

Supporting Information

Diastereoselective Diaza-Cope Rearrangement Reaction

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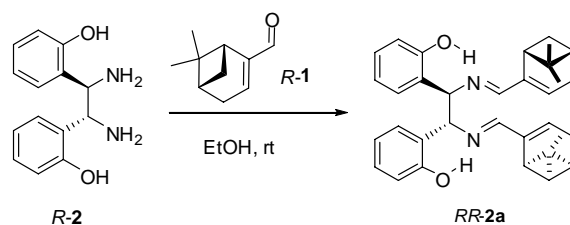
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General Information

Commercially available compounds (including (1*R*)-(-)-myrtenal) were used without further purification or drying. The ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 400 spectrometer (400 MHz and 100 MHz, respectively). The High resolution mass spectra (HRMS) were obtained from the Department of Chemistry University of Toronto, Optical rotations were measured at 589 nm using a Rudolph Autopol IV polarimeter. Melting points were recorded using an Electrothermal melting point apparatus. Spartan 06' for windows was used for all calculations.

Preparation and characterization of *RR*-2a, *RR*-3a, *RR*-3



Synthesis of *RR*-2a: To a clear solution of 22.4 mg (0.10 mmol) of (*R,R*)-bis-1,2-di-(2-hydroxyphenyl)-1,2-diaminoethane (*R*-2) in 0.20 mL of ethanol was added 30 mg (0.20 mmol) of (1*R*)-(-)-Myrtenal. The resulting clear reaction mixture was stirred for half an hour at room temperature to give *RR*-2a as a white precipitate. The solid was filtered, washed with 0.5 mL of ethanol and dried in vacuum (90 % yield).

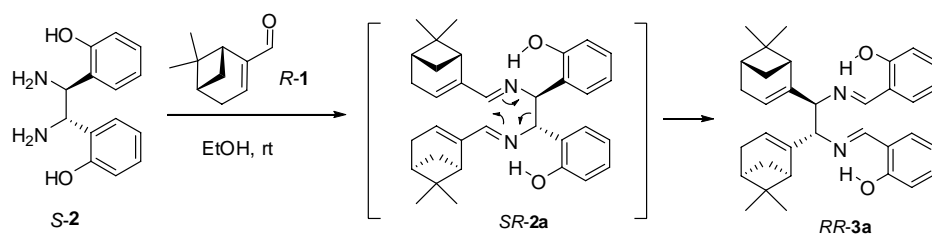
¹H NMR (400MHz, CDCl₃): δ 10.75 (s, 2H, ArOH), 7.53 (s, 2H, imine H), 7.04 (t, *J* = 7.6 Hz, 2H, ArH), 6.81 (d, *J* = 8.4 Hz, 2H, ArH), 6.46 (t, *J* = 7.6 Hz, 2H, ArH), 6.36 (d, *J* = 7.2 Hz, 2H, ArH), 6.06 (m, 2H, α-pinene), 4.64 (s, 2H, C*H), 2.86 (t, *J* = 5.2 Hz, 2H, α-pinene), 2.48 – 2.33 (m, 6H, α-pinene), 2.15 (s, 2H, α-pinene), 1.38 (s, 6H, α-pinene), 1.03 (d, *J* = 9.2 Hz, 2H, α-pinene), 0.81 (s, 6H, α-pinene).

¹³C-NMR (100 MHz, CDCl₃): δ 163.93, 156.82, 147.30, 138.81, 129.25, 128.80, 124.02, 119.94, 119.13 (7 aromatic and imine carbons, and 2 carbons of double bond of α-pinene), 78.48, 40.48, 40.44, 37.83, 32.76, 31.57, 26.33, 21.62 (8 carbons of α-pinene).

X-ray quality crystals for compound *RR*-2a was obtained by slow evaporation of its solution in CH₂Cl₂ / acetonitrile.

HRMS (ESI) calculated for C₃₄H₄₁N₂O₂ [M+H]⁺: 509.3162. Found: 509.3175.

[α]_D²⁷ + 200.6 (c = 1.0, CHCl₃), mp = 138°C.



Synthesis of *RR-3a*: To a clear solution of 22.4 mg (0.10 mmol) of (*S,S*)-bis-1,2-di-(2-hydroxyphenyl)-1,2-diaminoethane (*S-2*) in 0.20 mL of ethanol was added 30 mg (0.20 mmol) of (1*R*)-(-)-Myrtenal. The resulting clear reaction mixture was stirred for half an hour at room temperature to give *RR-3a* as a yellow precipitate. The solid was filtered, washed with 0.5 mL of ethanol and dried in vacuum (90 % yield).

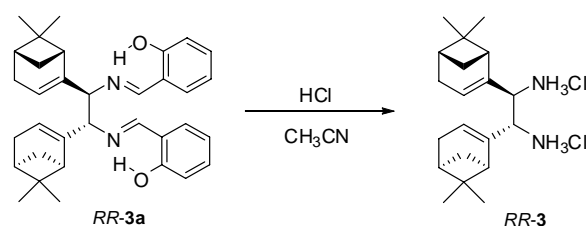
¹H NMR (400MHz, CDCl₃): δ 13.13 (s, 2H, ArOH), 8.18 (s, 2H, imine H), 7.21 (t, *J* = 7.8 Hz, 2H, ArH), 7.09 (d, *J* = 7.6 Hz, 2H, ArH), 6.88 (d, *J* = 8.0 Hz, 2H, ArH), 6.76 (t, *J* = 7.6 Hz, 2H, ArH), 5.43 (m, 2H, α-pinene), 4.08 (s, 2H, C*H), 2.54 (t, *J* = 5.2 Hz, 2H, α-pinene), 2.45 (dt, *J* = 8.8, 5.6 Hz, 2H, α-pinene), 2.27 (dt, *J* = 18, 2.8 Hz, 2H, α-pinene), 2.20 (dt, *J* = 18, 2.8 Hz, 2H, α-pinene), 2.08 (s, 2H, α-pinene), 1.31 (s, 6H, α-pinene), 1.29 (d, *J* = 6.1 Hz, 2H, α-pinene), 0.64 (s, 6H, α-pinene).

¹³C-NMR (100 MHz, CDCl₃): 165.48, 161.03, 145.86, 132.31, 131.74, 121.53, 118.88, 118.71, 116.93 (7 aromatic and imine carbons, and 2 carbons of double bond of α-pinene), 78.22, 42.68, 41.01, 38.34, 31.63, 31.53, 26.30, 21.18 (8 carbons of α-pinene).

X-ray quality crystals for compound *RR-3a* was obtained from DMSO-*d*₆

HRMS (ESI) calculated for C₃₄H₄₁N₂O₂ [M+H]⁺: 509.3162. Found: 509.3183.

[α]_D²⁷ -66.4 (c = 1.0, CHCl₃), mp = 184°C.



Synthesis of *RR-3*: To a slurry of *RR-3a* (1.0 mmol) in 10 mL of acetonitrile was added 0.2 mL of 37 % HCl solution. Stirring the reaction mixture at ambient temperature for 3 hrs afforded white precipitate. The solid was filtered, and the diamine dihydrochloride salt was washed with acetonitrile (2 x 3 mL) to afford analytically pure *RR-3*•2HCl in 95 % yield.

^1H NMR (400MHz, D_2O): δ 5.91 (m, 2H), 4.22 (s, 2H, C*H), 2.55 (dt, $J = 9.2, 5.6$ Hz, 2H), 2.35 – 2.33 (m, 6H), 2.14 (s, 2H), 1.34 (s, 6H), 1.20 (d, $J = 12.0$ Hz, 2H), 0.70 (s, 6H).

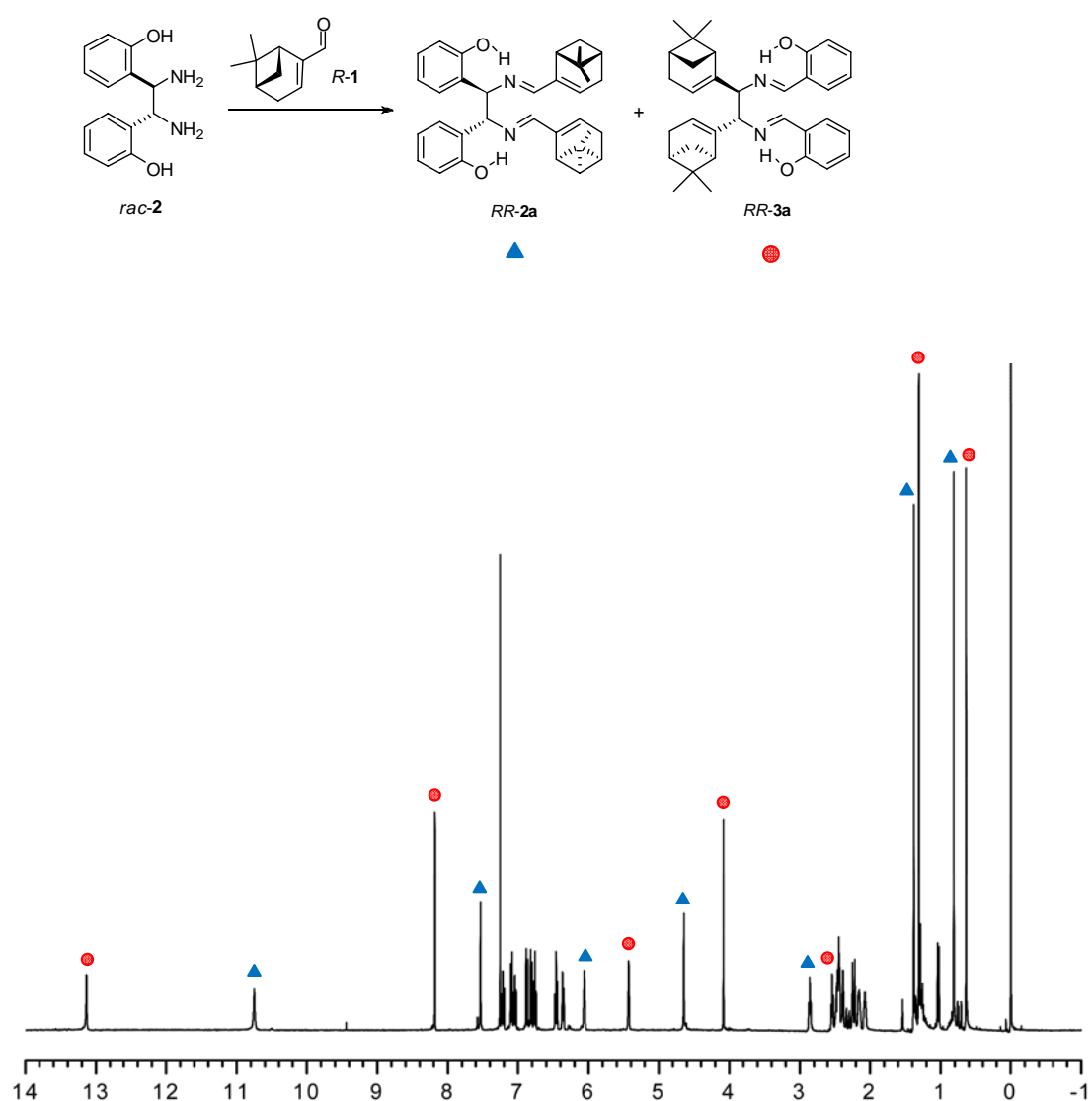
^{13}C -NMR (100 MHz, $\text{D}_2\text{O}/\text{CD}_3\text{OD}$): δ 138.76, 131.33 (2 carbons of double bond of α -pinene), 58.14, 41.48, 41.14, 38.65, 32.44, 32.02, 26.02, 21.53 (8 carbons of α -pinene).

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{33}\text{N}_2$ $[\text{M}+\text{H}]^+$: 301.2638. Found: 301.2652.

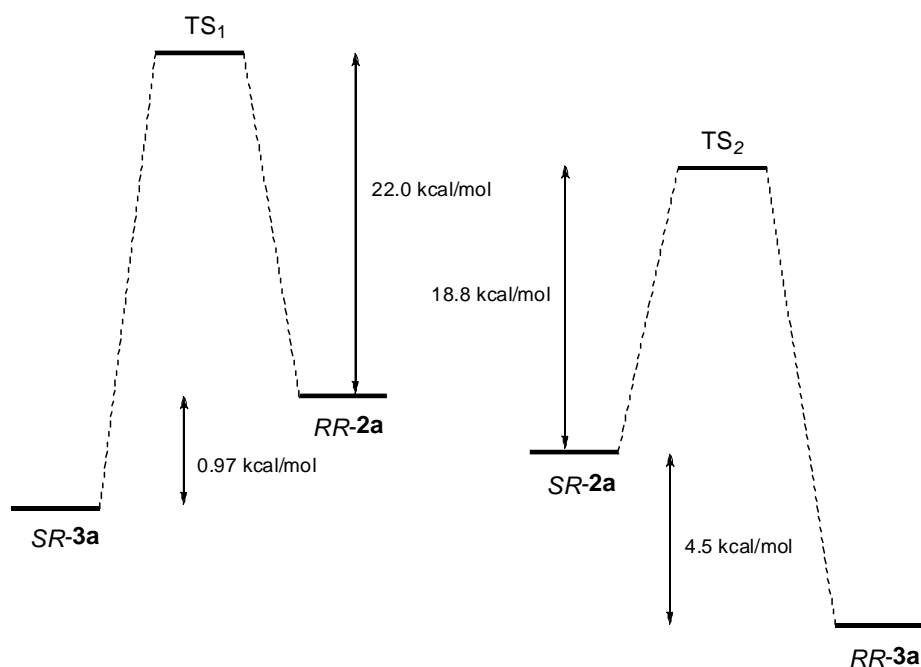
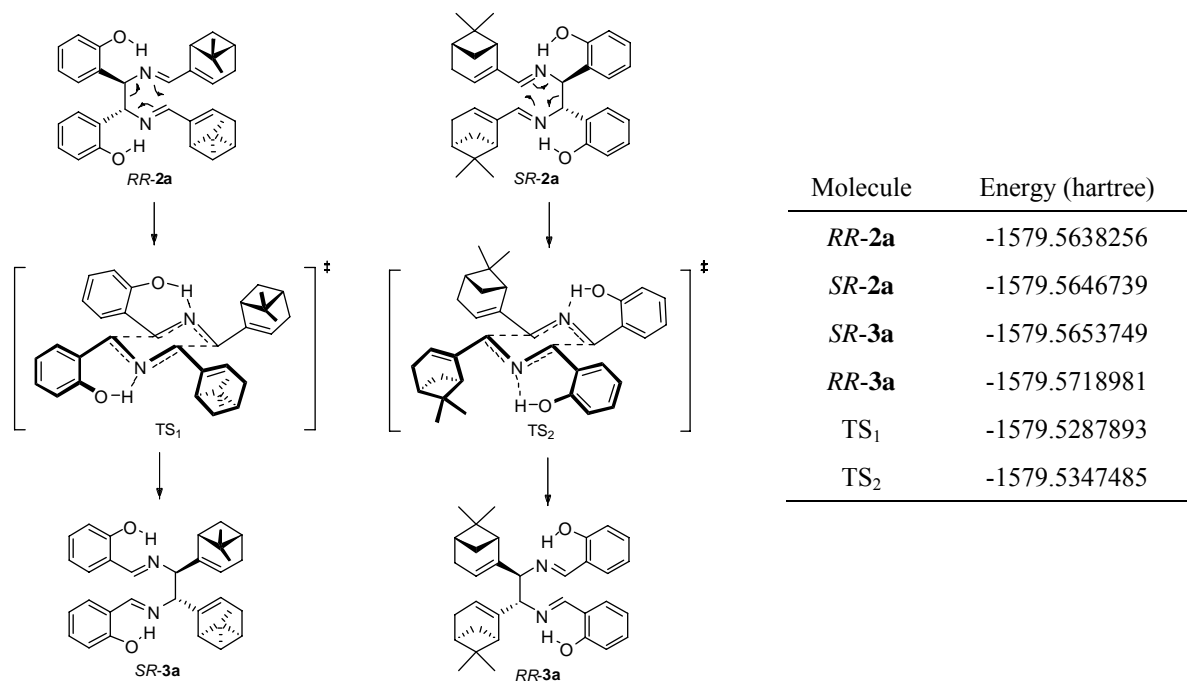
$[\alpha]_{\text{D}}^{27}$ -22.1 (c = 1.0, CHCl_3).

^1H NMR spectrum for enantioselective reaction between (*R*)-(-)-myrtenal and racemic bis-1,2-di-(2-hydroxyphenyl)-1,2-diaminoethane.

49mg of *rac*-bis-1,2-di-(2-hydroxyphenyl)-1,2-diaminoethane (0.20 mmol) was mixed with 2.2 equiv of (*R*)-(-)-myrtenal (0.44 mmol) in EtOH (0.2 ml). After stirring the mixture at ambient temperature for half an hour, the solvent was removed by nitrogen blowing. The crude mixture was dissolved in CDCl_3 for ^1H NMR.

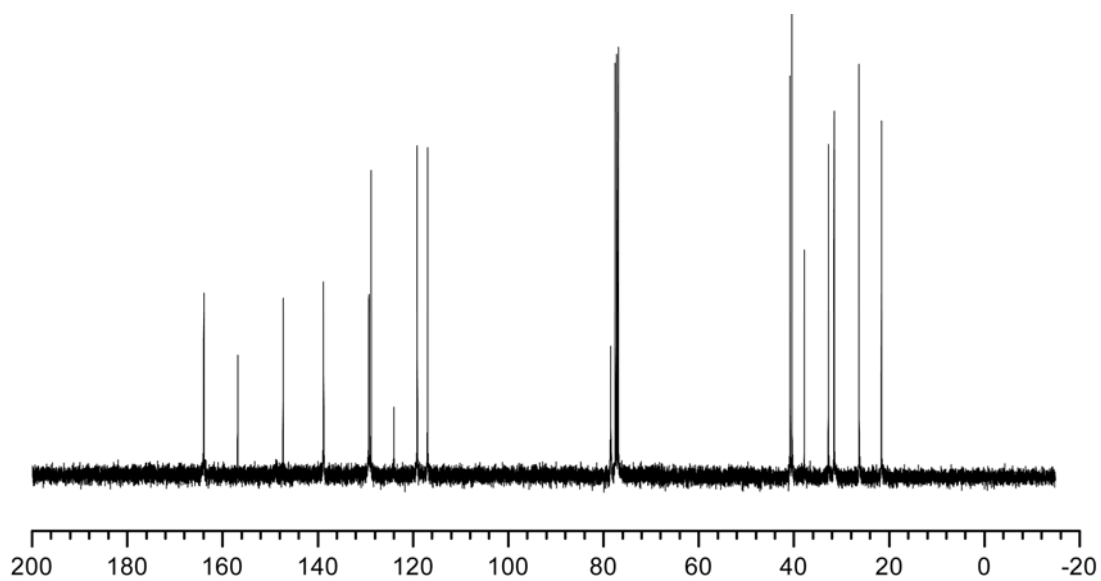
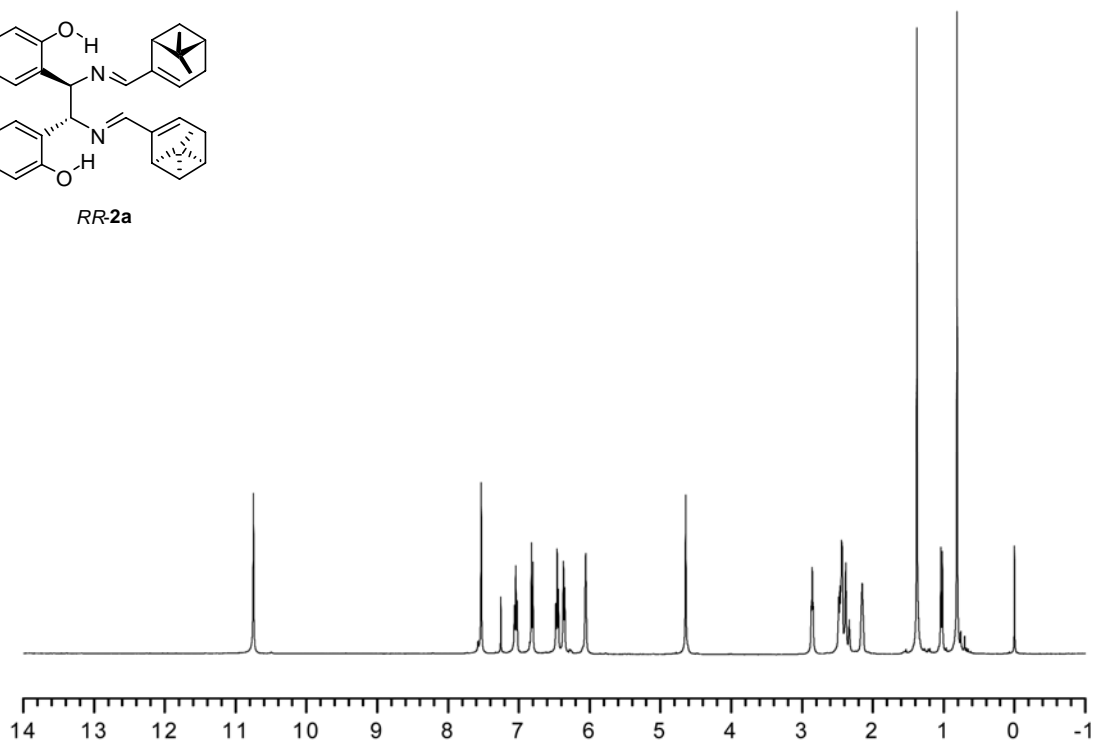
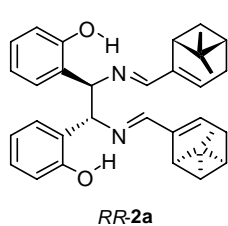


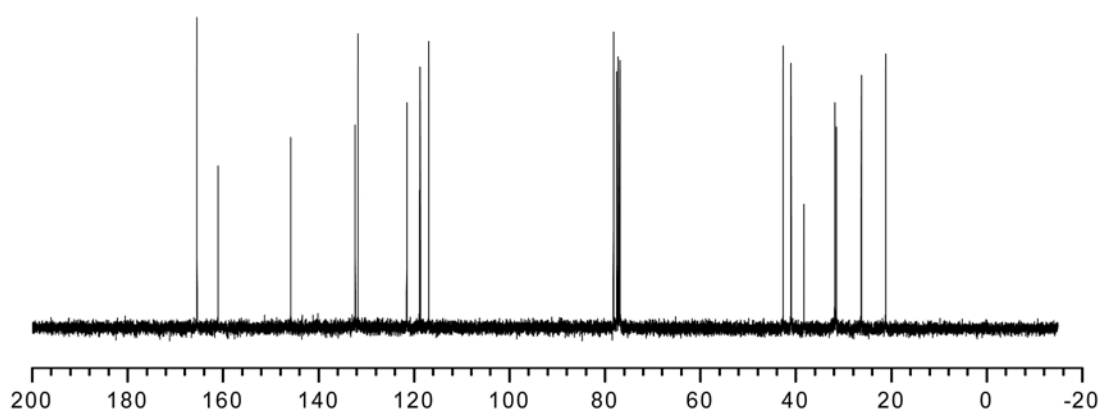
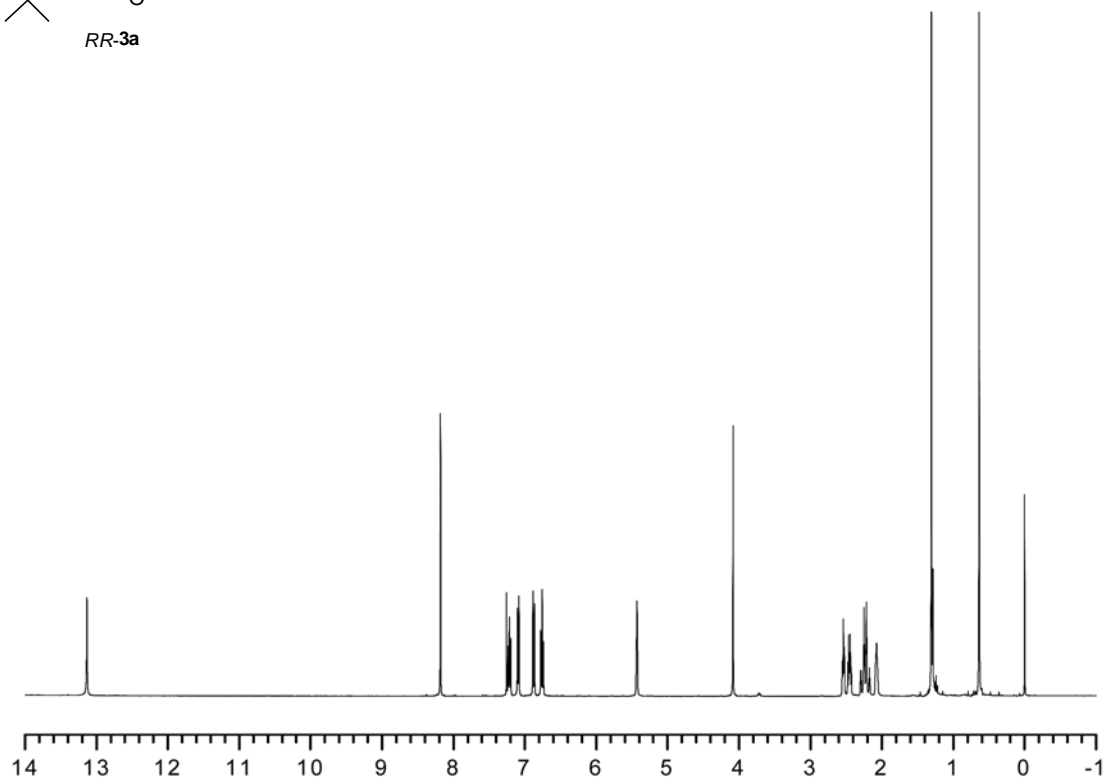
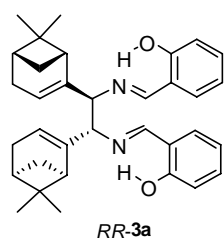
Calculation results

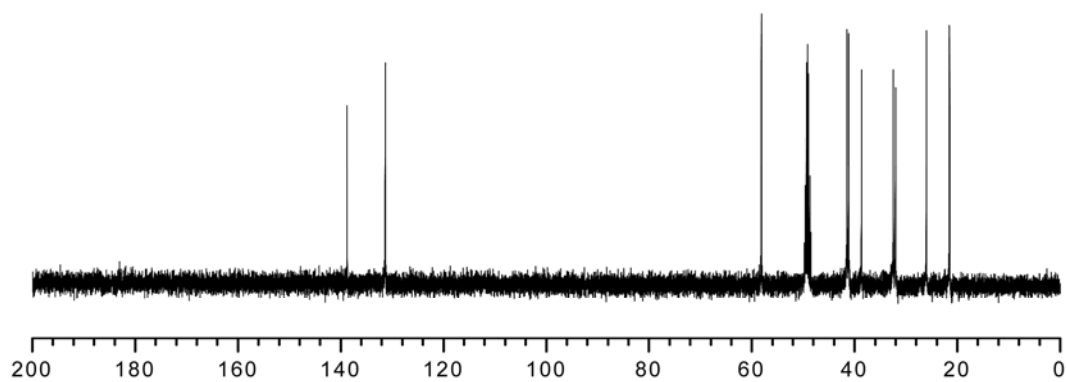
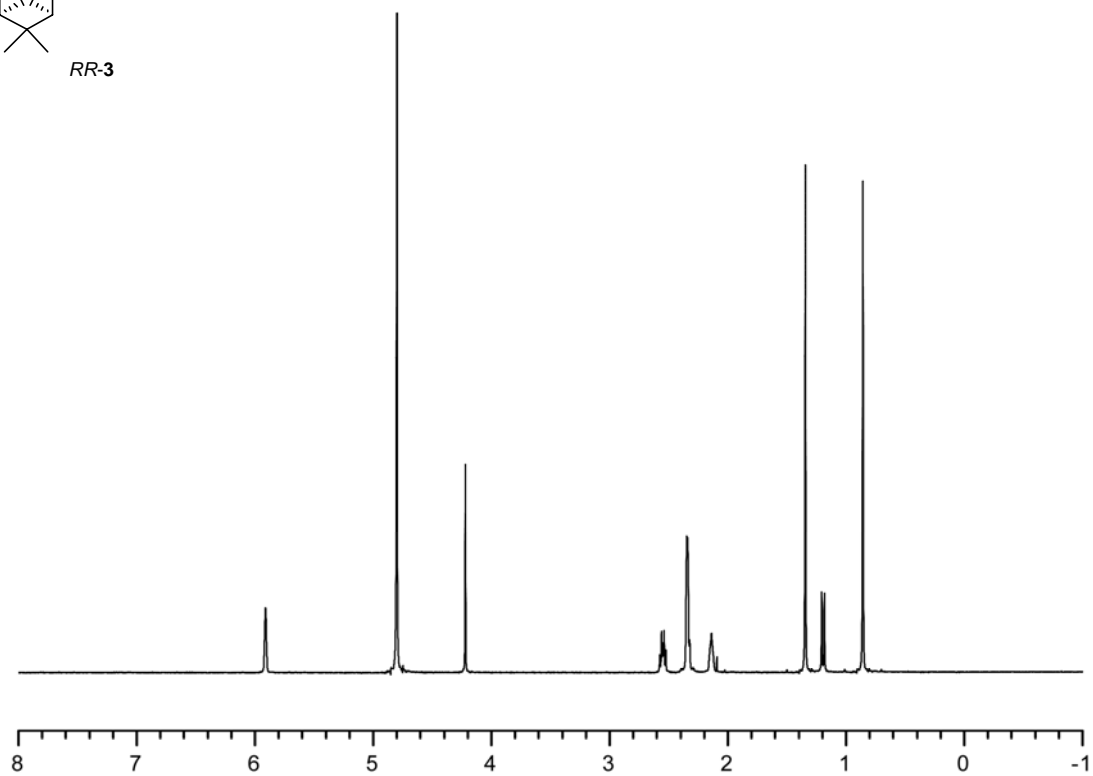
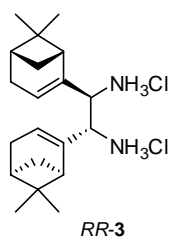


Equilibrium geometries and transition state geometries were obtained by DFT computation at the B3LYP / 6-31G* level

^1H and ^{13}C NMR spectra







^1H NMR signal for alkene C-H of *RR*-**2a** and *RR*-**3a** is a multiplet in CDCl_3

