

Intramolecular and Intermolecular Hydrogen Bond Formation by Some ortho-Substituted Phenols: An Experimental and Theoretical Investigation.

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SUPPORTING MATERIAL

TABLE OF CONTENTS

Title	page
Experimental details	S-2
Table S1. Parameters used for calculation of the equilibrium constant $K_{\text{ArOH/S}}^{\text{S}}$ for HB complex formation between DMSO and methoxyphenols.	S-6
Table S2. Values $K_A^{H_i}$, $\log K_A^{H_i}$, and α_2^H for methoxyphenols calculated from IR measurements of HB complex formation with DMSO	S-10
Table S3. Parameters used for calculation of the equilibrium constant $K_{\text{ArOH/S}}^{\text{S}}$ for HB complex formation between DMSO and 2,4-dinitrophenol.	S-13
Table S4. Parameters used for calculation of the equilibrium constant $K_{\text{ArOH/S}}^{\text{S}}$ for HB complex formation between DMSO and 2-methoxymethylphenol.	S-17
Table S5. Parameters used for calculation of the equilibrium constant $K_{\text{ArOH/S}}^{\text{S}}$ for HB complex formation between 4-F-phenol and 1,3-dinitrobenzene.	S-19
Table S6. Kinetic data for the reaction of dp⁺ph with 2,4-dimethoxyphenol in heptane.	S-20
Table S7. Kinetic data for the reaction of dp⁺ph with 2,4,6-trimethoxyphenol in heptane.	S-20
Table S8. Kinetic data for the reaction of dp⁺ph with 2-methoxymethylphenol in heptane.	S-21
Figure S1. OH-stretching region of 2,6-dimethoxyphenol in CCl ₄ containing various concentrations of DMSO.	S-6
Figure S2. OH-stretching region of 2,4-dimethoxyphenol in CCl ₄ containing various concentrations of DMSO.	S-7
Figure S3. OH-stretching region of 2,4,6-trimethoxyphenol in CCl ₄ containing various concentrations of DMSO.	S-7
Figure S4. Plots of $[\text{ArOH}]_{\text{o}}/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,6-dimethoxyphenol	S-8
Figure S5. Plots of $[\text{ArOH}]_{\text{o}}/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,4-dimethoxyphenol	S-8

Figure S6. Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,4,6-trimethoxyphenol	S-9
Figure S7. OH-stretching region of 2-nitrophenol in CCl_4 containing various concentrations of DMSO.	S-10
Figure S8. OH-stretching region of 2,6-dinitrophenol in CCl_4 containing various concentrations of DMSO.	S-10
Figure S9. OH-stretching region of 2,4-nitro phenol in CCl_4 .	S-11
Figure S10. OH-stretching region of 2,4-dinitrophenol in CCl_4 containing various concentrations of DMSO.	S-11
Figure S11 Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,4-di- NO_2 -phenol in CCl_4 containing various concentrations of DMSO.	S-12
Figure S12. OH-stretching region of 2,4,6-trinitrophenol in CCl_4 containing various concentrations of THF.	S-13
Figure S13. OH-stretching region of 2,4,6-trinitrophenol in CCl_4 containing various concentrations of DMSO.	S-13
Figure S14. OH-stretching region of 2,4-diformylphenol in CCl_4 containing various concentrations of DMSO.	S-14
Figure S15. OH-stretching region of 2-hydroxyacetophenone in CCl_4 containing various concentrations of DMSO.	S-14
Figure S16. OH-stretching region of 7-hydroxyindanone in CCl_4 containing various concentrations of DMSO.	S-15
Figure S17. OH-stretching region of 2-formylphenol in CCl_4 containing various concentrations of DMSO.	S-15
Figure S18. OD-stretching band of O-deuterio 2-methoxymethylphenol (20.5 mM) in CCl_4 .	S-16
Figure S19 Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2-methoxymethylphenol in CCl_4 containing various concentrations of DMSO.	S-17
Figure S20. Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{HBA}]_{\text{free}}$ for 4-fluorophenol in CCl_4 containing various concentrations of 3,5-dinitrobenzene.	S-18
Figure S21. OH-stretching region of 2-methoxymethylphenol (20.5 mM) in CCl_4 .	S-21
Figure S22. Example of LDBS partitioning..	S-22
Parameters used for calculation the ratio of free to internally H-bonded hydroxyl group in 2-methoxymethyl phenol	S-22

EXPERIMENTAL DETAILS

Synthesis of 2,4- dimethoxyphenol and 2,4,6-trimethoxyphenols. These phenols were prepared according to method described by Matsumoto et al. (Matsumoto M., Kobayashi H., Hotta Y. J. Org. Chem.1984, 49, 4741-4743): About 37 mmol of 2,4- dimethoxybenzaldehyde (or 2,4,6-trimethoxybenzaldehyde) was stirred with 48 mmol of 31% H₂O₂ in 30 mL methanol in the presence of 0.5 mL H₂SO₄ under argon atmosphere at room temperature during 12 hours. Resulting 2,4- dimethoxyphenol (85% yield) and 2,4,6-trimethoxyphenol (78%), respectively, were purified by column chromatography on SiO₂.

Synthesis of 2-methoxymethylphenol. Procedure described by De Jonge et al. (De Jonge, J.; Bibo, B. H. *Rec. Trav. Chim. Pays-Bas* **1955**, 74, 1448-1452) was followed: 4 g of 2-hydroxybenzyl alcohol was heated in sealed ampoule with 20 mL of anhydrous methanol during 4 hours at 150°C. After that time the excess of methanol was evaporated under reduced pressure and yellowish oil (3.95g) was distilled under vacuum. Main fraction (colorless oil, 1.5 g) was analyzed by GC MS indicating 2-methoxymethylphenol. The oil was stored at -80°C during two years to give single crystal.

Kinetic Measurements.

Solutions of **dpph**[•] and the phenol were prepared in nitrogen-purged solvents and were kept under nitrogen, with additional nitrogen-purging when necessary, until they were taken-up into the glass syringes of the stopped-flow apparatus with their gastight Teflon plungers. The decay of **dpph**[•] in the presence of a known concentration of phenols was followed at 517 nm on an Applied Photophysics Stopped-Flow Spectrophotometer, SX 18 MV equipped with a 150 W xenon lamp. All measurements were carried out at 23 ± 2 °C in heptane. The concentration of **dpph**[•] was (8.5 ± 1.0) × 10⁻⁵ M. Phenols were always used in large excess over [**dpph**[•]]. These measurements lead to determination of first order rate constants, k_{exptl} for each phenol concentration. Bimolecular rate constants, $k^{\text{S}}/\text{M}^{-1} \text{s}^{-1}$, were calculated from the slopes of the linear plots of k_{exptl} vs. phenol concentration: $k_{\text{exptl}} = k^{\text{S}}[\text{phenol}] + \text{const}$

Infrared Measurements.

Experiments were done in CCl₄ (or cyclohexane) with DMSO as HBAs and with a SHIMADZU FTIR 8201PC apparatus with a 1.03 mm (or 2.5 mm) CaF₂ cell at ambient temperatures and a baseline correction was made using the same concentration of the HBA.

For α_2^{H} determination: the formation of *intermolecular* HB complex with HBA is described by:



and the equilibrium constant is given by:

$$K^{\text{i}} = \frac{[\text{ArOH} \cdots \text{HBA}]_{\text{intermolecular}}}{[\text{ArOH}]_{\text{free}}[\text{HBA}]_{\text{free}}} \quad (1)$$

where [ArOH]_{free} denotes the concentration of phenol molecules not participating in an *intermolecular* HB. Values of [ArOH]_{free} were determined from the decrease

in the peak height of the internally hydrogen bonded OH. The concentration of free phenols was determined by using a calibration curve. Equation 1 can be transformed to the form: $[\text{ArOH}]_o / [\text{ArOH}]_{\text{free}} = 1 + K^i [\text{HBA}]_{\text{free}}$, where $[\text{ArOH}]_o$ is the total concentration of phenol, and values of K^i were determined from the plots of the ratio $[\text{ArOH}]_o / [\text{ArOH}]_{\text{free}}$ versus $[\text{HBA}]_{\text{free}}$. Values of α_2^H were calculated using the equations:

$$\log K_A^{\text{H}_i} = (\log K^i - D_B) / L_B \quad (2)$$

$$\alpha_2^H = (\log K_A^{\text{H}_i} + 1.1) / 4.636 \quad (3)$$

The Equations and D_B and L_B values are from work by Abraham et al.s' (*J. Chem. Soc., Perkin Trans. 2* **1989**, 699-711).

Value β_2^H for 1,3-dinitrobenzene was calculated from the equation:

$$\beta_2^H = (\log K_B^H + 1.1) / 4.636 \quad (4)$$

where $\log K_B^H$ is connected to the experimental equilibrium constants K^i by the equation: $\log K^i = L_A \log K_B^H + D_A$ (see Abraham et al. *J. Chem. Soc., Perkin Trans. 2* **1990**, 521-529.). For the reference acid, 4-fluorophenol, $L_A=1.000$ and $D_A=0.000$,³¹ and hence $\log K_B^H = \log K^i$.

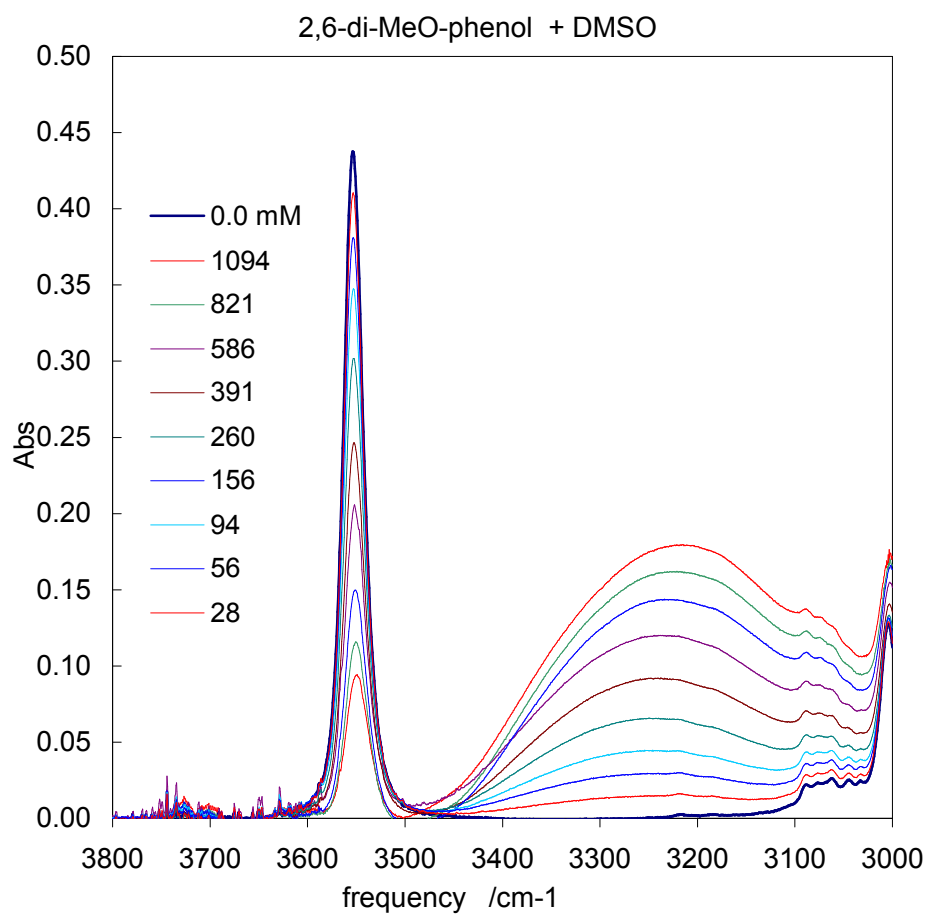
Table S1. Parameters used for calculation of the equilibrium constant $K^S_{\text{ArOH/S}}$ for HB complex formation between DMSO and phenols. $[\text{ArOH}]_o$ = total concentration of phenol, $[\text{ArOH}]_{\text{free}}$ = concentration of non-hydrogen bonded phenol calculated from IR measurements, $[\text{HB}] = [\text{ArOH}]_o - [\text{ArOH}]_{\text{free}}$, $[\text{DMSO}]_o$ = total concentration of DMSO in CCl_4 , $[\text{DMSO}]_{\text{free}}$ = concentration of free (i.e. non-hydrogen bonded) DMSO.

$[\text{ArOH}]_o$	$[\text{ArOH}]_{\text{free}}$	$[\text{HB}]$	$[\text{DMSO}]_o$	$[\text{DMSO}]_{\text{free}}$	$[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$
2,6-di-MeO-phenol + DMSO (band at 3554 cm^{-1})					
21.35	21.35	0.0	0.0	0.0	1.00
21.35	19.81	1.5	28.1	26.6	1.08
21.35	18.40	2.9	56.2	53.3	1.16
21.35	16.86	4.5	93.7	89.2	1.27
21.35	14.56	6.8	156.0	149.2	1.47
21.35	11.88	9.5	260.0	250.5	1.80
21.35	9.68	11.7	391.0	379.3	2.21
21.35	7.12	14.2	586.0	571.8	3.00
21.35	5.44	15.9	821.0	805.1	3.92
21.35	4.38	17.0	1094.0	1077.0	4.87
21.35	3.59	17.8	1406.0	1388.2	5.95
2,4-di-MeO-phenol + DMSO (band at 3566 cm^{-1})					
15.63	15.63	0.0	0.0	0.0	1.00
15.63	13.60	2.0	28.1	26.1	1.15
15.63	12.39	3.2	56.2	53.0	1.26
15.63	11.14	4.5	93.7	89.2	1.40
15.63	9.58	6.1	156.0	149.9	1.63
15.63	7.34	8.3	260.0	251.7	2.13
15.63	6.13	9.5	391.0	381.5	2.55
15.63	4.80	10.8	586.0	575.2	3.25
15.63	3.48	12.2	821.0	808.8	4.49
15.63	3.07	12.6	1094.0	1081.4	5.09
15.63	2.74	12.9	1406.0	1393.1	5.71
2,4-di-MeO-phenol + DMSO (band at 3566 cm^{-1})					
17.40	17.39	0.0	0.0	0.00	1.00
17.40	16.20	1.2	28.1	26.90	1.07
17.40	14.83	2.6	56.2	53.63	1.17
17.40	13.50	3.9	93.7	89.80	1.29
17.40	11.58	5.8	156.0	150.18	1.50
17.40	9.90	7.5	260.0	252.50	1.76
17.40	8.29	9.1	391.0	381.89	2.10

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Table S1. Continue

[ArOH] _o	[ArOH] _{free}	[HB]	[DMSO] _o	[DMSO] _{free}	[ArOH] _o /[ArOH] _{free}
2,4,6-tri-MeO-phenol + DMSO (band at 3563 cm ⁻¹)					
13.56	13.56	0.0	0.0	0.0	1.00
13.56	12.99	0.6	28.1	27.5	1.04
13.56	12.03	1.5	56.2	54.7	1.13
13.56	11.12	2.4	93.7	91.3	1.22
13.56	9.89	3.7	156.0	152.3	1.37
13.56	7.85	5.7	260.0	254.3	1.73
13.56	6.30	7.3	391.0	383.7	2.15
13.56	5.06	8.5	586.0	577.5	2.68
13.56	4.19	9.4	821.0	811.6	3.24
13.56	3.81	9.8	1094.0	1084.2	3.56
13.56	3.08	10.5	1406.0	1395.5	4.41

**Figure S1.** OH-stretching region of 2,6-dimethoxyphenol in CCl₄ containing various concentrations of DMSO.

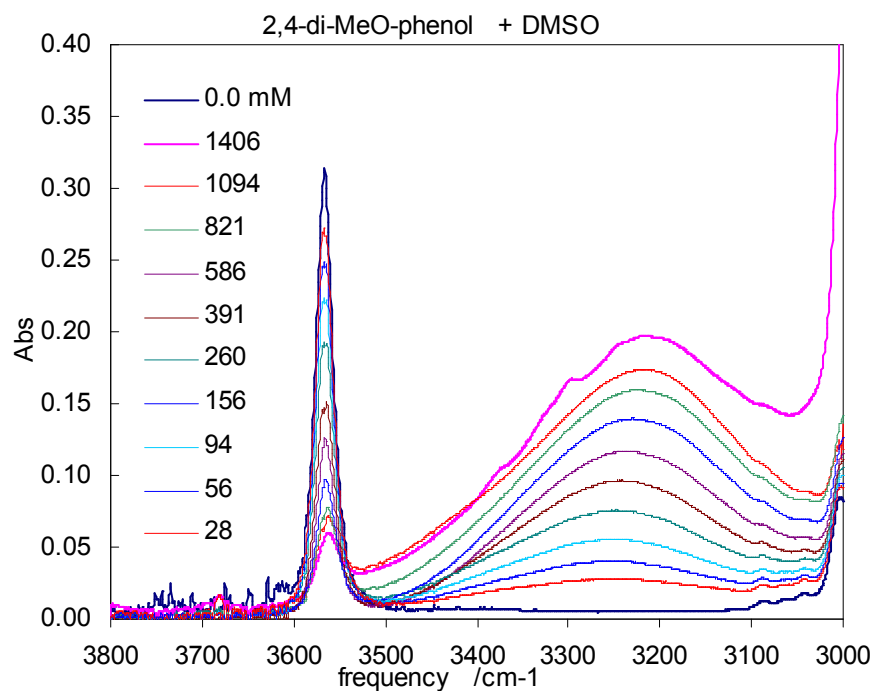


Figure S2. OH-stretching region of 2,4-dimethoxyphenol in CCl_4 containing various concentrations of DMSO (in mM).

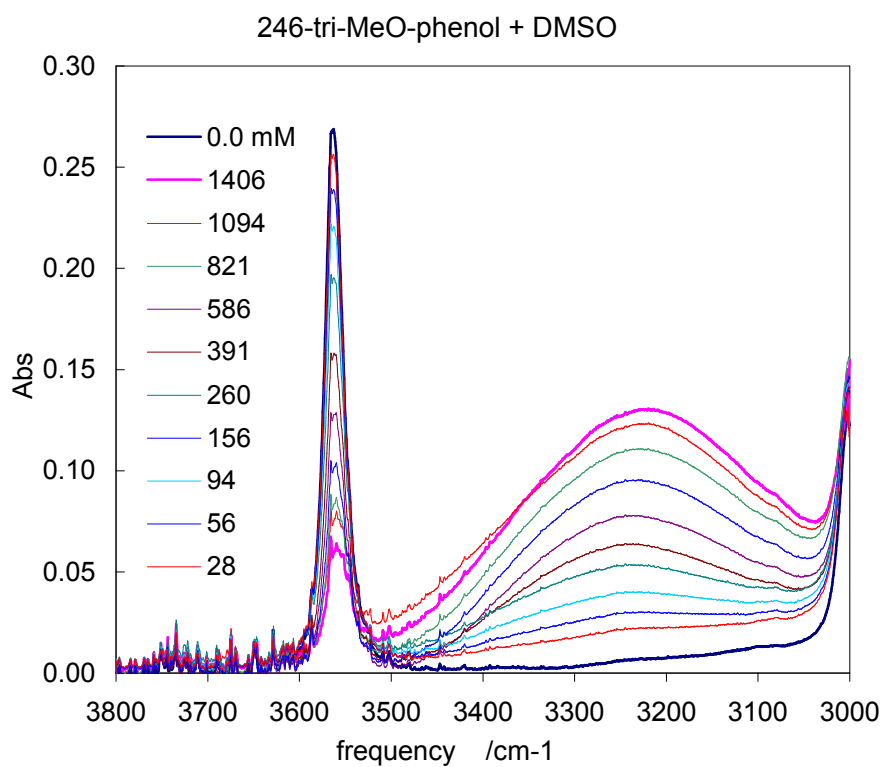


Figure S3. OH-stretching region of 2,4,6-trimethoxyphenol in CCl_4 containing various concentrations of DMSO (in mM).

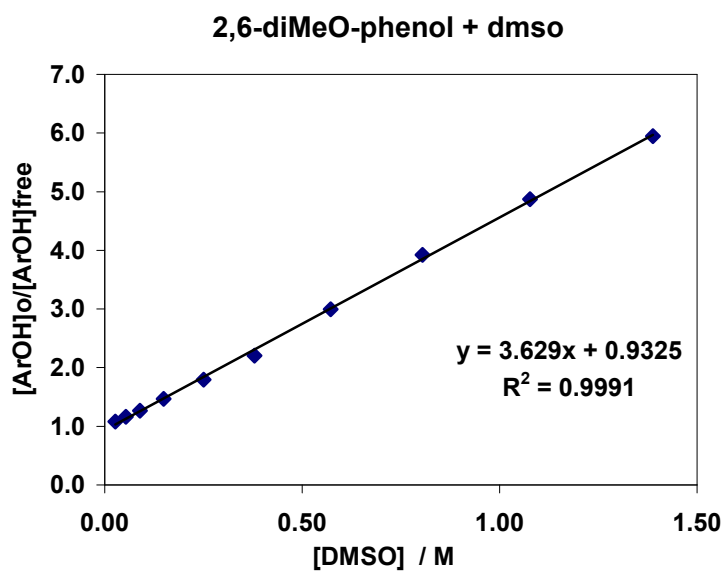


Figure S4. Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,6-dimethoxyphenol (data from Table S1)

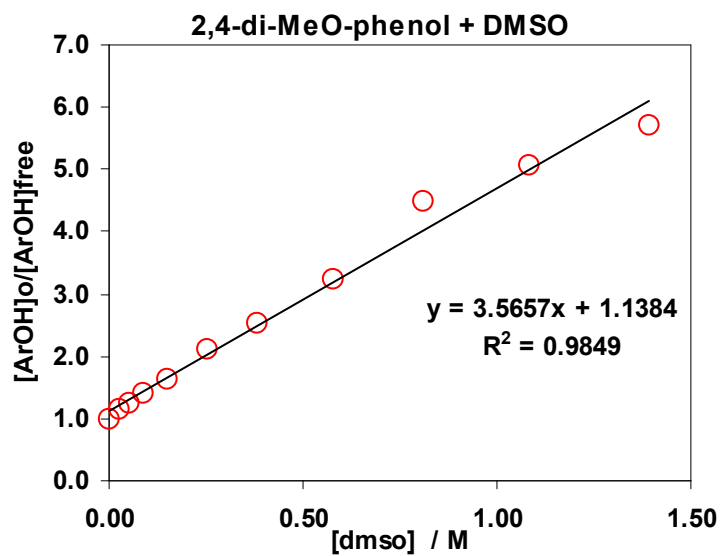


Figure S5. Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,4-dimethoxyphenol (data from Table S1)

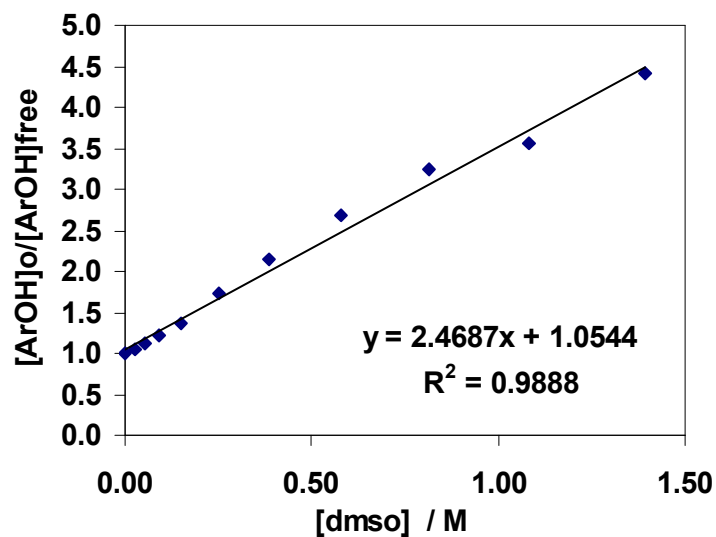


Figure S6. Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,4,6-trimethoxyphenol (data from Table S1).

Table S2. Values $K_A^{H_i}$, $\log K_A^{H_i}$, and α_2^H for methoxyphenols calculated from IR measurements of HB complex formation with DMSO ($L_B=1.24$ and $D_B=0.266$).

phenol	$K_A^{H_i}$	$\log K_A^{H_i}$	α_2^H
2,6-dimethoxyphenol	3.630	0.24	0.29
2,4-dimethoxyphenol	2.700	0.13	0.27
2,4-dimethoxyphenol	3.560	0.23	0.29
2,4,6-trimethoxyphenol	2.470	0.12	0.26

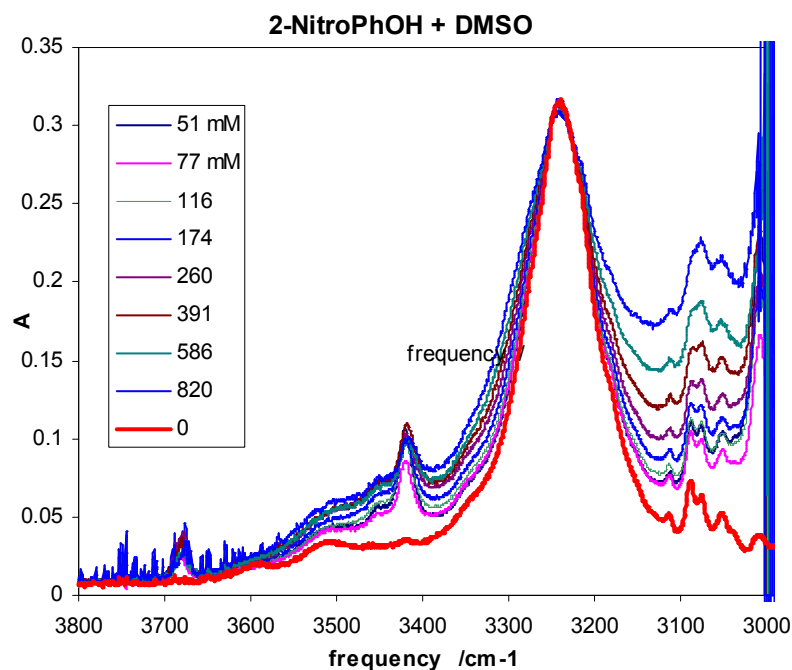


Figure S7. OH-stretching region of 2-nitrophenol in CCl_4 containing various concentrations of DMSO(in mM).

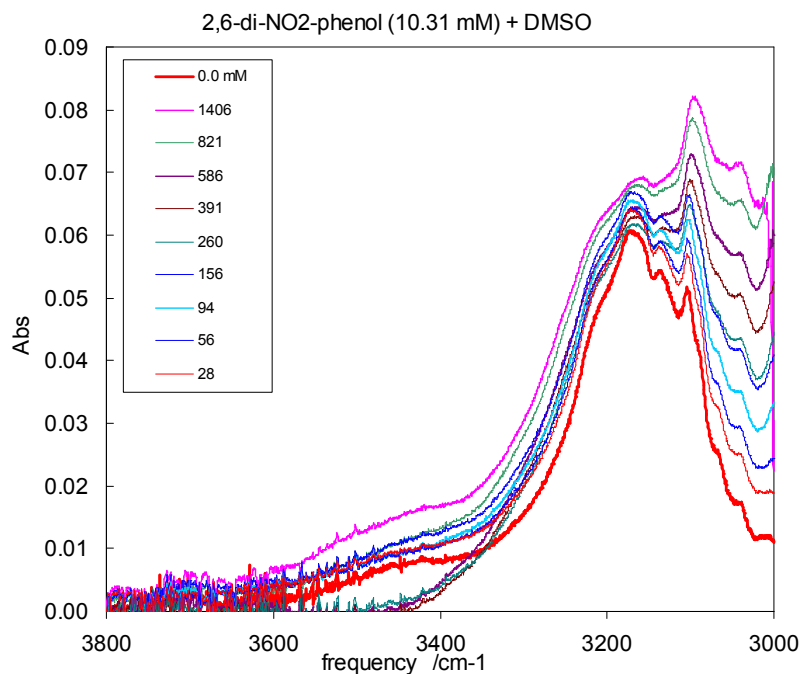


Figure S8. OH-stretching region of 2,6-dinitrophenol in CCl_4 containing various concentrations of DMSO(in mM).

Figure S9. OH-stretching region of 2,4-dinitro phenol in CCl₄. Concentration of phenol in mM units.

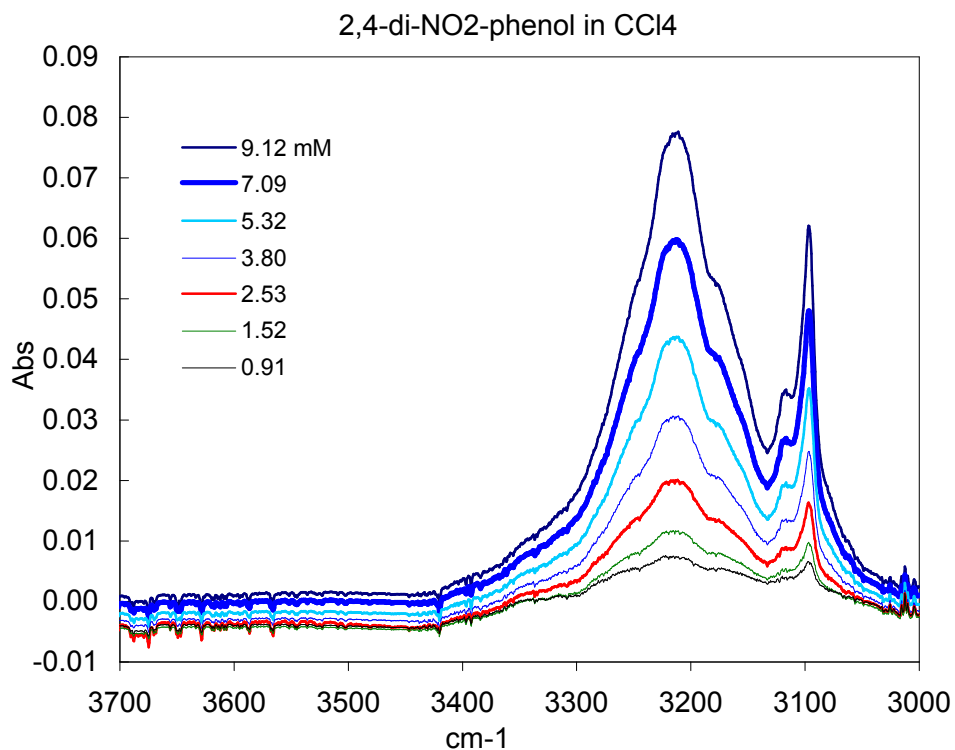


Figure S10. OH-stretching region of 2,4-dinitrophenol in CCl₄ containing various concentrations of DMSO (in mM).

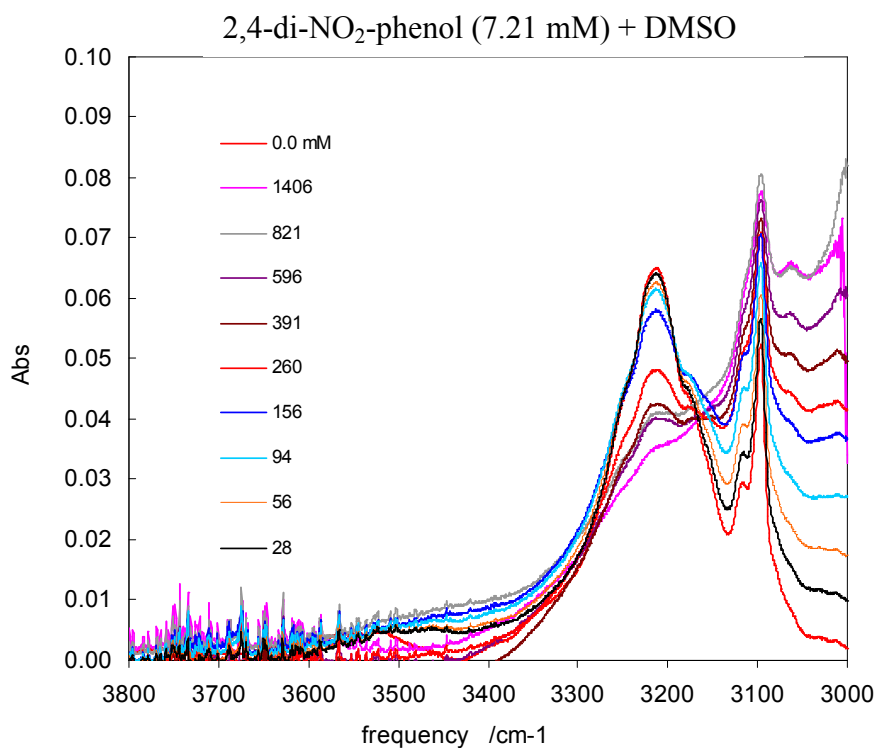


Table S3. Parameters used for calculation of the equilibrium constant $K^S_{\text{ArOH/S}}$ for HB complex formation between DMSO and 2,4-dinitrophenol. $[\text{ArOH}]_o$ = total concentration of phenol, $[\text{ArOH}]_{\text{free}}$ = concentration of non-hydrogen bonded phenol calculated from IR measurements, $[\text{HB}] = [\text{ArOH}]_o - [\text{ArOH}]_{\text{free}}$, $[\text{DMSO}]_o$ = total concentration of DMSO in CCl_4 , $[\text{DMSO}]_{\text{free}}$ = concentration of free (i.e. non-hydrogen bonded) DMSO.

$[\text{ArOH}]_o$	$[\text{ArOH}]_{\text{free}}$	$[\text{HB}]$	$[\text{DMSO}]_o$	$[\text{DMSO}]_{\text{free}}$	$[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$
2,4-di- NO_2 -phenol + DMSO					
7.21	7.21	0.0	0.0	0.00	1.00
7.21	6.62	0.6	28.1	27.51	1.09
7.21	5.94	1.3	56.2	54.93	1.21
7.21	5.27	1.9	93.7	91.76	1.37
7.21	4.26	3.0	156.0	153.05	1.69
7.21	3.14	4.1	260.0	255.93	2.29
2,4-di- NO_2 -phenol + DMSO					
19.72	19.72	0.0	0.0	0.00	1.00
19.72	15.78	3.9	51.0	47.06	1.25
19.72	14.23	5.5	77.0	71.51	1.39
19.72	12.63	7.1	116.0	108.91	1.56
19.72	10.10	9.6	174.0	164.38	1.95
19.72	7.51	12.2	260.0	247.79	2.63
19.72	5.91	13.8	391.0	377.19	3.34

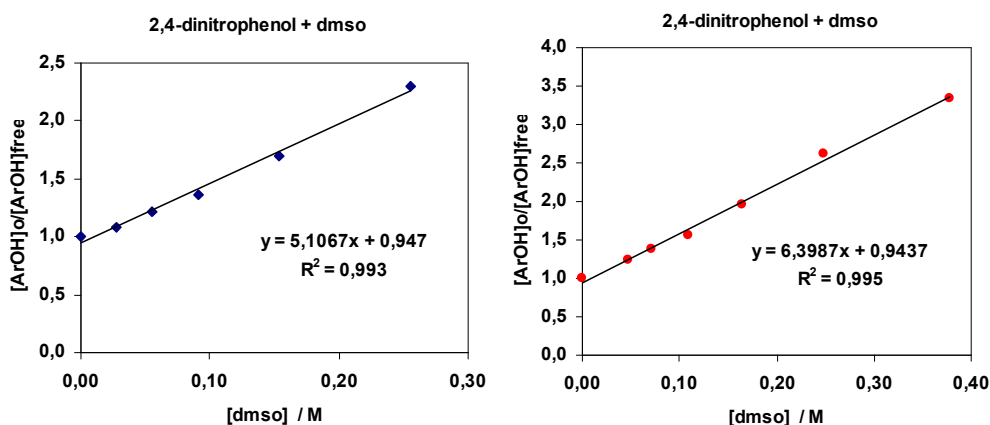


Figure S11 Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2,4-di- NO_2 -phenol in CCl_4 containing various concentrations of DMSO.

From these two series of measurements two values of K were obtained: 5.11 and 6.40 M^{-1} , thus, the mean $K = 5.7 \text{ M}^{-1}$.

Figure S12. OH-stretching region of 2,4,6-trinitrophenol in CCl_4 containing various concentrations of THF (in mM).

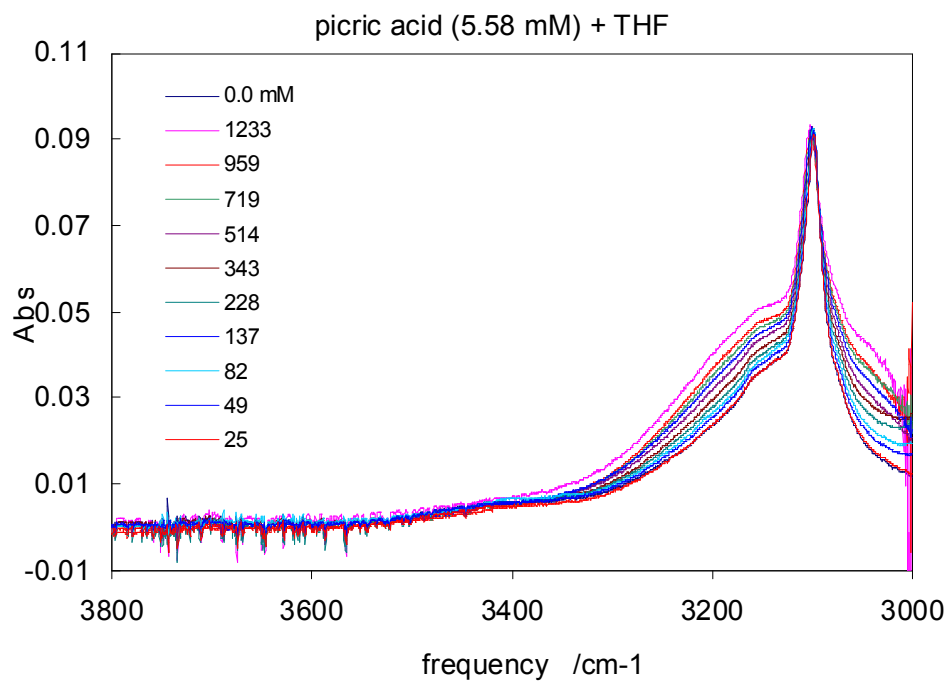


Figure S13. OH-stretching region of 2,4,6-trinitrophenol in CCl_4 containing various concentrations of DMSO (in mM).

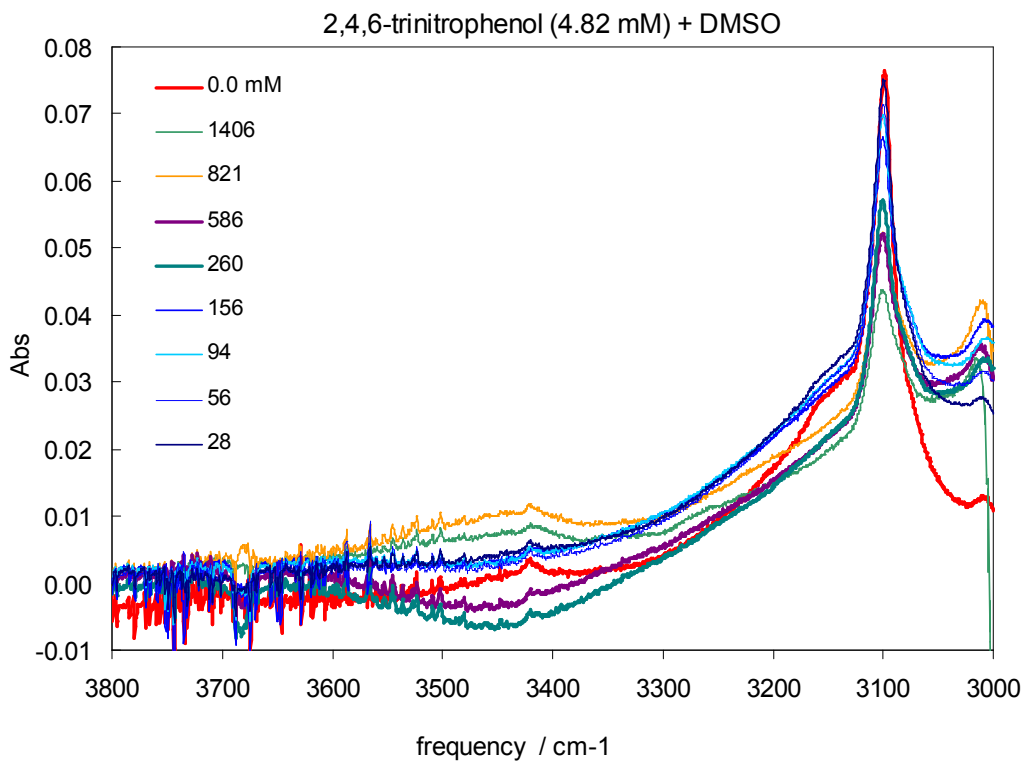


Figure S14. OH-stretching region of 2,4-diformylphenol in CCl_4 containing various concentrations of DMSO (in mM).

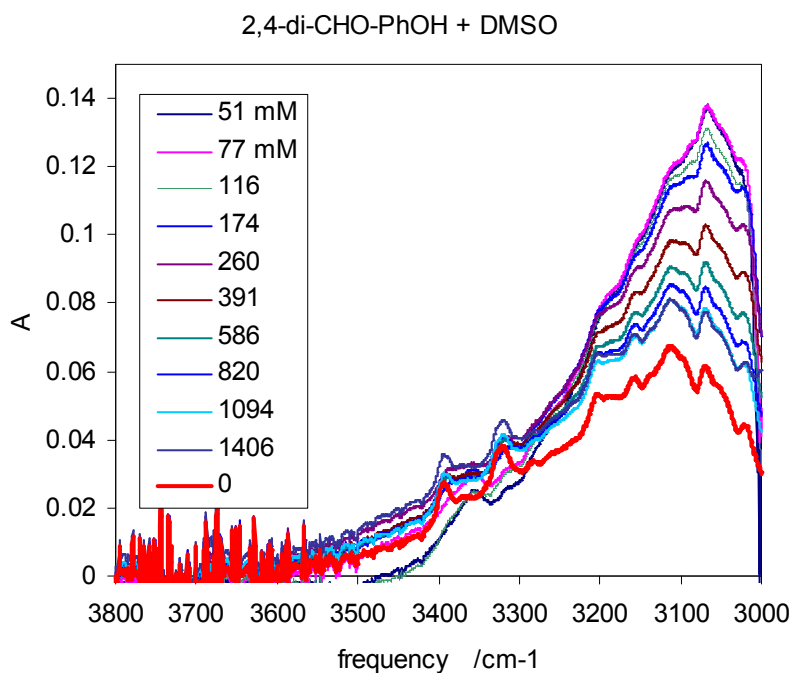


Figure S15. OH-stretching region of 2-hydroxyacetophenone in CCl_4 containing various concentrations of DMSO (in mM).

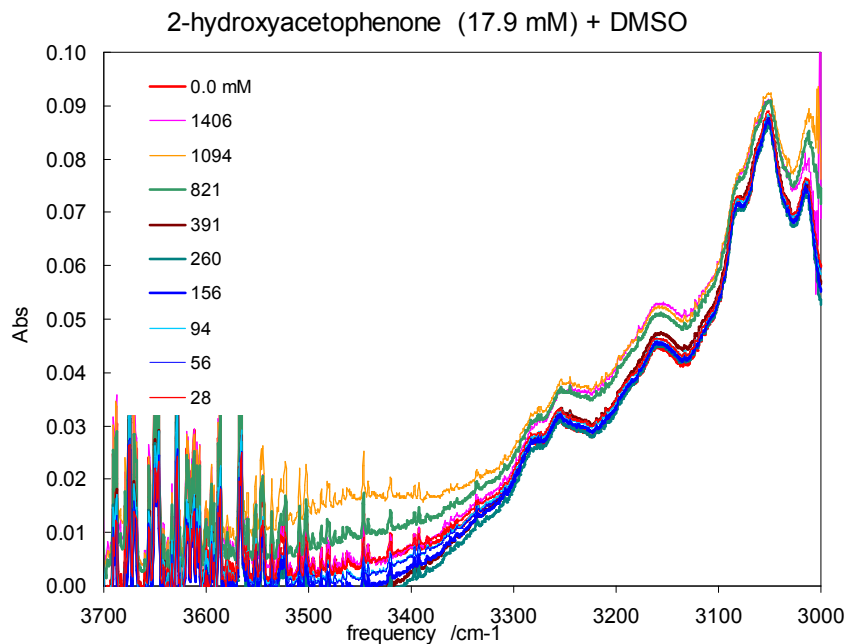


Figure S16. OH-stretching region of 7-hydroxyindanone in CCl_4 containing various concentrations of DMSO (in mM).

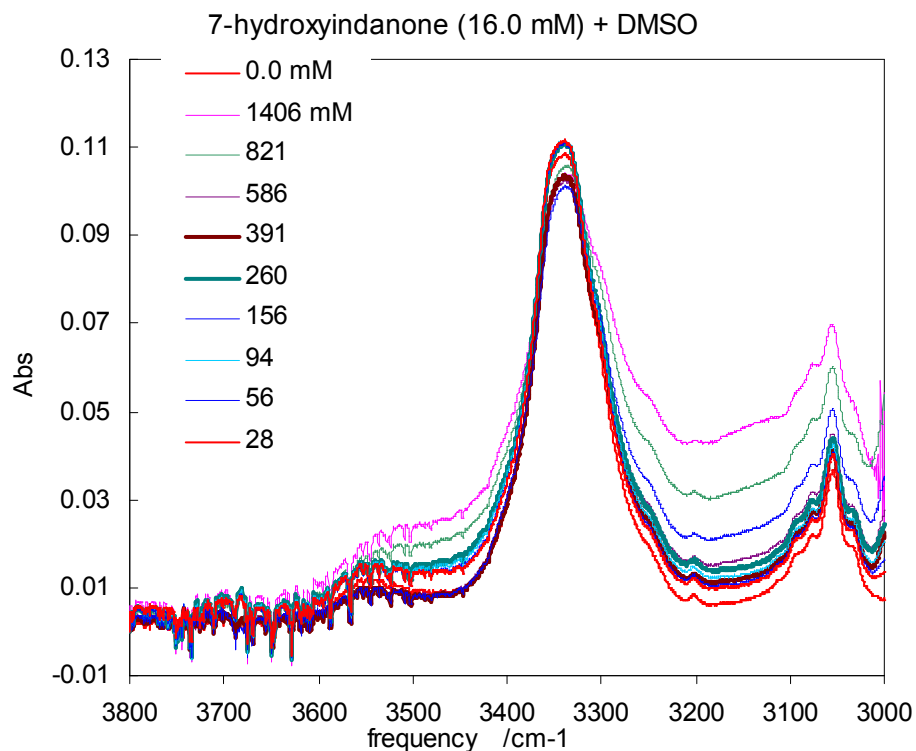
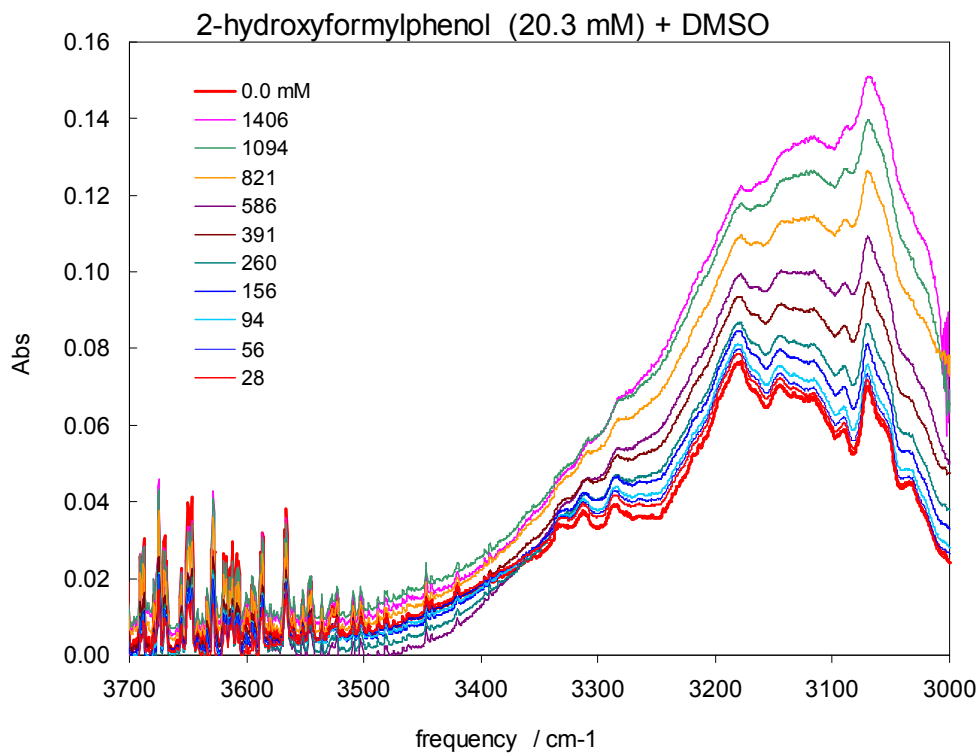


Figure S17. OH-stretching region of 2-formylphenol (salicylaldehyde) in CCl_4 containing various concentrations of DMSO (in mM).



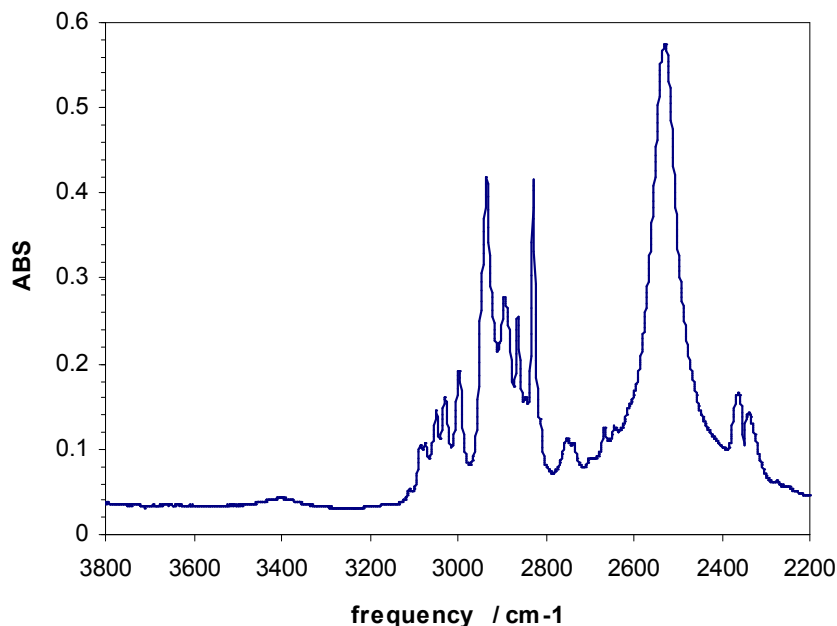


Figure S18. OD-stretching band of O-deuterio 2-methoxymethylphenol (20.5 mM) in CCl₄

Table S4. Parameters used for calculation of the equilibrium constant $K_{\text{ArOH/S}}^{\text{S}}$ for HB complex formation between DMSO and 2-methoxymethylphenol. [ArOH]_o = total concentration of phenol, [ArOH]_{free} = concentration of non-hydrogen bonded phenol calculated from IR measurements, [HB] = [ArOH]_o - [ArOH]_{free}, [DMSO]_o = total concentration of DMSO in CCl₄, [DMSO]_{free} = concentration of free (i.e. non-hydrogen bonded) DMSO.

[ArOH] _o	[ArOH] _{free}	[HB]	[DMSO] _o	[DMSO] _{free}	[ArOH] _o /[ArOH] _{free}
0.359	0.359	0.0000	0.0	0.0	1.00
0.359	0.175	0.1836	15.0	14.8	2.05
0.359	0.123	0.2364	30.0	29.8	2.93
0.359	0.068	0.2906	50.0	49.7	5.25
0.359	0.042	0.3169	80.0	79.7	8.53

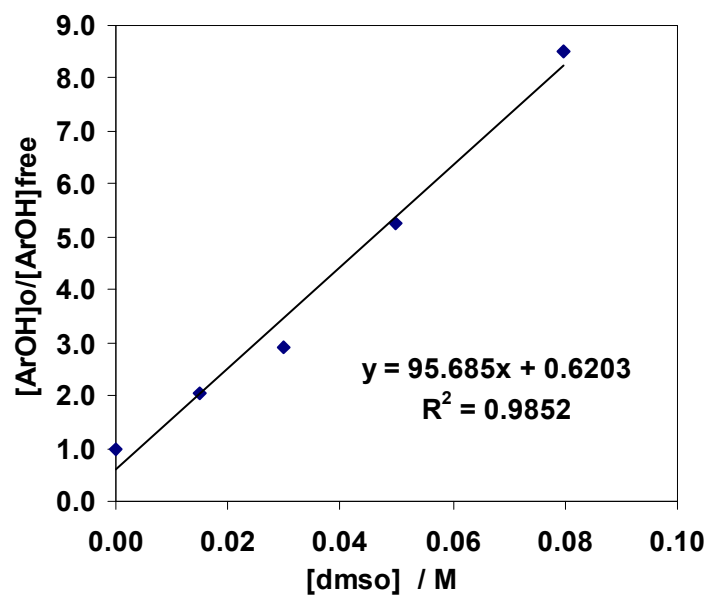


Figure S19 Plots of $[\text{ArOH}]_o/[\text{ArOH}]_{\text{free}}$ vs. $[\text{DMSO}]_{\text{free}}$ for 2-methoxymethylphenol in CCl_4 containing various concentrations of DMSO.

$L_B = 1.24$, $D_B = 0.266$, $K = 95.7 \text{ M}^{-1}$, $\log K_A^{H_i} = 1.398$, $\alpha_2^H = 0.53$

Table S5. Parameters used for calculation of the equilibrium constant $K^S_{\text{ArOH/S}}$ for HB complex formation between 4-F-phenol and 1,3-dinitrobenzene. $[\text{ArOH}]_0$ = total concentration of 4-F-phenol, $[\text{ArOH}]_{\text{free}}$ = concentration of non-hydrogen bonded phenol calculated from IR measurements, $[\text{HB}] = [\text{ArOH}]_0 - [\text{ArOH}]_{\text{free}}$, $[\text{HBA}]_0$ = total concentration of 1,3-dinitrobenzene in CCl_4 , $[\text{HBA}]_{\text{free}}$ = concentration of free (i.e. non-hydrogen bonded) 3,5-dinitrobenzene.

$[\text{ArOH}]_0$	$[\text{ArOH}]_{\text{free}}$	$[\text{HB}]$	$[\text{HBA}]_0$	$[\text{HBA}]_{\text{free}}$	$[\text{ArOH}]_0/[\text{ArOH}]_{\text{free}}$
14.16	14.16	0.00	0.0	0.00	1.000
14.16	14.12	0.04	9.9	9.84	1.003
14.16	14.13	0.03	14.8	14.80	1.002
14.16	13.85	0.31	22.2	21.93	1.022
14.16	13.65	0.51	31.1	30.64	1.037
14.16	13.46	0.70	41.5	40.82	1.052
14.16	13.25	0.91	55.4	54.45	1.069
14.16	12.89	1.27	71.2	69.91	1.099
14.16	12.43	1.73	91.5	89.79	1.139
14.16	12.05	2.11	114.4	112.29	1.175
2.88	2.88	0.00	0.0	0.00	1.00
2.88	2.88	0.00	9.9	9.89	1.00
2.88	2.84	0.04	14.8	14.79	1.01
2.88	2.80	0.08	22.2	22.16	1.03
2.88	2.75	0.13	31.1	31.01	1.05
2.88	2.68	0.20	41.5	41.33	1.07
2.88	2.60	0.28	55.4	55.08	1.11
2.88	2.48	0.40	71.2	70.78	1.16
2.88	2.42	0.46	91.5	91.06	1.19
2.88	2.30	0.58	114.4	113.82	1.25

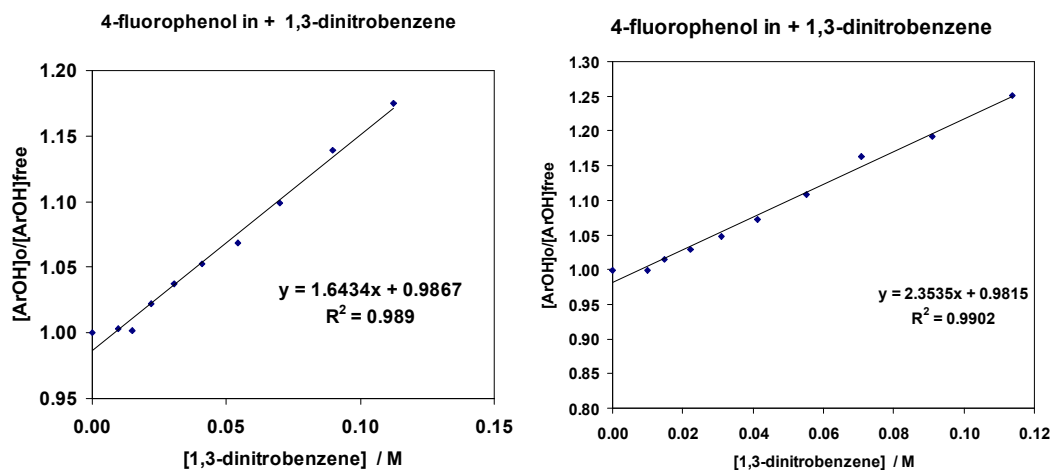


Figure S20. Plots of $[\text{ArOH}]_0/[\text{ArOH}]_{\text{free}}$ vs. $[\text{HBA}]_{\text{free}}$ for 4-fluorophenol in CCl_4 containing various concentrations of 1,3-dinitrobenzene.

$L_A = 1.000$, $D_A = 0.000$, $K = 1.88 \text{ M}^{-1}$, $\log K_B^{H_1} = 0.259$, $\beta_2^H = 0.30$ (after statistical correction $\beta_2^H = 0.23$).

Table S6. Kinetic data for the reaction of **dpph[•]** with 2,4-dimethoxyphenol in heptane. Concentration [CU], pseudo-first-order rate constant k_{ex} , R^2 for each data set The calculated mean bimolecular rate constant is denoted as ($k^S \pm$ absolute error).

[PhOH] $\times 10^5$ /M	k_{ex} /s-1	[PhOH] $\times 10^5$ /M	k_{ex} /s-1
112.2	0.330	65.5	0.194
87.3	0.252	46.8	0.157
65.5	0.192	31.2	0.112
46.8	0.149	20.8	0.077
31.2	0.100	13.9	0.051
20.8	0.058	9.2	0.032
13.9	0.041	6.2	0.023
9.2	0.031	65.5	0.194
6.2	0.020		
112.2	0.330		
$k = 291 \text{ M}^{-1}\text{s}^{-1}$		$k = 295 \text{ M}^{-1}\text{s}^{-1}$	
$\Delta k^a = 9$		$\Delta k^a = 30$	
$R^2 = 0.9979$		$R^2 = 0.9859$	

^a calculated as the confidence interval of the slope for the 90% confidence level.

$$k^S = 290 \pm 30 \text{ M}^{-1}\text{s}^{-1}$$

Table S7. Kinetic data for the reaction of **dpph[•]** with 2,4,6-trimethoxyphenol in heptane. Symbols are the same as described in Table S5.

[PhOH] $\times 10^5$ /M	k_{ex} /s-1	[PhOH] $\times 10^5$ /M	k_{ex} /s-1
121.6	0.405	121.6	0.368
94.6	0.354	94.6	0.298
70.9	0.276	70.9	0.230
50.7	0.212	50.7	0.178
33.8	0.146	33.8	0.117
20.3	0.100	22.5	0.082
12.2	0.042	15.0	0.055
7.3	0.033	10.0	0.037
4.4	0.019	6.7	0.026
$k = 340 \text{ M}^{-1}\text{s}^{-1}$		$k = 300 \text{ M}^{-1}\text{s}^{-1}$	
$\Delta k^a = 30$		$\Delta k^a = 12$	
$R^2 = 0.9845$		$R^2 = 0.9969$	

^a calculated as the confidence interval of the slope for the 90% confidence level.

$$k^S = 320 \pm 20 \text{ M}^{-1}\text{s}^{-1}$$

Table S8. Kinetic data for the reaction of **dp^{ph}•** with 2-methoxymethylphenol in heptane. Symbols are the same as described in Table S5.

[PhOH] /mM	10 ³ ×k _{ex} /s-1	[PhOH] /mM	10 ³ ×k _{ex} /s-1	[PhOH] /mM	10 ³ ×k _{ex} /s-1
17.3	2.20	20.7	1.13	22.9	1.17
13.4	2.01	16.1	0.93	17.8	1.00
10.1	1.85	12.5	0.77	13.4	0.78
7.2	1.75	9.4	0.58	9.5	0.60
4.8	1.70	7.1	0.45	6.4	0.45
3.2	1.52	5.0	0.35	4.2	0.31
2.1	1.38	3.6	0.25	2.8	0.22
		2.4	0.18		
k = 4.9×10⁻² M⁻¹s⁻¹		k = 5.2×10⁻² M⁻¹s⁻¹		k = 4.8×10⁻² M⁻¹s⁻¹	
Δk^a = 0.8×10⁻²		Δk^a = 0.3×10⁻²		Δk^a = 0.4×10⁻²	
R² = 0.9604		R² = 0.9958		R² = 0.9923	

^a calculated as the confidence interval of the slope for the 90% confidence level.

$$k^S = (5.0 \pm 0.5) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$

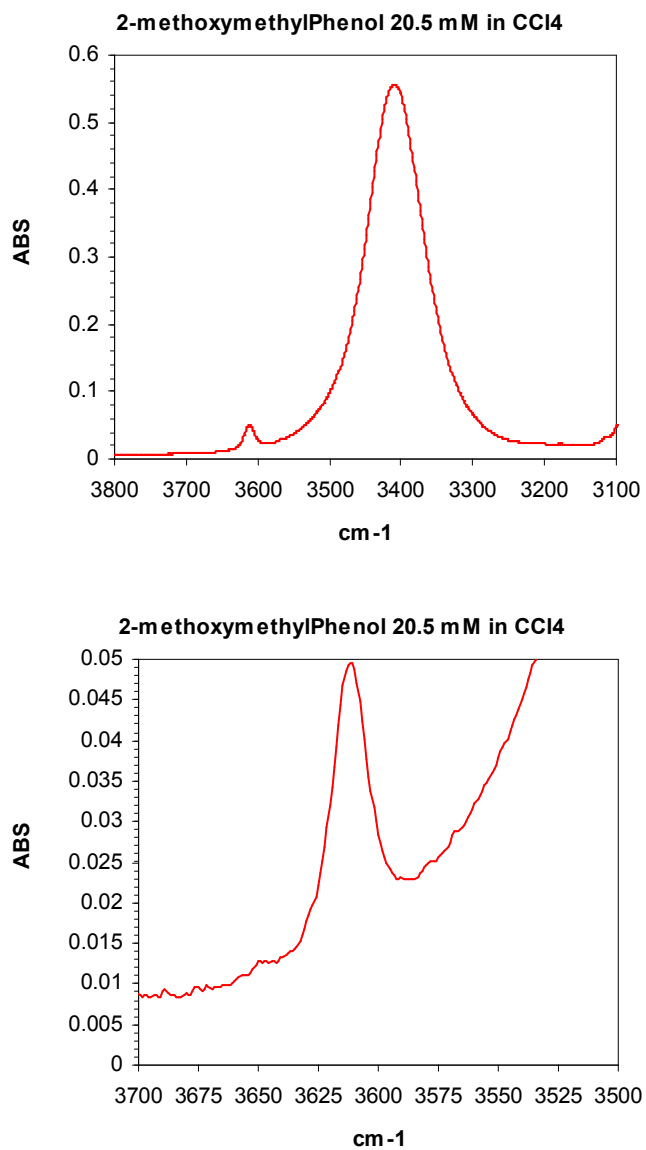
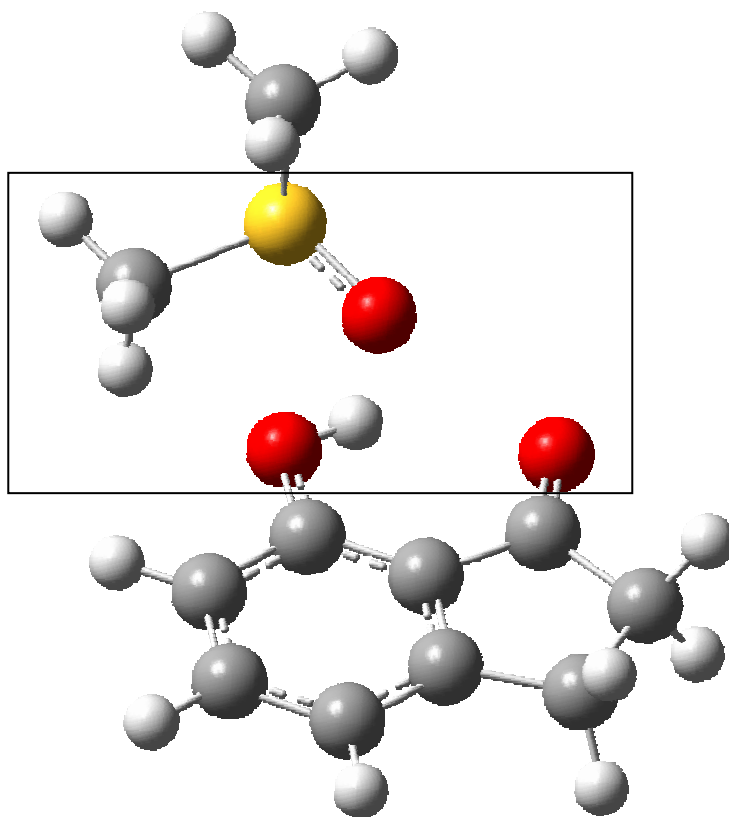


Figure S21. OH-stretching region of 2-methoxymethylphenol (20.5 mM) in CCl₄. Lower panel shows the same plot limited to the region 3500-3700 cm⁻¹ with free OH stretching band.



FigureS22.

Example of LDBS partitioning. The atoms contained in the rectangle are assigned 6-311++G(2d,2p) basis functions. The remaining atoms are represented by 6-31G(d) basis sets.

Parameters used for calculation the ratio of free to internally H-bonded hydroxyl group in 2-methoxymethyl phenol

Method 1- Peak intensity measurements in cyclohexane.

Free OH band height after baseline subtraction = **0.0366** a.u. ,
concentration of free OH = 0.277 mM (calculated on phenol in cyclohexane)
Total concentration of 2-methoxymethylphenol = **18.6 mM**
%free OH=0.277 / 18.6 *100%= 1.49 %

Method 2- Peak intensity measurements in CCl₄.

Free OH band height after baseline subtraction = **0.032** a.u. ,
concentration of free OH = **0.395 mM** (calculated on phenol in cyclohexane)
Total concentration of 2-methoxymethylphenol = **20.5 mM**
%free OH=0. 395 / 20.5 *100%= 1.92 % (see Figure S21)
Free OH band height after baseline subtraction = **0.0305** a.u. ,
concentration of free OH = **0.372 mM** (calculated on phenol in cyclohexane)
Total concentration of 2-methoxymethylphenol = **16.68 mM**
%free OH=0. 370 / 16.68 *100%= 2.23 %

Mean value =2.1% of free OH in CCl₄

Method 3- Area ratio measurements in CCl₄.

(Area of free OH) /(Area of H-Bonded OH) *100% = 0.72 / 37.16 *100% = 1.9%