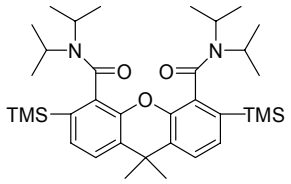
Supporting information: experimental data for 1b, 1c, 2a and syn/anti-2c; cif files of anti-2c and syn-2c.

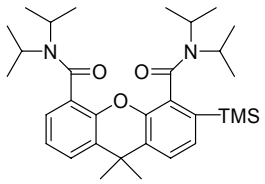
N,N,N',N'-Tetraisopropyl-3,6-bis(trimethylsilyl)-9,9-dimethyl-9H-xanthene-4,5-dicarboxamide 1b



To a solution of *N,N,N',N'*-tetraisopropyl-9,9-dimethyl-9H-xanthene-4,5-dicarboxamide **1a** (502 mg, 1.08 mmol) in dry THF (20 mL) was added *N,N,N',N'*-tetramethylethylenediamine (0.81 mL, 5.37 mmol) and the solution was cooled at -78ºC under nitrogen and stirred for 5 min. *n*-Butyllithium (2.4 mL, 5.52 mmol, 2.3 M in hexanes) was added and the mixture was stirred for 1 h. Freshly distilled trimethylsilyl chloride (2 mL) was added and the mixture was allowed to warm to room temperature. The mixture was partitioned between AcOEt and H_2O and the organic phase was washed with H_2O, dried, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (Petrol to petrol:AcOEt 30%) to yield **1b** (461 mg, 70%), followed by mono-silylated **1b'** (103 mg, 18%).

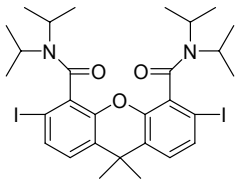
M.p. 190-192 ºC. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.31 (s, 18H), 0.99 (d, *J* = 6.9 Hz, 6H), 1.03 (d, *J* = 6.9 Hz, 6H), 1.53 (d, *J* = 6.9 Hz, 6H), 1.54 (d, *J* = 6.9 Hz, 6H), 1.62 (s, 6H), 3.39 (septet, *J* = 6.9 Hz, 2H), 4.30 (septet, *J* = 6.9 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 0.7 (CH_3), 21.5 (CH_3), 21.8 (CH_3), 21.9 (CH_3), 22.2 (CH_3), 32.9 (CH_3), 33.8 (Cq), 45.7 (CH), 49.6 (CH), 124.9 (CH), 129.7 (CH), 130.1 (Cq), 131.9 (Cq), 137.0 (Cq), 145.8 (Cq), 167.7 (Cq). IR (film) 1634 cm^{-1}. HRMS Calcd for $C_{35}H_{57}O_3N_2Si_2$: 6.9.3902. Found: 609.3903.

N,N,N',N'-Tetraisopropyl-3-trimethylsilyl-9,9-dimethyl-9H-xanthene-4,5-dicarboxamide 1b'



^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.308 (s, 9H), 0.95 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.44 (d, *J* = 6.9 Hz, 3H), 1.46 (s, 3H), 1.53 (d, *J* = 6.9 Hz, 6H), 1.60 (d, *J* = 6.9 Hz, 3H), 1.75 (s, 3H), 3.50 (septet, *J* = 6.9 Hz, 1H), 3.52 (septet, *J* = 6.9 Hz, 1H), 3.77 (septet, *J* = 6.9 Hz, 1H), 4.01 (septet, *J* = 6.9 Hz, 1H), 6.95 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.05 (dd, *J* = 7.8 and 7.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 0.5 (CH_3), 19.9 (CH_3), 20.1 (CH_3), 21.1 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 21.88 (CH_3), 21.93 (CH_3), 22.2 (CH_3), 29.1 (CH_3), 34.0 (Cq), 35.0 (CH_3), 45.6 (CH), 45.9 (CH), 50.4 (CH), 123.0 (CH), 124.5 (CH), 125.8 (CH), 125.9 (CH), 127.8 (Cq), 129.9 (CH), 130.4 (Cq), 130.7 (Cq), 131.9 (Cq), 136.5 (Cq), 145.7 (Cq), 146.2 (Cq), 167.8 (Cq), 168.2 (Cq). IR (film) 1640 cm^{-1}. HRMS Calcd for $C_{32}H_{49}O_3N_2Si$: 537.3507. Found: 537.3515.

N,N,N',N'-Tetraisopropyl-3,6-diiodo-9,9-dimethyl-9H-xanthene-4,5-dicarboxamide 1c



Method A

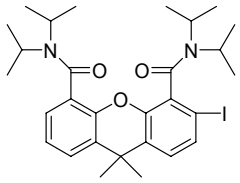
To a solution of *N,N,N',N'*-tetraisopropyl-9,9-dimethyl-9H-xanthene-4,5-dicarboxamide **1a** (100 mg, 0.21 mmol) in dry THF (10 mL) was added *N,N,N',N'*-tetramethylethylenediamine (0.13 mL, 0.86 mmol) and the solution was cooled to -78ºC under nitrogen and stirred for 5 min. *n*-Butyllithium (0.37 mL, 0.86 mmol, 2.35 M in hexanes) was added and the mixture was stirred for 1 h. A solution of Iodine (350 mg, 1.38 mmol) in dry THF (3 mL) was added, the mixture stirred for 30 min at -78ºC and then it was allowed to warm to room temperature. The mixture was partitioned between AcOEt and H_2O and the organic phase was washed with H_2O, dried, filtered and the solvent was removed under reduced pressure. The crude

product was purified by flash chromatography (Petrol to petrol:AcOEt 20%) to yield the title compound (21 mg, 14%) with a mono-iodinated product **1c'** (30 mg, 24%) eluting second.

Method B
To a solution of **1b** (50 mg, 0.082 mmol) in DCM (10 mL) was added ICl (0.35 mL, 0.35 mmol, 1 M in DCM). The solution was stirred at rt for 1 h and $Na_2S_2O_3$ aqueous saturated solution was added. After decolouration the mixture was extracted with DCM and the organic extracts were dried, filtered and the solvent was removed under reduced pressure to yield **1c** (59 mg, quantitative).

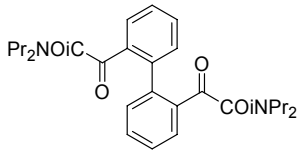
M.p. 300-302 ºC. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.15 (d, *J* = 6.9 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.55 (d, *J* = 6.9 Hz, 6H), 1.59 (s, 6H), 1.59 (d, *J* = 6.9 Hz, 6H), 3.44 (septet, *J* = 6.9 Hz, 2H), 4.13 (septet, *J* = 6.9 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 20.7 (CH_3), 21.5 (CH_3), 22.1 (CH_3), 22.6 (CH_3), 33.4 (CH_3), 34.2 (Cq), 46.4 (CH), 51.4 (CH), 92.2 (Cq), 127.6 (CH), 129.6 (Cq), 132.1 (Cq), 134.7 (CH), 145.8 (Cq), 166.7 (Cq). IR (film) 1644 cm^{-1}. HRMS Calcd for $C_{29}H_{39}O_3N_2I_2$: 717.1045. Found: 717.1052.

***N,N,N',N'*-Tetraisopropyl-3-iodo-9,9-dimethyl-9H-xanthene-4,5-dicarboxamide 1c'**



M.p. 254-255 ºC. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.99 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.45 (d, *J* = 6.9 Hz, 3H), 1.53 (d, *J* = 6.9 Hz, 3H), 1.55 (s, 3H), 1.57 (d, *J* = 6.9 Hz, 3H), 1.64 (d, *J* = 6.9 Hz, 3H), 1.67 (s, 3H), 3.53 (septet, *J* = 6.9 Hz, 1H), 3.54 (septet, *J* = 6.9 Hz, 1H), 3.83 (septet, *J* = 6.9 Hz, 1H), 3.84 (septet, *J* = 6.9 Hz, 1H), 6.97 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 20.0 (CH_3), 20.1 (CH_3), 20.3 (CH_3), 20.9 (CH_3), 21.7 (CH_3), 22.0 (CH_3), 22.1 (CH_3), 22.2 (CH_3), 31.4 (CH_3), 34.0 (Cq), 34.3 (CH_3), 45.7 (CH), 46.1 (CH), 51.41 (CH), 51.44 (CH), 91.5 (Cq), 123.4 (CH), 125.9 (CH), 126.2 (CH), 127.2 (CH), 127.7 (Cq), 129.7 (Cq), 129.9 (Cq), 131.7 (Cq), 133.9 (CH), 145.3 (Cq), 146.2 (Cq), 166.6 (Cq), 167.9 (Cq). IR (film) 1643 cm^{-1}. HRMS Calcd for $C_{29}H_{40}O_3N_2I$: 591.2078. Found: 591.2075.

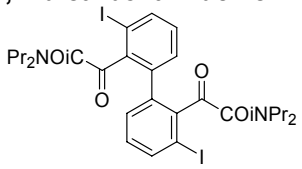
***N,N,N',N'*-Tetraisopropylbiphenyl-2,2'-dicarboxamide**[1] **2a**



To a solution of diphenic acid (10 g, 41 mmol), in dry DCM (250 mL) was added oxalyl chloride (11 mL, 126 mmol) followed by three drops of DMF. The mixture was stirred at rt under nitrogen for 1.5 h and the solvent was removed under reduced pressure. The residue was redisolved in dry DCM (250 mL), and freshly distilled diisopropylamine (50 mL, 357 mmol) and pyridine (20 mL, 247 mmol) were added. The mixture was stirred overnight under nitrogen at rt and then it was washed with NaOH 1N (x2), and HCl 3N (x2). The organic phase was dried, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (Petrol:AcOEt 20%) to yield the title compound (12.8 g, 74%).
^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.80 (d, J = 6.6 Hz, 6H), 1.08 (d, J = 6.6 Hz, 6H), 1.34 (d, J = 6.6 Hz, 6H), 1.49 (d, J = 6.6 Hz, 6H), 3.38 (septet, J = 6.6 Hz, 2H), 3.96 (septet, J = 6.6 Hz, 2H), 7.24-7.34 (m, 6H), 7.50-7.53 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 19.9 (CH_3), 20.6 (CH_3), 20.9 (CH_3), 21.3 (CH_3), 45.9 (CH), 50.7 (CH), 126.7 (CH), 127.6 (CH), 128.0 (CH), 130.6 (CH), 136.5 (Cq), 138.6 (Cq), 170.1 (Cq). IR (film) cm^{-1}. MS (ES+) 431 (100, M+Na).

[1] J. Clayden, A. Lund, L. H. Youssef, *Org. Lett.* **2001**, *3*, 4133-4136.

***N,N,N',N'*-Tetraisopropylbiphenyl-3,3'-diiodo-2,2'-dicarboxamide 2c**



To a solution of *N,N,N',N'*-tetraisopropylbiphenyl-2,2'-dicarboxamide **2a**[1] (2 g, 4.90 mmol) in dry THF (200 mL) was added *N,N,N',N'*-tetramethylethylenediamine (7.5 mL, 48.9 mmol) and the solution was cooled at -78ºC under nitrogen and stirred for 5 min. *s*-Butyllithium (40 mL, 48 mmol, 1.2 M in hexanes) was added and the mixture was stirred for 1 h. Freshly distilled trimethylsilyl chloride (8 mL) was added and the mixture was allowed to warm to room temperature gradually overnight. The mixture was partitioned between AcOEt and H_2O and the organic phase was washed with H_2O, dried, filtered and the solvent was removed under reduced pressure. The crude product **2b** was dissolved in DCM (100 mL) and ICl (20 mL, 20 mmol, 1 M in DCM) was added and the solution was stirred at room temperature 24 h. $Na_2S_2O_3$ aqueous saturated solution was added, and after decolouration the mixture was extracted with DCM. The organic extracts were dried, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (Petrol to AcOEt) to yield **2c** (95:5 *syn*:*anti*) (1.079g, 33%).

Conversion of *syn*-2c to *anti*-2c

A solution of **2c** (95:5 *syn*:*anti*) (195 mg, 0.42 mmol) in toluene (20 mL) was stirred at reflux for 2 h. The solvent was evaporated under reduced pressure to yield **2c** (10:90 *syn*:*anti*) (195 mg, quantitative).

Anti-**2c**: M.p. 254-256 ºC. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.75-0.97 (m, 6H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.27-1.33 (m, 6H), 1.55 (d, *J* = 6.6 Hz, 6H), 3.34-3.44 (m, 2H), 3.73 (septet, *J* = 6.6 Hz, 2H), 6.99 (t, *J* = 7.9 Hz, 2H), 7.57-7.61 (m, 2H), 7.81 (dd, *J* = 7.9 and 1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 19.9 (CH_3), 20.0 (CH_3), 21.0 (CH_3), 21.4 (CH_3), 46.3 (CH), 50.8 (CH), 94.1 (Cq), 128.6 (CH), 134.5 (Cq), 139.1 (CH), 142.5 (Cq), 168.3 (Cq). IR (film) 1630 cm^{-1}.

Conversion of *anti*-2c to *syn*-2c

A solution of **2c** (10:90 *syn*:*anti*) (10 mg, 0.015 mmol) in toluene (1 mL) was treated with $TiCl_4$ (4 μL, 0.03 mmol) and stirred at 90 ºC for 1 h. The solution was partitioned between DCM and NH_4Cl aqueous saturated solution and extracted with DCM. The organic extracts were dried, filtered and the solvent was removed under reduced pressure to yield **2c** (97:3 *syn*:*anti*) (10 mg, quantitative). Other metal-promoted switches were carried out in a similar way, as detailed in Table 2.

Syn-**2c** :M.p. 248-250 ºC. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.28 (d, *J* = 6.6 Hz, 6H), 1.19 (d, *J* = 6.6 Hz, 6H), 1.18 (d, *J* = 6.6 Hz, 6H), 1.63 (d, *J* = 6.6 Hz, 6H), 3.37 (septet, *J* = 6.6 Hz, 2H), 3.79 (septet, *J* = 6.6 Hz, 2H), 7.00 (t, *J* = 7.9 Hz, 2H), 7.84 (dd, *J* = 7.9 and 1 Hz, 2H), 7.99 (dd, *J* = 7.9 and 1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 19.3 (CH_3), 19.9 (CH_3), 20.5 (CH_3), 46.8 (CH), 50.7 (CH), 95.5 (Cq), 129.3 (CH), 130.6 (CH), 134.5 (Cq), 139.8 (CH), 142.9 (Cq), 169.2 (Cq). IR (film) 1624 cm^{-1}. HRMS Calcd for $C_{26}H_{34}O_2N_2I_2Na$: 683.0602. Found: 683.0606.