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FACILE SYNTHESIS OF 2-ARYLPYRROLES FROM 4-OXO-BUTANOIC ACIDS AND THEIR USE IN THE PREPARATION OF BIS(PYRROLYL)METHANES

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Abstract – A range of 3-aroyl-propionic acids have been cyclised to unsaturated lactones which, upon reduction using DIBAL-H and reaction with an ammonia source, gave 2-arylpyrroles (Ar = Ph, 1-naphthyl, *o*-phenoxyphenyl and 4-methyl-2-methylsulfanylphenyl) in excellent yields. Reaction of 2,6-disubstituted aroylpropanals (Ar = 2,4,6-$Me_3C_6H_2$, anthracenyl and 2-Me-naphthalen-1-yl) with an ammonia source failed to generate pyrroles. The arylpyrroles react readily with ketones or aldehydes in ethanol or under eutectic mix melt conditions to give bis-(pyrrolyl)methanes in excellent isolated yields.

INTRODUCTION

General routes to substituted pyrroles have been much examined due to the ubiquitous role of pyrroles in natural products and as key intermediates in drug manufacture.[1] Recently, there has been a growing interest in functionalized 2-arylpyrroles as precursors for the synthesis of: i.) 5,5-diaryl-4-bora-3a,4a-diaza-s-indacenes (BODIPY®) as dyes or chromophores, ii.) as end caps for oligopyrroles in electrochemical studies of these conducting polymers or iii.) tris-(pyrrolyl)methanes or amines as chelating ligands in anionic sensors. We were interested in developing routes to potentially bidentate or tetradentate bis-(arylpyrrolyl)methanes or pyrrolylmethenes as C_2-symmetric supporting ligands in olefin oligomerisation/polymerisation catalysis, as indicated in Figure 1. Although there have

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been a number of recent reports on the use of bis-(pyrrolyl)methane ligands in coordination chemistry or in catalysis there has been no report where the steric environment around the metal centre has been adjusted by altering the *ortho*-substituent of the pyrrole apart from bis-(iminopyrrolyl)methanes.

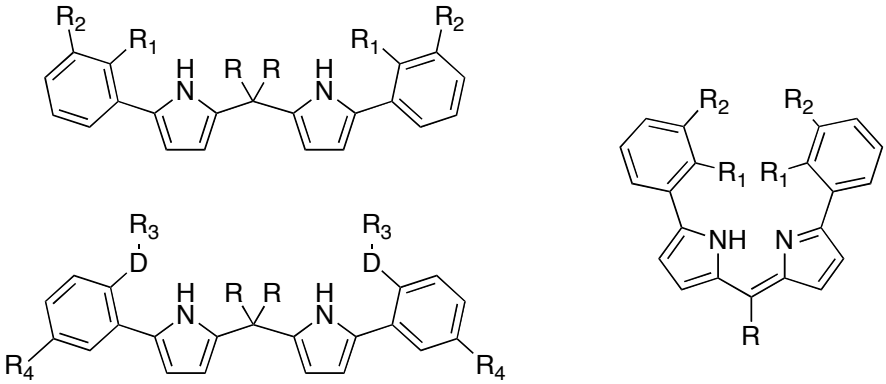
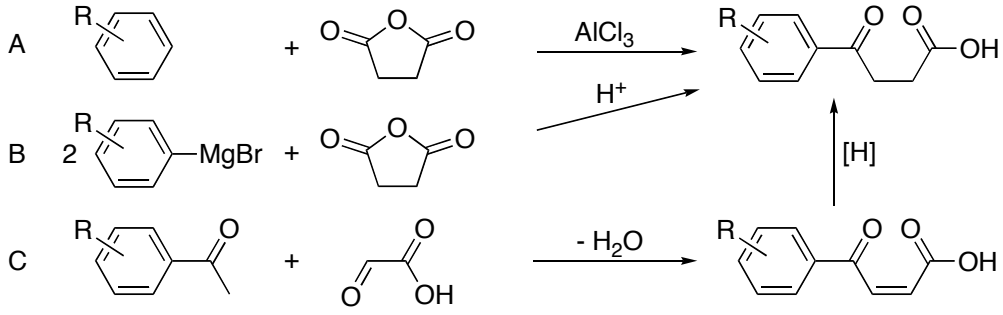


Figure 1. Targeted 2,2'-(bis-5,5'-arylpyrrolyl)methanes or pyrrolylmethenes

Simple 2-arylpyrroles have been synthesized by the high temperature isomerization of 1-arylpyrrole,[2] decarboxylation of arylpyrroles[3] or more recently by coupling reactions,[4] especially Suzuki[5] or Stille[6]methodologies, for example coupling 2-bromo *N*-Boc protected pyrroles with arylboronic acids to generate a series of dyes with tunable characteristics (Ar = Ph, 1-naph, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$ and 4-FC_6H_4), or coupling bromoarenes with 2-R_3Sn functionalized *N*-Boc-pyrroles for oligopyrroles (Ar = Ph, anthracenyl). As we were interested in generating a library of bispyrrolylmethanes or arylpyrrolylimines, we decided to investigate alternative routes to the required 2-arylpyrroles, which may offer general routes to large quantities of the required 2-arylpyrrole precursors avoiding the use of expensive reagents or multi-step preparations of precursors. We turned to the synthesis of a 4-oxobutanal, the Paal-Knorr precursor for pyrroles, and examined methods for its general synthesis.



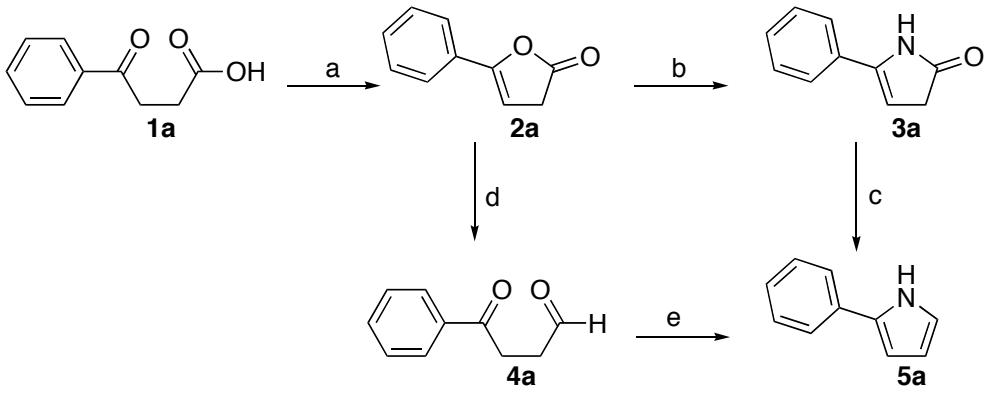
Scheme 1. General synthetic routes to 4-aryl-4-oxobutanoic acids

After examining known routes to 4-oxobutanals, including $C_1 + C_3$,[7] $C_2 + C_2$[7b,8] (especially the Trofimov reaction or variations of this[1a,1g,9]) or $C_3 + C_1$[10] coupling chemistry, as well as alternative approaches, e.g.

ozonolysis of 5-oxopent-1-ene[11] or methathesis,[12] we decided that the available routes were either too complicated, formed highly functionalized products or were not sufficiently general. The commercially available, or readily synthesized, 4-oxobutanoic acids (see Scheme 1) appeared to offer a key source of the required 4 carbon synthon for the Paal-Knorr synthesis of the pyrrole framework. We report here the facile generation of the 4-aryl-4-oxobutanal by DIBAL-H (i-Bu_2AlH) reduction of 5-aryl-*3H*-furan-2-ones formed from 4-aryl-4-oxobutanoic acid and their conversion into 2-arylpyrroles. The pyrroles have been used to generate new asymmetric bidentate and tetradentate bis-(pyrrolyl)methanes.

RESULTS AND DISCUSSION

The initial target for this research was the previously reported unsaturated lactam 5-phenyl-1,3-dihydro-pyrrolidin-2-one (**3a**) formed by cyclisation of the commercially available benzoylpropionic acid to the unsaturated γ-lactone (5-phenyl-*3H*-furanone) followed by reaction with NH_3 in ethanol (Scheme 2).

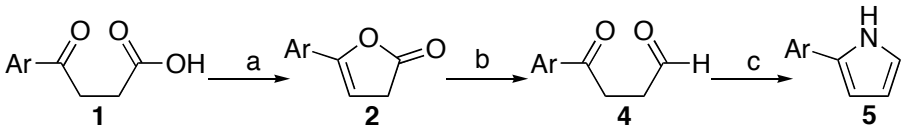


Scheme 2. Synthesis of 5-phenylpyrrole; (a) Ac_2O, cat H^+ (b) NH_3, EtOH, reflux
(c) $LiAlH_4$ (d) DIBAL-H, -78°C, H^+ (e) NH_4OAc, EtOH

It was expected that a simple reduction would then allow formation of the required pyrrole. During this work it was realized that formation of the γ-lactone effectively protected the arylketone as an enolester. This should allow reduction using DIBAL-H to the required Paal-Knorr precursor, the ketoaldehyde, allowing access not only to the required pyrroles but also the analogous furans and thiophenes. Reaction of **2a** with 1.1 eq. of DIBAL-H followed by an acid workup resulted in formation of the required ketoaldehyde (**4a**) (in > 95 % NMR yield). Reaction of the crude intermediate (**4a**) with NH_4OAc resulted in quantitative formation (NMR) of phenylpyrrole (**5a**) proving the synthetic route from 4-oxo-butanoic acids in three simple reaction steps in a high overall isolated yield (>90%).

An extensive literature search indicated only two previously reported DIBAL-H reductions of unsaturated γ-lactones to form keto-aldehydes or furans. Reduction of 5-alkyl-*3H*-furanones to form ketoaldehydes as perfume precursors[13] and a recent report, published after the commencement of this study, of the isomeric 5-alkyl-*5H*-furanones as intermediates in the synthesis of Litseaverticillols A, C, D, F and G.[14] An alternate, direct palladium catalyzed reduction of **1a** to **4a** has recently been reported in the presence of excess pivalic anhydride,[15] while reactions using triethyl orthoformate or orthoacetate result in moderate yields of ketoaldehydes and 2 or 2,5-furans via intermediate 3 carboxy species.[16]

The simplicity of the new methodology encouraged development of the chemistry and a range of keto-acids were formed using the routes outlined in Scheme 1, **1d** and **1e** Path A, **1b** and **1g**[17,18] Path B and **1b**, **1c** and **1f** via intermediate 4-oxobutenoic acids (Ar = 1-naphthyl (**I**), *o*-(Ph)C_6H_4 (**II**) and 9-anthracenyl (**III**)) Path C, Scheme 3. The majority of the keto-acids have been previously reported, **1b**, **d**, **e**, **f** and **g**,[17,19] or are commercially available, i.e. benzoylpropionic acid (**1a**). The keto-acids were cyclised using Ac_2O in an acid catalyzed reaction (yields > 80%, non-optimized) and reduced with DIBAL-H at low temperature. Reaction of the crude products (**4a-d)** with NH_4OAc generated the required pyrroles in excellent overall recrystallized yield, generally > 75%. However keto-acids (**1e-g)**, with di-*ortho*-substituted aryl groups, were cyclised and reduced to form the required ketoaldehydes (**4h-j**) but did not generate the required pyrrole on reaction with an ammonia source. This is presumably due to the sterically demanding aryl substituents impeding nucleophilic attack on the arylketone by ammonia or the enamine formed from **4e-g** upon reaction with the ammonia source.



1 **2** **4** **5**

1a Ar = Ph
1b Ar = 1-Napthyl
1c Ar = *o*-(PhO)C_6H_4
1d Ar = 4-Me-2(MeS)C_6H_4
1e Ar = Mesityl
1f Ar = Anthracenyl
1g Ar = 2-Me-napth-1-yl

5a Ar = Ph
5b Ar = 1-Napthyl
5c Ar = *o*-(PhO)C_6H_4
5d Ar = 4-Me-2(MeS)C_6H_4

Scheme 3. Substituted pyrrole synthesis from 4-keto-butanoic acids, a. Ac_2O, b. DIBAL-H, –78°C, c. NH_4OAc

Reaction of 2-phenylpyrrole with a range of ketones R_2CO (R = Ph, Py or R,R = fluorenyl) allowed a new set of bis(pyrrolyl)methanes, (**6a-c)**, to be generated (Figure 2). Blocking the pyrrole 2-position enables reactions to be carried out under eutectic mix melt conditions, resulting in yields of > 95% (NMR, crude

product). Similarly, reaction of naphthalenyl- or 2-phenoxyphenyl-pyrroles allowed generation of potentially C_2-symmetric bis(pyrrolyl)methanes (**7a**) and tetradentate bis(pyrrolyl)methanes (**8a-b**).

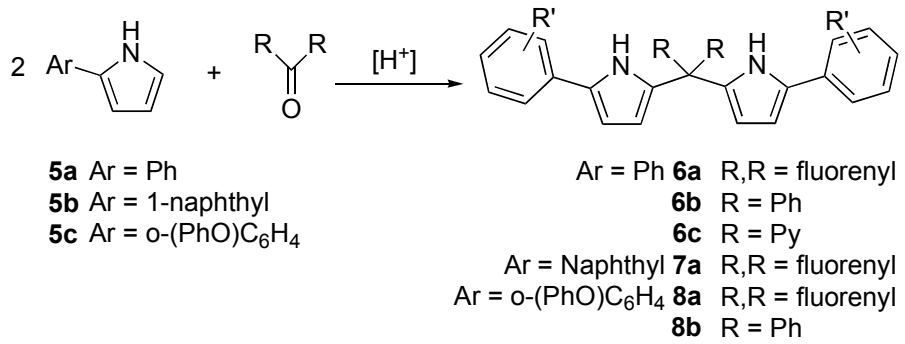


Figure 2. Synthesis of new bis(pyrrolyl)methanes

In summary, we have developed a facile synthesis of 2-arylpyrroles from 4-oxobutanoic acids via cyclization and subsequent DIBAL-H reduction of resultant unsaturated furanones. The 4-oxobutanoic acids are readily generated by simple Friedel-Crafts or Grignard chemistry using succinic anhydride as a C_4 synthon or via condensation of arylketones with glyoxylic acid and reduction of the substituted acrylic acids. We are currently exploiting this chemistry to develop routes to substituted pyrroles as precursors to bis(pyrrolyl)methanes. The metal complexation chemistry of the bis(pyrrolyl)methanes is currently under investigation.

EXPERIMENTAL

2'-Phenoxyacetophenone[20] was prepared by literature methods. ^{1}H-^{1}H, ^{1}H-^{13}C correlation and DEPT spectra were recorded on all compounds and NOESY spectra were collected, where required, to identify proton proximity.

4-Naphthalen-1-yl-4-oxobut-2-enoic acid (**I**)

A solution of 1-acetylnaphthalene (50 g, 0.294 mol) and glyoxylic acid monohydrate (27 g, 0.35 mol) in acetic acid 25 mL containing a catalytic amount of *p*-toluenesulphonic acid (0.25 g) was refluxed overnight. A sample was taken for ^{1}H NMR and indicated 90% completion of reaction. The reaction mix was cooled and ether (200 mL) added. The reaction mix was washed with 4 x 100 mL of water, dried over Na_2SO_4, filtered and the solvent removed. The residue was triturated in hexane and the crude product collected by filtration. Analytically pure material was obtained by recrystallization from ethanol. Yield 51.2 g (77%).[21,22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57(d, *J* = 82 Hz, Ar-H), 7.91(pseudo-t, 2H *J* = 8.5 Hz, Ar-H) overlapping 7.87(, 1H *J* = 15.8 Hz, CH), 7.53-7.67(m, 3H, Ar-H), 6.83(d, 1H *J* = 15.8 Hz, CH), COOH not identified. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.8, 170.7, 142.0, 133.9, 133.9, 131.6,

130.4, 129.5, 128.7, 128.4, 126.9, 125.5, 124.4. IR (KBr: CO cm^{-1}) υ 1700, 1667. CI-MS (m/z) 244($M+NH_4^+$ 85%), 246($MH_2+NH_4^+$ 100%). Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C 74.42; H, 4.46.

4-Oxo-4-(2-phenoxyphenyl)but-2-enoic acid (**II**)

As above for **I**. Yield 71%. ^1H NMR (400 MHz, $CDCl_3$) δ 11.50(br s, 1H, COOH), 7.91(d, 1H *J* = 15.6 Hz, CH), 7.81(dd, 1H *J* = 7.8 & 1.8 Hz, H_e), 7.46(ddd, 1H *J* = 8.7 & 7.0 & 1.4 Hz, H_c), 7.37(brdd, 2H *J* = 6.5 & 5.4 Hz, *m*-Ph-H), 7.21(dt, 1H *J* = 7.5 & 1.0 Hz, H_d), 7.16(tt, 1H *J* = 7.4 & 1.1 Hz, *p*-Ph-H), 7.01(brd, 2H *J* = 8.7 Hz, *o*-Ph-H), 6.93(dd, 1H *J* = 8.3 & 0.9 Hz, H_b), 6.70(d, 1H *J* = 15.6 Hz, CH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.5, 171.0, 156.7, 155.9, 142.2, 134.5, 131.0, 130.1, 129.4, 129.3, 124.3, 123.6, 119.1, 118.9. IR (KBr: CO cm^{-1}) υ 1700, 1663. CI-MS (m/z) 286($M+NH_4^+$ 100%), 269($M+H^+$ 60%). Anal. Calcd for $C_{16}H_{12}O_4$: C 71.64; H 4.51. Found: C 71.63; H 4.37.

4-Anthracen-9-yl-4-oxobut-2-enoic acid (**III**)

As above for **I**. Crude material was obtained by slurrying in $CHCl_3$ and collecting the red crystalline material, which was identified as the $CHCl_3$ adduct. Dried in a vacuum oven overnight at 60 °C. Yield 72%. Analytically pure material obtained by recrystallization from toluene / ethanol.[23,24] ^1H NMR (400 MHz, methanol-d_4) δ 8.59(s, 1H, H_5), 8.03-8.07(m, 2H, H_4), 7.73-7.77(m, 2H, H_1), 7.44-7.52(m, 4H, H_3 & H_2), 7.44 (d, 1H *J* = 15.9 Hz, CH), 6.20(d, 1H *J* = 15.9 Hz, CH), COOH not identified. $^{13}C\{^1H\}$ NMR (100 MHz, methanol-d_4) δ 201.2, 168.1, 142.6, 136.8, 134.0, 132.4, 130.5, 130.0, 129.5, 128.3, 126.7, 125.5. IR (KBr: CO cm^{-1}) υ 1700, 1661. CI-MS (m/z) 294($M+NH_4^+$ 10%), 144(NapthOH 100%). Anal. Calcd for $C_{18}H_{12}O_3$: C 78.25; H 4.38. Found C 78.17, H 4.29.

4-Naphthalen-1-yl-4-oxo-butyric acid (**1b**)

Method A. To a solution of **I** (50 g, 0.221 mol) in 100 mL of 90/10 HOAc/H_20 was added zinc dust (excess) in portions until no further reaction was noted. The reaction mix was diluted with 200 mL of 2 M HCl and 200 mL of ether added. The mix was filtered to remove excess zinc dust and the organic phase separated and washed with 100 mL 2 M HCl then 3 x 100 mL of distilled water. The ether layer was dried over Na_2SO_4, filtered and the solvent removed in vacuo to leave a crude product which was slurried in cold 96% ethanol and the product recovered by filtration. Yield 44.6 g (88%).

Method B: A Grignard formed from 1-bromonapthalene (100g, 0.483 mole) was added to a slurry of succininc anhydride (50 g, 0.50 mol) in 500 mL of thf at 0°C. The solution was allowed to warm to rt and then refluxed for 4 h. To the cooled solution was added 500 ml of 2M HCl and 500 mL of ether.

The phases were separated and the organic phase washed with 500 mL, 2 M HCl and 3 x 500 mL of distilled water. The organic phase dried over Na_2SO_4 and the solvent removed under vacuum. The crude product was slurried in cyclohexane and filtered. Yield 48 g (44%).[19g,i] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63(dd, 1H *J* = 7.7 & 0.9 Hz, H_g), 8.01(d, 1H *J* = 8.2 Hz, H_c), 7.95(dd, 1H *J* = 7.2 & 1.2 Hz, H_a), 7.88(dd, 1H *J* = 8.0 & 1.5, H_d), 7.49-7.61(m, 3H, H_f, H_e & H_b), 3.93(t, 2H *J* = 6.4 Hz, CH_2), 2.90(t, 2H *J* = 6.4 Hz, CH_2), COOH not identified. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.8, 135.2, 133.9, 132.9, 130.1, 128.4, 128.0, 127.8, 126.5, 125.7, 124.3, 84.8, 360.3, 28.4. IR (KBr: CO cm^{-1}) υ 1718, 1691. CI-MS (m/z) 246($M+NH_4^+$ 100%), 229($M+H^+$ 80%). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found C, 73.80; H, 5.19.

4-Oxo-4-(2-phenoxyphenyl)butyric acid (**1c**)

As above for **I**. Yield 94.5 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60(s, 1H, COOH), 7.88(dd, 1H *J* = 7.8 & 1.8 Hz, H_e), 7.43(ddd, 1H *J* = 8.6 & 7.0 & 1.5 Hz, H_d) overlapping 7.38(dd, 2H *J* = 8.6 & 7.5 Hz, *m*-Ph-H), 7.05(m, 2H, H_d & *p*-Ph-H), 7.05(br d, 2H, *o*-Ph-H), 6.89(dd, 1H *J* = 8.3 & 0.9 Hz, H_b), 3.37(t, 2H *J* = 6.4 Hz, CH_2), 2.74(t, 2H *J* = 6.4 Hz, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 179.1, 156.6, 156.1, 133.8, 130.7, 130.1, 129.3, 124.1, 123.4, 119.2, 118.9, 38.2, 28.5. IR (KBr: CO cm^{-1}) υ 1709, 1671. CI-MS (m/z) 288($M+NH_4^+$ 95%), 271($M+H^+$ 100%). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H 5.22. Found: C, 70.90; H, 5.16.

4-(5-Methyl-2-methylsulfanyl-phenyl)-4-oxo-butyric acid (**1d**)

To a mechanically stirred, degassed slurry of 4-methylsulfanyltoluene (138.23 g, 1.0 mol) and succinic anhydride (100.0 g, 1.0 mol) in 1.5 L of DCM at –20°C was slowly added $AlCl_3$ (266.6 g, 2 mol) and the red solution allowed to warm to rt over 4 h. The reaction mix was deactivated by pouring onto 3 L of ice and 1 L of 2M HCl. The organic phase was separated, the aqueous phase extracted with 500 mL of DCM and the combined organic extracts washed with 500 mL of 2 M HCl then 3 x 500 mL of distilled water. The organic fraction was dried over Na_2SO_4, filtered and the DCM removed under vacuum to leave a crude product which was slurried in a minimum of 96 % ethanol, filtered and washed with 2 x 100 mL of 96% ethanol. The crude material was dried in vacuum oven at 60°C overnight. Analytically pure material was obtained by recrystallization from toluene / ethanol. Yield 211.0 g (88.5%).[19a,25,26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69(d, 1H *J* = 1.8 Hz, H_e), 7.30(ddd, 1H *J* = 8.2 & 1.8 & 0.5 Hz, H_c), 7.21(d, 1H *J* = 8.2 Hz, H_b), 3.29(t, 2H *J* = 6.7 Hz, CH_2), 2.81(t, 2H *J* = 6.7 Hz, CH_2), 2.40(s, 3H, SMe), 2.37(s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.7, 179.1, 172.1, 139.0, 133.7, 133.4, 133.3, 130.9,

125.3, 34.5, 28.2, 20.7, 16.1. IR (KBr: CO cm^{-1}) υ 1700, 1667. CI-MS (m/z) 256($M+NH_4^+$ 100%), 239($M+H^+$ 30%). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.45; H, 5.78.

4-Oxo-4-(2,4,6-trimethylphenyl)butyric acid (**1h**)

Made as for **1d** above by Friedel-Crafts chemistry. Analytically pure material obtained by recrystallization from hot heptane. Yield 19.2g (FW 220.26 95.1%).[27] ^1H NMR (400 MHz, $CDCl_3$) δ 7.261(s, 2H, *m*-Ph-H), 3.03(t, 2H *J* = 6.5 Hz, CH_2), 2.77(t, 2H *J* = 6.5 Hz, CH_2), 2.28(s, 3H, Me), 2.201(s, 6H, Me), COOH not located. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 208.2, 177.9, 138.7, 138.6, 132.7, 128.5, 39.2, 27.4, 21.0, 19.0. IR (KBr: CO cm^{-1}) υ 1715, 1697. CI-MS (m/z) 238($M+NH_4^+$ 100%), 221($M+H^+$ 100%). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.84; H, 7.41.

4-Anthracen-9-yl-4-oxo-butyric acid (**1i**)

A deep yellow solution of anthracenoyl acrylic acid (**III**) (20g, 72.4 mmol) in ethanol containing 0.5 g of Pd/C was placed in a Parr reactor and pressurized with 4 Bar of H_2. The reaction was monitored by opening the reactor every hour and stopped when the yellow color was discharged and an off white precipitate had formed. The solids were dissolved in toluene, filtered and the solvent removed under vacuum to leave a product which could be used without further purification. Analytically pure material was obtained by recrystallization from toluene / ethanol. Yield 19.5 g (96.8 %).[28,29] ^1H NMR (250 MHz, acetone-d_6) δ 10.90(s, 1H, OH), 8.64(s, 1H, H_5), 8.11-8.14(m, 2H, H_4), 8.03-8.06(m, 2H, H_1), 7.52-7.58(m, 4H, H_3 & H_2), 3.39(t, 2H *J* = 5.95 Hz, CH_2), 2.94(t, 2H *J* = 5.95 Hz, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 208.4, 174.3, 137.4, 132.0, 129.5, 128.9, 127.8, 127.5, 126.5, 125.4, 41.5, 27.8. IR (KBr: CO cm^{-1}) υ 1700br. CI-MS (m/z) 296($M+NH_4^+$ 100%), 279($M+H^+$ 30%). Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.67; H, 5.15.

4-(2-Methylnaphthalen-1-yl)-4-oxo-butyric acid (**1j**)

A Grignard reagent made from 1-bromo-2-methylnaphthalene (90% dried by passage through a basic alumina column, 90 g, 0.40 mol) in thf was slowly added to a slurry of succinic anhydride (40 g, 0.40 mol) in 100 mL of thf at 0ºC. The reaction mix was allowed to warm to rt and then refluxed for 4 h. The cooled solution was deactivated by addition of 100 mL of 2 M HCl, extracted with 2 x 100 mL of ether. The combined organic fractions were washed with distilled water (3 x 100 mL), dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was slurried in hexane and the crude product collected by filtration. Analytically pure material was obtained by recrystallization from toluene / ethanol. Yield 33.0 g (39.2%, theoretical 50%) cf ref.[17] ^1H NMR (400

MHz, $CDCl_3$) δ 11.60(br s, 1H, OH), 7.83(d, 1H *J* = 7.8 Hz, Naphth-H), 7.79(d, 1H *J* = 8.4 Hz, Hc), 7.65(d, 1H *J* = 8.0 Hz, naphth-H), 7.43-5.51(m, 2H, He & Hf), 7.31(d, 1H *J* = 8.4 Hz, Hb), 3.21(t, 2H *J* = 6.3 Hz, C*H*$_2$CH$_2$CO$_2$H), 2.91(t, 2H *J* = 6.3 Hz, CH$_2$C*H*$_2$CO$_2$H), 2.43(s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 207.8, 178.5, 137.6, 131.7, 130.5, 129.3, 129.0, 128.5, 128.2, 127.0, 125.5, 123.9, 39.7, 27.5, 19.2. IR (KBr: CO cm^{-1}) υ 1711, 1701. CI-MS (m/z) 260(M+NH_4^+ 100%). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.19; H, 5.86.

5-Phenyl-3H-furan-2-one (**2a**)

Benzoylpropionic acid (83 g, 466 mmol), was slurried in 100 mL of Ac_2O with 50 mL of HOAc containing a catalytic amount of *p*-toluene sulphonic acid (0.5 g). The slurry was allowed to stir for 4 h during which time the initial solid dissolved giving a clear warm solution before the product precipitated. The slurry was diluted with 150 mL of distilled water, stirred for 30 min and the product collected by filtration to give an off white crystalline solid which was washed with 50/50 H_2O/HOAc then H_20 and dried in a vacuum oven at 60°C overnight. The crude product could be used without further purification. Analytically pure material was obtained by sublimation. Yield 62 g (84%).[30-33] ^1H NMR (250 MHz, $CDCl_3$) δ 7.60(m, 2H *J* = 3.9 & 0.8 Hz, *o*-Ph-H), 7.36-7.42(m, 3H, *p* & *m*-Ph-H), 5.79(t, 1H *J* = 1.4 Hz, CH), 3.42(d, 2H *J* = 1.4 Hz, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.0, 153.9, 129.6, 128.7, 128.4, 124.7, 97.7, 34.7. IR (KBr: CO cm^{-1}) υ 1804, 1786. CI-MS (m/z) 178(M+NH_4^+ 100%), 161(M+H^+ 50%). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.80, H, 4.74.

5-Naphthalen-1-yl-3H-furan-2-one (**2b**)

As above for **2a**. Yield 38.5 g (93.4%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.28(brd, 1H *J* = 7.8 Hz, Hg), 7.88-7.92(m, 2H, Ar-H), 7.71(brd, 1H *J* = 7.1 Hz, Ha), 7.47-7.58(m, 3H, Ar-H), 5.81(t, 1H *J* = 2.4 Hz, CH), 3.40(d, 2H *J* = 2.4 Hz, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.0, 154.1, 133.7, 130.5, 130.3, 128.7, 127.0, 126.9, 126.5, 126.2, 125.0, 124.9, 103.0, 34.7. IR (KBr: CO cm^{-1}) υ 1795. CI-MS (m/z) 228(M+NH_4^+ 100%), 211(M+H^+ 25%). Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.83; H, 4.90.

5-(2-Phenoxylphenyl)-3H-furan-2-one (**2c**)

As above for **2a**. Yield 71%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77(dd, 1H *J* = 7.8 & 1.6 Hz, H_a), 7.378(dd, 2H *J* = 8.5 & 7.5 Hz, *m*-PhH), 7.29(dt, 1H *J* = 7.8 & 1.7 Hz, H_c), 7.13-7.19(m, 2H, H_b & *p*-Ph-H), 7.02(br dd, 2H *J* = 8.6 & 1.0 Hz, *o*-Ph-H), 6.90(dd, 1H *J* = 7.7 & 1.5 Hz, H_d), 6.15(t, 1H *J* = 2.7 Hz, CH), 3.40(d, 2H *J* = 2.7 Hz, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.6, 156.0, 154.9, 149.7, 130.2, 130.0, 127.7,

123.9, 123.5, 119.7, 118.9, 118.7, 104.0, 35.0. IR (KBr: CO cm^{-1}) υ 1710. CI-MS (m/z) 270($M+NH_4^+$ 100%), 253($M+H^+$ 20%). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.29; H, 4.92.

5-(4-methyl-2-methylsulfanylphenyl)-3H-furan-2-one (**2d**)

As above for **2a**. Yield 85%. ^1H NMR (400 MHz, $CDCl_3$). δ 7.47(s, 1H, He), 7.14-7.21(m, 2H, Hb & Hc), 6.08(t, 1H *J* = 2.5 Hz, C*H*), 3.46(d, 2H *J* = 2.5 Hz, CH_2), 2.49(s, 3H, SMe), 2.33(s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.6, 151.8, 134.8, 133.8, 130.5, 129.0, 126.8, 126.4, 104.2, 35.1, 20.8, 16.4. IR (KBr: CO cm^{-1}) υ 1784. CI-MS (m/z) 238($M+NH_4^+$ 100%), 221($M+H^+$ 75%). Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49. Found: C, 65.63; H, 5.42.

5-(2,4,6-Trimethylphenyl)-3H-furan-2-one (**2e**)

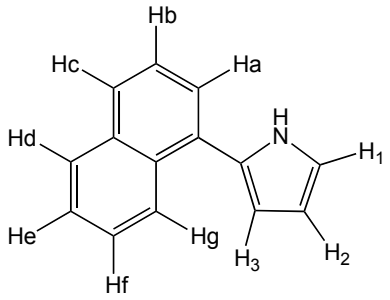
As above for **2a**. The off white solid was recrystallized from ether at low temperature. Yield 7.5g (82%).[19b] ^1H NMR (250 MHz, $CDCl_3$) δ 6.91(s, 2H, *m*-Ph-H), 5.39(t, 1H *J* = 2.4 Hz, CH), 3.43(d, 2H *J* = 2.4 Hz, CH_2), 2.30(s, 9H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.7, 153.3, 139.5, 137.8, 128.4, 126.1, 103.6, 34.4, 21.2, 20.2. IR (KBr: CO cm^{-1}) υ 1814. CI-MS (m/z) 220($M+NH_4^+$ 100%). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H 6.98. Found: C, 77.09; H, 6.90.

5-Anthracen-9-yl-3H-furan-2-one (**2f**)

As above for **2a**. Yield 96.7%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.538(s, 1H, H_5), 8.18(br d, 2H *J* = 8.7 Hz, H_4), 8.02(br d, 2H *J* = 8.6 Hz, H_1), 7.47-7.56(m, 4H, H_3 & H_2), 5.81(t, 1H *J* = 2.4 Hz, CH), 3.701(d, 2H *J* = 2.4 Hz, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5, 151.5, 131.1, 130.6, 129.8, 128.7, 126.8, 125.5, 125.4, 122.9, 107.0, 34.8. IR (KBr: CO cm^{-1}) υ 1785sh, 1772. CI-MS (m/z) 278($M+NH_4^+$ 100%). Anal. Calcd for $C_{14}H_{10}O_2$: C, 83.06; H, 4.65. Found: C, 83.39; H, 4.76.

5-(2-Methylnaphthalen-1-yl)-3H-furan-2-one (**2g**)

As above for **2a** but the reaction required heating for 4 h at 60°C to complete reaction. The product was a tacky oil which solidified on standing. Yield 83% cf ref.[17] ^1H NMR (250 MHz, $CDCl_3$) δ 7.96(br d, 1H *J* = 7.3 Hz, Ar-H), 7.83(brd, *J* = 8.3 Hz, Hd & Ar-H), 7.42-7.55(m, 3H, Ar-H), 7.37(d, 1H *J* = 8.4 Hz, Hc),5.60(t, 1H *J* = 2.4 Hz, CH), 3.56(d, 2H *J* = 2.4 Hz, CH_2), 2.53(s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.4, 152.2, 136.4, 132.2, 131.8, 129.9, 128.4, 128.1, 126.9, 125.4, 125.2, 124.7, 105.2, 34.5, 20.6. IR (KBr: CO cm^{-1}) υ 1792. CI-MS (m/z) ($M+H^+$ 100%). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.51; H, 5.49.



Proton labelling for aryl-pyrroles

2-Phenylpyrrole (**5a**)

A slurry of **2a** (25 g, 156.0 mmol) in anhydrous toluene (1L) at –78°C was slowly added DIBAL-H (114 mL of 1.5 M, 171.1 mmol) over 1 h. The solution was reacted at -78°C for 4 h then deactivated by slow addition of HOAc (50 mL) at –78°C. After allowing the reaction mix to warm to rt, distilled water (200 mL) was added and the organic phase separated. The organic phase was then washed with brine (3 x 200 mL). A sample of the organic phase was taken and dried under vacuum. Diagnostic peaks for the keto-aldehyde (**4a**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.89(s, 1H, CHO), 3.32(t, 2H J = 6.3 Hz, CH_2CH$_2$CHO)[34], 2.92(t, 2H J = 6.3 Hz, CH$_2$CH_2CHO).[7b] To the toluene fraction was added NH_4OAc (24 g, excess) and the toluene removed under reduced pressure. The residue was extracted with toluene, washed with distilled water (3 x 100 mL), dried over Na_2SO_4 and the solvent removed under reduced pressure to generate a product which could be used without further purification. Analytically pure material was obtained by sublimation. Yield 14.7 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43(br s, 1H, NH), 7.49(br dd, 2H J = 8.3 & 1.2 Hz, *o*-Ph-H), 7.39(t, 2H J =7.8 Hz, *m*-Ph-H), 7.24(tt, 1H J = 7.4 & 1.1 Hz, *p*-Ph-H), 6.86-6.88(m, 1H, H_1), 6.55-6.57(m, 1H, H_3), 6.33(pseudo-q, 1H J = 2.9 Hz, H_2) ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 132.8, 132.1, 128.9, 126.2, 123.9, 118.9, 110.1, 105.9. CI-MS (m/z): 144(M+H$^+$ 100%). Anal. Calcd for $C_{10}H_9N$: C, 83.88; H 6.34; N 9.78. Found: C, 83.98; H, 6.46; N, 9.81. Lit.[40]

2-(1-Naphthalenyl)pyrrole (**5b**)

As above for **5a**. Diagnostic peaks of the keto-aldehyde (**4b**) ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.93(s, 1H, CHO), 3.36(t, 2H J = 6.2 Hz, CH_2CH$_2$CHO), 2.99(t, 2H J = 6.2 Hz, CH$_2$CH_2CHO). Product recrystallized from hexane at low temperature. Yield 55.3%.[5d,e,9e,35,36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42(br s, 1H, N-H), 8.31-8.34(m, 1H, H_g), 7.90-7.93(m, 1H, Ar-H), 7.83(pent, 1H J = 4.8 Hz, Ar-H), 7.485-7.551(m, 8H, Ar-H), 6.982(ddd, 1H J = 3.4 & 1.9 & 0.7 Hz, H_1), 6.552(ddd, 3.7 & 2.3 & 1.2 Hz, H_3), 6.44(pseudo-q, 1H J = 2.91 Hz, H_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.0, 131.5, 131.4, 130.5,

128.4, 127.5, 126.4, 126.1, 126.0, 125.8, 125.5, 118.4, 109.49, 109.47. CI-MS (m/z) 194($M+H^+$ 100%). Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.21; H, 5.62; N, 7.33.

2-(2-Phenoxyphenyl)pyrrole (**5c**)

As above for **5a**, yield 90.5%. Diagnostic peaks for the keto-aldehyde (**4c**). ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.84(s, 1H, CHO), 3.38(t, 2H *J* = 6.2 Hz, CH_2), 2.84(t, 2H *J* =6.2 Hz, CH_2). Analytically pure material obtained by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67(brs, 1H, NH), 7.77(dd, 1H *J* = 7.5 & 1.9 Hz, H_e), 7.39(dd, 2H *J* = 8.2 & 7.7 Hz, *m*-Ph-H), 7.09-7.2(m, 5H, Hc & H_d and *o* & *p*-Ph-H), 6.85-6.90(m, 2H, Hb & pyrrol-H_1), 6.723(brs, 1H, pyrrol-H_3), 6.33(pseudo-q, 1H *J* = 3.0 Hz, pyrrol-H_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.5, 152.5, 130.0, 129.0, 127.0, 126.7, 124.0, 123.9, 123.6, 119.4, 119.3, 118.7, 109.1, 106.9. CI-MS (m/z) 236($M+H^+$ 100%). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.78; H, 5.54; N, 5.78.

2-(4-methyl-2-methylsulfanyphenyl)pyrrole (**5d**)

As above for **5a**, yield 83.4%. {Diagnostic peaks for the keto-aldehyde (**4d**), ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.84 (s, 1H, CHO), 3.24(t, 2H *J* = 6.4 Hz, CH_2), 2.861(t, 2H *J* =6.4 Hz, CH_2), 2.31(s, 3H, Me), 2.29(s, 3H, Me)}. Analytically pure material obtained by recrystallization from ethanol at low temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69(br s, 1H, NH), 7.35(br d, 1H *J* = 1.1 Hz, *p*-Ph-H), 7.30(d, 1H J = 7.9 Hz, *m*-Ph-H), 6.85-6.90(dd, 1H *J* = 7.9 & 1.1 Hz, *o*-Ph-H),6.90(br, 1H, pyrrol-H_1), 6.53(br, 1H, pyrrol-H_3), 6.30(pseudo-q, 1H *J* = 2.2 Hz, pyrrol-H_2), 2.35(s, 3H, Me), 2.33(s, 3H, SMe). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.7, 132.9, 131.0, 130.8, 129.8, 129.5, 127.7, 127.4, 118.4, 109.0, 108.7, 21.0, 17.8. CI-MS (m/z) 204($M+H^+$ 100%). Anal. Calcd for $C_{16}H_{13}NO$: C, 70.98; H, 6.45; N, 6.89. Found: C, 70.85; H, 6.57; N, 6.69.

2-(2,4,6-Trimethylphenyl)pyrrole (**5e**)

Attempted Prep. Diagnostic peaks for the keto-aldehyde (**4e**), ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.91(s, 1H, CHO). 6.85(s, 2H, *m*-Ph), 3.04(t, 2H *J* = 6.1 Hz, CH_2), 2.88(t, 2H *J* = 6.1 Hz, CH_2), 2.28(s, 3H, Me), 2.21(s, 6H, Me).

2-(9-Anthracenyl)pyrrole (**5f**)

Attempted Prep. Diagnostic peaks for the keto-aldehyde (**4f**), ^{1}H NMR (250 MHz, $CDCl_3$) δ 10.04(s, 1H, CHO), 3.39(t, 2H *J* = 5.9 Hz, CH_2), 3.09(t, 2H *J* =5.9 Hz, CH_2).

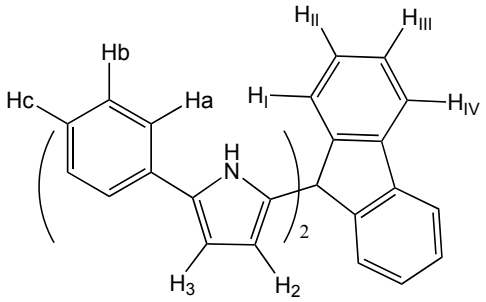
2-(2-Methylnaphthalen-1-yl)pyrrole (**5g**)

Attempted Prep. Diagnostic peaks for the keto-aldehyde (**4g**), ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.97(s, 1H, CHO), 3.12(t, 2H *J* = 5.9 Hz, CH_2), 2.99(t, 2H *J* =5.9 Hz, CH_2), 2.43(s, 3H, Me).

9,9-Bis-(5-phenylpyrrol-2-yl)fluorene (**6a**)

Method A: Phenylpyrrole (**5a)** (1.43 g, 10.0 mmol) and fluorenone (2.0 g, excess) were dissolved in EtOH (5 mL) and heated for 16 h with a catalytic amount of formic acid. The reaction was monitored by ^{1}H NMR spectroscopy and allowed to react until no pyrrole remained. The product was recovered by filtration and washed with EtOH. Yield 1.35g (55%).

Method B: Phenylpyrrole (**5a)** (1.43 g, 10.0 mmol) and fluorenone (1.0 g, excess) were heated for 16 h at 100°C under dinitrogen with a catalytic amount of formic acid. The product was slurried in EtOH and recovered by filtration and then washed with EtOH. Yield 2.15g (88%). Crystals suitable for structural analysis can be grown by slow vapor diffusion of hexane into a toluene solution of **6a**.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21(brs, 2H, NH), 7.83(d, 2H *J* = 7.6 Hz, fluor-H), 7.60(d, 2H *J* = 7.5 Hz, fluor-H), 7.45(dt, 2H *J* = 7.2 & 0.8 Hz, fluor-H), 7.29-7.39(m, 10H, Ar-H, 7.17(tt, 2H *J* = 7.1 & 1.6 Hz, *m*-Ph), 6.45(dd, 2H *J* = 3.5 & 2.7 Hz, pyr-H), 6.18(dd, 2H *J* = 3.5 & 2.7 Hz, pyr-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.8, 139.7, 133.9, 132.5, 131.8, 128.8, 128.4, 128.1, 126.2, 125.3, 123.7, 120.6, 109.4, 106.3. CI-MS (m/z): 449(M+H^+ 100%), 306(M-(Phenyl-pyrrole)+H^+ 70%). Anal. Calcd for $C_{33}H_{24}N_2$: C, 88.36; H, 5.39; N, 6.25. Found: C, 88.14; H, 5.54; N, 6.37.

1,1-Bis-(5-phenylpyrrol-2-yl)diphenylmethane (**6b**)

As above **6a** (Method B) Yield 89% ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21(s, 2H, NH), 7.23-7.38(m, 18H, Ar-H), 7.18(t, 2H *J* = 7.2 Hz, Ar-H), 6.51(t, 2H *J* = 3.0 Hz, H_3), 6.09(t, 2H *J* = 3.0 Hz, H_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.5, 136.1, 132.6, 131.8, 129.3, 128.9, 128.1, 127.1, 126.1, 123.6, 111.6, 105.9, 56.2. CI-MS (m/z) 451(M+H^+ 2.5%), 144(Phenyl-pyrrole+H^+ 100%). Anal. Calcd for $C_{33}H_{26}N_2$: C, 87.97; H, 5.82; N, 6.22. Found: C, 87.85; H, 5.86; N, 6.32.

1,1-Bis-(5-phenylpyrrol-2-yl)dipyrid-2-ylmethane (**6c**)

Phenylpyrrole (**5a)** (1.43 g, 10.0 mmol) and dipyridylketone (1.2 g, excess) were dissolved in 5 mL of EtOH and heated to reflux. The reaction was monitored by NMR and allowed to react until no pyrrole remained. The product was recovered by filtration and washed with EtOH. Yield 1.88g (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21(s, 2H, NH), 8.63(d, 2H *J* = 4.0 Hz, H_{IV}), 7.64(dt, 2H *J* = 7.8 & 1.5 Hz, H_{II}), 7.50(d, 4H *J* = 7.8 Hz, Ha), 7.36(t, 4H *J* = 7.7 Hz, Hb), 7.17-7.21(m, 4H. Hc & H_{III}), 6.98(d, 2H *J* = 8.0 Hz, H_I), 6.55(t, 2H *J* = 3.0 Hz, H_3), 6.08(t, 2H *J* = 3.0 Hz, H_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 148.4, 137.0, 133.9, 132.8, 132.0, 128.8, 126.0, 123.7, 123.6, 121.7, 111.9, 105.5, 58.3. CI-MS (m/z) 453(M+H^+ 8%), 144(Phenyl-pyrrole+H^+ 100%). Anal. Calcd for $C_{31}H_{24}N_4$: C, 82.27; H, 5.35; N, 12.38. Found: C, 82.45; H, 5.45; N, 12.53.

9,9-Bis-(5-(1-naphthalenyl)pyrrol-2-yl)fluorene (**7a**)

2-Naphthalen-1-ylpyrrole (**5b)** (1 g, 5.17 mmol) and fluorenone (1 g, excess) were dissolved in 5 mL of EtOH and heated to reflux. The reaction was monitored by NMR and allowed to react until no naphthalenylpyrrole remained. The product was recovered by filtration and washed with EtOH. Crystals suitable for structural analysis were grown by vapour diffusion of hexane into a toluene solution of **7a.** Yield 1.31g (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31(br s, 2H, NH), 8.27(br d, 2H *J* = 7.6 Hz, Ar-), 7.87(dd, 2H *J* = 7.7 & 1.8 Hz, Ar-H), 7.83(ddd, 2H *J* = 7.4 & 1.3 & 0.6 Hz, Ar-H), 7.87(br d, 2H *J* = 7.7 Hz, Ar-H), 7.71(ddd, 2H *J* = 7.5 & 1.2 & 0.6 Hz, Ar-H), 7.38-7.52(m, 12H, Ar-H), 6.43(dd, 2H *J* = 3.5 & 2.7 Hz, Py-H), 6.28(dd, 2H *J* = 3.5 & 2.7 Hz, Py-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.1, 139.7, 134.0, 133.7, 131.3, 131.2, 130.4, 128.4, 128.3, 128.0, 127.4, 126.3, 125.93, 125.90, 125.7, 125.4, 125.3, 120.6, 109.6, 108.6, 84.9. CI-MS (m/z) 549(M+H^+ 0.5%), 358(M-(Naphthalenyl-pyrrole)+H^+ 30%), 194(Naphthalenyl-pyrrole+H^+ 100%). Anal. Calcd for $C_{41}H_{28}N_2$: C, 89.75; H, 5.14; N, 5.11. Found: C, 89.96; H, 4.91; N, 5.26.

9,9-Bis-(5-(2-phenoxyphenyl)pyrrol-2-yl)fluorene (**8a**)

As above for **6a** (Method B). Yield 84 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38(s, 2H, NH), 7.64-7.68(m, 4H, He & Fl-H), 7.27(dt, 2H *J* = 7.5 & 1.1 Hz, H_c), 7.17-7.24(m, 6H, Ar-H), 6.99-7.14(m, 8H, Ar-H), 6.89(dd, 2H *J* = 8.0 & 1.5 Hz, H_b), 6.74(br dd, 4H *J* = 8.7 & 1.1 Hz, Ar-H), 6.53(dd, 2H *J* = 3.7 & 2.7 Hz, H_2), 6.05(dd, 2H *J* = 3.7 & 2.7 Hz, H_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.6, 150.9, 148.8, 139.5, 133.6, 129.7, 127.9, 127.8, 126.7, 126.5, 125.0, 124.5, 124.3, 123.0, 120.7, 120.2, 117.7, 107.8, 107.3, 55.9. CI-MS (m/z) 633(M+H^+ 50%), 398(M-$PhOC_6H_4$-pyrrole$^+$ 100%). Anal. Calcd for $C_{45}H_{32}N_2O_2$: C, 85.42; H, 5.10; N, 4.43. Found: C, 85.49; H, 5.16; N, 4.44.

Bis-(5-(2-phenoxyphenyl)pyrrol-2-yl)diphenylmethane (**8b**)

As above for **6a** (Method A). Yield 87 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38(s, 2H, NH), 7.65(dd, 2H *J* = 7.8 & 1.6 Hz, H_e), 7.20(t, 4H *J* = 7.9 Hz, Ar-H), *7*.00-7.16(m, 16H, Ar-H), 6.79(dd, 2H *J* = 8.0 & 1.0 Hz, H_b), 6.73(d, 4H *J* = 7.9 Hz, Ar-H), 6.53(dd, 2H *J* = 3.4 & 2.9 Hz, H_2), 6.00(dd, 2H *J* = 3.4 & 2.9 Hz, H_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.3, 151.7, 150.3, 145.4, 136.1, 129.6, 129.1, 127.8, 127.7, 126.6, 126.4, 124.0, 123.9, 123.4, 119.7, 118.6, 110.2, 107.0, 56.2. CI-MS (m/z) 635(M+H$^+$ 15%), 402(M-PhOC_6H_4-pyrrole$^+$ 45%), 236(PhOC_6H_4-pyrrole+H$^+$ 100%). Anal. Calcd for $C_{45}H_{34}N_2O_2$: C, 85.15; H, 5.40; N, 4.41. Found: C, 85.22; H, 5.53; N, 4.39.

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