Electronic Supplementary Material (ESI) for ChemComm.

A Vinylogous Norrish Reaction as a Strategy for Light-Mediated Ring Expansion

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Supporting Information

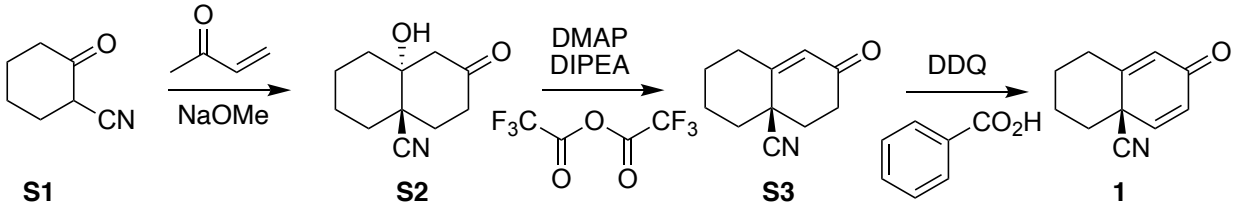
I. Materials and general methods

Infrared spectra were recorded on a Nexus 470 FT-IR spectrometer. Solid samples were handled as pressed KBr pellets or as CCl_4 thin films while liquid samples were analyzed neat between KBr plates. ^1H and ^{13}C NMR spectra were recorded on Bruker RDQ-400 (BBFO probe), Bruker DRX-400 (BBO probe), Bruker DRY-400 (BBO probe), or Bruker CFI-600 spectrometers (BBO probe). Spectra were obtained in $CDCl_3$ and the chemical shifts (ppm) are relative to the $CHCl_3$ peaks (7.27 ppm for ^1H-NMR and 77.0 ppm for ^{13}C-NMR). For the photochemical reaction studies C_6D_6 and CD_3CN were used as NMR solvents. GenTech 5890 Series II SSQ 7000 and Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS instruments were used for LR MS and HR MS analyses respectively at the University of Calgary. Elemental analyses were performed on PerkinElmer Series II CHNS/O 2400 instrument at the University of Calgary. X-ray structure determination was performed at the University of Calgary, using a Nonius Kappa APEX2 CCD (Mo sealed tube (2.0 kW), 4-circle Kappa-geometry goniometer) and Bruker SMART APEX2 CCD (Cu sealed tube (1.5 kW), 3-circle fixed Chi goniometer) both using APEX2 1k CCD X-ray detector. All melting points are uncorrected. Boiling points are uncorrected and refer to measured air-bath temperatures using a Kugelrohr short path distillation apparatus. Anhydrous solvents were prepared by standard methods (Na/benzophenone for THF, LAH for ether and CaH_2 for DCM, CH_3CN, HMPA and benzene). “DriSolv” EMD Millipore grade DMF was used. Chloroform stored over K_2CO_3 was used for work with acid sensitive compounds. A LZC-4V photoreactor (Luzchem Research Inc.) was used for irradiation of the divinyl ketones and equipped with:

1. 14x8W Hitachi FL8BL-B lamps (1.2W UV Output) for UV-A irradiation (315-400 nm with 365 nm spectral peak)
2. 14x7.2W USHIO G8T5 lamps (2.2W UV Output) for UV-C irradiation (200-280 nm with 254 nm spectral peak)

A 5 mm *Wilmad*® quartz NMR tube was used for simultaneous samples irradiation and the reaction monitoring when small amounts (less than 10 mg) of the irradiated starting materials were used. A 4 mL or 9 mL cylindric quartz cuvette was used for the irradiation up to 400 mg of starting materials. 100 or 200 mL quartz round bottom flasks were used for reactions up to 5 g.

Preparation of the substrate **1** for irradiation experiments



(4a*S*,8a*R*)-8a-hydroxy-2-oxodecahydronaphthalene-4a-carbonitrile (S2). To a solution of 1-cyano-cyclohexanone (**S1)**[1] (18.87 g, 153 mmol) and methylvinylketone (13.4 g, 15.6 mL, 191 mmol) in dry benzene (300 mL) at ambient temperature was added a freshly prepared solution of NaOMe (6.25 mL, 15 mmol, 2.4 M) in methanol over 5 minutes. The mixture was stirred for 2 hours (until the starting nitrile and intermediate Michael addition products were consumed by ^{1}H NMR spectroscopy). A solution of NH_4Cl (aq, sat., 20 mL), water (10 mL) and Et_2O (40 mL) were added to the reaction mixture and stirred vigorously for 15 minutes. The white powder was removed by filtration, washed with benzene (2x30 mL), water (2x25 mL) and dried *in vacuo* to yield 16.67 g of the target product **S2**. The combined biphasic liquor was separated, and the aqueous layer was extracted with $CHCl_3$ (3x75 mL). The combined organic extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was subjected to SiO_2 column chromatography (800 g, 25 - 40% Et_2O in $CHCl_3$) furnishing an additional amount of **S2** (1.12 g, 60% combined yield) and 7.6 g (26% yield) of the target product **S3** of 95% purity**.**

S2: mp: 186-187 °C ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (d, *J*=14.9 Hz, 1H), 2.76 (dt, *J*=13.9 Hz, *J*=6.7 Hz, 1H), 2.55-2.48 (m, 1H), 2.36 (dd, *J*=15.2 Hz, *J*=2.3 Hz, 1H), 2.23 (dt, *J*=13.6 Hz, *J*=4.8 Hz, 1H), 2.08-1.95 (m, 3H), 1.88-1.55 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5 (C=O), 122.3 (CN), 74.0 (C), 52.8 (CH_2), 43.5 (C), 38.6 (CH_2), 36.1 (CH_2), 31.7 (CH_2), 30.7 (CH_2), 22.5 (CH_2), 23.3 (CH_3), 19.6 (CH_2); IR (film, cm^{-1}) 3369, 2934, 2861, 2233, 1705, 1453, 1413, 1197, 997, 971; LRMS (EI) 193 [M^+] (80), 175 (10), 166 (18), 150 (17), 136 (100), 124 (80), 108 (48), 93 (22), 81 (21), 71 (32), 58 (53), 47 (62); Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.01, H, 7.73; N, 7.15.

7-oxo-1,2,3,4,4a,5,6,7-octahydronaphthalene-4a-carbonitrile (S3). To a solution of alcohol **S2** (17.71 g, 91.8 mmol), DMAP (12.2 g, 100 mmol) and diisopropylethylamine (DIPEA) (46.6 g, 64 mL, 367 mmol) in DCM (400 mL) at 0 °C was added trifluoroacetic anhydride (TFAA) (42 g, 28 mL, 200 mmol). After 15 minutes, the reaction mixture was allowed to warm to ambient temperature and was stirred for 16 hours. All the volatile components were removed *in vacuo* and the residue was diluted with toluene (360 mL) and

[1] The compound was prepared from 1,5-dicianopentane according to the published procedure: Dehli, J.R.; Gotor, V. *J. Org. Chem.* **2002**, *67*, 6816-19.

after 30 minutes of stirring at ambient temperature the mixture was refrigerated. After 12 hours the white powder (ca. 26 g, consisted mostly of TFA*DMAP and TFA*DIPEA salts) was removed by filtration. The filtrate was diluted with Et_2O (300 mL) and toluene in the amount enough to get ca. 1000 ml of total volume. The solution was passed through SiO_2 plug (300 g) to remove polar impurities. An additional amount (300 mL) of the 30% Et_2O/toluene mixture was used to remove all of the target product from the SiO_2. The solvents were removed *in vacuo* and crystallization of the residue (21.7 g) from 5% hexanes/EtOAc mixture, (500 mL, slow cooling technique) furnished 11.9 g of the target **S3**. SiO_2 column chromatography (500 g, 4 - 6% Et_2O in $CHCl_3$) of the concentrated mother liquor gave an additional 4.7 g of **S3** of 95% purity. It was combined with the product (7.6 g) of the same quality from previous step and recrystallized from 5% hexanes/EtOAc mixture to furnish 7.4 g of pure **S3** (19.3 g in total, 73% yield after 2 steps).

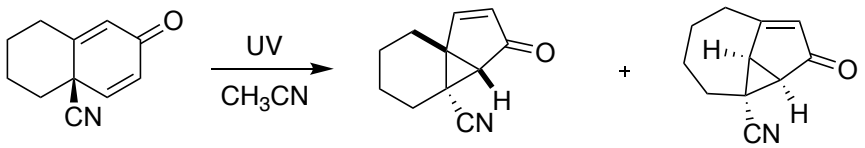
S3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96(s, 1H, CH=C), 2.73-2.64 (m, 1H), 2.56-2.48 (m, 3H), 2.43 (ddd, *J*=13.8 Hz, *J*=8.3 Hz, *J*=4.7 Hz, 1H), 2.30 (dq, *J*=11.5 Hz, *J*=2.4 Hz, 1H), 2.05-1.96 (m, 2H), 1.94-1.85 (m, 2H), 1.54-1.38 (m, 2H). All other data are in agreement with the literature.[2]

7-oxo-1,2,3,4,4a,7-hexahydronaphthalene-4a-carbonitrile (1). To a solution of **S3** (10.45 g, 59 mmol) in dry chlorobenzene (200 mL) was added benzoic acid (14.4 g, 120 mmol) followed by DDQ (24 g, 106 mmol) and the mixture was stirred at 88°C for 24 hours. After cooling down to ambient temperature, the solid by-products were removed by filtration and the organic solution was concentrated *in vacuo* and the residue was redissolved in EtOAc (300 mL) and the solution was washed with a 1:1 mixture (5x80 mL) of $NaHCO_3$ (aq, sat) solution and water to remove the leftover benzoic acid and most of the corresponding hydroquinone byproduct. After drying over Na_2SO_4 and filtering, the organic solution was concentrated *in vacuo* and the residue was redissolved in toluene (200 mL) and subjected to two consecutive SiO_2 column purifications (500 g, 20 - 30% Et_2O in toluene and 400 g, 30% EtOAc in hexanes) to furnish 8.25 g (79% yield) of the target **1** as a yellow oil solidifying upon storage.

1: mp: 42-43°C; UV-Vis: 229.0 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J*=9.8 Hz, 1H, C<u>H</u>=CH), 6.40 (dd, *J*=9.8 Hz, *J*=1.7 Hz, 1H, CH=C<u>H</u>), 6.24 (s, 1H, CH=C), 2.68-2.55 (m, 2H), 2.53-2.45 (m, 1H), 2.16-2.10 (m, 1H), 2.10-1.90 (m, 2H), 1.51-1.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4 (C=O), 156.3 (<u>C</u>=CH), 143.8 (<u>C</u>H=CH), 130.1 (CH=C), 125.8 (C=<u>C</u>H), 117.1 (CN), 41.0 (C), 39.3 (CH_2), 33.3 (CH_2), 29.2 (CH), 27.4 (CH_2), 22.5 (CH_2); IR (film, cm^{-1}) 2940, 2860, 2229, 1665, 1635, 1609, 1446, 1393, 1260, 878; LRMS (EI) 173 $[M]^+$ (100), 158 (44), 144 (71), 130 (64), 117 (69), 103 (59), 89 (25), 76 (22), 67 (20); LRMS (CI) 174 $[M+H]^+$; Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.08, H, 6.39; N, 8.19.

[2] Liu, H-J.; Ly, T-W.; Tai, C-L.; Wu, J-D.; Liang, J-K.; Guo, J-C.; Tseng, N-W.; Shia, K-S. *Tetrahedron* **2003**, *59*, 1209-1226.

Irradiation of **1**



1 **2** **3**

3-oxo-3a,3b,4,5,6,7-hexahydro-3H-cyclopenta[1,3]cyclopropa[1,2]benzene-3b-carbonitrile (2) and 2-oxo-2,2a,2a1,2b,3,4,5,6-octahydrocyclopropa[cd]azulene-2b-carbonitrile (3). A solution of **1** (3.33 g, 19.2 mmol) in dry CH_3CN (90 mL) in a quartz flask (200 mL) was irradiated under stirring in (UV-C LZC-4V photoreactor) for 6 hours. A solution containing **1**, **2** and **3** in 1:1:1 ratio (by ^{1}H NMR) was concentrated, and the residue was redissolved in 20% Et_2O in benzene mixture (100 mL) and passed through short plug of SiO_2 (50 g) to eliminate polar by-products. An additional amount (200 mL) of the same solvent mixture was used to take off all the valuable compounds from SiO_2. The combined solution was concentrated and the residue (3.10 g) was redissolved in CH_3CN (90 mL) and UV-C irradiated for 6 additional hours to give a solution containing **1**, **2** and **3** in a 0.4:1.25:1 ratio (by ^{1}H NMR, 85% conversion). According to TLC (Silica gel, 7% Et_2O in benzene) the reaction mixture showed two spots with R_f 0.45 and 0.35 (after 3 runs). The first spot (R_f 0.45) represented target product **2**. The second spot consisted of two components, namely, starting material **1** and target product **3**. The reaction mixture was concentrated and purified using SiO_2 column chromatography (450 g, 7 - 9% Et_2O in benzene[3]) which furnished 1.17 g of the target product **2** (35%) and 1.63 g of the mixture containing **1**, **2** and **3** in a 0.37:0.10:1.0 ratio. In order to separate the starting material from the target products (mostly **3**) in this mixture, column chromatography exploiting aluminum oxide instead of silica gel was used. The Et_2O/Benzene system for chromatography was also substituted with $CHCl_3$/hexanes. According to TLC (aluminum oxide, 1:1 $CHCl_3$/hexanes) the second combined fraction from the previous chromatography showed two spots with R_f 0.41 and 0.35 (after 3 runs). The first spot (R_f 0.41) represented the starting material **1**. The second spot consisted of target product **3** contaminated with target product **2**. So that the mixture was forwarded to the aluminum oxide column chromatography (450 cm^3, 1:1 - 2:1 $CHCl_3$/hexanes) to furnish 0.38 g of the starting material **1**, 0.25 g of the mixed fraction and 0.93 g of the target product **3** (27%) containing ca. 1 % of **1**. Recrystallization from hexane/EtOAc gave analytically pure sample.

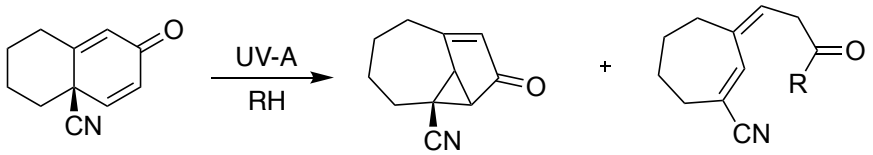
2: viscous oil; UV-Vis: 223.3, 260.9 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J*=5.6 Hz, *J*=1.1 Hz, 1H, CH=CH), 6.00 (dd, *J*=5.6 Hz, *J*=1.1 Hz, 1H, CH=CH), 2.35-2.26 (m, 1H), 2.25-2.08 (m, 2H), 2.20 (s, 1H), 1.98-1.91 (m, 1H), 1.63-1.55 (m, 1H), 1.51-1.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1 (C=O), 162.7 (<u>C</u>H=CH), 131.2 (CH=C<u>H</u>), 119.9 (CN), 40.6

[3] Benzene can be substituted by toluene however benzene produces consistently better separation on silica gel than toluene.

(C), 39.2 (C), 38.3 (CH), 29.7 (CH_2), 23.1 (CH_2), 20.5 (CH_2), 19.9 (CH_2); IR (film, cm^{-1}) 3399, 3056, 2931, 2861, 2236, 1702, 1442, 1333, 1164, 878, 821, 742, 490; LRMS (EI) 173 [M^+] (100), 158 (8), 145 (12), 130 (8), 117 (10), 103 (7); HRMS (ESI) calcd. for $C_{11}H_{11}NO$ 173.0841, found 173.0842.

3: mp: 58-59 °C (Hexane/ EtOAc); UV-Vis: 220.0, 261.1, 330.2 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (s, 1H, CH=C), 3.21 (d, *J*=4.8 Hz, 1H, C^1H), 3.04-2.88 (m, 1H), 2.69 (d, *J*=4.8 Hz, 1H, C^2H), 2.38 (dd, *J*=15.4 Hz, *J*=7.0 Hz, 1H), 2.28 (dt, *J*=12.0 Hz, *J*=5.4 Hz, 1H), 2.17-2.15 (m, 1H), 2.01-1.95 (m, 1H),), 1.50 (dq, *J*=15.1 Hz, *J*=2.4 Hz, 1H), 1.39 (dd, *J*=11.9 Hz, *J*=10.6 Hz, 1H), 1.12-1.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4 (C=O), 172.7 (C=CH), 129.0 (CH=C), 120.6 (CN), 39.3 (CH), 37.9 (CH), 32.9 (C), 32.3 (CH_2), 29.1 (CH_2), 27.3 (CH_2), 25.9 (CH_2); IR (film, cm^{-1}) 3372, 3067, 2944, 2858, 2237, 1751, 1692, 1596, 1456, 1276, 1180, 1067, 1040, 908, 878, 566; LRMS (ESI) 196 [M+Na^+]; HRMS (ESI) calcd. for $C_{11}H_{11}NaNO$ 196.0733, found 196.0732; Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.18, H, 6.41; N, 8.21.

Table SI-1. Irradiation of **1** in the presence of varying nucleophiles



1 **A** **B**

Entry	Solvent, trap (eq.), time, conversion	R	**A**:**B** by ^{1}H NMR	*Z*:*E* for **B** by ^{1}H NMR	**A** and **B** isolated yield (respectively)
1	d-MeOH, d-MeOH (excess), 4 hr , 98%[a]	d-MeO	1:1.30	77:23	N/A
2	MeOH, MeOH (excess), 18 hr, 98%[b]	MeO	1:1.70	80:20	28% and 48%
3	d-CH_3CN, d-MeOH (20 eq.), 14 hr, 98%[a]	d-MeO	1:1.13	73:27	N/A
4	d-CH_3CN, d-MeOH (5 eq.), 15 hr, 98%[a]	d-MeO	1:0.98	76:24	N/A
5	d-CH_3CN, d-MeOH (3 eq.), 19 hr, 98%[a]	d-MeO	1:0.97	77:23	N/A

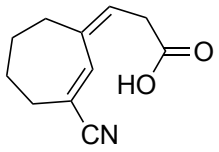
6	d-CH_3CN, D_2O (40 eq.), 12 hr, 98%[a]	OD	1:1.60	81:19	N/A
7	CH_3CN, H_2O (40 eq.), 19 hr, 97%[b]	OH	1:1.10	79:21	39% and 39%
8	d-CH_3CN, d-*t*-BuOH (20 eq.), 12 hr, 99%[a]	d-*t*-BuO	1:0.94	82:18	N/A
9	CH_3CN, *t*-BuOH (20 eq.), 28 hr, 99%[b]	*t*-BuO	1:1	83:17	46% and 33%
10	CH_3CN, Allyl alcohol (30 eq.), 21 hr, 99%[b]	AllylO	1:1	80:20	41% and 42%
11	CH_3CN, TMS-propargyl alcohol (4 eq.), 27 hs, 99%[b]	TMS-propargylO	1:1	83:17	36% and 49%
12	d-CH_3CN, Propargyl alcohol (4 eq.), 14 hr, 98%[a]	PropargylO	1:1.15	84:16	N/A
13	CH_3CN, Propargyl alcohol (4 eq.), 36 hr, 97%[b]	PropargylO	1:0.95	82:18	55% and 41%
14	d-CH_3CN, PhOH (4 eq.), 24 hr, 98%[a]	PhO	1:0.92	53:47	N/A
15	CH_3CN, PhOH (4 eq.), 57 hr, 85%[b]	PhO	1:0.81	75:25	49% and 32%
16	CH_3CN, Acetamide (4 eq.), 42 hr, 98%[b]	AcNH	1:0.69	84:16	67% and 24%
17	CH_3CN, Acrylamide (4 eq.), 44 hr, 75%[b]	AcrylNH	1:0.23	87:13	64% and 15%

[a] 10-20 mg (Quartz NMR tube). [b] 100-130 mg (Quartz cuvette);

n-$PrNH_2$, PhSH, $HSCH_2C(O)OH$ - complicated mixtures are formed.

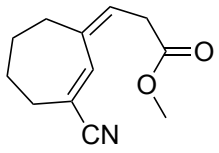
General Irradiation Procedure A

A solution of **1** (0.58 mmol, 100 mg) was combined with the respective alcohol or amine (see Table SI-1) in anhydrous CH_3CN and irradiated with UV-A light in a 9 mL quartz cuvette for the time indicated. The solvent and volatile components was removed *in vacuo* and the residue was purified by column chromatography to furnish the final product.



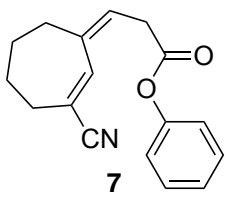
5

(*Z*)-3-(3-cyanocyclohept-2-en-1-ylidene)propanoic acid (5). General irradiation procedure A was followed to afford a viscous oil (39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 and 6.73 (s, 1H, CH=C), 5.76 and 5.64 (t, *J*=7.3 Hz, 1H, C=CH), 3.16 and 3.14 (d, *J*=7.5 Hz, 2H, $CH_2C(=O)$), 2.42-2.33 (m, 4H, CH_2), 1.78-1.65 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8 (C=O), 148.3 (CH),141.9 (CH), 140.4 (C), 138.9 (C), 128.4 (CH), 125.5 (CH), 121.4 and 121.1 (C), 116.7 (C), 113.5 (C), 35.3 (CH_2), 33.5 and 33.3 (CH_2), 30.5 and 30.2 (CH_2), 27.7 and 27.2 (CH_2), 26.4 and 26.3 (CH_2,) 25.0 (CH_2); IR (film, cm^{-1}) 3123, 2934, 2860, 2213, 1708, 1416, 1167; LRMS (ESI) 306 $[M-H]^-$; HRMS (ESI) calcd. for $C_{11}H_{12}NO_2$ 190.0874, found 190.0870.



6

(*Z*)-methyl 3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (6). General irradiation procedure A was followed to afford a viscous oil (48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H, CH=C), 5.74 (t, *J*=7.4 Hz, 1H, C=CH), 3.71 (s, 3H, CH_3O), 3.17 (d, *J*=7.4 Hz, 2H, $CH_2C(=O)$), 2.50-2.36 (m, 4H, CH_2), 1.80-1.70 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2 (C=O), 142.0 (CH), 138.4 (C), 126.5 (CH), 121.3 (C), 116.3 (C), 52.0 (CH_3), 35.3 (CH_2), 33.6 (CH_2), 30.5 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 2934, 2854, 2210, 1741, 1433, 1336, 1193, 1161; LRMS (ESI) 228 $[M+H]^+$; HRMS (ESI) calcd. for $C_{12}H_{15}NNaO_2$ 228.0995, found 228.0994.

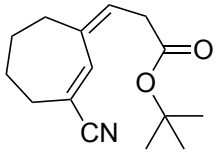


7

A solution of **1** (100 mg, 0.58 mmol) and phenol (223 mg, 2.32 mmol) in dry CH_3CN (5 mL) was irradiated using UV-A light in a 9 mL quartz cuvette for 48 hours (the reaction mixture consisted of **1**, **7**, and **3** in a 0.24:0.8[4]:1 ratio according to ^{1}H NMR). The solvent was removed *in vacuo* and the residue was stirred under *high vacuo* at ambient temperature for 3 hours to eliminate the excess phenol via sublimation. SiO_2 column chromatography (5 - 8% Et_2O in benzene) of the crude material furnished 11 mg of **7** and 37 mg of a 10:3 mixture of **7** and **7'** correspondingly (32% combined yield) and 49 mg (49% yield) of **3**.

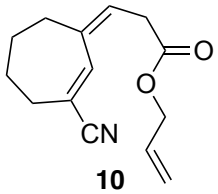
7: Viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dt, *J*=6.3 Hz, *J*=1.0 Hz, 2H, Ph), 7.25 (t, *J*=6.4 Hz, 1H, Ph), 7.11 (m, 3H, Ph, C=CH), 5.85 (t, *J*=7.3 Hz, 1H, C=CH), 3.42 (d, *J*=7.3 Hz, 2H, $CH_2C(=O)$), 2.54-2.41 (m, 4H, CH_2), 1.85-1.75 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3 (C=O), 150.5 (C), 141.9 (CH), 139.0 (C), 129.5 (CH), 126.0 (CH), 125.7 (CH), 121.4 (CH), 121.2 (C), 116.7 (C), 35.3 (CH_2), 33.9 (CH_2), 30.6 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 2937, 2854, 2250, 2316,2203, 1751, 1589,1492, 1190, 1127, 692; LRMS (ESI) 290 [M+Na$^+$]; HRMS (ESI) calcd. for $C_{17}H_{17}NNaO_2$ 290.1151, found 290.1157.

7': ^{1}H NMR (400 MHz, $CDCl_3$) (characteristic signals only) δ 5.97 (t, *J*=7.6 Hz, 1H, C=CH), 3.45 (d, *J*=7.5 Hz, 2H, $CH_2C(=O)$).



8

(*Z*)-tert-butyl 3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (8). General irradiation procedure A was followed to afford a viscous oil (33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H, CH=C), 5.75 (t, *J*=7.4 Hz, 1H, C=CH), 3.08 (d, *J*=7.4 Hz, 2H, $CH_2C(=O)$), 2.52-2.38 (m, 4H, CH_2), 1.85-1.70 (m, 4H, CH_2), 1.48 (s, 9H, *t*-BuO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0 (C=O), 142.4 (CH), 138.0 (C), 127.4 (CH), 121.4 (C), 115.8 (C), 81.2 (C), 35.3 (CH_2), 35.0 (CH_2), 30.5 (CH_2), 28.0 (CH_3), 27.2 (CH_2), 26.4 (CH_2); IR (film, cm^{-1}) 2980, 2937, 2851, 2210, 1732, 1452, 1371,1336, 1147, 951, 845; LRMS (ESI) 248 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{22}NO_2$ 248.1645, found 248.1644.

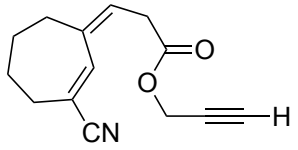


10

(*Z*)-allyl 3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (10). General irradiation procedure A was followed to afford a viscous oil (42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H, CH=C), 6.00-5.88 (m, 1H, CH=C), 5.76 (t, *J*=7.5 Hz, 1H, C=CH), 5.38-5.22 (m, 2H,

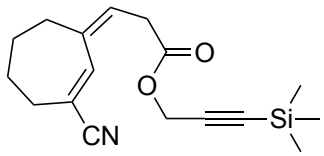
[4] 3:1 dr

C=CH_2), 4.65-4.60 (m, 2H, CH_2C=C), 3.20 (d, *J*=7.4 Hz, 2H, CH_2C(=O)), 2.52-2.41 (m, 4H, CH_2), 1.85-1.72 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4 (C=O), 142.1 (CH), 138.5 (C), 131.8 (CH), 126.4 (CH), 121.3 (C), 118.6 (CH_2), 116.3 (C), 65.6 (CH_2), 35.3 (CH_2), 33.7 (CH_2), 30.5 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 2937, 2864, 2213, 1742, 1161, 984, 938; LRMS (ESI) 254 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{14}H_{17}NNaO_2$ 254.1151, found 254.1149.



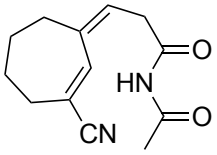
15

(*Z*)-prop-2-yn-1-yl 3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (15). General irradiation procedure A was followed to afford a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H, CH=C), 5.74 (t, *J*=7.4 Hz, 1H, C=CH), 4.71 (d, *J*=2.5 Hz, 2H, CH_2O), 3.22 (d, *J*=7.4 Hz, 2H, CH_2C(=O)), 2.50 (t, *J*=2.5 Hz, 1H), 2.50-2.40 (m, 4H, CH_2), 1.83-1.70 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9 (C=O), 141.9 (CH), 138.8 (C), 125.7 (CH), 121.2 (C), 116.6 (C), 75.2 (C), 52.4 (CH_2), 35.3 (CH_2), 33.4 (CH_2), 30.6 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 3286, 2934, 2854, 2207, 2130, 1742, 1429, 1326, 1147, 991, 675; LRMS (ESI) 252 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{14}H_{15}NNaO_2$ 252.0995, found 252.0990.



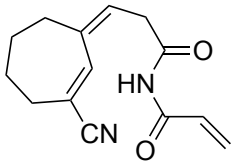
16

(*Z*)-3-(trimethylsilyl)prop-2-yn-1-yl 3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (16). General irradiation procedure A was followed to afford a viscous oil (49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H, CH=C), 5.74 (t, *J*=7.4 Hz, 1H, C=CH), 4.71 (s, 2H, CH_2O), 3.21 (d, *J*=7.4 Hz, 2H, CH_2C(=O)), 2.50-2.40 (m, 4H, CH_2), 1.83-1.70 (m, 4H, CH_2), 0.18 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0 (C=O), 141.9 (CH), 138.7 (C), 125.97 (CH), 121.2 (C), 116.6 (C), 98.5 (C), 92.5 (C), 53.2 (CH_2), 35.3 (CH_2), 33.5 (CH_2), 30.5 (CH_2), 27.2 (CH_2), 26.3 (CH_2), -0.4 (CH_3); IR (film, cm^{-1}) 3305, 2937, 2854, 2220, 2187, 1752, 1333, 1253, 1060, 1037, 841, 762; LRMS (ESI) 324 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{23}NNaO_2Si$ 324.1390, found 324.1390.



S4

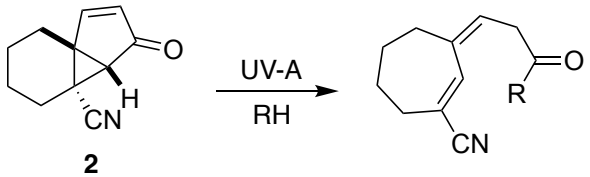
(*Z*)-N-acetyl-3-(3-cyanocyclohept-2-en-1-ylidene)propenamide (S4). General irradiation procedure A was followed to afford a viscous oil (24%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (br s, 1H, NH), 7.06 (d, *J*=1.3 Hz, 1H, CH=C), 5.77 (t, *J*=7.3 Hz, 1H, C=CH), 3.43 (d, *J*=7.3 Hz, 2H, $CH_2C(=O)$), 2.50-2.42 (m, 4H, CH_2), 2.37 (s, 3H, CH_3), 1.82-1.70 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1 (C=O), 170.8 (C=O), 142.0 (CH), 139.4 (C), 125.6 (CH), 121.2 (C), 116.7 (C), 36.6 (CH_2), 35.4 (CH_2), 30.5 (CH_2), 27.1 (CH_2), 26.3 (CH_2), 25.1 (CH_3); IR (film, cm^{-1}) 3293, 3196, 2927, 2857, 2213, 1741, 1705, 1499, 1379, 1273, 1220, 1151, 1028; LRMS (ESI) 255 [M+Na$^+$]; HRMS (ESI) calcd. for $C_{13}H_{16}N_2NaO_2$ 255.1104, found 255.1107.



S5

(*Z*)-N-(3-(3-cyanocyclohept-2-en-1-ylidene)propanoyl)acrylamide (S5). General irradiation procedure A was followed to afford a viscous oil (15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (br s, 1H, NH), 7.06 (d, *J*=1.3 Hz, 1H, CH=C), 6.53-6.45 (m, 2H, C<u>H</u>$_2$=CH), 5.98-5.92 (m, 1H, C<u>H</u>=CH$_2$), 5.82 (t, *J*=7.4 Hz, 1H, C=CH), 3.65 (d, *J*=7.4 Hz, 2H, $CH_2C(=O)$), 2.52-2.42 (m, 4H, CH_2), 1.82-1.70 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (C=O), 164.3 (C=O), 142.1 (CH), 139.2 (C), 131.7 (CH_2), 129.7 (CH), 125.6 (CH), 121.2 (C), 116.6 (C), 36.9 (CH_2), 35.4 (CH_2), 30.6 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 3286, 3199, 2934, 2861, 2363, 2213, 1735, 1685, 1619, 1492, 1174, 978, 802, 679; LRMS (ESI) 267 [M+Na$^+$]; HRMS (ESI) calcd. for $C_{14}H_{16}N_2NaO_2$ 267.1104, found 267.1104.

Table SI-2. Irradiation of **2** in the presence of various nucleophilic traps



2

Entry	Solvent, trap (eq.), time, conversion	R	*d.r.* (by ^{1}H NMR)	Yield[5]

[5]By ^{1}H NMR with mesitylene (0.33 eq) as an internal standard.

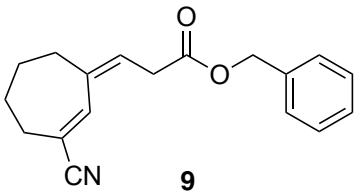
1	d-CH_3CN, MeOH (5 eq.), 5 hr, 100%	*d*-OMe	95:5	95%
2	d-CH_3CN, D_2O (10 eq.), 5 hr, 100%	OD	94:6	91%
3	CH_3CN, *t*-BuOH (10 eq.), 5 hr, 100%	*t*-BuO	95:5	94%
4	CH_3CN, Allyl alcohol (5 eq.), 5 hr, 100%	CH_2=CH-CH_2O	94:6	94%
5	CH_3CN, TMS-propargyl alcohol (4 eq.), 5 hr, 100%	TMS-propargyl-O	95:5	93%
6	d-CH_3CN, Propargyl alcohol (4 eq.), 14 hr, 98%	propargyl-O	93:7	93%
7	d-CH_3CN, PhOH (4 eq.), 10 hr, 100%	PhO	95:5	93%
8	d-CH_3CN, PhOH (1.2 eq.), 6 hr, 100%	PhO	96:4	94%
9	d-CH_3CN, BnOH (4 eq.), 5 hr, 100%	BnO	94:6	92%
10	d-CH_3CN, *(S)-methyl lactate* (4 eq.), 5 hr, 100%	MeOC(O)CH(Me)O	94:6	92%
11	d-CH_3CN, *p*-OH-benzaldehyde (1.2 eq.), 2.5 hr, 98%	H(O)CC_6H_4-*p*-O	81:19	92%
12	d-CH_3CN, Acetic acid (4 eq.), 2 hr, 98%	AcO	97:7	75%
13	d-CH_3CN, Benzoic acid (1.2 eq.), 2.5 hr, 100%	BzO	97:3	93%
14	d-CH_3CN, $PhNH_2$ (1.2 eq.), 2.5 hr, 100%	C_6H_5NH	97:3	89%

15	d-CH_3CN, $PhCH_2CH_2NH_2$ (1.2 eq.), 2.5 hr, 100%	$PhCH_2CH_2NH$	95:5	88%
16	d-CH_3CN, n-$C_{10}H_{21}NH_2$ (1.2 eq.), 1.5 hr, 100%	n-$C_{10}H_{21}NH$	97:3	92%
17	d-CH_3CN, *dl*-Alanine-OBn (1.2 eq.), 2 hr, 100%	BnO(O)CCHMeNH	98:2	94%
18	d-CH_3CN, Acetamide (4 eq.), 42 hr, 69%	AcNH	93:7	33%
19	d-CH_3CN, Acetamide (1.2 eq.), 24 hr, <1%	AcNH	N/A	N/A
20	d-CH_3CN, n-$C_8H_{17}SH$ (1.2 eq.), 4 hr, 91%	n-$C_8H_{17}S$	97:3	96%
21	d-CH_3CN, PhSH (1.2 eq.), 1.5 hr, 100%	PhS	35:65	91%
22	d-CH_3CN, (*R*)-mandelic acid (4 eq.), 2.5 hr, 100%	PhCH(C(O)OH)O	95:5	88%
23	d-CH_3CN, *m*-NH_2-phenol (1.2 eq.), 2.5 hr, 96%	C_6H_4(HO)-*m*-NH	97:3	91%
24	d-CH_3CN, *p*-NH_2-benzoic acid (1.2 eq.), 3 hr, 98%	C_6H_4(HO(O)C)-*p*-NH	98:2	78%[6]
25	d-CH_3CN, *p*-NH_2-salicylic acid (1.2 eq.), 3.5 hr, 96%	C_6H_3(HO(O)C)-*o*-OH-*p*-NH	91:9	76%[6]
26	d-CH_3CN, $HO(O)CCH_2SH$ (1.2 eq.), 4 hr, 98%	$HO(O)CCH_2S$	97:3	91%

[6] Isolated yield, the product precipitates in course of the reaction

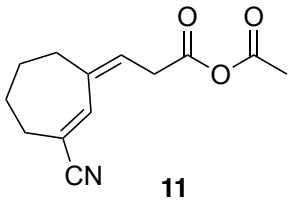
General Irradiation Procedure B

A solution of **2** (0.1 mmol) with the corresponding nucleophilic trap (Table SI-2) in anhydrous *d*-CH_3CN (0.6 ml) was combined with mesitylene (0.33 eq.) as an internal standard for yield determination and was irradiated with UV-A light in a 5 mm quartz NMR tube. Mesitylene (0.33 eq) was added as an internal standard to the reaction mixture for NMR yield determination. The solution was concentrated *in vacuo* and the residue was subjected to SiO_2 column chromatography to furnish the desired 7-membered ring product.



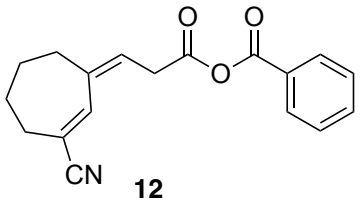
9

(*Z*)-benzyl 3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (9). General irradiation procedure B was followed to afford a viscous oil (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H, Ph), 7.01 (d, *J*=1.3 Hz, 1H, C=CH), 5.77 (t, *J*=7.4 Hz, 1H, C=CH), 5.15 (s, 2H, CH_2O), 3.22 (d, *J*=7.4 Hz, 2H, $CH_2C(=O)$), 2.52-2.38 (m, 4H, CH_2), 1.82-1.70 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 (C=O), 142.1 (CH), 138.6 (C), 135.6 (C), 128.6 (CH), 128.4 (CH), 128.3 (CH), 126.4 (CH), 121.3 (C), 116.47 (C), 66.8 (CH_2), 35.3 (CH_2), 33.8 (CH_2), 30.5 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 2934, 2847, 2203, 1731, 1449, 1153, 971, 742, 702; LRMS (ESI) 304 [M+Na^+]; HRMS (ESI) calcd. for $C_{18}H_{19}NNaO_2$ 304.1308, found 304.1315.



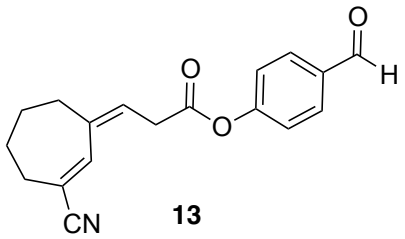
11

(*Z*)-acetic (*Z*)-3-(3-cyanocyclohept-2-en-1-ylidene)propanoic anhydride (11) General irradiation procedure B was followed to afford a viscous oil (75%). ^{1}H NMR (600 MHz, CD_3CN) δ 7.10 (q, *J* = 1.5 Hz, 1H), 5.72 (tdq, *J* = 8.0, 1.8, 0.9 Hz, 1H), 3.38 (d, *J* = 7.4 Hz, 2H), 2.50 – 2.47 (m, 2H), 2.47 – 2.43 (m, 2H), 2.21 (s, 3H), 1.80 – 1.75 (m, 2H), 1.75 – 1.70 (m, 2H). ^{13}C NMR (150 MHz, CD_3CN) δ 167.2, 166.7, 141.9, 139.5, 124.8, 121.1, 34.7, 34.2, 30.2, 27.0, 26.1, 21.5, 19.6. HRMS was not able to be acquired due to the instability of this compound.



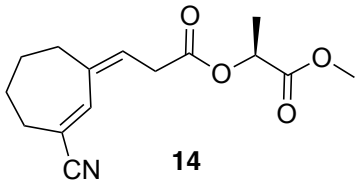
12

benzoic (*Z*)-3-(3-cyanocyclohept-2-en-1-ylidene)propanoic anhydride (12). General irradiation procedure B was followed to afford a viscous oil (93%). **(**Contains ca. 25% of benzoic acid). ^{1}H NMR (400 MHz, CD_3CN) δ 8.13-8.06 (m, 2H, Ph), 7.78-7.72 (m, 1H, Ph), 7.63-7.57 (m, 2H, 2H, Ph), 7.18 (d, *J*=1.2 Hz, 1H, CH=C), 5.81 (t, *J*=7.4 Hz, 1H, C=CH), 3.57 (d, *J*=7.4 Hz, 2H, $CH_2C(=O)$), 2.55-2.45 (m, 4H, CH_2), 1.82-1.67 (m, 4H, CH_2); ^{13}C NMR (150 MHz, CD_3CN) δ 167.2 (C=O), 162.2 (C=O), 141.9 (CH), 139.9 (C), 134.8 (CH), 130.3 (CH), 129.0 (CH), 124.7 (CH), 121.1 (C), 116.8 (C), 34.7 (CH_2), 34.5 (CH_2), 30.3 (CH_2), 27.0 (CH_2), 26.1 (CH_2); IR (film, cm^{-1}) 2947, 2860, 2210, 1808, 1735, 1695, 1605, 1459, 1250, 1074, 1034, 1011, 991, 712; LRMS (ESI) 313 $[M+NH_4]^+$; HRMS (ESI) calcd. for $C_{18}H_{21}N_2O_3$ 313.1547, found 313.1542.



13

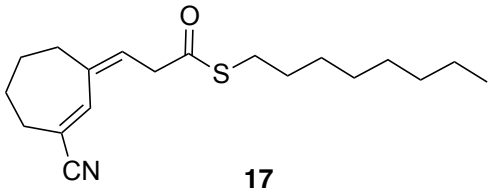
(*Z*)-4-formylphenyl 3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (13). General irradiation procedure B was followed to afford a viscous oil (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.0 (s, 1H, C(=O)H), 7.97 (d, *J*=8.6 Hz, 2H, Ar), 7.32 (d, *J*=8.6 Hz, 2H, Ar), 7.09 (d, *J*=1.3 Hz, 1H, CH=C), 5.83 (t, *J*=7.4 Hz, 1H, C=CH), 3.47 (d, *J*=7.4 Hz, 2H, $CH_2C(=O)$), 2.55-2.45 (m, 4H, CH_2), 1.87-1.72 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8 (C=O), 168.6 (C=O), 155.2 (C), 141.7 (CH), 139.5 (C), 134.2 (C), 131.2 (CH), 125.0 (CH), 122.2 (CH), 121.1 (C), 117.1 (C), 35.4 (CH_2), 33.8 (CH_2), 30.7 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 2937, 2848, 2216, 1768, 1702, 1605, 1502, 1213, 1161, 1123, 858; LRMS (ESI) 318 $[M+Na^+]$; HRMS (ESI) calcd. for $C_{18}H_{17}NNaO_3$ 318.1101, found 318.1108.



14

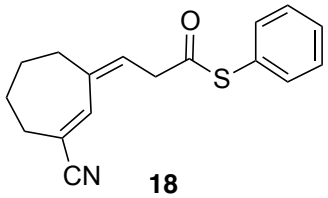
(*S,Z*)-1-methoxy-1-oxopropan-2-yl-3-(3-cyanocyclohept-2-en-1-ylidene)propanoate (14). General irradiation procedure B was followed to afford a viscous oil (92%). ^{1}H NMR (400 MHz, $CDCl_3$) Viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H, CH=C), 5.76 (t, *J*=7.3 Hz, 1H, C=CH), 5.11 (q, *J*=7.1 Hz, 1H, CHMe), 3.76 (s, 3H, OMe), 3.26 (dd, *J*=7.4 Hz, *J*=2.0 Hz, 2H, $CH_2C(=O)$), 2.52-2.40 (m, 4H, CH_2), 1.82-1.68 (m, 4H, CH_2), 1.51 (d, *J*=7.1

Hz, CH_3CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9 (C=O), 170.2 (C=O), 142.0 (CH), 138.8 (C), 125.9 (CH), 121.2 (C), 116.5 (C), 69.0 (CH), 52.4 (CH_3), 35.3 (CH_2), 33.4 (CH_2), 30.6 (CH_2), 27.2 (CH_2), 26.3 (CH_2), 16.9 (CH_3); IR (film, cm^{-1}) 2940, 2850, 2210, 1735, 1220, 1163, 1091; LRMS (ESI) 300 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{15}H_{19}NNaO_4$ 300.1206, found 300.1202.



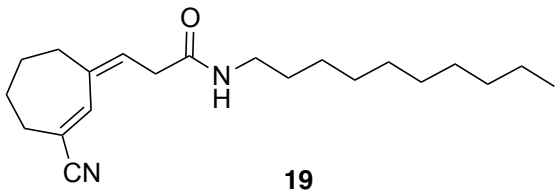
17

(*Z*)-S-octyl 3-(3-cyanocyclohept-2-en-1-ylidene)propanethioate (17). General irradiation procedure B was followed to afford a viscous oil (96%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J*=0.8 Hz, 1H, CH=C), 5.71 (t, *J*=7.6 Hz, 1H, C=CH), 3.37 (d, *J*=7.7 Hz, 2H, $CH_2C(=O)$), 2.87 (t, *J*=7.3 Hz, 2H, CH_2S), 2.50-2.45 (m, 2H, CH_2), 2.42 (t, *J*=6.3 Hz, 2H, CH_2), 1.82-1.73 (m, 4H, CH_2), 1.60-1.52 (m, 2H, CH_2), 1.40-1.20 (m, 10H, CH_2), 0.89 (t, *J*=6.7 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5 (C=O), 142.0 (CH), 139.4 (C), 126.0 (CH), 121.2 (C), 116.7 (C), 43.3 (CH_2), 35.3 (CH_2), 31.8 (CH_2), 30.6 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 27.1 (CH_2), 26.3 (CH_2), 22.6 (CH_2), 14.1 (CH_3); IR (film, cm^{-1}) 2933, 2854, 2213, 1688, 1452,1060, 987; LRMS (ESI) 342 $[M+Na^+]$; HRMS (ESI) calcd. for $C_{19}H_{29}NNaOS$ 342.1862, found 342.1859.



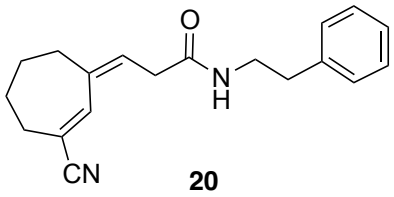
18

(*Z*)- and (*E*)-S-phenyl 3-(3-cyanocyclohept-2-en-1-ylidene)propanethioate (18) (*Z*:*E*=2:1). General irradiation procedure B was followed to afford a viscous oil (91%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 5H, Ph), 7.05 and 6.83 (s, 1H, CH=C), 5.87 and 5.75 (t, *J*=7.5 Hz, 1H, C=CH), 3.51 and 3.48 (d, *J*=7.5 Hz, 2H, $CH_2C(=O)$), 2.54-2.41 (m, 4H, CH_2), 1.90-1.72 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5 and 194.4 (C=O), 148.3 (CH),141.8 (CH), 141.4 (C), 139.9 (C), 134.5 and 134.4 (CH), 129.6 and 129.5 (CH), 129.3 (CH), 128.2 (CH), 127.3 and 127.2 (C), 125.4(CH), 121.4 and 121.2 (C), 117.0 and 113.9 (C), 42.9 and 42.8 (CH_2), 35.4 (CH_2), 30.6 and 30.2 (CH_2), 27.7 and 27.1 (CH_2), 26.5 and 26.3 (CH_2,) 25.1 (CH_2); IR (film, cm^{-1}) 3392, 3053, 2934, 2854, 2210, 1701, 1476, 1446, 981, 748, 696; LRMS (ESI) 306 $[M+Na^+]$; HRMS (ESI) calcd. for $C_{17}H_{17}NNaOS$ 306.0923, found 306.0915.



19

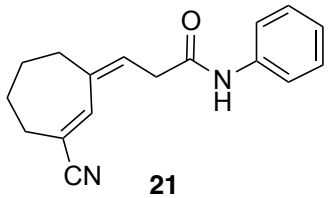
(*Z*)-3-(3-cyanocyclohept-2-en-1-ylidene)-N-decylpropanamide (19). General irradiation procedure B was followed to afford a viscous oil (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J*=1.1 Hz, 1H, CH=C), 5.79 (t, *J*=7.6 Hz, 1H, C=CH), 5.53 (bs, 1H, NH), 3.28-3.20 (m, 2H, CH_2), 3.05 (d, *J*=7.6 Hz, 2H, $CH_2C(=O)$), 2.50-2.40 (m, 4H, CH_2), 1.82-1.70 (m, 4H, CH_2), 1.55-1.46 (m, 2H, CH_2), 1.35-1.20 (m, 16H, CH_2), 0.86 (t, *J*=6.9 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 (C=O), 142.1 (CH), 138.7 (C), 128.1 (CH), 121.3 (C), 116.3 (C), 39.8 (CH_2), 36.1 (CH_2), 35.4 (CH_2), 31.9 (CH_2), 30.5 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.2 (CH_2), 26.9 (CH_2), 26.4 (CH_2), 22.7 (CH_2), 14.1 (CH_3); IR (film, cm^{-1}) 3296, 2921, 2851, 2210, 1632, 1566,1463, 706; LRMS (ESI) 353 [M+Na^+]; HRMS (ESI) calcd. for $C_{21}H_{34}N_2NaO$ 353.2563, found 353.2559.



20

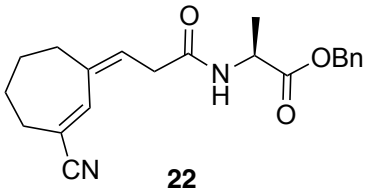
A solution of **2** (19 mg, 0.11 mmol) and 2-phenylethylamine (14 mg, 0.12 mmol) in dry *d*-CH_3CN (0.6 mL) was UV-A irradiated in 5 mm quartz NMR tube for 2 hours (conversion of **2** was 98%, *Z*:*E* = 95:5 according to ^{1}H NMR). Mesitylene (4.4 mg, 0.037 mmol. 0.33 eq.) was added to the solution and used as internal standard for yield determination (92%, combined for two diastereomers). The solution was concentrated *in vacuo* and the residue was subjected to SiO_2 column chromatography (7 g, 40% EtOAc in hexanes) to furnish 24 mg (88% yield) of *Z*-**20**.

(*Z*)-3-(3-cyanocyclohept-2-en-1-ylidene)-N-phenethylpropanamide (20). Viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J*=6.3 Hz, 2H, Ph), 7.26 (t, *J*=6.3 Hz, 1H, Ph), 7.18 (d, *J*=6.8 Hz, 2H, Ph), 6.96 (d, *J*=1.3 Hz, 1H, CH=C), 5.71 (t, *J*=7.6 Hz, 1H, C=CH), 5.56 (bs, 1H, NH), 3.55 (m, 2H, CH_2), 3.01 (d, *J*=7.7 Hz, 2H, $CH_2C(=O)$), 2.82 (t, *J*=6.8 Hz, 2H, CH_2), 2.42-2.47 (m, 2H, CH_2), 2.39 (t, *J*=6.2 Hz, 2H, CH_2), 2.42-2.47 (m, 2H, CH_2), 1.78-1.65 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 (C=O), 150.5 (C), 141.8 (CH), 138.9 (C), 138.6 (C), 128.7 (CH), 127.7 (CH), 126.6 (CH), 121.2 (C), 116.4 (C), 40.6 (CH_2), 36.0 (CH_2), 35.5 (CH_2), 35.3 (CH_2), 30.5 (CH_2), 27.1 (CH_2), 26.4 (CH_2); IR (film, cm^{-1}) 3286, 2931, 2851, 2213, 1648, 1542,1453, 748, 699; LRMS (ESI) 295 [M+H^+]; HRMS (ESI) calcd. for $C_{19}H_{22}N_2NaO$ 317.1624, found 317.1628.



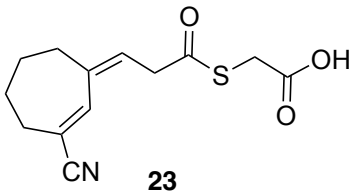
21

(*Z*)-3-(3-cyanocyclohept-2-en-1-ylidene)-N-phenylpropanamide (21). General irradiation procedure B was followed to afford a viscous oil (89%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.61 (br s, 1H, NH), 7.51 (d, *J*=7.7 Hz, 2H, Ar), 7.32 (t, *J*=7.6 Hz, 2H, Ar), 7.12 (t, *J*=7.4 Hz, 1H, Ar), 7.10 (s, 2H, CH=C), 5.88 (t, *J*=7.5 Hz, 1H, C=CH), 3.24 (d, *J*=7.4 Hz, 2H, $CH_2C(=O)$), 2.55-2.42 (m, 4H, CH_2), 1.84-1.70 (m, 4H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1 (C=O), 142.2 (CH), 138.9 (C), 137.7 (C), 129.0 (CH), 127.6 (CH), 124.5 (CH), 121.3 (C), 119.9 (CH), 116.4 (C), 36.9 (CH_2), 35.4 (CH_2), 30.5 (CH_2), 27.2 (CH_2), 26.4 (CH_2); IR (film, cm^{-1}) 3313, 2937, 2850, 2216, 1658, 1602, 1546,1496, 1439, 1323, 1247, 1177, 765, 682; LRMS (ESI) 267 M+H$^+$]; HRMS (ESI) calcd. for $C_{17}H_{19}N_2NaO$ 267.1492, found 267.1483



22

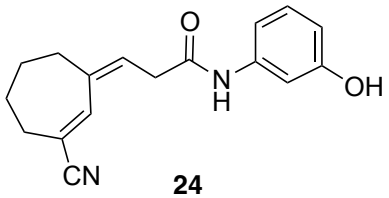
(*S*,*Z*)-benzyl 2-(3-(3-cyanocyclohept-2-en-1-ylidene)propanamido)propanoate (22). General irradiation procedure B was followed to afford a viscous oil (94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H, Ph), 7.01 (d, *J*=1.3 Hz, 1H, CH=C), 6.20 (d, *J*=7.0 Hz, 1H, NH), 5.76 (t, *J*=7.5 Hz, 1H, C=CH), 5.19 (q, *J*=19.5 Hz, *J*=12.2 Hz, 2H, CH_2Ph), 4.63 (pent, J=7.2 Hz, 1H, CHN), 3.10 (d, *J*=7.2 Hz, 2H, $CH_2C(=O)$), 2.48-2.40 (m, 4H, CH_2), 1.82-1.70 (m, 4H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7 (C), 169.1 (C=O), 150.5 (C), 141.9 (CH), 139.2 (C), 135.2 (C), 128.6 (CH), 128.5 (CH), 128.1 (CH), 127.2 (CH), 121.2 (C), 116.6 (C), 67.3 (CH_2), 40.6 (CH_2), 48.3 (CH), 35.7 (CH_2), 35.4 (CH_2), 30.6 (CH_2), 27.2 (CH_2), 26.3 (CH_2), 18.5 (CH_3); IR (film, cm^{-1}) 3292, 2931, 2858, 2200, 1742, 1652, 1532,1449, 1200, 1151, 745, 696; LRMS (ESI) 375 [M+Na$^+$]; HRMS (ESI) calcd. for $C_{21}H_{24}N_2NaO_3$ 375.1679, found 375.1672.



23

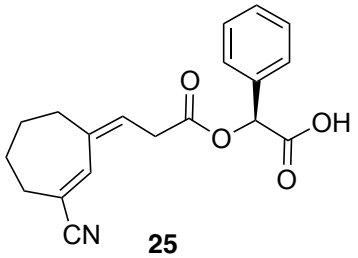
(*Z*)-2-((3-(3-cyanocyclohept-2-en-1-ylidene)propanoyl)thio)acetic acid (23). General irradiation procedure B was followed to afford a viscous oil (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H, CH=C), 5.72 (t, *J*=7.7 Hz, 1H, C=CH), 3.77 (s, 2H, CH_2S), 3.46 (d, *J*=7.6 Hz, 2H, $CH_2C(=O)$), 2.55-2.48 (m, 2H, CH_2), 2.45 (t, *J*=6.1 Hz, 2H, CH_2), 1.85-1.72 (m, 4H, CH_2);

^{13}C NMR (150 MHz, $CDCl_3$) δ 194.6 (C=O), 173.2 (C=O), 141.6 (CH), 140.5 (C), 124.6 (CH), 121.1 (C), 117.3 (C), 42.7 (CH_2), 35.4 (CH_2), 31.1 (CH_2), 30.6 (CH_2), 27.1 (CH_2), 26.2 (CH_2); IR (film, cm^{-1}) 3223, 2924, 2854, 2206, 1692, 1399,1164, 1057, 659; LRMS (ESI) 264 $[M-H]^-$; HRMS (ESI) calcd. for $C_{13}H_{15}NO_3S$ 264.0700, found 264.0696.



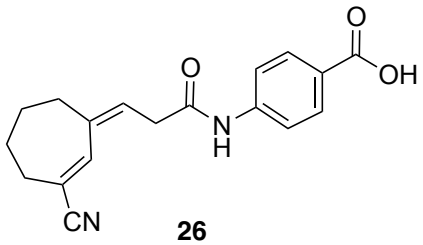
24

(*Z*)-3-(3-cyanocyclohept-2-en-1-ylidene)-N-(3-hydroxyphenyl)propenamide (24). General irradiation procedure B was followed to afford a viscous oil (91%). mp: 158-160 °C (CH_3CN); ^{1}H NMR (400 MHz, CD_3CN) δ 8.24 (br s, 1H, NH), 7.21 (s, 2H, CH=C, Ar), 7.13 (t, *J*=8.1 Hz, 2H, Ar), 7.05-6.90 (m, 2H, Ar, OH), 6.96 (dd, *J*=8.0 Hz, *J*=1.6 Hz, 1H, Ar), 5.83 (t, *J*=7.6 Hz, 1H, C=CH), 3.20 (d, *J*=7.6 Hz, 2H, $CH_2C(=O)$), 2.55-2.42 (m, 4H, CH_2), 1.82-1.70 (m, 4H, CH_2); ^{13}C NMR (150 MHz, CD_3OD) δ 169.8 (C=O), 157.5 (C), 142.4 (CH), 139.4 (C), 138.3 (C), 129.1 (CH), 128.0 (CH), 120.8 (C), 115.7 (C), 110.9 (CH), 107.0 (CH), 36.0 (CH_2), 34.8 (CH_2), 30.1 (CH_2), 27.0 (CH_2), 26.1 (CH_2); IR (film, cm^{-1}) 3306, 2927, 28.60, 2213, 1702, 1658, 1609, 1552,1452, 1233, 1151, 868, 789, 689; LRMS (ESI) 305 $[M+Na^+]$; HRMS (ESI) calcd. for $C_{17}H_{18}N_2NaO_2$ 305.1260, found 305.1263; Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.12, H, 6.58; N, 9.82.



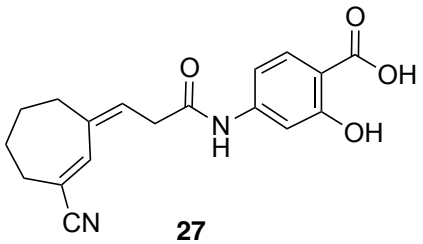
25

(*S*,*Z*)-2-((3-(3-cyanocyclohept-2-en-1-ylidene)propanoyl)oxy)-2-phenylacetic acid (25). General irradiation procedure B was followed to afford a viscous oil (88%). ^{1}H NMR (600 MHz, $CDCl_3$) Viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2H, Ph), 7.45-7.38 (m, 3H, Ph), 7.02 (s, 1H, CH=C), 6.96 (s, 1H, CHPh), 5.76 (t, *J*=7.3 Hz, 1H, C=CH), 3.32 (dq, *J*=17.8 Hz, *J*=7.6 Hz, 2H, $CH_2C(=O)$), 2.45-2.36 (m, 4H, CH_2), 1.80-1.68 (m, 4H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.7 (C=O), 170.1 (C=O), 142.0 (CH), 139.0 (C), 132.8 (C), 129.6 (CH), 128.9 (CH), 127.6 (CH), 125.5 (CH), 121.1 (C), 116.5 (C), 74.4 (CH), 35.3 (CH_2), 33.4 (CH_2), 30.6 (CH_2), 27.2 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 3153, 2927, 2210, 1745, 1150, 1027, 728, 696; LRMS (ESI) 348 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{19}H_{19}NNaO_4$ 348.1206, found 348.1193.



26

(*Z*)-4-(3-(3-cyanocyclohept-2-en-1-ylidene)propanamido)benzoic acid (26). General irradiation procedure B was followed to afford a viscous oil (78%). mp: 211-212 °C (CH_3CN); ^{1}H NMR (400 MHz, CD_3OD) δ 7.98 (d, *J*=6.9 Hz, 2H, Ar), 7.68 (d, *J*=6.9 Hz, 2H, Ar), 7.24 (d, *J*=1.0 Hz, 1H, CH=C), 5.86 (t, *J*=7.6 Hz, 1H, C=CH), 3.33[7] (d, *J*=7.7 Hz, 2H, $CH_2C(=O)$), 2.55-2.45 (m, 4H, CH_2), 1.85-1.72 (m, 4H, CH_2); ^{13}C NMR (150 MHz, CD_3OD) δ 170.2 (C=O), 168.0 (C=O), 142.8 (C), 142.3 (CH), 138.5 (C), 130.4 (CH), 125.7 (CH), 120.8 (C), 118.7 (CH), 115.8 (C), 36.0 (CH_2), 34.9 (CH_2), 30.1 (CH_2), 27.0 (CH_2), 26.1 (CH_2); IR (film, cm^{-1}) 3332, 2941, 2216, 1702, 1678, 1602, 1532,1396, 1297, 1163, 868, 755; LRMS (ESI) 333 [M+Na^+]; HRMS (ESI) calcd. for $C_{18}H_{18}N_2NaO_3$ 333.1210, found 333.1205; Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.44, H, 5.81; N, 9.15.

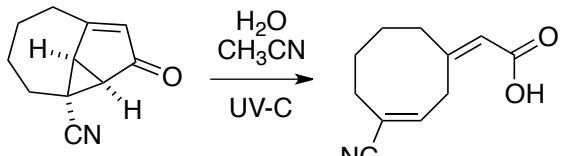


27

(*Z*)-4-(3-(3-cyanocyclohept-2-en-1-ylidene)propanamido)-2-hydroxybenzoic acid (27). General irradiation procedure B was followed to afford a viscous oil (76%). mp: 213-215 °C (CH_3CN); ^{1}H NMR (600 MHz, 20% CD_3OD in $CDCl_3$) δ 7.76 (d, *J*=8.7 Hz, 1H, Ar), 7.18 (d, *J*=1.9 Hz, 1H, Ar), 7.11 (d, *J*=1.0 Hz, 1H, CH=C), 7.08 (dd, *J*=8.7 Hz, *J*=1.9 Hz, 1H, Ar), 5.81 (t, *J*=7.4 Hz, 1H, C=CH), 3.21 (d, *J*=7.5 Hz, 2H, $CH_2C(=O)$), 2.48-2.38 (m, 4H, CH_2), 1.82-1.70 (m, 4H, CH_2); ^{13}C NMR (150 MHz, 20% CD_3OD in $CDCl_3$) δ 171.9 (C=O), 169.7 (C=O), 162.4 (C), 144.8 (C), 142.7 (CH), 138.4 (C), 131.4 (CH), 127.8 (CH), 121.3 (C), 115.7 (C), 110.6 (CH), 108.4 (C), 106.7 (CH), 36.4 (CH_2), 35.2 (CH_2), 30.3 (CH_2), 27.0 (CH_2), 26.3 (CH_2); IR (film, cm^{-1}) 3303, 3116, 2937, 2864, 2216, 1661, 1598, 1536, 1512,1422, 1237, 1154, 755; LRMS (ESI) 349 [M+Na^+]; HRMS (ESI) calcd. for $C_{18}H_{18}N_2NaO_4$ 349.1159, found 349.1161; Anal. Calcd. for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35, H, 5.49; N, 8.48.

Irradiation of **3** in the presence of water

[7] Overlapped with residual CH_3 signal of CD_3OD.



3 **4**

A solution of **3** (51 mg, 0.29 mmol) and water (0.30 mL, 1.67 mmol) in anhydrous CH_3CN (3 mL) was irradiated with UV-C light in 4 a mL quartz cuvette for 2 hours (ca. 50% conversion according to ^1H NMR). The solvent was removed *in vacuo*. Two consecutive purifications by SiO_2 column chromatography (1:2 - 1:1 EtOAc/Hexanes and 1 - 5% MeOH in $CHCl_3$) of the crude material furnished 23.0 mg of the recovered started material and 15.0 mg (65% yield BRSM) of crystalline **4**. Recrystallization of the last compound from acetonitrile furnished X-ray grade final product.

(*Z*)-2-((*E*)-4-cyanocyclooct-3-en-1-ylidene)acetic acid (4). mp: 99-100 °C (CH_3CN); ^1H NMR (400 MHz, $CDCl_3$) δ 6.60 (t, *J*=6.3 Hz, 1H, CH=CCN), 5.88 (s, 1H, C=CHC(=O)), 3.70 (d, *J*=6.3 Hz, 2H, CH_2), 2.49 (br s, 2H, CH_2), 2.40 (br s, 2H, CH_2), 1.77 (br s, 4H, CH_2); ^{13}C NMR (150 MHz, CD_3OD) δ 171.30 (C=O), 162.8 (C), 144.7 (CH), 120.2 (C), 117.7 (CH), 114.1 (C), 38.9 (CH_2), 32.8 (CH_2), 27.3 (CH_2), 26.9 (CH_2), 24.3 (CH_2); IR (film, cm^{-1}) 2927, 2864, 2213, 1685, 1635, 1622, 1469, 1463, 1412, 1270, 1204, 944, 931, 885; LRMS (ESI) 209 $[M+NH_4]^+$; HRMS (ESI) calcd. for $C_{11}H_{17}N_2O_2$ 209.1285, found 209.1284; Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.25, H, 6.95; N, 7.42.

II. Computational Methods

All structures were optimized using uM06-2X[8] with the default 2 triple-ζ split valence def2-TZVP[9] basis set. Vibrational analysis verified that each structure was either a minimum or transition state. All calculations were performed in Gaussian 09.e01[10]. Figures were created using Vesta.[11]

Other Pathways Studied

Upon irradiation, we envisioned that compound **2** could undergo ring opening in various positions which may or may not lead to the observed product. A comparison between the various energy profiles derived from the pathways a-d are summarized in Scheme S1.

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[8] Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120* (1–3), 215–241.

[9] (a) F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, **2005**, *7* 3297-3305; (b) F. Weigend, Accurate Coulomb-fitting basis sets for H to Rn, *Phys. Chem. Chem. Phys.*, **2006**, *8,* 1057-1065.

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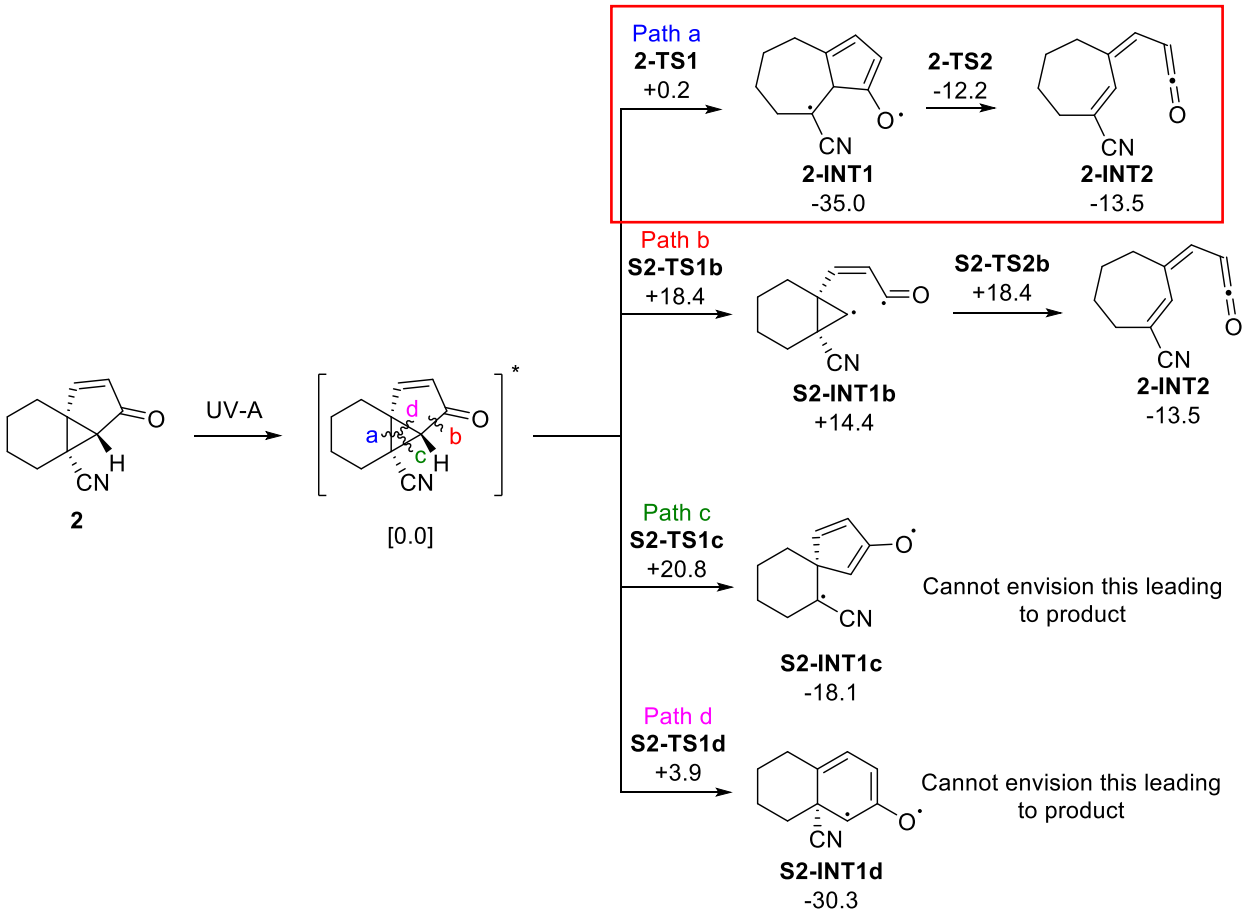


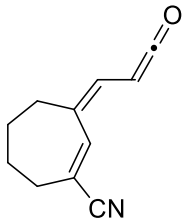
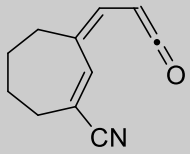
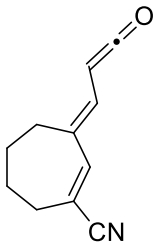
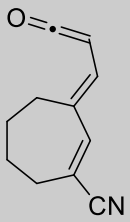
Scheme S1 – Other pathways studied for compound **2** (relative free energies in kcal/mol).

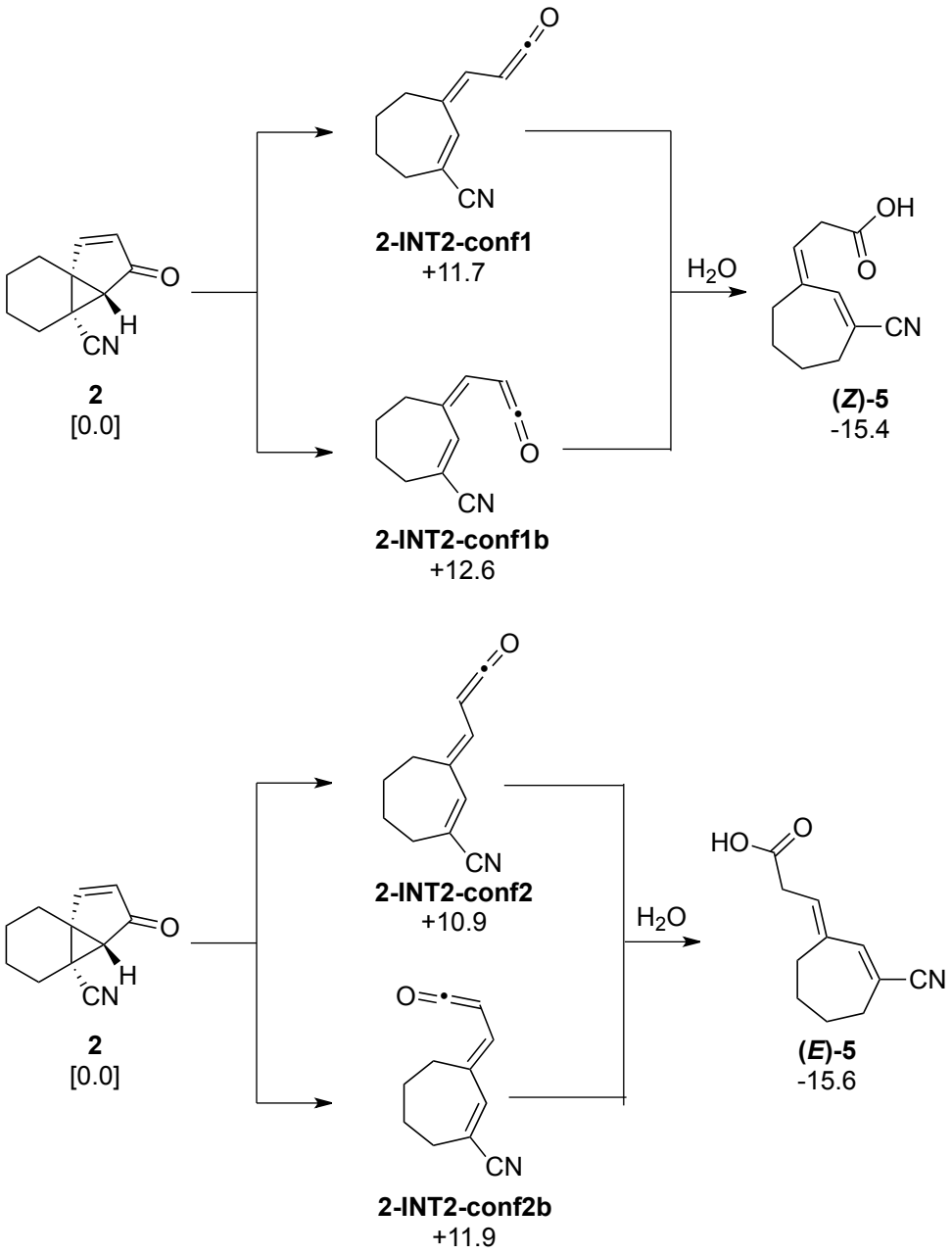
According to Scheme S1, one can see that path a (expansion of the six membered ring) is preferred over path b (opening of the 5 membered ring). Path d seems to be thermodynamically accessible albeit it does not lead to any intermediary that could lead to the observed product.

Furthermore, **2-INT2** has various possible conformations which were also computed (Table S1).

Interestingly, in the triplet state conformation 1b seems to be the lowest energy. However, for the singlet state, conformation 2, which arises from the isomerization of the exocyclic double bond, appears to be the most stable. Conformations 1 and 1b, after nucleophilic attack on the ketene, will produce the same product with a *Z* exocyclic double bond while conformations 2 and 2b would give rise to the *E* isomer (Scheme S2).

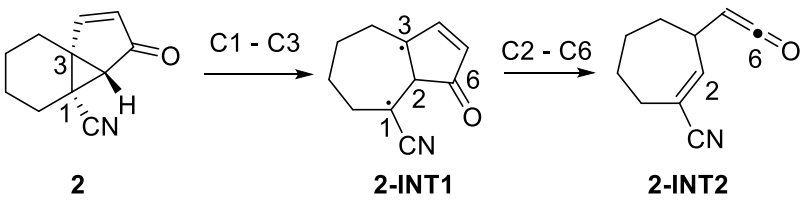
Table S1 – Conformations of intermediary **2-INT2** (relative free energies in kcal/mol).

2-INT2	**Relative Energy**	
Conformation	Triplet state	Singlet state
 **2-INT2-conf1**	0.8	-0.9
 **2-INT2-conf1b**	0.0	0.0
 **2-INT2-conf2**	1.4	-1.7
 **2-INT2-conf2b**	1.5	-0.7



Scheme S2 – Product formation (relative energies in kcal/mol for the singlet state).

To better understand the energy profile of this transformation, we examined the possibility of a conical intersection to play a role (Figure S1). For this purpose, we performed two scans on compound **2,** by expanding the C1 – C3 bond by 0.1 Å for ten steps, until **2-INT1** was reached. The other scan focused on the bond distance between C2 and C6 where we increased it by 0.2 Å for five steps until **2-INT2** was reached (Scheme S3) Single point energies were then determined for the ground state to help determine if there was any crossing in the Potential Energy Surfaces (PES).



Scheme S3 – Atom labelling for the scans performed

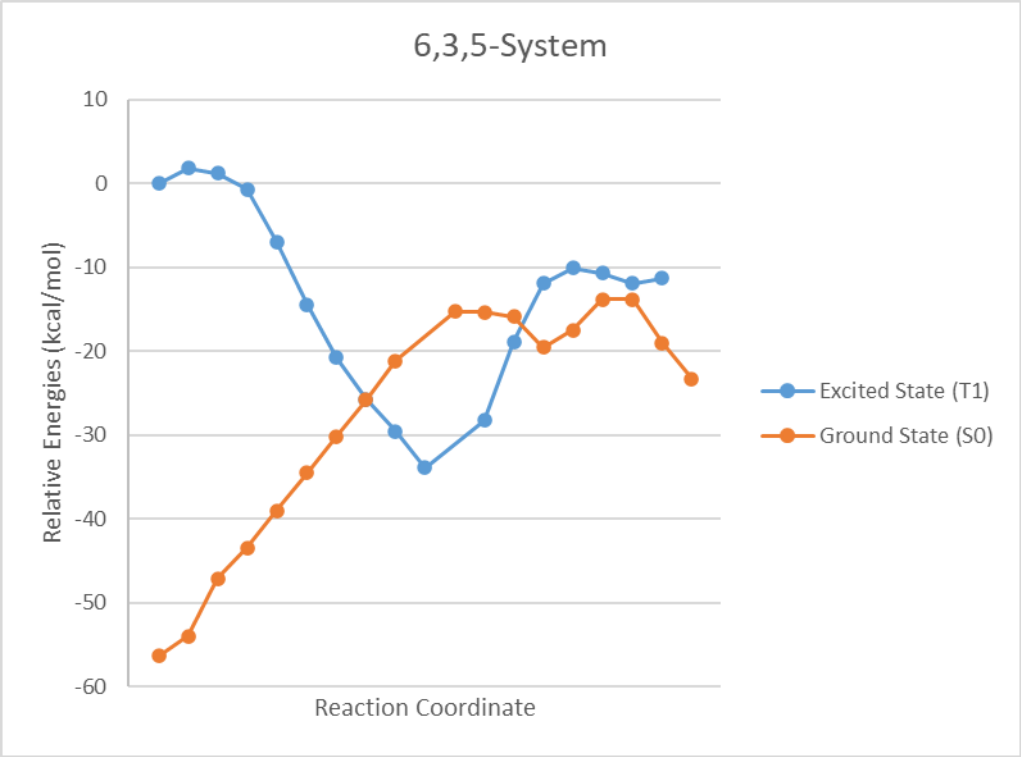
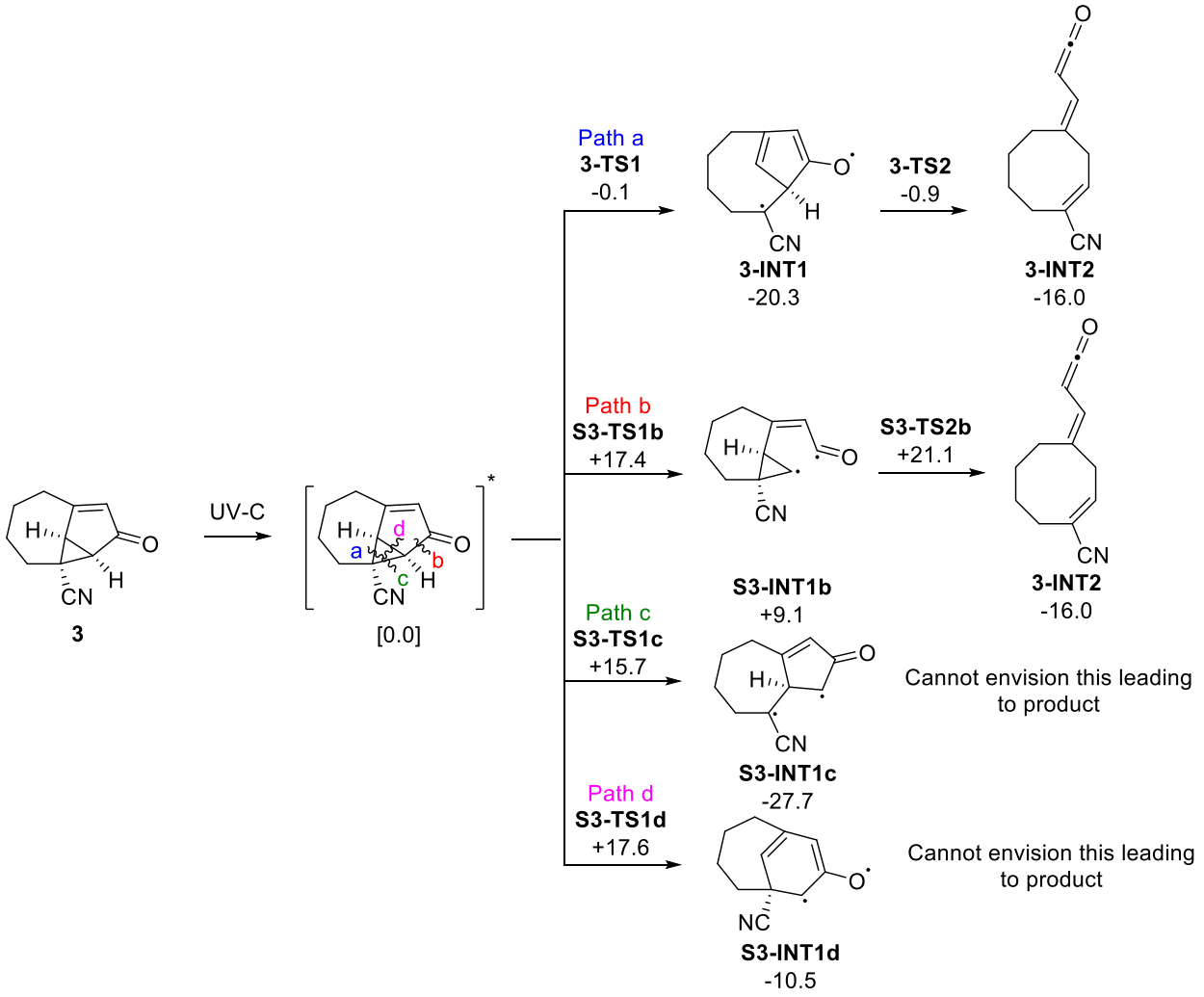


Figure S1 – Conical Intersection in the 6,3,5-system.

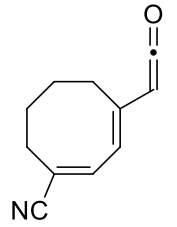
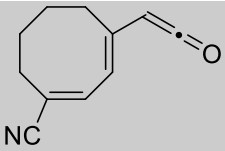
Similarly, to compound **2**, the 7,3,5-system (**3**) could also undergo ring opening reactions at multiple positions which we also computed (Scheme S4).



Scheme S4 – Other pathways studied for compound **3** (relative free energies in kcal/mol).

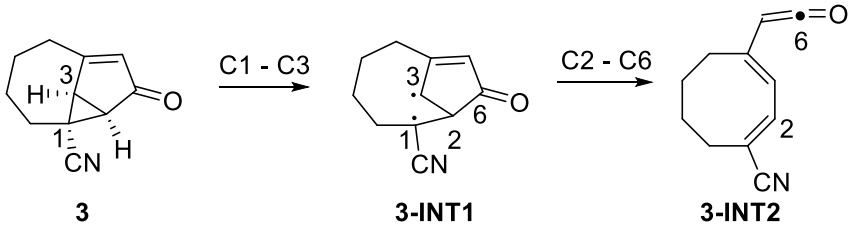
For compound **3**, path a seems the most favorable of all. The possible conformations of **3-INT2** were also computed even though for this system only two possible conformations are possible (Table S2).

Table S2 – Conformations of intermediary **3-INT2** (relative energies in kcal/mol).

3-INT2	**Relative Energies**	
Conformation	Triplet state	Singlet state
 **3-INT2-conf1**	0.0	0.0
 **3-INT2-conf2**	0.4	-1.2

In a similar fashion to compound **2**, here we also observe a change in the stability of this conformers between the triplet state and the singlet state. These differences may be due to strain geometries in the triplet state in order to accommodate the unpaired electrons. In both systems the energy difference between the different conformations of **INT2** are fairly low (<2 kcal/mol).

Scans were also performed for this system, starting from **3** we scanned the increase in bond length between atoms C1 and C3 by 0.087 Å for ten steps and between atoms C2 and C6 by increasing the bond distance 0.2 Å for five steps (Scheme S5). Single points were then performed to obtain the ground state energies and study the possibility of PES intersection (Figure S2).



Scheme S5 – Atom labelling for the scans.

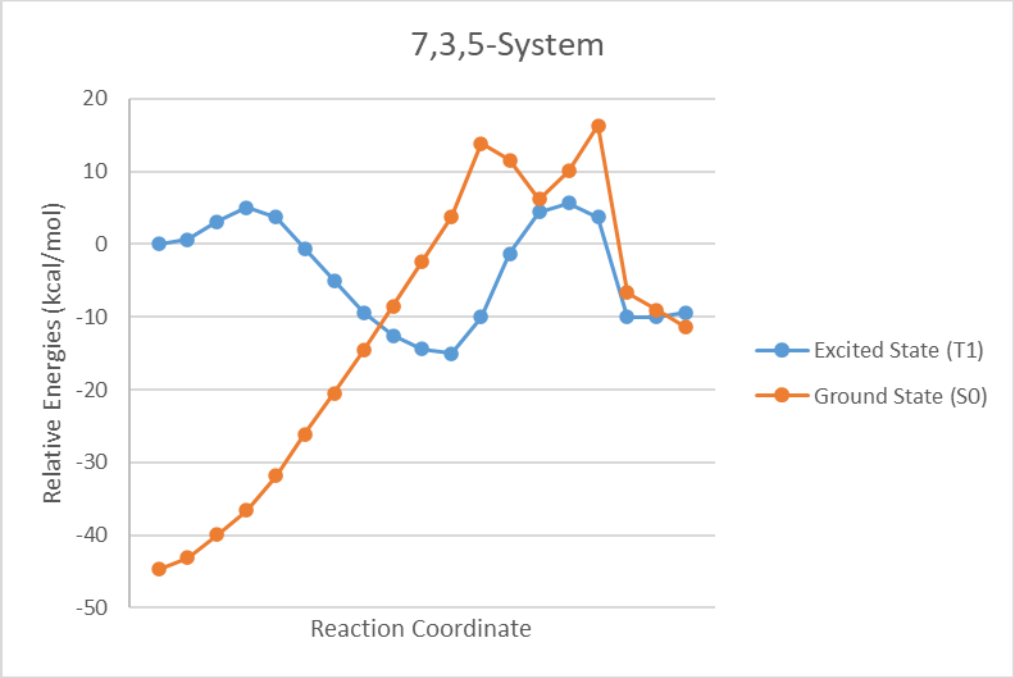
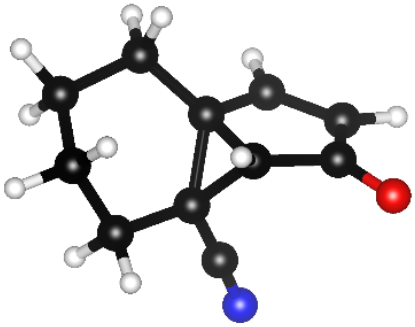


Figure S2 – Conical Intersections in compound **3**.

III. Atom Coordinates



2 (triplet)

HF = -554.9608495 hartrees

Zero-point correction= 0.193784 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.156692

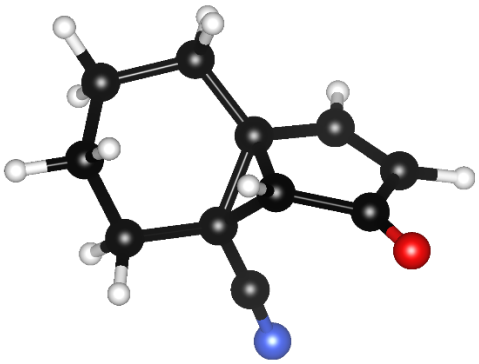
Sum of electronic and zero-point Energies= -554.767066

Sum of electronic and thermal Free Energies= -554.804158

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.508787	1.354901	0.560367
2	6	0	0.210018	0.752001	0.033760
3	6	0	0.198786	-0.725873	-0.437320
4	6	0	1.512702	-1.490304	-0.531407
5	6	0	2.758227	-0.638619	-0.287182
6	6	0	2.566296	0.304589	0.894444
7	1	0	1.279936	1.984858	1.434531
8	1	0	1.478018	-2.321757	0.191028
9	1	0	1.564531	-1.952608	-1.528059
10	1	0	3.625196	-1.295801	-0.129496
11	1	0	2.975334	-0.035966	-1.184817
12	1	0	2.283345	-0.270167	1.792849
13	1	0	3.506583	0.817402	1.141992
14	6	0	-0.441055	-0.330228	0.883197
15	1	0	0.010903	-0.529314	1.858001
16	6	0	-0.936088	-1.124754	-1.303516
17	1	0	-0.816797	-1.455809	-2.333137
18	6	0	-2.144407	-1.007295	-0.626748
19	1	0	-3.138943	-1.167406	-1.037094
20	6	0	-1.902519	-0.578661	0.684369
21	8	0	-2.733973	-0.316525	1.641810

22	1	0	1.909697	2.023262	-0.217341
23	6	0	-0.636281	1.703574	-0.654681
24	7	0	-1.281831	2.488503	-1.202090



2 (singlet)

HF = -555.070753 hartrees

Zero-point correction= 0.197319 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.161403

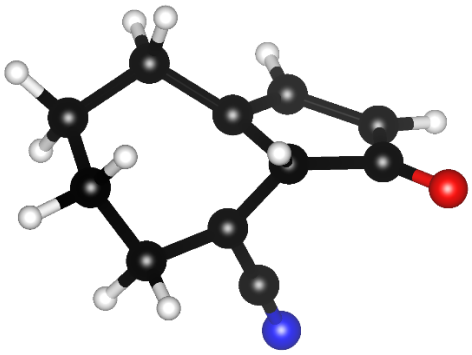
Sum of electronic and zero-point Energies= -554.873434

Sum of electronic and thermal Free Energies= -554.909350

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.531452	1.322606	0.593420
2	6	0	0.218373	0.746863	0.068726
3	6	0	0.196456	-0.697985	-0.441509
4	6	0	1.490563	-1.484452	-0.594667

5	6	0	2.751651	-0.664552	-0.314352
6	6	0	2.574491	0.248655	0.893670
7	1	0	1.315631	1.935038	1.482060
8	1	0	1.447812	-2.352668	0.082284
9	1	0	1.533350	-1.891092	-1.616024
10	1	0	3.603973	-1.343735	-0.172298
11	1	0	2.986693	-0.039974	-1.192191
12	1	0	2.286958	-0.344021	1.778306
13	1	0	3.523264	0.741560	1.148618
14	6	0	-0.428710	-0.361815	0.879560
15	1	0	0.027684	-0.607149	1.839988
16	6	0	-0.966731	-1.015052	-1.338948
17	1	0	-0.820525	-1.249079	-2.395223
18	6	0	-2.146539	-0.923799	-0.712860
19	1	0	-3.138865	-1.052584	-1.141237
20	6	0	-1.924139	-0.565814	0.722206
21	8	0	-2.743963	-0.486012	1.594673
22	1	0	1.931212	2.003144	-0.174445
23	6	0	-0.624670	1.744703	-0.569437
24	7	0	-1.254096	2.570358	-1.073154



DD_SM1_A_TS1.log

HF = -554.9586503 hartrees

Zero-point correction= 0.191893 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.154802

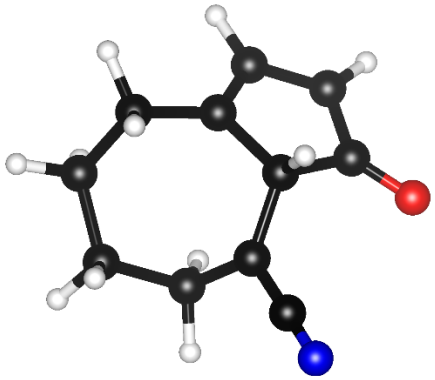
Sum of electronic and zero-point Energies= -554.766758

Sum of electronic and thermal Free Energies= -554.803849

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.498175	1.396320	0.565755
2	6	0	0.177095	0.800681	0.119912
3	6	0	0.181911	-0.884704	-0.370074
4	6	0	1.550994	-1.525154	-0.452513
5	6	0	2.748444	-0.585885	-0.316036
6	6	0	2.583344	0.363470	0.862934
7	1	0	1.302269	2.020204	1.455032
8	1	0	1.599331	-2.284607	0.346622

9	1	0	1.607255	-2.071709	-1.404757
10	1	0	3.661252	-1.188792	-0.208273
11	1	0	2.863193	0.005683	-1.239463
12	1	0	2.341922	-0.208418	1.774857
13	1	0	3.521896	0.895986	1.071740
14	6	0	-0.444001	-0.309765	0.895351
15	1	0	-0.011486	-0.511837	1.880650
16	6	0	-0.864079	-1.230644	-1.254347
17	1	0	-0.729717	-1.750530	-2.199540
18	6	0	-2.162208	-0.942173	-0.608629
19	1	0	-3.148921	-1.062527	-1.051769
20	6	0	-1.947913	-0.479337	0.727400
21	8	0	-2.778057	-0.229986	1.596431
22	1	0	1.855928	2.072355	-0.224949
23	6	0	-0.632942	1.653663	-0.702534
24	7	0	-1.253056	2.340750	-1.396417



DD_SM1_A_INT1.log

HF = -555.0149648 hartrees

Zero-point correction= 0.193890 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155019

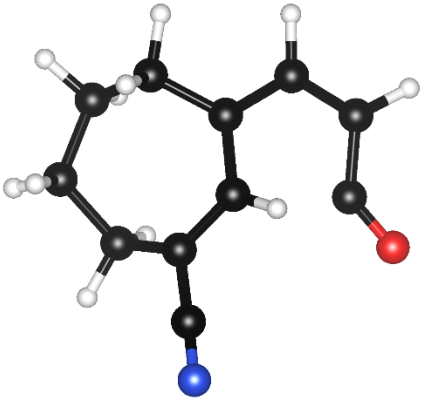
Sum of electronic and zero-point Energies= -554.821075

Sum of electronic and thermal Free Energies= -554.859945

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.808157	-1.127560	-1.150023
2	6	0	0.227154	-1.117460	-0.063111
3	6	0	-0.416323	1.232094	0.583829
4	6	0	-1.823809	0.970418	1.000239
5	6	0	-2.668726	0.376749	-0.145053
6	6	0	-2.251243	-1.016723	-0.613699
7	1	0	-0.710643	-2.056463	-1.727435
8	1	0	-1.835349	0.274610	1.855693
9	1	0	-2.288295	1.911122	1.331809
10	1	0	-3.717945	0.337615	0.185556
11	1	0	-2.633784	1.073249	-0.999223
12	1	0	-2.379089	-1.743346	0.205376
13	1	0	-2.937802	-1.328944	-1.415234
14	6	0	0.645340	0.166610	0.574692
15	1	0	1.003754	-0.026863	1.602562
16	6	0	0.098947	2.409976	0.061572

17	1	0	-0.472018	3.337508	-0.008230
18	6	0	1.419206	2.250970	-0.374290
19	1	0	2.058529	3.001794	-0.834277
20	6	0	1.835693	0.867266	-0.158090
21	8	0	2.871481	0.328363	-0.458592
22	1	0	-0.611788	-0.289147	-1.841966
23	6	0	0.823446	-2.319830	0.350348
24	7	0	1.294773	-3.324729	0.702232



DD_SM1_A_TS2b.log

HF = -554.9769284 hartrees

Zero-point correction= 0.192216 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.153369

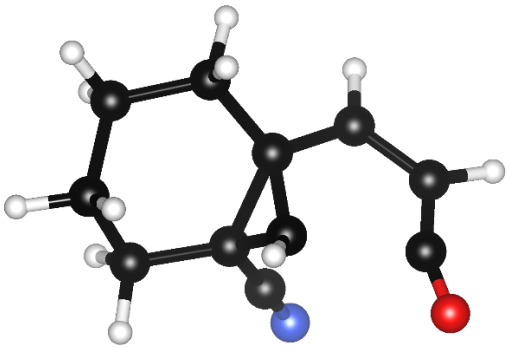
Sum of electronic and zero-point Energies= -554.784712

Sum of electronic and thermal Free Energies= -554.823559

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.696148	-0.730651	0.936701
2	6	0	0.659894	-1.114990	-0.095570
3	6	0	-0.239004	1.189598	-0.568440
4	6	0	1.062236	1.915159	-0.755020
5	6	0	2.061708	1.762067	0.401185
6	6	0	2.676424	0.371137	0.526640
7	1	0	2.262950	-1.631483	1.206282
8	1	0	1.541769	1.550631	-1.679422
9	1	0	0.844170	2.983200	-0.899406
10	1	0	2.868372	2.494122	0.245225
11	1	0	1.566816	2.037235	1.347535
12	1	0	3.160501	0.093183	-0.424093
13	1	0	3.474551	0.411427	1.283484
14	6	0	-0.309242	-0.259305	-0.594175
15	1	0	-1.040172	-0.691758	-1.286118
16	6	0	-1.438656	1.898964	-0.386607
17	1	0	-1.464420	2.976207	-0.564843
18	6	0	-2.561337	1.243526	0.078245
19	1	0	-3.525815	1.737965	0.223736
20	6	0	-2.402457	-0.134051	0.490721
21	8	0	-3.141150	-1.007871	0.774034
22	1	0	1.160355	-0.413804	1.850489
23	6	0	0.567854	-2.497393	-0.441434

24	7	0	0.519817	-3.621189	-0.721231



DD_SM1_B_TS1.log

HF = -554.9271796 hartrees

Zero-point correction= 0.190121 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.152306

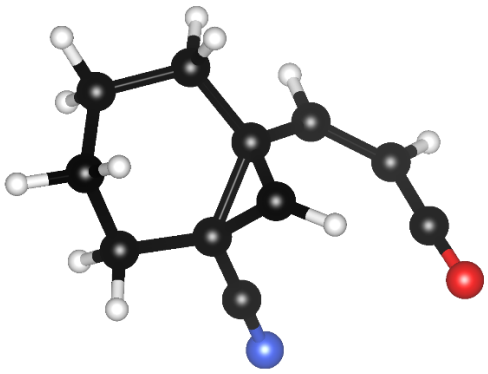
Sum of electronic and zero-point Energies= -554.737058

Sum of electronic and thermal Free Energies= -554.774873

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.663146	1.350906	0.506099
2	6	0	0.309620	0.779377	0.085172
3	6	0	0.198445	-0.746852	-0.348386
4	6	0	1.484137	-1.569377	-0.437130
5	6	0	2.768229	-0.752291	-0.287763
6	6	0	2.674622	0.259851	0.849746

7	1	0	1.512162	2.039598	1.351865
8	1	0	1.442678	-2.350495	0.339398
9	1	0	1.482971	-2.095023	-1.402622
10	1	0	3.614635	-1.436545	-0.132834
11	1	0	2.967553	-0.207617	-1.225547
12	1	0	2.394682	-0.251546	1.786845
13	1	0	3.652286	0.727607	1.032800
14	6	0	-0.295132	-0.256439	0.945108
15	1	0	-0.081383	-0.500209	1.986877
16	6	0	-0.915061	-1.100468	-1.253460
17	1	0	-0.738917	-1.392653	-2.286160
18	6	0	-2.202435	-0.945532	-0.718681
19	1	0	-3.120251	-1.091607	-1.290709
20	6	0	-2.385270	-0.541125	0.575994
21	8	0	-2.944381	-0.268357	1.576487
22	1	0	2.051338	1.950417	-0.332129
23	6	0	-0.537788	1.724607	-0.613240
24	7	0	-1.171114	2.505571	-1.180062



DD_SM1_B_INT1.log

HF = -554.9323617 hartrees

Zero-point correction= 0.190536 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.151175

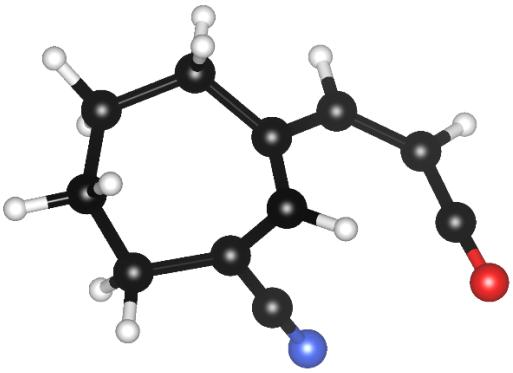
Sum of electronic and zero-point Energies= -554.741826

Sum of electronic and thermal Free Energies= -554.781186

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.799896	1.455330	0.097674
2	6	0	0.425224	0.789050	0.083123
3	6	0	0.288009	-0.798729	-0.002081
4	6	0	1.607489	-1.596349	-0.042609
5	6	0	2.865287	-0.766667	-0.290956
6	6	0	2.893898	0.499078	0.557692
7	1	0	1.749269	2.344397	0.745073
8	1	0	1.702335	-2.132496	0.914646
9	1	0	1.514198	-2.366993	-0.820871
10	1	0	3.749374	-1.389901	-0.092687
11	1	0	2.911541	-0.477003	-1.354378
12	1	0	2.752836	0.243130	1.621652
13	1	0	3.868577	1.000489	0.474309
14	6	0	-0.004603	-0.042291	1.216440

15	1	0	-0.792668	0.015623	1.964352
16	6	0	-0.802267	-1.405270	-0.794759
17	1	0	-0.513996	-2.003559	-1.658212
18	6	0	-2.190594	-1.214589	-0.600266
19	1	0	-2.897091	-1.705113	-1.275548
20	6	0	-2.811121	-0.460517	0.323215
21	8	0	-3.392365	0.165894	1.104883
22	1	0	2.026071	1.806516	-0.921484
23	6	0	-0.592862	1.557694	-0.606819
24	7	0	-1.400238	2.176759	-1.154263



DD_SM1_B_TS2.log

HF = -554.9255103 hartrees

Zero-point correction= 0.189548 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.150663

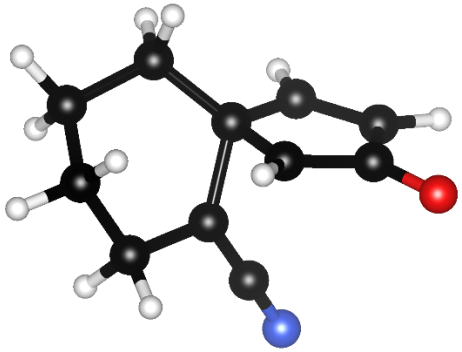
Sum of electronic and zero-point Energies= -554.735962

Sum of electronic and thermal Free Energies= -554.774847

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.809975	1.528093	0.129917
2	6	0	0.423931	0.919114	0.157816
3	6	0	0.260391	-0.973619	0.109865
4	6	0	1.638277	-1.625651	-0.007623
5	6	0	2.803706	-0.719652	-0.401439
6	6	0	2.908204	0.525163	0.472058
7	1	0	1.836089	2.375188	0.837837
8	1	0	1.863433	-2.093618	0.965574
9	1	0	1.557235	-2.445357	-0.735686
10	1	0	3.731466	-1.307835	-0.343008
11	1	0	2.686384	-0.409368	-1.453413
12	1	0	2.845538	0.239744	1.536155
13	1	0	3.883761	1.012631	0.331747
14	6	0	0.011732	-0.031270	1.189040
15	1	0	-0.771246	0.020530	1.947879
16	6	0	-0.795308	-1.556956	-0.634341
17	1	0	-0.526301	-2.258750	-1.424282
18	6	0	-2.191022	-1.281931	-0.517568
19	1	0	-2.896957	-1.805177	-1.167110
20	6	0	-2.797923	-0.405619	0.295241
21	8	0	-3.376013	0.324442	0.976706
22	1	0	1.990412	1.943828	-0.873150

23	6	0	-0.595392	1.565574	-0.602643
24	7	0	-1.435876	2.067597	-1.225447



DD_SM1_C_TS1.log

HF = -554.9249114 hartrees

Zero-point correction= 0.191122 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.153865

Sum of electronic and zero-point Energies= -554.733789

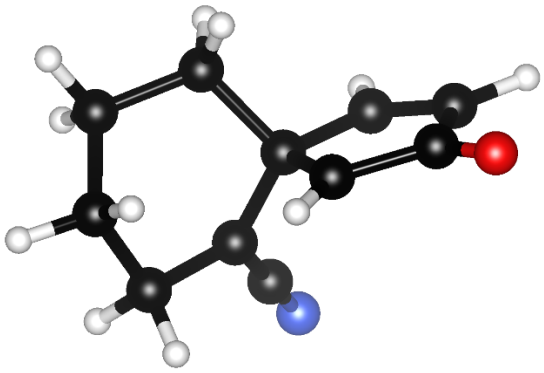
Sum of electronic and thermal Free Energies= -554.771047

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	1.574216	1.270292	0.701539
2	6	0	0.326346	0.817963	-0.009865
3	6	0	0.159161	-0.675029	-0.464362
4	6	0	1.474182	-1.440669	-0.680992
5	6	0	2.747451	-0.671584	-0.328820
6	6	0	2.571944	0.140599	0.948535

7	1	0	1.291872	1.771904	1.644343
8	1	0	1.414046	-2.363661	-0.084902
9	1	0	1.502053	-1.748517	-1.735633
10	1	0	3.581964	-1.380644	-0.235132
11	1	0	3.006540	0.017294	-1.149945
12	1	0	2.232562	-0.516228	1.766674
13	1	0	3.526568	0.574656	1.276331
14	6	0	-0.512736	-0.561390	0.853142
15	1	0	-0.036908	-0.599599	1.832776
16	6	0	-0.949190	-0.871884	-1.422045
17	1	0	-0.797316	-0.965855	-2.495725
18	6	0	-2.156425	-0.833726	-0.745338
19	1	0	-3.151233	-0.897638	-1.183773
20	6	0	-1.917829	-0.652647	0.644579
21	8	0	-2.816500	-0.558615	1.603115
22	1	0	2.054853	2.045304	0.080088
23	6	0	-0.543786	1.815565	-0.514115
24	7	0	-1.247571	2.643850	-0.919081



DD_SM1_C_INT1.log

HF = -554.9871865 hartrees

Zero-point correction= 0.193027 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.154250

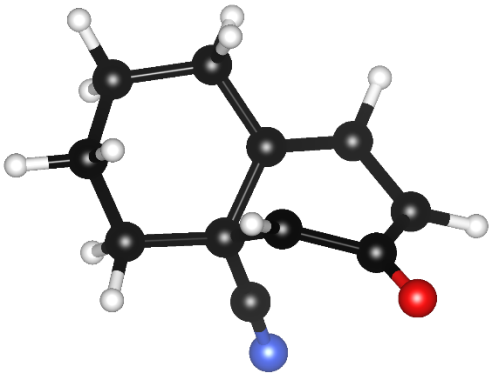
Sum of electronic and zero-point Energies= -554.794159

Sum of electronic and thermal Free Energies= -554.832936

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.993320	-0.060405	-1.130950
2	6	0	-0.975671	0.702633	-0.333476
3	6	0	0.119836	-0.080412	0.351221
4	6	0	-0.554473	-1.120089	1.323651
5	6	0	-1.973059	-1.524609	0.899815
6	6	0	-2.137260	-1.502175	-0.617888
7	1	0	-1.708506	-0.050190	-2.199468
8	1	0	0.105701	-1.998741	1.382043
9	1	0	-0.577684	-0.676291	2.329572
10	1	0	-2.210063	-2.517137	1.307606
11	1	0	-2.701000	-0.821115	1.336251
12	1	0	-1.385765	-2.161153	-1.079984
13	1	0	-3.118091	-1.898249	-0.914297
14	6	0	1.022848	-0.776130	-0.635740
15	1	0	0.711010	-1.467881	-1.416858

16	6	0	1.113387	0.784489	1.111984
17	1	0	0.776000	1.462860	1.898377
18	6	0	2.376856	0.590174	0.721418
19	1	0	3.272288	1.065594	1.118617
20	6	0	2.413175	-0.403858	-0.397577
21	8	0	3.390539	-0.809958	-0.994761
22	1	0	-2.958759	0.465631	-1.070839
23	6	0	-1.030205	2.099745	-0.240054
24	7	0	-1.088877	3.260022	-0.149623



DD_SM1_D_TS1.log

HF = -554.9533084 hartrees

Zero-point correction= 0.192255 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155317

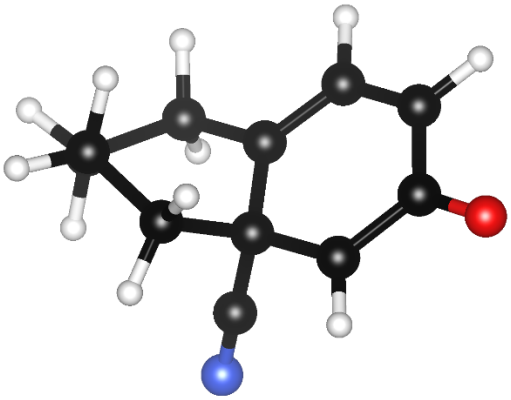
Sum of electronic and zero-point Energies= -554.761053

Sum of electronic and thermal Free Energies= -554.797991

Standard orientation:

Center Atomic Atomic Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	1.469297	1.312549	0.616142
2	6	0	0.179052	0.681419	0.075794
3	6	0	0.280295	-0.705844	-0.558980
4	6	0	1.596693	-1.456080	-0.552083
5	6	0	2.819277	-0.599638	-0.237986
6	6	0	2.545744	0.291743	0.967206
7	1	0	1.201452	1.936812	1.481853
8	1	0	1.519887	-2.264942	0.192753
9	1	0	1.700406	-1.950102	-1.529949
10	1	0	3.685588	-1.251874	-0.059895
11	1	0	3.067965	0.034881	-1.104592
12	1	0	2.239232	-0.324931	1.829461
13	1	0	3.454430	0.828089	1.274982
14	6	0	-0.573675	-0.209257	1.002851
15	1	0	-0.165499	-0.402382	1.998794
16	6	0	-0.814702	-1.192410	-1.283640
17	1	0	-0.705564	-2.084996	-1.904191
18	6	0	-2.117893	-0.838270	-0.709676
19	1	0	-3.083260	-0.959812	-1.198778
20	6	0	-2.000430	-0.488314	0.695653
21	8	0	-2.907030	-0.443244	1.518144
22	1	0	1.864108	1.988625	-0.157339
23	6	0	-0.597726	1.665411	-0.680749
24	7	0	-1.176871	2.461247	-1.282206



DD_SM1_D_INT1.log

HF = -555.0082318 hartrees

Zero-point correction= 0.193705 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155732

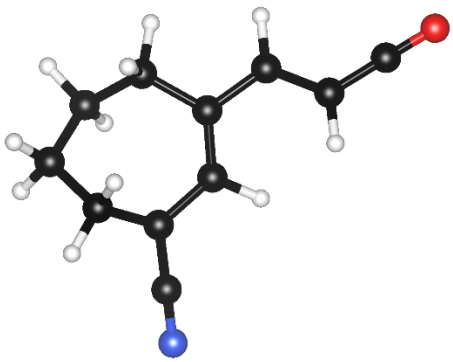
Sum of electronic and zero-point Energies= -554.814526

Sum of electronic and thermal Free Energies= -554.852500

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.907191	0.576645	1.472750
2	6	0	0.105494	0.562683	0.114408
3	6	0	0.239667	-0.816363	-0.510638
4	6	0	1.642692	-1.220175	-0.866194
5	6	0	2.678133	-0.599505	0.092979
6	6	0	2.064594	-0.432398	1.482179
7	1	0	0.192310	0.344038	2.274989

8	1	0	1.705985	-2.318709	-0.848779
9	1	0	1.861584	-0.909695	-1.903538
10	1	0	3.571620	-1.237374	0.134862
11	1	0	3.010904	0.379291	-0.284760
12	1	0	1.691702	-1.412166	1.821743
13	1	0	2.820106	-0.111264	2.212778
14	6	0	-1.322828	0.967497	0.350288
15	1	0	-1.537856	1.974164	0.712334
16	6	0	-0.852946	-1.642860	-0.669168
17	1	0	-0.676946	-2.645432	-1.068196
18	6	0	-2.159972	-1.263142	-0.350784
19	1	0	-3.007336	-1.934464	-0.483230
20	6	0	-2.440744	0.068841	0.168161
21	8	0	-3.590055	0.435583	0.445599
22	1	0	1.269890	1.600751	1.643652
23	6	0	0.717671	1.552846	-0.805229
24	7	0	1.192109	2.323112	-1.521308



DD_SM1_INT_conf1_T.log

HF = -554.9747473 hartrees

Zero-point correction= 0.191305 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.150345

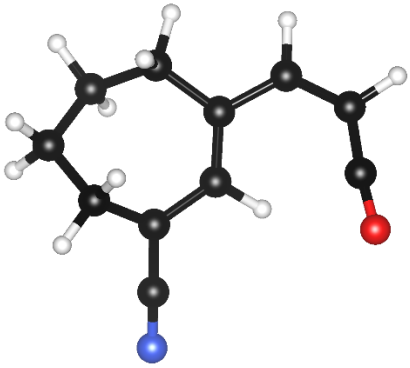
Sum of electronic and zero-point Energies= -554.783442

Sum of electronic and thermal Free Energies= -554.824402

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.618827	0.842795	0.191275
2	6	0	0.207201	0.627619	-0.087272
3	6	0	2.420231	-0.166270	0.959552
4	6	0	0.284566	-1.912184	-0.033242
5	6	0	2.804014	-1.405883	0.133536
6	6	0	1.653710	-1.936171	-0.722395
7	1	0	-0.378268	1.524859	-0.306449
8	1	0	0.371926	-2.262899	1.011872
9	1	0	1.800459	-0.488433	1.813260
10	1	0	3.148698	-2.184789	0.832256
11	1	0	3.324085	0.301784	1.372191
12	1	0	-0.377391	-2.642688	-0.522804
13	1	0	3.657873	-1.163042	-0.516179
14	1	0	1.884295	-2.966724	-1.029773
15	1	0	1.578259	-1.342610	-1.647232
16	6	0	-0.431915	-0.576481	-0.069156
17	6	0	-1.890236	-0.660927	-0.126267

18	1	0	-2.338850	-1.584094	-0.495911
19	6	0	-2.733621	0.407646	0.256346
20	1	0	-2.326254	1.303157	0.736026
21	6	0	-4.068592	0.429770	0.094701
22	8	0	-5.215899	0.463423	-0.040402
23	6	0	2.211137	2.063063	-0.184314
24	7	0	2.704347	3.074319	-0.485803



DD_SM1_INT_conf1b_T.log

HF = -554.9760978 hartrees

Zero-point correction= 0.191365 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.150498

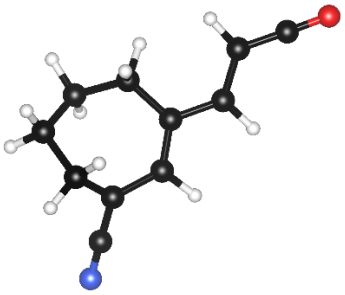
Sum of electronic and zero-point Energies= -554.784732

Sum of electronic and thermal Free Energies= -554.825600

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	1.025123	0.959821	0.073658
2	6	0	-0.204133	0.303529	-0.323461
3	6	0	1.982920	0.306812	1.026679
4	6	0	0.597192	-2.080162	0.056208
5	6	0	2.816892	-0.818868	0.393209
6	6	0	1.990532	-1.751675	-0.492738
7	1	0	-0.971904	0.958119	-0.745465
8	1	0	0.647784	-2.287347	1.141224
9	1	0	1.381509	-0.117982	1.847911
10	1	0	3.289385	-1.389325	1.208709
11	1	0	2.648421	1.060850	1.467903
12	1	0	0.241979	-3.018938	-0.395624
13	1	0	3.632797	-0.381878	-0.201341
14	1	0	2.547718	-2.687811	-0.643744
15	1	0	1.863518	-1.298851	-1.488682
16	6	0	-0.464678	-1.033872	-0.219133
17	6	0	-1.815183	-1.557310	-0.407229
18	1	0	-1.933054	-2.594835	-0.718495
19	6	0	-2.996935	-0.829577	-0.177109
20	1	0	-3.971711	-1.305553	-0.318448
21	6	0	-3.105767	0.439200	0.279526
22	8	0	-3.297386	1.531334	0.606831
23	6	0	1.273205	2.274814	-0.366937
24	7	0	1.486804	3.362373	-0.723522



DD_SM1_INT_conf2_T.log

HF = -554.9743659 hartrees

Zero-point correction= 0.191566 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.150904

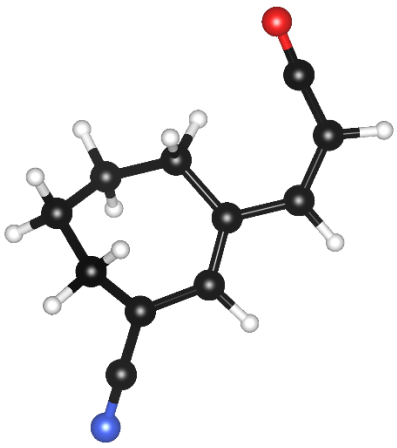
Sum of electronic and zero-point Energies= -554.782799

Sum of electronic and thermal Free Energies= -554.823462

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.983692	-0.651831	0.315550
2	6	0	-0.570869	-1.004236	0.127258
3	6	0	-2.349833	0.608416	1.040262
4	6	0	0.250511	1.378968	-0.182626
5	6	0	-2.273886	1.844124	0.124086
6	6	0	-1.076661	1.802490	-0.823927
7	1	0	-0.330846	-2.071740	0.147998
8	1	0	0.390330	1.890109	0.788355
9	1	0	-1.628665	0.730133	1.864352
10	1	0	-2.230223	2.744396	0.757650

11	1	0	-3.352487	0.525541	1.481984
12	1	0	1.061445	1.745116	-0.829208
13	1	0	-3.197272	1.916952	-0.469927
14	1	0	-0.949492	2.796771	-1.276515
15	1	0	-1.290067	1.108567	-1.652778
16	6	0	0.453943	-0.114786	-0.010450
17	6	0	1.810488	-0.622200	-0.009137
18	1	0	1.938620	-1.703359	0.062488
19	6	0	2.972080	0.190948	-0.020518
20	1	0	2.918568	1.281908	-0.054742
21	6	0	4.231102	-0.276615	0.028979
22	8	0	5.321069	-0.660924	0.067938
23	6	0	-2.987231	-1.507068	-0.169928
24	7	0	-3.822025	-2.223752	-0.554350



DD_SM1_INT_conf2b_T.log

HF = -554.974164 hartrees

Zero-point correction= 0.191583 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.150910

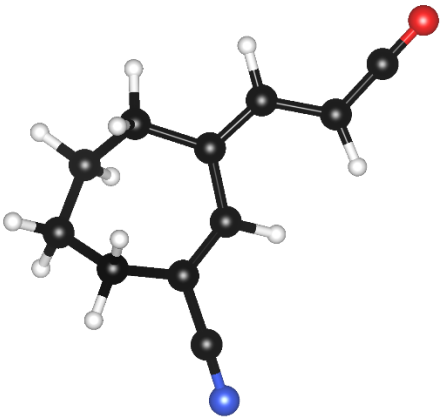
Sum of electronic and zero-point Energies= -554.782581

Sum of electronic and thermal Free Energies= -554.823254

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.999919	-0.355059	-0.325486
2	6	0	0.797648	-1.168460	-0.123350
3	6	0	1.899494	0.976472	-1.007690
4	6	0	-0.783859	0.781285	0.265730
5	6	0	1.422106	2.088963	-0.055897
6	6	0	0.330634	1.620029	0.903514
7	1	0	0.934799	-2.253432	-0.157688
8	1	0	-1.119663	1.246057	-0.680746
9	1	0	1.167069	0.866792	-1.823935
10	1	0	1.060835	2.933522	-0.663993
11	1	0	2.861977	1.253155	-1.459487
12	1	0	-1.649311	0.824033	0.945165
13	1	0	2.275722	2.460786	0.530463
14	1	0	-0.121295	2.499986	1.383758
15	1	0	0.783724	1.022614	1.710815
16	6	0	-0.465243	-0.685310	0.047937
17	6	0	-1.569641	-1.627203	0.064332
18	1	0	-1.323068	-2.688536	0.046756

19	6	0	-2.951629	-1.324671	0.010746
20	1	0	-3.670586	-2.149549	0.018212
21	6	0	-3.573365	-0.135489	-0.092110
22	8	0	-4.169724	0.852937	-0.184133
23	6	0	3.249657	-0.845205	0.091390
24	7	0	4.289038	-1.255863	0.421293



DD_SM1_INT_conf1.log

HF = -555.0457446 hartrees

Zero-point correction= 0.194655 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155104

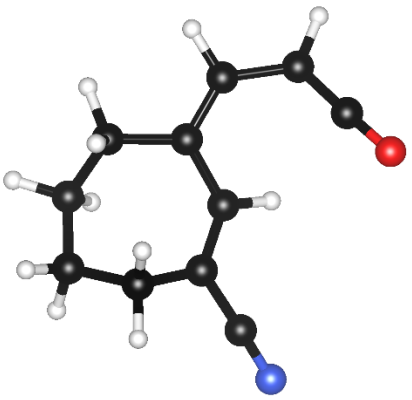
Sum of electronic and zero-point Energies= -554.851090

Sum of electronic and thermal Free Energies= -554.890641

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-1.584191	0.825311	-0.191397
2	6	0	-0.270715	0.627816	0.067041
3	6	0	-2.498024	-0.214470	-0.804785
4	6	0	-0.271950	-1.947812	-0.162920
5	6	0	-2.772078	-1.412466	0.113021
6	6	0	-1.506147	-2.006211	0.747308
7	1	0	0.284611	1.477105	0.473692
8	1	0	-0.567864	-2.173938	-1.201798
9	1	0	-2.030991	-0.564854	-1.737338
10	1	0	-3.283494	-2.180601	-0.488377
11	1	0	-3.446447	0.257189	-1.093233
12	1	0	0.437469	-2.738212	0.121443
13	1	0	-3.475192	-1.119349	0.906984
14	1	0	-1.707038	-3.050372	1.027711
15	1	0	-1.271747	-1.476664	1.683622
16	6	0	0.468020	-0.621906	-0.095255
17	6	0	1.824696	-0.616027	-0.100356
18	1	0	2.334530	-1.582919	-0.145261
19	6	0	2.685694	0.555439	-0.075856
20	1	0	2.304391	1.574325	-0.156720
21	6	0	4.008628	0.458169	0.004346
22	8	0	5.157834	0.380705	0.067726
23	6	0	-2.152974	2.112227	0.110633
24	7	0	-2.632379	3.138890	0.342398



DD_SM1_INT_conf1b.log

HF = -555.0444546 hartrees

Zero-point correction= 0.194511 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155222

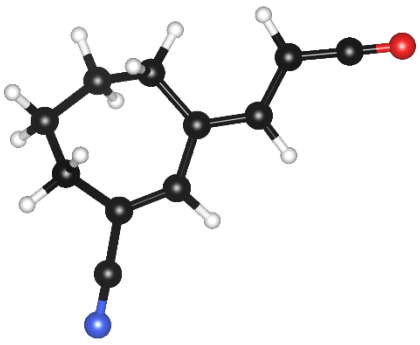
Sum of electronic and zero-point Energies= -554.849944

Sum of electronic and thermal Free Energies= -554.889233

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.898937	0.981199	-0.108580
2	6	0	0.179540	0.277005	0.303122
3	6	0	-1.996091	0.391824	-0.968143
4	6	0	-0.769663	-2.093277	-0.124396
5	6	0	-2.869429	-0.619158	-0.213560
6	6	0	-2.058932	-1.652955	0.579622
7	1	0	0.931657	0.804699	0.899443

8	1	0	-0.966570	-2.221175	-1.203067
9	1	0	-1.519711	-0.103365	-1.827207
10	1	0	-3.503769	-1.131142	-0.954423
11	1	0	-2.621204	1.196242	-1.377090
12	1	0	-0.464648	-3.085759	0.239129
13	1	0	-3.550950	-0.087577	0.467362
14	1	0	-2.692218	-2.531785	0.768501
15	1	0	-1.796643	-1.246593	1.568674
16	6	0	0.406051	-1.151276	0.086342
17	6	0	1.661043	-1.659654	0.164228
18	1	0	1.775189	-2.746977	0.128449
19	6	0	2.918423	-0.930964	0.267932
20	1	0	3.813668	-1.425197	0.650205
21	6	0	3.121362	0.313285	-0.157468
22	8	0	3.333417	1.381391	-0.536841
23	6	0	-1.025888	2.357004	0.292541
24	7	0	-1.153857	3.464188	0.600703



DD_SM1_INT_conf2.log

HF = -555.0472532 hartrees

Zero-point correction= 0.194709 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155237

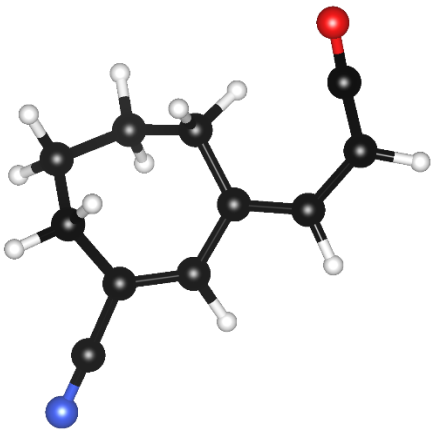
Sum of electronic and zero-point Energies= -554.852544

Sum of electronic and thermal Free Energies= -554.892016

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.928316	-0.660505	-0.173088
2	6	0	0.629447	-0.904069	0.117840
3	6	0	2.435232	0.619285	-0.805372
4	6	0	-0.245495	1.518839	-0.135286
5	6	0	2.302471	1.856565	0.088889
6	6	0	0.920951	2.002903	0.739699
7	1	0	0.375978	-1.899931	0.493129
8	1	0	-0.082559	1.818635	-1.185005
9	1	0	1.870451	0.778686	-1.736741
10	1	0	2.519370	2.740451	-0.531717
11	1	0	3.484009	0.487701	-1.101889
12	1	0	-1.159408	2.036867	0.186450
13	1	0	3.072220	1.831843	0.874747
14	1	0	0.763496	3.058748	1.003403
15	1	0	0.892834	1.443443	1.687248
16	6	0	-0.487793	0.025468	-0.028158

17	6	0	-1.735311	-0.506904	0.013615
18	1	0	-1.823347	-1.587296	0.158655
19	6	0	-2.981139	0.222437	-0.137724
20	1	0	-3.016354	1.289585	-0.360993
21	6	0	-4.167956	-0.369711	-0.042523
22	8	0	-5.201732	-0.874393	0.036127
23	6	0	2.890013	-1.699782	0.079821
24	7	0	3.683535	-2.518677	0.273914



DD_SM1_INT_conf2b.log

HF = -555.0465537 hartrees

Zero-point correction= 0.195055 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.156237

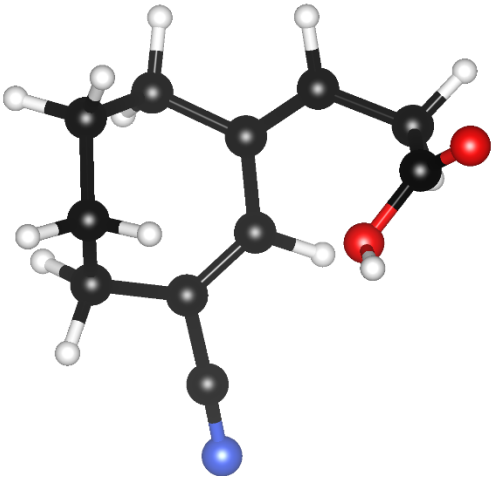
Sum of electronic and zero-point Energies= -554.851499

Sum of electronic and thermal Free Energies= -554.890317

Standard orientation:

Center Atomic Atomic Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-1.959331	-0.348681	0.229683
2	6	0	-0.887145	-1.055528	-0.194383
3	6	0	-1.855530	1.014256	0.880922
4	6	0	0.838096	0.882510	-0.231614
5	6	0	-1.414332	2.127411	-0.075540
6	6	0	-0.215288	1.739628	-0.946443
7	1	0	-1.057317	-2.071757	-0.562318
8	1	0	1.037017	1.286006	0.778018
9	1	0	-1.127103	0.931678	1.702409
10	1	0	-1.165768	3.012914	0.530726
11	1	0	-2.816183	1.275565	1.343681
12	1	0	1.785833	0.980155	-0.785661
13	1	0	-2.253963	2.418647	-0.724379
14	1	0	0.261582	2.655925	-1.323331
15	1	0	-0.560149	1.186608	-1.833553
16	6	0	0.501064	-0.595443	-0.183431
17	6	0	1.466334	-1.548418	-0.209676
18	1	0	1.151736	-2.593521	-0.268796
19	6	0	2.907918	-1.371726	-0.149307
20	1	0	3.567052	-2.212131	-0.377094
21	6	0	3.562107	-0.277752	0.232934
22	8	0	4.173022	0.639224	0.575542
23	6	0	-3.265259	-0.939036	0.109253
24	7	0	-4.325532	-1.392458	0.020225



DD_SM1_Prod_conf1.log

HF = -631.4365632 hartrees

Zero-point correction= 0.224652 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.183415

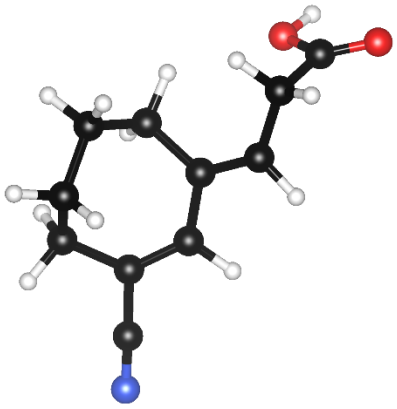
Sum of electronic and zero-point Energies= -631.211911

Sum of electronic and thermal Free Energies= -631.253149

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.508392	-0.270084	0.666068
2	6	0	1.735297	0.719095	-0.186844
3	6	0	0.556454	0.497543	-0.806019
4	6	0	1.610477	-1.285019	1.381156
5	6	0	1.176127	-2.458533	0.502573
6	6	0	0.756091	-2.035701	-0.911346

7	1	0	3.270230	-0.783854	0.053392
8	1	0	0.718898	-0.750345	1.747168
9	1	0	0.337904	-2.978058	0.992200
10	1	0	3.071648	0.312883	1.408480
11	1	0	0.075582	1.356159	-1.282115
12	1	0	2.134183	-1.671639	2.267411
13	1	0	1.996066	-3.189614	0.418669
14	1	0	0.231981	-2.865439	-1.406702
15	1	0	1.656119	-1.825282	-1.510553
16	6	0	-0.118312	-0.803452	-0.927499
17	6	0	-1.452117	-0.897875	-1.076394
18	1	0	-1.884704	-1.896900	-1.188907
19	6	0	-2.429774	0.245212	-1.035801
20	1	0	-3.345955	0.002274	-1.584596
21	1	0	-1.993097	1.156703	-1.472105
22	6	0	-2.850190	0.589656	0.381000
23	8	0	-3.966649	0.525781	0.808422
24	8	0	-1.807578	0.991688	1.124679
25	1	0	-2.147569	1.200509	2.008721
26	6	0	2.293352	2.047004	-0.266860
27	7	0	2.765392	3.100824	-0.319439



DD_SM1_Prod_conf2.log

HF = -631.4369119 hartrees

Zero-point correction= 0.224803 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.183418

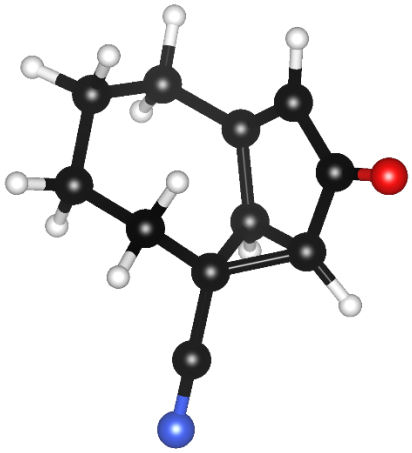
Sum of electronic and zero-point Energies= -631.212109

Sum of electronic and thermal Free Energies= -631.253494

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.801108	0.907556	-0.277294
2	6	0	-2.357003	-0.534460	-0.101372
3	6	0	-1.103446	-0.966315	0.157416
4	6	0	-2.013682	1.895481	0.590756
5	6	0	-0.654584	2.294755	0.010826
6	6	0	0.092787	1.132401	-0.651531
7	1	0	-2.749661	1.194943	-1.342135
8	1	0	-1.876705	1.440229	1.584480

9	1	0	-0.034996	2.727212	0.812123
10	1	0	-3.866262	0.953351	-0.010926
11	1	0	-0.967783	-2.029693	0.374544
12	1	0	-2.618160	2.801003	0.745563
13	1	0	-0.788937	3.086765	-0.742928
14	1	0	1.116337	1.429917	-0.911603
15	1	0	-0.396999	0.892123	-1.608624
16	6	0	0.112197	-0.139098	0.163096
17	6	0	1.187078	-0.584826	0.839476
18	1	0	1.116436	-1.552480	1.346324
19	6	0	2.510227	0.123401	0.958254
20	1	0	2.947865	-0.042173	1.949831
21	1	0	2.395090	1.204278	0.797819
22	6	0	3.513225	-0.401042	-0.050997
23	8	0	4.485424	-1.050948	0.204594
24	8	0	3.177063	-0.056478	-1.304632
25	1	0	3.840760	-0.443328	-1.896798
26	6	0	-3.407738	-1.521770	-0.140742
27	7	0	-4.269228	-2.291321	-0.183527



DD_SM2_3.log

HF = -554.9574511 hartrees

Zero-point correction= 0.194481 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.157792

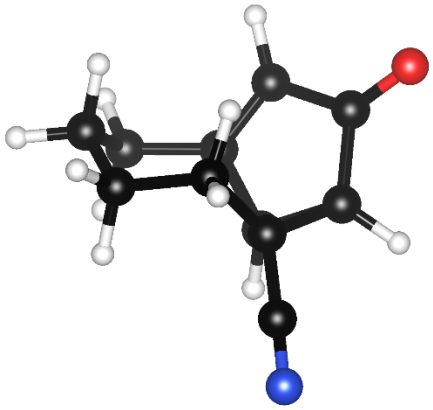
Sum of electronic and zero-point Energies= -554.762970

Sum of electronic and thermal Free Energies= -554.799659

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.387521	1.289745	-0.380528
2	6	0	-0.308213	0.834752	1.263030
3	1	0	0.293850	0.060726	1.761240
4	6	0	0.588078	2.019682	0.849055
5	1	0	0.064768	2.614442	0.080157
6	1	0	0.697829	2.683673	1.719385

7	6	0	2.000286	1.659488	0.365276
8	1	0	2.491634	1.060300	1.150672
9	1	0	2.587425	2.586594	0.266745
10	6	0	2.082509	0.873195	-0.961737
11	1	0	1.783501	1.524546	-1.798439
12	6	0	1.178975	-0.314030	-0.900044
13	6	0	-0.273044	-0.163815	-1.168101
14	1	0	-0.643853	0.187495	-2.134407
15	6	0	-1.061246	0.221817	0.085461
16	6	0	-2.357736	0.809546	-0.169740
17	6	0	-0.957254	-1.245946	-0.385503
18	1	0	-1.878854	-1.735956	-0.700167
19	6	0	1.386695	-1.458720	-0.117395
20	1	0	2.340007	-1.788571	0.294488
21	6	0	0.164224	-2.059883	0.177433
22	8	0	-0.094771	-3.128262	0.867314
23	1	0	-1.052597	1.173840	1.996866
24	1	0	3.127461	0.574276	-1.137768



DD_SM2_2.log (singlet)

HF = -555.0674164 hartrees

Zero-point correction= 0.197819 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.162218

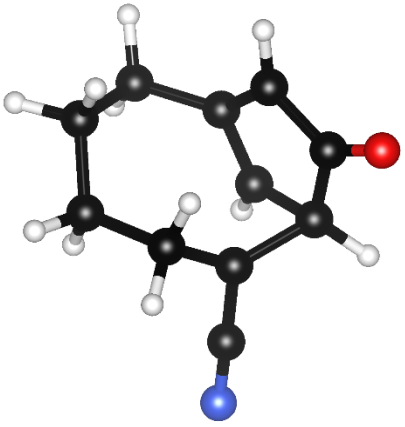
Sum of electronic and zero-point Energies= -554.869598

Sum of electronic and thermal Free Energies= -554.905198

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.584389	-0.452916	-0.389565
2	6	0	-0.675407	0.566305	1.278602
3	1	0	0.227715	0.198358	1.784114
4	6	0	-0.495435	2.036429	0.854672
5	1	0	-1.264571	2.288434	0.103914
6	1	0	-0.706149	2.673883	1.726090
7	6	0	0.897221	2.426923	0.337046
8	1	0	1.636391	2.187341	1.119018
9	1	0	0.924499	3.518662	0.200924
10	6	0	1.371053	1.764088	-0.977650
11	1	0	0.782235	2.143308	-1.826469
12	6	0	1.185515	0.288398	-0.837837
13	6	0	-0.158299	-0.300535	-1.150921
14	1	0	-0.617385	-0.156270	-2.130686
15	6	0	-1.024046	-0.332226	0.088496

16	6	0	-2.450592	-0.410915	-0.176838
17	6	0	-0.237724	-1.569390	-0.378096
18	1	0	-0.812961	-2.439187	-0.694164
19	6	0	1.941041	-0.574511	-0.134899
20	1	0	2.926524	-0.384796	0.291529
21	6	0	1.149618	-1.790445	0.202253
22	8	0	1.505507	-2.749243	0.833407
23	1	0	-1.492258	0.487545	2.008873
24	1	0	2.424957	2.022360	-1.152412



DD_SM2_A_TS1.log

HF = -554.955561 hartrees

Zero-point correction= 0.192537 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155708

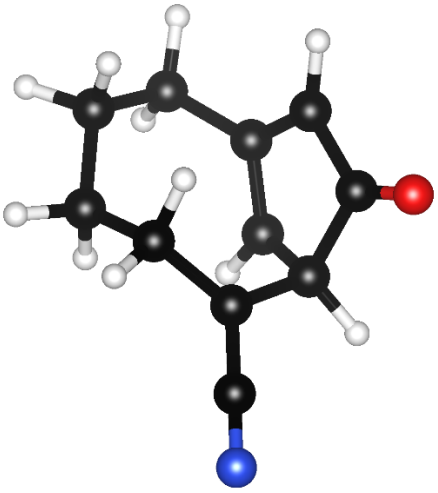
Sum of electronic and zero-point Energies= -554.763024

Sum of electronic and thermal Free Energies= -554.799853

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.587502	0.106699	0.436686
2	6	0	0.575517	0.558339	-1.329680
3	1	0	-0.288633	0.062138	-1.799770
4	6	0	0.192222	2.002693	-0.921786
5	1	0	0.922861	2.372588	-0.182002
6	1	0	0.317677	2.636608	-1.811964
7	6	0	-1.236074	2.218693	-0.406172
8	1	0	-1.943578	1.784276	-1.133790
9	1	0	-1.445108	3.300013	-0.384683
10	6	0	-1.539799	1.634936	0.993742
11	1	0	-0.946652	2.166365	1.753914
12	6	0	-1.176257	0.192948	0.988815
13	6	0	0.111353	-0.283183	1.284217
14	1	0	0.755816	0.109737	2.071505
15	6	0	1.116694	-0.302670	-0.207840
16	6	0	2.483278	-0.088763	0.141600
17	6	0	0.428849	-1.480212	0.439611
18	1	0	1.070903	-2.293541	0.785087
19	6	0	-1.820842	-0.807567	0.105842
20	1	0	-2.854233	-0.790150	-0.240880
21	6	0	-0.900633	-1.864130	-0.199262
22	8	0	-1.108113	-2.898526	-0.822207
23	1	0	1.361808	0.611565	-2.097168

24	1	0	-2.604315	1.795210	1.226090



DD_SM2_A_INT1.log

HF = -554.9881076 hartrees

Zero-point correction= 0.193921 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.156120

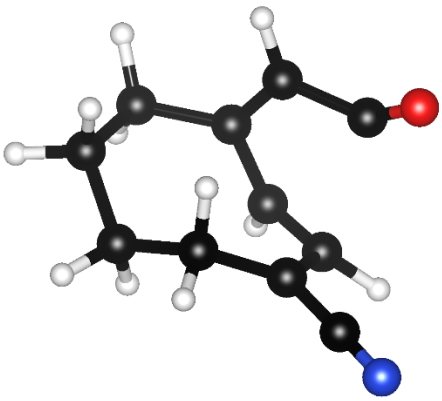
Sum of electronic and zero-point Energies= -554.794187

Sum of electronic and thermal Free Energies= -554.831988

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.686212	-1.294876	0.255274
2	6	0	-0.320229	-1.210832	-0.904620
3	1	0	0.020329	-0.504852	-1.684138
4	6	0	0.933313	-1.930486	-0.305932

5	1	0	0.771431	-2.144778	0.762360
6	1	0	0.981054	-2.914428	-0.793748
7	6	0	2.313449	-1.273256	-0.521211
8	1	0	2.349377	-0.870679	-1.547026
9	1	0	3.084945	-2.056420	-0.470976
10	6	0	2.706686	-0.141815	0.463326
11	1	0	2.955702	-0.569179	1.446210
12	6	0	1.498821	0.728077	0.568656
13	6	0	0.461909	0.405555	1.442823
14	1	0	0.555456	-0.242161	2.314413
15	6	0	-1.262316	-0.477936	0.025499
16	6	0	-2.589839	-0.917067	0.143052
17	6	0	-0.837963	0.759714	0.796388
18	1	0	-1.652693	1.124365	1.433054
19	6	0	1.058965	1.639192	-0.395099
20	1	0	1.649699	2.084408	-1.195192
21	6	0	-0.385758	1.822912	-0.259150
22	8	0	-1.129893	2.537960	-0.879169
23	1	0	-0.925614	-1.961663	-1.428286
24	1	0	3.590714	0.391500	0.087364



DD_SM2_A_TS2.log

HF = -554.9546657 hartrees

Zero-point correction= 0.191351 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.153525

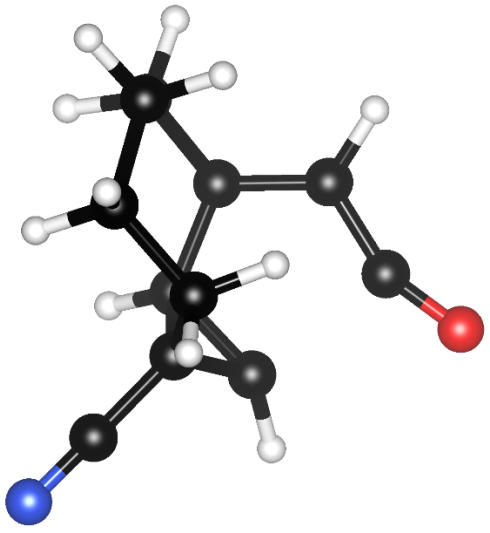
Sum of electronic and zero-point Energies= -554.763315

Sum of electronic and thermal Free Energies= -554.801141

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.635480	-1.262364	-0.070902
2	6	0	-0.181979	-1.385326	-0.728685
3	1	0	-0.041053	-0.728495	-1.607654
4	6	0	1.208102	-1.870645	-0.229497
5	1	0	1.188317	-2.012426	0.863554
6	1	0	1.358139	-2.873797	-0.653095
7	6	0	2.438035	-1.037217	-0.641954

8	1	0	2.310270	-0.733284	-1.693868
9	1	0	3.330409	-1.680024	-0.611418
10	6	0	2.718203	0.233471	0.198353
11	1	0	3.170906	-0.047286	1.161642
12	6	0	1.388437	0.871873	0.430002
13	6	0	0.594377	0.441642	1.531651
14	1	0	1.026387	0.324691	2.528801
15	6	0	-1.131592	-0.701716	0.241432
16	6	0	-2.515178	-0.998580	0.072407
17	6	0	-0.786131	0.213374	1.255692
18	1	0	-1.547057	0.418582	2.014237
19	6	0	0.747197	1.654647	-0.498824
20	1	0	1.233641	2.040601	-1.400177
21	6	0	-0.642201	1.973790	-0.235066
22	8	0	-1.536738	2.390197	-0.878849
23	1	0	-0.729059	-2.257322	-1.112496
24	1	0	3.417743	0.891847	-0.335496



DD_SM2_B_TS1.log

HF = -554.9260421 hartrees

Zero-point correction= 0.191346 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.154169

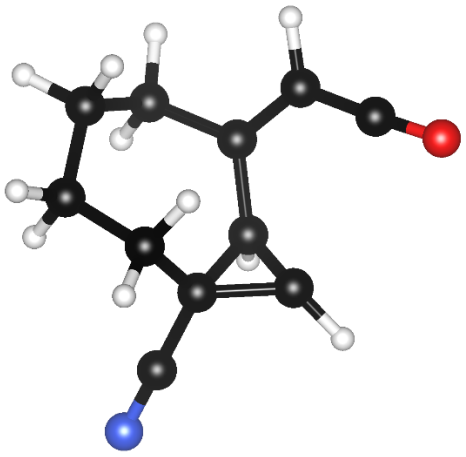
Sum of electronic and zero-point Energies= -554.734696

Sum of electronic and thermal Free Energies= -554.771873

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.187573	-1.850373	-0.364707
2	6	0	-0.861221	0.213861	1.287755
3	1	0	0.148061	0.259529	1.718999
4	6	0	-1.336428	1.620569	0.885877
5	1	0	-2.158085	1.529648	0.154047
6	1	0	-1.775363	2.100928	1.773201
7	6	0	-0.245348	2.551436	0.343509
8	1	0	0.551331	2.631943	1.102669
9	1	0	-0.666986	3.562545	0.226470
10	6	0	0.398356	2.123335	-0.991889
11	1	0	-0.349818	2.196981	-1.798027
12	6	0	0.916727	0.722240	-0.926061
13	6	0	-0.023537	-0.402099	-1.149217

14	1	0	-0.507859	-0.508308	-2.127499
15	6	0	-0.864993	-0.769242	0.114254
16	6	0	-2.156064	-1.377422	-0.147450
17	6	0	0.289549	-1.581838	-0.349493
18	1	0	0.325441	-2.648734	-0.565684
19	6	0	2.058433	0.346822	-0.177803
20	1	0	2.836825	1.049761	0.128717
21	6	0	2.208946	-0.932962	0.277659
22	8	0	2.739606	-1.867342	0.764109
23	1	0	-1.520471	-0.201322	2.063198
24	1	0	1.206552	2.830175	-1.238865



DD_SM2_B_INT1.1.log

HF = -554.9372161 hartrees

Zero-point correction= 0.191275 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.152046

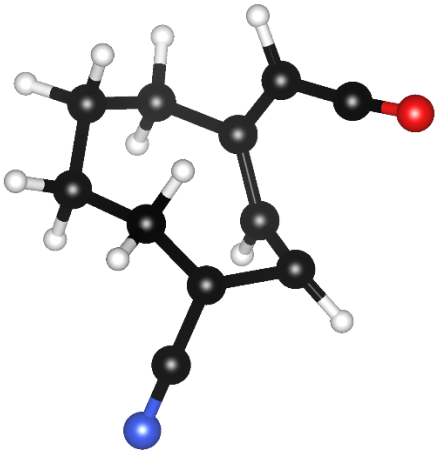
Sum of electronic and zero-point Energies= -554.745941

Sum of electronic and thermal Free Energies= -554.785170

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.302816	-1.800784	-0.541432
2	6	0	-1.067248	0.187290	1.330593
3	1	0	-0.062586	0.297231	1.767129
4	6	0	-1.582660	1.545481	0.835354
5	1	0	-2.411338	1.381485	0.124585
6	1	0	-2.018766	2.087109	1.688307
7	6	0	-0.516471	2.442114	0.200032
8	1	0	0.264928	2.649087	0.951533
9	1	0	-0.972518	3.412661	-0.052346
10	6	0	0.161261	1.873310	-1.061927
11	1	0	-0.605699	1.714769	-1.838788
12	6	0	0.873958	0.578974	-0.809163
13	6	0	0.067810	-0.665740	-0.889191
14	1	0	-0.270589	-0.948047	-1.897643
15	6	0	-0.993734	-0.864985	0.225531
16	6	0	-2.277371	-1.392402	-0.200615
17	6	0	0.185615	-1.744846	0.089165
18	1	0	0.267602	-2.825869	-0.004211
19	6	0	2.187774	0.572674	-0.263976
20	1	0	2.761500	1.501547	-0.193551

21	6	0	2.847352	-0.503213	0.198230
22	8	0	3.462963	-1.407024	0.581303
23	1	0	-1.718628	-0.205630	2.125037
24	1	0	0.864391	2.625400	-1.454643



DD_SM2_B_TS2.log

HF = -554.9165009 hartrees

Zero-point correction= 0.189428 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.150529

Sum of electronic and zero-point Energies= -554.727073

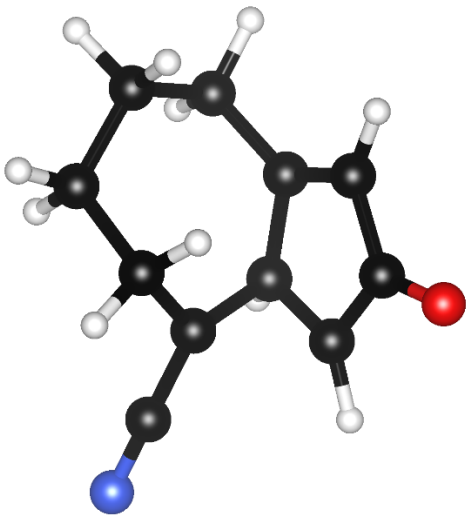
Sum of electronic and thermal Free Energies= -554.765972

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	7	0	-3.492679	-1.495537	-0.371225

2	6	0	-0.900336	0.166964	1.349312
3	1	0	0.130655	0.171039	1.726651
4	6	0	-1.308104	1.574235	0.841074
5	1	0	-2.127376	1.461306	0.110744
6	1	0	-1.738216	2.128091	1.689212
7	6	0	-0.201276	2.462228	0.251791
8	1	0	0.594016	2.579238	1.008016
9	1	0	-0.614780	3.470220	0.088520
10	6	0	0.441599	1.983994	-1.070145
11	1	0	-0.310263	1.997157	-1.873337
12	6	0	0.931368	0.583260	-0.869856
13	6	0	0.122495	-0.492712	-1.232467
14	1	0	-0.527966	-0.393170	-2.110915
15	6	0	-1.070055	-0.944959	0.335229
16	6	0	-2.401381	-1.247289	-0.054117
17	6	0	-0.009376	-1.672759	-0.397294
18	1	0	-0.161765	-2.688881	-0.765230
19	6	0	2.079562	0.394318	-0.018255
20	1	0	2.622264	1.248753	0.394443
21	6	0	2.606635	-0.793693	0.308716
22	8	0	3.140926	-1.771765	0.601399
23	1	0	-1.542052	-0.088965	2.207139
24	1	0	1.250038	2.676570	-1.351776



DD_SM2_C_TS1v2.log

HF = -554.9298181 hartrees

Zero-point correction= 0.192025 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155227

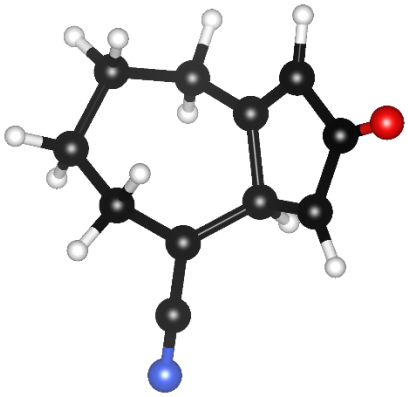
Sum of electronic and zero-point Energies= -554.737793

Sum of electronic and thermal Free Energies= -554.774591

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.443175	1.261433	-0.330889
2	6	0	-0.275117	0.903727	1.248269
3	1	0	0.316430	0.084190	1.695471
4	6	0	0.674663	2.067469	0.866816
5	1	0	0.156817	2.738536	0.161161
6	1	0	0.850393	2.660002	1.777219

7	6	0	2.038956	1.661296	0.304484
8	1	0	2.556555	1.037210	1.052272
9	1	0	2.652168	2.566627	0.172641
10	6	0	2.001650	0.885025	-1.028987
11	1	0	1.624144	1.540053	-1.830017
12	6	0	1.122339	-0.313282	-0.894599
13	6	0	-0.332670	-0.240178	-1.138252
14	1	0	-0.732385	0.130781	-2.089303
15	6	0	-1.056794	0.378214	0.082856
16	6	0	-2.367891	0.865870	-0.137520
17	6	0	-0.925661	-1.396551	-0.446438
18	1	0	-1.938910	-1.773380	-0.572336
19	6	0	1.359959	-1.435119	-0.097429
20	1	0	2.321057	-1.734953	0.323281
21	6	0	0.140450	-2.106824	0.183125
22	8	0	-0.002926	-3.191490	0.907540
23	1	0	-0.987327	1.243231	2.011985
24	1	0	3.027391	0.591714	-1.300414



DD_SM2_C_INT1.log

HF = -554.9991231 hartrees

Zero-point correction= 0.193928 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155283

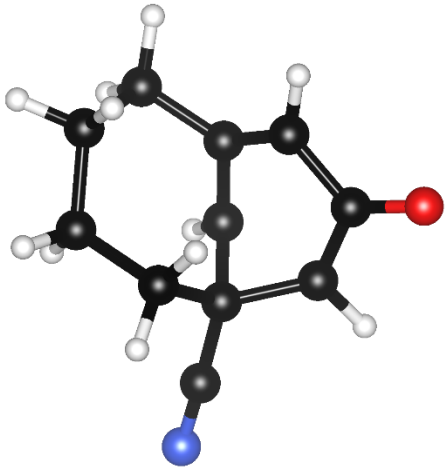
Sum of electronic and zero-point Energies= -554.805195

Sum of electronic and thermal Free Energies= -554.843840

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.797813	-2.576346	-0.550810
2	6	0	-1.385688	0.147656	1.267918
3	1	0	-0.462023	0.350514	1.837629
4	6	0	-1.966415	1.478812	0.742900
5	1	0	-2.782632	1.249758	0.038130
6	1	0	-2.426971	2.009748	1.589575
7	6	0	-0.952300	2.410541	0.081259
8	1	0	-0.219118	2.746007	0.832888
9	1	0	-1.480893	3.311198	-0.265872
10	6	0	-0.179118	1.811170	-1.108757
11	1	0	-0.894502	1.427707	-1.855754
12	6	0	0.744569	0.711984	-0.682078
13	6	0	0.243342	-0.725552	-0.569324
14	1	0	0.090176	-1.133421	-1.587970
15	6	0	-1.068562	-0.816907	0.165746

16	6	0	-2.013992	-1.779085	-0.224505
17	6	0	1.406892	-1.434031	0.061765
18	1	0	1.439022	-2.488350	0.331961
19	6	0	2.022236	0.813479	-0.283402
20	1	0	2.634766	1.715328	-0.279002
21	6	0	2.529469	-0.508435	0.194263
22	8	0	3.638503	-0.763417	0.621756
23	1	0	-2.108920	-0.312976	1.954840
24	1	0	0.405163	2.608449	-1.589511



DD_SM2_D_TS1b.log

HF = -554.9275771 hartrees

Zero-point correction= 0.192375 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.155903

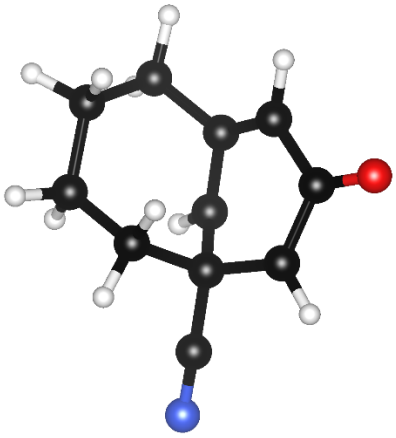
Sum of electronic and zero-point Energies= -554.735202

Sum of electronic and thermal Free Energies= -554.771674

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.220751	1.648551	-0.411320
2	6	0	-0.267774	0.846627	1.280278
3	1	0	0.219536	0.019474	1.819652
4	6	0	0.784850	1.898106	0.845377
5	1	0	0.351413	2.533009	0.052088
6	1	0	0.948062	2.569031	1.701148
7	6	0	2.177224	1.395270	0.403039
8	1	0	2.564666	0.714909	1.179987
9	1	0	2.866755	2.253475	0.370660
10	6	0	2.235212	0.657534	-0.965684
11	1	0	2.065966	1.374928	-1.782962
12	6	0	1.112132	-0.317130	-0.879319
13	6	0	-0.178127	0.136207	-1.149103
14	1	0	-0.399284	0.799689	-1.991831
15	6	0	-1.065887	0.260246	0.089206
16	6	0	-2.279526	1.019652	-0.187773
17	6	0	-1.197980	-1.195504	-0.193874
18	1	0	-2.154602	-1.590682	-0.541082
19	6	0	1.163472	-1.496778	-0.033443
20	1	0	2.093759	-1.980142	0.270633
21	6	0	-0.122608	-2.116648	0.195173
22	8	0	-0.302772	-3.282248	0.562288
23	1	0	-0.976741	1.307996	1.981839

24	1	0	3.221977	0.190952	-1.102453



DD_SM2_D_INT1.log

HF = -554.9730046 hartrees

Zero-point correction= 0.193515 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.156676

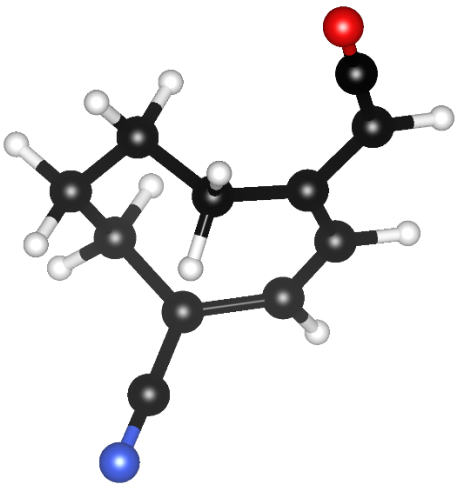
Sum of electronic and zero-point Energies= -554.779489

Sum of electronic and thermal Free Energies= -554.816329

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.949533	2.112001	-0.546983
2	6	0	-0.143383	0.998493	1.210723
3	1	0	0.112903	0.137243	1.845755
4	6	0	1.151581	1.762482	0.847469
5	1	0	0.942763	2.502349	0.057537

6	1	0	1.413721	2.354323	1.737390
7	6	0	2.411714	0.934874	0.494728
8	1	0	2.573512	0.207862	1.307503
9	1	0	3.276755	1.615241	0.504466
10	6	0	2.412317	0.147385	-0.843918
11	1	0	2.524630	0.837202	-1.694315
12	6	0	1.073259	-0.527933	-0.872561
13	6	0	-0.010325	0.362306	-1.162224
14	1	0	0.116496	1.211043	-1.834682
15	6	0	-0.992256	0.442727	-0.029937
16	6	0	-2.097258	1.367966	-0.324826
17	6	0	-1.492627	-0.951797	0.246575
18	1	0	-2.514575	-1.143401	0.575477
19	6	0	0.811971	-1.720197	-0.265283
20	1	0	1.604400	-2.422031	0.004181
21	6	0	-0.566686	-2.069819	0.143968
22	8	0	-0.900343	-3.206234	0.464429
23	1	0	-0.802048	1.649627	1.801576
24	1	0	3.251081	-0.562497	-0.859725



DD_SM2_INT_conf1_T.log

HF = -554.9767844 hartrees

Zero-point correction= 0.191933 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.151706

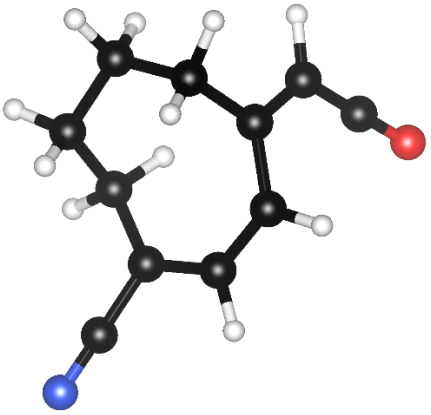
Sum of electronic and zero-point Energies= -554.784852

Sum of electronic and thermal Free Energies= -554.825078

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.999745	0.837492	1.135635
2	6	0	2.012016	-0.435609	0.332641
3	6	0	-0.633024	0.524610	-0.655365
4	6	0	1.197585	-1.601431	0.724689
5	6	0	-1.059929	-0.732496	0.060751
6	6	0	-0.165978	-1.676736	0.623523
7	1	0	3.036341	1.172556	1.304650

8	1	0	0.206304	0.307165	-1.332977
9	1	0	1.550170	0.625894	2.117362
10	1	0	-1.458326	0.834018	-1.316046
11	1	0	1.726296	-2.438794	1.192123
12	1	0	-0.628546	-2.572197	1.049602
13	6	0	1.227529	1.970307	0.441776
14	1	0	1.683941	2.155151	-0.545586
15	1	0	1.367813	2.891169	1.028331
16	6	0	-0.269786	1.716946	0.267690
17	1	0	-0.739304	1.568905	1.254597
18	1	0	-0.715638	2.632440	-0.148494
19	6	0	2.778320	-0.478610	-0.850719
20	7	0	3.410085	-0.493814	-1.828279
21	6	0	-2.467474	-0.969123	0.228509
22	1	0	-2.833834	-1.844798	0.769568
23	6	0	-3.430164	-0.164680	-0.237472
24	8	0	-4.274858	0.522646	-0.625641



DD_SM2_INT_conf2_T.log

HF = -554.9746521 hartrees

Zero-point correction= 0.191236 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.150118

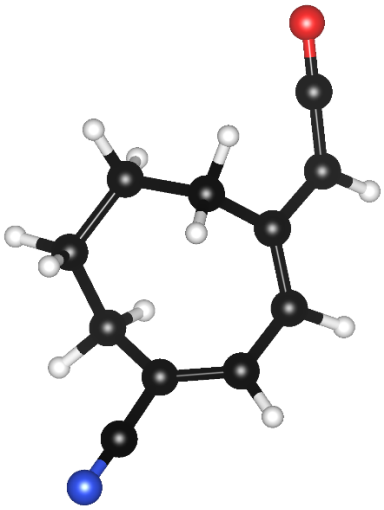
Sum of electronic and zero-point Energies= -554.783416

Sum of electronic and thermal Free Energies= -554.824534

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.170618	0.383702	1.080864
2	6	0	1.552808	-0.633298	0.034285
3	6	0	-0.842014	1.822837	-0.946281
4	6	0	0.721409	-1.136536	-0.996004
5	6	0	-1.274958	0.403348	-0.697426
6	6	0	-0.548303	-0.721819	-1.309485
7	1	0	1.868869	0.257587	1.919032
8	1	0	-0.180190	1.845842	-1.826266
9	1	0	0.167247	0.152776	1.469894
10	1	0	-1.725813	2.435585	-1.195814
11	1	0	1.155167	-1.925426	-1.615584
12	1	0	-1.044645	-1.247728	-2.136655
13	6	0	1.225685	1.858305	0.605976
14	1	0	1.916605	1.940223	-0.249043
15	1	0	1.668831	2.462077	1.411325
16	6	0	-0.123538	2.476166	0.243492

17	1	0	-0.786429	2.434974	1.125383
18	1	0	0.026914	3.544083	0.019512
19	6	0	2.889013	-1.119108	0.079006
20	7	0	3.983182	-1.503789	0.129021
21	6	0	-2.390209	0.154585	0.154741
22	1	0	-2.980685	0.978482	0.566221
23	6	0	-2.801585	-1.065942	0.537136
24	8	0	-3.180212	-2.110674	0.861379



DD_SM2_INT_conf1.log

HF = -555.0481072 hartrees

Zero-point correction= 0.194744 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.156435

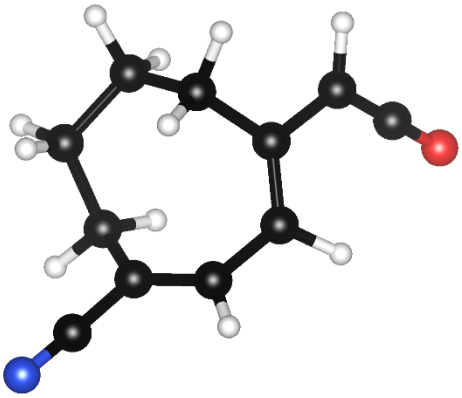
Sum of electronic and zero-point Energies= -554.853363

Sum of electronic and thermal Free Energies= -554.891672

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.516706	0.776357	1.046965
2	6	0	2.005398	-0.385201	0.209394
3	6	0	-0.850616	0.444129	-0.902253
4	6	0	1.302988	-1.503948	-0.078994
5	6	0	-1.077566	-0.795467	-0.066163
6	6	0	-0.105755	-1.687012	0.242938
7	1	0	2.379584	1.153858	1.613914
8	1	0	-0.020607	0.266238	-1.601646
9	1	0	0.786935	0.392203	1.776852
10	1	0	-1.748381	0.596075	-1.523175
11	1	0	1.830771	-2.331958	-0.563614
12	1	0	-0.392391	-2.629343	0.720096
13	6	0	0.889606	1.939741	0.262921
14	1	0	1.481828	2.122479	-0.649400
15	1	0	0.968939	2.853940	0.869700
16	6	0	-0.574925	1.732224	-0.105492
17	1	0	-1.192625	1.732370	0.808764
18	1	0	-0.907451	2.593669	-0.703338
19	6	0	3.369956	-0.296021	-0.252413
20	7	0	4.463005	-0.192773	-0.614240
21	6	0	-2.450443	-1.047005	0.374079
22	1	0	-2.691992	-1.888690	1.025754

23	6	0	-3.477512	-0.278248	0.029895
24	8	0	-4.377834	0.386411	-0.254936



DD_SM2_INT_conf2.log

HF = -555.0459034 hartrees

Zero-point correction= 0.194659 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.156098

Sum of electronic and zero-poin t Energies= -554.851245

Sum of electronic and thermal Free Energies= -554.889806

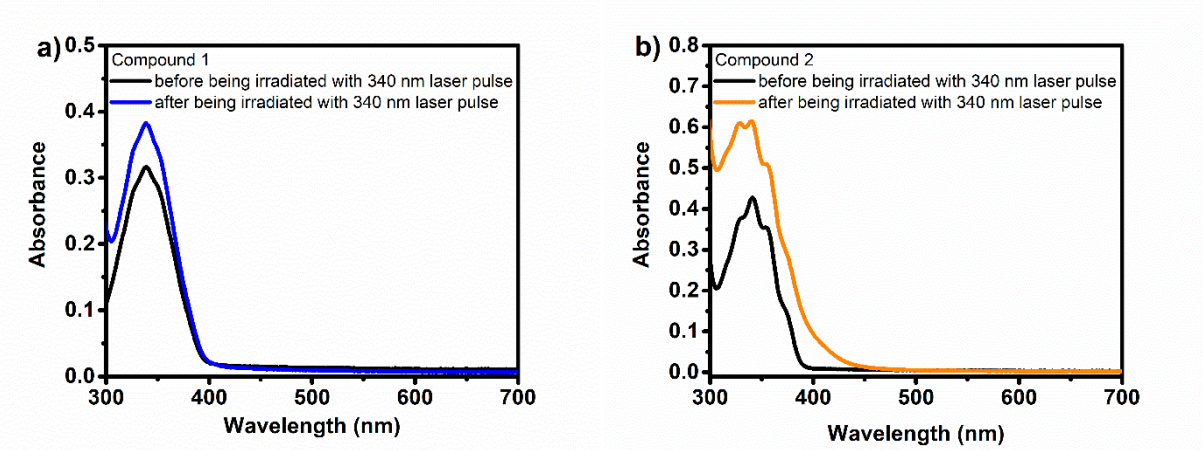
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.394097	0.406081	1.188795
2	6	0	1.711735	-0.676014	0.180550
3	6	0	-0.433851	1.261592	-1.136380
4	6	0	0.808871	-1.417997	-0.500464

5	6	0	-1.194461	0.039791	-0.673413
6	6	0	-0.626563	-1.175647	-0.480087
7	1	0	2.162582	0.354801	1.973119
8	1	0	0.441874	0.949195	-1.724392
9	1	0	0.427593	0.167967	1.659729
10	1	0	-1.098325	1.811504	-1.820283
11	1	0	1.176868	-2.267585	-1.084507
12	1	0	-1.276536	-2.047278	-0.347408
13	6	0	1.347997	1.836641	0.627285
14	1	0	2.166207	1.965219	-0.100905
15	1	0	1.551745	2.541462	1.446754
16	6	0	0.019004	2.214475	-0.016505
17	1	0	-0.769318	2.265913	0.753422
18	1	0	0.111758	3.228430	-0.433102
19	6	0	3.113416	-0.964216	-0.008205
20	7	0	4.243407	-1.166610	-0.144266
21	6	0	-2.636991	0.256091	-0.494284
22	1	0	-3.154726	1.085967	-0.978264
23	6	0	-3.380879	-0.518439	0.286437
24	8	0	-4.022228	-1.182935	0.977917

IV. Transient Absorption Spectroscopy Results

Below is a steady state absorbance spectrum of compounds **1**, **2** and **3** both before and after laser excitation under anhydrous conditions. In the case of compounds **1** and **2** they are reactive, as expected, and will form products.



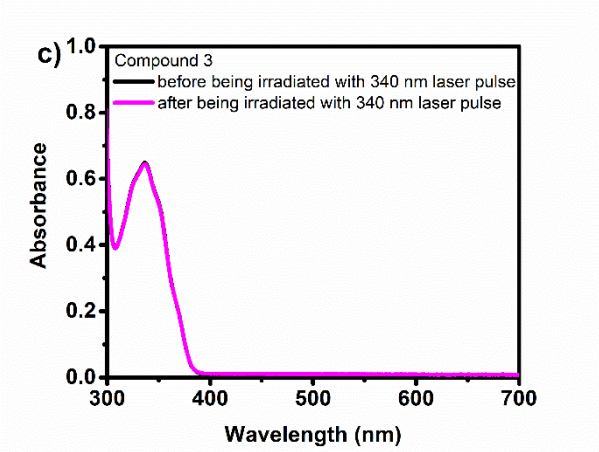


Figure S1. Steady state absorbance of (a) compound 1, (b) compound 2 and (c) compound 3, before and after being irradiated of the 340 nm laser pulse.

Compound **1** was excited with 250 fs pulses of 340nm excitation, and the induced excited state absorbance spectra were recorded. Drastic differences have been demonstrated between the first scan and the following scans in this experiment. The ESA spectrum of the first scan lacks the features that exist in the second to fifth scans at around 610nm and 800nm. This could be attributed to the conversion of compound **2** to new species (See Scheme 3 in manuscript, **B** and **C***) which have different excited absorbance spectra than compound **2** (Figure S2.a). Kinetics analysis of the different scans also shows a similar trend. The first scan's kinetics is a growth signal, indicative of the formation of **B** and **C***, while the second to fifth scans are identical decay signals that can be attributed to the conversion of these intermediates to a product. (Figure S2.b).

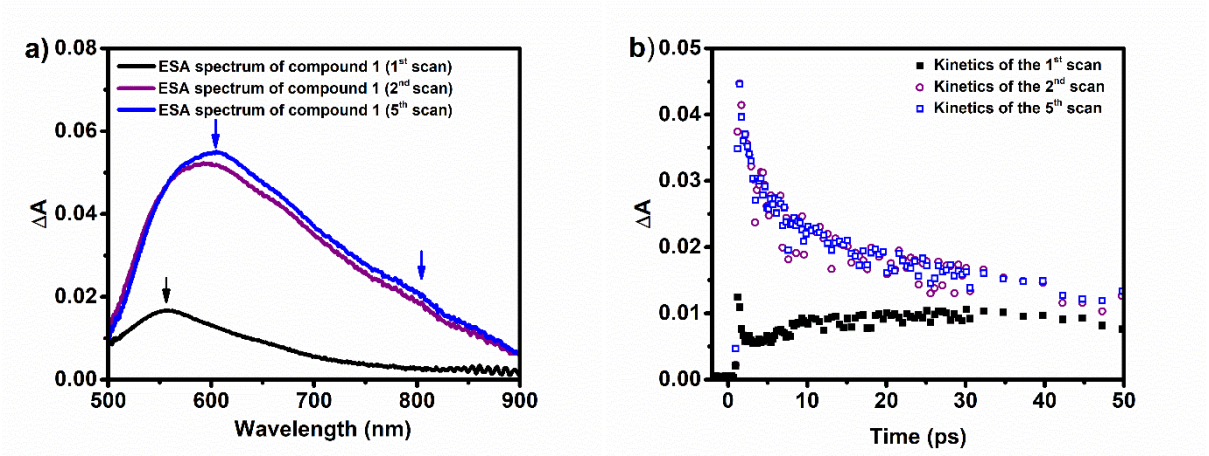


Figure S2. Excited state absorbance (ESA) of compound 1 at 3 ps, in the 1st, 2nd and 5th scans (a), Kinetics of the induced absorbance of compound 1, monitored at 650nm in the 1st, 2nd and 5th scans.

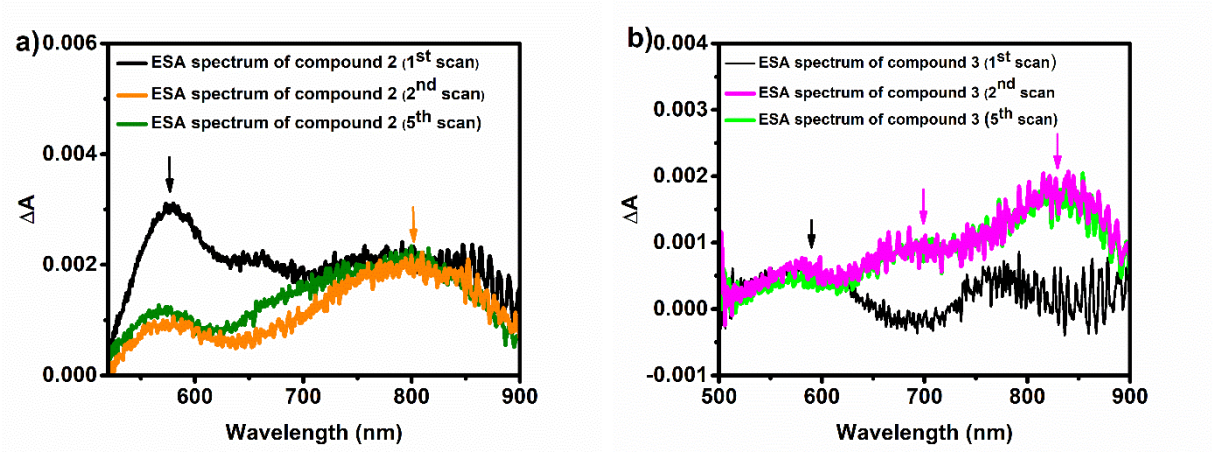


Figure S3. Excited state absorbance (ESA) of compound **2** (a) and compound **3** (b) at 3 ps, in the 1st, 2nd and 5th scans.