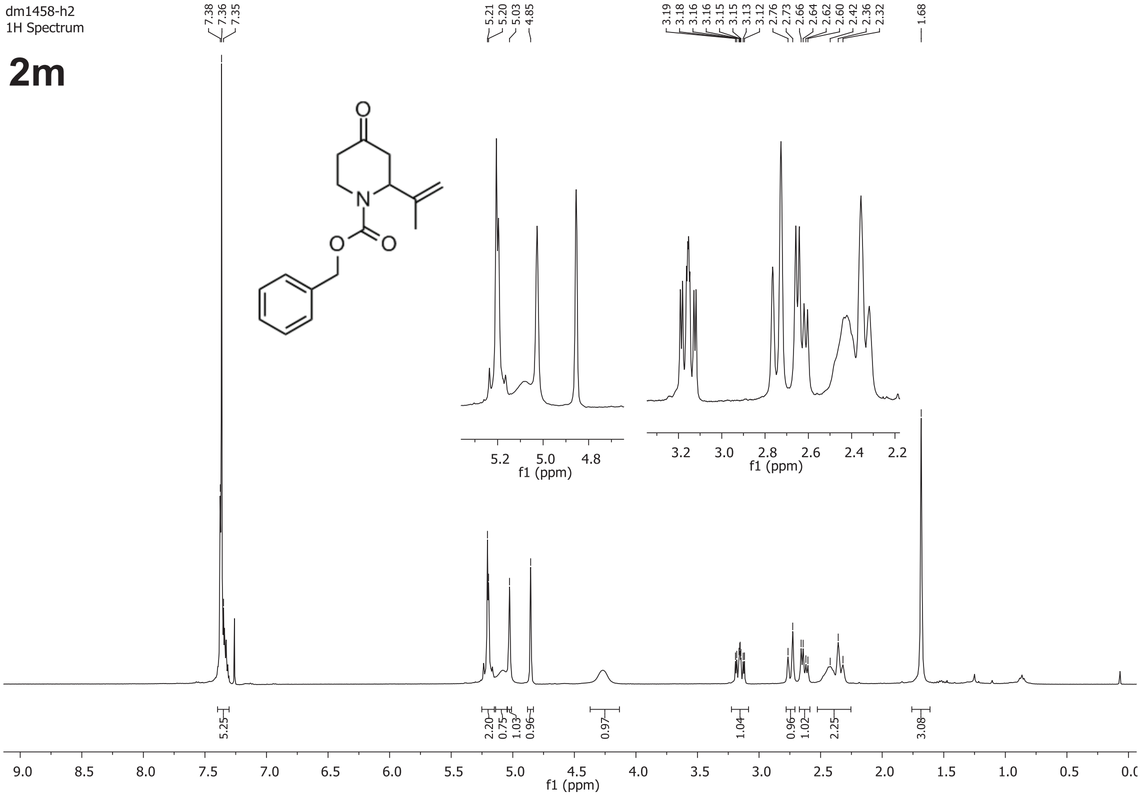


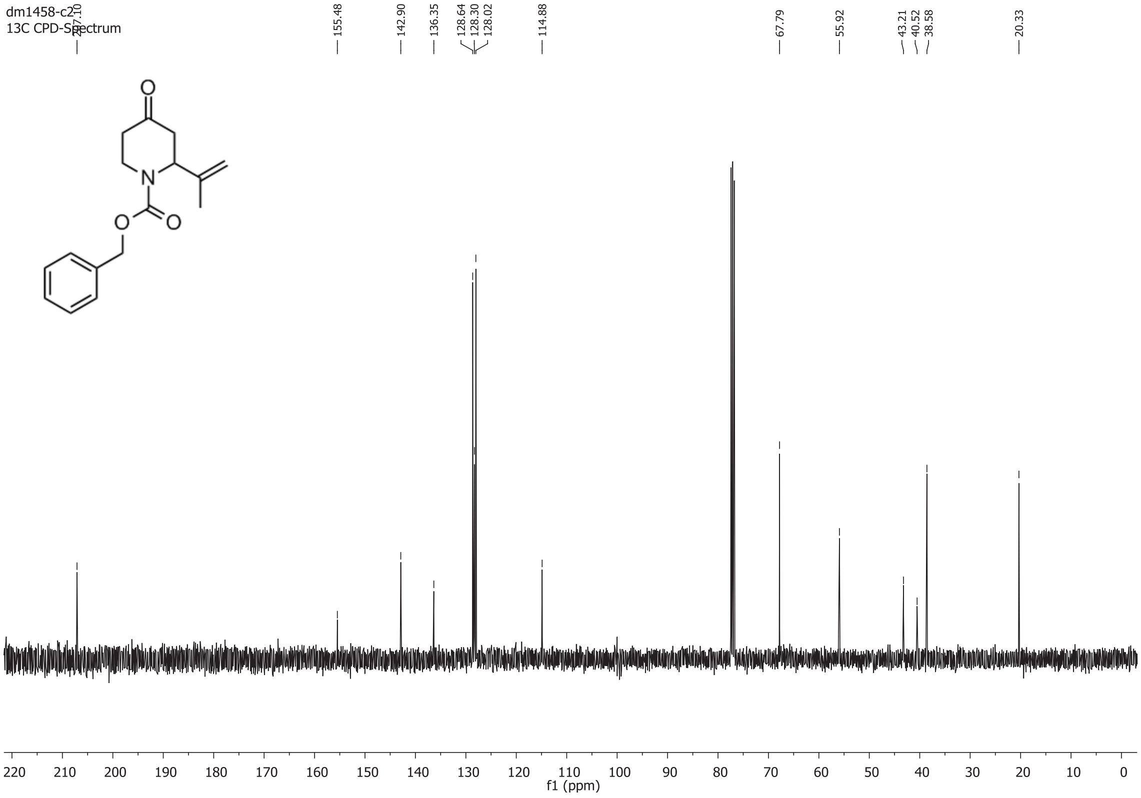
- NMR-spectra were recorded at 55°C.

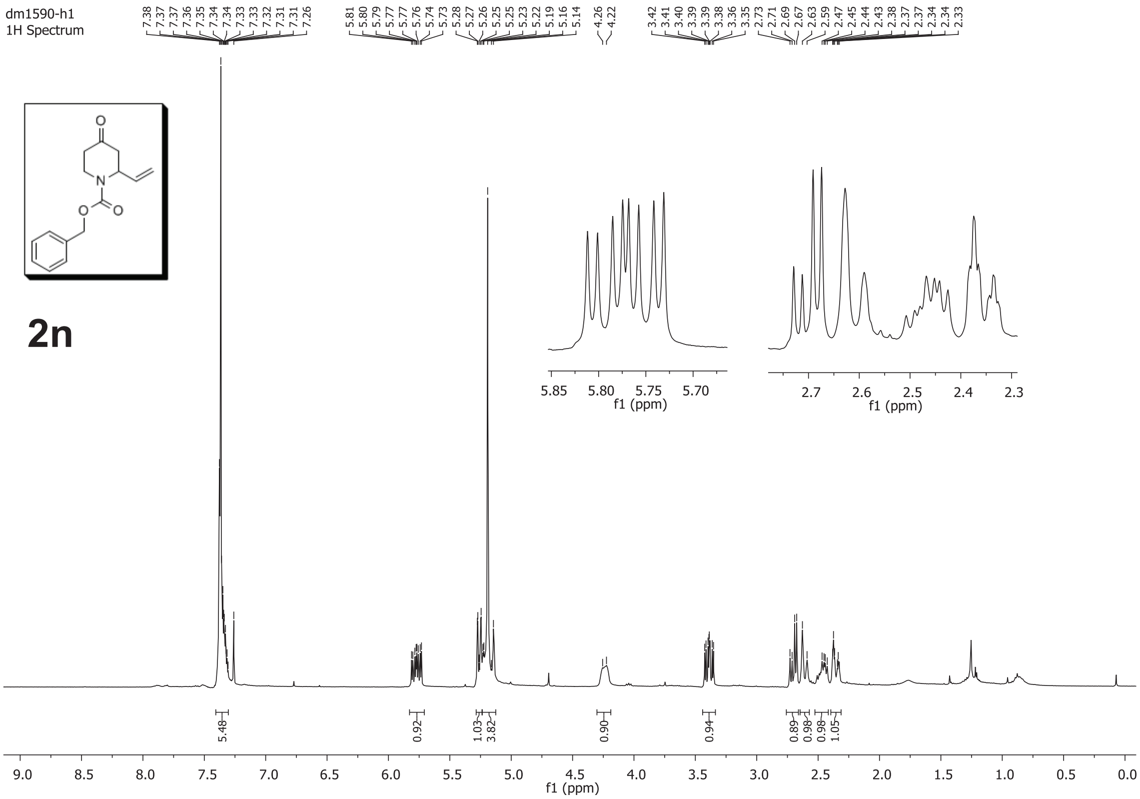




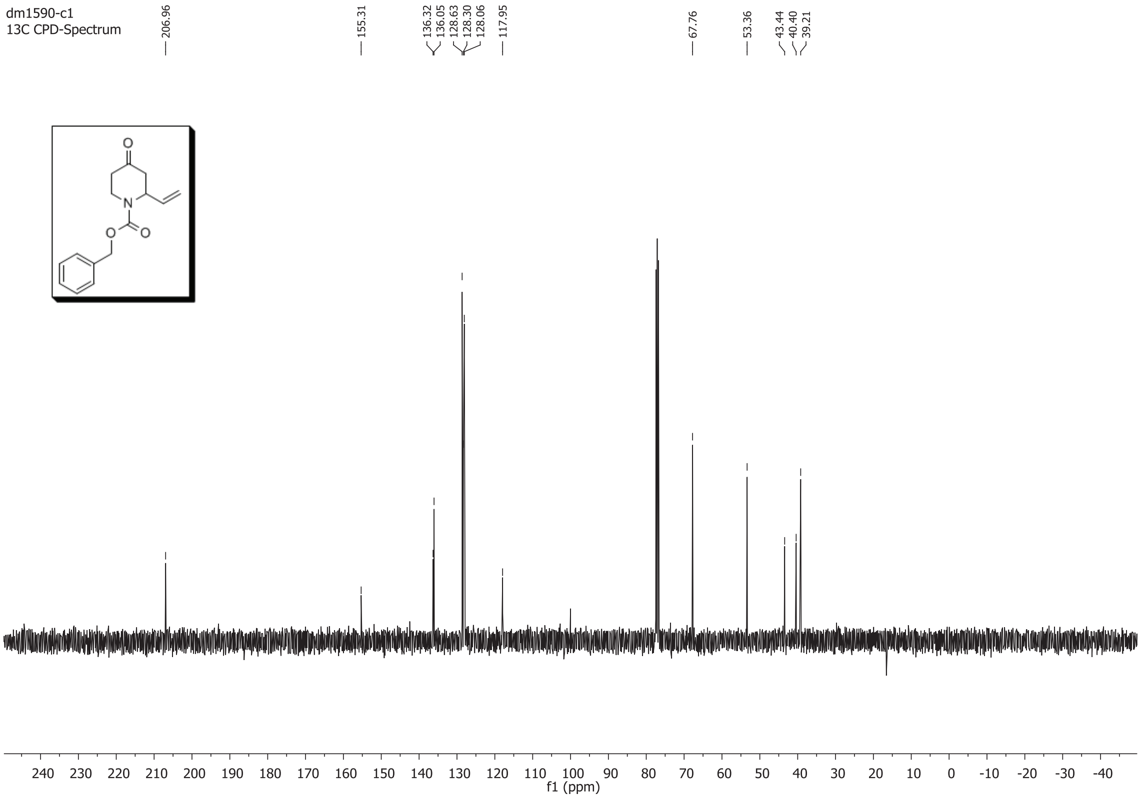
2m


dm1458-h2
1H Spectrum
7.38
7.36
7.35
5.21
5.20
5.03
4.85
3.19
3.18
3.16
3.16
3.15
3.15
3.13
3.12
2.76
2.73
2.66
2.64
2.62
2.60
2.42
2.36
2.32
1.68
O
N
O
O
5.2
5.0
4.8
f1 (ppm)
3.2
3.0
2.8
2.6
2.4
2.2
f1 (ppm)
5.25
2.20
0.75
1.03
0.96
0.97
1.04
0.96
1.02
2.25
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


dm1458-c2
13C CPD-Spectrum
207.10
155.48
142.90
136.35
128.64
128.30
128.02
114.88
67.79
55.92
43.21
40.52
38.58
20.33
O
N
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

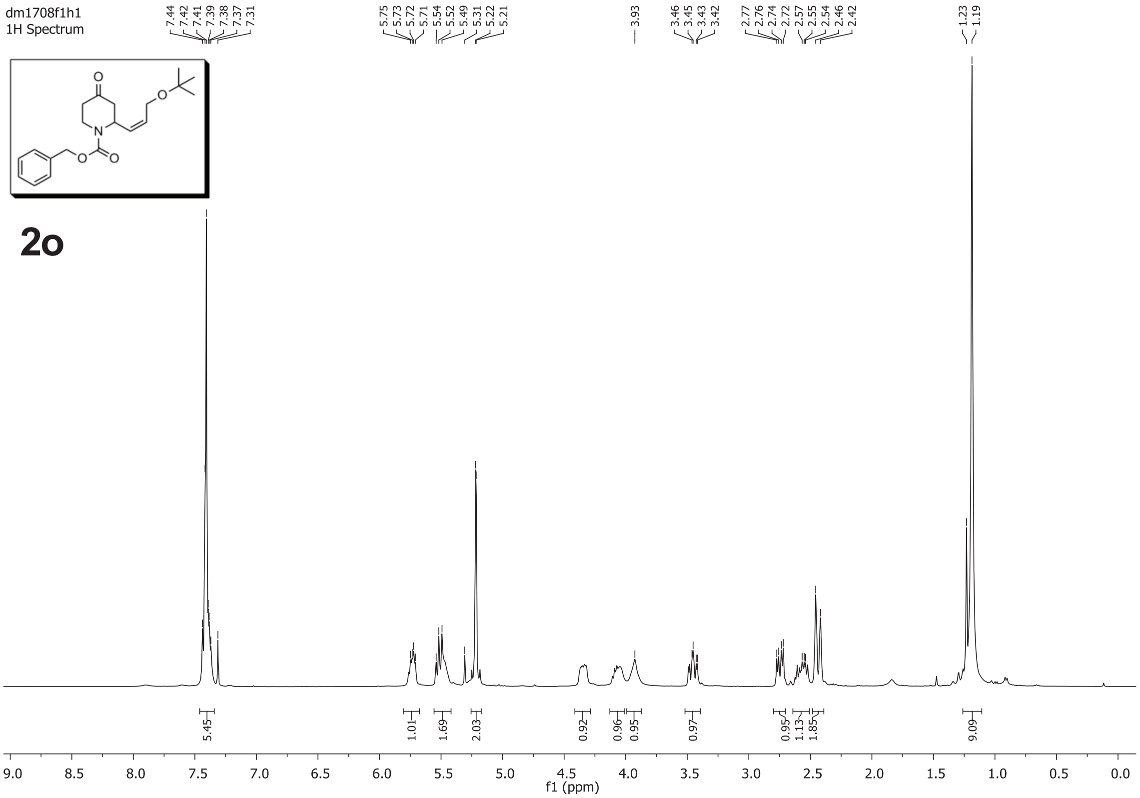

dm1590-h1
1H Spectrum
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.26
5.81
5.80
5.79
5.77
5.77
5.76
5.74
5.73
5.28
5.27
5.26
5.25
5.25
5.23
5.22
5.19
5.16
5.14
4.26
4.22
3.42
3.41
3.40
3.39
3.39
3.38
3.36
3.35
2.73
2.71
2.69
2.67
2.63
2.59
2.47
2.45
2.44
2.43
2.38
2.37
2.37
2.34
2.34
2.33
O
N
O
O
5.85
5.80
5.75
5.70
f1 (ppm)
2.7
2.6
2.5
2.4
2.3
f1 (ppm)
5.48
0.92
1.03
3.82
0.90
0.94
0.89
0.98
0.98
1.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

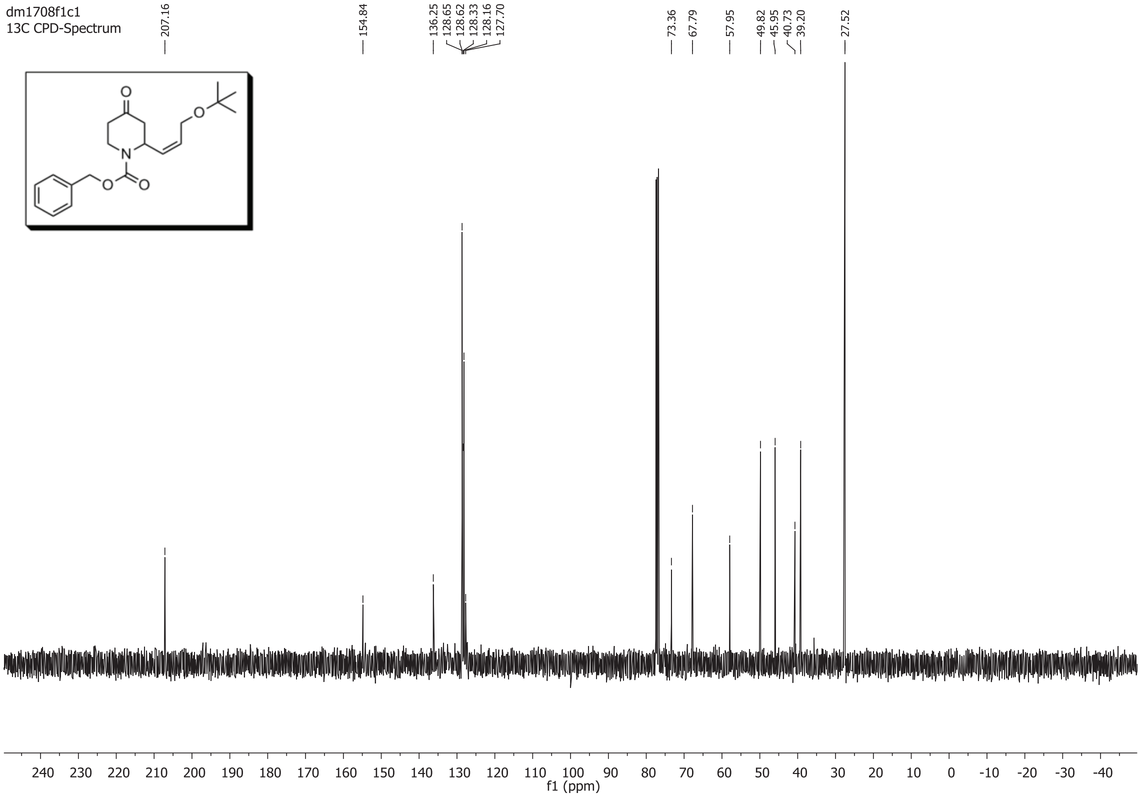
2n

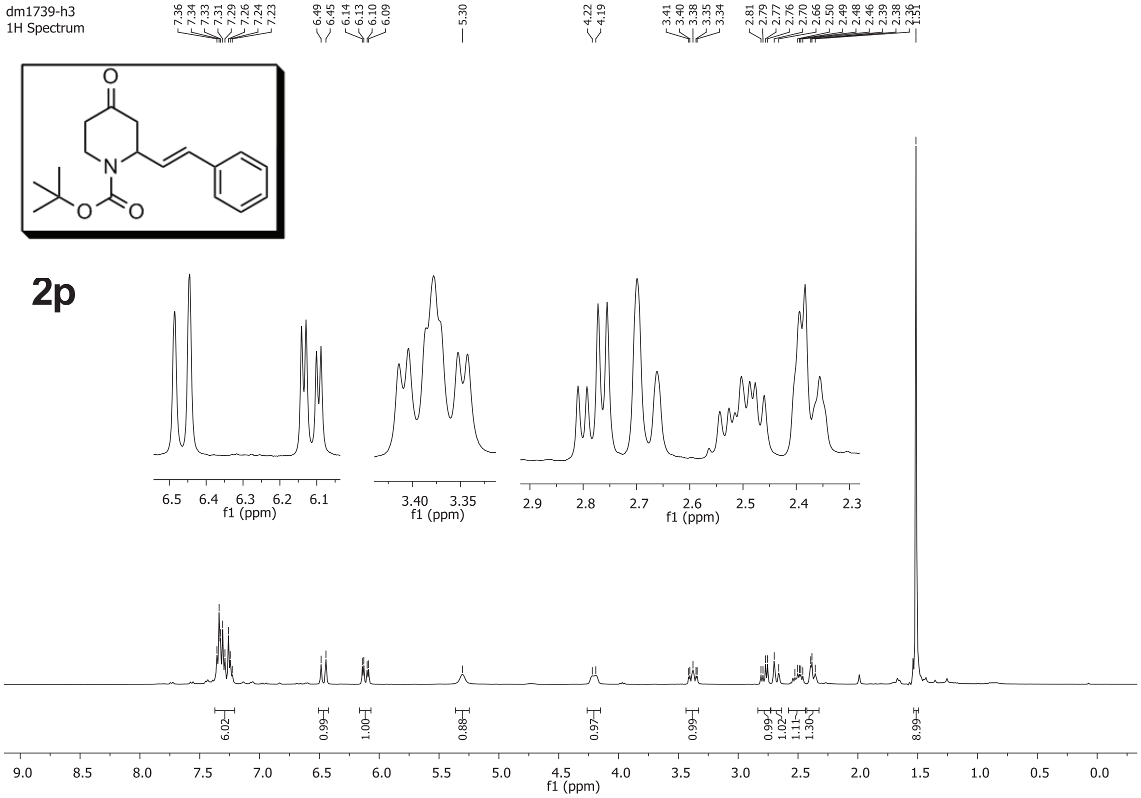

dm1590-c1
13C CPD-Spectrum
206.96
155.31
136.32
136.05
128.63
128.30
128.06
117.95
67.76
53.36
43.44
40.40
39.21
O
N
O
O
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

- NMR-spectra were recorded at 55°C.

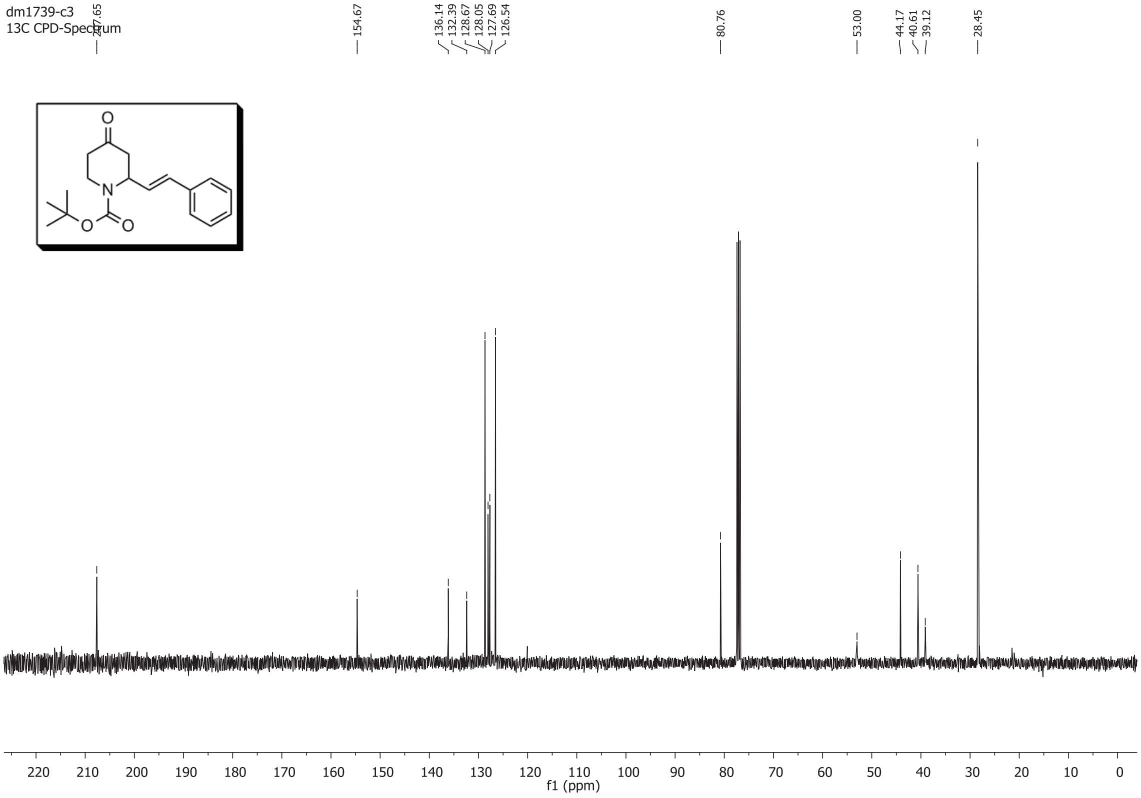
2o



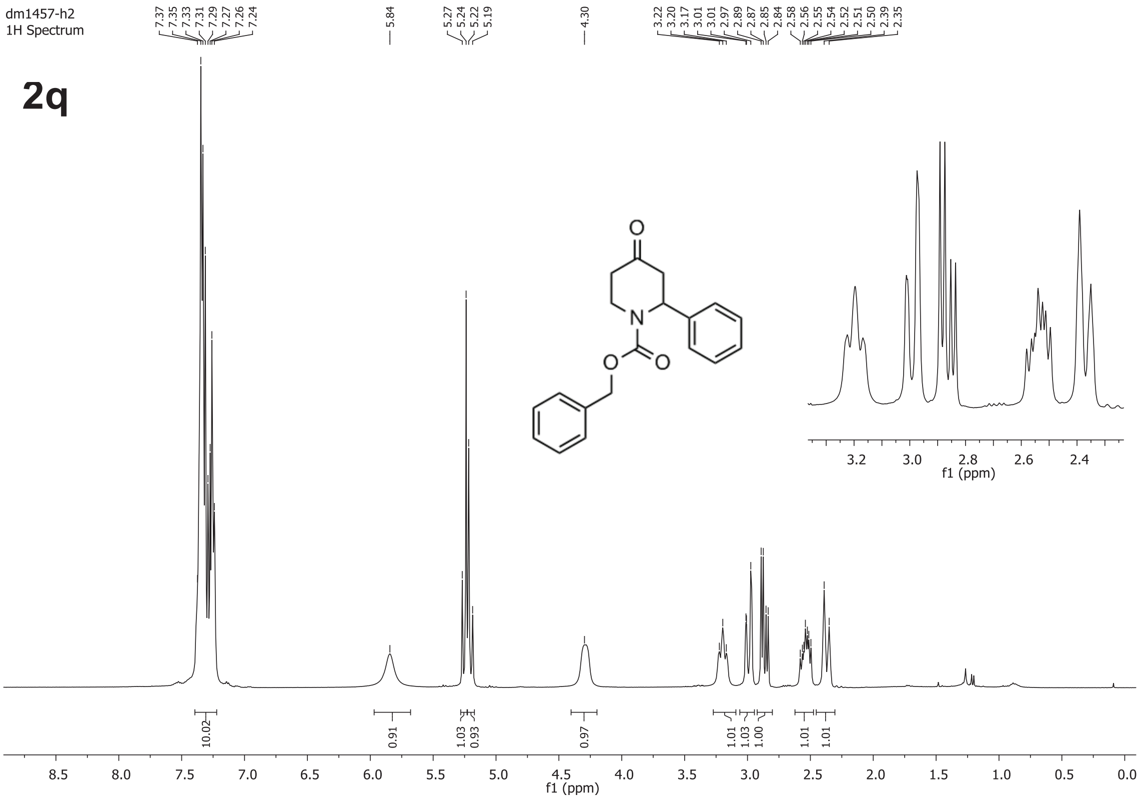


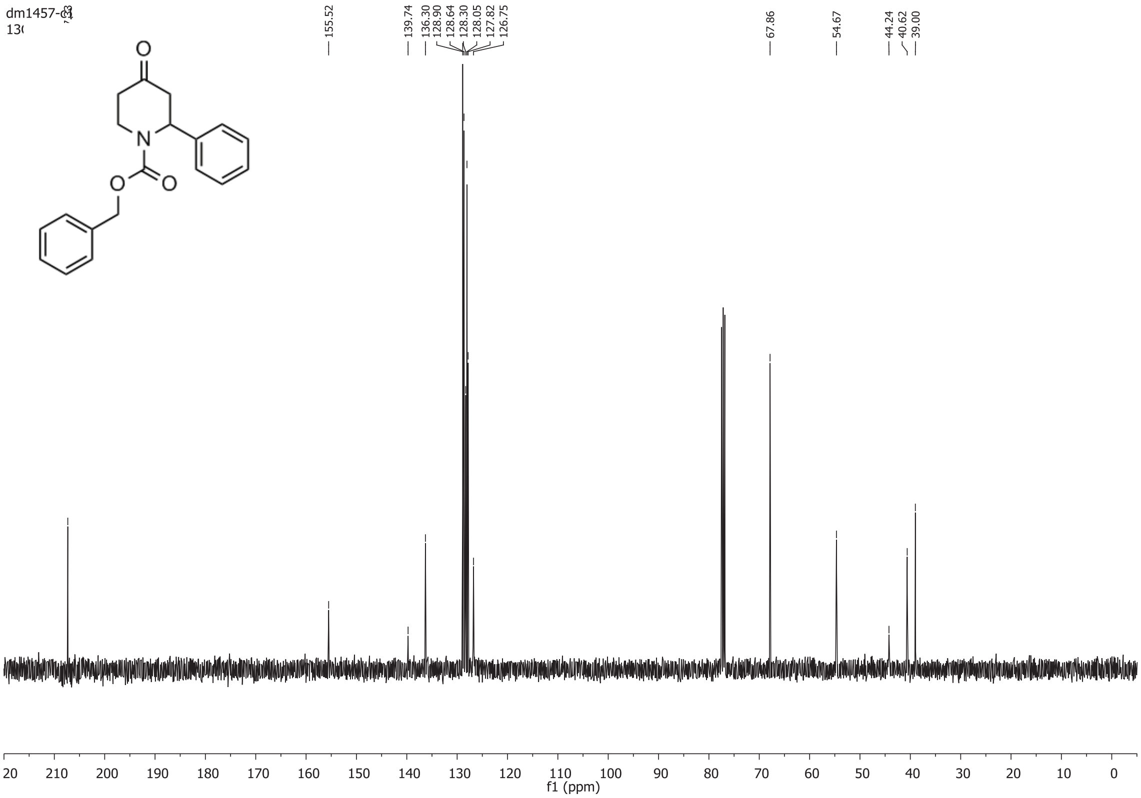

dm1739-h3
1H Spectrum
7.36
7.34
7.33
7.31
7.29
7.26
7.24
7.23
6.49
6.45
6.14
6.13
6.10
6.09
5.30
4.22
4.19
3.41
3.40
3.38
3.35
3.34
2.81
2.79
2.77
2.76
2.70
2.66
2.50
2.49
2.48
2.46
2.39
2.38
2.36
1.51
6.02
0.99
1.00
0.88
0.97
0.99
0.99
1.02
1.11
1.30
8.99
f1 (ppm)

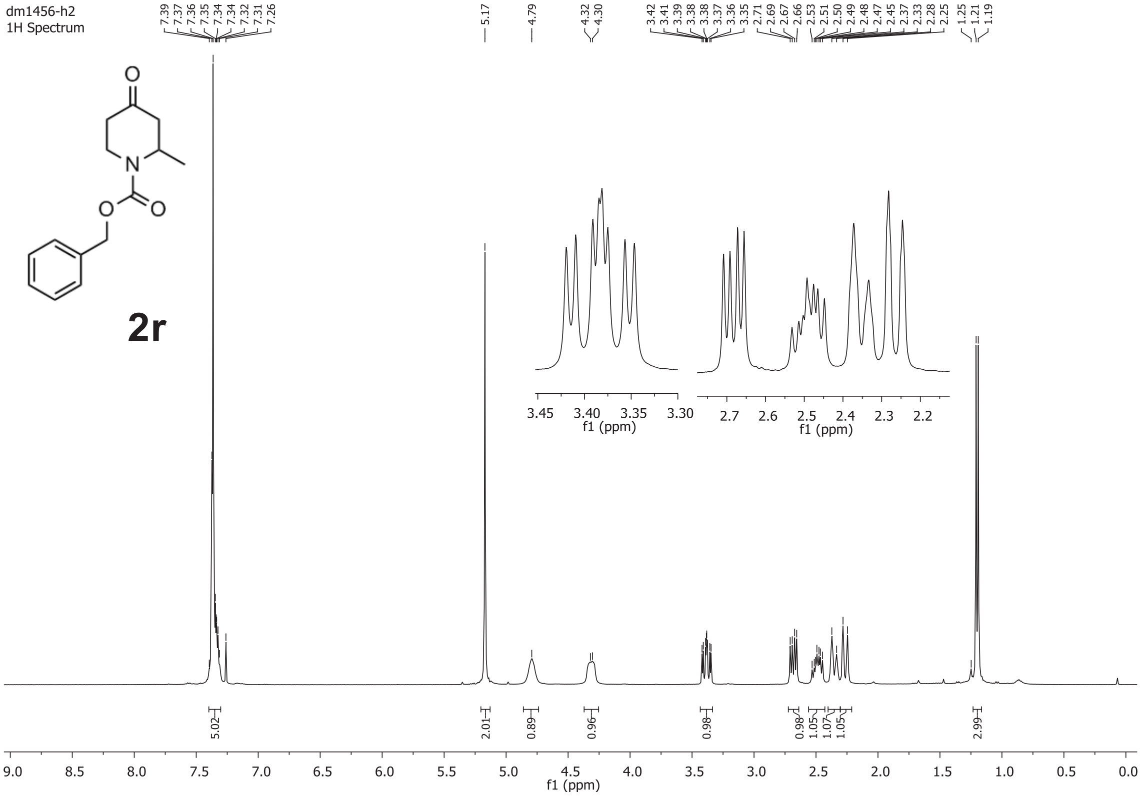
2p


dm1739-c3
13C CPD-Spectrum
207.65
154.67
136.14
132.39
128.67
128.05
127.69
126.54
80.76
53.00
44.17
40.61
39.12
28.45
f1 (ppm)

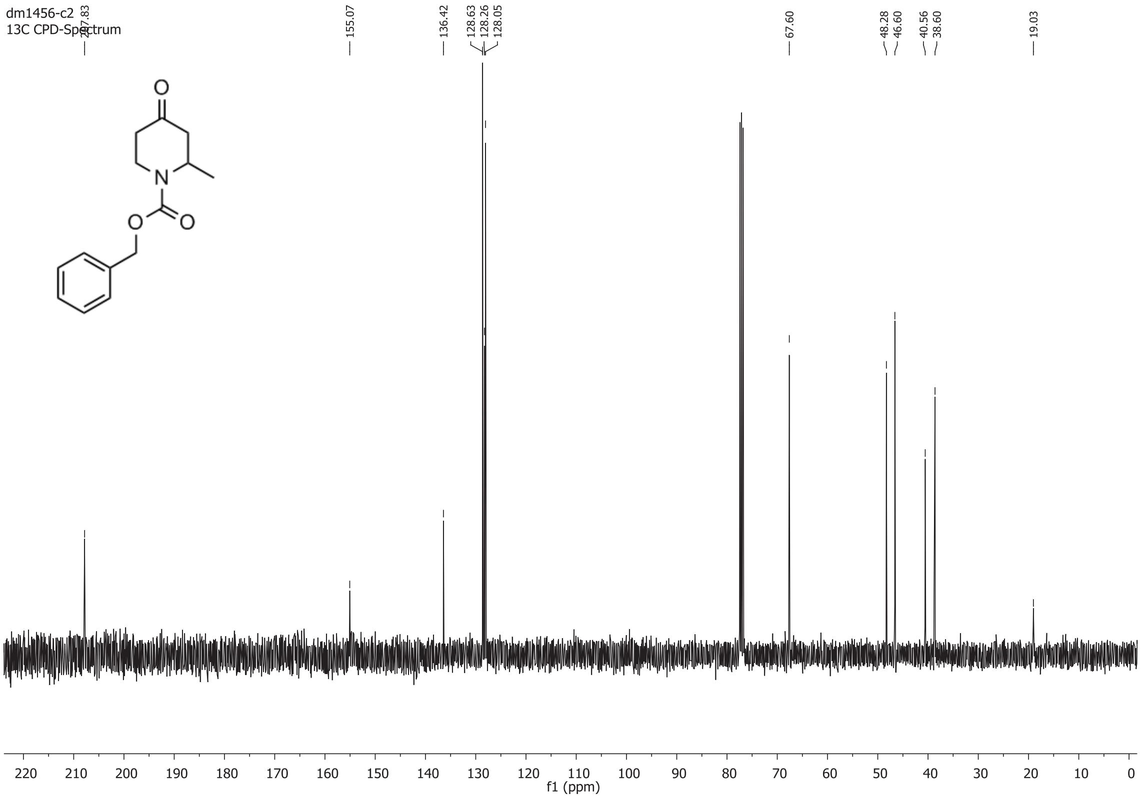
2q

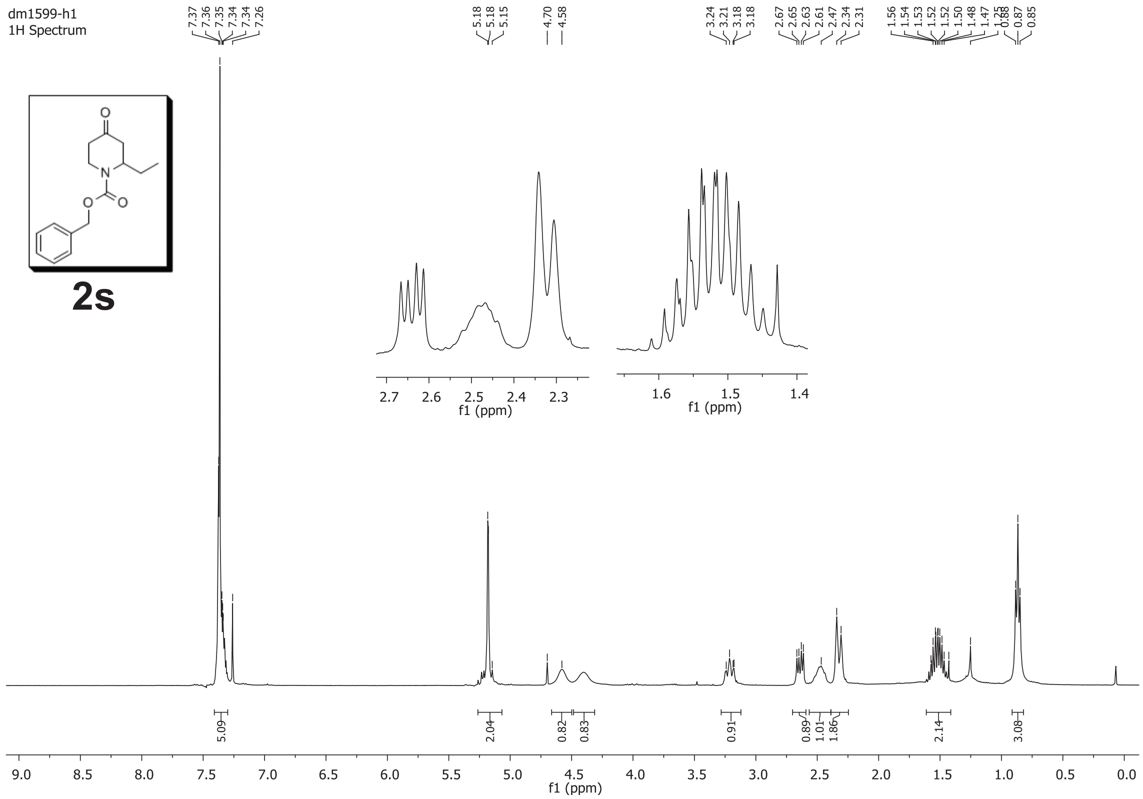

dm1457-h2
1H Spectrum
7.37
7.35
7.33
7.31
7.29
7.27
7.26
7.24
5.84
5.27
5.24
5.22
5.19
4.30
3.22
3.20
3.17
3.01
2.97
2.89
2.87
2.85
2.84
2.58
2.56
2.55
2.54
2.52
2.51
2.50
2.39
2.35
O
N
O
O
3.2
3.0
2.8
2.6
2.4
f1 (ppm)
10.02
0.91
1.03
0.93
0.97
1.01
1.03
1.00
1.01
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

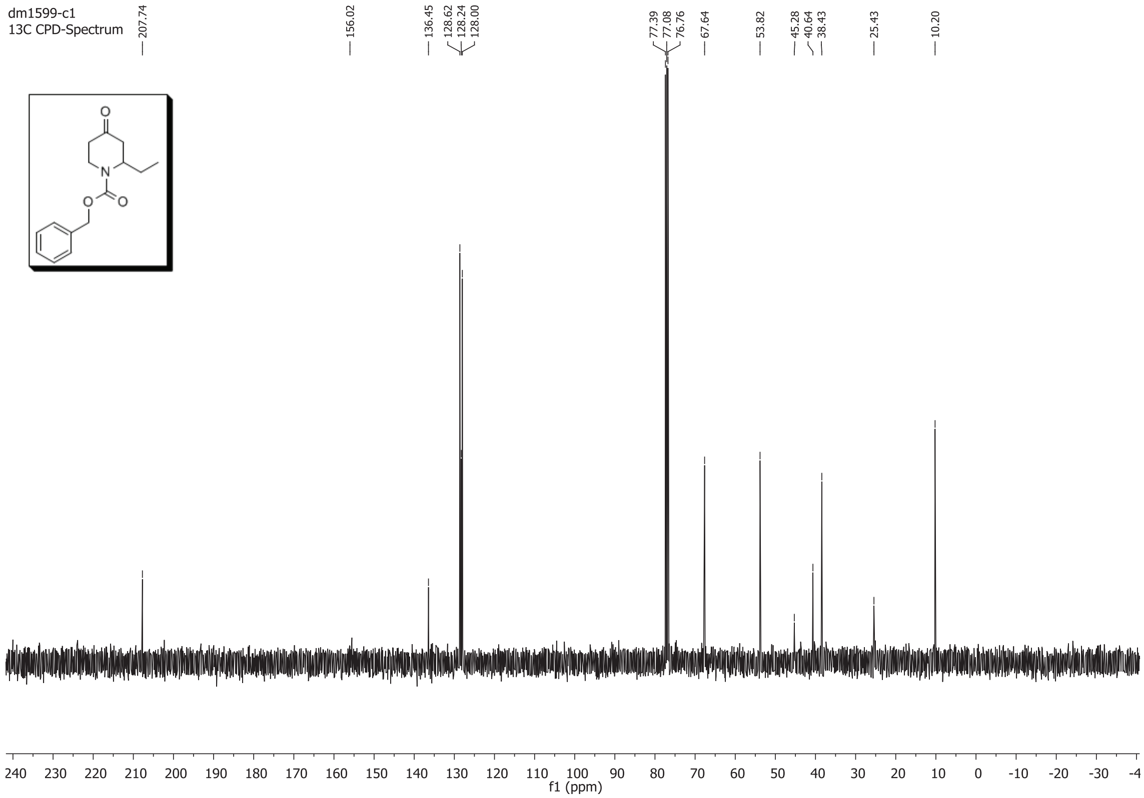

dm1457-c
13
155.52
139.74
136.30
128.90
128.64
128.30
128.05
127.82
126.75
67.86
54.67
44.24
40.62
39.00
O
N
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

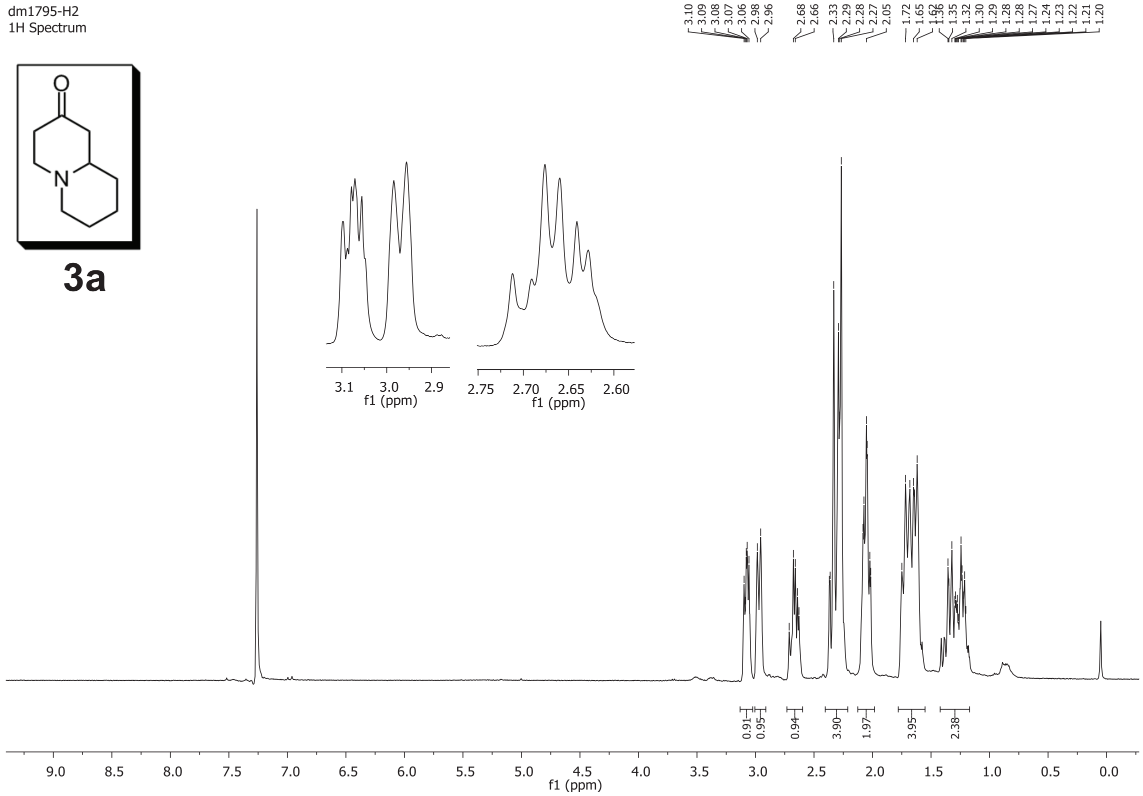

dm1456-h2
1H Spectrum
7.39
7.37
7.36
7.35
7.34
7.34
7.32
7.31
7.26
5.17
4.79
4.32
4.30
3.42
3.41
3.39
3.38
3.38
3.37
3.36
3.35
2.71
2.69
2.67
2.66
2.53
2.51
2.50
2.49
2.48
2.47
2.45
2.37
2.33
2.28
2.25
1.25
1.21
1.19
O
N
O
O
5.02
2.01
0.89
0.96
0.98
0.98
1.05
1.07
1.05
2.99
3.45 3.40 3.35 3.30
2.7 2.6 2.5 2.4 2.3 2.2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

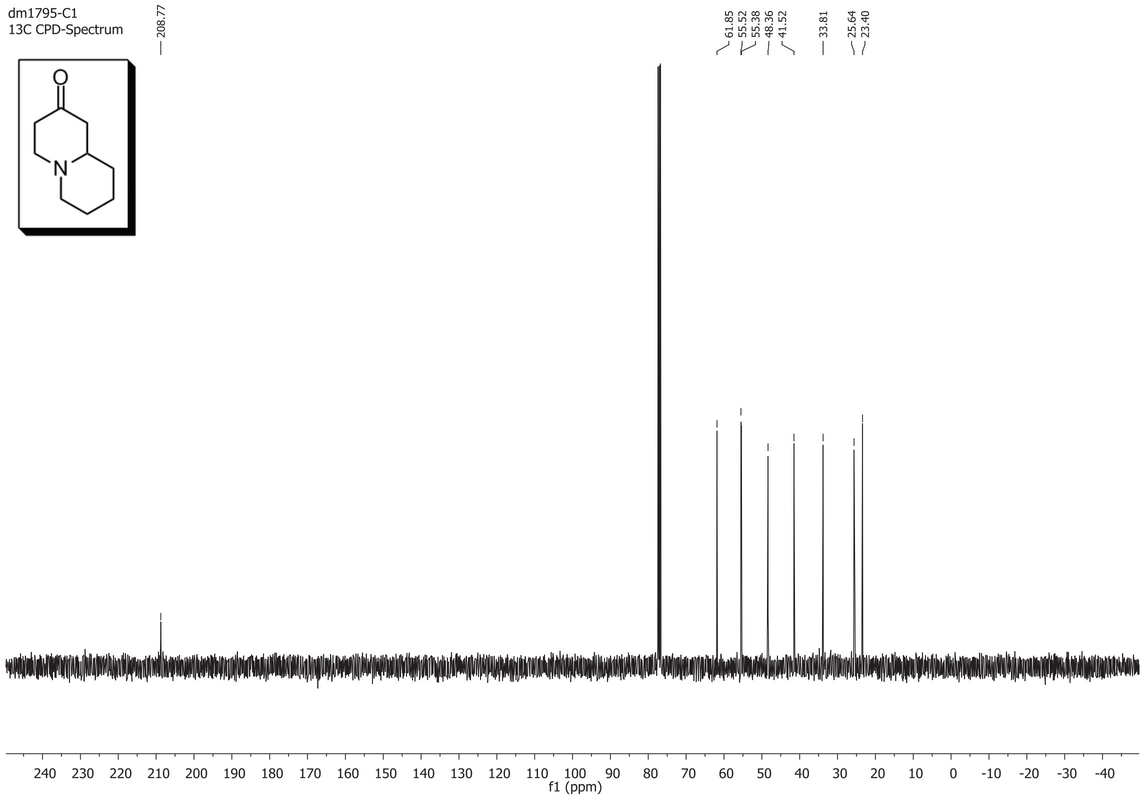
2r


dm1456-c2
13C CPD-Spectrum
207.83
155.07
136.42
128.63
128.26
128.05
67.60
48.28
46.60
40.56
38.60
19.03
O
N
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


dm1599-h1
1H Spectrum
2s
7.37
7.36
7.35
7.34
7.34
7.26
5.18
5.18
5.15
4.70
4.58
3.24
3.21
3.18
3.18
2.67
2.65
2.63
2.61
2.47
2.34
2.31
1.56
1.54
1.53
1.52
1.52
1.50
1.48
1.47
1.25
0.88
0.87
0.85
5.09
2.04
0.82
0.83
0.91
0.89
1.01
1.86
2.14
3.08
f1 (ppm)


dm1599-c1
13C CPD-Spectrum
207.74
156.02
136.45
128.62
128.24
128.00
77.39
77.08
76.76
67.64
53.82
45.28
40.64
38.43
25.43
10.20
f1 (ppm)


dm1795-H2
1H Spectrum
3a
3.10
3.09
3.08
3.07
3.06
2.98
2.96
2.68
2.66
2.33
2.29
2.28
2.27
2.05
1.72
1.65
1.62
1.36
1.35
1.32
1.30
1.29
1.28
1.28
1.27
1.24
1.23
1.22
1.21
1.20
3.1
3.0
2.9
f1 (ppm)
2.75
2.70
2.65
2.60
f1 (ppm)
0.91
0.95
0.94
3.90
1.97
3.95
2.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


dm1795-C1
13C CPD-Spectrum
208.77
61.85
55.52
55.38
48.36
41.52
33.81
25.64
23.40
240
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
-20
-30
-40
f1 (ppm)