Conversion of Ni(II)−Allylporphyrins to α,β-Unsaturated Formylporphyrins via a Nickel-Promoted Reaction

ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · AUGUST 2007

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Conversion of Ni(II)-Allylporphyrins to α,β-Unsaturated Formylporphyrins via a Nickel-Promoted Reaction

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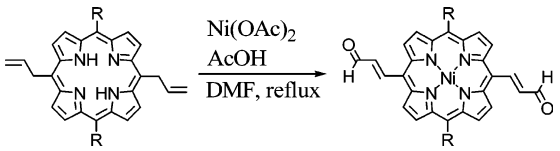
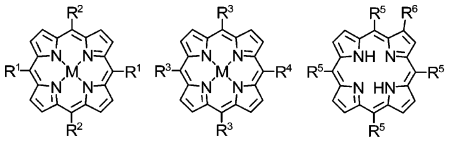
Received March 16, 2007



A new route to α,β-unsaturated formylporphyrins begins with the synthesis of allyl-substituted porphyrins via the Suzuki cross-coupling reaction of bromoporphyrins and allylboronic acid pinacol ester in 50−95% yield. Treatment of allyl-substituted porphyrins with nickel acetate in *N*,*N*-dimethylformamide (DMF) then affords mono- and diacroleinylporphyrins in up to 70% yield.

Porphyrins containing unsaturated side chains or extended π-conjugated substituents are of growing interest due to their potential applications in medicine[1] (photodynamic therapy, HIV treatment, neutron capture therapy) and as optical devices in material sciences.[2−4] Allyl-substituted porphyrins can be employed in electronic devices and it has been shown that they can be linked covalently to silicon wafers.[5] Previous syntheses of *meso*-allylporphyrins used the condensation of 5-allyldipyrromethane with a dipyrromethane-dicarbinol in 44% yield,[5] while 2,3-diallylporphyrins were prepared in 14−48% yield through Suzuki coupling reactions.[6]

The acroleinyl group as a substituent in the β-position has been shown to be a useful precursor for the synthesis of benzochlorins.[7] One method for their synthesis involves three steps using a sequence of formylation and Wittig reaction to yield the nickel(II) monoacroleinylporphyrin complex in 85%.[8] Alternatively, vinylogous Vilsmeier formylation may be used to prepare the monoacroleinylporphyrin in 85% yield and the 5,10-diacroleinylporphyrin in 55% yield.[7a] For the preparation of porphyrins with α,β-unsaturated substituents in the 5,15-positions, the Heck reaction has been employed to yield the bis(2-methoxycarbonylethenyl)-substituted porphyrin in 72% yield.[9] Here, we report a new synthetic route to mono- and diacroleinylporphyrins in the meso position from allyl-substituted precursors via a Ni-catalyzed reaction in up to 70% yield. A series of allylporphyrins with different substitution patterns in meso and β-positions have been prepared by the Suzuki cross-coupling of bromoporphyrins with allylboronic acid pinacol ester.



1 R¹=Ph; R³=H; M=2H
2 R¹=3-OMePh; R²=H; M=2H
3 R¹=3-OMePh; R²=H; M=Ni
4 R¹=4-MePh; R²=H; M=2H
5 R¹=4-MePh; R²=H; M=Ni
6 R¹=n-C_6H_{13}; R²=H; M=2H
7 R¹=n-C_6H_{13}; R²=H; M=Ni
8 R³=4-MePh; R⁴=H
9 R¹=Ph; R²=Br; M=2H
10 R¹=Ph; R²=allyl; M=Zn
11 R¹=3-OMePh; R²=Br; M=2H
12 R¹=3-OMePh; R²=Br; M=Ni
13 R¹=4-MePh; R²=Br; M=2H
14 R¹=4-MePh; R²=Br; M=Ni
15 R¹=*n*-C_6H_{13}; R²=Br; M=2H
16 R¹=*n*-C_6H_{13}; R²=Br; M=Ni
17 R³=4-MePh; R⁴=Br; M=2H
18 R³=4-MePh; R⁴=allyl; M=Ni
19 R⁵=Ph; R⁶=H
20 R⁵=Ph; R⁶=Br

To introduce the allyl substituent into the porphyrin moiety, the Suzuki cross-coupling reaction was chosen.[10] With high regio- and stereoselectivity as well as tolerance toward a wide range of functional groups, this method provides a very straightforward approach for the introduction of various substituents.[11] Hence it has been widely used in porphyrin chemistry, mostly with brominated porphyrins and organoboron reagents as coupling partners[12] but also as a powerful tool for the preparation of porphyrin arrays.[13] Therefore the 5,15-substituted compounds **1**−**7**[14−16] and the 5,10,15-substituted compound **8**[17] were brominated according to standard conditions (*N*-bromosuccinimide, NBS, in chloroform in the presence of pyridine)[18] to give the corresponding 5,15-dibromoporphyrins **9**−**16** in 62−90% yield and the 5-bromoporphyrin **17** in 84% yield.

Likewise, tetraphenylporphyrin **19** was brominated according to the literature[19] to yield the β-monobrominated analogue **20**. The Suzuki cross-coupling reaction of the bromo compounds **9**, **11**−**15**, **17,** and **19** was carried out under standard conditions

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10.1021/jo070550g CCC: $37.00
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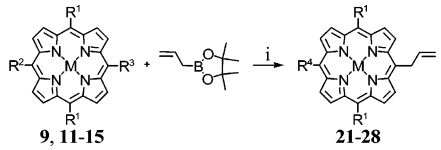
SCHEME 1



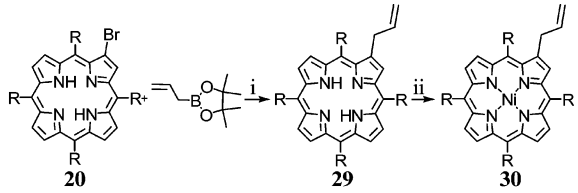
9, **11-15**
17

21-28

i: porphyrin (1 equiv.), boronic ester (10-20 equiv.), K_3PO_4 (20-40 equiv.), Pd-catalyst (0.1 equiv.), THF, reflux.

Entry	R^1	R^2	R^3	R^4	M	Product	Yield
9	Ph	Br	Br	Allyl	2H	**21**	88 %
11	3-MeOPh	Br	Br	Allyl	2H	**22**	95 %
12	3-MeOPh	Br	Br	Allyl	Ni	**23**	55 %
13	4-MePh	Br	Br	Allyl	2H	**24**	86 %
14	4-MePh	Br	Br	Allyl	Ni	**25**	88 %
15	*n*-C_6H_{13}	Br	Br	Allyl	2H	**26**	50 %
16	*n*-C_6H_{13}	Br	Br	Allyl	Ni	**27**	95 %
17	4-MePh	4-MePh	Br	4-MePh	2H	**28**	74 %

SCHEME 2



20 **29** **30**

R=Ph

i: porphyrin (1 equiv.), boronic ester (5 equiv.), K_2CO_3 (10 equiv.), $Pd(PPh_3)_4$ (0.1 equiv.),toluene, reflux; ii: porphyrin (1 equiv.), $Ni(OAc)_2$ (2 equiv.), AcOH (0.2 mL), DMF, reflux.

described in the literature.[20−22] The meso-brominated compounds **9**, **11**−**15**, and **17** were reacted with allylboronic acid pinacol ester in the presence of K_3PO_4 and a Pd catalyst under reflux in tetrahydrofuran (THF). In the course of our ongoing studies on the use of different Pd catalysts,[23] two different types of catalysts were applied, namely, $Pd(PPh_3)_4$ and $Pd(dppf)Cl_2$. Both resulted in similar yields, but use of the $Pd(dppf)Cl_2$ catalyst gave quicker formation of the product (Scheme 1). Suzuki coupling of the β-brominated porphyrin **20** was carried out with allylboronic acid pinacol ester in the presence of K_2CO_3 and $Pd(PPh_3)_4$ under reflux in toluene (Scheme 2).

The *meso*-allylporphyrins **21**−**28** were obtained in 50−95% yield and the β-allylporphyrin **29** was obtained in 66% yield. The crystal structure of compound **24** shows the diallyl substitution pattern (Figure 1). The C52−C53 bond length is 1.313(2) Å, clearly indicating the unsaturated bond character. The molecular conformation is flat, with a Δ24 of 0.03 Å.[24] The allyl group is nearly perpendicular to the molecular plane with a C5−C51−C52−C53 torsion angle of 2.6°. Compound **26** gave the lowest yield of 50% in the coupling reaction of the free-base porphyrins, due to the electron-donating effect of the alkyl substituent.[25] The yield can be improved from 50% to 95% by use of the nickel-chelated analogue, as Ni(II) decreases

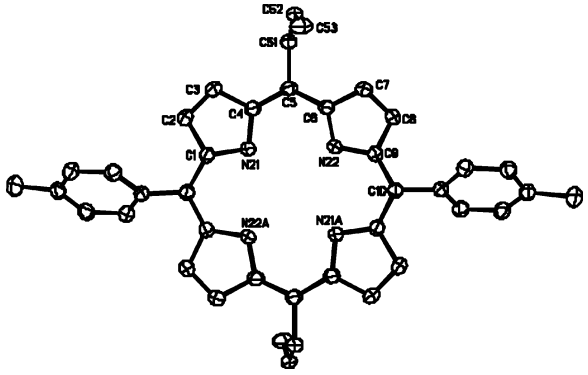
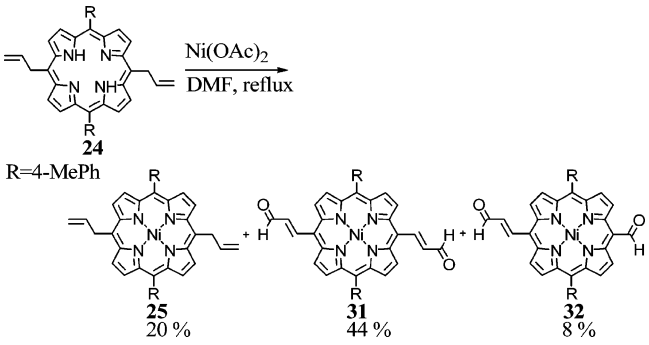


FIGURE 1. View of the molecular structure of **24** in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn for 50% occupancy.

SCHEME 3



the electron density on the macrocycle by π-back-bonding into semifilled metal d-orbitals. However, compounds **22** and **23** showed the inverse reactivity; here the free-base coupling product could be obtained in 95% yield while the nickel analogue was formed in 55% yield.

Initially, we were interested in studying metathesis reactions with the free base allyl compounds. However, no reaction was observed upon treatment of compound **24** with Grubbs I catalyst.[6,26] Thus, we intended to use related metal complexes and observed surprising results during the insertion of Ni(II). The metalation was carried out with nickel(II) acetate (3 equiv) in *N*,*N*-dimethylformamide (DMF) using standard reaction conditions.[25] The insertion of Ni(II), monitored by thin-layer chromatography (TLC), proceeded very slowly and the reaction mixture was heated to reflux overnight. Surprisingly, in addition to the expected red Ni(II) derivative **25**, two additional green fractions were obtained and identified as compounds **31** and **32**, the main product being the 5,15-diacroleinylporphyrin **31** (Scheme 3).

Further investigation of this reaction involved the use of different quantities of $Ni(OAc)_2$. Use of 4, 6, and 8 equiv of $Ni(OAc)_2$ (with respect to **24**) showed that the yield of compound **31** remained stable. On the other hand, the yields of compounds **25** and **32** decreased with more equivalents of $Ni(OAc)_2$ to traces only. When less than 3 equiv of $Ni(OAc)_2$ was used, no formation of the acroleinylporphyrins was observed. To examine the role of the metal and the ligand, the reaction

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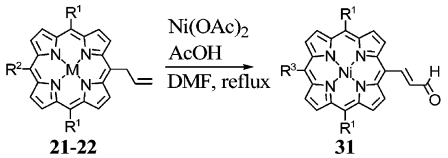
SCHEME 4



21-22
24; 26-28

31
33-36

Entry	R^1	R^2	R^3	M	Product	Yield
21	Ph	Allyl	Acroleinyl	2H	**33**	60 %
22	3-MeOPh	Allyl	Acroleinyl	2H	**34**	52 %
24	4-MePh	Allyl	Acroleinyl	2H	**31**	70 %
26	*n*-C_6H_{13}	Allyl	Acroleinyl	2H	**35**	20 %
27	*n*-C_6H_{13}	Allyl	Acroleinyl	Ni	**35**	20 %
28	4-MePh	4-MePh	4-MePh	2H	**36**	26 %

was carried out with different transition(II) salts, namely, Pd(OAc)$_2$, Zn(OAc)$_2$, $NiCl_2$, and $ZnCl_2$. However, none of these salts resulted in the formation of mono- or diacroleinyl- or the monoacroleinylmonoformylporphyrins. This led to the conclusion that nickel(II) as well as the acetate played a significant role in the reaction mechanism. It has been reported previously that acetic acid can promote the reaction of a nickel reagent with an allylic group.[27] Consequently, the reaction was carried out with the addition of 0.1 mL of glacial acetic acid (DMF/glacial acetic acid 200:1 v/v) in an attempt to increase the yield. Indeed, this improved the yield of **31** to 60%. A further increase of the amount of glacial acetic acid in the reaction mixture to 0.2 mL (DMF/glacial acetic acid 100:1 v/v) gave the 5,15-diacroleinylporphyrin **31** in 70% yield.

In order to examine if the reaction is applicable for other porphyrin systems, compounds **21**−**22**, **24**, and **26**−**28** were treated under the optimized reaction conditions (Scheme 4). All reactions resulted in the formation of the respective nickel(II) acroleinylporphyrins in varying yields. The yields of the dihexyl- and tritolyl-substituted allylporphyrins **35** and **36** were lower in comparison to the reaction of compound **31**. In the case of compound **36**, the main product turned out to be [5-allyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) **18** in 28% yield, whereas no identified byproduct was formed in the reaction of compound **35**. The remaining starting material underwent decomposition. Reaction of **26** under milder reaction conditions, for example, lower temperature (60 °C, 36 h), gave the same result. The more stable nickel(II) derivative **27** was also subjected to the optimized reaction conditions giving the same result as the corresponding free base **26**. Compound **34** has been reported previously but only as a byproduct in less than 5% yield.[15] Interestingly, treatment of the β-allyl-substituted compound **29** under the same conditions [Ni(OAc)$_2$ in the presence of glacial acetic acid in DMF under reflux for 3 days] led only to the formation of the standard nickel(II) complex **30**, on the basis of spectroscopic evidence.

To study the influence of the central metal in more detail, compound **21** was metalated with Zn(II) by a standard procedure[25] to give compound **10** in 77% yield. This compound was then subjected to the reaction conditions used for the formation of diacroleinporphyrins. However, only decomposition took place and small amounts of starting material were recovered. Thus, the inserted nickel(II) must be crucial for the activation of the *meso*-allyl substituent. Hence, compound **25** was synthesized in larger amounts by treating compound **13** with nickel(II) acetate under standard conditions [4 equiv of Ni(OAc)$_2$ in DMF heated to reflux] to obtain compound **14**,[25] followed by Suzuki cross-coupling reaction with allylboronic acid pinacol ester to obtain compound **25** in 88% yield. Treatment of the preformed Ni(II) complex **25** with Ni(OAc)$_2$ and glacial acetic acid in DMF gave **31** in 70% yield, which is identical to that observed with the free base **24**. Due to the observation that palladium(II) reagents often react similarly to nickel(II) reagents,[28] compound **25** was treated with Pd(OAc)$_2$ in the presence of glacial acetic acid in DMF under reflux for 12 h. Again, only decomposition was observed under these conditions.

To investigate the mechanism the reaction was carried out with 1 equiv of compound **24** and 3 equiv of Ni(OAc)$_2$ in DMF-d_7 at 115 °C in a sealed Schlenk tube (in the absence of acetic acid). The conversion of the starting material was followed by ^{1}H NMR measurements (see Supporting Information). Over a period of 24 h, samples were removed from the reaction mixture and analyzed at room temperature. After 1 h, the ratio between the starting material **24** and the nickel(II) analogue **25** was already 4:3, as indicated by the shift of the ^{1}H NMR signals to lower field. The signals for the β-protons, for example, appear at ∼10.0 and ∼9.1 ppm for the free base **24**, whereas the signals for the β-protons of the nickel(II) complex **25** appear at ∼9.6 and ∼8.9 ppm. The first characteristic signal of compound **31,** namely, the formyl-H signal of the acrolein system at ∼10.3 ppm, was observed after 2 h, and consumption of the starting material was complete after 5 h at a 4:1 ratio of **25** to **31**. After a period of 24 h, compound **31** can be clearly identified as the main product. Thus, conversion to **31** occurs as soon as **25** is formed. The reaction proceeded only under thermal conditions (115 °C), which could be a reason why no intermediates were detected in measurements carried out at room temperature. At present only speculations are possible for the exact reaction mechanism. In accordance with related studies that show that Ni catalysts are sometimes more effective than their Pd analogues for the reaction of allylic systems,[29−31] the formation of a nickel-η^1- and/or nickel-η^3-allyl complex may be surmised as the first reaction step.[32−34] The nickel-η^3-allyl complex produces a partial positive charge at the carbon atoms C_1 and C_3 of the allyl system, making it susceptible to nucleophilic attacks (Figure 2). In one case, the experimental data indicated that the reaction proceeds via a radical chain mechanism initiated by heat, light, or a reducing agent.[32] All other reported reactions required a polar, coordinating solvent, such as DMF, as well as stoichiometric amounts of the nickel reagent. This is in line with our observation that at least 3 equiv of Ni(OAc)$_2$ is required for the reaction of free base porphyrins. One equivalent of nickel(II) acetate is required for metal insertion into the porphyrin core. The remaining 2 equiv can then form two nickel-

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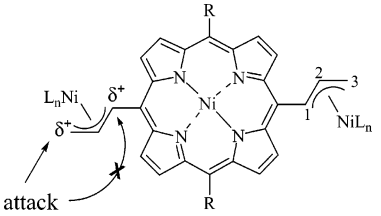

FIGURE 2. Possible structure of the intermediate during formation of the diacroleinylporphyrins.

η^3-allyl complexes, which are subsequently attacked at the C_3-positions only as the C_1-positions are shielded by the porphyrin macrocycle.

In conclusion, we have used a straightforward and convenient method for the preparation of a series of new allylporphyrins via the Suzuki cross-coupling reaction. Moreover, a novel pathway to porphyrins with α,β-unsaturated substituents in the meso position has been demonstrated. To our knowledge, the reaction of allylporphyrins with $Ni(OAc)_2$ in the presence of glacial acetic acid in DMF to acroleinylporphyrins is the first example of a Ni-catalyzed reaction for porphyrins. Both the allyl- and acroleinylporphyrins are useful precursors for further reactions.[7,35−38]

Experimental Section

Selected experimental procedures are presented. Full details of all compounds and of general techniques used are provided in the Supporting Information.

5,15-Diallyl-10,20-bis(4-methylphenyl)porphyrin (24). 5,15-Dibromo-10,20-bis(4-methylphenyl)porphyrin **13** (100 mg, 0.154 mmol, 1 equiv) was placed into a round-bottom flask under argon atmosphere and dissolved in anhydrous THF (60 mL). Allylboronic acid pinacol ester (20 equiv), K_3PO_4 (40 equiv), and $Pd(PPh_3)_4$ (0.1 equiv) were added, and the reaction mixture was heated under reflux at 80 °C for 48 h. The progress of the reaction was followed by TLC. After consumption of the starting material, the solvent was evaporated to dryness under reduced pressure and the residue was dissolved in dichloromethane. The crude product was washed with a saturated solution of sodium bicarbonate, water, and brine. The organic phase was dried with sodium sulfate and the solvent was evaporated to dryness under reduced pressure. Purification of the product was carried out by column chromatography on silica (CH_2Cl_2/C_6H_{14}, 1:1 v/v) and the title product was obtained in 75 mg (0.132 mmol, 86%) yield as dark purple crystals: mp >300 °C; R_f = 0.60 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ = −2.63 (br s, 2H, N*H*), 2.74 (s, 6H, $C_6H_4CH_3$), 5.14 (d, 2H, J = 17.2 Hz, CH_2CH═CH_2), 5.21 (d, 2H, J = 10.3 Hz, CH_2CH═CH_2), 5.73 (d, 4H, J = 5.1 Hz, CH_2CH═CH_2), 6.84 (m, 2H, CH_2CH═CH_2), 7.57 (d, 4H, J = 8.1 Hz, *H*arom), 8.08 (d, 4H, J = 7.6 Hz, *H*arom), 8.90 (d, 4H, J = 4.8 Hz, β-pyrrole-*H*), 9.41 (d, 4H, J = 4.8 Hz, β-pyrrole-*H*) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 21.5, 38.8, 115.6, 116.1, 119.3, 127.3, 127.8 (br), 131.9 (br), 134.4, 137.3, 139.5, 141.5 ppm; UV/vis (CH_2Cl_2) λ_{max} (lg ϵ) = 419 (5.3), 517 (3.0), 553 (3.9), 595 (2.8), 653 (3.9) nm; HRMS (ES+) [$C_{40}H_{34}N_4$] calcd for [M + H]$^+$ 571.2862, found 571.2872.

[5,15-Diacroleinyl-10,20-bis(4-methylphenyl)porphyrinato]-nickel(II) (31). 5,15-Diallyl-10,20-bis(4-methylphenyl)porphyrin **24** (42 mg, 0.074 mmol, 1 equiv) was placed into a round-bottom flask and dissolved in DMF (20 mL). $Ni(OAc)_2{\cdot}4H_2O$ (3 equiv) and glacial acetic acid (0.2 mL) were added, and the reaction mixture was heated under reflux at 115 °C for 12 h. The progress of the reaction was followed by TLC. After consumption of the starting material, the solvent was evaporated to dryness. The crude product was purified by column chromatography on silica (ethyl acetate/C_6H_{14}, 1:2 v/v) and the title product was obtained as the third column fraction in 34 mg (0.052 mmol, 70%) yield as green crystals: mp >300 °C; R_f = 0.54 (ethyl acetate/C_6H_{14}, 1:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.65 (s, 6H, $C_6H_4CH_3$), 6.60 (dd, 2H, J = 7.6, 15.8 Hz, CH═C*H*CHO), 7.49 (d, 4H, J = 7.6 Hz, *H*arom), 7.79 (d, 4H, J = 7.6 Hz, *H*arom), 8.73 (d, 4H, J = 5.3 Hz, β-pyrrole-*H*), 9.20 (d, 4H, J = 5.3 Hz, β-pyrrole-*H*), 9.51 (d, 2H, J = 15.2 Hz, C*H*═CHCHO), 10.04 (d, 2H, J = 7.6 Hz, CH═CHC*H*O) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 21.4, 110.1, 120.8, 127.9, 131.4, 133.2, 134.0, 136.2, 138.0, 140.6, 141.7, 141.9, 150.5, 191.9 ppm; UV/vis (CH_2Cl_2) λ_{max} (lg ϵ) = 443 (5.2), 622 (4.4) nm; LRMS (ES+) [$C_{40}H_{28}N_4NiO_2$] calcd for [M + H]$^+$ 655.4, found 655.3.

[5-Acroleinyl-15-formyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) (32). The title compound was obtained as a side product of the synthesis of [5,15-diacroleinyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) **31** as the second column fraction in 8.3 mg (0.013 mmol, 13%) yield as light green crystals: mp >300 °C; R_f = 0.65 (CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.65 (s, 6H, $C_6H_4CH_3$), 6.63 (dd, 2H, J = 7.5, 15.8 Hz, CH═C*H*CHO), 7.50 (d, 4H, J = 7.9 Hz, *H*arom), 7.80 (d, 4H, J = 7.9 Hz, *H*arom), 8.73 (d, 2H, J = 5.3 Hz, β-pyrrole-*H*), 8.80 (d, 2H, J = 4.9 Hz, β-pyrrole-*H*), 9.22 (d, 2H, J = 4.5 Hz, β-pyrrole-*H*), 9.55 (d, 2H, J = 15.8 Hz, C*H*═CHCHO), 9.72 (d, 2H, J = 5.3 Hz, β-pyrrole-*H*), 10.08 (d, 2H, J = 7.5 Hz, CH═CHC*H*O), 11.97 (s, 1H, C*H*O) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 21.5, 29.7, 107.0, 112.6, 121.5, 128.0, 131.6, 131.9, 133.3, 133.7, 135.6, 136.3, 138.2, 140.1, 141.6, 142.5, 143.4, 143.8, 150.4, 192.0, 192.5 ppm; UV/vis (CH_2Cl_2) λ_{max} (lg ϵ) = 438 (3.4), 622 (2.6) nm; HRMS (ES+) [$C_{38}H_{26}N_4NiO_2$] calcd for [M + H]$^+$ 629.1487, found 629.1491.

[5-Acroleinyl-10,15,20-tris(4-methylphenyl)porphyrinato]-nickel(II) (36). With 5-allyl-10,15,20-tris(4-methylphenyl)porphyrin **28** (40 mg, 0.065 mmol; 1 equiv) as starting material and $Ni(OAc)_2$ (2 equiv), the product was obtained following the procedure for compound **32** as the third fraction in 11.6 mg (0.017 mmol, 26%) yield as dark green crystals: mp 105 °C; R_f = 0.48 (CH_2Cl_2/C_6H_{14}, 2:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.63 (s, 3H, CH_3), 2.64 (s, 6H, CH_3), 6.65 (dd, 1H, J = 8.2, 15.8 Hz, CH═C*H*CHO), 7.47 (t, 6H, J = 7.6 Hz, *H*arom), 7.83 (d, 6H, J = 7.6 Hz, *H*arom), 8.62 (d, 2H, J = 4.7 Hz, β-pyrrole-*H*), 8.67 (d, 2H, J = 4.7 Hz, β-pyrrole-*H*), 8.81 (d, 2H, J = 5.3 Hz, β-pyrrole-*H*), 9.26 (d, 2H, J = 5.3 Hz, β-pyrrole-*H*), 9.60 (d, 1H, J = 15.8 Hz, C*H*═CHCHO), 10.05 (d, 1H, J = 8.2 Hz, CH═CHC*H*O) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 21.4, 108.0, 120.0, 121.3, 127.8, 130.6, 132.3, 132.9, 133.4, 134.0, 137.1, 137.7, 141.1, 141.3, 141.5, 142.3, 143.2, 151.6, 192.1 ppm; UV/vis (CH_2Cl_2) λ_{max} (lg ϵ) = 437 (5.1), 552 (4.1), 598 (4.1) nm; HRMS (ES+) [$C_{44}H_{32}N_4NiO$] calcd for [M + H]$^+$ 691.2008, found 691.2025.

Acknowledgment. This work was generously supported by a Science Foundation Ireland Research Professorship grant (SFI 04/RP1/B482). We are grateful to Frontier Scientific, Inc. for a gift of $Pd(dppf)Cl_2$.

Supporting Information Available: Experimental procedures and spectroscopic data for all compounds and X-ray crystallographic data (in CIF format for **21**. This material is available free of charge via the Internet at http://pubs.acs. org.

JO070550G

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