

Supporting Information for

Solid-State Photolysis of

α -Azidoacetophenones

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Preparation of azide **1**.

We have previously published the preparation of azides **1a-c**.¹ We prepared azide **1d** as described in the literature.²

Mp (ethyl acetate/hexanes): 83-86°C, lit.² 85°C. IR (KBr): 2092, 1684 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): 5.71 (s, 1H), 7.88 (d, 2H, 7 Hz), 7.52 (t, 1H, 7 Hz), 7.36 (t, 7H, 7 Hz) ppm. ¹³C NMR (60 MHz, CDCl₃): 67.8, 128.2, 128.7, 128.8, 129.3, 129.5, 133.7, 133.8, 134.3, 194.3 ppm. MS (m/z relative intensity): 209 (10% (M⁺-N₂), 105 (100%), 77 (60%).

Solution Photolysis of Azides 1d. A solution of azide **1d** (100 mg, 0.42 mmol) in toluene (10 mL) was bubbled with argon for 20 minutes and irradiated for 3 hours. HPLC analysis of the reaction mixture showed remaining starting material (28%) and formation of **2d:6:7:8** in the ratio of 47:17:11:25, respectively.

A solution of azide **1d** (100 mg, 0.42 mmol) in toluene (10 mL) was bubbled with oxygen for 20 minutes and irradiated for 3 hours. HPLC analysis of the reaction mixture showed remaining starting material (20%) and formation of benzoic acid (36%), benzonitrile (24%), deoxybenzoin (2%) benzaldehyde (3%) and **2d** (15%). The ratio of **2d:6:7:8:9** is 18:3:4:30:45.

Benzonitrile, benzaldehyde, deoxybenzoin and benzoic acid were characterized with an authentic sample injection on the HPLC chromatographer and GC-MS analysis of the reaction mixtures.

Solid state photolysis of azides 1. Crystals of azide **1** (~1 mmol) were dried under vacuum for a period of 24 h. The dried crystals were stored in Pyrex test tubes which were flushed with argon for 15 minutes and sealed. The solid samples were photolyzed for 12 h in an ice-bath. The reacted crystals were dissolved in anhydrous ethyl acetate. GC-MS analysis of the reaction mixture showed formation of **2** only and no remaining starting material. ¹H-NMR spectra of irradiated crystals of **1d**, that were dissolved in CDCl₃, confirmed that only **2d** was formed and no remaining starting.

Reduction of imine 2a-c with sodium cyanoborohydride. Irradiated crystal of azide **1b** (19.5 mg, 0.10 mmol) were dissolved in methanol (1 mL) and NaBH₃CN (13 mg, 0.2 mmol) added to the solution. The resulting solution was stirred at 25°C for 30 minutes maintaining the pH between 6 and 7. The solution was then poured into water (5 mL) and brought to pH >10 by adding aqueous KOH (6N). After saturating the solution with sodium chloride, it was extracted with diethyl ether (20 mL). The extract was dried with MgSO₄ and the solvent evaporated to give amine **12b** (20.5 mg, 0.095 mmol, 95% yield) as the only product (100% conversion by GC/MS and ¹H-NMR spectra).

Irradiated crystals of azides **1a** and **1c** were treated similarly and GC-MS analysis and $^1\text{H-NMR}$ spectra of the reacted crystals showed formation of only **12a** and **12c**, respectively.

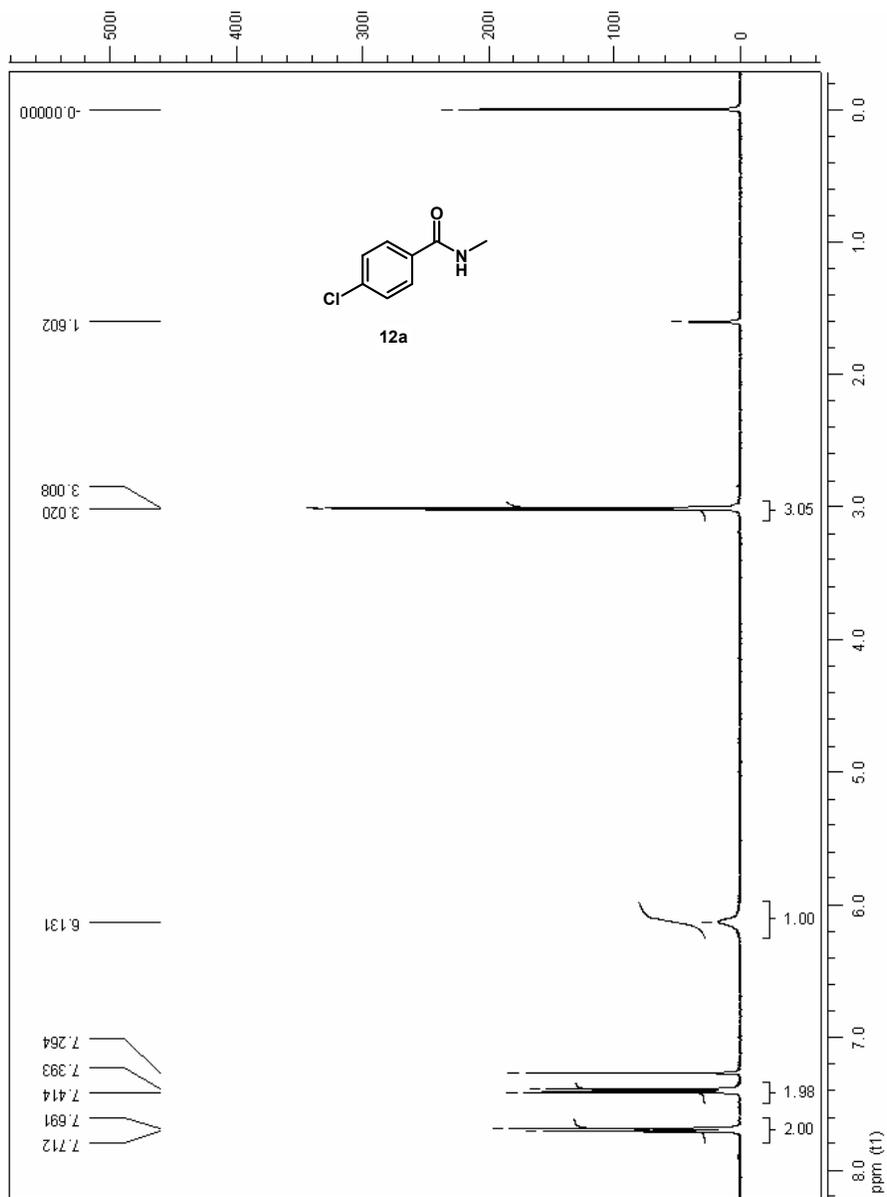


Figure 1. Reduction of **2a**, formed from solid-state photolysis of **1a**, with NaBH_3CN to form **12a**.

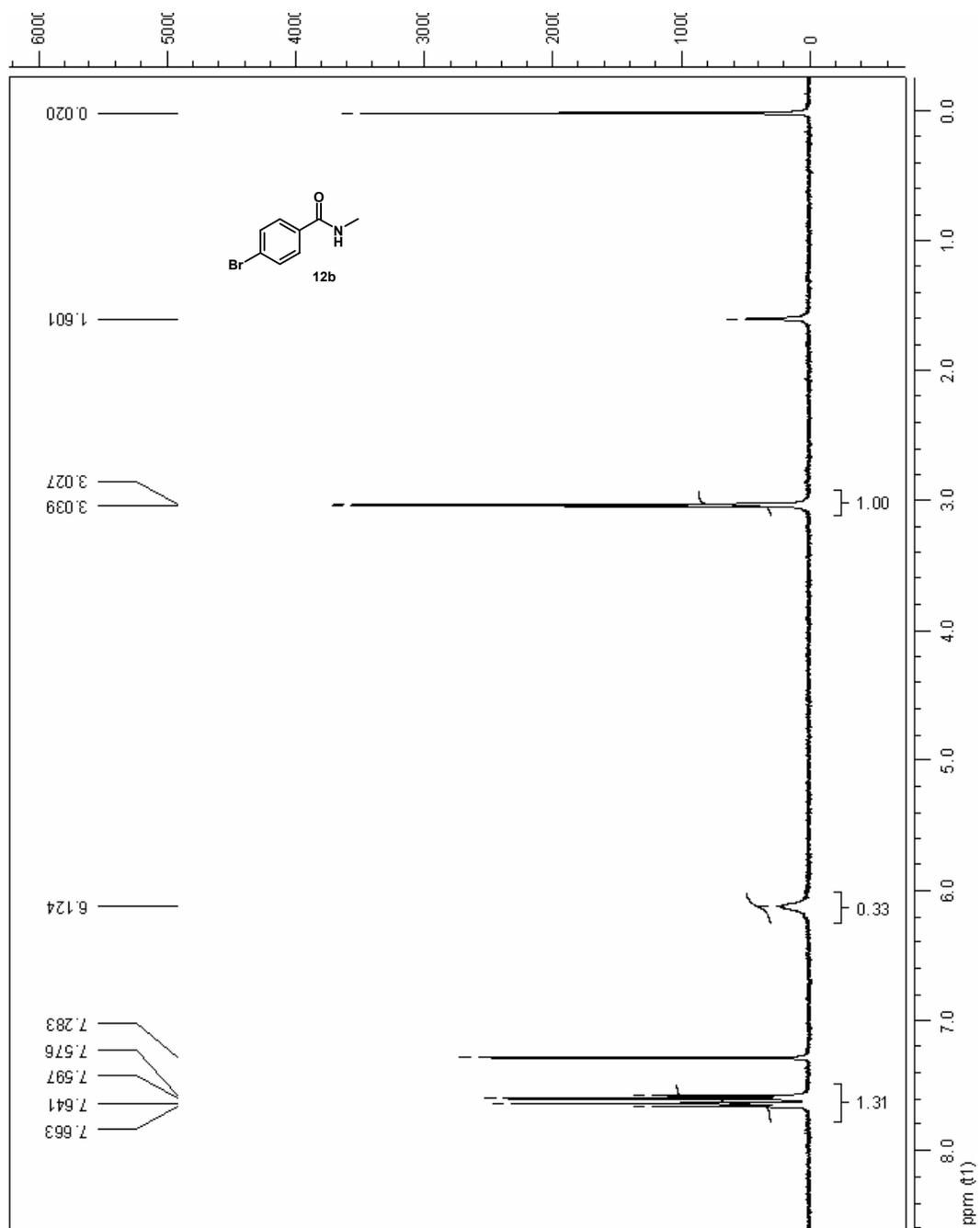


Figure 2. Reduction of **2b**, formed from solid-state photolysis of **1b**, with NaBH_3CN , to form **12b**.

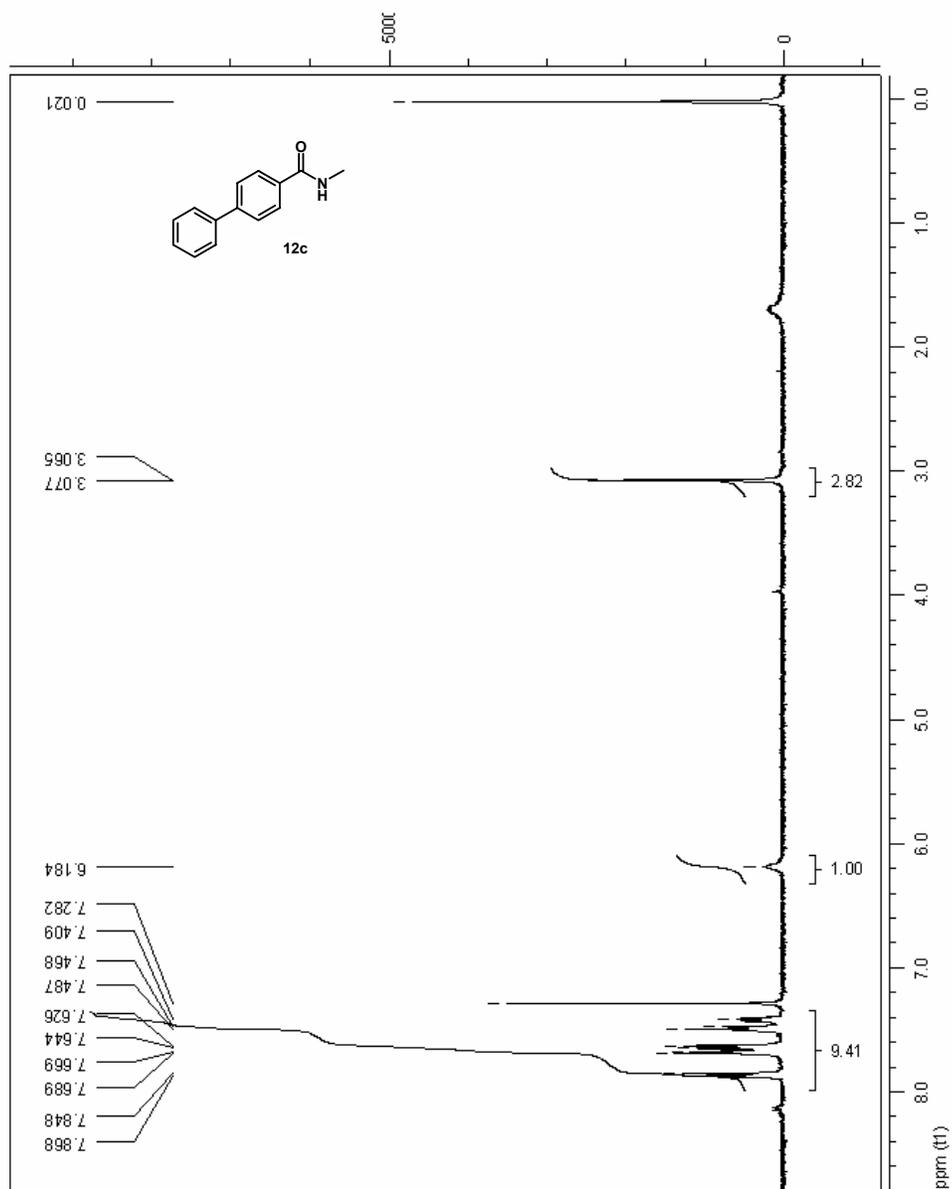


Figure 3. Reduction of **2c**, formed from solid-state photolysis of **1c**, with NaBH_3CN , to form **12c**.

Reduction of imine 2a-c with butyl triphenylphosphonium tetraborate. A mortar was charged with the irradiated crystals (~1 mmol) and reducing agent (~1 mmol) added. The solid mixture was grounded at room temperature with a pestle for a period of 15 minutes. The mixture was then extracted with acetone (12-20 mL). Evaporation of the solvent gave corresponding N-methyl-benzamides products. The products were identified by comparing their GC and GC/MS chromatography and ¹H-NMR spectra with those of a standard. p-Chloro N-methyl benzamide is commercially available whereas we prepared p-bromo N-methyl benzamide, p-phenyl N-methyl benzamide.

Preparation of N-benzylidenebenzamide 2d.

Preparation of 1,1,1-trimethyl-N-(phenylmethylene)-silanamine was made by a method described by Colvin et al.³ To 1,1,1,3,3,3-hexamethyldisilazane (23 mL, 0.11 mol) was added a solution of butyl lithium in hexane (1.55 M, 64.5 mL, 0.10 mol). The solvent was removed under vacuum until a white precipitate was formed. The resulting slurry was cooled in an ice bath and benzaldehyde (10.6 g, 0.09 mol) was added over 10 minutes. Fractional distillation of the reaction mixture gave 1,1,1-trimethyl-N-(phenylmethylene)-silanamine as a pale yellow liquid (7.2 g, 30 mmol, 30% yields) and its IR and ¹H-NMR and MS spectra are identical to those in the literature.³

Bp: 45°C (0.15 mmHg). IR (neat): 2960, 2800, 1650, 1250 cm⁻¹. ¹H-NMR (250 MHz, CDCl₃): 0.27 (s, 9 H, SiMe₃), 7.3 (m, 3 H, ArH), 7.7 (m, 2 H, ArH), 8.9 (s, 1 H, CH=N) ppm. MS (m/e): (M⁺) 177.

Preparation of substituted N-methylene carboxamide was prepared following the literature.³ The 1,1,1-trimethyl-N-(phenylmethylene)-silanamine (4.82 g, 20 mmol) was dissolved in anhydrous chloroform (30 mL) and the solution cooled to 0°C. A solution of benzoyl chloride (2.78 g, 20 mmol) in anhydrous chloroform (50 mL) was added dropwise over a period of 30 minutes with stirring. After the addition was complete the mixture was refluxed for 3 hours and the solvent is evaporated under vacuum. The remaining oil was purified by fractional distillation to yield N-methylene carboxamide (2.4 g, 11 mmol).

Bp: 116°C (0.02 torr). IR (neat): 1675, 1620, 1595, 1570 cm⁻¹. ¹H-NMR (CDCl₃): 7.40-7.85 (m, 6 H, p-HAr), 8.05-8.45 (m, 4H, o-HAr), 8.90 (s, 1H, CH=N) ppm. GC-MS (m/e): 209 (M⁺).

Preparation of Butyl triphenylphosphonium tetraborate

To a solution of butyl triphenylphosphonium bromide (1.9 g, 5 mmol) in methanol (15 mL), was added sodium borohydride (0.2 mg, 5 mmol) in one portion. The reaction mixture was stirred at room temperature for 90 minutes. The resulting white solid was collected, washed with water and dried in a desiccator under vacuum over calcium

chloride to yield white solid (1.6 g, 4.5 mmol, 89% yields). The melting point (270°C) is identical to the one in the literature.⁵

General procedure for preparation of N-methyl-amides derivatives 12b and 12c.

In freshly distilled MeOSO₂F (0.5 mL) was dissolved of p-bromo benzonitrile (2 mmol) and the mixture was left standing for 65-70 h at 20°C protected from atmospheric moisture. Then the reaction mixture was poured into water (15 mL), heated for 15-20 minutes until complete decomposition of the residual MeOSO₂F, cooled and extracted with chloroform (3 x 10 mL). The extract was washed with water, dried over Na₂SO₄, the solvent was distilled off and the residue was purified on a column packed with silica gel.

p-Bromo N-methyl benzamide.⁶ [92% yield, 390 mg, 1.3 mmol] Mp: 163-164°C (Lit.^{6a} 163-164°C. IR (Chloroform): 3480, 3400, 1660, 1530 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): 7.62-7.60 (d, J 8.4 Hz, 2 H), 7.52-7.50 (d, 8.4 Hz, 2 H), 6.38 (brs, 1H), 2.96 (d, 3.6 Hz, 3 H) ppm. MS: m/z (intensity): 215 (39), 213 (41), 185 (98), 183 (100), 157 (46), 155 (50), 117 (5), 104 (8), 76 (44), 58 (11).

p-Phenyl N-methyl benzamide. [85% yield, 358 mg, 1.36 mmol]. Mp: 164-172°C (Lit.⁷ 167°C. IR (Chloroform): 3468, 3341, 1634, 1549 cm⁻¹. ¹H-NMR (250 MHz, CDCl₃): 7.84-7.81 (d, 7.7 Hz, 2 H), 7.66-7.61 (m, 4 H), 7.48-.37 (m, 3 H), 6.21 (brs, 1 H), 3.04 (d, 4.8 Hz, 3 H) ppm. MS (m/z (intensities)): 211 (50), 181 (100), 152 (55), 127 (6), 102 (3), 76 (10).

Molecular Modeling

All were done by using Gaussian03⁶ at a B3LYP⁷ level of theory and 6-31+G(d) as the basis set. IRC calculations were done for all transition state calculation to verify that they correlated with the right starting material and product.

Heat of formation:

Methane

Energy = -40.5206149 a.u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.631791	0.631791	0.631791
3	1	0	-0.631791	-0.631791	0.631791
4	1	0	-0.631791	0.631791	-0.631791
5	1	0	0.631791	-0.631791	-0.631791

Zero-point correction= 0.045014
Thermal correction to Energy= 0.047879
Thermal correction to Enthalpy= 0.048823
Thermal correction to Gibbs Free Energy= 0.027688
Sum of electronic and zero-point Energies= -40.475601
Sum of electronic and thermal Energies= -40.472736
Sum of electronic and thermal Enthalpies= -40.471792
Sum of electronic and thermal Free Energies= -40.492927

Methyl Radical

Energy = -39.8426441 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	1.084050	0.000000
3	1	0	0.938815	-0.542025	0.000000
4	1	0	-0.938815	-0.542025	0.000000

Zero-point correction= 0.029876
Thermal correction to Energy= 0.032931
Thermal correction to Enthalpy= 0.033875
Thermal correction to Gibbs Free Energy= 0.011769
Sum of electronic and zero-point Energies= -39.812769
Sum of electronic and thermal Energies= -39.809713
Sum of electronic and thermal Enthalpies= -39.808769
Sum of electronic and thermal Free Energies= -39.830875

Methyl Azide

Energy=-204.1016545a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.394760	-0.633813	-0.000781
2	7	0	-0.716941	-0.097698	0.001803
3	7	0	-1.798678	0.272312	-0.000944
4	6	0	1.548374	0.285610	-0.000078
5	1	0	2.441217	-0.340155	-0.006299
6	1	0	1.554071	0.925002	-0.892177
7	1	0	1.560480	0.915883	0.898396

Zero-point correction= 0.050452
Thermal correction to Energy= 0.054924
Thermal correction to Enthalpy= 0.055869
Thermal correction to Gibbs Free Energy= 0.023869
Sum of electronic and zero-point Energies= -204.051203
Sum of electronic and thermal Energies= -204.046730
Sum of electronic and thermal Enthalpies= -204.045786
Sum of electronic and thermal Free Energies= -204.077785

Azido methylene radical

Energy=-203.4488072 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-0.589163	-0.437275	0.000000
2	7	0	0.000000	0.661135	0.000000
3	7	0	0.397908	1.740663	0.000000
4	6	0	0.106317	-1.603487	0.000000
5	1	0	-0.490511	-2.503150	0.000000
6	1	0	1.191394	-1.627588	0.000000

Zero-point correction= 0.036163
Thermal correction to Energy= 0.040569
Thermal correction to Enthalpy= 0.041513
Thermal correction to Gibbs Free Energy= 0.009637
Sum of electronic and zero-point Energies= -203.412644
Sum of electronic and thermal Energies= -203.408238
Sum of electronic and thermal Enthalpies= -203.407294
Sum of electronic and thermal Free Energies= -203.439170

Calculated Atom Energy

C: Energy: -37.8513345a.u.

N: Energy: -54.4856359a.u.

H: Energy: -0.5002728a.u.

Calculation of resonance stabilization energy of an azido substituent

	E ₀ (kcal/mol)	$\Delta H_f(0K)$ kcal/mol ⁸	H(298)-H(0) ⁸
C	-37.8513345	169.98	0.25
H	-0.5002728	51.63	1.01
N	-54.4856359	112.53	1.04
	Atomization Energy (kcal/mol)	$\Delta H_f(0K)$ (kcal/mol)	H(298K)-H(0)
CH₄	376.5	-14.5484	-16.329
CH₃·	324.87	35.82839	35.05843
CH₃N₃	662.46	-116.996	-119.997
·CH₂N₃	610.83	-81.8503	-83.8831
		RSE	-15 kcal/mol

Azide 1a



B3LYLP 631+G(d) = -1008.08776a.u

ZPE= 0.132224 a.u.

N₃ stretching = 2256 cm⁻¹

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.685539	-1.129964	-0.001400
2	6	0	0.030490	0.106675	-0.125135
3	6	0	0.800277	1.282283	-0.157530
4	6	0	2.187757	1.230602	-0.071006
5	6	0	2.815594	-0.012814	0.052071
6	6	0	2.075626	-1.196092	0.088975
7	1	0	0.124088	-2.058713	0.028848
8	1	0	0.290040	2.235635	-0.251913
9	1	0	2.780488	2.139227	-0.097809
10	1	0	2.579935	-2.151952	0.185658
11	6	0	-1.455720	0.234308	-0.220530
12	8	0	-2.001070	1.322108	-0.306125
13	6	0	-2.305137	-1.047906	-0.176811
14	1	0	-1.930527	-1.773854	-0.902937
15	1	0	-2.198017	-1.503435	0.821327
16	7	0	-3.707963	-0.841025	-0.522358
17	7	0	-4.361198	-0.093239	0.220737
18	7	0	-5.102837	0.538288	0.812466
19	17	0	4.562352	-0.087911	0.162242

TD DFT Azide 1a

Excited State	1:	Triplet-A	3.1765 eV	390.32 nm	f=0.0000
44A -> 51A		-0.17020			
47A -> 52A		0.27424			
48A -> 51A		-0.15127			
49A -> 51A		0.65697			
49A -> 57A		-0.12483			
50A -> 51A		0.25070			
44B -> 51B		0.17020			
47B -> 52B		-0.27424			
48B -> 51B		0.15127			
49B -> 51B		-0.65697			
49B -> 57B		0.12483			
50B -> 51B		-0.25070			
Excited State	2:	Triplet-A	3.2358 eV	383.16 nm	f=0.0000
46A -> 51A		0.11758			
48A -> 51A		-0.42302			
48A -> 57A		-0.10868			
49A -> 51A		-0.28560			
50A -> 51A		0.47613			
46B -> 51B		-0.11758			
48B -> 51B		0.42302			
48B -> 57B		0.10868			
49B -> 51B		0.28560			
50B -> 51B		-0.47613			
Excited State	3:	Singlet-A	3.6359 eV	341.00 nm	f=0.0010
48A -> 51A		-0.30252			
49A -> 51A		-0.12887			
50A -> 51A		0.59547			
48B -> 51B		-0.30252			
49B -> 51B		-0.12887			
50B -> 51B		0.59547			
Excited State	4:	Triplet-A	3.8217 eV	324.42 nm	f=0.0000
48A -> 51A		0.11612			
48A -> 53A		-0.21142			
50A -> 53A		-0.66525			
48B -> 51B		-0.11612			
48B -> 53B		0.21142			
50B -> 53B		0.66525			
Excited State	5:	Triplet-A	4.0488 eV	306.22 nm	f=0.0000
47A -> 51A		0.66064			
48A -> 51A		-0.24628			
49A -> 52A		0.13226			
50A -> 51A		-0.10613			
47B -> 51B		-0.66064			
48B -> 51B		0.24628			
49B -> 52B		-0.13226			
50B -> 51B		0.10613			

Excited State	6:	Triplet-A	4.1406 eV	299.44 nm	f=0.0000
46A -> 53A		-0.19110			
47A -> 51A		-0.18862			
48A -> 51A		-0.29492			
48A -> 53A		-0.12640			
48A -> 55A		0.18407			
50A -> 51A		-0.28545			
50A -> 54A		-0.15987			
50A -> 55A		0.41836			
50A -> 56A		0.14829			
50A -> 57A		0.20223			
46B -> 53B		0.19110			
47B -> 51B		0.18862			
48B -> 51B		0.29492			
48B -> 53B		0.12640			
48B -> 55B		-0.18407			
50B -> 51B		0.28545			
50B -> 54B		0.15987			
50B -> 55B		-0.41836			
50B -> 56B		-0.14829			
50B -> 57B		-0.20223			
Excited State	7:	Triplet-A	4.1788 eV	296.70 nm	f=0.0000
46A -> 53A		-0.19644			
47A -> 51A		0.17270			
48A -> 51A		0.33814			
48A -> 57A		0.11751			
50A -> 51A		0.34386			
50A -> 53A		0.13089			
50A -> 54A		-0.14828			
50A -> 55A		0.33630			
50A -> 56A		0.12359			
50A -> 57A		0.20506			
46B -> 53B		0.19644			
47B -> 51B		-0.17270			
48B -> 51B		-0.33814			
48B -> 57B		-0.11751			
50B -> 51B		-0.34386			
50B -> 53B		-0.13089			
50B -> 54B		0.14828			
50B -> 55B		-0.33630			
50B -> 56B		-0.12359			
50B -> 57B		-0.20506			
Excited State	8:	Singlet-A	4.2502 eV	291.72 nm	f=0.0171
48A -> 51A		0.52641			
49A -> 51A		0.12552			
50A -> 51A		0.32012			
50A -> 53A		-0.25194			
48B -> 51B		0.52641			
49B -> 51B		0.12552			
50B -> 51B		0.32012			
50B -> 53B		-0.25194			
Excited State	9:	Triplet-A	4.3516 eV	284.91 nm	f=0.0000
47A -> 52A		0.68377			

48A -> 52A	-0.15997
49A -> 51A	-0.22361
49A -> 52A	0.13551
47B -> 52B	-0.68377
48B -> 52B	0.15997
49B -> 51B	0.22361
49B -> 52B	-0.13551

Excited State 10: Singlet-A 4.3740 eV 283.46 nm f=0.0096

48A -> 51A	0.19976
48A -> 53A	0.13700
50A -> 51A	0.16401
50A -> 53A	0.60467
48B -> 51B	0.19976
48B -> 53B	0.13700
50B -> 51B	0.16401
50B -> 53B	0.60467

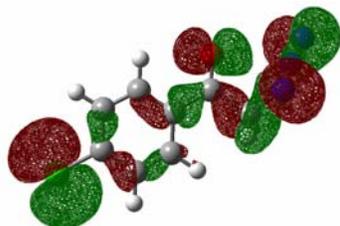
Excited State 11: Singlet-A 4.7033 eV 263.61 nm f=0.0479

47A -> 51A	0.55010
48A -> 51A	-0.15843
49A -> 51A	0.22392
49A -> 52A	-0.31057
47B -> 51B	0.55010
48B -> 51B	-0.15843
49B -> 51B	0.22392
49B -> 52B	-0.31057

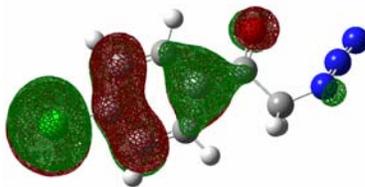
Excited State 12: Triplet-A 4.7169 eV 262.85 nm f=0.0000

47A -> 51A	-0.14714
47A -> 52A	-0.14028
49A -> 52A	0.66755
50A -> 52A	0.18371
47B -> 51B	0.14714
47B -> 52B	0.14028
49B -> 52B	-0.66755
50B -> 52B	-0.18371

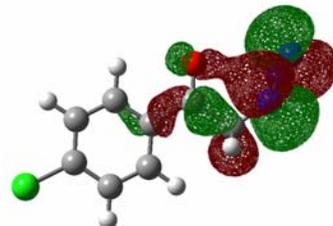
48a



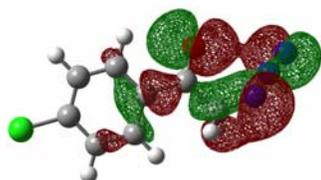
49a



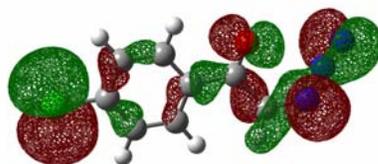
50a



46a



47



TS1 for Azide 1a

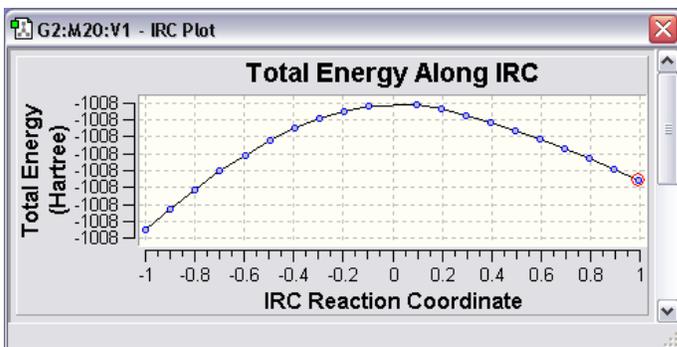


B3LYLP 631+G(d) = -1007.96492613 a.u

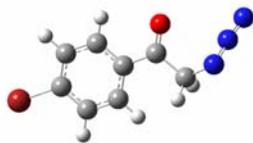
ZPE= 0.127198 a.u.

Imaginary frequencies 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.705099	-1.023584	-0.556092
2	6	0	-0.049897	0.203287	-0.326582
3	6	0	-0.819043	1.318281	0.074108
4	6	0	-2.196715	1.205511	0.247903
5	6	0	-2.817586	-0.026722	0.031935
6	6	0	-2.078020	-1.144549	-0.371039
7	1	0	-0.138961	-1.882164	-0.907349
8	1	0	-0.325615	2.271411	0.237183
9	1	0	-2.785318	2.065541	0.552265
10	1	0	-2.577718	-2.091192	-0.549985
11	6	0	1.382822	0.389221	-0.622102
12	8	0	2.050677	1.415146	-0.480414
13	6	0	2.284759	-0.912903	0.591827
14	1	0	2.201917	-0.324916	1.505534
15	1	0	1.666217	-1.799316	0.523463
16	7	0	3.548245	-1.140819	0.072101
17	7	0	4.413324	-0.248668	0.207476
18	7	0	5.316188	0.442056	0.253397
19	17	0	-4.552797	-0.175280	0.254801



Azide 1b



B3LYLP 631+G(d) = -3119.6203721 a.u

ZPE= -0.132478 a.u.

N₃ stretching = 2256 cm⁻¹

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.045896	-1.118167	-0.026444
2	6	0	-0.709458	0.114297	-0.141328
3	6	0	0.050189	1.295808	-0.183200
4	6	0	1.438852	1.253500	-0.114534
5	6	0	2.075774	0.014804	0.002050
6	6	0	1.345569	-1.173366	0.047438
7	1	0	-0.600759	-2.050602	0.011139
8	1	0	-0.468762	2.245220	-0.269859
9	1	0	2.022157	2.167695	-0.149194
10	1	0	1.855242	-2.126716	0.138282
11	6	0	-2.197518	0.232131	-0.208355
12	8	0	-2.751033	1.317151	-0.276731
13	6	0	-3.040076	-1.054208	-0.158714
14	1	0	-2.662357	-1.783303	-0.879776
15	1	0	-2.931985	-1.502677	0.842634
16	7	0	-4.443290	-0.855146	-0.507540
17	7	0	-5.101776	-0.103976	0.227738
18	7	0	-5.849473	0.528091	0.811088
19	35	0	3.972911	-0.053097	0.100004

TD_DFT for Azide 1b

Excited State	1:	Triplet-A	3.1470 eV	393.98 nm	f=0.0000
53A -> 60A		-0.22993			
56A -> 61A		0.26725			
57A -> 60A		-0.10009			
58A -> 60A		0.64303			
58A -> 66A		-0.10828			
59A -> 60A		0.27038			
53B -> 60B		0.22993			
56B -> 61B		-0.26725			
57B -> 60B		0.10009			
58B -> 60B		-0.64303			
58B -> 66B		0.10828			
59B -> 60B		-0.27038			
Excited State	2:	Triplet-A	3.2220 eV	384.80 nm	f=0.0000
54A -> 60A		0.11910			
57A -> 60A		-0.43715			
57A -> 66A		-0.10300			
58A -> 60A		-0.26539			
59A -> 60A		0.47452			
54B -> 60B		-0.11910			
57B -> 60B		0.43715			
57B -> 66B		0.10300			
58B -> 60B		0.26539			
59B -> 60B		-0.47452			
Excited State	3:	Singlet-A	3.6183 eV	342.66 nm	f=0.0011
57A -> 60A		-0.30227			
58A -> 60A		-0.14748			
59A -> 60A		0.59190			
57B -> 60B		-0.30227			
58B -> 60B		-0.14748			
59B -> 60B		0.59190			
Excited State	4:	Triplet-A	3.8195 eV	324.61 nm	f=0.0000
57A -> 60A		0.12694			
57A -> 62A		-0.20664			
59A -> 62A		-0.65351			
59A -> 63A		0.10318			
57B -> 60B		-0.12694			
57B -> 62B		0.20664			
59B -> 62B		0.65351			
59B -> 63B		-0.10318			
Excited State	5:	Triplet-A	4.0311 eV	307.57 nm	f=0.0000
56A -> 60A		0.67143			
57A -> 60A		-0.21977			
58A -> 61A		0.12715			
56B -> 60B		-0.67143			
57B -> 60B		0.21977			
58B -> 61B		-0.12715			
Excited State	6:	Triplet-A	4.1293 eV	300.26 nm	f=0.0000
54A -> 62A		-0.14336			
56A -> 60A		-0.19919			

57A -> 60A	-0.36692
57A -> 62A	-0.10969
57A -> 64A	-0.10272
57A -> 65A	0.13991
59A -> 60A	-0.34248
59A -> 64A	-0.23533
59A -> 65A	0.27521
59A -> 66A	0.18979
54B -> 62B	0.14336
56B -> 60B	0.19919
57B -> 60B	0.36692
57B -> 62B	0.10969
57B -> 64B	0.10272
57B -> 65B	-0.13991
59B -> 60B	0.34248
59B -> 64B	0.23533
59B -> 65B	-0.27521
59B -> 66B	-0.18979

Excited State 7: Triplet-A 4.1724 eV 297.15 nm f=0.0000

54A -> 62A	-0.22779
56A -> 60A	0.11992
57A -> 60A	0.27536
57A -> 62A	-0.11383
57A -> 65A	0.10247
57A -> 66A	0.13437
59A -> 60A	0.27352
59A -> 62A	0.12093
59A -> 64A	-0.29915
59A -> 65A	0.32642
59A -> 66A	0.28366
54B -> 62B	0.22779
56B -> 60B	-0.11992
57B -> 60B	-0.27536
57B -> 62B	0.11383
57B -> 65B	-0.10247
57B -> 66B	-0.13437
59B -> 60B	-0.27352
59B -> 62B	-0.12093
59B -> 64B	0.29915
59B -> 65B	-0.32642
59B -> 66B	-0.28366

Excited State 8: Singlet-A 4.2322 eV 292.95 nm f=0.0278

57A -> 60A	0.53800
58A -> 60A	0.11386
59A -> 60A	0.32851
59A -> 62A	-0.22093
57B -> 60B	0.53800
58B -> 60B	0.11386
59B -> 60B	0.32851
59B -> 62B	-0.22093

Excited State 9: Triplet-A 4.3298 eV 286.35 nm f=0.0000

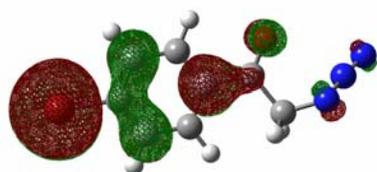
56A -> 61A	0.69525
57A -> 61A	-0.13314
58A -> 60A	-0.22657

58A -> 61A	0.11420
56B -> 61B	-0.69525
57B -> 61B	0.13314
58B -> 60B	0.22657
58B -> 61B	-0.11420

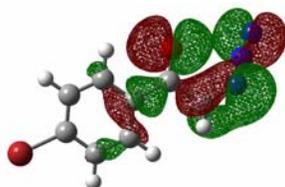
Excited State 10: Singlet-A 4.3697 eV 283.74 nm f=0.0168

57A -> 60A	0.16857
57A -> 62A	0.13542
59A -> 60A	0.15314
59A -> 62A	0.60642
57B -> 60B	0.16857
57B -> 62B	0.13542
59B -> 60B	0.15314
59B -> 62B	0.60642

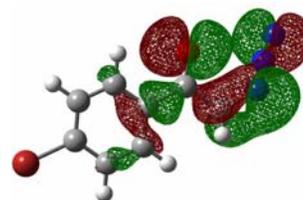
58



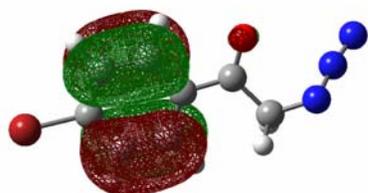
56



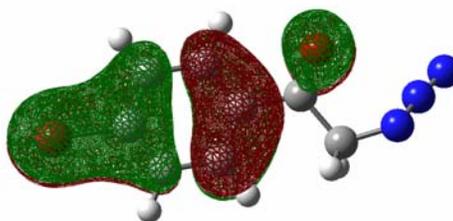
55



54



53



TS1 for Azide 1b

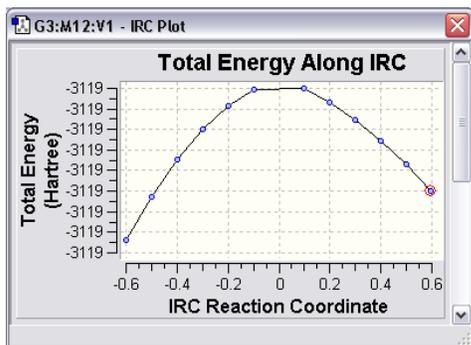


UB3LYLP 631+G(d) = -3119.49767497 a.u.

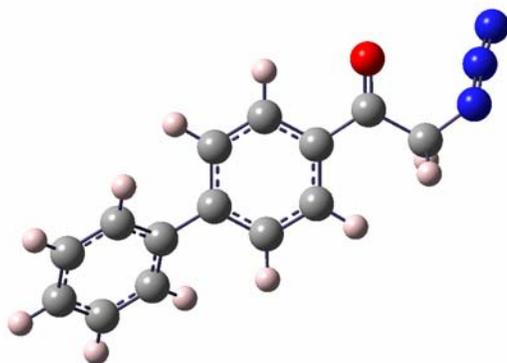
ZPE= 0.127337a.u.

Imaginary frequencies 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.034560	-0.980774	0.617312
2	6	0	-0.695893	0.237249	0.362412
3	6	0	0.066775	1.355091	-0.041493
4	6	0	1.447865	1.253149	-0.191372
5	6	0	2.075318	0.028628	0.044900
6	6	0	1.341375	-1.090908	0.451302
7	1	0	-0.598994	-1.839796	0.970226
8	1	0	-0.433956	2.300853	-0.224202
9	1	0	2.030849	2.116771	-0.495667
10	1	0	1.844589	-2.031668	0.648840
11	6	0	-2.136151	0.408770	0.623609
12	8	0	-2.813934	1.423196	0.452069
13	6	0	-2.994272	-0.921174	-0.596586
14	1	0	-2.907413	-0.335416	-1.511286
15	1	0	-2.361945	-1.796612	-0.514587
16	7	0	-4.260470	-1.166859	-0.092643
17	7	0	-5.137644	-0.288383	-0.239685
18	7	0	-6.050947	0.387712	-0.295627
19	35	0	3.961686	-0.116205	-0.163277



Azide 1c



B3LYP/6-31G(d) = -779.55763839 a.u.

ZPC= 0.222825 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.598166	-1.038284	-0.358652
2	6	0	-1.273694	0.168124	-0.107695
3	6	0	-0.514147	1.312620	0.191311
4	6	0	0.873498	1.252231	0.234209
5	6	0	1.557816	0.046577	-0.017366
6	6	0	0.792864	-1.096206	-0.312818
7	1	0	-1.146760	-1.944052	-0.599636
8	1	0	-1.035330	2.242529	0.396549
9	1	0	1.438166	2.144094	0.491255
10	1	0	1.293726	-2.033952	-0.536111
11	6	0	-2.760376	0.290684	-0.138608
12	8	0	-3.327219	1.342842	0.110458
13	6	0	-3.590620	-0.963853	-0.466262
14	1	0	-3.218638	-1.435435	-1.379155
15	1	0	-3.460719	-1.692286	0.350692
16	7	0	-5.003036	-0.691249	-0.716914
17	7	0	-5.652536	-0.201657	0.218690
18	7	0	-6.392770	0.217290	0.977786
19	6	0	3.040576	-0.015576	0.027039
20	6	0	3.821150	1.040714	-0.476425
21	6	0	3.701025	-1.131000	0.573027
22	6	0	5.215008	0.982581	-0.437231
23	1	0	3.333479	1.901492	-0.926220
24	6	0	5.094856	-1.187724	0.615742
25	1	0	3.118948	-1.947338	0.992623
26	6	0	5.857912	-0.131474	0.109857
27	1	0	5.799002	1.805471	-0.841473
28	1	0	5.584711	-2.054436	1.052205
29	1	0	6.943354	-0.176007	0.141902

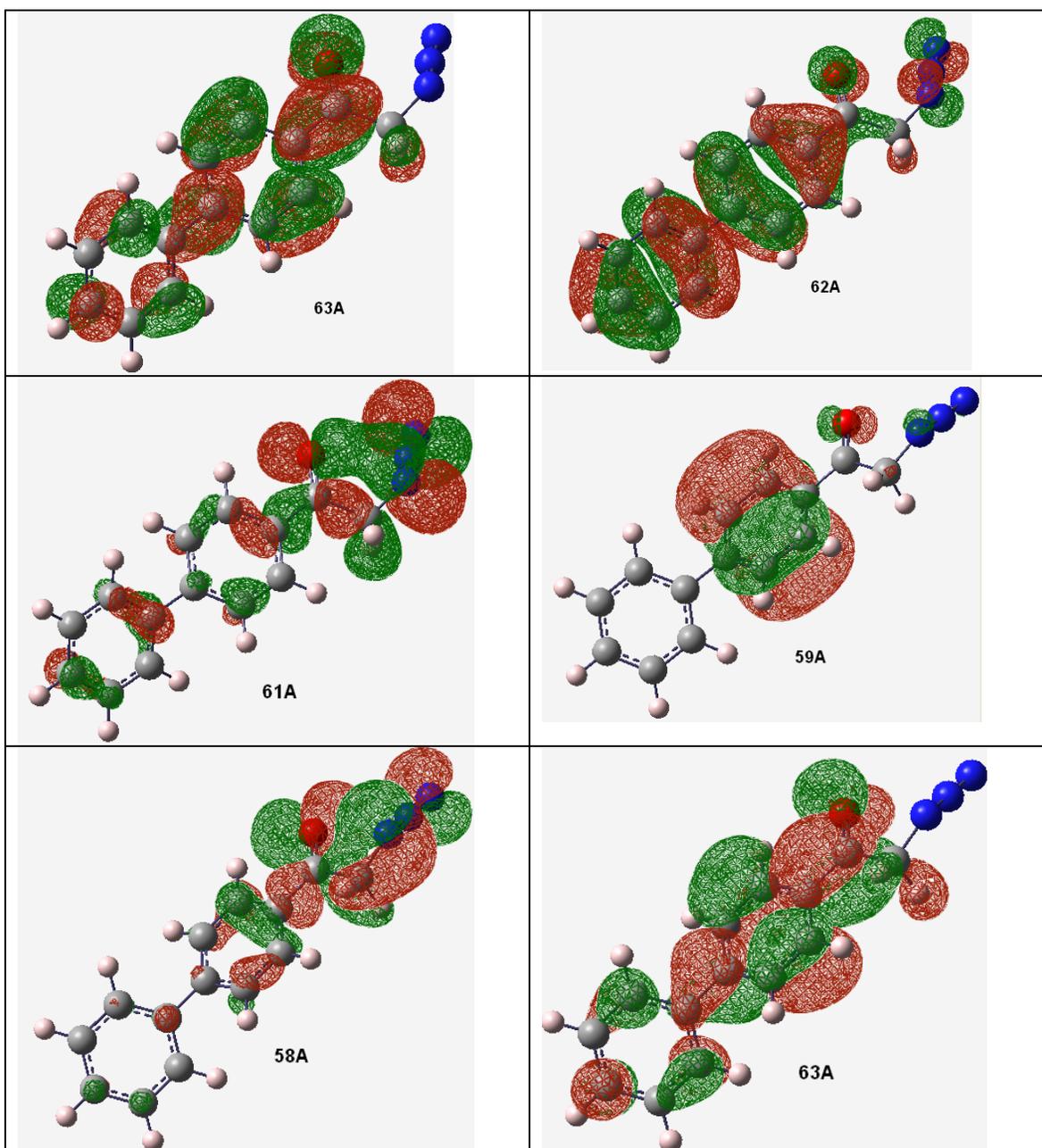
TD-DFT calculations 1c

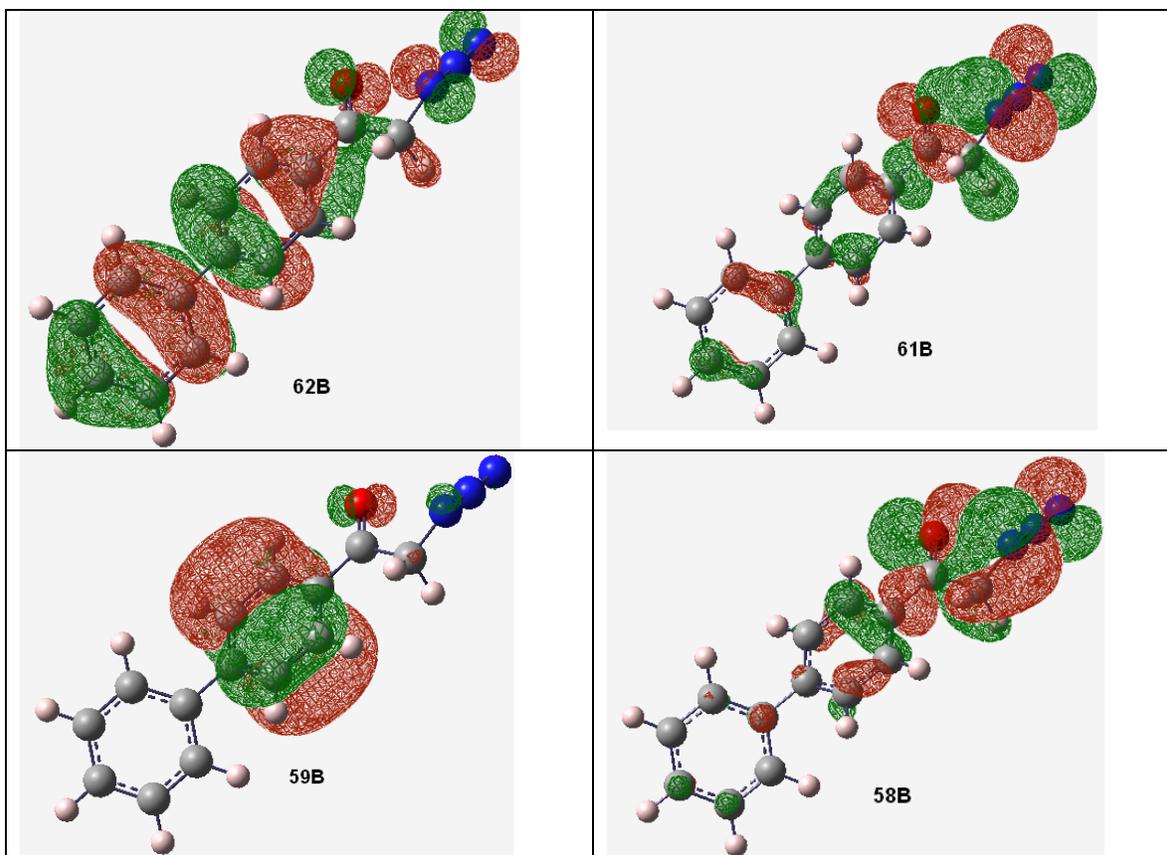
Excited State	1:	Triplet-A	2.9161 eV	425.17 nm	f=0.0000
57A -> 63A		0.23016			
57A -> 66A		-0.10223			
59A -> 65A		0.18977			
60A -> 67A		0.12711			
61A -> 63A		0.11813			
62A -> 63A		0.68195			
62A -> 66A		0.13447			
57B -> 63B		-0.23016			
57B -> 66B		0.10223			
59B -> 65B		-0.18977			
60B -> 67B		-0.12711			
61B -> 63B		-0.11813			
62B -> 63B		-0.68195			
Excited State	2:	Triplet-A	3.2272 eV	384.19 nm	f=0.0000
56A -> 63A		0.10199			
58A -> 63A		-0.43165			
58A -> 66A		0.12832			
61A -> 63A		0.52491			
61A -> 66A		-0.11368			
56B -> 63B		-0.10199			
58B -> 63B		0.43165			
58B -> 66B		-0.12832			
61B -> 63B		-0.52491			
61B -> 66B		0.11368			
Excited State	3:	Singlet-A	3.6217 eV	342.34 nm	f=0.0039
58A -> 63A		-0.29808			
61A -> 63A		0.57616			
62A -> 63A		-0.17983			
58B -> 63B		-0.29808			
61B -> 63B		0.57616			
62B -> 63B		-0.17983			
Excited State	4:	Triplet-A	3.7248 eV	332.86 nm	f=0.0000
57A -> 63A		0.38437			
57A -> 66A		0.15596			
58A -> 63A		-0.12563			
59A -> 63A		0.16962			
59A -> 65A		0.17870			
60A -> 65A		-0.11306			
60A -> 66A		0.13820			
60A -> 67A		-0.39825			
61A -> 66A		-0.10654			
62A -> 66A		-0.37168			
62A -> 67A		-0.12517			
57B -> 63B		-0.38437			
57B -> 66B		-0.15596			
58B -> 63B		0.12563			
59B -> 63B		-0.16962			
59B -> 65B		-0.17870			
60B -> 65B		0.11306			
60B -> 66B		-0.13820			

60B -> 67B	0.39825			
61B -> 66B	0.10654			
62B -> 66B	0.37168			
62B -> 67B	0.12517			
Excited State	5:	Triplet-A	3.8123 eV	325.22 nm f=0.0000
56A -> 69A	-0.10226			
58A -> 64A	-0.23509			
61A -> 64A	-0.62215			
62A -> 64A	0.19835			
56B -> 69B	0.10226			
58B -> 64B	0.23509			
61B -> 64B	0.62215			
62B -> 64B	-0.19835			
Excited State	6:	Triplet-A	3.8781 eV	319.70 nm f=0.0000
57A -> 63A	-0.12321			
59A -> 63A	0.69307			
57B -> 63B	0.12321			
59B -> 63B	-0.69307			
Excited State	7:	Singlet-A	4.0976 eV	302.58 nm f=0.5666
58A -> 63A	-0.15011			
61A -> 63A	0.10703			
62A -> 63A	0.63112			
58B -> 63B	-0.15011			
61B -> 63B	0.10703			
62B -> 63B	0.63112			
Excited State	8:	Triplet-A	4.1223 eV	300.77 nm f=0.0000
60A -> 63A	0.64115			
60A -> 66A	0.25100			
62A -> 67A	0.16582			
60B -> 63B	-0.64115			
60B -> 66B	-0.25100			
62B -> 67B	-0.16582			
Excited State	9:	Triplet-A	4.1418 eV	299.35 nm f=0.0000
56A -> 64A	-0.24501			
58A -> 63A	0.20064			
58A -> 64A	-0.13961			
58A -> 69A	-0.21174			
58A -> 70A	-0.13041			
61A -> 63A	0.16017			
61A -> 68A	-0.13644			
61A -> 69A	-0.49975			
61A -> 70A	-0.25341			
62A -> 69A	0.15852			
56B -> 64B	0.24501			
58B -> 63B	-0.20064			
58B -> 64B	0.13961			
58B -> 69B	0.21174			
58B -> 70B	0.13041			
61B -> 63B	-0.16017			
61B -> 68B	0.13644			
61B -> 69B	0.49975			
61B -> 70B	0.25341			

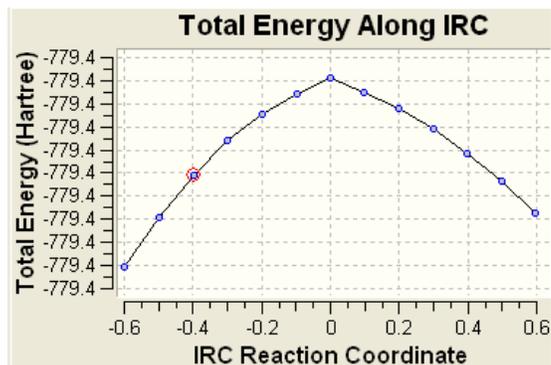
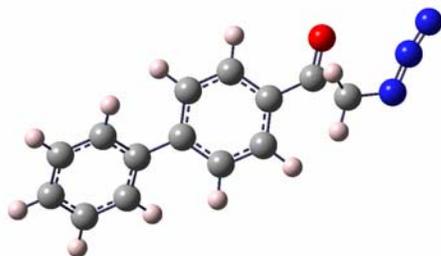
62B -> 69B

-0.15852





TS1 for Azide 1c



UB3LYP/631+G(d) 779.43437659 a.u.

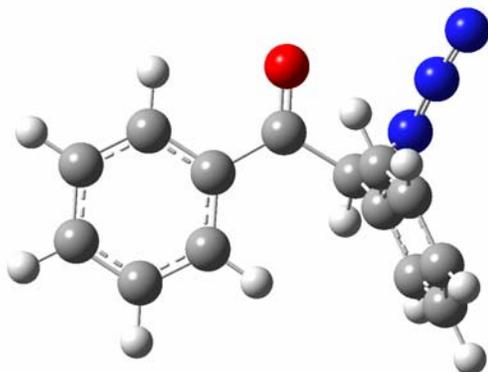
ZPC= 0.217710 a.u.

imaginary frequencies = 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.582230	-1.130539	-0.274218
2	6	0	1.267297	0.089996	-0.435839
3	6	0	0.512097	1.282498	-0.466976
4	6	0	-0.869255	1.245792	-0.329380
5	6	0	-1.558246	0.032031	-0.147584
6	6	0	-0.796353	-1.154028	-0.124911
7	1	0	1.138036	-2.064492	-0.277621
8	1	0	1.027860	2.225949	-0.615289
9	1	0	-1.430792	2.174287	-0.385829
10	1	0	-1.296214	-2.106016	0.029117
11	6	0	2.711577	0.148507	-0.714934
12	8	0	3.408591	1.152063	-0.870141
13	6	0	3.524628	-0.711407	0.896619
14	1	0	3.405439	0.136695	1.568866
15	1	0	2.898225	-1.573438	1.089276
16	7	0	4.810534	-1.089867	0.541830
17	7	0	5.668069	-0.193772	0.398534
18	7	0	6.567334	0.487409	0.243652
19	6	0	-3.031767	0.000478	0.008238
20	6	0	-3.796016	-1.051494	-0.527554
21	6	0	-3.707588	1.022168	0.699299
22	6	0	-5.181317	-1.081114	-0.377391
23	1	0	-3.302111	-1.837527	-1.091810
24	6	0	-5.092739	0.993127	0.848942
25	1	0	-3.137635	1.832024	1.146135
26	6	0	-5.836924	-0.059076	0.311674
27	1	0	-5.750854	-1.900343	-0.808470
28	1	0	-5.591006	1.790312	1.394436
29	1	0	-6.916980	-0.081982	0.428298

Azide 1d.



B3LYLP 631+G(d) = -779.55031839 a.u

ZPE= 0.223111 a.u.

N₃ stretching = 2246 cm⁻¹

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.036743	-0.873850	-0.749290
2	6	0	-1.887252	0.320737	-0.024479
3	6	0	-2.974681	0.807630	0.723022
4	6	0	-4.185390	0.119764	0.738846
5	6	0	-4.325355	-1.068901	0.012891
6	6	0	-3.249206	-1.565196	-0.727676
7	1	0	-1.209335	-1.283035	-1.319660
8	1	0	-2.848565	1.729925	1.281252
9	1	0	-5.020884	0.507661	1.315552
10	1	0	-5.270039	-1.606503	0.025581
11	1	0	-3.352051	-2.490851	-1.287481
12	6	0	-0.619346	1.112984	-0.006875
13	8	0	-0.488204	2.090080	0.714391
14	6	0	0.559552	0.681131	-0.911567
15	1	0	0.163161	0.330920	-1.866618
16	6	0	1.376461	-0.442553	-0.279518
17	6	0	1.900154	-1.455514	-1.096569
18	6	0	1.661419	-0.460874	1.093895
19	6	0	2.690586	-2.469939	-0.554094
20	1	0	1.695222	-1.442840	-2.165179
21	6	0	2.455743	-1.474998	1.636329
22	1	0	1.265158	0.314498	1.743935
23	6	0	2.969950	-2.481809	0.816046
24	1	0	3.089266	-3.248102	-1.199923
25	1	0	2.669663	-1.476505	2.701874
26	1	0	3.585107	-3.270933	1.240517
27	7	0	1.379057	1.848849	-1.305942
28	7	0	2.045115	2.400712	-0.418010
29	7	0	2.736339	2.996645	0.265274

TD-DFT calculations 1d

Excited State 1: Triplet-A 3.1421 eV 394.59 nm f=0.0000
57 -> 63 0.29805
58 -> 63 -0.10393
61 -> 63 -0.38488
62 -> 63 0.50283

This state for optimization and/or second-order correction.

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 3.2707 eV 379.08 nm f=0.0000
57 -> 63 0.11113
58 -> 63 0.43278
58 -> 64 0.11429
58 -> 65 -0.18067
59 -> 63 0.53461
59 -> 65 0.18678
59 -> 66 0.12027
60 -> 63 0.14939

Excited State 3: Triplet-A 3.6222 eV 342.29 nm f=0.0000
57 -> 67 0.14267
60 -> 65 -0.11003
60 -> 66 0.36282
60 -> 67 -0.10167
61 -> 63 -0.29438
61 -> 64 0.32110
61 -> 67 0.24888
62 -> 63 -0.23107
62 -> 64 0.27130

Excited State 4: Triplet-A 3.7699 eV 328.88 nm f=0.0000
57 -> 63 0.17713
57 -> 64 -0.18759
60 -> 66 -0.25027
61 -> 64 -0.17101
61 -> 67 -0.16259
62 -> 64 0.43618
62 -> 65 0.25532
62 -> 67 -0.25512

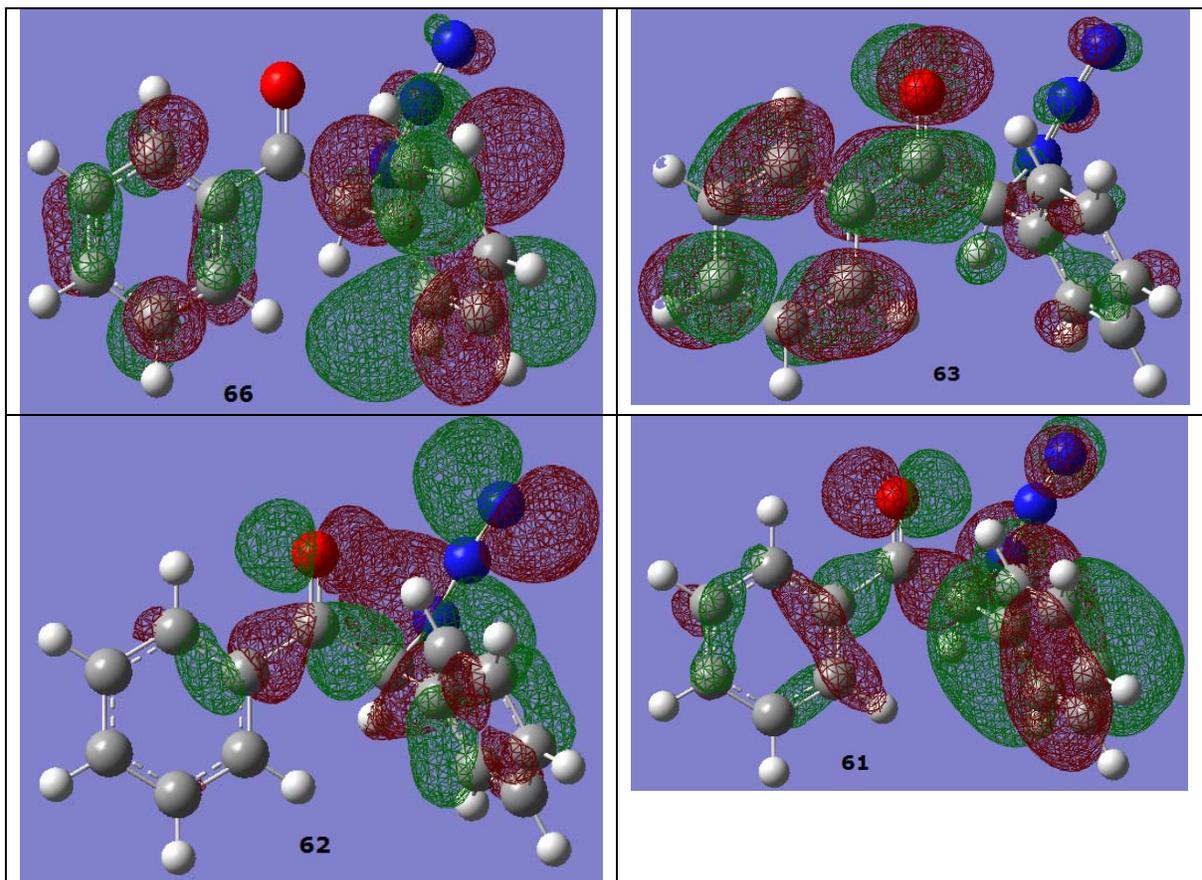
Excited State 5: Triplet-A 3.8572 eV 321.44 nm f=0.0000
58 -> 63 0.51073
59 -> 63 -0.46411
61 -> 63 -0.14188

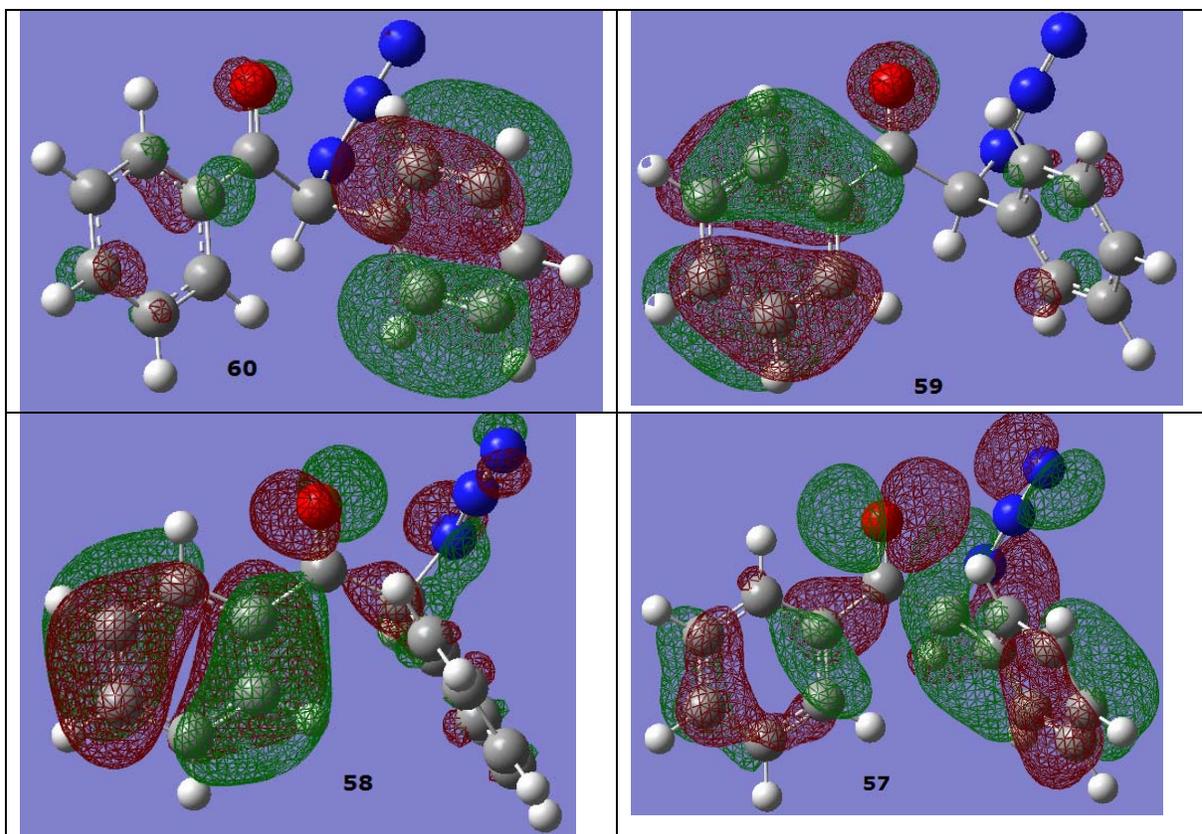
Excited State 6: Triplet-A 4.0142 eV 308.87 nm f=0.0000
57 -> 63 -0.15750
58 -> 63 0.17577
60 -> 66 0.13770
61 -> 63 0.30047
61 -> 64 0.15803
62 -> 63 0.36295
62 -> 64 0.23506
62 -> 65 0.10067
62 -> 68 -0.11841

62 -> 69	0.21855
62 -> 70	-0.15538
62 -> 72	0.10850

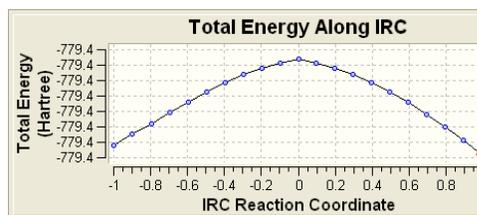
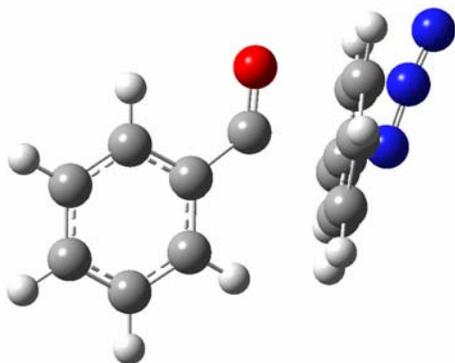
Excited State 7: Triplet-A 4.1814 eV 296.51 nm f=0.0000

56 -> 64	-0.22537
56 -> 65	-0.11873
56 -> 67	0.12684
57 -> 69	-0.12504
60 -> 66	-0.12710
61 -> 63	-0.19892
61 -> 67	-0.10029
62 -> 63	-0.18029
62 -> 66	-0.11170
62 -> 67	0.16237
62 -> 68	-0.14586
62 -> 69	0.36855
62 -> 70	-0.25530
62 -> 72	0.24386





Transition State for α -cleavage of 1d



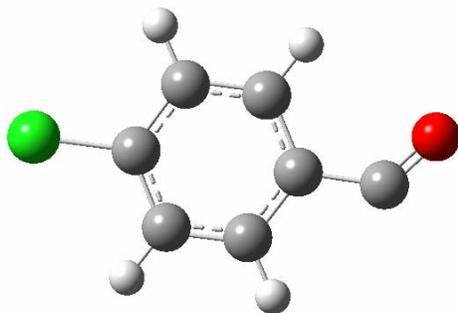
B3LYP- 631+G(d)= -779.43380631 a.u.

ZPE= 0.218077 a.u.

imaginary frequency = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.365786	-0.555374	-1.081449
2	6	0	1.704782	-0.711060	0.156600
3	6	0	2.364482	-0.279950	1.332406
4	6	0	3.629265	0.293572	1.260351
5	6	0	4.266299	0.459998	0.026996
6	6	0	3.624817	0.030115	-1.140777
7	1	0	1.904489	-0.919241	-1.995404
8	1	0	1.864179	-0.406000	2.286978
9	1	0	4.119793	0.620337	2.174021
10	1	0	5.253542	0.910071	-0.024985
11	1	0	4.117149	0.141454	-2.103453
12	6	0	0.436942	-1.425591	0.301734
13	8	0	-0.209332	-1.635764	1.337459
14	6	0	-0.814341	-0.763634	-0.974496
15	1	0	-0.186780	-0.693684	-1.857017
16	7	0	-1.696659	-1.846378	-1.185808
17	7	0	-2.522810	-2.170620	-0.319178
18	7	0	-3.332886	-2.609718	0.351863
19	6	0	-1.262328	0.548323	-0.465630
20	6	0	-2.081641	0.705135	0.670159
21	6	0	-0.814409	1.700934	-1.141647
22	6	0	-2.465076	1.976529	1.086439
23	1	0	-2.383154	-0.158249	1.250389
24	6	0	-1.202524	2.968669	-0.720540
25	1	0	-0.165611	1.594222	-2.006890
26	6	0	-2.034458	3.111546	0.393028
27	1	0	-3.095196	2.083061	1.964995
28	1	0	-0.856260	3.845180	-1.260945
29	1	0	-2.336593	4.100703	0.725440

Benzoyl Radical 4a



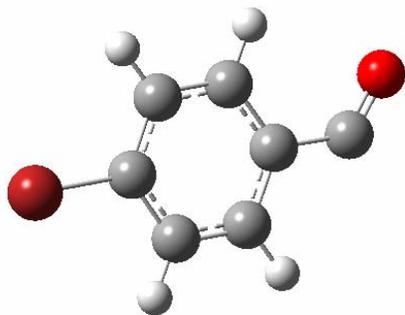
B3LYP/(631+G(d) = -804.5319681 a.u.

ZPE = 0.087961

0 Imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	1.272461	0.000000
2	6	0	1.224725	0.612755	0.000000
3	6	0	1.269796	-0.794146	0.000000
4	6	0	0.077135	-1.530887	0.000000
5	6	0	-1.154980	-0.878899	0.000000
6	6	0	-1.179443	0.517789	0.000000
7	1	0	-0.049357	2.356627	0.000000
8	1	0	2.152924	1.176871	0.000000
9	1	0	0.123092	-2.616311	0.000000
10	1	0	-2.083400	-1.440174	0.000000
11	6	0	2.562065	-1.512677	0.000000
12	8	0	3.668085	-1.062032	0.000000
13	17	0	-2.722572	1.347110	0.000000

Benzoyl Radical 4b



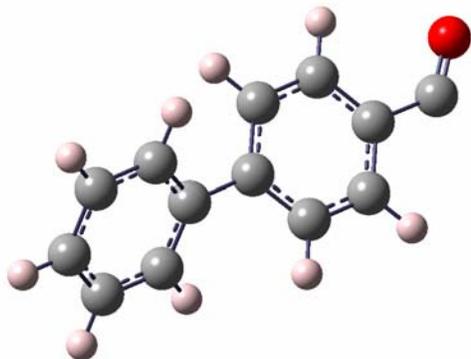
B3LYP/(631+G(d)) = -2916.0640543 a.u

ZPC= 0.088352

0 Imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.121299	-0.220936	0.000000
2	6	0	-0.935710	-1.599359	0.000000
3	6	0	0.365502	-2.135525	0.000000
4	6	0	1.475657	-1.280253	0.000000
5	6	0	1.298022	0.102262	0.000000
6	6	0	0.000000	0.616501	0.000000
7	1	0	-2.119663	0.203844	0.000000
8	1	0	-1.789774	-2.270496	0.000000
9	1	0	2.475244	-1.705874	0.000000
10	1	0	2.151696	0.771265	0.000000
11	6	0	0.581959	-3.597789	0.000000
12	8	0	-0.230412	-4.473228	0.000000
13	35	0	-0.253114	2.499362	0.000000

Benzoyl Radical 4c



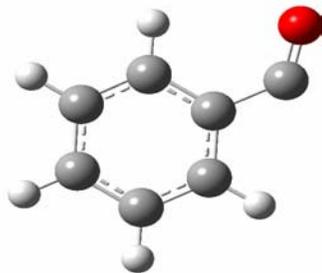
B3LYP/631+G(d) = -576.00190036 a.u.

ZPC= 0.178594 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.023264	1.348128	0.430243
2	6	0	-2.813436	0.224659	0.116256
3	6	0	-2.160047	-0.971138	-0.253215
4	6	0	-0.773328	-1.033532	-0.292361
5	6	0	0.022578	0.078892	0.039331
6	6	0	-0.638920	1.270511	0.400157
7	1	0	-2.502939	2.288703	0.687984
8	1	0	-2.759930	-1.835344	-0.520415
9	1	0	-0.294576	-1.956505	-0.607844
10	1	0	-0.053464	2.142652	0.676703
11	6	0	-4.280706	0.298614	0.021854
12	8	0	-5.065444	-0.613733	-0.240540
13	6	0	1.502305	0.003014	0.004817
14	6	0	2.276329	1.104266	-0.402523
15	6	0	2.174724	-1.173561	0.381213
16	6	0	3.667891	1.032118	-0.431416
17	1	0	1.780967	2.014991	-0.727132
18	6	0	3.566033	-1.246158	0.351718
19	1	0	1.601092	-2.029489	0.725755
20	6	0	4.320034	-0.143363	-0.054393
21	1	0	4.243671	1.893912	-0.758716
22	1	0	4.062667	-2.164054	0.655294
23	1	0	5.404904	-0.199702	-0.077395

Benzoyl Radical 1d



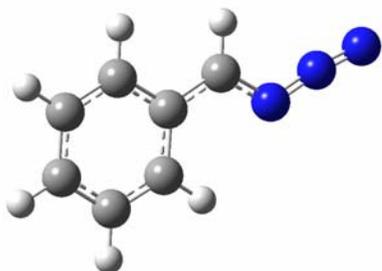
B3LYP/(631+G(d)) = -344.93693666 a.u

ZPC= 0.097615

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.740243	-1.687392	0.000000
2	6	0	-1.030590	-0.331115	0.000000
3	6	0	0.000000	0.618977	0.000000
4	6	0	1.331101	0.183368	0.000000
5	6	0	1.627578	-1.168928	0.000000
6	1	0	-1.555297	-2.400183	0.000000
7	1	0	-2.060778	0.008923	0.000000
8	1	0	2.127636	0.919981	0.000000
9	1	0	2.662155	-1.496470	0.000000
10	6	0	-0.301314	2.062024	0.000000
11	8	0	-1.360220	2.600295	0.000000
12	6	0	0.594489	-2.121524	0.000000
13	1	0	0.821918	-3.167074	0.000000

10p



UB3LYP 631+G(d) -434.52969465 a.u.

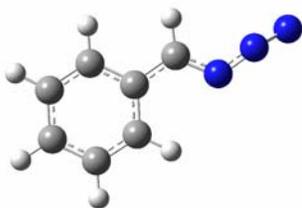
ZPE= 0.118596 a.u.

IR stretching of N₃ = 2226 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.004336	1.172075	-0.327985
2	1	0	1.109716	2.226578	-0.180274
3	6	0	-0.372125	0.503868	-0.153468
4	6	0	-1.484311	1.275008	0.210269
5	6	0	-0.512517	-0.875341	-0.358395
6	6	0	-2.736890	0.666940	0.369080
7	1	0	-1.377119	2.328065	0.366735
8	6	0	-1.765096	-1.483409	-0.199584
9	1	0	0.336662	-1.464124	-0.636116
10	6	0	-2.877283	-0.712269	0.164153
11	1	0	-3.586070	1.255723	0.646801
12	1	0	-1.872289	-2.536466	-0.356050
13	1	0	-3.833655	-1.176542	0.285408
14	7	0	2.173455	0.361199	-0.697499
15	7	0	2.874759	-0.144361	0.180229
16	7	0	3.764083	-0.776047	0.752853

Transition State for 10p

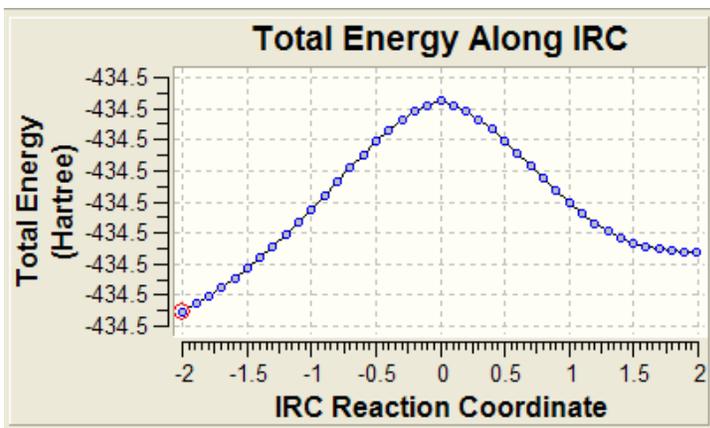


UB3LYP 631+G(d) -434.52474050 a.u.

ZPE= 0.117384

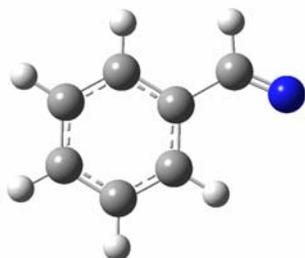
imaginary frequencies= 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-1.949884	-0.319786	-0.006163
2	7	0	-3.205215	-0.111728	-0.154936
3	7	0	-4.321449	-0.085292	0.166480
4	6	0	-1.090379	0.687758	-0.033490
5	1	0	-1.404221	1.728055	-0.078895
6	6	0	0.401487	0.306280	-0.013241
7	6	0	0.778010	-1.037112	-0.013872
8	6	0	1.376298	1.303745	0.005619
9	6	0	2.129052	-1.382872	0.005035
10	1	0	0.009234	-1.823259	-0.027966
11	6	0	2.727810	0.958052	0.023537
12	1	0	1.079718	2.362598	0.005939
13	6	0	3.104310	-0.384999	0.023387
14	1	0	2.425898	-2.441729	0.005173
15	1	0	3.496191	1.744726	0.037990
16	1	0	4.169497	-0.657860	0.038233



Reversed IRC

11p

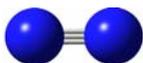


B3LYP-631+G(d) = 325.05892472 a.u.

ZPE= 0.108787 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.999976	0.530929	0.000185
2	1	0	-2.351417	1.560436	0.000579
3	6	0	-0.608404	0.233822	0.000101
4	6	0	0.330979	1.299448	-0.000011
5	6	0	-0.110759	-1.096907	0.000126
6	6	0	1.697123	1.044921	-0.000094
7	1	0	-0.030168	2.325721	-0.000031
8	6	0	1.257810	-1.337723	0.000042
9	1	0	-0.813790	-1.924168	0.000265
10	6	0	2.172593	-0.274188	-0.000069
11	1	0	2.398363	1.875612	-0.000179
12	1	0	1.620349	-2.362745	0.000062
13	1	0	3.241178	-0.470856	-0.000134
14	7	0	-2.928673	-0.486544	-0.000320



Nitrogen

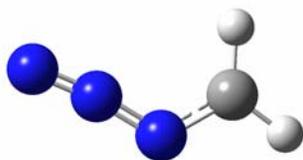
B3LYP/(631+G(d)) = -109.52977937 a.u

ZPC= **0.005592**

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	0.000000	0.000000	0.547768
2	7	0.000000	0.000000	-0.547768

Azido imine radical 10h



B3LYP/(631+G(d) = -203.44880419 a.u

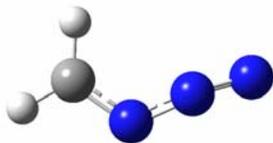
ZPC= 0.036167a.u.

0 Imaginary frequencies

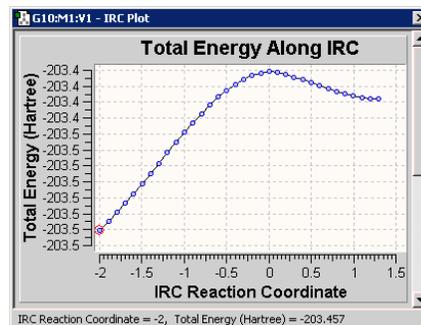
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.699720	-0.281060	0.000000
2	1	-2.131213	-0.597350	-0.926647
3	1	-2.131214	-0.597347	0.926648
4	7	-0.514121	0.587994	0.000000
5	7	0.613471	0.091647	0.000000
6	7	1.966471	-0.268062	0.000000

Transition State for 10h



Reversed IRC



UB3LYP/(631+G(d) = -203.447047 a.u

ZPC= 0.035609

imaginary frequencies = 1

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	-0.512318	-0.529957	-0.041866
2	7	0.664884	-0.070099	0.167904
3	7	1.761643	0.201097	-0.103312
4	6	-1.564852	0.274059	-0.022597
5	1	-2.531722	-0.206104	-0.090668
6	1	-1.478624	1.354468	0.067168

11h

B3LYP/631+G(d) = **-93.9890409 a.u.**

ZPC = -0.025347 a.u.

0 Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.742633	0.000029	0.000039
2	6	0	-0.505858	-0.000038	-0.000143
3	1	0	-1.081772	0.938404	0.000293
4	1	0	-1.081511	-0.938381	0.000293

Product 2a

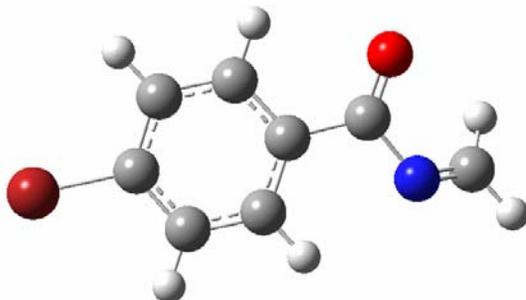
B3LYP/631+G(d) = -898.63527725 a.u.

ZPC= 0.122033 a.u.

0 Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.438344	1.215131	0.115389
2	6	0	0.053528	1.333083	0.046711
3	6	0	-0.754197	0.195718	-0.117563
4	6	0	-0.151631	-1.068263	-0.218377
5	6	0	1.235320	-1.198272	-0.151211
6	6	0	2.017541	-0.054066	0.016444
7	1	0	2.065803	2.091117	0.243532
8	1	0	-0.420221	2.307010	0.119787
9	1	0	-0.771020	-1.946822	-0.362858
10	1	0	1.705667	-2.172689	-0.233188
11	6	0	-2.231222	0.373345	-0.166628
12	8	0	-2.770693	1.469517	-0.211473
13	7	0	-2.979081	-0.837269	-0.218020
14	6	0	-4.029520	-0.911701	0.495725
15	1	0	-4.656015	-1.801836	0.426311
16	1	0	-4.341942	-0.113841	1.180365
17	17	0	3.762815	-0.209885	0.101238

Product 2b



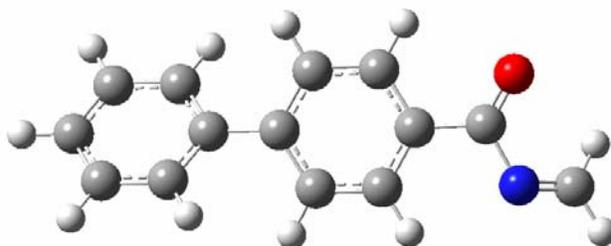
B3LYP/631+G(d) = -3010.1677266 a.u.

ZPC= 0.122323a.u.

0 Imaginary Frequencies

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.714750	1.269046	0.091217
2	6	-0.672631	1.361164	0.037308
3	6	-1.458795	0.208334	-0.120890
4	6	-0.835127	-1.044273	-0.229273
5	6	0.554643	-1.147097	-0.174925
6	6	1.315739	0.011431	-0.015044
7	1	1.324134	2.158218	0.213991
8	1	-1.164825	2.325443	0.116170
9	1	-1.439500	-1.933991	-0.369121
10	1	1.039891	-2.113537	-0.261792
11	6	-2.938968	0.358413	-0.159371
12	8	-3.498435	1.444986	-0.194557
13	7	-3.666049	-0.864563	-0.212938
14	6	-4.711488	-0.959595	0.505726
15	1	-5.322916	-1.860150	0.436220
16	1	-5.032698	-0.170662	1.196649
17	35	3.212486	-0.121651	0.060184

Product 2c



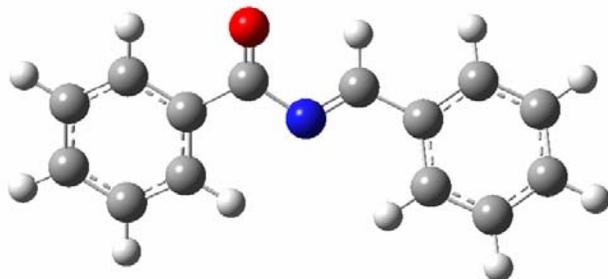
B3LYP/631+G(d) = -670.1044069 a.u.

ZPC= 0.212567a.u.

0 Imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.103464	1.264010	-0.299718
2	6	0	-1.283930	1.323975	-0.360657
3	6	0	-2.055042	0.163540	-0.180673
4	6	0	-1.403145	-1.057261	0.056464
5	6	0	-0.012454	-1.111387	0.117283
6	6	0	0.768722	0.045267	-0.058296
7	1	0	0.684555	2.166832	-0.466369
8	1	0	-1.790768	2.263916	-0.556407
9	1	0	-1.990259	-1.959915	0.188385
10	1	0	0.474381	-2.060311	0.324637
11	6	0	-3.536517	0.273583	-0.234510
12	8	0	-4.122912	1.294529	-0.566718
13	7	0	-4.240471	-0.926036	0.076769
14	6	0	-5.260585	-0.831658	0.830258
15	1	0	-5.854649	-1.723604	1.034181
16	1	0	-5.578058	0.113573	1.287395
17	6	0	2.251219	-0.015537	0.006838
18	6	0	2.954794	-1.103660	-0.540610
19	6	0	2.989491	1.014160	0.617873
20	6	0	4.348042	-1.160073	-0.479714
21	1	0	2.407916	-1.898119	-1.041546
22	6	0	4.382600	0.957079	0.681241
23	1	0	2.466731	1.852972	1.069848
24	6	0	5.068305	-0.130178	0.132151
25	1	0	4.871610	-2.005747	-0.918544
26	1	0	4.932092	1.759506	1.167075
27	1	0	6.153254	-0.174245	0.180128

Product 2d



B3LYP/631+G(d) = - 670.1164805a.u.

ZPC= 0.21332a.u.

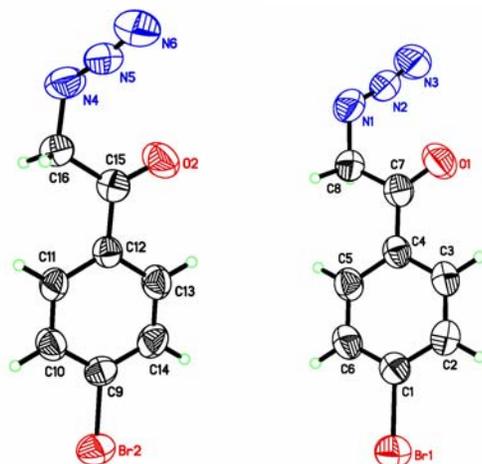
0 Imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.778964	-0.220017	0.206694
2	6	0	-3.599521	-0.923689	-0.027743
3	6	0	-2.373682	-0.242089	-0.110898
4	6	0	-2.346687	1.153647	0.041112
5	6	0	-3.530353	1.855871	0.276434
6	6	0	-4.746460	1.171547	0.359734
7	1	0	-5.724290	-0.752720	0.270484
8	1	0	-3.605079	-2.002477	-0.148548
9	1	0	-1.399993	1.677116	-0.035087
10	1	0	-3.504209	2.936499	0.390852
11	6	0	-1.131440	-1.034908	-0.345033
12	8	0	-1.152850	-2.241684	-0.559868
13	7	0	0.068454	-0.281553	-0.345599
14	6	0	1.121596	-0.868242	0.097080
15	1	0	-5.667669	1.719882	0.541243
16	6	0	2.453469	-0.260150	0.072261
17	6	0	2.677566	1.012351	-0.486697
18	6	0	3.536230	-0.973019	0.615620
19	6	0	3.959543	1.553711	-0.499086
20	1	0	1.836267	1.555447	-0.905772
21	6	0	4.820959	-0.428228	0.603024
22	1	0	3.366228	-1.957705	1.045696
23	6	0	5.033322	0.835759	0.045995
24	1	0	4.128651	2.535855	-0.932737
25	1	0	5.652376	-0.986924	1.024149
26	1	0	6.032781	1.263056	0.034267
27	1	0	1.055091	-1.878957	0.522616

Crystallographic Data:

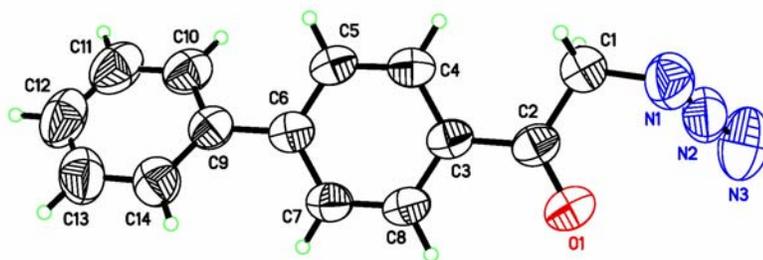
Azide **1a** crystallizes in an almost completely planar configuration excepting the torsion angles that are about the carbonyl carbon and N1 of the azide, at 76° and the torsion angle about the ketone and methylene carbons that is 11°. The molecules are arranged in stacking sheets, held together by non-traditional H bonds of types C-H...N, (2.51 Å, 128°) and C-H...O (2.53 Å, 160.4°) that allow for maximum π -stacking interaction, with narrow channels between the sheets. In this lattice the azide moieties cross at N2, and this allows the distances between the azides to be short, at 3.378Å for the distance from N1 to N1, and that from N1 to N3 to be 3.328 Å.

Monoclinic, $P2_1/c$, $a=12.6761(11)$ Å, $b=9.1007(8)$ Å, $c=7.4679(7)$ Å, $\alpha=90^\circ$,
 $\beta=93.289(2)^\circ$, $\gamma=90^\circ$, $Z=4$, $R= 5.17\%$.



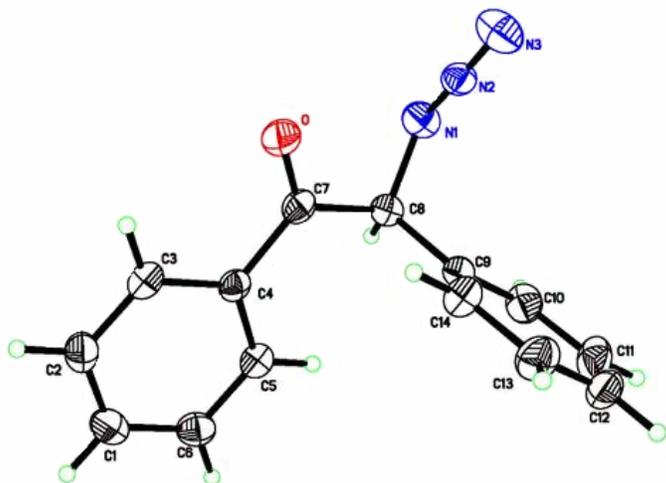
Azide 1b crystallizes with two independent molecule in the unit cell, which almost related by an inversion center. Both are almost completely planar. There are two important torsion angles, that around the carbonyl carbon and N1 is approximately 67° in both molecules, and the torsion angle around ketone carbon and methylene carbon in molecule 1 is -14.1° and the torsion angle around the carbonyl carbon and methylene carbon in molecule 2 is 11.4° . Molecules are arranged in stacking sheets, held in place by four non-traditional hydrogen bonds of type C-H...N (2.69 to 2.76 Å, 127 - 165°) and three of type C-H...O (2.55 to 2.68 Å, 126 - 148°). Interactions between the π - orbitals of the phenyl rings have been maximized with there being channels between sheets. The azide groups are oriented so that they are directed towards each other, with the distance between N1 to N1 of another molecule is 3.707 Å or 3.975 Å and the distance from N1 to N3 being 3.366 Å to 3.761 Å.

Triclinic, P_{-1} , $a=9.2953(3)$ Å, $b=10.7596(3)$ Å, $c=10.7786(2)$ Å, $\alpha=93.674(1)^\circ$, $\beta=110.314(1)^\circ$, $\gamma=111.876(1)^\circ$, $Z=4$, $R= 3.72\%$.



Azide **1c** has one molecule in the unit cell that exhibits three interesting torsion angles; that about the carbonyl carbon and N1 of the azide, at 68.2° around the ketone and methylene carbons of 173.9° and a dihedral angle of 37.5° between the two phenyl rings. Molecules are arranged in zig-zagging sheets down the bc plane to increase π -stacking interactions, with void volumes down the ac plane. This long-range structure is held together via a network of bifurcated non-traditional H bonds of type C-H...O, (2.53\AA , 144° and 2.55\AA , 156.1°). The azide moieties in this crystal lattice cross at N1 with the distance from N1 to another molecule's N1 at 3.999\AA the distance from N1 to N3 is significantly shorter at 3.328\AA .

Orthorhombic, $a = 10.5307(9)\text{\AA}$, $b = 7.9709(7)\text{\AA}$, $c = 29.396(3)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $Z = 8$, $R = 5.17\%$.



1d exhibited is not as flat as azides **1a-1c**. The dihedral angle about the keto and methylene carbon is 76° , making the molecule close like a book. The molecules are arranged in stacks to maximize π -stacking interactions. A T-stacking arrangement is also observed between H4 and the α -phenyl ring. There are no hydrogen bonds in this crystal structure. The azide groups are directed toward each other, and the distance from N1 to N1 one another molecule is 5.39 \AA . The distance from N1 to N3 is much shorter though at 3.23 \AA .

Orthorhombic $a = 5.9414(5) \text{ \AA}$, $b = 14.8154(13) \text{ \AA}$, $c = 26.690(2) \text{ \AA}$, $\alpha = 90^\circ(1)$, $\beta = 90^\circ(1)$, $\gamma = 90^\circ(1)$, $Z = 8$, $R = 4.5 \%$.

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