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# A ONE-POT FOUR-COMPONENT PROCEDURE FOR THE SYNTHESIS OF DISPIRO[TETRAHYDROQUINOLINE-BIS(2,2-DIMETHYL-1,3-DIOXANE-4,6-DIONE)] DERIVATIVES

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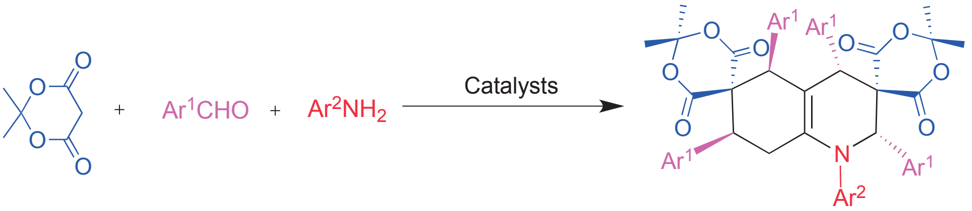
**Abstract –** A simple and efficient procedure for the diastereoselective synthesis of dispiro[tetrahydroquinoline-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] derivatives through one-pot four-component reaction of aromatic aldehydes, 2,2-dimethyl-1,3-dioxane-4,6-dione, arylamines and acetone in the presence of potassium dihydrogen phosphate (KDP) is described. The procedure involves initial Knoevenagel reaction, followed by Diels-Alder, Michael additon and intramolecular reactions. The main advantages of the protocol are the high isolated yields, broad substrate scope, mild conditions, and easy operation.

## INTRODUCTION

Hydroquinoline ring compounds made up of an important structural unit in a many naturally occurring alkaloids and therapeutics,[1-3] have exhibited an amazingly wide spectrum of biological properties including significant pharmacological activities, dopamine $D_2$-receptor, agonist to serotonin, and inhibitory activity against acetylcholinesterase.[4-8] Hydroquinoline ring compounds with Meldrum's acid structure are attractive building blocks in the synthesis of natural products and in medicinal chemistry and are also the starting materials for the synthesis of exotic amino acids that are used to modify the physical properties and biological activities of peptides, peptidomimetics, and proteins.[9-12] Therefore, the development of a simple and efficient methodology for the synthesis of hydroquinoline ring compounds has drawn great attention of synthetic as well as medicinal chemist.

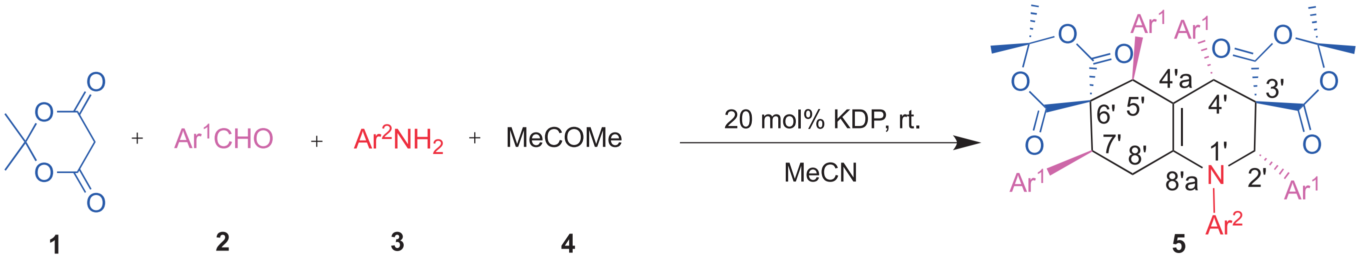
The three-component reaction procedure for the synthesis of dispiro[tetrahydroquinoline-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] derivatives has been reported in the literature. It involved the use of organic Brønsted acids or ionic liquids such as AcOH,[13] benzoic acid,[14] $Cl_3CCO_2H$,[15] citric acid,[16] salicylic acid,[17] phthalic acid,[18] and 4-(sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate[19] (Scheme 1) from low yields, long reaction times, high catalyst loading, environmentally unfavorable solvents, and tedious work-up, to waste production. Thus, an efficient, and enviromently friendly method using ecnomical catalyst is actively desirable.



**Catalysts**: AcOH, benzoic acid, $Cl_3CCO_2H$, citric acid, salicylic acid, phthalic acid, 4-(sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate

**Scheme 1.** Reported systhesis of dispiro[tetrahydroquinoline-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] derivatives

Multicomponent reactions with the properties of easy operation, high efficiency, high selectivity and atomic economy have been widely used in the fields of the total synthesis of natural products, heterocyclic compounds and combinatorial chemistry.[20-22] Our group has successfully prepared many dispiro compounds containing 1,3-dioxane-4,6-dione structure by Yonemitsu reaction,[23] and Biginelli-like reaction.[24,25] In continuation of our efforts toward the development of novel dispiro compounds, herein we would explore the synthesis of dispiro[tetrahydroquinoline-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] derivatives through one-pot four-component reaction of aromatic aldehydes, 2,2-dimethyl-1,3-dioxane-4,6-dione, arylamines and acetone in the presence of potassium dihydrogen phosphate (KDP)[25] as an inorganic acid salt catalyst(Scheme 2).

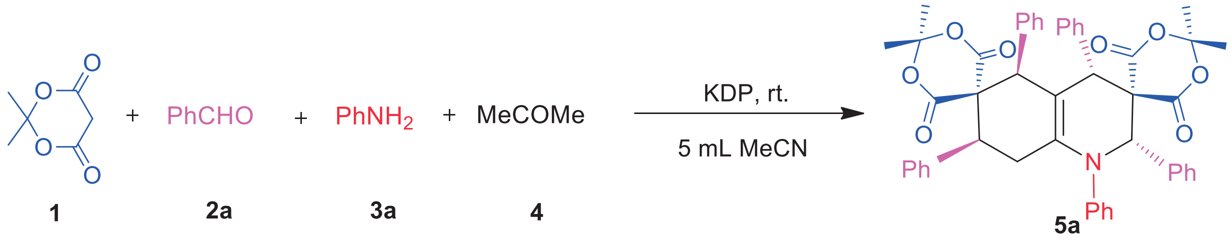


**Scheme 2.** The four-component synthesis of dispiro[tetrahydroquinoline-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] derivatives

## RESULTS AND DISCUSSION

At the outset of the experiment, the one-pot four-component reaction between Meldrum's acid, benzaldehyde, aniline and acetone was chosen a pattern to optimize the reaction conditions under different solvents in the presence of potassium dihydrogen phosphate (KDP). Different solvents including water, ethanol, ethyl acetate, acetone and acetonitrile were examined (Table 1, Entries 1-5). Results show that the yield reached to 86% effectively in MeCN (Table 1, entry 5). The reaction was just proceeded in the presence of different catalysts (Table 1, Entries 7-9), the product in 30% yield was only detected in the absence of catalysts. However, it was found that the best yield was obtained in the presence of KDP (Table 1, entry 5). Encouraged by this lead results, the reaction model at different concentrations of KDP which resulted in different yields was investigated. Finally, we determined 20 mol% KDP was sufficient to push the reaction forward and higher amounts of the catalyst did not improve the results to any greater extent. We also investigated the effect of reaction time on the reaction and found that 20 h gave the best result (Table 1, entry 5). Optimal results for the reaction conditions of 2,2-dimethyl-1,3-dioxane-4,6-dione (**1**, 2 mmol), benzaldehyde (**2a**, 4 mmol), aniline (**3a**, 1 mmol) and acetone (**4**, 2 mmol) furnished **5a** in 86% yield.

**Table 1.** Optimization of reaction conditions for the synthesis of **5a**[a]



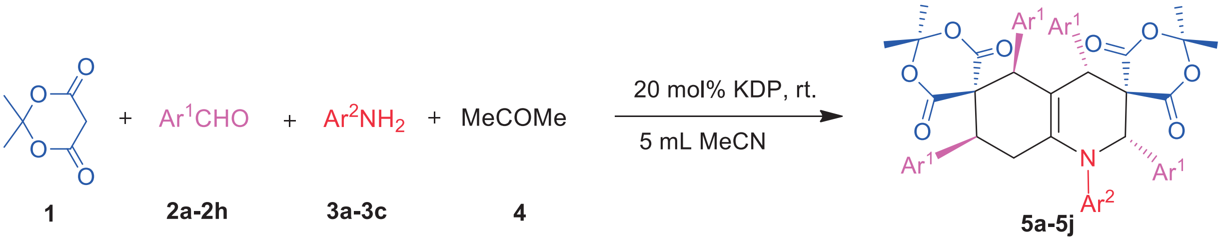
| Entry | Solvents/5 mL | Catalysts/mol% | Time(h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $H_2O$ | KDP/20 | 32 | 42 |
| 2 | EtOH | KDP/20 | 32 | 35 |
| 3 | $MeCO_2Et$ | KDP/20 | 32 | 56 |
| 4 | MeCOMe | KDP/20 | 24 | 64 |
| 5 | MeCN | KDP/20 | 20 | 86 |
| 6 | MeCN | none | 24 | 30 |
| 7 | MeCN | iodine/20 | 24 | 65 |
| 8 | MeCN | $CCl_3CO_2H$/20 | 24 | 75 |
| 9 | MeCN | malonic acid/20 | 24 | 76 |
| 10 | MeCN | KDP/15 | 20 | 70 |
| 11 | MeCN | KDP/25 | 20 | 86 |
| 12 | MeCN | KDP/20 | 24 | 86 |
| 13 | MeCN | KDP/20 | 12 | 80 |

[a]Reaction conditions: 2,2-dimethyl-1,3-dioxane-4,6-dione (**1**, 2 mmol), benzaldehyde (**2a**, 4 mmol), aniline (**3a**, 1 mmol) and acetone (**4**, 2 mmol) in MeCN (5 mL) at room temperature; [b]Isolated yield.

Under optimized conditions, a number of substrates including different aldehydes and arylamines have been investigated. Aromatic aldehydes bearing either electron-withdrawing functional groups, such as

$NO_2$ and F, Cl substituents, or electron-donating groups, such as Me and MeO, can be tolerated with good yields. The good results were also obtained by arylamines with either electron-withdrawing such as F or electron-donating groups such as MeO substituents. All the results are summaried in Table 2.

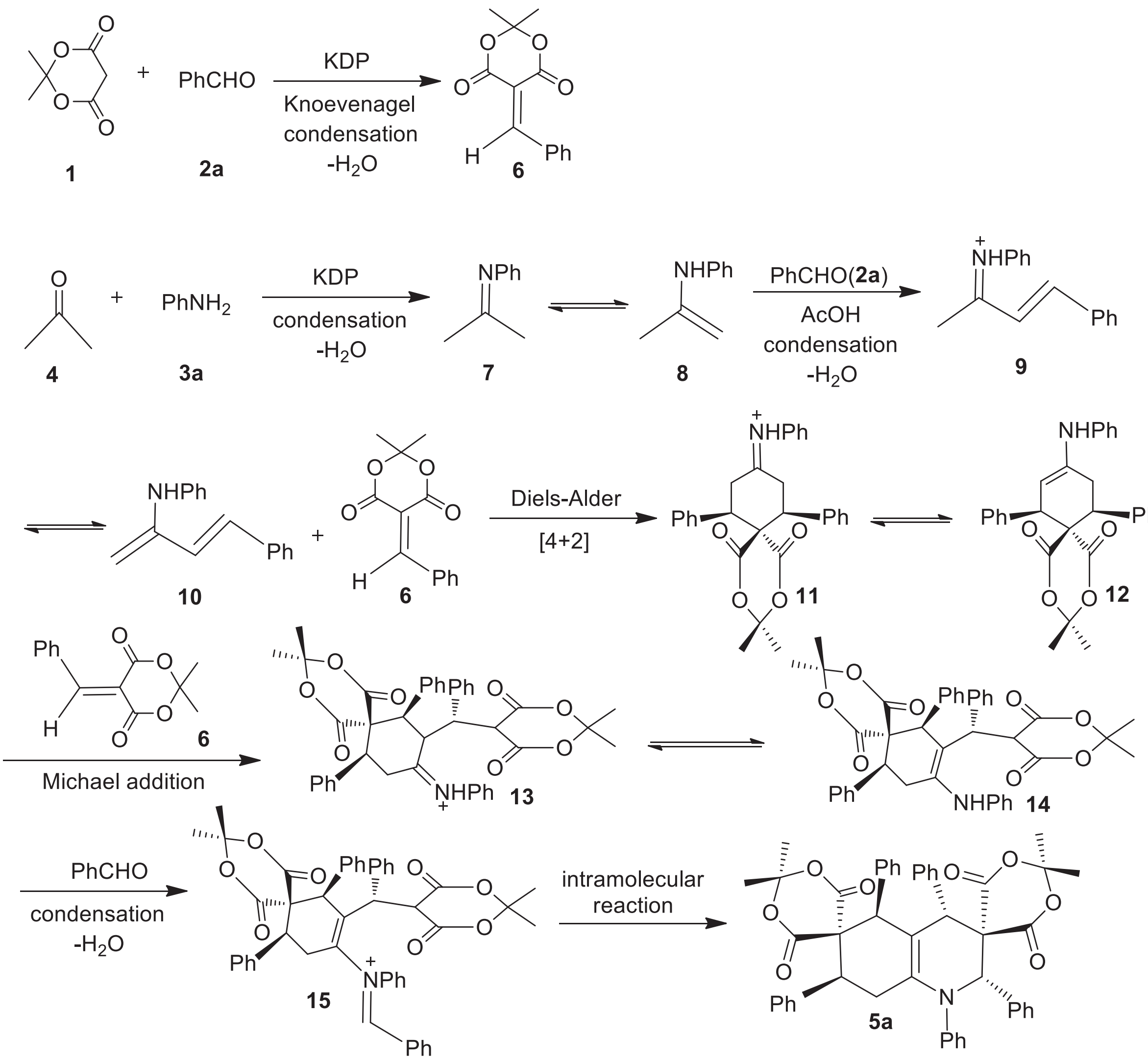
**Table 2.** Synthesis of dispiro[tetrahydroquinoline-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] derivatives[a]



| Entry | Ar$^1$ | Ar$^2$ | Time(h) | Product | Yields (%)[b] |
|---|---|---|---|---|---|
| 1 | **2a** ($C_6H_5$) | **3a** ($C_6H_5$) | 20 | **5a** | 86 |
| 2 | **2b** (4-$FC_6H_4$) | **3a** ($C_6H_5$) | 12 | **5b** | 72 |
| 3 | **2c** (4-$ClC_6H_4$) | **3a** ($C_6H_5$) | 20 | **5c** | 81 |
| 4 | **2d** (4-$MeC_6H_4$) | **3a** ($C_6H_5$) | 24 | **5d** | 82 |
| 5 | **2e** (4-$MeOC_6H_4$) | **3a** ($C_6H_5$) | 32 | **5e** | 65 |
| 6 | **2f** (4-$NO_2C_6H_4$) | **3a** ($C_6H_5$) | 12 | **5f** | 86 |
| 7 | **2g** (2-$MeC_6H_5$) | **3a** ($C_6H_4$) | 24 | **5g** | 63 |
| 8 | **2h** (2-$ClC_6H_5$) | **3a** ($C_6H_4$) | 24 | **5h** | 71 |
| 9 | **2a** ($C_6H_4$) | **3b** (4-$MeOC_6H_4$) | 32 | **5i** | 80 |
| 10 | **2a** ($C_6H_4$) | **3c** (4-$FC_6H_4$) | 20 | **5j** | 74 |

[a] Reaction conditions: 2,2-dimethyl-1,3-dioxane-4,6-dione (**1**, 2 mmol), different aldehydes (**2**, 4 mmol), arylamines (**3**, 1 mmol), and acetone (**4**, 2 mmol) in MeCN (5 mL) at room temperature; [b] Isolated yield.

A plausible mechanism for the combination reaction of Knoevengel condensation, Diels-Alder, Michael addition and intramolecular synthesis of 1',2',4',5',7'-pentaphenyl-*1'H*-dispiro[1',5',7',8'-tetrahydroquinoline-5,3':6',5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)](**5a**)[13,26] is depicted in Scheme 3. In this reaction, first the Knoevenagel condensation of Meldrum's acid and benzaldehyde was carried out to generate benzylidene Meldrum's acid **6** in the presence of KDP. Acetone undergoes condensation with aniline to give imine **7** and tautomerized to enamine **8**. **8** reacts with aldehyde to form reactive 2-amino-1,3-butadiene **10**. Dienamine acts as an activated 1,3-diene, and a concerted [4 + 2] cycloaddition would take place with benzylidene Meldrum's acid **6** as dienophiles (Diels-Alder), to furnish enamine **12**. The reaction of **12** with benzylidene Meldrum's acid generated **14** by Michael addition reaction, and **14** could form an iminium salt with the aldehydes, which then undergoes intramolecular reaction leading to **5a**.



**Scheme 3.** Proposed mechanism for the formation of **5a**

In summary, a four-component synthetic procedure of dispiro[tetrahydroquinoline-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] derivatives catalyzed by potassium dihydrogen phosphate (KDP) in MeCN, has been developed. The operation and work-up procedures were very simple and no column chrommatography purification was also needed. It provides an effective method for the synthesis of hydroquinoline ring compounds with Meldrum's acid structure.

## EXPERIMENTAL

2,2-Dimethyl-1,3-dioxane-4,6-dione was prepared according to ref.[27] The other chemicals were purchased from Aladdin, Aldrich and Fluka Chemical Companies and without further purification. Melting points were measured on XT-4 digital micro melting point apparatus and are uncorrected. $^1$H NMR spectra were recorded on a BRUKER AVANCE 400 MHz spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. $^{13}$C NMR data were collected on a BRUKER AVANCE 100 MHz instrument with

$CDCl_3$ as the solvent and TMS as the internal standard. The analytical MS of the compounds was performed on Agilent LC-MSD Trap VL Apparatus.

**General procedure of the preparation of products 5a, 5b, 5c, 5d, 5e, 5f, 5g, 5h, 5i, and 5j.**

**1',2',4',5',7'-Pentaphenyl-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5'']bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5a):** To a 25 mL tube equiped with a stirring bar were added MeCN (5 mL), 2,2-dimethyl-1,3-dioxane-4,6-dione (**1**, 2 mmol), benzaldehyde (**2a**, 4 mmol), aniline (**3a**, 1 mmol), acetone (**4**, 2 mmol) and 20 mol% KDP. After the reaction was stirred vigorously for 20 h at room temperature, MeCN was recycled by filtration. The residue was washed with water. Then, the residue was purified by recrytallization from absolute EtOH to afford the pure product **5a**; a white solid; mp 246-248 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.34 (3H, s, $CH_3$), 0.36 (s, 3H, $CH_3$), 0.59 (s, 3H, $CH_3$), 0.61 (s, 3H, $CH_3$), 2.56 (dd, *J*=17.6, 6.0 Hz, 1H, H'-8'), 2.61-2.69 (m, 1H, H''-8'), 4.02 (dd, *J*=12.0, 6.0 Hz, 1H, H-7'), 4.64 (s, 1H, H-4'), 4.66 (s, 1H, H-5'), 5.25 (s, 1H, H-2'), 6.03 (d, *J*=7.6 Hz, 1H, 1CH, HAr), 6.06 (d, *J*=7.6 Hz, 1H, 1CH, HAr), 6.69 (d, *J*=7.6 Hz, 1H, 1CH, HAr), 6.73 (d, *J*=8.0 Hz, 1H, 1CH, HAr), 6.98-7.57 (m, 21H, 21CH, HAr). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 27.9 ($CH_3$), 28.2 ($CH_3$), 28.4 ($CH_3$), 28.5 ($CH_3$), 32.7 (C-8'), 47.6 (C-4'), 50.8 (C-5'), 53.1 (C-7'), 61.5 (C-3'), 61.7 (C-6'), 70.0 (C-2'), 102.1 (C-4'a), 105.3 [$C(CH_3)_2$], 105.5 [$C(CH_3)_2$], 126.6, 127.1, 127.2, 127.9, 128.0, 128.0, 128.1, 128.4, 128.4, 128.5, 128.5, 128.7, 128.8, 129.4, 129.4, 129.5, 130.8, 131.3, 131.6, 135.2, 136.2, 137.2, 138.5, 142.3, 144.6 (C-8'a), 161.9 (C=O), 164.1 (C=O), 168.2 (C=O), 169.5 (C=O).

**1'-Phenyl-,2',4',5',7'-tetra(4-flurophenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5''] bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5b).** a white solid; mp 218-220 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.46 (s, 3H, $CH_3$), 0.49 (s, 3H, $CH_3$), 0.68 (s, 3H, $CH_3$), 0.72 (s, 3H, $CH_3$), 2.52 (brs, 1H, H'-8'), 2.54 (brs, 1H, H''-8'), 3.95 (dd, *J*=9.6, 7.6 Hz, 1H, H-7'), 4.57 (brs, 2H, H-4' and H-5'), 5.21 (s, 1H, H-2'), 6.05-6.12 (m, 2H, 2CH, HAr), 6.49-6.56 (m, 2H, 2CH, HAr), 6.77-7.54 (m, 17H, 17CH, HAr). $^{13}$C NMR (100 MHz, $CDCl_3$) δ28.0 ($CH_3$), 28.3 ($CH_3$), 28.8 ($CH_3$), 28.9 ($CH_3$), 32.8 (C-8'), 46.9 (C-4'), 49.8 (C-5'), 52.1 (C-7'), 61.5 (C-3'), 61.7 (C-6'), 69.3 (C-2'), 101.6 (C-4'a), 105.5 [$C(CH_3)_2$], 105.7 [$C(CH_3)_2$], 114.9, 115.0, 115.1, 115.1, 115.1, 115.2, 115.3, 115.3, 115.6, 115.6, 115.7, 15.8, 115.8, 115.9, 126.9, 130.4, 130.4, 130.7, 130.8, 130.9, 130.9, 131.0, 130.0, 130.1, 130.1, 131.9 (d, $J_{CF}$=3.1 Hz, $C_{Ar\text{-}F}$), 132.5, 132.6 (d, $J_{CF}$=3.1 Hz, $C_{Ar\text{-}F}$), 132.7, 132.9 (d, $J_{CF}$=3.1 Hz, $C_{Ar\text{-}F}$), 133.0, 133.1, 133.9 (d, $J_{CF}$=3.1Hz, $C_{Ar\text{-}F}$), 142.5, 144.1 (C-8'a), 160.8 (d, $J_{CF}$=246.5 Hz, $C_{Ar\text{-}F}$), 161.2 (d, $J_{CF}$= 246.5 Hz, $C_{Ar\text{-}F}$), 161.9 (C=O), 163.3 (d, $J_{CF}$=246.5 Hz, $C_{Ar\text{-}F}$), 163.6 (d, $J_{CF}$ =246.5 Hz, $C_{Ar\text{-}F}$), 164.0 (C=O), 168.0 (C=O), 169.4 (C=O). ESI+MS *m/z*=845.3$[M+H]^+$.

**1'-Phenyl-,2',4',5',7'-tetra(4-chlorophenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3': 6',5'']bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5c).** a white solid; mp 188-190 °C. $^1$H NMR (400 MHz,

$CDCl_3$) δ 0.48 (s, 3H, $CH_3$), 0.50 (s, 3H, $CH_3$), 0.69 (s, 3H, $CH_3$), 0.72 (s, 3H, $CH_3$), 2.51 (brs, 1H, H'-8'), 2.53 (brs, 1H, H''-8'), 3.93 (t, *J*=8.4 Hz, 1H, H-7'), 4.54 (brs, 2H, H-4' and H-5'), 5.20 (s, 1H, H-2'), 6.07 (dd, *J*=12.8, 8.4 Hz, 2H, 2CH, HAr), 6.81-7.49 (m, 19H, 19CH, HAr). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.0 ($CH_3$), 28.3 ($CH_3$), 28.8 ($CH_3$), 28.9 ($CH_3$), 32.5 (C-8'), 47.0 (C-4'), 49.9 (C-5'), 52.3 (C-7'), 61.2 (C-3'), 61.3 (C-6'), 69.4 (C-2'), 101.1 (C-4'a), 105.5 [$C(CH_3)_2$], 105.8 [$C(CH_3)_2$], 127.1, 128.2, 128.3, 128.4, 128.6, 128.9, 129.0, 129.5, 130.1, 130.6, 130.7, 130.9, 132.1, 132.5, 132.8, 133.3, 133.6, 133.7, 134.1, 134.4, 134.5, 135.4, 136.5, 142.7, 143.8 (C-8'a), 161.7 (C=O), 163.9 (C=O), 167.8 (C=O), 169.2 (C=O).

**1'-Phenyl-2',4',5',7'-tetra(4-methylphenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydro–quinoline-5,3':6',5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] (5d).** a white solid; mp 241-243 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 3H, $CH_3$), 0.41(s, 3H, $CH_3$), 0.62 (s, 3H, $CH_3$), 0.65 (s, 3H, $CH_3$), 2.16 (s, 3H, $ArCH_3$), 2.20 (s, 6H, $2ArCH_3$), 2.21 (s, 3H, $ArCH_3$), 2.44-2.63 (m, 2H, H'-8', H''-8'), 3.93 (dd, *J*=11.6, 5.6 Hz, 1H, H-7'), 4.55 (s, 1H, H-4'), 4.57 (s, 1H, H-5'), 5.18 (s, 1H, H-2'), 5.93 (dd, *J*=8.0, 1.2 Hz, 1H, 1CH, HAr), 5.96 (dd, *J*=8.0, 1.2 Hz, 1H, 1CH, HAr), 6.53 (t, *J*=7.2 Hz, 2H, 2CH, HAr), 6.85-7.43 (m, 17H, 17CH, HAr); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.9 ($ArCH_3$), 21.0 ($ArCH_3$), 21.0 ($ArCH_3$), 21.0 ($ArCH_3$), 27.9 ($CH_3$), 28.3 ($CH_3$), 28.5 ($CH_3$), 28.6 ($CH_3$), 32.8 (C-8'), 47.3 (C-4'), 50.3 (C-5'), 52.6 (C-7'), 61.8 (C-3'), 61.8 (C-6'), 69.9 (C-2'), 102.6 (C-4'a), 105.1 [$C(CH_3)_2$], 105.3 [$C(CH_3)_2$], 126.3, 128.3, 128.4, 128.6, 128.7, 128.8, 129.1, 129.1, 129.2, 129.3, 129.3, 130.7, 131.2, 131.5, 132.2, 133.2, 134.2, 135.6, 136.6, 136.7, 137.5, 137.9, 142.1, 144.7 (C-8'a), 162.0 (C=O), 164.2 (C=O), 168.4 (C=O), 169.8 (C=O).

**1'-Phenyl-2',4',5',7'-tetra(4-methoxylphenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydro–quinoline-5,3':6', 5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] (5e).** a yellow solid; mp 204-206 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 0.45 (s, 3H, $CH_3$), 0.48 (s, 3H, $CH_3$), 0.67 (s, 3H, $CH_3$), 0.72 (s, 3H, $CH_3$), 2.46-2.60 (m, 2H, H'-8', H''-8'), 3.67 (s, 3H, $ArCH_3O$), 3.70 (s, 6H, $2ArCH_3O$), 3.72 (s, 3H, $ArCH_3O$), 3.92 (dd, 1H, *J*=12.0, 6.0 Hz, H-7'), 4.53 (brs, 2H, H-4', H-5'), 5.15 (s, 1H, H-2'), 5.98-6.04 (m, 2H, 2CH, HAr), 6.29-6.34 (m, 2H, 2CH, HAr), 6.59-7.52 (m, 17H, 17CH, HAr); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.1 ($CH_3$), 28.4 ($CH_3$), 28.7 ($CH_3$), 28.8 ($CH_3$), 32.9 (C-8'), 46.9 (C-4'), 49.9 (C-5'), 52.2 (C-7'), 55.1 ($CH_3O$), 55.2 ($CH_3O$), 55.3 ($CH_3O$), 55.3 ($CH_3O$), 61.9 (C-3'), 62.1 (C-6'), 69.6 (C-2'), 102.8 (C-4'a), 105.2 [$C(CH_3)_2$], 105.4 [$C(CH_3)_2$], 112.7, 113.5, 113.6, 113.7, 113.8, 114.0, 114.1, 114.4, 126.4, 127.2, 128.4, 129.5, 129.8, 130.3, 130.5, 130.6, 132.0, 132.2, 132.6, 142.1, 144.7 (C-8'a), 158.7 ($C_{Ar\text{-}O}$), 158.8 ($C_{Ar\text{-}O}$), 159.1 ($C_{Ar\text{-}O}$), 159.3 ($C_{Ar\text{-}O}$), 162.2 (C=O), 164.3 (C=O), 168.5 (C=O), 169.9 (C=O). ESI+MS *m/z*=893.3$[M+H]^+$.

**1'-Phenyl-,2',4',5',7'-tetra(4-nitrophenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5''] bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5f).** a light yellow solid; mp 195-198 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 0.42 (s, 3H, $CH_3$), 0.46 (s, 3H, $CH_3$), 0.64 (s, 3H, $CH_3$), 0.67 (s, 3H, $CH_3$), 2.63 (brs, 1H, H'-8'), 2.64 (brs, 1H, H''-8'), 4.12 (t, *J*=8.4 Hz, 1H, H-7'), 4.72 (brs, 1H, H-4'), 4.73 (brs, 1H, H-5'), 5.42 ( s, 1H, H-2'), 6.31 (dd, *J*=15.6, 8.0 Hz, 2H, 2CH, HAr), 7.13-8.43 (m, 19H, 2CH, HAr). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.0 ($CH_3$), 28.4 ($CH_3$), 29.1 ($CH_3$), 29.2 ($CH_3$), 32.4 (C-8'), 47.5 (C-4'), 50.2 (C-5'), 52.7 (C-7'), 60.7 (C-3'), 60.8 (C-6'), 69.6 (C-2'), 99.5 (C-4'a), 106.1 [$C(CH_3)_2$], 106.2 [$C(CH_3)_2$], 123.0, 123.3, 123.4, 123.9, 124.1, 128.0, 129.9, 130.5, 130.8, 130.9, 132.0, 132.4, 141.2, 142.8, 142.9, 143.8, 143.8, 144.5 (C-8'a), 147.6 ($C_{Ar\text{-}NO2}$), 147.6 ($C_{Ar\text{-}NO2}$), 148.0 ($C_{Ar\text{-}NO2}$), 148.1 ($C_{Ar\text{-}NO2}$), 161.2 (C=O), 163.4 (C=O), 167.0 (C=O), 168.4 (C=O). ESI+MS *m/z*=953.2$[M+H]^+$.

**1'-Phenyl-2',4',5',7'-tetra(2-methylphenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydro–quinoline-5,3':6',5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] (5g).** a white solid; mp 214-216 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.48 (s, 3H, $CH_3$), 0.51 (s, 3H, $CH_3$), 1.12 (s, 3H, $CH_3$), 1.16 (s, 3H, $CH_3$), 2.12 (s, 3H, $ArCH_3$), 2.30 (s, 6H, $2ArCH_3$), 2.51 (s, 3H, $ArCH_3$), 2.53 (dd, *J*=14.4, 6.0 Hz,1H, H'-8'), 2.66-2.74 (m, 1H, H''-8'), 4.31 (dd, *J*=11.6, 5.6 Hz, 1H, H-7'), 4.74 (s, 1H, H-4'), 4.81 (s, 1H, H-5'), 5.61 (s, 1H, H-2'), 6.73-7.82 (m, 21H, 21CH, HAr); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 17.6 ($ArCH_3$), 17.8 ($ArCH_3$), 19.6 ($ArCH_3$), 19.8 ($ArCH_3$), 28.1 ($CH_3$), 28.3 ($CH_3$), 28.5 ($CH_3$), 29.0 ($CH_3$), 34.4 (C-8'), 42.8 (C-4'), 46.1 (C-5'), 48.9 (C-7'), 58.8 (C-3'), 59.3 (C-6'), 65.2 (C-2'), 104.1 (C-4'a), 105.2 [$C(CH_3)_2$], 105.3 [$C(CH_3)_2$], 125.4, 126.1, 126.4, 126.5, 126.6 127.1, 127.4, 127.5, 127.6, 128.3, 130.1, 130.8, 130.9, 131.2, 131.7, 131.8, 133.3, 134.5, 135.3, 137.6, 137.9, 138.1, 139.6, 139.6, 144.1, 144.5 (C-8'a), 162.7 (C=O), 165.0 (C=O), 168.1 (C=O), 169.6 (C=O).

**1'-Phenyl-,2',4',5',7'-tetra(2-chlorophenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5''] bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5h).** a white solid; mp 230-232 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.36 (s, 3H, $CH_3$), 0.38 (s, 3H, $CH_3$), 0.61 (s, 3H, $CH_3$), 0.64 (s, 3H, $CH_3$), 2.52 (dd, *J*=16.8, 6.0 Hz, 1H, H'-8'), 2.61-2.67 (m, 1H, H''-8'), 3.99 (dd, *J*=12.0, 6.0 Hz, 1H, H'-7'), 4.62 (s, 1H, H-4'), 4.64(s, 1H, H-5'), 5.18 (s, 1H, H-2'), 6.04 (d, *J*=7.6 Hz, 1H, 1CH, HAr), 6.08 (d, *J*=8.0 Hz, 1H, 1CH, HAr), 6.70-7.52 (m, 22H, 22CH, HAr). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.0 ($CH_3$), 28.2 ($CH_3$), 28.6 ($CH_3$), 28.7 ($CH_3$), 32.8 (C-8'), 47.6 (C-4'), 50.8 (C-5'), 53.0 (C-7'), 61.4 (C-3'), 61.7 (C-6'), 70.1 (C-2'), 102.8 (C-4'a), 105.4 [$C(CH_3)_2$], 105.6 [$C(CH_3)_2$], 127.1, 127.3, 128.0, 128.1, 128.1, 128.2, 128.5, 128.6, 128.8, 128.8, 129.2, 129.4, 129.5, 130.9, 131.3, 131.6, 135.1, 136.1, 137.0, 138.4, 140.7 (d, $^2J_{CF}$ 3.0 Hz, $C_{Ar}$), 142.1, 143.8 (C-8'a), 160.8 (d, $^1J_{CF}$ 246.0 Hz, $C_{Ar}$), 161.9 (C=O), 164.2 (C=O), 168.1 (C=O), 169.4 (C=O).

**1'-(4-Methoxylphenyl)-2',4',5',7'-tetraphenyl-1'*H*-dispiro[2',4',5',7',8'-tetrahydro–quinoline-5,3':6', 5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] (5i).** a white solid; mp 218-220 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.36 (s, 3H, $CH_3$), 0.38 (s, 3H, $CH_3$), 0.62 (s, 3H, $CH_3$), 0.64 (s, 3H, $CH_3$), 2.54 (dd, *J*=14.4, 5.2 Hz, 1H, H'-8'), 2.68-2.76 (m, 1H, H''-8'), 3.73 (s, 3H, $ArOCH_3$), 4.01 (dd, *J*=13.2, 5.6 Hz, 1H, H-7'), 4.64(s, 1H, H-4'), 4.68 (s, 1H, H-5'), 5.21 (s, 1H, H-2'), 6.04 (d, *J*=8.0 Hz, 1H, 1CH, HAr), 6.08 (d, *J*=8.0 Hz, 1H, 1CH, HAr), 6.70-7.56 (m, 22H, 22CH, HAr); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.0 ($CH_3$), 28.2 ($CH_3$), 28.4 ($CH_3$), 28.5 ($CH_3$), 32.6 (C-8'), 47.4 (C-4'), 50.5 (C-5'), 53.1 (C-7'), 55.6 ($OCH_3$), 61.6 (C-3'), 61.9 (C-6'), 70.0 (C-2'), 102.1(C-4'a), 105.2 [$C(CH_3)_2$], 105.3 [$C(CH_3)_2$], 127.0, 127.1, 127.8, 128.0, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 129.3, 129.4, 129.6, 130.7, 131.2, 131.5, 135.4, 136.2, 137.1, 137.4, 138.5, 142.6 (C-8'a), 157.6 ($C_{Ar\text{-}O}$), 161.8 (C=O), 164.2 (C=O), 168.1 (C=O), 169.4 (C=O).

**1'-(4-Fluropentaphenyl)-,2',4',5',7'-tetraphenyl-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5'']bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5j).** a white solid; mp 241-243 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 0.36 (s, 3H, $CH_3$), 0.38 (s, 3H, $CH_3$), 0.61 (s, 3H, $CH_3$), 0.64 (s, 3H, $CH_3$), 2.52 (dd, *J*= 16.8, 6.0 Hz, 1H, H'-8'), 2.61-2.67 (m, 1H, H''-8'), 3.99 (dd, *J*=12.0, 5.6 Hz, 1H, H'-7'), 4.62 (s, 1H, H-4'), 4.64 (s, 1H, H-5'), 5.18 (s, 1H, H-2'), 6.04 (d, *J*=7.6 Hz, 1H, 1CH, HAr), 6.08 (d, *J*=8.0 Hz, 1H, 1CH, HAr), 6.70-7.52 (m, 22H, 22CH, HAr). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.0 ($CH_3$), 28.2 ($CH_3$), 28.5 ($CH_3$), 28.6 ($CH_3$), 32.8 (C-8'), 47.6 (C-4'), 50.8 (C-5'), 53.0 (C-7'), 61.4 (C-3'), 61.7 (C-6'), 70.1 (C-2'), 102.8 (C-4'a), 105.4 [$C(CH_3)_2$], 105.6 [$C(CH_3)_2$], 127.1, 127.3, 128.0, 128.1, 128.1, 128.2, 128.5, 128.6, 128.8, 128.8, 129.2, 129.4, 129.5, 130.9, 131.3, 131.6, 135.1, 136.1, 137.0, 138.4, 140.7 (d, $J_{CF}$= 3.0 Hz, $C_{Ar}$), 142.1, 143.8 (C-8'a), 160.8 (d, $J_{CF}$=246.0 Hz, $C_{Ar}$), 161.9 (C=O), 164.2 (C=O), 168.1 (C=O), 169.4 (C=O).

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