Supporting Information:

Substituted Pyridines from Isoxazoles: Scope and Mechanism

Seokjoo Lee, Rashmi Jena, and Aaron L. Odom*

Table of Contents

General Considerations

Syntheses and handling of materials were carried out under an inert nitrogen atmosphere, either in a MBraun glovebox or by standard Schlenk techniques, except as noted and for column chromatography and preparation of GC samples. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Agilent DDR2 500 MHz

NMR spectrometer equipped with a 5 mm PFG OneProbe operating at 499.84 MHz (^{1}H) and 125.73 MHz (^{13}C), respectively. The chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to residual protio signals of the solvent ($CDCl_3$: δ_H = 7.26 ppm ^{1}H NMR, δ_C = 77.16 ppm ^{13}C NMR and C_6D_6: δ_H = 7.16 ppm ^{1}H NMR, δ_C = 128.06 ppm ^{13}C NMR). GCMS data was collected on an Agilent 5973 MSD with a 6890N series GC. GCFID data were collected on a Hewlett Packard 6890 series GC system and standardized against dodecane as an internal standard. 5,6,7,8-Tetrahydroquinoline was used for reaction optimization, and the yield was quantified *in situ* utilizing GCFID standardized calibration curves. Pyrrolidine, cyclohexanone, and $TiCl_4$ were purchased from Acros Organics and used as received. 5,6,7,8-Tetrahydroquinoline, isoxazole (**1a**), 3-aminoisoxazole, 4-bromoisoxazole (**1c**), 3-methylisoxazole (**1e**), 3-bromo-5-methylpyridine (**3u**), 3-bromo-6-methylpyridine (**3v**) were purchased from Fisher Scientific and used as received. Zinc and titanium powder were purchased and stored under N_2 from Alfa Aesar and used as received. All materials were purchased commercially, dried prior to use, and stored under N_2. 1,4-Dioxane was dried over Na/benzophenone and distilled under N_2. $CDCl_3$ and C_6D_6 were purchased commercially and dried over P_2O_5 and CaH_2, respectively, and distilled under N_2. All the glassware was dried in the oven at 140 °C overnight before use. $TiCl_4(THF)_2$,[1] 4-(p-tolyl)-isoxazole (**1b**),[2] 3-(*N*-acetylamino)isoxazole (**1d**),[3] other isoxazoles (**1f** and **1g**),[4] enamines (**2a**-**c**, **2g, 2f**),[5] and diarylenamines (**2d**, **2e**)[6] were prepared according to the literature procedures.

Procedure for GC-FID calibration (*n*-dodecane vs substituted pyridines)

Pyridine solution (0.4 M) in dioxane and n-dodecane solution (1.6 M) in dioxane were prepared in two 5 mL volumetric flasks separately (0.266 g of 5,6,7,8-tetrahydroquinoline (**3a**), 0.3441 g for 3-bromo-5-methylpyridine (**3u**), 0.3441 g of 3-bromo-6-methylpyridine (**3v**), and 1.36 g of dodecane). Then, 0.2, 0.4, 0.6, 0.8 mL of the pyridine solution was transferred into 4 different GC vials, and 0.2 mL of the n-dodecane solution was transferred to each vial. The solution in every vial was diluted to 1 mL with dioxane. All samples were analyzed by GC-FID. Ethyl acetate and DCM were used as wash solvents to prevent any

contamination between samples. The integrations of peaks were calculated and inserted into the equation to plot the graph (Fig. 1-3S).

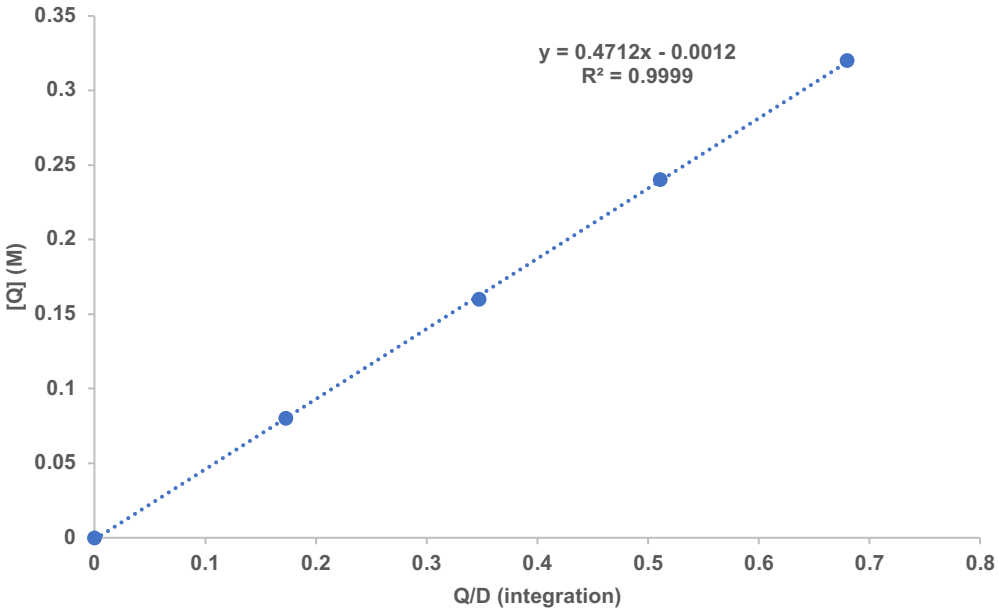


Fig. 1S. GC-FID calibration curve: n-dodecane vs. 5,6,7,8-tetrahydroquinoline (**3a**)

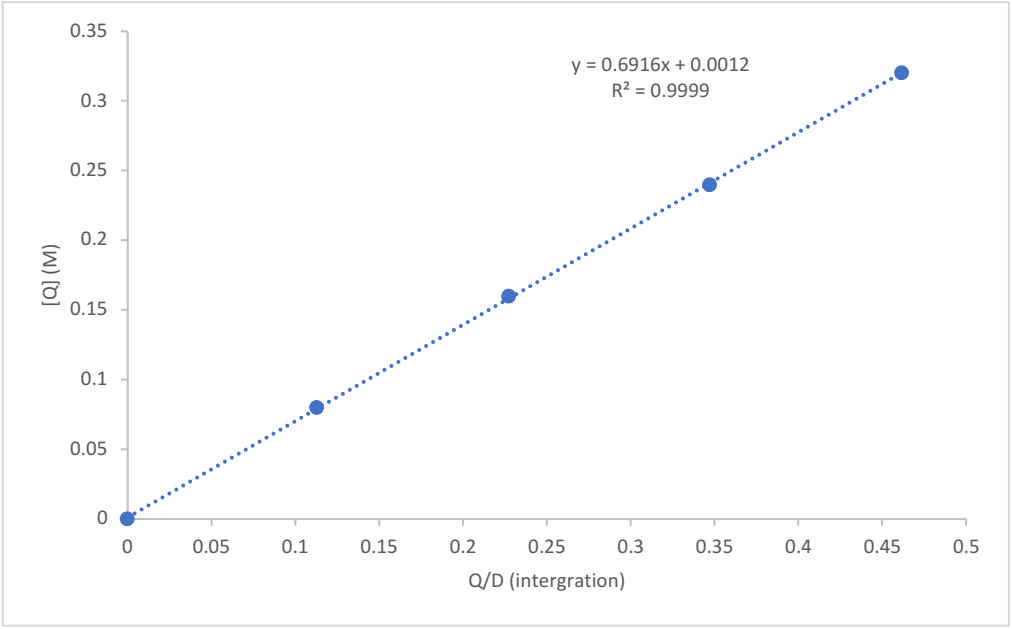


Fig. 2S. GC-FID calibration curve: n-dodecane vs. 3-bromo-5-methylpyridine (**3u**)

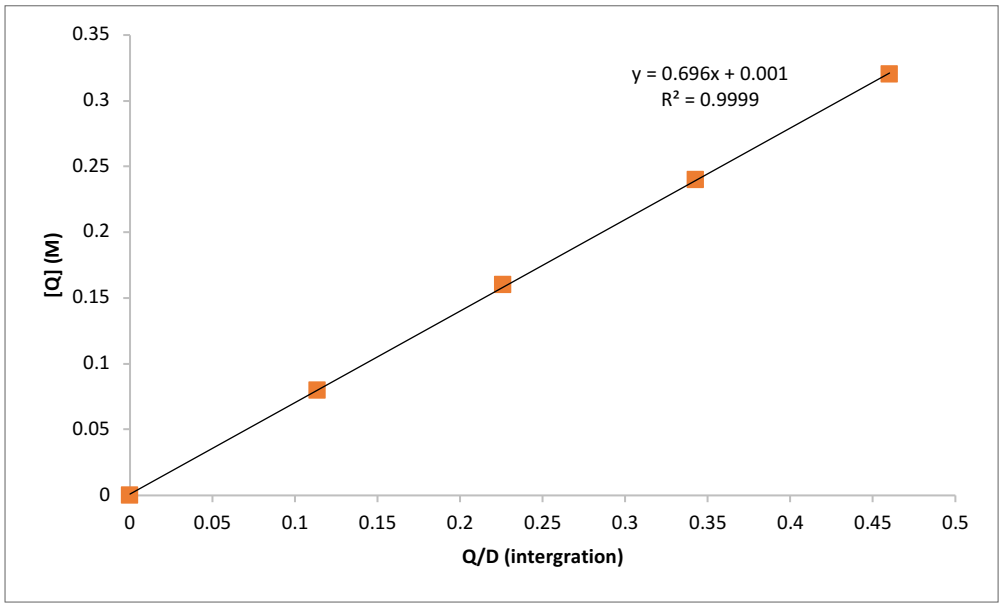
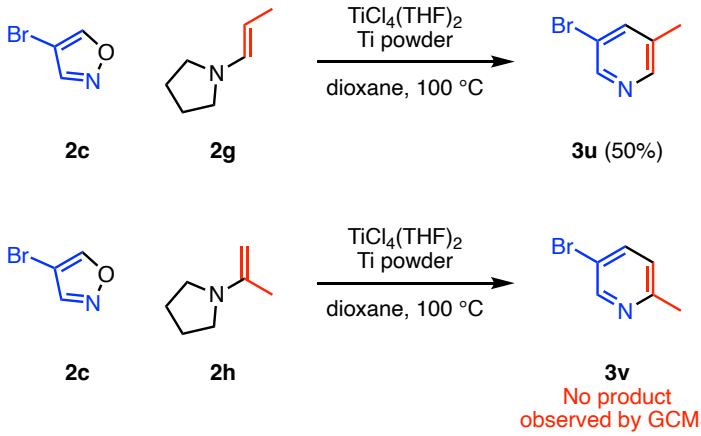


Fig. 3S. GC-FID calibration curve: n-dodecane vs. 3-bromo-6-methylpyridine (**3v**)

Reactions of 4-bromoisoxazoles with enamines 2g and 2h (Scheme 1S)



Scheme 1S. Reactions of 4-bromoisoxazoles (**2c**) with enamines **2g** and **2h**

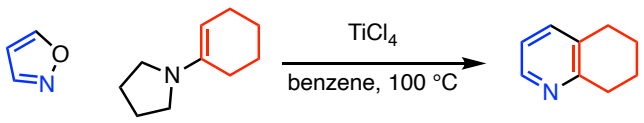
A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. In 15 mL pressure tube, 4-bromoisoxazole (**1c**, 0.069 g, 1 mmol), dodecane (0.170 g), and corresponding enamine (**2g** or **2h**, 0.45 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction

was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature for 10 min. 0.3~0.35 mL) of reaction mixture was taken into a GC vial and diluted to 1 mL. Yield was calculated based on the GC-FID calibration curves above. The diluted reaction mixtures were analyzed by GCMS and GCFID.

The top reaction between 4-bromoisoxazole (**1c**) and 1-methyl-1-(1-pyrroldinyl)ethene (**2g**) results in 50% GC yield of 3-bromo-5-methylpyridine (**3u**). However, the bottom reaction between 4-bromoisoxazole (**1c**) and 2-methyl-1-(1-pyrroldinyl)ethene (**2h**) did not give the corresponding pyridine (**3v**). As we mentioned in the paper, terminal enamines are less reactive and less nucleophilic.

Reactions of isoxazole with 1-(1-cyclohexenyl)pyrrolidine in benzene (Scheme 2S)

In the reactions of isoxazole (**1a**) and 1-(1-cyclohexenyl)pyrrolidine (**2a**) in dioxane, 5,6,7,8-tetrahydroquinoline-*N*-oxide was not observed but only 5,6,7,8-tetrahydroquinoline (**3a**) was observed. From this result, it was hypothesized that tetrahydroquinoline-*N*-oxide, the intermediate of the reaction was reduced in the reaction by a radical reaction. Since ethereal solvents can be good hydrogen radical donors, $TiCl_4$ and benzene were used in place of $TiCl_4(THF)_2$ and dioxane, respectively. However, the pyridine synthesis between isoxazole and 1-(1-cyclohexenyl)pyrrolidine gives 31% GC yield of 5,6,7,8-tetrahydroquinoline (**3a**). In this reaction, benzene was used in place of dioxane as solvent to observe pyridine-*N*-oxide. However, 5,6,7,8-tetrahydroquinoline was only observed by GCMS and GCFID.



1a **2a** (4 equiv) **3a** (31%)

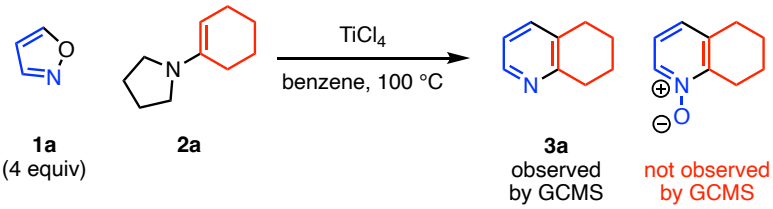
Scheme 2. The reaction of isoxazole with 1-(1-cyclohexenyl)pyrrolidine in benzene

A 15 mL pressure tube was charged with $TiCl_4$ (0.190 g, 1 mmol, 1 equiv) and benzene (1.5 mL). To the reaction mixture, isoxazole (**1a**, 0.069 g, 1 mmol), dodecane (0.170 g), and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.605 g, 4 mmol, 4 equiv) in benzene (1 mL) were added. The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was

heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature for 10 min. 0.3~0.35 mL) of reaction mixture was taken into a GC vial and diluted to 1 mL. Yield was calculated based on the GC-FID calibration curves above.

Reactions of isoxazole with 1-(1-cyclohexenyl)pyrrolidine in benzene (Scheme 3S)

Since the intermediate tetrahydroquinoline-*N*-oxide was not observed in the previous reaction in benzene, it was assumed that 1-(1-cyclohexenyl)pyrrolidine may act as reductant. To suppress this reductant role of the enamine, excess amount (4 equiv) of isoxazole was used in the reaction. However, we were not able to observe tetrahydroquinoline-*N*-oxide. 5,6,7,8-Tetrahydroquinoline was only observed by GCMS.



Scheme 3S. The reaction of isoxazole with 1-(1-cyclohexenyl)pyrrolidine in benzene

A 15 mL pressure tube was charged with $TiCl_4$ (0.190 g, 1 mmol, 1 equiv) and benzene (1.5 mL). To the reaction mixture, isoxazole (**1a**, 0.276 g, 4 mmol), dodecane (0.170 g), and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.151 g, 1 mmol, 0.25 equiv) in benzene (1 mL) were added. The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature for 10 min. 0.3~0.35 mL) of reaction mixture was taken into a GC vial and diluted to 1 mL. The sample was analyzed by GCMS.

Synthesis of Pyridine Derivatives

*Synthesis of 5,6,7,8-tetrahydroquinoline (**3a**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. Isoxazole (**1a**, 0.069 g, 1 mmol) and 1-(1-cyclohexenyl)pyrrolidine

(**2a**, 0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature for 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by silica gel auto-column chromatography, eluted with hexane to get a colorless oil (101 mg, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.34 (d, J = 4.0 Hz, 1H), 7.33 (d, J = 3.0 Hz, 1H), 7.01 (dd, J = 4.0 Hz, 3.0 Hz, 1H), 2.92 (t, J = 6.5 Hz, 2H), 2.76 (t, J = 6.5 Hz, 2H), 1.94-1.85 (m, 2H), 1.84-1.75 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 157.496, 146.886, 136.878, 132.392, 120.981, 32.622, 28.880, 23.187, 22.797. MS (EI): m/z 133 (M^+). The ^{1}H and ^{13}C{^{1}H} NMR spectroscopy of the compound matches that in the literature.[7]

*Synthesis of 3-(4-tolyl)-5,6,7,8-tetrahydroquinoline (**3b**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Tolylisoxazole (**1b**, 0.160 g, 1 mmol) and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (8:2) to get a colorless solid (92 mg, 41%). Mp = 58-60 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (s, 1H), 7.53 (s, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 2.96 (t, J = 6.0 Hz, 4H), 2.83

(t, J = 6.0 Hz, 4H), 2.40 (s, 3H), 1.96-1.91 (m, 4H), 1.90-1.82 (m, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 156.077, 145.154, 137.682, 135.308, 135.128, 134.024, 132.206, 129.820, 126.935, 32.307, 29.006, 23.278, 22.880, 21.282. MS (EI): m/z 223 (M^+).

*Synthesis of 3-bromo-5,6,7,8-tetrahydroquinoline (**3c**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Bromoisoxazole (**1c**, 0.148 g, 1 mmol) and 1-(1-cyclohexenyl) pyrrolidine (0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (9:1) to get a colorless oil (150 mg, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.39 (s, 1H), 7.49 (s, 1H), 2.85 (t, J = 6.5 Hz, 4H), 2.75 (t, J = 6.5 Hz, 4H), 1.92-1.82 (m, 4H), 1.81-1.73 (m, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 156.097, 147.707, 139.047, 134.312, 117.332, 32.103, 28.753, 22.920, 22.388. MS (EI): m/z 211 (M^+). The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy of the compound matches that in the literature.[8]

*Synthesis of 2-(N-acetoamino)-5,6,7,8-tetrahydroquinoline (**3d**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 3-(*N*-acetoamino)isoxazole (**1d**, 0.126 g, 1 mmol) and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum

block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (6:4) to get an amber solid (40 mg, 21%). m.p. = 127-129 °C. ^{1}H NMR (DMSO, 500 MHz): δ 10.35 (s, 1H), δ 7.80 (d, J = 8.5 Hz, 1H), 7.7.41 (d, J = 8.5 Hz, 1H), 2.71 (t, J = 6.5 Hz, 4H), 2.66 (t, J = 6.5 Hz, 4H), 2.04 (s, 3H), 1.84-1.75 (m, 4H), 1.75-1.66 (m, 4H). ^{13}C{^{1}H} NMR (DMSO, 126 MHz): δ 154.603, 149.499, 138.633, 126.907, 110.851, 31.509, 27.380, 23.810, 22.590, 22.371. MS (EI): m/z 190 (M^+).

*Synthesis of 2-methyl-5,6,7,8-tetrahydroquinoline (**3e**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 3-Methylisoxazole (**1e**, 0.083 g, 1 mmol) and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane to get a yellow oil (108 mg, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 2.87 (t, J = 6.5 Hz, 4H), 2.71 (t, J = 6.5 Hz, 4H), 2.48 (s, 3H), 1.91-1.84 (m, 4H), 1.82-1.74 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 156.548, 155.159, 137.592, 129.057, 120.575, 32.690, 28.516,

24.292, 23.332, 22.933. MS (EI): m/z 147 (M^+). The ^1H and $^{13}C\{^1H\}$ NMR spectroscopy of the compound matches that in the literature.[9]

*Synthesis of 3-ethyl-2-(thiopheny-2-yl)-5,6,7,8-tetrahydroquinoline (**3f**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Ethyl-3-(thiopheny-2-yl)-isoxazole (**1f**, 0.180 g, 1 mmol) and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (8:2) to get an amber oil (176 mg, 72%). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.36 (d, J = 3.5 Hz, 1H), 7.35 (d, J = 3.5 Hz, 1H), 7.25 (s, 1H), 7.08 (dd, J = 5.0 Hz, 4.0 Hz, 1H), 2.92 (t, J = 6.5 Hz, 4H), 2.81 (q, J = 6.0 Hz, 4H), 2.77 (t, J = 6.5 Hz, 4H), 2.17 (s, 1H), 1.93-1.86 (m, 4H), 1.85-1.77 (m, 4H), 1.25 (t, 6.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 154.574, 148.344, 137.987, 133.565, 131.122, 127.383, 126.582, 126.253, 32.274, 28.581, 25.890, 23.381, 22.949, 14.960. MS (EI): m/z 243 (M^+).

*Synthesis of 3-methyl-2-(4-tolyl)-5,6,7,8-tetrahydroquinoline (**3g**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-methyl-3-(4-tolyl)-isoxazole (**1g**, 0.187 g, 1 mmol) and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C

aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (8:2) to get an amber oil (194 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, J = 8.0 Hz, 2H), 7.24 (s, 1H), 7.23 (d, J = 3.0 Hz, 2H), 2.93 (t, J = 7.0 Hz, 4H), 2.77 (t, J = 7.0 Hz, 4H), 2.39 (s, 3H), 2.26 (s, 3H), 1.94-1.86 (m, 4H), 1.85-1.77 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 155.970, 154.424, 139.233, 137.327, 130.520, 129.002, 128.922, 127.756, 32.389, 28.517, 23.482, 22.980, 21.400, 19.701. MS (EI): m/z 237 (M^+).

*Synthesis of 2,3-dimethyl-5,6,7,8-tetrahydroquinoxaline (**3h**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 3,4-dimethyl-1,2,5-oxadiazole (**1h**, 0.98 g, 1 mmol) and 1-(1-cyclohexenyl)pyrrolidine (**2a**, 0.605 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (8:2) to get a colorless oil (31 mg, 19%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.61 (t, J = 6.0 Hz, 4H), 2.51 (t, J = 6.0 Hz, 4H), 2.36 (s, 3H), 1.85-1.79 (m, 4H), 1.78-1.71 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 116.106, 25.135, 23.551, 23.035, 22.940, 22.796. MS (EI): m/z 162 (M^+).

*Synthesis of 3-phenylpyridine (**3i**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. Isoxazole (**1a**, 0.069 g, 1 mmol) and 1-pyrrolidinyl-2-phenylethene (**2b**, 0.693 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (9:1) to get a yellow oil (131 mg, 84%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.85 (s, 1H), δ 8.59 (d, J = 5.0 Hz, 1H), 7.88 (d, J = 5.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.37 (dd, J = 8.0 Hz, 4.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 148.605, 148.472, 137.988, 136.769, 134.505, 129.216, 128.233, 127.292, 123.694. MS (EI): m/z 155 (M^+). The ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy of the compound matches that in the literature.[10]

*Synthesis of 3-bromo-5-phenylpyridine (**3j**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Bromoisoxazole (**1c**, 0.148 g, 1 mmol) and 1-pyrrolidinyl-2-phenylethene (**2b**, 0.693 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried

with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (9:1) to get white solid (133 mg, 86%). m.p. = 47-49 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.76 (s, 1H), 8.66 (s, 1H), 8.03 (s, 1H), 7.57 (d, J = 7.0 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 148.001, 145.823, 140.878, 139.599, 138.077, 129.015, 128.962, 128.434, 119.083. MS (EI): m/z 211 (M^+). The ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy of the compound matches that in the literature[11]

*Synthesis of 3-(4-tolyl)-5-phenylpyridine (**3k**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. (4-Tolyl)isoxazole (**1b**, 0.159 g, 1 mmol) and 1-pyrrolidinyl-2-phenylethene (**2b**, 0.693 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (9:1) to get white solid (197 mg, 80%). m.p. = 128-130 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.81 (d, 2.0 Hz, 1H), 8.80 (d, 2.0 Hz, 1H), 8.07 (s, 1H), 7.65 (d, J = 7.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.51 (t, 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 7.0 Hz, 2H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 145.154, 137.682, 135.308, 135.128, 134.024, 132.206, 129.820, 126.935, 32.307, 29.006, 22.278, 22.879, 21.282. MS (EI): m/z 245 (M^+).

*Synthesis of 3-methyl-2-phenylpyridine (**3l**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The

solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. Isoxazole (1a, 0.069 g, 1 mmol) and 1-(1-phenylprop-1-en-1-yl)pyrrolidine (**2c**, 0.750 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (9:1) to get a colorless oil (113 mg, 67%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.53 (d, J = 4.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1 Hz), 7.53 (d, J = 7.0 Hz, 2H), 7.45 (t, J = 7.0 Hz, 2H), 7.39(t, J = 7.0 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 158.794, 147.082, 140.695, 138.662, 130.973, 129.067, 128.286, 128.058, 122.210, 20.211. MS (EI): m/z 169 (M^+). The ^{1}H and ^{13}C{^{1}H} NMR spectroscopy of the compound matches that in the literature.[12]

*Synthesis of 3-bromo-5-methyl-6-phenylpyridine (**3m**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Bromoisoxazole (**1c**, 0.148 g, 1 mmol) and 1-(1-phenylprop-1-en-1-yl)pyrrolidine (**2c**, 0.750 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane

and ethyl acetate (8:2) to get a colorless oil (208 mg, 84%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.58 (s, 1H), δ 7.74 (s, 1H), 7.50 (s, J = 7.0 Hz, 2H), 7.45 (t, J = 7.0 Hz, 2H), 7.41 (t, J = 7.0 Hz, 1H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 147.847, 145.669, 140.766, 137.962, 132.781, 128.880, 128.827, 128.303, 128.283, 118.949, 19.982. MS (EI): m/z 247 (M^+). The ^{1}H and ^{13}C{^{1}H} NMR spectroscopy of the compound matches that in the literature.[13]

*Synthesis of 3-methyl-2-phenyl-5-(4-tolyl)pyridine (**3n**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. (4-Tolyl)isoxazole (**1b**, 0.159 g, 1 mmol) and 1-(1-phenylprop-1-en-1-yl)pyrrolidine (**2c**, 0.750 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (8:2) to get a white solid (200 mg, 77%). m.p. = 80-81 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.76 (s, 1H), δ 8.66 (s, 1H), 8.03 (s, 1H), 7.57 (d, J = 7.0 Hz, 2H), 7.49 (t, J = 7.0 Hz, 2H), (t, J = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 159.562, 147.642, 139.605, 137.960, 135.045, 134.966, 134.358, 129.907, 129.278, 128.787, 126.988, 126.587, 123.133, 44.429, 21.294 . MS (EI): m/z 259 (M^+).

*Synthesis of 2-(N-acetoamino)-5-methyl-6-phenylpyridine (**3o**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 3-*(N*-Acetoamino)isoxazole (**1d**, 0.126 g, 1 mmol) and 1-(1-phenylprop-1-en-1-yl)pyrrolidine (**2c**, 0.750 g, 4 mmol, 4 equiv) were added to the solution in

dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (7:3) to get an amber solid (147 mg, 65%). m.p. = 159 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (s br, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.29 (m, 4H), 7.20 (t, J = 7.0 Hz, 1H), 2.10 (s, 3H), 1.90 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 168.761, 156.566, 148.985, 141.148, 140.033, 128.870, 128.410, 128.263, 128.806, 112.552, 24.690, 19.325. MS (EI): m/z 226 (M^+).

*Synthesis of 2,3-diphenylpyridine (**3p**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. Isoxazole (**1a**, 0.069 g, 1 mmol) and 1-(1,2-diphenylvinyl)pyrrolidine (**2d**, 1 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (9:1) to get white solid (207 mg, 90%). m.p. = 56-58 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.71 (dd, J = 5.0 Hz, 2.0 Hz, 1H), 7.74 (dd, J = 5.0 Hz, 2.0 Hz, 1H), 7.39-7.32 (m, 2H), 7.31-7.23 (m, 6H), 7.21-7.17 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 157.227, 148.372, 140.107, 139.956, 138.791, 136.271, 130.016, 129.684, 128.462, 128.036,

127.960, 127.376, 122.248. MS (EI): m/z 231 (M^+). The ^1H and $^{13}C\{^1H\}$ NMR spectroscopy of the compound matches that in the literature.[14]

*Synthesis of 3-bromo-5,6-diphenylpyridine (**3q**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Bromoisoxazole (**1c**, 0.148 g, 1 mmol) and 1-(1,2-diphenylvinyl)pyrrolidine (**2d**, 1 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and dichloromethane (9:1 to 4:6) to get white solid (273 mg, 88%). m.p. = 103-105 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.74 (s, 1H), 7.88 (s, 1H), 7.34-7.20 (m, 8H), 7.19-7.13 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 155.631, 149.103, 140.831, 138.905, 138.512, 137.616, 129.745, 129.423, 128.509, 128.180, 128.029, 127.801, 119.043. MS (EI): m/z 310 (M^+).

*Synthesis of 3-methyl-5,6-diphenyl-2-(4-tolyl)pyridine (**3r**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Methyl-3-(4-tolyl)isoxazole (0.174 g, 1 mmol) and 1-(1,2-diphenylvinyl)pyrrolidine (**2d**, 1 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5

min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and dichloromethane (9:1 to 4:6) to get white solid (306 mg, 91%). m.p. = 119-122 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.76 (s, 1H), δ 8.66 (s, 1H), 8.03 (s, 1H), 7.57 (d, J = 7.0 Hz, 2H), 7.49 (t, J = 7.0 Hz, 2H), (t, J = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 148.001, 145.823, 140.878, 139.599, 138.077, 129.015, 128.962, 128.434, 119.083. MS (EI): m/z 334 (M^+).

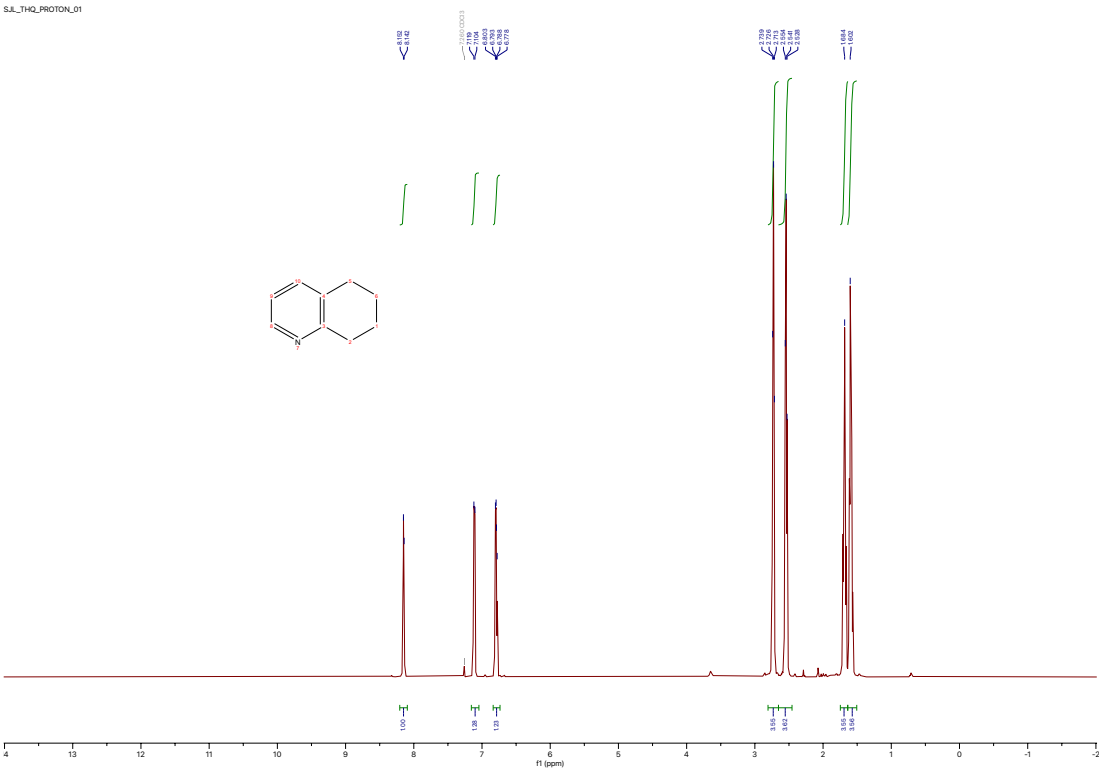
*Synthesis of 2,3-di-(4-tolyl)pyridine (**3s**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5 mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. Isoxazole (**1a**, 0.069 g, 1 mmol) and 1-(1,2-di(4-tolyl)vinyl)pyrrolidine (**2e**, 1 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and ethyl acetate (9:1) to get a colorless oil (174 mg, 67%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.73 (d, J = 5.0 Hz, 1H), δ 7.76 (d, J = 8.0 Hz, 1H), 7.40-7.30 (m, 3H), 7.20-7.10 (m, 6H), 2.42 (s, 3H), 2.19 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 157.209, 148.179, 138.696, 137.608, 137.474, 137.271, 137.001, 136.002, 129.862, 129.485, 129.182, 128.741, 121.935, 21.393, 21.312. MS (EI): m/z 259 (M^+). The ^{1}H and ^{13}C{^{1}H} NMR spectroscopy of the compound matches that in the literature.[15]

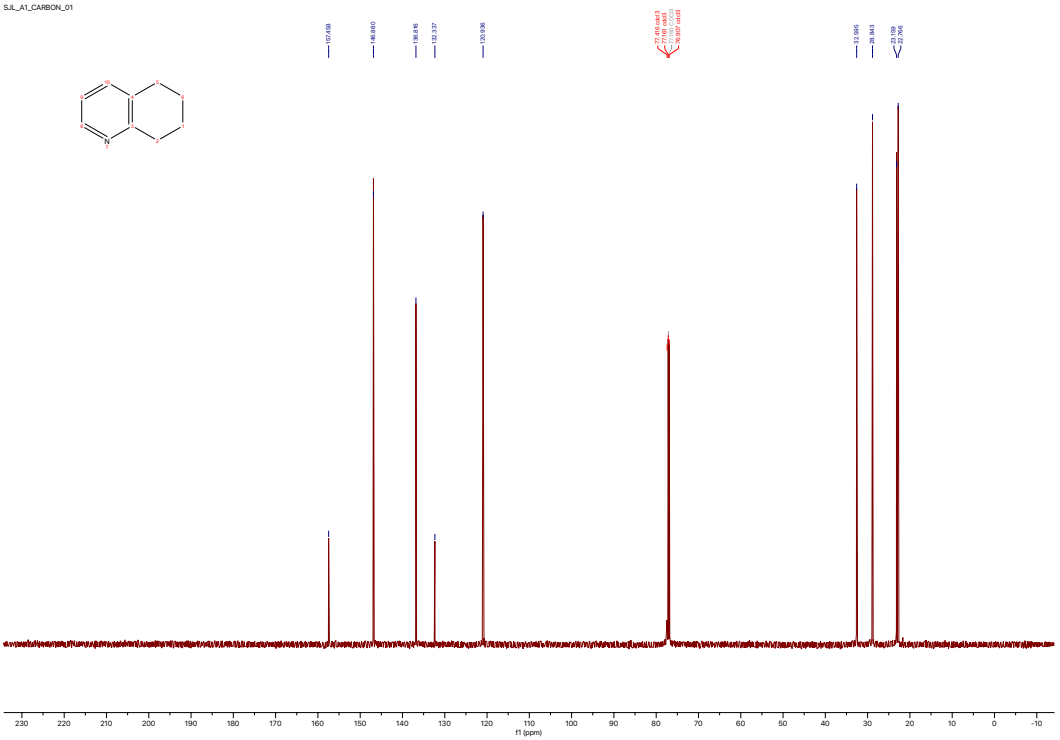
*Synthesis of 3-bromo-5,6-di-(4-tolyl)pyridine (**3t**).* A 15 mL pressure tube was charged with $TiCl_4(THF)_2$ (0.334 g, 1 mmol, 1 equiv), titanium powder (0.056 g, 1.0 mmol, 1.0 equiv), and dioxane (0.5

mL). The solution was stirred for 1 h over which solids form, and then 1 mL dioxane was added to the solution and stirring was continued for an additional 1 h. 4-Bromoisoxazole (**1c**, 0.148 g, 1 mmol) and 1-(1,2-di(4-tolyl)vinyl)pyrrolidine (**2e**, 1 g, 4 mmol, 4 equiv) were added to the solution in dioxane (1 mL). The pressure tube was sealed and transferred from the glovebox to a preheated 100 °C aluminum block. The reaction was heated with stirring for 12 h. After heating, the pressure tube was cooled to room temperature over 10 min. Then, 2 mL of 20% aqueous K_2CO_3 was added, and the mixture was stirred for 5 min. After stirring, solids were removed by vacuum filtration and were washed with CH_2Cl_2 (~10 mL). The filtrate was dried with Na_2SO_4 and filtered through a piece of cotton. The solvent was removed under reduced pressure. The product was purified by a silica gel auto-column chromatography, eluted with hexane and dichloromethane (9:1 to 4:6) to get white solid (285 mg, 84%). m.p. = 93-95 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.69 (s, 1H), δ 7.83 (s, 1H), 7.22 (d, J = 7.5 Hz, 2H), 7.09 (t, J = 8.0 Hz, 2H), 7.07-7.02 (m, 5H), 2.34 (s, 3H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ155.763, 148.995, 140.830, 138.069, 137.671, 137.523, 136.477, 135.949, 129.731, 129.366, 129.353, 128.871, 118.815, 21.417, 21.345. MS (EI): m/z 337 (M^+).

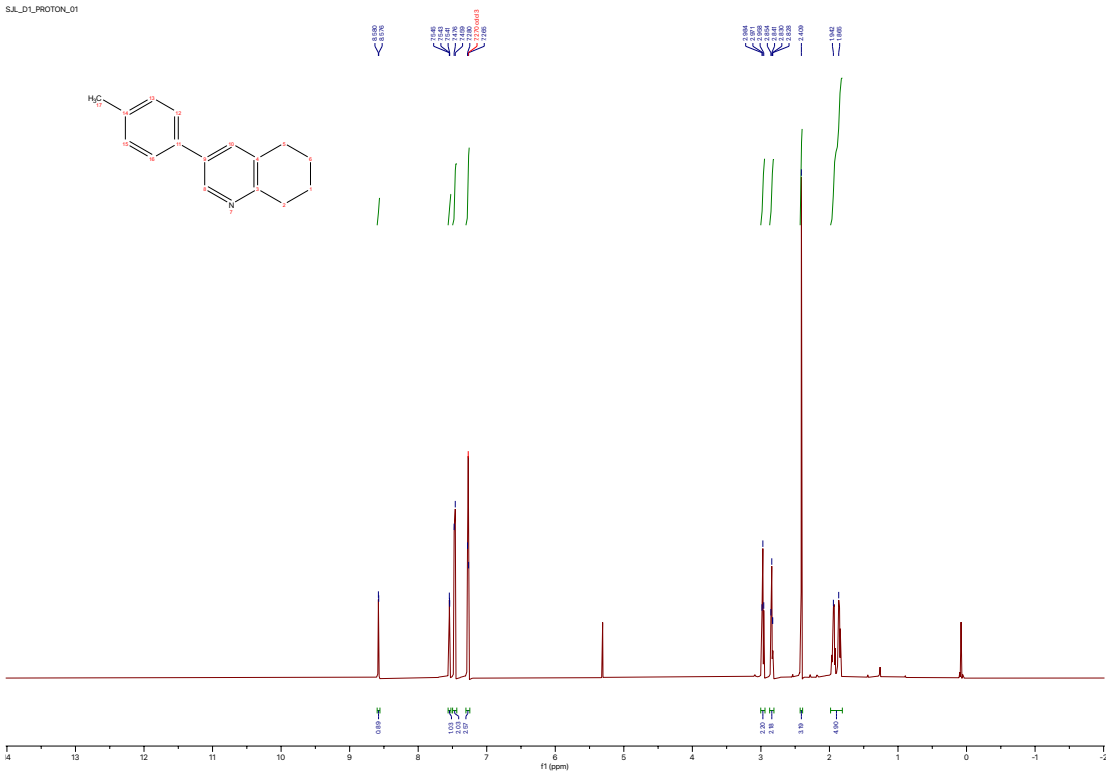
Spectral Data for Pyridine Derivatives

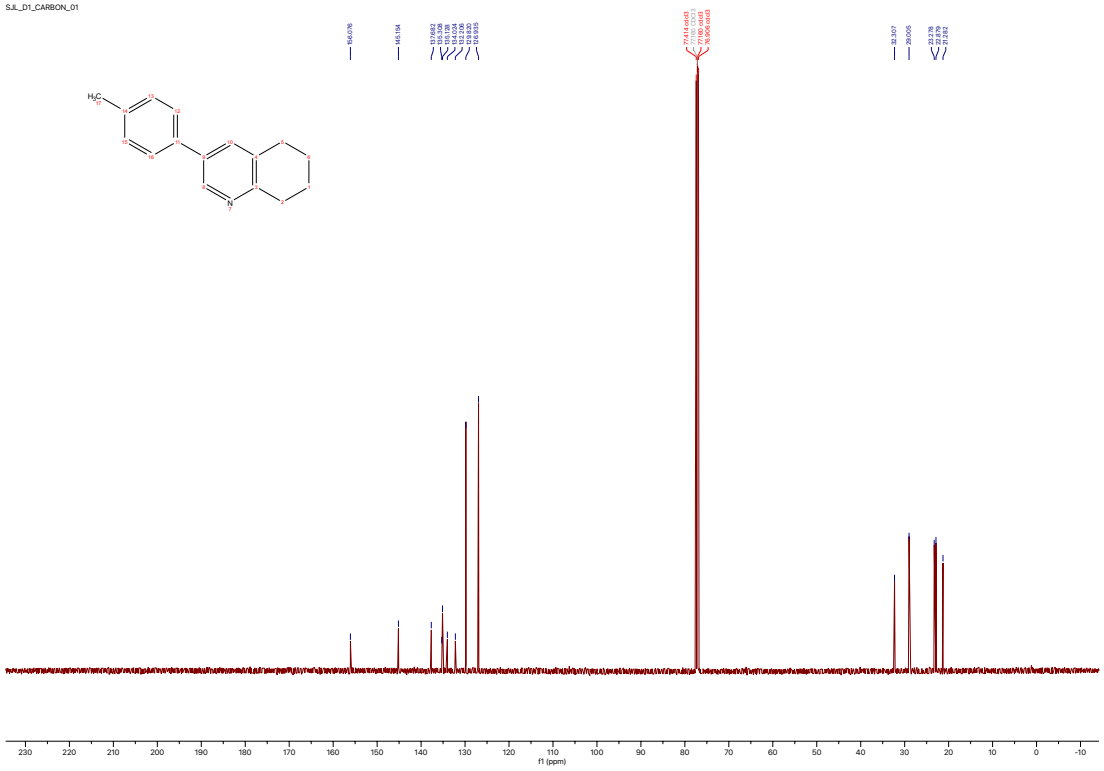
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 5,6,7,8-tetrahydroquinoline (**3a**)*



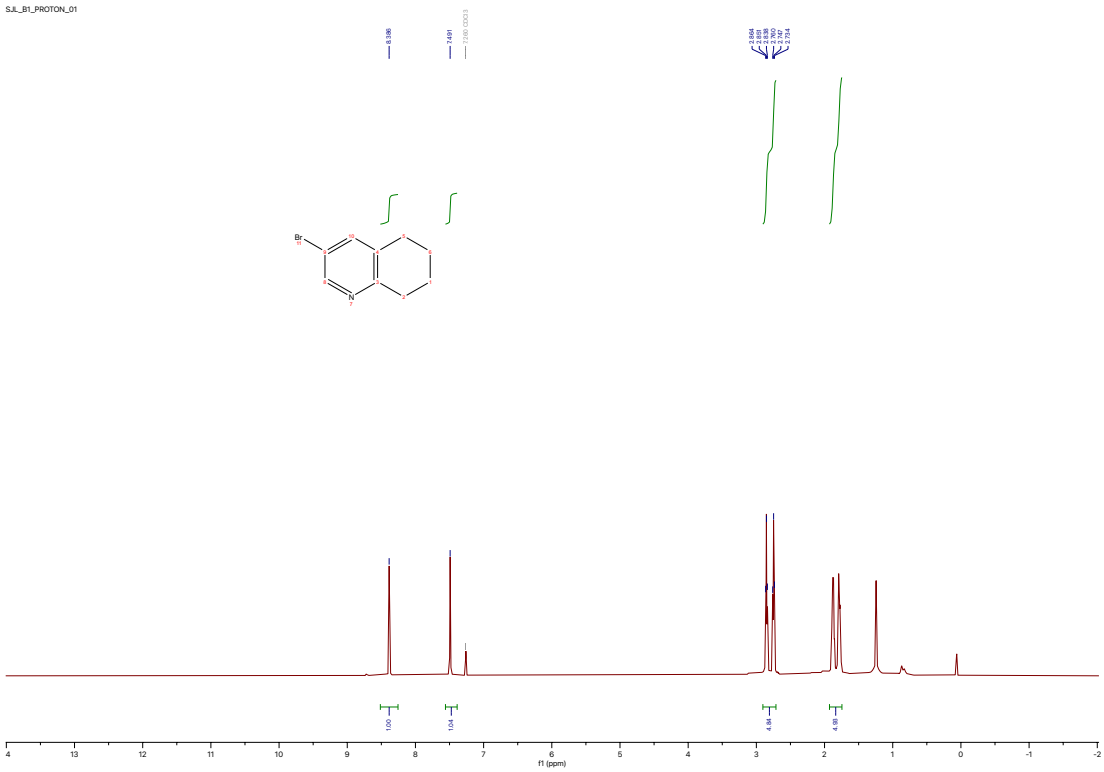


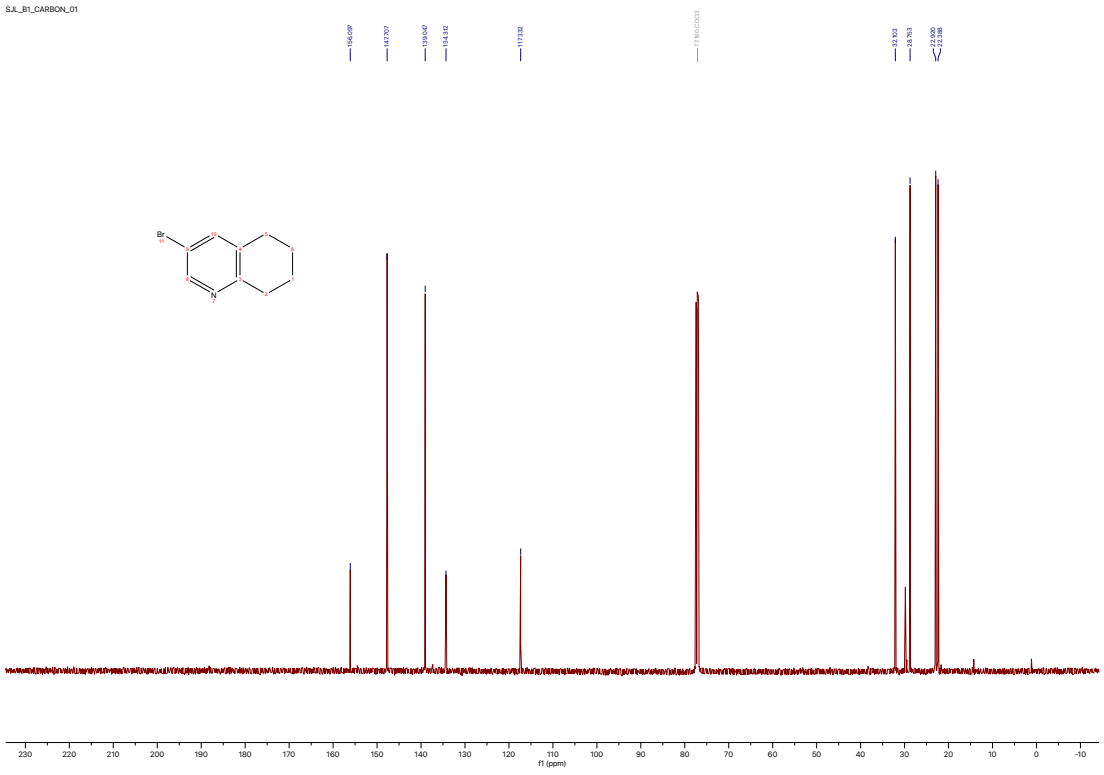
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-(4-tolyl)-5,6,7,8-tetrahydroquinoline (**3b**)*



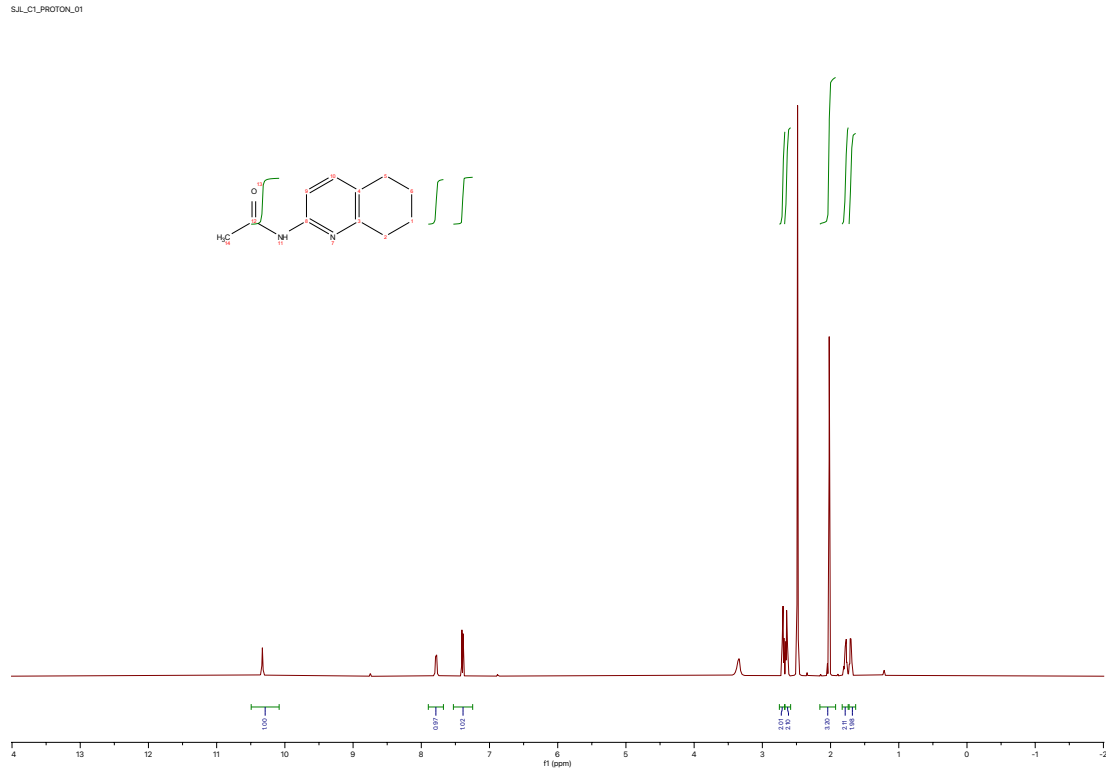


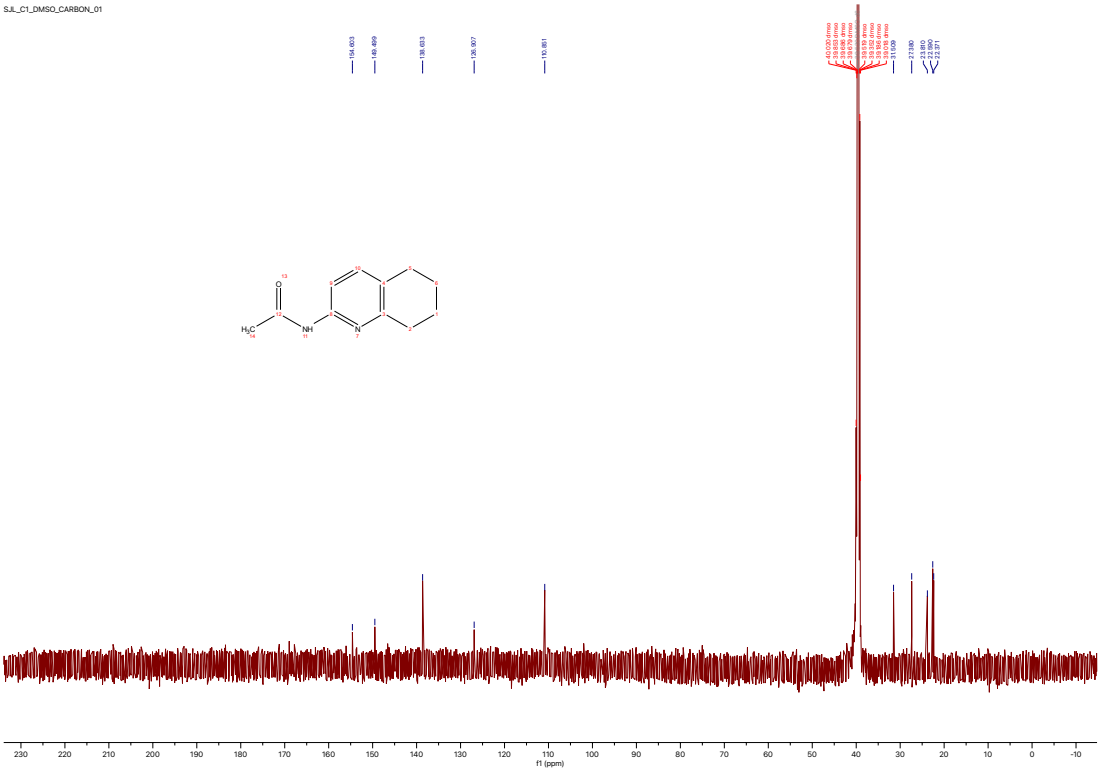
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-bromo-5,6,7,8-tetrahydroquinoline (**3c**)*



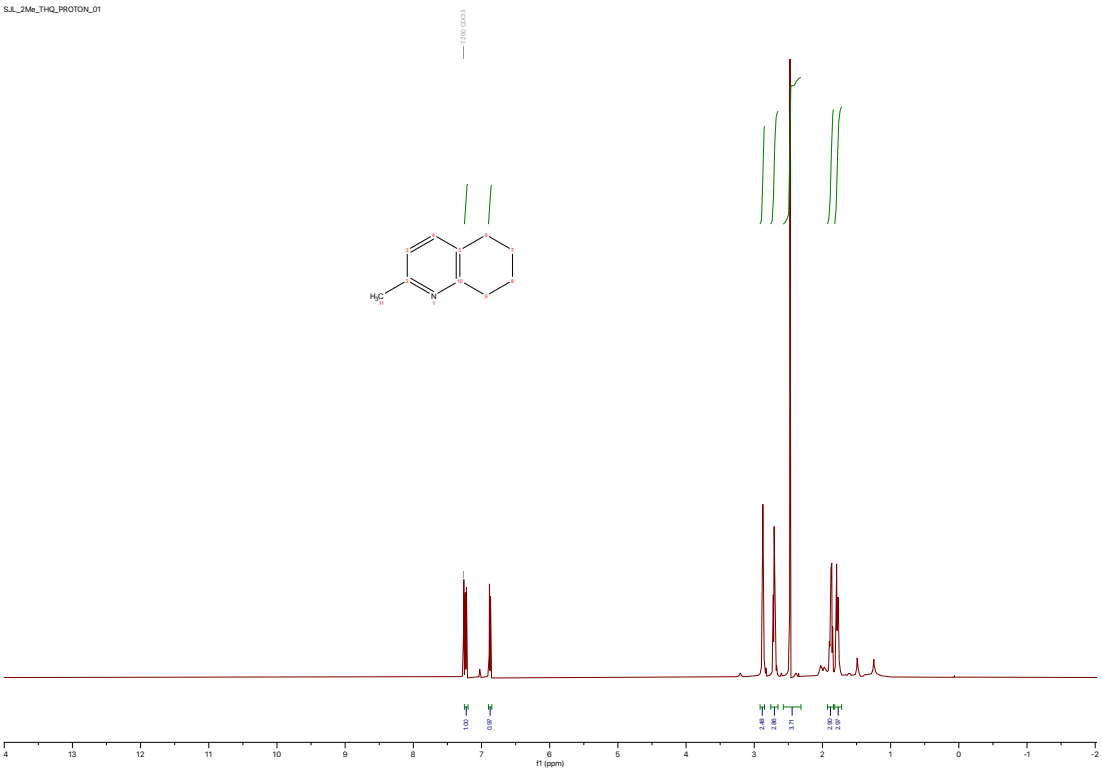


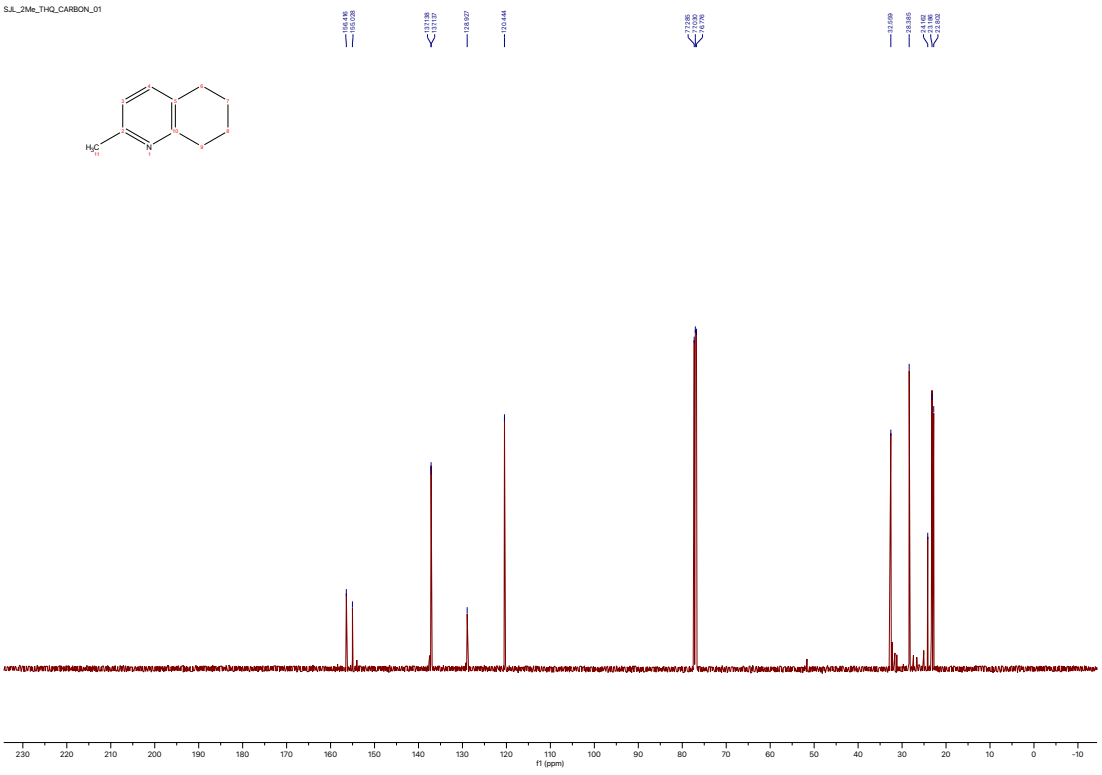
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 2-(N-acetylamino)-5,6,7,8-tetrahydroquinoline (**3d**)*



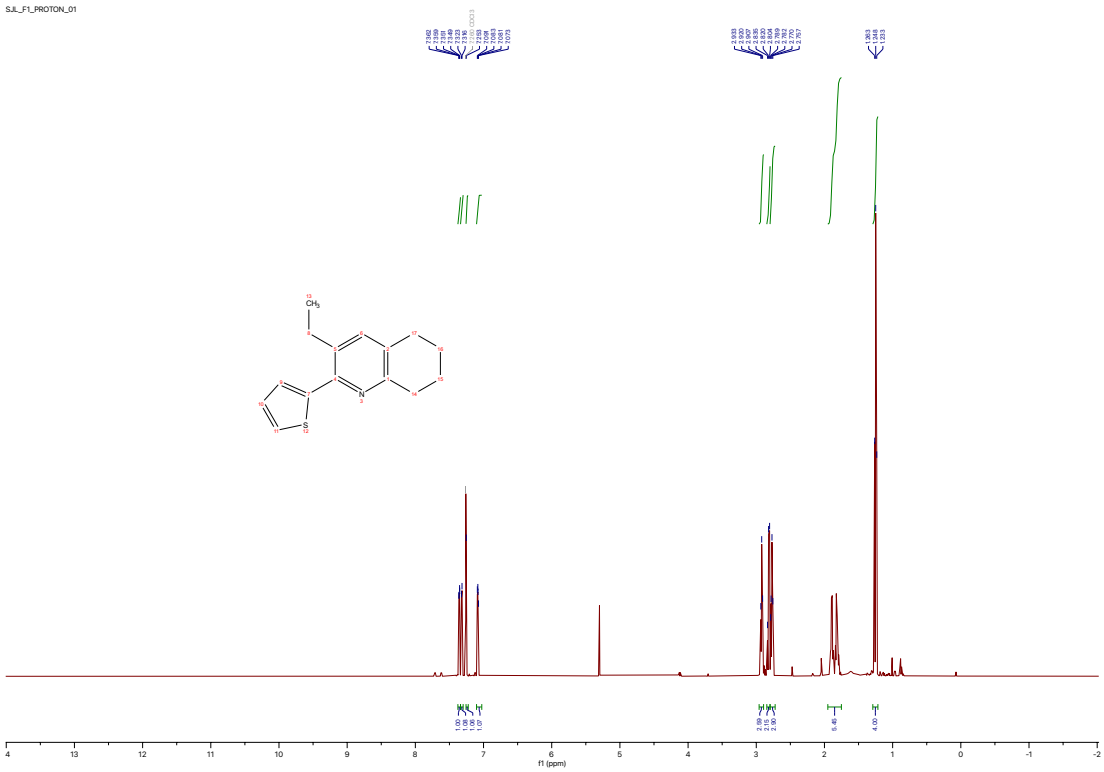


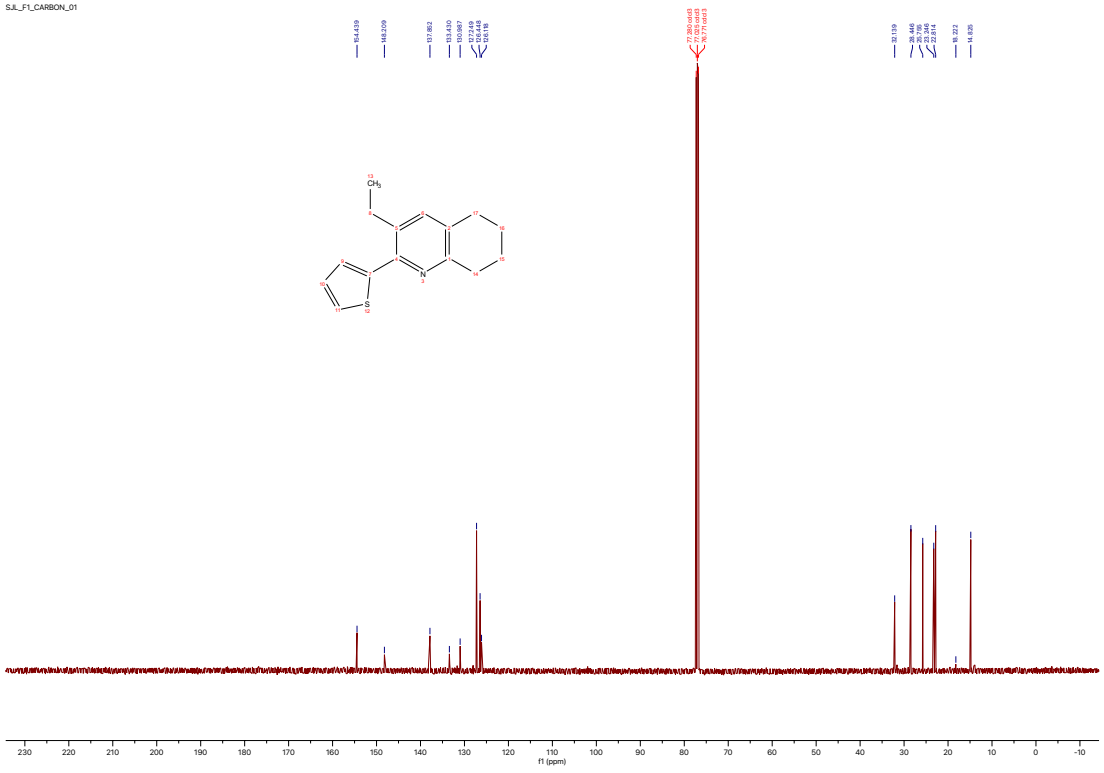
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 2-methyl-5,6,7,8-tetrahydroquinoline (**3e**)*



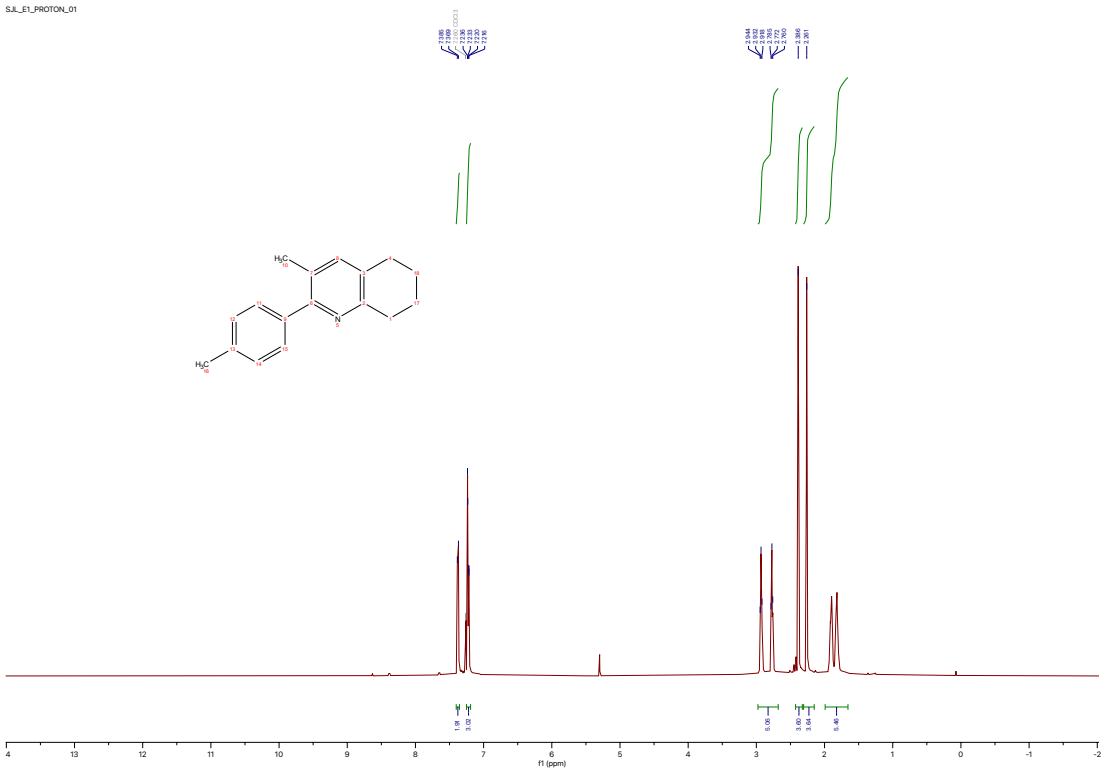


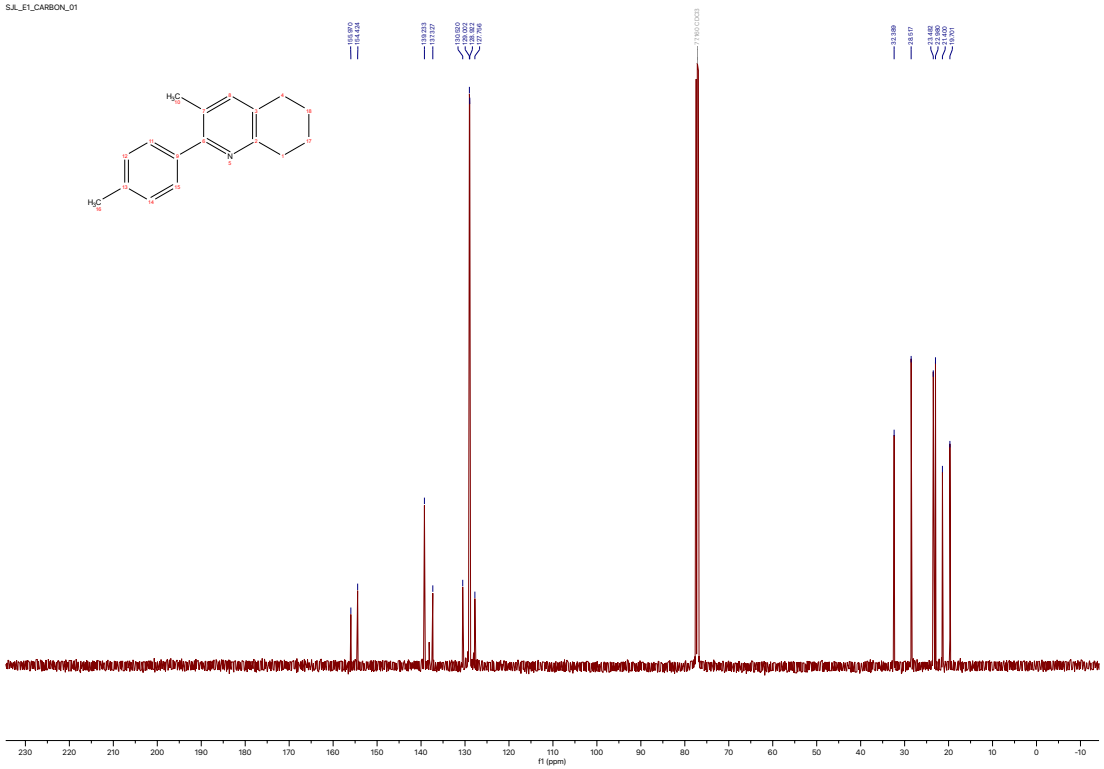
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-ethyl-2-(thiopheny-2-yl)-5,6,7,8-tetrahydroquinoline (**3f**)*



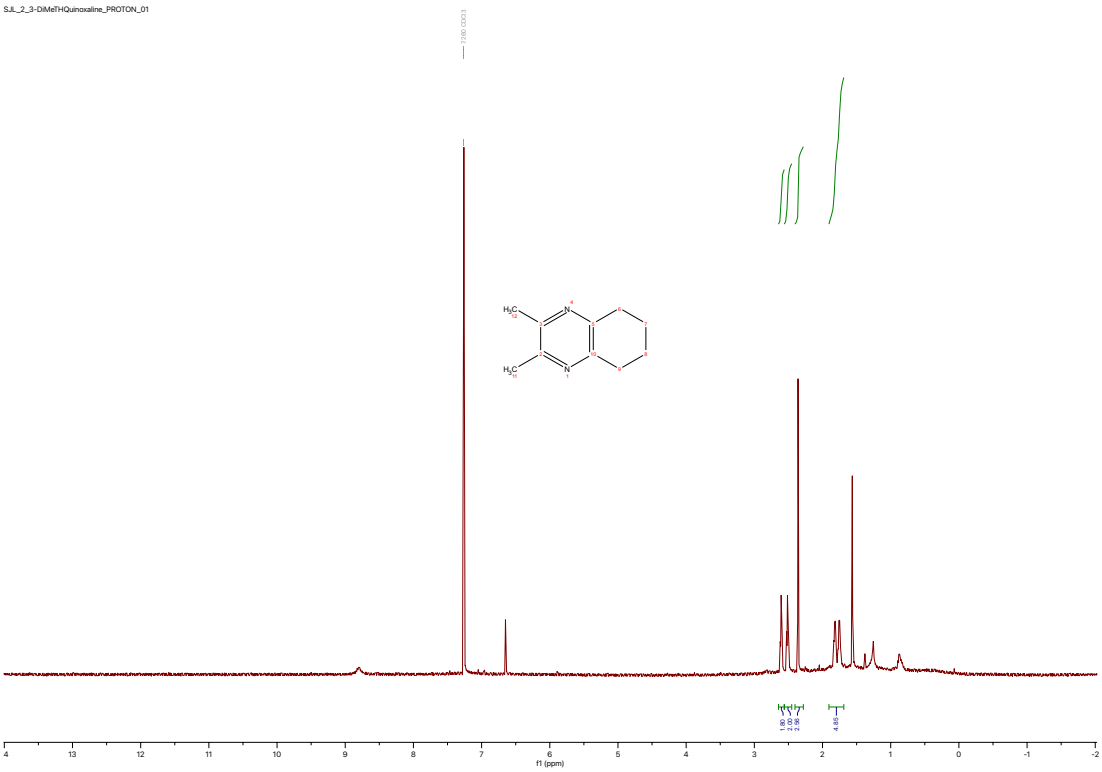


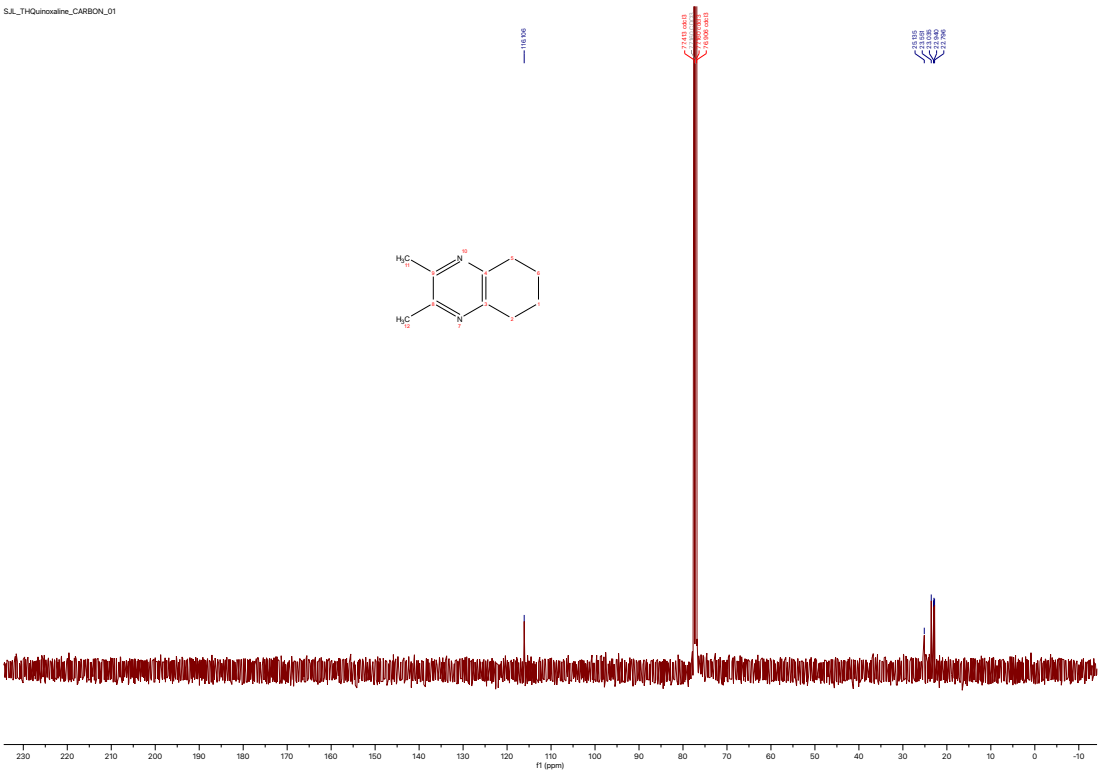
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-methyl-2-(4-tolyl)-5,6,7,8-tetrahydroquinoline (**3g**)*



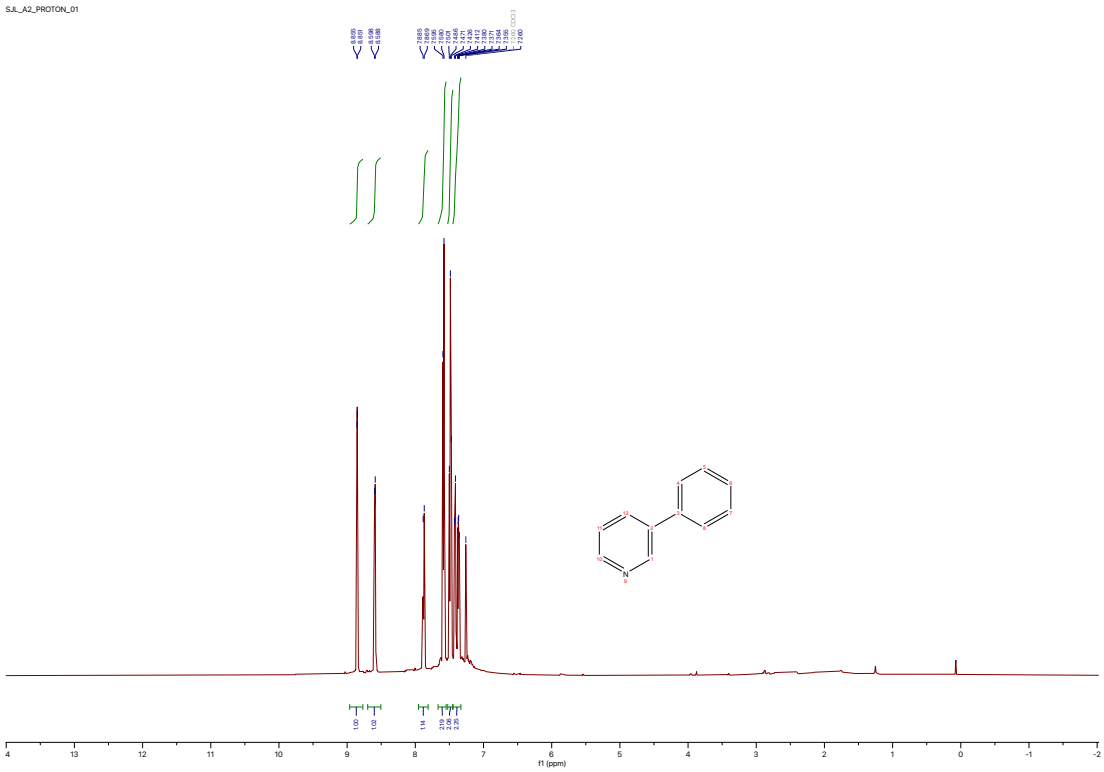


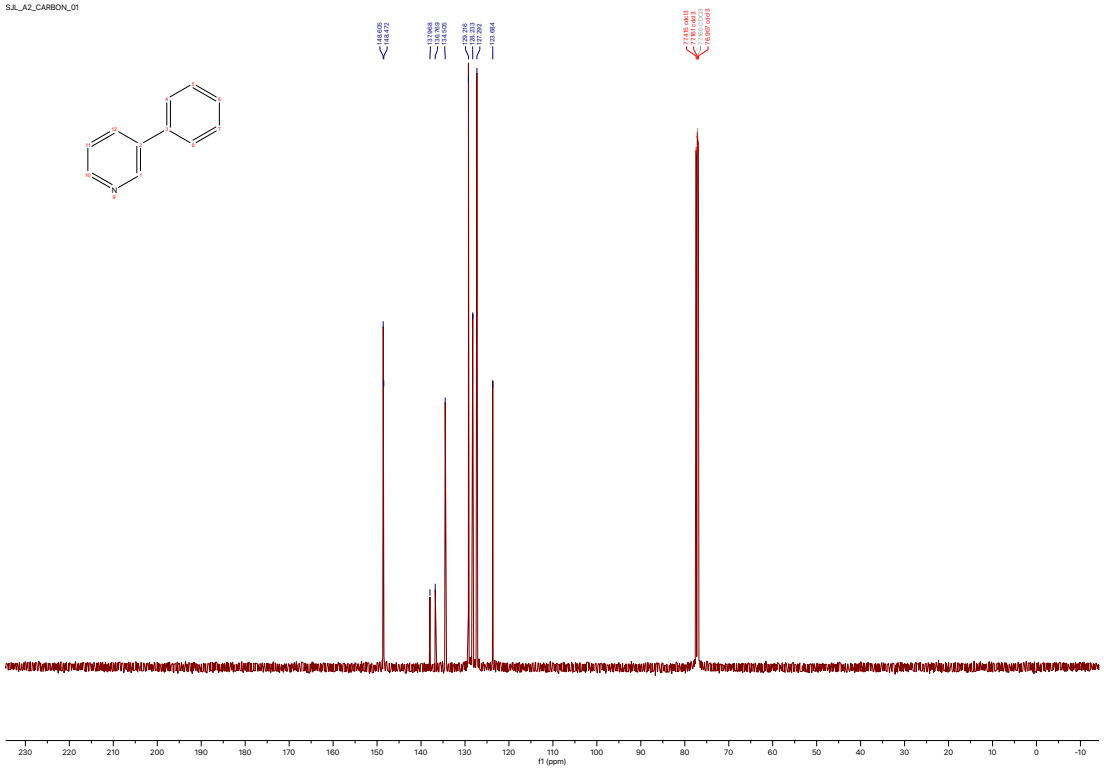
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 2,3-dimethyl-5,6,7,8-tetrahydroquinoxaline (**3h**)*



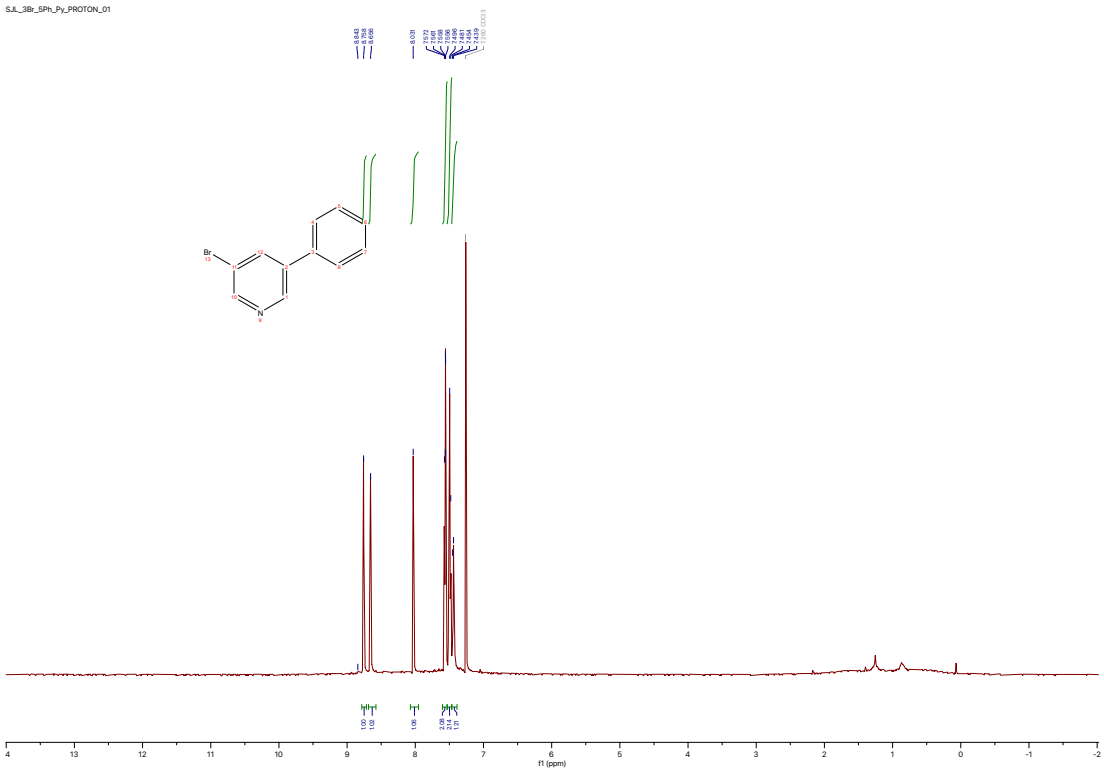


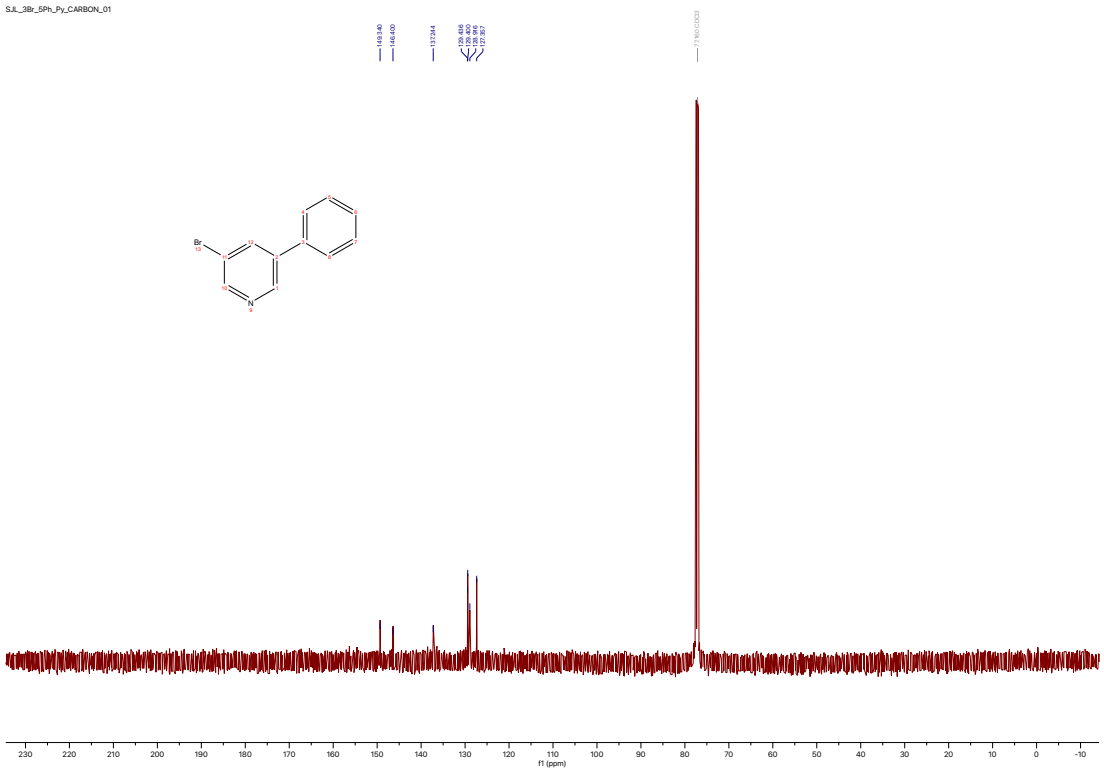
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-phenylpyridine (**3i**)*



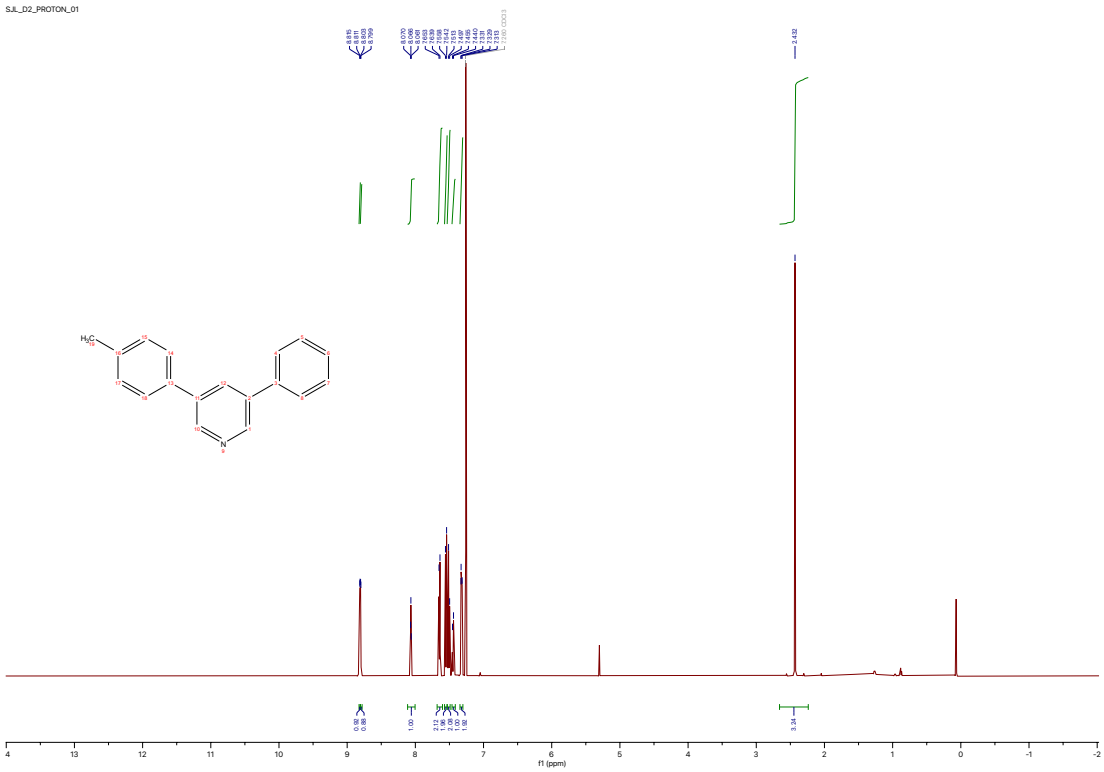


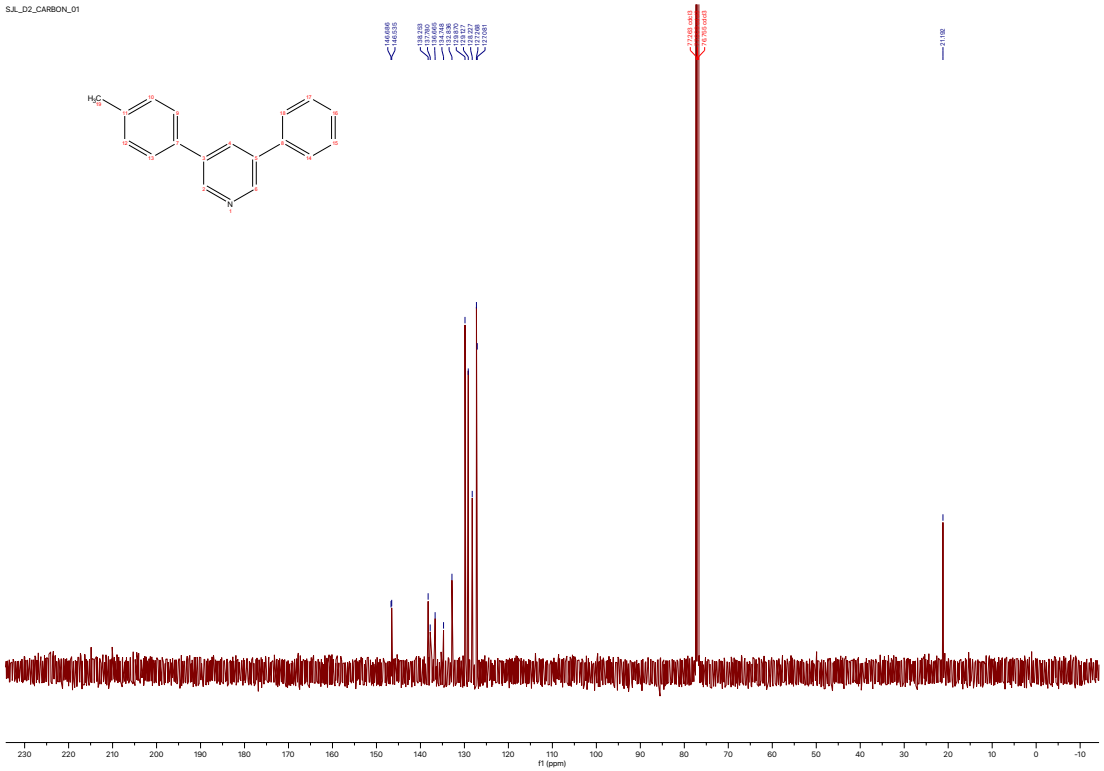
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-bromo-5-phenylpyridine (**3j**)*



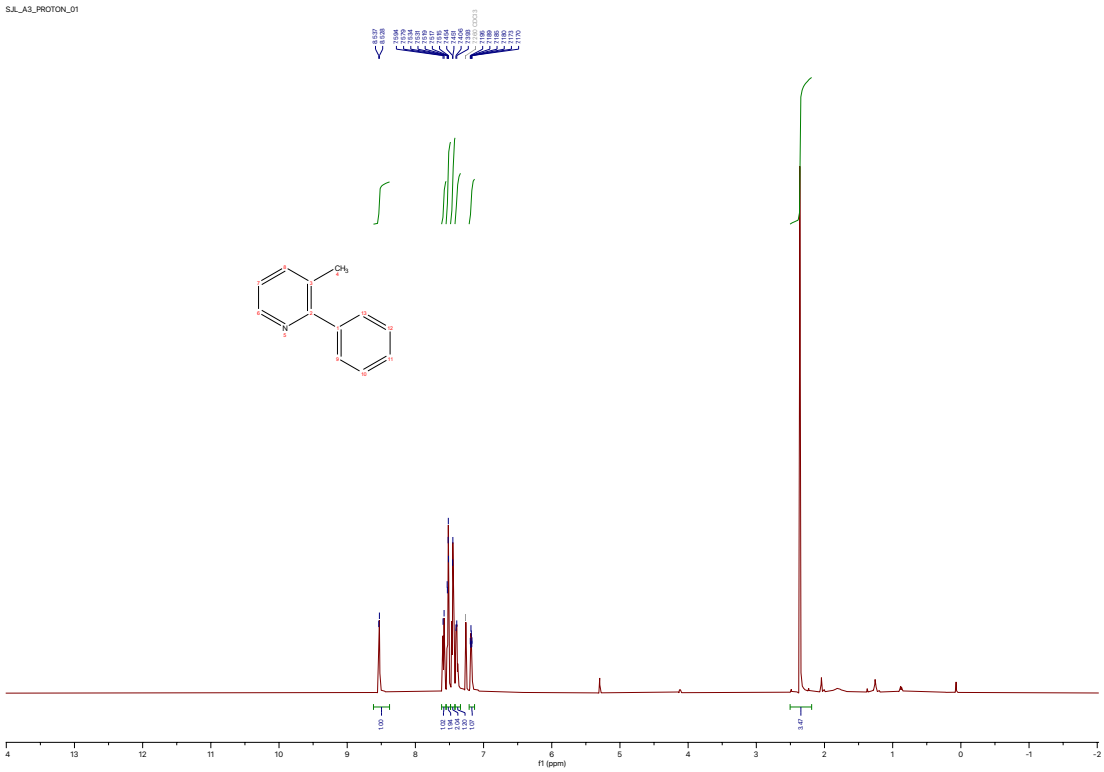


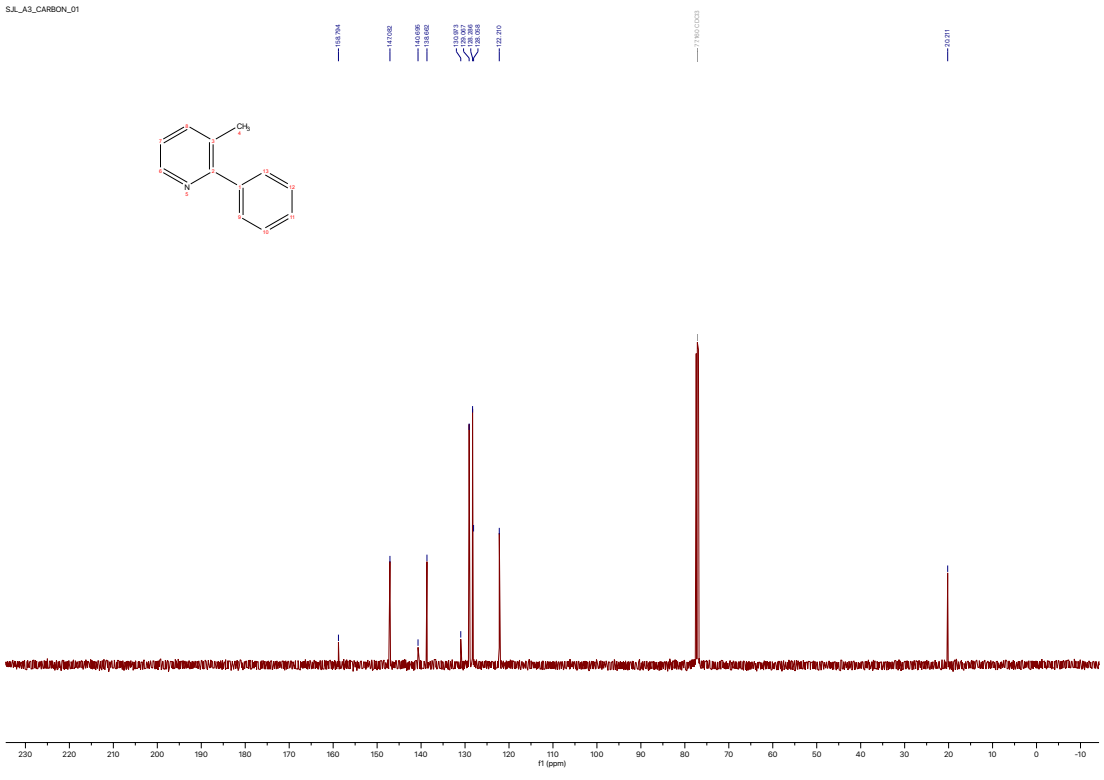
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-(4-tolyl)-5-phenylpyridine (**3k**)*



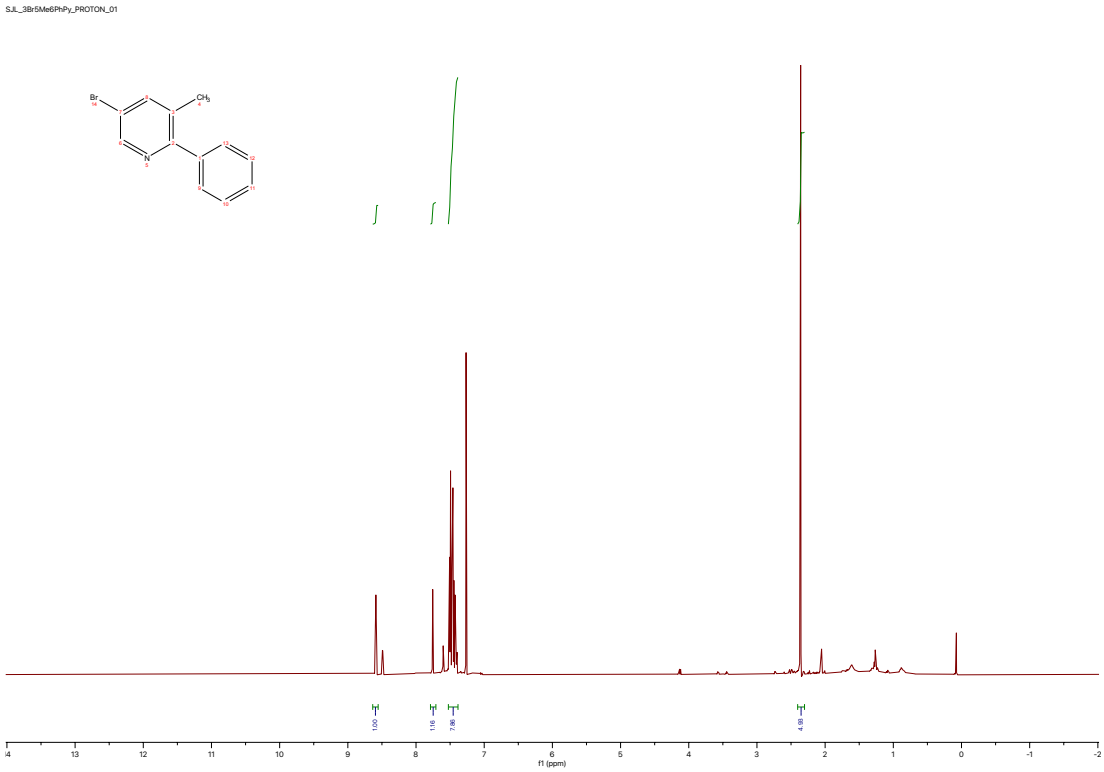


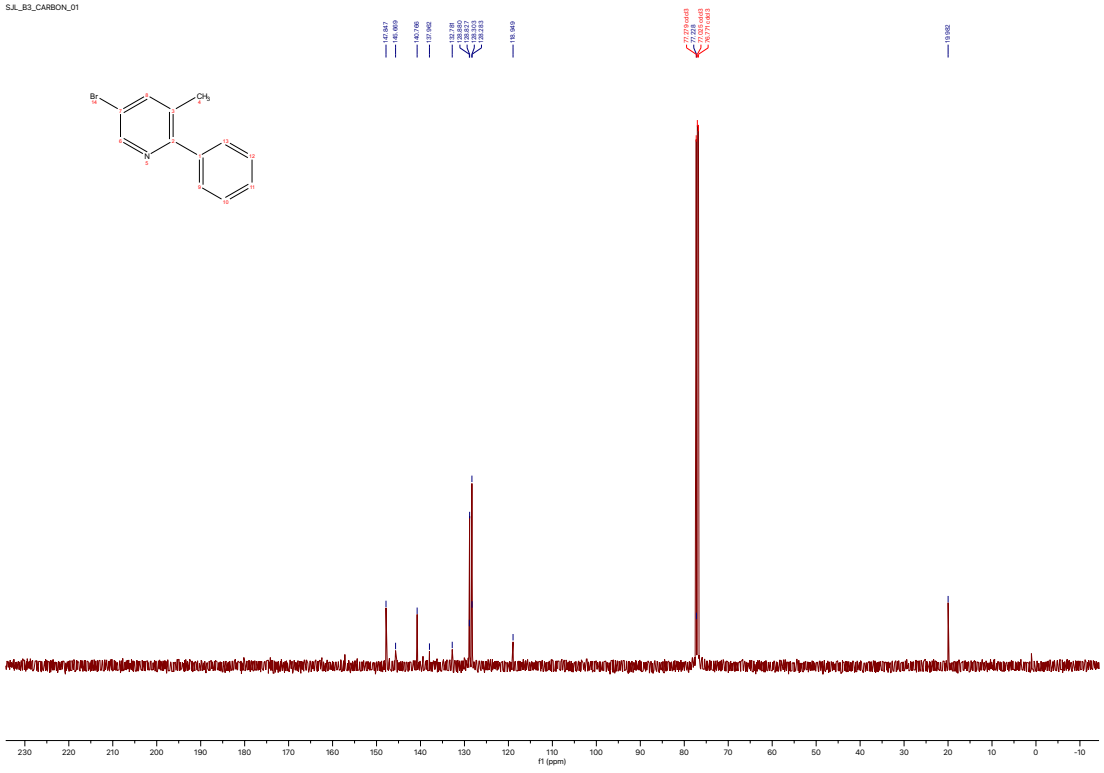
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-methyl-2-phenylpyridine (**3l**)*



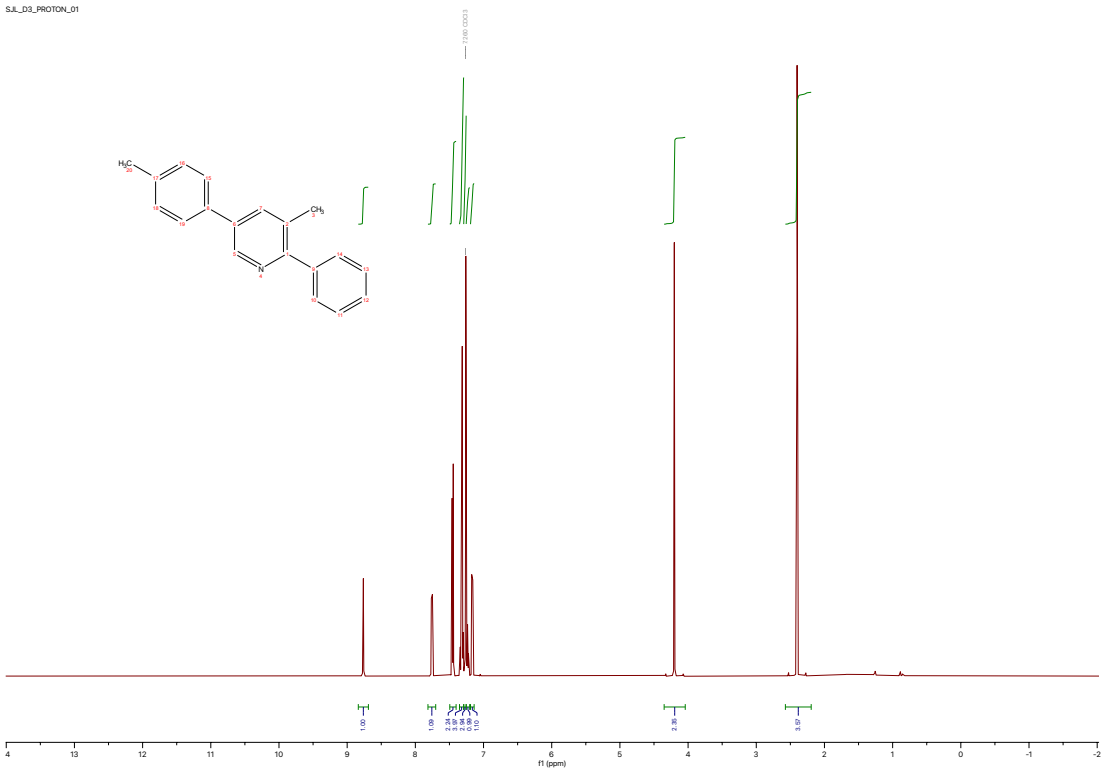


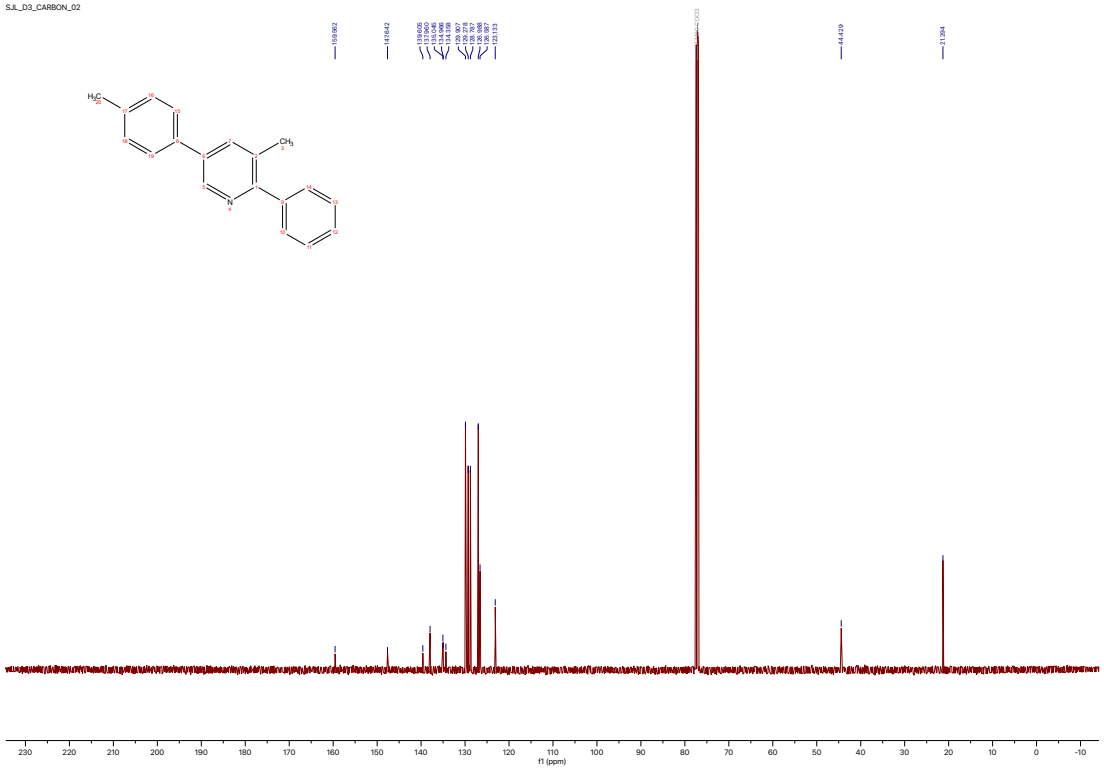
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-bromo-5-methyl-6-phenylpyridine (**3m**)*



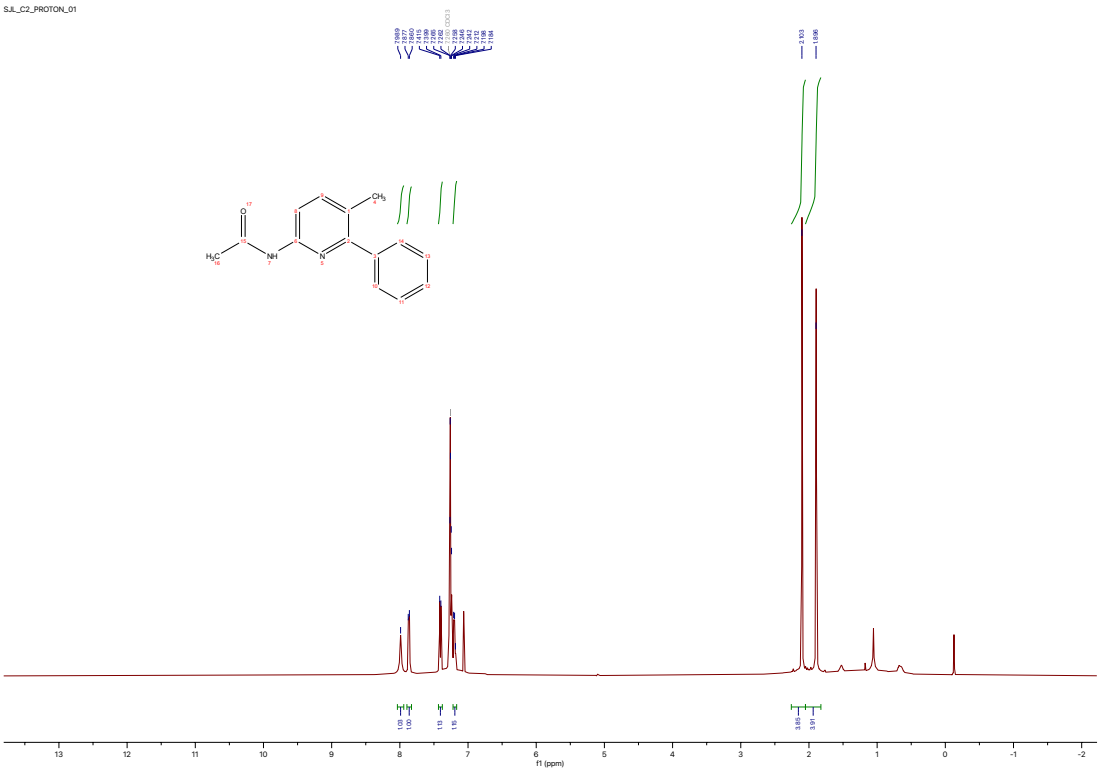


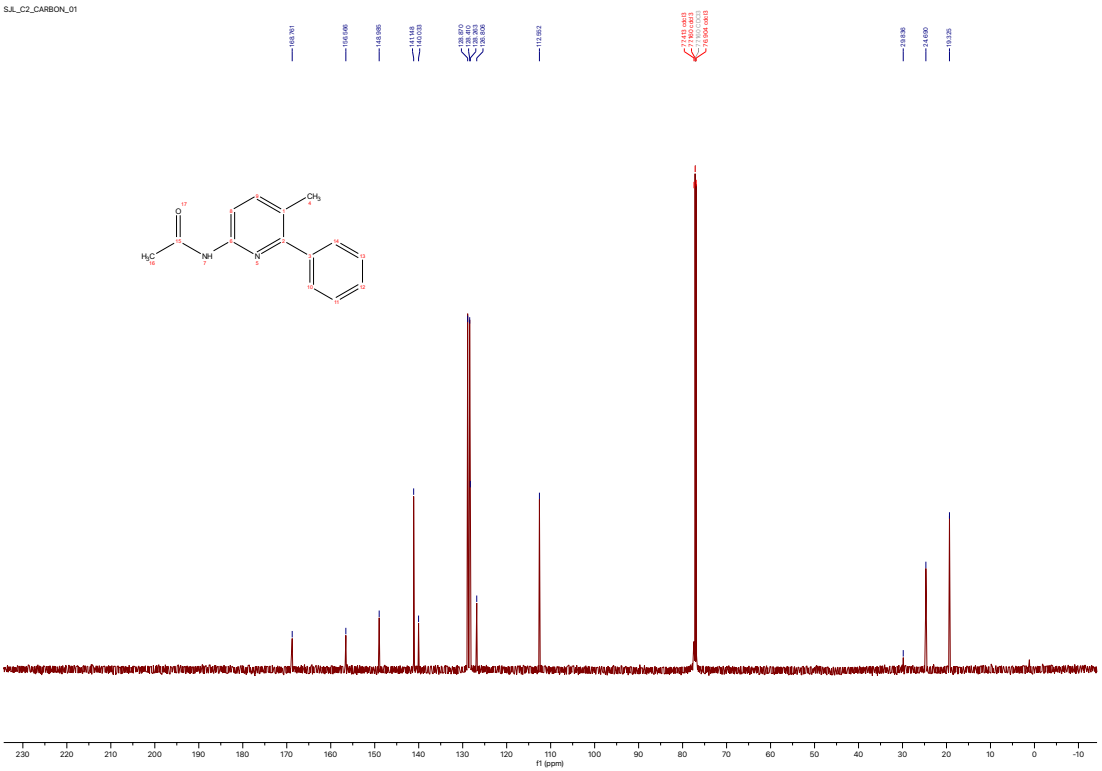
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-methyl-2-phenyl-5-(4-tolyl)pyridine (**3n**)*



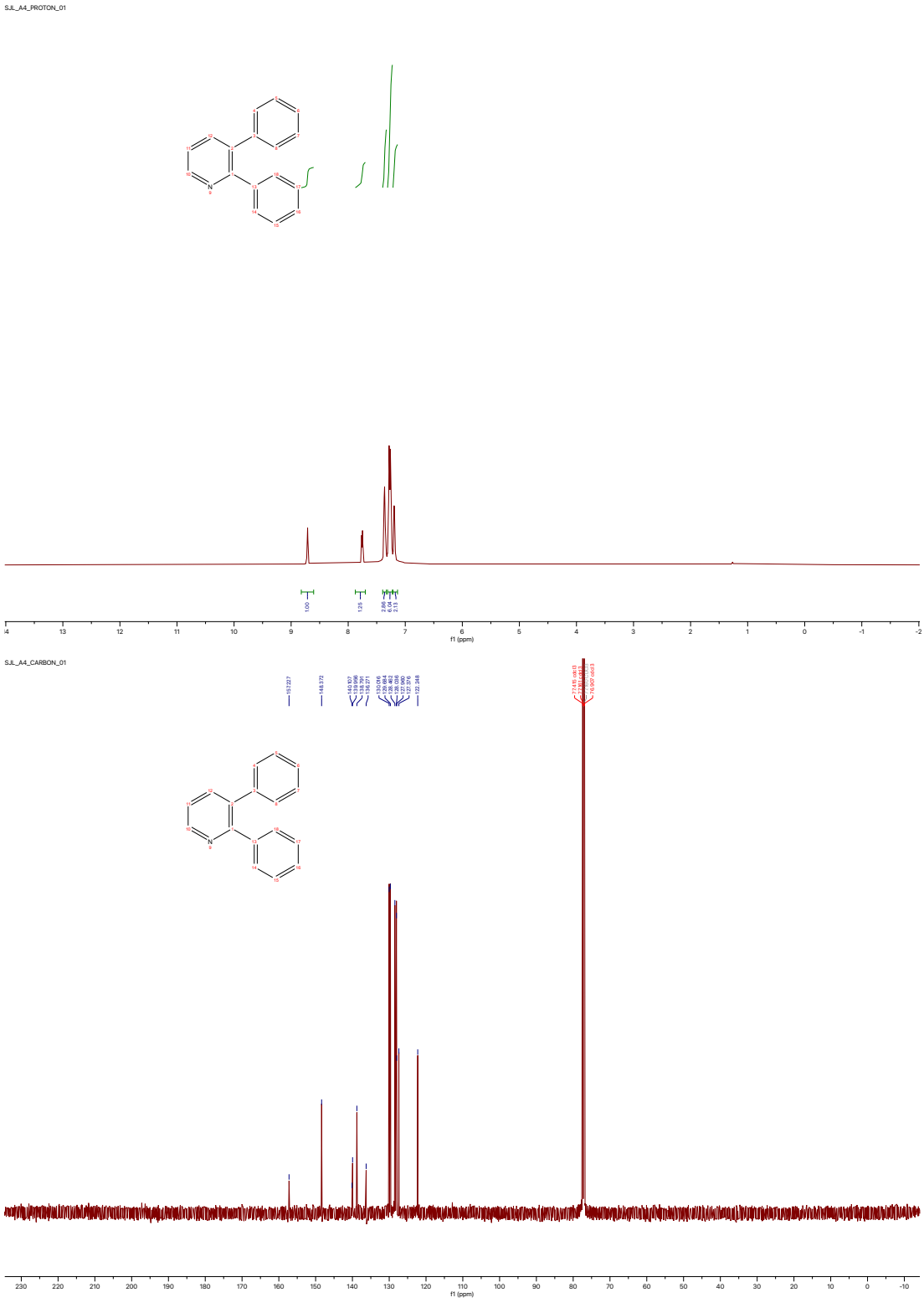


*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 2-(N-acetoamino)-5-methyl-6-phenylpyridine (**3o**)*

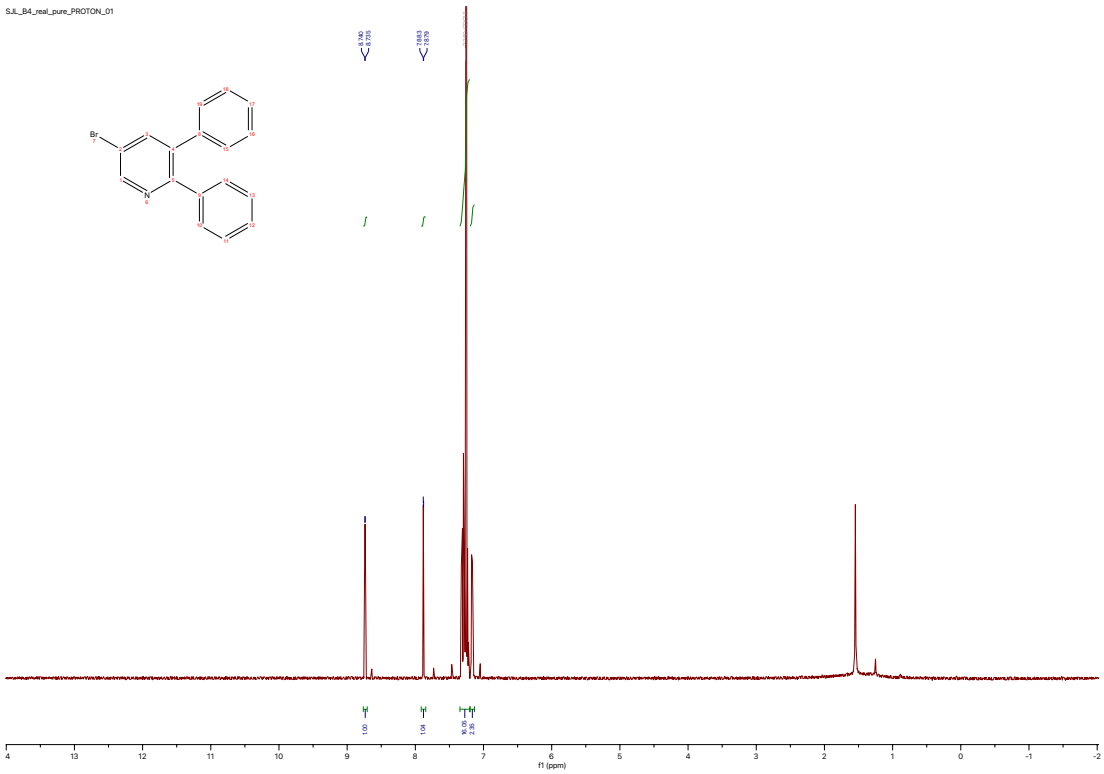


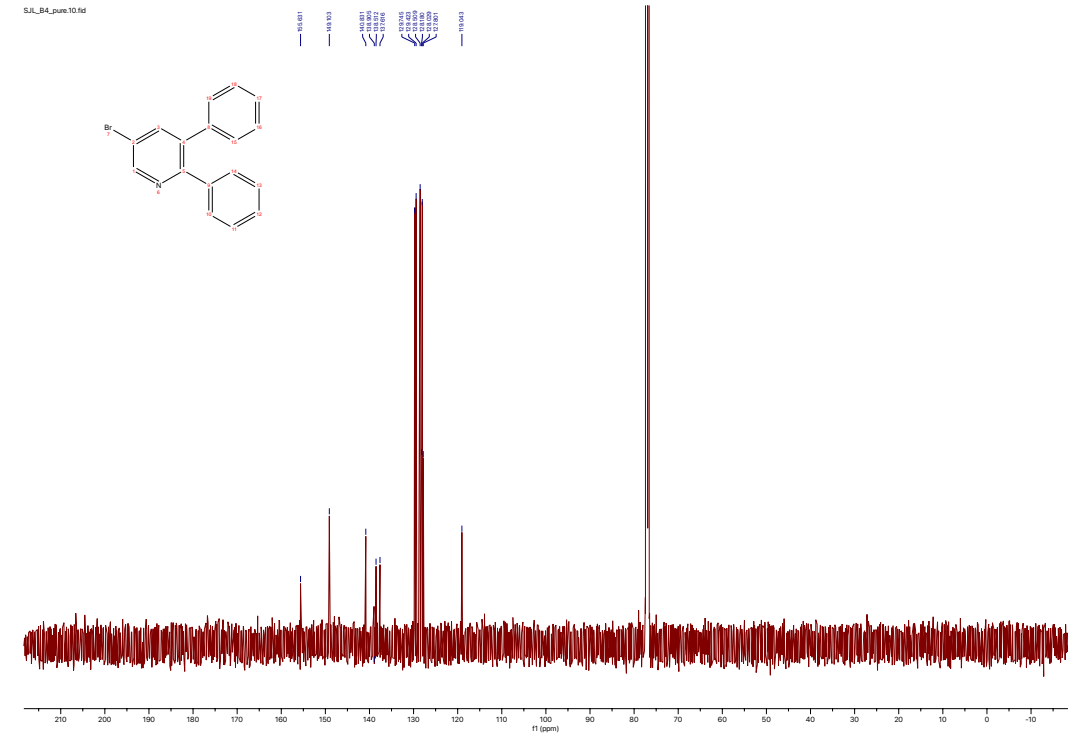


*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 2,3-diphenylpyridine (**3p**)*

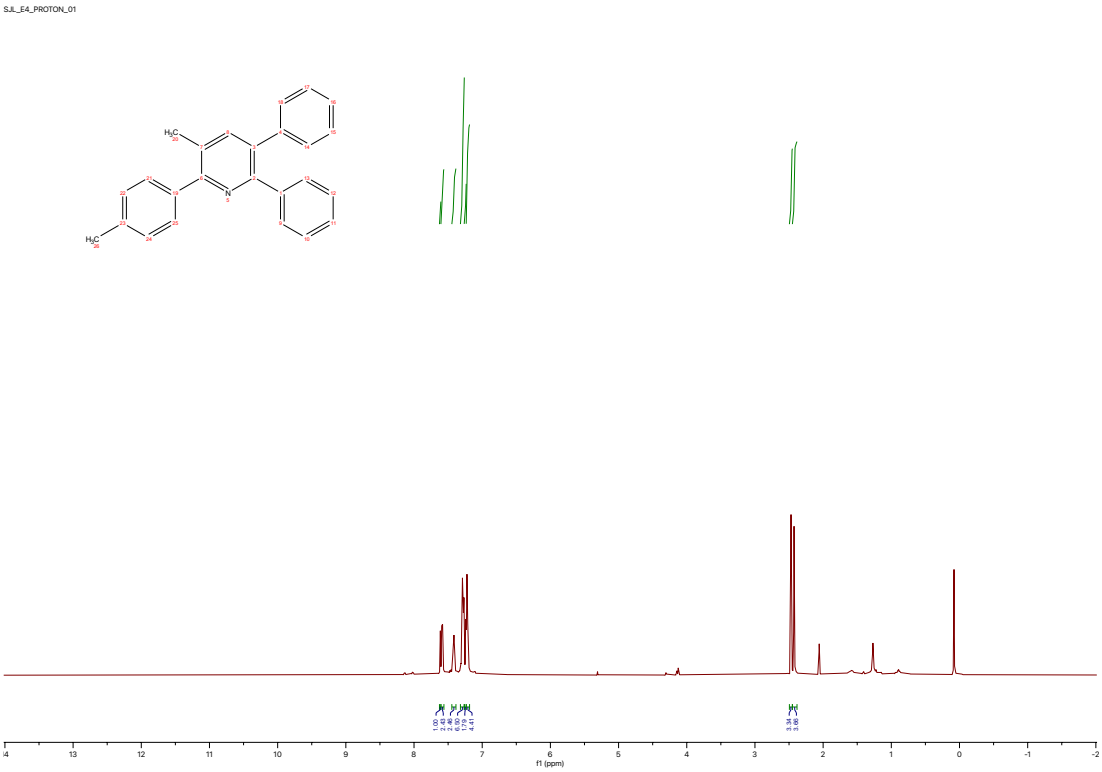


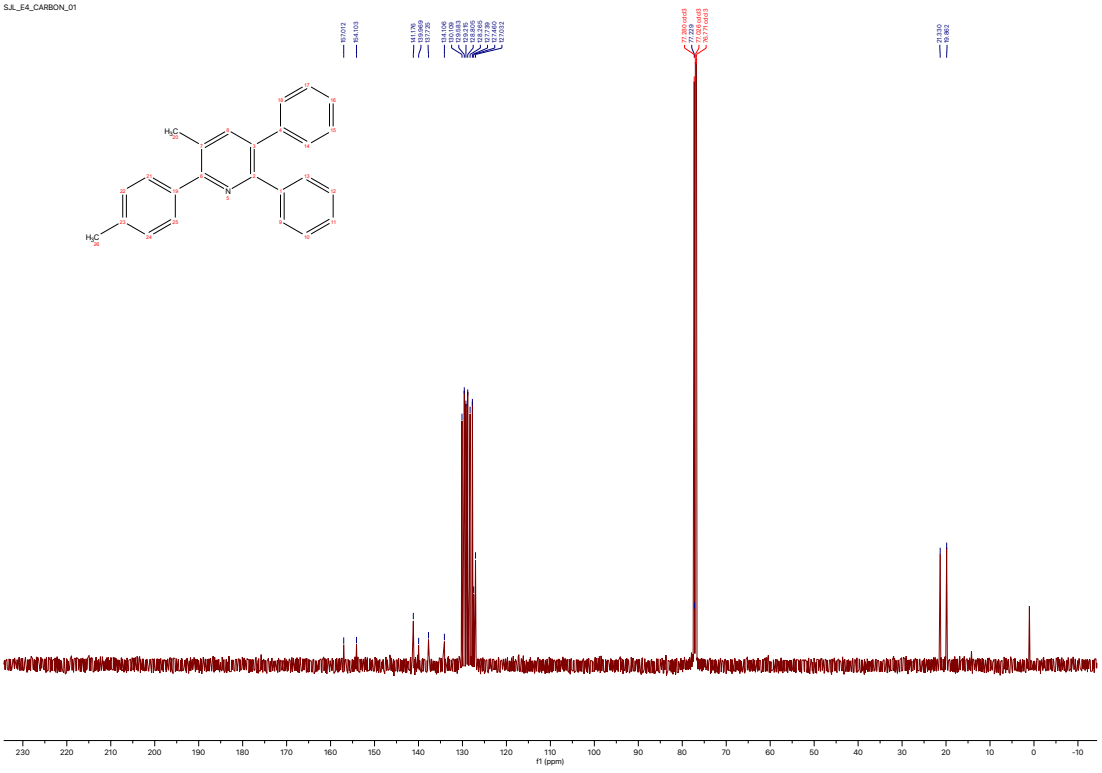
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-bromo-5,6-diphenylpyridine (**3q**)*



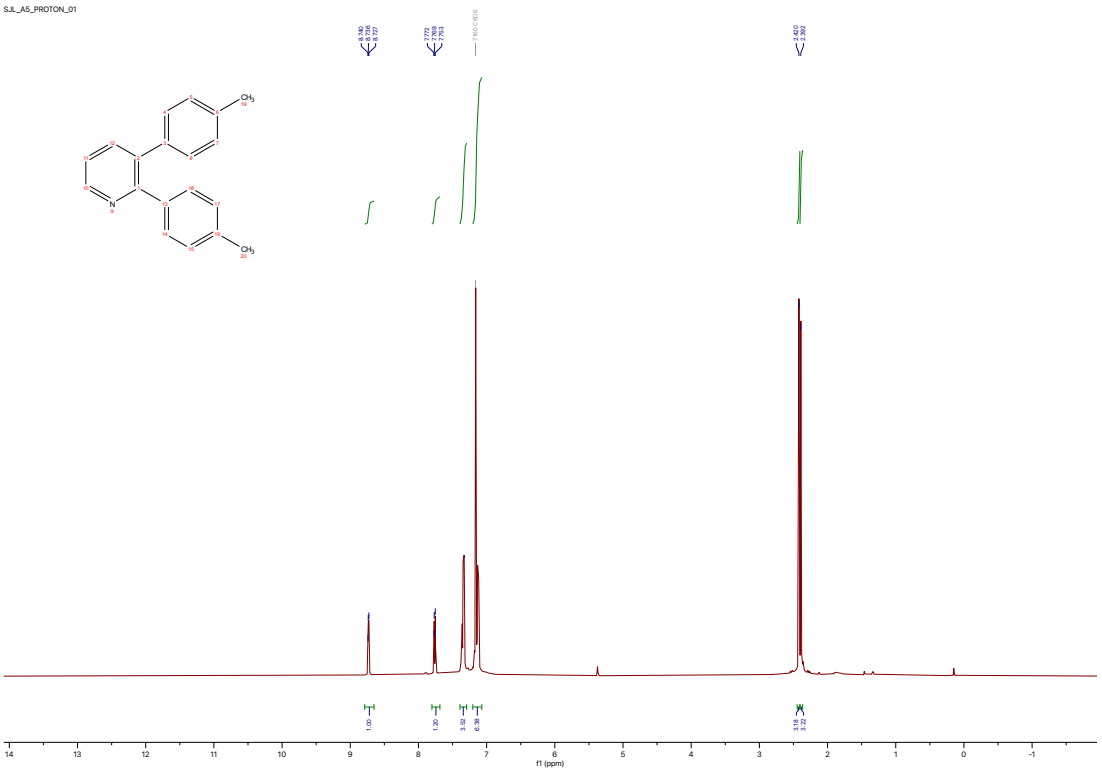


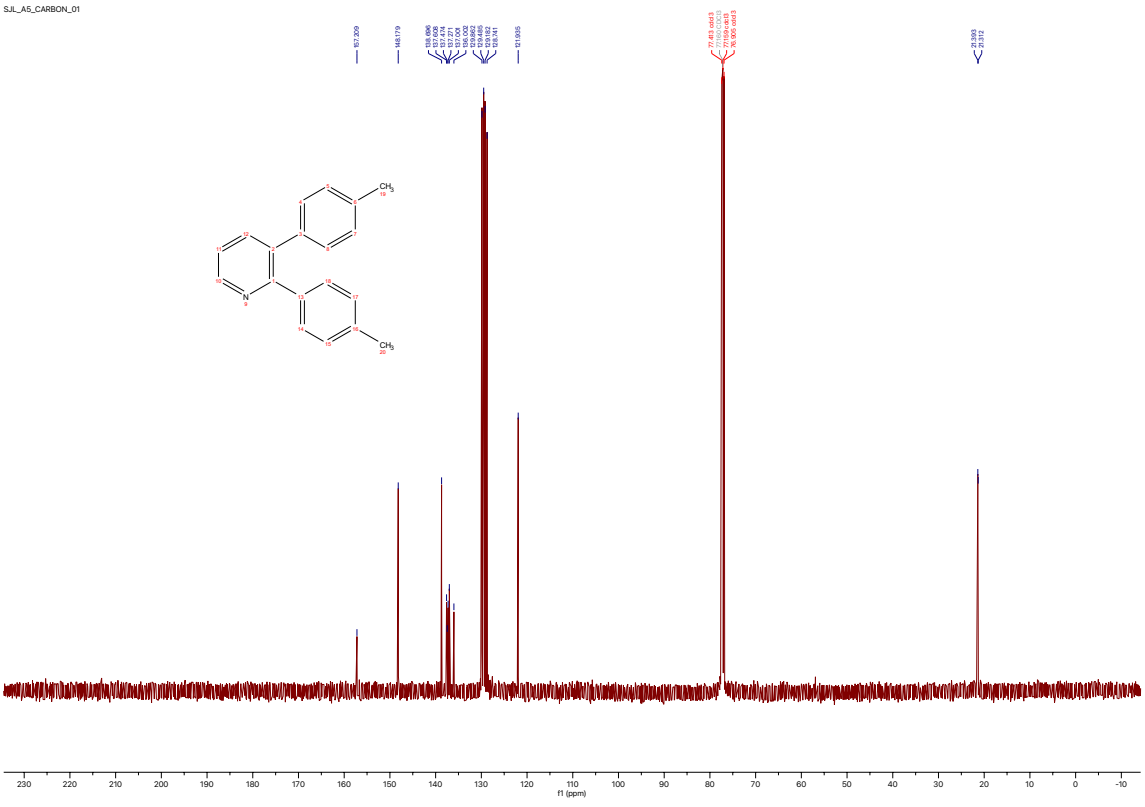
*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-methyl-5,6-diphenyl-2-(4-tolyl)pyridine (**3r**)*



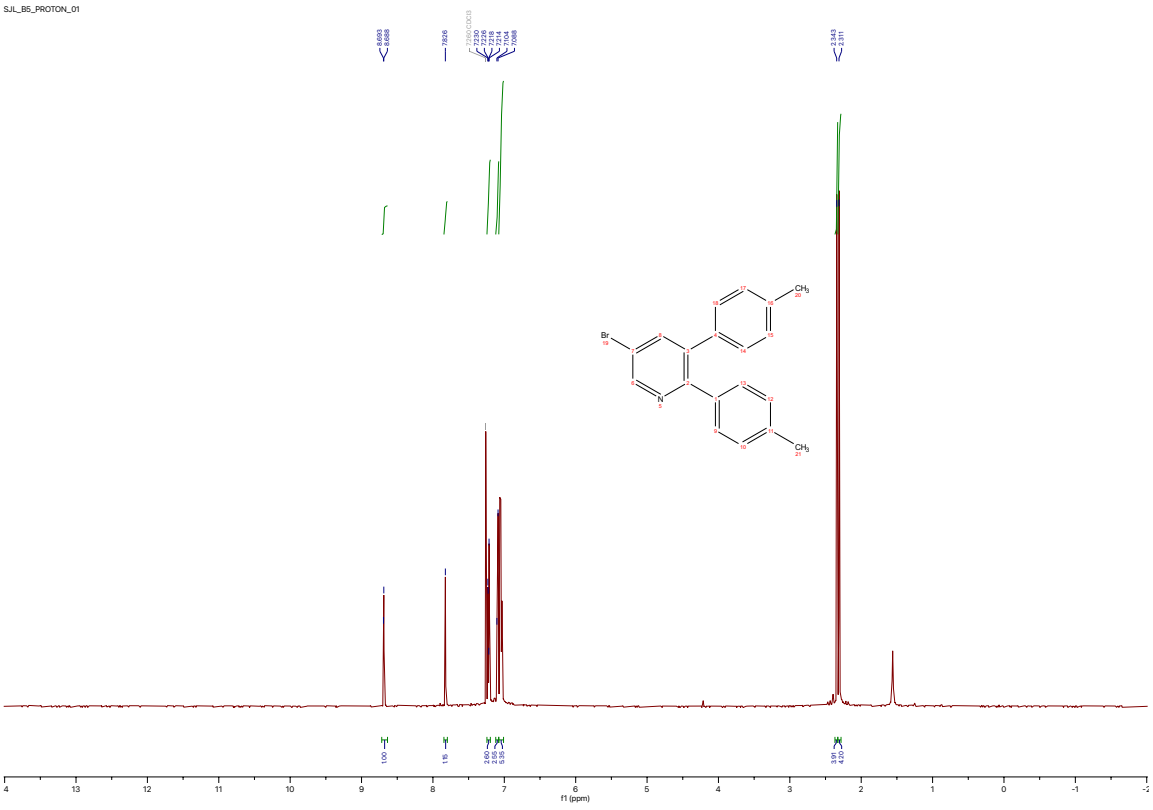


*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 2,3-di-(4-tolyl)pyridine (**3s**)*





*^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of 3-bromo-5,6-di-4-tolylpyridine (**3t**)*



References

1. Görl, C.; Betthausen, E.; Alt, H. G. Di- and Trinuclear Iron/titanium and Iron/zirconium Complexes with Heterocyclic Ligands as Catalysts for Ethylene Polymerization. *Polyhedron* **2016**, *118*, 37–51. https://doi.org/10.1016/j.poly.2016.07.033.
2. Pei, Z.; Mendonca, R.; Gazzard, L.; Pastor, R.; Goon, L.; Gustafson, A.; VanderPorten, E.; Hatzivassiliou, G.; Dement, K.; Cass, R.; Yuen, P.-W.; Zhang, Y.; Wu, G.; Lin, X.; Liu, Y.; Sellers, B. D. Aminoisoxazoles as Potent Inhibitors of Tryptophan 2,3-Dioxygenase 2 (TDO2). *ACS Med. Chem. Lett.* **2018**, *9* (5), 417–421. https://doi.org/10.1021/acsmedchemLett.7b00427.
3. Tóth, B. L.; Kovács, S.; Sályi, G.; Novák, Z. Mild and Efficient Palladium-Catalyzed Direct Trifluoroethylation of Aromatic Systems by C-H Activation. *Angew. Chem. Int. Ed Engl.* **2016**, *55* (6), 1988–1992. https://doi.org/10.1002/anie.201510555.
4. Jia, Q.-F.; Benjamin, P. M. S.; Huang, J.; Du, Z.; Zheng, X.; Zhang, K.; Conney, A. H.; Wang, J. letterSynthesis of 3, 4-Disubsituted Isoxazoles via Enamine [3+2] Cycloaddition. *Advanced online publication:* **2012**, *10*, 12. https://doi.org/10.1055/s-0032-1317923.
5. Liu, Y.-P.; Zhu, C.-J.; Yu, C.-C.; Wang, A.-E.; Huang, P.-Q. Tf_2O-Mediated Intermolecular Coupling of Secondary Amides with Enamines or Ketones: A Versatile and Direct Access to β-Enaminones. *European J. Org. Chem.* **2019**, *2019* (42), 7169–7174. https://doi.org/10.1002/ejoc.201901354.
6. Timofeeva, D. S.; Mayer, R. J.; Mayer, P.; Ofial, A. R.; Mayr, H. Which Factors Control the Nucleophilic Reactivities of Enamines? *Chemistry* **2018**, *24* (22), 5901–5910. https://doi.org/10.1002/chem.201705962.
7. Anderson, E. D.; Boger, D. L. Inverse Electron Demand Diels-Alder Reactions of 1,2,3-Triazines: Pronounced Substituent Effects on Reactivity and Cycloaddition Scope. *J. Am. Chem. Soc.* **2011**, *133* (31), 12285–12292.
8. Zhao, L.; Tsukano, C.; Kwon, E.; Takemoto, Y.; Hirama, M. Total Syntheses of Complanadines A and B. *Angew. Chem. Int. Ed Engl.* **2013**, *52* (6), 1722–1725. https://doi.org/10.1002/anie.201208297.
9. Bell, T. W.; Khasanov, A. B.; Drew, M. G. B. Role of Pyridine Hydrogen-Bonding Sites in Recognition of Basic Amino Acid Side Chains. *J. Am. Chem. Soc.* **2002**, *124* (47), 14092–14103. https://doi.org/10.1021/ja0273694.
10. Wolf, C.; Lerebours, R. Palladium-Phosphinous Acid-Catalyzed NaOH-Promoted Cross-Coupling Reactions of Arylsiloxanes with Aryl Chlorides and Bromides in Water. *Org. Lett.* **2004**, *6* (7), 1147–1150. https://doi.org/10.1021/ol049851s.
11. Qiu, D.; Jin, L.; Zheng, Z.; Meng, H.; Mo, F.; Wang, X.; Zhang, Y.; Wang, J. Synthesis of Pinacol Arylboronates from Aromatic Amines: A Metal-Free Transformation. *J. Org. Chem.* **2013**, *78* (5), 1923–1933. https://doi.org/10.1021/jo3018878.
12. Bolliger, J. L.; Frech, C. M. The 1,3-Diaminobenzene-Derived Aminophosphine Palladium Pincer Complex C6H3[NHP(piperidinyl)2]2Pd(cl) - A Highly Active Suzuki-Miyaura Catalyst with Excellent Functional Group Tolerance. *Adv. Synth. Catal.* **2010**, *352* (6), 1075–1080. https://doi.org/10.1002/adsc.200900848.
13. Zhou, Q.; Zhang, B.; Su, L.; Jiang, T.; Chen, R.; Du, T.; Ye, Y.; Shen, J.; Dai, G.; Han, D.; Jiang, H. Palladium-Catalyzed Highly Regioselective 2-Arylation of 2,x-Dibromopyridines and Its Application in the Efficient Synthesis of a 17β-HSD1 Inhibitor. *Tetrahedron* **2013**, *69* (51), 10996–11003. https://doi.org/10.1016/j.tet.2013.10.065.
14. Jin, Z.; Li, Y.-J.; Ma, Y.-Q.; Qiu, L.-L.; Fang, J.-X. Biphenyl-Based Diaminophosphine Oxides as Air-Stable Preligands for the Nickel-Catalyzed Kumada-Tamao-Corriu Coupling of Deactivated Aryl Chlorides, Fluorides, and Tosylates. *Chemistry - A European Journal*. 2012, pp 446–450. https://doi.org/10.1002/chem.201103050.

15. Yang, Z.-Y.; Luo, H.; Zhang, M.; Wang, X.-C. Borane-Catalyzed Reduction of Pyridines via a Hydroboration/Hydrogenation Cascade. *ACS Catal.* **2021**, *11* (17), 10824–10829. https://doi.org/10.1021/acscatal.1c02876.

DFT Study for Reaction Mechanism

Computational method

All calculations were performed with the Gaussian 16 B.01. Density functional theory (DFT) calculations using the aug-cc-PVDZ basis set and the B3LYP-D3 functional were employed to optimize geometry and to find transition states. The reported energies in this work are Gibbs free energy (ΔG) and enthalpies (ΔH), all in the gas phase at 298 K. The solvent effect with several solvents was estimated with SMD solvation model. To simplify the calculations, ethenamine was employed for enamines. All figures of structures were prepared by using GaussView6.

Computational Modeling of the Gas Phase Mechanistic Pathway

Both Path A and B share an initial [4 + 2]-cycloaddition (Scheme 1), which is where our investigations into the mechanism began. The cycloaddition step gives us four possible isomers: endo and exo of **I1-1** and **I1-2**. Calculation of the energy barrier for the cycloaddition step (Fig. 1) gave us clarity about the relative stability of these species.

The energy of isomers **I1-1** both exo/endo is ~1-2 kcal/mol lower than **I1-2** (Fig. 4S). However, the activation energy for the formation of **I1-1** is approximately 14 kcal/mol lower than **I1-2**; therefore, **I1-1** would be the more favored regioisomer over **I1-2**. The energy barrier for the formation of endo isomers is always slightly lower than exo isomers; whereas, thermodynamically **I1-1** exo is slightly more stable than **I1-1** endo. We can say that **I1-1** exo is the thermodynamic product, and **I1-1** endo is slightly favored kinetically. In all likelihood, both endo and exo **I1-1** are generated; however, both lead to the same observed final product after amine elimination.

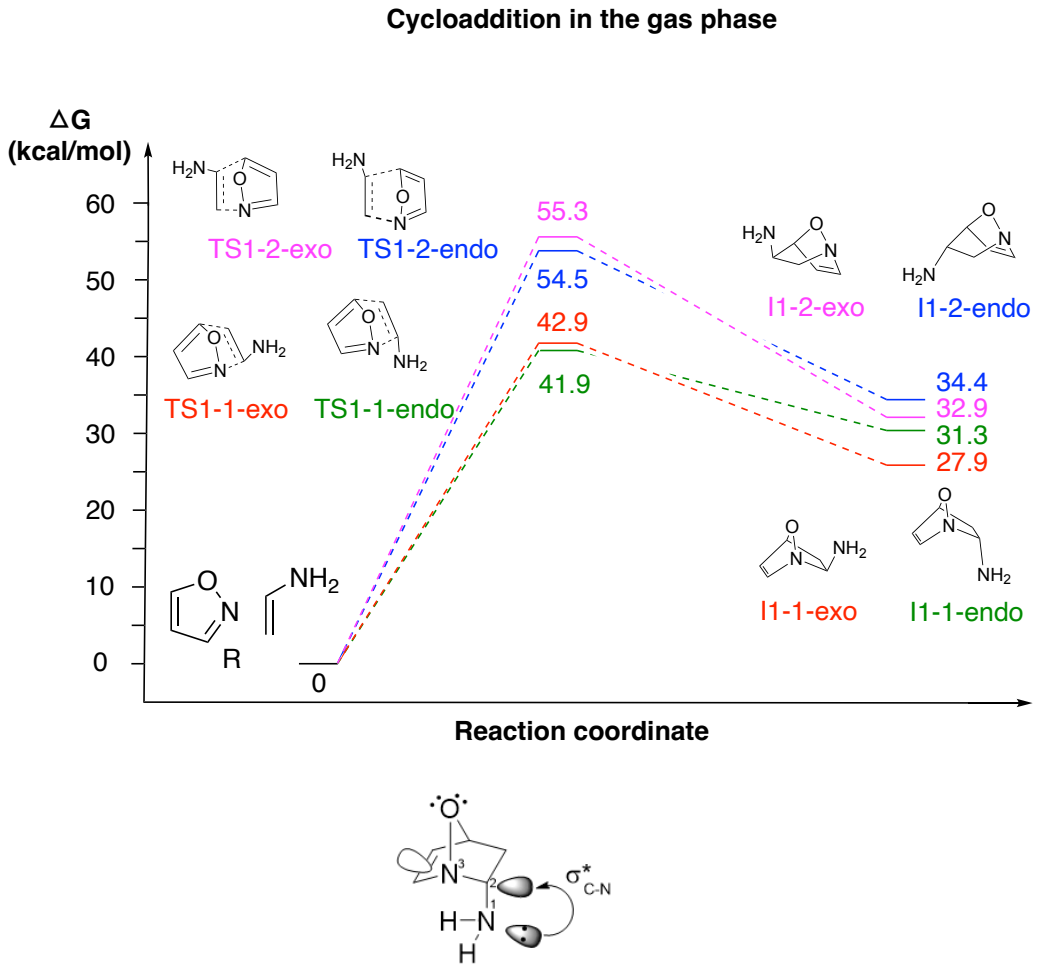


Fig. 4S. (Top) Free energy profile for cycloaddition (CA) reaction, (bottom) **I1-1** endo. Since **TS1-1** endo/exo is far lower in energy than **TS1-2** endo/exo (Fig. 1), we only consider this pathway going forward. We proposed two possible mechanisms to access the pyridine N-oxide from **I1-1**. Path A is amine loss followed by ring-opening, and Path B ring opening followed by amine loss (Scheme 1).

According to the NBO calculations, for **I1-1**, the lone pair present on N1 donates its electron density into the C2-N3 antibonding orbital (Fig. 4S bottom). Furthermore, there is donation from N1 to the antibonding orbital of the C-H bond at C2. With another regioisomer **I1-2**, there are no such secondary interactions possible.

The cycloaddition step follows a concerted mechanism in the gas phase. The transition states for the cycloaddition step are symmetrical, i.e., 2 bonds are being made to the electron-rich olefin, and asynchronous, i.e., the asymmetric dienophile leads to a different amount of bond making in the two new

bonds. All the transition states were asynchronous, but the symmetry changes when incorporating solvent models into our calculations (vide infra).

To quantify the trend in the symmetry of the transition state (TS), we used bond length ratios τ (Eq 1S). This ratio τ can be used to discern the nature of the TS. Subjectively, when τ < ~0.7, the transition state looks asymmetric, and, when τ > 0.7, the transition state looks symmetric.

$$\tau = \frac{(C-C\ bond\ length\ in\ TS)/(C-C\ bond\ length\ in\ Product)}{(C-N\ bond\ length\ in\ TS)/(C-N\ bond\ length\ in\ Product)} \qquad \textbf{(1S)}$$

Table 1S. The τ value for cycloaddition in different solvents with their dielectric constant (κ). See Fig. 4S for structures.

	No solvent	**Heptane**	**1,4-Dioxane**	**THF**	**DCM**	**EtOH**	**H_2O**
κ	0	1.92	2.21	7.52	8.93	24.6	78.5
TS1-1-endo	0.693	0.678	0.676	0.682	0.684	0.692	0.695
TS1-1-exo	0.745	0.708	0.699	0.649	0.649	0.591	0.588
TS1-2-endo	0.909	0.896	0.893	0.882	0.878	0.885	0.845
TS1-2-exo	0.873	0.865	0.864	0.857	0.854	0.844	0.823

After the cycloaddition step, this reaction mechanism divaricates into two pathways. In **Path A**, **I1** (cycloaddition products, *endo* and *exo*) eliminates ammonia and forms a double bond within the pyridine ring to make **I2_α** (Fig. 5S). Then, C–O bond cleavage of norbornadiene-like **I2_α** leads to pyridine-N-oxide (**I3)**. In **Path B**, C–O bond cleavage in **I1** leads to dihydropyridine-*N*-oxide **I2_β**, and, losing ammonia, the pyridine ring aromatizes to give pyridine-*N*-oxide (**I3)**.

In **Path A**, norbornadiene-like **I2_α** (plus ammonia) is roughly 26 kcal/mol higher in energy than the initial cycloaddition products (**I1**), and the transition state energy is 61.5 kcal/mol (**TS2_α**). The activation energy for the formation of the pyridine-*N*-oxide (**TS3_α**) is 60 kcal/mol, and this is an exergonic by 100 kcal/mol.

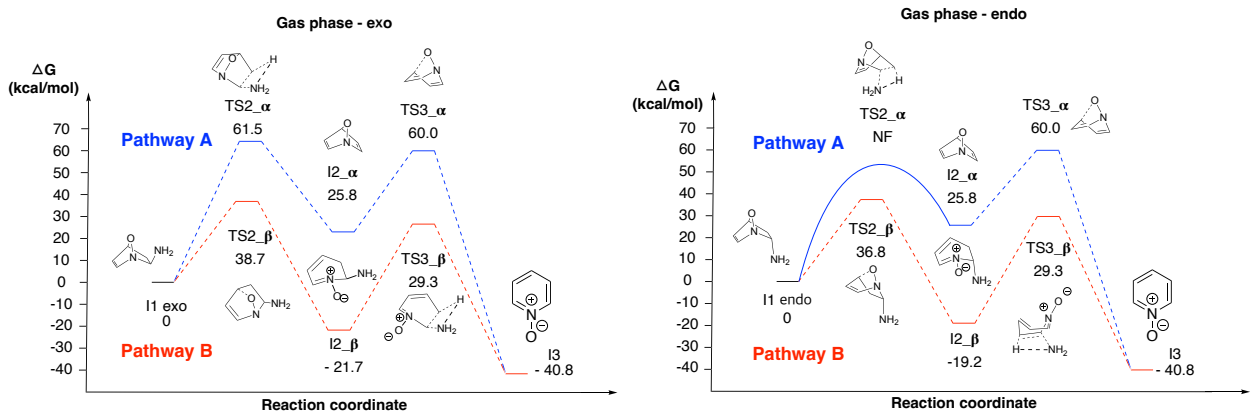


Fig. 5S. Energy diagram for two pathway mechanism for exo (right) and endo (left). Energy values for **I1** in each energy diagram are set to 0; however, **I1-1** endo is ~1.5 kcal/mol higher in energy than **I1-1** exo.

In **Path B**, cyclohexadiene-like **I2_β** is 21.7 kcal/mol lower in energy than the initial cycloaddition product **I1**, and the activation energy is 38.7 kcal/mol. Elimination of the amine to make the pyridine-*N*-oxide (**Step 2** in **Path B**) is also exergonic with an activation barrier of 29.3 kcal/mol.

Effects on Solvent on the Mechanistic Pathway

To get more realistic data we added a solvent model and reoptimized the pathway. It was noticed that **TS1-1** (Fig. 4S), both exo and endo, are asymmetric when a solvent model is used; whereas, **TS1-2** endo/exo were both symmetric. The asymmetric transition states for **TS1-1** endo/exo show more C–N bond formation than C–C bond. While the nature of the transition state is different with the inclusion of the solvent model, the energy of the transition state is similar to the gas phase calculation.

To investigate the effect of solvent polarity on the energies and structures, the compounds and transition states were reoptimized in different solvents using the SMD model. The energies were recalculated in heptane, dioxane, THF, DCM, ethanol (EtOH), and H_2O. Figure 4 shows variation of τ value (Eq. 1S) in different solvents. The only transition state structure showing structural changes (by this metric) as a function of solvent polarity is **TS1-1** exo, which gets more asymmetric as the polarity is increased. The other isomers of the transition state showed little energy change with solvent polarity.

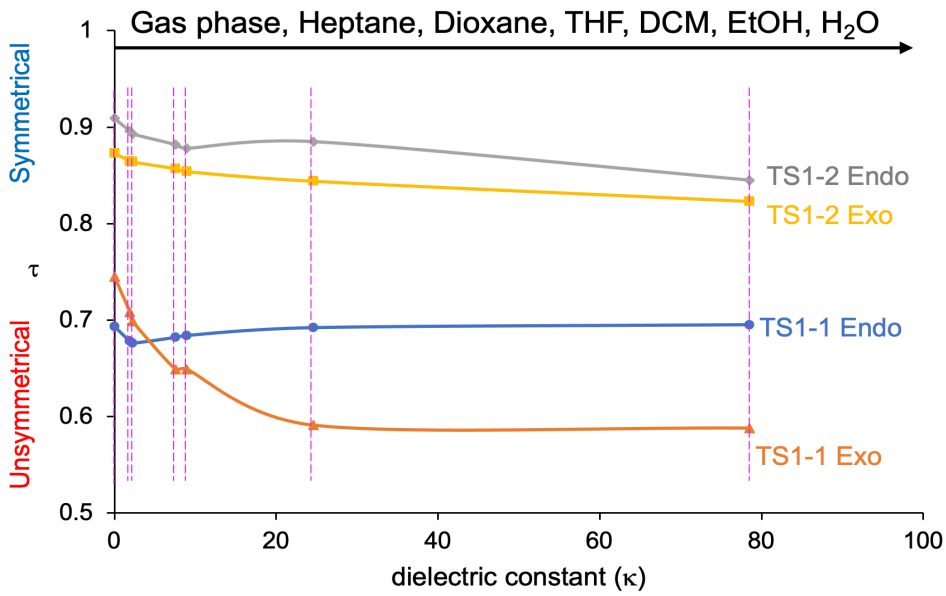
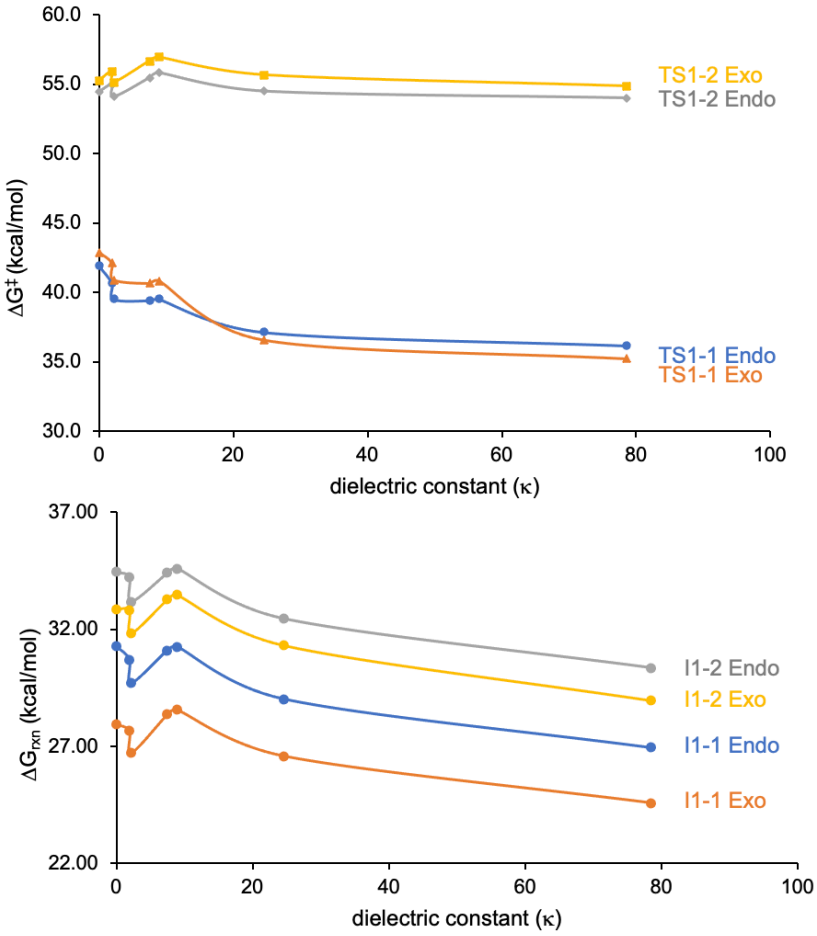


Fig. 6S. Correlation between τ (Eq. 1S) and dielectric constant (κ) of different solvents. The dielectric constants for the solvents are (left to right) represented by the vertical lines: gas phase (0), heptane, dioxane, THF, dichloromethane, EtOH, and water.

It was observed that **I1-1** endo/exo are energetically favored products irrespective of the solvent polarity (Fig. 7S). In low polarity solvents, **I1-1** exo is slightly less kinetically favored than *endo* isomer but in high polarity solvents, **I1-1** exo is both kinetically and thermodynamically favored product.



E (kcal/mol)	Gas Phase	Heptane	Dioxane	THF	DCM	EtOH	H_2O
Reactants	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TS1-1-endo	41.93	40.69	39.51	39.42	39.52	37.13	36.17
TS1-1-exo	42.89	42.12	40.90	40.64	40.83	36.56	35.22
TS1-2-endo	54.46	54.97	54.10	55.45	55.81	54.50	54.02
TS1-2-exo	55.25	55.92	55.13	56.67	56.94	55.67	54.86
I1-1-endo	31.27	30.70	29.70	31.10	31.24	29.01	26.94
I1-1-exo	27.94	27.66	26.70	28.36	28.55	26.57	24.57
I1-2-endo	34.44	34.23	33.18	34.40	34.59	32.45	30.35
I1-2-exo	32.86	32.82	31.84	33.28	33.46	31.31	28.95

Fig. 7S. Energy barrier $\Delta G^{\ddagger}$ (kcal/mol) of cycloaddition transition states in different solvents (top), free energy for cycloaddition products ΔG_{rxn} (kcal/mol) (middle), and the table of the transition state energy barrier ($\Delta G^{\ddagger}$) and free energy of cycloaddition products (ΔG_{rxn}) in different solvents. See Fig 4S for structures.

Input Files for Calculated Structures

Gas phase

Enamine

Zero-point correction= 0.068536 (Hartree/Particle)

Thermal correction to Energy= 0.072490

Thermal correction to Enthalpy= 0.073434

Thermal correction to Gibbs Free Energy= 0.043867

Sum of electronic and zero-point Energies= -133.904049

Sum of electronic and thermal Energies= -133.900095

Sum of electronic and thermal Enthalpies= -133.899151

Sum of electronic and thermal Free Energies= -133.928718

%chk=eneamine.chk

opt=calcall freq b3lyp/aug-cc-pvdz scf=(qc,maxcycle=600)

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.34782233

H 0.94716921 0.00000000 1.89365212

H 0.94164247 -0.01044363 -0.54625521

H -0.92722554 -0.00229978 -0.57737189

N -1.11429162 -0.06923289 2.17241399

H -1.00796633 0.32196915 3.10013323

H -2.00660723 0.15987070 1.74775490

1 2 2.0 4 1.0 5 1.0

2 3 1.0 6 1.0

3

4

5

6 7 1.0 8 1.0

7

8

Isoxazole

Zero-point correction= 0.057503 (Hartree/Particle)

Thermal correction to Energy= 0.061104

Thermal correction to Enthalpy= 0.062049

Thermal correction to Gibbs Free Energy= 0.031287

Sum of electronic and zero-point Energies= -246.014287

Sum of electronic and thermal Energies= -246.010685

Sum of electronic and thermal Enthalpies= -246.009741

Sum of electronic and thermal Free Energies= -246.040503

%chk=isoxazole.chk

opt=calcall freq b3lyp/aug-cc-pvdz scf=(qc,maxcycle=600)

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.18714946
C	0.86473601	0.00000000	1.13365854
O	-1.27343458	-0.00000000	1.74883784
N	-1.26839185	0.00000000	0.34354479
H	0.26067470	-0.00000000	-1.05610309
H	1.94848522	0.00000000	1.15545321
H	0.13761140	0.00000000	3.26453969

1 3 1.0 5 2.0 6 1.0

2 3 2.0 4 1.0 8 1.0

3 7 1.0

4 5 1.0

5

6

7

8

TS1-1-endo

Zero-point correction= 0.128669 (Hartree/Particle)

Thermal correction to Energy= 0.135481

Thermal correction to Enthalpy= 0.136425

Thermal correction to Gibbs Free Energy= 0.098057

Sum of electronic and zero-point Energies= -379.871783

Sum of electronic and thermal Energies= -379.864971

Sum of electronic and thermal Enthalpies= -379.864027

Sum of electronic and thermal Free Energies= -379.902395

%chk=TS1.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz scf=(qc,maxcycle=600)

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.17083335
C	0.86208892	0.00000000	1.12772671
C	0.83299138	0.06712128	9.30152225
C	0.12414789	0.07990156	8.16657357
O	-1.26057329	0.00000000	1.73185536
N	-1.25671581	0.00000000	0.35042800
H	1.91944912	0.06764409	9.26378999
H	-0.96235871	0.07655710	8.16912213
H	0.25453484	0.00000000	-1.05053483
H	1.93889331	0.00000000	1.15088209
H	0.13147162	-0.00000000	3.24213867
N	0.32406562	-0.01120616	10.58495978
H	0.90537030	0.37225981	11.31452717
H	-0.65232227	0.22474995	10.69447636
H	0.63144567	0.08187087	7.20992462

1 3 1.0 7 2.0 10 1.0

2 3 2.0 6 1.0 12 1.0

3 11 1.0

4 5 2.0 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 2.25005113

C 0.87597857 0.00000000 1.00969615

C -1.67287559 -1.29803818 1.15498189

C -0.66257787 -1.40410048 2.33189052

O -1.12070685 0.80114217 1.78706748

N -1.36131191 0.07732914 0.53719546

H -2.69329284 -1.18613166 1.54131607

H 0.06282010 -2.21548468 2.19974948

H 0.14419158 -0.09140943 -1.07177776

H 1.95824101 -0.08852023 0.97375506

H 0.40549714 0.41210285 3.17781246

N -1.54551196 -2.33695332 0.15399493

H -1.32130528 -3.23099568 0.58066030

H -2.40900181 -2.45390652 -0.37037842

H -1.18490639 -1.53794048 3.28573349

1 3 2.0 7 1.0 10 1.0

2 3 1.0 5 1.0 6 1.0 12 1.0

3 11 1.0

4 5 1.0 7 1.0 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 2.25005113

C 0.87597857 0.00000000 1.00969615

C -1.73973760 -1.59319396 1.28755974

C -0.79693292 -1.68881869 2.34848560

O -1.12070685 0.80114217 1.78706748

N -1.36131191 0.07732914 0.53719546

H -2.76015484 -1.48128744 1.67389392

H -0.07153494 -2.50020289 2.21634456

H 0.14419158 -0.09140943 -1.07177776

H 1.95824101 -0.08852023 0.97375506

H 0.40549714 0.41210285 3.17781246

N -1.61237396 -2.63210910 0.28657278

H -1.38816729 -3.52615147 0.71323815

H -2.47586382 -2.74906231 -0.23780058

H -1.31926144 -1.82265869 3.30232858

1 3 1.5 7 1.5 10 1.0

2 3 1.5 5 0.5 6 1.0 12 1.0

3 11 1.0

4 5 1.5 7 0.5 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

TS1-1-exo

Zero-point correction= 0.128590 (Hartree/Particle)

Thermal correction to Energy= 0.135560

Thermal correction to Enthalpy= 0.136504

Thermal correction to Gibbs Free Energy= 0.097707

Sum of electronic and zero-point Energies= -379.869986

Sum of electronic and thermal Energies= -379.863017

Sum of electronic and thermal Enthalpies= -379.862072

Sum of electronic and thermal Free Energies= -379.900869

%chk=TS2.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz scf=(qc,maxcycle=600)

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-1.53442125	-0.52845528	-0.02008667
C	-1.53442125	-0.52845528	2.15074668
C	-0.67233234	-0.52845528	1.10764004
C	-0.70142987	-0.46133399	9.28143558
C	-1.41027336	-0.44855372	8.14648690
O	-2.79499454	-0.52845528	1.71176868
N	-2.79113706	-0.52845528	0.33034132
H	0.38502787	-0.46081118	9.24370332
H	-2.49677996	-0.45189818	8.14903546
H	-1.27988641	-0.52845528	-1.07062151
H	0.40447206	-0.52845528	1.13079542
H	-1.40294963	-0.52845528	3.22205199
N	-1.21035563	-0.53966144	10.56487310
H	-0.62905095	-0.15619547	11.29444049
H	-2.18674353	-0.30370533	10.67438968
H	-0.90297559	-0.44658441	7.18983795

1 3 1.0 7 2.0 10 1.0

2 3 2.0 6 1.0 12 1.0

3 11 1.0

4 5 2.0 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

Title Card Required

0 1

C	-1.62894017	-0.53610502	-0.06400123
C	-1.32499850	1.60206454	0.57437368
C	-2.27109380	0.63411760	-0.12517340
C	0.56609432	0.40615780	-0.27247620
C	-0.10735634	1.80872008	-0.36079817
O	-0.74065483	0.73251531	1.57664249
N	-0.37412702	-0.36730550	0.67550333
H	0.56449882	-0.13784978	-1.22277384
H	-0.39110999	2.08947351	-1.38032504
H	-1.85391390	-1.50489926	-0.50234163
H	-3.20090980	0.87876531	-0.63090002

H -1.74578841 2.49481929 1.04473155

N 1.91519152 0.48601038 0.22838947

H 1.92669717 0.95119741 1.13499602

H 2.29854309 -0.44775776 0.36482588

H 0.56421000 2.57374417 0.04548253

1 3 2.0 7 1.0 10 1.0

2 3 1.0 5 1.0 6 1.0 12 1.0

3 11 1.0

4 5 1.0 7 1.0 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

Title Card Required

0 1

C -2.15240728 0.22975930 -0.11280289

C -1.84846561 2.36792886 0.52557202

C -2.79456092 1.39998192 -0.17397505

C 0.24186483 1.33592287 -0.52215947

C -0.37864535 2.61738351 -0.60327730

O -1.26412195 1.49837963 1.52784083

N -0.89759413 0.39855882 0.62670168

H 0.24026932 0.79191529 -1.47245711

H -0.66239900 2.89813694 -1.62280417

H -2.37738102 -0.73903494 -0.55114328

H -3.72437691 1.64462963 -0.67970168

H -2.26925552 3.26068361 0.99592989

N 1.59096203 1.41577545 -0.02129380

H 1.60246767 1.88096248 0.88531276

H 1.97431359 0.48200731 0.11514261

H 0.29292099 3.38240760 -0.19699660

1 3 1.5 7 1.5 10 1.0

2 3 1.5 5 0.5 6 1.0 12 1.0

3 11 1.0

4 5 1.5 7 0.5 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

TS1-2-endo

Zero-point correction= 0.128284 (Hartree/Particle)

Thermal correction to Energy= 0.135222

Thermal correction to Enthalpy= 0.136166

Thermal correction to Gibbs Free Energy= 0.097476

Sum of electronic and zero-point Energies= -379.851627

Sum of electronic and thermal Energies= -379.844690

Sum of electronic and thermal Enthalpies= -379.843746

Sum of electronic and thermal Free Energies= -379.882435

%chk=TS3.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz scf=(qc,maxcycle=600)

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C -0.88414629 -0.32520325 0.00000000

C -0.88414629 -0.32520325 2.17083335

C -0.02205738 -0.32520325 1.12772671

C -0.75999840 -0.24530169 8.16657357

C -0.05115491 -0.25808196 9.30152225

O -2.14471958 -0.32520325 1.73185535

N -2.14086210 -0.32520325 0.35042799

H -0.62961145 -0.32520325 -1.05053484

H 1.05474702 -0.32520325 1.15088209

H -0.75267467 -0.32520325 3.24213866

H 1.03530283 -0.25755915 9.26378999

H -0.25270063 -0.24333238 7.20992462

H -1.84650500 -0.24864615 8.16912213

N -0.56008067 -0.33640941 10.58495977

H -1.53646857 -0.10045330 10.69447635

H 0.02122401 0.04705656 11.31452716

1 3 1.0 7 2.0 8 1.0

2 3 2.0 6 1.0 10 1.0

3 9 1.0

4 5 2.0 13 1.0 12 1.0

5 11 1.0 14 1.0

6 7 1.0

7

8

9

10

11

12

13

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C	-1.63019696	0.68927789	0.00000000
C	-0.40308053	0.82517287	1.87779991
C	-0.95519878	1.60659441	0.69813412
C	-0.14538786	-1.09507136	0.50100458
C	0.72167729	-0.12097967	1.34927757
O	-1.45647374	-0.14427631	2.08809974
N	-1.56761874	-0.60171704	0.69319836
H	-2.12110331	0.73748644	-0.96850074
H	-0.75920679	2.64348381	0.44424786
H	-0.18677583	1.36246632	2.80546961
H	1.12866334	-0.66199714	2.21751639
H	-0.09297319	-2.12270732	0.87367392
H	0.10515156	-1.07475018	-0.56582340
N	1.75455748	0.56831093	0.57045212
H	2.34145744	1.12507853	1.19104997
H	2.37673479	-0.11637795	0.14392389

1 3 2.0 7 1.0 8 1.0

2 3 1.0 5 1.0 6 1.0 10 1.0

3 9 1.0

4 5 1.0 7 1.0 12 1.0 13 1.0

5 11 1.0 14 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C -2.94310726 -0.33916849 0.00000000

C -1.71599083 -0.20327351 1.87779991

C -2.26810908 0.57814804 0.69813412

C -1.12803148 -2.23808317 0.45637385

C -0.36938814 -1.33604319 1.24503293

O -2.76938404 -1.17272269 2.08809974

N -2.88052904 -1.63016341 0.69319836

H -3.43401361 -0.29095993 -0.96850074

H -2.07211709 1.61503743 0.44424786

H -1.49968613 0.33401994 2.80546961

H 0.03759792 -1.87706065 2.11327175

H -1.07561680 -3.26571912 0.82904318

H -0.87749206 -2.21776198 -0.61045413

N 0.66349205 -0.64675258 0.46620748

H 1.25039201 -0.08998499 1.08680533

H 1.28566936 -1.33144146 0.03967925

1 3 1.5 7 1.5 8 1.0

2 3 1.5 5 0.5 6 1.0 10 1.0

3 9 1.0

4 5 1.5 7 0.5 12 1.0 13 1.0

5 11 1.0 14 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

TS1-2-exo

Zero-point correction= 0.128257 (Hartree/Particle)

Thermal correction to Energy= 0.135190

Thermal correction to Enthalpy= 0.136134

Thermal correction to Gibbs Free Energy= 0.097515

Sum of electronic and zero-point Energies= -379.850431

Sum of electronic and thermal Energies= -379.843498

Sum of electronic and thermal Enthalpies= -379.842553

Sum of electronic and thermal Free Energies= -379.881172

%chk=TS4.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz scf=(qc,maxcycle=600)

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-0.57926826	-0.32520325	0.00000000
C	-0.57926826	-0.32520325	2.17083335
C	0.28282065	-0.32520325	1.12772671
C	-0.45512037	-0.24530169	8.16657357
C	0.25372312	-0.25808196	9.30152225
O	-1.83984155	-0.32520325	1.73185535
N	-1.83598407	-0.32520325	0.35042799

H -0.32473342 -0.32520325 -1.05053484

H 1.35962505 -0.32520325 1.15088209

H -0.44779664 -0.32520325 3.24213866

H 1.34018086 -0.25755915 9.26378999

H 0.05217740 -0.24333238 7.20992462

H -1.54162697 -0.24864615 8.16912213

N -0.25520264 -0.33640941 10.58495977

H -1.23159054 -0.10045330 10.69447635

H 0.32610204 0.04705656 11.31452716

1 3 1.0 7 2.0 8 1.0

2 3 2.0 6 1.0 10 1.0

3 9 1.0

4 5 2.0 13 1.0 12 1.0

5 11 1.0 14 1.0

6 7 1.0

7

8

9

10

11

12

13

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C	-2.17724292	-0.18599562	0.00000000
C	-3.97323550	-1.39692251	0.61253180
C	-2.65162670	-1.42679591	-0.13777443
C	-4.30500935	0.85668057	-0.04968782
C	-4.97584218	-0.55246442	-0.22060038
O	-3.66049867	-0.45912457	1.67759310
N	-3.10116106	0.60242098	0.82971730
H	-1.30739374	0.30685105	-0.42623111
H	-2.24817746	-2.25164485	-0.71794040
H	-4.36892272	-2.32865994	1.02436892
H	-4.99766727	-0.87557991	-1.26704418
H	-4.97812988	1.53748420	0.48305472
H	-3.97794301	1.32162675	-0.98611972
N	-6.32988799	-0.67689614	0.32547044
H	-6.34217976	-0.34117478	1.28866742
H	-6.96985420	-0.07516021	-0.19070513

1 3 2.0 7 1.0 8 1.0

2 3 1.0 5 1.0 6 1.0 10 1.0

3 9 1.0

4 5 1.0 7 1.0 12 1.0 13 1.0

5 11 1.0 14 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	-2.78993439	0.40481400	0.00000000
C	-4.58592698	-0.80611289	0.61253180
C	-3.26431818	-0.83598629	-0.13777443
C	-5.20237830	1.50761568	-0.25764329
C	-5.79302919	0.21058413	-0.39052923
O	-4.27319015	0.13168505	1.67759310
N	-3.71385253	1.19323060	0.82971730
H	-1.92008522	0.89766067	-0.42623111
H	-2.86086893	-1.66083523	-0.71794040
H	-4.98161419	-1.73785033	1.02436892
H	-5.81485428	-0.11253136	-1.43697303

H	-5.87549883	2.18841931	0.27509926
H	-4.87531196	1.97256187	-1.19407518
N	-7.14707499	0.08615241	0.15554159
H	-7.15936676	0.42187377	1.11873857
H	-7.78704120	0.68788834	-0.36063398

1 3 1.5 7 1.5 8 1.0

2 3 1.5 5 0.5 6 1.0 10 1.0

3 9 1.0

4 5 1.5 7 0.5 12 1.0 13 1.0

5 11 1.0 14 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

I1-1 endo

Zero-point correction= 0.132540 (Hartree/Particle)

Thermal correction to Energy= 0.138743

Thermal correction to Enthalpy= 0.139687

Thermal correction to Gibbs Free Energy= 0.102681

Sum of electronic and zero-point Energies= -379.892455

Sum of electronic and thermal Energies= -379.886253

Sum of electronic and thermal Enthalpies= -379.885309

Sum of electronic and thermal Free Energies= -379.922314

%chk=I1N.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-0.17544496	-1.27014475	-0.63381447
C	-1.06900567	-0.42073047	0.31597016
C	0.44198878	1.41836854	-0.08311413
C	1.26486459	0.72403180	-0.87641270
C	1.22195026	-0.68130375	-0.29319254
H	-1.43226714	-1.02748483	1.15052695
H	-0.44964201	-1.15071188	-1.68826158
H	0.10115958	2.44782549	-0.13928463
H	1.78726156	1.04982393	-1.77129236
H	-0.22746992	-2.33281058	-0.37317295
N	-0.06014925	0.55052329	0.98224831
O	1.05468826	-0.38559222	1.11387635
N	-2.19232531	0.20104180	-0.32879690

H -1.91102817 0.77953972 -1.11606194

H -2.73209797 0.76832119 0.31942214

H 2.08778190 -1.33204911 -0.44366422

1 2 1.0 5 1.0 7 1.0 10 1.0

2 6 1.0 11 1.0 13 1.0

3 4 2.0 8 1.0 11 1.0

4 5 1.0 9 1.0

5 12 1.0 16 1.0

6

7

8

9

10

11 12 1.0

12

13 14 1.0 15 1.0

14

15

16

I1-1 exo

Zero-point correction= 0.132491 (Hartree/Particle)

Thermal correction to Energy= 0.138703

Thermal correction to Enthalpy= 0.139647

Thermal correction to Gibbs Free Energy= 0.102598

Sum of electronic and zero-point Energies= -379.894804

Sum of electronic and thermal Energies= -379.888592

Sum of electronic and thermal Enthalpies= -379.887647

Sum of electronic and thermal Free Energies= -379.924697

%chk=I1X.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.99183102	-0.21223765	-0.54478675
C	0.32162386	1.19287018	-0.63269700
C	-0.89185609	0.98256591	0.31086586
C	-1.84864286	0.02386368	-0.39169185
C	-1.20788537	-1.14701772	-0.34025413
N	0.04904560	-0.98910691	0.39444583
O	-0.30656627	0.10707191	1.30001022
H	-1.30666766	1.87242526	0.79271075
H	-2.78513631	0.27043804	-0.88282256
H	-1.44542083	-2.11430553	-0.77388607
H	0.99909880	-0.74687074	-1.50196088
H	0.03640908	1.47403932	-1.65195968
H	1.00016488	1.95449979	-0.23267147
N	2.33782539	-0.13247161	-0.04005880
H	2.33432659	0.31100371	0.87701952
H	2.72123535	-1.06702183	0.08416262

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

I2_α

Zero-point correction= 0.126331 (Hartree/Particle)

Thermal correction to Energy= 0.135225

Thermal correction to Enthalpy= 0.136169

Thermal correction to Gibbs Free Energy= 0.091625

Sum of electronic and zero-point Energies= -379.846568

Sum of electronic and thermal Energies= -379.837674

Sum of electronic and thermal Enthalpies= -379.836730

Sum of electronic and thermal Free Energies= -379.881273

%chk=I2-1_NH3.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-2.02660273	-0.18781117	-0.32158089
C	0.01225212	-0.75247566	0.48761132
C	-1.50101750	-1.06957762	0.52858847
H	-3.04753819	0.03233497	-0.61512705
H	-1.99282417	-1.82188505	1.13632153
C	-0.39578158	1.46082558	0.22721327
H	-0.57740048	2.53031741	0.21511404
C	0.20453974	0.65470939	1.10168925
H	0.70293877	0.88823363	2.03608712
H	0.72982580	-1.52668843	0.76504397
O	0.12934760	-0.40609691	-0.91120099
N	-0.92128145	0.63334887	-0.90472042
N	3.15725008	-0.26460810	-0.12062838
H	2.38801188	-0.14900195	-0.78069973
H	3.96450333	-0.58746236	-0.65012043
H	3.38558148	0.66771850	0.21930153

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 1.0 14 0.5

12

13 14 1.0 15 1.0 16 1.0

14

15

16

I2__β endo

Zero-point correction= 0.131584 (Hartree/Particle)

Thermal correction to Energy= 0.138804

Thermal correction to Enthalpy= 0.139748

Thermal correction to Gibbs Free Energy= 0.100161

Sum of electronic and zero-point Energies= -379.921427

Sum of electronic and thermal Energies= -379.914207

Sum of electronic and thermal Enthalpies= -379.913263

Sum of electronic and thermal Free Energies= -379.952850

%chk=I2-2N.chk

opt=(calcall,tight) freq b3lyp/aug-cc-pvdz geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	-0.58789118	-0.65054582	0.35647587
C	0.59945383	-1.42989753	-0.20948513
C	1.90469365	-0.72065960	0.01959088
C	1.90846092	0.62728527	0.05140207
C	0.68541651	1.39115819	-0.08022122
N	-0.50025212	0.82621494	0.00618942
O	-1.60394996	1.46074412	-0.05325409
H	2.83132088	-1.29047744	0.08245895
H	2.83531337	1.19254688	0.15014129
H	0.67537405	2.46979246	-0.21781782
H	0.42799744	-1.57401938	-1.29065230
H	0.59586177	-2.43056920	0.24415444
H	-0.53379024	-0.63629895	1.46333416
N	-1.84053948	-1.15410635	-0.16836815
H	-2.12075610	-1.98799485	0.34034028
H	-2.55498262	-0.43773562	-0.03725001

1 2 1.0 6 1.0 13 1.0 14 1.0

2 3 1.0 11 1.0 12 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

I2_β_exo

Zero-point correction= 0.132350 (Hartree/Particle)

Thermal correction to Energy= 0.139362

Thermal correction to Enthalpy= 0.140306

Thermal correction to Gibbs Free Energy= 0.101391

Sum of electronic and zero-point Energies= -379.926003

Sum of electronic and thermal Energies= -379.918992

Sum of electronic and thermal Enthalpies= -379.918048

Sum of electronic and thermal Free Energies= -379.956962

%chk=I2-2X.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.39182318	0.92498171	-0.30534961
C	-1.06649386	0.95351854	-0.76808140
C	-1.91281117	-0.05119911	-0.03307431
C	-1.34309165	-1.19939004	0.38814619
C	0.06789577	-1.46516302	0.19564312
N	0.89602553	-0.51563850	-0.19078883
O	2.15054838	-0.66306470	-0.35478030
H	-2.97876514	0.13225575	0.09638443
H	-1.93183114	-1.97997097	0.87038857
H	0.51709496	-2.43868648	0.37985773
H	1.06043815	1.35522339	-1.05669583
H	-1.10630977	0.73336278	-1.84892831
H	-1.43746860	1.97792065	-0.63593162
N	0.57797998	1.62224698	0.94103923
H	-0.01624830	1.23911759	1.67320059
H	1.54673057	1.56254703	1.24451018

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

I3

Zero-point correction= 0.129145 (Hartree/Particle)

Thermal correction to Energy= 0.138027

Thermal correction to Enthalpy= 0.138971

Thermal correction to Gibbs Free Energy= 0.094571

Sum of electronic and zero-point Energies= -379.952773

Sum of electronic and thermal Energies= -379.943891

Sum of electronic and thermal Enthalpies= -379.942947

Sum of electronic and thermal Free Energies= -379.987346

%chk=I3_NH3.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-1.14897497	-1.23136829	-0.00000000
C	-2.30146874	-0.46065540	0.00000001
C	-2.21698402	0.93451520	0.00000000
C	-0.94281412	1.50901391	-0.00000000
C	0.19469473	0.71489612	-0.00000002
N	0.09247187	-0.65267506	-0.00000002
H	-3.11352814	1.55196830	0.00000002
H	-1.12994742	-2.31729095	-0.00000000
H	-3.26487398	-0.96936850	0.00000002
H	-0.81224314	2.59061595	0.00000000
H	1.21633189	1.09200139	-0.00000003
O	1.14653989	-1.39491133	-0.00000003
N	3.51153736	0.59039990	-0.00000006
H	2.95919126	-0.27150414	-0.00000005
H	4.11898369	0.56019245	0.81634820
H	4.11898490	0.56019300	-0.81634744

1 2 1.5 6 1.5 8 1.0

2 3 1.5 9 1.0

3 4 1.5 7 1.0

4 5 1.5 10 1.0

5 6 1.5 11 1.0

6 12 1.0

7

8

9

10

11

12 14 0.5

13 14 1.0 15 1.0 16 1.0

14

15

16

I2-1 (without NH3)

Zero-point correction= 0.090279 (Hartree/Particle)

Thermal correction to Energy= 0.095032

Thermal correction to Enthalpy= 0.095976

Thermal correction to Gibbs Free Energy= 0.062247

Sum of electronic and zero-point Energies= -323.304118

Sum of electronic and thermal Energies= -323.299365

Sum of electronic and thermal Enthalpies= -323.298421

Sum of electronic and thermal Free Energies= -323.332151

%chk=I2-1.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C -0.48448483 -0.67888251 1.19056230

C 0.33783302 1.06105591 -0.00000000

C -0.48448483 0.65239965 1.24744321

H -0.95587102 -1.44078893 1.80241687

H -0.95797396 1.31584415 1.96365615

C -0.48448483 -0.67888251 -1.19056230

H -0.95587102 -1.44078893 -1.80241687

C -0.48448483 0.65239965 -1.24744321

H -0.95797396 1.31584415 -1.96365615

H 0.82736026 2.03860915 -0.00000000

O 1.30130728 -0.01032896 -0.00000000

N 0.31292990 -1.10780415 0.00000000

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 1.0

12

I3 (without NH_3)

Zero-point correction= 0.092635 (Hartree/Particle)

Thermal correction to Energy= 0.097707

Thermal correction to Enthalpy= 0.098651

Thermal correction to Gibbs Free Energy= 0.064572

Sum of electronic and zero-point Energies= -323.407838

Sum of electronic and thermal Energies= -323.402765

Sum of electronic and thermal Enthalpies= -323.401821

Sum of electronic and thermal Free Energies= -323.435900

%chk=I3.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-0.00000000	-1.18114406	0.28568423
C	-0.00000000	-1.19627916	-1.10057461
C	-0.00000000	0.00000000	-1.82412224
C	0.00000000	1.19627916	-1.10057461
C	0.00000000	1.18114406	0.28568423
N	0.00000000	0.00000000	0.98512743
H	-0.00000000	-0.00000000	-2.91248950
H	-0.00000000	-2.06580882	0.91575002
H	-0.00000000	-2.16134098	-1.60642677
H	0.00000000	2.16134098	-1.60642677
H	0.00000000	2.06580882	0.91575002

O 0.00000000 -0.00000000 2.26517112

1 2 1.5 6 1.5 8 1.0

2 3 1.5 9 1.0

3 4 1.5 7 1.0

4 5 1.5 10 1.0

5 6 1.5 11 1.0

6 12 1.0

7

8

9

10

11

12

Biradical

Zero-point correction= 0.087296 (Hartree/Particle)

Thermal correction to Energy= 0.092978

Thermal correction to Enthalpy= 0.093922

Thermal correction to Gibbs Free Energy= 0.056845

Sum of electronic and zero-point Energies= -323.332751

Sum of electronic and thermal Energies= -323.327069

Sum of electronic and thermal Enthalpies= -323.326125

Sum of electronic and thermal Free Energies= -323.363202

%chk=BR.chk

opt=(calcall,tight,maxcycle=500) freq ub3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 3

C	1.12186144	-1.16171475	0.05130517
C	-1.05535375	0.00000106	-0.32246401
C	-0.22836885	-1.24564691	-0.17890003
H	1.70823354	-2.07535483	0.17375176
H	-0.74016426	-2.20670851	-0.22655216
C	1.12186295	1.16171386	0.05130555
H	1.70823617	2.07535299	0.17375349
C	-0.22836712	1.24564750	-0.17890039
H	-0.74016102	2.20670996	-0.22655212
H	-1.52505980	0.00000007	-1.35029000
O	-2.19557473	0.00000032	0.47230680
N	1.82338646	-0.00000098	0.16333670

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11

12

TS2_α_exo (amine loss from I1-1 Exo)

Zero-point correction= 0.128601 (Hartree/Particle)

Thermal correction to Energy= 0.135067

Thermal correction to Enthalpy= 0.136011

Thermal correction to Gibbs Free Energy= 0.098481

Sum of electronic and zero-point Energies= -379.794247

Sum of electronic and thermal Energies= -379.787782

Sum of electronic and thermal Enthalpies= -379.786838

Sum of electronic and thermal Free Energies= -379.824367

%mem=4GB

%Nprocs=1

%chk=TS1X.chk

opt=(calcall,tight,qst3,noeigentest,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.55924133

C 1.52620463 0.00000000 1.83811661

C 2.06017478 -1.36835255 1.42504870

C 1.98750898 -1.34008105 0.09159477

N 1.50087697 -0.03060650 -0.34779198

O 1.99333162 0.81694265 0.74182411

H 1.85715601 0.42226036 2.79114337

H 2.34794956 -2.18722934 2.07747078

H 2.17772355 -2.10736005 -0.65352713

H -0.44512933 -0.90455313 -0.43094197

H -0.52132014 -0.86003451 1.99267615

H -0.46513994 0.91960919 1.93137246

N -0.67136281 1.15573737 -0.53512294

H -0.22656476 2.00294710 -0.18568704

H -0.58535715 1.17248963 -1.54909559

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.33226020
C	1.50445488	0.00000000	1.69399426
C	2.08909620	-1.35496647	1.23087643
C	1.99793623	-1.29518150	-0.09752692
N	1.41836051	0.02942814	-0.47909202
O	1.99493286	0.83319428	0.61901328
H	1.78948967	0.40194519	2.66789442
H	2.45548288	-2.15676797	1.86337534
H	2.23129758	-2.00568341	-0.88344829
H	-0.79501056	-0.04334300	-0.73690174
H	-0.83101661	-0.01364103	2.02886615
H	1.08472007	3.98659347	2.62825746
N	0.72065798	3.05979286	2.41670622
H	1.18460311	2.73835041	1.56687326
H	-0.26207046	3.18007018	2.17859146

1 11 1.0 2 2.0 6 1.0

2 3 1.0 12 1.0

3 4 1.0 8 1.0 7 1.0

4 5 2.0 9 1.0

5 10 1.0 6 1.0

6 7 1.0

7 15 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C 0.82177355 -0.09009585 -0.72034797

C 0.26621281 1.23539663 -0.65019319

C -0.83905803 1.00069895 0.39754924

C -1.89578427 0.09356631 -0.25035232

C -1.30311097 -1.10568361 -0.34725241

N 0.03876803 -1.00684670 0.22959162

O -0.20178619 0.01884389 1.26741729

H -1.19328611 1.84528197 0.99630696

H -2.86864374 0.39582054 -0.62918036

H -1.59820691 -2.02958427 -0.83420011

H 1.05425714 -0.58337035 -1.67061585

H -0.01325016 1.71082786 -1.59114403

H 2.89010347 0.56945379 -0.33856397

N 2.28652037 -0.13556432 0.08351758

H 2.02069127 0.18814942 1.01971496

H 2.74540714 -1.05374754 0.14015955

1 2 1.5 6 1.0 11 1.0 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7 13 0.5 15 0.5

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0

15

16

TS3_α (ring opening from I2-2)

Zero-point correction= 0.129228 (Hartree/Particle)

Thermal correction to Energy= 0.135722

Thermal correction to Enthalpy= 0.136666

Thermal correction to Gibbs Free Energy= 0.098972

Sum of electronic and zero-point Energies= -379.833384

Sum of electronic and thermal Energies= -379.826890

Sum of electronic and thermal Enthalpies= -379.825946

Sum of electronic and thermal Free Energies= -379.863640

%mem=4GB

%Nprocs=4

%chk=TS3.chk

opt=(calcall,tight,qst3) freq b3lyp/aug-cc-pvdz geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.33200977

C 1.50631533 0.00000000 1.69340004

C 2.08948054 -1.35908818 1.23349720

C 1.99866229 -1.29795388 -0.09432913

N 1.42345053 0.02990814 -0.47045308

O 1.99869839 0.83280604 0.62372576

H 1.80598906 0.38774641 2.67058924

H 2.44787029 -2.16393754 1.86672210

H 2.22041540 -2.01092067 -0.88116212

H -0.77882040 -0.04742856 -0.75384631

H -0.83540647 -0.02601213 2.02377754

H 0.80576048 0.54418068 -2.62970601

N 0.00473195 0.52697760 -3.26359083

H 0.34822833 0.24282384 -4.17883647

H -0.31008664 1.49079580 -3.36086777

1 11 1.0 2 2.0 6 1.0

2 3 1.0 12 1.0

3 4 1.0 8 1.0 7 1.0

4 5 2.0 9 1.0

5 10 1.0 6 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38644869
C	1.20670795	0.00000000	2.09178147
C	2.39256150	0.00000000	1.35197828
C	2.36477607	0.00000000	-0.03502465
N	1.17114986	0.00000000	-0.71027026
O	1.14010734	-0.00000000	-1.99907211
H	1.22158965	0.00000000	3.18027495
H	3.36423262	0.00000000	1.84469201
H	3.24616479	0.00000000	-0.67463753
H	-0.89210235	0.00000000	-0.61947017
H	-0.95841796	0.00000000	1.90449648
H	3.08158069	0.00000000	-2.88135851
N	4.10508708	0.00000000	-2.86137572
H	4.41765135	0.81634732	-3.38311177
H	4.41765021	-0.81634821	-3.38311106

1 2 1.5 6 1.5 11 1.0

2 3 1.5 12 1.0

3 4 1.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C	1.24814029	-1.18630544	-0.52132968
C	2.12089546	-0.35279221	0.07646749
C	1.45926861	0.82482064	0.63915938
C	0.55555788	1.50276758	-0.28465633
C	-0.30407420	0.64616026	-0.87429960
N	-0.11584018	-0.71167496	-0.39619887
O	-0.29406076	-0.60305446	0.97617161
H	1.87085280	1.34044183	1.50626779
H	0.48182195	2.58548877	-0.35490712

H -1.22317999 0.87810762 -1.40306824

H 1.42199540 -2.20213347 -0.86389012

H 3.17361148 -0.57380722 0.23779456

H -3.53271280 -0.93269765 -0.26833083

N -3.28066854 -0.00880880 0.07830559

H -2.48229328 -0.14609588 0.70103041

H -4.06077675 0.31061287 0.64893605

1 2 2.0 6 1.0 11 1.0

2 3 1.0 12 1.0

3 4 1.0 7 0.5 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

TS3_β_endo (ring opening from I1-1 endo)

Zero-point correction= 0.129370 (Hartree/Particle)

Thermal correction to Energy= 0.135841

Thermal correction to Enthalpy= 0.136785

Thermal correction to Gibbs Free Energy= 0.099147

Sum of electronic and zero-point Energies= -379.833455

Sum of electronic and thermal Energies= -379.826984

Sum of electronic and thermal Enthalpies= -379.826040

Sum of electronic and thermal Free Energies= -379.863678

%mem=4GB

%Nprocs=4

%chk=TS2N.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.55629234

C 1.53000171 0.00000000 1.82935800

C 2.04918838 -1.37769929 1.44290625

C 1.97983124 -1.37600992 0.10734000

N 1.50735077 -0.07178616 -0.35747976

O 2.00350188 0.79074382 0.71321005

H 1.86834128 0.43580033 2.77348718

H 2.33320177 -2.18554650 2.11116355

H 2.18132363 -2.16046275 -0.61594118

H -0.31047778 0.97500808 -0.38672650

H -0.46826433 0.90978031 1.94735169

H -0.51433586 -0.87155700 1.97718875

N -0.82475875 -1.01728225 -0.59083152

H -0.77393716 -1.00081551 -1.60596413

H -0.57869007 -1.94819603 -0.26460499

1 2 1.0 11 1.0 6 1.0 14 1.0

2 3 1.0 13 1.0 12 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 10 1.0 6 1.0

6 7 1.0

7

8

9

10

11

12

13

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.52888511

C 1.39186542 0.00000000 2.09620954

C 2.37116786 -0.61202886 1.40024341

C 2.11781380 -1.21795110 0.10976481

N 1.00326171 -0.99830658 -0.55504052

O 0.75402649 -1.46724688 -1.71361184

H 1.57858815 0.42262571 3.08302522

H 3.38357682 -0.69715511 1.79534744

H 2.84189990 -1.85155470 -0.39692190

H 0.39302350 0.96601510 -0.37497925

H -0.57693941 0.87127003 1.86825845

H -0.55097122 -0.89417834 1.86942420

N -1.30496255 -0.35057793 -0.52185480

H -1.91665765 0.46068320 -0.50289977

H -1.19350302 -0.65124963 -1.49035179

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 13 1.0 12 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	1.08633558	0.03717126	0.39558703
C	0.31024060	1.42046110	0.36110345
C	-1.09672612	1.16898801	-0.01488234
C	-1.33671180	0.18912278	-1.03195442
C	-0.73707334	-1.02102778	-0.81410256
N	0.05487933	-1.01301253	0.37462562
O	-0.77605336	-0.81091170	1.39722861
H	-1.88514906	1.86073180	0.27797545
H	-2.14259601	0.28589285	-1.75909377

H -1.07269679 -1.96806855 -1.22804262

H 1.56754536 -0.06063712 1.37496699

H 0.39696197 1.98031773 1.29891870

H 0.81455111 1.99851468 -0.42942053

N 2.07856258 -0.05111932 -0.64934591

H 2.58683556 -0.93017568 -0.59217866

H 1.65249188 0.00134864 -1.57241928

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

TS3_β_exo (Ring opening from I1-1 exo)

Zero-point correction= 0.129228 (Hartree/Particle)

Thermal correction to Energy= 0.135722

Thermal correction to Enthalpy= 0.136666

Thermal correction to Gibbs Free Energy= 0.098972

Sum of electronic and zero-point Energies= -379.833384

Sum of electronic and thermal Energies= -379.826890

Sum of electronic and thermal Enthalpies= -379.825946

Sum of electronic and thermal Free Energies= -379.863640

%mem=4GB

%Nprocs=4

%chk=TS2X.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.55924133
C	1.52620463	0.00000000	1.83811661
C	2.06017478	-1.36835255	1.42504870
C	1.98750898	-1.34008105	0.09159477
N	1.50087697	-0.03060650	-0.34779198
O	1.99333162	0.81694265	0.74182411
H	1.85715601	0.42226036	2.79114337

H 2.34794956 -2.18722934 2.07747078

H 2.17772355 -2.10736005 -0.65352713

H -0.44512933 -0.90455313 -0.43094197

H -0.52132014 -0.86003451 1.99267615

H -0.46513994 0.91960919 1.93137246

N -0.67136281 1.15573737 -0.53512294

H -0.58535715 1.17248963 -1.54909559

H -0.22656476 2.00294710 -0.18568704

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.53010891
C	1.39143916	0.00000000	2.10039877
C	2.38629713	-0.59293416	1.41030685
C	2.14258596	-1.20097416	0.11605766
N	1.02056572	-1.00384919	-0.53343854
O	0.74972935	-1.50350074	-1.69302237
H	1.56604508	0.43008306	3.08589732
H	3.39763783	-0.66506280	1.80869035
H	2.87921568	-1.83217830	-0.37728053
H	-0.94804655	-0.37486185	-0.39553219
H	-0.53400449	-0.89363680	1.89430647
H	-0.57602384	0.87105852	1.86604874
N	0.25100415	1.31238923	-0.54301603
H	0.28324850	1.28570635	-1.55919916
H	1.13473468	1.69078292	-0.20717727

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C	0.93973558	0.08934461	-0.58175770
C	0.28528108	1.41444414	-0.02993143
C	-1.09200947	1.12528545	0.41719588
C	-1.86053307	0.19506882	-0.35776468
C	-1.23346576	-0.99806614	-0.58412083
N	0.09848009	-1.02135636	-0.07459242
O	-0.00116984	-0.90124216	1.25822839
H	-1.58369133	1.76147525	1.15251240
H	-2.93832296	0.29031583	-0.48542912
H	-1.74151921	-1.93914088	-0.77972665
H	0.89344983	0.04864835	-1.67687746
H	0.26505879	2.10518913	-0.88975747

H 0.89209155 1.87771050 0.75579397

N 2.31412904 0.02140897 -0.15704698

H 2.76363415 -0.79803491 -0.55869295

H 2.33634386 -0.09305554 0.85609854

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

TS2_β_endo (amine loss from I2_β endo)

Zero-point correction= 0.129256 (Hartree/Particle)

Thermal correction to Energy= 0.135918

Thermal correction to Enthalpy= 0.136862

Thermal correction to Gibbs Free Energy= 0.098915

Sum of electronic and zero-point Energies= -379.845307

Sum of electronic and thermal Energies= -379.838645

Sum of electronic and thermal Enthalpies= -379.837701

Sum of electronic and thermal Free Energies= -379.875648

%mem=4GB

%Nprocs=1

%chk=TS4N_TS.chk

opt=(calcall,tight,ts,verytight,noeigentest,maxcycle=500) freq

b3lyp/aug-cc-pvdz geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.45442619
C	1.31312532	0.00000000	1.99392573
C	2.43373664	0.23575411	1.18512099
C	2.23079243	0.77278621	-0.10892224
N	1.01260091	0.76146819	-0.67411958
O	0.70702202	1.30633044	-1.82399504
H	1.44516407	-0.06348227	3.07637914
H	3.44532458	0.21343849	1.58622530
H	3.00961647	1.24982870	-0.69691177
H	-0.93906693	0.10630263	-0.53990988
H	-0.64671895	0.65661773	2.04108449

H 1.52546215 -1.51785156 0.00028303

N 0.58915124 -1.59591631 -0.42257213

H 0.65703039 -1.71665291 -1.43216400

H 0.05099333 -2.33632602 0.02338804

1 2 1.3 6 1.2 11 0.5 13 0.5 14 0.5

2 3 1.2 11 0.5 12 1.0 13 0.2

3 4 1.8 8 1.0

4 5 1.3 9 1.0

5 6 1.8 10 1.0

6 7 1.0

7 13 0.3

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0

15

16

TS2_β_exo (amine loss from I2_β_exo)

Zero-point correction= 0.129256 (Hartree/Particle)

Thermal correction to Energy= 0.135917

Thermal correction to Enthalpy= 0.136862

Thermal correction to Gibbs Free Energy= 0.098915

Sum of electronic and zero-point Energies= -379.845307

Sum of electronic and thermal Energies= -379.838645

Sum of electronic and thermal Enthalpies= -379.837701

Sum of electronic and thermal Free Energies= -379.875648

%mem=4GB

%Nprocs=4

%chk=TS4X.chk

opt=(calcall,tight,qst3,noeigentest,maxcycle=500) freq b3lyp/aug-cc-pvdz

geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.53023647
C	1.39502894	0.00000000	2.09578067
C	2.37869871	-0.61176277	1.40405129
C	2.13622792	-1.22170308	0.11263388
N	1.01176171	-1.01256635	-0.54201330
O	0.73615095	-1.48894184	-1.69073449

H 1.58044566 0.43776773 3.07590983

H 3.38969543 -0.68801694 1.80473750

H 2.86540534 -1.85401004 -0.38931342

H -0.94840116 -0.36828461 -0.40196604

H -0.53297725 -0.89673293 1.89091530

H -0.57797215 0.87164007 1.86291843

N 0.26102181 1.30888387 -0.54130302

H 1.14628712 1.68061261 -0.20354765

H 0.28812843 1.27821779 -1.55740402

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38728131
C	1.20043305	0.00000000	2.10318505
C	2.39277213	0.00000000	1.37382493
C	2.36500338	0.00000000	-0.01234575
N	1.17986258	0.00000000	-0.69901698
O	1.18508586	0.00000000	-1.98818213
H	1.20735543	0.00000000	3.19175833
H	3.36137373	-0.00000000	1.87257298
H	3.24451967	0.00000000	-0.64955935
H	-0.89402259	-0.00000000	-0.62183156
H	-0.96160787	0.00000000	1.89935754
H	-0.77366922	0.00000000	-2.83140645
N	-1.79657014	0.00000000	-2.79092817
H	-2.11952028	0.81634826	-3.30629865
H	-2.11952144	-0.81634738	-3.30629934

1 2 1.5 6 1.5 11 1.0

2 3 1.5 12 1.0

3 4 1.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	0.08475011	-1.00929196	0.38954841
C	-1.03334505	-0.39755404	1.11786218
C	-1.50282233	0.78163624	0.56991502
C	-0.78451914	1.39611823	-0.49819111
C	0.55780489	1.03731588	-0.68656572
N	1.09947327	-0.06074571	-0.07056262
O	2.22552684	0.17316458	0.59692908
H	-2.39375548	1.26802277	0.96856885
H	-1.18092115	2.26997372	-1.01172136
H	1.29849218	1.70421075	-1.12202320
H	0.56751730	-1.88715923	0.82335053

H -1.38084264 -0.81403875 2.06018509

H -1.00216117 -0.49731520 -1.31629757

N -0.58863569 -1.43046866 -1.05156803

H 0.10117255 -1.71131578 -1.75201932

H -1.32079027 -2.12854031 -0.92597377

1 2 1.5 6 1.0 11 1.0 13 0.5 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0

15

16

TS3_α (ring opening from I2-2, without NH_3)

Zero-point correction= 0.087360 (Hartree/Particle)

Thermal correction to Energy= 0.092346

Thermal correction to Enthalpy= 0.093290

Thermal correction to Gibbs Free Energy= 0.059064

Sum of electronic and zero-point Energies= -323.248926

Sum of electronic and thermal Energies= -323.243940

Sum of electronic and thermal Enthalpies= -323.242996

Sum of electronic and thermal Free Energies= -323.277223

%mem=4GB

%Nprocs=4

%chk=TS3_wo_NH3.chk

opt=(calcall,tight,qst3) freq b3lyp/aug-cc-pvdz geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.33249554
C	1.50771074	0.00000000	1.68753518
C	2.08931749	-1.35940299	1.22601466
C	1.99406791	-1.29742983	-0.10162649
N	1.41654044	0.02960666	-0.47933886
O	1.99486766	0.83257371	0.61712942
H	1.80964668	0.38755450	2.66420691
H	2.45465935	-2.16192498	1.85830925
H	2.22217588	-2.00818076	-0.88894383
H	-0.79673413	-0.04394323	-0.73508651

H -0.83425505 -0.02201169 2.02592678

1 11 1.0 2 2.0 6 1.0

2 3 1.0 12 1.0

3 4 1.0 8 1.0 7 1.0

4 5 2.0 9 1.0

5 10 1.0 6 1.0

6 7 1.0

7

8

9

10

11

12

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.38634146

C 1.20410705 0.00000000 2.09678585

C 2.39241573 0.00000000 1.36022120

C 2.36214735 0.00000000 -0.02578979

N 1.17343765 0.00000000 -0.71229641

O 1.15946304 -0.00000000 -1.99226382

H 1.21598907 0.00000000 3.18508825

H 3.36294258 0.00000000 1.85550735

H 3.23988077 0.00000000 -0.66547617

H -0.89149064 0.00000000 -0.62037009

H -0.95948178 0.00000000 1.90269933

1 2 1.5 6 1.5 11 1.0

2 3 1.5 12 1.0

3 4 1.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7

8

9

10

11

12

Title Card Required

0 1

C -0.45409171 -0.59515511 -1.21375208

C -0.45409171 0.75262425 -1.22661036

C 0.10524498 1.32011474 0.00000000

C -0.45409171 0.75262425 1.22661036

C -0.45409171 -0.59515511 1.21375208

N 0.15407509 -1.10902668 0.00000000

O 1.41382126 -0.56402896 0.00000000

H 0.58402487 2.29864788 0.00000000

H -0.71901960 1.35744118 2.09110446

H -0.63417508 -1.27421497 2.04171916

H -0.63417508 -1.27421497 -2.04171916

H -0.71901960 1.35744118 -2.09110446

1 2 2.0 6 1.0 11 1.0

2 3 1.0 12 1.0

3 4 1.0 7 0.5 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7

8

9

10

11

12

TS_Biradical (N-O cleavage from I2_α)

Zero-point correction= 0.087093 (Hartree/Particle)

Thermal correction to Energy= 0.092091

Thermal correction to Enthalpy= 0.093035

Thermal correction to Gibbs Free Energy= 0.058755

Sum of electronic and zero-point Energies= -323.260597

Sum of electronic and thermal Energies= -323.255599

Sum of electronic and thermal Enthalpies= -323.254655

Sum of electronic and thermal Free Energies= -323.288935

%mem=4GB

%Nprocs=4

%chk=TSR.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.26295050
C	0.88780008	0.00000000	0.99365998
H	0.10435710	-0.04397503	-1.07900258
H	1.97192271	-0.02204696	0.95491092
C	-1.55462742	-1.29751131	1.25273125
H	-2.24921502	-2.00829547	0.81752470
C	-0.74108519	-1.35948782	2.30622879
H	-0.59216372	-2.16206527	3.02107233
H	0.42552905	0.38756596	3.19244783
O	-1.07643582	0.83245900	1.78932004
N	-1.37571255	0.02960157	0.58636418

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 1.0

12

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.49591517
C	0.71181387	0.00000000	1.17323294
H	0.53005411	0.02028883	-0.95508841
H	1.80104347	0.03720666	1.17949228
C	-2.05640389	0.00457851	1.08142824
H	-3.14362640	0.02846971	0.97683775
C	-1.49316148	0.00490930	2.33279221
H	-2.10515600	0.04590268	3.23369572
H	0.29430176	-0.93424965	3.05949621

O 0.46264714 0.97509246 3.37152891

N -1.35885761 -0.00526795 -0.08801713

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11

12

Title Card Required

0 1

C -1.19630840 -0.86892763 -0.07591932

C -0.07096172 1.12166026 -0.15368977

C -1.35143899 0.38490956 -0.50328835

H -1.90212930 -1.69712202 -0.13891124

H -2.22448608 0.80438220 -0.99577589

C 1.14099205 -0.91060231 -0.27575134

H 2.02422185 -1.54525039 -0.20504869

C 1.13816570 0.38518483 -0.73551604

H 2.01665839 0.89550901 -1.12731975

H -0.10208588 2.19881349 -0.38690538

O 0.22445779 0.88468503 1.20457321

N 0.06135242 -1.20102298 0.52605203

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 0.5

12

In 1,4-dioxane

Enamine

Zero-point correction= 0.068466 (Hartree/Particle)

Thermal correction to Energy= 0.072411

Thermal correction to Enthalpy= 0.073355

Thermal correction to Gibbs Free Energy= 0.043812

Sum of electronic and zero-point Energies= -133.905785

Sum of electronic and thermal Energies= -133.901841

Sum of electronic and thermal Enthalpies= -133.900896

Sum of electronic and thermal Free Energies= -133.930439

%chk=eneamine.chk

# opt=calcall freq b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane)
scf=(qc,maxcycle=600) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-1.25611076	-0.19663277	0.01314654
C	-0.06575363	0.43013315	0.00049825
H	-0.02436375	1.52229660	-0.00536861
H	-2.17873080	0.38018942	0.00678221
H	-1.33712187	-1.28560215	0.01436371
N	1.18442722	-0.17223587	-0.07946532
H	1.95741765	0.34791818	0.31466431
H	1.22299457	-1.16015320	0.14394687

1 2 2.0 4 1.0 5 1.0

2 3 1.0 6 1.0

3

4

5

6 7 1.0 8 1.0

7

8

Isoxazole

Zero-point correction= 0.057630 (Hartree/Particle)

Thermal correction to Energy= 0.061228

Thermal correction to Enthalpy= 0.062172

Thermal correction to Gibbs Free Energy= 0.031415

Sum of electronic and zero-point Energies= -246.017103

Sum of electronic and thermal Energies= -246.013506

Sum of electronic and thermal Enthalpies= -246.012561

Sum of electronic and thermal Free Energies= -246.043318

%chk=isoxazole.chk

# opt=calcall freq b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane)
scf=(qc,maxcycle=600) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.61819600	-0.96588700	0.00000000
C	0.00000000	1.13010200	0.00000000
C	1.12822700	0.36593600	0.00000000
O	-1.09589200	0.34942900	0.00000000
N	-0.69473100	-0.99523300	0.00000000
H	1.16481300	-1.90602500	0.00000000

H 2.16098400 0.69439800 0.00000000

H -0.17408900 2.20192000 0.00000000

1 3 1.5 5 2.0 6 1.0

2 3 2.0 4 1.0 8 1.0

3 7 1.0

4 5 1.0

5

6

7

8

TS1-I-endo

Zero-point correction= 0.128697 (Hartree/Particle)

Thermal correction to Energy= 0.135453

Thermal correction to Enthalpy= 0.136397

Thermal correction to Gibbs Free Energy= 0.098170

Sum of electronic and zero-point Energies= -379.880260

Sum of electronic and thermal Energies= -379.873504

Sum of electronic and thermal Enthalpies= -379.872560

Sum of electronic and thermal Free Energies= -379.910787

%chk=TS1.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane)

scf=(qc,maxcycle=600) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.18525469
C	0.86596214	0.00000000	1.13313420
C	-7.57957227	-0.00049825	3.27682996
C	-8.89861311	-0.01314654	3.01241200
O	-1.27197387	0.00000000	1.74649261
N	-1.26759683	0.00000000	0.34327262
H	-7.23090629	0.00536861	4.31267075
H	-9.28437825	-0.01436371	1.99084341
H	0.25832848	0.00000000	-1.05636953
H	1.94945173	0.00000000	1.15601841
H	0.13623331	0.00000000	3.26253828
N	-6.55086670	0.07946532	2.34539801
H	-6.79335098	-0.14394687	1.38692555
H	-5.66230347	-0.31466431	2.62562974
H	-9.62036541	-0.00678221	3.82667558

1 3 1.0 7 2.0 10 1.0

2 3 2.0 6 1.0 12 1.0

3 11 1.0

4 5 2.0 8 1.0 13 1.0

5 16 1.0 9 1.0

6 7 1.0

7

8

9

10

11

12

13 15 1.0 14 1.0

14

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.24779242
C	0.87703471	0.00000000	1.00780718
C	-1.67499509	-1.28990241	1.15103613
C	-0.66470981	-1.40495607	2.32807991
O	-1.11792567	0.80141511	1.78817359
N	-1.35961742	0.08103159	0.53719980
H	-2.69478086	-1.17492089	1.53963222
H	0.05882252	-2.21773918	2.19218908
H	0.14188693	-0.09427391	-1.07132598
H	1.95905643	-0.08717643	0.96965668
H	0.40537368	0.41026923	3.17674791

N -1.54527989 -2.32508906 0.14586634

H -1.37304913 -3.23187155 0.56823007

H -2.38552174 -2.40004623 -0.42145507

H -1.18657263 -1.54041536 3.28215798

1 3 2.0 7 1.0 10 1.0

2 3 1.0 5 1.0 6 1.0 12 1.0

3 11 1.0

4 5 1.0 7 1.0 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 2.24779242

C 0.87703471 0.00000000 1.00780718

C -1.74222093 -1.58213043 1.28188136

C -0.79525782 -1.68088734 2.34384826

O -1.11792567 0.80141511 1.78817359

N -1.35961742 0.08103159 0.53719980

H -2.76200670 -1.46714891 1.67047746

H -0.07172549 -2.49367045 2.20795742

H 0.14188693 -0.09427391 -1.07132598

H 1.95905643 -0.08717643 0.96965668

H 0.40537368 0.41026923 3.17674791

N -1.61250573 -2.61731708 0.27671158

H -1.44027497 -3.52409958 0.69907530

H -2.45274758 -2.69227426 -0.29060983

H -1.31712064 -1.81634663 3.29792633

1 3 1.5 7 1.5 10 1.0

2 3 1.5 5 0.5 6 1.0 12 1.0

3 11 1.0

4 5 1.5 7 0.5 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

TS1-I-exo

Zero-point correction= 0.128283 (Hartree/Particle)

Thermal correction to Energy= 0.135358

Thermal correction to Enthalpy= 0.136302

Thermal correction to Gibbs Free Energy= 0.097179

Sum of electronic and zero-point Energies= -379.877479

Sum of electronic and thermal Energies= -379.870404

Sum of electronic and thermal Enthalpies= -379.869460

Sum of electronic and thermal Free Energies= -379.908583

%chk=TS2BCDIOCARTESIAN.chk

opt=(calcall,qst3) freq b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane)

scf=(qc,maxcycle=600) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 2.18525469

C 0.86596214 0.00000000 1.13313420

C -7.57957227 -0.00049825 3.27682996

C -8.89861311 -0.01314654 3.01241200

O -1.27197387 0.00000000 1.74649261

N -1.26759683 0.00000000 0.34327262

H -7.23090629 0.00536861 4.31267075

H -9.28437825 -0.01436371 1.99084341

H 0.25832848 0.00000000 -1.05636953

H 1.94945173 0.00000000 1.15601841

H 0.13623331 0.00000000 3.26253828

N -6.55086670 0.07946532 2.34539801

H -6.79335098 -0.14394687 1.38692555

H -5.66230347 -0.31466431 2.62562974

H -9.62036541 -0.00678221 3.82667558

1 3 1.0 7 2.0 10 1.0

2 3 2.0 6 1.0 12 1.0

3 11 1.0

4 5 2.0 8 1.0 13 1.0

5 16 1.0 9 1.0

6 7 1.0

7

8

9

10

11

12

13 15 1.0 14 1.0

14

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.25011467
C	0.87952098	0.00000000	1.00538892
C	-1.63567114	-1.33909314	1.13291768
C	-0.65882313	-1.39946626	2.34623038
O	-1.12344683	0.78779498	1.78883988
N	-1.36064838	0.05635140	0.53816868
H	-1.39877773	-2.06647861	0.34883812
H	0.06154014	-2.22177550	2.28271130
H	0.13692335	-0.08347660	-1.07474634
H	1.96264691	-0.07123315	0.96696557
H	0.40465467	0.42235879	3.17410919
N	-3.00687227	-1.50705730	1.53926665
H	-3.25293061	-0.80344713	2.23364966
H	-3.63015479	-1.37272761	0.74553911
H	-1.22650156	-1.49815024	3.27849326

1 3 2.0 7 1.0 10 1.0

2 3 1.0 5 1.0 6 1.0 12 1.0

3 11 1.0

4 5 1.0 7 1.0 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 2.22589609

C 0.89370120 0.00000000 1.04292516

C -1.38773444 -2.05032810 1.58674941

C -0.54472644 -1.77140942 2.66072335

O -1.17573323 0.63046051 1.76239591

N -1.29260430 0.18359733 0.38343723

H -1.02041679 -2.47568229 0.65719254

H 0.37095838 -2.36508427 2.73448231

H 0.19199420 -0.18454220 -1.05735123

H 1.95118798 -0.24272124 1.02585931

H 0.33899999 0.47034416 3.15489571

N -2.68337789 -2.21864404 1.84647802

H -3.08581727 -1.85416089 2.70213459

H -3.32911715 -2.46396682 1.10665084

H -1.04009733 -1.71679656 3.63807449

1 3 1.5 7 1.5 10 1.0

2 3 1.5 5 0.5 6 1.0 12 1.0

3 11 1.0

4 5 1.5 7 0.5 8 1.0 13 1.0

5 9 1.0 16 1.0

6 7 1.0

7

8

9

10

11

12

13 14 1.0 15 1.0

14

15

16

I1-I-endo

Zero-point correction= 0.132481 (Hartree/Particle)

Thermal correction to Energy= 0.138695

Thermal correction to Enthalpy= 0.139639

Thermal correction to Gibbs Free Energy= 0.102613

Sum of electronic and zero-point Energies= -379.899341

Sum of electronic and thermal Energies= -379.893127

Sum of electronic and thermal Enthalpies= -379.892183

Sum of electronic and thermal Free Energies= -379.929210

%chk=I1N.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C -0.17093221 -1.27029869 -0.63360824

C -1.06961543 -0.42827312 0.31710169

C 0.43466408 1.42004686 -0.08021721

C 1.25841316 0.72937170 -0.87548373

C 1.22371006 -0.67641019 -0.29762587

H -1.43259597 -1.03596244 1.15022377

H -0.44539213 -1.15040440 -1.68783897

H 0.08498076 2.44666588 -0.13595152

H 1.77546356 1.05689869 -1.77297817

H -0.21559597 -2.33392935 -0.37545686

N -0.06255131 0.54763258 0.98365065

O 1.05958973 -0.38421764 1.11385312

N -2.18939329 0.19813415 -0.32878370

H -1.90430679 0.77332289 -1.11759492

H -2.72440074 0.77327079 0.31743045

H 2.09130364 -1.32310730 -0.45372726

1 2 1.0 5 1.0 7 1.0 10 1.0

2 6 1.0 11 1.0 13 1.0

3 4 2.0 8 1.0 11 1.0

4 5 1.0 9 1.0

5 12 1.0 16 1.0

6

7

8

9

10

11 12 1.0

12

13 14 1.0 15 1.0

14

15

16

I1-I-exo

Zero-point correction= 0.132466 (Hartree/Particle)

Thermal correction to Energy= 0.138681

Thermal correction to Enthalpy= 0.139625

Thermal correction to Gibbs Free Energy= 0.102574

Sum of electronic and zero-point Energies= -379.901311

Sum of electronic and thermal Energies= -379.895096

Sum of electronic and thermal Enthalpies= -379.894152

Sum of electronic and thermal Free Energies= -379.931204

%chk=I1X.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 0.99221062 -0.21248454 -0.54589937

C 0.32022071 1.19139044 -0.63288225

C -0.89457839 0.98330579 0.30667737

C -1.84648830 0.02057327 -0.39325196

C -1.20547675 -1.15005281 -0.33762513

N 0.05060262 -0.98742572 0.39723966

O -0.30959438 0.11072809 1.30265709

H -1.31202623 1.87494388 0.78271210

H -2.78086766 0.26610976 -0.88959368

H -1.43859403 -2.11849707 -0.77186860

H 0.99470783 -0.75190817 -1.49931715

H 0.03534363 1.47359650 -1.65188058

H 0.99594120 1.95472570 -0.23060669

N 2.33834865 -0.13253788 -0.04086391

H 2.34214814 0.32454365 0.86954408

H 2.72211591 -1.06598657 0.09301163

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

I2_α

Zero-point correction= 0.125939 (Hartree/Particle)

Thermal correction to Energy= 0.135039

Thermal correction to Enthalpy= 0.135983

Thermal correction to Gibbs Free Energy= 0.090137

Sum of electronic and zero-point Energies= -379.850682

Sum of electronic and thermal Energies= -379.841583

Sum of electronic and thermal Enthalpies= -379.840639

Sum of electronic and thermal Free Energies= -379.886485

%chk=I2-2_NH3.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	1.66719518	-0.99051379	0.21237444
C	0.76203196	0.90124588	-0.64088476
C	2.07914877	0.15277931	-0.33474379
H	2.19658509	-1.83455616	0.64257813
H	3.08737933	0.51461301	-0.50902963
C	-0.22554518	0.05545987	1.21439430

H -0.68210155 -0.25446105 2.14795066

C 0.10044960 1.24630619 0.71369097

H -0.02765841 2.23610981 1.13972664

H 0.76946432 1.66442432 -1.42312452

O -0.05901872 -0.23094731 -1.01333716

N 0.17377790 -1.00051559 0.23204472

N -3.24860808 -0.22456935 -0.15116105

H -2.33978741 -0.36555770 -0.59196616

H -3.35197602 0.78155988 -0.02814120

H -3.95562628 -0.51062374 -0.82646929

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 1.0 14 0.5

12

13 14 1.0 15 1.0 16 1.0

14

15

16

I2_β_endo

Zero-point correction= 0.131697 (Hartree/Particle)

Thermal correction to Energy= 0.138888

Thermal correction to Enthalpy= 0.139832

Thermal correction to Gibbs Free Energy= 0.100384

Sum of electronic and zero-point Energies= -379.928812

Sum of electronic and thermal Energies= -379.921622

Sum of electronic and thermal Enthalpies= -379.920677

Sum of electronic and thermal Free Energies= -379.960126

%chk=I2-1N_1.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-0.59561068	-0.64095887	0.36004656
C	0.59327031	-1.43447604	-0.18339784
C	1.89940864	-0.72299396	0.02166009
C	1.91016426	0.62475157	0.03817776
C	0.68811141	1.39127157	-0.08746741
N	-0.49691480	0.83127999	0.00632246
O	-1.60267743	1.47487864	-0.04381468

H 2.82433877 -1.29665606 0.07884658

H 2.83975530 1.18828991 0.11991844

H 0.68592609 2.47010173 -0.22686124

H -0.56354222 -0.62217560 1.46641484

H 0.59291495 -2.42191418 0.29796429

H 0.42785345 -1.60834420 -1.26150136

N -1.83625518 -1.14685851 -0.18928684

H -2.02310386 -2.07339431 0.18652949

H -2.60259677 -0.53145233 0.07584211

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

I2_β_exo

Zero-point correction= 0.132294 (Hartree/Particle)

Thermal correction to Energy= 0.139302

Thermal correction to Enthalpy= 0.140247

Thermal correction to Gibbs Free Energy= 0.101354

Sum of electronic and zero-point Energies= -379.933814

Sum of electronic and thermal Energies= -379.926805

Sum of electronic and thermal Enthalpies= -379.925861

Sum of electronic and thermal Free Energies= -379.964753

%chk=I2-1X.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 0.39024790 0.92841555 -0.30623075

C -1.06839518 0.95034567 -0.76805658

C -1.91150562 -0.05793632 -0.03730583

C -1.34047768 -1.20271188 0.38981692

C 0.07242438 -1.46054086 0.19865049

N 0.89534893 -0.51084120 -0.18893036

O 2.15612742 -0.66244607 -0.35835110

H -2.97921699 0.12182787 0.08573956

H -1.92554184 -1.98668507 0.87100560

H 0.52065902 -2.43512745 0.38207004

H 1.05656479 1.36120856 -1.05701566

H -1.11003080 0.73334911 -1.84926650

H -1.44669180 1.97179987 -0.63382926

N 0.57086691 1.62280637 0.94334723

H -0.02090484 1.23267146 1.67438639

H 1.53886942 1.57133505 1.25155503

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

I3

Zero-point correction= 0.128942 (Hartree/Particle)

Thermal correction to Energy= 0.137918

Thermal correction to Enthalpy= 0.138862

Thermal correction to Gibbs Free Energy= 0.093830

Sum of electronic and zero-point Energies= -379.958684

Sum of electronic and thermal Energies= -379.949707

Sum of electronic and thermal Enthalpies= -379.948763

Sum of electronic and thermal Free Energies= -379.993795

%chk=I3_NH3.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-1.13139946	-1.23830180	0.00001455
C	-2.30209479	-0.49537926	0.00003896
C	-2.24984242	0.90093798	0.00002146
C	-0.99096730	1.50690851	-0.00002117
C	0.16307814	0.73728500	-0.00004463
N	0.09245537	-0.62917504	-0.00002638
H	-3.16108601	1.49684771	0.00004037
H	-1.09195831	-2.32387177	0.00002719
H	-3.25283424	-1.02731723	0.00007104

H -0.88520619 2.59111950 -0.00003598

H 1.17275708 1.14180311 -0.00007332

O 1.17162772 -1.34755811 -0.00004534

N 3.56981602 0.58285335 0.00005740

H 2.93301551 -0.21945571 0.00004171

H 4.17192854 0.48838908 0.81629033

H 4.17181713 0.48849950 -0.81627081

1 2 1.5 6 1.5 8 1.0

2 3 1.5 9 1.0

3 4 1.5 7 1.0

4 5 1.5 10 1.0

5 6 1.5 11 1.0

6 12 1.0

7

8

9

10

11

12 14 0.5

13 14 1.0 15 1.0 16 1.0

14

15

16

I2_α (without NH3)

Zero-point correction= 0.090351 (Hartree/Particle)

Thermal correction to Energy= 0.095100

Thermal correction to Enthalpy= 0.096045

Thermal correction to Gibbs Free Energy= 0.062320

Sum of electronic and zero-point Energies= -323.309924

Sum of electronic and thermal Energies= -323.305175

Sum of electronic and thermal Enthalpies= -323.304231

Sum of electronic and thermal Free Energies= -323.337955

%chk=I2-2.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C -0.48399108 -0.67951871 1.19081180

C 0.33558496 1.06268953 -0.00000000

C -0.48399108 0.65181256 1.24561710

H -0.95695339 -1.44215622 1.80099327

H -0.95898070 1.31683624 1.95963765

C -0.48399108 -0.67951871 -1.19081180

H -0.95695339 -1.44215622 -1.80099327

C -0.48399108 0.65181256 -1.24561710

H -0.95898070 1.31683624 -1.95963765

H 0.82156632 2.04161253 -0.00000000

O 1.30384581 -0.00967854 -0.00000000

N 0.31168737 -1.10817252 0.00000000

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 1.0

12

Biradical

Zero-point correction= 0.087274 (Hartree/Particle)

Thermal correction to Energy= 0.092966

Thermal correction to Enthalpy= 0.093911

Thermal correction to Gibbs Free Energy= 0.056795

Sum of electronic and zero-point Energies= -323.339605

Sum of electronic and thermal Energies= -323.333913

Sum of electronic and thermal Enthalpies= -323.332969

Sum of electronic and thermal Free Energies= -323.370084

%chk=Biradical_Triplet.chk

opt=(calcall,maxcycle=500) freq ub3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 3

C	-1.12081734	-1.16285298	-0.05124530
C	1.05545353	-0.00015193	0.32091301
C	0.22900078	-1.24612771	0.17968015
H	-1.70672539	-2.07694054	-0.17209259
H	0.73847430	-2.20824847	0.23309194
C	-1.12058428	1.16298167	-0.05122245
H	-1.70633263	2.07718621	-0.17196680
C	0.22925512	1.24605541	0.17967984
H	0.73887632	2.20809784	0.23316291
H	1.52139537	-0.00008786	1.35149535
O	2.19017509	-0.00005018	-0.47363658
N	-1.82013365	0.00013821	-0.16448995

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11

12

I3 (without NH_3)

Zero-point correction= 0.092713 (Hartree/Particle)

Thermal correction to Energy= 0.097778

Thermal correction to Enthalpy= 0.098722

Thermal correction to Gibbs Free Energy= 0.064001

Sum of electronic and zero-point Energies= -323.415284

Sum of electronic and thermal Energies= -323.410219

Sum of electronic and thermal Enthalpies= -323.409275

Sum of electronic and thermal Free Energies= -323.443996

%chk=I3.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C -0.00000000 0.28552634 1.18001547

C 0.00000000 -1.10080685 1.19648629

C 0.00000000 -1.82278125 0.00000000

C 0.00000000 -1.10080685 -1.19648629

C -0.00000000 0.28552634 -1.18001547

N -0.00000000 0.98068260 0.00000000

H 0.00000010 -2.91136714 0.00000000

H -0.00000000 0.91178829 2.06748546

H -0.00000003 -1.60610689 2.16161217

H -0.00000003 -1.60610689 -2.16161217

H -0.00000000 0.91178829 -2.06748546

O -0.00000000 2.26940998 -0.00000000

1 2 1.5 6 1.5 8 1.0

2 3 1.5 9 1.0

3 4 1.5 7 1.0

4 5 1.5 10 1.0

5 6 1.5 11 1.0

6 12 1.0

7

8

9

10

11

12

TS2_α_endo

Zero-point correction= 0.128708 (Hartree/Particle)

Thermal correction to Energy= 0.135259

Thermal correction to Enthalpy= 0.136204

Thermal correction to Gibbs Free Energy= 0.098488

Sum of electronic and zero-point Energies= -379.797289

Sum of electronic and thermal Energies= -379.790737

Sum of electronic and thermal Enthalpies= -379.789792

Sum of electronic and thermal Free Energies= -379.827508

%chk=TS1N_TS.chk

opt=(calcall,tight,ts,verytight,noeigentest,maxcycle=500) freq

b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane) geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	-0.83328103	-0.72638177	0.31774671
C	-0.03081477	-1.27535350	-0.73788146
C	1.26811193	-0.52453820	-0.50968356
C	1.04892535	0.94342752	-0.87213036
C	0.25319485	1.41455571	0.09158878
N	0.00078019	0.32499650	1.06495714
O	1.28194904	-0.36349027	0.98924219
H	2.19694123	-0.99510023	-0.84270075
H	1.40352292	1.44601749	-1.76820529
H	-0.21978407	2.38188687	0.23538355

H -1.36968358 -1.37053733 1.01799489

H 0.04112015 -2.36378200 -0.76826756

H -2.86867285 -0.47272456 -0.56119980

N -2.17520007 0.20723751 -0.25256103

H -2.60646483 0.84715905 0.42258455

H -1.84845015 0.71910615 -1.07414051

1 2 1.5 6 1.0 11 1.0 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7 13 0.3

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0

15

16

TS2_α_exo

Zero-point correction= 0.128351 (Hartree/Particle)

Thermal correction to Energy= 0.134973

Thermal correction to Enthalpy= 0.135918

Thermal correction to Gibbs Free Energy= 0.098043

Sum of electronic and zero-point Energies= -379.805584

Sum of electronic and thermal Energies= -379.798962

Sum of electronic and thermal Enthalpies= -379.798017

Sum of electronic and thermal Free Energies= -379.835892

%chk=TS1X_TS.chk

opt=(calcall,tight,ts,verytight,noeigentest,maxcycle=500) freq

b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane) geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	0.79919263	-0.06048530	-0.73236172
C	0.22266683	1.23431147	-0.65381274
C	-0.87793321	0.99188291	0.39472313
C	-1.92272874	0.05706997	-0.24066376
C	-1.29627364	-1.12269216	-0.34389336
N	0.05242235	-0.98466391	0.22233501
O	-0.21721064	0.02946666	1.26493944
H	-1.24899551	1.83365872	0.98787050
H	-2.91176424	0.33097697	-0.59967515
H	-1.57047818	-2.05801742	-0.82221391

H 1.07183912 -0.55015797 -1.67025905

H -0.02247003 1.75380868 -1.58023316

H 2.99025600 0.53141024 -0.36211883

N 2.36641660 -0.13411026 0.09202333

H 2.14560634 0.21248401 1.02717667

H 2.80227579 -1.05899865 0.15547971

1 2 1.5 6 1.0 11 1.0 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7 13 0.2 15 0.3

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0

15

16

TS3_*α*

Zero-point correction= 0.123688 (Hartree/Particle)

Thermal correction to Energy= 0.132610

Thermal correction to Enthalpy= 0.133554

Thermal correction to Gibbs Free Energy= 0.089312

Sum of electronic and zero-point Energies= -379.792294

Sum of electronic and thermal Energies= -379.783373

Sum of electronic and thermal Enthalpies= -379.782429

Sum of electronic and thermal Free Energies= -379.826671

%mem=4GB

%Nprocs=4

%chk=TS3.chk

opt=(calcall,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.33232546

C 1.50339939 0.00000000 1.69484882

C 2.09030710 -1.35315681 1.23308390

C 1.99877440 -1.29476068 -0.09521375

N 1.41820921 0.02735817 -0.47695663

O 1.99624562 0.83708833 0.62195934

H 1.80049606 0.38701675 2.67277881

H 2.45470462 -2.15381258 1.86868807

H 2.22751105 -2.00661951 -0.88177132

H -0.79258524 -0.02963267 -0.73956240

H -0.83458180 -0.02275882 2.02556737

H 0.84557932 2.67377652 -0.21477367

N 0.07929809 3.29369866 -0.47678763

H -0.50756202 3.38598287 0.35097654

H 0.48445372 4.21185307 -0.65167128

1 11 1.0 2 2.0 6 1.0

2 3 1.0 12 1.0

3 4 1.0 8 1.0 7 1.0

4 5 2.0 9 1.0

5 10 1.0 6 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38713418
C	1.20260710	0.00000000	2.09826216
C	2.39328369	0.00000000	1.36701569
C	2.36183160	-0.00000000	-0.01915610
N	1.17602892	-0.00000000	-0.69939730
O	1.17494056	-0.00000000	-1.99581004
H	1.21241695	0.00000000	3.18701238
H	3.36333550	-0.00000000	1.86286142
H	3.24310339	-0.00000000	-0.65427638
H	-0.89674450	0.00000454	-0.61557760
H	-0.96070374	0.00000000	1.90069743
H	-0.74087042	0.00014938	-2.83531600
N	-1.76167848	0.00019299	-2.91996593
H	-2.01713632	0.81644068	-3.47330144
H	-2.01720903	-0.81612046	-3.47317133

1 2 1.5 6 1.5 11 1.0

2 3 1.5 12 1.0

3 4 1.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	-0.25676844	0.69927474	0.87719299
C	0.62971008	1.50901797	0.26397519
C	1.49216222	0.77806367	-0.65729073
C	2.10608742	-0.41900175	-0.08969181
C	1.20213733	-1.20351668	0.52910885
N	-0.14192315	-0.67423354	0.42605532
O	-0.33610412	-0.57699314	-0.95900712
H	1.90510428	1.25708062	-1.54478399
H	3.14242323	-0.69528943	-0.27223823
H	1.33624951	-2.22464560	0.87577155
H	-1.14311522	0.98545993	1.43514832
H	0.61101315	2.59513757	0.32107574
H	-2.47574234	-0.09811814	-0.67008450

N -3.31158344 0.01166390 -0.09194558

H -4.10145356 0.13654028 -0.72274341

H -3.45107172 -0.88526037 0.37137628

1 2 2.0 6 1.0 11 1.0

2 3 1.0 12 1.0

3 4 1.0 7 0.5 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

$END

TS3_β_endo

Zero-point correction= 0.129192 (Hartree/Particle)

Thermal correction to Energy= 0.135680

Thermal correction to Enthalpy= 0.136624

Thermal correction to Gibbs Free Energy= 0.098960

Sum of electronic and zero-point Energies= -379.841689

Sum of electronic and thermal Energies= -379.835201

Sum of electronic and thermal Enthalpies= -379.834257

Sum of electronic and thermal Free Energies= -379.871921

%mem=4GB

%Nprocs=4

%chk=TS2N.chk

opt=(calcall,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.55579174
C	1.52736733	0.00000000	1.83465332
C	2.04933331	-1.37426567	1.44697805
C	1.98451146	-1.37343227	0.11137293
N	1.51023026	-0.07003704	-0.35377527
O	2.00527026	0.79493974	0.71918726
H	1.86095638	0.43366479	2.78120317
H	2.32908215	-2.18245071	2.11682046
H	2.18424147	-2.15822647	-0.61218588

H -0.31327816 0.97210287 -0.38987995

H -0.46915863 0.90889415 1.94789985

H -0.51272183 -0.87244354 1.97658138

N -0.81305056 -1.02612442 -0.59116322

H -0.75043258 -1.01904924 -1.60636605

H -0.56384044 -1.95334716 -0.25576520

1 2 1.0 11 1.0 6 1.0 14 1.0

2 3 1.0 13 1.0 12 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 10 1.0 6 1.0

6 7 1.0

7

8

9

10

11

12

13

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52675812
C	1.38808481	0.00000000	2.10137937
C	2.38680565	-0.59047234	1.41518502
C	2.15880157	-1.20975933	0.12503729
N	1.04089967	-1.02244374	-0.53819998
O	0.78252796	-1.53239418	-1.68051185
H	1.55797035	0.42723775	3.08958784
H	3.39646682	-0.65368886	1.82183264
H	2.90032939	-1.84365575	-0.35786156
H	0.38988664	0.95231430	-0.38794890
H	-0.57605518	0.87149142	1.86168127
H	-0.54654735	-0.89223040	1.88747947
N	-1.30410528	-0.23010923	-0.52746039
H	-1.26774170	-0.31593029	-1.54034669
H	-1.69588580	-1.09855979	-0.16734145

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	-1.08523753	-0.03809327	0.40009728
C	-0.30554232	-1.41845948	0.36973314
C	1.09780199	-1.16600005	-0.00975776
C	1.33320417	-0.19525087	-1.03564333
C	0.73127518	1.01306809	-0.82085459
N	-0.06173254	1.01947857	0.36661240
O	0.78378124	0.82349169	1.39320124
H	1.89165463	-1.84664086	0.29553166
H	2.13772261	-0.29559537	-1.76406954
H	1.05335044	1.95611589	-1.25562819
H	-1.56294908	0.06154715	1.38043107
H	-0.39045393	-1.97837315	1.30740736
H	-0.80129717	-2.00237244	-0.42234116
N	-2.07996105	0.04386712	-0.64379909

H -2.57740289 0.93060083 -0.60035292

H -1.65802814 -0.02822188 -1.56772986

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

$END

TS3_β_exo

Zero-point correction= 0.129312 (Hartree/Particle)

Thermal correction to Energy= 0.135783

Thermal correction to Enthalpy= 0.136727

Thermal correction to Gibbs Free Energy= 0.099095

Sum of electronic and zero-point Energies= -379.841325

Sum of electronic and thermal Energies= -379.834854

Sum of electronic and thermal Enthalpies= -379.833909

Sum of electronic and thermal Free Energies= -379.871541

%mem=4GB

%Nprocs=4

%chk=TS2X.chk

opt=(calcall,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.55884618
C	1.52356036	0.00000000	1.84269864
C	2.06021476	-1.36399623	1.42508182
C	1.99177152	-1.33294203	0.09140018
N	1.50245045	-0.02349091	-0.34461796
O	1.99425409	0.82346765	0.74911636
H	1.85001208	0.41790060	2.79908695
H	2.34421096	-2.18524568	2.07669792
H	2.18137692	-2.09856099	-0.65604397
H	-0.43548086	-0.90679281	-0.43367359

H -0.52062504 -0.86017806 1.99266189

H -0.46458288 0.91956889 1.93255773

N -0.67285265 1.15455677 -0.53647725

H -0.24379535 2.00582861 -0.17727427

H -0.57996454 1.17910280 -1.55003323

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.53016459

C 1.39213642 0.00000000 2.09886543

C 2.38136795 -0.60399775 1.40920932

C 2.14021869 -1.21200509 0.11634943

N 1.01766423 -1.00785701 -0.53752228

O 0.74594425 -1.49598449 -1.69040980

H 1.57149307 0.43419302 3.08211032

H 3.39217141 -0.67969226 1.81046145

H 2.87376987 -1.84418957 -0.38026059

H -0.94672005 -0.36984305 -0.40237204

H -0.53341168 -0.89532582 1.89306896

H -0.57699052 0.87150647 1.86490683

N 0.26394261 1.30983438 -0.53936550

H 1.15060033 1.67928134 -0.20148335

H 0.29201553 1.28581964 -1.55588181

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	0.93805394	0.09067171	-0.58278232
C	0.28553980	1.41205538	-0.02624424
C	-1.09184304	1.12384715	0.41475217
C	-1.85977480	0.19616078	-0.36196033
C	-1.23001825	-0.99576416	-0.58336439
N	0.10274663	-1.02524941	-0.07713928
O	-0.00684546	-0.90161265	1.26550934
H	-1.58320643	1.75529407	1.15494678
H	-2.93757316	0.29157521	-0.49052647
H	-1.73785118	-1.93481450	-0.79239554
H	0.88793468	0.05120347	-1.67697408
H	0.26004202	2.10912238	-0.88106334
H	0.88822290	1.87433988	0.76328407
N	2.31451499	0.02295000	-0.16089715
H	2.34448243	-0.07483999	0.85372447

H 2.76013512 -0.80470866 -0.55122089

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

$END

TS2_β_endo

Zero-point correction= 0.130416 (Hartree/Particle)

Thermal correction to Energy= 0.137238

Thermal correction to Enthalpy= 0.138182

Thermal correction to Gibbs Free Energy= 0.099880

Sum of electronic and zero-point Energies= -379.886008

Sum of electronic and thermal Energies= -379.879187

Sum of electronic and thermal Enthalpies= -379.878243

Sum of electronic and thermal Free Energies= -379.916545

%mem=4GB

%Nprocs=1

%chk=TS4N_1.chk

opt=(calcall,qst3,verytight,maxcycle=500) freq b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3 scf=xqc

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.52919565
C	1.38761368	0.00000000	2.10259003
C	2.37918129	-0.58989346	1.40572138
C	2.14184987	-1.17479332	0.10252580
N	1.02753579	-0.96499226	-0.56152382
O	0.79516957	-1.41539725	-1.73735766
H	1.56079221	0.40614479	3.09903866
H	3.38941550	-0.67253675	1.80696124
H	2.88391224	-1.78350608	-0.40945288
H	0.35950915	0.97637320	-0.37799539

H -0.57642705 0.87072387 1.87024625

H -0.54663257 -0.89567731 1.87394927

N -1.29894725 -0.39087532 -0.50680660

H -1.24847943 -0.51312616 -1.51616546

H -1.97781492 0.33917074 -0.30484034

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 16 1.0 15 1.0

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.38713418

C 1.20260710 0.00000000 2.09826216

C 2.39328369 0.00000000 1.36701569

C 2.36183160 -0.00000000 -0.01915610

N 1.17602892 -0.00000000 -0.69939730

O 1.17494056 -0.00000000 -1.99581004

H 1.21241695 0.00000000 3.18701238

H 3.36333550 -0.00000000 1.86286142

H 3.24310339 -0.00000000 -0.65427638

H -0.89674450 0.00000454 -0.61557760

H -0.96070374 0.00000000 1.90069743

H -2.01720904 -0.81612047 -3.47317133

N -1.76167848 0.00019299 -2.91996593

H -2.01713632 0.81644068 -3.47330144

H -0.74087042 0.00014938 -2.83531600

1 2 1.5 6 1.5 11 1.0

2 3 1.5 12 1.0

3 4 1.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7 16 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	-0.29475911	0.87507724	-0.42105897
C	1.05545198	0.69105575	-0.96820739
C	1.80335991	-0.31668535	-0.37383692
C	1.18235970	-1.22853528	0.50903810
C	-0.22266241	-1.31465939	0.48869543
N	-0.96740555	-0.36381626	-0.09921720
O	-2.21596389	-0.53935448	-0.51707251
H	2.85112831	-0.45930301	-0.64574084
H	1.75166536	-1.98194811	1.04941789
H	-0.77657361	-2.18591490	0.83243981
H	-0.98299309	1.51281262	-0.97495939
H	1.33553421	1.16475919	-1.90661616
H	0.51889749	0.99301859	1.53882524
N	-0.10634241	1.61656681	1.01400793
H	0.37258122	2.50986688	0.88312588

H -0.96879347 1.75477290 1.54877099

1 2 1.5 6 1.0 11 1.0 13 0.5 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 2.0 8 1.0

4 5 1.5 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7 16 0.5

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0

15

16

$END

TS2_β_exo

Zero-point correction= 0.130213 (Hartree/Particle)

Thermal correction to Energy= 0.137110

Thermal correction to Enthalpy= 0.138055

Thermal correction to Gibbs Free Energy= 0.099557

Sum of electronic and zero-point Energies= -379.885931

Sum of electronic and thermal Energies= -379.879034

Sum of electronic and thermal Enthalpies= -379.878090

Sum of electronic and thermal Free Energies= -379.916588

%mem=4GB

%Nprocs=1

%chk=TS4X_2.chk

opt=(calcall,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.53016459
C	1.39213642	0.00000000	2.09886543
C	2.38136795	-0.60399775	1.40920932
C	2.14021869	-1.21200509	0.11634943
N	1.01766423	-1.00785701	-0.53752228
O	0.74594425	-1.49598449	-1.69040980
H	1.57149307	0.43419302	3.08211032
H	3.39217141	-0.67969226	1.81046145
H	2.87376987	-1.84418957	-0.38026059
H	-0.94672005	-0.36984305	-0.40237204
H	-0.53341168	-0.89532582	1.89306896

H -0.57699052 0.87150647 1.86490683

N 0.26394261 1.30983438 -0.53936550

H 1.15060033 1.67928134 -0.20148335

H 0.29201553 1.28581964 -1.55588181

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 1.38713418

C 1.20260710 0.00000000 2.09826216

C 2.39328369 0.00000000 1.36701569

C 2.36183160 -0.00000000 -0.01915610

N 1.17602892 -0.00000000 -0.69939730

O 1.17494056 -0.00000000 -1.99581004

H 1.21241695 0.00000000 3.18701238

H 3.36333550 -0.00000000 1.86286142

H 3.24310339 -0.00000000 -0.65427638

H -0.89674450 0.00000454 -0.61557760

H -0.96070374 0.00000000 1.90069743

H -2.01713632 0.81644068 -3.47330144

N -1.76167848 0.00019299 -2.91996593

H -0.74087042 0.00014938 -2.83531600

H -2.01720903 -0.81612046 -3.47317133

1 2 1.5 6 1.5 11 1.0

2 3 1.5 12 1.0

3 4 1.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0

7 15 0.5

8

9

10

11

12

13 14 1.0

14 15 1.0 16 1.0

15

16

Title Card Required

0 1

C	0.29559837	0.87136522	-0.43021896
C	-1.05103923	0.67864067	-0.97815448
C	-1.79952739	-0.32504785	-0.37870319
C	-1.18035814	-1.22794646	0.51430257
C	0.22457122	-1.30823919	0.50249516
N	0.96815787	-0.36142294	-0.09564354
O	2.21545004	-0.54341990	-0.51743360
H	-2.84520623	-0.47343145	-0.65540416
H	-1.74981729	-1.97639848	1.06143361
H	0.78103285	-2.17202959	0.86055305
H	0.98559300	1.50772189	-0.98314788
H	-1.33432223	1.15271301	-1.91551113
H	-0.40618769	0.94581874	1.59033751
N	0.09853757	1.63013108	1.01327175
H	0.95893969	1.91112408	1.49040481
H	-0.51596948	2.43824960	0.88907896

1 2 1.5 6 1.0 11 1.0 13 0.5 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7 13 0.5 15 0.5

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0

15

16

$END

TS3_α (without NH_3)

Zero-point correction= 0.087392 (Hartree/Particle)

Thermal correction to Energy= 0.092390

Thermal correction to Enthalpy= 0.093335

Thermal correction to Gibbs Free Energy= 0.059082

Sum of electronic and zero-point Energies= -323.256273

Sum of electronic and thermal Energies= -323.251275

Sum of electronic and thermal Enthalpies= -323.250331

Sum of electronic and thermal Free Energies= -323.284584

%mem=4GB

%Nprocs=1

%chk=TS3_wo_NH3.chk

opt=(calcall,tight,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.33245884
C	1.50432484	0.00000000	1.69175469
C	2.08727514	-1.35610873	1.22999200
C	1.99543813	-1.29644196	-0.09795846
N	1.41643063	0.02860668	-0.47727030
H	1.80285761	0.38558690	2.66984929
H	-0.79521921	-0.04736275	-0.73689479
H	-0.83408406	-0.02452976	2.02628810
H	2.44967219	-2.15799575	1.86508456
H	2.22269736	-2.00811192	-0.88504794
O	1.99485944	0.83597270	0.62029410

1 8 1.0 2 2.0 6 1.0

2 3 1.0 9 1.0

3 4 1.0 7 1.0 12 1.0

4 5 2.0 10 1.0

5 11 1.0 6 1.0

6 12 1.0

7

8

9

10

11

12

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38643103
C	1.20497892	0.00000000	2.09414021
C	2.39280371	0.00000000	1.35800248
C	2.35986439	0.00000000	-0.02803720
N	1.17167373	0.00000000	-0.70912580
H	1.21791134	0.00000000	3.18264927
H	-0.89484737	0.00000000	-0.61567460
H	-0.95905480	0.00000000	1.90316112
H	3.36386446	0.00000000	1.85180115

H 3.23983176 0.00000000 -0.66479811

O 1.15636363 0.00000000 -1.99776224

1 2 1.5 6 1.5 8 1.0

2 3 1.5 9 1.0

3 4 1.5 7 1.0

4 5 1.5 10 1.0

5 6 1.5 11 1.0

6 12 1.0

7

8

9

10

11

12

Title Card Required

0 1

C -0.45413252 -0.59244330 -1.21169369

C -0.45413252 0.75528443 -1.22649645

C 0.10301631 1.31963632 0.00000000

C -0.45413252 0.75528443 1.22649645

C -0.45413252 -0.59244330 1.21169369

N 0.14456339 -1.11657663 0.00000000

H 0.59931236 2.28966917 0.00000000

H -0.63418117 -1.26853146 -2.04299117

H -0.71047197 1.36146904 -2.09295689

H -0.71047197 1.36146904 2.09295689

H -0.63418117 -1.26853146 2.04299117

O 1.41989160 -0.56642742 0.00000000

1 2 1.5 6 1.5 8 1.0

2 3 1.5 9 1.0

3 4 1.0 7 1.0 12 0.5

4 5 2.0 10 1.0

5 6 1.0 11 1.0

6 12 1.0

7

8

9

10

11

12

$END

TS_Biradical (N-O bond cleavage)

Zero-point correction= 0.083679 (Hartree/Particle)

Thermal correction to Energy= 0.089330

Thermal correction to Enthalpy= 0.090274

Thermal correction to Gibbs Free Energy= 0.053863

Sum of electronic and zero-point Energies= -323.228569

Sum of electronic and thermal Energies= -323.222918

Sum of electronic and thermal Enthalpies= -323.221974

Sum of electronic and thermal Free Energies= -323.258385

%mem=4GB

%Nprocs=4

%chk=TS_Triplet_tight.chk

opt=(calcall,tight,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 3

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.26385229
C	0.88541595	0.00000000	0.99573347
H	0.10459459	-0.04736275	-1.07909569
H	1.96976683	-0.02452976	0.95997829
C	-1.55626460	-1.29644196	1.25276083
H	-2.24911242	-2.00811193	0.81558980
C	-0.74247336	-1.35610873	2.30615072
H	-0.59127153	-2.15799575	3.02156123
H	0.42685107	0.38558690	3.19314719
O	-1.07855491	0.83597270	1.78911942

N -1.37562983 0.02860667 0.58455560

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 1.0

12

Title Card Required

0 3

C 0.00000000 0.00000000 0.00000000

C 0.00000000 0.00000000 2.49530166

C 0.71177590 0.00000000 1.17287906

H 0.53019650 0.02042814 -0.95494646

H 1.80125402 0.03337534 1.17687504

C -2.05780787 -0.00025861 1.08394351

H -3.14521709 0.01987853 0.98105555

C -1.49321045 -0.00025188 2.33434877

H -2.10617356 0.03285028 3.23505977

H 0.29501441 -0.93725722 3.05540626

O 0.45853923 0.97451118 3.36649154

N -1.35910551 -0.00643468 -0.08489379

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11

12

Title Card Required

0 3

C 0.78867248 1.07835322 0.39651059

C -1.12628970 -0.00000263 -0.28043453

C -0.61056669 1.06402309 0.64855498

H 1.55703755 1.76468157 0.73889480

H -1.17222025 1.62675705 1.38792936

C 0.78867755 -1.07834941 0.39651125

H 1.55704553 -1.76467559 0.73889342

C -0.61056195 -1.06402519 0.64855592

H -1.17221296 -1.62676083 1.38793101

H -2.17457132 -0.00000534 -0.58428307

O -0.23144223 -0.00000096 -1.39435188

N 1.12526702 0.00000234 -0.48181997

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 0.5

12

$END

With $TiCl_4$ in 1,4-dioxane

SM

Zero-point correction= 0.135120 (Hartree/Particle)

Thermal correction to Energy= 0.153040

Thermal correction to Enthalpy= 0.153984

Thermal correction to Gibbs Free Energy= 0.085761

Sum of electronic and zero-point Energies= -3070.620773

Sum of electronic and thermal Energies= -3070.602853

Sum of electronic and thermal Enthalpies= -3070.601909

Sum of electronic and thermal Free Energies= -3070.670132

%chk=CAR_TiCl4.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	1.59557709	0.97189487	-1.31371403
C	2.71092069	1.76621794	-0.96237094
C	2.51421677	2.02613990	0.36454098
O	1.37492898	1.46680547	0.79122371
H	1.33452797	0.53341361	-2.26971316
H	3.53465276	2.07891264	-1.59191137
N	0.80723987	0.78136651	-0.27424235
H	3.07831072	2.57614612	1.11057016
C	3.82332869	-0.99215444	1.10840806
H	3.74324093	-0.70631283	2.15490508
H	4.76216582	-0.78156417	0.59260810

C 2.79992486 -1.62083168 0.50055616

H 1.87775619 -1.81809232 1.04852214

N 2.78947306 -2.11380735 -0.79448770

H 1.88505303 -2.20350187 -1.23823384

H 3.52184489 -1.79719340 -1.41770876

Ti -1.30180986 -0.04206899 0.02282558

Cl -0.59642544 -0.64098572 2.03424965

Cl -1.88954868 2.08958943 -0.23087979

Cl -3.37434974 -0.86755704 0.18705184

Cl -0.72426239 -1.30288476 -1.75068063

1 2 1.0 5 1.0 7 2.0

2 3 2.0 6 1.0

3 4 1.0 8 1.0 10 0.5

4 7 1.0 10 0.5

5

6

7 17 0.5

8

9 10 1.0 11 1.0 12 2.0

10

11

12 13 1.0 14 1.0

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

I1A_M_endo

Zero-point correction= 0.138517 (Hartree/Particle)

Thermal correction to Energy= 0.154247

Thermal correction to Enthalpy= 0.155191

Thermal correction to Gibbs Free Energy= 0.094347

Sum of electronic and zero-point Energies= -3070.600144

Sum of electronic and thermal Energies= -3070.584414

Sum of electronic and thermal Enthalpies= -3070.583470

Sum of electronic and thermal Free Energies= -3070.644315

%chk=CAIN_TiCl4.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 2.40230243 -0.94563332 0.97596667

C 3.28541075 0.22161324 1.00593100

C 2.77371458 1.31369960 -0.08601274

C 2.80473744 0.76111258 -1.46862348

C 1.57286474 0.22307472 -1.64953398

N 0.74761280 0.48449157 -0.57764892

O 1.39106973 1.53664624 0.15364387

H 3.32051109 2.24113573 0.10900984

H 3.66054022 0.71727603 -2.13292330

H 1.19474499 -0.38438525 -2.46370107

H 1.49309198 -0.97120924 1.57191581

H 3.23615632 0.71248130 1.98274811

H 4.32311442 -0.02989247 0.75484946

N 2.63685406 -1.98216306 0.21736443

H 3.44595096 -2.01564440 -0.39398376

H 1.91884628 -2.69007215 0.08407031

Ti -1.16291025 0.03823426 -0.02312059

Cl -1.63011491 2.23217286 -0.35401693

Cl -3.33783488 -0.58029785 -0.34118273

Cl -0.90138637 -0.15094975 2.18422979

Cl -0.53436597 -2.06995548 -0.92296287

1 2 1.0 11 1.0 14 2.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

I1A_M_exo

Zero-point correction= 0.138385 (Hartree/Particle)

Thermal correction to Energy= 0.154343

Thermal correction to Enthalpy= 0.155287

Thermal correction to Gibbs Free Energy= 0.092845

Sum of electronic and zero-point Energies= -3070.597165

Sum of electronic and thermal Energies= -3070.581207

Sum of electronic and thermal Enthalpies= -3070.580263

Sum of electronic and thermal Free Energies= -3070.642705

%chk=CAIX_TiCl4.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	1.47687997	-1.44685823	1.10866310
C	2.71832527	-1.76154040	0.67428429
C	2.88036239	-1.00291013	-0.60251257
O	1.54028808	-0.77028828	-1.02179750
H	0.99164705	-1.69244988	2.04630963
H	3.48127686	-2.33717889	1.18622821
N	0.79168720	-0.66531913	0.19684323
H	3.41644841	-1.49828667	-1.41914044
C	3.57059149	0.42669415	-0.37681183
H	4.53615561	0.23453279	0.10913898
H	3.73292793	0.89870702	-1.35402753
C	2.73664198	1.27515962	0.48383127
H	2.55673501	1.00450602	1.52289896
N	2.20425809	2.38662742	0.06744181
H	1.54640783	2.90137013	0.64402497
H	2.29185606	2.68429772	-0.89942223
Ti	-1.16247066	-0.04274200	-0.01043023

Cl -1.51861951 -1.90719453 -1.22762714

Cl -1.04569840 0.13635403 2.27827460

Cl -0.54084119 1.72439531 -1.27169060

Cl -3.39894844 0.51201601 0.04416748

1 2 2.0 5 1.0 7 1.0

2 3 1.0 6 1.0

3 4 1.0 8 1.0 9 1.0

4 7 1.0

5

6

7 17 0.5

8

9 10 1.0 11 1.0 12 1.0

10

11

12 13 1.0 14 2.0

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

I1_M_endo

Zero-point correction= 0.140085 (Hartree/Particle)

Thermal correction to Energy= 0.155035

Thermal correction to Enthalpy= 0.155980

Thermal correction to Gibbs Free Energy= 0.096807

Sum of electronic and zero-point Energies= -3070.599313

Sum of electronic and thermal Energies= -3070.584362

Sum of electronic and thermal Enthalpies= -3070.583418

Sum of electronic and thermal Free Energies= -3070.642590

%chk=I1N_N_TiCl4_2.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	2.03212536	-1.11128662	0.48273468
C	3.33995999	-0.35625333	0.81928027
C	2.97722701	1.10097230	0.44330829
C	2.85203359	1.16408712	-1.06686250
C	1.71017592	0.53023988	-1.33653488
N	1.10394793	0.11164053	-0.06282110
O	1.58225764	1.14024414	0.83772118

H 3.52608810 1.89639473 0.95217792

H 3.58177453 1.56033827 -1.76615284

H 1.23167583 0.25539823 -2.26857518

H 1.48947763 -1.41798390 1.37649334

H 3.56210393 -0.43268503 1.88851576

H 4.19104500 -0.74387729 0.24911501

N 2.19921021 -2.20430489 -0.39558819

H 2.69573650 -1.97378232 -1.25082831

H 1.33700439 -2.69255396 -0.61111721

Ti -1.21205052 0.02895029 0.02789219

Cl -1.08821968 2.12380481 -0.68455302

Cl -3.45430158 -0.10397850 0.09039640

Cl -0.88564414 -0.41401719 2.18423558

Cl -0.93648719 -1.57804523 -1.51523873

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

I1_M_exo

Zero-point correction= 0.140576 (Hartree/Particle)

Thermal correction to Energy= 0.155312

Thermal correction to Enthalpy= 0.156257

Thermal correction to Gibbs Free Energy= 0.097721

Sum of electronic and zero-point Energies= -3070.598870

Sum of electronic and thermal Energies= -3070.584134

Sum of electronic and thermal Enthalpies= -3070.583189

Sum of electronic and thermal Free Energies= -3070.641725

%chk=I1X_N_TiCl4.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-2.05815499	-1.09967682	0.55139662
C	-3.41231400	-0.68760453	-0.07941188
C	-3.09194738	0.70548331	-0.66425543
C	-2.83447634	1.64416123	0.50303910
C	-1.64907602	1.26655696	0.97709347
N	-1.14119633	0.16455754	0.13400116
O	-1.74197607	0.48429250	-1.14530576
H	-3.72164748	1.05494542	-1.48573342
H	-3.51755877	2.38382485	0.90833643
H	-1.08184168	1.56360848	1.85113106
H	-2.04975384	-1.07959500	1.64268845
H	-4.22436329	-0.67048167	0.65430828
H	-3.67183062	-1.38653242	-0.88171514
N	-1.59481006	-2.35191396	0.08801730
H	-1.52855375	-2.40105253	-0.92402806
H	-0.70736865	-2.62331818	0.49964564
Ti	1.17946685	0.04854087	-0.02474363
Cl	1.06198529	2.23013888	-0.38685251
Cl	0.88217126	-0.76237407	2.05990265
Cl	3.41797631	-0.10537015	0.03938656
Cl	0.86835613	-1.21213960	-1.82062070

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

I2_M_*α*

Zero-point correction= 0.137768 (Hartree/Particle)

Thermal correction to Energy= 0.153394

Thermal correction to Enthalpy= 0.154338

Thermal correction to Gibbs Free Energy= 0.094571

Sum of electronic and zero-point Energies= -3070.569049

Sum of electronic and thermal Energies= -3070.553423

Sum of electronic and thermal Enthalpies= -3070.552479

Sum of electronic and thermal Free Energies= -3070.612246

%chk=I2-2_TiCl4_NH3.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-2.02590892	-0.89689588	1.02112376
C	-3.39449852	0.64706708	0.07466280
C	-3.27558569	-0.46335874	1.13883548
H	-1.45077101	-1.68546695	1.48599169
H	-4.06260089	-0.82046226	1.79415604
C	-2.04237484	-0.48410081	-1.35071054
H	-1.50577628	-1.12105741	-2.04064122
C	-3.29306955	-0.03579774	-1.30360556
H	-4.09320037	-0.17266031	-2.02330471
H	-4.14362648	1.42841403	0.21756628
O	-2.05600747	1.19455901	0.15781056
N	-1.36206154	-0.07534061	-0.06563302
N	0.80994132	0.38411982	-2.20509835

H -0.07436411 0.81878342 -2.46872606

H 0.92791226 -0.46206377 -2.76153565

H 1.54357877 1.03555089 -2.48301755

Ti 1.02053077 0.02384030 0.02966862

Cl 0.77985394 2.29332667 0.04892852

Cl 0.91744997 -0.25375285 2.25900294

Cl 3.24409441 -0.05292222 -0.30721649

Cl 0.64146625 -2.21400067 -0.54320904

1 3 2.0 4 1.0 12 1.0

2 3 1.0 8 1.0 10 1.0 11 1.0

3 5 1.0

4

5

6 7 1.0 8 2.0 12 1.0

7

8 9 1.0

9

10

11 12 1.0

12 17 0.5

13 14 1.0 15 1.0 16 1.0 17 0.5

14

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

I2_M_β_endo

Zero-point correction= 0.139609 (Hartree/Particle)

Thermal correction to Energy= 0.155428

Thermal correction to Enthalpy= 0.156372

Thermal correction to Gibbs Free Energy= 0.094102

Sum of electronic and zero-point Energies= -3070.639981

Sum of electronic and thermal Energies= -3070.624162

Sum of electronic and thermal Enthalpies= -3070.623218

Sum of electronic and thermal Free Energies= -3070.685488

%chk=I2-1N_O_TiCl4.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C 2.62191535 -1.09990439 0.41743348

C 3.70209378 -0.66903103 -0.57380122

C 4.19284059 0.72962473 -0.34738314

C 3.39317957 1.66127758 0.20845678

C 2.03266523 1.32252496 0.57074302

N 1.64460220 0.08652986 0.61317526

O 0.41811886 -0.26574134 0.95542173

H 5.18943218 0.99677136 -0.70046570

H 3.70382691 2.69652697 0.33575224

H 1.28453294 2.07875320 0.80383971

H 3.03908465 -1.23379887 1.42481063

H 4.52314760 -1.39234342 -0.50576221

H 3.30955436 -0.74082895 -1.60414927

N 1.96749084 -2.28708934 0.00611038

H 1.27322725 -2.59916488 0.67852604

H 1.51308939 -2.17871120 -0.89795525

Ti -1.34960246 0.02738163 0.02769112

Cl -0.12138578 -0.01125942 -1.89797067

Cl -1.54175833 2.04775408 0.98651758

Cl -2.01413786 -1.74299600 1.24160374

Cl -3.28921276 0.15551874 -1.14043700

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7 17 0.5

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

I2_M_β_exo

Zero-point correction= 0.139814 (Hartree/Particle)

Thermal correction to Energy= 0.155602

Thermal correction to Enthalpy= 0.156546

Thermal correction to Gibbs Free Energy= 0.094578

Sum of electronic and zero-point Energies= -3070.640028

Sum of electronic and thermal Energies= -3070.624240

Sum of electronic and thermal Enthalpies= -3070.623296

Sum of electronic and thermal Free Energies= -3070.685263

%chk=I2-1X_O_TiCl4.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-2.67876663	1.12716710	-0.32010476
C	-4.06868556	0.54654494	-0.59887953
C	-4.28086977	-0.80054008	0.02262919
C	-3.23843101	-1.62673847	0.24361349
C	-1.89361385	-1.21221044	-0.09074507
N	-1.64212937	0.01743081	-0.43454294
O	-0.43368680	0.47186514	-0.71787319
H	-5.29949795	-1.12281789	0.23951784
H	-3.36467085	-2.63140711	0.64220668
H	-1.05546677	-1.90327306	-0.06563280
H	-2.37908460	1.83609903	-1.09570700
H	-4.22004085	0.44918466	-1.68713753
H	-4.81018240	1.27204098	-0.24204943
N	-2.59370816	1.75755696	0.96185993
H	-2.81573144	1.12011391	1.72342721
H	-1.67325702	2.15500044	1.13115567
Cl	3.47408938	-0.37995950	0.81645528
Cl	0.42740072	-0.15919613	1.97795497
Ti	1.42368828	0.03178987	-0.06310201

Cl 2.00698457 1.97674943 -1.00479388

Cl 1.40795754 -1.80697567 -1.36284282

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7 19 0.5

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 19 1.0

18 19 1.0

19 20 1.0 21 1.0

20

21

I3_M

Zero-point correction= 0.139406 (Hartree/Particle)

Thermal correction to Energy= 0.155678

Thermal correction to Enthalpy= 0.156622

Thermal correction to Gibbs Free Energy= 0.094200

Sum of electronic and zero-point Energies= -3070.686696

Sum of electronic and thermal Energies= -3070.670423

Sum of electronic and thermal Enthalpies= -3070.669479

Sum of electronic and thermal Free Energies= -3070.731901

%chk=I3_NH3_TiCl4.chk

opt=(calcall,tight,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	2.41641319	-1.26140355	0.07185339
C	3.72391567	-1.19510782	-0.38370483
C	4.44055020	-0.00252597	-0.25869876
C	3.82222972	1.10034920	0.33328655
C	2.51165106	0.99767298	0.77583673
N	1.84511210	-0.17079825	0.63403076
O	0.59683620	-0.27085021	1.09732912
H	5.46759539	0.06469738	-0.61482370
H	4.34236817	2.04837906	0.45474901

H 1.94980651 1.80054902 1.23876271

H 1.78128024 -2.13884160 0.01713102

H 4.16599571 -2.08156320 -0.83414348

Ti -1.12694661 -0.00393722 -0.01461512

Cl -0.33393472 -1.26623228 -1.73505521

Cl -0.13317896 2.01129279 -0.74415478

Cl -1.96660291 -1.72215694 1.29473134

Cl -3.15357672 0.56600061 -0.88371994

N -1.68506579 1.23306265 1.78808493

H -1.02421152 1.05889458 2.54481366

H -2.61392212 0.98946606 2.12917127

H -1.67567389 2.23070845 1.58036686

1 2 2.0 6 1.0 11 1.0

2 3 1.0 12 1.0

3 4 2.0 8 1.0

4 5 1.0 9 1.0

5 6 2.0 10 1.0

6 7 1.0

7 13 0.5

8

9

10

11

12

13 14 1.0 15 1.0 16 1.0 17 1.0 18 0.5

14

15

16

17

18 19 1.0 20 1.0 21 1.0

19

20

21

TS1A_M_endo

Zero-point correction= 0.136165 (Hartree/Particle)

Thermal correction to Energy= 0.152273

Thermal correction to Enthalpy= 0.153217

Thermal correction to Gibbs Free Energy= 0.089738

Sum of electronic and zero-point Energies= -3070.597550

Sum of electronic and thermal Energies= -3070.581442

Sum of electronic and thermal Enthalpies= -3070.580498

Sum of electronic and thermal Free Energies= -3070.643977

%mem=4GB

%Nprocs=4

%chk=TSCA1N_TiCl4.chk

opt=(calcall,tight,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.41364132
C	1.32820809	0.00000000	1.73428166
O	2.08101064	-0.02127551	0.62715644
H	-0.83565367	0.00075089	-0.68994851
H	-0.85126506	0.01477073	2.08279242
N	1.23155236	-0.00000648	-0.47069764
H	1.87079180	0.01272012	2.67380798
C	1.40225003	3.33813872	1.25613310
H	2.42916575	3.30986576	1.61379262
H	0.61260026	3.52324019	1.98688891
C	1.14037052	3.18766165	-0.05567887
H	1.95537998	3.00775088	-0.75779357
N	-0.10168101	3.28135853	-0.66296870
H	-0.21745749	2.78619644	-1.53723491
H	-0.91593221	3.24761141	-0.06224089
Ti	2.17509420	-0.33142551	-2.52356837
Cl	3.78912411	1.00226388	-1.80365282
Cl	2.26382474	-2.45171808	-1.85256115
Cl	2.98141136	-0.67398337	-4.58180212
Cl	0.23848372	0.58350149	-3.21711624

1 2 1.0 5 1.0 7 2.0

2 3 2.0 6 1.0

3 4 1.0 8 1.0 10 0.5

4 7 1.0 10 0.5

5

6

7 17 0.5

8

9 10 1.0 11 1.0 12 2.0

10

11

12 13 1.0 14 1.0

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.35360026
C	1.43705374	0.00000000	1.74791907

O 2.10250403 -0.51174350 0.59777682

H -0.82504326 0.10098707 -0.69551596

H -0.85383712 0.06454603 2.01908823

N 1.28074477 -0.10820509 -0.50539051

H 1.72011425 -0.61302147 2.60978997

C 2.00073667 1.49030232 2.03901065

H 3.04628187 1.37942050 2.34193211

H 1.40573078 1.90808424 2.86090586

C 1.90286565 2.28847216 0.81501689

H 2.69880835 2.27153194 0.07105422

N 0.84235170 2.97629438 0.51114845

H 0.72536796 3.34072717 -0.43453897

H 0.03692758 3.00488466 1.12906562

Ti 2.08731877 0.19204273 -2.29321350

Cl 3.72514401 1.77206162 -2.36451794

Cl 1.25005280 -0.79108189 -4.14047339

Cl 3.56821756 -1.48815612 -1.87703285

Cl 0.40893269 1.91815501 -2.53015352

1 2 2.0 5 1.0 7 1.0

2 3 1.0 6 1.0

3 4 1.0 8 1.0 9 1.0

4 7 1.0

5

6

7 17 0.5

8

9 11 1.0 10 1.0 12 1.0

10

11

12 13 1.0 14 2.0

13

14 15 1.0 16 1.0

15

16

17 19 1.0 21 1.0 20 1.0 18 1.0

18

19

20

21

Title Card Required

0 1

C	-1.56068986	-0.41664602	-1.55361634
C	-2.77633891	-1.01776356	-1.32042825
C	-2.71824683	-1.40057851	0.06161079
O	-1.39714089	-1.36734281	0.43638921
H	-1.21200954	0.10514862	-2.43665484
H	-3.62851656	-1.08074752	-1.98611160
N	-0.74304431	-0.50303347	-0.48266572
H	-3.25492460	-2.24187252	0.49843314

C -3.55013926 -0.00680850 1.13259172

H -3.40607530 -0.42274451 2.12922938

H -4.57512029 -0.06262986 0.75830454

C -2.81715977 1.15702597 0.84869328

H -1.90693894 1.38809445 1.39953871

N -3.08839624 1.95520439 -0.18165922

H -2.44782244 2.68802268 -0.45626632

H -3.90900642 1.81443759 -0.75652388

Ti 1.26299334 0.00503499 0.00074951

Cl 0.60589467 0.49433624 2.09107805

Cl 3.43120503 0.63755397 0.30615553

Cl 1.75319148 -2.15895659 -0.31819991

Cl 0.97954525 1.53198939 -1.66846805

1 2 1.5 5 1.0 7 1.5

2 3 1.5 6 1.0

3 4 1.0 8 1.0 9 0.5 10 0.5

4 7 1.0 10 0.5

5

6

7 17 0.5

8

9 10 1.0 11 1.0 12 1.5

10

11

12 13 1.0 14 1.5

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

$END

TS1A_M_exo

Zero-point correction= 0.136296 (Hartree/Particle)

Thermal correction to Energy= 0.152371

Thermal correction to Enthalpy= 0.153315

Thermal correction to Gibbs Free Energy= 0.090657

Sum of electronic and zero-point Energies= -3070.594139

Sum of electronic and thermal Energies= -3070.578064

Sum of electronic and thermal Enthalpies= -3070.577120

Sum of electronic and thermal Free Energies= -3070.639778

%mem=4GB

%Nprocs=4

%chk=TSCA1X_TiCl4.chk

opt=(calcall,tight,qst3,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.41172325
C	1.31975392	0.00000000	1.73616980
O	2.07684079	-0.00276001	0.62985397
H	-0.83276626	0.00886339	-0.68322591
H	-0.84931611	0.00806009	2.07184349
N	1.22834756	-0.00803815	-0.46717500
H	1.86014311	0.00446907	2.66894333
C	0.35409351	3.40690756	0.07023131
H	1.25111496	2.85138149	0.30429845
H	-0.25454744	3.76206708	0.89563480
C	0.03579263	3.65602568	-1.20747613
H	0.67455875	3.28133826	-2.00149417
N	-1.02005847	4.42781997	-1.66929801
H	-1.37274730	4.18234523	-2.58264492
H	-1.76169439	4.60745663	-1.00604945
Ti	2.27047699	-0.01327902	-2.47964372
Cl	3.19357088	1.86816994	-1.76241962
Cl	3.16342605	-1.92205518	-1.74959399
Cl	3.25911651	-0.02644722	-4.50608769

Cl 0.17797785 0.16649766 -3.24751194

1 2 1.0 5 1.0 7 2.0

2 3 2.0 6 1.0

3 4 1.0 8 1.0 10 0.5

4 7 1.0 10 0.5

5

6

7 17 0.5

8

9 10 1.0 11 1.0 12 2.0

10

11

12 13 1.0 14 1.0

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.34241083
C	1.42952972	0.00000000	1.76826169
O	2.13834566	-0.34640085	0.57525590
H	-0.83394854	0.06997895	-0.67793530
H	-0.85017274	0.06513217	2.00120256
N	1.27243975	-0.08363540	-0.53374716
H	1.69397333	-0.72850566	2.53650706
C	1.94942137	1.40540769	2.29794795
H	1.30854101	1.68236805	3.13955475
H	2.97793402	1.29488720	2.64279224
C	1.84110604	2.42543733	1.24988819
H	0.86451775	2.72120851	0.88074720
N	2.86055245	2.96468761	0.68225222
H	2.75788794	3.60793058	-0.09504000
H	3.81000839	2.71572665	0.94183523
Ti	2.15656119	-0.24606450	-2.32019258
Cl	2.83168787	-2.34432776	-1.78833603
Cl	0.10225628	0.38242858	-3.15459370
Cl	3.81781924	1.18714710	-1.73049201
Cl	2.97027972	-0.43956851	-4.54390678

1 2 2.0 5 1.0 7 1.0

2 3 1.0 6 1.0

3 4 1.0 8 1.0 9 1.0

4 7 1.0

5

6

7 17 0.5

8

9 10 1.0 11 1.0 12 1.0

10

11

12 13 1.0 14 2.0

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

Title Card Required

0 1

C	1.36184068	-1.64145690	0.88793038
C	2.57015346	-1.99196093	0.34455669
C	2.76419053	-1.06226095	-0.73630996
O	1.55405065	-0.46030317	-0.97240208

H 0.86999144 -2.02945817 1.77229713

H 3.28751407 -2.71115597 0.72088414

N 0.74357370 -0.66724818 0.17851990

H 3.29501512 -1.29505413 -1.65929275

C 3.98238758 0.35033506 -0.17394078

H 4.74702924 -0.24733024 0.32031756

H 4.28422119 0.76093612 -1.14084906

C 3.22689866 1.20126861 0.65105863

H 3.06195491 0.95286792 1.69975007

N 2.58193858 2.27332142 0.21275855

H 1.86977417 2.71973281 0.77538574

H 2.61916690 2.54262881 -0.76299492

Ti -1.25944409 0.00886510 -0.00070970

Cl -1.46245088 -1.49484945 -1.65963180

Cl -1.35207622 -0.50509022 2.20985369

Cl -0.50733598 2.02564530 -0.65276832

Cl -3.47053184 0.58700991 -0.04506456

1 2 1.5 5 1.0 7 1.5

2 3 1.5 6 1.0

3 4 1.0 8 1.0 9 0.5 10 0.5

4 7 1.0 10 0.5

5

6

7 17 0.5

8

9 10 1.0 11 1.0 12 1.5

10

11

12 13 1.0 14 1.5

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

$END

TS1B_M_endo

Zero-point correction= 0.138167 (Hartree/Particle)

Thermal correction to Energy= 0.153197

Thermal correction to Enthalpy= 0.154141

Thermal correction to Gibbs Free Energy= 0.093916

Sum of electronic and zero-point Energies= -3070.597091

Sum of electronic and thermal Energies= -3070.582061

Sum of electronic and thermal Enthalpies= -3070.581117

Sum of electronic and thermal Free Energies= -3070.641342

%mem=4GB

%Nprocs=4

%chk=TSCA2N_TiCl4.chk

opt=(calcall,tight,qst3,noeigentest,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.46398179
C	1.53477539	0.00000000	2.00369583
C	2.27322098	-1.21242491	1.55352784
C	2.84326523	-0.84867460	0.37774769
N	2.63585520	0.48690498	0.11030542
O	2.21294573	1.06519233	1.35231457
H	1.49621962	0.20911482	3.07698166
H	2.26486376	-2.19059067	2.02122026
H	3.37272877	-1.45112674	-0.35134077
H	0.05668454	0.93241582	-0.55665139
H	-0.46348186	0.91491679	1.84563731
H	-0.49409839	-0.88450006	1.88428216
N	-0.02970606	-1.10151641	-0.70047476

H -0.04617341 -2.01132975 -0.25161632

H 0.15254435 -1.07539438 -1.70074482

Ti 3.08716230 1.79544412 -1.38662238

Cl 4.52582626 2.76389495 0.07402412

Cl 4.23552720 2.57856030 -3.19825968

Cl 1.27657371 3.09760990 -1.33452384

Cl 2.48194591 -0.08609230 -2.70676701

1 2 1.0 11 1.0 14 2.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.54837528
C	1.52062342	0.00000000	1.85553659
C	2.06368987	-1.35658163	1.45228294
C	2.04356718	-1.34408843	0.12009376
N	1.56259466	-0.02057838	-0.31772685
O	2.00746149	0.82715312	0.76959244
H	1.83212173	0.42513617	2.81215755
H	2.30845296	-2.18334905	2.11153410
H	2.24538662	-2.10597407	-0.62153171
H	-0.30229373	0.97027824	-0.39974861
H	-0.47283286	0.90878619	1.93482587
H	-0.50721622	-0.87778232	1.96533002
N	-0.65841123	-1.11453039	-0.59797428
H	-1.34074878	-1.55614443	0.00417907
H	-1.05810768	-0.92052877	-1.50787405
Ti	2.41829419	0.82285527	-2.32124507
Cl	4.37937968	0.37204019	-1.38672868
Cl	3.23228077	1.63086058	-4.25462986

Cl 1.29332550 2.66206314 -1.75684391

Cl 1.30665674 -0.89204811 -3.21285923

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

Title Card Required

0 1

C	2.19128531	-1.18346434	0.58831223
C	3.32450429	-0.23826008	0.87015847
C	2.89883627	1.18570546	0.34696348
C	2.81225967	1.14345831	-1.15538150
C	1.62780196	0.55735496	-1.39660112
N	0.95928793	0.30236063	-0.16904587
O	1.52215047	1.27233309	0.72819191
H	3.46080390	2.00007411	0.81101461
H	3.58517288	1.42369059	-1.86314848
H	1.18103606	0.21845888	-2.32423216
H	1.47165366	-1.37679084	1.37834906
H	3.48011598	-0.17293387	1.95254795
H	4.25387582	-0.56809993	0.39142197
N	2.37917919	-2.18744912	-0.28348041
H	3.05629994	-2.07250253	-1.02802190
H	1.60315887	-2.80409216	-0.49087761
Ti	-1.18431698	0.02748401	0.02308521
Cl	-1.34680714	2.13049800	-0.70549586
Cl	-3.42388320	-0.35733400	0.06108517
Cl	-0.84487354	-0.26772152	2.20979675
Cl	-0.77924449	-1.68334033	-1.41912070

1 2 1.0 6 0.5 11 1.0 14 1.5

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

$END

TS2_M_α_endo

Zero-point correction= 0.136494 (Hartree/Particle)

Thermal correction to Energy= 0.151615

Thermal correction to Enthalpy= 0.152559

Thermal correction to Gibbs Free Energy= 0.093175

Sum of electronic and zero-point Energies= -3070.500495

Sum of electronic and thermal Energies= -3070.485374

Sum of electronic and thermal Enthalpies= -3070.484430

Sum of electronic and thermal Free Energies= -3070.543814

%chk=PathA_1N_TS.chk

opt=(calcall,tight,ts,verytight,noeigentest,maxcycle=500) freq

b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane) geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	-2.02538849	0.79253838	0.84043547
C	-3.23364755	0.08558855	1.04490892
C	-2.99961034	-1.18215474	0.26347671
C	-2.92372437	-0.84542777	-1.22369263
C	-1.77445650	-0.19102055	-1.38511799
N	-1.11513308	-0.13393534	-0.04347466
O	-1.52456714	-1.40998599	0.49335305
H	-3.55268991	-2.07738378	0.55410740
H	-3.69840381	-1.02919348	-1.96217018
H	-1.30585867	0.30364451	-2.22654124
H	-1.45862779	1.24429939	1.65226495
H	-3.61345843	0.00413021	2.06125879

H -2.91461636 2.00553505 -0.88163930

N -2.21289720 2.22868957 -0.17494454

H -1.36621584 2.60722422 -0.61060758

H -2.60965793 2.92271468 0.45669724

Ti 1.18998134 -0.05150255 0.03164518

Cl 1.09851267 -1.83843848 -1.26743103

Cl 3.43155927 0.11350867 0.11466150

Cl 0.88858988 -0.21487461 2.22806616

Cl 0.90920005 1.92871915 -1.03985644

1 2 1.5 6 1.0 11 1.0 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0 17 0.3

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

TS2_M_ α_exo

Zero-point correction= 0.136305 (Hartree/Particle)

Thermal correction to Energy= 0.151471

Thermal correction to Enthalpy= 0.152415

Thermal correction to Gibbs Free Energy= 0.092685

Sum of electronic and zero-point Energies= -3070.501130

Sum of electronic and thermal Energies= -3070.485964

Sum of electronic and thermal Enthalpies= -3070.485020

Sum of electronic and thermal Free Energies= -3070.544749

%chk=PathA_1X_TS.chk

opt=(calcall,tight,ts,verytight,noeigentest,maxcycle=500) freq

b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane) geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C -2.16477139 -0.96631168 0.63386387

C -3.43763593 -0.66271067 0.10027893

C -3.16086876 0.63371589 -0.66661200

C -2.84322306 1.71116403 0.38224144

C -1.65883590 1.36410358 0.88683732

N -1.20564893 0.14421432 0.15279271

O -1.80631943 0.38015529 -1.15243289

H -3.80038151 0.91571064 -1.50754363

H -3.49701358 2.51402283 0.71110038

H -1.06967015 1.71788480 1.72288306

H -1.97600790 -1.24477626 1.67051251

H -4.30564863 -0.72119879 0.75533404

H -1.48935590 -2.20878618 -1.14460802

N -1.46450400 -2.40109782 -0.14246000

H -2.14560279 -3.13179338 0.05756645

H -0.52771827 -2.71074851 0.13344644

Ti 1.17528140 0.07667113 -0.00569187

Cl 0.90589735 -1.15457532 -1.83737635

Cl 1.07018264 2.24375671 -0.39360009

Cl 3.40668080 -0.10736957 0.10851402

Cl 0.83423004 -0.77827680 2.05505106

1 2 1.5 6 1.0 11 1.0 14 0.5

2 3 1.0 12 1.0 13 0.5

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0 17 0.5

7

8

9

10

11

12

13 14 0.5

14 15 1.0 16 1.0 17 0.3

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

TS3_M_α_endo

Zero-point correction= 0.133665 (Hartree/Particle)

Thermal correction to Energy= 0.150077

Thermal correction to Enthalpy= 0.151021

Thermal correction to Gibbs Free Energy= 0.088695

Sum of electronic and zero-point Energies= -3070.531927

Sum of electronic and thermal Energies= -3070.515515

Sum of electronic and thermal Enthalpies= -3070.514571

Sum of electronic and thermal Free Energies= -3070.576897

%chk=PathA_2_TS.chk

opt=(calcall,tight,ts,verytight,noeigentest,maxcycle=500) freq

b3lyp/aug-cc-pvdz scrf=(smd,solvent=1,4-dioxane) geom=connectivity

empiricaldispersion=gd3

Title Card Required

0 1

C	-2.36852656	-1.26367176	0.69756181
C	-2.73402031	-0.16676650	1.39305042
C	-2.71911842	1.01220239	0.54818072
C	-3.42083322	0.88618429	-0.72666298
C	-3.05882638	-0.23614400	-1.37157332
N	-2.03173823	-1.00618513	-0.69100954
O	-1.03639558	0.08575310	-0.50539660
H	-2.41161858	1.98359010	0.93619965
H	-4.04386546	1.68054204	-1.13084838
H	-3.30817397	-0.52102733	-2.39024823
H	-2.08298698	-2.22827889	1.10732386
H	-2.80822813	-0.11570983	2.47565515
Ti	0.95347565	0.01465249	-0.00904371
Cl	0.57118458	-0.21737631	2.22610277
Cl	0.57569773	2.33415708	-0.08836526
Cl	0.87984802	-2.23368965	-0.53393770

Cl 3.23517899 0.17915335 0.06186079

N 1.24239344 0.26615707 -2.24000060

H 0.34157712 0.24155014 -2.71557452

H 1.82322052 -0.47575743 -2.62761591

H 1.68568023 1.15792529 -2.45525658

1 2 2.0 6 1.0 11 1.0

2 3 1.0 12 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0 13 0.3

7 13 0.3

8

9

10

11

12

13 14 1.0 15 1.0 16 1.0 17 1.0 18 0.5

14

15

16

17

18 19 1.0 20 1.0 21 1.0

19

20

21

TS3_M_β_endo

Zero-point correction= 0.136324 (Hartree/Particle)

Thermal correction to Energy= 0.151727

Thermal correction to Enthalpy= 0.152672

Thermal correction to Gibbs Free Energy= 0.090921

Sum of electronic and zero-point Energies= -3070.553699

Sum of electronic and thermal Energies= -3070.538296

Sum of electronic and thermal Enthalpies= -3070.537352

Sum of electronic and thermal Free Energies= -3070.599102

%chk=PathB_1N_TS.chk

opt=(calcall,tight,ts,noeigentest,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	2.54499835	0.90978691	-0.55626679
C	2.99366118	-0.41481963	-1.29552682
C	2.61558063	-1.56839012	-0.47165981
C	2.81218923	-1.46576847	0.94093781
C	2.24862706	-0.35081324	1.48279854
N	1.62323191	0.53137654	0.53987309

O 0.69038202 -0.32432547 -0.09986487

H 2.32972419 -2.51984745 -0.92178517

H 3.11086122 -2.31403842 1.55540452

H 2.04615345 -0.21477287 2.54262714

H 1.91495010 1.47040215 -1.25380588

H 2.60588881 -0.48684628 -2.31527526

H 4.09540666 -0.39031778 -1.34222469

N 3.65696526 1.71932630 -0.13983251

H 3.34286660 2.60075624 0.25875331

H 4.25256602 1.25143489 0.53908618

Ti -1.27429379 0.00685217 -0.02078907

Cl -3.54825802 0.16564218 -0.08895001

Cl -1.16664005 -0.08965243 2.22966140

Cl -0.93138634 2.05454878 -0.89242638

Cl -1.26187609 -1.85805659 -1.31937226

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0 17 0.3

7 17 0.3

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

TS3_M_ β_exo

Zero-point correction= 0.137014 (Hartree/Particle)

Thermal correction to Energy= 0.152008

Thermal correction to Enthalpy= 0.152953

Thermal correction to Gibbs Free Energy= 0.093783

Sum of electronic and zero-point Energies= -3070.550126

Sum of electronic and thermal Energies= -3070.535132

Sum of electronic and thermal Enthalpies= -3070.534187

Sum of electronic and thermal Free Energies= -3070.593357

%chk=PathB_1X_TS.chk

opt=(calcall,tight,ts,noeigentest,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-2.41541502	-0.92162261	0.57227359
C	-3.17612466	-0.51862512	-0.71829355
C	-2.77688716	0.85828656	-1.12516812
C	-2.57697350	1.81902434	-0.07956260
C	-1.74977420	1.36059638	0.89142962
N	-1.19949778	0.04645299	0.57210843
O	-0.82691062	0.10348486	-0.81427705
H	-2.92000102	1.17484314	-2.16072602
H	-2.91322950	2.85088579	-0.15615678
H	-1.46798375	1.82888557	1.82825535
H	-2.96551659	-0.66593867	1.48419765
H	-4.26358055	-0.49847904	-0.53341902
H	-2.99578889	-1.23555376	-1.52529757
N	-2.10280744	-2.30242941	0.57236067
H	-1.52232655	-2.56218935	-0.22213378
H	-1.60606449	-2.57592072	1.41616075
Ti	0.98378004	-0.01651334	-0.06935692
Cl	1.87445395	-0.35612910	1.98796881
Cl	0.82528633	2.33559749	0.37511507
Cl	0.99379797	-2.29992051	-0.51919528
Cl	2.47786169	0.40426149	-1.68778091

1 2 1.0 6 1.0 11 1.0 14 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0 17 0.3

7 17 0.3

8

9

10

11

12

13

14 15 1.0 16 1.0

15

16

17 18 1.0 19 1.0 20 1.0 21 1.0

18

19

20

21

Calcs with pyrrolidine in place of NH_2

I1_M_endo (with pyrrolidine)

Zero-point correction= 0.231786 (Hartree/Particle)

Thermal correction to Energy= 0.250714

Thermal correction to Enthalpy= 0.251658

Thermal correction to Gibbs Free Energy= 0.180932

Sum of electronic and zero-point Energies= -3226.551358

Sum of electronic and thermal Energies= -3226.532429

Sum of electronic and thermal Enthalpies= -3226.531485

Sum of electronic and thermal Free Energies= -3226.602211

%chk=I1_M_endo.chk

opt=(calcall,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	-1.93456022	0.23221586	-0.55042571
C	-1.65492295	1.69040358	-1.02910806
C	-0.43072309	2.05141835	-0.15500803
C	-0.90689560	2.18969569	1.27459818
C	-1.23191040	0.94977791	1.64534356
N	-0.91758679	0.01036258	0.57010286

O	0.19949765	0.71836730	-0.07822399
H	0.28001973	2.77596762	-0.55006529
H	-1.02248301	3.11783185	1.82455768
H	-1.68258542	0.56572079	2.55341307
H	-1.63635238	-0.48828006	-1.33193023
H	-1.39874442	1.71003556	-2.09297074
H	-2.49152025	2.36850949	-0.83936016
Ti	2.18463428	-0.24419775	-0.05867590
Cl	2.02817466	-0.19998824	2.15486247
Cl	4.22998935	-1.13601806	-0.16447546
Cl	2.72636362	1.63736128	-1.15246635
Cl	1.13748827	-1.89463930	-1.12102294
C	-4.32203408	0.17911328	-1.05265825
C	-3.46651338	-1.39381994	0.43217592
C	-5.56297467	-0.44333206	-0.38919012
H	-4.07655313	-0.35751859	-1.99239037
H	-4.44717484	1.24128847	-1.29250998
C	-4.98996209	-1.48581543	0.61198902
H	-2.90293739	-1.56890486	1.35565493
H	-3.11318508	-2.12688591	-0.32091128
H	-6.13925139	0.32626486	0.13889800
H	-6.22412846	-0.89809989	-1.13676491
H	-5.26910231	-1.22754350	1.64088754

H -5.35263195 -2.50197140 0.41556881

N -3.26135558 -0.01652149 -0.05138511

1 2 1.0 6 1.0 11 1.0 31 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.0 7 1.0 8 1.0

4 5 2.0 9 1.0

5 6 1.0 10 1.0

6 7 1.0

7 14 0.5

8

9

10

11

12

13

14 15 1.0 16 1.0 17 1.0 18 1.0

15

16

17

18

19 21 1.0 22 1.0 23 1.0 31 1.0

20 24 1.0 25 1.0 26 1.0 31 1.0

21 24 1.0 27 1.0 28 1.0

22

23

24 29 1.0 30 1.0

25

26

27

28

29

30

31

TS3_M_ β_endo (with pyrrolidine)

Zero-point correction= 0.228554 (Hartree/Particle)

Thermal correction to Energy= 0.247681

Thermal correction to Enthalpy= 0.248625

Thermal correction to Gibbs Free Energy= 0.177734

Sum of electronic and zero-point Energies= -3226.517823

Sum of electronic and thermal Energies= -3226.498695

Sum of electronic and thermal Enthalpies= -3226.497751

Sum of electronic and thermal Free Energies= -3226.568643

%chk= TS3_M_beta_endo.chk

opt=(calcall,ts,noeigentest,maxcycle=500) freq b3lyp/aug-cc-pvdz

scrf=(smd,solvent=1,4-dioxane) geom=connectivity empiricaldispersion=gd3

Title Card Required

0 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.58494837
C	1.38948506	0.00000000	2.05453270
C	2.30790100	-0.86339612	1.38110784
C	2.29792145	-0.70920337	0.03122402
N	1.36608591	0.26692192	-0.46082480
O	1.71889576	1.43527033	0.26184788
H	1.68024680	0.51889340	2.96860406
H	3.11364927	-1.38272096	1.89744110
H	3.06112485	-1.08608216	-0.64446686
H	-0.57430093	0.89043461	-0.31536748
H	-0.58794885	0.81744909	2.00987597
H	-0.43180507	-0.96025311	1.90792759
C	-0.44334838	-1.23744698	-2.06110831
C	-1.90037580	-1.51525709	-0.26971483
C	-1.28370957	-2.46709504	-2.43618115
H	0.59026412	-1.28587783	-2.41779535

H	-0.89475916	-0.31150678	-2.46681393
C	-2.26954436	-2.64319354	-1.24856940
H	-2.52856932	-0.62030792	-0.45544401
H	-2.02941893	-1.80566634	0.77988326
H	-1.79849589	-2.31725094	-3.39262913
H	-0.64176895	-3.35055081	-2.54005262
H	-3.31905046	-2.56644642	-1.55701874
H	-2.13494672	-3.62189586	-0.77197913
N	-0.48877602	-1.22842351	-0.58253676
Ti	2.42849226	3.03515331	-0.68573137
Cl	4.09051235	1.76237474	-1.53053762
Cl	0.55655930	3.09778903	-1.93285935
Cl	2.45111215	3.82293572	1.44633279
Cl	3.26464799	4.98968770	-1.52166394

1 2 1.0 6 1.0 11 1.0 26 1.0

2 3 1.0 12 1.0 13 1.0

3 4 1.5 7 0.5 8 1.0

4 5 1.5 9 1.0

5 6 1.5 10 1.0

6 7 1.0 27 0.3

7 27 0.3

8

9

10

11

12

13

14 16 1.0 17 1.0 18 1.0 26 1.0

15 19 1.0 20 1.0 21 1.0 26 1.0

16 19 1.0 22 1.0 23 1.0

17

18

19 24 1.0 25 1.0

20

21

22

23

24

25

26

27 28 1.0 29 1.0 30 1.0 31 1.0

28

29

30

31