SUPPORTING INFORMATION

A Modular Synthesis of Unsymmetrical Tetraarylazadipyrromethenes

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References

- 8b:** Rogers, M.A.T. *J. Chem. Soc.* **1943**, 596.
- 8g:** Rogers, M.A.T. *J. Chem. Soc.* **1943**, 596.
- 8i:** Dannhardt, G.; Kiefer, W.; Krämer, G.; Maehrlein, S.; Nowe, U.; Fiebich, B. *Eur. J. Med. Chem.* **2000**, *35*, 499-510.
- 8j:** Kumar, C. V.; Ramaiah, D.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 2818-2825.
- 4-Bromomethylbenzaldehyde: Wen, L.; Li, M.; Schlenoff, J.B. *J. Am. Chem. Soc.* **1997**, *119*, 7726.

Experimental Procedures

Reagents and Solvents. All reactions were performed under nitrogen atmosphere. Toluene was distilled over CaH₂, under nitrogen, immediately before use. UV/Vis spectra were measured using spectroscopic grade CHCl₃, freshly distilled over CaCO₃. Column chromatography was performed on Silica gel 60 (0.040-0.063nm) or Aluminium Oxide 90. Melting points are uncorrected.

Instrumentation. ¹H NMR and ¹³C NMR were recorded in CDCl₃ (internal Me₄Si) or DMSO-*d*₆ on a 300MHz and 500MHz instruments. Some NMRs are carried out in using trifluoroacetic acid as co-solvent to increase solubility.

4-Morpholin-4-ylmethyl-benzaldehyde.

To a stirred solution of 4-bromomethyl-benzaldehyde (7.92 g, 40 mmol) in THF (200 mL) was added morpholine (1.05 mL, 120 mmol) and the resulting mixture was heated at reflux for 2 h. The solvent was removed under reduced pressure and the resulting oil was partitioned between Et₂O (200 mL) and water (200 mL). The organic layer was washed with NaHCO₃ (aq) (100 mL), saturated NaCl (aq) (100 mL), dried over Na₂SO₄ and the solvent removed under reduced pressure. The resulting material was purified by chromatography on silica gel (1:1 EtOAc:cyclohexane) to give a white solid (6.9 g, 84%), mp 51-54 °C. ¹H NMR (CDCl₃) δ: 10.00 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 3.72 (t, *J* = 4.4 Hz, 4H), 3.58 (s, 2H), 2.46 (t, *J* = 4.4 Hz, 4H). ¹³C NMR (CDCl₃) δ: 191.9, 145.3, 135.6, 129.8, 129.5, 67.0, 63.0, 53.7. IR (KBr disk) cm⁻¹: 1699. ES-MS: *m/z* 206 [M+H]⁺. HRMS Calcd for C₁₂H₁₆NO₂ [M+H]⁺: 206.1181. Found 206.1181. Anal. Calcd for C₁₂H₁₅NO₂: C, 70.22; H, 7.37; N, 6.82. Found C, 69.99; H, 7.52; N, 6.76.

4-Diethylaminomethyl-benzaldehyde.

To a stirred solution of 4-bromomethyl-benzaldehyde (1.98 g, 10 mmol) in THF (50 mL) was added diethylamine (2.06 mL, 30 mmol) and the resulting mixture was heated at reflux for 2 h. The solvent was removed under reduced pressure and the resulting oil was partitioned between Et₂O (100 mL) and water (100 mL). The organic layer was extracted 1M HCl (aq) (100 mL), the aqueous layer was neutralised with 2M NaOH (aq) and extracted with Et₂O (2x100 mL). The organic layer was washed with saturated NaCl (aq)

(100 mL), dried over Na₂SO₄ and the solvent removed under reduced pressure and distilled (75-80 °C at 0.1 mbar) to give a colorless oil (1.9 g, 95%). This oil was stored at -5 °C, under nitrogen. ¹H NMR (CDCl₃) δ: 9.99 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 3.63 (s, 2H), 2.53 (q, *J* = 7.1 Hz, 4H), 1.05 (t, *J* = 7.1, 6H). ¹³C NMR (CDCl₃) δ: 192.1, 148.1, 135.3, 129.8, 129.2, 57.5, 47.1, 11.9. IR (neat) cm⁻¹: 1705. ES-MS: *m/z* 192 [M+H]⁺. HRMS Calcd for C₁₂H₁₈NO [M+H]⁺: 192.1392. Found: 192.1388. Anal. Calcd for C₁₂H₁₇NO: C, 75.35; H, 8.96; N, 7.32. Found: C, 74.98; H, 8.90; N, 7.36.

Synthesis of 8b, e, f, g, i, j.

METHOD A: A stirred solution of aldehyde (10 mmol), acetophenone (10 mmol) and NaOH (1 mmol) in MeOH (50 mL) was heated at reflux for 16 h. The solvent was removed under reduced pressure and the resulting yellow material was recrystallized from MeOH and washed with water to give pale yellow crystalline solids.

METHOD B: Aldehyde (10 mmol) and acetophenone (10 mmol) were dissolved in EtOH (16 mL), and KOH (1 mmol) in H₂O (4 mL) was added. The solution was stirred overnight with the resulting precipitate collected by filtration and washed with cold EtOH.

3-(4-Dimethylamino-phenyl)-1-phenyl-propenone (8b). Method B. Yellow solid (1.91 g, 76%), mp 111-112 °C (lit mp 110-111 °C). ¹H NMR (CDCl₃) δ: 7.98-8.02 (m, 2H), 7.79 (d, *J* = 15.5 Hz, 1H), 7.43-7.56 (m, 5H), 7.32 (d, *J* = 15.5 Hz, 1H), 6.64-6.69 (m, 2H), 3.00 (s, 6H). ¹³C NMR (CDCl₃) δ: 190.8, 152.3, 146.0, 139.3, 132.3, 130.6, 128.7, 128.5, 122.9, 117.1, 112.0, 40.3. IR (KBr disk) cm⁻¹: 1649. ES-MS: *m/z* 252 [M+H]⁺. Anal. Calcd for C₁₇H₁₇NO: C, 81.24; H, 6.82; N, 5.57. Found C, 80.95; H, 6.82; N, 5.49.

3-(4-Diethylaminomethyl-phenyl)-1-phenyl-propenone (8e). Method A. Yellow oil (2.70 g, 92%). ¹H NMR (CDCl₃) δ: 8.02 (d, *J* = 7.0 Hz, 2H), 7.81 (d, *J* = 15.8 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.46-7.55 (m, 4H), 7.39 (d, *J* = 8.2 Hz, 2H), 3.58 (s, 2H), 2.52 (q, *J* = 7.1 Hz, 4H), 1.04 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (CDCl₃) δ: 190.7, 144.9, 143.2, 138.4, 133.5, 132.8, 129.5, 128.7, 128.5, 128.4, 121.6, 57.4, 46.9, 11.8. IR (neat) cm⁻¹: 1663. ES-MS: *m/z* 294 [M+H]⁺. HRMS Calcd for C₂₀H₂₄NO [M+H]⁺: 294.1864. Found:

294.1863. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.38; H, 7.70; N, 4.88.

3-(4-Morpholin-4-ylmethyl-phenyl)-1-phenyl-propenone (8f). Method A. Yellow solid (2.52 g, 82%), mp 100-101 °C. 1H NMR ($CDCl_3$) δ : 8.02 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 15.6 Hz, 1H), 7.59 (d, J = 15.6 Hz, 1H), 7.49-7.60 (m, 5H), 7.39 (d, J = 8.1 Hz, 2H), 3.72 (t, J = 4.5 Hz, 4H), 3.52 (s, 2H), 2.46 (t, J = 4.5 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ : 190.6, 144.6, 140.9, 138.3, 133.9, 132.8, 129.7, 128.6, 128.5, 128.5, 121.8, 67.0, 63.1, 53.7. IR (KBr disk) cm^{-1} : 1601. ES-MS: m/z 308 $[M+H]^+$. HRMS Calcd for $C_{20}H_{22}NO_4$ $[M+H]^+$: 308.1651. Found 308.1640.

N-[4-(3-Oxo-3-phenyl-propenyl)-phenyl]-acetamide (8g). Method A. Yellow solid (1.96 g, 74%), mp 181-182 °C (lit. 180-182 °C). 1H NMR ($CDCl_3$) δ : 8.01 (d, J = 7.0 Hz, 2H), 7.91 (bs, 1H), 7.76 (d, J = 15.8 Hz, 1H), 7.56-7.64 (m, 5H), 7.48-7.53 (m, 2H), 7.46 (d, J = 15.8 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$) δ : 190.8, 168.7, 144.4, 140.3, 138.2, 132.8, 130.5, 129.5, 128.7, 128.5, 120.9, 119.7, 24.7. IR (KBr disk) cm^{-1} : 1693, 1644. ES-MS: m/z 266 $[M+H]^+$.

1-(4-Fluoro-phenyl)-3-phenyl-propenone (8i). Method B. Yellow solid (2.21 g, 98%), mp 79-80 °C (lit. 84-86 °C). 1H NMR ($CDCl_3$) δ : 8.06 (dd, J = 8.8, 5.4 Hz, 2H), 7.82 (d, J = 15.7 Hz, 1H), 7.63-7.66 (m, 2H), 7.51 (d, J = 15.7 Hz, 1H), 7.42-7.44 (m, 3H), 7.18 (t, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 188.8, 165.6 (d, J = 254.0 Hz), 145.1, 134.7, 134.5

(d, $J = 3.5$ Hz), 131.1 (d, $J = 9.4$ Hz), 130.7, 129.0, 128.5, 121.5, 115.8 (d, $J = 21.7$ Hz).
IR (KBr disk) cm^{-1} : 1664. ES-MS: m/z 227 $[\text{M}+\text{H}]^+$.

3-(4-Diethylaminomethyl-phenyl)-1-(4-methoxy-phenyl)-propenone (8j). Method A.

Yellow solid (3.0 g, 93%), mp 87-88 °C. ^1H NMR (CDCl_3) δ : 8.05 (d, $J = 8.9$ Hz, 2H), 7.80 (d, $J = 15.6$, 1H), 7.55 (d, $J = 8.1$ Hz, 2H), 7.53 (d, $J = 15.6$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 8.9$ Hz, 2H), 3.89 (s, 3H), 3.58 (s, 2H), 2.54 (q, $J = 7.1$ Hz, 4H), 1.05 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (CDCl_3) δ : 188.5, 163.4, 144.0, 143.2, 133.7, 131.3, 130.8, 129.4, 128.3, 121.3, 113.9, 57.5, 55.5, 47.0, 11.9. IR (KBr disk) cm^{-1} : 1656. ES-MS: m/z 324 $[\text{M}+\text{H}]^+$. HRMS Calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 324.1954. Found: 324.1964. Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 77.98; H, 7.73; N, 4.22.

ORTEP Diagram of 10b.

Figure 1. Perspective drawing of **10b**. Thermal ellipsoids drawn at the 50% probability level.

Table 1. Crystal data and structure refinement for **10b**.

Identification code	10b	
Empirical formula	$C_{34} H_{26} N_3 O Cl_3$	
Molecular formula	$C_{33} H_{25} N_3 O \times C H Cl_3$	
Formula weight	598.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n (#14)	
Unit cell dimensions	a = 17.506(4) Å	$\alpha = 90^\circ$.
	b = 6.9612(16) Å	$\beta = 103.629(4)^\circ$.
	c = 24.205(5) Å	$\gamma = 90^\circ$.
Volume	2866.7(11) Å ³	
Z	4	
Density (calculated)	1.388 Mg/m ³	
Absorption coefficient	0.353 mm ⁻¹	
F(000)	1240	
Crystal size	0.40 x 0.15 x 0.10 mm ³	
Theta range for data collection	1.63 to 22.00°.	
Index ranges	-18 ≤ h ≤ 18, -7 ≤ k ≤ 7, -25 ≤ l ≤ 25	
Reflections collected	14495	
Independent reflections	3527 [R(int) = 0.0619]	
Completeness to theta = 22.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9655 and 0.6951	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3527 / 0 / 399	
Goodness-of-fit on F ²	1.043	
Final R indices [I > 2σ(I)]	R1 = 0.0743, wR2 = 0.1742	
R indices (all data)	R1 = 0.0991, wR2 = 0.1875	
Largest diff. peak and hole	0.990 and -0.597 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
N(1)	5824(2)	7609(5)	663(2)	26(1)
C(1)	5671(3)	7792(6)	1177(2)	25(1)
N(2)	4930(2)	8030(5)	1276(2)	25(1)
C(2)	6226(3)	7821(6)	1718(2)	23(1)
C(5)	7081(3)	7655(6)	1825(2)	22(1)
C(6)	7549(3)	8325(6)	2337(2)	26(1)
C(7)	8362(3)	8204(6)	2457(2)	28(1)
C(8)	8723(3)	7422(6)	2055(2)	28(1)
O	9520(2)	7279(5)	2114(1)	38(1)
C(11)	10013(3)	7919(7)	2636(2)	38(1)
C(9)	8266(3)	6741(6)	1545(2)	29(1)
C(10)	7463(3)	6860(6)	1433(2)	27(1)
C(3)	5780(3)	8054(6)	2119(2)	26(1)
C(4)	4983(3)	8185(6)	1836(2)	24(1)
C(12)	4294(3)	8401(6)	2069(2)	29(1)
C(13)	3599(3)	9142(7)	1733(2)	35(1)
C(14)	2945(3)	9344(8)	1957(2)	47(2)
C(15)	2959(3)	8782(9)	2503(3)	55(2)
C(16)	3649(4)	8033(9)	2834(2)	58(2)
C(17)	4306(3)	7866(8)	2625(2)	41(1)
C(18)	5266(3)	7546(6)	193(2)	24(1)
N(3)	4460(2)	7605(5)	165(2)	25(1)
C(19)	5394(3)	7363(6)	-379(2)	24(1)
C(22)	6148(3)	7181(6)	-536(2)	25(1)
C(23)	6830(3)	8053(7)	-220(2)	31(1)
C(24)	7534(3)	7854(7)	-372(2)	39(1)
C(25)	7579(3)	6791(8)	-845(2)	42(1)
C(26)	6913(3)	5921(7)	-1165(2)	35(1)
C(27)	6207(3)	6123(7)	-1012(2)	30(1)
C(20)	4657(3)	7327(6)	-730(2)	24(1)

C(21)	4098(3)	7477(6)	−383(2)	23(1)
C(28)	3241(3)	7530(6)	−571(2)	24(1)
C(29)	2774(3)	7063(7)	−200(2)	32(1)
C(30)	1964(3)	7194(7)	−370(2)	36(1)
C(31)	1617(3)	7823(7)	−915(2)	36(1)
C(32)	2079(3)	8271(7)	−1287(2)	32(1)
C(33)	2884(3)	8114(6)	−1119(2)	27(1)
Cl(1A) ^{a)}	1250(3)	7478(7)	1320(2)	101(2)
Cl(2A) ^{a)}	−226(3)	8654(10)	585(3)	206(4)
Cl(3A) ^{a)}	149(2)	4789(7)	749(1)	105(2)
C(34A) ^{a) c)}	302(8)	6840(20)	1074(6)	85(4)
Cl(1B) ^{b)}	1018(8)	7110(30)	1196(10)	356(15)
Cl(2B) ^{b)}	−342(4)	6792(15)	480(3)	145(4)
Cl(3B) ^{b)}	440(4)	10225(10)	815(3)	125(3)
C(34B) ^{b) c)}	238(8)	7910(20)	1027(6)	34(3)

^{a)} s.o.f = 0.606(5) ^{b)} s.o.f. = 0.394(5) [s.o.f.: site occupation factor; the sum of the s.o.f.'s a) and b) is constrained to be 1] ^{c)} refinement of only isotropic temperature factors possible

Table 3. Bond lengths [Å] and angles [°] for **10b**.

N(1)–C(18)	1.314(5)
N(1)–C(1)	1.340(6)
C(1)–N(2)	1.383(6)
C(1)–C(2)	1.435(6)
N(2)–C(4)	1.341(5)
N(2)–H(1N2)	0.8800
C(2)–C(3)	1.392(6)
C(2)–C(5)	1.461(6)
C(5)–C(6)	1.395(6)
C(5)–C(10)	1.398(6)
C(6)–C(7)	1.386(6)
C(6)–H(6)	0.9500
C(7)–C(8)	1.391(6)
C(7)–H(7)	0.9500
C(8)–O	1.373(5)
C(8)–C(9)	1.387(6)
O–C(11)	1.424(5)
C(11)–H(11A)	0.9800
C(11)–H(11B)	0.9800
C(11)–H(11C)	0.9800
C(9)–C(10)	1.371(6)
C(9)–H(9)	0.9500
C(10)–H(10)	0.9500
C(3)–C(4)	1.404(6)
C(3)–H(3)	0.9500
C(4)–C(12)	1.455(6)
C(12)–C(17)	1.392(7)
C(12)–C(13)	1.393(7)
C(13)–C(14)	1.386(7)
C(13)–H(13)	0.9500
C(14)–C(15)	1.373(8)
C(14)–H(14)	0.9500
C(15)–C(16)	1.384(8)
C(15)–H(15)	0.9500

C(16)–C(17)	1.367(7)
C(16)–H(16)	0.9500
C(17)–H(17)	0.9500
C(18)–N(3)	1.397(6)
C(18)–C(19)	1.460(6)
N(3)–C(21)	1.331(5)
N(3)–H(1N3)	0.8800
C(19)–C(20)	1.367(6)
C(19)–C(22)	1.462(6)
C(22)–C(27)	1.392(6)
C(22)–C(23)	1.396(6)
C(23)–C(24)	1.374(7)
C(23)–H(23)	0.9500
C(24)–C(25)	1.381(7)
C(24)–H(24)	0.9500
C(25)–C(26)	1.379(7)
C(25)–H(25)	0.9500
C(26)–C(27)	1.380(7)
C(26)–H(26)	0.9500
C(27)–H(27)	0.9500
C(20)–C(21)	1.435(6)
C(20)–H(20)	0.9500
C(21)–C(28)	1.461(6)
C(28)–C(29)	1.388(6)
C(28)–C(33)	1.389(6)
C(29)–C(30)	1.382(7)
C(29)–H(29)	0.9500
C(30)–C(31)	1.386(7)
C(30)–H(30)	0.9500
C(31)–C(32)	1.381(7)
C(31)–H(31)	0.9500
C(32)–C(33)	1.377(6)
C(32)–H(32)	0.9500
C(33)–H(33)	0.9500
Cl(1A)–C(34A)	1.686(14)
Cl(2A)–C(34A)	1.828(16)

Cl(3A)–C(34A)	1.619(16)
C(34A)–H(34A)	1.0000
Cl(1B)–C(34B)	1.44(2)
Cl(2B)–C(34B)	1.660(15)
Cl(3B)–C(34B)	1.752(16)
C(34B)–H(34B)	1.0000
C(18)–N(1)–C(1)	122.5(4)
N(1)–C(1)–N(2)	125.0(4)
N(1)–C(1)–C(2)	127.4(4)
N(2)–C(1)–C(2)	107.7(4)
C(4)–N(2)–C(1)	109.8(4)
C(4)–N(2)–H(1N2)	125.1
C(1)–N(2)–H(1N2)	125.1
C(3)–C(2)–C(1)	105.4(4)
C(3)–C(2)–C(5)	127.2(4)
C(1)–C(2)–C(5)	127.4(4)
C(6)–C(5)–C(10)	117.5(4)
C(6)–C(5)–C(2)	119.6(4)
C(10)–C(5)–C(2)	122.9(4)
C(7)–C(6)–C(5)	121.7(4)
C(7)–C(6)–H(6)	119.2
C(5)–C(6)–H(6)	119.2
C(6)–C(7)–C(8)	119.3(4)
C(6)–C(7)–H(7)	120.3
C(8)–C(7)–H(7)	120.3
O–C(8)–C(9)	115.3(4)
O–C(8)–C(7)	125.0(4)
C(9)–C(8)–C(7)	119.7(4)
C(8)–O–C(11)	117.4(4)
O–C(11)–H(11A)	109.5
O–C(11)–H(11B)	109.5
H(11A)–C(11)–H(11B)	109.5
O–C(11)–H(11C)	109.5
H(11A)–C(11)–H(11C)	109.5
H(11B)–C(11)–H(11C)	109.5

C(10)–C(9)–C(8)	120.3(4)
C(10)–C(9)–H(9)	119.8
C(8)–C(9)–H(9)	119.8
C(9)–C(10)–C(5)	121.5(4)
C(9)–C(10)–H(10)	119.3
C(5)–C(10)–H(10)	119.3
C(2)–C(3)–C(4)	108.9(4)
C(2)–C(3)–H(3)	125.6
C(4)–C(3)–H(3)	125.6
N(2)–C(4)–C(3)	108.2(4)
N(2)–C(4)–C(12)	122.2(4)
C(3)–C(4)–C(12)	129.6(4)
C(17)–C(12)–C(13)	118.4(4)
C(17)–C(12)–C(4)	121.4(4)
C(13)–C(12)–C(4)	120.1(4)
C(14)–C(13)–C(12)	119.9(5)
C(14)–C(13)–H(13)	120.1
C(12)–C(13)–H(13)	120.1
C(15)–C(14)–C(13)	121.2(5)
C(15)–C(14)–H(14)	119.4
C(13)–C(14)–H(14)	119.4
C(14)–C(15)–C(16)	118.7(5)
C(14)–C(15)–H(15)	120.6
C(16)–C(15)–H(15)	120.6
C(17)–C(16)–C(15)	120.8(5)
C(17)–C(16)–H(16)	119.6
C(15)–C(16)–H(16)	119.6
C(16)–C(17)–C(12)	120.9(5)
C(16)–C(17)–H(17)	119.5
C(12)–C(17)–H(17)	119.5
N(1)–C(18)–N(3)	125.3(4)
N(1)–C(18)–C(19)	125.1(4)
N(3)–C(18)–C(19)	109.6(4)
C(21)–N(3)–C(18)	106.5(4)
C(21)–N(3)–H(1N3)	126.7
C(18)–N(3)–H(1N3)	126.7

C(20)–C(19)–C(18)	104.9(4)
C(20)–C(19)–C(22)	128.0(4)
C(18)–C(19)–C(22)	127.1(4)
C(27)–C(22)–C(23)	117.6(4)
C(27)–C(22)–C(19)	120.5(4)
C(23)–C(22)–C(19)	121.9(4)
C(24)–C(23)–C(22)	121.0(4)
C(24)–C(23)–H(23)	119.5
C(22)–C(23)–H(23)	119.5
C(23)–C(24)–C(25)	120.4(5)
C(23)–C(24)–H(24)	119.8
C(25)–C(24)–H(24)	119.8
C(26)–C(25)–C(24)	119.8(5)
C(26)–C(25)–H(25)	120.1
C(24)–C(25)–H(25)	120.1
C(25)–C(26)–C(27)	119.8(5)
C(25)–C(26)–H(26)	120.1
C(27)–C(26)–H(26)	120.1
C(26)–C(27)–C(22)	121.5(5)
C(26)–C(27)–H(27)	119.2
C(22)–C(27)–H(27)	119.2
C(19)–C(20)–C(21)	108.0(4)
C(19)–C(20)–H(20)	126.0
C(21)–C(20)–H(20)	126.0
N(3)–C(21)–C(20)	111.0(4)
N(3)–C(21)–C(28)	121.3(4)
C(20)–C(21)–C(28)	127.7(4)
C(29)–C(28)–C(33)	119.1(4)
C(29)–C(28)–C(21)	120.8(4)
C(33)–C(28)–C(21)	120.1(4)
C(30)–C(29)–C(28)	120.7(4)
C(30)–C(29)–H(29)	119.7
C(28)–C(29)–H(29)	119.7
C(29)–C(30)–C(31)	119.6(5)
C(29)–C(30)–H(30)	120.2
C(31)–C(30)–H(30)	120.2

C(32)–C(31)–C(30)	120.0(5)
C(32)–C(31)–H(31)	120.0
C(30)–C(31)–H(31)	120.0
C(33)–C(32)–C(31)	120.3(4)
C(33)–C(32)–H(32)	119.8
C(31)–C(32)–H(32)	119.8
C(32)–C(33)–C(28)	120.3(4)
C(32)–C(33)–H(33)	119.8
C(28)–C(33)–H(33)	119.8
Cl(3A)–C(34A)–Cl(1A)	116.1(9)
Cl(3A)–C(34A)–Cl(2A)	107.1(8)
Cl(1A)–C(34A)–Cl(2A)	110.5(9)
Cl(3A)–C(34A)–H(34A)	107.6
Cl(1A)–C(34A)–H(34A)	107.6
Cl(2A)–C(34A)–H(34A)	107.6
Cl(1B)–C(34B)–Cl(2B)	113.9(14)
Cl(1B)–C(34B)–Cl(3B)	101.3(12)
Cl(2B)–C(34B)–Cl(3B)	109.0(9)
Cl(1B)–C(34B)–H(34B)	110.7
Cl(2B)–C(34B)–H(34B)	110.7
Cl(3B)–C(34B)–H(34B)	110.7

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	31(2)	17(2)	27(2)	0(2)	5(2)	1(2)
C(1)	35(3)	16(3)	24(3)	-1(2)	8(2)	0(2)
N(2)	28(2)	23(2)	22(2)	-1(2)	5(2)	-4(2)
C(2)	32(3)	12(2)	23(3)	-1(2)	5(2)	-2(2)
C(5)	30(3)	14(2)	21(2)	1(2)	2(2)	-1(2)
C(6)	33(3)	21(3)	22(3)	2(2)	5(2)	1(2)
C(7)	34(3)	22(3)	24(3)	2(2)	-3(2)	-1(2)
C(8)	26(3)	22(3)	35(3)	2(2)	6(2)	1(2)
O	34(2)	44(2)	33(2)	-6(2)	3(2)	2(2)
C(11)	35(3)	36(3)	36(3)	-4(2)	-4(2)	0(2)
C(9)	32(3)	24(3)	27(3)	-7(2)	4(2)	3(2)
C(10)	32(3)	23(3)	23(3)	0(2)	0(2)	-2(2)
C(3)	40(3)	18(3)	19(2)	-1(2)	3(2)	0(2)
C(4)	34(3)	16(2)	21(3)	2(2)	6(2)	-1(2)
C(12)	38(3)	19(3)	32(3)	-6(2)	11(2)	-1(2)
C(13)	40(3)	28(3)	38(3)	0(2)	13(3)	0(2)
C(14)	39(3)	46(4)	58(4)	0(3)	19(3)	3(3)
C(15)	53(4)	62(4)	61(4)	2(3)	33(3)	8(3)
C(16)	68(4)	70(5)	45(3)	1(3)	32(3)	-1(4)
C(17)	44(3)	48(3)	34(3)	-4(3)	13(3)	-3(3)
C(18)	30(3)	17(3)	23(3)	1(2)	1(2)	-1(2)
N(3)	31(2)	17(2)	24(2)	-1(2)	3(2)	-1(2)
C(19)	35(3)	15(2)	20(2)	1(2)	3(2)	-1(2)
C(22)	33(3)	17(3)	24(2)	3(2)	6(2)	1(2)
C(23)	40(3)	25(3)	31(3)	0(2)	13(2)	-3(2)
C(24)	38(3)	39(3)	39(3)	-1(3)	8(3)	-3(2)
C(25)	45(3)	40(3)	47(3)	6(3)	21(3)	1(3)
C(26)	47(3)	32(3)	30(3)	1(2)	18(3)	3(3)
C(27)	42(3)	25(3)	24(3)	4(2)	8(2)	1(2)
C(20)	36(3)	17(2)	18(2)	-1(2)	4(2)	-2(2)
C(21)	35(3)	12(2)	22(3)	5(2)	4(2)	-2(2)

C(28)	31(3)	15(2)	24(3)	-2(2)	0(2)	0(2)
C(29)	36(3)	30(3)	27(3)	1(2)	3(2)	-3(2)
C(30)	31(3)	35(3)	42(3)	4(2)	9(2)	0(2)
C(31)	34(3)	27(3)	42(3)	0(2)	0(3)	3(2)
C(32)	40(3)	25(3)	24(3)	2(2)	-3(2)	-1(2)
C(33)	37(3)	21(3)	23(3)	-2(2)	4(2)	-2(2)
Cl(1A) ^{a)}	45(3)	86(3)	141(3)	-19(2)	-37(2)	0(2)
Cl(2A) ^{a)}	123(4)	149(6)	290(8)	-42(5)	-62(5)	74(4)
Cl(3A) ^{a)}	80(2)	163(4)	62(2)	1(2)	-3(2)	-56(3)
Cl(1B) ^{b)}	87(8)	380(30)	500(30)	120(20)	-144(11)	-35(10)
Cl(2B) ^{b)}	132(6)	220(11)	78(4)	-18(5)	15(4)	-112(7)
Cl(3B) ^{b)}	110(5)	94(5)	173(7)	-2(4)	40(5)	-16(4)

^{a)} s.o.f = 0.606(5) ^{b)} s.o.f. = 0.394(5) [s.o.f.: site occupation factor; the sum of the s.o.f.'s a) and b) is constrained to be 1]

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10b**.

Atom	x	y	z	U(eq)
H(1N2) ^{a)}	4489	8074	1011	30
H(6)	7305	8878	2611	31
H(7)	8669	8650	2811	34
H(11A)	9890	9259	2703	56
H(11B)	10565	7820	2617	56
H(11C)	9925	7117	2948	56
H(9)	8511	6189	1272	34
H(10)	7158	6392	1080	33
H(3)	5982	8115	2519	31
H(13)	3574	9508	1351	42
H(14)	2477	9881	1728	56
H(15)	2505	8905	2651	66
H(16)	3666	7630	3212	70
H(17)	4777	7378	2862	50
H(1N3) ^{b)}	4235	7708	452	30
H(23)	6807	8796	105	38
H(24)	7993	8450	-150	47
H(25)	8067	6660	-949	51
H(26)	6941	5184	-1490	42
H(27)	5750	5527	-1237	37
H(20)	4536	7220	-1133	29
H(29)	3012	6648	175	38
H(30)	1648	6854	-116	43
H(31)	1062	7947	-1032	43
H(32)	1839	8691	-1662	38
H(33)	3197	8405	-1380	33
H(34A)	55	6776	1407	102
H(34B)	-13	7967	1357	41

^{a)} s.o.f = 0.67(6) ^{b)} s.o.f. = 0.33(6) [s.o.f.: site occupation factor; the sum of the s.o.f.'s a) and b) is constrained to be 1]

Table 6. Torsion angles [°] for **10b**.

C(18)–N(1)–C(1)–N(2)	–3.4(7)
C(18)–N(1)–C(1)–C(2)	178.0(4)
N(1)–C(1)–N(2)–C(4)	–179.4(4)
C(2)–C(1)–N(2)–C(4)	–0.6(5)
N(1)–C(1)–C(2)–C(3)	179.5(4)
N(2)–C(1)–C(2)–C(3)	0.8(5)
N(1)–C(1)–C(2)–C(5)	–0.1(7)
N(2)–C(1)–C(2)–C(5)	–178.9(4)
C(3)–C(2)–C(5)–C(6)	–20.6(7)
C(1)–C(2)–C(5)–C(6)	159.0(4)
C(3)–C(2)–C(5)–C(10)	160.1(4)
C(1)–C(2)–C(5)–C(10)	–20.4(7)
C(10)–C(5)–C(6)–C(7)	–0.4(6)
C(2)–C(5)–C(6)–C(7)	–179.8(4)
C(5)–C(6)–C(7)–C(8)	1.0(7)
C(6)–C(7)–C(8)–O	177.8(4)
C(6)–C(7)–C(8)–C(9)	–1.3(7)
C(9)–C(8)–O–C(11)	–178.6(4)
C(7)–C(8)–O–C(11)	2.3(6)
O–C(8)–C(9)–C(10)	–178.2(4)
C(7)–C(8)–C(9)–C(10)	0.9(7)
C(8)–C(9)–C(10)–C(5)	–0.3(7)
C(6)–C(5)–C(10)–C(9)	0.0(6)
C(2)–C(5)–C(10)–C(9)	179.4(4)
C(1)–C(2)–C(3)–C(4)	–0.6(5)
C(5)–C(2)–C(3)–C(4)	179.0(4)
C(1)–N(2)–C(4)–C(3)	0.2(5)
C(1)–N(2)–C(4)–C(12)	–178.5(4)
C(2)–C(3)–C(4)–N(2)	0.3(5)
C(2)–C(3)–C(4)–C(12)	178.8(4)
N(2)–C(4)–C(12)–C(17)	156.0(4)
C(3)–C(4)–C(12)–C(17)	–22.4(7)
N(2)–C(4)–C(12)–C(13)	–23.4(7)
C(3)–C(4)–C(12)–C(13)	158.2(5)

C(17)–C(12)–C(13)–C(14)	0.5(7)
C(4)–C(12)–C(13)–C(14)	180.0(4)
C(12)–C(13)–C(14)–C(15)	–1.6(8)
C(13)–C(14)–C(15)–C(16)	1.1(9)
C(14)–C(15)–C(16)–C(17)	0.5(9)
C(15)–C(16)–C(17)–C(12)	–1.6(9)
C(13)–C(12)–C(17)–C(16)	1.1(8)
C(4)–C(12)–C(17)–C(16)	–178.4(5)
C(1)–N(1)–C(18)–N(3)	–1.8(7)
C(1)–N(1)–C(18)–C(19)	179.5(4)
N(1)–C(18)–N(3)–C(21)	–179.0(4)
C(19)–C(18)–N(3)–C(21)	–0.2(5)
N(1)–C(18)–C(19)–C(20)	179.0(4)
N(3)–C(18)–C(19)–C(20)	0.2(5)
N(1)–C(18)–C(19)–C(22)	1.3(7)
N(3)–C(18)–C(19)–C(22)	–177.6(4)
C(20)–C(19)–C(22)–C(27)	–29.1(7)
C(18)–C(19)–C(22)–C(27)	148.1(4)
C(20)–C(19)–C(22)–C(23)	150.6(5)
C(18)–C(19)–C(22)–C(23)	–32.1(7)
C(27)–C(22)–C(23)–C(24)	–0.7(7)
C(19)–C(22)–C(23)–C(24)	179.5(4)
C(22)–C(23)–C(24)–C(25)	0.5(7)
C(23)–C(24)–C(25)–C(26)	–0.2(8)
C(24)–C(25)–C(26)–C(27)	0.2(7)
C(25)–C(26)–C(27)–C(22)	–0.5(7)
C(23)–C(22)–C(27)–C(26)	0.7(7)
C(19)–C(22)–C(27)–C(26)	–179.5(4)
C(18)–C(19)–C(20)–C(21)	–0.1(5)
C(22)–C(19)–C(20)–C(21)	177.6(4)
C(18)–N(3)–C(21)–C(20)	0.1(5)
C(18)–N(3)–C(21)–C(28)	–178.9(4)
C(19)–C(20)–C(21)–N(3)	0.0(5)
C(19)–C(20)–C(21)–C(28)	178.9(4)
N(3)–C(21)–C(28)–C(29)	–22.1(6)
C(20)–C(21)–C(28)–C(29)	159.1(4)

N(3)–C(21)–C(28)–C(33)	155.7(4)
C(20)–C(21)–C(28)–C(33)	–23.1(7)
C(33)–C(28)–C(29)–C(30)	–0.7(7)
C(21)–C(28)–C(29)–C(30)	177.2(4)
C(28)–C(29)–C(30)–C(31)	–0.9(7)
C(29)–C(30)–C(31)–C(32)	1.5(7)
C(30)–C(31)–C(32)–C(33)	–0.6(7)
C(31)–C(32)–C(33)–C(28)	–1.0(7)
C(29)–C(28)–C(33)–C(32)	1.6(6)
C(21)–C(28)–C(33)–C(32)	–176.3(4)

Symmetry transformations used to generate equivalent atoms:

UV Vis Spectra 10a-10k (CHCl₃ at 4x10⁻⁶M)

2,4-Diphenyl-1*H*-pyrrole (6a)

Dimethyl-[4-(5-phenyl-1*H*-pyrrol-3-yl)-phenyl]-amine (6b)

4-(4-Methoxy-phenyl)-2-phenyl-1*H*-pyrrole (6c)

4-(4-Bromo-phenyl)-2-phenyl-1*H*-pyrrole (6d)

Diethyl-[4-(5-phenyl-1H-pyrrol-3-yl)-benzyl]-amine (6e)

4-[4-(5-Phenyl-1*H*-pyrrol-3-yl)-benzyl]-morpholine (6f)

N-[4-(5-Phenyl-1H-pyrrol-3-yl)-phenyl]-acetamide (6g)

2-(4-Methoxy-phenyl)-4-phenyl-1H-pyrrole (6h)

2-(4-Fluoro-phenyl)-4-phenyl-1*H*-pyrrole (6i)

Diethyl- $\{4-[5-(4\text{-methoxy-phenyl})-1H\text{-pyrrol-3-yl}]\text{-benzyl}\}$ -amine (6j)

2-Nitroso-3,5-diphenyl-1H-pyrrole (7a)

3-(4-Methoxy-phenyl)-2-nitroso-5-phenyl-1H-pyrrole (7b)

5-(4-Methoxy-phenyl)-2-nitroso-3-phenyl-1H-pyrrole (7c)

5-(4-Fluoro-phenyl)-2-nitroso-3-phenyl-1H-pyrrole (7d)

4,4-Dimethoxy-1,3-diphenyl-butan-1-one (9a)

(3,5-Diphenyl-1H-pyrrol-2-yl)-[3-(4-dimethylamino-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (10a)

**(3,5-diphenyl-1H-pyrrol-2-yl)-[3-(4-methoxy-phenyl)-5-phenyl-pyrrol-2-ylidene]-
amine (10b)**

[3-(4-Bromo-phenyl)-5-phenyl-pyrrol-2-ylidene]-(3,5-diphenyl-1H-pyrrol-2-yl)-amine (10c)

[3-(4-Diethylamino-methyl-phenyl)-5-phenyl-pyrrol-2-ylidene]-(3,5-diphenyl-1H-pyrrol-2-yl)-amine (10d)

(3,5-Diphenyl-1H-pyrrol-2-yl)-[3-(4-morpholin-4-ylmethyl-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (10e)

**N-{4-[2-(3,5-Diphenyl-1H-pyrrol-2-ylimino)-5-phenyl-2H-pyrrol-3-yl]-phenyl}-
acetamide (10f)**

**(3,5-Diphenyl-1H-pyrrol-2-yl)-[5-(4-fluoro-phenyl)-3-phenyl-pyrrol-2-ylidene]-
amine (10g)**

[3-(4-Diethylamino-methyl-phenyl)-5-(4-methoxy-phenyl)-pyrrol-2-ylidene]-[5-(4-methoxy-phenyl)-3-phenyl-1H-pyrrol-2-yl]-amine (10h)

[5-(4-methoxy-phenyl)-3-phenyl]-1H-pyrrol-2-yl)-[3-(4-methoxy-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (10i)

[3-(4-Diethylamino-methyl-phenyl)-5-(4-methoxy-phenyl)-pyrrol-2-ylidene]-[5-(4-fluoro-phenyl)-3-phenyl-1H-pyrrol-2-yl]-amine (10j)

[illegible]