CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Reactions of Nitroheteroarenes with Carbanions: Bridging Aromatic, Heteroaromatic, and Vinylic Electrophilicity

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Competition experiments

Following notations are used throughout this paper: **3a**, **3b**, **3c**, ..., **4a**, **4b**, ..., **7**, etc. denote the nitroheteroarene. The additional letter (o = *ortho*, p = *para* or *pseudo-para*) indicates the position of CH_2SO_2Ph substituent in relation to the nitro group.

Calibration factors for GC/HPLC analysis

GC and HPLC calibration factors $f_{GC/HPLC}$ for the VNS products of nitroheteroarenes were determined according to the following procedure: Approximately $n = 4 \times 10^{-2}$ mmol of a VNS product of a nitroheteroarene (P_x^y) and the same amount of diphenylsulfone (**2**) were dissolved in $CHCl_3$ (3 mL) and the resultant solution was injected three times on the GC. In case of HPLC the experiments were only performed once. The integrated peak areas *a* were evaluated according to the following equation:

$$f(P_x^y) = \frac{a(\mathbf{2}) \cdot n(P_x^y)}{a(P_x^y) \cdot n(\mathbf{2})} \qquad \text{(S1)}$$

The calibration factors of the individual injections were averaged (last column of table 1).

TABLE 1: GC calibration factors

		$a(X)^a$			$f_{GC}{}^b$			$f_{GC}{}^c$
X	n / mmol	I	II	III	I	II	III	
3bo	9.11×10^{-3}	3.50×10^6	3.37×10^6	3.53×10^6	1.50	1.49	1.50	1.49
2	4.40×10^{-2}	2.53×10^7	2.42×10^7	2.55×10^7				
3co	3.89×10^{-2}	1.09×10^7	1.08×10^7	1.01×10^7	1.18	1.14	1.15	1.15
2	5.22×10^{-2}	1.72×10^7	1.65×10^7	1.55×10^7				
3do	2.66×10^{-2}	6.95×10^6	7.51×10^6	7.35×10^6	1.33	1.31	1.32	1.32
2	4.49×10^{-2}	1.56×10^7	1.67×10^6	1.64×10^6				

3eo2	2.14×10^{-2} 3.48×10^{-2}	1.02×10^{7} 3.21×10^{7}	5.95×10^{6} 1.84×10^{7}	5.17×10^{6} 1.62×10^{7}	1.93	1.90	1.92	1.92
4ao2	2.37×10^{-2} 3.39×10^{-2}	9.58×10^{6} 1.81×10^{7}	1.02×10^{7} 1.92×10^{7}	9.80×10^{6} 1.88×10^{7}	1.32	1.32	1.34	1.33
4ap2	2.26×10^{-2} 3.99×10^{-2}	6.95×10^{6} 2.18×10^{7}	6.75×10^{6} 2.21×10^{7}	6.97×10^{6} 2.26×10^{7}	1.78	1.86	1.84	1.83
4bo2	3.84×10^{-2} 5.04×10^{-2}	8.25×10^{6} 1.61×10^{7}	8.11×10^{6} 1.62×10^{7}	6.62×10^{6} 1.27×10^{7}	1.48	1.52	1.46	1.49
4co2	3.32×10^{-2} 4.58×10^{-2}	3.64×10^{6} 1.71×10^{7}	3.49×10^{6} 1.59×10^{7}	3.73×10^{6} 1.72×10^{6}	3.40	3.30	3.34	3.35
4cp2	2.30×10^{-2} 3.48×10^{-2}	4.20×10^{6} 1.28×10^{7}	3.50×10^{6} 1.09×10^{7}	3.59×10^{6} 1.10×10^{7}	2.01	2.05	2.02	2.03
4do2	1.91×10^{-2} 2.79×10^{-2}	6.82×10^{6} 1.60×10^{7}	6.90×10^{6} 1.65×10^{7}	7.20×10^{6} 1.68×10^{7}	1.61	1.64	1.60	1.61
5ap2	3.03×10^{-2} 3.34×10^{-2}	4.01×10^{6} 2.10×10^{7}	4.23×10^{6} 2.17×10^{7}	4.03×10^{6} 2.15×10^{7}	4.74	4.65	4.84	4.74
5bo2	2.46×10^{-2} 2.52×10^{-2}	1.04×10^{7} 1.75×10^{7}	9.77×10^{6} 1.69×10^{7}	9.63×10^{6} 1.72×10^{7}	1.64	1.69	1.74	1.69
6ao2	4.83×10^{-2} 5.13×10^{-2}	3.97×10^{6} 1.63×10^{7}	3.98×10^{6} 1.66×10^{7}	3.98×10^{6} 1.66×10^{7}	3.87	3.93	3.92	3.91
6ap2	3.16×10^{-2} 3.34×10^{-2}	9.38×10^{5} 1.41×10^{7}	8.37×10^{5} 1.35×10^{7}	9.02×10^{5} 1.37×10^{7}	14.2	15.3	14.4	14.6
6bo2	2.45×10^{-2} 3.25×10^{-2}	1.86×10^{6} 1.44×10^{7}	1.78×10^{6} 1.37×10^{7}	1.58×10^{6} 1.22×10^{7}	6.44	6.42	6.47	6.44
7o2	2.84×10^{-2} 5.31×10^{-2}	1.07×10^{7} 3.18×10^{7}	1.06×10^{7} 3.16×10^{7}	1.10×10^{7} 3.28×10^{7}	1.59	1.59	1.59	1.59
8o2	2.61×10^{-2} 4.86×10^{-2}	4.72×10^{6} 2.56×10^{7}	4.90×10^{6} 2.62×10^{7}	4.77×10^{6} 2.56×10^{7}	2.92	2.88	2.89	2.89

[a]integrated peak area, [b]calibration factor, [c]averaged calibration factor.

TABLE: HPLC calibration factors

X	n / mmol	a(X)[a]	f_{HPLC}(X)[b]
3bo[c]	3.29×10^{-2}	1.30×10^{7}	6.63×10^{-2}
2[c]	5.04×10^{-2}	1.32×10^{6}	
3co	3.89×10^{-2}	9.32×10^{6}	2.63×10^{-1}
2	5.22×10^{-2}	3.28×10^{6}	
3do	3.85×10^{-2}	9.28×10^{6}	1.92×10^{-1}
2	5.27×10^{-2}	2.44×10^{6}	
3eo	2.14×10^{-2}	1.65×10^{7}	2.04×10^{-1}
2	3.48×10^{-2}	5.49×10^{6}	
4ao	2.37×10^{-2}	2.15×10^{7}	2.92×10^{-1}
2	3.39×10^{-2}	8.98×10^{6}	
4ap	2.26×10^{-3}	3.96×10^{7}	1.54×10^{-1}
2	3.99×10^{-2}	1.07×10^{7}	
4bo	3.84×10^{-2}	5.51×10^{6}	4.92×10^{-1}
2	5.04×10^{-2}	3.56×10^{6}	
4co	3.94×10^{-2}	2.97×10^{6}	6.77×10^{-1}
2	5.27×10^{-2}	2.69×10^{6}	
4cp	3.66×10^{-2}	8.17×10^{6}	2.49×10^{-1}
2	5.04×10^{-2}	2.80×10^{6}	
4do	4.02×10^{-2}	1.41×10^{7}	2.21×10^{-1}
2	5.04×10^{-2}	3.92×10^{6}	
5bo	4.03×10^{-2}	1.46×10^{7}	2.75×10^{-1}
2	5.27×10^{-2}	5.23×10^{6}	
6ao[c]	4.83×10^{-2}	4.74×10^{6}	1.00×10^{-1}
2[c]	5.13×10^{-2}	5.06×10^{5}	

6ap[c]	4.66×10^{-2}	1.23×10^{7}	1.00×10^{-1}
2[c]	5.13×10^{-2}	1.36×10^{6}	
6bo	3.70×10^{-2}	5.41×10^{6}	4.61×10^{-1}
2	5.18×10^{-2}	3.49×10^{6}	
7o	2.52×10^{-2}	2.15×10^{7}	1.73×10^{-1}
2	5.41×10^{-2}	7.96×10^{6}	
8o	4.45×10^{-2}	1.32×10^{7}	3.40×10^{-1}
2	5.27×10^{-2}	5.31×10^{6}	

[a]integrated peak area, [b]calibration factor, [c]evaluation at 280 nm

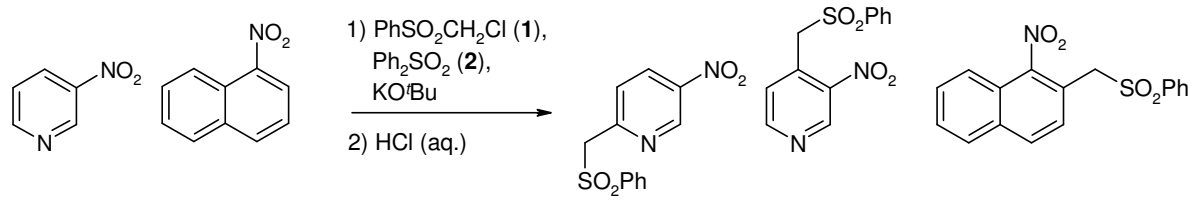
For the quantitative evaluation of the competition experiments the following equation was used.

$$\frac{k_A}{k_B} = \frac{\ln\left(\frac{[A]_0 - \sum[P_A]}{[A]_0}\right)}{\ln\left(\frac{[B]_0 - \sum[B_A]}{[B]_0}\right)} \qquad \text{(S2)}$$

$[A]_0$ = molarity of compound A at start, $[B]_0$ = molarity of compound B at start, $[P_x]$ = molarity of product P_x^y at the end.

Quantitative analysis of reaction mixtures

Competition experiments with nitropyridines 4a-d



4a **3e** **4ao** **4ap** **3eo**

n(**1**) = 0.125 mmol, n(**2**) = 0.056 mmol, n(**4a**) = 0.176 mmol, n(**3e**) = 0.527 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**4ao**)[a]	a(**4ap**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{4a})}{k(\mathbf{3e})}$	$\frac{k(\mathbf{4a^o})}{k(\mathbf{4a^p})}$
$1_{(GC)}$	0	1.15×10^7	7.94×10^6	5.86×10^5	1.28×10^6	1.7×10^1	9.8
	0	1.32×10^7	9.70×10^6	7.23×10^5	1.51×10^6	1.8×10^1	9.7
	0	1.29×10^7	9.20×10^6	6.86×10^5	1.45×10^6	1.7×10^1	9.7
$2_{(GC)}$	0	1.16×10^7	7.55×10^6	4.10×10^5	1.25×10^6	1.6×10^1	1.3×10^1
	0	1.14×10^7	7.53×10^6	4.11×10^5	1.26×10^6	1.6×10^1	1.3×10^1
	0	1.13×10^7	6.80×10^6	3.66×10^5	1.09×10^6	1.6×10^1	1.4×10^1
$3_{(GC)}$	0	1.09×10^7	7.22×10^6	4.63×10^5	1.14×10^6	1.7×10^1	1.1×10^1
	0	1.17×10^7	8.29×10^6	5.22×10^5	1.42×10^6	1.6×10^1	1.2×10^1

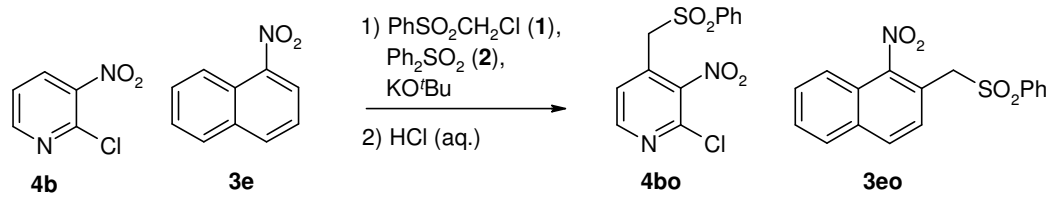
[a] integrated peak area.

k(**4a**)/k(**3e**) = $(1.7 \pm 0.1) \times 10^1$, k(**4a**^{o})/k(**4a**^{p}) = $(1.2 \pm 0.2) \times 10^1$

No.	a(**1**)[a]	a(**2**)[a]	a(**4ao**)[a]	a(**4ap**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{4a})}{k(\mathbf{3e})}$	$\frac{k(\mathbf{4a^o})}{k(\mathbf{4a^p})}$
$1_{(HPLC)}$	0	5.80×10^6	2.63×10^7	4.07×10^6	1.23×10^7	1.3×10^1	1.2×10^1
$2_{(HPLC)}$	0	6.15×10^6	2.79×10^7	4.97×10^6	1.35×10^7	1.3×10^1	1.1×10^1
$3_{(HPLC)}$	0	5.32×10^6	2.33×10^7	3.02×10^6	1.16×10^7	1.2×10^1	1.5×10^1

[a] integrated peak area.

k(**4a**)/k(**3e**) = $(1.3 \pm 0.1) \times 10^1$, k(**4a**^{o})/k(**4a**^{p}) = $(1.2 \pm 0.2) \times 10^1$



n(**1**) = 0.125 mmol, n(**2**) = 0.050 mmol, n(**4b**) = 0.150 mmol, n(**3e**) = 0.600 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**4bo**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{4b})}{k(\mathbf{3e})}$
$1_{(GC)}$	0	3.75×10^6	1.72×10^6	3.12×10^5	1.9×10^1
	0	3.88×10^6	1.70×10^6	2.92×10^5	2.0×10^1
	0	3.71×10^6	1.70×10^6	3.13×10^5	1.9×10^1
$2_{(GC)}$	0	4.89×10^6	2.83×10^6	5.56×10^5	1.8×10^1
	0	5.03×10^6	2.99×10^6	6.06×10^5	1.8×10^1
	0	5.04×10^6	3.08×10^6	6.55×10^5	1.7×10^1
$3_{(GC)}$	0	3.86×10^6	2.22×10^6	4.53×10^5	1.8×10^1
	0	3.53×10^6	1.80×10^6	3.07×10^5	2.1×10^1
	0	3.77×10^6	2.23×10^6	4.79×10^5	1.9×10^1

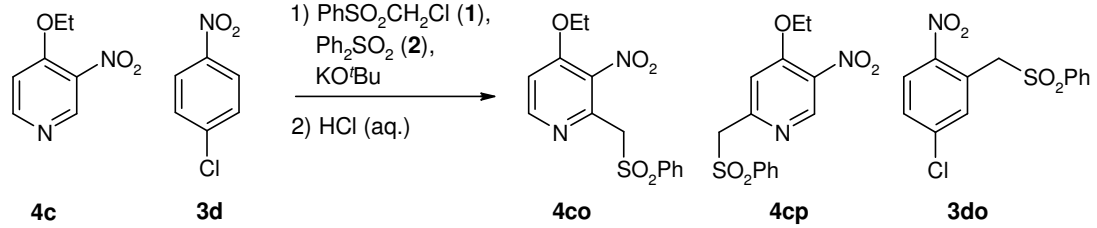
[a] integrated peak area.

k(**4b**)/k(**3e**) = $(1.9 \pm 0.1) \times 10^1$

No.	a(**1**)[a]	a (**2**)[a]	a(**4bo**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{4b})}{k(\mathbf{3e})}$
$1_{(HPLC)}$	0	9.01×10^5	1.50×10^6	8.04×10^5	2.1×10^1
$2_{(HPLC)}$	0	1.77×10^6	4.03×10^6	2.33×10^6	2.1×10^1
$3_{(HPLC)}$	0	1.08×10^6	2.32×10^6	1.32×10^6	2.1×10^1

[a] integrated peak area.

k(**4b**)/k(**3e**) = $(2.1 \pm 0.01) \times 10^1$



4c **3d** **4co** **4cp** **3do**

n(**1**) = 0.126 mmol, n(**2**) = 0.050 mmol, n(**4c**) = 0.362 mmol, n(**3d**) = 0.303 mmol, n(KO^{t}Bu) = 0.504 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**4co**)[a]	a(**4cp**)[a]	a(**3do**)[a]	$\frac{k(\mathbf{4c})}{k(\mathbf{3d})}$	$\frac{k(\mathbf{4c^p})}{k(\mathbf{4c^o})}$
$1_{(GC)}$	0	5.27×10^6	7.63×10^5	2.37×10^6	9.73×10^5	5.2	1.9
	0	5.74×10^6	7.86×10^5	2.43×10^6	1.02×10^6	5.1	1.9
	0	5.59×10^6	7.20×10^5	2.29×10^6	9.97×10^5	4.8	1.9
$2_{(GC)}$	0	5.05×10^6	7.16×10^5	2.32×10^6	1.16×10^6	4.2	2.0
	0	5.00×10^6	6.83×10^5	2.21×10^6	1.07×10^6	4.3	2.0
	0	4.83×10^6	6.09×10^5	1.97×10^6	9.86×10^5	4.2	2.0
$3_{(GC)}$	0	5.98×10^6	8.62×10^5	2.83×10^6	1.40×10^6	4.2	2.0
	0	6.75×10^6	8.91×10^5	2.96×10^6	1.53×10^6	4.0	2.0
	0	6.41×10^6	8.53×10^5	2.78×10^6	1.39×10^6	4.2	2.0

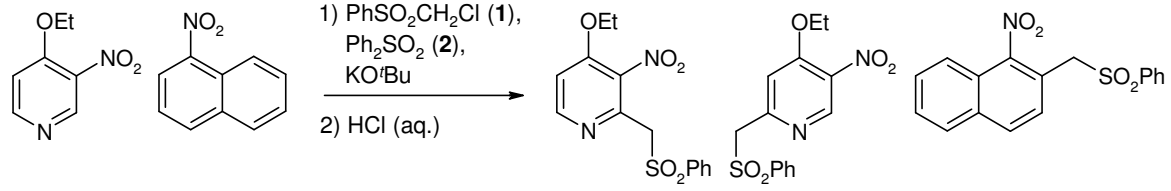
[a] integrated peak area.

k(**4c**)/k(**3d**) = 4.5 ± 0.4, k(**4c**^{p})/k(**4c**^{o}) = 2.0 ± 0.04

No.	a(**1**)[a]	a(**2**)[a]	a(**4co**)[a]	a(**4cp**)[a]	a(**3do**)[a]	$\frac{k(\mathbf{4c})}{k(\mathbf{3d})}$	$\frac{k(\mathbf{4c^p})}{k(\mathbf{4c^o})}$
$1_{(HPLC)}$	0	1.43×10^6	7.81×10^5	5.52×10^6	1.96×10^6	4.6	2.6
$2_{(HPLC)}$	0	8.95×10^5	5.20×10^5	3.73×10^6	1.52×10^6	4.0	2.6
$3_{(HPLC)}$	0	1.74×10^6	1.01×10^6	7.34×10^6	3.02×10^6	3.9	2.7

[a] integrated peak area.

k(**4c**)/k(**3d**) = 4.2 ± 0.3, k(**4c**^{p})/k(**4c**^{o}) = 2.6 ± 0.03



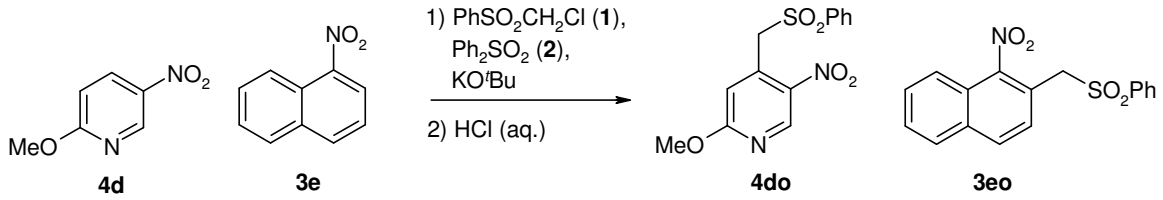
4c **3e** **4co** **4cp** **3eo**

n(**1**) = 0.126 mmol, n(**2**) = 0.055 mmol, n(**4c**) = 0.653 mmol, n(**3e**) = 0.246 mmol, n(KO^{t}Bu) = 0.504 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**4co**)[a, b]	a(**4cp**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{3e})}{k(\mathbf{4c})}$
$1_{(GC)}$	0	8.35×10^6		8.20×10^5	2.10×10^6	4.5
	0	7.70×10^6		8.01×10^5	2.15×10^6	4.7
	0	8.42×10^6		9.61×10^5	2.62×10^6	4.8
$2_{(GC)}$	0	6.69×10^6		7.70×10^5	2.12×10^6	4.9
	0	6.88×10^6		7.76×10^5	2.12×10^6	4.8
	0	7.10×10^6		8.07×10^5	2.25×10^6	4.9
$3_{(GC)}$	0	1.03×10^7		8.98×10^5	2.43×10^6	4.7
	0	1.10×10^7		8.53×10^5	2.30×10^6	4.7
	0	1.10×10^7		9.65×10^5	2.62×10^6	4.7

[a] integrated peak area, [b] peak in chromatogram is too small and not separated completely from **3eo** so that evaluation is not possible. Thus, the molarity of **4co** in the product mixture is calculated by the known ratio $k(\mathbf{4c}^p)/k(\mathbf{4c}^o) = 2.0 \pm 0.04$.

k(**3e**)/k(**4c**) = 4.8 ± 0.1



n(**1**) = 0.125 mmol, n(**2**) = 0.050 mmol, n(**4d**) = 0.300 mmol, n(**3e**) = 0.300 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**4do**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{4d})}{k(\mathbf{3e})}$
$1_{(GC)}$	0	3.63×10^6	1.92×10^6	4.55×10^5	3.8
	0	3.62×10^6	2.03×10^6	4.89×10^5	3.7
	0	3.87×10^6	2.03×10^6	4.68×10^5	3.9
$2_{(GC)}$	0	3.63×10^6	1.92×10^6	4.55×10^5	3.8
	0	3.62×10^6	2.03×10^6	4.89×10^5	3.7
	0	3.87×10^6	2.03×10^6	4.68×10^5	3.9
$3_{(GC)}$	0	2.68×10^6	1.24×10^6	3.14×10^5	3.5
	0	2.72×10^6	1.31×10^6	3.42×10^5	3.4
	0	2.75×10^6	1.36×10^6	3.46×10^5	3.5

[a] integrated peak area.

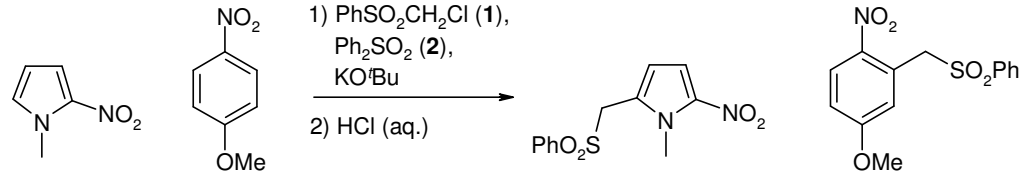
k(**4d**)/k(**3e**) = 3.7 ± 0.2

No.	a(**1**)[a]	a (**2**)[a]	a(**4do**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{4d})}{k(\mathbf{3e})}$
$1_{(HPLC)}$	0	1.45×10^6	5.64×10^6	2.17×10^6	3.0
$2_{(HPLC)}$	0	1.13×10^6	4.57×10^6	1.25×10^6	4.2
$3_{(HPLC)}$	0	8.92×10^5	3.02×10^6	8.65×10^5	4.0

[a] integrated peak area.

k(**4d**)/k(**3e**) = 3.7 ± 0.5

Competition experiments with nitropyrroles 5a-b



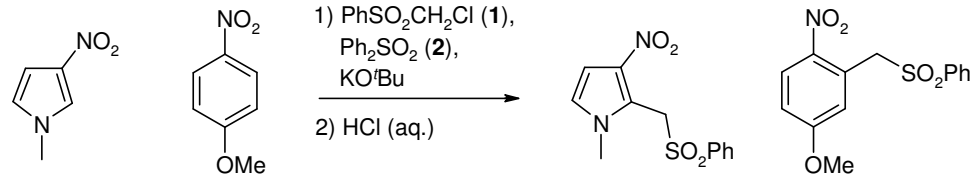
5a **3b** **5ap** **3bo**

n(**1**) = 0.125 mmol, n(**2**) = 0.049 mmol, n(**5a**) = 0.302 mmol, n(**3b**) = 0.300 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**5ap**)[a]	a(**3bo**)[a]	$\frac{k(\mathbf{3b})}{k(\mathbf{5a})}$
$1_{(GC)}$	0	5.31×10^6	3.49×10^5	2.34×10^6	2.2
	0	5.36×10^6	3.28×10^5	2.25×10^6	2.2
	0	5.49×10^6	3.66×10^5	2.52×10^6	2.3
$2_{(GC)}$	0	7.01×10^6	5.91×10^5	3.64×10^6	2.0
	0	7.43×10^6	6.08×10^5	3.79×10^6	2.0
	0	7.59×10^6	6.13×10^5	3.86×10^6	2.1
$3_{(GC)}$	0	4.98×10^6	3.23×10^5	2.22×10^6	2.2
	0	5.02×10^6	3.26×10^5	2.24×10^6	2.3
	0	5.02×10^6	3.07×10^5	2.09×10^6	2.2

[a] integrated peak area.

k(**3b**)/k(**5a**) = 2.2 ± 0.1



5b **3b** **5bo** **3bo**

n(**1**) = 0.125 mmol, n(**2**) = 0.050 mmol, n(**5b**) = 0.199 mmol, n(**3b**) = 0.299 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**5bo**)[a]	a(**3bo**)[a]	$\frac{k(\mathbf{5b})}{k(\mathbf{3b})}$
$1_{(GC)}$	0	5.10×10^6	3.21×10^6	1.87×10^6	3.2
	0	5.20×10^6	3.43×10^6	1.99×10^6	3.3
	0	5.57×10^6	3.43×10^6	2.00×10^6	3.2
$2_{(GC)}$	0	6.25×10^6	3.61×10^6	2.60×10^6	2.6
	0	6.69×10^6	3.83×10^6	2.74×10^6	2.6
	0	6.76×10^6	4.06×10^6	2.93×10^6	2.6
$3_{(GC)}$	0	7.72×10^6	4.30×10^6	3.12×10^6	2.5
	0	1.30×10^7	6.36×10^6	4.59×10^6	2.5
	0	1.30×10^7	6.21×10^6	4.48×10^6	2.5

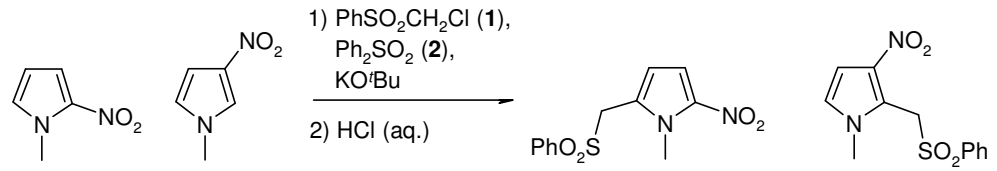
[a] integrated peak area.

k(**5b**)/k(**3b**) = 2.8 ± 0.3

No.	a(**1**)[a]	a(**2**)[a]	a(**5bo**)[a]	a(**3bo**)[a]	$\frac{k(\mathbf{5b})}{k(\mathbf{3b})}$
$1_{(HPLC)}$	0	3.24×10^6	1.65×10^7	6.00×10^6	3.6
$2_{(HPLC)}$	0	3.25×10^6	1.65×10^7	7.60×10^6	2.8
$3_{(HPLC)}$	0	5.59×10^6	2.95×10^7	1.34×10^7	2.9

[a] integrated peak area.

k(**5b**)/k(**3b**) = 3.1 ± 0.4



5a **5b** **5ap** **5bo**

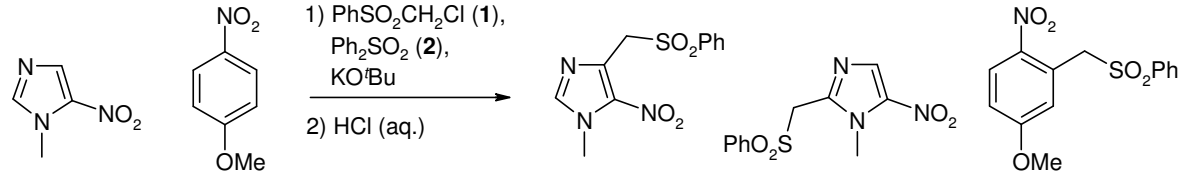
n(**1**) = 0.125 mmol, n(**2**) = 0.050 mmol, n(**5a**) = 0.174 mmol, n(**5b**) = 0.050 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**5ap**)[a]	a(**5bo**)[a]	$\frac{k(\mathbf{5b})}{k(\mathbf{5a})}$
$1_{(GC)}$	0	1.12×10^7	9.15×10^5	2.96×10^6	5.0
	0	1.08×10^7	8.81×10^5	2.83×10^6	5.0
	0	1.06×10^7	8.59×10^5	2.76×10^6	5.0
$2_{(GC)}$	0	8.42×10^6	1.04×10^6	2.89×10^6	4.7
	0	8.81×10^6	1.04×10^6	2.95×10^6	4.8
	0	8.23×10^6	9.99×10^5	2.80×10^6	4.7
$3_{(GC)}$	0	1.00×10^7	9.04×10^5	3.01×10^6	5.4
	0	9.75×10^6	9.40×10^5	3.11×10^6	5.5
	0	9.21×10^6	9.07×10^5	2.94×10^6	5.4

[a] integrated peak area.

k(**5b**)/k(**5a**) = 5.0 ± 0.3

Competition experiments with nitroimidazoles 6a-b



6a **3b** **6ao** **6ap** **3bo**

n(**1**) = 0.125 mmol, n(**2**) = 0.050 mmol, n(**6a**) = 0.300 mmol, n(**3b**) = 0.300 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**6ao**)[a]	a(**6ap**)[a]	a(**3bo**)[a]	$\frac{k(\mathbf{6a})}{k(\mathbf{3b})}$	$\frac{k(\mathbf{6a^o})}{k(\mathbf{6a^p})}$
$1_{(GC)}$	7.45×10^5	5.43×10^6	6.21×10^5	1.73×10^5	2.80×10^5	1.3×10^1	9.6×10^{-1}
	8.87×10^5	6.56×10^6	7.55×10^5	1.95×10^5	3.44×10^5	1.2×10^1	1.0
	8.90×10^5	8.39×10^6	6.91×10^5	1.93×10^5	3.70×10^5	1.1×10^1	9.6×10^{-1}
$2_{(GC)}$	8.81×10^5	8.51×10^6	7.04×10^5	2.02×10^5	3.75×10^5	1.1×10^1	9.3×10^{-1}
	8.92×10^5	8.40×10^6	7.45×10^5	2.10×10^5	3.99×10^5	1.1×10^1	9.5×10^{-1}
	1.01×10^6	8.28×10^6	7.17×10^5	2.02×10^5	4.40×10^5	9.2	9.5×10^{-1}
$3_{(GC)}$	9.45×10^5	7.76×10^6	5.92×10^5	1.72×10^5	3.56×10^5	9.5	9.2×10^{-1}
	9.81×10^5	8.09×10^6	6.83×10^5	1.97×10^5	4.16×10^5	9.4	9.3×10^{-1}

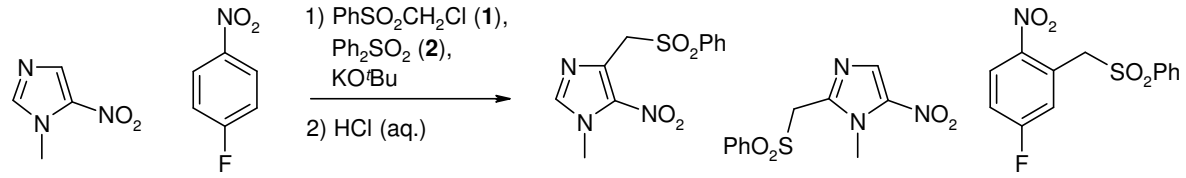
[a] integrated peak area.

k(**6a**)/k(**3b**) = $(1.1 \pm 0.1) \times 10^1$, k(**6a**^{o})/k(**6a**^{p}) = 1.0 ± 0.03

No.	a(**1**)[a]	a(**2**)[a]	a(**6ao**)[a]	a(**6ap**)[a]	a(**3bo**)[a]	$\frac{k(\mathbf{6a})}{k(\mathbf{3b})}$	$\frac{k(\mathbf{6a^o})}{k(\mathbf{6a^p})}$
$1_{(HPLC)}$	0	4.10×10^6	1.87×10^6	1.81×10^6	5.10×10^5	1.2×10^1	1.0
$2_{(HPLC)}$	0	4.24×10^6	1.59×10^6	2.00×10^6	6.20×10^5	9.4	8.0×10^{-1}
$3_{(HPLC)}$	0	3.53×10^6	1.20×10^6	1.52×10^6	5.17×10^5	8.5	7.9×10^{-1}

[a] integrated peak area at 280 nm.

k(**6a**)/k(**3b**) = 9.9 ± 1.4, k(**6a**^{o})/k(**6a**^{p}) = $(8.7 \pm 1.1) \times 10^{-1}$



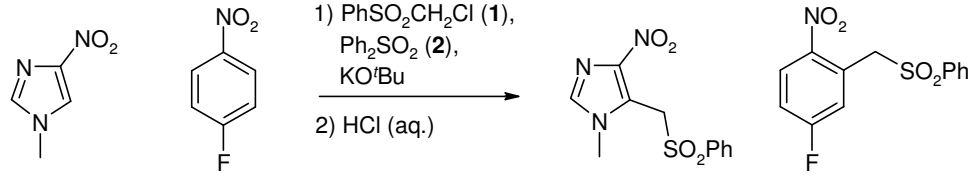
6a **3c** **6ao** **6ap** **3co**

n(**1**) = 0.123 mmol, n(**2**) = 0.047 mmol, n(**6a**) = 0.529 mmol, n(**3c**) = 0.176 mmol, n(KO^{t}Bu) = 0.492 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**6ao**)[a]	a(**6ap**)[a]	a(**3co**)[a]	$\frac{k(\mathbf{3c})}{k(\mathbf{6a})}$	$\frac{k(\mathbf{6a}^{o})}{k(\mathbf{6a}^{p})}$
$1_{(GC)}$	0	6.46×10^6	1.74×10^5	5.28×10^4	2.62×10^6	6.6	8.8×10^{-1}
	0	6.71×10^6	1.83×10^5	5.75×10^4	2.86×10^6	6.8	8.5×10^{-1}
	0	6.52×10^6	1.71×10^5	4.77×10^4	2.81×10^6	7.6	9.6×10^{-1}
$2_{(GC)}$	0	4.98×10^6	1.36×10^5	3.95×10^4	2.18×10^6	7.3	9.2×10^{-1}
	0	5.33×10^6	1.51×10^5	4.32×10^4	2.38×10^6	7.2	9.4×10^{-1}
	0	7.61×10^6	2.29×10^5	7.14×10^4	3.45×10^6	6.6	8.6×10^{-1}
$3_{(GC)}$	0	7.47×10^6	2.16×10^5	6.44×10^4	3.34×10^6	6.9	9.0×10^{-1}
	0	7.75×10^6	2.27×10^5	6.77×10^4	3.49×10^6	6.9	9.0×10^{-1}

[a] integrated peak area.

k(**3c**)/k(**6a**) = 7.0 ± 0.3, $k(\mathbf{6a}^{o})/k(\mathbf{6a}^{p}) = (9.0 \pm 0.4) \times 10^{-1}$



6b **3c** **6bo** **3co**

n(**1**) = 0.125 mmol, n(**2**) = 0.050 mmol, n(**6b**) = 0.300 mmol, n(**3c**) = 0.299 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**6bo**)[a]	a(**3co**)[a]	$\frac{k(\mathbf{6b})}{k(\mathbf{3c})}$
$1_{(GC)}$	0	6.57×10^6	2.05×10^6	2.18×10^6	6.1
	0	6.44×10^6	1.89×10^6	2.13×10^6	5.7
	0	6.22×10^6	1.73×10^6	2.02×10^6	5.5
$2_{(GC)}$	0	8.42×10^6	2.18×10^6	2.30×10^6	6.0
	0	9.71×10^6	2.14×10^6	2.50×10^6	5.3
	0	9.56×10^6	2.68×10^6	3.13×10^6	5.5
$3_{(GC)}$	0	9.44×10^6	2.52×10^6	2.80×10^6	5.7
	0	8.13×10^6	2.59×10^6	2.60×10^6	6.6
	0	1.01×10^7	2.39×10^6	2.84×10^6	5.2

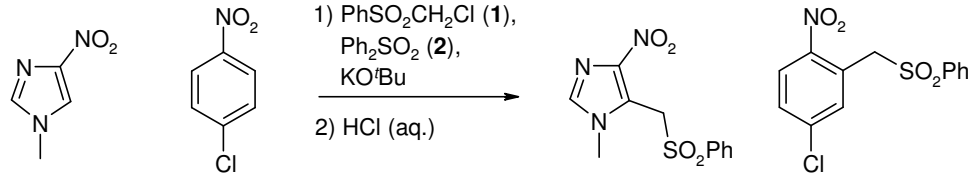
[a] integrated peak area.

k(**6b**)/k(**3c**) = 5.7 ± 0.4

No.	a(**1**)[a]	a(**2**)[a]	a(**6bo**)[a]	a(**3co**)[a]	$\frac{k(\mathbf{6b})}{k(\mathbf{3c})}$
$1_{(HPLC)}$	0	3.04×10^6	1.43×10^7	5.34×10^6	5.6
$2_{(HPLC)}$	0	3.54×10^6	1.76×10^7	5.98×10^6	6.2
$3_{(HPLC)}$	0	5.93×10^6	3.06×10^7	9.71×10^6	6.8

[a] integrated peak area.

k(**6b**)/k(**3c**) = 6.2 ± 0.5



6b **3d** **6bo** **3do**

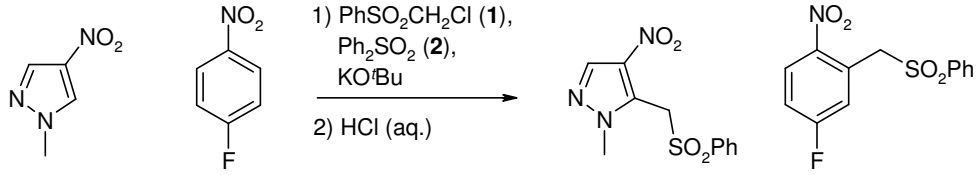
n(**1**) = 0.071 mmol, n(**2**) = 0.027 mmol, n(**6b**) = 0.133 mmol, n(**3d**) = 0.268 mmol, n(KO^{t}Bu) = 0.284 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**6bo**)[a]	a(**3do**)[a]	$\frac{k(\mathbf{6b})}{k(\mathbf{3d})}$
$1_{(GC)}$	0	7.68×10^6	9.16×10^5	5.35×10^6	1.7
	0	7.28×10^6	8.89×10^5	4.92×10^6	1.8
	0	7.05×10^6	7.17×10^5	4.11×10^6	1.8
$2_{(GC)}$	0	6.23×10^6	7.51×10^5	3.96×10^6	1.9
	0	6.53×10^6	7.64×10^5	4.07×10^6	1.9
	0	6.53×10^6	8.08×10^5	4.11×10^6	2.0
$3_{(GC)}$	0	6.68×10^6	7.52×10^5	4.30×10^6	1.8
	0	6.52×10^6	7.18×10^5	4.16×10^6	1.8
	0	6.58×10^7	6.63×10^5	4.08×10^6	1.6

[a] integrated peak area.

k(**6b**)/k(**3d**) = 1.8 ± 0.1

Competition experiments with nitropyrazole 7



7 **3c** **7o** **3co**

n(**1**) = 0.126 mmol, n(**2**) = 0.053 mmol, n(**7**) = 0.186 mmol, n(**3c**) = 0.292 mmol, n(KO^{t}Bu) = 0.504 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**7o**)[a]	a(**3co**)[a]	$\frac{k(\mathbf{7})}{k(\mathbf{3c})}$
$1_{(GC)}$	0	1.05×10^7	3.90×10^6	8.27×10^6	1.0
	0	1.05×10^7	3.86×10^6	8.23×10^6	1.0
	0	1.11×10^7	3.96×10^6	7.86×10^6	1.1
$2_{(GC)}$	0	1.32×10^7	3.76×10^6	8.21×10^6	9.9×10^{-1}
	0	1.56×10^7	4.58×10^6	1.04×10^7	9.5×10^{-1}
	0	1.50×10^7	4.39×10^6	9.66×10^6	9.8×10^{-1}
$3_{(GC)}$	0	1.12×10^7	3.74×10^6	7.97×10^6	1.0
	0	1.07×10^7	3.81×10^6	7.58×10^6	1.1
	0	1.11×10^7	3.87×10^6	7.85×10^6	1.1

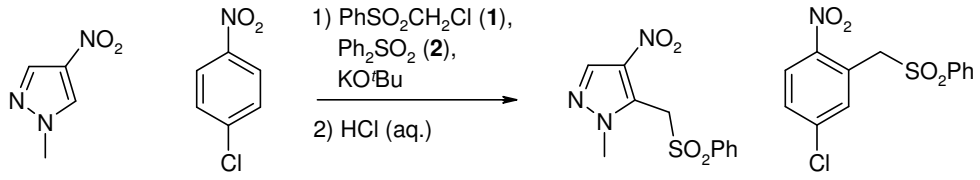
[a] integrated peak area.

k(**7**)/k(**3c**) = 1.0 ± 0.1

No.	a(**1**)[a]	a(**2**)[a]	a(**7o**)[a]	a(**3co**)[a]	$\frac{k(\mathbf{7})}{k(\mathbf{3c})}$
$1_{(HPLC)}$	0	2.21×10^6	9.95×10^6	9.46×10^6	1.1
$2_{(HPLC)}$	0	4.91×10^6	1.97×10^7	1.80×10^7	1.1
$3_{(HPLC)}$	0	7.54×10^6	3.11×10^7	2.97×10^7	1.1

[a] integrated peak area.

k(**7**)/k(**3c**) = 1.1 ± 0.02



7 **3d** **7o** **3do**

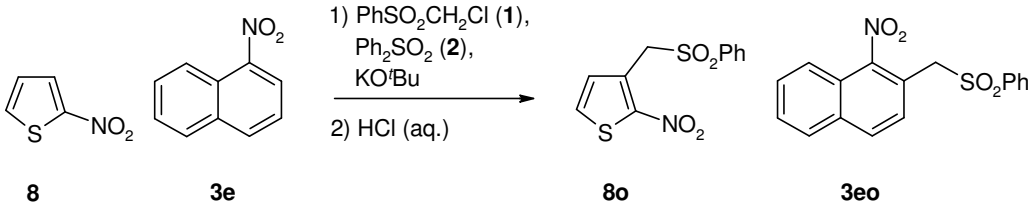
n(**1**) = 0.099 mmol, n(**2**) = 0.042 mmol, n(**7**) = 0.479 mmol, n(**3d**) = 0.151 mmol, n(KO^{t}Bu) = 0.396 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**7o**)[a]	a(**3do**)[a]	$\frac{k(\mathbf{3d})}{k(\mathbf{7})}$
$1_{(GC)}$	0	1.03×10^7	2.96×10^6	3.20×10^6	3.0
	0	1.02×10^7	2.73×10^6	2.97×10^6	3.0
	0	1.03×10^7	3.14×10^6	3.40×10^6	3.0
$2_{(GC)}$	0	9.96×10^6	2.75×10^6	2.74×10^6	2.7
	0	9.59×10^6	2.73×10^6	2.70×10^6	2.7
	0	9.47×10^6	2.45×10^6	2.42×10^6	2.7
$3_{(GC)}$	0	1.06×10^7	2.88×10^6	2.45×10^6	2.3
	0	1.10×10^7	3.10×10^6	2.65×10^6	2.3
	0	1.01×10^7	2.69×10^6	2.26×10^6	2.3

[a] integrated peak area.

k(**3d**)/k(**7**) = 2.7 ± 0.3

Competition experiments with nitrothiophene 8



8 **3e** **8o** **3eo**

n(**1**) = 0.125 mmol, n(**2**) = 0.050 mmol, n(**8**) = 0.201 mmol, n(**3e**) = 0.500 mmol, n(KO^{t}Bu) = 0.500 mmol

No.	a(**1**)[a]	a(**2**)[a]	a(**8o**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{8})}{k(\mathbf{3e})}$
$1_{(GC)}$	0	2.53×10^6	6.86×10^5	6.10×10^5	4.6
	0	2.60×10^6	7.14×10^5	6.41×10^5	4.5
	0	2.55×10^6	7.08×10^5	6.35×10^5	4.6
$2_{(GC)}$	0	5.13×10^6	1.06×10^6	1.23×10^6	3.4
	0	4.61×10^6	8.42×10^5	8.28×10^5	4.0
	0	4.47×10^6	8.51×10^5	8.51×10^5	4.0
$3_{(GC)}$	0	3.66×10^6	6.86×10^5	7.84×10^5	3.5
	0	3.83×10^6	7.39×10^5	8.67×10^5	3.4
	0	3.70×10^6	7.09×10^5	8.04×10^5	3.5

[a] integrated peak area.

k(**8**)/k(**3e**) = 3.9 ± 0.5

No.	a(**1**)[a]	a(**2**)[a]	a(**8o**)[a]	a(**3eo**)[a]	$\frac{k(\mathbf{8})}{k(\mathbf{3e})}$
$1_{(HPLC)}$	0	9.89×10^5	2.59×10^6	2.37×10^6	5.0
$2_{(HPLC)}$	0	2.37×10^6	5.21×10^6	6.21×10^6	3.8
$3_{(HPLC)}$	0	1.87×10^6	3.25×10^6	4.13×10^6	3.5

[a] integrated peak area.

k(**8**)/k(**3e**) = 4.1 ± 0.7

Kinetic experiments

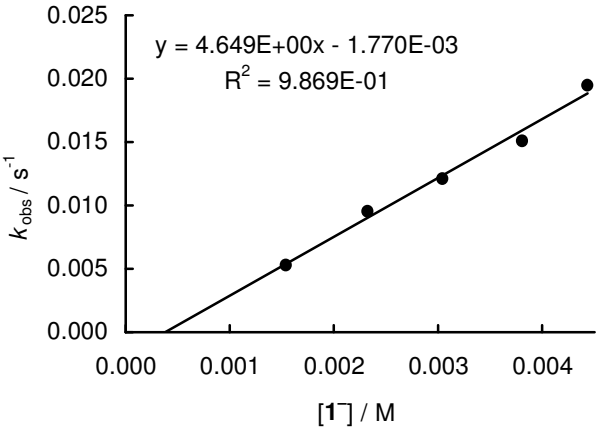
The temperature of the solutions during all kinetic studies was kept constant (–40 ± 0.1°C) by using a bath thermostat. Dry DMF for kinetics was purchased (< 50 ppm H_2O).
Rate constants k_{obs} (s^{-1}) were obtained by fitting the single exponential $A_t = A_0\exp(-k_{obs}t) + C$ to the observed time-dependent absorbance of the minor component.

reactions of 1^- with Michael acceptors

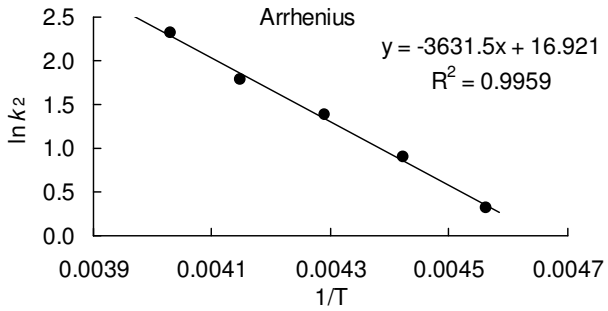
reaction of $\mathbf{1}^-$ with **10b**
(DMF, –40 °C, 400 nm)

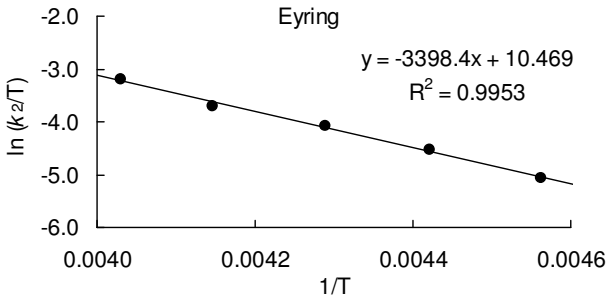
[**10b**] / M	[$\mathbf{1}^-$] / M	k_{obs} / s^{-1}
7.64×10^{-5}	1.58×10^{-3}	5.31×10^{-3}
7.89×10^{-5}	2.36×10^{-3}	9.57×10^{-3}
7.90×10^{-5}	3.08×10^{-3}	1.21×10^{-2}
8.07×10^{-5}	3.85×10^{-3}	1.51×10^{-2}
8.11×10^{-5}	4.47×10^{-3}	1.95×10^{-2}

$k_2 = 4.65 \pm 0.31$ M^{-1} s^{-1}



[**10b**] / M	[$\mathbf{1}^-$] / M	T / K	k_{obs} / s^{-1}	k_2 / M^{-1} s^{-1}
7.87×10^{-5}	3.07×10^{-3}	219.2	4.19×10^{-3}	1.38
8.01×10^{-5}	3.13×10^{-3}	226.2	7.58×10^{-3}	2.46
7.90×10^{-5}	3.08×10^{-3}	233.2	1.21×10^{-2}	3.98
7.95×10^{-5}	3.10×10^{-3}	241.2	1.83×10^{-2}	5.97
7.85×10^{-5}	3.06×10^{-3}	248.2	3.07×10^{-2}	1.02×10^{1}





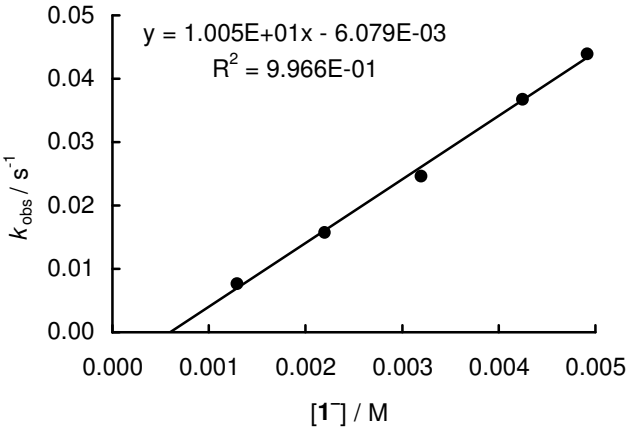
$E_A = (3.02 \pm 0.11) \times 10^1$ kJ mol^{-1}
$\ln(A) = (1.69 \pm 0.06) \times 10^1$

$\Delta H^{\ddagger} = (2.83 \pm 0.11) \times 10^1$ kJ mol^{-1}
$\Delta S^{\ddagger} = (-1.11 \pm 0.05) \times 10^2$ J mol^{-1} K^{-1}
k_2 (20 °C) = 9.31×10^1 m^{-1} s^{-1}

reaction of **1**$^-$ with **10a**
(DMF, –40 °C, 400 nm)

[**10a**] / M	[**1**$^-$] / M	k_{obs} / s^{-1}
8.73×10^{-5}	1.34×10^{-3}	7.66×10^{-3}
8.52×10^{-5}	2.24×10^{-3}	1.58×10^{-2}
8.21×10^{-5}	3.23×10^{-3}	2.46×10^{-2}
8.17×10^{-5}	4.29×10^{-3}	3.68×10^{-2}
8.09×10^{-5}	4.95×10^{-3}	4.39×10^{-2}

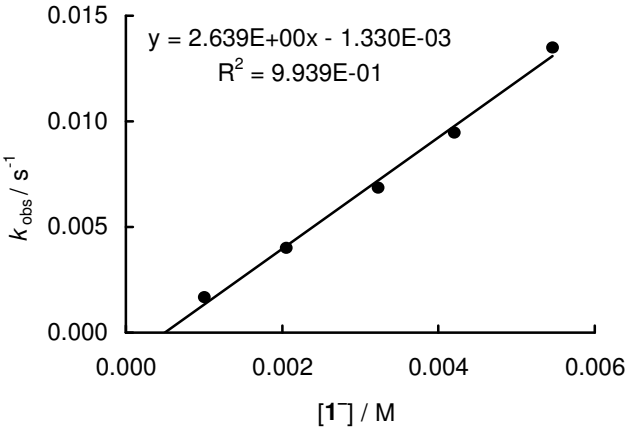
$k_2 = (1.00 \pm 0.03) \times 10^1$ M^{-1} s^{-1}



reaction of **1**$^-$ with **10c**
(DMF, –40 °C, 420 nm)

[**10c**] / M	[**1**$^-$] / M	k_{obs} / s^{-1}
7.43×10^{-5}	1.04×10^{-3}	1.66×10^{-3}
7.45×10^{-5}	2.09×10^{-3}	4.00×10^{-3}
7.16×10^{-5}	3.27×10^{-3}	6.84×10^{-3}
7.11×10^{-5}	4.24×10^{-3}	9.46×10^{-3}
7.12×10^{-5}	5.49×10^{-3}	1.35×10^{-2}

$k_2 = 2.64 \pm 0.12$ M^{-1} s^{-1}



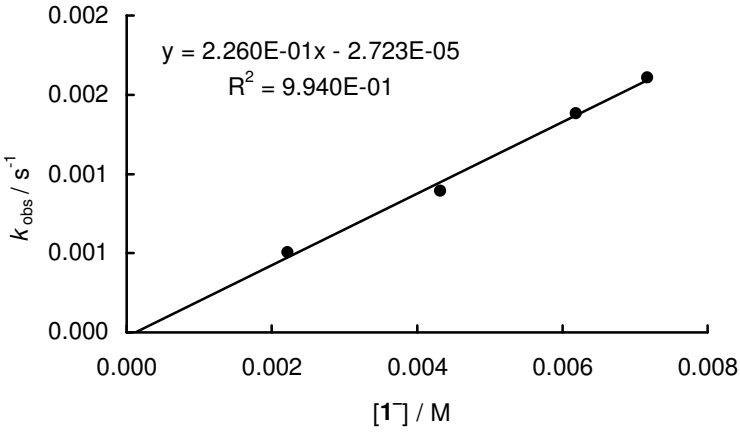
reactions of $\mathbf{1}^-$ with arenes

reaction of $\mathbf{1}^-$ with **3b**

(DMF, –40 °C, KO^{t}Bu, 18-K-6, 425 nm, excess of the nucleophile)

[**3b**] / M	[**1**] / M	[KO^{t}Bu] / M	[18-K-6] / M	k_{obs} / s^{-1}
2.14×10^{-4}	2.22×10^{-3}	2.30×10^{-3}	2.34×10^{-3}	5.05×10^{-4}
2.08×10^{-4}	4.32×10^{-3}	4.48×10^{-3}	4.57×10^{-3}	8.93×10^{-4}
1.99×10^{-4}	6.19×10^{-3}	6.51×10^{-3}	6.54×10^{-3}	1.38×10^{-3}
1.79×10^{-4}	7.17×10^{-3}	7.52×10^{-3}	7.56×10^{-3}	1.61×10^{-3}

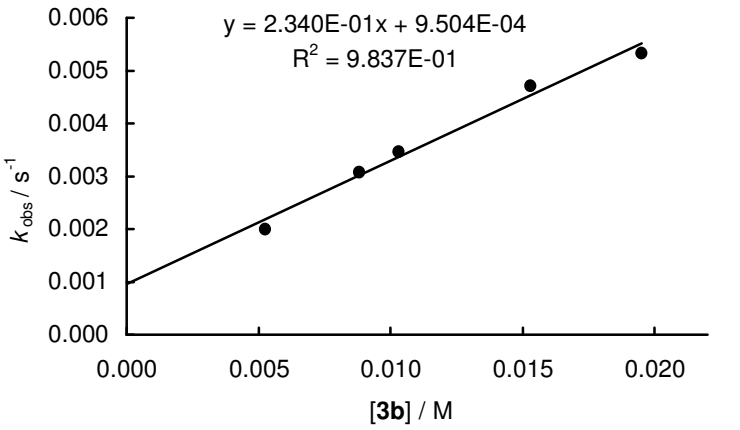
$k_2 = (2.26 \pm 0.12) \times 10^{-1}$ M^{-1} s^{-1}



(DMF, –40 °C, KO^{t}Bu, 18-K-6, 425 nm, excess of the electrophile)

[**1**] / M	[KO^{t}Bu] / M	[18-K-6] / M	[**3b**] / M	k_{obs} / s^{-1}
5.04×10^{-4}	3.40×10^{-4}	3.40×10^{-4}	5.24×10^{-3}	2.00×10^{-3}
5.17×10^{-4}	3.32×10^{-4}	3.52×10^{-4}	8.80×10^{-3}	3.08×10^{-3}
5.15×10^{-4}	3.46×10^{-4}	3.50×10^{-4}	1.03×10^{-2}	3.47×10^{-3}
5.43×10^{-4}	3.65×10^{-4}	3.70×10^{-4}	1.53×10^{-2}	4.71×10^{-3}
5.27×10^{-4}	3.54×10^{-4}	3.54×10^{-4}	1.95×10^{-2}	5.33×10^{-3}

$k_2 = (2.34 \pm 0.17) \times 10^{-1}$ M^{-1} s^{-1}

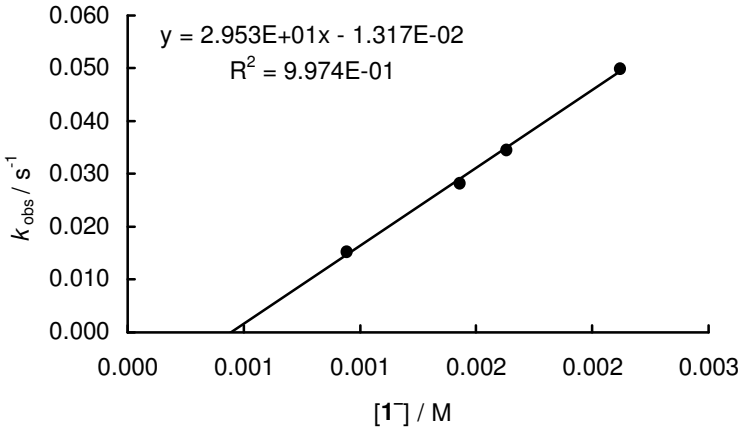


reaction of $\mathbf{1}^-$ with **3d**

(DMF, –40 °C, KO^{t}Bu, 18-K-6, 425 nm, excess of the nucleophile)

[**3d**] / M	[**1**] / M	[KO^{t}Bu] / M	[18-K-6] / M	k_{obs} / s^{-1}
9.31×10^{-5}	1.21×10^{-3}	9.42×10^{-4}	9.47×10^{-4}	1.53×10^{-2}
9.39×10^{-5}	1.84×10^{-3}	1.43×10^{-3}	1.41×10^{-3}	2.82×10^{-2}
8.04×10^{-5}	2.11×10^{-3}	1.63×10^{-3}	1.64×10^{-3}	3.46×10^{-2}
8.72×10^{-5}	2.74×10^{-3}	2.12×10^{-3}	2.11×10^{-3}	5.00×10^{-2}

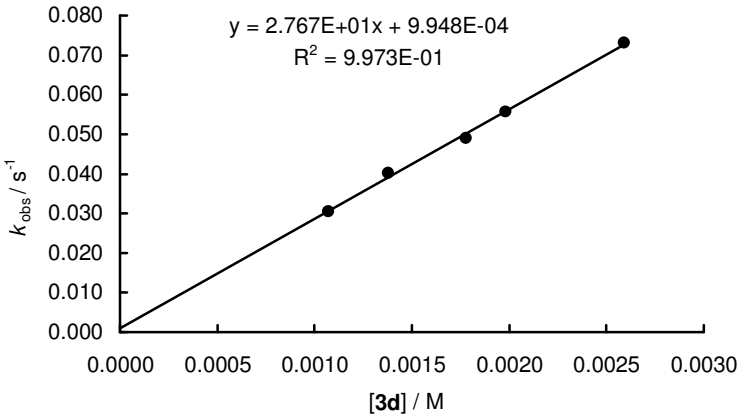
$k_2 = (2.95 \pm 0.11) \times 10^1$ M^{-1} s^{-1}



(DMF, –40 °C, KO^{t}Bu, 18-K-6, 425 nm, excess of the electrophile)

[**1**] / M	[KO^{t}Bu] / M	[18-K-6] / M	[**3d**] / M	k_{obs} / s^{-1}
2.05×10^{-4}	1.38×10^{-4}	1.40×10^{-4}	1.07×10^{-3}	3.05×10^{-2}
2.59×10^{-4}	1.69×10^{-4}	1.69×10^{-4}	1.38×10^{-3}	4.02×10^{-2}
2.62×10^{-4}	1.71×10^{-4}	1.70×10^{-4}	1.78×10^{-3}	4.90×10^{-2}
2.40×10^{-4}	1.56×10^{-4}	1.54×10^{-4}	1.98×10^{-3}	5.57×10^{-2}
2.50×10^{-4}	1.63×10^{-4}	1.61×10^{-4}	2.59×10^{-3}	7.31×10^{-2}

$k_2 = (2.77 \pm 0.08) \times 10^1$ M^{-1} s^{-1}

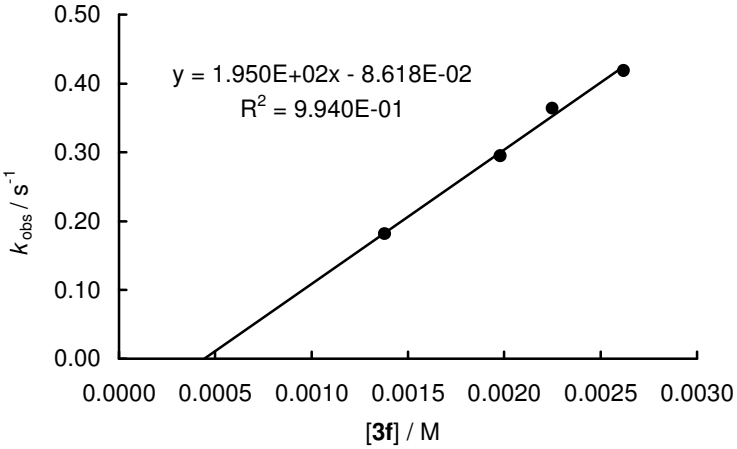


reaction of **1**$^-$ with **3f**

(DMF, –40 °C, KO^{t}Bu, 18-K-6, 425 nm, excess of the electrophile)

[**1**] / M	[KO^{t}Bu] / M	[18-K-6] / M	[**3f**] / M	k_{obs} / s^{-1}
2.77×10^{-4}	1.83×10^{-4}	1.87×10^{-4}	1.38×10^{-3}	1.82×10^{-1}
2.87×10^{-4}	1.90×10^{-4}	1.94×10^{-4}	1.98×10^{-3}	2.95×10^{-1}
2.79×10^{-4}	1.85×10^{-4}	1.88×10^{-4}	2.25×10^{-3}	3.64×10^{-1}
2.73×10^{-4}	1.81×10^{-4}	1.84×10^{-4}	2.62×10^{-3}	4.19×10^{-1}

$k_2 = (1.95 \pm 0.11) \times 10^2$ M^{-1} s^{-1}



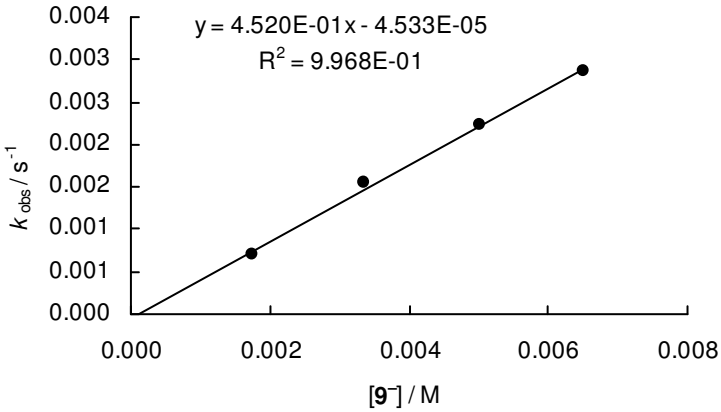
reactions of 9$^-$ with Michael acceptors

reaction of **9**$^-$ with **10a**

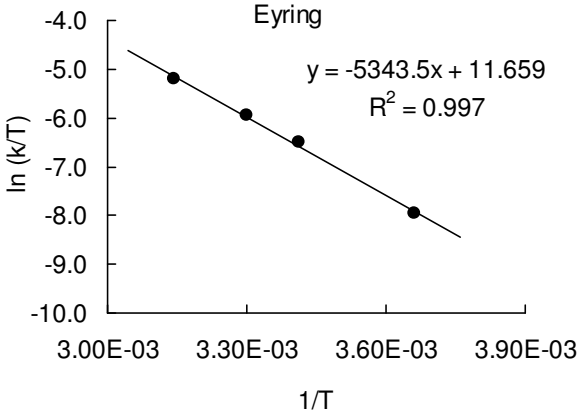
(DMF, 20 °C, 380 nm)

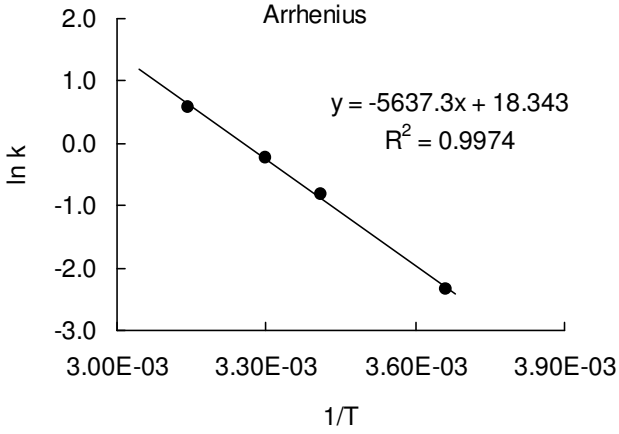
[**10a**] / M	[**9**$^-$] / M	k_{obs} / s^{-1}
5.82×10^{-5}	1.78×10^{-3}	6.98×10^{-4}
5.64×10^{-5}	3.37×10^{-3}	1.54×10^{-3}
5.58×10^{-5}	5.04×10^{-3}	2.22×10^{-3}
5.46×10^{-5}	6.53×10^{-3}	2.87×10^{-3}

$k_2 = (4.52 \pm 0.18) \times 10^{-1}$ M^{-1} s^{-1}



[**10a**] / M	[**9**$^-$] / M	T / K	k_{obs} / s^{-1}	k_2 / M^{-1} s^{-1}
5.54×10^{-5}	5.01×10^{-3}	273.2	4.79×10^{-4}	9.62×10^{-2}
5.57×10^{-5}	5.03×10^{-3}	293.2	2.22×10^{-3}	4.44×10^{-1}
5.51×10^{-5}	6.58×10^{-3}	303.2	5.24×10^{-3}	7.99×10^{-1}
5.59×10^{-5}	5.05×10^{-3}	318.2	8.87×10^{-3}	1.77





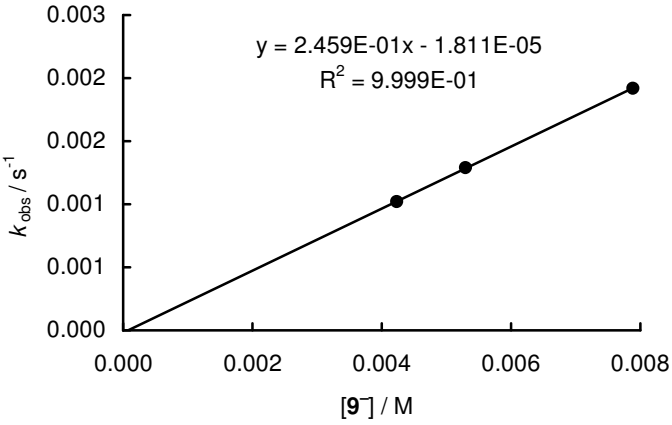
$\Delta H^{\ddagger} = (4.44 \pm 0.17) \times 10^{1}$ kJ mol^{-1}
$\Delta S^{\ddagger} = (-1.01 \pm 0.06) \times 10^{2}$ J mol^{-1} K^{-1}
k_2 (–40 °C) = $(3.01 \pm 0.57) \times 10^{-3}$ M^{-1} s^{-1}

$E_A = (4.69 \pm 0.17) \times 10^{1}$ kJ mol^{-1}
$\ln(A) = (1.83 \pm 0.07) \times 10^{1}$

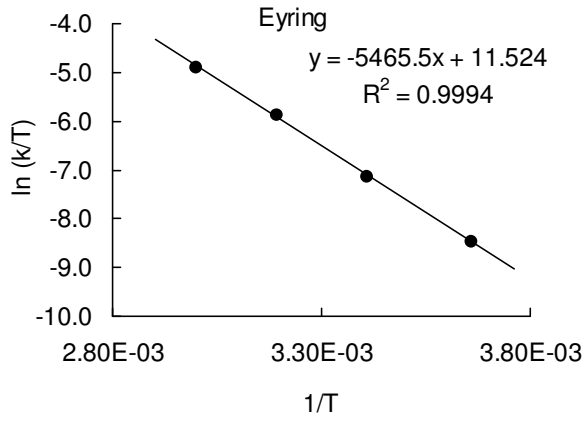
reaction of $\mathbf{9}^-$ with **10b**
(DMF, 20 °C, 390 nm)

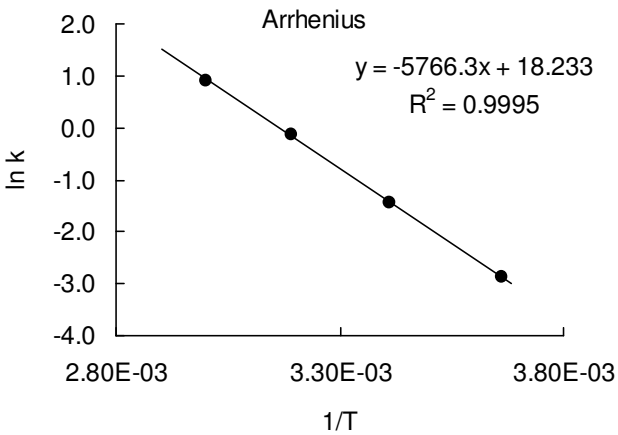
[**10b**] / M	[$\mathbf{9}^-$] / M	k_{obs} / s^{-1}
6.97×10^{-5}	4.23×10^{-3}	1.02×10^{-4}
6.71×10^{-5}	5.30×10^{-3}	1.29×10^{-3}
6.49×10^{-5}	7.89×10^{-3}	1.92×10^{-3}

$k_2 = (2.46 \pm 0.02) \times 10^{-1}$ M^{-1} s^{-1}



[**10b**] / M	[$\mathbf{9}^-$] / M	T / K	k_{obs} / s^{-1}	k_2 / M^{-1} s^{-1}
6.53×10^{-5}	7.94×10^{-3}	273.2	4.43×10^{-4}	5.60×10^{-2}
6.80×10^{-5}	8.26×10^{-3}	293.2	1.92×10^{-3}	2.34×10^{-1}
6.59×10^{-5}	8.01×10^{-3}	313.2	7.03×10^{-3}	8.81×10^{-1}
6.56×10^{-5}	7.97×10^{-3}	338.2	1.94×10^{-2}	2.44





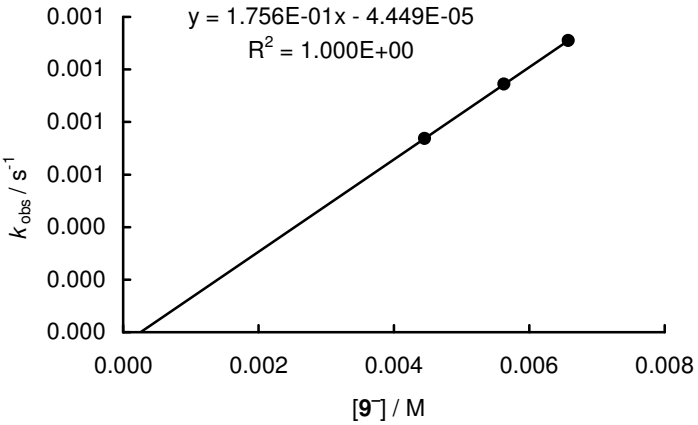
$\Delta H^{\ddagger} = (4.54 \pm 0.08) \times 10^{1}$ kJ mol^{-1}
$\Delta S^{\ddagger} = (-1.02 \pm 0.03) \times 10^{2}$ J mol^{-1} K^{-1}
k_2 (–40 °C) = $(1.56 \pm 0.15) \times 10^{-3}$ M^{-1} s^{-1}

$E_A = (4.79 \pm 0.08) \times 10^{1}$ kJ mol^{-1}
$\ln(A) = (1.82 \pm 0.03) \times 10^{1}$

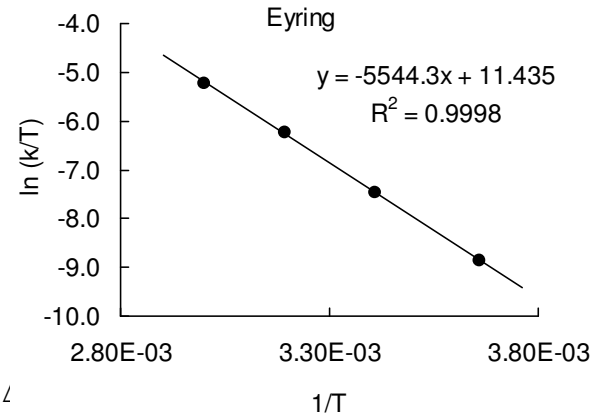
reaction of $\mathbf{9}^-$ with **10c**
(DMF, 20 °C, 380 nm)

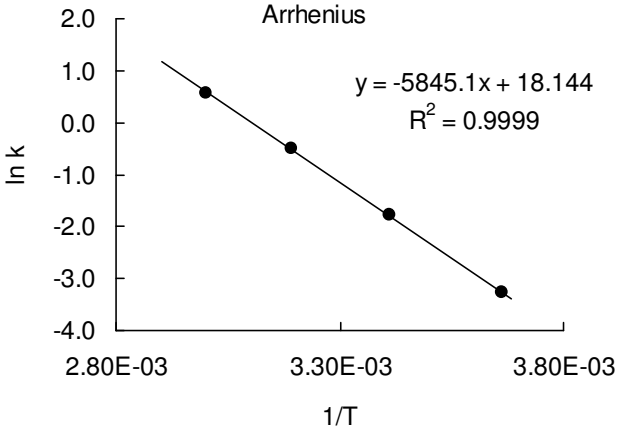
[**10c**] / M	[$\mathbf{9}^-$] / M	k_{obs} / s^{-1}
5.57×10^{-5}	4.48×10^{-3}	7.37×10^{-4}
5.66×10^{-5}	5.66×10^{-3}	9.44×10^{-4}
5.53×10^{-5}	6.60×10^{-3}	1.11×10^{-3}

$k_2 = (1.76 \pm 0.004) \times 10^{-1}$ M^{-1} s^{-1}



[**10c**] / M	[$\mathbf{9}^-$] / M	T / K	k_{obs} / s^{-1}	k_2 / M^{-1} s^{-1}
5.58×10^{-5}	6.66×10^{-3}	273.2	2.52×10^{-4}	3.80×10^{-2}
5.53×10^{-5}	6.60×10^{-3}	293.2	1.11×10^{-3}	1.69×10^{-1}
5.53×10^{-5}	6.60×10^{-3}	313.2	3.97×10^{-3}	6.04×10^{-1}
5.51×10^{-5}	6.57×10^{-3}	333.2	1.17×10^{-2}	1.79





$\Delta S^{\ddagger} = (-1.02 \pm 0.01) \times 10^{2}$ J mol^{-1} K^{-1}
k_2 (–40 °C) = $(1.01 \pm 0.05) \times 10^{-3}$ M^{-1} s^{-1}

$\ln(A) = (1.82 \pm 0.02) \times 10^{1}$

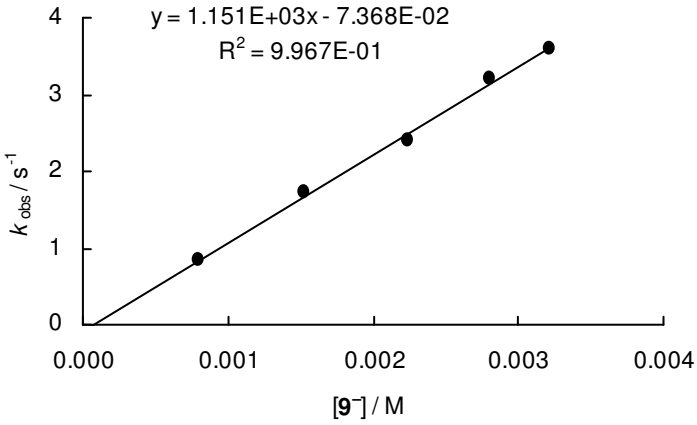
reactions of 9^- with quinone methides

reaction of $\mathbf{9}^-$ with **12a**

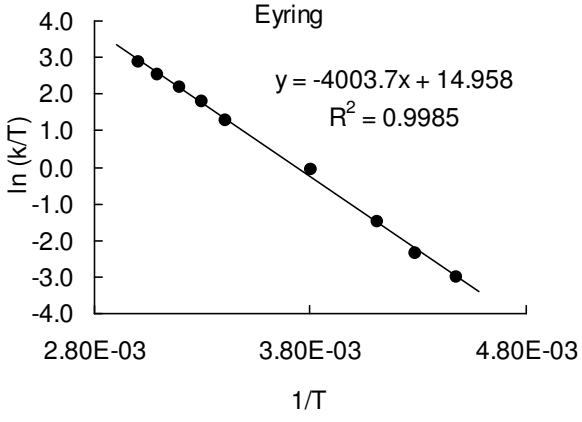
(DMF, 20 °C, stopped flow, 400 nm)

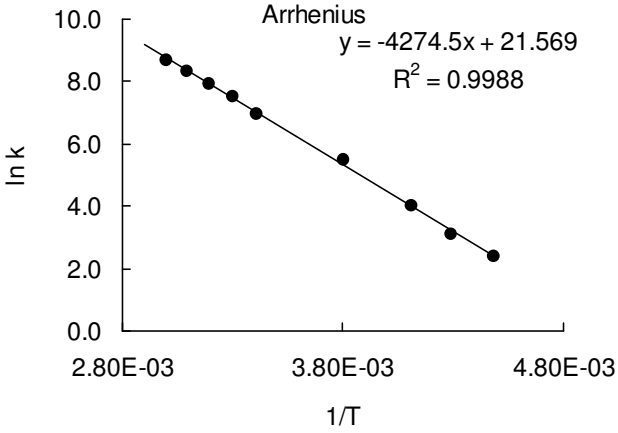
[**12a**] / M	[$\mathbf{9}^-$] / M	k_{obs} / s^{-1}
4.25×10^{-5}	8.03×10^{-4}	8.48×10^{-1}
4.25×10^{-5}	1.53×10^{-3}	1.73
4.25×10^{-5}	2.25×10^{-3}	2.41
4.25×10^{-5}	2.81×10^{-3}	3.22
4.25×10^{-5}	3.21×10^{-3}	3.62

$k_2 = (1.15 \pm 0.04) \times 10^3$ M^{-1} s^{-1}



[**12a**] / M	[$\mathbf{9}^-$] / M	T / K	k_{obs} / s^{-1}	k_2 / M^{-1} s^{-1}
2.06×10^{-5}	2.08×10^{-4}	223.2	2.20×10^{-3}	1.11×10^1
2.06×10^{-5}	2.09×10^{-4}	233.2	4.44×10^{-3}	2.24×10^1
2.09×10^{-5}	2.11×10^{-4}	243.2	1.12×10^{-2}	5.58×10^1
2.06×10^{-5}	2.08×10^{-4}	263.2	4.80×10^{-2}	2.42×10^2
4.25×10^{-5}	2.25×10^{-3}	293.2	2.41	1.07×10^3
4.25×10^{-5}	2.25×10^{-3}	303.2	4.16	1.85×10^3
4.25×10^{-5}	2.25×10^{-3}	313.2	6.15	2.74×10^3
4.25×10^{-5}	2.25×10^{-3}	323.2	9.10	4.05×10^3
4.25×10^{-5}	2.25×10^{-3}	333.2	1.31×10^1	5.85×10^3





$\Delta H^{\ddagger} = (3.33 \pm 0.05) \times 10^1$ kJ mol^{-1}

$\Delta S^{\ddagger} = (-7.32 \pm 0.18) \times 10^1$ J mol^{-1} K^{-1}

k_2 (–40 °C) $= (2.55 \pm 0.23) \times 10^1$ M^{-1} s^{-1}

$E_A = (3.55 \pm 0.05) \times 10^1$ kJ mol^{-1}

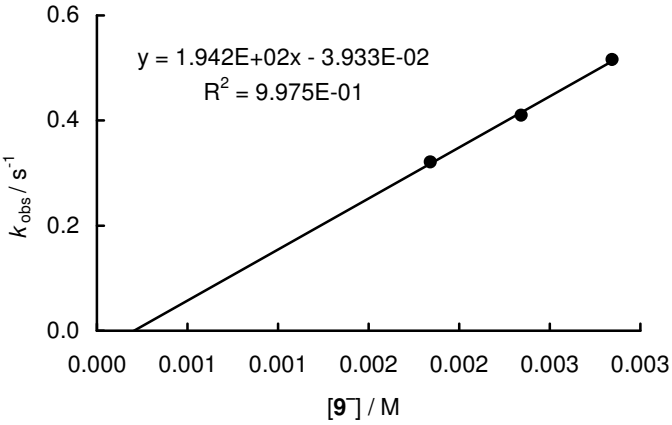
$\ln(A) = (2.16 \pm 0.02) \times 10^1$

reaction of $\mathbf{9}^-$ with **12b**

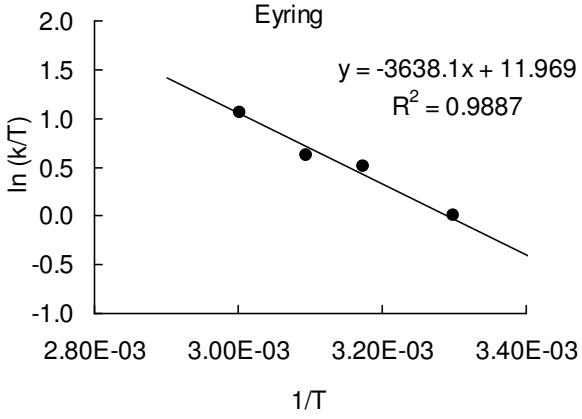
(DMF, 20 °C, stopped flow, 500 nm)

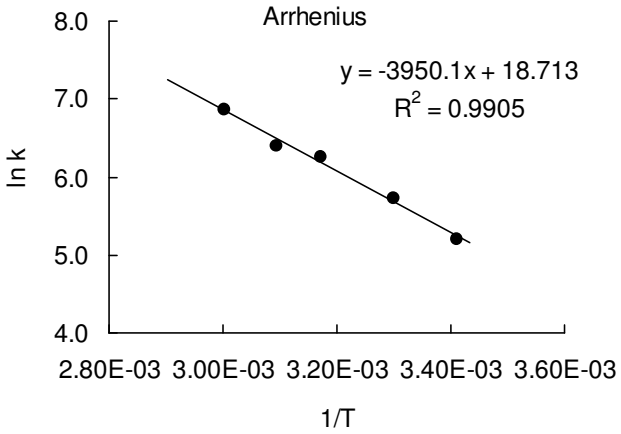
[**12b**] / M	[$\mathbf{9}^-$] / M	k_{obs} / s^{-1}
2.48×10^{-5}	1.84×10^{-3}	3.21×10^{-1}
2.48×10^{-5}	2.34×10^{-3}	4.10×10^{-1}
2.48×10^{-5}	2.84×10^{-3}	5.16×10^{-1}

$k_2 = (1.94 \pm 0.10) \times 10^2$ M^{-1} s^{-1}



[**12b**] / M	[$\mathbf{9}^-$] / M	T / K	k_{obs} / s^{-1}	k_2 / M^{-1} s^{-1}
2.48×10^{-5}	2.84×10^{-3}	293.2	5.16×10^{-1}	1.81×10^2
2.48×10^{-5}	2.84×10^{-3}	303.2	8.68×10^{-1}	3.05×10^2
2.48×10^{-5}	2.84×10^{-3}	315.2	1.48	5.20×10^2
2.48×10^{-5}	2.84×10^{-3}	323.2	1.72	6.05×10^2
2.48×10^{-5}	2.84×10^{-3}	333.2	2.73	9.60×10^2





$\Delta H^{\ddagger} = (3.02 \pm 0.19) \times 10^1$ kJ mol^{-1}

$\Delta S^{\ddagger} = (-9.80 \pm 0.60) \times 10^1$ J mol^{-1} K^{-1}

k_2 (–40 °C) = 6.15 ± 1.52 M^{-1} s^{-1}

$E_A = (3.28 \pm 0.19) \times 10^1$ kJ mol^{-1}

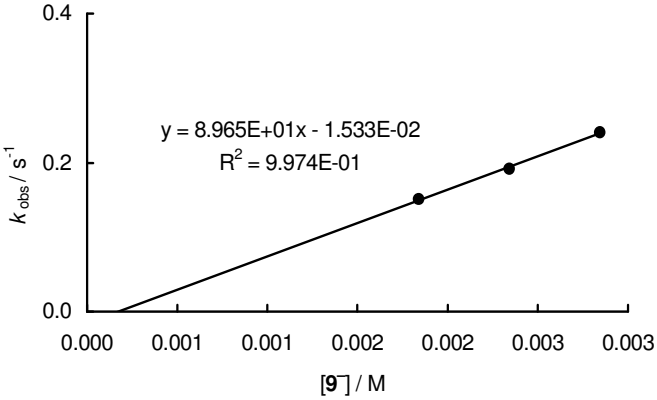
$\ln(A) = (1.87 \pm 0.07) \times 10^1$

reaction of $\mathbf{9}^-$ with **12c**

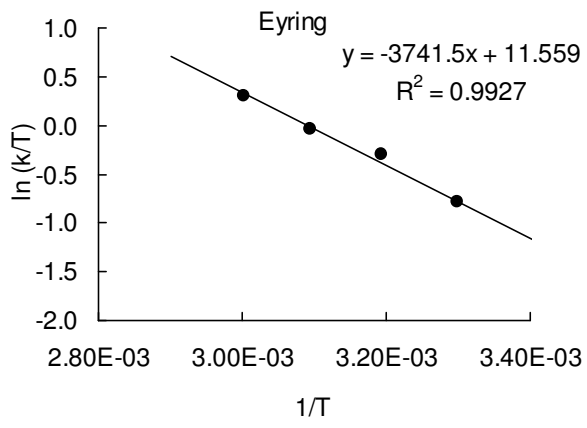
(DMF, 20 °C, stopped flow, 500 nm)

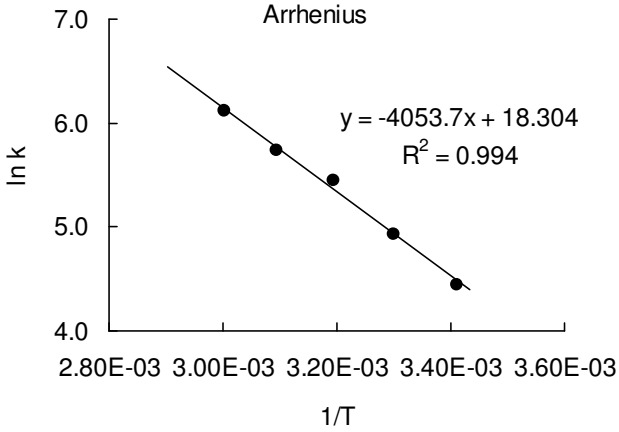
[**12c**] / M	[$\mathbf{9}^-$] / M	k_{obs} / s^{-1}
2.46×10^{-5}	1.84×10^{-3}	1.15×10^{-1}
2.46×10^{-5}	2.34×10^{-3}	1.92×10^{-1}
2.46×10^{-5}	2.84×10^{-3}	2.41×10^{-1}

$k_2 = (8.97 \pm 0.46) \times 10^1$ M^{-1} s^{-1}



[**12c**] / M	[$\mathbf{9}^-$] / M	T / K	k_{obs} / s^{-1}	k_2 / M^{-1} s^{-1}
2.46×10^{-5}	2.84×10^{-3}	293.2	2.41×10^{-1}	8.47×10^1
2.46×10^{-5}	2.84×10^{-3}	303.2	3.95×10^{-1}	1.39×10^2
2.46×10^{-5}	2.84×10^{-3}	313.2	6.61×10^{-1}	2.32×10^2
2.46×10^{-5}	2.84×10^{-3}	323.2	8.78×10^{-1}	3.09×10^2
2.46×10^{-5}	2.84×10^{-3}	333.2	1.28	4.50×10^2





$\Delta H^{\ddagger} = (3.11 \pm 0.15) \times 10^1$ kJ mol^{-1}

$\Delta S^{\ddagger} = (-1.01 \pm 0.05) \times 10^2$ J mol^{-1} K^{-1}

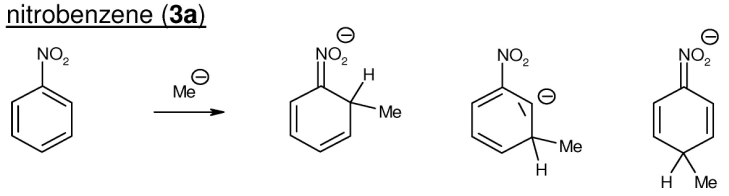
k_2 (–40 °C) = 2.62 ± 0.53 M^{-1} s^{-1}

$E_A = (3.37 \pm 0.15) \times 10^1$ kJ mol^{-1}

$\ln(A) = (1.83 \pm 0.06) \times 10^1$

Quantum chemical calculations

nitrobenzene (**3a**)



3a **3a_a2** **3a_a3** **3a_a4**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
3a	-436.7505850	-436.639283	-436.8744693	-436.7631673			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
3a_a4	-476.6780191	-476.528437	-476.8357953	-476.6862132	-0.1023	-64.2	-268.6
3a_a2	-476.6752506	-476.525670	-476.8328866	-476.6833060	-0.0994	-62.4	-260.9
3a_a3	-476.6392896	-476.491290	-476.7982246	-476.6502250	-0.0663	-41.6	-174.1

3a

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C6H5N1O2\FLSCH\27-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\benz_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\0,1\C,0,-2.17905546
88,0.0008036248,-1.2583757933\C,0,-2.1830975788,0.0065715483,0.1392452
47\C,0,-0.9807971742,0.0061676169,0.843350263\C,0,0.2119813906,-0.0000
793966,0.1224164094\C,0,0.2402212606,-0.005896306,-1.2710240296\C,0,-0
.9705600042,-0.005409152,-1.9604417178\H,0,-3.1198173755,0.0011509853,
-1.8016541994\H,0,-3.1231915502,0.0113934177,0.6826968459\H,0,-0.94998
77472,0.010541839,1.9258471909\H,0,1.1931992019,-0.010633846,-1.785395
9021\H,0,-0.9697456832,-0.0098840795,-3.0463141257\N,0,1.4875378506,-0
.0005504748,0.8590337111\O,0,1.4378395224,0.0046671125,2.088694132\O,0
,2.5277384336,-0.0061249383,0.2013761105\\Version=x86-Linux-G03RevB.03
\State=1-A\HF=-436.8744693\RMSD=8.809e-09\Dipole=-1.6914014,0.0006206,
-0.9767622\PG=C01 [X(C6H5N1O2)]\\@

methyl anion

1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C1H3(1-)\FLSCH\21-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\me_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,-0.
083113744,-0.143957206,-0.0587702946\H,0,-0.0007490109,-0.0012971953,1
.062101736\H,0,1.0011095043,-0.0012972643,-0.3547399313\H,0,-0.5016780
294,0.8663376953,-0.354740037\\Version=x86-Linux-G03RevB.03\State=1-A1
\HF=-39.8524446\RMSD=7.584e-09\Dipole=0.3918045,0.6786252,0.2770476\PG
=C03V [C3(C1),3SGV(H1)]\\@

3a_a2

1\1\GINC-CICUM83\SP\RB3LYP\6-311+G(d,p)\C7H8N1O2(1-)\FLSCH\27-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\benz_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,2.4
712081309,-0.442189168,-0.2435626036\C,0,1.8903826702,0.7406979902,-0.
5521672583\C,0,0.4228978487,1.035846641,-0.295111022\C,0,-0.3267052624
,-0.2595562638,-0.0322362513\C,0,0.3402600373,-1.4585245008,0.30107940
63\C,0,1.7099803546,-1.5665738047,0.2496805077\H,0,3.5442186042,-0.567
8954271,-0.4049796565\H,0,2.4925373245,1.5577765002,-0.9528963493\H,0,
-0.0228898895,1.5216266942,-1.1787770365\H,0,-0.2855230016,-2.30131665
77,0.5786199122\H,0,2.2100112035,-2.4983831351,0.5028004588\N,0,-1.702
9465429,-0.24405304,-0.1265660843\O,0,-2.2816502294,0.8472711087,-0.43
98672359\O,0,-2.3841231302,-1.2954746621,0.0839864371\C,0,0.2636071845
,2.0592141542,0.8635054001\H,0,-0.7971251619,2.2805528142,1.0124714749
\H,0,0.6810793216,1.6516023389,1.7922920421\H,0,0.7947184937,2.9965462
909,0.6363490616\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-476.83288
66\RMSD=6.481e-09\Dipole=2.1205685,0.4634475,0.1783077\PG=C01 [X(C7H8N
1O2)]\\@

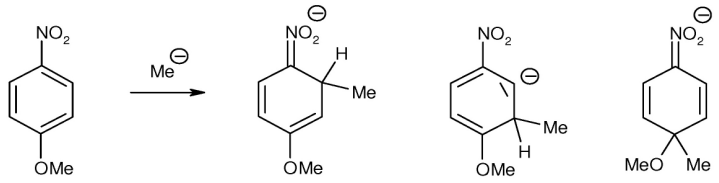
3a_a3

1\1\GINC-CICUM85\SP\RB3LYP\6-311+G(d,p)\C7H8N1O2(1-)\FLSCH\27-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\benz_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-2.
0650112402,0.7658163766,-0.6104997465\C,0,-1.7830226734,-0.7066920091,
-0.3707768681\C,0,-0.2885934173,-0.8926141534,-0.5172536952\C,0,0.5491
857393,0.096095773,-0.0326694659\C,0,0.1153671063,1.4031355622,0.29889
2113\C,0,-1.1892898917,1.7201681913,-0.1406790683\H,0,-2.9978567046,1.
0569108394,-1.0949884422\H,0,-2.2948944007,-1.3133775287,-1.138920685\
H,0,0.1244032447,-1.7853560153,-0.9710294445\H,0,0.8061905361,2.140451
4095,0.6820850391\H,0,-1.4862714245,2.7723858591,-0.1705214043\C,0,-2.
3217458364,-1.2003517928,1.0031771172\H,0,-3.4087365356,-1.0371452455,
1.0848361779\H,0,-2.1137415238,-2.2715115166,1.1545643203\H,0,-1.83462
78228,-0.6413821248,1.8103140062\N,0,1.9807945674,-0.1813115991,0.0187
512227\O,0,2.405303661,-1.2788828495,-0.3832509164\O,0,2.7495255815,0.
6832400783,0.4746583609\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-47
6.7982246\RMSD=5.767e-09\Dipole=-0.9738916,-0.1326295,0.002016\PG=C01
[X(C7H8N1O2)]\\@

3a_a4

1\1\GINC-CICUM84\SP\RB3LYP\6-311+G(d,p)\C7H8N1O2(1-)\FLSCH\27-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\benz_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-1.
9115425075,-0.1309277689,-1.1021920671\C,0,-1.7897341099,-0.181694354,
0.4084691205\C,0,-0.6060221498,-0.1668656678,1.0675280783\C,0,0.649764
1466,-0.1502452065,0.3754961569\C,0,0.620129139,-0.1760692875,-1.05790
48278\C,0,-0.5430194994,-0.1910523905,-1.7526085242\H,0,-2.5219776164,
-0.9936691441,-1.450612999\H,0,-2.722031036,-0.2059549364,0.975291845\
H,0,-0.5716683993,-0.1822179485,2.1526028233\H,0,1.5765871625,-0.19834
29656,-1.5712223268\H,0,-0.5191348023,-0.2224900791,-2.8432483752\N,0,
1.844467132,-0.1454913438,1.0646934188\O,0,1.8387032951,-0.137572845,2
.3351778559\O,0,2.9414336511,-0.145850038,0.4236859446\C,0,-2.70215848
45,1.1239655808,-1.5637283846\H,0,-2.8184341635,1.1419301194,-2.657751
0212\H,0,-3.7073627196,1.1486025123,-1.1168662566\H,0,-2.1728431253,2.
0352994789,-1.2623153368\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-4
76.8357953\RMSD=5.355e-09\Dipole=-2.4561028,0.1461151,-1.4175461\PG=C0
1 [X(C7H8N1O2)]\\@

1-methoxy-4-nitrobenzene (**3b**)



3b **3b_a2** **3b_a3** **3b_a4**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
3b	-551.2758602	-551.129185	-551.4335495	-551.2868743			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
3b_a4	-591.2093414	-591.024865	-591.4012137	-591.2167373	-0.1091	-68.5	-286.5
3b_a2	-591.1973919	-591.012627	-591.3883925	-591.2036276	-0.0960	-60.2	-252.0
3b_a3	-591.1618228	-590.978314	-591.3530839	-591.1695751	-0.0619	-38.9	-162.6

3b

1\1\GINC-CICUM85\SP\RB3LYP\6-311+G(d,p)\C7H7N1O3\FLSCH\27-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\ani_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\0,1\C,0,-1.461634892
8,-0.1541642415,-0.7537782843\C,0,-1.5035152698,0.0016021426,0.6444702
181\C,0,-0.3310919366,0.1385554572,1.3669235758\C,0,0.8926077453,0.119
9963598,0.6894524631\C,0,0.9524889462,-0.0331366345,-0.6930179148\C,0,
-0.2260620173,-0.1709839437,-1.4208733272\H,0,-2.4709241105,0.01122834
06,1.1353581641\H,0,-0.3416907308,0.259462289,2.4430708166\H,0,1.91749

13998,-0.0429714865,-1.1847491098\H,0,-0.1730255725,-0.2897904641,-2.4
963094716\N,0,2.1339348884,0.2642529695,1.4477646757\O,0,2.0478771494,
0.398228799,2.6702228623\O,0,3.1966320963,0.2438779793,0.8228489305\C,
0,-2.7047926575,-0.4411860603,-2.7765356037\H,0,-3.7614966898,-0.52037
05687,-3.0351955618\H,0,-2.2673808683,0.4241358858,-3.2896362914\H,0,-
2.1832406623,-1.3542981966,-3.0889337731\O,0,-2.6651688069,-0.27976491
13,-1.3627973259\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-551.43354
95\RMSD=3.111e-09\Dipole=-1.7935751,-0.2819807,-1.7473749\PG=C01 [X(C7
H7N1O3)]\\@

3b_a2

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C8H10N1O3(1-)\FLSCH\28-Nov-200
7\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUES
S=READ\\ani_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,1.7
270998384,0.1439160506,0.1706062221\C,0,0.9778012418,1.1432667047,-0.3
433922191\C,0,-0.538733147,1.1402267003,-0.2723137242\C,0,-1.038435469
8,-0.2651027724,0.0191183515\C,0,-0.2014227105,-1.2542095431,0.5753117
075\C,0,1.1552201412,-1.0700970968,0.7049832127\H,0,1.4767041007,2.012
3336672,-0.7689787765\H,0,-0.9535347051,1.4586278022,-1.2415854456\H,0
,-0.677317642,-2.17819575,0.8892567792\H,0,1.7940923201,-1.8105201054,
1.1770879881\N,0,-2.3626013763,-0.5558447173,-0.2432063088\O,0,-3.1021
490659,0.3572370676,-0.7318820408\O,0,-2.8332535666,-1.7114423425,-0.0
110865979\C,0,-1.0526265705,2.1766827823,0.7645130291\H,0,-2.146677674
,2.1750409722,0.7741393954\H,0,-0.6826248519,1.9280559559,1.7665306773
\H,0,-0.7003131892,3.1891077366,0.5154329383\C,0,3.7953747648,-0.63333
6408,-0.6597244557\H,0,4.8698175191,-0.4474238015,-0.5444698139\H,0,3.
5837526075,-1.6788554918,-0.3931414404\H,0,3.5181074952,-0.4897407077,
-1.7163091399\O,0,3.1242195228,0.2847558047,0.1792021707\\Version=x86-
Linux-G03RevB.03\State=1-A\HF=-591.3883925\RMSD=6.849e-09\Dipole=2.938
9872,0.4358718,0.0149354\PG=C01 [X(C8H10N1O3)]\\@

3b_a3

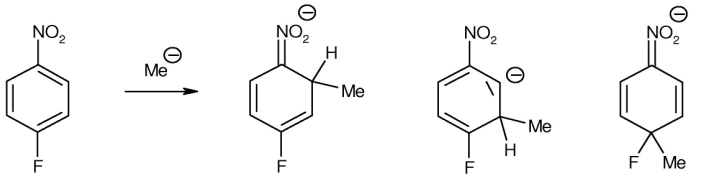
1\1\GINC-CICUM99\SP\RB3LYP\6-311+G(d,p)\C8H10N1O3(1-)\FLSCH\28-Nov-200
7\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUES
S=READ\\ani_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-1.
2723712352,-0.1046422182,-0.8506866306\C,0,-1.422995062,0.1285925549,0
.6336684454\C,0,-0.1015296832,-0.2720188458,1.2434912303\C,0,1.0677181
894,0.0621302191,0.5700090673\C,0,1.1002889993,0.4188467431,-0.7944744
746\C,0,-0.1007197854,0.1873781256,-1.5122055912\H,0,-2.2175832426,-0.
5403884201,1.0025225388\H,0,-0.0620390942,-0.8067786905,2.1841087336\H

,0,2.0157475962,0.7311434544,-1.2756508639\H,0,-0.071985253,0.19900024
45,-2.6013264516\C,0,-1.864712999,1.5824731901,0.9716791212\H,0,-2.821
837957,1.8378775443,0.4909553623\H,0,-1.9708406623,1.7100540695,2.0591
677728\H,0,-1.1041614339,2.2894223708,0.6211382623\N,0,2.3370434284,-0
.0889783835,1.2598578709\O,0,2.3434492187,-0.5205728596,2.427591575\O,
0,3.3944158328,0.2169620051,0.6755995196\C,0,-2.329918675,-1.042987070
5,-2.7743364964\H,0,-3.2771782914,-1.5364312539,-3.0237253459\H,0,-2.1
638105009,-0.2257723257,-3.4967965378\H,0,-1.4996919558,-1.7592304082,
-2.8809180825\O,0,-2.4429252636,-0.5757246568,-1.4558596585\\Version=x
86-Linux-G03RevB.03\State=1-A\HF=-591.3530839\RMSD=2.503e-09\Dipole=-1
.8571417,-0.1751999,-1.5297653\PG=C01 [X(C8H10N1O3)]\\@

3b_a4

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C8H10N1O3(1-)\FLSCH\30-Nov-200
7\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUES
S=READ\\ani_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,1.6
785845933,0.036597147,-0.4094591554\C,0,0.827353779,-1.1999379275,-0.4
920355888\C,0,-0.5223523003,-1.1996647851,-0.3273443215\C,0,-1.2508909
132,0.0104650574,-0.1206749339\C,0,-0.5234907389,1.2387200493,-0.11541
90231\C,0,0.8262220672,1.2683430453,-0.2777651718\H,0,1.3555456241,-2.
1376741215,-0.6660068406\H,0,-1.0898836685,-2.124210515,-0.3694727295\
H,0,-1.0916831814,2.1562365679,0.0024356977\H,0,1.3546414176,2.2219657
932,-0.2853317678\N,0,-2.6313611618,-0.0034327718,0.037207859\O,0,-3.2
50879131,-1.105196986,0.0137732719\O,0,-3.2511411769,1.0857741226,0.20
40614994\C,0,2.0372748275,-0.1785216511,2.0017440581\H,0,2.8515410054,
-0.2337549659,2.7360655032\H,0,1.3989411463,0.6855605657,2.2420731652\
H,0,1.4176971339,-1.0845168475,2.0887957757\O,0,2.6404932607,-0.061766
3109,0.7346395808\C,0,2.6602985091,0.1397724986,-1.590163507\H,0,3.304
926341,1.0207735616,-1.4768226296\H,0,3.3025337144,-0.7492155637,-1.63
29154427\H,0,2.1094860349,0.2237377197,-2.5323647008\\Version=x86-Linu
x-G03RevB.03\State=1-A\HF=-591.4012137\RMSD=3.261e-09\Dipole=2.5435787
,0.0004399,-0.0302837\PG=C01 [X(C8H10N1O3)]\\@

1-fluoro-4-nitrobenzene (**3c**)



3c **3c_a2** **3c_a3** **3c_a4**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
3c	-535.9833544	-535.879511	-536.1420483	-536.0382049			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
3c_a4	-575.9307597	-575.788397	-576.1282417	-575.9858790	-0.1269	-79.6	-333.2
3c_a2	-575.9166114	-575.774192	-576.1102320	-575.9678126	-0.1088	-68.3	-285.8
3c_a3	-575.8779723	-575.736954	-576.0721326	-575.9311143	-0.0722	-45.3	-189.4

3c

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C6H4F1N1O2\FLSCH\28-Nov-2007\0
\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=R
EAD\\fbenzn_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\0,1\C,0,-1.7856
306794,0.0006645851,-1.031174273\C,0,-1.8155663317,0.0149671101,0.3616
321691\C,0,-0.6108105865,0.0145114831,1.0566748556\C,0,0.5847209582,-0
.0002176248,0.33766733\C,0,0.6099069695,-0.0145111467,-1.057196753\C,0
,-0.5942553057,-0.0140702108,-1.7532671572\H,0,-2.7692183058,0.0261357
291,0.8778581335\H,0,-0.5819264238,0.025301638,2.139070356\H,0,1.56182
89133,-0.0256663406,-1.5731917969\H,0,-0.6238041827,-0.0248728991,-2.8
372764959\N,0,1.8564478488,-0.0006909424,1.0720700802\O,0,1.8061487251
,0.0120809528,2.3019715689\O,0,2.8965498186,-0.0138312269,0.413764682\
F,0,-2.948199271,0.0010972759,-1.7025397548\\Version=x86-Linux-G03RevB
.03\State=1-A\HF=-536.1420483\RMSD=4.919e-09\Dipole=-1.1512067,0.00042
85,-0.6648043\PG=C01 [X(C6H4F1N1O2)]\\@

3c_a2

1\1\GINC-CICUM91\SP\RB3LYP\6-311+G(d,p)\C7H7F1N1O2(1-)\FLSCH\28-Nov-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\fbenzn_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0
,2.0943430264,-0.1937133655,-0.1112588047\C,0,1.4593441577,0.937889253
5,-0.4686897621\C,0,-0.0380338361,1.1002200811,-0.2673977155\C,0,-0.67
94877552,-0.2574114958,-0.0197945139\C,0,0.0713932067,-1.390946685,0.3
506750865\C,0,1.4474636268,-1.3848939848,0.3584900398\H,0,2.0339373809
,1.7799450353,-0.8481166555\H,0,-0.4902512461,1.5340902796,-1.17332057
13\H,0,-0.488574964,-2.2832447026,0.611527479\H,0,2.0419888452,-2.2496
75326,0.6325003984\N,0,-2.0504455486,-0.3649519543,-0.1614478219\O,0,-

2.7088316286,0.6658091366,-0.5094638551\O,0,-2.6407011762,-1.4691528827,0.0406776962\F,0,3.4618309272,-0.2655708855,-0.2347148214\C,0,-0.3359088993,2.1090886359,0.8753916186\H,0,-1.4172094493,2.230788017,0.9867046754\H,0,0.086270624,1.7477615122,1.8209611921\H,0,0.1120605804,3.0904921674,0.6581052073\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-576.110232\RMSD=3.870e-09\Dipole=1.8807416,0.5906945,0.2838529\PG=C01 [X(C7H7F1N1O2)]\\@

3c_a3

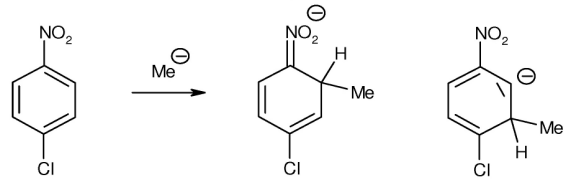
1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C7H7F1N1O2(1-)\FLSCH\28-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\fbenzn_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,1.7899191535,-0.5153141174,-0.2272575116\C,0,1.3939200297,0.9319493685,-0.2446360979\C,0,-0.1006104207,0.9366218886,-0.4842213309\C,0,-0.8868526796,-0.1007257471,-0.0026005128\C,0,-0.384828256,-1.3426019966,0.4383665289\C,0,0.9978392941,-1.5417046587,0.2002110956\H,0,-0.5612947315,1.7638903956,-1.0092853594\H,0,-1.0300204128,-2.1065328521,0.8451660995\H,0,1.4451635554,-2.5292308745,0.3137780561\H,0,1.9073236836,1.4219093558,-1.0934441416\C,0,1.8468418866,1.7100152626,1.030503055\H,0,2.9397891817,1.6706400429,1.1585771395\H,0,1.5396468874,2.7647693316,0.9686734486\H,0,1.3794084414,1.2723727101,1.9200789148\F,0,3.0954622316,-0.7781958897,-0.6172428595\N,0,-2.3372388126,0.0535524834,-0.0626987106\O,0,-2.8170134403,1.0966616757,-0.5388517518\O,0,-3.0649714405,-0.8589569864,0.3673944013\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-576.0721326\RMSD=6.662e-09\Dipole=1.1021318,0.1427709,0.1412828\PG=C01 [X(C7H7F1N1O2)]\\@

3c_a4

1\1\GINC-CICUM85\SP\RB3LYP\6-311+G(d,p)\C7H7F1N1O2(1-)\FLSCH\28-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\fbenzn_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-1.6118407506,0.1324552463,-0.9300029401\C,0,-1.5063826345,0.1536632423,0.554433405\C,0,-0.3265990618,0.0317228581,1.2217761611\C,0,0.9140000876,-0.053784471,0.5271458665\C,0,0.8933606775,0.0102549064,-0.8956625355\C,0,-0.2746369738,0.1319879177,-1.5834616505\H,0,-2.4408449068,0.2352003535,1.1089874227\H,0,-0.2980382623,0.0188736996,2.3065951272\H,0,1.8460028567,-0.0188552726,-1.4147371509\H,0,-0.2629271664,0.1968754837,-2.6711429795\N,0,2.1181520516,-0.1538867371,1.2219308916\O,0,2.107093213,-0.1890204707,2.4835190643\O,0,3.2036406091,-0.2083173537,0.5802819599\F,0,-2.3149567621,-1.123831561,-1.3223650625\C,0,-2.569233424

4,1.1904485853,-1.4923306357\H,0,-2.6756417118,1.0709371511,-2.5779636
729\H,0,-3.562789037,1.0865493581,-1.0381753176\H,0,-2.1960981028,2.20
03233199,-1.2875883269\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-576
.1282417\RMSD=3.113e-09\Dipole=-1.7722331,0.8741117,-1.0299323\PG=C01
[X(C7H7F1N1O2)]\\@

1-chloro-4-nitrobenzene (**3d**)



3d **3d_a2** **3d_a3**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
3d	-896.3448212	-896.242048	-896.4956875	-896.3929143			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
3d_a2	-936.2837216	-936.142337	-936.4663983	-936.3250137	-0.1113	-69.9	-292.3
3d_a3	-936.2512143	-936.110835	-936.4333917	-936.2930124	-0.0793	-49.8	-208.3

3d

1\1\GINC-CICUM83\SP\RB3LYP\6-311+G(d,p)\C6H4Cl1N1O2\FLSCH\27-Nov-2007\
0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=
READ\\clbenz_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\0,1\C,0,-1.424
2704906,0.0005343557,-0.8224868863\C,0,-1.4422231515,0.0063357543,0.57
46348576\C,0,-0.2372237066,0.0058839675,1.2706090421\C,0,0.9572853484,
-0.000359197,0.5528127637\C,0,0.9819272768,-0.0061634401,-0.8405577471
\C,0,-0.2231689338,-0.0057109642,-1.5363644013\H,0,-2.3869063184,0.011
1273343,1.1068467729\H,0,-0.2111273475,0.0102692618,2.3532461903\H,0,1
.9326647145,-0.0109152329,-1.359093465\H,0,-0.2343939121,-0.0101438811
,-2.620593681\N,0,2.2307350181,-0.0008369849,1.2882035697\O,0,2.179141
4636,0.0043651973,2.5176216597\O,0,3.2697697754,-0.0064093914,0.629012
0824\Cl,0,-2.9400370724,0.0011030652,-1.6978109715\\Version=x86-Linux-
G03RevB.03\State=1-A\HF=-896.4956875\RMSD=1.677e-09\Dipole=-1.1665239,
0.0004376,-0.6736434\PG=C01 [X(C6H4Cl1N1O2)]\\@

3d_a2

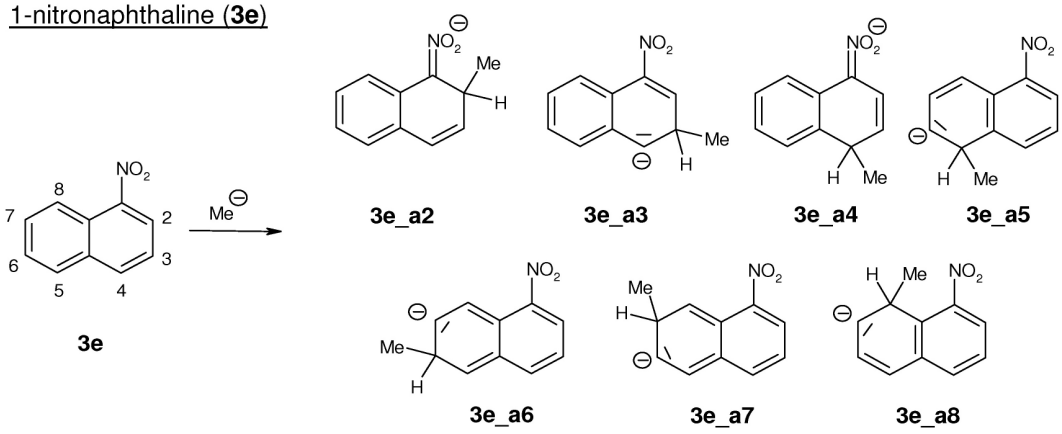
1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C7H7Cl1N1O2(1-)\FLSCH\27-Nov-2
007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GU
ESS=READ\\clbenz_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,
0,-1.3739800007,-0.0335964561,-1.0207533293\C,0,-1.4605100393,-0.14743
48459,0.3194202818\C,0,-0.2356066857,0.028094251,1.2044186441\C,0,1.02

8273677,-0.0975976681,0.3707154042\C,0,1.0201776446,0.0349299084,-1.02
97560438\C,0,-0.1481148462,0.1185818246,-1.7546680333\H,0,-2.420840915
7,-0.3097229051,0.8014540089\H,0,-0.2257773956,-0.7612732146,1.9721861
51\H,0,1.9853558851,0.0500763211,-1.5261991715\H,0,-0.159350138,0.2208
986409,-2.8329880317\N,0,2.2212297732,-0.3338484495,1.030438302\O,0,2.
2006251619,-0.4525209746,2.2954509509\O,0,3.308086292,-0.4379802595,0.
388212343\C,0,-0.3052378076,1.372243752,1.9787517375\H,0,0.5667411483,
1.4620838087,2.6329688166\H,0,-0.3187416917,2.2153759221,1.277925786\H
,0,-1.2170153146,1.425900031,2.5921415476\Cl,0,-2.8810990161,-0.146689
0694,-2.0005079729\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-936.466
3983\RMSD=5.673e-09\Dipole=-2.1714185,0.5041241,-0.716754\PG=C01 [X(C7
H7Cl1N1O2)]\\@

3d_a3

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C7H7Cl1N1O2(1-)\FLSCH\27-Nov-2
007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GU
ESS=READ\\clbenz_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,
0,1.4913972666,-0.292724231,-0.0399963093\C,0,0.9582934173,1.116155961
1,-0.1374721551\C,0,-0.5019774778,0.9546495288,-0.5075015453\C,0,-1.22
50453608,-0.0964787438,0.0244746694\C,0,-0.6363537266,-1.2312529218,0.
629017823\C,0,0.7593677705,-1.3428247352,0.4589634441\H,0,1.472948009,
1.6490560772,-0.9517807216\H,0,-0.9768513644,1.6577188594,-1.180686560
9\H,0,-1.2349464228,-2.0071505551,1.0830742027\H,0,1.2586146418,-2.283
5337612,0.6874229726\C,0,1.1872557702,1.9439750766,1.1583617757\H,0,2.
2579716569,2.0266123335,1.3952703996\H,0,0.7712801274,2.9568795376,1.0
506893136\H,0,0.6846010271,1.457787774,2.0019129724\N,0,-2.6731828221,
-0.0999426361,-0.1654292261\O,0,-3.2050619623,0.8285797824,-0.79588233
44\O,0,-3.3415005113,-1.0282378304,0.3187842328\Cl,0,3.2149138772,-0.5
570298256,-0.507423494\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-936
.4333917\RMSD=6.663e-09\Dipole=1.2125337,0.3013243,0.1906006\PG=C01 [X
(C7H7Cl1N1O2)]\\@

1-nitronaphthaline (**3e**)



	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
3e	-590.3881395	-590.227291	-590.5457952	-590.3849467			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
3e_a4	-630.3353855	-630.135917	-630.5246592	-630.3251907	-0.1195	-75.0	-313.7
3e_a2	-630.3329354	-630.133479	-630.5216696	-630.3222132	-0.1165	-73.1	-305.9
3e_a5	-630.3129034	-630.114089	-630.5027969	-630.3039825	-0.0983	-61.7	-258.0
3e_a7	-630.3116741	-630.112933	-630.5012907	-630.3025496	-0.0968	-60.8	-254.3
3e_a8	-630.2918261	-630.093796	-630.4825192	-630.2844891	-0.0788	-49.4	-206.8
3e_a3	-630.2888651	-630.091001	-630.4783248	-630.2804607	-0.0748	-46.9	-196.3
3e_a6	-630.2891149	-630.091322	-630.4776634	-630.2798705	-0.0742	-46.5	-194.7

3e

1\1\GINC-CICUM84\SP\RB3LYP\6-311+G(d,p)\C10H7N1O2\FLSCH\27-Nov-2007\0\
\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=RE
AD\\naph_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\0,1\C,0,-2.7552752
853,0.0234233942,-1.5971933487\C,0,-2.7059822612,-0.0009416421,-0.2240
870256\C,0,-1.4625291465,-0.010490375,0.463377117\C,0,-0.2362936968,-0
.0079233993,-0.2913689953\C,0,-0.3254285394,0.0233984499,-1.7109149722
\C,0,-1.5521111137,0.0420597944,-2.3384649771\H,0,-2.3721768668,-0.030
988223,2.4218021392\H,0,-3.7112890605,0.0331236069,-2.1128492328\H,0,-
3.6207104317,-0.0072169366,0.3632481623\C,0,-1.428585202,-0.0162894789
,1.8821163025\C,0,0.9748333446,0.0026739633,0.4742094338\H,0,0.5810169
459,0.0280132003,-2.2979376842\H,0,-1.5916078769,0.0692018616,-3.42387
93285\C,0,0.977222489,0.0217239577,1.8538631506\C,0,-0.2357787827,0.00
16032362,2.5674936078\H,0,1.92764279,0.0441863517,2.3722685042\H,0,-0.
218396218,-0.0009448918,3.6528219073\N,0,2.3063141864,-0.0151491123,-0
.1578661704\O,0,3.2496410753,0.4381734659,0.4917665715\O,0,2.420470246
9,-0.5012682892,-1.2848407004\\Version=x86-Linux-G03RevB.03\State=1-A\
HF=-590.5457952\RMSD=1.544e-09\Dipole=-1.9032961,0.0287662,0.6302397\P
G=C01 [X(C10H7N1O2)]\\@

3e_a2

1\1\GINC-CICUM95\SP\RB3LYP\6-311+G(d,p)\C11H10N1O2(1-)\FLSCH\28-Nov-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\naph_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-
0.7158133992,2.2515922273,-0.4825166118\C,0,0.6224268341,2.1669140548,
-0.4574127534\C,0,1.3221678635,0.925004386,-0.1613220888\C,0,0.5675548
455,-0.2936604141,-0.0208460058\C,0,-0.8672725397,-0.2252806416,-0.128
9194089\C,0,-1.6171302441,1.0981248064,-0.1313038152\H,0,3.2459263732,
1.8666397779,-0.1829618468\H,0,-1.1984095688,3.202508618,-0.7136556082
\H,0,1.2345631367,3.0432234869,-0.6771561643\C,0,2.7181053092,0.920177
2554,-0.0593195124\C,0,1.3281853447,-1.4739551876,0.2126334537\H,0,-2.
4189421953,1.0229574898,-0.8801828851\C,0,2.7146705939,-1.4434411281,0
.3179122075\C,0,3.4341974218,-0.2500052032,0.1857919237\H,0,0.78979895
72,-2.4052945842,0.3063467432\H,0,3.2450557195,-2.3766769763,0.5070188
055\H,0,4.5194582243,-0.2341476327,0.2637463792\N,0,-1.6772543111,-1.3
356504535,-0.2297397127\O,0,-2.9390615859,-1.1634302932,-0.3222421556\
O,0,-1.209135737,-2.5167528056,-0.2541390565\C,0,-2.3338369548,1.37959
27695,1.2181139372\H,0,-2.9080594578,2.3177343123,1.174814973\H,0,-3.0
202225478,0.5569325294,1.4338190601\H,0,-1.6023403293,1.4667633964,2.0
305702731\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-630.5216696\RMSD
=5.273e-09\Dipole=1.6969983,2.1048357,0.3095574\PG=C01 [X(C11H10N1O2)]
\\@

3e_a3

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C11H10N1O2(1-)\FLSCH\30-Nov-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\naph_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,0
.7830942564,2.2569012252,-0.1771549393\C,0,-0.5819909989,1.9281880021,
-0.7240489541\C,0,-1.1958578354,0.7240445941,-0.400842775\C,0,-0.41080
27159,-0.4042656497,0.1020755374\C,0,1.0182111625,-0.2329553442,-0.065
5924502\C,0,1.5675686156,0.9914474589,-0.3823140428\H,0,-3.2007362981,
1.3039898782,-1.0032837673\H,0,1.2453513627,3.0550864089,-0.7798931745
\H,0,-1.1368934311,2.6894059461,-1.2724524076\C,0,-2.6072629546,0.5039
417041,-0.560287979\C,0,-1.0835846026,-1.5437345826,0.5888837582\H,0,2
.5760431255,1.0228852933,-0.7780295006\C,0,-2.4638703131,-1.6679814952
,0.5079946703\C,0,-3.2196286113,-0.6424415559,-0.1098032367\H,0,-0.498
7799777,-2.3536599383,1.0056931422\H,0,-2.9544589748,-2.5622066784,0.8
869059432\H,0,-4.2992965478,-0.7544364992,-0.2158262955\N,0,1.92291828
55,-1.3685470961,-0.1250293334\O,0,3.1386307863,-1.1542076681,-0.30416
69883\O,0,1.4870125814,-2.5269311472,0.0054208111\C,0,0.7769044204,2.7

54021894,1.2936549052\H,0,1.796492677,2.9607822945,1.6548433074\H,0,0.1776112015,3.6717390683,1.3879175638\H,0,0.3324093831,1.9923569166,1.9439129777\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-630.4783248\RMSD=2.290e-09\Dipole=-0.7754534,1.035891,0.2102647\PG=C01 [X(C11H10N1O2)]\\@

3e_a4

1\1\GINC-CICUM91\SP\RB3LYP\6-311+G(d,p)\C11H10N1O2(1-)\FLSCH\27-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\naph_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-2.5572830712,-0.3762164423,-1.8753737247\C,0,-2.4885811619,-0.3525740073,-0.4821758041\C,0,-1.2813321831,-0.2012610021,0.204843946\C,0,-0.0518772185,-0.1022346618,-0.5227449236\C,0,-0.1469205594,-0.1112530453,-1.9396003986\C,0,-1.3671134128,-0.2416704771,-2.5938370309\H,0,-3.5134147501,-0.4902963933,-2.3829222004\H,0,-3.4051962575,-0.4447761957,0.1020204755\C,0,-1.3374155677,-0.0929848958,1.7269546315\C,0,1.1903573033,-0.0611155511,0.2341255673\H,0,0.7725747463,-0.0246875653,-2.499706722\H,0,-1.3832426864,-0.2488198754,-3.6834228282\C,0,1.1428614108,-0.3235415539,1.6499143243\C,0,-0.0053847373,-0.4136339687,2.3520979428\H,0,2.1023512771,-0.4726224263,2.1322554296\H,0,0.0152327871,-0.6371353122,3.4184005891\H,0,-2.1004449339,-0.8041770528,2.0896712205\N,0,2.4489959363,0.1083943298,-0.3277239239\O,0,3.4748705538,0.0764857717,0.4183842546\O,0,2.5898196736,0.3122346302,-1.5718220367\C,0,-1.8209035698,1.3167809593,2.1651116933\H,0,-2.8153498418,1.5456421316,1.7580970697\H,0,-1.8710831003,1.3858883369,3.260976458\H,0,-1.1203640071,2.0806887706,1.8103028916\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-630.5246592\RMSD=8.119e-09\Dipole=-3.0343194,-0.1331447,0.6577641\PG=C01 [X(C11H10N1O2)]\\@

3e_a5

1\1\GINC-CICUM85\SP\RB3LYP\6-311+G(d,p)\C11H10N1O2(1-)\FLSCH\03-Dec-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\naph_an_4sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-0.6415647682,2.4941087919,-0.3532040739\C,0,0.7023947908,2.0314965836,-0.3888774486\C,0,1.0227088258,0.7050886295,-0.243532634\C,0,-0.0176337807,-0.3214911516,-0.1306140989\C,0,-1.3765934563,0.198228777,-0.0203052935\C,0,-1.6468149493,1.5824536693,-0.1467297825\H,0,-0.8638291692,3.5534599186,-0.4588773758\H,0,1.5113648501,2.7547816369,-0.504662528\C,0,2.4932247595,0.3113524764,-0.1012531012\C,0,0.3727833909,-1.6583109555,-0.2001761866\H,0,-2.6842746762,1.8854402007,-0.0804904932\C,0,1.

7317955505,-2.0035142697,-0.5082293773\C,0,2.7452402736,-1.1055104878,
-0.5544907286\H,0,-0.3736023879,-2.4334877248,-0.1455891807\H,0,1.9362
141482,-3.0502407498,-0.7434782529\H,0,3.7634110446,-1.3996697041,-0.8
06261453\H,0,3.0915906741,1.0150293735,-0.7031059973\C,0,2.9571005685,
0.4907782541,1.3715017892\H,0,4.0175604101,0.2222909523,1.4810689863\H
,0,2.8201486783,1.5292369023,1.7037526091\H,0,2.371866183,-0.161087907
,2.0291244201\N,0,-2.5049775556,-0.6297853115,0.1892168101\O,0,-3.6552
676722,-0.111097391,0.2475241553\O,0,-2.35866409,-1.8708198116,0.32240
92458\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-630.5027969\RMSD=3.8
23e-09\Dipole=2.2583159,1.2545642,-0.1142077\PG=C01 [X(C11H10N1O2)]\\@

3e_a6

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C11H10N1O2(1-)\FLSCH\01-Dec-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\naph_an_5sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-
2.5272216091,-0.0585930444,-1.5011951501\C,0,-2.3661216523,-0.11027256
18,-0.0046153559\C,0,-1.1611347184,-0.1209235725,0.6586229057\C,0,0.12
05630161,-0.1296961054,-0.0651217915\C,0,0.0178291564,-0.09203159,-1.5
047011354\C,0,-1.1680834395,-0.0697620629,-2.1577873055\H,0,-2.0105742
097,-0.1498914865,2.6643747962\H,0,-3.112040787,-0.9331909298,-1.87794
62612\H,0,-3.2814062234,-0.112889228,0.5905939313\C,0,-1.0759907159,-0
.1327275331,2.1041105186\C,0,1.3117571029,-0.1191960814,0.6903618477\H
,0,0.9307320399,-0.0893655587,-2.0874238463\H,0,-1.154456196,-0.041923
8872,-3.2499993414\C,0,1.3540423479,-0.0876504944,2.0914058726\C,0,0.1
239915492,-0.1124434036,2.7758474661\H,0,2.3046513612,-0.0810283615,2.
6056151615\H,0,0.1275024167,-0.1199308608,3.8661297917\N,0,2.627626553
8,-0.1495304643,0.0445430005\O,0,3.5871520896,0.3613152505,0.643170333
3\O,0,2.7659760166,-0.7034420639,-1.0558346307\C,0,-3.3526089573,1.175
3444018,-1.9676020579\H,0,-3.4928894882,1.1833230757,-3.0606329141\H,0
,-4.3479908413,1.1740240739,-1.500365832\H,0,-2.8440712784,2.102313205
7,-1.676786996\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-630.4776634
\RMSD=5.168e-09\Dipole=-0.8240226,0.0630656,0.0613052\PG=C01 [X(C11H10
N1O2)]\\@

3e_a7

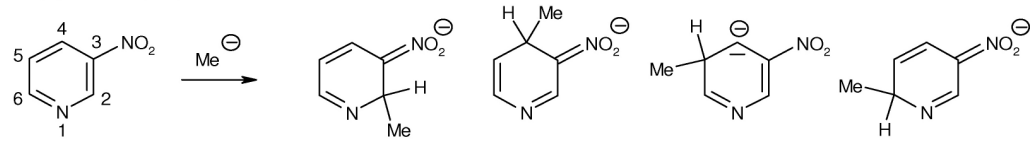
1\1\GINC-CICUM91\SP\RB3LYP\6-311+G(d,p)\C11H10N1O2(1-)\FLSCH\01-Dec-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\naph_an_6sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-
1.1013632925,-0.1139525096,-2.2003852019\C,0,-1.1626491846,-0.12467432
02,-0.7875922449\C,0,0.066711156,-0.1123212559,0.0275374345\C,0,1.3111

154548,-0.104757239,-0.7719930102\C,0,1.3009194752,-0.098772931,-2.146
8260426\C,0,0.0907684795,-0.0988065916,-2.8879608873\H,0,-0.7533408083
,-0.1317651056,1.9751977045\H,0,-2.051014298,-0.1189490158,-2.72133612
51\C,0,0.1567862235,-0.1151153866,1.3946474249\C,0,2.5720776781,-0.118
2743741,-0.0548175185\H,0,2.2564029947,-0.0949478661,-2.6737183065\H,0
,0.1061106888,-0.0913606025,-3.9750466554\C,0,2.6608078001,-0.12040802
8,1.2866207847\C,0,1.4482572191,-0.0678135908,2.1774596705\H,0,3.48087
16868,-0.13731039,-0.6593178579\H,0,3.6402746439,-0.1368138082,1.76858
76863\H,0,1.4887149022,-0.9353582575,2.8716978621\C,0,1.5017893237,1.1
796233805,3.1019887387\H,0,0.6330398061,1.1992122513,3.7724585321\H,0,
2.4122939051,1.1856077804,3.7209697032\H,0,1.4861856655,2.0964230156,2
.501548862\N,0,-2.4555233696,-0.1441996361,-0.2322748061\O,0,-3.467839
05,-0.1490403996,-0.9924975754\O,0,-2.6049356497,-0.1576725344,1.01909
84941\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-630.5012907\RMSD=7.5
09e-09\Dipole=2.7252623,0.1458161,0.0323001\PG=C01 [X(C11H10N1O2)]\\@

3e_a8

1\1\GINC-CICUM87\SP\RB3LYP\6-311+G(d,p)\C11H10N1O2(1-)\FLSCH\03-Dec-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\naph_an_7sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,2
.9932011213,-0.3439867055,-0.5381290689\C,0,2.5217860516,0.9335742921,
-0.1183260344\C,0,1.1364348269,1.1401738179,-0.0012518162\C,0,0.224542
1722,0.0075161785,-0.0747243338\C,0,0.8231359122,-1.3915854399,0.07959
58816\C,0,2.1921431267,-1.4459954091,-0.5684691956\H,0,1.2315158275,3.
292793794,0.2079733849\H,0,4.0231636039,-0.4217345879,-0.8974113555\H,
0,3.1875133204,1.7945923226,-0.1127990215\C,0,0.5559998101,2.440769357
1,0.1324408073\C,0,-1.146109777,0.2883272171,-0.1054751706\H,0,0.16133
83386,-2.1217934255,-0.3915055418\H,0,2.5425113139,-2.3989358088,-0.96
1562587\C,0,-1.6998952153,1.5761986197,0.0117859718\C,0,-0.8116145525,
2.6493212997,0.1390614917\H,0,-2.7742299439,1.7050598268,0.0063875979\
H,0,-1.2044788516,3.6617127618,0.2295009862\N,0,-2.1513556129,-0.77606
43323,-0.2636582429\O,0,-3.2182959695,-0.668469623,0.3588040821\O,0,-1
.9256166695,-1.7166793638,-1.0337493318\C,0,0.9124923429,-1.7607410906
,1.5891647918\H,0,1.3580877287,-2.758678961,1.7085225211\H,0,1.5501835
017,-1.0400308622,2.1132722258\H,0,-0.0775093517,-1.7607756615,2.06875
15397\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-630.4825192\RMSD=1.6
93e-09\Dipole=-0.0941962,0.6276168,0.2803741\PG=C01 [X(C11H10N1O2)]\\@

3-nitropyridine (**4a**)



4a **4a_a2** **4a_a4** **4a_a5** **4a_a6**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
4a	-452.7826697	-452.683381	-452.9102153	-452.8109266			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
4a_a6	-492.7283198	-492.590062	-492.8888725	-492.7506147	-0.1189	-74.6	-312.2
4a_a4	-492.7285464	-492.590152	-492.8882535	-492.7498591	-0.1182	-74.2	-310.3
4a_a2	-492.7261678	-492.587916	-492.8866351	-492.7483833	-0.1167	-73.2	-306.4
4a_a5	-492.6879627	-492.551463	-492.8495676	-492.7130679	-0.0814	-51.1	-213.7

4a

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C5H4N2O2\FLSCH\20-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\3no2pyridin_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C,
0,-2.4602105888,-0.0859852393,0.0003200806\C,0,-1.840698517,1.16719513
34,-0.0005094237\C,0,-0.4509259502,1.2224425269,-0.0007055348\C,0,0.23
38398245,0.0106012711,-0.0002461219\C,0,-0.4616837934,-1.1994321227,0.
0000707029\N,0,-1.7964573066,-1.2499658581,0.0006870402\H,0,0.09895102
19,2.1561223456,-0.0011314174\H,0,-3.5459863942,-0.1599865928,0.000183
6569\H,0,-2.4352285611,2.0751434457,-0.0008145322\H,0,0.0798290297,-2.
1399978785,0.0007761985\N,0,1.7032665099,0.0062934817,0.0002178329\O,0
,2.2735124508,1.0964956447,0.0012841918\O,0,2.268093128,-1.0858086574,
-0.0011499713\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-452.9102153\
RMSD=2.651e-09\Dipole=-1.4315285,0.8097399,-0.000528\PG=C01 [X(C5H4N2O
2)]\\@

4a_a2

1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C6H7N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\3no2pyd_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,
1\C,0,2.3775280592,-0.4312687165,-0.3089914693\C,0,1.6689702321,-1.539
0565531,0.2740887534\C,0,0.2918202801,-1.4468138241,0.3266604395\C,0,-
0.3428785722,-0.252750981,-0.0297962826\C,0,0.4779592007,0.9960424592,
-0.3030160054\N,0,1.8882767863,0.7158695482,-0.6584245845\H,0,-0.33541
32086,-2.2864866698,0.6122186724\H,0,3.4436877939,-0.5783182962,-0.533
9641451\H,0,2.1964495794,-2.4554967503,0.5250728585\N,0,-1.7212892223,
-0.1885003488,-0.1220783615\O,0,-2.2540837495,0.9225009705,-0.42826442

11\O,0,-2.4342178312,-1.2135274411,0.093730859\H,0,0.0250605018,1.5360001124,-1.146139138\C,0,0.4633487365,1.9728524286,0.894671217\H,0,-0.5659044943,2.2794072169,1.1061227534\H,0,0.8820357619,1.4881679068,1.7853802219\H,0,1.071096145,2.85932497,0.6693979796\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-492.8866351\RMSD=3.845e-09\Dipole=1.497528,-0.207676,0.5224453\PG=C01 [X(C6H7N2O2)]\\@

4a_a4

1\1\GINC-CICUM87\SP\RB3LYP\6-311+G(d,p)\C6H7N2O2(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\3no2pyd_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,-2.0259544179,0.0680050363,-1.4115864906\C,0,-2.0716192794,0.2441537818,-0.0733475847\C,0,-0.843604486,0.1300869325,0.8060857511\C,0,0.3659017111,0.0956344749,-0.1053258275\C,0,0.2443139421,-0.0993190017,-1.4929037182\N,0,-0.8857810465,-0.1533164637,-2.1797604991\H,0,-2.9521498128,0.1170437051,-1.99057074\H,0,-3.0295107587,0.4273976932,0.4155440555\H,0,1.1715796736,-0.2003885113,-2.0556409861\N,0,1.6238418079,0.280754225,0.4542785542\O,0,1.7023731891,0.4893066941,1.7019308913\O,0,2.6642924537,0.2564843111,-0.2618264683\H,0,-0.7664575892,1.00563743,1.4738835739\C,0,-0.9394938897,-1.1033708634,1.7433061991\H,0,-1.0206267592,-2.0243752452,1.1533437129\H,0,-0.0500697586,-1.1604812694,2.3770054113\H,0,-1.8297769486,-1.0343683345,2.386603228\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-492.8882535\RMSD=4.089e-09\Dipole=-1.6645127,-0.2662447,0.5139361\PG=C01 [X(C6H7N2O2)]\\@

4a_a5

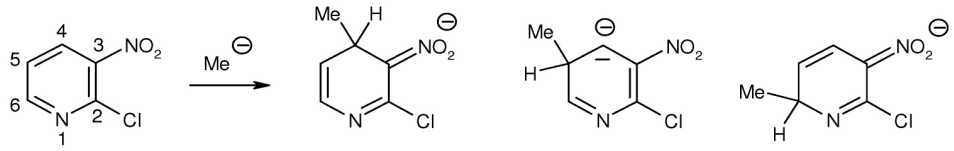
1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C6H7N2O2(1-)\FLSCH\22-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\pyd_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,1.9646532137,0.7495796105,-0.6850308113\C,0,1.7747204349,-0.720313612,-0.340948172\C,0,0.3044228451,-0.9193313235,-0.5681027208\C,0,-0.5217386945,0.0569248251,-0.0221043917\C,0,-0.0126998985,1.3384777486,0.3128517639\H,0,2.7810665874,1.052326349,-1.3464314195\H,0,2.3548255636,-1.3398597425,-1.0424074733\H,0,-0.093356272,-1.7189067856,-1.182206769\H,0,-0.62587395,2.0911178042,0.7930020443\C,0,2.2538245444,-1.0587497562,1.0932652436\H,0,2.070787957,-2.1170394178,1.3309350851\H,0,3.3279579722,-0.847716948,1.2119037449\H,0,1.7066327632,-0.4488794487,1.8206520897\N,0,-1.947682361,-0.1594441675,0.0280808879\O,0,-2.6883450189,0.7371415667,0.4747340026\O,0,-2.4052568067,-1.2515679082,-0.3589953185\N,0,1.18306512,1.6972790198,-0.2067869229\\Version=x86-Linux-G03RevB.

03\State=1-A\HF=-492.8495676\RMSD=8.307e-09\Dipole=1.0390885,-0.736453
7,0.0377307\PG=C01 [X(C6H7N2O2)]\\@

4a_a6

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C6H7N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\3no2pyd_an_4sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,
1\C,0,-1.897113773,0.1815221435,-1.0156639721\C,0,-1.7858215028,0.2825
590247,0.4934862235\C,0,-0.5912953186,0.2208194131,1.1178310969\C,0,0.
6156203972,0.1331464842,0.3425817599\C,0,0.4848409146,0.2183751546,-1.
0792346631\N,0,-0.6247629433,0.2846422655,-1.7517193111\H,0,-0.4993864
997,0.2664557118,2.1985110151\H,0,-2.7095318651,0.3850633678,1.0647698
673\H,0,1.4122890142,0.2566393389,-1.6531376654\N,0,1.8576116537,0.067
7424444,0.9465438976\O,0,1.9310175107,0.0368982013,2.2110080579\O,0,2.
9044510308,0.031129757,0.2349445243\H,0,-2.5465274814,0.9996863533,-1.
3870074811\C,0,-2.6021263887,-1.1283336383,-1.4434913744\H,0,-3.611769
6049,-1.1946736408,-1.0129666471\H,0,-2.678486298,-1.1789627657,-2.537
1383505\H,0,-2.0249025416,-1.993656492,-1.0974779253\\Version=x86-Linu
x-G03RevB.03\State=1-A\HF=-492.8888725\RMSD=3.592e-09\Dipole=-2.277226
9,-0.1298558,-0.4315175\PG=C01 [X(C6H7N2O2)]\\@

2-chloro-3-nitropyridine (**4b**)



4b **4b_a4** **4b_a5** **4b_a6**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
4b	-912.3674805	-912.276998	-912.5229645	-912.4324820			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
4b_a6	-952.3250659	-952.195437	-952.5113186	-952.3816897	-0.1284	-80.6	-337.2
4b_a4	-952.3242535	-952.194509	-952.5098222	-952.3800777	-0.1268	-79.6	-333.0
4b_a5	-952.2856604	-952.157463	-952.4720496	-952.3438522	-0.0906	-56.9	-237.9

4b

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C5H3Cl1N2O2\FLSCH\21-Nov-2007\
0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=
READ\\3no2clpyd_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C
,0,-2.5715389766,-0.0316668117,0.0619303882\C,0,-2.1601382668,-1.36368
36425,0.0723563957\C,0,-0.7948009632,-1.6208458798,0.0424977764\C,0,0.
0946229256,-0.5482083614,0.0228219949\C,0,-0.4203824962,0.7604229548,-

0.0105103486\N,0,-1.7220549669,0.9993932048,0.0057304319\H,0,-0.396385
5808,-2.6288097552,0.0377738415\H,0,-3.6269828732,0.2287279881,0.09253
71156\H,0,-2.8834905315,-2.1713468903,0.1018883637\N,0,1.5307094356,-0
.8763399467,0.0420013416\O,0,1.8585477719,-1.9244920722,-0.5150057725\
O,0,2.2903627663,-0.1164802359,0.6301095322\Cl,0,0.5981423566,2.168336
7505,-0.154219356\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-912.5229
645\RMSD=9.629e-09\Dipole=-1.7119436,-0.7911473,0.0629921\PG=C01 [X(C5
H3Cl1N2O2)]\\@

4b_a4

1\1\GINC-CICUM89\SP\RB3LYP\6-311+G(d,p)\C6H6Cl1N2O2(1-)\FLSCH\21-Nov-2
007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GU
ESS=READ\\clpyd_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-2.3182364134,0.1607920739,-0.943737087\C,0,-2.3578179612,0.274
5844076,0.3976169261\C,0,-1.1242018915,0.0346036412,1.2352269972\C,0,0
.1054472712,0.1785498087,0.3454763827\C,0,-0.0507919567,-0.0546455838,
-1.0397427563\N,0,-1.1805187885,-0.1302996038,-1.6871070491\H,0,-3.220
7555297,0.2919666913,-1.5430671197\H,0,-3.2981045732,0.4929533379,0.90
35115847\N,0,1.2869377133,0.545029165,0.9893037934\O,0,1.2635865683,0.
6050717037,2.2554583493\O,0,2.3281914109,0.8318619743,0.3545517255\Cl,
0,1.3706386035,-0.3879491808,-2.0963989539\H,0,-1.0467669745,0.8025059
883,2.0170051141\C,0,-1.1875240048,-1.3276177297,1.9723124761\H,0,-0.2
940741212,-1.4557025107,2.5911251113\H,0,-2.0753952555,-1.380754456,2.
6200999447\H,0,-1.2461663735,-2.1520090367,1.2517321406\\Version=x86-L
inux-G03RevB.03\State=1-A\HF=-952.5098222\RMSD=9.841e-09\Dipole=-1.612
5417,-0.4728153,0.118197\PG=C01 [X(C6H6Cl1N2O2)]\\@

4b_a5

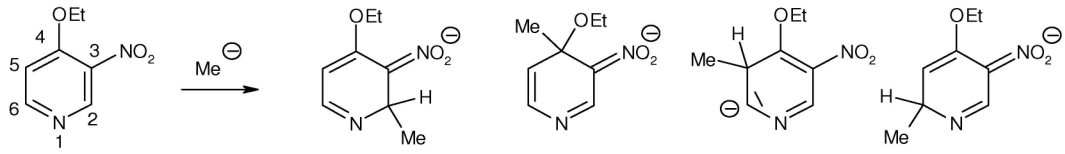
1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C6H6Cl1N2O2(1-)\FLSCH\21-Nov-2
007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GU
ESS=READ\\clpyd_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-0.1206910992,0.8664718703,-0.1963958543\C,0,-0.2456495134,-0.5
461164682,-0.0637356545\C,0,0.8898588864,-1.3277828029,-0.2686127227\C
,0,2.2160871982,-0.6448505323,-0.1534943578\C,0,1.9951568958,0.5989355
536,-0.997498592\N,0,0.9432714917,1.3751334534,-0.8200705893\H,0,0.787
850347,-2.3395839963,-0.645018907\H,0,3.000021745,-1.2666017812,-0.609
8504693\H,0,2.719968242,0.8943408305,-1.7584166987\C,0,2.6523069514,-0
.3111685148,1.2933559625\H,0,2.7639118813,-1.22857897,1.888719601\H,0,
3.6065583934,0.2363246844,1.2999923705\H,0,1.8984472657,0.3171543882,1
.779647404\Cl,0,-1.310505811,2.0512728514,0.40503989\N,0,-1.5236811887

,-1.2245396281,-0.0399896672\O,0,-1.5215020894,-2.4583155564,0.1368161926\O,0,-2.573211301,-0.5856575736,-0.1995714829\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-952.4720496\RMSD=2.227e-09\Dipole=1.2861952,-0.098643,0.2240011\PG=C01 [X(C6H6Cl1N2O2)]\\@

4b_a6

1\1\GINC-CICUM84\SP\RB3LYP\6-311+G(d,p)\C6H6Cl1N2O2(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\clpyd_an_4sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,2.3283170066,-0.0018773968,-0.2754078857\C,0,1.7689622322,-1.3631170264,-0.6203295652\C,0,0.453261535,-1.6073164174,-0.4737418053\C,0,-0.4734728329,-0.5603809421,-0.101074865\C,0,0.0860936348,0.7614452523,-0.163055052\N,0,1.3191707435,1.0638980806,-0.325577137\H,0,0.0249209477,-2.5877284766,-0.64869748\H,0,2.4562054739,-2.1446171367,-0.9427128493\N,0,-1.7869661269,-0.9160918021,0.2037983986\O,0,-2.1208021121,-2.1298179305,0.0719187971\O,0,-2.6084312651,-0.0677479502,0.6235042043\Cl,0,-1.0029388503,2.209640106,-0.1981001875\H,0,3.1105598014,0.2765594231,-1.0034633702\C,0,3.0102521142,0.007130025,1.1132761617\H,0,3.8403288834,-0.7124597619,1.1428851954\H,0,3.3992363661,1.0069440999,1.3437476793\H,0,2.2866615442,-0.2719978209,1.8870092377\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-952.5113186\RMSD=3.043e-09\Dipole=2.1748636,0.0037734,-0.1448257\PG=C01 [X(C6H6Cl1N2O2)]\\@

4-ethoxy-3-nitropyridine (**4c**)



4c **4c_a2** **4c_a4** **4c_a5** **4c_a6**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
4c	-606.6198547	-606.455337	-606.7920359	-606.6275182			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
4c_a4	-646.5625743	-646.359844	-646.7662182	-646.5634879	-0.1152	-72.3	-302.5
4c_a6	-646.5591281	-646.355790	-646.7625061	-646.5591680	-0.1109	-69.6	-291.1
4c_a2	-646.5583348	-646.355008	-646.7619948	-646.5586680	-0.1104	-69.3	-289.8
4c_a5	-646.5236215	-646.321842	-646.7266179	-646.5248384	-0.0766	-48.0	-201.0

4c

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C7H8N2O3\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA

D\\oetpyd_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C,0,-1.5619219681,0.0115677737,-2.2227235304\C,0,-1.6954607769,0.0219109692,-0.8374305995\C,0,-0.5432269922,0.0179007579,-0.0344061023\C,0,0.6904895677,-0.0016478756,-0.7250799671\C,0,0.7049060427,-0.0263537924,-2.1201592495\N,0,-0.393092882,-0.0114890213,-2.8770238218\H,0,-2.6836246826,0.0286095826,-0.3951762496\N,0,1.9821579463,0.0224983202,-0.0363289018\O,0,2.0475487817,0.5728914556,1.0597981568\O,0,2.9358317582,-0.4922564178,-0.6247661799\H,0,1.6645774419,-0.0507845178,-2.6275651538\H,0,-2.4558608315,0.0165666534,-2.8438301396\O,0,-0.5483681416,-0.0056888674,1.3030321611\C,0,-1.8036718612,-0.0316034736,2.0061657785\C,0,-1.4833007827,-0.0601260262,3.4886110179\H,0,-2.372359691,-0.919808103,1.7015870794\H,0,-2.3846642481,0.8608947671,1.7407634251\H,0,-2.4125137145,-0.0744834231,4.0679698716\H,0,-0.9006591226,-0.9509236681,3.7410238898\H,0,-0.905329164,0.8234042559,3.7743191527\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-606.7920359\RMSD=4.122e-09\Dipole=-2.3323591,-0.0149961,0.6771551\PG=C01 [X(C7H8N2O3)]\\@

4c_a2

1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C8H11N2O3(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\oetpyd_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,0.9938988777,-2.324987109,-0.5340764146\C,0,-0.3027162625,-1.8371532651,-0.1621569284\C,0,-0.4714426387,-0.4609780129,-0.0471428727\C,0,0.668133604,0.3769445588,-0.1303126039\C,0,2.0464756931,-0.2737964256,-0.0753028811\N,0,2.1008823056,-1.6593705539,-0.5822207156\H,0,-1.1306343288,-2.5313714634,-0.0959330476\N,0,0.6263421861,1.7549479936,-0.257078606\O,0,-0.4591861661,2.381186171,-0.3926210242\O,0,1.7328637033,2.3824643068,-0.2395639118\H,0,1.0520552139,-3.3780617838,-0.8443820484\O,0,-1.6998240547,0.1118236726,0.1449530315\C,0,-2.8418327547,-0.7215388704,0.1523011704\C,0,-4.0552292561,0.1852352398,0.2985780222\H,0,-2.7939606512,-1.4422533665,0.984488332\H,0,-2.8990424021,-1.3038100998,-0.7799996666\H,0,-4.9797390235,-0.4057737482,0.3069224336\H,0,-3.9947937077,0.756989292,1.2304126165\H,0,-4.0965332119,0.8984667955,-0.5305047207\H,0,2.7118798544,0.3340477436,-0.6989418866\C,0,2.6434429703,-0.2526195585,1.3497395338\H,0,3.6403624576,-0.713422375,1.3521049224\H,0,2.7206280044,0.7822958941,1.6985823566\H,0,2.0039970948,-0.8165815123,2.0404390421\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-646.7619948\RMSD=5.299e-09\Dipole=-2.2527561,-1.9169212,0.642483\PG=C01 [X(C8H11N2O3)]\\@

4c_a4

1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C8H11N2O3(1-)\FLSCH\22-Nov-200
7\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUES
S=READ\\oetpyd_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,
1\C,0,0.2257960799,2.5813417319,0.1210183734\C,0,-0.505354144,1.644884
8031,0.7729388371\C,0,-0.2739117837,0.1635464914,0.6160515962\C,0,1.07
35858583,0.0006431635,-0.0396518468\C,0,1.6956757148,1.0724622304,-0.7
039248797\N,0,1.3198961587,2.3433434515,-0.6822080175\H,0,-1.315713698
5,1.9594667566,1.4292630625\N,0,1.6869410488,-1.2639939794,-0.13747753
93\O,0,1.1467460447,-2.2632819084,0.3961717662\O,0,2.778883409,-1.3830
55312,-0.7498358483\H,0,2.5897634354,0.834425546,-1.2757049545\H,0,-0.
0274808889,3.6378621605,0.2462851954\O,0,-1.2555057648,-0.4421620447,-
0.3427126997\C,0,-2.6174794239,-0.1623663692,-0.1445723976\C,0,-3.3940
057184,-0.8402625982,-1.2691781442\H,0,-2.8145414574,0.9233617578,-0.1
616191589\H,0,-2.9839663386,-0.5377971044,0.8294262141\H,0,-4.47257712
78,-0.6560887195,-1.172383246\H,0,-3.0586618323,-0.4598825174,-2.24021
00897\H,0,-3.2197073648,-1.9218307516,-1.2537501152\C,0,-0.466511476,-
0.5449511294,1.9743916709\H,0,-1.3744419313,-0.1707920719,2.4669245183
\H,0,-0.5373168509,-1.6232316646,1.8428280815\H,0,0.3790234498,-0.3247
355144,2.635314389\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-646.766
2182\RMSD=3.624e-09\Dipole=-2.4437628,0.5474825,0.8215544\PG=C01 [X(C8
H11N2O3)]\\@

4c_a5

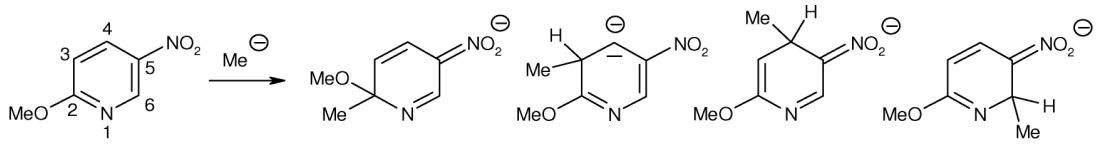
1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C8H11N2O3(1-)\FLSCH\06-Dec-200
7\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUES
S=READ\\oetpy_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1
\C,0,1.7725475764,-1.369828965,-0.9634848596\C,0,1.1169381148,-1.57354
47809,0.3873219418\C,0,0.0402711508,-0.5357601223,0.3023022361\C,0,0.4
794052612,0.7649287502,-0.0323728033\C,0,1.7101747232,0.894573748,-0.7
495695955\H,0,1.8779346092,-2.2126758968,-1.6496967584\H,0,0.639815909
5,-2.5612458855,0.4228168228\H,0,2.148072235,1.8703625912,-0.921419093
2\C,0,2.083305412,-1.4318217134,1.5817994519\H,0,1.5451152671,-1.50736
30841,2.5371971281\H,0,2.8586392395,-2.2106066373,1.5464048004\H,0,2.5
819686359,-0.457380155,1.5468985129\N,0,-0.2607255365,1.9434612621,0.2
632048444\O,0,0.2087767559,3.0563325377,-0.0554405151\O,0,-1.350471132
,1.8540449802,0.8745601042\N,0,2.2231239571,-0.1812846523,-1.358006491
6\C,0,-2.1886285273,-0.5956514372,-0.590282253\H,0,-2.3941966199,0.477
0077129,-0.5088009377\H,0,-1.7544786508,-0.7970310509,-1.5819689107\C,
0,-3.4625167298,-1.4012911441,-0.3766283003\H,0,-3.8756274643,-1.20053

15788,0.6181459554\H,0,-4.2188347677,-1.1334027229,-1.1252222718\H,0,-3.2629187063,-2.4766916068,-0.4518745965\O,0,-1.2572131887,-0.9897905137,0.4154574072\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-646.7266179\RMSD=4.508e-09\Dipole=-1.24909,-1.6363691,0.1250628\PG=C01 [X(C8H11N2O3)]\\@

4c_a6

1\1\GINC-CICUM87\SP\RB3LYP\6-311+G(d,p)\C8H11N2O3(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\oetpyd_an_4sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,1.8915374121,-1.5898700408,-0.3014600896\C,0,0.3800507921,-1.5205047919,-0.2801940262\C,0,-0.2730749848,-0.3395383711,-0.1280313644\C,0,0.4998376298,0.8915294091,-0.1033137468\C,0,1.885972083,0.7640672929,-0.4602399331\N,0,2.5679139963,-0.3259770845,-0.6238242242\H,0,-0.1613140766,-2.4536526694,-0.3998841911\N,0,-0.0070760712,2.15916715,0.1591084433\O,0,-1.1977029161,2.3080030614,0.5373715817\O,0,0.7558106342,3.1634890914,0.0316220622\H,0,2.4099509356,1.7054105058,-0.6253116242\O,0,-1.6429322648,-0.2292273649,-0.0888597695\C,0,-2.4022653302,-1.4162460884,-0.1420787149\C,0,-3.865722756,-1.0238703851,0.0026235113\H,0,-2.0989412021,-2.1033756626,0.6644544368\H,0,-2.2338314329,-1.9444897978,-1.0953165267\H,0,-4.5094588843,-1.911867314,-0.0334002037\H,0,-4.0281326193,-0.5069848742,0.9537844251\H,0,-4.1596514993,-0.3433856381,-0.8032534354\H,0,2.1963843884,-2.322656829,-1.0722382611\C,0,2.4683704463,-2.122539589,1.033473106\H,0,2.0771878449,-3.1245171795,1.2607885467\H,0,3.564108843,-2.1713102217,0.9839114965\H,0,2.188196847,-1.4517836961,1.8537323545\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-646.7625061\RMSD=5.190e-09\Dipole=-1.3455811,-2.9852914,-0.0413707\PG=C01 [X(C8H11N2O3)]\\@

2-methoxy-5-nitropyridine (**4d**)



4d **4d_a2** **4d_a3** **4d_a4** **4d_a6**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
4d	-567.3213298	-567.186503	-567.4830699	-567.3482431			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
4d_a6	-607.2663195	-607.092510	-607.4607799	-607.2869704	-0.1180	-74.0	-309.7
4d_a2	-607.2607941	-607.087778	-607.4555084	-607.2824923	-0.1135	-71.2	-298.0
4d_a4	-607.2595314	-607.085905	-607.4521583	-607.2785319	-0.1095	-68.7	-287.6
4d_a3	-607.2213838	-607.049318	-607.4163813	-607.2443155	-0.0753	-47.3	-197.7

4d

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C6H6N2O3\FLSCH\22-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\omepyd_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C,0,-1.
5549075319,-0.1798529091,-0.4101892153\C,0,-1.3804876841,0.4085259538,
0.8622887382\C,0,-0.0923270587,0.608220241,1.3115322033\C,0,0.96554159
81,0.2157310985,0.4793028644\C,0,0.6979429664,-0.3565308648,-0.7597071
646\N,0,-0.5483167493,-0.5531807275,-1.2017944009\H,0,0.1199750055,1.0
536749368,2.2760405759\H,0,-2.2483295918,0.6861598321,1.449296345\N,0,
2.3447145245,0.4067812901,0.9111768962\O,0,2.5296669136,0.9180466882,2
.0172735264\O,0,3.2407936229,0.0464377683,0.1461245323\H,0,1.512805961
2,-0.6621853552,-1.4079428119\O,0,-2.8181140912,-0.361261473,-0.819605
4608\C,0,-3.0216466815,-0.9576311312,-2.1097504557\H,0,-2.5844703043,-
1.9588708634,-2.1479286759\H,0,-4.1043324678,-1.0064073714,-2.23033561
43\H,0,-2.5738982414,-0.3441333154,-2.8960098911\\Version=x86-Linux-G0
3RevB.03\State=1-A\HF=-567.4830699\RMSD=4.478e-09\Dipole=-1.8630411,-0
.2291224,-0.5208942\PG=C01 [X(C6H6N2O3)]\\@

4c_a2

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C7H9N2O3(1-)\FLSCH\22-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\omepyd_an_4sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1
\C,0,-1.6309642729,-0.307341309,0.2661386051\C,0,-0.8222995377,-1.1181
083898,-0.7182358015\C,0,0.5208716981,-0.99784026,-0.8162871932\C,0,1.
2151866967,-0.0974068924,0.0533415938\C,0,0.4353800573,0.6358167227,0.
9911736015\N,0,-0.8582837642,0.5645936425,1.1406977237\H,0,1.101867783
5,-1.5737222138,-1.5298461682\H,0,-1.3742431709,-1.8015778849,-1.36239

98639\N,0,2.5971805851,0.0485329423,-0.0067155165\O,0,3.2495218524,-0.6203280949,-0.8549438089\O,0,3.1775314355,0.8438841874,0.7817432309\H,0,0.970134468,1.3179235757,1.6536319729\O,0,-2.6199347771,0.5052438469,-0.4636585539\C,0,-2.062976561,1.5334698225,-1.2508845069\H,0,-1.3683326371,1.1458566365,-2.0128056019\H,0,-2.9001625945,2.0309303754,-1.7565683766\H,0,-1.5244093722,2.2715374497,-0.6402974801\C,0,-2.5343674434,-1.1961731687,1.1345355543\H,0,-3.1264852818,-0.564038114,1.8044133102\H,0,-3.2116447528,-1.788510864,0.5066779998\H,0,-1.9209340978,-1.8751837219,1.7355006944\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-607.4555084\RMSD=4.515e-09\Dipole=-2.0364051,-0.3481429,-0.5054478\PG=C01 [X(C7H9N2O3)]\\@

4c_a3

1\1\GINC-CICUM94\SP\RB3LYP\6-311+G(d,p)\C7H9N2O3(1-)\FLSCH\22-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\omepyd_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,-0.9192364661,0.4025158992,-0.854877634\C,0,-1.027057342,0.1081726278,0.5188578192\C,0,0.0937005726,-0.2188819681,1.2827298439\C,0,1.4186944026,0.2164623464,0.7198702144\C,0,1.2922115652,-0.15638271,-0.740167594\H,0,-1.7594766812,0.7298248959,-1.4519581489\H,0,0.014039356,-0.7992072421,2.1931230977\H,0,2.2373150827,-0.3674140694,1.1634704733\C,0,1.7463464606,1.7220708062,0.9143276416\H,0,1.7976632318,1.9634510896,1.9851977647\H,0,2.7016581084,1.9963203785,0.4414537451\H,0,0.954170485,2.3343533758,0.4689310199\N,0,0.2520942005,0.0896216647,-1.484722028\C,0,2.2557826826,-1.2885467102,-2.5833259237\H,0,3.1891758812,-1.8129243856,-2.8200803707\H,0,1.4072569405,-1.9834507148,-2.6348378439\H,0,2.0774147314,-0.4962823845,-3.3220306781\O,0,2.4164972245,-0.7634564637,-1.279863442\N,0,-2.3485255186,-0.0032338049,1.0925363284\O,0,-3.3472711674,0.2738543228,0.3999760132\O,0,-2.4575822024,-0.3706288227,2.277080508\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-607.4163813\RMSD=7.295e-09\Dipole=1.9046221,-0.1949204,-0.8653169\PG=C01 [X(C7H9N2O3)]\\@

4c_a4

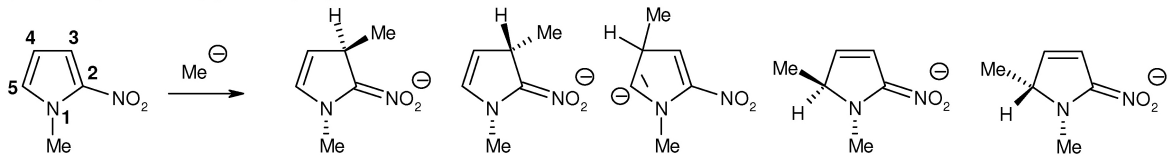
1\1\GINC-CICUM99\SP\RB3LYP\6-311+G(d,p)\C7H9N2O3(1-)\FLSCH\22-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\omepyd_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,-1.5570222604,-0.1966866119,-0.6345351097\C,0,-1.4396896093,0.2671860484,0.6307811874\C,0,-0.093986703,0.3781626444,1.3173488365\C,0,0.9798472916,0.2089836641,0.2620120731\C,0,0.6834422853,-0.2671641139,-1

.0209578151\N,0,-0.5287404299,-0.5140750433,-1.4962404546\H,0,-2.33784
00289,0.5047770209,1.1965621206\N,0,2.2930330655,0.5531655702,0.573806
453\O,0,2.5339283192,1.0198852899,1.7238316226\O,0,3.2169996058,0.4159
319557,-0.2749575543\H,0,1.521919363,-0.4371741959,-1.6940033474\O,0,-
2.8393234242,-0.3621400225,-1.1415404402\C,0,-2.9490383363,-0.65361357
12,-2.5215891054\H,0,-2.4591704691,-1.5971377936,-2.7884539622\H,0,-4.
0250428084,-0.7257258536,-2.7207424616\H,0,-2.5132670037,0.1343988706,
-3.1498510701\H,0,0.0188869597,1.3733653436,1.7804419292\C,0,0.0369561
406,-0.6423812844,2.480030515\H,0,-0.0599734209,-1.6663589787,2.099177
937\H,0,1.0071466027,-0.5329601495,2.9738772875\H,0,-0.7585964997,-0.4
831563897,3.2228170627\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-607
.4521583\RMSD=7.727e-09\Dipole=-2.1131482,-0.5200159,-0.4364348\PG=C01
[X(C7H9N2O3)]\\@

4c_a6

1\1\GINC-CICUM94\SP\RB3LYP\6-311+G(d,p)\C7H9N2O3(1-)\FLSCH\22-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\omepyd_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1
\C,0,-1.6353976199,-0.2986511132,-0.2629259677\C,0,-1.4431079653,-0.10
37555277,1.1518382696\C,0,-0.1870758702,0.3029033871,1.5440680365\C,0,
0.8607995151,0.3813150883,0.6181949249\C,0,0.6696600376,-0.1384326244,
-0.7969254589\N,0,-0.747081689,-0.2565225346,-1.1914320198\H,0,0.02622
49406,0.590727153,2.5691624687\H,0,-2.2889284011,-0.1616882326,1.82737
57259\N,0,2.0829501712,0.9102085395,0.9817353068\O,0,2.2762666074,1.35
34001936,2.1531890834\O,0,3.0079863059,0.9453553925,0.1116184578\O,0,-
2.9600054659,-0.5016711322,-0.6077437442\C,0,-3.2115955894,-0.67864789
47,-1.9907256376\H,0,-2.6447991428,-1.5238376929,-2.3988410885\H,0,-4.
2877850343,-0.8648865048,-2.0773738735\H,0,-2.9357083163,0.2113281255,
-2.5692371946\H,0,1.1525011666,0.5602593643,-1.4943254604\C,0,1.357885
1476,-1.5058720736,-1.0082983177\H,0,2.4287994231,-1.4116457816,-0.804
8831103\H,0,0.9279301005,-2.2548237727,-0.3316802549\H,0,1.2097003778,
-1.8510657751,-2.0401856923\\Version=x86-Linux-G03RevB.03\State=1-A\HF
=-607.4607799\RMSD=4.793e-09\Dipole=-2.3102606,-1.1405621,-1.0980786\P
G=C01 [X(C7H9N2O3)]\\@

1-methyl-2-nitropyrrole (**5a**)



5a **5a_a3** **5a_a3b** **5a_a4** **5a_a5** **5a_a5b**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
2no2pyr_1	-453.9817612	-453.858886	-454.1128507	-453.9899755			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
5a_a5	-493.9019402	-493.741420	-494.0686996	-493.9081794	-0.0974	-61.1	-255.8
5a_a3b	-493.8959986	-493.735209	-494.0634580	-493.9026684	-0.0919	-57.7	-241.4
5a_a5b	-493.8963622	-493.735858	-494.0625848	-493.9020806	-0.0913	-57.3	-239.8
5a_a3	-493.8939805	-493.733189	-494.0609018	-493.9001103	-0.0894	-56.1	-234.7
5a_a4	-493.8325631	-493.674382	-494.0029282	-493.8447471	-0.0340	-21.3	-89.3

5a

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C5H6N2O2\FLSCH\19-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\2no2pyr_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C,0,0.
0958437494,-0.3569785473,0.0000137483\C,0,-0.5697044656,-1.5749629135,
0.0000304537\C,0,-1.943895597,-1.2813514531,-0.00000858\C,0,-2.0665013
002,0.1015816318,-0.0000499296\N,0,-0.8284342063,0.6746769497,-0.00005
7274\H,0,-0.0853245543,-2.5394258328,0.0000461209\H,0,-2.761481897,-1.
9883058503,-0.000019902\H,0,-2.9502176699,0.7243117346,-0.0000729139\C
,0,-0.5931895412,2.1180894882,0.0000930711\H,0,-1.5692545109,2.6076722
18,0.000085312\H,0,-0.0294518295,2.4169292451,0.8848216356\H,0,-0.0293
466781,2.4170986018,-0.884508568\N,0,1.5015308695,-0.1575976533,-0.000
0123488\O,0,1.9352777271,1.0053311416,-0.000099905\O,0,2.211982701,-1.
1673441951,0.0000577918\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-45
4.1128507\RMSD=3.220e-09\Dipole=-2.0259826,0.5939485,0.0000657\PG=C01
[X(C5H6N2O2)]\\@

5a_a3

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\2no2pyr_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,
1\C,0,0.1439788,-0.0785520192,0.0865818146\C,0,-1.171082849,-0.7509489
539,0.4160237322\C,0,-2.1142101731,0.430765519,0.2646348224\C,0,-1.428
9150347,1.5165950668,-0.1394881063\N,0,-0.0641817545,1.291705891,-0.32
07790926\H,0,-3.1934644145,0.369605151,0.3675785653\H,0,-1.8117999335,
2.5158670153,-0.3349103632\C,0,0.85231192,2.3208990346,0.1597455139\H,

0,0.6321660938,3.2695490298,-0.3494749846\H,0,0.7752017999,2.4830225041,1.2518090224\H,0,1.8621448868,1.9783126427,-0.074131974\N,0,1.3237026274,-0.6923013722,0.0284157034\O,0,2.3816155599,-0.0740253996,-0.3858241112\O,0,1.401798068,-1.9206047572,0.4258595135\H,0,-1.180427175,-1.1627037762,1.4455950623\C,0,-1.5141025648,-1.9400430914,-0.5138517153\H,0,-0.7052773693,-2.6722375689,-0.4478147494\H,0,-2.4648758754,-2.4116451172,-0.2210013155\H,0,-1.6055037372,-1.600853592,-1.5532651263\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-494.0609018\RMSD=6.969e-09\Dipole=-2.4484793,1.6525839,0.0840607\PG=C01 [X(C6H9N2O2)]\\@

5a_a3b

1\1\GINC-CICUM84\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\2no2pyr_an_1bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,0.1769520543,-0.0758743468,-0.0384858016\C,0,-1.0123051043,-0.9797452444,-0.2832665832\C,0,-2.0922584857,0.0607190224,-0.5280333762\C,0,-1.5679827974,1.2980386329,-0.4245909883\N,0,-0.1955107589,1.3098196872,-0.1915158594\H,0,-3.1186959053,-0.1662703461,-0.8001410771\H,0,-2.0819609193,2.252943532,-0.5138636616\C,0,0.3504006759,2.2889914748,0.7369231484\H,0,0.0679321798,3.3005242854,0.4127140735\H,0,-0.0043033411,2.1401854546,1.7749500685\H,0,1.4363278394,2.1751207336,0.7112706833\N,0,1.4456284583,-0.4797333613,-0.163373477\O,0,2.4106803454,0.3738252165,-0.1999141843\O,0,1.6859687161,-1.7452226238,-0.2076116476\C,0,-1.3248517363,-1.9733858947,0.8580418558\H,0,-2.1873938504,-2.6134988188,0.6130108927\H,0,-0.4442279301,-2.6033690356,1.0150787903\H,0,-1.5493913967,-1.4357732107,1.7878974161\H,0,-0.822030703,-1.601749483,-1.1800147056\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-494.063458\RMSD=9.241e-09\Dipole=-2.6402861,1.198514,0.3799736\PG=C01 [X(C6H9N2O2)]\\@

5a_a4

1\1\GINC-CICUM94\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\2no2pyr_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,-0.38073167,-0.2921850861,-0.0994086784\C,0,0.7275398408,-1.1229547718,-0.1895964948\C,0,1.9788980134,-0.2972719083,-0.4154319273\C,0,1.3847817045,1.0761917953,-0.2195604941\N,0,-0.0008903692,1.0413626902,-0.164826983\H,0,0.6438273981,-2.1841211075,-0.3796854939\H,0,2.4434622186,-0.4396388817,-1.4425886091\H,0,1.8370807607,2.0117993203,-0.5428356315\C,0,-0.7825500114,2.2165847681,0.154431085\H,0,-0.1526322727,3.0912772483,-0.0452021637\H,0,-1.6886413864,2.2545413638,-0.4499670558

\H,0,-1.0937601886,2.2389287219,1.2092364091\N,0,-1.7158208137,-0.6589
3901,0.0392407144\O,0,-2.630926417,0.222293891,0.1726017374\O,0,-1.980
8254624,-1.8960262777,0.0164364933\C,0,3.1630446668,-0.6110073866,0.54
59347458\H,0,3.5286665541,-1.6393924864,0.3937046444\H,0,4.0122986423,
0.073130688,0.378245004\H,0,2.8347963252,-0.5097759993,1.587681514\\Ve
rsion=x86-Linux-G03RevB.03\State=1-A\HF=-494.0029282\RMSD=4.531e-09\Di
pole=0.9808353,1.6501208,-0.4395411\PG=C01 [X(C6H9N2O2)]\\@

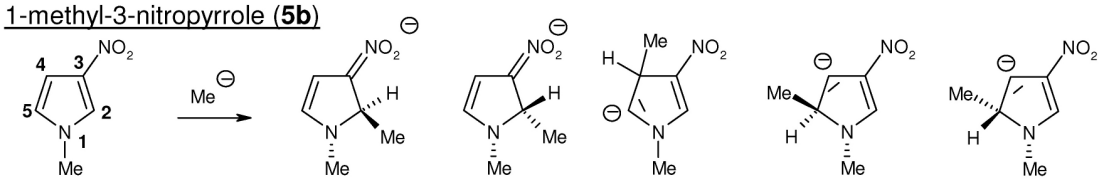
5a_a5

1\1\GINC-CICUM84\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\2no2pyr_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,
1\C,0,-0.6158305897,-0.1916609966,0.0659421107\C,0,-0.583531805,-0.373
7345738,1.4739362986\C,0,0.690245693,-0.2695190396,1.9341047552\C,0,1.
62578837,-0.037497985,0.7674976347\N,0,0.714761646,0.1329069695,-0.392
2264917\H,0,-1.4853601405,-0.529775816,2.0525145182\H,0,1.0297647535,-
0.3674214121,2.9602560863\H,0,2.2761211852,-0.9280113382,0.5951942597\
C,0,1.1705265588,-0.5160933247,-1.6084401568\H,0,2.1220233606,-0.07094
46107,-1.9327859851\H,0,1.3352754202,-1.6076231738,-1.4823383308\H,0,0
.4092892374,-0.3561955026,-2.3738330376\N,0,-1.731220913,-0.0438327482
,-0.6831907738\O,0,-1.6353224882,0.2901372859,-1.9197703699\O,0,-2.876
1935934,-0.2760688585,-0.15359269\C,0,2.5657482954,1.1712216441,0.9303
958141\H,0,3.2445855472,1.0280203138,1.7843118864\H,0,3.1796394131,1.3
196733153,0.0313993968\H,0,1.9783256085,2.0799169099,1.0994878043\\Ver
sion=x86-Linux-G03RevB.03\State=1-A\HF=-494.0686996\RMSD=4.251e-09\Dip
ole=2.8492826,-0.1830007,1.1369414\PG=C01 [X(C6H9N2O2)]\\@

5a_a5b

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\2no2pyr_an_3bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-0.5941043223,0.1747633736,0.0813579237\C,0,-0.5739235202,0.252
5197782,1.4995027232\C,0,0.7066440516,0.2770786593,1.9520470766\C,0,1.
6553469784,0.0943974974,0.7868848108\N,0,0.767099122,0.2466585985,-0.3
908803545\H,0,-1.4845722625,0.3335286542,2.0787527415\H,0,1.0402739709
,0.3214597081,2.983837844\C,0,1.1484925855,-0.4291427815,-1.6142416372
\H,0,2.1375917269,-0.0721935286,-1.9391768415\H,0,1.2020526338,-1.5332
674417,-1.5306761724\H,0,0.3958595198,-0.1798905872,-2.3637267926\N,0,
-1.6939888858,0.3359701571,-0.6857078111\O,0,-1.583519833,0.4690519605
,-1.9612129197\O,0,-2.8520558442,0.3234368138,-0.1298078207\C,0,2.4018

622608,-1.2626397779,0.8812551418\H,0,3.1028715148,-1.4184252751,0.050
3609626\H,0,2.9789506613,-1.291859113,1.8155294936\H,0,1.6888470323,-2
.0947806398,0.8987383598\H,0,2.4450507642,0.8752562464,0.7498072529\\V
ersion=x86-Linux-G03RevB.03\State=1-A\HF=-494.0625848\RMSD=2.618e-09\D
ipole=2.9058038,-0.7271645,1.1521253\PG=C01 [X(C6H9N2O2)]\\@



	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
5b	-453.9836782	-453.860911	-454.1160379	-453.9932707			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
5b_a2	-493.9065635	-493.745874	-494.0745059	-493.9138164	-0.0998	-62.6	-262.0
5b_a2b	-493.9028691	-493.742154	-494.0704834	-493.9097683	-0.0957	-60.1	-251.4
5b_a4	-493.8625540	-493.702615	-494.0323023	-493.8723633	-0.0583	-36.6	-153.2
5b_a5	-493.8557752	-493.697120	-494.0251767	-493.8665215	-0.0525	-32.9	-137.8
5b_a5b	-493.8513463	-493.692734	-494.0197237	-493.8611114	-0.0471	-29.5	-123.6

5b

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C5H6N2O2\FLSCH\19-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\3no2pyr_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C,0,-0
.243109833,0.1490237719,-0.9290188118\C,0,-0.2279799252,-0.0216535119,
0.4442635323\C,0,1.1099508669,-0.2459889299,0.8664470254\C,0,1.8729395
098,-0.2041826919,-0.2738583872\N,0,1.0443050772,0.0394696875,-1.35770
09323\H,0,1.4427467239,-0.4042894972,1.88057447\H,0,2.9375115921,-0.32
33597694,-0.4156472454\C,0,1.478260758,0.0899879247,-2.745898758\H,0,2
.4071246621,0.6616188924,-2.8216117917\H,0,1.6439129937,-0.9169826783,
-3.1441638568\H,0,0.711983787,0.5874257042,-3.3436134374\H,0,-1.068274
3887,0.3367336639,-1.597857951\N,0,-1.3865362761,0.0357545323,1.279319
5596\O,0,-1.2254075798,-0.1313496121,2.4917376094\O,0,-2.4770618248,0.
2474952081,0.7356851178\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-45
4.1160379\RMSD=5.093e-09\Dipole=1.9726308,-0.0157606,-2.1877528\PG=C01
[X(C5H6N2O2)]\\@

5b_a2

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS

=READ\\3no2pyr_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,
1\C,0,-0.1934756849,0.2035334609,-0.8307355759\C,0,-0.1261802339,-0.07
1576576,0.6568003572\C,0,1.2466086277,-0.252629813,1.0252893317\C,0,2.
0229918412,-0.0730806401,-0.0694277406\N,0,1.2523367682,0.317507524,-1
.2091793598\H,0,1.5796529123,-0.4691125515,2.0316726828\H,0,3.10521902
61,-0.0780719228,-0.1537742546\C,0,1.6051712103,-0.3017844264,-2.46764
70373\H,0,2.6740352618,-0.1492859967,-2.6707089254\H,0,1.4080094275,-1
.3942453338,-2.4999655808\H,0,1.0415466106,0.1629283985,-3.287347747\N
,0,-1.2034687503,-0.3705413259,1.4094067908\O,0,-1.0611003321,-0.68644
94889,2.6404968979\O,0,-2.370738468,-0.3267088918,0.8706034258\H,0,-0.
6507439844,-0.6589851581,-1.363172751\C,0,-0.9775689136,1.4576388279,-
1.2392245737\H,0,-2.0088089633,1.3462180476,-0.8946405476\H,0,-0.53479
42062,2.3448044128,-0.7722685909\H,0,-0.9667628902,1.5996487643,-2.330
5174597\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-494.0745059\RMSD=3
.775e-09\Dipole=2.0729352,0.5405103,-2.4274412\PG=C01 [X(C6H9N2O2)]\\@

5b_a2b

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\3no2pyr_an_1bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-0.5069026244,0.6504925791,-0.3502020601\C,0,0.621625877,-0.315
6981329,-0.0556942342\C,0,0.0618905846,-1.5926658231,0.2764406616\C,0,
-1.2802294045,-1.5318476148,0.0979375187\N,0,-1.6770303112,-0.27658184
44,-0.4481806895\H,0,0.6436264624,-2.4541807848,0.5745308709\H,0,-2.02
62905479,-2.3126077416,0.2052702523\C,0,-2.9920154039,0.2232113163,-0.
1399972482\H,0,-3.7341203718,-0.5578211376,-0.3579197408\H,0,-3.143503
4701,0.5353515956,0.9135482122\H,0,-3.22772958,1.0868696174,-0.7764518
954\N,0,1.9197279401,0.0288144167,-0.0924208218\O,0,2.8265244697,-0.83
48245573,0.1753585388\O,0,2.2304746119,1.2389554493,-0.4133108214\C,0,
-0.6332758963,1.7373511068,0.7413066753\H,0,-1.4271236701,2.467719325,
0.5264804922\H,0,-0.8276848899,1.2850907581,1.7215390086\H,0,0.3290600
211,2.2549780188,0.7748500189\H,0,-0.3676688047,1.1708646196,-1.312766
2563\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-494.0704834\RMSD=6.07
5e-09\Dipole=-3.5108797,0.0369976,0.2295443\PG=C01 [X(C6H9N2O2)]\\@

5b_a4

1\1\GINC-CICUM87\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\3no2pyr_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,
1\C,0,-0.4175840079,-0.0582599091,-1.1686207634\C,0,-0.4300746642,-0.0

587257029,0.234079372\C,0,1.0005069588,-0.1397047443,0.7606024118\C,0,1.8119543101,-0.0741587347,-0.5512363001\N,0,0.8537089586,-0.1342224706,-1.5907584579\H,0,1.1420914324,-1.0930681967,1.315114761\H,0,2.6080971011,-0.8157041028,-0.6988159424\C,0,1.2418828633,-0.1160429186,-2.9775778937\H,0,1.80028405,0.801120233,-3.2130232044\H,0,1.9016596984,-0.969688658,-3.1948333793\H,0,0.3578635792,-0.1886066589,-3.61862949\H,0,-1.2473578842,0.0981908232,-1.8437729568\N,0,-1.5682812727,-0.1422457317,0.9803474018\O,0,-1.4741497383,-0.2766878899,2.2449437929\O,0,-2.7052380347,-0.0798115731,0.4019528088\C,0,1.3708980877,0.9780789059,1.7613207528\H,0,0.7288789326,0.9289938624,2.6467451043\H,0,2.42287538,0.8789535327,2.0677704207\H,0,1.2572148068,1.9599609075,1.2857437897\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-494.0323023\RMSD=4.435e-09\Dipole=1.5563608,-0.2316538,-2.2064752\PG=C01 [X(C6H9N2O2)]\\@

5b_a5

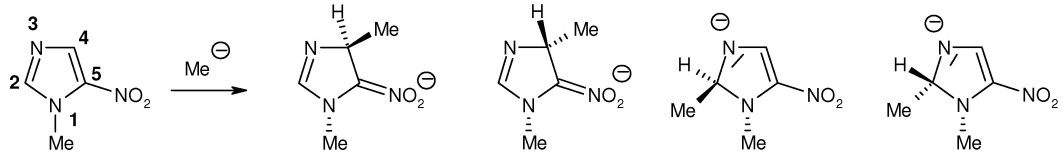
1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\3no2pyr_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,-0.6423138888,0.0855708059,-0.8988694306\C,0,-0.5781870221,0.1395917872,0.4868792428\C,0,0.7113510439,-0.1237788773,0.9952242822\C,0,1.6062550235,-0.0970774037,-0.2251681025\N,0,0.6410210063,-0.3121083753,-1.345125731\H,0,1.0545485476,0.3227885602,1.9245482782\C,0,1.0715754485,0.1263557877,-2.650276289\H,0,1.3707846271,1.196654475,-2.6610233848\H,0,1.9316854892,-0.463114543,-2.9949902288\H,0,0.2594798605,-0.0049219732,-3.3760570043\H,0,-1.5128442342,-0.095153549,-1.5176628589\N,0,-1.7528414627,0.3807280022,1.2580428775\O,0,-2.8541535565,0.5678756946,0.6860432385\O,0,-1.6381439561,0.4221080971,2.5003823008\H,0,2.1135740632,0.9051699211,-0.4054910602\C,0,2.7373601912,-1.1399901474,-0.2374356223\H,0,3.3569146356,-1.0882275976,-1.1482373844\H,0,3.3996411682,-0.9723178355,0.6230167749\H,0,2.311094362,-2.1451168937,-0.148051954\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-494.0251767\RMSD=8.440e-09\Dipole=1.2271309,-0.1342404,-1.7697096\PG=C01 [X(C6H9N2O2)]\\@

5b_a5b

1\1\GINC-CICUM93\SP\RB3LYP\6-311+G(d,p)\C6H9N2O2(1-)\FLSCH\21-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\3no2pyr_an_3bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\C,0,-0.5172215134,-0.2351821015,-0.9080496897\C,0,-0.5069283998,-0.2833054612,0.4797476713\C,0,0.8015259641,-0.2883050128,1.0206832691\C,0,1.6982362241,0.0674360976,-0.1521715156\N,0,0.8264638243,-0.27492316

,-1.3137584943\H,0,1.0084927924,0.149103017,1.9945896527\C,0,1.2108573928,0.0960255645,-2.6474088912\H,0,1.1642288874,1.1832779427,-2.8588472211\H,0,2.2406805843,-0.2344819723,-2.8439740726\H,0,0.5514060059,-0.4043979135,-3.3703002404\H,0,-1.3097060405,-0.5051096221,-1.5933947794\N,0,-1.72593591,-0.3726257958,1.2024619396\O,0,-2.8273706114,-0.3814340726,0.5915341951\O,0,-1.6624022482,-0.4180316659,2.4513517789\C,0,2.162146777,1.5574968883,-0.1618263102\H,0,2.7323548796,1.7541717293,0.7554378536\H,0,2.8119196533,1.8107897816,-1.0172164174\H,0,1.2921176746,2.225426596,-0.1679154031\H,0,2.6312943712,-0.5352068101,-0.2482384834\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-494.0197237\RMSD=6.854e-09\Dipole=1.4985342,0.6591329,-2.1617774\PG=C01 [X(C6H9N2O2)]\\@

1-methyl-5-nitroimidazole (**6a**)



6a **6a_a4** **6a_a4b** **6a_a2** **6a_a2b**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
6a	-470.0262963	-469.915070	-470.1611650	-470.0499387			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
6a_a2	-509.9642525	-509.814673	-510.1330922	-509.9835127	-0.1128	-70.8	-296.2
6a_a4b	-509.9577280	-509.807962	-510.1283838	-509.9786178	-0.1079	-67.7	-283.3
6a_a2b	-509.9585186	-509.808864	-510.1269098	-509.9772552	-0.1066	-66.9	-279.8
6a_a4	-509.9552280	-509.805514	-510.1255408	-509.9758268	-0.1051	-66.0	-276.0

6a

1\1\GINC-CICUM95\SP\RB3LYP\6-311+G(d,p)\C4H5N3O2\FLSCH\19-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\5no2imid_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C,0,-0.2559350988,0.0009820364,0.2680811073\C,0,-0.2046068618,0.059217072,1.6482250921\C,0,1.8065458249,0.1086943323,0.9455302311\N,0,1.055031064,0.0335151799,-0.1830611474\H,0,-1.0409502353,0.0545979298,2.3319952846\H,0,2.8872938633,0.14879144,0.899456584\C,0,1.5743697353,-0.0019983045,-1.5495579033\H,0,2.6636236507,0.042826216,-1.4871254259\H,0,1.2684144353,-0.9214936124,-2.0499549846\H,0,1.1997535075,0.8473702734,-2.122021069\N,0,-1.396894426,-0.0776744563,-0.5747579965\O,0,-1.2184423284,-0.120671923,-1.8002532135\O,0,-2.4972571002,-0.0978108333,-0.0199565928\N,0,1.0883231633,0.1262162744,2.0600558437\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-470.161165\RMSD=5.974e-09\Dipole=1.7102542,0.0465

793,-0.4869229\PG=C01 [X(C4H5N3O2)]\\@

6a_a2

1\1\GINC-CICUM84\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\5no2imid_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-0.5918561438,-0.1818527698,0.053570319\C,0,-0.4923451304,-0.36
02931466,1.4508332094\C,0,1.587729406,-0.0415986487,0.7754215431\N,0,0
.7211190855,0.1586371932,-0.4216399978\H,0,-1.355609876,-0.5283000049,
2.0890874639\H,0,2.2224864971,-0.9432995697,0.6193511846\C,0,1.1844756
767,-0.517618679,-1.6209835803\H,0,2.1475002597,-0.0923939189,-1.93606
20986\H,0,1.3272476121,-1.6094776856,-1.4769784662\H,0,0.442392208,-0.
3578753577,-2.4051895145\N,0,-1.7352348438,-0.0462398145,-0.6655799326
\O,0,-1.6706213639,0.2887761633,-1.8961863037\O,0,-2.8547939719,-0.292
0713376,-0.1042166348\N,0,0.7195017647,-0.2715025432,1.9356005162\C,0,
2.5190620748,1.1534667511,1.005043851\H,0,3.145922469,0.9841702838,1.8
897129337\H,0,3.1709426053,1.3169501032,0.1365385497\H,0,1.9223435656,
2.0577026536,1.164787302\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-5
10.1330922\RMSD=2.978e-09\Dipole=2.3736212,-0.0802718,0.2286809\PG=C01
[X(C5H8N3O2)]\\@

6a_a2b

1\1\GINC-CICUM86\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\imid_an_2bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1\
C,0,0.5281184342,-0.2895073687,-0.0199928369\C,0,-0.055119939,-1.57531
71329,-0.0146277367\C,0,-1.7339762495,-0.2040652516,-0.4709121888\N,0,
-0.4884654728,0.617513482,-0.4730657676\H,0,0.512698335,-2.480629966,0
.1806258197\C,0,-0.5419206001,1.9560683928,0.0839935176\H,0,-1.2649652
144,2.5616133752,-0.480855762\H,0,-0.8283572346,1.9968895883,1.1534218
978\H,0,0.4555659581,2.3870801521,-0.0171739546\N,0,1.854386029,-0.016
0119338,0.0553374306\O,0,2.27539855,1.1672304598,-0.1890634403\O,0,2.6
613292389,-0.9445048798,0.4024563099\N,0,-1.3292656491,-1.6071382897,-
0.3097268537\C,0,-2.7535543039,0.1486983322,0.6328129427\H,0,-3.151297
9854,1.1660597575,0.5278338211\H,0,-3.5873247239,-0.5595246752,0.57156
5453\H,0,-2.296056168,0.0499309999,1.6238348955\H,0,-2.2519536771,-0.0
790285124,-1.4418509796\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-51
0.1269098\RMSD=2.287e-09\Dipole=-2.4827923,0.722858,0.1761054\PG=C01 [
X(C5H8N3O2)]\\@

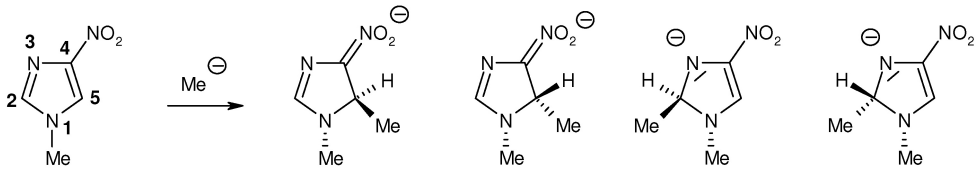
6a_a4

1\1\GINC-CICUM94\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\5no2imid_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-0.1565462341,-0.0878335855,-0.1459684648\C,0,1.184280272,-0.73
64611368,-0.4075084256\C,0,1.4576053527,1.4181409166,0.0625520181\N,0,
0.1011187625,1.2711928132,0.2430156343\H,0,1.2652527563,-1.1532305178,
-1.4291089961\H,0,1.8944008643,2.4062487581,0.2186751572\C,0,-0.815818
2478,2.3601256378,-0.055705213\H,0,-0.5004906331,3.2603884943,0.487622
843\H,0,-0.8554914425,2.5948755232,-1.1347776782\H,0,-1.8072123114,2.0
336193134,0.2622791074\N,0,-1.3355608067,-0.6919120666,-0.0478587907\O
,0,-2.3838679397,-0.0518120516,0.3603744787\O,0,-1.4224026393,-1.93004
28063,-0.4053125003\N,0,2.1551241623,0.3870392754,-0.2690982978\C,0,1.
5287118934,-1.8836389307,0.5603034563\H,0,0.7498178417,-2.6461727375,0
.4808736698\H,0,2.5093337848,-2.3144950731,0.3175023381\H,0,1.56038072
82,-1.5126324597,1.5919876852\\Version=x86-Linux-G03RevB.03\State=1-A\
HF=-510.1255408\RMSD=9.867e-09\Dipole=1.6121492,1.8545374,0.0771005\PG
=C01 [X(C5H8N3O2)]\\@

6a_a4b

1\1\GINC-CICUM84\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\5imid_an_1bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1
\C,0,0.1687068686,-0.1288270253,0.0631303052\C,0,-1.1665088558,-0.7534
796116,-0.2839310626\C,0,-1.3107565572,1.4573681316,-0.432020398\N,0,0
.0187383616,1.2883540305,-0.1303605978\H,0,-1.6914397633,2.4742903734,
-0.5471255179\C,0,0.7669073782,2.2556498889,0.6497389911\H,0,0.5933672
16,3.2633885781,0.250051425\H,0,0.4867223557,2.2452671283,1.718957329\
H,0,1.821542861,1.988303824,0.5598445583\N,0,1.3449816881,-0.743603483
5,-0.1215705836\O,0,2.4406223069,-0.0698327868,-0.1787343515\O,0,1.353
8957283,-2.0267242866,-0.1885975379\N,0,-2.0479080399,0.4105280191,-0.
5854084551\C,0,-1.781634996,-1.647803943,0.8023709737\H,0,-2.754220796
7,-2.0466154588,0.481766596\H,0,-1.0920737206,-2.4746914169,0.99918362
6\H,0,-1.9277899613,-1.0801125751,1.72975112\H,0,-1.0632195672,-1.3817
684723,-1.1881294218\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-510.1
283838\RMSD=2.591e-09\Dipole=-1.5172755,1.8329101,0.5812018\PG=C01 [X(
C5H8N3O2)]\\@

1-methyl-4-nitroimidazole (**6b**)



6b **6b_a5** **6b_a5b** **6b_a2** **6b_a2b**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
6b	-470.0274563	-469.916497	-470.1636808	-470.0527215			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
6b_a5	-509.9575732	-509.808599	-510.1278684	-509.9788942	-0.1054	-66.1	-276.8
6b_a5b	-509.9549223	-509.805836	-510.1249210	-509.9758347	-0.1024	-64.2	-268.7
6b_a2	-509.9249401	-509.777450	-510.0963146	-509.9488245	-0.0753	-47.3	-197.8
6b_a2b	-509.9201896	-509.772690	-510.0907757	-509.9432761	-0.0698	-43.8	-183.3

6b

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C4H5N3O2\FLSCH\19-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\4no2imid_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\0,1\C,0,-
0.262860755,-0.2208068596,-0.9291185302\C,0,-0.2078676431,0.030131286,
0.4235722778\C,0,1.7611505207,0.3328961693,-0.2610185876\N,0,1.0197190
038,-0.0217672071,-1.3646703657\H,0,2.8191987335,0.5479250462,-0.33278
51111\C,0,1.5049011316,-0.1589334234,-2.7316664269\H,0,2.5726814039,0.
067699926,-2.7479238106\H,0,1.354144204,-1.1810323789,-3.0907224612\H,
0,0.9845634392,0.5384223775,-3.3944511859\H,0,-1.0753218445,-0.5099865
77,-1.5759010656\N,0,-1.3336131426,-0.0531962614,1.3228627652\O,0,-2.4
131863016,-0.3759658636,0.8111616931\O,0,-1.1537975902,0.1952180172,2.
509484484\N,0,1.0437035205,0.3725679462,0.8369507174\\Version=x86-Linu
x-G03RevB.03\State=1-A\HF=-470.1636808\RMSD=3.098e-09\Dipole=1.6623557
,-0.159851,-2.9284996\PG=C01 [X(C4H5N3O2)]\\@

6b_a2

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\4no2imid_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-0.0191728798,1.1118662765,-0.1812193176\C,0,0.7070676935,-0.04
10029207,0.0412171672\C,0,-1.3493031648,-0.7045377113,0.3156745373\N,0
,-1.3683112429,0.6996041644,-0.2451981368\H,0,-1.725368318,-0.62541059
86,1.3857274381\C,0,-2.3936783202,1.5750508154,0.264980246\H,0,-3.3863
329833,1.2293136977,-0.0533272377\H,0,-2.3960218794,1.6247792768,1.376
2111909\H,0,-2.254033834,2.5929126792,-0.120014306\H,0,0.3059772276,2.

0850147279,-0.5162076472\N,0,2.1444787169,-0.0097521062,-0.0042342752\
O,0,2.7678684285,-1.067139781,0.1927672035\O,0,2.7242771649,1.08212045
63,-0.2353045289\N,0,0.0123338405,-1.1689207307,0.2478902449\C,0,-2.32
93379226,-1.6232426486,-0.4237916079\H,0,-2.2710305684,-2.6324140901,0
.0011910617\H,0,-3.3695990043,-1.2724211285,-0.3410177866\H,0,-2.05371
70257,-1.6769421273,-1.4826350898\\Version=x86-Linux-G03RevB.03\State=
1-A\HF=-510.0963146\RMSD=6.667e-09\Dipole=-2.2480076,1.0712703,-0.2461
044\PG=C01 [X(C5H8N3O2)]\\@

6b_a2b

1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\4imid_an_2bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1
\C,0,-0.0968332267,1.0846224224,0.0142196011\C,0,0.6996579953,-0.03511
89835,-0.1267270077\C,0,-1.3229009609,-0.8262105043,-0.4542191046\N,0,
-1.3755458252,0.678013289,-0.3825497884\C,0,-2.5645192172,1.384130104,
0.0010479503\H,0,-3.4156184691,1.0348013588,-0.6002719228\H,0,-2.84516
33703,1.2735755947,1.0685376108\H,0,-2.4392567413,2.459317287,-0.19263
58409\H,0,0.1589019316,2.1151344637,0.2035003176\N,0,2.1126058337,0.06
36296428,0.0636390371\O,0,2.8086292975,-0.9574078585,-0.1027834991\O,0
,2.6127565113,1.1739729051,0.3971998446\N,0,0.0791082821,-1.1750460915
,-0.483841548\C,0,-2.0527076442,-1.5037271008,0.7408962669\H,0,-3.1367
011565,-1.3042130287,0.7587106458\H,0,-1.9004548484,-2.58547972,0.6586
658709\H,0,-1.6116185367,-1.1711422389,1.6884300186\H,0,-1.8705349915,
-1.1428675983,-1.3723076053\\Version=x86-Linux-G03RevB.03\State=1-A\HF
=-510.0907757\RMSD=3.046e-09\Dipole=-2.7796229,1.1256125,0.2182158\PG=
C01 [X(C5H8N3O2)]\\@

6b_a5

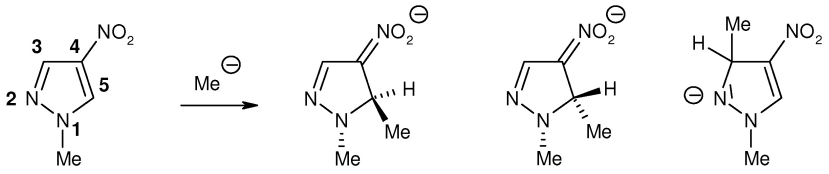
1\1\GINC-CICUM94\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\4no2imid_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1
,1\C,0,-0.2326393614,0.0406156969,-0.8415777562\C,0,-0.0826023705,0.01
66799797,0.6679473958\C,0,1.9377765863,0.0894388628,-0.0399027316\N,0,
1.1875676073,0.2542143611,-1.2287652253\H,0,3.023612047,0.1309795304,-
0.0863315357\C,0,1.6540938451,-0.3543043229,-2.4505044484\H,0,2.732014
5806,-0.1793573732,-2.5625719831\H,0,1.4805526947,-1.4491068173,-2.489
5056665\H,0,1.152770721,0.09095924,-3.3198743147\N,0,-1.1066538024,-0.
2956471062,1.4953568655\O,0,-2.2679029157,-0.4510222592,0.958632887\O,
0,-0.942521656,-0.4233467138,2.7455879131\N,0,1.2521355097,0.003376233

9,1.0503316209\H,0,-0.5885075542,-0.9427064053,-1.2282654416\C,0,-1.15
81074454,1.118554388,-1.4200275564\H,0,-2.1652417037,0.9443388126,-1.0
3461725\H,0,-0.8187809901,2.1124309625,-1.1064610068\H,0,-1.1754959476
,1.0879017855,-2.520211449\\Version=x86-Linux-G03RevB.03\State=1-A\HF=
-510.1278684\RMSD=6.460e-09\Dipole=1.8080495,0.4229685,-3.2885391\PG=C
01 [X(C5H8N3O2)]\\@

6b_a5b

1\1\GINC-CICUM87\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\21-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\4imid_an_1bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) frequenz\\-1,1
\C,0,-0.5045838229,0.6566234613,-0.3418132374\C,0,0.6016829283,-0.3353
119401,-0.036812132\C,0,-1.1766863895,-1.5074802351,0.1400188405\N,0,-
1.6486956159,-0.2880369306,-0.3844402979\H,0,-1.8744904224,-2.32557007
14,0.30334784\C,0,-3.0020388633,0.150605891,-0.1821935682\H,0,-3.67920
44092,-0.7065905689,-0.2949378734\H,0,-3.1972593899,0.6002862552,0.810
1763599\H,0,-3.2832728221,0.895037305,-0.9403753034\N,0,1.9070585997,-
0.0038736176,-0.0866294873\O,0,2.1882881693,1.212919213,-0.4207417018\
O,0,2.825713643,-0.8428888904,0.1657545253\N,0,0.1030528973,-1.5880614
621,0.2988096686\C,0,-0.6344760701,1.7759719501,0.7158366116\H,0,-1.43
23344287,2.4947855249,0.4764218462\H,0,-0.827531469,1.3546937851,1.710
4908718\H,0,0.3256041759,2.2975690877,0.7328223313\H,0,-0.3768235961,1
.1468954101,-1.3224469305\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-
510.124921\RMSD=2.883e-09\Dipole=-4.0207801,0.5720153,0.0506899\PG=C01
[X(C5H8N3O2)]\\@

1-methyl-4-nitropyrazole (**7**)



7 **7a5** **7a5b** **7a3**

	B3LYP/6-31G(d)		B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)				
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn}	/ kcal mol^{-1}	/ kJ mol^{-1}
7	-470.0135178	-469.902460	-470.1492359	-470.0381781			
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583			
7_a5	-509.9513237	-509.801980	-510.1196309	-509.9702872	-0.1114	-69.9	-292.4
7_a5b	-509.9474427	-509.797985	-510.1154747	-509.9660170	-0.1071	-67.2	-281.1
7_a3	-509.9123397	-509.763616	-510.0846098	-509.9358861	-0.0769	-48.3	-202.0

7

1\1\GINC-CICUM83\SP\RB3LYP\6-311+G(d,p)\C4H5N3O2\FLSCH\27-Nov-2007\0\\
#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=REA
D\\pyraz_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\0,1\C,0,-0.2725708
271,0.0675360432,-0.9567913443\C,0,-0.2370269491,0.0001633188,0.427428
1651\C,0,1.124162788,-0.1310936254,0.7751876641\N,0,1.0111146768,-0.02
25110016,-1.3543658262\H,0,-1.1039312293,0.1694591106,-1.6371525497\H,
0,1.5571420037,-0.2135577242,1.761363195\C,0,1.5333989601,-0.003600554
6,-2.7107612266\H,0,2.2194768328,0.8387922637,-2.8291085913\H,0,2.0695
199185,-0.9345049729,-2.9115757981\H,0,0.7005861945,0.0992708645,-3.40
84397117\N,0,1.8816012212,-0.1444978104,-0.3137466546\N,0,-1.365223346
2,0.0549138955,1.3014127263\O,0,-1.146907955,-0.019877153,2.5128454572
\O,0,-2.4809702218,0.1732738758,0.7848335663\\Version=x86-Linux-G03Rev
B.03\State=1-A\HF=-470.1492359\RMSD=8.630e-09\Dipole=0.9788812,0.01317
05,-2.0632033\PG=C01 [X(C4H5N3O2)]\\@

7_a3

1\1\GINC-CICUM85\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\27-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR)\\pyraz_an_2sp b3
lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C\C,1,1.40348514\C,2,1.52377
069,1,107.17511765\N,1,1.33629339,2,106.88046337,3,-0.87418593,0\H,1,1
.07942349,4,123.26188194,2,179.49620519,0\C,4,1.43994558,1,125.5989519
,2,179.36513761,0\H,6,1.0977533,4,109.42423778,1,123.40304532,0\H,6,1.
09832762,4,109.95981021,1,-118.48153357,0\H,6,1.09344216,4,110.0224533
4,1,2.58241688,0\N,4,1.36106666,1,117.47330916,2,0.,0\N,2,1.35561414,1
,125.69573679,4,172.7030664,0\O,11,1.27806265,2,118.82310379,1,-175.55
857199,0\O,11,1.27870534,2,119.61309223,1,4.04356088,0\H,3,1.11270769,
2,110.50656416,1,120.37322726,0\C,3,1.54466693,2,114.53133679,1,-120.5
1718595,0\H,15,1.09873633,3,110.1004063,2,176.43035502,0\H,15,1.094751
23,3,109.80533632,2,-62.82348771,0\H,15,1.09721549,3,110.20641025,2,57
.38553876,0\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-510.0846098\RM
SD=9.561e-09\Dipole=1.4681071,-0.3170927,-2.3658303\PG=C01 [X(C5H8N3O2
)]\\@

7_a5

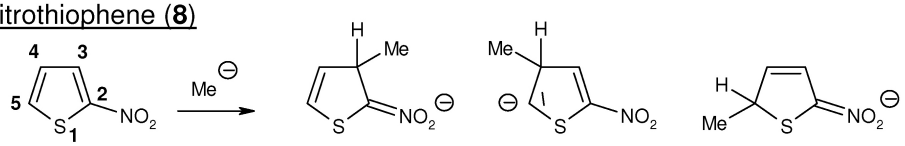
1\1\GINC-CICUM83\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\27-Nov-2007
\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS
=READ\\pyraz_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-0
.2129935043,0.1268756659,-0.8627111527\C,0,-0.1287848047,-0.0414805536
,0.6319032136\C,0,1.2489847628,-0.161942654,0.9480549498\N,0,1.2286917

094,0.3549126921,-1.1831931459\H,0,1.6415179638,-0.3700490142,1.9376402903\C,0,1.6960994463,-0.2751663574,-2.3964621782\H,0,2.7645589045,-0.0666974844,-2.5164843849\H,0,1.5570735268,-1.3761610135,-2.4058580453\H,0,1.1583797908,0.1401366757,-3.2589214605\N,0,2.0557527329,-0.0044452436,-0.0657024419\N,0,-1.1710806175,-0.3475753976,1.4439898176\O,0,-0.9697371143,-0.5731165053,2.6792827234\O,0,-2.3449472598,-0.3996521562,0.9450931447\H,0,-0.5786667469,-0.8086623243,-1.3464301303\C,0,-1.0882473819,1.2783290546,-1.3705957801\H,0,-2.1203057815,1.105547021,-1.0537131697\H,0,-0.7368487689,2.2273119972,-0.9506751084\H,0,-1.0521317778,1.3507881459,-2.4673588596\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-510.1196309\RMSD=8.152e-09\Dipole=0.9410889,0.3508414,-2.127248\PG=C01 [X(C5H8N3O2)]\\@

7_a5b

1\1\GINC-CICUM96\SP\RB3LYP\6-311+G(d,p)\C5H8N3O2(1-)\FLSCH\28-Nov-2007\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=READ\\pyraz_an_1bsp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-0.5191581288,0.6728803253,-0.3775676271\C,0,0.602101303,-0.2938318821,-0.0935252786\C,0,-0.0017701175,-1.525818437,0.2670451009\N,0,-1.650365513,-0.2974957499,-0.4806650913\H,0,0.5287265831,-2.4006978077,0.6263227692\C,0,-2.9741717341,0.1349513065,-0.1066903219\H,0,-3.6667544121,-0.6958366656,-0.2810584234\H,0,-3.0827787184,0.4446896313,0.9511258093\H,0,-3.2792943352,0.9803594765,-0.7380997296\N,0,-1.3004021911,-1.5448646495,0.128341015\N,0,1.9188514452,0.0170602127,-0.0877054728\O,0,2.7821916051,-0.87131172,0.2050866376\O,0,2.2699677647,1.208239182,-0.3937880962\C,0,-0.6549677945,1.7592030395,0.7150610287\H,0,-1.4639111837,2.4717924796,0.5008189374\H,0,-0.8383436963,1.3067878285,1.6968844228\H,0,0.2945944442,2.3004513836,0.7510013055\H,0,-0.3983009955,1.1898291721,-1.3431139904\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-510.1154747\RMSD=9.685e-09\Dipole=-2.4800662,0.6773573,0.2187181\PG=C01 [X(C5H8N3O2)]\\@

2-nitrothiophene (**8**)



8 **8a3** **8a4** **8a5**

	B3LYP/6-31G(d)		B3LYP/6-31G(d)// B3LYP/6-31G(d)		627.509	4.184
	E_{tot}	H_{298}	E_{tot}	"H_{298}"	H_{rxn} / kcal mol^{-1}	/ kJ mol^{-1}
8	-757.4989054	-757.421717	-757.6308831	-757.5536947		
methyl anion	-39.7902953	-39.758609	-39.8524446	-39.8207583		
8_a5	-797.4500601	-797.333612	-797.6147879	-797.4983398	-0.1239	-77.7 -325.3
8_a3	-797.4377288	-797.321360	-797.6029970	-797.4866282	-0.1122	-70.4 -294.5
8_a4	-797.3747228	-797.260456	-797.5408517	-797.4265849	-0.0521	-32.7 -136.9

8

1\1\GINC-CICUM87\SP\RB3LYP\6-311+G(d,p)\C4H3N1O2S1\FLSCH\27-Nov-2007\0
\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUESS=R
EAD\\thio_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\0,1\C,0,-2.135024
7594,-0.0118853121,-0.669486531\C,0,-2.1207148116,0.0256270005,0.70413
37338\C,0,-0.8044890532,0.0361982468,1.2355355399\C,0,0.1361277644,0.0
06086214,0.2374767237\S,0,-0.549020223,-0.035477255,-1.3579980396\H,0,
-2.9992536268,-0.0270983249,-1.3209833438\H,0,-3.0180743807,0.04493935
13,1.3118447248\H,0,-0.5438560611,0.0641262336,2.2856886648\N,0,1.5609
75236,0.0064533208,0.407691199\O,0,1.9946993714,0.0366789263,1.5603833
208\O,0,2.2507113964,-0.0236365914,-0.6164303962\\Version=x86-Linux-G0
3RevB.03\State=1-A\HF=-757.6308831\RMSD=3.477e-09\Dipole=-2.0801846,0.
0032525,-0.1098041\PG=C01 [X(C4H3N1O2S1)]\\@

8_a3

1\1\GINC-CICUM90\SP\RB3LYP\6-311+G(d,p)\C5H6N1O2S1(1-)\FLSCH\27-Nov-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\thio_an_1sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-
2.0327699076,0.1152214887,-0.969381563\C,0,-2.0758139348,0.0977281779,
0.3720551031\C,0,-0.7410931352,0.0222773485,1.0826440836\C,0,0.2745863
266,0.0231420787,-0.032049589\S,0,-0.4146964746,0.079758031,-1.6811604
748\H,0,-2.8947070665,0.1503900523,-1.6304238711\H,0,-3.01061257,0.118
1186525,0.931506028\H,0,-0.5860776081,0.912820423,1.7239368945\N,0,1.5
770230787,0.2601609139,0.1280070629\O,0,2.049166729,0.3568154672,1.322
9171213\O,0,2.3328536932,0.377452149,-0.9022029244\C,0,-0.6255993234,-
1.2014158925,2.0231539984\H,0,0.3891878707,-1.2191346365,2.4301644523\
H,0,-1.3480692362,-1.1437004964,2.8523055003\H,0,-0.8057628791,-2.1316

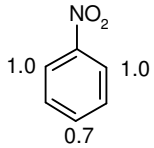
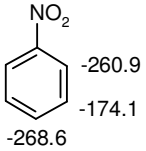
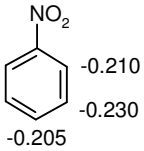
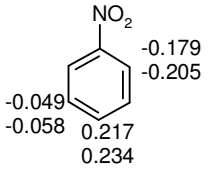
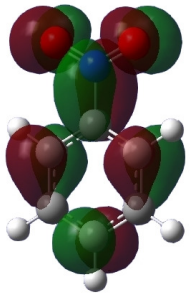
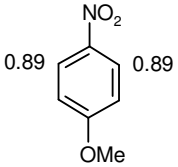
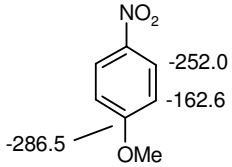
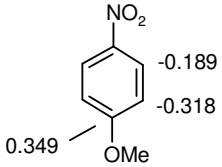
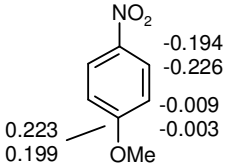
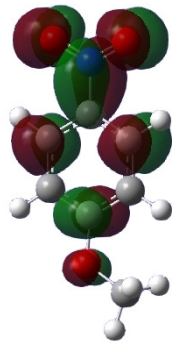
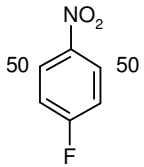
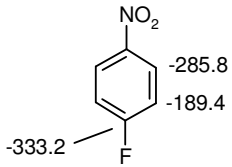
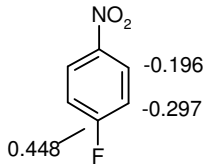
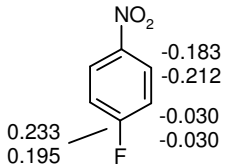
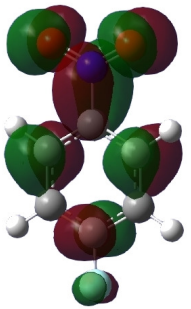
090255,1.4707833778\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-797.60
2997\RMSD=4.617e-09\Dipole=-3.0781112,-0.4500609,0.1312449\PG=C01 [X(C
5H6N1O2S1)]\\@

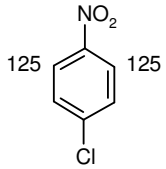
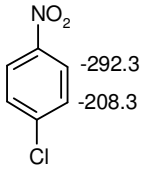
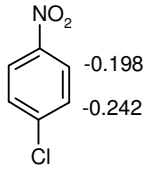
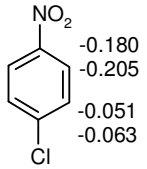
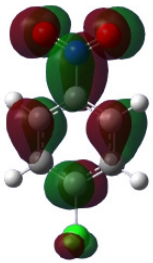
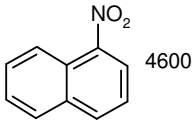
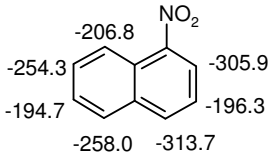
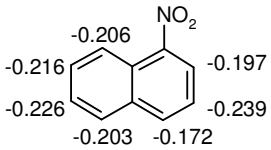
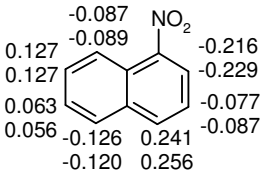
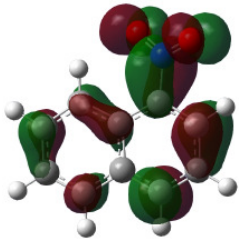
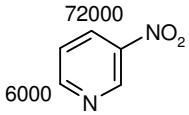
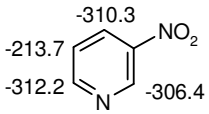
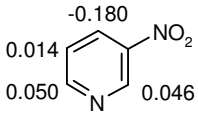
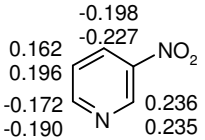
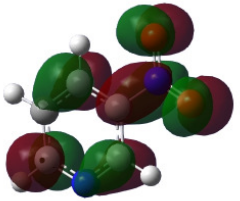
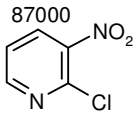
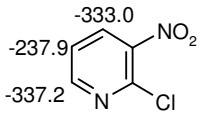
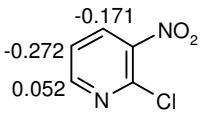
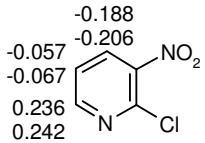
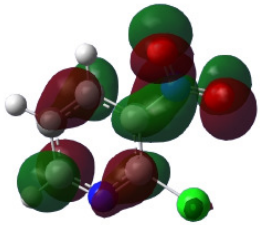
8_a4

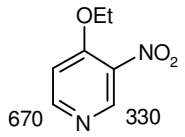
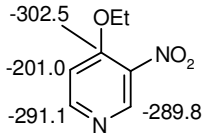
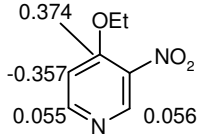
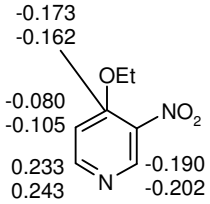
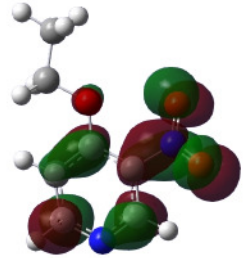
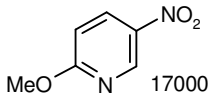
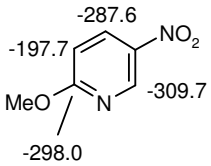
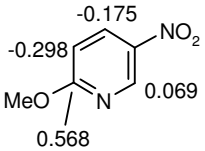
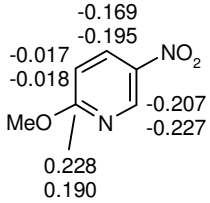
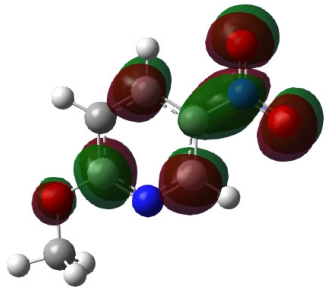
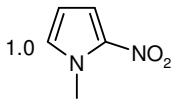
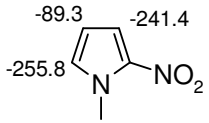
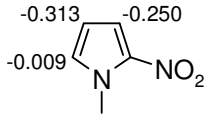
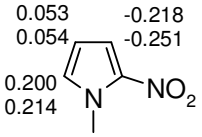
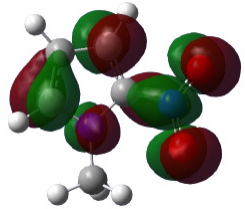
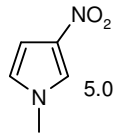
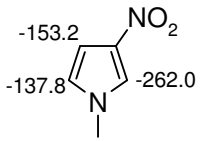
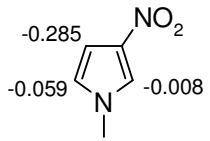
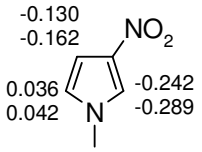
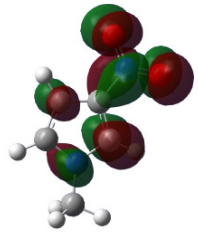
1\1\GINC-CICUM87\SP\RB3LYP\6-311+G(d,p)\C5H6N1O2S1(1-)\FLSCH\27-Nov-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\thio_an_2sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-
1.7526146184,-0.6093702461,-0.8397733343\C,0,-1.8799074569,-0.25660475
12,0.6242532731\C,0,-0.4380075135,-0.4449738277,1.0642923878\C,0,0.480
9146894,-0.1531043099,0.0904289315\S,0,-0.221089704,0.0224713692,-1.50
21532229\H,0,-2.6081466972,-0.5053719801,-1.5109581783\H,0,-2.54852833
53,-0.9850591182,1.1231647177\H,0,-0.1353185705,-0.6043399474,2.093826
3375\N,0,1.8763694884,-0.0666764288,0.2646435585\O,0,2.3486298802,-0.3
474773985,1.3943071013\O,0,2.599415182,0.2864932717,-0.7000957073\C,0,
-2.4372975349,1.1564254144,1.0016473262\H,0,-3.4754017725,1.2739126477
,0.6533445507\H,0,-2.4218829534,1.3213062384,2.0920494831\H,0,-1.83075
87176,1.9403845918,0.531737088\\Version=x86-Linux-G03RevB.03\State=1-A
\HF=-797.5408517\RMSD=8.532e-09\Dipole=-1.2855746,0.4338407,0.215659\P
G=C01 [X(C5H6N1O2S1)]\\@

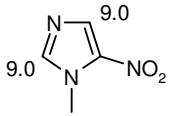
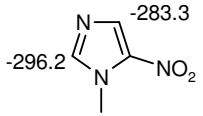
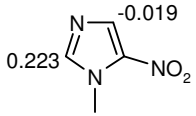
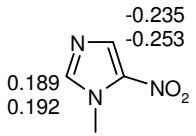
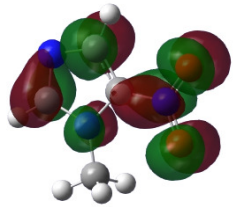
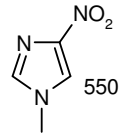
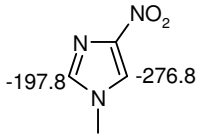
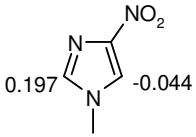
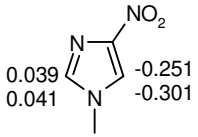
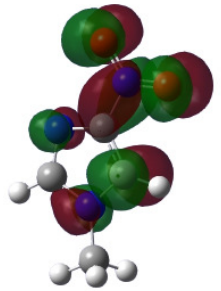
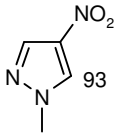
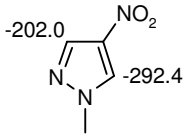
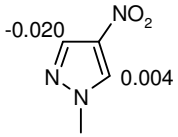
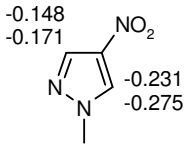
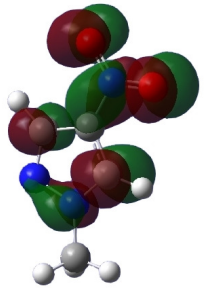
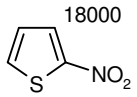
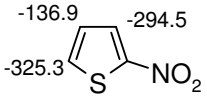
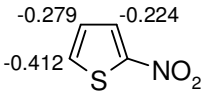
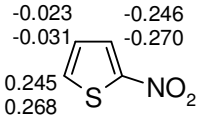
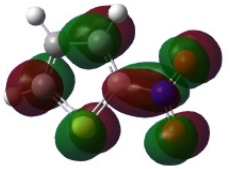
8_a5

1\1\GINC-CICUM85\SP\RB3LYP\6-311+G(d,p)\C5H6N1O2S1(1-)\FLSCH\27-Nov-20
07\0\\#P B3LYP/6-311+G(D,P) SCF=TIGHT POP=(NPA,REGULAR) GEOM=CHECK GUE
SS=READ\\thio_an_3sp b3lyp/6-311+G(d,p)//B3LYP/6-31G(d) sp\\-1,1\C,0,-
1.8908132353,-0.1129992966,-0.5939019783\C,0,-1.7462678116,-0.14395791
68,0.9130986635\C,0,-0.4717246922,-0.1392341941,1.3832654491\C,0,0.547
4274558,-0.1540964746,0.400447786\S,0,-0.1376235877,-0.1859680941,-1.2
574318551\H,0,-2.4214110867,-1.0034067727,-0.9713029742\H,0,-2.6332177
5,-0.1316935898,1.5430713915\H,0,-0.1976031302,-0.1301467726,2.4335144
298\N,0,1.8829943763,-0.1523936383,0.5917310036\O,0,2.3546424809,-0.13
74988333,1.7793678683\O,0,2.6432892235,-0.1705206504,-0.4346665466\C,0
,-2.6403960479,1.1260565731,-1.1139247356\H,0,-2.7067312051,1.12947832
06,-2.210261239\H,0,-3.6654343953,1.1477344578,-0.7125591087\H,0,-2.12
73933111,2.0398230521,-0.7971915252\\Version=x86-Linux-G03RevB.03\Stat
e=1-A\HF=-797.6147879\RMSD=5.653e-09\Dipole=-3.2059545,0.2245006,-0.49
08584\PG=C01 [X(C5H6N1O2S1)]\\@

no.	partial reactivities (experimental)	methyl anion affinities / kJ mol^{-1}	charges (NPA)	E(LUMO) / eV	LUMO coefficients $2p_z$ $3p_z$	LUMO
3a				-2.43		
3b				-2.16		
3c				-2.51		

no.	partial reactivities (experimental)	methyl anion affinities / kJ mol^{-1}	charges (NPA)	E(LUMO) / eV	LUMO coefficients $2p_z$ $3p_z$	LUMO
3d				-2.67		
3e				-2.47		
4a				-2.76		
4b				-2.78		

no.	partial reactivities (experimental)	methyl anion affinities / kJ mol^{-1}	charges (NPA)	E(LUMO) / eV	LUMO coefficients $2p_z$ $3p_z$	LUMO
4c				-2.29		
4d				-2.42		
5a				-2.04		
5b				-1.72		

no.	partial reactivities (experimental)	methyl anion affinities / kJ mol^{-1}	charges (NPA)	E(LUMO) / eV	LUMO coefficients $2p_z$ $3p_z$	LUMO
6a				-2.42		
6b				-1.93		
7				-2.09		
8				-2.66		

Calculation of k_2 (20 °C) from k_2 (–40 °)

In order to calculate second-order rate constants k_2 (20 °C) from k_2 (–40 °C) and Eyring activation entropy $\Delta S^{\ddagger}$ = −111 J mol^{-1} K^{-1}, the following transformation of the Eyring equation was used:

$$k_{T_2} = \mathrm{e}^{\left\{\ln T_2 + \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^{\neq}}{R} - \left[\frac{T_1}{T_2}\left(\ln\frac{T_1}{k_{T_1}} + \ln\frac{k_b}{h} + \frac{\Delta S^{\neq}}{R}\right)\right]\right\}} \tag{S3}$$

k_{T_2} second-order rate constant at temperature T_2

k_{T_1} second-order rate constant at temperature T_1

k_b Boltzman’s constant

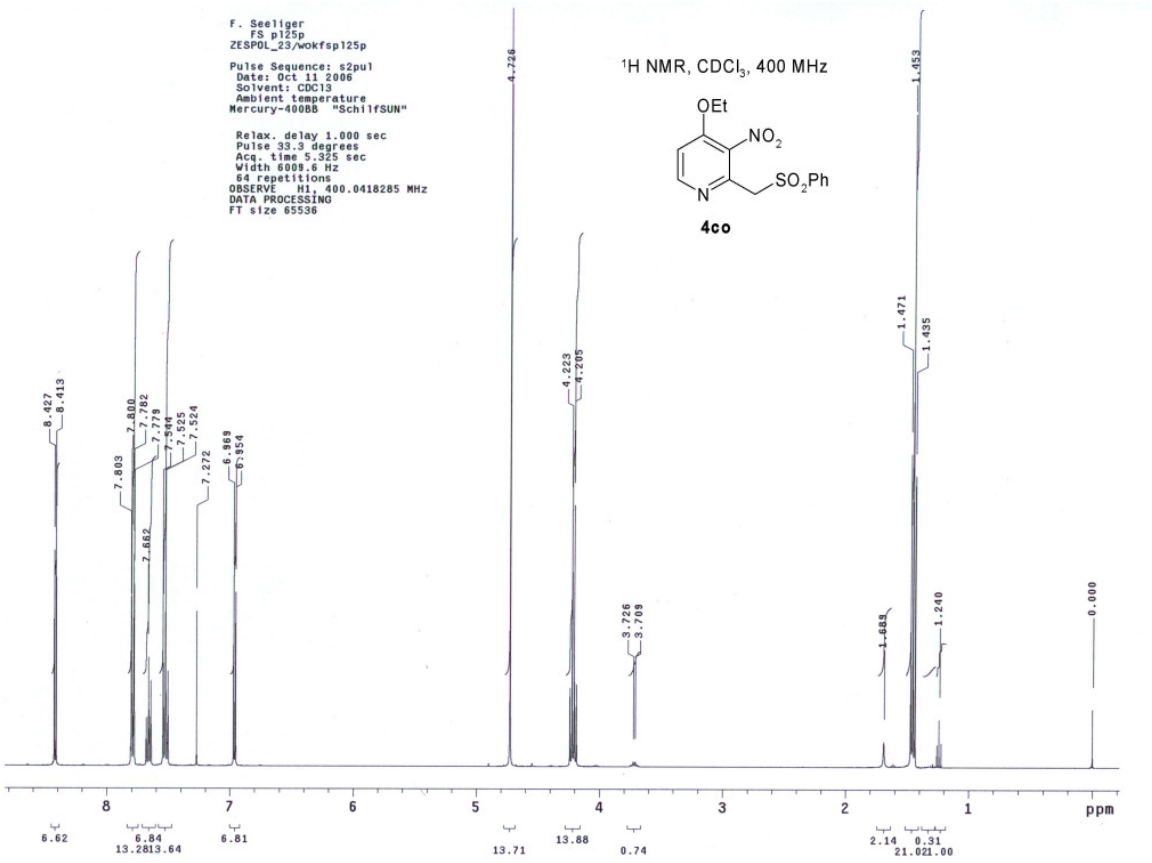
h Planck's constant

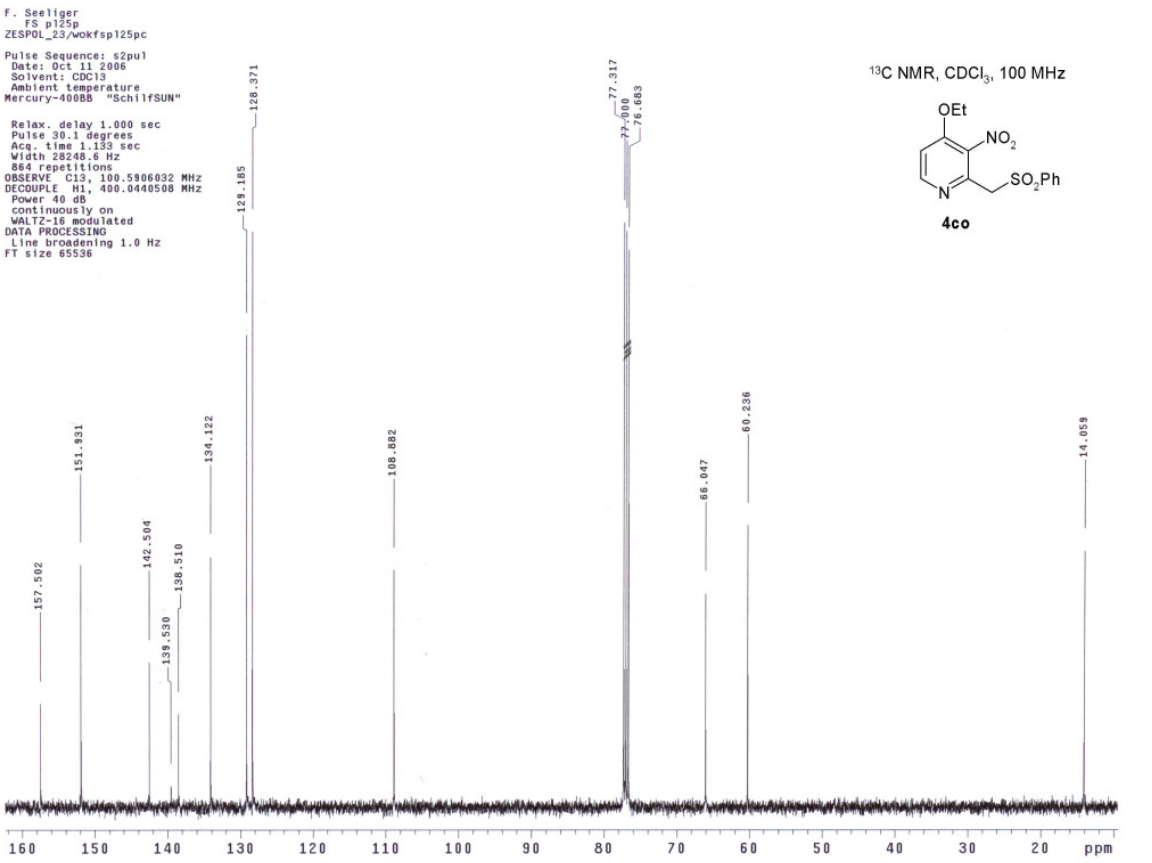
$\Delta S^{\ddagger}$ Eyring activation entropy

R Gas constant

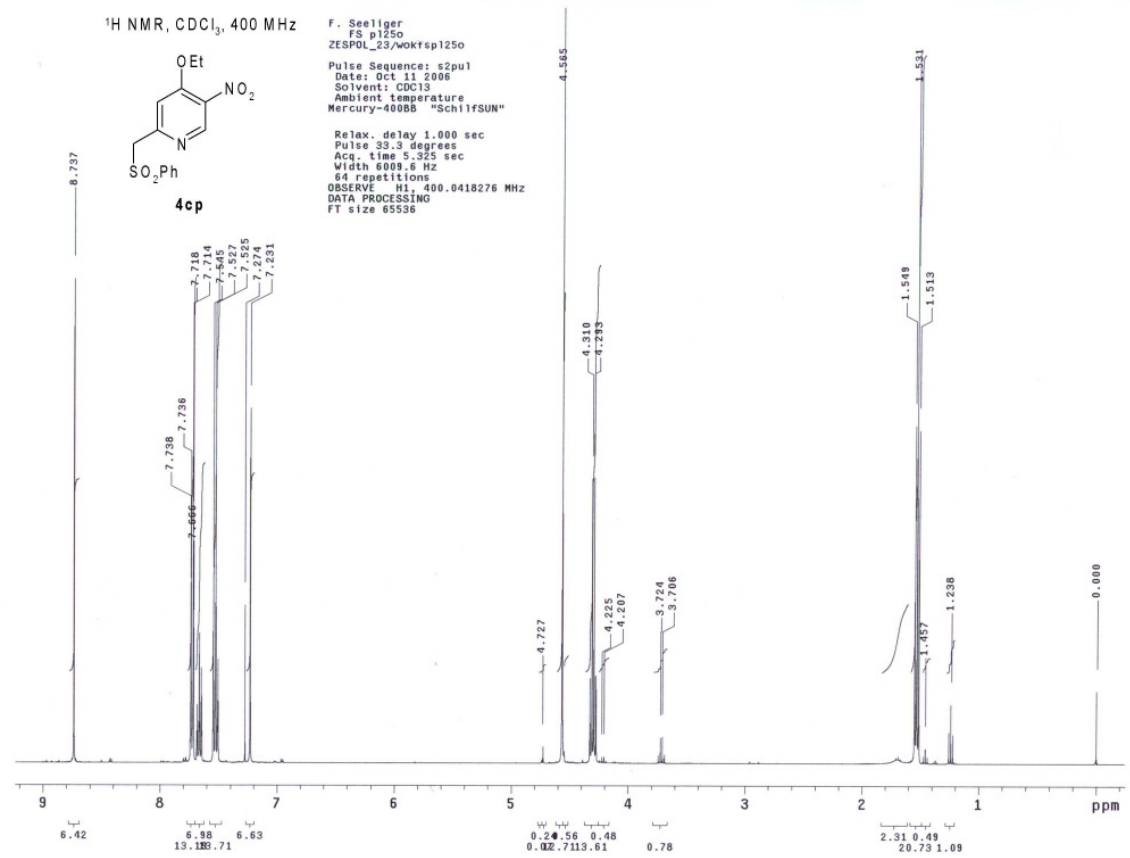
NMR spectra

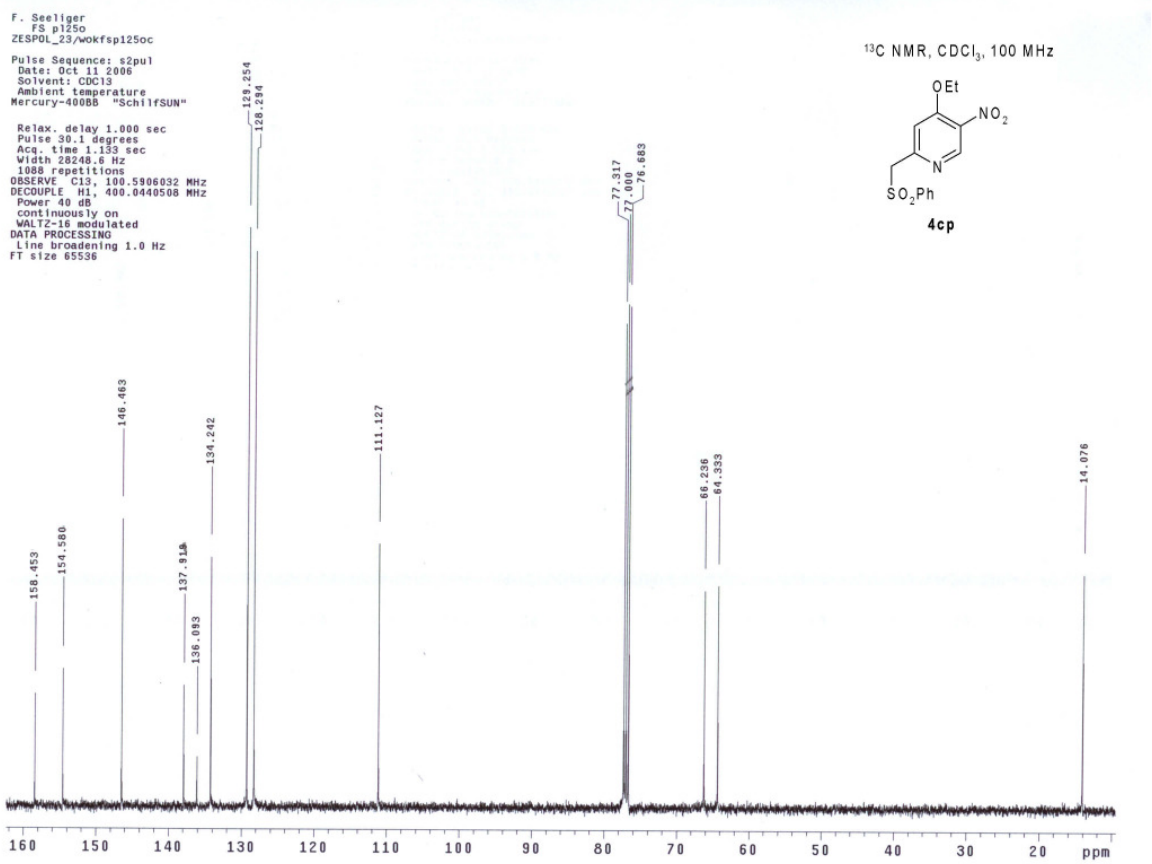
4co



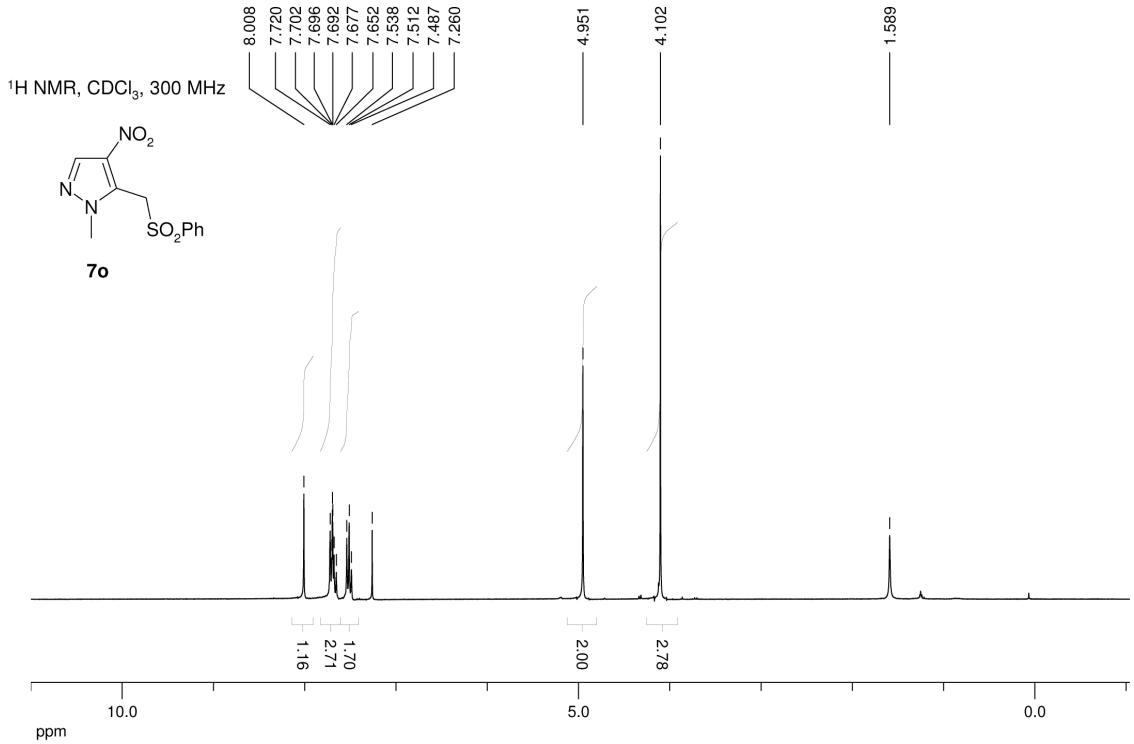


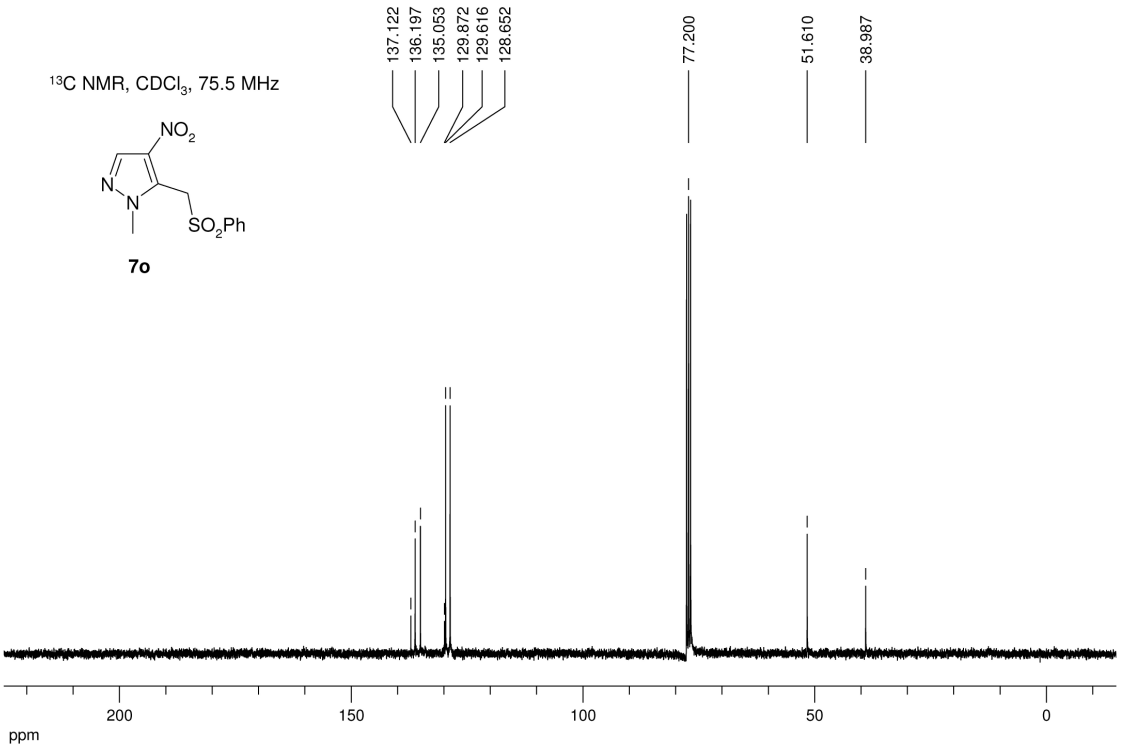
4cp


1H NMR, CDCl3, 400 MHz
OEt
NO2
N
SO2Ph
4cp
F. Seeliger
FS p125o
ZESPOL_23/wokfsp125o
Pulse Sequence: s2pul
Date: Oct 11 2006
Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 1.000 sec
Pulse 33.3 degrees
Acq. time 5.325 sec
Width 6009.6 Hz
64 repetitions
OBSERVE H1, 400.0418276 MHz
DATA PROCESSING
FT size 65536
8.737
7.738
7.736
7.718
7.714
7.645
7.642
7.525
7.274
7.231
4.727
4.565
4.310
4.293
4.225
4.207
3.724
3.706
1.549
1.531
1.513
1.457
1.238
0.000
ppm

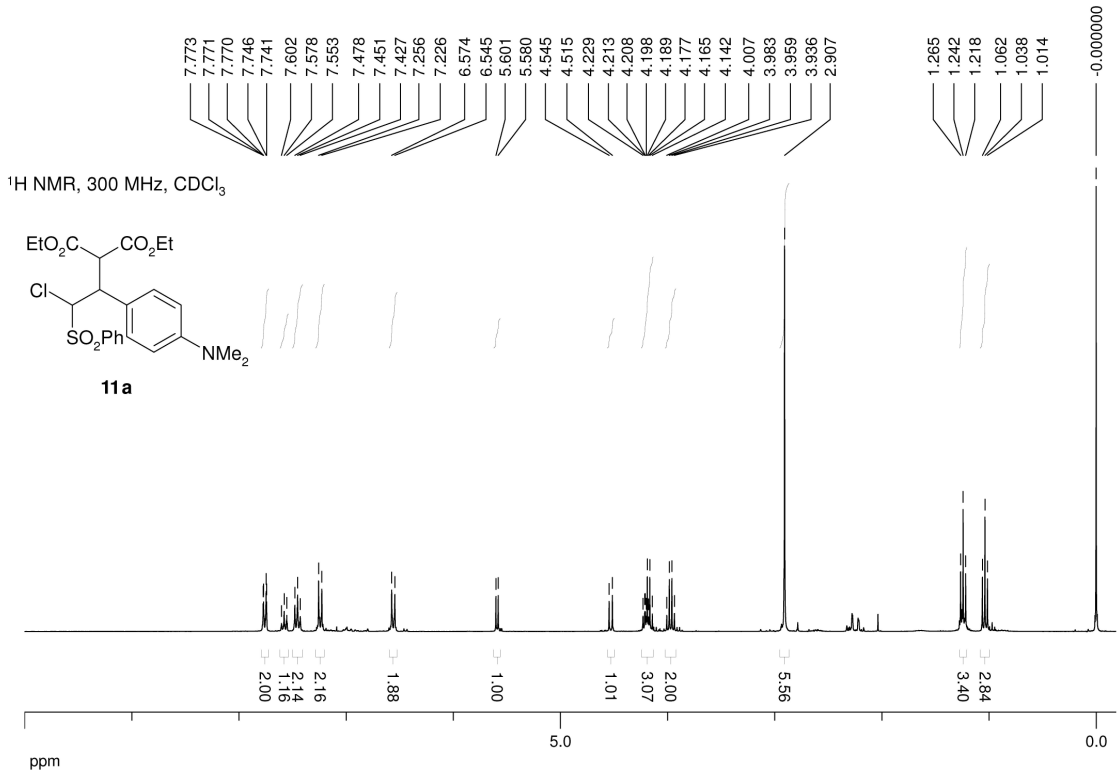

F. Seeliger
FS p125o
ZESPOL_23/wokfsp125oc
Pulse Sequence: s2pul
Date: Oct 11 2006
Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 1.000 sec
Pulse 30.1 degrees
Acq. time 1.133 sec
Width 28248.6 Hz
1088 repetitions
OBSERVE C13, 100.5906032 MHz
DECOUPLE H1, 400.0440508 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
13C NMR, CDCl3, 100 MHz
OEt
NO2
N
SO2Ph
4cp
158.453
154.580
146.463
137.918
136.093
134.242
129.254
128.284
111.127
77.317
77.000
76.683
66.236
64.333
14.076
ppm

7o


8.008
7.720
7.702
7.696
7.692
7.677
7.652
7.538
7.512
7.487
7.260
4.951
4.102
1.589
^{1}H NMR, $CDCl_3$, 300 MHz
NO_2
N
N
SO_2Ph
7o
1.16
2.71
1.70
2.00
2.78
10.0
5.0
0.0
ppm


137.122
136.197
135.053
129.872
129.616
128.652
77.200
51.610
38.987
^{13}C NMR, $CDCl_3$, 75.5 MHz
NO_2
N
N
SO_2Ph
7o
200
150
100
50
0
ppm

11a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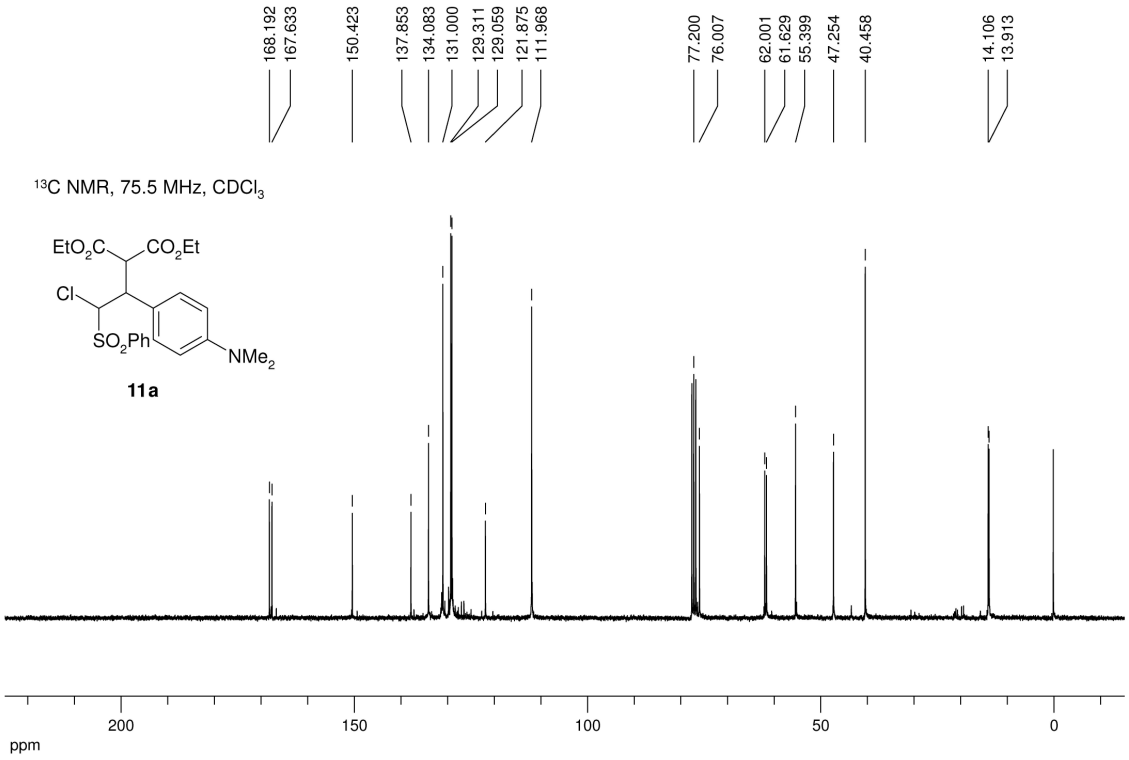
7.771
7.770
7.746
7.741
7.602
7.578
7.553
7.478
7.451
7.427
7.256
7.226
6.574
6.545
5.601
5.580
4.545
4.515
4.229
4.213
4.208
4.198
4.189
4.177
4.165
4.142
4.007
3.983
3.959
3.936
2.907
1.265
1.242
1.218
1.062
1.038
1.014
-0.000000
1H NMR, 300 MHz, CDCl3
EtO2C
CO2Et
Cl
SO2Ph
NMe2
11a
2.00
2.14
1.16
2.16
1.88
1.00
1.01
3.07
2.00
5.56
3.40
2.84
5.0
0.0
ppm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167.633
150.423
137.853
134.083
131.000
129.311
129.059
121.875
111.968
77.200
76.007
62.001
61.629
55.399
47.254
40.458
14.106
13.913
13C NMR, 75.5 MHz, CDCl3
EtO2C
CO2Et
Cl
SO2Ph
NMe2
11a
200
150
100
50
0
ppm