

Reactions of 2-(pyrrol-1-yl)benzyl radicals and related species under flash vacuum pyrolysis conditions

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Supplementary Information

Full experimental details for products **5**, **7**, **25**, **26** (not given in main paper)

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NOE results

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The following pyrroles and related compounds were made by the method given in the main paper, unless stated otherwise:

***N*-[2-(benzyloxy)phenyl]pyrrole 5aa**

Reaction of *N*-(2-hydroxyphenyl)pyrrole **4a** (0.80 g, 50 mmol) with benzyl bromide (1.03 g, 55 mmol) as described in the main paper gave *N*-[2-(benzyloxy)phenyl]pyrrole **5aa** (1.05 g, 85%), bp 160-165 °C (0.005 Torr) (Found C, 82.0; H, 6.2; N, 5.65; C₁₇H₁₅NO requires C, 81.9; H 6.05; N, 5.6%), δ_{H} 7.42-7.05 (9H, m), 7.15 (2H, t, ³*J* and ⁴*J* 2.1), 6.42 (2H, t, ³*J* and ⁴*J* 2.1) and 5.13 (2H, s); δ_{C} 151.62 (quat), 136.54 (quat), 130.95 (quat), 128.38, 127.69, 127.18, 126.85, 125.69, 121.97, 121.46, 114.71, 108.70 and 70.81; *m/z* 249 (M⁺, 15%), 172 (20), 158 (42), 91 (100), 77 (23), 65 (28), 63 (12) and 51(22).

***N*-[2-(Allylamino)phenyl]pyrrole 5b**

N-(2-Aminophenyl)pyrrole **4b** (3.95 g, 25 mmol) was alkylated with allyl bromide (3.03 g, 25 mmol) as described in the main paper giving a mixture of starting material, mono- and di-allylated products. These were separated by chromatography on 6% deactivated alumina using hexane as eluent. The crude product was then purified by bulb to bulb distillation to give *N*-[2-(allylamino)phenyl]pyrrole **5b** (2.11 g, 43%), bp 145-150 °C (0.1 Torr) (Found: M⁺ 198.1153. C₁₃H₁₄N₂ requires *M* 198.1157); δ_{H} 7.43-7.28 (2H, m), 6.98 (2H, t, ³*J* and ⁴*J* 2.0), 6.92-6.86 (2H, m), 6.53 (2H, t, ³*J* and ⁴*J* 2.0), 6.08-5.95 (1H, m), 5.41-5.26 (2H, m), 4.16 (1H, br) and 3.87 (2H, m); δ_{C} 143.56 (quat), 134.94, 128.88, 127.30 (quat), 127.13, 121.90, 116.64, 116.00, 111.46, 109.55 and 45.86; *m/z* 198 (M⁺, 100%), 197 (52), 183 (17), 171 (24), 169 (39), 157 (35), 156 (26), 155 (12), 131 (12), 130 (15), 118 (11), 77 (20) and 51(15).

***N*-[2-(Allylthio)phenyl]pyrrole 5c**

Reaction of 2-aminothiophenol **3c** (6.25 g, 50 mmol) with 2,5-dimethoxytetrahydrofuran (6.60 g, 50 mmol) as described in the main paper gave *N*-(2-mercaptophenyl)pyrrole **4c** (6.28 g, 72%), bp 110-115 °C (0.05 Torr) [lit.,¹ 119-121 °C (1.0 Torr)] δ_{H} 7.41-7.20 (4H, m), 6.85 (2H, t, ³*J* and ⁴*J* 2.2), 6.39 (2H, t, ³*J* and ⁴*J* 2.2) and 3.41 (1H, s) spectrum compatible with that previously reported;¹ *m/z* 175 (M⁺, 6%), 174 (9), 173 (17), and 40 (100).

Treatment of *N*-(2-mercaptophenyl)pyrrole **4c** (2.00 g, 11.4 mmol) with allyl bromide under the conditions described in the main paper gave *N*-[2-(allylthio)phenyl]pyrrole **5c** (2.46 g, 100%), bp 118-120 °C (0.03 Torr) (Found C, 72.3; H, 6.2; N, 6.35. C₁₃H₁₃NS requires C, 72.5; H, 6.1; 6.5%) δ_{H} 7.47-7.26 (4H, m), 6.91 (2H, t, ³*J* and ⁴*J* 2.2), 6.36 (2H, t, ³*J* and ⁴*J* 2.2), 5.84-5.68 (1H, m), 5.17-5.03 (2H, m) and 3.35-3.30 (2H, m); δ_{C} 133.00, 132.78 (quat), 130.06, 127.50, 126.91, 126.53, 121.98, 117.87, 108.96, 108.80 (quat) and 35.86; *m/z* 215 (M⁺, 8%), 175 (16), 174 (100), 173 (20) and 45 (9).

bis-[2-(Pyrrol-1-yl)benzyl] oxalate 5d

A mixture of methyl 2-aminobenzoate **3da** (3.02 g, 20 mmol), 2,5-dimethoxytetrahydrofuran (1.98 g, 20 mmol) and glacial acetic acid (15 cm³) in dioxane (30 cm³) was heated under reflux for 2 h. The volatiles were then removed on a rotary evaporator and the residue azeotroped with xylene to remove any remaining acetic acid to give *N*-[2-(carbomethoxy) phenyl]pyrrole **4da** (3.65 g, 91%), which was then reduced to the hydroxymethyl compound.

A solution of *N*-[2-(carbomethoxy) phenyl]pyrrole **4da** (6.00 g, 30 mmol) in dry ether (100 cm³) was added dropwise to an ice-cold suspension of lithium aluminium hydride (1.26 g, 33 mmol) in dry ether (100 cm³). The mixture was then heated under reflux for 2 h. Wet ether (50 cm³), then water (50 cm³) were added followed by aqueous sodium tartrate (1 M, 50 cm³). The solution was filtered and the ether layer was separated. The aqueous layer was extracted with ether (2 × 50 cm³) and the combined organic extracts

washed with water ($3 \times 50 \text{ cm}^3$) and dried (MgSO_4). The solvent was removed to yield the crude product, which was purified by bulb to bulb distillation to yield *N*-[2-(hydroxymethyl)phenyl]pyrrole **4d** (4.38 g, 85%), bp 155-160 °C (0.4 Torr) [lit.,² 120 °C (0.2 Torr)] (Found: M^+ 173.0846 $\text{C}_{11}\text{H}_{11}\text{NO}$ requires M^+ 173.0840); δ_{H} 7.57-7.53 (1H, m), 7.43-7.27 (3H, m), 6.86 (2H, t, 3J and 4J 2.1), 6.34 (2H, t, 3J and 4J 2.1), 4.53 (2H, s) and 2.07 (1H, br); spectrum compatible with literature data;² m/z 173 (M^+ , 100%), 155 (16), 154 (32), 144 (41), 115 (35), 105 (25), 89 (10), 77 (50), 51(24) and 50(14).

A solution of *N*-[2-(hydroxymethyl)phenyl]pyrrole **4d** (4.00 g, 23 mmol) and triethylamine (3.03 g, 30 mmol) in dry ether (200 cm^3) was cooled in ice and a solution of oxalyl chloride (1.51 g, 11.5 mmol) in dry ether (20 cm^3) was added dropwise. The mixture was stirred for 2 h. Water (100 cm^3) was added and the mixture was extracted with dichloromethane ($3 \times 50 \text{ cm}^3$). The combined extracts were dried (MgSO_4) and the solvent was removed to provide crude product which was recrystallised to yield bis-[2-(pyrrol-1-yl)benzyl] oxalate **5d** (3.51 g, 75%), mp 153-155 °C (from ethanol) (Found: C, 71.8; H, 4.95; N, 7.0. $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4$ requires C, 72.0; H, 5.05; N, 7.0%); δ_{H} 7.57-7.31 (8H, m), 6.84 (4H, t, 3J and 4J 2.1), 6.30 (4H, t, 3J and 4J 2.1) and 5.15 (4H, s); δ_{C} 184.31 (quat), 156.83 (quat), 140.90 (quat), 130.70, 129.78, 127.77, 126.92, 122.43, 109.50 and 64.44; m/z 400 (M^+ , 7%), 399 (20), 172 (22), 157 (16), 156 (100), 155 (55), 154 (35), 129 (11) and 128 (12).

1-(2-Benzylaminophenyl)pyrazole 7

A solution of 1-(2-aminophenyl)pyrazole **6** (2.04 g, 13 mmol)³ and re-distilled benzaldehyde (1.3 g, 13 mmol) in ethanol (20 cm^3) was kept for *ca.* 48 h in the presence of 4A molecular sieves. Removal of the solvent under reduced pressure gave crude 1-(2-*N*-benzyliminophenyl)pyrazole as an oil, which was freed from unchanged amine by bulb-to-bulb distillation at 120-123 °C (0.02 Torr) (2.56 g, 80%) (Found M^+ , 247.1120. $\text{C}_{16}\text{H}_{13}\text{N}_3$ requires M 247.1109); δ_{H} 8.47 (1H, s), 8.1-7.1 (11H, m) and 6.40 (1H, t, 3J 2.1); δ_{C} 161.08, 143.45 (quat), 140.21, 135.82 (quat), 133.89 (quat), 132.12, 131.67, 128.93, 128.77, 127.52, 126.61, 124.30, 119.34 and 106.28; m/z 247 (M^+ , 31%), 219 (15), 170 (70), 145 (11), 144 (100), 143 (13), 118 (11), 117 (19), 90 (19), 89 (18) and 77 (26).

Sodium borohydride (0.72 g, 19 mmol) was added to a solution of 1-(2-*N*-benzyliminophenyl)pyrazole (1.12 g, 4.5 mmol) in methanol (20 cm^3) and the resulting solution was heated under reflux for a further 15 min. The reaction mixture was added to water (30 cm^3) and then extracted with dichloromethane ($2 \times 30 \text{ cm}^3$). The extracts were dried (MgSO_4) and the solvents were removed under reduced pressure to yield 1-(2-benzylaminophenyl)pyrazole **7** (0.76 g, 67%) as an oil which crystallised, mp 76-77 °C (from *n*-hexane) (Found: C, 77.05; H, 6.1; N 17.0. $\text{C}_{16}\text{H}_{15}\text{N}_3$ requires C, 77.1; H, 6.0; N, 16.85%); δ_{H} 7.78-7.74 (2H, m), 7.40-7.15 (7H, m), 6.79-6.71 (2H, m), 6.47 (1H, t, 3J 2.1), 6.10-5.75 (1H, br s) and 4.43 (2H, s); δ_{C} 141.84 (quat), 140.25, 138.75 (quat), 129.85, 128.46, 128.25, 126.68, 125.93 (quat), 123.69, 116.09, 112.17, 106.05 and 47.13 (1 peak overlapping); m/z 249 (M^+ , 100%), 248 (19), 195 (18), 180 (29), 172 (28), 170 (14), 145 (34), 144 (17), 131 (20), 130 (15), 106 (17), 104 (13), 92 (10), 91 (83), 89 (12), 78 (15) and 77 (37).

The following 2,5-diarylpyrroles were made by the general method described in the main paper:

2,5-Di-*p*-tolyl-*N*-(2-mercaptophenyl)pyrrole 25b

2-Aminothiophenol **3c** (1.32 g, 10.5 mmol) and 4,4'-dimethyldiphenacyl⁴ (2.73 g, 10.3 mmol) gave 2,5-di-*p*-tolyl-*N*-(2-mercaptophenyl)pyrrole **25b** (55%), mp 114-117 °C; (Found: C, 79.5; H, 5.9; N, 3.85. $\text{C}_{24}\text{H}_{21}\text{NS} \cdot 0.33\text{H}_2\text{O}$ requires C, 79.75; H, 6.0; N 3.9%); (Found: M^+ , 355.1387. $\text{C}_{24}\text{H}_{21}\text{NS}$ requires M 355.1395); δ_{H} 7.29-6.99 (12H, m), 6.55 (2H, s), 3.14 (1H, s) and 2.29 (6H, s); δ_{C} 136.70 (quat), 136.02 (quat), 135.33 (quat),

133.54 (quat), 130.80, 129.81 (quat), 129.13, 128.61, 128.54, 127.88, 125.59, 109.64 and 20.99; m/z 355 (M^+ , 100%), 354 (45), 264 (37) and 91 (42).

2,5-Di-(thien-2-yl)-*N*-(2-mercaptophenyl)pyrrole 25c

A slightly different method was used to make **25c**. A solution of 1,4-di(thien-2-yl)-1,4-butanedione⁵ (1.25 g, 5 mmol), 2-aminothiophenol **3c** (0.63 g, 5 mmol) and *p*-toluenesulfonic acid (80 mg, 0.46 mmol) in toluene (15 cm³) was heated under reflux with stirring for 24 h under nitrogen. The toluene was evaporated and the residue was worked up as described above to give 2,5-di-(thien-2-yl)-*N*-(2-mercaptophenyl)pyrrole **25c** (0.47 g, 28%); mp 132-135 °C (from propan-2-ol); (Found: C, 62.3; H, 3.75; N, 4.0. C₁₈H₁₃NS₃·0.5H₂O requires C, 62.05; H, 4.0; N, 4.0%); δ_H 7.38 (3H, m), 7.22 (1H, m), 7.06 (2H, dd, ³*J* 5.1, ⁴*J* 1.2), 6.83 (2H, dd, ³*J* 3.7, 5.1), 6.64 (2H, s), 6.63 (2H, dd, ³*J* 3.7, ⁴*J* 1.2) and 3.11 (1H, s, SH); δ_C 135.52 (quat), 134.92 (quat), 133.95 (2 quat), 131.10, 129.87, 129.37, 128.94 (2 quat), 126.80 (2 CH), 126.06, 123.80 (2 CH), 123.48 (2 CH) and 109.96 (2 CH); m/z 339 (M^+ , 100%), 306 (29), 217 (48), 218 (20), 195 (29), 194 (28), 150 (26) and 111 (32).

2,5-Diphenyl-*N*-(2-hydroxyphenyl)pyrrole 25d

2-Aminophenol **3a** (1.42 g, 13 mmol) and 1,2-dibenzoylthane (3.09 g, 13 mmol) gave 2,5-diphenyl-*N*-(2-hydroxyphenyl)pyrrole **25d** (3.90 g, 96%), mp 177-181 °C (from ethanol) (lit.,⁶ 183 °C) (Found. M^+ 311.1316. C₂₂H₁₇NO requires M 311.1310) δ_H 8.04 (1H, d, ³*J* 7.0), 7.59-6.77 (13H, m), 6.58 (2H, s) and 5.32 (1H, br. s); δ_C 136.09 (quat), 133.04 (quat), 132.18 (quat), 129.89, 129.84, 127.97, 127.82, 126.61, 125.74 (quat), 120.65, 116.28 and 110.45; m/z 311 (M^+ , 60%), 133 (10), 105 (100) and 77 (32).

2,5-Di-(thien-2-yl)-*N*-(2-hydroxyphenyl)pyrrole 25e

Using the method described above for **25c** using 1,4-di(thien-2-yl)-1,4-butanedione⁵ (1.25 g, 5 mmol), 2-aminophenol **3a** (0.55 g, 5 mmol) and *p*-toluenesulfonic acid (80 mg, 0.46 mmol) in toluene (15 cm³) 2,5-di-(thien-2-yl)-*N*-(2-hydroxyphenyl)pyrrole **25e** (1.09 g, 68%) was obtained mp 95-98 °C; (Found M^+ , 323.04367. C₁₈H₁₃NOS₂ requires M 323.04331) δ_H 7.40 (1H, m), 7.21 (1H, dd, ³*J* 7.8, ⁴*J* 1.7), 6.95-7.05 (4H, m), 6.81 (2H, dd, ³*J* 3.7, 5.1), 6.64 (2H, dd, ³*J* 3.7, ⁴*J* 1.1), 6.63 (2H, s) and 5.25 (1H, br s, OH); δ_C 153.46 (quat), 133.76 (2 quat), 131.28, 130.72, 130.07 (2 quat), 127.02 (2 CH), 124.86 (quat), 124.15 (2 CH), 123.72 (2 CH), 121.04, 116.62 (CH) and 110.43 (2 CH); m/z 323 (M^+ , 100%), 282 (34), 217 (30), 195 (15), 194 (10), 150 (23) and 111 (31).

The following allyl and related derivatives were made by the general method described in the main paper, unless stated otherwise:

2,5-Di-*p*-tolyl-*N*-[2-(allylthio)phenyl]pyrrole 26b

2,5-Di-*p*-tolyl-*N*-(2-mercaptophenyl)pyrrole **25b** (1.00 g, 2.80 mmol) gave 2,5-di-*p*-tolyl-*N*-[2-(allylthio)phenyl]pyrrole **26b** (1.09 g, 98%) mp 124-126 °C; (Found: M^+ , 395.1719. C₂₇H₂₅NS requires M 395.1708); δ_H 7.20-6.84 (12H, m), 6.40 (2H, s), 5.47 (1H, m), 4.91-4.82 (2H, m), 3.23-3.19 (2H, m) and 2.16 (6H, s); δ_C 137.78 (quat), 137.01 (quat), 135.70 (quat), 135.63 (quat), 132.83, 130.50, 130.20 (quat), 128.39 (4CH), 128.20, 127.99 (4CH), 127.70, 125.35, 117.59, 109.00, 34.86 and 20.94; m/z 395 (M^+ , 100%), 354 (60), 262 (20), and 91(7).

2,5-Di-(thien-2-yl)-*N*-[(2-allylthio)phenyl]pyrrole 26c

2,5-Di-(thien-2-yl)-*N*-(2-mercaptophenyl)pyrrole **25c** (0.467 g, 1.38 mmol) gave 2,5-di-(thien-2-yl)-*N*-[(2-allylthio)phenyl]pyrrole **26c** (0.42 g, 82%) bp 68-72 °C (1.5 Torr); (Found M^+ , 379.05190. C₂₁H₁₇NS₃ requires M 379.05176); δ_H 7.50-7.20 (4H, m), 6.99 (2H, dd, ³*J* 5.1, ⁴*J* 1.2), 6.77 (2H, dd, ³*J* 3.6, 5.1), 6.59 (2H, s), 6.57 (2H, dd, ³*J* 3.6, ⁴*J* 1.2), 5.58 (1H, m), 4.98 (2H, m) and 3.37 (2H, m); δ_C 139.07 (quat), 136.59 (quat), 134.54 (2 quat), 132.69, 131.06, 129.72, 129.57 (2 quat), 127.99, 126.73 (2 CH), 125.80,

123.60 (2 CH), 123.53 (2 CH), 117.92, 109.55 (2 CH) and 34.77; m/z 379 (M^+ , 100%), 337 (44), 303 (29), 217 (93), 203 (36), 162 (43), 111 (60) and 84 (64).

2,5-Diphenyl-*N*-[2-(allyloxy)phenyl]pyrrole 26d

2,5-Diphenyl-*N*-(2-hydroxyphenyl)pyrrole **25d** (3.11 g, 0.01 mol) gave 2,5-diphenyl-*N*-[2-(allyloxy)phenyl]pyrrole **26d** (3.23 g, 95%), mp 106-108 °C (from ethanol) (Found: C, 85.0; H, 6.0; N, 3.95. $C_{25}H_{21}NO$ requires C, 85.45; H, 6.0; N, 4.0%) δ_H 7.52-7.03 (12H, m), 6.87-6.77 (2H, m), 6.50 (2H, s), 5.51 (1H, m), 5.01 (2H, m) and 4.16 (2H, m); δ_C 154.37 (quat), 136.10 (quat), 133.51 (quat), 132.70, 130.69, 128.92, 128.47 (quat), 127.99, 127.58, 125.93, 120.48, 116.72, 113.17, 109.10 and 68.64; m/z 351 (M^+ , 100%), 310 (12) and 191 (21).

2,5-Di-(thien-2-yl)-*N*-[2-(allyloxy)phenyl]pyrrole 26e

2,5-Di-(thien-2-yl)-*N*-(2-hydroxyphenyl)pyrrole **25e** (0.549 g, 1.70 mmol) gave 2,5-di-(thien-2-yl)-*N*-[2-(allyloxy)phenyl]pyrrole **26e** (0.58 g, 95%) mp 61-64 °C; (Found M^+ , 363.07313. $C_{21}H_{17}NOS_2$ requires M 363.07461) δ_H 7.42 (1H, m), 7.28 (1H, dd, 3J 7.8, 4J 1.8), 7.01-6.90 (4H, m), 6.79 (2H, dd, 3J 3.7, 5.1), 6.60 (2H, dd, 3J 3.7, 4J 1.7), 6.57 (2H, s), 5.65 (1H, m), 5.08-5.00 (2H, m) and 4.38 (2H, m); δ_C 155.98 (quat), 135.01 (quat), 132.49 (2 quat), 131.55 (2 quat), 130.48, 130.04, 126.65 (2 CH), 123.50 (4 CH), 120.76, 116.73, 113.56, 109.37 (2 CH) and 68.81 (one CH signal overlapping); m/z 363 (M^+ , 100%), 322 (25), 289 (14), 214 (14), 203 (22), 152 (16), 79 (53) and 65 (98).

2,5-Di-*p*-tolyl-*N*-[2-(benzylamino)phenyl]pyrrole 26f

Benzylamine (10.72 g, 0.1 mol) was added over 30 min to a stirred, ice-cooled suspension of 2-fluoronitrobenzene **27** (10 g, 0.071 mol), and anhydrous potassium carbonate (13.8 g, 0.1 mol) in DMSO (100 cm³). After 1 h water (50 cm³) was added and the product extracted with dichloromethane (3 × 50 cm³). The combined organic extracts were dried (MgSO₄) and the solvent evaporated to give *N*-benzyl-2-nitroaniline **28** an orange solid. (14.5 g, 89%) mp 69-72 °C (lit.,⁷ 72 °C); δ_H 8.46 (1H, br s, NH), 8.16 (1H, dd, 3J 8.6, 4J 1.6), 7.35-7.20 (6H, m), 6.77 (1H, d, 3J 8.6), 6.60 (1H, dt, 3J 8.3, 4J 1.3) and 4.55 (2H, d, 3J 5.7); δ_C 145.13 (quat), 137.23 (quat), 136.09, 132.29 (quat), 128.81 (2 CH), 127.58, 126.92 (2 CH), 126.75, 115.60, 114.07 and 46.98.

A solution of *N*-benzyl-2-nitroaniline **28** (8.0 g, 0.035 mol) in methanol was hydrogenated over 5% Pd/C (20 mg) at 20 bar for 24 h. The product was dissolved in hexane, filtered and the filtrate concentrated to give *N*-benzyl-*o*-phenylenediamine⁸ **29** as an oil. (6.80 g, 98%) which was sufficiently pure for the next stage; δ_H 7.3-7.1 (5H, m), 6.55-6.8 (4H, m), 4.27 (2H, s, CH₂) and 3.38 (2H, br s, NH₂); δ_C 139.28 (quat), 137.58 (quat), 134.03 (quat), 128.47 (2 CH), 127.65 (2 CH), 127.13, 120.60, 118.68, 116.39, 111.84 and 48.50 (CH₂).

Using the method described for **25c**, a solution of 4,4'-dimethyldiphenacyl⁴ (4.00 g, 15 mmol), *N*-benzyl-*o*-phenylenediamine **29** (6.00 g, 30 mmol) and PTSA (80 mg, 0.46 mmol) in toluene (50 cm³) gave 2,5-di-*p*-tolyl-*N*-[2-(benzylamino)phenyl]pyrrole **26f** (1.66 g, 25%) as a white solid mp 163-165 °C (from toluene); (Found: C, 86.55; H, 6.55; N, 6.55. $C_{31}H_{28}N_2$ requires C, 86.9; H, 6.55; N, 6.55 %); δ_H 7.15-7.00 (13H, m), 6.74 (2H, dd, 3J 7.9, 4J 2.1), 6.58 (1H, td, 3J 7.5, 4J 1.3), 6.53 (2H, s), 6.40 (1H, dd, 3J 8.2, 4J 1.2), 4.08 (2H, s) and 2.23 (6H, s); δ_C 144.36 (quat), 138.57 (quat), 135.70 (quat), 135.15 (quat), 129.89 (quat), 129.82, 129.02, 128.46 (4 CH), 127.99 (2 CH), 127.48 (4 CH), 126.42, 126.25 (2 CH), 124.33 (quat), 116.34, 110.94, 109.26 (2 CH), 46.61 and 20.83; m/z 428 (M^+ , 100%), 351 (9), 337 (27), 247 (12), 219 (13) and 91 (47).

NOE results:

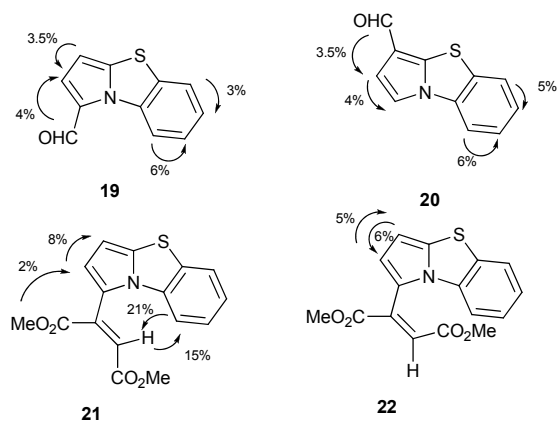


Fig. 1 NOE enhancements for **19-22**.

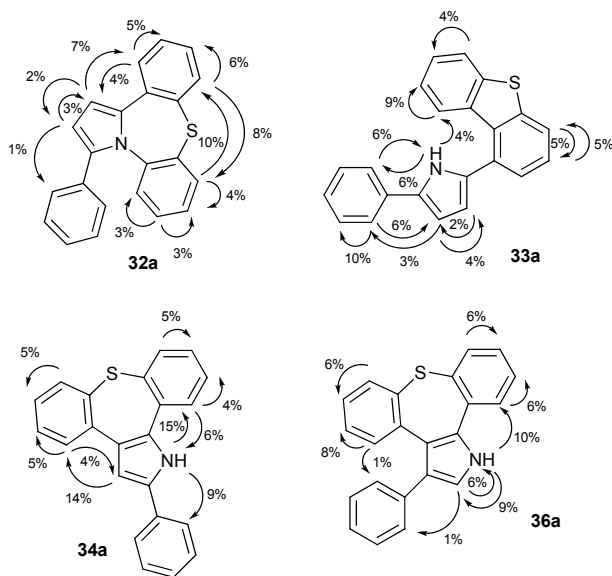


Fig. 2 NOE enhancements for **32a, 33a, 34a** and **36a**.

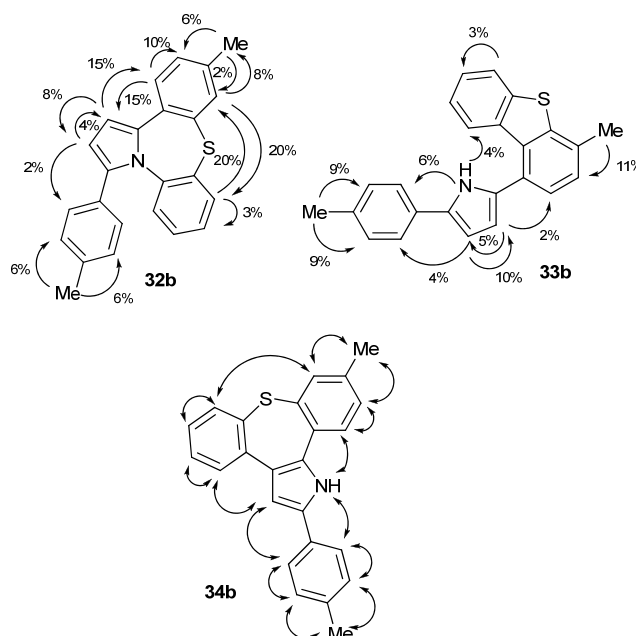


Fig. 3 NOE enhancements for **32b** and **33b**; NOESY correlations for **34b**.

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