Electronic supplementary materials *Mendeleev Commun*., 2016, **26**, 129−130

Cyclometallated Pt^{II} complexes of 2-(2-thienyl)-4-(cycloalkylimino)-substituted quinazolines

Emiliya V. Nosova, Tatyana N. Moshkina, Dmitry S. Kopchuk, Galina N. Lipunova, Pavel A. Slepukhin and Valery N. Charushin

General. Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were measured on the instrument Boetius. ^{1}H NMR spectra were acquired on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, using TMS as internal reference. For ligands **2a** and **2b** mass spectra were recorded on a SHIMADZU GCMS-QP2010 Ultra instrument with electron ionization (EI) of the sample. For complexes **3a** and **3b** mass spectra were recorded on MicrOTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer. The absorption spectra in the range 220–800 nm were recorded on a UV–2600 spectrophotometer (λ = 310 nm) produced by Shimadzu. The fluorescence spectra were registered using a Varian Cary Eclipse spectrofluorometer (Xenon lamp), and solutions in acetonitrile with a concentration of 10^{-4} mol L^{-1} were used for spectra recording. The structure of compound **3a** was determined on an Xcalibur E X-ray diffractometer.

Starting 2-(thiophen-2-yl)-3H-quinazolin-4-one **1** was synthesized as described in literature[1].

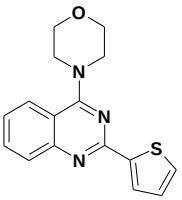
4-(Morpholin-4-yl)-2-(thiophen-2-yl)quinazoline (2a). To quinazolinone **1** (0.7 g, 3.1 mmol) phosphorous oxychloride (4 ml) was added, and reaction mixture was refluxed for 2 h. After cooling the mixture was poured into ice (70 ml), precipitate formed was filtered off and washed with saturated water solution of sodium hydrocarbonate. After drying on air 4-chloroquinazoline obtained (without further purification) was dissolved in acetonitrile (62 ml), morpholine (0.65 ml, 7.4 mmol) was added, and reaction mixture was refluxed for 6 h and

concentrated in vacuum. The residue was washed with water and quinazoline **2a** obtained was recrystallized from ethanol. Yield 0.79 g (86%), mp 155-157 ^{0}C. ^{1}H NMR (DMSO-d_6): 3.80 (m, 4H, N(CH_2)$_2$), 3.85 (m, 4H, O(CH_2)$_2$), 7.14 (dd, 1H, H-4', J 5.2, 3.7), 7.43 (dd, 1H, H-5', J 3.7, 1.5), 7.54 (dd, 1H, H-3', J 5.2, 1.3), 7.76 (m, 2H, H-5, H-7), 7.95 (m, 2H, H-6, H-8). MS (m/z, I_{rel} %): 297 $[M]^+$ (100), 296 (76), 266 (34), 254 (12), 252 (35), 241 (18), 240 (81), 239 (90), 213 (15), 212 (50), 211 (73), 140 (10), 110 (22), 106 (20), 103 (27), 102 (44), 86 (25), 84 (14), 76 (13), 75 (13), 39 (11). Calcd for $C_{16}H_{15}N_3OS$: C 64.62; H 5.08; N 14.13. Found: C 64.57; H 4.98; N 14.21.

4-(Piperidin-1-yl)-2-(thiophen-2-yl)quinazoline (2b) was synthesized by similar method. Yield 84%, mp 105-107 ^{0}C. ^{1}H NMR (DMSO-d_6): 1.80 (m, 6H, (CH_2)$_3$), 3.78 (m, 4H, N(CH_2)$_2$), 7.14 (dd, 1H, H-4', J 4.9, 3.8), 7.43 (m, 1H, H-5'), 7.54 (d, 1H, H-3', J 4.9), 7.75 (m, 2H, H-5, H-7), 7.88 (m, 1H, H-6), 7.94 (m, 1H, H-8). MS (m/z, I_{rel} %): 295 $[M]^+$ (100), 294 (42), 267 (15), 266 (72), 252 (20), 240 (26), 239 (42), 227 (20), 213 (16), 212 (60), 211 (54), 110 (24), 103 (28), 102 (40), 84 (82), 76 (14), 75 (13), 56 (11), 41 (13), 39 (19). Calcd for $C_{17}H_{17}N_3S$: C 69.12; H 5.80; N 14.22. Found: C 69.18; H 5.88; N 14.13.

Platinum(II) acac complex of 4-(morpholin-4-yl)-2-(thiophen-2-yl)quinazoline (3a). The starting ligand **2a** (250 mg, 0.84 mmol) was dissolved in glacial acetic acid (37 ml) and solution of potassium tetrachloroplatinate (348.3 mg, 0.84 mmol) in water (6.2 ml) was added with vigorous stirring. The mixture was stirred and refluxed for 10 h in argon atmosphere, after cooling dimeric dichloro complex was filtered off, washed with acidic acid (8 ml) and dried. Resulting solid was treated with 2 ml of DMSO, the mixture was heated 5 min for reflux, and after cooling 15 ml of water was added, precipitate was filtered off, washed with water and dried in vacuum. Chloroform (15 mL) was added to the residue, impurities were filtered off, and chloroform solution was concentrated in vacuum. The residue of DMSO-chloro complex was dissolved in acetone (54 ml) and sodium acetylacetonate[2] (1.18 g, 8.4 mmol) was added. The suspension was stirred under reflux for 12 h. Then solvent was removed, and the product was isolated by column chromatography on silica with DCM as eluent to give orange crystals of **3a**. Yield 258 mg, 0.44 mmol, 52%. Mp 166-168 ^{0}C. ^{1}H NMR ($CDCl_3$): 2.00 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.90 (m, 4H, N(CH_2)$_2$), 3.99 (m, 4H, O(CH_2)$_2$), 5.58 (s, 1H, CH=), 7.34 (m, 2H, arom.), 7.52 (m, 1H, arom.), 7.70 (m, 2H, arom.), 9.15 (m, 1H, arom.). ESI-MS, m/z: found 597.1073, 596.1029, 595.1054, 594.1039, 593.1033, 592.1016, 591.1013, 590.0988, 598.0910, calculated 596.1013, 595.1089, 594.1055, 593.1058, 592.1027, 591.1026, 590.1003, 588.0987. Calcd for $C_{21}H_{21}N_3O_3PtS$: C 42.71; H 3.58; N 7.12. Found: C 42.56; H 3.49; N 7.17.

Platinum(II) acac complex of 4-(piperidin-1-yl)-2-(thiophen-2-yl)quinazoline (3b) was synthesized by similar method. Yield 56%, mp 188-190 ^{0}C. ^{1}H NMR ($CDCl_3$): 1.99 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.82 (m, 6H, $(CH_2)_3$), 3.92 (m, 4H, $N(CH_2)_2$), 5.57 (s, 1H, CH=), 7.31 (m, 2H, arom.), 7.50 (m, 1H, arom.), 7.68 (m, 2H, arom.), 9.07 (m, 1H, arom.). ESI-MS, m/z: found 594.1310, 593.1309, 592.1290, 591.1285, 590.1277, 589.1277, 588.1252, 586.1200, calculated 594.1221, 593.1296, 592.1262, 591.1266, 590.1234, 589.1233, 588.1210, 586.1194. Calcd for $C_{22}H_{23}N_3O_2PtS$: C 44.89; H 3.94; N 7.14. Found: C 44.98; H 4.05; N 7.06.



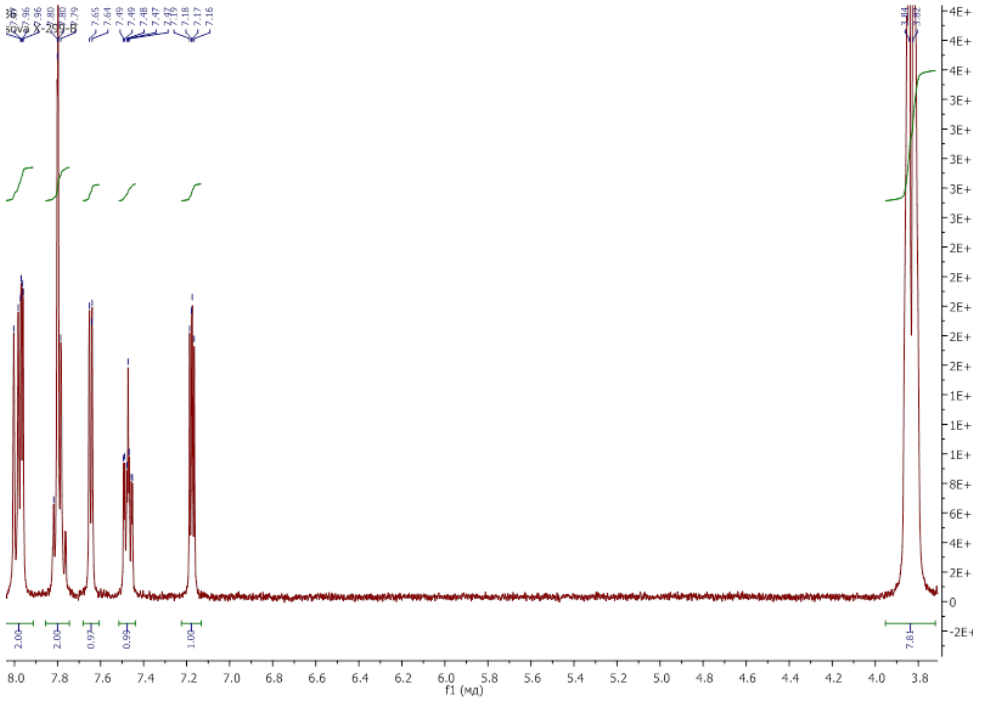


Figure S1 NMR ^{1}H spectra of quinazoline **2a** in DMSO-d_6.

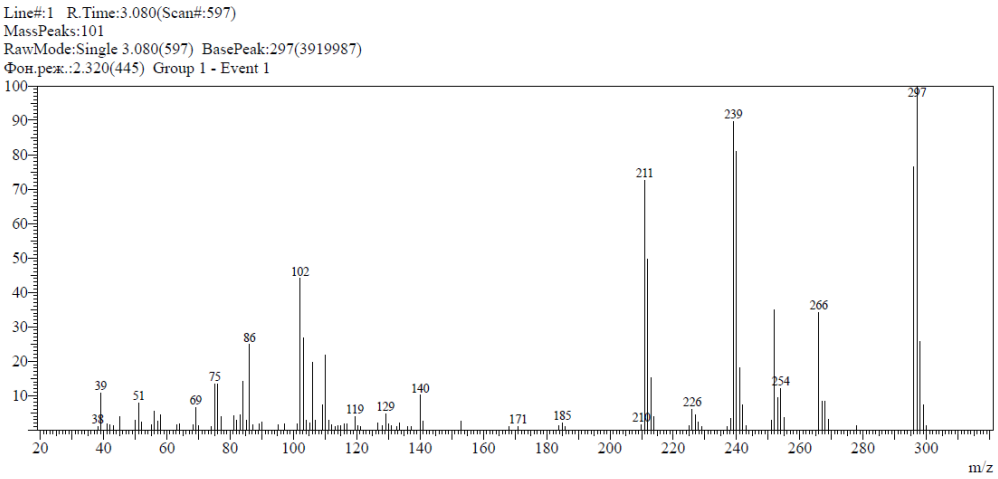


Figure S2 Mass spectra (EI) of quinazoline **2a.**

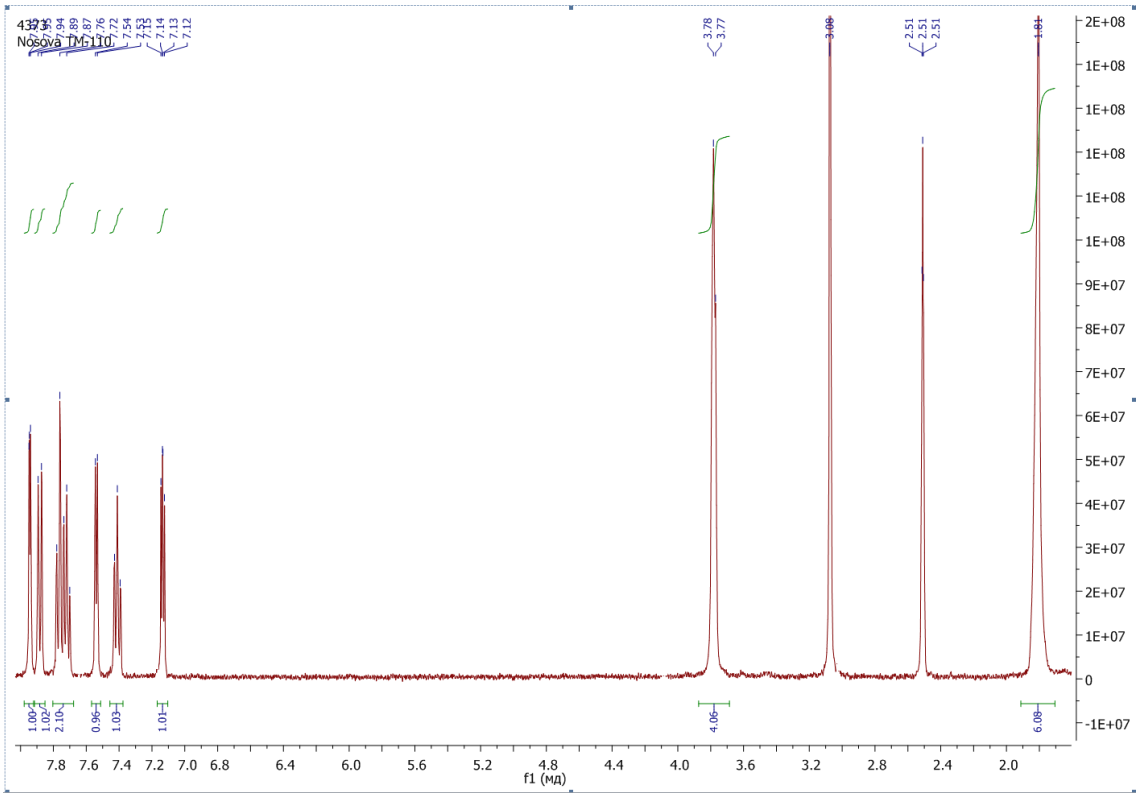


Figure S3 NMR ^{1}H spectra of quinazoline **2b** in DMSO-d_6.

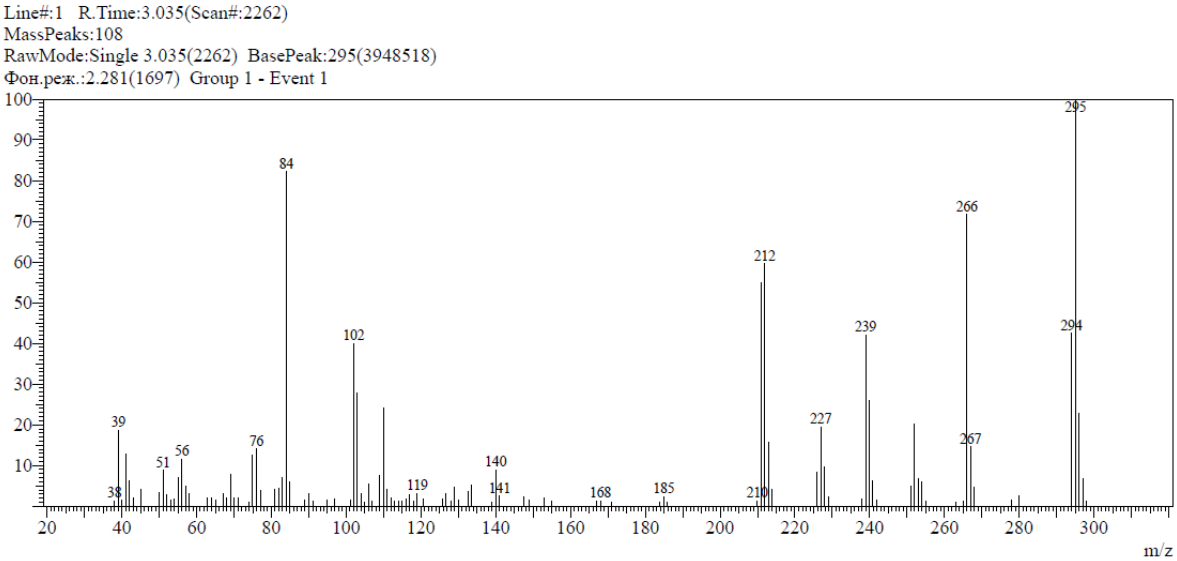
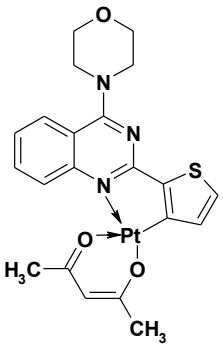


Figure S4 Mass spectra (EI) of quinazoline **2b.**



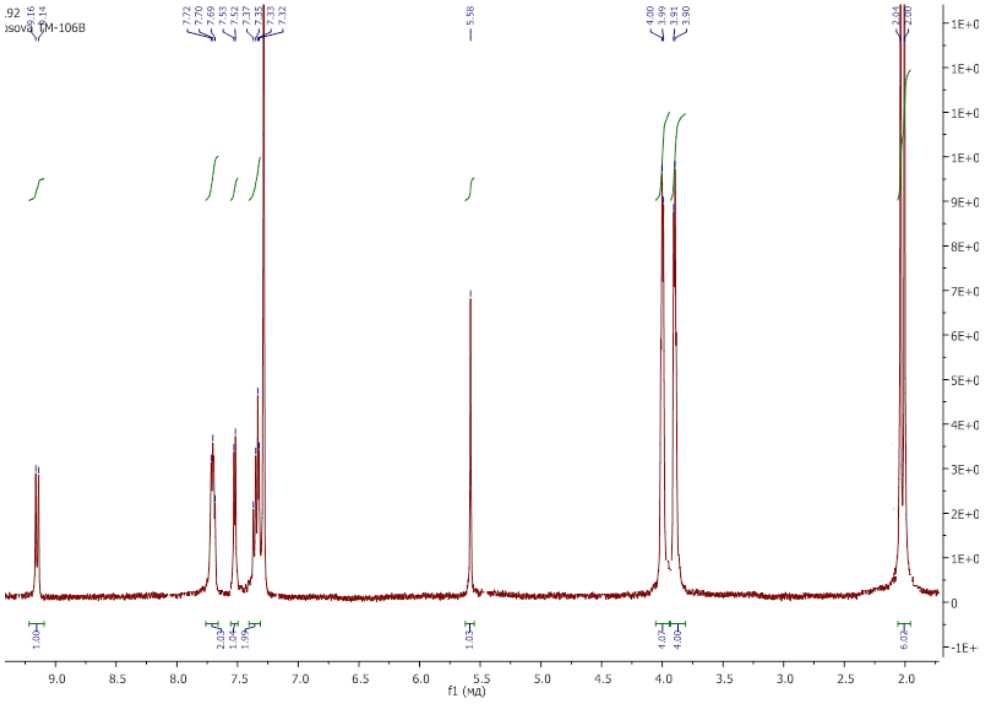


Figure S5 NMR ^{1}H spectra of complex **3a** in $CDCl_3$.

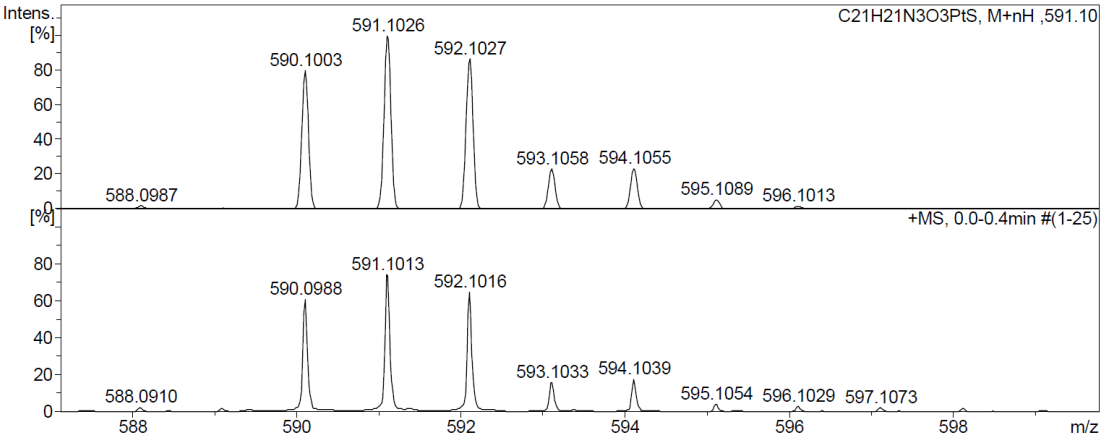


Figure S6 Mass spectra (electrospray ionization) of complex **3a** and calculated data.

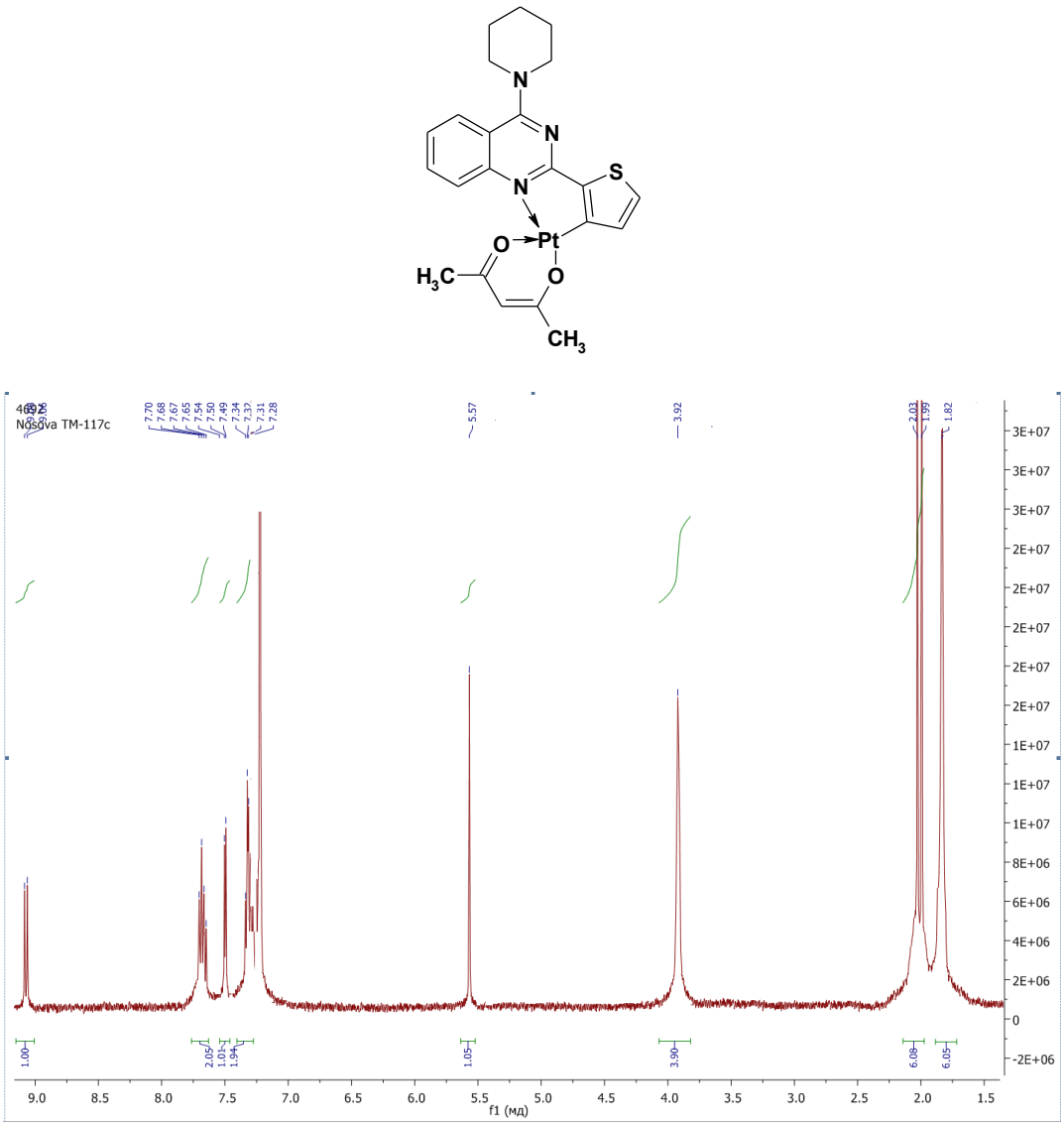


Figure S7 NMR ^{1}H spectra of complex **3b** in $CDCl_3$.

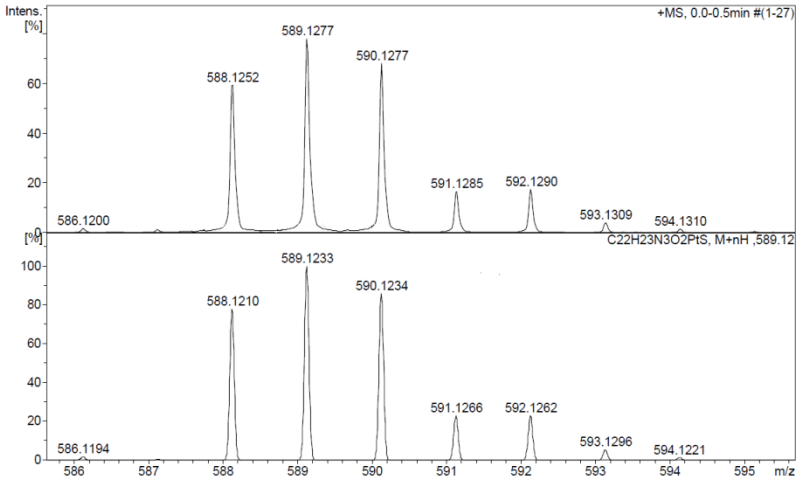


Figure S8 Mass spectra (electrospray ionization) of complex **3b** and calculated data.

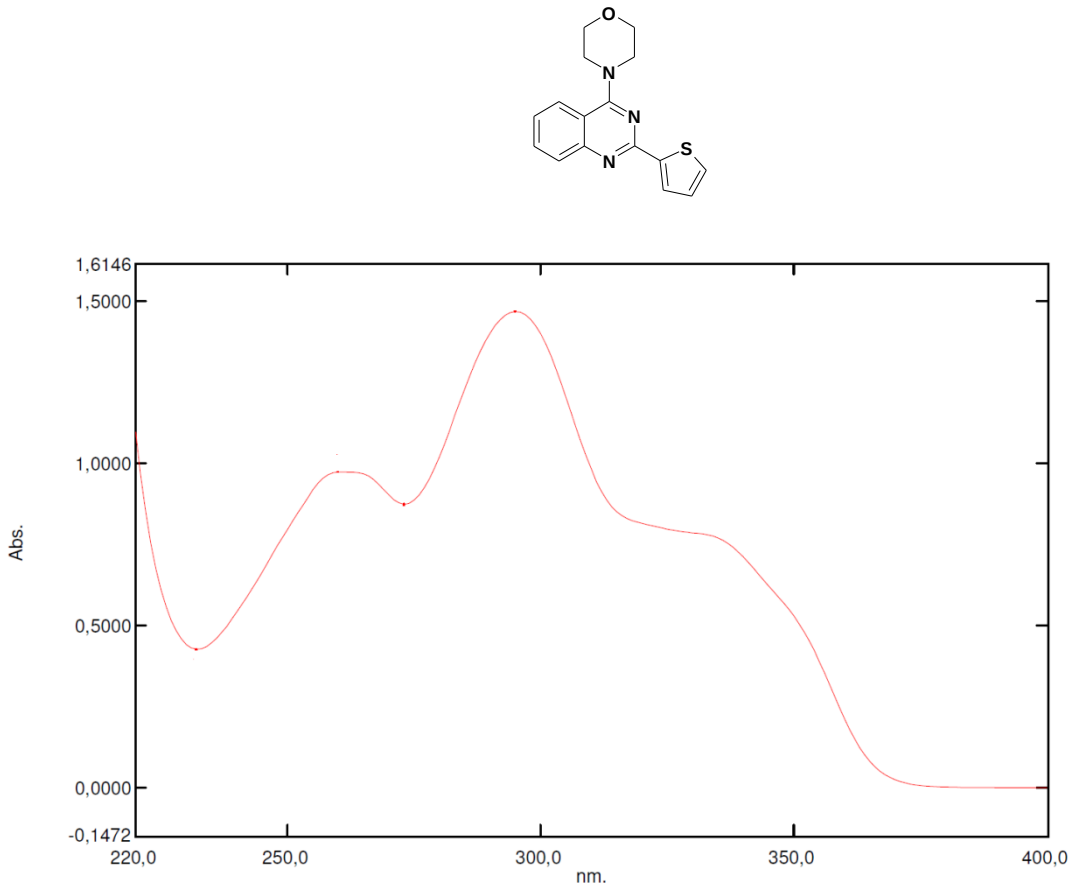


Figure S9 Absorption spectra of ligand **2a** in acetonitrile

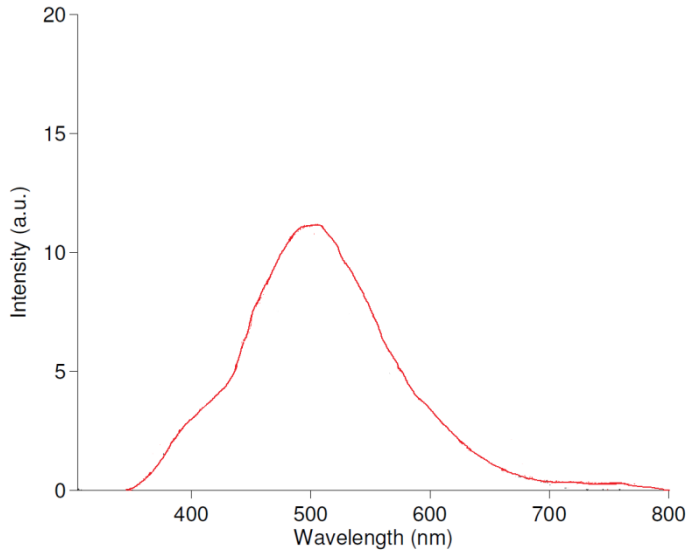
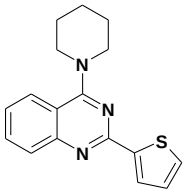


Figure S10 Emission spectra of ligand **2a** in acetonitrile (exitation at 295 nm).



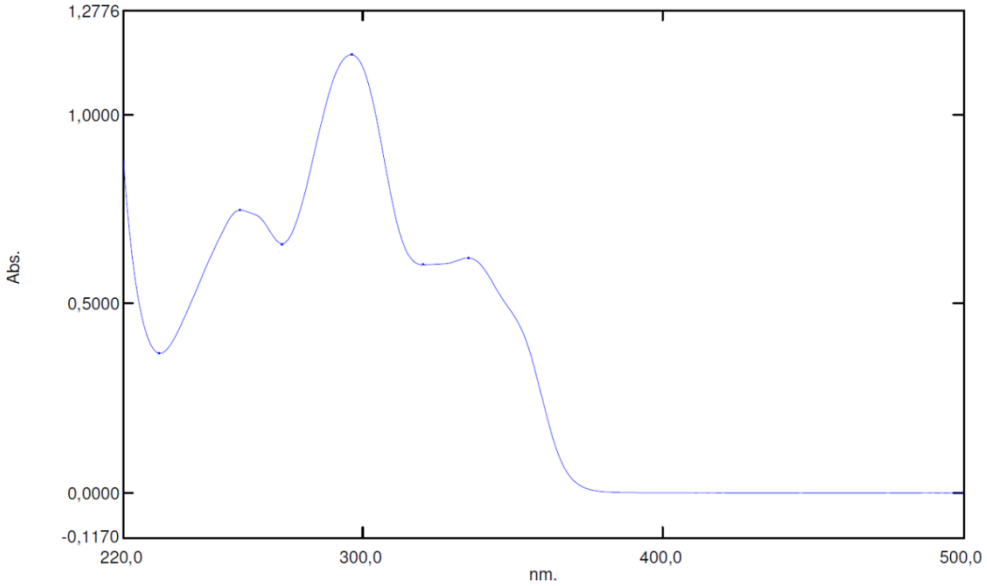


Figure S11 Absorption spectra of ligand **2b** in acetonitrile.

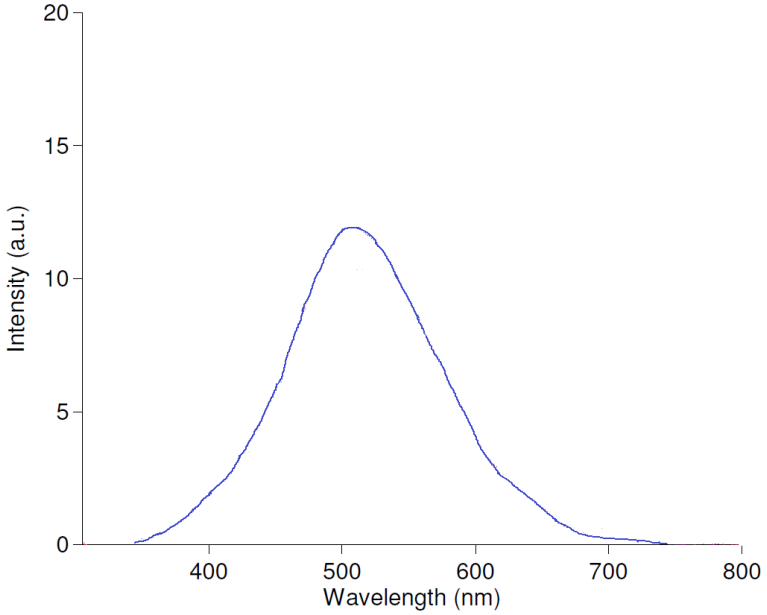


Figure S12 Emission spectra of ligand **2b** in acetonitrile (exitation at 295 nm).

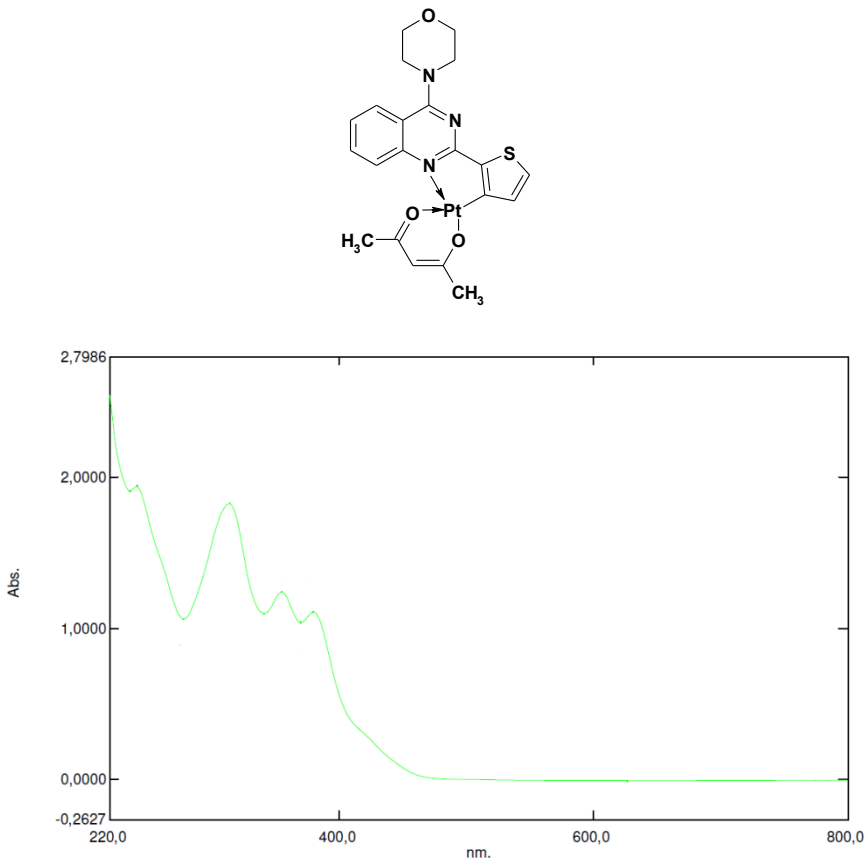


Figure S13 Absorption spectra of complex **3a** in acetonitrile.

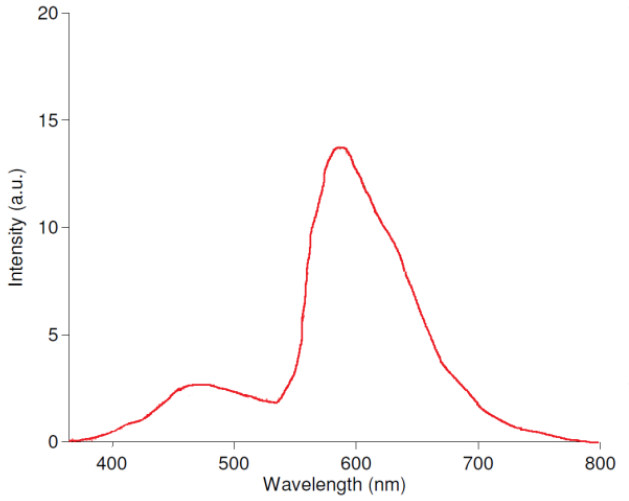


Figure S14 Emission spectra of complex **3a** in acetonitrile (exitation at 380 nm).

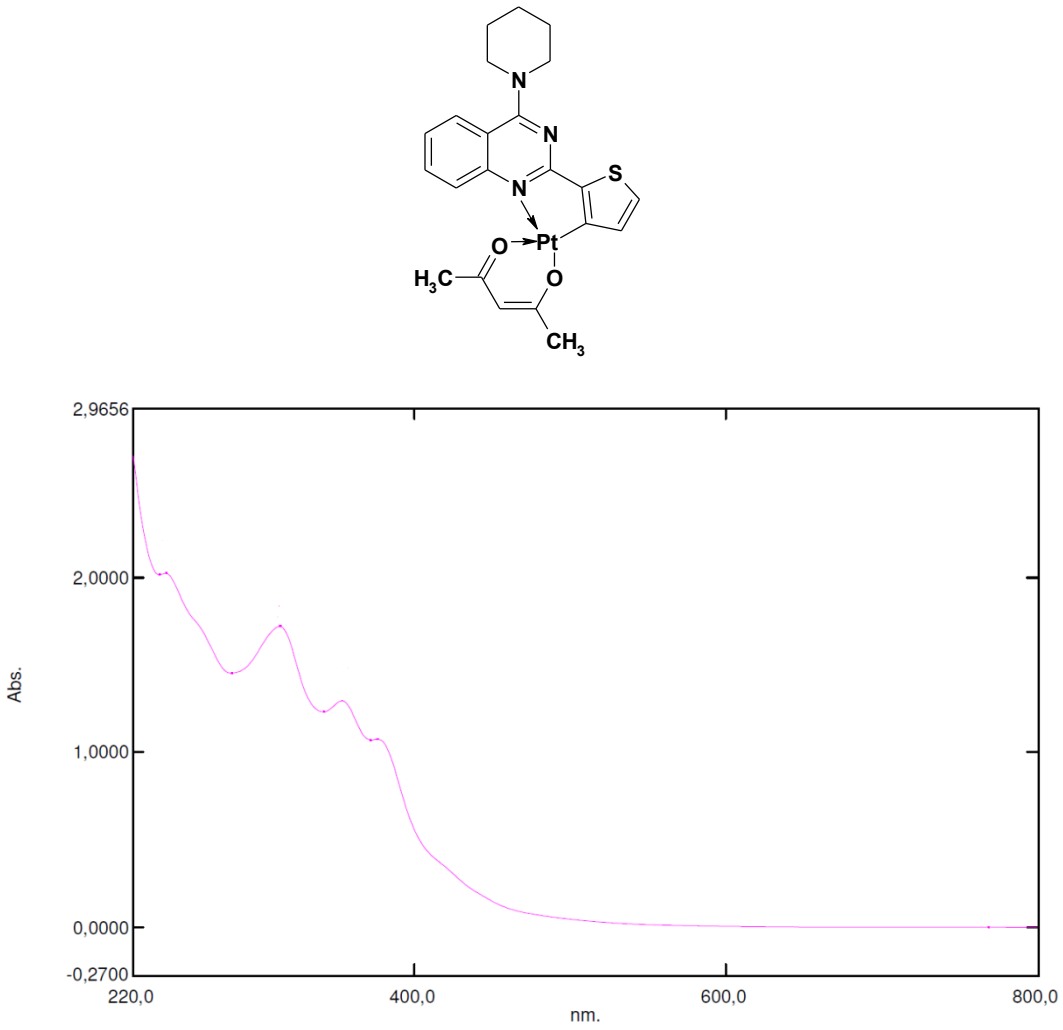


Figure S15 Absorption spectra of complex **3b** in acetonitrile.

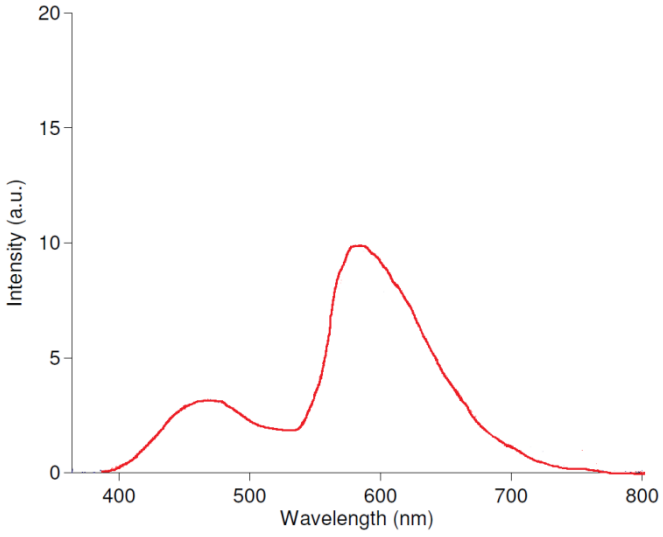


Figure S16 Emission spectra of complex **3b** in acetonitrile (exitation at 380 nm).

Table S1 Selected bond lengths of complex **3a**.

Bond	Bond length (Å)	Bond	Bond length (Å)
Pt(1)-O(1)	2.099(4)	N(1)-C(10)	1.391(6)
Pt(1)-O(2)	2.007(4)	N(3)-C(2)	1.351(6)
Pt(1)-N(1)	2.062(4)	N(3)-C(4)	1.335(6)
Pt(1)-C(12)	1.952(5)	N(16)-C(4)	1.364(6)
S(15)-C(11)	1.727(5)	N(16)-C(17)	1.476(6)
S(15)-C(14)	1.709(6)	N(16)-C(21)	1.456(6)
O(1)-C(23)	1.263(6)	C(2)-C(11)	1.426(7)
O(2)-C(25)	1.278(6)	C(4)-C(5)	1.430(6)
O(3)-C(18)	1.441(8)	C(5)-C(6)	1.413(6)
O(3)-C(20)	1.412(8)	C(5)-C(10)	1.423(6)
N(1)-C(2)	1.357(6)		

Table S2 Selected bond angles of complex **3a**.

Angle	(°)	Angle	(°)
O(2)-Pt(1)-O(1)	90.27(15)	C(9)-C(10)-C(5)	118.4(5)
O(2)-Pt(1)-N(1)	169.29(16)	C(2)-C(11)-S(15)	129.2(4)
N(1)-Pt(1)-O(1)	100.29(15)	C(12)-C(11)-S(15)	113.3(4)
C(12)-Pt(1)-O(1)	176.52(18)	C(12)-C(11)-C(2)	117.5(5)
C(12)-Pt(1)-O(2)	88.80(19)	C(11)-C(12)-Pt(1)	114.6(4)
C(12)-Pt(1)-N(1)	80.77(19)	C(7)-C(6)-H(6)	119.5
C(14)-S(15)-C(11)	89.7(3)	C(13)-C(12)-Pt(1)	134.8(4)
C(23)-O(1)-Pt(1)	124.0(4)	N(1)-C(10)-C(5)	120.9(5)
C(25)-O(2)-Pt(1)	126.0(4)	N(1)-C(10)-C(9)	120.5(5)
C(20)-O(3)-C(18)	109.6(5)	S(15)-C(14)-H(14)	123.3
C(2)-N(1)-Pt(1)	113.2(3)	C(13)-C(14)-S(15)	113.4(4)
C(2)-N(1)-C(10)	115.8(4)	N(16)-C(17)-H(17A)	109.0
C(10)-N(1)-Pt(1)	130.6(3)	N(16)-C(17)-H(17B)	109.0
C(4)-N(3)-C(2)	118.4(4)	O(1)-C(23)-C(24)	125.8(6)
C(4)-N(16)-C(17)	121.2(4)	O(2)-C(25)-C(24)	126.3(5)
C(4)-N(16)-C(21)	119.4(4)	O(2)-C(25)-C(26)	113.4(6)
C(21)-N(16)-C(17)	108.9(4)	C(18)-C(17)-N(16)	113.1(6)
N(1)-C(2)-C(11)	113.7(4)	O(3)-C(18)-H(18A)	109.2
N(3)-C(2)-N(1)	125.4(5)	O(3)-C(18)-H(18B)	109.2
N(3)-C(2)-C(11)	120.9(5)	C(17)-C(18)-O(3)	112.0(6)
N(3)-C(4)-N(16)	116.4(5)	O(3)-C(20)-H(20A)	108.8
N(3)-C(4)-C(5)	120.5(5)	O(3)-C(20)-H(20B)	108.8
N(16)-C(4)-C(5)	123.0(5)	O(3)-C(20)-C(21)	113.8(6)
C(6)-C(5)-C(10)	118.7(5)	N(16)-C(21)-H(21A)	108.9
C(10)-C(5)-C(4)	116.2(4)	N(16)-C(21)-H(21B)	108.9
C(5)-C(6)-H(6)	119.5	C(20)-C(21)-N(16)	113.6(5)
C(7)-C(6)-C(5)	120.9(5)	O(1)-C(23)-C(22)	116.2(6)

References

1 R. J. Abdel-Jalil, W. Voelter and M. Saeed, *Tetrahedron Lett.*, 2004, **45**, 3475.

2 T. Kataoka, H. Shimizu, K. Tomimatsu, K. Tanaka, M. Hori and M. Kido, *Chem. Pharm. Bull.*, 1990, **38**, 874.