SUPPORTING INFORMATION

Copper-Mediated Synthesis of Tertiary Diaryl Squaramides

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General information:

All reactions are carried out in oven dried round bottom flasks under nitrogen atmosphere. Commercially available anhydrous DMF was used in this study without any further purification. Silica gel (230-400) mesh was used for column chromatography. ^1H and ^{13}C spectra were recorded at 400 and 100 MHz respectively. The spectra are reported in ppm referenced to the appropriate solvent peak. High resolution mass spectra were obtained on a Time-of-Flight mass spectrometer connected to a capillary HPLC system. Samples were ionized using electrospray ionization within a mass range of 105 Da to 2800 Da in both positive and negative modes.

Experimental procedures

3,4-bis(methyl amino)cyclobut-3-ene-1,2-dione (**1a**):

Squaric acid (2.28 g, 20 mmol) was stirred with ethanol (30 ml) in a 100 ml RB flask under nitrogen atmosphere for 30 minutes, and then triethyl orthoformate (8 ml) was syringed in. The reaction was refluxed for 24 hours to obtain diethyl squarate. The obtained diethyl squarate was cooled to 5-10 °C followed by the addition of 2M methylamine in THF (26 ml). After the complete addition of methylamine, the reaction was stirred at room temperature for 24 hr. The precipitated solid was filtered and washed with diethyl ether (2 × 100 ml) and dried under vacuum to get title compound in 85% yield. ^1H NMR (400 MHz, d_6 DMSO): δ 7.4(2H, br.), 3.1(6H, s) ppm. ^{13}C NMR (100 MHz, DMSO- d_6): δ 182.5, 168.3, 30.2 ppm. mp: >250°C

3,4-bis(tert-butyl amino)cyclobut-3-ene-1,2-dione (**1b**, Ref: Schmidt, A. H. *Synthesis* 1980, 961)

Similar to procedure **1a**, using tert-butyl amine. Pale yellow solid was obtained in 50% yield. ^1H NMR (DMSO- d_6): δ 7.62(2H, s), 1.37(18H, s) ppm. ^{13}C NMR (DMSO- d_6): δ 180.8, 168.3, 52.2, 30.2 ppm.

3,4-bis(cyclohexyl amino)cyclobut-3-ene-1,2-dione (**1c**, Ref: Frauenhoff, G. R.; Takusagawa, F.; Busch, H. *Inorg Chem* **1992**, 31(19), 4002)

Similar to procedure **1a**, using cyclohexyl amine. Pale yellow solid obtained in 70% yield. ^1H NMR(DMSO- d_6): δ 7.32(2H, b), 3.76(2H, S), 1.89(8H, b), 1.67(8H, b), 1.54(4H, b), 1.29(2H, b) ppm. ^{13}C NMR(DMSO- d_6): δ 181.8, 166.9, 51.9, 33.7, 24.7, 23.9 ppm.

3,4-bis(dodecyl amino)cyclobut-3-ene-1,2-dione (**1d**, Ref. Hutchings, M. G.; Ferguson, I. Allen, S.; Zyss, J.; Ledoux, I. *J. Chem. Res., Synop.* **1998**, 5, 244)

Similar to procedure **1a**, using dodecyl amine. Pale white solid obtained in 82% yield. ^1H NMR (at 90 °C in Toluene- d_8): δ 7.88(2H, broad singlet), 3.75(4H, broad multiplet), 1.76(4H, m), 1.45(4H, m), 1.32 (32H, broad multiplet), 0.90(6H, t, $J=6.4\text{Hz}$) ppm. ^{13}C NMR(Toluene- d_8): 183.3, 168.8, 45.2, 32.3, 31.7, 30.1, 30.1, 30.0, 30.0, 29.8, 29.7, 27.1, 22.9, 13.9 ppm. mp 172-174 °C. (lit.² 173-174 °C)

General procedure for diarylation:

3,4-bis(N-methyl-N-phenyl amino)cyclobut-3-ene-1,2-dione (**2a**):

To a 25 ml RB flask was added Copper Iodide (95 mg, 0.5 mmol), L-proline (58 mg, 0.5 mmol), potassium carbonate (345 mg, 3 mmol) and anhydrous DMF (1 ml). The mixture was stirred at room temperature under nitrogen atmosphere for 20 minutes.

Bromobenzene (471 mg, 3 mmol) and 3,4-bis(methyl amino)cyclobut-3-ene-1,2-dione (140 mg, 1 mmol) were then added and the reaction temperature increased to 120 °C and maintained for 18 hr. The reaction mixture was cooled to room temperature, diluted with ethylacetate (15 ml), filtered and concentrated. The residue was chromatographed (2:3 Ethyl acetate / hexane) to yield the title compound in 65% yield. ^1H NMR (CDCl_3): δ 7.02(4H, t, $J=7.6\text{Hz}$), 6.89(2H, t, $J=7.2\text{Hz}$), 6.61(4H, d, $J=7.6\text{Hz}$), 3.70(6H, s) ppm. ^{13}C NMR (CDCl_3): δ 186.7, 167.6, 142.8, 128.8, 125.0, 121.2, 39.2 ppm. mp. 174-175 °C.

N, N'-dimethyl N, N'-(4, 4-dichloro) cyclobut-3-ene-1,2-dione (**2b**):

Solid was obtained in 44% yield. ^1H NMR (CDCl_3): δ 7.03(4H, d, $J=8.8\text{Hz}$), 6.55(4H, d, $J=8.8\text{Hz}$), 3.7(6H, s) ppm. ^{13}C NMR (CDCl_3): δ 186.5, 167.3, 141.3, 130.9, 128.7, 122.7, 39.3 ppm. HRMS calculated for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2$ ($M+1$) 361.0501. Found 361.0502. mp $>250^\circ\text{C}$

3,4-bis(N-methyl-N-o-tolyl amino)cyclobut-3-ene-1,2-dione (**2c**):

Pale yellow color solid obtained in 20% yield. ^1H NMR (CDCl_3): δ 6.96-6.91(4H, m), 6.85(2H, d), 6.65(2H, d, $J=6.4\text{Hz}$), 3.64(6H, s), 2.21(6H, s) ppm. Due to restricted rotation aromatic signals are broad. ^{13}C NMR (CDCl_3): δ 185.7, 168.8, 142.8, 132.50, 131.5, 127.2, 127.1, 124.8, 40.8, 18.1 ppm. HRMS calculated for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$ ($M+1$) 321.1597. Found 321.1600. mp $160-162^\circ\text{C}$

3,4-bis(N-methyl-N-p-tolyl amino)cyclobut-3-ene-1,2-dione (**2d**):

Pale yellow color solid obtained in 70% yield. ^1H NMR (CDCl_3): δ 6.80(4H, d, $J=8\text{Hz}$), 6.50(4H, d, $J=8\text{Hz}$), 3.64(6H, s), 2.21(6H, s) ppm. ^{13}C NMR (CDCl_3): δ 186.4, 167.5, 140.6, 135.0, 129.0, 121.4, 39.3, 20.8 ppm. HRMS calculated for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$ ($M+1$) 321.1597. Found 321.1598. mp $193-195^\circ\text{C}$.

3,4-bis(N-(4-(dimethyl amino)phenyl)-N-methyl amino)cyclobut-3-ene-1,2-dione (**2e**):

Brown color solid obtained in 55% yield. ^1H NMR (CDCl_3): δ 6.54(4H, d, $J=8.8\text{Hz}$), 6.3(4H, d, $J=8.8\text{Hz}$), 3.60(6H, s), 2.89(12H, s) ppm. ^{13}C NMR (CDCl_3): δ 185.9, 167.3, 148.3, 133.2, 122.7, 112.4, 40.8, 40.0 ppm. HRMS calculated for $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_2$ ($M+1$) 379.2128. Found 379.2129. mp 180-183 $^\circ\text{C}$

N, N'-dimethyl N, N'(4,4' dicarbomethoxy) cyclobut-3-ene-1,2-dione (**2f**):

Pale yellow color solid obtained in 10% yield. ^1H NMR (CDCl_3): δ 7.69(4H, d, $J=8.8\text{Hz}$), 6.67(4H, d, $J=8.8\text{Hz}$), 3.90(6H, s), 3.76(6H, s) ppm. ^{13}C NMR (CDCl_3): δ 187.1, 167.7, 165.9, 146.1, 130.4, 126.3, 119.9, 52.2, 38.4 ppm. HRMS calculated for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_6$ ($M+1$) 409.1394. Found 409.1391. mp >250 $^\circ\text{C}$

Note: Reaction time was only 3 hours

N, N'dimethyl N, N'(3,3' dicarbomethoxy) cyclobut-3-ene-1,2-dione (**2g**):

Pale yellow color solid obtained in 21% yield.. ^1H NMR(CDCl_3): δ 7.45(2H, d, $J = 7.6\text{Hz}$), 7.18(2H, t, $J=4\text{Hz}$), 7.06(2H, t, $J=8\text{Hz}$), 6.80(2H, d, $J=8\text{Hz}$), 3.92(6H, s), 3.78(6H, s) ppm. ^{13}C NMR (CDCl_3): δ 186.9, 167.3, 165.8, 142.8, 130.7, 128.9, 125.7, 124.2, 121.7, 52.4, 38.6 ppm. HRMS calculated for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_6$ ($M+1$) 409.1394. Found 409.1391. mp 166-168 $^\circ\text{C}$

Note: Reaction time was only 3 hours

N, N'dimethyl N, N' (diethyl 4,4'diphenyl diacetate) cyclobut-3-ene-1,2-dione (**2h**):

Solid obtained in 45% yield. ^1H NMR (CDCl_3): δ 6.91 (4H, d, $J=8.0\text{Hz}$), 6.53 (4H, d, $J=8.4\text{Hz}$), 4.19 (4H, q, $J=7.2\text{Hz}$), 3.64 (6H, s), 3.46 (4H, s), 1.30 (6H, t, $J=6.8\text{ Hz}$) ppm. ^{13}C NMR (CDCl_3): 186.6, 171.1, 167.7, 141.7, 131.1, 129.5, 121.5, 60.9, 40.4, 39.2, 14.3 ppm. HRMS calculated for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_6$ ($M+1$) 465.2020. Found 465.2024. mp 157-160 $^\circ\text{C}$

3-(N-methyl-N-phenyl amino)-4-(methyl amino) cyclobut-3-ene-1,2-dione (**7a**):

^1H NMR (400 MHz, CDCl_3): δ 7.49 (2H, t, $J=7.6\text{Hz}$), 7.33 (1H, t, $J=7.6\text{Hz}$), 7.11 (2H, d, $J=7.6\text{Hz}$), 3.97 (1H, br), 3.81 (3H, s), 3.29 (3H, s), ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 184.9, 183.9, 168.3, 164.9, 141.6, 129.8, 126.8, 122.6, 38.8, 31.7 ppm. HRMS calculated for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ ($M+1$) 217.0971. Found 217.0971. mp 213-215 $^\circ\text{C}$.

3-(N-tert-butyl-N-phenyl amino)-4-(tert-butyl amino)cyclobut-3-ene-1,2-dione (**7b**):

Pale white solid obtained in 96% yield. ^1H NMR (CDCl_3): δ aromatic signal are broad due to restricted rotation of phenyl 7.48 (3H, m), 7.25 (2H, m), 3.40 (1H, br), 1.48 (9H, s), 1.09 (9H, s) ppm. ^{13}C NMR (CDCl_3): δ 182.7, 181.8, 169.8, 168.2, 140.1, 130.1, 129.1, 129.0, 60.0, 52.8, 30.6, 30.3 ppm. HRMS calculated for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_2$ ($M+1$) 301.1910. Found 301.1915. mp 200-202 $^\circ\text{C}$

3-(N-cyclohexyl-N-phenyl amino)-4-(cyclohexyl amino)cyclobut-3-ene-1,2-dione(7c):

^1H NMR (CDCl_3): δ 7.48(2H, d, $J=6.4\text{Hz}$), 7.23(2H, t, $J=6\text{Hz}$), 7.30(1H, t, 8Hz), 4.59(1H, m), 3.31(1H, m), 3.89(1H, broad singlet), cyclohexyl ring proton 0.82-2.05(20H, m) ppm. ^{13}C NMR (CDCl_3): δ 183.3, 182.7, 167.5, 166.1, 137.3, 129.3, 129.1, 128.9, 60.5, 52.1, 34.0, 32.5, 25.4, 25.0, 24.9, 23.6 ppm. HRMS calculated for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$ ($M+1$) 353.2223. Found 353.2227. mp 185-188 $^\circ\text{C}$

N-dodecyl N-(ethyl 4-phenyl acetate) cyclobut-3-ene-1,2-dione (7d):

Obtained as viscous liquid. ^1H NMR(CDCl_3): δ 7.35 (2H, d, $J=8.4\text{Hz}$), 7.07(2H, d, $J=8.4\text{Hz}$), 4.17(2H, q, $J=7.2\text{Hz}$), 4.11(1H, m), 3.99(2H, m), 3.65(2H, s), 3.55(2H, q), 1.57(2H, m), 1.43(2H, m), 1.28(3H, t, $J=6.8\text{Hz}$), 1.22(36H, m), 0.86(6H, t). ^{13}C NMR(CDCl_3): δ 184.3, 183.3, 171.0, 167.5, 165.0, 138.6, 133.4, 131.8, 130.6, 124.5, 61.1, 51.7, 44.7, 40.5, 31.9, 31.2, 29.6, 29.6, 29.6, 29.5, 29.7, 29.3, 29.3, 29.2, 29.1, 29.0, 26.2, 26.2, 22.6, 14.2 ppm. HRMS calculated for $\text{C}_{38}\text{H}_{62}\text{N}_2\text{O}_4$ ($M+1$) 611.4782. Found 611.4783.

3-(N-methyl-N-(naphthalen-1-yl)amino)-4-(methyl amino)cyclobut-3-ene-1,2-dione(7e):

Pale yellow solid was obtained in 10% yield. ^1H NMR (CDCl_3): δ 7.99(1H, d, $J=7.6\text{Hz}$), 7.96(1H, d, $J=8.0\text{Hz}$), 7.92(1H, d, $J=8.8\text{Hz}$), 7.67(1H, t, $J=5.6$), 7.64(1H, t, $J=6.8$), 7.57(1H, t, $J=8\text{Hz}$), 7.45(1H, d, $J=7.6\text{Hz}$), 3.88(3H, s), 3.38(1H, s), 2.95(3H, s) ppm. ^{13}C NMR (CDCl_3): 184.1, 183.4, 168.7, 166.8, 137.9, 134.4, 130.1, 129.4, 129.1, 128.9,

128.1, 127.5, 125.4, 124.1, 122.2, 40.8, 31.4 ppm. HRMS calculated for $C_{16}H_{14}N_2O_2$ (M+1) 267.1128. Found 267.1125. mp 220-222 °C

3-(N-(anthracen-10-yl)-N-methyl amino)-4-(methyl amino)cyclobut-3-ene-1,2-dione(7f):

Solid obtained in 12% yield. 1H NMR ($CDCl_3$): δ 8.62(1H, s), 8.15(2H, d, $J=8.4$ Hz), 8.04(2H, d, $J=8.8$ Hz), 7.69(2H, t of d), 7.63(2H, t of d), 3.96(3H, s) ppm, 2.95 (1H, s), 2.72 (3H, s) ppm. ^{13}C NMR ($CDCl_3$): 183.9, 183.2, 169.0, 167.5, 131.4, 129.2, 128.8, 128.5, 128.1, 126.4, 121.8, 40.5, 31.2 ppm. HRMS calculated for $C_{20}H_{16}N_2O_2$ (M+1) 317.1284. Found 317.1287. mp >250 °C

3-(N-methyl-N-(phenanthren-9-yl)amino)-4-(methyl amino)cyclobut-3-ene-1,2-dione(7g)

Light brown solid was obtained in 30% yield. 1H NMR ($CDCl_3$): δ 8.82(1H, d, $J=8.4$ Hz), 8.75(1H, d, $J=8.0$ Hz), 7.98(1H, t, $J=8.8$ Hz), 7.78(5H, multiplet), 7.74(1H, s), 3.9 (3H, s), 3.7 (1H, br), 2.95 (3H, s) ppm. ^{13}C NMR ($CDCl_3$): 184.1, 183.3, 168.6, 166.8, 136.5, 131.5, 130.5, 129.1, 128.3, 128.3, 128.1, 127.8, 127.6, 124.9, 123.7, 123.2, 122.8, 40.8, 31.4 ppm. HRMS Calculated for $C_{20}H_{16}N_2O_2$ (M+1) 317.1284. Found 317.1283

3-(N-methyl-N-(pyren-1-yl)amino)-4-(methyl amino)cyclobut-3-ene-1,2-dione (7h):

Yellow solid was obtained in 55% yield. Temperature was raised to 120 °C. 1H NMR ($CDCl_3$): δ 8.33 (1H, d, $J=7.2$ Hz), 8.28-8.11(7H, m), 7.94(1H, d, $J=8$ Hz), 4.00(6H, s), 3.2(1H, br.), 2.84(3H, s) ppm. ^{13}C NMR ($CDCl_3$): 183.4, 168.8, 131.5, 131.1, 130.8, 130.0, 128.9, 127.1, 126.9, 126.5, 126.4, 125.2, 124.1, 120.7, 41.3, 31.4 ppm. HRMS Calculated for $C_{22}H_{16}N_2O_2$ (M+1) 341.1284. Found 341.1287. mp 188-190 °C

N, N' didodecyl N, N' (diethyl 4,4' diphenyl diacetate) cyclobut-3-ene-1,2-dione (**8c**):

^1H NMR (CDCl_3): δ 6.85 (4H, d, $J=8.4\text{Hz}$), 6.40(4H, d, $J=8.0\text{Hz}$), 4.21(4H, q, $J=7.2\text{Hz}$), 3.99(6H,t), 3.46(4H,s), 1.33-1.23(40H, m), 1.57(4H, br.), 0.87 (6H, t, $J=6.8\text{Hz}$) ppm. ^{13}C NMR (CDCl_3): δ 186.2, 171.1, 167.6, 140.2, 131.1, 129.4, 122.8, 60.9, 52.8, 40.5, 31.9, 29.9, 29.6, 29.5, 29.3, 29.3, 26.4, 22.7, 14.3, 14.1 ppm. HRMS calculated for $\text{C}_{48}\text{H}_{72}\text{N}_2\text{O}_6$ ($M+1$) 773.5463. Found 773.5463.

3,4-bis(N-methyl-N-(naphthalen-1-yl)amino)cyclobut-3-ene-1,2-dione (**8d**):

^1H NMR ($\text{DMSO}-d_6$): Broad signals in the aromatic region are observed due to syn and anti mixture at room temperature. Therefore ^1H NMR was taken at 80°C ^1H NMR: δ 7.60(2H, d, $J=7.6\text{Hz}$), 7.47- 7.35(6H, m), 7.15(2H, d, $J=8\text{Hz}$), 6.97(2H, d, $J=7.6\text{Hz}$), 6.82(2H, t, $J=8\text{Hz}$), 3.46(6H, s) ppm. ^{13}C NMR ($\text{DMSO}-d_6$) at 80°C : 185.5, 169.5, 140.3, 134.1, 128.7, 127.6, 127.0, 126.9, 126.3, 125.6, 123.4, 122.6, 41.9 ppm. HRMS calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$ ($M+1$) 393.1597. Found 393.1596. mp $228-230^\circ\text{C}$

3,4-bis(N-methyl-N-(phenanthren-10-yl)amino)cyclobut-3-ene-1,2-dione (**8f**):

Solid obtained in 14 % yield. ^1H NMR (CDCl_3 mixture of syn and anti isomer): δ 8.0 (2H, t, $J=8\text{Hz}$), 7.94(2H, d, $J=8\text{Hz}$), 7.53-7.38(6H, t), 7.27-7.19(2H, m), 7.11-7.04(2H, m), 6.92(2H, s), 6.72(2H, t $J=8\text{Hz}$), 3.72 (6H, s) ppm. ^{13}C NMR (CDCl_3): 185.9, 169.4, 138.4, 131.0, 130.4, 129.2, 128.9, 128.2, 127.8, 127.1 126.9, 126.7, 126.6, 126.5, 126.3,

125.3, 125.1, 124.1, 123.6, 123.3, 122.9, 122.5, 122.2, 122.9, 121.6, 42.0, 41.7 ppm.
HRMS calculated for $C_{34}H_{24}N_2O_2$ (M+1) 493.1910. Found 493.1913.

3-(N-methyl-N-(pyren-1-yl)amino)-4-(N-methyl-N-phenylamino)cyclobut-3-ene-1,2-dione (9):

A 25 ml RB flask was charged with copper iodide (95 mg, 0.5mmol), L-proline (58 mg, 0.5 mmol), potassium carbonate (345 mg, 3 mmol) and anhydrous DMF (1 ml). The mixture was stirred at room temperature under nitrogen atmosphere for 20 minutes. To this 3-(N-methyl-N-(pyren-1-yl)amino)-4-(methyl amino)cyclobut-3-ene-1,2-dione (340 mg, 1 mmol) and bromobenzene (471 mg, 3 mmol) were added and the temperature increased to 120 °C and maintained for 18 hr. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (15 ml), filtered and concentrated. The residue upon column chromatography (2:3 Ethyl acetate / hexane) gives the title compound in 51% yield. 1H NMR ($CDCl_3$): δ 8.24 (1H, d, $J=8Hz$), 8.12-8.06 (5H, m), 7.94 (1H, d, $J=8Hz$), 7.86 (1H, t, $J=8Hz$), 7.42 (1H, d, $J=8Hz$), 6.23 (2H, t, $J=8Hz$), 6.13 (2H, d, $J=8Hz$), 5.75 (1H, t, $J=7.2Hz$), 4.02 (3H, s), 3.43 (3H, s) ppm. ^{13}C NMR ($CDCl_3$): 186.6, 186.2, 169.9, 167.6, 143.0, 136.9, 130.9, 130.6, 130.4, 128.4, 127.8, 127.8, 126.8, 126.5, 125.9, 125.7, 125.2, 124.9, 124.8, 124.1, 123.8, 122.6, 122.0, 120.9, 42.2, 39.9 ppm. HRMS calculated for $C_{28}H_{20}N_2O_2$ (M+1) 417.1597. Found 417.1599. mp 187-190 °C.