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Reactions of nitroxides with metalloporphyrin alkyls bearing beta hydrogens: Aliphatic carbon–carbon bond activation by metal centered radicals

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Abstract

Nitroxide-induced beta-hydrogen atom abstraction and beta-elimination of rhodium porphyrin alkyls have been observed. Rhodium(II) porphyrin radical were proposed intermediates to form first and subsequently reacted via aliphatic carbon–carbon bond activation with alkyl substituted nitroxides to yield rhodium porphyrin alkyl complexes.

Keywords: Rhodium porphyrin; Nitroxides; Carbon–carbon bond activation

1. Introduction

2,2,6,6-Tetramethylpiperidinoxy (TEMPO) and related nitroxide radicals have been shown to react with organometallic and inorganic complexes in various modes. They can act as: (1) coordinating ligands [1,2], (2) trapping agents for alkyl radicals generated from homolysis of metal–alkyls [3–6], (3) reagents in reactions with metal hydrides [7–9], (4) hydrogen atom abstractors with metal–alkyls [10,11], and (5) alkyl transfer agents with metal radicals [11,12].

The importance of nitroxide radicals in organometallic chemistry is exemplified particularly as efficient alkyl radical traps in the estimations of bond dissociation energies of metal–alkyl bonds by kinetic methods. Various bond energy estimations have thus been accomplished in vitamin B_{12} and related models [3,4], cyclopentadienyl metal–alkyl complexes [3b], and ruthenium porphyrin alkyl complexes [5,6]. These radicals can behave as reagents rather than as innocent traps in the reactions with organometallic complexes. James and Dolphin have remarked in the report on the reactivity of Ru(oep)$(CH_3)_2$ and Ru(oep)$(C_6H_5)_2$ (oep = octaethylporphyrinate): "the rate of decomposition of Ru(oep)$(CH_3)_2$ was found to be dependent on the concentration of TEMPO which also appears to react with Ru(oep)CH_3" [6]. While nitroxyls are well-known ligands for a variety of transition metal complexes [1,2], TEMPO has been reported to react with Ru(oep)CH_3 to yield Ru(oep)CO [10]. We have also reported recently that rhodium(II) porphyrin reacts with alkyl nitroxides via carbon–carbon bond activation (CCA) to yield alkyl rhodium porphyrins [11,12]. During the investigation of the mechanism of 1,2-rearrangements of rhodium porphyrin alkyls [13], we have observed that TEMPO did not act as a radical trap but reacted directly with rhodium porphyrin alkyls bearing beta hydrogens via a novel beta-hydrogen abstraction/elimination process to generate rhodium porphyrin radical which then underwent aliphatic CCA with nitroxides [11]. We now disclose further details on the reactions of rhodium porphyrin alkyls with nitroxides and the subsequent carbon–carbon bond activation.

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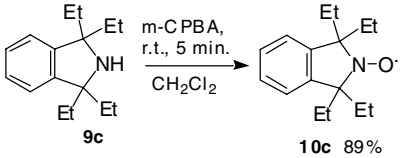
2. Results and discussion

Rhodium porphyrin chlorides were prepared form the metalation of porphyrins with $RhCl_3$ in refluxing PhCN (Fig. 1, Eq. (1)). High yields of (PhCN)Rh(por)Cl were obtained if the reactions were monitored carefully to avoid further carbon–hydrogen bond activation of PhCN in giving *meta*-cyanophenyl rhodium porphyrins [14] and were further heated under high vaccum to remove the weakly coordinating PhCN. Then, alkyl rhodium porphyrin complexes were synthesized by the reactions of the corresponding rhodium porphyrin chlorides with $NaBH_4$/RI according to the literature procedure (Fig. 1, Eq. (1), Table 1) [13–15].

The alkyl nitroxides were prepared according to the literature methods (Scheme 1 and Eq. (3)). *N*-benzylphthalaimide (**7**) reacted with Grignard reagents to yield amines **8a**–**c**. Subsequent debenzylation produced the methyl and ethyl amines **9a**–**c**. Oxidation of the resultant methylamines **9a**, **b** with sodium tungstate gave TMINOs **10a**, **b** (tetramethylisoindolylnitroxyl) in good yields [16]. The method was not effective for the preparation of **10c**. Instead, **9c** was successfully oxidized with *m*-CPBA to generate TEINO **10c** (tetraethylisoindolylnitroxyl) (Eq. (3)) [17].

$$H_2por \xrightarrow[PhCN]{RhCl_3} (PhCN)Rh(por)Cl \quad \textbf{1-3}\ 84\text{-}94\% \qquad (1)$$

$$Rh(por)Cl \xrightarrow[2.\ RBr\ or\ RI,\ 0\ ^\circ C,\ 15\ min]{1.\ NaBH_4,\ EtOH,\ 50\ ^\circ C,\ 1\ h} Rh(por)R \quad \textbf{4-6} \qquad (2)$$



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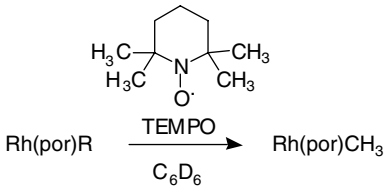

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Table 2 lists the results of the thermal reactions of TEMPO and rhodium porphyrin alkys (Eq. (4)). In the presence of excess TEMPO, $Rh(por)CH_3$ was formed from the thermolysis of $Rh(por)CH_2CH_2R$. Complexes with electron rich porphyrins of ttp and bttp reacted slower than that of bocp. The phenylethyl complexes were the most reactive while Rh(ttp)Et was the least reactive. No simple electronic effect exists for the beta-substituent of phenyl, cyanao, and methyl groups. The reactivity appears to decrease with increasing bond strengths of beta C–H bonds [18] (Table 2, entries 1, 7 and 8).

The reactions likely occurred via two consecutive steps with the formation of fairly long-lived intermediates. $Rh(bocp)CH_2CH_2Ph$ **6c** reacted with TEMPO (5 equiv.) completely within the first hour of the reaction without any $Rh(bocp)CH_3$ **6a** formed as determined by TLC analysis. Then after a total reaction time of 7 h, $Rh(bocp)CH_3$ **6a** was formed in 45% isolated yield. Increasing the amount

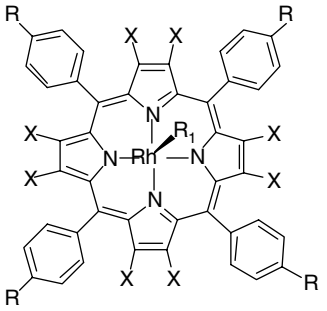
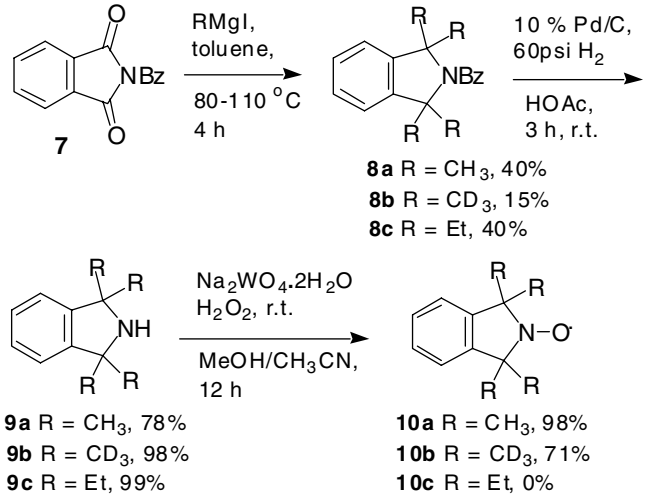


Fig. 1. Structures of rhodium porphyrins.

Table 1
Compound numbering and synthesis of Rh(por)R

Entry	Rh(por)Cl[a]	Rh(por)R	% Yield
1	Rh(ttp)Cl (**1**)	$Rh(ttp)CH_3$ (**4a**)	91
2	Rh(ttp)Cl (**1**)	$Rh(ttp)CH_2CH_3$ (**4b**)	59
3	Rh(ttp)Cl (**1**)	$Rh(ttp)CH_2CH_2CH_3$ (**4c**)	54
4	Rh(ttp)Cl (**1**)	$Rh(ttp)CH_2CH_2Ph$ (**4d**)	78
5	Rh(ttp)Cl (**1**)	$Rh(ttp)CH_2CH_2CN$ (**4e**)	79
6	Rh(bttp)Cl (**2**)	$Rh(bttp)CH_3$ (**5a**)	92
7	Rh(bttp)Cl (**2**)	$Rh(bttp)CH_2CH_2Ph$ (**5b**)	74
8	Rh(bocp)Cl (**3**)	$Rh(bocp)CH_3$ (**6a**)	97
9	Rh(bocp)Cl (**3**)	$Rh(bocp)CD_3$ (**6a–d$_3$**)	48
10	Rh(bocp)Cl (**3**)	$Rh(bocp)CH_2CH_3$ (**6b**)	69
11	Rh(bocp)Cl (**3**)	$Rh(bocp)CH_2CH_2Ph$ (**6c**)	85
12	Rh(bocp)Cl (**3**)	Rh(bocp) CH_2CH_2Ph (**6c***)	64
13	Rh(bocp)Cl (**3**)	$Rh(bocp)CH(CH_3)Ph$ (**6d**)	55
14	Rh(bocp)Cl (**3**)	$Rh(bocp)CH_2CH_2CN$ (**6e**)	71

[a] As mono PhCN adduct.



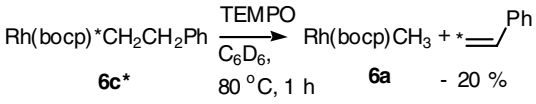
Scheme 1. Preparation of nitroxides.

Table 2
Summary of Thermolysis of Rh(por)R with TEMPO

Entry	Complex	TEMPO (equiv.)	Temp (°C)	Time for disappearance of complex	Total reaction time	% Yield of Rh(por)Me
1	Rh(ttp)CH_2CH_2Ph (**4d**)	5	80	48 h	6 d	**4a** 70[b]
2	Rh(bttp)CH_2CH_2Ph (**5b**)	5	80	48 h	6 d	**5a** 25b
3	Rh(bocp)CH_2CH_2Ph (**6c**)	5	80	15 min	7 h	**6a** 45b
4	Rh(bocp)CH_2CH_2Ph (**6c**)	15	80	15 min	90 min	**6a** 81[a]
5	Rh(bocp)CH_2CH_2Ph (**6c***)	15	80	15 min	90 min	**6a** 81a
6	Rh(bocp)$CH(CH_3)Ph$ (**6d**)	5	120	3 d	3 d	**6a** 70b
7	Rh(ttp)$CH_2CH_2CH_3$ (**4c**)	10	120	7d	7 d	**4a** 74b
8	Rh(ttp)CH_2CH_2 (**4b**)	10	120	N.A.[c]	14db	**4a** 10[d] (51[e])
9	Rh(ttp)CH_2CH_2CN (**4e**)	10	120	12 h	24 h	**4a** 86b
10	Rh(bocp)CH_2CH_2CN (**6e**)	10	120	12 h	24 h	**6a** 86b

[a] Isolated yield from column chromatography.
[b] Estimated yields from ^{1}H NMR integration.
[c] Only 19% of starting material converted.
[d] Based on 100% of starting material.
[e] Based on 19% staring material converted.

of TEMPO to 15 equiv. did not increase the rate of disappearance of **6c** but accelerated the rate of the formation and the yield of product **6a** (90 min and 81%). Since starting materials disappeared completely in most cases before Rh(por)CH_3 formed, a relatively stable rhodium porphyrin intermediate must be involved. More electron rich porphyrin rhodium alkyls such as **4d** and **5b** reacted with excess TEMPO similarly. The rate of disappearance of **3** was also found to be much faster than that of 1,2-rearangement to Rh(bocp)$CH(CH_3)Ph$ (10 h at 80 °C) [13a].



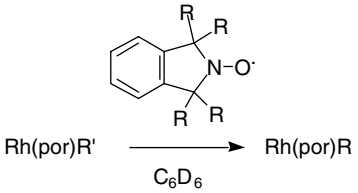
6c* 6a (5)

In order to elucidate the mechanism of the formation of Rh(por)CH_3 complexes especially the source of Me group in the product, the ^{13}C enriched phenylethyl rhodium complex **6c*** was reacted with TEMPO (Eq. (5)). The rhodium methyl group in **6a** was found to be un-enriched with ^{13}C and appeared as a broad singlet at −4.84 ppm in the ^{1}H NMR spectrum of the reaction mixture without any $^1J_{C-H}$ coupling observed. Therefore, the rhodium methyl group did not come from the α-carbon of the phenylethyl ligand of **6c***.

The proton coupled ^{13}C NMR spectrum of the reaction mixture also showed two enhanced triplets at 73.7 and 113.8 ppm with the $^1J_{C-H}$ equal to 148 and 157 Hz, respectively. At least two products were formed. The resonance at 113.8 ppm was assigned to the terminal sp^2 carbon of styrene and was quantified in 20% yield by ^{1}H NMR spectroscopy (cf. $\delta(C_6H_5CH{=}CH_2) = 112.3$ ppm, $^1J_{C-H}(CH_2{=}CH_2) = 156$ Hz in $CDCl_3$) [10]. The low yield of styrene was accounted by the partial oligomerization catalyzed by TEMPO [19]. However, the signal at 73.7 ppm could not be unambiguously assigned and is unlikely to be TEMPO–$^*CH_2CH_2Ph$. Therefore, the CH_2CH_2Ph fragment remained intact without any carbon–carbon bond cleavage. Only the Rh–C bond was cleaved in the reaction. Furthermore, the source of Me group in the products did not originate from the alkyl fragment of the starting (por)Rh–alkyl complexes.

We propose that the Me group in the product was transferred from one of the methyl groups in TEMPO via a carbon–carbon cleavage [12]. Labeling experiments were carried out to test the validity of the proposal. When TMINO–$(CD_3)_4$ was reacted with Rh(bocp)CH_2CH_2Ph, Rh(bocp)CD_3 was isolated 76% yield (Table 2, entries 1, Eq. (6)). Furthermore, ethyl–methine bond cleavage was also observed in the slower reaction of TEINO with Rh(bocp)CH_2CH_2Ph and Rh(bocp)Et was isolated in 90% yield. Indeed, this type of carbon–carbon bond activation in TMINO and TEINO with rhodium(II) porphyrin radical has been reported [12]. Therefore, the origin of alkyl group was identified to come form the alkyl group of nitroxides.

The generation of rhodium(II) porphyrin radical from the reactions of Rh(por)CH_2CH_2R with alkyl nitroxides could not be ascertained with pre-coordination of nitroxide. Attempted detection of such coordination in a mixture of nitroxide and Rh(por) CH_2CH_2R was not successful as no change in its visible spectrum was observed. Presumably, the strong *trans*-alkyl group does not favor TEMPO coordination. Therefore, the formation of Rh(por)R from the reaction of alkyl nitroxides with Rh(por)CH_2CH_2R involes a two step reaction: Firstly, rhodium(II) porphyrin radicals are generated and secondly, Rh^{II}(por) radicals undergo CCA with nitroxides to produce Rh(por)alkyl (Scheme 2) [8]. Kinetic studies by ^{1}H NMR proved to be difficult as the accuracy of integration was hampered by broadening caused by the excess TEMPO added.



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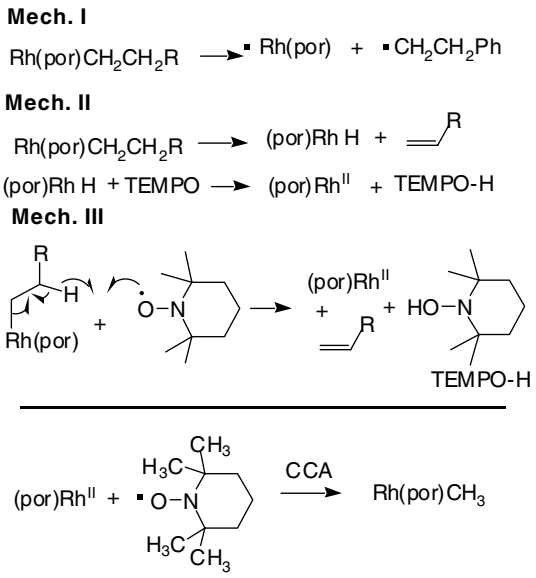

Scheme 2. Proposed mechanism for Rh(por)CH_3 from Rh(por)-CH_2CH_2R.

Three mechanistic possibilities exist for the generation of Rh(por) radicals: (**I**) homolysis of a rhodium alkyl bond, (**II**) beta-hydride elimination of Rh(por)CH_2CH_2R to Rh(por)H – hydrogen abstraction with TEMPO [11] and (**III**) beta-hydrogen abstraction of Rh(por)CH_2CH_2R with TEMPO – Rh-alkyl homolysis.

Mechanism **I** is disfavored based on the unlikely homolysis of the rather strong Rh–C bond at 120 °C (B.D.E. ~60 kcal/mol) [12,13] as well as the absence of $PhCH_2CH_2$–TEMPO in the presence of excess, efficient spin trap of TEMPO. Though mechanism **II** is apparently supported by the established intermediate of Rh(por)H, which is generated via beta-hydride elimination in the 1,2-rearrangements of Rh(por)CH_2CH_2R [13] and is known to react with TEMPO to give Rh(por) radical,[7] the rates of disappearance of the starting materials were, however, much faster in the presence of TEMPO. In the absence of TEMPO, the 1,2-rearrangements of Rh(bocp)CH_2CH_2Ph and Rh(ttp)CH_2CH_2Ph took 10 h [13a] and 144 h [13b] at 80 °C, respectively. Similarly, the 1,2-rearrangements of Rh(bocp)CH_2CH_2CN and Rh(ttp)CH_2CH_2CN at 140 °C required 9 and 24 days, respectively, and the rearrangement of Rh(ttp)Pr into Rh(ttp)CH(Me)Me took 52 h at 120 °C. All these rearrangements are much slower than the reactions with TEMPO. Furthermore, the formation of 1,2-rearrangement products as the intermediates is unlikely since Rh(bocp)$CH(CH_3)Ph$ (**6e**) is also much less reactive than Rh(bocp)CH_2CH_2Ph in the reaction with TEMPO (Table 2, entry 6). Therefore, Rh(por)CH_2CH_2Ph and other alkyls must react with TEMPO directly. Mechanism **III** remains the most probable. Abstraction of the fairly weak C–H bond α to Ph, CN, and Me groups in these rhodium complexes is energetically feasible at the reaction temperature from 80 to 120 °C and the reaction rates increased with decreasing C–H bond strengths (bond disscoication energy (B.D.E.) $PhCH_2$–H = 88 kcal/mol, ^{18}Me(H)(CN)C–H = 90 kcal/mol [18], Me(Me)CH_2–H = 95 kcal/mol [18], $MeCH_2$–H = 98 kcal/mol [18], TEMPO–H = 70 kcal/mol [18]). The hydrogen abstraction step may be synchronous with the homolysis of Rh–C bond to generate a Rh(por) radical. Alternatively, a sufficiently long-lived carbon-centered radical stabilized by the beta-Rh(por) could exist before Rh–C homolysis [20–22a]. The detailed nature of the transfer of methyl or ethyl group from the nitroxides to Rh(II) porphyrins is not very clear at this stage. It is likely that Rh(II)-nitroxide adduct can initially form as TEMPO–transition metal complexes are reported in the literature [22,23]. Then the alkyl group can transfer in an SH2 or S_N2 like manner to give the rhodium porphyrin alkyls. Further studies are required to understand the details of the carbon carbon bond cleavage (see Table 3).

Table 3
Summary of reactions of Rh(por)CH_2CH_2Ph with nitroxides at 80 °C

Entry	Complex	Nitroxide (5 equiv.)	Total reaction time	Rh(por)R % yield
1	Rh(ttp)CH_2CH_2Ph (**4d**)	TMINO	6 d	**4a** 70
2	Rh(bocp)CH_2CH_2Ph (**6c**)	TMINO	14 h	**6a** 76
3	Rh(bocp)CH_2CH_2Ph (**6c**)	TMINO–Me_d	18 h	**6a**–**d**$_3$ 76
4	Rh(bocp)CH_2CH_2Ph (**6c**)	TEINO	54 h	**6b** 90

3. Summary

In conclusion, we have discovered a non-radical trapping pathway for reactions of nitroxides with rhodium porphyrin alkyls bearing beta hydrogens. Rhodium(II) porphyrins are formed by the beta-hydrogen elimination of the alkyl group. Subsequently rhodium porphyrins can coordinate with excess nitroxides to form Rh(II)-nitroxides adducts. Then these adducts undergo carbon–carbon bond activation at the methine–alkyl bonds of the nitroxides to yield rhodium porphyrin alkyls. In view of the roles of nitroxides as reagents, the innocent nature of TEMPO and related nitroxides as radical traps in the determination of bond energies of metal–alkyls bearing β-hydrogens, especially stronger ones, needs to be cautioned.

4. Experimental

All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Rhodium trichloride ($RhCl_3 \cdot xH_2O$) was obtained from Johnson Matthey. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under N_2. Benzene was distilled from sodium. Dichloromethane and acetonitrile were distilled from calcium

hydride. Benzene-d_6 was vacuum distilled from sodium, degassed twice by freeze–thaw–pump cycle and stored in a Teflon screwhead stoppered flask. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) was sublimed under high vacuum.

Thin layer chromatography was performed on precoated silica gel plates. Column chromatography was performed on silica gel (70–230 and 230–400 mesh) or neutral aluminum oxide (activity I, 70–230 mesh).

^{1}H NMR spectra were recorded on either a Bruker WM-250 (250 MHz), Bruker DPX-300 (300 MHz) or a Bruker AMX-500 (500 MHz) spectrometer. Chemical shifts were referenced with the residual solvent protons in C_6D_6 (δ 7.15 ppm), $CDCl_3$ (δ 7.24 ppm) or with tetramethylsilane (d 0.00 ppm) as the internal standard. Chemical shifts (d) were reported as part per million (ppm) in δ scale downfield from TMS. Coupling constants (J) were reported in Hertz (Hz). ^{13}C NMR spectra were recorded on either a Bruker WM-250 (62.89 MHz), Bruker DPX-300 (75.47 MHz) or a Bruker AMX-500 (125.77 MHz) spectrometer. Chemical shifts were referenced to the solvent peak of C_6D_6 (δ 128.0 ppm) or $CDCl_3$ (δ 77.0 ppm). Coupling constants (J) were reported in Hertz (Hz).

Mass spectra were recorded on either a VG7070F mass spectrometer (E.I. 70 ev), Hewlett–Packard 5989B mass spectrometer (FAB-MS and E.I. 70 ev), Bruker APEX 47e FT-ICR mass spectrometer (FAB-MS and ESI-MS) or MAT-95L spectrometer (FAB-MS). Fast atom bombardment spectra were obtained using 3-nitrobenzyl alcohol (NBA) as the matrix. Electrospray ionization spectra were obtained with a solvent mixture of acetone with 3% of acetic acid.

IR spectra were obtained on a FT-IR spectrophotometer. Samples were prepared either as neat film on KBr plates or as a KBr pressed disk.

4.1. Chloro(5,10,15,20-tetratoylporphyrinato)(benzonitrile)rhodium(III) [Rh(ttp)Cl(PhCN)] (1)

A solution of H_2ttp (350 mg, 0.522 mmol) and $RhCl_3 \cdot xH_2O$ (206 mg, 0.78 mmol) in benzonitrile (30 mL) was refluxed in air for 2 h until the solution was changed from purple to bright red in color. The solvent was then removed under high vacuum and the crude product was purified by column chromatography over silica gel (70–230 mesh) eluting with a solvent mixture of hexane/CH_2Cl_2 (1:4). The major red band was collected. After removal of solvent by rotary evaporation, a red solid (401 mg, 0.44 mmol, 84%) was obtained and was further purified by recrystallization from CH_2Cl_2/CH_3OH. $R_f = 0.29$ (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.70 (s, 12H), 5.33 (d, 2H, $J = 7.5$ Hz), 6.63 (m, 2H), 6.95 (t, 1H, $J = 7.5$ Hz), 7.50–7.56 (m, 8H), 8.07 (d, 4H, $J = 7.5$ Hz), 8.20 (d, 4H, $J = 7.5$ Hz) 8.94 (s, 8H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 21.49, 121.05, 127.04, 127.50, 128.25, 131.16, 132.16, 133.26, 134.14, 134.76, 137.10, 139.51, 142.66; UV–Vis (CH_2Cl_2), λ_{max}, nm (log e) 424.0 (5.39), 535.0 (4.34), 570.5 (3.76); HRMS (ESI): Calc. for $(C_{48}H_{36}N_4RhCl)^+$ (after vacuum removal of PhCN): m/z 806.1678. Found: m/z 806.1669. Anal. Calc. for $C_{48}H_{36}N_4RhCl$ (after vacuum removal of PhCN): C, 61.46; H, 4.13; N, 5.73. Found: C, 61.72; H, 4.61; N, 5.86%.

4.2. Preparation of chloro[5,10,15,20-tetrakis(p-tert-butylphenyl)porphyrinato](benzonitrile)rhodium(III) [Rh(bttp)(Cl)(PhCN)] (2)

A solution mixture of *p-tert*-butyltoluene (44.8 g, 300 mmol), NBS (81.9 g, 460 mmol) and benzoylperoxide (0.27 g, 1.1 mmol) in CCl_4 (200 mL) was refluxed in air for 4 h. The reaction mixture was cooled to rt and was filtered. The filtrate was rotary evaporated and the yellow oily liquid obtained was added to a solution mixture of hexamethylenetetramine (115 g, 820 mmol) in H_2O (100 mL) and EtOH (100 mL). The mixture was refluxed in air for 4 h. Concentrated HCl (50 mL) was added and the mixture was refluxed for another 30 min. The reaction mixture was cooled to room temperature and was worked up by extraction with diethyl ether. The combined organic extract was dried ($MgSO_4$) and filtered. After rotary evaporation, a yellow oily liquid of *p-tert*-butylbenzaldehyde (41.5 g, 256 mmol, 86%) was obtained. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.34 (s, 9H), 7.53 (d, 2H, $J = 8.4$ Hz), 7.79 (d, 2H, $J = 8.4$ Hz), 9.96 (s, 1H).

Pyrrole (23.5 mL, 0.34 mol) was added dropwise to a refluxing solution of *p-tert*-butylbenzaldehyde (55 g, 0.34 mol) in propionic acid (1.25 L). The resulting mixture was refluxed in air for another 30 min. The resulting black solution was cooled to room temperature, and MeOH (1.5 L) was added to crystallize the porphyrin. The mixture was filtered and the purple solid obtained was washed with MeOH. After purified by recrystallization from $CHCl_3$/MeOH, purple crystals of 5,10,15,20-tetrakis(*p-tert*-butylphenyl)porphyrin [22] [H_2(bttp)] (9.55 g, 0.011 mol, 13%) was obtained. $R_f = 0.71$ (hexane/$CH_2Cl_2 = 1:1$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ − 2.76 (s, 2H), 1.60 (s, 36H), 7.75 (d, 8H, $J = 8.2$ Hz), 8.14 (d, 8H, $J = 8.2$ Hz), 8.86 (s, 8H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 31.8, 34.9, 121.1, 123.2, 123.7, 128.2, 131.1, 132.2, 133.3, 134.1, 134.6, 139.4, 142.6, 150.3; UV–Vis (CH_2Cl_2), λ_{max}, nm (log e) 419.0 (5.67), 517.0 (4.23), 553.0 (4.02), 591.0 (3.73), 648.0 (3.78); HRMS (FAB): Calc. for $(C_{60}H_{62}N_4)^+$: m/z 838.4969. Found: m/z 838.4962.

2 was synthesized from H_2(bttp) (300 mg, 0.358 mmol) and $RhCl_3 \cdot xH_2O$ (200 mg, 0.752 mmol). Red solid (311 mg, 0.319 mmol, 89%) was obtained and was further purified by recrystallization from CH_2Cl_2/CH_3OH. $R_f = 0.50$ (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.60 (s, 36H), 5.31 (d, 2H, $J = 7.7$ Hz), 6.60–6.66 (m, 2H), 6.97 (t, 1H, $J = 7.8$ Hz), 7.68–7.76 (m, 8H), 8.08 (d, 4H, $J = 8.0$ Hz), 8.24 (d, 4H, $J = 8.0$ Hz), 8.93 (s, 8H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 31.8, 34.9, 121.1, 123.2, 123.7, 128.2, 131.1, 132.2, 133.3, 134.1, 134.6, 139.4, 142.6, 150.3; UV–Vis (CH_2Cl_2), λ_{max}, nm (log e) 425.0

(5.30), 535.5 (4.25), 571.0 (3.74); HRMS (FAB): Calc. for $(C_{60}H_{60}N_4RhCl)^+$: m/z 974.3556. Found: m/z 974.3560.

4.3. Preparation of chloro[2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(p-tert-butylphenyl)porphyrinato](benzonitrile)rhodium(III) [Rh(bocp)(Cl)(PhCN)] (3) [13a,24]

A suspension of H_2(bttp) (1.0 g, 1.2 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.6 g, 2.4 mmol) in DMF (100 mL) was refluxed for 1.5 h. The color of the suspension changed from purple to reddish purple. The reaction mixture was cooled to room temperature and was worked up by extraction with $CHCl_3/H_2O$. The combined organic extract was rotary evaporated and the reddish purple residue obtained was purified by recrystallization with $CHCl_3$/MeOH to give a reddish purple crystalline solid of 5,10,15,20-tetrakis(*p-tert*-butylphenyl)porphyrinato nickel(II) Ni(bttp) (0.94 g, 1.1 mmol, 87%). $R_f = 0.51$ (hexane/$CH_2Cl_2 = 2:1$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.55 (s, 36H), 7.68 (d, 8H, $J = 8.2$ Hz), 7.94 (d, 8H, $J = 8.2$ Hz), 8.77 (s, 8H); UV–Vis (CH_2Cl_2), λ_{max}, nm (log e) 414.0 (5.47), 528.0 (4.31), 614.0 (3.04).

Ni(bttp) (0.94 g, 1.1 mmol) and NCS (1.68 g, 12.6 mmol) were dissolved in *o*-dichlorobenzene (100 mL) and the mixture was heated at 140 °C. The reaction was monitored by UV–Vis spectroscopy until the Soret band shifted from 416 to 442 nm (about 2.5 h). The solvent was then removed under high vacuum. The dark red residue was purified by flash column chromatography over neutral alumina using $CHCl_3$ as the eluent. The major red band was collected. After removal of solvent by rotary evaporation, a dark red solid of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(*p-tert*-butylphenyl)porphyrinto nickel(II) [Ni(bocp)] (1.0 g, 0.86 mmol, 82%) was obtained. $R_f = 0.17$ (hexane/$CH_2Cl_2 = 2:1$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.49 (s, 36H), 7.64 (d, 8H, $J = 8.3$ Hz), 7.78 (d, 8H, $J = 8.3$ Hz); UV–Vis (CH_2Cl_2), λ_{max}, nm (log e) 442.5 (5.42), 554.5 (4.31). HRMS (FAB): Calc. for $(C_{60}H_{52}^{35}Cl_6^{37}Cl_2N_4Ni)^+$: m/z 1170.0989. Found: m/z 1170.0979.

Concentrated sulfuric acid (100 mL) was added to a solution of Ni(bocp) (1.0 g, 0.86 mmol) in CH_2Cl_2 (150 mL). The mixture was stirred at room temperature for 30 min. The resulting green suspension was then poured onto ice cubes and the mixture was extracted with CH_2Cl_2/H_2O. The combined green organic extract was neutralized with Na_2CO_3, washed with saturated NaCl solution, dried ($MgSO_4$), and filtered. The solvent was then removed by rotary evaporation. The greenish blue crude product obtained was purified by column chromatography over silica gel (100–200 mesh) eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1). The fast moving brown fraction was discarded. The column was then eluted with CH_2Cl_2 and the major green band was collected. After removal of solvent by rotary evaporation, a greenish blue solid of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(*p-tert*-butylphenyl)porphyrin [H_2(bocp)] (0.85 g, 0.76 mmol, 88%) were obtained. $R_f = 0.26$ (hexane/$CH_2Cl_2 = 2:1$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.52 (s, 36H), 7.74 (d, 8H, $J = 7.8$ Hz), 8.06 (d, 8H, $J = 7.8$ Hz); UV–Vis (CH_2Cl_2), λ_{max}, nm (log e) 359.5 (4.28), 457.0 (5.22), 555.5 (3.86), 612.0 (4.04), 723.0 (3.78). LRMS (FAB): Calc. for $(C_{60}H_{54}^{35}Cl_6^{37}Cl_2N_4)^+$: m/z 1114. Found: m/z 1114.

[Rh(bocp)(Cl)(PhCN)]**3** was synthesized from H_2(bocp) (500 mg, 0.45 mmol) and $RhCl_3 \cdot xH_2O$ (142 mg, 0.54 mmol). The crude product was purified by column chromatography over silica gel (70–230 mesh) eluting with a solvent mixture of hexane/CH_2Cl_2 (2:3). The fast moving green fraction was discarded and the major red fraction that eluted off with CH_2Cl_2 was collected. After rotary evaporation, a reddish brown solid (573 mg, 0.423 mmol, 94%) was obtained. The product was further purified by recrystallization from CH_2Cl_2/CH_3OH. $R_f = 0.62$ (hexane/$CH_2Cl_2 = 2:3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.55 (s, 36H), 5.69 (d, 2H, $J = 7.7$ Hz), 6.77–6.83 (m, 2H), 7.12 (t, 1H, $J = 7.3$ Hz), 7.61–7.76 (m, 8H), 8.01 (m, 8H); UV–Vis (CH_2Cl_2), λ_{max}, nm (log e) 373.0 (4.36), 449.0 (5.18), 561.5 (4.24); IR (KBr, cm^{-1}) n 2862, 2267, 1596; HRMS (FAB): Calc. for $(C_{60}H_{52}^{35}Cl_7^{37}Cl_2N_4Rh)^+$: m/z 1250.0379. Found: m/z 1250.0376. Anal. Calc. for $C_{60}H_{52}Cl_9N_4Rh$: C, 57.60; H, 4.19; N, 4.48. Found: C, 57.43; H, 4.36; N, 4.62%.

4.4. Preparation of (5,10,15,20-tetratoylporphyrinato)2-ethylrhodium(III) [Rh(ttp)CH_2CH_3] (4b)

A suspension of Rh(ttp)Cl (100 mg, 0.110 mmol) in EtOH (50 mL) and a solution of $NaBH_4$ (41 mg, 0.120 mmol) in aq NaOH (0.1 M, 3 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannular. The solution mixture was heated at 50 °C under N_2 for 1 h to give a brown suspension. The solution was then cooled to 30 °C under N_2 and ethyl bromide (119 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After stirred at room temperature for another 15 min under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250–400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (4:1) as the eluent. The major orange fraction was collected and gave a reddish orange solid (45 mg, 0.063 mmol, 59%) as the product after rotary evaporation. ^{1}H NMR ($CDCl_3$, 300 MHz) δ − 4.86 (dq, 2H, $^2J_{Rh-H} = 3.0$ Hz, $^3J_{H-H} = 6.0$ Hz), −4.45 (t, 3H, $J = 6.0$ Hz), 2.69 (s, 12H), 7.53 (t, 8H, $J = 6.3$ Hz), 8.03 (d, 4H, $J = 7.2$ Hz), 8.08 (d, 4H, $J = 7.5$ Hz), 8.71 (s, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.4 (d, $J = 27.0$ Hz), 13.2, 21.7, 122.5, 127.5, 131.5, 133.8, 134.1, 137.3, 139.5, 143.4. LRMS (FAB): Calc. for $(C_{50}H_{41}N_4Rh)^+$: m/z 800. Found: m/z 800. Anal. Calc. for $C_{50}H_{41}N_4Rh$: C, 74.99; H, 5.16; N, 6.99. Found: C, 75.11; H, 5.24; N, 6.80%.

4.5. Preparation of [2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(p-tert-butylphenyl)porphyrinato]phenethyl-1-^{13}C-rhodium(III) [Rh(bocp)*CH_2CH_2Ph] (*6c)

Lithium aluminum hydride (140 mg, 3.66 mmol) in freshly distilled THF (20 mL) was stirred at room temperature under N_2 for 30 min. The gray suspension was then cooled to 0 °C and phenylacetic-*carboxy*-^{13}C acid (250 mg, 1.83 mmol) in THF (5 mL) was added dropwise. The resulting mixture was stirred at room temperature for about 16 h under N_2. Diethyl ether (saturated with H_2O) was then added dropwise to destroy with excess LAH. The gray suspension was filtered and the filtrate was dried ($MgSO_4$) and filtered. After removal of solvent, the colorless oily liquid of 2-phenylethanol-*1*-^{13}C (Ph–CH_2–$^{13}CH_2$–OH) was obtained without further purification. $R_f = 0.16$ (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.83–2.87 (m, 2H), 3.81 (dt, 2H, $^3J_{H-H} = 7.0$ Hz, $^1J_{C-H} = 150.5$ Hz), 4.99 (bs, 1 H), 7.32–7.20 (m, 5 H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 39.7 (d, $^1J_{C-C} = 36.0$ Hz), 64.0 (^{13}C enriched), 126.9, 129.0, 129.6, 139.9.

Triphenylphosphine (580 mg, 2.2 mmol) was dissolved in freshly distilled CH_2Cl_2 (15 mL) at 0 °C in a round bottom flask fitted with a drying tube. Bromine (350 mg, 2.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The mixture was stirred at rt for 1 h and then cooled to 0 °C. The crude reaction product of 2-phenylethanol-*1*-^{13}C was dissolved in CH_2Cl_2 (5 mL) and the solution was added dropwise to the reaction mixture. The mixture was then stirred at room temperature for another 90 min and then worked up by washing with saturated aqueous $Na_2S_2O_3$ aq, $NaHCO_3$ aq, H_2O and brine successively. The organic extract was dried ($MgSO_4$) and filtered. Hexane was added to the filtrate and the precipitated triphenylphosphine oxide was filtered. The filtrate was rotary evaporated and purified by silica gel column chromatography using hexane as the eluent. The first fast moving colorless fraction was discarded and the following colorless fraction [$R_f = 0.36$ (hexane)] was collected. After removal of solvent, a colorless oily liquid (182.4 mg, 0.98 mmol, 54% from phenylacetic-*carboxy*-^{13}C acid) was collected. $R_f = 0.36$ (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.14–3.19 (m, 2H), 3.57 (dt, 2H, $^3J_{H-H} =$ 7.5 Hz, $^1J_{C-H} = 153$ Hz), 7.20–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 125.8 Hz) δ 32.9 (^{13}C enriched), 39.4 ($^1J_{C-C} =$ 35.0 Hz), 126.9, 128.6, 138.9; LRMS (EI): Anal. Calc. *m*/*z* (rel int) 187 ($M^+ + 2$, 100), 185 (M^+, 78).

*__6c__ was synthesized from 2-phenylethyl-*1*-^{13}C bromide (100 mg, 0.074 mmol) and **10** (55 mg, 0.30 mmol). A reddish orange solid (62.6 mg, 0.047 mmol, 64%) was obtained after purified by column chromatography. The product was further purified by recrystallization from CH_2Cl_2/CH_3OH. $R_f = 0.59$ (hexane/$CH_2Cl_2 = 5:1$); ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta -3.99$ (dt, 2H, $^3J_{H-H} = 6.6$ Hz, $^1J_{C-H} = 143.2$ Hz), −2.53 to (−2.48) (m, 2H), 1.52 (s, 36H), 5.06 (d, 2H, $J = 7.7$ Hz), 6.46–6.50 (m, 2H), 6.60 (t, 1H, $J = 7.2$ Hz), 7.67–7.74 (m, 8 H), 7.86 (d, 4H, $J = 7.5$ Hz), 7.94 (d, 4H, $J = 7.5$ Hz); ^{13}C NMR (C_6D_6, 125.8 MHz) δ 19.04 (^{13}C enriched, d, $^1J_{Rh-C} = 26.9$ Hz); LRMS (FAB): $(C_{67}^{13}C_1H_{61}N_4Rh^{35}Cl_6^{37}Cl_2)^+$ *m*/*z* 1321. Found: *m*/*z* 1322 ($M^+ + 1$).

4.6. Preparation of 2-benzyl-1,1,3,3-tetramethylisoindoline (*8a*)

A solution of MeMgI, prepared from methyl iodide (4.8 mL, 60 mmol) and magnesium powder (1.52 g, 62.5 mmol) in anhydrous diethyl ether (35 mL) under N_2, was concentrated by high vacuum until the suspension did not boil at 80 °C. The residue was allowed to cool to 60 °C, and a solution of *N*-benzylphthalimide (**7**) [25] (2.37 g, 10 mmol) in toluene (30 mL) was added dropwise with stirring through a cannula under N_2. Solvents were partially removed by high vacuum until the reaction mixture was slightly refluxed at 110 °C. The reaction mixture was heated at 110 °C for 4 h. The solvents were then further removed until ~15 mL was left. The slurry reaction mixture was diluted with hexane (25 mL). It was then filtered through celite and washed with hexane (3 × 5 mL). The yellow organic filtrate turned to a purple suspension after standing in air for 2 h. After rotary evaporation, the purple crude product was chromatographed through alumina (basic, grade I, 70–230 mesh) eluting with hexane to give a white solid of 2-benzyl-1,1,3,3-tetramethylisoindoline (**8a**) (1.05 g, 40%). $R_f = 0.14$ (hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (s, 12H), 3.99 (s, 2H), 7.09–7.16 (m, 2H), 7.19–7.31 (m, 5 H), 7.43–7.48 (m, 2H). GCD (column program: initial temperature 100 °C, duration 2 min; increment rate 20 °C/min; final temperature 280 °C, duration 15 min) t_R 9.96 min; LRMS (EI): Calc. for $(C_{19}H_{23}N)^+$: *m*/*z* 265. Found: *m*/*z* 265.

4.7. Preparation of 1,1,3,3-tetramethylisoindoline (*9a*) [17]

2-Benzyl-1,1,3,3-tetramethylisoindoline (**8a**) (550 mg, 2.1 mmol) and 10% Pd/C (50 mg) were suspended in HOAc (10 mL) in a 25 mL conical flask with a magnetic stirrer bar. The reaction flask was placed in a high pressure reactor. The reactor was charged with hydrogen (60 psi) and released (20 psi) for three cycles and was finally pressurized with hydrogen at 60 psi. After stirring for 3 h at room temperature, the reaction mixture was then neutralized with NaOH to pH 9 and extracted with ether (3 × 10 mL). The organic extract was then dried over $MgSO_4$, filtered and rotary evaporated to dryness. The crude oily product was purified by chromatography over a short alumina column eluting with hexane:ethyl acetate (3:1) to yield colorless crystals (286 mg, 78%), $R_f = 0.06$ (hexane:ethyl acetate = 3:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.48 (s, 12H), 2.13 (br s, 1H), 7.10–7.15 (m, 2H); 7.23–7.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 31.79, 63.02, 121.42, 127.17, 148.42.

4.8. Preparation of 1,1,3,3-tetramethylisoindolin-2-oxyl (**10a**) [25]

To the pale yellow solution of 1,1,3,3-Tetramethylisoindoline (**9a**) (148 mg, 0.84 mmol) in MeOH:CH_3CN (14:1) (2 mL), $NaHCO_3$ (56 mg, 0.67 mmol) and $Na_2WO_4 2H_2O$ (8 mg, 0.025 mmol) were added to a suspension [16]. 30% H_2O_2 (~0.3 mL) was then added and the suspension turned to pink in color. After 12 h, a bright yellow solution formed and 30% H_2O_2 (~0.3 mL) was added. The reaction mixture was stirred for 2 days. The product was extracted from hexane (3 × 5 mL). The organic layer was washed with H_2O, brine, dried over $MgSO_4$, filtered and rotary evaporated to dryness to give a yellow solid (157 mg, 98%). $R_f = 0.63$ (hexane:ethyl acetate = 3:1); GCD (column program: initial temperature 100 °C, duration 2 min; increment rate 20 °C/min; final temperature 280 °C, duration 15 min) t_R 6.51 min; LRMS (EI): Calc. for $(C_{12}H_{16}NO)^+$: *m/z* 190. Found: *m/z* 190.

4.9. Reactions of porphyrinatorhodium(III) alkyls with nitroxides

General procedure. Rh(por)R (recrystallized from CH_2Cl_2/CH_3OH, ~0.01 mmol) and TEMPO (5–10 equiv.) were dissolved in C_6D_6 (0.40 mL) in an NMR tube. The solution was degassed for three freeze–thaw–pump cycles and the NMR tube was flame sealed under high vacuum. The reaction mixture was heated in an oil bath and protected from light and the progress of the reaction was monitored by ^1H NMR spectroscopy. The composition of the reaction mixture were estimated by ^1H NMR integration with reference to either the residual proton resonance of C_6D_6 or tetrakis(trimethylsilyl)silane (1.0 mg added as the internal standard).

4.10. Reaction between Rh(bocp) CH_2CH_2 Ph and 1,1,3,3-tetramethyl-isoindolin-2-oxyl (**12a**)

To a Teflon screwhead stoppered flask, Rh(bocp)(CH_2-CH_2Ph) (13 mg, 9.8 mmol) and 1,1,3,3-tetramethyl-isoindolin-2-oxyl **12a** (9.4 mg, 0.049 mmol) were charged with benzene (2 mL) to form a red solution. The reaction mixture was degassed by freeze–pump–thaw method (three cycles) and filled with N_2. The reaction mixture was then heated at 80 °C for 14 h in the absence of light. After removal of solvent by rotary evaporation, the crude product was chromatographed on silica gel (70–230 mesh) using hexane:CH_2Cl_2 (10:1) to hexane:CH_2Cl_2(5:1) as the gradient eluent to give the red solid of Rh(bocp)CH_3 **6a** (9.2 mg, 76%) was obtained. $R_f = 0.23$ (hexane:CH_2Cl_2 = 5:1); ^1H NMR ($CDCl_3$, 300 MHz) δ −4.87 (d, $^2J_{RhH} = 2.7$ Hz, 3H), 1.53 (s, 36H), 7.68 (d, $J = 8.6$ Hz, 8H), 7.90 (m, 8H).

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Appendix A. Supplementary material

Supplementary data associated with this article for the compound characterization can be found. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.009.

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