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Phenalenyl based Aluminum Compound for Catalytic C-H Arylation of Arene and Heteroarenes at Room Temperature

Pavan K. Vardhanapu[†], Jasimuddin Ahmed[†], Anex Jose[†], Bikash Kumar Shaw[†], Tamal K. Sen[†], Amita A. Mathews[‡] and Swadhin K. Mandal*[,†]

[†] *Department of Chemical Sciences, Indian Institute of Science Education and Research-Kolkata, Mohanpur-741246, India.*

[‡] *Department of Chemical Sciences, Loyola College, University of Madras, Nungambakkam, Chennai-600034, India.*

**E-mail: swadhin.mandal@iiserkol.ac.in*

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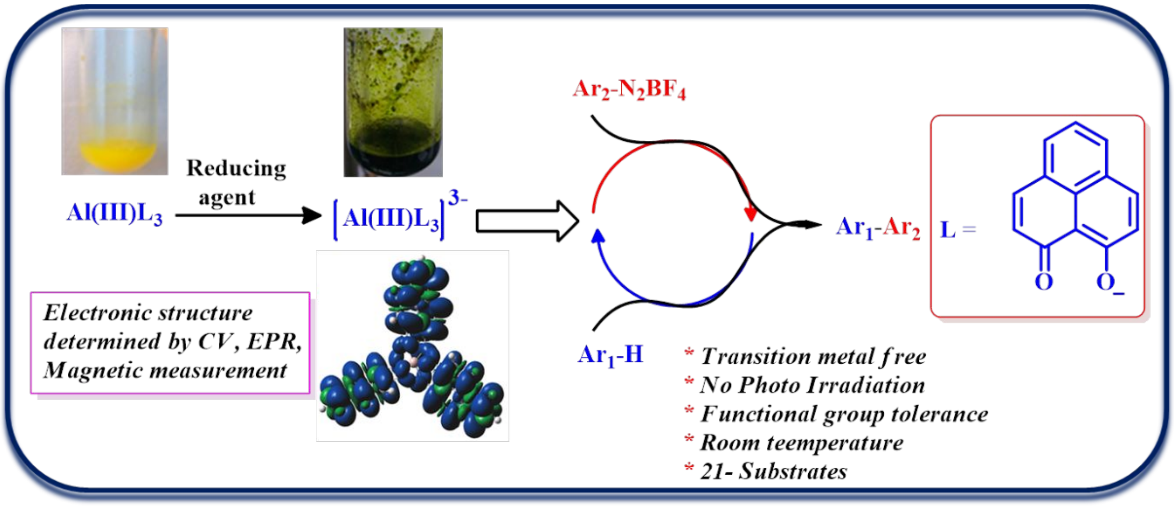


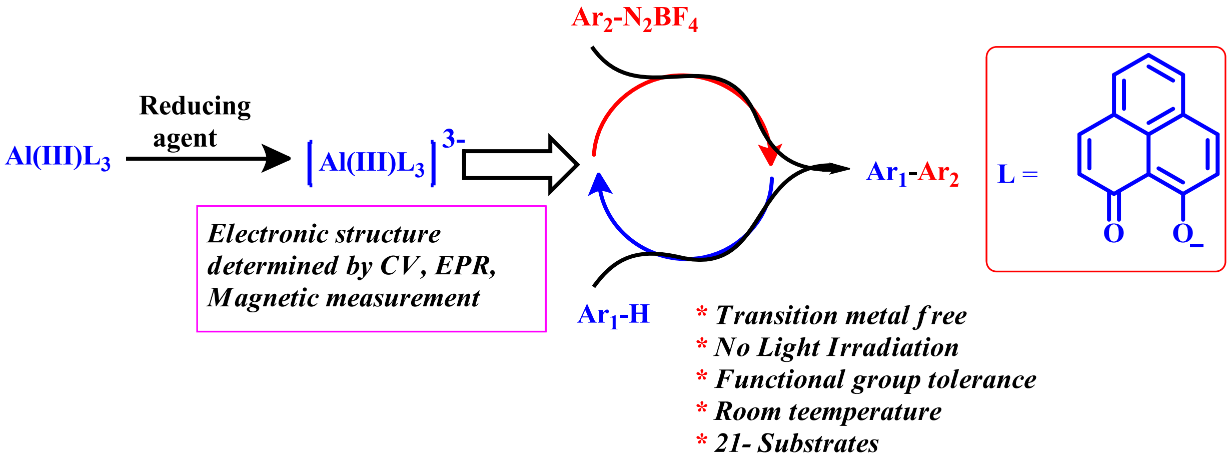
ABSTRACT: Main group metal based catalysis has been considered to be a cost effective alternative way to the transition metal based catalysis, due to the high abundance of main group metals in the Earth crust. Among the main group metals, aluminum is the most abundant (7-8%) in the Earth crust making the development of aluminum based catalyst very attractive. So far aluminum based compounds have been popularly used as Lewis acids in a variety of organic reactions but chemical transformation demanding a redox based process has never utilized Al(III) complex as a catalyst. Herein, we tuned the redox non-innocence behavior of phenalenyl ligand by coupling with Al(III) ion, subsequently can store the electron upon reduction with K to carry out direct C-H arylation of heteroarenes/mesitylene at ambient temperature. A mechanistic investigation revealed that a three-electron reduced phenalenyl based triradical aluminum(III) complex plays the key role in such catalysis. The electronic structure of the catalytically active triradical species has been probed using EPR spectroscopy, magnetic susceptibility measurements, and electronic structure calculations using a DFT method.

INTRODUCTION

The characteristics of most of the transition metal mediated catalysis are facile substrate activation and their rearrangement triggered by switching of different accessible redox states.[1] On the other hand, substrate activation by Lewis acidic non-transition metals such as alkali, alkaline earth metals or by other main group metals is very well-known which works through entirely different mechanism than that of a typical transition metal mediated process involving redox switching.[2] It has long been discussed and considered as an open challenge to mimic the transition metal like behavior by a main group element in catalysis.[3] The major impetus of mimicking transition metals by a main group element stems from its low-toxicity, less expenses and high abundance. However, designing redox chemistry to devise a catalytic organic transformation with the compounds of main group elements is extremely challenging. One school of thought introduced by Power, Roesky, Bertrand and others considered that the use of low-valent main group complexes may introduce feasibility on the oxidative addition process, however, the reverse reductive elimination was not favorable which is essential to complete the catalytic cycle as it regenerates the active catalytic species.[3,4,5] As a result, the chemistry of low-valent main group elements can mimic the transition metals only half-way in which the small molecules activation by oxidative addition could be accomplished.[6] However, the reductive elimination reaction which is the hallmark of transition metal mediated catalytic process; often the last step of a typical catalytic cycle remained elusive in such design using low-valent main group chemistry. It thus warrants devising conceptually new strategy to achieve such goal. Keeping this aim in mind, herein, we have taken advantage of well-known redox non-innocent ligand phenalenyl (PLY) and synthesized an Al(III) based complex (Scheme 1) for designing direct C-H arylation catalysis at ambient temperature.

Early HMO calculations predicted that phenalenyl can exist in three redox active states such as cation, neutral radical and anion using its unique non-bonding molecular orbital (NBMO).[7-12] In recent years, we have explored the cationic state of phenalenyl by coordinating with appropriate metal ions and it is capable of accepting electron(s) to form phenalenyl based radical.[13] The in situ generated phenalenyl radical can show spectacular range of properties

Scheme 1. Redox catalysis of Al(III) complex, 1



spanning from spin based device, fuel cell application and transition metal mimicking catalysis.[14-19]

In the present work, the phenalenyl based Al(III) complex was used to store electrons by reducing it with a chemical reductant. Subsequently the stored electron was transferred through a single electron transfer (SET) process to generate the aryl radical from aryl diazonium coupling partner which can couple with arene/heteroarene partner delivering a facile route to C-H functionalization under mild conditions. There has been seminal effort by König and co-workers to avoid transition metal as catalyst to couple aryl diazonium salt with heteroarene partner under light stimulation, however this method failed to activate arene partner.[20] It may be noted that the coupling between aryl diazonium salt and arene partner was successfully accomplished in 2017 by Lee and co-workers using a dual gold and ruthenium based photoredox catalyst, which induces electron transfer process to activate the aryl diazonium coupling partner while the Au based catalyst acts as an Lewis-acid for electrophilic activation of arene partner.[21] More recently, this coupling reaction between aryl diazonium partner and arene/heteroarene partner was further modified by Ackerman and co-workers using an efficient Mn(I) based catalyst under blue LED irradiation.[22] Recently, we have reported the catalytic protocol for this direct C-H arylation of arenes and heteroarenes by redox active phenalenyl assisted Fe(III) complex under ambient conditions.[23] However, all these recent reports failed to provide a completely transition metal free direct C-H arylation catalysis at ambient conditions without using external light stimulation activating both arene and heteroarene coupling partner. The present work addresses this concern.

RESULTS AND DISCUSSION

First we prepared the aluminum(III) complex (**1**) with 9-hydroxyphenalenone (PLY) ligand using anhydrous $AlCl_3$ precursor following earlier method after modification.[24] Complex **1** was obtained as yellow precipitate after 16 h reflux in dichloroethane at 100 ^{o}C. The product was crystallized from $CHCl_3$/hexane and yielded 77% of crystallized product. Complex **1** was further characterized by ^{1}H and ^{13}C NMR spectroscopy and matched with the earlier report.[24]

To understand the redox behavior of complex **1**, cyclic voltammetric (CV) experiment was carried out in chloroform which shows three, quasi-reversible, single-electron reductions at -1.28 V ($E_1^{1/2}$), -1.52 V ($E_2^{1/2}$) and -1.78 V ($E_3^{1/2}$), (Figure 1b).[25] The CV result clearly indicates that there are three consecutive one electron reductions which may be attributed to gradual acceptance of three electrons into three phenalenyl units. This observation is in consonance with previous study carried out on a similar PLY based complexes.[26-28] It clearly reveals that three consecutive one electron reduction processes are generating a radical, bi-radical and tri-radical species, respectively *(vide infra*, Figure 1a). It may be noted that the differences between the consecutive reduction potentials ($\Delta E_{2\text{-}1}$ = -0.24 V and $\Delta E_{3\text{-}2}$ = -0.26 V, respectively) matches very well with earlier electrochemical results.[25] Its worth to note that the ΔE is considered as the disproportionation potential and is directly correlated to the on-site Coulomb correlation energy (U).[27] The observed ΔE values are in close agreement to bis-phenalenyl-boron complexes ($\Delta E_{2\text{-}1}$ values are -0.29 V and -0.28 V),[27] tris-phenalenyl-silicon ($\Delta E_{2\text{-}1}$ = -0.24 V and $\Delta E_{3\text{-}2}$ = -0.32 V, respectively) and tris-phenalenyl-germanium complexes ($\Delta E_{2\text{-}1}$ = -0.22 V and $\Delta E_{3\text{-}2}$ = -0.28 V, respectively)[28] bearing the same O,O-phenalenyl ligand. These identical ΔE values observed for **1** strongly suggests that successive electron reduction processes occur into phenalenyl moieties. After having this information on redox behavior of complex **1**, three electrons were chemically injected to **1** by reduction with 3 equiv. K yielding a tri-radical paramagnetic compound **IV** (Figure 2a). Further, the DFT calculation at the level B3LYP/6-31+g* reveals that three electrons

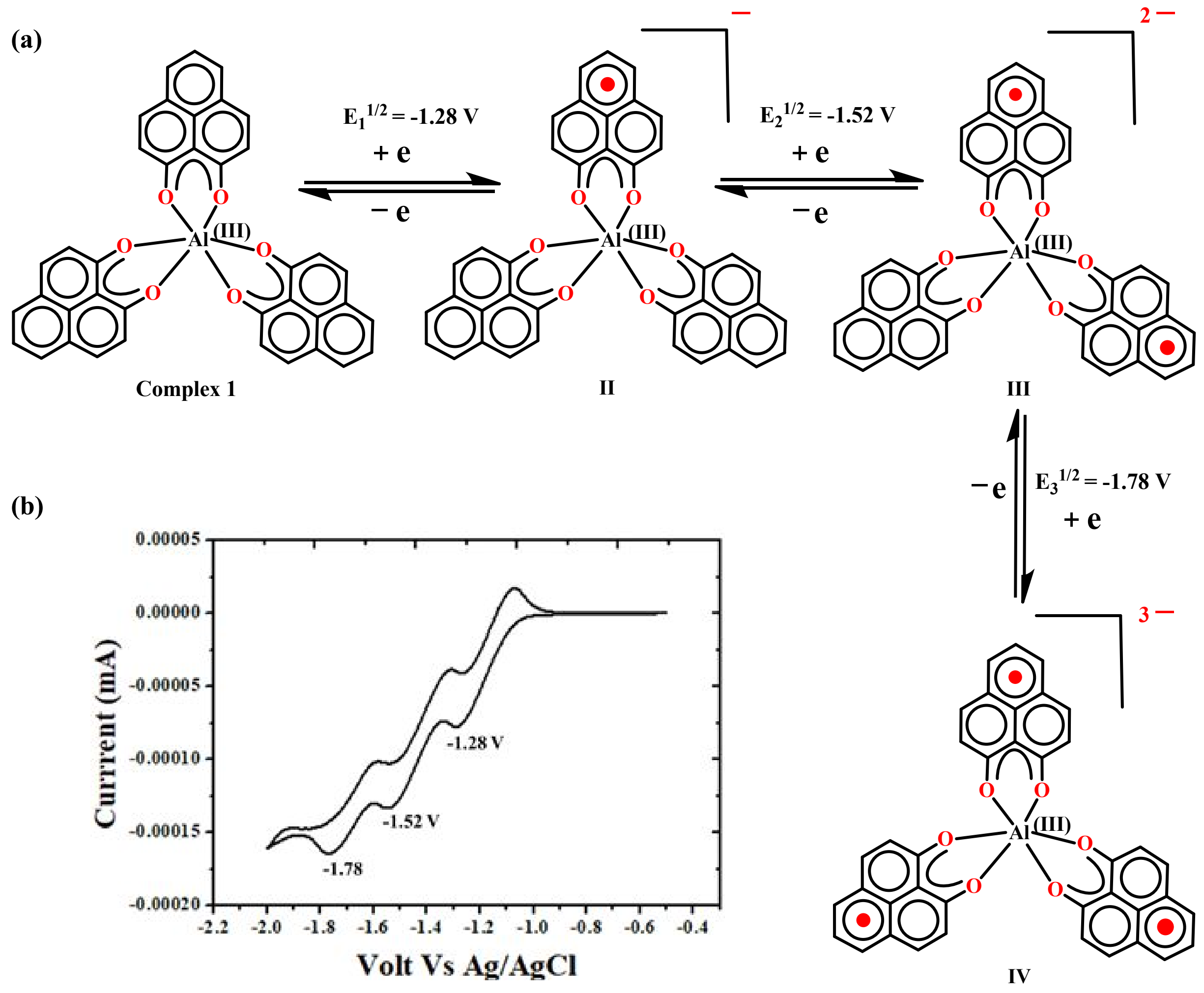


Figure 1. (a) Redox process for **1**. (b) Cyclic voltammetry of complex **1** in chloroform at a scan rate of 0.1 V s^{-1} acquired using Pt working electrode, Pt-wire as the counter electrode and reference electrode, internally referenced to Ag/AgCl.

after reduction populates on PLY moieties as shown in spin density plot (Figure 2b). The natural bond orbital (NBO) analysis of three electrons reduced species **IV** revealed empty 3s and 3p orbitals on aluminum, which clearly supports the presence of Al(III) center and is consistent with other experimental results (see below). To further explore the electronic spin structure of the catalytically active species **IV**, we have performed variable temperature dc magnetic susceptibility measurements in an applied field of 0.01 Tesla in temperature range 2 – 300K. The μ_{RT} value obtained from the variation of effective magnetic moment (μ_{eff}) as a function of temperature (Figure 3a) is 3.92 μB. This is close to the theoretical value (3.87 μB) of tri-radical species **IV** generated after successive reduction of three PLY moieties present in complex **1**. The existence of a significant antiferromagnetic coupling between these radical spins is revealed from the continuous decrease in the μ_{eff} values upon lowering down the temperature to 2K.

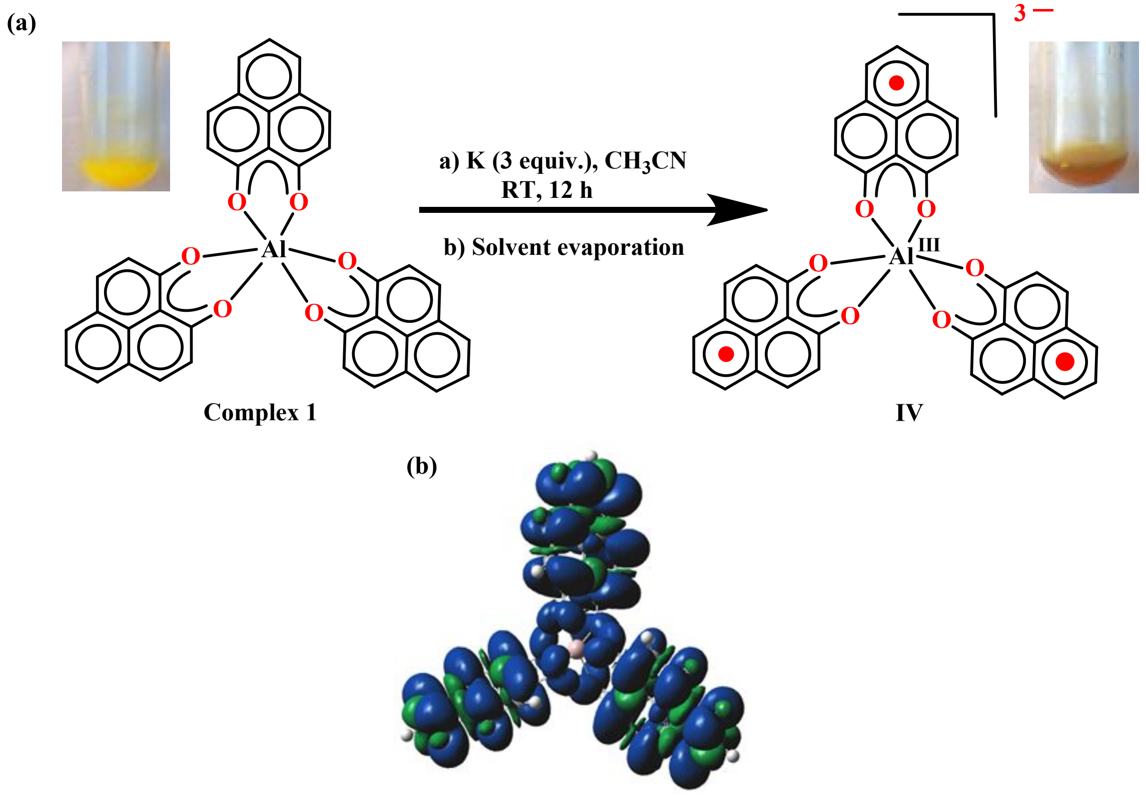


Figure 2. (a) Preparation of three electron reduced species **IV** from complex **1**. (b) Spin density plot of **IV**, Isovalue = 0.02, density = 0.0004 e-/au3.

To understand the strength of this super-exchange coupling, the experimental data were fitted using the following spin Hamiltonian (1) considering three PLY units as equilateral triangular sites.[29] The molar susceptibility is plotted in the form of $\chi_M T$ vs. T. The sharp fall in the $\chi_M T$ values indicates a significant contribution of temperature independent paramagnetism (TIP) in the species **IV**. The best fit is obtained considering the super-exchange coupling J between the three $S = \frac{1}{2}$ PLY•¯ centers and the Lande g factor (from EPR studies, Figure 3b) as ~ 1.99, the extracted parameters are found as $J = -25.38$ (2) cm^{-1}, TIP = $6 \times 10^{-2} \text{cm}^3 \text{mol}^{-1}$. Good agreement factor (R^2) in the order of 10^{-5} is obtained in the least squares fitting procedure (Figure 3a).

$$H = -(JS_iS_j + JS_jS_k + JS_iS_k)\ldots\ldots\ldots\ldots\ldots(1)$$

where, the specific terms carry their usual meaning [$S_i = S_j = S_k = \frac{1}{2}$;(PLY•¯)]

Furthermore, the X-band EPR spectroscopy of species **IV** reveals a sharp singlet line with resonance at $g = \sim 1.9998$ (Figure 3b). This EPR signal at g = ~2 is indicative of a phenalenyl based radical.[30] The magnetic susceptibility along with EPR measurements, DFT studies, catalytic results with **IV** and CV result of complex **1** provide a consistent picture of the tri-radical species **IV**. This observation encouraged us to check if such reduced species **IV** can initiate any single electron transfer (SET) process. In this context, we studied direct C-H arylation of arenes and heteroarenes with aryl diazonium salt coupling partners under ambient conditions using **1** in the presence of a chemical reductant. In order to design such reaction, furan (**1a**) was taken as the arene partner and 4-chloroaryl diazonium salt **2a** was taken as the aryl diazonium-coupling partner to obtain the arylated product **3a** (Table 1) under different conditions using phenalenyl supported aluminium complex **1**.

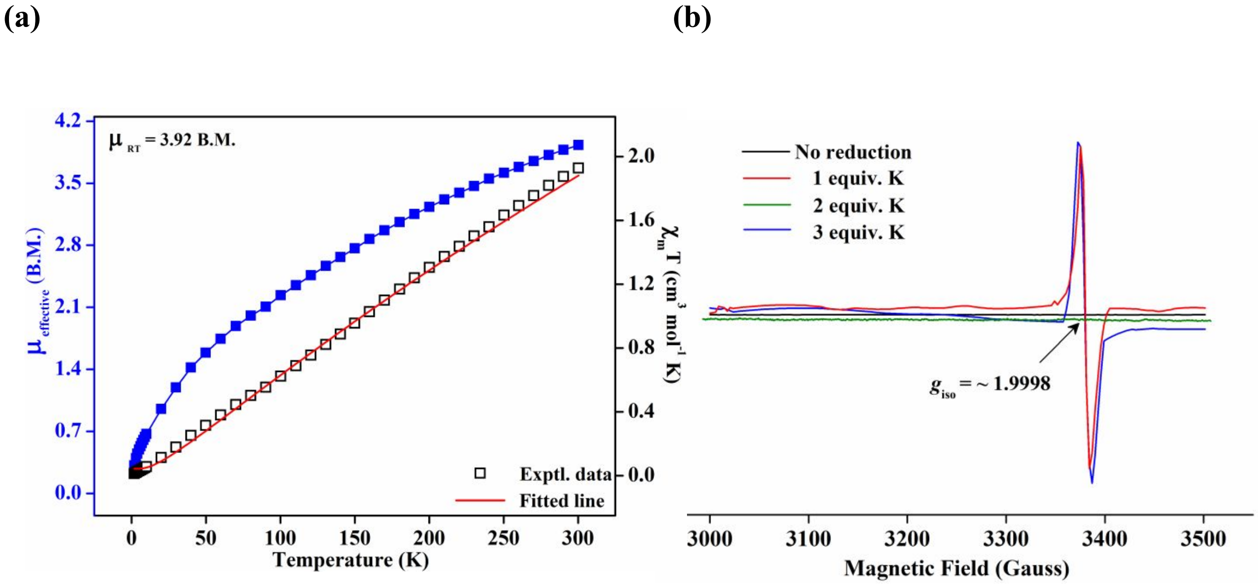
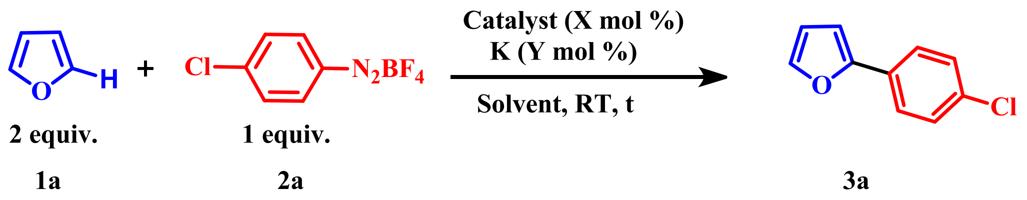


Figure 3. (a) Variation of μ_{eff} values as a function of temperature for reduced tri-radical species **IV** (Blue). Variation of $\chi_M T$ values with temperature (Black). Solid line (Red) represents the theoretically fitted curve and the points are the experimental data (Black). (b) EPR spectrum of complex **1** and gradual change in the EPR spectrum of complex **1** on addition of 1/2/3 equivalents of K. The signal intensities in the EPR spectra are not normalized.

The first reaction was carried out by using 10 mol % of **1** and 40 mol % of K in DMSO for 24 h which afforded 74% of the arylated product **3a** (Table 1, entry 1). However, the reaction did not proceed at all when it was carried out without addition of any reducing agent (K) (Table 1, entry 2). Use of 40 mol% of an organic amine tetrakis diamino ethylene (TDAE) as the reducing agent with 10 mol % of complex **1**, afforded less than 10% yield of the arylated product **3a** (Table 1, entry 3), indicating the necessity of a strong reducing agent (such as K) to reduce **1**. The reaction was optimized under various catalyst and potassium loadings (Table 1, entries 4-8), we found that 5 mol% of **1** and 4 equiv. K (20 mol %) are the effective combinations to afford 72% yield of **3a** (Table 1, entry 4). Taking these combinations of catalyst and K, reactions were performed in DMF, THF and DMA and we obtained lesser yield in other solvents than in DMSO (Table 1, entries 9-11). A blank reaction without **1** was carried out keeping other conditions fixed which afforded only 16% yield of product **3a** (Table 1, entry 12), confirming the necessity of complex **1** to succeed this reaction. When this reaction was carried out for 12 h instead of 24 h, only 41% yield of **3a** (Table 1, entry 13), was obtained. As a control, the reaction using catalytic amount of Al(acac)$_3$ having identical coordination environment around Al(III) ion in complex **1**, was performed keeping other parameters same, when it resulted in only 26% yield of product **3a** (Table 1, entry 14). This result (Table 1, entry 14) clearly establishes the role of phenalenyl ligand to initiate redox process for the direct C-H arylation of heteroarene. Overall, we found 5 mol % of complex **1** with 20 mol % of K in DMSO solvent can afford the best isolated yield72% of C-H arylated product of furan within 24 h.

With this optimized reaction conditions, the substrate scope was screened over the range of heteroarene (furan and thiophene) partners as well as in different aryl diazonium salt coupling partners. The C-H arylation of heteroarenes has been accomplished by König and co-workers with aryl coupling partners using organic dye in the presence of light.[24] At first, C-H arylation of furan (**1a**) was carried out with differently substituted aryl diazonium salt coupling partners. Electron withdrawing group containing aryl diazonium salt coupling partners (**2a**, **2b**, **2c** and **2d**) yielded 72-82% of arylated products **3a**, **3b**, **3c** and **3d**, respectively whereas electron donating group containing aryl diazonium salt coupling partners (**2f** and **2g**) afforded slightly less yield (69% and 65%) of corresponding products **3f** and **3g**, respectively. Phenyl group containing aryl diazonium salt coupling partner (**2e**) yielded 68% of product **3e** (Table 2). Next C-H arylation of thiophene (**1b**) was carried out with differently substituted aryl diazonium salt coupling partners.

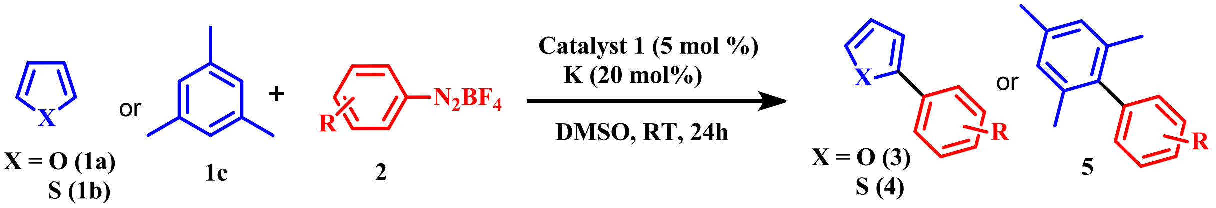
Table 1. Optimization study for C-H arylation of furan[a]

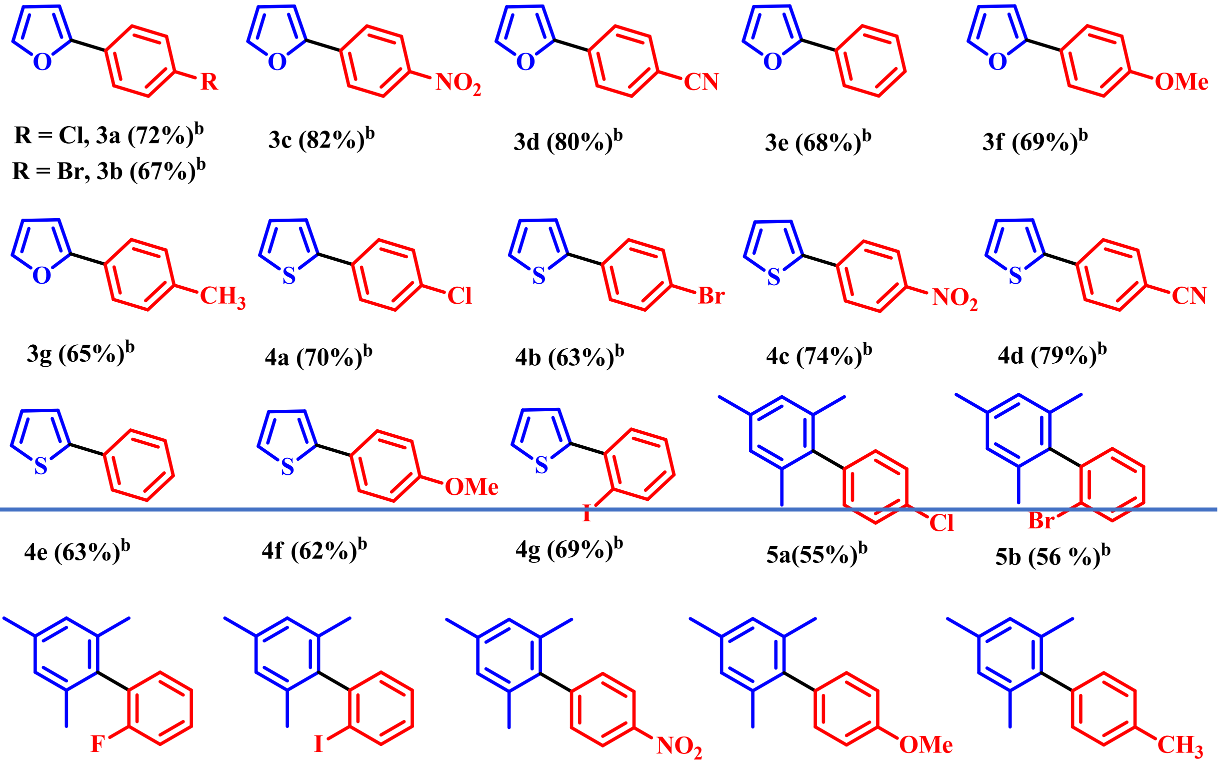


Entry	Catalyst (mol %)	Reductant (mol %)	Solvent	Time (h)	Yield[b] (%)
1	**1** (10)	K (40)	DMSO	24	74
2	**1** (10)	None	DMSO	24	NR
3	**1** (10)	TDAE (40)	DMSO	24	<10
4	**1 (5)**	**K (20)**	**DMSO**	**24**	**72**
5	**1** (2)	K (8)	DMSO	24	21
6	**1** (5)	K (5)	DMSO	24	15
7	**1** (5)	K (10)	DMSO	24	19
8	**1** (5)	K (15)	DMSO	24	52
9	**1** (5)	K (20)	DMF	24	15
10	**1** (5)	K (20)	THF	24	NR
11	**1** (5)	K (20)	DMA	24	<10
12	None	K (20)	DMSO	24	16
13	**1** (5)	K (20)	DMSO	12	41
14	Al(acac)$_3$	K (20)	DMSO	24	26

^{a}Reaction conditions: Furan (0.64 mmol), **2a** (0.32 mmol), K (x mol % loading). ^{b} Isolated yield, NR stands for "No Reaction.

Table 2. Substrate scopes for C-H arylation of heteroarenes/mesitylene using aluminum complex 1 under ambient conditions.^{a}

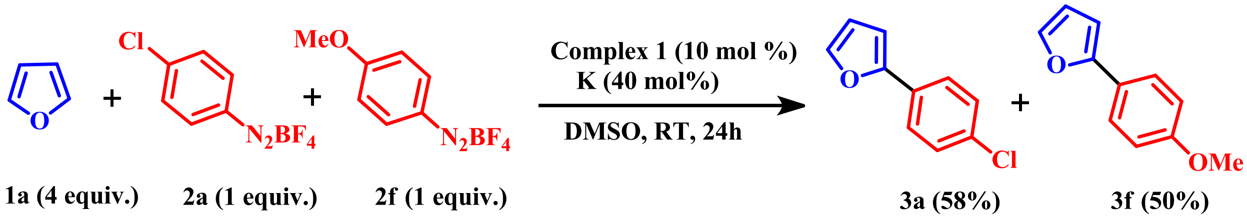




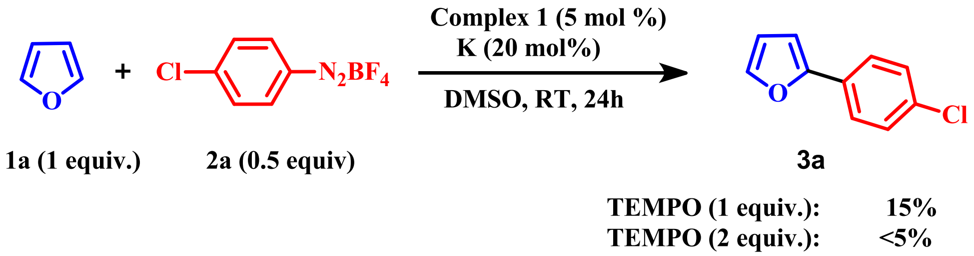
R = Cl, 3a (72%)^b
R = Br, 3b (67%)^b
3c (82%)^b
3d (80%)^b
3e (68%)^b
3f (69%)^b
3g (65%)^b
4a (70%)^b
4b (63%)^b
4c (74%)^b
4d (79%)^b
4e (63%)^b
4f (62%)^b
4g (69%)^b
5a(55%)^b
5b (56 %)^b
5c (60%)^b
5d (64%)^b
5e (61%)^b
5f (52%)^b
5g (42%)^b

^{a}Reaction conditions: Heteroarene/mesitylene (0.64 mmol), **2** (0.32 mmol), catalyst **1** (5 mol %, 0.016 mmol), K (2.49 mg, 20 mol % loading, 0.064 mmol). ^{b}Isolated yield.

(a) Competition reaction between furan and mixture of two electronically biased aryl diazonium salts 2a and 2f.



(b) Reaction inhibition in presence of TEMPO.



(c) TEMPO trapped intermediate formation.

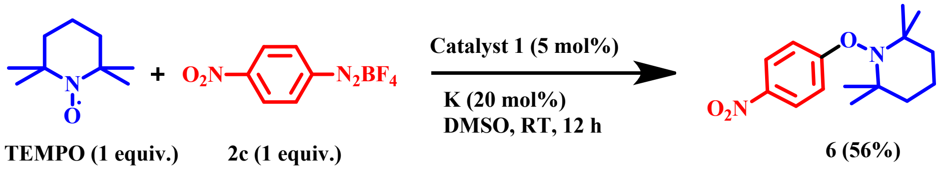


Figure 4. Mechanistic investigation: (a) Competition reaction between furan and mixture of two aryl diazonium salts **2a** and **2f**. (b) Reaction inhibition of furan arylation in presence of TEMPO. (c) Trapping of aryl radical by TEMPO.

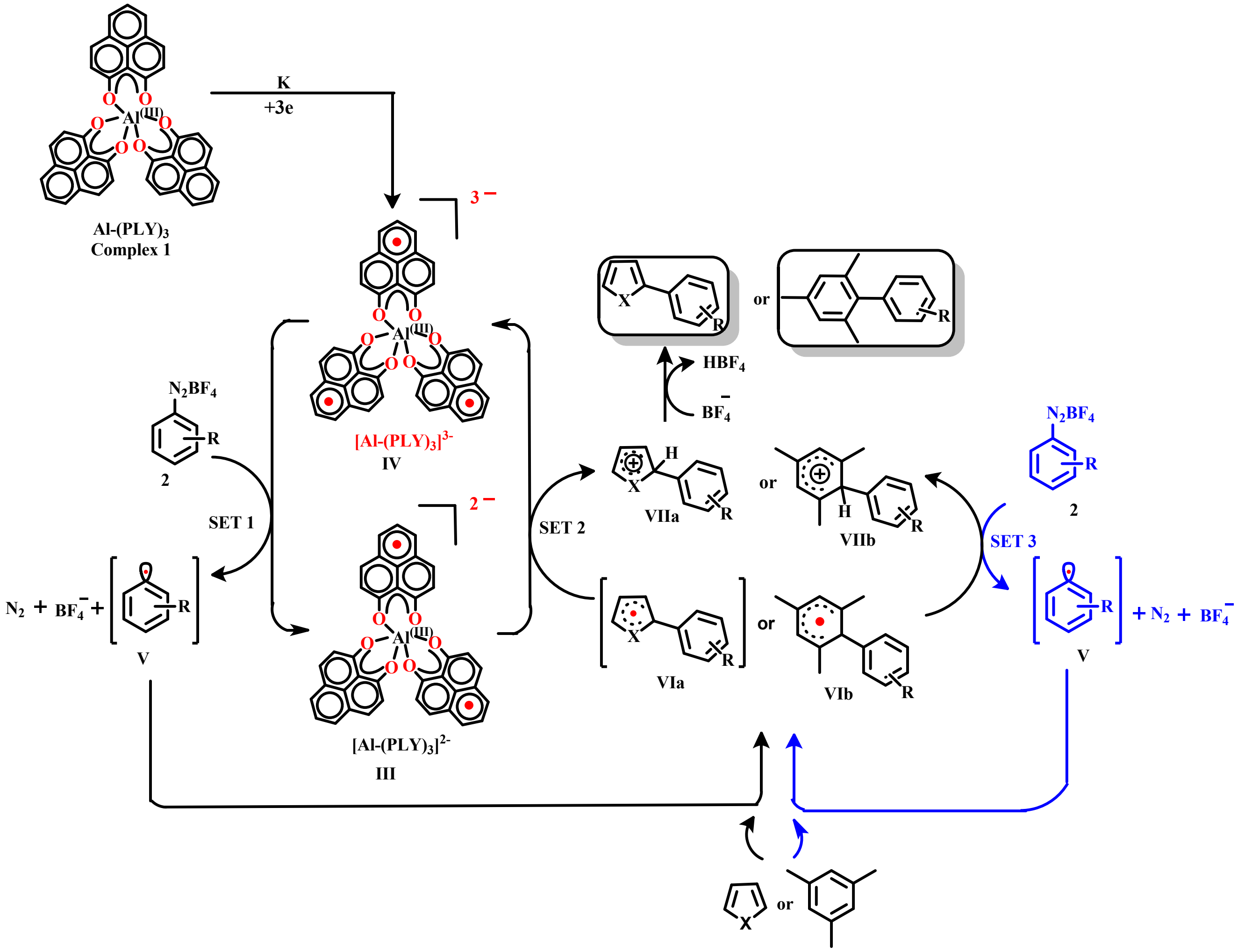
Electron withdrawing group containing aryl diazonium salt coupling partners (**2a**, **2b**, **2c** and **2d**) yielded 70-79% of arylated products **4a**, **4b**, **4c** and **4d**, respectively whereas electron donating group containing aryl diazonium salt coupling partner (**2f**) afforded slightly less yield of 62% of corresponding product **4f**, respectively. Phenyl group containing aryl diazonium salt coupling partner (**2e**) yielded 63% of product **4e** (Table 2). Aryl diazonium salt coupling partner (**2g**) containing ortho-substitution afforded 69% of corresponding product **4g**.

After successful C-H arylation of heteroarenes, direct C-H arylation of arene (mesitylene) was attempted. Electron withdrawing groups such as Cl, Br, F, I, NO_2, containing aryl diazonium salt coupling partners yielded 55-64% of arylated products **5a**, **5b**, **5c**, **5d** and **5e**, respectively whereas aryl diazonium salt coupling partners containing electron donating groups such as OMe, or Me afforded less yield of 52% or 42% of corresponding product **5f** or **5g** (Table 2). Almost similar yields of arylated products of mesitylene have been reported by Lee and co-workers under Au and Ru based dual catalysis in the presence of light with aryl diazonium salt as the coupling partners[21] whereas the present method avoids use of any expensive and rare metals and avoids light stimulation. With this versatile and efficient C-H arylation of arenes and heteroarenes in hand, the mechanistic pathway for the reaction was investigated. At first, an intermolecular competitive reaction was carried out for the arylation of furan with substituted aryl diazonium salt coupling partners of which one bears an electron donating substituent (**2f**) while the other bears an electron withdrawing substituent (**2a**), to afford respective arylated products **3f** (50%) and **3a** (58%, Figure 4a). This indicates the present catalytic system is biased towards the aryl diazonium coupling partners having electron withdrawing groups than the aryl diazonium coupling partners containing electron donating groups. This result indicates that a radical intermediate might be involved during the catalytic cycle.[30]

Next, the reaction between furan **1a** and aryl diazonium salt coupling partner **2a** was carried out in the presence of a well-known radical scavenger 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) under different TEMPO loadings (Figure 4b). In presence of 1 equiv. TEMPO, only 15% of arylated product **3a** was obtained while in presence of 2 equiv. TEMPO, the reaction was arrested almost completely (<5%). This reaction inhibition in presence of a radical scavenger, confirms a radical mediated pathway for this arylation process. Furthermore, the reaction between TEMPO and aryl diazonium salt coupling partner **2c** was performed with our optimized conditions in absence of any arene or heteroarene partner, which resulted in the formation of a TEMPO-trapped product **6** with 56% yield (Figure 4c). The arrest of TEMPO-trapped aryl radical **6** clearly establishes a radical mediated SET process is operative which can further be supported by previous reports for direct C-H arylation.[31-34] As described earlier, we were able to isolate the active catalytic species **IV** by performing stoichiometric reaction between $Al(PLY)_3$ complex **1** and K. Using this triradical species **IV** in 5 mol % without further addition of the reducing agent (K) (see above for details on electronic structure of **IV**), a catalytic reaction was carried out under the optimized conditions and the direct C-H arylation of furan afforded 74% yield of the arylated product **3a**. This result establishes that species **IV** (Figure 2a) is the catalytically active species for this arylation reaction.

Taking these results in account along with the previous literature supports,[20,33] we sketch a plausible mechanistic cycle for the catalytic reaction (Scheme 2). Complex **1** forms the catalytically active triradical species **IV** upon reduction with K metal. The electronic structure of this species is well understood by magnetic, spectroscopic and theoretical studies as described above. In the first step of mechanistic cycle, species **IV** transfers an electron(SET1) to the aryl diazonium salt and forms the aryl radical. This aryl radical was trapped and isolated as

Scheme 2. Plausible mechanistic cycle for C-H arylation using complex 1.



compound **6** using TEMPO and characterized by ^{1}H and ^{13}C NMR spectroscopy. During this process, species **IV** transforms into species **III** as also indicated by electrochemistry data and theoretical calculations. We have studied the electron transfer process in this key step of catalytic cycle. The process takes place by transfer of an electron from HOMO of **IV** (Energy = 3.99 eV) to the low-lying LUMO of substrate **2** (Energy = -8.18 eV). Figure 5 displays the HOMO of **IV**, which clearly shows that it is delocalized over PLY moieties. Hence the first electron transfer from **IV** to the diazonium salt takes place from PLY moiety of **IV**.

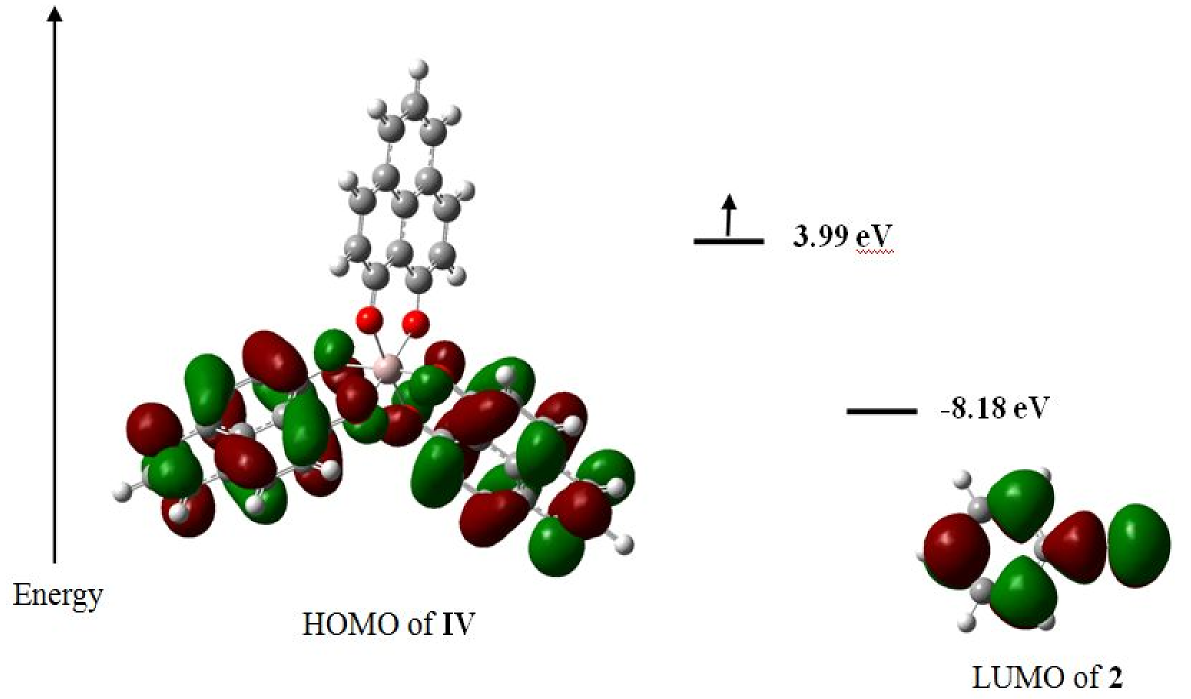


Figure 5. Energy levels and plot of HOMO of **IV** and LUMO of **2** (Isovalue = 0.02 e^{-}/au^{3})

It is found from DFT calculations that the orbital occupancy on aluminum atom remains the same in **IV** and **III** supporting the fact that the electron transfer takes place from a PLY unit. Further, the biarylated radical intermediate **VI** is formed by reaction of aryl radical **V** with the arene/heteroarene partner. However, the exact pathway of the arene activation is not clear, which traditionally requires a Lewis acid as reported earlier.[19,21] The biarylated radical **VI** forms a cationic biaryl intermediate **VII** by transferring an electron to species **III** (SET2) thus regenerating the catalytically active species **IV** for the catalytic cycle to continue. Further, the BF_4^- counter anion abstracts a proton from the cationic biaryl intermediate **VII** to yield the desired product.[20] There can be two probable fate of the second electron released from species **VII**. It can either be consumed by species **III** to regenerate the active catalyst species **IV** or it can be captured by aryl diazonium salt coupling partner (**2**) and used in radical propagation process forming species **V**, which will further continue the reaction forming species **VI**. But the inefficiency of this chain propagation process (through SET 3) has been confirmed by the reaction optimization study in absence of catalyst but in presence of 20 mol % of K yielding only 16% of product **3a** (Table 1, entry 12).

CONCLUSION

In conclusion, we have shown an aluminum supported phenalenyl complex is highly accessible for redox transformation reaction and thus mimics the transition metal mediated catalysis. A radical based SET process plays key role for such direct arylation of arenes and heteroarenes. Magnetic susceptibility, EPR measurement, CV, catalytic experiment and DFT studies indicate involvement of a tri-radical species during this catalysis. This study establishes that by taking the advantage of the non-innocence behavior of phenalenyl ligand, it is possible to design catalysts of main group elements, which may take part in redox catalysis, such a phenomena is usually considered as the hallmark of transition metals mediated catalysis.

EXPERIMENTAL SECTION

General methods and Instrumentation. Unless stated otherwise, reactions were performed in flame–dried glassware under inert atmosphere (N_2), using standard Schlenk techniques or inside a MBraun Glovebox maintained under nitrogen. All solvents were distilled from Na/benzophenone or calcium hydride prior to use. All other chemicals were purchased from commercial sources and used as received. Deuterated solvents were purchased from Cambridge

Isotope Laboratories. NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer. All chemical shifts were reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Thin-layer chromatography (TLC) and open-column chromatography were performed on silica gel (Merck silica gel 100-200 mesh). Evaporation of solvents was performed under reduced pressure using a rotary evaporator.

General Procedure for the Synthesis of Aryldiazonium tetrafluoroborate.[35] Substituted aniline (10 mmol) was dissolved in 5 mL of distilled water at room temperature then 4 mL of 46% hydrofluoroboric acid was added to the mixture. The resulting reaction mixture was cooled down to 0-5 ^{o}C using an ice bath. Sodium nitrite (0.69 g) was dissolved in 1.5 mL of water and cooled down to 0-5 ^{o}C separately, this cold sodium nitrite solution was added drop-wise to the main reaction mixture. The resulting mixture was stirred for 30 min maintaining the temperature 0-5 ^{o}C and the precipitate was collected by filtration after washing the residue with ice cold water. The final residue was dissolved in minimum amount of acetone and then diethyl ether was added. Pure product was collected as crystals from this mixture of acetone and diethyl ether solvent. The final aryldiazonium tetrafluoroborate crystals were washed with diethyl ether and dried under vacuum.

Synthetic procedure of Complex 1.[24] In an oven dried Schlenk flask, 9-hydroxyphenalenone (1 g, 5.09 mmol) was dissolved in 50 mL of dichloroethane and anhydrous aluminum chloride (0.225 g, 1.69 mmol) was added under N_2 atmosphere. Then the reaction mixture was refluxed for 16h at 100 ^{o}C. The yellow precipitate was filtered and washed thoroughly with fresh dichloroethane. The crude product was purified by column chromatography and by recrystallization from $CHCl_3$/hexane yielding to pure yellow powder. Single crystals of the complex **1** were obtained in chloroform, the molecular structure was resolved by X-ray single-crystal diffraction and matched with literature report (yellow crystals, 77 % yield, 0.796 g, 1.301 mmol). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 8.01(d, J = 9.3 Hz, 2H), 7.94 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ 179.0, 141.2, 132.7, 127.7, 127.6, 125.1, 122.7, 113.2 ppm.

General Procedure for C-H Arylation of Heteroarenes. In a glove box, catalyst **1** (9.80 mg, 5 mol %, 0.016 mmol) and K (2.49 mg, 20 mol %, 0.064 mmol) were taken in a 25 mL pressure tube and subsequently DMSO (1 mL) was added in to the reaction mixture, which resulted in a dark green colored solution. Subsequently, furan/thiophene (**1a/1b**, 0.64 mmol) and diazo coupling partner **2** (0.32 mmol) were added to the reaction mixture and allowed to stir for 24 h at room temperature. After completion of the reaction, product was extracted in dichloromethane (25 mL) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired product.

General Procedure for C-H Arylation of Mesitylene. In a glove box, catalyst **1** (9.80 mg, 5 mol %, 0.016 mmol) and K (2.49 mg, 20 mol %, 0.064 mmol) were taken in a 25 mL pressure tube, subsequently DMSO (1 mL) was in to the reaction mixture, which resulted in a dark green colored solution. Subsequently, mesitylene **1c** (0.64 mmol) and diazo coupling partner **2** (0.32 mmol) were added to the reaction mixture and allowed to stir for 24 h at room temperature. After completion of the reaction, product was extracted in dichloromethane (25 mL) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired product.

General Procedure for Inhibition of C-H Arylation Reaction in Presence of TEMPO (Radical Scavenger). Furan (**1a**, 0.64 mmol), diazo coupling partner (**2a**, 0.32 mmol), catalyst **1** (9.80 mg, 5 mol%, 0.016 mmol), K (2.49 mg, 20 mol%, 0.064 mmol) and required amount of TEMPO (with respect to diazo coupling partner **2a**) were taken in a 25 mL pressure tube and subsequently added DMSO (1 mL) in to the reaction mixture inside a nitrogen filled glovebox. Then, the reaction mixture was allowed to stir for 24 h at room temperature. After completion of the reaction, product was extracted in dichloromethane (25 mL) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and product **3a** was purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc.

General Procedure for Synthesis of TEMPO-Trapped Intermediate (2,2,6,6-tetramethyl-1-(4-nitrophenoxy) piperidine), (6).[36] TEMPO (0.32 mmol), diazo coupling partners **2c** (0.32 mmol), catalyst **1** (9.80 mg, 5 mol%, 0.016 mmol) and K (2.49 mg, 20 mol%, 0.064 mmol) were taken in a 25 mL pressure tube, subsequently DMSO (1 mL) was added in to the reaction mixture inside the glovebox. Subsequently, the reaction mixture was allowed to stir for 12 h at room temperature. After completion of the reaction, product was extracted in dichloromethane (25 mL) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and product **6** was purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc. Colorless solid, Yield: 0.0498 g (56%, 0.179 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.14 (d, J = 8.5 Hz, 2H), 7.26 (s, 2H), 1.65 – 1.60 (m, 5H), 1.45 – 1.42 (m, 1H), 1.24 (s, 6H), 1.0 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 168.7, 141.2, 125.5, 114.2, 60.8, 39.6, 32.2, 20.4, 16.8 ppm.

General Procedure of Sample Preparation for Magnetic Study. Catalyst **1**(100 mg, 0.163 mmol) and K (19.10 mg, 0.490 mmol) were added in a 25 mL Schlenk flask, subsequently acetonitrile (3 mL) was added in to the reaction mixture inside the nitrogen filled glovebox. Then, the reaction mixture was allowed to stir for 12 h at room temperature. After solvent evaporation and after multiple washing with acetonitrile, a dark brown colored solid was obtained for magnetic study.

General Procedure of Sample Preparation for EPR Study. A series of reactions was performed with catalyst **1** (100 mg, 0.163 mmol) by varying the equivalents of K (1, 2, 3 equivalent) with respect to catalyst **1** in a 25 mL Schlenk flask, subsequently acetonitrile (3mL) was added into the reaction mixture inside a glovebox under N_2 atmosphere. The reaction mixture drastically changes from yellow to brown color. After solvent evaporation, a brown colored solid was obtained which was taken for EPR measurement.

*2-(4-chlorophenyl)furan **(3a)**.*[37] Colorless solid. Yield: 0.0415 g (72%, 0.234 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.60 – 7.58 (m, 2H), 7.46 (m, 1H), 7.36 – 7.33 (m, 2H), 6.64 – 6.63 (m, 1H), 6.47 – 6.46 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 152.9, 142.3, 132.9, 129.3, 128.8, 125.0, 111.7, 105.4 ppm.

*2-(4-Bromophenyl)furan **(3b)**.*[38] Colorless solid. Yield: 0.0478 g (67%, 0.214 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.55 – 7.47 (m, 5H), 6.65 (d, J = 3.3 Hz, 1H), 6.48 – 6.47 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 152.9, 142.3, 131.7, 129.7, 125.2, 121.0, 111.7, 105.5 ppm.

*2-(4-nitrophenyl)furan **(3c)**.*[38] Yellow solid. Yield: 0.0496 g (82%, 0.262 mmol); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.24 – 8.22 (m, 2H), 7.80 – 7.76 (m, 2H), 7.56 (d, J = 1.72 Hz, 1H), 6.87 – 6.86 (m, 1H), 6.55 – 6.54 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 151.7, 146.4, 144.1, 136.4, 124.2, 123.9, 112.4, 108.9 ppm.

2-(4-Cyanophenyl)furan ***(3d)***.[20] Brown solid. Yield: 0.0433 g (80%, 0.256 mm0l); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.74 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 1.5 Hz, 1H), 6.81 (d, J = 3.4 Hz, 1H), 6.52 (dd, J_1 = 3.7 Hz, J_2 = 2.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm) 152.0, 143.6, 134.6, 132.5, 124.0, 119.0, 112.2, 110.2, 108.1.

2-Phenylfuran ***(3e).***[20] Pale yellow solid. Yield: 0.0314 g (68%, 0.217 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.70 (d, J = 7.9 Hz, 2H), 7.48 (m, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.30-7.25 (m, 1H), 6.69 (d, J = 3.2 Hz, 1H), 6.50-6.48 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 154.0, 142.0, 131.0, 128.6, 127.3, 123.7, 111.6, 105.0 ppm.

2-(4-Methoxyphenyl)furan ***(3f).***[39] Colorless solid. Yield: 0.0384 g (69%, 0.221 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.60 (d, J= 8.7 Hz, 2H), 7.42 (s, 1H), 6.92 (d, J= 8.8 Hz, 2H), 6.51 (d, J= 3.2 Hz, 1H), 6.45 – 6.44 (m, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ 159.0, 154.2, 141.3, 125.2, 124.0, 114.1, 111.5, 103.3, 55.31 ppm.

2-(p-tolyl)-furan ***(3g)***.[39] Colorless solid. Yield: 0.0329 g (65%, 0.208 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.57 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 1.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 3.3 Hz, 1H), 6.47 – 6.46 (m, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ 154.2, 141.6, 137.1, 129.3, 128.2, 123.7, 111.5, 104.1, 21.2 ppm.

2-(4-Chlorophenyl)thiophene ***(4a)***.[37] Colorless solid. Yield: 0.0436 g (70%, 0.224 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.55-7.53 (m, 2H), 7.36-7.34 (m, 2H), 7.30-7.29 (m, 2H), 7.10-7.07 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm) 143.0, 133.1, 132.9, 128.9, 128.1, 127.0, 125.1, 123.4 ppm.

2-(4-Bromophenyl)thiophene ***(4b).***[39] Colorless solid. Yield: 0.0482 g (63%, 0.201 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.51-7.47 (m, 4H), 7.29 (d, J = 4.1 Hz, 2H), 7.09-7.06 (m, 1H) ppm;

^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm) 143.1, 133.1, 131.9, 128.1, 127.4, 125.2, 123.4, 121.2 ppm.

2-(4-nitrophenyl)thiophene ***(4c).***[39] Yellow solid. Yield: 0.0486 g (74%, 0.237 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 8.28 – 8.22 (m, 2H), 7.76 – 7.73 (m, 2H), 7.49 – 7.43 (m, 2H), 7.16 – 7.14 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ 146.63, 141.6, 140.6, 128.6, 127.6, 126.0, 125.7, 124.4 ppm.

2-(4-Cyanophenyl)thiophene ***(4d)***.[40] Yellow solid. Yield: 0.0468 g (79%, 0.253 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.73-7.64 (m, 4H), 7.43-7.40 (m, 2H), 7.14-7.12 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ (ppm) 142.0, 138.6, 132.7, 128.5, 127.0, 126.1, 125.1, 119.0, 110.5 ppm.

2-Phenylthiophene ***(4e)***.[40] Colorless solid. Yield: 0.0323 g (63%, 0.201 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.63 – 7.59 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.26 – 7.25 (m, 1H), 7.10-7.07 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ 144.4, 134.4, 128.8, 128.0, 127.4, 125.9, 124.7, 123.1 ppm.

2-(4-Methoxyphenyl)thiophene ***(4f)***.[36] Pale yellow solid, Yield: 0.0377 g (62%, 0.198 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.60 (d, J = 8.8 Hz, 2H), 7.28-7.26 (m, 2H), 7.12-7.10 (m, 1H), 6.99 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ 159.1, 144.3, 127.9, 127.3, 127.2, 123.8, 122.0, 114.2, 55.3 ppm.

2-(2-Iodo-phenyl)thiophene ***(4g)***.[41] Colorless oil, Yield: 0.063 g (69%, 0.220 mmol); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.97–7.53 (m, 1H), 7.44–7.36 (m, 3H), 7.18–7.17 (m, 1H), 7.11–7.10 (m, 1H), 7.05–7.02 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) 144.9, 139.9, 139.3, 131.2, 129.3, 128.0, 127.6, 126.7, 125.8, 99.5 ppm.

4'-Chloro-2,4,6-trimethylbiphenyl ***(5a)***.[42] Yellow oil, Yield: 0.0406 g (55%, 0.176 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.39 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.94 (s, 2H), 2.33 (s, 3H), 2.00 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 139.4, 137.7, 136.9, 135.8, 132.4, 130.7, 128.6, 128.1, 21.00, 20.6 ppm.

2'-Bromo-2,4,6-trimethylbiphenyl ***(5b)***.[43] Colorless liquid. Yield: 0.0493 g (56%, 0.179 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.67 (d, J= 8.1 Hz, 1H), 7.38 (t, J= 7.5 Hz, 1H), 7.22 (t, J = 6.7 Hz, 1H), 7.14 (d, J= 7.2 Hz, 1H), 6.95 (s, 2H), 2.35 (s, 3H), 1.96 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 141.8, 137.9, 137.2, 135.7, 132.6, 130.8, 128.5, 127.9, 127.6, 124.1, 21.1, 20.1 ppm.

2'-Fluoro-2,4,6-trimethylbiphenyl ***(5c)***.[44] Colorless oil, Yield: 0.0411 g (60%, 0.192 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.38 – 7.33 (m, 1H), 7.23 – 7.21 (m, 1H), 7.20 – 7.13 (m, 2H), 6.98 (s, 2H), 2.36 (s, 3H), 2.05 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.6 (d, $J_{C\text{–}F}$ = 242 Hz), 137.3, 136.5, 131.6, 128.8 (d, $J_{C\text{–}F}$ = 7.8 Hz), 128.1, 124.1, 115.6 (d, $J_{C\text{–}F}$ = 22.4 Hz), 21.1, 20.3 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ 115.0 – 115.03 (m) ppm.

2'-Iodo-2,4,6-trimethylbiphenyl ***(5d)***.[45] Colorless solid, Yield: 0.0659 g (64%, 0.204 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.95 –7.93 (m, 1H), 7.42 –7.39 (m, 1H), 7.14 –7.12 (m, 1H), 7.04 –7.01(m, 1H), 6.95 (s, 2H), 2.35(s, 3H), 1.93(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 146.0, 141.1, 139.0, 137.3, 135.5, 129.7, 128.5, 128.4, 128.1, 100.8, 21.2, 20.3 ppm.

4'-Nitro-2,4,6-trimethylbiphenyl ***(5e)***.[21] Yellow solid, Yield: 0.0471 g (61%, 0.195 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.29 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 6.97 (s, 2H), 2.34 (s, 3H), 1.99 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 148.5, 146.8, 137.6, 136.7, 135.2, 130.4, 128.3, 123.7, 21.0, 20.5 ppm.

4'-Methoxy-2,4,6-trimethylbiphenyl ***(5f)***.[46] Yellow oil, Yield: 0.0376 g (52%, 0.166 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.05 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 6.93 (s, 2H), 3.85 (s, 3H), 2.32 (s, 3H), 2.01 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 158.1, 138.8, 136.4, 136.0, 133.2, 130.30, 128.0, 113.7, 55.2, 21.0, 20.8 ppm.

4'-Methyl-2,4,6-trimethylbiphenyl ***(5g)***.[21] Colorless oil, Yield: 0.0283 g (42%, 0.134 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.22 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.93 (s, 2H), 2.40 (s, 3H), 2.32 (s, 3H), 2.00 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 139.0, 138.0, 136.3, 136.1, 136.0, 129.1, 129.0, 128.0, 21.2, 21.0, 20.7 ppm.

Computational Methods

All the theoretical calculations performed to interpret the experimental observation were performed using Gaussian09 quantum chemistry package.[47] All the Density Functional Theory (DFT) calculations were performed at B3LYP/6-31+g* level of theory.[48] Unrestricted calculations were performed for open shell molecules. Frequency calculations were performed to confirm the optimization to a minimum for all structures.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website, at DOI:…………

General experimental procedures, computational details and spectroscopic data of all compounds (PDF).

AUTHOR INFORMATION

Corresponding Authors

*E-mail: swadhin.mandal@iiserkol.ac.in

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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