Supporting Information for

Amphiphilic Polymeric Nanoreactors Containing Rh(I)-NHC Complexes for the Aqueous Biphasic Hydrogenation of Alkenes

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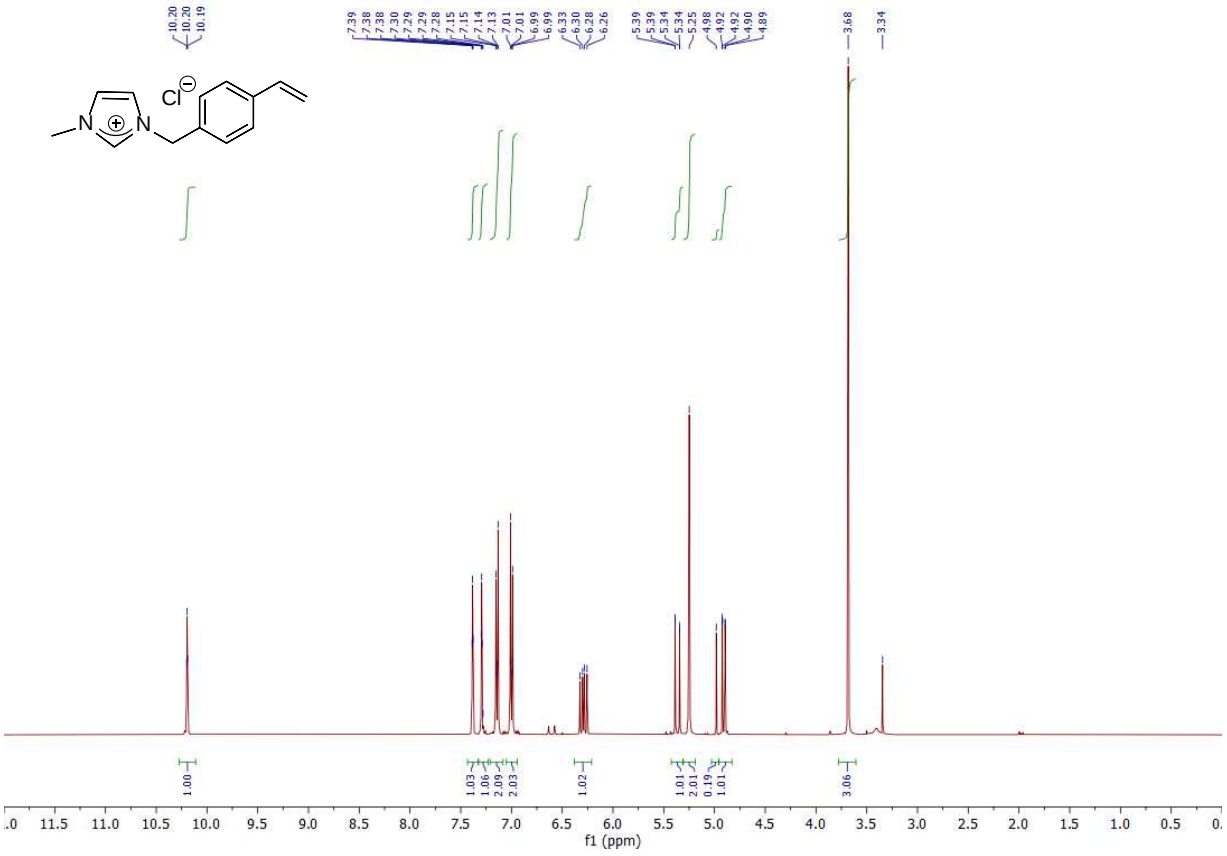
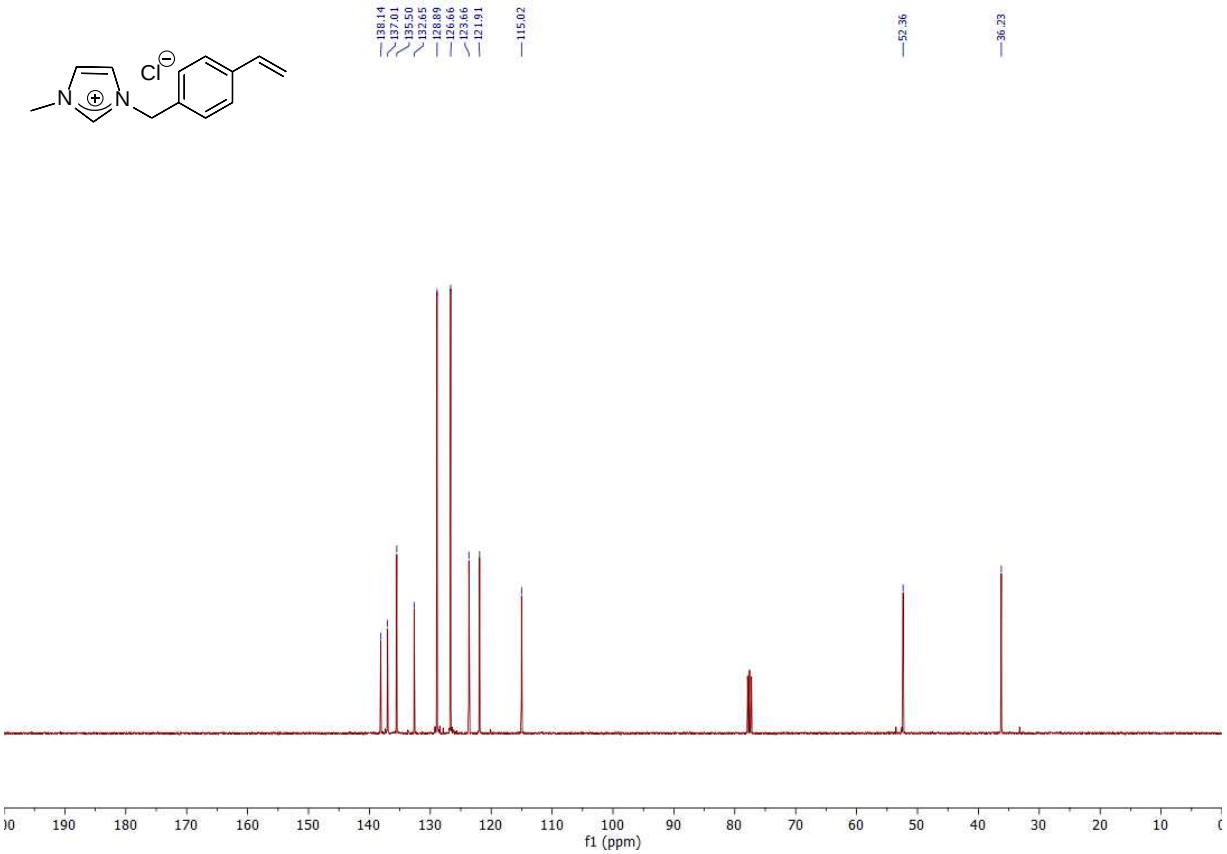
NMR analyses

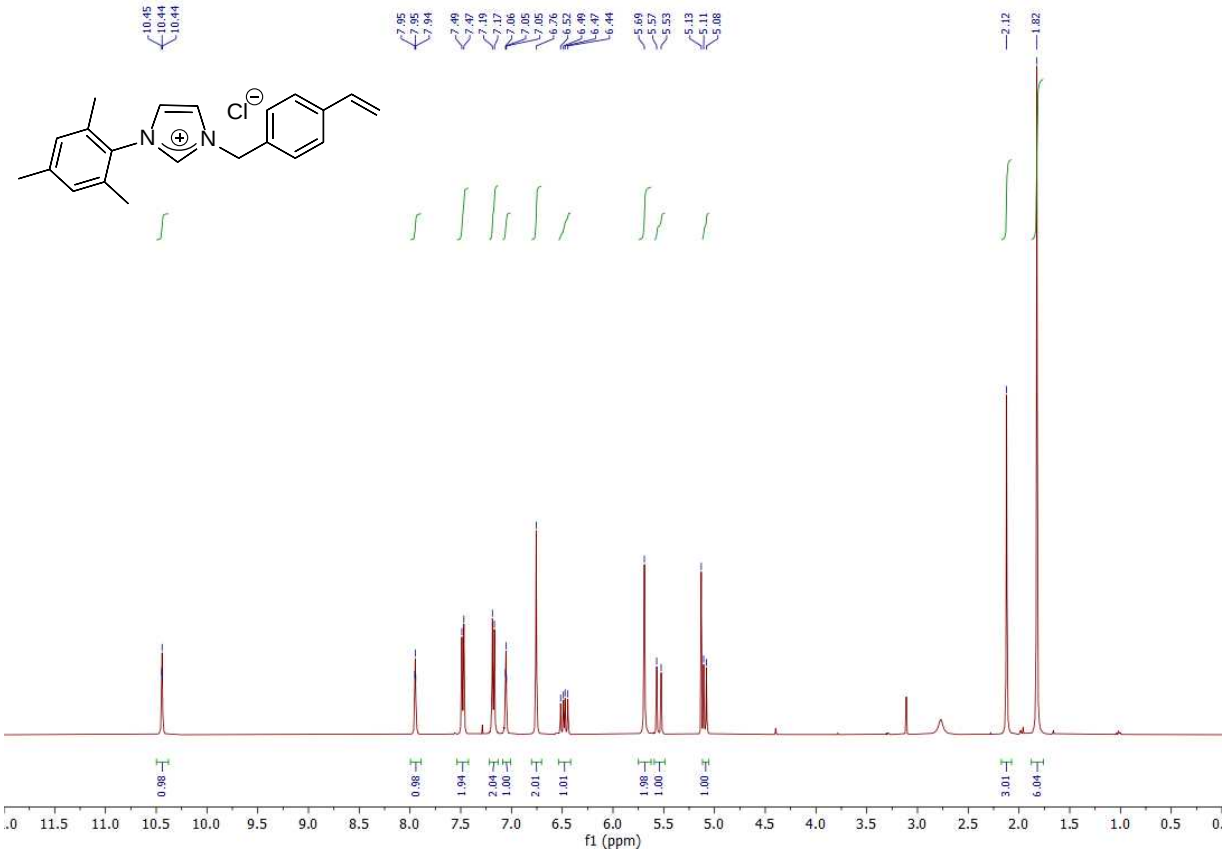
^{1}H NMR spectrum of compound **1a**



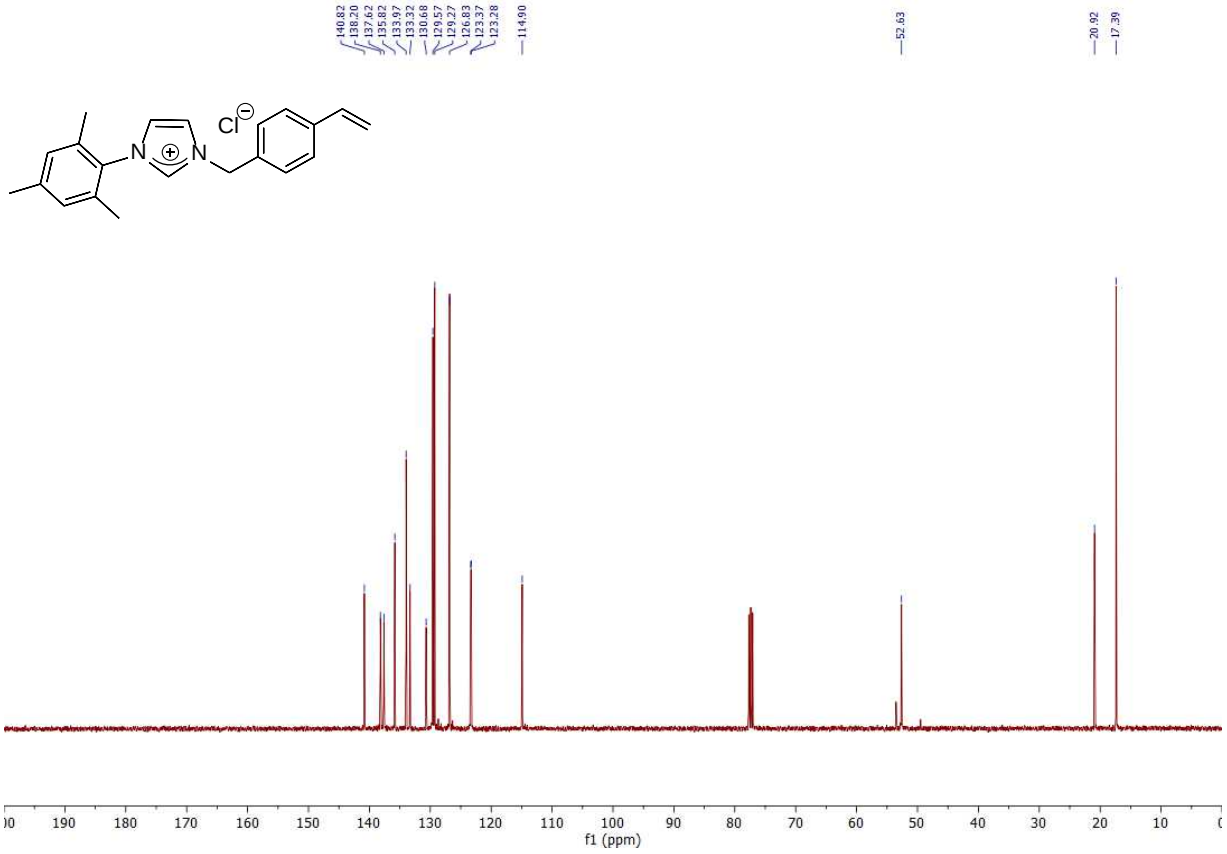
^{13}C NMR spectrum of compound **1a**



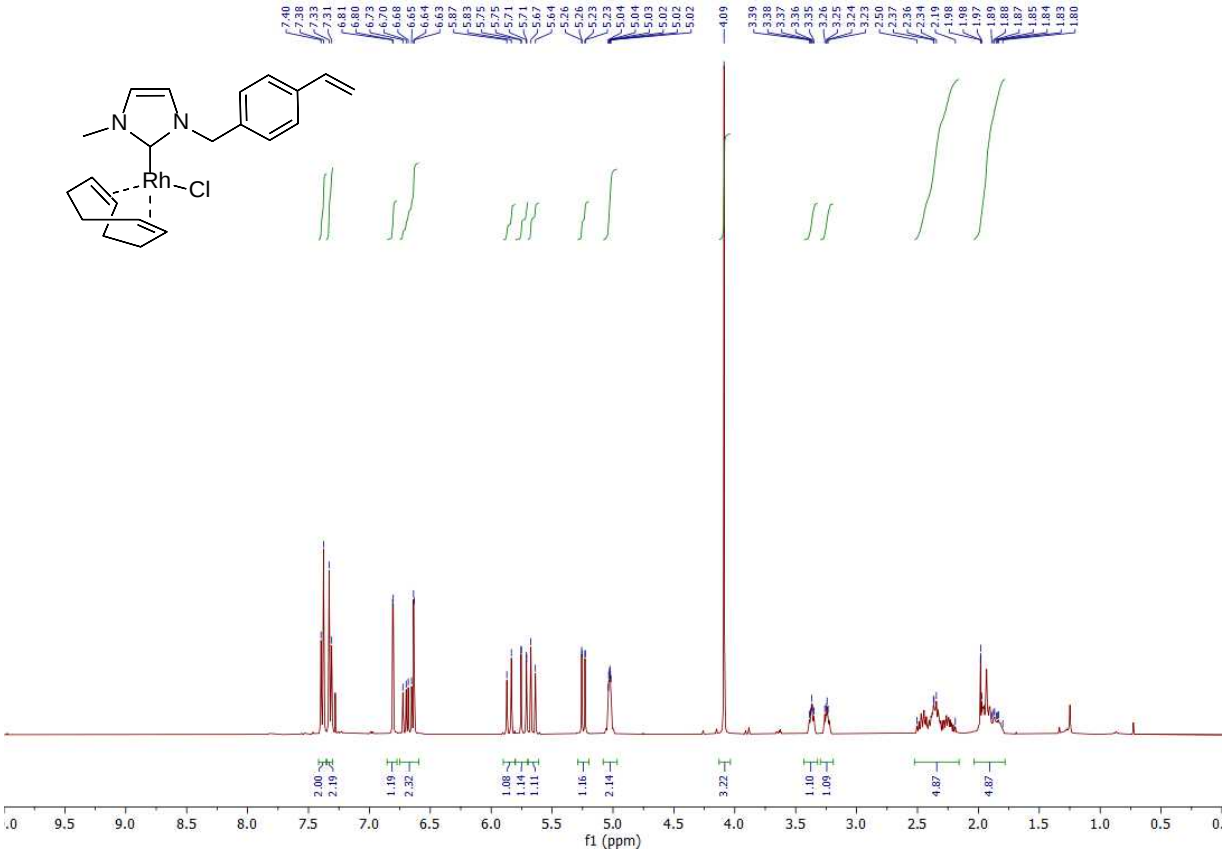
^{1}H NMR spectrum of compound **1b**



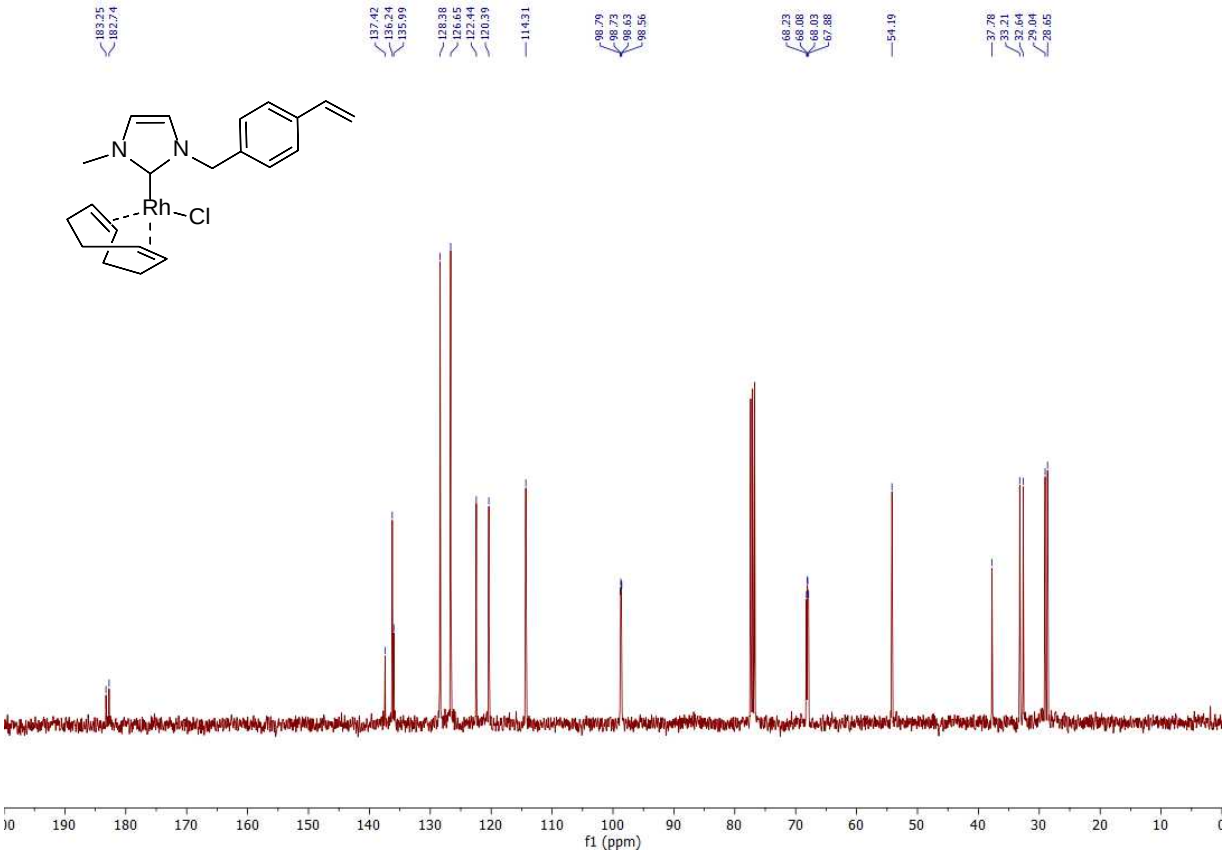
^{13}C NMR spectrum of compound **1b**



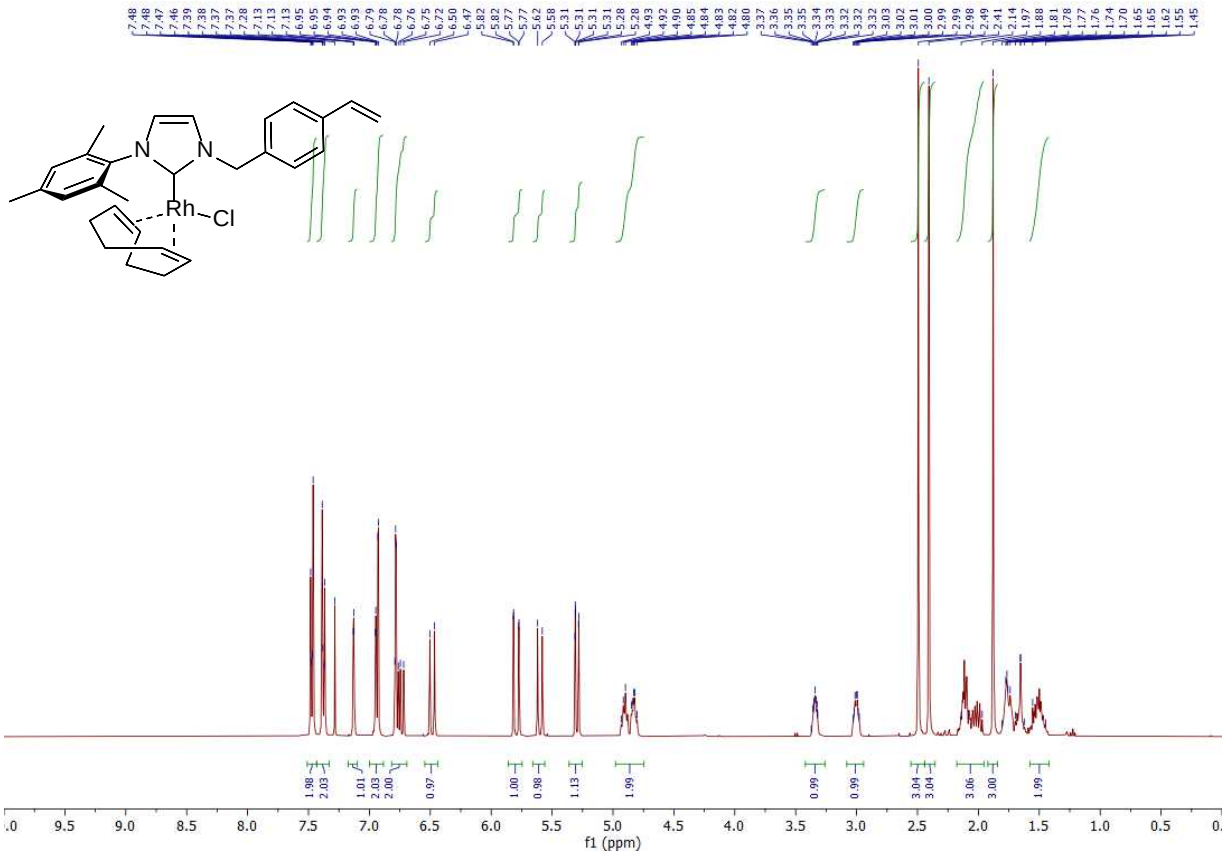
^{1}H NMR spectrum of polymerizable rhodium(I) complex **2a**



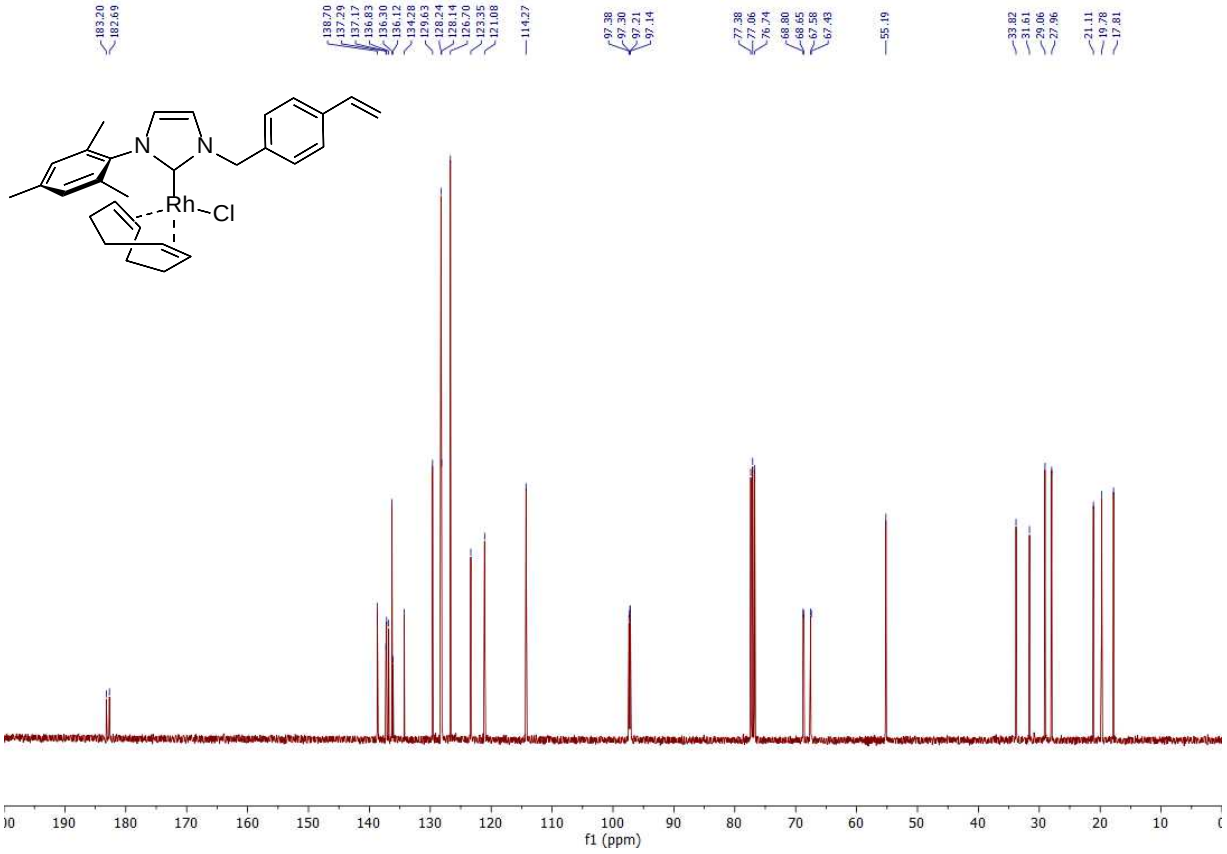
^{13}C NMR spectrum of polymerizable rhodium(I) complex **2a**



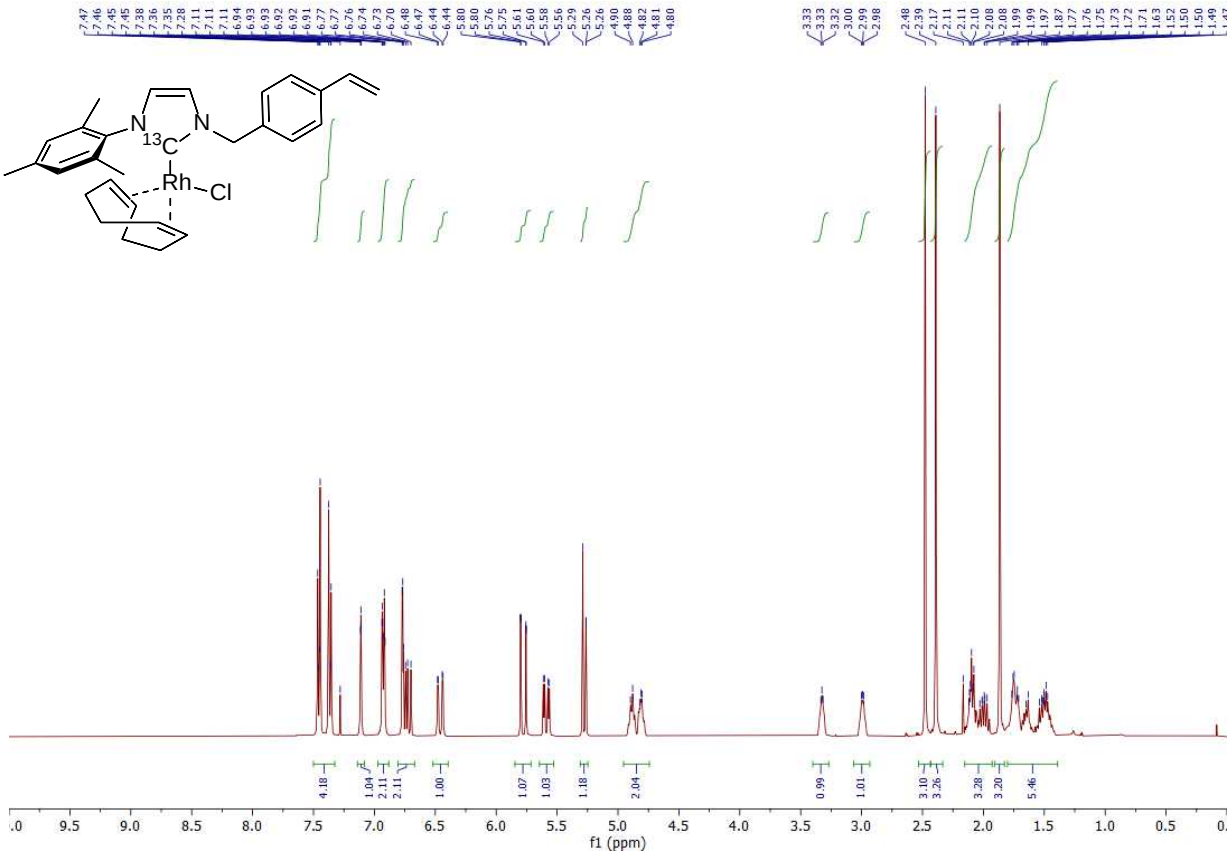
^{1}H NMR spectrum of polymerizable rhodium(I) complex **2b**



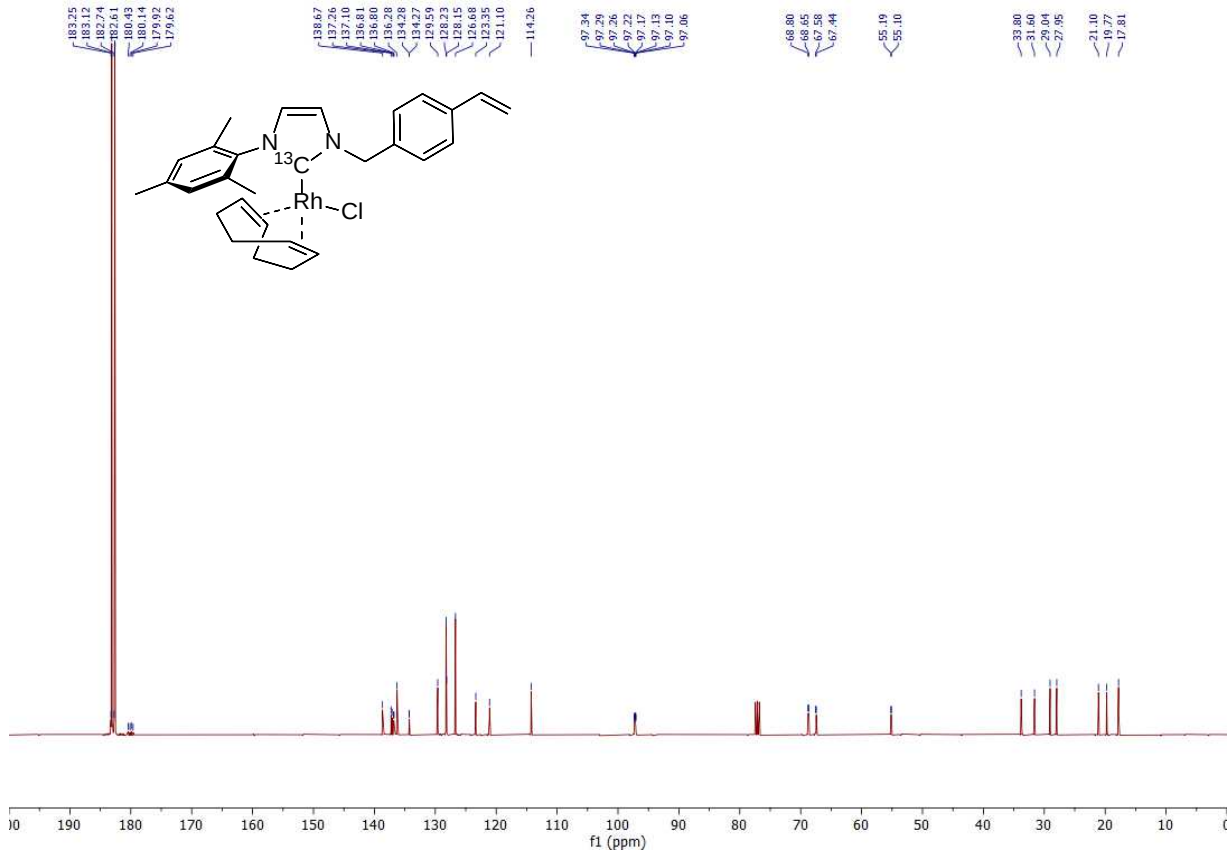
^{13}C NMR spectrum of polymerizable rhodium(I) complex **2b**



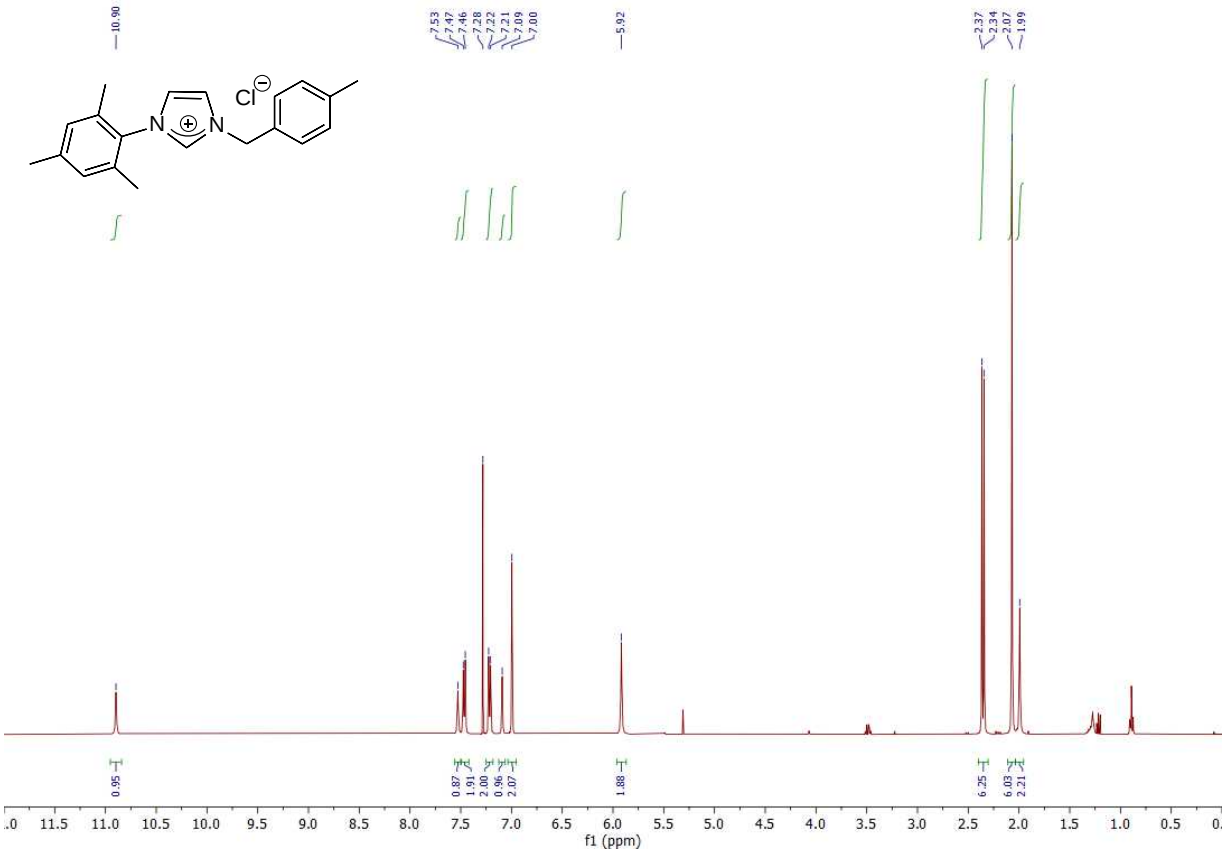
^{1}H NMR spectrum of ^{13}C-labelled polymerizable rhodium(I) complex **2b***



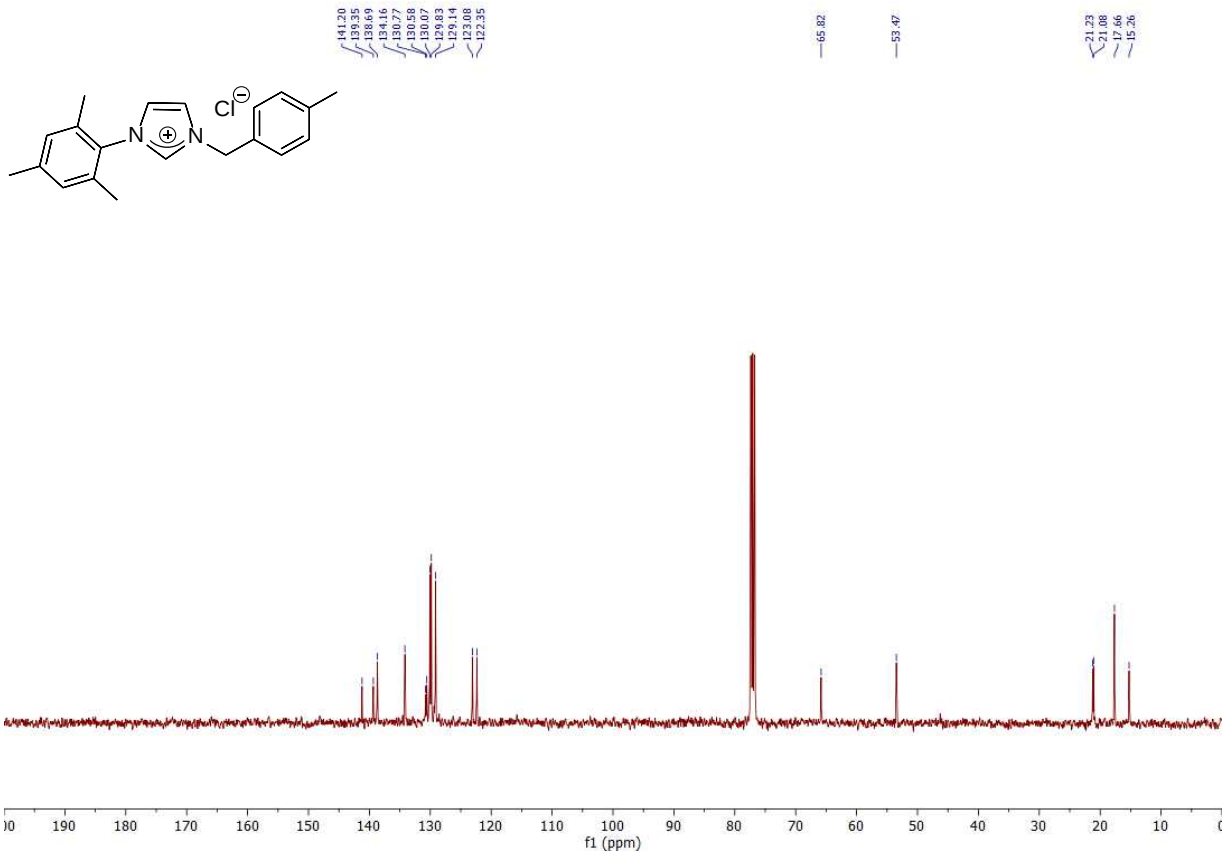
^{13}C NMR spectrum of ^{13}C-labelled polymerizable rhodium(I) complex **2b***



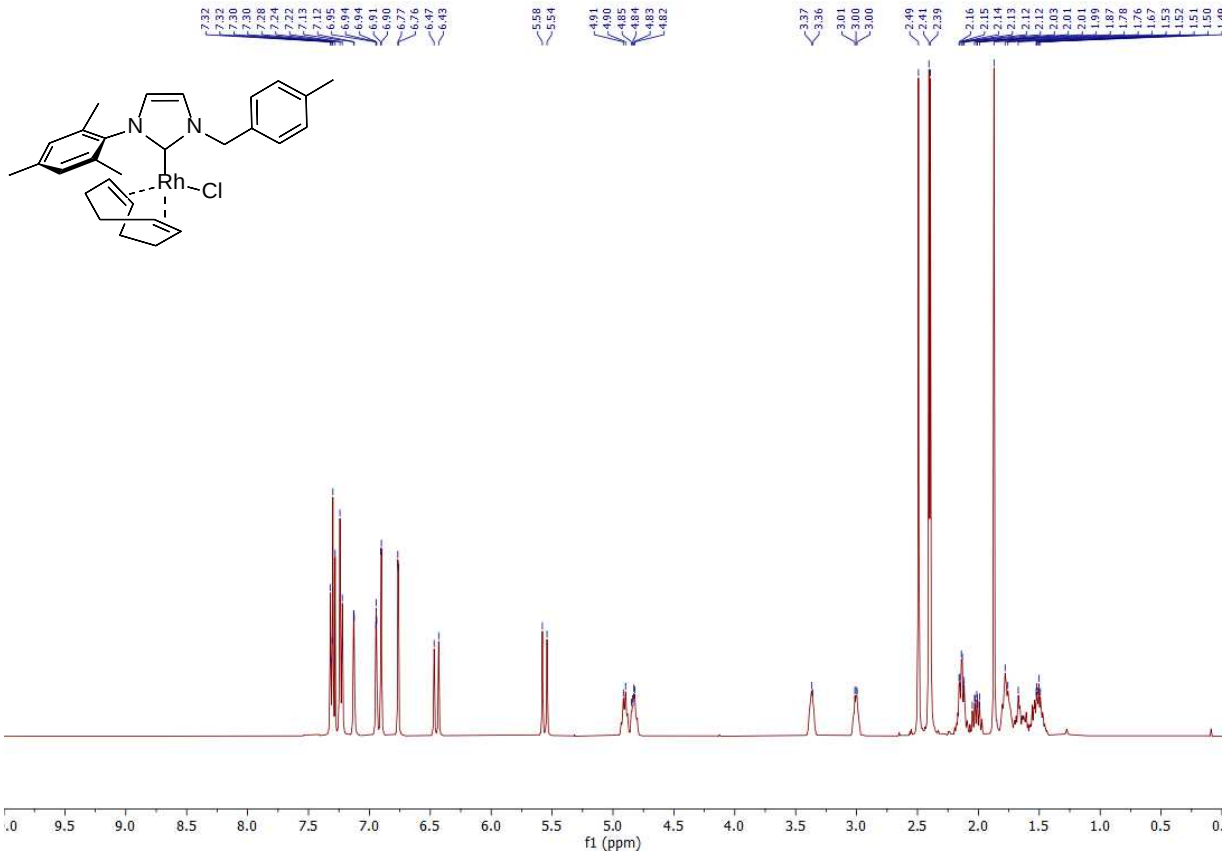
^{1}H NMR spectrum of compound **6b**



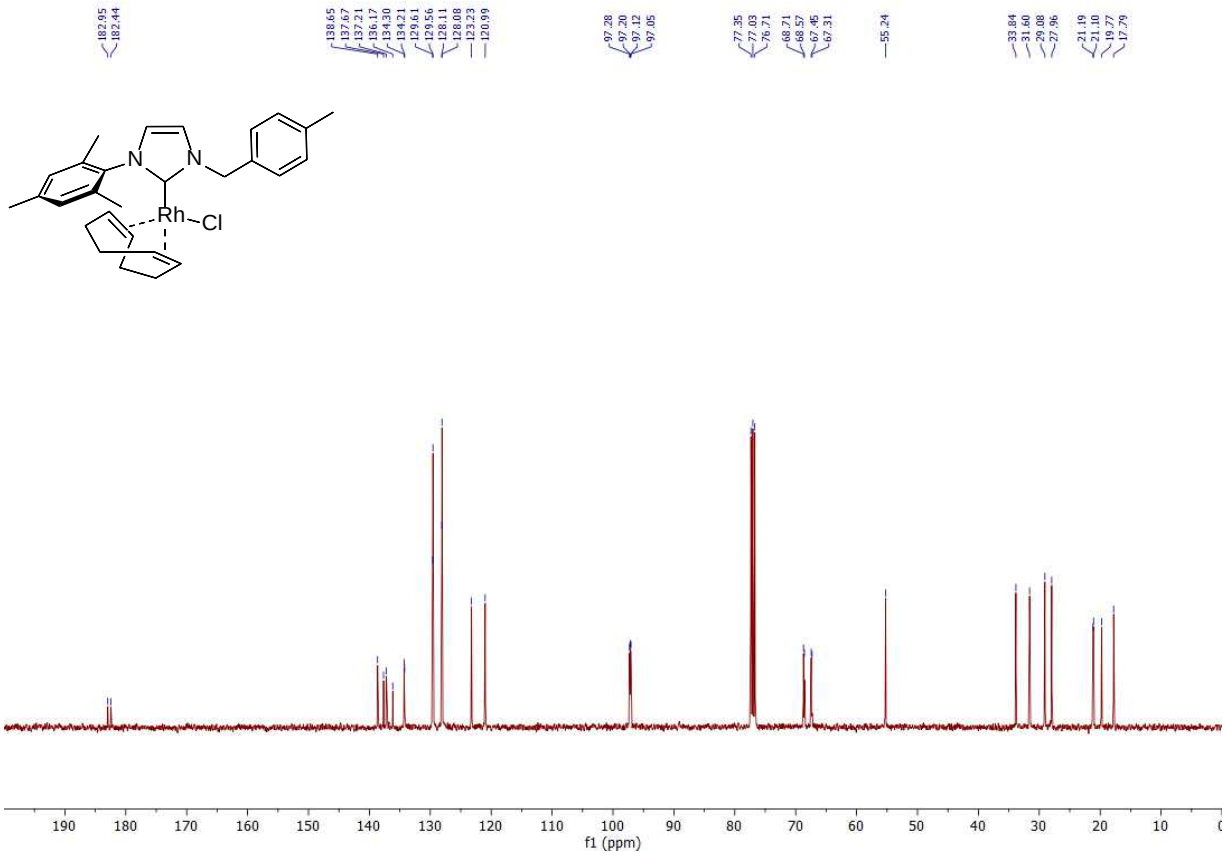
^{13}C NMR spectrum of compound **6b**



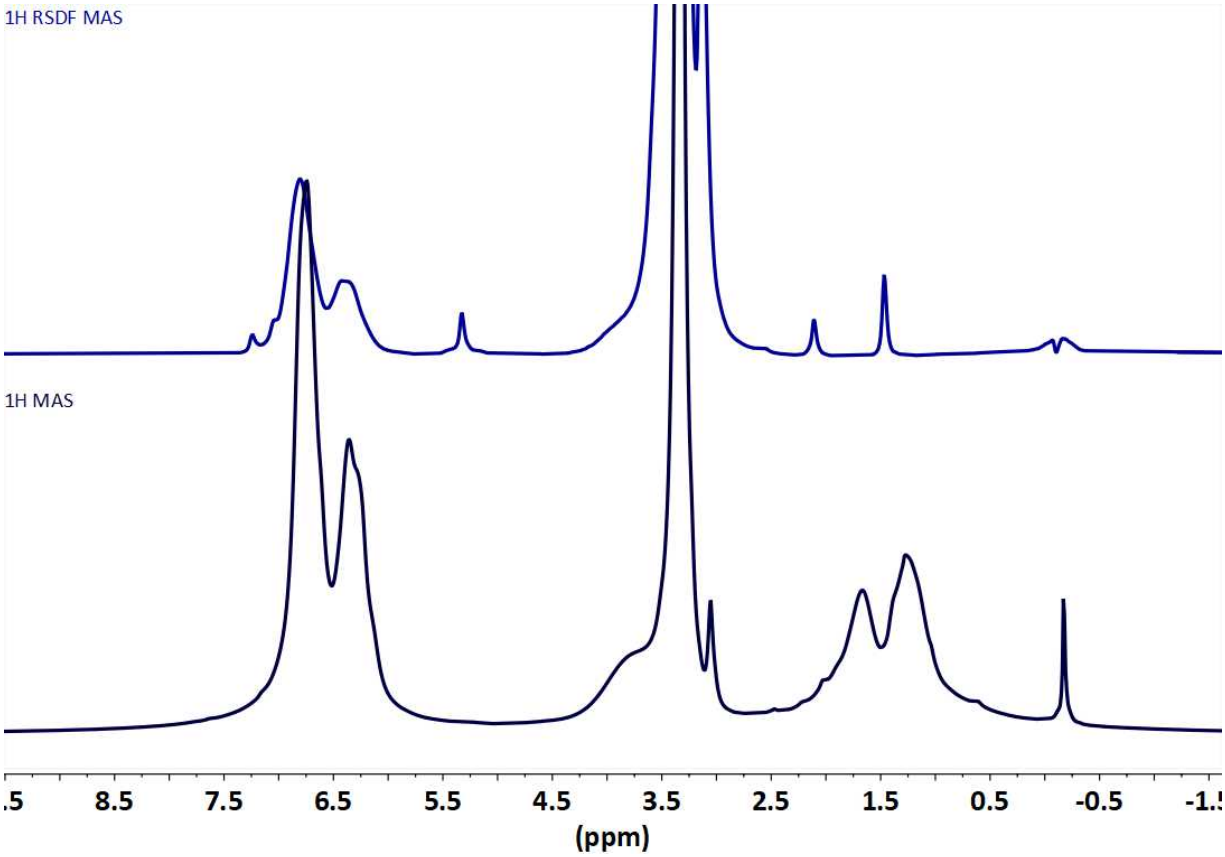
^{1}H NMR spectrum of model rhodium(I) complex **7b**



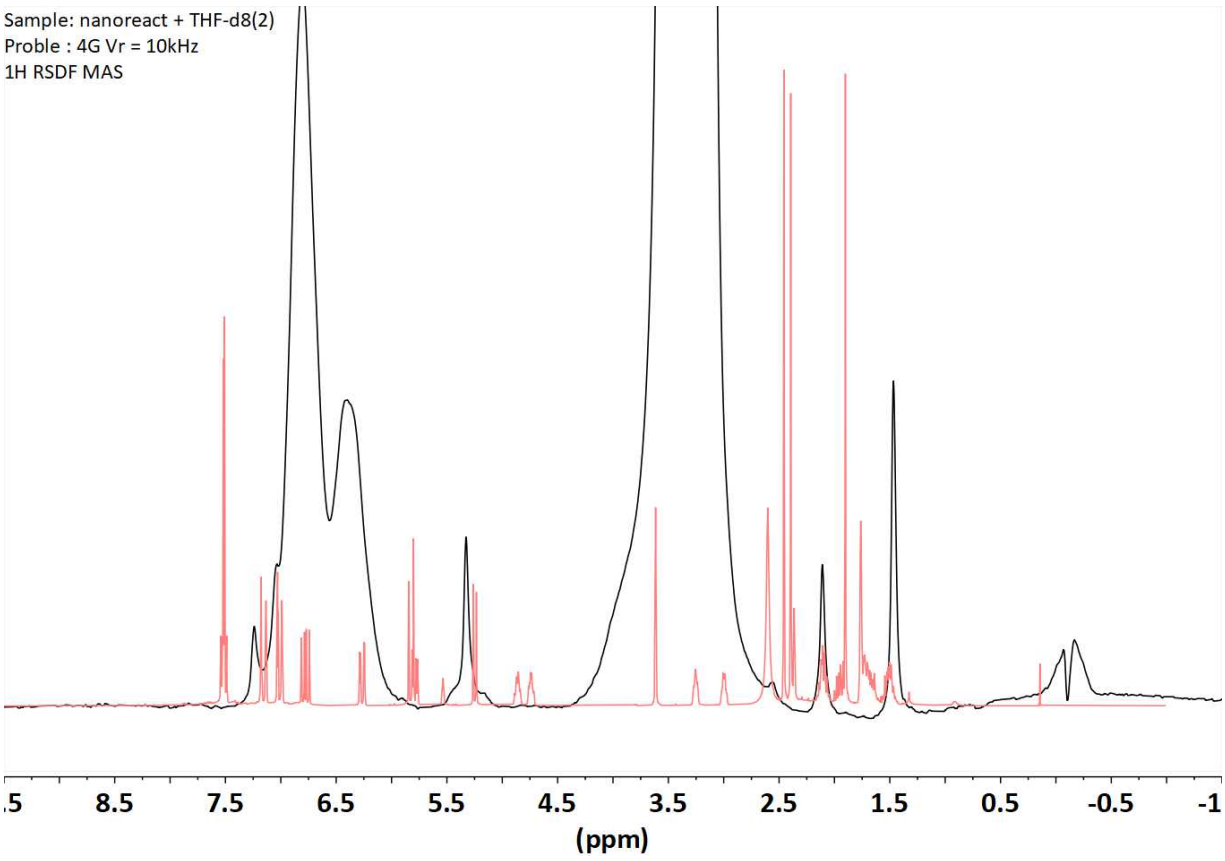
^{13}C NMR spectrum of model rhodium(I) complex **7b**



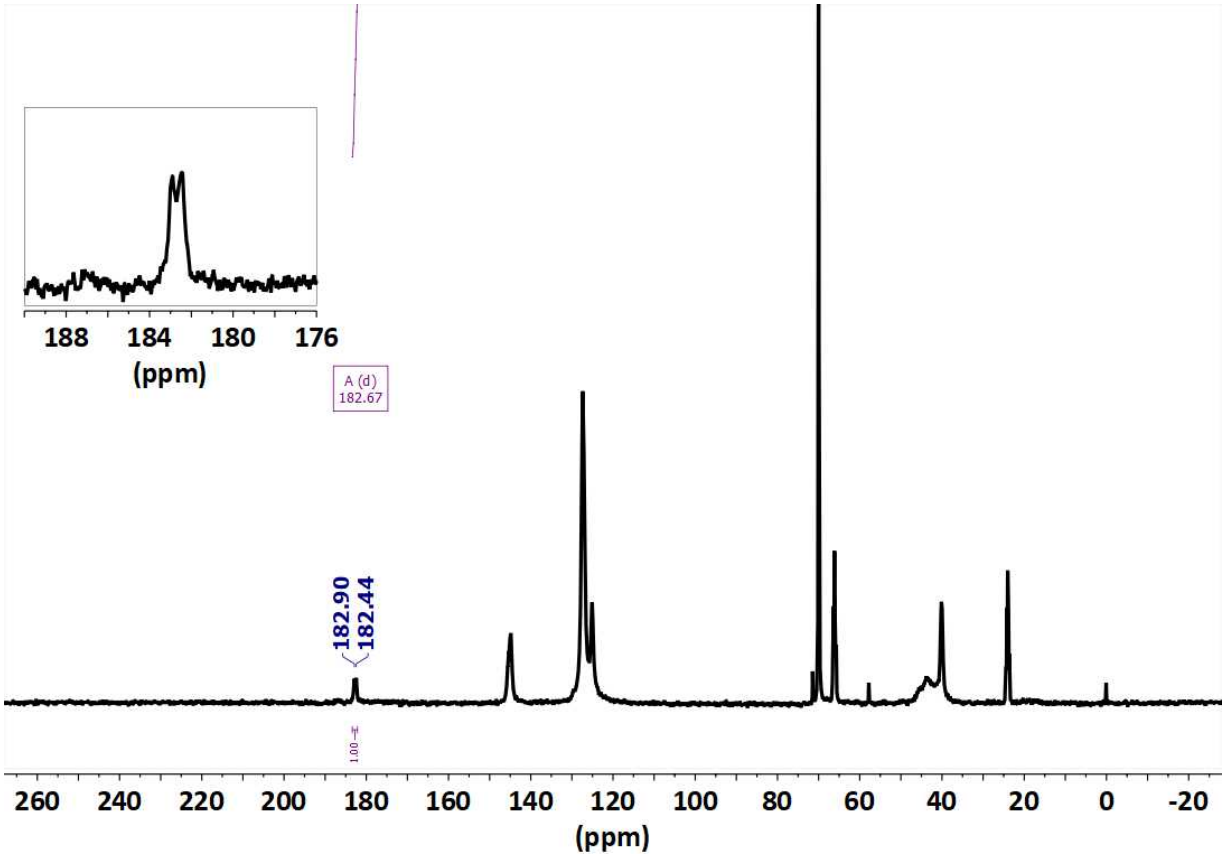
^{1}H-DFSE MAS (blue) and ^{1}H-MAS (black) NMR spectra of nanoreactors Rh-NHC^{mes}@CCM **5b***



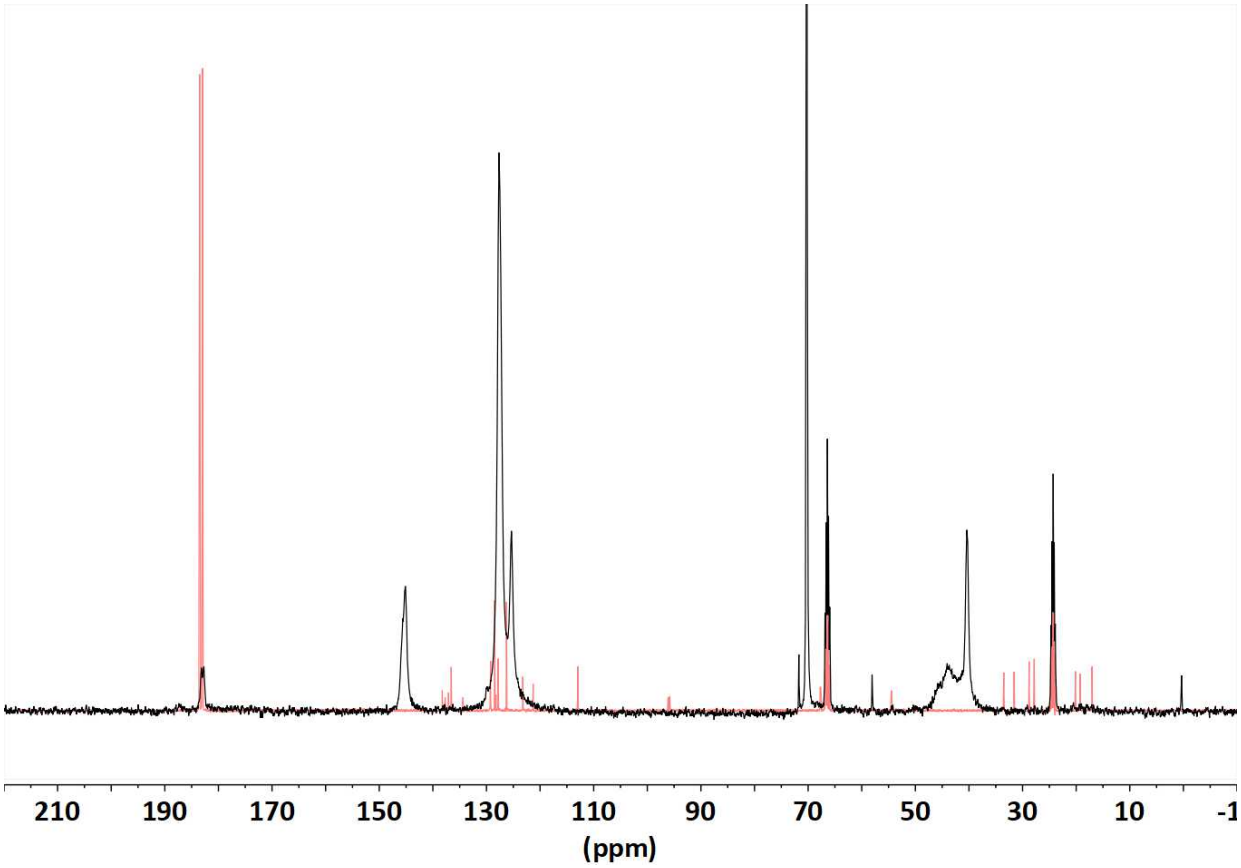
^{1}H-DFSE MAS NMR spectrum of nanoreactors Rh-NHC^{mes}@CCM **5b*** (black) and ^{1}H NMR spectrum of ^{13}C-labelled polymerizable rhodium(I) complex **2b*** (THF-d_8) (red)



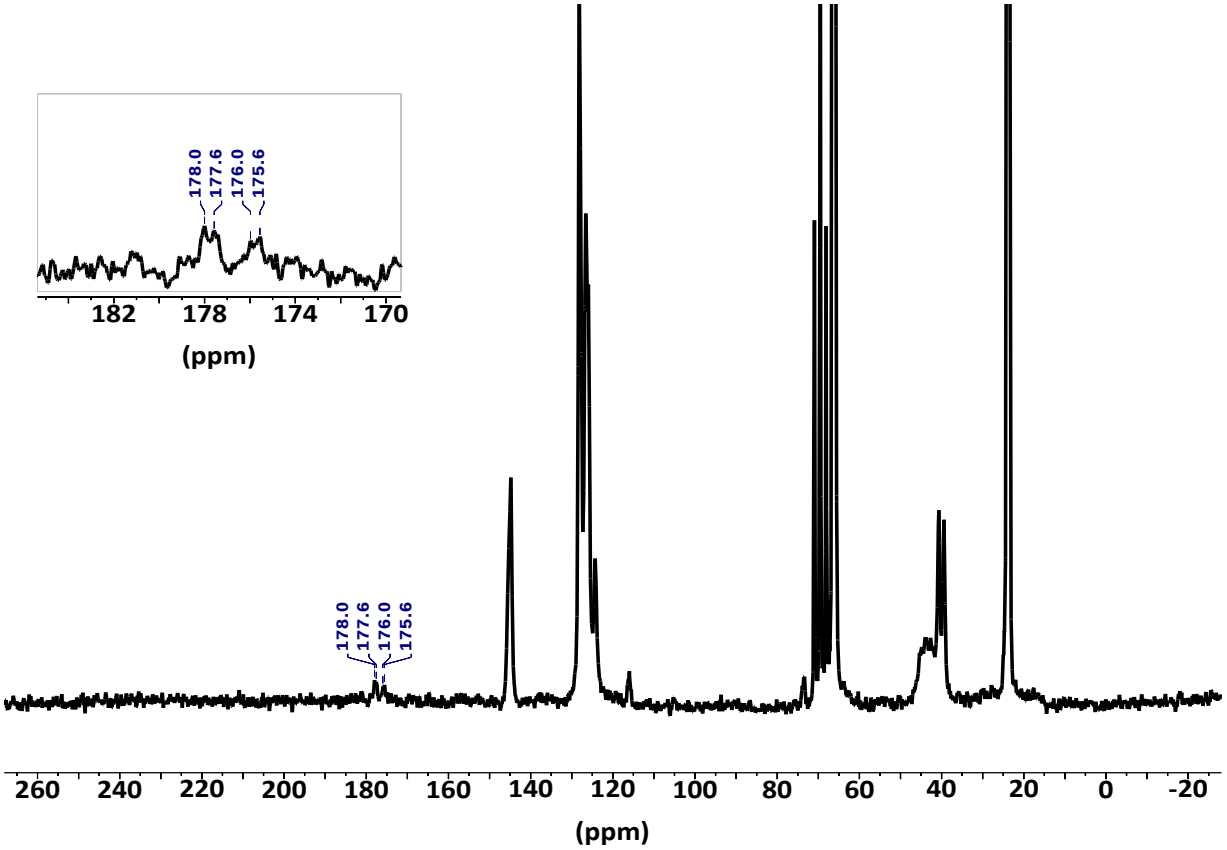
^{13}C-MAS NMR spectrum of nanoreactors Rh-NHC^{mes}@CCM **5b***



^{13}C-MAS NMR spectrum of nanoreactors Rh-NHC^{mes}@CCM **5b*** (black) and ^{13}C NMR spectrum of ^{13}C-labelled polymerizable rhodium(I) complex **2b*** (THF-d_8) (red)

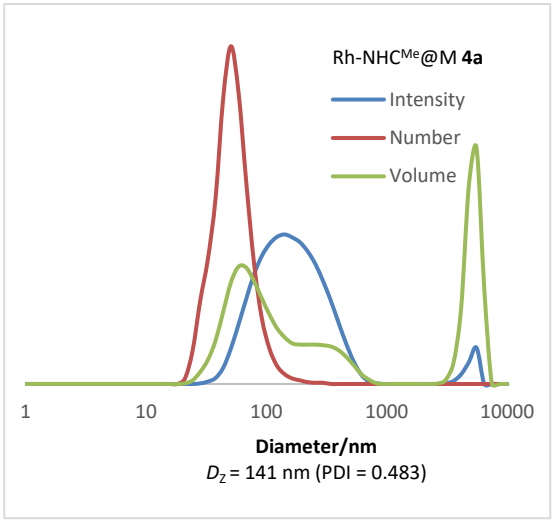


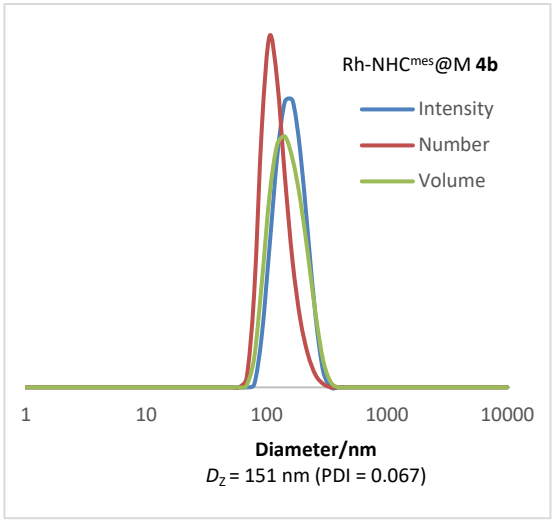
^{13}C-MAS NMR spectrum of nanoreactors Rh-NHC^{mes}@CCM **5b*** recovered after 5 runs hydrogenation.



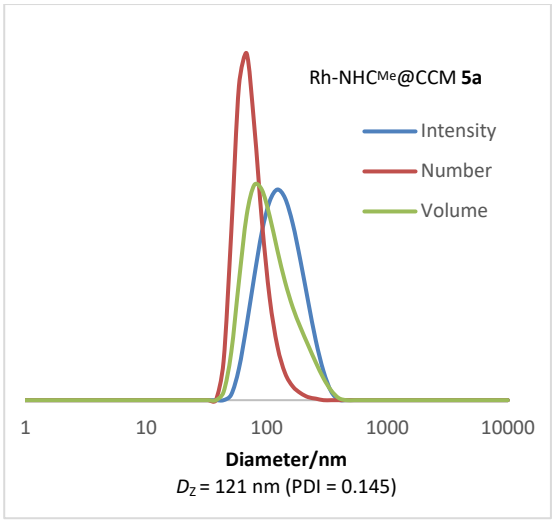
DLS analyses

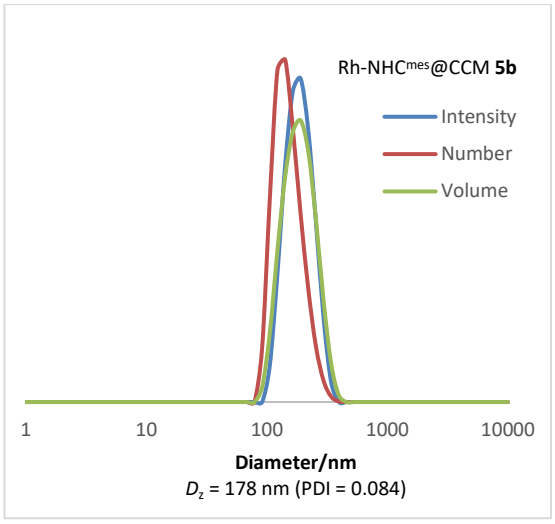
DLS analyses of Rh-NHC^{Me}@M **4a** (left) and Rh-NHC^{mes}@M **4b** (right), 45 µm filter



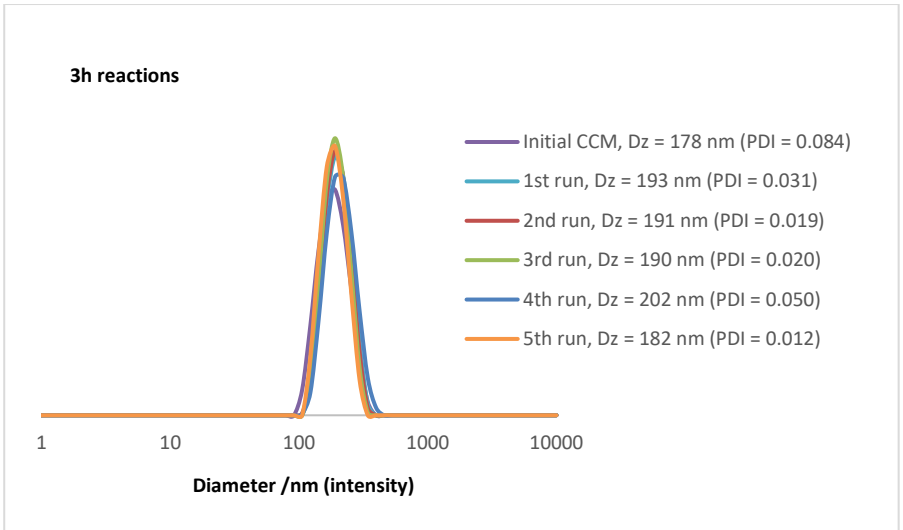


DLS analyses of Rh-NHC^{Me}@CCM **5a** (left) and Rh-NHC^{mes}@CCM **5b** (right), 45 µm filter



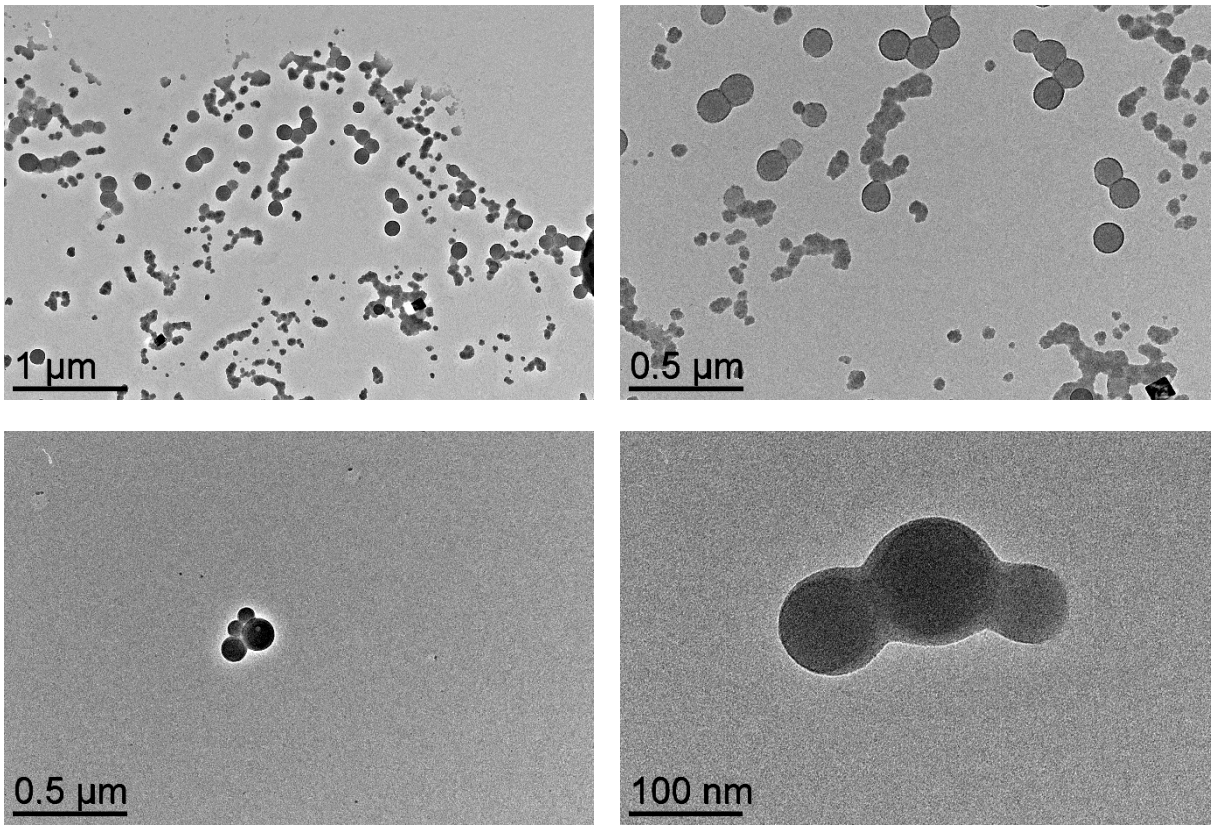


DLS analyses of Rh-NHC^{mes}@CCM **5b** after hydrogenation, 10 000/1 Sty/Rh ratio , 45 µm filter

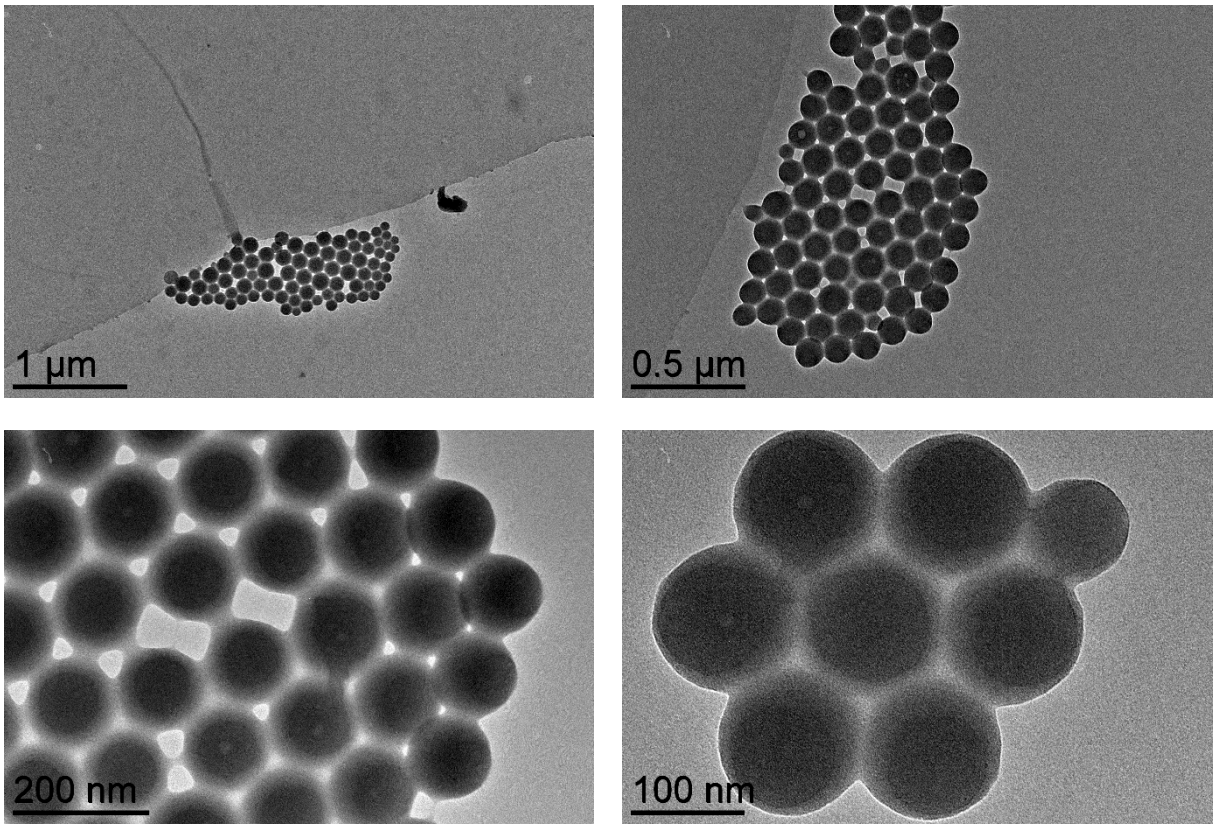


TEM analyses

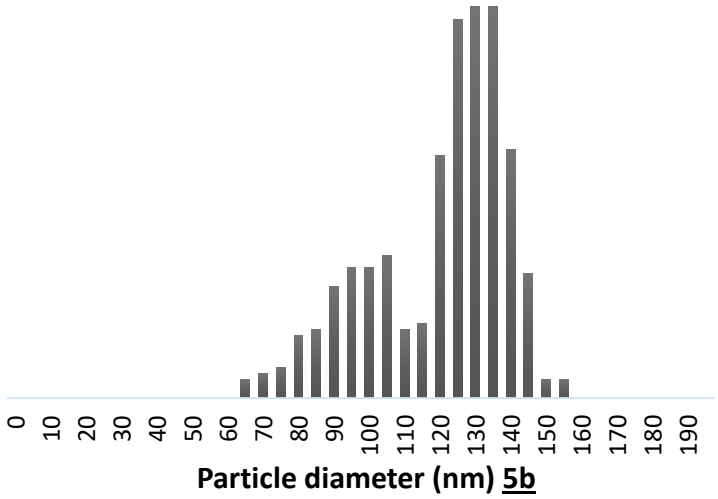
TEM images of Rh-NHC^{mes}@M **4b**:



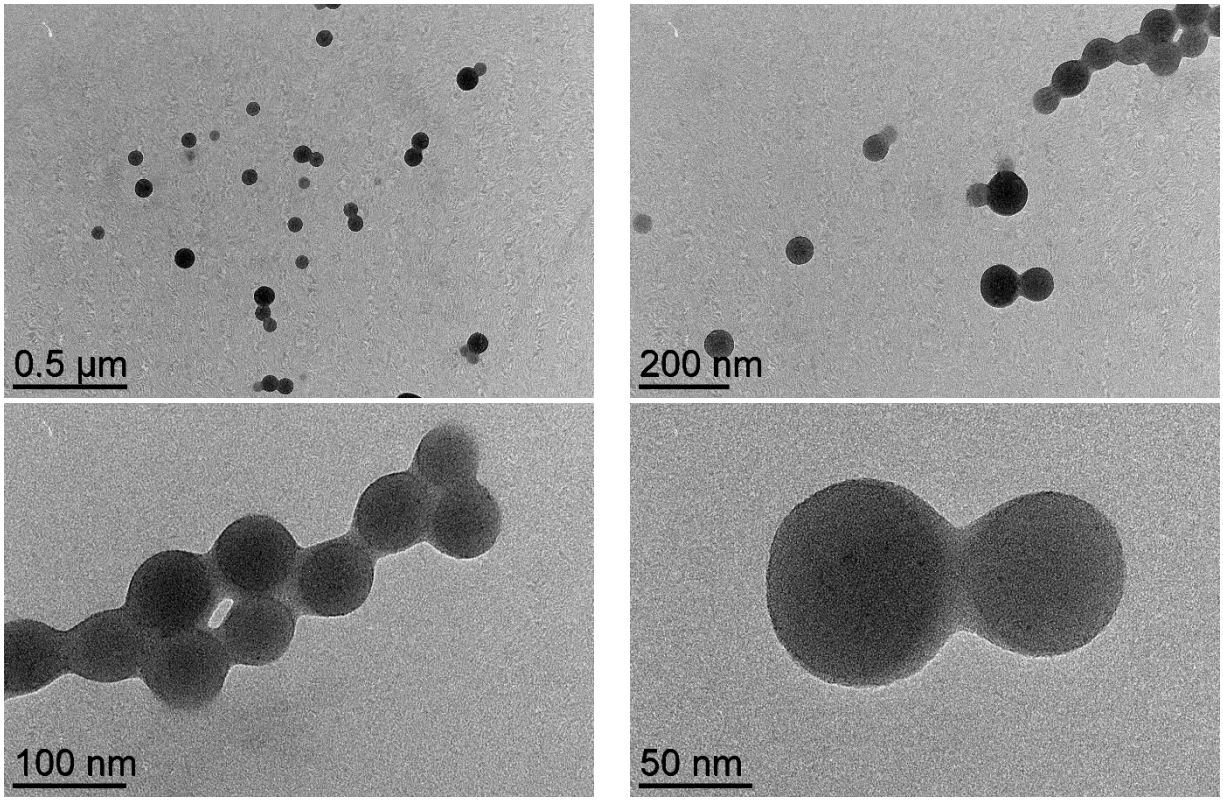
TEM images of Rh-NHC^{mes}@CCM **5b**:



Size distribution of Rh-NHC^{mes}@CCM **5b** measured on 431 particles, mean diameter: 123.3 ± 19.2 nm



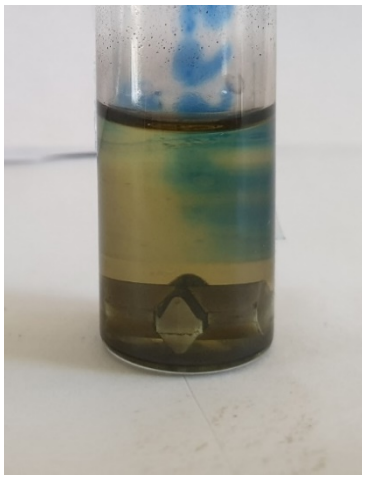
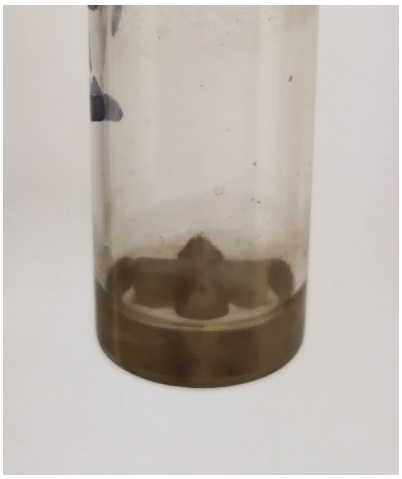
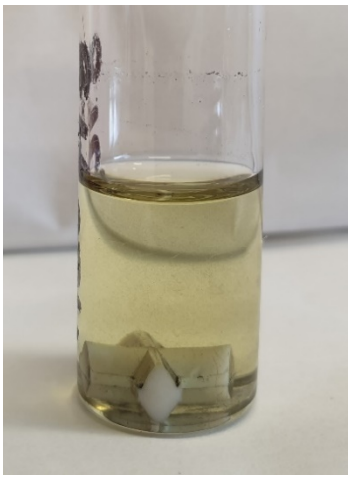
TEM images of Rh-NHC^{mes}@CCM **5b*** after 5 hydrogenation runs:



Photos of catalytic mixtures after hydrogenation

The reactions were carried out at a 1000/1 styrene/Rh ratio, 6h at 80°C, 20 bar H_2.

Reaction mixtures with **7b** under “wet toluene” conditions (left), “on-water” conditions (middle) or toluene/DME 1:1 conditions (right):

Biphasic mixture with **7b** incorporated into “blank” (non-functionalized polystyrene core) CCMs: “blank” CCMs + **7b** (aqueous phase) + styrene/toluene solution, after 1 run hydrogenation.

Aqueous phases containing **5b***, recovered after 1 run (left) and after 5 runs/4 recycles (right).

X-Ray diffraction analyses

Table 1. Crystal data and structure refinement.

Identification code	**2a**	**2b**
Empirical formula	C_{21} H_{26} Cl N_2 Rh	C_{29} H_{34} Cl N_2 Rh
Formula weight	444.80	548.94
Temperature, K	173(2)	173(2)
Wavelength, Å	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1/c
a, Å	12.4856(3)	17.8663(7)
b, Å	10.6263(2)	15.7110(6)
c, Å	15.2385(4)	9.4111(4)
α, °	90.0	90.0
β, °	98.181(2)	96.939(4)
γ, °	90.0	90.0
Volume, $Å^3$	2001.20(8)	2622.32(18)
Z	4	4
Density (calc), Mg/m^3	1.476	1.390
Abs. coefficient, mm^{-1}	8.153	0.772
F(000)	912	1136
Crystal size, mm^3	0.500 x 0.270 x 0.050	0.5 x 0.35 x 0.1
Theta range, °	4.290 to 61.163	2.891 to 26.371°.
Reflections collected	9274	36687
Indpt reflections (R_{int})	3054 (0.0333)	5344 (0.1512)
Absorption correction	Sphere	Multiscan
Max. / min. transmission	0.10401 and 0.03020	0.7461 / 0.6609
Refinement method	F^2	F^2
Data /restraints/parameters	3054 / 0 / 227	5344 / 20 / 359
Goodness-of-fit on F^2	1.045	1.206
R1, wR2 [I>2σ(I)]	0.0378, 0.1002	0.0518, 0.1011
R1, wR2 (all data)	0.0411, 0.1045	0.0542, 0.1024
Residual density, $e.Å^{-3}$	1.239 / -0.299	0.529 / -0.901

Table 2. Bond lengths [Å] and angles [°] for **2a**.

Rh(1)-Cl(1)	2.3763(10)	Rh(1)-C(1)	2.030(4)
Rh(1)-C(11)	2.200(4)	Rh(1)-C(15)	2.105(4)
Rh(1)-C(12)	2.189(4)	Rh(1)-C(16)	2.095(4)
N(2)-C(1)	1.353(5)	N(5)-C(1)	1.350(5)
N(2)-C(3)	1.377(5)	N(5)-C(4)	1.374(5)
N(2)-C(21)	1.462(5)	N(5)-C(51)	1.474(5)
C(11)-C(12)	1.382(6)	C(14)-C(15)	1.532(6)
C(11)-C(18)	1.508(7)	C(15)-C(16)	1.413(6)
C(12)-C(13)	1.498(7)	C(16)-C(17)	1.520(7)
C(13)-C(14)	1.529(7)	C(17)-C(18)	1.510(8)
C(3)-C(4)	1.336(6)	C(54)-C(55)	1.396(7)
C(51)-C(52)	1.505(6)	C(55)-C(56)	1.388(7)
C(52)-C(57)	1.382(6)	C(55)-C(58)	1.473(7)
C(52)-C(53)	1.399(6)	C(56)-C(57)	1.383(7)
C(53)-C(54)	1.370(7)	C(58)-C(59)	1.311(9)

C(11)-Rh(1)-Cl(1)	93.65(14)	C(12)-Rh(1)-Cl(1)	89.40(13)
C(1)-Rh(1)-C(11)	162.78(16)	C(1)-Rh(1)-C(12)	160.44(15)
C(1)-Rh(1)-C(15)	92.28(16)	C(1)-Rh(1)-C(16)	90.07(17)
C(15)-Rh(1)-Cl(1)	160.17(12)	C(16)-Rh(1)-Cl(1)	160.49(12)
C(15)-Rh(1)-C(12)	82.50(17)	C(16)-Rh(1)-C(12)	97.49(18)
C(16)-Rh(1)-C(11)	81.47(19)	C(15)-Rh(1)-C(11)	90.61(17)
C(1)-Rh(1)-Cl(1)	89.36(10)	N(5)-C(1)-N(2)	104.3(3)
C(1)-N(2)-C(3)	111.0(3)	C(1)-N(5)-C(4)	111.0(3)
C(1)-N(2)-C(21)	124.8(3)	C(1)-N(5)-C(51)	124.0(3)
C(3)-N(2)-C(21)	124.1(3)	C(4)-N(5)-C(51)	125.0(3)
N(2)-C(1)-Rh(1)	128.4(3)	N(5)-C(1)-Rh(1)	127.3(3)
C(4)-C(3)-N(2)	106.7(3)	C(3)-C(4)-N(5)	107.1(3)
C(12)-C(11)-C(18)	123.6(4)	C(57)-C(52)-C(51)	122.2(4)
C(11)-C(12)-C(13)	126.2(4)	C(53)-C(52)-C(51)	119.6(4)
C(12)-C(13)-C(14)	114.0(4)	C(54)-C(53)-C(52)	121.4(4)
C(13)-C(14)-C(15)	113.5(4)	C(53)-C(54)-C(55)	120.5(4)
C(16)-C(15)-C(14)	123.6(4)	C(56)-C(55)-C(54)	117.9(4)
C(15)-C(16)-C(17)	125.5(4)	C(56)-C(55)-C(58)	120.7(5)
C(18)-C(17)-C(16)	114.8(4)	C(54)-C(55)-C(58)	121.3(5)
C(11)-C(18)-C(17)	111.7(4)	C(57)-C(56)-C(55)	121.5(4)
N(5)-C(51)-C(52)	112.0(3)	C(52)-C(57)-C(56)	120.4(4)
C(57)-C(52)-C(53)	118.2(4)	C(59)-C(58)-C(55)	126.7(6)

Table 3. Bond lengths [Å] and angles [°] for **2b**.

Rh(1)-Cl(1)	2.3839(9)	Rh(1)-C(1)	2.034(3)
Rh(1)-C(12)	2.187(4)	Rh(1)-C(16)	2.096(3)
Rh(1)-C(11)	2.195(4)	Rh(1)-C(15)	2.095(4)
N(2)-C(1)	1.359(4)	N(5)-C(1)	1.351(4)
N(2)-C(3)	1.388(4)	N(5)-C(4)	1.381(5)
N(2)-C(21)	1.440(4)	N(5)-C(51)	1.459(5)
C(3)-C(4)	1.328(5)	C(21)-C(22)	1.386(4)
C(12)-C(11)	1.377(7)	C(21)-C(26)	1.387(5)
C(12)-C(13)	1.492(7)	C(22)-C(23)	1.384(5)
C(11)-C(18)	1.513(7)	C(22)-C(221)	1.489(5)
C(17)-C(18)	1.516(7)	C(23)-C(24)	1.378(5)
C(16)-C(17)	1.493(5)	C(24)-C(25)	1.377(5)
C(15)-C(16)	1.392(5)	C(24)-C(241)	1.510(5)
C(15)-C(14)	1.521(5)	C(25)-C(26)	1.393(5)
C(13)-C(14)	1.527(7)	C(26)-C(261)	1.504(5)
C(51)-C(52A)	1.508(6)	C(51)-C(52B)	1.508(6)
C(52A)-C(53A)	1.391(12)	C(52B)-C(53B)	1.361(12)
C(52A)-C(57A)	1.391(11)	C(52B)-C(57B)	1.415(12)
C(53A)-C(54A)	1.383(15)	C(53B)-C(54B)	1.388(15)
C(54A)-C(55A)	1.395(16)	C(54B)-C(55B)	1.388(17)
C(55A)-C(56A)	1.397(18)	C(55B)-C(56B)	1.399(18)
C(55A)-C(58A)	1.489(16)	C(55B)-C(58B)	1.468(14)
C(56A)-C(57A)	1.391(16)	C(56B)-C(57B)	1.381(16)
C(58A)-C(59A)	1.290(13)	C(58B)-C(59B)	1.289(14)

C(1)-Rh(1)-C(15)	96.54(13)	C(16)-Rh(1)-C(11)	81.00(16)
C(1)-Rh(1)-C(16)	92.29(13)	C(1)-Rh(1)-Cl(1)	87.78(10)
C(1)-Rh(1)-C(12)	162.34(16)	C(15)-Rh(1)-Cl(1)	157.49(11)
C(15)-Rh(1)-C(12)	81.72(16)	C(16)-Rh(1)-Cl(1)	163.48(11)
C(16)-Rh(1)-C(12)	97.02(15)	C(12)-Rh(1)-Cl(1)	87.50(12)
C(1)-Rh(1)-C(11)	160.86(15)	C(11)-Rh(1)-Cl(1)	93.63(12)
C(15)-Rh(1)-C(11)	89.44(15)	N(5)-C(1)-N(2)	103.7(3)
N(2)-C(1)-Rh(1)	129.9(2)	N(5)-C(1)-Rh(1)	125.9(2)
C(1)-N(2)-C(3)	110.9(3)	C(1)-N(5)-C(4)	111.7(3)
C(1)-N(2)-C(21)	125.6(3)	C(1)-N(5)-C(51)	123.3(3)
C(3)-N(2)-C(21)	123.4(3)	C(4)-N(5)-C(51)	124.6(3)
C(4)-C(3)-N(2)	107.0(3)	C(3)-C(4)-N(5)	106.7(3)

C(12)-C(11)-C(18)	123.9(4)	C(16)-C(15)-C(14)	124.1(4)
C(11)-C(18)-C(17)	112.8(3)	C(15)-C(14)-C(13)	112.7(4)
C(16)-C(17)-C(18)	113.0(4)	C(12)-C(13)-C(14)	113.4(4)
C(15)-C(16)-C(17)	126.5(3)		
C(22)-C(21)-N(2)	119.5(3)	C(26)-C(21)-N(2)	118.2(3)
C(22)-C(21)-C(26)	122.3(3)	C(25)-C(24)-C(241)	121.4(4)
C(23)-C(22)-C(21)	117.6(3)	C(23)-C(24)-C(241)	120.4(4)
C(23)-C(22)-C(221)	120.6(3)	C(24)-C(25)-C(26)	122.0(3)
C(21)-C(22)-C(221)	121.7(3)	C(21)-C(26)-C(25)	117.4(3)
C(24)-C(23)-C(22)	122.3(3)	C(21)-C(26)-C(261)	122.2(3)
C(25)-C(24)-C(23)	118.3(3)	C(25)-C(26)-C(261)	120.4(3)
N(5)-C(51)-C(52B)	111.6(3)	C(59A)-C(58A)-C(55A)	127.3(15)
N(5)-C(51)-C(52A)	111.6(3)	C(53B)-C(52B)-C(57B)	121.4(10)
C(53A)-C(52A)-C(57A)	114.6(10)	C(53B)-C(52B)-C(51)	126.2(8)
C(53A)-C(52A)-C(51)	120.0(7)	C(57B)-C(52B)-C(51)	112.4(8)
C(57A)-C(52A)-C(51)	125.4(8)	C(52B)-C(53B)-C(54B)	117.8(14)
C(54A)-C(53A)-C(52A)	123.6(15)	C(53B)-C(54B)-C(55B)	120.4(15)
C(53A)-C(54A)-C(55A)	121.0(16)	C(54B)-C(55B)-C(56B)	117.9(12)
C(54A)-C(55A)-C(56A)	113.5(12)	C(54B)-C(55B)-C(58B)	121.1(15)
C(54A)-C(55A)-C(58A)	121.9(14)	C(56B)-C(55B)-C(58B)	118.5(16)
C(56A)-C(55A)-C(58A)	123.4(14)	C(57B)-C(56B)-C(55B)	119.3(15)
C(57A)-C(56A)-C(55A)	124.0(13)	C(56B)-C(57B)-C(52B)	119.1(14)
C(56A)-C(57A)-C(52A)	121.1(13)	C(59B)-C(58B)-C(55B)	126.6(15)