J. Braz. Chem. Soc., Vol. 221, No. 5, 941-945, 2010.
Printed in Brazil - ©2010 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Short Report

Silica Supported Perchloric Acid: An Efficient Catalyst for the Synthesis of 14-Aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones

Li Qiang Wu, Yan Fang Wu, Chun Guang Yang, Li Min Yang and Li Juan Yang*

School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan 453003, China

Este trabalho descreve a obtenção de 14-aril-14*H*-dibenzo[*a,i*]xanteno-8,13-dionas, com excelentes rendimentos e em um curto tempo de reação, a partir da reação de condensação do β-naftol com aldeídos aromáticos e 2-hidroxinaftaleno-1,4-dionas na presença de sílica suportada em ácido perclórico em um meio livre de solvente. A reação é muito simples e o catalisador pode ser separado facilmente da mistura reacional e, ainda, ser reutilizado por muitas vezes em reações subseqüentes.

The condensation of β-naphthol with aromatic aldehydes and 2-hydroxynaphthalene-1,4-dione in presence of silica supported perchloric acid under solvent-free media to afford the corresponding 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones in excellent yields and short reaction times is described. The reaction work-up is very simple and the catalyst can be easily separated from the reaction mixture and reused several times in subsequent reactions.

Keywords: dibenzo[*a,i*]xanthenes**,** β-naphthol, 2-hydroxynaphthalene-1,4-dione, silica supported perchloric acid, solvent-free

Introduction

Xanthenes and benzoxanthenes have been reported to posses diverse biological and therapeutic properties such as antibacterial,[1] antiviral,[2] and anti-inflammatory activities,[3] as well as photodynamic therapy[4] and for antagonism of the paralyzing action of zoxazolamine.[5] The other useful applications of this heterocycles are as dyes,[6] fluorescent materials for visualization of biomolecules,[7] and in laser technologies.[8] Many procedures have been developed for the synthesis of xanthenes and benzoxanthenes, which include trapping of benzynes by phenols,[9] cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone,[10] cyclodehydrations,[11] and intramolecular phenyl carbonyl reaction of aldehydes with 5,5-dimethylcyclohexane-1,3-dione[12] or β-naphthol.[13] Furthermore, the synthesis of benzoxanthenes and their related products include the reaction of β-naphthol with formamide,[14] carbon monoxide,[15] 2-naphthol-1-methanol,[16] aldehydes and cyclic 1,3-dicarbonyl compounds.[17]

In recent years, the use of heterogeneous catalysts has received considerable interest in various disciplines including organic synthesis. They are advantageous over their homogeneous counterparts due to the prime advantage that in most of the cases the catalyst can be recovered easily and reused. Silica supported perchloric acid ($HClO_4$-SiO_2) has been used as an efficient heterogeneous catalyst for many organic transformations because of its low cost, ease of preparation, catalyst recycling, and ease of handling.[18] We now report a simple and efficient route to synthesis of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones using $HClO_4$-SiO_2 as an efficient catalyst under solvent-free conditions (Scheme 1).

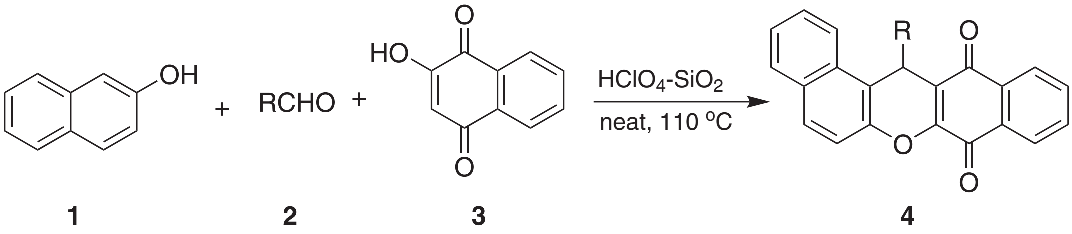
Results and Discussion

Initially, to optimize the amount of catalyst and the reaction temperature, the reaction of β-naphthol, benzaldehyde and 2-hydroxy-1,4-naphthoquinone was studied under solvent-free conditions in the presence of $HClO_4$-SiO_2 at different temperatures. The results were summarized in Table 1, and showed that the reaction using 5 mol % $HClO_4$-SiO_2 at 110 °C proceeded in highest yield.

Based on the optimized reaction conditions, several syntheses of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones from the condensation of β-naphthol, 2-hydroxynaphthalene-1,4-dione, and a wide range of aromatic aldehydes utilizing $HClO_4$-SiO_2 under solvent-free

---

*e-mail: wliq870@163.com



Scheme 1.

conditions at 110 °C were examined. All reactions were complete with in 1-2 h, as indicated in Table 2; in all cases the reactions afforded the desired products in excellent yields. When this reaction was carried out with aliphatic aldehyde such as butanal or pentanal, TLC and ^{1}H NMR spectra of the reaction mixture showed a combination of starting materials and numerous products, the yield of the expected product was very poor.

Table 1. Amounts of catalyst and temperature optimization for the synthesis of 14-phenyl-14*H*-dibenzo[*a,i*]xanthene-8,13-dione[a]

Entry	$HClO_4$-SiO_2 / mol %	Temp. / °C	time / h	Yield / %[b]
1	5	50	3	49
2	5	80	2	64
3	5	90	1.5	72
4	5	100	1	82
5	0	110	5	0
6	1	110	2	52
7	2	110	2	61
8	3	110	1.5	74
9	4	110	1	82
10	5	110	1	92
11	6	110	1	92
12	7	110	1	91
13	5	120	1	90
14	5	130	0.5	91

[a]Reaction conditions: β-naphthol (1 mmol); benzaldehyde (1 mmol); 2-hydroxynaphthalene-1,4-dione (1 mmol); neat. [b]Isolated yield.

The reusability of the catalyst was checked by separating $HClO_4$-SiO_2 from the reaction mixture by simple filtration, washing with $CHCl_3$, and drying in a vaccum oven at 60 °C for 10 h prior to reuse in subsequent reactions. The recovered catalyst can be reused at least three additional times in subsequent reactions without significant loss in product yield (Table 3).

Although the detailed mechanism of the above reaction remains to be fully clarified, the formation of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones could be explained by a reaction sequence presented in Scheme 2. We proposed that the reaction proceeded *via* a reaction sequence of condensation, addition, cyclization and dehydration. First, the condensation of aldehyde (**2**) and β-naphthol (**1**) gave the intermediate *ortho*-quinone methide (**5**). The addition of 2-hydroxynaphthalene-1,4-dione (**3**) to (**5**) leading to the formation of (**6**), which on intermolecular cyclization gave rise to (**7**). In the last step, the intermediate product (**7**) undergoes dehydration to afford the desired product (**4**). In β-naphthol the electron density at the benzylic C-1 position (which is in conjugation with the aromatic ring) is higher than that at the C-3 position. Thus the regioselective formation of the *ortho*-quinone methide from this compound involving the C-1 and C-2 positions is favored. In simple phenolic compounds and α-naphthol (which are weaker nucleophiles

Table 2. Preparation of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones catalyzed by $HClO_4$-SiO_2[a]

Entry	R	time / h	Product	Yield / %[b]
1	C_6H_5	1	**4a**	92
2	4-Cl-C_6H_4	1	**4b**	94
3	4-MeO-C_6H_4	1	**4c**	89
4	4-Me-C_6H_4	1	**4d**	90
5	4-NO_2-C_6H_4	1.5	**4e**	89
6	3-NO_2-C_6H_4	2	**4f**	88
7	2,4-Cl_2-C_6H_3	1.5	**4g**	87
8	3,4-Cl_2-C_6H_3	1.5	**4h**	92
9	2-Cl-C_6H_4	2	**4i**	88

[a]Reaction conditions: β-naphthol (1 mmol); aldehyde (1 mmol); 2-hydroxynaphthalene-1,4-dione (1 mmol); $HClO_4$-SiO_2 (0.05 mmol); 110 °C; neat. [b]Isolated yield.

Table 3. Effect of reusability of $HClO_4$-SiO_2 catalyst on 14-phenyl-14*H*-dibenzo[*a,i*]xanthene-8,13-dione synthesis [a]

Run	Cycle	Yield / %[b]
1	0	92
2	1	91
3	2	89
4	3	88

[a]Reaction conditions: β-naphthol (1 mmol); benzaldehyde (1 mmol); 2-hydroxynaphthalene-1,4-dione (1 mmol); $HClO_4$-SiO_2 (0.05 mmol); 110 °C; neat. [b]Isolated yield.

compared to β-naphthol) the electron density at the *ortho* position of the hydroxyl group is not sufficient for the reaction of these compounds with the aldehydes leading to the formation of the corresponding *ortho*-quinone methides.

Conclusions

In conclusion, we have developed a simple and efficient protocol for the synthesis of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones using $HClO_4$-SiO_2 under solvent-free conditions. Short reaction times, simple work-up in isolation of the products in high yields with high purity, mild reaction conditions and recyclability of supported catalyst are features of this procedure.

Experimental

NMR spectra were determined on Bruker AV-400 spectrometer at room temperature using TMS as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Mass spectra were recorded on a Finnigan LCQ Advantage mass spectrometer. Elemental analysis were performed by a Vario-III elemental analyzer. Melting points were determined on a XT-4 binocular microscope and were uncorrected. Commercially available reagents were used throughout without further purification unless otherwise stated.

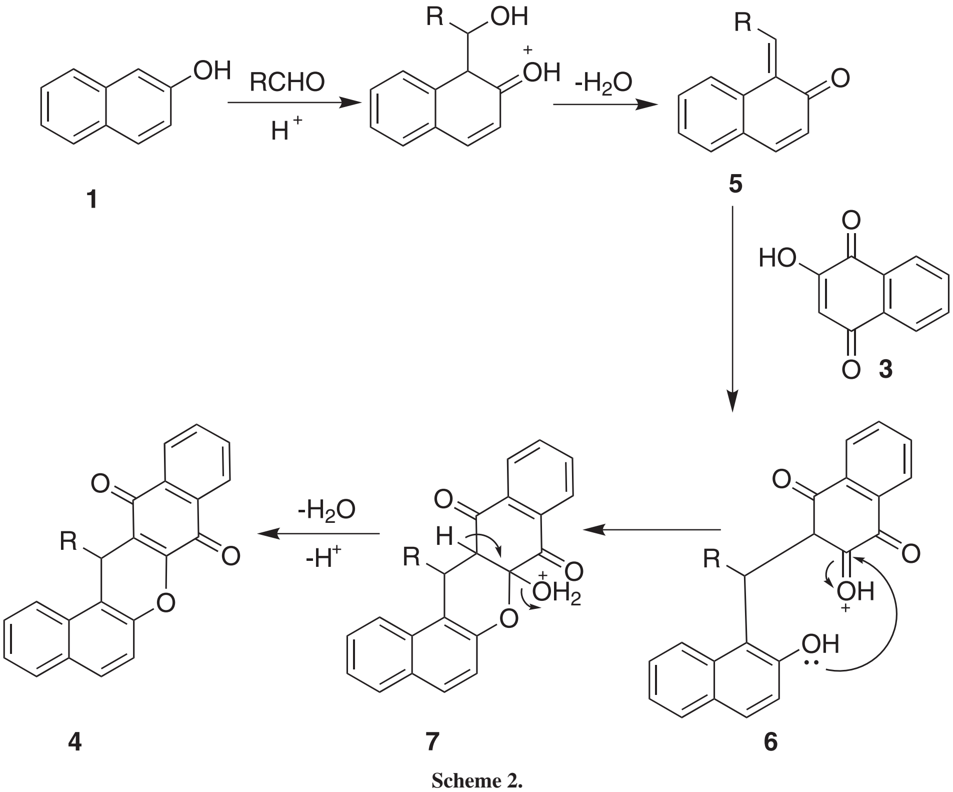
Preparation of $HClO_4$-SiO_2 catalyst

$HClO_4$ (1.8 g, 12.5 mmol, as 70% aqueous solution) was added to a suspension of SiO_2 (230-400 mesh, 23.7 g) in Et_2O (70.0 mL). The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to furnish $HClO_4$-SiO_2 (0.5 mmol g^{-1}) as a free flowing powder (50 mg = 0.025 mmol of $HClO_4$).

General procedure for the preparation of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-diones

A mixture of β-naphthol (1 mmol), aldehyde (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and $HClO_4$-SiO_2 (100 mg, 0.05 mmol) was heated at 110 °C for an appropriate time and monitored by TLC until the final conversion. After cooling, the reaction mixture was washed with $CHCl_3$ and filtered to recover the catalyst. Solvent was evaporated and the crude product puried by silica gel column chromatography using $CHCl_3$ as eluent to afford the pure product.

*14-Phenyl-14H-dibenzo[a,i]xanthene-8,13-dione (**4a**)*: Yellow powder, mp 319-320 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, 1H, J 7.6 Hz), 8.12 (d, 1H, J 7.6 Hz), 7.99 (d, 1H, J 8.4 Hz), 7.91-7.77 (m, 3H), 7.61-7.41 (m, 6H), 7.20 (t, 2H, J 8.0 Hz), 7.12-7.09 (m, 1H), 5.95 (s, 1H);



Scheme 2.

^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.3, 157.2, 147.3, 143.1, 135.1, 131.9, 131.2, 131.0, 130.9, 130.0, 129.5, 129.4, 128.6, 127.5, 126.8, 125.5, 124.5, 123.8, 116.9, 116.8, 116.6, 35.2; MS (ESI): *m/z* 389 [M+H]$^+$; Anal. Calc. for $C_{27}H_{16}O_3$: C, 83.49; H, 4.15. Found: C, 83.25; H, 4.12%.

*14-(4-Chlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4b**)*: Yellow powder, mp 305-306 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.16 (d, 1H, *J* 7.6 Hz), 8.13 (d, 1H, *J* 7.6 Hz), 7.92-7.77 (m, 4H), 7.62-7.44 (m, 4H), 7.34 (d, 2H, *J* 8.4 Hz), 7.15 (d, 2H, *J* 8.4 Hz), 5.90 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.2, 157.3, 147.2, 141.6, 135.2, 132.7, 131.9, 131.4, 130.8, 130.7, 130.0, 120.0, 129.8, 129.5, 128.7, 127.6, 125.7, 124.6, 123.6, 116.8, 116.3, 116.0, 34.6; MS (ESI): *m/z* 423 [M+H]$^+$; Anal. Calc. for $C_{27}H_{15}ClO_3$: C, 76.69; H, 3.58. Found: C, 76.48; H, 3.62%.

*14-(4-Methoxylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4c**)*: Yellow powder, mp 279-280 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.16 (d, 1H, *J* 8.0 Hz), 8.12 (d, 1H, *J* 7.6 Hz), 7.98 (d, 1H, *J* 8.4 Hz), 7.89-7.76 (m, 4H), 7.60-7.43 (m, 5H), 7.31 (d, 2H, *J* 8.4 Hz), 5.90 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.4, 158.3, 157.0, 147.2, 135.5, 135.1, 131.9, 131.2, 131.0, 130.0, 129.6, 129.4, 128.5, 127.4, 125.5, 124.5, 123.8, 117.1, 116.8, 113.9, 55.1, 34.3; MS (ESI): *m/z* 419 [M+H]$^+$; Anal. Calc. for $C_{28}H_{18}O_4$: C, 80.37; H, 4.34. Found: C, 80.50; H, 4.27%.

*14-(4-Methylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4d**)*: Yellow powder; mp 255-256 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.16 (d, 1H, *J* 8.0 Hz), 8.11 (d, 1H, *J* 7.6 Hz), 7.99 (d, 1H, *J* 8.0 Hz), 7.89-7.76 (m, 3H), 7.60-7.42 (m, 4H), 7.29 (d, 2H, *J* 8.0 Hz), 7.00 (d, 2H, *J* 7.6 Hz), 5.90 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.3, 178.2, 157.1, 147.2, 140.3, 136.5, 135.1, 131.9, 131.2, 131.0, 130.9, 120.0, 129.4, 129.3, 129.2, 128.5, 128.4, 127.4, 125.5, 124.5, 123.8, 117.0, 116.8, 116.7, 34.7, 21.0; MS (ESI): *m/z* 403 [M+H]$^+$; Anal. Calc. for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51. Found: C, 83.49; H, 4.63%.

*14-(4-Nitrophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4e**)*: Yellow powder, mp 332-333 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.20 (d, 1H, *J* 7.6 Hz), 8.15 (d, 1H, *J* 7.6 Hz), 8.06 (d, 2H, *J* 8.8 Hz), 7.97-7.81 (m, 4H), 7.66-7.49 (m, 6H), 6.06 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.2, 178.0, 157.8, 150.0, 147.3, 146.7, 135.3, 132.0, 131.7, 130.7, 130.4, 130.3, 130.0, 129.6, 128.8, 127.9, 125.9, 124.8, 123.9, 123.3, 116.8, 115.4, 115.0, 35.3; MS (ESI): *m/z* 434 [M+H]$^+$; Anal. Calc. for $C_{27}H_{15}NO_5$: C, 74.82; H, 3.49; N, 3.23. Found: C, 74.91; H, 3.38; N, 3.29%.

*14-(3- Nitrophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4f**)*: Yellow powder, mp 304-305 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.22 (d, 1H, *J* 8.0 Hz), 8.15 (d, 1H, *J* 8.0 Hz), 8.12 (s, 1H), 8.00-7.82 (m, 6H), 7.66-7.61 (m, 2H), 7.52-7.41 (m, 3H), 6.06 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.1, 178.0, 157.7, 148.6, 147.3, 145.1, 135.3, 135.1, 132.0, 131.7, 130.6, 130.4, 130.1, 129.6, 129.4, 128.9, 127.8, 125.9, 124.9, 123.3, 122.1, 117.0, 115.3, 115.2, 35.2; MS (ESI): *m/z* 434 [M+H]$^+$; Anal. Calc. for $C_{27}H_{15}NO_5$: C, 74.82; H, 3.49; N, 3.23. Found: C, 74.76; H, 3.56; N, 3.25%.

*14-(2,4-Dichlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4g**)*: Yellow powder, mp 301-302 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.20 (d, 1H, *J* 8.4 Hz), 8.16-8.11 (m, 2H), 7.89-7.80 (m, 3H), 7.65-7.45 (m, 4H), 7.31-7.27 (m, 2H), 7.07-7.05 (m, 1H), 6.14 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.1, 157.6, 147.1, 139.2, 135.2, 134.0, 133.1, 132.6, 131.8, 131.5, 131.1, 130.6, 130.1, 130.0, 129.8, 129.5, 128.7, 127.7, 127.5, 125.7, 124.7, 123.7, 116.8, 33.2; MS (ESI): *m/z* 457 [M+H]$^+$; Anal. Calc. for $C_{27}H_{14}Cl_2O_3$: C, 70.91; H, 3.09. Found: C, 70.82; H, 3.11%.

*14-(3,4-Dichlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4h**)*: Yellow powder, mp 260-261 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.19 (d, 1H, *J* 7.6 Hz), 8.16 (d, 1H, *J* 7.6 Hz), 7.95-7.82 (m, 4H), 7.65-7.43 (m, 5H), 7.31-7.30 (m, 2H), 5.92 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.2, 178.0, 157.6, 147.3, 143.2, 135.2, 132.7, 132.0, 131.6, 131.1, 130.7, 130.5, 130.4, 130.1, 129.6, 128.8, 128.2, 127.8, 125.8, 124.7, 123.4, 116.8, 115.6, 115.4, 34.6; MS (ESI): *m/z* 457 [M+H]$^+$; Anal. Calc. for $C_{27}H_{14}Cl_2O_3$: C, 70.91; H, 3.09. Found: C, 70.95; H, 3.02%.

*14-(2-Chlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (**4i**)*: Yellow powder, mp 281-282 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.25-8.22 (m, 2H), 8.14 (d, 1H, *J* 7.2 Hz), 7.89-7.83 (m, 3H), 7.65-7.29 (m, 6H), 7.08-7.04 (m, 2H), 6.22 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 178.2, 178.1, 157.4, 147.1, 135.2, 133.3, 131.8, 131.4, 131.3, 130.8, 130.2, 130.1, 129.8, 129.4, 128.6, 128.2, 127.6, 127.1, 125.6, 124.7, 124.0, 116.8, 116.7, 115.6, 33.5; MS (ESI): *m/z* 423 [M+H]$^+$; Anal. Calc. for $C_{27}H_{15}ClO_3$: C, 76.69; H, 3.58. Found: C, 76.79; H, 3.41%.

Supplementary Information

^{1}H NMR, ^{13}C NMR spectra of compounds **4a-i** are available free of charge at http://jbcs.sbq.org.br, as pdf file.

Acknowledgment

We are pleased to acknowledge the financial support from Xinxiang Medical University.

References

1. Hideu, T.; *Jpn. Kokai Tokkyo Koho 56005480* **1981.** *(CA 95:80922b).*
2. Lamberk, R. W.; Martin, J. A.; Merrett, J. H.; Parkes, K. E. B.; Thomas, G. J.; *PCT Int. Appl.WO 9706178* **1997**. (*CA 126:212377y).*
3. Poupelin, J. P.; Saint-Rut, G.; Fussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, Lakroix, G. R.; *Eur. J. Med. Chem.* **1978**, *13,* 67.
4. Ion, R. M.; Frackowiak, D.; Planner, A.; Wiktorowicz, K.; *Acta Biochim. Pol.* **1998**, *45*, 833.
5. Saint-Ruf, G.; De, A.; Hieu, H. T.; *Bull. Chim. Ther.* **1972**, *7,* 83.
6. Banerjee, A.; Mukherjee, A. K.; *Stain Technol.* **1981**, *56,* 83.
7. Knight, C. G.; Stephenes, T.; *Biochem. J.* **1989**, *258*, 683.
8. Sirkecioglu, O.; Tulinli, N.; Akar, A.; *J. Chem. Res.* **1995,** 502.
9. Knight, D. W.; Little P. B.; *J. Chem. Soc. Perkin Trans I* **2001**, 1771.
10. Jha, A.; Beal, J.; *Tetrahedron Lett.* **2004**, *45*, 8999.
11. Bekaert, A.; Andrieux, J.; Plat, M.; *Tetrahedron Lett.* **1992**, *33*, 2805.
12. Zhang, Z. H.; Tao, X.Y.; *Aust. J. Chem.* **2008**, *61*, 77; Lu, H. Y.; Li, J. J.; Zhang, Z. H.; *Appl. Organomet. Chem.* **2009**, *23*, 165.
13. Ohishi, T.; Kojima, T.; Matsuoka, T.; Shiro, M.; Kotsuko, H.; *Tetrahedron Lett.* **2001**, *42*, 2493; Liu, Y. H.; Tao, X. Y.; Lei, L. Q.; Zhang, Z. H.; *Synth. Commun.* **2009**, *39*, 580
14. Papini, P.; Cimmarusti, R.; *Gazz. Chim. Ital.* **1947**, *77*, 142.
15. Ota, K.; Kito, T.; *Bull. Chem. Soc. Jpn.* **1976***, 48*, 1167.
16. Sen, R. N.; Sarkar, N.; *J. Am. Chem. Soc.* **1925**, *47*, 1079.
17. Das, B.; Laxminarayana, K.; Krishnaiah, M.; Srinivas, Y.; *Synlett* **2007**, 3107; Wang, H. J.; Ren, X. Q.; Zhang, Y. Y.; Zhang, Z. H.; *J. Braz. Chem. Soc.* **2009**, *20*, 1939; Shaterian, H. R.; Ghashang, M. *J. Braz. Chem. Soc.* **2008**, *19*, 1053.
18. Misra, A. K.; Tiwari, P.; Agnihotri, G.; *Synthesis* **2005**, 260; Agnihotri, G.; Misra, A. K.; *Tetrahedron Lett.* **2007**, *48*, 7553; Tiwari, P.; Misra, A. K.; *Tetrahedron Lett.* **2007**, *48,* 7422; Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. H.; *J. Mol. Catal. A: Chem.* **2007**, *275*, 25; Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. H.; *Tetrahedron Lett***.** **2007**, *48*, 6801; Das, B.; Damodar, K.; Chowdhury, N.; Kumar, R. A.; *J. Mol. Catal. A: Chem.* **2007**, *274*, 148; Misra, A. K.; Tiwari, P.; Madhusudan, S. K.; *Carbohydr. Res.* **2005**, *340*, 325; Kumar, R.; Kumar, D.; Chakraborti, A. K.; *Synthesis* **2007**, 299; Mandal, P. K.; Misra, A. K.; *Lett. Org. Chem.* **2006**, *3*, 848; Khan, A. T.; Ghosh, S.; Choudhury, L. H.; *Eur. J. Org. Chem*. **2006**, *9*, 2226; Agnihotri, G.; Misra, A. K.; *Tetrahedron Lett.* **2006**, *47,* 3653; Khan, A. T.; Parvin, T.; Choudhury, L. H.; *Synthesis* **2006**, 2497; Wu, L. Q; Yang, C. G.; Zhang, C.; Yang, L. M.; *Lett. Org. Chem.* **2009**, *6*, 234.

Received: October 6, 2009
Web Release Date: March 11, 2010

J. Braz. Chem. Soc., Vol. 00, No. 00, S1-S10, 2010.
Printed in Brazil - ©2010 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

Silica Supported Perchloric Acid: An Efficient Catalyst for the Synthesis of 14-Aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones

Li Qiang Wu,* Yan Fang Wu, Chun Guang Yang, Li Min Yang and Li Juan Yang

School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan 453003, China

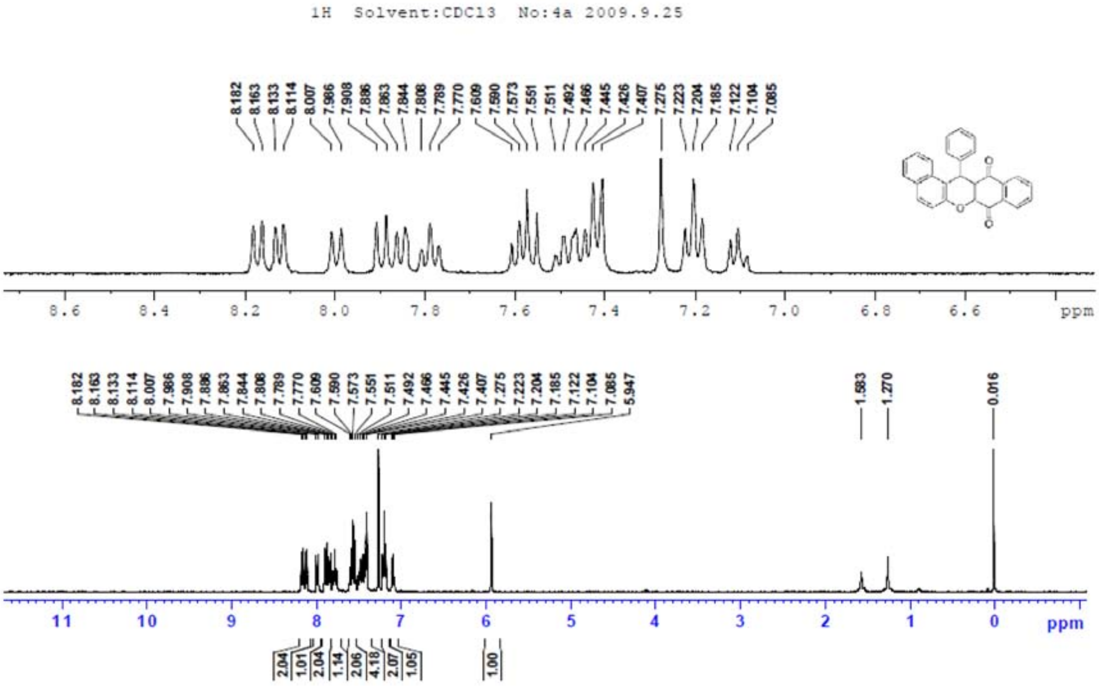


Figure S1a. ^{1}H NMR of **4a** (400 MHz, $CDCl_3$).

---

*e-mail: wliq870@163.com

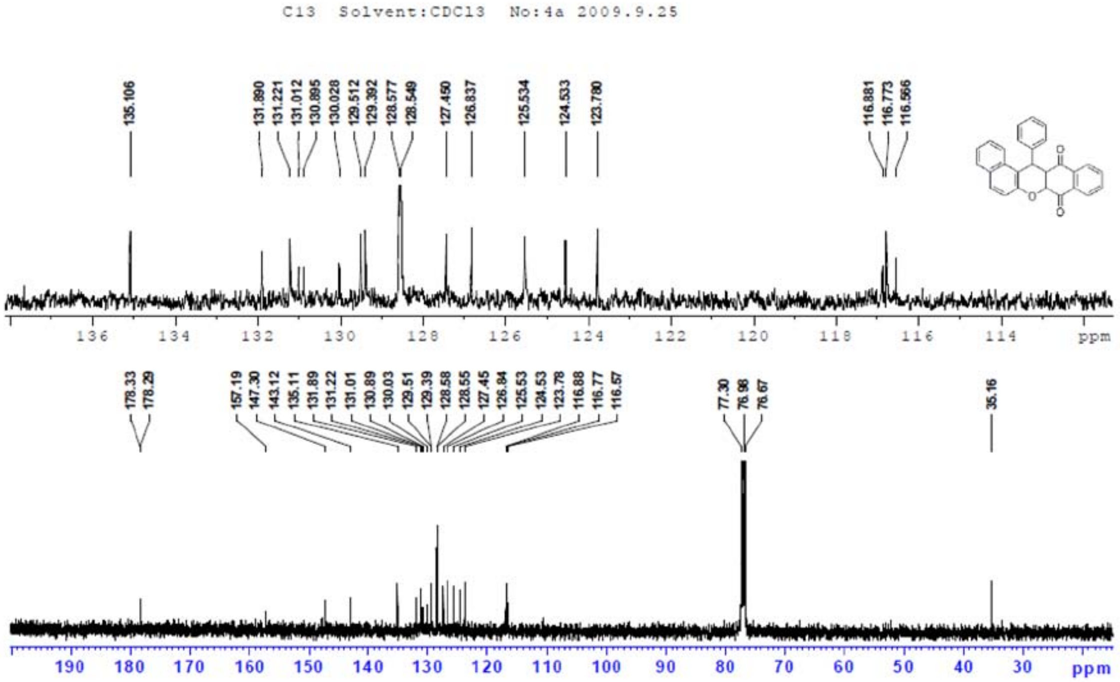


Figure S1b. ^{13}C NMR of **4a** (400 MHz, CDCl$_3$).

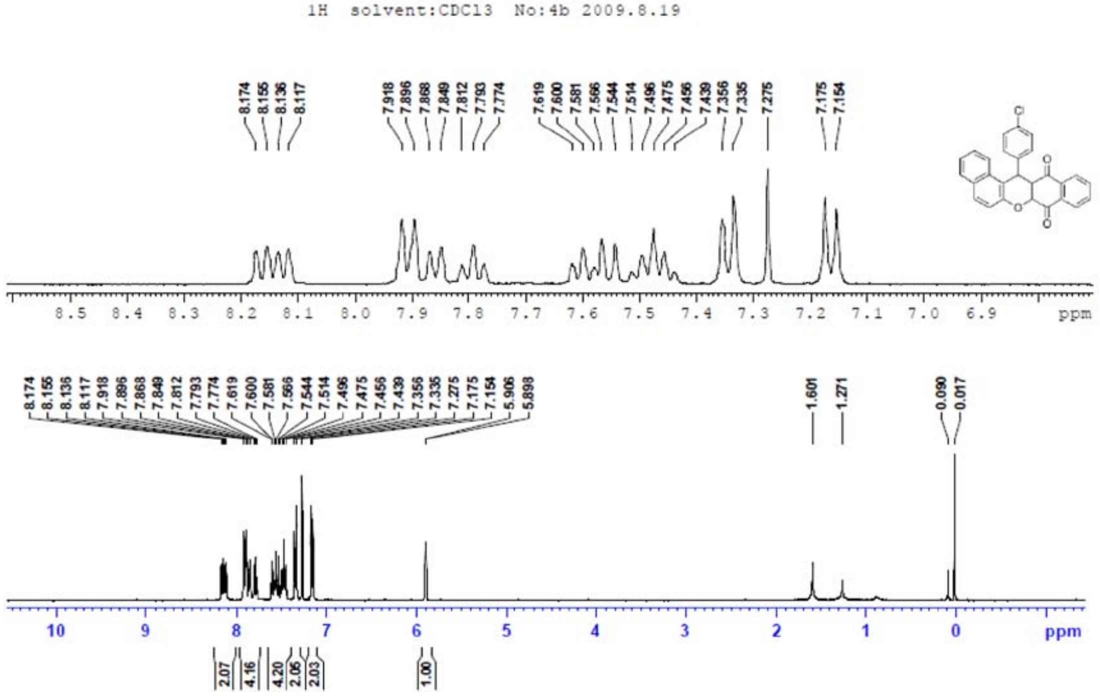


Figure S2a. ^{1}H NMR of **4b** (400 MHz, CDCl$_3$).

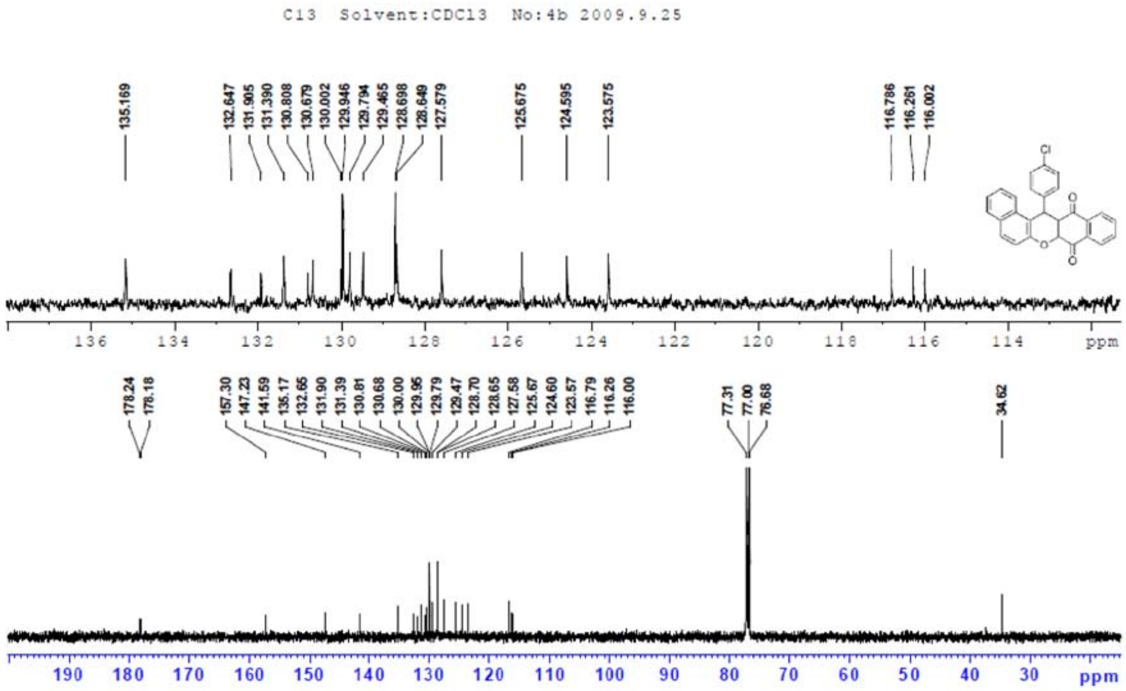


Figure S2b. ^{13}C NMR of **4b** (400 MHz, $CDCl_3$).

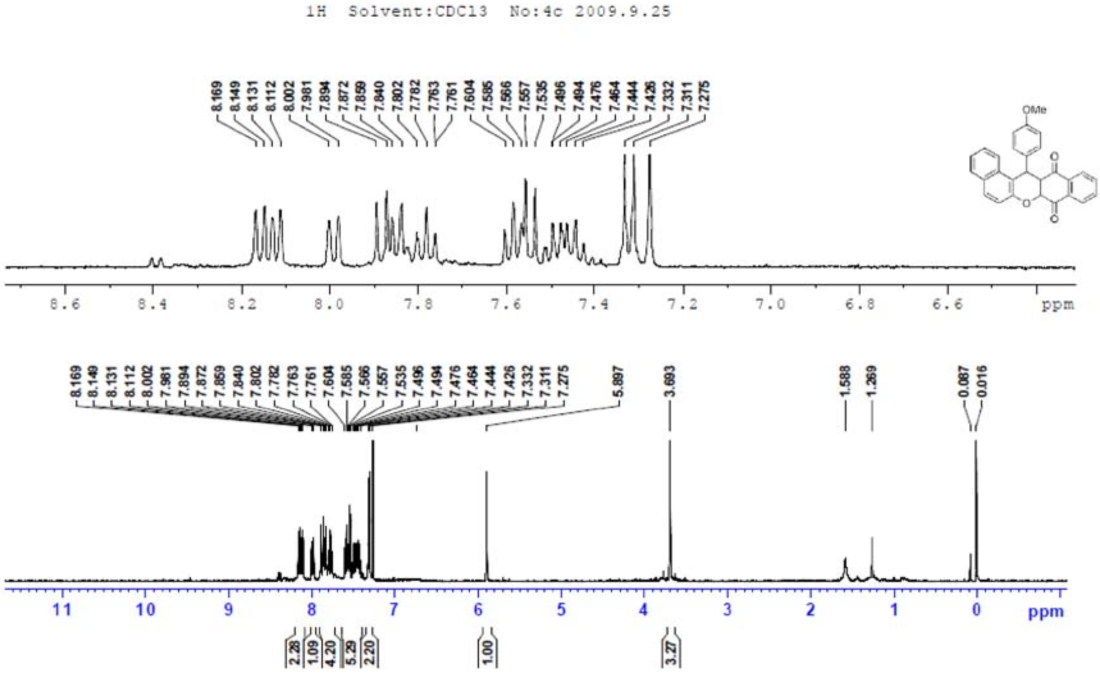


Figure S3a. ^{1}H NMR of **4c** (400 MHz, $CDCl_3$).

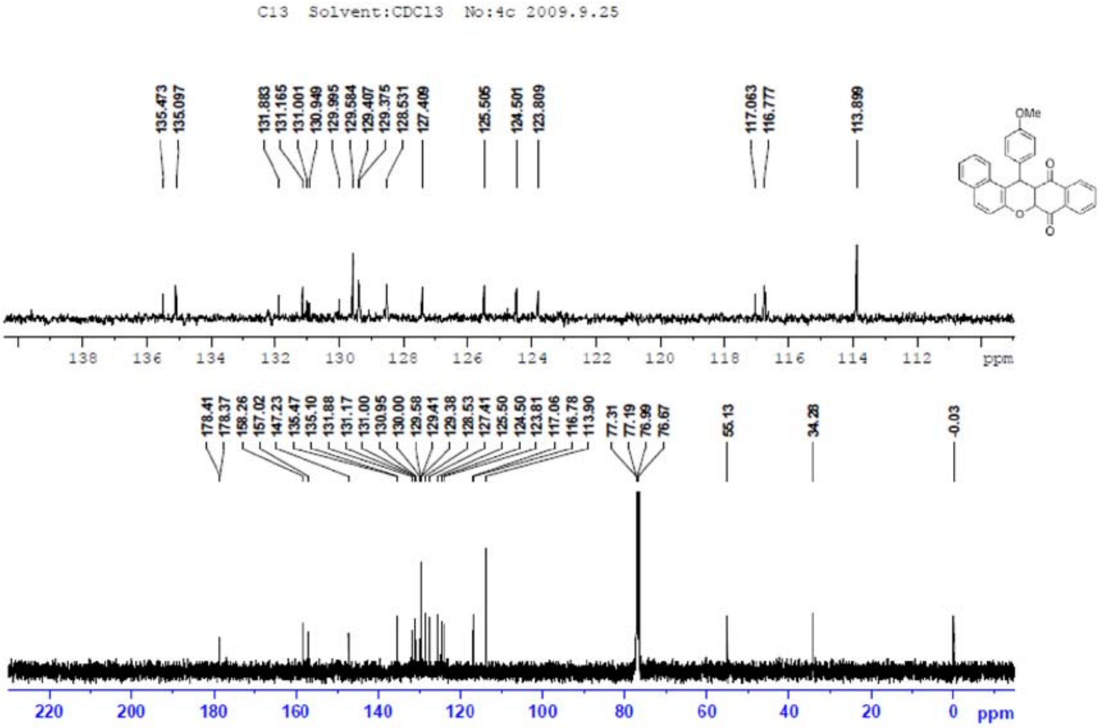


Figure S3b. ^{13}C NMR of **4c** (400 MHz, CDCl$_3$).

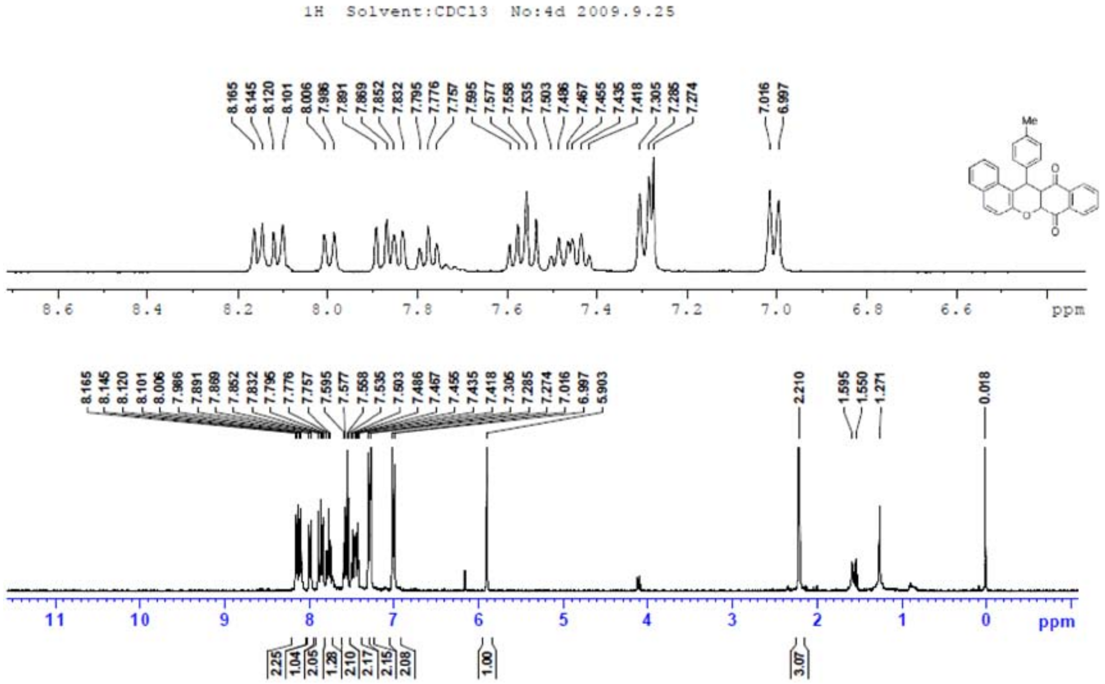


Figure S4a. ^{1}H NMR of **4d** (400 MHz, CDCl$_3$).

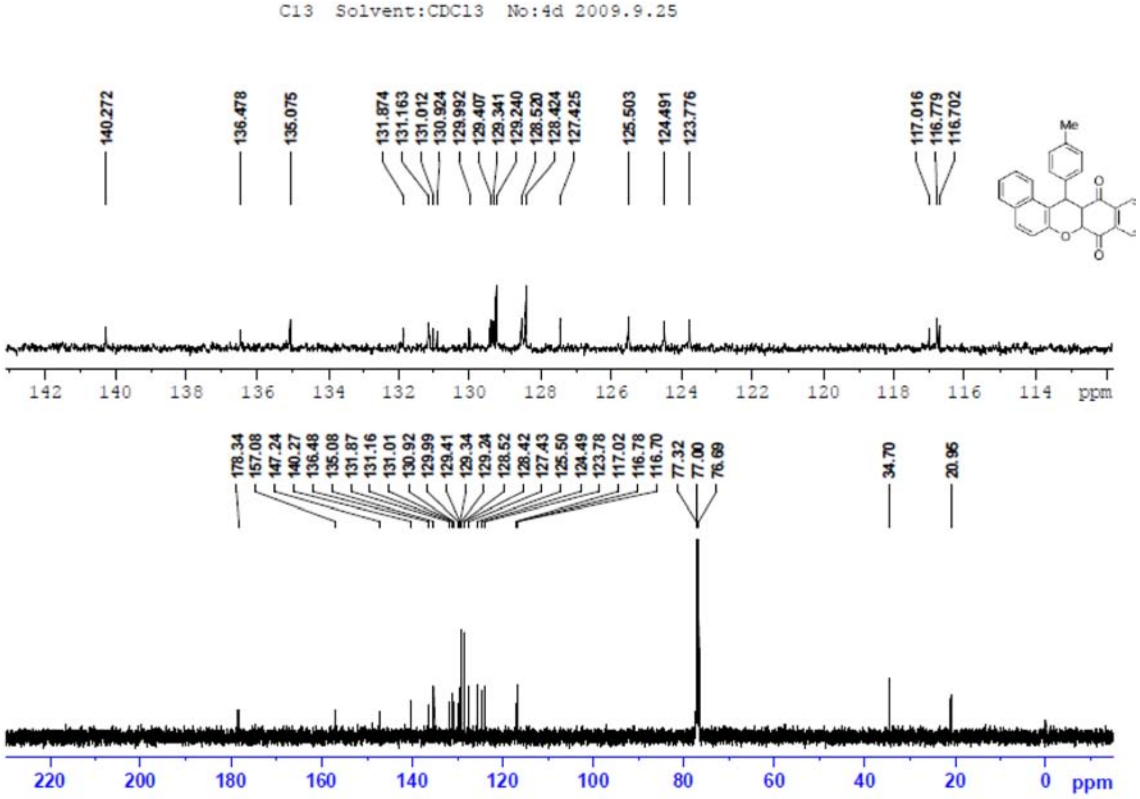


Figure S4b. ^{13}C NMR of **4d** (400 MHz, $CDCl_3$).

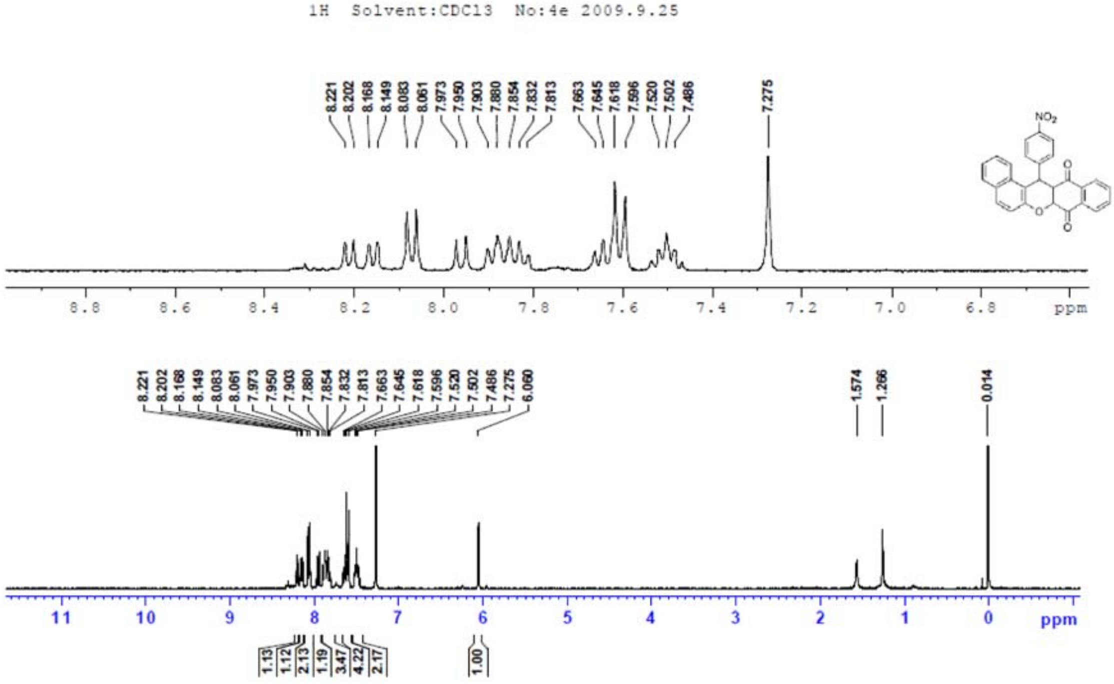


Figure S5a. ^{1}H NMR of **4e** (400 MHz, $CDCl_3$).

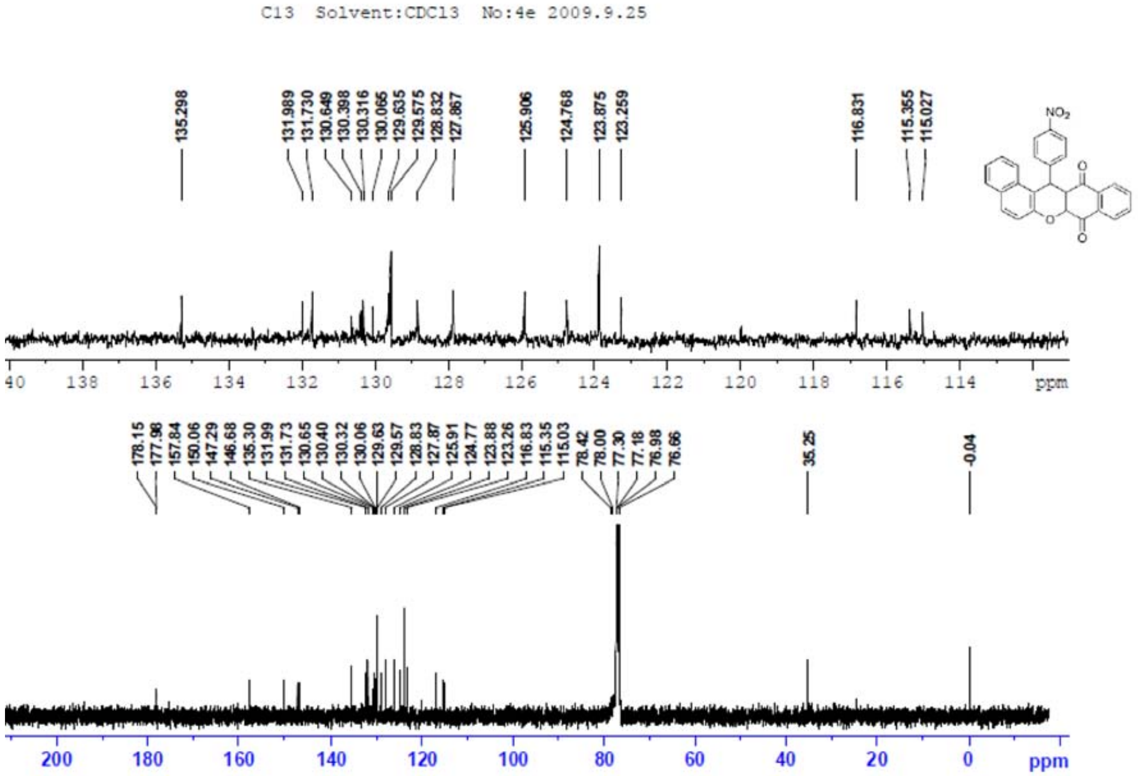


Figure S5b. ^{13}C NMR of **4e** (400 MHz, CDCl$_3$).

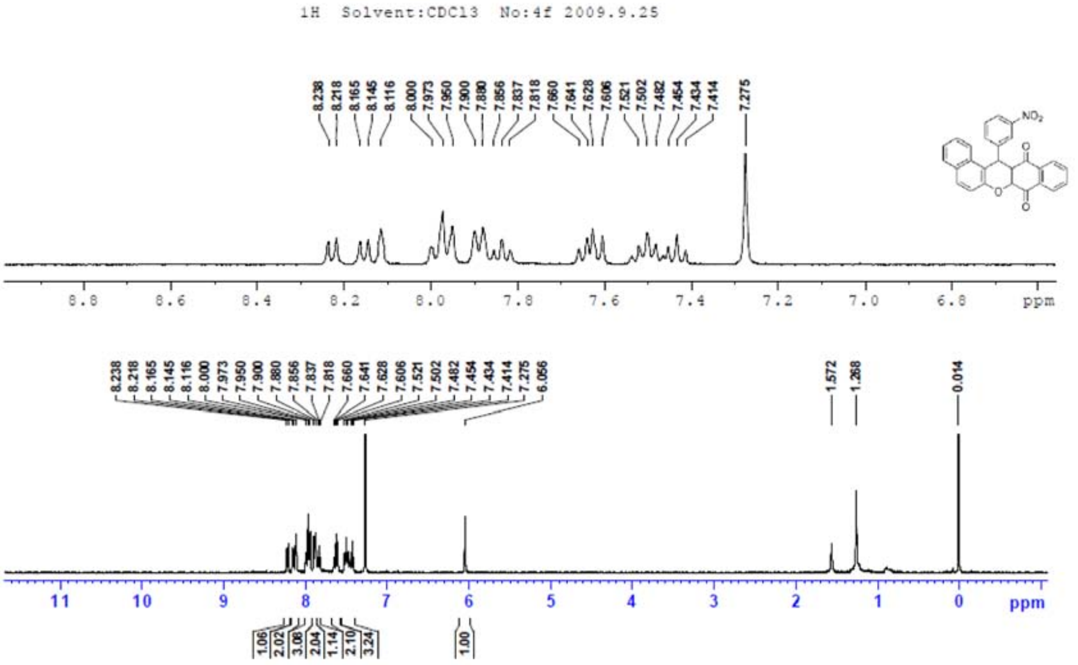


Figure S6a. ^{1}H NMR of **4f** (400 MHz, CDCl$_3$).

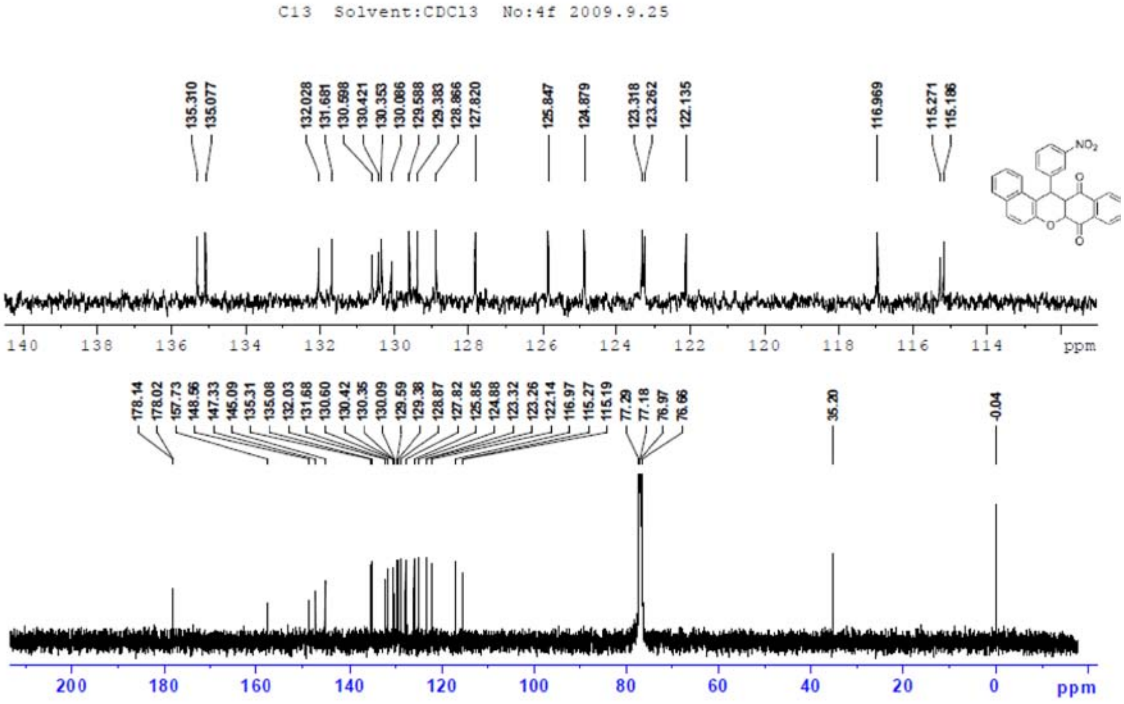


Figure S6b. ^{13}C NMR of **4f** (400 MHz, CDCl$_3$).

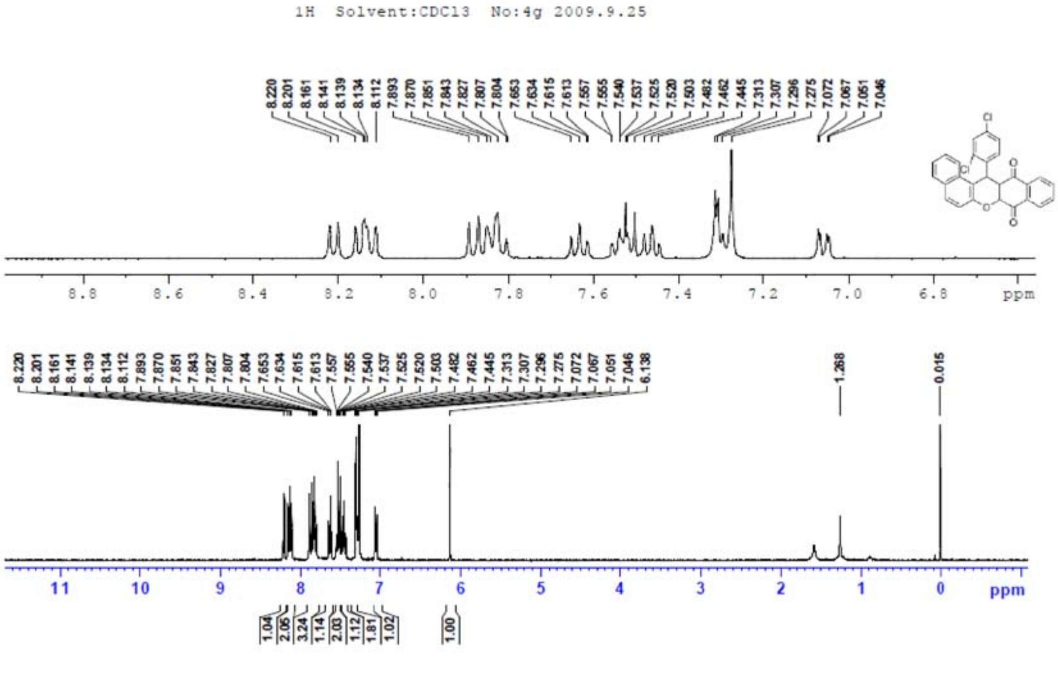


Figure S7a. ^{1}H NMR of **4g** (400 MHz, CDCl$_3$).

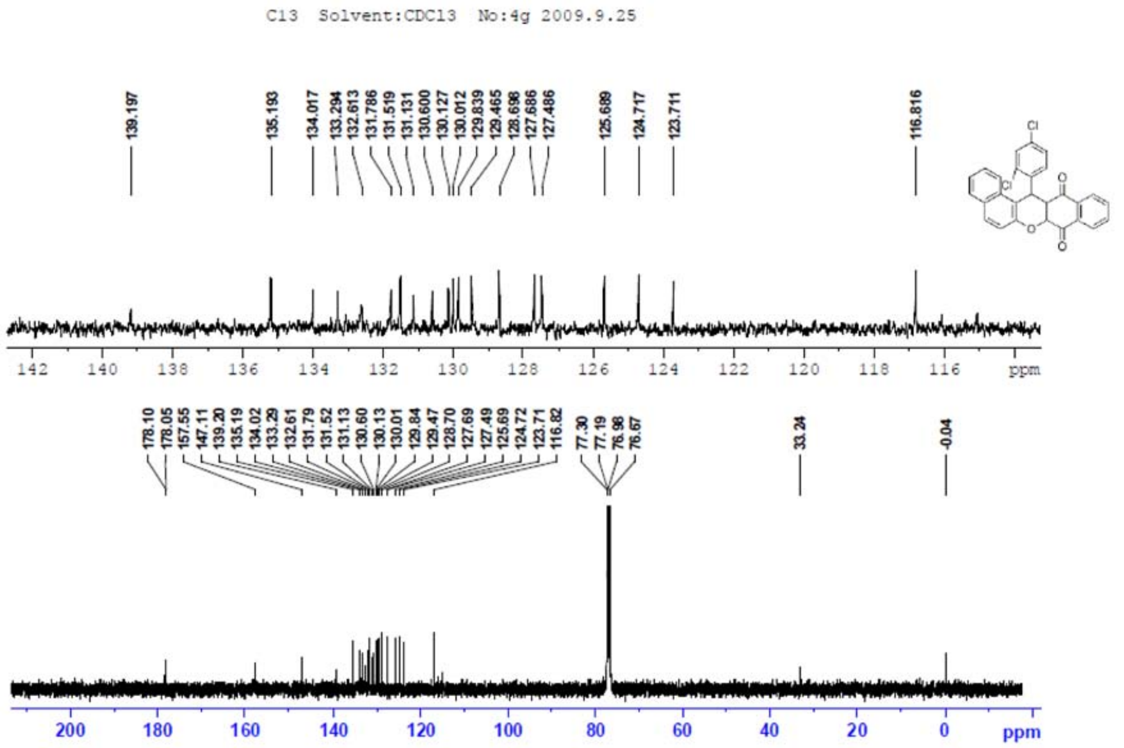


Figure S7b. ^{13}C NMR of **4g** (400 MHz, CDCl$_3$).

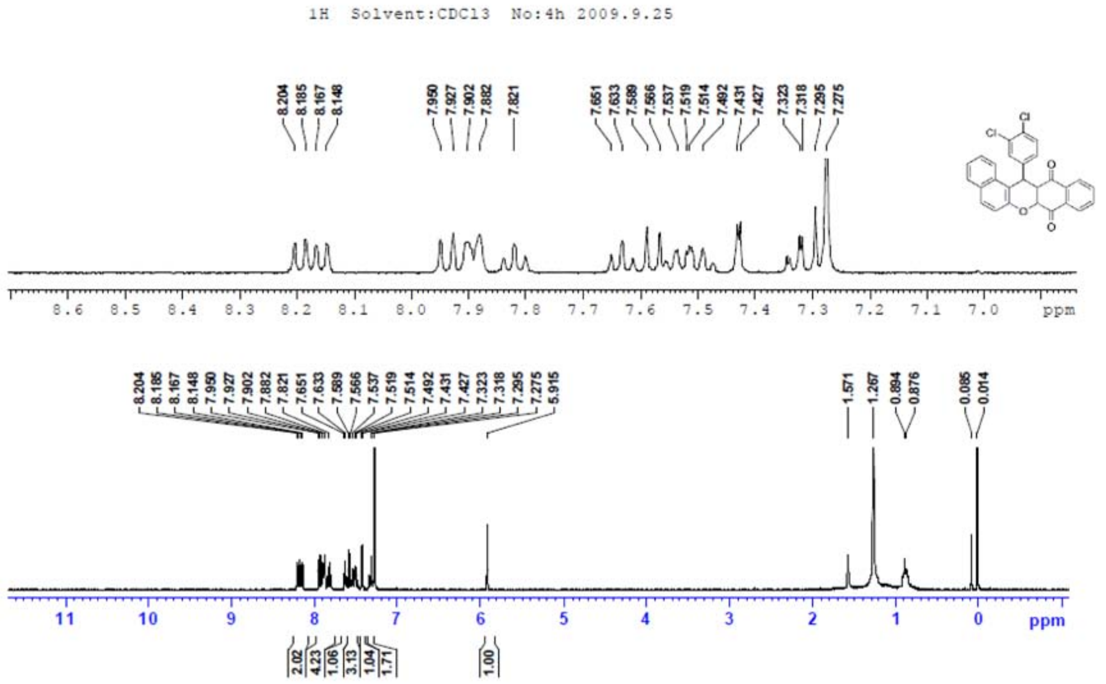


Figure S8a. ^{1}H NMR of **4h** (400 MHz, CDCl$_3$).

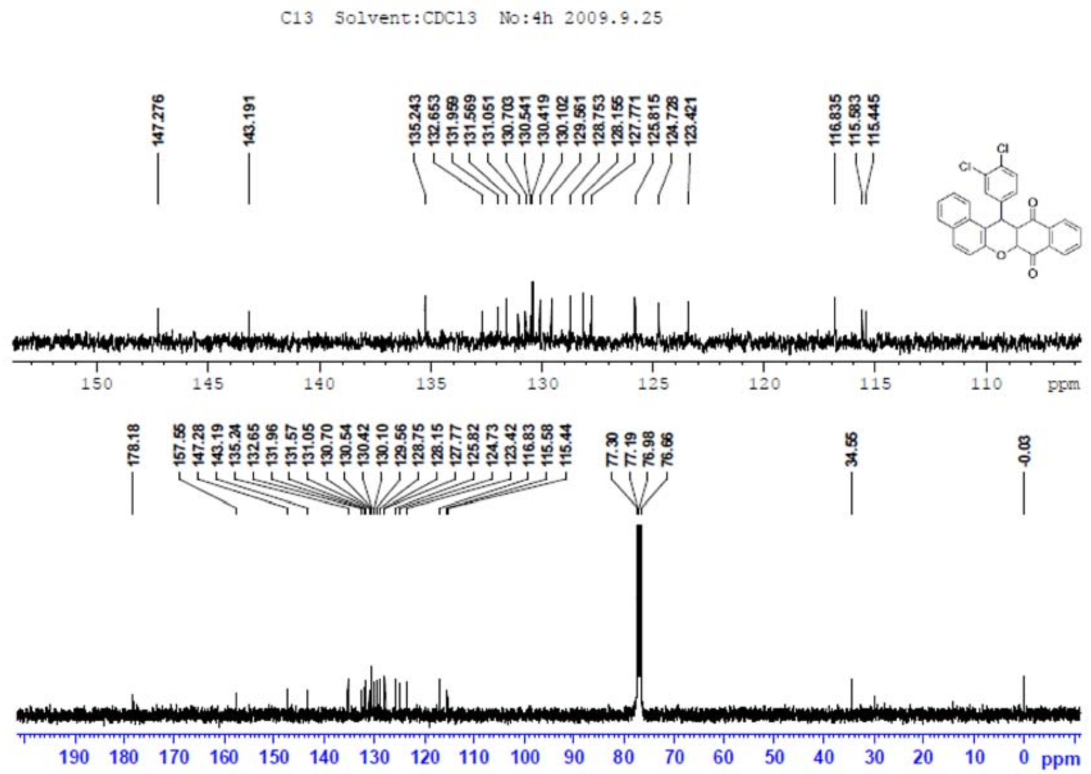


Figure S8b. ^{13}C NMR of **4h** (400 MHz, CDCl$_3$).

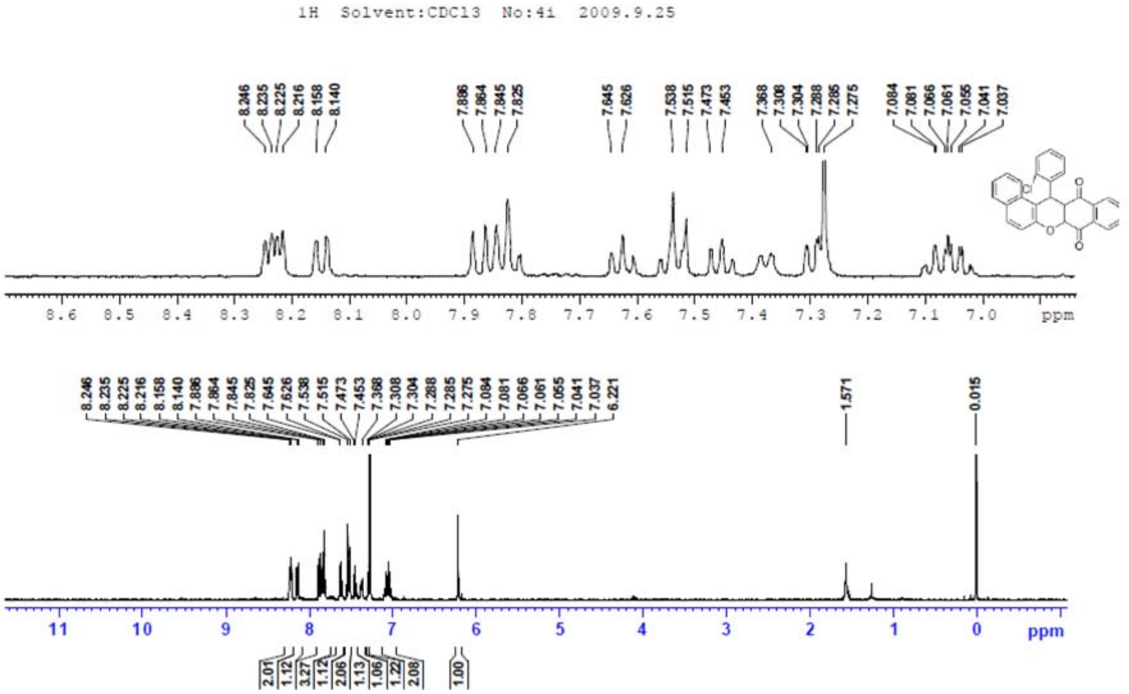


Figure S9a. ^{1}H NMR of **4i** (400 MHz, CDCl$_3$).

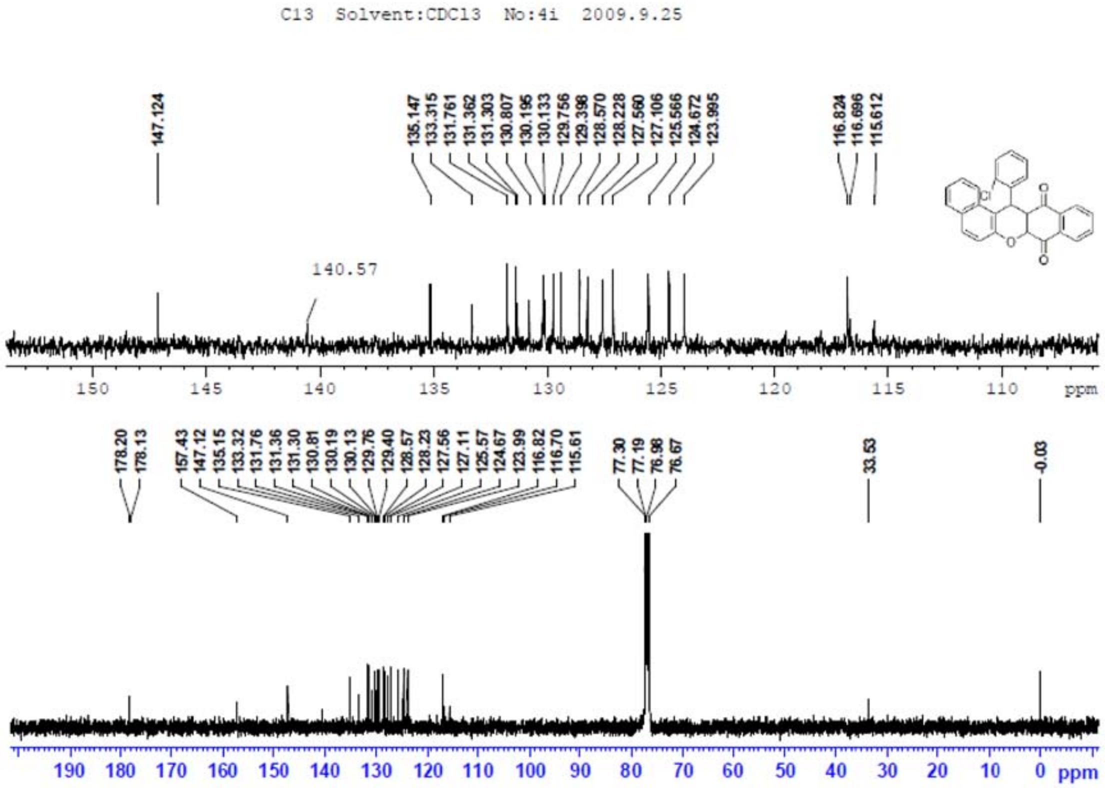


Figure S9b. ^{13}C NMR of **4i** (400 MHz, $CDCl_3$).