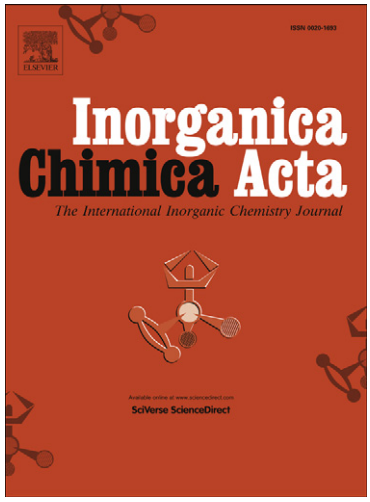

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Ru(II)-Arene Complexes with N-Substituted 3,4-Dihydroquinazoline Ligands and Catalytic Activity for Transfer Hydrogenation Reaction

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ABSTRACT

In this study, N-coordinated 3,4-dihydroquinazoline ruthenium(II) complexes were synthesized by the cleavage reaction of $[RuCl_2(p\text{-cymene})]_2$ with N-substituted 3,4-dihydroquinazolines. In addition, the X-ray crystal structure of 2,4,6-trimethylbenzyl substituted 3,4-dihydroquinazoline Ru(II) complex (1a) is reported. Furthermore, the resulting piano-stool complexes were evaluated as transfer hydrogenation catalysts for reduction of acetophenone in the presence of 2-propanol and KOH at 82°C. All the complexes showed good to excellent performance after 1h in the conversion of acetophenone to alcohol and the reaction rate was found to be sensitive to changes on the N-substituent. Additionally, the most active catalyst 1a was used in transfer hydrogenation of different ketones to investigate the effect of substituents on ketones.

Keywords: 3,4-Dihydroquinazoline; ruthenium(II) complexes; transfer hydrogenation reaction

1. Introduction

Ru(II)-arene complexes of the type $[(\eta^6\text{- arene})RuCl_2]_2$ are very versatile electrophiles since they can be used to introduce a variety of ligands with C_{NHC}-, P-, O- or S- donor atoms.[1-6] The resulting monomeric complexes, in neutral, mono- or dicationic forms, can be used as catalysts for a number of organic transformations or as biologically active compounds.[7-9]The Ru(II) complexes with ligands bearing N-donor atoms are attracting interest of researchers due to their potential to promote the catalytic reaction of organic compounds.[10-12] In this context, (η^6-arene)Ru(II) complexes containing N-bonded heterocycles, such as N-alkybenzazole, N-alkylimidazoline and N-alkyl-1,4,5,6-tetrahydropyrimidine were prepared and used successfully as catalysts for transfer hydrogenation or for the cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran. [13-19]

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However the development of new ligands is still of considerable importance, in order to find more efficient ruthenium catalysts. Recent studies showed that complexes derived from six-membered heterocyclic rings such as tetrahydropyrimidine exhibit superior activity as compared with five-membered analogues[19] and that the substitution pattern on the heterocyclic ring is also an important factor to affect the catalytic activity. Nevertheless, six-membered systems and their metal complexes have not been studied in detail. It is worth noting that although the quinazoline skeleton is a common structural motif among heterocycles and has been found to show remarkable biological activities and applications as pharmaceutical agents,[20-27] quinazoline containing complexes are rarely found in the literature.[28-32] Therefore, it seems of interest to examine the influence of benzene annulation at the 5,6-position of the reduced pyrimidines having alkyl- and aryl- substituents at the nitrogen atom. Thus, we wish to report here the synthesis and transfer hydrogenation activity of N-coordinated quinazoline Ru(II)-(arene) complexes.

2. Experimental

2.1. General

Unless otherwise specified all reactions were performed under argon using standard Schlenk techniques. Starting compounds and reagents were purchased from Merck (4-methylbenzaldehyde, 4-dimethylaminobenzaldehyde, sodium borohydride) Sigma-Aldrich (2-aminobenzylamine) Alfa Aesar (2,4,6-trimethylbenzaldehyde, 2,4,6-trimethoxybenzaldehyde, 3,4,5-trimethoxybenzaldehyde, 4-isopropylbenzaldehyde, 1-methylimidazole, p-anisidine) and Acros Organics (p-toluidine, p-anisaldehyde, 1,2-dimethylimidazole, N,N-dimethylformamide dimetyhl acetal) and used as received. Solvents like dichloromethane, ethanol, diethyl ether, toluene were obtained from Riedel-de Haën, Merck and J.T. Baker. The synthesis of **Ab+Bb**,[33] **Ad+Bd**, [34] **Ae+Be,** [35] **Cb**, [36] **Ce**,[37-38] **E** , **F** [39-47] have been reported previously. The spectroscopic data of these compounds were given in supplementary material. $[RuCl_2(p\text{-cymene})]_2$ was prepared by following a literature protocol. [48] ^{1}H NMR and ^{13}C NMR spectra were taken with a Varian AS 400 Mercury instrument operating at 399.88 MHz (^{1}H), 100.56 (^{13}C). As solvents d_1-$CDCl_3$ was employed. Chemical shifts (δ) are given in ppm relative to TMS; coupling constants (*J*) in Hz. The multiplicities of the signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; hept, heptet; m, multiplet. Elemental analysis of samples were done using on a LECO
CHNS model 932 elemental analyzer. FTIR Spectra were recorded on a Perkin Elmer Spectrum 100 series. MS analyses were performed using Bruker HCT Ultra Mass

Spectrometry (ESI) Agilent 1200 Capillary HPLC. Melting points were recorded with a Gallenkamp electrothermal melting point apparatus.

2.2. X-ray crystallography

For the crystal structure determination, the single-crystal of the Ru (II) complex **1a** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo K_α radiation (λ=0.71073 Å) and oscillation scans technique with $\Delta\omega=5^\circ$ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2>2\sigma(F^2)$. H atoms were positioned geometrically and refined using a riding model. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc., 2005) software.[49] The structure was solved by direct methods using SHELXS-97[50] and refined by a full-matrix least-squares procedure using the program SHELXL-97.[50] The final difference Fourier maps showed no peaks of chemical significance. Details of the crystal parameters, data collection and refinement are summarized in Table 1.

CCDC-883056 contains the supplementary crystallographic data for complex **1a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre.

Table 1

2.3. General procedure for the synthesis of compounds (**A+B**)

Substituted benzaldehyde derivatives (16.4 mmol) were added to a solution of 2-aminobenzylamine (16.4 mmol) in methanol (10 mL). The mixture was stirred at room temperature for 3 h. The light-yellow precipitate was filtered and washed with cold methanol (Scheme 1). [34]

2.4 General procedure for the synthesis of compounds (**C**)

The mixture of **Aa** and **Ba** (15.9 mmol) was dissolved in methanol (30 mL) and $NaBH_4$ (31.7 mmol) was added slowly under Ar (Scheme 1). The mixture was stirred for 2 h at room temperature. After that time the mixture was refluxed for 24 h. Then the solvent was removed

and the solid was extracted with CH_2Cl_2/H_2O. The dried organic phase was concentrated and the product was washed with Et_2O.

Ca: (96%). mp 72-74 °C, ^{1}H NMR δ 7.09-7.02, 6.69-6.62 (m, 4H, $NH_2C_6H_4CH_2NH$), 6.85 (s, 2H, $C_6H_2(CH_3)_3$-2,4,6), 4.68 (s, 2H, NH_2), 3.91 (s, 2H, $NH_2C_6H_4CH_2NH$), 3.76 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.34, 2.26 (s, 9H, $C_6H_2(CH_3)_3$-2,4,6). ^{13}C NMR δ 147.2, 130.1, 128.6, 124.3 117.8, 115.9 ($NH_2C_6H_4CH_2NH$), 137.1, 136.8, 133.7, 129.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 53.8($CH_2C_6H_2(CH_3)_3$-2,4,6), 47.3 ($NH_2C_6H_4CH_2NH$), 21.1, 19.7 ($C_6H_2(CH_3)_3$-2,4,6). Anal. Calcd (%) for $C_{17}H_{22}N_2$ (254.37): C 80.27, H 8.72, N 11.01 Found: C 80.23, H 8.74, N 11.03.

Cc: (87%). Liquid, ^{1}H NMR δ 7.23-7.15 (m, 4H, $C_6H_4(CH(CH_3)_2)$-4), [7.09-7.05 (m, 1H) 7.01 (d, *J* 7.2 Hz, 1H), 6.68-6.63 (m, 2H) ($NH_2C_6H_4CH_2NH$)], 4.66 (s, 2H, NH_2), 3.81 (s, 2H, $NH_2C_6H_4CH_2NH$) 3.74 (s, 2H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 2.89 (hept, *J* 6.7 Hz, 1H, $C_6H_4(CH(CH_3)_2)$-4), 1,24 (d, *J* 6.7 Hz, 6H, $C_6H_4(CH(CH_3)_2)$-4). ^{13}C NMR δ 147.2, 130.2, 128.6, 124.2, 117.9, 115.9 ($NH_2C_6H_4CH_2NH$), 147.9, 137.9, 128.4, 126.7 ($C_6H_4(CH(CH_3)_2)$-4), 53.3, ($CH_2C_6H_4(CH(CH_3)_2)$-4), 52.7 ($NH_2C_6H_4CH_2NH$), 34.1 ($C_6H_4(CH(CH_3)_2)$-4), 24.3 ($C_6H_4(CH(CH_3)_2)$-4). Anal. Calcd (%) for $C_{17}H_{22}N_2$ (254.37): C 80.27, H 8.72, N 11.01 Found: C 80.22, H 8.75, N 11.02.

Cd: (88%). Liquid, ^{1}H NMR δ 7.07, 6.61 (d, *J* 8.8 Hz, 4H, $C_6H_4(N(CH_3)_2)$-4), [6.97 (t, *J* 1.6 Hz, 1H), 6.91 (d, *J* 7.6 Hz, 1H), 6.56-6.52 (m, 2H) ($NH_2C_6H_4CH_2NH$)], 4.60 (s, 2H, NH_2), 3.71(s, 2H, $NH_2C_6H_4CH_2NH$), 3.59 (s, 2H, $CH_2C_6H_4(N(CH_3)_2)$-4), 2.85 (s, 6H, $C_6H_4(N(CH_3)_2)$-4). ^{13}C NMR δ 147.3, 130.2, 128.6, 124.4, 117.9, 115.9, ($NH_2C_6H_4CH_2NH$), 150.1, 129.3, 128.5, 112.9 ($C_6H_4(N(CH_3)_2)$-4), 53.0 ($CH_2C_6H_4(N(CH_3)_2)$-4), 52.5 ($NH_2C_6H_4CH_2NH$), 41.0 ($C_6H_4(N(CH_3)_2)$-4). Anal. Calcd (%) for $C_{16}H_{21}N_3$ (255.36): C 75.26, H 8.29, N 16.45 Found: C 75.29, H 8.28, N 16.43.

Cf: (81%). mp 68-70 °C, ^{1}H NMR δ [7.05 (t, *J* 8 Hz, 1H), 6.97-6.95 (m, 1H), 6.63-6.60 (m, 2H) ($NH_2C_6H_4CH_2NH$)], 6.14 (s, 2H, $C_6H_2(OCH_3)_3$-2,4,6), 3.83, 3.81 (s, 9H, $C_6H_2(OCH_3)_3$-2,4,6), 3.82 (s, 2H, $NH_2C_6H_4CH_2NH$), 3.79 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-2,4,6). ^{13}C NMR δ 147.5, 130.1, 128.2, 124.9, 117.5, 115.7, ($NH_2C_6H_4CH_2NH$), 160.6, 159.7, 109.4, 90.6 ($C_6H_2(OCH_3)_3$-2,4,6), 55.7, 55.3 ($C_6H_2(OCH_3)_3$-2,4,6), 52.2 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 40.9 ($NH_2C_6H_4CH_2NH$). Anal. Calcd (%) for $C_{17}H_{22}N_2O_3$ (302.37): C 67.53, H 7.33, N 9.26 Found: C 67.55, H 7.32, N 9.28.

Cg: (70%). mp 68-70 ^{o}C, ^{1}H NMR δ [7.06 (d, *J* 7.6 Hz, 1H), 6.99 (d, *J* 6.8 Hz, 1H), 6.67-6.62 (m, 2H) ($NH_2C_6H_4CH_2NH$)], 6.52 (s, 2H, $C_6H_2(OCH_3)_3$-3,4,5), 3.85, 3.83 (s, 9H, $C_6H_2(OCH_3)_3$-3,4,5), 3.81 (s, 2H, $NH_2C_6H_4CH_2NH$), 3.72 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5). ^{13}C NMR δ 147.0, 130.3, 128.7, 123.9, 118.0, 115.9 ($NH_2C_6H_4CH_2NH$), 153.5, 137.3, 136.1, 105.3 ($C_6H_2(OCH_3)_3$-3,4,5), 61.1, 56.4 ($C_6H_2(OCH_3)_3$-3,4,5), 53.7 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 52.4 ($NH_2C_6H_4CH_2NH$) . Anal. Calcd (%) for $C_{17}H_{22}N_2O_3$ (302.37): C 67.53, H 7.33, N 9.26 Found: C 67.56, H 7.34, N 9.24.

2.5 General procedure for the synthesis of compounds (**D**)

The monosubstituted diamine **C** (11.8 mmol) was heated with $Me_2NCH(OMe)_2$ (12.9 mmol) on an oil bath for 2 h at 90 ^{o}C and 1 h at 110 ^{o}C in order to distill MeOH and Me_2NH formed. Following the completion of the process, volatiles were removed under vacuo and the residue was crystallized from Et_2O.

Da: (82%). mp 147-149 ^{o}C, ^{1}H NMR δ [7.13 (t, *J* 8 Hz, 1H), 7.02 (d, *J* 7.6 Hz, 1H), 6.95 (t, *J* 7.6 Hz, 1H), 6.77 (d, *J* 7.2 Hz, 1H) ($NC_6H_4CH_2N$)], 6.97 (s, 1H, NC*H*N), 6.89 (s, 2H, $C_6H_2(CH_3)_3$-2,4,6), 4.41 (s, 2H, $NC_6H_4CH_2N$), 4.27 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.33, 2.28 (s, 9H, $C_6H_2(CH_3)_3$-2,4,6). ^{13}C NMR δ 149.5 (N*C*HN), 142.2, 120.4 ($NCC_5H_4CCH_2N)_{benzylamine}$, 128.5, 124.8 ($NCCHC_2H_2CHCCH_2N)_{benzylamine}$, 125.8, 124.7 ($NCCHC_2H_2CHCCH_2N)_{benzylamine}$, 138.2, 127.2 $[CC(CH_3)CHC(CH_3)CHC(CH_3)]_{benzyl}$, 138.0 $[CC(CH_3)CHC(CH_3)CHC(CH_3)]_{benzyl}$, 129.8 $[CC(CH_3)CHC(CH_3)CHC(CH_3)]_{benzyl}$, ($C_6H_2(CH_3)_3$-2,4,6), 50.6 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 46.8 ($NC_6H_4CH_2N$), 21.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 20.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6). $\upsilon_{(CN)=}$1614cm^{-1}. Anal. Calcd (%) for $C_{18}H_{20}N_2$ (264.36): C 81.78, H 7.62, N 10.60 Found: C 81.52, H 7.75, N 10.73.

Db: (46%). mp 100-102 ^{o}C, ^{1}H NMR δ 7.23 (s, 1H, NC*H*N), 7.18 (s, 4H, $CH_2C_6H_4(CH_3)$-4), [7.14 (t, *J* 7.2 Hz, 1H), 7.07 (d, *J* 8 Hz, 1H), 6.96 (t, *J* 7.6 Hz, 1H), 6.75 (d, *J* 7.6 Hz, 1H) ($NC_6H_4CH_2N$)], 4.38 (s, 2H, $NC_6H_4CH_2N$), 4.26 (s, 2H, $CH_2C_6H_4(CH_3)$-4), 2.35 (s, 3H, $C_6H_4(CH_3)$-4). ^{13}C NMR δ 150.3 (N*C*HN), 141.9, 128.5, 125.9, 124.9, 124.8, 120.6 ($NC_6H_4CH_2N$), 138.2, 132.2, 129.8, 127.9 ($C_6H_4(CH_3)$-4), 56.8 ($CH_2C_6H_4(CH_3)$-4), 46.5 ($NC_6H_4CH_2N$), 21.3 ($C_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1617cm^{-1}. Anal. Calcd (%) for $C_{16}H_{16}N_2$ (236.31): C 81.32, H 6.82, N 11.85 Found: C 81.20, H 6.89, N 11.90.

Dc: (70%). mp 117-119 ^{o}C, ^{1}H NMR δ 7.25-7.22 (m, 4H, $C_6H_4(CH(CH_3)_2)$-4), 7.19 (s, 1H, NC*H*N), [7.14 (t, *J* 7.6 Hz, 1H), 7.07 (d, *J* 8 Hz, 1H), 6.93-6.97 (m, 1H), 6.76 (d, *J* 7.6 Hz,

1H) ($NC_6H_4CH_2N$)], 4.39 (s, 2H, $NC_6H_4CH_2N$), 4.25 (s, 2H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 2.91 (hept, *J* 6.7 Hz, 1H, $C_6H_4(CH(CH_3)_2)$-4), 1.25 (d, *J* 6.7 Hz, 6H, $C_6H_4(CH(CH_3)_2)$-4). ^{13}C NMR δ 150.2 (NCHN), 141.8, 128.5, 125.8, 124.9, 124.8, 120.5 ($NC_6H_4CH_2N$), 149.2, 132.5, 128.0, 127.2 ($C_6H_4(CH(CH_3)_2)$-4), 56.9 ($CH_2C_6H_4(CH(CH_3)_2)$-4), 46.6 ($NC_6H_4CH_2N$), 34.1 ($C_6H_4(CH(CH_3)_2)$-4), 24.2 ($C_6H_4(CH(CH_3)_2)$-4). $\upsilon_{(CN)=}$1617cm^{-1}. Anal. Calcd (%) for $C_{18}H_{20}N_2$(264.36): C 81.78, H 7.62, N 10.60 Found: C 81.60, H 7.72, N 10.68.

Dd: (74%). mp 138-140 °C, ^{1}H NMR δ 7.22 (s, 1H, NCHN), 7.15, 6.71 (d, *J* 8.8 Hz, 4H, $C_6H_4(N(CH_3)_2)$-4), [7.12 (t, *J* 7.6 Hz, 1H), 7.06 (d, *J* 8 Hz, 1H), 6.95 (t, *J* 7.2 Hz, 1H), 6.76 (d, *J* 7.6 Hz, 1H) ($NC_6H_4CH_2N$)], 4.38 (s, 2H, $NC_6H_4CH_2N$), 4.20 (s, 2H, $CH_2C_6H_4(N(CH_3)_2)$-4), 2.95 (s, 6H, $C_6H_4(N(CH_3)_2)$-4). ^{13}C NMR δ 150.3 (NCHN), 142.1, 128.4, 125.9, 124.8, 124.7, 120.7 ($NC_6H_4CH_2N$), 150.7, 129.2, 122.3, 112.8 ($C_6H_4(N(CH_3)_2)$-4), 56.8, ($CH_2C_6H_4(N(CH_3)_2)$-4), 46.3 ($NC_6H_4CH_2N$), 40.7 ($C_6H_4(N(CH_3)_2)$-4). $\upsilon_{(CN)=}$1614cm^{-1}. Anal. Calcd (%) for $C_{17}H_{19}N_3$(265.35): C 76.95, H 7.22 N, 15.84 Found: C 76.80, H 7.27, N 15.93.

De: (78%). mp 83-85 °C, ^{1}H NMR δ 7.19 (s, 1H, NCHN), 7.17, 6.89 (d, *J* 2.8 Hz, 4H, $C_6H_4(OCH_3)$-4), [7.12-7.10 (m, 1H), 7.05 (d, *J* 7.2 Hz, 1H), 6.95-6.93 (m, 1H), 6.73 (d, *J* 6.8 Hz, 1H) ($NC_6H_4CH_2N$)], 4.34 (s, 2H, $NC_6H_4CH_2N$), 4.19 (s, 2H, $CH_2C_6H_4(OCH_3)$-4), 3.78 (s, 3H, $C_6H_4(OCH_3)$-4). ^{13}C NMR δ 150.2 (NCHN), 141.9, 128.5, 125.9, 124.9, 124.8, 120.6 ($NC_6H_4CH_2N$), 159.8, 129.3, 127.1, 114.6 ($C_6H_4(OCH_3)$-4), 56.6 ($CH_2C_6H_4(OCH_3)$-4), 46.4 ($NC_6H_4CH_2N$), 55.5 ($C_6H_4(OCH_3)$-4). $\upsilon_{(CN)=}$1615cm^{-1}. Anal. Calcd (%) for $C_{16}H_{16}N_2O$ (252.31): C 76.16, H 6.39, N 11.10 Found: C 76.23, H 6.42, N 11.84.

Df: (96%). mp 148-150 °C, ^{1}H NMR δ 7.18 (s, 1H, NCHN), [7.05 (t, *J* 8.8 Hz, 1H), 6.94 (d, *J* 8 Hz, 1H), 6.86 (t, *J* 7.2 Hz, 1H), 6.73 (d, *J* 7.2 Hz, 1H) ($NC_6H_4CH_2N$)], 6.09 (s, 2H, $C_6H_2(OCH_3)_3$-2,4,6), 4.38 (s, 2H, $NC_6H_4CH_2N$), 4.25 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-2,4,6), 3.82, 3.79 (s, 9H, $C_6H_2(OCH_3)_3$-2,4,6). ^{13}C NMR δ 151.2 (NCHN), 142.3, 128.1, 125.7, 124.4, 124.1, 121.1 ($NC_6H_4CH_2N$), 161.7, 160.1, 103.9, 90.6 ($C_6H_2(OCH_3)_3$-2,4,6), 55.8, 55.4 ($C_6H_2(OCH_3)_3$-2,4,6), 46.2 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 44.7 ($NC_6H_4CH_2N$). $\upsilon_{(CN)=}$1612cm^{-1}. Anal. Calcd (%) for $C_{18}H_{20}N_2O_3$(312.36): C 69.21, H 6.45, N 8.97 Found: C 69.40, H 6.46, N 8.87.

Dg: (66%). mp 125-127 °C, ^{1}H NMR δ 7.17 (s, 1H, NCHN), [7.14 (t, *J* 7.6 Hz, 1H), 7.06 (d, *J* 7.6 Hz, 1H), 6.96 (t, *J* 7.6 Hz, 1H), 6.77 (d, *J* 7.2 Hz, 1H)($NC_6H_4CH_2N$)], 6.47 (s, 2H, $C_6H_2(OCH_3)_3$-3,4,5), 4.41 (s, 2H, $NC_6H_4CH_2N$), 4.22 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.85, 3.83 (s, 9H, $C_6H_2(OCH_3)_3$-3,4,5). ^{13}C NMR δ 150.2 (NCHN), 141.7, 128.6, 125.9, 125.1,

124.9, 120.5 ($NC_6H_4CH_2N$), 153.9, 138.1, 130.9, 104.9 ($C_6H_2(OCH_3)_3$-3,4,5), 61.1, 56.5 ($C_6H_2(OCH_3)_3$-3,4,5), 57.4 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 46.6 ($NC_6H_4CH_2N$). $\upsilon_{(CN)=}$1618cm^{-1}. Anal. Calcd (%) for $C_{18}H_{20}N_2O_3$ (312.36): C 69.21, H 6.45, N 8.97 Found: C 69.44, H 6.35, N 8.79.

2.6 General procedure for the synthesis of Ru(II) complexes (**1**-**3**)

3,4-Dihydroquinazoline derivatives (0.76 mmol) were dissolved in dry toluene (10 mL) and then $[RuCl_2(p\text{-cymene})]_2$ (0.38 mmol) was added to the solution. The mixture was refluxed for 4h under Ar. After that time the solvent was removed under vacuo and red/orange crystals were obtained by crystallization with CH_2Cl_2/Et_2O. 1-Methylimidazol- and 1,2-dimethylimidazol Ru(II) complexes were synthesized using the same procedure.

1a: (81%). mp 226-228 ^oC, ^1H NMR δ 7.74 (s, 1H, NC*H*N), [7.94 (d, *J* 8.4 Hz, 1H), 7.18 (t, *J* 7.6 Hz, 1H), 7.00 (t, *J* 7.2 Hz, 1H), 6.78 (d, *J* 7.6 Hz, 1H) ($NC_6H_4CH_2N$)], 6.93 (s, 2H, $C_6H_2(CH_3)_3$-2,4,6), 5.15, 5.39 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.49 (s, 2H, $NC_6H_4CH_2N$), 4.34 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.84 (hept, *J* 7.1 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.36, 2.29 (s, 9H, $C_6H_2(CH_3)_3$-2,4,6), 2.01 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.21 (d, *J* 7.1 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 155.3 (N*C*HN), 140.4, 128.2, 126.9, 125.7, 125.5, 120.8 ($NC_6H_4CH_2N$), 138.9, 138.5, 129.8, 126.6, ($C_6H_2(CH_3)_3$-2,4,6), 102.9, 96.7, 82.1, 81.9 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 51.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 47.7 ($NC_6H_4CH_2N$), 30.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 22.5 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 21.2, 20.4 ($C_6H_2(CH_3)_3$-2,4,6), 18.3 ($(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1622 cm^{-1}. Anal. Calcd (%) for $C_{28}H_{34}Cl_2N_2Ru$ (570.56): C 58.94, H 6.01, N 4.92 Found: C 58.90, H 6.05, N 4.97.

1b: (90%). mp 210-212 ^oC, ^1H NMR δ 8.16 (s, 1H, NC*H*N), [8.07 (d, *J* 8 Hz, 1H), 7.19 (s, 1H), 7.00 (t, *J* 7.2 Hz, 1H), 6.76 (d, *J* 7.6 Hz, 1H) ($NC_6H_4CH_2N$)], 7.19 (s, 4H, $C_6H_4(CH_3)$-4), 5.49, 5.29 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.42 (s, 2H, $NC_6H_4CH_2N$), 4.31 (s, 2H, $CH_2C_6H_4(CH_3)$-4), 3.03 (hept, *J* 6.9 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.22 (s, 3H, $C_6H_4(CH_3)$-4), 2.16 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.32 (d, *J* 6.9 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 155.6 (N*C*HN), 140.6, 128.3, 126.9, 125.8, 125.7, 120.9 ($NC_6H_4CH_2N$), 138.7, 130.8, 129.9, 128.5 ($C_6H_4(CH_3)$-4), 102.6, 97.4, 82.7, 81.7 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 57.8 ($CH_2C_6H_4(CH_3)$-4), 46.3 ($NC_6H_4CH_2N$), 30.8 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 22.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 21.4 ($C_6H_4(CH_3)$-4), 18.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1623 cm^{-1}. Anal. Calcd (%) for $C_{26}H_{30}Cl_2N_2Ru$ (542.51): C 57.56, H 5.57, N 5.16 Found: C 57.51, H 5.62, N 5.19.

1c: (47%). mp 214-216 °C, ^{1}H NMR δ 8.11 (s, 1H, NC*H*N), [8.05 (d, *J* 8 Hz, 1H), 7.17 (t, *J* 7.2 Hz, 1H), 6.98 (t, *J* 7.6 Hz, 1H), 6.78 (d, *J* 7.2 Hz, 1H) ($NC_6H_4CH_2N$)], 7.22 (s, 4H, $C_6H_4(CH(CH_3)_2)$-4), 5.49, 5.27 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.42 (s, 2H, $NC_6H_4CH_2N$), 4.23 (s, 2H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 3.02 (hept, *J* 7.0 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.90 (hept, *J* 7.0 Hz, 1H, $C_6H_4(CH(CH_3)_2)$-4), 2.19 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.30 (d, *J* 7.0 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.25 (d, *J* 7.0 Hz, 6H, $C_6H_4(CH(CH_3)_2)$-4). ^{13}C NMR δ 155.6 (N*C*HN), 140.6, 128.1, 126.9, 125.9, 125.6, 120.9 ($NC_6H_4CH_2N$), 149.6, 131.3, 128.6, 127.3 ($C_6H_4(CH(CH_3)_2)$-4), 102.6, 97.4, 82.7, 81.7 $(CH_3)_2CHC_6H_4(CH_3)$-4), 57.6 ($CH_2C_6H_4(CH(CH_3)_2)$-4), 46.4 ($NC_6H_4CH_2N$), 34.1 ($C_6H_4(CH(CH_3)_2)$-4), 30.8 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 24.1 ($C_6H_4(CH(CH_3)_2)$ -4), 22.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 18.7 ($(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1622 cm^{-1} Anal. Calcd (%) for $C_{28}H_{34}Cl_2N_2Ru$ (570.56): C 58.94, H 6.01, N 4.92 Found: C 58.91, H 6.04, N 4.95.

1d: (82%). mp 198-200 °C, ^{1}H NMR δ 8.14 (s, 1H, NC*H*N), [8.05 (d, *J* 8 Hz, 1H), 7.19 (t, *J* 7.2 Hz, 1H), 6.97 (t, *J* 7.2 Hz, 1H), 6.73 (d, *J* 7.2 Hz, 1H) ($NC_6H_4CH_2N$)], 6.69 (d, *J* 8.2 Hz, 4H, $C_6H_4(N(CH_3)_2)$-4), 5.49, 5.27 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.40 (s, 2H, $NC_6H_4CH_2N$), 4.24 (s, 2H, $CH_2C_6H_4(N(CH_3)_2)$-4), 3.01 (hept, *J* 6.9 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.96 (s, 6H, $C_6H_4(N(CH_3)_2)$-4), 2.21 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.32 (d, *J* 6.9 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 155.4 (N*C*HN), 140.8, 128.4, 128.1, 125.8, 125.5, 120.9 ($NC_6H_4CH_2N$), 150.9, 129.7, 129.2, 126.8 ($C_6H_4(N(CH_3)_2)$-4), 102.6, 97.4, 82.7, 81.7, $(CH_3)_2CHC_6H_4(CH_3)$-4), 57.7 ($CH_2C_6H_4(N(CH_3)_2)$-4), 46.1 ($NC_6H_4CH_2N$), 40.6 ($C_6H_4(N(CH_3)_2)$-4), 30.8 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 22.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 18.7 ($(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1621 cm^{-1}. Anal. Calcd (%) for $C_{27}H_{33}Cl_2N_3Ru$ (571.55): C 56.74, H 5.82, N 7.35 Found: C 56.81, H 5.79, N 7.33.

1e: (89%). mp 204-206 °C, ^{1}H NMR δ 8.09 (s, 1H, NC*H*N), [8.04 (d, *J* 8.4 Hz, 1H), 7.16 (t, *J* 7.2 Hz, 1H), 6.98 (t, *J* 7.6 Hz, 1H), 6.78 (d, *J* 7.2 Hz, 1H) ($NC_6H_4CH_2N$)], 7.22 , 6.89 (d, *J* 8.4 Hz, 4H, $C_6H_4(OCH_3)$-4), 5.49, 5.27 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.39 (s, 2H, $NC_6H_4CH_2N$), 4.19 (s, 2H, $CH_2C_6H_4(OCH_3)$-4), 3.79 (s, 3H, $C_6H_4(OCH_3)$-4); 3.01 (hept, *J* 7.1 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.18 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.31 (d, *J* 7.1 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 155.4 (N*C*HN), 140.6, 126.8, 125.9, 125.8, 125.6, 120.9, ($NC_6H_4CH_2N$), 160.0, 130.1, 128.1, 114.6 ($C_6H_4(OCH_3)$-4), 102.6, 97.4, 82.7, 81.7 $(CH_3)_2CHC_6H_4(CH_3)$-4), 57.3 ($CH_2C_6H_4(OCH_3)$-4), 46.2 ($NC_6H_4CH_2N$), 55.6 ($C_6H_4(OCH_3)$-4), 30.8 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 22.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 18.6

$(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1622cm^{-1}. Anal. Calcd (%) for $C_{26}H_{30}Cl_2N_2ORu$ (558.50): C 55.91, H 5.41, N 5.02 Found: C 55.87, H 5.44, N 5.06.

1f: (61%). mp 227-229 ^{o}C, ^{1}H NMR δ 8.09 (s, 1H, NC*H*N), [8.07(d, *J* 8 Hz, 1H), 7.14 (t, *J* 8 Hz, 1H), 6.96 (t, *J* 6.8 Hz, 1H), 6.76 (d, *J* 7.6 Hz, 1H) ($NC_6H_4CH_2N$)], 6.12 (s, 2H, $C_6H_2(OCH_3)_3$-2,4,6), 5.44, 5.20 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.49 (s, 2H, $NC_6H_4CH_2N$), 4.37 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-2,4,6), 3.88, 3.82 (s, 9H, $C_6H_2(OCH_3)_3$-2,4,6), 2.98 (hept, *J* 6.9 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.11 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.28 (d, *J* 6.9 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 156.4 (N*C*HN), 141.5, 127.9, 126.7, 125.5, 124.9, 121.5 ($NC_6H_4CH_2N$), 162.2, 160.1, 102.5, 90.5 ($C_6H_2(OCH_3)_3$-2,4,6), 102.6, 96.9, 82.7, 81.9 (($CH_3)_2CHC_6H_4(CH_3)$-4), 56.1 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 46.6 ($NC_6H_4CH_2N$), 55.7, 45.8 ($C_6H_2(OCH_3)_3$-2,4,6), 30.7 $(CH_3)_2CHC_6H_4(CH_3)$-4), 22.5 (($CH_3)_2CHC_6H_4(CH_3)$-4), 18.4 $(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1606 cm^{-1}. Anal. Calcd (%) for $C_{28}H_{34}Cl_2N_2O_3Ru$ (618.56): C 54.37, H 5.54, N 4.53 Found: C 54.33, H 5.52, N 4.57.

1g: (77%). mp 213-215 ^{o}C, ^{1}H NMR δ 8.16 (s, 1H, NC*H*N), [7.99 (d, *J* 8 Hz, 1H), 7.19 (t, *J* 7.2 Hz, 1H), 7.00 (t, *J* 7.6 Hz, 1H), 6.79 (d, *J* 7.2 Hz, 1H) ($NC_6H_4CH_2N$)], 6.53 (s, 2H, $C_6H_2(OCH_3)_3$-3,4,5), 5.50, 5.29 (d, *J* 5.6 Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.42 (s, 2H, $NC_6H_4CH_2N$), 4.24 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.87, 3.83 (s, 9H, $C_6H_2(OCH_3)_3$-3,4,5), 3.02 (hept, *J* 7.0 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.19 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.31 (d, *J* 7.0 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 155.6 (N*C*HN), 140.2, 128.1, 126.7, 126.0, 125.7, 120.9 ($NC_6H_4CH_2N$), 153.8, 138.4, 129.4, 106.4 ($C_6H_2(OCH_3)_3$-3,4,5), 102.6, 97.2, 82.7, 81.6 (($CH_3)_2CHC_6H_4(CH_3)$-4), 56.8 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 46.4 ($NC_6H_4CH_2N$), 61.0, 58.2 ($C_6H_2(OCH_3)_3$-3,4,5), 30.8 $(CH_3)_2CHC_6H_4(CH_3)$-4), 22.5 ($CH_3)_2CHC_6H_4(CH_3)$-4), 18.6 (($CH_3)_2CHC_6H_4(CH_3)$-4).$\upsilon_{(CN)=}$1621 cm^{-1}. Anal. Calcd (%) for $C_{28}H_{34}Cl_2N_2O_3Ru$ (618.56): C 54.37, H 5.54, N 4.53 Found: C 54.34, H 5.52, N 4.55.

2: (70%). mp 223-225 ^{o}C, ^{1}H NMR δ 8.49 (s, 1H, NC*H*N), [8.12 (d, *J* 8.4 Hz, 1H), 7.07 (d, *J* 8.8 Hz, 1H), 6.75 (s, 1H), $(CH_3)C_6H_3$)], 7.21, 7.09 (d, *J* 7.6 Hz, 4H, (C_6H_4 (CH_3)), 5.49, 5.28 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.91 (s, 2H, $NC_6H_3CH_2N$), 3.02 (hept, *J* 6.9 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.35 (s, 3H, ($C_6H_3(CH_3)$)), 2.29 (s, 3H, $C_6H_4(CH_3)$) 2.21 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.29 (d, *J* 6.9 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 152.9 (N*C*HN), 140.1, 136.3, 129.2, 126.9, 126.2, 121.1, ($C_6H_3(CH_3)$), 138.2, 136.1, 130.5, 119.2 ($C_6H_4(CH_3)$), 102.6, 97.4, 82.8, 81.8 (($CH_3)_2CHC_6H_4(CH_3)$-4), 47.7 ($NC_6H_3CH_2N$), 30.8 (($CH_3)_2CHC_6H_4(CH_3)$-4), 22.6 (($CH_3)_2CHC_6H_4(CH_3)$-4), 21.0 ($C_6H_4(CH_3)$ and $C_6H_3(CH_3)$),

18.7 ($(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1619 cm^{-1}. Anal. Calcd (%) for $C_{26}H_{30}Cl_2N_2Ru$ (542.51): C 57.56, H 5.57, N 5.16 Found: C 57.51, H 5.55, N 5.19.

3: (80%). mp 209-211 ^oC, ^1H NMR δ 8.35 (s, 1H, NC*H*N), [8.19 (d, *J* 8.8 Hz, 1H), 6.79 (d, *J* 9.2 Hz, 1H), 6.45 (s, 1H) $(OCH_3)C_6H_3$)], 7.14, 6.92, (d, *J* 8.4 Hz, 4H, $C_6H_4(OCH_3)$), 5.49, 5.27 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 4.91 (s, 2H, $NC_6H_3CH_2N$), 3.80, (s, 3H, $C_6H_3(OCH_3)$), 3.78 (s, 3H, $C_6H_4(OCH_3)$), 3.03 (hept, *J* 7.0 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.21 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.29 (d, *J* 7.0 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 152.2 (N*C*HN), 157.9, 134.1, 128.4, 122.4, 113.4, 110.9, ($C_6H_3(OCH_3)$), 158.1, 135.9, 121.2, 115.2 ($C_6H_4(OCH_3)$), 102.6, 97.3, 82.8, 81.7 $(CH_3)_2CHC_6H_4(CH_3)$-4), 48.3 ($NC_6H_3CH_2N$), 55.8 ($C_6H_4(OCH_3)$), 55.7 ($C_6H_3(OCH_3)$), 30.8 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 22.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 18.7 ($(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1615cm^{-1}. Anal. Calcd (%) for $C_{26}H_{30}Cl_2N_2O_2Ru$ (574.50): C 54.36, H 5.26, N 4.88 Found: C 54.38, H 5.24, N 4.85.

1-Methylimidazole Ru(II): (83%). mp 182-184 ^oC, ^1H NMR δ 7.87 (s, 1H, NC*H*N), 7.29, 6.88 (s, 2H,N*H*C=C*H*N), 5.45, 5.27 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 3.64 (s, 3H, NCH_3), 2.97 (hept, *J* 7.0 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.18 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.28 (d, *J* 7.0 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 140.5 (N*C*HN), 132.2, 121.1, (NH*C*=*C*HN), 102.7, 97.4, 82.7, 81.6 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 34.8 (N*C*H_3), 30.9 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 22.4 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 18.7 ($(CH_3)_2CHC_6H_4(CH_3)$-4). $\upsilon_{(CN)=}$1536 cm^{-1}. Anal. Calcd (%) for $C_{14}H_{20}Cl_2N_2Ru$ (388.29): C 43.30, H 5.19, N 7.21 Found: C 43.37, H 5.16, N 7.23.

1,2-Dimethylimidazole Ru(II): (80%). mp 218-220 ^oC, ^1H NMR δ 7.29, 6.74 (d, J 1.6 Hz, 2H, N*H*C=C*H*N), 5.41, 5.22 (d, *J 5.6* Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 3.54 (s, 3H, NCH_3), 2.92 (hept, *J* 7.0 Hz, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 2.67 (s, 3H, NC(CH_3)N), 2.09 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-4), 1.28 (d, *J* 7.0 Hz, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-4). ^{13}C NMR δ 147.9 (N*C*(CH_3)N), 129.9, 120.5 (NH*C*=*C*HN), 102.7, 97.3, 82.7, 81.5 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 34.8 (N*C*H_3), 30.7 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 22.5 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 18.5 ($(CH_3)_2CHC_6H_4(CH_3)$-4), 14.3 (NC(*C*H_3)N). $\upsilon_{(CN)=}$1508 cm^{-1}. Anal. Calcd (%) for $C_{15}H_{22}Cl_2N_2Ru$ (402.32): C 44.78, H 5.51, N 6.96 Found: C 44.73, H 5.53, N 6.93.

2.7 General procedure for the transfer hydrogenation reaction

The Ru(II) complexes (1 mol %) and acetophenone (1 mmol) were placed in a two necked flask and 10 mL 2-propanol was added to the mixture which was stirred for 10 min at

room temperature. Then 0.4 mol % KOH was added to the mixture and it was heated at 82 ^{o}C for the desired period of time. After that, volatiles were removed under reduced pressure and conversions were determined by ^{1}H NMR spectroscopy.

3. Results and discussion

3.1 Synthesis of N-benzyl or -aryl substituted 3,4-dihydroquinazolines, (**D**, **E** and **F**) and their ruthenium(II) complexes (**1**-**3**)

The synthesis of N-benzyl substituted 3,4-dihydroquinazolines were performed in a three-step reaction, starting from commercially available 2-aminobenzylamine (Scheme 1). The reaction of 2-aminobenzylamine with different benzaldehyde derivatives to obtain imine compounds resulted with the formation of ring-chain tautomerizm, so the mixture of 2-aryl-1,2,3,4-tetrahydroquinazolines (**B**) and 2-aminobenzyl substituted imines (**A**) were obtained with different ratios depending on the substituents of the benzaldehydes. The tautomeric mixture (without any separation) was reduced to mono substituted benzylamine derivatives (**C**), then the ring was closed with $Me_2NCH(OMe)_2$ to obtain the target compound **D**.

N-aryl substituted 3,4-dihydroquinazolines (**E** and **F**) were obtained by the reaction of *p*-substituted aniline derivatives with formalin and formic acid in a one-step reaction.[39-47] 3,4-Dihydroquinazolines (**D**, **E** and **F**) were characterized by spectroscopic methods and the data for the intermediates (**A**, **B**) are given in the supplementary material.

The ^{1}H and ^{13}C NMR of **D**, **E** and **F** showed that the NCHN resonances occurred between 6.97-7.47 ppm and 145.9-151.2 ppm, respectively. The ^{1}H NMR values showed that the C_2-*H* signals shifted to low field in the N-aryl 3,4-dihydroquinazolines as compared to N-benzyl analogues due to an electron withdrawing effect of the aryl substituent.

The ESI mass spectra of compounds (**1a** and **2**) contained peaks at *m/z* values assignable to the N-ligands which indicates decomposition of the complexes under the conditions (supplementary material).

Scheme 1. Synthesis of N-alkyl and N-aryl substituted quinazolines (**D**, **E** and **F**) and their complexation with [(*p*-cymene)$RuCl_2$]$_2$ dimer.

N-substituted-3,4-dihydroquinazolines were used as nucleophiles to cleave [(*p*-cymene)$RuCl_2$]$_2$ dimer and the resultant piano-stool ruthenium(II) complexes (**1-3**) were

obtained in high yield. All complexes have been isolated as orange solids and are stable in the solid state and in solution. The structures of the complexes were confirmed by IR and NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of complex **1a** were given as a sample in supplementary material. The structure of **1a** was also confirmed by X-ray crystallography. The presence of the –C=N– group in the complexes was verified by the υ(C=N) vibrations between 1606-1622 cm^{-1}. ^{1}H and ^{13}C NMR chemical shifts and the integrations of the signals were consistent with the proposed structures. The protons of *p*-cymene displayed two doublets at *ca* 5.15-5.50 ppm. The chemical shift of C_2-*H* is sensitive to formation of complexes. C_2-*H* shifts to low field *ca.* 1 ppm when complexes are formed (7.74-8.49 ppm). In addition, the signals of the N-substituents have been assigned to the corresponding protons. The imino carbons C_2 appeared as typical singlets between 152.2-156.4 ppm in ^{13}C NMR spectra.

3.2 Crystal structures:

The molecular structure of complex **1a** including atom-numbering is shown in Fig. 1. Crystal data and additional data collection parameters and refinement details are presented in Table 1. Selected bond distances and angles are given in Table 2. The complex (**1a**) crystallizes in the triclinic space groups *P*-1 (no:2). The complex adopt a distorted piano-stool type structure with the ruthenium atom being η^6-coordinated *p*-cymene ligand with an average Ru–C distances of 2.145(5)-2.208(5) Å, while the distances between the ruthenium atom and the centroid of the *p*-cymene ring is 1.656(5)Å which is similar to those observed for *p*-cymene ruthenium complexes.[51-52] The ruthenium atom is also directly coordinated to nitrogen atoms of the 3-(2,4,6-trimethylbenzyl)-3,4-dihydroquinazoline ligand, with a normal distance (Ru-N1=2.165(3) Å) and average Ru-C distance is 2.175(3) Å. The Ru–Cl bond lengths are also normal and comparable with the other ruthenium(II) half-sandwich complexes.[51] The angles between the nitrogen heteroaromatic ligands and chlorine ligands in the complex are close to those observed in the ruthenium(II) arene compounds. In the crystal structure of complex (**1a**) no classical hydrogen bonds are present.

Figure 1. The molecular structure of (**1a**). Displacement ellipsoids are drawn at the 40% probability level.

Table 2

3.3 Transfer hydrogenation reaction

Catalytic transfer hydrogenation is an important way to achieve reduction reactions which is one of the most fundamental and useful reactions in organic synthesis, to drive a large number of chemical processes. Whilst direct hydrogenation of unsaturated molecules is more widely applied, transfer hydrogenation is an attractive alternative because the use of a potentially dangerous high pressure of H_2 is avoided. In general, secondary alcohols (often 2-propanol) or an HCOOH/NEt_3 mixture is used as a hydrogen-donor source under the catalytic influence of metal complexes. The protocols are simple, mild and the reaction can be highly chemo- and enantioselective.[53-54] Transfer hydrogenation has been described for the reduction of carbonyl, imine, nitro and olefin functionalities in the presence of Ru(II), Rh(I) and Ir(I) complexes.[53] The capability of ruthenium(II) complexes to dehydrogenate alcohols and deliver the hydride and a proton to a ketone has made them useful as transfer hydrogenation catalysts. Also the ligand moiety is as important as metal species in the progression of a catalytic reaction. The established mechanism[54-55] involving complexes operates via a mono- or dihydride intermediate and may incorporate a coordinated -NH functionality. However non -NH containing catalysts which display excellent activity are also known.[56]

The transfer hydrogenation reactions of acetophenone were carried out in the presence of catalyst (1 mol %) (**1-3**) and KOH (0.4 mol %) in 2-propanol (10 mL) and the mixtures were analyzed in periods of 5-60 min (Fig. 2).

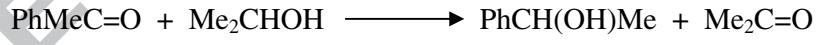


Figure 2. Time-dependent in conversions of acetophenone: yields are recorded as the average of three runs. Reaction conditions: (1 mol %) **1-3**, 0.4 mol % KOH, 82°C.

All the complexes showed good to excellent performance after 1h in the conversion of acetophenone to alcohol. The reaction rate was sensitive to changes on the N-substituent: **1a** and **1f** were found to be the most active catalysts whereas complexes **2** and **3** showed significantly lower activity in comparison to **1**. Clearly, It appears that electron donating substituents on the N atom increased the yield. In addition, each complex has different

initiation period, thus they didn't show similar catalytic behavior in 1h reaction time. [57] The most efficient complex **1a** was used to investigate effect of catalyst loading. Decreasing the load of catalyst to 0.5 mol % and 0.1 mol % resulted in 74% and 50% conversions, respectively. Thus, the rest of catalytic reactions were carried out with 1 mol % catalyst loading. It was observed that the efficiency of the complexes was reduced if KOH is not used. For example, **1a** exhibits only 44% conversion in the absence of KOH. The decrease of the activity in the absence of base suggests that the reaction may not proceed by the outher-sphere bifunctional mechanism proposed by Noyori et al. [58] The base facilitates the formation of [Ru]-H species as active species via β-elemination of [Ru]-$OCHMe_2$. Subsequently the ketone coordinates to [Ru]-H intermediates and then reduced to seconder alcohol by the inner-sphere mechanism. [52, 59] However, we have not observed any sign of [Ru]-H signal in the ^{1}H NMR experiment (see Supplementary Material, Fig.E).

When [(*p*-cymene)$RuCl_2$]$_2$ dimer was used in transfer hydrogenation reaction of acetophenone, 15% conversion was obtained at the end of 60 min period. In order to compare the efficiency of benzimidazole and 3,4-dihydroquinazoline ligand, the corresponding N^1-2,4,6-trimethylbenzyl substituted benzimidazole Ru(II) complex was synthesized [16] and used in transfer hydrogenation reaction of acetophenone under the same condition. The conversion was lower (46%) than the corresponding 3,4-dihydroquinazoline bearing ruthenium complex **1a** (Fig. 3).

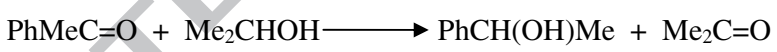


Figure 3. The comparison of **1a** with benzimidazole, 1-methylimidazole, 1,2-dimethylimidazole complexes and [(*p*-cymene)$RuCl_2$]$_2$ in the time-dependent conversions of acetophenone: yields are recorded as the average of three runs. Reaction conditions: 1 mol % cat., 0.4 mol % KOH, 82^{o}C.

Additionally, the catalyst **1a** was used in transfer hydrogenation of different ketones to investigate the effect of substituents on ketones. It was observed that electron-withdrawing groups in the *para* position of the acetophenone increased the yield whereas electron donating groups at the *para* position of the acetophenone decreased (Fig. 4).

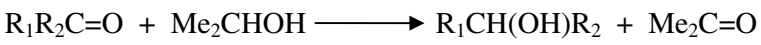


Figure 4. Time-dependent in conversions of different ketones catalyzed with **1a**: yields are recorded as the average of three runs. Reaction conditions: 1 mol % **1a**, 0.4 mol % KOH, 82°C.

Additional experiments were carried out with **1a** to understand mechanism of transfer hydrogenation reaction with 3,4-dihydroquinazoline Ru(II) complexes. The complex **1a** showed NC*H*N resonance at 7.93 ppm in d_1-methanol. But when base (KOH) was added to this solution NC*H*N resonance of complex immediately shifts to high field *ca.* 1 ppm (6.97 ppm). This observation suggests that the C_2-*H* functionality on the dihydroquinazoline plays an important role. Besides, the chemical shift (acidity) of C_2-*H* of **1-3** is related with the catalytic conversion. Thus, complex **1a** was found to be the least acidic and the most effective catalyst. To support this hypothesis, 1-methyl and 1,2-dimethylimidazole Ru(II) complexes were synthesized and tested. 1,2-Dimethylimidazole Ru(II) complex which do not contain C_2-*H*, showed much lower activity than 1-methylimidazole complex (Fig. 3).

4. Conclusion

In this study we reported a straightforward synthesis of N-coordinated- imidazole, benzimidazole and 3,4-dihydroquinazoline ruthenium(II) complexes. The resulting piano-stool ruthenium complexes bearing 3,4-dihydroquinazoline ligand (**1-3**) showed good to excellent activity as transfer hydrogenation catalysts for reduction of acetophenone at 82°C. Among the complexes studied, 2,4,6-trimethylbenzyl and 2,4,6-trimethoxybenzyl substituted complexes, **1a** and **1f** were found to be the most active catalysts. It is worth mentioning that C_2-*H* functionality in the quinazoline complexes appears to play an important role in the catalytic steps.

Supplementary Material

Ru(II)-Arene Complexes with N-Substituted 3,4-Dihydroquinazoline Ligands and Catalytic Activity for Transfer Hydrogenation Reaction

Deniz Mercan, Engin Çetinkaya*, Ertan Şahin

^{1}H NMR data for the intermediates (A, B):

Aa+Ba (78%). (Ba/Aa)(%): 45/55. **Aa**: ^{1}H NMR δ 8.69 (s, 1H, *H*C=N), [7.07 (d, *J* 7.6 Hz, 2H), 7.01 (t, *J* 7.6 Hz, 1H), 6.94 (d, *J* 7.2, 1H) ($NH_2C_6H_4CH_2N$)], 6.84 (s, 2H, $C_6H_2(CH_3)_3$-2,4,6), 4.74 (s, 2H, $NH_2C_6H_4CH_2N$), 2.38, 2.26 (s, 9H, $C_6H_2(CH_3)_3$-2,4,6). **Ba**: ^{1}H NMR δ 5.61 (s, 1H, HN-C*H*-NH), 6.84 (s, 2H, $C_6H_2(CH_3)_3$-2,4,6), 6.65-6.72 (m, 4H, $NHC_6H_4CH_2NH$), [4.29 (d, *J* 16.8 Hz, 1H) and 4.02 (d, *J* 16.4 Hz, 1H) ($NHC_6H_4CH_2NH$)], 2.46, 2.25, (s, 9H, $C_6H_2(CH_3)_3$-2,4,6).

Ab+Bb (70%) (Bb/Ab)(%): 45/55 **Ab**: ^{1}H NMR δ 8.28 (s, 1H, *H*C=N), [7.59(d, *J* 7.6 Hz, 2H), Other signals overlap with the ring hydrogens ($NH_2C_6H_4CH_2N$)], 4.71 (s, 2H, $NH_2C_6H_4CH_2N$), Other signals overlap with the ring hydrogens **Bb**: ^{1}H NMR δ 5.15 (s, 1H, HN-C*H*-NH), [7.36 (d, *J* 7.2 Hz, 2H) and 7.17 (d, *J* 7.2 Hz, 2H, $C_6H_4(CH_3)$-4)], [7.01 (t, *J* 7.6 Hz, 1H), 6.90 (d, *J* 7.6 Hz, 1H), 6.69 (t, *J* 7.2 Hz, 1H), 6.53 (d, *J* 8 Hz, 1H), ($NHC_6H_4CH_2NH$)], [4.21(d, *J* 16.4 Hz, 1H) and 3.93 (d, *J* 16.4 Hz, 1H) ($NHC_6H_4CH_2NH$)], 2.34 (s, 3H,$C_6H_4(CH_3)$-4).

Ac+Bc (70%). (Bc/Ac)(%): 83/17 **Ac**: ^{1}H NMR δ 8.29 (s, 1H, *H*C=N) ,[7.63(d, *J* 8 Hz, 2H), Other signals overlap with the ring hydrogens ($NH_2C_6H_4CH_2N$)], 4.71 (s, 2H, $NH_2C_6H_4CH_2N$), **Bc**: ^{1}H NMR δ 5.16 (s, 1H, HN-C*H*-NH), [7.40 (d, *J* 8 Hz, 2H) and 7.23 (d, *J* 8.4 Hz, 2H) $C_6H_4(CH(CH_3)_2)$-4)], [7.05 (t, *J* 6.8 Hz, 1H), 6.90 (d, *J* 7.6 Hz, 1H), 6.68 (m, 1H), 6.52 (d, *J* 8 Hz, 1H), ($NHC_6H_4CH_2NH$)], [4.22 (d, *J* 16.4 Hz, 1H) and 3.94 (d, *J* 16.8 Hz, 1H) ($NHC_6H_4CH_2NH$)], 2.90 (hept, *J* 8 Hz, 1H, $C_6H_4(CH(CH_3)_2)$-4), 1.26 (d, *J* 8 Hz, 6H, $C_6H_4(CH(CH_3)_2)$-4).

Ad+Bd (70%) (Bd/Ad)(%): 45/55 **Ad**: ^{1}H NMR δ 8.25 (s, 1H, *H*C=N), [7.63(d, *J* 9.2 Hz, 2H), 7.17-7.09 (m, 2H) ($NH_2C_6H_4CH_2N$)], 6.74-6.69 (m, 4H $CH_2C_6H_4(N(CH_3)_2)$-4), 4.72 (s, 2H, $NH_2C_6H_4CH_2N$), 3.02 (s, 6H, $CH_2C_6H_4(N(CH_3)_2)$-4). **Bd**: ^{1}H NMR δ 5.16 (s, 1H, HN-C*H*-NH), [7.39 (d, *J* 8.8, 2H), 6.76 (d, *J* 8., 2H) ($CH_2C_6H_4(N(CH_3)_2)$-4)], [7.06(t, *J* 7.2Hz, 1H), 6.95(d, *J* 7.2 Hz, 1H), 6.74-6.69 (m, 1H), 6.56(d, *J* 7.6 Hz, 1H) ($NHC_6H_4CH_2NH$)], [4.28 (d, *J*

16.8 Hz, 1H) and 3.99 (d, *J* 16.8 Hz, 1H), ($NHC_6H_4C\mathit{H}_2NH$)], 2.97 (s, 6H, $CH_2C_6H_4(N(C\mathit{H}_3)_2)$-4).

Ae+Be (70%) (Be/Ae)(%): 45/55 **Ae**: ^{1}H NMR δ 8.25 (s, 1H, *H*C=N), [7.64 (d, *J* 8 Hz, 2H); Other signals overlap with the ring hydrogens,($NH_2C_6\mathit{H}_4CH_2N$)], 4.69 (s, 2H, $NH_2C_6H_4C\mathit{H}_2N$), 3.79 (s, 3H, $CH_2C_6H_4(OC\mathit{H}_3)$-4), Other signals overlap with the ring hydrogens **Be**: ^{1}H NMR δ 5.13 (s, 1H, HN-C*H*-NH), [7.67 (t, *J* 8 Hz, 1H), 6.90 (d, *J* 6.4 Hz, 1H), 6.69 (t, *J* 7.6Hz, 1H), 6.52 (d, *J* 8 Hz, 1H) ($NHC_6\mathit{H}_4CH_2NH$)], [7.39 (d, *J* 8.4 Hz, 4H), 6.88 (d, *J* 8 Hz, 2H, ($CH_2C_6\mathit{H}_4(OCH_3)$-4)], [4.21(d, *J* 16.8 Hz, 1H) and 3.93 (d, *J* 16.8 Hz, 1H) ($NHC_6H_4C\mathit{H}_2NH$)], 3.78(s, 3H, $CH_2C_6H_4(OC\mathit{H}_3)$-4).

Af+Bf (96%). (Bf/Af)(%): 83/17. **Af**: ^{1}H NMR δ 8.65 (s, 1H, *H*C=N), 4.72 (s, 2H, $NH_2C_6H_4C\mathit{H}_2N$), Other signals overlap with the ring hydrogens. **Bf**: ^{1}H NMR δ 5.65 (s, 1H, HN-*H*C-NH), [7.02 (t, *J* 7.6 Hz, 1H), 6.95 (d, *J* 7.6 Hz, 1H), 6.72 (t, *J* 7.6Hz, 1H), 6.58 (d, *J* 7.6 Hz, 1H), ($NHC_6\mathit{H}_4CH_2NH$)], 6.14 (s, 2H, $C_6\mathit{H}_2(OCH_3)_3$-2,4,6), [4.26 (d, *J* 16.4 Hz, 1H) and 4.02 (d, *J* 16.8 Hz, 1H) ($NHC_6H_4C\mathit{H}_2NH$)], 3.82, 3.81 (s, 9H, $C_6H_2(OC\mathit{H}_3)_3$-2,4,6).

Ag+Bg (56%). (Bg/Ag)(%): 89/11. **Ag**: ^{1}H NMR δ 8.23 (s, 1H, *H*C=N), 4.72 (s, 2H, $NH_2C_6H_4C\mathit{H}_2N$), Other signals overlap with the ring hydrogens. **Bg**: ^{1}H NMR δ 5.13 (s, 1H, HN-*H*C-NH), [7.04 (t, *J* 8 Hz, 1H), 6.94 (d, *J* 7.2 Hz, 1H), 6.72 (t, *J* 7.6 Hz, 1H), 6.59 (d, *J* 8.4 Hz, 1H) ($NHC_6\mathit{H}_4CH_2NH$)], 6.75 (s, 2H, $CH_2C_6\mathit{H}_2(OCH_3)_3$-3,4,5), [4.25 (d, *J* 16.8 Hz, 1H), and 3.98 (d, *J* 16.4 Hz, 1H) ($NH_2C_6H_4C\mathit{H}_2NH$)], 3.85, 3.83 (s, 9H, $CH_2C_6H_2(OC\mathit{H}_3)_3$-3,4,5).

^{1}H NMR and ^{13}C NMR data for the intermediates (Cb, Ce):

Cb: (78%). Liquid, ^{1}H NMR δ 7.18, 7.12 (d, *J* 8 Hz, 4H, $CH_2C_6\mathit{H}_4(CH_3)$-4), [7.06-7.04 (m, 1H), 7. 00 (d, *J* 6.8 Hz, 1H),6.71-6.66 (m, 2H) ($NH_2C_6\mathit{H}_4CH_2NH$)], 4.70 (s, 2H, NH_2), 3.79 (s, 2H, $NH_2C_6H_4C\mathit{H}_2NH$) 3.72 (s, 2H, $C\mathit{H}_2C_6H_4(CH_3)$-4), 2.32 (s, 3H, $CH_2C_6H_4(C\mathit{H}_3)$-4). ^{13}C NMR δ 147.2, 130.2, 128.6, 124.2, 117.9, 115.9 ($NH_2\mathit{C}_6H_4CH_2NH$), 137.5, 136.8, 129.4, 128.4 ($\mathit{C}_6H_4(CH_3)$-4), 53.3 ($\mathit{C}H_2C_6H_4(CH_3)$-4), 52.6 ($NH_2C_6H_4\mathit{C}H_2NH$), 21.4 ($C_6H_4(\mathit{C}H_3)$-4).

Ce: (92%). Liquid, ^{1}H NMR δ 7.19, 6.83 (d, *J* 8.4 Hz, 4H, $CH_2C_6\mathit{H}_4(OCH_3)$-4), [7.06-7.04 (m; 1H), 6.98 (d, *J* 7.2 Hz, 1H), 6.69-6.62 (m, 2H), ($NH_2C_6\mathit{H}_4CH_2NH$)], 4.65 (s, 2H, NH_2), 3.77 (s, 2H, $NH_2C_6H_4C\mathit{H}_2NH$) 3.71 (s, 2H, $C\mathit{H}_2C_6H_4(OCH_3)$-4), 3.79 (s, 3H, $CH_2C_6H_4(OC\mathit{H}_3)$-4)^{13}C NMR δ 147.2, 130.2, 128.6, 124.2, 117.9, 115.9 ($NH_2\mathit{C}_6H_4CH_2NH$),

158.9, 132.7, 129.6, 114.1 ($C_6H_4(CH_3)$-4), 55.5 ($C_6H_4(OCH_3)$-4), 52.9 ($CH_2C_6H_4(OCH_3)$-4), 52.5 ($NH_2C_6H_4CH_2NH$).

^{1}H NMR and ^{13}C NMR data for the compounds (E,F):

E: (40%). mp 157-159 ^{o}C, ^{1}H NMR δ 7.47 (s, 1H, NC*H*N), [7.08 (d, *J* 8 Hz, 1 H), 7.02 (d, *J* 8 Hz, 1H), 6.76 (s, 1H) $(CH_3)C_6H_3$)], 7.19, 7.02 (d, *J* 8 Hz, 4H, (C_6H_4 (CH_3)), 4.83 (s, 2H, $NC_6H_3CH_2N$), 2.34 (s, 3H, ($C_6H_3(CH_3)$), 2.29 (s, 3H, $C_6H_4(CH_3)$). ^{13}C NMR δ 146.5 (N*C*HN), 141.2, 135.5, 129.3, 126.5, 124.8, 121.2, ($C_6H_3(CH_3)$), 139.0, 134.4, 130.3, 118.3 ($C_6H_4(CH_3)$), 47.4 ($NC_6H_3CH_2N$), 21.3, 20.9 ($C_6H_4(CH_3)$ and $C_6H_3(CH_3)$). $\upsilon_{(CN)=}$1619 cm^{-1}. Anal. Calcd (%) for $C_{16}H_{16}N_2$ (236.31): C 81.32, H 6.82, N 11.85 Found: C 81.35, H 6.81, N 11.83.

F: (46%). mp 134-136 ^{o}C, ^{1}H NMR δ 7.33 (s, 1H, NC*H*N), [7.09 (d, *J* 8.8 Hz, 1H), 6.74 (dd, *J* 8.8, 2.8 Hz, 1 H), 6.47 (d, *J* 2.8 Hz, 1 H) $(CH_3)C_6H_3$)], 7.05, 6.91 (d, *J* 8 Hz, 4H, (C_6H_4 (OCH_3)), 4.82 (s, 2H, $NC_6H_3CH_2N$), 3.78 (s, 3H, ($C_6H_3(OCH_3)$), 3.75 (s, 3H, $C_6H_4(OCH_3)$). ^{13}C NMR δ 145.9 (N*C*HN), 157.8, 137.2, 122.3, 120.3, 115.0, 111.4 ($C_6H_3(OCH_3)$), 157.1, 135.0, 125.9, 113.6 ($C_6H_4(OCH_3)$), 47.9 ($NC_6H_3CH_2N$), 55.8, 55.7 ($C_6H_4(OCH_3)$ and $C_6H_3(OCH_3)$). $\upsilon_{(CN)=}$1620 cm^{-1}. Anal. Calcd (%) for $C_{16}H_{14}N_2O_2$ (268.31): C 71.62, H 6.01, N 10.44 Found: C 71.65, H 6.04, N 10.40.

Figure A: ^{1}H NMR spectrum of complex **1a**

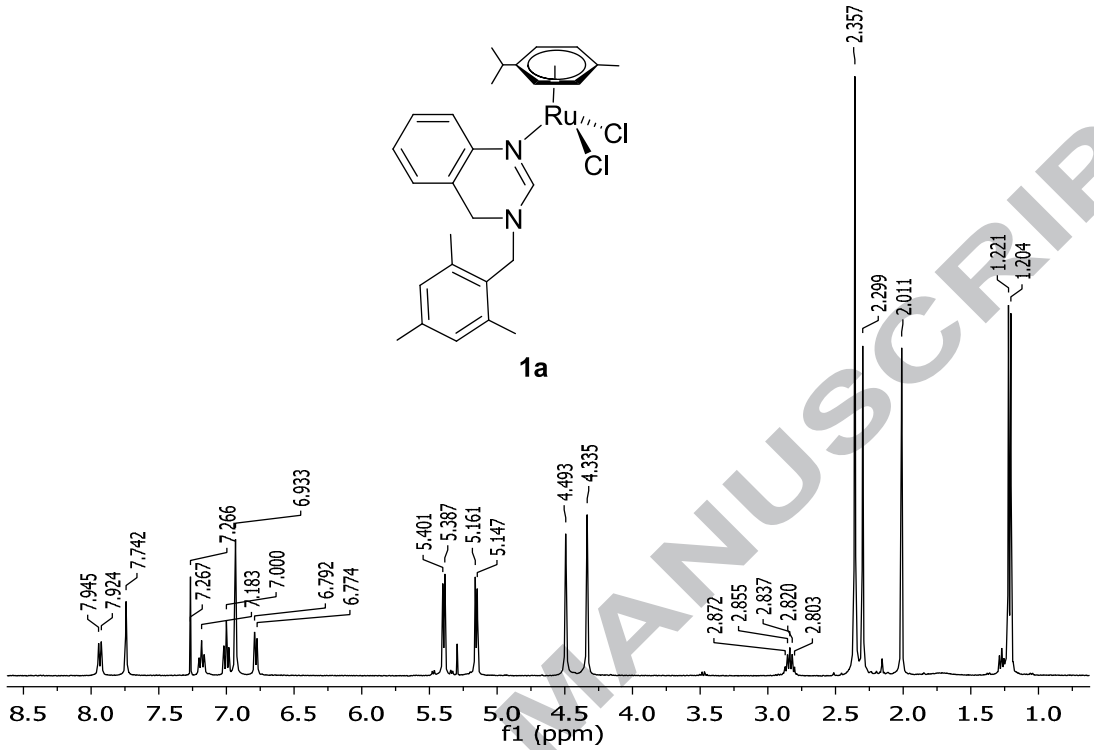


Figure B: ^{13}C NMR spectrum of complex **1a**

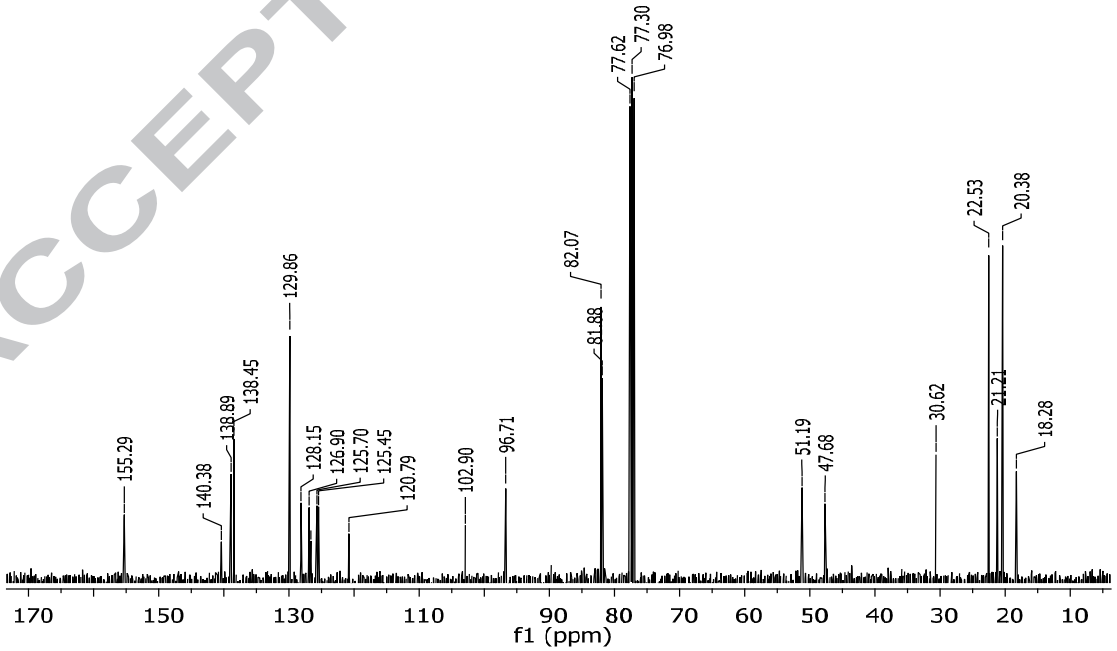


Figure C: ^{1}H NMR spectrum of complex **1a** in CD_3OD

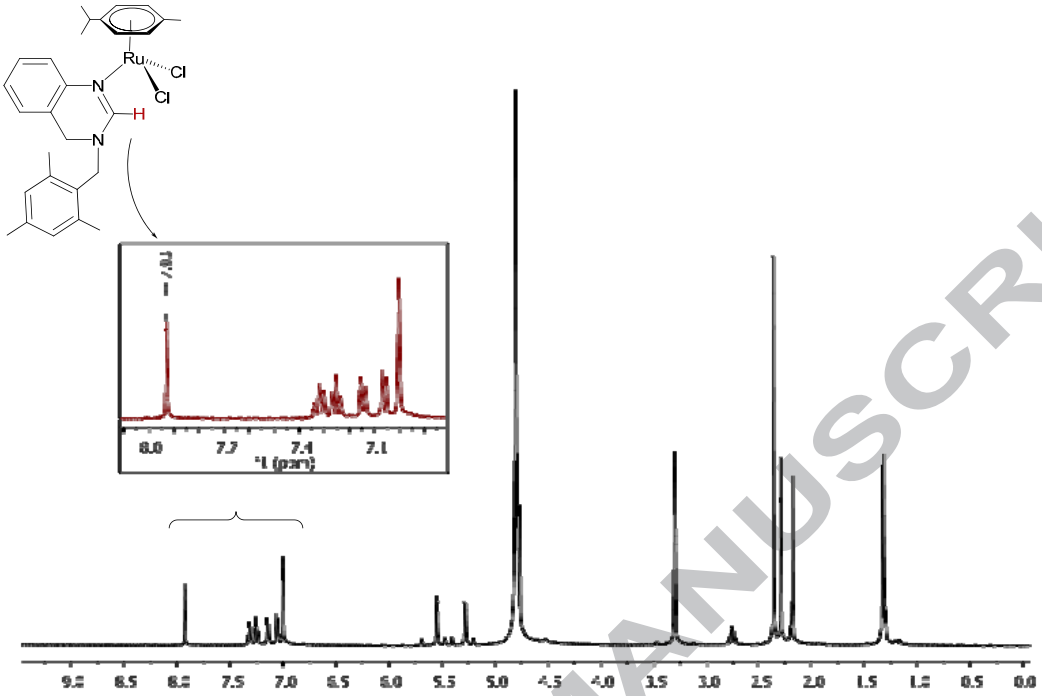


Figure D: ^{1}H NMR spectrum of complex **1a+**KOH in CD_3OD

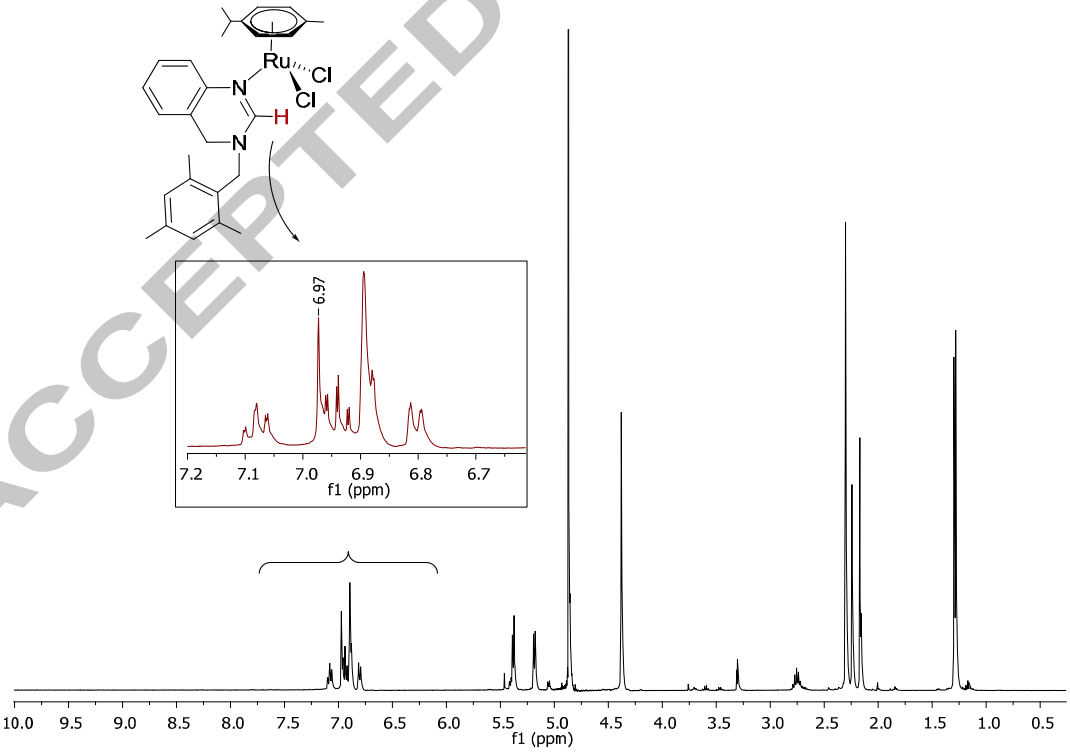


Figure E: ^{1}H NMR spectrum of complex **1a+**KOH+2-propanol in CD_3OD

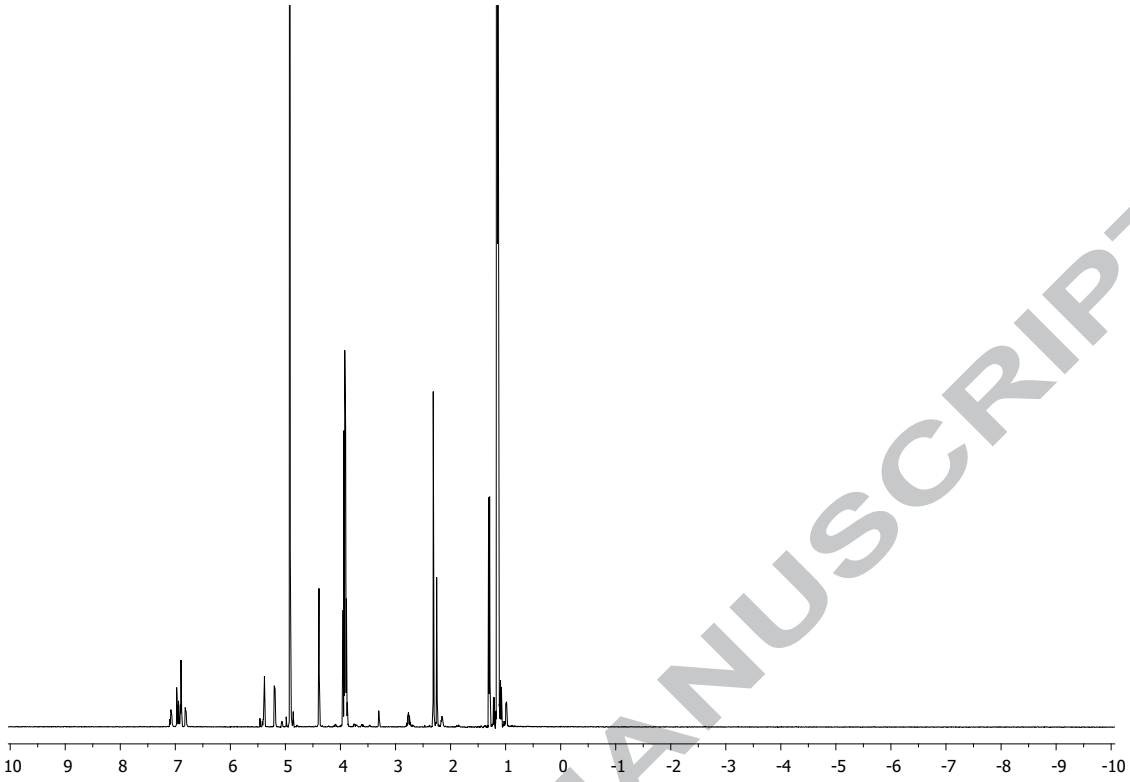


Table A: The NC*H*N resonances of ligands (**D**,**E-F**) and complexes **1-3**.

Ligand	NC*H*N	Complex	NC*H*N
Da	6.97	**1a**	7.74
Db	7.23	**1b**	8.16
Dc	7.19	**1c**	8.11
Dd	7.22	**1d**	8.14
De	7.19	**1e**	8.09
Df	7.18	**1f**	8.09
Dg	7.17	**1g**	8.16
E	7.47	**2**	8.49
F	7.33	**3**	8.35

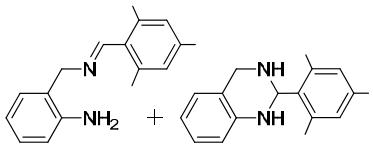
Table B: Influence of catalyst and low catalyst loading transfer hydrogenation of acetophenon

Entry	Catalyst	Mol %	Yield	TON	TOF
1	**1a**	1	97	97	97
2	**1b**	1	73	73	73
3	**1c**	1	78	78	78
4	**1d**	1	86	86	86
5	**1e**	1	72	72	72
6	**1f**	1	94	94	94
7	**1g**	1	66	66	66
8	**2**	1	69	69	69
9	**3**	1	65	65	65
10	**1a**	0.5	74	148	148
11	**1a**	0.1	50	500	500

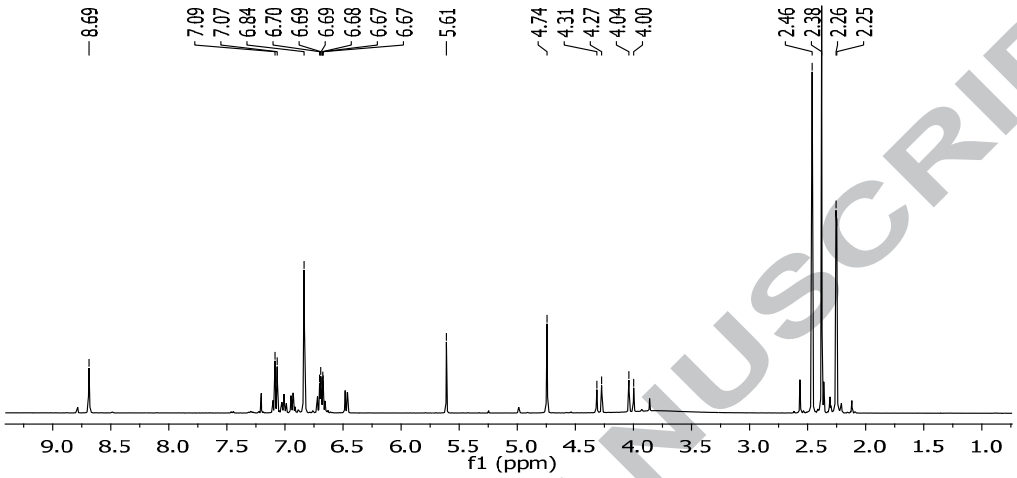
Reaction conditions: 1 mmol acetophenone, 0.4 mol % KOH,1h, 82^{o}C.

Spectral Data:

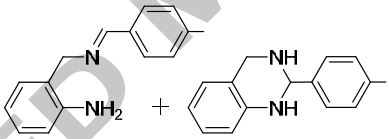
^{1}H spectrum of Aa+Ba



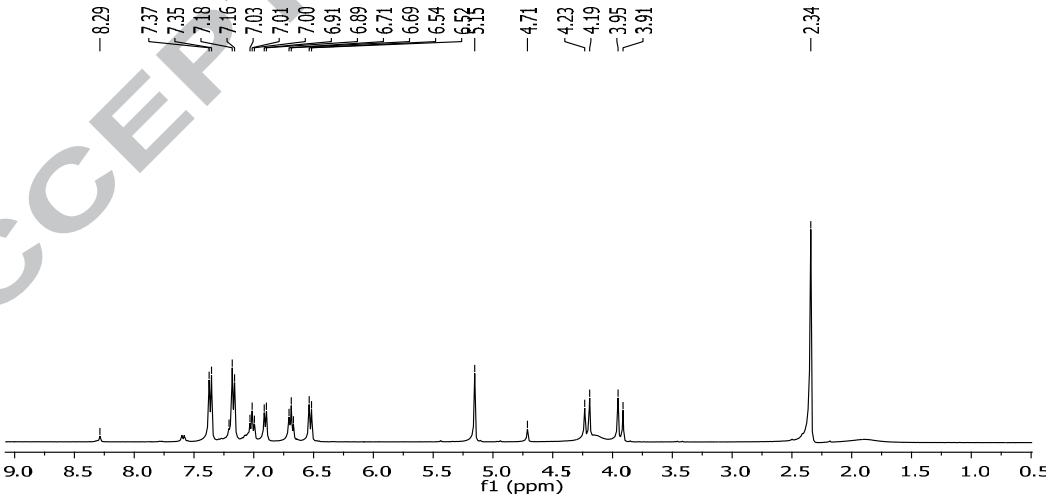
Aa+Ba



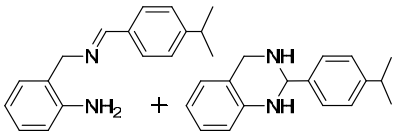
^{1}H spectrum of Ab+Bb



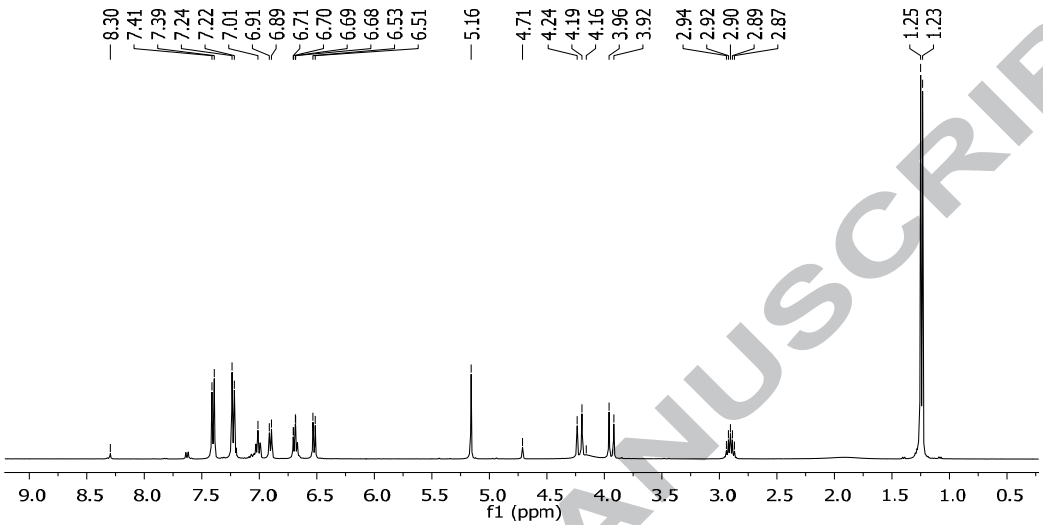
Ab+Bb



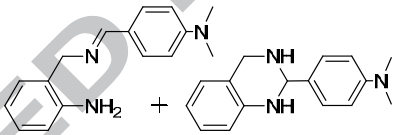
^{1}H spectrum of Ac+Bc



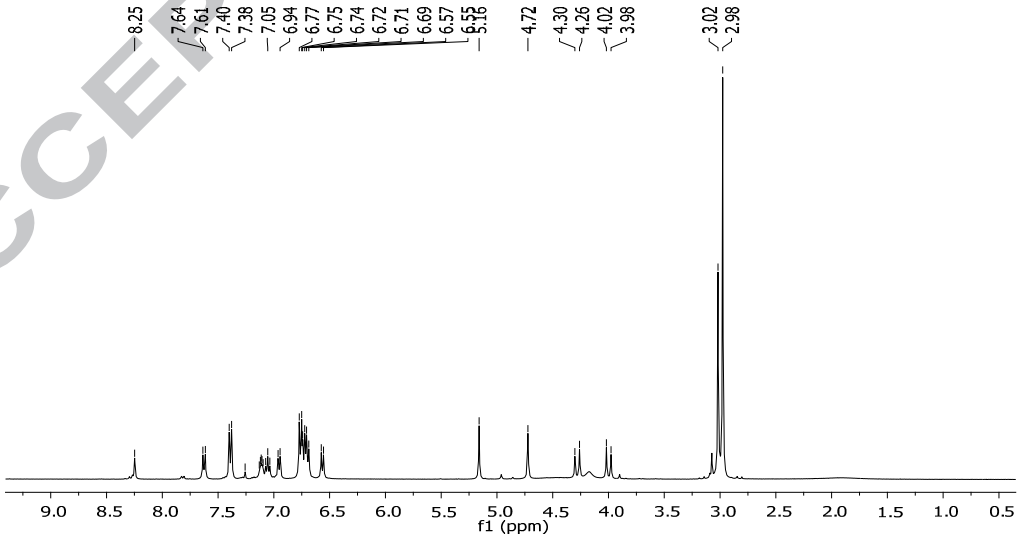
Ac+Bc



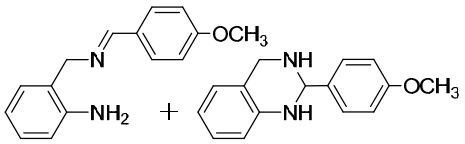
^{1}H spectrum of Ad+Bd



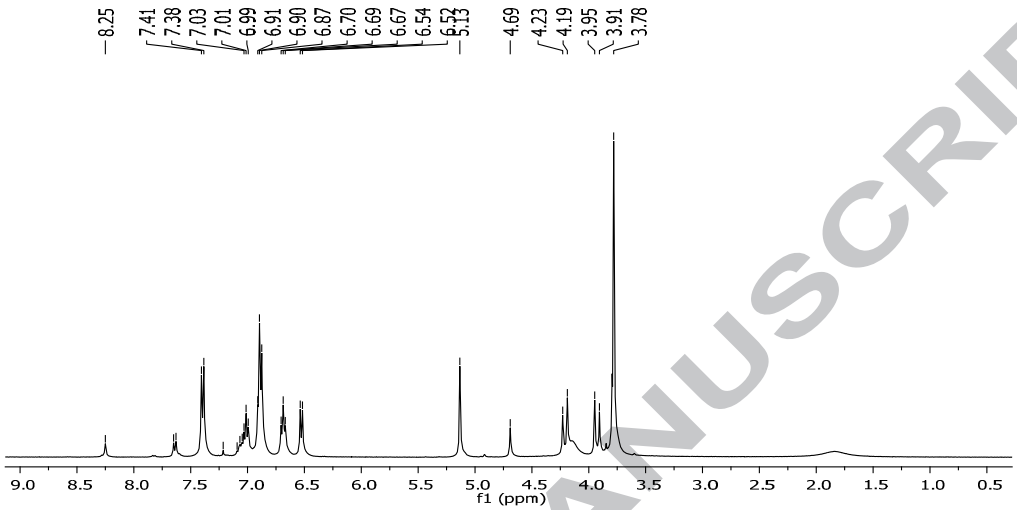
Ad+Bd



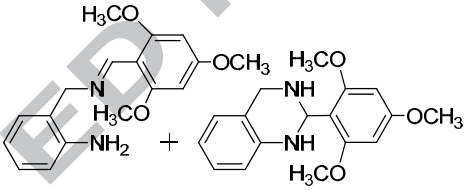
^{1}H spectrum of Ae+Be



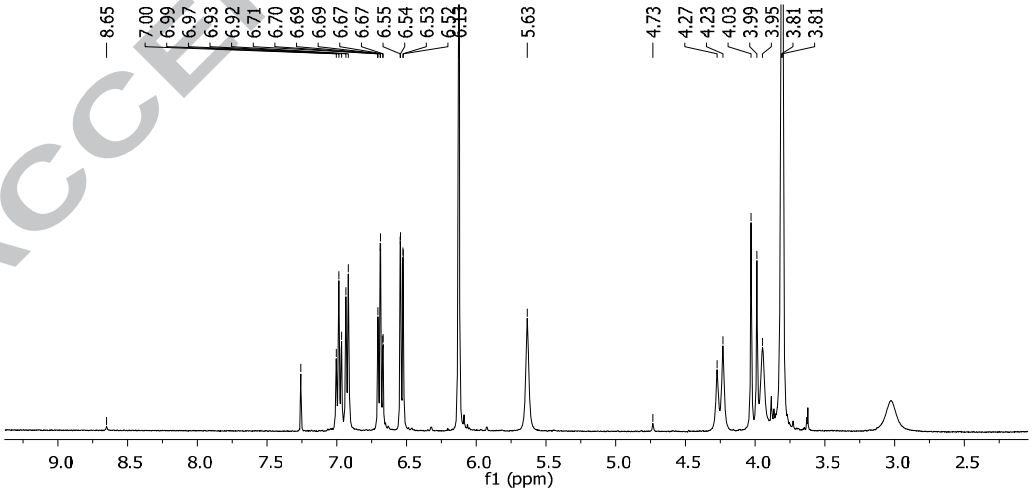
Ae+Be



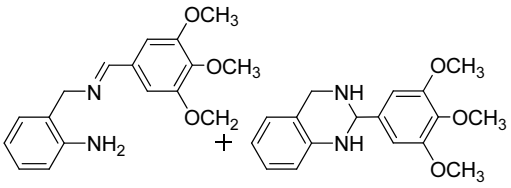
^{1}H spectrum of Af+Bf



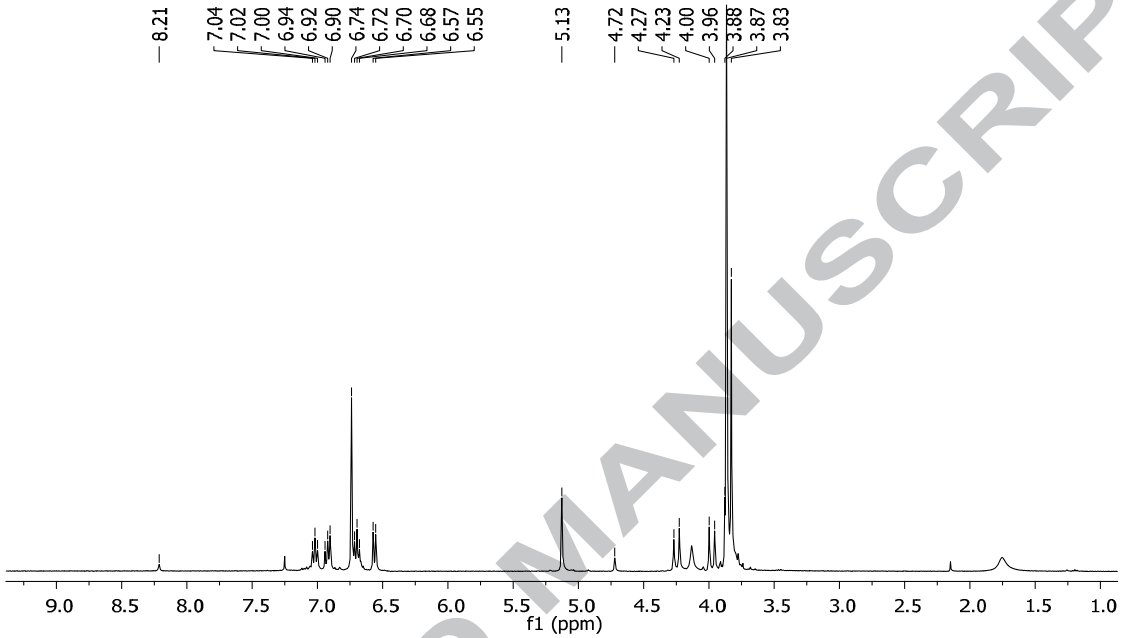
Af+Bf



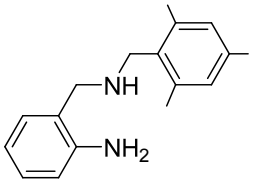
^{1}H spectrum of Ag+Bg



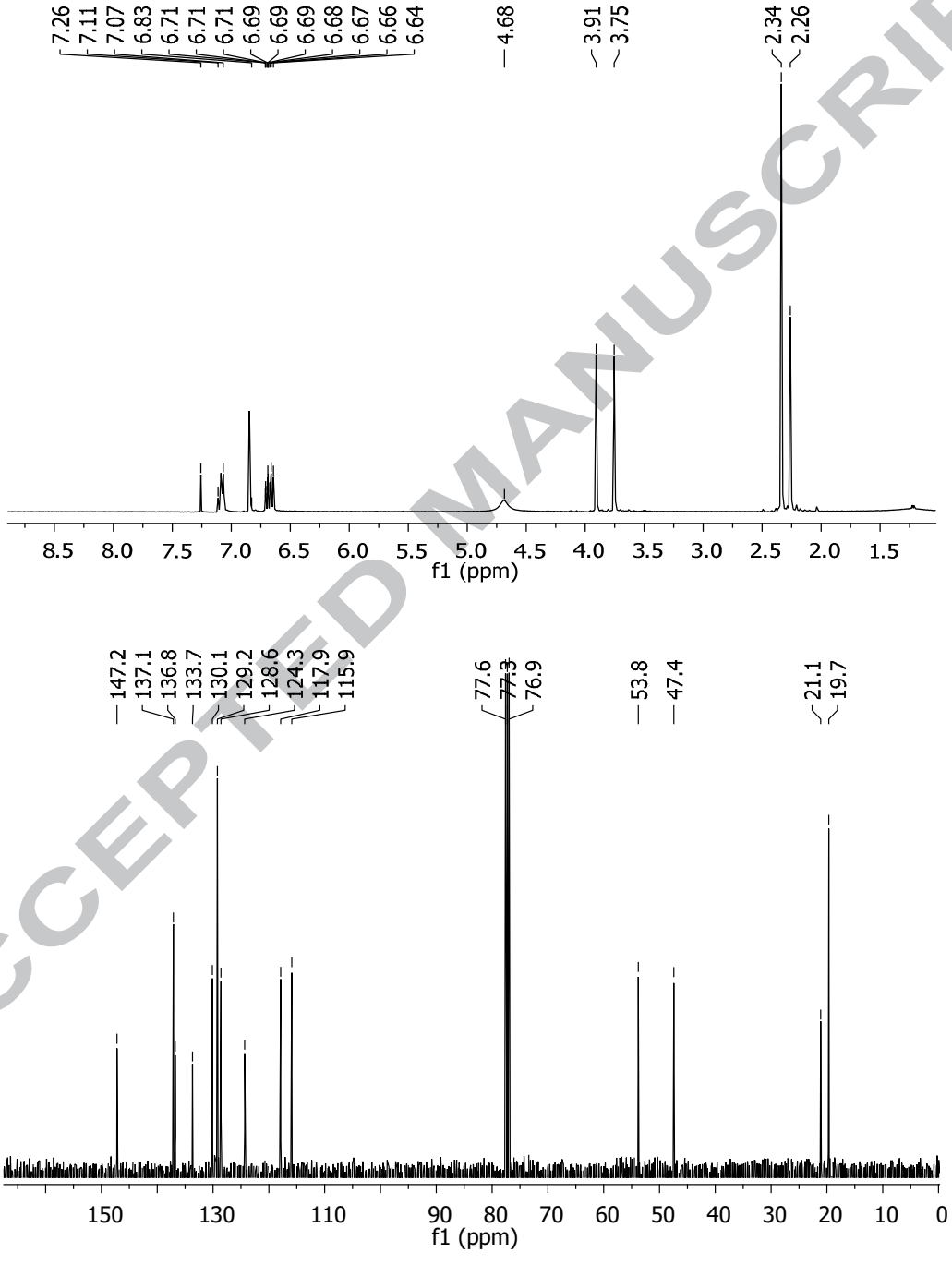
Ag+Bg



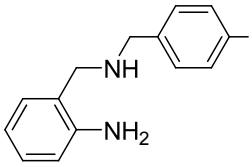
^{1}H and ^{13}C spectrum of Ca



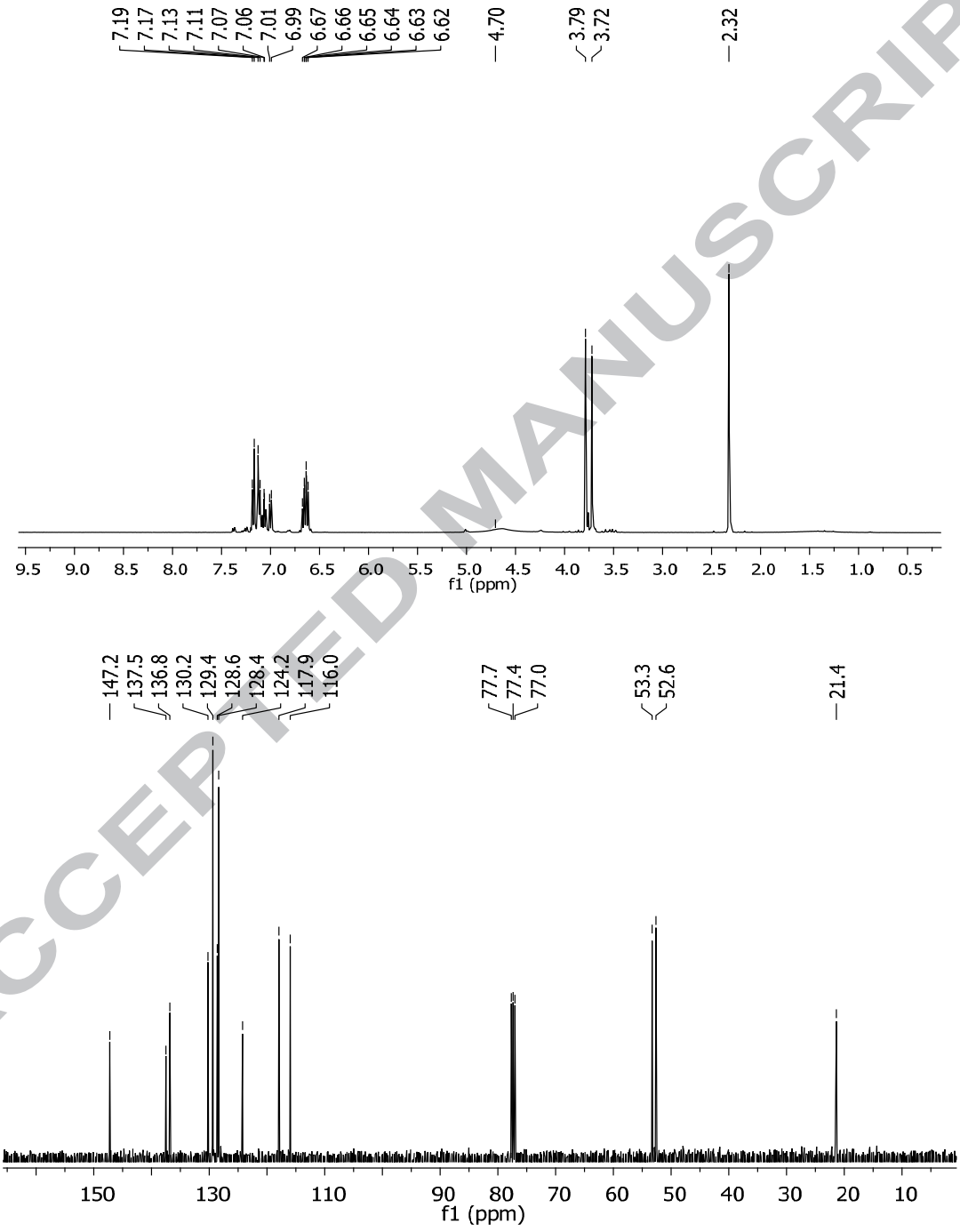
Ca



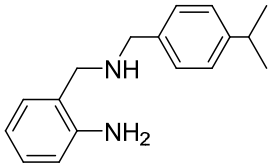
^{1}H and ^{13}C spectrum of Cb



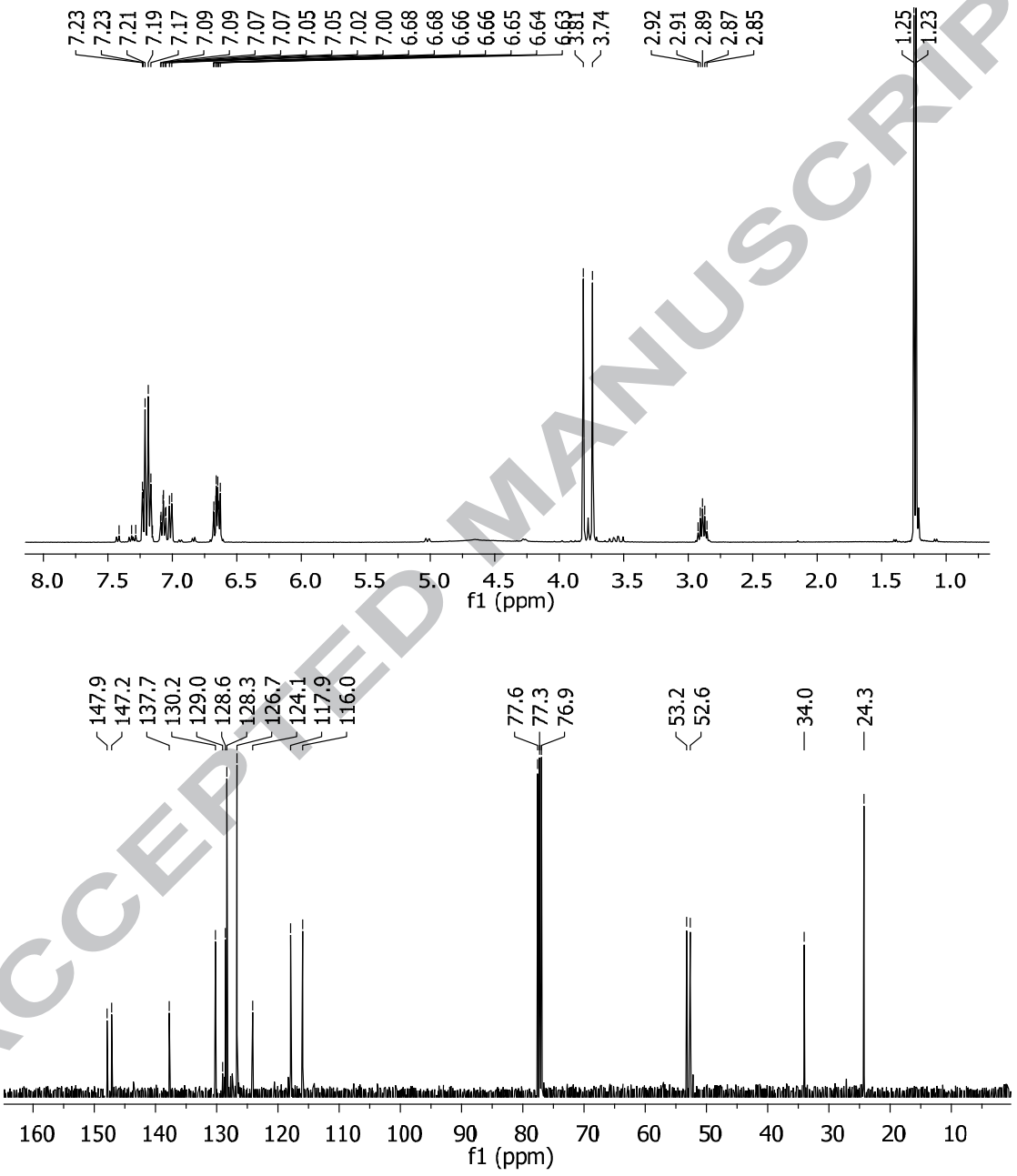
Cb



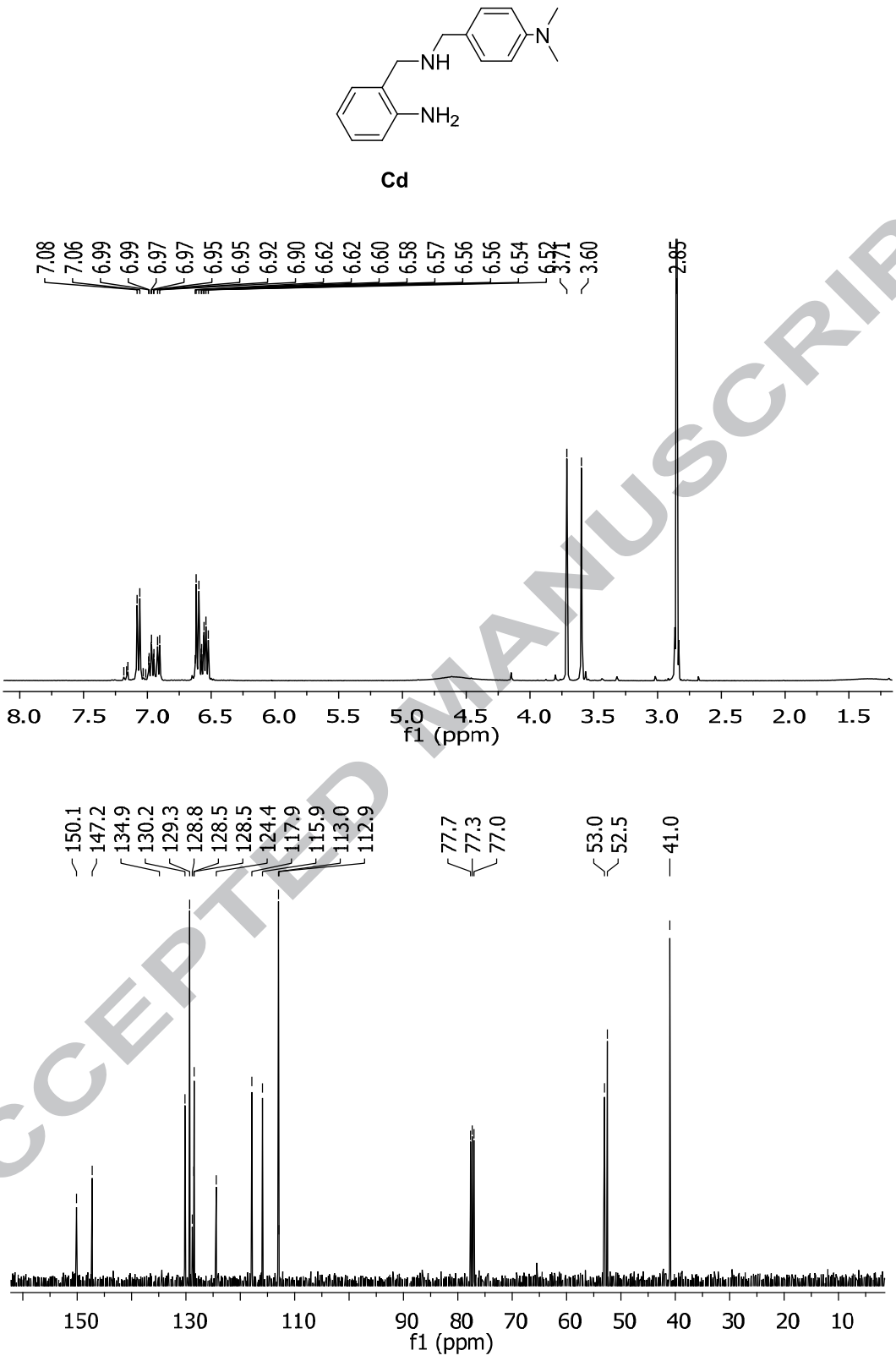
^{1}H and ^{13}C spectrum of Cc



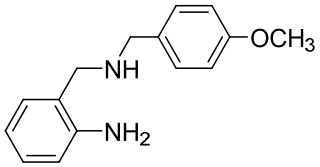
Cc



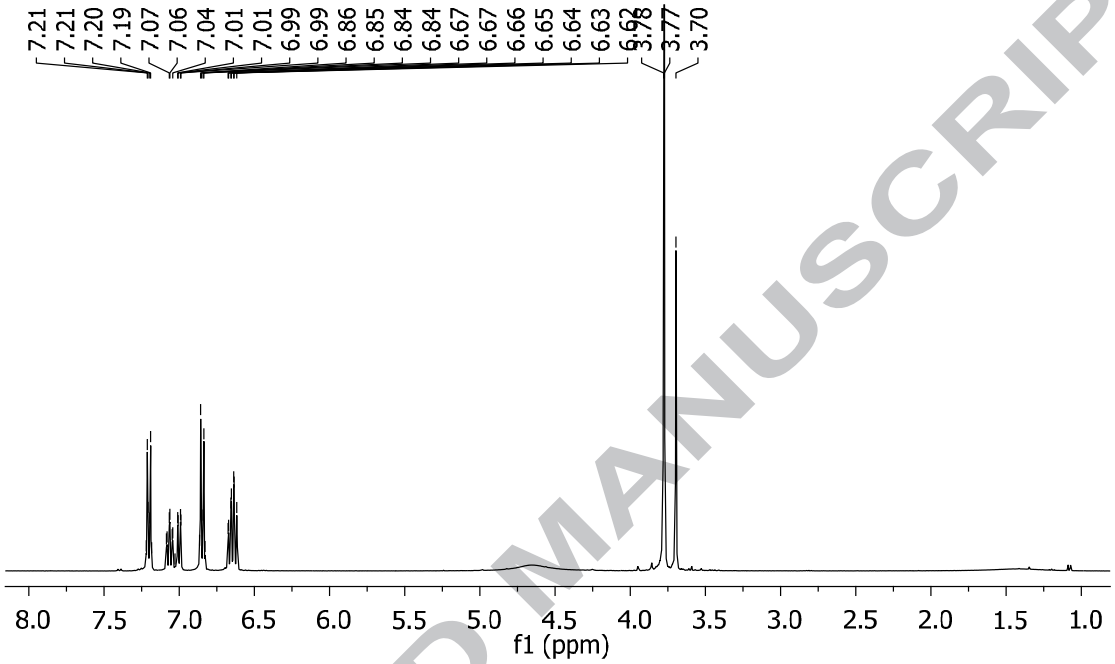
^{1}H and ^{13}C spectrum of Cd

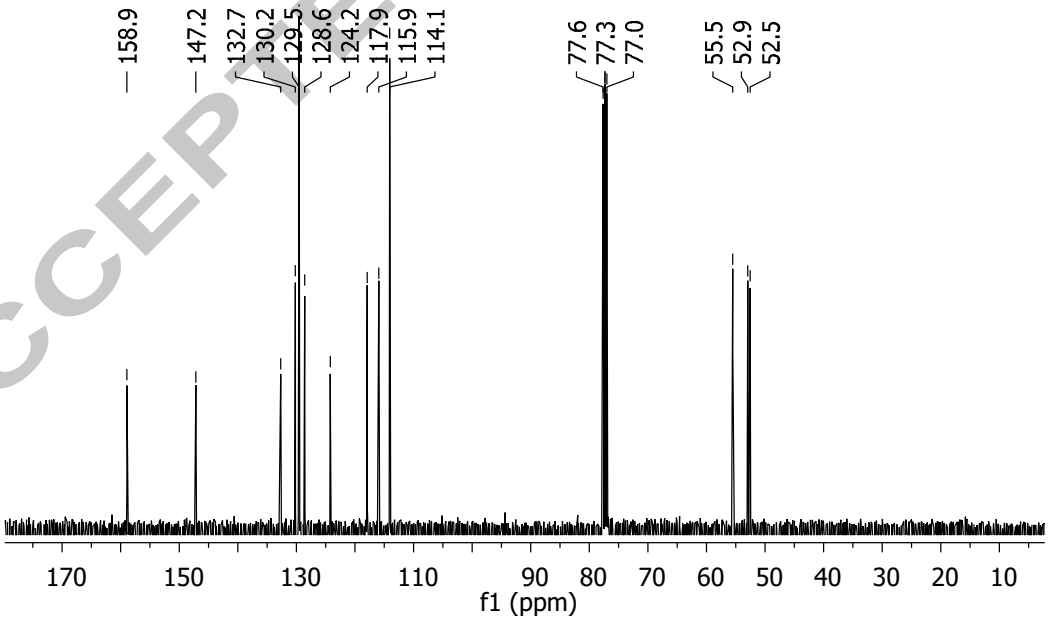


^{1}H and ^{13}C spectrum of Ce

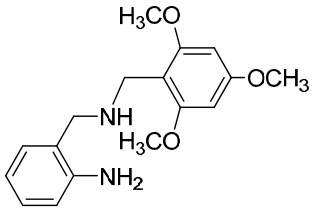


Ce

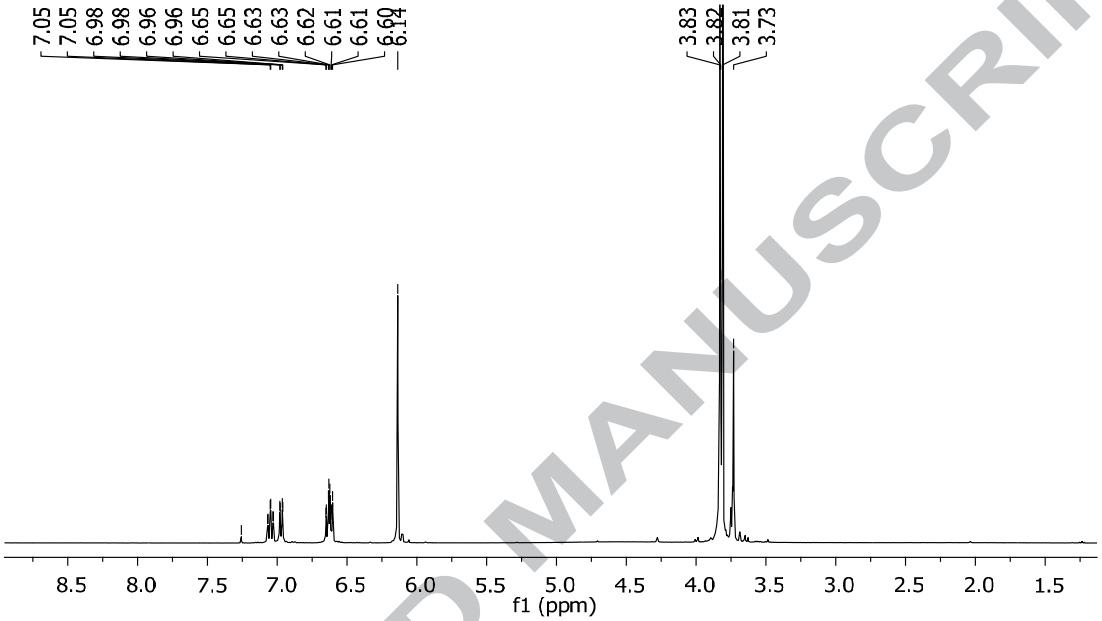


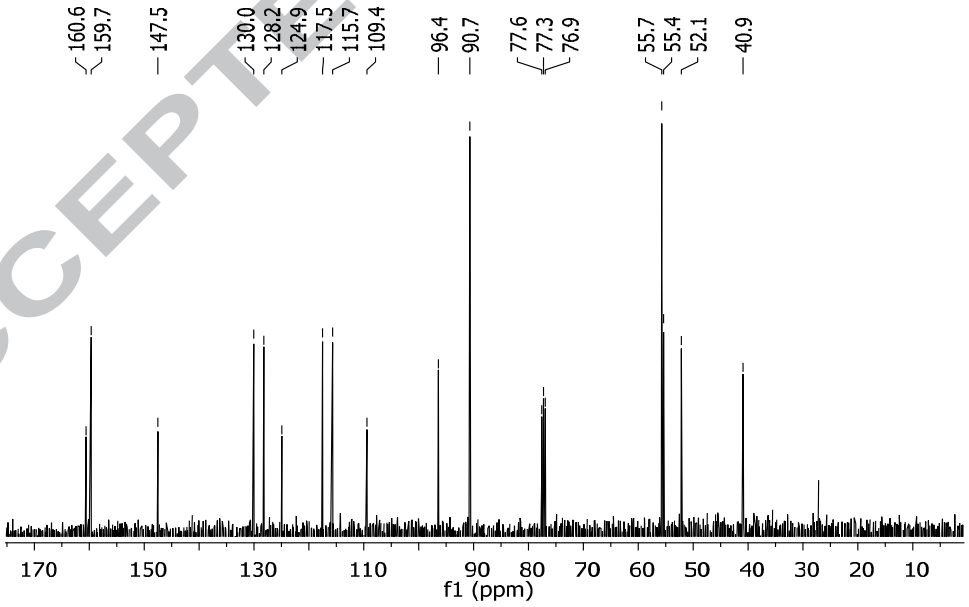


^{1}H and ^{13}C spectrum of Cf

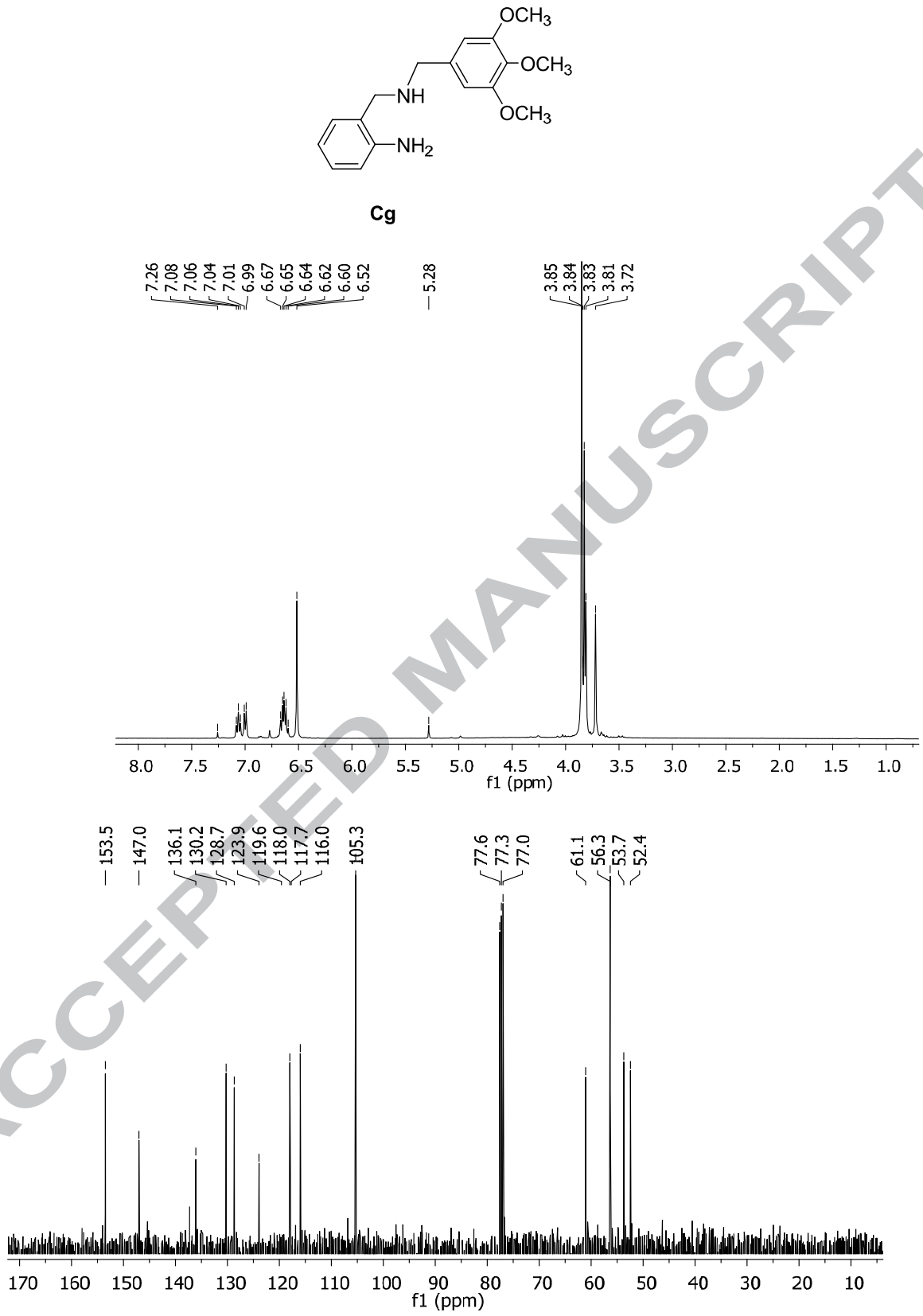


Cf

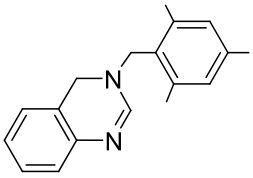




^{1}H and ^{13}C spectrum of Cg



^{1}H and ^{13}C spectrum of Da



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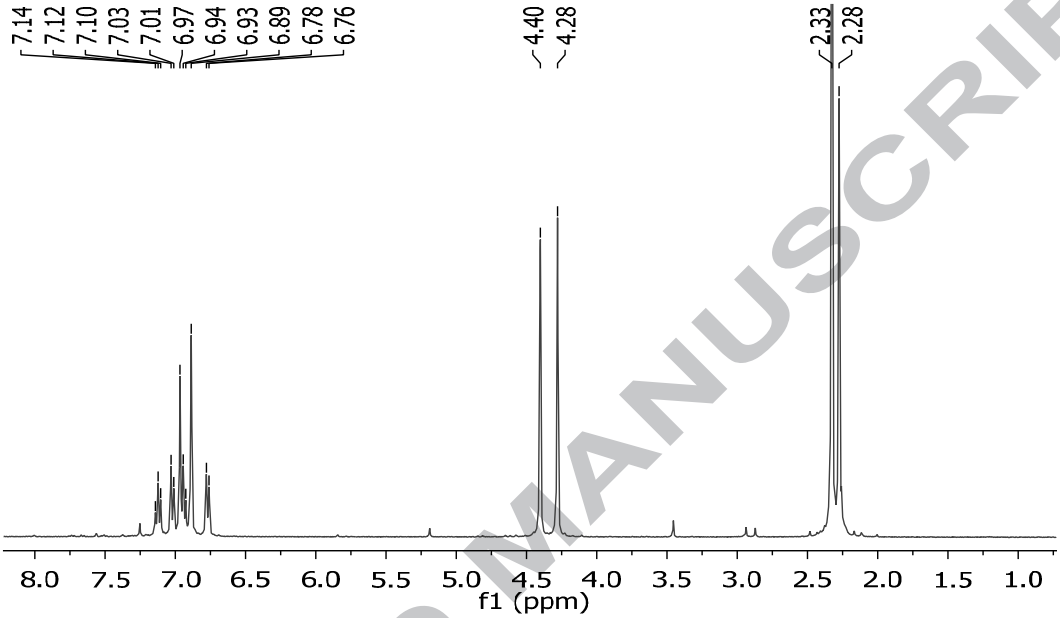
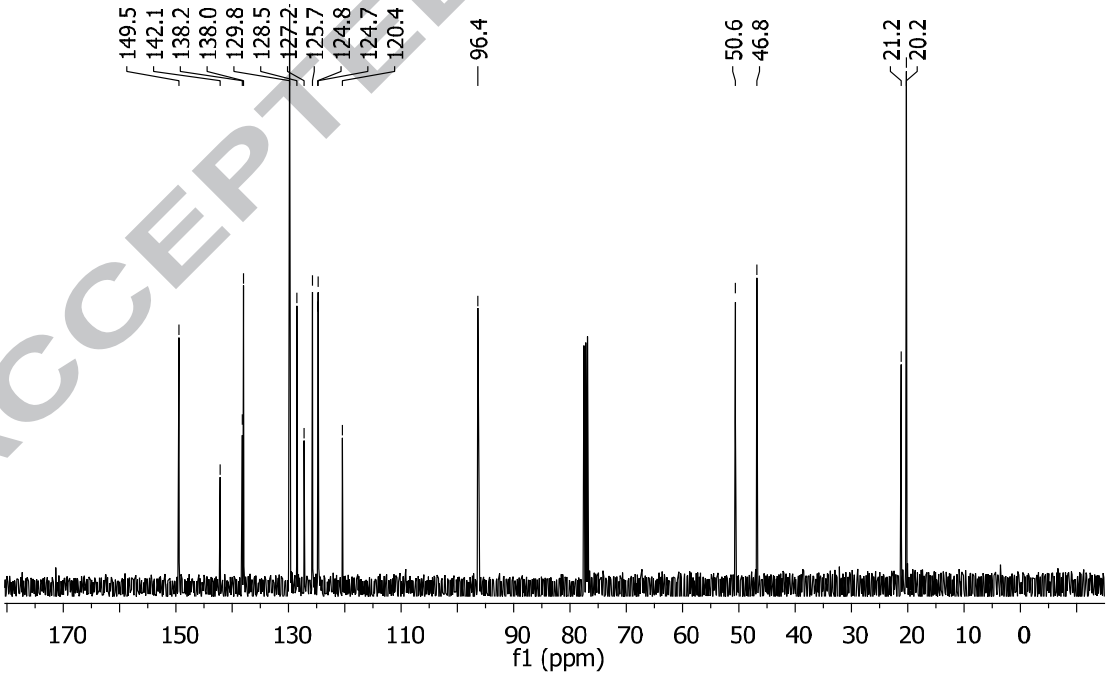
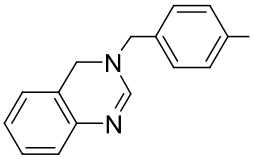
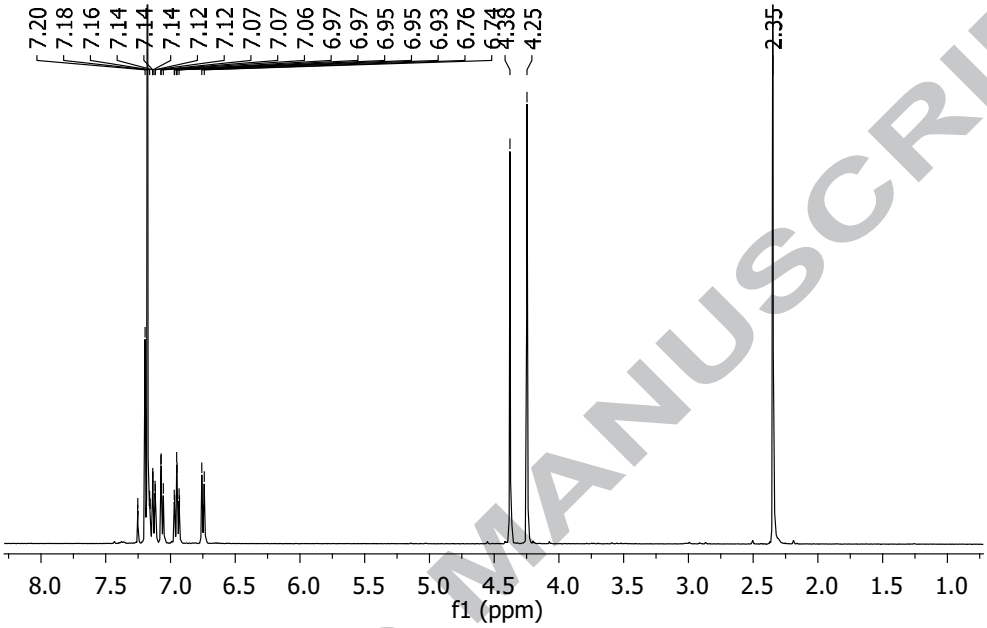


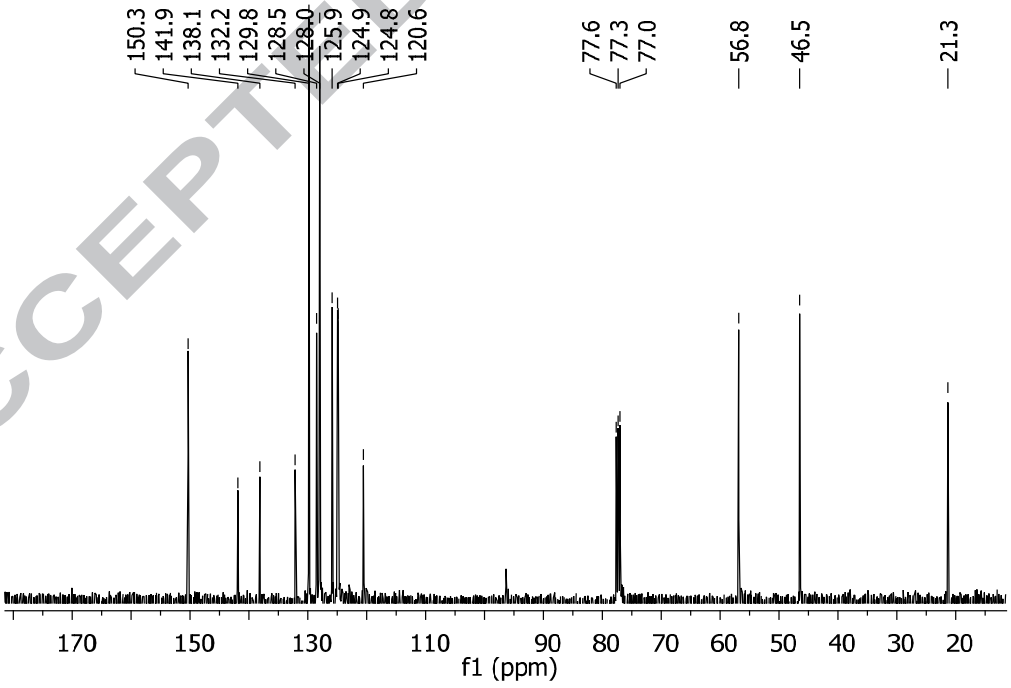


^{1}H and ^{13}C spectrum of Db

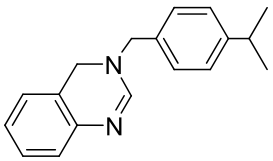


Db

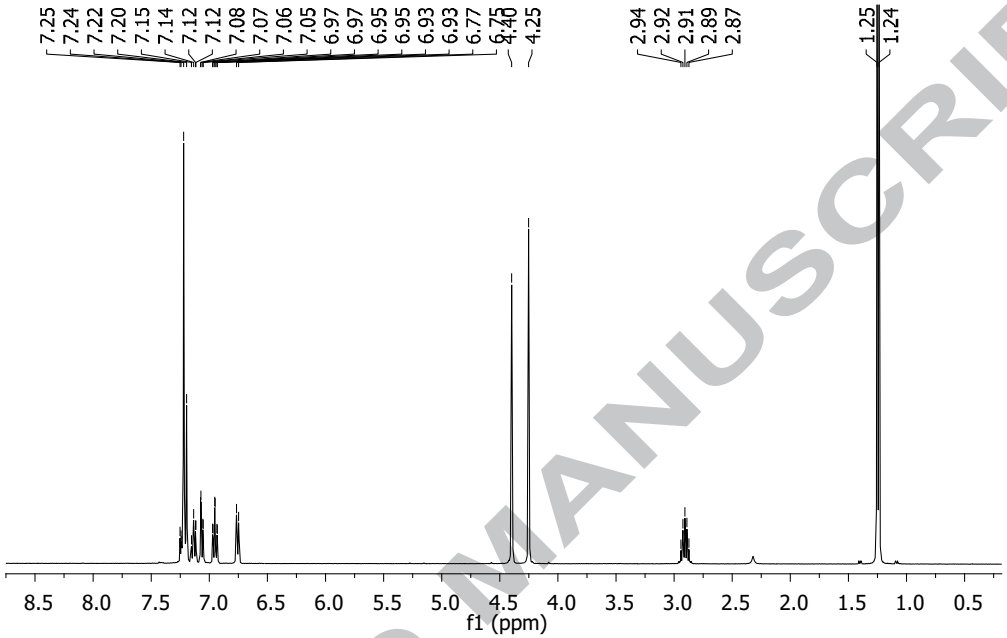


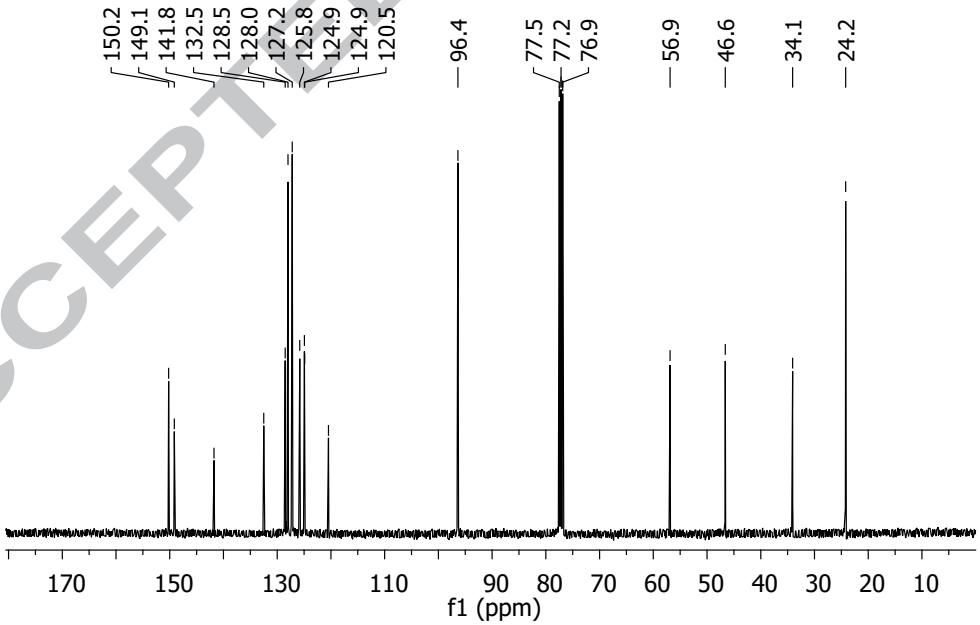


^{1}H and ^{13}C spectrum of Dc

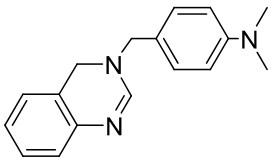


Dc

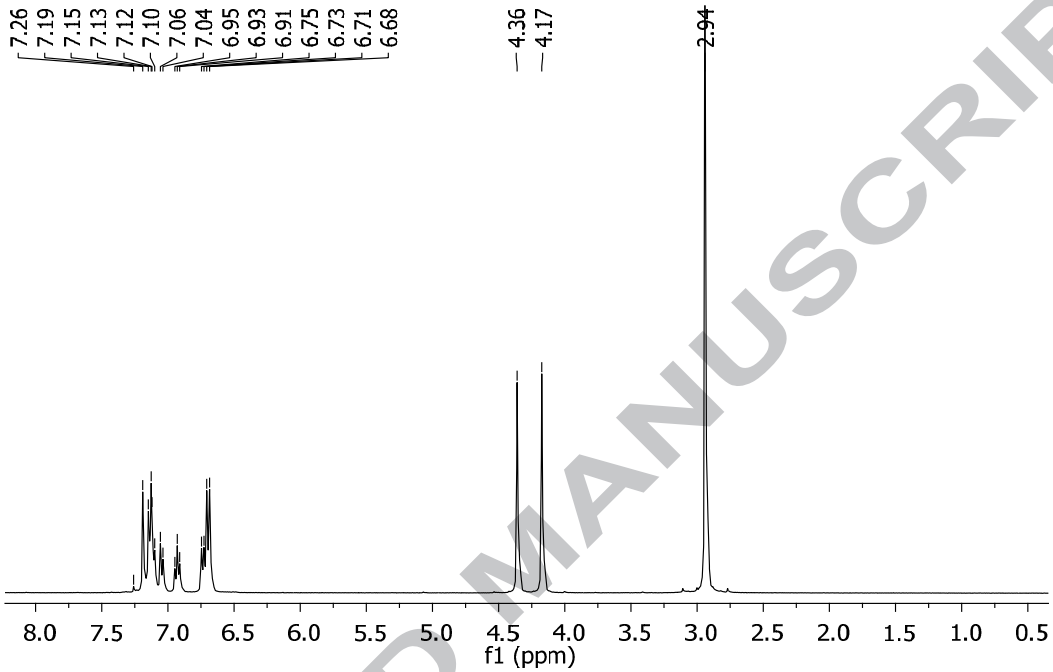


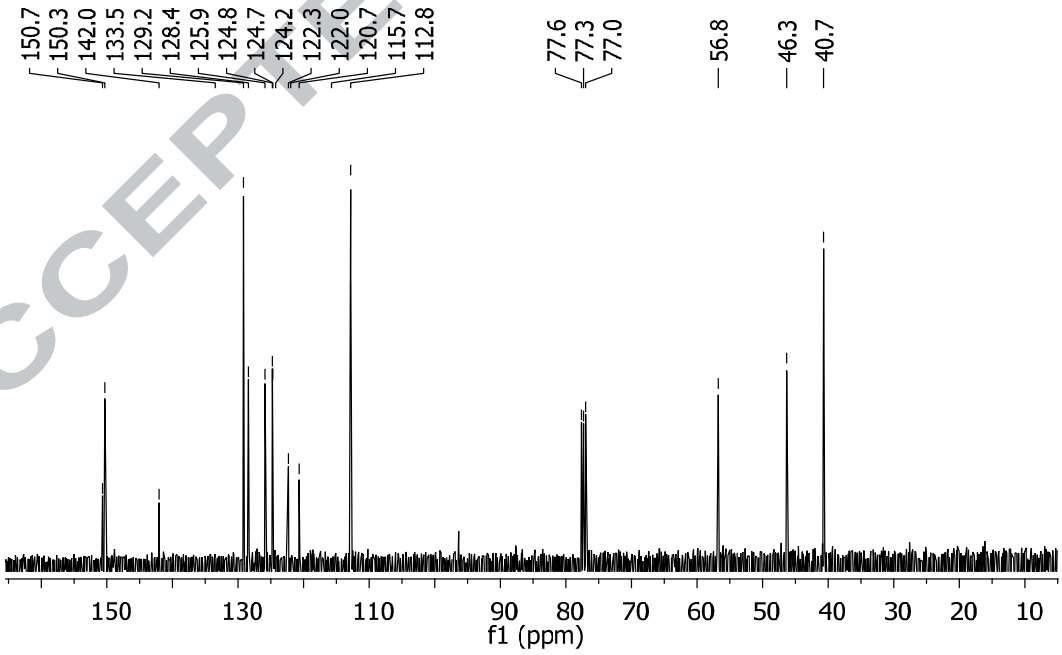


^{1}H and ^{13}C spectrum of Dd

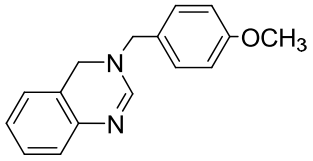


Dd

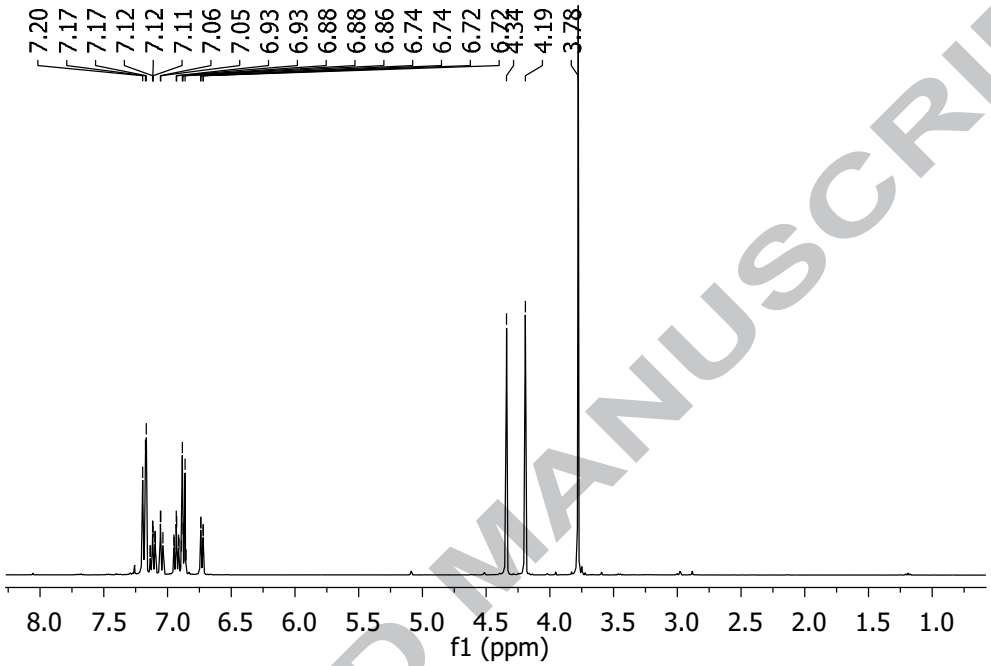


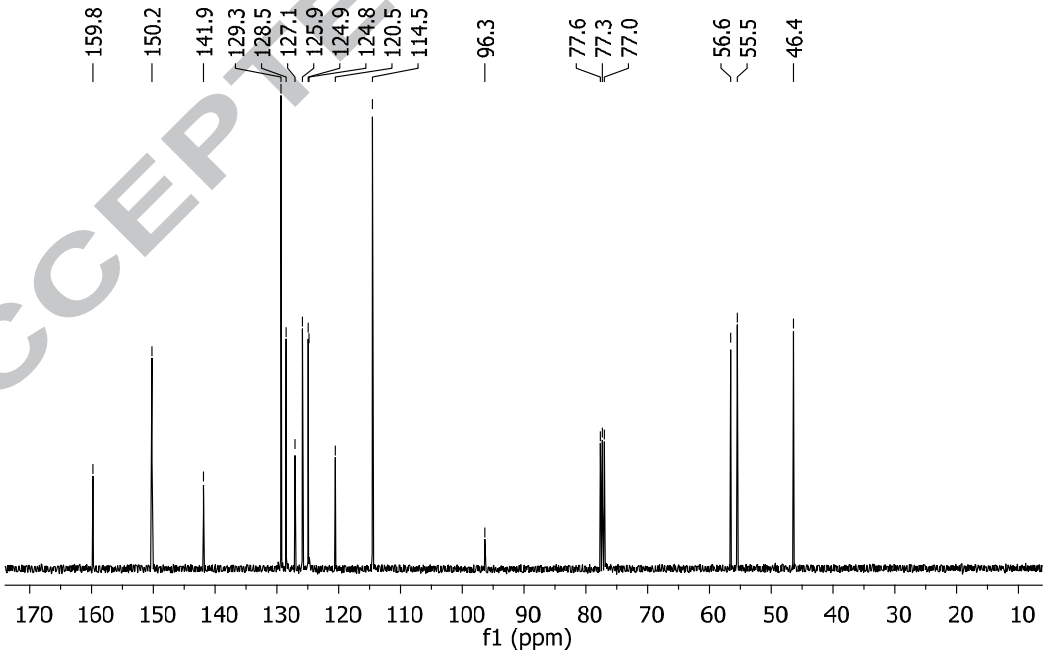


^{1}H and ^{13}C spectrum of De

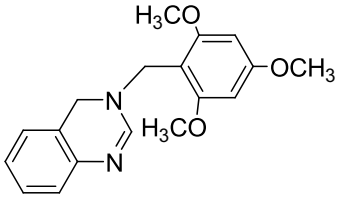


De

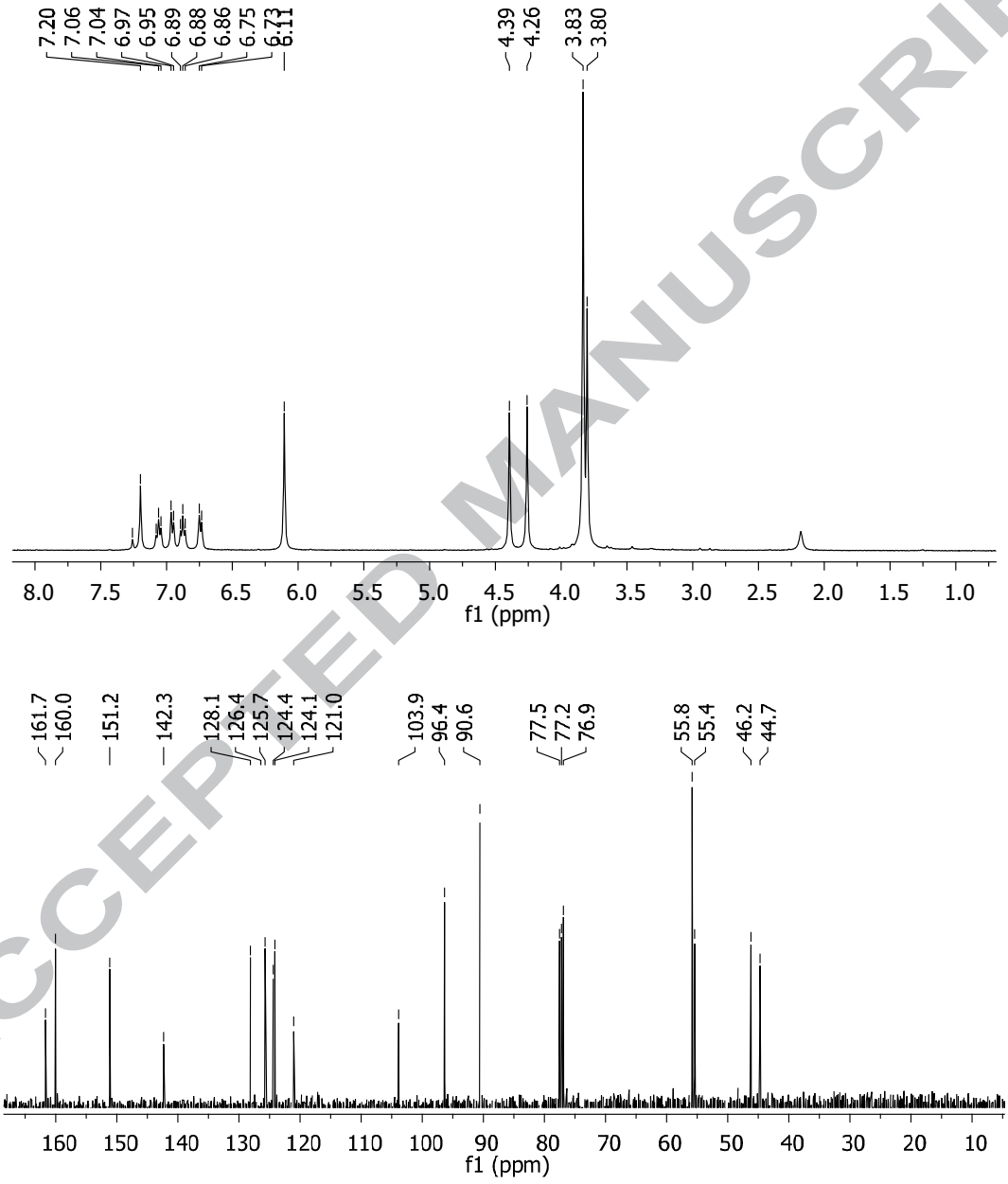




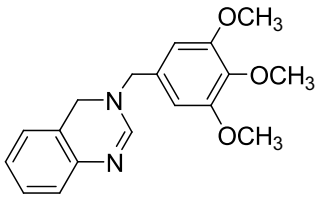
^{1}H and ^{13}C spectrum of Df



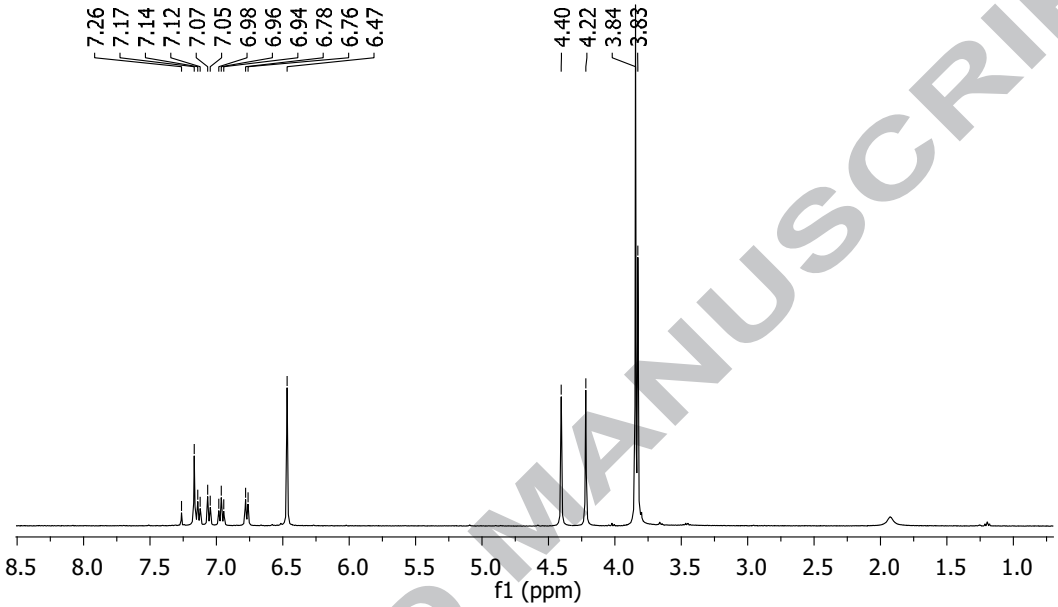
Df

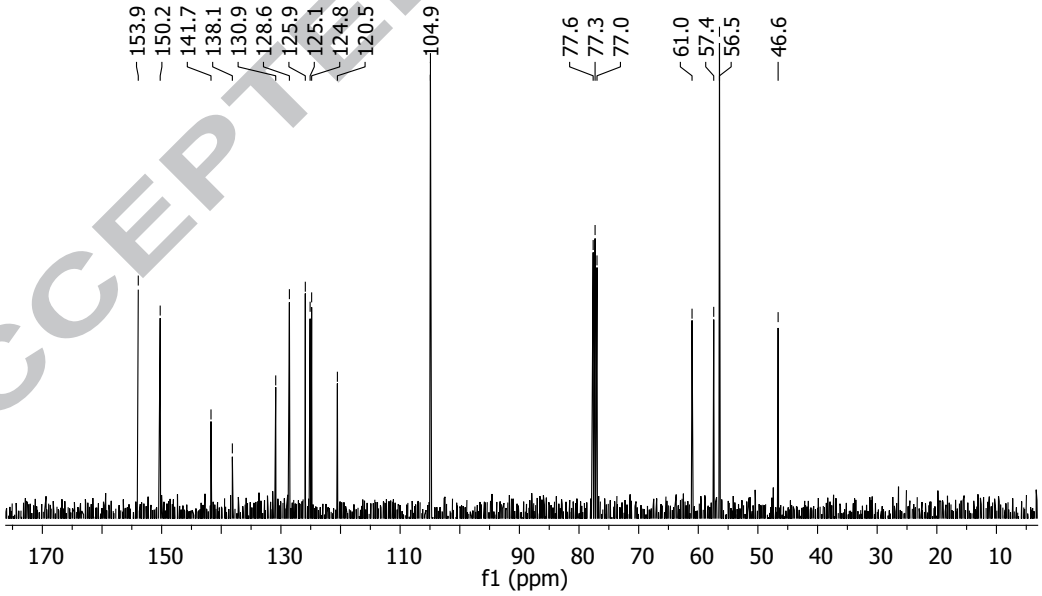


^{1}H and ^{13}C spectrum of Dg

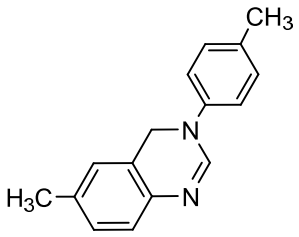


Dg

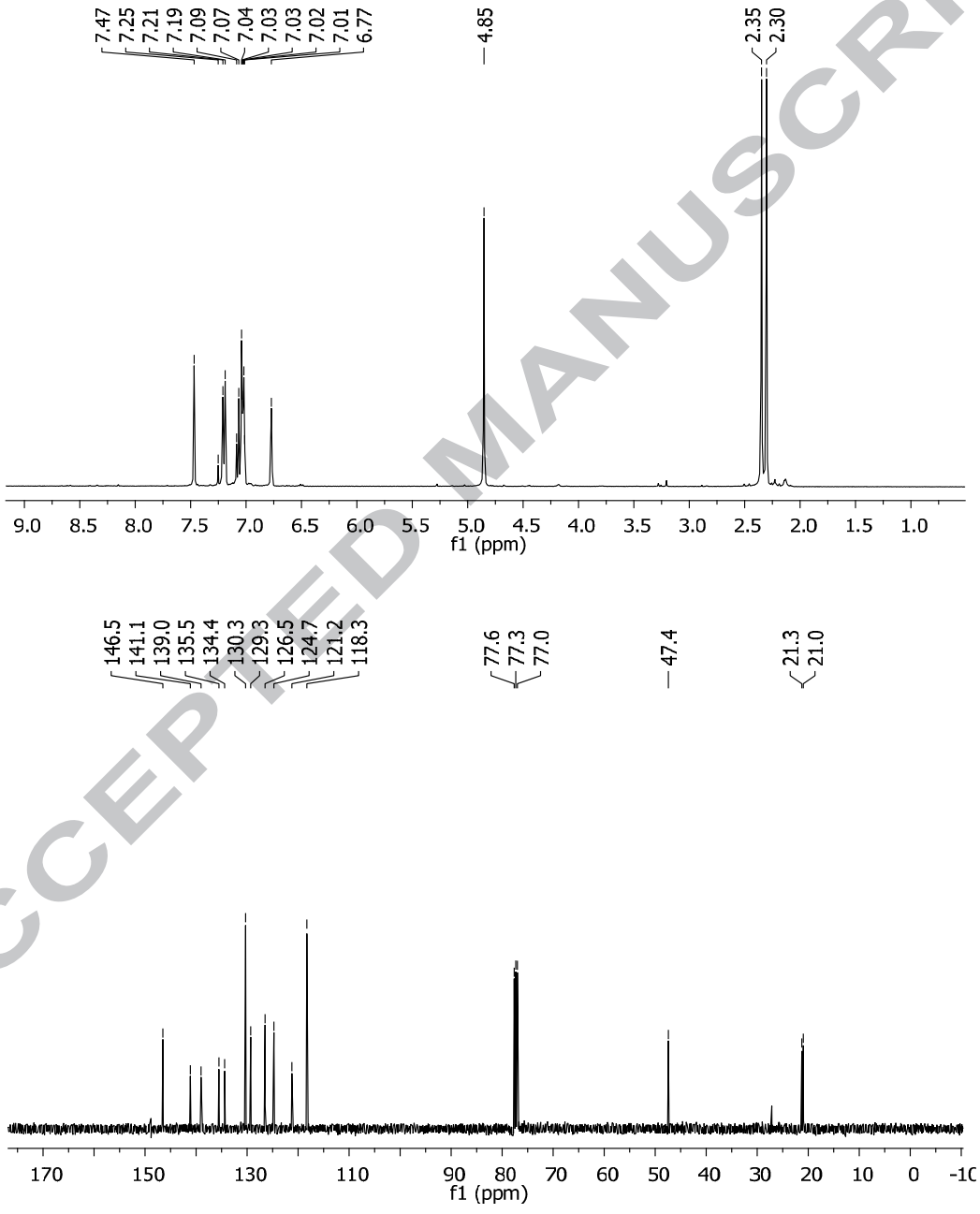




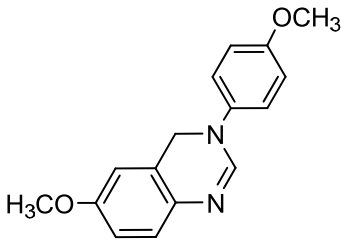
^{1}H and ^{13}C spectrum of E



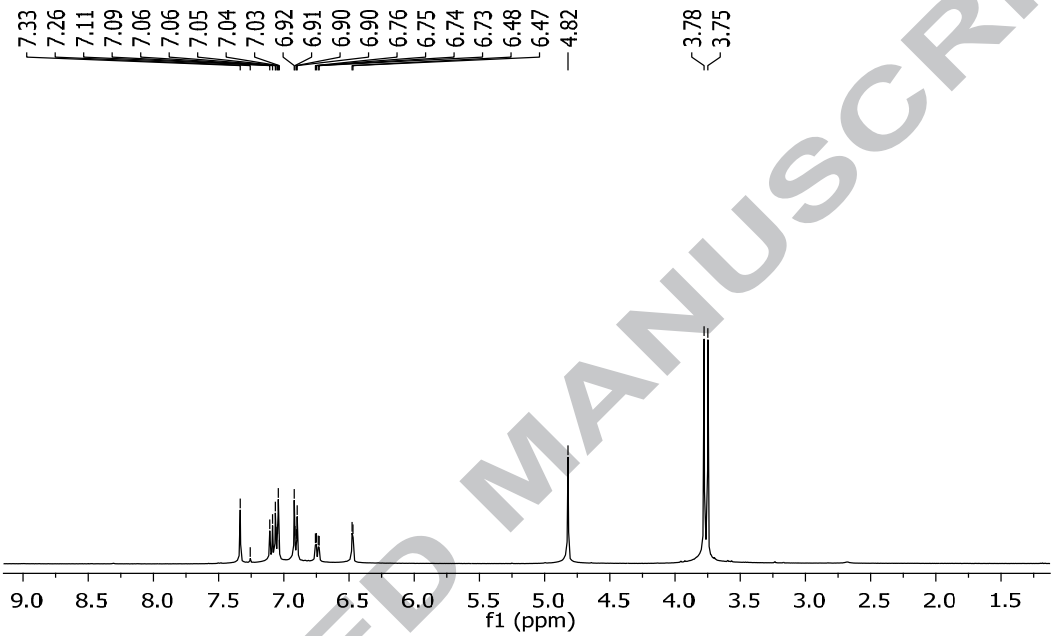
E

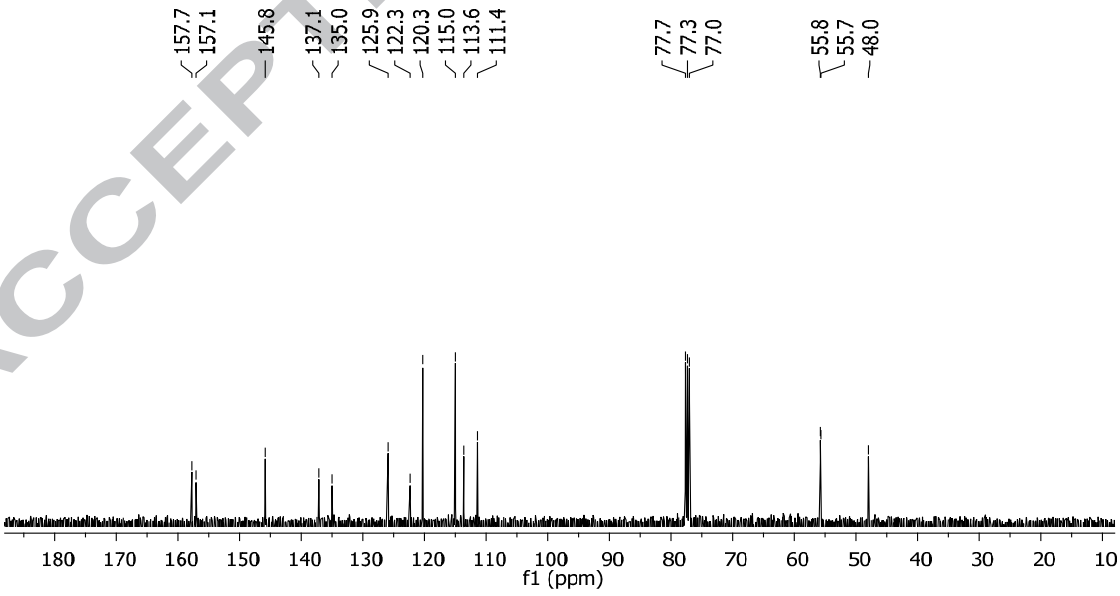


^{1}H and ^{13}C spectrum of F

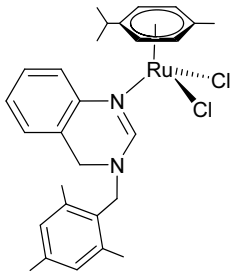


F

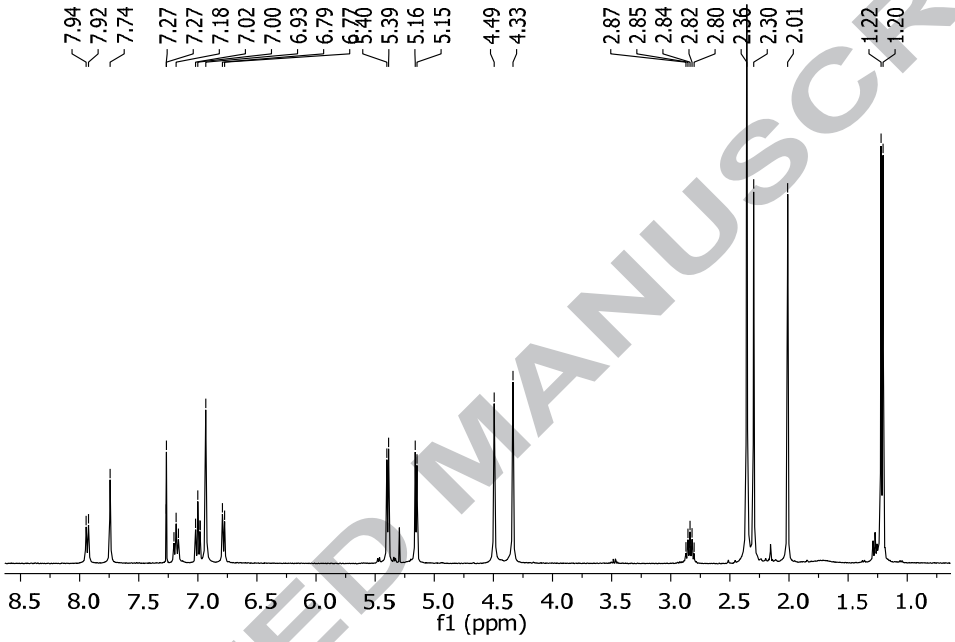


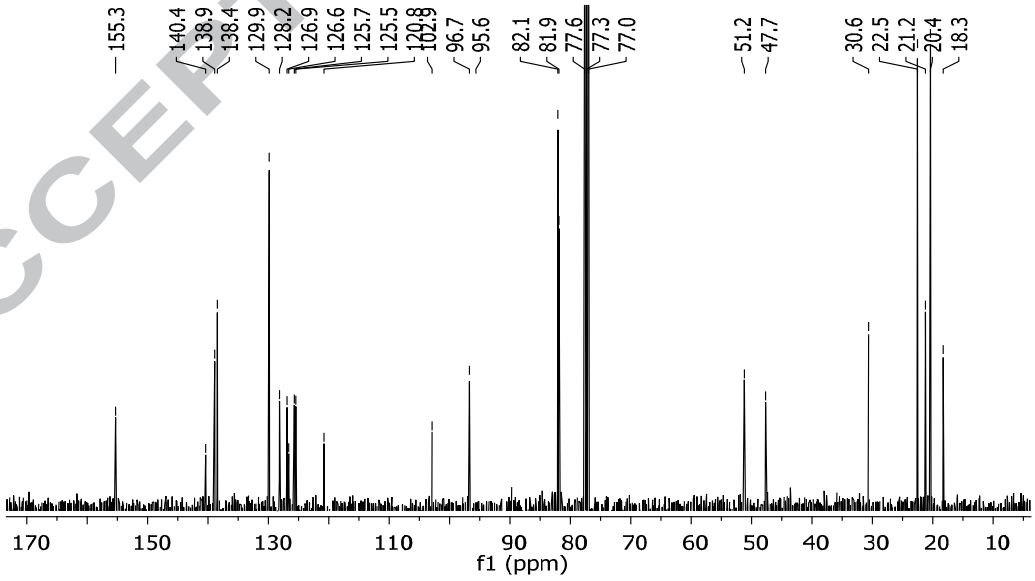


^{1}H and ^{13}C spectrum of 1a

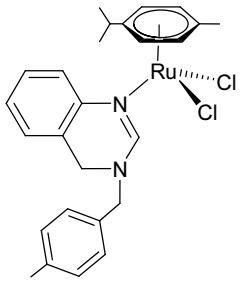


1a

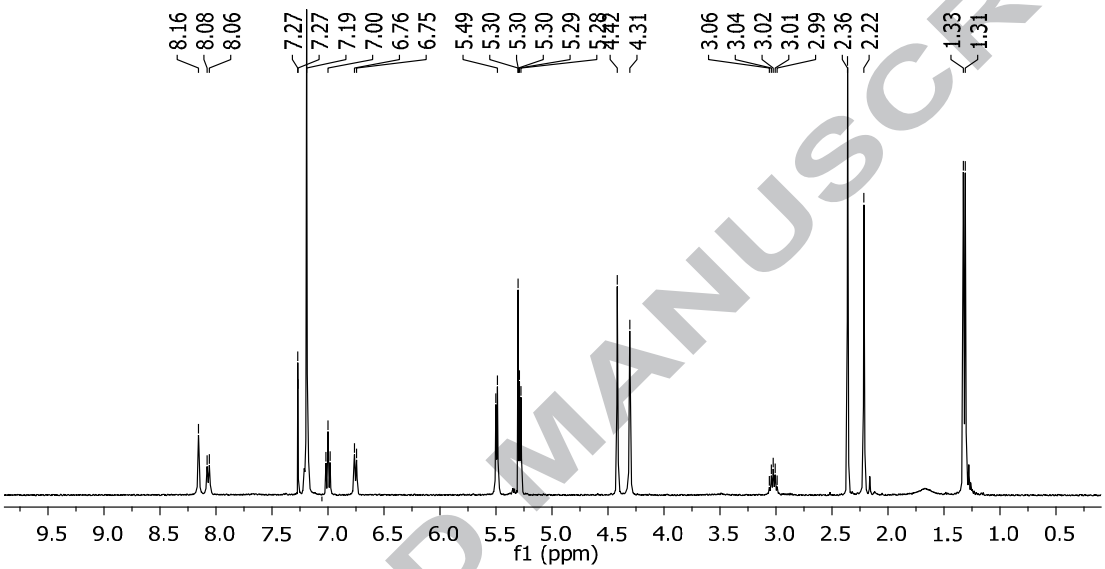


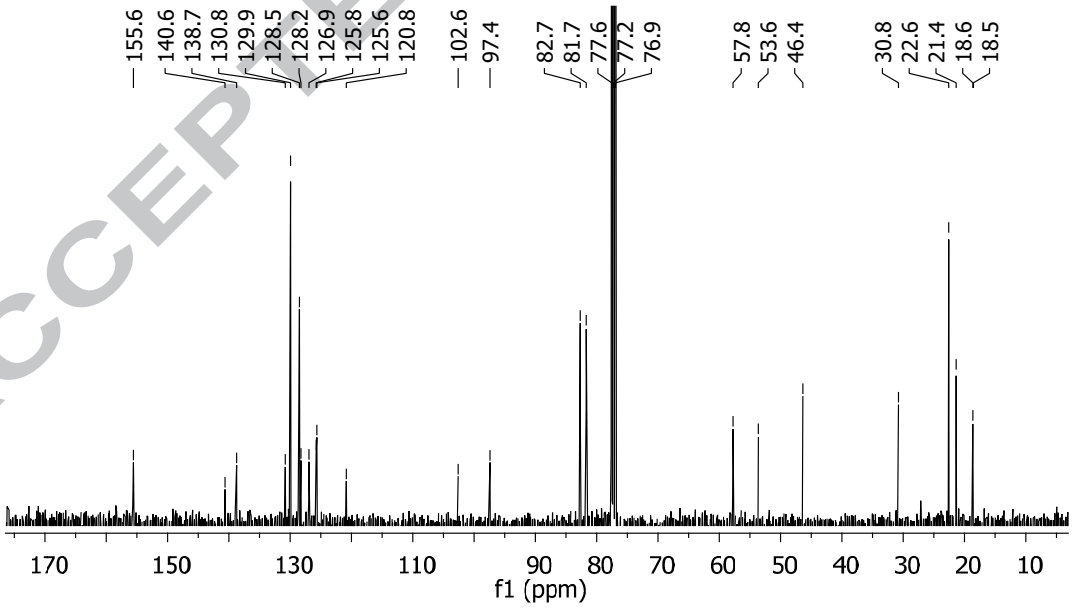


^{1}H and ^{13}C spectrum of 1b

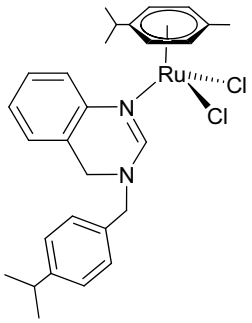


1b

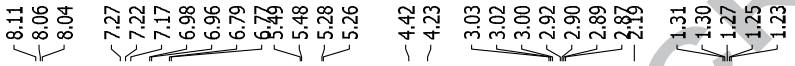


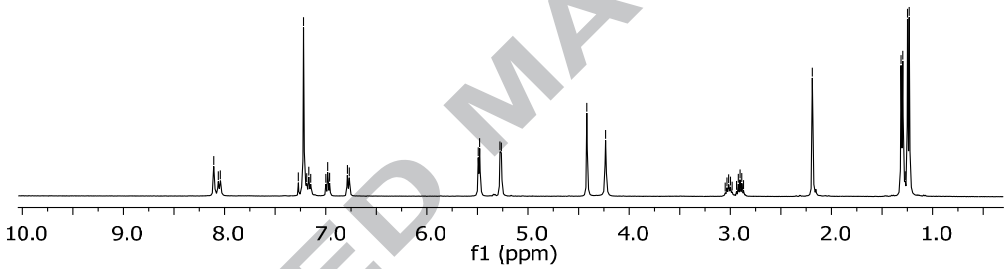


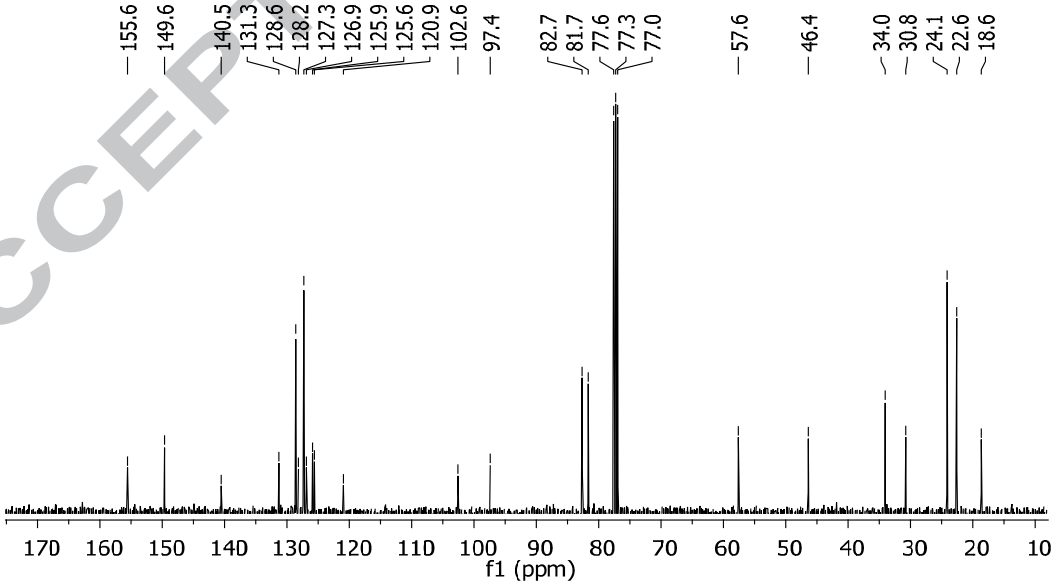
^{1}H and ^{13}C spectrum of 1c



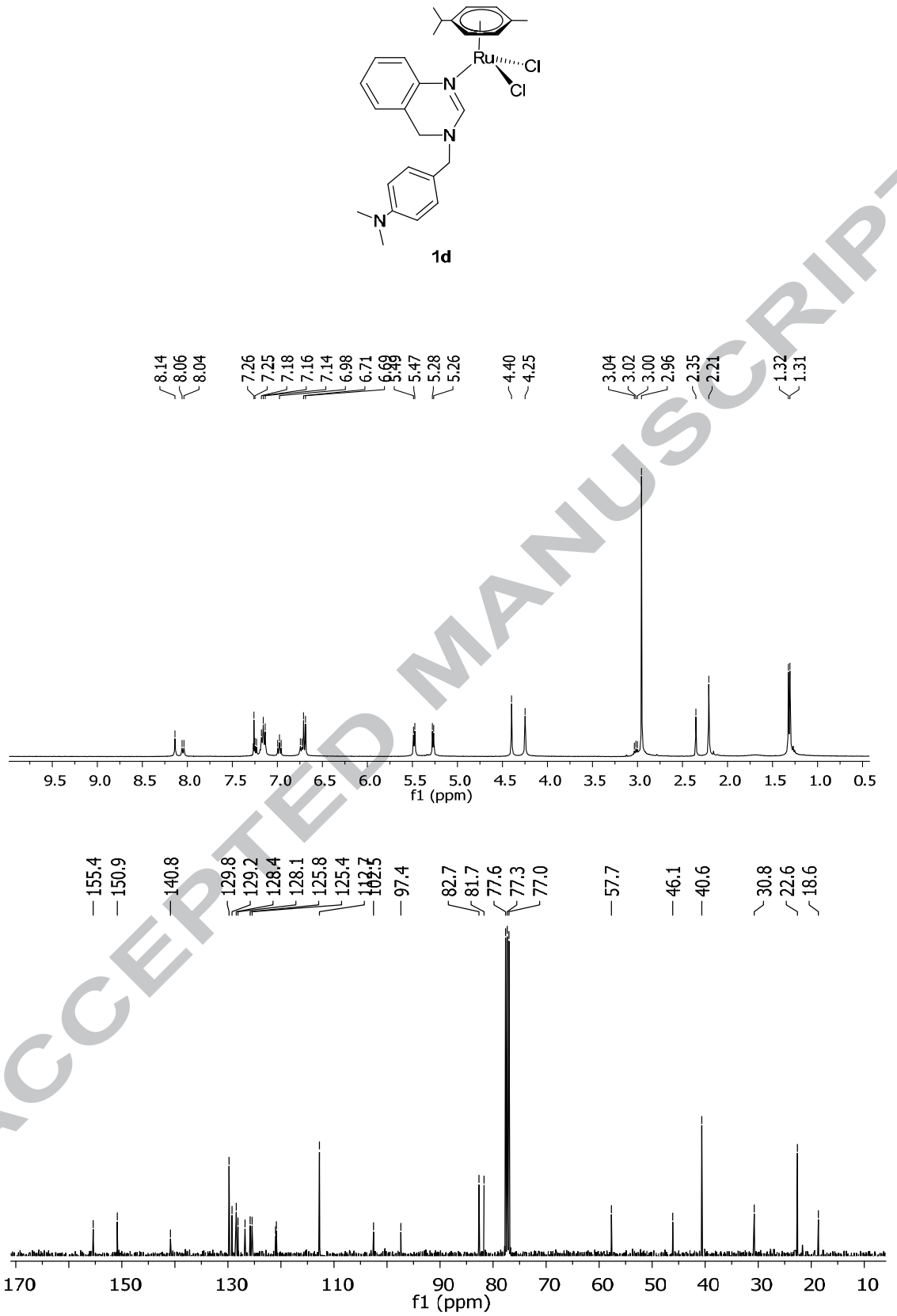
1c



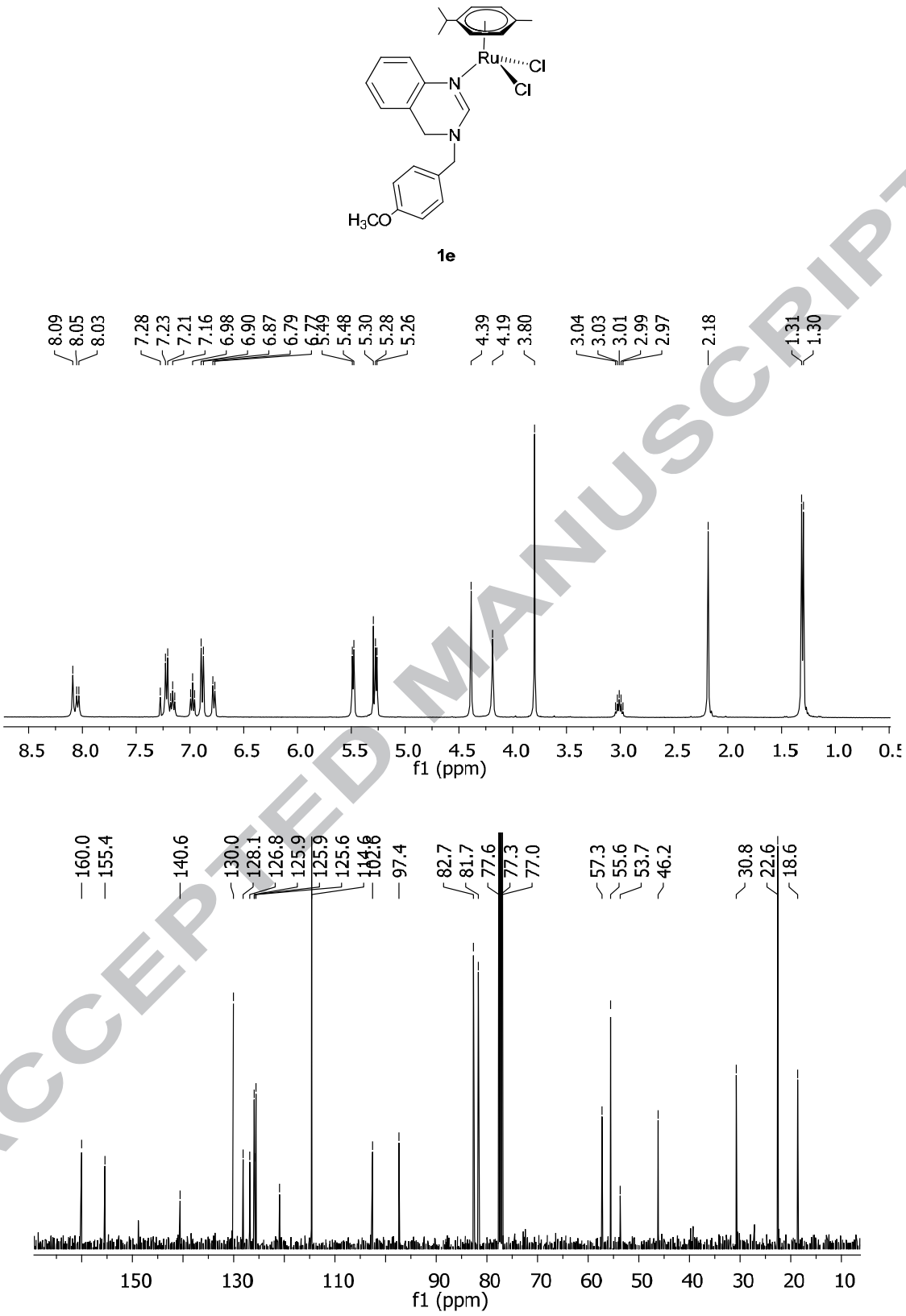




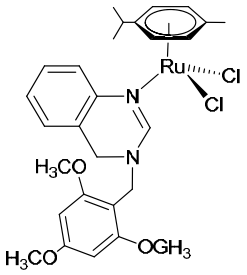
^{1}H and ^{13}C spectrum of 1d



^{1}H and ^{13}C spectrum of 1e



^{1}H and ^{13}C spectrum of 1f



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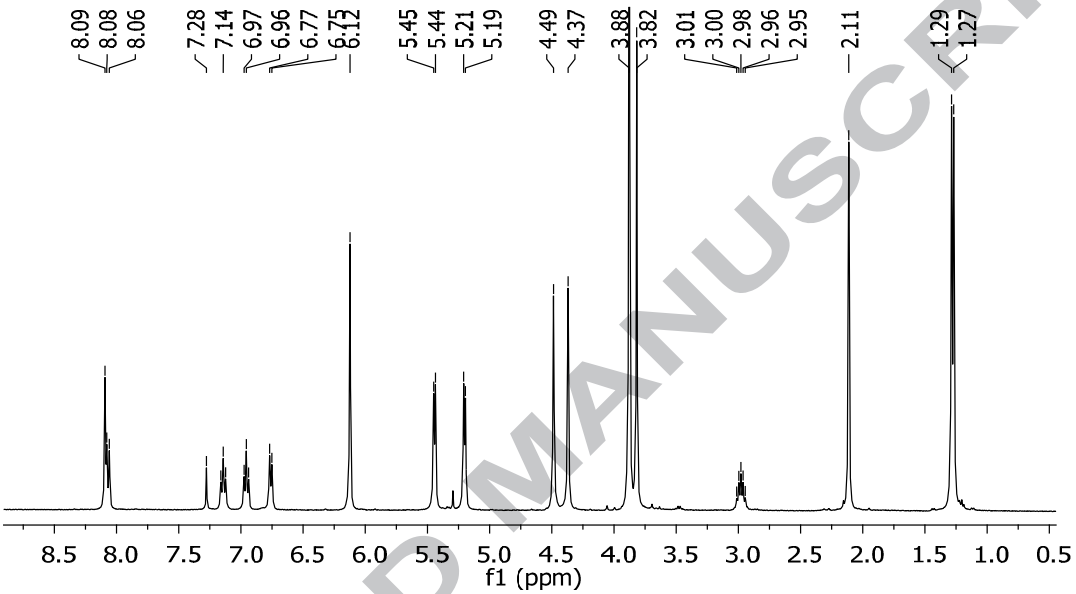
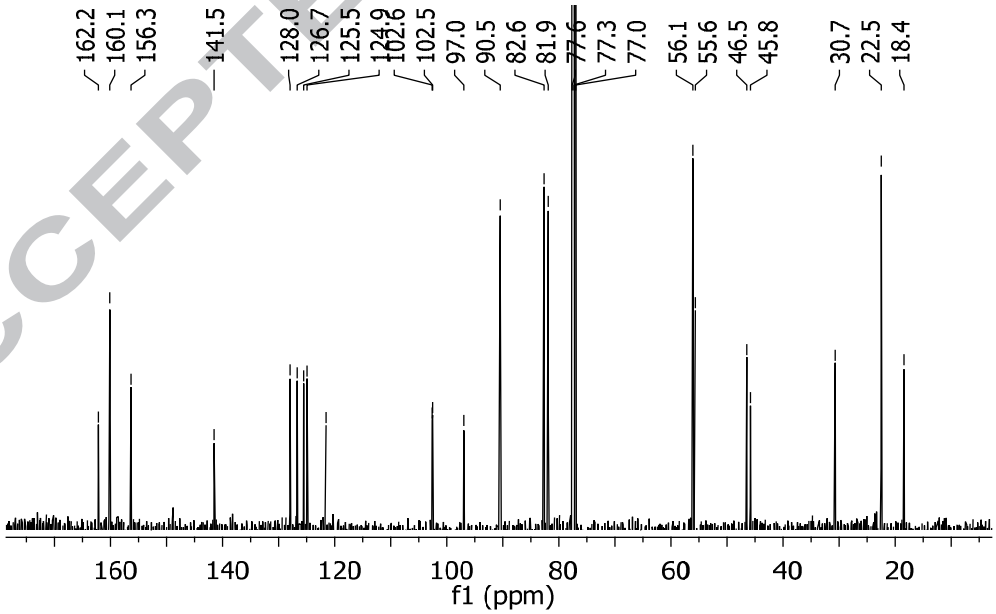
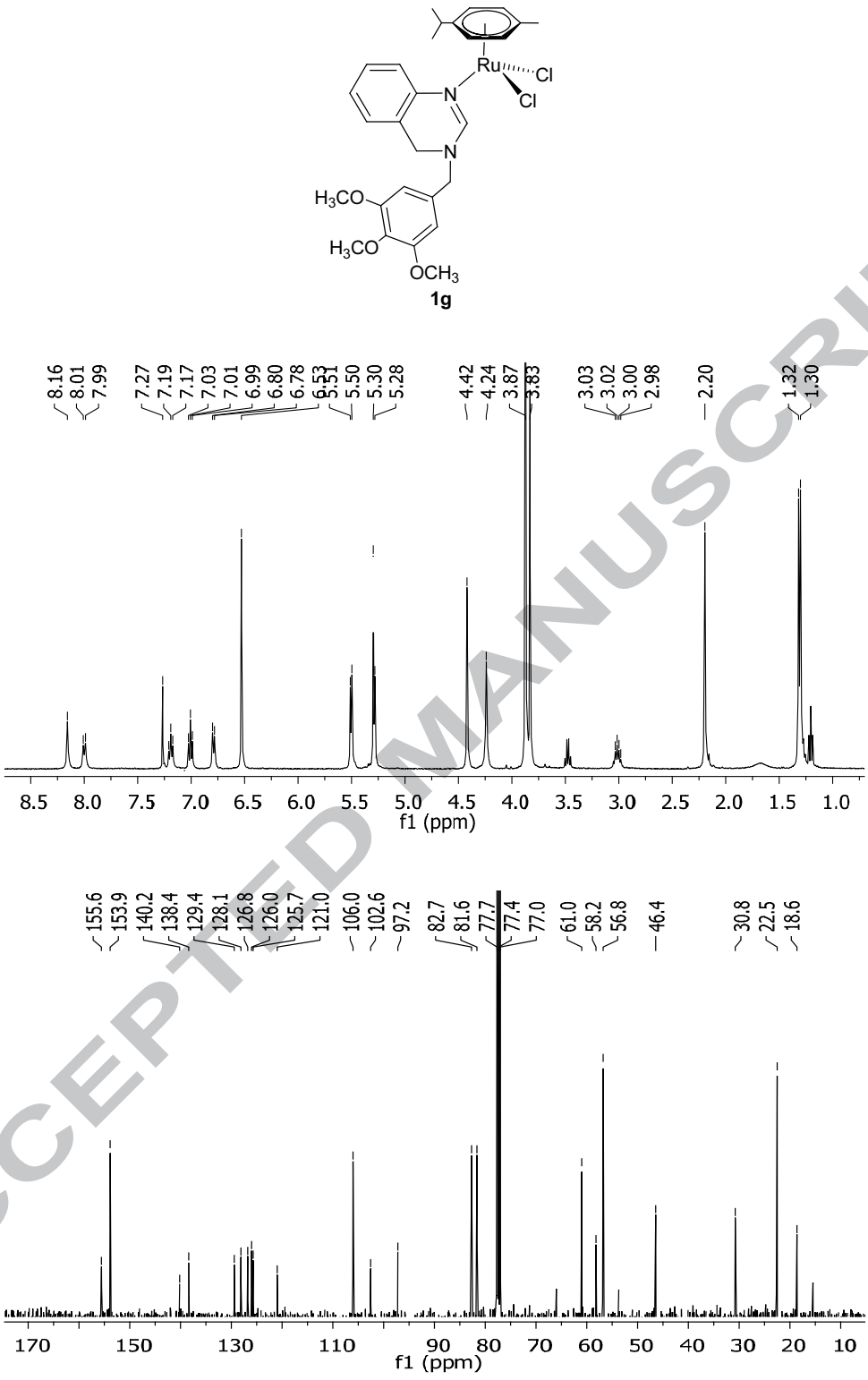
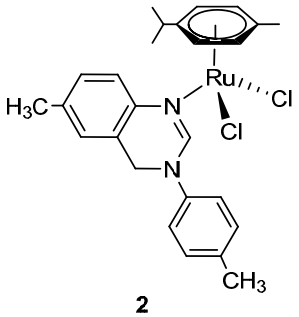




^{1}H and ^{13}C spectrum of 1g



^{1}H and ^{13}C spectrum of 2



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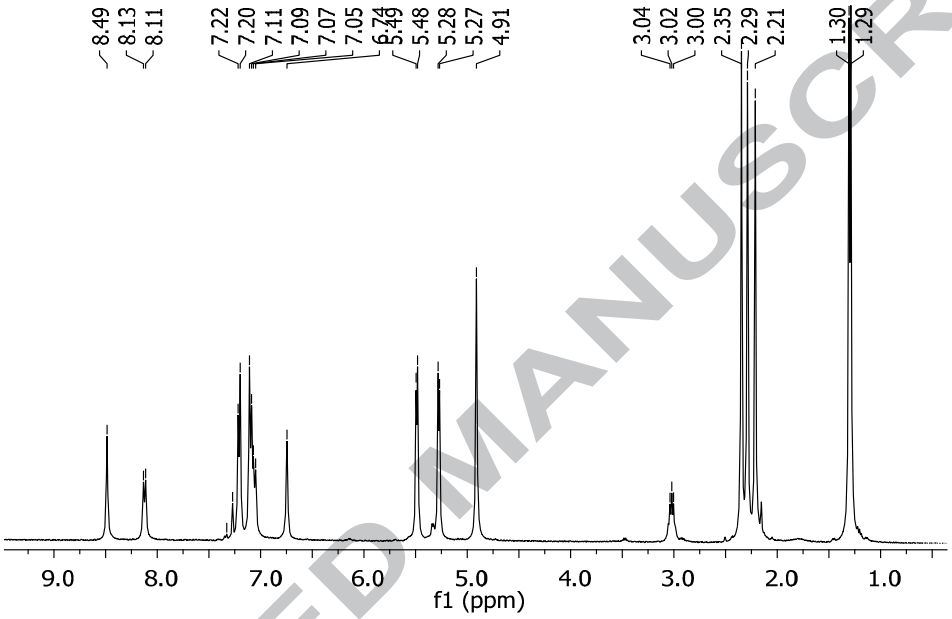
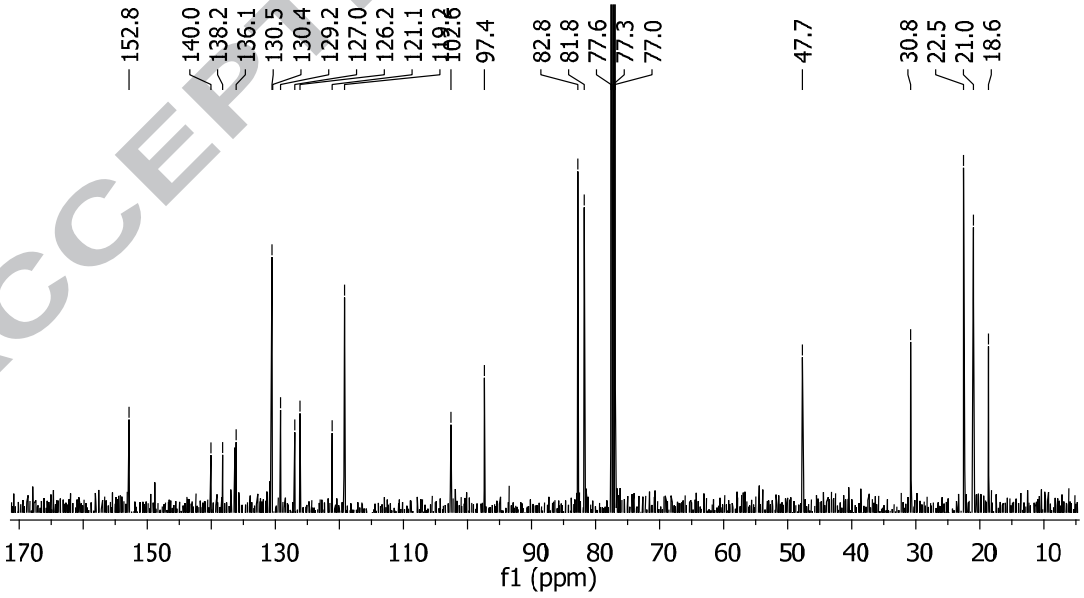
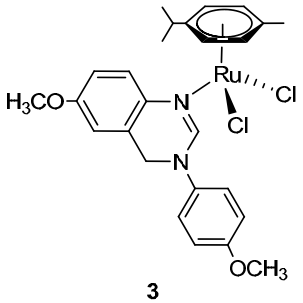




^{1}H and ^{13}C spectrum of 3



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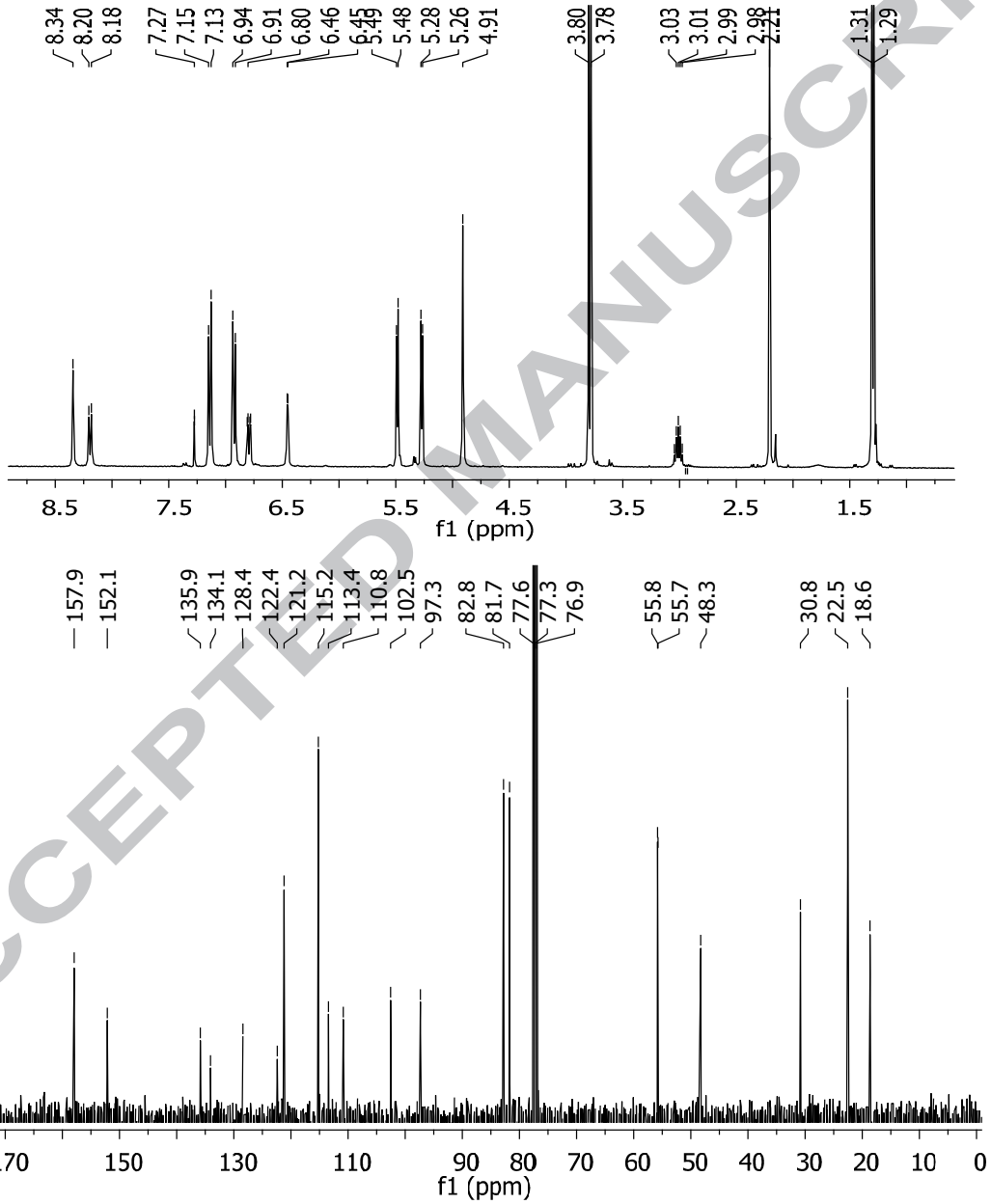
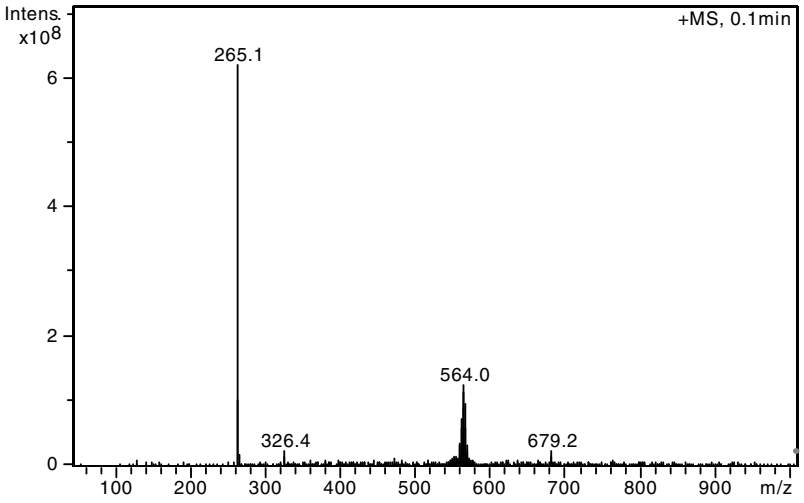
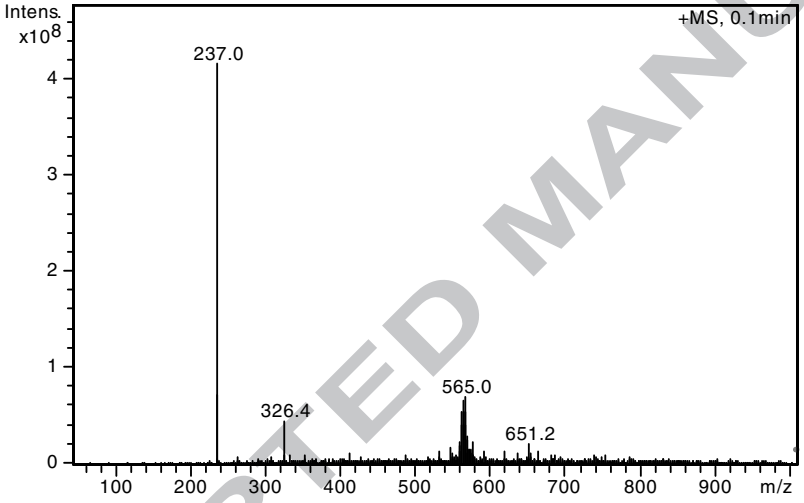


Electrospray ionization mass spectra of complex 1a



Electrospray ionization mass spectra of complex 2



Acknowledgements

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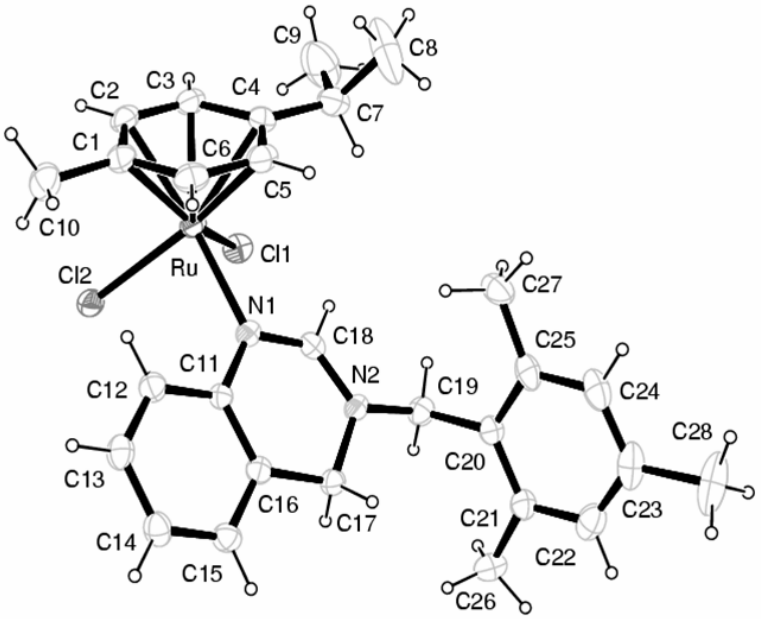


Figure 1

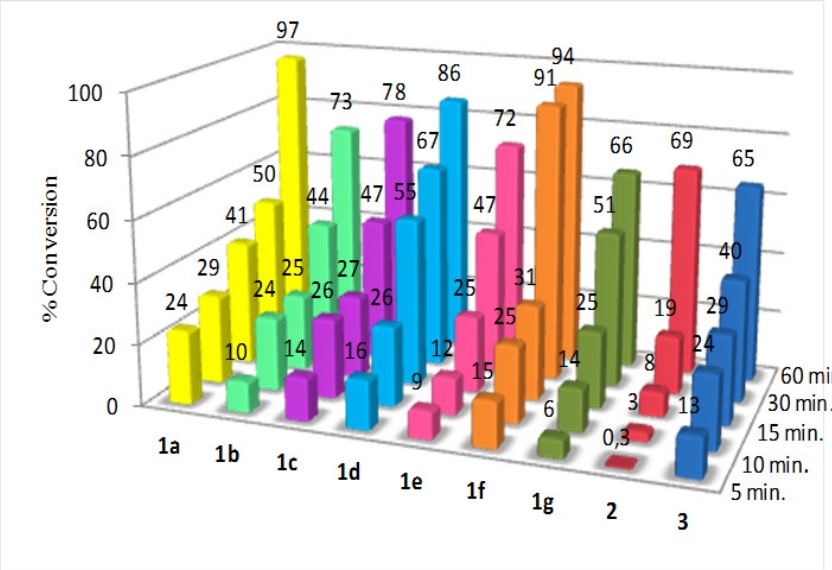


Figure 2

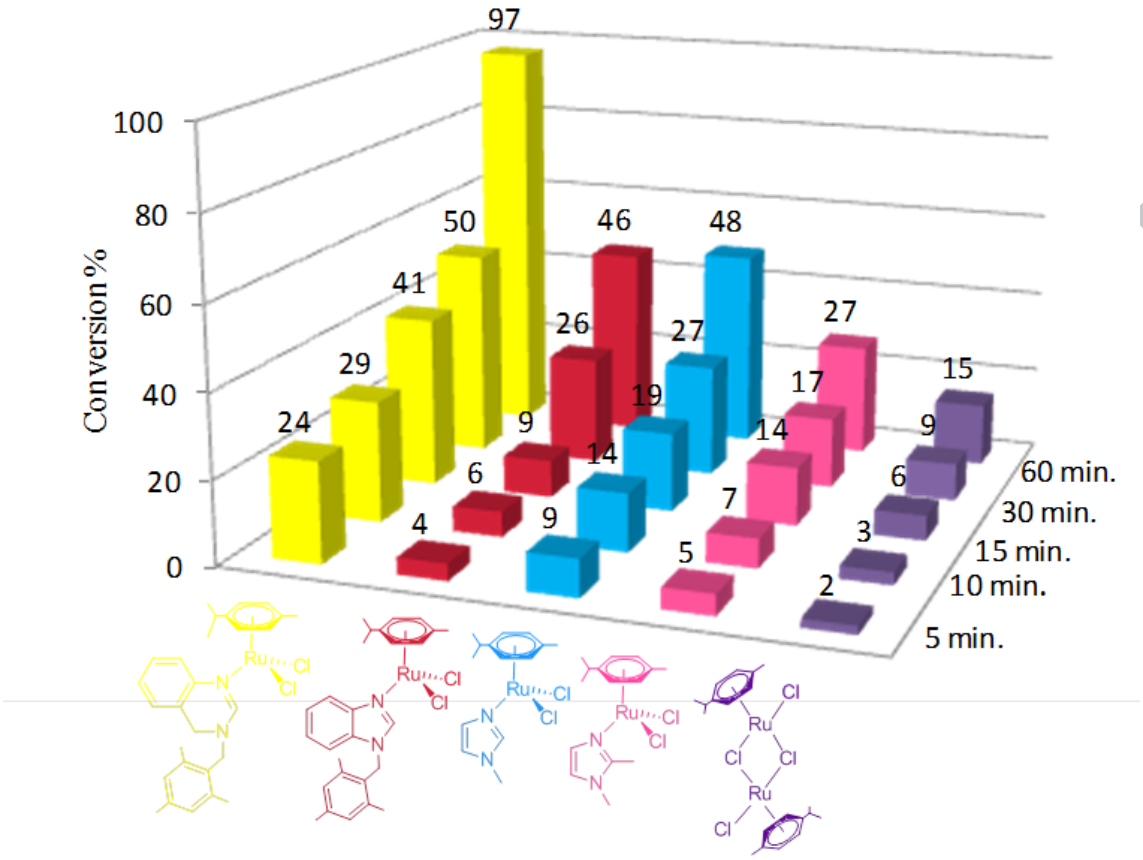


Figure 3

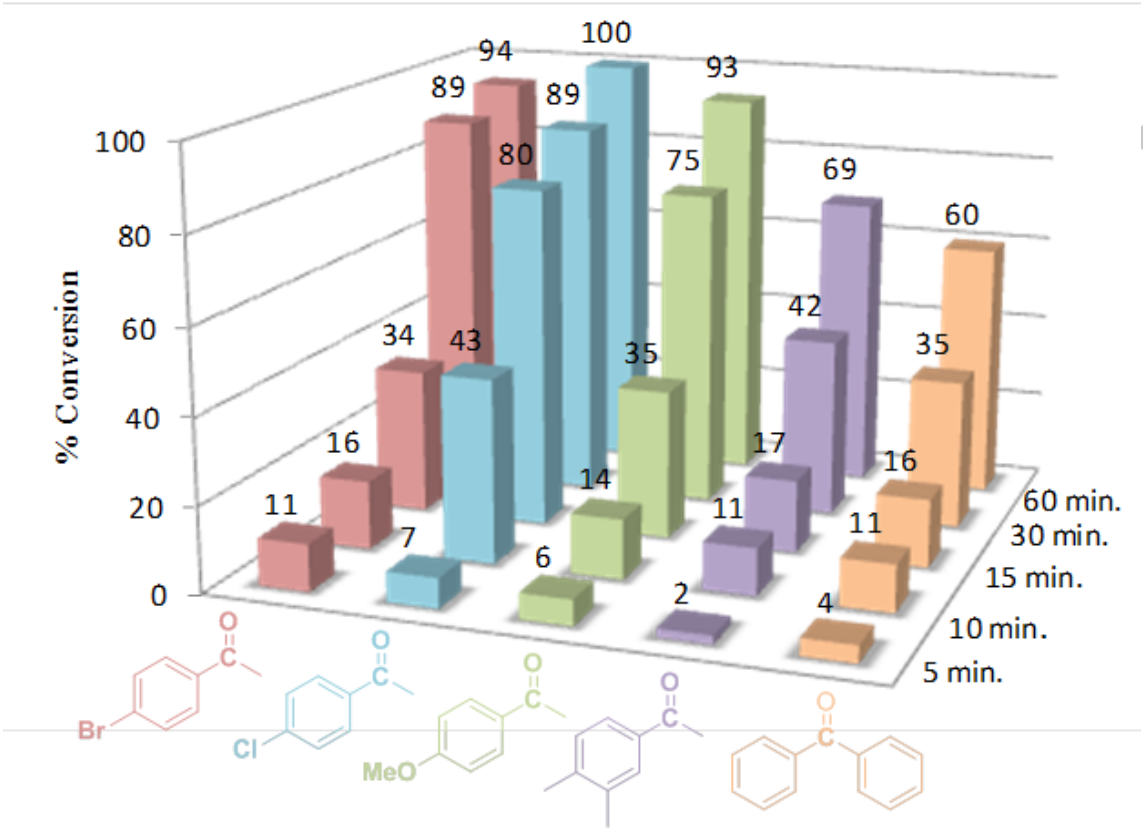
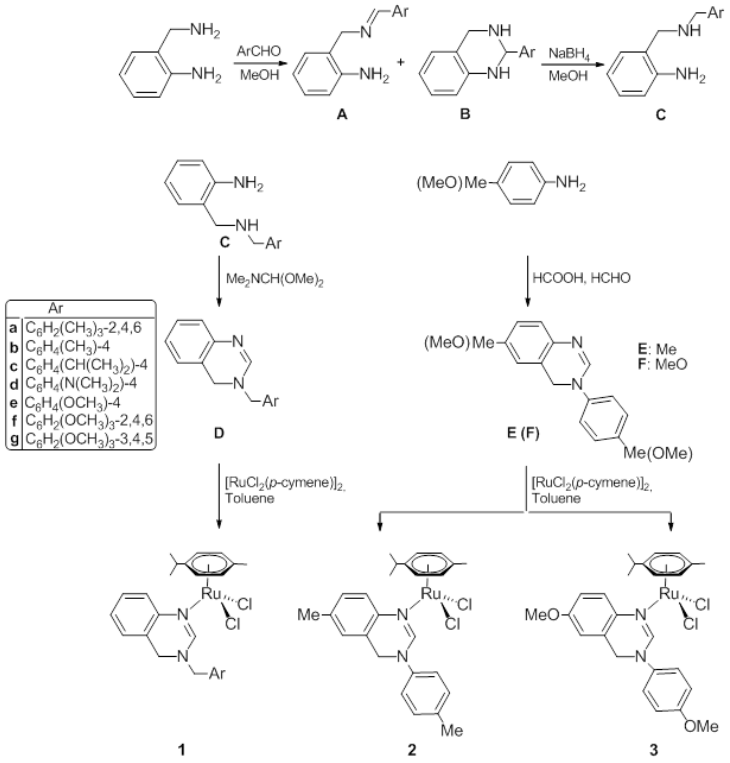


Figure 4



Scheme 1

Table 1. Crystal data and structure refinement details of Ru(II) complex **1a**

Empirical formula	$C_{28}H_{34}N_2Cl_2Ru$
Formula weight	570.54
Temperature (K)	293(2)
Crystal size (mm)	0.21x0.14x0.11
Crystal system	Triclinic
Space group	*P*-1
a (Å)	7.3631(1)
b (Å)	13.5745(4)
c (Å)	13.7274(2)
α (°)	87.45(5)
β (°)	74.65(5)
γ(°)	86.92(5)
V (Å^3)	1320.55(5)
Z	2
$\rho_{calcd.}$ [g/cm3]	1.435
μ (mm^{-1})	0.815
F(000)	588
Θ- range (°)	2.1 – 26.4
Index ranges	-8<*h*< 9, -16<*k*< 16, -17<*l*< 17
Reflections collected	28514
Independent reflections	3386 [R_{int} = 0.101]
Data / restraints / parameters	3386/0/304
Final *R* indices [$F^2 > 2\sigma(F^2)$]	R_1 = 0.079, wR_2 = 0.163
R indices (all data)	R_1 = 0.135, wR_2 = 0.193
Goodness-of-fit on F^2	1.069
Largest diff. peak and hole	0.537 and –0.547 e Å^{-3}

Table 2. Selected bond lengths (Å) and bond angles (˚) for the structure of **1a**

Ru-C(3)	2.159(5)	Ru-N(1)	2.165(4)
Ru-Cl(1)	2.424(5)	Ru-Cl(2)	2.411 (5)
Ru-C(5)	2.145(8)	Ru-C(2)	2.180(6)
N(2)-C(19)	1.469(5)	N(2) -C(18)	1.327(5)
N(1)-C(11)	1.422(5)	N(1) -C(18)	1.299(6)
C(16)-C(11)	1.392(6)	C(16) -C(15)	1.389(6)
C(3)-Ru-C(5)	68.2(3)	C(19)-N(2)-C(18)	120.3(6)
C(11)-N(1)-C(18)	115.7(6)	C(11)-C(16)-C(15)	120.7(7)
C(11)-C(16)-C(17)	121.5(6)	C(15)-C(16)-C(17)	117.8(7)

Graphical abstract

Ru(II)-Arene Complexes with N-Substituted 3,4-Dihydroquinazoline Ligands and Catalytic Activity for Transfer Hydrogenation Reaction

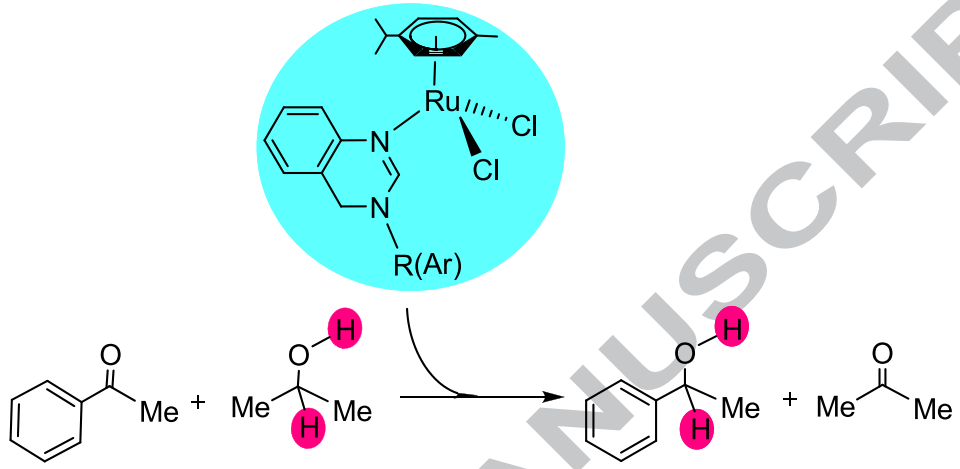
Deniz Mercan, Engin Çetinkaya*, Ertan Şahin

The evaluation of N-coordinated 3,4-dihydroquinazoline ruthenium(II) complexes showed good to excellent performance in the conversion of acetophenone to alcohol after 1h in the presence of 2-propanol and KOH at 82^{o}C. The reaction rate was sensitive to changes on the N-substituent: electron donating substituents on the N atom increased the yield. The most active catalyst, 2,4,6-trimethylbenzyl substituted complex 1a, was used in transfer hydrogenation of different ketones to investigate the effect of substituents on ketones. It was observed that electron-withdrawing groups in the *para* position of the acetophenone increased the yield.

Graphical abstract

Ru(II)-Arene Complexes with N-Substituted 3,4-Dihydroquinazoline Ligands and Catalytic Activity for Transfer Hydrogenation Reaction

Deniz Mercan, Engin Çetinkaya*, Ertan Şahin



Highlights

*Quinazoline-metal complexes are rarely found in the literature.

*3,4-dihydoquinazoline Ru(II) complexes were synthesized and used as homogenous catalyst.

*They showed good to excellent catalytic activity in transfer hydrogenation reaction of acetophenone and its derivatives.