SUPPORTING INFORMATION

Fig. 1 ESI Low field region of the ^{1}H NMR spectrum for **[1a]Cl** in CD_3OD at 25 ºC.
Fig. 2 ESI ^{1}H NMR spectrum for **[2a]Cl** in CD_3SOCD_3 at 25 ºC.
Fig. 3 ESI ^{1}H NMR spectrum for **[3a]Cl** in CD_3SOCD_3 at 25 ºC.
Fig. 4 ESI DSC curve for the *aphen*/DNA system at $C_D/C_P = 1$, $C_P = 4 \times 10^{-4}$ M, I = 2.5 mM (NaCac), pH = 7, scan rate = 1 ºC/min and P = 3 atm.
Fig. 5 ESI Aquation curve of **[1a]Cl** at λ = 300 nm, I = 2.5 mM, pH = 6 and T = 25 ºC.
Fig. 6 ESI Low field region of the ^{1}H NMR spectra in D_2O (I = 0.1 M) at 25 ºC for reaction between **[1a]Cl** and 9-MeG (1:1, 5 mM, pH = 6).
Fig. 7 ESI Low field region of the ^{1}H NMR spectra in D_2O (I = 2.5 mM) at 25 ºC for the reaction between **[1a]Cl** and 5'-dGMP (1:1, 5 mM, pH = 6).
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Table 1 ESI. ^{1}H NMR Chemical shifs, δ (ppm), for complexes **[1a]Cl**, **[1a](BF$_4$)**, **[1b]Cl** and **[1b](BF$_4$)**.
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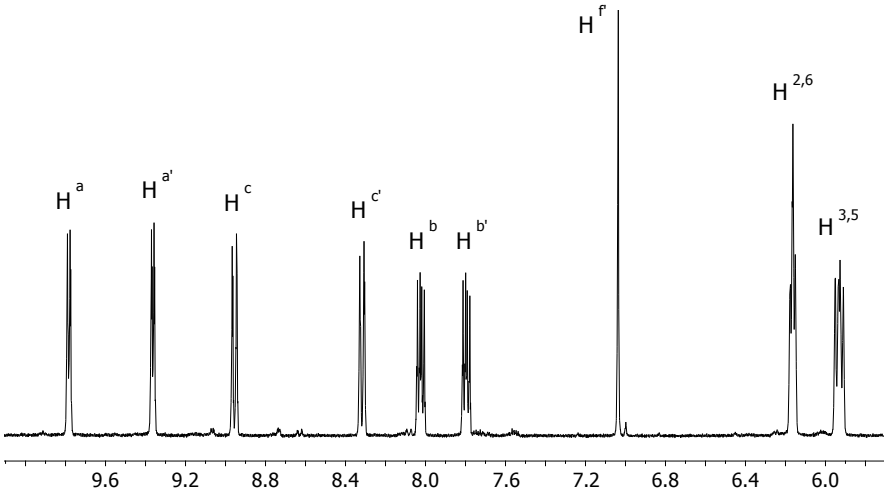

Fig. 1 ESI Low field region of the ^{1}H NMR spectrum for **[1a]Cl** in CD_3OD at 25 ºC.

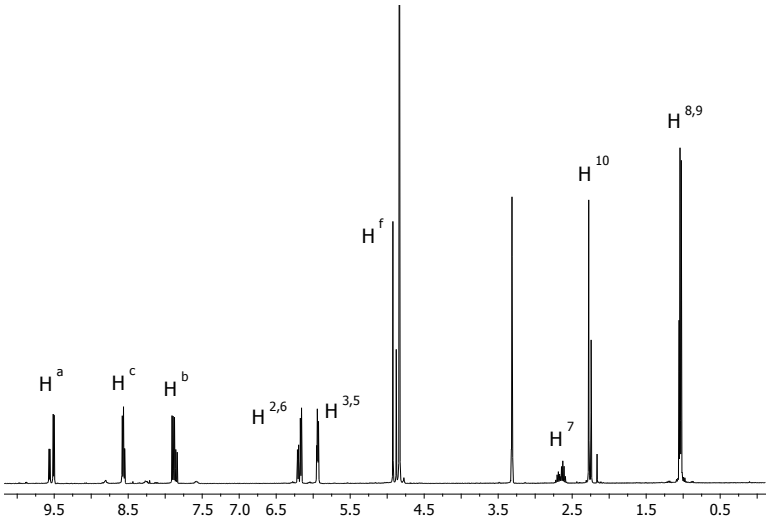

Fig. 2 ESI ^{1}H NMR spectrum for **[2a]Cl** in CD_3SOCD_3 at 25 ºC.

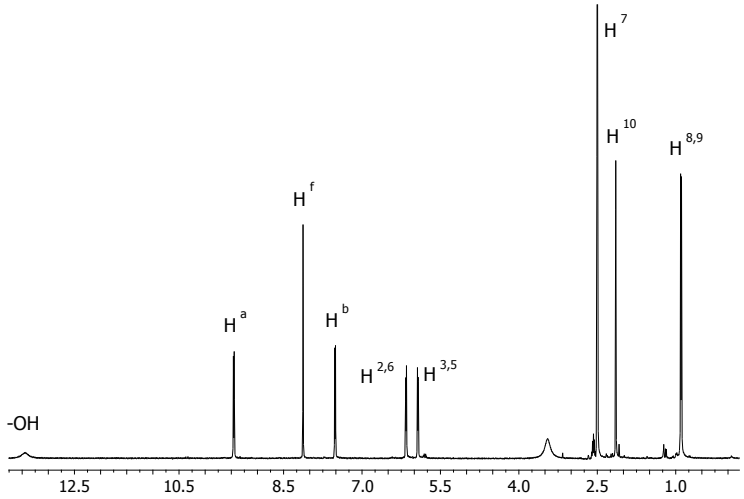

Fig. 3 ESI ^{1}H NMR spectrum for **[3a]Cl** in CD_3SOCD_3 at 25 ºC.

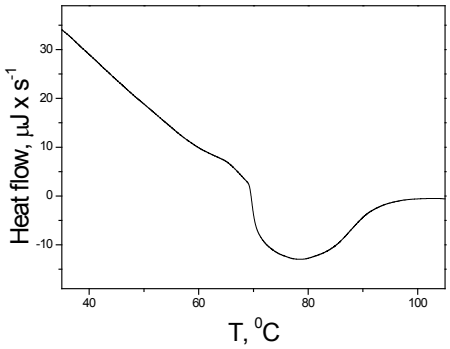

Fig. 4 ESI DSC curve for the *aphen*/DNA system at $C_D/C_P = 1$, $C_P = 4 \times 10^{-4}$ M, I = 2.5 mM, pH = 7, scan rate 1 ºC/min and P = 3 atm.

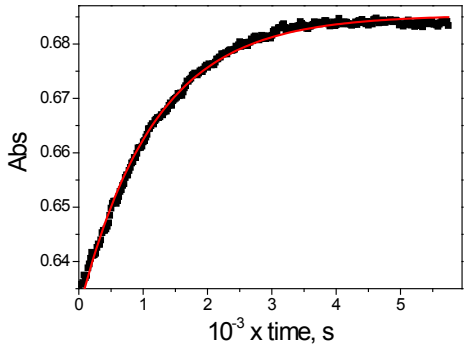

Fig. 5 ESI Aquation curve of **[1a]Cl** at λ = 300 nm, I = 2.5 mM, pH = 6 and T = 25 ºC,.

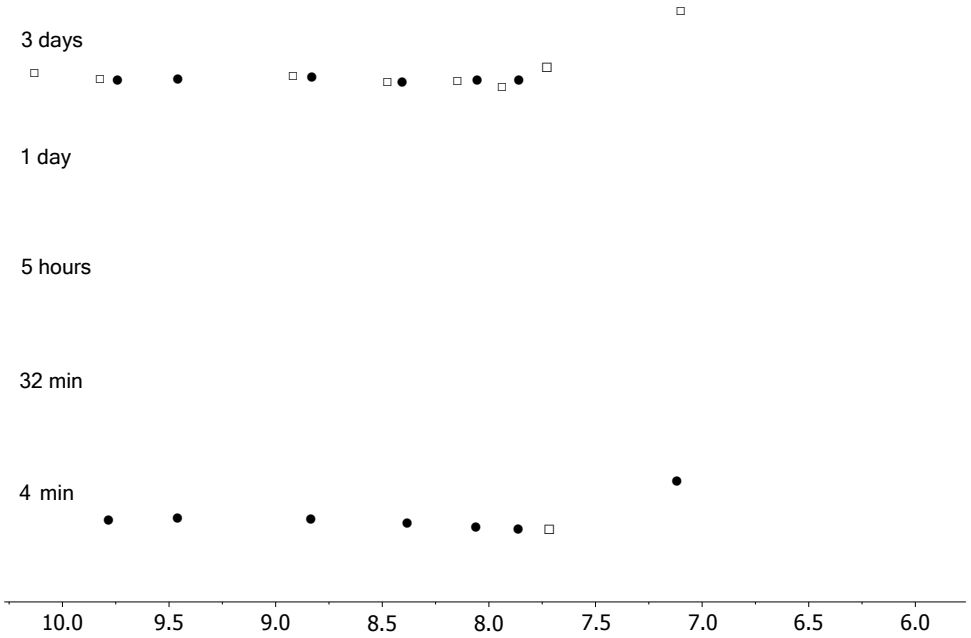

Fig. 6 ESI Low field region of the ^{1}H NMR spectra in D_2O (I = 0.1 M) at 25 ºC for reaction between **[1a]Cl** and 9-MeG (1:1, 5 mM, pH = 6). (● = Ru-Cl, ▲ = 9-MeG, ■ = adduct Ru-N7).

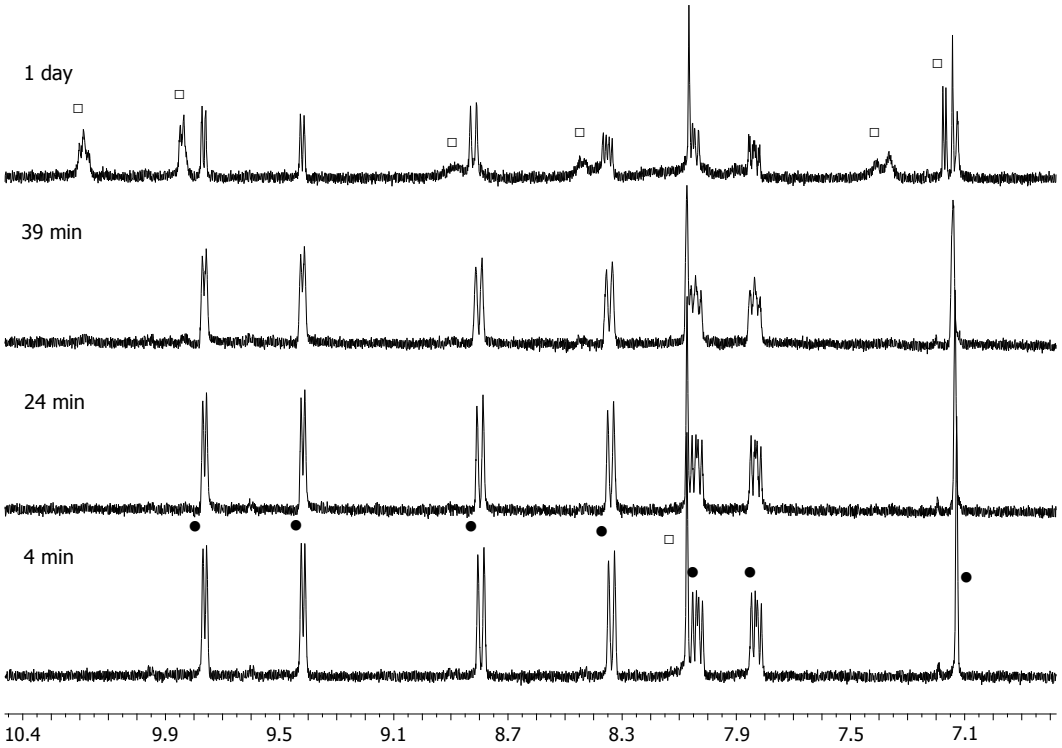

Fig. 7 ESI Low field region of the ^{1}H NMR spectra in D_2O (I = 0.1 M) at 25 ºC for the reaction between **[1a]Cl** and 5'-dGMP (1:1, 5 mM, pH = 6). (● = Ru-Cl, ▲ = 5'-dGMP, ■ = adduct Ru-N7).

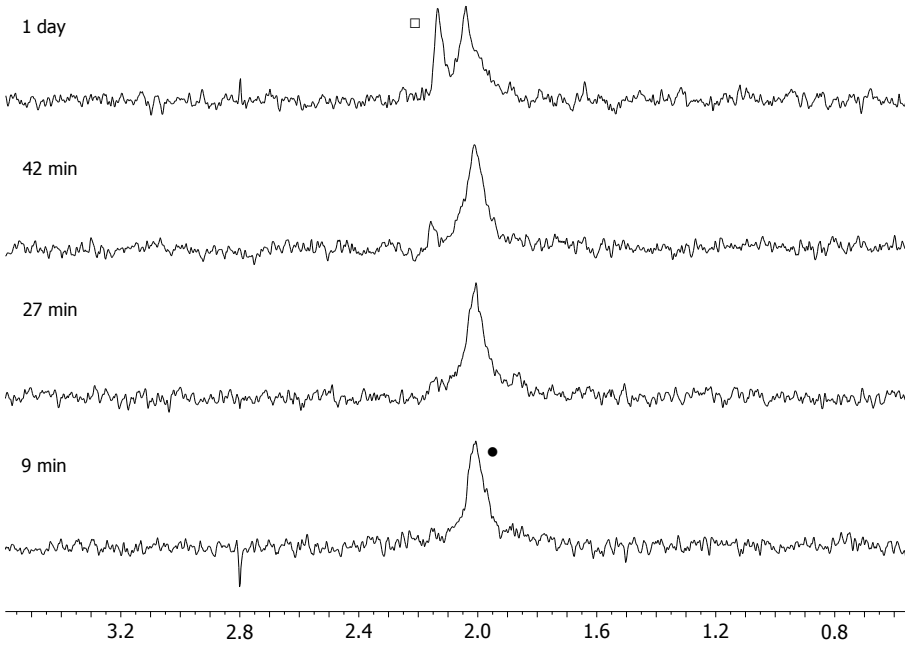

Fig. 8 ESI ^{31}P NMR spectra in D_2O (I = 0.1 M) at 25 ºC for the reaction between **[1a]Cl** and 5'-dGMP (1:1, 5 mM, pH = 6). (● = 5'-dGMP, ▲= adduct Ru-N7).

Table 1 ESI ^{1}H NMR Chemical shifs, δ (ppm), for complexes **[1a]Cl**, **[1a](BF$_4$)**, **[1b]Cl** and **[1b](BF$_4$)**.

Compounds	*Aphen*							*p*-cym/bz				
	H^{a} (dd)	$H^{a'}$ (dd)	H^{c} (dd)	$H^{c'}$ (dd)	H^{b} (dd)	$H^{b'}$ (dd)	$H^{f'}$ (s)	$H^{2,6}$ (m)	$H^{3,5}$ (m)	H^{7} (sept)	H^{10} (s)	$H^{8,9}$ (d)
[1a]Cl	9.78	9.36	8.96	8.32	8.02	7.79	7.04	6.16	5.93	2.62	2.26	0.97
[1a](BF$_4$)	9.78	9.36	8.95	8.32	8.02	7.79	7.04	6.16	5.92	2.62	2.26	0.97
[1b]Cl	9.86	9.44	8.95	8.31	8.01	7.78	7.03	6.22*				
[1b](BF$_4$)	9.86	9.44	8.95	8.32	8.01	7.79	7.05	6.18*				

(*)Just one singlet for the 6 protons of **bz**.

Table 2 ESI ^{1}H NMR Chemical shifs, δ (ppm), for complexes **[2a]Cl**, **[2a](BF$_4$)**, **[2b]Cl** and **[2b](BF$_4$)**.

ephen region	H^{aM}	H^{am}	H^{cM}	H^{cm}	H^{bM}	H^{bm}
ephen	8.80 dd	-	8.21 dd	-	7.54 dd	-
[2a]Cl	9.51 dd	9.56 dd	8.57 dd	8.55 dd	7.89 dd	7.85 dd
[2a](BF$_4$)	9.46 dd	9.51 dd	8.56 dd	8.55 dd	7.88 dd	7.85 dd
[2b]Cl	9.56 dd	9.60 dd	8.56 dd	8.54 dd	7.87 dd	7.82 dd
[2b](BF$_4$)	9.56 dd	9.60 dd	8.56 dd	8.55 dd	7.87 dd	7.83 dd

aromatic region	$H^{2,6M}$	$H^{2,6m}$	$H^{3,5M}$	$H^{3,5m}$	H^{fM}	H^{fm}
ephen					4.74 s	
[2a]Cl	6.16 d	6.20 d	5.93 d	5.94 d	4.92 s	4.87 s
[2a](BF$_4$)	6.12 d	6.16 d	5.90 d	5.90 d	4.91 s	4.91 s
[2b]Cl	6.18 s *	6.19 s *	----	----	4.91 s	4.86 s
[2b](BF$_4$)	6.18 s *	6.19 s *	----	----	4.91 s	4.86 s

***** Just one singlet for the 6 protons of **bz**.

p-cym region	H^{7M}	H^{7m}	H^{10M}	H^{10m}	$H^{8,9M}$	$H^{8,9m}$
[2a]Cl	2.62 sept	2.68 sept	2.27 s	2.24 s	1.03 d	1.04 d
[2a](BF$_4$)	2.62 sept	2.68 sept	2.27 s	2.24 s	1.04 d	1.04 d

Note: M and m refer to major and minor isomers, respectively.

Table 3 ESI ^{13}C NMR Chemical shifs, δ (ppm), for complexes **[1a]Cl** and **[1a](BF$_4$)**.

	aphen region											
	C^{a} (s)	$C^{a'}$ (s)	C^{e} (s)	C^{f} (s)	$C^{e'}$ (s)	$C^{c'}$ (s)	C^{c} (s)	$C^{d'}$ (s)	$C^{b'}$ (s)	C^{b} (s)	C^{d} (s)	$C^{f'}$ (s)
[1a]Cl	156.46	151.48	147.90	146.25	141.26	136.35	134.98	134.31	127.22	125.97	125.17	103.04
[1a](BF$_4$)	156.47	151.50	147.90	146.24	141.26	136.35	134.96	134.30	127.23	125.98	125.17	103.06

	p-cym region								
	C^{1} (s)	C^{4} (s)	C^{2} (s)	C^{6} (s)	C^{3} (s)	C^{5} (s)	C^{7} (s)	$C^{8,9}$ (s)	C^{10} (s)
[1a]Cl	105.65	104.91	87.71	87.45	85.38	85.13	32.34	22.20	18.90
[1a](BF$_4$)	105.65	104.93	87.72	87.45	85.37	85.13	32.34	22.19	18.89

Table 4 ESI ^{13}C NMR Chemical shifs, δ (ppm), for complexes **[2a]Cl**, **[2a](BF$_4$)**, **[2b]Cl** and **[2b](BF$_4$)**.

Isomer **M**	C^{a}	C^{e}	C^{c}	C^{d}	C^{b}	C^{1}	C^{4}	$C^{2,6}$	$C^{3,5}$	C^{f}	C^{7}	$C^{8,9}$	C^{10}
[2a]Cl	156.65	151.57	141.91	134.85	129.02	106.24	105.34	87.46	85.40	55.90	32.40	22.29	18.96
[2a](BF$_4$)	----	-----	----	----	----	----	----	----	----	----	----	----	----
[2b]Cl	156.66	151.84	142.02	134.83	128.82	88.25*	----	----	----	55.89	----	----	----
[2b](BF$_4$)	----	----	----	----	----	----	----	----	----	----	----	----	----

Isomer **m**	C^{a}	C^{e}	C^{c}	C^{d}	C^{b}	C^{1}	C^{4}	$C^{2,6}$	$C^{3,5}$	C^{f}	C^{7}	$C^{8,9}$	C^{10}
[2a]Cl	156.32	151.91	142.00	135.17	128.68	106.61	105.28	88.02	85.38	55.62	32.29	22.32	18.91
[2a](BF$_4$)	----	----	----	----	----	----	----	----	----	----	----	----	----
[2b]Cl	156.35	152.17	142.06	135.22	128.42	88.40*	----	----	----	55.55	----	----	----
[2b](BF$_4$)	----	----	----	----	----	----	----	----	----	----	----	----	----

***** Just one singlet for the 6 C atoms of **bz**.

Note: M and m refer to major and minor isomers, respectively.

Table 5 ESI ^{1}H NMR Chemical shifs, δ (ppm), for complex **[3a]Cl**.

	$H_{(OH)}$	H^{a}	H^{f}	H^{b}	$H^{2,6}$	$H^{3,5}$	H^{7}	H^{10}	$H^{8,9}$
DMSO	13.45	9.45 d	8.13 s	7.51 d	6.16 d	5.93 d	2.57_{sept}	2.15 s	0.90 d
CD_3OD		9.37 d	8.22 s	7.32 d	6.08 d	5.84 d	2.61_{sept}	2.24 s	0.98 d

Table 6 ESI ^{13}C NMR Chemical shifs, δ (ppm), for complex **[3a]Cl**.

	C^{c}	C^{a}	C^{e}	C^{d}	C^{f}	C^{b}	C^{1}	C^{4}	$C^{2,6}$	$C^{3,5}$	C^{7}	$C^{8,9}$	C^{10}
[3a]Cl	165.29	157.01	148.54	123.81	121.23	111.32	104.41	103.90	86.66	84.29	32.30	22.24	18.93

Table 7 ESI Molar conductivity, Λ_M ($S \cdot cm^2 \cdot mol^{-1}$), for all complexes.

	H_2O	CH_3CN
[1a]Cl	90	
[1a](BF_4)		98
[1b]Cl	91	
[1b](BF_4)		113
[2a]Cl	74	
[2a](BF_4)	65	
[2b]Cl		78
[2b](BF_4)	96	
[3a]Cl	89	

Table 8 ESI Crystal data and structure refinement for **[2a](BF_4)**.

Empirical formula	$C_{22}H_{22}BClF_4N_2ORu$
Formula weight	553.75
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	17.274(6)
b(Å)	16.130(6)
c(Å)	16.903(6)
β(°)	96.644(5)
Volume($Å^3$)	4678(3)
Z	8
Density (calculated) (g/cm^3)	1.572
Absorption coefficient (mm^{-1})	0.833
F(000)	2224
Crystal size (mm^3)	0.41 x 0.41 x 0.32
Index ranges	$-20 \le h \le 20$ $-19 \le k \le 19$ $-20 \le l \le 20$
Reflections collected	43230
Independent reflections	8237 [R(int) = 0.1085]
Data / restraints / parameters	8237 / 54 / 621
Goodness-of-fit on F^2	1.026
Final R indices [$I>2\sigma(I)$]	R1 = 0.0591, wR2 = 0.1517
Largest diff. peak and hole, $e.Å^{-3}$	1.577 and -0.900

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] GOF = $\{\Sigma\,[w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

Table 9 ESI Some Intermolecular hydrogen bonding parameters for complex **[2a](BF$_4$)**.[a]

Interaction	d(D---A) Å	d(H---A) Å	d(D-H) Å	D-H---A (º)	Bond strength[b]
C5-H5---F7	3.238	2.313	0.980	156.97	weak
C6-H6---Cl2	3.615	2.698	0.980	156.07	weak
C36-H36---F3	3.073	2.144	0.978	157.95	strong
C35-H35---Cl1	3.687	2.771	0.980	155.86	weak
C32-H32---F6	3.411	2.591	0.931	147.34	weak
C31-H31---F5	3.356	2.546	0.929	145.88	weak
C47-H47---F8	3.429	2.637	0.929	143.50	weak
O3-H2(O3)---F7	3.343	2.600	0.817	151.81	weak
C19-H19C---O1	3.320	2.613	0.959	130.79	weak
C22-H22C---O1	3.628	2.695	0.959	164.48	weak
C49-H49B---O2	3.397	2.698	0.959	130.20	weak

[a] Calculated with Mercury, versión 3.0. [b] Bond strength according to Steiner [*].
[*]T. Steiner, *Angew. Chem.-Int. Edit.*, 2002, **41**, 48-76.