Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Domino Rh-catalyzed Hydroformylation Double Cyclization of *o*-Amino Cinnamyl Derivatives: Applications to the Formal Total Syntheses of Physostigmine and Physovenine.

Wen-Hua Chiou,* Chien-Lun Kao, Jui-Chi Tsai and Yun-Man Chang

wchiou@dragon.nchu.edu.tw

Department of Chemistry, National Chung Hsing University, Taichung 402 Taiwan, R.O.C.

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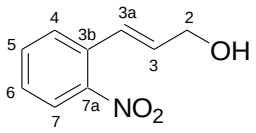
General Methods: All NMR spectra, i.e., ^{1}H, ^{13}C, DEPT, gCOSY, gHSQC, gHMBC, ROESY, were recorded on a Varian 600 or 400 MHz NMR spectrometer, which provided all necessary data for the full assignment of each compound. Melting points were measured on a Büchi 535 melting point apparatus and uncorrected. High-resolution mass spectrometry (HRMS) analyses were conducted at the Instrument Center of National Chung Hsing University. GC-MS analyses were performed on an HP 5890 Series GC system equipped with an Rtx-®-5MS capillary column (50 m X 0.25 mm, 0.5 μm). IR spectra were measured on a Bruker Equinox 55 or Bruker Tensor 27 spectrophotometer. TLC analyses were performed on Merck DC-alufolien with Kieselgel 60F-254, and were visualized with UV light, iodine chamber, 10% sulfuric acid or 10% PMA solution. Purifications were performed by flash chromatography on silica gel 60 (Merck, 230-400 mesh ASTM). Microwave reactions were performed in a *Discover* system of CEM.

Materials: Chemicals, reagents and solvents were purchased from Sigma Aldrich Company or Acros Organic Fischer Company. The reagents were used as received. Dichloromethane, pyridine, triethylamine, acetonitrile, DMSO and methanol were dried and distilled over calcium hydride under argon before use. Ether was dried and distilled over sodium-benzophenone ketyl under argon before use. THF was dried and distilled over potassium metal under argon before use. Toluene and benzene were dried and distilled over sodium metal under argon or argon before use. The reaction flasks were dried in a 110 °C oven and allowed to cool to room temperature in a desiccator over "*Drierite*" (calcium sulfate) and assembled under argon atmosphere.

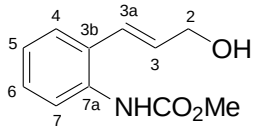
***ortho*-nitrocinnamyl alcohol (1):**



To a solution of 2-nitrocinnamaldehyde[1] (3.88 g, 21.7 mmol, 1.0 eq.) in MeOH (50 mL) in an ice bath, was added $NaBH_4$ (902 mg, 23.8 mmol, 1.1 eq.) in portions. The reaction mixture was allowed to be stirred for 30 min at room temperature. Upon completion of the reaction monitored by TLC analysis, water (20 mL) was added, and the reaction mixture was allowed to be stirred for 1 h. The reaction mixture was concentrated under reduced pressure to remove excess MeOH, and then extracted with CH_2Cl_2 (20 mL). The resulting aqueous layer was extracted with CH_2Cl_2 (20 mL X4). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. Purification of the crude product by flash chromatography on silica gel, using EtOAc/n-Hex as the eluant to give the titled product as a yellow solid (3.89 g, 21.7 mmol, 99%): mp 61-62 °C, [lit.[2] 56-57 ^oC]; R_f = 0.16; EtOAc/n-Hex = 1/1; ^{1}H-NMR[3] (600 MHz, 25 ^oC, $CDCl_3$, δ): 2.29 (s, 1H, -OH), 4.36 (d, *J* = 4.8 Hz, 2H, H-2), 6.33 (ddd, *J* = 15.6, 5.4, 5.4 Hz, 1H, H-3), 7.06 (d, *J* = 15.6 Hz, 1H, H-3a), 7.37 (t, *J* = 8.4 Hz, 1H, H-6), 7.54 (t, *J* = 7.8 Hz, 1H, H-5), 7.58 (d, *J* = 6.6 Hz, 1H, H-4), 7.89 (d, *J* = 7.8 Hz, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^oC, $CDCl_3$, δ): 63.1 (t, C-2), 124.4 (d, C-7), 125.7 (d, C-3a), 128.0 (d, C-6), 128.7 (d, C-4), 132.5 (s, C-3b), 133.1 (d, C-5), 134.1 (d, C-3), 147.7 (s, C-7a). EI-HRMS (m/z): $[M]^+$ calcd for $C_9H_9NO_3^+$, 179.0582; found, 179.0579 (Δ = 1.7 ppm).

[1] Preparation of *o*-nitrocinnamaldehyde, see R. E. Buckles and M. P. Bellis. *Org. Synth.* **1963**, *Coll. Vol. 4*, 722.
[2] Penjišević, J., Šukalović, V., Andrić, D., Kostić-Rajačić, S., Šoškić, V. and Roglić, G. *Arch. Pharm.* **2007,** *340*, 456.
[3] The numbering for pyrrolidinoindolines was used throughout the article for consistency.

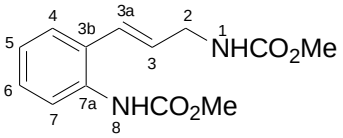
(*E*)- 3-(2-methoxycarbonylaminophenyl)-2-propenol (2a):



To a solution of 2-nitrocinnamyl alcohol (**1**) (3.41 g, 19.0 mmol, 1.0 eq.) in MeOH (200 mL), was added concentrated ammonia aqueous solution (28%, 160 mL), water (57.0 mL) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 39.1 g, 141 mmol, 7.4 eq.) in sequence. The reaction mixture was allowed to be stirred at 80 ^oC for 4 h. Upon completion of the reaction monitored by TLC analysis, the solution was cool down to room temperature, and diluted with CH_2Cl_2 (100 mL). The solid precipitate was filtered off by a short celite column, to give a two-phased resulting filtrate. After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (70 mL X 4). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was used directly without further purification.

To a mixture of the crude product and $NaHCO_3$ (3.197 g, 38.1 mmol, 2.0 eq.) in acetone (38 mL) in an ice bath, methyl chloroformate (1.8 mL, 23.2 mmol 1.2 eq.) was added slowly. The reaction mixture was allowed to be stirred for 2 h. Upon completion of the reaction monitored by TLC analysis, the reaction mixture was concentrated under reduced pressure to remove excess solvent, affording a crude residue. The crude residue was partitioned with CH_2Cl_2 (70 mL) and water (30 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (30 mL X 5) again. The combined organic layers were dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was purified by flash chromatography on silica gel, using EtOAc/n-hex as the eluant to give the titled product as a light yellow solid (3.31 g, 16.0 mmol, 84%): mp 100-102 °C; R_f = 0.18; EtOAc/n-Hex = 1/1; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.12 (s, 1H, -OH), 3.77 (s, 3H, -OC<u>H</u>$_3$), 4.33 (dd, *J* = 1.2, 4.8 Hz, 2H, H-2), 6.24 (ddd, *J* = 5.4, 5.4, 15.6 Hz, 1H, H-3), 6.70 (d, *J* = 15.6 Hz, 1H, H-3a), 6.71 (brs, 1H, N<u>H</u>CO_2Me), 7.10 (t, *J* = 7.2 Hz, 1H, H-5), 7.26 (t, *J* = 7.8 Hz, 1H, H-6), 7.36 (d, *J* = 7.2 Hz, 1H, H-4), 7.73 (br, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 52.4 (q, -NHCO$_2$<u>C</u>H$_3$), 63.2 (t, C-2), 122.3 (d, C-7), 124.7 (d, C-5), 125.3 (d, C-3a), 126.9 (d, C-4), 128.3 (d, C-6), 129.0 (s, C-3b), 132.5 (d, C-3), 134.5 (s, C-7a), 154.7(s, -NH<u>C</u>O$_2$Me). EI-HRMS (m/z): $[M]^+$ calcd for $C_{11}H_{13}NO_3^+$, 207.0895; found, 207.0890 (Δ = 2.4 ppm).

(*E*)-*N*-methoxycarbonyl-3-(2-methoxycarbonylaminophenyl)-2-propeneamine (2b):



To a solution of alcohol **2a** (707 mg, 3.41 mmol, 1.0 eq.) in ether (35 mL) in an ice bath, was slowly added PBr_3 (130 μL, 1.36 mmol, 0.4 eq.). The reaction mixture was allowed to be stirred at room temperature for 30 min. Upon completion of the reaction monitored by TLC analysis, the solution was quenched with sat. $NaHCO_3$ (17 mL), followed by addition of CH_2Cl_2 (35 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (15 mL X 4). The combined organic layers were dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a brown crude solid. The crude bromide product was used directly without further purification: R_f = 0.64; EtOAc/n-Hex = 1/1.

To a mixture of the crude bromide in acetone (11 mL) and water (4 mL) in an ice bath, NaN_3 (355 mg, 5.46 mmol, 1.6 eq.) was added. The reaction mixture was allowed to be stirred at room temperature for 4 h. Upon completion of the reaction monitored by TLC analysis, the reaction mixture was concentrated under reduced pressure to remove excess solvent, affording a crude residue. The crude residue was partitioned with CH_2Cl_2 (15 mL) and water (15 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (15 mL X 4) again. The combined organic layers were dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude azide product was used directly without further purification: R_f = 0.30; EtOAc/n-Hex = 1/5.

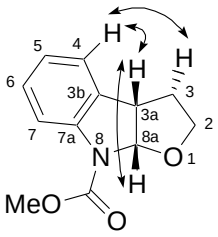
To the crude azide product in THF (17 mL) and water (3.5 mL) in an ice bath, PPh_3 (1.93 g, 7.36 mmol, 2.2 eq.) was added. The reaction mixture was allowed to be stirred at room temperature for 2 h. Upon completion of the reaction monitored by TLC analysis, the reaction mixture was partitioned with CH_2Cl_2 (30 mL) and $HCl_{(aq)}$ solution (1 N, 10 mL). After separation of the aqueous layer, the organic layer was extracted with $HCl_{(aq)}$ (1 N, 10 mL X 3) again. The combined aqueous layers was added with CH_2Cl_2 (25 mL) in an ice bath, and then adding NaOH solution (6 N, ~8 mL) until pH value had reached about 12. After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (15 mL X 5). The combined organic layers were dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a light brown crude solid. The crude amine product was used directly without further purification: R_f = 0.27; MeOH/CH_2Cl_2/Et_3N = 1/20/0.02.

To a mixture of the crude amine product and K_2CO_3 (943 mg, 6.82 mmol, 2.0 eq.) in acetone (14 mL) in an ice bath, methyl chloroformate (264 μL, 3.41 mmol, 1.0 eq.) was added slowly. The reaction mixture was allowed to be stirred at room temperature for 5 h. Upon completion of the reaction monitored by TLC analysis, the reaction mixture was concentrated under reduced pressure to remove excess solvent, affording a crude residue. The crude residue was partitioned with CH_2Cl_2 (15 mL) and water (17 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (20 mL X 4) again. The combined organic layers were dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was purified by flash chromatography on silica gel, using EtOAc/h-Hex as the eluant to give the titled product as a white solid (747 mg, 2.83 mmol, 83% over 4 steps): mp 115-117 °C; R_f = 0.31; EtOAc/n-Hex = 1/1; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 3.70 (s, 3H, -NHCO$_2$C<u>H</u>$_3$ at N-1), 3.78 (s, 3H, -NHCO$_2$C<u>H</u>$_3$ at N-8), 4.00 (br, 2H, H-2), 5.06 (br, 1H, -N<u>H</u>CO$_2$Me at N-1), 6.07 (ddd, *J* = 15.6, 5.4, 5.4 Hz, 1H, H-3), 6.61 (d, *J* = 15.6 Hz, 1H, H-3a), 6.71 (brs, 1H, -N<u>H</u>CO$_2$Me at N-8), 7.09 (dd, *J* = 7.2, 7.2 Hz, 1H, H-5), 7.26 (dd, *J* = 7.8, 7.8 Hz, 1H, H-6), 7.33 (d, *J* = 7.2 Hz, 1H, H-4), 7.73 (br, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 43.1 (t, C-2), 52.2 (q, -NHCO$_2$<u>C</u>H$_3$ at N-1), 52.4 (q, -NHCO$_2$<u>C</u>H$_3$ at N-8), 122.2 (d, C-7), 124.6 (d, C-5), 126.5 (d, C-3a), 127.0 (d, C-4), 128.4 (d, C-6), 128.8 (s, C-3b), 129.9 (d, C-3), 134.5 (s, C-7a), 154.5 (s, -NH<u>C</u>O$_2$Me at N-8); 157.0 (s, -NH<u>C</u>O$_2$Me at N-1), EI-HRMS (m/z): $[M]^+$ calcd for $C_{13}H_{16}N_2O_4^+$, 264.1110; found, 264.1105 (Δ = 1.9 ppm).

General procedure of Bicyclization Reaction:

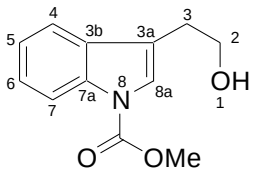
$Rh(acac)(CO)_2$ (5.1 mg, 20 μmol, 2 mol%) and $P(OPh)_3$ (21 μL, 80 μmol, 8 mol%) were dissolved in the solvent (1 mL) under argon. The resulting catalyst solution was degassed by a frozen-thawed procedure at least three times. Substrate carbamate **2** (**2b**, 261 mg, 0.98 mmol, 1.00 eq.) was placed in a 50 mL flask. The catalyst solution was transferred to the reaction flask containing the substrate by a pipette, and the total volume was adjusted to 20 mL with the solvent. The reaction flask was placed in a 300 mL stainless steel autoclave and then was pressurized up to desired pressure with CO followed by H_2. The reaction mixture was stirred at desired temperature. Upon completion of the reaction, the gas was carefully released in a good ventilated hood and the reaction mixture was concentrated under reduced pressure to give a crude residue. The crude product was purified by flash chromatography on silica gel using EtOAc/n-Hex as the eluant to give the product**.**

***cis*-3,3a,8,8a-tetrahydro-8-methoxycarbonyl-2*H*-furo[2,3-b]indole (3a):** Yellow solid (142 mg, 0.648 mmol, 65%); mp 93-95 °C; R_f = 0.21; EtOAc/n-Hex = 1/3; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.10 (dd, *J* = 5.4, 12.0 Hz, 1H, H-3α), 2.33 (dddd, *J* = 7.8, 7.8, 12.6, 12.6 Hz, 1H, H-3β), 3.45 (ddd, *J* = 4.8, 8.4, 11.6 Hz, 1H, H-2α), 3.89 (s, 3H, - $CO_2C\underline{H}_3$ at N-8), 3.94-4.01 (m, 2H, H-3a and H-2β), 6.17 (brs, 1H, H-8a), 7.02 (t, *J* = 7.2 Hz, 1H, H-5), 7.18 (d, *J* = 7.2 Hz, 1H, H-4), 7.22 (t, *J* = 7.2 Hz, 1H, H-6), 7.84 (brs, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 33.5 (t, C-3), 44.9 (d, C-3a), 52.6 (q, -O$\underline{C}H_3$), 66.2 (t, C-2), 92.9 (d, C-8a), 114.0 (d, C-7), 123.0 (d, C-5), 124.1 (d, C-4), 128.0 (d, C-6), 130.8 (s, C-3b), 142.3 (s, C-7a), 153.2 (s, -$\underline{C}O_2$Me); EI-HRMS (m/z): $[M]^+$ calcd for $C_{12}H_{13}NO_3^+$, 219.0895; found, 219.0900 (Δ = 2.3 ppm).



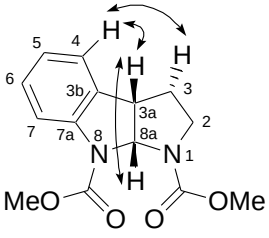
Key nOe Signals

***N*-methoxycarbonyltryptaphol (4a):** Yellow oil (44 mg, 0.201 mmol, 20%); R_f = 0.21; EtOAc/n-Hex = 1/3; ^{1}H-NMR (400 MHz, 25 ^{o}C, $CDCl_3$, δ): 1.90 (brs, 1H, -O$\underline{H}$), 2.97 (t, *J* = 6.4 Hz, 2H, H-3), 3.94 (t, *J* = 6.4 Hz, 2H, H-2), 4.02 (s, 3H, -$CO_2C\underline{H}_3$ at N-8), 7.28 (t, *J* = 7.6 Hz, 1H, H-5), 7.37 (t, *J* = 7.6 Hz, 1H, H-6), 7.50 (s, 1H, H-8a), 7.56 (d, *J* = 7.6 Hz, 1H, H-4), 8.18 (d, *J* = 5.2 Hz, 1H, H-7); ^{13}C-NMR (100 MHz, 25 ^{o}C, $CDCl_3$, δ): 28.3 (t, C-3), 53.6 (q, -$CO_2\underline{C}H_3$ at N-8), 61.7 (t, C-2), 115.1 (d, C-7), 118.0 (s, C-3a),



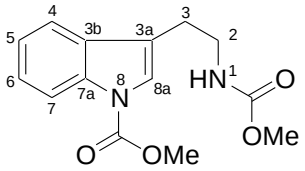
118.9 (d, C-4), 122.7 (d, C-5), 122.9 (d, C-8a), 124.6 (d, C-6), 130.4 (s, C-3b), 135.5 (s, C-7a), 151.3 (s, -$\underline{C}O_2CH_3$ at N-8); EI-HRMS (m/z): $[M]^+$ calcd for $C_{12}H_{13}NO_3^+$, 219.0895; found, 219.0901 (Δ = 2.7 ppm).

***cis*-1,2,3,3a,8,8a-hexahydro-1,8-dimethoxycarbonyl-pyrrolo[2,3-b]indole (3b):** Yellow oil (217 mg, 0.785 mmol, 80%); R_f = 0.36; EtOAc/n-Hex = 1/1; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.08 (dd, *J* = 6.0, 12.0 Hz, 1H, H-3α), 2.17 (dddd, *J* = 7.8, 7.8, 12.0, 12.0 Hz, 1H, H-3β), 2.91 (ddd, *J* = 6.0, 12.0, 12.0 Hz, 1H, H-2α), 3.73 (s, 3H, - $CO_2C\underline{H}_3$ at N-1), 3.80-3.88 (m, 1H, H-2β), 3.85 (s, 3H, - $CO_2C\underline{H}_3$ at N-8), 4.01 (dd, *J* = 7.2, 7.2 Hz, 1H, H-3a), 6.40 (d, *J* = 6.0 Hz, 1H, H-8a), 7.03 (t, *J* = 7.8 Hz, 1H, H-5), 7.16 (d, *J* = 7.2 Hz, 1H, H-4), 7.22 (t, *J* = 7.8 Hz, 1H, H-6), 7.69 (d, *J* = 7.2 Hz, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 31.3 (t, C-3), 44.8 (t, C-2), 45.4 (d, C-3a), 52.6 (q, - $CO_2\underline{C}H_3$ at N-1), 52.7 (q, - $CO_2\underline{C}H_3$ at N-8), 76.4 (d, C-8a), 115.9 (d, C-7), 123.5 (d, C-5), 123.9 (d, C-4), 128.3 (d, C-6), 131.5 (s, C-3b), 142.3 (s, C-7a), 154.0 (s, C-9), 155.2 (s, C-10); EI-HRMS (m/z): $[M]^+$ calcd for $C_{14}H_{16}N_2O_4^+$, 276.1110; found, 276.1116 (Δ = 2.2 ppm).



Key nOe Signals

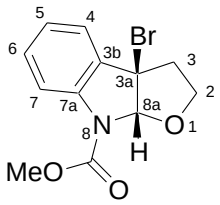
***N,N*-dimethoxycarbonyltryptamine (4b):** white solid (45 mg, 0.163 mmol, 17%); mp 76-78 °C; R_f = 0.48; EtOAc/n-Hex = 1/1; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.91 (t, *J* = 6.0 Hz, 2H, H-3), 3.51 (q, *J* = 6.0 Hz, 2H, H-2), 3.67 (s, 3H, -$CO_2C\underline{H}_3$ at N-1), 4.02 (s, 3H, -$CO_2C\underline{H}_3$ at N-8), 4.84 (brs, 1H, N$\underline{H}$), 7.26 (t, *J* = 7.2 Hz, 1H, H-5), 7.34 (t, *J* = 7.2 Hz, 1H, H-6), 7.43 (s, 1H, H-8a), 7.54 (d, *J* = 7.2 Hz, 1H, H-4), 8.16 (brs, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 25.6 (t, C-3), 40.5 (t, C-2), 52.0 (q, -$CO_2\underline{C}H_3$ at N-1), 53.7 (q, -$CO_2\underline{C}H_3$ at N-8), 115.2 (d, C-7), 118.4 (s, C-3a), 118.9 (d, C-4), 122.7 (d, C-8a), 122.9 (d, C-5), 124.8 (d, C-6), 130.3 (s, C-3b), 135.6 (s, C-7a), 151.4 (s, -$\underline{C}O_2CH_3$ at N-8), 157.0 (s, -$\underline{C}O_2CH_3$ at N-1); EI-HRMS (m/z): $[M]^+$ calcd for $C_{14}H_{16}N_2O_4^+$, 276.1110; found, 276.1104 (Δ = 2.2 ppm).



General procedure of Benzylic Bromination:

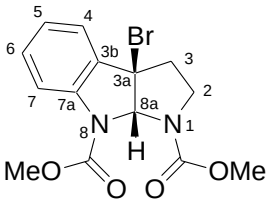
A mixture of compound **3a** (188 mg, 0.858 mmol, 1.0 eq.) and AIBN (14 mg, 0.053 mmol, 10 mol%), and 1,3-dibromo-5,5-dimethylhydantoin (DMHDT-Br_2, 246 mg, 0.860 mmol, 1.0 eq.) in CCl_4 (20 mL) was allowed to be stirred at 80 ^oC. As a white suspension has been observed, the reaction was cooled down to room temperature. The reaction mixture was concentrated under reduced pressure to remove excess volatile compounds, and then purified by flash chromatography on silica gel, using EtOAc/n-Hex as the eluant to give the titled product.

***cis*-3,3a,8,8a-tetrahydro-3a-bromo-8-methoxycarbonyl-furo[2,3-b]indole (5a):**



Colorless oil, (190 mg, 0.637 mmol, 74%); R_f = 0.68; EtOAc/n-Hex = 1/2; ^{1}H-NMR (600 MHz, 25 ^oC, $CDCl_3$, δ): 2.81 (dd, *J* = 4.2, 13.2 Hz, 1H, H-3), 2.90 (ddd, *J* = 7.8, 10.8, 12.6 Hz, 1H, H-3), 3.50 (ddd, *J* = 4.8, 9.0, 13.2 Hz, 1H, H-2), 3.91 (s, 3H, -$CO_2C\underline{H}_3$), 4.02 (t, *J* = 7.8 Hz, 1H, H-2), 6.23 (s, 1H, H-8a), 7.11 (t, *J* = 7.2 Hz, 1H, H-5), 7.31 (t, *J* = 7.2 Hz, 1H, H-6), 7.42 (d, *J* = 7.2 Hz, 1H, H-4), 7.86 (brs, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^oC, $CDCl_3$, δ): 44.9 (t, C-3), 53.2 (q, -$CO_2\underline{C}H_3$), 61.6 (s, C-3a), 68.0 (t, C-2), 100.6 (d, C-8a), 114.8 (d, C-7), 124.2 (d, C-5), 124.8 (d, C-4), 130.6 (d, C-6), 131.5 (s, C-3b), 141.4 (s, C-7a), 152.9 (s, -$\underline{C}O_2$Me); EI-HRMS (m/z): $[M]^+$ calcd for $C_{12}H_{12}BrNO_3^+$, 297.0001; found, 296.9995 (Δ = 2.0 ppm).

***cis*-1,2,3,3a,8,8a-hexahydro-3a-bromo-1,8-dimethoxycarbonyl-pyrrolo[2,3-b]indole (5b):** Colorless oil, (89 mg, 0.25 mmol, 59%); R_f = 0.27; EtOAc/n-Hex = 1/2; ^{1}H-NMR (600 MHz, 25 ^oC, $CDCl_3$, δ): 2.76 (ddd, *J* = 8.4, 12.0, 12.0 Hz, 1H, H-3), 2.83-2.91 (m, 2H, H-2 and H-3), 3.73 (s, 3H, -$CO_2C\underline{H}_3$ at N-1), 3.76-3.80 (m, 1H, H-2), 3.90 (s, 3H, -$CO_2C\underline{H}_3$ at N-8), 6.41 (s, 1H, H-8a), 7.12 (t, *J* = 7.8 Hz, 1H, H-5), 7.32 (t, *J* = 7.2 Hz, 1H, H-6), 7.38 (d, *J* = 7.8 Hz, 1H, H-4), 7.70 (d, *J* = 7.8 Hz, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^oC, $CDCl_3$, δ): 41.1 (t, C-3), 46.2 (t, C-2), 52.8 (q, -$CO_2\underline{C}H_3$ at N-1), 53.1 (q, -$CO_2\underline{C}H_3$ at N-8), 61.9 (s, C-3a), 84.1 (d, C-8a), 117.0 (d, C-7), 123.8 (d, C-4), 124.5 (d, C-5), 130.6 (d, C-6), 132.1 (s, C-3b), 141.4 (s, C-7a), 153.7 (s, -$\underline{C}O_2$Me at N-8), 154.6 (s, -$\underline{C}O_2$Me at N-1); EI-

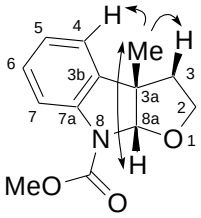


HRMS (m/z): $[M]^+$ calcd for $C_{14}H_{15}BrN_2O_4{}^+$, 354.0215; found, 354.0222 (Δ = 2.0 ppm).

General procedure for Methylation of Bromides: 5 to 6.

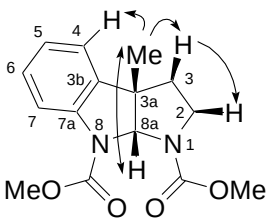
To a solution of bromide **5** (**5b**, 275 mg, 0.750 mmol, 1.0 eq.) in toluene (16 mL), was added $Zn(CH_3)_2$ (1.2 M in ether, 2.9 mL, 3.48 mmol, 4.6 eq.) in an ice bath. The reaction mixture was allowed to be stirred under reflux overnight. Upon completion of the reaction monitored by TLC analysis, the reaction was quenched with saturated NH_4Cl solution (20 mL). After separation of the organic layer, the aqueous layer was extracted with EtOAc (10 mL X 4) again. The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was purified by flash chromatography on silica gel, using EtOAc/n-Hex as the eluant to give the titled product.

***cis*-3,3a,8,8a-tetrahydro-8-methoxycarbonyl-3a-methyl-furo[2,3-b]indole (6a):** Colorless oil, (363 mg, 1.56 mmol, 69%); R_f = 0.12; EtOAc/n-Hex = 1/4; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 1.49 (s, 3H, -C<u>H</u>$_3$ at C-3a), 2.12 (ddd, *J* = 7.2, 11.4, 11.4 Hz, 1H, H-3), 2.19 (dd, *J* = 4.8, 12.0 Hz, 1H, H-3), 3.47 (ddd, *J* = 4.8, 9.0, 13.8 Hz, 1H, H-2), 3.87 (s, 3H, -CO_2C<u>H</u>$_3$), 3.98 (t, *J* = 7.8 Hz, 1H, H-2), 5.69 (s, 1H, H-8a), 7.03 (t, *J* = 7.8 Hz, 1H, H-5), 7.16 (d, *J* = 7.8 Hz, 1H, H-4), 7.22 (t, *J* = 7.2 Hz, 1H, H-6), 7.84 (brs, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 25.0 (q, -<u>C</u>H$_3$ at C-3a), 41.2 (t, C-3), 52.3 (s, C-3a), 52.8 (q, -CO_2<u>C</u>H$_3$), 67.8 (t, C-2), 98.8 (d, C-8a), 114.2 (d, C-7), 122.8 (d, C-4), 123.3 (d, C-5), 128.2 (d, C-6), 135.4 (s, C-3b), 141.8 (s, C-7a), 153.5 (s, -<u>C</u>O$_2$Me); EI-HRMS (m/z): $[M]^+$ calcd for $C_{13}H_{15}N_1O_3{}^+$, 233.1052; found, 233.1044 (Δ = 3.4 ppm).



Key NOE Signals

***cis*-1,2,3,3a,8,8a-hexahydro-1,8-dimethoxycarbonyl-3a-methyl-pyrrolo[2,3-b]indole (6b):** Colorless oil, (165 mg, 0.570 mmol, 74%); R_f = 0.46; EtOAc/n-Hex = 1/1; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 1.40 (s, 3H, -C<u>H</u>$_3$ at C-3a), 1.96 (ddd, *J* = 7.8, 12.0, 12.0 Hz, 1H, H-3β), 2.15 (dd, *J* = 6.0, 12.0 Hz, 1H, H-3α), 2.89 (ddd, *J* = 6.0, 12.0, 12.0 Hz, 1H, H-2α), 3.67 (s, 3H, -CO_2C<u>H</u>$_3$ at N-1), 3.77 (t, *J* = 7.8 Hz, 1H, H-2β), 3.84 (s, 3H, -CO_2C<u>H</u>$_3$ at N-8),



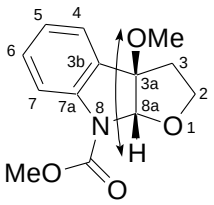
Key nOe Signals

5.90 (s, 1H, H-8a), 7.02 (t, *J* = 7.2 Hz, 1H, H-5), 7.10 (d, *J* = 7.2 Hz, 1H, H-4), 7.20 (t, *J* = 8.4 Hz, 1H, H-6), 7.66 (d, *J* = 7.8 Hz, 1H, H-7); ^{13}C-NMR (100 MHz, 25 ^{o}C, $CDCl_3$, δ): 24.9 (q, -$\underline{C}H_3$ at C-3a), 37.7 (t, C-3), 46.0 (t, C-2), 52.5 (q, -$CO_2\underline{C}H_3$ at N-1), 52.7 (q, -$CO_2\underline{C}H_3$ at N-8), 52.7 (s, C-3a), 81.9 (d, C-8a), 116.1 (d, C-7), 122.3 (d, C-4), 123.7 (d, C-5), 128.2 (d, C-6), 136.1 (s, C-3b), 141.4 (s, C-7a), 154.0 (s, -$\underline{C}O_2$Me at N-8), 155.0 (s, -$\underline{C}O_2$Me at N-1); EI-HRMS (m/z): $[M]^+$ calcd for $C_{15}H_{18}N_2O_4^+$, 290.1267; found, 290.1258 (Δ = 3.1 ppm).

General procedure for Methoxy Substitution of Bromides: 5 to 6'.

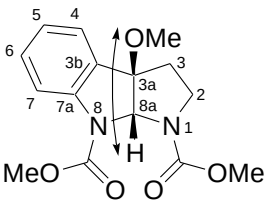
To a solution of bromide **5** (**5b**, 190 mg, 0.535 mmol, 1.0 eq.) in MeOH (12 mL), was added $Ti(O\text{-}^{i}Pr)_4$ (45 μL, 0.15 mmol, 25 mol%). The reaction mixture was allowed to be stirred under reflux for 48 h. The reaction mixture was concentrated under reduced pressure to remove excess volatile compounds, and then partitioned with CH_2Cl_2 (15 mL) and saturated $NaHCO_3$ (15 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (15 mL X 4) again. The combined organic layers were dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was purified by flash chromatography on silica gel, using EtOAc/h-Hex as the eluant to give the titled product.

***cis*-3,3a,8,8a-tetrahydro-8-methoxycarbonyl-3a-methoxy-furo[2,3-b]indole (6a'):**



Colorless oil, (423 mg, 1.70 mmol, 87% brsm value); R_f = 0.13; EtOAc/n-Hex = 1/4; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.32 (dd, *J* = 4.8, 12.0 Hz, 1H, H-3), 2.52 (ddd, *J* = 7.2, 12.0, 12.0 Hz, 1H, H-3), 3.07 (s, 3H, -OC<u>H</u>$_3$ at C-3a), 3.55 (ddd, *J* = 4.8, 9.0, 12.0 Hz, 1H, H-2), 3.89 (s, 3H, - $CO_2C\underline{H}_3$ at N-8), 4.07 (ddd, *J* = 1.2, 9.0, 9.0 Hz, 1H, H-2), 5.92 (s, 1H, H-8a), 7.11 (t, *J* = 7.2 Hz, 1H, H-5), 7.33 (d, *J* = 8.4 Hz, 1H, H-4), 7.35 (t, *J* = 7.2 Hz, 1H, H-6), 7.91 (brs, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 40.0 (t, C-3), 53.0 (q, -$CO_2\underline{C}H_3$ at N-8), 53.2 (q, -O<u>C</u>H$_3$ at C-3a), 67.6 (t, C-2), 92.4 (s, C-3a), 94.3 (d, C-8a), 114.7 (d, C-7), 123.5 (d, C-5), 124.6 (d, C-4), 127.8 (s, C-3b), 130.6 (d, C-6), 143.7 (s, C-7a), 153.2 (s, -<u>C</u>O_2Me at N-8); EI-HRMS (m/z): $[M]^+$ calcd for $C_{13}H_{15}NO_4^+$, 249.1001; found, 249.1005 (Δ = 1.6 ppm).

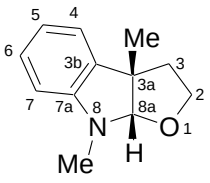
***cis*-1,2,3,3a,8,8a-hexahydro-1,8-dimethoxycarbonyl-3a-methoxy-pyrrolo[2,3-b]indole** (**6b'**): Colorless oil, (133 mg, 0.434 mmol, 81%); R_f = 0.56; EtOAc/n-Hex = 1/1; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.23-2.30 (m, 2H, H-3), 2.83 (ddd, *J* = 7.2, 12.0, 12.0 Hz, 1H, H-2), 3.02 (s, 3H, -OC<u>H</u>$_3$ at C-3a), 3.70 (s, 3H, -CO_2C<u>H</u>$_3$ at N-1), 3.82 (s, 3H, -CO_2C<u>H</u>$_3$ at N-8), 3.85-3.88 (m, 1H, H-2), 6.13 (s, 1H, H-8a), 7.07 (t, *J* = 7.2 Hz, 1H, H-5), 7.24 (d, *J* = 7.2 Hz, 1H, H-4), 7.31 (t, *J* = 7.2 Hz, 1H, H-6), 7.73 (d, *J* = 8.4 Hz, 1H, H-7); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 37.2 (t, C-3), 45.2 (t, C-2), 52.62 (q, -CO_2<u>C</u>H$_3$ at N-1), 52.72 (q, -O<u>C</u>H$_3$ at C-3a), 52.78 (q, -CO_2<u>C</u>H$_3$ at N-8), 78.0 (d, C-8a), 91.7 (s, C-3a), 116.1 (d, C-7), 123.7 (d, C-5), 124.2 (d, C-4), 128.1 (s, C-3b), 130.5 (d, C-6), 143.6 (s, C-7a), 153.6 (s, -<u>C</u>O_2Me at N-8), 155.1 (s, -<u>C</u>O_2Me at N-1); EI-HRMS (m/z): $[M]^+$ calcd for $C_{15}H_{18}N_2O_5^+$, 306.1216; found, 306.1205 (Δ = 3.6 ppm).



General procedure of Hydrogenation Reduction: 6a to 7a and 6a' to 7a'.

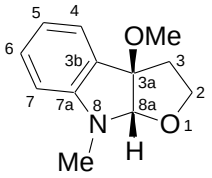
To a solution of carbamate **6a** (101 mg, 0.433 mmol, 1.0 eq.) in MeOH solution (1.5 mL), was added $NaOH_{(aq)}$ solution (1 N, 4.3 mL) at room temperature. The reaction mixture was allowed to be stirred under microwave reactor. Upon completion of the reaction monitored by TLC analysis, the reaction mixture was cooled down to room temperature, and then concentrated under reduced pressure to remove volatile substances. The syrup was partitioned with EtOAc (10 mL) and saturated NH_4Cl solution (10 mL). After separation of the organic layer, the aqueous layer was extracted with EtOAc (10 mL X 4) again. The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a residue (~134 mg). To the residue in EtOAc (2 mL), was added formalin solution (37%, 1.6 mL). After stirred at room temperature overnight, the solution was transferred into a flask with activated Pd/C (9.1 mg, 20 mol/%) and EtOAc (10 mL). The reaction mixture was allowed to be stirred under ambient hydrogen pressure, and monitored by TLC analysis. As the starting material has been disappeared (~ 2 d), the solid catalyst was removed by a short celite column, and the reaction mixture was partitioned with EtOAc (5 mL). After separation of the organic layer, the aqueous layer was extracted with EtOAc (15 mL X 4) again. The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was purified by flash chromatography on silica gel, using EtOAc/n-Hex/Et_3N as the eluant to give the titled product.

***cis*-3,3a,8,8a-tetrahydro-3a,8-dimethylfuro[2,3-b]indole (7a)**



Colorless oil, (52 mg, 0.275 mmol, 64%); R_f = 0.54; EtOAc/Hex = 1/2; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 1.47 (s, 3H, -C<u>H</u>$_3$ at C-3a), 2.06 (ddd, *J* = 7.2, 11.4, 11.4 Hz, 1H, H-3), 2.14 (ddd, *J* = 1.2, 4.8, 12.0 Hz, 1H, H-3), 2.93 (s, 3H, -C<u>H</u>$_3$ at N-8), 3.46 (ddd, *J* = 4.8, 8.4, 11.4 Hz, 1H, H-2), 3.96 (ddd, *J* = 1.2, 8.4, 8.4 Hz, 1H, H-2), 5.08 (s, 1H, H-8a), 6.38 (d, *J* = 7.8 Hz, 1H, H-7), 6.69 (t, *J* = 7.2 Hz, 1H, H-5), 7.05 (d, *J* = 7.2 Hz, 1H, H-4), 7.11 (ddd *J* = 1.2, 7.8, 7.8 Hz, 1H, H-6); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 24.7 (q, -<u>C</u>H$_3$ at C-3a), 30.8 (q, -<u>C</u>H$_3$ at N-8), 41.7 (t, C-3), 52.3 (s, C-3a), 67.3 (t, C-2), 104.8 (d, C-7), 104.9 (d, C-8a), 117.2 (d, C-5), 122.4 (d, C-4), 128.1 (d, C-6), 134.4 (s, C-3b), 150.4 (s, C-7a); EI-HRMS (m/z): $[M]^+$ calcd for $C_{12}H_{15}NO^+$, 189.1154; found, 189.1151 (Δ = 1.6 ppm).

cis-3,3a,8,8a-tetrahydro-3a-methoxy-8-methylfuro[2,3-b]indole (7a')



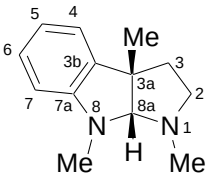
Colorless oil, (43 mg, 0.210 mmol, 70%), R_f = 0.58; EtOAc/Hex = 1/2; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.27 (ddd, J = 1.8, 5.4, 12.0 Hz, 1H, H-3), 2.44 (ddd, J = 7.8, 12.0, 12.0 Hz, 1H, H-3), 2.92 (s, 3H, -NC$\underline{H}_3$), 3.11 (s, 3H, -OC$\underline{H}_3$), 3.55 (ddd, J = 4.8, 9.0, 11.4 Hz, 1H, H-2), 4.04 (ddd, J = 1.8, 7.8, 9.0 Hz, 1H, H-2), 5.32 (s, 1H, H-8a), 6.44 (d, J = 7.8 Hz, 1H, H-7), 6.74 (t, J = 7.2 Hz, 1H, H-5), 7.19-7.23 (m, 2H, H-4 and H-6); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 30.8 (q, -N$\underline{C}H_3$), 40.5 (t, C-3), 53.1 (q, -O$\underline{C}H_3$), 67.0 (t, C-2), 93.5 (s, C-3a), 100.0 (d, C-8a), 105.8 (d, C-7), 117.5 (d, C-5), 124.4 (d, C-4), 126.2 (s, C-3b), 130.2 (d, C-6), 152.0 (s, C-7a); EI-HRMS (m/z): $[M]^+$ calcd for $C_{12}H_{15}NO^+$, 205.1103; found, 205.1102 (Δ = 0.5 ppm).

General procedure of Red-Al Reduction of 6b to 7b and 6b' to 7b'

Deoxyeseroline (7b):

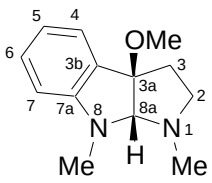
To a solution of dicarbamate **6b** (303 mg, 1.04 mmol, 1.0 eq.) in toluene (5.2 mL), was added "*Red-Al"* (2.0 mL, 70% in toluene, 6.93 mmol, 6.9 eq.) via a syringe at room temperature. The reaction mixture was allowed to be stirred under reflux for 1 h. Upon completion of the reaction monitored by TLC analysis, the reaction mixture was cooled down to room temperature, followed by addition of EtOAc (5 mL) and saturated potassium sodium tartrate solution (7 mL). The reaction mixture was kept stirring until the reaction mixture turned to be clear. After separation of the organic layer, the aqueous layer was extracted with EtOAc (10 mL X 5) again. The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was purified by flash chromatography on silica gel, using EtOAc/n-Hex/Et_3N as the eluant to give the titled product.

***cis*-1,2,3,3a,8,8a-hexahydro-1,3a,8-trimethylpyrrolo[2,3-b]indole (7b):** Pale yellow oil, (164 mg, 0.811 mmol, 78%); R_f = 0.17; EtOAc/Et_3N = 2/0.01; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 1.44 (s, 3H, -C<u>H</u>$_3$ at C-3a), 1.94-1.98 (m, 2H, H-3 X2), 2.55 (s, 3H, -C<u>H</u>$_3$ at N-1), 2.63 (ddd, *J* = 7.8, 7.8, 7.8 Hz, 1H, H-2), 2.72 (ddd, *J* = 5.4, 5.4, 9.6 Hz, 1H, H-2), 2.95 (s, 3H, -C<u>H</u>$_3$ at N-8), 4.11 (s, 1H, H-8a), 6.41 (d, *J* = 7.8 Hz, 1H, H-7), 6.68 (t, *J* = 7.2 Hz, 1H, H-5), 7.00 (d, *J* = 7.2 Hz, 1H, H-4), 7.08 (ddd *J* = 1.8, 7.2, 7.2 Hz, 1H, H-6); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 27.3 (q, -<u>C</u>H$_3$ at C-3a), 36.5 (q, -<u>C</u>H$_3$ at N-8), 38.4 (q, -<u>C</u>H$_3$ at N-1), 40.8 (t, C-3), 52.6 (s, C-3a), 53.2 (t, C-2), 97.4 (d, C-8a), 106.5 (d, C-7), 117.4 (d, C-5), 122.2 (d, C-4), 127.6 (d, C-6), 136.6 (s, C-3b), 151.9 (s, C-7a); EI-HRMS (m/z): $[M]^+$ calcd for $C_{13}H_{18}N_2^+$, 202.1470; found, 202.1473 (Δ = 1.5 ppm).



CPC-1 (7b'):

***cis*-1,2,3,3a,8,8a-hexahydro-3a-methoxy-1,8-dimethylpyrrolo[2,3-b]indole (7b'):**



Yellow oil, (116 mg, 0.531 mmol, 71%): R_f = 0.23; EtOAc/n-Hex/Et_3N = 2/1/0.01; ^{1}H-NMR (600 MHz, 25 ^{o}C, $CDCl_3$, δ): 2.12 (ddd, *J* = 4.2, 6.0, 12.0 Hz, 1H, H-3α), 2.34 (ddd, *J* = 7.2, 8.4, 14.4 Hz, 1H, H-3β), 2.56 (s, 3H, -C<u>H</u>$_3$ at N-1), 2.61 (ddd, *J* = 6.0, 8.4, 8.4 Hz, 1H, H-2α), 2.77 (ddd, *J* = 4.8, 7.2, 9.0 Hz, 1H, H-2β), 2.95 (s, 3H, -C<u>H</u>$_3$ at N-8), 3.03 (s, 3H, -OC<u>H</u>$_3$ at C-3a), 4.33 (s, 1H, H-8a), 6.49 (d, *J* = 7.8 Hz, 1H, H-7), 6.73 (t, *J* = 7.8 Hz, 1H, H-5), 7.14 (d, *J* = 7.8 Hz, 1H, H-4), 7.17 (t, *J* = 7.8 Hz, 1H, H-6); ^{13}C-NMR (150 MHz, 25 ^{o}C, $CDCl_3$, δ): 36.1 (q, -<u>C</u>H$_3$ at N-8), 38.6 (q, -<u>C</u>H$_3$ at N-1), 39.2 (t, C-3), 52.31 (q, -O<u>C</u>H$_3$ at C-3a), 52.35 (t, C-2), 91.7 (d, C-8a), 94.0 (s, C-3a), 107.7 (d, C-7), 117.8 (d, C-5), 123.9 (d, C-4), 128.0 (s, C-3b), 129.6 (d, C-6), 153.0 (s, C-7a); EI-HRMS (m/z): $[M]^+$ calcd for $C_{13}H_{18}N_2O^+$, 218.1419; found, 218.1409 (Δ = 4.6 ppm).

Computational Details: All calculations were performed at the level of B3LYP[4]/6-31++G**, using *Gausian* 09.[5] Stationary points for each reaction, i.e. reactant and product, were achieved by IRC calculation of the corresponding transition state, followed by geometry optimization. All geometries have been confirmed as either stationary points or saddle points by vibrational analyses at the same level. Thermal corrections were calculated at 1 atm 298.15 K in the gas phase. The solvent correlation were performed in the CPCM model.[6]

Four possible double cyclization pathways.

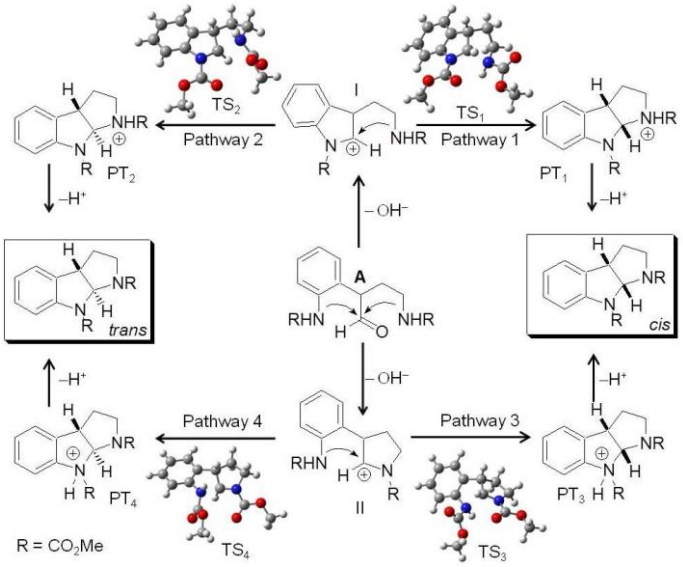


Table 1: Calculated at the level of B3LYP/++G** in the gas phase.

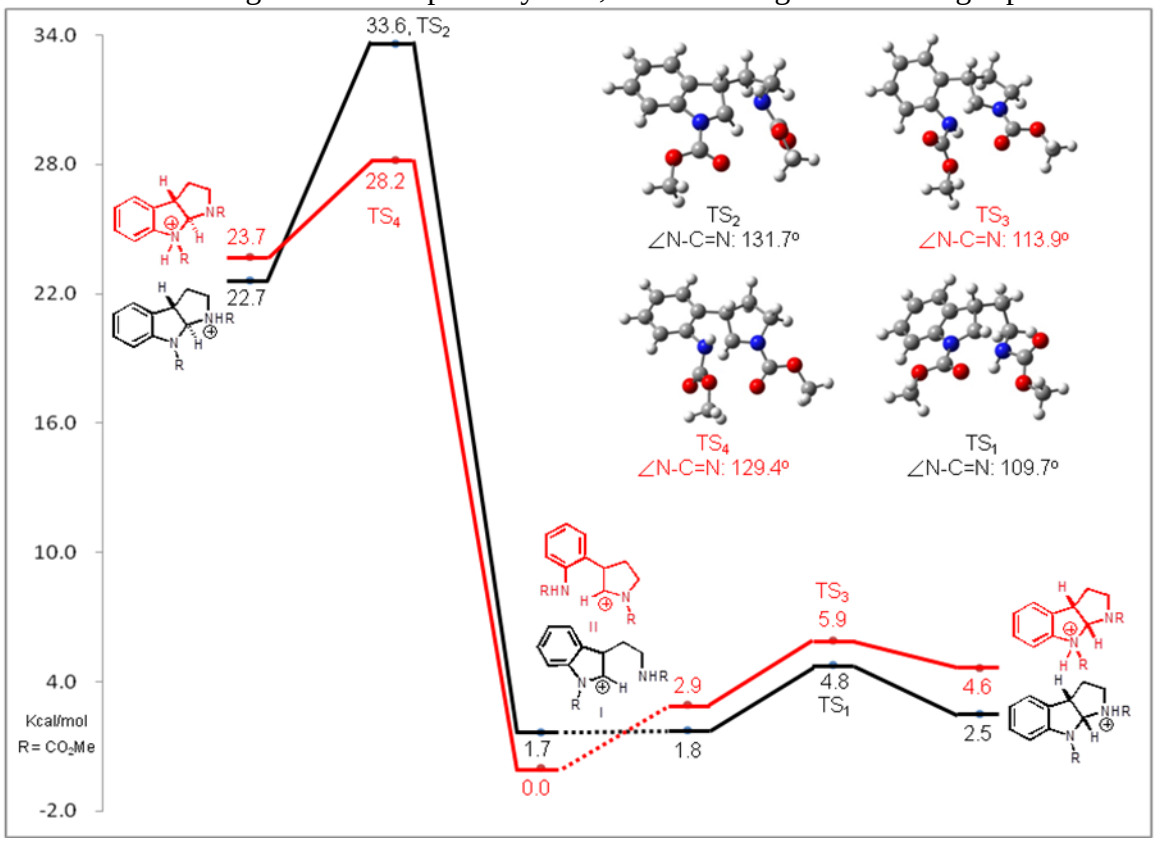
	Sum of the electric and thermal Free Energies (Hartree)			Kcal/mol		Imag.ν
	Reactant	TS	Product	$\Delta G^{\ddagger}$	ΔG	cm^{-1}
Indolinium, *cis* addn	-953.720891	-953.716086	-953.719666	3.02	0.77	-169.66
Indolinium, *trans* addn	-953.721041	-953.670089	-953.687583	31.97	20.99	-271.20
Pyrrolinium, *cis* addn	-953.719000	-953.714217	-953.716313	3.00	1.69	-149.59
Pyrrolinium, *trans* addn	-953.723692	-953.678685	-953.685888	28.24	23.72	-217.66

Table 2: Calculated at the level of B3LYP/++G** in the solvent of acetonitrile.

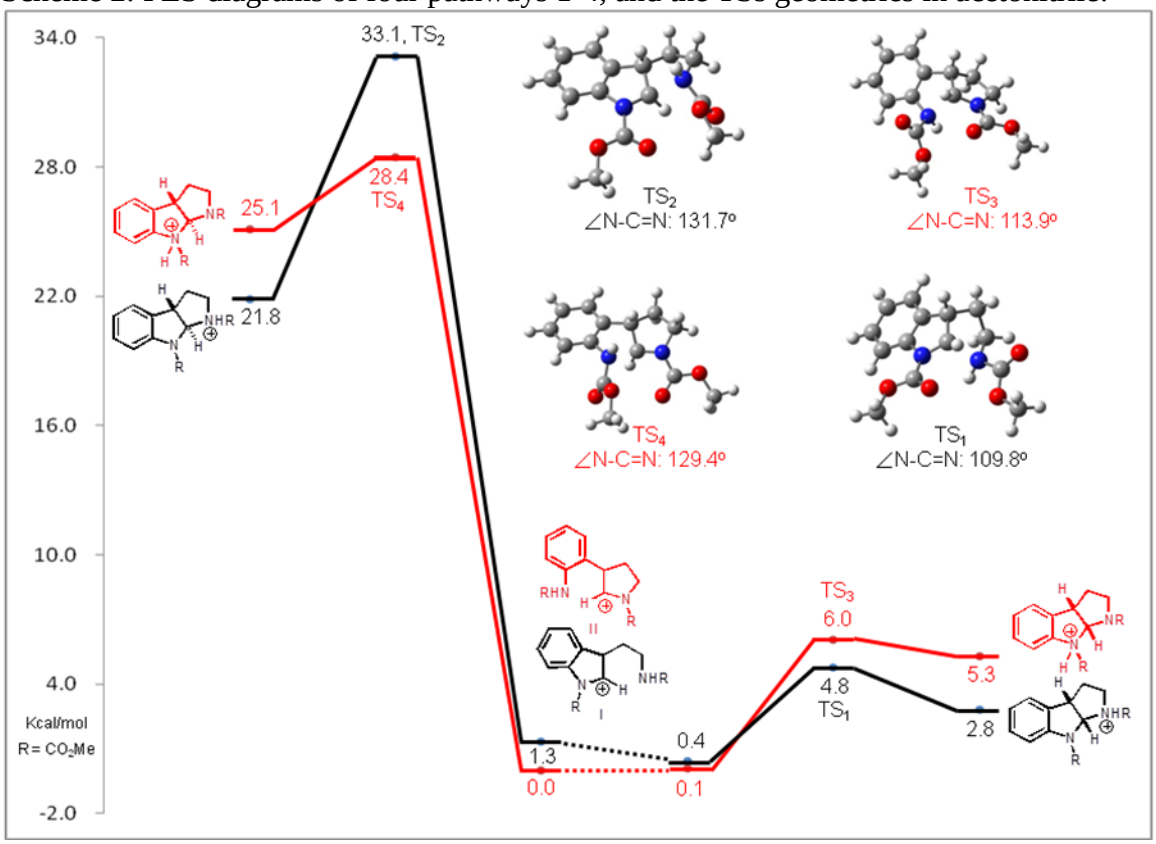
	Sum of the electric and thermal Free Energies (Hartree)			Kcal/mol		Imag.ν
	Reactant	TS	Product	$\Delta G^{\ddagger}$	ΔG	cm^{-1}
Indolinium, *cis* addn	-953.793000	-953.786101	-953.789229	4.33	2.37	-211.20
Indolinium, *trans* addn	-953.791571	-953.740930	-953.758889	31.78	20.51	-295.23
Pyrrolinium, *cis* addn	-953.793527	-953.784068	-953.785237	5.94	5.20	-202.17
Pyrrolinium, *trans* addn	-953.793686	-953.748363	-953.753698	28.44	25.09	-250.59

[4] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; (b) Lee C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
[5] *Gaussian 09*, *Gaussian, Inc.*; 340 Quinnipiac St Bldg 40 Wallingford, CT 06492 USA.
[6] Tomasi, B. Mennucci, and R. Cammi, "Quantum mechanical continuum solvation models," *Chem. Rev.*, **2005**, *105*, 2999-3093.

Scheme 1: PES diagrams of four pathways 1-4, and the TSs geometries in gas phase:

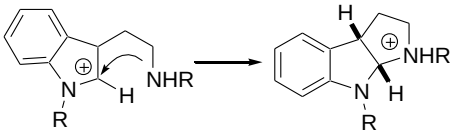


Scheme 2: PES diagrams of four pathways 1-4, and the TSs geometries in acetonitrile:



Computed Cartesian Coordinates of All Geometries:

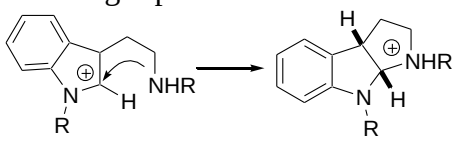
The *cis* addition of indolinium in acetonitrile:



R = COOMe

	Cyclization	of **Indolinium**	with **alkylcarbamat**		in a **cis** manner	in **acetonitrile**						
	Reactant				Transition State				Product			
C	-0.0915199549	-0.1046809115	1.1711784715	C	-0.2981958013	-0.2593955290	0.8675072672	C	-0.3660101144	-0.2913372232	0.7093557193
H	-1.0158250821	0.2049238001	1.6399678669	H	-1.1252493560	0.0658926869	1.4850526395	H	-0.9658921413	0.0473708571	1.5492091380
C	0.5241008856	-1.4530864455	1.1753377131	C	0.4753667208	-1.5348401509	1.1092688132	C	0.3997675499	-1.6212967556	0.9093070260
H	0.7464095648	-1.6570632903	2.2389285653	H	0.6215866633	-1.6182163722	2.1958774164	H	0.4270158275	-1.8816407326	1.9710668734
C	-0.4090626877	-2.5961505679	0.7038674922	C	-0.3232657133	-2.7499890323	0.6117963724	C	-0.3794243321	-2.6879207615	0.1107366013
H	0.1474657088	-3.5366534978	0.7449606812	H	0.3110303112	-3.6350435475	0.5257826310	H	0.2667396488	-3.4951923795	-0.2395950527
H	-1.2402009949	-2.6779430068	1.4091155936	H	-1.1220541898	-2.9765965431	1.3222423615	H	-1.1661248927	-3.1242358008	0.7302088028
C	-0.9489498108	-2.3743846657	-0.7125751837	C	-0.9132854170	-2.3649220747	-0.7457114152	C	-0.9793511918	-1.9278835727	-1.0648494297
H	-1.6283675899	-3.1943713177	-0.9646150195	H	-1.7275167569	-3.0272445345	-1.0424457162	H	-1.8514936919	-2.3923581335	-1.5241944931
H	-0.1350836176	-2.3721300256	-1.4404146185	H	-0.1507478059	-2.3626363009	-1.5259892163	H	-0.2435063350	-1.6963155502	-1.8356040522
N	-1.6427905635	-1.0900727554	-0.8373892890	N	-1.4150101200	-0.9641096004	-0.6329198167	N	-1.3894293984	-0.5756051194	-0.4573112733
H	-1.3470802617	-0.4697344265	-1.5816726731	H	-1.1809848420	-0.3833109251	-1.4380939929	H	-1.3187505868	0.1668878594	-1.1608479743
C	-2.9680287617	-0.9800403874	-0.4840063321	C	-2.8027825899	-0.8151851282	-0.3007968723	C	-2.8025610848	-0.5911827365	0.0308759247
O	-3.5760529286	-1.8013603335	0.1891208500	O	-3.3959313347	-1.6048917500	0.4000739808	O	-3.1002811311	-1.1445921990	1.0550529238
O	-3.4912478961	0.1690257890	-0.9548112277	O	-3.2725367393	0.3036684375	-0.8327171836	O	-3.5465419917	0.0515201751	-0.8335403642
C	-4.8713066879	0.4289748158	-0.6139240699	C	-4.6540032294	0.6391663219	-0.5247390851	C	-4.9804687786	0.1166774629	-0.5446414039
H	-5.1028095009	1.3865248771	-1.0772173166	H	-4.8370018637	1.5748012555	-1.0477529035	H	-5.3996192852	0.6847959606	-1.3705473599
H	-5.5148598394	-0.3557384041	-1.0160579338	H	-5.3128234424	-0.1485391956	-0.8917949685	H	-5.3837545651	-0.8952663224	-0.5131328356
H	-4.9890759786	0.4897922194	0.4696727891	H	-4.7693240291	0.7645288856	0.5524675524	H	-5.1294572404	0.6288150728	0.4056864157
N	0.7068284424	0.7887420012	0.6259357140	N	0.5451034700	0.7038583278	0.4022799012	N	0.5998683281	0.6880496728	0.2945213230
C	1.9077191077	0.1584000568	0.1166096395	C	1.8116661101	0.1167550453	0.0280098192	C	1.8714489762	0.0742630270	0.0633320348
C	1.8100789398	-1.2056389522	0.4244033173	C	1.7892565616	-1.2268199815	0.4223538893	C	1.7849160858	-1.2829689382	0.3963765058
C	0.3059511449	2.1913961208	0.5988908295	C	0.1382702420	2.0642638555	0.4124252623	C	0.2080127530	2.0150217790	0.2646148785
O	-0.7417971404	2.5406204201	1.0819251185	O	-0.9801745829	2.3918904488	0.7513185458	O	-0.9650669462	2.3351614035	0.4225207139
O	1.2205914366	2.9162885462	0.0029213279	O	1.1188248580	2.8615527211	0.0239662120	O	1.2198108477	2.8498991587	0.0393765761
C	2.9958017946	0.7073798261	-0.5547050681	C	2.9050618167	0.6860669312	-0.6168545160	C	3.0497537345	0.6363996785	-0.4243150302
H	3.0606368862	1.7607597832	-0.7840944531	H	2.9135483894	1.7224398896	-0.9222708675	H	3.1117835513	1.6835693056	-0.6847737018
C	2.8328584272	-2.0720741270	0.0532920545	C	2.8897413764	-2.0413352567	0.1791336308	C	2.8929097498	-2.1110096879	0.2513477398
H	2.7788306533	-3.1307033647	0.2853259655	H	2.8881464902	-3.0833533458	0.4834882267	H	2.8337423086	-3.1633660950	0.5134358833
C	4.0136171986	-0.1786645535	-0.9239185556	C	4.0064856697	-0.1463442157	-0.8559654771	C	4.1583485075	-0.2089422680	-0.5666185254
H	4.8788344046	0.2084600027	-1.4518361306	H	4.8759258402	0.2670200518	-1.3570828763	H	5.0878427954	0.2059785479	-0.9440755854
C	3.9364895317	-1.5456486212	-0.6277126565	C	4.0045070339	-1.4897029746	-0.4652251847	C	4.0886821503	-1.5656201842	-0.2342299221
H	4.7435852324	-2.2051493696	-0.9294352423	H	4.8725465072	-2.1100577839	-0.6634680161	H	4.9624942522	-2.1983600689	-0.3516419549
C	0.9493807584	4.3482909174	-0.0988089057	C	0.8219432805	4.2857490877	0.0103980188	C	0.8817182286	4.2583831344	-0.0470228538
H	1.8115499944	4.7538892039	-0.6216967920	H	1.7352162440	4.7557533127	-0.3469385952	H	1.8256178270	4.7595378251	-0.2513010490
H	0.0330376816	4.5012862649	-0.6688098536	H	-0.0097854731	4.4810435790	-0.6671311051	H	0.1722973310	4.4222597863	-0.8593504524
H	0.8600715031	4.7694133793	0.9025413317	H	0.5803327017	4.6194194046	1.0200662677	H	0.4597992544	4.5987678222	0.8994692340

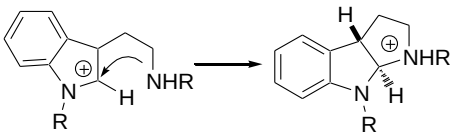
The *cis* addition of indolinium in gas phase:



R = COOMe

	Cyclization	of **Indolinium**	with **alkylcarbamate**		in a **cis** manner	in **gas**					
	Reactant				Transition State				Product		
C	-0.1532913657	-0.1394239951	1.0658293010	C	0.4721677658	0.0308625822	-0.2051102120	C	-0.3600763316	-0.2274413681	0.6963478914
H	-1.0899782556	0.1660969068	1.5144711569	H	-0.5521050351	0.2803773231	0.0439535629	H	-0.7996932164	0.0798714524	1.6452754705
C	0.4903708332	-1.4771131993	1.1243640295	C	0.8605362875	-1.0489255711	-1.1893592843	C	0.2861649340	-1.6387095276	0.6679451471
H	0.6912146022	-1.6492862858	2.1987314058	H	0.2094689675	-1.9142664223	-0.9915866541	H	0.1227345674	-2.1571310247	1.6153614508
C	-0.4145052185	-2.6438884225	0.6613910582	C	0.6281248792	-0.5648053018	-2.6301246704	C	-0.4283183924	-2.4002492633	-0.4903261721
H	0.1597901421	-3.5746446202	0.6950292661	H	1.1337716568	-1.2087347121	-3.3542540990	H	0.2697373520	-3.0063077977	-1.0714116477
H	-1.2464956521	-2.7444577390	1.3626355915	H	-0.4411816321	-0.5791697525	-2.8568007304	H	-1.1995274219	-3.0637946469	-0.0902491113
C	-0.9608016353	-2.4151830135	-0.7511217516	C	1.1603426727	0.8683518412	-2.7061744625	C	-1.0560637102	-1.3087329171	-1.3584025980
H	-1.6903444372	-3.1996412774	-0.9798489972	H	0.7708021148	1.4016135693	-3.5756498387	H	-1.9150697225	-1.6127595406	-1.9572600185
H	-0.1569079350	-2.4684845807	-1.4895148751	H	2.2519728502	0.8839053163	-2.7335935191	H	-0.3258318731	-0.8120179380	-2.0006032835
N	-1.5723688212	-1.0847250064	-0.8814314535	N	0.7498735469	1.5679789064	-1.4519533535	N	-1.4976914988	-0.2670706046	-0.3331894049
H	-1.4026868586	-0.6061308047	-1.7598664870	H	1.4866374647	2.1446364509	-1.0462383734	H	-1.5772474675	0.7044258090	-0.7023841543
C	-2.8700531946	-0.8925843450	-0.3966979421	C	-0.4859511615	2.3098530361	-1.5171847886	C	-2.8205885467	-0.6107542590	0.2928807031
O	-3.3560453557	-1.5578141920	0.4973337735	O	-1.4499193555	1.8909371090	-2.1104756347	O	-2.8908537870	-1.2098942042	1.3283959726
O	-3.4493489827	0.1428015064	-1.0184155972	O	-0.3713703031	3.4254949116	-0.8135228827	O	-3.7652947523	-0.1561847113	-0.4956373789
C	-4.7842568244	0.4901792924	-0.5670066581	C	-1.5754183938	4.2400474889	-0.6897829021	C	-5.1486046914	-0.3847177030	-0.0617847897
H	-5.0880060207	1.3209285499	-1.2008368287	H	-1.2641782372	5.1091615640	-0.1151146722	H	-5.7564246299	0.0721649967	-0.8385553017
H	-5.4533132788	-0.3622017120	-0.6933224937	H	-1.9270478830	4.5257835660	-1.6816470936	H	-5.3304595790	-1.4573559602	0.0098935491
H	-4.7577397010	0.7902278791	0.4820045454	H	-2.3427877288	3.6731859349	-0.1611723573	H	-5.3035936937	0.0995563479	0.9025121009
N	0.6639341551	0.7671788988	0.5612291032	N	1.3863153047	0.0835777870	0.7993523935	N	0.6711884091	0.6972678876	0.2446816317
C	1.8863493887	0.1458624422	0.0931216704	C	2.5599335861	-0.6840300800	0.4431999514	C	1.9403132809	0.0317647047	0.1827346899
C	1.7934928049	-1.2189964624	0.4029441578	C	2.2820858464	-1.3508668126	-0.7574446528	C	1.7495299144	-1.3313524031	0.4324989289
C	0.2420149131	2.1646943805	0.5303438067	C	1.0779420810	0.8187968590	1.9823334229	C	0.3167943366	2.0009657010	-0.0261305274
O	-0.8397470396	2.4845438577	0.9472497318	O	0.0689364020	1.4831648654	2.0591689702	O	-0.8717425584	2.3249278161	-0.1263383512
O	1.1850845920	2.9214748731	0.0132080770	O	2.0100686636	0.6576238659	2.9066177685	O	1.3458397774	2.8183096568	-0.1862794855
C	2.9898271691	0.7029210773	-0.5456238080	C	3.7832181020	-0.7970727507	1.0946664421	C	3.2029366988	0.5627427985	-0.0702160826
H	3.0518369153	1.7570078702	-0.7739996161	H	3.9862907849	-0.2827578676	2.0233155160	H	3.3486603405	1.6180244271	-0.2512049149
C	2.8374696880	-2.0747135832	0.0679059344	C	3.2479483802	-2.1665782577	-1.3371396716	C	2.8353131894	-2.2011036217	0.4349025544
H	2.7922438685	-3.1331924616	0.3050080300	H	3.0472495698	-2.7007774271	-2.2611311849	H	2.6973327921	-3.2592081717	0.6386043968
C	4.0276220564	-0.1735010382	-0.8805944118	C	4.7469170971	-1.6191469107	0.4964795107	C	4.2862632126	-0.3249825711	-0.0704174073
H	4.9056497532	0.2200935445	-1.3818550904	H	5.7126280412	-1.7312217870	0.9784353377	H	5.2811907400	0.0641682786	-0.2613627147
C	3.9560641816	-1.5395106525	-0.5814706961	C	4.4883472916	-2.2955281493	-0.6999148402	C	4.1128208107	-1.6893052271	0.1792295619
H	4.7798056340	-2.1909044804	-0.8541678482	H	5.2537626608	-2.9283290331	-1.1366707148	H	4.9710978835	-2.3527655442	0.1825577168
C	0.8870929952	4.3534817405	-0.0537593171	C	1.7736002596	1.3396694610	4.1745659910	C	1.0291993520	4.1983098915	-0.5287409062
H	1.7746135622	4.7987646144	-0.4968260394	H	2.6386250339	1.0939485705	4.7864742520	H	1.9964358004	4.6869280243	-0.6249459614
H	0.0082721074	4.5104456869	-0.6796747686	H	1.7011171013	2.4145899975	4.0055160013	H	0.4780788132	4.2305592553	-1.4694139982
H	0.7129212142	4.7325737512	0.9535280407	H	0.8541188679	0.9638968994	4.6246087527	H	0.4402856677	4.6501159577	0.2699334440

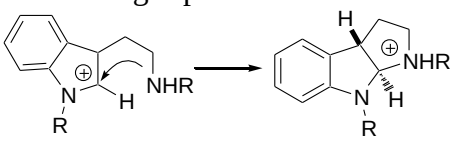
The *trans* addition of indolinium in acetonitrile:



R = COOMe

	Cyclization	of **Indolinium**	with **alkylcarbamate**		in a **trans** manne	in acetonitrile					
	Reactant				Transition State				Product		
C	-0.6707930692	-1.3654905447	-0.8564058873	C	-0.6319421416	-1.7375629114	0.0063748708	C	-0.6622071808	-1.8002893713	-0.3973553995
N	-0.8883515638	0.9067414202	-0.4887544467	N	-0.5707248871	0.5807555446	0.0285607294	N	-0.5644454112	0.5256835038	-0.2005749253
C	-2.0961936958	0.3082937892	0.0403802660	C	-1.9631791060	0.1796494598	-0.1508913572	C	-1.9484283978	0.1263770792	-0.0549475324
C	-0.0955723207	-0.0058393213	-0.9934027204	C	0.1559130234	-0.5180835727	0.3769177717	C	0.1887569325	-0.6674070261	0.1457042424
C	-1.9896460986	-1.0704751917	-0.1845430562	C	-2.0522215824	-1.2139462395	0.0417493000	C	-2.0350102168	-1.2853943817	-0.0520096147
H	-0.8125761512	-1.7613620753	-1.8754989614	H	-0.4934648444	-1.8391424673	-1.0826750195	H	-0.5976160742	-1.7522101155	-1.4971077563
H	0.8420639983	0.2804728264	-1.4493639633	H	0.7760926306	-0.4211947923	1.2615081342	H	0.3306471751	-0.7394698039	1.2301099434
C	-0.4916703540	2.3200520139	-0.5468183277	C	-0.0342413964	1.8626214180	0.3197479190	C	0.0190580212	1.7677687682	-0.0628949507
C	0.2336880412	-2.3761686152	-0.0781095403	C	0.0808084146	-2.9334411766	0.6092774583	C	0.1421783253	-3.0187347917	0.0393786044
H	-0.3591096949	-3.2885066184	0.0362059601	H	-0.3225724469	-3.8804515818	0.2491043284	H	-0.1126387046	-3.9305810573	-0.5022856552
H	0.4287541689	-1.9878161000	0.9246974030	H	0.0318779952	-2.9282410966	1.7003920073	H	0.0565470360	-3.2059483018	1.1123273766
C	1.5512633901	-2.7474790661	-0.7664820335	C	1.5598463663	-2.7590362784	0.1126092213	C	1.5813192476	-2.5663766754	-0.3341236219
H	1.3693950981	-3.0745145560	-1.7930975545	H	1.7990755635	-3.4737804052	-0.6748102843	H	1.9040528893	-2.9133320597	-1.3140420594
H	1.9832103833	-3.5930198065	-0.2206813005	H	2.2708940706	-2.8787937769	0.9277036808	H	2.3275890156	-2.8145509432	0.4172861863
N	2.5258743449	-1.6588269967	-0.8252314504	N	1.7802949387	-1.3764892782	-0.4656662178	N	1.5405636148	-0.9825263417	-0.4380921079
C	3.3037092638	-1.3495345799	0.2520106412	C	2.9509514598	-0.6736694711	-0.0518528330	C	2.7096681708	-0.3578726009	0.2746342603
H	2.8841970188	-1.3827691515	-1.7298789188	H	1.6708662154	-1.3315645199	-1.4781916982	H	1.5849005793	-0.7058999614	-1.4254713642
O	0.5789992000	2.6347780091	-0.9979891840	O	1.1257282493	1.9863017773	0.6581904637	O	1.2269272052	1.8917293027	0.1156293927
O	3.1378954061	-1.7898419193	1.3850751230	O	3.3952675011	-0.7490601999	1.0737415443	O	2.7989147240	-0.4038219710	1.4696442657
C	-3.1945342807	0.8955159187	0.6608994866	C	-3.0775923173	0.9618187600	-0.4154275168	C	-3.0814750776	0.9198326580	0.0931477167
H	-3.2625848301	1.9600179809	0.8299140283	H	-3.0046667952	2.0282035643	-0.5750556119	H	-3.0218784208	1.9991383062	0.0884459225
C	-3.0182510559	-1.9156086960	0.2176059486	C	-3.2835687576	-1.8482361514	-0.0132305628	C	-3.2612906661	-1.9147304667	0.1065159636
H	-2.9596411176	-2.9860623250	0.0505413904	H	-3.3601311347	-2.9229882935	0.1146623163	H	-3.3289294113	-2.9979952870	0.0972029551
C	-4.1365499831	-1.3505225441	0.8414029817	C	-4.4291499782	-1.0663312667	-0.2336466586	C	-4.4089463517	-1.1254488063	0.2757219713
H	-4.9512951542	-1.9919196401	1.1610246553	H	-5.4055766174	-1.5396058925	-0.2502545265	H	-5.3748720606	-1.6008124905	0.4126074665
C	-4.2192231794	0.0311877047	1.0595948556	C	-4.3218770164	0.3101233664	-0.4430662523	C	-4.3135462245	0.2681919074	0.2598476612
H	-5.0948830893	0.4464244486	1.5472343826	H	-5.2149918124	0.8984132271	-0.6273650888	H	-5.2086027013	0.8698882713	0.3840399177
O	4.2732463417	-0.4710209951	-0.0917760427	O	3.4001617479	0.0772867211	-1.0485469955	O	3.5360398601	0.0976296165	-0.6302796311
C	5.1433816503	-0.0341937192	0.9734578548	C	4.5221125188	0.9502353131	-0.7456455737	C	4.7568026707	0.7337750968	-0.1370754701
H	5.8383144058	0.6619899208	0.5063329389	H	4.7432210723	1.4566382729	-1.6823622696	H	5.3081697734	1.0027051687	-1.0339984322
H	4.5683183855	0.4680225848	1.7540968866	H	4.2295183902	1.6646111709	0.0248937084	H	4.4854553086	1.6170770715	0.4409880460
H	5.6832427720	-0.8832011555	1.3976956060	H	5.3736280489	0.3548105020	-0.4141910392	H	5.3132759654	0.0218097799	0.4721840896
O	-1.4436059239	3.0758043759	-0.0640245881	O	-0.9269983679	2.8201477699	0.1512419723	O	-0.8483032607	2.7694535273	-0.1939380791
C	-1.1925749693	4.5164770858	-0.0656608223	C	-0.4703910388	4.1789181192	0.4048380266	C	-0.2979144596	4.1099565404	-0.1196834613
H	-2.0883911250	4.9504413900	0.3703593718	H	-1.3341475079	4.8051554321	0.1945488454	H	-1.1540369023	4.7699406774	-0.2437422060
H	-0.3129411953	4.7276312799	0.5421279890	H	-0.1630854081	4.2735637645	1.4466632607	H	0.1740464012	4.2667868805	0.8510792972
H	-1.0482450172	4.8528908683	-1.0922499716	H	0.3579109500	4.4169921885	-0.2632850531	H	0.4258406060	4.2602092971	-0.9220220119

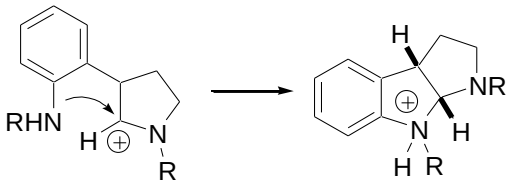
The *trans* addition of indolinium in gas phase:



R = COOMe

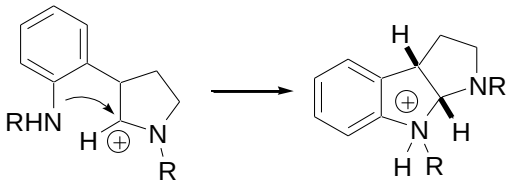
	Cyclization	of **Indolinium**	with **alkylcarbamat**	in a **trans** manne	in **gas**						
	Reactant				Transition State				Product		
C	-0.6723880374	-1.4768162753	-1.0418901732	C	-0.6382700000	-1.7425360000	-0.0174060000	C	-0.6738285943	-1.8126199724	-0.4101499724
N	-0.7257317297	0.8129586703	-0.6709687750	N	-0.5752040000	0.5767700000	-0.0463790000	N	-0.5686378996	0.5122079393	-0.2387731455
C	-1.8320287961	0.2631721340	0.0882409502	C	-1.9769180000	0.1702210000	-0.1665490000	C	-1.9560419298	0.1164335140	-0.0647859697
C	-0.0311445730	-0.1439494958	-1.2484831895	C	0.1602340000	-0.5143320000	0.3096680000	C	0.1750282468	-0.6757433784	0.1256202563
C	-1.8278637604	-1.1199561693	-0.1324230352	C	-2.0594010000	-1.2185710000	0.0604960000	C	-2.0451087293	-1.2949223444	-0.0528131546
H	-1.0477012698	-1.7552142536	-2.0441190942	H	-0.5275250000	-1.8634800000	-1.1093530000	H	-0.6113530842	-1.7677730851	-1.5133907607
H	0.7581195487	0.1197071993	-1.9359854443	H	0.7915020000	-0.4024120000	1.1868870000	H	0.3153506432	-0.7410588110	1.2122891415
C	-0.3135243637	2.1990143488	-0.8649189616	C	-0.0208970000	1.8629690000	0.2173130000	C	0.0385650276	1.7496006123	-0.1087060924
C	0.2308424584	-2.6347272264	-0.5384223877	C	0.1019400000	-2.9208460000	0.5897870000	C	0.1400274979	-3.0265764808	0.0285760497
H	-0.3356649779	-3.5588094309	-0.6843996443	H	-0.3185140000	-3.8840030000	0.2949640000	H	-0.1132955517	-3.9475696211	-0.5000722292
H	0.3772832101	-2.5185783678	0.5374308364	H	0.1133160000	-2.8755820000	1.6819630000	H	0.0611832629	-3.2081339623	1.1038977448
C	1.6049897164	-2.7635301898	-1.2347053162	C	1.5482680000	-2.7700040000	0.0017110000	C	1.5771015242	-2.5667762365	-0.3545425368
H	1.6017551704	-2.2629473225	-2.2126338148	H	1.7033060000	-3.4565700000	-0.8324340000	H	1.8938238919	-2.9163964432	-1.3373112715
H	1.8128878293	-3.8165455444	-1.4326545057	H	2.3101270000	-2.9554740000	0.7577370000	H	2.3313398690	-2.8217241972	0.3886329846
N	2.7198627947	-2.2846487512	-0.4190738389	N	1.7773820000	-1.3682390000	-0.5280790000	N	1.5344947311	-0.9911330404	-0.4468558757
C	2.7524834199	-1.0749660227	0.1833202159	C	2.9362600000	-0.6737430000	-0.0286230000	C	2.6992734041	-0.3599200381	0.2928626313
H	3.5551862182	-2.8495721927	-0.3499747751	H	1.7186690000	-1.2922110000	-1.5428340000	H	1.5867335951	-0.6900431337	-1.4259756816
O	0.5534507082	2.4779746291	-1.6497563538	O	1.1559770000	1.9761780000	0.4837810000	O	1.2557950314	1.8416242025	0.0109677644
O	1.8240604338	-0.2516972577	0.1576283616	O	3.2932680000	-0.7850090000	1.1188240000	O	2.7608700055	-0.4183578065	1.4844898808
C	-2.7734339669	0.8976933570	0.8900554530	C	-3.0977270000	0.9479510000	-0.4113180000	C	-3.0824017059	0.9145770273	0.0931146370
H	-2.7650763808	1.9656779637	1.0520687504	H	-3.0287490000	2.0107930000	-0.5954190000	H	-3.0186561239	1.9935927425	0.0803123857
C	-2.7958629177	-1.9171594722	0.4679484187	C	-3.2922820000	-1.8522320000	0.0598620000	C	-3.2714954966	-1.9207257436	0.1221076663
H	-2.8150077090	-2.9910830872	0.3112253975	H	-3.3705580000	-2.9234720000	0.2162110000	H	-3.3477723536	-3.0037016638	0.1200448799
C	-3.7555946581	-1.3026234955	1.2815603286	C	-4.4432390000	-1.0733980000	-0.1394550000	C	-4.4121103227	-1.1262536196	0.3019978068
H	-4.5204356695	-1.9072074169	1.7577053340	H	-5.4199770000	-1.5448570000	-0.1120380000	H	-5.3777015625	-1.5968268778	0.4536908076
C	-3.7414944455	0.0812892298	1.4864842902	C	-4.3420310000	0.2969910000	-0.3832080000	C	-4.3126468402	0.2664980135	0.2783853289
H	-4.4940624928	0.5374189799	2.1210897794	H	-5.2410610000	0.8807930000	-0.5511050000	H	-5.2050384488	0.8697991388	0.4107363678
O	3.9024550871	-0.8724536260	0.8334343488	O	3.4445460000	0.0854560000	-0.9860000000	O	3.5401951246	0.0843483465	-0.6062307976
C	4.0534875078	0.3855818773	1.5328175706	C	4.5294880000	0.9764330000	-0.5897630000	C	4.7170656872	0.7952539180	-0.0968471334
H	5.0459971443	0.3392473618	1.9769773341	H	4.8421270000	1.4604790000	-1.5121910000	H	5.3083504349	1.0161673088	-0.9818776836
H	3.9839417784	1.2177243756	0.8299895823	H	4.1476710000	1.7019920000	0.1294660000	H	4.3804074181	1.7071035062	0.3966389152
H	3.2891498769	0.4803947385	2.3062241356	H	5.3421440000	0.3938880000	-0.1546590000	H	5.2582825397	0.1506719098	0.5960095697
O	-1.0121692198	3.0007195984	-0.0892338575	O	-0.9213250000	2.8227540000	0.1089970000	O	-0.8138578361	2.7641769318	-0.1819285212
C	-0.6942920872	4.4237385243	-0.1972814341	C	-0.4422230000	4.1788040000	0.3536790000	C	-0.2337291087	4.0964117481	-0.1223628212
H	-1.3636712866	4.9104873055	0.5080955111	H	-1.3168880000	4.8105080000	0.2160730000	H	-1.0840146809	4.7724384978	-0.1848530067
H	0.3500509410	4.5820618492	0.0730759691	H	-0.0591560000	4.2531300000	1.3718850000	H	0.3011987141	4.2266163434	0.8191141690
H	-0.8799355019	4.7601914553	-1.2177589661	H	0.3393660000	4.4254880000	-0.3659300000	H	0.4432156192	4.2432857553	-0.9651613335

The *cis* addition of pyrrolinium in acetonitrile:



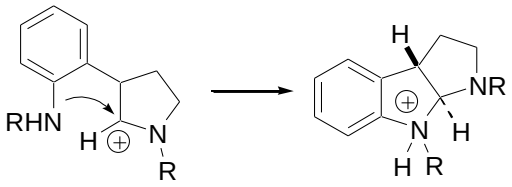
	Cyclization	of **Pyrrolinium**	with **arylcarbamate**		in a **cis** manner		in **acetonitrile**				
	Reactant				Transition State				Product		
C	-0.4699006484	-0.8488662480	0.7381936411	C	-0.3040611896	-0.6790077258	0.6383474463	C	-0.2938692776	-0.6608308188	0.6419572706
H	-0.4993451371	-0.0505293399	1.4715383281	H	-0.4023799986	-0.0624752789	1.5262386706	H	-0.4721595117	-0.1803875725	1.6028769726
C	0.6909672924	-1.7194018165	0.4074693645	C	0.7538654861	-1.7586643863	0.5434923442	C	0.7583949938	-1.7811925451	0.6452514579
H	0.7827679036	-2.3908640837	1.2771323501	H	0.7585891754	-2.3039610533	1.4944084848	H	0.7988913526	-2.2328701841	1.6401622637
C	2.0118735201	-1.0012046147	0.2341966085	C	2.0779709435	-1.0896988328	0.2906845437	C	2.0450121703	-1.0915035426	0.2812762793
C	2.0588359905	0.2970841077	-0.2976376564	C	1.9694952570	0.2048739330	-0.2170762701	C	1.8261335586	0.1850335040	-0.2253049903
N	0.8225524735	0.9347964962	-0.6648963914	N	0.5817552332	0.6436173231	-0.3821385921	N	0.3730070097	0.5121958748	-0.2275350972
H	0.5074865256	0.8002548995	-1.6216238713	H	0.2522573711	0.5590948205	-1.3481876054	H	-0.0051783013	0.4709786526	-1.1832471736
C	0.4526631611	2.1536068534	-0.1168913998	C	0.2359971787	1.9581847096	0.1331523984	C	0.0632129722	1.8734763144	0.3301672606
O	0.8736717122	2.5977543163	0.9388943262	O	0.6183922195	2.3469178210	1.2102936541	O	0.2334676838	2.1195601382	1.4919169105
O	-0.4757882181	2.7409614486	-0.8912045943	O	-0.5576452676	2.5672261603	-0.7284116406	O	-0.3513748822	2.6339050170	-0.6517438026
C	-1.0298606192	3.9821881801	-0.3961203714	C	-1.0995773051	3.8547665756	-0.3155046495	C	-0.7076602710	4.0104717338	-0.3056916419
H	-1.7496326252	4.2919045794	-1.1515688586	H	-1.6959921579	4.1891261223	-1.1607514745	H	-1.0120470772	4.4596394537	-1.2471416907
H	-0.2419667516	4.7294915697	-0.2876374995	H	-0.2821470693	4.5473032705	-0.1135792973	H	0.1659936211	4.5126516216	0.1094582079
H	-1.5259098663	3.8176534371	0.5621283270	H	-1.7185281811	3.7169974893	0.5717114228	H	-1.5289329959	3.9955671914	0.4106258849
N	-1.5679808094	-1.2580149444	0.1742029756	N	-1.4498509167	-1.1256304075	0.0644169629	N	-1.4533696528	-1.1901540581	0.0285253373
C	-1.3678041455	-2.4490840847	-0.7128572969	C	-1.2955490645	-2.4360078892	-0.6310172063	C	-1.2991396306	-2.6086451982	-0.3825594984
C	0.1648934184	-2.5253054418	-0.8204958164	C	0.2260138205	-2.6638298466	-0.6092470275	C	0.2236509855	-2.8007334392	-0.3996447064
C	-2.8489029908	-0.6450754585	0.4622649955	C	-2.6656614213	-0.4586314646	0.2706931552	C	-2.6391280652	-0.4993350852	0.1237984397
O	-2.9477277021	0.3094470351	1.1938195022	O	-2.7384727696	0.6114255067	0.8482352087	O	-2.6954280844	0.6574916302	0.5298986862
O	-3.7909013353	-1.2944521260	-0.1846710066	O	-3.6725174341	-1.1510146368	-0.2507835069	O	-3.6762934353	-1.2300019858	-0.2953197009
C	-5.1550873058	-0.8103893497	-0.0031677777	C	-4.9929075681	-0.5611206871	-0.1212566687	C	-4.9674264330	-0.5725765185	-0.2864393835
H	-5.7659095058	-1.4720213896	-0.6118585520	H	-5.6622782378	-1.2625389342	-0.6143266732	H	-5.6645982863	-1.3165538955	-0.6667874057
H	-5.2221657371	0.2203073777	-0.3519935690	H	-5.0137067809	0.4103718949	-0.6168639800	H	-4.9459298030	0.3036242225	-0.9364980286
H	-5.4264620384	-0.8811964186	1.0503078375	H	-5.2494675555	-0.4555379394	0.9336138134	H	-5.2323567168	-0.2807122341	0.7309159893
C	3.2123070939	-1.6410058119	0.5687495999	C	3.3468792642	-1.6408362319	0.4762276093	C	3.3556569008	-1.5668350989	0.3428539675
H	3.1858430308	-2.6445126768	0.9831992369	H	3.4534084333	-2.6441718274	0.8762439213	H	3.5631047239	-2.5566427209	0.7362323818
C	3.2836087885	0.9440265367	-0.4854646476	C	3.0782425642	0.9742008426	-0.5554282945	C	2.8307826608	1.0212276834	-0.6919527613
H	3.2997975656	1.9479529278	-0.8968598783	H	2.9702042501	1.9785148721	-0.9511250542	H	2.6244586372	2.0088519596	-1.0902205935
C	4.4724141146	0.2979128443	-0.1441978710	C	4.3438958053	0.4118066017	-0.3657269358	C	4.1387712644	0.5302218348	-0.6227012940
H	5.4214801121	0.8039601415	-0.2893039156	H	5.2273323804	0.9896529010	-0.6160181831	H	4.9582975878	1.1506183005	-0.9690561854
C	4.4362253808	-0.9974213329	0.3808038025	C	4.4756615544	-0.8843270505	0.1470392781	C	4.3956490604	-0.7474705365	-0.1088120615
H	5.3580231637	-1.5038473837	0.6487228432	H	5.4647807631	-1.3058811164	0.2945202350	H	5.4182983455	-1.1071628865	-0.0595020601
H	0.5216273769	-3.5552667565	-0.8096406233	H	0.4782733292	-3.7121941863	-0.4459762568	H	0.5103808535	-3.8237073728	-0.1516128170
H	0.5065250721	-2.0553911471	-1.7455137550	H	0.6716485795	-2.3552253835	-1.5586457038	H	0.6239897296	-2.5671291868	-1.3903694395
H	-1.8138815563	-3.3112936792	-0.2124913752	H	-1.8462735533	-3.1911352288	-0.0651463602	H	-1.7903927420	-3.2557658578	0.3508765976
H	-1.8761957041	-2.2802016470	-1.6608700113	H	-1.7070671377	-2.3776457367	-1.6388597684	H	-1.7587229452	-2.7701733946	-1.3581945750

The *cis* addition of pyrrolinium in gas phase:



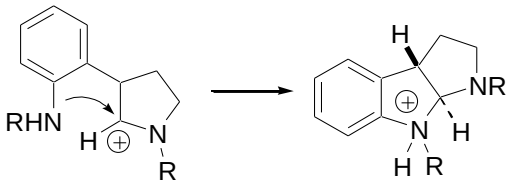
	Cyclization	of **Pyrrolinium**	with **arylcarbamate**		in a **cis** manner	in **gas**					
	Reactant				Transition State				Product		
C	-0.4820349478	-0.7587219406	0.6720503507	C	-0.3210277390	-0.6923257382	0.6303288732	C	-0.3096778468	-0.6702926642	0.6734897315
H	-0.5158937377	0.1267586589	1.3026472543	H	-0.4047849733	-0.0204029162	1.4794124007	H	-0.5281229353	-0.1969083363	1.6315243609
C	0.6864698683	-1.6577103243	0.4734815351	C	0.7529982253	-1.7501228668	0.5264446380	C	0.7715712467	-1.7689480167	0.7113796633
H	0.7764879596	-2.2155785673	1.4218153095	H	0.7696065145	-2.2968049963	1.4790080481	H	0.8574909420	-2.1601967252	1.7299440687
C	2.0050432774	-0.9565699322	0.2244006278	C	2.0786643823	-1.0783234758	0.2738309752	C	2.0316046692	-1.0718637417	0.2671911569
C	2.0396688628	0.2961466154	-0.4049068821	C	1.9847521484	0.2131621347	-0.2484228148	C	1.7724478367	0.1885346260	-0.2607368475
N	0.7960933789	0.9366332690	-0.7707196194	N	0.6135163051	0.6769782293	-0.4405714685	N	0.3214893699	0.5129364259	-0.1754078861
H	0.6590731489	1.0623468776	-1.7706978629	H	0.2942121551	0.6097833192	-1.4096338220	H	-0.1139685034	0.5137741664	-1.1060657782
C	0.3538407787	2.0466862943	-0.0282706830	C	0.2551315906	1.9738253084	0.1081048888	C	0.0403586153	1.8673882057	0.4455492002
O	0.5292480757	2.1643699323	1.1677778103	O	0.6042267175	2.3210672875	1.2057502194	O	0.1376404721	2.0370336033	1.6235574482
O	-0.3365697699	2.8791154830	-0.8152914119	O	-0.5186074049	2.6090312971	-0.7606705100	O	-0.2455346949	2.6973361646	-0.5299323263
C	-0.9652462974	4.0066929929	-0.1494886284	C	-1.1099985713	3.8592178248	-0.2952823464	C	-0.6240924685	4.0563009384	-0.1298867599
H	-1.4467474297	4.5699952083	-0.9464224533	H	-1.6388619663	4.2554587804	-1.1591226858	H	-0.7699367096	4.5875878675	-1.0670983124
H	-0.2085377027	4.6104722839	0.3531351616	H	-0.3222478663	4.5384296276	0.0317996887	H	0.1795938347	4.4972276799	0.4602181288
H	-1.6984085736	3.6463912821	0.5742610853	H	-1.7963922726	3.6430031953	0.5244307464	H	-1.5480044986	4.0046503835	0.4465530284
N	-1.5720026573	-1.2463971777	0.1445140770	N	-1.4594149778	-1.1424565261	0.0682553784	N	-1.4391318710	-1.2357077282	0.0218396217
C	-1.3516871934	-2.5473401315	-0.5641553164	C	-1.3051756360	-2.4599019064	-0.6141476035	C	-1.2901487773	-2.6890262693	-0.2240493263
C	0.1832720529	-2.6101899126	-0.6555741014	C	0.2208671054	-2.6621343226	-0.6208507251	C	0.2342118344	-2.8652517412	-0.2544142535
C	-2.8547896997	-0.5813507712	0.2979692271	C	-2.6824821409	-0.4489011998	0.2519757822	C	-2.6122980343	-0.5038887455	-0.0099608507
O	-2.9454358526	0.4999013035	0.8170492672	O	-2.7285192606	0.6459626525	0.7688207915	O	-2.6223966553	0.6946404998	0.2435822984
O	-3.7991328532	-1.3473119895	-0.2111487271	O	-3.6908587703	-1.1678277736	-0.2215036891	O	-3.6564347591	-1.2458989031	-0.3714615099
C	-5.1625085199	-0.8231881994	-0.1362010050	C	-5.0162137287	-0.5760418180	-0.0931708920	C	-4.9289126277	-0.5533631210	-0.4840150412
H	-5.7785726334	-1.5906107815	-0.5984482166	H	-5.6909306874	-1.3080432255	-0.5312965813	H	-5.6399560016	-1.3227619260	-0.7778201259
H	-5.2188255732	0.1167136748	-0.6863004182	H	-5.0509997878	0.3678487025	-0.6387616953	H	-4.8621725330	0.2268363412	-1.2439530461
H	-5.4341703833	-0.6713015239	0.9088725799	H	-5.2436249343	-0.4118394569	0.9607971979	H	-5.2005384661	-0.1173588723	0.4782438283
C	3.2107899328	-1.5753917597	0.5772289290	C	3.3404222374	-1.6362381911	0.4857898695	C	3.3495358569	-1.5315909484	0.2719503432
H	3.1957619321	-2.5396807317	1.0779582985	H	3.4366980378	-2.6350805346	0.9008830864	H	3.5927861600	-2.5070095960	0.6816515722
C	3.2621323023	0.9115545981	-0.6877171220	C	3.1095120579	0.9687966170	-0.5666541188	C	2.7430677496	1.0205546246	-0.8026568292
H	3.2731838947	1.8864822855	-1.1659025735	H	3.0169028483	1.9763787652	-0.9595078185	H	2.5041103577	1.9967120050	-1.2119319235
C	4.4576591900	0.2801750120	-0.3444747790	C	4.3675779971	0.3999236029	-0.3527414252	C	4.0575046166	0.5434385809	-0.7925589702
H	5.4045041072	0.7630082642	-0.5628061664	H	5.2596320171	0.9711311154	-0.5870024932	H	4.8516297465	1.1603645169	-1.1992375979
C	4.4312414784	-0.9638863117	0.2911168609	C	4.4810170513	-0.8928471059	0.1698382393	C	4.3550294264	-0.7160362536	-0.2569476353
H	5.3583741958	-1.4544195900	0.5690136100	H	5.4638127517	-1.3203335719	0.3395899147	H	5.3827804754	-1.0641349908	-0.2513696700
H	0.5614036595	-3.6267062068	-0.5387222682	H	0.4969331410	-3.7080096313	-0.4769752982	H	0.5413017091	-3.8677772060	0.0493760931
H	0.5250486410	-2.2327162761	-1.6230350024	H	0.6474860193	-2.3381472288	-1.5750833400	H	0.6148861075	-2.6903881426	-1.2657934175
H	-1.7881540207	-3.3412352403	0.0484308295	H	-1.8364181233	-3.2155799006	-0.0290136773	H	-1.7588637774	-3.2579515649	0.5869610801
H	-1.8624378916	-2.5291796680	-1.5267825763	H	-1.7469854625	-2.4242180732	-1.6109467330	H	-1.7757038670	-2.9638301366	-1.1612545164

The *trans* addition of pyrrolinium in acetonitrile:



	Cyclization	of **Pyrrolinium**	with **arylcarbamate**		in a **trans** manne	in **acetonitrile**					
	Reactant				Transition State				Product		
C	0.2531110065	-0.6558317687	0.6860161936	C	0.6893336250	-1.6823931118	0.4641032017	C	0.6976139204	-1.8082478108	0.3853930231
N	-1.8359904754	-1.2518733556	-0.1180586366	N	-1.5172706641	-1.0823543335	0.1958088955	N	-1.5075173199	-1.1188207535	0.2335697641
C	-1.6542798516	-2.1498118284	1.0686663882	C	-1.4877159360	-2.5200377797	0.6545896982	C	-1.5094057624	-2.6260085303	0.3055642955
C	-0.8344136061	-0.4518684044	-0.3067740968	C	-0.2624579536	-0.6735073243	-0.1327336045	C	-0.1966063028	-0.6986019166	-0.1461559979
C	-0.1512725254	-1.9982874865	1.3645358528	C	-0.0734481900	-2.9876197725	0.2086473197	C	-0.0624276458	-3.0405425806	-0.1004262196
H	0.1379903743	0.1634626470	1.4106383543	H	0.6097791654	-1.5510875332	1.5559205383	H	0.5822923165	-1.8053477001	1.4820437715
H	-0.8456274212	0.2839761687	-1.1026026046	H	-0.1219663468	-0.2477182648	-1.1234899189	H	-0.0872158419	-0.5358992541	-1.2238615445
C	-3.0291128064	-1.1988606032	-0.9505885285	C	-2.6385956141	-0.3925211907	-0.2855448413	C	-2.5941030295	-0.3478000939	-0.0944300844
C	1.6471940403	-0.5551782874	0.0852933329	C	2.0516859392	-1.1737152232	0.0943210908	C	2.0582793877	-1.2294608598	0.1132485746
C	2.4626487074	0.5667025998	0.3307611508	C	2.0586365941	0.2285850197	0.2114183202	C	1.9423630366	0.1640258281	0.2174947697
N	1.9975568926	1.6691652355	1.1062857541	N	0.7456542616	0.7773171143	0.6074106034	N	0.4945522956	0.5522694110	0.4466263086
C	0.9923320891	2.5063603321	0.6936669784	C	0.3217363095	2.0343687646	0.0302311412	C	0.0957823844	1.8541185436	-0.2071598980
H	2.6423221768	2.0623058265	1.7818564396	H	0.5948604667	0.7792771576	1.6208124563	H	0.2916463674	0.6240386084	1.4540485000
O	-3.1006732899	-0.4721662144	-1.9095471549	O	-2.5443369548	0.7064015023	-0.8026397937	O	-2.4886299850	0.8272502231	-0.4360047449
O	0.2279239793	2.2806085753	-0.2386223298	O	0.5766084642	2.3416694388	-1.1094950551	O	0.2427804530	2.0214659683	-1.3841851682
O	0.9418498465	3.5997379892	1.4771038646	O	-0.3952861359	2.6978082930	0.9201288346	O	-0.3362869251	2.6554616685	0.7311257487
C	-0.1054644045	4.5509841847	1.1805361763	C	-1.0131034954	3.9334247693	0.4601364830	C	-0.8209892482	3.9651660302	0.2967884750
H	0.0184454199	5.3457675996	1.9140257644	H	-1.5365502306	4.3234134239	1.3296340686	H	-1.0966897009	4.4746462519	1.2161582812
H	-1.0849227147	4.0810829408	1.2871351479	H	-1.7088275720	3.7079817956	-0.3487723761	H	-1.6848564941	3.8212939746	-0.3519847464
H	0.0138828534	4.9423457906	0.1686488420	H	-0.2409339505	4.6261887704	0.1245207783	H	-0.0208501928	4.4911136333	-0.2236117595
O	-3.9202630893	-2.0355013053	-0.4712717790	O	-3.7535629172	-1.0817096748	-0.0754470898	O	-3.7452087734	-1.0144010128	0.0435347240
C	-5.1888439667	-2.1146352676	-1.1888379800	C	-4.9889149698	-0.4550280045	-0.5116283080	C	-4.9553446929	-0.2665236740	-0.2280384645
H	-5.7709130778	-2.8497978045	-0.6394083474	H	-5.7716915898	-1.1576053530	-0.2345855023	H	-5.7666348967	-0.9703548759	-0.0524212123
H	-5.0039314691	-2.4417382313	-2.2121514994	H	-4.9664470105	-0.3046258168	-1.5916578165	H	-4.9610372920	0.0761282970	-1.2639680891
H	-5.6720372489	-1.1375768644	-1.1751732029	H	-5.1212401051	0.4976871572	0.0028914251	H	-5.0301871425	0.5846763138	0.4506772591
C	3.7749277054	0.6035068720	-0.1580429724	C	3.1983745380	0.9874353553	-0.0136414269	C	3.0076061189	1.0416120494	0.1346365796
C	2.1571291567	-1.5914090593	-0.7115730010	C	3.2237152769	-1.8360638232	-0.2525885374	C	3.3187009021	-1.7783151144	-0.0957415407
C	3.4598080956	-1.5479840532	-1.2083389383	C	4.3827391690	-1.0842067792	-0.4889646522	C	4.4193870176	-0.9158053121	-0.2000576172
C	4.2776743766	-0.4537364222	-0.9151476485	C	4.3713358737	0.3086405866	-0.3692706317	C	4.2698376567	0.4699454129	-0.0812741801
H	0.4017579780	-2.8312992207	0.9277918882	H	-0.0733620777	-3.2782208317	-0.8460642468	H	0.0220969878	-3.1751289273	-1.1828435996
H	0.0491990285	-1.9811496307	2.4357784662	H	0.2889774172	-3.8204221095	0.8133027181	H	0.2391531743	-3.9637523157	0.3961592332
H	-2.2971760159	-1.7731470861	1.8673156424	H	-1.6181700192	-2.5706504749	1.7383986992	H	-1.7445603101	-2.9376692656	1.3261211340
H	-1.9626099150	-3.1595872046	0.8033093483	H	-2.3037362067	-3.0511377146	0.1678310915	H	-2.2677564598	-3.0217407679	-0.3698450361
H	4.3915682824	1.4723670188	0.0507859661	H	3.1880469586	2.0678732113	0.0757961344	H	2.8886782579	2.1159426167	0.2214226057
H	5.2962331102	-0.4129119524	-1.2877624070	H	5.2772112532	0.8762742688	-0.5543386151	H	5.1363146178	1.1173308984	-0.1615437669
H	3.8334385459	-2.3670365017	-1.8142821346	H	5.3009482912	-1.5913320735	-0.7675784796	H	5.4066469224	-1.3320219553	-0.3724157639
H	1.5383592127	-2.4551222280	-0.9351512894	H	3.2380343363	-2.9174014392	-0.3401316023	H	3.4462001988	-2.8526590085	-0.1741536139

The *trans* addition of pyrrolinium in gas phase:

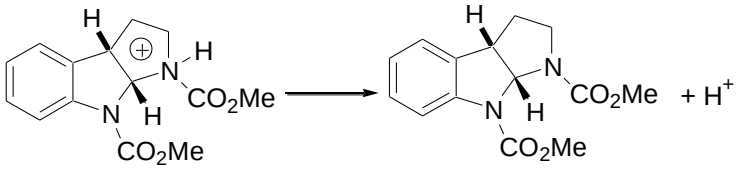


	Cyclization	of **Pyrrolinium**	with **arylcarbamate**	in a **trans** manne	in **gas**						
	Reactant				Transition State				Product		
C	0.2500657288	-0.6596700739	0.7392302377	C	0.6890995044	-1.6751677027	0.4803198175	C	0.7014665607	-1.8310167765	0.3637015217
N	-1.8309809169	-1.2565070636	-0.0970907108	N	-1.5208266901	-1.0862307831	0.2106387757	N	-1.5027563013	-1.1480182705	0.2323777719
C	-1.6588176177	-2.1679667899	1.0804295610	C	-1.4890924139	-2.5248133376	0.6602813316	C	-1.5117592175	-2.6550259527	0.2101739262
C	-0.8340218459	-0.4389046394	-0.2553910483	C	-0.2703020358	-0.6674746259	-0.1099931311	C	-0.1964058974	-0.7186893179	-0.1536367977
C	-0.1587923023	-2.0114285291	1.3990897651	C	-0.0695095236	-2.9841921571	0.2195317137	C	-0.0487146971	-3.0533423549	-0.1700589424
H	0.1533888225	0.1536358243	1.4719121047	H	0.6052326564	-1.5498008751	1.5747123276	H	0.5682429093	-1.8601247085	1.4590426702
H	-0.8393791366	0.3129142082	-1.0375869370	H	-0.1303468508	-0.2068504228	-1.0859258658	H	-0.0869995155	-0.5532945356	-1.2327385034
C	-3.0114673625	-1.2030094903	-0.9610113882	C	-2.6500798491	-0.3812801743	-0.2654368848	C	-2.5912548553	-0.3365581559	-0.0131367081
C	1.6343196225	-0.5574868062	0.1136778466	C	2.0534856794	-1.1697628885	0.1075394399	C	2.0628586017	-1.2328911876	0.1255674265
C	2.4469600371	0.5731872684	0.3294476804	C	2.0702040314	0.2330331715	0.2255555264	C	1.9292681349	0.1584789411	0.2470345836
N	2.0064425837	1.6808213537	1.1102607816	N	0.7696632720	0.7953154218	0.6365778564	N	0.4721356372	0.5353083239	0.4327687968
C	0.9492706260	2.4952958995	0.7554204922	C	0.3379752966	2.0511406703	0.0437624372	C	0.0751900594	1.8267632510	-0.2728240361
H	2.7127170235	2.1403889569	1.6734107158	H	0.6297747205	0.8126897953	1.6504275520	H	0.2330827027	0.6365053899	1.4290912320
O	-3.0640938847	-0.4618658592	-1.9034912453	O	-2.5463416633	0.7377159676	-0.7212042057	O	-2.4640009336	0.8638336837	-0.2244666901
O	0.0693049829	2.1907168432	-0.0396300643	O	0.5882313631	2.3397855498	-1.0959637545	O	0.1644188185	1.9236969972	-1.4579212967
O	1.0081202758	3.6477462452	1.4360155077	O	-0.3746097233	2.7170714617	0.9395325002	O	-0.2598852774	2.6870243340	0.6570932680
C	-0.0558765617	4.5981158731	1.1887739822	C	-1.0286357267	3.9301254095	0.4589729613	C	-0.8042540230	3.9641250498	0.1858274925
H	0.1882221879	5.4592556155	1.8079673246	H	-1.5142734266	4.3501402236	1.3368069025	H	-0.9489866298	4.5512059890	1.0892931641
H	-1.0172074900	4.1718250657	1.4819660184	H	-1.7559708696	3.6596705525	-0.3074557881	H	-1.7499074882	3.7657355729	-0.3189703717
H	-0.0768534327	4.8722006725	0.1327943619	H	-0.2811331146	4.6141843861	0.0560269082	H	-0.0902260088	4.4367667060	-0.4888587179
O	-3.9023631366	-2.0636719592	-0.5137611071	O	-3.7554213020	-1.0982212256	-0.1168241079	O	-3.7410734026	-1.0052580126	0.0549623178
C	-5.1541715205	-2.1408199867	-1.2686655363	C	-4.9930958822	-0.4650374403	-0.5522241691	C	-4.9517942457	-0.2229733582	-0.1209933087
H	-5.7430758315	-2.8925300858	-0.7489495055	H	-5.7696804967	-1.1956342319	-0.3371300679	H	-5.7637022173	-0.9426283996	-0.0376996669
H	-4.9380335420	-2.4422908857	-2.2940522537	H	-4.9399901335	-0.2495199792	-1.6200567667	H	-4.9496983991	0.2513092665	-1.1033915131
H	-5.6454761483	-1.1675189362	-1.2514829449	H	-5.1517775480	0.4551586830	0.0116387289	H	-5.0214231911	0.5344274212	0.6614215544
C	3.7453919740	0.6076000271	-0.1959881629	C	3.2113196233	0.9825945236	-0.0244024499	C	2.9872442867	1.0478248080	0.1972503033
C	2.1278129322	-1.5955097435	-0.6917756964	C	3.2162410279	-1.8405197938	-0.2535202223	C	3.3345757864	-1.7640082459	-0.0607840784
C	3.4151763473	-1.5520586195	-1.2233643537	C	4.3766844918	-1.0970516997	-0.5067475392	C	4.4277690746	-0.8886139402	-0.1278274567
C	4.2330777831	-0.4515959762	-0.9581860408	C	4.3745035360	0.2955264585	-0.3934093833	C	4.2604726774	0.4933004331	0.0049155629
H	0.4070357369	-2.8383703689	0.9657300322	H	-0.0632212866	-3.2725206921	-0.8368629480	H	0.0642014654	-3.1583304186	-1.2538748251
H	0.0293049905	-2.0093024634	2.4736147510	H	0.2940218587	-3.8223860992	0.8175157000	H	0.2432780646	-3.9930081108	0.3019789731
H	-2.3169436396	-1.8106312933	1.8773189853	H	-1.6266998153	-2.5865556334	1.7439445891	H	-1.7889351106	-3.0287702880	1.1993160528
H	-1.9636926792	-3.1766199899	0.8031039616	H	-2.3053135405	-3.0549389262	0.1712138319	H	-2.2479328350	-3.0105102548	-0.5121320412
H	4.3655715367	1.4810958531	-0.0170262691	H	3.2066676734	2.0646776236	0.0465943421	H	2.8542232009	2.1209623471	0.2865372683
H	5.2404930805	-0.4071506046	-1.3588818590	H	5.2801317331	0.8566122224	-0.5979343163	H	5.1218418938	1.1502615055	-0.0492896225
H	3.7774523669	-2.3724725248	-1.8338046465	H	5.2876012120	-1.6103965207	-0.7969451545	H	5.4232405469	-1.2915980567	-0.2832193648
H	1.5089394100	-2.4655540173	-0.8932073399	H	3.2255392123	-2.9222299118	-0.3420374873	H	3.4798238253	-2.8354856746	-0.1520399445

Proton affinity calculations:[7]

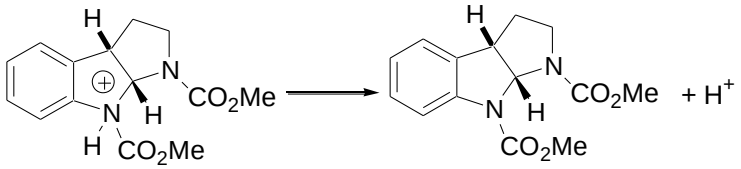
$(B\text{-}H)^+ \rightarrow B + H^+$; Proton affinity = ΔE_{ele}+ ZPVE + 5RT/2

For the cis tricyclic product: Proton affinity (Kcal/mol):



PT1

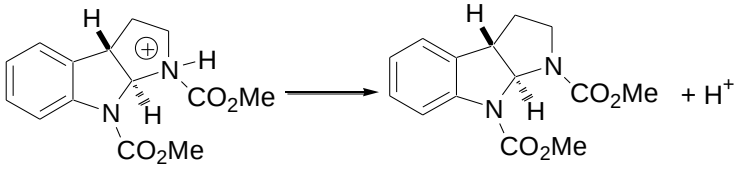
P. A. = 627.5 * ((-953. 325218)-(-953.671746))+ 5/2*1.987*298.15/1000= 218.9



PT3

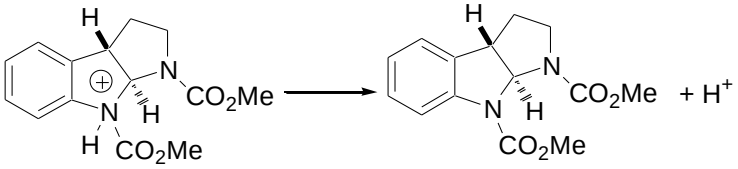
P. A. = 627.5 * ((-953. 668688)-(-953.325218))+ 5/2*1.987*298.15/1000= 217.0

For the trans tricyclic product: Proton affinity (Kcal/mol):



PT2

P. A. = 627.5 * ((-953. 640847)-(-953.288930))+ 5/2*1.987*298.15/1000= 222.3



PT4

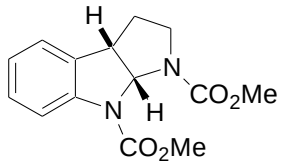
P. A. = 627.5 * ((-953. 638898)-(-953.288930))+ 5/2*1.987*298.15/1000= 221.1

Experimental proton affinity values: [8]

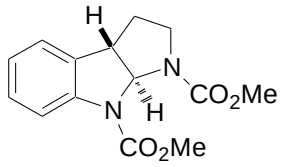
$Me_2N\text{-}CO_2Me$: 210.1 Kcal/mol.
Glutamic acid: 218.4 Kcal/mol

[7] J. S.Rao and G. N.Sastry, "*Proton affinity of five-membered heterocyclic amines: Assessment of computational procedures*", *Int. J. Quantum Chem.*, **2006**, *106*, 5, 1217-1224.

[8] For an excellent reference for the experimental proton affinity values, see E. P. L. Hunter and S. G. Lias, "*Evaluated Gas Phase Basicities and Proton Affinities of Molecules: An Update*", *J. Phys. Chem. Ref. Data*, **1998**, *27*, 3, 413-656.



cis in gas phase				cis in acetonitrile			
	X	Y	Z		X	Y	Z
C	-0.4260478711	-0.3813517695	0.7370383221	C	0.4206966948	-0.3249912649	-0.7610621863
H	-0.8244818227	-0.1123276183	1.7144236059	H	0.8361774930	0.0353804232	-1.6996439432
C	0.2426534748	-1.7938090579	0.6318395744	C	-0.3315778359	-1.6948836142	-0.8389069017
H	0.1872490293	-2.3259251481	1.5864681296	H	-0.3161909848	-2.0923392274	-1.8573734805
C	-0.5748712992	-2.5337666497	-0.4641366683	C	0.4423730010	-2.6257848016	0.1333708047
H	0.0552681889	-3.1809513486	-1.0805485317	H	-0.2200342882	-3.3232248932	0.6520431689
H	-1.3513078226	-3.1523736651	-0.0009030389	H	1.1882875336	-3.2068023165	-0.4182501665
C	-1.2330241312	-1.3967990663	-1.2648044326	C	1.1504761040	-1.6534725352	1.0881632618
H	-2.1499904720	-1.6835177172	-1.7759157072	H	2.0422352247	-2.0626213743	1.5570934882
H	-0.5401322067	-0.9771559630	-2.0038392414	H	0.4753704258	-1.2963943161	1.8737158858
N	-1.5154915115	-0.3926700531	-0.2258827453	N	1.5030038841	-0.5285179168	0.1957688070
C	-2.7873748166	-0.0620967131	0.1891127668	C	2.7939276435	-0.2208486883	-0.1518547562
O	-3.0898464599	0.3402653454	1.2982356713	O	3.1400091119	0.3409997818	-1.1857757804
O	-3.6865540119	-0.2352747984	-0.8181649601	O	3.6665959530	-0.5995117325	0.8133172809
C	-5.0436452441	0.1007040272	-0.4814190416	C	5.0595360117	-0.3470521365	0.5384983458
H	-5.6183976957	-0.0869275969	-1.3886187763	H	5.5939641332	-0.7229412590	1.4100297359
H	-5.4047139474	-0.5243656165	0.3390487585	H	5.3760845318	-0.8794571682	-0.3608923283
H	-5.1152604433	1.1510604928	-0.1903263209	H	5.2369612395	0.7233382294	0.4157871999
N	0.6601552539	0.5670836741	0.3637441098	N	-0.6069782785	0.6361701464	-0.2705816295
C	1.8675110737	-0.1182134292	0.0818169811	C	-1.8530146187	-0.0127659031	-0.0552559048
C	1.6714260529	-1.4978367446	0.2487151612	C	-1.7361372858	-1.3679528757	-0.3977587234
C	0.4051360654	1.9174148682	0.4441497412	C	-0.3010502209	1.9727694543	-0.2229245581
O	-0.6613942630	2.3830407456	0.8027221469	O	0.7877100655	2.4298205356	-0.5512588921
O	1.4707740415	2.6712568024	0.0742617783	O	-1.3232836229	2.7270739740	0.2291678773
C	3.1157355444	0.3819944685	-0.3039673715	C	-3.0659694540	0.5037857129	0.4138719432
H	3.2731840079	1.4413964280	-0.4415070889	H	-3.1657018898	1.5431440934	0.6893101226
C	2.7185980262	-2.3900930065	0.0465874674	C	-2.8302915410	-2.2206853567	-0.2916165171
H	2.5618082643	-3.4571105185	0.1838000278	H	-2.7344810211	-3.2684937083	-0.5631711726
C	4.1599658312	-0.5287361293	-0.5051731038	C	-4.1593585706	-0.3665153596	0.5170506144
H	5.1337804336	-0.1492992308	-0.8013105897	H	-5.1062429759	0.0254395434	0.8769690397
C	3.9758510411	-1.9028436481	-0.3314573415	C	-4.0542562332	-1.7158575288	0.1668269949
H	4.8022228229	-2.5892041353	-0.4878870684	H	-4.9161890761	-2.3704922012	0.2506298334
C	1.2581013625	4.0938058346	0.1477550004	C	-1.0774515191	4.1487525419	0.2963032723
H	2.1977277047	4.5395710390	-0.1788477513	H	-2.0033249144	4.5777327592	0.6767277572
H	0.4396721774	4.3925301818	-0.5108955213	H	-0.2501114305	4.3599881090	0.9763485181
H	1.0242396223	4.3936047164	1.1716540581	H	-0.8526292897	4.5435628736	-0.6962650113
Sum of electronic and zero-point Energies			-953.325218				-953.341871
Sum of electronic and thermal Energies			-953.307290				-953.323907
Sum of electronic and thermal Enthalpies			-953.306346				-953.322963
Sum of electronic and thermal Free Energies			-953.372357				-953.389231

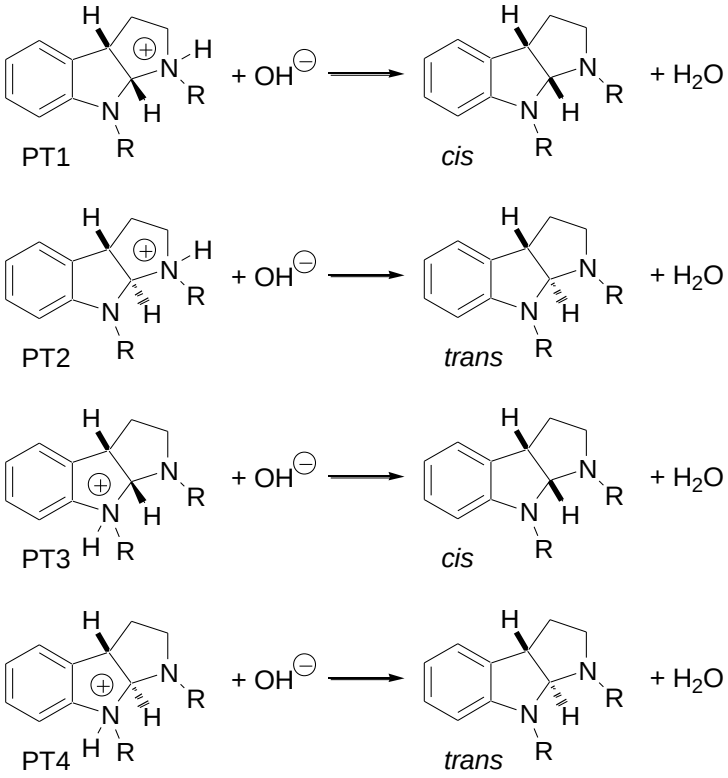


trans in gas phase				trans in acetonitrile			
	X	Y	Z		X	Y	Z
C	-0.7091873496	-1.5328357786	-0.5190415361	C	-0.4441489286	-1.6049419736	-0.6190354835
N	-0.5253881921	0.7161779637	0.0025720006	N	-0.5817007176	0.6040378013	0.0897286163
C	-1.8984959184	0.3483391343	0.1819907628	C	-1.8905880102	0.0216448134	0.2263372049
C	0.2062510998	-0.5633063355	0.2155288423	C	0.3246267869	-0.5773729838	0.2023141786
C	-2.0477247721	-1.0493622487	-0.0246415324	C	-1.8365743599	-1.3579958824	-0.0992333108
H	-0.6646546783	-1.2336765238	-1.5810460872	H	-0.4443698368	-1.2239198292	-1.6546466243
H	0.1736068040	-0.7330652472	1.3031421012	H	0.3105869878	-0.8410725983	1.2698995428
C	0.0402342206	1.9304380279	-0.3006308627	C	-0.2394891015	1.8737102204	-0.2845404219
C	0.0763298317	-2.8347472781	-0.4265091275	C	0.5109128365	-2.7904574629	-0.6122679184
H	-0.2629599302	-3.6191590219	-1.1082923233	H	0.2856132290	-3.5539866886	-1.3599686671
H	0.0891279299	-3.2376731373	0.5927311636	H	0.5729406145	-3.2661385675	0.3723230339
C	1.4774897362	-2.2892938234	-0.8332593846	C	1.8270789034	-2.0351751449	-0.9531584096
H	1.5824006471	-2.2643993125	-1.9233324191	H	1.9370918127	-1.9122050590	-2.0346794154
H	2.3057537668	-2.8712361694	-0.4277767129	H	2.7192407776	-2.5283228616	-0.5687679428
N	1.5203122056	-0.8896386485	-0.2858123575	N	1.6752880065	-0.6791085201	-0.3032945018
C	2.6051279754	-0.4543507046	0.4521369505	C	2.6907654427	-0.1442248160	0.4545651576
O	1.2132401554	2.1077542701	-0.5696961467	O	0.8968519799	2.2478249962	-0.5480122932
O	2.5401463080	0.2998364510	1.4049889546	O	2.5271476131	0.5664007144	1.4388480660
C	-2.9904696369	1.1325789194	0.5464565680	C	-3.0736359821	0.6091274552	0.6664018079
H	-2.8821287126	2.1963075196	0.7071588546	H	-3.1165739165	1.6591786072	0.9238664165
C	-3.2846563413	-1.6564985460	0.1303735748	C	-2.9720978064	-2.1486215322	0.0059798651
H	-3.3992661237	-2.7234341506	-0.0396164639	H	-2.9352195693	-3.2022780118	-0.2544926380
C	-4.3862837456	-0.8726790378	0.5079128286	C	-4.1688494089	-1.5641670770	0.4521813685
H	-5.3584202844	-1.3360977219	0.6456160305	H	-5.0629238149	-2.1723922889	0.5494786982
C	-4.2334674885	0.5011675588	0.7037397287	C	-4.2131894028	-0.2042718125	0.7705599408
H	-5.0915739982	1.1005005577	0.9940217939	H	-5.1433326174	0.2374046120	1.1157720181
O	3.7599223053	-0.9791517092	-0.0288610681	O	3.9017931333	-0.4872948522	-0.0362960574
C	4.9519326483	-0.5533178870	0.6548797568	C	5.0445269773	0.0051068825	0.6943633346
H	5.7721823175	-1.0531578072	0.1395580633	H	5.9119459967	-0.3834076801	0.1626621601
H	5.0591958436	0.5316721869	0.5891558336	H	5.0545926503	1.0969269132	0.6938127938
H	4.9205727804	-0.8490243473	1.7064850206	H	5.0302223747	-0.3645152717	1.7217455689
O	-0.8893231785	2.9239714748	-0.2902687556	O	-1.3238446833	2.6833972833	-0.3343947721
C	-0.3897170603	4.2199623207	-0.6657137190	C	-1.0776079273	4.0391708793	-0.7615779068
H	-1.2515187425	4.8853274969	-0.6092398490	H	-2.0543301724	4.5211679207	-0.7510700890
H	0.3932783900	4.5429233348	0.0238911353	H	-0.3979837916	4.5409079509	-0.0698472413
H	0.0120141877	4.1976432201	-1.6815706190	H	-0.6569730754	4.0531118643	-1.7691770790
Sum of electronic and zero-point Energies			-953.288930				-953.305808
Sum of electronic and thermal Energies			-953.270910				-953.287784
Sum of electronic and thermal Enthalpies			-953.269966				-953.286839
Sum of electronic and thermal Free Energies			-953.335680				-953.352565

Calculations of the Energy changes in the neutralization in the gas phase:

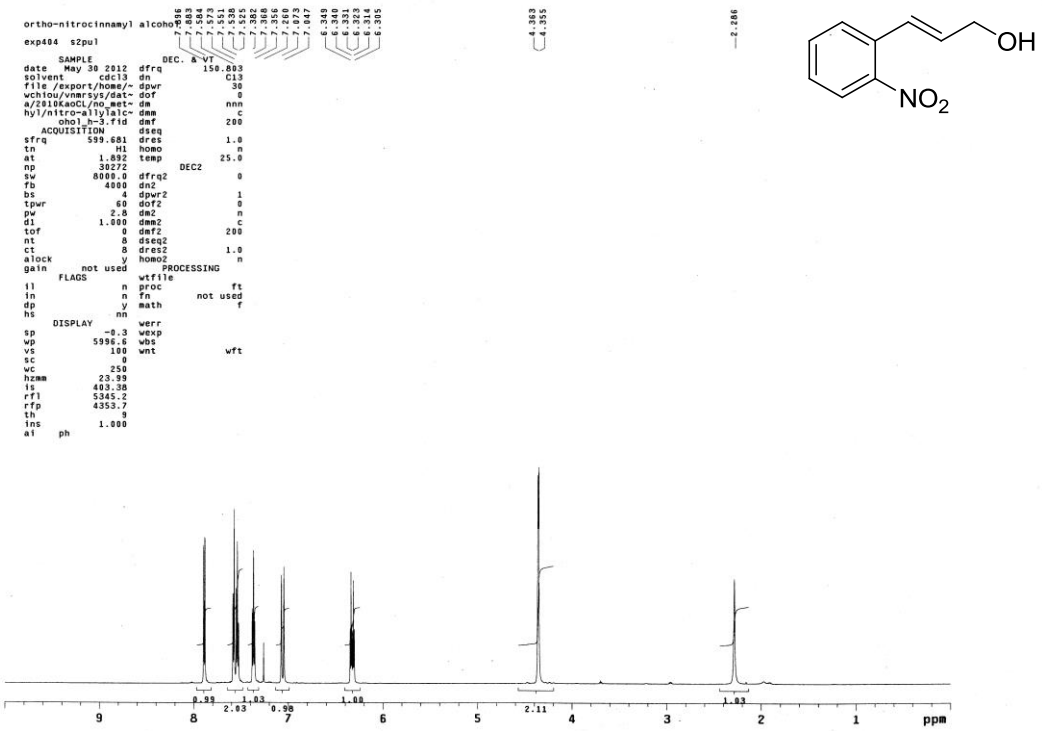
$$(PT\text{-}H)^{+} + OH^{-} \rightarrow PT + H_2O$$

R = CO_2Me

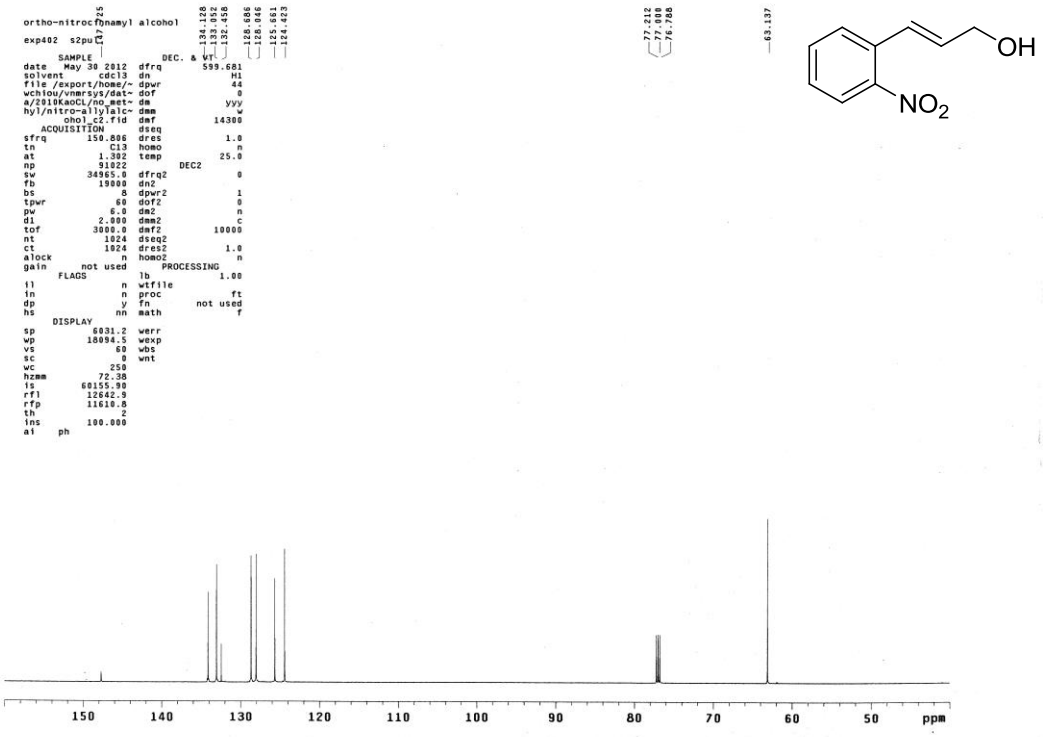


	Protonated tricycl	Hydroxide	Sum	Neutral tricycle	water	Sum	ΔG, Kcal/mol
PT1 cis	-953.719666	-75.811565	-1029.531231	-953.372357	-76.430498	-1029.802855	-170.4
PT2 trans	-953.687583	-75.811565	-1029.499148	-953.335680	-76.430498	-1029.766178	-167.6
PT3 cis	-953.716313	-75.811565	-1029.527878	-953.372357	-76.430498	-1029.802855	-172.5
PT4 trans	-953.685888	-75.811565	-1029.497453	-953.335680	-76.430498	-1029.766178	-168.6

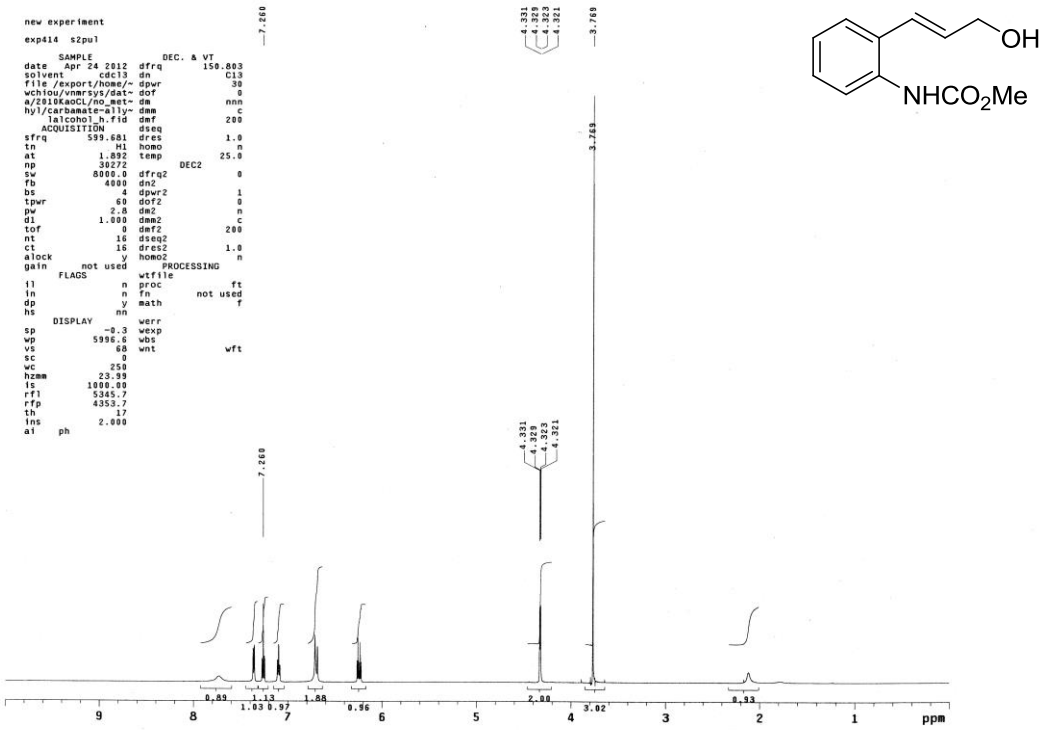
1 ^{1}H-NMR



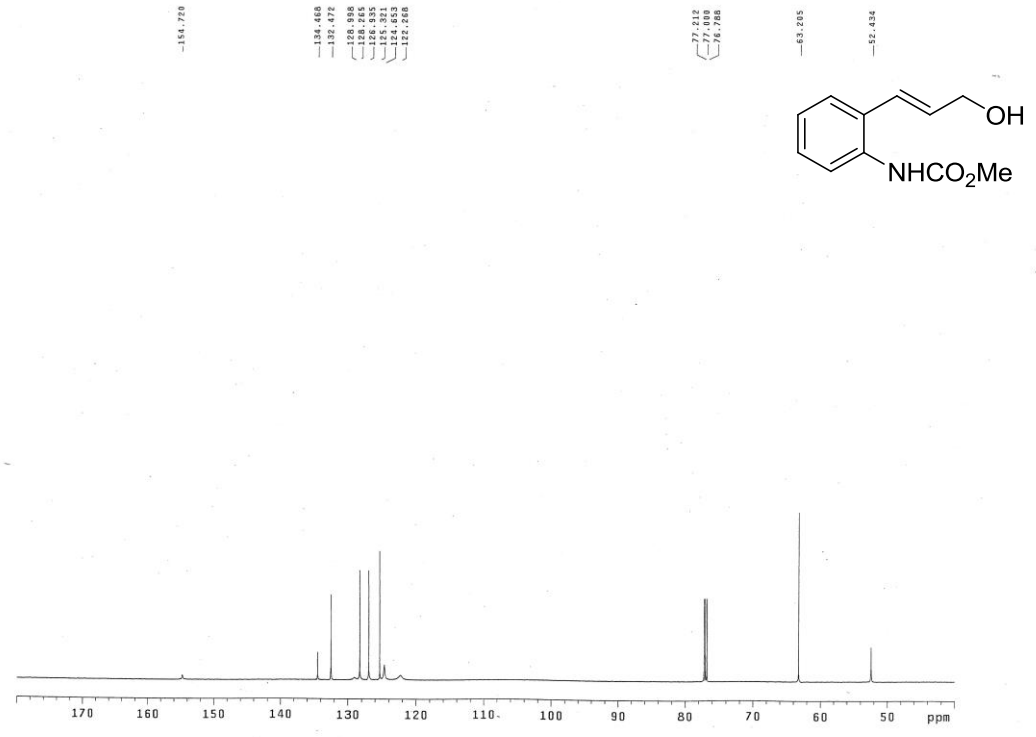
1 ^{13}C-NMR



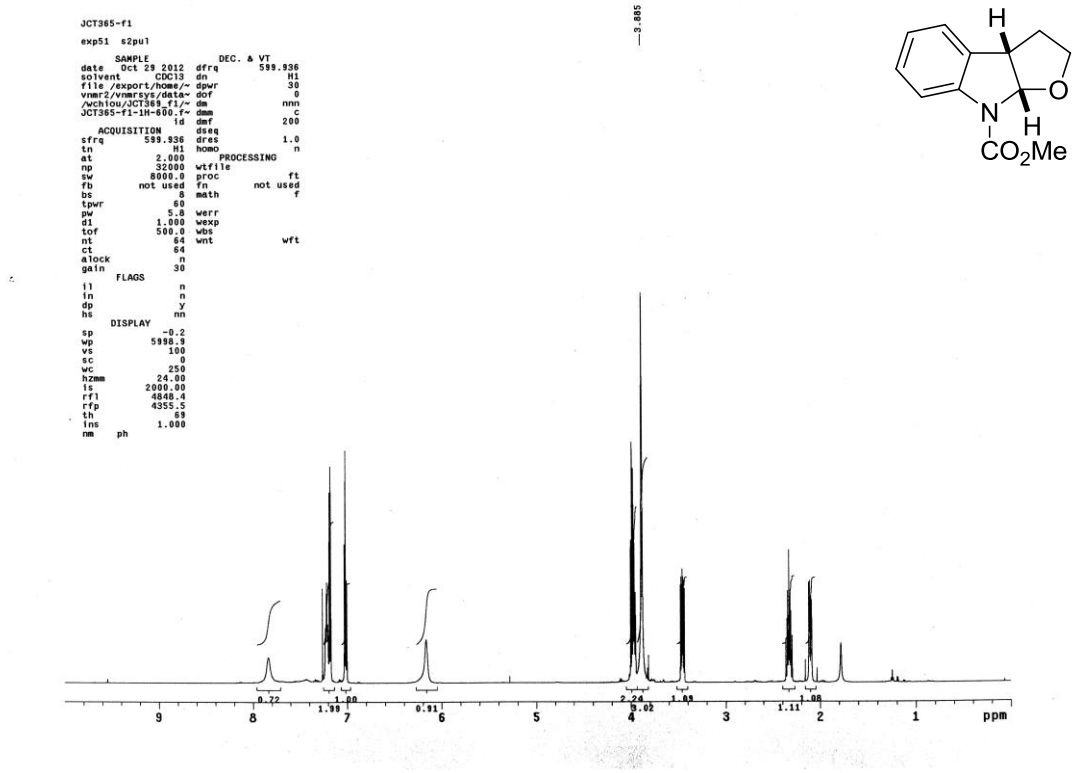
2a ^{1}H-NMR



2a ^{13}C-NMR



3a ^{1}H-NMR



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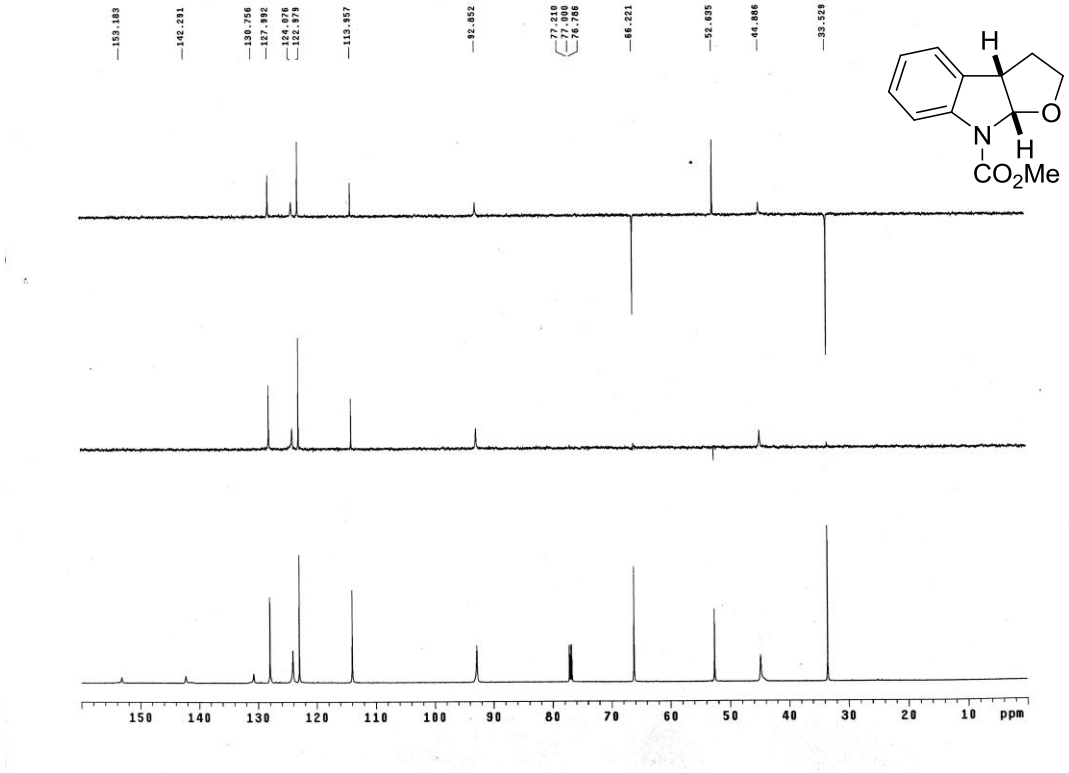
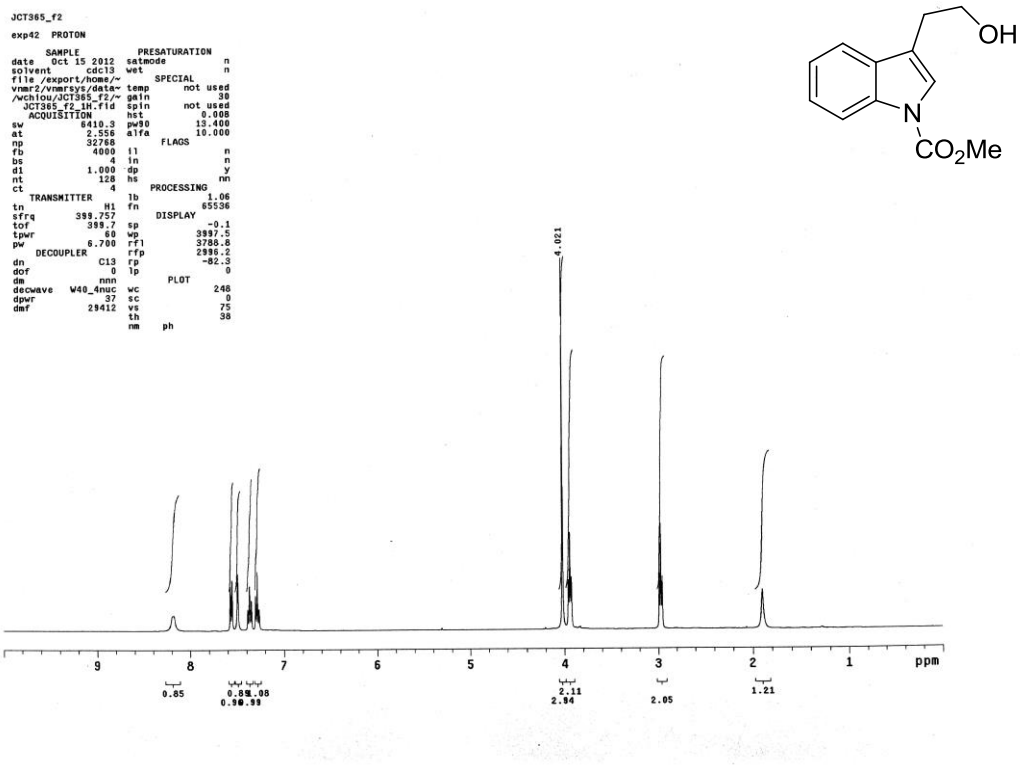


4a ^{1}H-NMR



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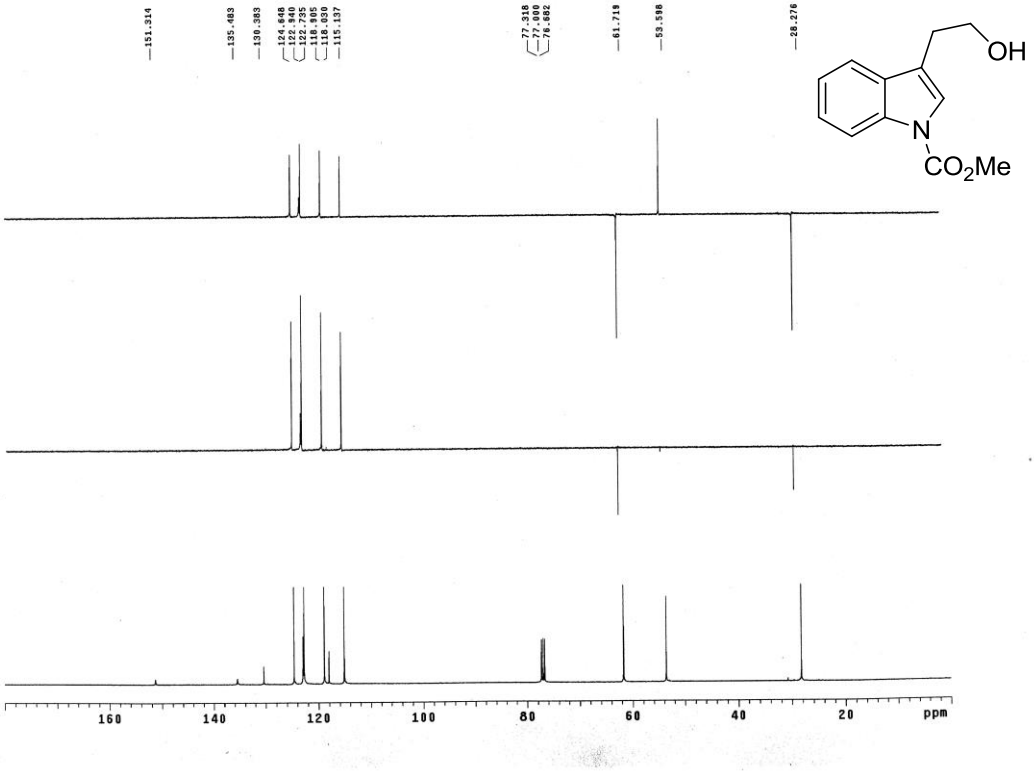
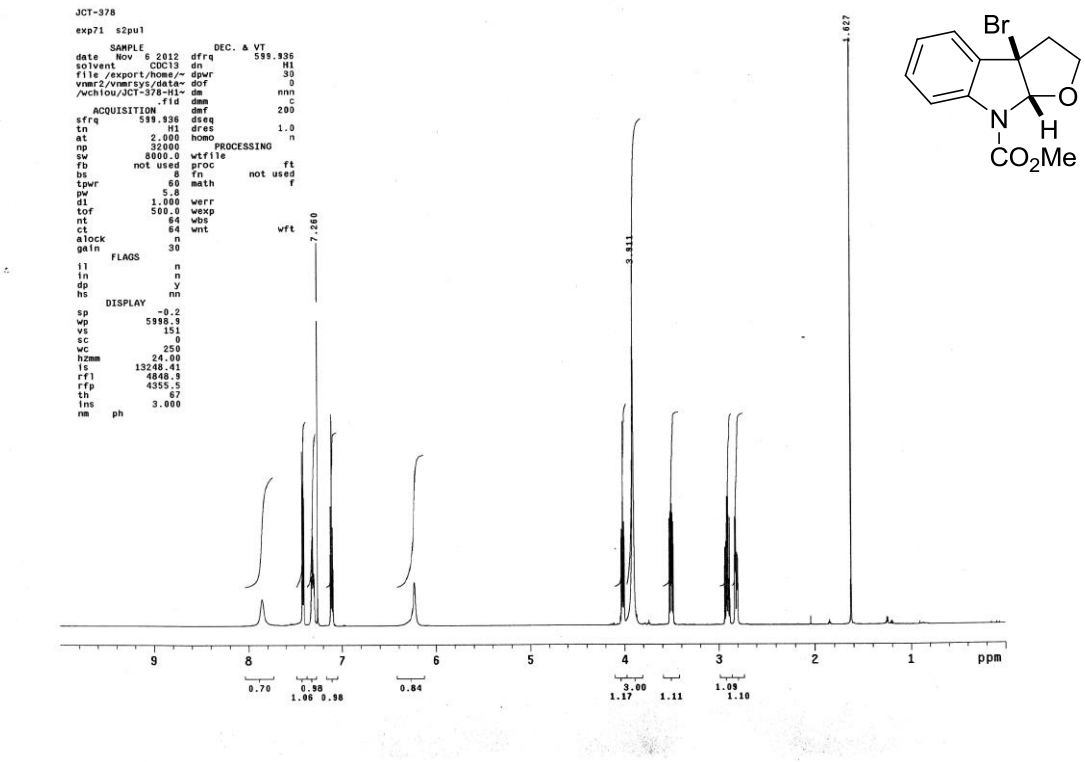


5a ^{1}H-NMR



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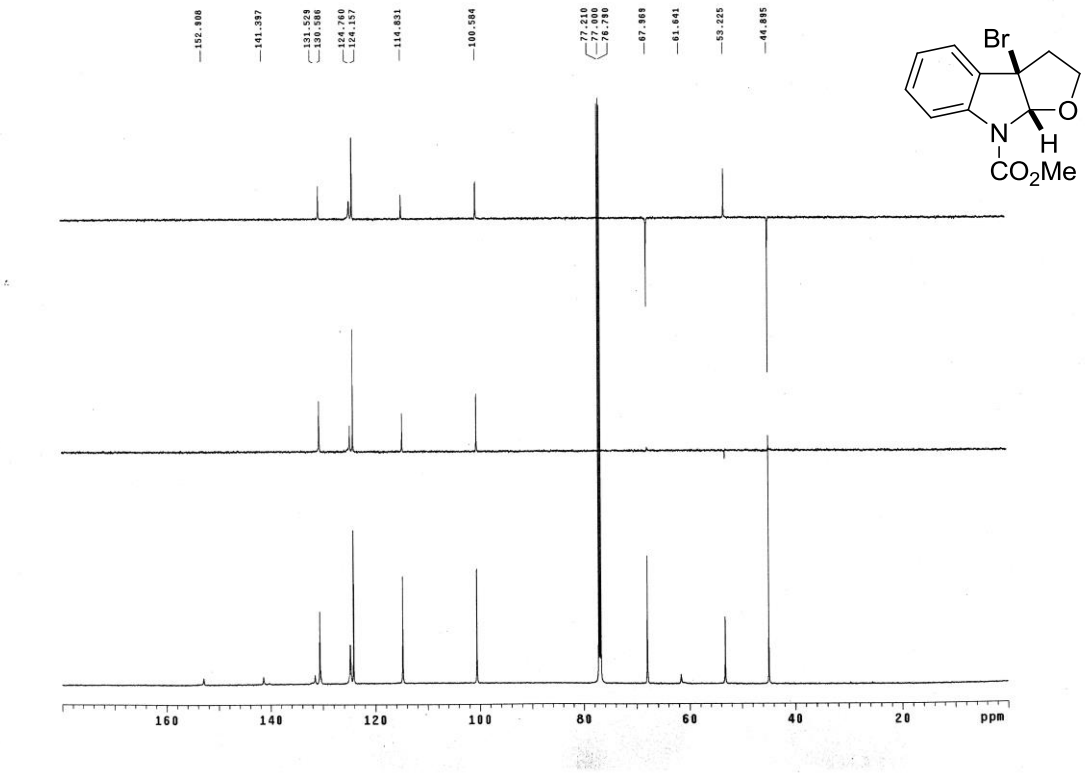
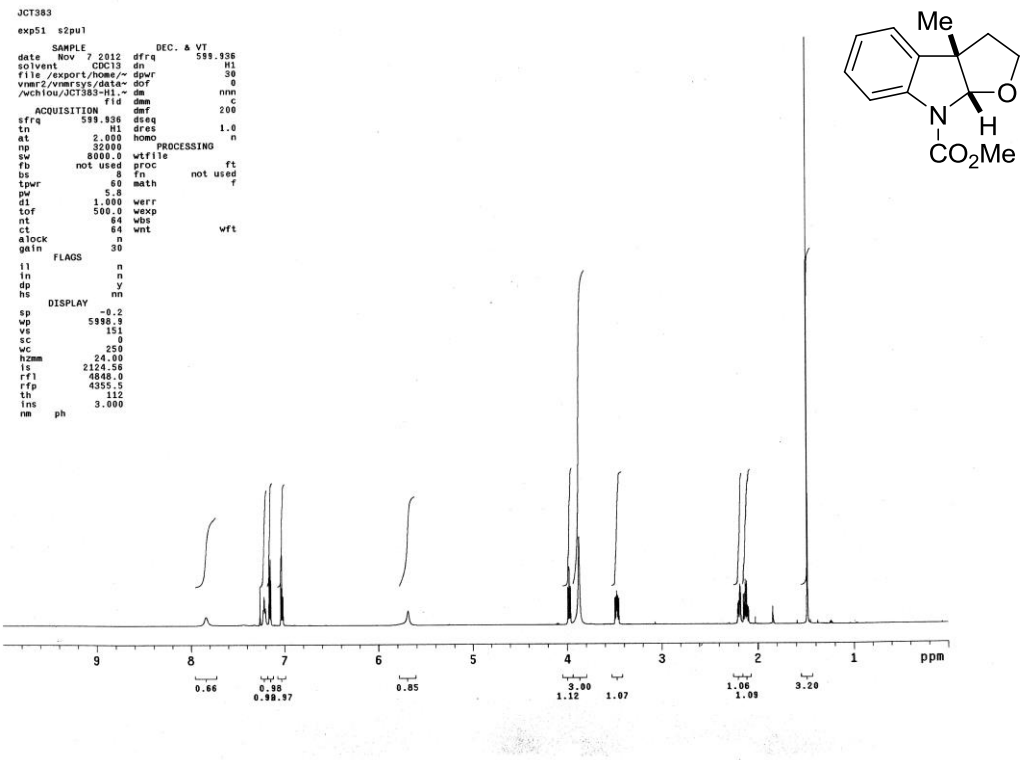
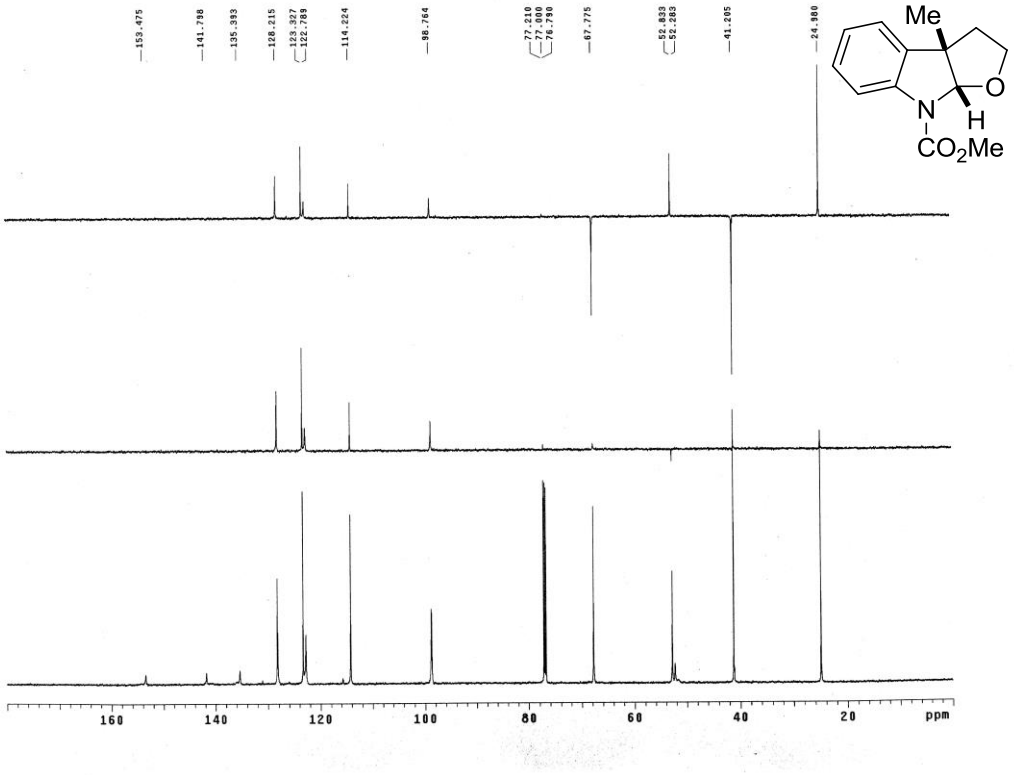


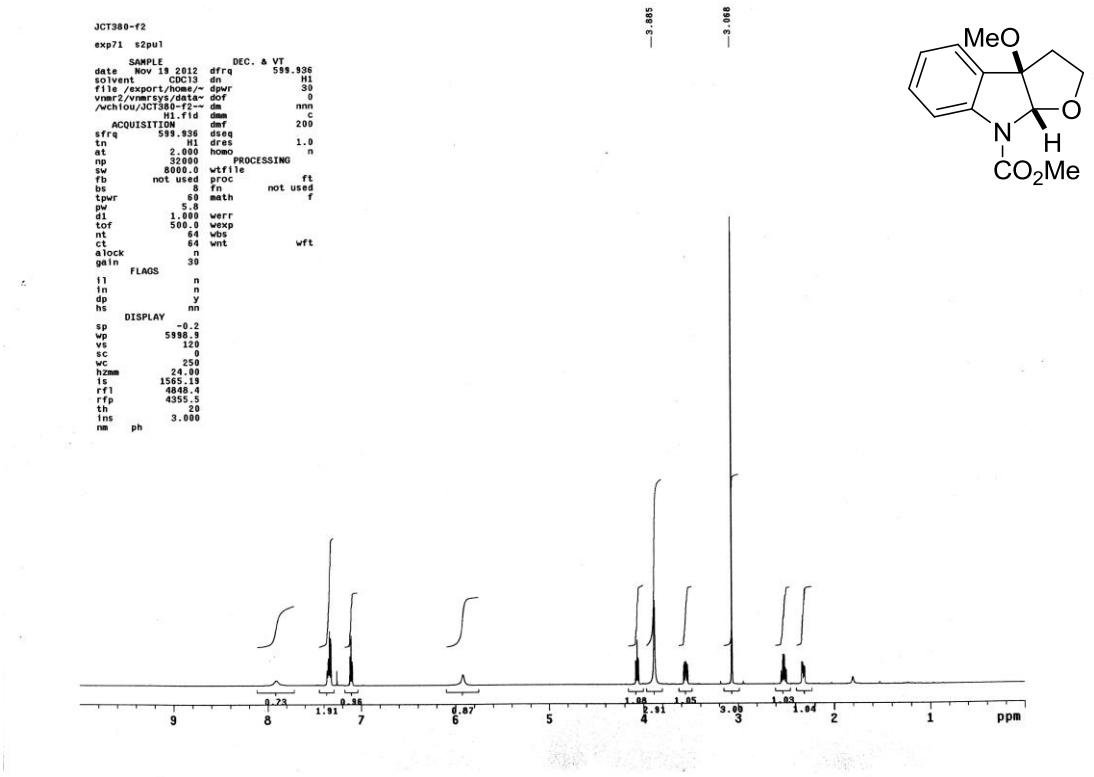
6a ^{1}H-NMR



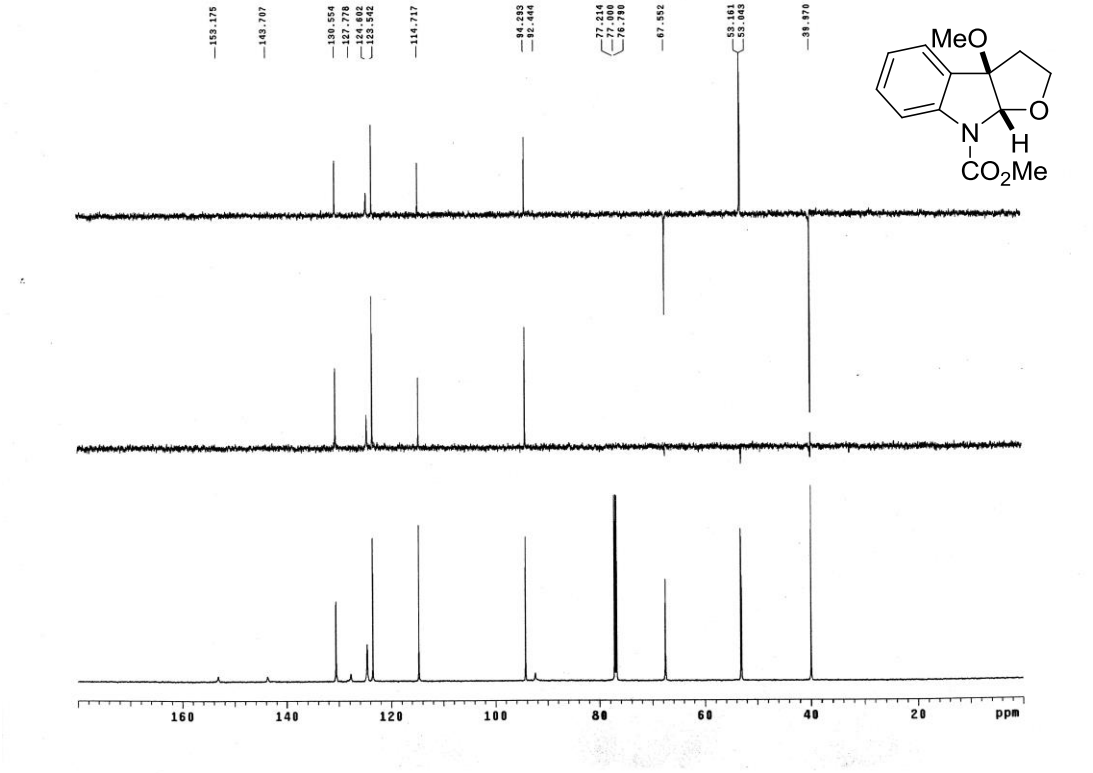
6a ^{13}C-NMR



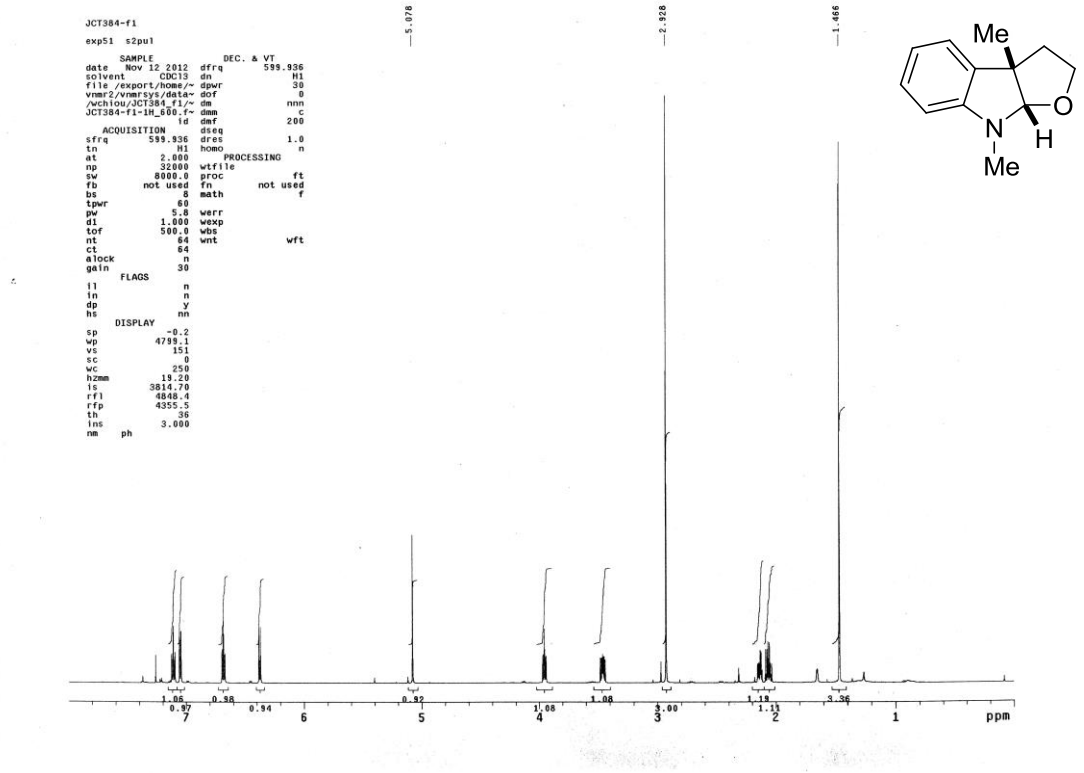
6a' ^{1}H-NMR



6a' ^{13}C-NMR



7a ^{1}H-NMR



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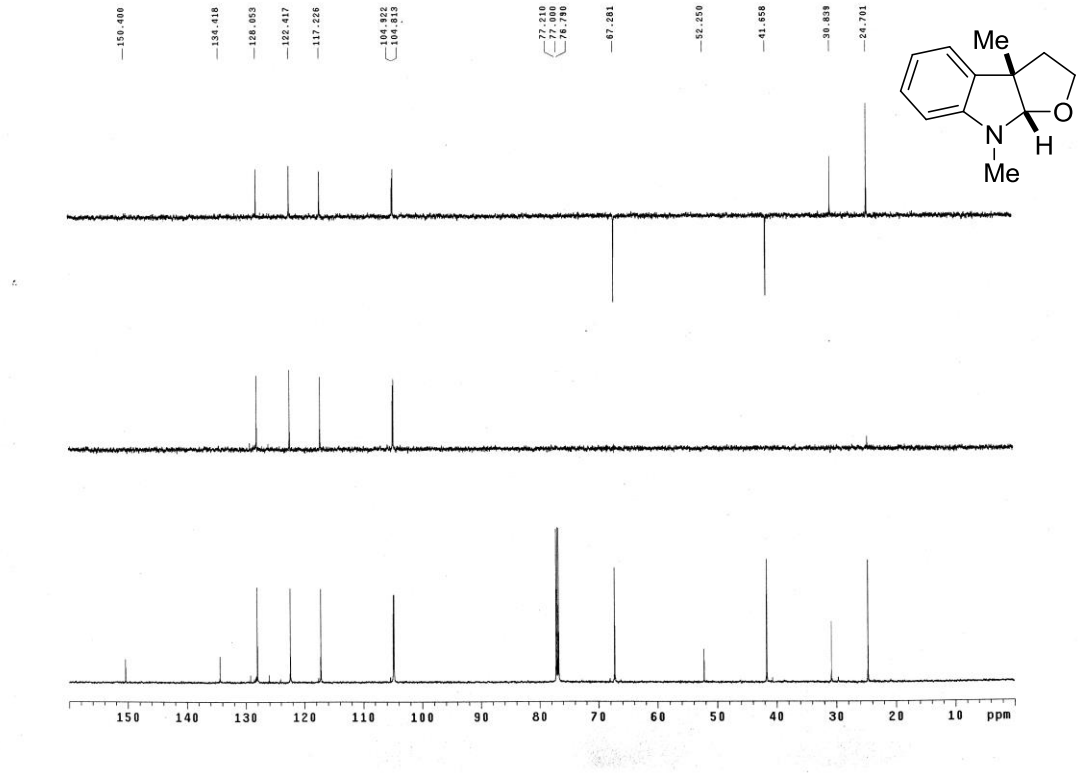

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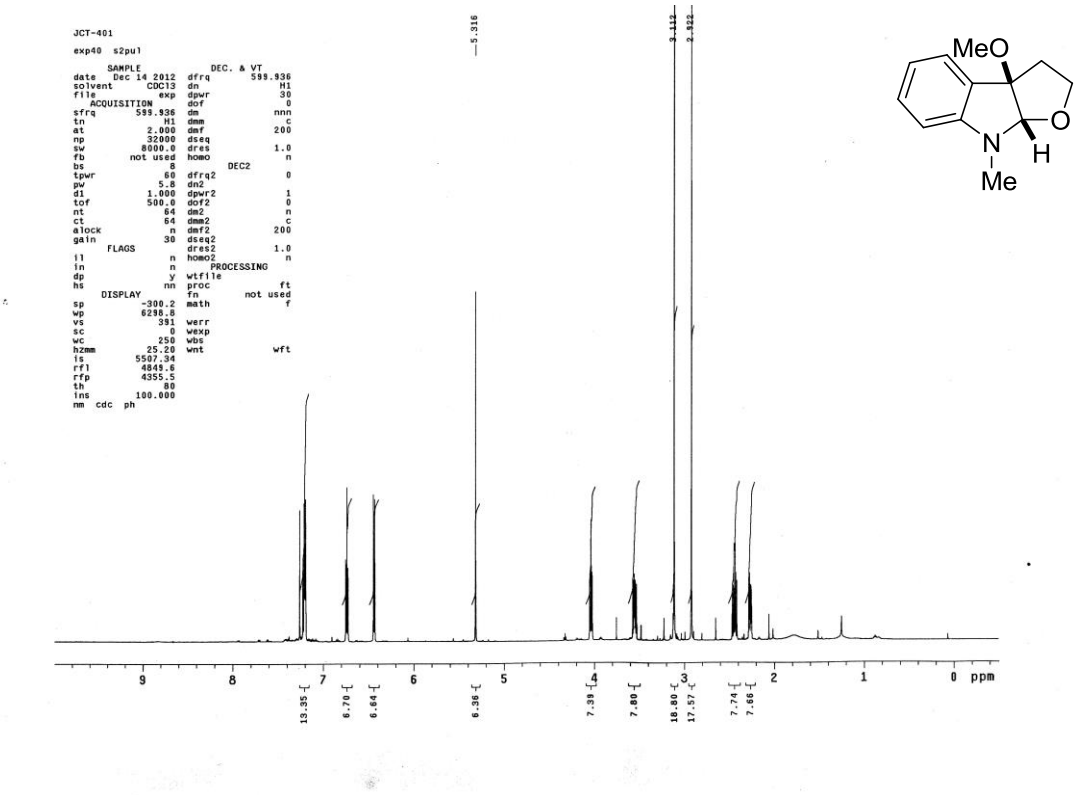
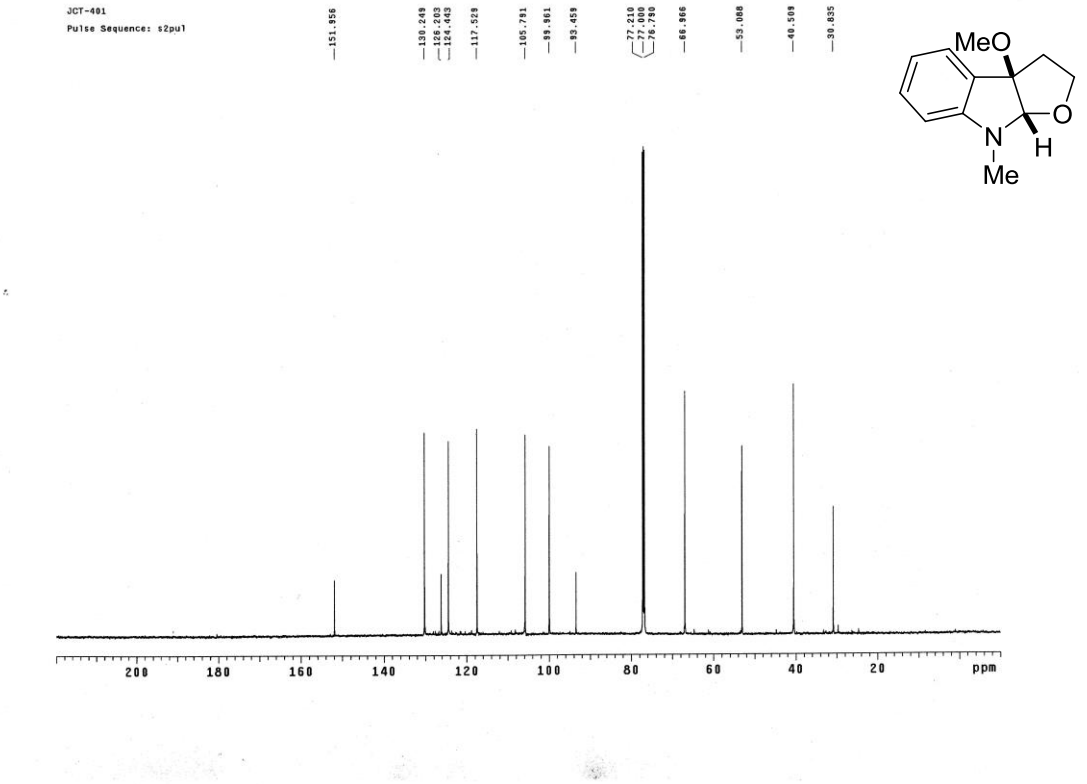
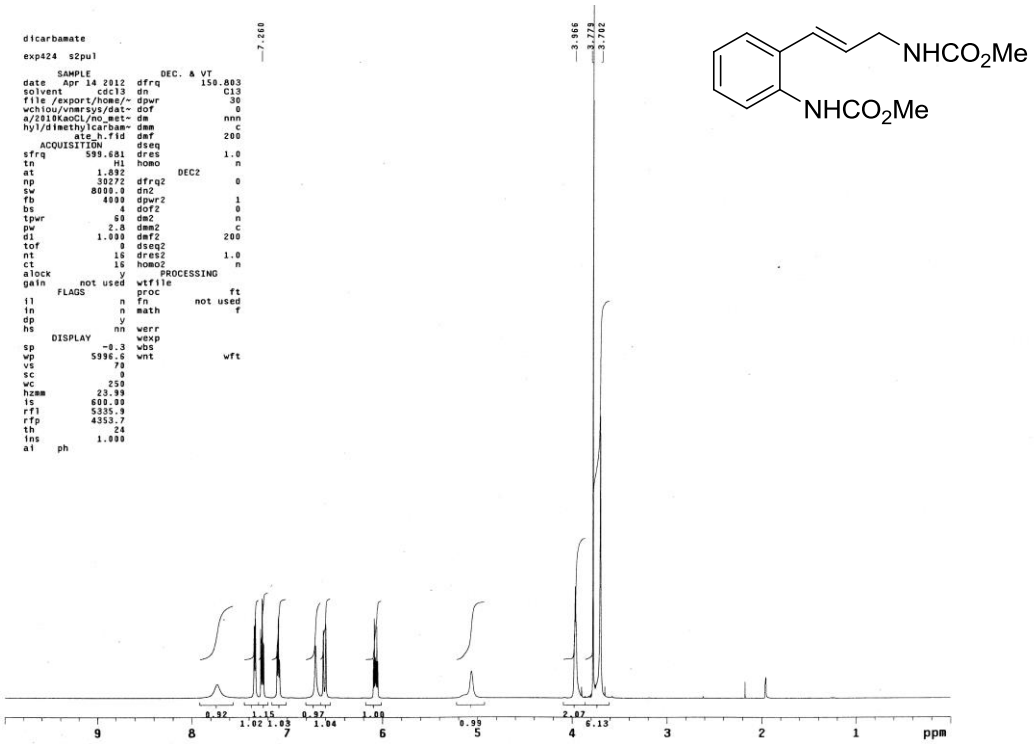


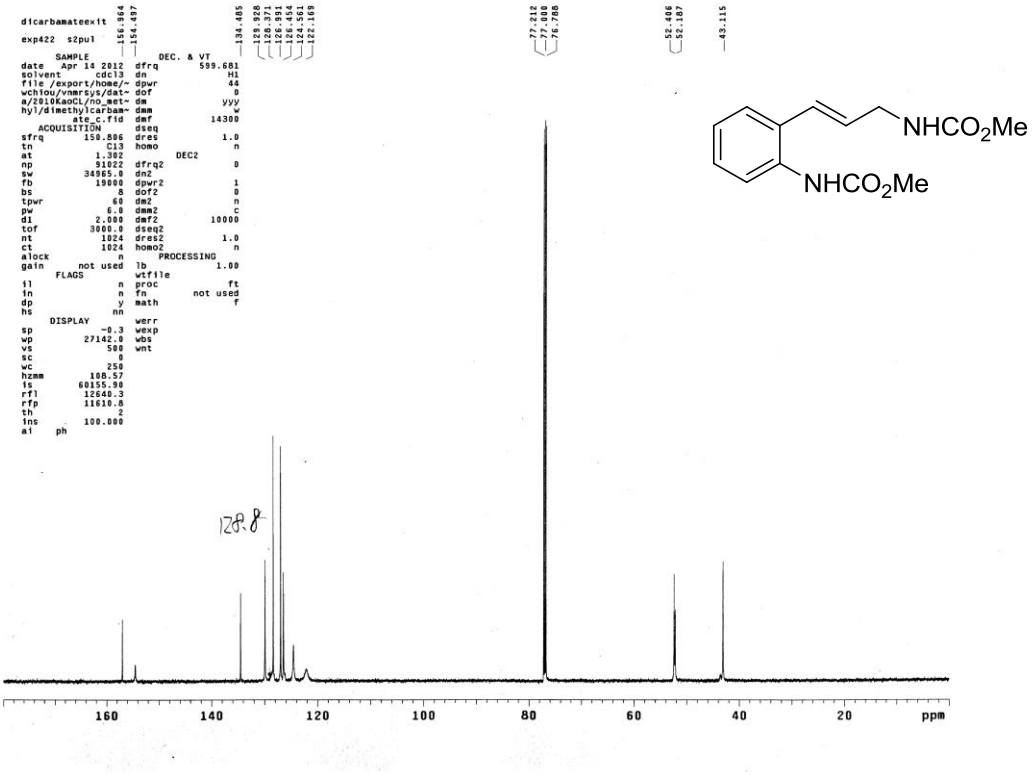
7a' ^{13}C-NMR



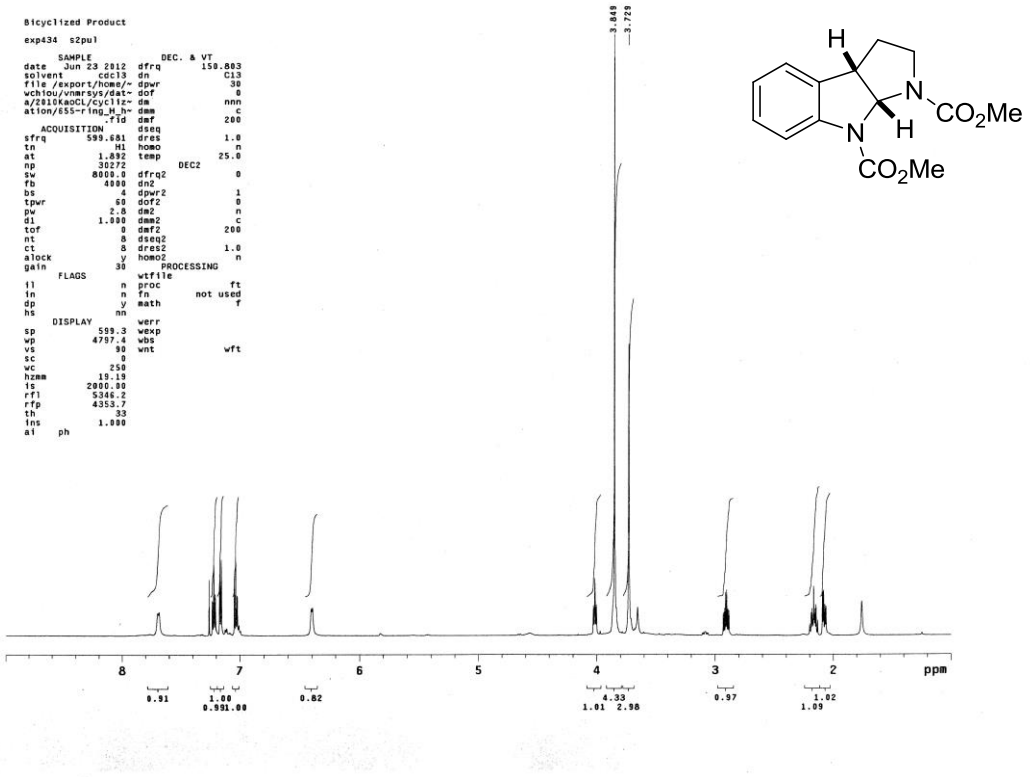
2b ^{1}H-NMR



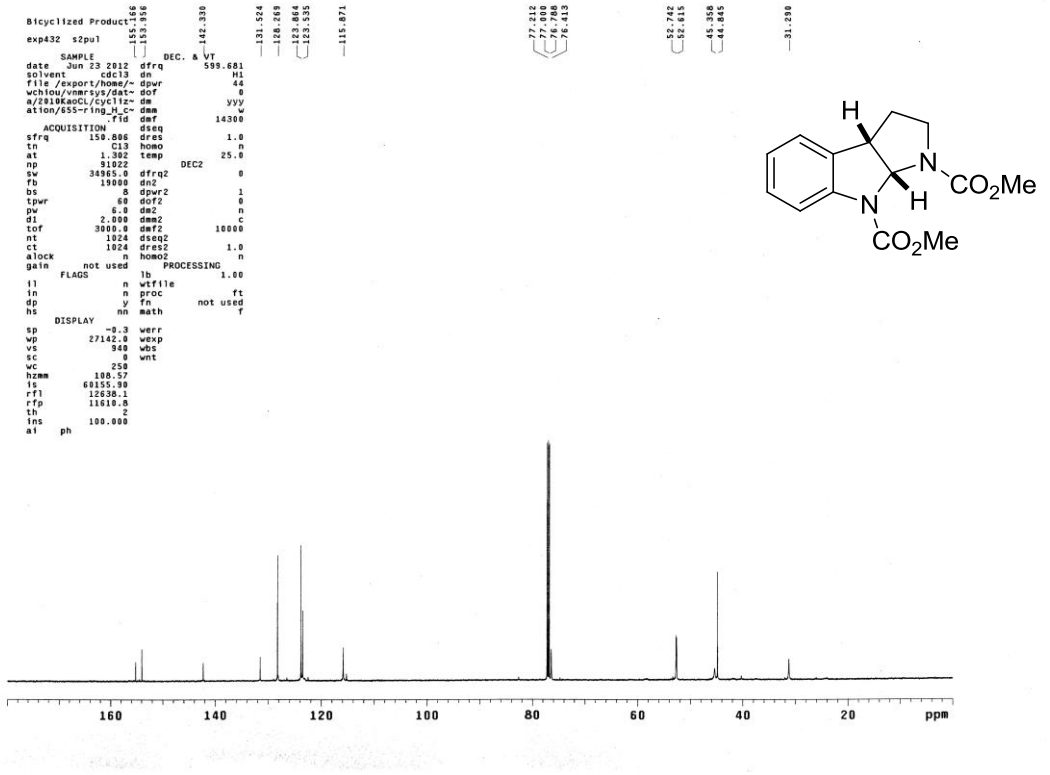
2b ^{3}C-NMR



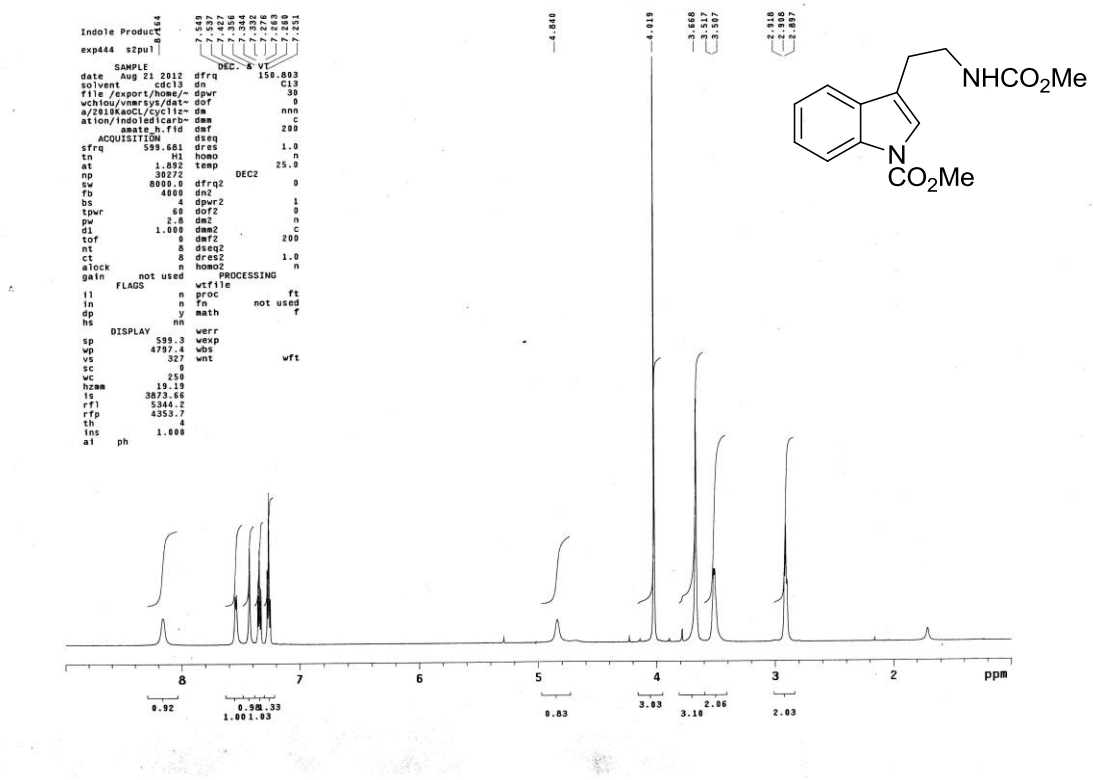
3b ^{1}H-NMR



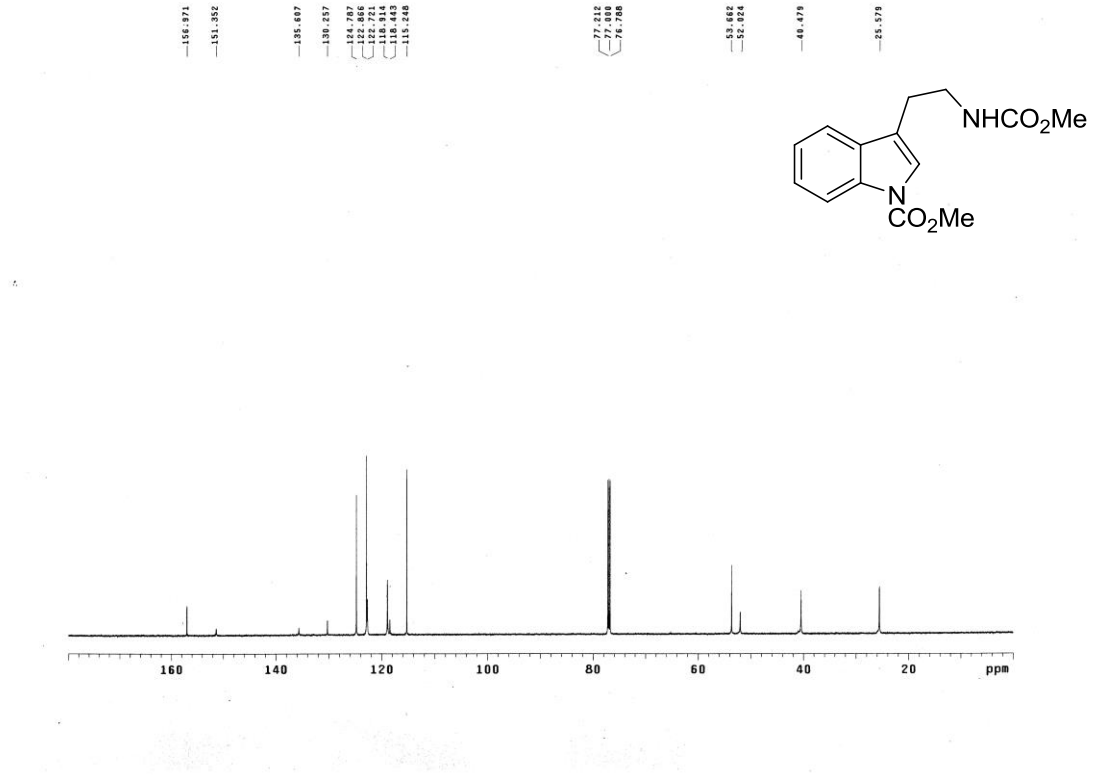
3b ^{13}C-NMR



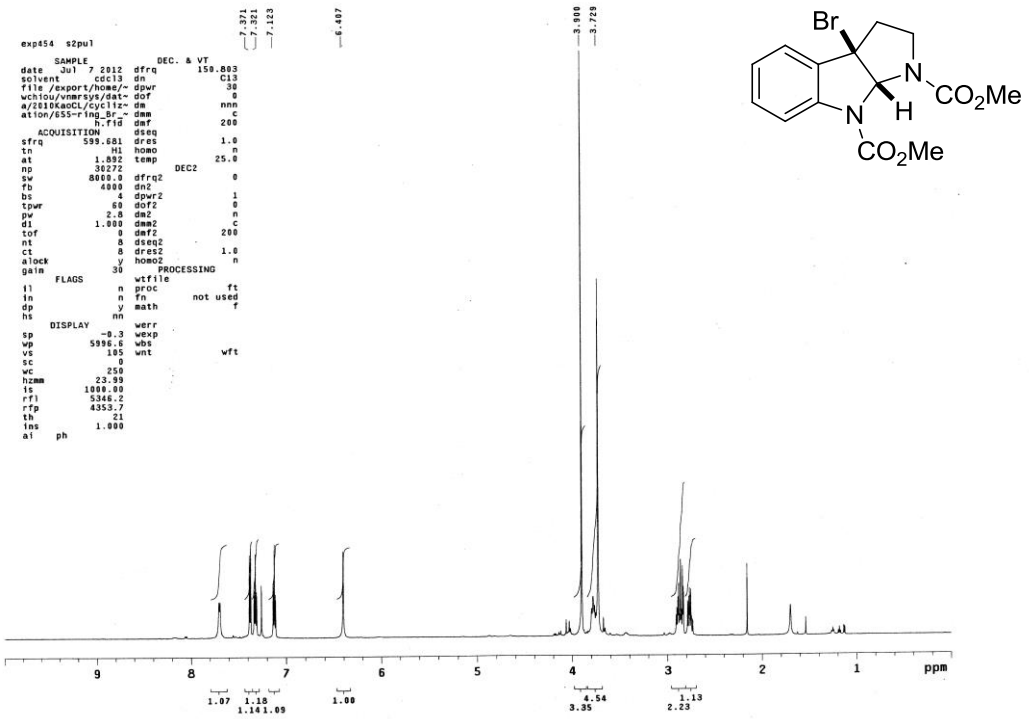
4b ^{1}H-NMR



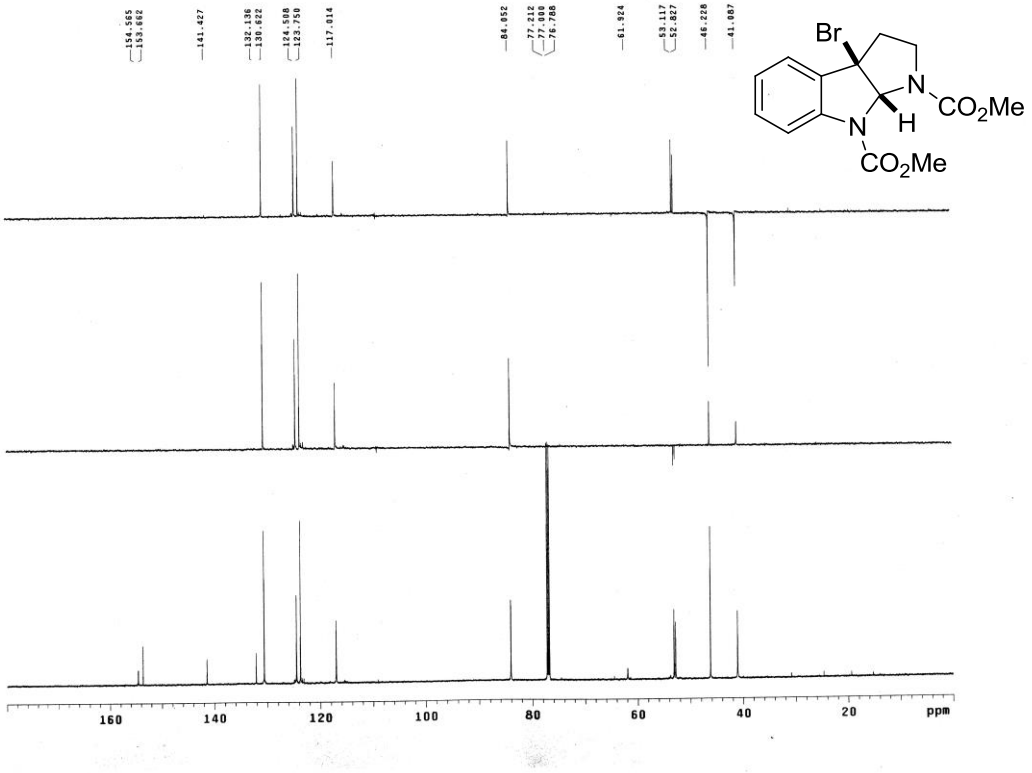
4b ^{13}C-NMR



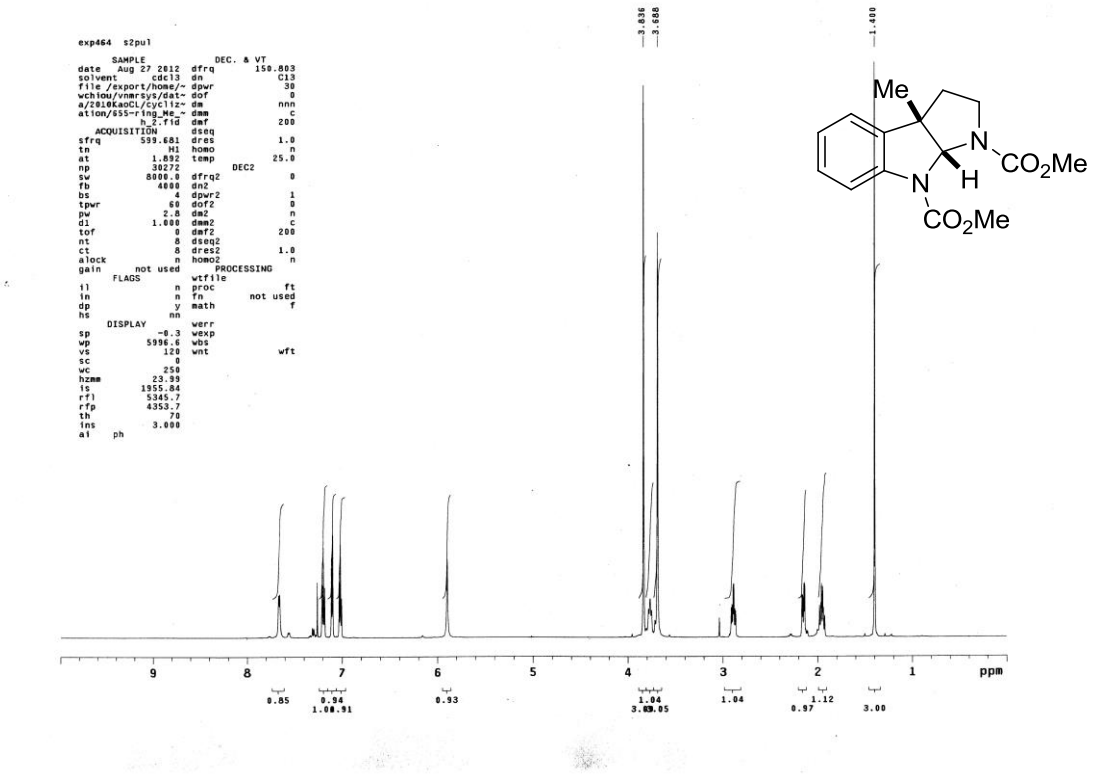
5b ^{1}H-NMR



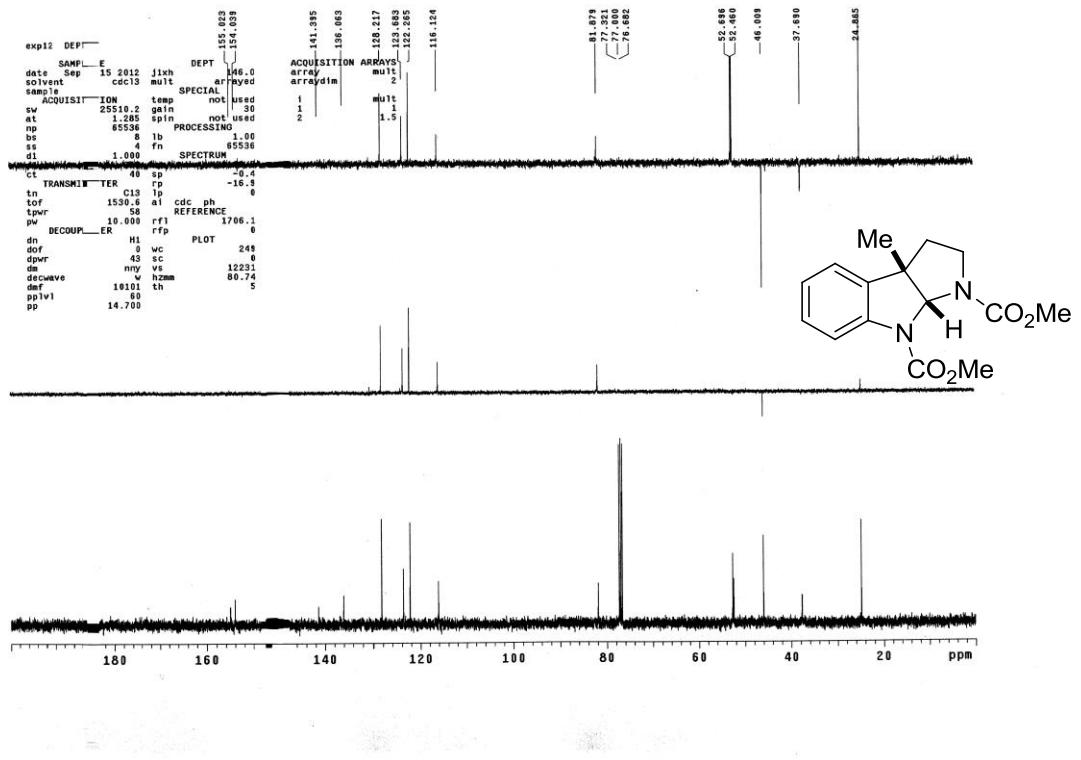
5b ^{13}C-NMR



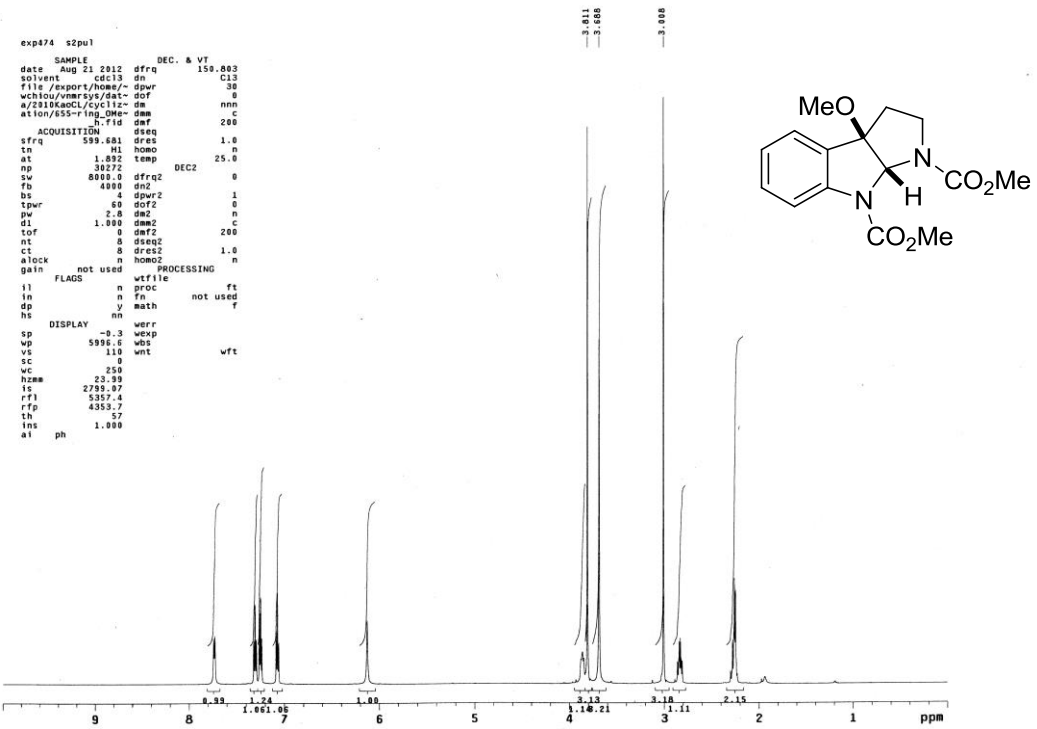
6b ^{1}H-NMR



6b' ^{13}C-NMR



6b' ^{1}H-NMR



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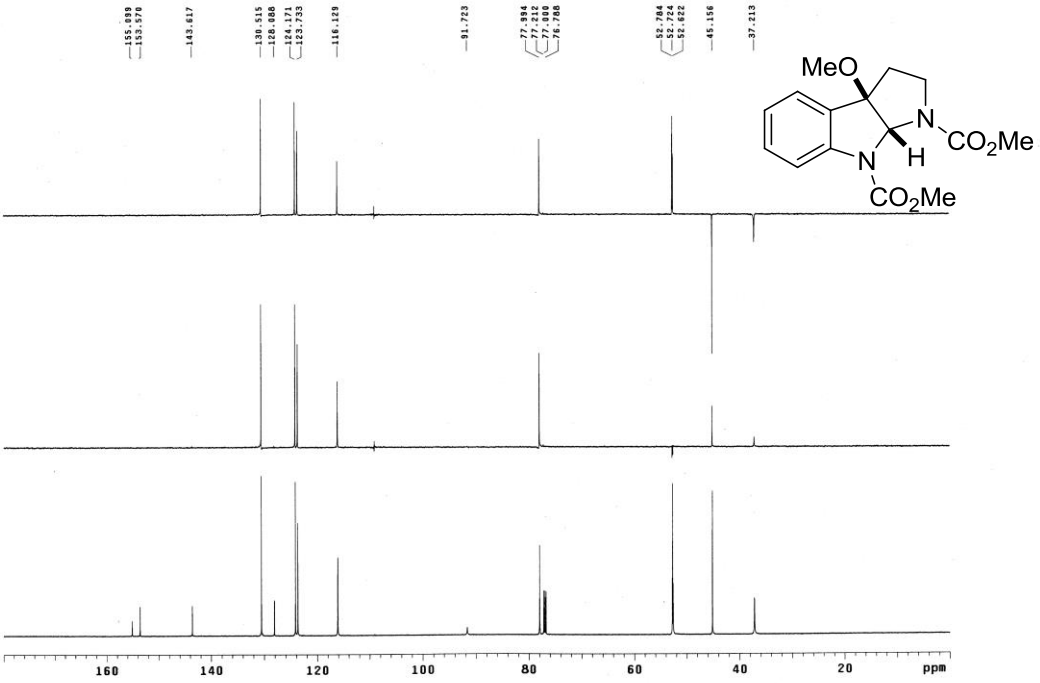
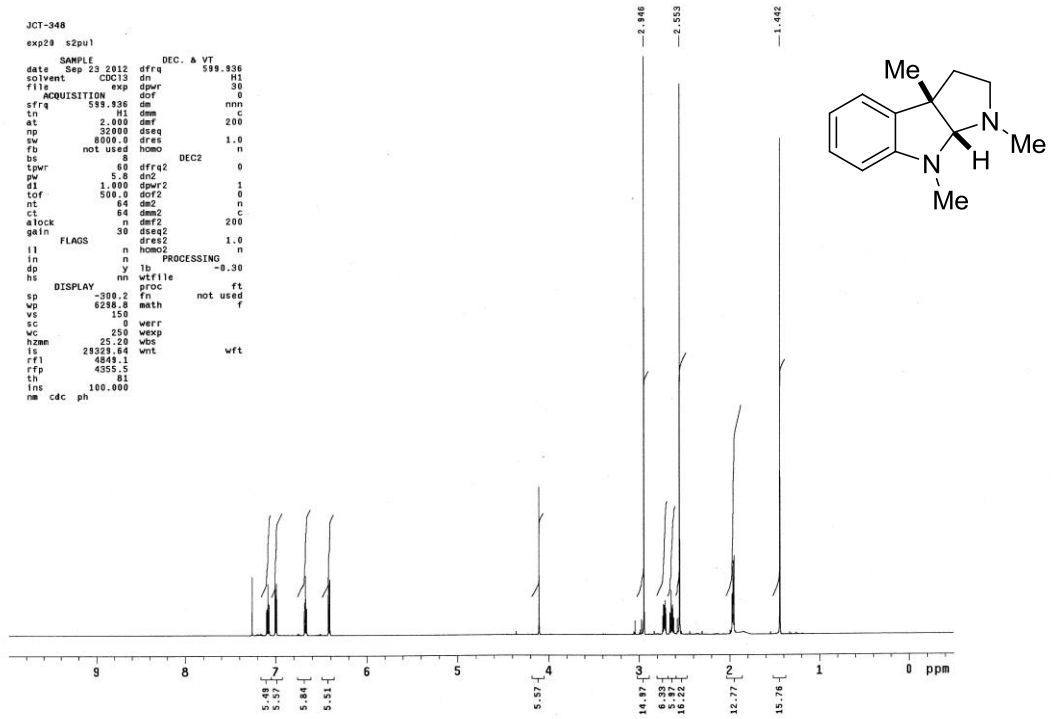
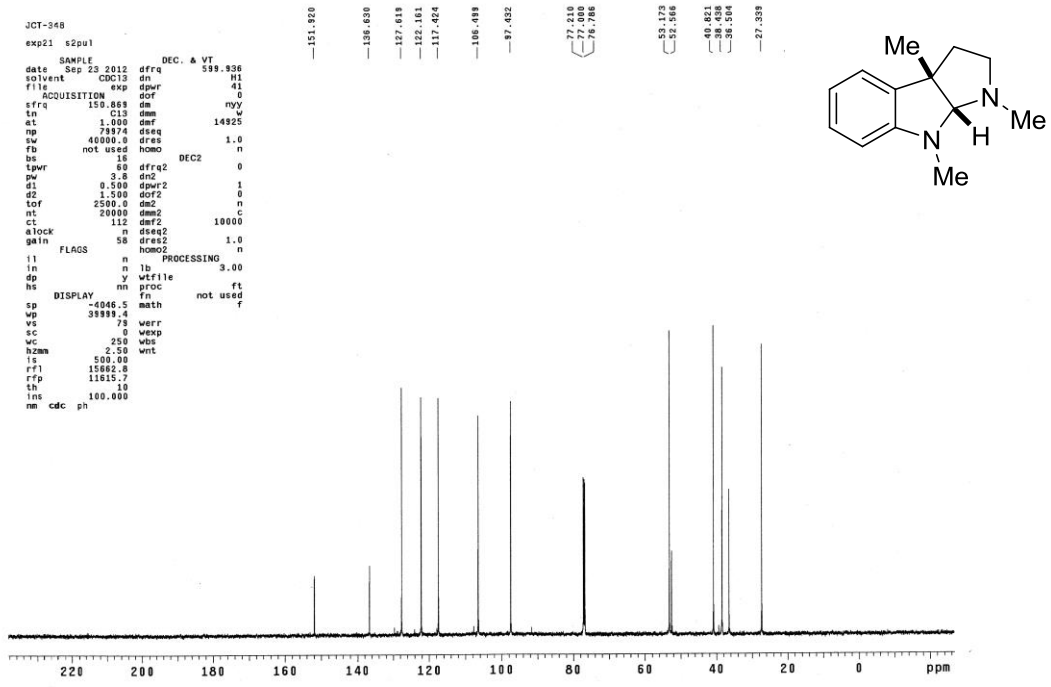


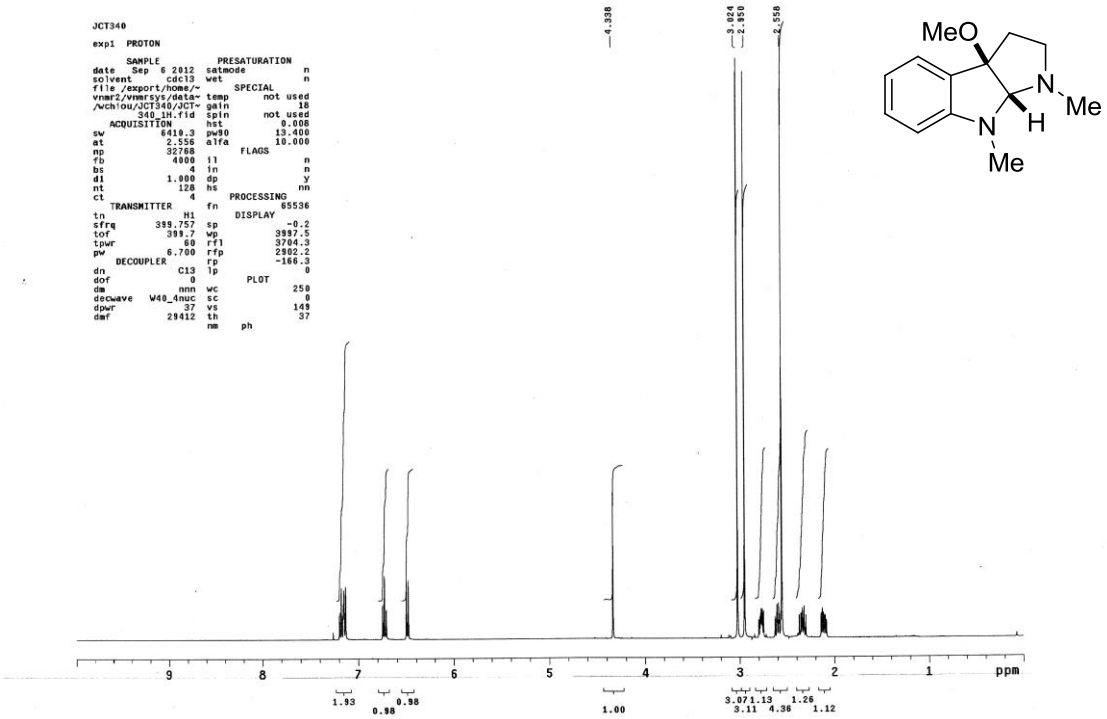
7b ^{1}H-NMR



7b ^{13}C-NMR



7b' ^{1}H-NMR



7b' ^{13}C-NMR