Electronic Supplementary Information

The Oxidation of Ni(II) N-Confused Porphyrins (NCPs) with Azo Radical Initiators and an Unexpected Intramolecular Nucleophilic Substitution Reaction via a Proposed Ni(III) NCP Intermediate

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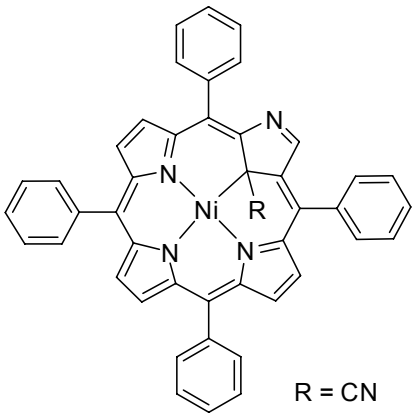
Contents

General: ^{1}H (300MHz) and ^{19}F (282MHz) NMR spectra were recorded with a Brucker AM-300 or Varian-VXR (300MHz) spectrometer. Chemical shifts are reported in parts per million (ppm)

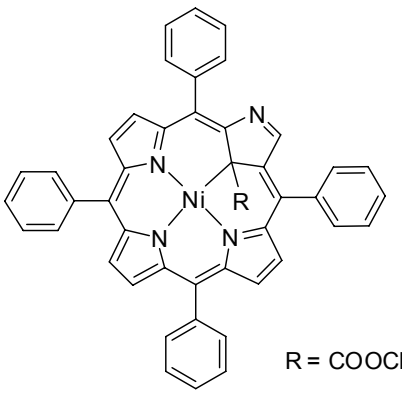
relative to TMS as an internal standard (δ_{TMS} = 0 ppm) for ^{1}H NMR spectra. MS and HRMS were recorded on a Hewlett-Packard HP-5989A spectrometer and a Finnigan MAT-8483 mass spectrometer. UV/Vis spectra were measured with a Varian Cary 100 spectrophotometer. Elementary analyses were obtained on a Perkin Elmer 2400 Series Elemental Analyzer. TLC analysis were performed on silica gel plate and column chromatography over silica gel (mesh 300-400).Unless otherwise noted, reagents were commercial available and used as received. The solvent toluene was treated with Na and redistilled before using. The starting N-confused porphyrins and Ni(II) N-Confused Porphyrins were synthesized according to the literatures (G. Richard Geier III, Denise M. Haynes, Jonathan S. Lindsey. **1999**, *9*, 1455, and Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem.* **1994**, *104***,** 805; *Angew. Chem. Int. Ed.* **1994**, *33*, 779.).

Typical procedure for synthesis of 21-C cyano- or alkoxycarbonyl-substituted Ni(II) N-confused porphyrins. A mixture of **Ni1** (67 mg, 0.1 mmol) and AIBN (66 mg, 0.4 mmol) was stirred in 10 mL anhydrous toluene at 60 ^{o}C for about 4 hours. The reaction course was monitored by TLC. When **Ni1** was totally consumed, the reaction mixture was cooled. After chromatography on silica gel column using CH_2Cl_2 as an eluent (the first yellow-greenish band was collected) and crystallization from CH_2Cl_2/MeOH, a purple solid **Ni1a** was obtained.



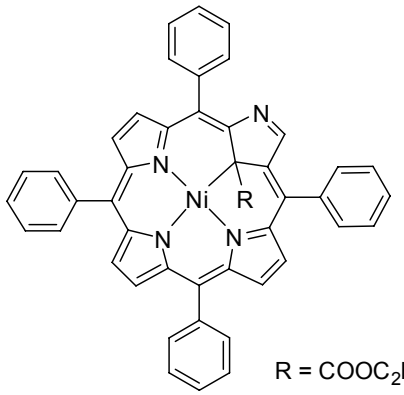
Ni1a

Ni1a: yield 45%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 8.73 (d, *J* = 5.0 Hz, 1H), 8.70 (d, *J* = 5.0 Hz, 1H), 8.51 ~ 8.62 (m, 4H), 7.65 ~ 8.20 (m, 20H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 430 (18.0), 714 (1.0) nm. HRMS (MALDI): Calcd. for $[C_{45}H_{27}N_5Ni+H]^+$: 696.16927. Found: 696.1691.



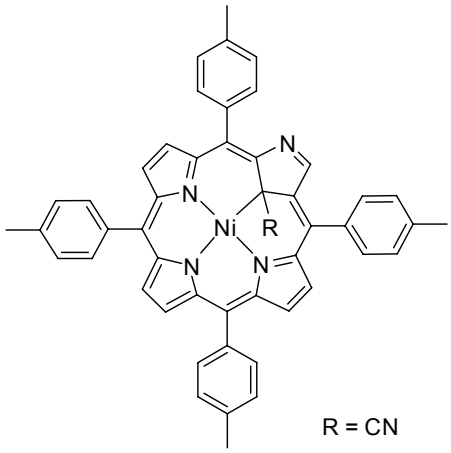
Ni1b

Ni1b: yield 38%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 8.69 (d, *J* = 5.1 Hz, 1H), 8.66 (d, *J* = 5.1 Hz, 1H), 8.52 ~ 8.56 (m, 2H), 8.49 (d, *J* = 5.0 Hz, 1H), 8.44 (d, *J* = 5.0 Hz, 1H), 7.63 ~ 8.22 (m, 20H), 1.60 (s, 3H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 434 (6.5), 699 (1.0) nm. MS (MALDI): *m*/*z* 729.2 ($[C_{46}H_{30}N_4NiO_2+H]^+$). Anal. Calcd. for $C_{46}H_{30}N_4NiO_2 \cdot CH_2Cl_2 \cdot H_2O$: C, 67.28; H, 4.12; N, 6.73. Found: C, 67.35; H, 4.16; N, 6.67.



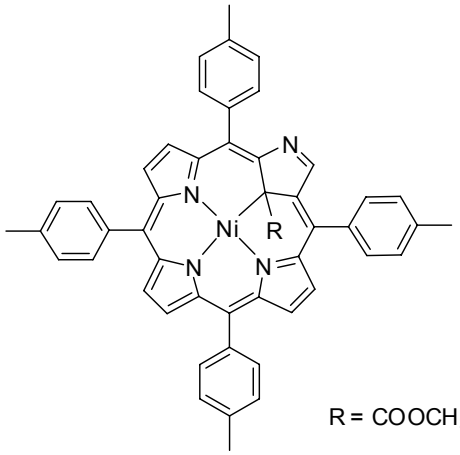
Ni1c

Ni1c: yield 37%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.69 (d, *J* = 5.0 Hz, 1H), 8.66 (d, *J* = 5.0 Hz, 1H), 8.54 (d, *J* = 5.0 Hz, 2H), 8.49 (d, *J* = 4.8 Hz, 1H), 8.45 (d, *J* = 4.8 Hz, 1H), 7.64 ~ 8.24 (m, 20H), 2.00 (q, *J* = 7.1 Hz, 2H), -0.41 (t, *J* = 7.1 Hz, 3H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 435 (11.0), 696 (1.0) nm. MS (MALDI): *m*/*z* 743.2 ($[C_{47}H_{32}N_4NiO_2+H]^+$). Anal. Calcd. for $C_{47}H_{32}N_4NiO_2 \cdot CH_3OH$: C, 74.34; H, 4.68; N, 7.22. Found: C, 74.10; H, 5.10; N, 6.82.



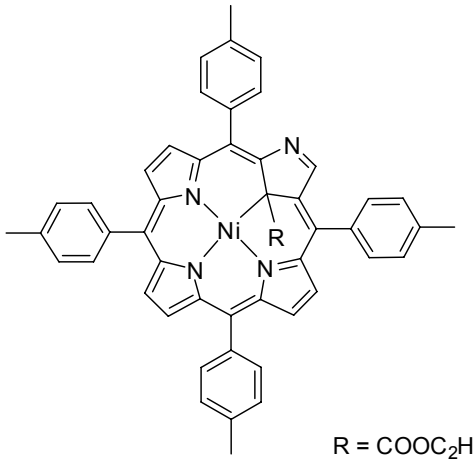
Ni2a

Ni2a: yield 42%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 8.68 ~ 8.73(m, 2H), 8.50 ~ 8.61(m, 4H), 7.46 ~ 8.05 (m, 16H), 2.61 ~ 2.71 (m, 12H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 434 (15.5), 716 (1.0) nm. MS (MALDI): *m*/*z* 752.2 ($[C_{49}H_{35}N_5Ni+H]^+$). Anal. Calcd. for $C_{49}H_{35}N_5Ni \cdot H_2O$: C, 76.38; H, 4.84; N, 9.09. Found: C, 76.59; H, 5.07; N, 8.89.



Ni2b

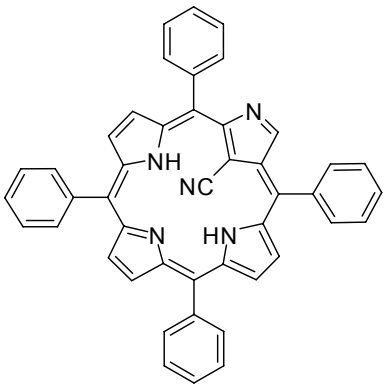
Ni2b: yield 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.97 (s, 1H), 8.65 ~ 8.71 (m, 2H), 8.43 ~ 8.58 (m, 4H), 7.45 ~ 8.16 (m, 16H), 2.60 ~ 2.69 (m, 12H), 1.60 (s, 3H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 436 (10.9), 700 (1.0) nm. MS (MALDI): *m*/*z* 785.2 ($[C_{50}H_{38}N_4NiO_2+H]^+$). Anal. Calcd. for $C_{50}H_{38}N_4NiO_2 \cdot 1.5H_2O$: C, 73.90; H, 5.09; N, 6.89. Found: C, 73.93; H, 5.15; N, 6.75.



Ni2c

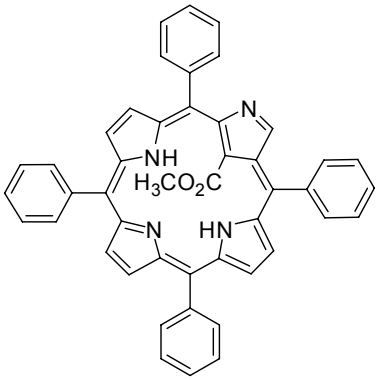
Ni2c: yield 39%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 8.63 ~ 8.70 (m, 2H), 8.51 ~ 8.56 (m, 2H), 8.48 (d, *J* = 5.0 Hz, 1H), 8.44 (d, *J* = 5.0Hz, 1H), 7.40 ~ 8.19 (m, 16H), 2.60 ~ 2.68 (m, 12H), 1.97 (q, *J* = 7.6 Hz, 2H), -0.43 (t, *J* = 7.6 Hz, 3H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 437 (32.5), 727 (1.0) nm. MS (MALDI): *m*/*z* 799.3 ($[C_{51}H_{40}N_4NiO_2+H]^+$). Anal. Calcd for $C_{51}H_{40}N_4NiO_2 \cdot 2H_2O$: C, 73.30; H, 5.31; N, 6.70. Found: C, 73.41; H, 5.07; N, 6.27.

Typical Procedure for the demetallation of 21-C cyano- or alkoxycarbonyl-substituted Ni(II) N-confused porphyrins. Solution of **Ni1a** (20 mg, 0.029 mmol) in 5 mL of dichloromethane was shaken with 5 mL concentrated hydrochloric acid for 5 min. Then the water layer was removed, and organic layer was washed with water and dried with sodium carbonate. Chromatography on a silica gel column with dichloromethane/methanol 100:1 (V/V) as an eluent (green band was collected) and crystallization from CH_2Cl_2/MeOH, gave **1a.**



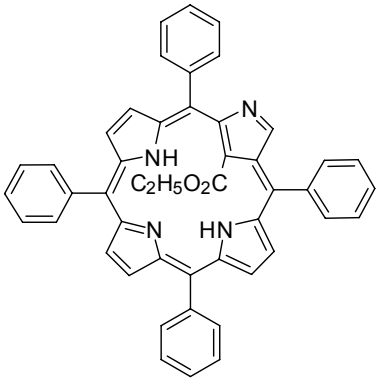
1a

1a: yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.12 (d, *J* = 5.0 Hz, 1H), 9.07 (d, *J* = 5.0 Hz, 1H), 8.68 ~ 8.76 (m, 2H), 8.60 ~ 8.65 (m, 2H), 8.43 ~ 8.52 (m, 4H), 8.15 ~ 8.30 (m, 4H), 7.73 ~ 7.98 (m, 13H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 454 (18.6), 554 (1.0), 601 (1.2), 710 (1.6) nm. MS (MALDI): *m*/*z*, 640.2 ($[C_{45}H_{29}N_5+H]^+$). Anal. Calcd for $C_{45}H_{29}N_5 \cdot CH_2Cl_2 \cdot CH_3OH$: C, 74.60; H, 4.66; N, 9.25. Found: C, 74.80; H, 4.83; N, 8.89.



1b

1b: yield 74%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.17 (d, *J* = 5.0 Hz, 1H), 9.12 (d, *J* = 5.0 Hz, 1H), 8.68 ~ 8.74 (m, 2H), 8.52 ~ 8.56 (m, 2H), 8.39 ~ 8.49 (m, 4H), 8.19 ~ 8.28 (m, 2H), 8.05 ~ 8.13 (m, 2H), 7.69 ~ 7.93 (m, 13H), 0.29 (s, 3H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 463 (15.1), 566 (1.0), 617 (1.3), 717 (1.3) nm. HRMS (MALDI): Calcd. for $[C_{46}H_{32}N_4O_2+H]^+$: 673.25980. Found: 673.2615.

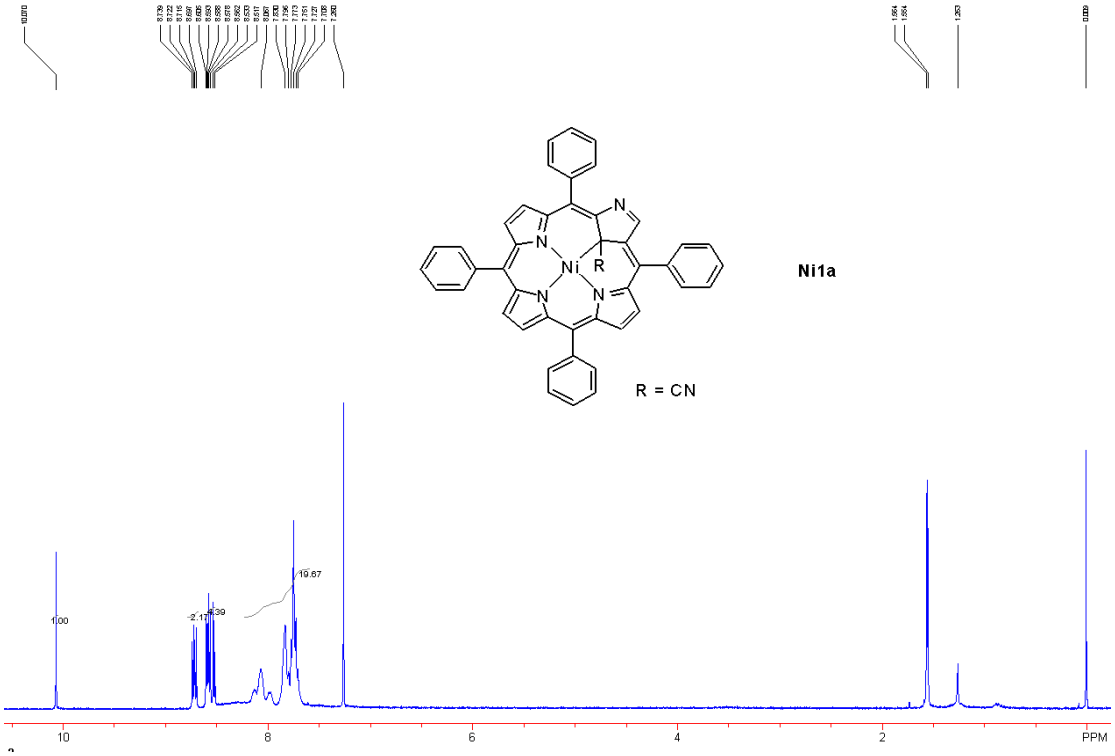


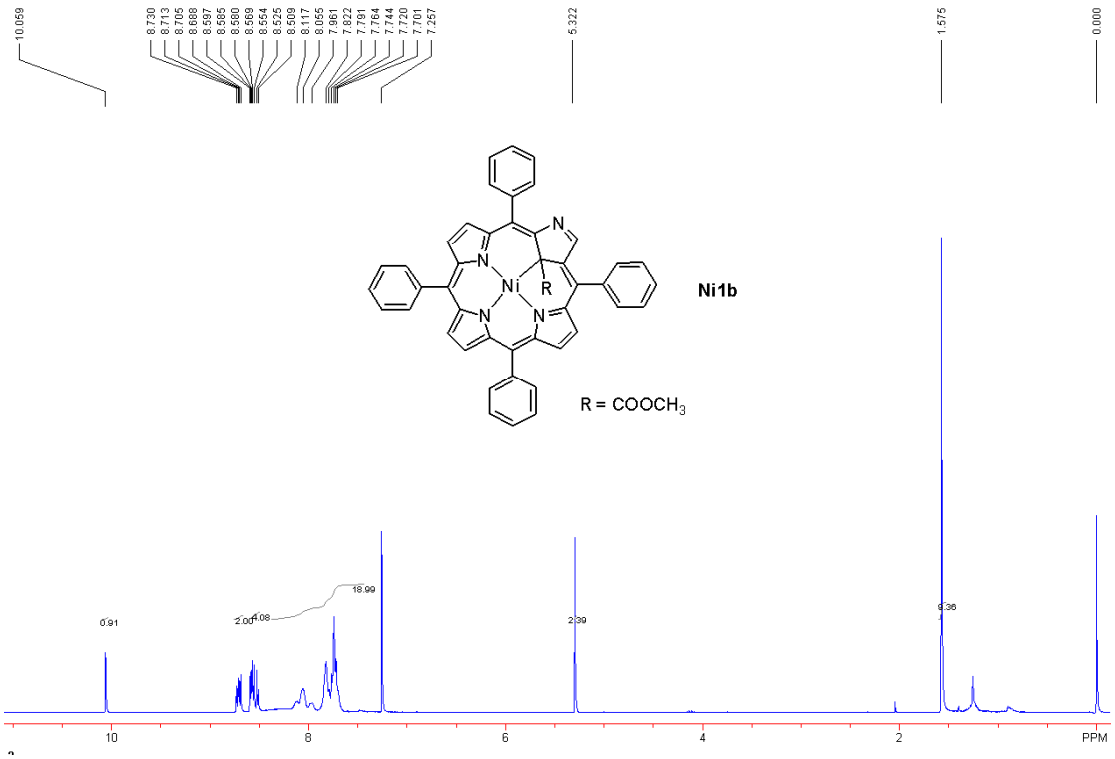
1c

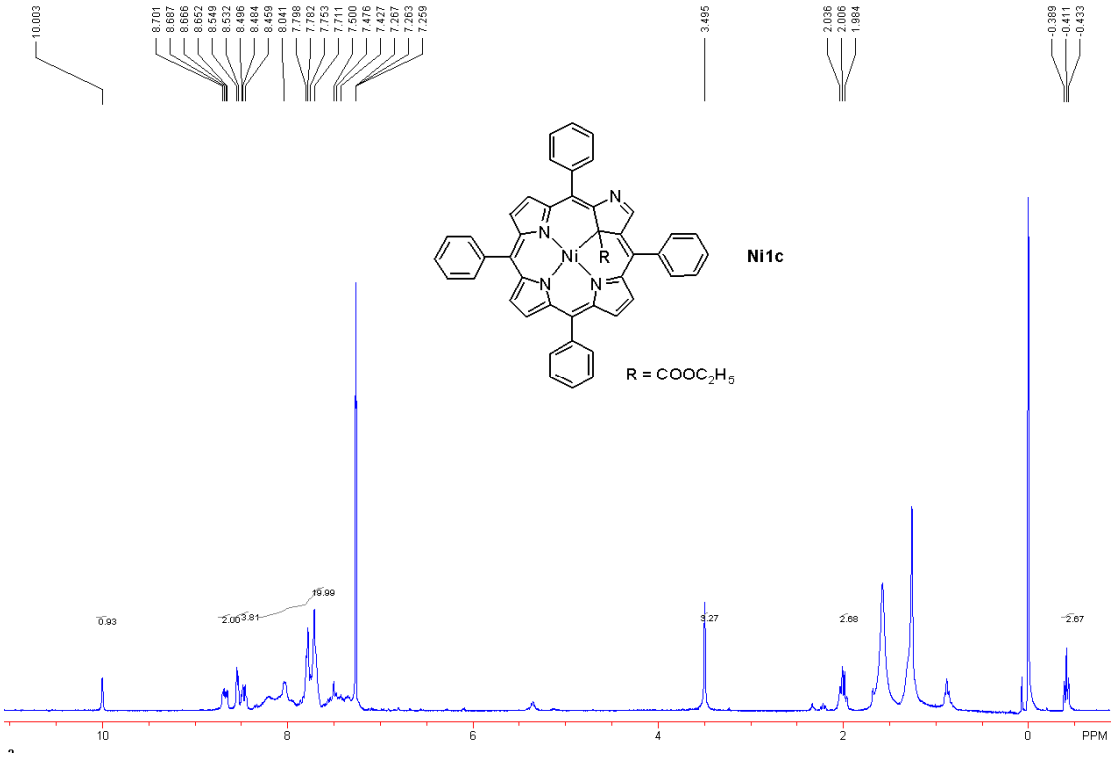
1c: yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.16 (d, *J* = 5.0 Hz, 1H), 9.11 (d, *J* = 5.0 Hz, 1H), 8.70 ~ 8.75 (m, 2H), 8.50 ~ 8.56 (m, 2H), 8.40 ~ 8.47(m, 4H), 8.15 ~ 8.27 (m, 2H), 8.03 ~ 8.14 (m, 2H), 7.68 ~ 7.94 (m, 13H), 0.87 (q, *J* = 6.9 Hz, 2H), -1.51 (t, *J* = 6.9 Hz, 3H). UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 463 (16.2), 565 (1.0), 616 (1.3), 717 (1.3) nm. HRMS (MALDI): Calcd. for $[C_{47}H_{34}N_4O_2+H]^+$: 687.27545. Found: 687.2781

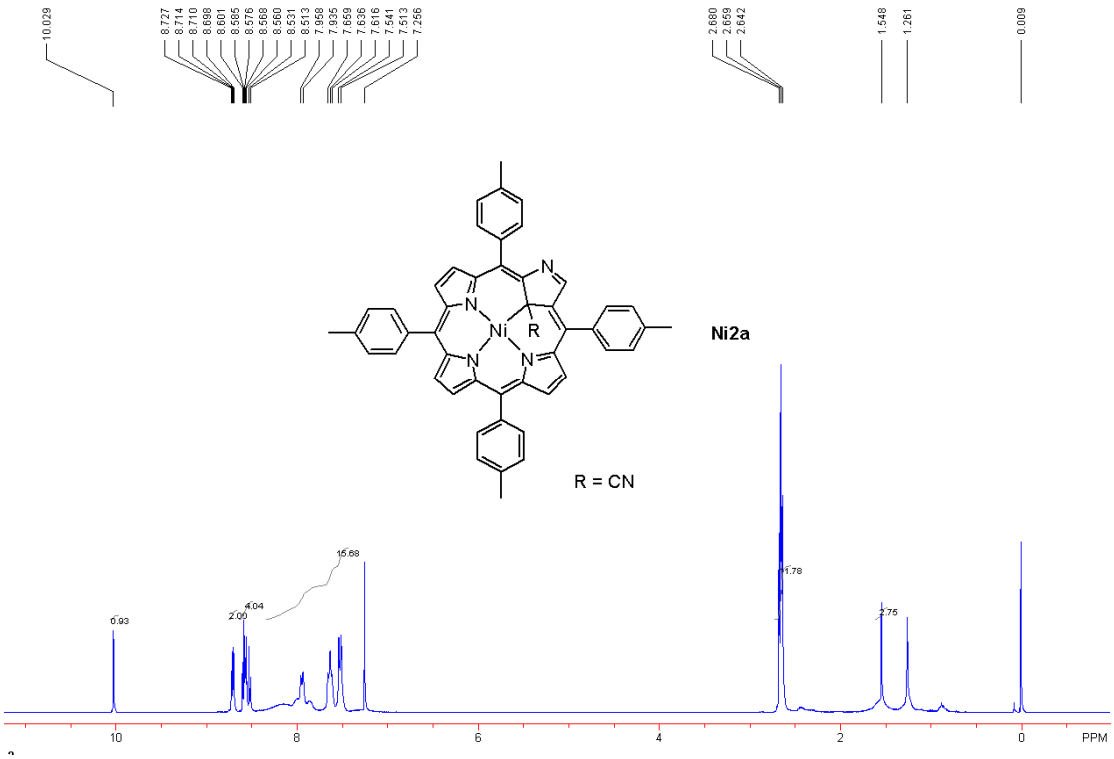
Copies of ^{1}H NMR spectra

Extra peaks at 1.5 ppm in the ^{1}H NMR spectra of most of the products are the signals of water. And the small signals at 1.3 ppm in some of the ^{1}H NMR spectra are the singals of small amount of impurities.




10.059
8.730
8.713
8.705
8.688
8.597
8.585
8.580
8.569
8.554
8.525
8.509
8.117
8.055
7.961
7.822
7.791
7.764
7.744
7.720
7.701
7.257
5.322
1.575
0.000
Ni1b
R = COOCH3
0.91
2.00
4.08
18.99
2.39
9.36
10
8
6
4
2
PPM


10.003
8.701
8.687
8.666
8.652
8.649
8.532
8.486
8.484
8.459
8.041
7.798
7.782
7.753
7.711
7.500
7.476
7.427
7.267
7.263
7.259
3.495
2.036
2.006
1.984
-0.399
-0.411
-0.433
Ni1c
R = COOC2H5
0.93
2.00
3.81
19.99
3.27
2.68
2.67
10
8
6
4
2
0
PPM


10.029
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8.710
8.698
8.601
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8.576
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8.560
8.531
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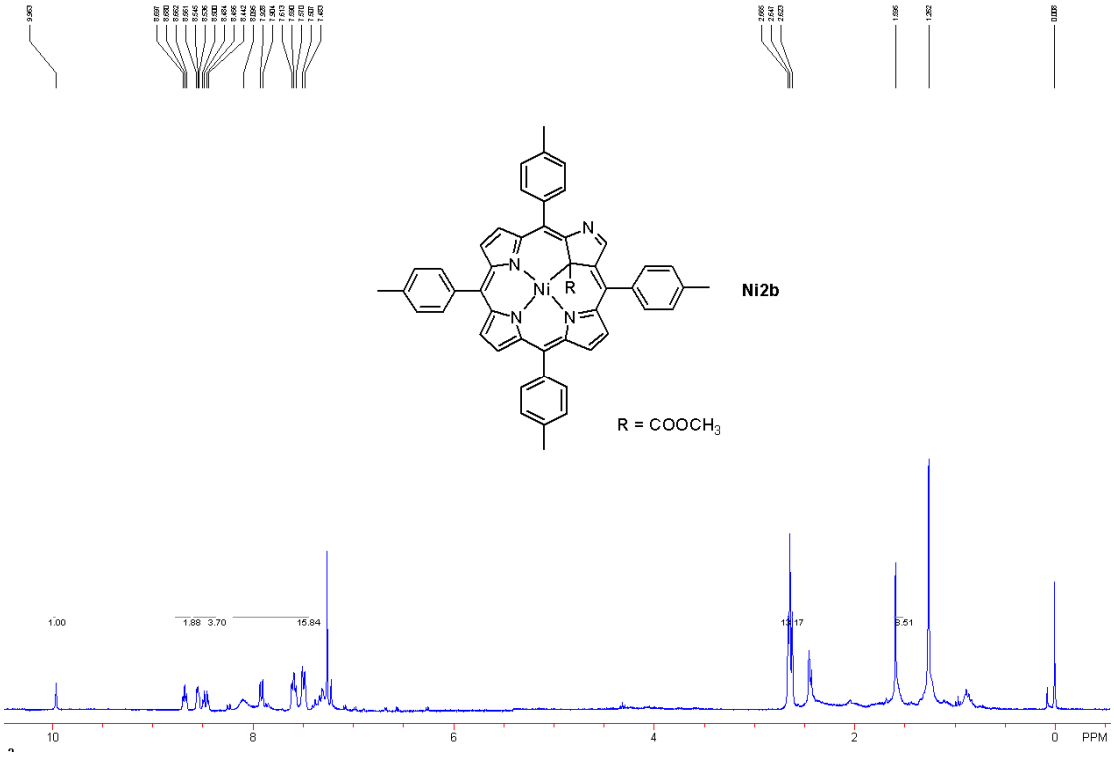
7.935
7.659
7.636
7.616
7.541
7.513
7.256
2.680
2.659
2.642
1.548
1.261
0.009
Ni2a
R = CN
15.68
11.78
4.04
2.00
0.93
2.75
10
8
6
4
2
0
PPM


Ni2b
R = COOCH3
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13.17
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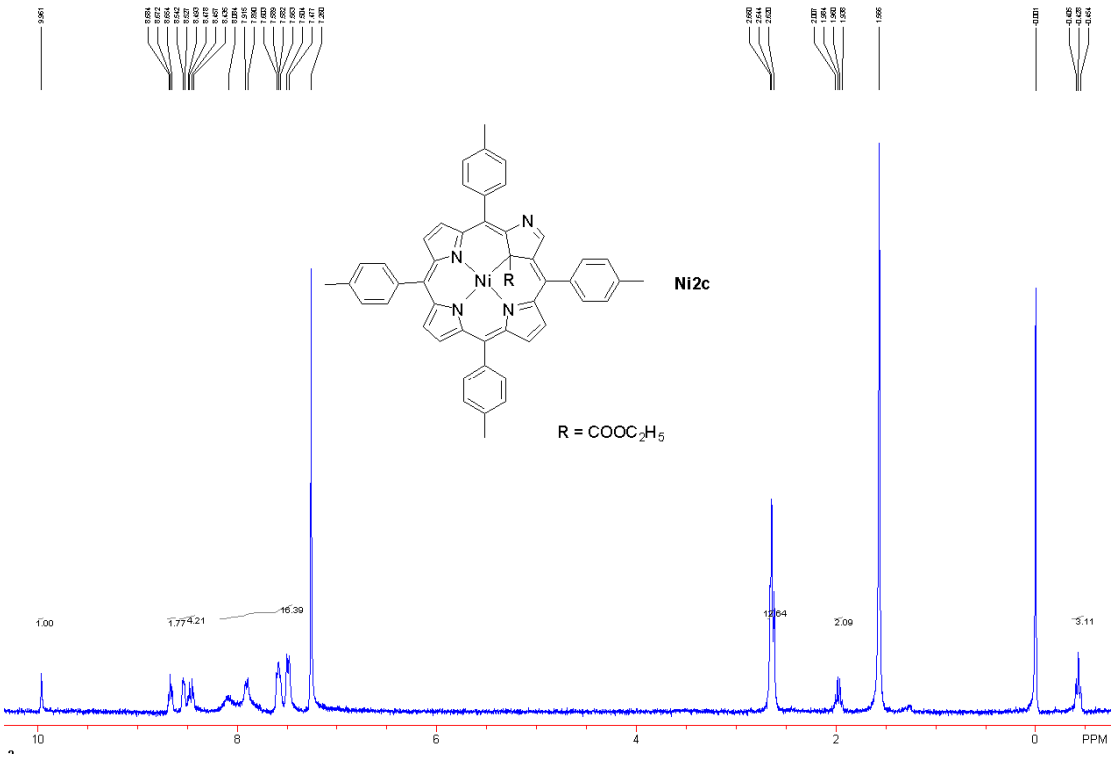
10
8
6
4
2
0
PPM


Ni2c
R = COOC2H5
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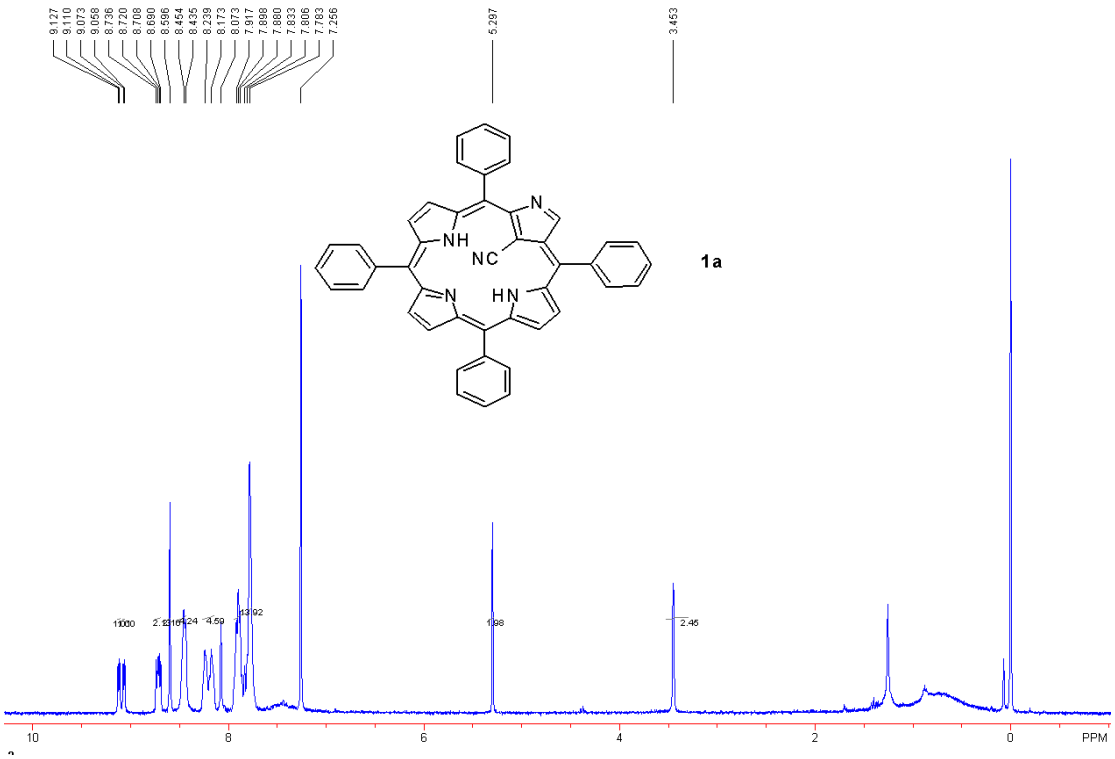
4.21
16.39
12.64
2.09
3.11
10
8
6
4
2
0
PPM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3.453
2.46
10
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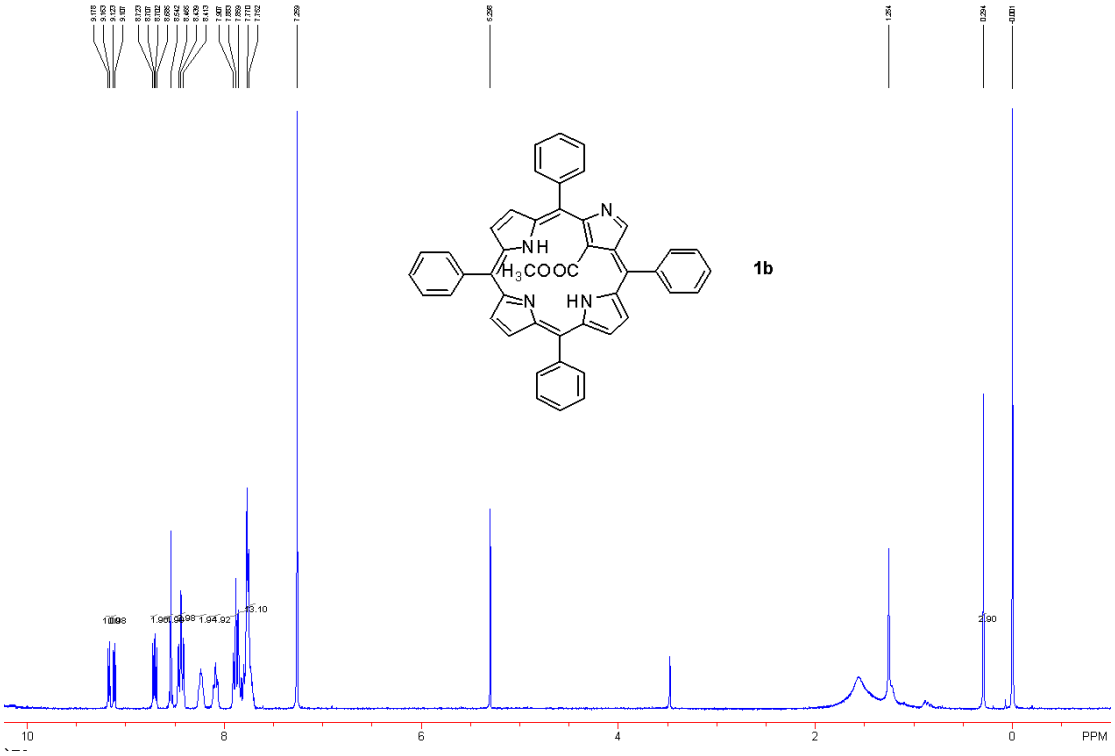
6
4
2
0
PPM


NH
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N
HN
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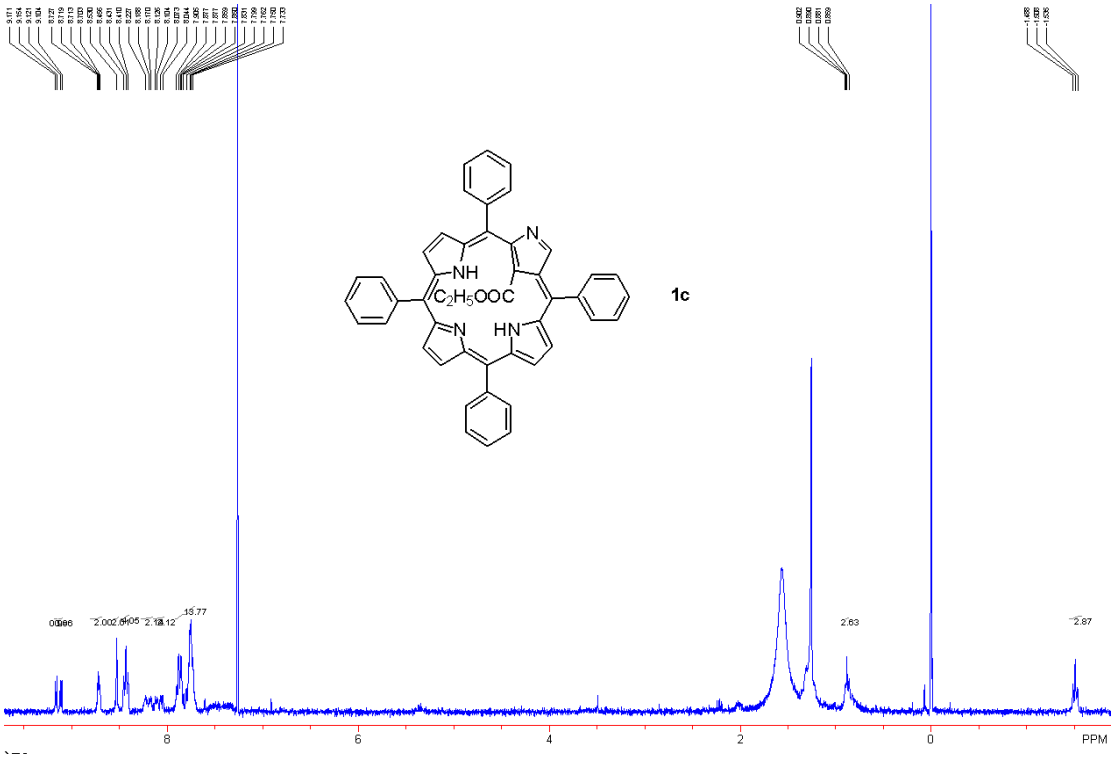
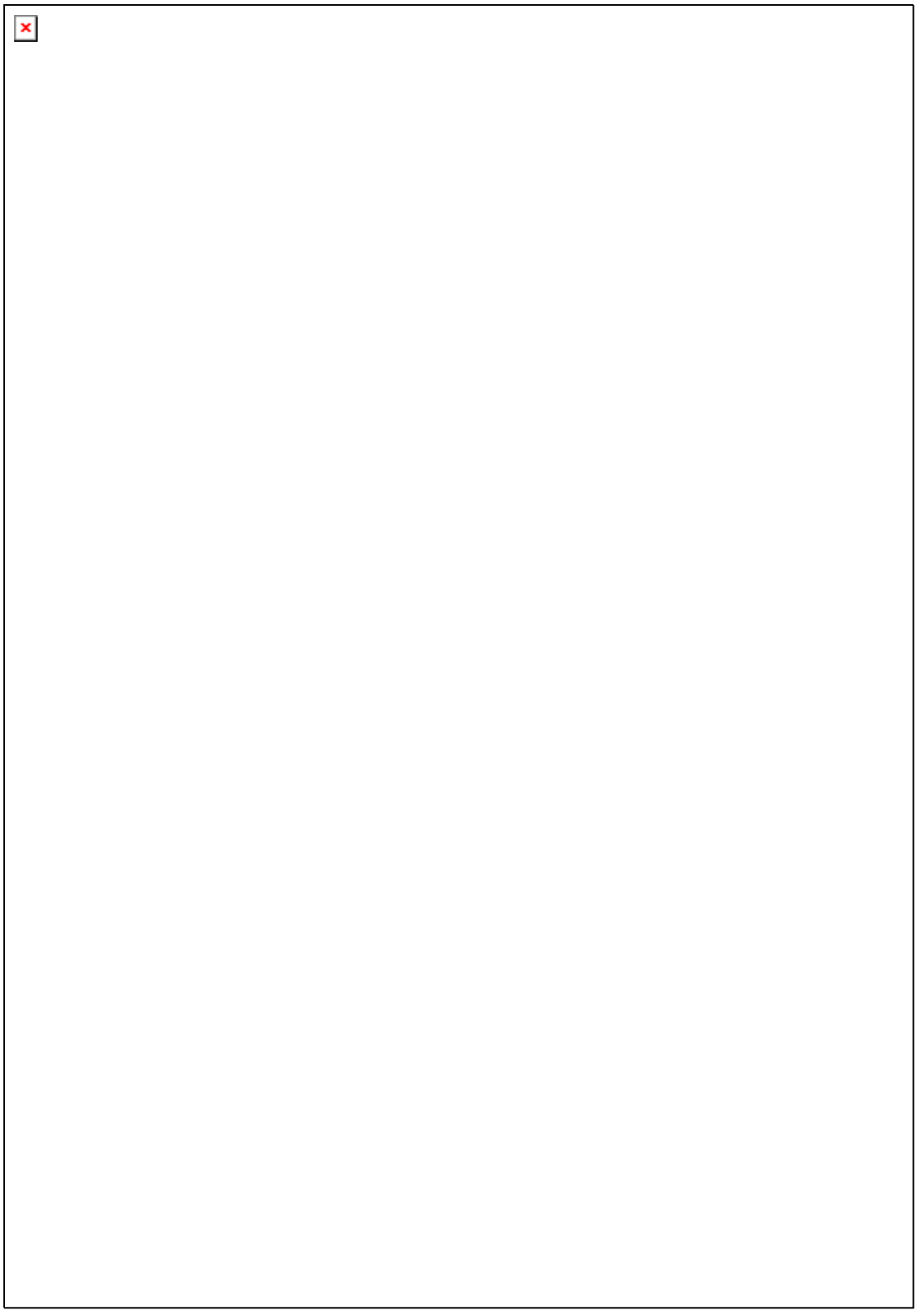
1.94
13.10
2.90
10
8
6
4
2
0
PPM


NH
C2H5OOC
N
HN
1c
16.77
2.63
2.87
8
6
4
2
0
PPM

Copies of the MS spectrum of the proposed Ni(III) intermediates.



Copies of the HRMS report of the proposed Ni(III) intermediates.

Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

SIOC

Instrument:

IonSpec 4.7 Tesla FTMS

Card Serial Number: I082633

Sample Serial Number: Inter3

Operator : HuaQin Date: 2008/10/21

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 827.2880 ± 0.004
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
N	14.003074	0	5
O	15.994915	0	5
Ni	57.935348	0	1

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:

Number of Hits = 5

m/z	Delta m/z	DBE	Formula
827.28905	-0.00105	33.5	$C_{53}H_{45}N_4O_2Ni^{+1}$
827.28909	-0.00109	41.0	$C_{56}H_{37}N_5O_3^{+1}$
827.28637	0.00163	29.0	$C_{50}H_{47}N_3O_5Ni^{+1}$
827.29039	-0.00239	33.0	$C_{55}H_{47}NO_3Ni^{+1}$
827.29043	-0.00243	40.5	$C_{58}H_{39}N_2O_4^{+1}$