

Potentiometric Determination of Acid Dissociation Constants of Novel Biaryl Monomers

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5 Electronic Supporting Information.

Figure ESI1. Linear plot of experimentally determined dielectric constants of water in various THF-water mixtures at 25°C.¹⁸

Figure ESI1. Autoprotolysis constant of H₂O at various THF-water mixtures measured at 25°C.¹⁹

Table ESI1. Yasuda-Shedlovsky parameters in THF-water mixtures and aqueous p*K*_s for analytes **A8H** and **A9**.

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Table ESI2. Summary of the p*K*_s and p*K*_s + log [H₂O] values for basic monomers **M1**, **M3** and **M5** in THF-water mixtures.

Table ESI3. p*K*_s and p*K*_s + log [H₂O] values for acidic monomers **M2**, **M4**, **M6** and **M7** in THF-water mixtures.

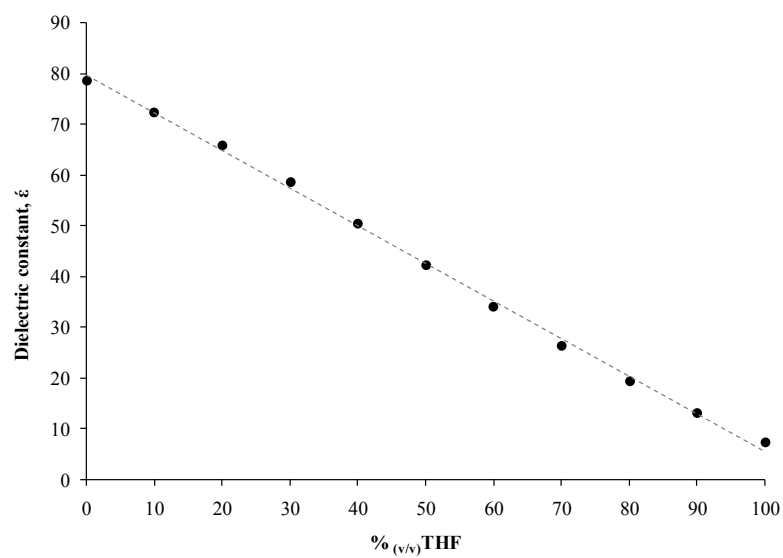


Figure ESI1. Linear plot of experimentally determined dielectric constants of water in various THF-water mixtures at 25°C.¹⁸

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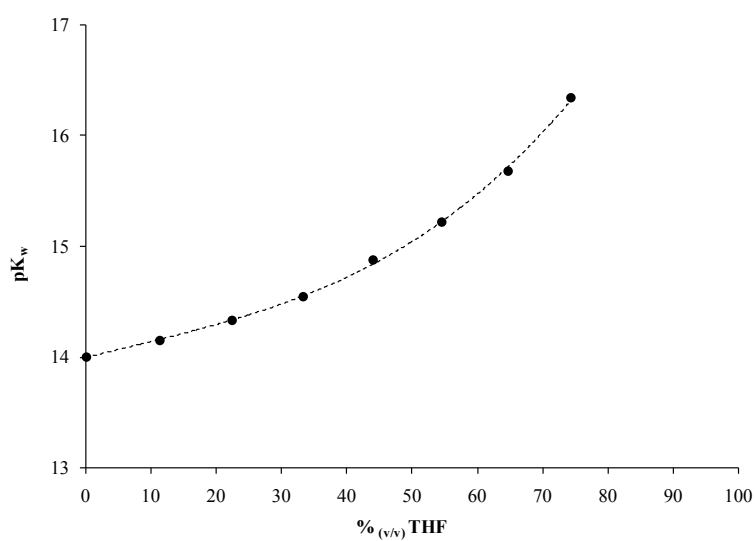
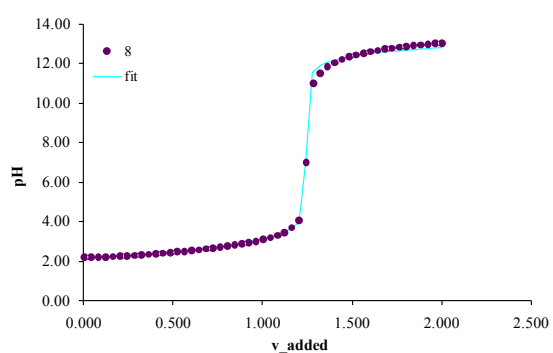
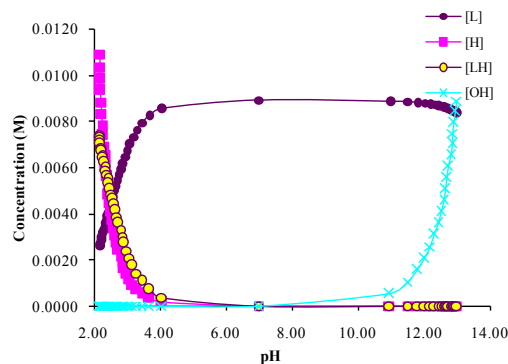


Figure ESI2 Autoprotolysis constant of H₂O at various THF-water mixtures measured at 25 °C.¹⁹

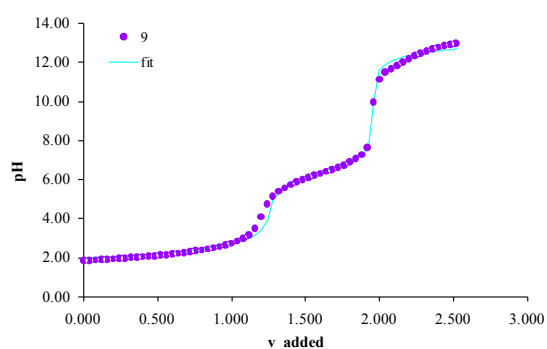
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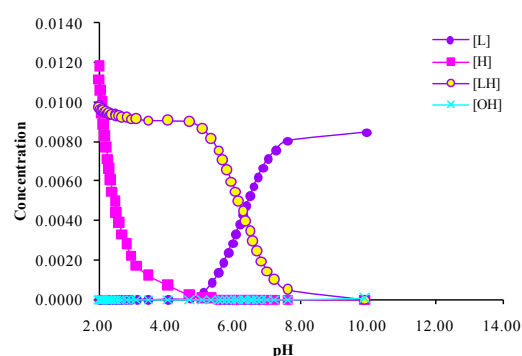
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8b



9a



9b

Figure ES13 (a) Titration curves for **A8H** and **A9** at 50:50 THF:H₂O mixture and their (b) corresponding species equilibrium concentrations. The species equilibrium plots show the equivalence point of the 5 species involved in the titration, including the monomer [L], acid [H], protonated monomer [LH] and base [OH]. The first endpoint obtained for the titration of **A9** is due to the presence of excess H⁺ when the system was pre-acidified prior to titration and has been taken account during the processing of titration results.

Table ESI1 Yasuda-Shedlovsky parameters in THF-water mixtures and aqueous pK_a s for analytes **A8H** and **A9**.

Analyte	Yasuda-Shedlovsky Parameters	THF in water (%)				
		0	40	45	50	55
A8H	p_sK_a		3.19 ± 0.09	2.67 ± 0.05	2.42 ± 0.07	2.32 ± 0.08
	$p_sK_a + \log [H_2O]$	$5.74 \pm 0.88^*$	4.71 ± 0.26	4.15 ± 0.16	3.86 ± 0.22	3.72 ± 0.26
	pK_a (aqueous)	$3.98 \pm 0.61^*$ (3.83) ²¹				
	slope	-1.64 ± 0.44				
A9	p_sK_a		5.73 ± 0.03	5.92 ± 0.05	6.14 ± 0.04	6.36 ± 0.05
	$p_sK_a + \log [H_2O]$	$6.65 \pm 0.30^*$	7.25 ± 0.08	7.40 ± 0.12	7.58 ± 0.10	7.76 ± 0.12
	pK_a (aqueous)	$4.90 \pm 0.22^*$ (4.19) ²²				
	slope	0.86 ± 0.17				

*error = 2s where s = standard deviation for 95% confidence interval.

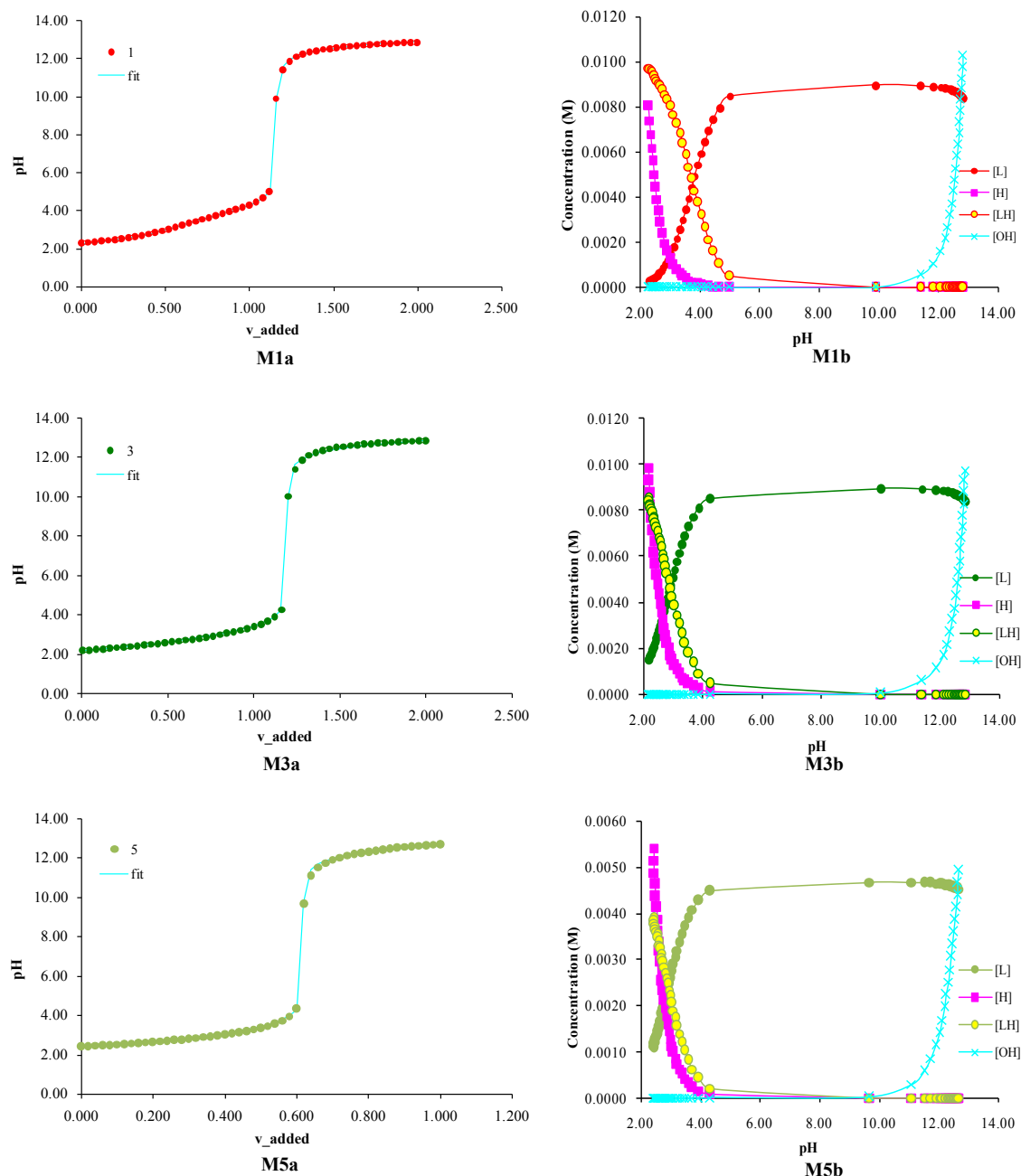


Figure ESI4. Titration curves (a) and corresponding species equilibrium concentration plots (b) for basic monomers in their acidic forms **M1H**, **M3H**, and **M5H** at 50:50 THF:H₂O mixtures. The species equilibrium plots show the equivalence point of the species involved in the titration, including the 5 monomer [L], acid [H], protonated monomer [LH] and base [OH].

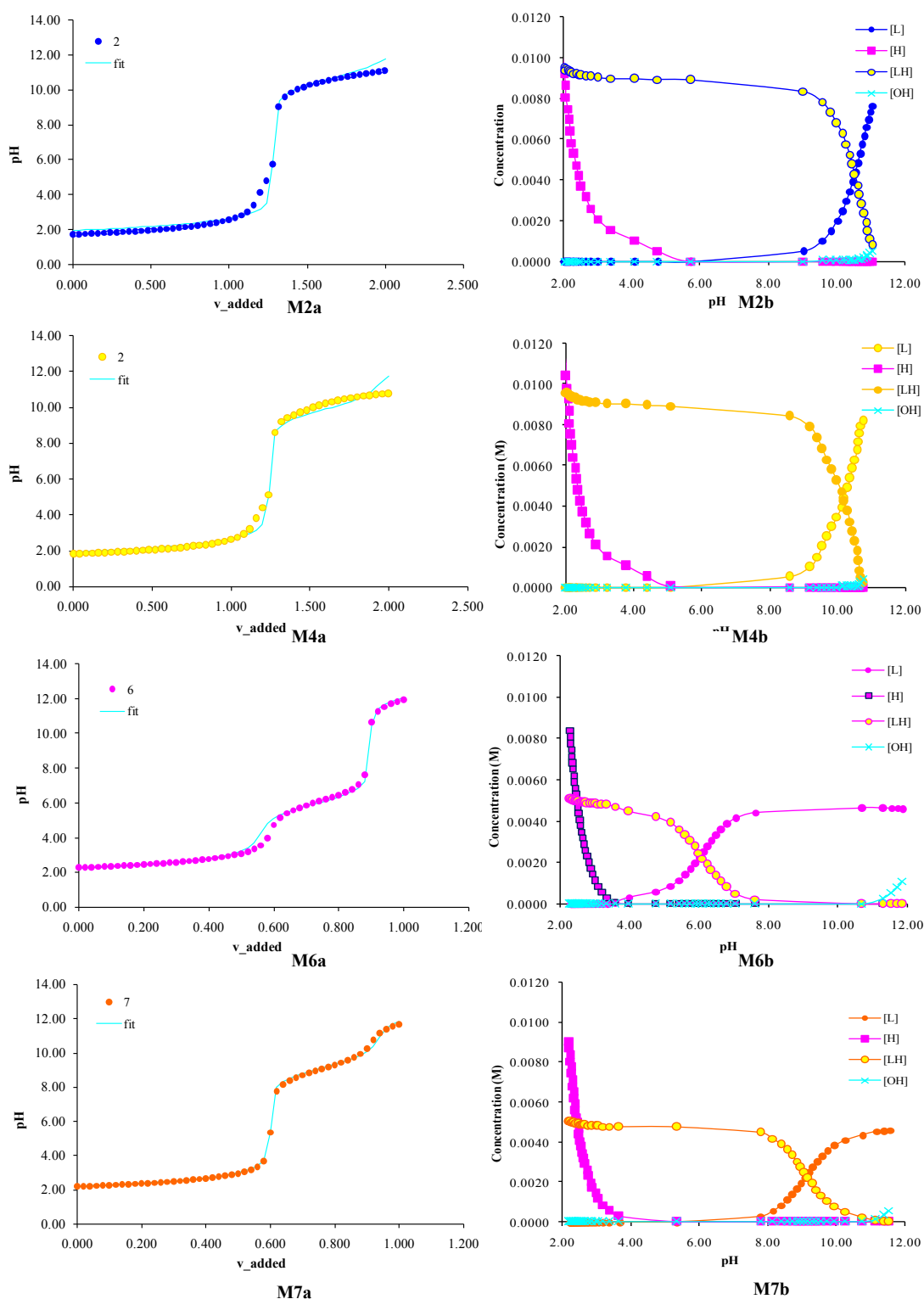


Figure ES15. Titration curves (a) and their corresponding species equilibrium concentrations (b) for acidic monomers **M2**, **M4**, **M6** and **M7** at 50:50 v/v THF:H₂O mixture. The species equilibrium plots show the equivalence point of the species involved in the titration, including the monomer [L], acid [H], protonated monomer [LH] and base [OH]. The first endpoint obtained for the titration of **M6** is due to the presence of excess H⁺ when the system was pre-acidified prior to titration and has been taken account during the processing of titration results.

Table ESI2. Summary of the p_sK_a and $p_sK_a + \log [H_2O]$ values for basic monomers (in acidic forms) **M1**, **M3** and **M5** in THF-water mixtures.

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% THF (v/v)	M1H		M3H		M5H	
	p_sK_a	$p_sK_a + \log$	p_sK_a	$p_sK_a + \log$	p_sK_a	$p_sK_a + \log$
		$[H_2O]^*$		$[H_2O]^*$		$[H_2O]^*$
0		6.58 ± 1.12		6.01 ± 0.78		4.65 ± 0.52
35	4.24 ± 0.02	5.80 ± 0.06				
40	4.22 ± 0.02	5.74 ± 0.06	$3.38 \pm .09$	4.90 ± 0.26		
45	4.08 ± 0.03	5.56 ± 0.08	3.30 ± 0.05	4.78 ± 0.14	$2.89 \pm .03$	4.37 ± 0.10
50	3.62 ± 0.01	5.06 ± 0.02	2.76 ± 0.02	4.20 ± 0.06	2.82 ± 0.04	4.26 ± 0.12
55	3.62 ± 0.02	5.02 ± 0.06	2.69 ± 0.05	4.09 ± 0.16	2.84 ± 0.07	4.24 ± 0.12
R^2		0.93		0.92		0.91

Blank entries means the monomer is insoluble at this composition, thus no titration was done.

*error = $2s$ where s = standard deviation for 95% confidence interval.

Table ES13. p_sK_a and $p_sK_a + \log [H_2O]$ values for acidic monomers M2, M4, M6 and M7 in THF-water mixtures.

% THF (v/v)	M2		M4	
	p_sK_a	$p_sK_a + \log$	p_sK_a	$p_sK_a + \log$
		$[H_2O]^*$		$[H_2O]^*$
0		11.29 ± 0.42		13.05 ± 0.42
40	10.07 ± 0.09	11.59 ± 0.10	10.33 ± 0.13	11.85 ± 0.15
45	10.25 ± 0.20	11.73 ± 0.23	10.29 ± 0.11	11.77 ± 0.13
50	10.39 ± 0.13	11.83 ± 0.15	10.05 ± 0.12	11.49 ± 0.14
55	10.48 ± 0.15	11.88 ± 0.17	9.54 ± 0.18	10.94 ± 0.21
R^2		0.94		0.91

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% THF (v/v)	M6		M7	
	p_sK_a	$p_sK_a + \log$	p_sK_a	$p_sK_a + \log$
		$[H_2O]^*$		$[H_2O]^*$
0		6.44 ± 0.13		9.91 ± 0.11
40	5.43 ± 0.03	6.95 ± 0.04	8.79 ± 0.03	10.31 ± 0.04
45	5.70 ± 0.03	7.18 ± 0.04	8.86 ± 0.01	10.34 ± 0.01
50	5.80 ± 0.05	7.24 ± 0.06	9.03 ± 0.02	10.47 ± 0.02
55	6.05 ± 0.03	7.45 ± 0.04	9.22 ± 0.02	10.62 ± 0.02
R^2		0.96		0.95

Blank entries means the monomer is insoluble at this composition, thus no titration was done.

*error = $2s$ where s = standard deviation for 95% confidence interval.

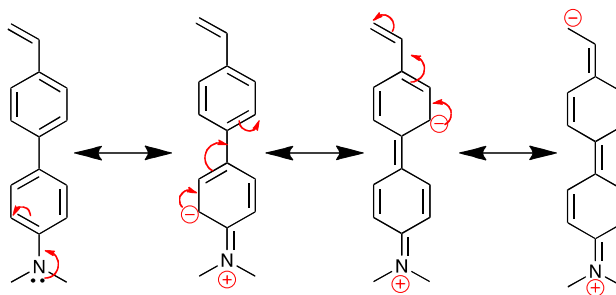


Figure ES16. Resonance structures of **M5** showing delocalisation of the lone pair from nitrogen.

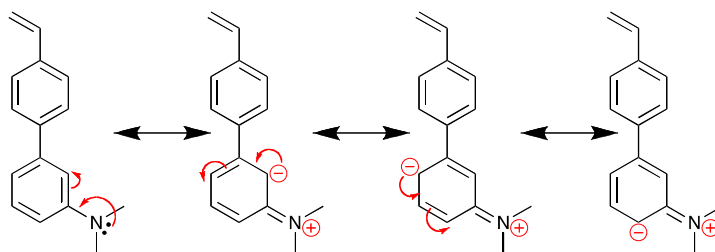


Figure ES17. Resonance structures of **M3** showing delocalisation of the lone pair from nitrogen.

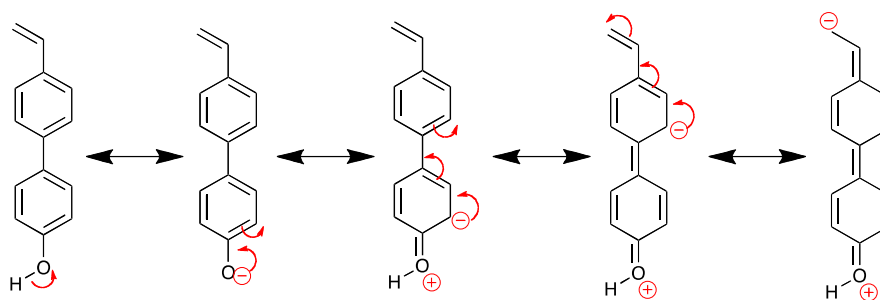


Figure ES18. Resonance structures of **M2**. Delocalisation of electrons from the oxygen by resonance stabilisation.

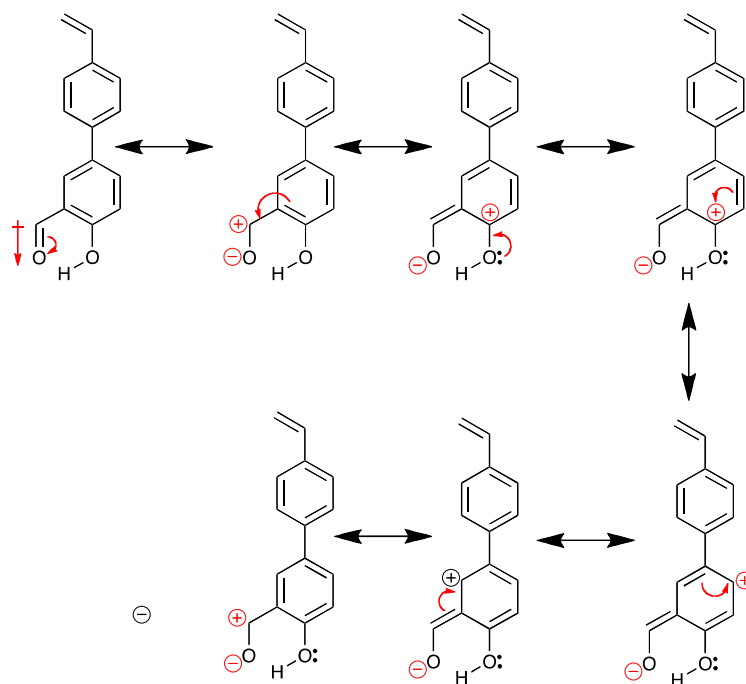


Figure ESI9. Resonance structures of **M7**. Delocalisation of electrons by inductive effect of carbonyl group ortho to hydroxyl group imparts a stronger effect on the acidity of **M7**.

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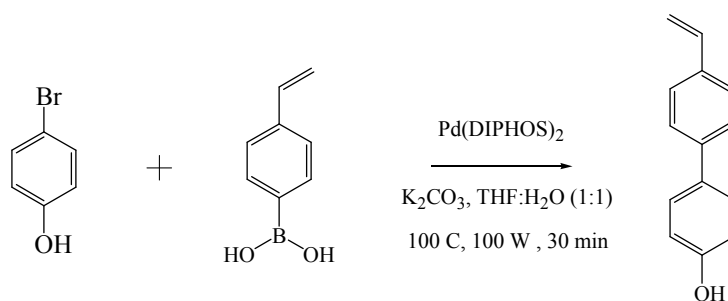


Figure ESI10. General reaction scheme for the microwave-assisted Suzuki cross coupling of aryl bromide with 4-vinylphenyl boronic acid using **M2** as a representative product.

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