Regioselective Functionalisation of Tetrabromo Phenanthroline Ruthenium Complexes

Sven Rau*[a], Reinald Fischer[a], Michael Jäger[a], Bernhard Schäfer[a], Susann Meyer[b], Günter Kreisel[b], Helmar Görls[a], Manfred Rudolf[a], William Henry[c], Johannes G. Vos[c]

[a] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität, 07743 Jena, Germany
E-mail: Sven.Rau@uni-jena.de

[b] Institut für Technische Chemie und Umweltchemie, Friedrich-Schiller-Universität, 07743 Jena, Germany

[c] National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

Abstract

Structural, photophysical and -chemical characterisation and reactivity of a novel polypyridyl ruthenium complex based on 3,5,6,8-tetra-bromophenanthroline are discussed.

Signal storage at a molecular level is great challenge for chemistry.[1] The possibility of connecting different functionalities selectively to one ligand of a metal complex may open the route towards higher integrated molecular units capable of processing various external stimuli in a predesignated order. The implementation of this concept demands ligands with a multitude of potential connecting groups which can selectively be transformed.[2] 3-bromo- and 3,8-dibromophenanthrolines have proved useful for the preparation of mononuclear[3] and multiheteronuclear complexes.[4] These systems have found applications ranging from DNA photoprobes[5] to metalloligands in catalysis.[6] A very useful feature of this bromophenanthroline ruthenium complexes is their susceptibility towards nucleophilic aromatic substitution which is very well established.[7]

We have improved a bromination reaction of phenanthroline first published by Dénes and Chira[8] which allows now the selective formation of 3,5,6,8,-tetrabromophenanthroline (Br_4phen) in an one step multigram reaction, figure 1.[8]

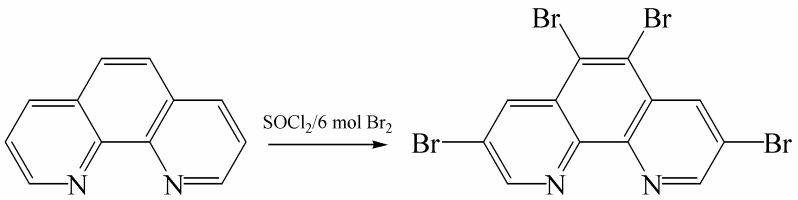

Figure 1 Improved preparation of 3,5,6,8,-tetrabromophenanthroline (Br_4phen)

Br_4phen readily forms a complex with $(tbbpy)_2RuCl_2$ resulting in $[(tbbpy)_2Ru(Br_4phen)]^{2+}$, **1**. The structural characterisation using two dimensional NMR spectroscopy suggests that a symmetrical complex is formed indicated by the presence of only two signals for the four phenanthroline based protons. ^{13}C, HSQC, HMBC allows the complete assignment of all signals in the ^{1}H- and ^{13}C-NMR spectra which together with mass spectroscopy suggests that Br_4phen coordinates in a similar fashion as the unsubstituted phenanthroline. The X-ray crystallographic characterisation confirms this assumption and as apparent from table 1 shows no significant differences compared with the parent complex $[(tbbpy)_2Ru(phen)]^{2+}$, **2** (see supporting information), the molecular structure is depicted in figure 2.

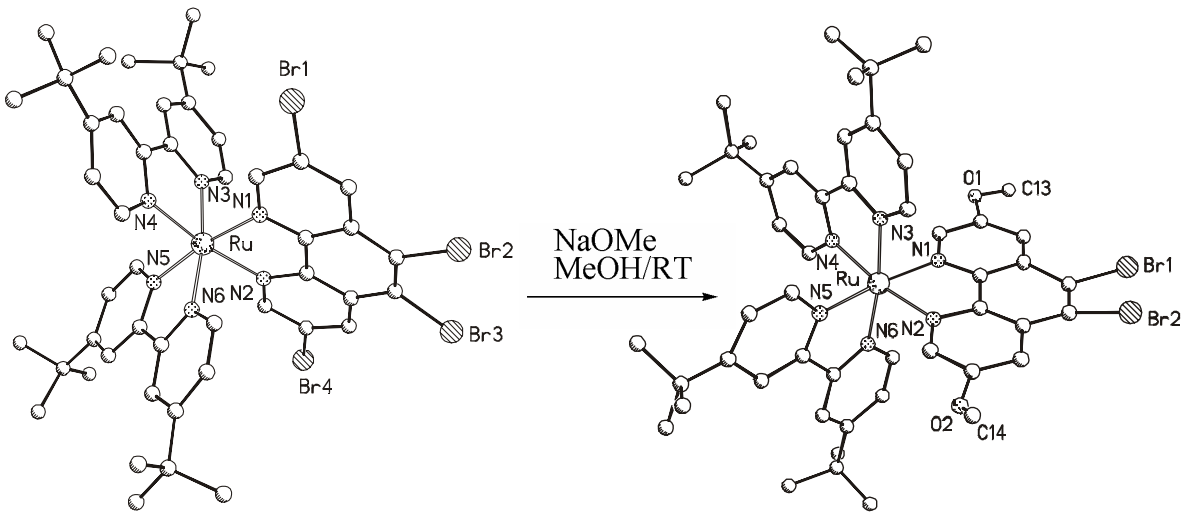

Figure 2. Regioselective nucleophilic substitution of **1** with NaOMe leading to **3;** molecular structure of **1**, Anions and hydrogen atoms omitted and structural motive of **3** confirming the regioselective substitution

Reaction of **1** with NaOMe at room temperature in methanol leads to the selecetive formation of one product that still contains two bromine and two new methoxy functions, confirmed by ESI-MS. The fact that all bipyridine based signals in the ^{1}H-NMR did not change their position together with only one new signal at 4.15 ppm for the methoxy function suggests the formation of a symmetrical species where substitution at the phenanthroline moiety has taken place. The regioselective formation of the 5,6-dibromo-3,8-dimethoxyphenanthroline ruthenium complex **3** could be confirmed by a structural motive depicted figure 2.

Table 1 Ru-N bond length in Å, angles in °

	1	**2**
Ru-N1	2.046(5)	2.055(4)
Ru-N2	2.060(5)	2.056(5)
Ru-N3	2.064(5)	2.053(4)
Ru-N4	2.052(5)	2.055(4)
Ru-N5	2.047(5)	2.060(4)
Ru-N6	2.071(5)	2.074(4)
C2-Br1	1.891(6)	----
C5-Br2	1.883(6)	----
N1-Ru-N2	79.27(19)	79.9(2)
N3-Ru-N4	78.21(19)	77.88(16)
N5-Ru-N6	78.25(19)	78.99(16)

Photophysical investigation of compounds **1** to **3** suggests that the tetrabromo-substitution lowers the electron density of the phenanthroline ligand considerably. The absorption and emission wavelength of **1** are redshifted compared with **2**, see table 2. This finding correlates well with the data obtained for the oxidation potential of RuII/III which clearly shows that the four bromine substituents significantly decrease the electron density at the metal centre (difference of 137 mV). Introduction of the methoxy groups increases the electron density as expected.[9] The introduction of two methoxy groups has a pronounced influence on the photophyiscal properties which is in agreement with an electron donating substituent.

Table 2 Photophysical and electrochemical properties of complexes **1-3** in acetonitrile

Compound	$E_{1/2}$ ox in V (vs Fc/Fc^+)	λ_{max} in nm	λ_{em} in nm
1	0.92	470	680
2	0.783	444	610
3	0.845	450	615

In conclusion, rutheniumpolypyridyl complexes based on the ligand Br_4phen are readily obtainable. Most importantly a regioselective nucleophilic substitutions with NaOMe at the 3,8 position is possible. It is evident from the conventional reactivity of bromine substituted aromatics that **1** and **3** are potentially very interesting synthon in itself opening the possibility to derivatise the previously not easily accessible 5,6 position. Initial investigations of the photochemical reactivity of **3** suggest that Br_2OMe_2phen is very photolabile.

Acknowledgement

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reduction of the ruthenium centre of **3** suggesting an involvment of the methoxy function as observed previously: L. O'Brien, M. Duati, S. Rau, A.L. Guckian, T.E. Keyes, N.M. Boyle, A. Serr, H. Görls, J.G. Vos, *J. Chem. Soc. Dalton Trans.* **2004**, 514.

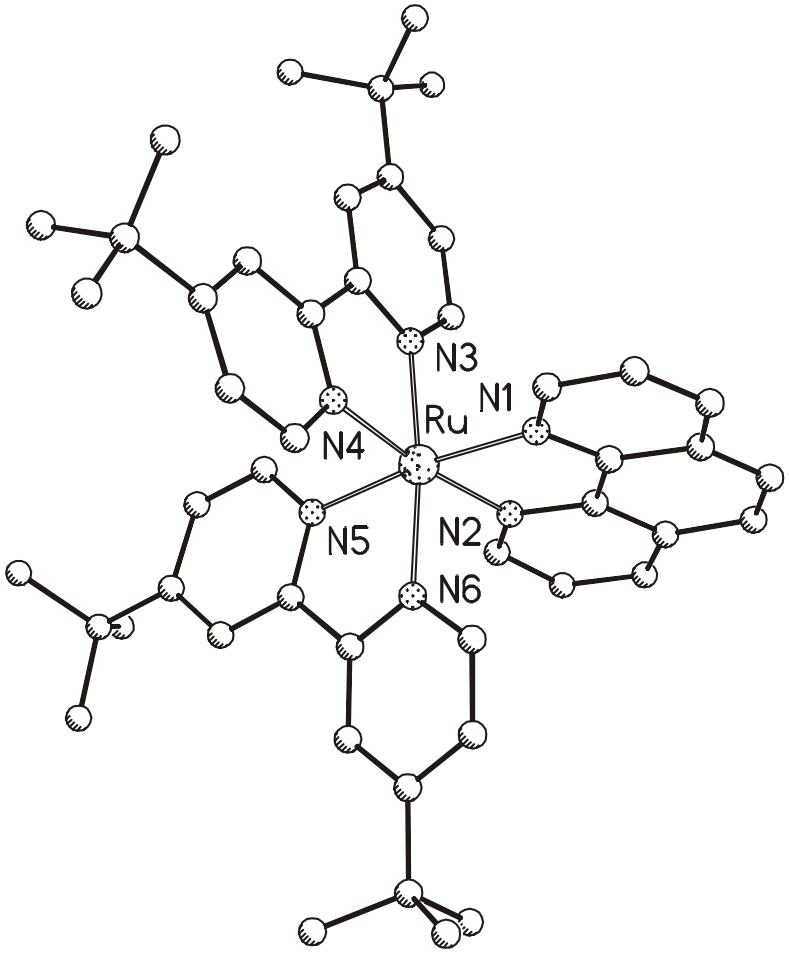


Figure S1. Moleculare structure of $(tbbpy)_2Ru(phen)$, **2**, Anions and hydrogen atoms omitted (Ru-N bond length in Å, angles in °, Ru-N1 2.061(5), Ru-N2 2.056(5), Ru-N3 2.053(4), Ru-N4 2.055(4), Ru-N5 2.060(4), Ru-N6 2.074(4), N1-Ru-N2 79.9(2), N3-Ru-N4 77.88(16), N5-Ru-N6 78.99(16))

Experimental conditions

Methods and Materials

1,10-phenanthroline was received from Aldrich and used without further purification, $(tbbpy)_2RuCl_2$ was prepared according to literature methods.[1] All manipulations were carried out under Argon using standard Schlenk techniques and the used solvents were dried and distilled if not stated otherwise. The NMR spectra were recorded on a Bruker 400 MHz and

200 MHz spectrometer. The mass spectroscopy was carried out on a SSQ 170, Finigan Mat. The Electrospray mass spectroscopy was performed on a Finnnigan MAT 95 XL double focussing sector field instrument (Thermo Finnigan GmbH, Bremen, Germany) adjusted to a mass resolution of about 2000.

UV-VIS spectra were obtained using a Varian Cary 1 UV-vis or a Shimadzu UV 3100 UV-vis-NIR spectrometer. Emission spectra are not corrected and were recorded using a Perkin Elmer LS50B spectrometer equipped with a Hamamatsu R928 red sensitive detector.

Electrochemical investigation

The electrochemical oxidation of the compounds was investigated in 3-electrode technique by means of cyclic square-wave voltammetry using an home-built computer controlled instrument based on the PCI-6110E data acquisition board (National Instruments). The experiments were performed in acetonitrile containing 0.25M tetra-n-butylammonium-hexafluorophosphate under a blanket of solvent-saturated argon. The ohmic resistance of the solvent which had to be compensated for was determined by measuring the impedance of the system at potentials where the faradaic current was negligibly small. The reference electrode was an Ag\AgCl electrode in acetonitrile containing 0.25M tetra-n-butylammonium chloride. The potential of this reference system was calibrated by measuring the potential of the ferrocenium/ferrocene couple at the end of each experiment. The latter was found to be at *0.803±0.001V* throughout the measurements.

The working electrode was a 1.5 mm Pt disk electrode (Bioanalytical Systems Inc., West Lafayette, USA).

Crystal Structure Determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects [2,3]. **1** was corrected for absorption effects[4].

The structures were solved by direct methods (SHELXS [5]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97 [6]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [6]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. The quality of the data for compound **3** is insufficient for full structural refinement. We will therefore only publish the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. Further informations can be obtained directly at the authors.

Synthesis

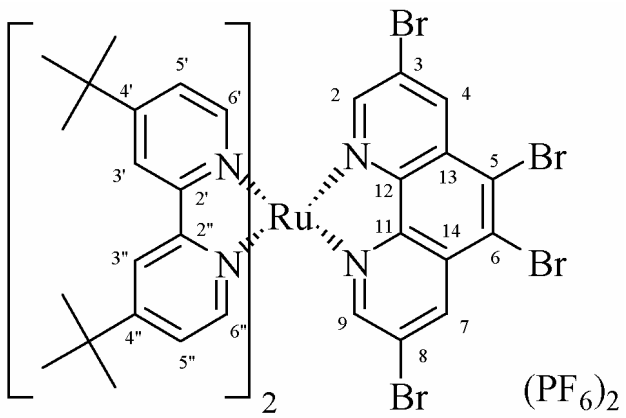
3,5,6,8,-tetrabromophenanthroline (Br_4phen):

4,0 g (20 mmol) of 1,10-phenanthroline monohydrate were dissolved in 200 ml $SOCl_2$. 9.3 g (120 mmol) of freshly distilled Br_2 were carefully added. This mixture was refluxed for 31 h and cooled to room temperature and the bright yellow precipitate filtered of (3,5,6,8,-tetrabromophenanthroline). The precipitate was washed with aqueous NH_3 until the washing solution was colourless. The white solid was recrystallised from toluene.

3,5,6,8,-tetrabromophenanthroline (Br_4phen) ^{1}H-NMR ($CDCl_3$): 9.16 (2H, d), 8.91 (2H, d); ^{13}C-NMR ($CDCl_3$): 122,0; 125,1; 129,6; 139,0; 143,6; 152,4; ; MS(DCI with H_2O): 497 ($M+H^+$) 417 ($M-Br+H^+$), 338 ($M-Br_2+H^+$), 257 (M^+-Br_3) Yield 5.22 g (52 % of theory based on phen)

$[(tbbpy)_2Ru(Br_4phen)](PF_6)_2$ (1): 3,5,6,8-Tetrabromo-1,10-phenanthroline (1.15 g, 2.32 mmol) and $[(tbbpy)_2RuCl_2]$ (1.5 g, 2.11 mmol) were refluxed in a mixture of 80 mL ethanol and 20 mL H_2O for 8 hours. The crude reaction mixture was filtered, washed twice with ethanol/H_2O (80:20), and the combined filtrate was concentrated to the half volume. Upon addition of NH_4PF_6 and stirring at room temperature for 1 hour the crude product precipitated. Recrystallisation from aceton/water gave the desired product. Crystalls suitable for X-ray analysis were obtained from aceton/water.

Crystal Data for **1** [7]: $C_{48}H_{52}Br_4N_6Ru]^{2+} * 2\ [PF_6]^-$, Mr = 1423.61 gmol^{-1}, bourdeux-red prism, size 0.02 x 0.02 x 0.01 mm^3, tetragonalic, space group $I4_1/a$, a = b = 32.5281(3), c = 20.5151(4) Å, V = 21706.6(5) Å^3 , T= -90 °C, Z = 16, $\rho_{calcd.}$ = 1.742 gcm^{-3}, μ (Mo-K_α) = 33.74 cm^{-1}, psi-scan, transmin: 0.5565, transmax: 0.7367, F(000) = 11264, 20023 reflections in h(-42/42), k(-29/29), l(-19/26), measured in the range $2.66° \leq \Theta \leq 27.49°$, completeness Θ_{max} = 99.8 %, 12423 independent reflections, R_{int} = 0.053, 7520 reflections with $F_o > 4\sigma(F_o)$, 652 parameters, 0 restraints, $R1_{obs}$ = 0.065, wR^2_{obs} = 0.135, $R1_{all}$ = 0.129, wR^2_{all} = 0.163, GOOF = 1.018, largest difference peak and hole: 1.217 / -1.151 e Å^{-3}.



^{1}H-NMR	in d_6-DMSO 400MHz		in d_6 acetone 400 MHz	
Proton	Chemical Shift (ppm)	Integration, multiplicity	Chemical Shift (ppm)	Integration, multiplicity
CH_3(*tert*-butyl)	1.362	18H, s	1.300	18H, s
CH_3(*tert*-butyl)	1.391	18H, s	1.388	18H, s
5'	7.310	2H, d(lc)	7.600	2H, d(lc)
6",6'	7.527	4H, m	7.857	4H, m
5"	7.599	2H, d(lc)	7.359	2H, d(lc)
2,9	8.055	2H, s(lc)	8.340	2H, s(lc)
3'	8.788	2H, s(lc)	8.838	2H, s(lc)
3"	8.792	2H, s(lc)	8.801	2H, s(lc)
4,7	8.997	2H, s(lc)	8.988	2H, s(lc)

^{13}C-NMR in d_6-DMSO 400MHz

Carbon	Chemical shift (ppm)
CH_3(*tert*-butyl)	29.962
CH_3(*tert*-butyl)	30.001
C(*tert*-butyl)	35.378
C(*tert*-butyl)	35.508
3',3"	121.741
11,12	122.572
5'	124.261
5"	124.685
13,14	126.074

5,6	130.765
4,7	138.459
3,8	145.802
6' or 6"	150.732 and 151.974
2,9	153.667
2' or 2"	156.006 and 156.610
4' or 4"	161.934 and 162.267

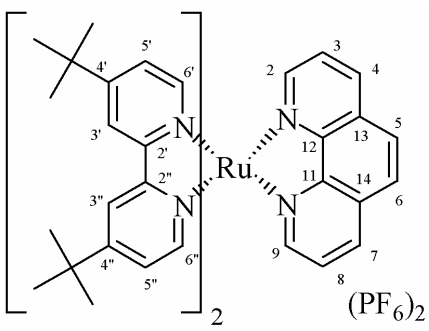
MS (Micro-ESI in $CHCl_3$ + Methanol); m/z(relative intensity) with matching isotop pattern 1279(100) (**1** + PF_6), 1201(34) (**1**-Br + PF_6), 567(51) ($\mathbf{1}^{2+}$)

Synthesis of **[(tbbpy)$_2$Ru(phen)](PF$_6$)$_2$ 2:**

1,10-phenanthroline (0.018 g, 0.09 mmol) and [(tbbpy)$_2$RuCl$_2$] (0.06 g, 0.085 mmol) were reacted and purified according to **1**. Yield 96 mg (95%). Crystalls suitable for X-ray analysis were obtained from aceton/water.

Crystal Data for **2** [7]: $[C_{48}H_{56}N_6Ru]^{2+}$ * 2 $[PF_6]^-$ * 2 C_3H_6O, Mr = 1224.15 gmol^{-1}, red-brown prism, size 0.12 x 0.10 x 0.09 mm^3, triclinic, space group P-1, a = 12.1999(7), b = 13.3243(7), c = 18.989(1) Å, α = 76.854(2), β = 74.819(3), γ = 78.206(3)°, V = 2866.3(3) Å^3 , T= -90 °C, Z = 2, $\rho_{calcd.}$ = 1.418 gcm^{-3}, μ (Mo-K$_\alpha$) = 4.13 cm^{-1}, psi-scan, transmin: 0.9521, transmax: 0.9637, F(000) = 1264, 19624 reflections in h(-15/15), k(-17/14), l(-24/24), measured in the range 2.11° ≤ Θ ≤ 27.44°, completeness Θ_{max} = 97.4 %, 12753 independent reflections, R_{int} = 0.062, 6757 reflections with $F_o > 4\sigma(F_o)$, 664 parameters, 0 restraints, $R1_{obs}$ = 0.074, wR^2_{obs} = 0.194, $R1_{all}$ = 0.138, wR^2_{all} = 0.220, GOOF = 0.955, largest difference peak and hole: 1.402 / -1.062 e Å^{-3}.

^{1}H-NMR	in d$_3$-Acetonitrile 400MHz	
proton	Chemical Shift (ppm)	Integration, multiplicity
CH_3(*tert*-butyl)	1.322	18H, s
CH_3(*tert*-butyl)	1.437	18H, s
5''	7.200	2H, d(lc)
6''	7.405	2H, d
5'	7.463	2H, d(lc)



6'	7.705	2H, d
3,8	7.753	2H, m
2,9	8.058	2H, s(lc)
5,6	8.299	2H, s
3''	8.456	2H, s(lc)
3'	8.504	2H, s(lc)
4,7	8.613	2H, s(lc)

^{13}C-NMR in d_3-acetonitrile 200MHz

δ in ppm 164.16; 164.01; 158.73; 158.44; 153.83; 152.71; 149.35; 138.09; 132.59; 129.68; 127.66; 126.22; 126.06; 123.07; 123.00; 122.00; 36.96; 36.85; 31.38, 31.14

MS FAB in nba m/z(relative intensity) with matching isotop pattern

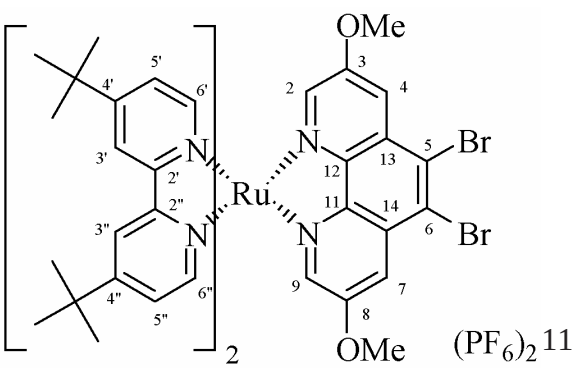
980(22) **2**+PF_6; 834(15) **2**

Synthesis of **[(tbbpy)$_2$Ru(OMe$_2$Br$_2$phen)](PF$_6$)$_2$ 3:**

200 mg of **1**, 0.14 mmol, were dissolved in 100 ml of a freshly prepared 1 M solution of NaOMe in MeOH. The solution was stirred for 6 h and 200 ml H_2O were added. The pH of the solution was slowly adjusted to 7 by adding diluted HCl. The resulting opaque orange solution was extracted with CH_2Cl_2 until colorless and the solvent was removed from the combined organic phases. The precipitate was dissolved in a minimal amount of EtOH and concentrated aqueous NH_4PF_6 added. The precipitate was recrystallised from aceton/water. Yield 170 mg (90%)

Crystal Data for **3** : $C_{52}H_{61}Br_2F_{12}N_6O_2P_2Ru$, Mr = 1304.72 gmol^{-1}, red prism, size 0.02 x 0.02 x 0.01 mm^3, monoclinic, space group $P2_1/n$, a = 13.983(3), b = 39.063(5), c = 10.4711(15) Å, β = 100.945(13)°, V = 5615.4(17) Å^3 , T= -153 °C, Z = 4, $\rho_{calcd.}$ = 1.543 gcm^{-3}, μ (Mo-K$_\alpha$) = 6.22 cm^{-1}, F(000) = 2654, 21731 reflections in h(-15/13), k(-45/45), l(-12/12), measured in the range 1.52° ≤ Θ ≤ 14.56°, completeness Θ$_{max}$= 72.1 %, 6903 independent reflections.

^{1}H-NMR in d_6-aceton 400MHz		
proton	Chemical Shift (ppm)	Integration, multiplicity
CH_3(*tert*-butyl)	1.367	18H, s



CH_3(*tert*-butyl)	1.428	18H, s
CH_3(OMe)	2.831	6H, s
5''	7.397	2H, d(lc)
5'	7.618	2H, d(lc)
6''	7.828	2H, d
2,9	7.845	2H, s(lc)
6'	7.939	2H, d
4,7	8.174	2H, s(lc)
3''	8.844	2H, s(lc)
3'	8.879	2H, s(lc)

MS FAB in nba m/z(relative intensity) with matching isotop pattern
1181(5) **3**+PF_6; 1035(5) **3**

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(7) CCDC 216455 and 216456 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).