Supporting Information

Room Temperature Catalytic Dehydrogenation of Cyclic Amines with Liberation of H₂ Using Water as a Solvent

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Table of Contents

1. Mechanistic Studies

1.1 UV-Visible spectra of proton reduction catalysts

Solutions of 10^{-4} M was prepared for all Co-based proton reduction catalysts used for the present catalytic study as well as for $[Ru(bpy)_3]^{2+}$ using analytical grade acetonitrile. Then the solution-state UV-Visible spectra were recorded and are given in Figure S1. From the UV-visible absorption spectra of proton reduction catalysts, it is found that the proton reduction catalysts do not absorb in the visible-light region. However, the photoredox catalyst $[Ru(bpy)_3]^{2+}$ absorbs the visible-light, hence initiates the redox reaction *via* single electron transfer process and not the proton reduction catalysts.
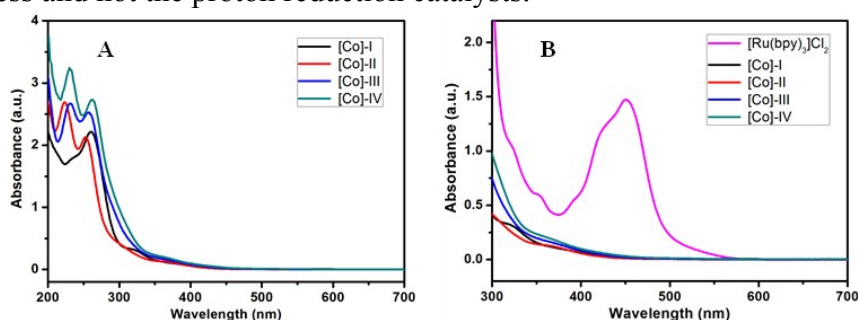

Figure S1. (A) UV-Visible spectra of proton reduction catalysts used for the present study. (B) Comparison of UV-Visible spectral absorbance of $[Ru(bpy)_3]Cl_2$ with proton reduction catalysts used for the present study.

1.2 Detection of liberated gas

The liberated hydrogen gas was detected and quantified after completion of the reaction for substrate **1a**.
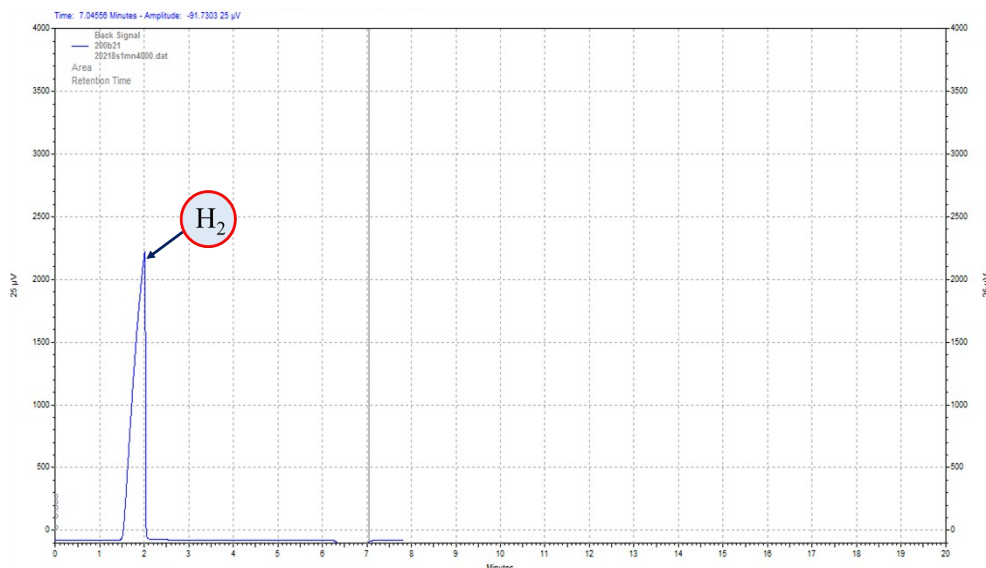

Figure S2. GC analysis.

1.3 Quantification of hydrogen gas

The evolved hydrogen gas was quantified by the hydrogenation of styrene, and it is observed that 76% of hydrogen gas was evolved from the hydrogenation reaction while the isolated yield of **2a** is 93%. The evolved hydrogen gas was utilized for hydrogenation of styrene. Simultaneously two parallel reactions were carried out. In one reaction vial, visible-light mediated photoredox catalytic acceptorless dehydrogenation of **1a** was carried out under the optimal reaction condition. Whereas in another reaction vial thermal hydrogenation of styrene **5** was carried out using RhCl(PPh$_3$)$_3$ as the catalyst. Both the reaction vials are connected to each other by a cannula and were allowed to continue for 12 h. After the stipulated time, the reaction mixture was analyzed in GC for hydrogenation of styrene and the results are given below.
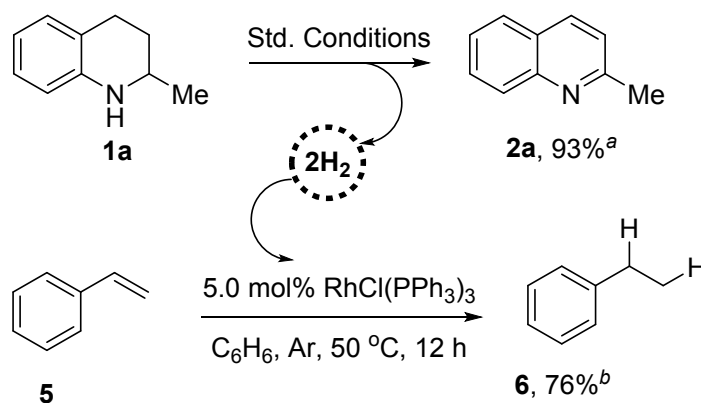

Figure S3. Quantification of hydrogen.

Reaction conditions: Substrate (0.25 mmol), [Ru(bpy)$_3$]Cl$_2$ (1.0 mol %), [Co] (2.5 mol %), water 8.0 mL, ambient temperature, 12 h, 36 W blue LED, [a]Isolated yield, [b]GC yield using n-decane as internal standard.

1.4 Cyclic voltammetric analysis

1.4a Cyclic voltammetry of proton reduction catalyst IV

Redox potentials of proton reduction catalyst and photocatalyst were judged through cyclic voltammetric (CV) investigations. Typically three electrode systems comprising glassy carbon (GC, 3mm dia.) was used as working electrode and Ag/Ag$^+$ (0.1M TBAP in acetonitrile) as reference electrode and platinum wire was used as counter electrode, respectively. CVs were recorded in acetonitrile containing 0.1M TBAP as electrolytic medium. Solutions were purged with argon for 30 minutes before scans and also jacketed during the measurements. Potentials were calibrated using the ferrocene as internal standard.
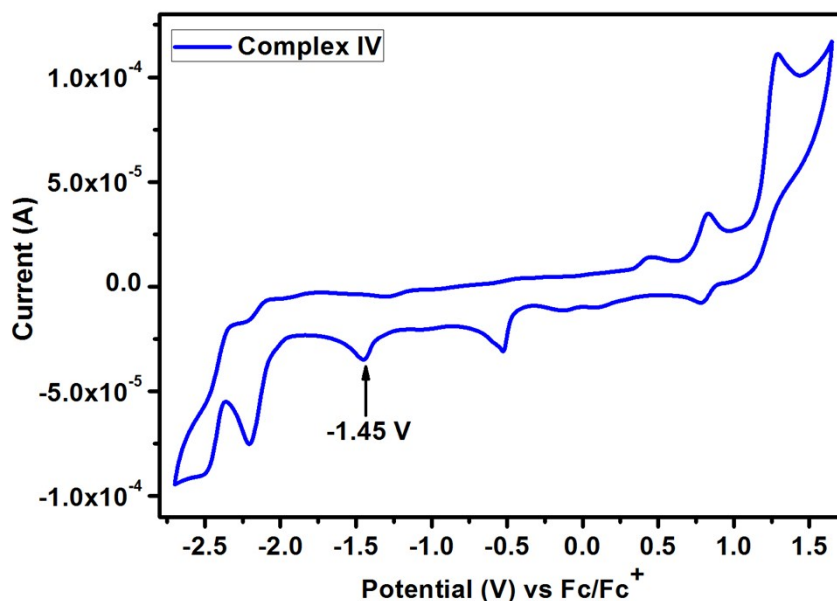
Figure S4. CV of **IV** (0.001 M) in 0.1 M NBu_4PF_6 in degassed CH_3CN with scan rate 100 mV/s.

1.4b   Cyclic voltammetry of partially saturated *N*-heterocycles

In order get insight into the oxidation potential of the partially saturated *N*-heterocycles, we recorded the cyclic voltammetry data for few of the compounds. The cyclic voltammetry was measured at 10 mV s^{-1} scan rate using Ag/AgCl as reference electrode, Pt wire as counter electrode and glassy carbon electrode as working electrode in anhydrous degassed acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The oxidation potential for **1a**, **3f** and **3h** are given below.
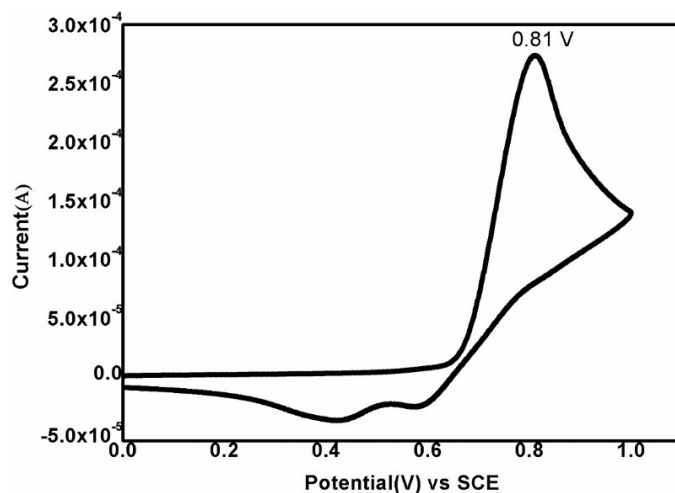

Figure S5. CV of **1a** (0.01 M) in 0.1 M NBu_4PF_6 in degassed MeCN with scan rate 10 mV/s.
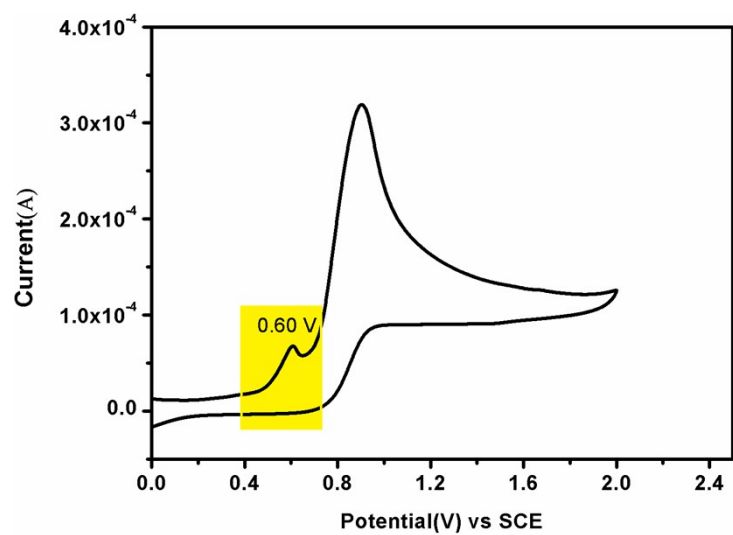
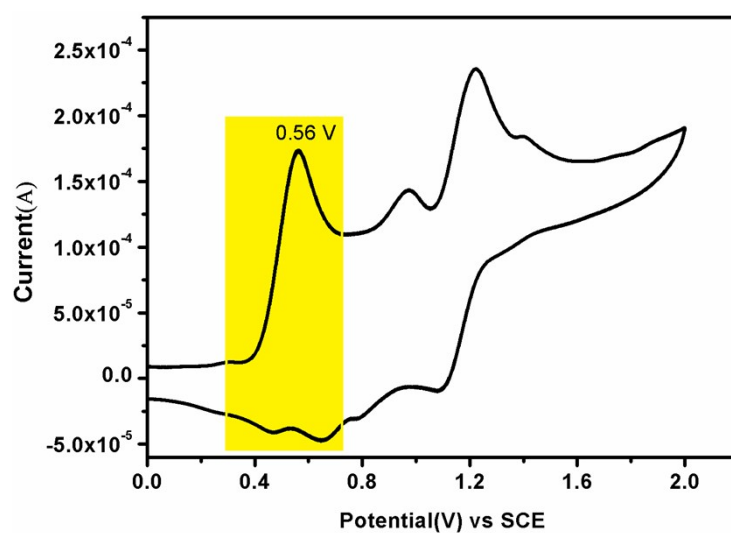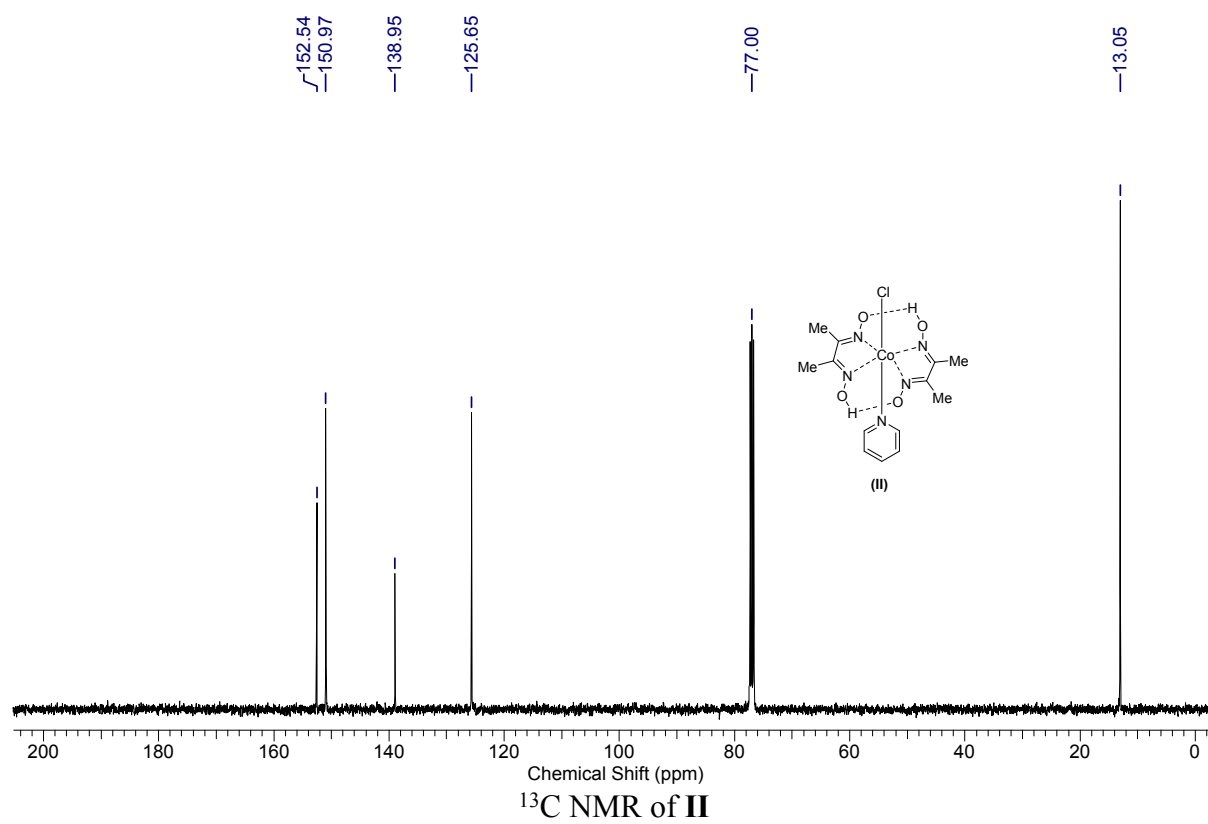**Figure S6.** CV of **3f** (0.01 M) in 0.1 M NBu$_4$PF$_6$ in degassed MeCN with scan rate 10 mV/s.

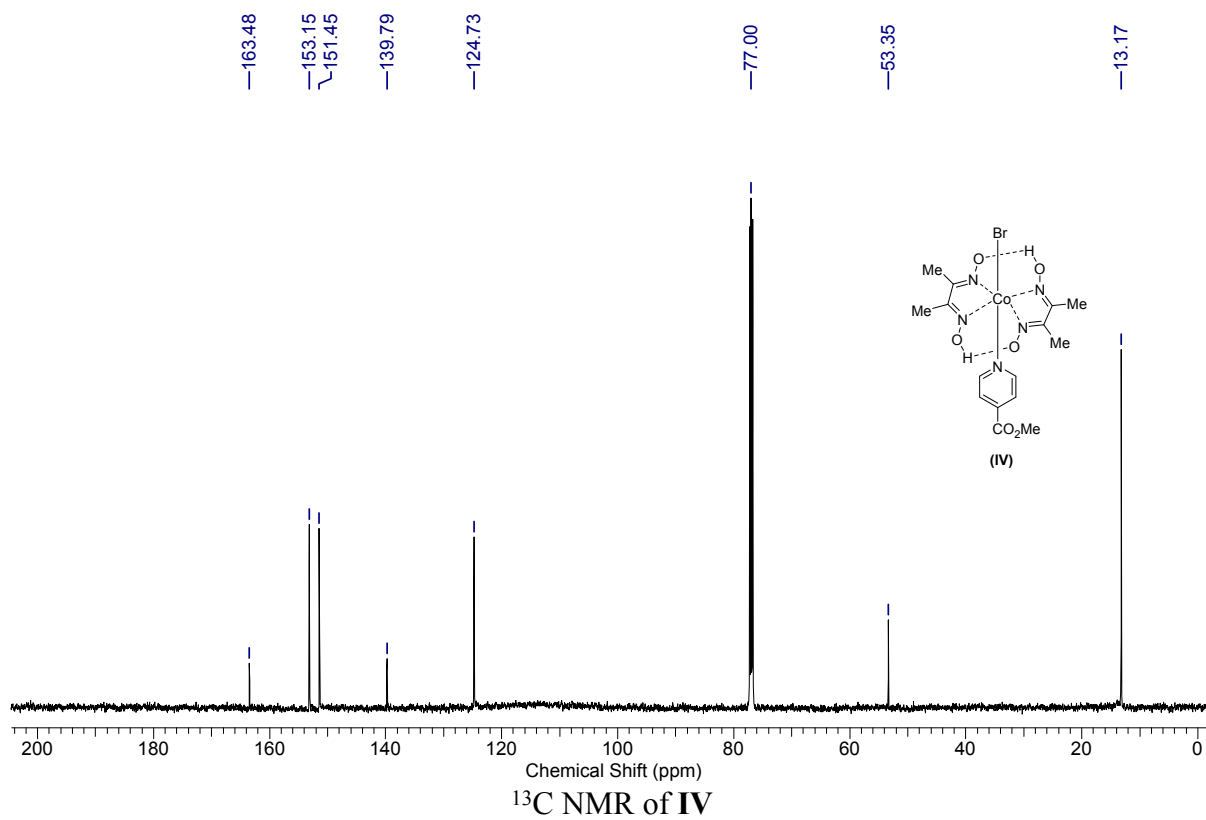**Figure S7.** CV of **3h** (0.01 M) in 0.1 M NBu$_4$PF$_6$ in degassed MeCN with scan rate 10 mV/s.

2. Copy of ¹H and ¹³C NMR Spectra

8.26
8.25
7.73
7.71
7.69
7.27
7.25
7.24
7.22

2.40

(II)

2.00 0.96 2.04

11.86
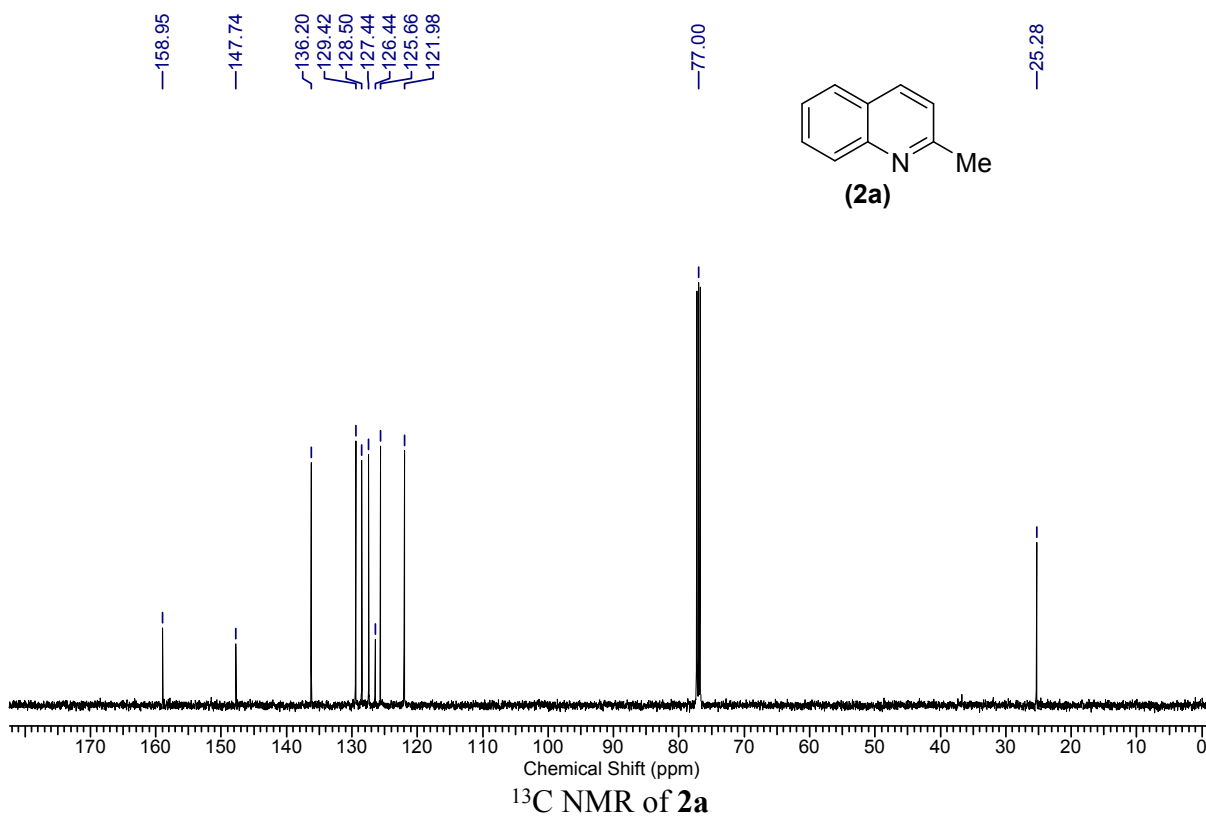
10 9 8 7 6 5 4 3 2 1 0

Chemical Shift (ppm)

¹H NMR of **II**

152.54
150.97
138.95
125.65
77.00
13.05

(II)

200 180 160 140 120 100 80 60 40 20 0

Chemical Shift (ppm)

¹³C NMR of **II**

8.41
8.40
7.77
7.75
7.27
3.92
2.39

2.00
1.94
2.95
11.95

10 9 8 7 6 5 4 3 2 1 0

Chemical Shift (ppm)

^{1}H NMR of **IV**

163.48
153.15
151.45
139.79
124.73
77.00
53.35
13.17

200 180 160 140 120 100 80 60 40 20 0

Chemical Shift (ppm)

^{13}C NMR of **IV**

^{1}H NMR of **2a**

^{13}C NMR of **2a**

^{1}H NMR of **2b**

^{13}C NMR of **2b**

8.76
8.10
8.09
7.95
7.94
7.69
7.68
7.66
7.54
7.52
7.51
7.27
7.18
7.17

2.65

Me

(2c)

1.05 1.10 1.00 0.99 0.98 0.98

3.13

Chemical Shift (ppm)

¹H NMR of **2c**

150.01
147.88
144.10
129.90
128.95
128.17
126.13
123.68
121.74

77.00

18.48

Me

(2c)

Chemical Shift (ppm)

¹³C NMR of **2c**

8.92, 8.92, 8.92, 8.91
8.92, 8.92, 8.92
8.05, 7.99, 7.98, 7.97, 7.97
8.07, 8.05, 7.99, 7.98, 7.97, 7.97
7.79, 7.77, 7.77
7.79, 7.78, 7.77, 7.77
7.43, 7.42, 7.41, 7.40
7.43, 7.42, 7.40

0.94   1.00 1.91 0.95 0.99

^{1}H NMR of **2d**

150.69, 146.79, 135.01, 132.91, 131.18, 129.76, 129.31, 121.85, 120.42, 77.00

^{13}C NMR of **2d**

8.87
8.86
8.86

8.11
8.10
8.09
8.08
8.07

7.49
7.47
7.47
7.42
7.41
7.40
7.39

8.87
8.86

8.11
8.10
8.09
8.08
8.07

7.47
7.42
7.41

7.39
7.27

0.96

1.99

1.00 2.01

F

(2e)

0.96   1.99   1.00 2.01

Chemical Shift (ppm)

^{1}H NMR of **2e**

161.30
159.33
149.63
149.60
145.33
135.35
135.31
131.96
131.88
128.85
128.77
121.70
119.78
119.57
110.71
110.53

77.00

F

(2e)

Chemical Shift (ppm)

^{13}C NMR of **2e**

^{1}H NMR of **2f**

^{13}C NMR of **2f**

^{1}H NMR of **2g**

^{13}C NMR of **2g**

8.76, 8.75, 8.75, 8.04, 8.02, 8.01, 7.99, 7.38, 7.37, 7.36, 7.35, 7.34, 7.34, 7.06, 7.05

8.76, 8.76, 8.75, 8.75, 8.04, 8.02, 8.01, 7.99, 7.38, 7.37, 7.36, 7.35, 7.34, 7.34, 7.33, 7.27, 7.06, 7.05

3.92

MeO — quinoline structure **(2h)**

0.99 1.07 1.00 1.04 1.04 1.07

0.99 1.07 1.00 1.04 1.04 1.07 3.38

Chemical Shift (ppm)

^{1}H NMR of **2h**

157.70, 147.87, 144.41, 134.69, 130.81, 129.26, 122.19, 121.29, 105.10, 77.00, 55.46

MeO — quinoline structure **(2h)**

Chemical Shift (ppm)

^{13}C NMR of **2h**

^{1}H NMR of **2i**

^{13}C NMR of **2i**

8.00
7.99
7.69
7.67
7.42
7.41
7.27
7.25

−2.72

1.90 1.00 0.97 1.04

3.11

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

^{1}H NMR of **2j**

160.15
148.17
135.85
135.13
128.62
127.69
126.63
124.78
122.14
−77.00
−25.30

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

^{13}C NMR of **2j**

^{1}H NMR of **4a**

^{13}C NMR of **4a**

^{1}H NMR of **4b**

^{13}C NMR of **4b**

7.61
7.59

7.32
7.31
7.27
7.22
7.20
7.19
7.19
7.14
7.14
7.13

8.40
7.61
7.59
7.32
7.31
7.22
7.20
7.19
7.14
7.13
6.41

4.77

2.26

1.00

1.01

1.03 1.03

7.6   7.5   7.4   7.3   7.2   7.1

(4c)

0.99   1.00 1.01 1.03 1.03   0.98   2.20   1.06

9   8   7   6   5   4   3   2   1   0

Chemical Shift (ppm)

^{1}H NMR of **4c**

137.49
136.33
128.00
122.15
120.58
119.90
110.97
100.52
77.00
58.60

(4c)

170 160 150 140 130 120 110 100   90   80   70   60   50   40   30   20   10   0

Chemical Shift (ppm)

^{13}C NMR of **4c**

^{1}H NMR of **4d**

^{13}C NMR of **4d**

^{1}H NMR of **4e**

^{13}C NMR of **4e**

8.71, 8.69, 8.25, 8.24, 7.97, 7.95, 7.94, 7.78, 7.76, 7.75, 7.74, 7.51, 7.50, 7.48, 7.27

8.71, 8.69 | 8.25, 8.24, 7.97, 7.95, 7.94, 7.78, 7.78, 7.76, 7.76, 7.75, 7.74 | 7.51, 7.50, 7.48

1.00   1.94   2.02   2.03   1.99

8.5   8.0   7.5

Chemical Shift (ppm)

1.00 1.94 2.02 2.03 1.99

9   8   7   6   5   4   3   2   1   0

Chemical Shift (ppm)

^{1}H NMR of **4f**

149.01   135.92, 130.18, 129.35, 128.11, 126.50, 125.57   77.00

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Chemical Shift (ppm)

^{13}C NMR of **4f**

^{1}H NMR of **4g**

^{13}C NMR of **4g**

^{1}H NMR of **4h**

^{13}C NMR of **4h**

3. Copy of HRMS Data

200A116 #292 RT: 1.30 AV: 1 NL: 4.58E7
T: FTMS + p ESI Full ms [100.0000-1500.0000]

404.0526
R=56306
C $_{13}$ H $_{20}$ O $_4$ N $_5$ Cl Co = 404.0530
-1.1180 ppm

426.0344
R=55106
C $_{13}$ H $_{19}$ O $_4$ N $_5$ Cl Co Na = 426.0350
-1.3012 ppm

410.1061
R=49602

391.2836
R=51000

421.9569
R=48000

441.9993
R=55904

449.1102
R=46600

460.0099
R=51502

467.0484
R=36400

483.0262
R=50006

Relative Abundance

m/z

HRMS of II

200A122 #269 RT: 1.20 AV: 1 NL: 4.88E8
T: FTMS + p ESI Full ms [100.0000-1500.0000]

448.0025
R=53606
C $_{13}$ H $_{20}$ O $_4$ N $_5$ Br Co = 448.0025
-0.0356 ppm

564.1160
R=47107

413.2543
R=53902

485.0738
R=49102

503.9595
R=48202

528.9744
R=45206

543.9332
R=40106

576.1346
R=42200

608.2715
R=33000

Relative Abundance

m/z

HRMS of III

506.0078
R=50506
$C_{15} H_{22} O_6 N_5 Br Co = 506.0080$
-0.4865 ppm

483.0756
R=51106

426.0812
R=54007
$C_{15} H_{21} O_6 N_5 Co = 426.0818$
-1.5449 ppm

413.2542
R=53502

474.4259
R=42400

541.9363
R=42500

558.9572
R=43902

577.0609
R=33600

592.8544
R=41700

(IV)

HRMS of IV

144.0809
R=94307
$C_{10} H_{10} N = 144.0808$
0.6641 ppm

116.9862
R=103902

134.9966
R=97907
$C_6 H_5 Cl Na = 134.9972$
-4.4583 ppm

160.0757
R=89307

110.0580
R=100002

120.0446
R=94202

125.9864
R=99902

152.9471
R=88102

167.0227
R=86507

181.0384
R=83507

(2a)

HRMS of 2a

144.0808
R=94503
C₁₀ H₁₀ N = 144.0808
-0.0772 ppm

115.0544
R=96002
C₉ H₇ = 115.0542
1.4843 ppm

158.0966
R=83502

216.9224
R=56500

237.0732
R=72007

277.0679
R=65107

301.1410
R=45100

319.1148
R=62907

Me

(2c)

Relative Abundance

m/z

HRMS of **2c**

207.9759
R=79002
C₉ H₇ N Br = 207.9756
1.0683 ppm

209.9729
R=78107

206.9672
R=55500
C₉ H₆ N Br = 206.9678
-2.9946 ppm

208.9787
R=79202

210.9758
R=79002

211.9792
R=74202

Br

(2d)

Relative Abundance

m/z

HRMS of **2d**

148.0556
R=90119
C$_9$H$_7$NF = 148.0557
-0.5581 ppm

108.0813
R=98844

122.0965
R=99454

136.1120
R=94232

164.1435
R=78464

177.1119
R=79202

199.0940
R=76357

229.1410
R=64524

251.6014
R=71513

Relative Abundance

m/z

(2e)

HRMS of **2e**

144.0808
R=94607
C$_{10}$H$_{10}$N = 144.0808
0.4523 ppm

116.9862
R=102502

129.0571
R=85102
C$_9$H$_7$N = 129.0573
-1.4502 ppm

134.9966
R=97505

149.0121
R=91602

152.9468
R=104600

160.0759
R=75502

167.0225
R=71400

174.0914
R=69600

Relative Abundance

m/z

(2f)

HRMS of **2f**

188.0704
R=82207
$C_{11}H_{10}O_2N$ = 188.0706
-1.2313 ppm

191.0771
R=66200

129.0566
R=91407

149.0119
R=88702

181.0489
R=74600

216.4706
R=62300

226.9508
R=70302

245.0780
R=44800

288.9211
R=62702

301.1404
R=55600

Relative Abundance

m/z

MeO$_2$C — quinoline

(2g)

HRMS of **2g**

160.0754
R=90007
$C_{10}H_{10}ON$ = 160.0757
-1.5683 ppm

145.0520
R=94407
C_9H_7ON = 145.0522
-1.6820 ppm

182.0573
R=82907
$C_{10}H_9ONNa$ = 182.0576
-1.8588 ppm

212.0068
R=57600

226.9510
R=71502

245.0780
R=61700

264.9541
R=51300

288.9212
R=64602

315.6865
R=45000

Relative Abundance

m/z

MeO — quinoline

(2h)

HRMS of **2h**

175.0503
R=84607
$C_9 H_7 O_2 N_2$ = 175.0502
0.6825 ppm

149.0122
R=91802
$C_7 H_7 Cl Na$ = 149.0128
-4.1048 ppm

161.0472
R=89807
$C_9 H_7 O_2 N$ = 161.0471
0.5010 ppm

172.0945
R=75102

191.0454
R=77502

203.0527
R=77000

212.1072
R=62300

(2i)

Relative Abundance

m/z

HRMS of **2i**

178.0419
R=86106
$C_{10} H_9 N Cl$ = 178.0418
0.4595 ppm

122.0732
R=95402

144.0806
R=92102
$C_{10} H_{10} N$ = 144.0808
-0.9245 ppm

190.0860
R=65200

204.4389
R=48700

225.1118
R=73407

237.0731
R=71707

256.8203
R=60900

277.0677
R=64207

297.0821
R=59607

(2j)

Relative Abundance

m/z

HRMS of **2j**

132.0809
R=99507
C₉ H₁₀ N = 132.0808
0.8399 ppm

$C_9 H_{10} N = 132.0808$

116.9862
R=105202

149.0122
R=92202

114.0917
R=95702

121.0174
R=102502

125.9865
R=99402

134.9965
R=97607

144.0808
R=93507

152.9471
R=89302

158.0965
R=89202

163.0390
R=88907

(4b)

HRMS of **4b**

148.0756
R=93102
C₉ H₁₀ O N = 148.0757
-0.3558 ppm

$C_9 H_{10} O N = 148.0757$

146.0599
R=86502
C₉ H₈ O N = 146.0600
-1.1293 ppm

$C_9 H_8 O N = 146.0600$

147.0502
R=63400

147.7857
R=60900

(4c)

HRMS of **4c**

S32

212.0682
R=76707
$C_{11} H_{11} O_2 N Na$ = 212.0682
-0.1111 ppm

(4d)

205.0863
R=65802

206.1176
R=70000

208.0690
R=57500

209.0696
R=70702

213.0760
R=69400

214.0897
R=54000

215.1045
R=65500

216.9228
R=71302

218.0648
R=51300

219.1744
R=71902

HRMS of **4d**

148.0758
R=92907
$C_9 H_{10} O N$ = 148.0757
0.6747 ppm

(4e)

130.1591
R=89700

134.9965
R=96907

140.0682
R=94607

145.0172
R=92102

152.9470
R=90502

158.0124
R=89402

163.0389
R=87407

167.0226
R=87302

171.1491
R=84102

174.0913
R=86207

177.0434
R=85007

181.0383
R=84407

188.0706
R=82407

195.0540
R=79207

201.1120
R=67500

HRMS of **4e**

S33

180.0807
R=83703
$C_{13} H_{10} N = 180.0808$
-0.6549 ppm

152.0618
R=85907
$C_{12} H_8 = 152.0621$
-1.9697 ppm

226.9512
R=72802
$H_3 O_{14} = 226.9517$
-2.3968 ppm

288.9216
R=63102

331.1049
R=57807
$C_{16} H_{11} O N_8 = 331.1050$
-0.4368 ppm

362.9256
R=54700

Relative Abundance

m/z

(4f)

HRMS of **4f**

159.0916
R=89707
$C_{10} H_{11} N_2 = 159.0917$
-0.2885 ppm

131.0604
R=98202
$C_8 H_7 N_2 = 131.0604$
0.1486 ppm

152.9469
R=84002

173.0121
R=84402

194.0963
R=81407
$C_{14} H_{12} N = 194.0964$
-0.5009 ppm

226.9512
R=75202
$H_3 O_{14} = 226.9517$
-2.1951 ppm

Relative Abundance

m/z

(4g)

HRMS of **4g**

HRMS of **4h**