Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Vertically π-Expanded Coumarin – the Synthesis via the Scholl Reaction and Photophysical Properties

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Table of Contents

General information

All chemicals were used as received unless otherwise noted. Reagent grade solvents (MeCN, CH_2Cl_2, hexane, toluene) were distilled prior to use. All reported NMR spectra were recorded on 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. UV-Vis absorption spectra were recorded in THF. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh) and dry column vacuum chromatography (DCVC) was performed on preparative thin layer chromatography silica (Merck 107747). Mass spectra were obtained via EI or electrospray MS. All calculations were done with aid of the Gaussian 09 package.[1]

Table S1. (I) Transition energies (ΔE) and oscillator strengths (f) for the $S_0 \rightarrow S_i$ transitions of isomers A and B of compound **4** calculated by TDDFT B3LYP/6-31G(d,p) method for B3LYP/6-31G(d,p) optimized structures in the S_0 state. (II) Transition energies and oscillator strengths for the $S_1 \rightarrow S_0$ transitions of isomers A and B of compound **4** optimized in the S_1 state. (III) Triplet state energies for A and B isomers in their geometries in the S_0 state.

A		**B**	
ΔE [nm]	f	ΔE [nm]	f
(I) $S_0 \rightarrow S_i$ absorption			
408.12	0.2631	411.69	0.2555
381.55	0.0730	378.54	0.0711
320.60	0.0393	323.95	0.0524
319.65	0.0001	323.71	0.0001
311.87	0.0573	313.68	0.0414
297.74	0.0337	298.04	0.0390
276.85	0.0317	277.19	0.0390
266.56	0.0270	264.84	0.0230
257.61	0.0395	258.26	0.0593
253.70	0.0690	254.08	0.0486
252.24	0.0299	251.61	0.0165
241.42	0.0157	240.81	0.0323
237.43	0.0545	237.30	0.0473
232.29	0.0159	233.28	0.0277
226.08	0.0001	227.28	0.0001
225.32	0.0381	224.77	0.0507
217.33	0.5210	219.39	0.0233
217.08	0.0790	218.03	0.0001
216.51	0.0001	217.69	0.5775
209.66	0.0000	211.27	0.0000
(II) $S_0 \rightarrow S_i$ fluorescence			
461.91	0.2480	467.14	0.2396
(III) $S_0 \rightarrow T_i$			
725.83		736.66	
486.01		480.14	
397.28		402.84	
359.67		360.42	

Table S2. Solvent effect on absorption $S_0 \rightarrow S_1$ and fluorescence $S_1 \rightarrow S_0$ transitions in compound **4** calculated by TDDFT B3LYP/6-31G(d,p) method within PCM model.

	absorption		fluorescence	
solvent	ΔE [nm]	f	ΔE [nm]	f
		A		
isolated	408.12	0.263	461.91	0.248
nonane	418.71	0.361	475.32	0.338
methanol	439.18	0.540	501.24	0.509
acetonitrile	439.35	0.541	501.45	0.510
		B		
isolated	411.69	0.256	467.14	0.240
nonane	421.40	0.354	479.51	0.329
methanol	440.94	0.538	503.83	0.503
acetonitrile	441.10	0.539	504.03	0.504

Table S3. $S_0 \rightarrow S_i$ transitions energies calculated by TDDFT B3LYP/6-31G(d,p) method for two dimers of the A isomer, B3LYP/6-31G(d,p) optimized.

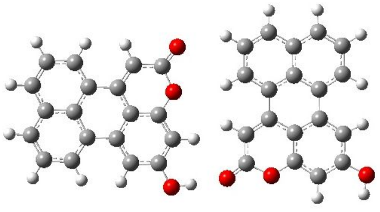
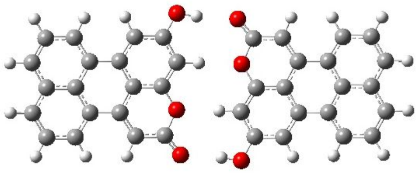
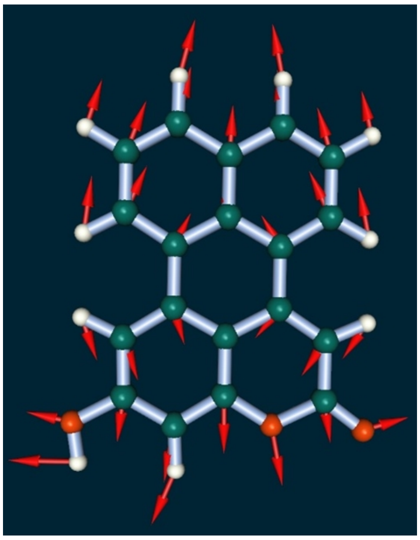
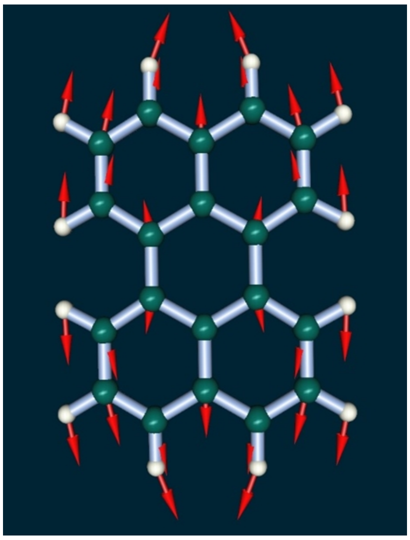
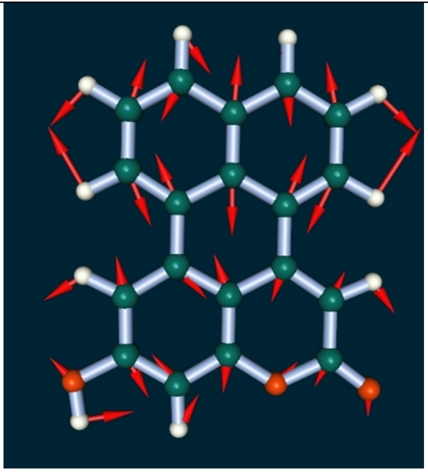
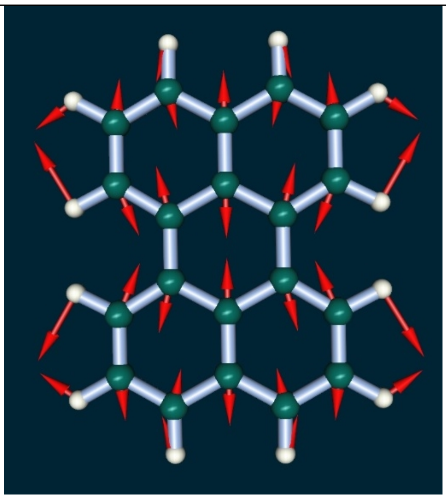
			
ΔE [nm]	f	ΔE [nm]	f
471.29	0.0001	437.89	0.0111
423.89	0.1456	437.53	0.0237
414.60	0.3402	430.42	0.4872
410.51	0.0108	429.74	0.0033
404.78	0.0019	399.32	0.0020
395.36	0.1506	397.13	0.1865
371.57	0.0706	385.86	0.0002
335.14	0.0002	385.34	0.0000
331.98	0.0113	330.06	0.2439
328.32	0.0918	328.97	0.0020
327.00	0.0786	317.91	0.0577
315.54	0.0265	317.69	0.0003
314.53	0.0628	314.85	0.0012
305.82	0.0001	314.48	0.0077
301.29	0.0769	295.76	0.0011

Table S4. Comparison of the photophysical parameters of compound **4**, perylene and 7-HC.

	$S_0 \rightarrow S_1$		$S_1 \rightarrow S_0$		ν_{00}	$\mu(S_0)$	$\mu(S_1)$
molecule	E [cm^{-1}]	f	E [cm^{-1}]	f	E [cm^{-1}]	[D]	[D]
4	24503	0.2631	21649	0.2480	22214	5.12	5.96
	24290	0.2555	21407	0.2396	22032	7.59	8.11
perylene	23343	0.3610	20781	0.3576	21310	0	0
7-HC	33631	0.2818				3.94	
	33882	0.2875				6.39	

Table S5. Graphical presentation of vibrations dominating in the spectra of **4** and the corresponding vibrations in perylene.

<table>
<tr><th>4</th><th>Perylene</th></tr>
<tr><td>
A 359.8 cm^{-1} in S$_0$
A 355.2 cm^{-1} in S$_1$
B 360.0 cm^{-1} in S$_0$
B 354.8 cm^{-1} in S$_0$</td><td>
357 cm^{-1} in S$_0$</td></tr>
<tr><td>
A 1626.7 cm^{-1} in S$_0$
A 1631.1 cm^{-1} in S$_1$
B 1625.4 cm^{-1} in S$_0$
B 1630.5 cm^{-1} in S$_1$</td><td>
1617 cm^{-1} in S$_0$</td></tr>
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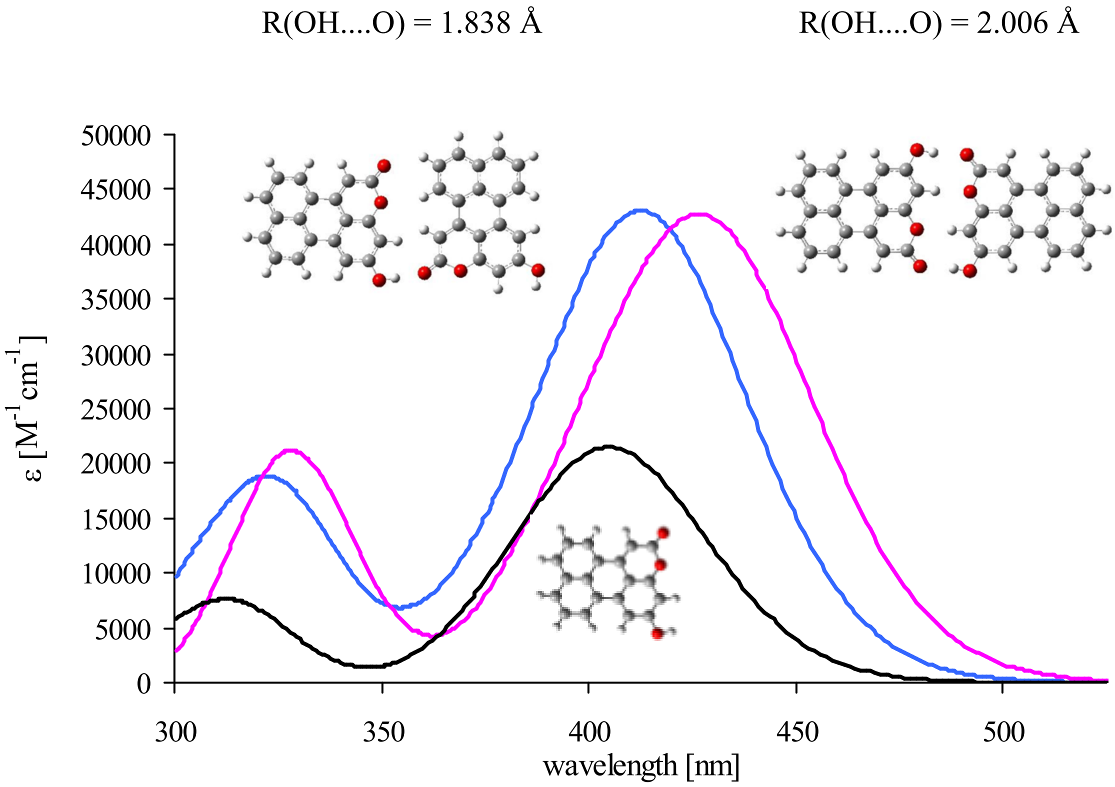

Figure S1. Simulation of the absorption spectra of two dimmers of the isomer A (with optimized geometry). The spectra of dimmers are shifted to low energy as compare with that of the monomer but are characterized by lower oscillator strength (see Table S3).

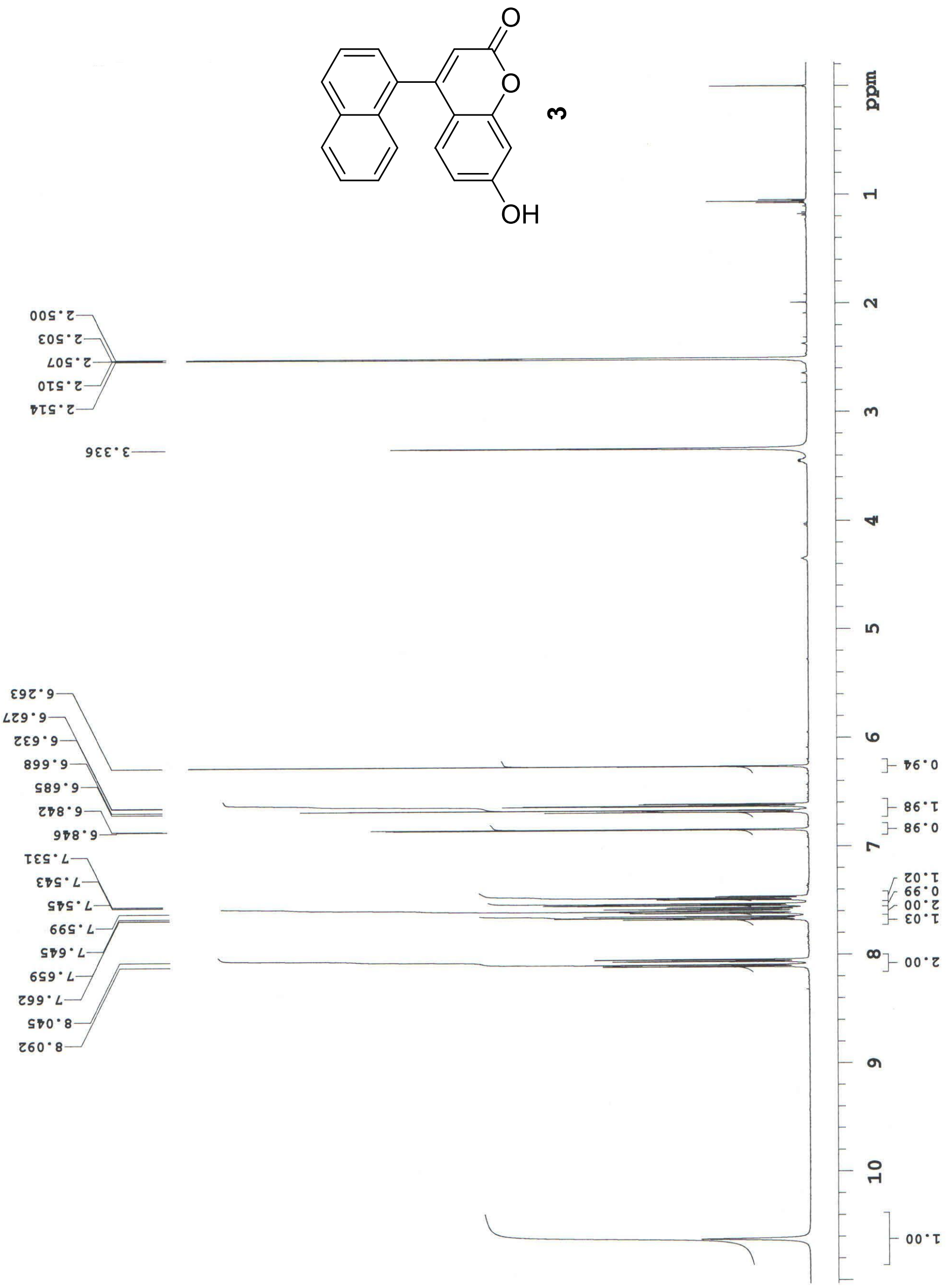

Figure S2. ^{1}H NMR spectrum of compound **3**.

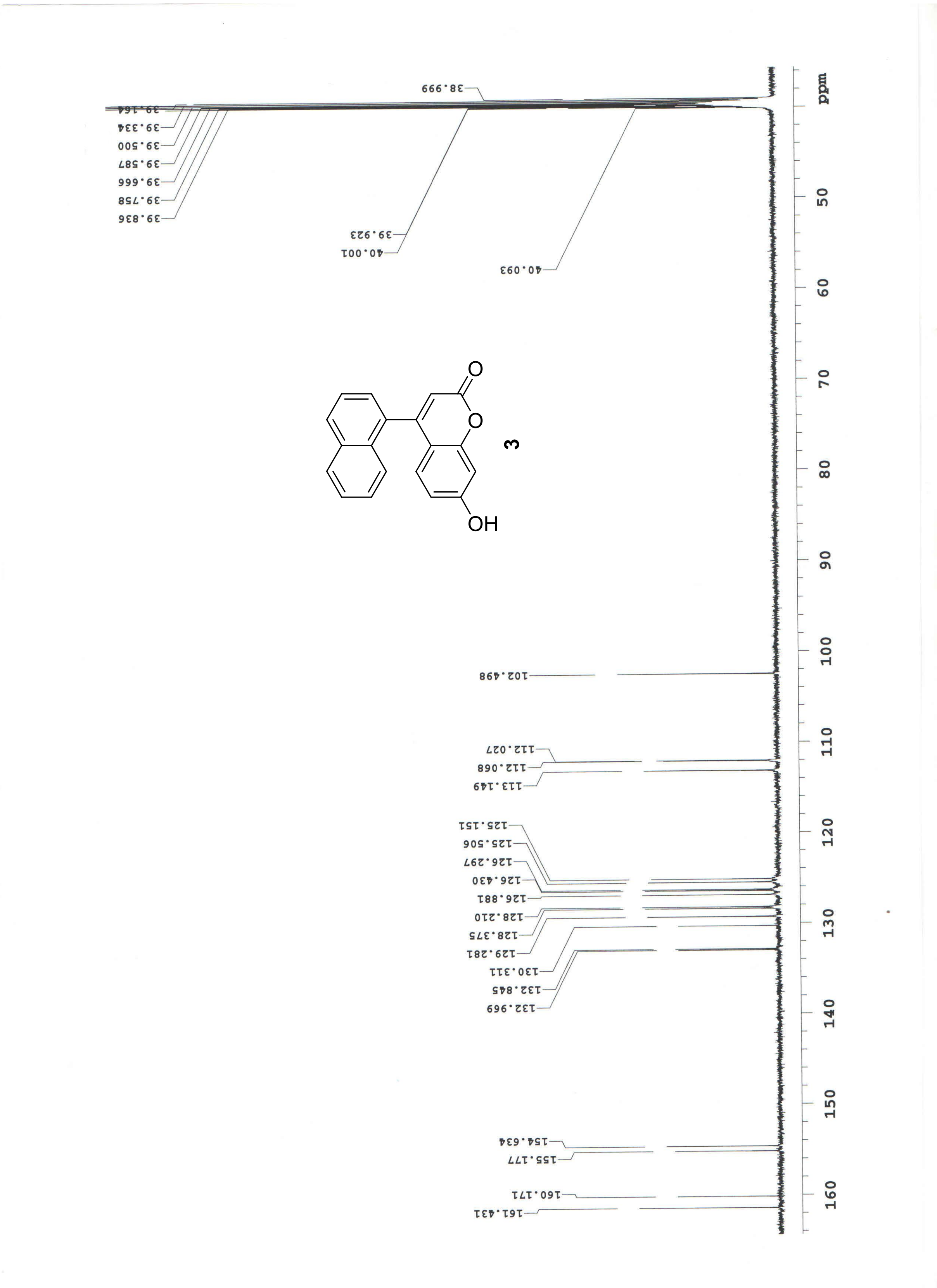

Figure S3. ^{13}C NMR spectrum of compound **3**.

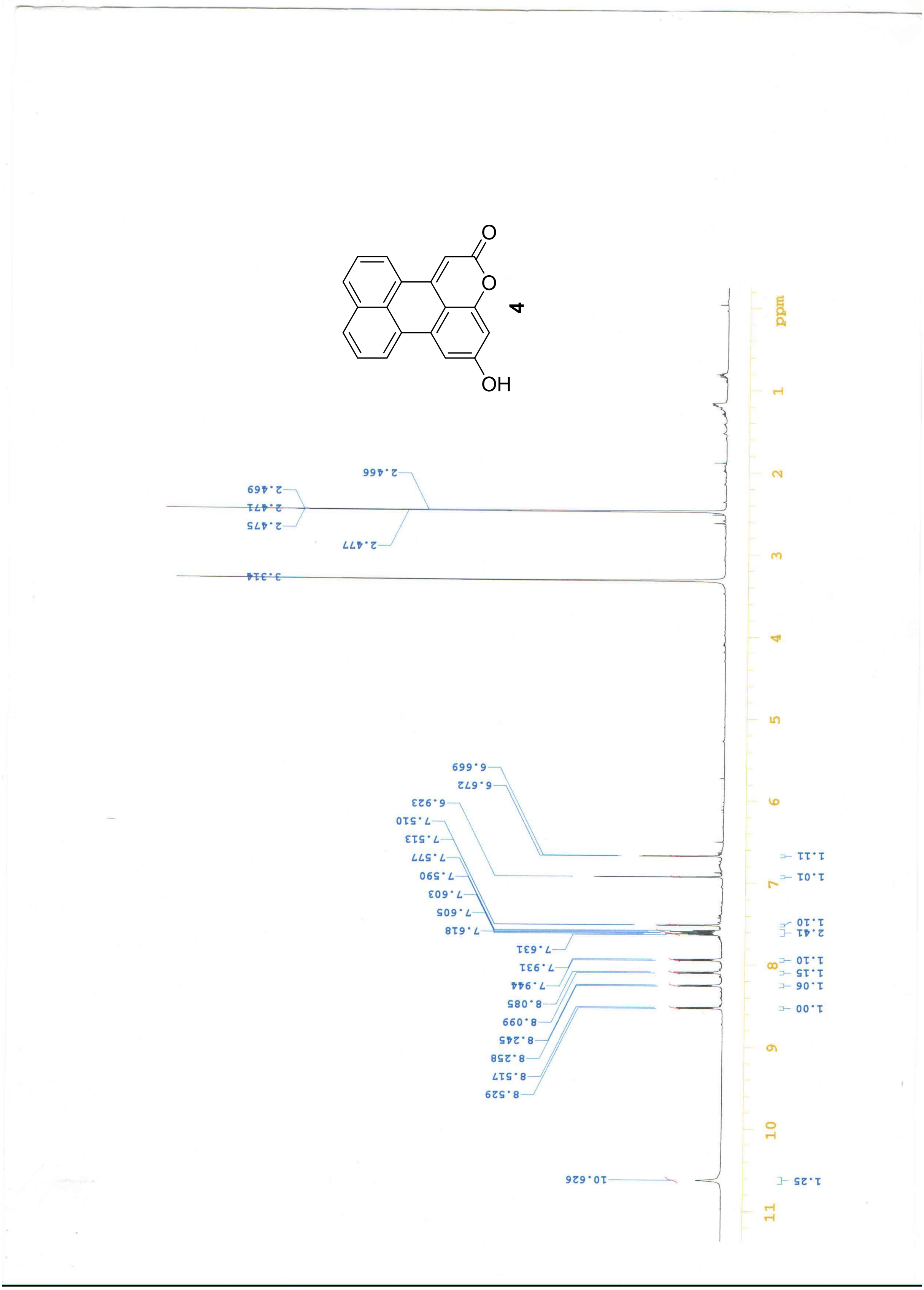

Figure S4. ^{1}H NMR spectrum of compound **4**.

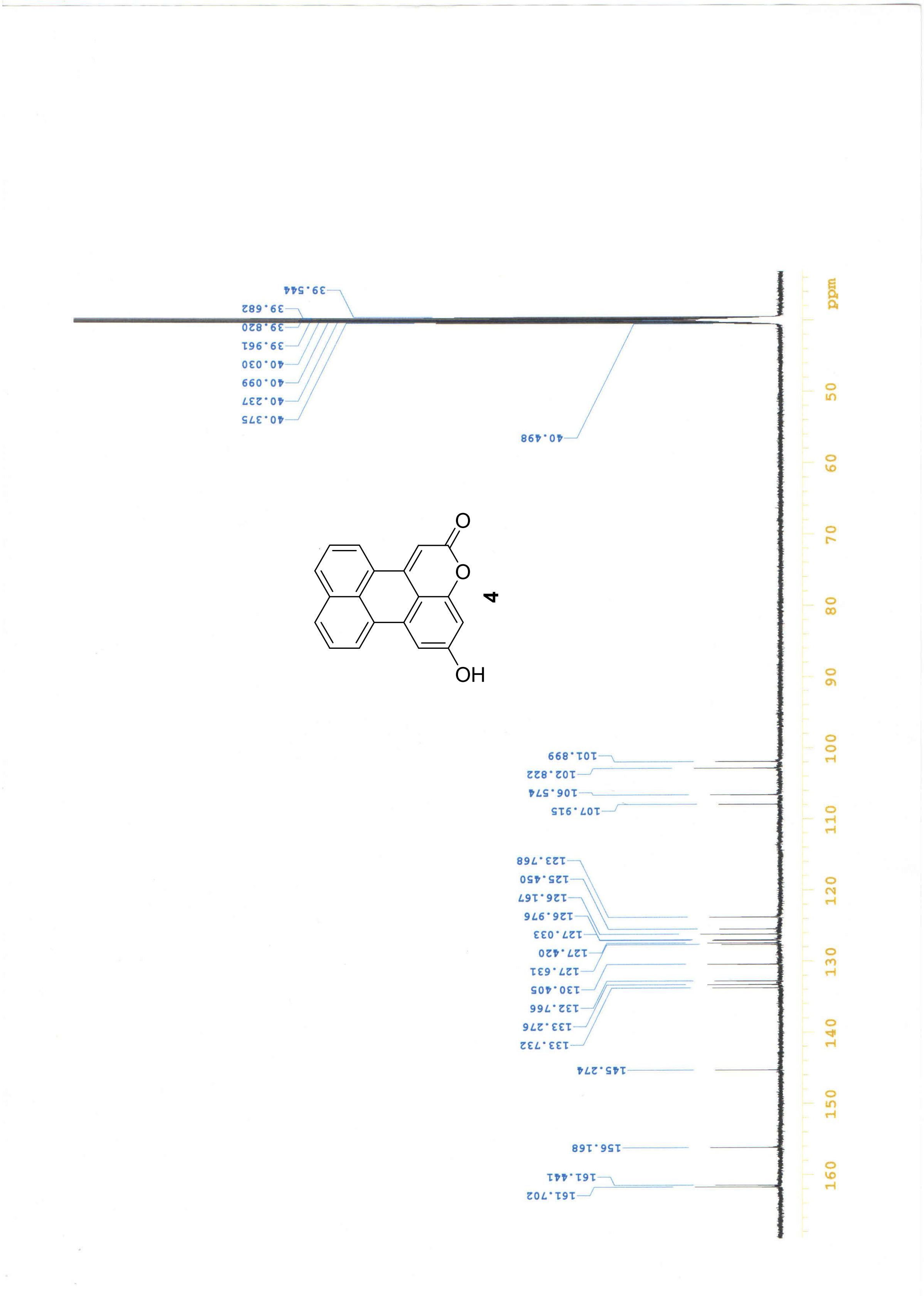

Figure S5. ^{13}C NMR spectrum of compound **4**.

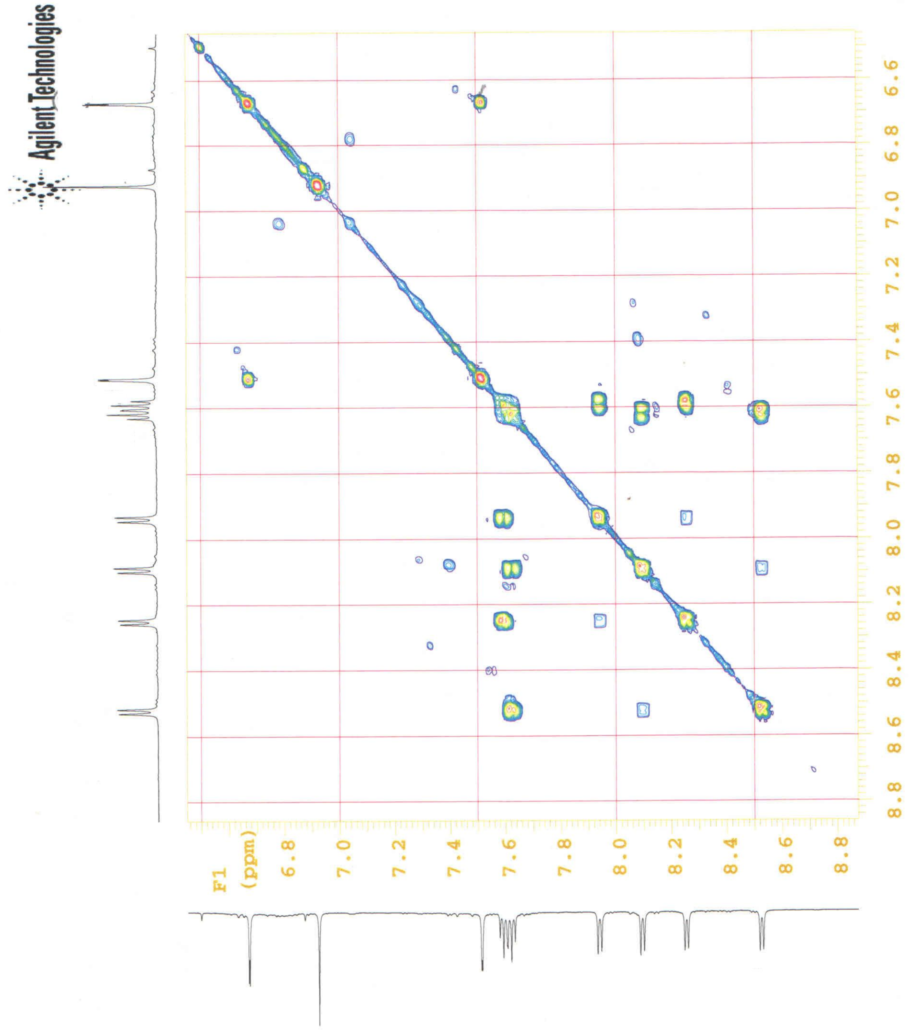

Figure S6. COSY spectrum of compound **4**.

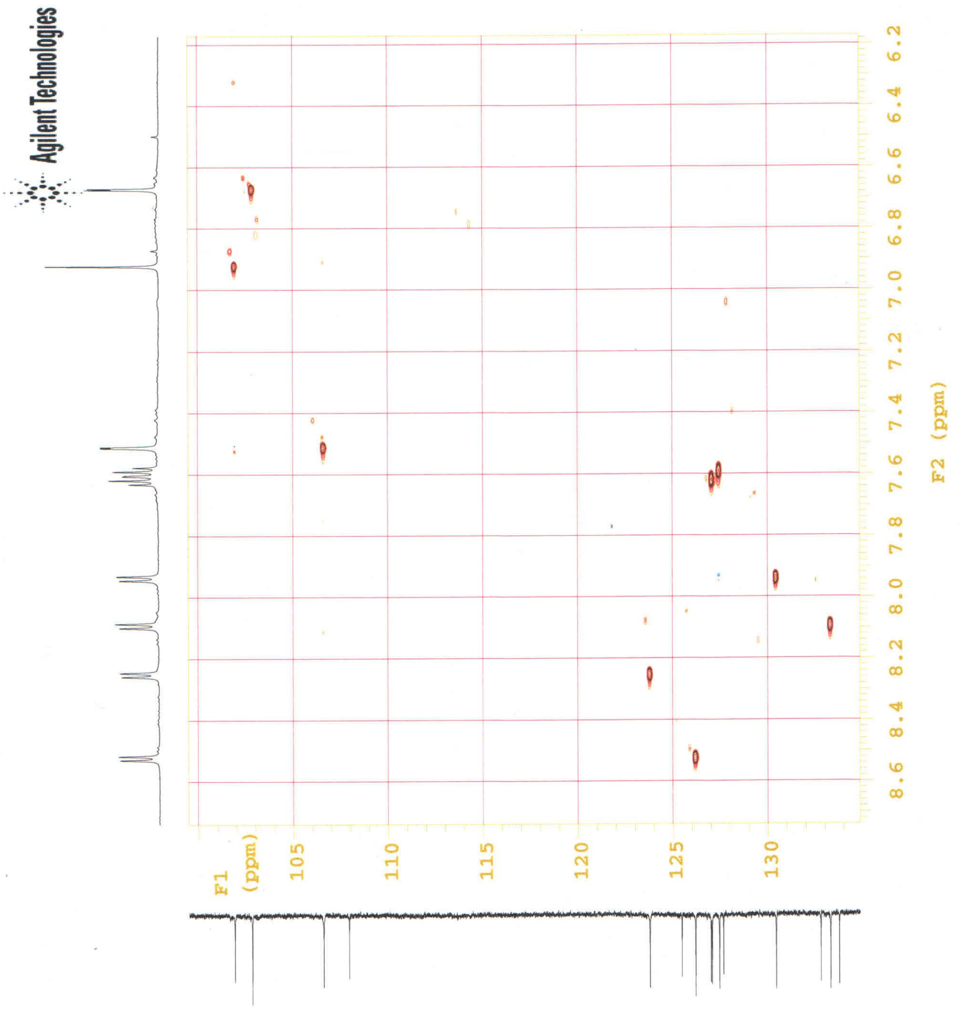

Figure S7. HSQC spectrum of compound **4**.

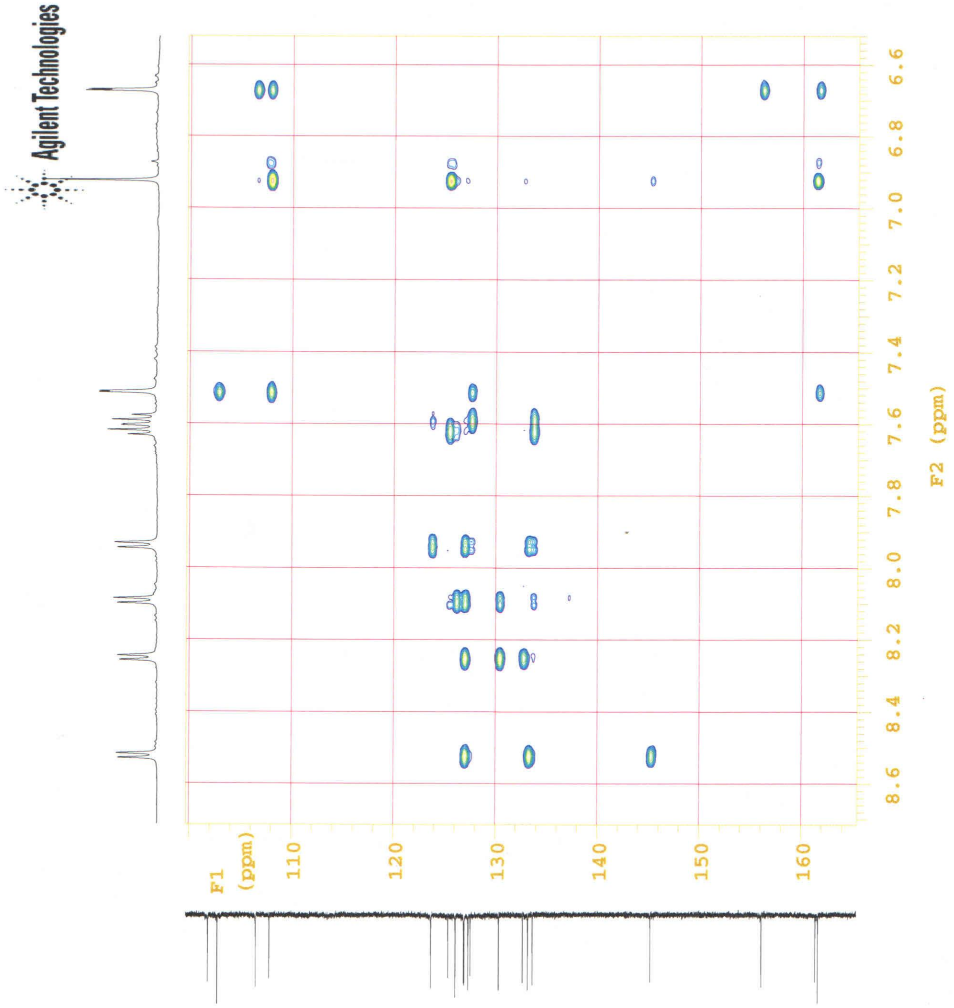

Figure S8. HMBC spectrum of compound **4**.

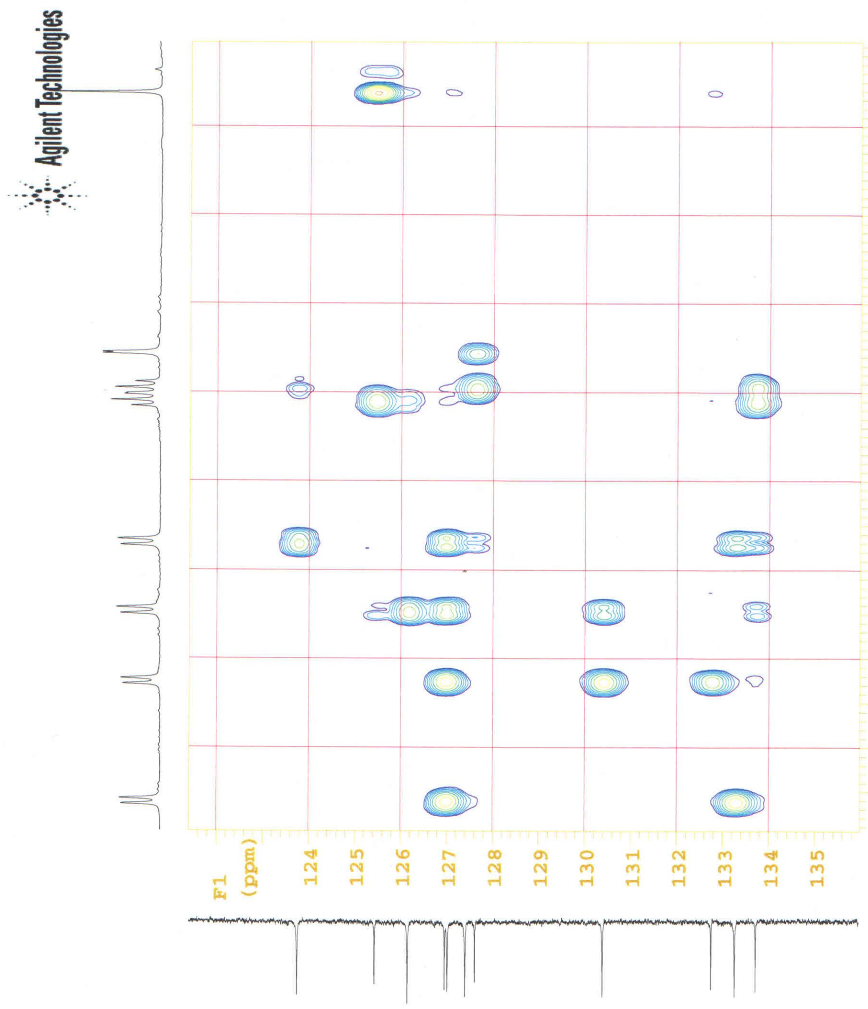

Figure S9. HMBC spectrum of compound **4**.

References

(1) Gaussian 09, Revision B.01, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J.; Gaussian Inc., Wallingford CT, **2010**.