Supporting Information

for

Double N-arylation reaction of polyhalogenated 4,4’-bipyridines.

Expedious synthesis of functionalized 2,7-diazacarbazoles

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1. Characterization of compounds 3

3,6-Dichloro-9-(4-pentylphenyl)-2,7-diazacarbazole (3a). Mp 128–130 °C; $^1$H NMR (250 MHz, CDCl$_3$) δ 8.65 (s, 2H, H$_a$), 8.00 (s, 2H, H$_b$), 7.45 (s, 4H, H$_c,d$), 2.75 (t, $J = 7.5$ Hz, 2H, CH$_2$), 1.73 (quint, $J = 7.5$ Hz, 2H, CH$_2$), 1.39 (m, 4H, CH$_2$), 0.93 (t, $J = 7$ Hz, 3H, CH$_3$); $^{13}$C NMR (63 MHz, CDCl$_3$) δ 144.3, 141.6, 137.3, 133.9, 132.6, 130.5, 129.1, 126.1, 115.8, 35.7, 31.2, 31.0, 22.5, 14.0; MS (70 eV) m/z (%): 383 (95, M$^+$), 326 (100), 290 (15); HRMS m/z: calcd for C$_{21}$H$_{20}$Cl$_2$N$_3$ (M + H)$^+$ 384.1029, found: 384.1058.
3,6-Dichloro-9-(4-methoxyphenyl)-2,7-diazacarbazole (3b). Mp 178–180 °C; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \( \delta \) 8.61 (s, 2H, H\textsubscript{a}), 8.03 (s, 2H, H\textsubscript{b}), 7.47 (d, \( J = 8.8 \) Hz, 2H, H\textsubscript{c}), 7.17 (d, \( J = 8.8 \) Hz, 2H, H\textsubscript{d}), 3.95 (s, 3H, OCH\textsubscript{3}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \( \delta \) 160.3, 141.9, 137.9, 134.1, 129.3, 128.1, 127.8, 116.1, 116.05, 55.0; MS (70 eV) m/z (%): 343 (100, M\textsuperscript{+}), 328 (40), 300 (10), 264 (15); HRMS m/z: calcd for C\textsubscript{17}H\textsubscript{12}Cl\textsubscript{2}N\textsubscript{3}O (M + H)\textsuperscript{+} 344.0352, found: 344.0365.
3,6-Dichloro-9-(4-thiomethylphenyl)-2,7-diazacarbazole (3c). Mp 196–198 °C; $^1$H NMR (250 MHz, CDCl$_3$) δ 8.65 (d, $J$ = 1 Hz, 2H, H$_a$), 8.03 (d, $J$ = 1 Hz, 2H, H$_b$), 7.46 and 7.52 (2d, AB syst., $J$ = 9 Hz, 4H, H$_{c,d}$), 2.61 (s, 3H, SCH$_3$); $^{13}$C NMR (63 MHz, CDCl$_3$) δ 141.7, 140.6, 137.1, 133.6, 131.6, 129.1, 127.7, 126.6, 115.8, 15.4; MS (70 eV) m/z (%): 359 (100, M$^+$), 344 (45), 108 (12); HRMS m/z: calcd for C$_{17}$H$_{12}$Cl$_2$N$_3$S (M + H)$^+$ 360.0123, found: 360.0144.
3,6-Dichloro-9-phenyl-2,7-diazacarbazole (3d). Mp 227–229 °C; $^1$H NMR (250 MHz, CDCl$_3$) δ 8.69 (d, $J = 1$ Hz, 2H, H$_a$), 8.05 (d, $J = 1$ Hz, 2H, H$_b$), 7.97 (d, $J = 7.5$ Hz, 2H, H$_c$), 7.59 (dt, $J = 7.5$, 1 Hz, 3H, H$_{d,e}$); $^{13}$C NMR (63 MHz, CDCl$_3$) δ 141.9, 137.2, 135.2, 133.8, 130.7, 129.3, 129.2, 126.3, 115.9; MS (70 eV) m/z (%): 313 (100, M$^+$), 277 (10), 243 (12), 77 (18), 51 (17); HRMS m/z: calcd for C$_{16}$H$_{10}$Cl$_2$N$_3$ (M + H)$^+$ 314.0246, found: 314.0257.
3,6-Dichloro-9-(4-chlorophenyl)-2,7-diazacarbazole (3e). Mp > 250 °C; $^1$H NMR (250 MHz, $d_6$-DMSO) δ 8.66 (s, 2H, H$_a$), 8.06 (s, 2H, H$_b$), 7.68 (d, $J = 8.7$ Hz, 2H, H$_c$), 7.53 (d, $J = 8.7$ Hz, 2H, H$_d$); $^{13}$C NMR (63 MHz, $d_6$-DMSO) δ 141.2, 137.5, 134.8, 134.5, 133.8, 131.2, 129.9, 129.1, 117.4; MS (70 eV) m/z (%): 347 (100), 277 (25), 241 (15), 75 (20); HRMS m/z: calcd for C$_{16}$H$_9$Cl$_3$N$_3$ (M + H)$^+$ 347.9857, found: 347.9882.
3,6-Dichloro-9-(4-fluorophenyl)-2,7-diazacarbazole (3f). Mp > 250 °C; $^1$H NMR (250 MHz, $d_6$-DMSO) $\delta$ 8.72 (d, $J = 1$ Hz, 2H, $H_a$), 8.61 (d, $J = 1$ Hz, 2H, $H_b$), 7.88 (dd, $J = 9$, 5 Hz, 2H, $H_c$), 7.57 (t, $J = 9$ Hz, 2H, $H_d$); $^{13}$C NMR (63 MHz, $d_6$-DMSO) $\delta$ 140.4, 137.1, 134.0, 131.1, 129.0, 128.9, 117.6, 117.2, 116.7; MS (70 eV) m/z (%): 331 (100, M$^+$), 261 (12), 233 (10), 75 (12); HRMS m/z: calcd for C$_{16}$H$_9$Cl$_2$FN$_3$ (M + H)$^+$ 332.0152, found: 332.0161.
3,6-Dichloro-9-(4-trifluoromethylphenyl)-2,7-diazacarbazole (3g). Mp > 250 °C; $^1$H NMR (250 MHz, d$_6$-DMSO) δ 8.83 (d, $J = 0.8$ Hz, 2H, H$_a$), 8.59 (d, $J = 0.8$ Hz, 2H, H$_b$), 8.06 (s, 4H, H$_c,d$); $^{13}$C NMR (63 MHz, d$_6$-DMSO) δ 141.5, 139.4, 137.2, 134.9, 130.3, 129.0 (t, $J = 38.6$ Hz), 128.3 (d, $J = 4.3$ Hz), 127.8, 122.5 (t, $J = 325$ Hz), 117.5; MS (70 eV) m/z (%): 381 (100, M$^+$), 277 (12); HRMS m/z: calcd for C$_{17}$H$_9$Cl$_2$F$_3$N$_3$ (M + H)$^+$ 382.0120, found: 382.0127.
2. Synthesis and characterization of compounds 9.
To a mixture of 2a (50 mg, 0.13 mmol), 8 (144 mg, 0.39 mmol) and PdCl₂(PPh₃)₂ (9.1 mg, 0.013 mmol) under argon, degassed toluene (1.5 mL) was added. After heating at 100 °C for 18 h, the mixture was cooled to room temperature. Water was added and the mixture was extracted with diethyl ether, washed with brine and concentrated. The residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate/triethylamine 9:0.5:0.5) to give separately 9a (22 mg, 40%) and 9b (20 mg, 33%).

3-Chloro-6-(2-pyridyl)-9-(4-pentylphenyl)-2,7-diazacarbazole (9a). ¹H NMR (250 MHz, CDCl₃) δ 9.16 (s, 1H, Hₐ), 8.97 (s, 1H, Hₐ'), 8.72 (d, J = 5 Hz, 1H, Hₖ), 8.68 (s, 1H, Hₐ), 8.45 (d, J = 7.5 Hz, 1H, Hₖ), 8.14 (s, 1H, Hₐ'), 7.83 (t, J = 7.5 Hz, 1H, Hₖ), 7.50 (m, 4 H, H_c,d), 7.28 (dd, J = 7.5, 5 Hz, 1H, Hₔ), 2.77 (t, J = 7.5 Hz, 2H, CH₂), 1.75 (quint, J = 7.5 Hz, 2H, CH₂), 1.42 (m, 4H, CH₂), 0.95 (m, 3H, CH₃); ¹³C NMR (63 MHz, CDCl₃) δ 156.2, 149.1, 147.8, 144.0, 141.6, 138.2, 137.1, 137.0, 133.8, 133.6, 133.0, 131.0, 130.4, 127.3, 126.1, 123.1, 120.9, 116.0, 113.3, 35.7, 31.5, 31.0, 22.5, 14.0; MS (70 eV) m/z (%): 426 (75, M⁺), 369 (42), 167 (35); HRMS m/z: calcd for C₂₆H₂₄ClN₄ (M + H)⁺ 427.1684, found: 427.1716.
3,6-Bis(2-pyridyl)-9-(4-pentylphenyl)-2,7-diazacarbazole (9b). Mp 148–150 °C; \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 9.32 (s, 2H, H\(_a\)), 9.01 (s, 2H, H\(_b\)), 8.74 (d, \(J = 4.8\ Hz, 2H, H_c\)), 8.44 (d, \(J = 7.5\ Hz, 2H, H_d\)), 7.82 (t, \(J = 7.5\ Hz, 2H, H_e\)), 7.59 (d, \(J = 8.3\ Hz, 2H, H_c\)), 7.49 (d, \(J = 8.3\ Hz, 2H, H_d\)), 7.28 (dd, \(J = 7.5, 4.8\ Hz, 2H, H_g\)), 2.78 (t, \(J = 7.5\ Hz, 2H, CH_2\)), 1.75 (quint, \(J = 7.5\ Hz, 2H, CH_2\)), 1.42 (m, 4H, CH\(_2\)), 0.96 (t, \(J = 5.5\ Hz, 3H, CH_3\)); \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 156.5, 149.2, 147.9, 143.6, 137.9, 136.9, 133.6, 133.5, 130.2, 129.0, 126.1, 122.9, 120.8, 113.7, 35.7, 31.5, 31.0, 22.5, 14.1; MS (70 eV) m/z (%): 469 (100, M\(^+\)), 412 (98); HRMS m/z: calcd for C\(_{31}\)H\(_{28}\)N\(_5\) (M + H\(^+\)) 470.2339, found: 470.2359.
3. Synthesis and characterization of 3-Chloro-6-(4-formylphenyl)-9-(4-pentylphenyl)-2,7-diazacarbazole (10).

A Schlenk tube was charged with 3a (50 mg, 0.13 mmol), 4 (58.5 mg, 0.39 mmol), Pd2(dba)3 (2.4 mg, 0.0026 mmol), SPhos (4.3 mg, 0.0104 mmol) and K3PO4 (55 mg, 0.26 mmol). The Schlenk tube was evacuated under vacuum, filled with argon (three times) and degassed toluene (1.5 mL) was added. The mixture was then heated at 90 °C for 24 h. After cooling, the mixture was filtered through a pad of silica gel (dichloromethane/ethyl acetate, 1:1). The filtrate was concentrated to give a residue, which was purified by column chromatography (silica gel: cyclohexane/ethyl acetate 9:1) to afford the starting material 3a (12 mg, 24%) and 10 (25 mg, 42%) separately. Mp 141–143 °C; 

$^1$H NMR (200 MHz, CDCl3) δ 10.09 (s, 1H, CHO), 9.05 (s, 1H, Hα), 8.72 (s, 1H, Hα'), 8.53 (s, 1H, Hb), 8.28 (d, $J = 7.5$ Hz, 2H, Hc), 8.16 (s, 1H, Hb'), 8.02 (d, $J = 7.5$ Hz, 2H, Hf), 7.50 (m, 4H, Hd,e), 2.78 (t, $J = 7$ Hz, 2H, CH2), 1.76 (m, 2H, CH2), 1.42 (m, 4H, CH2), 0.96 (m, 3H, CH3); 

$^{13}$C NMR (63 MHz, CDCl3) δ 192.2, 147.5, 145.8, 145.3, 144.5, 142.0, 138.0, 137.3, 136.2, 135.0, 134.2, 133.1, 130.8, 130.6, 128.3, 127.5, 126.4, 116.1, 113.4, 36.0, 31.8, 31.3, 22.8, 14.3; MS (70 eV) m/z (%): 453 (100, M$^+$), 396 (70); HRMS m/z: calcd for C28H25ClN3O (M + H)$^+$ 454.1681, found: 454.1692.
4. Synthesis and characterization of compounds 11.

To a degassed toluene solution (1.3 mL) containing Pd(PPh$_3$)$_4$ (10 mg, 0.0085 mmol) and 1b (78 mg, 0.17 mmol), degassed solutions of phenylboronic acid (41 mg, 0.34 mmol) in methanol (0.7 mL) and Na$_2$CO$_3$ (71 mg, 0.34 mmol) in water (0.7 mL) were successively added. After heating for 15 h at 100 °C, the reaction mixture was cooled to room temperature, extracted with ethyl acetate and dried over MgSO$_4$. After concentration, the residue was purified by chromatography on silica gel (dichloromethane/cyclohexane 7:3) to give compound 11a (75 mg, 95%). Compound 11b was obtained similarly in 94% yield (89 mg) by using 4-methylsulfanylphenylboronic acid (56 mg, 0.33 mmol).

![Chemical Structure](image)

5,5′-Dibromo-2,2′-diphenyl-4,4′-bipyridine (11a). Mp 247–249 °C; $^1$H NMR (250 MHz, d$_6$-DMSO) $\delta$ 9.00 (s, 2H, H$_a$), 8.18 (m, 3H, H$_{b,c}$), 7.50 (m, 3H, H$_{d,e}$); $^{13}$C NMR (63 MHz, d$_6$-DMSO) $\delta$ 155.3, 151.2, 147.4, 136.9, 129.7, 128.8, 126.6, 121.6, 118.9; MS (70 eV) m/z (%): 466 (75, M$^+$), 387 (35), 77 (100), 51 (72); HRMS m/z$^+$ calcd for C$_{22}$H$_{15}$Br$_2$N$_2$ (M + H)$^+$ 464.9597, found: 464.9631.
5,5'-Dibromo-2,2'-bis-(4-methylsulfanylphenyl)-4,4'-bipyridine (11b). Mp 215–216 °C; \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 8.89 (s, 2H, H\(_a\)), 7.95 (d, \(J = 8.2\) Hz, 4H, H\(_c\)), 7.61 (s, 2H, H\(_b\)), 7.33 (d, \(J = 8.2\) Hz, 4H, H\(_d\)), 2.53 (s, 6H, SCH\(_3\)); \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 155.9, 152.1, 147.5, 141.1, 127.1, 126.3, 120.9; MS (70 eV) m/z (%): 558 (100, M\(^+\)), 279 (10); HRMS m/z: calcd for C\(_{24}\)H\(_{19}\)Br\(_2\)N\(_2\)S\(_2\) (M + H\(^+\)) 556.9351, found: 556.9362.
5. Synthesis and characterization of compounds 12.

These were obtained according to the general procedure of the double N-arylation reaction.

3,6-Diphenyl-9-(4-pentylphenyl)-2,7-diazacarbazole (12a). 11a (35 mg, 0.075 mmol), 6a (12.2 mg, 0.075 mmol), Pd₂(dba)₃ (6.9 mg, 0.0075 mmol), XPhos (10.7 mg, 0.0225 mmol), NaOr-Bu (21.6 mg, 0.225 mmol). 12a: m = 27 mg, 77% yield. Mp 131–133 °C; ¹H NMR (250 MHz, CDCl₃) δ 9.04 (s, 2H, Hₐ), 8.52 (s, 2H, H₅), 8.12 (d, J = 7.5 Hz, 4H, Hₐ), 7.56 (d, J = 8.3 Hz, 2H, H₇), 7.51 (d, J = 8.3 Hz, 2H, H₈), 7.49 (t, J = 7.5 Hz, 4H, Hₙ), 7.40 (t, J = 7.5 Hz, 2H, Hₖ), 2.77 (t, J = 7.5 Hz, 2H, CH₂), 1.76 (quint, J = 7.5 Hz, 2H, CH₂), 1.40 (m, 4H, CH₂), 0.96 (t, J = 7.5 Hz, 2H, CH₃); ¹³C NMR (63 MHz, CDCl₃) δ 148.9, 143.5, 139.9, 136.9, 134.2, 133.5, 130.2, 128.8, 128.6, 128.1, 126.8, 126.0, 112.1, 35.7, 31.5, 31.0, 22.6, 14.1; MS (70 eV) m/z (%): 467 (100, M⁺), 410 (60); HRMS m/z: calcd for C₃₃H₃₀N₃ (M + H)⁺ 468.2434, found: 468.2474.
3,6-Bis-(4-methylsulfanylphenyl)-9-(4-pentylphenyl)-2,7-diazacarbazole (**12b**). **11b** (42 mg, 0.075 mmol), **6a** (12.2 mg, 0.075 mmol), Pd$_2$(dba)$_3$ (6.9 mg, 0.0075 mmol), XPhos (10.7 mg, 0.0225 mmol), NaOt-Bu (21.6 mg, 0.225 mmol). **12b**: m = 34 mg, 81% yield; Mp 166–168 °C; $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 9.00 (s, 2H, H$_a$), 8.45 (s, 2H, H$_b$), 8.04 (d, $J = 8.3$ Hz, 4H, H$_c$), 7.53 (d, $J = 8.3$ Hz, 2H, H$_d$), 7.46 (d, $J = 8.3$ Hz, 2H, H$_e$), 7.38 (d, $J = 8.3$ Hz, 4H, H$_f$), 2.76 (t, $J = 7.5$ Hz, 2H, CH$_2$), 2.55 (s, 6H, SCH$_3$), 1.75 (quint, $J = 7.5$ Hz, 2H, CH$_2$), 1.41 (m, 4H, CH$_2$), 0.95 (t, $J = 7.5$ Hz, 2H, CH$_3$); $^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 148.3, 143.5, 138.6, 136.8, 136.7, 134.1, 133.5, 130.2, 128.6, 127.1, 126.8, 126.0, 111.6, 35.6, 31.5, 31.0, 22.5, 15.8, 14.0; MS (70 eV) m/z (%): 559 (100, M$^+$), 280 (15); HRMS m/z: calcd for C$_{35}$H$_{34}$N$_3$S$_2$ (M + H)$^+$ 560.2189, found: 560.2196.
3,6-Bis-(4-methylsulfanylphenyl)-9-(4-methoxyphenyl)-2,7-diazacarbazole (12c). 11b (64 mg, 0.1 mmol), 6b (12.7 mg, 0.1 mmol), Pd$_2$(dba)$_3$ (9.2 mg, 0.01 mmol), XPhos (14.3 mg, 0.03 mmol), NaOt-Bu (29 mg, 0.3 mmol). 12c: m = 38 mg, 73% yield; Mp > 250 °C; $^1$H NMR (200 MHz, CDCl$_3$) δ 8.94 (d, $J = 0.8$ Hz, 2H, H$_a$), 8.47 (d, $J = 0.8$ Hz, 2H, H$_b$), 8.05 (d, $J = 8.5$ Hz, 4H, H$_e$), 7.54 (d, $J = 9$ Hz, 2H, H$_c$), 7.39 (d, $J = 8.5$ Hz, 4H, H$_h$), 7.17 (d, $J = 9$ Hz, 2H, H$_d$), 3.95 (s, 3H, OCH$_3$), 2.55 (s, 6H, SCH$_3$); $^{13}$C NMR (63 MHz, CDCl$_3$) δ 159.5, 148.3, 138.6, 137.1, 136.7, 134.0, 128.5, 128.4, 127.7, 127.7, 126.8, 115.5, 111.6, 55.7, 15.8; HRMS m/z: calcd for C$_{31}$H$_{26}$N$_3$OS$_2$ (M + H)$^+$ 520.1512, found: 520.1492.
32

ppm (t1)

0 50 100 150 200

159.498
148.255
138.610
137.117
136.738
134.037
128.527
128.417
127.694
127.077
126.780
115.494
111.639

77.508
77.000
76.492
55.677
29.690
15.797

grease

N
NN
OMe
MeS SMe

55.677
29.690
15.797

159.498
148.255
138.610
137.117
136.738
134.037
128.527
128.417
127.694
127.077
126.780
115.494
111.639

77.508
77.000
76.492
6. X-ray structure determination

General. The crystal structure analysis was performed at low temperature (T = 110 K) on an Oxford Diffraction SuperNova CCD diffractometer by using Cu Kα radiation (λ = 1.5418 Å). The structures were solved by direct methods with the program SIR92 (Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. J. Appl. Crystallogr. 1993, 26, 343) and full-matrix least-square refinements on F² in SHELXL-97 (Sheldrick, G. M. SHELXL-97, University of Göttingen, Germany, 1997) were performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in difference Fourier maps and refined isotropically according to a riding model.
Crystallographic data of compound 3b

Residual density was found within the channels parallel to [010], but refinement of the disordered \( n \)-hexane molecules was not successful; this is due to the fact that the \( n \)-hexane molecules are \( \sim 2.7 \) times longer than the crystallographic \( b \) axis. The final model was then constructed by inserting carbon atoms with partial occupancies into these channels. CCDC 818528 contains the detailed crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

ORTEP-3 view of 3b in space group \( C2/c \). Atomic displacement ellipsoids are drawn at the 50% probability level. Disordered carbon atoms of the \( n \)-hexane solvent molecule are not shown.
Table S1. Crystal data and structure refinement for 3b.

| Property                      | Value                                                                 |
|-------------------------------|----------------------------------------------------------------------|
| Identification code           | 3b                                                                  |
| Empirical formula             | C18.5 H11 Cl2 N3 O                                                   |
| Formula weight                | 362.21                                                              |
| Temperature                   | 110(2) K                                                            |
| Wavelength                    | 1.54184 Å                                                          |
| Crystal system                | Monoclinic                                                          |
| Space group                   | C 2/c                                                               |
| Unit cell dimensions          | $a = 30.9380(7)$ Å, $\alpha = 90^\circ$, $b = 3.88160(10)$ Å, $\beta = 108.837(2)^\circ$, $c = 28.1690(6)$ Å, $\gamma = 90^\circ$ |
| Volume                        | 3201.61(13) Å³                                                      |
| Z                             | 8                                                                   |
| Density (calculated)          | 1.503 Mg/m³                                                         |
| Absorption coefficient        | 3.710 mm$^{-1}$                                                     |
| F(000)                        | 1480                                                                |
| Crystal size                  | 0.1267 x 0.0689 x 0.0272 mm³                                         |
| Theta range for data collection| 3.32 to 76.30°                                                      |
| Index ranges                  | -38<=$h<=$36, -4<=$k<=$4, -34<=$l<=$34                               |
| Reflections collected         | 10777                                                               |
| Independent reflections       | 3340 [R(int) = 0.0167]                                              |
| Completeness to theta = 76.30°| 99.9 %                                                              |
| Absorption correction         | Analytical                                                          |
| Max. and min. transmission    | 0.907 and 0.725                                                     |
| Refinement method             | Full-matrix least-squares on F$^{2}$                                |
| Data / restraints / parameters| 3340 / 24 / 237                                                     |
| Goodness-of-fit on F$^{2}$     | 1.101                                                               |
| Final R indices [I>2sigma(I)] | R1 = 0.0410, wR2 = 0.1310                                             |
| R indices (all data)          | R1 = 0.0454, wR2 = 0.1354                                             |
| Largest diff. peak and hole   | 0.893 and -0.237 e.Å$^{-3}$                                         |
Crystallographic data of compound 12c

Residual density was found within the channels parallel to [100], but refinement of the disordered chloroform molecules was not successful. The final model was then constructed by inserting chlorine atoms with partial occupancies into these channels. CCDC 818527 contains the detailed crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

ORTEP-3 view of 12c in space group $P\overline{1}$. Atomic displacement ellipsoids are drawn at the 50% probability level. Disordered chlorine atoms of the chloroform molecules are not show.
| Identification code | 12c |
|---------------------|-----|
| Empirical formula   | C31 H25 Cl0.85 N3 O S2 |
| Formula weight      | 549.92 |
| Temperature         | 110(2) K |
| Wavelength          | 1.54184 Å |
| Crystal system      | Triclinic |
| Space group         | P - 1 |
| Unit cell dimensions| $a = 9.64985(16)$ Å, $\alpha = 99.0852(12)^\circ$. |
|                     | $b = 16.5066(2)$ Å, $\beta = 91.9074(13)^\circ$. |
|                     | $c = 17.1719(3)$ Å, $\gamma = 93.8073(12)^\circ$. |
| Volume              | 2692.30(7) Å³ |
| Z                   | 4 |
| Density (calculated)| 1.357 Mg/m³ |
| Absorption coefficient| 2.817 mm⁻¹ |
| F(000)              | 1145.8 |
| Crystal size        | 0.1661 x 0.1078 x 0.0735 mm³ |
| Theta range for data collection | 3.45 to 76.43°. |
| Index ranges        | $-12\leq h \leq 12$, $-20\leq k \leq 20$, $0\leq l \leq 21$ |
| Reflections collected| 44453 |
| Independent reflections | 11242 [R(int) = 0.0250] |
| Completeness to theta = 76.43° | 99.5 % |
| Absorption correction| Analytical |
| Max. and min. transmission | 0.862 and 0.725 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 11242 / 0 / 717 |
| Goodness-of-fit on F² | 1.067 |
| Final R indices [I>2sigma(I)] | $R1 = 0.0602$, $wR2 = 0.1638$ |
| R indices (all data) | $R1 = 0.0671$, $wR2 = 0.1689$ |
| Largest diff. peak and hole | 1.020 and -0.825 e.Å⁻³ |