

Interaction, Bond Formation or Reaction Between a Dimethylamino Group and an Adjacent Alkene or Aldehyde Group in Aromatic Systems Controlled by Remote Molecular Constraints.

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Synthesis:

Peri-Diphenylnaphthalenes.	p. 2
Acenaphthenes.	p. 6
9,9-Dimethylfluorenes.	p. 10

X-ray Crystallography.

Peri-Diphenylnaphthalenes.	p. 20
Acenaphthenes.	p. 25
9,9-Dimethylfluorenes.	p. 29

I. Synthesis of Compounds.

General. Solution NMR spectra were measured on a Jeol ECLIPSE 400 ECX or ECZ spectrometer at 400 MHz for ^1H and at 100.6 MHz for ^{13}C using CDCl_3 as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated Total Reflection sampling on solids or oils and are reported in cm^{-1} . Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Swansea. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University.

A. DIPHENYLS DERIVATIVES.

Experimental details for preparation and characterisation of **16**, **17** and **18** have been previously described.^{S1}

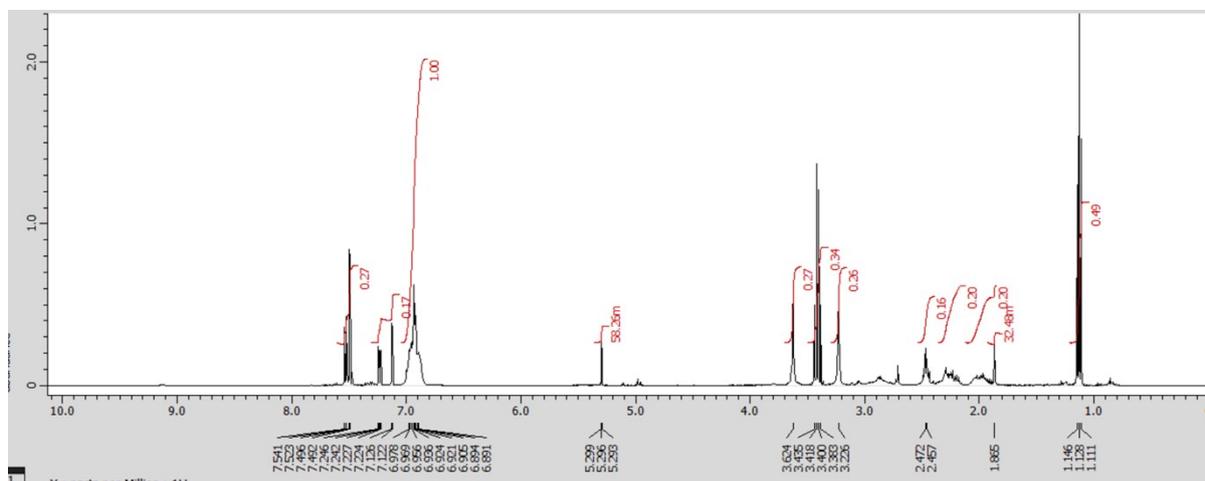
Preparation of methyl (*E*)-2-cyano-3-(8'-(dimethylamino)-4',5'-diphenylnaphthalen-1'-yl)propenoate, **19/20**.

Dimethylamino-aldehyde **17** (75 mg, 0.21 mmol), methyl cyanoacetate (0.075 mL, 0.85 mmol) and ethylenediamine diacetate (6 mg, 0.03 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and refluxed for 24 h. The solvent was removed *in vacuo* and the crude product purified by flash column chromatography (4:1 hexane: ethyl acetate) to give **19/20** as a yellow solid (80 mg, 87%), m.p. 165-168°C. (**19** in the solid state, **20** in CDCl_3 solution). δH (400 MHz, CDCl_3 , 24 °C): 8.95 (1H, s, 3-*H*), 7.58 (1H, d, $J = 7.3$ Hz, Ar-*H*₁), 7.39-7.51 (3H, m, Ar-*H*₃), 6.87-6.97 (10H, m, Ar-*H*₁₀), 3.94 (3H, s, OCH_3), 2.77 (6H, s, 8'- $\text{N}(\text{CH}_3)_2$); δC (100 MHz, CDCl_3 , 24 °C): 161.8 (C=O), 156.7 (3-C), 148.4 (8'-C), 142.9, 142.3, 142.0, 138.9, 132.6, 131.6, 131.5, 130.5, 129.9, 129.8, 127.9, 126.4, 126.2, 126.1, 118.7 (Ar- C_{21}), 117.4 (CN), 87.5 (2-C), 52.7 (OCH_3), 45.7 ($\text{N}(\text{CH}_3)_2$); $\nu_{\text{max}}/\text{cm}^{-1}$: 2167 (C \equiv N), 1638 (C=O), 1433, 1371, 1345, 1276, 1250, 1189, 1095, 918, 849, 756, 695; Found: C, 80.53; H, 5.70; N, 6.57%. Calc. for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_2$: C, 80.53; H, 5.59; N, 6.48%.

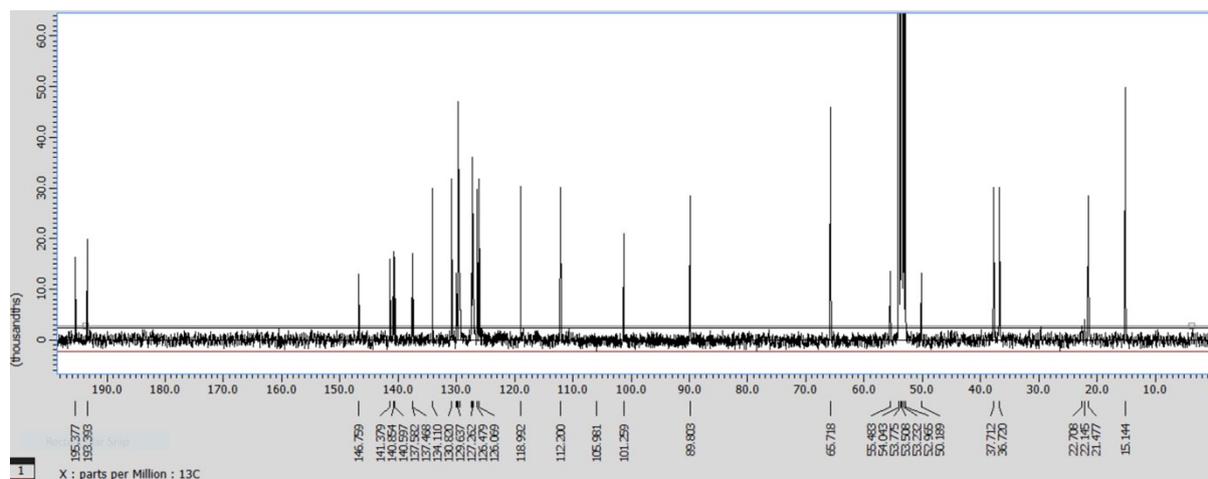
Preparation of 1-(1',1'-dimethyl-5',6'-diphenyl-1',2'-dihydrobenzo[cd]indol-1'-ium-2'-yl)-2,6-dioxocyclohexan-1-ide, **21.**

Dimethylamino-aldehyde **17** (100 mg, 0.28 mmol), 1,3-cyclohexandione (28 mg, 0.25 mmol) and ethylenediamine diacetate (5 mg, 0.03 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and refluxed for 24 h. The solvent was removed *in vacuo* and the crude oil triturated with Et₂O, yielding a precipitate which was isolated give **21** as a yellow solid (35 mg, 31%), m.p. decomp. > 150°C. δ H (400 MHz, CD₂Cl₂, 24 °C): 7.53 (1H, d, J = 7.3 Hz, 8'-H), 7.49-7.52 (2H, m, 4'-, 7'-H), 7.23 (1H, dd, J = 7.3, 1.4 Hz, 3'-H), 7.12 (1H, d, J = 1.4 Hz, 2'-H), 6.85-7.04 (10H, m, Ar-H₁₀), 3.62 (3H, s, NCH₃), 3.23 (3H, s, NCH₃), 2.43-2.50 (2H, m, CH₂CH₂CH₂), 2.17-2.32 (2H, m, CH₂CH₂CH₂), 1.90-2.06 (2H, m, CH₂CH₂CH₂); δ C (100 MHz, CD₂Cl₂, 24 °C): 195.4 & 193.4 (C=O), 146.8 (8a'-C), 141.4, 140.9, 140.6, 137.6, 137.5, 134.1, 130.8, 130.0, 129.6, 127.5, 127.3, 127.1, 126.5, 126.0 (Ar-C₁₄), 119.0 (3'-C), 112.2 (8'-C), 101.3 (Ar-C₁), 89.8 (2-C), 55.5 & 50.2 (N(CH₃)₂), 37.7 & 36.7 (3-, 5-C), 21.5 (4-C); $\nu_{\max}/\text{cm}^{-1}$: 3028, 2965, 2927, 2868, 1587, 1522 (C=O), 1444, 1431, 1401, 1384, 1349, 1179, 1120, 1073, 998, 982, 941, 844, 754, 726, 697; HRMS (ESI) calcd for C₃₁H₂₈NO₂ ([M+H]⁺): 446.2120, found: 446.2137.

¹H NMR spectrum for **21**.



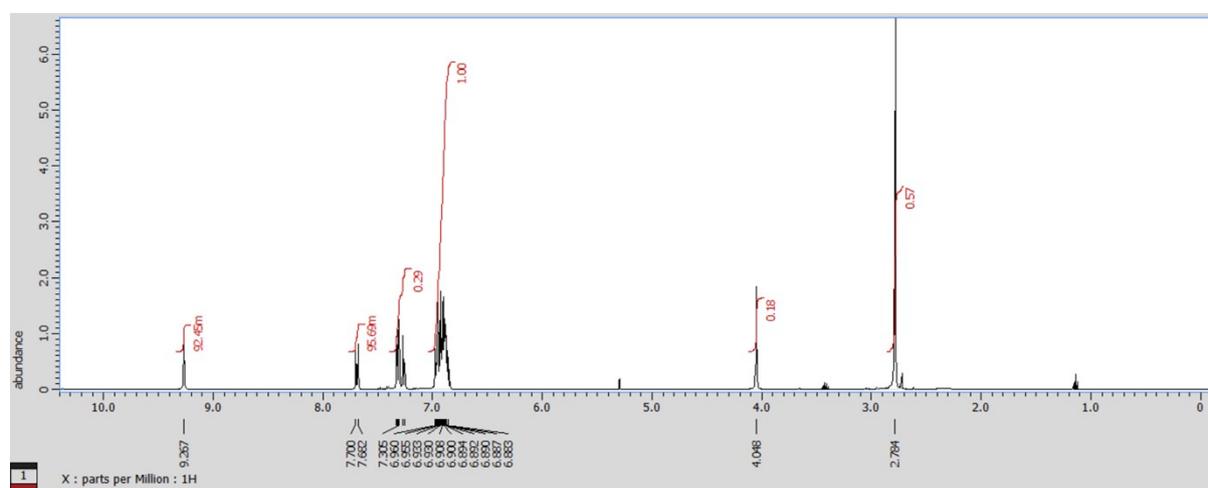
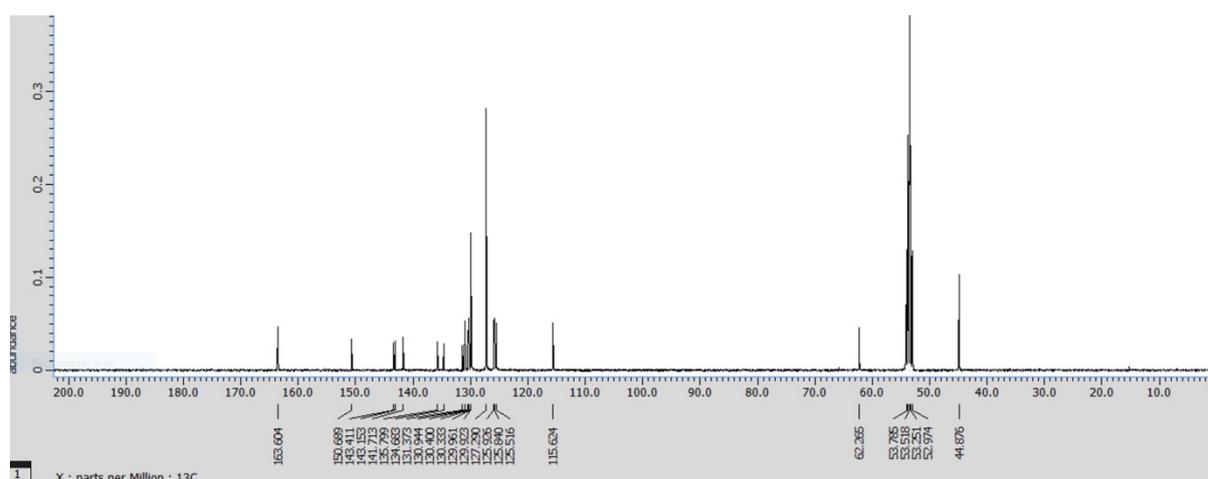
^{13}C NMR spectrum for **21**.



(diethyl ether present)

Preparation of N, N-Bis(4',5'-diphenyl-8'-dimethylamino-naphthalen-1'-methylidene)-1,2-ethanediamine, **22**.

Dimethylamino aldehyde **17** (100 mg, 0.28 mmol), nitromethane (0.05 mL, 0.85 mmol) and ethylenediamine diacetate (8 mg, 0.04 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and stirred at room temperature for 24 h. The solvent was removed *in vacuo* and the crude oil triturated with Et₂O, and the resultant precipitate **22** was isolated as a yellow solid (22 mg, 69%), m.p. 218-221°C. δH (400 MHz, CD₂Cl₂, 24 °C): 9.27 (2H, s, 2 x N=CH), 7.69 (2H, d, J = 7.3 Hz, 2 x 2'-H), 7.30-7.33 (4H, m, 2 x 3'-, 6'-H), 7.26 (2H, d, J = 7.8 Hz, 2 x 7'-H), 6.87-6.96 (20H, m, 4 x Ph-H₅), 4.05 (4H, s, 1-,2-H₂), 2.78 (12H, s, 2 x 8'-N(CH₃)₂); δC (100 MHz, CDCl₃, 24 °C): 163.6 (2 x N=CH), 150.7 (2 x 8'-C), 143.4, 143.2, 141.7, 135.8, 134.7, 131.4, 130.9, 130.4, 130.3, 130.0, 129.9, 127.3 (Ar-C₃₄), 125.9 (2 x 2'-C), 125.8, 125.5 (Ar-C₄), 115.6 (2 x 7'-C), 62.3 (1-,2-C), 44.9 (2 x N(CH₃)₂); $\nu_{\text{max}}/\text{cm}^{-1}$: 3075, 2865, 1632, 1492, 1440, 1390, 1354, 1276, 1183, 1146, 1114, 1036, 928, 833, 758, 695; HRMS (ESI) calcd for C₅₂H₄₇N₄ ([M+H]⁺): 727.3800, found: 727.3771.

¹H NMR spectrum for **22**.¹³C NMR spectrum for **22**.

Preparation of 2-hydroxy-1,1-dimethyl-5,6-diphenyl-1,2-dihydrobenzo[cd]indol-1-ium chloride, **26**.

Dimethylamino-aldehyde **17** (75 mg, 0.21 mmol) was dissolved in anhydrous diethyl ether (5 mL) and ethereal hydrochloric acid (1M, 0.32 mL, 0.32 mmol) was added dropwise with immediate formation of a white precipitate. The solution was stirred for a further 1 h. before the solid was collected by careful filtration under a flow of nitrogen. The solid was washed with cold anhydrous diethyl ether and dried under vacuum to give **26** as an off-white solid (61 mg, 74%), m.p. decomp. > 150°C. δ_H (400 MHz, CDCl₃, 24 °C): 7.81 (1H, d, J = 7.3 Hz, 3-H),

7.70 (1H, d, $J = 7.3$ Hz, 4-*H*), 7.63 (2H, AB system, $J = 7.6$ Hz, 7-,8-*H*), 7.31 (1H, s, 2-*H*), 6.86-7.03 (11H, m, *OH*, Ar-*H*₁₀), 3.84 (3H, s, N(*CH*₃)), 3.43 (3H, s, N(*CH*₃)); δ_C (100 MHz, CDCl₃, 24 °C): 144.0 (8a-*C*), 142.1, 141.6, 140.0, 139.9 (Ar-*C*₄), 134.3 (4-*C*), 131.7 (7-*C*), 131.3, 129.4, 129.1, 127.4, 126.9, 126.7 (Ar-*C*₁₃), 122.7 (3-*C*), 113.7 (8-*C*), 110.5 (2-*C*), 53.5 & 48.7 (N(*CH*₃)₂); $\nu_{\max}/\text{cm}^{-1}$: 3050, 2957, 1492, 1466, 1442, 1291, 1176, 1133, 1105, 930, 861, 842, 821, 762, 697; Found: C, 77.20; H, 5.58; N, 3.58%. Calc. for C₂₅H₂₂NOCl: C, 77.41; H, 5.72; N, 3.61%.

Preparation of 2-hydroxy-1,1-dimethyl-5,6-diphenyl-1,2-dihydrobenzo[*cd*]indol-1-ium monomalonate, 27.

Dimethylamino-aldehyde **17** (100 mg, 0.28 mmol) and Meldrum's acid (82 mg, 0.56 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and stirred at room temperature for 24 h. The solvent was removed *in vacuo* and the crude oil triturated with Et₂O, yielding a precipitate which was isolated and recrystallised from ethyl acetate to give **27** as an off-white solid (63 mg, 49%), m.p. 168-171°C. δ_H (400 MHz, CDCl₃, 24 °C): 7.80 (1H, d, $J = 7.3$ Hz, 3-*H*), 7.72 (1H, br s, 2-*H*), 7.70 (1H, d, $J = 6.9$ Hz, 4-*H*), 7.58 (2H, m, 7-, 8-*H*), 6.86-7.06 (10H, m, Ar-*H*₁₀), 3.50 (6H, s, N(*CH*₃)₂), 3.31 (2H, s, (O=C)₂CH₂); δ_C (100 MHz, CDCl₃, 24 °C): 173.4 (2 x C=O), 144.4 (8a-*C*), 141.9, 141.8, 140.0, 139.8 (Ar-*C*₄), 134.1 (4-*C*), 132.3 (Ar-*C*₁), 131.5 (7-*C*), 129.4, 129.3, 127.7, 127.4, 127.3, 126.9, 126.7 (Ar-*C*₉), 123.1 (3-*C*), 113.7 (8-*C*), 49.6 (N⁽⁺⁾(*CH*₃)₂), 38.8 (CH₂); $\nu_{\max}/\text{cm}^{-1}$: 3051, 2415 br, 2117 br, 1890 br, 1724 (C=O), 1588, 1485, 1465, 1440, 1407, 1366, 1260, 1180, 1139, 1098, 985, 930, 869, 821, 753, 712, 695; Found: C, 73.50; H, 5.27; N, 2.87%. Calc. for C₂₈H₂₅NO₅: C, 73.88; H, 5.53; N, 3.08%.

B. ACENAPHTHENE DERIVATIVES.

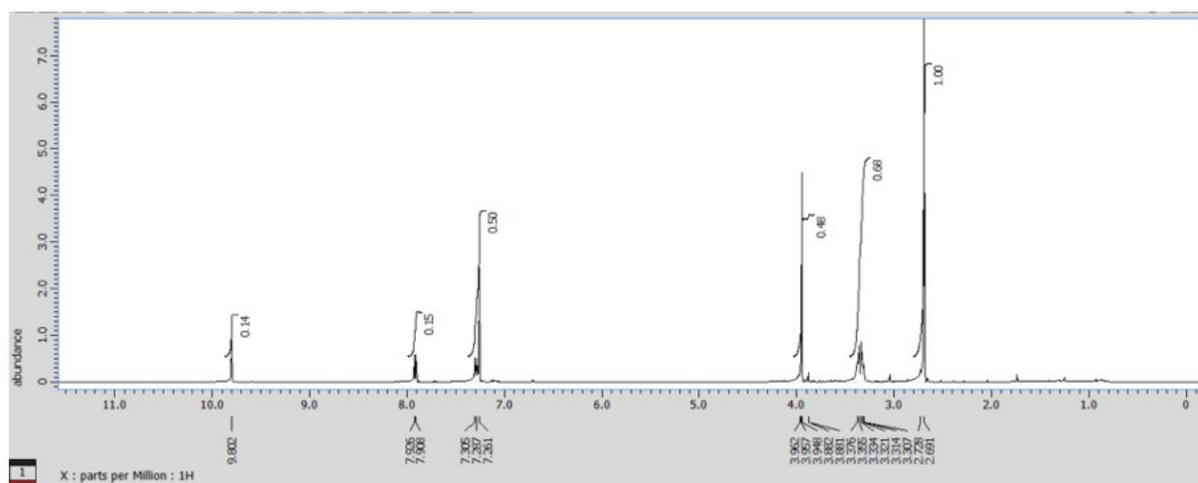
Experimental details for preparation and characterisation of **28** and **29** have been previously described.^{S1}

Preparation of methyl (*E*)-2-cyano-3-(6'-(dimethylamino)-1',2'-dihydroacenaphthylen-5'-yl)propenoate, 30.

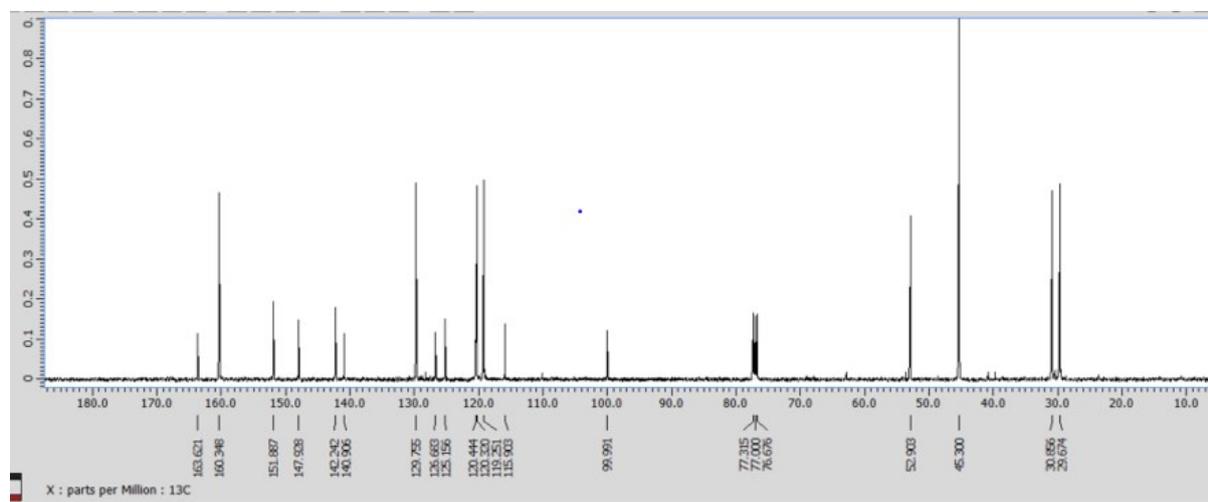
Dimethylamino-aldehyde **28** (100 mg, 0.44 mmol) was dissolved in anhydrous MeOH (10 mL). Methyl cyanoacetate (0.12 mL, 1.33 mmol) and ethylenediamine diacetate (8 mg, 0.04 mmol) were added and the deep orange solution was heated to reflux for 16 h. The solvent was

removed *in vacuo* to yield a crude dark orange solid which was purified by flash column chromatography (1:4 EtOAc:petrol 40-60), to give **30** as an orange solid (120 mg, 88%), m.p. 82-85°C. δ H (400 MHz, CDCl₃, 24 °C): 9.80 (1H, s, 3-*H*), 7.92 (1H, d, *J* = 7.3 Hz, 4'-*H*), 7.29 (1H, d, *J* = 7.3 Hz, 3'-*H*), 7.26 (2H, s, 7'-, 8'-*H*), 3.95 (3H, s, OCH₃), 3.31-3.438 (4H, m, 1'-, 2'-*H*), 2.69 (6H, s, N(CH₃)₂); δ C (100 MHz, CDCl₃, 24 °C): 163.6 (C=O), 160.3 (3-C), 151.9 (2a'-C), 147.9 (6'-C), 142.2 (8a'-C), 140.9 (5'-C), 129.7 (4'-C), 126.7 (5a'-C), 125.1 (2a''-C), 120.4 & 120.3 (7'-, 8'-C), 119.3 (3'-C), 115.9 (C≡N), 100.0 (2-C), 52.9 (OCH₃), 45.3 (N(CH₃)₂), 30.9 & 29.7 (1'-, 2'-C); $\nu_{\max}/\text{cm}^{-1}$: 2922, 2849, 2825, 2786, 2223 (C≡N), 1727 (C=O), 1589, 1436, 1263, 1246, 1209, 1088, 957, 842, 829, 764, 751; HRMS (ESI) calcd for C₁₉H₁₉N₂O₂ ([M+H]⁺): 307.1440, found: 307.1447.

¹H NMR spectrum for **30**.



¹³C NMR spectrum for **30**.



Preparation of 1',2',3',4'-Tetrahydro-1',2,2-trimethyl-*spiro*[1,3-dioxane-5,3'-acenaphth[5,6-bc]azepine]-4,6-dione, 34.

Dimethylamino-aldehyde **28** (120 mg, 0.53 mmol) was dissolved in anhydrous DMSO (10 mL) under nitrogen and Meldrum's acid (115 mg, 0.8 mmol) was added, the deep orange solution was stirred at room temperature. After 24 h, a precipitate had formed which was collected via filtration and dried under vacuum to give **34** as a yellow solid (150 mg, 80%), m.p. 198-201°C. δ H (400 MHz, CDCl₃, 24 °C): 7.08-7.14 (2H, m, 6'-, 9'-H), 6.99 (1H, d, J = 6.9 Hz, 5'-H), 6.75 (1H, d, J = 7.3 Hz, 10'-H), 3.70-3.90 (4H, m, 2'-, 4'-H₂), 3.25-3.35 (4H, m, 8'-, 7'-H₂), 3.08 (3H, s, NCH₃), 1.86 (3H, s, 2-CH₃), 1.75 (3H, s, 2-CH₃); δ C (100 MHz, CDCl₃, 24 °C): 169.0 (2 x C=O), 148.4, 145.5, 141.2, 137.9, 129.0 (Ar-C₅), 128.2 (5'-C), 124.7 (Ar-C₁), 119.5 & 119.1 (6'-, 9'-C), 110.3 (10'-C), 104.9 (2-C), 63.6 (3'-C), 55.3 (2'-C), 41.5 (4'-C), 40.8 (NCH₃), 30.5 & 29.6 (7'-,8'-C), 29.4 & 29.0 (2-CH₃); $\nu_{\max}/\text{cm}^{-1}$: 1772, 1735 (C=O), 1589, 1502, 1472, 1448, 1422, 1388, 1295, 1276, 1239, 1176, 1151, 1129, 1101, 1082, 1030, 941, 913, 820, 777; Found: C, 71.65; H, 5.99; N, 4.05%. Calc. for C₂₁H₂₁NO₄: C, 71.72; H, 5.98; N, 3.98%.

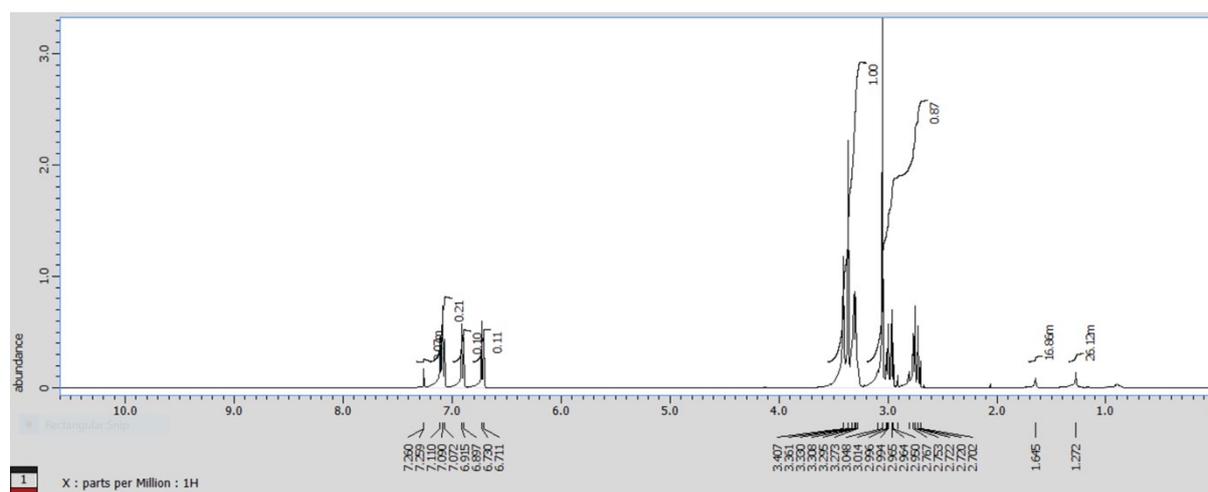
Preparation of 1',2',3',4'-Tetrahydro-1'-methyl-*spiro*[cyclohexan-1,3'-acenaphth[5,6-bc]azepine]-2,6-dione, 35.

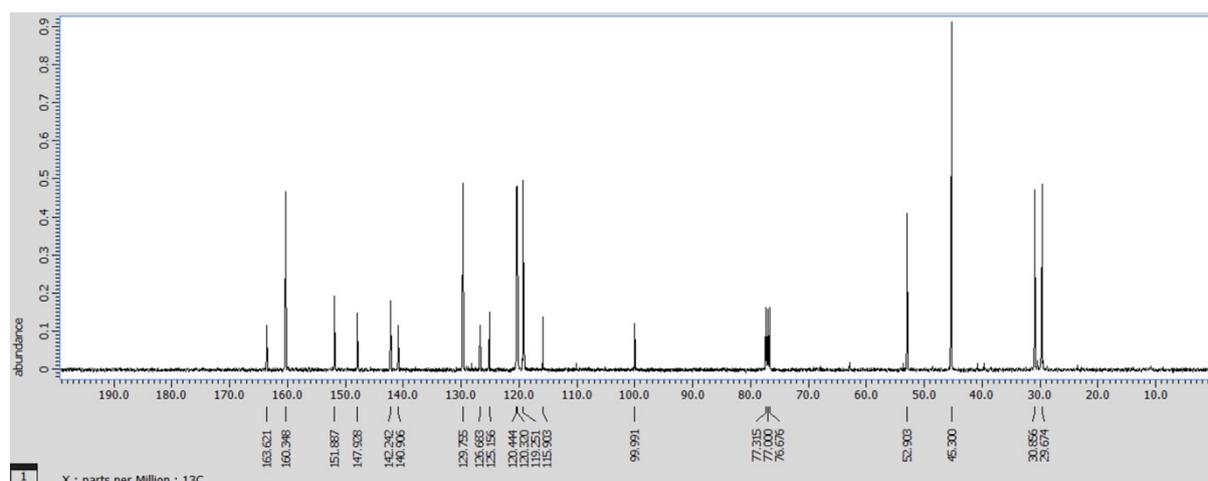
Dimethylamino-aldehyde **28** (100 mg, 0.44 mmol) was dissolved in anhydrous DMSO (10 mL) under nitrogen and 1,3-cyclohexanedione (88 mg, 0.79 mmol) was added, and the deep orange solution was stirred at room temperature. After 24 h, H₂O (20 mL) was added to produce a pale orange precipitate. The precipitate was collected via filtration and dried under vacuum to give **35** as a pale orange solid (84 mg, 59%), m.p. decomp. > 155°C. δ H (400 MHz, CDCl₃, 24 °C): 7.08 (1H, d, J = 7.8 Hz, 9'-H), 7.04 (1H, d, J = 6.9 Hz, 6'-H), 6.94 (1H, d, J = 6.9 Hz, 5'-H), 6.78 (1H, d, J = 7.8 Hz, 10'-H), 3.63-3.72 (4H, m, 2'-, 4'-H₂), 3.22-3.33 (4H, m, 7'-, 8'-H₂), 3.03 (3H, s, NCH₃), 2.62-3.00 (4H, m, 3-, 5-H₂), 2.10-2.25 (1H, m, 4-H _{α}), 1.75-1.89 (1H, m, 4-H _{β}); δ C (100 MHz, CDCl₃, 24 °C): 207.5 (2 x C=O), 149.6, 145.4, 141.2, 137.1, 129.4 (Ar-C₅), 127.0 (5'-C), 125.3 (Ar-C₁), 119.4 & 119.3 (6'-, 9'-C), 109.9 (10'-C), 73.7 (3'-C), 57.8 (2'-C), 40.8 (4'-C), 40.6 (NCH₃), 37.9 (3-, 5-C), 30.7 & 29.7 (7', 8'-C), 18.5 (4-C); $\nu_{\max}/\text{cm}^{-1}$: 1718, 1684 (C=O), 1593, 1504, 1470, 1431, 1317, 1272, 1190, 1108, 1079, 1004, 834, 767; Found: C, 78.90; H, 6.65; N, 4.37%. Calc. for C₂₁H₂₁NO₂: C, 78.90; H, 6.58; N, 4.38%.

Preparation of 1',2',3',4'-Tetrahydro-1'-methyl-*spiro*[cyclopentan-1,3'-acenaphth[5,6-bc]azepine]-2,5-dione, **36**.

Dimethylamino-aldehyde **28** (100 mg, 0.44 mmol) was dissolved in anhydrous DMSO (10 mL) under nitrogen and 1,3-cyclopentanedione (65 mg, 0.67 mmol) was added, the deep orange solution was stirred at room temperature for 24 h to give a pale orange solution, H₂O (20 mL) was added to produce a pale orange precipitate. The precipitate was dissolved by the addition of DCM (30 mL) and the organic layer separated. The aqueous solution was extracted further with DCM (2 x 30 mL). The combined organics were washed with H₂O (30 mL) and brine (30 mL), dried over MgSO₄ and filtered. The solvent was removed *in vacuo* to give a crude orange solid which was purified by flash column chromatography (1:2 EtOAc:petrol 40-60), to give **36** as an off-white solid (54 mg, 40%), m.p. 180-183°C. δ H (400 MHz, CDCl₃, 24 °C): 7.07-7.11 (2H, 2 overlapping d, 6'-, 9'-H), 6.91 (1H, d, J = 6.9 Hz, 5'-H), 6.72 (1H, d, J = 7.3 Hz, 10'-H), 3.41 (2H, br s, 4'-H₂), 3.36 (2H, s, 2'-H₂), 3.25-3.34 (4H, m, 7'-, 8'-H₂), 3.05 (3H, s, NCH₃), 2.91-3.01 (2H, m, 3- or 4-H₂), 2.70-2.81 (2H, m, 3- or 4-H₂); δ C (100 MHz, CDCl₃, 24 °C): 213.6 (2 x C=O), 148.6, 145.3, 141.1, 137.5, 128.8 (Ar-C₅), 127.6 (5'-C), 124.9 (Ar-C₁), 119.3 & 119.1 (6'-, 9'-C), 110.3 (10'-C), 63.5 (3'-C), 59.0 (2'-C), 41.1 (NCH₃), 38.9 (4'-C), 34.7 (3-, 4-C), 30.5 & 29.5 (7'-, 8'-C); $\nu_{\max}/\text{cm}^{-1}$: 2917, 1707 (C=O), 1591, 1502, 1470, 1416, 1285, 1271, 1149, 1101, 1077, 1037, 1000, 943, 834, 805, 766; HRMS (ESI) calcd for C₂₀H₂₀NO₂ ([M+H]⁺): 306.1494, found: 306.1486.

¹H NMR spectrum of **36**.



¹³C NMR spectrum of **36**.

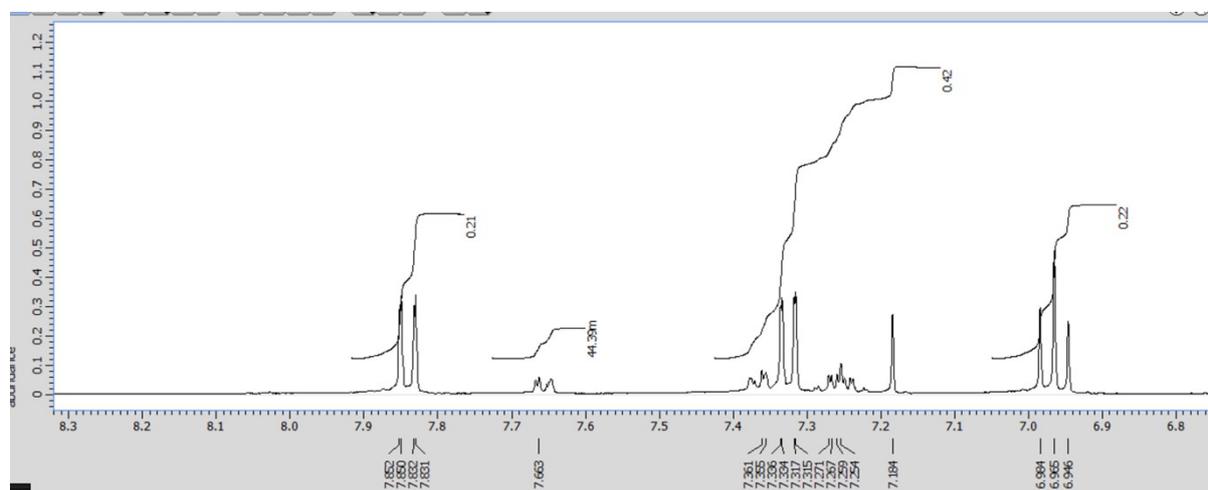
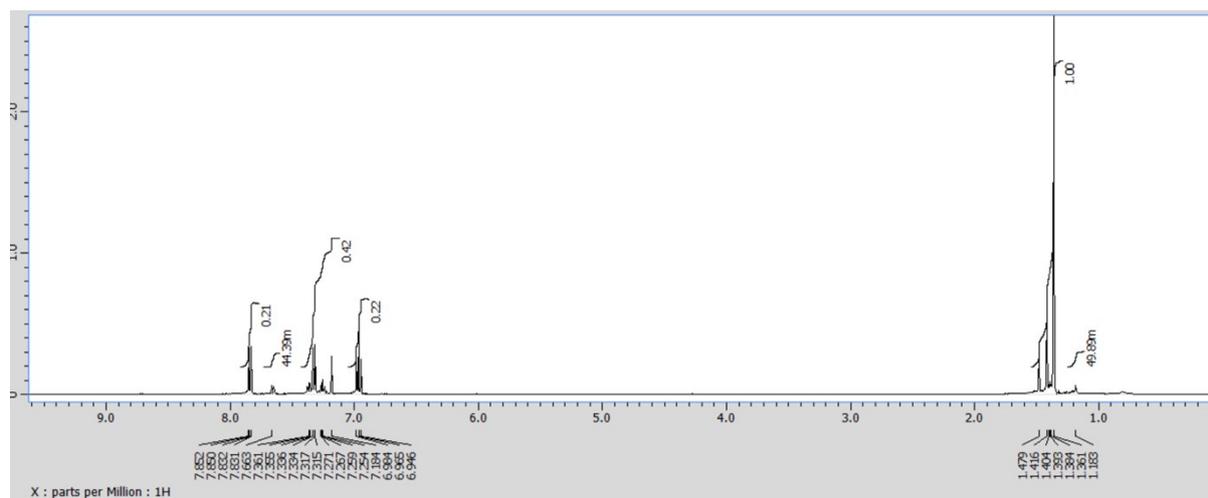
C. FLUORENE DERIVATIVES.

Preparation of 4,5-diiodo-9,9-dimethyl-9H-fluorene, 43.

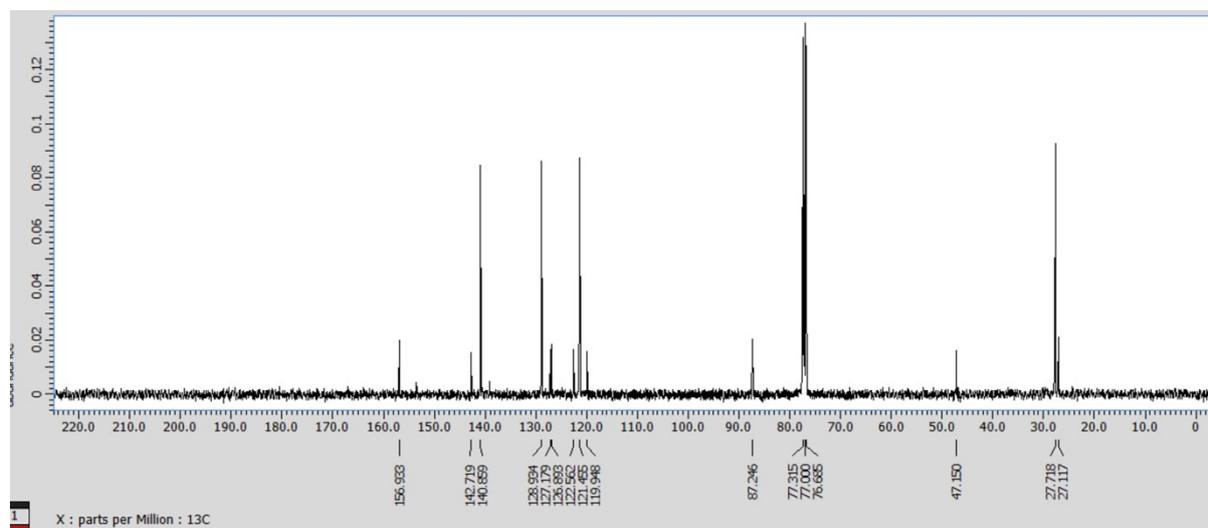
9, 9-Dimethylfluorene **42**^{S2} (1.00 g, 5.15 mmol) was stirred in anhydrous TMEDA (3.09 mL, 20.62 mmol) whilst *n*-BuLi (1.6M in hexanes, 12.89 mL, 20.62 mmol) was steadily added, producing an orange solution which was heated to 60°C for 5 h.^{S3} The deep brown solution was diluted with anhydrous THF (100 mL), cooled to -78°C and iodine (13.09 g, 51.50 mmol) added. The reaction was allowed to warm to room temperature and stirred for 16h. The deep brown solution was quenched with sat. sodium thiosulfate solution (150 mL) and stirred for 10 min. The aqueous layer was washed with EtOAc (3 x 40 mL) and the combined organic layers washed with sat. sodium thiosulfate solution (3 x 40 mL), H₂O (40 mL), brine (40 mL) and dried over MgSO₄. The solvent was removed *in vacuo* to give a crude thick brown oil which was first purified by flash column chromatography (hexanes), to give two close running bands (*R_f*: 0.32 and 0.27). The faster band contained a mono-iodinated-9,9-dimethyl-fluorene (δ H (400 MHz, CDCl₃, 24 °C): 8.82 (1H, d, *J* = 6.8 Hz, Ar-*H*₁), 7.83 (1H, d, *J* = 6.8 Hz Ar-*H*₁), 7.41-7.46 (4H, m, Ar-*H*₄), 7.00 (1H, t, *J* = 7.6 Hz, Ar-*H*₁), 1.48 (6H, s, 2 x CH₃), δ C (100 MHz, CDCl₃, 24 °C): 156.6, 154.1, 140.3, 139.0, 128.2, 128.1, 126.2, 122.4, 122.3 (Ar-C₁₁), 88.2 (*C*-I), 46.4 (9-C), 27.3 (2 x CH₃)). The slower band contained starting material **42** and the diiodo compound **43**. Increasing the polarity of the solvent eluted further materials. The mixture of **42** and **43** co-eluted in most solvent combinations, however they just separated (*R_f*: 0.54 (**42**), 0.49 (**43**)) in hexane/ethyl acetate 59/5, though to gain a reasonable amount of material for further reactions it was necessary to accept some **42** as impurity. The product was

obtained as a pale yellow solid (570 mg, 25%), m.p. 50-53°C. δH (400 MHz, CDCl_3 , 24 °C): 7.93 (2H, d, $J = 7.8$ Hz, 3, 6-*H*), 7.40 (2H, d, $J = 7.2$ Hz, 1, 8-*H*), 7.04 (2H, t, $J = 7.7$ Hz, 2, 7-*H*), 1.43 (6H, s, 9-(CH_3)₂); δC (100 MHz, CDCl_3 , 24 °C): 156.9, 142.7 (Ar- C_4), 140.8 (3, 6- C), 128.9 (2, 7- C), 121.5 (1, 8- C), 87.3 (4, 5- C), 47.1 (9- C), 27.7 (9-(CH_3)₂); $\nu_{\text{max}}/\text{cm}^{-1}$: 2957, 2920, 2857, 1442, 1392, 1075, 931, 779, 762, 732, 661. Crystal structure determined (p. 29). This synthesis was not optimised.

^1H NMR spectrum of **43**.

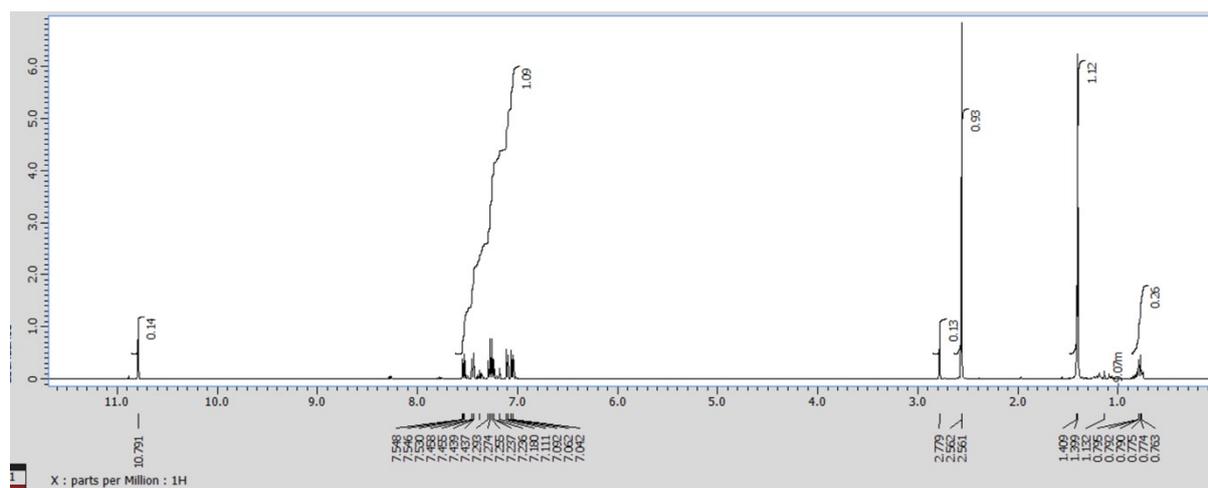
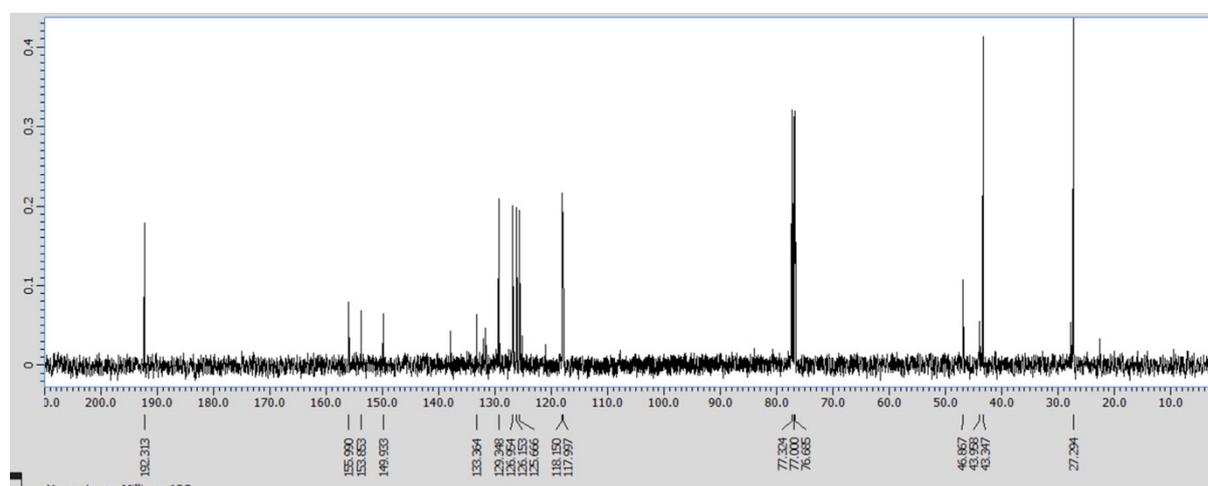


^{13}C NMR spectrum of **43**.



Preparation of 4-(dimethylamino)-9, 9-dimethyl-9H-fluorene-5-carbaldehyde, **44**.

The *di*-iodo-fluorene **43** (0.4 g, 0.90 mmol) was dissolved in anhydrous Et_2O (15 mL) under nitrogen and cooled to -78°C . *n*-BuLi (1.6M in hexanes, 0.62 mL, 0.99 mmol) was steadily added, and the orange solution was stirred at -78°C for 2h. Anhydrous DMF (0.36 mL, 4.63 mmol) was added and the reaction was allowed to warm to room temperature. After 16 h. the resulting green/yellow solution was quenched with H_2O (10 mL) and stirred for 10 min. The aqueous solution was washed with Et_2O (3 x 30 mL) and the combined organic layers washed with H_2O (40 mL), brine (40 mL) and dried over MgSO_4 . The solvent was removed *in vacuo* to give a yellow/green oil which was purified by flash column chromatography (5:95 EtOAc/petrol 40-60), to give **44** as a yellow solid (100 mg, 42%), m.p. $80\text{--}83^\circ\text{C}$. δH (400 MHz, CDCl_3 , 24°C): 10.86 (1H, s, CHO), 7.61 (1H, dd, $J = 7.3, 0.9$ Hz, 6-*H*), 7.52 (1H, dd, $J = 7.3, 0.9$ Hz, 8-*H*), 7.34 (2H, m, 2-,7-*H*), 7.17 (1H, d, $J = 7.3$ Hz, 1-*H*), 7.12 (1H, d, $J = 7.8$ Hz, 3-*H*), 2.63 (6H, s, $\text{N}(\text{CH}_3)_2$), 1.47 (6H, s, 9-(CH_3) $_2$); δC (100 MHz, CDCl_3 , 24°C): 192.5 ($\text{C}=\text{O}$), 156.1, 154.0 (Ar- C_2), 150.1 (4-*C*), 138.1 (Ar- C_1), 133.5 (5-*C*), 131.8 (Ar- C_1), 129.5 & 127.1 (2-,7-*C*), 126.3 (6-*C*), 125.8 (8-*C*), 118.3 (3-*C*), 118.1 (1-*C*), 47.0 (9-*C*), 43.5 ($\text{N}(\text{CH}_3)_2$), 27.4 (9-(CH_3) $_2$); $\nu_{\text{max}}/\text{cm}^{-1}$: 2950, 2834, 2786, 1677 ($\text{C}=\text{O}$), 1581, 1481, 1455, 1381, 1317, 1289, 1224, 1200 1181, 1118, 985, 795, 764, 726; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{NO}$ ($[\text{M}+\text{H}]^+$): 266.1545, found: 266.1538.

¹H NMR spectrum of **44**.¹³C NMR spectrum of **44**.

Preparation of 2-cyano-2-(4'-dimethylamino-9',9'-dimethyl-9H-fluoren-5'-yl)-propenenitrile, **45**.

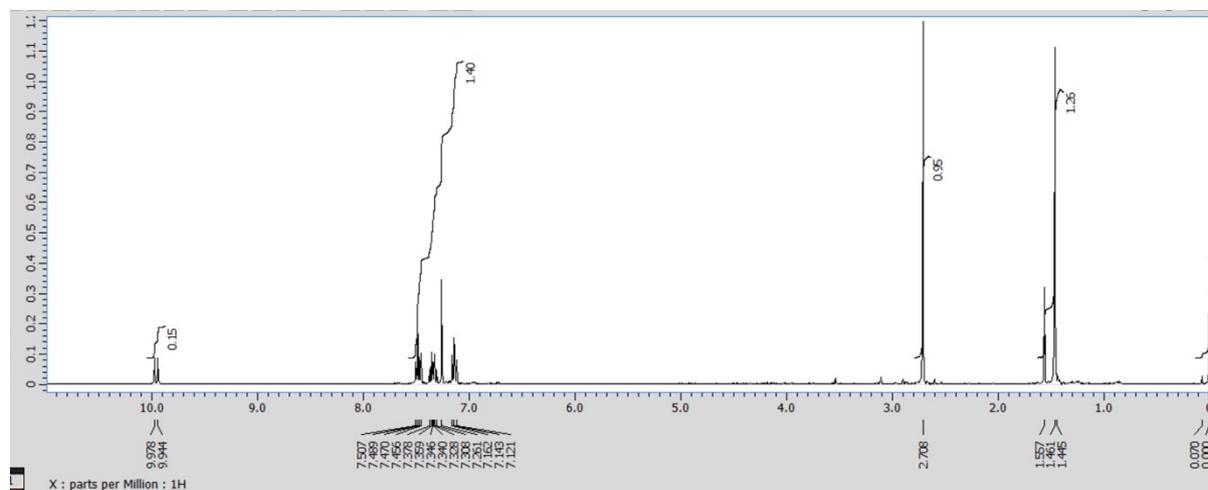
Dimethylamino-aldehyde **44** (100 mg, 0.38 mmol) was dissolved in anhydrous MeOH (15 mL). Malononitrile (30 mg, 0.45 mmol) and ethylenediamine diacetate (10 mg, 0.06 mmol) were added and the solution was heated to reflux for 2 h. The solvent was removed *in vacuo* to yield a crude orange solid which was purified by flash column chromatography (3:97 EtOAc:petrol 40-60), to give **45** as an orange solid (70 mg, 59%), m.p. 122-125°C. δ H (400 MHz, CDCl₃, 24 °C): 9.07 (1H, s, CH), 7.67 (1H, dd, J = 7.8 Hz, 6'-H), 7.56 (1H, d, J = 7.3 Hz, 8'-H), 7.39 (2H, m, 2', 7'-H), 7.22 (1H, d, J = 7.8 Hz, 1'-H), 7.19 (1H, d, J = 7.8 Hz, 3'-H), 2.68 (6H, s,

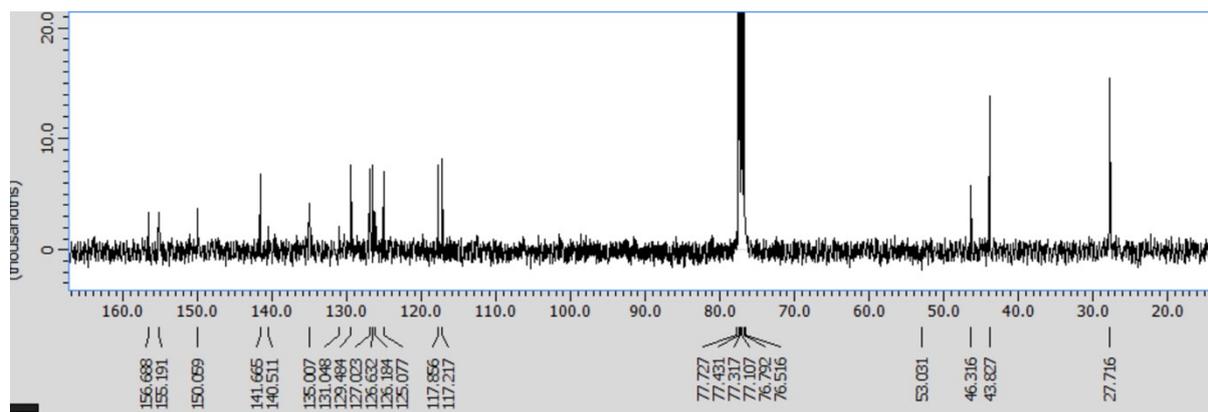
$N(CH_3)_2$, 1.48 (6H, s, 9'-(CH_3)₂); δC (100 MHz, $CDCl_3$, 24 °C): 163.8 (3-C), 156.1, 154.6, 149.1, 138.3, 131.6 (Ar- C_5), 129.9 (2'- or 7'-C), 127.8 (6'-C), 127.4 (2'- or 7'-C), 126.3 (Ar- C_1), 126.1 (8'-C), 118.9 (3'-C), 118.8 (1'-C), 114.6 (2 x $C\equiv N$), 112.9 ($C(CN)_2$), 46.9 (9'-C), 44.2 ($N(CH_3)_2$), 27.1 (9'-(CH_3)₂); ν_{max}/cm^{-1} : 2942, 2862, 2223 ($C\equiv N$), 1582, 1481, 1459, 1314, 1183, 1043, 984, 879, 797, 764, 730; Found: C, 80.27; H, 6.23; N, 13.36%. Calc. for $C_{21}H_{19}N_3$: C, 80.41; H, 6.06; N, 13.40%.

Preparation of *E*-2-(4'-Dimethylamino-9',9'-dimethyl-9*H*-fluorene-5'-yl)-1-nitroethene, **46**.

Dimethylamino-aldehyde **44** (55 mg, 0.21 mmol) was dissolved in anhydrous MeOH (5 mL). Nitromethane (0.03 mL, 0.56 mmol) and ethylenediamine diacetate (5 mg, 0.03 mmol) were added and the solution was heated to reflux for 24 h. The solvent was removed *in vacuo* to yield a crude orange solid which was purified by flash column chromatography (5:95 EtOAc:petrol 40-60), to give **46** as an orange solid (40 mg, 63%), m.p. 99-102°C. δH (400 MHz, $CDCl_3$, 24 °C): 9.93 (1H, d, $J = 13.7$ Hz, 2-*H*), 7.45-7.52 (3H, m, 1-, 6'-, 8'-*H*), 7.29-7.39 (2H, m, 2'-, 7'-*H*), 7.10-7.18 (2H, m, 1'-, 3'-*H*), 2.72 (6H, s, $N(CH_3)_2$), 1.46 (6H, s, 9'-(CH_3)₂); δC (100 MHz, $CDCl_3$, 24 °C): 156.7, 155.2, 150.1 (Ar- C_3), 141.7 (3-C), 140.2, 135.0 (2-C), 131.1 (Ar- C_2), 129.5 & 127.0 (2'-, 7'-C), 126.6, 126.2, 125.1 (Ar- C_3), 117.9 & 117.2 (1'-, 3'-C), 46.3 (9'-C), 43.8 ($N(CH_3)_2$), 27.7 (9'-(CH_3)₂); ν_{max}/cm^{-1} : 2957, 2860, 1623, 1582, 1545, 1500, 1481, 1332, 1259, 1090, 985, 969, 799, 732; *HRMS* (ESI) calcd for $C_{19}H_{21}N_2O_2$ ($[M+H]^+$): 309.1603, found: 309.1594.

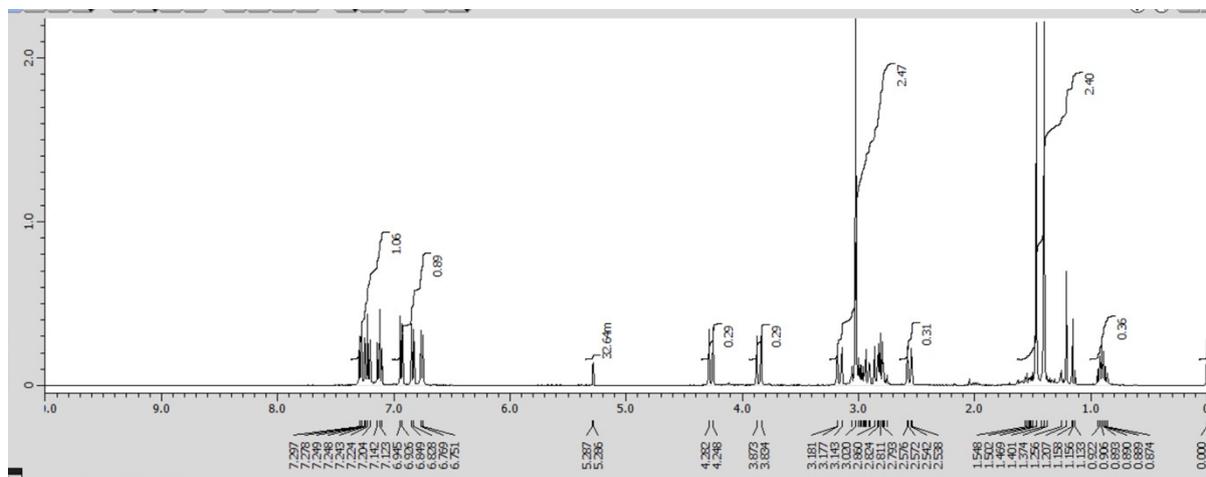
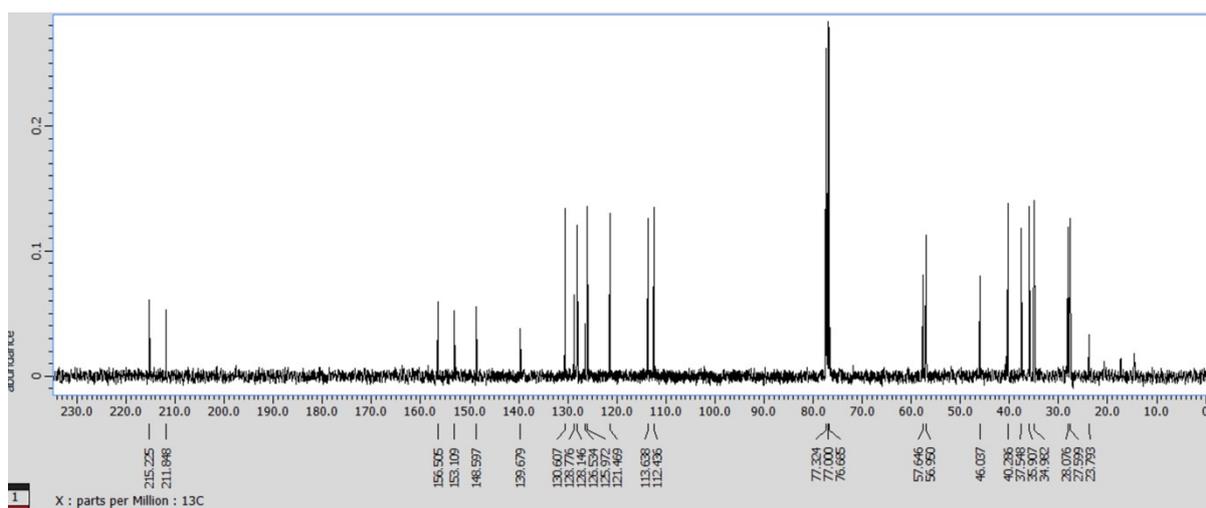
1H NMR spectrum of **46**.



¹³C NMR spectrum of **46**

Preparation of 1',8',8'-Trimethyl-1',2',3',4'-tetrahydro-8'*H*-spiro[cyclopentane-1,3'-fluoreno[4,5-*bcd*]azocine]-2,5-dione, **47.**

Dimethylamino-aldehyde **44** (100 mg, 0.38 mmol) was dissolved in anhydrous DMSO (10 mL) under nitrogen and 1,3-cyclopentandione (44 mg, 0.45 mmol) was added, and the deep orange solution was stirred at room temperature. After 24 h, the solution was diluted with water (15 mL) and extracted with EtOAc (3 x 20 mL). The combined organics were washed with brine (1 x 20 mL), dried over MgSO₄ and filtered. The solvent was removed *in vacuo* to yield a crude brown oil which was purified by flash column chromatography (10:90 EtOAc:petrol 40-60), to give **47** as an orange solid (53 mg, 41%), m.p. 60-63°C. δ H (400 MHz, CDCl₃, 24 °C): 7.30 (1H, d, J = 7.3 Hz, 7'-*H*), 7.23 (1H, t, J = 7.8 Hz, 10'-*H*), 7.12 (1H, t, J = 7.3 Hz, 6'-*H*), 6.95 (1H, d, J = 7.8 Hz, 9'-*H*), 6.85 (1H, d, J = 8.2 Hz, 5'-*H*), 6.77 (1H, d, J = 7.3 Hz, 11'-*H*), 4.26 (1H, d, J = 13.7 Hz, 4'-*H*_α), 3.86 (1H, d, J = 15.1 Hz, 2'-*H*_α), 3.16 (1H, dd, J = 13.1, 1.4 Hz, 4'-*H*_β), 3.02 (3H, s, NCH₃), 2.75-2.90 (4H, m, 3-, 4-*H*₂), 2.57 (1H, d, J = 13.7, 1.9 Hz, 2-*H*), 1.47 (3H, s, 8'-CH₃), 1.40 (3H, s, 8''CH₃); δ C (100 MHz, CDCl₃, 24 °C): 215.3 & 212.0 (2 x C=O), 156.7, 153.3, 148.7, 139.8 (Ar-C₄), 130.7 (5'-C), 128.9 (Ar-C₁), 128.3 (10'-C), 126.7 (Ar-C₁), 126.1 (6'-C), 121.6 (7'-C), 113.8 (9'-C), 112.6 (11'-C), 57.8 (3'-C), 57.1 (2'-C), 46.2 (8'-C), 40.4 (NCH₃), 37.7 (4'-C), 36.1 & 35.1 (3-, 4-C), 28.2 & 27.7 (2 x 8'-CH₃); ν_{\max} /cm⁻¹: 2957, 2920, 2862, 1714 (C=O), 1584, 1485, 1442, 1420, 1280, 1168, 1153, 1129, 987, 907, 790, 728;

¹H NMR spectrum of **47**.¹³C NMR spectrum of **47**.

Preparation of 1',2,2,8',8'-Pentamethyl-1',2',3',4'-tetrahydro-8'*H*-*spiro*[1,3-dioxane-5,3'-fluoreno[4,5-*bcd*]azocine]-4,6-dione, **48**.

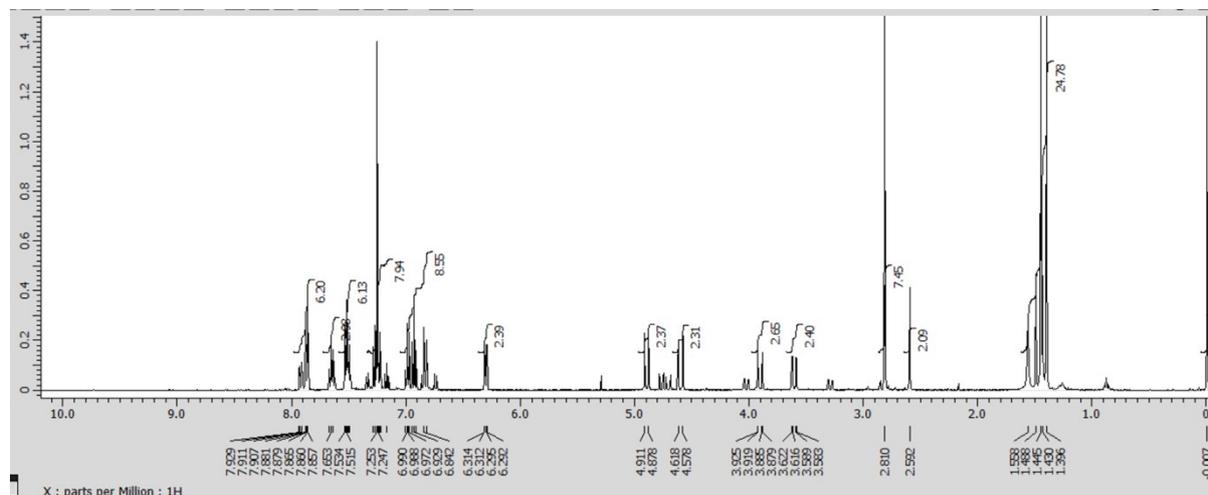
Dimethylamino-aldehyde **44** (143 mg, 0.54 mmol) was dissolved in anhydrous MeOH (10 mL). Meldrum's acid (109 mg, 0.76 mmol) and ethylenediamine diacetate (9 mg, 0.05 mmol) were added and the reaction heated to reflux for 5 h, with a precipitate forming after 15 min. The precipitate was filtered, washed with cold MeOH and dried *in vacuo* to give **48** as a pale yellow

solid (150 mg, 71%), m.p. 204-207°C. δ H (400 MHz, acetone- d_6 , 24 °C): 7.34 (1H, d, J = 7.8 Hz, 7'-H), 7.20 (1H, t, J = 8.2 Hz, 10'-H), 7.12 (1H, t, J = 7.8 Hz, 6'-H), 7.00 (1H, d, J = 7.3 Hz, 9'-H), 6.94 (1H, d, J = 7.3 Hz, 5'-H), 6.87 (1H, d, J = 8.2 Hz, 11'-H), 4.51 (1H, d, J = 13.3 Hz, 4'- H_α), 4.12 (1H, d, J = 15.1 Hz, 2'- H_α), 3.71 (1H, d, J = 15.6 Hz, 4'- H_β), 3.04 (1H, d, J = 13.7 Hz, 2'- H_β), 2.96 (3H, s, NCH₃), 1.81 (6H, m, 2-(CH₃)₂), 1.39 (6H, m, 8'-(CH₃)₂); δ C (100 MHz, acetone- d_6 , 24 °C): 168.9 & 166.2 (C=O), 156.6, 152.9, 148.9, 139.4 (Ar-C₄), 131.5 (5'-C), 129.7 (Ar-C₁), 128.4 (10'-C), 126.2 (Ar-C₁), 126.1 (6'-C), 121.4 (7'-C), 114.0 (9'-C), 112.7 (11'-C), 105.0 (2-C), 60.8 (2'-C), 50.1 (3'-C), 45.8 (8'-C), 40.3 (NCH₃), 39.1 (4'-C), 28.6 & 28.3 (2-(CH₃)₂), 27.8 & 27.0 (8'-(CH₃)₂); $\nu_{\max}/\text{cm}^{-1}$: 2965, 2868, 1778, 1735 (C=O), 1571, 1477, 1436, 1379, 1278, 1258, 1198, 1026, 948, 795, 740; Found: C, 73.49; H, 6.36; N, 3.86%. Calc. for C₂₄H₂₅NO₄: C, 73.57; H, 6.39; N, 3.58%.

Preparation of 3-Benzoyl-3-nitro-1,2,3,4-tetrahydro-1,8,8-trimethyl-8H-fluoreno[4,5-bcd]azocine, 49.

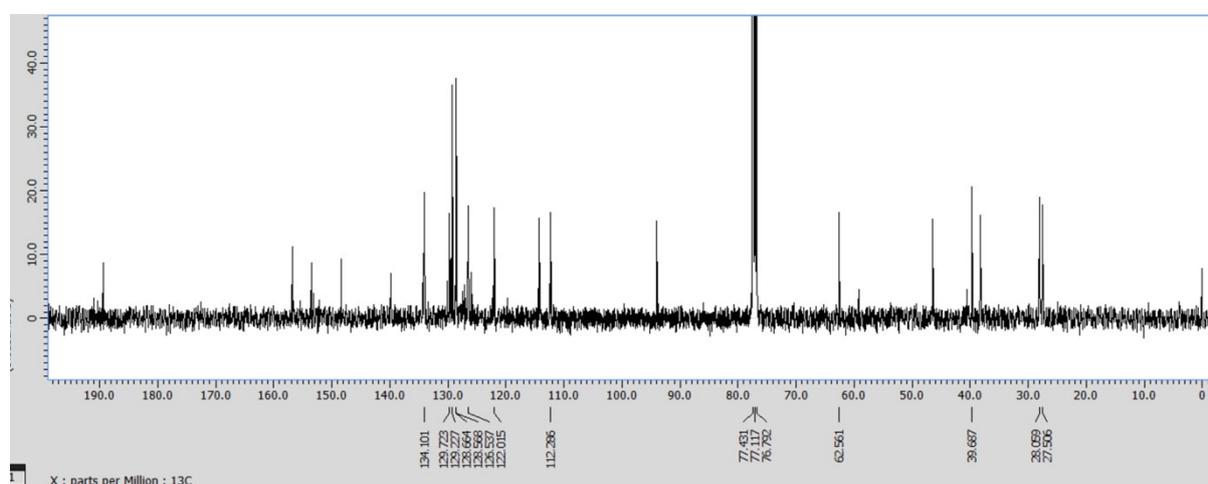
Dimethylamino-aldehyde **44** (55 mg, 0.21 mmol) was dissolved in anhydrous MeOH (10 mL). Benzoyl-nitromethane (69 mg, 0.42 mmol) and ethylenediamine diacetate (5 mg, 0.03 mmol) were added and the solution was refluxed for 4 h. The solvent was removed *in vacuo* to yield a crude yellow oil which was purified by flash column chromatography (5:95 EtOAc:petrol 40-60), to give **49** as an orange solid (65 mg, 76%), m.p. 172-175°C. δ H (400 MHz, CDCl₃, 24 °C): 7.87 (2H, dd, J = 8.2, 0.91 Hz, *ortho*-Ph-H), 7.65 (1H, t, J = 7.8 Hz, *para*-Ph-H), 7.51 (2H, t, J = 7.8 Hz, *meta*-Ph-H), 7.20-7.30 (2H, m, 7-, 10-H), 6.98 (1H, dd, J = 7.3, 0.9 Hz, Ar-H), 6.95 (1H, t, J = 7.3 Hz, 6-H), 6.83 (1H, d, J = 8.2 Hz, Ar-H), 6.30 (1H, dd, J = 7.8, 0.9 Hz, 5-H), 4.89 (1H, d, J = 13.3 Hz, 2- H_α), 4.60 (1H, d, J = 16.0 Hz, 4- H_α), 3.90 (1H, dd, J = 16.0, 2.3 Hz, 4- H_β), 3.60 (1H, dd, J = 13.3, 2.3 Hz, 2- H_β), 2.81 (3H, s, NCH₃), 1.44 (3H, s, 8-C(CH₃)), 1.40 (3H, s, 8-C(CH₃)); δ C (100 MHz, CDCl₃, 24 °C): 189.4 (C=O), 156.8 (8a-C), 153.5 (7a-C), 148.4 (11a-C), 139.9 (Ar-C₁), 134.1 (*p*-Ph-C), 129.7 (6-C), 129.2 (*m*-Ph-C), 128.7 (Ar-C₁), 128.6 (*o*-Ph-C), 128.5 (Ar-C₁), 126.5 (6-C), 126.4, 126.0, 120.0, 114.3, 112.3 (Ar-C₅), 94.0 (3-C), 62.6 (2-C), 46.4 (8-C), 39.7 (NCH₃), 38.2 (4-C), 28.1 & 27.5 (8-C(CH₃)₂); $\nu_{\max}/\text{cm}^{-1}$: 2980, 2821, 1686 (C=O), 1533, 1485, 1444, 1425, 1321, 1269, 1241, 1200, 1179, 1159, 1000, 922, 786, 728, 695; HRMS (ESI) calcd for C₂₆H₂₅N₂O₃ ([M+H]⁺): 413.1865, found: 413.1854.

^1H NMR spectrum of **49**.



(some evidence two non-interconverting conformers).

^{13}C NMR spectrum of **49**.



Preparation of 3-Nitro-1,2,3,4-tetrahydro-1,8,8-trimethyl-8*H*-fluoreno[4,5-*bcd*]azocine, **50**.

Recrystallisation of the fused azocine **49** from a DCM/hexanes solution gave two separate crystal types. Separation of the two crystal systems under a microscope gave two samples; the first the starting azocine **49** and the second a decomposition product **50** as pale yellow plates, m.p. 115-118°C. $\nu_{\text{max}}/\text{cm}^{-1}$: 2957, 2862, 1584, 1537, 1474, 1454, 1438, 1358, 1269, 1177, 984,

793, 730; *HRMS* (ESI) calcd for C₁₉H₂₁N₂O₂ ([M+H]⁺): 309.1603, found: 309.1595. Crystal structure was determined (p.29 and main article).

II. X-Ray Crystallography.

General.

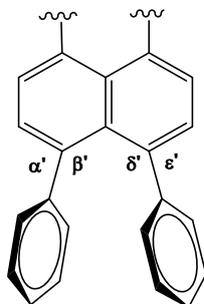
Low temperature (150K) X-ray diffraction data (MoK α for all compounds but for **22** and **44** which were measured with CuK α) were measured on an Rigaku Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire detector and an 700 series Cryostream low temperature system using the CrysAlis-Pro software package.^{S4} Structures were solved and refined using the SHELXS and SHELXL suite of programs^{S5} using the XSEED interface^{S6} or OLEX².^{S7} Molecular illustrations were made with Mercury,^{S8} and geometric analysis with PLATON.^{S9} Data are deposited at the Cambridge Crystallographic Data Centre with code numbers CCDC: 2069090-2069106 and 2069108.

A. DIPHENYL DERIVATIVES.

Table S1. Crystallographic data for dimethylamino-diphenyl-naphthalene derivatives **16 -19**, and **21-22** and salts **26-27**.

	16	17	18^{S1}	19
Formula	C ₂₄ H ₂₁ N	C ₂₅ H ₂₁ NO	C ₂₈ H ₂₁ N ₃ . C ₇ H ₈	C ₂₉ H ₂₄ N ₂ O ₂
Formula weight	323.42	351.43	491.61	432.50
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P-1</i>	<i>P2₁/n</i>
<i>a</i> [Å]	22.0584(7)	12.6676(5)	8.6981(5)	10.6932(3)
<i>b</i> [Å]	9.7183(2)	9.9541(3)	12.6447(6)	8.4601(3)
<i>c</i> [Å]	16.5596(4)	15.1783(6)	12.8788(7)	25.0272(8)
<i>α</i> [°]	90	90	81.679(4)	90
<i>β</i> [°]	99.142(3)	108.164(4)	77.685(4)	101.328(3)
<i>γ</i> [°]	90	90	78.768(4)	90
<i>V</i> [Å³]	3504.78(16)	1818.53(12)	1349.48(12)	2219.99(13)
<i>Z</i>	8	4	2	4
<i>ρ</i> [g cm⁻³]	1.226	1.284	1.210	1.294
<i>T</i> [K]	150	150	150	150
<i>λ</i> (Å)	0.71073	0.71073	0.71073	0.71073
<i>μ</i> (mm⁻¹)	0.070	0.078	0.071	0.082
unique refl.	3568	3708	6693	5513
Refl, <i>I</i> > 2σ<i>I</i>	2558	3300	4808	4823
<i>R</i>₁	0.0476	0.0721	0.0522	0.0399
<i>wR</i>₂	0.1137	0.1953	0.1233	0.1087
<i>Δρ</i>(r) [e Å⁻³]	0.15/-0.17	0.67/-0.32	0.30/-0.26	0.31/-0.23
Crystallisation solvent	<i>n</i> -hexane	EtOAc	Toluene	EtOAc

	21	22	26	27
Formula	C ₃₁ H ₂₇ NO ₂ . CHCl ₃	C ₅₂ H ₄₆ N ₄	C ₂₅ H ₂₂ NO. Cl.CH ₂ Cl ₂	C ₂₅ H ₂₂ NO. C ₃ H ₃ O ₄
Formula Weight	564.90	726.93	472.81	455.49
Crystal System	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>I2/a</i>	<i>Pbca</i>	<i>P2₁2₁2₁</i>	<i>P-1</i>
a[Å]	19.4622(12)	9.8042(2)	6.1138(3)	6.0395(3)
b[Å]	9.9340(8)	15.4073(4)	11.1707(5)	13.8019(8)
c[Å]	29.6756(15)	52.7317(11)	33.8350(17)	14.6137(9)
α[°]	90	90	90	67.400(5)
β [°]	93.325(5)	90	90	86.108(4)
γ[°]	90	90	90	81.742(4)
V [Å³]	5727.7(6)	7965.5(3)	2310.78(19)	1112.84(12)
Z	8	8	4	2
ρ [g cm⁻³]	1.310	1.212	1.359	1.359
T [K]	150	150	150	150
λ (Å)	0.71073	1.54184	0.71073	0.71073
μ (mm⁻¹)	0.350	0.542	0.415	0.093
unique refl.	5880	7645	5702	6361
Refl, I > 2σI	2821	5584	4042	4061
R₁	0.0805	0.0524	0.0594	0.0644
wR₂	0.1734	0.1423	0.1217	0.1563
Δρ(r) [e Å⁻³]	0.40/-0.37	0.21/-0.19	0.49/-0.64	0.44/-0.29
Crystallisation solvent	CHCl ₃	CH ₂ Cl ₂ /n-hexane	CH ₂ Cl ₂	EtOAc/CH ₂ Cl ₂

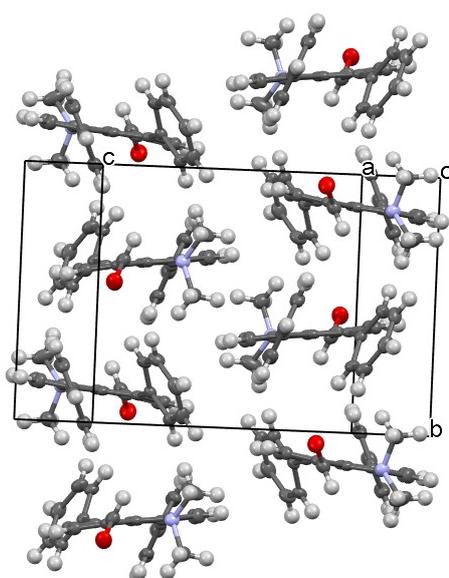
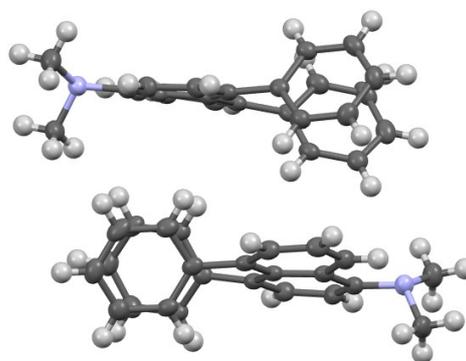
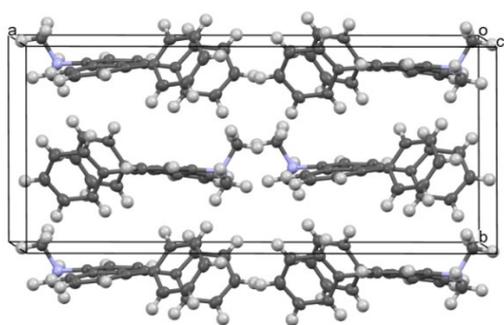
Table S2. Phenyl Group Orientations for *peri*-Diphenylnaphthalene Derivatives.

	$\alpha' / ^\circ$	$\beta' / ^\circ$	$\delta' / ^\circ$	$\epsilon' / ^\circ$	Phenyl/ Naphthyl planes/ $^\circ$	Phenyl/ Phenyl plane / $^\circ$
Parent ^{S10}	114.8(2)	125.8(2)	124.4(2)	115.8(2)	66.48(10)/ 67.10(10)	20.49(12)
16	116.12(13)	125.11(13)	125.80(14)	115.16(14)	59.36(4) / 57.01(4)	27.08(7)
17	116.5(2)	124.6(2)	125.1(2)	116.0(2)	59.23(7) 56.71(7)	20.69(10)
18	115.44(12)	125.88(12)	124.50(12)	116.02(12)	62.22(3) 63.21(3)	21.10(6)
19	116.75(9)	123.75(9)	123.10(9)	118.05(9)	60.12(4) 62.98(5)	16.97(6)
21	116.2(3)	124.9(3)	123.6(3)	117.9(3)	57.51(14) 53.06(13)	26.26(18)
22	115.75(18)	125.08(17)	124.91(17)	115.84(19)	57.08(8) 48.78(8)	30.50(10)
	116.89(17)	123.87(17)	124.85(17)	115.96(18)	56.71(8) 56.66(9)	34.21(11)
26	115.4(3)	125.6(3)	124.6(4)	116.3(4)	61.90(18) 53.69(16)	25.1(2)
27	116.98(16)	123.93(16)	124.96(16)	115.84(16)	55.78(8) 61.87(9)	22.78(11)

Parent = 1,8-diphenylnaphthalene, room temperature measurement.

Crystal packing diagrams of 16, 17 and 19.

There is a common packing motif with pairs of molecules oriented so that the two phenyls lie opposite a naphthalene.



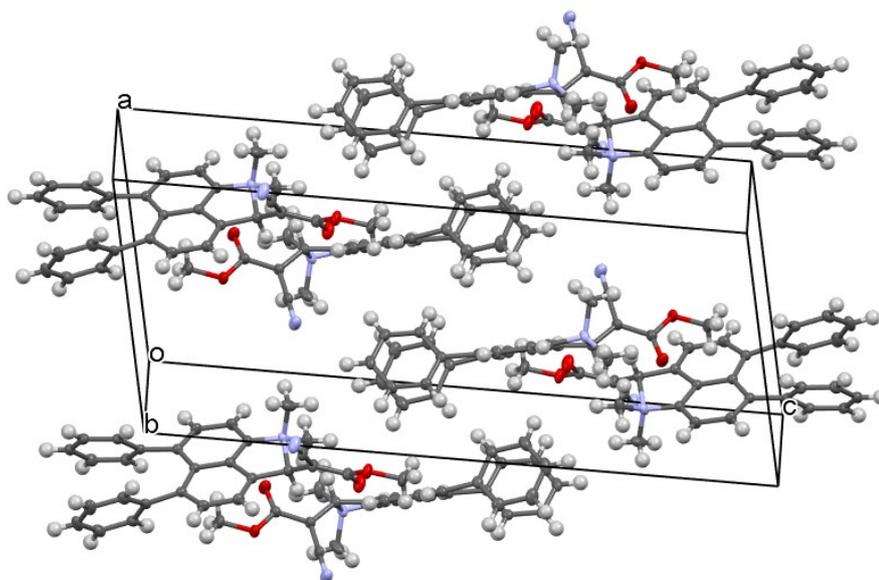


Figure S1. Crystal packing in **16**, and an isolated pair of molecules of **16** (top), crystal packing of **17** (middle) and crystal packing of **19** (with some molecules along the *b* axis omitted for clarity) (bottom).

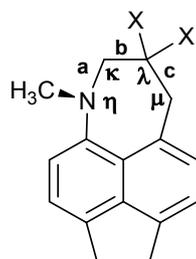
B. ACENAPHTHENE DERIVATIVES.

Table S3. Crystallographic data for the acenaphthene derivatives **28-30** and **34-36**.

	28	29^{S1}	30
Formula	C ₁₅ H ₁₅ NO	C ₁₈ H ₁₅ N ₃	C ₁₉ H ₁₈ N ₂ O ₂
Formula weight	225.28	273.33	306.35
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P2₁/c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	9.1836(6)	9.8149(4)	8.7457(5)
<i>b</i> [Å]	9.4806(5)	9.9853(4)	9.3638(7)
<i>c</i> [Å]	13.2584(8)	15.1587(6)	11.2739(7)
α [°]	90	84.234(3)	108.887(6)
β [°]	99.767(7)	78.977(4)	91.171(5)
γ [°]	90	80.518(3)	113.671(6)
<i>V</i> [Å³]	1137.62(12)	1434.64(10)	787.91(10)
<i>Z</i>	4	4	2
ρ [g cm⁻³]	1.315	1.265	1.291
<i>T</i> [K]	150	150	150
λ (Å)	0.71073	0.71073	0.71073
μ (mm⁻¹)	0.082	0.077	0.085
unique refl.	2341	5911	3915
Refl, $I > 2\sigma I$	1961	3884	2990
<i>R</i>₁	0.0487	0.0575	0.0506
<i>wR</i>₂	0.1119	0.1157	0.1360
$\Delta\rho(\mathbf{r})$ [e Å⁻³]	0.21/-0.21	0.23/-0.25	0.30/-0.21
Crystallisation solvent	CDCl ₃	CH ₃ OH	CH ₂ Cl ₂ / <i>n</i> -hexane

	34	35	36
Formula	C ₂₁ H ₂₁ NO ₄	C ₂₁ H ₂₁ NO ₂	C ₂₀ H ₁₉ NO ₂
Formula weight	351.39	319.39	305.36
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> [Å]	10.4257(3)	15.2740(6)	10.7625(5)
<i>b</i> [Å]	8.8243(3)	10.3218(4)	32.3176(10)
<i>c</i> [Å]	18.7805(7)	10.2175(3)	8.6130(3)
α [°]	90	90	90
β [°]	101.546(3)	93.356(3)	98.945(4)
γ [°]	90	90	90
<i>V</i> [Å³]	1692.83(10)	1608.08(10)	2959.3(2)
<i>Z</i>	4	4	8
ρ [g cm⁻³]	1.379	1.319	1.371
<i>T</i> [K]	150	150	150
λ (Å)	0.71073	0.71073	0.71073
μ (mm⁻¹)	0.096	0.084	0.088
unique refl.	3489	3307	6829
Refl, $I > 2\sigma I$	2736	2578	4795
<i>R</i>₁	0.0552	0.0514	0.1040
<i>wR</i>₂	0.1132	0.1111	0.2072
$\Delta\rho(r)$ [e Å⁻³]	0.22/-0.24	0.18/-0.26	0.53/-0.29
Crystallisation Solvent	CH ₂ Cl ₂ / n-hexane	CH ₂ Cl ₂ / <i>n</i> -hexane	CH ₂ Cl ₂ / <i>n</i> -hexane

Table S4. Selected geometric details for the azepine ring for *spiro* acenaphtho-azepines **34-36**.



34 X, X = (C(=O)O)₂CMe₂

35 X, X = (C(=O)CH₂)₂CH₂

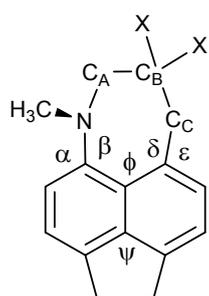
36 X, X = (C(=O)CH₂)₂

	a / Å	b / Å	c / Å	Σ ^a / °
34	1.457(2)	1.549(2)	1.560(2)	349.5(3)
35	1.470(2)	1.525(2)	1.562(2)	343.6(3)
36	1.453(4)	1.551(4)	1.529(4)	346.9(9)
	1.447(5)	1.551(5)	1.520(5)	348.3(9)

Σ^a = Sum of bond angles at nitrogen.

	η / °	κ / °	λ / °	μ / °
34	115.56(14)	113.02(14)	109.01(14)	116.19(14)
35	113.57(13)	114.02(13)	109.23(13)	115.66(13)
36	114.4(3)	113.3(3)	109.4(3)	117.0(3)
	113.8(3)	113.3(3)	110.0(3)	117.2(3)

Table S5: Selected angles around the acenaphthene ring, and deviations of selected atoms in the azepine ring from the acenaphthene plane for the *spiro* acenaphtho-azepines **34-36**.



34 X, X = (C(=O)O)₂CMe₂

35 X, X = (C(=O)CH₂)₂CH₂

36 X, X = (C(=O)CH₂)₂

	α / °	β / °	ϕ / °	δ / °	ϵ / °	ψ / °
3	122.86(1)	118.57(1)	127.35(1)	120.79(1)	119.73(1)	112.07(1)
4	6)	5)	7)	6)	6)	7)
3	122.76(1)	118.53(1)	127.14(1)	121.27(1)	119.75(1)	111.81(1)
5	5)	4)	5)	5)	5)	5)
3	123.2(3)	118.3(3)	127.3(3)	121.8(3)	119.6(3)	111.8(3)
6						
	121.6(2)	120.2(3)	126.1(3)	121.9(3)	118.8(4)	111.6(4)

Deviations from the acenaphthene plane / Å.

	N	C _A	C _B	C _C
34	0.303(2)	1.319(2)	0.731(3)	-0.383(2)
35	0.249(2)	1.354(2)	0.919(2)	-0.246(2)
36	0.242(4)	1.254(4)	0.670(4)	-0.389(4)
	0.183(4)	1.163(5)	0.551(5)	-0.450(4)

C. FLUORENE DERIVATIVES.

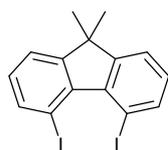
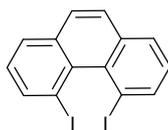
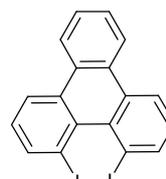
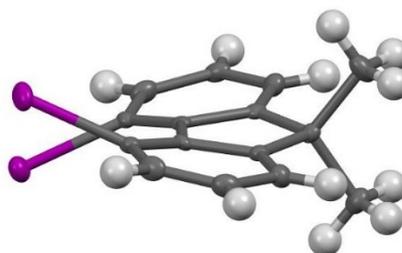
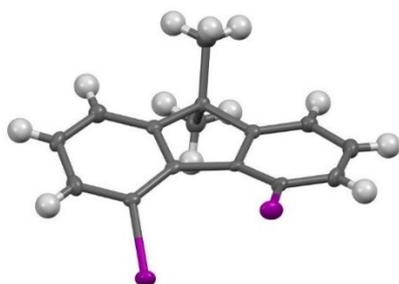
Table S6. Crystallographic data for the fluorene derivatives **43-45**, **48** and **50**.

	43	44	45	48	50
Formula	C ₁₅ H ₁₂ I ₂	C ₁₈ H ₁₉ NO	C ₂₁ H ₁₉ N ₃	C ₁₉ H ₂₀ N ₂ O ₂	C ₂₄ H ₂₅ NO ₄
Formula weight	446.05	265.34	313.39	308.37	391.45
Crystal system	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>I4₁cd</i>	<i>I2/a</i>	<i>P2₁</i>	<i>P2₁/n</i>
<i>a</i> [Å]	8.4109(2)	24.79560(10)	18.4256(4)	9.7431(3)	10.9539(3)
<i>b</i> [Å]	9.6735(3)	24.79560(10)	11.2921(3)	6.9459(2)	9.5493(3)
<i>c</i> [Å]	17.0655(5)	9.47440(10)	16.4939(4)	12.1403(4)	19.3902(6)
α [°]	90	90	90	90	90
β [°]	90.496(2)	90	99.223(2)	105.257(4)	104.652(3)
γ [°]	90	90	90	90	90
<i>V</i> [Å³]	1388.45(7)	5825.07(8)	3387.42(14)	792.63(4)	1962.30(11)
<i>Z</i>	4	16	8	2	4
ρ [g cm⁻³]	2.134	1.210	1.229	1.292	1.325
<i>T</i> [K]	150	150	150	150	150
λ (Å)	0.71073	1.54184	0.71073	0.71073	0.71073
μ (mm⁻¹)	4.506	0.579	0.074	0.085	0.090
unique refl.	2837	2152	3936	4532	3165
Refl, $I > 2\sigma I$	2477	2108	3251	3645	2904
$R_1(I > 2\sigma I)$	0.0289	0.0314	0.0478	0.0462	0.0510
wR_2	0.0646	0.0803	0.1188	0.0961	0.1109

$\Delta\rho(r)$ [$e \text{ \AA}^{-3}$]	0.96/-0.53	0.13/-0.17	0.29/-0.23	0.20/-0.20	0.28/-0.23
Crystallisation solvent	EtOAc/Petrol (40-60)	CH ₂ Cl ₂ / <i>n</i> -hexane	CDCl ₃ / <i>n</i> -hexane	CH ₂ Cl ₂ / <i>n</i> -hexane	(CH ₃) ₂ CO

Crystal Structure of 4,5-diiodo-9,9-dimethylfluorene **43**.

The diiodo compound **43** crystallises in space group $P2_1/c$ with four molecules in the unit cell. The molecule is strongly distorted to increase the I...I separation to 3.6392(4) Å (Fig. S2). This is achieved in three ways: (a) the C-I bonds are displaced apart in the plane of the fluorene, with the two bonds displaced from their symmetrical positions by 5.9 and 7.1°, (b) the iodo groups are displaced out of their respective phenyl ring planes by 0.614 and 0.598 Å and (c) the fluorene is twisted about the bond connecting the phenyl rings, by 21.4(8)°. The C-I bonds are 2.106(4) and 2.114(4) Å long. Similar distortions is seen in the 4,5-diiodo-phenanthrene **S1**,^{S10} 1,12-diiodo-triphenylene **S2**,^{S11} and a polybenzenoid system **S3**^{S12}: I...I separations **S1**: 3.602/3.610 Å, **S2**: 3.679/3.687 Å, **S3**: 3.636 Å, but with a larger twist about the bond between the relevant rings: **S1**: 33.7/34.6°, **S2**: 33.5°, **S3**: 40.3°.

**43****S1****S2**

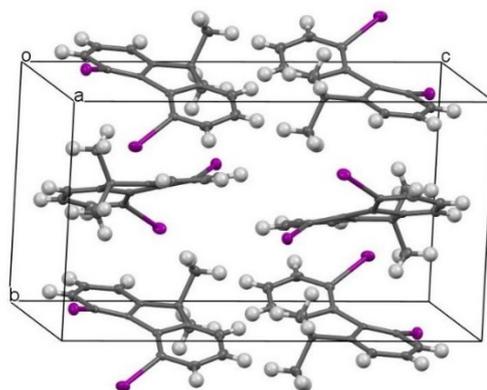
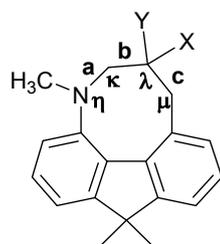


Figure S2: Two views of the molecular structure of **43** (top) and its crystal packing arrangement (below).

Table S7. Selected molecular geometry for fluoreno-azocines **48** and **50**.



48 X = Y = $-(\text{C}=\text{O})_2\text{CMe}_2$

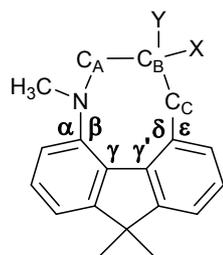
50 X = NO_2 , Y = H.

	a / Å	b / Å	c / Å	$\Sigma^a / ^\circ$
48	1.454(2)	1.565(2)	1.561(2)	350.6(2)
50	1.460(4)	1.525(4)	1.506(4)	348.8(4)

Σ^a = Sum of bond angles at nitrogen.

	$\eta / ^\circ$	$\kappa / ^\circ$	$\lambda / ^\circ$	$\mu / ^\circ$
48	118.26(13)	113.75(13)	108.14(12)	116.44(12)
50	116.1(2)	116.1(2)	112.0(2)	112.1(2)

Table S8. Selected angles around the fluorene ring, and deviations of selected atoms in the azocine ring from the fluorene plane for the *spiro* fluoreno-azepines **48** and **50**.



48 X = Y = -((C=O)O)₂CMe₂

50 X = NO₂, Y = H

	$\alpha / ^\circ$	$\beta / ^\circ$	$\gamma / ^\circ$	$\gamma' / ^\circ$	$\delta / ^\circ$	$\epsilon / ^\circ$
48	120.14(14)	122.97(14)	133.50(14)	133.35(14)	124.02(14)	117.80(14)
50	121.5(2)	121.0(2)	133.4(2)	134.0(2)	124.2(3)	117.6(2)

Deviations from the fluorene plane / Å

	N	C _A	C _B	C _C
48	0.389(3)	1.458(4)	0.953(4)	-0.306(4)
50	0.4379(19)	1.428(2)	0.829(2)	-0.391(2)

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