Synthesis of 3-Acyl-2-arylindole via Palladium-Catalyzed Isocyanide Insertion and Oxypalladation of Alkyne

Takeshi Nanjo, Sho Yamamoto, Chihiro Tsukano, Yoshiji Takemoto*

Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan

Table of Contents

General Experimental Details.....	S2
Preparation of o-Alkynylphenylfolmanilide.....	S2
Procedure for the Preparation of o-Alkynylphenylisocyanide.....	S5
Procedure for the Synthesis of 3-Acyl-2-arylindoles.....	S5
X-ray structure of 9	S13
References.....	S57
¹ H and ¹³ C NMR Spectra.....	S58

General Experimental Details

Unless otherwise noted, all reactions were performed under argon. $\text{Pd}(\text{OAc})_2$ and $\text{Ad}_2\text{P}^n\text{Bu}$ were purchased from Sigma Aldrich. DMF and Cs_2CO_3 were purchased from Wako Pure Chemical Industries, Ltd.. Unless otherwise noted, all other reagents were purchased from commercial suppliers and used as received.

Analytical thin-layer chromatography was performed with Merck Silica gel 60. Silica gel column chromatography was performed with Kanto silica gel 60 (particle size, 63–210 μm) or Fuji Silysia BW-300. Column chromatography using Aluminum oxide was performed with SIGMA-ALDRICH Aluminum oxide. All melting points (m.p.) were determined on YANAGIMOTO micro melting point apparatus and BÜCHI Melting Point M-565. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a JEOL JNM-LA 500 at 500 MHz. Chemical shifts are reported relative to Me_4Si (δ 0.00). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); sep (septet); m (multiplet); br (broad). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JEOL JNM-LA 500 at 126 MHz. Chemical shifts are reported relative to CDCl_3 (δ 77.0), $\text{DMF}-d_7$ (δ 162.7), and $\text{DMSO}-d_6$ (δ 39.5). Infrared spectra were recorded on a FT/IR-4100 (JASCO). Low and high resolution mass spectra were recorded on JEOL JMS-HX/HX 110A.

Preparation of α -Alkynylphenylformanilide

N-(2-(Phenylethynyl)phenyl)formanilide (S1): To formic acid (2.41 mL, 63.9 mmol) was added acetic anhydride (2.16 mL, 22.8 mmol) and the mixture was stirred at room temperature. After stirring for 10 min, to the mixture was added the solution of o -iodoaniline (3.99 g, 18.3 mmol) in CH_2Cl_2 (60 mL) and the mixture was stirred at room temperature. After stirring for 2 h, the mixture was concentrated under reduced pressure to give o -iodoformanilide² (4.42 g, 98%) as a white solid.

To the solution of the formanilide (1.01 g, 4.09 mmol), ethynyl benzene (499 mg, 4.89 mmol) and Et_3N (15 mL) were added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (140 mg, 0.20 mmol) and CuI (38.3 mg, 0.20 mmol) and stirred at room temperature. After stirring for 24h, the reaction mixture was diluted

with Et₂O and the precipitate was removed by filtration through Celite. The filtrate was acidified with saturated aqueous solution of NH₄Cl and extracted with Et₂O. The combined extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography (hexane/EtOAc = 90/10) to give **14** (0.614g, 68%) as a white solid: m.p. 96.8-97.9°C; ¹H NMR (500 MHz, CDCl₃) δ 8.83 (d, 0.35H, *J* = 11.5 Hz), 8.51(s, 0.65H), 8.44(d, 0.65H, *J* = 8.3 Hz), 7.99 (brs, 1H), 7.56-7.51 (m, 3H), 7.31-7.40 (m, 4H), 7.25-7.23 (m, 0.35H), 7.17-7.09 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 161.3, 159.0, 137.8, 137.6, 133.0, 131.9, 131.7, 131.6, 129.7, 129.7, 129.0, 128.5, 128.5, 124.5, 124.0, 122.2, 122.1, 120.0, 116.2, 113.5, 112.1, 96.5, 83.9, 83.7; IR (ATR) 3140, 1687, 1269 cm⁻¹; MS (FAB+) *m/z* = 221([M]⁺); HRMS (FAB+) Calcd for C₁₅H₁₂NO [M+H]⁺:222.0919; found:222.0916. The peaks of ¹H NMR and ¹³C NMR were observed as the mixture of amide rotamers. The spectroscopic data were in agreement with those reported in the literature.¹

N-(2-((4-Methoxyphenyl)ethynyl)phenyl)formamide (S2): The reaction was performed according to the procedure for **S1**. A white solid: m.p. 61.0-62.3°C; ¹H NMR (500 MHz, CDCl₃) δ 8.85 (d, 0.35H, *J* = 11.2 Hz), 8.52 (s, 0.65H), 8.44 (d, 0.65H, *J* = 8.3 Hz), 7.95 (brs, 1H), 7.55-7.46 (m, 3H), 7.37-7.29 (m, 1H), 7.26-7.24 (m, 0.35H), 7.18-7.07 (m, 1H), 6.91(t, 2H, *J* = 7.9 Hz), 3.85 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 161.3, 160.1, 158.9, 137.7, 137.4, 133.1, 133.1, 132.7, 131.7, 129.4, 129.3, 124.4, 123.9, 119.9, 116.0, 114.2, 114.1, 114.1, 114.1, 113.8, 112.4, 96.7, 96.6, 82.6, 82.4, 55.3; IR (ATR) 3273, 1658, 1507, 1246 cm⁻¹; MS (FAB+) *m/z* = 251([M]⁺); HRMS (FAB+) Calcd for C₁₆H₁₃NO₂ [M]⁺:251.0946; found:251.0941. The peaks of ¹H NMR and ¹³C NMR were observed as the mixture of amide rotamers.

N-(2-((4-Chlorophenyl)ethynyl)phenyl)formamide (S3): To formic acid (1.21 mL, 32.0 mmol) was added acetic anhydride (1.08 mL, 11.4 mmol) and the mixture was stirred at room temperature. After stirring for 10 min, to the mixture was added the solution of *o*-ethynylaniline (1.07 g, 9.13 mmol) in CH₂Cl₂ (30 mL) and the mixture was stirred at room temperature. After stirring for 1 h, the mixture was concentrated under reduced pressure to give *o*-ethynylformanilide (1.32 g, 100%) as a white solid.

To the solution of the formanilide (1.32 g, 9.13 mmol), 1-chloro-4-iodobenzene (1.81 g, 7.61 mmol) and Et₃N (28 mL) under Ar atmosphere were added Pd(PPh₃)₂Cl₂ (260.5 mg, 0.38 mmol) and CuI (76.5 mg, 0.38 mmol) and stirred at room temperature. After stirring for 12h, the reaction mixture was diluted with CHCl₃ and the precipitate was removed by filtration through Celite. The filtrate was acidified with saturated aqueous solution of NH₄Cl and extracted with CHCl₃. The combined extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography (100% CH₂Cl₂) to give **S3** (1.10g, 47%) as a white solid. Mixture of rotamers in a ratio of 0.65:0.35; m.p. 143.7-144.7°C; ¹H NMR (500 MHz, CDCl₃) δ 8.84 (d, 0.35H, *J* = 11.5 Hz), 8.52 (s, 0.65H), 8.44 (d, 0.65H, *J* = 8.3 Hz), 7.95-7.82 (m, 1H), 7.56-7.10 (m, 7.35H); ¹³C NMR (126 MHz, CDCl₃) δ 161.3, 158.8, 137.8, 137.6, 135.1, 133.0, 132.8, 132.8, 132.0, 130.0, 129.9, 128.9, 128.9, 124.6, 124.0, 120.7, 120.5, 120.1, 116.3, 113.3, 111.7, 95.3, 95.3, 84.9, 84.6; IR (ATR) 3263, 1654, 1085 cm⁻¹; MS (FAB+) *m/z* = 255 ([M]⁺); HRMS (FAB+) Calcd for C₁₅H₁₀ClNO [M]⁺:255.0451; found:255.0453. The peaks of ¹H NMR and ¹³C NMR were observed as the mixture of amide rotamers.

N-(4-Methoxy-2-(phenylethynyl)phenyl)formamide (S4): The reaction was performed according to the procedure for **S1**. A white solid: m.p. 121.0-122.0°C; ¹H NMR (500 MHz, CDCl₃) δ 8.63 (d, 0.35H, *J* = 11.5 Hz), 8.43 (s, 0.65H), 8.30 (d, 0.65H, *J* = 9.2 Hz), 7.89-7.83 (m, 1H), 7.55-7.52 (m, 2H), 7.40-7.33 (m, 3H), 7.12-7.00 (m, 1.35H), 6.92-6.86 (m, 1H), 3.79 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 161.8, 158.5, 156.7, 155.7, 131.7, 131.7, 131.5, 130.9, 129.1, 129.1, 128.6, 128.5, 122.1, 122.0, 121.6, 119.2, 117.0, 116.3, 115.9, 115.6, 113.3, 96.3, 96.2, 83.9, 55.7, 55.6; IR (ATR) 3265, 1658, 1532, 1219 cm⁻¹; MS (FAB+) *m/z* = 251 ([M]⁺); HRMS

(FAB+) Calcd for $C_{16}H_{13}NO_2$ $[M]^+$:251.0946; found:251.0947. The peaks of 1H NMR and ^{13}C NMR were observed as the mixture of amide rotamers.

N-(4-Chloro-2-(phenylethynyl)phenyl)formamide (S5): The reaction was performed according to the procedure for **S1**. A white solid: m.p. 118.8-119.5°C; 1H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, 0.25H, $J = 11.2$ Hz), 8.49 (s, 0.75H), 8.40 (d, 0.75H, $J = 8.9$ Hz), 7.99-7.88 (m, 1H), 7.58-7.13 (m, 7.25H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 158.8, 136.4, 136.2, 132.5, 131.7, 131.7, 131.4, 129.8, 129.7, 129.4, 128.9, 128.6, 128.6, 121.7, 121.5, 121.1, 117.3, 115.1, 113.6, 97.6, 82.6; IR (ATR) 3258, 1643, 1519, 1403 cm^{-1} ; MS (FAB+) $m/z = 255$ ($[M]^+$); HRMS (FAB+) Calcd for $C_{15}H_{10}ClNO$ $[M]^+$:255.0451; found:255.0448. The peaks of 1H NMR and ^{13}C NMR were observed as the mixture of amide rotamers.

Procedure for the Preparation of α -Alkynylphenylisocyanide³

1-Isocyano-2-(phenylethynyl)benzene (3a): To the solution of formanilide (44.3 mg, 0.200 mmol) and Et_3N (0.139 mL, 1.00 mmol) in THF (2 mL) were added $POCl_3$ (0.028 mL, 0.300 mmol) at 0 °C and stirred at the same temperature. After stirring for 1h, the reaction was quenched with saturated aqueous solution of $NaHCO_3$ and extracted with Et_2O . The combined extracts were washed with brine, dried over Na_2SO_4 , added toluene (5 mL), and concentrated under reduced pressure to 3 mL. The obtained solution was filtered through alumina column chromatography (hexane/ $EtOAc = 90/10$). To the obtained solution was added DMF (2 mL) and concentrated under reduced pressure to 2 mL. The solution was used for the synthesis of 3-acyl-2-arylindoles.

Procedure for the Synthesis of 3-Acyl-2-arylindoles

Phenyl(2-phenyl-1H-indol-3-yl)methanone (1a): To a stirred solution iodobenzene (20.4 mg, 0.100 mmol) in DMF (1 mL) were added Pd(OAc)₂ (1.1 mg, 0.0049 mmol), Ad₂P^{*t*}Bu (3.6 mg, 0.0101 mmol) and Cs₂CO₃ (97.7 mg, 0.300 mmol) at room temperature and the reaction mixture was heated to 100 °C. After stirring for 10 min freshly prepared 1-isocyano-2-(phenylethynyl)benzene in DMF (2 mL) was added for 3 h and stirred at 100 °C. After stirring for 1 h, the reaction mixture was neutralized by saturated aqueous solution of NH₄Cl and extracted with EtOAc. The combined extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography (hexane/EtOAc = 9/1) to give **1a** (23.2 mg, 78%) as a white solid; m.p. 224.8–225.8 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.65 (brs, 1H), 7.94 (d, 1H, *J* = 8.0 Hz), 7.65 (d, 2H, *J* = 7.0 Hz), 7.45 (d, 1H, *J* = 8.0 Hz), 7.37–7.16 (m, 10H); ¹³C NMR (126 MHz, DMF-*d*₇) δ 193.1, 144.7, 141.0, 137.0, 132.8, 132.0, 130.3, 130.0, 129.4, 129.1, 128.8, 128.5, 123.6, 122.0, 121.5, 113.4, 112.5; IR (ATR) 3053, 1563, 1448, 1421, 1216 cm⁻¹; MS (FAB+) *m/z* = 298 ([M+H]⁺); HRMS (FAB+) Calcd for C₂₁H₁₆NO [M+H]⁺: 298.1232; found: 298.1227. The spectroscopic data were in agreement with those reported in the literature.⁴

(2-(4-Methoxyphenyl)-1H-indol-3-yl)(phenyl)methanone (1b): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1b** in 83% yield as a white solid: m.p. 210.0–211.0 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.13 (brs, 1H), 7.75 (d, 1H, *J* = 8.0 Hz), 7.57–7.52 (m, 3H), 7.43 (t, 1H, *J* = 7.3 Hz), 7.37 (d, 2H, *J* = 8.5 Hz), 7.29–7.25 (m, 3H), 7.18 (t, 1H, *J* = 7.6 Hz), 6.86 (d, 2H, *J* = 8.6 Hz), 3.76 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 192.1, 159.4, 144.2, 139.9, 135.7, 131.2, 130.9, 129.0, 128.3, 127.8, 123.8, 122.6, 121.3, 120.4, 113.5, 111.7, 111.5, 55.2; IR (ATR) 3183, 1591, 1570, 1431, 1247 cm⁻¹; MS (FAB+) *m/z* = 328 ([M+H]⁺); HRMS (FAB+) Calcd for C₂₂H₁₈NO₂ [M+H]⁺: 328.1338; found: 328.1341.

Phenyl(2-(*p*-tolyl)-1H-indol-3-yl)methanone (1c): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1c** in 73% yield as a brown solid: m.p. 188.0-189.0 °C; ^1H NMR (500 MHz, $\text{DMF-}d_7$) δ 12.11 (brs, 1H), 7.76 (d, 1H, $J = 8.0$ Hz), 7.65 (d, 2H, $J = 7.4$ Hz), 7.57 (d, 1H $J = 8.0$ Hz), 7.43-7.40 (m, 3H), 7.29-7.24 (m, 3H), 7.16 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 7.10 (d, 2H $J = 8.0$ Hz), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMF-}d_7$) δ 193.1, 144.8, 141.0, 139.0, 137.0, 132.0, 130.2, 130.0, 129.9, 129.4, 129.4, 128.5, 123.4, 121.9, 121.4, 113.1, 112.4, 21.0; IR (ATR) 3144, 1567, 1428, 1210 cm^{-1} ; MS (FAB+) $m/z = 312$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: 312.1388; found: 312.1387.

(2-(4-Chlorophenyl)-1H-indol-3-yl)(phenyl)methanone (1d): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1d** in 93% yield as a white solid: m.p. 221.0-222.0 °C; ^1H NMR (500 MHz, $\text{DMF-}d_7$) δ 12.13 (brs, 1H), 7.65 (d, 1H, $J = 8.0$ Hz), 7.49-7.44 (m, 3H), 7.39 (d, 2H, $J = 8.3$ Hz), 7.29 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 7.20 (d, 2H, $J = 8.5$ Hz), 7.16-7.13 (m, 3H), 7.05 (dd, 1H, $J_1 = J_2 = 7.4$ Hz); ^{13}C NMR (126 MHz, $\text{DMF-}d_7$) δ 192.9, 143.4, 141.0, 137.0, 134.4, 132.1, 132.0, 131.6, 130.0, 129.2, 128.9, 128.6, 123.8, 122.1, 121.5, 113.7, 112.6; IR (ATR) 3134, 1598, 1567, 1416, 1208 cm^{-1} ; MS (FAB+) $m/z = 332$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{21}\text{H}_{15}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 332.0842; found: 332.0841.

Phenyl(2-(4-(trifluoromethyl)phenyl)-1H-indol-3-yl)methanone (1e): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1e** in 64% yield as a white solid; m.p. 224.0-225.0 °C; ^1H NMR (500 MHz, $\text{DMF-}d_7$) δ 12.40 (brs, 1H), 7.79-7.74 (m, 3H), 7.67-7.61 (m, 5H), 7.43 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 7.33-7.27 (m, 3H), 7.21 (dd, 1H, $J_1 = J_2$

= 7.4 Hz); ^{13}C NMR (126 MHz, $\text{DMF-}d_7$) δ 192.9, 142.8, 140.9, 137.2, 136.8, 132.2, 131.1, 130.0, 129.7 (q, J = 31.4 Hz), 129.1, 128.6, 125.6 (q, J = 3.6 Hz) 125.1 (q, J = 271.1 Hz) 124.1, 122.3, 121.7, 114.5, 112.7; IR (ATR) 3077, 1595, 1563, 1427, 1320 cm^{-1} ; MS (FAB+) m/z = 366 ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$:366.1106; found:366.1102.

Methyl 4-(3-benzoyl-1H-indol-2-yl)benzoate (1f): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1f** in 48% yield as a yellow solid; m.p. 214.0-215.0 °C; ^1H NMR (500 MHz, $\text{DMF-}d_7$) δ 12.24 (brs, 1H), 7.73 (d, 2H, J = 8.3 Hz), 7.67 (d, 1H, J = 8.0 Hz), 7.53-7.47 (m, 5H), 7.27 (dd, 1H, $J_1 = J_2$ = 7.4 Hz), 7.18-7.12 (m, 3H), 7.07 (dd, 1H, $J_1 = J_2$ = 7.4 Hz), 3.74(s, 3H); ^{13}C NMR (126 MHz, $\text{DMF-}d_7$) δ 193.0, 166.7, 143.0, 140.9, 137.3, 132.3, 130.5, 130.1, 130.1, 129.6, 129.3, 128.6, 124.0, 122.2, 121.6, 114.3, 112.7, 52.5 (One carbon peak was overlapping); IR (ATR) 3178, 1724, 1611, 1571, 1432, 1274, 1104 cm^{-1} ; MS (FAB+) m/z = 356 ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{23}\text{H}_{18}\text{NO}_3$ $[\text{M}+\text{H}]^+$:356.1287; found:356.1288.

4-(3-Benzoyl-1H-indol-2-yl)benzonitrile (1g): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1g** in 54% yield as a white solid; m.p. 250.0-251.2 °C; ^1H NMR (500 MHz, $\text{DMF-}d_7$) δ 12.29 (brs, 1H), 7.65-7.57 (m, 5H), 7.51-7.47 (m, 3H), 7.32 (dd, 1H, $J_1 = J_2$ = 7.4 Hz), 7.20-7.15 (m, 3H), 7.07 (dd, 1H, J = 7.4 Hz); ^{13}C NMR (126 MHz, $\text{DMF-}d_7$) δ 192.9, 142.4, 140.8, 137.3, 137.3, 132.6, 132.4, 131.1, 130.1, 129.1, 128.7, 124.2, 122.4, 121.7, 119.2, 114.6, 112.8, 111.9; IR (ATR) 3114, 2230, 1593, 1566, 1418, 1210 cm^{-1} ; MS (FAB+) m/z = 323 ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{22}\text{H}_{15}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$:323.1184; found:323.1192

Phenyl(2-(m-tolyl)-1H-indol-3-yl)methanone (1h): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1h** in 85% yield as a white solid; m.p. 153.0-154.2 °C; ^1H NMR (500 MHz, DMF- d_7) δ 11.98 (brs, 1H), 7.70 (d, 1H, $J = 8.0$ Hz), 7.44-7.41 (m, 3H), 7.21 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 7.15-7.06 (m, 5H), 7.04-6.98 (m, 2H), 6.90 (d, 1H, $J = 7.4$ Hz), 2.01 (s, 3H); ^{13}C NMR (126 MHz, DMF- d_7) δ 193.2, 145.1, 141.2, 138.2, 137.0, 132.5, 131.9, 131.3, 129.8, 129.7, 129.4, 128.7, 128.4, 127.2, 123.6, 122.0, 121.5, 113.3, 112.4, 21.0; IR (ATR) 3210, 1593, 1570, 1447, 1429, 1209, 887 cm^{-1} ; MS (FAB+) $m/z = 312$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{22}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$:312.1388; found:312.1387.

Phenyl(2-(o-tolyl)-1H-indol-3-yl)methanone (1i): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1i** in 85% yield as a white solid; m.p. 211.2-212.2 °C; ^1H NMR (500 MHz, DMF- d_7) δ 12.00 (brs, 1H), 7.94 (d, 1H, $J = 8.0$ Hz), 7.58-7.53 (m, 3H), 7.34-7.12 (m, 8H), 7.06 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 2.25 (s, 3H); ^{13}C NMR (126 MHz, DMF- d_7) δ 192.8, 145.1, 141.3, 137.4, 136.8, 133.2, 131.9, 131.5, 130.5, 129.4, 129.3, 128.7, 128.2, 125.9, 123.5, 122.1, 121.8, 114.7, 112.4, 20.2; IR (ATR) 3056, 1591, 1563, 1445, 1423, 1209, 883 cm^{-1} ; MS (FAB+) $m/z = 312$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$:312.1388; found:312.1387.

(5-Chloro-2-phenyl-1H-indol-3-yl)(phenyl)methanone (1j): The reaction was performed in DMF at 100 °C according to the procedure for **1a** with 10 mol% of $\text{Pd}(\text{OAc})_2$ and 20 mol% of $\text{Ad}_2\text{P}^n\text{Bu}$, and gave **1j** in 41% yield as a white solid; m.p. 261.8-263.6 °C; ^1H NMR (500 MHz,

DMF- d_7) δ 12.28 (brs, 1H), 7.74 (s, 1H), 7.48-7.46 (m, 3H), 7.33 (d, 2H, $J = 6.9$ Hz), 7.24 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 7.15-7.11 (m, 6H); ^{13}C NMR (126 MHz, DMF- d_7) δ 192.8, 146.4, 140.6, 135.5, 132.3, 132.1, 130.5, 130.4, 129.9, 129.4, 128.8, 128.5, 127.2, 123.7, 120.7, 114.1, 112.9; IR (ATR) 3160, 1595, 1563, 1409, 1215 cm^{-1} ; MS (FAB+) $m/z = 332$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{21}\text{H}_{15}\text{ClNO}$ $[\text{M}+\text{H}]^+$:332.0842; found: 332.0837.

(5-Methoxy-2-phenyl-1H-indol-3-yl)(phenyl)methanone (1k): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1k** in 69% yield as a white solid; m.p. 182.0-183.2 °C; ^1H NMR (500 MHz, DMF- d_7) δ 12.06 (brs, 1H), 7.60 (d, 2H, $J = 8.0$ Hz), 7.50-7.42 (m, 4H), 7.37 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 7.25-7.22 (m, 5H), 6.94 (dd, 1H, $J_1 = 8.9$ Hz, $J_2 = 2.6$ Hz), 3.80 (s, 3H); ^{13}C NMR (126 MHz, DMF- d_7) δ 193.0, 156.3, 145.4, 141.2, 132.9, 132.0, 131.8, 130.3, 130.2, 129.9, 129.0, 128.7, 128.4, 113.6, 113.2, 103.3, 55.7 (One carbon peak was overlapping); IR (ATR) 3173, 1597, 1414, 1271 cm^{-1} ; MS (FAB+) $m/z = 328$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$:328.1338; found:328.1347.

(4-Chlorophenyl)(2-phenyl-1H-indol-3-yl)methanone (1l): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1l** in 47% yield as a white solid; m.p. 226.4-228.0 °C; ^1H NMR (500 MHz, DMF- d_7) δ 12.23 (brs, 1H), 7.91 (d, 1H, $J = 8.0$ Hz), 7.61-7.59 (m, 3H), 7.47 (d, 2H, $J = 6.0$ Hz), 7.29-7.20 (m, 7H); ^{13}C NMR (126 MHz, DMF- d_7) δ 191.7, 145.2, 139.8, 137.1, 137.1, 132.6, 131.8, 130.5, 129.3, 129.2, 128.8, 128.6, 123.7, 122.2, 121.5, 113.1, 112.5; IR (ATR) 3133, 1592, 1445, 1412, 1274 cm^{-1} ; MS (FAB+) $m/z = 332$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{21}\text{H}_{15}\text{ClNO}$ $[\text{M}+\text{H}]^+$:332.0842; found:332.0837.

(4-Methoxyphenyl)(2-phenyl-1H-indol-3-yl)methanone (1m): The reaction was performed in DMF at 100 °C according to the procedure for **1a**, and gave **1m** in 60% yield as a white solid; m.p. 152.7-154.0 °C; ^1H NMR (500 MHz, DMF- d_7) δ 12.10 (brs, 1H), 7.71-7.67 (m, 3H), 7.58-7.54 (m, 3H), 7.33-7.24 (m, 4H), 7.15 (dd, 1H, $J_1 = J_2 = 7.4$ Hz), 6.85 (d, 2H, $J = 8.9$ Hz), 3.80 (s, 3H); ^{13}C NMR (126 MHz, DMF- d_7) δ 191.9, 163.3, 143.3, 137.0, 133.3, 132.9, 132.3, 130.0, 129.4, 129.0, 128.9, 123.4, 121.6, 121.2, 113.9, 113.6, 112.4, 55.8; IR (ATR) 3184, 1592, 1423, 1251 cm^{-1} ; MS (FAB+) $m/z = 328$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{22}\text{H}_{17}\text{NO}_2$ $[\text{M}]^+$: 327.1259; found: 327.1252.

6-Phenyl-11H-indolo[3,2-c]quinoline (5): The reaction was performed in toluene at 100 °C according to the procedure for **1a** with 10 mol% of $\text{Pd}(\text{OAc})_2$ and 20 mol% of $\text{Ad}_2\text{P}^n\text{Bu}$ to give **5** in 56% yield as a orange solid; m.p. 237.0-238.4 °C; ^1H NMR (500 MHz, DMSO- d_6) δ 8.57 (d, 1H, $J = 8.0$ Hz), 8.13 (d, 1H, $J = 8.3$ Hz), 7.82 (d, 2H, $J = 7.4$ Hz), 7.80-7.57 (m, 6H), 7.50 (d, 1H, $J = 8.0$ Hz), 7.43 (t, 1H, $J = 7.7$ Hz), 7.12 (t, 1H, $J = 7.6$ Hz); ^{13}C NMR (126 MHz, DMSO- d_6) δ 155.5, 144.9, 141.0, 140.7, 139.0, 129.4, 128.8, 128.5, 128.4, 125.6, 125.3, 121.9, 121.7, 121.0, 120.2, 116.3, 111.9 (Two carbon peak was overlapping); IR (ATR) 3057, 1558, 1512, 1361, 1242 cm^{-1} ; MS (FAB+) $m/z = 295$ ($[\text{M}+\text{H}]^+$); HRMS (FAB+) Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$: 295.1235; found: 295.1233. The spectroscopic data were in agreement with those reported in the literature.⁵

6-Phenylchromeno[4,3-b]indole (7): The reaction was performed in toluene at 100 °C according to the procedure for **1a** with 10 mol% of Pd(OAc)₂ and 20 mol% of Ad₂PⁿBu to give **7** in 73% yield as a yellow solid; m.p. 143.3-144.7 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.70 (1H, d, *J* = 7.9 Hz), 8.06-8.03 (2H, m), 7.94 (1H, d, *J* = 8.0 Hz), 7.82 (1H, d, *J* = 7.7 Hz), 7.75-7.65 (5H, m), 7.58 (1H, t, *J* = 7.4 Hz), 7.51 (1H, t, *J* = 7.7 Hz), 7.19 (1H, t, *J* = 7.4 Hz); ¹³C NMR (500 MHz, CDCl₃) δ: 158.2, 156.5, 155.3, 152.5, 132.5, 131.7, 131.0, 130.0, 129.2, 129.0, 128.4, 126.0, 125.2, 124.4, 122.7, 121.3, 120.0, 118.7, 118.1; IR (ATR) 3056, 1638, 1378, 1056 cm⁻¹; MS (FAB+) *m/z* = 296 ([M+H]⁺); HRMS (FAB+) Calcd for C₂₁H₁₄NO [M+H]⁺: 296.1075; found: 296.1075.

6-Phenyl-11H-benzo[a]carbazole-5-carbonitrile (9): The reaction was performed in DMF at 100 °C according to the procedure for **1a** with 10 mol% of Pd(OAc)₂ and 20 mol% of Ad₂PⁿBu to give **9** in 68% yield as a white solid; m.p. 282.0-282.8 °C; ¹H NMR (500 MHz, DMF-*d*₇) δ: 13.07 (1H, brs), 8.68 (1H, d, *J* = 8.0 Hz), 8.21 (1H, d, *J* = 8.0 Hz), 7.77-7.70 (2H, m), 7.62-7.55 (6H, m), 7.29 (1H, t, *J* = 7.7 Hz), 6.91 (1H, t, *J* = 7.4 Hz), 6.80 (1H, d, *J* = 8.0 Hz); ¹³C NMR (500 MHz, DMF-*d*₇) δ: 144.5, 140.6, 138.9, 138.7, 131.5, 129.9, 129.7, 129.6, 128.8, 127.6, 126.2, 123.6, 123.4, 121.7, 121.1, 120.9, 118.8, 116.8, 112.7, 100.6 (One carbon peak was overlapping); IR (ATR) 3273, 2213, 1371 cm⁻¹; MS (FAB+) *m/z* = 319 ([M+H]⁺); HRMS (FAB+) Calcd for C₂₃H₁₄N₂ [M]⁺: 318.1157; found: 318.1166. The structure of **9** was determined X-ray crystallography.

X-ray structure of 9

Data Collection

A colorless platelet crystal of $C_{47}H_{29}Cl_3N_4$ having approximate dimensions of 0.800 x 0.500 x 0.150 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-Axis RAPID diffractometer using graphite monochromated Mo-K α radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

$$\begin{aligned}a &= 7.366(2) \text{ \AA} & \alpha &= 64.891(4)^\circ \\b &= 16.750(3) \text{ \AA} & \beta &= 81.409(4)^\circ \\c &= 17.108(3) \text{ \AA} & \gamma &= 78.963(4)^\circ \\V &= 1870.4(5) \text{ \AA}^3\end{aligned}$$

For $Z = 2$ and F.W. = 756.13, the calculated density is 1.342 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$$P\bar{1} \text{ (\#2)}$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ to a maximum 2θ value of 55.0° . A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at $\chi=45.0^\circ$ and $\phi = 0.0^\circ$. The exposure rate was 120.0 [sec./ $^\circ$]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at $\chi=45.0^\circ$ and $\phi = 180.0^\circ$. The exposure rate was 120.0 [sec./ $^\circ$]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 16147 reflections that were collected, 7745 were unique ($R_{\text{int}} = 0.1109$); equivalent reflections were merged.

The linear absorption coefficient, μ , for Mo-K α radiation is 2.852 cm⁻¹. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.257 to 0.958. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction¹ was applied (coefficient = 0.008910).

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement³ on F^2 was based on 7745 observed reflections and 488 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0838$$

$$wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.2326$$

The standard deviation of an observation of unit weight⁴ was 1.03. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.47 and -0.43 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in F_{calc} ⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸.

All calculations were performed using the CrystalStructure⁹ crystallographic software package except for refinement, which was performed using SHELXL-97¹⁰.

References

(1) Larson, A.C. (1970), Crystallographic Computing, 291-294. F.R. Ahmed, ed. Munksgaard, Copenhagen (equation 22, with V replaced by the cell volume).

(2) SIR2008: M.C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna (2007)

(3) Least Squares function minimized: (SHELXL97)

$$\sum w(F_o^2 - F_c^2)^2 \quad \text{where } w = \text{Least Squares weights.}$$

(4) Standard deviation of an observation of unit weight:

$$[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations
 N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C.

Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(10) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$\text{C}_{47}\text{H}_{29}\text{Cl}_3\text{N}_4$
Formula Weight	756.13
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.800 X 0.500 X 0.150 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	$a = 7.366(2) \text{ \AA}$ $b = 16.750(3) \text{ \AA}$ $c = 17.108(3) \text{ \AA}$ $\alpha = 64.891(4)^\circ$ $\beta = 81.409(4)^\circ$ $\gamma = 78.963(4)^\circ$ $V = 1870.4(5) \text{ \AA}^3$
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.342 g/cm^3
F_{000}	780.00
$\mu(\text{MoK}\alpha)$	2.852 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoK α ($\lambda = 0.71075 \text{ \AA}$) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	23.0°C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range ($\chi=45.0$, $\phi=0.0$)	130.0 - 190.0°
Exposure Rate	120.0 sec./°
ω oscillation Range ($\chi=45.0$, $\phi=180.0$)	0.0 - 160.0°
Exposure Rate	120.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\text{max}}$	55.0°
No. of Reflections Measured	Total: 16147 Unique: 7745 ($R_{\text{int}} = 0.1109$)
Corrections	Lorentz-polarization

Absorption

(trans. factors: 0.257 - 0.958)

Secondary Extinction

(coefficient: 8.91000e-003)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0907 \cdot P)^2 + 1.1274 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	7745
No. Variables	488
Reflection/Parameter Ratio	15.87
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0838
Residuals: R (All reflections)	0.1730
Residuals: wR_2 (All reflections)	0.2326
Goodness of Fit Indicator	1.028
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.47 e ⁻ /Å ³

Minimum peak in Final Diff. Map

-0.43 e⁻/Å³

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
Cl1	0.5697(2)	0.25424(9)	0.29686(9)	3.34(3)
Cl2	0.9373(2)	0.1629(2)	0.2647(1)	4.78(4)
Cl3	0.8500(3)	0.3576(2)	0.1789(1)	5.02(4)
N1	0.2682(5)	0.3625(3)	0.5501(3)	1.98(7)
N2	0.1425(6)	0.7670(3)	0.2192(3)	2.63(8)
N3	0.6867(5)	0.1490(3)	-0.0396(3)	2.14(7)
N4	0.6191(6)	-0.2613(3)	0.2713(3)	2.71(8)
C1	0.2445(6)	0.3062(3)	0.5127(3)	1.96(8)
C2	0.2567(6)	0.2129(3)	0.5500(3)	2.22(9)
C3	0.2193(7)	0.1721(3)	0.4996(4)	2.6(1)
C4	0.1700(7)	0.2240(3)	0.4127(3)	2.35(9)
C5	0.1598(6)	0.3156(3)	0.3769(3)	2.08(9)
C6	0.2007(6)	0.3592(3)	0.4254(3)	1.77(8)
C7	0.2040(6)	0.4509(3)	0.4120(3)	1.70(8)
C8	0.1778(6)	0.5345(3)	0.3380(3)	1.72(8)
C9	0.1870(6)	0.6110(3)	0.3498(3)	1.87(8)
C10	0.2247(6)	0.6109(3)	0.4303(3)	1.66(8)
C11	0.2383(6)	0.6900(3)	0.4399(3)	2.07(9)
C12	0.2773(7)	0.6868(4)	0.5177(3)	2.44(9)
C13	0.3085(7)	0.6040(3)	0.5889(3)	2.33(9)
C14	0.2977(6)	0.5260(4)	0.5815(3)	2.11(9)
C15	0.2560(6)	0.5269(3)	0.5033(3)	1.79(8)
C16	0.2442(6)	0.4499(3)	0.4899(3)	1.54(8)
C17	0.1625(6)	0.6966(3)	0.2764(3)	2.02(8)
C18	0.1545(7)	0.5358(3)	0.2525(3)	2.05(9)
C19	-0.0091(7)	0.5787(3)	0.2088(3)	2.5(1)
C20	-0.0226(8)	0.5787(4)	0.1280(4)	2.9(1)
C21	0.1245(8)	0.5358(4)	0.0906(4)	3.1(1)

C22	0.2869(8)	0.4927(3)	0.1344(3)	2.7(1)
C23	0.3017(7)	0.4926(3)	0.2142(3)	2.24(9)
C24	0.5895(7)	0.2049(3)	-0.0008(3)	2.22(9)
C25	0.5538(7)	0.2980(3)	-0.0360(3)	2.55(9)
C26	0.4417(7)	0.3388(4)	0.0141(4)	2.7(1)
C27	0.3674(7)	0.2875(3)	0.0981(3)	2.52(9)
C28	0.4073(7)	0.1949(3)	0.1334(3)	2.12(9)
C29	0.5217(6)	0.1518(3)	0.0843(3)	1.88(8)
C30	0.5862(6)	0.0594(3)	0.0962(3)	1.90(8)

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ (continued)

atom	x	y	z	B_{eq}
C31	0.5675(6)	-0.0248(3)	0.1657(3)	1.85(8)
C32	0.6402(6)	-0.1023(3)	0.1519(3)	1.85(8)
C33	0.7408(6)	-0.1000(3)	0.0711(3)	2.01(9)
C34	0.8196(6)	-0.1785(3)	0.0576(3)	2.04(9)
C35	0.9165(7)	-0.1736(4)	-0.0195(3)	2.55(9)
C36	0.9395(7)	-0.0893(4)	-0.0865(3)	2.6(1)
C37	0.8646(7)	-0.0128(4)	-0.0760(3)	2.31(9)
C38	0.7638(6)	-0.0147(3)	0.0020(3)	1.93(8)
C39	0.6844(6)	0.0617(3)	0.0179(3)	1.86(8)
C40	0.6258(7)	-0.1893(4)	0.2194(3)	2.23(9)
C41	0.4721(7)	-0.0285(3)	0.2508(3)	2.11(9)
C42	0.5435(7)	0.0126(3)	0.2940(3)	2.42(9)
C43	0.4545(8)	0.0132(4)	0.3720(4)	3.1(1)
C44	0.2952(8)	-0.0276(3)	0.4080(4)	2.9(1)
C45	0.2218(7)	-0.0692(4)	0.3663(4)	2.9(1)
C46	0.3123(7)	-0.0705(3)	0.2876(3)	2.45(9)
C47	0.7587(8)	0.2556(4)	0.2193(4)	3.7(2)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B _{iso}
H1	0.2938	0.3455	0.6027	2.38
H2	0.2889	0.1795	0.6066	2.67
H3	0.7396	0.1666	-0.0912	2.57
H3A	0.2263	0.1105	0.5226	3.11
H4	0.1446	0.1958	0.3798	2.82
H5	0.1256	0.3487	0.3206	2.49
H11	0.2205	0.7447	0.3928	2.48
H12	0.2829	0.7392	0.5232	2.93
H13	0.3365	0.6019	0.6411	2.80
H14	0.3182	0.4718	0.6291	2.54
H19	-0.1068	0.6065	0.2336	3.00
H20	-0.1292	0.6073	0.0988	3.51
H21	0.1144	0.5358	0.0371	3.69
H22	0.3840	0.4644	0.1096	3.26
H23	0.4088	0.4640	0.2429	2.69
H25	0.6031	0.3318	-0.0911	3.06
H26	0.4155	0.4006	-0.0081	3.27
H27	0.2912	0.3158	0.1300	3.02
H28	0.3590	0.1616	0.1889	2.54
H34	0.8053	-0.2341	0.1017	2.44
H35	0.9662	-0.2254	-0.0272	3.05
H36	1.0061	-0.0858	-0.1383	3.14
H37	0.8804	0.0420	-0.1212	2.78
H42	0.6500	0.0394	0.2707	2.90
H43	0.5015	0.0408	0.4001	3.70
H44	0.2374	-0.0271	0.4600	3.46
H45	0.1151	-0.0956	0.3901	3.43
H46	0.2664	-0.0991	0.2601	2.94
H47	0.7135	0.2503	0.1709	4.45

Table 3. Anisotropic displacement parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cl1	0.0342(8)	0.0507(9)	0.0487(9)	-0.0106(6)	0.0089(6)	-0.0289(7)
Cl2	0.0353(9)	0.090(2)	0.088(2)	0.0022(8)	-0.0093(8)	-0.069(1)
Cl3	0.057(1)	0.087(2)	0.053(1)	-0.0375(9)	0.0102(8)	-0.0270(9)
N1	0.023(2)	0.028(2)	0.024(3)	-0.006(2)	-0.001(2)	-0.010(2)
N2	0.039(3)	0.031(3)	0.029(3)	-0.010(2)	-0.001(2)	-0.010(2)
N3	0.028(3)	0.030(3)	0.020(3)	-0.011(2)	-0.002(2)	-0.005(2)
N4	0.041(3)	0.032(3)	0.023(3)	-0.002(2)	-0.001(2)	-0.006(2)
C1	0.017(3)	0.030(3)	0.026(3)	-0.005(2)	-0.001(2)	-0.009(2)
C2	0.025(3)	0.030(3)	0.026(3)	-0.006(3)	-0.001(2)	-0.007(2)
C3	0.036(3)	0.023(3)	0.040(4)	-0.004(3)	-0.002(3)	-0.014(3)
C4	0.026(3)	0.037(3)	0.033(3)	-0.011(3)	0.000(2)	-0.019(3)
C5	0.021(3)	0.029(3)	0.027(3)	-0.007(2)	0.000(2)	-0.009(2)
C6	0.016(3)	0.025(3)	0.022(3)	-0.001(2)	-0.001(2)	-0.006(2)
C7	0.017(3)	0.026(3)	0.023(3)	-0.005(2)	0.001(2)	-0.011(2)
C8	0.017(3)	0.024(3)	0.022(3)	-0.002(2)	-0.003(2)	-0.007(2)
C9	0.027(3)	0.023(3)	0.017(3)	-0.005(2)	-0.002(2)	-0.004(2)
C10	0.019(3)	0.024(3)	0.019(3)	-0.009(2)	0.002(2)	-0.008(2)
C11	0.023(3)	0.026(3)	0.026(3)	-0.005(2)	-0.000(2)	-0.007(2)
C12	0.024(3)	0.036(3)	0.042(4)	-0.010(3)	0.001(2)	-0.023(3)
C13	0.027(3)	0.039(3)	0.025(3)	-0.004(3)	-0.004(2)	-0.014(3)
C14	0.016(3)	0.040(3)	0.021(3)	-0.005(2)	-0.000(2)	-0.010(2)
C15	0.022(3)	0.023(3)	0.018(3)	-0.004(2)	0.003(2)	-0.005(2)
C16	0.015(3)	0.022(3)	0.016(3)	-0.004(2)	0.001(2)	-0.004(2)
C17	0.023(3)	0.028(3)	0.030(3)	-0.011(2)	-0.000(2)	-0.014(3)
C18	0.036(3)	0.019(3)	0.020(3)	-0.006(2)	-0.001(2)	-0.004(2)
C19	0.035(3)	0.028(3)	0.031(3)	-0.002(3)	-0.005(3)	-0.012(3)
C20	0.050(4)	0.033(3)	0.030(3)	-0.011(3)	-0.015(3)	-0.009(3)
C21	0.065(4)	0.033(3)	0.025(3)	-0.017(3)	-0.003(3)	-0.014(3)
C22	0.045(4)	0.027(3)	0.034(3)	-0.011(3)	0.007(3)	-0.016(3)

C23	0.036(3)	0.024(3)	0.024(3)	-0.006(3)	-0.000(2)	-0.008(2)
C24	0.023(3)	0.034(3)	0.029(3)	-0.009(3)	-0.005(2)	-0.011(3)
C25	0.039(3)	0.026(3)	0.027(3)	-0.013(3)	-0.002(3)	-0.004(2)
C26	0.032(3)	0.031(3)	0.042(4)	-0.011(3)	-0.008(3)	-0.011(3)
C27	0.031(3)	0.031(3)	0.031(3)	-0.004(3)	-0.003(2)	-0.011(3)
C28	0.026(3)	0.033(3)	0.026(3)	-0.011(3)	-0.005(2)	-0.012(2)
C29	0.020(3)	0.027(3)	0.025(3)	-0.009(2)	-0.004(2)	-0.008(2)
C30	0.022(3)	0.029(3)	0.024(3)	-0.011(2)	-0.002(2)	-0.010(2)

Table 3. Anisotropic displacement parameters (continued)

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C31	0.021(3)	0.033(3)	0.020(3)	-0.009(2)	-0.004(2)	-0.011(2)
C32	0.023(3)	0.027(3)	0.023(3)	-0.006(2)	-0.005(2)	-0.010(2)
C33	0.022(3)	0.036(3)	0.023(3)	-0.010(3)	-0.005(2)	-0.012(2)
C34	0.025(3)	0.027(3)	0.030(3)	-0.006(2)	-0.006(2)	-0.014(2)
C35	0.030(3)	0.040(3)	0.033(3)	-0.006(3)	-0.004(2)	-0.020(3)
C36	0.032(3)	0.046(3)	0.028(3)	-0.012(3)	0.001(2)	-0.020(3)
C37	0.027(3)	0.039(3)	0.024(3)	-0.014(3)	-0.001(2)	-0.012(2)
C38	0.022(3)	0.033(3)	0.021(3)	-0.009(2)	-0.003(2)	-0.011(2)
C39	0.013(3)	0.031(3)	0.027(3)	-0.008(2)	-0.003(2)	-0.011(2)
C40	0.027(3)	0.033(3)	0.028(3)	-0.006(3)	-0.005(2)	-0.015(3)
C41	0.034(3)	0.025(3)	0.020(3)	-0.006(3)	-0.003(2)	-0.006(2)
C42	0.031(3)	0.030(3)	0.028(3)	-0.008(3)	-0.003(2)	-0.008(2)
C43	0.050(4)	0.037(3)	0.035(4)	-0.003(3)	-0.004(3)	-0.020(3)
C44	0.050(4)	0.031(3)	0.027(3)	-0.004(3)	0.005(3)	-0.014(3)
C45	0.029(3)	0.036(3)	0.043(4)	-0.010(3)	0.005(3)	-0.016(3)
C46	0.035(3)	0.024(3)	0.032(3)	-0.004(3)	-0.001(3)	-0.010(2)
C47	0.037(4)	0.074(4)	0.050(4)	-0.022(3)	0.006(3)	-0.041(4)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table 4. Fragment Analysis

fragment: 1

Cl(1)	Cl(2)	Cl(3)	C(47)
-------	-------	-------	-------

fragment: 2

N(1)	N(2)	C(1)	C(2)	C(3)
C(4)	C(5)	C(6)	C(7)	C(8)
C(9)	C(10)	C(11)	C(12)	C(13)
C(14)	C(15)	C(16)	C(17)	C(18)
C(19)	C(20)	C(21)	C(22)	C(23)

fragment: 3

N(3)	N(4)	C(24)	C(25)	C(26)
C(27)	C(28)	C(29)	C(30)	C(31)
C(32)	C(33)	C(34)	C(35)	C(36)
C(37)	C(38)	C(39)	C(40)	C(41)
C(42)	C(43)	C(44)	C(45)	C(46)

Table 5. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Cl1	C47	1.771(6)	Cl2	C47	1.801(6)
Cl3	C47	1.774(7)	N1	C1	1.391(8)
N1	C16	1.382(5)	N2	C17	1.169(5)
N3	C24	1.400(7)	N3	C39	1.376(6)
N4	C40	1.160(6)	C1	C2	1.406(7)
C1	C6	1.426(6)	C2	C3	1.389(9)
C3	C4	1.429(7)	C4	C5	1.381(7)
C5	C6	1.408(9)	C6	C7	1.458(7)
C7	C8	1.438(5)	C7	C16	1.402(8)
C8	C9	1.395(8)	C8	C18	1.488(8)
C9	C10	1.443(8)	C9	C17	1.451(6)
C10	C11	1.426(8)	C10	C15	1.436(5)
C11	C12	1.381(8)	C12	C13	1.409(6)
C13	C14	1.384(9)	C14	C15	1.410(8)
C15	C16	1.422(8)	C18	C19	1.418(7)
C18	C23	1.421(7)	C19	C20	1.400(9)
C20	C21	1.409(8)	C21	C22	1.411(8)
C22	C23	1.385(8)	C24	C25	1.399(7)
C24	C29	1.419(6)	C25	C26	1.397(8)
C26	C27	1.414(7)	C27	C28	1.392(7)
C28	C29	1.417(8)	C29	C30	1.464(7)
C30	C31	1.422(6)	C30	C39	1.412(7)
C31	C32	1.408(8)	C31	C41	1.501(7)
C32	C33	1.456(7)	C32	C40	1.436(6)
C33	C34	1.430(8)	C33	C38	1.438(6)
C34	C35	1.380(7)	C35	C36	1.413(7)
C36	C37	1.370(8)	C37	C38	1.417(7)
C38	C39	1.420(8)	C41	C42	1.409(9)
C41	C46	1.413(7)	C42	C43	1.399(8)

C43	C44	1.399(8)	C44	C45	1.402(10)
C45	C46	1.418(8)			

Table 6. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N1	H1	0.860	N3	H3	0.860
C2	H2	0.930	C3	H3A	0.930
C4	H4	0.930	C5	H5	0.930
C11	H11	0.930	C12	H12	0.930
C13	H13	0.930	C14	H14	0.930
C19	H19	0.930	C20	H20	0.930
C21	H21	0.930	C22	H22	0.930
C23	H23	0.930	C25	H25	0.930
C26	H26	0.930	C27	H27	0.930
C28	H28	0.930	C34	H34	0.930
C35	H35	0.930	C36	H36	0.930
C37	H37	0.930	C42	H42	0.930
C43	H43	0.930	C44	H44	0.930
C45	H45	0.930	C46	H46	0.930
C47	H47	0.980			

Table 7. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C1	N1	C16	109.8(4)	C24	N3	C39	109.3(4)
N1	C1	C2	129.0(5)	N1	C1	C6	108.5(4)
C2	C1	C6	122.5(6)	C1	C2	C3	117.9(5)
C2	C3	C4	120.7(5)	C3	C4	C5	120.7(6)
C4	C5	C6	120.3(5)	C1	C6	C5	117.9(4)
C1	C6	C7	105.4(5)	C5	C6	C7	136.6(4)
C6	C7	C8	132.9(5)	C6	C7	C16	107.9(4)
C8	C7	C16	119.1(5)	C7	C8	C9	117.0(5)
C7	C8	C18	119.7(5)	C9	C8	C18	123.2(4)
C8	C9	C10	124.3(4)	C8	C9	C17	118.5(5)
C10	C9	C17	117.2(5)	C9	C10	C11	123.1(4)
C9	C10	C15	118.5(5)	C11	C10	C15	118.4(5)
C10	C11	C12	121.2(4)	C11	C12	C13	119.9(6)
C12	C13	C14	120.3(6)	C13	C14	C15	121.3(4)
C10	C15	C14	118.8(5)	C10	C15	C16	116.3(5)
C14	C15	C16	124.9(4)	N1	C16	C7	108.4(5)
N1	C16	C15	126.8(5)	C7	C16	C15	124.8(4)
N2	C17	C9	177.7(7)	C8	C18	C19	122.0(5)
C8	C18	C23	118.5(4)	C19	C18	C23	119.5(5)
C18	C19	C20	119.6(5)	C19	C20	C21	120.3(5)
C20	C21	C22	120.1(6)	C21	C22	C23	119.9(5)
C18	C23	C22	120.5(5)	N3	C24	C25	128.7(4)
N3	C24	C29	108.9(4)	C25	C24	C29	122.3(5)
C24	C25	C26	118.0(4)	C25	C26	C27	121.0(5)
C26	C27	C28	120.6(5)	C27	C28	C29	119.7(4)
C24	C29	C28	118.4(4)	C24	C29	C30	105.6(5)
C28	C29	C30	135.8(4)	C29	C30	C31	134.1(5)
C29	C30	C39	107.2(4)	C31	C30	C39	118.7(5)

C30	C31	C32	118.4(4)	C30	C31	C41	119.4(5)
C32	C31	C41	122.2(4)	C31	C32	C33	122.9(4)
C31	C32	C40	121.1(5)	C33	C32	C40	115.9(5)
C32	C33	C34	123.2(4)	C32	C33	C38	118.4(5)
C34	C33	C38	118.4(4)	C33	C34	C35	121.5(4)
C34	C35	C36	119.5(5)	C35	C36	C37	120.6(5)
C36	C37	C38	121.8(4)	C33	C38	C37	118.3(5)
C33	C38	C39	116.8(4)	C37	C38	C39	124.9(4)
N3	C39	C30	109.0(5)	N3	C39	C38	126.3(4)

Table 7. Bond angles ($^{\circ}$) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C30	C39	C38	124.7(4)	N4	C40	C32	176.7(6)
C31	C41	C42	118.5(5)	C31	C41	C46	121.9(6)
C42	C41	C46	119.6(5)	C41	C42	C43	120.1(5)
C42	C43	C44	120.4(6)	C43	C44	C45	120.6(5)
C44	C45	C46	119.3(5)	C41	C46	C45	120.1(6)
Cl1	C47	Cl2	110.9(3)	Cl1	C47	Cl3	110.6(4)
Cl2	C47	Cl3	110.4(4)				

Table 8. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C1	N1	H1	125	C16	N1	H1	125
C24	N3	H3	125	C39	N3	H3	125
C1	C2	H2	121	C3	C2	H2	121
C2	C3	H3A	120	C4	C3	H3A	120
C3	C4	H4	120	C5	C4	H4	120
C4	C5	H5	120	C6	C5	H5	120
C10	C11	H11	119	C12	C11	H11	119
C11	C12	H12	120	C13	C12	H12	120
C12	C13	H13	120	C14	C13	H13	120
C13	C14	H14	119	C15	C14	H14	119
C18	C19	H19	120	C20	C19	H19	120
C19	C20	H20	120	C21	C20	H20	120
C20	C21	H21	120	C22	C21	H21	120
C21	C22	H22	120	C23	C22	H22	120
C18	C23	H23	120	C22	C23	H23	120
C24	C25	H25	121	C26	C25	H25	121
C25	C26	H26	119	C27	C26	H26	119
C26	C27	H27	120	C28	C27	H27	120
C27	C28	H28	120	C29	C28	H28	120
C33	C34	H34	119	C35	C34	H34	119
C34	C35	H35	120	C36	C35	H35	120
C35	C36	H36	120	C37	C36	H36	120
C36	C37	H37	119	C38	C37	H37	119
C41	C42	H42	120	C43	C42	H42	120
C42	C43	H43	120	C44	C43	H43	120
C43	C44	H44	120	C45	C44	H44	120
C44	C45	H45	120	C46	C45	H45	120
C41	C46	H46	120	C45	C46	H46	120

CI1	C47	H47	108	CI2	C47	H47	108
CI3	C47	H47	108				

Table 9. Torsion Angles(^o)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C1	N1	C16	C7	0.0(5)	C1	N1	C16	C15	179.6(4)
C16	N1	C1	C2	179.8(4)	C16	N1	C1	C6	-0.9(5)
C24	N3	C39	C30	-0.6(6)	C24	N3	C39	C38	178.3(5)
C39	N3	C24	C25	-178.5(5)	C39	N3	C24	C29	-0.3(6)
N1	C1	C2	C3	177.4(4)	N1	C1	C6	C5	-176.2(3)
N1	C1	C6	C7	1.3(5)	C2	C1	C6	C5	3.2(6)
C2	C1	C6	C7	-179.3(4)	C6	C1	C2	C3	-1.8(6)
C1	C2	C3	C4	0.0(7)	C2	C3	C4	C5	0.4(7)
C3	C4	C5	C6	1.0(7)	C4	C5	C6	C1	-2.7(6)
C4	C5	C6	C7	-179.2(4)	C1	C6	C7	C8	177.7(4)
C1	C6	C7	C16	-1.3(4)	C5	C6	C7	C8	-5.5(8)
C5	C6	C7	C16	175.5(5)	C6	C7	C8	C9	178.6(4)
C6	C7	C8	C18	-5.2(7)	C6	C7	C16	N1	0.8(5)
C6	C7	C16	C15	-178.8(4)	C8	C7	C16	N1	-178.4(4)
C8	C7	C16	C15	2.1(6)	C16	C7	C8	C9	-2.5(6)
C16	C7	C8	C18	173.7(4)	C7	C8	C9	C10	1.4(6)
C7	C8	C9	C17	179.6(4)	C7	C8	C18	C19	118.6(4)
C7	C8	C18	C23	-61.4(6)	C9	C8	C18	C19	-65.4(6)
C9	C8	C18	C23	114.6(5)	C18	C8	C9	C10	-174.7(4)
C18	C8	C9	C17	3.5(6)	C8	C9	C10	C11	178.2(4)
C8	C9	C10	C15	0.3(6)	C17	C9	C10	C11	0.0(6)
C17	C9	C10	C15	-177.9(4)	C9	C10	C11	C12	-179.0(4)
C9	C10	C15	C14	178.4(4)	C9	C10	C15	C16	-0.9(6)
C11	C10	C15	C14	0.4(6)	C11	C10	C15	C16	-178.9(4)
C15	C10	C11	C12	-1.1(6)	C10	C11	C12	C13	1.4(7)
C11	C12	C13	C14	-0.9(7)	C12	C13	C14	C15	0.2(7)
C13	C14	C15	C10	0.1(6)	C13	C14	C15	C16	179.3(4)

C10	C15	C16	N1	-179.8(4)	C10	C15	C16	C7	-0.3(6)
C14	C15	C16	N1	1.0(7)	C14	C15	C16	C7	-179.5(4)
C8	C18	C19	C20	179.2(4)	C8	C18	C23	C22	-179.5(4)
C19	C18	C23	C22	0.5(7)	C23	C18	C19	C20	-0.8(7)
C18	C19	C20	C21	0.7(7)	C19	C20	C21	C22	-0.3(8)
C20	C21	C22	C23	0.1(8)	C21	C22	C23	C18	-0.2(7)
N3	C24	C25	C26	175.6(5)	N3	C24	C29	C28	-175.5(4)
N3	C24	C29	C30	1.0(6)	C25	C24	C29	C28	2.8(8)
C25	C24	C29	C30	179.4(5)	C29	C24	C25	C26	-2.3(8)
C24	C25	C26	C27	0.3(8)	C25	C26	C27	C28	1.1(9)

Table 9. Torsion angles ($^{\circ}$) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C26	C27	C28	C29	-0.7(8)	C27	C28	C29	C24	-1.2(8)
C27	C28	C29	C30	-176.5(5)	C24	C29	C30	C31	179.6(5)
C24	C29	C30	C39	-1.4(6)	C28	C29	C30	C31	-4.8(11)
C28	C29	C30	C39	174.3(6)	C29	C30	C31	C32	176.0(5)
C29	C30	C31	C41	-4.1(9)	C29	C30	C39	N3	1.2(6)
C29	C30	C39	C38	-177.7(4)	C31	C30	C39	N3	-179.5(4)
C31	C30	C39	C38	1.6(8)	C39	C30	C31	C32	-3.0(7)
C39	C30	C31	C41	176.9(4)	C30	C31	C32	C33	2.8(7)
C30	C31	C32	C40	-180.0(4)	C30	C31	C41	C42	-58.1(6)
C30	C31	C41	C46	120.9(5)	C32	C31	C41	C42	121.8(5)
C32	C31	C41	C46	-59.2(6)	C41	C31	C32	C33	-177.0(4)
C41	C31	C32	C40	0.2(7)	C31	C32	C33	C34	178.2(5)
C31	C32	C33	C38	-1.1(7)	C40	C32	C33	C34	0.8(7)
C40	C32	C33	C38	-178.5(4)	C32	C33	C34	C35	-179.0(5)
C32	C33	C38	C37	178.8(4)	C32	C33	C38	C39	-0.4(7)
C34	C33	C38	C37	-0.5(7)	C34	C33	C38	C39	-179.7(4)
C38	C33	C34	C35	0.3(7)	C33	C34	C35	C36	0.3(8)
C34	C35	C36	C37	-0.8(8)	C35	C36	C37	C38	0.7(8)
C36	C37	C38	C33	-0.0(8)	C36	C37	C38	C39	179.2(5)
C33	C38	C39	N3	-178.6(4)	C33	C38	C39	C30	0.1(7)
C37	C38	C39	N3	2.3(8)	C37	C38	C39	C30	-179.1(5)
C31	C41	C42	C43	177.8(3)	C31	C41	C46	C45	-177.3(3)
C42	C41	C46	C45	1.7(6)	C46	C41	C42	C43	-1.2(6)
C41	C42	C43	C44	0.6(6)	C42	C43	C44	C45	-0.3(7)
C43	C44	C45	C46	0.8(7)	C44	C45	C46	C41	-1.4(6)

Table 10. Possible hydrogen bonds

Donor	H	Acceptor	D...A	D-H	H...A	D-H...A
N1	H1	N4 ¹	2.954(6)	0.86	2.13	160.42
N3	H3	N2 ²	2.976(6)	0.86	2.13	169.76

Symmetry Operators:

(1) -X+1,-Y,-Z+1

(2) -X+1,-Y+1,-Z

Table 11. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
N1	C5	3.599(8)	N1	C14	3.057(8)
N2	C8	3.523(6)	N2	C10	3.504(6)
N2	C11	3.568(7)	N3	C37	3.046(7)
N4	C31	3.557(6)	N4	C33	3.462(5)
N4	C34	3.513(6)	C1	C4	2.775(9)
C2	C5	2.842(7)	C3	C6	2.821(7)
C5	C8	3.463(7)	C5	C18	3.383(6)
C5	C23	3.308(6)	C6	C18	3.179(5)
C6	C23	3.403(6)	C7	C10	2.861(8)
C7	C23	3.149(7)	C8	C15	2.915(8)
C9	C16	2.753(5)	C9	C19	3.264(9)
C9	C23	3.566(8)	C10	C13	2.823(8)
C11	C14	2.796(6)	C11	C17	2.884(8)
C12	C15	2.827(8)	C17	C18	2.903(8)
C17	C19	3.190(9)	C18	C21	2.811(8)
C19	C22	2.824(8)	C20	C23	2.809(7)
C24	C27	2.782(8)	C25	C28	2.842(6)
C26	C29	2.813(7)	C28	C31	3.471(7)
C28	C41	3.389(6)	C28	C42	3.227(6)
C29	C41	3.190(6)	C29	C42	3.356(6)
C30	C33	2.876(8)	C30	C42	3.113(7)
C31	C38	2.906(7)	C32	C39	2.771(6)
C32	C46	3.223(7)	C33	C36	2.822(7)
C34	C37	2.789(6)	C34	C40	2.869(7)
C35	C38	2.836(8)	C40	C41	2.950(8)
C40	C46	3.171(7)	C41	C44	2.813(8)
C42	C45	2.820(8)	C43	C46	2.808(10)

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
N1	H2	2.776	N1	H14	2.797
N2	H11	2.964	N2	H19	3.442
N3	H25	2.770	N3	H37	2.784
N4	H34	2.904	N4	H46	3.342
C1	H3A	3.239	C1	H5	3.274
C2	H1	2.797	C2	H4	3.280
C3	H5	3.281	C4	H2	3.294
C5	H3A	3.273	C5	H23	3.233
C6	H1	3.114	C6	H2	3.321
C6	H4	3.257	C6	H23	3.182
C7	H1	3.084	C7	H5	2.937
C7	H23	2.995	C8	H5	3.347
C8	H19	2.713	C8	H23	2.639
C9	H11	2.699	C9	H19	3.181
C10	H12	3.284	C10	H14	3.291
C11	H13	3.251	C12	H14	3.258
C13	H11	3.253	C14	H1	2.893
C14	H12	3.259	C15	H1	2.763
C15	H11	3.299	C15	H13	3.271
C16	H14	2.703	C17	H11	2.558
C17	H19	3.044	C18	H5	2.883
C18	H20	3.275	C18	H22	3.276
C19	H5	3.511	C19	H21	3.274
C19	H23	3.290	C20	H22	3.282
C21	H19	3.276	C21	H23	3.260
C22	H5	3.290	C22	H20	3.281
C23	H5	2.752	C23	H19	3.294
C23	H21	3.258	C24	H26	3.238

C24	H28	3.281	C25	H3	2.800
C25	H27	3.279	C26	H28	3.277
C27	H25	3.290	C28	H26	3.269
C28	H42	3.127	C29	H3	3.121
C29	H25	3.307	C29	H27	3.269
C29	H42	3.119	C30	H3	3.097
C30	H28	2.943	C30	H42	2.959
C31	H28	3.361	C31	H42	2.640
C31	H46	2.712	C32	H34	2.713

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C32	H46	3.085	C33	H35	3.290
C33	H37	3.290	C34	H36	3.249
C35	H37	3.253	C36	H34	3.251
C37	H3	2.878	C37	H35	3.253
C38	H3	2.751	C38	H34	3.302
C38	H36	3.270	C39	H37	2.705
C40	H34	2.544	C40	H46	2.930
C41	H28	2.887	C41	H43	3.271
C41	H45	3.293	C42	H28	2.632
C42	H44	3.264	C42	H46	3.278
C43	H28	3.141	C43	H45	3.272
C44	H42	3.265	C44	H46	3.273
C45	H43	3.269	C46	H28	3.585
C46	H42	3.278	C46	H44	3.273
H1	H2	2.760	H1	H14	2.387
H2	H3A	2.329	H3	H25	2.758
H3	H37	2.369	H3A	H4	2.349
H4	H5	2.304	H5	H23	2.896
H11	H12	2.303	H12	H13	2.338
H13	H14	2.303	H19	H20	2.331
H20	H21	2.336	H21	H22	2.341
H22	H23	2.312	H25	H26	2.333
H26	H27	2.333	H27	H28	2.321
H28	H42	2.743	H28	H43	3.516
H34	H35	2.303	H35	H36	2.343
H36	H37	2.284	H42	H43	2.326
H43	H44	2.322	H44	H45	2.333
H45	H46	2.353			

Table 13. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
Cl1	C4	3.290(5)	Cl1	C5	3.290(5)
Cl3	C21 ¹	3.585(6)	N1	N4 ²	2.954(6)
N1	C9 ³	3.568(6)	N1	C10 ³	3.555(6)
N1	C11 ⁴	3.585(6)	N1	C12 ⁴	3.440(6)
N2	N3 ⁵	2.976(6)	N3	N2 ⁵	2.976(6)
N3	C33 ⁶	3.572(7)	N3	C35 ⁷	3.381(8)
N3	C36 ⁷	3.482(7)	N4	N1 ²	2.954(6)
N4	C17 ⁸	3.547(7)	C1	C11 ³	3.522(6)
C1	C12 ⁴	3.500(7)	C4	Cl1	3.290(5)
C4	C12 ³	3.600(7)	C5	Cl1	3.290(5)
C5	C12 ³	3.445(7)	C5	C13 ³	3.513(6)
C7	C13 ⁴	3.531(6)	C7	C15 ³	3.497(6)
C9	N1 ³	3.568(6)	C10	N1 ³	3.555(6)
C11	N1 ⁴	3.585(6)	C11	C1 ³	3.522(6)
C12	N1 ⁴	3.440(6)	C12	C1 ⁴	3.500(7)
C12	C4 ³	3.600(7)	C12	C5 ³	3.445(7)
C13	C5 ³	3.513(6)	C13	C7 ⁴	3.531(6)
C13	C16 ⁴	3.472(6)	C14	C15 ⁴	3.500(6)
C14	C16 ⁴	3.452(6)	C15	C7 ³	3.497(6)
C15	C14 ⁴	3.500(6)	C15	C15 ⁴	3.531(6)
C16	C13 ⁴	3.472(6)	C16	C14 ⁴	3.452(6)
C17	N4 ⁹	3.547(7)	C21	Cl3 ¹⁰	3.585(6)
C22	C25 ⁵	3.532(7)	C24	C34 ⁶	3.460(8)
C25	C22 ⁵	3.532(7)	C28	C35 ⁶	3.452(9)
C29	C34 ⁶	3.590(8)	C29	C35 ⁶	3.472(8)
C30	C36 ⁷	3.593(7)	C31	C37 ⁶	3.571(7)
C33	N3 ⁶	3.572(7)	C33	C39 ⁶	3.517(7)
C34	C24 ⁶	3.460(8)	C34	C29 ⁶	3.590(8)

C35	N3 ⁷	3.381(8)	C35	C28 ⁶	3.452(9)
C35	C29 ⁶	3.472(8)	C36	N3 ⁷	3.482(7)
C36	C30 ⁷	3.593(7)	C36	C39 ⁷	3.345(8)
C37	C31 ⁶	3.571(7)	C37	C38 ⁷	3.365(8)
C37	C39 ⁷	3.456(7)	C38	C37 ⁷	3.365(8)
C38	C38 ⁷	3.594(7)	C39	C33 ⁶	3.517(7)
C39	C36 ⁷	3.345(8)	C39	C37 ⁷	3.456(7)

Symmetry Operators:

(1) X+1,Y,Z	(2) -X+1,-Y,-Z+1
(3) -X,-Y+1,-Z+1	(4) -X+1,-Y+1,-Z+1
(5) -X+1,-Y+1,-Z	(6) -X+1,-Y,-Z
(7) -X+2,-Y,-Z	(8) X,Y-1,Z
(9) X,Y+1,Z	(10) X-1,Y,Z

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
Cl1	H4	3.383	Cl1	H5	3.396
Cl1	H12 ¹	3.464	Cl1	H13 ¹	3.232
Cl1	H23	3.253	Cl1	H27	3.443
Cl1	H28	3.527	Cl1	H43	3.349
Cl2	H4 ²	2.941	Cl2	H28 ²	3.182
Cl2	H36 ³	2.901	Cl2	H42	3.194
Cl3	H5 ²	3.327	Cl3	H13 ¹	3.463
Cl3	H21 ⁴	3.347	Cl3	H27 ²	3.251
N2	H3 ⁴	2.126	N2	H25 ⁴	3.422
N2	H34 ⁵	3.428	N2	H37 ⁴	2.899
N2	H46 ⁶	2.943	N3	H35 ³	3.583
N4	H1 ⁷	2.130	N4	H2 ⁷	3.148
N4	H11 ⁸	3.346	N4	H14 ⁷	3.173
N4	H19 ⁹	2.916	C1	H12 ¹	3.438
C2	H11 ¹⁰	3.525	C2	H12 ¹	3.554
C2	H45 ¹¹	3.453	C3	H43	3.524
C3	H43 ⁷	3.599	C3	H45 ¹¹	3.006
C4	H12 ¹⁰	3.378	C4	H43	3.599
C5	H12 ¹⁰	3.542	C6	H13 ¹	3.521
C7	H13 ¹	3.417	C9	H1 ¹⁰	3.520
C10	H14 ¹	3.560	C11	H1 ¹	3.405
C11	H45 ⁶	3.292	C11	H46 ⁶	3.585
C12	H1 ¹	3.587	C12	H45 ⁶	3.441
C13	H5 ¹⁰	3.441	C13	H23 ¹	3.466
C14	H19 ¹⁰	3.288	C15	H14 ¹	3.581
C17	H3 ⁴	3.098	C17	H25 ⁴	3.548
C17	H46 ⁶	3.535	C18	H25 ⁴	3.252
C19	H14 ¹⁰	3.233	C19	H25 ⁴	3.550

C19	H34 ⁵	3.049	C20	H25 ⁴	3.547
C20	H34 ⁵	3.015	C20	H35 ⁵	3.223
C21	H25 ⁴	3.267	C21	H26	3.590
C21	H27	3.456	C22	H25 ⁴	2.955
C22	H26	3.341	C22	H26 ⁴	3.078
C22	H27	2.989	C23	H13 ¹	3.574
C23	H25 ⁴	2.944	C24	H34 ¹²	3.452
C24	H35 ³	3.477	C25	H20 ¹³	3.333
C25	H34 ¹²	3.521	C26	H20 ¹³	2.983

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C26	H22	3.106	C26	H22 ⁴	3.447
C26	H47	3.239	C27	H22	3.079
C27	H35 ¹²	3.396	C27	H47	2.850
C28	H35 ¹²	3.361	C28	H47	2.846
C29	H36 ³	3.577	C29	H47	3.241
C30	H36 ³	3.340	C31	H37 ¹²	3.584
C33	H37 ³	3.453	C34	H3 ³	3.438
C34	H19 ⁹	3.587	C34	H20 ⁹	3.305
C35	H3 ³	3.429	C35	H20 ⁹	3.412
C36	H46 ¹²	3.555	C37	H46 ¹²	3.094
C38	H37 ³	3.404	C39	H36 ³	3.473
C40	H1 ⁷	3.106	C40	H2 ⁷	3.208
C40	H3 ¹²	3.586	C40	H19 ⁹	3.535
C41	H2 ⁷	3.129	C42	H2 ⁷	3.038
C42	H3A ⁷	3.424	C43	H2 ⁷	3.315
C43	H3A ⁷	3.050	C43	H4	3.487
C44	H3A	3.543	C44	H4	3.535
C44	H12 ⁸	3.564	C45	H3A ¹¹	3.587
C45	H11 ⁸	2.955	C45	H12 ⁸	3.194
C46	H2 ⁷	3.460	C46	H11 ⁸	2.997
C46	H36 ¹²	3.555	C46	H37 ¹²	3.184
C47	H42	3.567	H1	N4 ⁷	2.130
H1	C9 ¹⁰	3.520	H1	C11 ¹	3.405
H1	C12 ¹	3.587	H1	C40 ⁷	3.106
H1	H19 ¹⁰	3.274	H2	N4 ⁷	3.148
H2	C40 ⁷	3.208	H2	C41 ⁷	3.129
H2	C42 ⁷	3.038	H2	C43 ⁷	3.315
H2	C46 ⁷	3.460	H2	H42 ⁷	3.342

H2	H45 ¹¹	3.509	H3	N2 ⁴	2.126
H3	C17 ⁴	3.098	H3	C34 ³	3.438
H3	C35 ³	3.429	H3	C40 ¹²	3.586
H3	H46 ¹²	3.529	H3A	C42 ⁷	3.424
H3A	C43 ⁷	3.050	H3A	C44	3.543
H3A	C45 ¹¹	3.587	H3A	H42 ⁷	3.491
H3A	H43	3.124	H3A	H43 ⁷	2.863
H3A	H44	2.908	H3A	H45 ¹¹	2.723
H4	Cl1	3.383	H4	Cl2 ¹⁴	2.941

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H4	C43	3.487	H4	C44	3.535
H4	H12 ¹⁰	3.538	H4	H43	3.265
H4	H44	3.353	H5	Cl1	3.396
H5	Cl3 ¹⁴	3.327	H5	C13 ¹⁰	3.441
H5	H13 ¹⁰	3.379	H5	H27	3.535
H11	N4 ⁶	3.346	H11	C2 ¹⁰	3.525
H11	C45 ⁶	2.955	H11	C46 ⁶	2.997
H11	H45 ⁶	2.621	H11	H46 ⁶	2.680
H12	Cl1 ¹	3.464	H12	C1 ¹	3.438
H12	C2 ¹	3.554	H12	C4 ¹⁰	3.378
H12	C5 ¹⁰	3.542	H12	C44 ⁶	3.564
H12	C45 ⁶	3.194	H12	H4 ¹⁰	3.538
H12	H44 ⁶	3.553	H12	H45 ⁶	2.925
H13	Cl1 ¹	3.232	H13	Cl3 ¹	3.463
H13	C6 ¹	3.521	H13	C7 ¹	3.417
H13	C23 ¹	3.574	H13	H5 ¹⁰	3.379
H13	H23 ¹	2.672	H14	N4 ⁷	3.173
H14	C10 ¹	3.560	H14	C15 ¹	3.581
H14	C19 ¹⁰	3.233	H14	H19 ¹⁰	2.596
H19	N4 ⁵	2.916	H19	C14 ¹⁰	3.288
H19	C34 ⁵	3.587	H19	C40 ⁵	3.535
H19	H1 ¹⁰	3.274	H19	H14 ¹⁰	2.596
H19	H34 ⁵	2.702	H20	C25 ¹³	3.333
H20	C26 ¹³	2.983	H20	C34 ⁵	3.305
H20	C35 ⁵	3.412	H20	H25 ¹³	3.450
H20	H26 ¹³	2.851	H20	H34 ⁵	2.628
H20	H35 ⁵	2.859	H21	Cl3 ⁴	3.347
H21	H21 ¹³	2.931	H21	H26	3.114

H21	H27	3.407	H22	C26	3.106
H22	C26 ⁴	3.447	H22	C27	3.079
H22	H25 ⁴	3.310	H22	H26	2.617
H22	H26 ⁴	2.737	H22	H27	2.574
H23	Cl1	3.253	H23	C13 ¹	3.466
H23	H13 ¹	2.672	H23	H25 ⁴	3.296
H25	N2 ⁴	3.422	H25	C17 ⁴	3.548
H25	C18 ⁴	3.252	H25	C19 ⁴	3.550
H25	C20 ⁴	3.547	H25	C21 ⁴	3.267

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H25	C22 ⁴	2.955	H25	C23 ⁴	2.944
H25	H20 ¹³	3.450	H25	H22 ⁴	3.310
H25	H23 ⁴	3.296	H26	C21	3.590
H26	C22	3.341	H26	C22 ⁴	3.078
H26	H20 ¹³	2.851	H26	H21	3.114
H26	H22	2.617	H26	H22 ⁴	2.737
H27	Cl1	3.443	H27	Cl3 ¹⁴	3.251
H27	C21	3.456	H27	C22	2.989
H27	H5	3.535	H27	H21	3.407
H27	H22	2.574	H27	H47	3.172
H28	Cl1	3.527	H28	Cl2 ¹⁴	3.182
H28	H36 ¹²	3.540	H28	H47	3.159
H34	N2 ⁹	3.428	H34	C19 ⁹	3.049
H34	C20 ⁹	3.015	H34	C24 ¹²	3.452
H34	C25 ¹²	3.521	H34	H19 ⁹	2.702
H34	H20 ⁹	2.628	H35	N3 ³	3.583
H35	C20 ⁹	3.223	H35	C24 ³	3.477
H35	C27 ¹²	3.396	H35	C28 ¹²	3.361
H35	H20 ⁹	2.859	H35	H47 ³	3.246
H36	Cl2 ³	2.901	H36	C29 ³	3.577
H36	C30 ³	3.340	H36	C39 ³	3.473
H36	C46 ¹²	3.555	H36	H28 ¹²	3.540
H36	H42 ³	3.114	H36	H46 ¹²	3.369
H36	H47 ³	3.309	H37	N2 ⁴	2.899
H37	C31 ¹²	3.584	H37	C33 ³	3.453
H37	C38 ³	3.404	H37	C46 ¹²	3.184
H37	H46 ¹²	2.485	H42	Cl2	3.194
H42	C47	3.567	H42	H2 ⁷	3.342

H42	H3A ⁷	3.491	H42	H36 ³	3.114
H42	H47	3.300	H43	Cl1	3.349
H43	C3	3.524	H43	C3 ⁷	3.599
H43	C4	3.599	H43	H3A	3.124
H43	H3A ⁷	2.863	H43	H4	3.265
H43	H43 ⁷	3.094	H43	H44 ⁷	3.197
H44	H3A	2.908	H44	H4	3.353
H44	H12 ⁸	3.553	H44	H43 ⁷	3.197
H45	C2 ¹¹	3.453	H45	C3 ¹¹	3.006

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H45	C11 ⁸	3.292	H45	C12 ⁸	3.441
H45	H2 ¹¹	3.509	H45	H3A ¹¹	2.723
H45	H11 ⁸	2.621	H45	H12 ⁸	2.925
H46	N2 ⁸	2.943	H46	C11 ⁸	3.585
H46	C17 ⁸	3.535	H46	C36 ¹²	3.555
H46	C37 ¹²	3.094	H46	H3 ¹²	3.529
H46	H11 ⁸	2.680	H46	H36 ¹²	3.369
H46	H37 ¹²	2.485	H47	C26	3.239
H47	C27	2.850	H47	C28	2.846
H47	C29	3.241	H47	H27	3.172
H47	H28	3.159	H47	H35 ³	3.246
H47	H36 ³	3.309	H47	H42	3.300

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1	(2) X+1,Y,Z
(3) -X+2,-Y,-Z	(4) -X+1,-Y+1,-Z
(5) X-1,Y+1,Z	(6) X,Y+1,Z
(7) -X+1,-Y,-Z+1	(8) X,Y-1,Z
(9) X+1,Y-1,Z	(10) -X,-Y+1,-Z+1
(11) -X,-Y,-Z+1	(12) -X+1,-Y,-Z
(13) -X,-Y+1,-Z	(14) X-1,Y,Z

Reference

- (1) Yasuhara, A.; Kanamori, Y.; Kaneko, M.; Numata, A.; Kondo, Y.; Sakamoto, T.; *J. Chem. Soc., Perkin Trans.* **1999**, *1*, 529-534
- (2) Yamakawa, T.; Ideue, E.; Shimokawa, J.; Fukuyama, T.; *Angew. Chem. Int. Ed.*, **2010**, *49*, 9262-9265
- (3) Rainier, J. D.; Kennedy, A. R.; *J. Org. Chem.*, **2000**, *65*, 6213-6216
- (4) Kim, T.; Kim, K.; *Tetrahedron Lett.*, **2010**, *51*, 868-871
- (5) Xu, M.; Hou, Q.; Wang, S.; Yao, Z.; Wang, H.; *SYNTHESIS*, **2011**, *4*, 626-634

S1

S1

S59

S2

S60

S2

S3

S62

single pulse decoupled gated NOE

S3

S63

S4

S5

S5

single pulse decoupled gated NOE

1a

1b

1b

1c

1c

1d

1d

1e

single pulse decoupled gated NOE

1e

1f

1f

1g

1h

1i

1i

1j

1j

1k

1k

1l

single pulse decoupled gated NOE

1l

1m

1m

5

5

7

7

9

9