



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

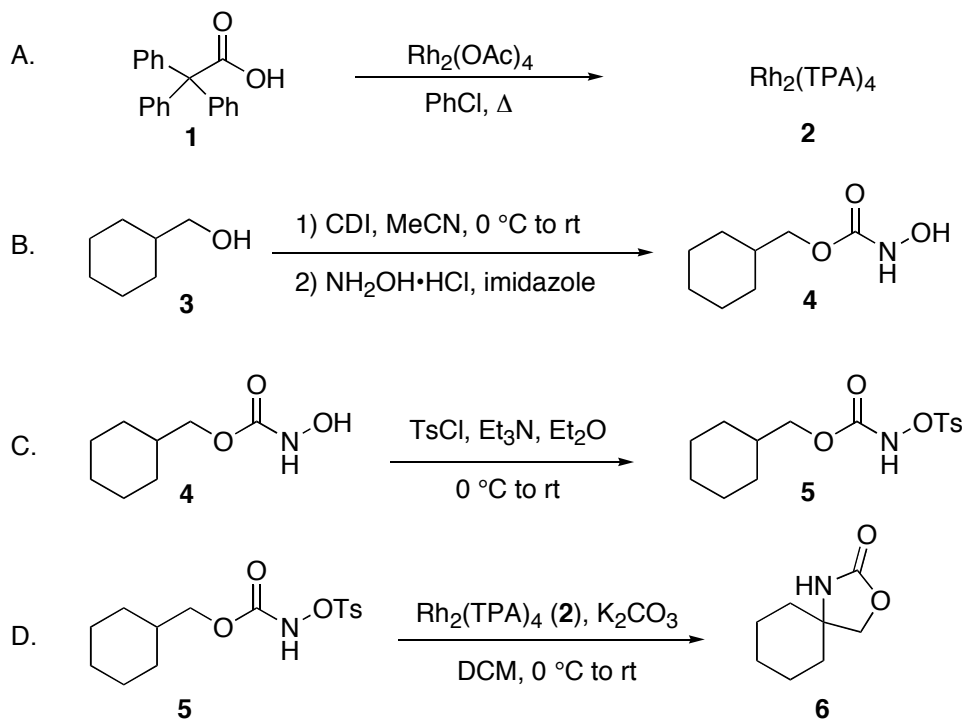
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

**PREPARATION OF 4-SPIROCYCLOHEXYLOXAZOLIDINONE  
BY C-H BOND NITRENE INSERTION  
[3-Oxa-1-azaspiro[4.5]decan-2-one]**



Submitted by Kim Huard and H el ene Lebel.<sup>1</sup>

Checked by Adam Rosenberg, Darla Seifried, and Kay Brummond.

## 1. Procedure

A. *Rhodium II tetrakis(triphenylacetate) dimer* (**2**). To a 250-mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar, a short-path distillation apparatus and a 100-mL receiving bulb (Note 1) is added rhodium (II) acetate dimer (1.26 g, 2.85 mmol) (Note 2), triphenylacetic acid (**1**) (6.55 g, 22.7 mmol, 8.0 equiv) (Note 3) and chlorobenzene (120 mL) (Note 3). The mixture is heated with an oil bath that is set to a temperature at which the solvent distills at a rate of 10 mL/hour (approximately 155 °C) (Note 4). The green mixture becomes homogeneous upon heating. After 7 h, the reaction is cooled to 25 °C and the residual solvent is concentrated at 65 °C by rotary evaporation (20–25 mmHg) and then at 0.5 mmHg. The solid residue is dissolved in 200 mL of dichloromethane. The solution is washed with saturated aqueous sodium bicarbonate (3 x 200 mL), saturated aqueous sodium chloride (100 mL), dried over magnesium sulfate (15 g), filtered and

concentrated at 40 °C by rotary evaporation (225 mmHg) and then at 0.5 mmHg. To the green solid, methanol (40 mL) is added and the residue is stirred in a 35 °C water bath (Note 5). After 5 minutes, dichloromethane is added portion wise with stirring and heating in a 35 °C water bath until the solid is completely dissolved (approximately 200 mL of DCM). The solution is left to rest at -19 °C for 72 h. The crystals are collected by suction filtration on a fritted glass funnel and dried at 0.5 mmHg to afford 3.01 g (78% yield) of the desired product (Notes 6 and 7).

*B. Cyclohexylmethyl N-hydroxycarbamate (4).* A 500-mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar and a 50-mL pressure-equalizing addition funnel fitted with a nitrogen inlet is flame-dried and maintained under nitrogen atmosphere. The flask is quickly opened to add 1,1'-carbonyldiimidazole (17.0 g, 105 mmol, 1.05 equiv) (Notes 8 and 9) followed by acetonitrile (200 mL) (Note 10) via cannula. The white suspension is cooled with an ice bath and cyclohexanemethanol (**3**) (12.3 mL, 100 mmol) (Note 11) is transferred to the addition funnel using a syringe. Cyclohexanemethanol (**3**) is added dropwise over a 30-minute time period. Addition of the alcohol results in the suspension becoming a homogeneous solution. The addition funnel is rinsed with acetonitrile (10 mL) and the solution is stirred in the ice bath for 1 h. The reaction of cyclohexanemethanol **3** ( $R_f = 0.63$  in 30% EtOAc/DCM) with 1,1'-carbonyldiimidazole to give a carbonylated intermediate ( $R_f = 0.59$  in 30% EtOAc/DCM) can be followed by TLC analysis using a potassium permanganate solution for visualization. Continued stirring does not improve the conversion as the intermediate can be hydrolyzed and the starting alcohol recovered. The solution is then warmed to ambient temperature. To the solution is then added hydroxylamine hydrochloride (20.9 g, 300 mmol, 3.0 equiv) (Note 12) followed by imidazole (13.6 g, 200 mmol, 2.0 equiv) (Note 12) and vigorous stirring is continued for 3.5 h (Note 13). The conversion of the intermediate ( $R_f = 0.59$  in 30% EtOAc/DCM) to cyclohexylmethyl *N*-hydroxycarbamate **4** ( $R_f = 0.52$  in 30% EtOAc/DCM) can be followed by TLC analysis using a potassium permanganate solution for visualization. The suspension is concentrated at 40 °C by rotary evaporation (130 mmHg) and at 0.5 mmHg. The white residue is dissolved in a 1:1 mixture of ethyl acetate and 10% hydrochloric acid (300 mL) and transferred to a 1-L separatory funnel. After vigorous shaking, the phases are separated and the aqueous phase is extracted with ethyl acetate (2 x 150 mL). The combined organic layers are washed with a saturated sodium chloride solution (100

mL), dried over magnesium sulfate (15 g), filtered and concentrated at 40 °C by rotary evaporation (75 mmHg) and then at 0.5 mmHg to afford 16.57 g of a light amber oil containing the title compound **4** and residual starting alcohol **3** in a ratio of roughly 7:1, as determined by NMR analysis (Note 14). This mixture is used without further purification for the next step. A 200 mg sample of the crude product is purified by silica gel chromatography (Note 15) to afford 167 mg (84% recovery) of the title compound as a white solid (Note 16).

*C. Cyclohexylmethyl N-tosylloxycarbamate (5).* A 500-mL, one-necked, round-bottomed flask containing the oily residue obtained from procedure B (15.9 g) is equipped with a magnetic stirring bar and a 50-mL pressure-equalizing addition funnel fitted with a nitrogen inlet. The system is flushed with nitrogen for 30 min and maintained under nitrogen atmosphere. Diethyl ether (200 mL) (Note 17) is added via cannula and the solution is cooled with an ice bath. The system is quickly opened to add *p*-toluenesulfonyl chloride (20.2 g, 106 mmol) (Note 18). Triethylamine (13.4 mL, 96.4 mmol) (Note 19) is introduced into the addition funnel using a syringe and is added dropwise over a 15-minute time period to the ethereal solution. The addition funnel is rinsed with diethyl ether (10 mL) and the solution is stirred in the ice bath for 1.5 h. Distilled water (75 mL) is added to the white suspension and the resulting clear mixture is transferred to a 500-mL separatory funnel. After vigorous shaking, the organic layer is separated and washed with a saturated sodium chloride solution (75 mL), dried over MgSO<sub>4</sub> (15 g), filtered and concentrated at 40 °C by rotary evaporation (225 mmHg and 20 mmHg) until the residue becomes solid and then at 0.5 mmHg for 12 h to afford a yellowish solid. The solid is dissolved in 50 mL of dichloromethane and is charged on a 6.5 x 11 cm silica gel column (200 g of dry silica) (Note 20). The system is eluted with a mixture of 5% ethyl acetate-dichloromethane. The first 150 mL are discarded and the next 800 mL are collected in a 1-L round-bottomed flask and concentrated at 40 °C by rotary evaporation (225 mmHg, then 20 mmHg) until the residue becomes a solid which is then dried at 0.5 mmHg. The inner surface of the flask is scratched with a spatula in order to loosen the product from the flask. To the 1-L flask is added a 6-cm egg-shaped magnetic stirring bar and 300 mL of hexane (Note 21). The suspension is vigorously stirred for 24 h and filtered on a fritted glass funnel. The white solid is dried at 0.5 mmHg for 8 h to afford 23.75 g (73% yield from **3**) of the desired product (Notes 22 and

23). The tosyloxycarbamate must be over 90% purity, as determined by GC/MS, to be used for the next step.

*D. 4-Spirocyclohexyloxazolidinone (6).* Using a 250-mL one-necked, round-bottomed flask equipped with a magnetic stirring bar, a solution of cyclohexylmethyl *N*-tosyloxycarbamate (**5**) (16.4 g, 50.0 mmol) in dichloromethane (50 mL) (Note 24) is prepared. A 1-L three-necked, round-bottomed flask equipped with a 6-cm egg-shaped magnetic stirring bar is charged with dichloromethane (75 mL) and distilled water (10 mL). Potassium carbonate (7.60 g, 55 mmol, 1.1 equiv) (Note 25) is added to the flask, which is fitted with a rubber septum, an internal thermometer, glass stopper and a short needle (through the septum) opened to the atmosphere, and the mixture is stirred until the white solid is dissolved. The dichloromethane solution containing **5** (Note 26) is taken up in a 60-mL glass syringe, which is installed on a syringe pump system set for an addition time of 60 minutes. Tetrakis(triphenylacetate) rhodium dimer (**2**) (0.678 g, 0.5 mmol, 0.01 equiv) is added to the biphasic solution and the dropwise addition is begun. Upon the addition of the tosyloxycarbamate **5** solution, the green reaction mixture becomes thicker, a white solid forms, and the internal temperature slowly rises to reach 30 °C when approximately half of the starting material is added. Then the mixture slowly cools down to room temperature. The starting material is added dropwise to avoid any significant rise of internal temperature. When the complete volume is added, the 250-mL flask and the syringe are rinsed with 10 mL of dichloromethane and this volume is added to the mixture which is stirred for a further 3 h to ensure complete consumption of the starting material. The dichloromethane is evaporated at 40 °C by rotary evaporation (225 mmHg) until only the residue and the water are left in the flask. The aqueous residue is dissolved in a 1:1 mixture of ethyl acetate and water (400 mL) and transferred to a 1-L separatory funnel. The phases are separated and the aqueous layer is extracted with ethyl acetate (2 x 100 mL). The combined organic extracts are washed with a saturated sodium chloride solution (100 mL), dried over MgSO<sub>4</sub> (15 g), filtered and concentrated at 40 °C by rotary evaporation (75 mmHg) and then at 0.5 mmHg to afford a yellowish solid. The solid is dissolved in 20 mL of dichloromethane and charged on a 6.5 x 22 cm column of silica gel (350 g of dry silica) (Note 20). The system is eluted with a mixture of 30% ethyl acetate-dichloromethane. Because the product is difficult to visualize by TLC, the first 900 mL are discarded and the next 1400 mL are collected and concentrated at 40 °C by rotary evaporation (225

mmHg then 20 mmHg) until the residue solidifies. It is then dried at 0.5 mmHg to afford 6.1 g (79% yield) of the title compound as a yellowish solid of purity higher than 98% as determined by NMR and GC/MS analysis (Note 27).

## 2. Notes

1. All glassware was flame-dried under vacuum and allowed to cool under an atmosphere of nitrogen.

2. Rhodium (II) acetate dimer was purchased from Strem Chemicals. It was stored and weighed in a glove box and was used without further purification.

3. Triphenylacetic acid (99%) and chlorobenzene (99%) were purchased from Aldrich Chemical Company, Inc. and used as received.

4. Slow distillation of the solvent (bp 132 °C) removes the acetic acid (bp 117 °C) formed from the ligand exchange. If the distillation rate is higher than 10 mL/hour, chlorobenzene is added in order to keep the total volume of the reaction mixture over 40 mL.

5. The solid is insoluble in methanol and the color changes from green to purple-blue.

6. A half-scale run provided 1.75 g (89%) of the rhodium II tetrakis(triphenylacetate) dimer.

7. Analytical data for Rhodium II tetrakis(triphenylacetate) dimer (**2**):  $R_f = 0.19$  (10% ethyl acetate/hexane);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.51 (residual MeOH), 6.63 (d,  $J = 7.5$  Hz, 24 H), 6.86 (t,  $J = 8.1$  Hz, 24 H), 7.07 (t,  $J = 7.5$  Hz, 12 H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 69.2 (residual MeOH), 126.8, 127.4, 130.7, 143.4, 192.9; IR (film) 3055, 1590, 1580, 1365  $\text{cm}^{-1}$ ; Analysis calc. for  $\text{C}_{80}\text{H}_{60}\text{O}_8\text{Rh}_2$ : C 70.90, H 4.46; found: C 67.96, H 4.73 %. The low value obtained for the carbon analysis is due to residual coordinated methanol from the recrystallization. Up to 2 equiv of MeOH per molecule of dimer (determined by  $^1\text{H NMR}$ ,  $\delta = 3.51$  and  $^{13}\text{C NMR}$ ,  $\delta = 69.2$ ) can be present and do not affect the reactivity of the catalyst.

8. 1,1'-Carbonyldiimidazole, reagent grade, was purchased from Aldrich Chemical Company, Inc. It was stored and weighed in a glove box to avoid hydrolysis and was used without further purification.

9. Short exposure to 1,1'-carbonyldiimidazole could cause serious temporary or residual injury. This reagent should be handled with careful attention to avoid contact with skin.

10. Acetonitrile was distilled over calcium hydride. If wet acetonitrile is used, hydrolysis of a reaction intermediate reduces the yield.
11. Cyclohexanemethanol (**3**), 99+%, was purchased from Aldrich Chemical Company, Inc. and was used as received.
12. Hydroxylamine hydrochloride (99%) and imidazole (99%) were purchased from Alfa Aesar and used as received.
13. An excess of hydroxylamine and imidazole is used in order to accelerate the reaction and minimize the hydrolysis of the intermediate.
14. The  $^1\text{H}$  NMR methylene resonances of the *N*-hydroxycarbamate (doublet at 3.96 ppm) and the starting alcohol (doublet at 3.44 ppm) are used to determine the product ratio.
15. Flash chromatography is performed on a 3 x 10 cm silica gel column (33 g of dry silica). The product is charged on the column and the system is eluted with 50 mL of 20% ethyl acetate-dichloromethane. At that point, fraction collection (8-mL fractions) is begun and elution is continued with 450 mL of a 20% ethyl acetate-dichloromethane mixture. Collected fractions were analyzed by TLC, eluting with 30% ethyl acetate-dichloromethane ( $R_f = 0.52$  for **4** and 0.63 for **3**). Visualization was accomplished by spraying with a potassium permanganate solution followed by heating. All the fractions (10-30) containing the desired product were combined and concentrated at 45 °C by rotary evaporation (40-50 mmHg) and then at 0.5 mmHg.
16. Analytical data for cyclohexylmethyl *N*-hydroxycarbamate (**4**): mp 33–34 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.85–1.04 (m, 2 H), 1.06–1.37 (m, 3 H), 1.40–1.90 (m, 6 H), 3.99 (dd,  $J = 6.3, 5.1$  Hz, 2 H), 7.03 (br s, 1 H), 7.28 (br s, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 25.7, 26.4, 29.6, 37.4, 71.5, 159.9; IR (film) 3291, 2922, 2851, 1712, 1449, 1267, 1121  $\text{cm}^{-1}$ ; HRMS (TOF $^+$ ) calc. for  $\text{C}_8\text{H}_{15}\text{NO}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 196.0950; found: 196.0940; Analysis calc. for  $\text{C}_8\text{H}_{15}\text{NO}_3$ : C 55.47, H 8.73, N 8.09; found: C 55.49, H 8.81, N 7.93 %.
17. Anhydrous diethyl ether was obtained by filtration through a drying column on a Sol-Tec solvent purification system.
18. *p*-Toluenesulfonyl chloride, 99+%, was purchased from Aldrich Chemical Company, Inc. and was used as received.
19. Triethylamine was purchased from Fisher Scientific and was freshly distilled from  $\text{CaH}_2$  (88–90 °C) under argon atmosphere prior to use.
20. UltraPure silica gel (32–63  $\mu\text{m}$ ) was purchased from EcoChrom.

21. Omnisolv grade hexane was purchased from EMD and was used as received.

22. A second run on approximately half-scale provided a 79% yield.

23. The physical properties of **5** are as follows:  $R_f$  0.68 (5% ethyl acetate/dichloromethane); mp 88–90 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.82–0.85 (m, 2 H), 1.0–1.3 (m, 3 H), 1.46–1.57 (m, 3 H), 1.63–1.67 (m, 3 H), 2.46 (s, 3 H), 3.83 (d,  $J = 6.3$  Hz, 2 H), 7.35 (d,  $J = 8.1$  Hz, 2 H), 7.87 (d,  $J = 8.1$  Hz, 2 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 21.9, 25.7, 26.3, 29.3, 37.1, 72.2, 129.7, 129.9, 130.5, 146.2, 155.9; IR (film) 3230, 2927, 2853, 1740, 1597, 1380, 1191, 1179  $\text{cm}^{-1}$ ; HRMS (TOF<sup>+</sup>) calc. for  $\text{C}_{15}\text{H}_{21}\text{NO}_5\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 350.1038; found: 350.1006; Analysis calc. for  $\text{C}_{15}\text{H}_{21}\text{NO}_5\text{S}$ : C 55.03, H 6.47, N 4.28, S 9.79; found: C 54.85, H 6.30, N 4.11, S 10.07 %.

24. Dichloromethane was purchased from Fisher Scientific and was used as received.

25. Granular potassium carbonate was purchased from J.T. Baker and was used as received.

26. The total volume added is approximately 60 mL.

27. Analytical data for 3-oxa-1-azaspiro[4.5]decan-2-one (**6**):  $R_f$  0.53 (30% ethyl acetate/dichloromethane); mp 81–82 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.20–1.72 (m, 10 H), 4.08 (s, 2H), 6.82 (br s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 22.7, 24.9, 37.2, 57.9, 75.8, 159.7; IR (film) 3230, 2932, 2858, 1745, 1397, 1251, 1031  $\text{cm}^{-1}$ ; HRMS (TOF<sup>+</sup>) calc. for  $\text{C}_8\text{H}_{13}\text{NO}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 178.0844; found: 178.0843; Analysis calc. for  $\text{C}_8\text{H}_{13}\text{NO}_2$ : C 61.91, H 8.44, N 9.03; found: C 61.99, H 8.61, N 8.94 %.

### Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with “Prudent Practices in the Laboratory”; National Academy Press; Washington, DC, 1995.

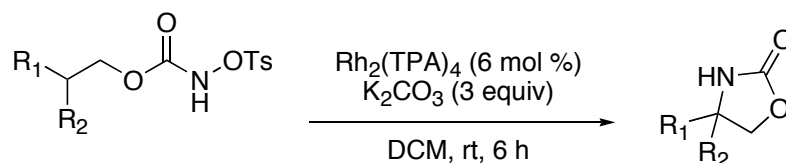
### 3. Discussion

This procedure describes an attractive method for the preparation of oxazolidinones using a rhodium-catalyzed nitrene C-H bond insertion reaction. It is well known that nitrene species are accessible by photolysis or thermolysis of acyl azides. However, their employment in the formation of oxazolidinones is limited to some specific cases,<sup>2</sup> because of their lack of



stability and selectivity.<sup>3</sup> Alternatively, metal nitrenes are prepared via the oxidation of carbamates using hypervalent iodine reagents which generate a stoichiometric amount of iodobenzene as byproduct.<sup>4</sup> In the described procedure, a tosyloxycarbamate is decomposed with a base to form a metal nitrene in the presence of a rhodium catalyst. The insertion reaction proceeds then smoothly, with total conversion. The only stoichiometric byproduct is potassium tosylate, which is simply removed by an aqueous work up. The starting material is a stable white solid easily prepared from the corresponding commercially available alcohol. The metal nitrene insertion is effective at ethereal, benzylic, tertiary, secondary, and even primary positions, providing an interesting route to various substituted oxazolidinones (Table 1).<sup>5</sup>

**Table 1. Oxazolidinone formation<sup>a,b</sup>**



Entry	Product	Isolated yield	Entry	Product	Isolated yield
1		92%	5		73%
2		84%	6		84%
3		87%	7		64%
4		71%	8		41%

<sup>a</sup> see reference 5; <sup>b</sup> 0.5 mmol scale

Chiral oxazolidinones can also be prepared by this method using an enantioenriched *N*-tosyloxycarbamate as starting material, as the C-H insertion occurs with total retention of configuration (Entry 5). The method

has been initially developed on a 0.5 mmol scale, using 6 mol% of rhodium dimer and 3 equivalents of potassium carbonate in dichloromethane at room temperature. Under the optimized reaction conditions on a 50 mmol scale, the catalyst loading is lowered to 1 mol% and 1.1 equivalent of base is used for complete conversion. The intermolecular version of the reaction has also been reported using 2,2,2-trichloroethyl *N*-tosyloxycarbamate as the source of nitrene and Troc-protected amines derived from various unfunctionalized substrates were isolated in good yields.<sup>6</sup>

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2. (a) Berndt, D. F.; Norris, P. *Tetrahedron Lett.* **2002**, *43*, 3961-3962; (b) Kan, C.; Long, C. M.; Paul, M.; Ring, C. M.; Tully, S. E. Rojas, C. M. *Org. Lett.* **2001**, *3*, 381-384; (c) Yuan, P.; Plourde, R.; Shoemaker, M. R.; Moore, C. L.; Hansen, D. E. *J. Org. Chem.* **1995**, *60*, 5360-5364; (d) Schneider, G.; Hackler, L.; Szanyl, J.; Sohar, P. *J. Chem. Soc. Perkin Trans. 1* **1991**, 37-42; (e) Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Gaur, S.; Hodgson, P. K. G. *Tetrahedron Asymm.* **1994**, *5*, 2447-2458.
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5. (a) Lebel, H.; Huard, K.; Lectard, S. *J. Am. Chem. Soc.* **2005**, *127*, 14198-14199; (b) Lebel, H.; Leogane, O.; Huard, K.; Lectard, S. *Pure Appl. Chem.* **2006**, *78*, 363-375.
6. Lebel, H.; Huard, K. *Org. Lett.* **2007**, *9*, 639-642.

## Appendix

### Chemical Abstracts Nomenclature; (Registry Number)

Rhodium II acetate: (15956-28-2)

Triphenylacetic acid: Benzeneacetic acid,  $\alpha,\alpha$ -diphenyl-; (595-91-5)

Rhodium (II) tetrakis(triphenylacetate);(142214-04-8)

Cyclohexylmethyl *N*-hydroxycarbamate: Carbamic acid, hydroxy-, cyclohexylmethyl ester; (869111-30-8)

1,1'-Carbonyldiimidazole: Methanone, di-1*H*-imidazol-1-yl-; (530-62-1)

Cyclohexanemethanol; (100-49-2)

Hydroxylamine hydrochloride; (5470-11-1)

Imidazole; (288-32-4)

*p*-Toluenesulfonyl chloride: Benzenesulfonyl chloride, 4-methyl-; (98-59-9)

Triethylamine; (121-44-8)

Cyclohexylmethyl *N*-tosyloxycarbamate: Benzenesulfonic acid, 4-methyl-, [(cyclohexylmethoxy)carbonyl]azanyl ester; (869111-41-1)

4-Spirocyclohexyloxazolidinone: 3-Oxa-1-azaspiro[4.5]decan-2-one: (81467-34-7)

Potassium carbonate; (584-08-7)



H  l  ne Lebel received her B.Sc. degree in biochemistry from the Universit   Laval in 1993. She conducted her Ph.D. studies in organic chemistry at the chemistry department of the Universit   de Montr  al under the supervision of professor Andr   B. Charette as a 1967 Science and Engineering NSERC Fellow. In 1998, she joined the research group of professor Eric Jacobsen at Harvard University as a NSERC Postdoctoral Fellow. She started her independent career in 1999 at the Universit   de Montr  al, where her research program focuses on the development of novel synthetic methods.



Kim Huard was born in Granby, Qu  bec, Canada in 1979. She received a B.Sc. degree in chemistry in 2004 from Universit   de Montr  al. She then received her Ph.D. in H  l  ne Lebel's research group at Universit   de Montr  al where she studied rhodium-catalyzed C-H bonds amination. She has been recipient of NSERC Postgraduate Scholarships. She is currently a postdoctoral fellow at University of California at Irvine under the guidance of Professor Larry Overman.



Adam Rosenberg obtained his B.S. in chemistry from the University of Rochester while performing undergraduate research in Dr. Boeckman's research group. He is currently pursuing graduate studies in the laboratory of Professor Kay Brummond at the University of Pittsburgh. His graduate work has included investigations into the total synthesis of 3 $\alpha$ -hydroxy-15-rippertene as well as novel multi-component cycloaddition reactions.

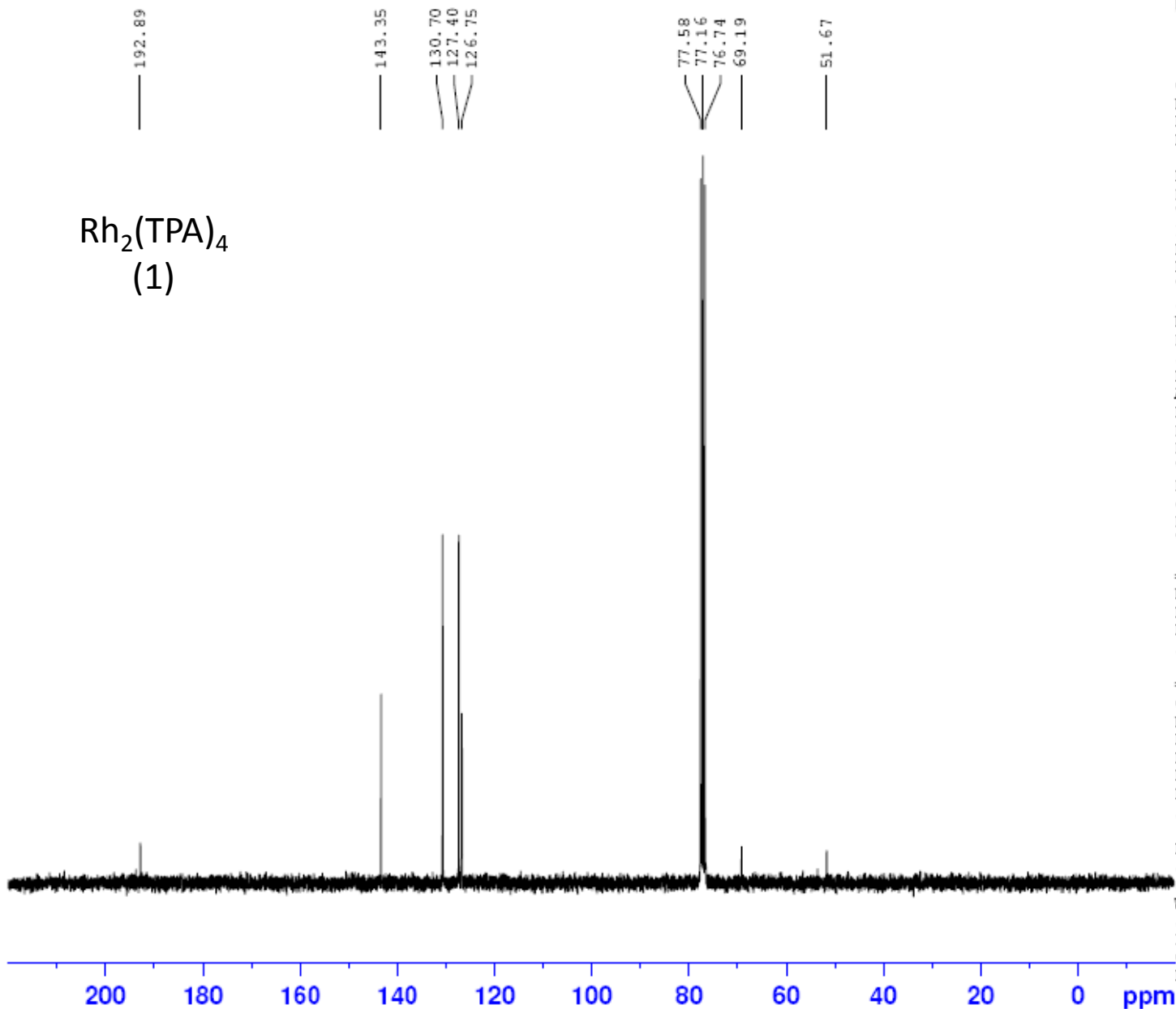


Darla Seifried is a graduate of the University of Pittsburgh with a Bachelor of Science in biology. She is currently earning her B.S. in chemistry from the University of Pittsburgh. Darla plans to attend graduate school beginning in the fall of 2009.

AJR-Rh2 (TPA) 4  
NMR 301a



$\text{Rh}_2(\text{TPA})_4$   
(1)



Current Data Parameters

NAME AJR-Rh2 (TPA) 4  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters

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DE 6.00 usec  
TE 300.0 K  
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d11 0.03000000 sec  
DELTA 11.89999962 sec  
TD0 1

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PL1 1.80 dB  
SFO1 75.5381641 MHz

==== CHANNEL f2 =====

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PL2 0.00 dB  
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F2 - Processing parameters

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Oxycarbamate

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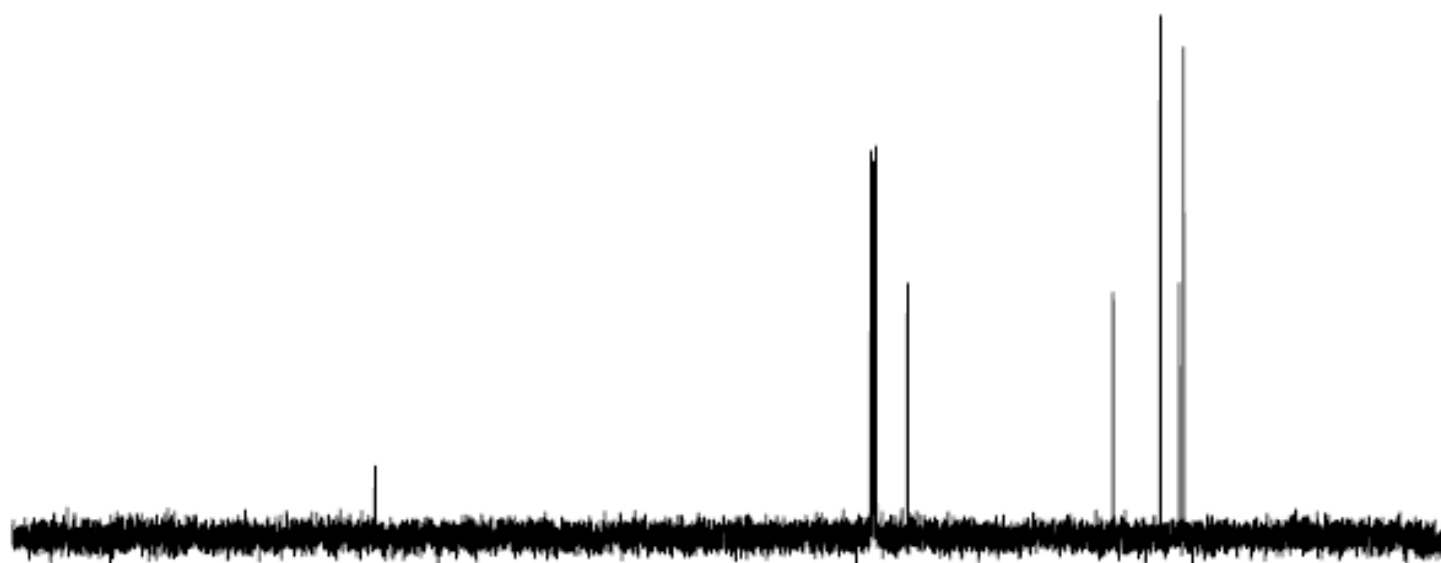
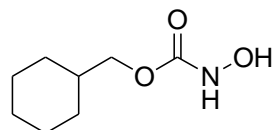
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PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20080521  
Time 15.48  
INSTRUM spect  
PROBHD 5 mm DUL 1H-13  
PULPROG zgpg  
TD 65536  
SOLVENT CDC13  
NS 17  
DS 4  
SWH 19115.941 Hz  
FIDRES 0.276427 Hz  
AQ 1.8089436 sec  
RG 5792.6  
DW 27.600 usec  
DE 6.00 usec  
TE 300.0 K  
D1 9.00000000 sec  
d11 0.03000000 sec  
DELTA 7.90000010 sec  
TD0 1

==== CHANNEL f1 =====  
NUC1 13C  
P1 9.00 usec  
PL1 1.90 dB  
SFO1 75.5381641 MHz

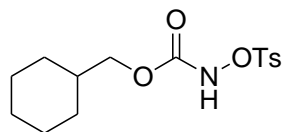
==== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 92.00 usec  
PL2 0.00 dB  
PL12 20.00 dB  
PL13 20.00 dB  
SFO2 300.3912015 MHz

F2 - Processing parameters  
SI 65536  
SF 75.5306001 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



200 180 160 140 120 100 80 60 40 20 0 ppm

AJR-4-29  
 NMR 500  
 Tosyloxycarbamate



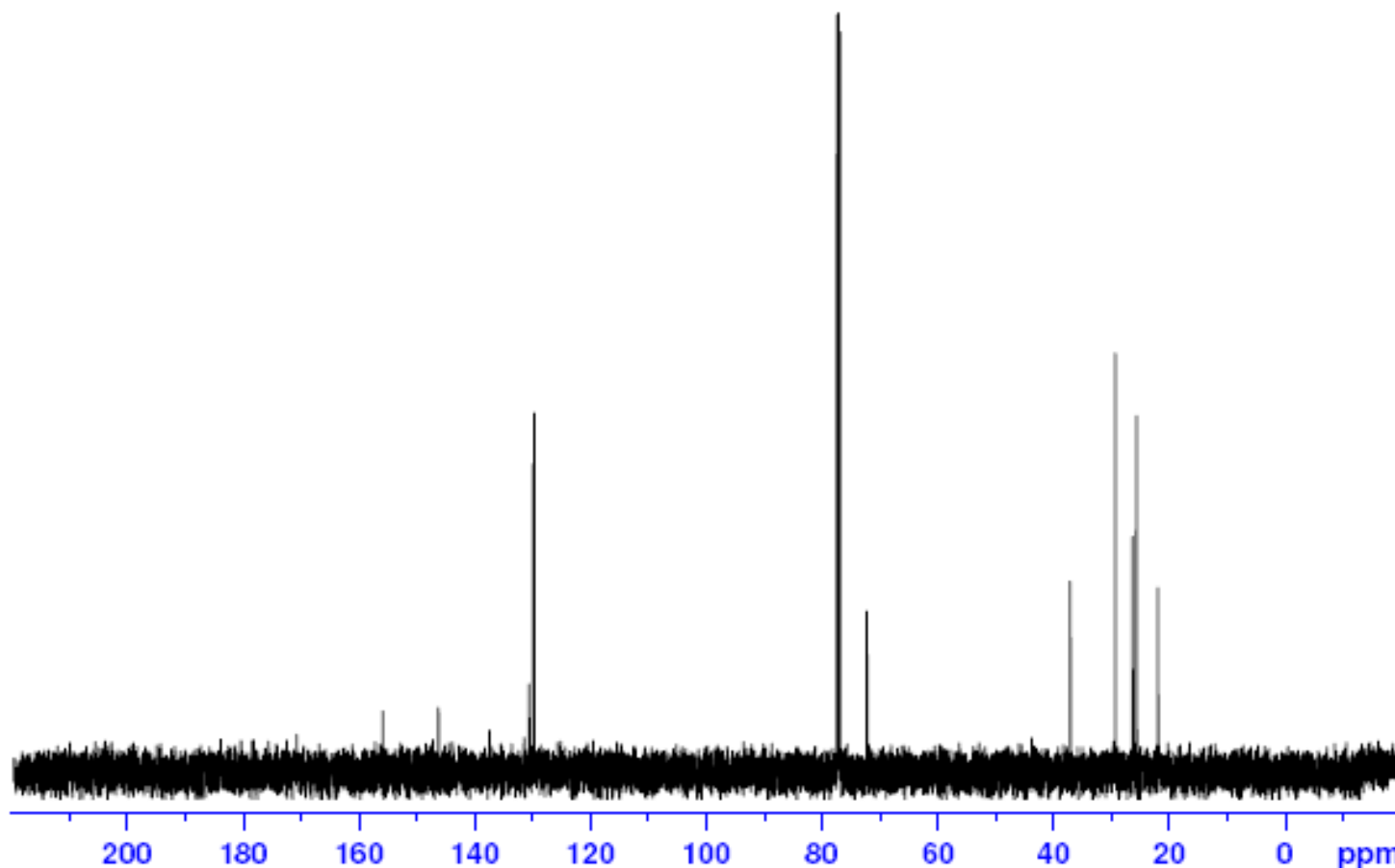
Current Data Parameters  
 NAME AJR-4-29  
 EXPNO 4  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20080512  
 Time 16.21  
 INSTRUM spect  
 PROBHD 5 mm Multinucl  
 PULPROG zgpg  
 TD 65536  
 SOLVENT CDCl3  
 NS 31  
 DS 4  
 SWH 30030.029 Hz  
 FIDRES 0.458222 Hz  
 AQ 1.0912244 sec  
 RG 32768  
 DW 16.650 usec  
 DE 6.00 usec  
 TE 298.2 K  
 D1 10.0000000 sec  
 d11 0.0300000 sec  
 DELTA 9.89999962 sec  
 TD0 1

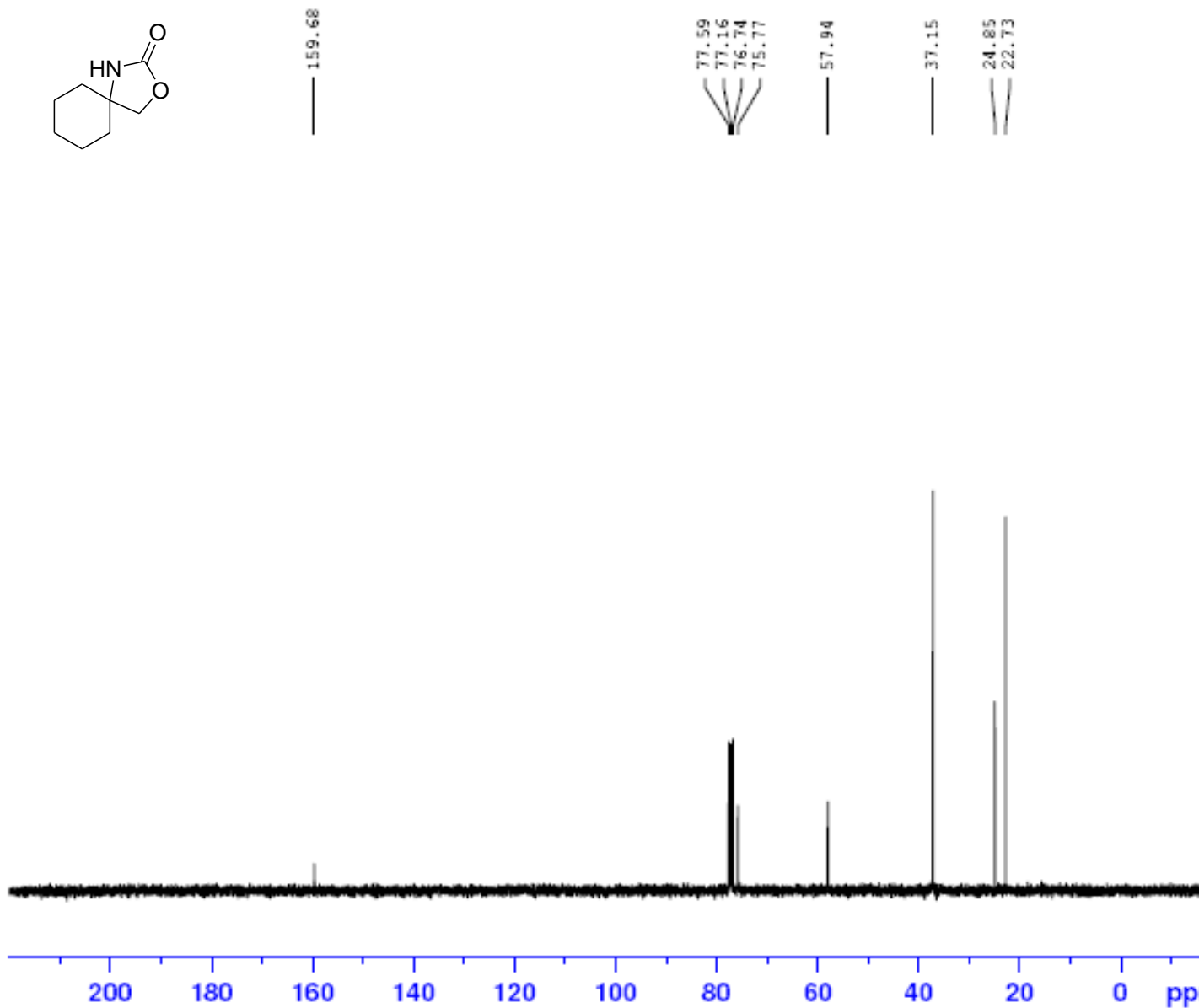
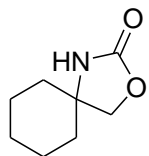
==== CHANNEL f1 =====  
 NUC1 13C  
 P1 9.00 usec  
 PL1 -2.00 dB  
 SFO1 125.7703643 MHz

==== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 100.00 usec  
 PL2 0.00 dB  
 PL12 20.63 dB  
 PL13 20.63 dB  
 SFO2 500.1320005 MHz

F2 - Processing parameters  
 SI 32768  
 SF 125.7577736 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



AJR-4-36  
NMR 300  
OrgSyn Final



Current Data Parameters  
NAME AJR-4-36  
EXPNO 2  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20080626  
Time 19.47  
INSTRUM spect  
PROBHD 5 mm DUL 1H-13  
PULPROG zgpg  
TD 65536  
SOLVENT CDCl3  
NS 21  
DS 4  
SWH 18115.941 Hz  
FIDRES 0.276427 Hz  
AQ 1.8088436 sec  
RG 8192  
DW 27.600 usec  
DE 6.00 usec  
TE 300.0 K  
D1 8.00000000 sec  
d11 0.03000000 sec  
DELTA 7.90000010 sec  
TD0 1

==== CHANNEL f1 =====  
NUC1 13C  
P1 9.00 usec  
PL1 1.80 dB  
SFO1 75.5381641 MHz

==== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 92.00 usec  
PL2 0.00 dB  
PL12 20.00 dB  
PL13 20.00 dB  
SFO2 300.3812015 MHz

F2 - Processing parameters  
SI 65536  
SF 75.5306024 MHz  
NDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



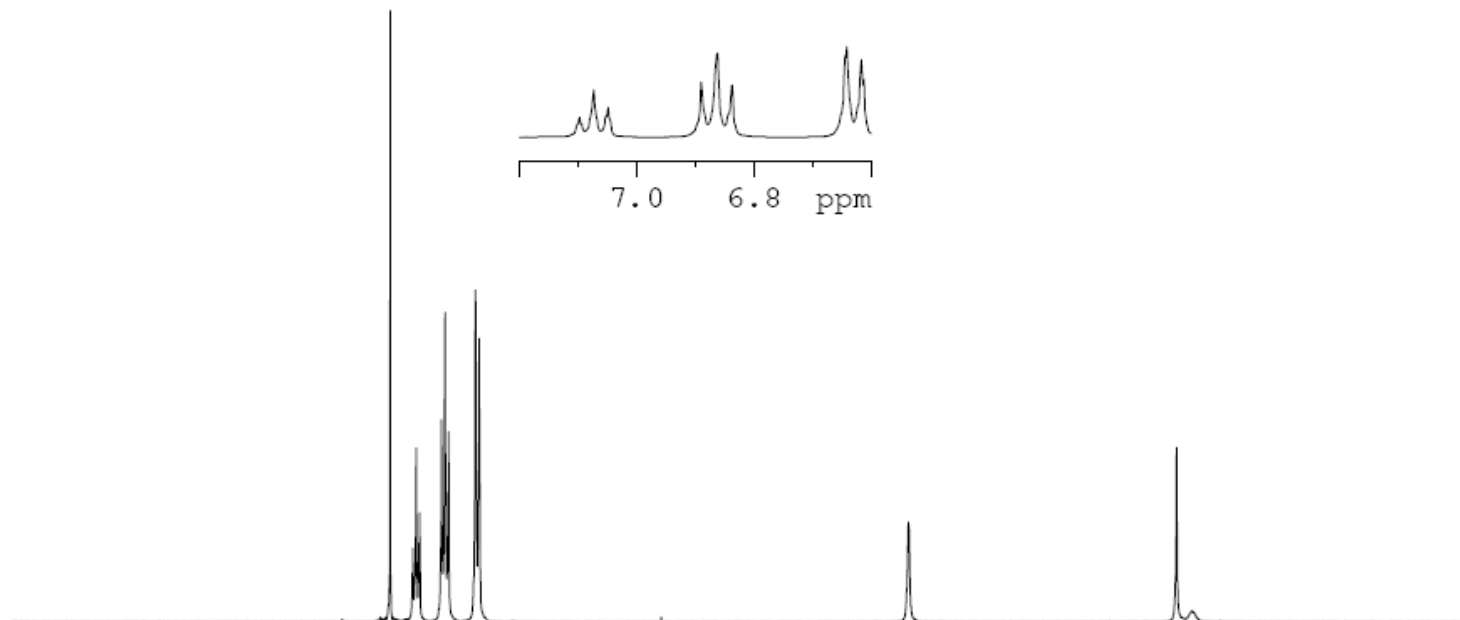
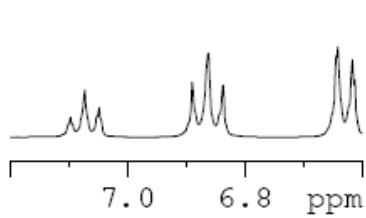
Rh2(TPA)4

7.261  
7.098  
7.073  
7.052  
7.049  
6.890  
6.863  
6.838  
6.645  
6.643  
6.618  
6.614

3.510

1.574

7.073  
7.052  
7.049  
6.890  
6.863  
6.838  
6.645  
6.643  
6.618  
6.614



Current Data Parameters  
NAME AJR-Rh2(TPA)4  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20080417  
Time 13.14  
INSTRUM spect  
PROBHD 5 mm Dual 13C/  
PULPROG zg  
TD 32768  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 6172.839 Hz  
FIDRES 0.188380 Hz  
AQ 2.6542580 sec  
RG 512  
DW 81.000 usec  
DE 6.00 usec  
TE 300.0 K  
D1 4.00000000 sec  
TD0 1

==== CHANNEL f1 =====  
NUC1 1H  
P1 5.00 usec  
PL1 4.00 dB  
SFO1 300.1318530 MHz

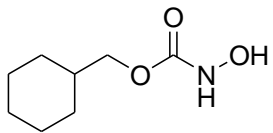
F2 - Processing parameters  
SI 16384  
SF 300.1300062 MHz  
WDW EM  
SSB 0  
LB 0.10 Hz  
GB 0  
PC 1.00

12.00  
23.95  
23.91

6.13

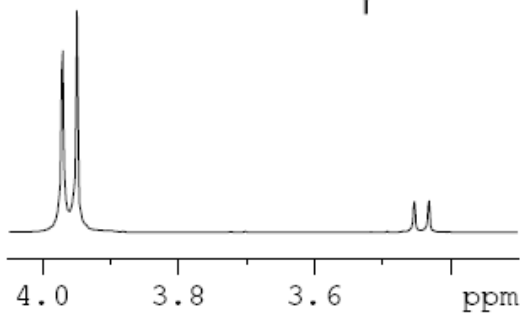
6.36



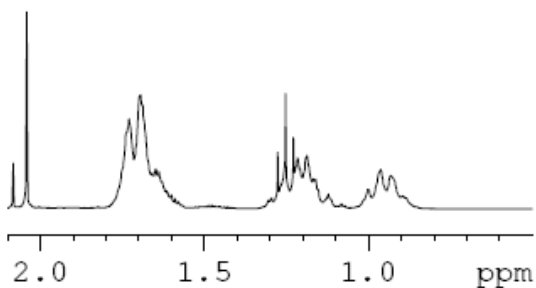


Crude

7.274  
7.261



4.153  
4.129  
4.105  
4.081  
3.971  
3.949  
3.453  
3.432  
2.084  
2.042  
1.730  
1.696  
1.690  
1.277  
1.253  
1.229  
1.216  
1.188  
1.001  
0.963  
0.932



Current Data Parameters  
 NAME AJR-4-22  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20080503  
 Time 13.30  
 INSTRUM spect  
 PROBHD 5 mm Dual 13C/  
 PULPROG zg  
 TD 32768  
 SOLVENT CDC13  
 NS 16  
 DS 2  
 SWH 6172.839 Hz  
 FIDRES 0.188380 Hz  
 AQ 2.6542580 sec  
 RG 90.5  
 DW 81.000 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 4.00000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 5.00 usec  
 PL1 4.00 dB  
 SFO1 300.1318530 MHz

F2 - Processing parameters  
 SI 16384  
 SF 300.1300062 MHz  
 WDW EM  
 SSB 0  
 LB 0.10 Hz  
 GB 0  
 PC 1.00

0.81

0.39

2.00

0.27

0.14

0.60

6.93

4.12

2.39

AJR-4-22  
 NMR 300  
 OxyCarbamate

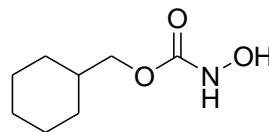
7.278  
 7.261  
 7.251  
 7.027

3.991  
 3.974  
 3.970  
 3.953

1.744  
 1.732  
 1.703  
 1.659  
 1.228  
 1.218  
 1.207  
 1.193  
 0.980  
 0.939



Current Data Parameters  
 NAME AJR-4-22  
 EXPNO 2  
 PROCNO 1

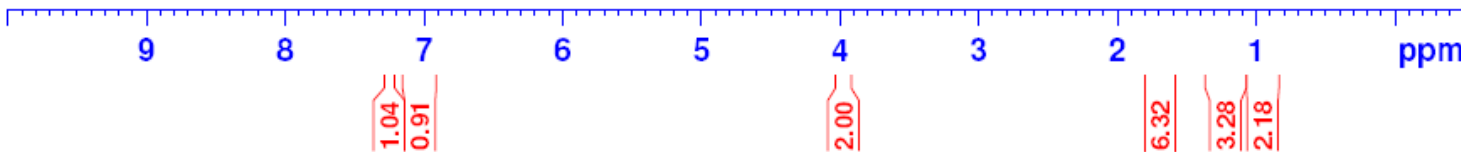
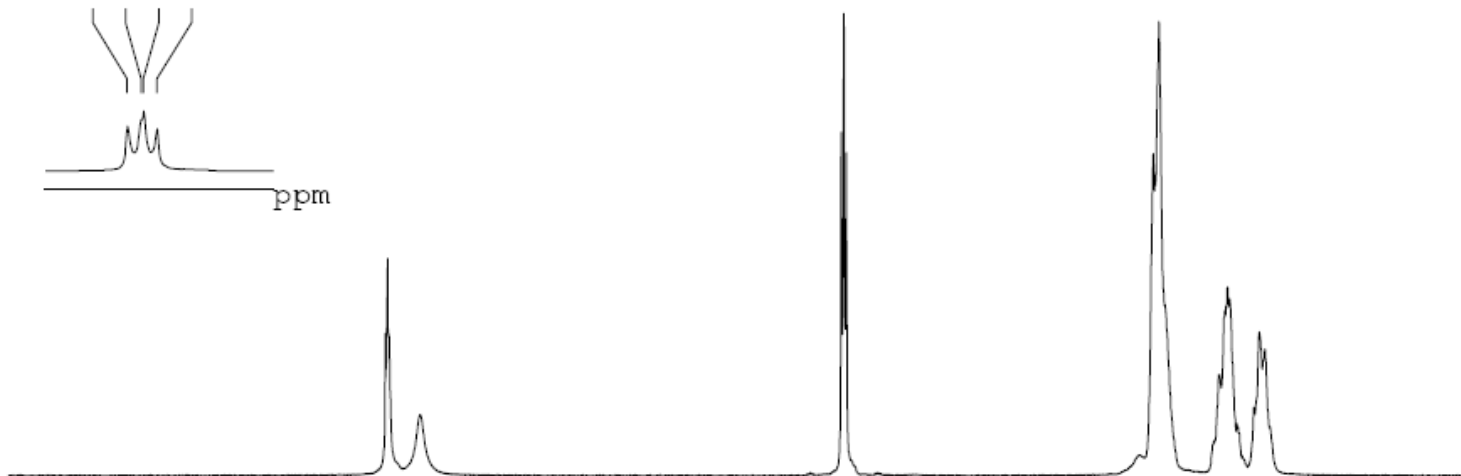
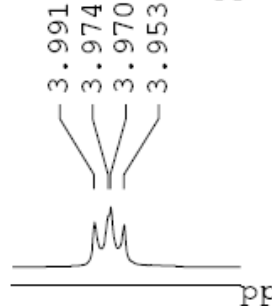
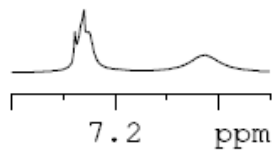
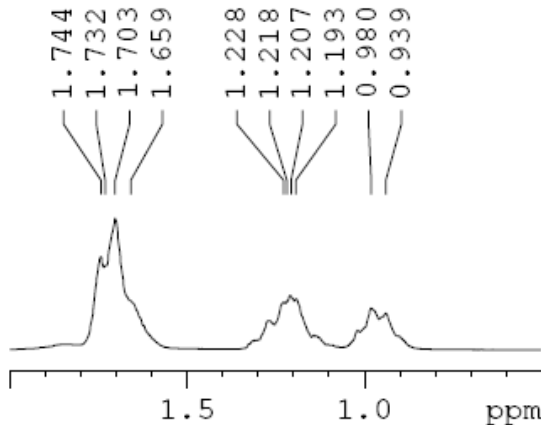
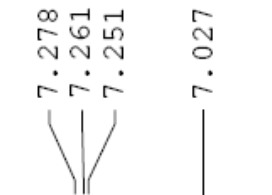


F2 - Acquisition Parameters

Date\_ 20080521  
 Time 11.32  
 INSTRUM spect  
 PROBHD 5 mm Dual 13C/  
 PULPROG zg  
 TD 32768  
 SOLVENT CDCl3  
 NS 9  
 DS 2  
 SWH 6172.839 Hz  
 FIDRES 0.188380 Hz  
 AQ 2.6542580 sec  
 RG 143.7  
 DW 81.000 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 4.00000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 5.00 usec  
 PL1 4.00 dB  
 SFO1 300.1318530 MHz

F2 - Processing parameters  
 SI 16384  
 SF 300.1300059 MHz  
 WDW EM  
 SSB 0  
 LB 0.10 Hz  
 GB 0  
 PC 1.00

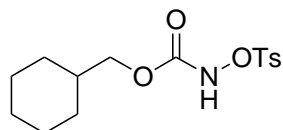


1.04  
 0.91

2.00

6.32  
 3.28  
 2.18

AJR-4-29  
 NMR 500  
 Tosyloxycarbamate



7.884  
 7.868  
 7.858  
 7.365  
 7.349  
 7.261

3.838  
 3.825

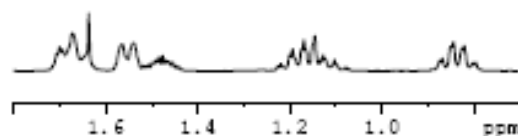
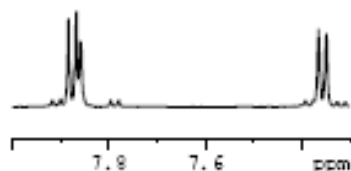
2.459  
 1.672  
 1.637  
 1.569  
 1.565  
 1.539  
 1.477  
 1.470  
 1.464  
 1.170  
 1.146  
 0.850  
 0.844  
 0.826  
 0.821

Current Data Parameters  
 NAME AJR-4-29  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20080512  
 Time 16.12  
 INSTRUM spect  
 PROBHD 5 mm Multinucl  
 PULPROG zg  
 TD 65536  
 SOLVENT CDCl3  
 NS 9  
 DS 2  
 SWH 10330.578 Hz  
 FIDRES 0.157632 Hz  
 AQ 3.1719923 sec  
 RG 32  
 DW 48.400 usec  
 DE 6.00 usec  
 TE 298.2 K  
 D1 8.00000000 sec  
 TDO 1

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 9.00 usec  
 PL1 0.00 dB  
 SFO1 500.1330885 MHz

F2 - Processing parameters  
 SI 32768  
 SF 500.1300135 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



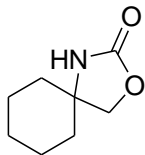
0.91  
 1.90  
 1.98

1.98

3.00

3.50  
 3.26  
 3.24  
 2.17

AJR-4-36  
NMR 300  
OrgSyn

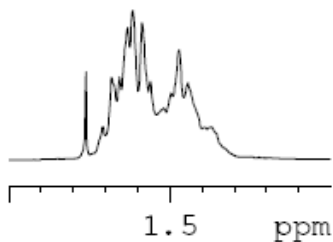


— 7.261

— 6.817

— 4.081

1.714  
1.682  
1.657  
1.632  
1.616  
1.587  
1.561  
1.472  
1.445



1.714  
1.682  
1.657  
1.632  
1.616  
1.587  
1.561  
1.472  
1.445  
1.356



Current Data Parameters  
NAME AJR-4-36  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20080522  
Time 10.39  
INSTRUM spect  
PROBHD 5 mm Dual 13C/  
PULPROG zg  
TD 32768  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 6172.839 Hz  
FIDRES 0.188380 Hz  
AQ 2.6542580 sec  
RG 90.5  
DW 81.000 usec  
DE 6.00 usec  
TE 300.0 K  
D1 4.00000000 sec  
TD0 1

==== CHANNEL f1 =====  
NUC1 1H  
P1 5.00 usec  
PL1 4.00 dB  
SFO1 300.1318530 MHz

F2 - Processing parameters  
SI 16384  
SF 300.1300062 MHz  
WDW EM  
SSB 0  
LB 0.10 Hz  
GB 0  
PC 1.00

9 8 7 6 5 4 3 2 1 ppm

0.98

2.00

10.68