Supplementary Material to:

Indaphyrin, a *meso*-Tetraphenylsecochlorin-Derived Chromophore Incorporating *o*-Phenyl-to-ß-Linkages

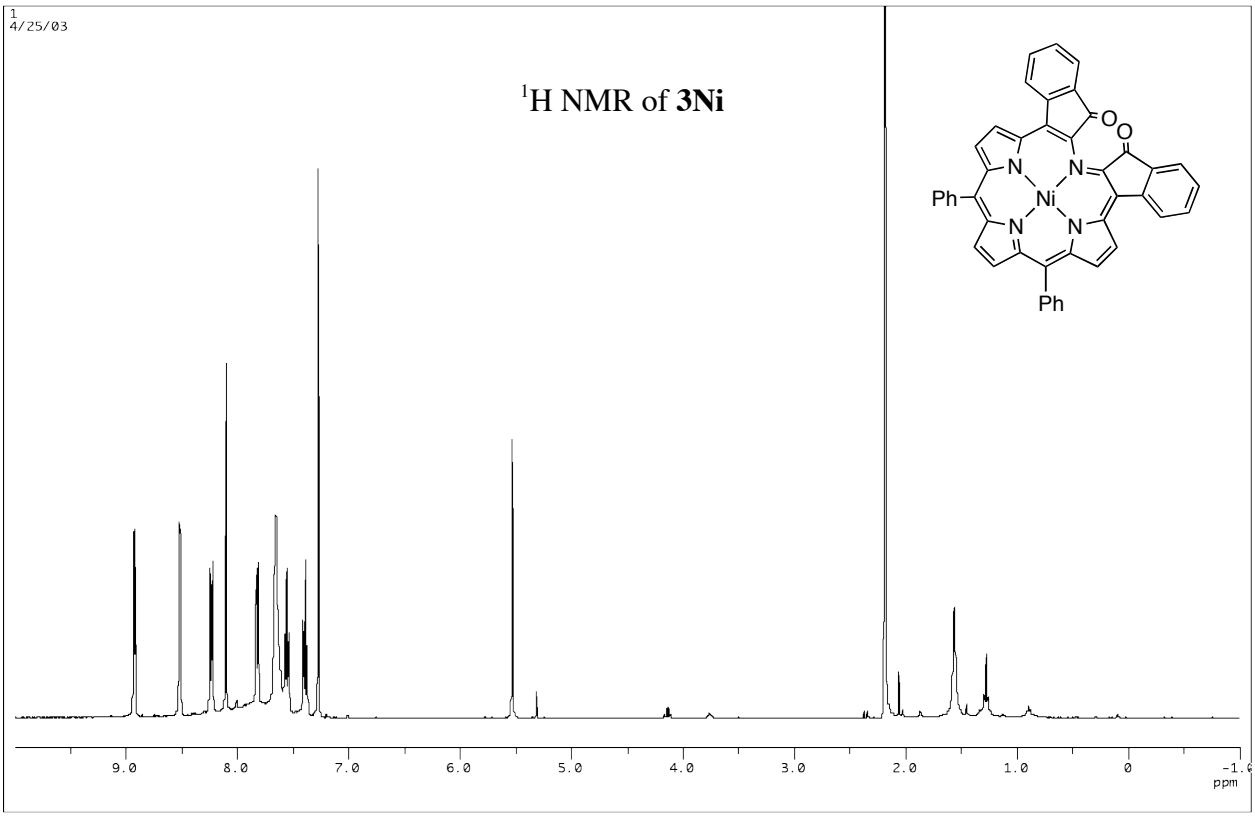
Jason R. McCarthy, Michael A. Hyland, and Christian Brückner*
University of Connecticut, Department of Chemistry, Storrs, CT 06269-3060, U.S.A.

General:

All solvents and reagents used were reagent grade or better, and were used as received. The analytical TLC plates were Silicycle ultra pure silica gel 60 (aluminum backed, 250 μm); preparative TLC plates (500 μm silica gel on glass) and the flash column silica gel (standard grade, 60Å, 32-63 mm) used were provided by Sorbent Technologies, Atlanta, GA. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX400 and were referenced to residual solvent peaks. All NMR analyses performed at ambient temperature in $CDCl_3$. UV-vis spectra were recorded on Cary 50 spectrophotometer, and IR spectra on a Perkin-Elmer Model 834 FT-IR. ESI mass spectra were recorded on a Micromass Quattro II in the solvents indicated. High resolution FAB mass spectra were provided by the Mass Spectrometry Facility, Department of Chemistry and Biochemistry, University of Notre-Dame (Bill Boggess).

*Preparation and spectroscopic data of **3Ni**:*

A solution of **1Ni** (29 mg) in $CHCl_3$ (10 mL, amylene-stabilized) was treated with TFA vapours, administered by pipette. After all the starting material was consumed (~15 min, TLC control), the reaction mixture was filtered through a plug of basic alumina. The resulting mixture was separated by preparative TLC chromatography to provide **3Ni** in 80% yield: UV-vis ($CHCl_3$) λ_{max}, nm (rel. intensity): 446 (1.00), 635 (0.20); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36-7.39 (t, 1H, *J* = 7. 3 Hz), 7.52-7.56 (t, 1H, 7.24 Hz), 7.65 (br. s, 3H), 8.20 (d, 1H, *J* = 7.6 Hz), 7.84 (d, 1H, *J* = 7.3 Hz), 8.09 (s, 1H), 8.21 (d, 1H, *J* = 7.64 Hz), 8.50 (d, 1H, *J* = 4.84 Hz), 8.9 (d, 1H, *J* = 4.9 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 110.7, 122.6, 124.9, 125.1, 125.3, 126.7, 127.9, 129.8, 130.2, 132.9, 134.9, 139.2, 139.8, 141.5, 141.8, 142.9, 148.5, 206.9 ppm; IR (KBr) $\nu_{C=O}$: 1599 cm^{-1}; HR-MS (FAB) *m/z*: calc'd for $C_{44}H_{24}N_4NiO_2$ 698.1253; found, 698.1262.


1
4/25/03
^{1}H NMR of **3Ni**
O
O
N
N
Ni
N
N
Ph
Ph
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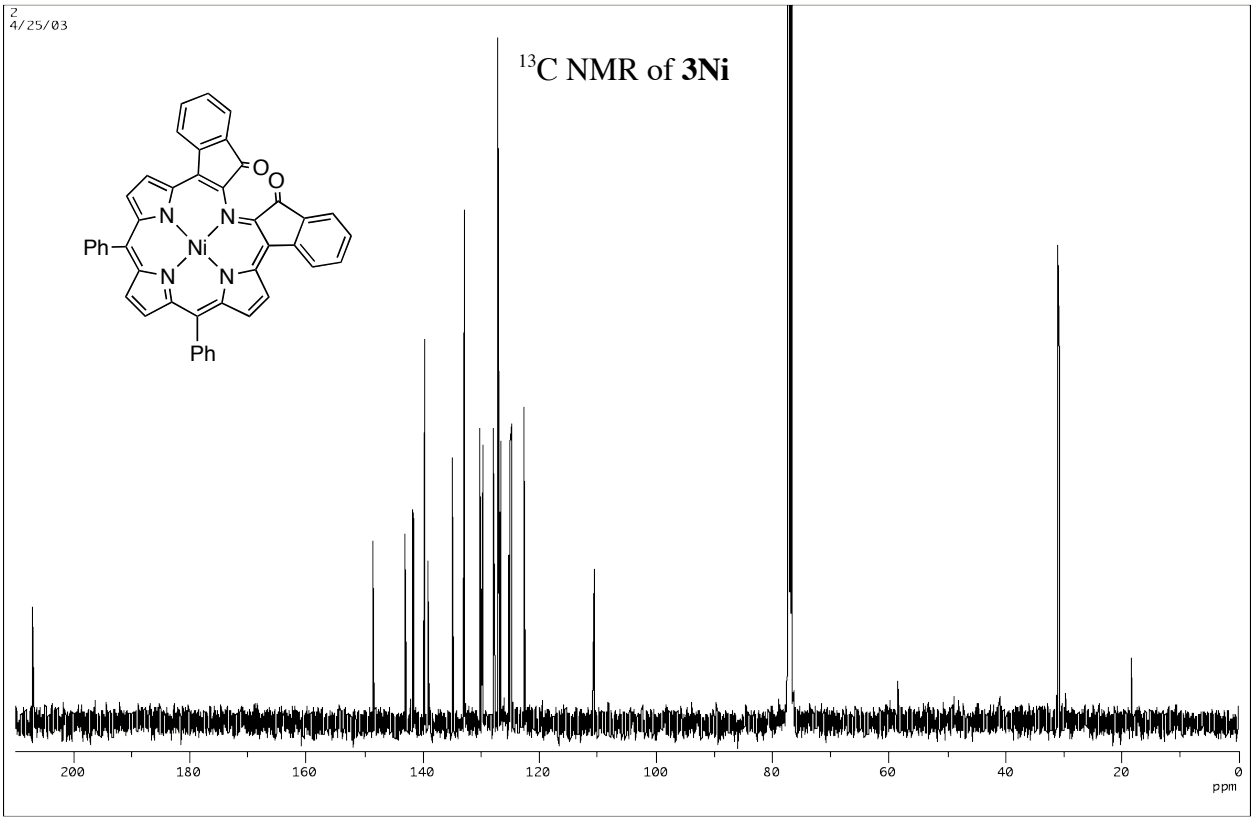
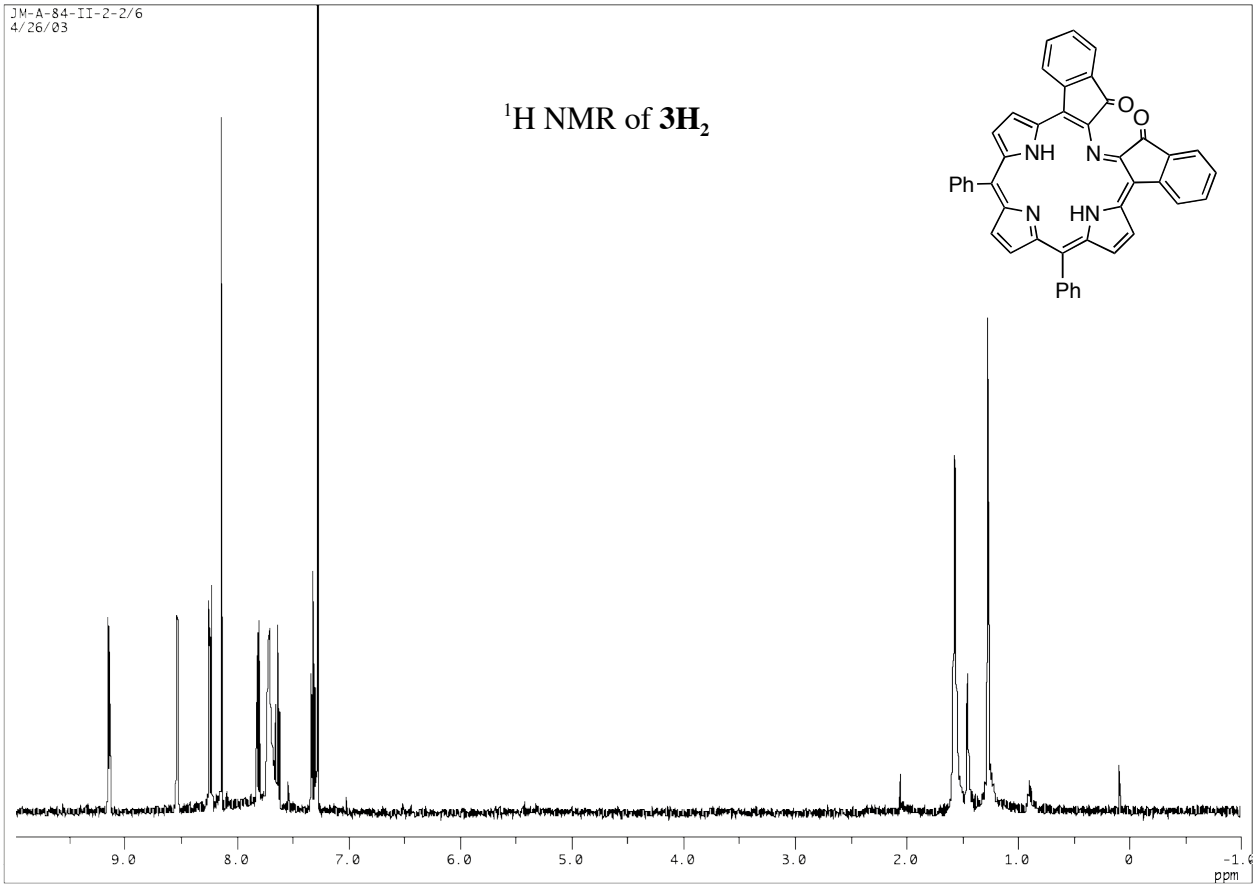
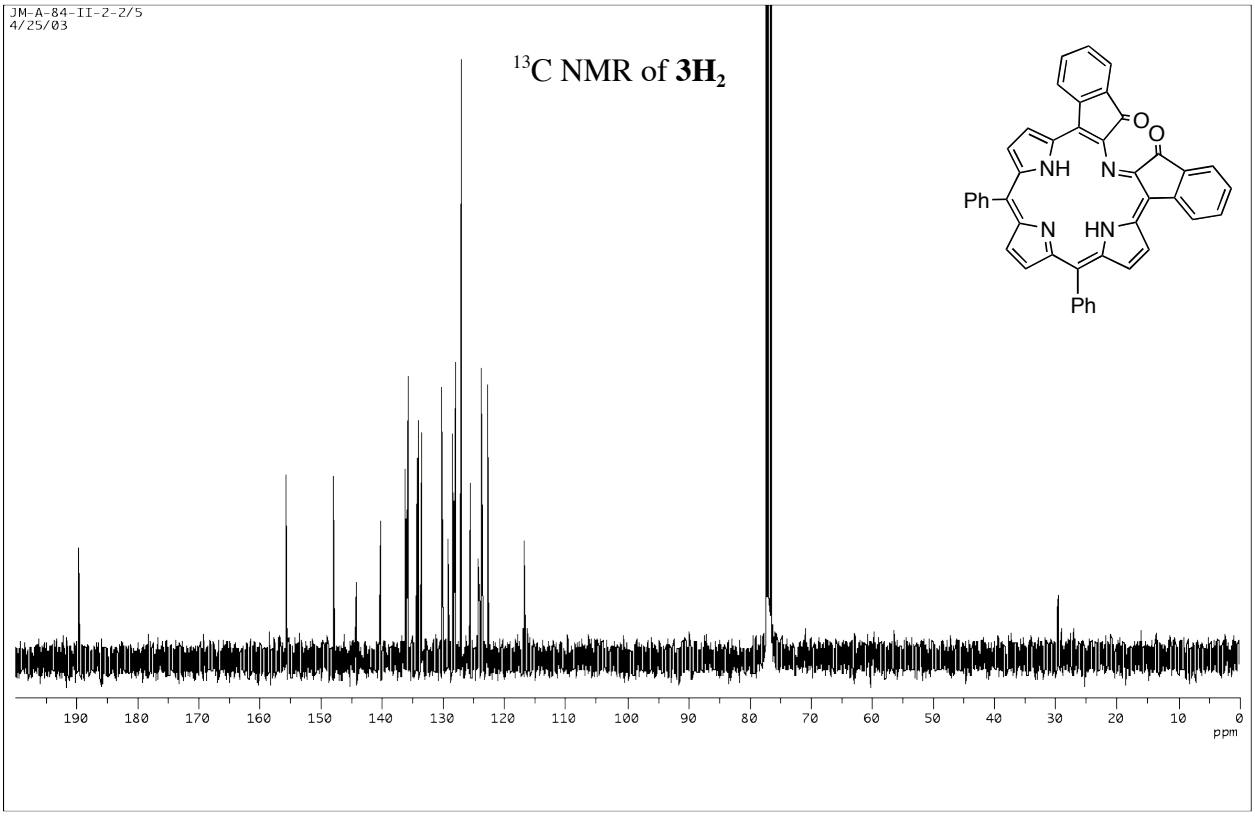
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm


2
4/25/03
^{13}C NMR of **3Ni**
O
O
N
N
Ni
N
N
Ph
Ph
200
180
160
140
120
100
80
60
40
20
0
ppm

Preparation of ***3H$_2$****:*

A slurry of acidified silica gel (silica gel wetted with conc HCl and air dried, ~500 mg) in $CHCl_3$ (10 mL, amylene-stabilized) containing **2H$_2$** (125 mg) was allowed to react for 12 h. The filtered solution was subjected to preparative TLC chromatography to provide **3H$_2$** in 30% yield: UV-vis (CH_2Cl_2) λ_{max} (log ε): 419 (4.65), 554 (4.61), 639 (4.05), 730 (3.62), 812 (3.29); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.49 (brs, 1H, exchangeable with D_2O), (7.32 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.71 (brs, 5H), 7.81 (d, J = 7.7 Hz, 1H), 8.14 (s, 1H), 8.24 (d, J = 7.7 Hz, 1H), 8.54 (d, J = 4.9 Hz, 1H), 9.15 (d, J = 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 116.7, 122.7, 123.7, 124.2, 125.5, 127.1, 128.1, 128.5, 129.4, 130.3, 133.6, 134.1, 134.4, 135.7, 136.2, 140.3, 144.3, 147.9, 155.6, 189.5; IR (KBr) $\nu_{C=O}$: 1699 cm^{-1}; LR-ESI-MS (70 V, CH_3CN) m/z = 643 (MH^+); HR-MS (FAB+ of MH+) calculated for $C_{44}H_{27}O_2N_4$: 643.2134, found: 643.2145.

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4/25/03
^{13}C NMR of **3H$_2$**
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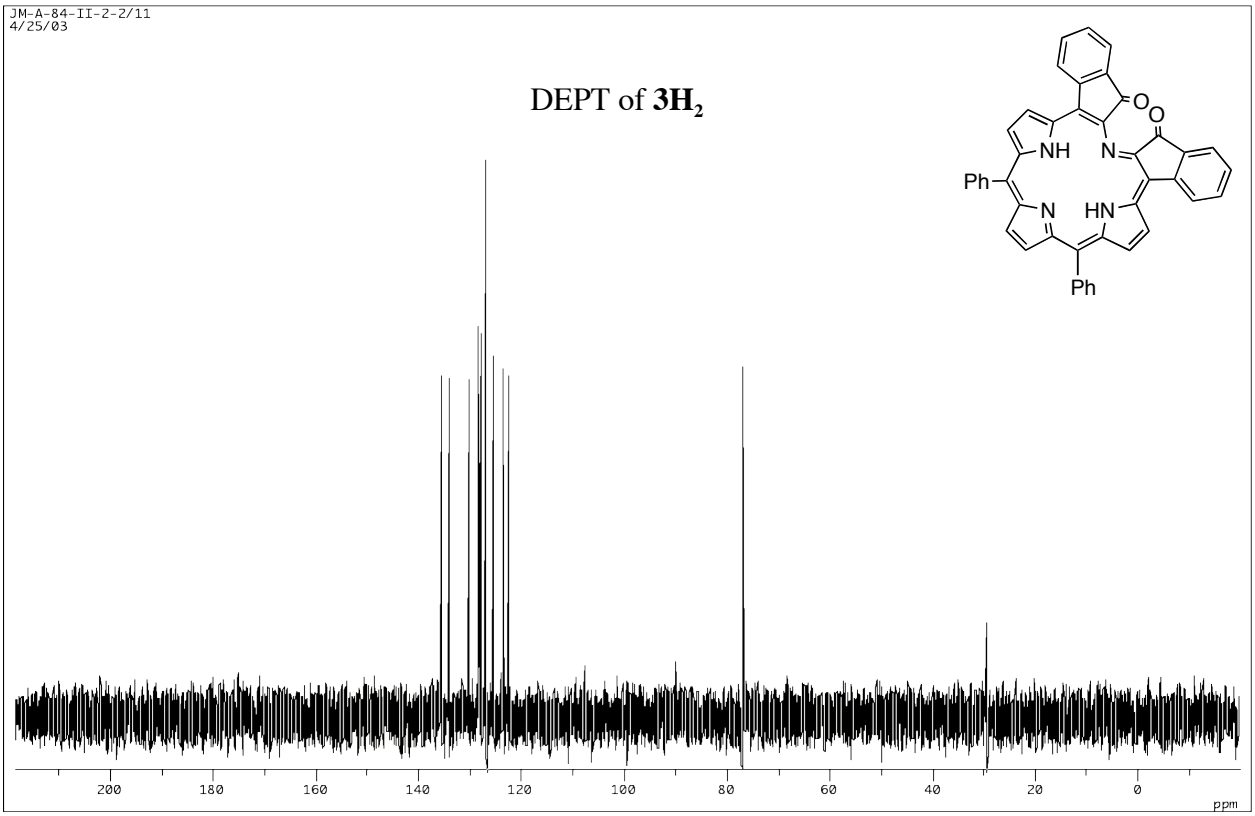
O
NH
N
Ph
N
HN
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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4/25/03
DEPT of **3H$_2$**
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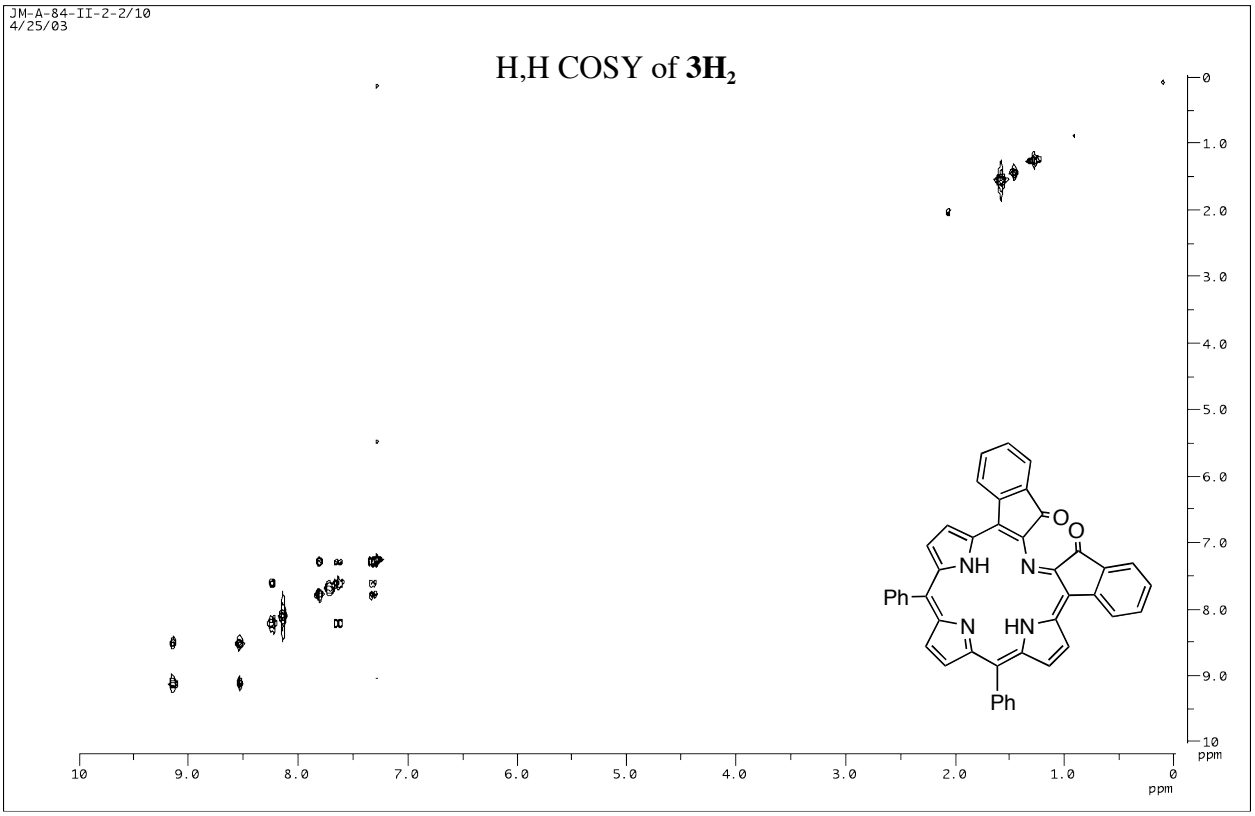
O
NH
N
Ph
N
HN
Ph
200 180 160 140 120 100 80 60 40 20 0
ppm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4/25/03
H,H COSY of 3H2
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O
NH
N
Ph
N
HN
Ph
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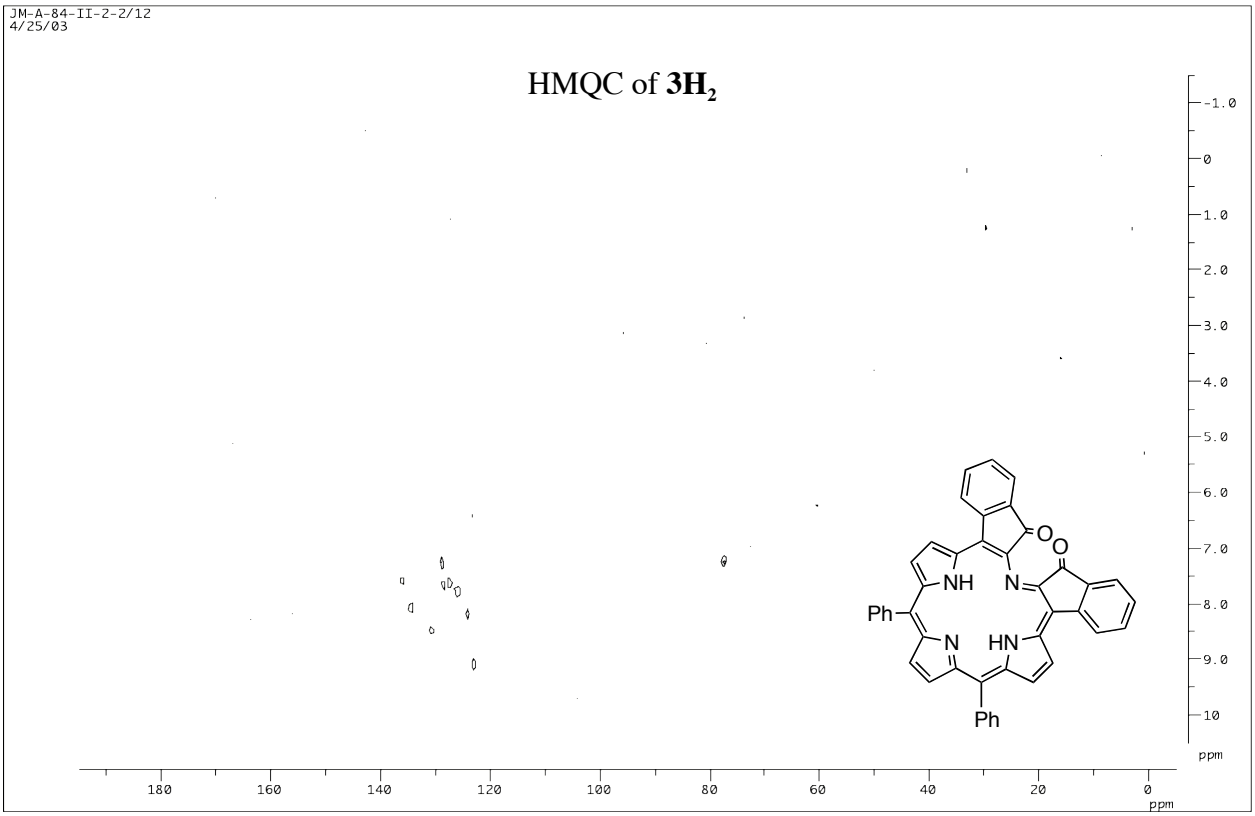
4.0
3.0
2.0
1.0
0
ppm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4/25/03
HMQC of 3H2
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NH
N
Ph
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HN
Ph
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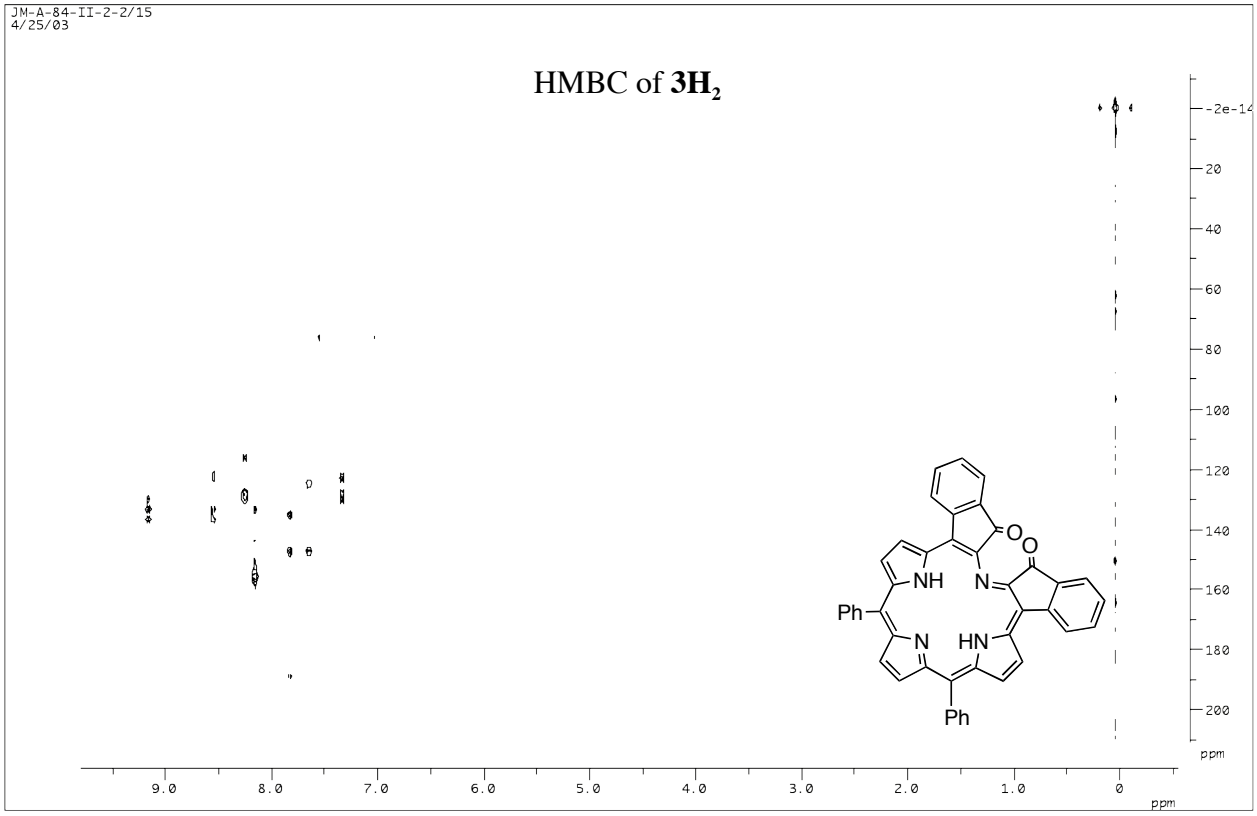
160
140
120
100
80
60
40
20
0
ppm


JM-A-84-II-2-2/15
4/25/03
HMBC of 3H2
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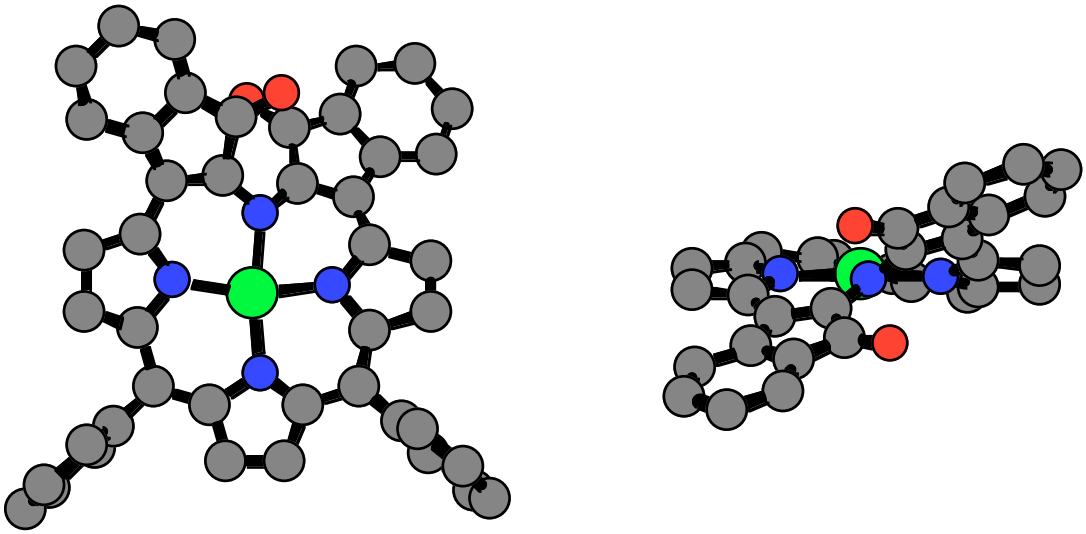
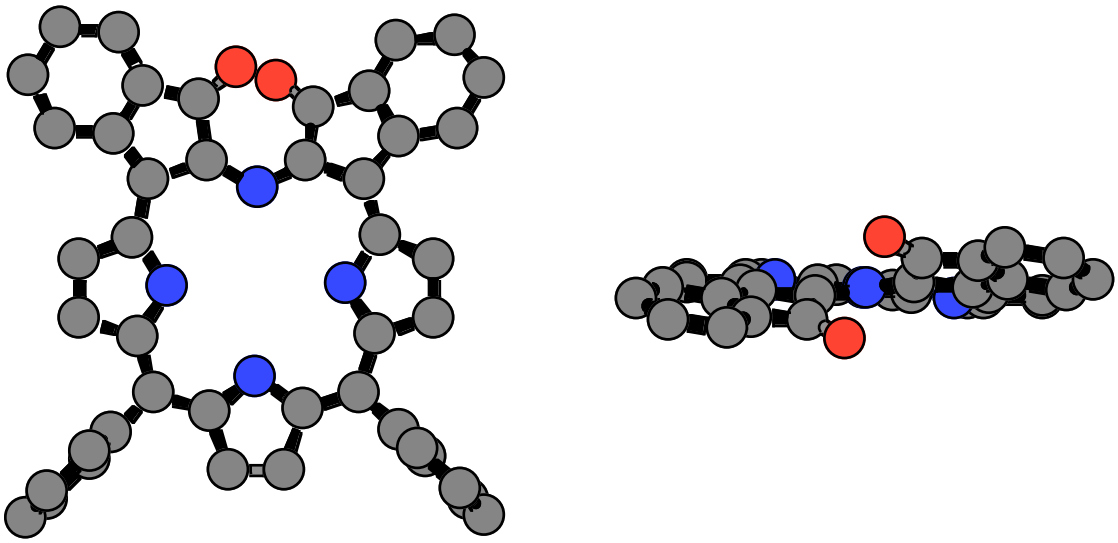
20
40
60
80
100
120
140
160
180
200
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm
O
O
NH
N
Ph
N
HN
Ph

*Molecular Modelling of **3Ni** and **3H$_2$**.*

Quantum CACHe 4.9 (Fujitsu 2002, Beaverton, OR) minimization of **3Ni** and **3H$_2$**. MM3 parameters. Ni-N bond distances locked at 1.89 Å according to crystallographic data obtained for [2,3-dimethoxymorpholinochlorinato] Ni(II). (C. Brückner, S. J. Rettig, and D. Dolphin, *J. Org. Chem.*, 1998, **63**, 2094.)



Minimization of **3Ni** (left), and view along C_2 axis (right, distal phenyl groups omitted for clarity). O-O distance = 2.88 Å, rms deviation of $C_{20}N_4$ chromophore from planarity = 0.56 Å.



Minimization of **3H$_2$** (left), and view along C_2 axis (right, distal phenyl groups omitted for clarity). O-O distance = 2.55 Å, rms deviation of $C_{20}N_4$ chromophore from planarity = 0.24 Å.