1,3-Dipolar Cycloaddition with Diazo Groups: Noncovalent Interactions Overwhelm Strain

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Materials

Silica gel (40 μm) was from SiliCycle (Québec, Canada). All chemicals and solvents were from Sigma–Aldrich (St. Louis, MO) and were used without further purification.

General Experimental

Temperature. All procedures were performed in air at ambient temperature (~22 °C) and pressure (1.0 atm) unless specified otherwise.

Solvent removal. The phrase "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator at water aspirator pressure (<20 torr) while maintaining the water-bath temperature below 40 °C. Residual solvent was removed from samples at high vacuum (<0.1 torr). The term "high vacuum" refers to vacuum achieved by mechanical belt-drive oil pump.

Instrumentation. ^{1}H and ^{13}C NMR spectra for all compounds were acquired on Bruker Spectrometers in the NMRFAM at the University of Wisconsin–Madison operating at operating at 400, 500, or 750 MHz for ^{1}H and 126 or 189 MHz for ^{13}C. Chemical shift data are reported in units of δ (ppm) relative to residual solvent or TMS. Electrospray ionization (ESI) mass spectrometry was performed with a Waters LCT instrument at the Mass Spectrometry Facility in the Department of Chemistry at the University of Wisconsin–Madison.

Kinetic Experiments

All kinetics experiments monitored with NMR spectroscopy were conducted in triplicate, and the rate constants are reported as an average of the three values. ^{1}H NMR experiments were carried out, monitoring diazo compound consumptions under pseudo-first-order conditions (5:1 diazo/alkyne).

The disappearance of the diazo group signal (monitored with NMR or UV spectroscopy) is advantageous for determination of rate constants during ligations. For OND cycloadditions, the extrusion of furan in the retro-Diels–Alder step might be slower for reactions of diazo compounds relative to analogous azide reactions, as the pyrazoline product must undergo a proton transfer step to generate the aromatic tautomer. Monitoring diazo compound consumption avoids possible complications arising from a slower second step, allowing for direct comparison of cycloaddition rates of alkynes and ONDs. Still, based on calculated energies of activation, the 1,3-dipolar cycloaddition is the rate-determining step (Figure S2), and consumption of the diazo compound does report on the overall rate of the reactions.

General procedure for OND and alkyne kinetic experiments. Stock solutions of diazoacetamide (0.3 M) and OND or alkyne (0.06 M) were prepared in CD_3OD. Equal volumes of each solution were added to generate a solution of 0.15 M dipole and 0.03 M dipolarophile. The NMR tube was inverted once and inserted into a spectrometer. An 8-scan NMR spectrum was acquired every 45 s, and the integrations were used to calculate concentrations from the known initial concentrations. A pseudo-first-order rate constant (k') was determined from the slope of the plot

of ln[diazo compound] versus time. A second-order rate constant (k) was calculated from the value of k' and the initial concentration of dipolarophile with the equation: $k = k'/$[dipolarophile].

Procedure for ethyl 4,4,4-trifluorobutynoate kinetic experiments. Diazoacetamide was dissolved in methanol to a concentration of 40 mM. In a clear 96-well plate, 50 µL of the diazoacetamide stock solution was combined with 50 µL of a stock solution of a ethyl 4,4,4-trifluorobutynoate (1 equiv) to produce a final concentration of 20 mM for the diazo compound. Absorbance was measured using an Infinite M1000 plate reader from Tecan (Männedorf, Switzerland), monitoring at 388 nm, which is a wavelength of maximal absorbance by diazoacetamide. Multiple readings were taken from each well (circle (filled) 3×3) every 60 s at ambient temperature, followed by an orbital mixing of 10 s. All assays were performed in triplicate with similar results, and an average of these values was used for rate determinations. The formation of final products was confirmed by mass spectrometry and NMR spectroscopy from identical assays. A second-order rate constant (k) was calculated as described above.

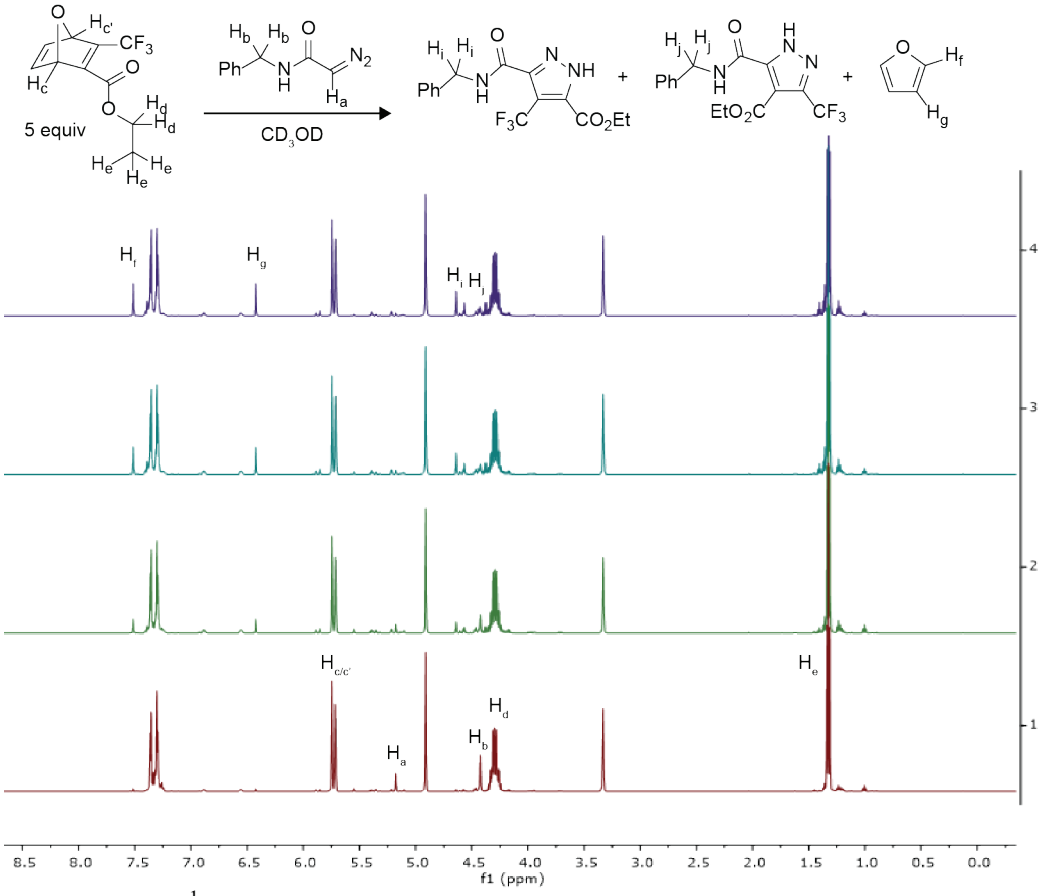
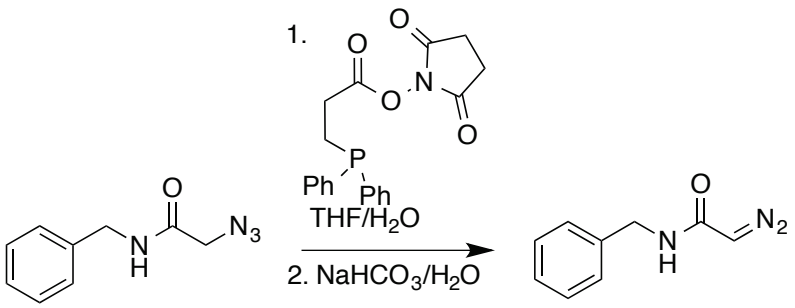
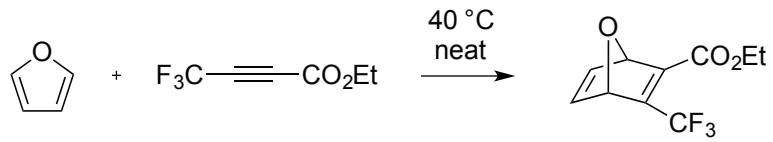


Figure S1. Sample ^{1}H NMR spectra taken at various time points during the cycloaddition of diazoacetamide **1** (R = Bn) with OND **4a**.

Synthetic Procedures

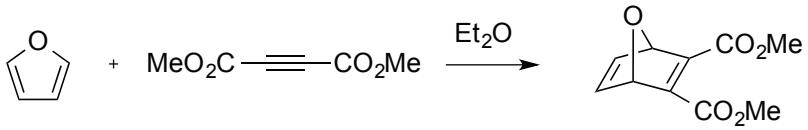


***N*-Benzyl-2-diazoacetamide (1, R = Bn)**. Diazoacetamide **1** (R = Bn) was synthesized as described previously.[1] Spectroscopic data were indistinguishable from those in the previous report.



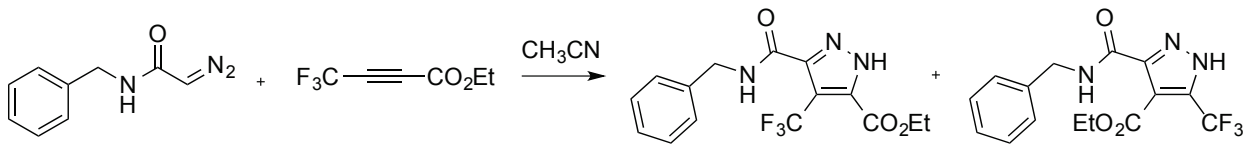
3a **4a**

Ethyl (1R,4S)-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (4a). OND **4a** was synthesized as described previously.[2] Spectroscopic data were indistinguishable from those in the previous report.



3b **4b**

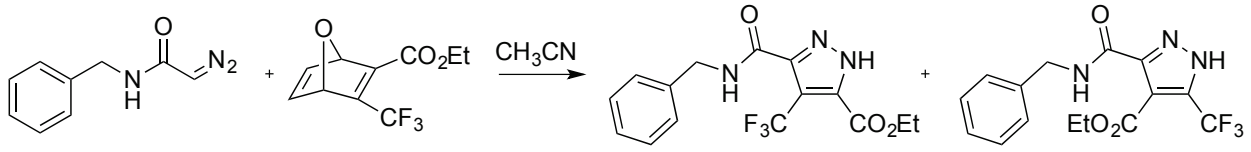
Dimethyl (1*R*,4*S*)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (4b). OND **4b** was synthesized as described previously.[2] Spectroscopic data were indistinguishable from those in the previous report.



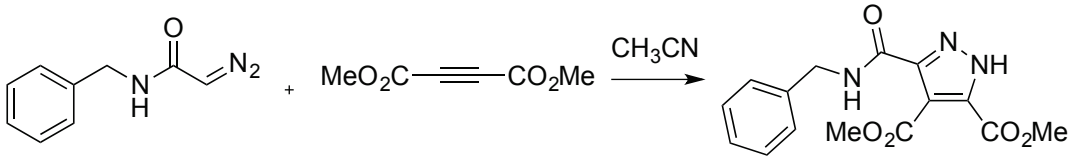
1 (R=Bn) **3a** **5a** **5a'**

Ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (5a) and **ethyl 5-(benzylcarbamoyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (5a′).** Pyrazoles **5a** and

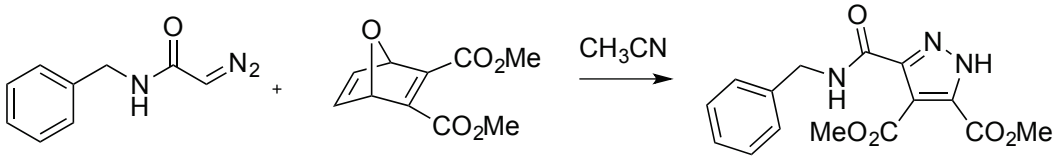
5a′ were synthesized as described previously.[3] Spectroscopic data were indistinguishable from those in the previous report.



Ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (**5a**) and **ethyl 5-(benzylcarbamoyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate** (**5a′**)**.** *N*-Benzyl-2-diazoacetamide (2.7 mg, 0.015 mmol) was dissolved in CH_3CN (0.25 mL). Ethyl (1*R*,4*S*)-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (12.9 mg, 0.055 mmol) was added, and the resulting solution was stirred overnight. The reaction mixture was concentrated to dryness, to provide a mixture of pyrazole **5a′** as the major product and pyrazole **5a** as the minor product. The regioisomeric ratio, as determined by integration of ^{1}H NMR spectra, was 0.75:1. Spectra were indistinguishable from those in the previous report.[3] ^{1}H NMR. **5a**: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.37–7.29 (m, 5H), 6.96 (s, 1H), 4.64 (d, J = 5.8 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H). **5a′**: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 10.49 (s, 1H), 7.39–7.29 (m, 5H), 4.69 (d, J = 5.7 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H).



Dimethyl 5-(benzylcarbamoyl)-1*H*-pyrazole-3,4-dicarboxylate (**5b**). *N*-Benzyl-2-diazoacetamide (8.5 mg, 0.05 mmol) was dissolved in CH_3CN (0.25 mL). Dimethyl acetylenedicarboxylate (33.8 mg, 0.24 mmol) was added, and the resulting solution was stirred overnight. The reaction mixture was concentrated under reduced pressure to dryness, and the product was purified by column chromatography on silica gel (50% v/v EtOAc in hexanes) and concentrated under high vacuum to provide pyrazole **5b** as a colorless oil (14.7 mg, quant.). **^{1}H NMR** (500 MHz, acetonitrile-d_3, δ): 7.40–7.22 (m, 5H), 4.55 (d, J = 6.0 Hz, 2H), 3.88 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (126 MHz, acetonitrile-d_3, δ): 167.06, 141.30, 131.24, 130.17, 129.92, 55.21, 55.09, 45.39. HRMS (ESI) calcd. for $C_{14}H_{15}N_3O_3$ $[M+H]^+$ 318.1085, found 318.1077.



1 (R=Bn) **4b** **5b**

Dimethyl 5-(benzylcarbamoyl)-1*H*-pyrazole-3,4-dicarboxylate (**5b**). *N*-Benzyl-2-diazoacetamide (13.1 mg, 0.075 mmol) was dissolved in CH_3CN (0.25 mL). Diethyl (1*R*,4*S*)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (89.3 mg, 0.38 mmol) was added, and the resulting solution was stirred overnight. The reaction mixture was concentrated under high vacuum, and pyrazole **5b** was purified and identified as described above.

Computational Methods

Optimizations were performed using Gaussian 09 software[4] at M06-2X level of theory[5] using the 6-31+G(2d,p) basis set. M06-2X has been shown to describe trends in reactivity accurately for other cycloadditions.[6] Solvation corrections were performed on gas-phase geometries using an IEFPCM dielectric continuum solvent model for methanol with UFF radii. This model does not explicitly include non-electrostatic contributions and should be considered as the first approximation of solvation effects.[7] Frequency calculations were performed to confirm each stationary point as minima or first-order saddle points. All ΔE values include zero-point corrections. Remote substituents (Bn in **1** and Et in **3a** and **4a**) were modeled as methyl groups.

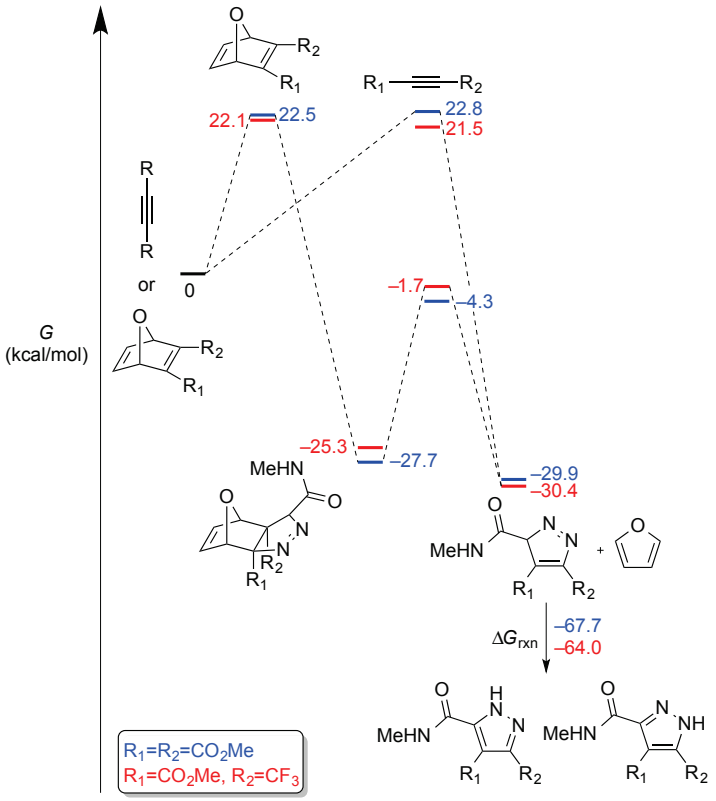
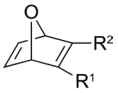


Figure S2. Calculated activation and reaction free energies for the cycloaddition of diazoacetamide **1** (R = Me) with alkynes or ONDs. Values were calculated at 298 K with the M06-2X/6-31+G(2d,p) level of theory. Energies (kcal/mol) include solvation corrections (MeOH) on gas-phase geometries with the IEFPCM model (radii = UFF).

Table S1. Calculated Activation Parameters for the Cycloaddition of Diazoacetamide 1 (R = Me) with Alkynes and ONDs[a]

dipolarophile		R_1	R_2	gas phase $\Delta E^{\ddagger}$	gas phase $\Delta H^{\ddagger}$	gas phase $\Delta G^{\ddagger}$	gas phase $\Delta S^{\ddagger}$	MeOH $\Delta E^{\ddagger}$	MeOH $\Delta H^{\ddagger}$	MeOH $\Delta G^{\ddagger}$	MeOH $\Delta S^{\ddagger}$
R^1—≡—R^2	**3a**	CO_2Et	CF_3	8.6	8.2	22.6	–48.5	9.6	9.7	21.5	–39.6
	3b	CO_2Me	CO_2Me	7.3	6.8	20.6	–46.1	9.8	9.4	22.8	–44.8
	**4a**	CO_2Et	CF_3	6.1	5.6	20.3	–49.5	8.2	7.7	22.1	–48.3
	4b	CO_2Me	CO_2Me	4.8	4.3	19.1	–49.7	7.8	7.2	22.5	–51.4

[a]Calculations were performed at the M06-2X/6-31+G(2d,p) level of theory. Energies are in kcal/mol or cal/mol·K. Solvation corrections were performed on gas-phase geometries with the IEFPCM model (radii = UFF).

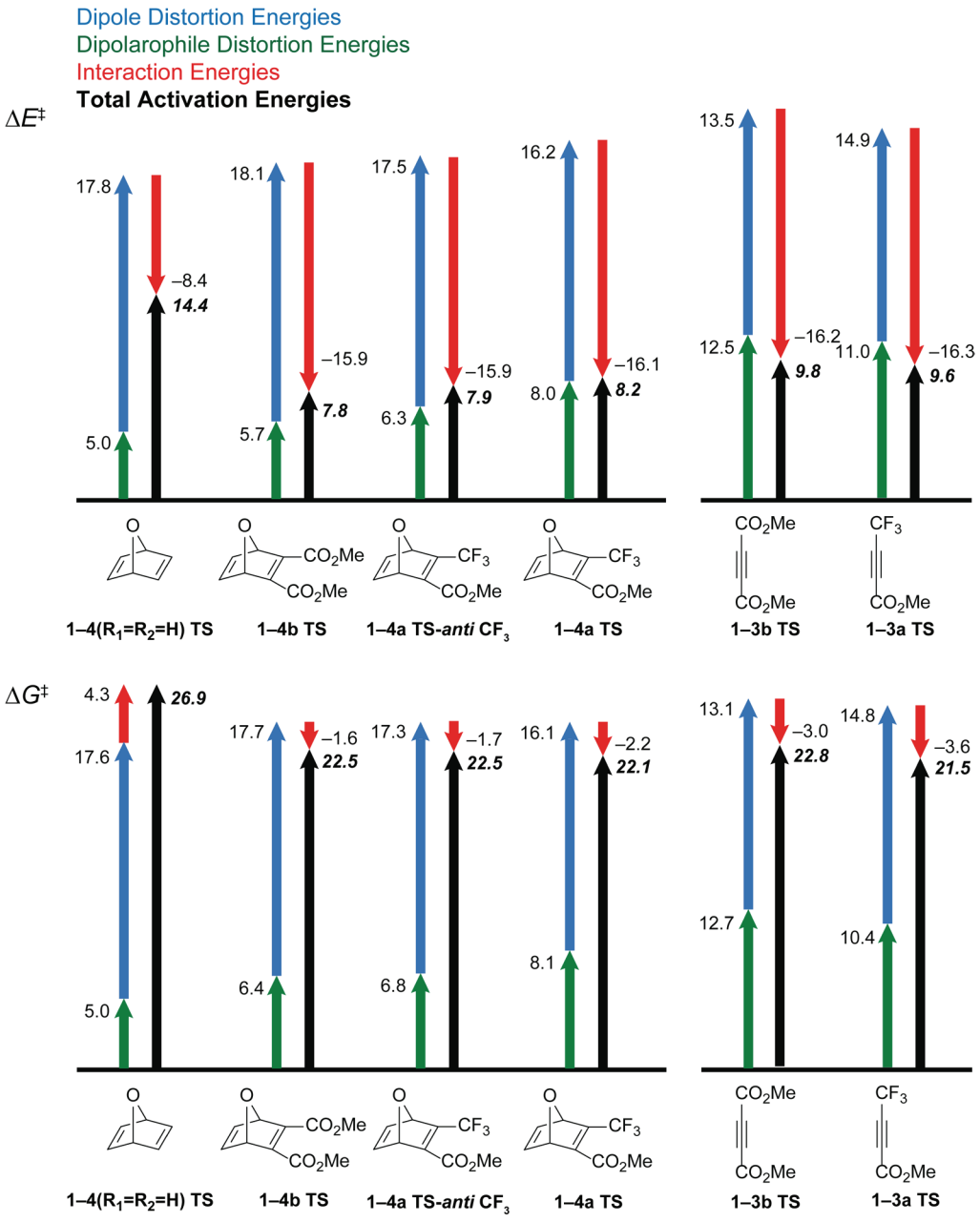
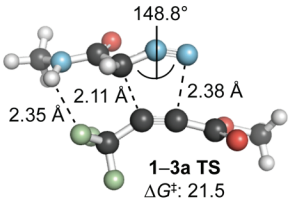


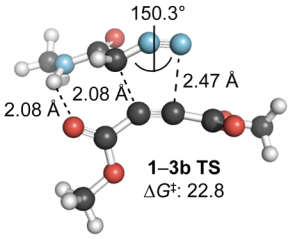
Figure S3. Distortion/interaction analysis for the cycloaddition of diazoacetamide **1** (R = Me) with OND and alkyne calculated at the M06-2X/6-31+G(2d,p) level of theory. Energies (kcal/mol) include solvation corrections (MeOH) on gas-phase geometries using IEFPCM model (radii = UFF).



Starting Alkyne	
$\pi_{C=C} \rightarrow \sigma^*_{C-F}$	2.41, 0.67
$\pi_{C=C} \rightarrow \sigma^*_{C-F}$	2.50, 0.66, 1.36
Total	7.60

Transition State	
$\pi_{C=C} \rightarrow \sigma^*_{C-F}$	7.57, 3.71, 0.66
$\pi_{C=C} \rightarrow \sigma^*_{C-F}$	3.39, 5.35
$\pi^*_{C=C} \rightarrow \sigma^*_{C-F}$	2.26, 8.00
$n_F \rightarrow \sigma^*_{N-H}$	1.22, 0.65
Total	32.81

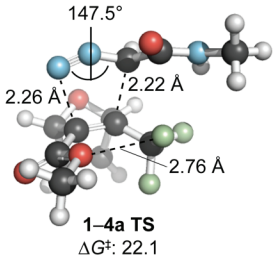
Transition State Stabilization: 25.21



Starting Alkyne	
$\pi_{C=C} \rightarrow \sigma^*_{C-O}$	2.53, 2.27
$\pi_{C=C} \rightarrow \sigma^*_{C=O}$	2.21, 1.90
$\pi_{C=C} \rightarrow \pi^*_{C=O}$	7.76, 8.74
Total	25.41

Transition State	
$\pi_{C=C} \rightarrow \sigma^*_{C-O}$	3.32
$\pi_{C=C} \rightarrow \sigma^*_{C=O}$	3.15
$\pi_{C=C} \rightarrow \pi^*_{C=O}$	19.60, 0.72
$\pi^*_{C=C} \rightarrow \sigma^*_{C-O}$	4.05
$\pi^*_{C=C} \rightarrow \sigma^*_{C=O}$	1.12
$n_O \rightarrow \sigma^*_{N-H}$	3.67, 1.51
Total	37.14

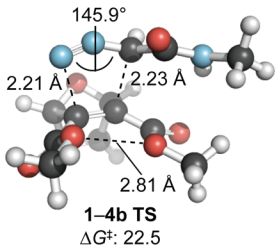
Transition State Stabilization: 11.73



Starting Alkyne	
$\pi_{C=C} \rightarrow \sigma^*_{C-F}$	4.68, 6.00
Total	10.68

Transition State	
$\pi_{C=C} \rightarrow \sigma^*_{C-F}$	6.47, 2.04, 1.32
$\pi^*_{C=C} \rightarrow \sigma^*_{C-F}$	5.86, 2.13
$n_F \rightarrow \sigma^*_{N-H}$	0.76, 0.62, 0.17
Total	19.37

Transition State Stabilization: 8.69



Starting Alkyne	
$\pi_{C=C} \rightarrow \pi^*_{C=O}$	20.06
Total	20.06

Transition State	
$\pi_{C=C} \rightarrow \pi^*_{C=O}$	22.51
$n_O \rightarrow \sigma^*_{N-H}$	0.38
Total	22.89

Transition State Stabilization 2.83

Figure S4. Natural bond orbital analysis for the cycloaddition of diazoacetamide **1** (R = Me) with alkynes and ONDs calculated at the M06-2X/6-31+G(2d,p) level of theory. Energies (kcal/mol) include solvation corrections (MeOH) on gas-phase geometries with the IEFPCM model (radii = UFF).

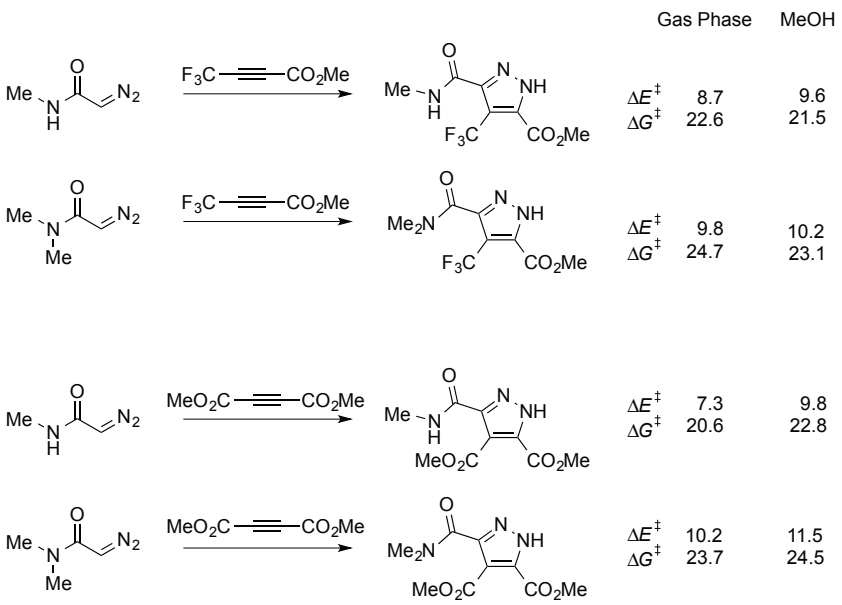


Figure S5. Calculated energies and free energies of activation (kcal/mol) for the cycloaddition of diazoacetamide **1** (R = Me) and its *N,N*-dimethyl analogue with alkynes **3a** and **3b** at the M06-2X/6-31+G(2d,p) level of theory. Solvation corrections (MeOH) were performed on gas-phase geometries with the IEFPCM model (radii = UFF).

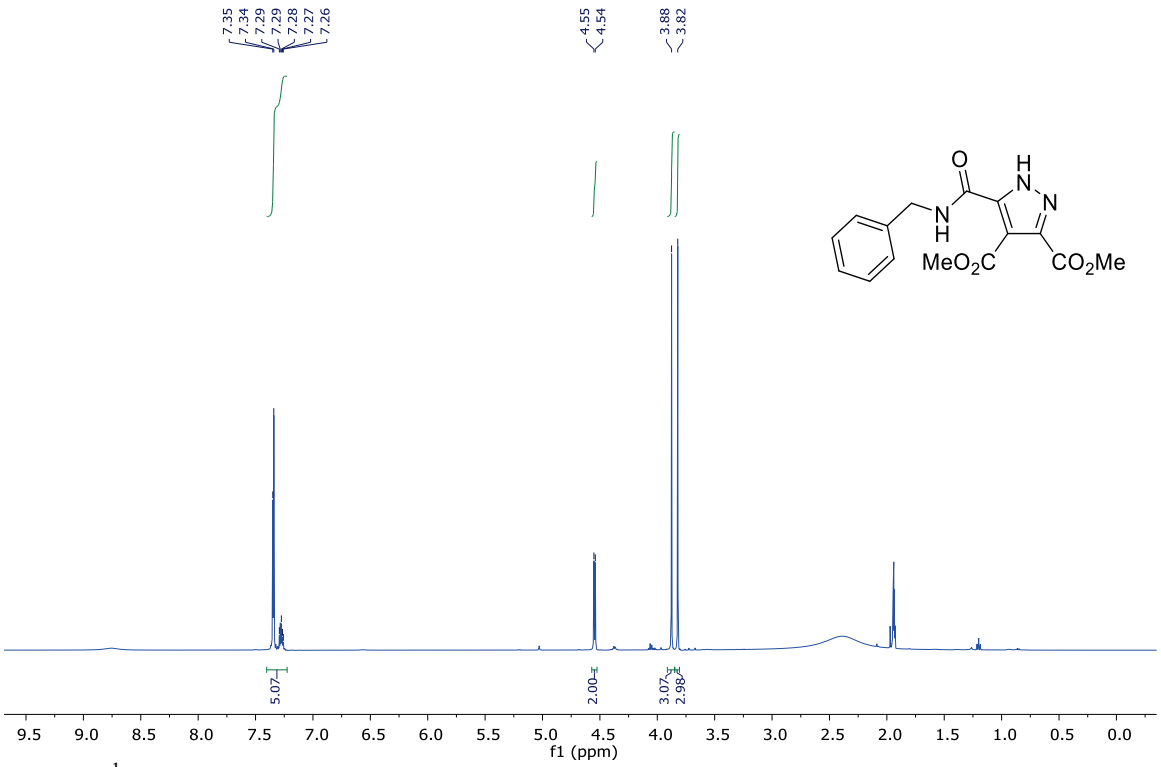


Figure S6. ^{1}H NMR spectrum of dimethyl 5-(benzylcarbamoyl)-1H-pyrazole-3,4-dicarboxylate (**3a**) in CD_3CN (500 MHz).

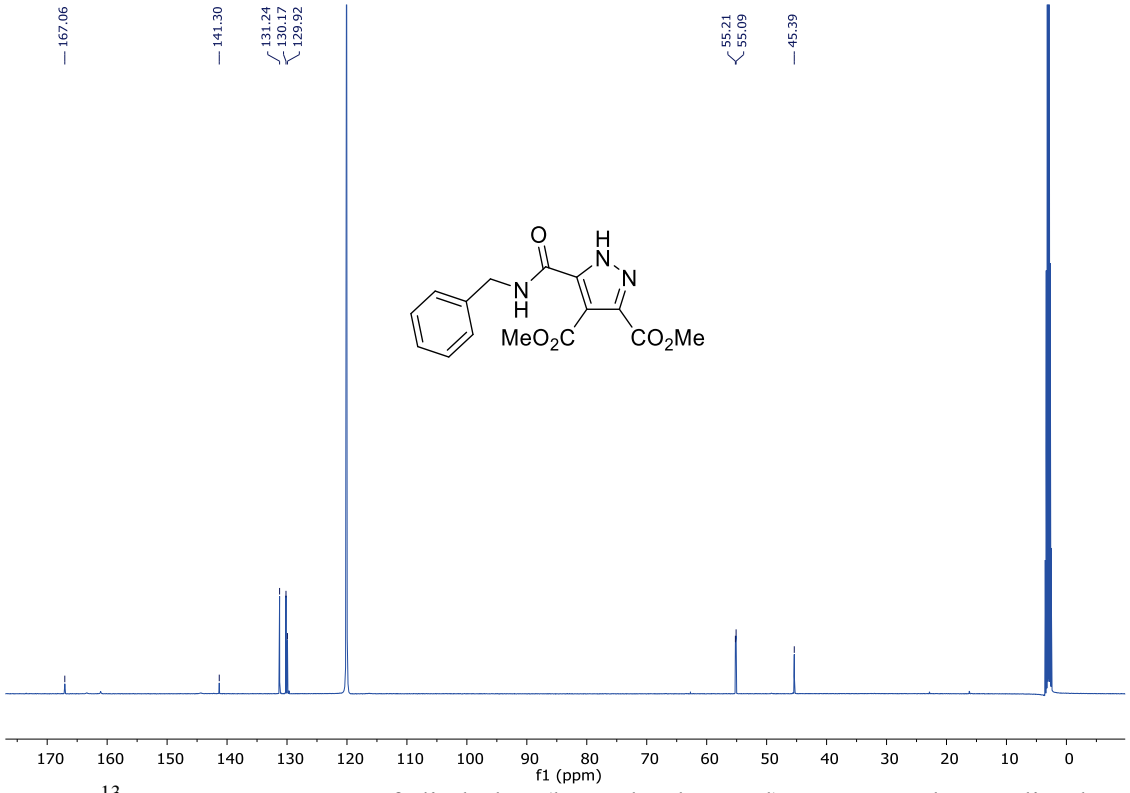


Figure S7. ^{13}C NMR spectrum of diethyl 5-(benzylcarbamoyl)-1H-pyrazole-3,4-dicarboxylate (**3a**) in CD_3CN (126 MHz).

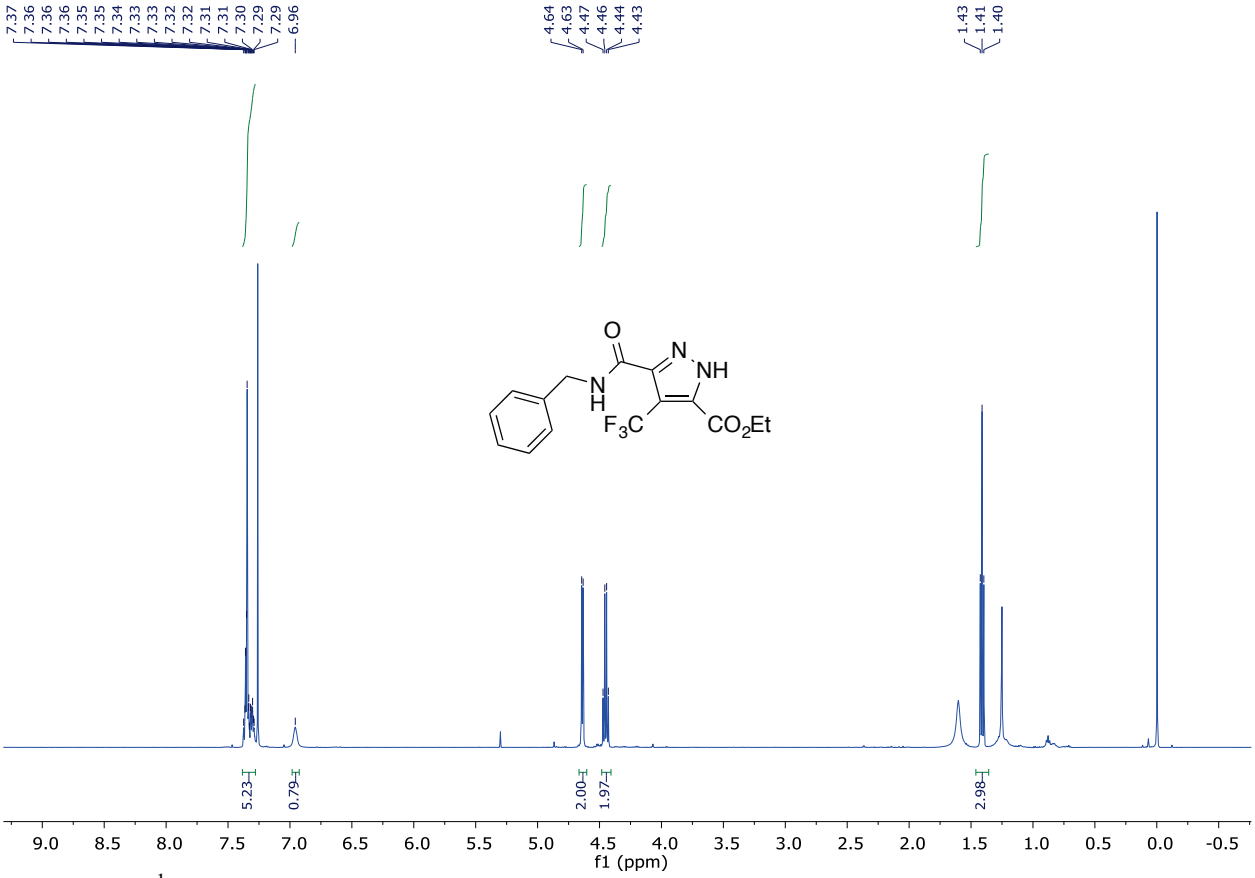


Figure S8. ^{1}H NMR spectrum of ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1H-pyrazole-5-carboxylate (**5a**) in CD_3Cl_3 (500 MHz).

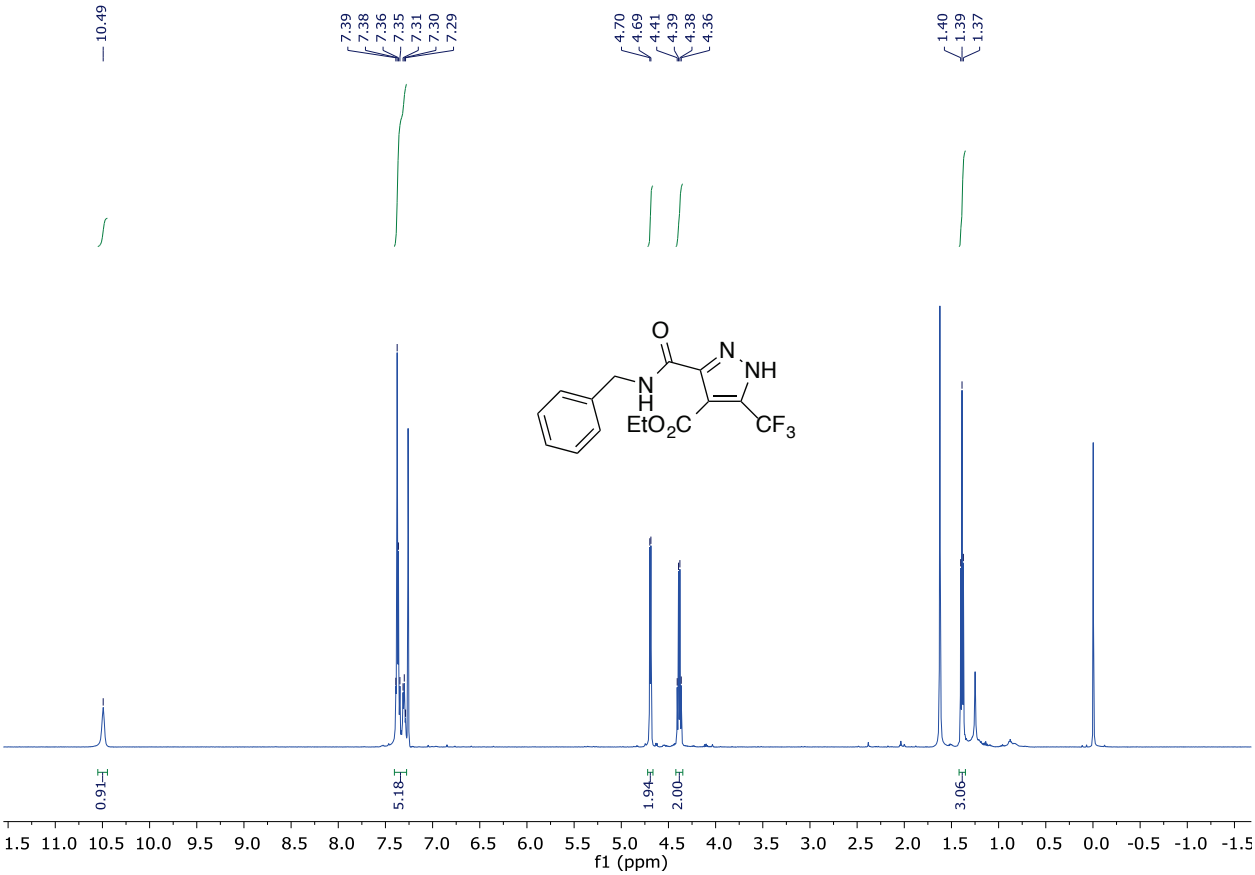
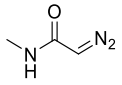


Figure S9. ^{1}H NMR spectrum of ethyl 5-(benzylcarbamoyl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate (**5a′**) in CD_3Cl_3 (500 MHz).

Cartesian coordinates, total energies, and imaginary frequencies (for TSs)

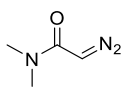
All energies include IEFPCM single point corrections. TS frequencies are from gas phase optimized structures.



(**1**, GS)

C	0.30852100	0.03905300	-0.02920200
N	-2.02771400	-0.22212300	0.01247700
N	-2.99960900	0.33676500	0.04001300
O	0.22780700	1.25507100	-0.03578400
N	1.50346700	-0.61999200	-0.05770900
H	1.51615300	-1.60579700	0.14568500
C	2.73859300	0.13170600	0.05051200
H	2.86639000	0.56630800	1.04724000
H	3.57565100	-0.53248600	-0.16735100
H	2.72785900	0.94470800	-0.67669500
C	-0.87166200	-0.83196100	-0.01577300
H	-0.89422800	-1.90863500	-0.05928700

HF: -356.6533518
Sum of electronic and zero-point Energies: -356.564190
Sum of electronic and thermal Energies: -356.556466
Sum of electronic and thermal Enthalpies: -356.555522
Sum of electronic and thermal Free Energies: -356.596282



(**1′**, GS)

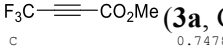
C	-0.03072100	-0.32329300	0.03512000
N	2.22317000	0.30315400	-0.01530900
N	3.26729000	-0.10269300	-0.02234200
O	0.29530300	-1.50174200	0.02846700
N	-1.33254300	0.09319500	0.08320400
C	-2.38529900	-0.89470700	-0.05843200
H	-3.14021900	-0.74963200	0.72027700
H	-2.87020400	-0.81139600	-1.03890400
H	-1.94604400	-1.88527900	0.04085200
C	0.98648700	0.73650800	-0.00226900
H	0.86382200	1.80277200	-0.07240800
C	-1.71523600	1.48750900	-0.00159100
H	-1.13517700	2.09856400	0.69400400
H	-1.60739900	1.89301800	-1.01621300
H	-2.76401000	1.57420400	0.28881700

HF: -395.9396332
Sum of electronic and zero-point Energies: -395.822047
Sum of electronic and thermal Energies: -395.813019
Sum of electronic and thermal Enthalpies: -395.812075
Sum of electronic and thermal Free Energies: -395.856254

MeN_3 (**2**, GS)

C	1.51977100	0.29700200	0.00000000
N	-0.71122300	-0.11313200	-0.00000400
N	-1.76425600	0.28699900	0.00000100
N	0.39482300	-0.65083800	0.00000100
H	2.42800900	-0.30193400	0.00056600
H	1.50928500	0.92898100	-0.89387800
H	1.50866600	0.92973700	0.89333200

HF: -204.0205204
Sum of electronic and zero-point Energies: -203.969418
Sum of electronic and thermal Energies: -203.965081
Sum of electronic and thermal Enthalpies: -203.964136
Sum of electronic and thermal Free Energies: -203.995767

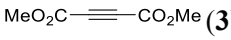


(**3a**, GS)

C	0.74787000	0.06985700	-0.00078600
C	-0.44533400	0.18237300	0.00047100
C	2.21160900	-0.06760900	-0.00061900
C	-1.89391600	0.38676100	0.00008000
O	-2.40531600	1.46988700	-0.00086600
O	-2.53855600	-0.77507700	0.00053900

C	-3.96791700	-0.66521700	-0.00089800
H	-4.29928900	-0.13062900	-0.89271700
H	-4.33674000	-1.68817600	-0.00020900
H	-4.30094800	-0.12871100	0.88912200
F	2.58365400	-1.25062900	-0.49133100
F	2.69710900	0.03279900	1.23744500
F	2.78302500	0.87916800	-0.74423200

HF: -642.0664486
Sum of electronic and zero-point Energies: -641.988580
Sum of electronic and thermal Energies: -641.979647
Sum of electronic and thermal Enthalpies: -641.978703
Sum of electronic and thermal Free Energies: -642.024050


(**3b**, GS)

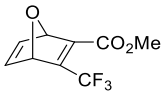
C	-0.59713900	0.19653200	0.06727900
C	0.59712800	0.19650700	-0.06721500
C	-2.03891700	0.24357900	0.28032400
O	-2.56598100	0.95078700	1.09241500
O	-2.67233900	-0.59376900	-0.53810600
C	-4.09694100	-0.60732300	-0.39197900
H	-4.50405900	0.38261600	-0.60552800
H	-4.45582500	-1.33845700	-1.11276500
H	-4.36597200	-0.89704400	0.62523900
C	2.03890300	0.24357600	-0.28034500
O	2.56593400	0.95079700	-1.09242700
O	2.67236100	-0.59378500	0.53807400
C	4.09697000	-0.60728900	0.39199300
H	4.50397000	0.38305300	0.60380200
H	4.45598800	-1.33716100	1.11398900
H	4.36606500	-0.89873600	-0.62472700

HF: -532.9212331
Sum of electronic and zero-point Energies: -532.804674
Sum of electronic and thermal Energies: -532.793973
Sum of electronic and thermal Enthalpies: -532.793029
Sum of electronic and thermal Free Energies: -532.842790


(**4**($R^1 = R^2 = H$), GS)

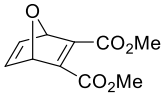
C	-1.24335900	-0.66463300	-0.49886300
C	0.00065000	-1.05690600	0.33337500
C	-0.00063500	1.05684300	0.33353400
C	-1.24448400	0.66337300	-0.49827400
H	-1.90417900	-1.35450400	-1.00308000
H	-1.90635300	1.35260600	-1.00198900
C	1.24450400	-0.66328800	-0.49833000
C	1.24330800	0.66472600	-0.49882300
H	0.00111000	-2.03360800	0.81115200
H	-0.00111500	2.03347500	0.81145500
O	0.00001600	-0.00011200	1.29399000
H	1.90408400	1.35464400	-1.00303600
H	1.90641300	-1.35241000	-1.00214000

HF: -307.2717524
Sum of electronic and zero-point Energies: -307.167050
Sum of electronic and thermal Energies: -307.162358
Sum of electronic and thermal Enthalpies: -307.161413
Sum of electronic and thermal Free Energies: -307.195084


(**4a**, GS)

C	1.90249800	-1.81969500	0.90953200
C	1.12055200	-1.81415000	-0.42207200
C	2.12293300	0.04702500	-0.37949500
C	2.53184800	-0.65083800	0.93896100
H	1.86263800	-2.60739400	1.64687900
H	3.15237500	-0.21300800	1.70643000
C	-0.00766200	-0.76936100	-0.26593800
C	0.62087400	0.40189400	-0.23400800
H	0.83724300	-2.76803200	-0.85745900
H	2.77493600	0.82013600	-0.77590500
O	2.01575900	-1.07375600	-1.24873600
C	-1.41240400	-1.15085000	-0.03796400
O	-1.73980200	-2.27613600	0.24437000
O	-2.25310000	-0.12800100	-0.17518500
C	-3.62864900	-0.43124400	0.06905400
H	-3.75577800	-0.80408500	1.08709100
H	-4.16261500	0.50629900	-0.06985200
H	-3.97744800	-1.18613100	-0.63816900
C	0.10836700	1.77876100	0.03985400
F	-0.62496600	1.84292100	1.15645200
F	-0.63531500	2.25810100	-0.95930600
F	1.14201900	2.62410000	0.20616900

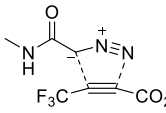
HF: -872.0536747
Sum of electronic and zero-point Energies: -871.900075
Sum of electronic and thermal Energies: -871.887320
Sum of electronic and thermal Enthalpies: -871.886375
Sum of electronic and thermal Free Energies: -871.940721


(**4b**, GS)

C	2.49419300	-0.96686800	0.98687200
C	1.77166500	-1.33117800	-0.32763300
C	2.10160900	0.74994100	-0.45911900
C	2.70887900	0.34113800	0.90054200
H	2.69645000	-1.65770500	1.79139300
H	3.14145000	1.02340900	1.61696400
C	0.35513000	-0.70461600	-0.23615100
C	0.56871100	0.61030900	-0.30593000
H	1.82381500	-2.36024300	-0.67288300
H	2.45615300	1.66137400	-0.93138700
O	2.37616700	-0.41643200	-1.23173200
C	-0.80721000	-1.55287000	0.09719600
O	-0.70821600	-2.46641700	0.87879200
O	-1.91621500	-1.24839000	-0.56823000
C	-3.04720600	-2.06606100	-0.25982600
H	-3.30759400	-1.96459700	0.79572000
H	-3.85292300	-1.70200400	-0.89398100
H	-2.82633500	-3.11317000	-0.47554400
C	-0.28033400	1.79505700	-0.08830900
O	-1.55210200	1.50405400	0.18893500
O	0.15870000	2.91804100	-0.13401500
C	-2.39401300	2.63626200	0.40971500
H	-2.40211000	3.27835900	-0.47296900
H	-3.38566300	2.23047800	0.60090600
H	-2.03846900	3.21056000	1.26762900

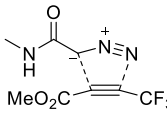
HF: -762.9035545
Sum of electronic and zero-point Energies: -762.711362
Sum of electronic and thermal Energies: -762.697579
Sum of electronic and thermal Enthalpies: -762.696635
Sum of electronic and thermal Free Energies: -762.754040

1,3-Dipolar cycloaddition transition states


(**1–3a**, TS)

C	1.39665200	0.20027500	-0.23740900
C	0.22946100	0.59384000	-0.30656600
C	-2.06396000	-1.26195400	-0.00264400
N	-0.06265200	-1.76959000	-1.18951100
N	1.02926600	-2.01006300	-1.04938000
O	-1.81504100	-2.10245200	0.83505800
C	2.83327200	0.07151900	-0.12909700
O	3.59923900	0.33441800	-1.01910100
O	3.19163400	-0.39213700	1.07213400
C	4.60035800	-0.56342700	1.24703700
H	5.11248600	0.39454500	1.13953300
H	4.72241700	-0.95608400	2.25433800
H	4.98942700	-1.26531100	0.50728600
N	-3.22231000	-0.56229200	-0.06355400
H	-3.25826500	0.24999000	-0.66075900
C	-4.15859600	-0.64356500	1.04380400
H	-3.75932100	-0.15652700	1.93927800
H	-5.09246400	-0.16424600	0.75044000
H	-4.34711900	-1.69247800	1.27373500
C	-1.06818200	-0.89089100	-1.06759000
H	-1.41250000	-0.50429600	-2.02236800
C	-0.69177200	1.71627900	-0.04964100
F	-1.39609500	1.53083200	1.07516400
F	-1.59932700	1.86318400	-1.04378100
F	-0.05289400	2.87675500	0.06234400

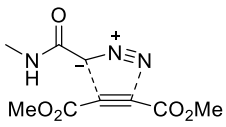
HF: -998.7063449
Sum of electronic and zero-point Energies: -998.537454
Sum of electronic and thermal Energies: -998.519662
Sum of electronic and thermal Enthalpies: -998.518718
Sum of electronic and thermal Free Energies: -998.586019
Frequencies: -391.3068


(**1–3a**, TS-*anti* CF_3)

C	1.51467600	0.14613400	-0.04558800
C	0.34117800	0.51465200	-0.11013700
C	-1.75473100	-1.53405100	-0.01936500
N	0.34013700	-1.85870900	-1.12530900
N	1.44987500	-1.90950200	-0.88829600
O	-1.50412900	-2.37237000	0.81914500
C	2.94735100	0.23865800	0.26610500
N	-2.90722200	-0.81872200	-0.06310900
H	-2.97852600	-0.06112200	-0.72450900
C	-3.85215200	-0.89560900	1.03693900
H	-3.46891000	-0.38289600	1.92465700
H	-4.79286100	-0.43997300	0.72641100
H	-4.02491600	-1.94325000	1.28547700
C	-0.77315000	-1.13462700	-1.07497400
H	-1.09347500	-0.73081400	-2.02980300
C	-0.75315600	1.44346000	0.16556800
O	-1.38891900	1.81230400	-0.96360000
O	-1.06895000	1.81816100	1.25879200
C	-2.43051200	2.77402200	-0.76529900
H	-2.84940300	2.96237000	-1.75203500
H	-3.18907900	2.37834800	-0.08454700
H	-2.02056500	3.69093700	-0.33849100
F	3.27158200	1.42504500	0.79485200
F	3.69302800	0.08271000	-0.83471500
F	3.31285300	-0.70171700	1.13937800

HF: -998.7031099

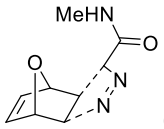
Sum of electronic and zero-point Energies: -998.534143
Sum of electronic and thermal Energies: -998.516355
Sum of electronic and thermal Enthalpies: -998.515411
Sum of electronic and thermal Free Energies: -998.583293
Frequencies: -398.4322



(**1–3b**, TS)

C	1.33164400	0.14431800	-0.24251400
C	0.15119200	0.49921800	-0.36690300
C	-2.00039200	-1.48947200	0.05255800
N	-0.06590900	-1.87516700	-1.24509500
N	1.02027800	-2.13781800	-1.12506100
O	-1.70232700	-2.42797300	0.76460200
C	2.75898600	0.02022700	-0.10390900
O	3.54547500	0.25370200	-0.98691500
O	3.09905500	-0.39949600	1.12194600
C	4.50351500	-0.56602000	1.32335100
H	5.02004900	0.38691500	1.19256500
H	4.61026000	-0.92544100	2.34500800
H	4.90415600	-1.29218300	0.61368500
N	-3.13735600	-0.77159300	0.17308500
H	-3.18483800	0.11423200	-0.31126600
C	-4.03304500	-1.03614800	1.28293200
H	-3.57504900	-0.77234500	2.24153100
H	-4.94524100	-0.45635000	1.14189000
H	-4.28094400	-2.09848300	1.30498500
C	-1.08786700	-1.02492200	-1.05630000
H	-1.50540800	-0.62462700	-1.97412000
C	-0.76495900	1.64654600	-0.33813100
O	-0.20709100	2.69673600	0.25233800
O	-1.88137700	1.66065000	-0.80616700
C	-1.02009300	3.87287300	0.30006500
H	-0.41461200	4.62267300	0.80458700
H	-1.27454500	4.19489900	-0.71127500
H	-1.93668900	3.67408900	0.85859700

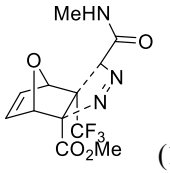
HF: -889.56044
Sum of electronic and zero-point Energies: -889.353176
Sum of electronic and thermal Energies: -889.334510
Sum of electronic and thermal Enthalpies: -889.333566
Sum of electronic and thermal Free Energies: -889.402783
Frequencies: -373.0388



(**1–4**($R^1 = R^2 = H$), TS)

C	-3.42035900	-0.68079600	0.56408600
C	-2.60417000	0.54585300	0.11280700
C	-1.47466300	-1.13071300	-0.53281300
C	-2.70995600	-1.73124100	0.16370200
H	-4.33002400	-0.65262400	1.14675600
H	-2.88872500	-2.78369500	0.33087300
C	-1.33284600	0.59287000	0.98561300
C	-0.58621700	-0.47703200	0.55301000
H	-3.13786500	1.47955500	-0.05126700
H	-0.98384700	-1.74350800	-1.28771100
O	-2.04599500	0.04550500	-1.10981000
H	0.13483300	-1.02638600	1.14408500
H	-1.27946600	1.07017500	1.95275700
N	-0.34492000	2.31252900	-0.04966100
N	0.43816100	1.70282300	-0.60923000
C	0.95678800	0.48384000	-0.78714000
H	0.79583500	0.07497200	-1.77918900
C	2.21123300	0.23434900	-0.03210500
O	2.54559800	0.90811100	0.92320600
N	2.88629400	-0.88213600	-0.42471900
H	2.66538500	-1.29664200	-1.31509100
C	4.11155400	-1.26679000	0.24785600
H	4.34457700	-2.30298500	0.00003200
H	4.95116100	-0.62542900	-0.03841400
H	3.96638800	-1.17691500	1.32518000

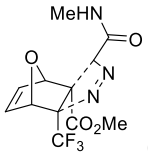
HF: -663.9045655
Sum of electronic and zero-point Energies: -663.708351
Sum of electronic and thermal Energies: -663.695749
Sum of electronic and thermal Enthalpies: -663.694805
Sum of electronic and thermal Free Energies: -663.748513
Frequencies: -496.1267



(**1–4a**, TS)

C	3.00925000	-1.63157000	-0.23373700
C	2.33801200	-0.97213100	0.97696800
C	0.81195300	-2.13119000	0.07540300
C	2.04930300	-2.35263200	-0.80735700
H	4.02189100	-1.44517900	-0.55955800
H	2.06644900	-2.91960500	-1.72643800
C	1.36500200	0.08158300	0.40897700
C	0.33423200	-0.65881600	-0.14112200
H	2.96369400	-0.65507100	1.80679700
H	0.03985900	-2.89816300	0.06404000
O	1.40194300	-1.98640800	1.35998800
N	0.44661700	0.66131600	2.39553800
N	-0.53054300	0.11928500	2.21674100
C	-1.29437200	-0.58820300	1.37006600
H	-1.36477000	-1.63652200	1.64841900
C	-2.53154600	0.15147200	0.94274300
O	-2.71338500	1.31668800	1.22317400
N	-3.39912000	-0.59745200	0.21534000
H	-3.05568100	-1.45980200	-0.17928900
C	-4.49308200	0.07032400	-0.46832000
H	-5.13511200	-0.68319400	-0.92437200
H	-5.07089100	0.64503700	0.25625500
H	-4.12135300	0.75546900	-1.23714200
C	1.87532100	1.40794500	0.05771000
O	3.03860200	1.71325700	0.17509200
O	0.92507200	2.23392500	-0.39053000
C	1.37384000	3.54032400	-0.75122500
H	2.11450900	3.47724200	-1.55094500
H	0.48579200	4.07240700	-1.08663600
H	1.81938400	4.03711400	0.11286300
C	-0.41658400	-0.35818000	-1.39840200
F	-1.18069700	0.72943300	-1.36072500
F	-1.23956100	-1.40035500	-1.69442800
F	0.40600600	-0.23408000	-2.45033000

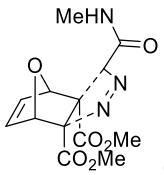
HF: -1228.6961454
Sum of electronic and zero-point Energies= -1228.451213
Sum of electronic and thermal Energies= -1228.430620
Sum of electronic and thermal Enthalpies= -1228.429675
Sum of electronic and thermal Free Energies= -1228.501826
Frequencies: -393.8664



(**1–4a**, TS-*anti* CF_3)

C	-3.05995500	-1.33059700	0.81957900
C	-2.51452300	-0.89809400	-0.55133300
C	-0.97094200	-2.06960400	0.30717900
C	-2.08869600	-2.06361300	1.35766100
H	-4.00144400	-1.01404400	1.24445500
H	-2.01939600	-2.50828400	2.33937100
C	-1.38043500	0.12322600	-0.28034700
C	-0.37207000	-0.63957500	0.27623700
H	-3.22304400	-0.63705200	-1.33332000
H	-0.26337200	-2.89535600	0.32967400
O	-1.72359000	-2.03373100	-0.90382600
N	-0.70784200	0.34903000	-2.36232700
N	0.27205300	-0.21727800	-2.25325300
C	1.09258200	-0.88014300	-1.43661100
H	1.04579100	-1.95793300	-1.56198500
C	2.40482500	-0.20632900	-1.17247600
O	2.72593800	0.83452400	-1.70679600
N	3.17857300	-0.86053700	-0.27051700
H	2.76878900	-1.59125000	0.29290600
C	4.44298400	-0.27907200	0.14259100
H	4.76897800	-0.76487400	1.06265400
H	5.20425600	-0.42164500	-0.62863500
H	4.32725000	0.79477400	0.31018100
C	-1.69022500	1.56071100	-0.03893800
C	0.62083200	-0.27721000	1.29672800
O	1.08966500	-1.08841400	2.06587700
O	0.96920800	1.00519700	1.26343600
C	1.91950000	1.41468000	2.24703300
H	2.80735000	0.78099800	2.20253800
H	2.16460400	2.44668000	2.00490300
H	1.47822200	1.34367400	3.24335200
F	-1.90864800	1.82424300	1.26450900
F	-2.82082400	1.89912300	-0.68595700
F	-0.73391700	2.39429200	-0.45152600

HF: -1228.6970692
Sum of electronic and zero-point Energies= -1228.451648
Sum of electronic and thermal Energies= -1228.431289
Sum of electronic and thermal Enthalpies= -1228.430345
Sum of electronic and thermal Free Energies= -1228.501143
Frequencies: -388.9384

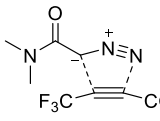


(**1–4b**, TS)

C	-3.09829100	-1.46845100	0.76302200
C	-2.59539900	-0.91459200	-0.57682500
C	-1.03807600	-2.17067900	0.10906700
C	-2.11838500	-2.25895400	1.19460500

H	-4.01920500	-1.17689900	1.24576600
H	-2.01892900	-2.79403000	2.12741000
C	-1.45200200	0.07346800	-0.24779200
C	-0.42440200	-0.74452800	0.20374500
H	-3.32986800	-0.57028600	-1.30055900
H	-0.33396100	-2.99569300	0.03070700
O	-1.82646700	-2.01580900	-1.06600600
N	-0.80221300	0.47343400	-2.32508400
N	0.18359000	-0.08964400	-2.27337300
C	1.01205200	-0.80591600	-1.50400700
H	0.99911200	-1.86768300	-1.73348300
C	2.31256600	-0.12796600	-1.19423900
O	2.59722400	0.97279900	-1.61916500
N	3.12666100	-0.85157100	-0.38483700
H	2.75205600	-1.64879000	0.10897800
C	4.38438100	-0.27598800	0.05423200
H	4.79975200	-0.90335900	0.84331900
H	5.09268900	-0.22717600	-0.77657100
H	4.23303500	0.74027300	0.42883200
C	-1.81066600	1.46460000	0.07307400
O	-2.93544100	1.78400000	0.38041500
O	-0.80321100	2.32703200	-0.06514400
C	-1.12067300	3.68654900	0.22683300
H	-1.44863200	3.78492500	1.26408500
H	-0.20124000	4.24386300	0.05699900
H	-1.91457400	4.04071700	-0.43397300
C	0.58100300	-0.54198700	1.26111500
O	1.06762400	-1.47421300	1.86677900
O	0.92462000	0.72468300	1.46882500
C	1.90315300	0.93575900	2.48635400
H	2.79350900	0.33599300	2.28725300
H	2.13631800	1.99831400	2.45188000
H	1.49731300	0.65846800	3.46167700

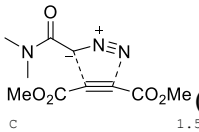
HF: -1119.5465392
Sum of electronic and zero-point Energies= -1119.263163
Sum of electronic and thermal Energies= -1119.241696
Sum of electronic and thermal Enthalpies= -1119.240752
Sum of electronic and thermal Free Energies= -1119.314507
Frequencies: -406.0472



(1′–3a, TS)

C	1.59902000	0.20231400	-0.21526400
C	0.44752100	0.64601000	-0.20992700
C	-1.82985500	-1.27663500	0.03045000
N	0.06681300	-1.59838600	-1.32864900
N	1.16073200	-1.85734900	-1.25101100
O	-1.39231100	-2.13729700	0.77082000
C	3.03328400	0.02555300	-0.15026100
O	3.78917800	0.34685400	-1.02975100
O	3.40171400	-0.55642500	0.99522200
C	4.80669700	-0.78926500	1.11927000
H	5.35186700	0.15503800	1.06751400
H	4.93866900	-1.25901100	2.09176800
H	5.15128400	-1.44839200	0.32009200
N	-3.08211000	-0.76596300	0.12398400
C	-3.91571500	-1.21036200	1.22810000
H	-3.91546500	-0.46483400	2.03229200
H	-4.94032500	-1.34280300	0.86947800
H	-3.53157700	-2.15259200	1.61201600
C	-0.92748700	-0.73514800	-1.05694100
H	-1.31415000	-0.27134800	-1.95745700
C	-0.40713000	1.79805300	0.12345300
F	-1.34247100	1.48304100	1.03477300
F	-1.06908100	2.25307000	-0.95889600
F	0.29350900	2.81861900	0.61135300
C	-3.60916900	0.36113900	-0.61879700
H	-2.91498400	0.71425300	-1.37613100
H	-4.54722700	0.07599100	-1.10612000
H	-3.80540100	1.19800800	0.06038900

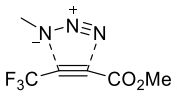
HF: -1037.9922725
Sum of electronic and zero-point Energies= -1037.794403
Sum of electronic and thermal Energies= -1037.775616
Sum of electronic and thermal Enthalpies= -1037.774671
Sum of electronic and thermal Free Energies= -1037.843433
Frequencies: -399.2234



(1′–3b, TS)

C	1.58066100	0.11818900	-0.29504800
C	0.40803500	0.50862000	-0.36487600
C	-1.76348100	-1.33254400	0.24477800
N	0.09401600	-1.90456500	-1.08462500
N	1.18498500	-2.16092500	-0.97519300
O	-1.25514100	-1.94443900	1.16838200
C	3.01277800	-0.01710300	-0.21415800
O	3.76583800	0.21155900	-1.12703500
O	3.39864500	-0.44456800	0.99480700
C	4.80814200	-0.62207600	1.13964600
H	5.32635300	0.32806500	0.99504200
H	4.95236900	-0.98933600	2.15391600
H	5.17588500	-1.34603800	0.41001300
N	-3.03899400	-0.87583500	0.25933100
C	-3.81625700	-1.05812300	1.47270100
H	-4.31210000	-0.11596500	1.72680800
H	-4.58185000	-1.82856800	1.32621600
H	-3.15376200	-1.36021000	2.28086600
C	-0.90135400	-1.01093800	-0.95320600
H	-1.29238400	-0.67539700	-1.90435400
C	-0.49954400	1.65856700	-0.27791700
O	0.07391900	2.68147600	0.35211200
O	-1.61859800	1.69122800	-0.72910100
C	-0.73598100	3.85369700	0.46172100
H	-0.12566100	4.57951800	0.99511800
H	-1.00003500	4.22386900	-0.53080700
H	-1.64809700	3.63070100	1.01867300
C	-3.76677000	-0.27559100	-0.84102400
H	-3.18617300	-0.27155600	-1.75842400
H	-4.68696100	-0.84541900	-1.01305500
H	-4.02232700	0.76138100	-0.60561800

HF: -928.8442383
Sum of electronic and zero-point Energies: -928.608411
Sum of electronic and thermal Energies: -928.588433
Sum of electronic and thermal Enthalpies: -928.587489
Sum of electronic and thermal Free Energies: -928.659928
Frequencies: -405.5642

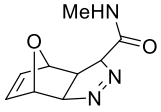


(2–3a, TS)

C	0.72199600	-0.03261400	0.12005900
C	-0.47475400	-0.27986000	-0.02341100
N	-0.45241300	2.20987100	-0.21239700
N	0.68307800	2.21579200	-0.08160100
C	2.14360000	-0.16335100	0.39570300
O	2.61244400	-0.17804700	1.50089300
O	2.84744800	-0.24818700	-0.73533600
C	4.26141700	-0.35973400	-0.54928500
H	4.49668900	-1.25641700	0.02677600
H	4.68231400	-0.42204500	-1.55057900
H	4.64058800	0.51788000	-0.02234500
N	-1.44731300	1.47791700	-0.39529800
C	-2.71238100	1.83802500	0.25345100
H	-3.42680400	1.06295000	-0.01792700
H	-3.06938800	2.79571000	-0.13032900
C	-1.61193900	-1.21676000	-0.06141600
F	-2.37409100	-1.04721000	-1.14716400
F	-1.19768800	-2.48299900	-0.05305100
F	-2.41097500	-1.04824600	1.00500400
H	-2.60884700	1.87861100	1.34131500

HF: -846.0675628
Sum of electronic and zero-point Energies: -845.937063
Sum of electronic and thermal Energies: -845.922841
Sum of electronic and thermal Enthalpies: -845.921897
Sum of electronic and thermal Free Energies: -845.979976
Frequencies: -407.7276

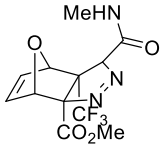
Oxanorbornadiene Intermediates



(1–4($R_1 = R_2 = H$), cycloadduct)

C	3.33522700	-0.30837300	-0.68370600
C	2.50646200	0.81217000	-0.07247800
C	1.65759100	-0.98929400	0.68812900
C	2.80426400	-1.43337500	-0.20857300
H	4.11434600	-0.18268900	-1.42235400
H	3.04455800	-2.45694600	-0.46009800
C	1.13596300	0.78091000	-0.82050300
C	0.50620400	-0.50958400	-0.24283500
H	2.95262900	1.79712800	0.04132700
H	1.36079600	-1.64604800	1.50379900
O	2.13432700	0.26111200	1.18619800
H	0.20023500	-1.25532800	-0.97406000
H	1.24402200	0.85056800	-1.90301100
N	0.28748100	1.89588800	-0.36364600
N	-0.64218000	1.52935700	0.35207800
C	-0.68531300	0.05290700	0.52469300
H	-0.61415200	-0.13073700	1.60334100
C	-2.03614900	-0.50502700	0.07324900
O	-2.14827400	-1.66417800	-0.27984400
N	-3.07124700	0.35590000	0.13693500
H	-2.87801300	1.31803800	0.37119200
C	-4.40494000	-0.06798000	-0.23933500
H	-5.09949500	0.75195400	-0.05745200
H	-4.44233200	-0.34814300	-1.29571700
H	-4.70524100	-0.93540000	0.35277800

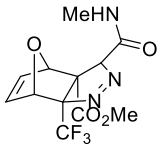
HF: -664.0109381
Sum of electronic and zero-point Energies: -663.807878
Sum of electronic and thermal Energies: -663.796575
Sum of electronic and thermal Enthalpies: -663.795631
Sum of electronic and thermal Free Energies: -663.846354



(**1**–**4a**, cycloadduct)

C	-2.94031200	-1.28523200	0.00356600
C	-2.10234700	-1.03460700	-1.23874400
C	-0.82718900	-2.10623600	0.09035500
C	-2.14139200	-1.95254600	0.83298700
H	-3.93069300	-0.89247500	0.17226100
H	-2.31737800	-2.24898800	1.85687000
C	-1.05520200	0.07704800	-0.87878400
C	-0.08432500	-0.71543600	0.05179700
H	-2.60271700	-0.87928800	-2.19117900
H	-0.17710600	-2.93830700	0.35343300
O	-1.24936200	-2.17483300	-1.26667200
N	-0.26309100	0.42566400	-2.08184500
N	0.87567200	-0.02960000	-2.05745900
C	1.16625800	-0.82978100	-0.85324000
H	1.25105200	-1.85967300	-1.21643200
C	2.53413200	-0.52646300	-0.24260800
O	2.93253300	-1.19212000	0.69229200
N	3.23632700	0.46903100	-0.81339300
H	2.87246200	0.90351400	-1.64726800
C	4.56223800	0.79656100	-0.32668000
H	4.91112600	1.69523800	-0.83502300
H	4.52479400	0.97861500	0.74939600
H	5.26339400	-0.02214100	-0.51159600
C	-1.70281600	1.36528500	-0.39297700
O	-2.88556600	1.52444200	-0.26959800
O	-0.78208600	2.29445100	-0.16337000
C	-1.27752500	3.53355400	0.35244300
H	-1.77257800	3.36112800	1.31030800
H	-0.40374700	4.16934900	0.47780000
H	-1.98486700	3.97561700	-0.35087300
C	0.14998500	-0.14343900	1.44505500
F	1.06922000	0.82385300	1.47115800
F	0.52969600	-1.10185900	2.29406100
F	-0.97550300	0.39067200	1.95711000

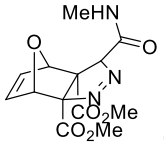
HF: -1228.7795947
Sum of electronic and zero-point Energies= -1228.529621
Sum of electronic and thermal Energies= -1228.510293
Sum of electronic and thermal Enthalpies= -1228.509348
Sum of electronic and thermal Free Energies= -1228.577289



(**1**–**4a**, cycloadduct-*anti* CF_3)

C	-3.02746900	-0.56109500	0.90611800
C	-2.29028000	-1.31084500	-0.19062000
C	-1.00078700	-1.38900200	1.50330200
C	-2.21727200	-0.60568400	1.96148300
H	-3.95770500	-0.02643400	0.77995400
H	-2.31608200	-0.12279500	2.92148000
C	-1.10964000	-0.37869400	-0.66822800
C	-0.14543800	-0.49053600	0.54955900
H	-2.85448100	-1.75447200	-1.00701800
H	-0.41776100	-1.91704500	2.25488800
O	-1.55828400	-2.28247800	0.53889700
N	-0.42007300	-1.01064300	-1.81234400
N	0.66460900	-1.49290400	-1.50424500
C	0.99985500	-1.31734300	-0.07808300
H	1.00102300	-2.32761600	0.34730500
C	2.41480100	-0.78545800	0.14143700
O	2.77127800	-0.46619400	1.26075200
N	3.21093800	-0.74527100	-0.93994100
H	2.83613300	-1.03795300	-1.82938500
C	4.58485900	-0.29766100	-0.82120300
H	5.07449300	-0.40656700	-1.78843700
H	4.62318200	0.75009000	-0.51110100
H	5.11501600	-0.89393200	-0.07491500
C	-1.59923500	0.98389200	-1.15441400
C	0.31517300	0.79508100	1.20128300
O	0.10473600	1.08214000	2.34619300
O	0.97689600	1.55722100	0.33089100
C	1.58433300	2.72506800	0.88867200
H	2.06353000	3.23472000	0.05510600
H	0.82468900	3.36080600	1.34685100
H	2.31850000	2.42347800	1.63934900
F	-1.86780600	1.82035600	-0.14682900
F	-2.73535000	0.83155200	-1.85422300
F	-0.72009300	1.58449100	-1.95317900

HF: -1228.7852935
Sum of electronic and zero-point Energies= -1228.534858
Sum of electronic and thermal Energies= -1228.515728
Sum of electronic and thermal Enthalpies= -1228.514784
Sum of electronic and thermal Free Energies= -1228.582067

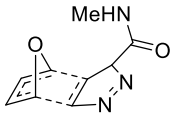


(**1**–**4b**, cycloadduct)

C	-3.16858400	-0.83321400	0.33513900
C	-2.41049600	-0.87000000	-0.98058100
C	-1.26794300	-2.06456100	0.36313200
C	-2.45914300	-1.58871500	1.16986400
H	-4.03657200	-0.22617700	0.53993400
H	-2.60060900	-1.75614600	2.22626500
C	-1.12290200	0.02327000	-0.82761900
C	-0.28825700	-0.85810800	0.15983500
H	-2.95084900	-0.70075800	-1.90952700
H	-0.77743300	-2.98871200	0.66228100
O	-1.80873700	-2.15798800	-0.95435700
N	-0.38981600	0.00776300	-2.10916700
N	0.64357200	-0.65067400	-2.06679800
C	0.89981100	-1.25492400	-0.74337600
H	0.90284100	-2.33892000	-0.90383600
C	2.29217900	-0.91563500	-0.20928700
O	2.60912200	-1.24492800	0.91913200
N	3.11674000	-0.27996100	-1.05940700
H	2.78494900	-0.06626900	-1.98748700
C	4.46990100	0.04688400	-0.65638400
H	4.96761200	0.56089900	-1.47816200
H	4.45772600	0.69523900	0.22354400
H	5.02610500	-0.85919300	-0.40323100
C	-1.39251300	1.45927800	-0.39994500
O	-2.16288100	1.76253800	0.47039100
O	-0.65800600	2.33202200	-1.08244500
C	-0.79133200	3.68896500	-0.65804000
H	-0.49577700	3.77903100	0.38980900
H	-0.12856800	4.26470100	-1.30075500
H	-1.82496700	4.02156000	-0.76948600
C	0.12264000	-0.20322200	1.45779100
O	-0.10679100	-0.64604600	2.54692200
O	0.77390500	0.94370000	1.22633500
C	1.35244300	1.54741000	2.38560100
H	2.08141900	0.86076900	2.82179600
H	1.83724100	2.45724300	2.03487200
H	0.57568100	1.77789500	3.11697500

HF: -1119.6332184
Sum of electronic and zero-point Energies= -1119.344760
Sum of electronic and thermal Energies= -1119.324483
Sum of electronic and thermal Enthalpies= -1119.323538
Sum of electronic and thermal Free Energies= -1119.394488

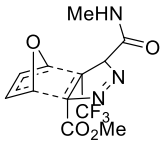
Oxanorbornadiene retro[4+2] Transition States



(**1**–**4**(R_1 = R_2 = H), retro [4+2] TS)

C	3.40873300	0.10263900	0.66436000
C	2.74307200	-0.83724300	-0.14731700
C	1.90300600	1.06797700	-0.66390800
C	0.80910800	-0.72661100	1.01435900
C	0.36061300	0.49590400	0.47308900
H	2.93030400	-1.88949000	-0.30035100
H	1.47988800	1.76570900	-1.37385600
O	2.11653400	-0.19460600	-1.15148600
H	0.17716200	1.38824900	1.05455200
H	1.21416200	-0.91811100	1.99530000
N	0.19015300	-1.81046800	0.34083300
N	-0.57793000	-1.41414700	-0.56232900
C	-0.67616800	0.05650100	-0.53381200
H	-0.52263700	0.42722800	-1.55226800
C	-2.07673700	0.53173500	-0.12015000
O	-2.27628700	1.70410700	0.13691200
N	-3.03432500	-0.41280100	-0.08840700
H	-2.77991700	-1.35765200	-0.33462800
C	-4.39877700	-0.06412300	0.25166900
H	-5.00284100	-0.97112900	0.25643700
H	-4.43687500	0.40231600	1.23916900
H	-4.81002900	0.64276600	-0.47385500
C	2.89846000	1.33099500	0.31456400
H	3.07187500	2.28582200	0.78659400
H	4.08378100	-0.13645000	1.47170000

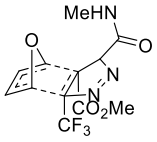
HF: -663.9601643
Sum of electronic and zero-point Energies: -663.761155
Sum of electronic and thermal Energies: -663.749262
Sum of electronic and thermal Enthalpies: -663.748317
Sum of electronic and thermal Free Energies: -663.799971
Frequencies: -542.7028



(**1**–**4a**, retro[4+2] TS)

C	-2.91940600	-1.14263200	-0.22253600
C	-2.15659800	-1.26328300	-1.40321700
C	-0.96638100	-2.16248100	0.13959600
C	-2.18823300	-1.75861700	0.76028000
H	-3.83530700	-0.57973800	-0.12702700
H	-2.39367500	-1.79667900	1.81734100
C	-0.60997300	0.31665200	-0.82193600
C	0.10269500	-0.51906300	0.09015700
H	-2.39215700	-0.99943700	-2.42436600
H	-0.28647300	-2.92756300	0.49177700
O	-1.17907700	-2.16003800	-1.22089300
N	-0.00529100	0.24226100	-2.10619500
N	0.99306900	-0.50310300	-2.10763300
C	1.31856000	-0.94493800	-0.74738700
H	1.51286900	-2.01824400	-0.74361000
C	2.65072900	-0.28935200	-0.29741100
O	3.35300600	-0.83334200	0.52689400
N	2.93405400	0.90584600	-0.84997600
H	2.39542600	1.22249300	-1.64055200
C	4.14293300	1.60741000	-0.46506200
H	5.03442600	1.04398600	-0.75487200
H	4.15325400	2.58245200	-0.95184600
H	4.15995500	1.74206100	0.61865900
C	-1.54220800	1.44651100	-0.62316600
O	-2.05031500	2.07420500	-1.51531200
O	-1.77440100	1.68005900	0.67414800
C	-2.69695400	2.73478600	0.94372800
H	-3.66760500	2.51518300	0.49283700
H	-2.77616000	2.78556500	2.02801200
H	-2.32337000	3.67663800	0.53813400
C	0.37522000	-0.24156700	1.55297300
F	1.05150400	-1.27257300	2.08278600
F	1.11885000	0.85840900	1.71187200
F	-0.71368900	-0.09132200	2.31060100

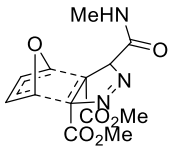
HF: -1228.7377166
Sum of electronic and zero-point Energies= -1228.490841
Sum of electronic and thermal Energies= -1228.470930
Sum of electronic and thermal Enthalpies= -1228.469986
Sum of electronic and thermal Free Energies= -1228.539732
Frequencies: -446.0222



(**1**–**4a**, retro[4+2] TS-*anti* CF_3)

C	3.16302300	-0.11722100	-0.83656600
C	2.60748000	-1.37603800	-0.55365200
C	1.32283000	-0.49881500	-2.03544100
C	2.36658400	0.43440900	-1.81410100
H	3.97257700	0.34414300	-0.29317300
H	2.39305000	1.43335100	-2.21848300
C	0.79110300	-0.48726600	0.61612100
C	0.07197200	-0.10922900	-0.53629800
H	2.95360900	-2.17696400	0.08276500
H	0.66697800	-0.55920400	-2.89285900
O	1.70783300	-1.70054300	-1.49089300
N	0.35037100	-1.74127000	1.09603700
N	-0.55249900	-2.21291600	0.37578000
C	-0.94484800	-1.24566300	-0.65871000
H	-0.92692500	-1.74827000	-1.62939500
C	-2.39227900	-0.75482400	-0.47709300
O	-2.85450500	0.05250700	-1.26089700
N	-3.06744700	-1.26910100	0.56208800
H	-2.61703600	-1.97344300	1.12671900
C	-4.44165700	-0.87938600	0.80925700
H	-5.07640000	-1.14314300	-0.04049300
H	-4.79649300	-1.39364900	1.70205000
H	-4.50588800	0.20046000	0.96324600
C	-0.38702900	1.29740800	-0.83013200
O	-0.18419200	1.89237000	-1.85287900
O	-1.07123200	1.78085200	0.20394500
C	-1.73045300	3.02662300	-0.04029000
H	-2.45440300	2.89701500	-0.84768700
H	-2.22847400	3.28183400	0.89304600
H	-1.00129400	3.79159700	-0.31273600
C	1.43673500	0.40811900	1.61960500
F	0.62725900	0.66148600	2.65773900
F	1.76330600	1.59039900	1.07510300
F	2.55873700	-0.11643100	2.14041000

HF: -1228.7404056
Sum of electronic and zero-point Energies= -1228.493763
Sum of electronic and thermal Energies= -1228.473815
Sum of electronic and thermal Enthalpies= -1228.472871
Sum of electronic and thermal Free Energies= -1228.543033
Frequencies: -434.0978

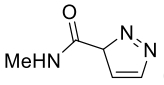


(**1**–**4b**, retro[4+2] TS)

C	-2.72438400	-1.24151500	1.18567300
C	-2.39559300	-1.85927900	-0.02755100
C	-0.60717700	-1.95526900	1.16581000
C	-1.60178500	-1.33708800	1.97597100
H	-3.63467600	-0.69929100	1.38817100
H	-1.41877300	-0.88245600	2.93622100
C	-0.90915800	-0.02465700	-0.67345100
C	0.13596500	-0.49563300	0.15664700
H	-2.98035800	-2.05272200	-0.91492000
H	0.26094900	-2.49315000	1.52237700
O	-1.24759200	-2.53175300	0.08706000
N	-0.78384900	-0.54681800	-1.98136400
N	0.24230200	-1.24203000	-2.10026200
C	1.04594100	-1.18834100	-0.86730200
H	1.32850700	-2.20868400	-0.59354000
C	2.31927400	-0.35882800	-1.12486700
O	2.41363000	0.45008600	-2.01535400
N	3.30988100	-0.58325000	-0.22241400
H	3.16762800	-1.23565200	0.53137200
C	4.49980300	0.24567900	-0.23955200
H	5.10769000	0.00891600	0.63382600
H	5.08241400	0.06478400	-1.14632000
H	4.22210800	1.30348200	-0.22028800
C	-1.79012300	1.08533100	-0.32463300
O	-1.78541900	1.60500900	0.77096200
O	-2.61390400	1.44664500	-1.31391900
C	-3.48411300	2.53258700	-1.00479300
H	-2.90648100	3.41645300	-0.72749800
H	-4.05690200	2.71676600	-1.91182500
H	-4.14670200	2.26755100	-0.17734200
C	0.79516200	0.35192400	1.21505000
O	1.01874800	-0.01668500	2.34160000
O	1.18168700	1.52067700	0.72251900
C	1.85201600	2.38102300	1.64384600
H	2.73936400	1.88534700	2.04535800
H	2.12559100	3.26482100	1.07128900
H	1.17914100	2.64108900	2.46337700

HF: -1119.5921381
Sum of electronic and zero-point Energies= -1119.307030
Sum of electronic and thermal Energies= -1119.286075
Sum of electronic and thermal Enthalpies= -1119.285131
Sum of electronic and thermal Free Energies= -1119.357223
Frequencies: -476.9720

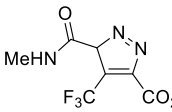
Pyrazoles



(**1**–**ethylene**, GS)

C	-2.47587600	0.18054400	-0.58368900
C	-1.57400500	1.06578300	-0.15071000
N	-2.12077100	-1.13880800	-0.15420300
N	-1.06769000	-1.10720300	0.51680000
C	-0.58980500	0.27265000	0.63077600
H	-0.61377800	0.53374700	1.69832100
C	0.86972500	0.46209700	0.18834200
O	1.32990100	1.57773600	0.06132900
N	1.56464100	-0.67177400	-0.01159700
H	1.09576300	-1.55357000	0.13061700
C	2.96379100	-0.61590000	-0.38864500
H	3.34544200	-1.63333000	-0.46916400
H	3.08242600	-0.10722000	-1.34845300
H	3.54018600	-0.06933200	0.36183700
H	-1.52137100	2.13085500	-0.31381700
H	-3.36410900	0.31041100	-1.18341300

HF: -434.0409219
Sum of electronic and zero-point Energies: -433.915399
Sum of electronic and thermal Energies: -433.906932
Sum of electronic and thermal Enthalpies: -433.905988
Sum of electronic and thermal Free Energies: -433.949645

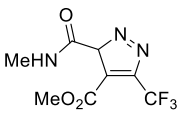


(**1**–**3/4a**, GS)

C	0.83659800	-0.94361200	-0.32149000
C	0.06080100	0.13707500	-0.46084200
N	0.08399200	-2.12923200	-0.61228700
N	-1.08681700	-1.82567500	-0.91285900
C	-1.27452200	-0.37822000	-0.86586000
H	-1.56378400	-0.03879900	-1.87001500
C	-2.43777300	0.02832700	0.07321500
O	-2.50389200	1.15264200	0.51339800
N	-3.34312600	-0.94001200	0.29661200
H	-3.16584100	-1.86248000	-0.07125800
C	-4.50386600	-0.67388300	1.12655000
H	-5.14441300	-1.55509300	1.12228200
H	-4.20319800	-0.44648300	2.15241800

H	-5.05802400	0.18115500	0.73333400
C	2.27659400	-1.08641300	0.03394800
O	2.99652000	-1.91112800	-0.45295400
O	2.63532700	-0.19138000	0.95102700
C	4.02282400	-0.20866000	1.30126100
H	4.63028000	0.01362900	0.42192700
H	4.14245500	0.56172600	2.05951800
H	4.29701600	-1.18958700	1.69325900
C	0.43168300	1.58632600	-0.34932500
F	-0.36386000	2.32886400	-1.12464600
F	1.68797500	1.79296900	-0.76784300
F	0.34138300	2.03746400	0.89712800

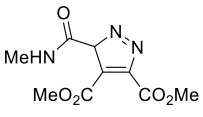
HF: -998.8089826
Sum of electronic and zero-point Energies: -998.635071
Sum of electronic and thermal Energies: -998.618594
Sum of electronic and thermal Enthalpies: -998.617650
Sum of electronic and thermal Free Energies: -998.681193



(**1–3/4a**, GS-*anti* CF_3)

C	0.96787800	-0.92307800	-0.16811700
C	0.14310700	0.07565900	-0.48699500
N	0.31478600	-2.18684700	-0.31199700
N	-0.85316700	-2.01609700	-0.71438700
C	-1.12107600	-0.59215500	-0.89863000
H	-1.33183300	-0.41270100	-1.96264700
C	-2.35620600	-0.09505400	-0.11947900
O	-2.48158700	1.08581700	0.12252800
N	-3.24459800	-1.04752900	0.20675500
H	-3.01084100	-2.00965300	0.01191400
C	-4.46443400	-0.70295500	0.91420100
H	-5.11288500	-1.57806900	0.93888500
H	-4.24662300	-0.38184700	1.93630600
H	-4.97319700	0.11273900	0.39731700
C	2.39269400	-0.91046200	0.28172300
C	0.32421800	1.55292300	-0.55687300
O	0.21162900	2.15693900	-1.58727900
O	0.59162300	2.07714700	0.62891900
C	0.69050000	3.50622500	0.64421900
H	1.50755800	3.83087700	-0.00245100
H	-0.24866000	3.94103300	0.29785800
H	0.88572200	3.77289300	1.68036300
F	2.50619400	-1.31765500	1.54863800
F	2.91150200	0.31672100	0.19444400
F	3.13543700	-1.72659800	-0.46905800

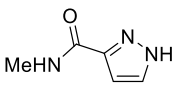
HF: -998.8106999
Sum of electronic and zero-point Energies: -998.636661
Sum of electronic and thermal Energies: -998.620115
Sum of electronic and thermal Enthalpies: -998.619171
Sum of electronic and thermal Free Energies: -998.683336



(**1–3/4b**, GS)

C	1.04492000	-0.70354000	-0.39212300
C	-0.08745400	0.00055500	-0.50817900
N	0.78361600	-2.09627700	-0.64681800
N	-0.42217000	-2.26544500	-0.90742300
C	-1.14241700	-0.99694300	-0.85656400
H	-1.56431900	-0.81114400	-1.85236100
C	-2.28775500	-1.05423100	0.18337500
O	-2.26535700	-1.81772700	1.11897500
N	-3.27777300	-0.16317500	-0.05097200
H	-3.09921000	0.58097100	-0.71138900
C	-4.33474100	0.00076100	0.93070800
H	-5.07615700	0.69371100	0.53370900
H	-4.80707800	-0.96442400	1.11983800
H	-3.94503000	0.38322000	1.87909000
C	2.44316100	-0.25105300	-0.13898000
O	2.93396400	0.72284500	-0.64095900
O	3.06593500	-1.08129300	0.69034700
C	4.43091400	-0.75295100	0.96300400
H	4.49428300	0.23434500	1.42441200
H	4.78613400	-1.52317000	1.64392200
H	5.00766300	-0.75642000	0.03634200
C	-0.36164600	1.44902200	-0.40323600
O	-1.31266500	1.96337900	-0.94558600
O	0.51651100	2.09490000	0.34531100
C	0.33165400	3.51146600	0.43012300
H	-0.63937700	3.73616900	0.87511500
H	1.14154700	3.87182400	1.06013600
H	0.38891100	3.95384600	-0.56580100

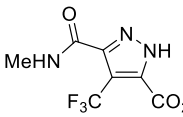
HF: -889.6585705
Sum of electronic and zero-point Energies: -889.445861
Sum of electronic and thermal Energies: -889.428519
Sum of electronic and thermal Enthalpies: -889.427575
Sum of electronic and thermal Free Energies: -889.493644



(**5**(R_1=R_2=H), GS)

C	2.70426000	0.34669300	0.00027200
C	1.55061200	1.09563200	-0.00010900
N	2.31650400	-0.95186300	0.00005300
N	0.99424000	-1.10281700	-0.00003300
C	0.51700200	0.13745300	-0.00011300
C	-0.94556400	0.41507500	-0.00020100
O	-1.37484400	1.55563400	0.00008300
N	-1.74031400	-0.67764300	-0.00079200
H	-1.30288100	-1.58547100	0.00105400
C	-3.18021600	-0.53647500	0.00046600
H	-3.63269700	-1.52828700	-0.01016900
H	-3.51406000	0.00414500	0.89042600
H	-3.51226400	0.02205100	-0.87886400
H	1.44091100	2.16656700	-0.00027900
H	3.74658200	0.62221900	0.00049200
H	2.90358000	-1.77031400	0.00018400

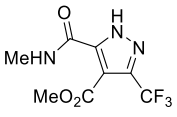
HF: -434.0962584
Sum of electronic and zero-point Energies: -433.968491
Sum of electronic and thermal Energies: -433.960020
Sum of electronic and thermal Enthalpies: -433.959076
Sum of electronic and thermal Free Energies: -434.002523



(**5a**, GS)

C	1.03006600	-0.87227300	-0.05903500
C	0.04696900	0.10458700	-0.03898200
N	0.37699500	-2.05420000	-0.04108500
N	-0.93602900	-1.93226200	0.00717800
C	-1.16439800	-0.62209100	0.01411600
C	-2.55974200	-0.10002900	0.15158800
O	-2.77789500	1.03286200	0.53056400
N	-3.52798100	-0.99145300	-0.15337300
H	-3.25695400	-1.93779500	-0.36931700
C	-4.92024500	-0.64694600	0.04979400
H	-5.54168500	-1.47188900	-0.29832200
H	-5.12749200	-0.45479400	1.10666600
H	-5.16776500	0.25473200	-0.51443600
C	2.51193100	-0.96483700	-0.03553800
O	3.06699300	-2.01846300	-0.23233200
O	3.11521000	0.16825600	0.26763000
C	4.54531000	0.10629200	0.32055900
H	4.94033900	-0.21924000	-0.64301100
H	4.86872300	1.11824800	0.55264600
H	4.85940000	-0.59257600	1.09781300
C	0.19712800	1.59109800	-0.15599800
F	-0.73977000	2.10909000	-0.95011300
F	1.37943700	1.91833200	-0.69742900
F	0.12157600	2.20293100	1.02782400
H	0.82677100	-2.96049600	-0.04953500

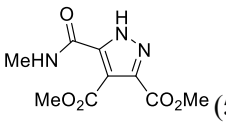
HF: -998.8666002
Sum of electronic and zero-point Energies: -998.690511
Sum of electronic and thermal Energies: -998.674974
Sum of electronic and thermal Enthalpies: -998.674030
Sum of electronic and thermal Free Energies: -998.734770



(**5a-*anti* CF_3**, GS)

C	-1.05675900	-0.94388400	-0.00024600
C	0.02122400	-0.01772000	-0.00069500
N	-0.62493100	-2.19216900	0.00145400
N	0.69590900	-2.08985500	0.00251800
C	1.15591200	-0.83027200	0.00087800
C	2.65441100	-0.71582700	0.00267500
O	3.30065000	-1.75526400	0.01187500
N	3.18873000	0.50648300	-0.00808200
H	2.56669200	1.30982100	-0.01033600
C	4.62989400	0.66200900	-0.00467500
H	4.86479100	1.72352000	-0.07394100
H	5.05999400	0.25235500	0.91312700
H	5.07126100	0.13310000	-0.85288700
C	-2.54252100	-0.70760600	-0.00263400
C	-0.02495200	1.45166100	-0.00077900
O	0.94679300	2.17830200	-0.00857300
O	-1.26775100	1.90971300	0.00942500
C	-1.41196300	3.33217800	0.00852100
H	-0.93551300	3.75766600	0.89340900
H	-0.95657700	3.75398700	-0.88915000
H	-2.48453000	3.51256700	0.02076000
F	-3.20325400	-1.86273500	-0.00908000
F	-2.93404900	-0.01716300	-1.08046700
F	-2.93954100	-0.02620400	1.07873000
H	1.29851600	-2.90455700	0.00505600

HF: -998.8752367
Sum of electronic and zero-point Energies: -998.698696
Sum of electronic and thermal Energies: -998.682657
Sum of electronic and thermal Enthalpies: -998.681713
Sum of electronic and thermal Free Energies: -998.743729



(5b, GS)

C	-1.04783600	-0.81498400	0.06801800
C	0.10845300	0.00891200	0.06208200
N	-0.72474600	-2.09959100	0.00327800
N	0.59912000	-2.11068200	-0.04299900
C	1.16627000	-0.89362200	-0.00654900
C	2.66379300	-0.88889600	-0.06475400
O	3.23521800	-1.95858000	-0.23049600
N	3.28478000	0.28500600	0.08224100
H	2.72589700	1.11222200	0.26940700
C	4.73261000	0.34307800	0.05838200
H	5.04008400	1.38376700	0.15549100
H	5.15715800	-0.24124900	0.87946900
H	5.11410800	-0.06381600	-0.88107100
C	-2.47136600	-0.42444300	0.27492100
O	-2.82345300	0.46104500	1.00651600
O	-3.29924800	-1.20248300	-0.42129200
C	-4.68741900	-0.94680200	-0.20432800
H	-4.92914400	0.08281100	-0.47501800
H	-5.21843900	-1.64985000	-0.84287500
H	-4.93986000	-1.11040200	0.84535800
C	0.18584900	1.47803300	0.02949200
O	1.16064400	2.12714900	0.34794900
O	-0.93294300	2.02700900	-0.42038700
C	-0.97227900	3.45522300	-0.41132300
H	-0.21895200	3.85663700	-1.09175300
H	-1.97429500	3.71930900	-0.74237500
H	-0.78809300	3.82805700	0.59754400
H	1.12727200	-2.97273500	-0.10578900

HF: -889.7227408
Sum of electronic and zero-point Energies: -889.507658
Sum of electronic and thermal Energies: -889.490629
Sum of electronic and thermal Enthalpies: -889.489685
Sum of electronic and thermal Free Energies: -889.553971

(GS)

C	-1.08801800	-0.34857900	0.00016200
C	-0.71771700	0.95597100	-0.00013500
C	0.71745100	0.95615600	0.00005700
C	1.08811300	-0.34829400	0.00013200
O	0.00016100	-1.15148400	-0.00020000
H	-2.04157800	-0.85003100	0.00024400
H	-1.37564500	1.80973400	-0.00024300
H	1.37513800	1.81009800	0.00010100
H	2.04182700	-0.84945300	0.00020800

HF: -229.9487337
Sum of electronic and zero-point Energies: -229.878038
Sum of electronic and thermal Energies: -229.874368
Sum of electronic and thermal Enthalpies: -229.873424
Sum of electronic and thermal Free Energies: -229.904281

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