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SUPPORTING INFORMATION

Hydrogen Atom Transfer (HAT) Processes Promoted by the Quinolinimide-*N*-Oxyl Radical. A Kinetic and Theoretical Study

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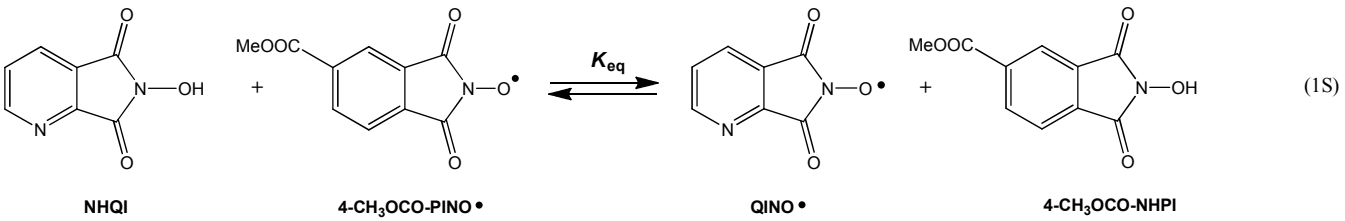
Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on a spectrometer operating at 300 MHz and 75 MHz, respectively. Spectrophotometric analyses for the HAT reactions promoted by PINO and QINO were performed with a diode array spectrophotometer thermostated by a circulating water bath. For reactions with $k_{obs} > 0.1$ s^{-1} the instrument was equipped with a rapid mixing accessory. EPR spectra were obtained using a X-band spectrometer. Laser flash photolysis experiments were carried out with an laser kinetic spectrometer providing 8 ns pulses, using the third armonic (355 nm) of a Nd:YAG laser. The laser energy was adjusted to ≤ 10 mJ/pulse by the use of the appropriate filter. The transient spectrum was obtained by a point-to-point technique, monitoring the change of absorbance (ΔA) after the laser flash at intervals of 10 nm over the spectral range 340-600 nm.

Determination of the O-H BDE values by EPR measurements

These determinations were done by using the EPR radical equilibration technique that has been largely used to measure BDE values of X-H bonds in many antioxidants.



(1S)

This consists in measuring the equilibrium constant, K_{eq}, for the hydrogen atom transfer reaction (Equation 1S) between NHQI and an appropriate reference hydroxylamine, that in the present case was represented by 4-CH_3OCO-NHPI (see Eq 1S). The equilibrating radicals were produced by photolyzing deoxygenated CH_3CN solution containing NHPI, the reference compound (in the range 0.01-0.02 M)

and di-*tert*butyl peroxide (10% v/v). The molar ratio of the two radicals was obtained from the EPR spectra and used to determine the equilibrium constant, K_{eq} (eq 2S).

$$K_{eq} = \frac{[\text{QINO}\bullet][\text{4-CH}_3\text{OCO-NHPI}]}{[\text{4-CH}_3\text{OCO-PINO}\bullet][\text{NHQI}]} \qquad (2S)$$

The equilibrium constant was found to be independent on the initial product concentrations and on the rate of initiation. The initial concentrations of the two reactants were used for this purpose since these were high enough to avoid significant consumption during the course of the experiment. Relative radical concentrations were determined by comparison of the digitized experimental spectra with computer simulated ones. In these cases an iterative least squares fitting procedure based on the systematic application of the Monte Carlo method was performed in order to obtain the experimental spectral parameters of the two species including their relative intensities.

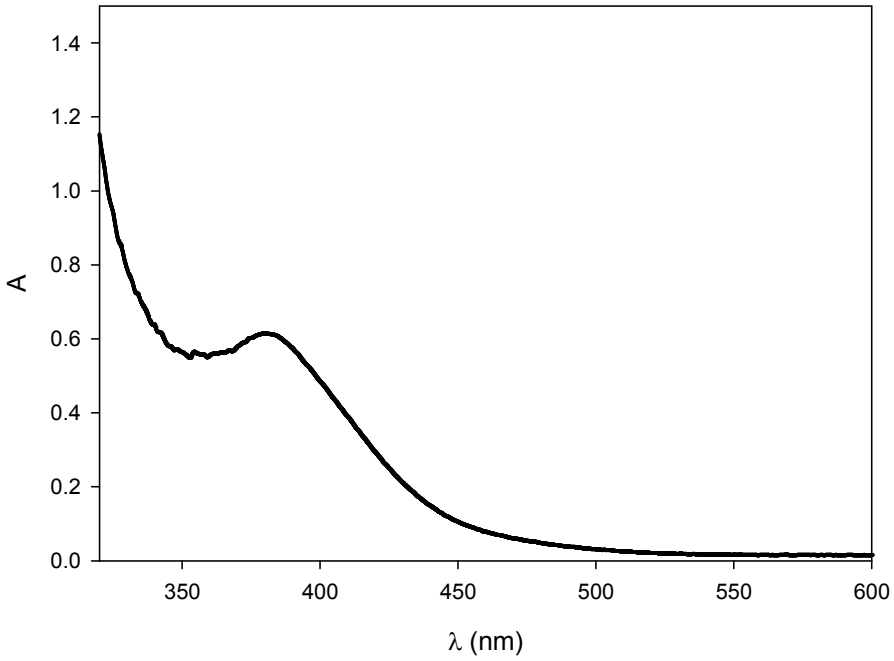


Figure S1. UV-vis spectrum of QINO generated by oxidation of NHQI (1 mM) with cerium(IV) ammonium nitrate (0.5 mM) in MeCN at T = 25 °C.

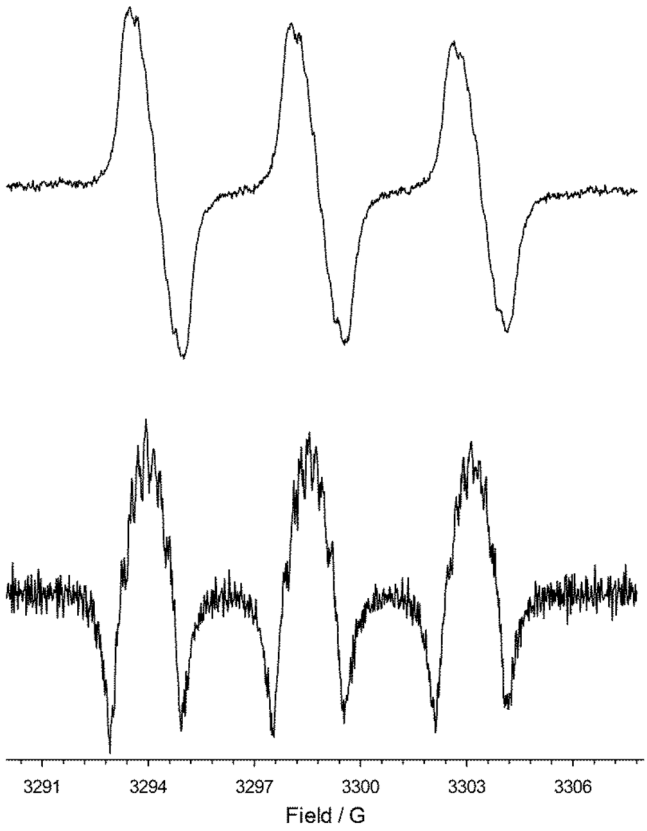


Figure S2. 1st (top) and 2nd derivative (bottom) EPR spectrum of QINO obtained by oxidation of NHQI 1 mM with cerium(IV) ammonium nitrate (CAN) 2 mM in CH_3CN at 25 °C. The 2nd derivative spectrum clearly shows unresolved hyperfine structure due to small coupling of the unpaired electron with the nitrogen and hydrogen aromatic nuclei.

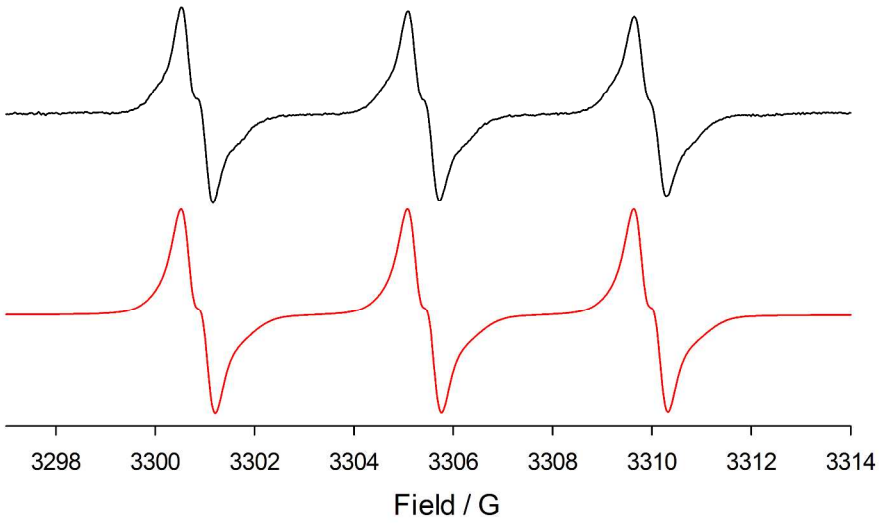


Figure S3. EPR spectrum observed under continuous irradiation of a CH_3CN solution containing di-*tert*-butyl peroxide (10% v/v) and an equimolar amount of NHQI and 4-CH_3OCO-NHPI. In red is reported the corresponding theoretical simulation.

Dependence of k_{obs} for the decay of QINO on the concentration of alkylaromatics

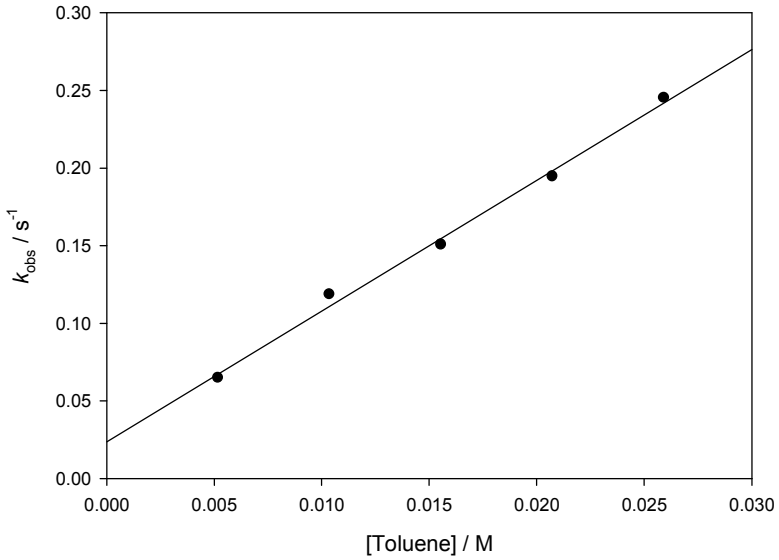


Figure S4. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of toluene in $CH_3CN/HClO_4$ 0.15 M at 25 °C (r^2=0.995).

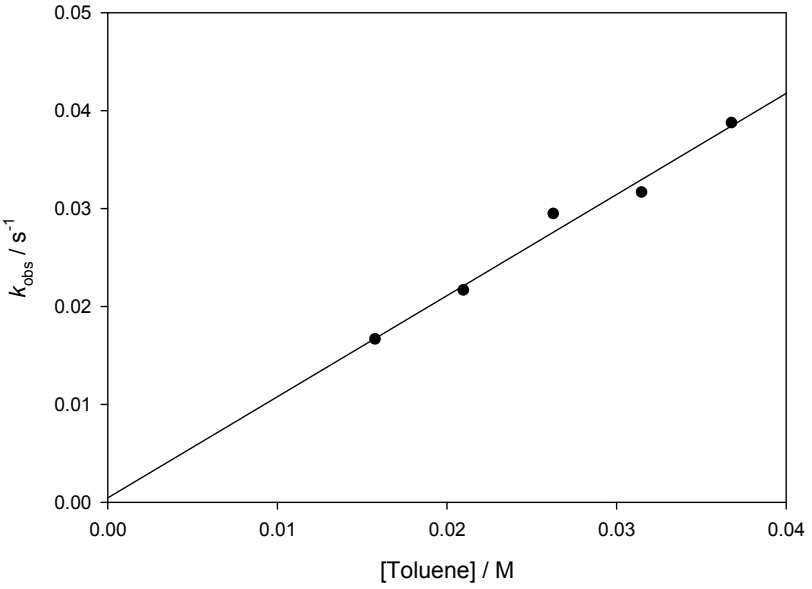


Figure S5. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of toluene in $CH_3CN/Mg(ClO_4)_2$ 0.15 M at 25 °C (r^2=0.982).

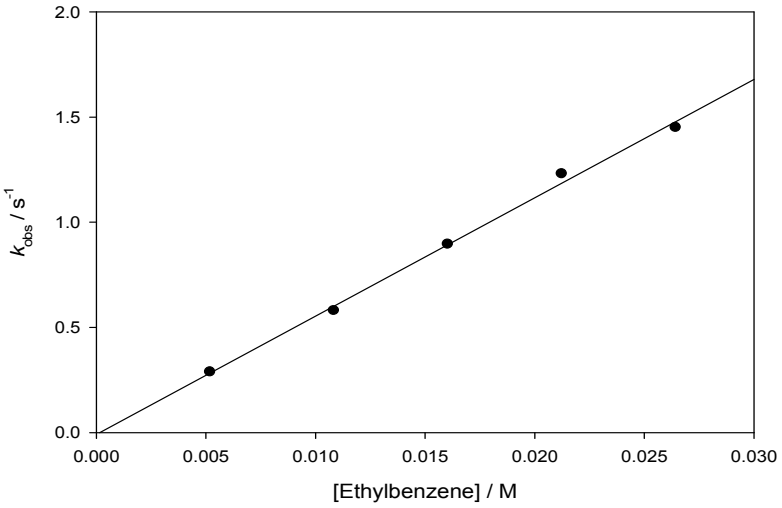


Figure S6. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of ethylbenzene in $CH_3CN/HClO_4$ 0.15 M at 25 °C (r^2=0.996).

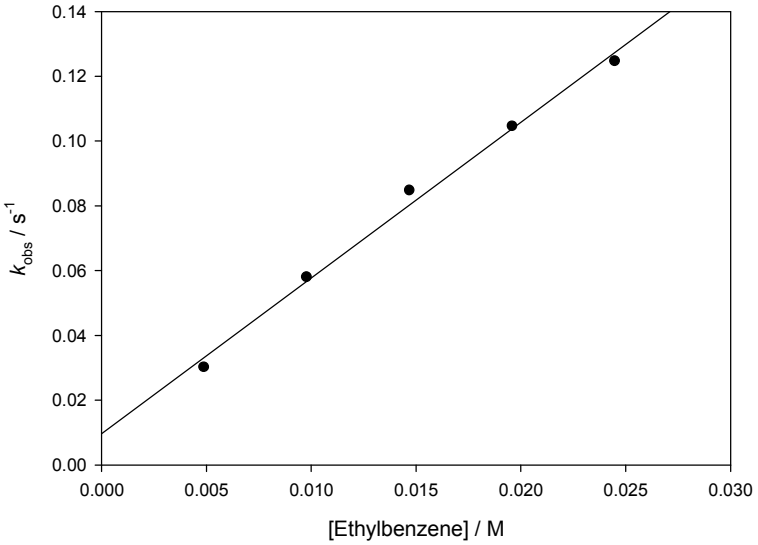


Figure S7. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of ethylbenzene in $CH_3CN/Mg(ClO_4)_2$ 0.15 M at 25 °C (r^2=0.993).

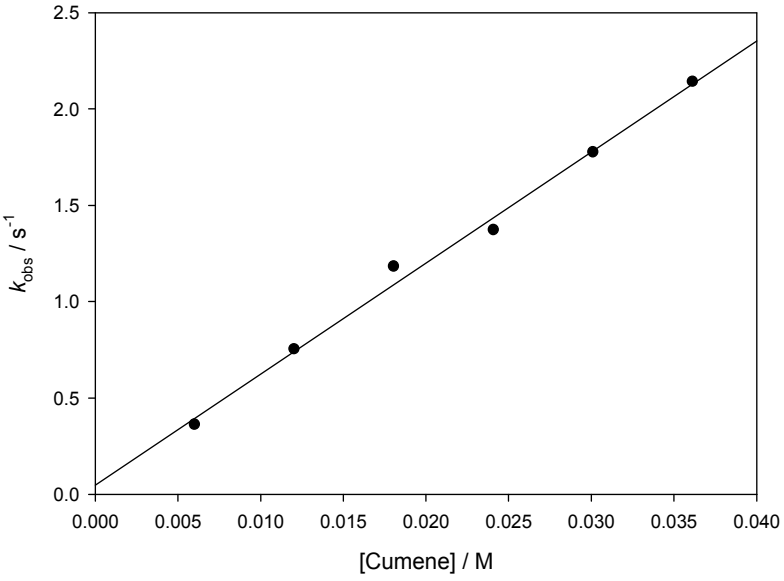


Figure S8. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of cumene in $CH_3CN/HClO_4$ 0.15 M at 25 °C (r^2=0.993).

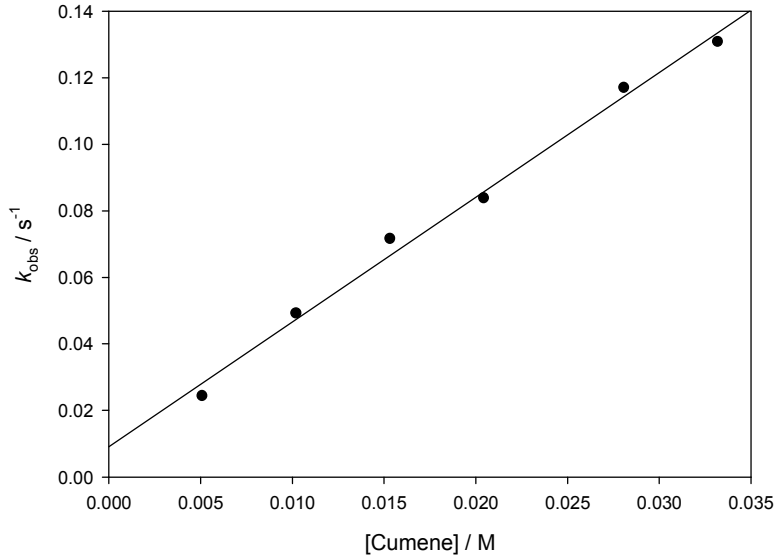


Figure S9. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of cumene in $CH_3CN/Mg(ClO_4)_2$ 0.15 M at 25 °C (r^2=0.992).

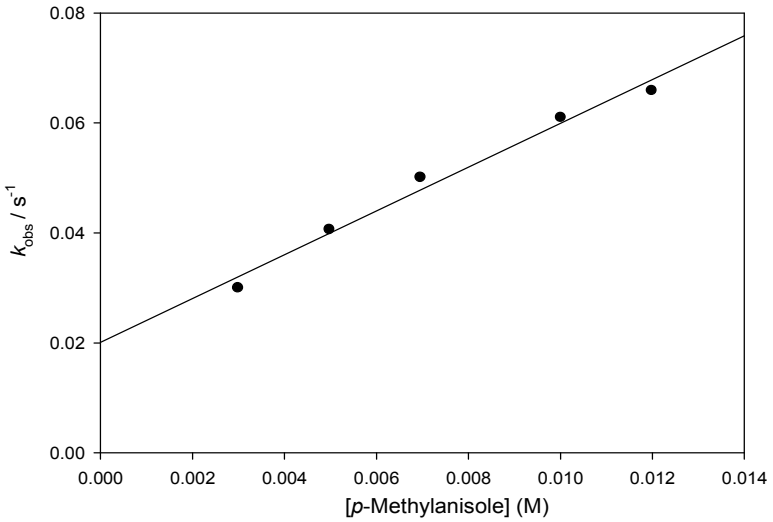


Figure S10. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *p*-methylanisole in CH_3CN at 25 °C (r^2=0.983).

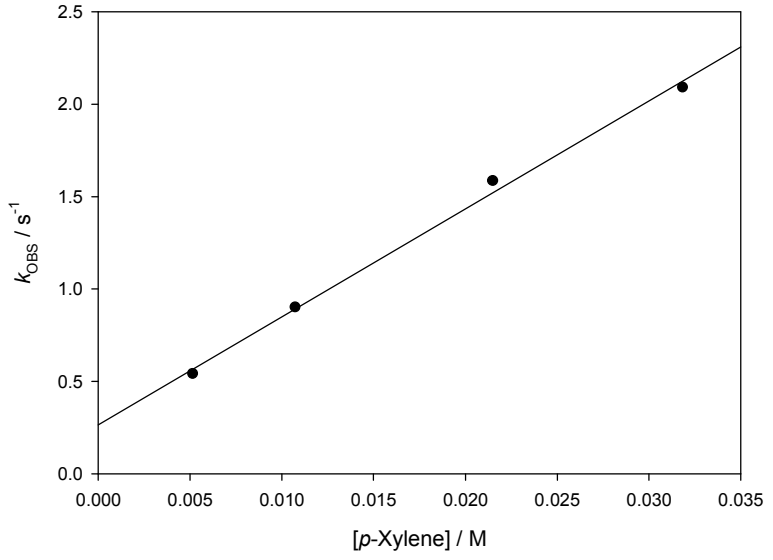


Figure S11. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *p*-xylene in $CH_3CN/HClO_4$ 0.15 M at 25 °C (r^2=0.996).

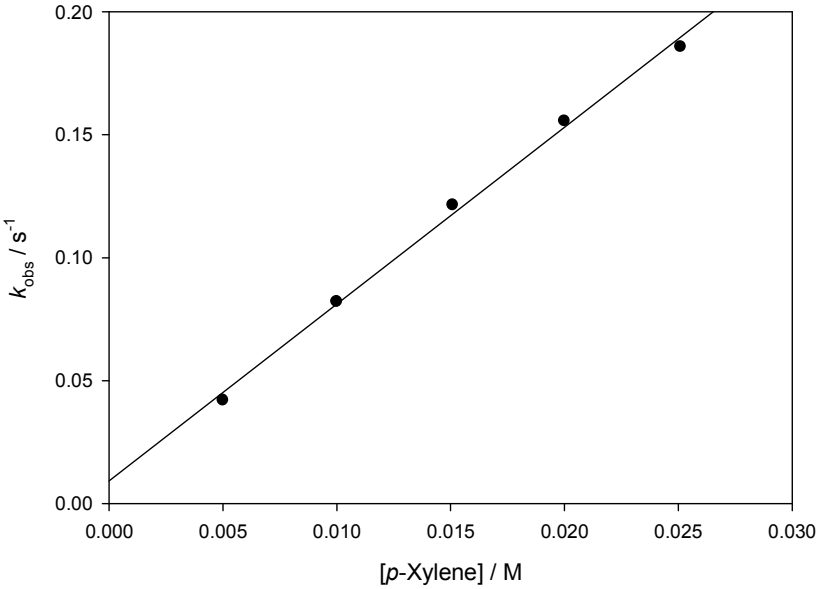


Figure S12. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *p*-xylene in $CH_3CN/Mg(ClO_4)_2$ 0.15 M at 25 °C (r^2=0.996).

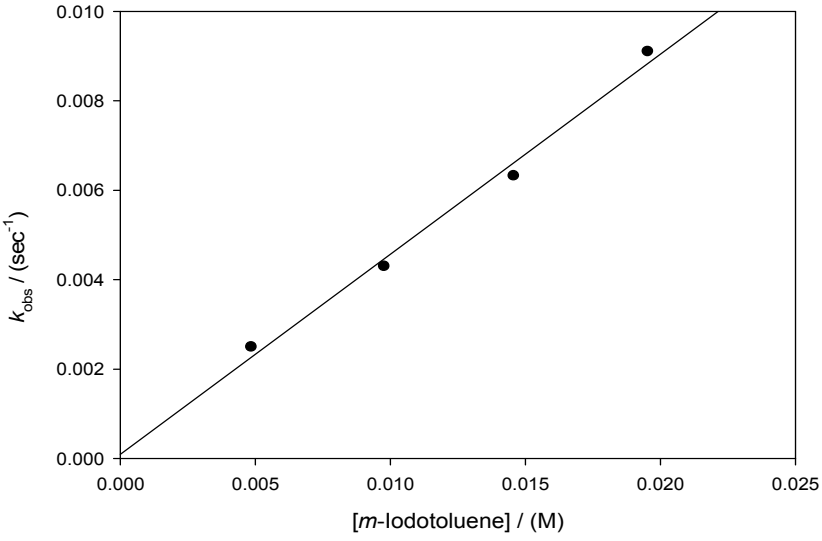


Figure S13. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *m*-iodotoluene in CH_3CN at 25 °C (r^2=0.990).

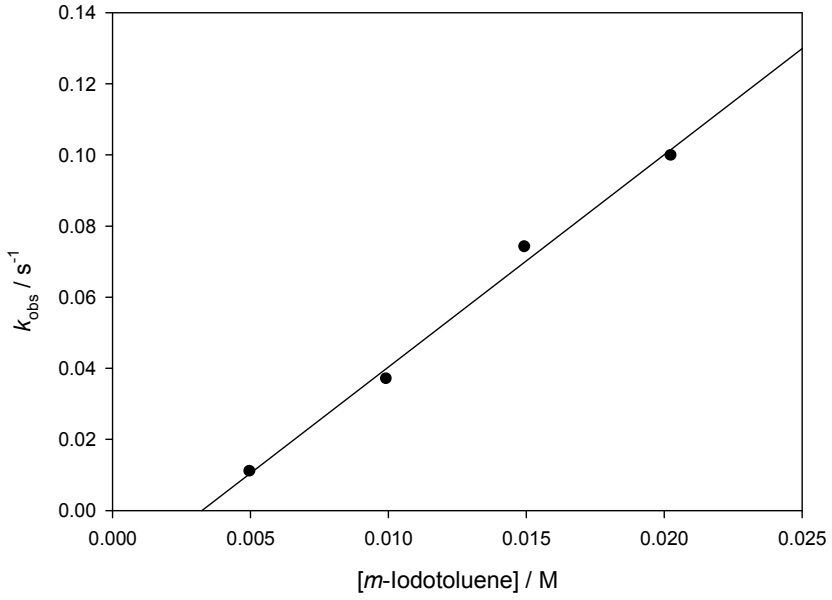


Figure S14. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *m*-iodotoluene in $CH_3CN/HClO_4$ 0.15 M at 25 °C (r^2=0.994).

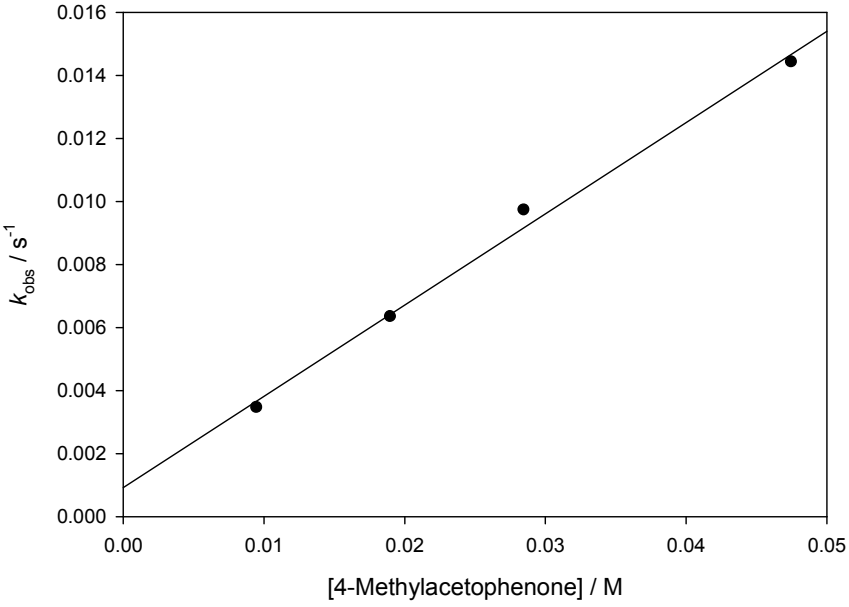


Figure S15. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of 4-methylacetophenone in CH_3CN at 25 °C (r^2=0.994).

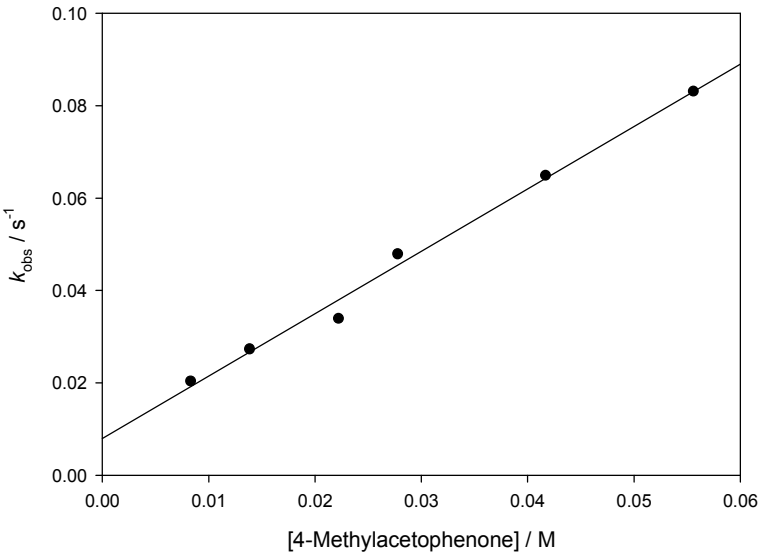


Figure S16. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of 4-methylacetophenone in $CH_3CN/HClO_4$ 0.15 M at 25 °C (r^2=0.992).

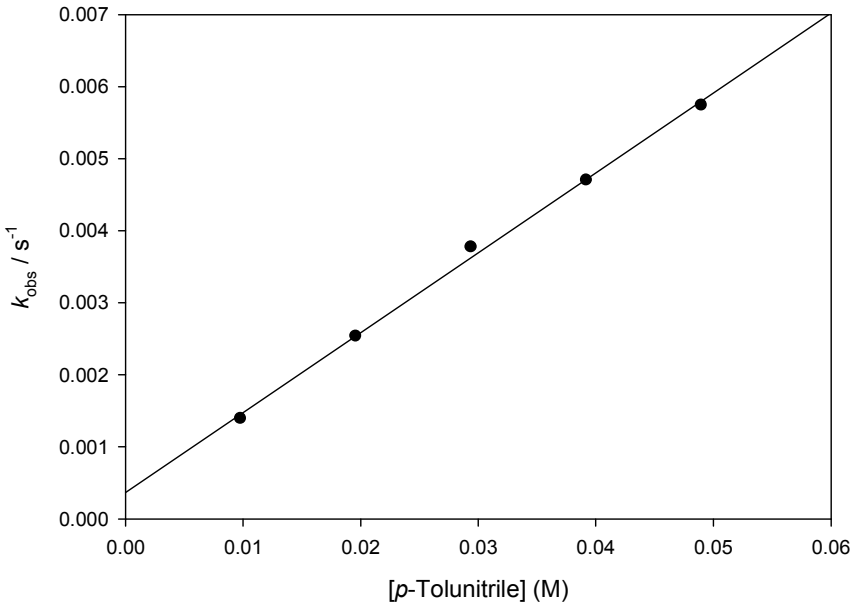


Figure S17. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *p*-tolunitrile in CH_3CN at 25 °C (r^2=0.998).

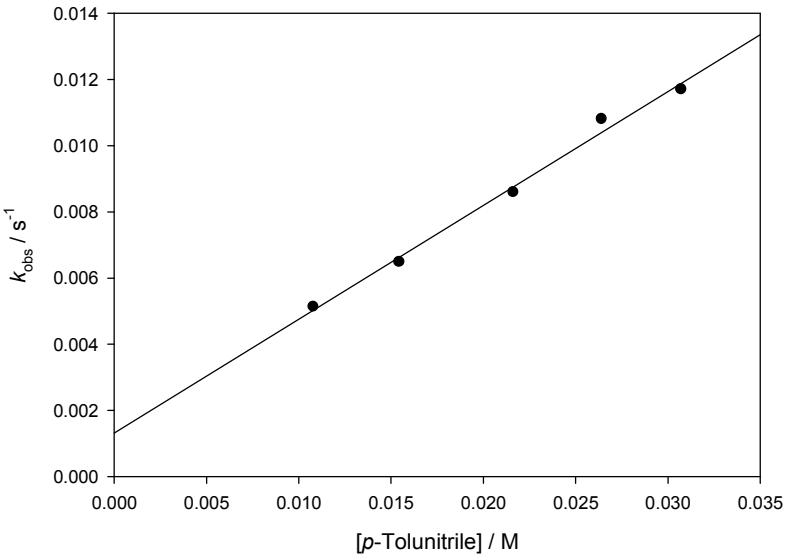


Figure S18. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *p*-tolunitrile in $CH_3CN/HClO_4$ 0.15 M at 25 °C (r^2=0.992).

Dependence of k_{obs} for the decay of PINO on the concentration of alkylaromatics

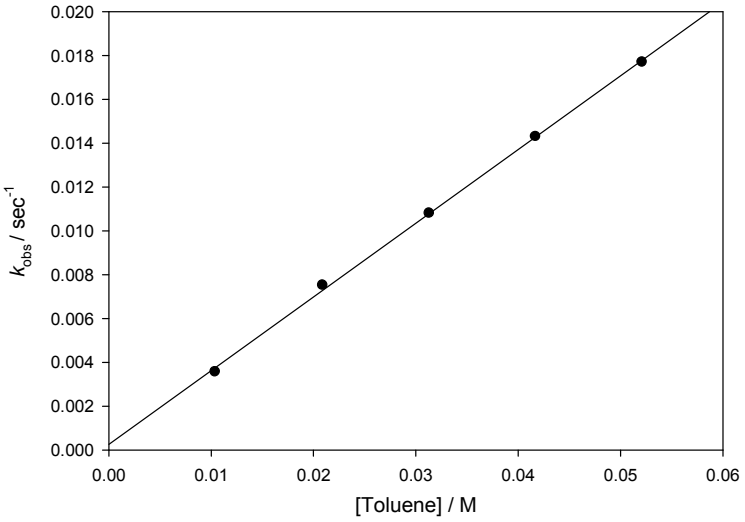


Figure S19. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of toluene in CH_3CN at 25 °C (r^2=0.999).

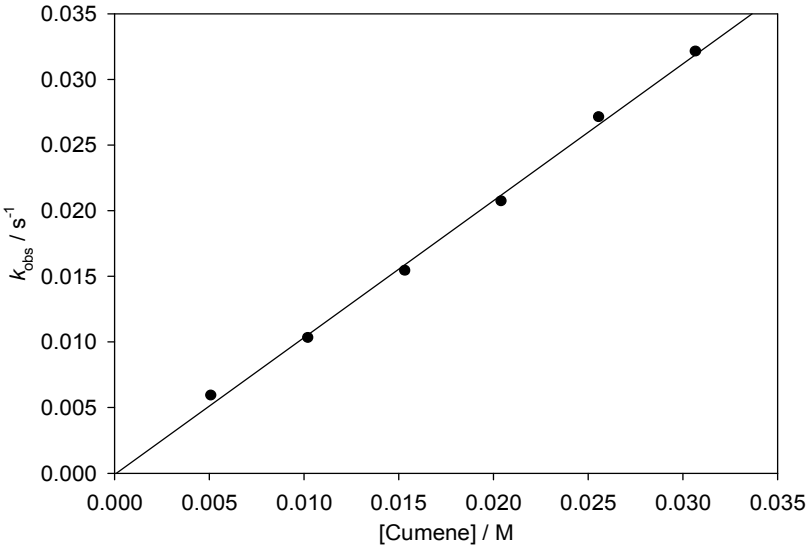


Figure S20. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of cumene in CH_3CN at 25 °C (r^2=0.997).

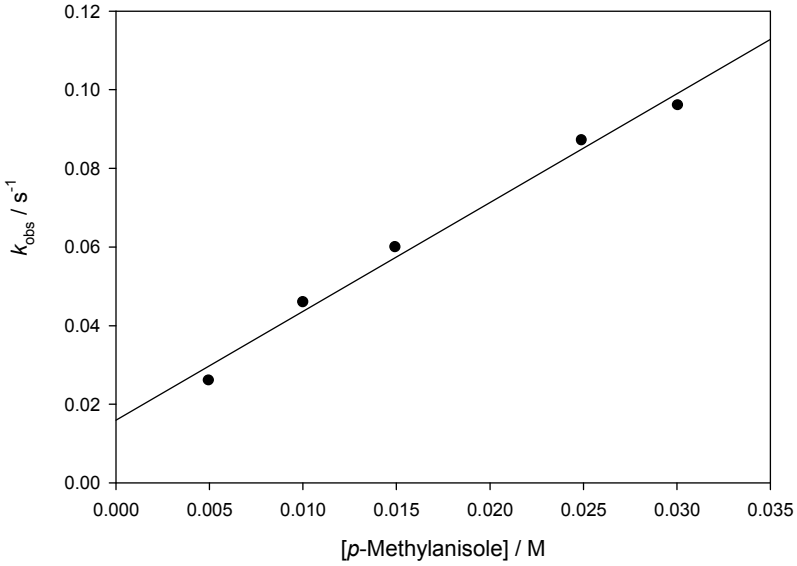


Figure S21. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of *p*-methylanisole in CH_3CN at 25 °C (r^2=0.988).

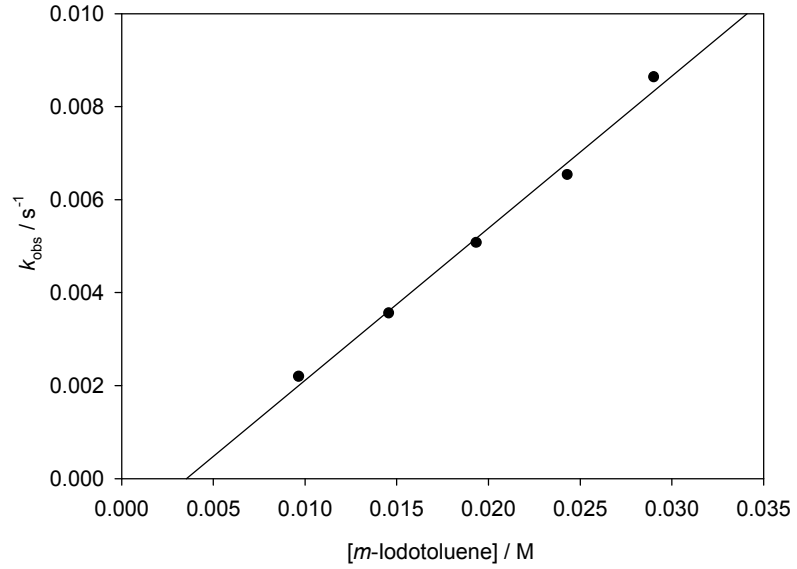


Figure S22. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of *m*-iodotoluene in CH_3CN at 25 °C (r^2=0.992).

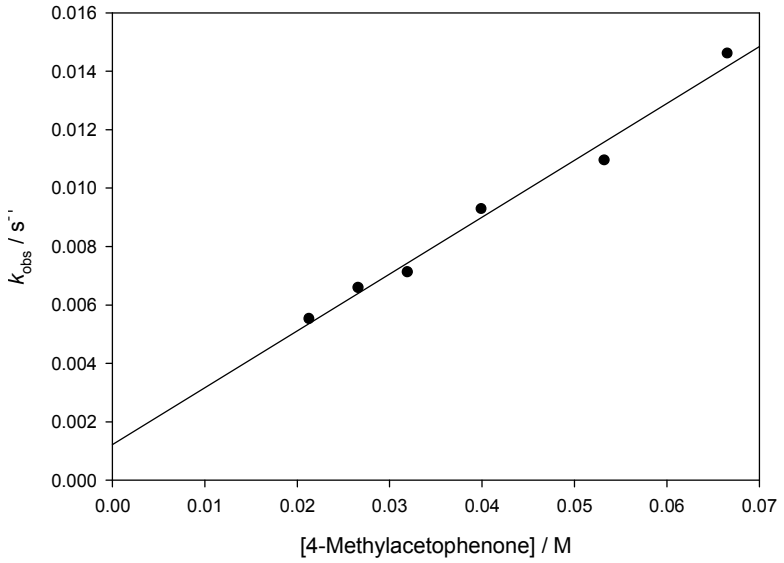


Figure S23. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of 4-methylacetophenone in CH_3CN at 25 °C (r^2=0.985).

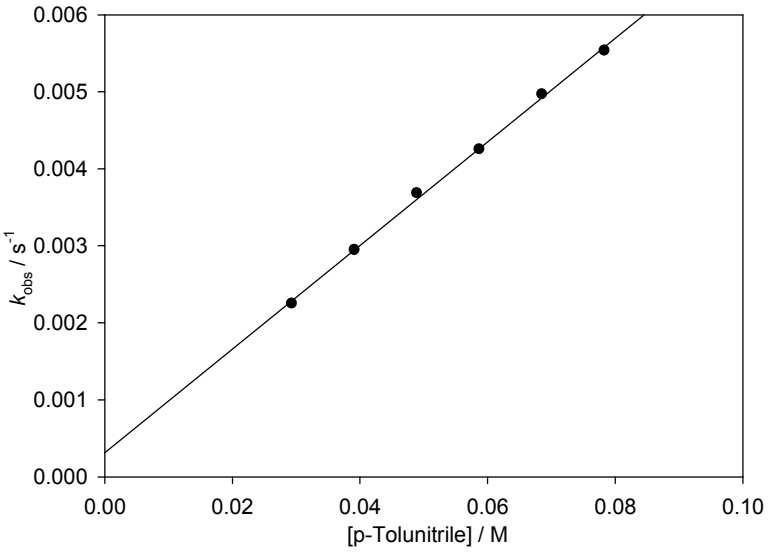


Figure S24. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of *p*-tolunitrile in CH_3CN at 25 °C (r^2=0.998).

Dependence of k_{obs} for the decay of QINO on the concentration of aliphatic hydrocarbons, alcohols, aldehydes, ethers and amides

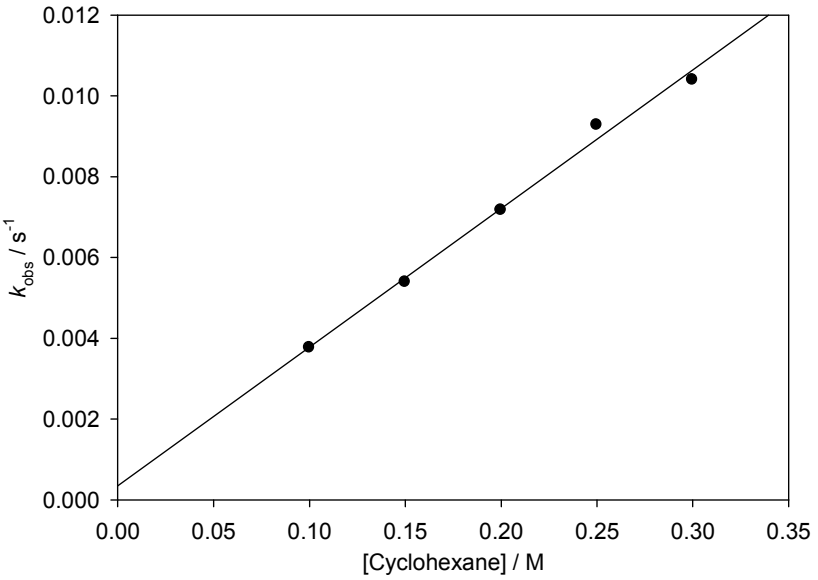


Figure S25. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of cyclohexane in CH_3CN at 25 °C (r^2=0.993).

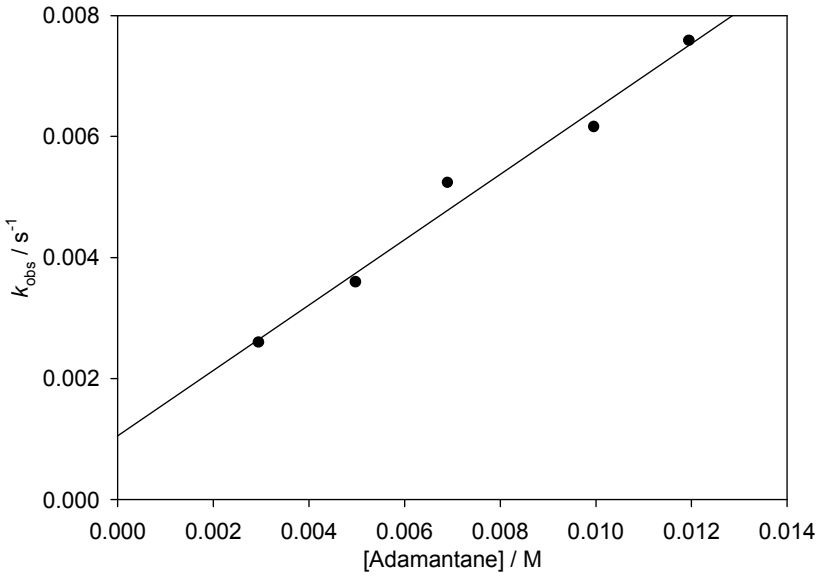


Figure S26. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of adamantane in CH_3CN at 25 °C (r^2=0.980).

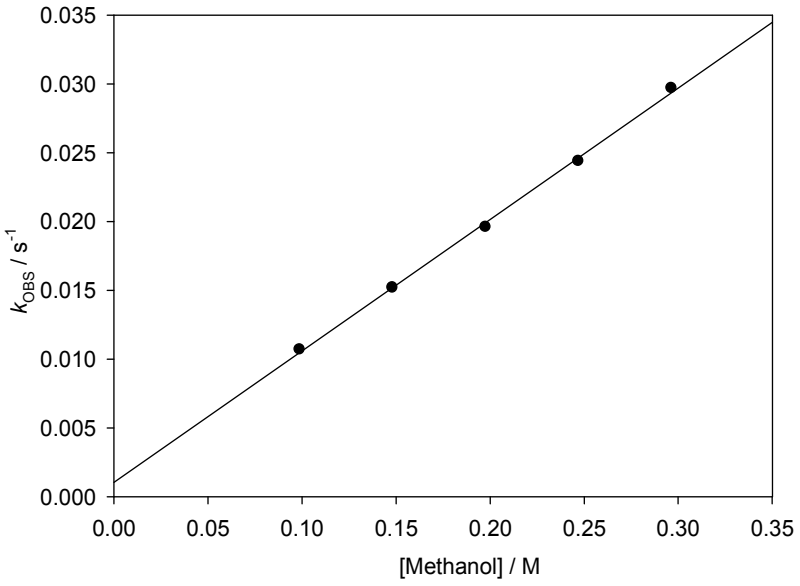


Figure S27. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of methanol in CH_3CN at 25 °C (r^2=0.999).

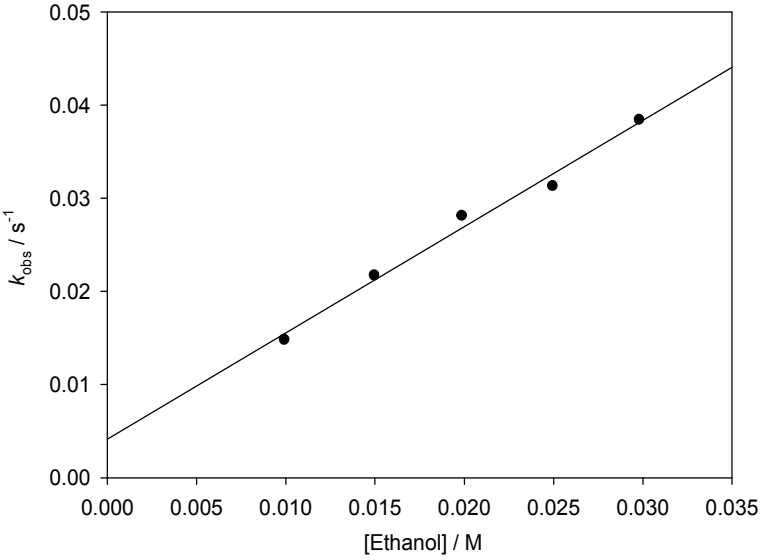


Figure S28. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of ethanol in CH_3CN at 25 °C (r^2=0.987).

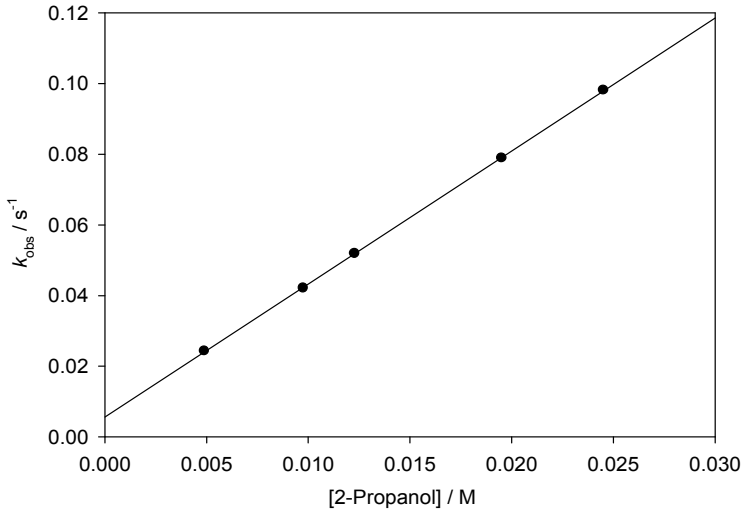


Figure S29. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of 2-propanol in CH_3CN at 25 °C (r^2=0.999).

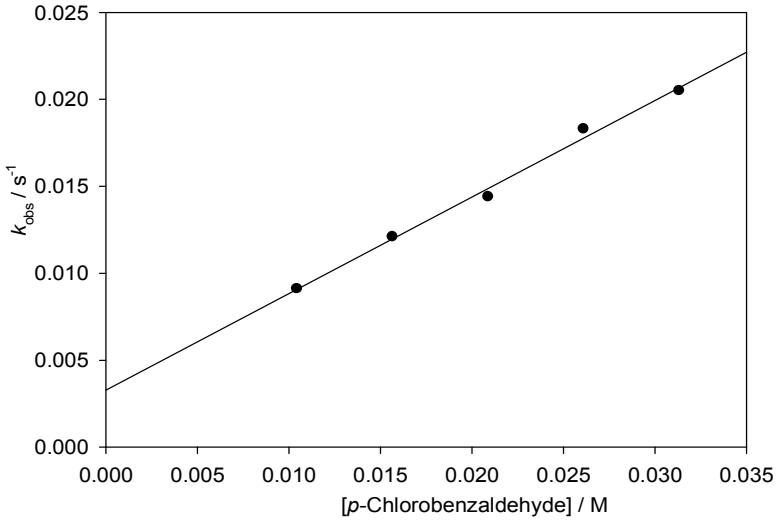


Figure S30. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *p*-chlorobenzaldehyde in CH_3CN at 25 °C (r^2=0.994).

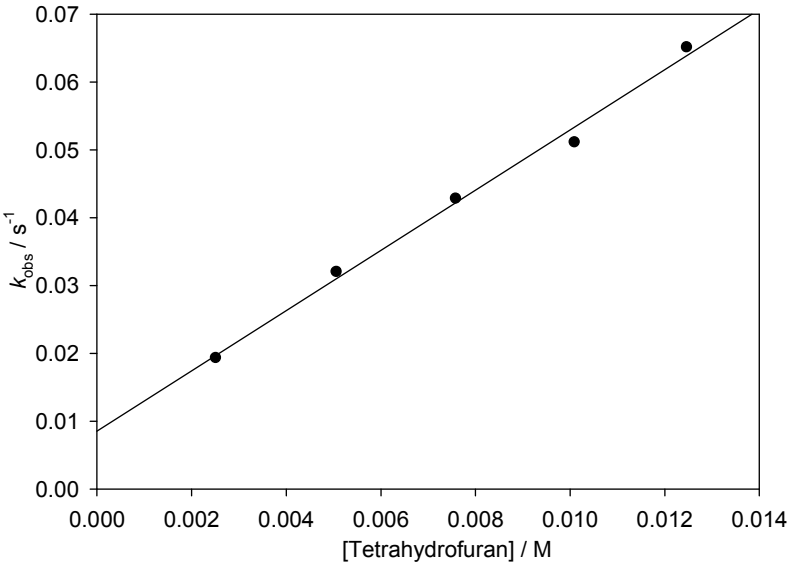


Figure S31. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of tetrahydrofuran in CH_3CN at 25 °C (r^2=0.993).

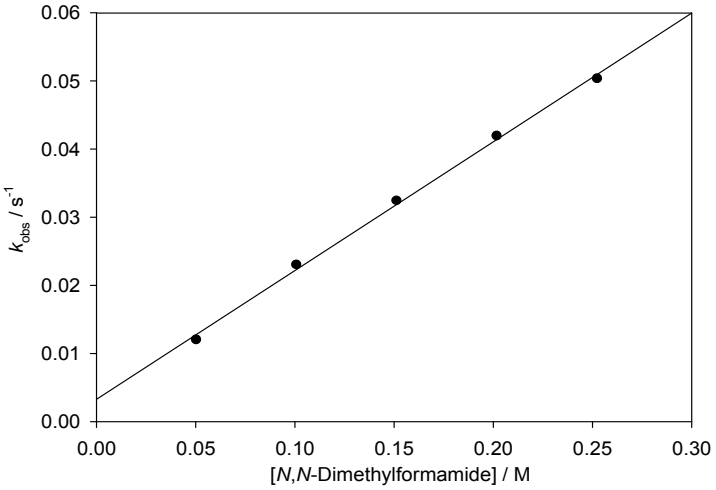


Figure S32. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of QINO on the concentrations of *N*,*N*-dimethylformamide in CH_3CN at 25 °C (r^2=0.998).

Dependence of k_{obs} for the decay of PINO on the concentration of aliphatic hydrocarbons, alcohols, aldehydes, ethers and amides

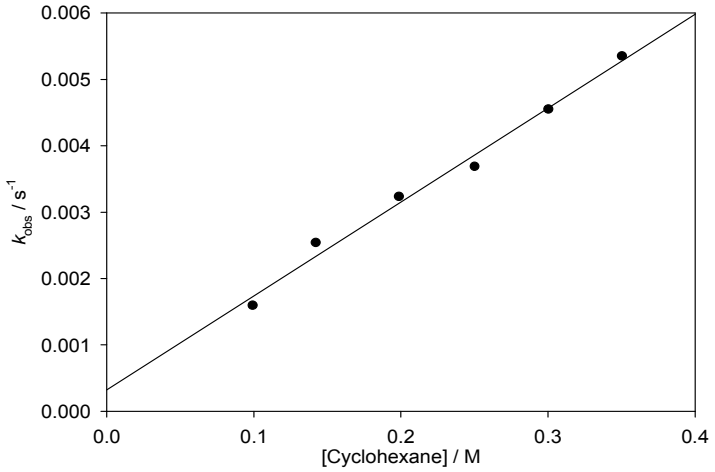


Figure S33. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of cyclohexane in CH_3CN at 25 °C (r^2=0.988).

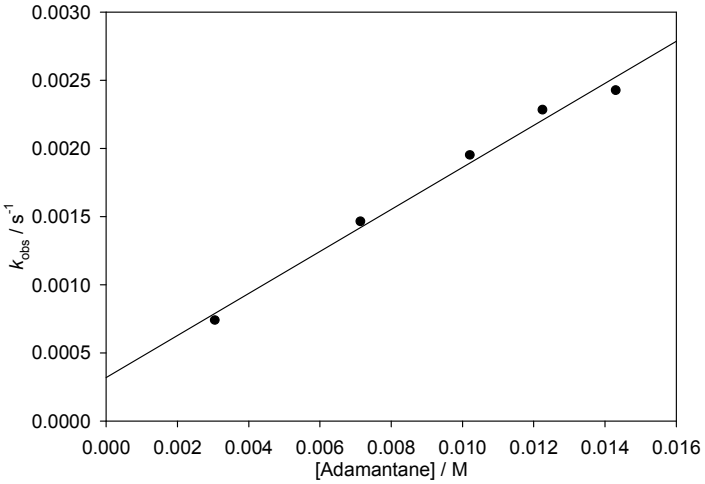


Figure S34. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of adamantane in CH_3CN at 25 °C (r^2=0.988).

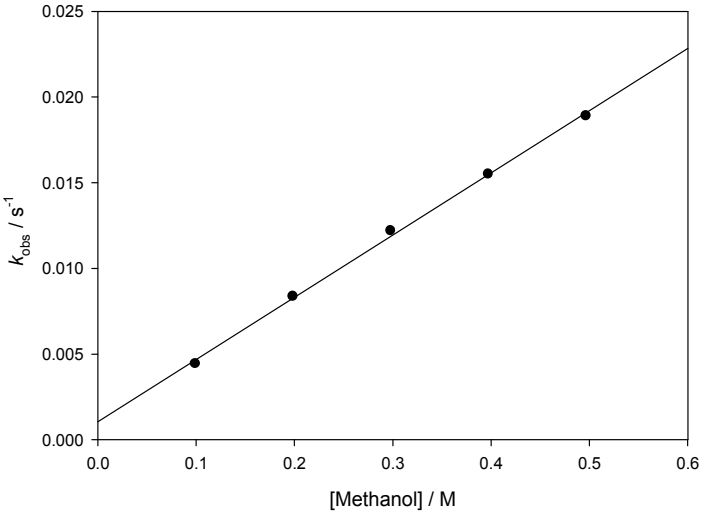


Figure S35. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of methanol in CH_3CN at 25 °C (r^2=0.998).

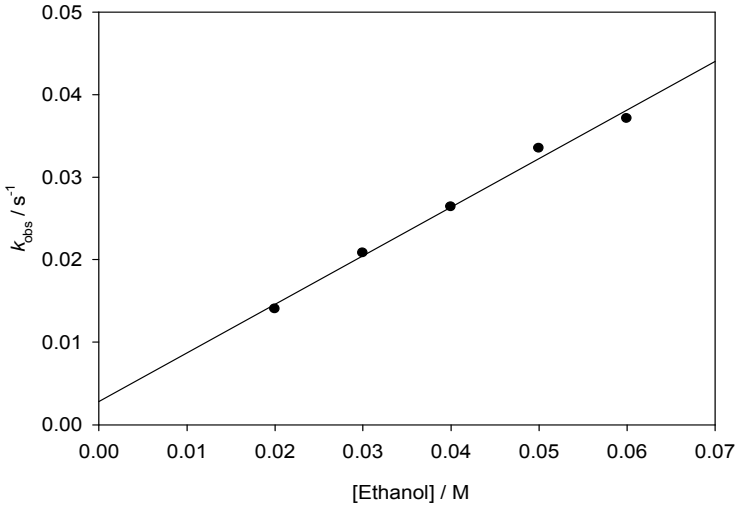


Figure S36. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of ethanol in CH_3CN at 25 °C (r^2=0.991).

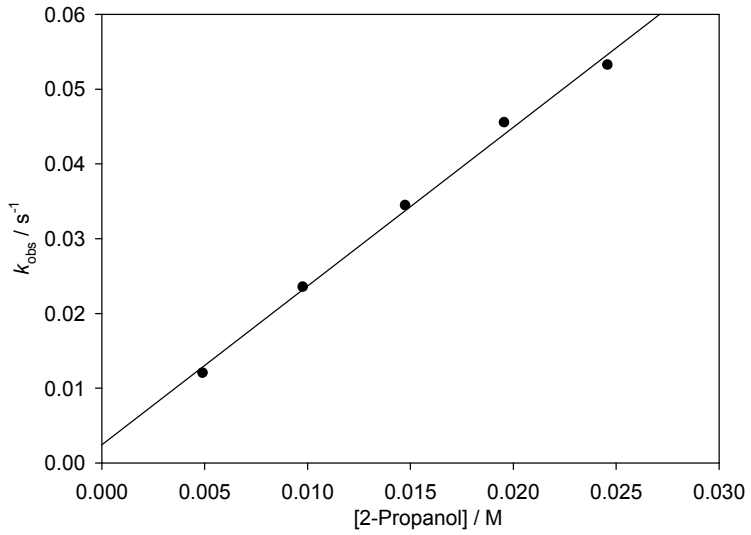


Figure S37. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of 2-propanol in CH_3CN at 25 °C (r^2=0.995).

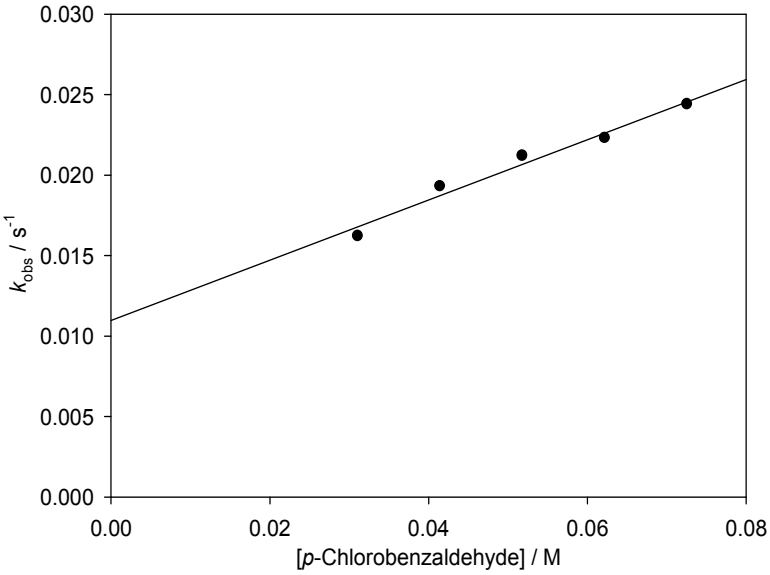


Figure S38. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of *p*-chlorobenzaldehyde in CH_3CN at 25 °C (r^2=0.972).

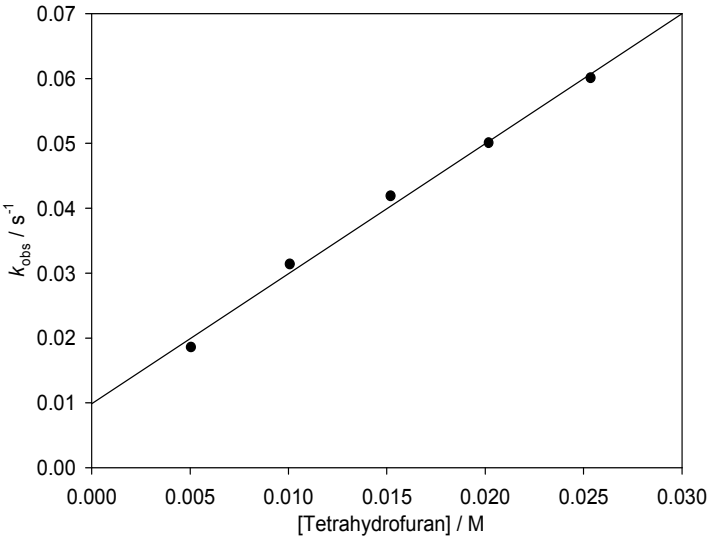


Figure S39. Dependence of pseudo-first order rate constants (k_{obs}) for the decay of PINO on the concentrations of tetrahydrofuran in CH_3CN at 25 °C (r^2=0.994).

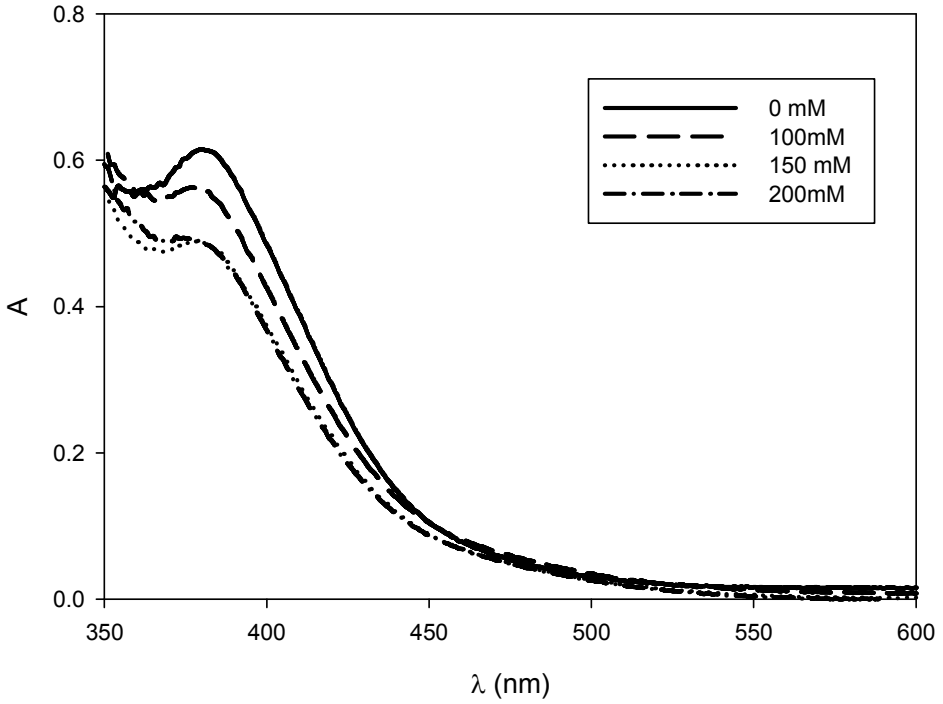


Figure S40. UV-vis spectra of QINO generated by oxidation of NHQI (1 mM) with cerium(IV) ammonium nitrate (0.5 mM) at T = 25 °C in MeCN/[$HClO_4$] (0-0.2 M).

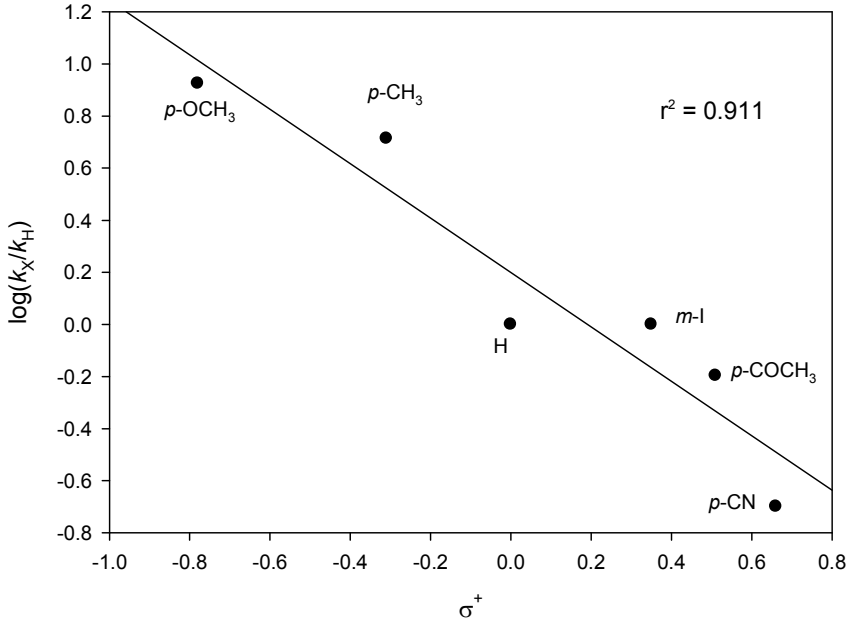


Figure S41. Hammett plot for the reaction of substituted toluenes with PINO in CH_3CN at 25 °C.

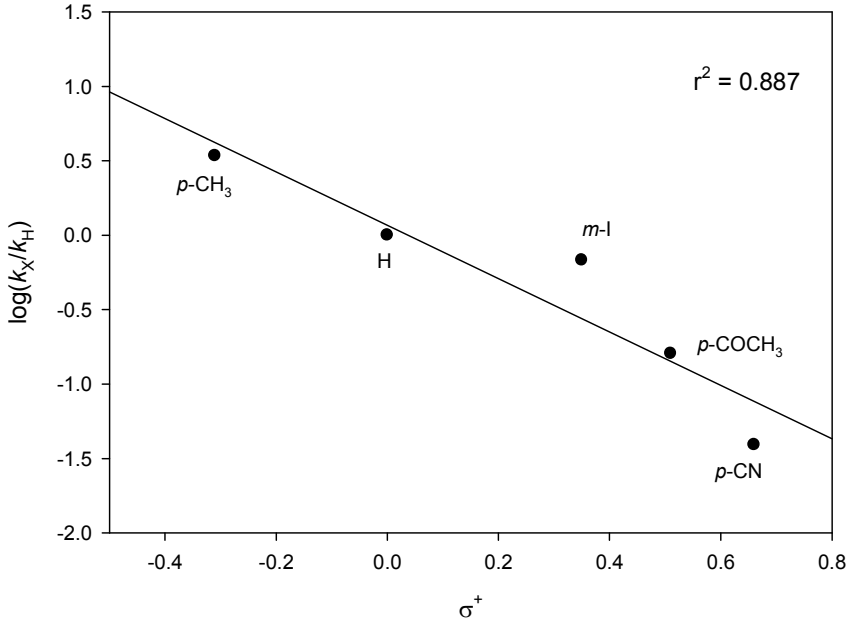


Figure S42. Hammett plot for the reaction of substituted toluenes with QINO in $CH_3CN/HClO_4$ 0.15 M at 25 °C.

Table S1. Gas phase computational results relative to reactants (QINO+toluene), of the hydrogen atom transfer between QINO with toluene. The data were obtained using B3LYP-DCP/6-31+G(2d,2p) approach. All values are in kcal/mol.

Molecule(s)/Complex	Electronic energy (Eel)	Eel+ZPVE (zero point vibrational energy correction)	Enthalpy change	Free energy change
QINO-toluene (pre-reaction complex)	-9.7	-9.0	-8.4	2.6
QINO-toluene (cisoid TS complex)	7.3	5.0	4.7	18.7
QINO-toluene (transoid TS complex)	12.7	10.1	10.1	21.9
NHQI-benzyl (post-reaction complex)	-0.4	-0.2	0.2	12.0
NHQI + Benzene (products)	9.5	8.9	8.9	10.1

Table S2. Gas phase computational results relative to reactants (PINO+toluene), of the hydrogen atom transfer between PINO with toluene. The data were obtained using B3LYP-DCP/6-31+G(2d,2p) approach. All values are in kcal/mol.

Molecule(s)/Complex	Electronic energy (Eel)	Eel+ZPVE (zero point vibrational energy correction)	Enthalpy change	Free energy change
PINO-toluene (pre-reaction complex)	-9.0	-8.4	-7.8	2.6
PINO-toluene (cisoid TS complex)	8.4	6.0	5.7	19.5
PINO-toluene (transoid TS complex)	13.5	10.9	10.8	22.7
NHPI-benzyl (post-reaction complex)	0.8	0.8	1.3	12.9
NHPI + Benzene (products)	10.5	9.9	9.9	11.0

Table S3. Solvent phase computational results relative to reactants (QINO+toluene), of the hydrogen atom transfer between QINO with toluene in acetonitrile solvent. The data were obtained using B3LYP-DCP/6-31+G(2d,2p) approach with the SMD solvation (acetonitrile) model. All values are in kcal/mol.

Molecule(s)/Complex	Electronic energy (Eel)	Eel+ZPVE (zero point vibrational energy correction)	Enthalpy change	Free energy change
QINO-toluene (pre-reaction complex)	-6.3	-5.7	-5.1	5.5
QINO-toluene (cisoid TS complex)	9.8	7.5	7.8	19.6
QINO-toluene (transoid TS complex)	13.7	11.1	11.6	21.8
NHQI-benzyl (post-reaction complex)	2.4	2.4	3.4	13.3
NHQI + Benzene (products)	11.7	10.5	10.8	10.3

Table S4. Solvent phase computational results relative to reactants (PINO+toluene), of the hydrogen atom transfer between PINO with toluene in acetonitrile solvent. The data were obtained using B3LYP-DCP/6-31+G(2d,2p) approach with the SMD solvation (acetonitrile) model. All values are in kcal/mol.

Molecule(s)/Complex	Electronic energy (Eel)	Eel+ZPVE (zero point vibrational energy correction)	Enthalpy change	Free energy change
PINO-toluene (pre-reaction complex)	-6.0	-5.3	-4.1	4.6
PINO-toluene (cisoid TS complex)	11.0	8.7	9.0	20.6
PINO-toluene (transoid TS complex)	14.9	12.4	12.9	23.0
NHPI-benzyl (post-reaction complex)	3.7	3.7	4.7	14.4
NHPI + Benzene (products)	12.8	11.6	11.9	11.4

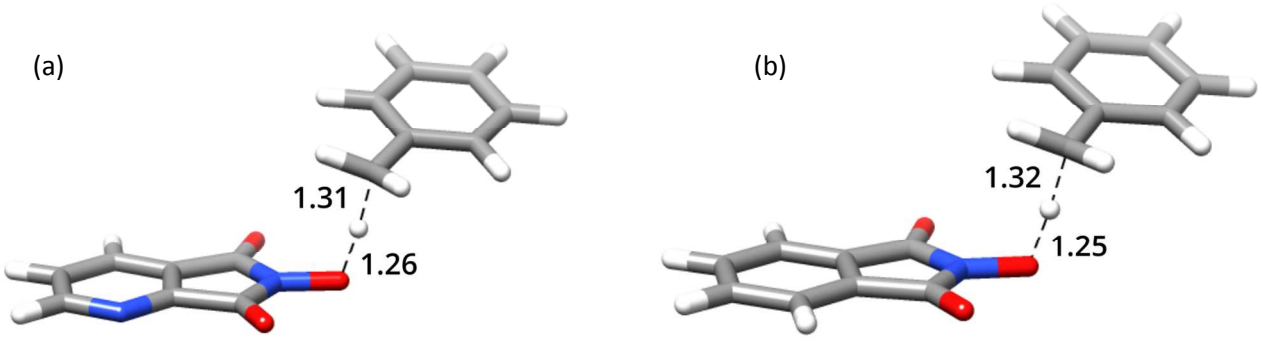


Figure S43. Optimized structures of the transition states for the reaction of (a) QINO and (b) PINO with toluene. Structures were obtained using the B3LYP-DCP/6-31+G(2d,2p) with the SMD solvation (acetonitrile) model. Key distances shown are in Angstroms. Key: Carbon = grey; Hydrogen = White; Oxygen = red; Nitrogen = blue.

Cartesian coordinates of the optimized structures of the reaction steps

Optimized cartesian coordinates (in Angstroms) of the structures studied computationally in this work are presented as below. The geometries of the molecules are given in the order of the total number of atoms, followed by the overall charge and spin multiplicity, followed by their composite atomic symbols and the respective x, y, z coordinates.

A. Gas-phase optimized geometries:

- **NHQI**

16
0 1

C	-0.535593	-0.664893	0.000000
C	-0.532287	0.726750	0.000000
C	-1.728249	1.411607	0.000000
C	-2.880894	0.625859	0.000000
C	-2.774150	-0.764100	0.000000
N	-1.609263	-1.434587	0.000000
C	0.886854	-1.131120	0.000000
C	0.872066	1.224775	0.000000
H	-1.761578	2.495175	0.000000
H	-3.863182	1.083846	0.000000
H	-3.671002	-1.376524	0.000000
O	1.286918	2.357540	0.000000
O	1.391069	-2.232643	0.000000
N	1.626724	0.048138	0.000000
O	3.005301	0.030092	0.000000
H	3.202205	-0.928145	0.000000

- **NHPI**

17
0 1

C	-0.490751	-0.704990	0.000000
C	-0.525836	0.688415	0.000000
C	-1.719085	1.377650	0.000000
C	-2.896957	0.624165	0.000000
C	-2.861159	-0.768163	0.000000
C	-1.645640	-1.458398	0.000000
C	0.928306	-1.129588	0.000000
C	0.868658	1.217824	0.000000
H	-1.733779	2.461492	0.000000
H	-3.855336	1.131665	0.000000

H	-3.791710	-1.324923	0.000000
H	-1.604789	-2.541530	0.000000
O	1.264489	2.357674	0.000000
O	1.447985	-2.229611	0.000000
N	1.650489	0.056239	0.000000
O	3.030642	0.063200	0.000000
H	3.244248	-0.890955	0.000000

- **QINO**

15

0 2

C	-1.122022	-0.640587	-0.834131
C	-1.314020	-0.848658	0.529023
C	-2.464263	-0.379847	1.140101
C	-3.365291	0.283041	0.316451
C	-3.077412	0.439825	-1.043970
N	-1.966857	-0.011463	-1.639796
C	0.178294	-1.231952	-1.254410
C	-0.170955	-1.581954	1.099773
H	-2.640458	-0.527290	2.199488
H	-4.291587	0.682290	0.712902
H	-3.782265	0.958260	-1.687737
O	0.037119	-1.947104	2.224223
O	0.721107	-1.277049	-2.318686
N	0.721204	-1.798002	-0.024100
O	1.826826	-2.399279	0.052308

- **PINO**

16

0 2

C	-1.074486	-0.658748	-0.864891
C	-1.302316	-0.847890	0.498433
C	-2.451746	-0.379415	1.109062
C	-3.376510	0.290226	0.310803
C	-3.148319	0.479679	-1.054611
C	-1.988443	0.005225	-1.663227
C	0.218367	-1.255392	-1.244648
C	-0.173195	-1.580444	1.098518
H	-2.615988	-0.533341	2.169267
H	-4.289567	0.671825	0.754224

H	-3.888038	1.005188	-1.648384
H	-1.798710	0.145171	-2.721111
O	0.018009	-1.937967	2.228684
O	0.775897	-1.308759	-2.306712
N	0.741769	-1.812622	-0.007653
O	1.844133	-2.417580	0.092641

- **Toluene**

15

0 1

C	0.118626	2.516833	-0.529887
C	1.265840	1.849528	-0.944288
C	2.067307	1.164811	-0.030958
C	1.686020	1.160283	1.310642
C	0.539887	1.825790	1.730958
C	-0.248622	2.508531	0.811299
H	-0.491813	3.041460	-1.257741
H	0.260436	1.807472	2.779392
H	-1.144870	3.025940	1.136446
H	2.293832	0.626182	2.035516
H	1.542855	1.858053	-1.994689
C	3.323693	0.474021	-0.476301
H	3.241020	0.120993	-1.508174
H	4.182687	1.154524	-0.431403
H	3.554391	-0.384785	0.160427

- **Benzyl**

14

0 2

C	1.128434	-1.207388	0.000000
C	-0.252216	-1.213313	0.000008
C	-0.989072	0.000000	-0.000004
C	-0.252216	1.213313	0.000008
C	1.128434	1.207388	0.000000
C	1.831551	0.000000	-0.000007
H	1.670567	-2.147415	0.000004
H	1.670567	2.147415	0.000004
H	2.915926	0.000000	-0.000019
H	-0.794149	2.154002	0.000017

H -0.794150 -2.154001 0.000017
C -2.390179 0.000000 -0.000005
H -2.948584 -0.928687 -0.000010
H -2.948584 0.928687 -0.000010

- **H**

1
0 2
H 0.000000 0.000000 0.000000

- **QINO-toluene pre-reaction complex**

30
0 2
C -1.541190 1.883290 -0.605070
C -1.652950 1.570250 0.743900
C -1.999540 0.281470 1.157330
C -2.224290 -0.686620 0.178300
C -2.111700 -0.378480 -1.174260
C -1.770650 0.908870 -1.571810
H -1.269280 2.890960 -0.902950
H -2.284770 -1.151610 -1.915970
H -1.678610 1.151050 -2.625340
C 1.528960 0.370260 -0.070640
C 1.256330 -0.739740 -0.867660
N 1.423440 -0.699950 -2.240310
C 1.872300 0.493020 -2.799050
C 2.142830 1.607420 -1.999800
C 1.973970 1.559460 -0.619230
C 1.278650 0.045500 1.343070
C 0.806580 -1.861910 -0.027040
H 2.015260 0.562020 -3.871900
H 2.490930 2.522820 -2.465710
H 2.178470 2.415800 0.012820
O 0.475590 -2.979290 -0.317620
O 1.389810 0.713200 2.336320
N 0.850610 -1.342520 1.330090
O 0.543060 -2.004470 2.358820
H -2.482220 -1.697650 0.478840
H -1.460500 2.333460 1.492510
C -2.122870 -0.043060 2.616780

H	-1.195260	0.184740	3.152310
H	-2.921880	0.546040	3.080540
H	-2.347310	-1.100690	2.771660

- **PINO-toluene pre-reaction complex**

31
0 2

C	-1.553083	1.860688	-0.633587
C	-1.653100	1.573115	0.722024
C	-1.996355	0.292619	1.162862
C	-2.229112	-0.693890	0.204266
C	-2.128482	-0.411451	-1.154859
C	-1.791263	0.868221	-1.579603
H	-1.284050	2.862526	-0.952954
H	-2.307547	-1.198650	-1.880121
H	-1.709234	1.090481	-2.638316
C	1.530222	0.363065	-0.065634
C	1.259401	-0.734308	-0.880621
C	1.434602	-0.674952	-2.251495
C	1.890447	0.524694	-2.789958
C	2.159966	1.626280	-1.972659
C	1.982589	1.558706	-0.593913
C	1.268522	0.018546	1.341297
C	0.799242	-1.866733	-0.059780
H	1.218888	-1.536377	-2.872866
H	2.039697	0.609209	-3.860831
H	2.513700	2.547295	-2.422989
H	2.185800	2.405138	0.051761
O	0.467214	-2.978748	-0.369071

- **QINO-toluene cisoid transition state complex**

30
0 2

C	-0.653681	2.293036	1.145693
C	-1.719612	1.410905	1.145857
C	-2.223426	0.888930	-0.062514
C	-1.613858	1.291782	-1.267946
C	-0.544804	2.170584	-1.262893
C	-0.057936	2.674301	-0.056945
H	-0.276465	2.681121	2.085891
H	-0.077734	2.454480	-2.199480

H	0.785156	3.356819	-0.054166
C	1.325515	-0.655041	0.733454
C	1.342874	-0.702814	-0.655103
N	2.310963	-0.234484	-1.428149
C	3.334246	0.322080	-0.763619
C	3.413525	0.419068	0.627214
C	2.381414	-0.083328	1.414481
C	0.065885	-1.251532	1.232631
C	0.080970	-1.349431	-1.134098
H	4.139919	0.713747	-1.378440
H	4.281235	0.885958	1.079032
H	2.393879	-0.030334	2.497301
O	-0.309791	-1.565641	-2.250440
O	-0.329119	-1.367698	2.367361
N	-0.617059	-1.662328	0.064126
O	-1.831434	-2.203025	0.078933
H	-1.974657	0.880537	-2.204841
H	-2.164359	1.093903	2.083421
C	-3.278209	-0.096393	-0.060406
H	-3.894744	-0.155943	0.835382
H	-3.820557	-0.238956	-0.994000
H	-2.603654	-1.265609	0.016387

- **PINO-toluene cisoid transition state complex**

31

0 2

C	-0.102848	1.517025	0.861584
C	-1.324000	0.884479	1.013807
C	-2.059348	0.455726	-0.109471
C	-1.519666	0.694254	-1.389381
C	-0.298072	1.327225	-1.536214
C	0.418911	1.738555	-0.412789
H	0.453065	1.831685	1.738283
H	0.105621	1.493899	-2.529141
H	1.381899	2.223783	-0.529604
C	1.155445	-1.801346	0.506602
C	1.042548	-1.910848	-0.875641
C	2.119240	-1.679340	-1.708533
C	3.329806	-1.327732	-1.110865
C	3.443065	-1.217886	0.275736
C	2.349323	-1.456188	1.108355

C	-0.161070	-2.083232	1.124824
C	-0.352732	-2.269098	-1.221645
H	2.016162	-1.767187	-2.784100
H	4.198456	-1.137097	-1.731814
H	4.397979	-0.943584	0.710905
H	2.422183	-1.373395	2.186793
O	-0.861982	-2.431010	-2.304233
O	-0.486933	-2.067349	2.287195
N	-1.011334	-2.376311	0.029066
O	-2.308115	-2.642172	0.156040
H	-2.063387	0.350549	-2.263155
H	-1.715752	0.688500	2.006466
C	-3.289645	-0.281692	0.049077
H	-3.801651	-0.186268	1.005489
H	-3.949909	-0.330464	-0.815592
H	-2.866165	-1.567913	0.116450

- **QINO-toluene transoid transition state complex**

30

0 2

C	-5.430850	0.518547	-0.016320
C	-4.248928	1.087559	0.425611
C	-3.105703	0.295521	0.636354
C	-3.182497	-1.083071	0.361760
C	-4.365144	-1.646968	-0.082082
C	-5.494831	-0.850827	-0.270233
H	-6.307549	1.139631	-0.165281
H	-4.410678	-2.710483	-0.290074
H	-6.420606	-1.295319	-0.619314
C	2.531263	-0.775537	-0.136235
C	3.007200	0.525914	-0.021314
N	4.244644	0.865031	0.304372
C	5.066598	-0.171636	0.528897
C	4.688104	-1.512458	0.440509
C	3.378385	-1.840037	0.098862
C	1.097415	-0.741778	-0.506701
C	1.888590	1.478725	-0.316456
H	6.087906	0.084617	0.796073
H	5.420547	-2.286162	0.639813
H	3.035693	-2.865449	0.018495
O	1.860135	2.679660	-0.290134

O	0.318670	-1.658009	-0.639524
N	0.797372	0.628257	-0.644654
O	-0.399894	1.081134	-1.006327
H	-2.294090	-1.694634	0.481877
H	-4.196465	2.153881	0.621895
C	-1.862454	0.887437	1.075918
H	-1.915099	1.898856	1.477057
H	-1.182827	0.231091	1.622266
H	-1.145133	1.040334	-0.024382

- **PINO-toluene transoid transition state complex**

31

0 2

C	-3.670083	0.248004	-3.667534
C	-2.883057	0.427370	-2.542865
C	-3.217414	-0.193553	-1.325910
C	-4.354061	-1.022967	-1.284301
C	-5.136202	-1.201216	-2.411481
C	-4.800835	-0.565138	-3.606535
H	-3.405557	0.740912	-4.596900
H	-6.009000	-1.843556	-2.365598
H	-5.415299	-0.707508	-4.488983
C	-1.879330	-3.388207	3.299233
C	-0.598431	-2.893362	3.529204
C	-0.001945	-2.984151	4.770930
C	-0.732617	-3.594869	5.791608
C	-2.015960	-4.090568	5.561209
C	-2.611375	-3.991313	4.302602
C	-2.245303	-3.137808	1.884747
C	-0.076523	-2.299139	2.274073
H	0.995318	-2.592889	4.936526
H	-0.297436	-3.685655	6.780857
H	-2.558523	-4.559869	6.374596
H	-3.608269	-4.371109	4.110189
O	0.970198	-1.736654	2.064379
O	-3.283964	-3.359117	1.305061
N	-1.102488	-2.527051	1.322762
O	-1.015027	-2.169304	0.043811
H	-4.595292	-1.540165	-0.361278
H	-2.001181	1.058705	-2.589116
C	-2.387291	-0.028219	-0.154135

H	-1.654939	0.777709	-0.181043
H	-2.885940	-0.139995	0.810161
H	-1.633378	-1.119833	-0.106966

- **NHQI-benzyl post-reaction complex**

30

0 2

C	0.646283	2.051705	-1.416389
C	1.785729	1.275737	-1.348882
C	2.363164	0.938926	-0.095929
C	1.726471	1.423901	1.077085
C	0.585047	2.195952	0.996073
C	0.037808	2.519035	-0.248248
H	0.217790	2.292223	-2.383712
H	0.103802	2.539069	1.905364
H	-0.862639	3.120791	-0.306308
C	-1.395855	-0.710295	-0.650158
C	-1.371354	-0.588953	0.733182
N	-2.294280	0.009609	1.469112
C	-3.317164	0.522950	0.769086
C	-3.436681	0.453441	-0.620026
C	-2.448835	-0.182385	-1.367741
C	-0.167109	-1.407384	-1.104523
C	-0.112894	-1.220665	1.251464
H	-4.087546	1.019111	1.352898
H	-4.300162	0.897150	-1.102311
H	-2.492551	-0.258231	-2.448418
O	0.304314	-1.320469	2.375695
O	0.189175	-1.675940	-2.227017
N	0.527172	-1.678800	0.082967
O	1.716949	-2.356978	0.108050
H	2.137081	1.158623	2.045589
H	2.244806	0.899098	-2.257040
C	3.514229	0.137573	-0.018654
H	4.027832	-0.183676	-0.918398
H	3.981462	-0.070567	0.937794
H	2.411355	-1.660074	0.071916

- **NHPI-benzyl post-reaction complex**

31

0 2

C	0.633268	2.042918	-1.367390
C	1.771947	1.263618	-1.339310
C	2.397936	0.933741	-0.108075
C	1.812482	1.432727	1.085607
C	0.673566	2.211026	1.043137
C	0.075073	2.523587	-0.180117
H	0.164374	2.273647	-2.318048
H	0.236021	2.572527	1.967647
H	-0.826684	3.125370	-0.207010
C	-1.406098	-0.706675	-0.627000
C	-1.382891	-0.609944	0.759787
C	-2.399398	0.009303	1.457825
C	-3.457155	0.538509	0.716755
C	-3.480441	0.441450	-0.674733
C	-2.446721	-0.187943	-1.369988
C	-0.168636	-1.388671	-1.084441
C	-0.129303	-1.224724	1.265995
H	-2.366418	0.080109	2.539110
H	-4.275748	1.032469	1.229035
H	-4.316783	0.861430	-1.223066
H	-2.449930	-0.267970	-2.451128
O	0.276973	-1.325652	2.399422

B. <u>Optimized geometries in Acetonitrile solvent:</u>

- **NHQI**

16
0 1

C	-0.536418	-0.660660	0.000000
C	-0.533697	0.729348	0.000000
C	-1.731203	1.413364	0.000000
C	-2.882419	0.625619	0.000000
C	-2.778285	-0.763698	0.000000
N	-1.609004	-1.431840	0.000000
C	0.880050	-1.134328	0.000000
C	0.871573	1.211204	0.000000
H	-1.777364	2.496543	0.000000
H	-3.864629	1.083363	0.000000
H	-3.676108	-1.373674	0.000000
O	1.310956	2.339663	0.000000

O	1.364004	-2.248233	0.000000
N	1.625298	0.036560	0.000000
O	3.004792	0.048557	0.000000
H	3.247395	-0.900019	0.000000

- **NHPI**

17

0 1

C	-0.493266	-0.708994	0.000000
C	-0.526065	0.686307	0.000000
C	-1.718052	1.378348	0.000000
C	-2.897711	0.625850	0.000000
C	-2.864271	-0.766193	0.000000
C	-1.649692	-1.460045	0.000000
C	0.922839	-1.136260	0.000000
C	0.866978	1.204299	0.000000
H	-1.741256	2.462283	0.000000
H	-3.854923	1.135608	0.000000
H	-3.795452	-1.322015	0.000000
H	-1.619947	-2.543808	0.000000
O	1.281263	2.344448	0.000000
O	1.442396	-2.238147	0.000000
N	1.647502	0.049577	0.000000
O	3.028750	0.082628	0.000000
H	3.280684	-0.863719	0.000000

- **QINO**

15

0 2

C	-1.119843	-0.643169	-0.826871
C	-1.315056	-0.849536	0.536303
C	-2.468189	-0.378398	1.143099
C	-3.363932	0.282781	0.314048
C	-3.075031	0.439070	-1.046490
N	-1.960750	-0.015182	-1.637341
C	0.172995	-1.230558	-1.246270
C	-0.173517	-1.580119	1.099220
H	-2.658126	-0.518266	2.201002
H	-4.291049	0.683261	0.706362
H	-3.780376	0.957292	-1.688715
O	0.060133	-1.957626	2.216975

O	0.718891	-1.276560	-2.315730
N	0.718153	-1.795476	-0.028657
O	1.825118	-2.397283	0.044504

- **PINO**

16

0 2

C	-1.073356	-0.658894	-0.866786
C	-1.301840	-0.848580	0.500475
C	-2.451624	-0.379960	1.111217
C	-3.375232	0.289480	0.311130
C	-3.146977	0.478985	-1.054700
C	-1.987622	0.005266	-1.665297
C	0.213490	-1.253176	-1.243116
C	-0.177391	-1.577643	1.096164
H	-2.625047	-0.528883	2.170774
H	-4.288383	0.671205	0.754151
H	-3.886925	1.004506	-1.648106
H	-1.807023	0.150252	-2.724202
O	0.033165	-1.944986	2.224137
O	0.789143	-1.317343	-2.299576
N	0.736380	-1.809661	-0.008137
O	1.840100	-2.415413	0.092269

- **Toluene**

15

0 1

C	0.117892	2.517500	-0.531004
C	1.266281	1.849374	-0.946184
C	2.068474	1.163476	-0.031577
C	1.687038	1.159163	1.311887
C	0.539619	1.825654	1.732427
C	-0.250047	2.509113	0.811741
H	-0.492625	3.042748	-1.259170
H	0.260243	1.807661	2.781459
H	-1.146722	3.027030	1.137119
H	2.295531	0.625069	2.036679
H	1.543978	1.857946	-1.996736
C	3.323827	0.472874	-0.476672
H	3.240895	0.121888	-1.509619
H	4.181994	1.154908	-0.431244

H 3.554911 -0.384769 0.162132

- **Benzyl**

14
0 2
C 1.129126 -1.208764 0.000000
C -0.252908 -1.215280 0.000001
C -0.989671 0.000000 0.000004
C -0.252908 1.215280 0.000001
C 1.129126 1.208764 0.000000
C 1.832812 0.000000 -0.000001
H 1.671680 -2.149093 0.000001
H 1.671681 2.149093 0.000001
H 2.917765 0.000000 -0.000005
H -0.795595 2.156047 0.000003
H -0.795596 -2.156047 0.000003
C -2.391560 0.000000 0.000001
H -2.948812 -0.930753 -0.000002
H -2.948812 0.930753 -0.000002

- **H**

1
0 2
H 0.000000 0.000000 0.000000

- **QINO-toluene pre-reaction complex**

30
0 2
C -0.105819 1.796855 -1.648353
C -0.260158 0.568900 -2.281415
C 0.716386 -0.425215 -2.170007
C 1.847852 -0.156963 -1.398080
C 2.005365 1.071134 -0.759152
C 1.029704 2.054012 -0.883747
H -0.879561 2.552405 -1.743669
H 2.888818 1.253319 -0.155201
H 1.146273 3.008633 -0.380976
C -1.099930 -0.003364 1.110876
C 0.141309 -0.079698 1.734975
N 0.669172 0.855745 2.513808
C -0.093454 1.944907 2.676317

C	-1.351239	2.120610	2.087692
C	-1.883467	1.126783	1.279204
C	-1.357197	-1.234062	0.354504
C	0.786316	-1.374239	1.417537
H	0.315953	2.725762	3.310007
H	-1.897422	3.037847	2.272900
H	-2.853297	1.226831	0.805713
O	1.837162	-1.847269	1.757871
O	-2.304580	-1.587036	-0.297568
N	-0.172405	-2.049692	0.565126
O	-0.017559	-3.213661	0.102548
H	2.613318	-0.920685	-1.293704
H	-1.153516	0.373789	-2.868392
C	0.547202	-1.741826	-2.867319
H	-0.415154	-2.202798	-2.620385
H	0.569640	-1.614229	-3.956063
H	1.341824	-2.441006	-2.594901

- **PINO-toluene pre-reaction complex**

31

0 2

C	-1.551321	1.873700	-0.609291
C	-1.675645	1.555596	0.738712
C	-2.038498	0.268053	1.142400
C	-2.266776	-0.694991	0.157933
C	-2.142337	-0.381626	-1.192977
C	-1.785078	0.905244	-1.582234
H	-1.261035	2.878338	-0.900959
H	-2.314499	-1.149312	-1.941179
H	-1.678164	1.149705	-2.634135
C	1.569044	0.386342	-0.059344
C	1.292638	-0.734394	-0.848129
C	1.444075	-0.702705	-2.223105
C	1.881186	0.490074	-2.793452
C	2.154493	1.611592	-2.004934
C	2.001364	1.574213	-0.621339
C	1.335769	0.070519	1.353528
C	0.855957	-1.845909	0.003029
H	1.227141	-1.573226	-2.831466
H	2.009705	0.552557	-3.868403
H	2.490905	2.526044	-2.480998

H	2.209217	2.441755	-0.005655
O	0.535644	-2.977739	-0.258401

- **QINO-toluene cisoid transition state**

30

0 2

C	-0.107012	1.521124	0.894258
C	-1.334336	0.895387	1.022406
C	-2.043002	0.458293	-0.116964
C	-1.473186	0.685998	-1.387913
C	-0.244441	1.310875	-1.510248
C	0.447350	1.726277	-0.370943
H	0.428889	1.846115	1.779994
H	0.184931	1.470513	-2.493783
H	1.415951	2.205458	-0.468354
C	1.155337	-1.795640	0.540439
C	1.062640	-1.907177	-0.840342
N	2.046841	-1.686589	-1.698576
C	3.211358	-1.323895	-1.134137
C	3.405244	-1.183335	0.240587
C	2.353492	-1.425358	1.119727
C	-0.161739	-2.103308	1.137491
C	-0.330796	-2.297242	-1.204453
H	4.034411	-1.133982	-1.816389
H	4.378907	-0.884062	0.610329
H	2.466723	-1.323743	2.193127
O	-0.821747	-2.509049	-2.288571
O	-0.499885	-2.130869	2.299046
N	-1.001468	-2.380364	0.033941
O	-2.301962	-2.652603	0.149571
H	-2.006521	0.350204	-2.271409
H	-1.760414	0.722072	2.005405
C	-3.275732	-0.275280	0.017336
H	-3.805985	-0.178562	0.964726
H	-3.915539	-0.328978	-0.863544
H	-2.863378	-1.549523	0.095836

- **PINO-toluene cisoid transition state**

31

0 2

C	-0.110659	1.535968	0.862363

C	-1.330976	0.901575	1.014989
C	-2.064574	0.469198	-0.110094
C	-1.527490	0.711206	-1.392242
C	-0.306716	1.346042	-1.539268
C	0.410811	1.756380	-0.413966
H	0.444783	1.856556	1.737638
H	0.096246	1.518919	-2.531807
H	1.373316	2.243443	-0.531058
C	1.161819	-1.818499	0.508861
C	1.048779	-1.928019	-0.876037
C	2.124226	-1.690984	-1.709041
C	3.333745	-1.333260	-1.110092
C	3.446868	-1.223659	0.275819
C	2.354350	-1.468026	1.110283
C	-0.151577	-2.110208	1.121693
C	-0.342390	-2.295077	-1.216016
H	2.030908	-1.773843	-2.786125
H	4.199971	-1.135031	-1.731923
H	4.399391	-0.941821	0.711232
H	2.436904	-1.380489	2.187875
O	-0.854342	-2.498003	-2.295601

- **QINO-toluene transoid transition state**

30

0 2

C	5.336285	0.262584	0.231734
C	4.215288	1.021441	-0.059125
C	3.060489	0.419561	-0.596645
C	3.067623	-0.971769	-0.817201
C	4.190942	-1.726634	-0.526277
C	5.329576	-1.113740	-0.000184
H	6.221679	0.739143	0.639557
H	4.186457	-2.796216	-0.708829
H	6.208991	-1.706835	0.228070
C	-2.488799	-0.776756	0.284164
C	-2.911122	0.487510	-0.106613
N	-4.085771	0.774560	-0.645503
C	-4.902951	-0.281485	-0.804002
C	-4.572943	-1.587814	-0.442105
C	-3.329190	-1.860848	0.121759

C	-1.119635	-0.675672	0.834807
C	-1.825863	1.470808	0.180919
H	-5.873264	-0.072879	-1.244269
H	-5.293478	-2.380690	-0.604682
H	-3.038811	-2.863531	0.414405
O	-1.779897	2.661727	-0.025352
O	-0.388711	-1.542135	1.259427
N	-0.804541	0.699375	0.767911
O	0.354523	1.210122	1.183157
H	2.180113	-1.445549	-1.225709
H	4.216895	2.092302	0.120243
C	1.881800	1.205018	-0.876766
H	2.032713	2.277797	-1.001840
H	1.161508	0.768991	-1.572026
H	1.153064	1.198985	0.213576

- **PINO-toluene transoid transition state**

31

0 2

C	-3.733700	-0.031173	-3.642614
C	-2.789936	0.151821	-2.645814
C	-3.088182	-0.167646	-1.306706
C	-4.362075	-0.689242	-1.008249
C	-5.303334	-0.869462	-2.007539
C	-4.993862	-0.542257	-3.328767
H	-3.492855	0.224590	-4.669271
H	-6.283736	-1.264605	-1.762346
H	-5.732213	-0.684735	-4.110938
C	-1.803787	-3.556851	3.137845
C	-0.716492	-2.775271	3.527596
C	-0.308009	-2.712227	4.844900
C	-1.026651	-3.464741	5.776867
C	-2.112937	-4.247509	5.387010
C	-2.519219	-4.304621	4.051739
C	-1.994121	-3.416771	1.677752
C	-0.160916	-2.102003	2.333913
H	0.537657	-2.103055	5.143746
H	-0.735617	-3.440451	6.821397
H	-2.651105	-4.820962	6.133898
H	-3.363569	-4.911744	3.745006
O	0.762549	-1.322106	2.236472

- **NHQI-benzyl post-reaction complex**

30
0 2
C 0.646283 2.051705 -1.416389
C 1.785729 1.275737 -1.348882
C 2.363164 0.938926 -0.095929
C 1.726471 1.423901 1.077085
C 0.585047 2.195952 0.996073
C 0.037808 2.519035 -0.248248
H 0.217790 2.292223 -2.383712
H 0.103802 2.539069 1.905364
H -0.862639 3.120791 -0.306308
C -1.395855 -0.710295 -0.650158
C -1.371354 -0.588953 0.733182
N -2.294280 0.009609 1.469112
C -3.317164 0.522950 0.769086
C -3.436681 0.453441 -0.620026
C -2.448835 -0.182385 -1.367741
C -0.167109 -1.407384 -1.104523
C -0.112894 -1.220665 1.251464
H -4.087546 1.019111 1.352898
H -4.300162 0.897150 -1.102311
H -2.492551 -0.258231 -2.448418
O 0.304314 -1.320469 2.375695
O 0.189175 -1.675940 -2.227017
N 0.527172 -1.678800 0.082967
O 1.716949 -2.356978 0.108050
H 2.137081 1.158623 2.045589
H 2.244806 0.899098 -2.257040
C 3.514229 0.137573 -0.018654
H 4.027832 -0.183676 -0.918398
H 3.981462 -0.070567 0.937794
H 2.411355 -1.660074 0.071916

- **NHPI-benzyl post-reaction complex**

31
0 2
C 0.670665 2.091442 -1.407248
C 1.795261 1.291601 -1.349172

C	2.379957	0.947060	-0.100944
C	1.774379	1.459798	1.077622
C	0.649930	2.258754	1.005540
C	0.088037	2.580417	-0.233895
H	0.233327	2.336175	-2.370019
H	0.196284	2.633499	1.917608
H	-0.800631	3.200687	-0.284616
C	-1.405917	-0.724908	-0.618898
C	-1.374478	-0.645345	0.771435
C	-2.382395	-0.026445	1.482452
C	-3.440377	0.519788	0.752112
C	-3.472193	0.439546	-0.639661
C	-2.446919	-0.189488	-1.349743
C	-0.178564	-1.410231	-1.086616
C	-0.125683	-1.276396	1.258374
H	-2.350535	0.039039	2.564284
H	-4.250038	1.016959	1.275225
H	-4.306382	0.874850	-1.179081
H	-2.464458	-0.249216	-2.432232
O	0.279607	-1.432953	2.390221