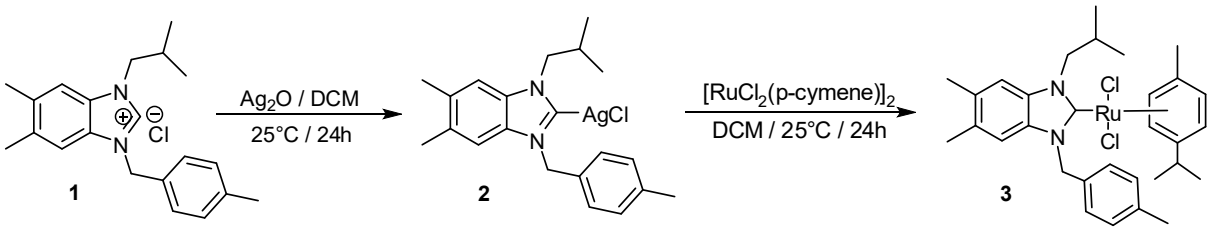

Preparation of benzimidazolium salts (1)

The benzimidazolium salts **1** were prepared by reactiong1-isobutyl-benzimidazole (1mmol) (**1**) with 4-methylbenzylchloride (1,1mmol) in dimethylformamide(DMF ; 5 mL) at 80°Cand the resulting mixturewas stirred for 24 hours. Diethyl ether (15 mL) was added toobtain a white crystalline solid, which was subsequently filteredoff. The solid was washed with diethyl ether (3×10 mL), driedunder vacuum, and the crude product was recrystallized fromDichloromethane/diethyl ether (1:3 ratio).

Preparation of silver(I)–NHC complexes (2)

A solution of benzimidazolium salt **1** (1.0 mmol) and Ag_2O(1.0 mmol) in dichloromethane(15mL) was stirred at room temperature for 24 h. The reaction mixture was filtered through celite and the solvent removed under reduced pressure. The crude product **2** was recrystallized from dichloromethane/diethyl ether (1:3).

Preparation of Ru(II)–NHC complexes (3)

The NHC ruthenium complexes **3** were synthesized by transmetallation via silver NHC complexes **2**. 10 mmol of Ag-NHC complex with 5 mmol of $[RuCl_2$ (p-cymene)$]_2$ dissolved in 30 ml of DCM and the mixture was stirred for 24 hours in the dark at room temperature, then the solution was filtered on celite and crystallized from DCM: diethyl ether (1: 2) at room temperature.

1-(isobutyl)-3-(4-methylbenzyl) -5.6-dimethylbenzimidazolium chloride, (1)

Yield 93%, $C_{21}H_{27}ClN_2$, M = 342.91g mol^{-1}, Mp: 223.2°C, ν(CN) = 1561 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.04 (d, 6H, $CH_{3\ (a,b)}$, J = 8 Hz), 2.31 (s, 3H, $CH_{3(e)}$), 2.38 (s, 3H, $CH_{3(c)}$), 2.42 (s, 3H, $CH_{3(d)}$), 2.39 (hept, 1H, $H_{2'}$, J = 4 Hz), 4.36 (d, 2H, $H_{1'}$, J = 8 Hz), 5.79 (s, 2H, $H_{1''}$), 7.15 – 7.39 (m, 6H, $H_{4,\ 7,3'',\ 4'',\ 6'',7''}$), 11.83 (s, 1H, H_2). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 19.8 ($C_{(c,d)}$), 20.6 ($C_{a,b}$), 21.1 (C_e), 28.7 ($C_{2'}$), 50.9 ($C_{1''}$), 54.2 ($C_{1'}$), 112.7 (C_4), 113.4 (C_7), 128.1 ($C_{3'';4'';6'';7''}$), 129.9 ($C_{8;9}$), 130.1 ($C_{2''}$), 130.2 ($C_{5''}$), 137.2 ($C_{5;6}$), 142.7 (C_2).

chloro-[1-(isobutyl)-3-(4-methylbenzyl) -5.6-dimethylbenzimidazole-2-ylidene]silver(I), (2)

Yield 93%, Mp: 161.2°C, ν(CN) = 1433 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.00 (d, 6H, $CH_{3\ (a,b)}$, J = 4 Hz), 2.31 (s, 3H, $CH_{3(c,d)}$), 2.34 (hept, 1H, $H_{2'}$, J = 4 Hz), 2.37 (s, 3H, $CH_{3(e)}$), 4.17 (d, 2H, $H_{1'}$, J = 8 Hz), 5.50 (s, 2H, $H_{1''}$), 7.12 – 7.26 (m, 6H, $H_{4,\ 7,3'',\ 4'',\ 6'',7''}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 20.3 ($C_{(c,d)}$), 20.4 (C_a), 20.4 (C_b), 21.1 (C_e), 29.2 ($C_{2'}$), 53.0 ($C_{1''}$), 56.7 ($C_{1'}$), 111.8 (C_4), 112.2 (C_7), 126.9 ($C_{3'';7''}$), 129.7 ($C_{4'';6''}$), 133.1 ($C_{2'';5''}$), 133.5 ($C_{8;9}$), 133.5 (C_5), 138.2 (C_6)C_2:

Ag-$C_{carbene}$: not observed. Elemental analysis % calcd. (found) for C21H26AgClN2: C, 56.079% (56.1); H, 5.827% (5.9); N, 6.228% (6.4).

Dichloro-[1-(isobutyl)-3-(4-methylbenzyl) -5.6-dimethylbenzimidazole-2-ylidene](p-cymene)ruthenium (II), (3)

Yield 79%, Mp: 167,8°C, ν(CN) = 1402 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 0.98 (d, 6H, $CH_{3\ (a,b)}$, *J* = 4 Hz), 1.27 (d, 6H, $CH_{3(g,h)}$, *J* = 4 Hz), 1.97 (s, 3H, $CH_{3(f)}$), 2.21 (s, 3H, $CH_{3(e)}$), 2.32 (d, 6H, $CH_{3(c,d)}$, *J* = 8 Hz), 2.66 (hept, 1H, $H_{2'}$, *J* = 8 Hz), 2.86 (hept, 1H, $H_{7'''}$, *J* = 4 Hz), 4.53 (d, 2H, $H_{1'}$, *J* = 8 Hz), 5.11 (s, 2H, $H_{1''}$), 5.38 (d, 2H, $H_{1''', 3'''}$, *J* = 8 Hz), 5.60 (d, 2H, $H_{4''', 6'''}$, *J* = 8 Hz), 6.78-7.22 (m, 6H, $H_{4,7,3',4',6',7'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 18.3 ($C_{(c,d)}$), 20.1 ($C_{(a,b)}$), 20.3 ($C_{(f,g,h)}$), 21.0 ($C_{(e,)}$), 27.9 ($C_{2'}$), 30.7 ($C_{7'''}$), 52.4 ($C_{1''}$), 55.7 ($C_{1'}$), 97.2 (C_4), 112.0 (C_7), 125.6 ($C_{3'';4'';6'';7''}$), 129.5 ($C_{1''';3''';4''';6'''}$), 131.6 (C_8), 131.9 (C_9), 134.1 ($C_{2'',2'''}$), 134.3 ($C_{5'',5'''}$), 134.9 (C_5), 136.9 (C_6), 187.9 (C_2). Elemental analysis % calcd. (found) for $C_{31}H_{40}Cl_2N_2Ru$: C, 60.676% (60.1); H, 6.734% (6.8); N, 4.565% (4.6).

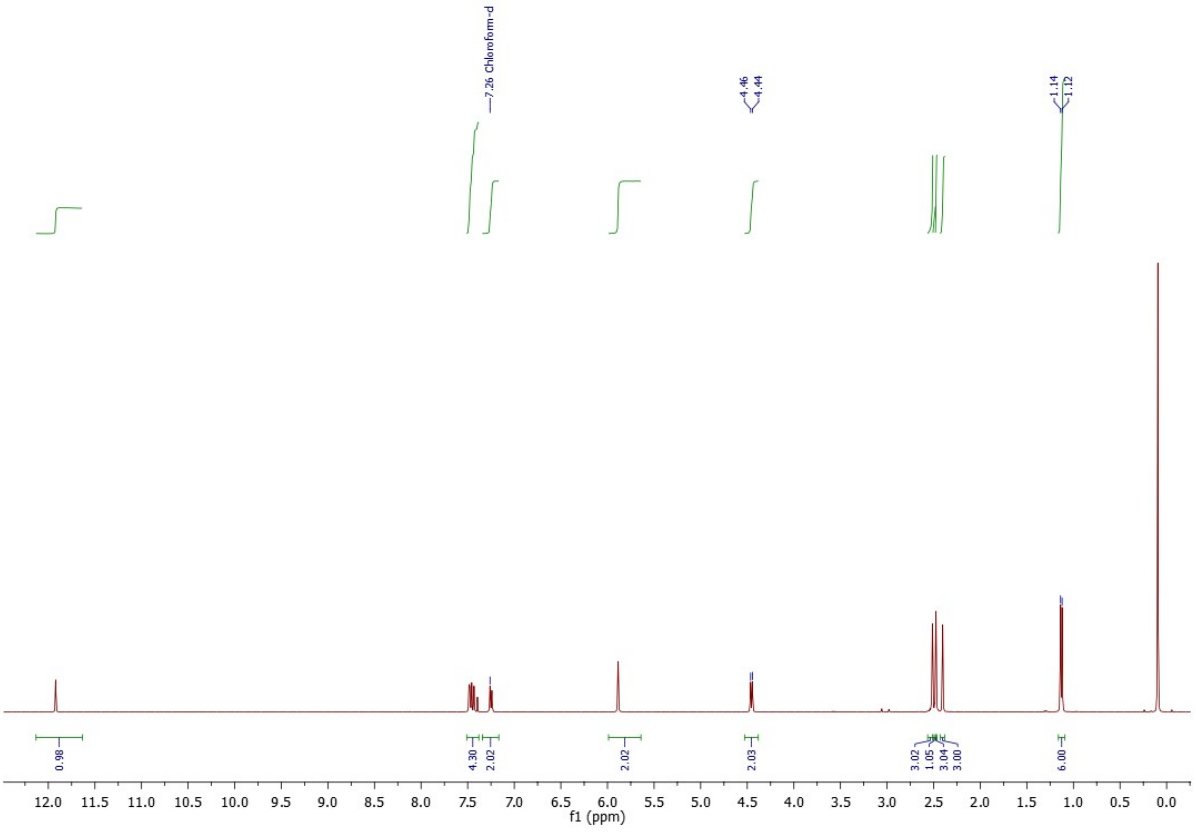

Figure S1: ^1H-NMR spectra of benzimidazole salt **1** in $CDCl_3$

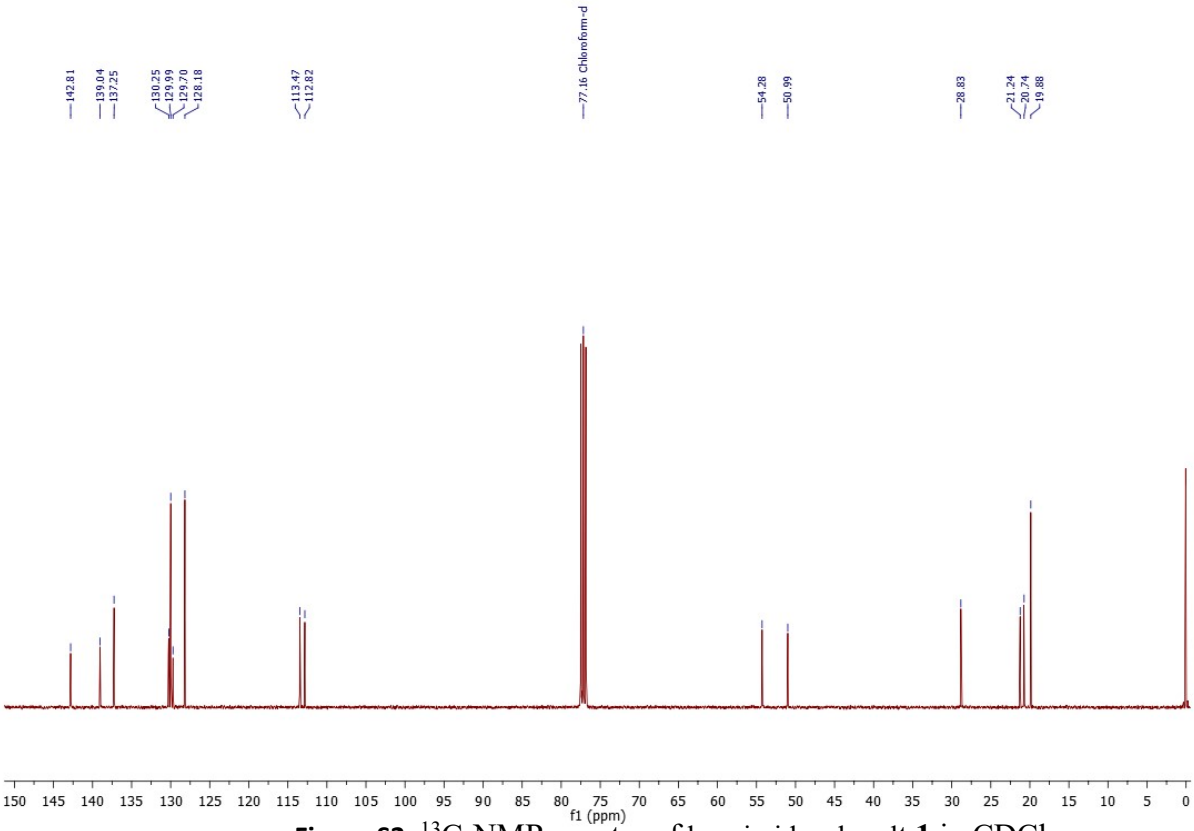

Figure S2: ^{13}C-NMR spectra of benzimidazole salt **1** in $CDCl_3$

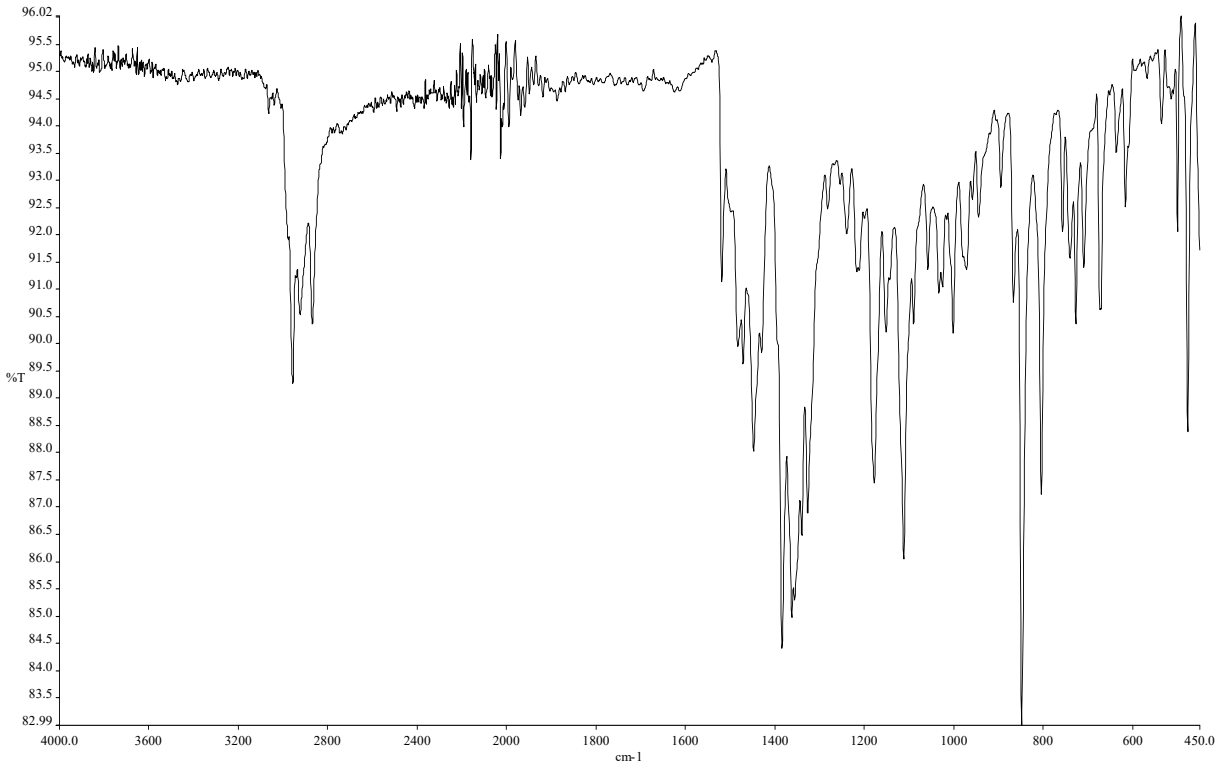

Figure S3. IR spectra on ATR unit of salt 1

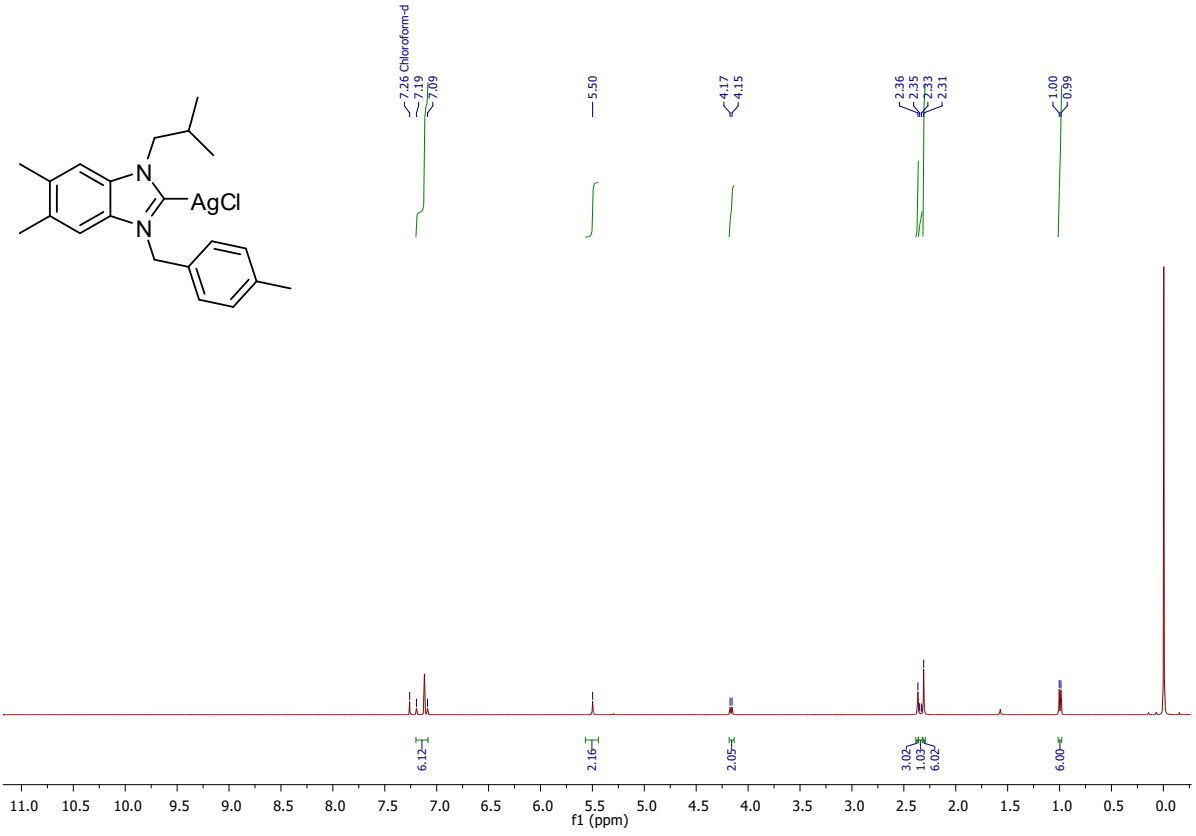

Figure S4. ^{1}H NMR spectrum (400 MHz, CDCl3) of complex **2**

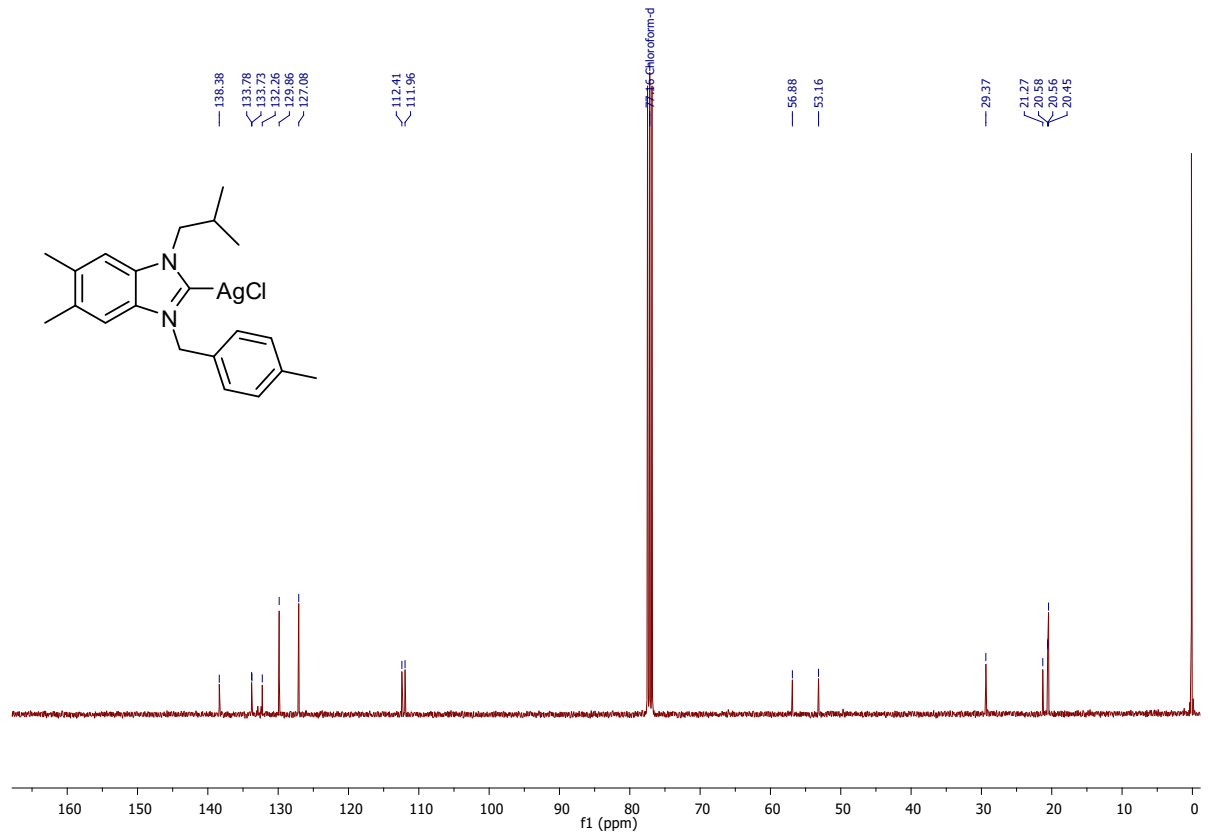

Figure S5: . ^{13}C NMR spectrum (100 MHz, CDCl3) of complex **2**

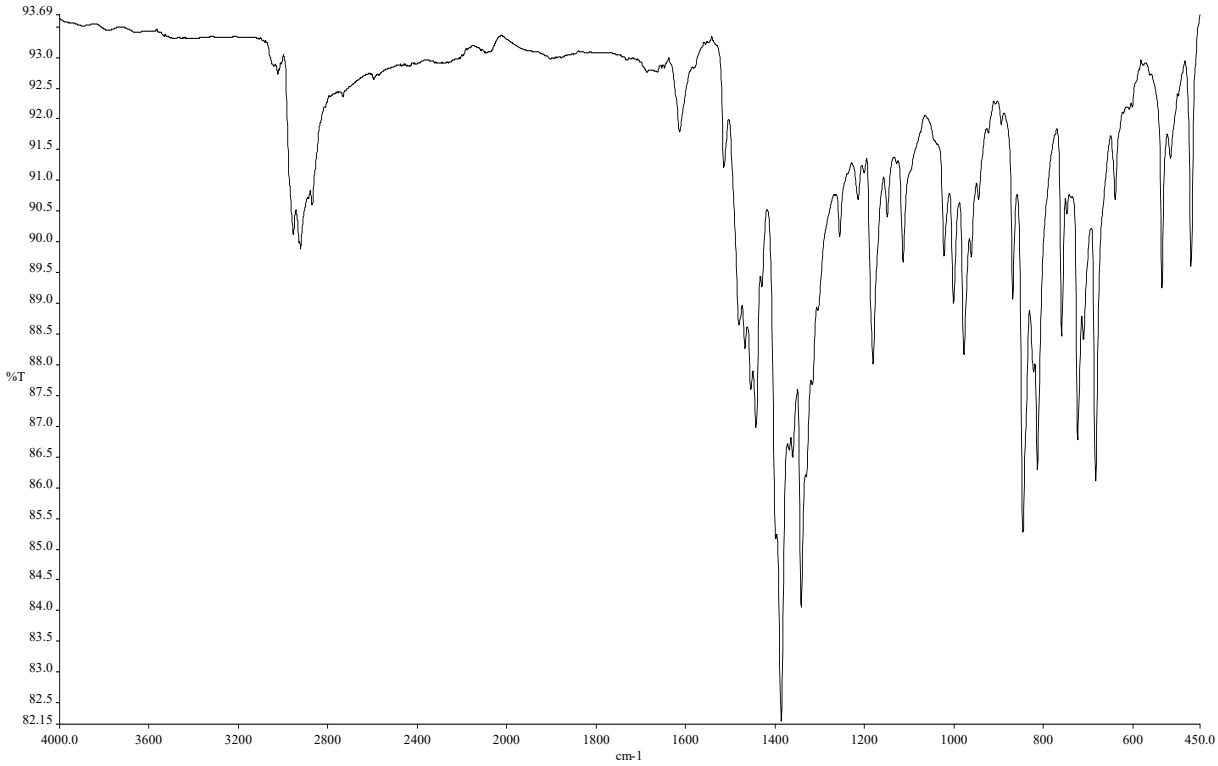

Figure S6. IR spectra on ATR unit of complex **2**

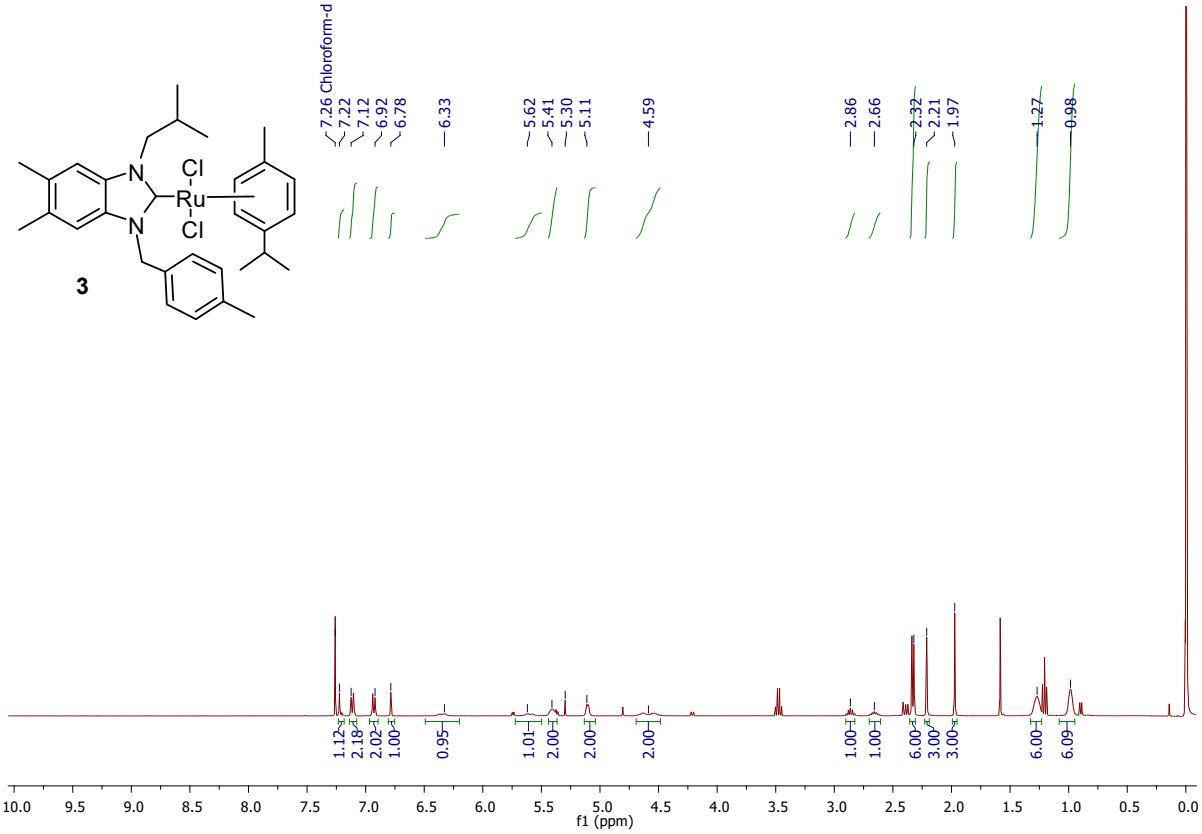

Figure S7. ^{1}H NMR spectrum (400 MHz, CDCl3) of complex**3**

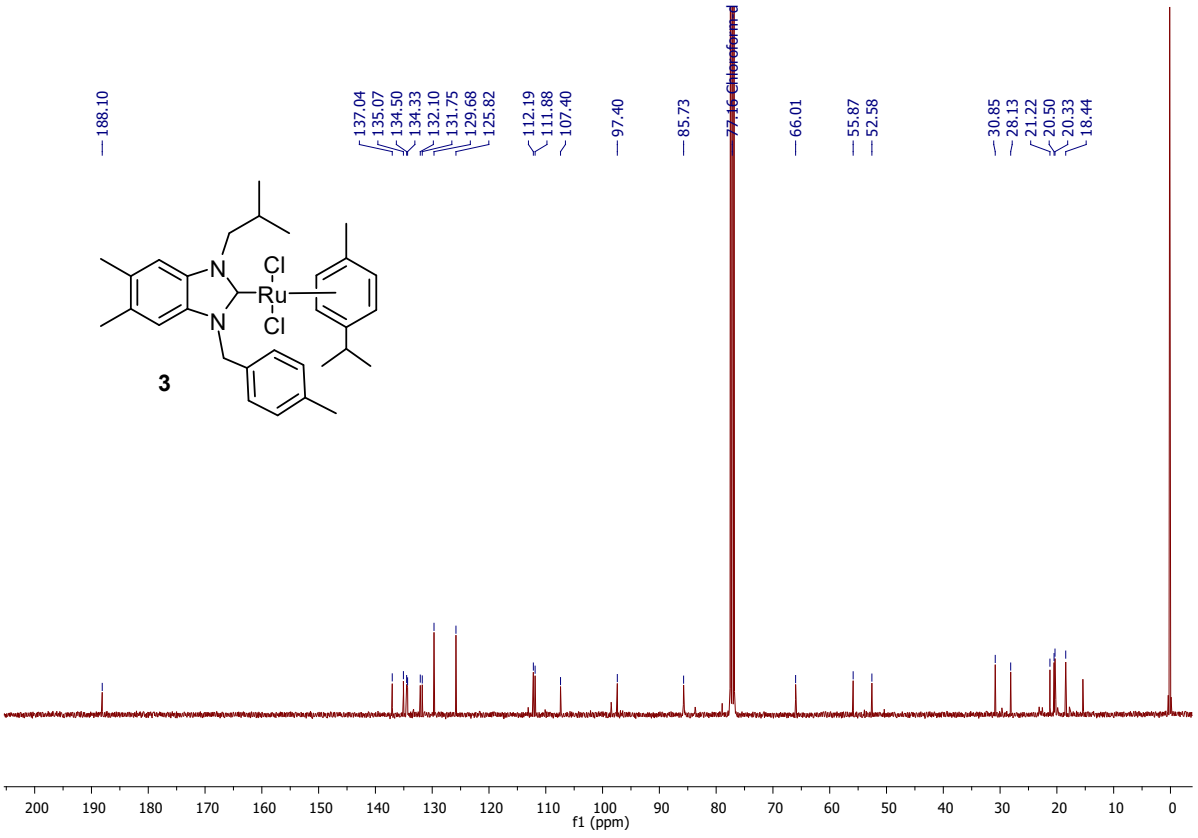

Figure S8. 13C NMR spectrum (100 MHz, CDCl3) ofcomplex 3

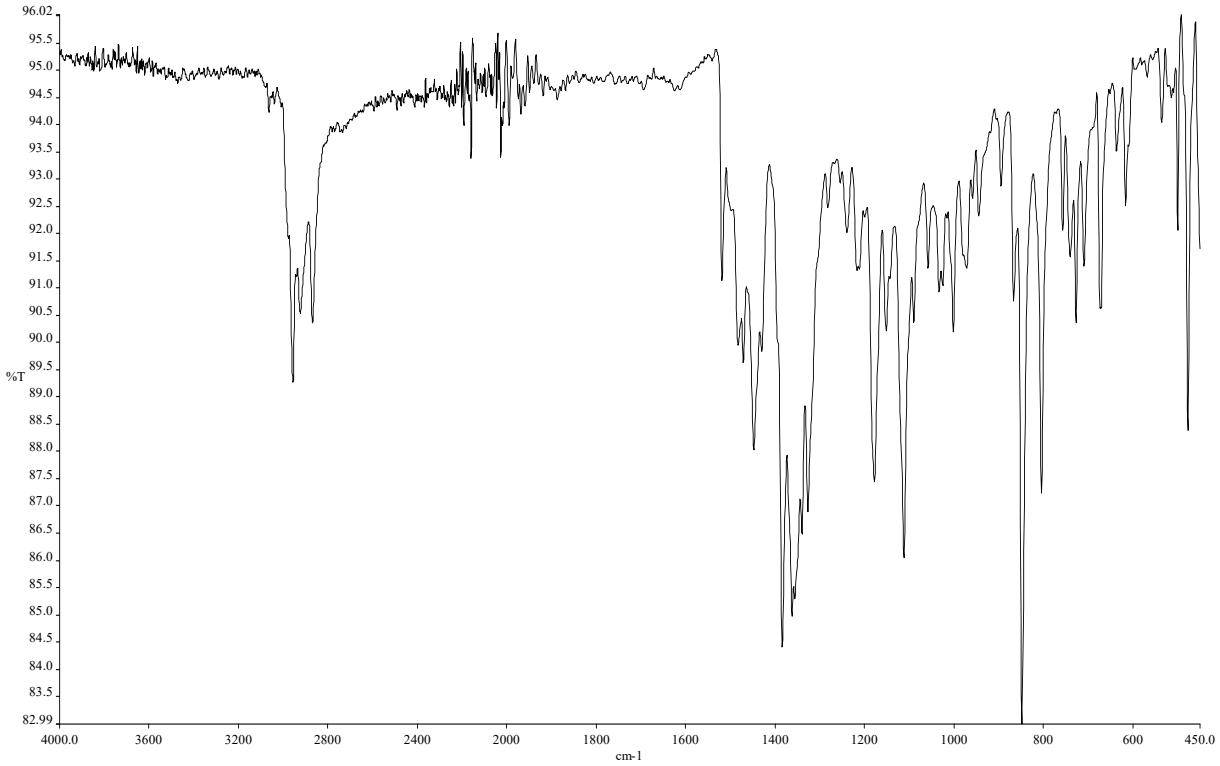

Figure S9. IR spectra on ATR unit of complex **3**

X-ray crystallography

X-ray data were collected on a STOE IPDS II diffractometer at room temperature using graphite-monochromated MoKα radiation by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA [1] while data reduction was applied using X-RED32 [1]. The structure was solved by direct methods with SIR2019 [2] and refined by means of the full-matrix least-squares calculations on F^2 using SHELXL-2018 [3]. All H atoms were located in difference maps and then treated as riding atoms, fixing the bond lengths at 0.98, 0.93, 0.97 and 0.96 Å for methine CH, aromatic CH, CH_2 and CH_3 atoms, respectively. In the complex, the isobutyl group of the NHC ligand and the isopropyl group of the *p*-cymene ligand were disordered over two sites and the refined site-occupancy factors of the disordered moieties are 0.591(12)/0.409(12)% and 0.58(4)/0.42(4)%, respectively. The displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for CH_3). Crystal data, data collection and structure refinement details are given in Table 1. Molecular graphic was generated by using OLEX2 [4].

Table 1. Crystal data and structure refinement parameters for complex **3**

CCDC depository	2085331
Color/shape	Brown/prism
Chemical formula	$[RuCl_2(C_{10}H_{14})(C_{21}H_{26}N_2)]$
Formula weight	612.62
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a, b, c (Å)	11.5940(5), 12.6166(5), 22.3958(9)
α, β, γ (°)	90, 95.492(4), 90
Volume (Å^3)	3260.9(2)
Z	4
$D_{calc.}$ (g/cm^3)	1.248
μ (mm^{-1})	0.664
Absorption correction	Integration
$T_{min.}$, $T_{max.}$	0.8533, 0.9632
F_{000}	1272
Crystal size (mm^3)	0.39 × 0.13 × 0.06
Diffractometer	STOE IPDS II
Measurement method	ω scan
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-26 \le l \le 26$
ϑ range for data collection (°)	$1.765 \le \vartheta \le 25.049$
Reflections collected	20762
Independent/observed	5782/2590
$R_{int.}$	0.1441
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5782/168/384
Goodness-of-fit on F^2	0.962
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0782$, $wR_2 = 0.1369$
R indices (all data)	$R_1 = 0.1846$, $wR_2 = 0.1723$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ (e/Å^3)	0.86, −0.33

Appendix A. Supplementary data

CCDC 2085331 contains the supplementary crystallographic data for the compound reported in this article. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/].