Organic Syntheses

Copper(II) Triflate as Additive in Low Loading Au(I)-Catalyzed Hydroalkylation of Unactivated Alkenes

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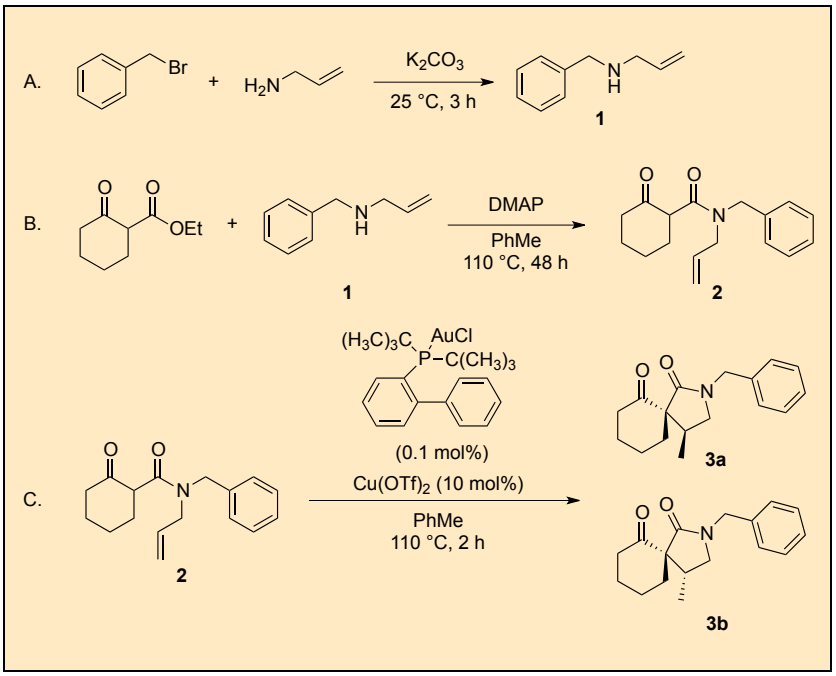

Procedure

A. *N-Allyl-N-benzylamine (**1**)*. A 500-mL one-necked, round-bottomed flask equipped with a magnetic stirring bar (5 x 2 cm Teflon-coated, ovoid-shaped) is charged with potassium carbonate (27.7 g, 0.2 mol, 1.2 equiv)

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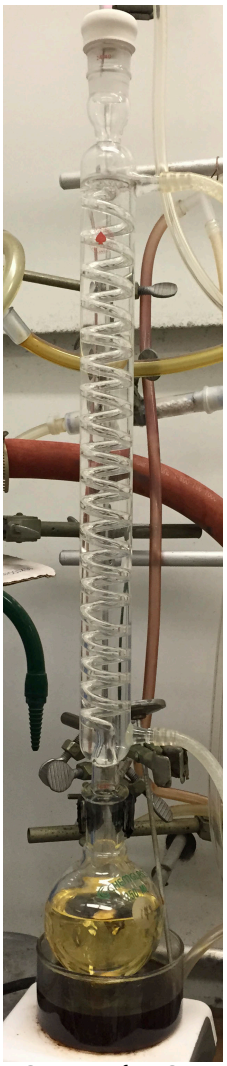
(Note 1) and then sealed with a rubber septum, into which is inserted a needle connected to a nitrogen/vacuum inlet line. The flask is evacuated and filled with nitrogen. Allylamine (150 mL, 114.5 g, 2.0 mol, 11.9 equiv) (Notes 1 and 2) is added via cannula into the flask. The septum is replaced with a 100 mL pressure-equalizing addition funnel, and the funnel is charged with benzyl bromide (20.0 mL, 28.6 g, 0.17 mol, 1.0 equiv) (Note 1), then sealed with the septum containing the nitrogen inlet needle. Benzyl bromide is then added dropwise over 30 min under a slight positive pressure of nitrogen. The reaction mixture is stirred at 25 °C for 3 h (Notes 3 and 4), then diluted with 50 mL of CH_2Cl_2, added via the addition funnel. The resulting mixture is filtered through a fritted funnel (porosity 3, 10 cm diameter). The solid residue is rinsed with CH_2Cl_2 (2 x 100 mL), and the filtrate is concentrated by rotary evaporation (40 °C, 10 mmHg) to afford a pale yellow liquid. The crude product is purified by vacuum distillation (69 ºC, 1 mmHg) to afford 21.0–21.7 g (85–88%) of *N*-allyl-*N*-benzyl-amine **1** as a colorless oil (Notes 5, 6, 7, and 8).

B. *N-Allyl-N-benzyl-2-oxocyclohexanecarboxamide* (**2**). A 250-mL one-necked, round-bottomed flask equipped with a magnetic stirring bar (3 x 1.5 cm Teflon-coated, ovoid-shaped) is sealed with a rubber septum, into which is inserted a needle connected to a nitrogen/vacuum inlet line. The flask is evacuated and filled with nitrogen, then charged with *N*-allyl-*N*-benzylamine **1** (15.0 g, 101.9 mmol, 2.0 equiv) using a syringe. The septum is removed and 4-dimethylaminopyridine (1.9 g, 15.6 mmol, 0.3 equiv), toluene (50 mL), and ethyl 2-oxocyclohexanecarboxylate (8.6 mL, 9.1 g, 53.6 mmol, 1.0 equiv) are added (Note 9). The neck is equipped with a 30 cm Graham-type water-cooled reflux condenser, the top of which is sealed with the septum containing a nitrogen inlet needle, and positive pressure of nitrogen is maintained. The resulting mixture is stirred at reflux in a pre-heated oil bath at 130 °C (external temperature) for 2 days (Notes 3 and 10). The reaction mixture is then allowed to cool down to room temperature (25 °C) and transferred to a 1 L separatory funnel. The flask is rinsed with EtOAc (50 mL) and the rinsate is added to the funnel. The solution is washed successively with 150 mL of aqueous 1 M HCl solution and 100 mL of a saturated aqueous NaCl solution, dried over 20 g of $MgSO_4$, filtered through a fritted funnel (porosity 3, 5 cm diameter), and concentrated by rotary evaporation (40 °C, 10 mmHg) to afford a brown oil. The crude product is purified by flash chromatography on a silica gel column (8 x 40 cm, 250 g of silica gel) using EtOAc:hexanes (15:85) (Note 11). Four 250 mL fractions are collected, then the solvent is changed to EtOAc:hexanes

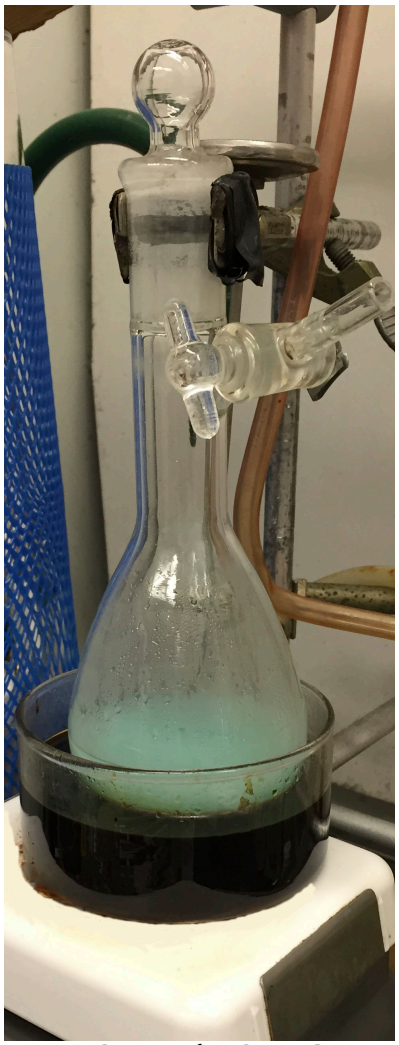
(25:75) and another six fractions (250 mL each) are collected. The desired product is obtained in fractions 6-10, which are concentrated by rotary evaporation (40 °C, 10 mmHg) and dried under vacuum (1.0 mmHg) for 2 h to give 10.7–13.0 g (73–90%) of *N*-allyl-*N*-benzyl-2-oxocyclohexanecarboxamide **2** as a yellow oil (Notes 12 and 13).

C. *N-Benzyl-4-methyl-2-azaspiro[4.5]decane-1,6-dione (**3**)*. An oven-dried 16 x 4 cm (150 mL) Schlenk tube equipped with a Teflon-coated magnetic stir bar (1.3 x 2.5 cm) is evacuated and filled with nitrogen. This procedure is repeated 3 times. While maintaining a stream of nitrogen, the tube is charged with copper (II) triflate (673 mg, 1.86 mmol, 0.1 equiv) and toluene (50 mL), followed by a solution of *N*-allyl-*N*-benzyl-2-oxocyclohexanecarboxamide **2** (5.0 g, 18.4 mmol, 1.0 equiv) in toluene (20 mL) and a solution of JohnPhosAuCl (5 mL of a 2.0 g/L in toluene, 0.02 mmol, 0.1 mol%), both added by syringe (Notes 14 and 15). The tube is sealed with a glass stopper and the stirred mixture is immersed in a preheated oil bath at 110 ºC (external temperature) for 2 h (see photo) (Notes 3, 16, and 17). The reaction mixture is allowed to cool down to room temperature (25 °C), then filtered through a fritted funnel (porosity 3, 5 cm diameter) into a 250-mL round-bottomed flask. The reaction vessel was rinsed with 50 mL of EtOAc, and the rinsate was passed through the fritted funnel. The filter cake was washed with EtOAc (2 x 15 mL), and the filtrate was concentrated by rotary evaporation (40 °C, 10 mmHg) to afford a brown oil (Note 18). The crude product is dissolved in 100 mL of CH_2Cl_2 and treated with 25 g of silica gel. The resulting mixture is placed on a rotary evaporator (25 °C, 100 mmHg) until the silica appears dry. The silica gel-adsorbed crude product is placed on a silica gel column (6 x 30 cm, 250 g of silica gel) prepared using EtOAc:hexanes (15:85). The column is eluted using the same solvent system and 100 mL fractions are collected. After 15 fractions are collected, the solvent is changed to EtOAc:hexanes (25:75) and another 20 fractions are collected. The minor diastereomer is found in fractions 4-16 (determined by TLC), which are combined, concentrated, and placed under vacuum (25 °C, 1 mmHg) to afford 1.52–1.53 g (31%) of compound **3b** (Note 19). The major diastereomer is found in fractions 18-30, which are similarly concentrated to afford 2.56–2.57 g (51%) of compound **3a** (Notes 19 and 20).

Set-up for Step A



Set-up for Step B



Set-up for Step C

Notes

1. Benzyl bromide (99%) was purchased from Alfa-Aesar, allylamine (98%) and potassium carbonate (99%, anhydrous, Redi-Dry™) from Sigma-Aldrich, and used as received. EtOAc and hexanes (both ACS grade) were purchased from Fisher and used as received.
2. A large excess of allylamine was used to ensure a complete conversion of benzyl bromide.
3. TLC was performed on Silica gel 60 F_{254} glass plates purchased from EMD Millipore and visualized with a permanganate stain (prepared from 2 g of $KMnO_4$, 13 g of K_2CO_3 and 200 mL of H_2O).
4. The progress of the reaction was followed by TLC analysis on silica gel with 15% EtOAc-hexanes as eluent and visualization with the $KMnO_4$ stain. Benzyl bromide, $R_f = 0.81$; allylamine $R_f = 0.00$; product **1** $R_f = 0.10$.
5. The submitters purified the product by flash chromatography on a column (8 x 40 cm) of 250 g of silica gel conditioned with EtOAc:cyclohexane (10:90) (Note 1) and eluted with 1.5 L of EtOAc:cyclohexane (10:90) followed by 2 L of EtOAc:cyclohexane (50:50) in 500 mL fractions. The desired product is obtained in fractions 3-6, which are concentrated by rotary evaporation (40 °C, 20 mmHg) and dried under vacuum (1.3 mmHg) for 2 h to give 17.34 g (70%) of **1** as yellow oil. Silica gel: Gerudan Si60 (40-63 μm) was purchased from Merck.
6. The submitters checked purity using GC analysis. GC conditions: Varian GC430 apparatus, column VF1-MS (15 m x 0.25 mm x 0.25 μm); vector gas: He; flow: 2 mL/min; injection temperature: 250 °C; temperature profile: initial temperature = 90 °C for 1 min, temperature gradient = 10 °C/min, final temperature = 250 °C for 5 min; detection: FID (250 °C).
7. *N*-Allyl-*N*-benzylamine (**1**) is bench-stable. Physical properties: GC Retention time: 2.96 min (Note 6); FT-IR (film): 3315, 3064, 3027, 2978, 2811, 1643, 1495, 1454, 1106, 918, 736, 698 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd. for $C_{10}H_{14}N$ $(M + H)^+$ 148.1121, found 148.1116; ^1H NMR (250 MHz, $CDCl_3$) δ: 1.35 (br s, 1 H), 3.28 (dd, *J*=6.0, 1.5 Hz, 2 H), 3.79 (s, 2 H), 5.10 (dt, *J*=10.5, 1.5 Hz, 1 H), 5.19 (dt, *J*=17.5, 1.5 Hz, 1 H), 5.93 (ddt, *J* =17.5, 6.0, 1.5 Hz, 1 H), 7.23-7.27 (m, 1 H), 7.30-7.34 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 51.7, 53.2, 115.9, 126.9, 128.1, 128.3, 136.8, 140.3.

Anal. calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.66; H, 8.92; N, 9.57.

8. *N*-Allyl-*N*-benzylamine (**1**) is also commercially available. The submitters and checkers only used the product prepared by the method described here.
9. 4-Dimethylaminopyridine (99%) was purchased from Alfa-Aesar, toluene (HPLC grade) from Fisher, and ethyl 2-oxocyclohexanecarboxylate (95%) from Sigma-Aldrich. All were used as received.
10. The progress of the reaction was followed by TLC analysis on silica gel with 15% EtOAc-hexanes as eluent. Ethyl 2-oxocyclohexanecarboxylate, R_f = 0.75 and 0.18 (the latter spot probably corresponds to the enol form); amine **1**, R_f = 0.19; product **2**, R_f = 0.34. The reaction does not reach full conversion after 2 days (~95% complete by NMR), but a longer reaction time (4-5 days) provides only slight increase in conversion (~ 2%).
11. Silica gel: SiliaFlash® P60 40-63μm (230-400 mesh) 60Å Irregular Silica Gel was purchased from Siliycle.
12. Unreacted starting material is found in fractions 2-3, which after concentration and drying under vacuum provides 0.66 g (7%) of starting ethyl 2-oxocyclohexanecarboxylate.
13. *N*-Allyl-*N*-benzyl-2-oxocyclohexanecarboxamide **2** is bench-stable. Physical properties: GC retention time: 12.21 min (see Note 6); FT-IR (film): 3063, 3029, 2940, 2865, 1709, 1648, 1448, 1180, 1128, 737, 700 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd. for $C_{17}H_{22}NO_2$ $(M + H)^+$ 272.1645. Found: 272.1657; ^1H NMR (500 MHz, $CDCl_3$, mixture of rotomeric forms) δ: 1.54–1.86 (m, 4 H), 1.95–2.12 (m, 6 H), 2.22–2.37 (m, 4 H), 2.51–2.59 (m, 2 H), 3.52–3.82 (m, 6 H), 4.19–4.50 (m, 4 H), 5.08–5.28 (m, 4 H), 5.70–5.83 (m, 2 H), 7.15–7.38 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of rotomeric forms) δ: 21.1, 23.4, 23.6, 26.7, 26.9, 50.1, 30.3, 30.4, 34.5, 41.8, 41.9, 48.0, 48.4, 49.0, 54.3, 54.4, 116.6, 117.1, 126.2, 127.1, 127.5, 127.8, 127.9, 128.4, 128.5, 128.8, 132.5, 133.1, 136.7, 137.1, 169.9, 170.1, 207.2, 207.4. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.11; H, 7.86; N, 5.17.
14. Copper (II) triflate (99%) was purchased from Alfa-Aesar, JohnPhosAuCl ((2-biphenyl)-di-*tert*-butylphosphine gold chloride, 98%) from Strem Chemicals, and toluene (HPLC grade) from Fisher. All were used as received.

15. The solution of gold complex was obtained by dissolving 20.0 mg JohnPhosAuCl in 10.0 ml of toluene with stirring for 15 min.
16. The progress of the reaction was followed by TLC analysis on silica gel with 15% EtOAc-hexanes as eluent and visualization with $KMnO_4$. Amide **2**, R_f = 0.19; minor diastereomer of **3**, R_f = 0.34; major diastereomer of **3**, R_f = 0.16.
17. The initial clear green solution turned brown during the course of the reaction.
18. NMR spectrum of the crude product shows the presence of two diastereomers, formed in ca. 2:1 ratio.
19. Both diastereomers of *N*-benzyl-4-methyl-2-azaspiro[4.5]decane-1,6-dione **3** are bench-stable. Physical properties of minor diastereomer: GC Retention time = 12.52 min (see Note 6); FT-IR (film): 2938, 2865, 1705, 1682, 1494, 1428, 1262, 1230, 701 cm^{-1}; HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{17}H_{22}NO_2$ (minor): 272.1645. Found: 272.1657. ^1H NMR (500 MHz, $CDCl_3$) (minor) δ: 1.10 (d, *J*=7.0 Hz, 3 H), 1.70–1.97 (m, 4 H), 2.15–2.34 (m, 4 H), 2.60 (ddd, *J*=16.0, 7.0, 6.5 Hz, 1 H), 3.09 (t, *J*=9.0 Hz, 1 H), 3.14 (dd, *J*=9.0, 8.0 Hz, 1 H), 4.45 (d, *J*=15.0 Hz, 1 H), 4.50 (d, *J*=15.0 Hz, 1 H), 7.23–7.35 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) (minor) δ: 13.4, 20.7, 26.9, 30.2, 31.6, 40.4, 46.8, 50.4, 61.5, 127.6, 128.0, 128.7, 136.3, 172.8, 208.4; Major diastereomer: GC Retention time = 12.39 min (see Note 6); FT-IR (film): 2937, 2867, 1705, 1682, 1440, 1264, 701 cm^{-1}; HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{17}H_{22}NO_2$ (major): 272.1645. Found: 272.1657. ^1H NMR (500 MHz, $CDCl_3$) (major) δ: 0.92 (d, *J*=7.0 Hz, 3H), 1.66–1.76 (m, 3 H), 1.98–2.03 (m, 1 H), 2.06–2.12 (m, 1 H), 2.23–2.32 (m, 1 H), 2.48 (dt, *J*=14.0, 4.5 Hz, 1 H), 2.71 (dd, *J*=9.5, 7.0 Hz, 1 H), 2.98 (app. sex, *J*=7.5 Hz, 1 H), 3.09 (ddd, *J*=12, 11.5, 6.0 Hz, 1 H), 3.25 (dd, *J*=9.5, 7.5 Hz, 1 H), 4.38 (d, *J*=14.5 Hz, 1 H), 4.48 (d, *J*=14.5 Hz, 1 H), 7.20–7.21 (m, 2 H), 7.26–7.34 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) (major) δ: 14.0, 21.2, 24.5, 34.6, 39.6, 41.7, 46.8, 51.3, 61.8, 127.5, 127.8, 127.9, 128.6, 136.2, 174.1, 208.9.
20. In the submitter's original procedure, the reaction was carried out in air. Compounds **3a** and **3b** were obtained in 69% overall yield. The isolated yields reported in Table 1 are those obtained when the reaction is carried in air.

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The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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Discussion

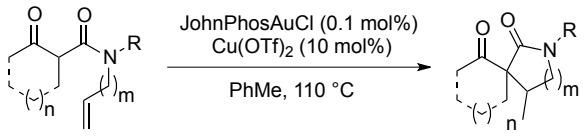
Homogeneous Au(I)-catalysis has become an essential tool in organic chemistry. The majority of reactions involve $[LAu]^+Y^-$ as the active species where Y^- is a weakly coordinating anion ($Y^- = TfO^-$, Tf_2N^-, BF_4^-, PF_6^-, SbF_6^-, …; L = PR_3, NHC, …).[2] These electrophilic compounds act as soft Lewis acids, which can coordinate and activate unsaturated C–C bonds towards nucleophilic attack. They are usually generated by anion metathesis

between LAuX (X= Cl, Br) and a silver salt (AgY), which ensures a fast and irreversible generation of $[LAu]^+Y^-$. However, these species may rapidly decay to give Au(0) (mirror, precipitate, or nanoparticles) and inactive $[L_2Au]^+Y^-$ under the reaction conditions.[3] Thus, some Au(I)-catalyzed reactions suffer from a limited scale (usually milligram scale) and restriction on temperature range (usually below 80 °C). A catalyst loading superior to 1 mol% is also often required.

Several groups have focused their efforts on the development of bulky ligands to circumvent these problems.[4] On our side, we decided to play on the anion metathesis itself. We have shown very recently that the use of copper salts as additives in Au(I)-catalyzed reactions allows the gradual delivery of $[LAu]^+$ from a reservoir of stable LAuX.[5] Thus, readily available, non-light-sensitive, and cheap Cu(II) salts can advantageously replace silver additives in Au(I)-catalyzed reactions. With the Au/Cu catalytic system, it becomes possible to carry out gram-scale reactions in a small amount of solvent, even at elevated temperature, without observing the formation of Au(0). Since then, we have worked on the scope of this Au/Cu catalytic system. The practical features of this method, including its operational simplicity, make it an expedient alternative to traditional methods.

In particular, it allows one to synthesize (spiro) lactams with low loadings of gold complex via hydroalkylation of unactivated alkenes. Lactams are valuable building blocks and are ubiquitous frameworks of compounds of biological interest. Che has reported similar transformations using 1 to 20 mol% of JohnPhosAuCl/AgOTf.[6] With some substrates, as shown in our preliminary communication, Che's procedure is not as efficient as the one we propose. With the Au/Cu catalytic system, the intramolecular hydroalkylation of readily accessible β-ketoamides can be performed on a 1 gram-scale using 0.1 mol% of JohnPhosAuCl and 10 mol% of copper(II) triflate at 110 °C with good yield (60-78%) (Table 1). In addition to substrate scope, this new Au/Cu system has many practical advantages. All the reactions can be carried out in standard glassware without precautions towards air and moisture and employs commercially available reagents and catalysts. This new catalytic system is also suitable to achieve highly selective transformations in a large scale.

Table 1. Gram-scale Hydroalkylation of Unactivated Alkenes



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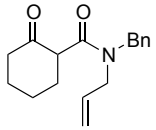
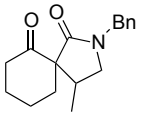
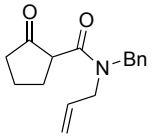
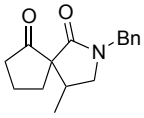
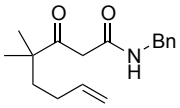
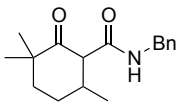
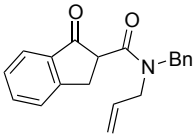
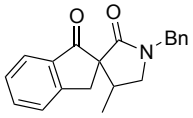
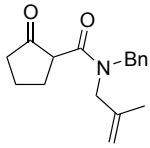
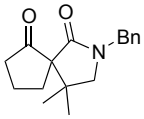
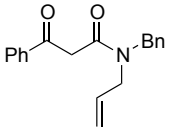
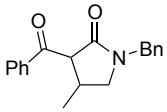
1		1.5		100 (73)	66/34
2		1.5		100 (69)	67/33
3		1.0		100 (78)	95/5
4		24		100 (60)	60/40
5		24		100 (70)	n/a
6		3		80 (60)	90/10

References

1. ICMMO (UMR CNRS 8182), LabEx CHARMMMAT Université Paris-sud 91405 Orsay, France. Fax: (+)33 169 154 747. sophie.bezzenine@u-psud.fr; vincent.gandon@u-psud.fr. We thank ANR JCJC HAONA, UPS, CNRS, CSC, and IUF for financial support.
2. Modern Gold-Catalyzed Synthesis, Hashmi, A. S. K.; Toste, F. D. Eds; Wiley-VCH: Weinheim, 2012.
3. See Chapter 8 in ref 2 and: Wang, W.; Hammond, G. B.; Xu, B. *J. Am. Chem. Soc.* **2012**, *134*, 5697.
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Appendix
Chemical Abstracts Nomenclature (Registry Number)

Potassium carbonate: carbonic acid, potassium salt (1:2); (584-08-7)
Allylamine: 2-propen-1-amine; (107-11-9)
Benzyl bromide: benzene, (bromomethyl)-; (100-39-0)
4-Dimethylaminopyridine: 4-pyridinamine,N,N-dimethyl-; (1122-58-3)
Ethyl 2-oxocyclohexanecarboxylate: cyclohexanecarboxylic acid, 2-oxo-, ethyl ester; (1655-07-8)
Copper (II) triflate: methanesulfonic acid, 1,1,1-trifluoro-, copper(2+) salt (2:1); (34946-82-2)
JohnPhosAuCl: gold, [[1,1'-biphenyl]-2-ylbis(1,1-dimethylethyl)phosphine]chloro-; (854045-93-5)

Weizhen Fang was born in 1985 in Anhui, China. He received his B.Eng. and M.S. from Southwest Jiaotong University in 2008 and 2011 respectively. He is now pursuing his Ph.D. in the group of Prof. Vincent Gandon at Université Paris-Sud (2011-2014). His current research interests include two-component catalyst system (Gold(I) complexes and Lewis acids) for asymmetric hydroalkylation and the synthesis of natural products.

Marc Presset was born in Thonon-les-bains (France) in 1981. After joining the ENS Cachan, he passed the Agrégation de Sciences Physiques in 2007. He then moved to Aix- Marseille Université, where he obtained his Ph.D. under the supervision of Prof. Rodriguez and Dr. Coquerel in 2010. After previous postdoctoral experiences with Prof. Molander at the University of Pennsylvania (USA) and in Janssen (Belgium), he is currently working with Prof. Gandon at the Université Paris-Sud.

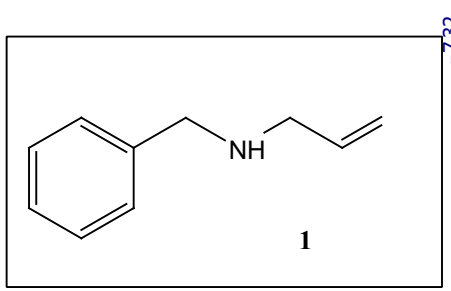
Amandine Guérinot was born in 1983 in Troyes (France). She received her engineer's diploma from ESPCI ParisTech in 2007 and then joined the organic chemistry laboratory at ESPCI where she prepared her Ph.D. under the supervision of Prof. Cossy and Dr. Reymond. After a one-year postdoctoral stay with Pr Canesi at UQAM (Montreal), she moved to Université Paris-Sud to work with Prof. Gandon. After an additional postodoctoral fellowship in Université Paris V in the group of Dr. Micouin, she was appointed associate professor in 2013 at ESPCI in the group of Pr Cossy.

Christophe Bour was born in Haguenau (France) in 1980. He studied chemistry at the University of Strasbourg and completed his Ph.D. with Dr. J. Suffert in 2006. He then joined the research group of Prof. Antonio Echavarren in Tarragona (Spain) as a post-doctoral fellow. In early 2009, he moved to the ECPM at the University of Strasbourg to work with Dr. G. Hanquet as a post-doctoral researcher. In September 2010, he was appointed associate professor at the Université Paris-Sud. His scientific interests include catalysis, coordination chemistry, and new synthetic methodologies.

Sophie Bezzenine-Lafollée was born in Paris, France in 1972. She received her Ph.D. prepared under the supervision of Dr. H. Rudler in 1998 in the University of Paris VI. She spent one post-doctoral year in Prof. Müller's group at the University of Geneva, Switzerland and then two years in the laboratory of Prof. J. Ardisson and Dr. A. Pancrazi at the University of Cergy-Pontoise. She became associate professor in 2001 in Orsay University. She worked with Dr. F. Guibé and then with Dr. J. Collin. Her main current research interests are enantioselective catalysis and applications in synthesis.

Vincent Gandon was born in Soissons, France, in 1973. He received his Ph.D. in 2002 from the University of Reims Champagne Ardenne (group of Prof. Jan Szymoniak). After a postdoctoral stay at the University of California, Riverside in the group of Prof. Guy Bertrand, he joined the faculty of the University Pierre et Marie Curie in Paris in 2003, as associate professor in the laboratory of Prof. Max Malacria. In 2009, he was appointed full Professor at the University of Paris-Sud. His research interests are focused on homogeneous catalysis using cobalt, gold, platinum, and gallium complexes.

Pavel K. Elkin was born in Kaliningrad, Russia, in 1991. He received his B.S. from D. Mendeleyev University of Chemical Technology of Russia in 2012 and M.S. from the University of Chicago in 2013. He is now pursuing his Ph.D. in the group of Prof. Viresh H. Rawal at the University of Chicago. His current research interests include development of novel dienes for asymmetric Diels-Alder reactions, new types of single-point hydrogen-bonding catalysts and the synthesis of natural products.



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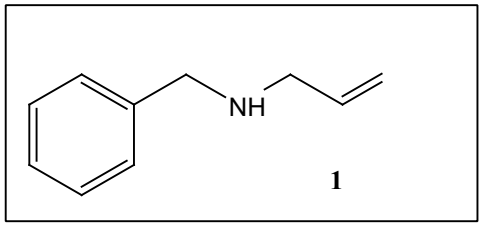

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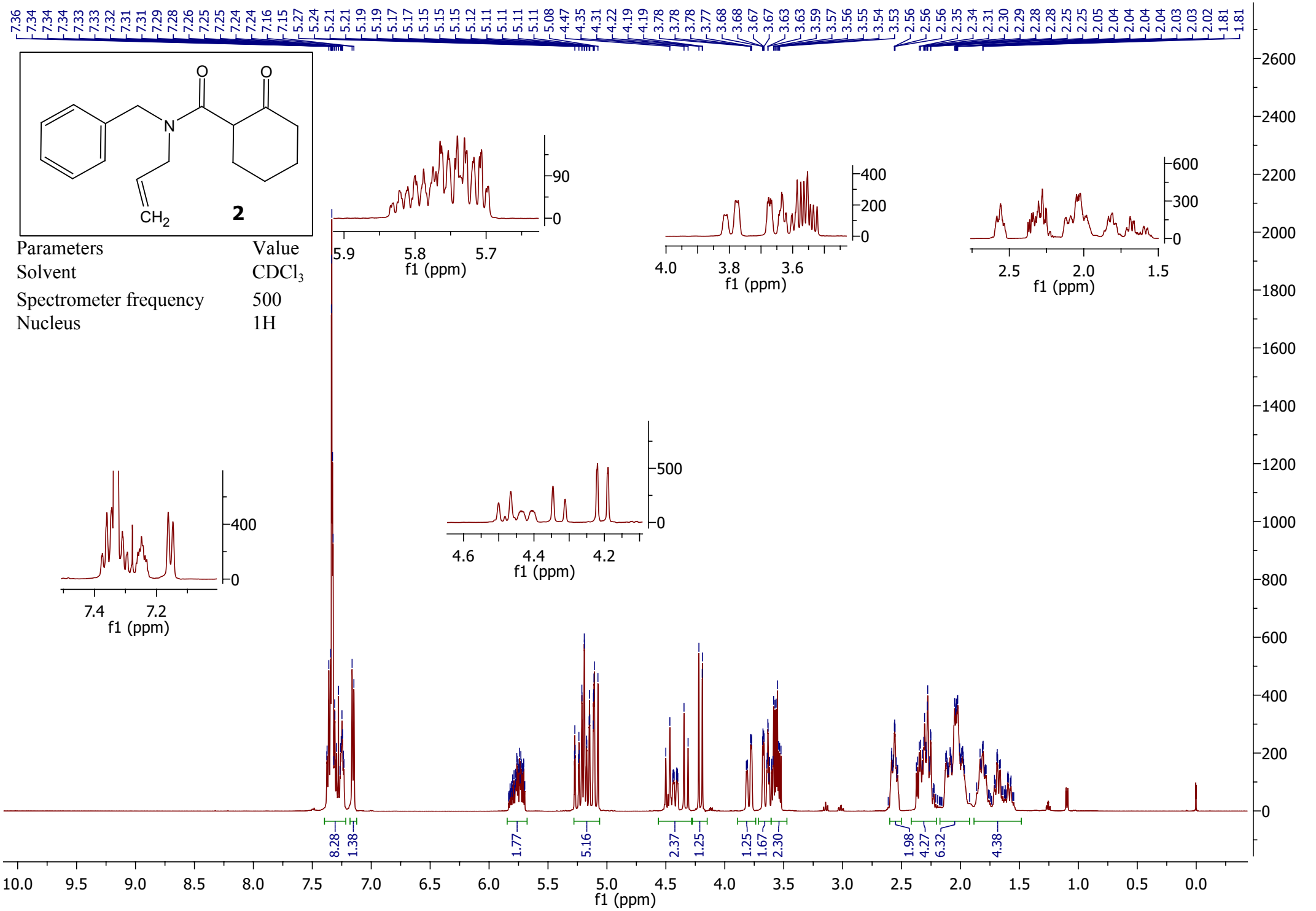
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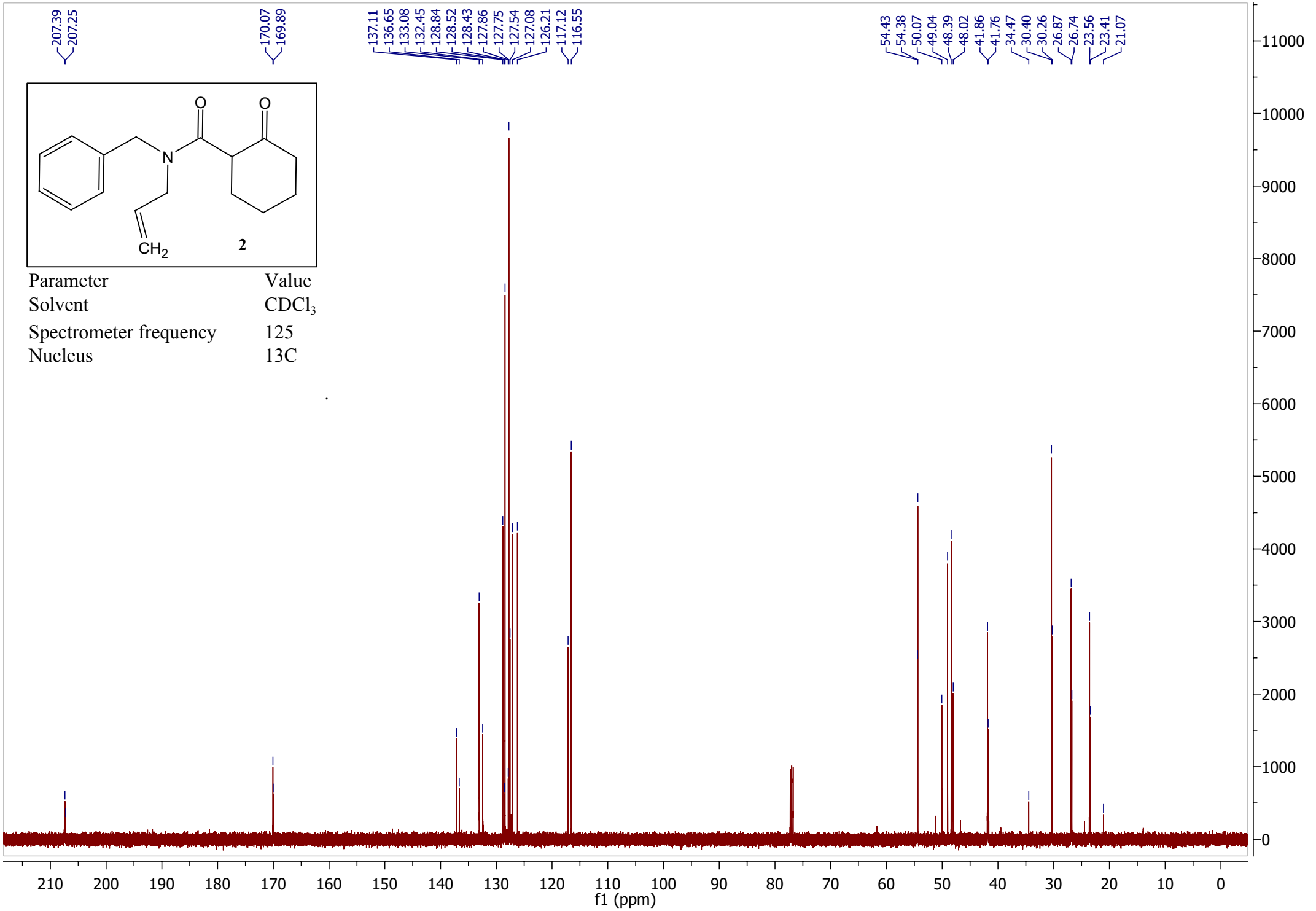
2.30
1.98
4.27
6.32
4.38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48.02
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41.76
34.47
30.40
30.26
26.87
26.74
23.56
23.41
21.07
O
O
N
CH2
2
Parameter
Value
Solvent
CDCl3
Spectrometer frequency
125
Nucleus
13C
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210
200
190
180
170
160
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70
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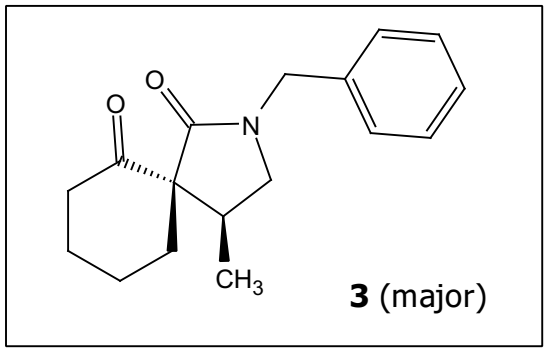
50
40
30
20
10
0
f1 (ppm)



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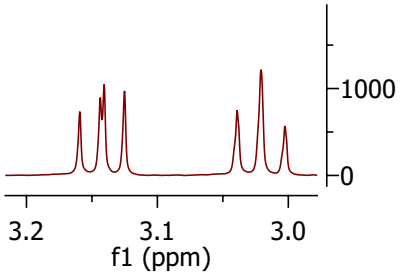
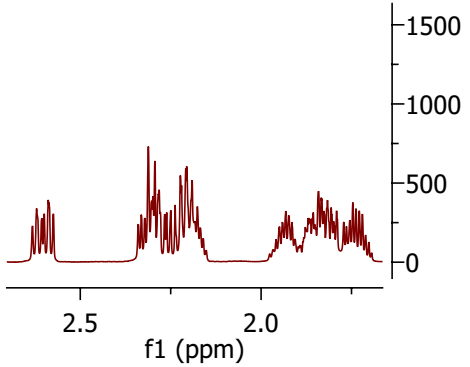
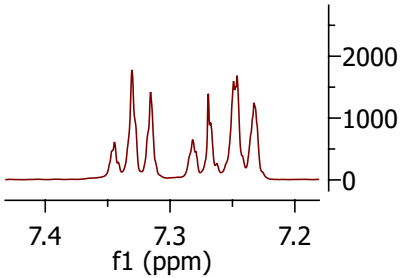
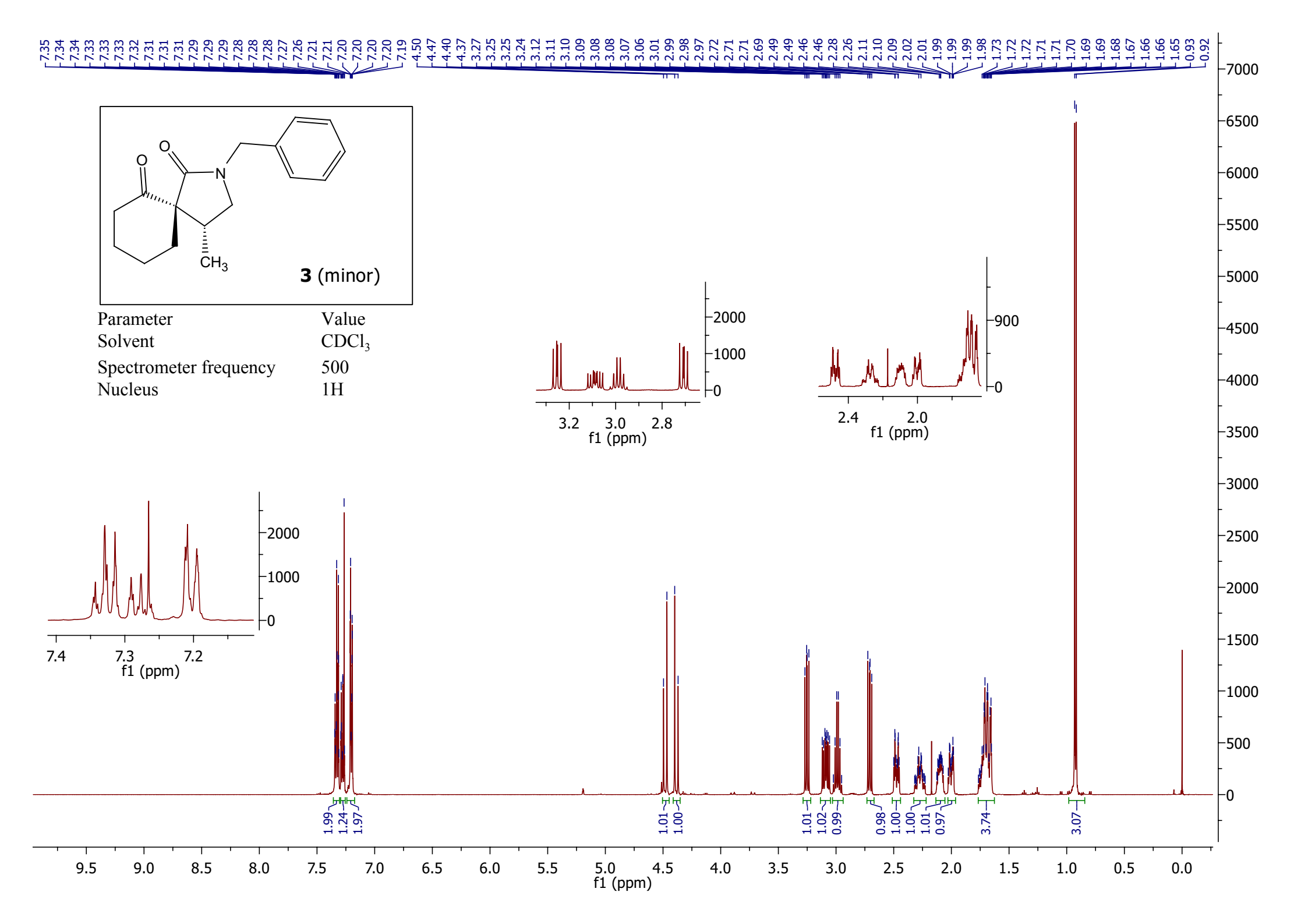
Nucleus	1H





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O
N
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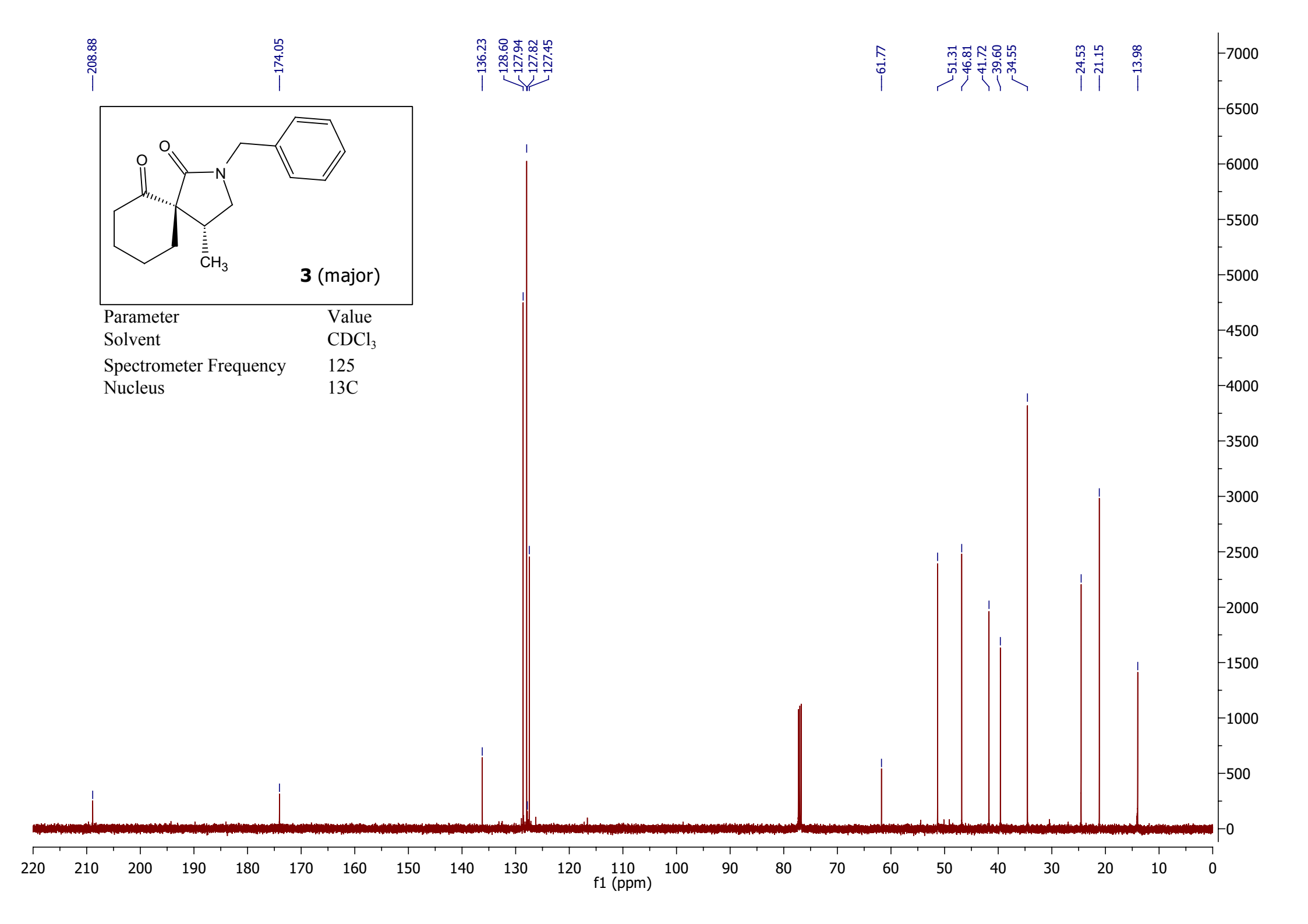
Spectrometer frequency 500
Nucleus 1H
f1 (ppm)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24.53
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Parameter Value
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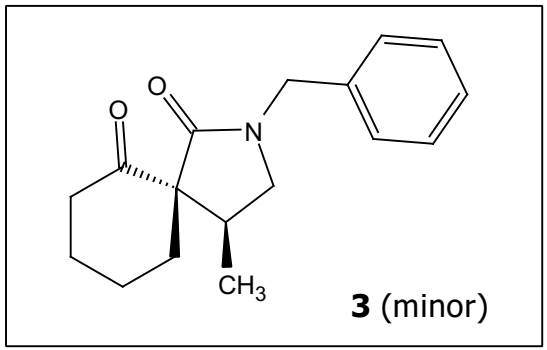
Nucleus 13C
f1 (ppm)



Parameter	Value
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Nucleus	13C