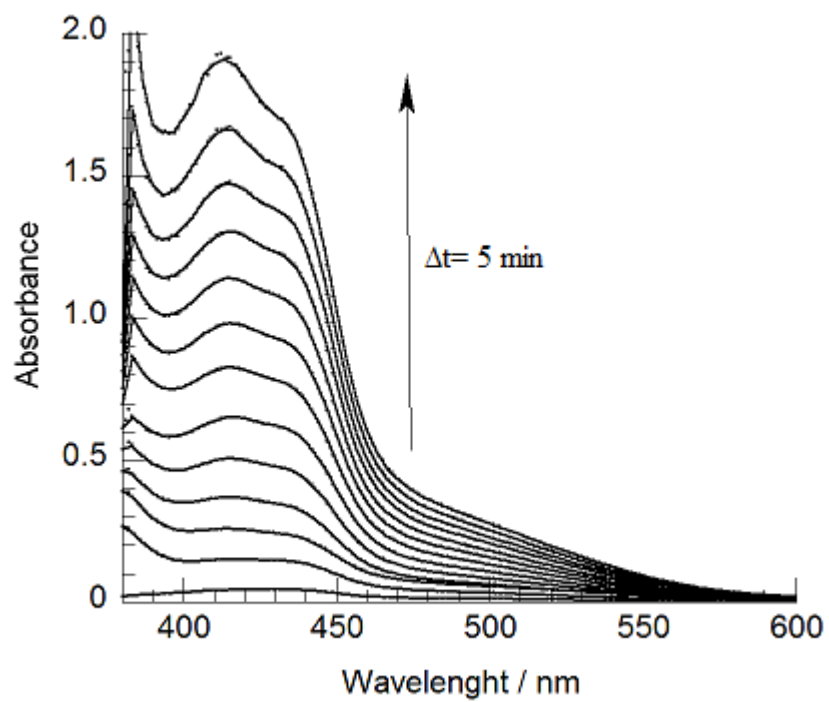


## Supplementary Material to the Paper

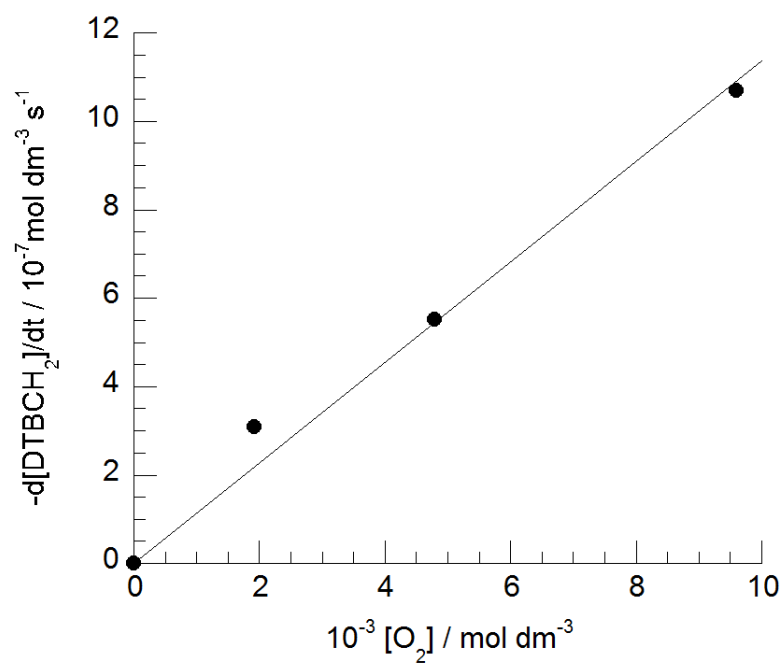
### Oxidation of 3,5-di-*tert*-butylcatechol and 2-aminophenol by molecular oxygen catalyzed by an organocatalyst†

Gábor Székely, Nárcisz Bagi, József Kaizer\* and Gábor Speier\*

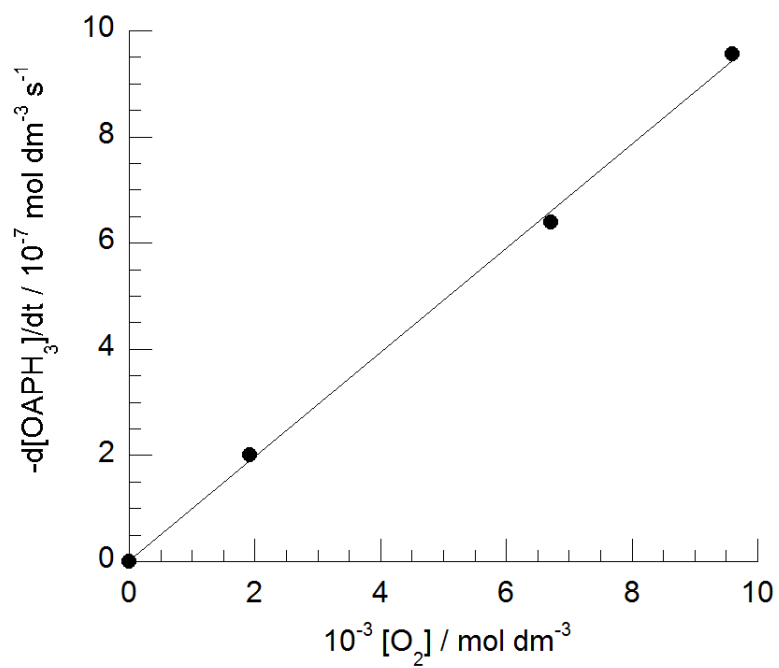
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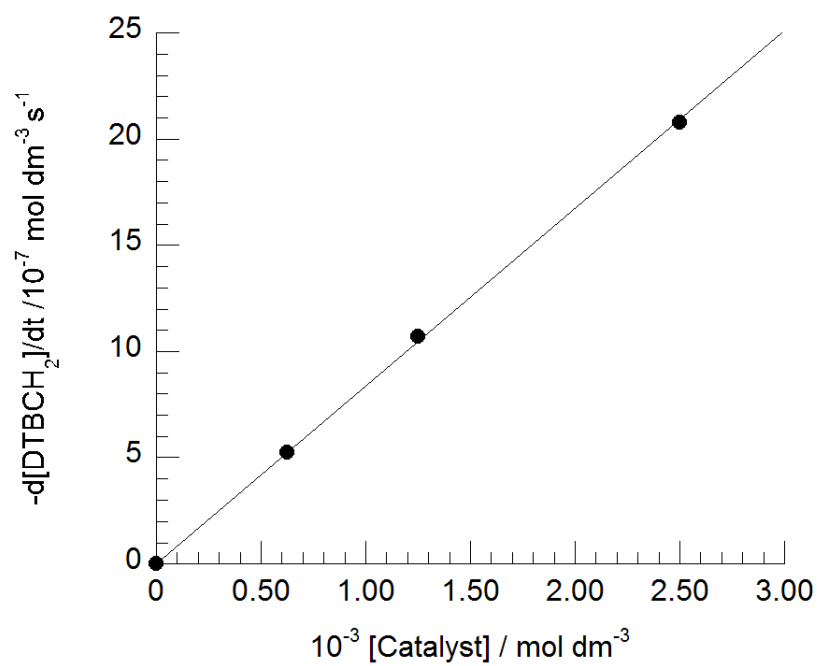
**Figure 1.** The catalytic oxidation of OAPH<sub>3</sub> followed by UV-vis spectroscopy. [OAPH<sub>3</sub>] =  $11.25 \times 10^{-2}$  M, [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$  M, [O<sub>2</sub>] =  $9.5 \times 10^{-3}$  M, T = 298.15 K, 20 mL MeOH.



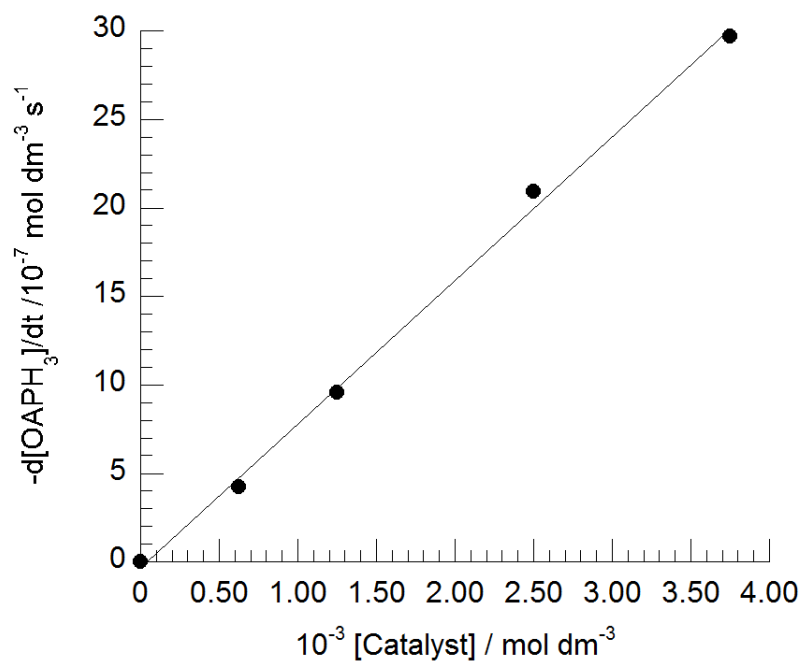
**Figure 2.** Plot of oxidation of DTBCH<sub>2</sub> versus dioxygen concentration. [DTBCH<sub>2</sub>] =  $12.5 \times 10^{-2}$  M, [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$  M, T = 298.15 K, 10 mL MeOH.



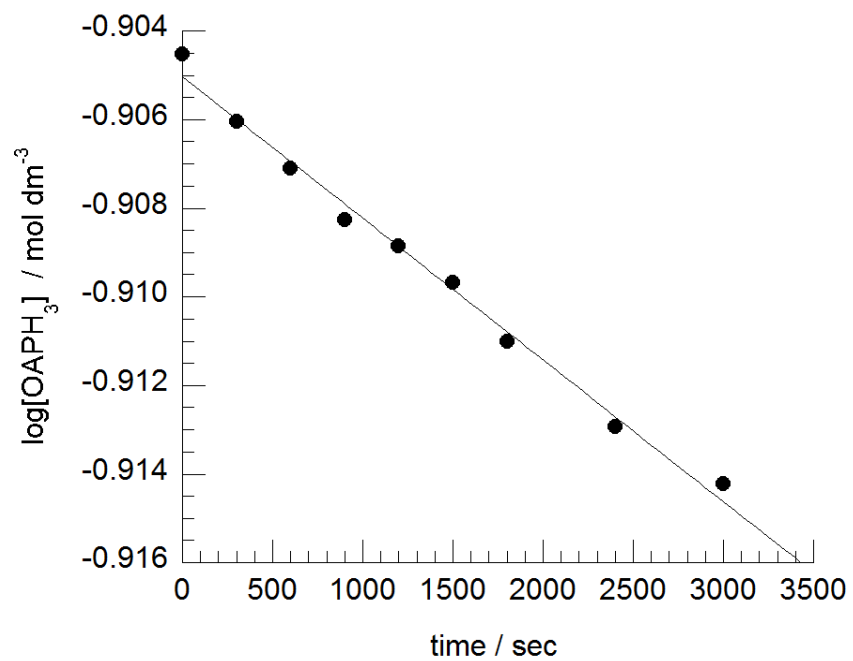
**Figure 3.** Plot of oxidation of OAPH<sub>3</sub> versus dioxygen concentration. [OAPH<sub>3</sub>] =  $12.5 \times 10^{-2}$  M, [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$  M, T = 298.15 K, 20 mL MeOH.



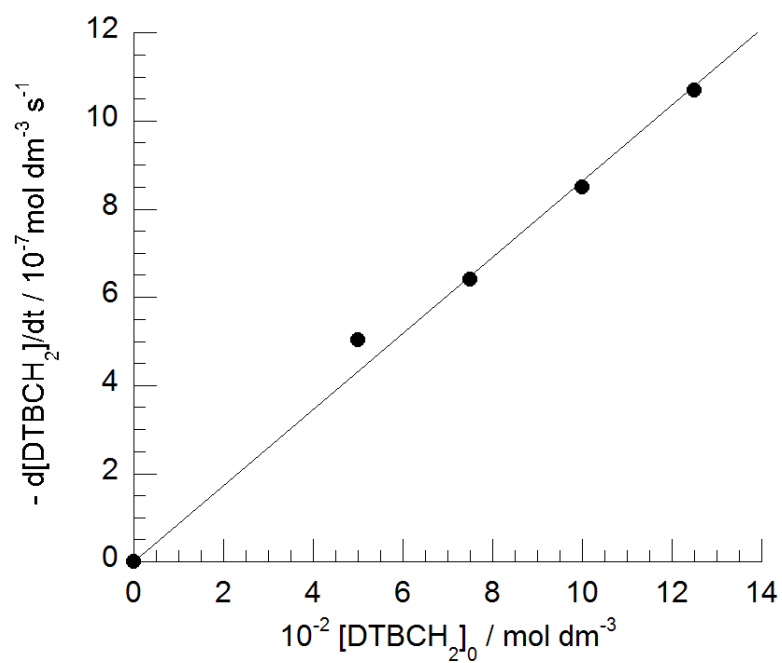
**Figure 4.** The dependence of reaction rate of the oxidation of DTBCH<sub>2</sub> on the catalyst concentration. [DTBCH<sub>2</sub>] = 12.5 × 10<sup>-2</sup> M, [O<sub>2</sub>] = 9.5 × 10<sup>-3</sup> M, T = 298.15 K, 10 mL MeOH.



**Figure 5.** The dependence of reaction rate of the oxidation of OAPH<sub>3</sub> on the catalyst concentration. [OAPH<sub>3</sub>] = 12.5 × 10<sup>-2</sup> M, [O<sub>2</sub>] = 9.5 × 10<sup>-3</sup> M, T = 298.15 K, 20 mL MeOH.

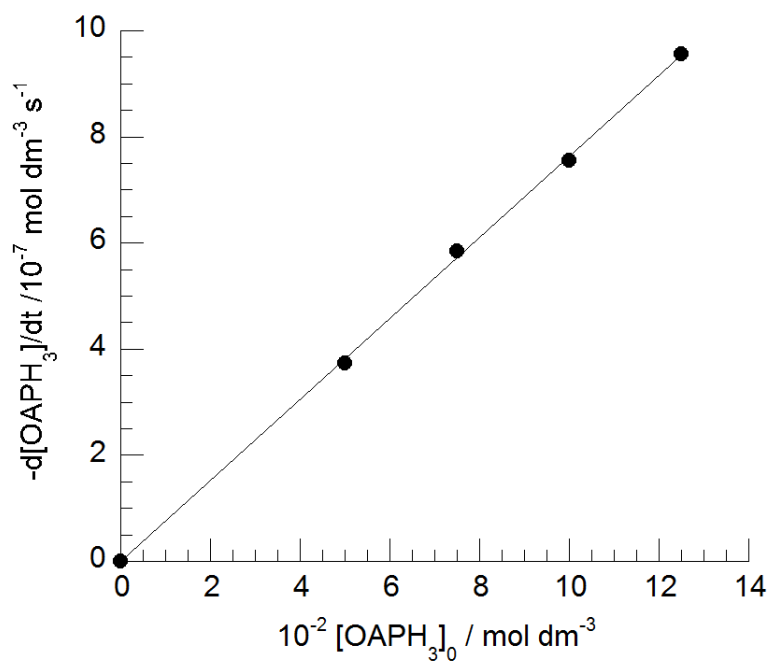


**Figure 6.** Time course of the oxidation of OAPH<sub>3</sub>. [OAPH<sub>3</sub>] =  $12.5 \times 10^{-2}$  M, [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$ , [O<sub>2</sub>] =  $9.5 \times 10^{-3}$  M, T = 298.15 K, 20 mL MeOH.

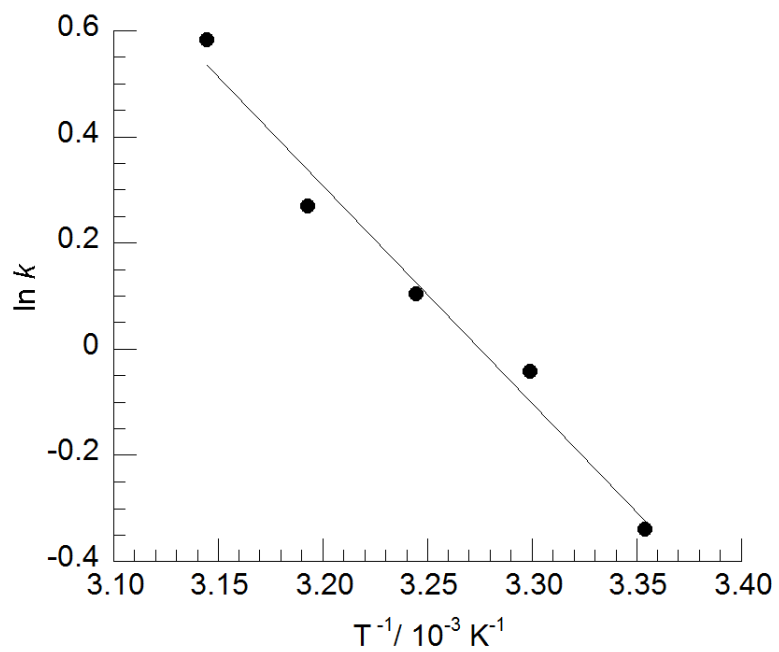


**Figure 7.** Rate dependence of the oxidation of DTBCH<sub>2</sub> on the initial concentration of DTBCH<sub>2</sub>. [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$  M, [O<sub>2</sub>] =  $9.5 \times 10^{-3}$  M, T = 298.15 K, 10 mL MeOH.

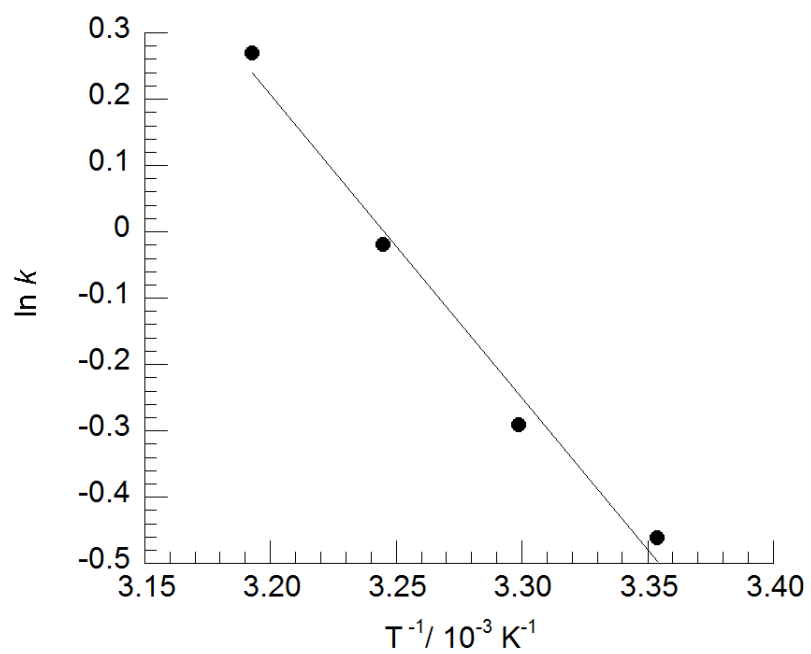




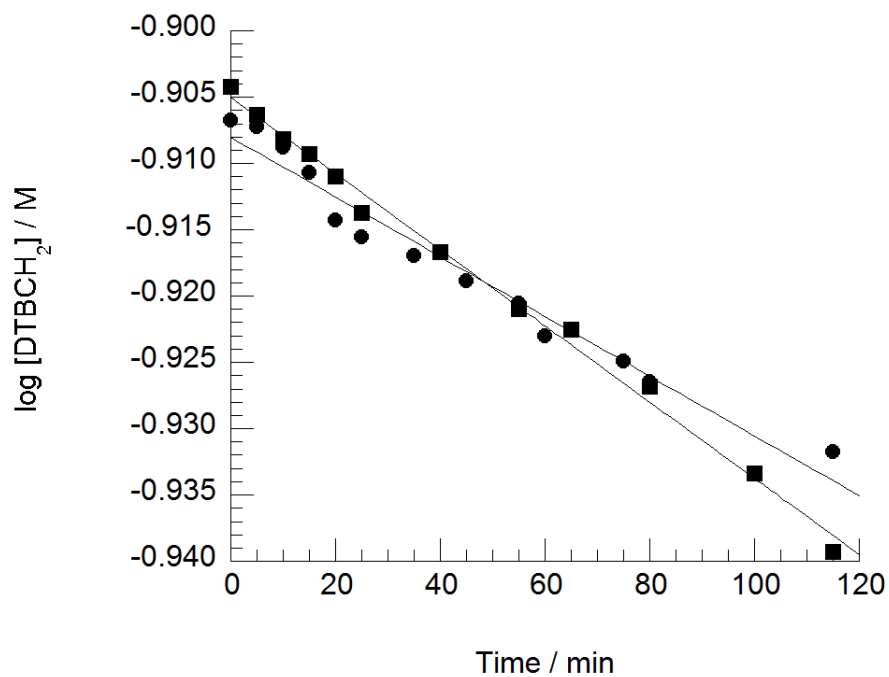
**Figure 8.** Rate dependence of the oxidation of OAPH<sub>3</sub> on the initial concentration of OAPH<sub>3</sub>. [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$  M, [O<sub>2</sub>] =  $9.5 \times 10^{-3}$  M, T = 298.15 K, 20 mL MeOH.



**Figure 9.** The Arrhenius plot on the oxidation of DTBCH<sub>2</sub>.



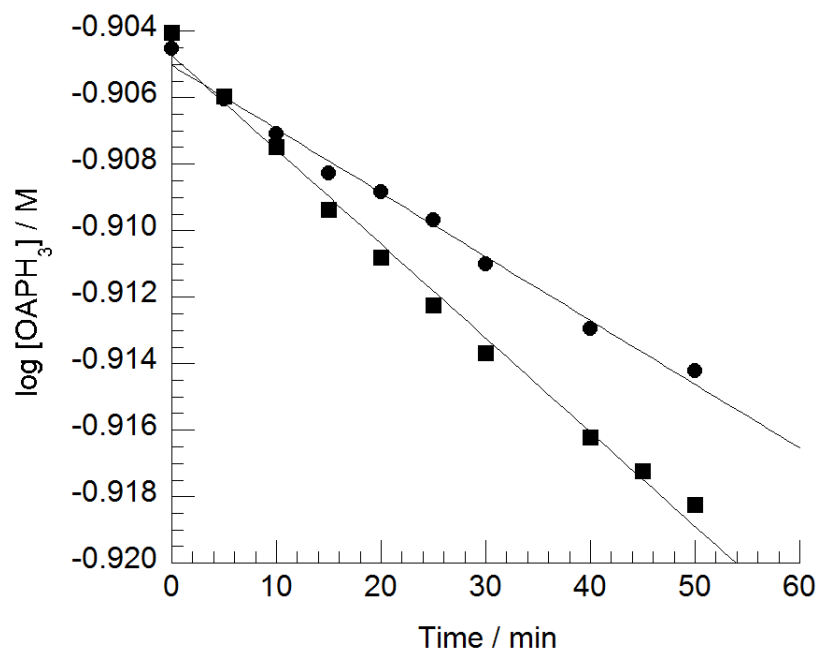
**Figure 10.** The Arrhenius plot on the oxidation of OAPH<sub>3</sub>.



**SFigure 11.** The Kinetic Isotope Effect data of DTBCH<sub>2</sub>.

(■ in MeOH, ● in MeOD)

[DTBCH<sub>2</sub>] =  $12.5 \times 10^{-2}$  M, [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$ , [O<sub>2</sub>] =  $9.5 \times 10^{-3}$  M,  
T = 298.15 K, 10 mL MeOD/MeOH.



**SFigure 12.** The Kinetic Isotope Effect data of OAPH<sub>3</sub>.

(■ in MeOH, ● in MeOD)

[OAPH<sub>3</sub>] =  $12.5 \times 10^{-2}$  M, [1,3,2-oxazaphosphole] =  $1.25 \times 10^{-3}$ , [O<sub>2</sub>] =  $9.5 \times 10^{-3}$  M,  
T = 298.15 K, 20 mL MeOD/MeOH.

**STable 1.** The kinetic data of the catalytic oxidation of DTBCH<sub>2</sub>.

Entry	Temp. (°C)	[O <sub>2</sub> ] (10 <sup>-3</sup> mol dm <sup>-3</sup> )	[1,3,2-oxazaphosphole] (10 <sup>-3</sup> mol dm <sup>-3</sup> )	[DTBCH <sub>2</sub> ] (10 <sup>-2</sup> mol dm <sup>-3</sup> )	-d[DTBCH <sub>2</sub> ]/dt (10 <sup>-7</sup> Ms <sup>-1</sup> )	<i>k</i> <sub>obs</sub> (M <sup>-2</sup> s <sup>-1</sup> )
1.	25	9.50	1.25	5.00	5.02 ± 0.30	0.84±0.08
2.	25	9.50	1.25	7.50	6.41 ± 0.17	0.71±0.09
3.	25	9.50	1.25	10.00	8.49 ± 0.03	0.70±0.09
4.	25	9.50	1.25	12.50	10.69 ±0.24	0.71±0.09
5.	25	9.50	0.625	12.50	5.25 ± 0.27	0.70±0.09
6.	25	9.50	2.500	12.50	20.80 ± 0.24	0.69±0.09
7. *	25	1.92	1.25	12.50	3.08 ± 0.12	1.03±0.10
8.	25	4.80	1.25	12.50	5.52 ± 0.25	0.74±0.09
						<b>avg.:0.76±0.11</b>
9.	30	9.48	1.25	12.50	14.20 ± 0.57	0.96±0.10
10.	35	9.46	1.25	12.50	16.40 ± 0.78	1.11±0.11
11.	40	9.44	1.25	12.50	19.32 ± 1.07	1.31±0.11
12.	45	9.42	1.25	12.50	24.40 ± 1.55	1.79±0.11
13.	25	9.50	1.25	12.50	10.20 ± 0.22	0.69±0.09

Mean value of the kinetic constant *k*<sub>obs</sub> and its standard deviations  $\sigma(k_{\text{obs}})$  were calculated as

$$k_{\text{obs}} = (\sum_i w_i k_i / \sum_i w_i) \text{ and } \sigma(k_{\text{obs}}) = (\sum_i w_i (k_i - k_{\text{obs}})^2 / (n-1) \sum_i w_i)^{1/2}, \text{ where } w_i = 1/\sigma_i^2$$

\* Under air

13. in MeOD

**STable 2.** The kinetic data of the catalytic oxidation of OAPH<sub>3</sub>.

Entry	Temp. (°C)	[O <sub>2</sub> ] (10 <sup>-3</sup> mol dm <sup>-3</sup> )	[1,3,2-oxazaphosphole] (10 <sup>-3</sup> mol dm <sup>-3</sup> )	[OAPH <sub>3</sub> ] (10 <sup>-2</sup> mol dm <sup>-3</sup> )	d[OAPH <sub>3</sub> ]/dt (10 <sup>-7</sup> Ms <sup>-1</sup> )	<i>k</i> <sub>obs</sub> (M <sup>-2</sup> s <sup>-1</sup> )
1.	25	9.50	1.25	5.00	3.73 ± 0.25	0.61±0.03
2.	25	9.50	1.25	7.50	5.85 ± 0.18	0.63±0.03
3.	25	9.50	1.25	10.00	7.56 ± 0.12	0.62±0.03
4.	25	9.50	1.25	12.50	9.56 ± 0.10	0.62±0.03
5.	25	9.50	0.63	12.50	4.26 ± 0.23	0.55±0.03
6.	25	9.50	2.50	12.50	20.90 ± 0.35	0.68±0.04
7.	25	9.50	3.75	12.50	29.70 ± 0.65	0.65±0.04
8. *	25	1.92	1.25	12.50	2.00 ± 0.32	0.65±0.04
9.	25	6.72	1.25	12.50	6.40 ± 0.16	0.59±0.03
						<b>avg.:0.62±0.03</b>
10.	25	9.50	1.25	12.50	9.56 ± 0.10	0.62±0.03
11.	30	9.48	1.25	12.50	11.25 ± 0.10	0.75±0.03
12.	35	9.46	1.25	12.50	14.70 ± 0.13	0.98±0.04
13.	40	9.44	1.25	12.50	19.50 ± 0.29	1.31±0.04
14.	25	9.50	1.25	12.50	6.53 ± 0.10	0.44±0.02

Mean value of the kinetic constant *k*<sub>obs</sub> and its standard deviations  $\sigma(k_{\text{obs}})$  were calculated as

$$k_{\text{obs}} = (\sum_i w_i k_i / \sum_i w_i) \text{ and } \sigma(k_{\text{obs}}) = (\sum_i w_i (k_i - k_2)^2 / (n-1) \sum_i w_i)^{1/2}, \text{ where } w_i = 1/\sigma_i^2$$

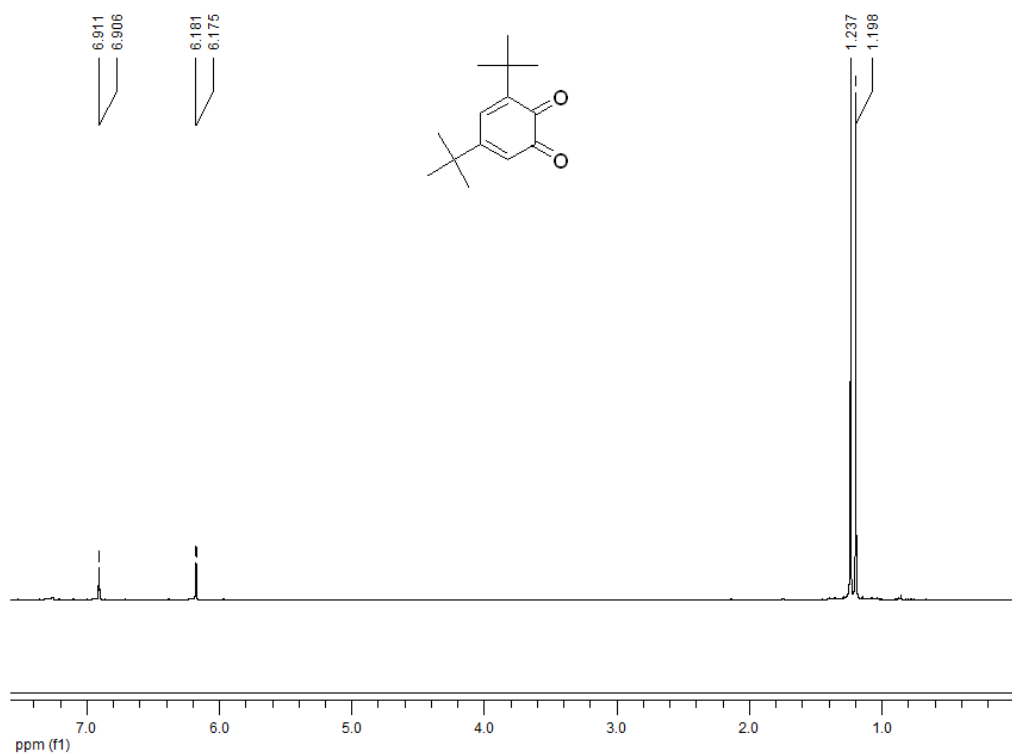
\* Under air

14. in MeOD

## Experiments details

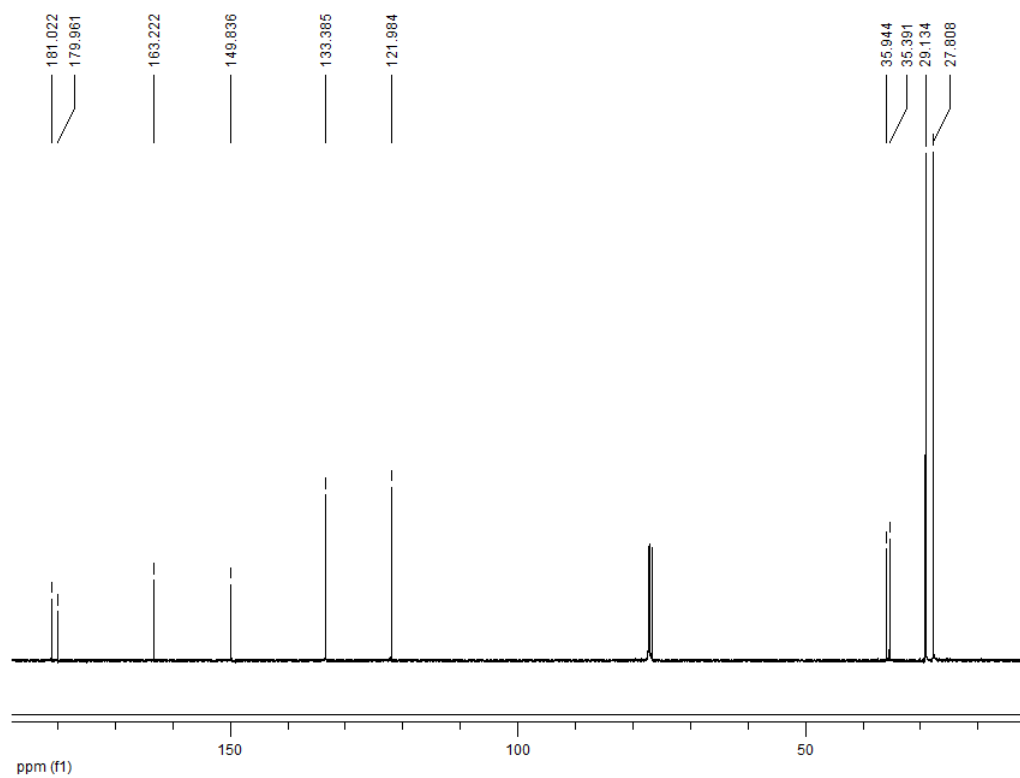
**Instruments:** Gas chromatographic – Mass Spectrometric (GC-MS) analyses were carried out on a GCMS-QP2010 SE instrument with secondary electron multiplier detector. NMR spectrum:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected on 400 MHz NMR spectrometers (Bruker Avance) using DMSO-d<sub>6</sub> and  $\text{CDCl}_3$  as solvent. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual protium in the NMR solvent ( $\delta$  (DMSO-d<sub>6</sub>) = 2.50, 39.52 and  $\delta$ ( $\text{CDCl}_3$ ) = 7.24, 77)).





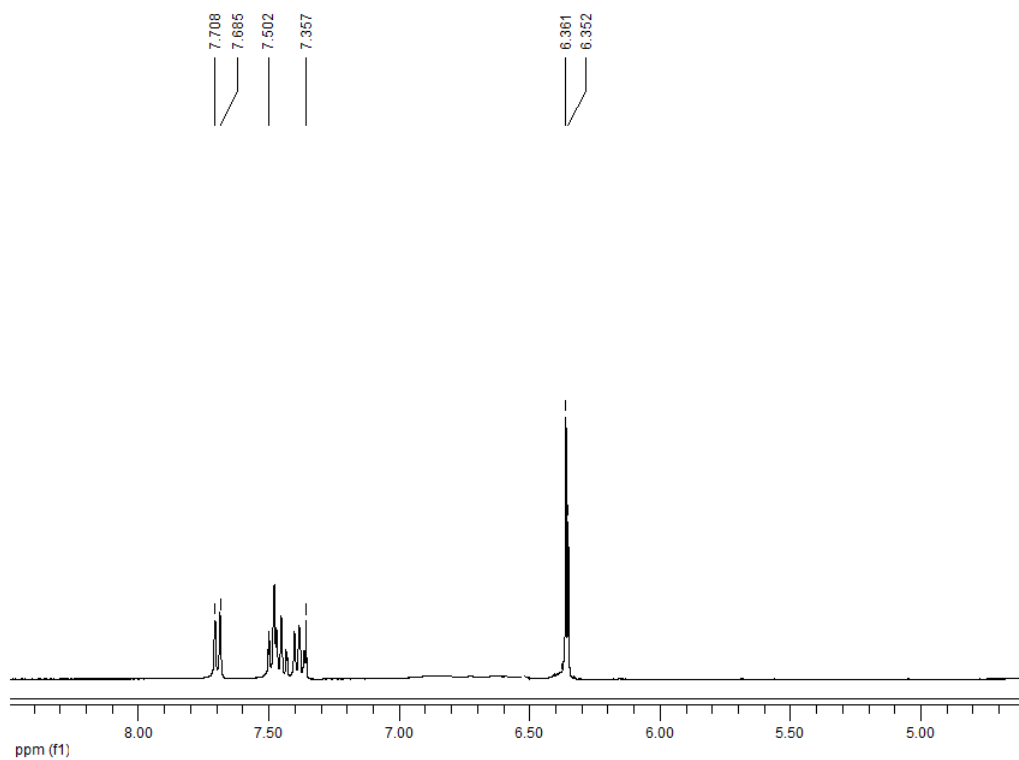
**Figure 13.** <sup>1</sup>H NMR spectrum of 3,5-di-*tert*-butylquinone.

(Uyanik, M.; Mutsuga, T.; Ishihara, K. *Molecules* **2012**, *17*, 8604-8616.)



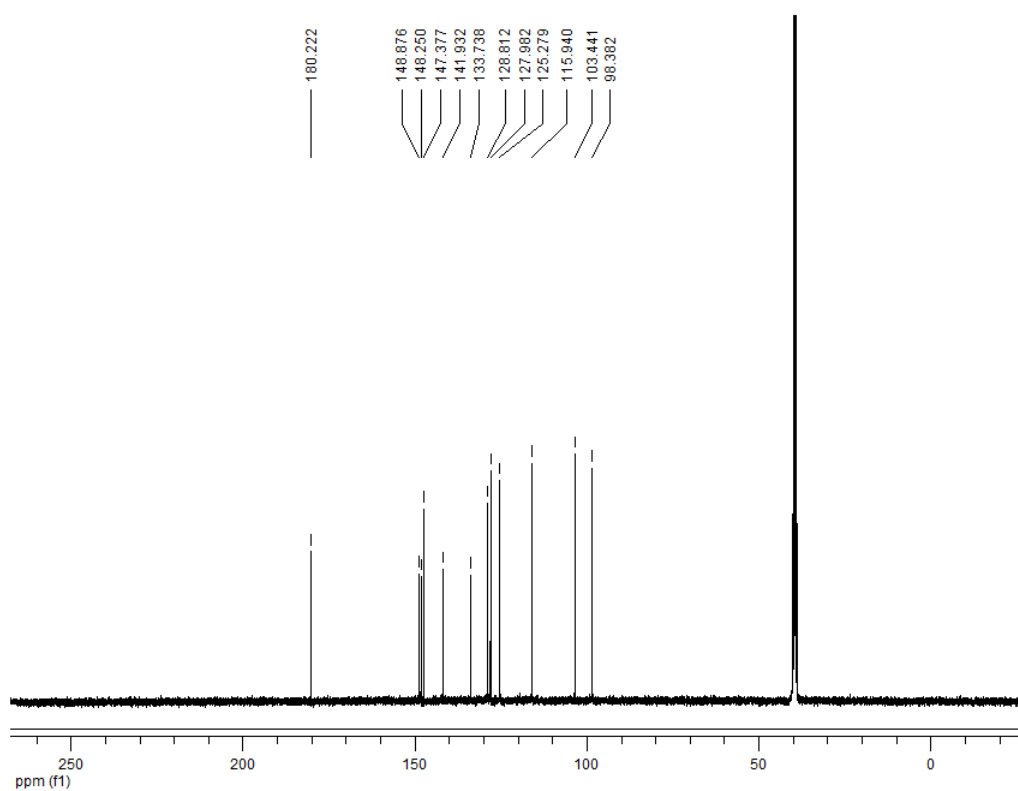
**Figure 14.**  $^{13}\text{C}$  NMR spectrum of 3,5-di-*tert*-butylquinone.

(Uyanik, M.; Mutsuga, T.; Ishihara, K. *Molecules* **2012**, *17*, 8604-8616.)



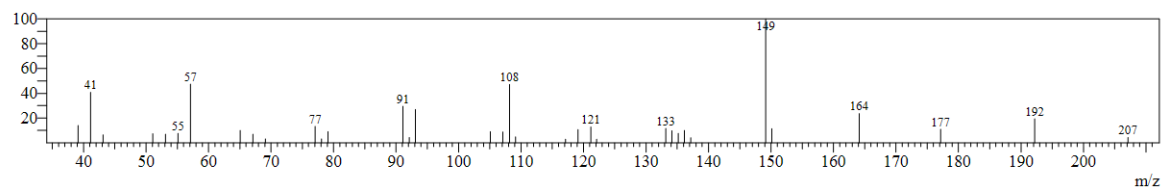
**Figure 15.** <sup>1</sup>H NMR spectrum of 2-aminophenoxazine-3-one.

(Suzuki, H., Furusko, Y., Higashi, T. Ohnishi, Y., Horinouchi, S. *J. Biol. Chem.* **2006**, *2*, 824-833.)



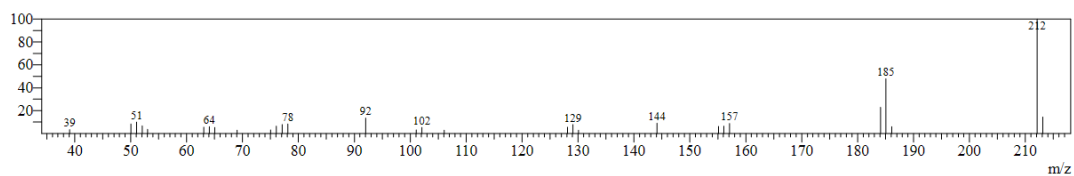
**SFigure 16.**  $^{13}\text{C}$  NMR spectrum of 2-aminophenoxazine-3-one.

(Suzuki, H., Furusko, Y., Higashi, T. Ohnishi, Y., Horinouchi, S. *J. Biol. Chem.* **2006**, *2*, 824-833.)



**Figure 17.** Mass spectrum of 3,5-di-*tert*-butylquinone.

([http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct\\_frame\\_top.cgi](http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi))



**Figure 18.** Mass spectrum of 2-aminophenoxazine-3-one.

(Friebe, A., Vilich, V., Hennig L., Kluge M., Sicker D. *Appl Environ Microbiol.* **1998**, *64*(7), 2386–2391.)