

Synthesis 12-Aryl or 12-Alkyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one Derivatives Catalyzed by Dodecatungstophosphoric Acid

Hong-Juan Wang, Xiao-Qian Ren, Yan-Yan Zhang and Zhan-Hui Zhang*

The College of Chemistry & Material Science, Hebei Normal University,
Shijiazhuang 050016, P. R. China

Um protocolo eficiente para a síntese de derivados de 12-aryl ou 12-alkyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one foi desenvolvido *via* reação de três componentes de aldeído, 2-naftol e 1,3-ciclohexadiona ou 5,5-dimetil-1,3-ciclohexadiona na presença de ácido 12-tungstosfórico ($H_3PW_{12}O_{40}$) sem o uso de solvente. A presente metodologia oferece muitas vantagens como altos rendimentos, procedimento simples, baixo custo, curto tempo de reação e condições brandas.

An efficient protocol for the synthesis of 12-aryl or 12-alkyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one derivatives has been developed *via* three-component reaction of aldehyde, 2-naphthol and 1,3-cyclohexadione or 5,5-dimethyl-1,3-cyclohexadione in the presence of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) under solvent-free conditions. The present methodology offers several advantages such as high yields, simple procedure, low cost, short reaction times, and mild conditions.

Keywords: xanthen, multi-component reaction, 2-naphthol, aldehydes, 12- tungstophosphoric acid, heteropoly acid, solvent-free conditions

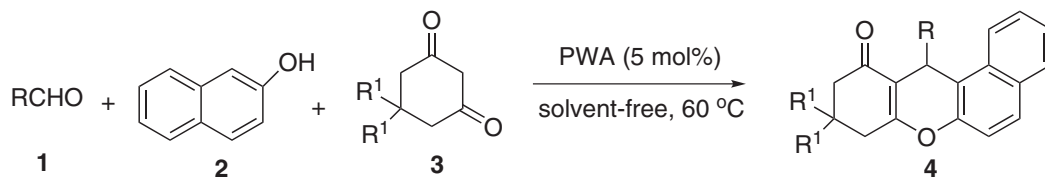
Introduction

Xanthenes and their derivatives have been received special attention due to their diverse array of biological activities such as anti-inflammatory, antibacterial and antiviral activities.¹⁻³ In addition to this, they can be employed as dyes,⁴ intracellular pH indicators,⁵ molecular probes in chemical biology,⁶ and fluorescent materials for visualization of biomolecules.⁷ In particular, the xanthen moiety is a core structure of a series of natural products with interesting biological and pharmacological activities.⁸⁻¹² Tetrahydroxanthenones are among the most important classes in the family of xanthenes due to their distinctive structure and great potential for further transformations.^{13,14} Consequently, the development of novel methods for the synthesis of these heterocyclic compounds has been received considerable interest in both organic and medicinal fields.¹⁵⁻¹⁸ The three-component reaction of aryl aldehydes, 2-naphthol and cyclic 1,3-dicarbonyl compounds has appeared as a novel alternative method for preparation of tetrahydroxanthenones.¹⁹ In this regard, $NaHSO_4 \cdot SiO_2$ was utilized to catalyze this reaction to afford 12-aryl or

12-alkyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one derivatives. However, this method needs to be further improved because some disadvantages such as relatively long reaction times and the use of harmful volatile organic solvent. Therefore, the development of efficient, mild and environmentally benign practical synthetic methods for accessing this type of heterocyclic compounds still remains a great need.

In recent years, the application of solid acids in organic synthesis is becoming an area of growing interest. Heteropoly acids (HPAs) are strong solid acids, harmless to the environment and highly stable toward humidity and have flexibility in modifying the acid strength.²⁰ In particular, the Keggin-type HPAs such as $H_3PW_{12}O_{40}$ (PWA), $H_3PMo_{12}O_{40}$ (PMoA) or $H_4SiW_{12}O_{40}$ (SiWA) are the most efficient catalysts for a variety of catalytic processes and has been used in various organic transformations.²¹ On the other hand, multi-component reactions (MCRs) offer significant advantages over conventional linear step synthesis, in terms of simple work-up and purification, and less time, energy and raw-material consuming. Thus, MCRs provide benefits in both economic and environment.²² In continuation of our ongoing project on the application of cheap and ecofriendly materials as catalysts for developing of new

*e-mail: zhanhui@mail.nankai.edu.cn



Scheme 1

synthetic methodology,²³ we herein describe a novel one-pot three-component synthesis of 12-aryl or 12-alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives by using PWA as a catalyst under solvent-free conditions (Scheme 1).

Results and Discussion

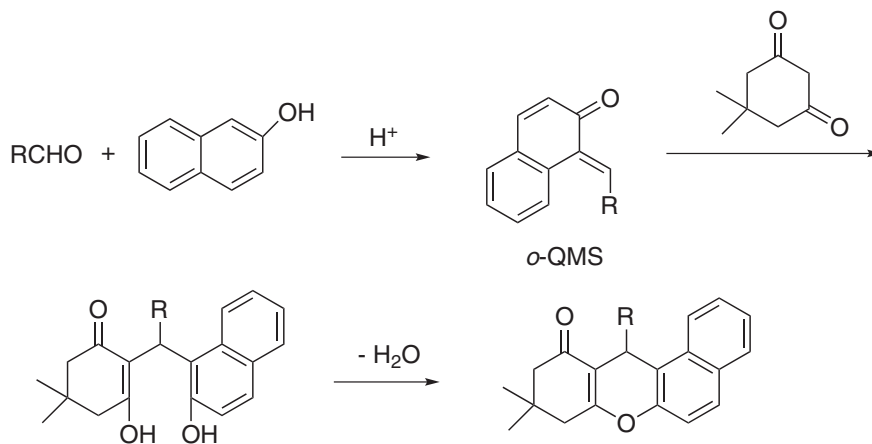
Initially, we investigated the activity of PWA in the condensation of 4-chlorobenzaldehyde (**1f**), 2-naphthol (**2**) and 5,5-dimethyl-1,3-cyclohexanedione. To our delight, the expected product 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*] xanthen-11-one (**4f**) was obtained in 92% isolated yield in 1 h in the presence of a catalytic amount of PWA (5 mol%) at 60 °C under solvent-free condition. Interestingly, under those conditions, the reaction could be scaled-up to a gram scale. No desired product was formed in the absence of PWA. The effect of other Keggin-type HPAs such as H₃PMo₁₂O₄₀ (PMoA) and H₄SiW₁₂O₄₀ (SiWA) for this transformation, was also studied and the results showed that PWA was the most effective catalyst. The desired product **4f** was obtained in 89% and 82% yields respectively in the presence of 5 mol% of PMoA and 5 mol% of SiWA.

To explore the scope and limitation of this reaction, we have extended the reaction of 2-naphthol and 5,5-dimethyl-1,3-cyclohexanedione with a variety of aromatic aldehydes under the optimized conditions. Gratifyingly, the corresponding 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one

derivatives could be obtained in high yields. It is worth noting that the electron property of the group on aromatic ring of aldehydes have a delicate effect on the yield of the product and reaction time. As shown in Table 1, aromatic aldehydes containing electron-withdrawing groups showed higher reactivity than those containing electron-donating groups. In addition, the use of 1,3-cyclohexanedione in place of 5,5-dimethyl-1,3-cyclohexanedione also gave similar results. Remarkably, aliphatic aldehydes also reacted with 2-naphthol and cyclic 1,3-dicarbonyl compounds under identical conditions and furnished the expected products in good yields. We have also tried to make benzoxanthen-11-ones using 1-naphthol or other phenol rather than 2-naphthol. Unfortunately, those substrates resulted only in traces of the corresponding products under the same conditions.

The catalyst could be recovered and reused without loss of catalytic activity. During the work-up of the reaction, PWA was recovered from the aqueous solution by evaporating to dryness, regenerated by heating at 150 °C. The recovered catalyst was applied to the preparation of **4f** and the yield was kept at 90-92% through three cycles of catalyst recycling.

According to the mechanism suggested by Das *et al.*¹⁹ we think that the reaction may proceed through *ortho*-quinone methides (*o*-QMs) formation from 2-naphthol with aldehydes. Subsequent addition of dimedone to the *o*-QMs forms intermediate **5**, followed by cyclization to give the corresponding products **4**, accompanied by loss of one H₂O (Scheme 2). During the reaction process, the hydrogen



Scheme 2

Table 1. Synthesis of 12-aryl or 12-alkyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one derivatives catalyzed by PWA^a

Entry	Aldehydes	R ¹	time / min	Yield / (%) ^b	mp / (°C)
a	Benzaldehyde	Me	70	86	149-150 ²⁴
b	4-Methylbenzaldehyde	Me	90	85	175-176 ²⁴
c	4-Methoxybenzaldehyde	Me	90	86	208-209 ²⁴
d	4-Hydroxybenzaldehyde	Me	90	81	150-151 ²⁴
e	4-Fluorobenzaldehyde	Me	65	94	185-186
f	4-Chlorobenzaldehyde	Me	60	92	187-188 ²⁴
g	4-Bromobenzaldehyde	Me	60	93	186-187 ²⁴
h	3,4-Dichlorobenzaldehyde	Me	60	92	181-182
i	4-Nitrobenzaldehyde	Me	50	90	174-175 ²⁴
j	2-Methyl-propionaldehyde	Me	40	82	oil ¹⁹
k	Butyraldehyde	Me	40	83	oil
l	Benzaldehyde	H	70	85	188-189 ²⁴
m	4-Methylbenzaldehyde	H	90	83	205-206 ²⁴
n	4-Methoxybenzaldehyde	H	90	81	181-182 ²⁴
o	4-Hydroxy-3-methoxybenzaldehyde	H	95	83	193-194 ²⁵
p	2-Chlorobenzaldehyde	H	75	90	245-246 ²⁵
q	3-Chlorobenzaldehyde	H	60	90	209-210 ²⁵
r	4-Chlorobenzaldehyde	H	60	91	205-206 ²⁴
s	4-Bromobenzaldehyde	H	60	92	208-209
t	4-Nitrobenzaldehyde	H	55	92	234-235 ²⁴
u	Butyraldehyde	H	45	81	
v	Cyclohexanecarbaldehyde	H	40	86	

^aReaction conditions: 2-naphthol (1 mmol), aldehydes (1.0 mmol), 1,3-cyclohexadione (1.2 mmol), PWA (0.05 mmol), reaction temperature: 60 °C.

^bIsolated yield.

ion is donated by the heteropoly acid. The hydrogen ion not only helps the dehydration but also benefits the enolization of dimedone to form the enolate intermediate. Only intermediate **5** was formed in the absence of a catalyst or in the presence of PWA at room temperature. These results lead us to assume that the step of cyclization is the rate-limiting step.

Conclusions

In conclusion, we have developed a simple, efficient and green process for the synthesis of 12-aryl or 12-alkyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one derivatives via three-component reaction catalyzed by 12-tungstophosphoric acid under solvent-free conditions. The simple experimental procedure, short reaction times, solvent-free conditions, and good yields are the advantage of the present method.

Experimental

General remarks

IR spectra were obtained by using a Shimadzu FTIR-8900 spectrometer. ¹H NMR spectra were determined on a

Varian 400 or a Bruker 400 spectrometer by using CDCl₃ as solvent and tetramethylsilane as internal standard. Elemental analyses were performed on a Vario EL III CHNOS elemental analyzer.

General procedure for synthesis of 12-aryl or 12-alkyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one derivatives

A mixture of 2-naphthol (1 mmol), aldehyde (1.0 mmol), cyclic 1,3-dicarbonyl compounds (1.2 mmol), PWA (0.05 mmol) was heated at 60 °C. The reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with ethyl acetate (2 × 10 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography using ethyl acetate-hexane (1:10) as eluent. The physical and spectral data of the known compounds were in agreement with those reported in literature. The spectral and analytical data for the new compounds were given below.

12-(4-Fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one (**4e**)

White solid, mp 185-186 °C; IR (KBr) ν_{\max} /cm⁻¹: 2935, 2881, 1651, 11618, 1595, 1508, 1465, 1398, 1375, 1226,

1184, 1014, 839; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.93 (s, 3H), 1.09 (s, 3H), 2.22 and 2.29 (AB system, *J* 16.4 Hz, 2H), 2.53 (s, 2H), 5.69 (s, 1H), 6.84 (t, *J* 8.4 Hz, 2H), 7.27-7.43 (m, 5H), 7.75 (t, *J* 8.0 Hz, 2H), 7.92 (d, *J* 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 27.0, 29.5, 32.1, 34.1, 41.5, 51.0, 114.0, 115.0, 115.2, 117.2, 117.5, 123.7, 125.0, 127.2, 128.5, 129.2, 130.0, 131.4, 131.5, 140.6, 147.8, 164.0, 197.0; Anal. Calc. for C₂₅H₂₁FO₂: C, 80.62; H, 5.68. Found: C, 80.45; H, 5.82.

*12-(3,4-Dichlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one (4h)*

White solid, mp 182-184 °C; IR (KBr) ν_{max}/cm⁻¹: 2962, 2891, 1649, 1637, 1618, 1597, 1398, 1385, 1373, 1234, 1002, 819; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.94 (s, 3H), 1.09 (s, 3H), 2.22 and 2.28 (AB system, *J* 16.0 Hz, 2H), 2.53 (s, 2H), 5.66 (s, 1H), 7.18-7.22 (m, 2H), 7.29-7.43 (m, 4H), 7.73-7.77 (m, 2H), 7.88 (d, *J* 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 27.2, 29.2, 32.4, 34.4, 41.4, 50.8, 113.4, 116.4, 117.2, 123.2, 125.2, 127.4, 128.0, 129.5, 130.1, 130.3, 131.0, 131.5, 132.2, 145.0, 147.8, 164.4, 196.8; Anal. Calc. for C₂₅H₂₀Cl₂O₂: C, 70.93; H, 4.76. Found: C, 71.18; H, 4.90.

*9,9-Dimethyl-12-propyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4k)*

Colorless liquid; IR (neat) ν_{max}/cm⁻¹: 3068, 2956, 2931, 2869, 1651, 1618, 1596, 1515, 1464, 1394, 1280, 1222, 1178, 1146, 1028, 813; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.73 (t, *J* 7.2 Hz, 3H), 0.86-0.97 (m, 2H), 1.13 (s, 3H), 1.19 (s, 3H), 1.75-1.80 (m, 2H), 2.36 and 2.38 (AB system, *J* 16.4 Hz, 2H), 2.51 and 2.53 (AB system, *J* 17.6 Hz, 2H), 4.74 (t, *J* 4.4 Hz, 1H), 7.20 (d, *J* 8.8 Hz, 1H), 7.43 (d, *J* 7.6 Hz, 1H), 7.53 (d, *J* 7.6 Hz, 1H), 7.69 (d, *J* 8.8 Hz, 1H), 7.81 (d, *J* 8.8 Hz, 1H), 8.10 (d, *J* 8.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 14.2, 18.4, 27.3, 28.0, 29.7, 32.1, 37.5, 41.4, 51.0, 112.9, 116.8, 118.4, 123.3, 124.8, 128.0, 128.6, 131.2, 131.5, 148.5, 166.2, 197.7; Anal. Calc. for C₂₂H₂₄O₂: C, 82.46; H, 7.55. Found: C, 82.62; H, 7.38.

*12-(4-Bromophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4s)*

White solid, mp 209-210 °C; IR (KBr) ν_{max}/cm⁻¹: 2941, 1651, 1616, 1596, 1485, 1400, 1229, 1190, 1172, 1130, 1010, 833; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.90-2.05 (m, 2H), 2.28-2.41 (m, 2H), 2.53-2.73 (m, 2H), 5.69 (s, 1H), 7.18-7.24 (m, 2H), 7.28-7.37 (m, 4H), 7.40 (t, *J* 8.0 Hz, 1H), 7.74-7.77 (m, 2H), 7.86 (d, *J* 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 20.4, 27.2, 34.2, 37.0, 115.0, 116.8, 117.0, 120.2, 123.5, 125.0, 127.1, 128.5, 129.0, 130.4, 131.2, 131.5, 144.0, 147.8, 164.2, 165.8, 197.0;

Anal. Calc. for C₂₃H₁₇BrO₂: C, 68.16; H, 4.23. Found: C, 68.31; H, 4.05.

*12-Propyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4u)*

White solid, mp 85-86 °C; IR (KBr) ν_{max}/cm⁻¹: 3068, 2956, 2929, 2869, 1635, 1622, 1591, 1515, 1458, 1434, 1400, 1244, 1076, 960, 814; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.75 (t, *J* 7.2 Hz, 3H), 0.87-0.98 (m, 2H), 1.17-1.28 (m, 2H), 1.70-1.81 (m, 2H), 2.02-2.16 (m, 2H), 2.37-2.75 (m, 2H), 4.77 (t, *J* 4.8 Hz, 1H), 7.21 (d, *J* 8.8 Hz, 1H), 7.43 (d, *J* 7.6 Hz, 1H), 7.53 (d, *J* 7.6 Hz, 1H), 7.68 (d, *J* 8.8 Hz, 1H), 7.81 (d, *J* 8.8 Hz, 1H), 8.10 (d, *J* 8.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 14.2, 18.4, 29.8, 31.2, 38.2, 41.6, 50.8, 112.1, 116.7, 117.6, 122.5, 124.1, 128.2, 131.0, 131.4, 145.0, 165.8, 197.5; Anal. Calc. for C₂₀H₂₀O₂: C, 82.16; H, 6.89. Found: C, 81.98; H, 7.02.

*12-Cyclohexyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4v)*

White solid, mp 186-187 °C; IR (KBr) ν_{max}/cm⁻¹: 2931, 1643, 1595, 1448, 1361, 1234, 1188, 1134, 993, 948, 833; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.96-1.11 (m, 6H), 1.26-1.80 (m, 5H), 2.09-2.15 (m, 2H), 2.31-2.40 (m, 2H), 2.56-2.77 (m, 2H), 4.68 (d, *J* 3.6 Hz, 1H), 7.24 (d, *J* 8.8 Hz, 1H), 7.44 (d, *J* 7.6 Hz, 1H), 7.55 (d, *J* 7.6 Hz, 1H), 7.71 (d, *J* 8.8 Hz, 1H), 7.83 (d, *J* 8.0 Hz, 1H), 8.11 (d, *J* 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 20.3, 26.3, 27.9, 28.5, 31.1, 32.6, 37.2, 45.5, 113.3, 116.7, 118.9, 123.7, 124.7, 126.6, 127.8, 128.5, 131.5, 131.6, 149.1, 168.5, 197.7; Anal. Calc. for C₂₅H₂₈O₂: C, 83.29; H, 7.83. Found: C, 83.51; H, 7.65.

Acknowledgments

We are grateful for financial support from National Natural Science Foundation of China (20872025), Nature Science Foundation of Hebei Province (B2008000149) and Natural Science Foundation of Hebei Education Department (2006318).

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br>, as PDF file.

References

- Chatterjee, S.; Iqbal, M.; Kauer, J. C.; Mallamo, J. P.; Senadhi, S.; Mallya, S.; Bozyczko-Coyne, D.; Siman, R.; *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1619.

2. Vieira, E.; Huwyler, J.; Jolidon, S.; Knofach, F.; Mutel, V.; Wichmann, J.; *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4628.
3. Hafez, H. N.; Hegab, M. I.; Ahmed-Farag, I. S.; El-Gazzar, A. B. A.; *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4538.
4. Sekar, N.; *Colourage* **1999**, *46*, 43.
5. Liu, J.; Diwu, Z.; Leung, W.-Y.; *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2903.
6. Kikuchi, K.; Komatsu, K.; Nagano, T.; *Curr. Opin. Chem. Biol.* **2004**, *8*, 182.
7. Sarma, R. J.; Baruah, J. B.; *Dyes Pigm.* **2005**, *64*, 91.
8. Itoh, T.; Ohguchi, K.; Inuma, M.; Nozawa, Y.; Akao, Y.; *Bioorg. Med. Chem.* **2008**, *16*, 4500.
9. Isakovic, A.; Jankovic, T.; Harhaji, L.; Kostic-Rajacic, S.; Nikolic, Z.; Vajs, V.; Trajkovic, V.; *Bioorg. Med. Chem.* **2008**, *16*, 5683.
10. Seo, E. J.; Curtis-Long, M. J.; Lee, B. W.; Kim, H. Y.; Ryu, Y. B.; Jeong, T.-S.; Lee, W. S.; Park, K. H.; *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6421.
11. Masullo, M.; Bassarello, C.; Suzuki, H.; Pizza, C.; Piacente, S.; *J. Agric. Food Chem.* **2008**, *56*, 5205.
12. Urbain, A.; Marston, A.; Grilo, L. S.; Bravo, J.; Purev, O.; Purevsuren, B.; Batsuren, D.; Reist, M.; Carrupt, P.-A.; Hostettmann, K.; *J. Nat. Prod.* **2008**, *71*, 895.
13. Lesch, B.; Bräse, S.; *Angew. Chem., Int. Ed.* **2004**, *43*, 115.
14. Shi, Y.-L.; Shi, M.; *Synlett* **2005**, 262.
15. Zhang, Z.-H.; Tao, X.-Y.; *Aust. J. Chem.* **2008**, *61*, 77.
16. Dabiri, M.; Baghbanzadeh, M.; Nikcheh, M. S.; Arzroomchilar, E.; *Bioorg. Med. Chem. Lett.* **2008**, *18*, 436.
17. Kamino, S.; Ichikawa, H.; Wada, S.-I.; Horio, Y.; Usami, Y.; Yamaguchi, T.; Koda, T.; Harada, A.; Shimanuki, K.; Arimoto, M.; Doi, M.; Fujita, Y.; *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4380.
18. Shaterian, H. R.; Ghashang, M.; *J. Braz. Chem. Soc.* **2008**, *19*, 1053.
19. Das, B.; Laxminarayana, K.; Krishnaiah, M.; Srinivas, Y.; *Synlett* **2007**, 3107.
20. Misono, M.; Ono, I.; Koyano, G.; Aoshima, A.; *Pure Appl. Chem.* **2000**, *72*, 1305; Kozhevnikov, I. V.; *Chem. Rev.* **1998**, *98*, 171.
21. Heydari, A.; Khaksar, S.; Sheykhan, M.; Tajbakhsh, M.; *J. Mol. Catal. A: Chem.* **2008**, *287*, 5; Yadav, J. S.; Reddy, B. V. S.; Reddy, A. S.; *J. Mol. Catal. A: Chem.* **2008**, *280*, 219; Yadav, J. S.; Reddy, B. V. S.; Aravind, S.; Kumar, G. G. K. S. N.; Madhavi, C.; Kunwar, A. C.; *Tetrahedron* **2008**, *64*, 3025; Yadav, J. S.; Reddy, B. V. S.; Pandurangam, T.; Rao, K. V. R.; Praneeth, K.; Kumar, G. G. K. S. N.; Madhavi, C.; Kunwar, A. C.; *Tetrahedron Lett.* **2008**, *49*, 4296; Wang, G.-W.; Shen, Y.-B.; Wu, X.-L.; Wang, L.; *Tetrahedron Lett.* **2008**, *49*, 5090; Heydaria, A.; Khaksar, S.; Sheykhan, M.; Tajbakhsh, M.; *J. Mol. Catal. A: Chem.* **2008**, *287*, 5; Wang, G.-W.; Shen, Y.-B.; Wu, X.-L.; *Eur. J. Org. Chem.* **2008**, 4367; Wang, R.; Huang, T.; Shi, L.; Li, B.; Lu, X.; *Synlett* **2007**, 2197; Kadam, S. T.; Kim S. S.; *Synthesis* **2008**, 267; Yadav, J. S.; Reddy, B. V. S.; Kumar, G. G. K. S. N.; Aravind, S.; *Synthesis* **2008**, 395; Chen, X.; She, J.; Shang, Z.; Wu, J.; Wu, H.; Zhang, P.; *Synthesis* **2008**, 3478; Chen, X.; She, J.; Shang, Z.; Wu, J.; Zhang, P.; *Synthesis* **2008**, 3931; da Silva Rocha, K. A.; Hoehne, J. L.; Gusevskaya, E. V.; *Chem. Eur. J.* **2008**, *14*, 6166.
22. Russowsky, D.; Lopes, F. A.; da Silva, V. S. S.; Canto, K. F. S.; D'Oca, M. G. M.; Godoi, M. N.; *J. Braz. Chem. Soc.* **2004**, *15*, 165; Vieira, Y. W.; Nakamura, J.; Finelli, F. G.; Brocksom, U.; *J. Braz. Chem. Soc.* **2007**, *18*, 448; Kazemizadeh, A. R.; Ramazani, A.; *J. Braz. Chem. Soc.* **2009**, *20*, 309.
23. Zhang, Z.-H.; Hu, J.-Y.; *J. Braz. Chem. Soc.* **2006**, *17*, 1447; Mo, L.-P.; Ma, Z.-C.; Zhang, Z.-H.; *Synth. Commun.* **2005**, *35*, 1997; Zhang, Z.-H.; Lin, J.; *Synth. Commun.* **2007**, *37*, 209; Zhang, Z.-H.; Li, J.-J.; Gao, Y.-Z.; Liu, Y.-H.; *J. Heterocycl. Chem.* **2007**, *44*, 1509; Zhang, Z.-H.; Li, T.-S.; Li, J.-J.; *Monatsh. Chem.* **2007**, *138*, 89; Liu, Y.-H.; Liu, Q.-S.; Zhang, Z.-H.; *J. Mol. Catal. A: Chem.* **2008**, *296*, 42; Liu, Y.-H.; Zhang, Z.-H.; Li, T.-S.; *Synthesis* **2008**, 3314; Lü, H.-Y.; Li, J.-J.; Zhang, Z.-H.; *Appl. Organomet. Chem.* **2009**, *23*, 165; Liu, Y.-H.; Liu, Q.-S.; Zhang, Z.-H.; *Tetrahedron Lett.* **2009**, *50*, 916.
24. Wang, R.-Z.; Zhang, L.-F.; Cui, Z.-S.; *Synth. Commun.* **2009**, *39*, 2101.
25. von Heinrich, H.; Manfred, S.; *Liebigs Ann. Chem.* **1941**, *641*, 78.

Received: January 8, 2009

Web Release Date: November 12, 2009

Synthesis 12-Aryl or 12-Alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one Derivatives Catalyzed by Dodecatungstophosphoric Acid

Hong-Juan Wang, Xiao-Qian Ren, Yan-Yan Zhang and Zhan-Hui Zhang*

The College of Chemistry & Material Science, Hebei Normal University,
Shijiazhuang 050016, P. R. China

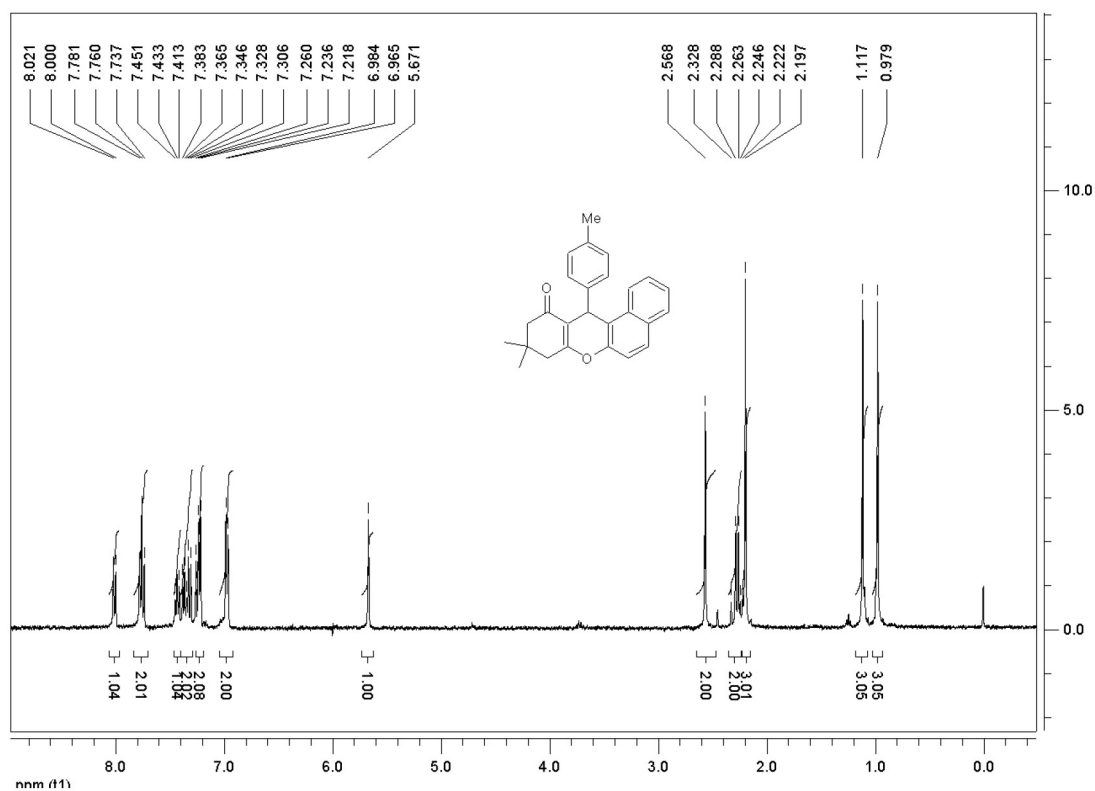
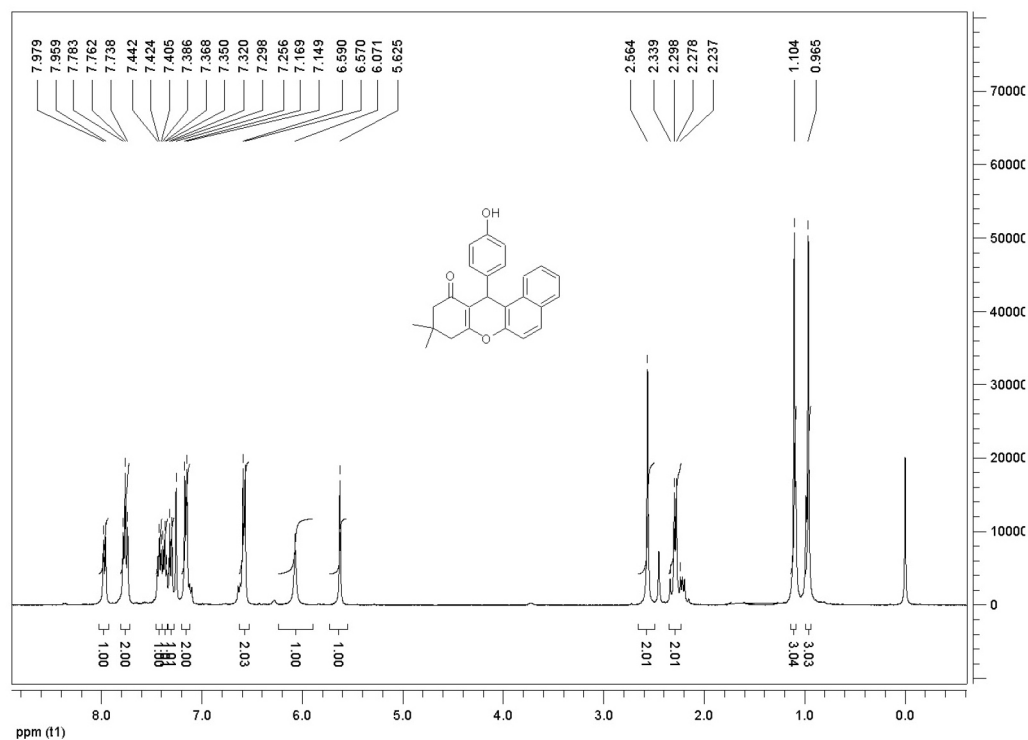
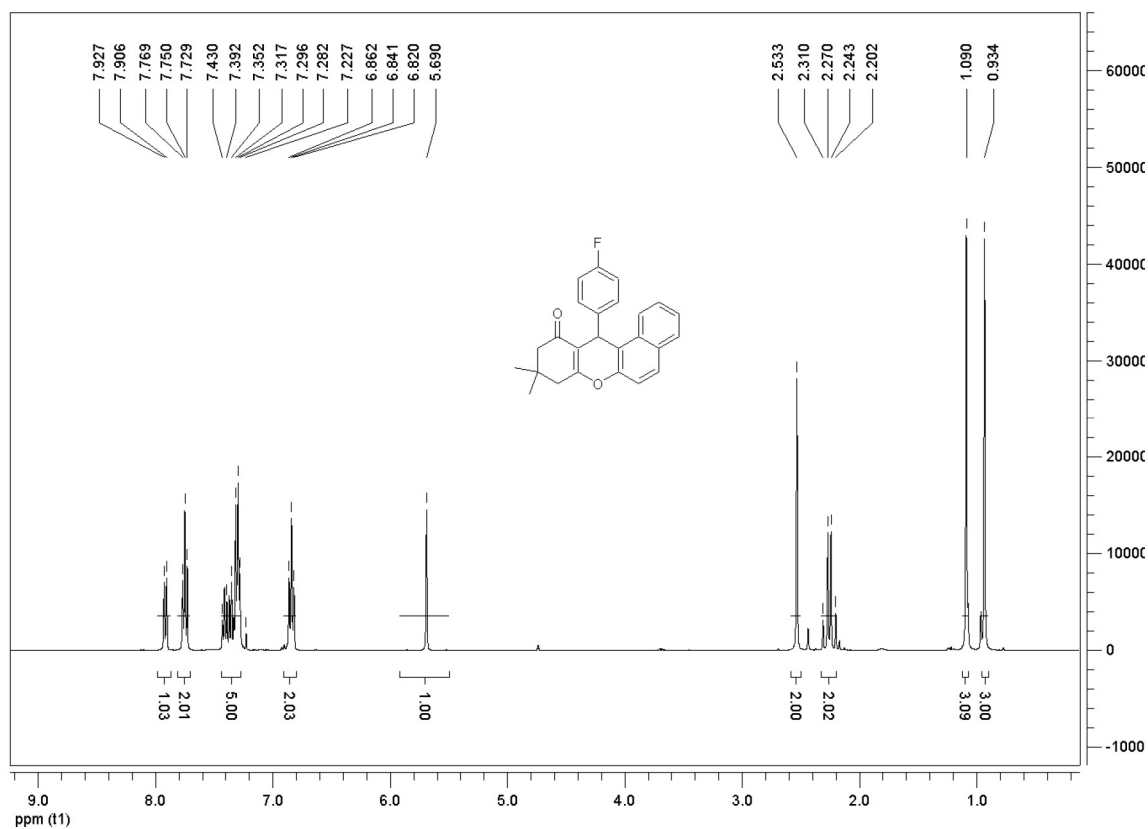
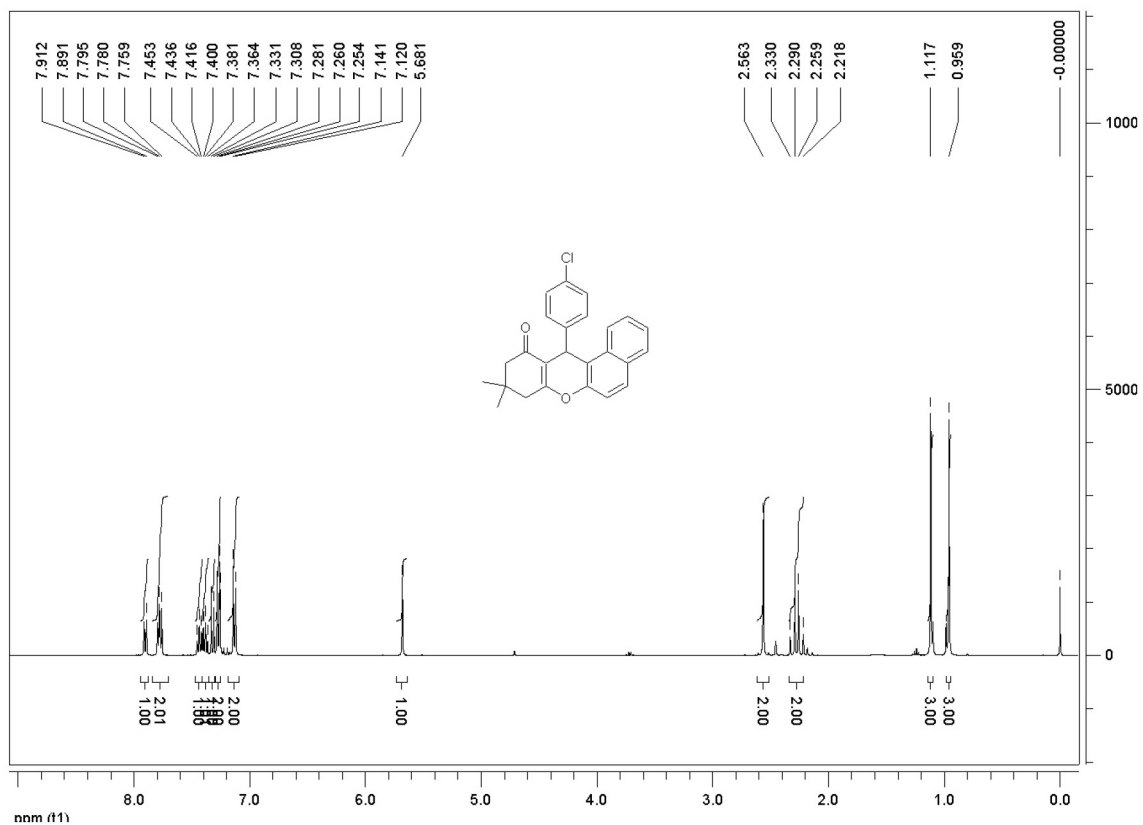
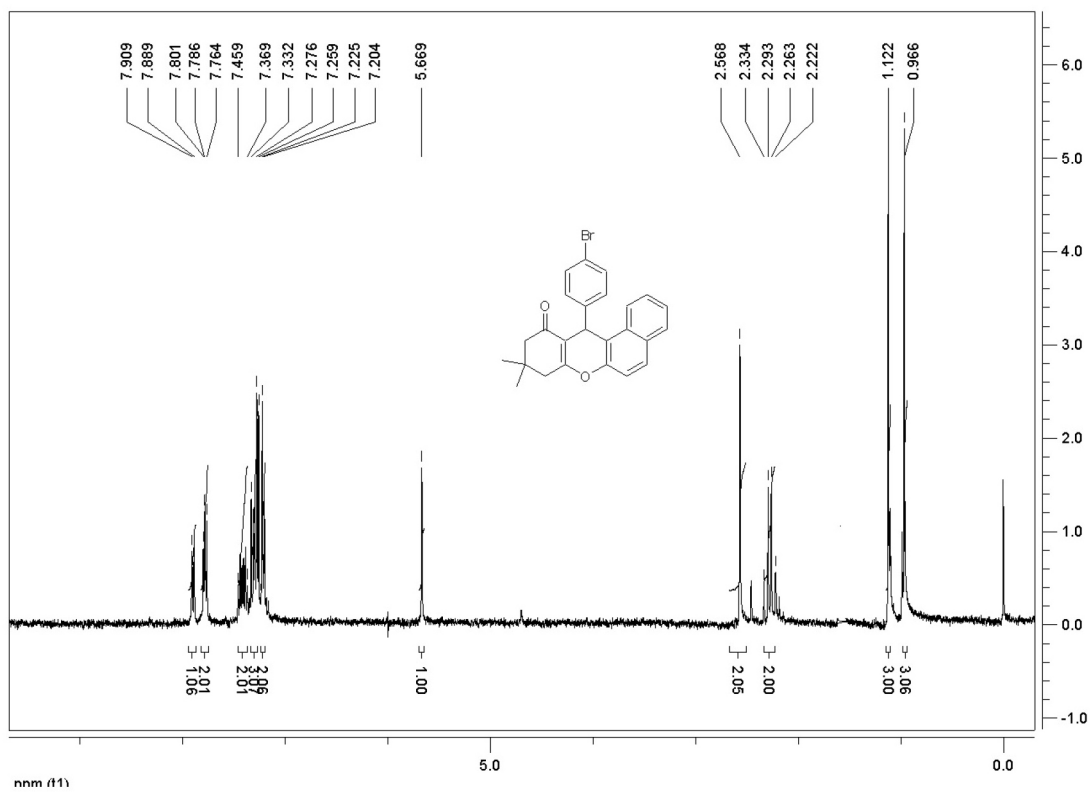


Figure S1. ¹H NMR of 4b (400 MHz, CDCl₃).

Figure S2. ^1H NMR of **4d** (400 MHz, CDCl_3).Figure S3. ^1H NMR of **4e** (400 MHz, CDCl_3).

Figure S4. ^1H NMR of **4f** (400 MHz, CDCl_3).Figure S5. ^1H NMR of **4g** (400 MHz, CDCl_3).

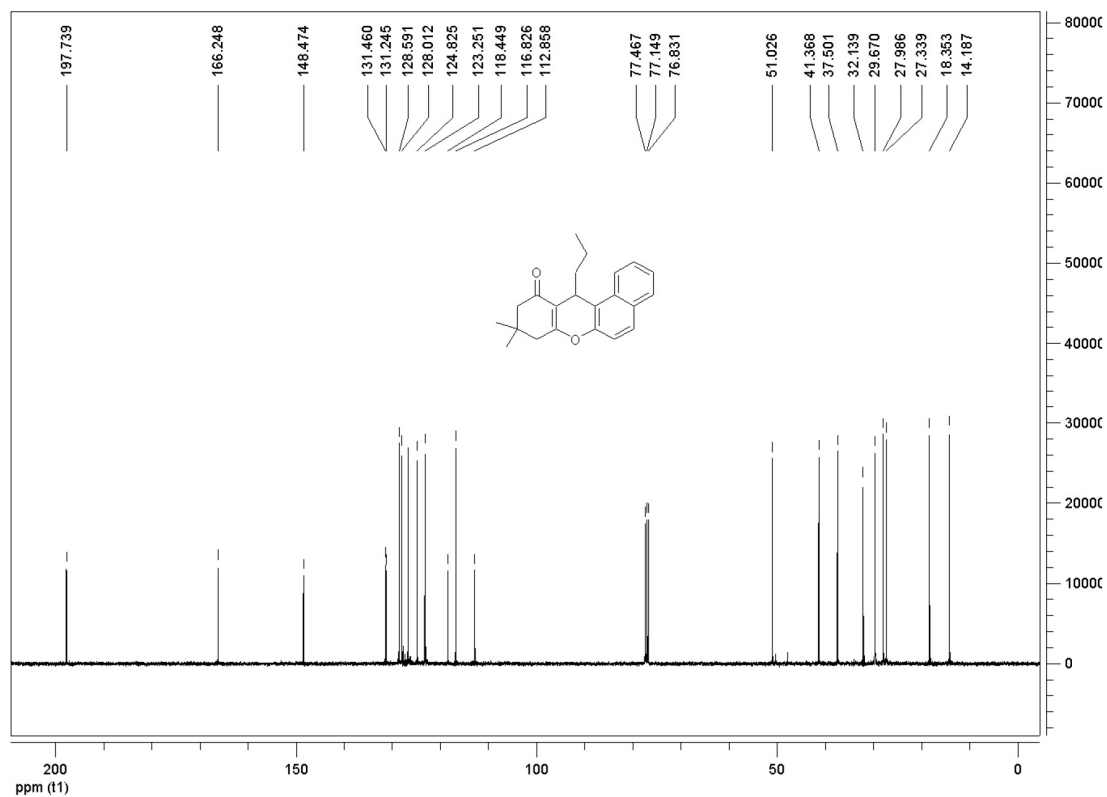


Figure S12. ^{13}C NMR of **4u** (100 MHz, CDCl_3).

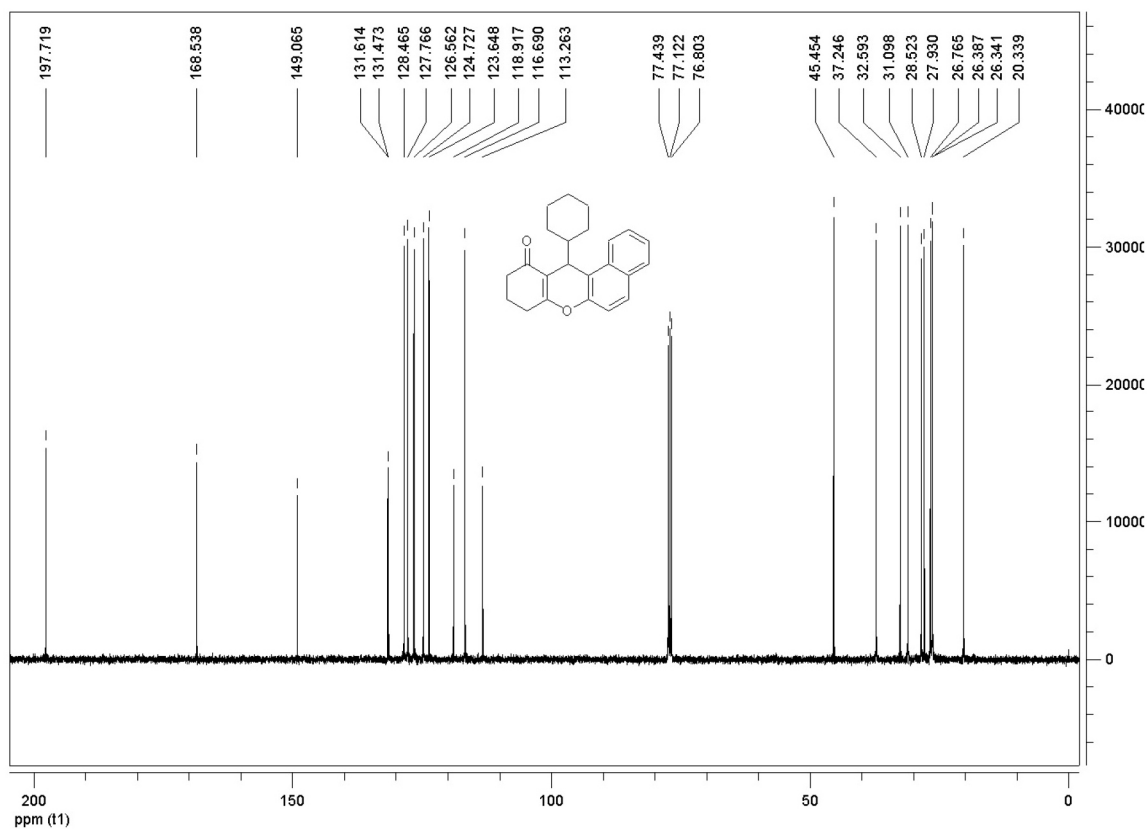


Figure S13. ^{13}C NMR of **4v** (100 MHz, CDCl_3).