Supplementary Material

Rapid cycloaddition of a diazo group with an unstrained dipolarophile

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Materials

Silica gel (40 μm) was from SiliCycle. All chemicals and solvents were from Sigma–Aldrich (St. Louis, MO) unless indicated otherwise, and were reagent-grade and used without further purification. Water was purified with an Arium Pro system from Sartorius (Göttingen, Germany).

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 400, 500, or 750 MHz for ^{1}H, and 126 or 189 MHz for ^{13}C. The 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 (Micromass) AutoSpec or a Waters LCT, and MALDI–TOF mass spectrometry was performed using a Bruker microflex LRF at the Mass Spectrometry Facility in the Department of Chemistry at the University of Wisconsin–Madison. Absorbance measurements were made with an Infinite M1000 plate reader from Tecan (Männedorf, Switzerland).

Procedures for kinetic experiments

***N*-Benzyl-2-diazoacetamide (1) + ethyl 4,4,4-trifluorocrotonate (2).** Diazoacetamide **1** was dissolved in 1:1 CH_3CN/H_2O at a concentration of 40 mM. In a clear 96-well plate, 50 μL of this stock solution was combined with 50 μL of a stock solution of ethyl 4,4,4-trifluorocrotonate (5 equiv) in 1:1 CH_3CN/H_2O to produce a final concentration of 20 mM of diazoacetamide **1**. Absorbance was monitored at the wavelength of maximum absorbance by diazoacetamide **1**, which is 388 nm.[1] Multiple readings were taken of each well every 60 s, followed by an orbital mixing period of 10 s. The formation of the expected products was confirmed by mass spectrometry and NMR spectroscopy. Reaction velocity was determined from the inverse of the slope of a semilog plot of of the concentration of diazoacetamide **1** as a function of time (Figure S1, panel A), and the slope was used to calculate a pseudo–first-order rate constant (k') for the reaction, which was converted to a second-order rate constant ($k = k'/[0.10\ \mathrm{M}]$) as the mean ± SD from triplicate measurements.

***N*-Benzyl-2-diazoacetamide (1) + methyl crotonate (9).** Diazoacetamide **1** was dissolved in CD_3CN at a concentration of 0.50 M. Methyl crotonate was dissolved in CD_3CN to a concentration of 4.50 M. Equal volumes of each solution were added to an NMR tube, which

was capped, sealed with parafilm, and inverted periodically to mix the contents. Multiple 16-scan NMR spectra were acquired over a 48 h period, and integration was used to determine the concentration of diazoacetamide **1**. Reaction velocity was determined from the inverse of the slope of a semilog plot of the concentration of diazoacetamide **1** as a function of time (Figure S1, panel B), and the slope was used to calculate a pseudo–first-order rate constant (k') for the reaction, which was converted to a second-order rate constant ($k = k'/[2.25\ \mathrm{M}]$) as the mean ± SD from triplicate measurements.

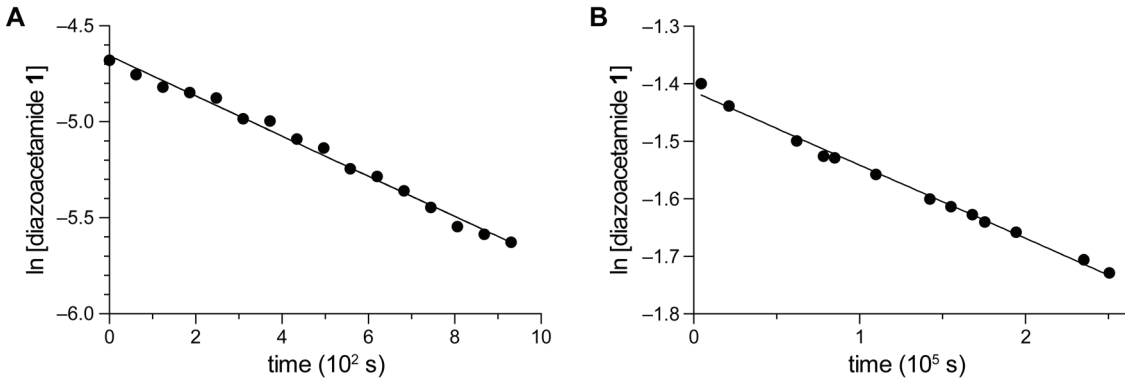


Figure S1. Representative kinetic plots for the cycloaddition of diazoacetamide **1** with a dipolarophile under pseudo-first order conditions. (A) Ethyl 4,4,4-trifluorocrotonate (**2**) in 1:1 CH_3CN/H_2O, $k = (1.05 \pm 0.11) \times 10^{-1}\ \mathrm{M^{-1}s^{-1}}$ from triplicate measurements; (B) Methyl crotonate in CD_3CN, $k = (5.8 \pm 0.2) \times 10^{-7}\ \mathrm{M^{-1}s^{-1}}$ from triplicate measurements.

Procedure for chemoselectivity experiment

N-Benzyl-2-diazoacetamide (**1**) (4.4 mg, 0.025 mmol) and *N*-benzyl-2-azidoacetamide (**10**) (4.8 mg, 0.025 mmol) were dissolved in 0.50 mL of CD_3CN, and their molar ratio was determined by ^{1}H NMR spectroscopy to be 1:1.08 **1**/**10** (Figure S2, top). A 0.2-mL aliquot of this solution was diluted with an additional 0.05 mL CD_3CN and 0.25 mL D_2O, affording a 0.5-mL solution that contained 0.02 M of both diazoacetamide **1** and azidoacetamide **10** in 1:1 CD_3CN/D_2O. Ethyl 4,4,4-trifluorocrotonate (**2**) (8.4 mg, 0.05 mmol) was added, and the reaction was monitored by ^{1}H-NMR spectroscopy (Figure S2, bottom). After ~1 h, diazoacetamide **1** was consumed completely but the azidoacetamide **10** had reacted to a neglible extent. Product distribution was analyzed by LCMS (Figure S3).

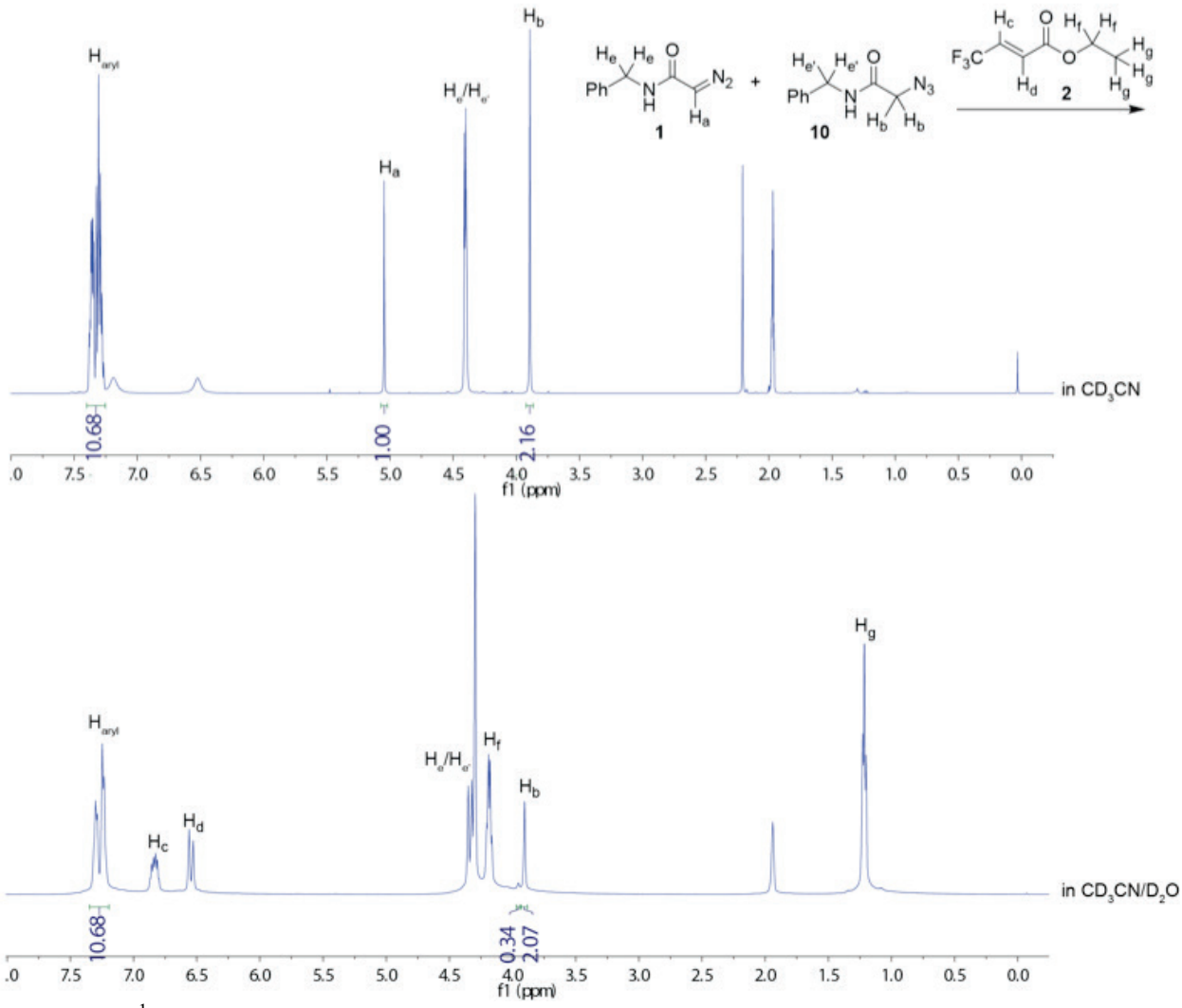


Figure S2. ^{1}H NMR spectrum of *N*-benzyl-2-diazoacetamide (**1**) and *N*-benzyl-2-azidoacetamide (**10**) in CD_3CN (top), and the reaction mixture with 5 equiv of ethyl trifluororcronate (**2**) in 1:1 CD_3CN/D_2O after 1 h (bottom).

Product distribution was assessed by reverse-phase chromatography with a Discovery BIO Wide Pore C5-5 column from Supelco (Bellefonte, PA). The column was eluted with 5–95% v/v B over 10 min, 95% v/v B for 2 min, 95–5% over 2 min, and 5% v/v B for 5 min (A: H_2O containing 0.1% v/v formic acid; B: acetonitrile containing 0.1% v/v formic acid). Absorbance at 254 nm and molecular mass were monitored with an LCMS-2020 instrument from Shimadzu (Kyoto, Japan).

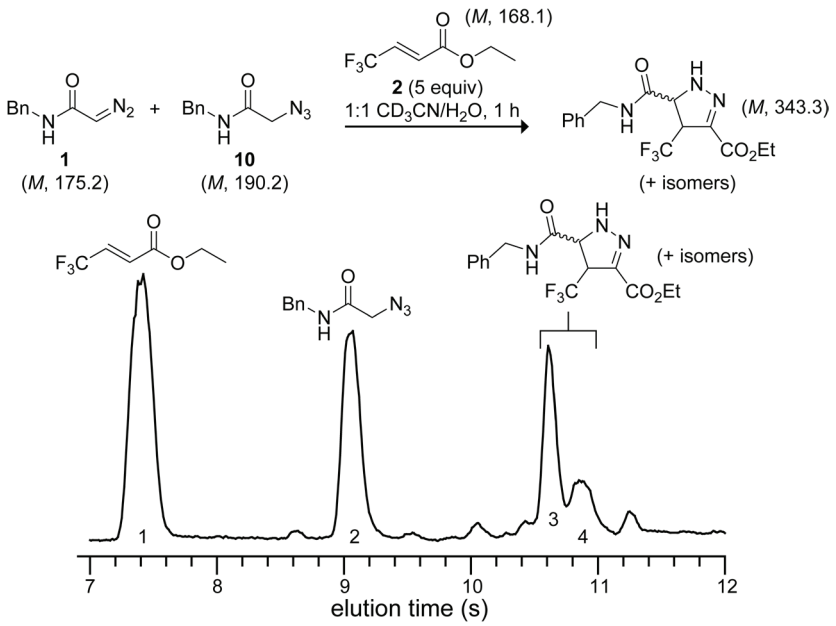


Figure S3. LCMS trace of the reaction of a 1:1 mixture of diazoacetamide **1** and azidoacetamide **10** with trifluorocrotonate **2** (5 equiv), showing selective reactivity for the more nucleophilic diazoacetamide **1**. Molecules were detected by absorbance at 254 nm during LCMS with a reverse-phase column. Reaction conditions: 1:1 CD_3CN/D_2O, ~1 h.

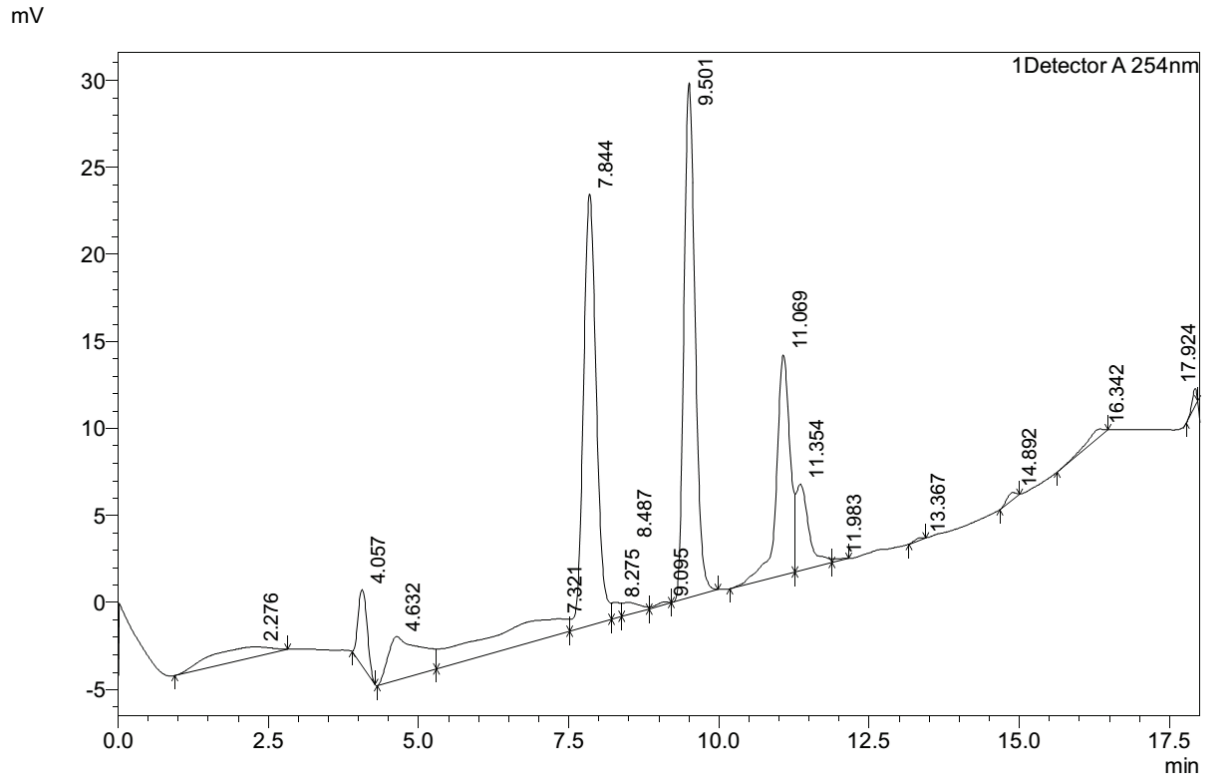


Figure S4. UV trace of the reaction of a 1:1 mixture of diazoacetamide **1** and azidoacetamide **10** with trifluorocrotonate **2** (5 equiv). Molecules were detected by absorbance at 254 nm during LCMS with a reverse-phase column. Reaction conditions: 1:1 CD_3CN/D_2O, ~1 h.

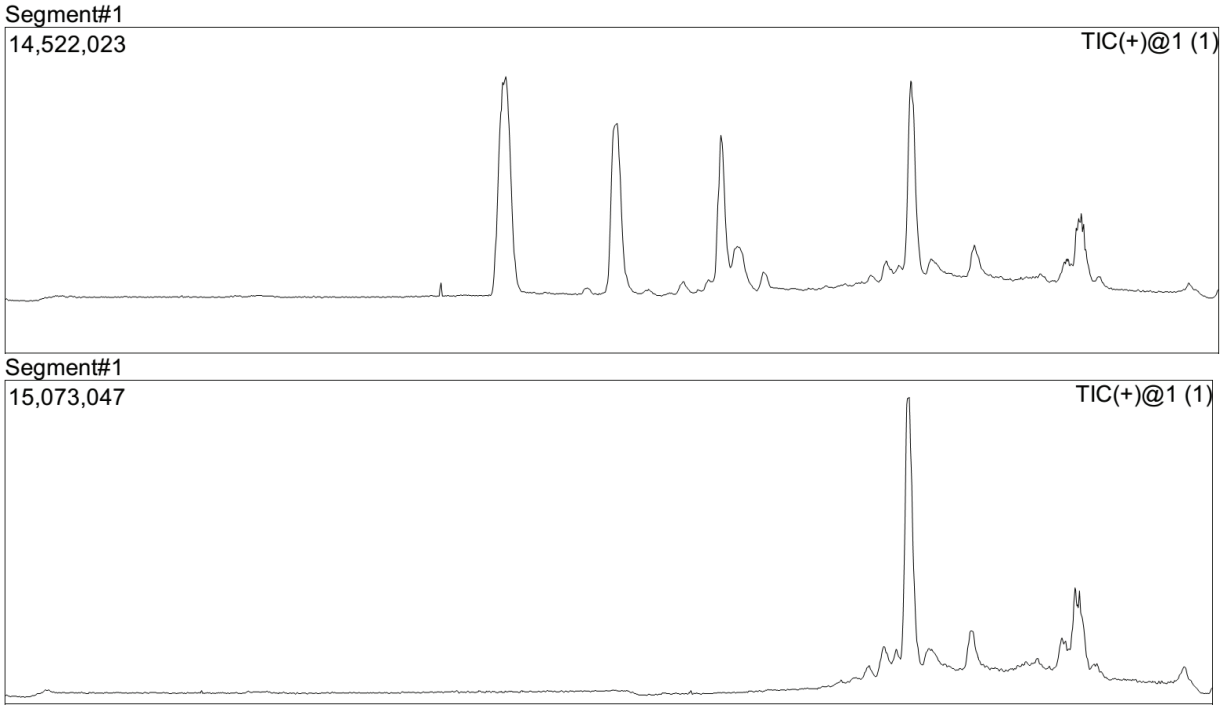


Figure S5. Top: Full LCMS trace of the reaction of a 1:1 mixture of diazoacetamide **1** and azidoacetamide **10** with trifluorocrotonate **2** (5 equiv). Reaction conditions: 1:1 CD_3CN/D_2O, ~1 h. Bottom: Full LCMS trace of the MeOH blank.

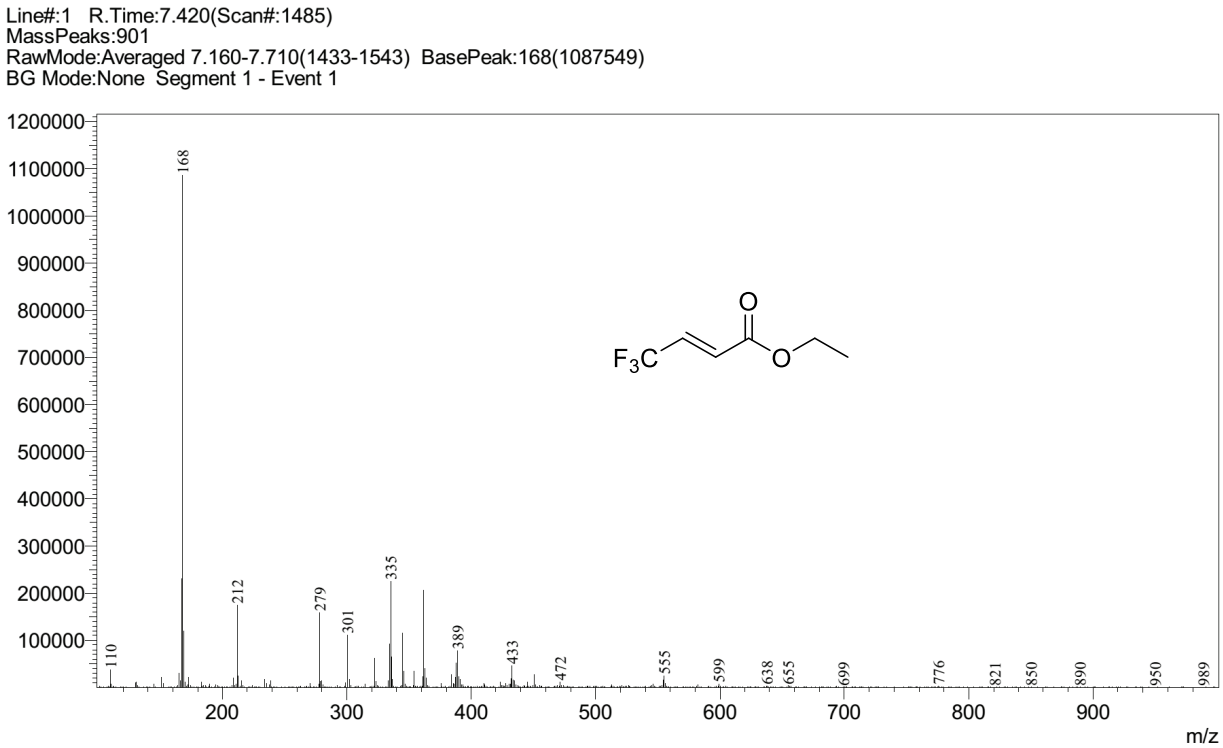


Figure S6. MS data for peak 1 (~7.4 min) from Figure S3, corresponding to unreacted ethyl trifluorocrotonate **2** (*M*, 168.1).

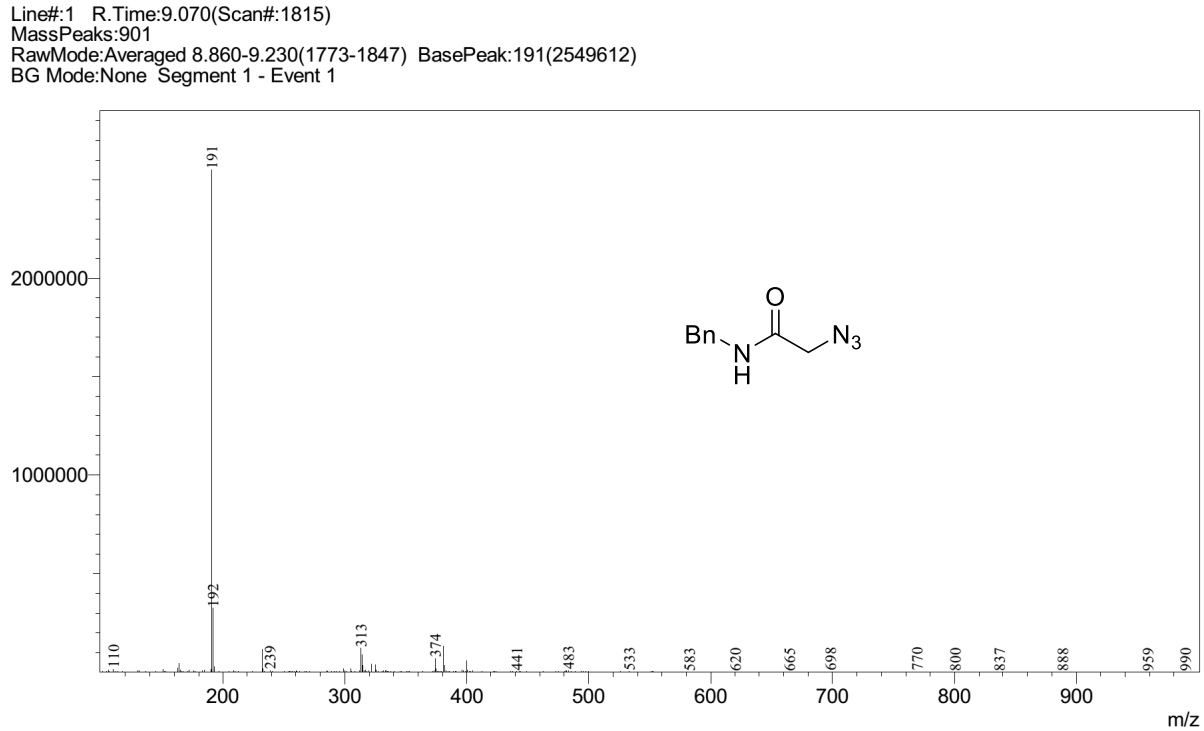


Figure S7. MS data for peak 2 (~9.1 min) from Figure S3, corresponding to unreacted azidoacetamide **10** (*M*, 190.2).

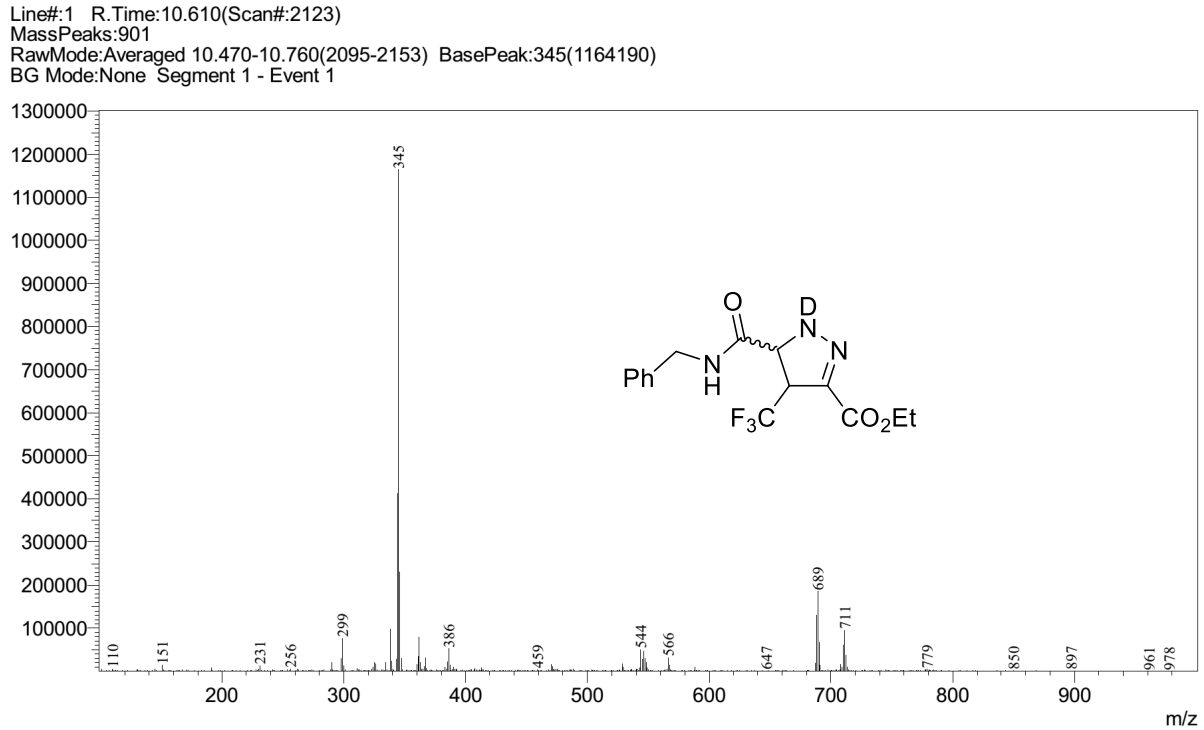


Figure S8. MS data for peak 3 (~10.6 min) from Figure S3, corresponding to an isomeric mixture of deuterated products from the cycloaddition of diazoacetamide **1** and trifluorocrotonate **2** (*M*, 344.3).

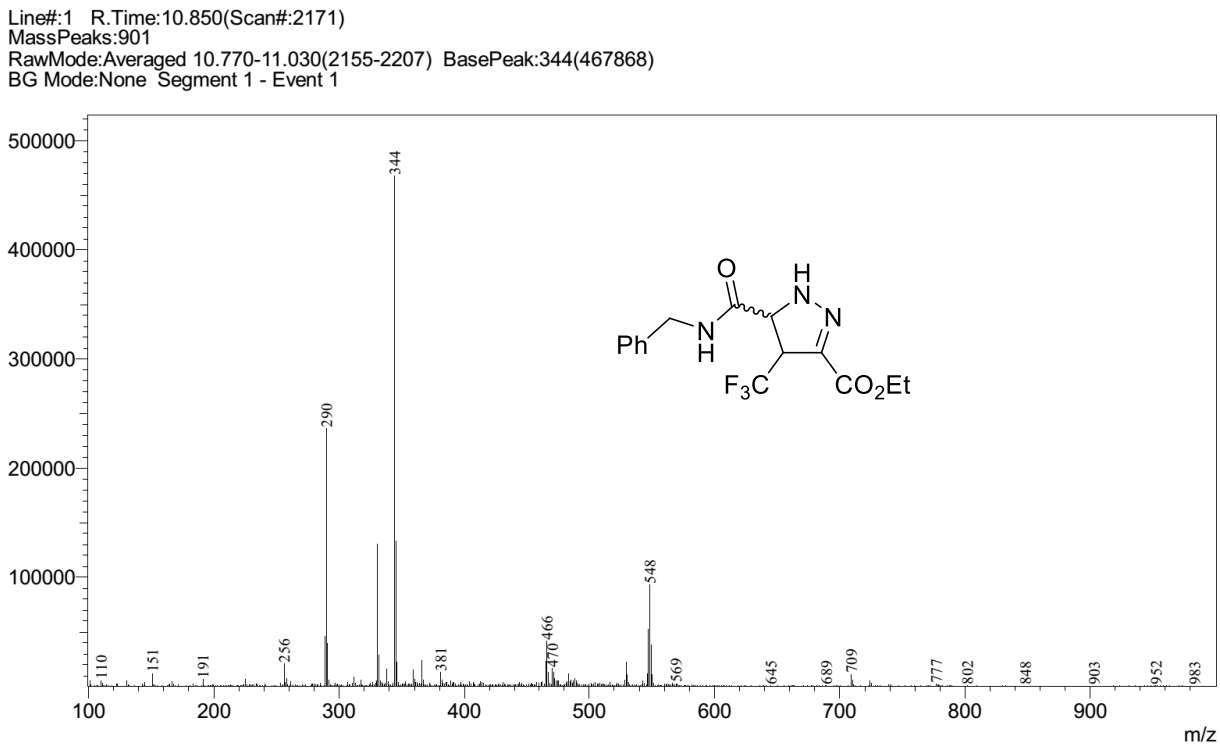
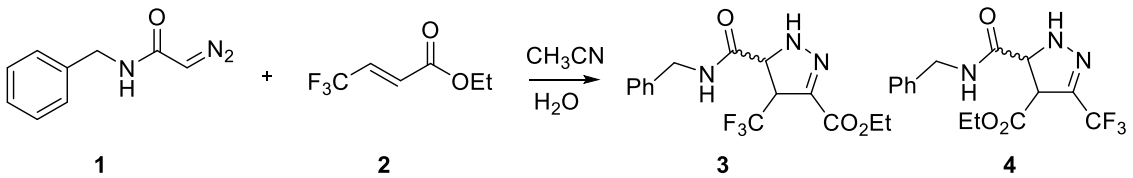
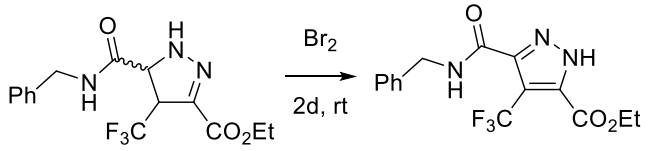


Figure S9. MS data for peak 4 (~10.9 min) from Figure S3, corresponding to an isomeric mixture of products from the cycloaddition of diazoacetamide **1** and trifluorocrotonate **2** (*M*, 343.3).

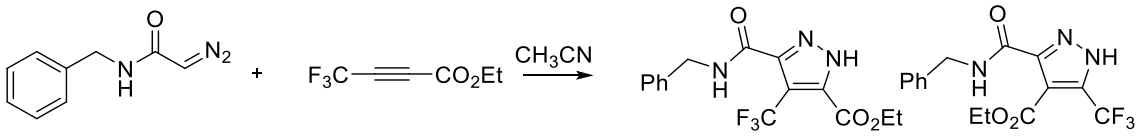
Chemical synthesis



Ethyl 5-(benzylcarbamoyl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (3): *N*-Benzyl-2-diazoacetamide (**1**) (31.8 mg, 0.18 mmol) was dissolved with stirring in 1.0 mL of CH_3CN, and 1.0 mL of water was added. Ethyl (*E*)-4,4,4-trifluorobut-2-enoate (**2**) (0.136 mL, 0.9 mmol) was added, and the reaction mixture was stirred overnight. The resulting solution was concentrated to dryness under high vacuum to provide the desired pyrazoline products as a mixture of isomers (62.5 mg, quant). Spectral characterization is provided for the major isomer (see HMBC for isomer determination). Ethyl 5-(benzylcarbamoyl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3**): ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.98 (s, 1H), 7.27-7.32 (m, 3H), 7.22 (d, J = 6.8 Hz, 2H), 7.14 (t, J = 5.8 Hz, 1H), 4.66 (dd, J = 5.4, 2.0 Hz, 1H), 4.47 (dd, J = 14.7, 5.9 Hz, 1H), 4.46–4.37 (m, 1H), 4.33 (dd, J = 14.6, 5.3 Hz, 1H), 4.19 (dq, J = 10.9, 7.1 Hz, 1H), 4.11 (dq, J = 10.8, 7.1 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, δ): 167.94, 161.48, 137.07, 134.82, 128.79, 127.89, 127.84, 124.39 (q), 64.15, 61.86, 51.75 (q), 44.08, 13.95. HRMS (ESI) calcd. for $C_{14}H_{17}N_3O_3$ $[M+H]^+$ 344.1217, found 344.1210.



Ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (6): Ethyl 5-(benzylcarbamoyl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate was oxidized using bromine for regioisomeric determination of pyrazoline product ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate.[2] The pyrazoline (0.032 mmol, 11.0 mg) was dissolved in 0.5 mL of DCM and cooled to 0 °C. Bromine (0.035 mmol, 1.8 µL) was added dropwise, and the reaction mixture was warmed to ambient temperature and stirred for 2 days. Sodium thiosulfate was added to the solution, and the organic layer was extracted with DCM. The resulting mixture was concentrated to dryness under high vacuum to provide the desired pyrazole product.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25–7.30 (m, 5H), 7.15 (t, J = 6.0 Hz, 1H), 4.57 (d, J = 5.8 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 159.50, 158.43, 137.25, 128.85, 127.93, 127.88, 124.43, 122.30, 120.16, 118.02, 112.25, 92.50, 62.90, 43.98, 13.92. HRMS (ESI) calcd. for $C_{14}H_{15}N_3O_3$ $[M+H]^+$ 342.1060, found 342.1057.



Synthesis of **ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (6):** *N*-benzyl-2-diazoacetamide (19.9 mg, 0.11 mmol) was dissolved in 0.25 mL of CH_3CN. Ethyl 4,4,4-trifluoro-2-butynoate (18.9 mg, 0.11 mmol) was added, and the resulting solution was stirred overnight. The resulting solution was concentrated to dryness, purified by column chromatography on silica gel (50% v/v EtOAc in hexanes) and concentrated to provide ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (**6**) as the major product (23.1 mg) and ethyl 5-(benzylcarbamoyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (**7**) as the minor product (2.1 mg). The regioisomeric ratio was determined by ^{1}H NMR from the crude reaction mixture to be 7.5:1. Major product, ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (**6**): ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25–7.30 (m, 5H), 7.15 (t, J = 6.0 Hz, 1H), 4.57 (d, J = 5.8 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 159.50, 158.43, 137.25, 128.85, 127.93, 127.88, 121.23 (q), 112.25, 92.50, 62.90, 43.98, 13.92. HRMS (ESI) calcd. for $C_{14}H_{15}N_3O_3$ $[M+H]^+$ 342.1060, meas. 342.1057. Minor product, ethyl 3-(benzylcarbamoyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (**7**): ^{1}H NMR (500 MHz, $CDCl_3$, δ): 10.49 (s, 1H), 7.41–7.28 (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). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 163.74, 156.98, 141.17, 137.20, 128.94, 127.93, 127.83, 109.74, 62.82, 44.00, 13.71. HRMS (ESI) calcd. for $C_{14}H_{15}N_3O_3$ $[M+H]^+$ 342.1060, found 342.1060.

NMR spectra of synthetic compounds

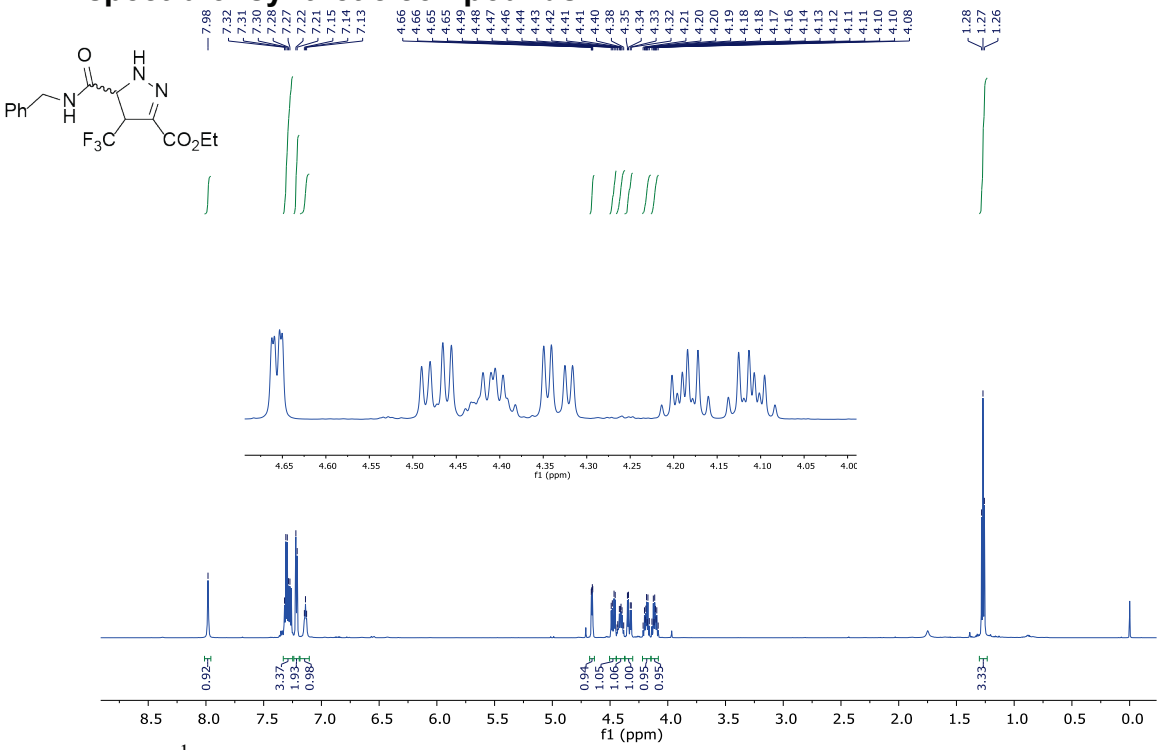


Figure S10. ^{1}H NMR spectrum of ethyl 5-(benzylcarbamoyl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole-5-carboxylate (**3**) (600 MHz).

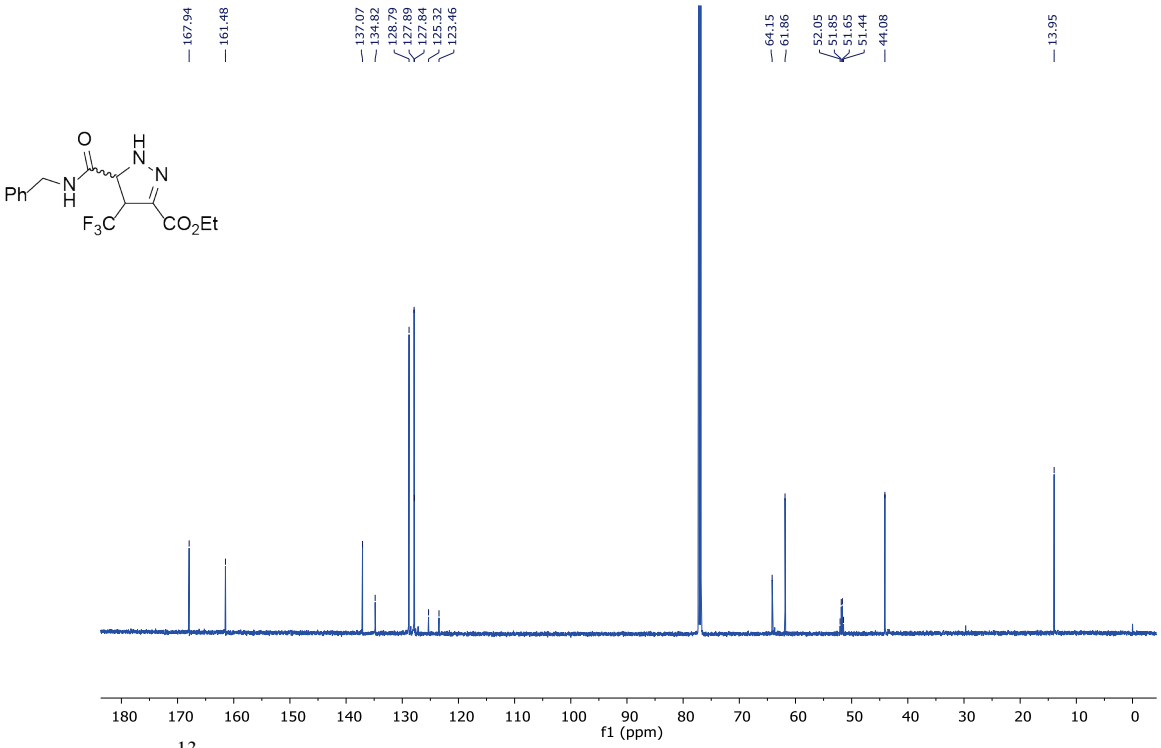


Figure S11. ^{13}C NMR spectrum of ethyl 5-(benzylcarbamoyl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole-5-carboxylate (**3**) (600 MHz).

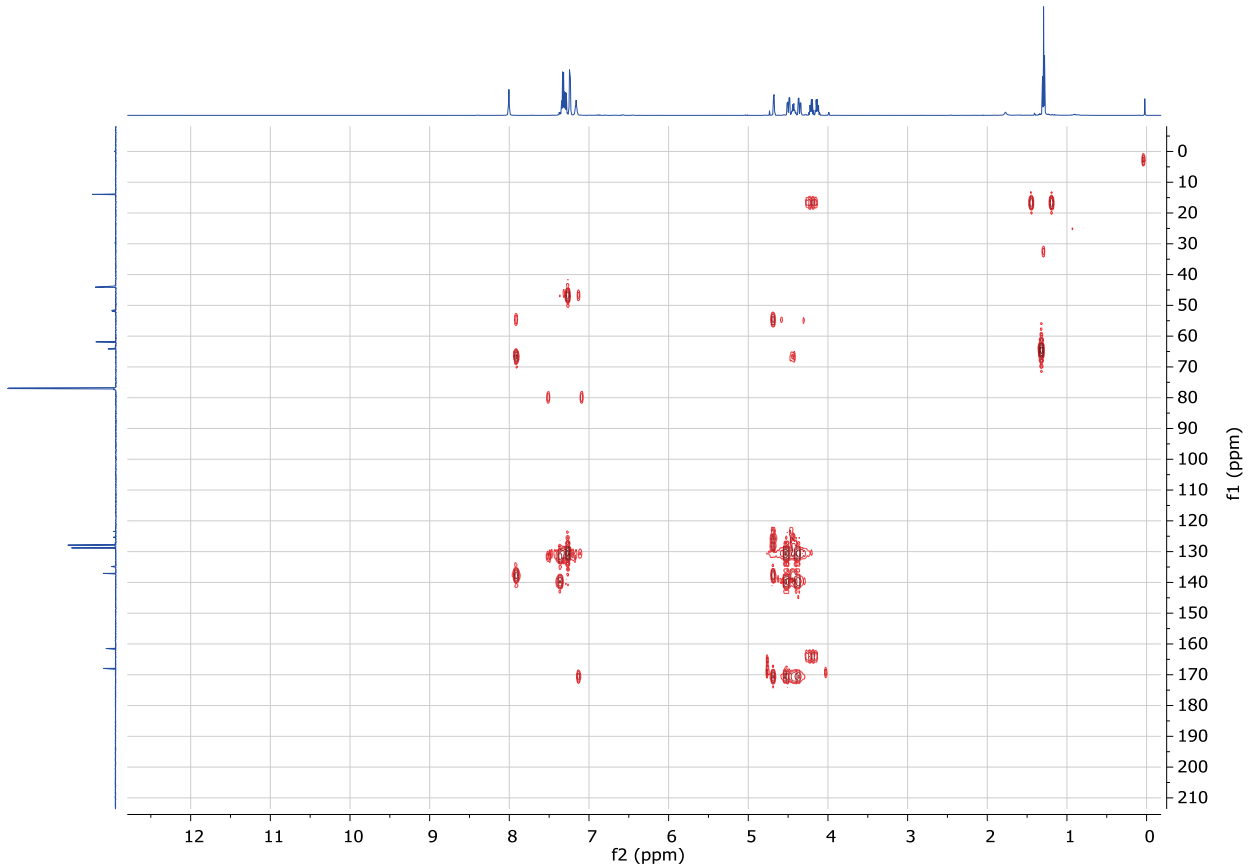


Figure S12. HMBC NMR spectrum of ethyl 5-(benzylcarbamoyl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole-5-carboxylate (**3**) (600 MHz).

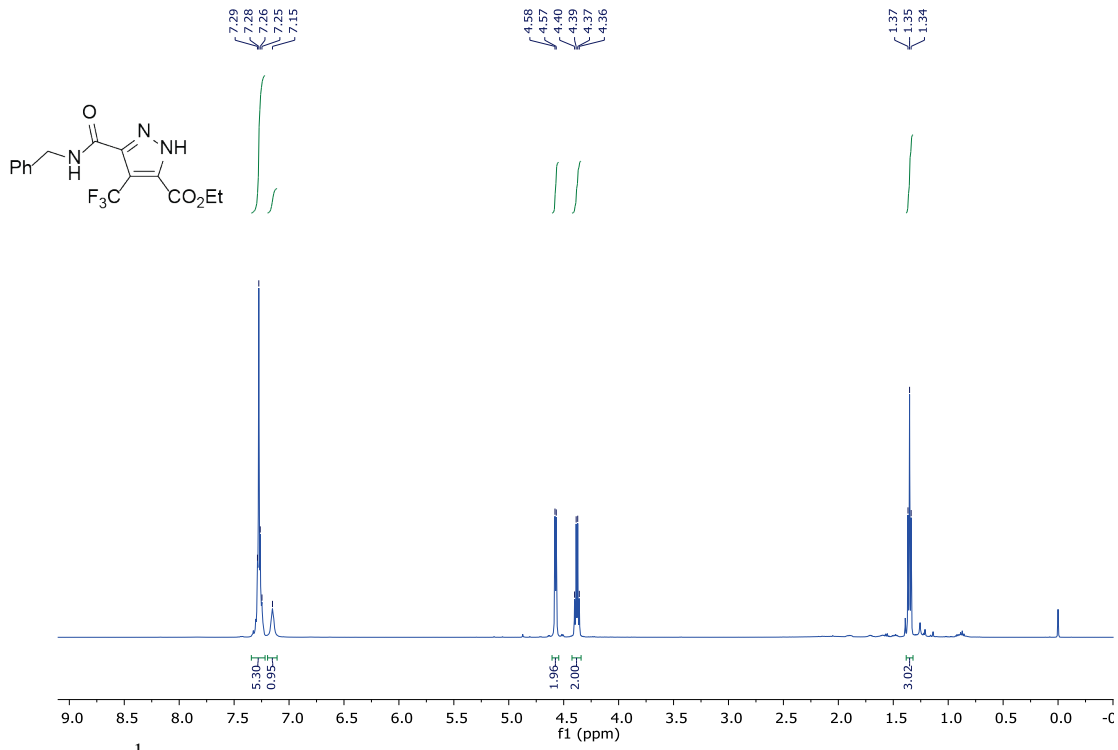


Figure S13. ^{1}H NMR spectrum of ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (**6**) (500 MHz).

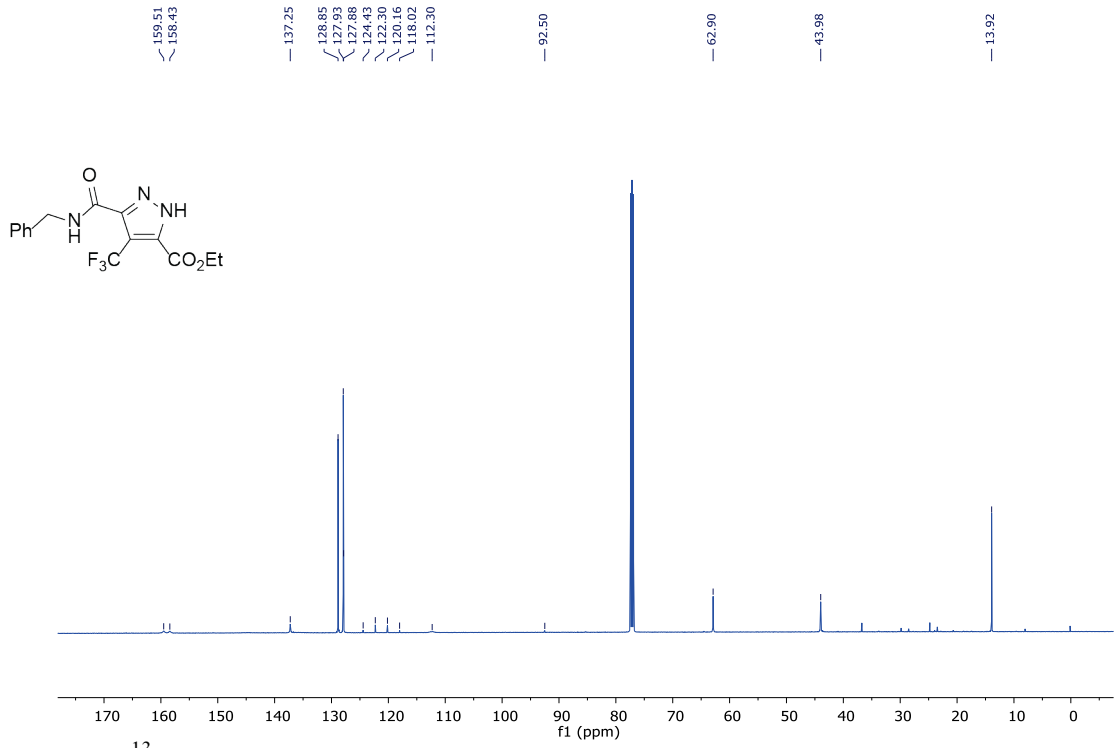


Figure S14. ^{13}C NMR spectrum of ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (**6**) (126 MHz).

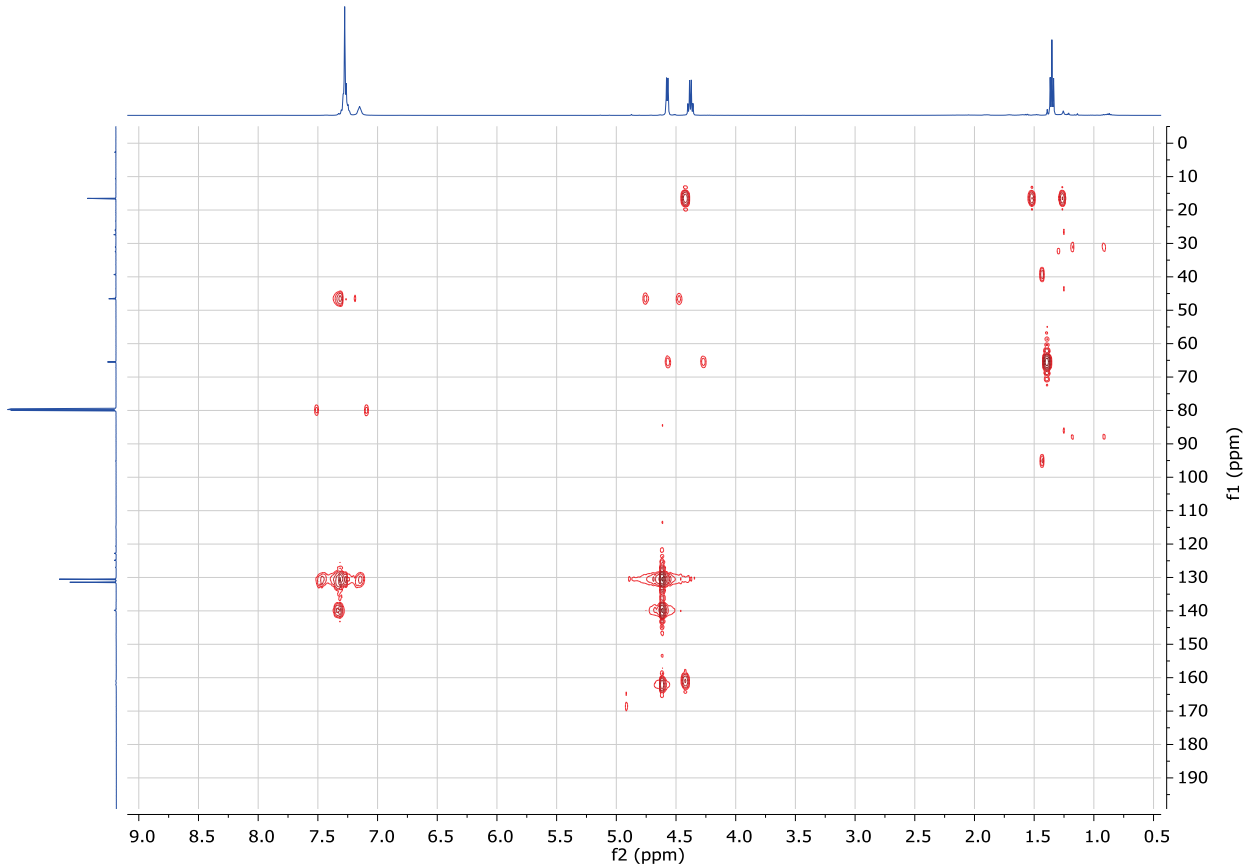


Figure S15. HMBC NMR spectrum of ethyl 3-(benzylcarbamoyl)-4-(trifluoromethyl)-1*H*-pyrazole-5-carboxylate (**6**) (126 MHz).

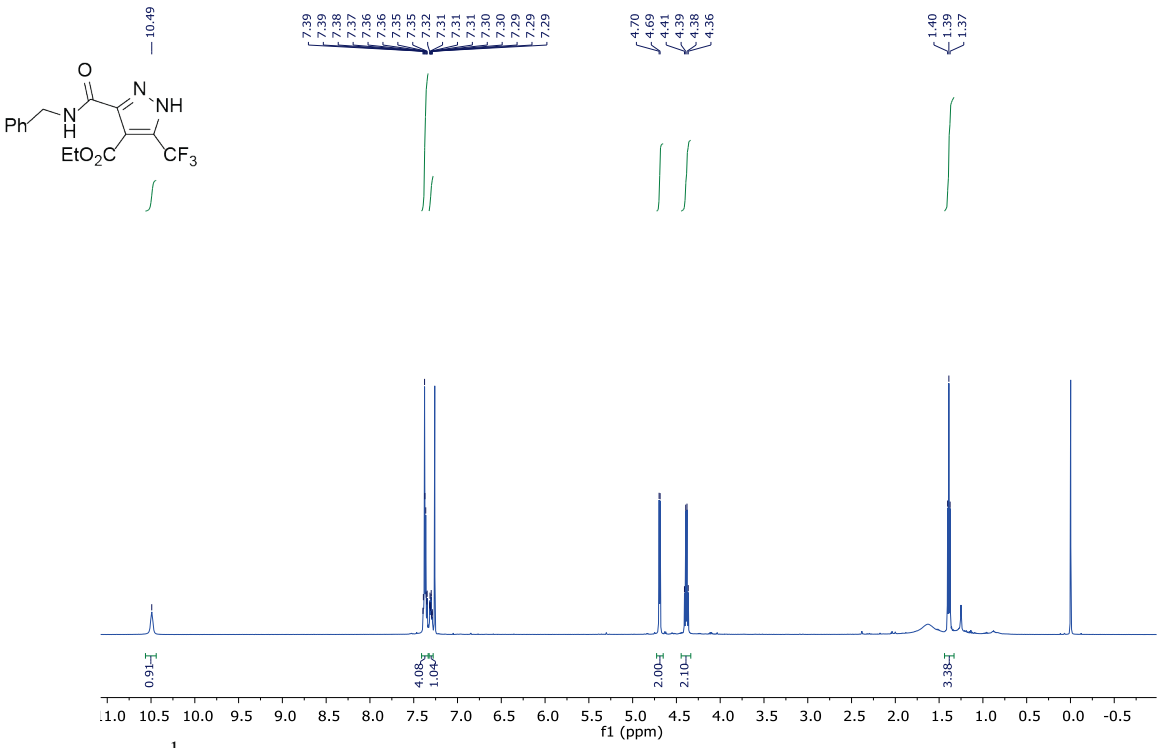


Figure S16. ^{1}H NMR spectrum of ethyl 3-(benzylcarbamoyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (**7**) (500 MHz).

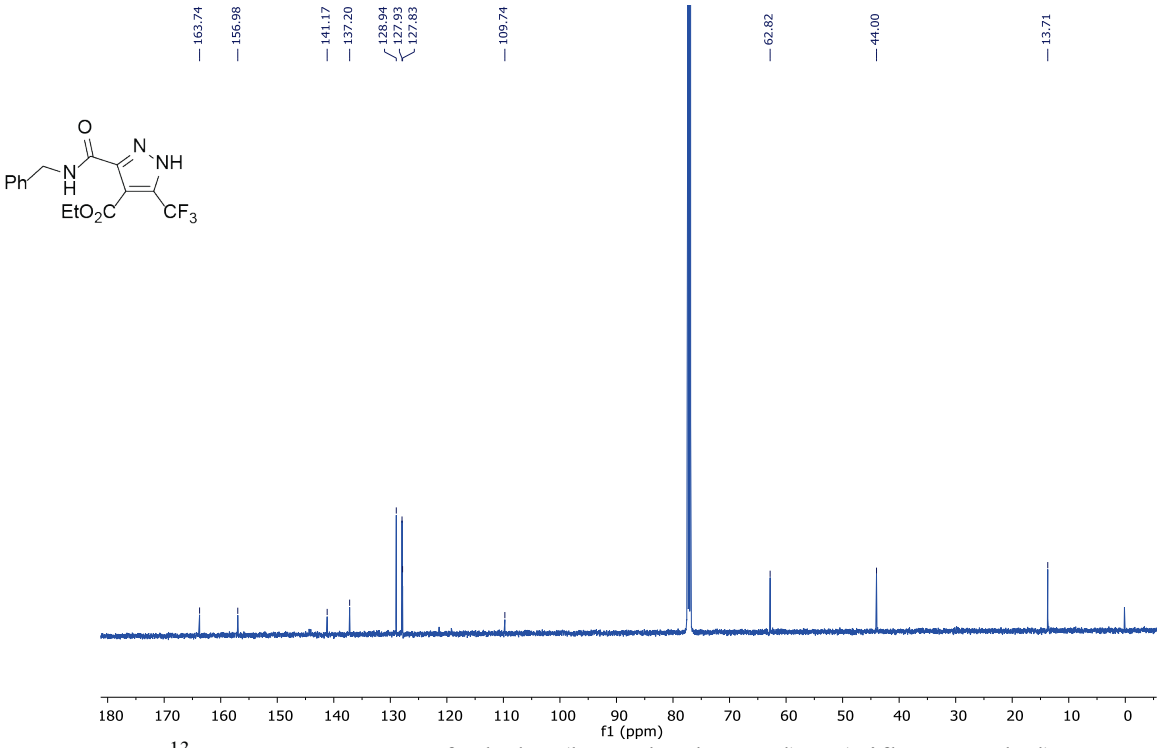


Figure S17. ^{13}C NMR spectrum of ethyl 3-(benzylcarbamoyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (**7**) (500 MHz).

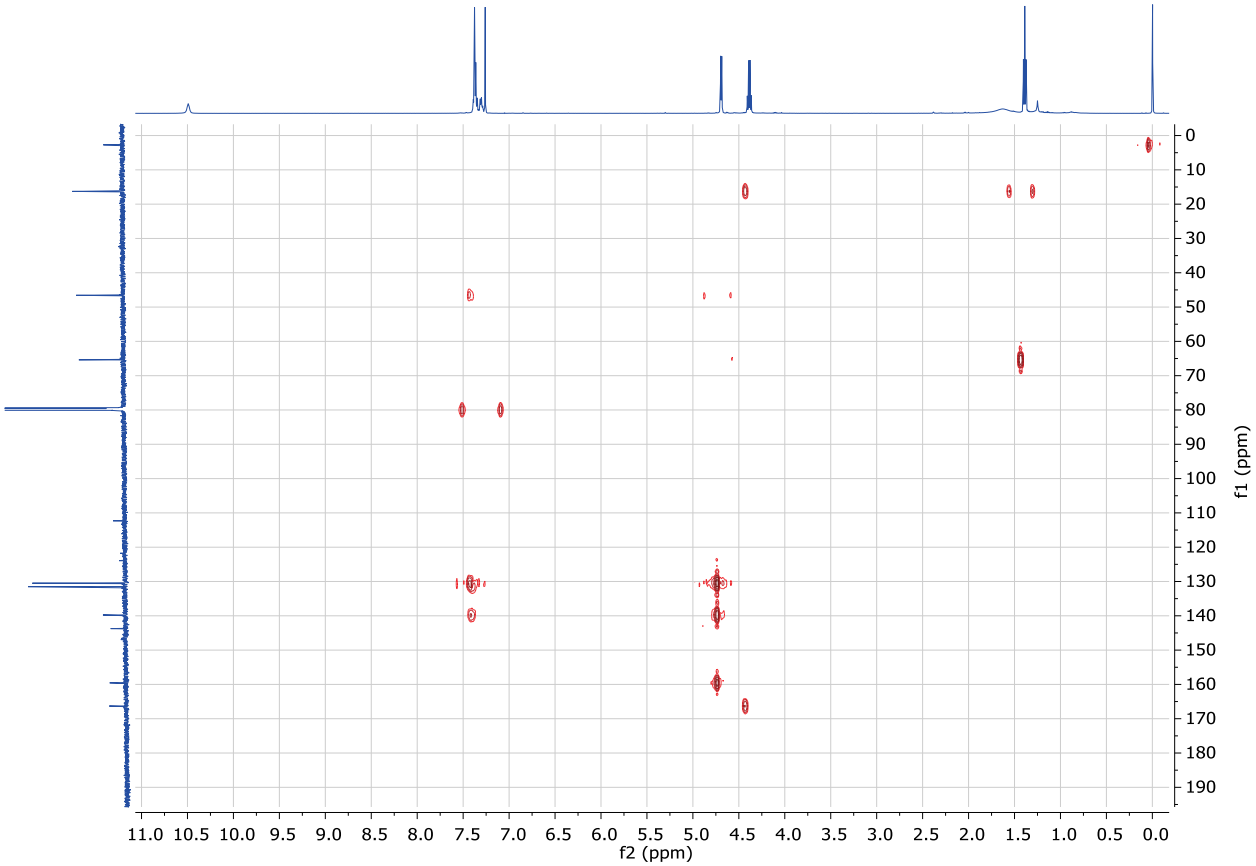
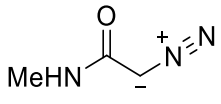


Figure S18. HMBC NMR spectrum of ethyl 3-(benzylcarbamoyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (**7**) (500 MHz).

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

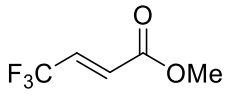
All energies include IEFPCM single point corrections. TS frequencies are from gas-phase optimized structures.



(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: –356.6537399
Sum of electronic and zero-point Energies: –356.564577
Sum of electronic and thermal Energies: –356.556859
Sum of electronic and thermal Enthalpies: –356.555915
Sum of electronic and thermal Free Energies: –356.596660



(GS)

C	0.35058000	–0.35213600	0.00006900
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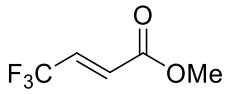
C	1.72695700	0.21684300	0.00001500
O	1.98587100	1.39098000	0.00005700
O	2.64383700	–0.75539400	–0.00010100
C	4.00079500	–0.30621600	0.00000600
H	4.19632700	0.29618200	0.88911000
H	4.60968000	–1.20773500	0.00128000
H	4.19712200	0.29406300	–0.89036900
H	0.24354600	–1.43050000	0.00009400
H	–0.56302600	1.54520200	0.00007600
C	–2.10273600	–0.02318400	0.00004700
F	–2.18803500	–1.35700500	0.00023200
F	–2.76314200	0.42302100	–1.07754300
F	–2.76338400	0.42332400	1.07719500

HF: –643.3352657
Sum of electronic and zero-point Energies: –643.233741
Sum of electronic and thermal Energies: –643.223845
Sum of electronic and thermal Enthalpies: –643.222901
Sum of electronic and thermal Free Energies: –643.270739

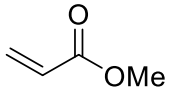


(TS)

C	–1.35681800	0.71409600	0.10830800
C	–0.04374300	0.76649000	–0.31198900
C	1.75038000	–1.46150400	0.39546300
N	0.06244300	–0.63767500	1.87773500
N	–1.06107100	–0.56635300	2.00731000
O	1.31791100	–2.59020900	0.47887200
C	–2.23222700	–0.31037300	–0.47995100
O	–1.85895000	–1.20061500	–1.20562400
O	–3.50896500	–0.15136800	–0.09841300
C	–4.41248400	–1.13631700	–0.59770000
H	–4.11167300	–2.13044400	–0.26100700
H	–5.38886300	–0.87198900	–0.19528700
H	–4.42781100	–1.11876500	–1.68931600
H	–1.81293900	1.51343800	0.67886500

N	2.81398300	–1.10792700	–0.36455000
H	3.01742500	–0.12892400	–0.49535100
C	3.44134200	–2.09300900	–1.22717500
H	2.77315300	–2.39434200	–2.03925200
H	4.35325600	–1.66482400	–1.64283600
H	3.69230900	–2.97941800	–0.64270200
C	1.11545300	–0.29853300	1.10937100
H	1.76267200	0.43395500	1.58513500
H	0.23946400	0.15344700	–1.16423100
C	0.69435500	2.06263100	–0.21211600
F	0.52714000	2.65397800	0.98058100
F	0.31439000	2.94017300	–1.14522100
F	2.03158300	1.90009400	–0.37774200

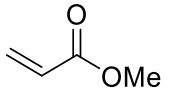
HF: –999.971634
Sum of electronic and zero-point Energies: –999.778892
Sum of electronic and thermal Energies: –999.761207
Sum of electronic and thermal Enthalpies: –999.760263
Sum of electronic and thermal Free Energies: –999.826272
Frequencies: –441.6732



(GS)

C	–0.03943800	0.10894500	–0.00045300
C	–1.31631500	–0.64908900	0.00001900
H	–1.24516000	–1.73078400	0.00023500
O	0.06165800	1.30836100	–0.00002800
C	–2.47544300	–0.00003800	0.00018800
H	–2.48947600	1.08560000	–0.00002100
H	–3.42123200	–0.52963600	0.00055100
O	1.01362000	–0.72245000	–0.00029400
C	2.28779800	–0.07991200	0.00031900
H	3.02378500	–0.88171200	0.00045600
H	2.39545500	0.54505300	–0.88867200
H	2.39478700	0.54476300	0.88959100

HF: –306.3696751
Sum of electronic and zero-point Energies: –306.273754
Sum of electronic and thermal Energies: –306.267156
Sum of electronic and thermal Enthalpies: –306.266212
Sum of electronic and thermal Free Energies: –306.304261

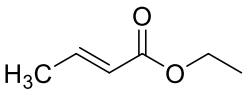


(TS)

C	–1.11363000	–0.29192500	0.94871500
C	0.00811400	–1.02448700	0.60594500
H	0.80472000	–1.13049600	1.33572500

H	–0.12466300	–1.84654300	–0.09119500
C	2.41406300	0.32184000	–0.12295500
N	0.28593100	1.19921400	–0.74069500
N	–0.64180300	1.65735400	–0.27764800
O	2.61332000	1.22005900	0.66961600
C	–2.31689100	–0.44910600	0.13202500
O	–2.35069200	–0.99585400	–0.95064800
O	–3.40027700	0.11283600	0.69726800
C	–4.59467600	0.02812400	–0.07387700
H	–4.86394800	–1.01605000	–0.24740200
H	–5.36285700	0.52993600	0.51230100
H	–4.46187800	0.52385300	–1.03803500
H	–1.18878900	0.26022000	1.87552800
N	3.33552500	–0.62536900	–0.42952400
H	3.08120400	–1.38412800	–1.04045700
C	4.60668800	–0.66716100	0.26856400
H	4.49388900	–1.05432500	1.28577700
H	5.29496600	–1.30375100	–0.28762000
H	5.01501100	0.34250200	0.32766000
C	1.08466800	0.11210400	–0.77540200
H	1.02595400	–0.41227100	–1.72518000

HF: –663.0040822
Sum of electronic and zero-point Energies: –662.816847
Sum of electronic and thermal Energies: –662.803260
Sum of electronic and thermal Enthalpies: –662.802316
Sum of electronic and thermal Free Energies: –662.858483
Frequencies: –511.6685

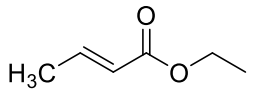


(GS)

C	–0.76910600	–0.46887500	0.00013700
C	–1.86802800	0.28367600	0.00047200
H	–1.73414900	1.36437800	0.00051200
C	0.56804700	0.16525400	–0.00010100
O	0.78772200	1.35009400	–0.00021900
O	1.54116200	–0.76264600	–0.00011800
C	2.86855600	–0.24192000	0.00015800
H	3.03454000	0.37276500	0.88744400
H	3.52716300	–1.10859000	0.00326800
H	3.03664500	0.36763200	–0.89026200
H	–0.80311600	–1.55341100	–0.00033300
C	–3.26458000	–0.24454100	–0.00012300
H	–3.80860800	0.11638200	–0.87910800
H	–3.28336100	–1.33638200	–0.00046700
H	–3.80952800	0.11607100	0.87838100

HF: –345.673176

Sum of electronic and zero-point Energies: –345.549053
Sum of electronic and thermal Energies: –345.540960
Sum of electronic and thermal Enthalpies: –345.540016
Sum of electronic and thermal Free Energies: –345.581686



(TS)

C	1.27747200	–0.79766900	–0.58805600
C	0.07728300	–1.15143000	0.01667100
H	0.12229900	–1.32063900	1.09053700
C	–2.30613300	0.53337900	–0.03106000
N	–0.13128200	1.43143500	–0.47188700
N	0.78962300	1.41425400	–1.13494400
O	–2.68134400	0.68534900	–1.17711200
C	2.35177300	–0.29555500	0.25933600
O	2.20051900	0.09315800	1.40145200
O	3.54148300	–0.25587400	–0.36778900
C	4.61120300	0.28584400	0.40040100
H	4.76890500	–0.30340800	1.30641000
H	5.48924000	0.24326700	–0.24211300
H	4.39301000	1.31816000	0.68290400
H	1.49823500	–1.04376600	–1.61894300
N	–3.12486100	0.11004800	0.96469000
H	–2.78490800	0.07424000	1.91119500
C	–4.51625400	–0.18832900	0.68525000
H	–4.58505100	–0.91279900	–0.13000300
H	–4.97301200	–0.60770400	1.58162800
H	–5.05855700	0.71300600	0.38721400
C	–0.87785100	0.67891900	0.37308600
H	–0.63337000	0.90660100	1.40861900
C	–0.93307000	–1.96421700	–0.75851900
H	–1.89717900	–2.01892800	–0.24671400
H	–1.10190100	–1.53776700	–1.75097800
H	–0.56387800	–2.98713700	–0.87983200

HF: –702.3020037
Sum of electronic and zero-point Energies: –702.086005
Sum of electronic and thermal Energies: –702.070388
Sum of electronic and thermal Enthalpies: –702.069443
Sum of electronic and thermal Free Energies: –702.129681
Frequencies: –525.4007

References and notes

1. Aronoff, M. R.; Gold, B.; Raines, R. T. *Org. Lett.* **2016**, *18*, 1538–1541.
2. Slobodyanyuk, E. Y.; Artamonov, O. S.; Shishkin, O. V.; Mykhailiuk, P. V. *Eur. J. Org. Chem.* **2014**, 2487–2495.