Supporting Information

1. Syntheses and characterization of 1b·PF_6 and [(η^6-p-cymene)Ru(*k*NPh,*k*^{2}NO)] (3a).

[(η^6-p-cymene)Ru(*k*NHBn,*k*NOH)Cl]PF_6 (1b·PF_6): KPF_6 (0.05 g, 0.26 mmol) was added to a CH_2Cl_2 (15.0 mL) solution of **1b** (0.15 g, 0.26 mmol), and the mixture was stirred overnight. The resulting suspension was filtered to remove insoluble KCl and the solvent was evaporated to dryness from the orange solution to afford an orange solid, which was identified as compound **1b·PF_6** (yield 0.16 g, 90 %). $C_{27}H_{38}ClF_6N_2OPRu$ (688.09): calcd. C 47.13, H 5.57, N 4.07; found C 46.80, H 4.89, N 3.32. IR (KBr): ν = 3300-3100 (NH/OH), 1646, 1614 (C=N) cm^{-1}. ^{1}H NMR (400.1 MHz, 293 K, $CDCl_3$): δ = 7.41 (overlapped, 5H, -C_6H_5), 5.85, 5.81 (both d, each 1H, $^3J_{HH}$ = 6, p-cymene-C_6H_4), 5.46, 5.44 (both d, each 1H, $^3J_{HH}$ = 8, p-cymene-C_6H_4), 4.78 (s, 1H, =CH_2), 4.61 (m, 2H, -CH_2Ph) 4.53 (br, 1H, =CH_2), 3.92 (m, 1H, NH), 3.61 (d, 1H, $^2J_{HH}$ = 14, -CH_2^6), 2.58 (spt, 1H, $^3J_{HH}$ = 6, p-cymene-$CHMe_2$), 2.55 (br, 1H, -CH^5), 2.32 (dd, 1H, $^2J_{HH}$ = 16, $^3J_{HH}$= 6, -CH_2^6), 1.97 (overlapped, 4H, p-cymene-CH_3 + $CH_2^{3,4}$), 1.81 (m, 1H, -$CH_2^{3,4}$), 1.64 (m, 1H, -$CH_2^{3,4}$), 1.66 (s, 3H, CH_3-C=), 1.36 (m, 1H, -$CH_2^{3,4}$), 1.19, 0.99 (both d, each 3H, $^3J_{HH}$ = 6, p-cymene-CH(C***H*****$_3$**)$_2$) ppm. ^{31}P NMR (161.9 MHz, 293 K, $CDCl_3$): δ = – 144.0 (spt, $J_{P\text{-}F}$ = 692 Hz, PF_6) ppm. ^{19}F NMR (376.5 MHz, 293 K, $CDCl_3$): δ = – 72.5 (d, $J_{P\text{-}F}$ = 692 Hz, PF_6) ppm.

[(η^6-p-cymene)Ru(*k*NPh,*k*^{2}NO)] (3a): A THF solution of **1a** (0.25 g, 0.44 mmol) was treated with NaOMe (0.05 g, 0.98 mmol) at room temperature. After stirring of the mixture during 2 hours, evaporation of the THF and extraction from the solid residue with toluene affords an orange solution from which an orange solid was isolated, washed with hexane (5x2 mL) and fully characterized as derivative **3a** (yield 0.18 g, 83 %). $C_{26}H_{34}N_2ORu$ (491.63): calcd. C 63.52, H 6.97, N 5.70; found C 63.99, H 6.90, N, 5.53. IR (KBr): ν = 1622, 1590 (C=N) cm^{-1}. ^{1}H NMR (plus HSQC, plus HMBC, plus COSY, 400.1 MHz, 293 K, $CDCl_3$): δ = 7.28 (m, 2H, $C_6H_5^{o/m}$), 7.16 (m, 1H, $C_6H_5^{p}$), 7.10 (m, 2H, $C_6H_5^{o/m}$), 5.26 (d, 1H, $^3J_{HH}$ = 6, p-cymene-C_6H_4), 5.12 (1H, =CH_2), 5.10, 5.02, 4.81 (both d, each 1H, $^3J_{HH}$ = 6, p-cymene-C_6H_4), 4,73 (br, 1H, =CH_2), 3.88 (d, 1H, $^2J_{HH}$ = 16, -CH_2^6), 2.63 (spt, 1H, $^3J_{HH}$ = 6, $CHMe_2$), 2.38 (br, 1H, -CH^5), 2.12 (s, 3H, p-cymene-CH_3), 1.85 (dd, 1H, $^2J_{HH}$ = 16, $^3J_{HH}$ = 6, -CH_2^6), 1.61 (overlapped, 4H, CH_3-C= + -CH_2^4), 1.47 (overlapped, 2H, 1-CH_2^4 + 1-CH_2^3), 1.25, 1.23 (overlapped, both d, each 3H, $^3J_{HH}$ = 6, CH(C***H*****$_3$**)$_2$), 1.17 (m, 1H, -CH_2^3), 1.05 (s, 3H, HNC-C***H*****$_3$**) ppm. ^{13}C-NMR (plus APT, plus gHSQC, plus HMBC, 100.6 MHz, 293 K, $CDCl_3$): δ = 163.4 (−, C=N-O), 158.3 (−, C_{ipso}-Ph), 144.9 (−, *C*=CH_2), 128.0, 126.6, 125.2 (+, -$C_6H_5^{o,m,p}$), 112.3 (−, =CH_2), 100.3, 89.9 (−, C_{ipso}-p-cymene), 83.1, 82.9, 82.6, 80.8 (+, p-cymene-C_6H_4), 77.7 (−, C-N-Ru), 42.1 (+, -CH^5), 33.8 (−, -CH_2^3), 31.4 (+, p-cymene-$CHMe_2$), 26.2 (−, -CH_2^4), 25.3 (-CH_2^6), 24.1, 24.0 (both +, p-cymene-CH(*C*H_3)$_2$), 23.8 (+, *C*H_3-CNH), 22.8 (+, *C*H_3-C=), 20.0 (+, p-cymene-CH_3) ppm. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, $CDCl_3$): δ = 329.0 (=NO), 263.5 (Ru-NPh) ppm.

Preligands a, b, c and compounds 1a, 1b and 2b

Syntheses and characterization of amino-oxime derivatives (2S,5R)-[NHR,NOH][1] (R = **a**, **b**, **c**) and ruthenium compounds [(η^6-p-cymene)Ru(*k*NHR,*k*NOH)Cl]Cl (R = Ph **1a**, Bn **1b**)[2] and [(η^6-p-cymene)Ru(*k*NHBn,k^2NO)Cl] (**2b**)[2] was reported elsewhere. During this work, we performed the IR and ^{15}N-^{1}H HMBC spectra of all these compounds, as well as the spectroscopic NMR characterization in methanol-d_4 of compounds **1a** and **1b**, since their NMR spectra in $CDCl_3$ changed dramatically with the concentration (see Dilution Spectra, page S9). Solubility in water of **1a**, **1b** and **2b** is given in mM concentration. Data are given in the following section:

(2S,5R)-[NHPh,NOH] (a). IR (KBr): ν = 3100-3300 (NH/OH), 1644, 1602 (C=N) cm^{-1}. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, $CDCl_3$): δ = 343.3 (=NOH), 84.1 (NHPh) ppm.

(2S,5R)-[NHBn,NOH] (b). IR (KBr): ν = 3100-3320 (NH/OH), 1644, 1602 (C=N) cm^{-1}. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, $CDCl_3$): δ = 340.0 (=NOH), 60.0 (NHBn) ppm.

(2S,5R)-[NH(2-pic),NOH] (c). IR (KBr): ν = 3086-3314 (NH/OH), 1650, 1595 (C=N) cm^{-1}. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, $CDCl_3$): δ = 343.3 (=NOH), 305.3 (=Npic), 51.8 (NH(2-pic)) ppm.

[(η^6-p-cymene)Ru(*k*NHPh,*k*NOH)Cl]Cl (1a): IR (KBr): ν = 3391-3151 (NH/OH), 1642, 1597 (C=N) cm^{-1}. Solubility in H_2O at 24 ºC (mM): 21± 2. Value of pH ([9.0 mM]) in H_2O at 24 ºC: 4.62.

^{1}H NMR (plus HMBC, gHSQC, plus COSY, 400.1 MHz, 293 K, CD_3OD): δ = 7.89, 7.65, 7.52, 7.41, 7.02 (all br, each 1H, C_6H_5), 6.19, 5.86, 5.52 (all d, each 1H, $^3J_{HH}$ = 6, C_6H_4), 5.39 (s, 1H, NH), 4.85, 4.85 (overlapped with CD_3OD, 2H, C_6H_4 + =CH_2), 4.60 (br, 1H, =CH_2), 3.66 (d, 1H, $^2J_{HH}$ = 15, CH_2^6), 2.71 (spt, 1H, $^3J_{HH}$ = 7, p-cymene-$CHMe_2$), 2.53 (m, 1H, -CH^5), 2.56 (m, 1H, -CH_2^6), 2.27 (s, 3H, p-cymene-CH_3), 1.78 (m, 1H, -CH_2^4), 1.79 (s, 3H, CH_3-C=), 1.67 (s, 3H, PhNC-CH_3), 1.55 (m, 3H, -CH_2^4+ -CH_2^3), 1.13, 0.62 (both d, each 3H, $^3J_{HH}$ = 7, p-cymene-CH(CH_3)$_2$) ppm. ^{13}C NMR (plus APT, plus gHSQC, plus HMBC, 100.6 MHz, 293 K, CD_3OD): δ = 170.2 (−, C=NO), 146.3 (−, =C-Me), 144.1 (−, C_{ipso}-Ph), 130.8, 130.8, 129.2, 125.6, 126.2, 114.2 (−, =CH_2), 106.3 (−, C_{ipso}, p-cymene-*C*CHMe$_2$), 98.8 (−, C_{ipso}, p-cymene-CMe), 87.3, 86.1, 87.9, 81.9 (all +, p-cymene-C_6H_4), 71.6 (−, C-NH), 49.9 (+, -CH^5), 36.0 (−, -CH_2^3), 31.9 (+, p-cymene-$CHMe_2$), 28.9 (−, -CH_2^6), 24.1 (+, p-cymene-CH(*C*H$_3$)$_2$), 24.7 (-CH_2^4), 22.6 (+, *C*H_3-C=), 22.2 (+, *C*H_3-CNPh), 19.0 (+, p-cymene-CH(*C*H$_3$)$_2$), 18.6 (+, p-cymene-CH_3) ppm. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, $CDCl_3$): δ = 272.1 (=NOH), 68.1 (NHPh) ppm. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, CD_3OD): δ = 266.5 (=NOH), 68.2 (NHPh) ppm.

[(η^6-p-cymene)Ru(*k*NHBn,*k*NOH)Cl]Cl (1b): IR (KBr): ν = 3400-3040 (NH/NOH), 1643, 1600 (C=N) cm^{-1}. Solubility in H_2O at 24 ºC (mM): 28 ± 4. Value of pH ([9.0 mM]) in H_2O at 24 ºC: 4.70.

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[1] Carman, R. M.; Mathew, P. C.; Saraswathi, G. N.; Singaram, B.; Verghese, J. *Aust. J. Chem.* **1977**, *30*, 1323

[2] Ibn El Alami, M. S.; El Amrani, M. A.; Dahdouh, A.; Roussel, P.; Suisse, I.; Mortreux, A. *Chirality* **2012**, *24*, 675-682 and references therein.

^{1}H NMR (plus gHSQC, plus HMBC, plus COSY, 400.1 MHz, 293 K, CD_3OD): δ = 7.45 (m, 5H, C_6H_5), 5.85, 5.84, 5.46, 5.33 (d, each 1H, $^{3}J_{HH}$ = 6, p-cymene-C_6H_4), 4.79 (m, 1H, =CH_2), 4.62 (second order system, 2H, -CH_2Ph), 4.60 (br, 1H, =CH_2), 4,02 (br, 1H, NH), 3.60 (d, 1H, $^{2}J_{HH}$ = 16, CH_2^{6}), 2.53 (overlapped, 3H, p-cymene-$CHMe_2$ + CH_2^{6} + CH^{5}), 2.14 (m, 1H, -CH_2^{3}), 1.99 (s, 3H, p-cymene-CH_3), 1.83 (m, 2H, -CH_2^{4}), 1.66, 1.65 (both s, each 3H, BnNC-CH_3 + CH_3-C=), 1.39 (m, 1H, -CH_2^{3}), 1.22, 1.02 (both d, each 3H, $^{3}J_{HH}$ = 8, p-cymene-CH(C*H*$_3$)$_2$) ppm. ^{13}C- NMR (plus APT, plus gHSQC, 100.6 MHz, 293 K, CD_3OD): δ = 170,8 (−, C=N), 145.9 (−, =*C*-CH_3), 137.1 (−, C_{ipso}-Ph), 130.1, 129.5, 129.4 (all +, -$C_6H_5^{(o,m,p)}$), 113.2 (−, =CH_2), 108.9, 98.8 (both −, C_{ipso}-p-cymene), 87.5, 84.8, 83.3, 83.2 (all +, -C_6H_4), 70.5 (−, C-NH), 55.9 (−, *C*H_2Ph), 39.4 (+, -CH^{5}), 35.4 (−, -CH_2^{3}), 32.5 (+, p-cymene-$CHMe_2$), 29.1 (−, -CH_2^{6}), 25.1 (-CH_2^{4}), 23.9 (+, p-cymene-CH(*C*H_3)$_2$), 22.3 (+, *C*H_3-C-NH), 20.8 (+, p-cymene-CH(*C*H_3)$_2$), 20.7 (+, *C*H_3-C=), 18.4 (+, p-cymene-CH_3) ppm. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, $CDCl_3$): δ = 272.0 (=NOH), 50.4 (NHBn) ppm. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, CD_3OD): δ = 266.7 (=NOH), 50.0 (NHBn) ppm.

[(η^{6}-p-cymene)Ru(*k*NHBn,*k*NO)Cl] (2b). IR (KBr): v = 3400-3060 (NH/NOH), 1700, 1643 (C=N) cm^{-1}. Solubility in H_2O at 24 ºC (mM): 20.0 ± 4. ^{15}N NMR (gHMBC, 40.5 MHz, 293 K, $CDCl_3$): δ = 291.7 (=NOH), 50.4 (NHBn) ppm.

2. ^{1}H NMR dilution data

Dilutions experiments were carried out from an initial stock solution. This initial stock solution (500μL) was diluted with 100 μL of $CDCl_3$ and the dilution process sequentially repeated for the next 9 samples.

OriginLab Software was used for least-squares curve fitting to the theoretical equation:

Dimerization model, Eq.1: δ = δm + ((δd-δm)*(1+((1-((8*Ka*C)+1)^(1/2)))/(4*Ka*C))) or

Infinite association model, Eq.1: δ = δm + ((δa-δm)*(1+((1-((4*Ka*C)+1)^(1/2)))/(2*Ka*C)))

Where δm = calculated chemical shift of the monomer, δd = calculated chemical shift of the dimer; Ka = association constant; C = Total concentration; δa = average chemical shift of aggregates.

1a. ^{1}H NMR dilution data of 1a and 1b in $CDCl_3$

Table S1. Tabulated ^{1}H NMR dilution data for the $-CH_2$[6] protons of **1a** at 22 ºC

Conc[a]	δ$-CH_2$[6]
65,185	3,752
32,592	3,780
21,728	3,799
16,296	3,810
13,037	3,818
10,864	3,824
9,312	3,829
8,148	3,831
7,243	3,836
6,518	3,839
δm[b]	3.871±0.003
δd[c]	3.619±0.009
Ka[d]	13.27±1.5
R[e]	0.99915

[a]Total milimolar concentration of compound.[b] calculated chemical shifts for the monomer. [c] calculated chemical shifts for the dimer. [d] Association constant of dimerization (M^{-1}). [e] goodness-of-fit value

Figure S1. Concentration dependence of ^{1}H NMR chemical shifts for the –CH_2^6 proton of **1a** in $CDCl_3$

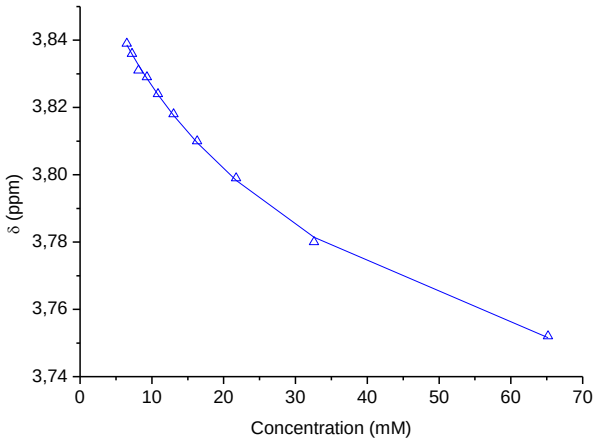
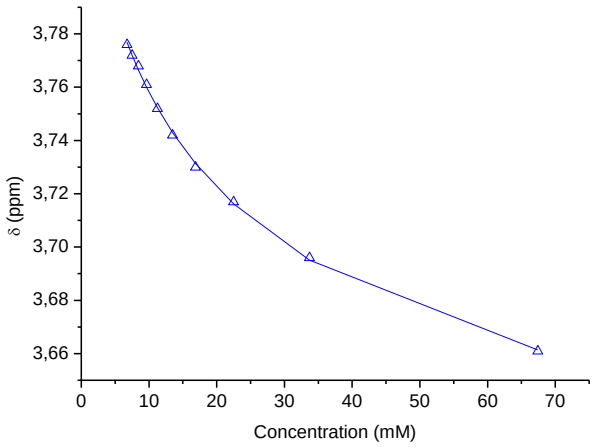


Table S2. Tabulated ^{1}H NMR dilution data for the –CH_2^6 protons of **1b** at 22 ºC

Conc[a]	δ–CH_2^6
67.406	3.661
33.703	3.696
22.469	3.717
16.851	3.730
13.481	3.742
11.234	3.752
9.629	3.761
8,426	3.768
7,489	3.772
6,741	3.776
δm[b]	3.849±0.006
δd[c]	3.542±0.007
Ka[d]	29.95±3.8
R[e]	0.99931

[a]Total milimolar concentration of compound.[b] Calculated chemical shifts for the monomer. [c] Calculated chemical shifts for the dimer. [d] Association constant of dimerization (M^{-1}). [e] goodness-of-fit value

Figure S2. Concentration dependence of ^{1}H NMR chemical shifts for the $-CH_2^6$ proton of **1b** in $CDCl_3$



3. DOSY NMR data

DOSY experiments were acquired in a Bruker Ultra Shield 400 spectrometer, using the ledbpgp2s pulse program. The gradient strength (g) was the variable parameter, while Δ (diffusion time) and δ (diffusion gradient length) were kept constant during the 2D-DOSY study. Appropriate Δ and δ values were selected for each sample by optimization of the attenuation of the ^{1}H NMR signals in 1D-versions of the diffusing ledbpgp1s pulse program. The values of Δ and δ were 40-100 ms and 1.5-2.5 ms, respectively; depending on the sample and the solution concentration (eddy current delay was set to 5 ms in all he experiments). The pulse gradients (g) were incremented from 2 to 95% of the maximum gradient strength in a linear ramp. The diffusion dimension was processed with Bruker topspin T1/T2 software.

Table S3. Full data of diffusion coefficients (Dt, $m^2 \cdot s^{-1}$) for solutions of TMSS (1mM) and TMSO (1mM) at various concentrations (C, mM) of compounds **1a**-**c**, **1b·PF$_6$**, **2b** and **3b** at 295 K.

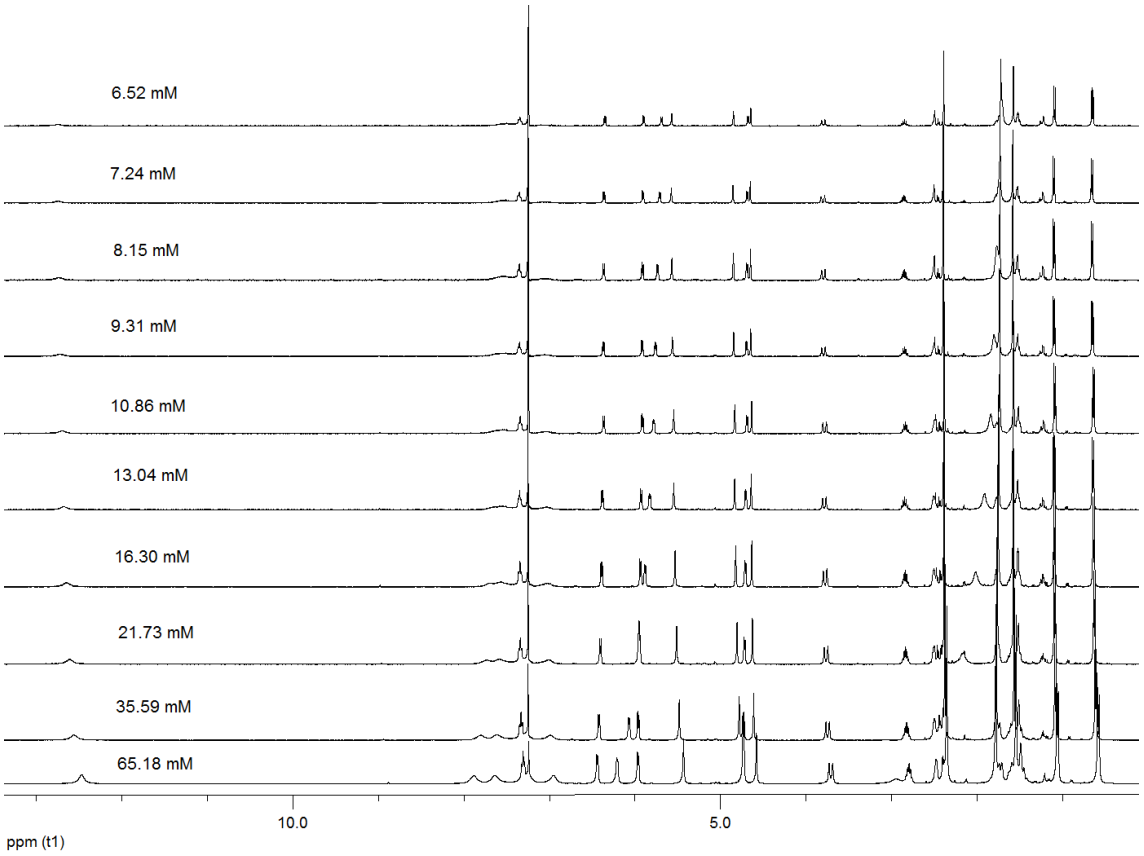
Compound	Solvent	C	$10^{10}\cdot Dt_{(s)}$	$10^{10}\cdot Dt_{(TMSS)}$	$10^{10}\cdot Dt_{(TMSO)}$
1a	$CDCl_3$	11.7	6.957	11.31	10.76
1a	$CDCl_3$	63.0	5.180	11.06	10.56
1a	$CDCl_3$:C_6D_6 [a]	5.31	6.685	10.88	10.13
1a	$CDCl_3$:C_6D_6 [a]	65.5	3.676	10.62	9.952
1a	CD_3OD	14.5	6.966	9.648	9.063
1a	CD_3OD	76.5	6.280	9.265	8.661
1a	$(CD_3)_2CO$	7.75	11.67	18.49	16.72
1a	$(CD_3)_2CO$	64.9	10.02	17.08	15.59
1c	$(CD_3)_2CO$	3.25	10.59	19.61	17.70
1c	$(CD_3)_2CO$	62.1	10.42	19.61	17.70
1b	$CDCl_3$	6.92	7.894	12.62	11.74
1b	$CDCl_3$	30.7	4.442	10.72	10.13
1b	$CDCl_3$	62.5	3.362	10.58	9.848
1b·PF$_6$	$CDCl_3$	6.10	5.473	10.71	10.17
1b PF$_6$	$CDCl_3$	52.3	4.346	10.62	10.07
2b	$CDCl_3$	7.38	5.739	11.03	10.46
2b	$CDCl_3$	81.2	4.830	11.03	10.27
3b	$CDCl_3$	5.82	8.542	11.49	10.66
3b	$CDCl_3$	87.1	7.341	10.67	9.914

[a] $CDCl_3$:C_6D_6 = 8:2

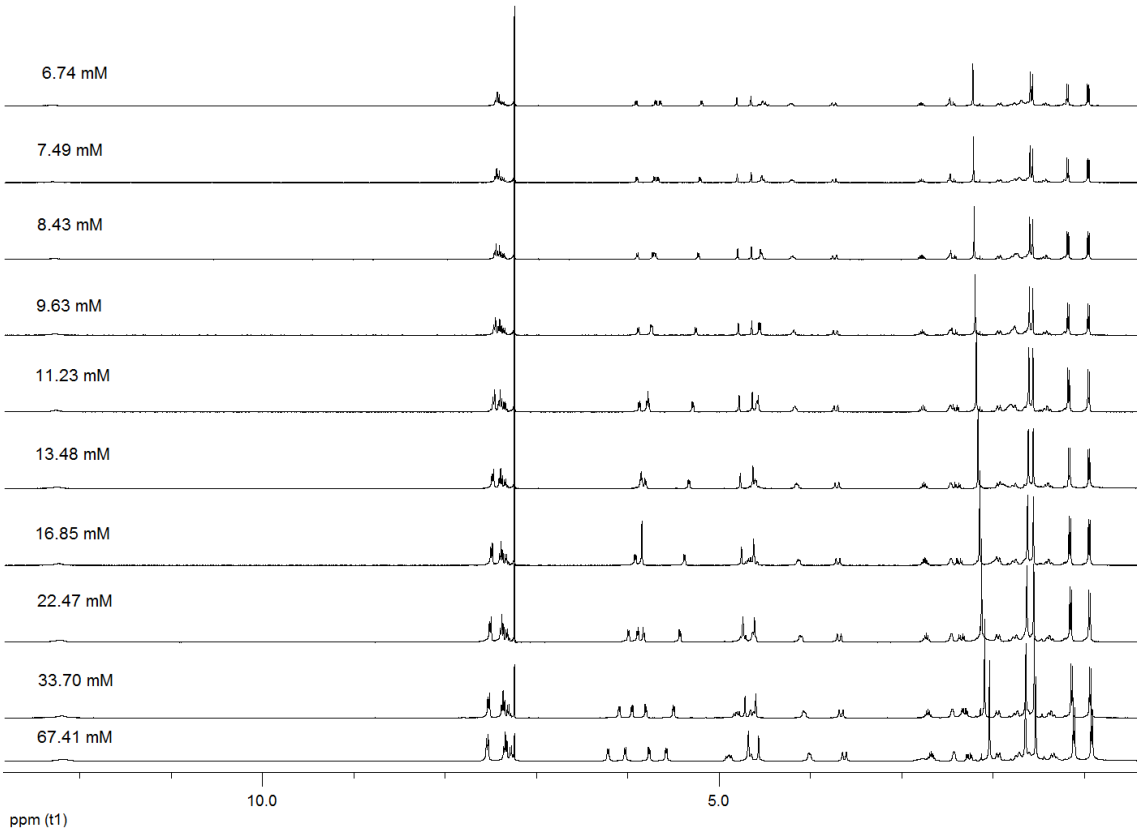
4. Selected NMR spectra

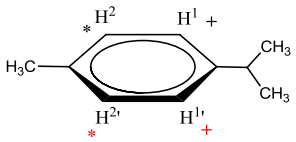
4a. Dilution Spectra

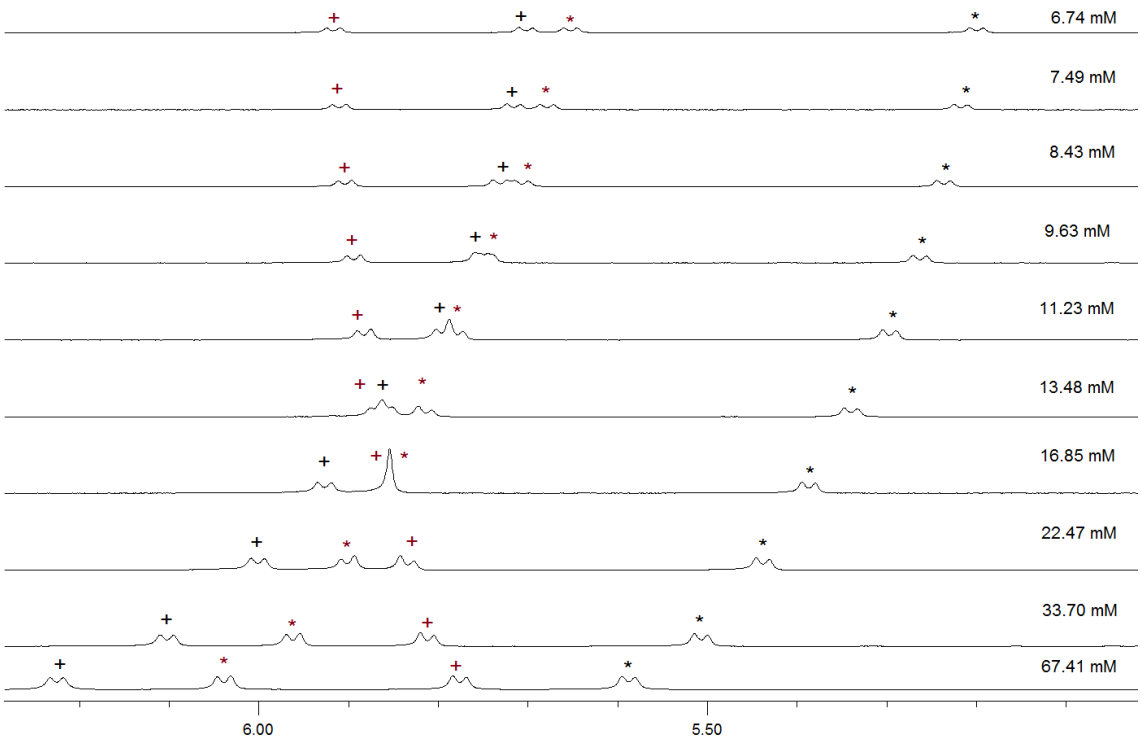
a) ^{1}H NMR of **1a** in $CDCl_3$ at different concentrations (25 ºC)



b) ^{1}H NMR (full and expansion) of **1b** in $CDCl_3$ at different concentrations (25 ºC)

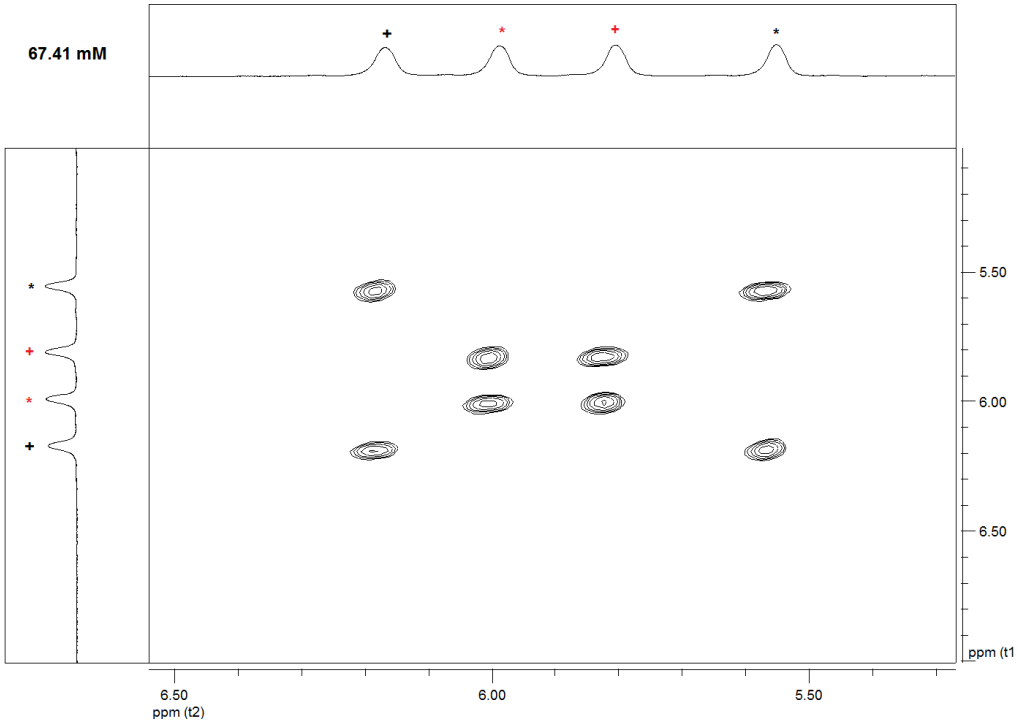




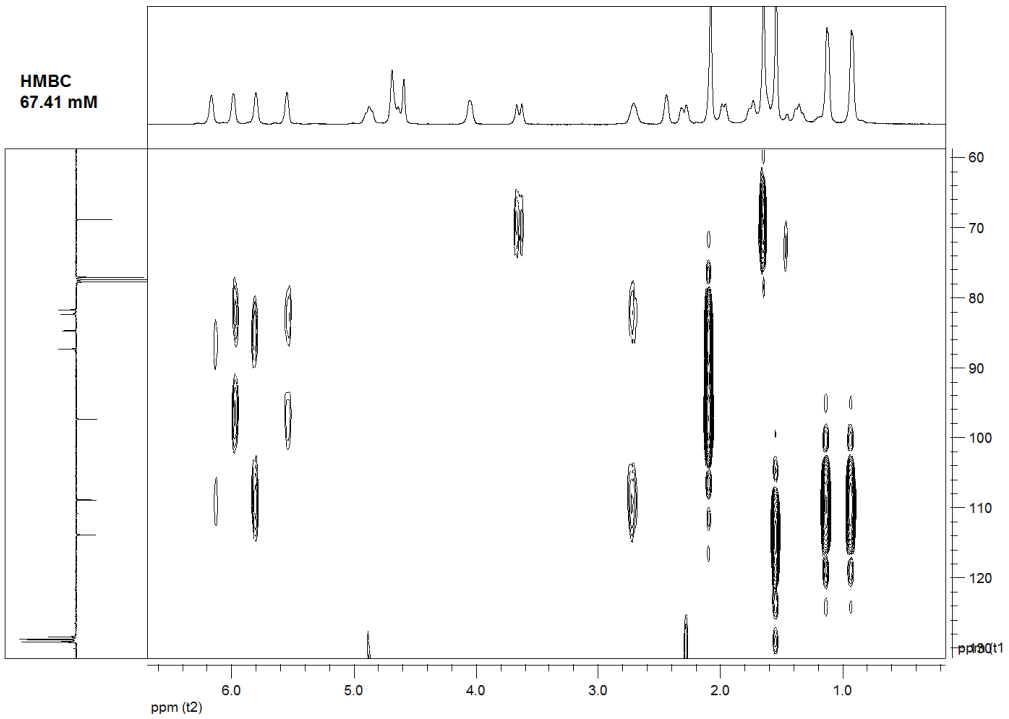


Assignment of p-cymene proton resonances of 1b in $CDCl_3$

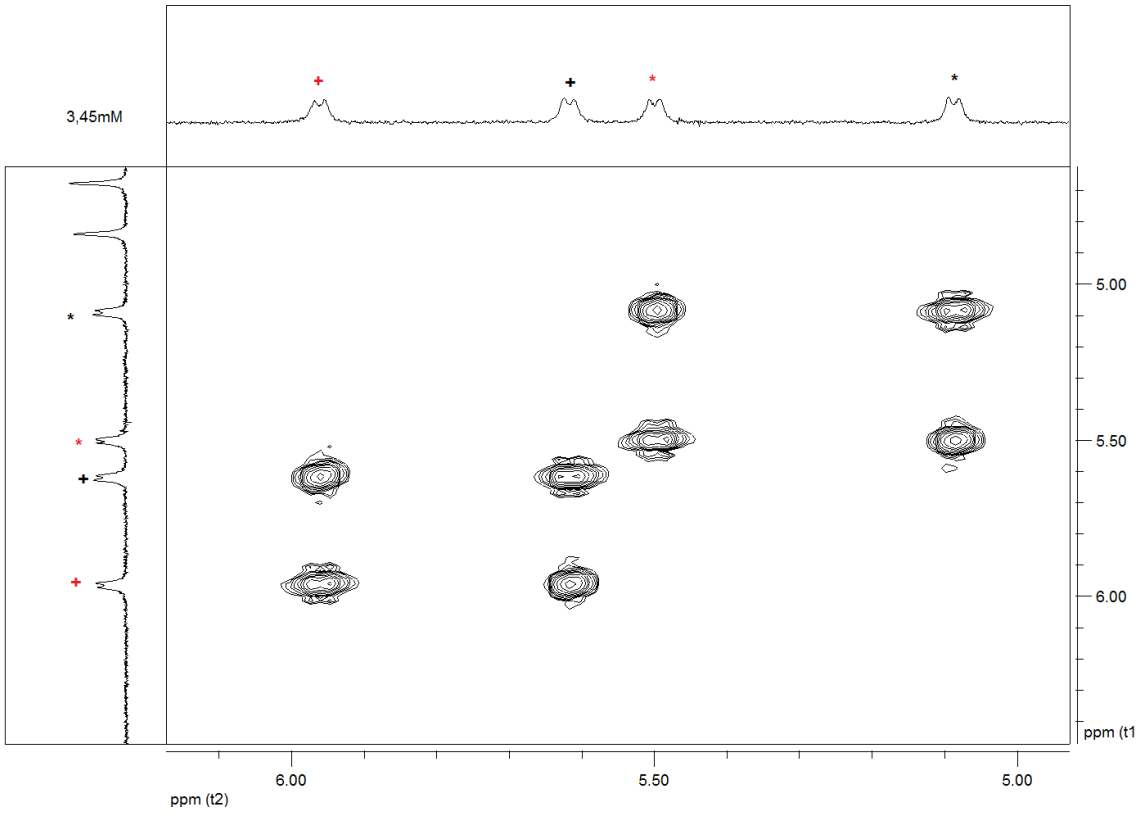
c) Expansion of ^{1}H-^{1}H COSY NMR spectrum of **1b** in $CDCl_3$ (67.41 mM)



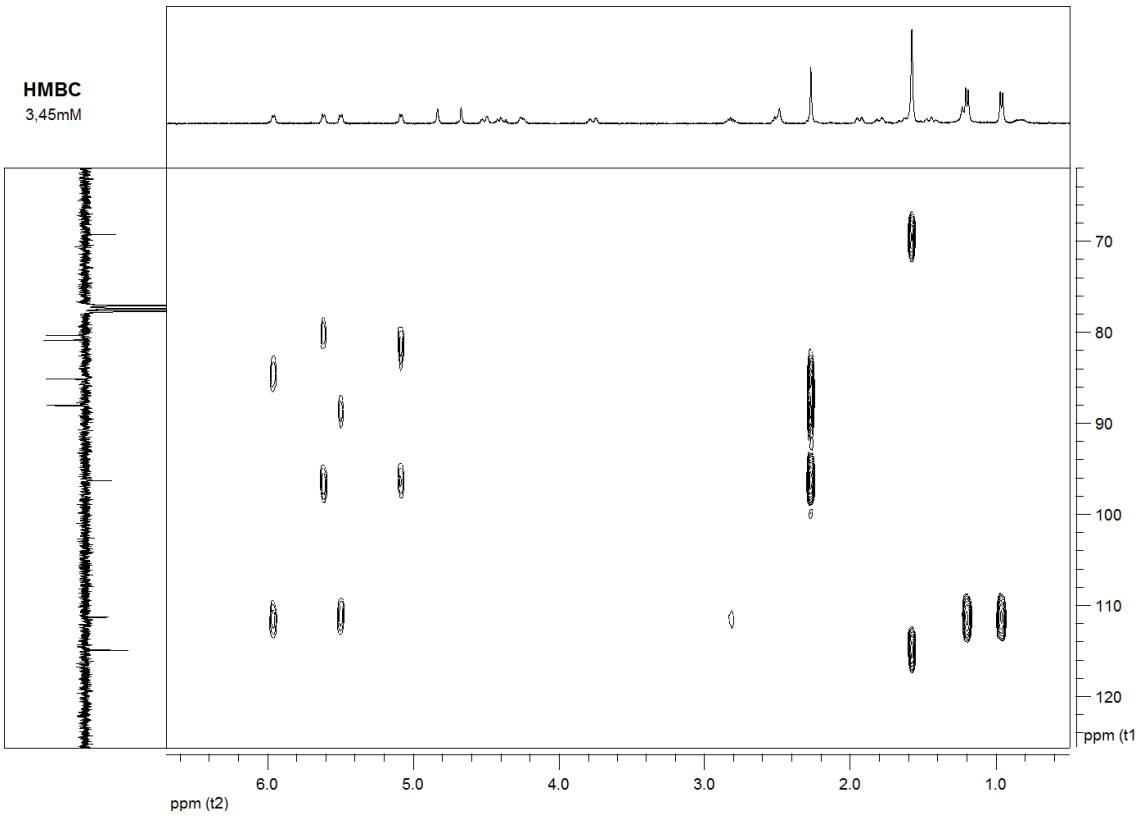
d) Expansion of ^{1}H-^{13}C HMBC NMR spectrum of **1b** in $CDCl_3$ (67.41 mM)



e) Expansion of ^{1}H-^{1}H COSY NMR spectrum of **1b** in $CDCl_3$ (3.45 mM)

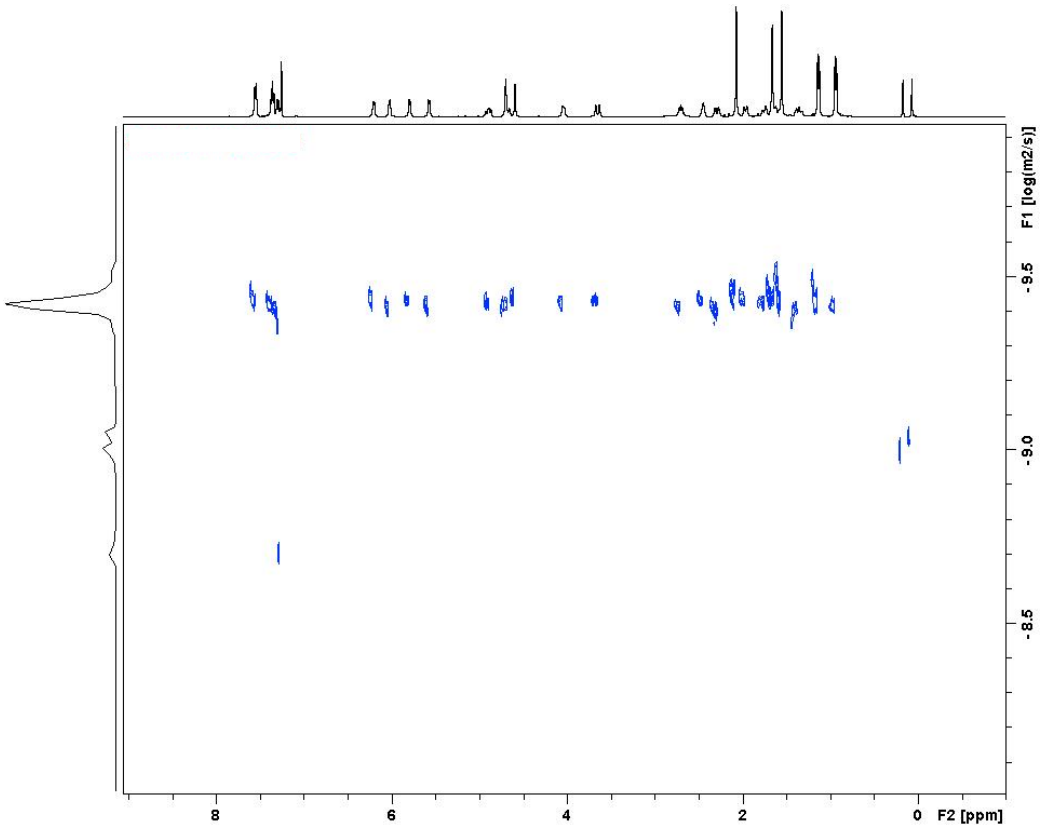


f) Expansion of ^{1}H-^{13}C HMBC NMR spectrum of **1b** in $CDCl_3$ (3.45 mM)

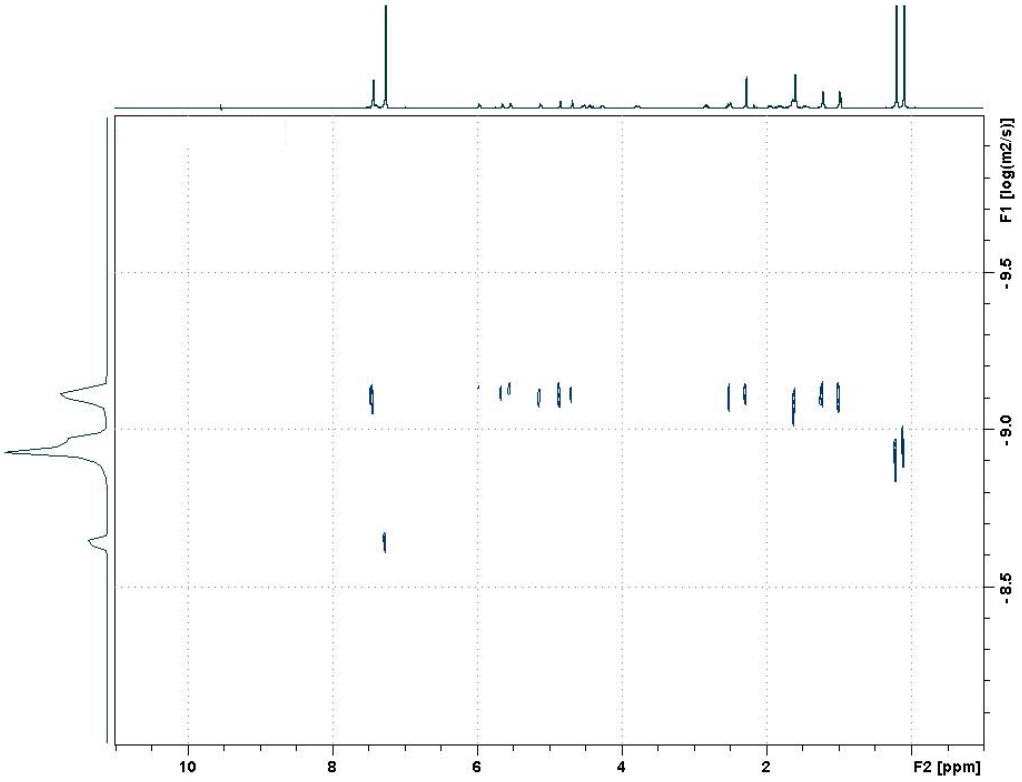


4b. DOSY spectra

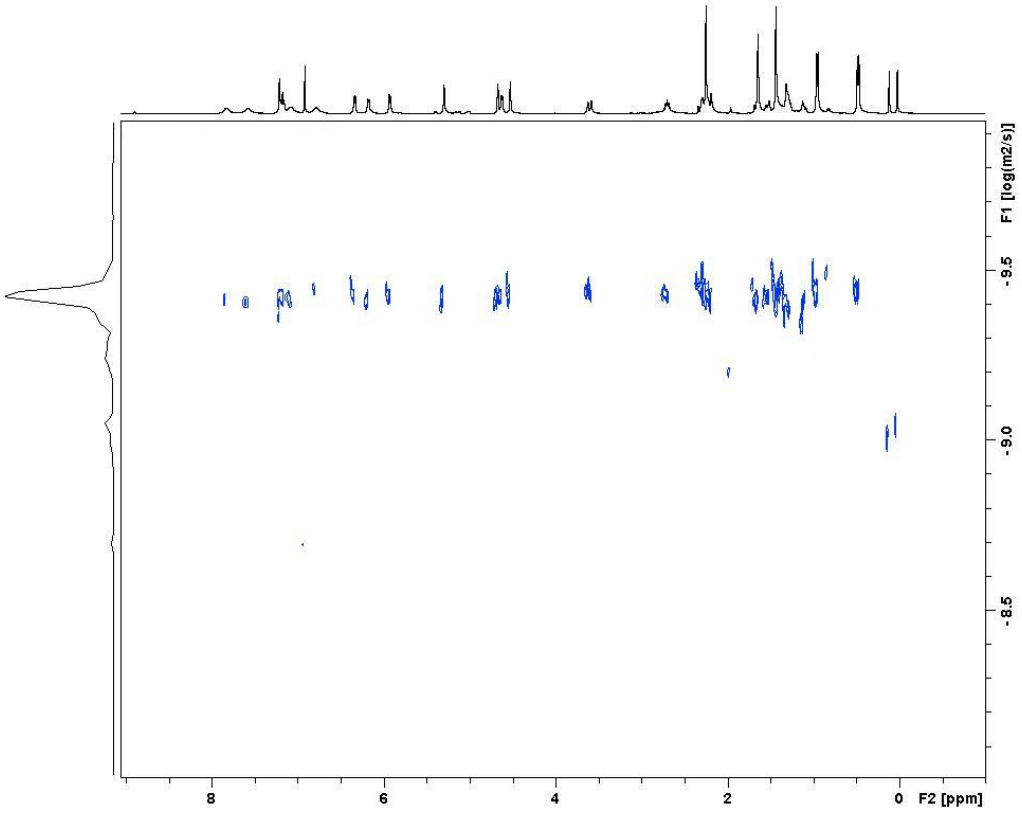
a) DOSY NMR of **1b**, (62,5mM), TMSS (1mM) and TMSO (1mM) in $CDCl_3$



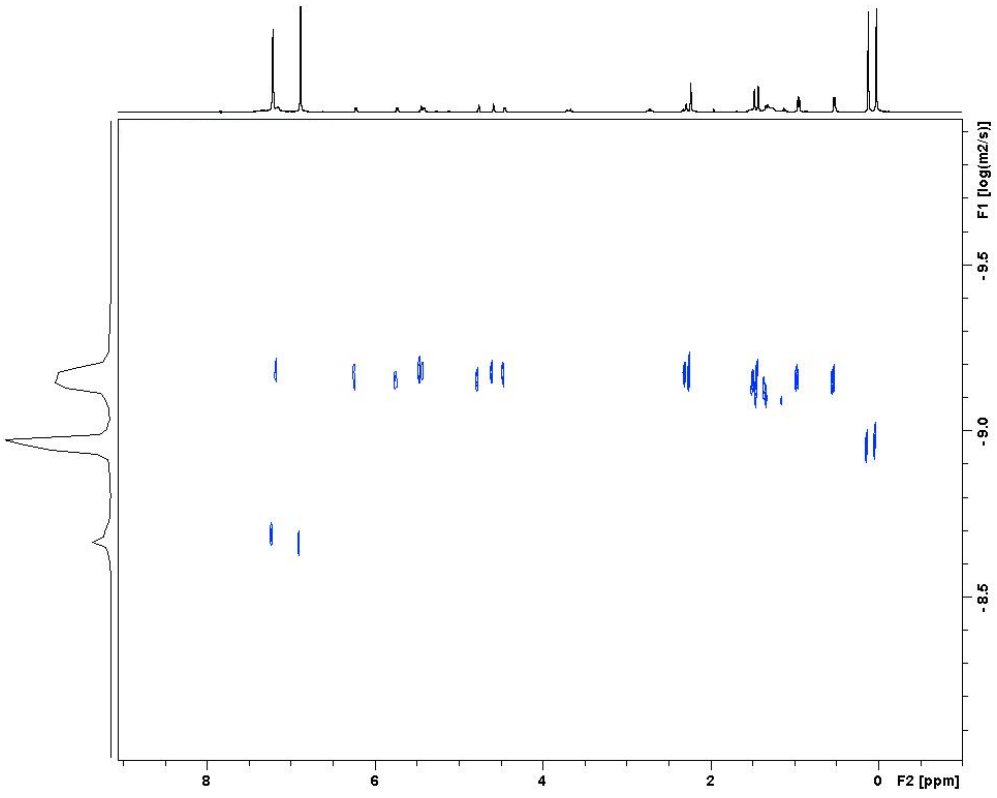
b) DOSY NMR of **1b**, (6.92 mM), TMSS (1mM) and TMSO (1mM) in $CDCl_3$



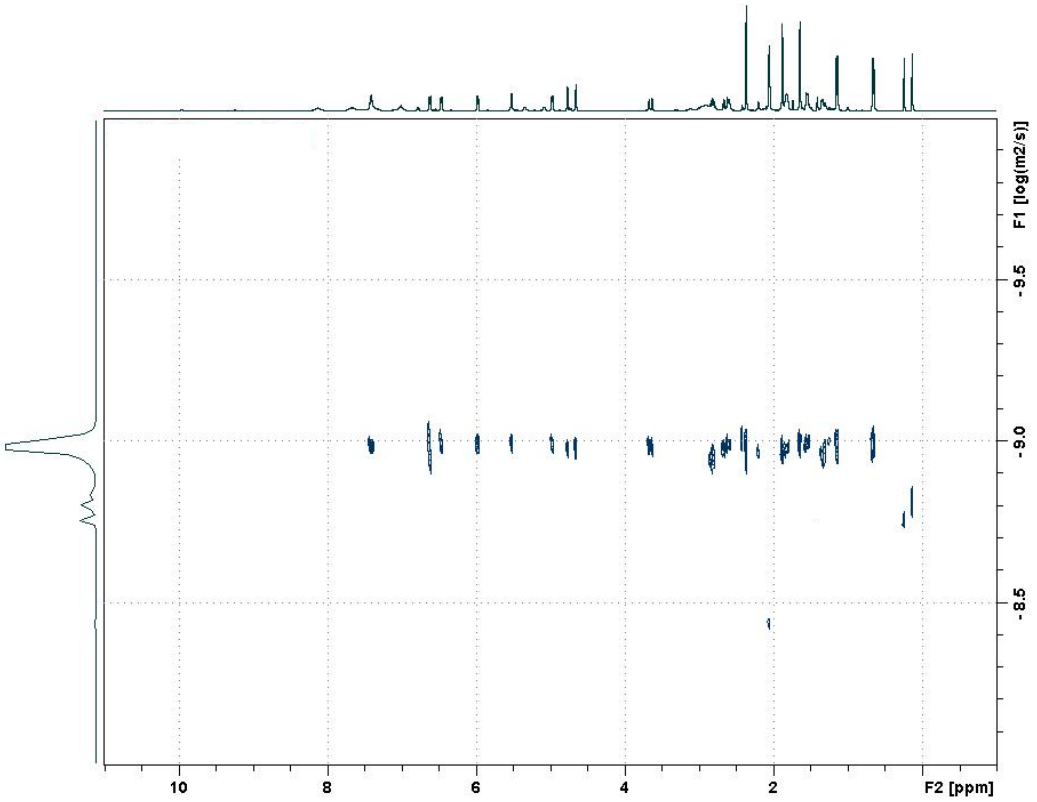
c) DOSY NMR of **1a**, (65.5 mM), TMSS (1mM) and TMSO (1mM) in C_6D_6:$CDCl_3$ (8:2)



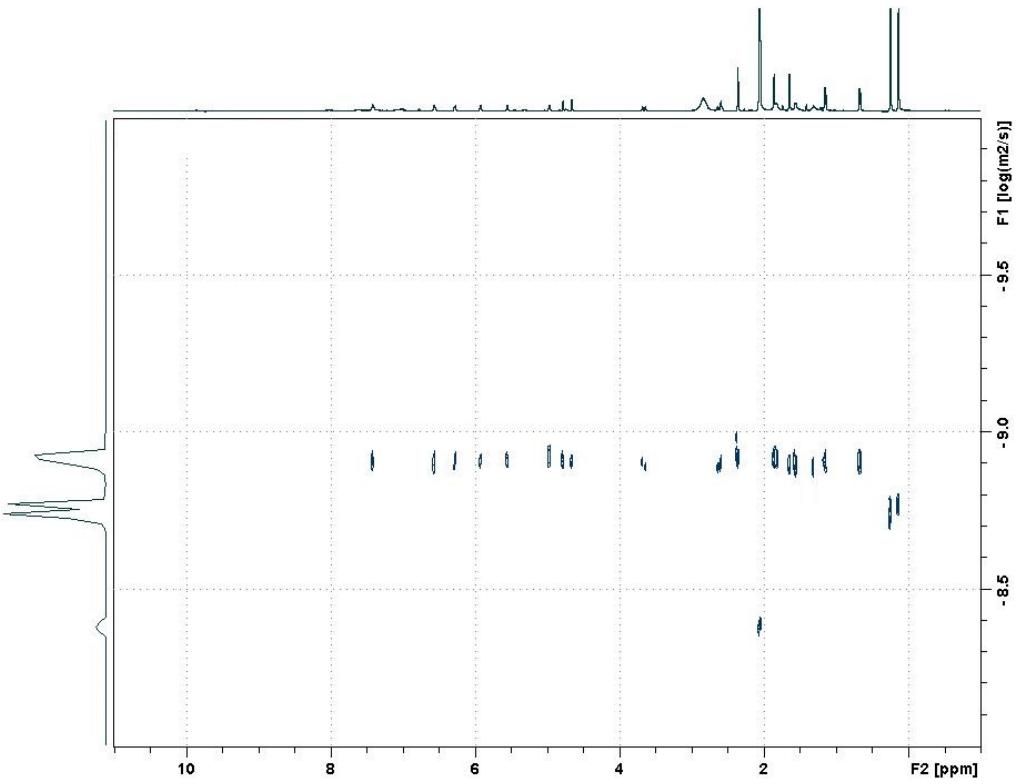
d) DOSY NMR of **1a**, (5.31 mM), TMSS (1mM) and TMSO (1mM) in C_6D_6:$CDCl_3$ (8:2)



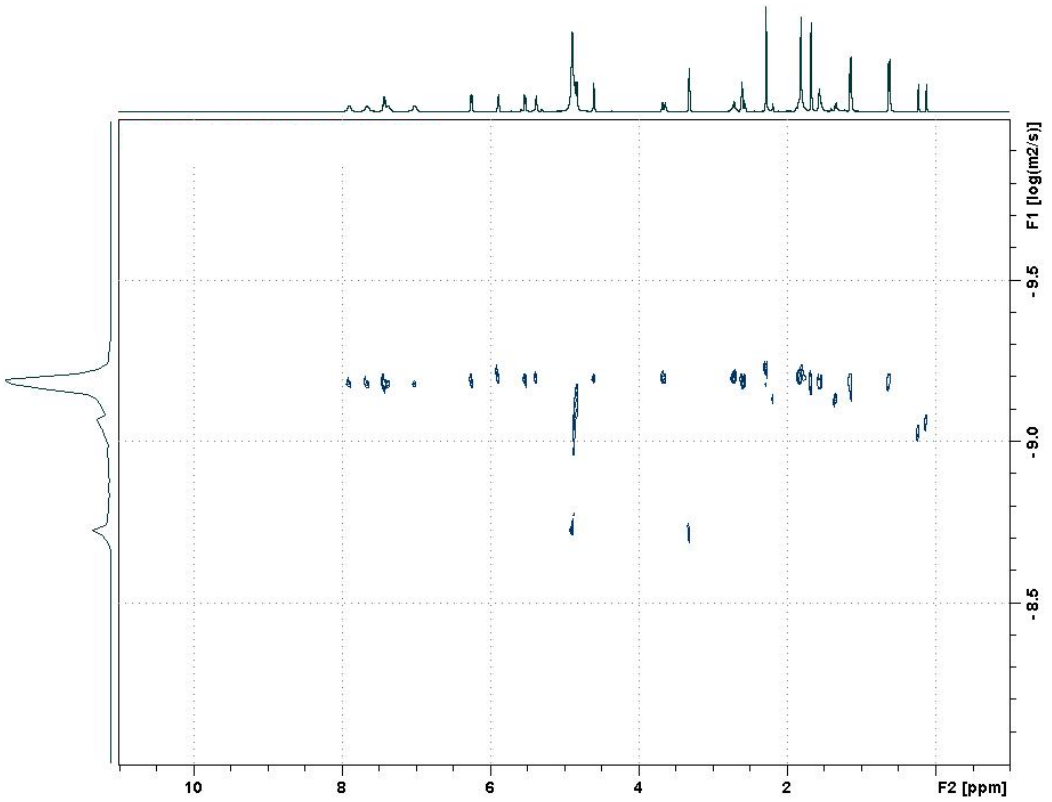
e) DOSY NMR of **1a**, (64.9 mM), TMSS (1mM) and TMSO (1mM) in acetone-d_6



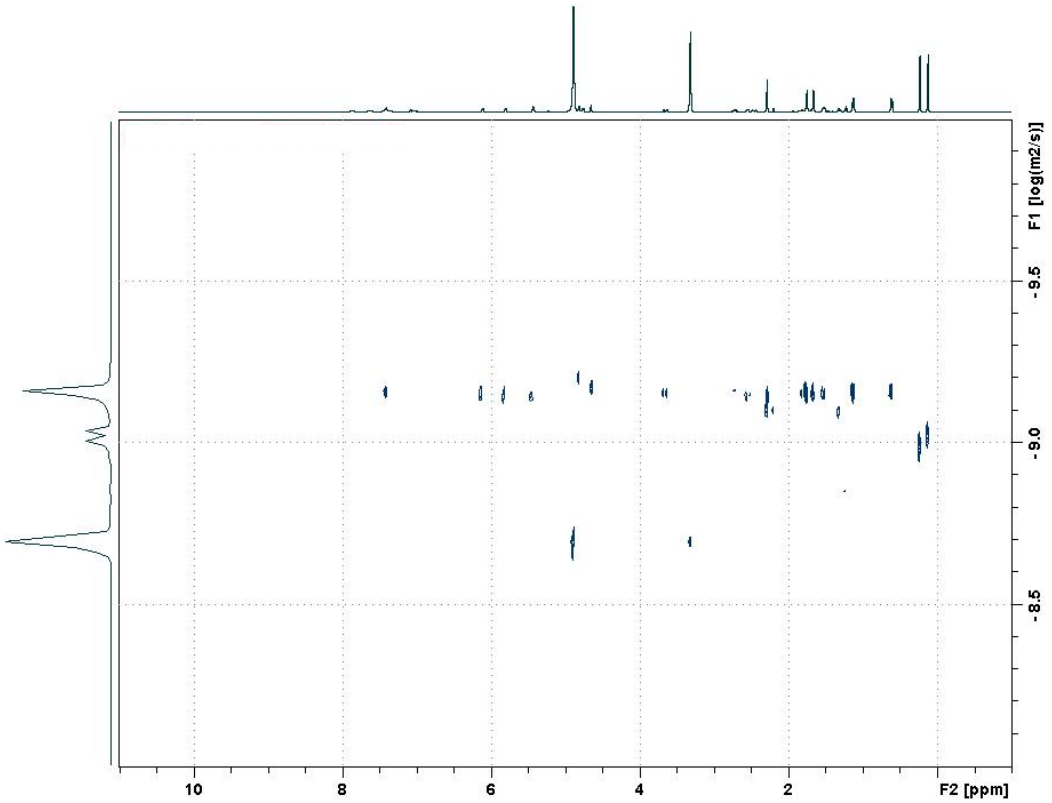
f) DOSY NMR of **1a**, (7.75 mM), TMSS (1mM) and TMSO (1mM) in acetone-d_6



g) DOSY NMR of **1a**, (76.5 mM), TMSS (1mM) and TMSO (1mM) in methanol-d_4

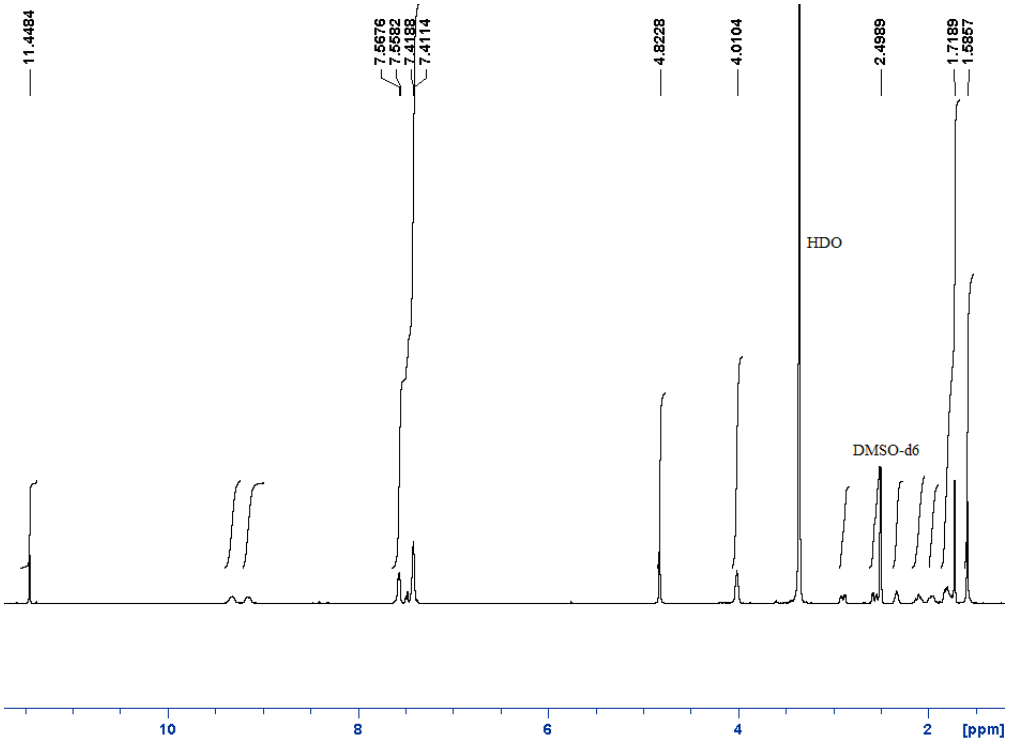


h) DOSY NMR of **1a**, (14.5 mM), TMSS (1mM) and TMSO (1mM) in methanol-d_4

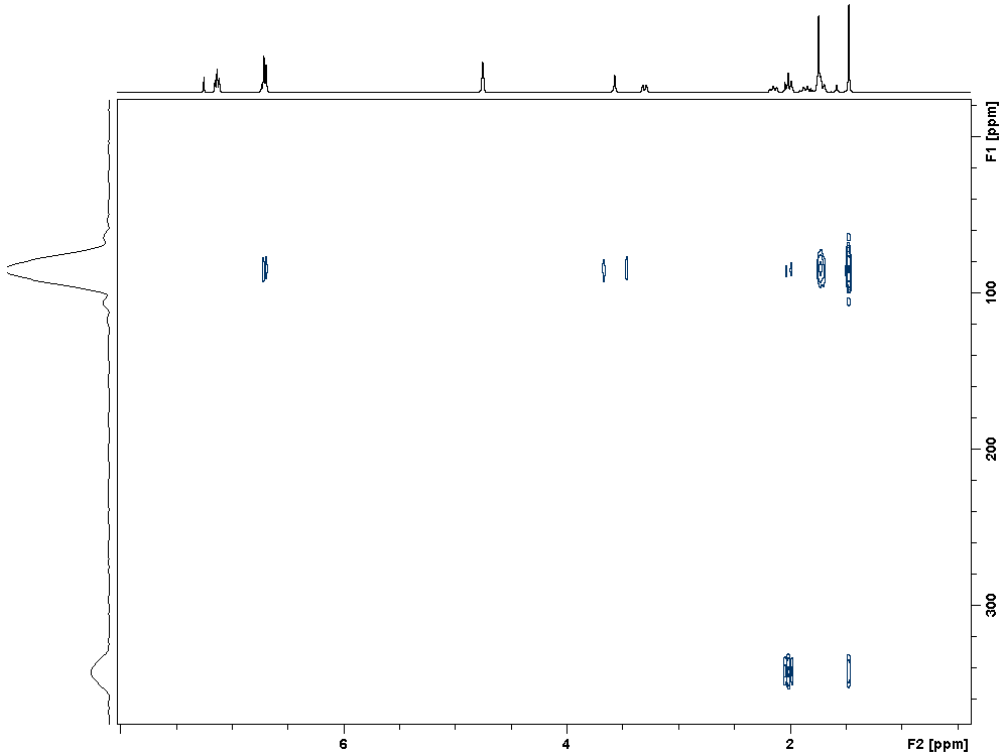


4c. Selected NMR spectra of amino-oxime compounds a, b, b·HCl, c and corresponding ruthenium compounds 1a-c, 2b, 3a and 3b.

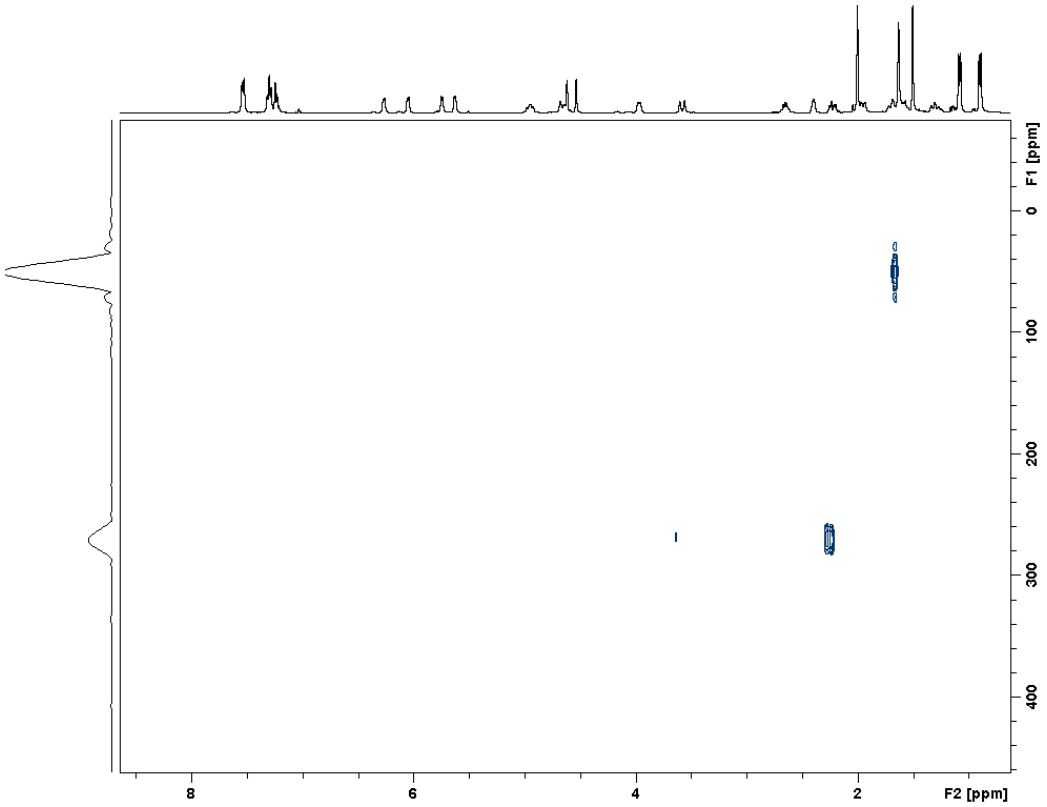
1. ^{1}H NMR of (2S,5R)-[ClH·NHBn,NOH] (**b·HCl**) in DMSO-d_6



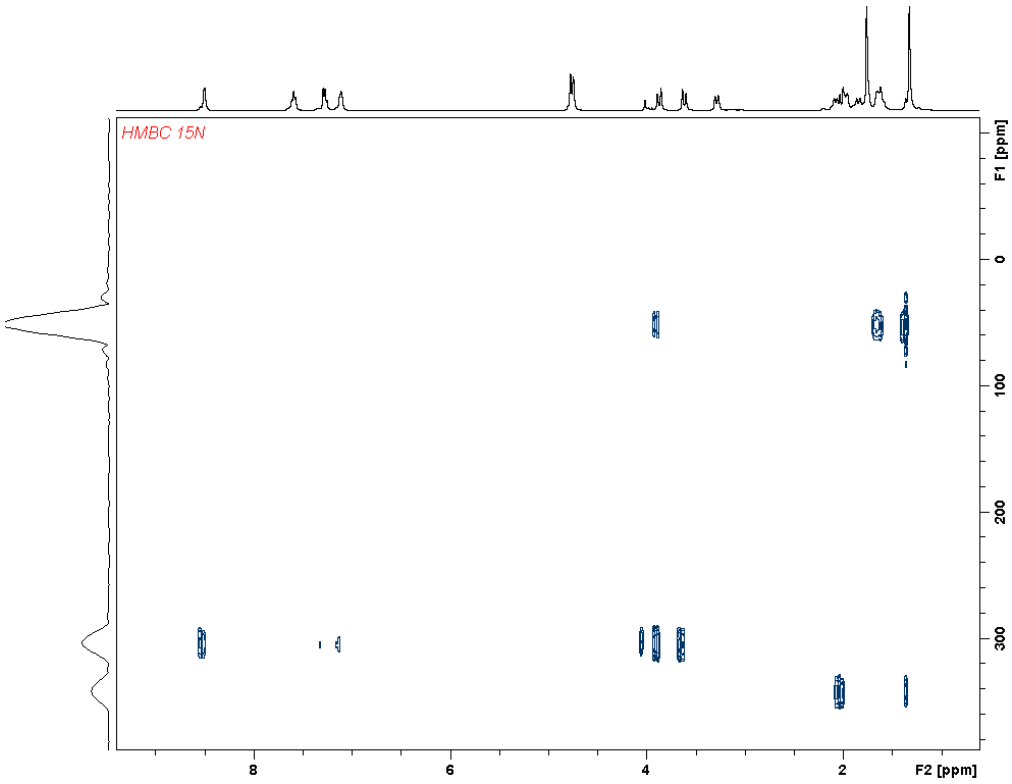
2. ^{1}H-^{15}N HMBC NMR of (2S,5R)-[NHPh,NOH] (**a**) in $CDCl_3$



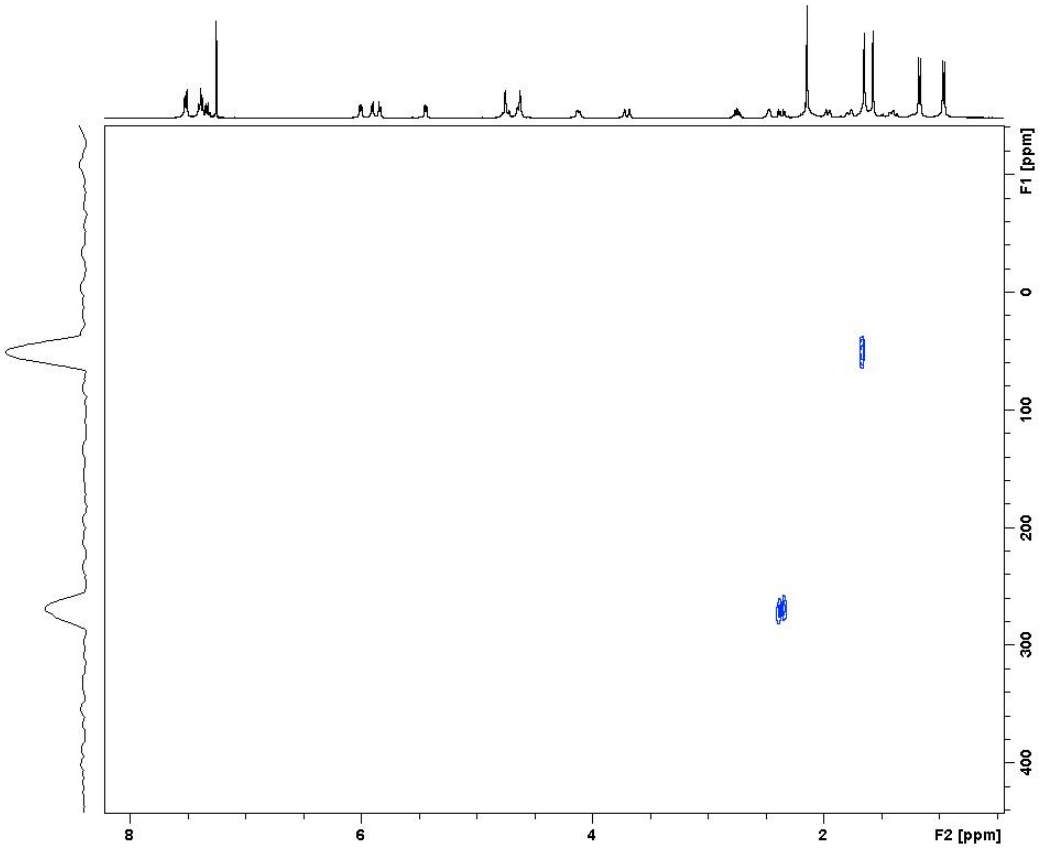
3. ^{1}H-^{15}N HMBC NMR of (2S,5R)-[NHBn,NOH] (**b**) in $CDCl_3$



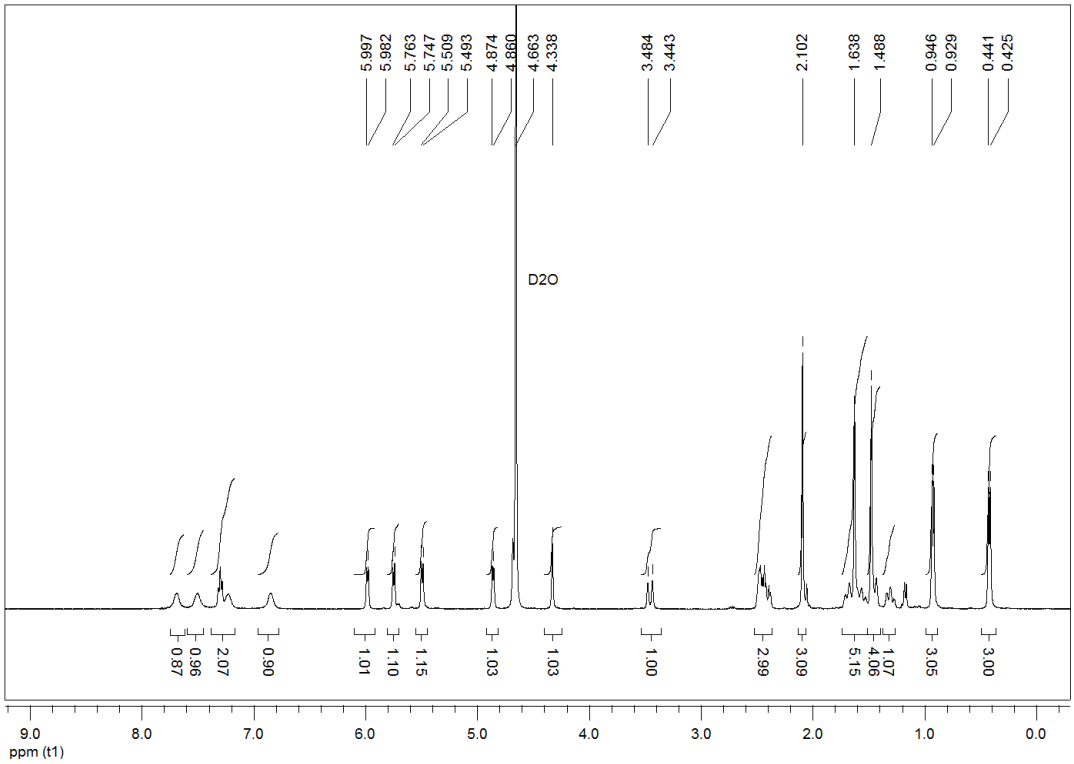
4. ^{1}H-^{15}N HMBC NMR of (2S,5R)-[NH(2-pic),NOH] (**c**) in $CDCl_3$



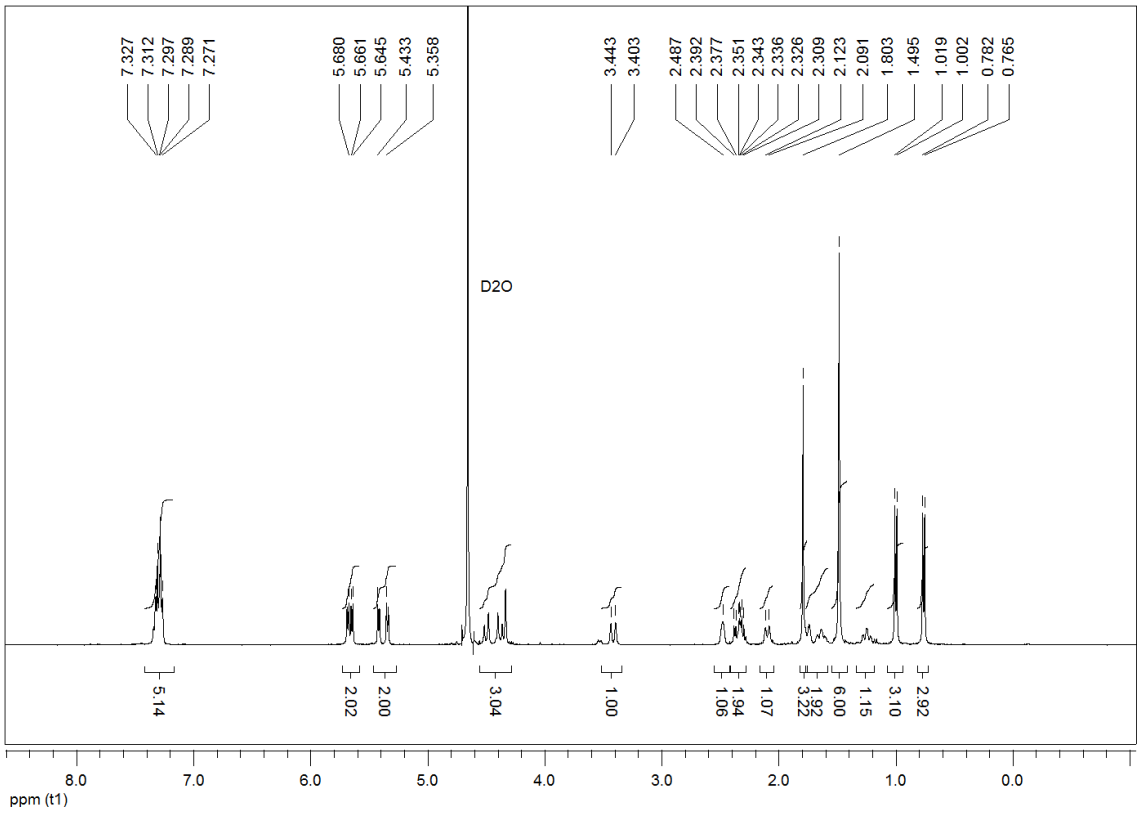
5. ^{1}H-^{15}N HMBC NMR of **1b** in $CDCl_3$



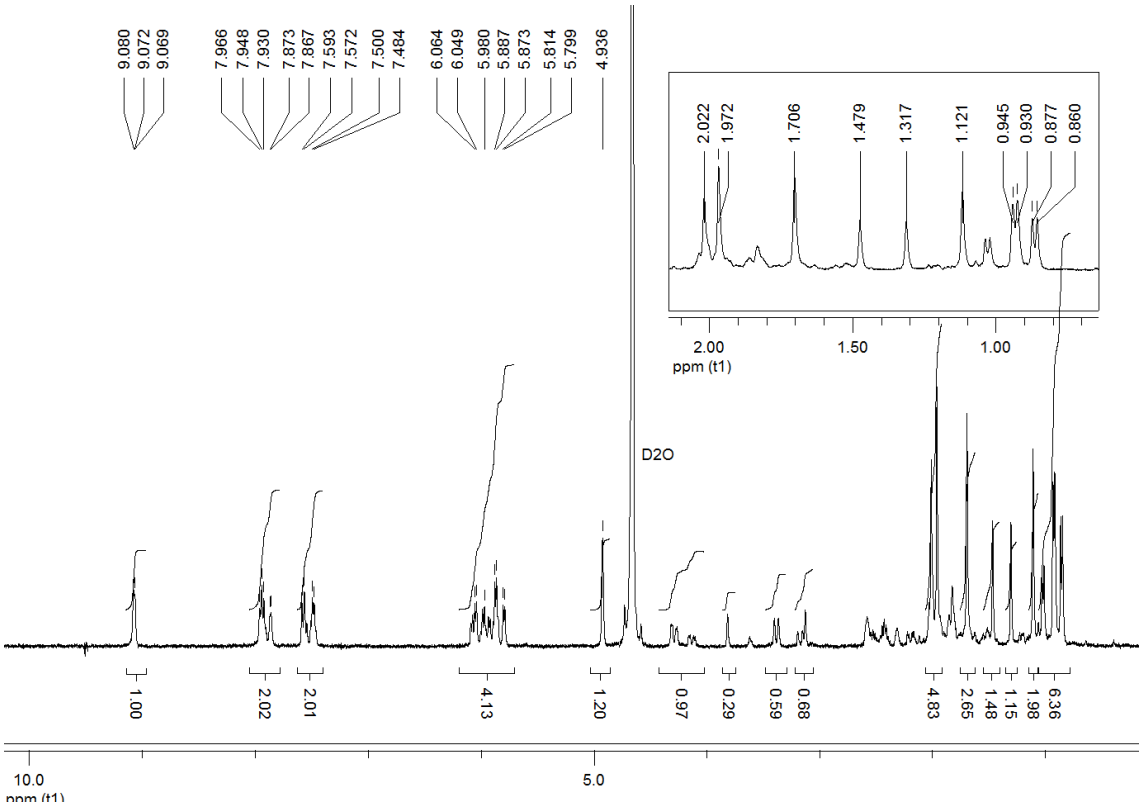
6. ^{1}H NMR of **1a** in D_2O



7. ^{1}H NMR of **1b** in D_2O

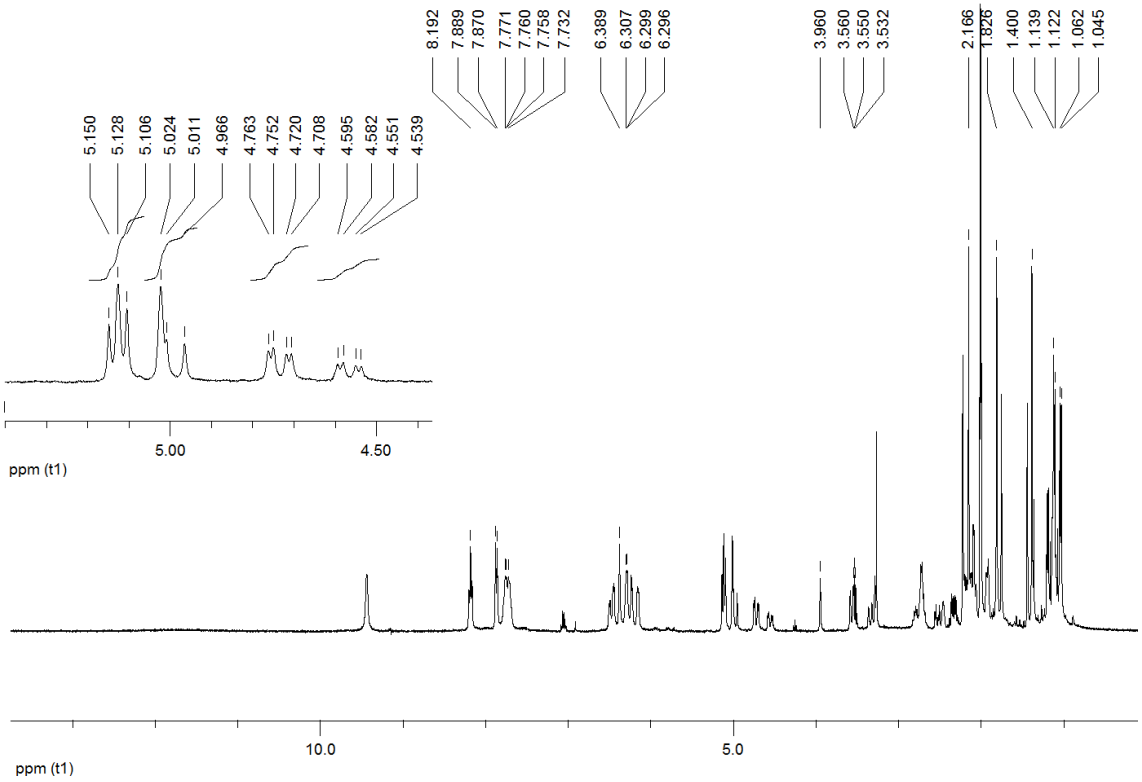


8. ^{1}H NMR of **1c** in D_2O

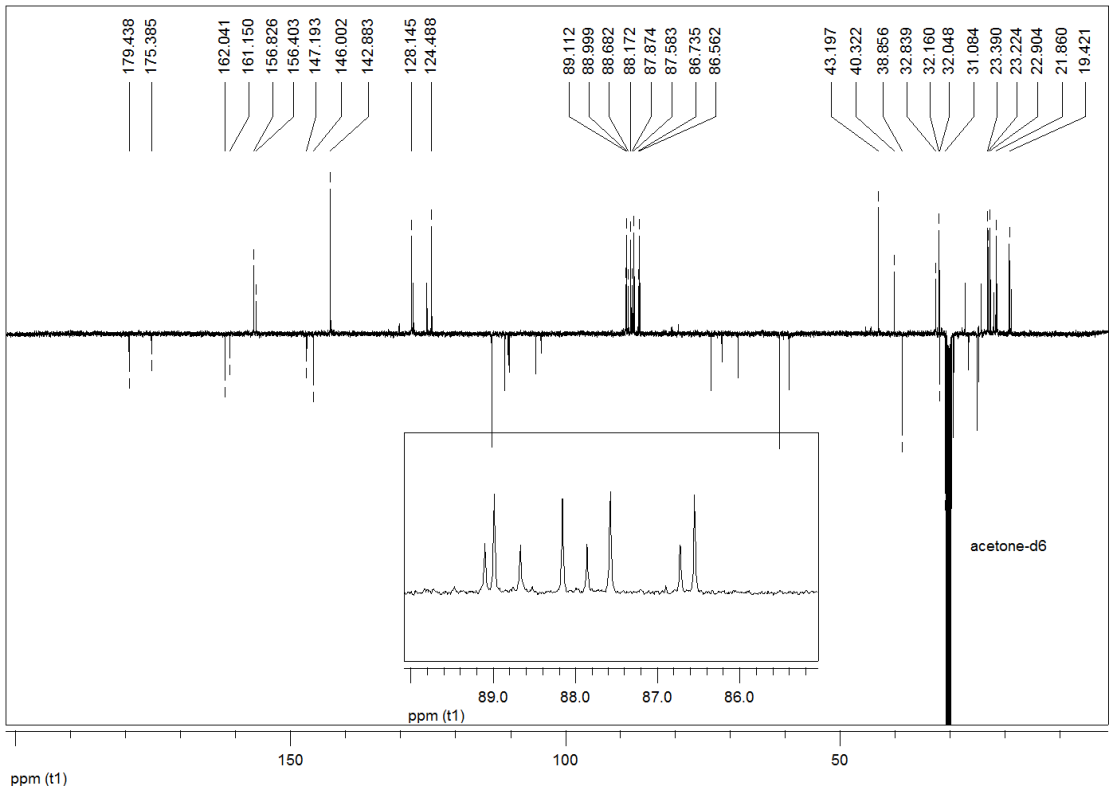


NMR spectra of 1c in acetone-d_6

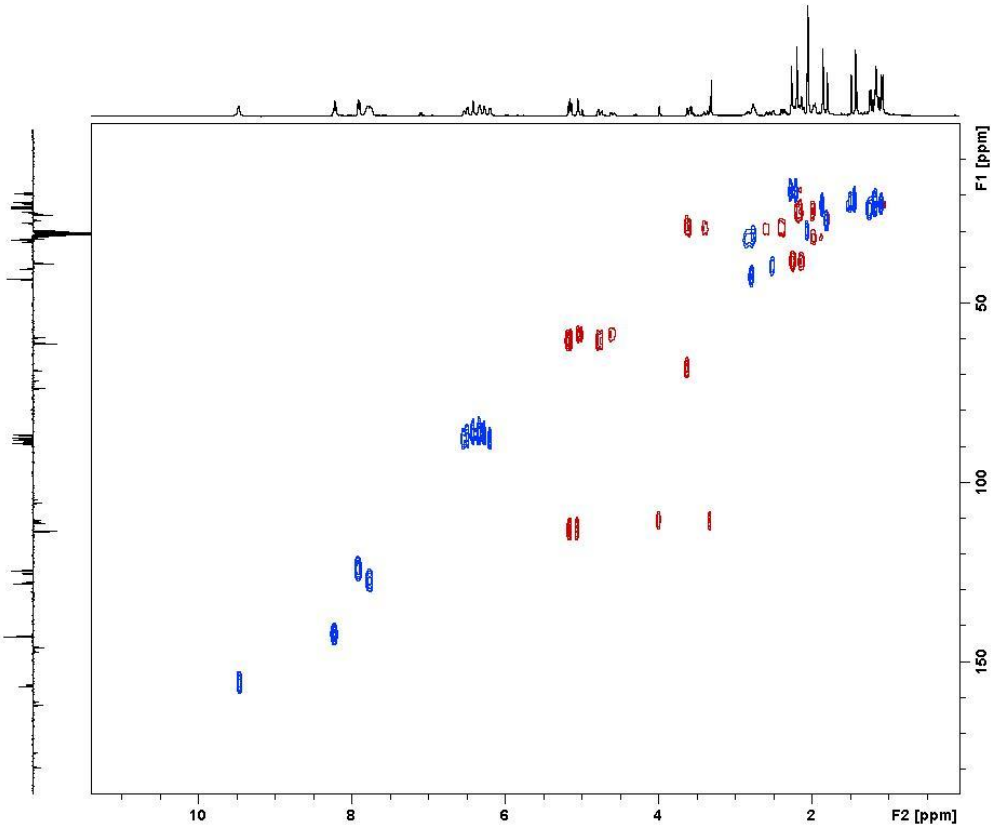
1. ^{1}H NMR of **1c**



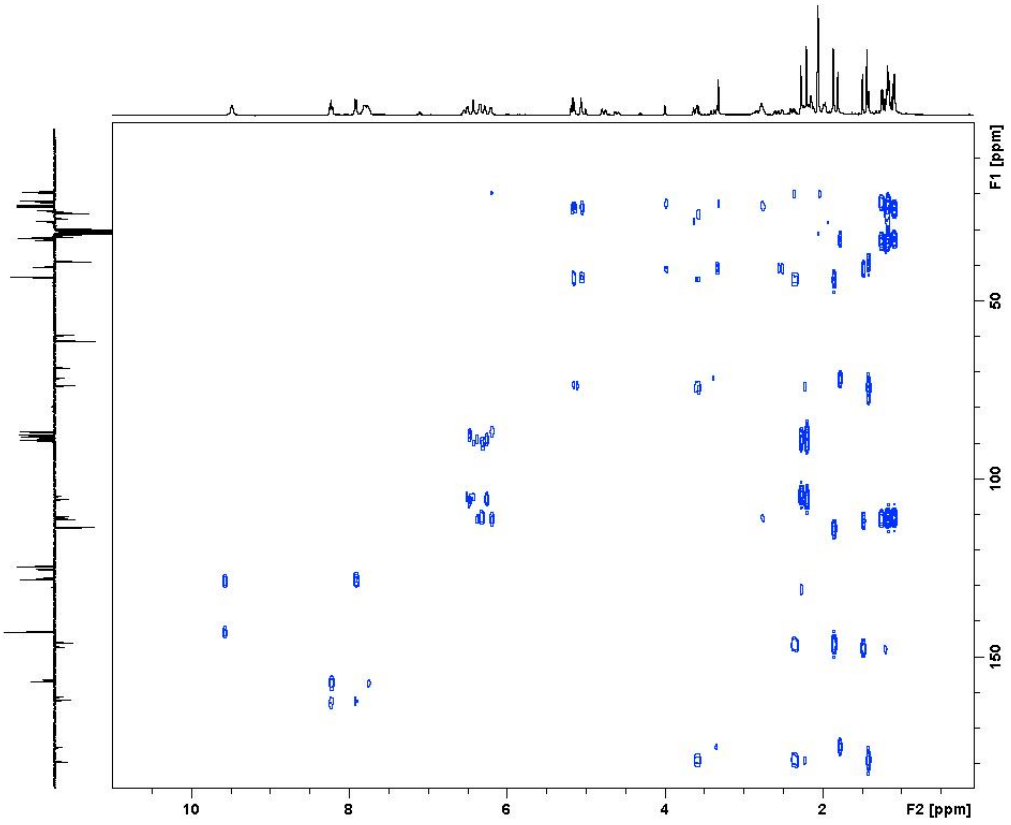
2. ^{13}C APT-NMR of **1c**



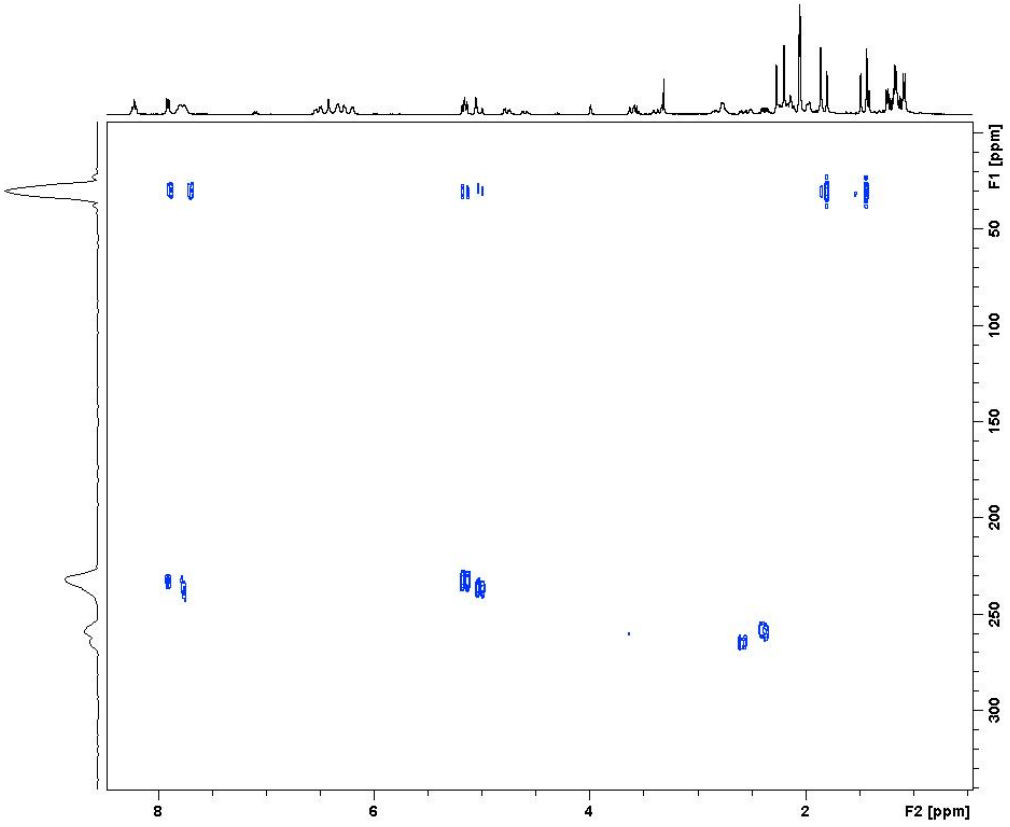
3. ^{1}H-^{13}CHSQC NMR of **1c**



4. ^{1}H-^{13}C HMBC NMR of **1c**

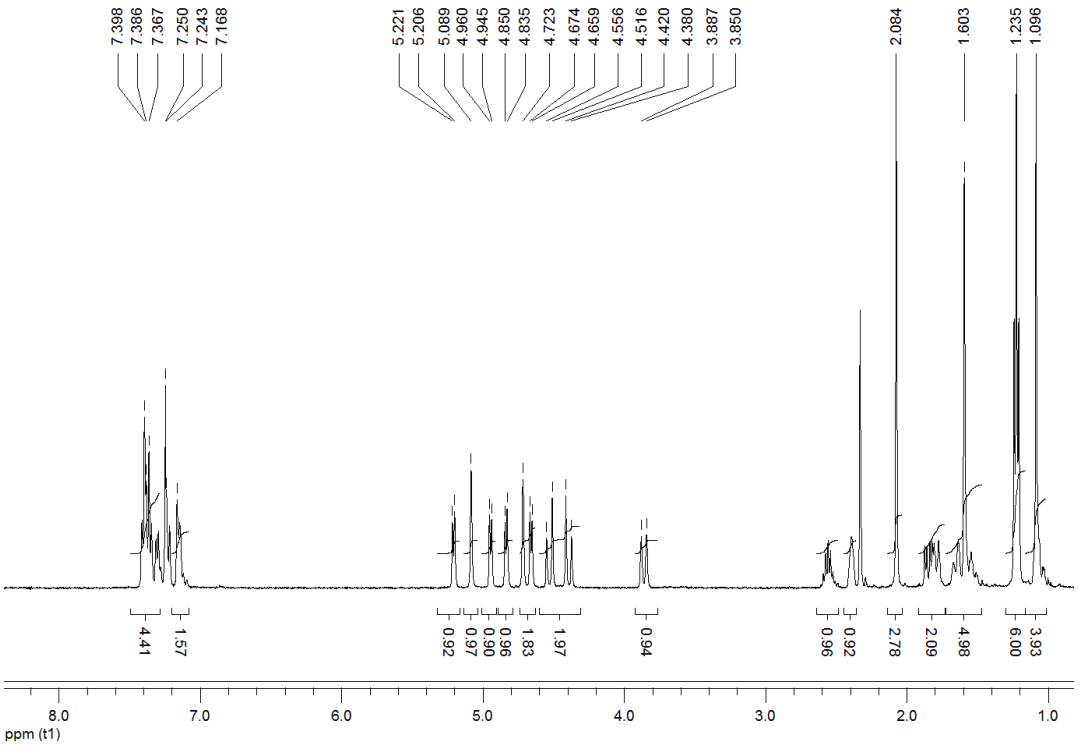


5. ^{1}H-^{15}N HMBC NMR of **1c**

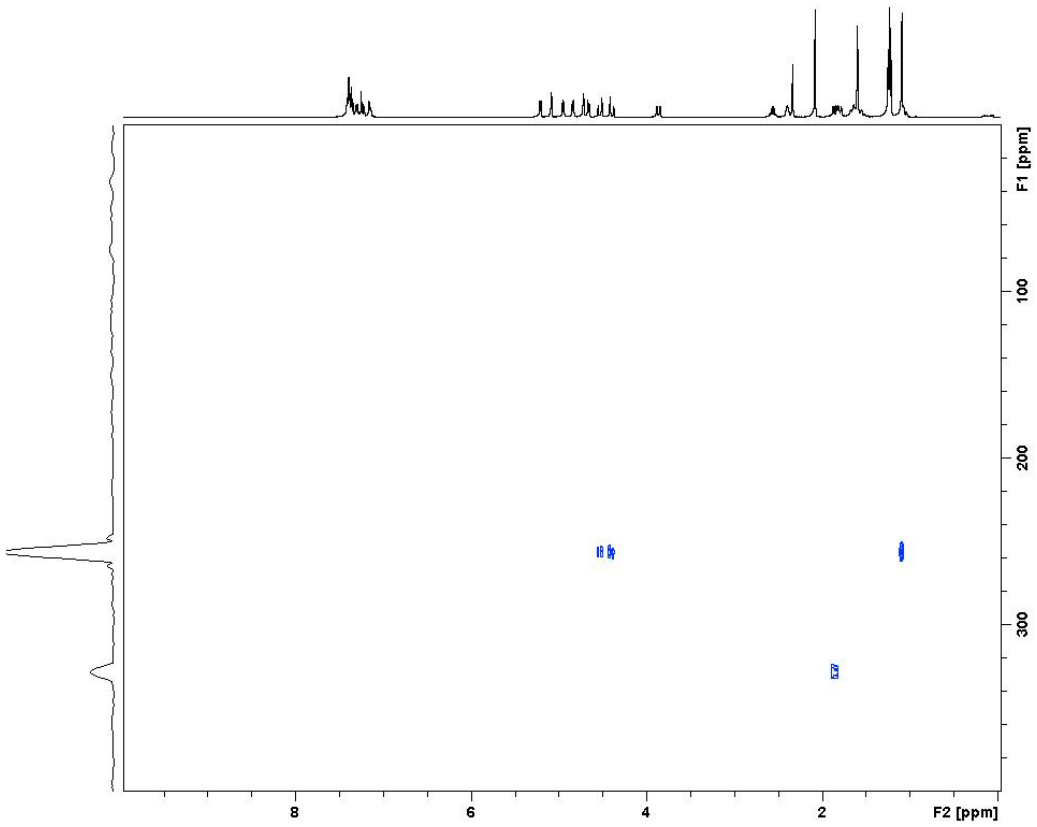


NMR spectra of 3b in $CDCl_3$

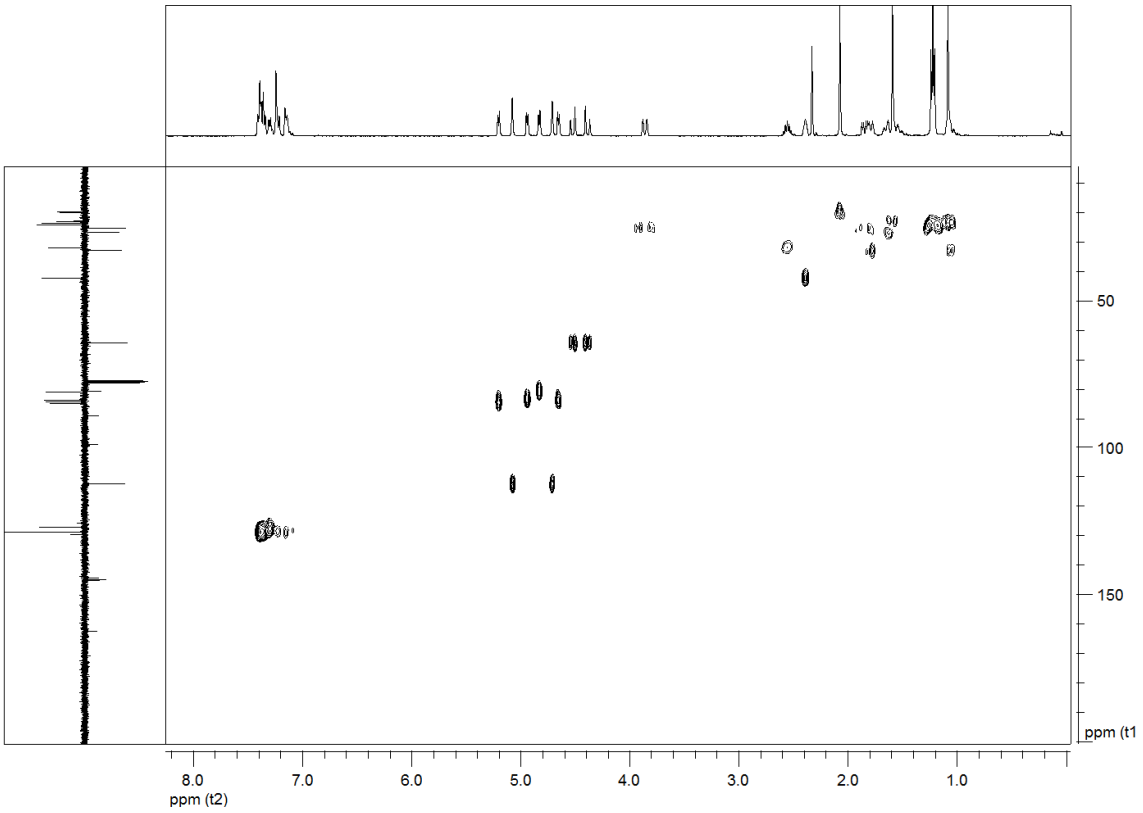
1. ^{1}H NMR of **3b**



2. ^{1}H-^{15}N HMBC NMR of **3b**

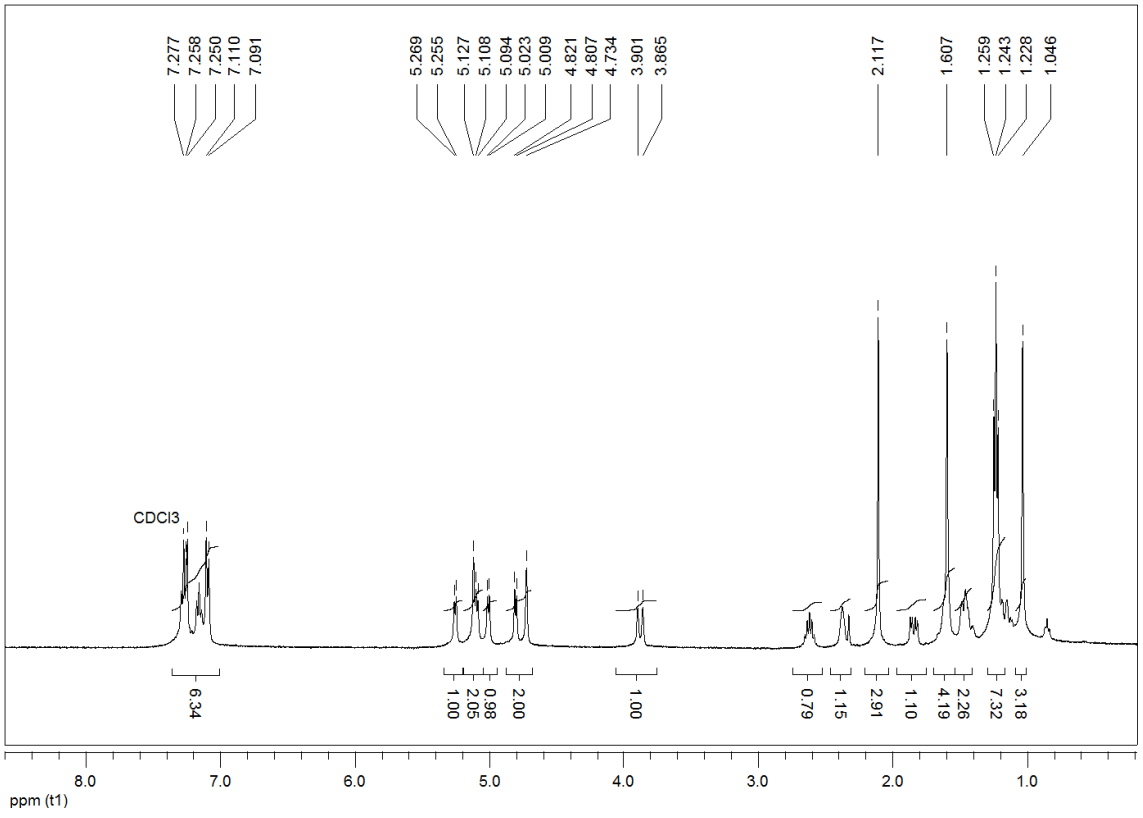


1. ^{13}C-^{1}H HSQC NMR of **3b**

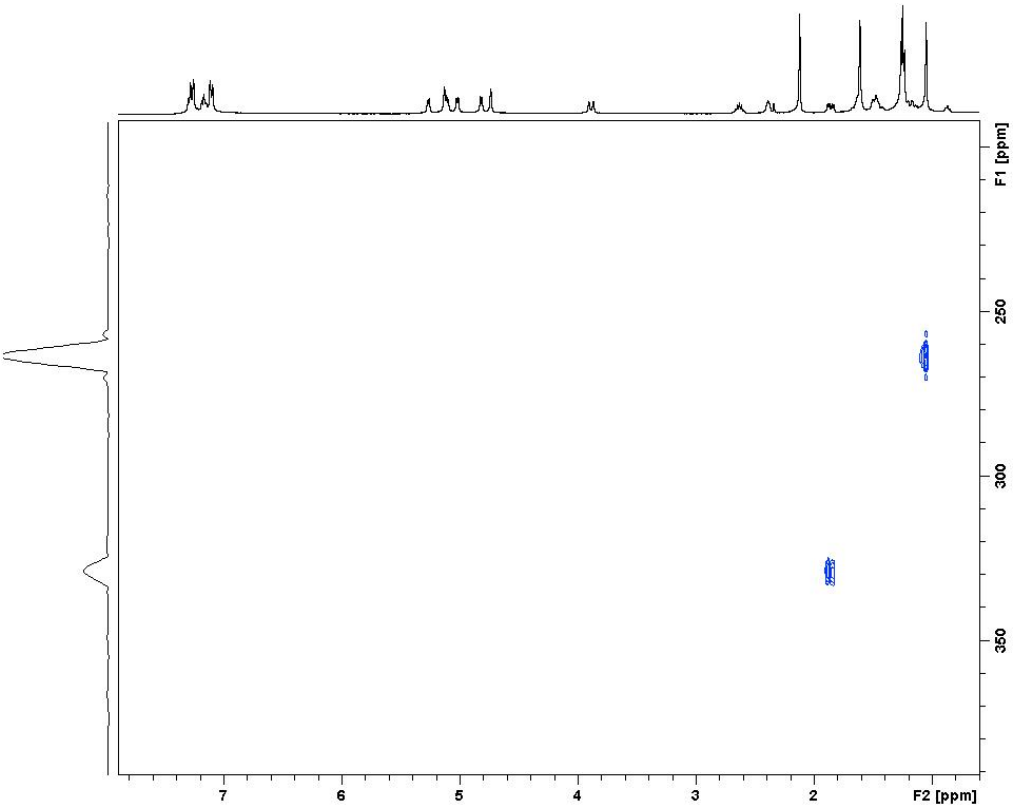


NMR spectra of 3a in $CDCl_3$

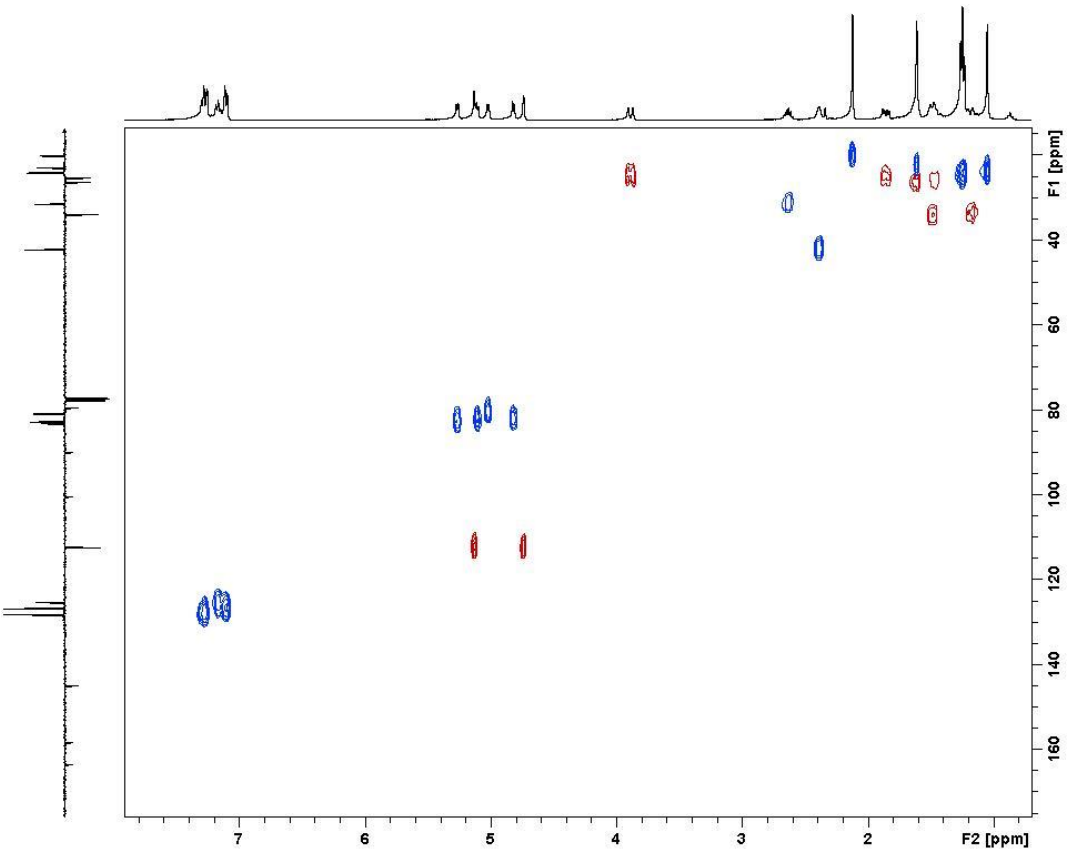
1. ^{1}H NMR of **3a**.



2. ^{1}H-^{15}N HMBC NMR of **3a**.



3. ^{1}H-^{13}C HSQC NMR of **3a**.



5. NMR experiments under physiological conditions.

Phosphate buffer saline (PBS) was prepared according to Cold Spring Harbor Protocols (http://cshprotocols.cshlp.org/content/2006/1/pdb.rec8247) using NaCl, KCl, Na_2HPO_4 and $KHPO_4$ in D_2O. Adjustment of pH to 7.40 was carried out using a DCl solution in D_2O (0.01M) with the help of a HANNA HI208 pHmeter. Compounds **1a**-**1c** were then dissolved in 2500 μL of the freshly prepared PBS (6-9 mM of ruthenium compounds), final pH measured (7.36-7.38) and time-dependent ^1H NMR spectra of 500 μL aliquots of final solutions were carried out at 25 ºC.

Figure S3. ^1H NMR spectrum (25 ºC) of: **A) 1b** in D_2O, **B)** Phosphate buffer saline (PBS) in D_2O, **C) 1b** in PBS solution after 24h at r.t. **D) 1b** in PBS solution after 48h at r.t. **E) 1b** in PBS solution after 72 h at r.t., **F) 1b** in PBS solution after 5 days at room temperature.

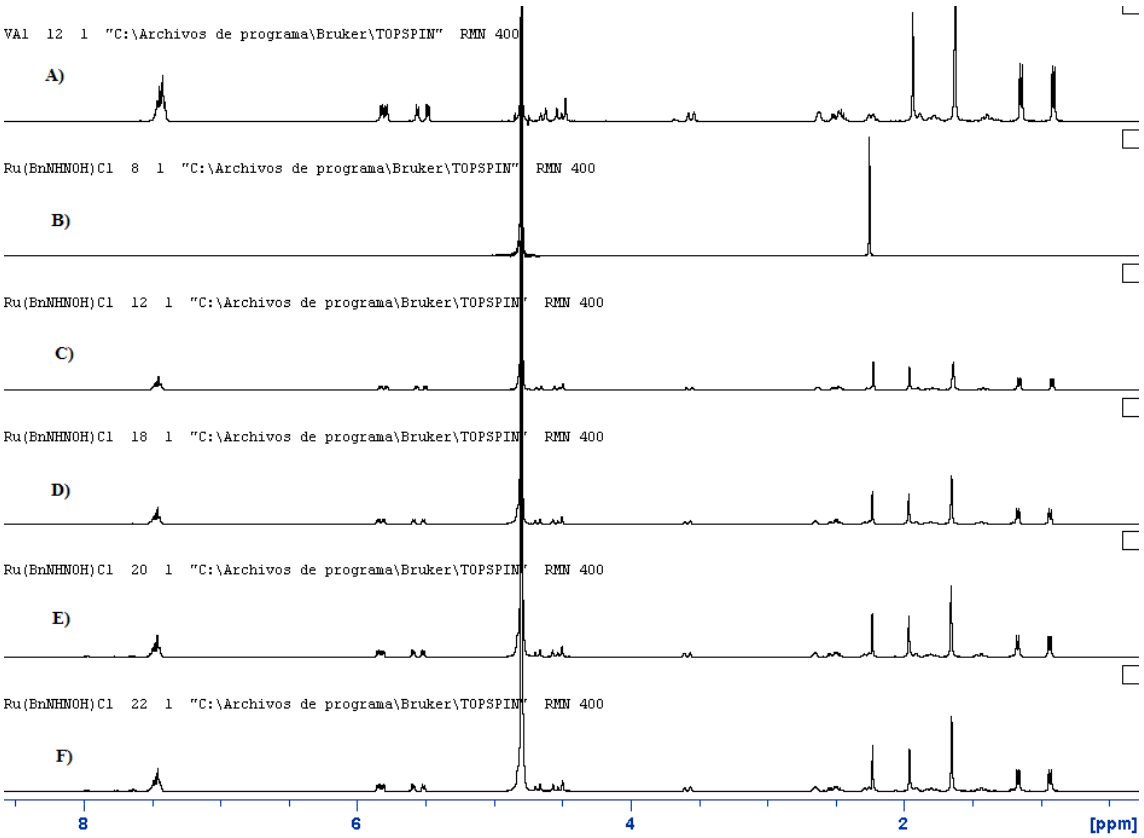
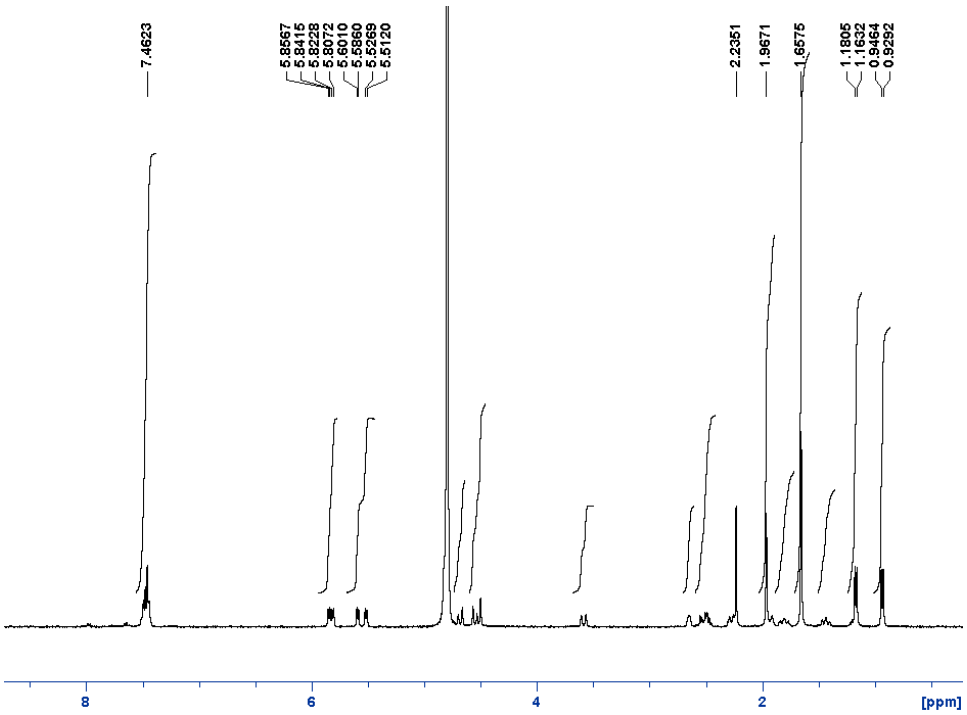
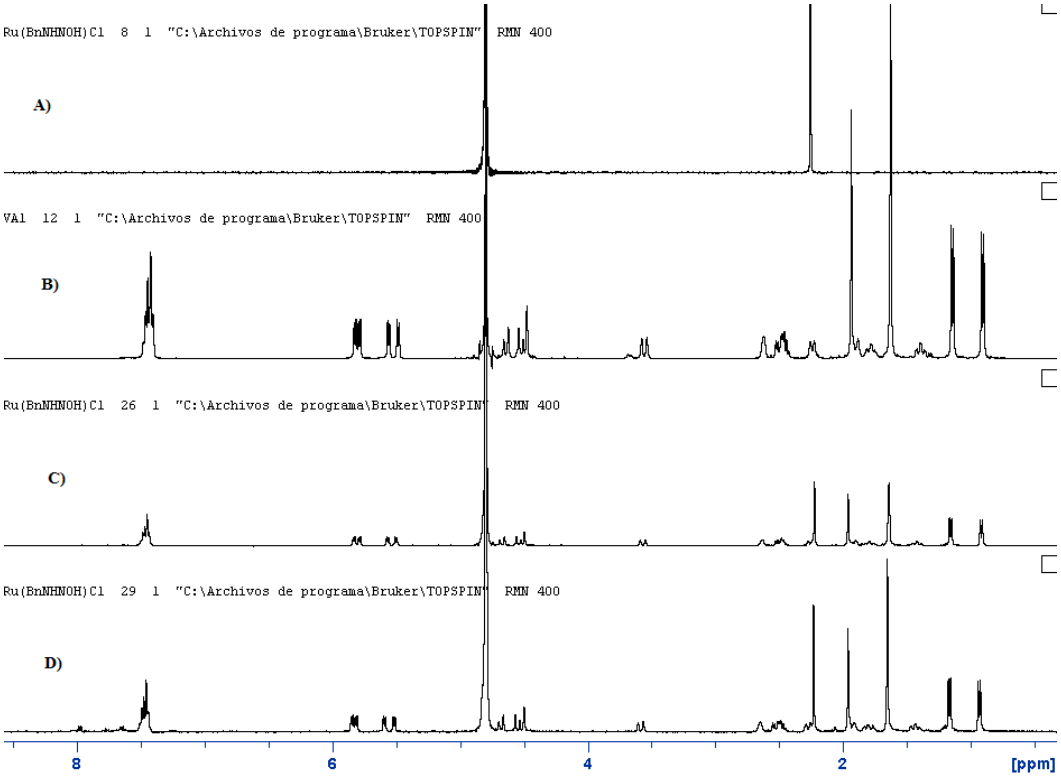


Figure S4. Full ^{1}H NMR spectrum (25 ºC) of **1b** in PBS solution after 72 h at r.t.



A 500 μL aliquot of **1b** in PBS (pH = 7.4), prepared as described above, was warmed up to ca. 36 ºC, and time-dependent ^{1}H NMR spectra were carried out at 25 ºC. Spectra of this experiment are shown in Figure S5.

Figure S5. ^{1}H NMR spectrum (25 ºC) of: **A)** Phosphate buffer saline (PBS) in D_2O, **B) 1b** in D_2O, **C) 1b** in PBS solution after 24h at 36 ºC **D) 1b** in PBS solution after 72h at 36 ºC.



6. *In vitro* assays.

Figure S6. Effect of derivatives A) **1a**, B) **1b** and C) **1c** on PC3 cells viability, compared to that of ammonium-oxime compounds **a·HCl**-**c·HCl** and ruthenium dimer $[(\eta^6\text{-p-cymene})RuCl_2]_2$. Cells were treated with increasing doses of organic and ruthenium compounds for 3 hours. Cell viability was measured by means of MTT assay. The results are expressed as a percentage of live cells compared to control. Data are the mean ± S.E.M. of at least three experiments. *, P < 0.05; **, P < 0.01; ***, P < 0.001 versus Control.