Supporting information for the article:

Hydrogen hyperfine splitting constants for phenoxyl radicals by DFT methods: regression analysis unravels hydrogen bonding effects

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Table 1S. Comparison between experimental *hsc*'s [a] in benzene and *hsc*'s computed at the B3LYP/6-311+G(2df,p)// B3LYP/6-31G(d) level for *ortho* hindered phenoxyl radicals (gauss).

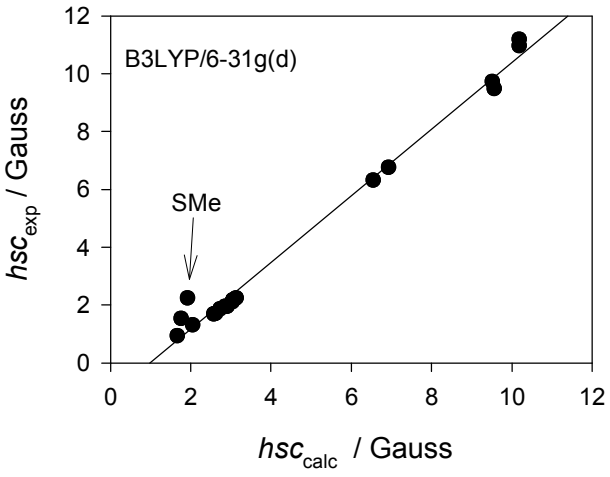
radical	***a* 2,6**		***a* 3,5 (2H)**		***a* 4**	
	calc	**exp**	**calc**	**exp**	**calc**	**exp**
1			2.38	1.95	8.37	9.72 (1H)
2			2.12	1.67	10.35	11.20 ($1CH_3$)
3			1.37	0.93	1.68	1.53 ($1OCH_3$)
4			1.62	1.30	2.20	2.24 ($1SCH_3$)
5			2.27	1.87	1.06 (^{35}Cl)	1.47 (^{35}Cl), 1.22 (^{37}Cl)
6			2.57	2.10	0.15	0.45 (1H)
7			2.60	2.17	1.06	1.37 (1N)
8			2.59	2.14	0.65	0.53 ($1CH_3$)
9			2.70	2.23	1.84	2.23 (1N)
10	6.85	6.75 ($2CH_3$)	2.41	1.94	8.41	9.48 (1H)
11	6.38	6.30 ($2CH_3$)	2.15	1.63	10.34	10.96 ($1CH_3$)

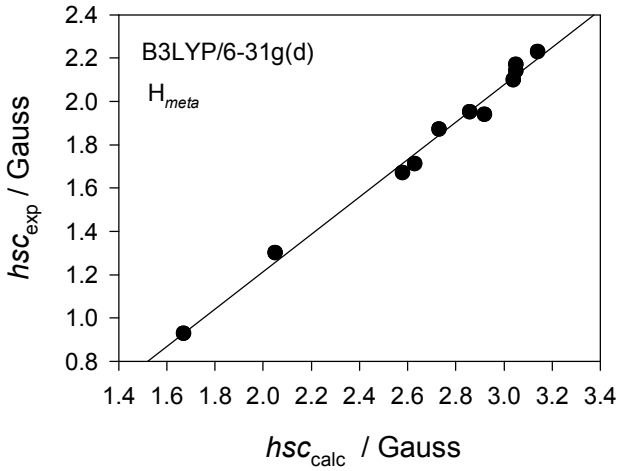
a) Measured by stationary photolysis of the parent phenols, from ref. 13 and 24. The values for radical **4** are from ref. 25.

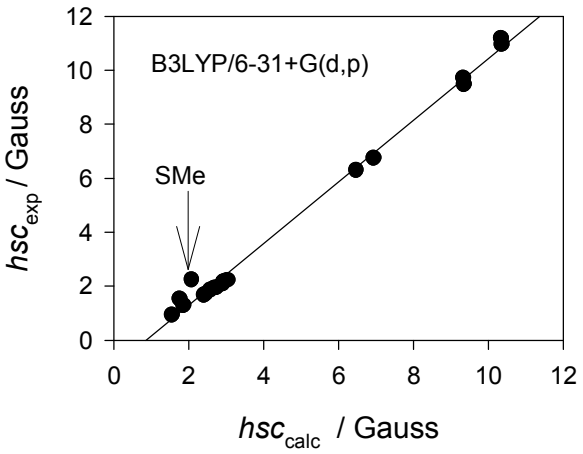
Table 2S. Experimental *hsc*'s in benzene solution and *hsc*'s calculated at the B3LYP/6-311+G(2df,p)// B3LYP/6-31G(d) level for unhindered phenoxyl radicals.

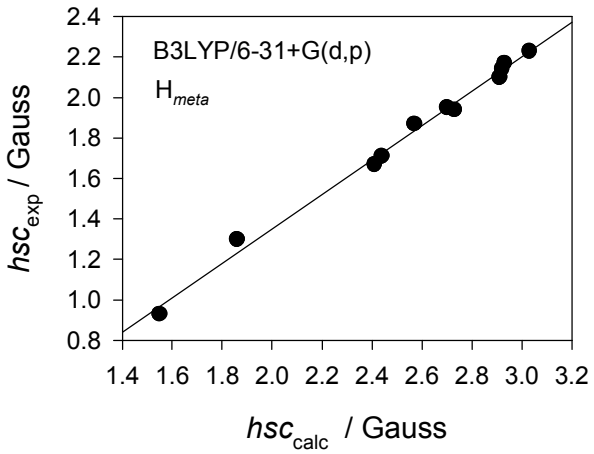
phenoxyl	***hcc* 2,6 (2H)**		***hcc* 3,5 (2H)**		***hcc* 4**	
	calc	**exp**	**calc**	**exp**	**calc**	**exp**
12	–6.47	6.57 [a] 6.60 [b] 6.85 [c]	2.56	1.84 [a] 1.88 [b] 2.02 [c]	–8.54	10.07 (1H)[a] 10.10 [b] 9.98 [c]
13	–6.17	6.32 [a] 5.93 [b] 6.48 [c]	2.29	1.56 [a] 1.47 [b] 1.79 [c]	10.66	11.99 ($1CH_3$) [a] 11.86 [b] 11.63 [c]
14	–5.62	5.57 [a] 5.38 [b] 5.75 [d] 5.75 [e] 5.91 [c]	1.54	0.70 [a] 0.57 [b] 0.80 [d] 0.85[e] 0.99 [c]	1.41	1.81 ($1OCH_3$) [a] 1.83 [b] 1.78 [d] 1.75 [e] 1.68 [c]

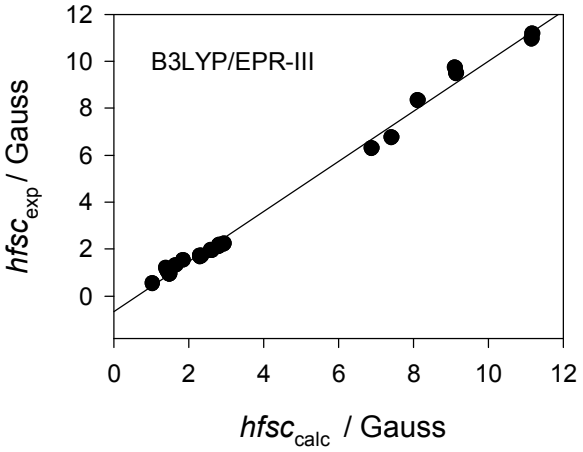
a) From ref. 13. b) From ref. 14. c) From this work, measured at low concentration of the parent phenol. d) From ref. 6. e) From ref. 4a.

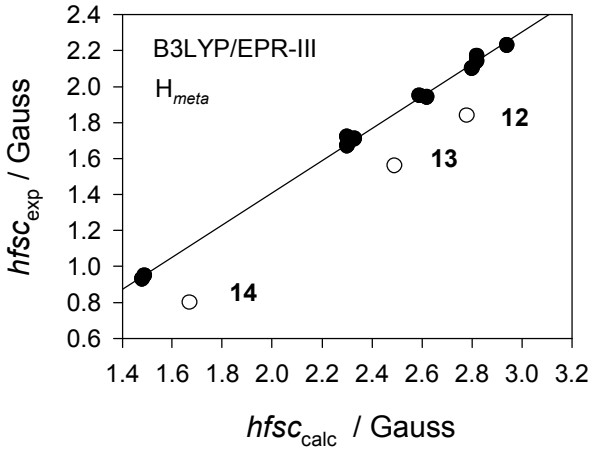


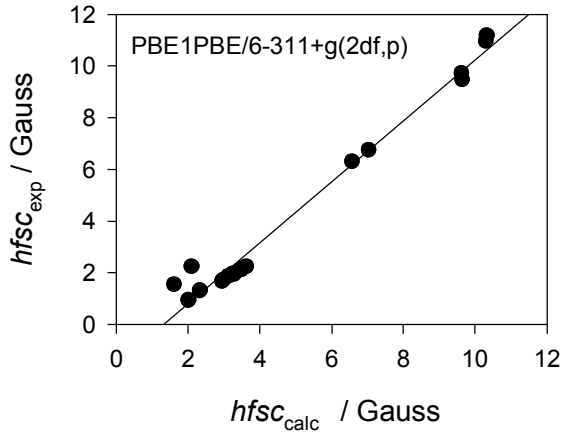


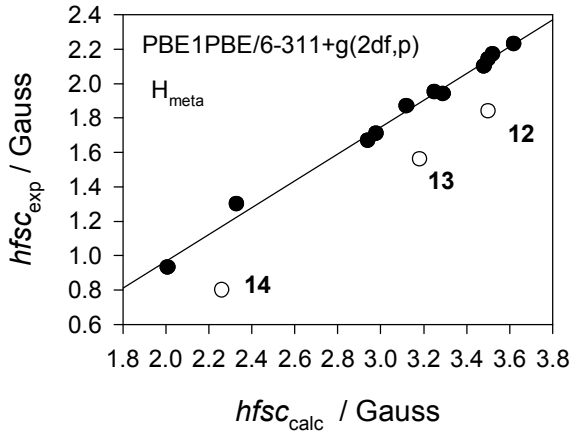


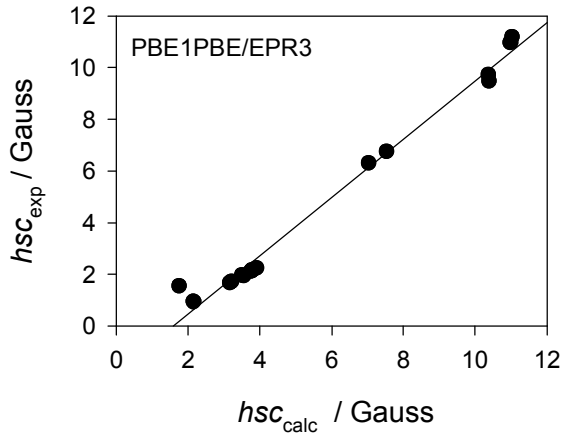












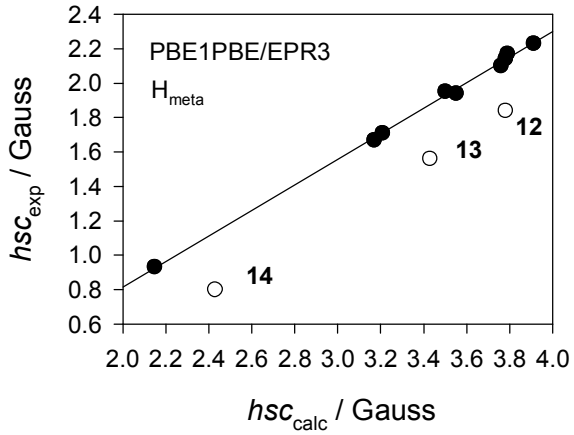


Table 3S. Hyperfine splitting constants of phenoxyl radical **(12)** measured in benzene solution at different parent phenol concentrations.

[PhOH] / M	***a*(2,6) / G**	***a*(3,5) / G**	***a*(4) / G**
0.005	6.86	2.00	9.92
0.015	6.83	2.01	9.99
0.058	6.85	2.00	9.98
0.52	6.75	1.96	10.03
1.0	6.70	1.91	10.01
2.0	6.63	1.87	10.01

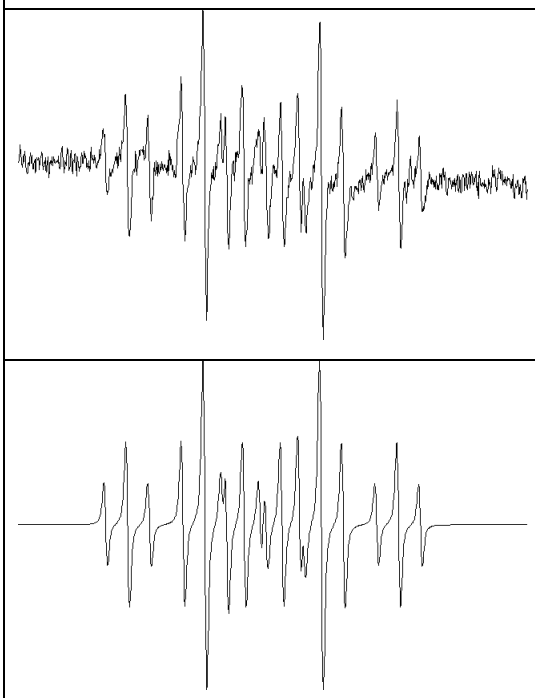
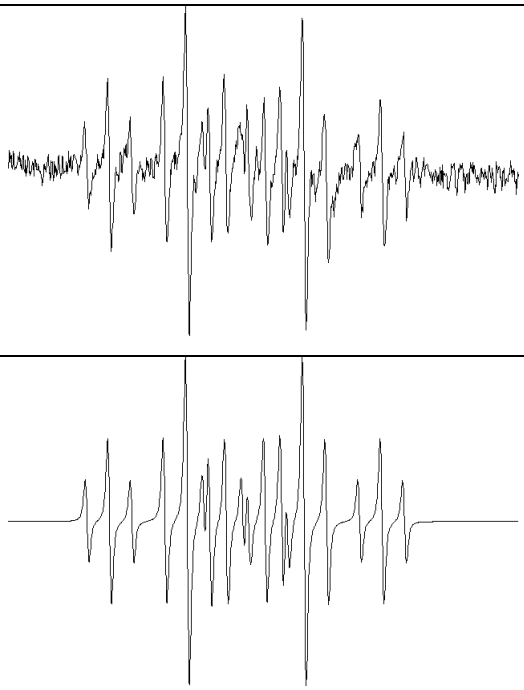
Table 4S. Hyperfine splitting constants of 4-methylphenoxyl radical (**13)** measured in benzene solution at different parent phenol concentrations.

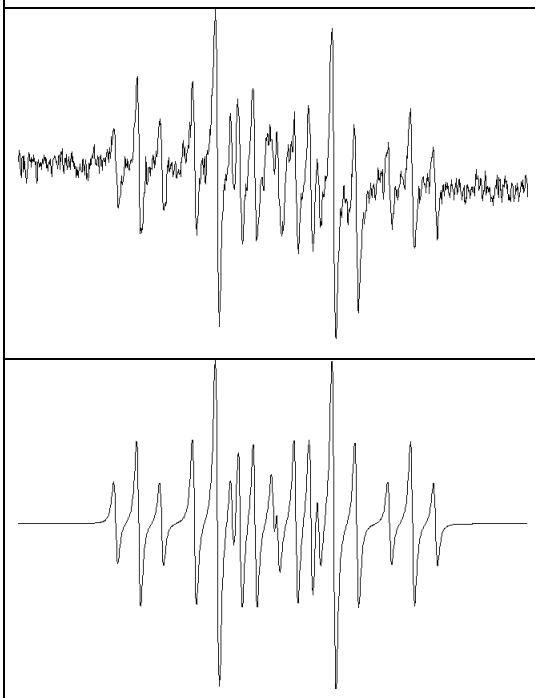
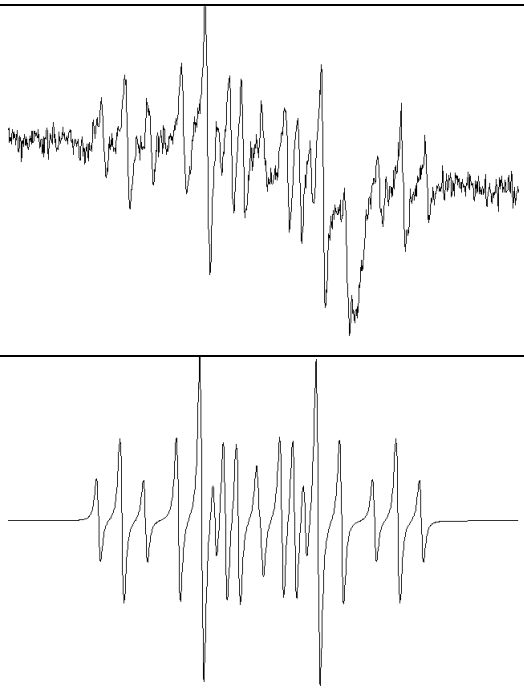
[4-MePhOH] / M	***a*(2,6) / G**	***a*(3,5) / G**	***a*(4) / G**
0.002	6.48	1.79	11.63
0.02	6.48	1.75	11.67
0.10	6.43	1.74	11.74
1.0	6.25	1.57	12.02
1.8	6.24	1.48	12.17

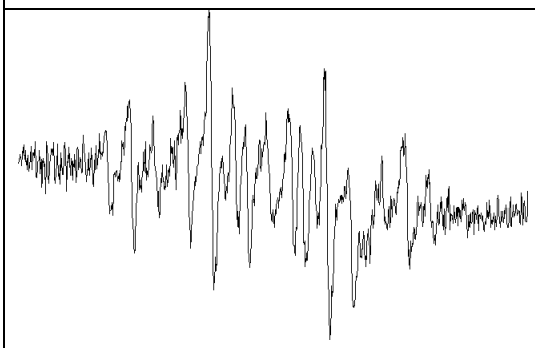
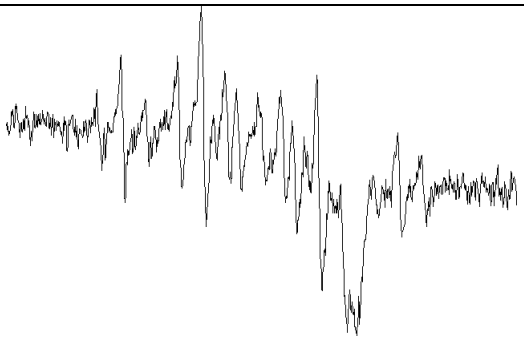
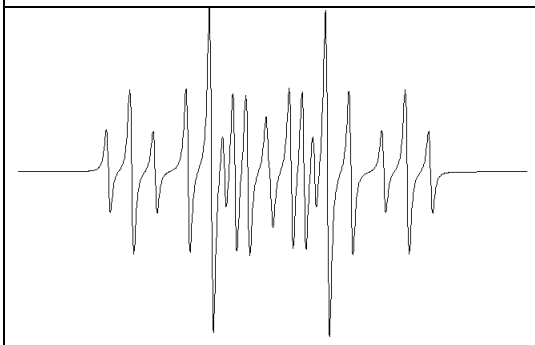
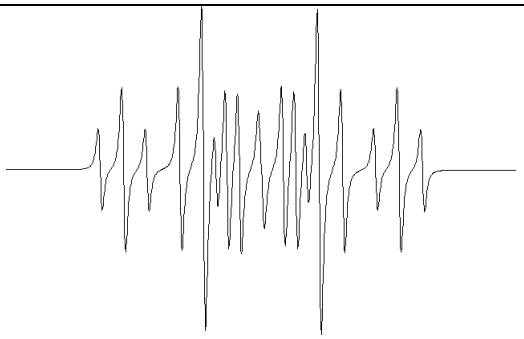
Table 5S. Hyperfine splitting constants of 4-methoxyphenoxyl radical (**14)** measured in benzene solution at different parent phenol concentrations.

[4-OMePhOH] / M	***a*(2,6) / G**	***a*(3,5) / G**	***a*(4) / G**
0.0007	5.91	0.99	1.68
0.002	5.90	0.99	1.63
0.019	5.85	0.85	1.71
0.068	5.72	0.80	1.74
0.31	5.51	0.66	1.82
0.58	5.38	0.54	1.87
0.72	5.37	0.52	1.89
1.0	5.31	0.48	1.92
1.3	5.29	0.46	1.93

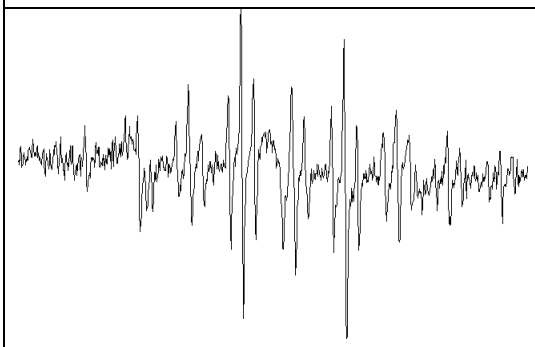
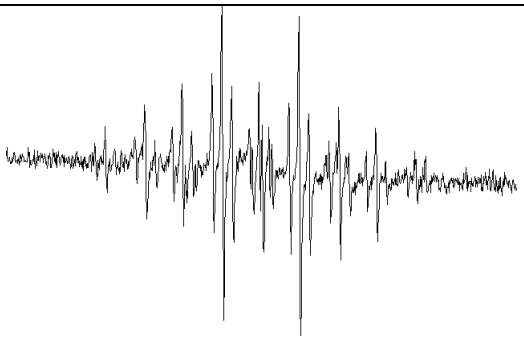
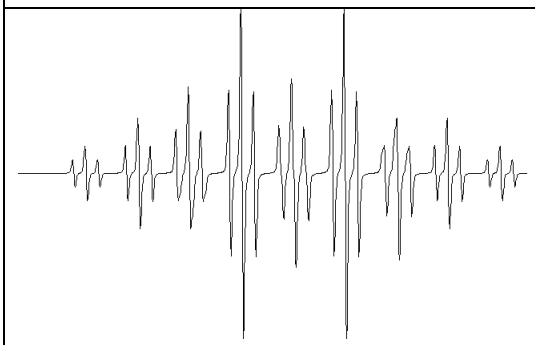
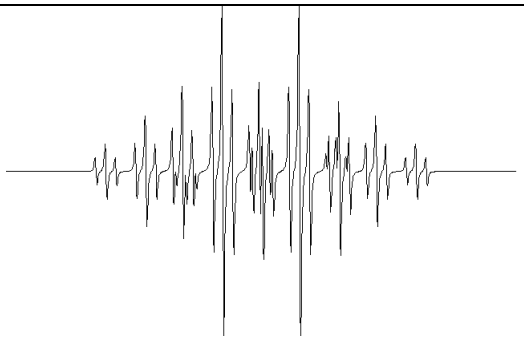
Phenoxyl radical (12). Experimental and simulated spectra.

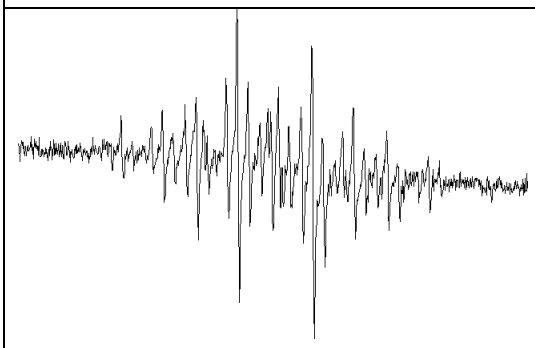
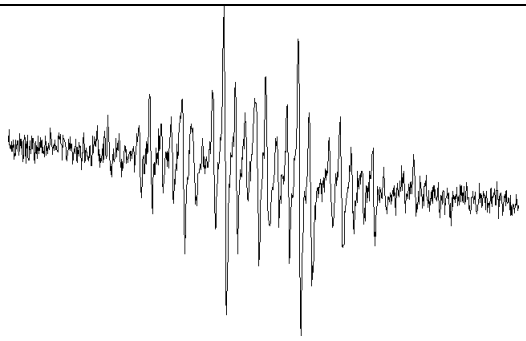
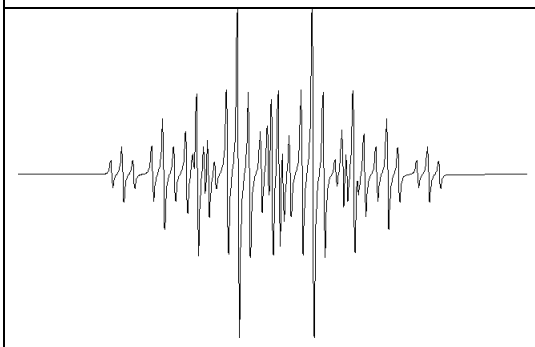
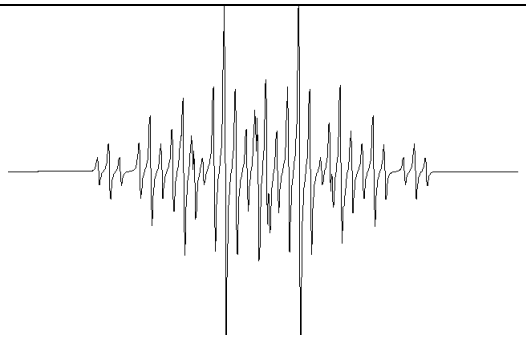
[PhOH] = 2.0 M	[PhOH] = 1.0 M
	

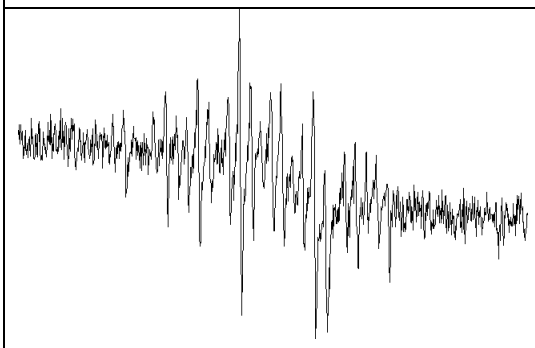
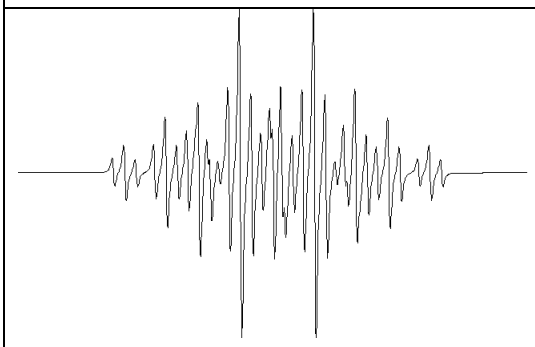
[PhOH] = 0.52 M	[PhOH] = 0.058 M
	

[PhOH] = 0.015 M	[PhOH] = 0.0052 M
	
	

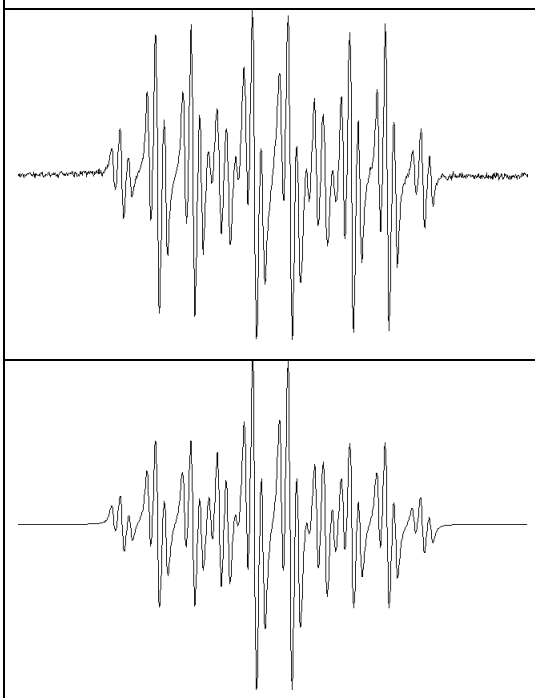
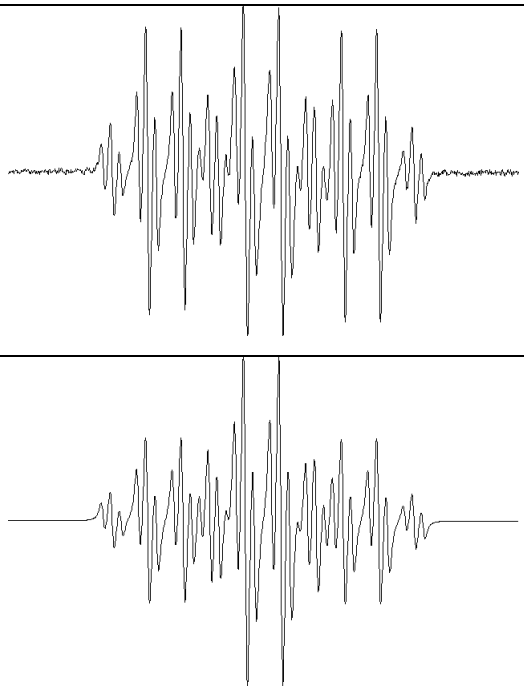
4-methyl phenoxyl radical (13). Experimental and simulated spectra.

[4-MePhOH] = 1.8 M	[4-MePhOH] = 1.0 M
	
	

[4-MePhOH] = 0.1 M	[4-MePhOH] = 0.02 M
	
	

[4-MePhOH] = 0.002 M	
	
	

4-methoxy phenoxyl radical (14). Experimental and simulated spectra.

[4-MeOPhOH] = 1.3 M	[4-MeOPhOH] = 1.0 M
	

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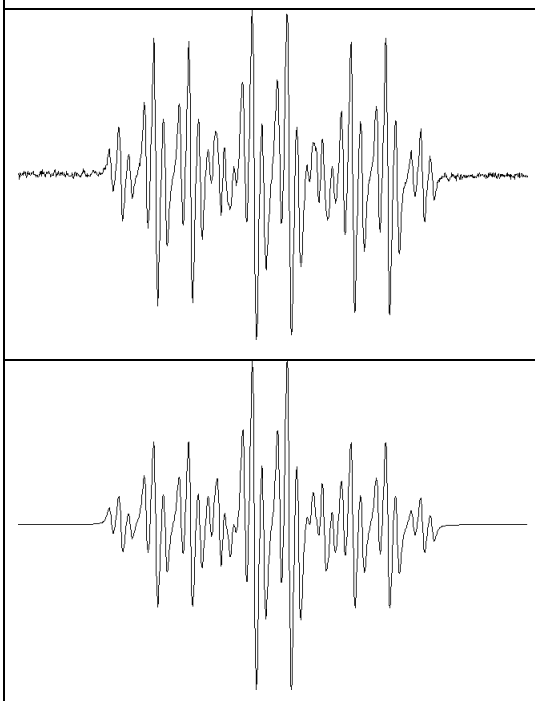	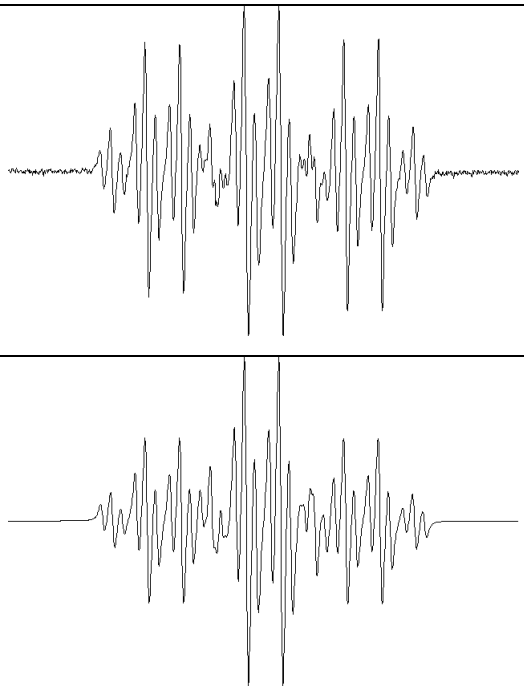

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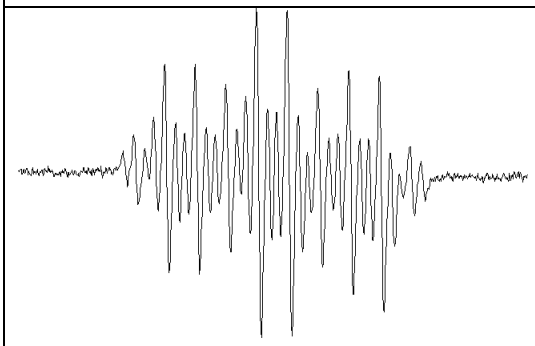
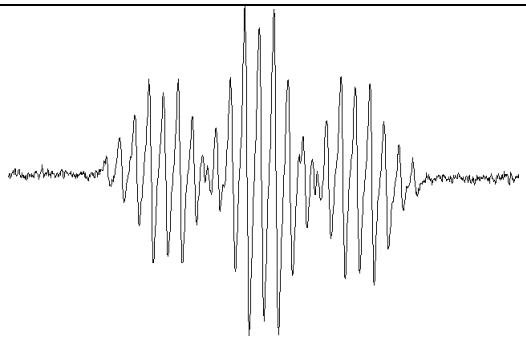
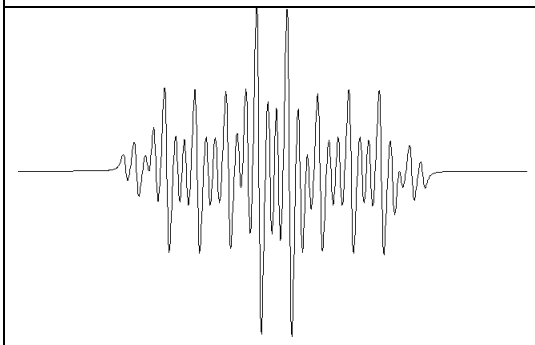
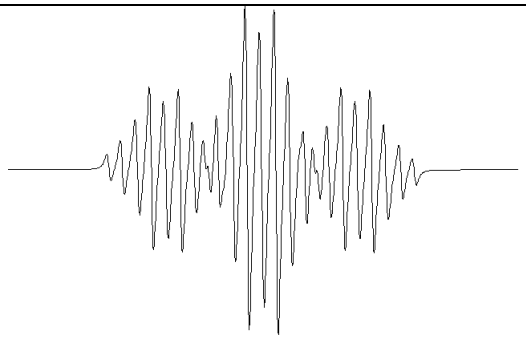
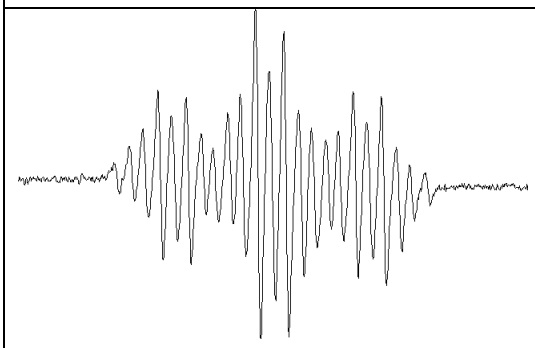
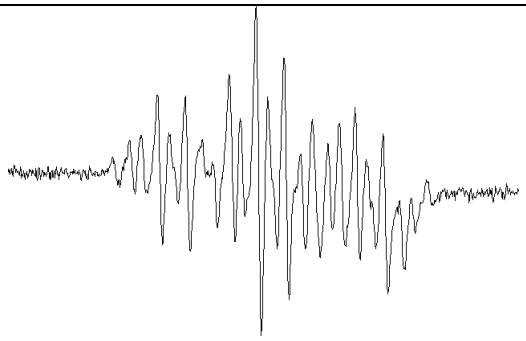
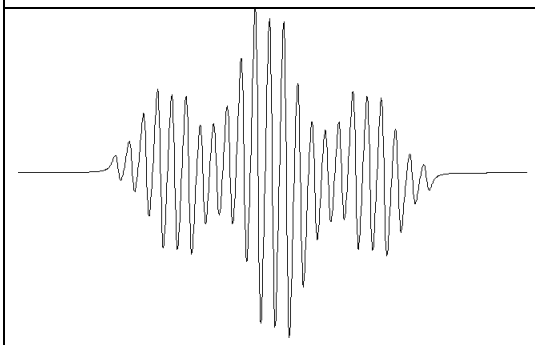
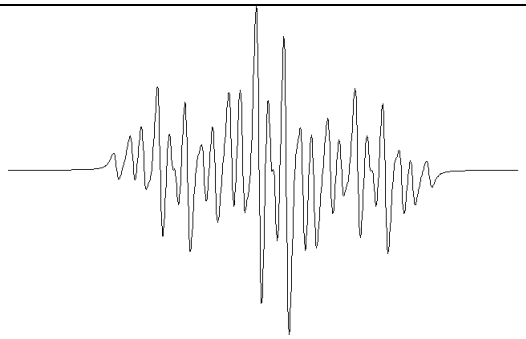
	
	

[4-MeOPhOH] = 0.019 M	[4-MeOPhOH] = 0.002 M
	
	

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