Electronic Supplementary Information

for

Rhodium-Catalyzed Enantioselective Desymmetrization of Bicyclic Hydrazines with Alkynylboronic Esters

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General Methods and Materials.

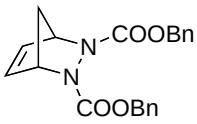
All reaction were carried out under argon atmosphere in a 25 mL Schlenk tube of an RR98072 6 place Carousel Reaction Station™ from Radleys Discovery Technologies, equipped with gas-tight threaded caps with a valve, cooling reflux head system and digital temperature controller.

MeOH (HPLC grade) were purchased from J. T. Baker and used as such. $[Rh(C_2H_4)_2Cl]_2$, $[Rh(cod)Cl]_2$, $[Rh(C_2H_4)_2acac]_2$ were purchased from Stream Chemical Co. and used without further purification. $[Rh(cod)OH]_2$ was prepared from $[Rh(cod)Cl]_2$ by a literature procedure.[1] Monophos was prepared following a previously dercribed procedure.[2] All phosphine ligands used are commercially available from Strem and were used without further purification. Analytical TLC were performed on Alugram SIL G/UV254 silica gel sheets (Macherey- Nagel) with detection by 0.5% Phosphomolybdic acid solution in 95% EtOH. Silica gel 60 (Macherey- Nagel 230- 400 mesh) was used for flash chromatography. Solvents for extraction and chromatography were HPLC grade.

^{1}H NMR spectra were recorded on Bruker Avance II 250 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: **δ 7.26**, deuteromethanol: **δ 3.31**). ^{13}C NMR spectra were recorded on a Bruker Avance II 250 spectrometer (62.5 MHz) with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: **δ 77.0**, deuteromethanol: **δ 49.0**). Analytical high performance liquid chromatography (HPLC) were performed on a Waters 600E equipped with Varian Prostar 325 detector using Daicel Chiralcel OD-H column with 0.5 mL and Daicel chiralpak AD-H column with detection at 220 nm. Mass spectra ESI-MS were measured on a Finnigan LC-Q Deca Termoquest spectrometer, equipped with a software Xcalibur.

Synthesis of bicyclic hydrazines 1a-b.

Cyclic hydrazines **1a-b** were prepared following a previously described procedure.[3]

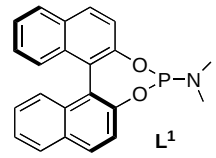


Dibenzyl 2,3-diaza-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (1c) was prepared in accordance with a previously described procedure.[4]

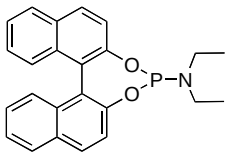
Synthesis of 1-alkynyldiisopropylboronates 2a-e.[5]

To a solution of an alkyne (10 mmol) in anhydrous diethyl ether (20.0 mL) was added BuLi (1.56 M in hexane, 6.4 mL, 10.0 mmol) at –78°C and the reaction mixture was stirred for three hours at –78°C. The resulting mixture was added *via cannula* to a solution of triisopropylborate (1.88 g, 10 mmol) in anhydrous diethyl ether at –78°C and slowly warmed to room temperature over 3 hours. The solvent was removed *in vacuo* and diethyl ether (10 mL) and a solution of hydrogen chloride in diethyl ether (1.5 M, 6.6 mL, 10 mmol) were added to the resulting powder at –78°C. The mixture was slowly warmed at room temperature over three hours. Filtration of the resulting suspension followed by distillation gave alkynylboronates **2a-e**.

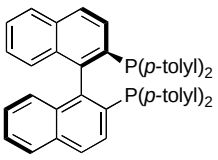
Figure 1. Description of Chiral Ligands Used in the Screening



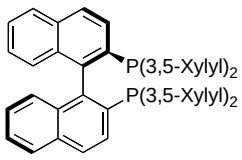
(S)-(-)-MONOPHOS



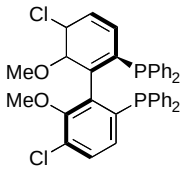
(rac)-Ethyl-MONOPHOS



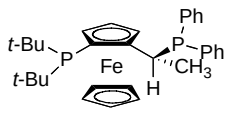
(R)-Tol-BINAP



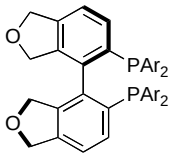
(R)-Xylyl-BINAP



(*R*)-Cl-MeO-BIPHEP

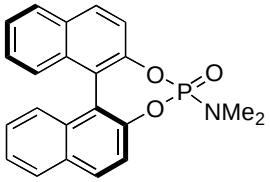


(R,S$_p$)-tert-Butyl-JOSIPHOS



(R)-DTBM-SEGPHOS

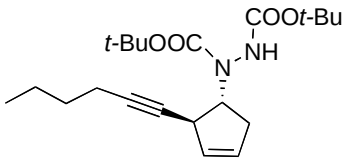
Ar=3,5-di-*t*-Bu-4-methoxyphenyl



Monophos oxide L[2] was prepared following a previously described procedure.[6]

Rhodium-Catalyzed Desymmetrization of Compounds 1a-c with Alkynylboronic Esters-RACEMIC VERSION (Scheme 1).

General procedure as follows: A dried schlenk tube was charged, under argon protection, with $[Rh(cod)Cl]_2$ (2.95 mg, 0.006 mmol) and racemic **L[1]** (8.64 mg, 0.024 mmol) in HPLC grade MeOH (1.0 mL) was added and the mixture was stirred for 30 min at room temperature. Cyclic hydrazine **1a- c** (0.2 mmol) in MeOH (1.0 mL), alkynylboronic ester (0.4 mmol) and a base (0.4 mmol) were then introduced and the reaction mixture was warmed at 65°C. The reaction was followed by TLC and was quenched with $NaHCO_3$ (2.0 mL). The solution was diluted with CH_2Cl_2 (20 mL). The acqueous phase was separated and extracted further with CH_2Cl_2 (10 mL) and Et_2O (10 mL). Combined organic fractions were dried over magnesium sulfate and filtered. Evaporation of the organic solution afforded a crude reaction mixture that was purified by silica gel column chromatography to give the pure compounds of type **3**.



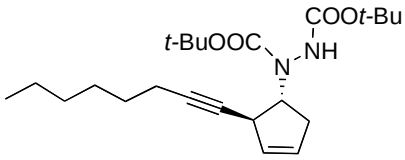
Di-*tert*-butyl 1-((1*R,2*S**)-2-(hex-1-ynyl)cyclopent-3-enyl) hydrazine-1,2-dicarboxylate (3aa)** (Scheme 1).

Using the general procedure described above, $[Rh(cod)Cl]_2$ (2.95 mg, 0.006 mmol) and rac-**L[1]** (8.64 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1a** (59.2 mg, 0.2 mmol) in MeOH (1.0 mL), 1-hexynyldiisopropylboronate **2a** (84 mg, 0.4 mmol) and $NaHCO_3$ (33.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 16 hours at 65°C (conversion= 85%). The product was isolated (Yield= 78%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J*= 7.0 Hz); 1.25- 1.54 (m, 4H); 1.44 (s, 9H); 1.45 (s, 9H); 2.08- 2.15 (m, 2H); 3.42- 3.58 (m, 1H); 4.72- 4.84 (m, 1H); 5.50- 5.57 (m, 1H); 5.59- 5.67 (m, 1H); 5.89 and 6.18 *NH* (coalescing br, s, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.6, 18.5, 21.9, 28.1, 28.2, 31.0, 34.8, 39.2, 65.9, 77.3, 78.7, 81.4, 89.4, 129.4, 130.6, 154.6, 155.8.

Anal. Calcd. For $C_{21}H_{34}N_2O_4$: C, 66.64%; H, 9.05%; N, 7.40. Found: C, 66.68%; H, 9.03%, N, 7.38%.



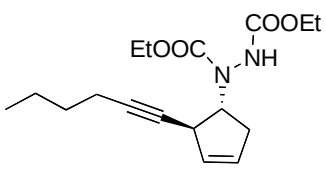
Di-*tert*-butyl 1-((1*R, 2*S**)-2-(oct-1-ynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3ab)** (Scheme 1).

Using the general procedure described above, $[Rh(cod)Cl]_2$ (2.95 mg, 0.006 mmol) and rac-**L**[1] (8.64 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1a** (59.2 mg, 0.2 mmol) in MeOH (1.0 mL), 1-octynyldiisopropylboronate **2b** (95.2 mg, 0.4 mmol) and $NaHCO_3$ (33.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (complete conversion). The product was isolated (Yield= 95%) by column chromatography eluting with hexanes/AcOEt 9:1, as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 0.77-0.89 (m, 3H); 1.16-1.29 (m, 8H); 1.32-1.52 (m, 18H); 2.02-2.16 (m, 2H); 2.39-2.65 (m, 2H); 3.41-3.63 (br,s, 1H); 4.70-4.89 (m, 1H); 5.50-5.59 (m, 1H); 5.60-5.70 (m, 1H); 6.03 and 6.31 *NH* (coalescing br, s, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.0, 18.8, 22.5, 28.1, 28.5, 28.9, 31.3, 34.6, 39.2, 65.7, 77.2, 78.7, 81.3, 89.4, 129.3, 130.6, 154.6, 155.8.

Anal. Calcd. For $C_{23}H_{38}N_2O_4$: C, 67.94%; H, 9.42%; N, 6.89. Found: C, 68.00%; H, 9.44%, N, 6.83%.



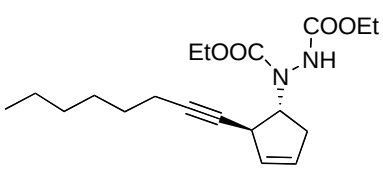
Diethyl 1-((1*R,2*S**)-2-(hex-1-ynyl)cyclopent-3-enyl) hydrazine -1,2-dicarboxylate (3ba)** (Scheme 1).

Using the general procedure described above, $[Rh(cod)Cl]_2$ (2.95 mg, 0.006 mmol) and rac-**L**[1] (8.64 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1b** (48 mg, 0.2 mmol) in MeOH (1.0 mL), 1-hexynyldiisopropylboronate **2a** (84 mg, 0.4 mmol) and $NaHCO_3$ (33.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 4 hours at 65°C (complete conversion). The product was isolated (Yield= 92%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 0.78-0.91 (m, 3H); 1.12-1.28 (m, 6H); 1.34-1.48 (m, 4H); 2.05-2.15 (m, 2H); 2.32-2.56 (m, 2H); 3.48-3.60 (br,s, 1H); 4.09-4.22 (m, 4H); 4.78-4.89 (m, 1H); 5.51-5.60 (m, 1H); 5.62-5.70 (m, 1H); 6.31-6.50 (br, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.5, 14.3, 14.4, 18.4, 21.8, 30.9, 34.6, 39.1, 62.2, 62.6, 65.8, 80.1, 129.1, 130.6 156.90, 158.16.

Anal. Calcd. For $C_{17}H_{26}N_2O_4$: C, 63.33%; H, 8.13%; N, 8.69. Found: C, 63.48%; H, 8.07%, N, 8.57%.



Diethyl 1-((1*R,2*S**)-2-(oct-1-ynyl)cyclopent-3-enyl) hydrazine-1,2-dicarboxylate (3bb)** (Scheme 1).

Using the general procedure described above, $[Rh(cod)Cl]_2$ (2.95 mg, 0.006 mmol) and rac-**L**[1] (8.64 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1b** (59.2 mg,

0.2 mmol) in MeOH (1.0 mL), 1-octynyldiisopropylboronate **2b** (95.2 mg, 0.4 mmol) and $NaHCO_3$ (33.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (complete conversion). The product was isolated (Yield= 84%) by column chromatography eluting with hexanes/AcOEt 9:1, as an oil.

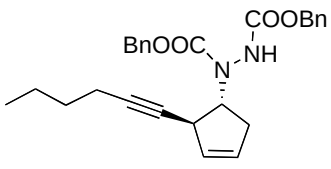
^{1}H NMR (250 MHz, $CDCl_3$) δ 0.78- 0.91 (m, 3H); 1.12- 1.40 (m, 6H); 2.08- 2-17 (m, 2H); 2.38- 2.70 (m, 2H); 3.53 (br, s, 1H); 4.09- 4.26 (m, 4H); 4.78- 4.91 (m, 1H); 5.49- 5.59 (m, 1H); 5.61- 5.70 (m, 1H); 6.20 and 6.39 *NH* (coalescing br, s, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.0, 14.3, 14.4, 18.8, 22.5, 28.5, 28.9, 29.7, 31.3, 34.7, 39.1, 62.2, 62.5, 65.9, 80.1, 81.8, 129.1, 130.6, 153.8, 156.8.

Anal. Calcd. For $C_{19}H_{30}N_2O_4$: C, 65.12%; H, 8.63%; N, 7.99. Found: C, 65.15%; H, 8.67%, N, 7.90%.

Rhodium-Catalyzed Desymmetrization of Compounds 1a-c with Alkynylboronic Esters. ASYMMETRIC VERSION (Scheme Table 2).

General procedure as follows: A dried schlenk tube was charged, under argon protection, with $[Rh(C_2H_4)Cl]_2$ (3.0-6.0 mol %) and chiral ligand (12 mol%). MeOH (1.0 mL) was added and the mixture was stirred for 30 min at room temperature. Cyclic hydrazine **1a-c** (0.2 mmol) in MeOH (1.0 mL), alkynylboronic ester (0.4 mmol) and a base (0.4 mmol) were then introduced and the reaction mixture was warmed at 65°C. The reaction was followed by TLC and was quenched with $NaHCO_3$ (2.0 mL). The solution was diluted with CH_2Cl_2 (20 mL). The acqueous phase was separated and extracted further with CH_2Cl_2 (10 mL) and Et_2O (10 mL). Combined organic fractions were dried over magnesium sulfate and filtered. Evaporation of the organic solution afforded a crude reaction mixture that was purified by silica gel column chromatography to give the pure compounds of type **3**.



(-)-Dibenzyl-1-((*1R,2S*)-2-(hex-1-ynyl)cyclopent-3-enyl) hydrazine-1,2-dicarboxylate (3ca) (Entry 1, Table 2).

Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Tol-BINAP (16.3 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1c** (72.8 mg, 0.2 mmol) in MeOH (1.0 mL), 1-hexynyldiisopropylboronate **2a** (84 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 81%). The product was isolated (Yield= 54%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

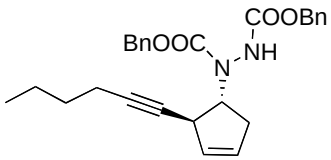
^{1}H NMR (250 MHz, $CDCl_3$) δ 0.78- 0.98 (m, 3H); 1.15- 1.50 (m, 4H); 2.02- 2.13 (m, 2H); 2.38- 2.71 (m, 2H); 3.49- 3.61 (m, 1H); 4.80- 4.92 (m, 1H); 5.01- 5.22 (m, 4H); 5.50- 5.69- (m, 2H); 6.49 *NH* (br, s, 1H); 7.12- 7.45 (m, 10H).

$[\alpha]^{20}_D$= -31.5 (*c* 1.5, $CHCl_3$).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.6, 18.4, 21.9, 30.9, 34.7, 39.1, 66.1, 67.9 (2C); 77.2, 127.8, 128.1, 128.5, 129.1, 130.6, 135.8, , 155.2, 157.2.

Anal. Calcd. For $C_{27}H_{30}N_2O_4$: C, 72.62%; H, 6.77%; N, 6.27. Found: C, 72.70%; H, 6.67%, N, 6.20%.

HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 93/7, retention times (min): 29.6 (minor, stereoisomer), 44.1 (major, stereoisomer).

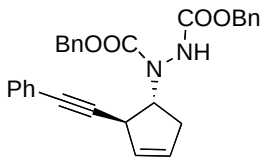


(-)-Dibenzyl-1-((*1R,2S*)-2-(hex-1-ynyl)cyclopent-3-enyl) hydrazine-1,2-dicarboxylate (3ca) (Entry 2, Table 2).

Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Xylyl-BINAP (17.6 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1c** (72.8 mg, 0.2 mmol) in MeOH (1.0 mL), 1-hexynyldiisopropylboronate **2a** (84 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 66%). The product was isolated (Yield= 43%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

For ^{1}H NMR, ^{13}C NMR and HPLC data see description for entry 1, Table 2

$[\alpha]^{20}_D$= -41.1 (*c* 1.3, $CHCl_3$).



(-)-Dibenzyl 1-((*1R,2S*)-2-(phenylethynyl)cyclopent-3-enyl) hydrazine-1,2-dicarboxylate (3cc) (Entry 4, Table 2).

Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Xylyl-BINAP (17.6 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1c** (72.8 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl phenylethynylboronate **2c** (92 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 85%). The product was isolated (Yield= 67%) by column chromatography eluting with hexanes/AcOEt 8:2, as a semisolid.

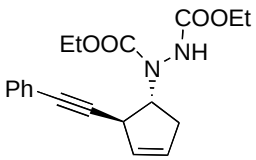
$[\alpha]^{20}_D$= -141.3 (*c* 1.5, $CHCl_3$).

^{1}H NMR (250 MHz, $CDCl_3$) δ 2.41- 2.79 (m, 2H); 3.77- 3.89 (br, s, 1H); 4.95- 5.23 (m, 5H); 5.59- 5.72 (m, 2H); 6.49 and 6.69 *NH* (coalescing br, s, 1H); 7.05- 7.40 (m, 15H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 34.9, 39.9, 65.8, 68.0, 68.4, 77.2, 127.8, 127.9, 128.1, 128.4, 128.5, 128.6, 129.8, 131.6, 131.7, 155.2, 157.2.

Anal. Calcd. For $C_{29}H_{26}N_2O_4$: C, 74.66%; H, 5.62%; N, 6.00. Found: C, 74.62%; H, 5.65%, N, 5.93%.

HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 52.2 (minor, stereoisomer), 63.7 (major, stereoisomer).



Diethyl 1-((*1R,2S*)-2-(phenylethynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3bc) (Entry 5, Table 2).

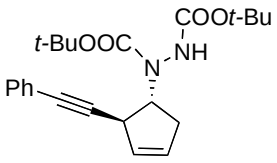
Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Tol-BINAP (16.3 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1b** (48.1 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl phenylethynylboronate **2c** (92 mg, 0.4 mmol) and CsF (60.8 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 75%). The product was isolated (Yield= 58%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 1.10- 1.31 (m, 6H); 2.39- 2.71 (m, 2H); 3.82 (br, s, 1H); 4.07- 4.30 (m, 4H); 4.90- 5.09 (m, 1H); 5.60- 5.69 (m, 1H); 5.70- 5.78 (m, 1H); 6.26- 6.58 *NH* (m, 1H); 7.20- 7.42 (m, 5H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.1, 14.4, 34.7, 39.8, 62.3, 62.7, 65.6, 77.2, 127.8, 128.1, 128.4, 128.6, 129.8, 131.6, 155.5, 156.1.

Anal. Calcd. For $C_{19}H_{22}N_2O_4$: C, 66.65%; H, 6.48%; N, 8.18. Found: C, 66.71%; H, 6.43%, N, 8.10%.

HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 92/8, retention times (min): 20.0 (minor, stereoisomer), 26.7 (major, stereoisomer).



(-)-Di-*tert*-butyl 1-((*1R,2S*)-2-(phenylethynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3ac) (Entry 6, Table 2).

Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Xylyl-BINAP (17.6 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1a** (59.2 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl phenylethynylboronate **2c** (92 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at

65°C (conversion= 83%). The product was isolated (Yield= 48%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

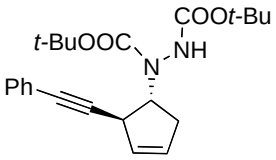
$[\alpha]^{20}_{D}$= -102.8 (*c* 1.0, $CHCl_3$).

^{1}H NMR (250 MHz, $CDCl_3$) δ 1.44 (s, 9H); 1.53 (s, 9H); 2.48- 2.72 (m, 2H); 3.83 (br, s, 1H); 5.62- 5.69 (m, 1H); 5.71- 5.78 (m, 1H); 5.98 and 6.25 *NH* (coalescing br, s, 1H); 7.18- 7.31 (m, 3H); 7.32- 7.48 (m, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 28.1, 28.2, 34.8, 39.9, 65.6, 77.2, 78.7, 81.54, 90.37, 127.6, 127.9, 128.1, 129.2, 131.6, 131.7, 154.5, 155.7.

Anal. Calcd. For $C_{23}H_{30}N_2O_4$: C, 69.32%; H, 7.59%; N, 7.03. Found: C, 69.50%; H, 7.40%, N, 6.96%.

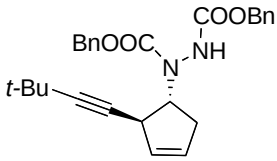
HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 97/3, retention times (min): 10.4 (major, stereoisomer), 11.3 (minor, stereoisomer).



(-)-Di-*tert*-butyl 1-((*1R,2S*)-2-(phenylethynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3ac) (Entry 7, Table 2).

Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Tol-BINAP (16.3 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1a** (59.2 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl phenylethynylboronate **2c** (92 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 80%). The product was isolated (Yield= 45%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

For ^{1}H NMR, ^{13}C NMR and HPLC data, see above description for entry 6, Table 2.



Dibenzyl 1-((*1R,2S*)-2-(3,3-dimethylbut-1-ynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3cd) (Entry 9, Table 2).

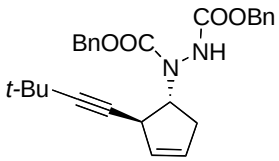
Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Tol-BINAP (16.3 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1c** (72.8 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl 3,3-dimethylbut-1-ynylboronate **2d** (84.1 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 55%). The product was isolated (Yield= 40%) by column chromatography eluting with hexanes/AcOEt 8:2, as a semisolid.

^{1}H NMR (250 MHz, $CDCl_3$) δ 1.08 (s, 9H); 2.45- 2.53 (m, 2H); 3.41- 3.54 (m, 1H); 4.73- 4.85 (m, 1H); 5.01- 5.20 (m, 4H); 5.44- 5.51 (m, 1H); 5.53- 5.60 (m, 1H); 7.13- 7.40 (m, 10H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 31.1, 34.8, 38.9, 65.9, 66.2, 68.2, 77.1, 127.8, 128.1, 128.4, 128.5, 129.1, 130.1, 135.5, 135.9, 156.6.

Anal. Calcd. For $C_{27}H_{30}N_2O_4$: C, 72.62%; H, 6.77%; N, 6.27. Found: C, 72.70%; H, 6.79%, N, 6.16%.

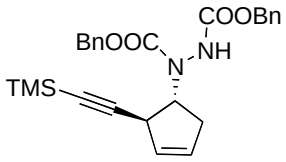
HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 93/7, retention times (min): 28.5 (minor, stereoisomer), 35.8 (major, stereoisomer).



Dibenzyl 1-((*1R,2S*)-2-(3,3-dimethylbut-1-ynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3cd) (Entry 10, Table 2).

Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Xylyl-BINAP (17.6 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1c** (72.8 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl 3,3-dimethylbut-1-ynylboronate **2d** (84.1 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 43%). The product was isolated (Yield= 36%) by column chromatography eluting with hexanes/AcOEt 8:2, as a semisolid.

For ^{1}H NMR, ^{13}C NMR and HPLC data see above descriptions for entry 9, Table 2.

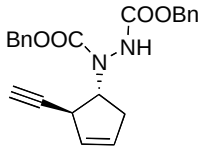


Dibenzyl 1-((1*R*,2*S*)-2-((trimethylsilyl)ethynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3ce) (Entry 11, Table 2).

Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Tol-BINAP (16.3 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1c** (72.8 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl (trimethylsilyl)ethynylboronate **2e** (90.5 mg, 0.4 mmol) and MeONa (21.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 38%). The product was isolated (Yield= 18%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 0.18 (s, 9H); 2.37- 2.70 (m, 2H); 3.60- 3.72 (m, 1H); 4.90- 5.02 (m, 1H); 5.10- 5.25 (m, 4H); 5.50- 5.60 (m, 1H); 5.62- 5.73 (m, 1H); 6.49 *NH* (br, s, 1H); 7.20- 7.43 (m, 10H).

HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 19.4 (minor, stereoisomer), 22.7 (major, stereoisomer).



Dibenzyl 1-((1*R*,2*S*)-2-(ethynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (4ce). Data not reported in Table 2.

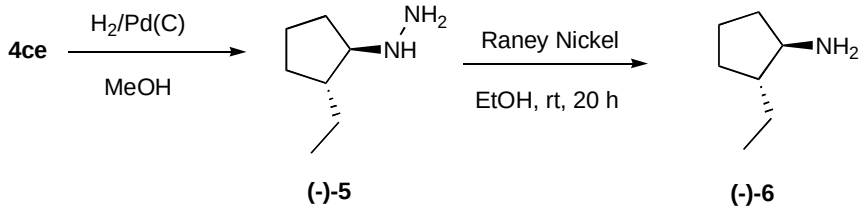
Using the general procedure described above, $[Rh(C_2H_4)Cl]_2$ (8.17 mg, 0.021 mmol) and *(R)*-Tol-BINAP (28.5 mg, 0.042 mmol) in MeOH (4.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1c** (255 mg, 0.7 mmol) in MeOH (1.0 mL), diisopropyl (trimethylsilyl)ethynylboronate **2e** (474 mg) and MeONa (113 mg) were added. The mixture was allowed to react for *4 days at 65°C*. The desilylated[7] product **4ce** was isolated in mixture with benzylic alcohol by column chromatography eluting with hexanes/AcOEt 8:2, as a brownish oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 2.08 (br s, 1H); 2.37- 2.57 (m, 2H); 3.55- 3.69 (m, 1H); 4.90- 5.29 (m, 5H); 5.50- 5.60 (m, 1H); 5.62- 5.72 (m, 1H); 6.50-6.65 *NH* (br, s, 1H); 7.20- 7.43 (m, 10H).

Determination of absolute sense of induction by chemical correlation.

The absolute configuration of the ring-opened adducts of type **3** was determined by chemical correlation with the known compound (i.e. (-)-(1*R*, 2*R*)-2-ethylcyclopentylamine,[8a] Scheme 1)**.**

Scheme 1



(-)-(1*R*, 2*R*)-2-Ethylcyclopentylamine. A solution of the above obtained dibenzyl 1-(-2-(ethynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (**4ce**) (55 mg) in MeOH (3.5 ml) was treated with Pd(C) (10 mg) and allowed to stir under hydrogen atmosphere for 16 h. The reaction mixture was filtered on celite and washed with MeOH. Evaporation of the organic solvent afforded crude (1*R*,2*R*)-2-ethylcyclopentyl)hydrazine (**5**), as grey semisolid (32 mg) $[\alpha]_D^{20}$= -7.2 (c= 2.1, MeOH). ^{1}H NMR (250 MHz, MeOD) δ 0.95 (t, *J*=6.1 Hz, 3H); 1.21-2.22 (m, 9H); 3.08- 3.21 (m, 1H). ESI-MS examination (2M + Na^+ = 279).

A solution of the crude hydrazine **5** (28 mg) in EtOH (2.1 ml) was treated with Raney nickel 2800 in suspension in 0.9 mL of EtOH (684 mg of slurry 50% in water, pre-washed with 2 X 2 mL water, 2 X 2 mL MeOH, 1 x 2 mL EtOH). After stirring for 20h at rt the reaction mixture was filtered on celite and washed with EtOH. Evaporation of the organic solvents afforded a crude oil (25 mg) consisting mainly of amine **6** as detected by ^{1}H NMR and ESI-MS examination (M+H = 114 and 2M + Na^+ = 249). ^{1}H NMR (250 MHz, MeOD) δ 0.95 (t, *J*=6.1 Hz, 3H); 1.21-2.22 (m, 9H); 2.98- 3.10 (m, 1H). The measurament of the optical rotatory power for this compound, $[\alpha]_D^{20}$= -9.1 (c= 0.5, MeOH) for a 79 : 21 enantiomeric ratio, gave the absolute sense of induction.[8]

It is assumed that all adducts of type **3** follow the same trend (i.e. (*R*)-Tol-Binap and (*R*)-xylyl-Binap gave products in which the major enantiomer has (1*R*, 2*S*) configuration.

Rhodium-Catalyzed Ring-Opening of Bicyclic Hydrazines 1a and 1c with Terminal Alkynes in the presence of Lewis-Acid.

Rhodium-Monophos Catalyzed Ring-Opening of bicyclic Hydrazine 1a with 1-Hexyne in the Presence of Lewis acid (Table 1). Under argon protection, a solution of $[Rh(cod)Cl]_2$ (4.91 mg, 0.01 mmol) and (+/-)-**L**[1] (17.1 mg, 0.048 mmol) in HPLC grade MeOH (1.0 mL) was stirred in a Sclenk tube for 30 minutes at room temperature. A solution of **1a** (59.2 mg, 0.2 mmol) in MeOH (1.0 mL) was then added, followed by the addition of 1-hexyne (82 mg, 1.0 mmol), MeONa (54 mg, 1.0 mmol) and Lewis acid (10 or 500 mol%, see Table 1). The mixture was allowed to react for 18 hours at 65°C and quenched with saturated aqueous $NaHCO_3$. After extraction with Et_2O (2 X 10 mL) and CH_2Cl_2 (10 mL), the organic phase dried over $MgSO_4$, filtered and concentrated *in vacuo*. Percentage conversions were determined by ^{1}H NMR examination of crude reaction mixture.

Rhodium-*(R)*-Tol-BINAP Catalyzed Ring-Opening of Bicyclic Hydrazine 1c with 1-Hexyne in the Presence Triisopropylborate (Entry 3, Table 2).

A solution of $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Tol-BINAP (16.3 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. A solution of **1c** (72.8 mg, 0.2 mmol) in MeOH (1.0 mL) was then added, followed by the addition of 1-hexyne (82 mg, 1.0 mmol), MeONa (54 mg, 1.0 mmol) and triisopropyl borate (188 mg, 1.0 mmol). The mixture was allowed to react for 18 hours at 65°C (conversion= 25%) and quenched with saturated aqueous $NaHCO_3$. After extraction with Et_2O (2 X 10 mL) and CH_2Cl_2 (10 mL), the organic phase dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture was

purified by column chromatography eluting with hexanes/AcOEt 8:2 to give compound **3ca**, as an oil (38% *ee*).

For ^{1}H NMR, ^{13}C NMR and HPLC data see above description of entry 1, Table 2.

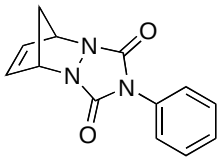
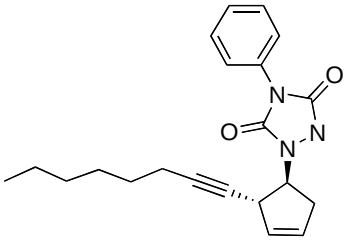
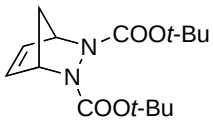
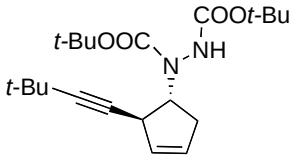
Rhodium-*(R)*-Tol-BINAP Catalyzed Ring-Opening of Bicyclic Hydrazine 1a Phenylacetylene in the presence triisopropyl borate (Entry 8, Table 2).

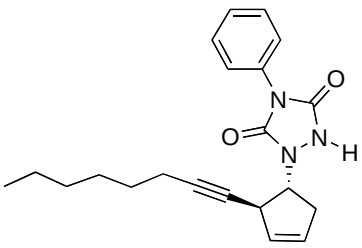
A solution of $[Rh(C_2H_4)Cl]_2$ (3.9 mg, 0.01 mmol) and *(R)*-Tol-BINAP (16.3 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. A solution of **1a** (59.2 mg, 0.2 mmol) in MeOH (1.0 mL) was then added, followed by the addition of phenylacetylene (102.1 mg, 1.0 mmol), MeONa (54 mg, 1.0 mmol) and triisopropyl borate (188 mg, 1.0 mmol). The mixture was allowed to react for 18 hours at 65°C and quenched with saturated aqueous $NaHCO_3$. After extraction with Et_2O (2 X 10 mL) and CH_2Cl_2 (10 mL), the organic phase dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture (conversion= 25%) was purified by column chromatography eluting with hexanes/AcOEt 8:2 to give compound **3ac**, as an oil (33% *ee*).

For ^{1}H NMR, ^{13}C NMR and HPLC data see above description of entry 6, Table 2.

Additional Results of the Ring-Opening Cyclic Hydrazines with Alkynylboronic Esters.

Table 3. Ring-opening cyclic hydrazines with alkynylboronic esters.

Entry	Hydrazine	Conditions	Boronic Ester	Product (yield%)
1	 **1d**	$[Rh(cod)Cl]_2$/ (+/-)-**L**^{1}	**2b**	 **3db** (55)
2	 **1a**	$[Rh(cod)Cl]_2$/ (+/-)-**L**^{1}	**2d**	 **3ad** (48)

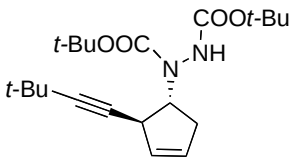


(1*R2*S**)-1-(2-(oct-1-ynyl)cyclopent-3-enyl)-4-phenyl-1,2,4-triazolidin-3,5-dione (3db)** (Entry 1, Table 3).

Using the general procedure described above, $[Rh(cod)Cl]_2$ (2.95 mg, 0.006 mmol) and rac-**L**^{1} (8.64 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1d** (48.2 mg, 0.2 mmol) in MeOH (1.0 mL), 1-octynyldiisopropylboronate **2b** (95.2 mg, 0.4 mmol) and $NaHCO_3$ (33.6 mg, 0.4 mmol) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 88%). The product was isolated (Yield= 55%) by column chromatography eluting with hexanes/AcOEt 6:4, as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 0.71- 0.96 (m, 3H); 1.03- 1.52 (m, 8H); 2.07- 2.20 (m, 2H); 2.42- 2.75 (m, 2H); 3.57 (br, s, 1H); 4.81- 4.99 (m, 1H); 5.59- 5.69 (m, 1H); 5.70- 5.84 (m, 1H); 7.34- 7.58 (m, 5H); 8.60- 8.93 (br, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.1, 18.8, 22.5, 28.5, 28.7, 31.3, 34.9, 39.8, 62.7, 78.4, 83.3, 128.8, 129.1, 130.8, 131.1, 153.1.



Di-*tert*-butyl 1-((1*R,2*S**)-2-(3,3-dimethylbut-1-ynyl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3ad)** (Entry 2, Table 3).

Using the general procedure described above, $[Rh(cod)Cl]_2$ (2.95 mg, 0.006 mmol) and rac- **L**[1] (8.64 mg, 0.024 mmol) in MeOH (1.0 mL) was stirred for 30 minutes at rt. Then a solution of hydrazine **1a** (59.2 mg, 0.2 mmol) in MeOH (1.0 mL), diisopropyl 3,3-dimethylbut-1-ynylboronate **2d** (84.1 mg, 0.4 mmol)**,** $NaHCO_3$ (33.6 mg, 0.4 mmol) and molecular sieves (4A, 100 mg) were added. The mixture was allowed to react for 18 hours at 65°C (conversion= 76%). The product was isolated (Yield= 48%) by column chromatography eluting with hexanes/AcOEt 8:2, as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 1.15 (s, 9H); 1.44 (s, 9H); 1.46 (s, 9H); 2.31. 2.70 (m, 2H); 3.41- 3.62 (m, 1H); 4.69- 4.91 (m, 1H); 5.48- 5.57 (m, 1H); 5.60- 5.68 (m, 1H); 5.88 and 6.18 *NH* (coalescing br, s, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 28.2, 31.2, 34.6, 39.0, 65.8, 77.2, 78.7, 81.2, 89.9, 129.2, 130.8, 154.7, 155.7.

Table 4. Additional results for the ring-opening of bicyclic hydrazines 1a with boronate 2a in different reaction conditions.[a]

Entry	Rhodium Source (5.0 mol%)	Ligand (24.0 mol%)	Base	Time (h)	Conversion (%)	*ee* (%)
1	$[Rh(cod)Cl]_2$	$P(OEt)_3$	$NaHCO_3$	96	70	N.a
2	$[Rh(cod)Cl]_2$	(+/-)-Et-Monoophos	$NaHCO_3$	18	77	N.a

[a] All reactions carried out in accordance with the general procedure.

Table 5. Additional results for the ring-opening of bicyclic hydrazines 1c with boronate 2a in different reaction conditions.[a]

Entry	Rhodium Source (3.0 mol%)	Ligand (6.0 mol%)	Base	Time (h)	Conversion (%)	*ee* (%)
1	$[Rh(cod)Cl]_2$	*t*-Bu-Josiphos	$NaHCO_3$	72	< 5	N.d
2[b]	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	$NaHCO_3$	48	28	N.a
3	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Tol-BINAP	CsF	36	42	39
4	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Biphep	CsF	48	< 5	N.d
5	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Tol-BINAP	K_2CO_3	18	74	46
6[b]	$[Rh(C_2H_4)_2Cl]_2$	(+/-)-**L**[2]	MeONa	48	<5	N.d
7	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Tol-BINAP	*t*-BuOK	18	40	N.d
8	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-DTBM-SEGPHOS	MeONa	48	<5	N.d

[a] All reactions carried out in accordance with the general procedure. [b]Reaction performed with 12 mol% of chiral ligand.

Table 6. Additional results for the ring-opening of bicyclic hydrazines 1a with boronate 2c in different reaction conditions.[a]

Entry	Rhodium Source (5.0 mol%)	Ligand (12.0 mol%)	Base	Time (h)	Conversion (%)	*ee* (%)
1[b]	$[Rh(C_2H_4)_2Cl]_2$	(+/-)-Et-Monophos	MeONa	18	21	N.d
2[b]	$[Rh(cod)Cl]_2$	*(S)*-**L**[1]	CsF	3	70	N.a
3	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Tol-BINAP	CsF	24	25	43
4	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Xylyl-BINAP	CsF	24	50	43

[a] All reactions carried out in accordance with the general procedure. [b]Reaction performed with 24 mol% of chiral ligand.

Table 7. Additional results for the ring-opening of bicyclic hydrazines 1a with boronate 2d in different reaction conditions.[a]

Entry	Rhodium Source (5.0 mol%)	Ligand (24.0 mol%)	Base	Time (h)	Conversion (%)	*Ee* (%)
1	$[Rh(cod)Cl]_2$	(+/-)-**L**[1]	$NaHCO_3$	18	76	-
2	$[Rh(cod)Cl]_2$	**L**[2]	$NaHCO_3$	18	12	-

[a] All reactions carried out in accordance with the general procedure.

Table 8. Additional results for the ring-opening of bicyclic hydrazines 1c with boronate 2d in different reaction conditions.[a]

Entry	Rhodium Source (3.0 mol%)	Ligand (6.0 mol%)	Base	Time (h)	Conversion (%)	*Ee* (%)
1[b]	$[Rh(C_2H_4)_2Cl]_2$	(+/-)-Et-Monophos	MeONa	24	< 5	N.a
2	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Xylyl-BINAP	-	18	< 5	N.d
3	$[Rh(C_2H_4)_2Cl]_2$	*(R)*-Tol-BINAP	MeONa	18	19	N.d
4[b]	$[Rh(C_2H_4)_2Cl]_2$	*(S)*- **L**[1]	MeONa	18	< 5	N.d

[a] All reactions carried out in accordance with the general procedure. [b]Reaction performed with 12 mol% of chiral ligand

Table 9. Additional results for the Rh-catalyzed ring-opening of bicyclic hydrazines 1a with 1-hexyne in the presence of Lewis acids.[a]

Entry	Rh source (5.0 mol%)	Ligand (24.0 mol%)	Base	Lewis Acid	Time(h)	Conv. (%)
1	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	MeONa	$B(OH)_3$	18	<5
2	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	MeONa	$Yb(OTf)_3$	18	<5
3	$[Rh(cod)Cl]_2$	(S)- **L**[1]	MeONa	I_2	18	58
4[b]	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	MeONa	$B(OiPr)_3$	18	64
5	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	MeONa	$Sc(OTf)_2$	18	82
6	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	MeONa	$Yb(OTf)_3$	18	68
7	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	MeONa	$In(OTf)_3$	18	<50
8	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	*t*-BuOK	$Yb(OTf)_3$	72	100
9	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	MeONa	$Cu(OTf)_2$	72	50
10[b]	$[Rh(cod)OH]_2$	(+/-)-Et-Monophos	MeONa	$B(OiPr)_3$	18	<5
11[b]	$[Rh(C_2H_4)_2acac]_2$	(+/-)-Et-Monophos	MeONa	$B(OiPr)_3$	18	14
12[b]	$[Rh(CO)_2Cl]_2$	(+/-)-Et-Monophos	MeONa	$B(OiPr)_3$	18	<5
13[b]	$[Rh(cod)Cl]_2$	(+/-)-Et-Monophos	-	$B(OiPr)_3$	18	<5

[a] All reactions carried out in the presence of 5.0 equiv. of 1-hexyne and 10 mol% of the Lewis acid. [b]Reaction performed with 5.0 eq. of the Lewis acid.

Table 10. Additional results for the Rh-catalyzed ring-opening of bicyclic hydrazines 1c with 1-hexyne in the presence of triisopropylborate.[a]

Entry	Rh source (5.0 mol%)	Ligand (12.0 mol%)	Base	Lewis Acid	Time (h)	Conv. (%)
1	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-Tol-Binap	MeONa	-	18	13
2	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-Tol-Binap	MeONa	$B(OiPr)_3$	18	21

[a] All reactions carried out in the presence of 5.0 equiv. of 1-hexyne and 5.0 equiv. of the Lewis acid.

Table 11. Additional results for the Rh-catalyzed ring-opening of bicyclic hydrazines 1a with phenylacetylene in the presence of Lewis acids.[a]

Entry	Rh source (5.0 mol%)	Ligand (12.0 mol%)	Base	Lewis acid	Time (h)	Conv. (%)
1	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-Tol-Binap	MeONa	-	18	<5
2	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-Tol-Binap	*t*-BuOK	$Yb(OTf)_3$	18	<5
3[b]	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-Tol-Binap	NaO*i*Pr	$B(OiPr)_3$	18	<5
4	$[Rh(cod)Cl]_2$	(*R*)-Tol-Binap	*t*-BuOK	$Yb(OTf)_3$	18	<5
5[b]	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-Tol-Binap	MeONa	$B(OiPr)_3$	18	25
6	$[Rh(C_2H_4)_2Cl]_2$	(*R*)-Xylyl-Binap	MeONa	$Yb(OTf)_3$	18	<5
7[c]	$[Rh(C_2H_4)_2Cl]_2$	(*S*)- **L**[1]	MeONa	-	18	16

[a] All reactions carried out in the presence of 5.0 equiv. of phenylacetylene and 10 mol% of the Lewis acid. [b]Reaction performed with 5.0 eq. of the Lewis acid. [c] [b]Reaction performed with 24 mol% of the chiral ligand.

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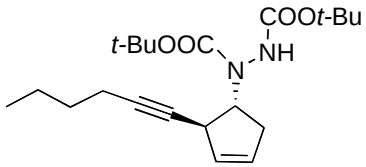
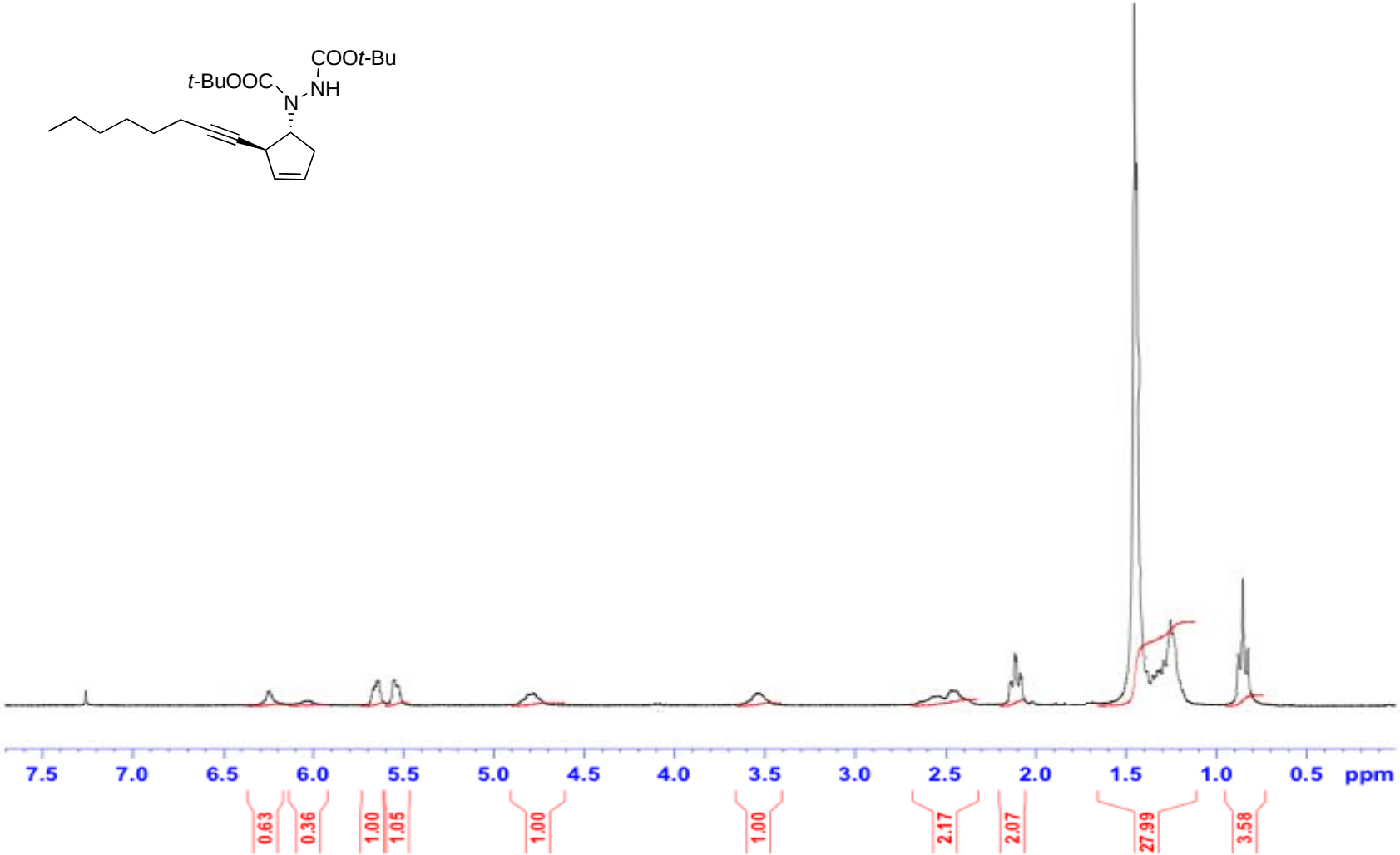
[8] (a) Biju P. J. et al. Patent No. WO 2005066147. (b) For the absolute configuration of related (1*S*, 2*S*)-(+)-*trans*-2-methylcyclopentylamine hydrochloride ($[\alpha]_D^{20}$= +29.2 (c= 4, MeOH), see: (b) H. C. Brown, K.-W. Kim, T. E. Cole, B. Singaram, *J. Am. Chem. Soc.* **1986**, *108*, 6761.

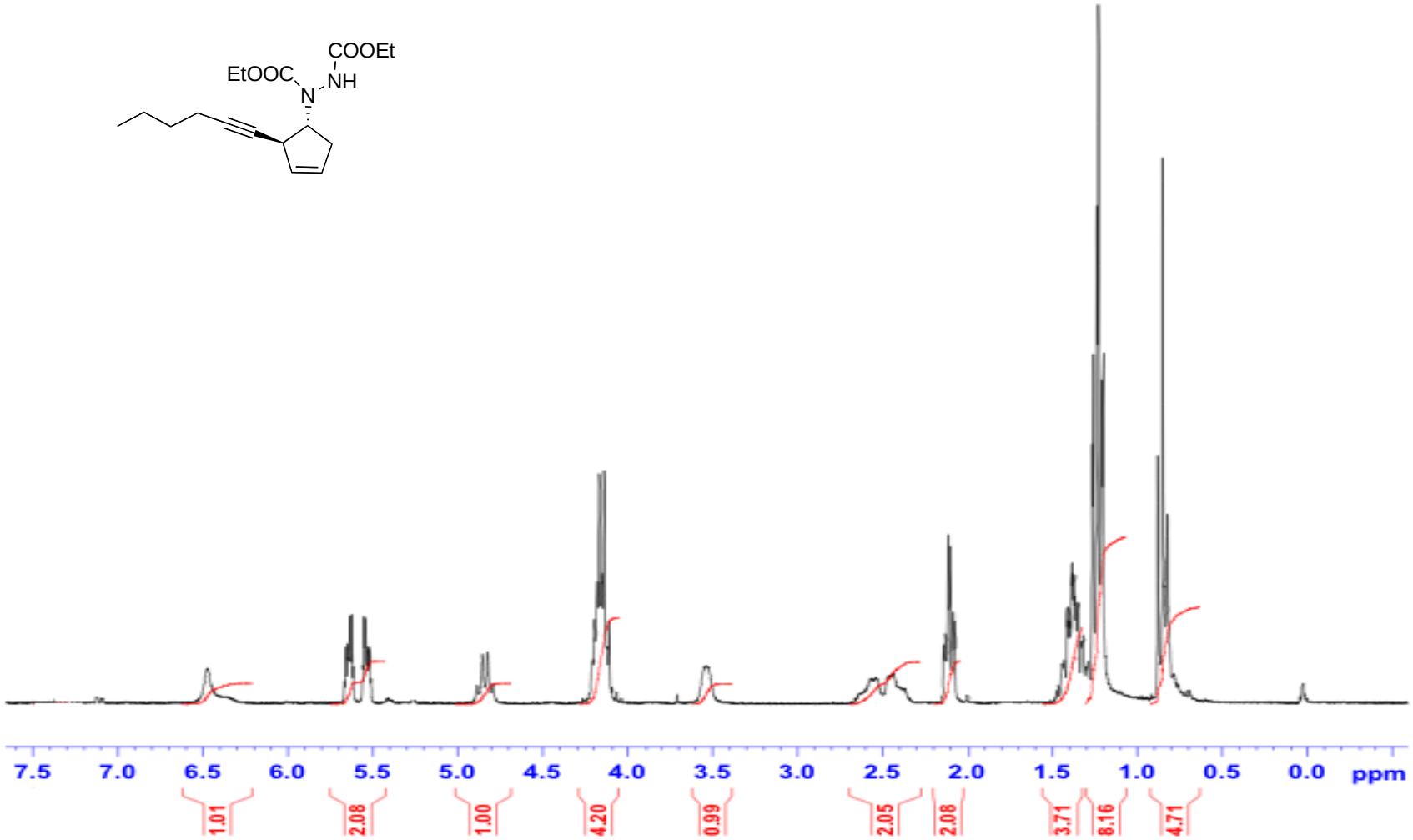
Di-*tert*-butyl 1-((1*R**,2*S**)-2-(hex-1-ynyl)cyclopent-3-enyl) hydrazine-1,2-dicarboxylate **(3aa)** ($CDCl_3$, 250 MHz).



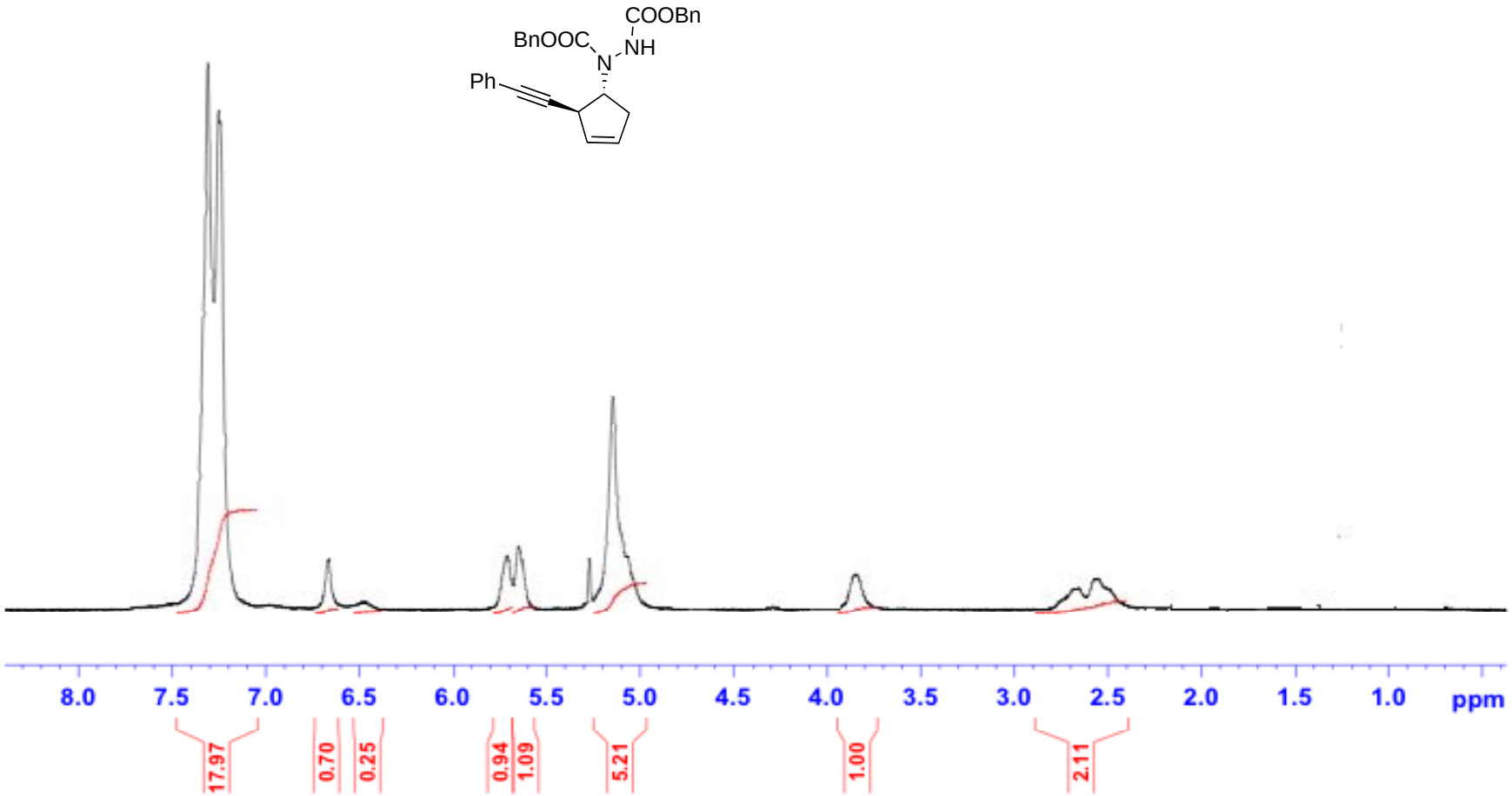
Di-*tert*-butyl 1-((1*R**, 2*S**)-2-(oct-1-ynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate **(3ab)** ($CDCl_3$, 250 MHz).



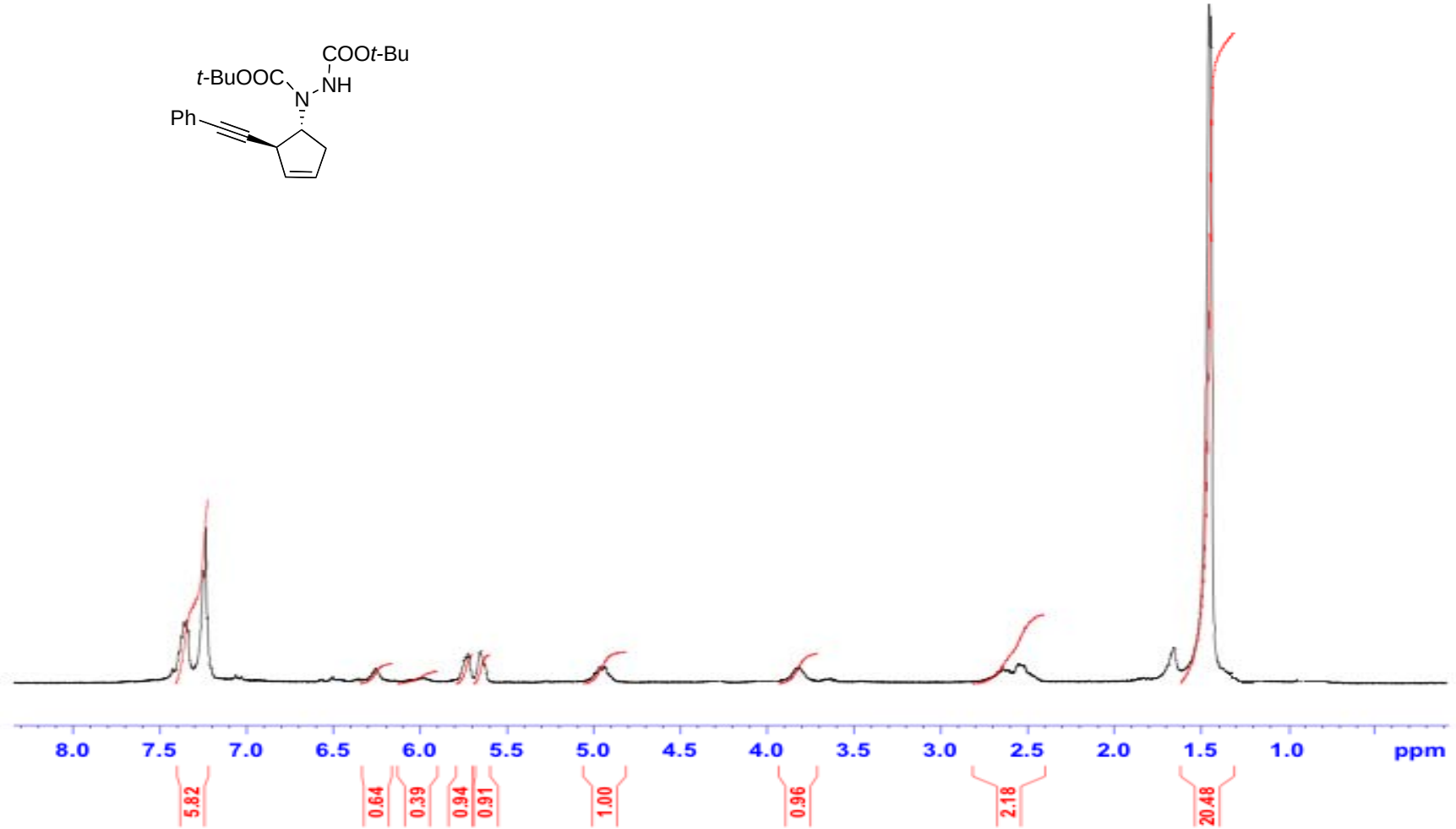
Diethyl 1-((1*R**,2*S**)-2-(hex-1-ynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate **(3ba)** ($CDCl_3$, 250 MHz).



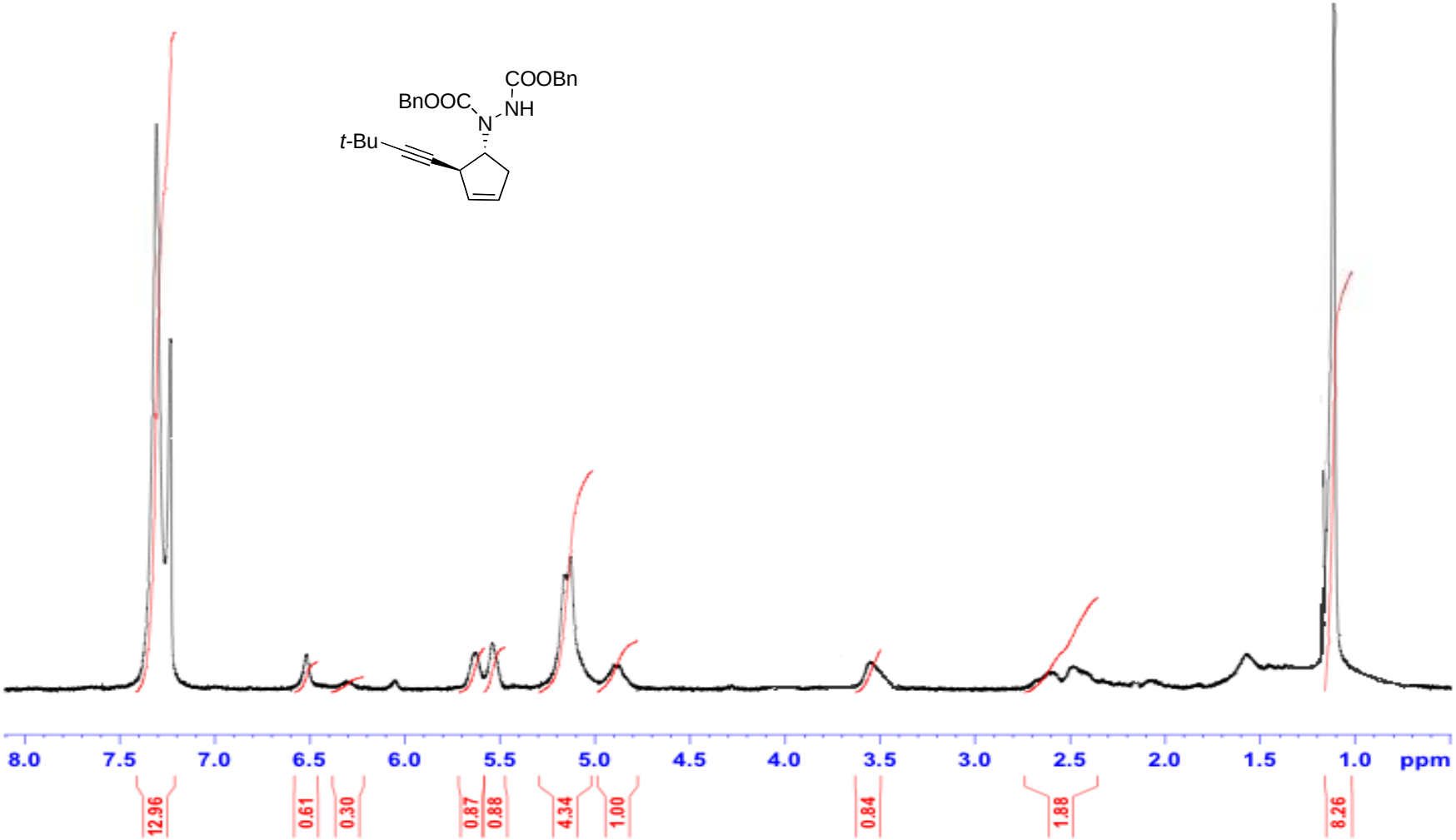
(-)-Dibenzyl 1-((*1R,2S*)-2-(phenylethynyl)cyclopent-3-enyl) hydrazine-1,2-dicarboxylate **(3cc)** ($CDCl_3$, 250 MHz).



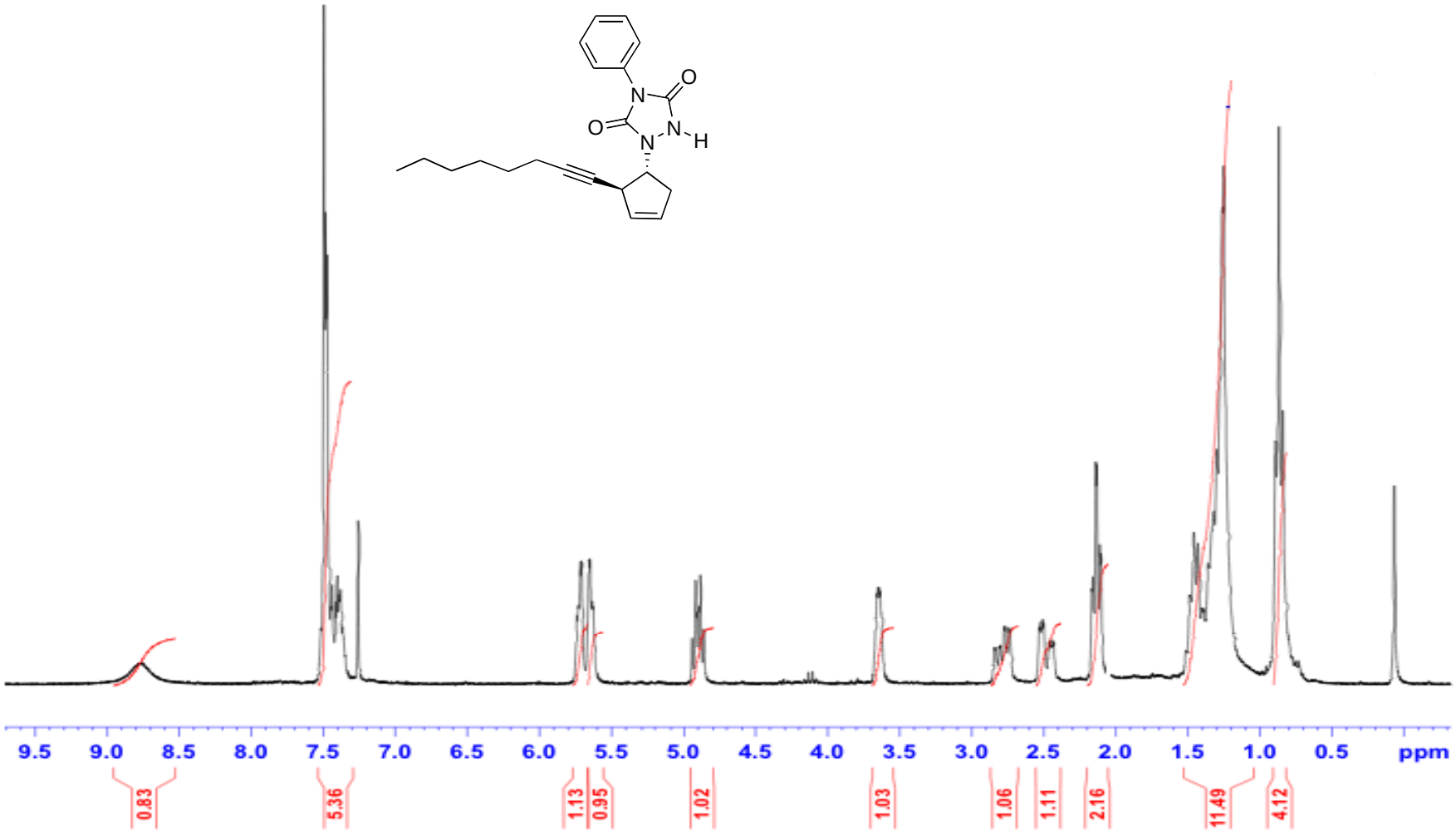
(-)-Di-*tert*-butyl 1-((*1R,2S*)-2-(phenylethynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate **(3ac)** ($CDCl_3$, 250 MHz).



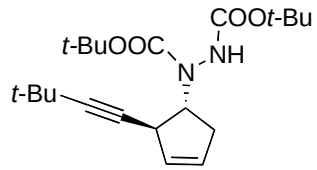
Dibenzyl 1-((*1R,2S*)-2-(3,3-dimethylbut-1-ynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate **(3cd)** ($CDCl_3$, 250 MHz).



(1*R**-2*S**)-1-(2-(oct-1-ynyl)cyclopent-3-enyl)-4-phenyl-1,2,4-triazolidin-3,5-dione **(3db)** ($CDCl_3$, 250 MHz).



Di-*tert*-butyl 1-((1*R**,2*S**)-2-(3,3-dimethylbut-1-ynyl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate **(3ad)** ($CDCl_3$, 250 MHz)



Di-*tert*-butyl 1-((1*R**,2*S**)-2-(3,3-dimethylbut-1-ynyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate **(3ad)** ($CDCl_3$, 62.5 MHz).