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(Ar-tpy)Ru^{II}(ACN)$_3$- A Water-Soluble Catalyst for Aldehyde-Amidation, Olefin Oxo-scissoring, and Alkyne-Oxygenation

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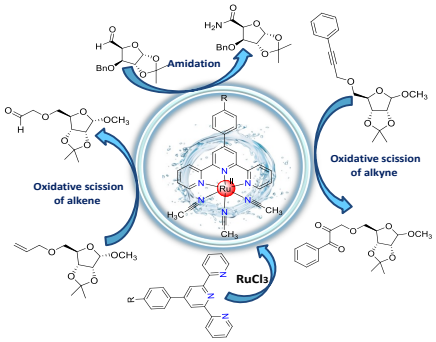


ABSTRACT: The synthetic chemists always look for developing new catalysts, sustainable catalysis, and their application in various organic transformations. Herein, we report a new class of water-soluble complexes, (Ar-tpy)Ru^{II}(ACN)$_3$ utilizing designed terpyridines possessing electron donating and withdrawing aromatic residues for tuning the catalytic activity of Ru(II)-complex. These complexes displayed excellent catalytic activity for several oxidative organic transformations including late-stage C-H functionalization of aldehydes with NH_2OR to valuable primary amides in nonconventional aqueous media with excellent yield. Its diverse catalytic power was established for direct oxo-scissoring of a wide range of alkenes to furnish aldehydes and/or ketones in high yield using a low catalyst loading in the water. Its smart catalytic activity under mild conditions was validated for dioxygenation of alkynes to highly demanding labile synthons, 1,2-diketones and/or acids. This general and sustainable catalysis was successfully employed on sugar-based substrates to obtain the chiral amides, aldehydes, and labile 1,2-diketones. The catalyst is recovered and reused with moderate turnover. The proposed mechanistic pathway is supported by isolation of the intermediates and their characterization. This multifaceted sustainable catalysis is a unique tool, especially for late-stage functionalization to furnish the targeted compounds through frequently used amidation and oxygenation processes in the academia and industry.

■ INTRODUCTION

The quest to find an efficient and inexpensive metal catalyst with a utilitarian application is still an obstacle for developing sustainable chemistry.[1] On the other hand; replacement of a frequently used toxic and volatile organic solvent with a nonconventional solvent like water is a serious consideration to the synthetic professionals of academia and industries.[2] Water is a non-toxic, abundant, inexpensive, and possesses unique physical and chemical properties, and the only solvent to carrying out thousands of organic transformations in biological systems. The design, synthesis, and development of new water-soluble catalysts are highly desirable and challenging to perform diverse organic transformations with hydrophobic substrates in water media.

Among the ruthenium catalysts,[3] Ru^{II}-complex catalyzed fundamental and applied organic synthesis is now an emerging research area because of its outstanding ability to acquire a range of oxidation states (-2 to +8) and coordination geometries. Some of the significant organic syntheses that have been studied using Ru^{II}-catalysts include C-H activations,[4] C-C couplings,[5] olefin metatheses,[6] dehydrogenations,[7a] hydrogenations,[7b,c] and oxygenations.[8] An array of monodentate, bidentate, η6, and a few tridentate ligands coordinated-Ru^{II}-complexes were examined as catalysts with great success.[9] However, the majority of these catalysts are quite substrate specific, relatively unstable (air/moisture sensitive), require hazardous organic solvents, catalyst loading, costly ligands and/or additives. Hence, the discovery of a chemically efficient, green, multifaceted substrate independent catalyst, which can catalyze various organic transformations, is of immense importance.[10]

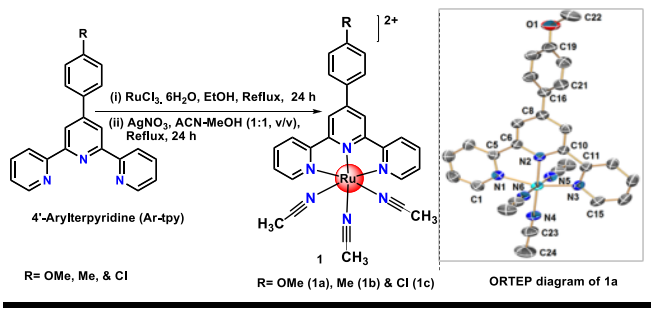
In search for a multifunctional catalyst, we choose Ru(II) as the metal center, π-acidic 4'-aryl-2,2':6',2''-terpyridine (Ar-tpy), and weakly coordinating acetonitrile molecules as ancillary ligands to facilitate substrate binding during catalysis in water. Although metal-tpy complexes with Ru^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, and Pd^{2+} have been exploited in supramolecular chemistry[11] and catalysis,[12] albeit the use of (Ar-tpy)Ru^{II}-complex is a rarity for generating smart catalyst. To the best of our knowledge, only Crabtree *et al.* has reported a (tpy)$Ru^{II}(PPh_3)Cl_2$ complex for catalytic transformation of oximes/aldehydes to amides,[13a] and cross-coupling of alcohols to ketones under refluxing toluene.[13b]

The syntheses of primary amides,[14] sugar-based chiral analogues, and analogous functionalities[15] are particularly important in biology and pharmaceutical industry,[16] and their direct synthesis are still considered as a contemporary challenge. The traditional methods to primary amides through activation of acids and analogs have several drawbacks such as use of harsh reaction conditions, racemization, degradation, and handling of hazardous chemicals. For instance, TCI, CDI, cyanuric chloride were frequently employed as activating agents.[17]An array of second generation strategies to primary amides was reported such as Pd^{II}-catalyzed carbonylation of aromatic halides using formamide as ammonia equivalent[18] and Cu_2O-guided coupling of aldehyde with NH_4Cl.[19] Primary amides were also directly achieved from primary alcohols and liquor NH_3 in the presence of MnO_2-based octahedral molecular sieves.[20] We and others introduced few synthetic routes to amides involving "green" catalytic strategies.[21]Aldehydes, ketones, and acids are essential synthons and industrial ingredients. These compounds are frequently synthesized through ozonolysis[22] of alkenes and alkynes. However, hazardous generation and handling difficulties of ozone and related strong oxidants have prompted scientists to search for alternative methods employing metal-based catalytic oxidation (e.g. Os and Ru)[23] in the presence of a sacrificial oxidant. However, most of the existing synthetic routes targeting these compounds are reaching their inherent limits, in term of high catalyst loading, over-oxidation, stringent reaction conditions, production of waste and by-product(s), higher overhead cost and use of toxic organic solvents, which have always been a concern for our health and environment. Herein, we report the design and synthesis of new (Ar-tpy)$Ru^{II}(ACN)_3$ complexes and introducing their broad range of C-N, C-O and C=O bond forming green catalytic activities through oxidative functionalization of aldehyde-C-H, alkenes, and alkynes to achieve valuable primary amides, aldehydes, ketones, 1,2-dicarbonyls, and/or acids, and also their sugar-based chiral analogues.

■ RESULTS AND DISCUSSION

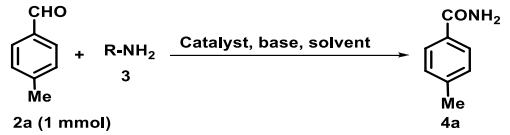
First, we synthesized the designed Ar-tpy[24] ligands possessing different functional groups on aromatic substituents (R = OMe, Me and Cl) by coupling 2-acetylpyridine with corresponding 4-substituted benzaldehydes under alkaline conditions. (Ar-tpy)$Ru^{II}(ACN)_3$ complexes (**1a-c**) were synthesized following a modified reported method[11e] (Scheme 1) and characterized thoroughly by NMR, ESI-MS, FT-IR, UV-Vis and fluorescence spectroscopies of **1a-c**, and single crystal X-ray diffraction analyses of **1a** (Supporting Information).

Scheme 1. Synthesis and Structure of (Ar-tpy)$Ru^{II}(ACN)_3$



With the as-synthesized (Ar-tpy)$Ru^{II}(ACN)_3$-complexes in hand, we performed a survey to establish their catalytic activity for direct functionalization of aldehydes [R-C(=O)-H] to valuable amides (Table 1). In our first experiment, a solution of 4-methyl benzaldehyde (**2a**), hydroxylamine hydrochloride (**3a**), catalyst **1a**, and sodium acetate was stirred in the water at ambient temperature. However, the desired amide (**4a**) was not detected (entry 1).

Table 1. Catalyst Screening for Amidation Reaction[a]



entry	**3**(1.1 mmol), catalyst	base(1.15 mmol)	solvent	temp (°C)[b]	time (h)	yield (%)
1	$NH_2OH.HCl$, **1a**	NaOAc	Water	25	24	NR[c]
2	$NH_2OH.HCl$, **1a**	NaOAc	Water	100	12	54
3	$NH_2OH.HCl$, **1b**	NaOAc	Water	100	12	74
4	**$NH_2OH.HCl$, 1c**	**NaOAc**	**Water**	**100**	**12**	**95**
5	$NH_2OH.HCl$, **1c**[d]	NaOAc	Water	100	12	94
6	$NH_2OH.HCl$, **1c**[e]	NaOAc	Water	100	24	54
7	$NH_2OH.HCl$,[f]**1c**	NaOAc	Water	100	24	62
8	$NH_2OH.HCl$,[g]**1c**	NaOAc	Water	100	24	34
9	$NH_2OH.HCl$, **1c**	NaOAc[h]	Water	100	12	74
10	$NH_2OH.HCl$, **1c**	NaOAc[i]	Water	100	12	56
11	$NH_2OH.HCl$,**1c**	NaOH	Water	100	12	34
12	$NH_2OH.HCl$, **1c**	Cs_2CO_3	Water	100	12	89
13	$NH_2OH.HCl$, **1c**	K_2CO_3	Water	100	12	37
14	$NH_2OH.HCl$, **1c**	$CaCO_3$	Water	100	12	71
15	$NH_2OH.HCl$, **1c**	DABCO	Water	100	12	45
16	$NH_2OH.HCl$, **1c**	NaOAc	Water	50	12	Trace
17	$NH_2OH.HCl$, **1c**	NaOAc	EDC	84	12	Trace
18	$NH_2OH.HCl$, **1c**	NaOAc	EtOH	79	12	Trace
19	$NH_2OH.HCl$, **1c**	NaOAc	PhMe	110	12	30
20	$NH_2OH.HCl$, **1c**	NaOAc	THF	66	12	0
21	$NH_2OH.HCl$, **1c**	NaOAc	ACN	82	12	20
22	$NH_2OMe.HCl$,**1c**	NaOAc	Water	100	12	73
23	$NH_2OBn.HCl$, **1c**	NaOAc	Water	100	12	Trace
24	$NH_2NH_2.2HCl$,**1c**	NaOAc	Water	100	12	0
25	$PhNHNH_2.HCl$, **1c**	NaOAc	Water	100	12	0
26	$NH_2OH.HCl$, [(*p*-Cymene) $Ru(II)Cl_2]_2$	NaOAc	Water	100	12	44
27	$NH_2OH.HCl$,$RuCl_3$	NaOAc	Water	100	12	Trace
28	$NH_2OH.HCl$,$Pd(OAc)_2$	NaOAc	Water	100	12	0

[a]**2a** (1 mmol), **3a** ($NH_2OH.HCl$, 1.1 mmol), Catalyst (1.12 mol%),NaOAc (1.15 mmol), Water (5 mL), 100 ºC and 12 h. [b]Bath temperature. [c]No reaction. [d]2.4 mol%. [e]0.6 mol%. [f]**3a** ($NH_2OH.HCl$, 2 mmol). [g]**3a**($NH_2OH.HCl$, 0.6 mmol). [h]2 mmol. [i]0.6 mmol.

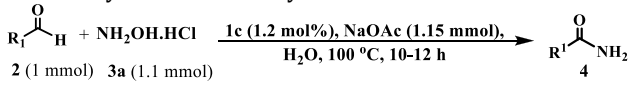
To our delight, the amidation reaction was successful at elevated temperature (bath temperature 100 °C), with a moderate yield (54%, entry 2). The catalyst screening revealed that **1c** (entries 3, 4) is the preferred catalyst to furnish **4a** with excellent yield (95%). There was no further improvement in changing catalyst loading (entries 5, 6), $NH_2OH.HCl$ (**3a**, entries 7, 8) or NaOAc (entries 9, 10). The other inorganic (entries 11-14) and organic (entry 15) bases were not effective. Only traces of **4a** was obtained by reducing the temperature to 50 °C (entry 16). Solvent variation experiments (entry 17-21) confirmed that water is the best reaction medium for C-H amidation by **1c**. Next, several substituted hydroxylamine salts (**2**, entries 23-25) were employed but, only $NH_2OMe.HCl$ afforded **4a** (71%, entry 22). The powerful catalytic activity of the **1c** was verified by comparing the insignificant results obtained from commercially used catalysts Ru(II), Ru(III) and Pd(II) (entries 26-28).

The substrate scope for the amidation reaction was validated utilizing different functional group decorated aromatic, metalized and chiral aliphatic aldehydes under the developed reaction conditions (entry 4, Table 1) to achieve corresponding primary amides (**4**, Scheme 2). Electron-deficient halogens (entries 1-3), and nitro (entries 4, 5) group substituted aromatic aldehydes (**2b**-**f**, Scheme 2) furnished corresponding amides (**4b**-**f**) in 10-12 h with high yield (74-90%). Aldehydes possessing activated aromatic (**2g**, entry 6) and conjugated residue (**2h**, entry 7) smoothly produced the desired products with high yield (79-90%). Aldehydes armed with phenolic -OH (entries 8, 9), carboxylic acid (**2k**, entry 10), heterocycles (entries 11, 12), sterically hindered (entry 13) and metal-containing aromatic residue (entry 14) were well-tolerated. Sensitive substrates (**2p**-**2t**) were also successfully converted to the corresponding amide derivatives (**4p**- **4t**, entries 15-19) in excellent to good yield (70-95%). Late-stage amidation of **2u** provided the desired amide (**4u**) in 70% yield (entry 20). The utility of the sustainable strategy was validated using sugar aldehydes as aliphatic substrates, which efficiently furnished desired optically pure primary amides (**4v** and **4w**) in good yield (72%, 71%, entries 21, 22).

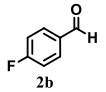
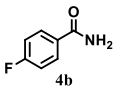
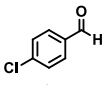
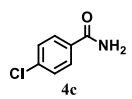
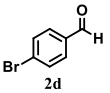
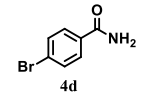
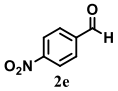
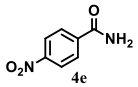
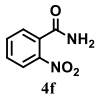
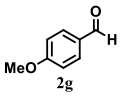
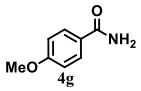
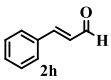
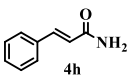
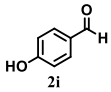
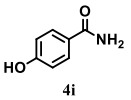
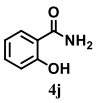
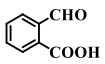
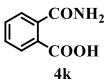
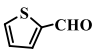
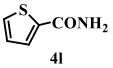
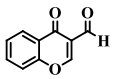
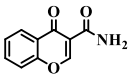
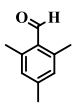
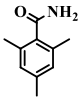
Having established the amidation catalysis, we moved on to explore oxidative scission of alkenes with the catalyst (Ar-tpy)$Ru^{II}(ACN)_3$ to furnish corresponding aldehydes and ketones.[25] We decided to screen the catalyst **1a**-**c** for the catalytic oxidative scission reactions under mild conditions in water, which will be especially useful for the late-functionalization and synthesis of labile sugar-based compounds. Unfortunately, the transformation of styrene (**5a**) to benzaldehyde (**6a**, Table 2) in the presence of catalyst **1a** was not successful in water (entry 1, Table 2) at ambient temperature. The main difficulty we faced during the development of oxidative scission of olefin was that the extremely low solubility of the highly hydrophobic olefin substrates, such as olefins or alkynes in water. Thus, we

started looking for a suitable phase-transfer catalyst (PTC),[26] surfactant[27]or β-cyclodextrin[28] to build up corresponding a phase-transfer protocol or hydrophobic nanoreactor for smooth running of the oxidative cleavage of styrene (**2a**) in water to aldehyde (**6a**). The results of catalyst screening (**1a-c)** revealed that the tetrabutylammonium iodide is a good PTC for the reaction using $NaIO_4$ as oxidant.

Scheme 2. Synthesized Primary Amides



2 (1 mmol) **3a** (1.1 mmol) **4**

entry	aldehyde (2)	amide (4)	time (h)	yield (%)
1	 2b	 4b	12	77
2	 2c	 4c	12	90
3	 2d	 4d	12	83
4	 2e	 4e	10	74
5	 2f	 4f	11	76
6	 2g	 4g	12	90
7	 2h	 4h	12	79
8	 2i	 4i	11	85
9	 2j	 4j	12	75
10	 2k	 4k	10	70
11	 2l	 4l	11	71
12	 2m	 4m	12	80
13	 2n	 4n	11	56
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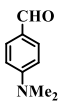
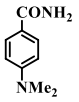
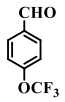
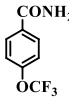
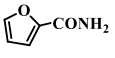
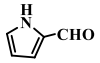
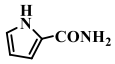
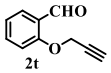
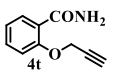
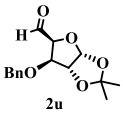
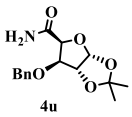
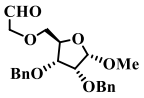
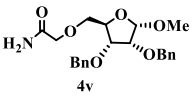
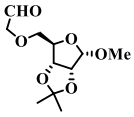
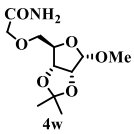
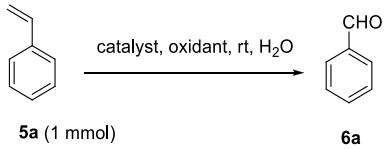
15	 2p	 4p	12	95

Continued

entry	aldehyde (2)	amide (4)	time (h)	yield (%)
16	 2q	 4q	12	90
17	 2r	 4r	12	77
18	 2s	 4s	12	74
19	 2t	 4t	12	70
20	 2u	 4u	12	70
21	 2v	 4v	11	72
22	 2w	 4w	11	71

The catalyst **1c** (entry 4, 80%) is the best one to afford **6a** with respect to **1a** (entry 2, 70%) or **1b** (entry 3, 69%) in 12 h at room temperature. The counter anion bromide, chloride, basic –OH and acidic -HSO_4 (entries 5-8) as well as less lipophilic counter cation Et_4N^+ (entry 9) of the PTC, were employed without any significant improvement (45-79%). Next, we started optimizing the reaction through changing the concentration of TBAI (entries 10, 11), which indicate 10 mol% of TBAI (entry 4) was the best to produce the desired product (**6a**, Table 2). *β*-CD (10 mol%), CTAB (10 mol%), SDS (10 mol%, entries 12-14) were all inferior to TBAI. No product was obtained using only $NAIO_4$ without any catalyst (entry 15), which proved the important role of the catalyst in the oxo-scissoring of the olefin. Next, we screened an array of oxidants (entries 16-21) among which only $PhI(OAc)_2$ (entry 16) and oxone (entry 17) furnished the desired product in diminished yield (46-60%). Rest of the oxidants (entries 18-21) failed to furnish the product. After screening several experiments, we found the best result for styrene (**5a**) to benzaldehyde (**6a**) with 80% yield using catalyst **1c** (1.12 mol%), sacrificial oxidant $NaIO_4$ (2 mmol) in the presence of phase transfer catalysts (PTC) tetrabutylammonium iodide (10 mol%) in water at ambient temperature (entry 4).

Table 2. Optimization Data of Oxo-scissoring of Alkenes[a]



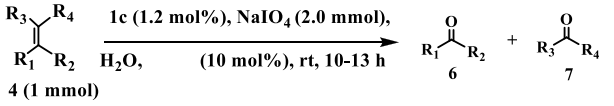
5a (1 mmol) **6a**

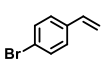
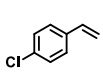
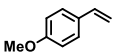
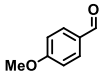
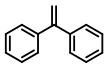
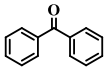
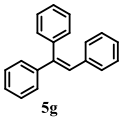
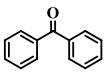
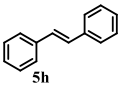
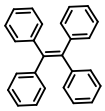
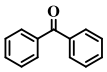
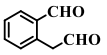
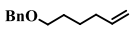
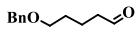
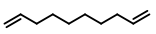
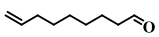
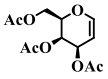
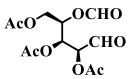
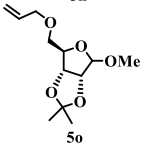
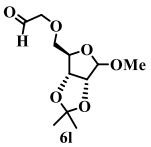
entry	PTC (mol %)	oxidant	catalyst	catalyst (mol%)	time (h)	yield (%)
1	-	$NaIO_4$	**1a**	1.0	12	-
2	TBAI (10)	$NaIO_4$	**1a**	1.0	12	70
3	TBAI (10)	$NaIO_4$	**1b**	1.0	12	69
4	**TBAI (10)**	**$NaIO_4$**	**1c**	**1.0**	**12**	**80**
5	TBAB (10)	$NaIO_4$	**1c**	1.0	12	77
6	TBAC (10)	$NaIO_4$	**1c**	1.0	12	72
7	TMAOH (10)	$NaIO_4$	**1c**	1.0	12	45
8	TBAHS (10)	$NaIO_4$	**1c**	1.0	12	49
9	TEAB (10)	$NaIO_4$	**1c**	1.0	12	79
10	TBAI (15)	$NaIO_4$	**1c**	1.0	12	79
11	TBAI (5)	$NaIO_4$	**1c**	1.0	12	51
12	β-CD (10)	$NaIO_4$	**1c**	1.0	12	75
13	CTAB (10)	$NaIO_4$	**1c**	1.0	12	67
14	SDS (10)	$NaIO_4$	**1c**	1.0	12	60
15	-	$NaIO_4$	-	-	12	-
16	TBAI (10)	$PhI(OAc)_2$	**1c**	1.0	12	60
17	TBAI (10)	Oxone	**1c**	1.0	12	46
18	TBAI (10)	TBHP	**1c**	1.0	12	-
19	TBAI (10)	H_2O_2	**1c**	1.0	12	-
20	TBAI (10)	O_2	**1c**	1.0	12	-
21	TBAI (10)	$K_2S_2O_8$	**1c**	1.0	12	-

[a]**5a** (1 mmol), $NaIO_4$ (2.0 mmol), Catalyst (1.12 mol%), Water (5 mL), 12 h.

We proceeded to examine the substrate scope of the reaction under the optimized conditions. The experimental data (Scheme 3) shows that the reaction is pretty general for terminal olefins possessing electron withdrawing and donating aromatic residues which afforded **6b**-**d** in high yield (80-85%, entries 2-4). 1,1´- Disubstituted (entries 5, 6), 1,2-disubstituted (entry 8), 1,1´,2-trisubstituted (entry 7), and 1,1´,2,2´ tetrasubstituted (entry 9) olefins were cleaved into respective ketones (**6e**-**f**) and/or aldehydes (**6a**) with excellent yield (80-90%). The cyclic substrates such as **5j** and **5k** were also took part in the reaction providing corresponding desired product **6g** and **6h** in 77% and 80% yield, respectively (entries 10, 11). Successful scission of

Scheme 3. Substrate Scope of Alkene-Scission Catalysis

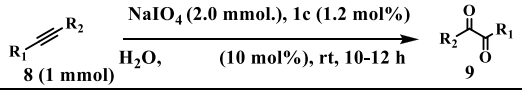


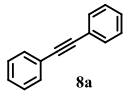
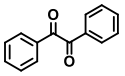
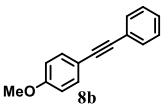
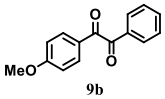
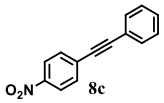
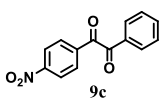
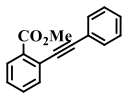
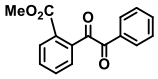
Entry	Olefin (5)	Product (6)	Time (h)	6, Yield (%)
1	 5a	 6a	10	80
2	 5b	 6b	10	81
3	 5c	 6c	10	83
4	 5d	 6d	12	76
5	 5e	 6e	12	77
6	 5f	 6f	13	85
7	 5g	 6f	12	80*
8	 5h	 6a	10	88
9	 5i	 6f	14	70
10	 5j	 6g	12	77
11	 5k	 6h	10	80
12	 5l	 6i	12	76
13	 5m	 6j	10	70
14	 5n	 6k	10	75
15	 5o	 6l	10	79

aliphatic (entries 12, 13) and sugar derivatives (entries 14, 15) to corresponding functionalized aldehyde (**6i**), terminal olefin possessing aldehyde (**6j**), labile optically pure aldehyde formate (**6k**) and ribose derivative (**6l**) produced the generality, robustness, and usefulness of the catalytic strategy under mild conditions.

Satisfied with the above results, we successfully established the oxidative transformation of an alkyne partner, diphenylacetylene (**8a**, entry 1, Scheme 4) to produce benzil (**9a**) in excellent yield (89%) under the same reaction conditions. Unsymmetrical aromatic alkynes carrying an electron donating (**8b**, entry 2) or withdrawing group (**8c**, entry 3) furnished 1,2-diketones (**9b**, **9c**) in excellent yield (93, 94%), respectively.

Scheme 4. Experimental Data of Oxygenation to Alkynes



entry	alkyne (8)	product (9)	time (h)	yield (%)
1	 8a	 9a	12	89
2	 8b	 9b	12	93
3	 8c	 9c	12	88
4	 8d	 9d	12	85
5	8e	9e	10	68
6	8f	9f	11	97
7	8g	9g	10	82
8	8h	9h	10	77
9	8i	9i	12	73
10	8j	9j	13	69

Alkyne-containing labile ester functionality (**8d**) was converted to the corresponding diketo derivative (**9d**) in 85% yield (entry 4). Gratifyingly, 1,4-diphenylbuta-1,3-diyne (**8e**, entry 5) selectively installed 1,2-diketone to one alkyne moiety to achieve valuable 1,4-diphenyl-1,2-diketobutyne (**9e**) in 10 h. Aliphatic substituted alkyne (**8f**) was also smoothly transformed into the desired 1,2-diketone (**9f**), in excellent yield (97%, entry 6). Exploration of reaction with terminal alkynes (**8g**, **h**, entries 7, 8) expectantly afforded benzoic acids (**9g**, **h**) in 10 h. The usefulness of the developed methodology was showcased by using ribose derivatives (**8i** and **8j**, entries 9, 10), which furnished the corresponding acid (**9i**) and diketo derivative (**9j**) in excellent yield (73 and 69%, respectively).

The developed procedure is extremely efficient as the synthesized catalyst (**1c**) was recovered and reused (Figure 1). The catalyst was recycled (Experimental Section) and reused 5 times successively during amidation of **2a** with some variation in the yield. Similarly, the oxo-scissoring of alkene **5a** were also performed without much loss of catalytic activity.

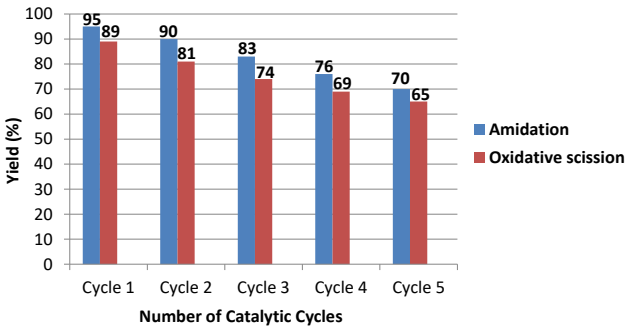
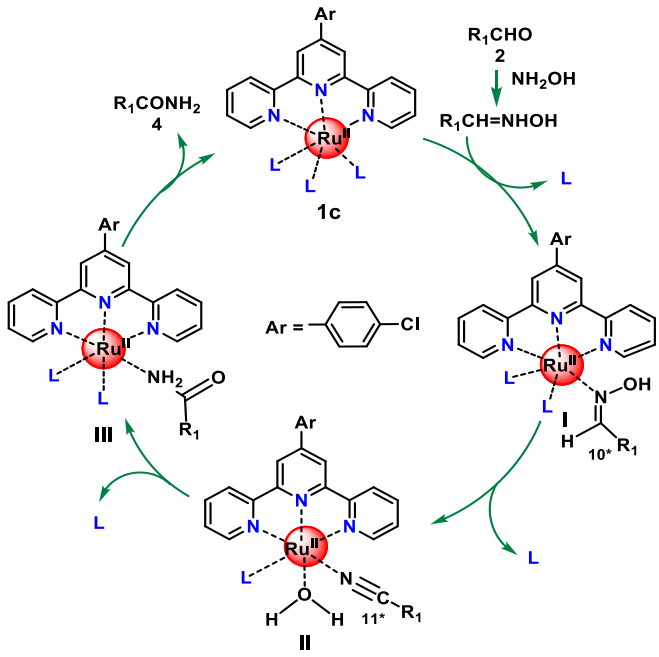


Figure 1. Catalytic Efficiency of the Recovered Catalyst

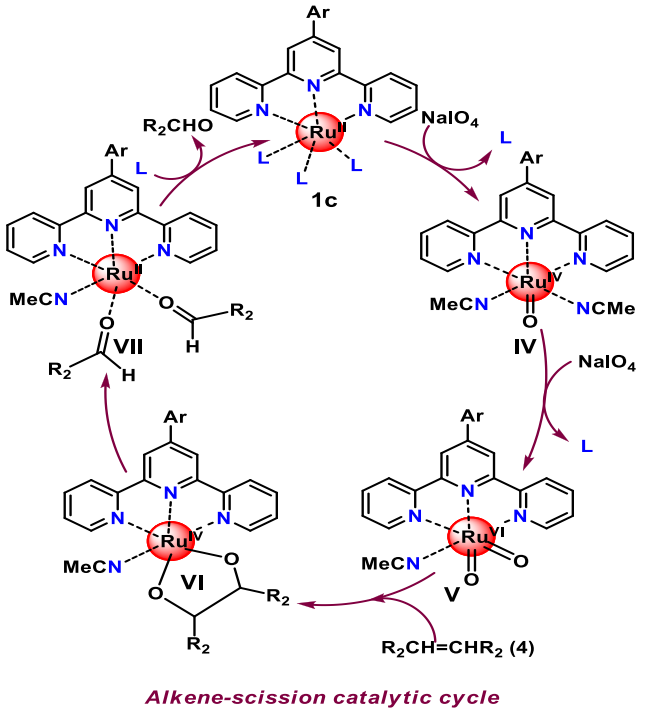
The (Ar-tpy)$Ru^{II}(ACN)_3$-catalyzed synthesis of amides from aldehydes is expected to proceed through dehydration and hydration mechanism (Scheme 5).[29] Herein, the amidation catalytic cycle (Scheme 5) is proposed through the formation of an oxime-**1c** complex (**I**), which is generated from the aldehyde (**2**), hydroxylamine hydrochloride (**3a**), sodium acetate and the catalyst (**1c**). The aldoxime undergoes Ru(II)-guided dehydration to yield the corresponding nitrile (**II**), which was confirmed by TLC monitoring. The coordinated water and nitrile molecule is expected to pass through a Ru^{II}-tuned hydration process (**III**). Moreover, conducting the reaction in non-aqueous media (EDC) furnished only the corresponding nitrile intermediate, which was isolated and characterized. The active catalyst (**1c**) is regenerated for the next cycle through the release of the product (**4**) and ligation. However, Wiliams *et al.* reported[29] a mechanism in which an oxime attacks the coordinated nitrile, instead of water. This pathway seems less probable for our case as the reaction also proceeds with NH_2OMe reagent (Table 1, entry 22), and the amidation reaction was arrested in the absence of water.

Progress of oxidative scission of alkene is presumed to proceed through oxidation of Ru(II) to Ru(VI) (**IV** and **V**, Scheme 6) in the presence of

Scheme 5. Proposed Catalytic Cycle of Amidation Reaction



$NaIO_4$, complexation with an olefin and formation of dioxo-Ru(IV)[25] cycloadduct (**VI**) by a concerted [3+2] cycloaddition with olefin (**5**). The Ru^{IV}-pinacol putative intermediate undergoes C-C bond cleavage with reduction of Ru(IV) to Ru(II) to achieve the desired product (**6**) surrounded intermediate **VII**. The release of the aldehyde (**4**) or ketone and ligation of MeCN regenerate the active catalyst **1c** for the next cycle. The reaction was run in H_2O^{18} medium and the mass spectrometry of the ongoing reaction was performed in a regular interval. It revealed that O^{18}-incorporation was minimal (Supporting Information). This labeling experiment indicates that the source of oxygen in the product is likely to be from $NaIO_4$.



Scheme 6. Proposed Mechanism for Olefin-Scission Catalysis

■ CONCLUSION

In conclusion, we have demonstrated synthesis of a new water-soluble multifaceted catalyst, (4-Cl-C_6H_4-tpy)$Ru^{II}(ACN)_3$ and its unprecedented catalytic activity with low catalyst loading for direct amidation of C-H with NH_2OR (R = H, Me) to obtain primary amides in nonconventional aqueous media with excellent yield. Diverse reactivity of the catalyst was established through development of two general methods for oxidative cleavage of alkenes to aldehydes and/or ketones, and selective oxygen installation to alkynes to achieve 1,2-diketones or acids in the water at ambient temperature. This strategy may be utilized as a unique tool for late-stage oxygen transfer process in the academia and industries. We believe that the research delineated herein opens up a new window for design and synthesis of novel multifaceted catalysts, developing green and sustainable chemistry and their outstanding application to catalyze the valuable organic transformation of academic, commercial and industrial interests.

■ EXPERIMENTAL SECTION

General Information. All reagents were purchased from commercial suppliers and used without further purification, unless otherwise

specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. CH_2Cl_2 was dried by distillation over P_2O_5. Petroleum ether used in our experiments was in the boiling range of 60-80 °C. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Reported melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra (Bruker Advance 300 or Bruker Advance 400) were recorded at ambient temperature using either 300 MHz spectrometers (300 MHz for ^{1}H and 75 MHz for ^{13}C) or 400 MHz spectrometers (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shift is reported in ppm and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) in thin film. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadruple mass spectrophotometer (Bruker). The optical rotation of the chiral compounds was measured in a polarimeter using standard 10 cm quartz cell in the sodium-D lamp (589 nm) at ambient temperature. X-RAY crystallographic data was taken in a CCD diffractometer.

General Procedure for Catalyst (1a-c) Preparation: (Ar-tpy)$RuCl_3$ were prepared according to reported literature procedure[11e]. To a clean, dry, aluminum foil wrapped round bottom flask (Ar-tpy)$RuCl_3$ (1.0 eqv.) and $AgNO_3$ (3.0 equiv.) were added under argon atmosphere. Dry MeOH and dry acetonitrile (1:1, v/v, 0.002 M) were introduced and argon was bubbled in the solution for 1 hour. After that, the solution was heated at reflux for 24 h under Ar. The solution was filtered through a sintered glass funnel and the filtrate was concentrated under reduced pressure to furnish the crude product. The crude product was purified by column chromatography (60-120 mesh silica gel) using ACN: water: saturated solution of KNO_3 (30:1:1) to get pure product.

General Procedure for Amidation: Hydroxylamine hydrochloride (**3a**, 1 mmol, 69.49 mg), sodium acetate (1.15 mmol, 94.3 mg) and **1c** (1.2 mol%, 9 mg) was stirred in water (5 mL), and 4–methyl benzaldehyde (**2a**, 1 mmol, 120 mg) was added dropwise to it. The solution was heated at 100 °C (bath temperature) under an argon atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction, the post-reaction mixture was filtered and washed with water. The crude amide was crystallized from ethanol to get the pure amide **4a** in 95% (128 mg, 0.95 mmol) yield. All primary amides were synthesized by the same procedure and characterized (**4a-q**) by recording NMR, IR, ESI-MS and melting points (solid products), and also comparing the reported data of the known compounds.

General Procedure for Oxo-scissoring of Alkenes: Styrene (1 mmol, 104.15 mg, 0.11 mL), $NaIO_4$ (2 mmol, 426 mg), TBAI (10 mol%,4 mg) and distilled water (1 mL) were sequentially added to a solution of the catalyst (**1c**, 1 mol%, 8 mg) under an inert atmosphere. The mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, it was filtered in case of solid compounds or extracted by EtOAc (3 x 15 mL) in case of liquid compounds, dried over activated Na_2SO_4, and the solvent was evaporated under reduced pressure. The catalyst was recovered from water extract. The solid products were purified by crystallization. For oils, the residue obtained after evaporation was purified by column chromatography on silica (60–120 mesh), which yielded benzaldehyde (87%, 150 mg) as an oily compound. However, all solid products were filtered through a sintered glass funnel and crystallized in ethanol to get pure product. All products were synthesized by the same procedure

and characterized (**6a**-**k**) by recording NMR, IR, ESI-MS and melting points (solid products), and also comparing the reported data of the known compounds.

General Procedure for Oxygenation of Alkynes. All products (**9a**-**i**) were synthesized by the same procedure as described above and characterized by recording NMR, IR, ESI-MS and melting points (solid products), and also comparing the reported data of the known compounds.

Catalyst Recovery and Recycling. After the reaction is over the product was either filtered or extracted with ethyl acetate. Water was then removed and the residue was taken up in acetonitrile. The mixture was stirred for 1 hour and filtered. The solvent was removed under reduced pressure to obtain a solid which was dried under high vacuum before using it in the next catalytic reaction. This process was repeated four times (as depicted in Figure 1.) without any significant loss in catalytic activity.

Characterization Data of Synthesized Primary Amides (4)

*4-Methylbenzamide (***4a***)*[30]*:* Yield: 95% (128 mg, 0.95 mmol); Characteristics: light pink solid, M. P.: 162-164 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.74 (2H, d, *J*=8.1 Hz), 7.27 (2H, d, *J*=8.4 Hz), 6.16 (2H, broad singlet), 2.43 (3H, s).

*4-Fluorobenzamide (***4b***)*[31]: Yield: 77% (107 mg, 0.77 mmol); Characteristic: Brown solid, M.P.: 118-120 °C; ^{1}H-NMR (300 MHz, DMSO-D_6): δ 7.97 – 7.88 (2H, m), 7.39 – 7.22 (2H, m).

*4-Chlorobenzamide (***4c***)*[32]: Yield: 90% (140 mg, 0.90 mmol); Characteristic: Brown solid, M.P.: 173-175 °C; ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.75 (2H, d, *J*= 8.4 Hz), 7.43(2H, d, *J*= 8.4 Hz), 5.89 (2H, broad singlet).

4-Bromobenzamide (**4d**)[33]: Yield: 83% (166.0 mg, 0.83 mmol); Characteristic: White solid, M.P.: 191-194 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.68 (2H, d, *J*= 8.7 Hz), 7.60 (2H, d, *J*= 8.4 Hz), 6.04 (1H, br s), 5.73 (1H, broad singlet).

4-Nitrobenzamide (**4e**)[34]: Yield: 74% (123 mg, 0.74 mmol); Characteristic: yellow solid, M.P.: 198-202 °C; ^{1}H-NMR (300 MHz, DMSO-D_6): δ 7.45 (2H, d, *J*=8.7 Hz), 7.33(2H, *J*=8.7 Hz), 6.35 (2H, broad singlet).

2-Nitrobenzamide (**4f**)[35]: Yield: 76% (126 mg, 0.76 mmol); Characteristic: Brown solid, M.P.: 178-180 °C; ^{1}H-NMR (300 MHz, DMSO-D_6): δ 8.14 (1H, broad singlet), 7.987 (1H, d, *J*= 7.8 Hz), 7.77 – 7.60 (4H, m).

4-Methoxybenzamide (**4g**)[36]: Yield: 90% (136.0 mg, 0.90 mmol); Characteristic: Off white solid, M.P.: 163-166 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78 (2H, d, *J*= 8.7 Hz), 6.94 – 6.3 (2H, d, *J*= 8.7 Hz), 5.80 (2H, broad singlet), 3.86 (3H, s).

Cinnamamide (**4h**)[37]: Yield: 79% (116 mg, 0.79 mmol); Characteristic: Off white solid, M.P.: 149-151 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.65 (1H, d, *J* = 15.6 Hz), 7.53 – 7.49 (2H, m), 7.38 – 7.36 (3H, m), 6.50 (1H, d, *J* = 15.9), 5.68 (2H, broad singlet).

4-Hydroxybenzamide (**4i**)[34]: Yield: 85% (116 mg, 0.85 mmol); Characteristic: Off white solid, M.P.: 161-163 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.39 (1H, s), 7.66- 7.61 (2H, m), 6.78-6.75 (3H, m), 5.90 (1H, broad singlet).

2-Hydroxybenzamide (**4j**)[14b]: Yield: 75% (103 mg, 0.75mmol); Characteristics: Pinkish solid, M.P.: 142-145 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 12.16 (1H, broad singlet), 7.48 – 7.36 (2H, m), 6.99 (1H, d, *J*=8.4 Hz), 6.85 (1H, t, *J*=7.8 Hz), 6.10 (2H, broad singlet).

2-Carbamoylbenzoic acid (**4k**)[38]: Yield: 70% (116 mg, 0.70 mmol); Characteristics: Pinkish solid; M.P.: 142-145 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.85 (1H, d, *J* = 7.5 Hz), 7.74 – 7.56 (3H, m), 6.76 (2H, broad singlet).

Thiophene-2-carboxamide (**4l**)[39]: Yield: 71% (90 mg, 0.71mmol); Characteristic: Off white solid, M.P.: 182-184 °C; ^{1}H-NMR (300 MHz, DMSO-D_6): δ 7.95 (1H, broad singlet), 7.72 (2H, d, *J*= 4.5 Hz), 7.37 (1H, broad singlet), 7.10 (1H, t, *J*= 4.2 Hz).

4-Oxo-4H-chromene-3-arboxamide (**4m**)[40]: Yield: 80% (151 mg, 0.80 mmol); Characteristic: Off white solid; M.P.: 166- 169 °C; ^{1}H-NMR (300 MHz, DMSO-D_6): δ 9.97 (1H, s), 9.49 (2H, broad singlet), 7.91 (1H, d, *J*=7.8 Hz), 7.64 – 7.59 (1H, m), 7.35 – 7.28 (2H, m).

2,4,6-Trimethylbenzamide (**4n**)[41]: Yield: 56% (91 mg, 0.56 mmol);Characteristic: Dark grey solid, M. P.: 148- 149 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.84 (2H, s), 6.05 (1H, broad singlet), 5.65 (1H, broad singlet), 2.36 (3H, s), 2.16 (6H, s).

Ferrocenecarboxamide (**4o**)[42]: Yield: 75% (194 mg, 0.75 mmol); Characteristic: Brown crystals; M.P.: 169-172 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.65 (2H, broad singlet), 4.69 (2H, s), 4.39 (2H, s), 4.24 (5H, s).

4-(dimethylamino)benzamide (**4p**)[33]: Yield: 95% (156 mg, 0.95 mmol); Characteristic: grey solid; M.P.: 209-210 °C; 1H-NMR (400 MHz, $CDCl_3$): δ 7.71 (2H, d, *J*= 8.8 Hz), 6.67 (2H, d, *J*= 9.2 Hz), 6.12 (6H, s), 5.65 (2H, broad singlet), 3.04 (6H, s).

4-(trifluoromethoxy)benzamide (**4q**)[14b]: Yield: 90% (185 mg, 0.90 mmol); Characteristic: White solid; M.P.: 152-154 °C; 1H-NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.85 (2H, m), 7.30 – 7.26 (2H,m), 6.02 (2H, broad singlet).

furan-2-carboxamide (**4r**)[14a]: Yield: 77% (86 mg, 0.77 mmol); Characteristic: light brown solid; M.P.: 139-141 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48 (1H, s), 7.17 (1H, d, J= 3.2 Hz), 6.53-6.52 (1H, m), 6.31 (1H, broad singlet), 6.05 (1H, broad singlet).

1H-pyrrole-2-carboxamide (**4s**)[14e]: Yield: 74% (81 mg, 0.74 mmol); Characteristic: brown solid; M.P.: 171-173 °C; 1H-NMR (400 MHz, $CDCl_3$): δ 9.48 (1H, broad singlet), 6.96 (1H, s), 6.62 (1H, s), 6.27-6.23 (1H, m), 5.60 (2H, broad singlet).

2-(prop-2-ynyloxy)benzamide (**4t**)[21a]: Yield: 70% (123 mg, 0.7 mmol); Characteristic: white solid;^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.23-8.21 (1H, m), 7.63 (1H, brs), 7.51- 7.46 (1H, m), 7.15-7.11 (1H, m), 7.07 (1H, d, *J*= 8.4 Hz), 6.24 (1H, broad singlet), 4.85-4.84 (2H, m), 2.61 (1H, s); ^{13}C{1H}-NMR (100 MHz, $CDCl_3$): 166.7, 155.8, 133.2, 132.8, 122.2, 121.6, 112.8, 77.4, 76.8, 56.8.

(3aR,5S,6R,6aR)-(-)-6-(Benzyloxy)-2,2-dimethyltetrahydro-furo[2,3-d][1,3]dioxole-5-carboxamide (**4u**):
Yield: 70% (205 mg, 0.70 mmol); Purified by column chromatography using 80% ethyl acetate in petroleum ether (Rf:0.6).Characteristic: light brown crystals; M. P.: 150 °C (decomposition); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.36- 7.28 (5H, m), 6.60 (1H, broad singlet), 6.17 (1H, broad singlet), 6.01 (1H, d, *J*=3.3 Hz), 4.74 (1H, d, *J*=3.3 Hz) 4.58- 4.64 (3H, m), 4.35 (1H, d, *J*= 3.3 Hz), 1.49 (3H, s), 1.32 (3H, s); ^{13}C{1H}-NMR (75MHz, $CDCl_3$): δ 170.7, 137.1, 128.4, 127.9, 127.7, 112.6, 105.5, 82.47, 82.40, 80.97, 73.13, 26.92, 26.30; FT-IR (film)(Solvent: Acetonitrile) υ_{max}(cm^{-1}): 3415, 3216, 2936, 1641, 1380, 1217, 1085, 1025, 755. HRMS (ESI-TOF) m/z: for $[M+ Na]^+$: Calcd for $C_{15}H_{19}NO_5Na$ 316.1161, Found 316.1144. $[\alpha]_D^{20}$-33.7[c 1.0, DCM].

2-(((2R,5R)-3,4-Bis(benzyloxy)-5-methoxytetrahydrofuran-2-yl)methoxy)acetamide (**4v**): Yield: 72% (289 mg, 0.72 mmol); Purified by column chromatography using 90% ethyl acetate in petroleum ether (Rf: 0.31). Characteristic: light yellow oil,1H-NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.29 (10H, m), 6.89 (1H , brs), 6.53 (1H, brs), 4.90 (1H, s), 4.69- 4.58 (3H, m), 4.41 (1H, d, *J*= 11.6 Hz), 4.28- 4.26 (1H, m), 4.03-3.99 (1H, m), 3.93 (2H, d, *J*= 0.8 Hz), 3.87 (1H, d, *J*= 4.8 Hz), 3.67 (1H, dd, J_1= 2.8 Hz, J_2= 10.8 Hz), 3.49 (1H, dd, J_1= 5 Hz, J_2= 10.4 Hz), 3.32 (3H, S); ^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ 173.7, 137.6, 137.5, 128.5, 128.1, 128.0, 127.9, 106.8, 80.1, 79.4, 77.6, 72.5, 72.4, 72.2, 70.2, 55.4.; FT-IR (Neat) υ_{max}(cm^{-1}): 3459, 3340, 2922, 2855, 1688, 1450, 1365, 1262, 1135, 1058, 938, 743, 709, 607; HRMS (ESI-TOF) m/z: for $[M+ Na]^+$: Calcd for $C_{22}H_{27}NO_6Na$ 424.1736; Found 424.1735. $[\alpha]_D^{20}$ +23.0[c 1.25, CH_2Cl_2].

2-(((3aR,4R,6S,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methoxy)acetamide (**4w**): Yield: 71% (186 mg, 0.71 mmol); Purified by column chromatography using 80% ethyl acetate in petroleum ether (Rf:0.4). Characteristic: light yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.06 (1H , broad singlet), 5.81 (1H, broad singlet), 5.00 (1H, s), 4.70 (1H, d, *J*= 6 Hz), 4.59 (1H, d, *J*= 6 Hz), 4.38 (1H, t, *J*= 5.2 Hz), 4.03 (1H, d, *J*= 15.6 Hz), 3.93 (1H, d, *J*= 15.6 Hz), 3.61-3.59 (2H, m), 3.35 (3H, s), 1.49 (3H, s), 1.33 (3H, s) ; ^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ 172.4, 112.6, 110.3, 85.5, 85.2, 81.8, 72.6, 70.4, 55.2, 26.5, 24.9. FT-IR (Neat) υ_{max}(cm^{-1}): 3463, 3320, 2900, 2855, 1688, 1450, 1365, 1262, 1135; HRMS (ESI-TOF) m/z: for $[M+ Na]^+$: Calcd for $C_{11}H_{19}NO_6Na$ 284.1110; Found 284.1109. $[\alpha]_D^{20}$ -40.8 [c 0.25, CH_2Cl_2].

Characterization Data of Aldehydes or Ketones (6).

Benzaldehyde (**6a**)[43] from **5a**: Yield: 80% (85 mg, 0.80 mmol) (entry 1), 88% (187 mg, 1.76 mmol) (entry 8); Characteristic: colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.76 (1H, s), 7.62 – 7.59 (2H, m), 7.35-7.32 (1H, m), 7.26-7.24 (2H, m).

4-Bromobenzaldehyde (**6b**)[44]: Yield: 81% (149 mg, 0.81 mmol); Characteristic: White solid; M.P.: 57-59 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): 9.96 (1H, s), 7.75 – 7.65 (4H, m).

4-Chlorobenzaldehyde (**6c**)[45]: Yield: 83% (117 mg, 0.83 mmol); Characteristic: Low melting solid; M.P.: 48-50 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.92 (1H, s), 7.78 – 7.74 (2H, m), 7.46 – 7.42 (2H,m).

4-Methoxybenzldehyde (**6d**)[46]: Yield: 76% (103 mg, 0.76 mmol); Characteristic: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.78 (1H, s), 7.75 – 7.72 (2H, m), 6.91 – 6.89 (2H, m), 3.78 (3H, s).

Acetophenone (**6e**)[47]: Yield: 77% (93 mg, 0.77 mmol); Characteristic: Colourless liquid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.98 – 7.95 (2H, m), 7.57 – 7.46 (3H, m), 2.61 (3H, s).

Benzophenone (**6f**)[48] from **5f**: Yield: 85% (156 mg, 0.85 mmol) (entry 6), 80 % (146 mg, 0.80 mmol) (entry 7), 70% (255 mg, 1.4 mmol) (entry 9); Characteristic: Colourless solid; M.P.: 48-50 °C; ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.82 – 7.79 (2H, m), 7.61 – 7.55 (1H, m), 7.49 – 7.44 (2H, m); ^{13}C{1H}-NMR (75MHz, $CDCl_3$): δ 196.5, 137.4, 132.3, 129.9, 128.1.

2-(Formylmethyl)benzaldehyde (**6g**)[49]: Yield: 77% (114 mg, 0.77 mmol); Characteristic: Oil;^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.04 (1H, s), 9.79 (1H, s), 7.85- 7.83 (1H, m), 7.61- 7.52 (2H, m), 7.27-7.24 (2H, m), 4.15 (2H, s); ^{13}C{1H}-NMR (100 MHz, CDCl3): 198.4, 193.4, 135.6, 134.1, 134.0, 132.8, 129.5, 128.2, 48.3.

Biphenyl-2,-2'-dicarbaldehyde (6**h**)[48]:Yield: 80 % (168 mg, 0.80 mmol); Characteristic: White solid; M.P.: 62-65 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.84 (2H, s), 8.08 – 8.07 (2H, d, *J*= 7.6 Hz), 7.69 - 7.66 (2H, m), 7.62 - 7.58 (2H, m), 7.37 – 7.35 (2H, d, *J*= 7.6 Hz).

5-(Benzyloxy)pentanal (**6i**)[50]: Yield: 76% (146 mg, 0.76 mmol) Characteristic: Light yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$): 9.76 (1H, t, *J*=1.5 Hz), 7.36 – 7.29 (5H, m), 4.50 (2H, s), 3.52 – 3.48 (2H, m), 2.49 – 2.44 (2H, m), 1.78 – 1.66 (4H, m).

Non-8-enal (**6j**)[51]: Yield: 70% (98 mg, 0.70 mmol); Characteristic: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.77 (1H, s), 5.76-5.69 (1H, m), 4.94- 4.85 (2H, m), 2.45 – 2.39 (2H, m), 2.05–2.00 (2H, t, *J*= 7 Hz), 1.65 – 1.51 (2H, m), 0.92 – 0.83 (6H, m); ^{13}C{1H}-NMR (75MHz, $CDCl_3$): δ 202.5, 138.7, 114.2, 43.7, 33.5, 31.4, 28.8, 28.6, 28.5.

(2R,3S,4S)-2-(Formyloxy)-5-oxopentane-1,3,4-triyltriacetate (**6k**)[48]: Yield: 75% (228 mg, 0.75 mmol); Characteristic: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.39 (1H, s), 7.98 (1H, s), 5.65 – 5.62 (1H, m), 5.39-5.29 (2H, m), 4.30-4.02 (2H, m), 2.14 (3H, s), 2.1- 1.97 (6H, s). ^{13}C{1H}-NMR (75 MHz, $CDCl_3$): 193.7, 170.3, 169.6, 169.4, 159.1, 75.6, 67.6, 66.9, 61.2, 60.2, 20.3, 20.2, 20.0.

2-(((3aR,4R,6R,6aR)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methoxy)acetaldehyde (**6l**): Yield: 79% (195 mg, 0.79 mmol); Purified by column chromatography using 50% ethyl acetate in petroleum ether (R_f:0.57). Characteristic: light yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.69 (1H, s), 5.27 (1H , s), 4.94 (1H, s), 4.69 (1H, d, *J*= 4.4 Hz), 4.55 (1H, d, *J*= 4.4 Hz), 4.33 (1H, m), 4.09 (2H, s), 3.56 (2H, m), 3.30 (3H, s), 1.45 (3H, s), 1.29 (3H, s); α:β=4:1;^{13}C{1H}-NMR (100MHz, $CDCl_3$): δ200.6, 112.8, 109.6, 85.3, 85.1, 82.2, 76.7, 72.9, 55.2, 26.7, 25.2; FT-IR (Neat) υ_{max}(cm^{-1}): 3450, 2940, 1739, 1475, 1381, 1211, 1110, 853; HRMS (ESI-TOF) m/z: for $[M+ Na]^+$: Calcd for $C_{11}H_{18}NaO_6$ 269.1001, Found 269.1001. $[\alpha]_D^{20}$-48.5[c 0.75, CH_2Cl_2].

Characterization Data of the Synthesized Alkynes (8)

1-Methoxy-4-(phenylethynyl)benzene (**8b**)[52]: Yield: 85% (177.0 mg, 0.85 mmol); Characteristic: white solid; M. P.: 70-73 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52 – 7.45 (4H, m), 7.35 – 7.31 (3H, m), 6.89 – 6.85 (2H, d, *J* = 8.4 Hz), 3.82 (3H, s).

1-Nitro-4-(phenylethynyl)benzene (**8c**)[53]: Yield: 72% (161 mg, 0.72mmol); Characteristic: Yellowish solid; M. P.: 72-75 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.25 – 8.20 (2H, dt, J_1 = 9 Hz, J_2 = 2.1 Hz), 7.69 – 7.65 (2H, dt, J_1 = 9 Hz, J_2 = 2.1 Hz), 7.58 – 7.53 (2H, m), 7.41 – 7.37 (3H, m).

1,4-Diphenylbuta-1,3-diyne (**8e**)[54]: Yield: 83% (168 mg, 0.83mmol); Characteristic: Colorless solid; M.P.: 85-87 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.52 (2H, m), 7.40 – 7.31 (3H, m).

Characterization Data of the 1,2-Dikitones or Acids (9).

Benzil (**9a**)[48]: Yield: 89% (187 mg, 0.89 mmol); Characteristic: Yellow solid, M.P.: 94-96 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.98 – 7.95 (2H, m), 7.68 – 7.62 (1H, m), 7.53 – 7.48 (2H, m); ^{13}C{1H}-NMR (75 MHz, $CDCl_3$): δ 194.5, 134.8, 132.9, 129.8, 128.9.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (**9b**)[55]: Yield: 93% (223 mg, 0.93 mmol); Characteristic: Yellow solid, M. P.: 138-141 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.96 – 7.91 (4H, t, *J*= 7.8 Hz), 7.62 – 7.59 (1H, t, *J*= 7.5 Hz), 7.49 – 7.44 (2H, t, *J*= 7.8 Hz), 6.96 – 6.93 (2H, d, *J*= 9 Hz), 3.84 (3H, s); ^{13}C{1H}-NMR (75 MHz, $CDCl_3$): δ 194.8, 193.1, 164.9, 134.7, 133.2, 132.3, 129.8, 128.9, 126.0, 114.4, 55.8.

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (**9c**)[56]: Yield: 88% (225 mg, 0.88 mmol); Characteristic: Deep yellow solid, M.P.: 142-144 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.29 (2H, d, *J*=9 Hz), 8.12-8.09 (2H, m), 7.93 – 7.90 (2H, m), 7.67 – 7.62 (1H, m), 7.51 – 7.46 (2H, m); ^{13}C{1H}-NMR (75 MHz, $CDCl_3$):192.8, 192.1, 151.2, 137.3, 135.4, 132.4, 130.9, 130.0, 129.2, 124.1.

Methyl 2-(2-oxo-2-phenylacetyl)benzoate (**9d**)[57]: Yield: 85% (228 mg, 0.85 mmol); Characteristic: light yellow solid, M.P.: 118- 120 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.21- 8.19 (2H, m), 8.02 (1H, d, *J*= 8 Hz), 7.71- 7.69 (2H, m), 7.66 - 7.63 (2H, m), 7.56- 7.52 (2H, t, *J*= 7.6 Hz), 3.67 (3H, s); ^{13}C{1H}-NMR (100 MHz, $CDCl_3$): 193.7, 189.0, 166.9, 138.8, 133.9, 133.1, 133.0, 131.6, 130.8, 130.1, 129.7, 129.6, 128.5, 52.7.

1,4-Diphenylbut-3-yne-1,2-dione (**9e**)[58]: Yield: 68% (159 mg, 0.68 mmol); Characteristic: Oil;^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.01 (2H, d, *J*= 7.2 Hz), 7.62 – 7.57 (3H, m), 7.49 – 7.42 (3H, m), 7.36 – 7.32 (2H, t, *J*= 7.6 Hz); ^{13}C{1H}-NMR (100 MHz, $CDCl_3$): 188.4, 178.5, 135.0, 134.8, 133.6, 131.6, 130.4, 128.9, 128.7, 119.2, 99.1, 87.0.

1-Phenylpentane-1,2-dione (**9f**)[59]: Yield: 97% (171 mg, 0.97 mmol); Characteristic: Off white solid; M. P.: 139- 140 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.94 (2H, dt, *J*= 7.8 Hz, 2.1 Hz), 7.63 – 7.26 (3H, m), 2.85 – 2.80 (2H, t, *J*= 7.2 Hz), 1.77 – 1.65 (2H, sextet, *J*=7.5 Hz), 1.00 (3H, t); ^{13}C{1H}-NMR (75 MHz, $CDCl_3$): δ 203.3, 192.5, 134.5, 132.0, 130.1, 128.8, 40.6, 16.4, 13.6.

Benzoic acid (**9g**)[60]: Yield: 82% (100 mg, 0.82 mmol); Characteristic: Off white solid; M. P.: 121- 123 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.81 (1H, broad singlet), 8.15 – 8.13 (2H, m), 7.67 – 7.60 (1H, m), 7.52-7.47 (2H, m).

4-Methylbenzoic acid (**9h**)[61]: Yield: 77% (105 mg, 0.77 mmol); Characteristic: Off white solid, M. P.: 179-181 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* = 8.1 Hz), 7.27 (2H, d, *J* = 8.1 Hz), 2.41 (3H, s).

2-(((2R,3R,4R,5S)-3,4-Bis(benzyloxy)-5-methoxytetrahydrofuran-2-yl)methoxy)acetic acid (**9i**): Yield: 73% (294 mg, 0.73 mmol); Purified by column chromatography using 60% ethyl acetate in petroleum ether (R_f:0.16). Characteristic: light yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.28 (10H, m), 4.93 (1H , s), 4.69-4.59 (4H, m), 4.50 (1H, d, *J*= 12 Hz), 4.34 (1H, m), 4.22 (2H, d, *J*= 1.6 Hz), 4.05-4.02 (1H, m), 3.86 (1H, d, *J*= 4.4 Hz), 3.72- 3.69 (1H, m), 3.63-3.59 (1H, m), 3.36 (3H, s); ^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ 172.5, 137.5, 137.47, 128.43, 128.31, 128.26, 127.98, 127.91, 107.1, 80.2, 79.6, 77.7, 72.6, 72.4, 68.4, 55.7; FT-IR (Neat) υ_{max}(cm^{-1}): 3442, 2922, 2863, 1730, 1466, 1381, 1262, 1211, 1143, 1101, 1041, 938, 743, 692; HRMS (ESI-TOF) m/z: for $[M+ Na]^+$: Calcd for $C_{22}H_{26}O_7Na$ 425.1576; Found 425.1576. $[\alpha]_D^{20}$ +16.4 [c 2.1, CH_2Cl_2].

3-(((3aR,4R,6S,6aR)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methoxy)-1-phenylpropane-1,2-dione (**9j**): Yield: 69% (242 mg, 0.69 mmol); Purified by column chromatography using 15% ethyl acetate in petroleum ether (R_f:0.45). Characteristic: light yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.07 (1H, m), 7.65- 7.49 (1H , m), 7.47-7.44 (2H, m), 7.42- 7.29 (1H, m), 4.96 (1H, m), 4.83 (1H, d, *J*= 5.9 Hz), 4.71 (1H, d, *J*= 3.7 Hz), 4.61-4.54 (1H, m), 4.48-4.42 (2H, m), 3.71-3.60 (2H, m), 3.42 (3H, s), 3.33- 3.30 (2H, m), 1.47 (3H, s), 1.29 (3H, s) α,β mixture; ^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ 172.6, 171.3, 133.6, 130.1, 129.4, 128.9, 128.4, 112.5, 110.5, 85.5, 85.1, 81.8, 73.8, 72.7, 68.3, 55.5, 26.5, 24.9; FT-IR (Neat) υ_{max}(cm^{-1}): 3433, 2931, 1739, 1594, 1459, 1381, 1211, 1092, 871; HRMS (ESI-TOF) m/z: for $[M+ Na]^+$: Calcd for $C_{18}H_{22}O_7Na$ 373.1263; Found 373.1263. $[\alpha]_D^{20}$ -33.4 [c 0.85, CH_2Cl_2].

Characterization Data of the Synthesized Arylterpyridines

4'-(4-Chlorophenyl)-2,2´:6´,2´´-terpyridine[62]: Yield: 82% (281.9 mg, 0.82 mmol); Characteristic: White solid; M. P.: 168- 171 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.73 – 8.65 (6H, m), 7.91 – 7.83 (4H, m), 7.49 – 7.47 (2H, d, *J*= 8.4 Hz), 7.38 – 7.34 (2H, m).

4'-(4-Methylphenyl)-2,2´:6´,2´´-terpyridine[63]: Yield: 87% (281.4 mg, 0.87 mmol); Characteristic: White solid, M. P.: 169- 171 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.66 – 8.58 (6H, m), 7.82 – 7.74 (4H, m), 7.29 – 7.19 (4H, m), 2.35 (3H, s).

4'-(4-Methoxylphenyl)-2,2´:6´,2´´-terpyridine[64]: Yield: 90% (305.4 mg, 0.90 mmol); Characteristic: White solid, M. P. : 170-173 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.74– 8.66 (6H, m), 7.90 – 7.85 (4H, m), 7.37 – 7.33 (2H, m), 7.03 – 7.02 (2H, d, *J* = 8.4 Hz).

Characterization Data of the Catalysts (1a-c).

Triacetonitrile4'-(4-methoxypheny)-2,2':6',2''-terpyridineruthenium(II) nitrate (**1a**): Yield: 52% (357.6 mg, 0.52 mmol); Characteristic: Dark red solid, M.P.: decomposes at 204 °C; R_f: 0.35 (30: 1: 1, ACN, Water, Saturated solution of KNO_3); ^{1}H-NMR (300 MHz, D_2O): δ8.78 (2H,d, *J*=5.4 Hz), 8.24 (4H, m, *J*= 5.1 Hz, 8.1 Hz), 7.97 (2H, t, *J*= 7.8 Hz), 7.66 (2H, d, *J*= 8.7 Hz), 7.54 (2H, m, *J*= 5.1 Hz, 7.2 Hz), 6.87 (2H, d, *J*= 8.7 Hz), 3.55 (3H, s), 2.60 (3H, s), 1.81 (6H, s); ^{13}C{1H}-NMR (75MHz, D_2O): δ 160.8, 158.4, 154.3, 149.0, 138.9, 138.7, 128.8, 127.8, 127.0, 123.6, 123.3, 119.6, 114.8, 55.4, 3.4, 2.5; FT-IR υ_{max} (KBr, cm^{-1}): 3455.5, 3043, 2964.1, 2630.1, 2421.3, 2302, 2262.2, 2073.2, 1650.6, 1446.7, 1049.5, 922; HRMS (ESI-TOF) m/z: for $[M]^{2+}$: Calcd for $C_{28}H_{26}N_6ORu$ 282.0606; Found 282.0607.

Triacetonitrile4'-(4-methylphenyl)-2,2':6',2''-terpyridine ruthenium(II) nitrate (**1b**)[10e]: Yield: 63% (423.1 mg, 0.63 mmol); Characteristic: Red solid, M.P.: decomposes at 198 °C; R_f: 0.30 (30: 1: 1, ACN, Water, Saturated solution of KNO_3); ^{1}H-NMR (300MHz, D_2O): δ 8.86 (2H, d, *J*=5.4 Hz), 8.45 (2H, s), 8.33 (2H, d, *J* = 8.1 Hz), 8.05 (2H, t, *J* = 7.8 Hz), 7.73 (2H, d, *J* = 6.9 Hz), 7.63 (2H, t, *J* = 6 Hz), 7.34 (2H, d, *J*= 6.9 Hz), 2.69 (3H, s), 2.30 (3H, s), 1.89 (6H, s); ^{13}C{1H}-NMR (75MHz, D_2O): δ 158.6, 158.4, 154.3, 149.6, 141.3, 138.7, 130.1, 127.8, 127.2, 127.1, 123.7, 123.2, 120.1, 30.2, 3.4, 2.5; FT-IR υ_{max}(KBr, cm^{-1}): 3684.3, 3013, 2953.3, 2630.1, 2416.3, 2302, 2242.3, 2073.2, 1615.7, 1461.6, 1044, 919.6; HRMS (ESI-TOF) m/z: for $[M]^{2+}$: Calcd for $C_{28}H_{26}N_6Ru$ 274.0631; Found 274.0766.

Triacetonitrile4'-(4-chlorophenyl)-2,2':6',2''-terpyridine ruthenium(II) nitrate (**1c**): Yield: 54% (373.7 mg, 0.54 mmol); Characteristic: Orange red solid; M.P.: decomposes at 210 °C; R_f: 0.35 (30: 1: 1, ACN, Water, Saturated solution of KNO_3); ^{1}H-NMR (300 MHz, D_2O): δ 8.79 (2H, d, *J*=5.1 Hz), 8.38 (2H,s), 8.30 (2H, d, *J*=8.1 Hz), 8.03-7.96 (2H, m, *J*= 8.1, 6.3 Hz), 7.70 (2H, d, *J* = 8.8 Hz), 7.57 (2H, t, *J* = 6.6 Hz), 7.38 (2H, d, *J* = 8.4 Hz), 2.62 (3H, s), 1.82 (6H, s); ^{13}C{1H}-NMR (75 MHz, D_2O): δ158.8, 158.3, 154.3, 148.6, 138.9, 135.9, 135.0, 129.4, 128.9, 127.8, 127.2, 123.8, 123.2, 120.3, 3.4, 2.5; FT-IR (film)(Solvent: Acetonitrile) υ_{max}(cm^{-1}): 3465.8, 3006.6, 2948.5, 2634.3, 2412, 2300.8, 2257.3, 2078.4, 1638.5, 1450, 1043.9, 923. HRMS (ESI-TOF) m/z: for $[M]^{2+}$: Calcd for $C_{27}H_{23}N_6ClRu$ 284.0358; Found 284.0357.

Characterization Data of the Isolated Intermediates

2-Nitrobenzaldehyde O-methyl oxime (**10**)[65]*:* ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.52 (1H, s), 7.97 – 7.88 (2H, m), 7.58 – 7.42 (2H, m), 3.94 (3H, s) Hz), 7.38 –7.34 (2H, m), ^{13}C{1H}-NMR (75 MHz, $CDCl_3$): 147.8, 144.9, 133.4, 130.1, 128.7, 127.3, 124.8, 62.5, 60.4.

2-Nitrobenzonitrile (**11**)[66]: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.30-8.26 (1H, m), 7.88 – 7.84 (1H, m), 7.80 – 7.75 (2H, m), ^{13}C{1H}-NMR (75 MHz, $CDCl_3$): 135.6, 135.4, 134.2, 133.6, 125.6, 114.9,108.2.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallography data, CIF file, NMR, ESI-MS, UV-Vis and Fluorescence spectra of synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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