Supporting information

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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1. Measurement

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.

2. General experimental procedure

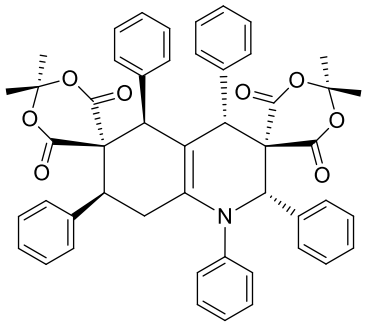
2.1 General procedure of the preparation of products 5a-5j

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**. **5b-5j** were synthesized from the same procedure.

3. Spectral data

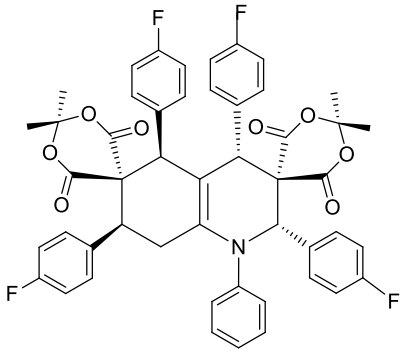
1',2',4',5',7'-Pentaphenyl-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5'']bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5a): a white solid; mp 246-248 °C. ^{1}H

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).

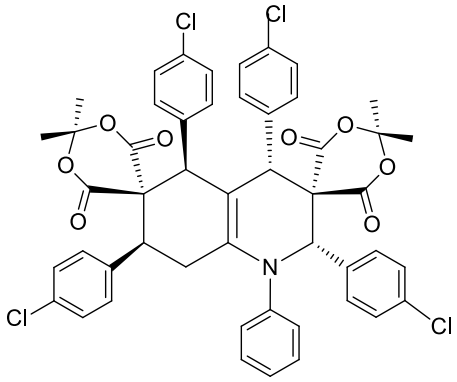


1'-Pentaphenyl-,2',4',5',7'-tetra(4-flurophenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5'']bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5b): a white solid; mp 218-220 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.46 (s, 3H, CH_3), 0.49 (s, 3H, CH_3), 0.68 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 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$[M+H]^+$.

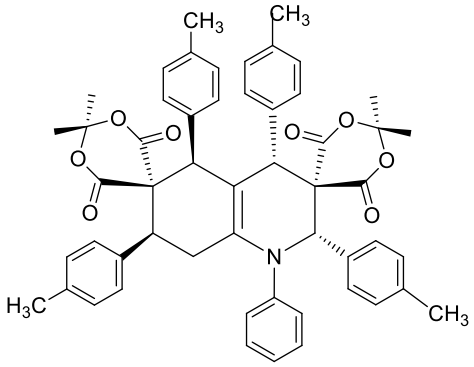


1'-Pentaphenyl-,2',4',5',7'-tetra(4-chlorophenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5'']bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5c). a white solid; mp 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48 (s, 3H, CH_3), 0.50 (s, 3H, CH_3), 0.69 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 2.51 (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).



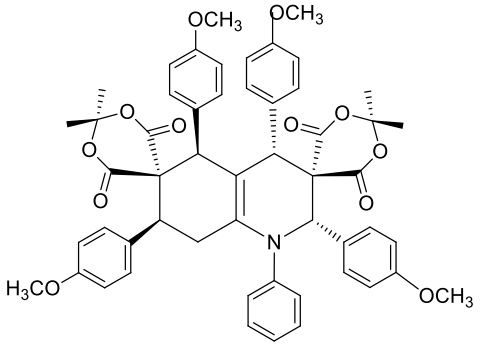
1'-Phenyl-2',4',5',7'-tetra(4-methylphenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydro–quinoline-5,3':6',5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] (**5d**). a white solid; mp

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).

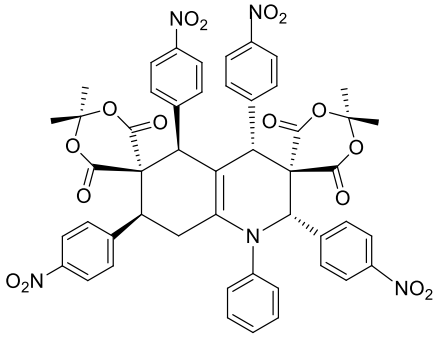


1'-Phenyl-2',4',5',7'-tetra(4-methoxylphenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydro –quinoline-5,3':6',5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] (**5e**). a yellow solid; mp 204-206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.45 (s, 3H, CH_3), 0.48 (s, 3H, CH_3), 0.67 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 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-O}),

158.8 (C_{Ar-O}), 159.1 (C_{Ar-O}), 159.3 (C_{Ar-O}), 162.2 (C=O), 164.3 (C=O), 168.5 (C=O), 169.9 (C=O). ESI+MS *m/z*=893.3$[M+H]^+$.

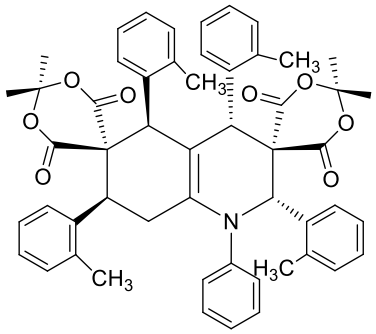


1'-Pentaphenyl-,2',4',5',7'-tetra(4-nitrophenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydroquinoline-5,3':6',5'']bis(2,2-dimetyl-1,3-dioxane-4,6-dione)] (5f). a light yellow solid; mp 195-198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.42 (s, 3H, CH_3), 0.46 (s, 3H, CH_3), 0.64 (s, 3H, CH_3), 0.67 (s, 3H, CH_3), 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-NO2}), 147.6 (C_{Ar-NO2}), 148.0 (C_{Ar-NO2}), 148.1 (C_{Ar-NO2}), 161.2 (C=O), 163.4 (C=O), 167.0 (C=O), 168.4 (C=O). ESI+MS *m/z*=953.2$[M+H]^+$.

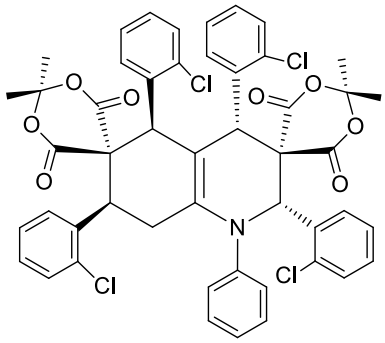


1'-Phenyl-2',4',5',7'-tetra(2-methylphenyl)-1'*H*-dispiro[2',4',5',7',8'-tetrahydro–quinoline-5,3':6',5''-bis(2,2-dimethyl-1,3-dioxane-4,6-dione)] (**5g**). a white solid; mp 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48 (s, 3H, CH_3), 0.51 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 2.12 (s, 3H, $ArCH_3$), 2.30 (s, 6H, $2ArCH_3$), 2.51 (s,

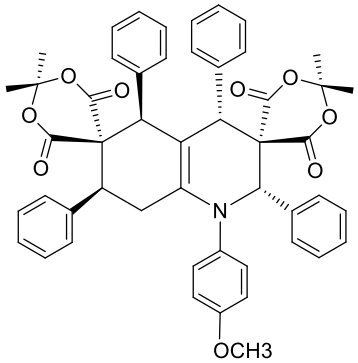
3H, $ArCH_3$), 2.53 (dd, *J*= 14.4, 6.0 Hz,1H, H'-8'), 2.66-2.74 (m, 1H, H''-8'), 4.31 (dd, *J*= 11.6, 5.6 Hz, 1H, H-7'), 4.74 (s, 1H, H-4'), 4.81 (s, 1H, H-5'), 5.61 (s, 1H, H-2'), 6.73-7.82 (m, 21H, 21CH, HAr); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6 ($ArCH_3$), 17.8 ($ArCH_3$), 19.6 ($ArCH_3$), 19.8 ($ArCH_3$), 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'-Pentaphenyl-,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. ^1H 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-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'-tetrahyd roquinoline-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).