Supporting information

A Repertoire of Pyridinium-Phenyl-Methyl Cross-talk Through Cascade of Intramolecular Electrostatic Interactions

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Legends for Figures S1 – S4:

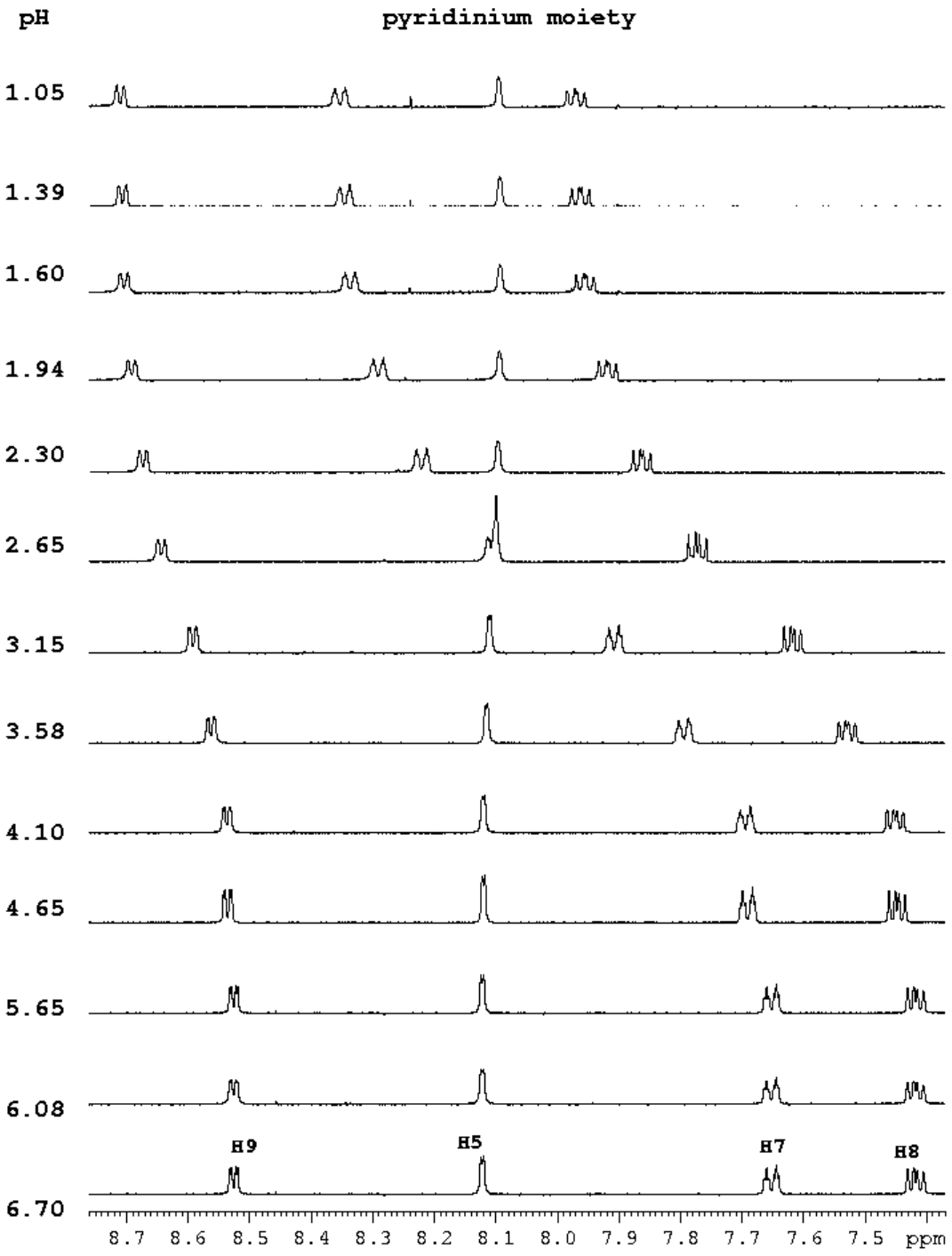
Figure S1A-S1B. ^{1}H NMR plots showing the relative shift of aromatic and methyl protons (see Scheme 1 for proton numbering) as a function of pH for compounds **1a** (only 13 representative pH-dependent chemical shifts including the lowest and highest pHs are shown out of total 35). Figure S1A shows the pH-dependent ^{1}H NMR plots [$7.37 \leq \delta$ (in ppm) ≤ 8.8] for aromatic protons (δH5, δH7, δH8 and δH9) of pyridinium moiety in **1a**. Figure S1B shows the pH-dependent ^{1}H NMR plots [$6.79 \leq \delta$ (in ppm) ≤ 7.35] for aromatic protons (δH14, δH13/H15 and δH12/H16) of phenyl moiety in **1a**. Panel (**C**) shows the pH-dependent ^{1}H NMR plots [$1.65 \leq \delta$ (in ppm) ≤ 2.02] for methyl group (δC$\underline{H}_3$) in **1a**.

Figure S2. ^{1}H NMR plots showing the relative shift of aromatic and methyl protons (see Scheme 1 for proton numbering) as a function of pH for compounds **2a** (only 13 representative pH-dependent chemical shifts including the lowest and highest pHs are shown out of total 30). It shows the pH-dependent ^{1}H NMR plots [$7.55 \leq \delta$ (in ppm) ≤ 9.1] for aromatic protons (δH5, δH7, δH8 and δH9) of pyridinium moiety in **2a**. The methyl group (δC$\underline{H}_3$) in **2a** did not shift as a function of pH so it is now shown.

Figure S3A-S3B. Figure S3A shows ^{1}H NMR plots [$6.78 \leq \delta$ (in ppm) ≤ 8.8] of **1b** [Panel (**A**)] compared to **1a**$^{+}$ [Panel (**B**)] and **1a** [Panel (**C**)] at 298 K. Similarly, Panels (**D**) – (**F**) show ^{1}H NMR plots [$7.55 \leq \delta$ (in ppm) ≤ 9.15] of **2b** [Panel (**D**)], **2a** [Panel (**E**)] compared to **2a**$^{+}$ [Panel (**F**)] at 298 K. Figure S3B shows ^{1}H NMR plots [$1.5 \leq \delta$ (in ppm) ≤ 4.8] of **1b** [Panel (**A**)] compared to **1a**$^{+}$ [Panel (**B**)] and **1a** [Panel (**C**)] at 298 K. Similarly, Panels (**D**) – (**F**) show ^{1}H NMR plots [$1.55 \leq \delta$ (in ppm) ≤ 4.6] of **2b** [Panel (**D**)], **2a** [Panel (**E**)] compared to **2a**$^{+}$ [Panel (**F**)] at 298 K.

Figure S4. NMR plots of selective homonuclear (^{1}H) decoupling experiments in D_2O at 298 K of **1a** [$2.70 \leq \delta$ (in ppm) ≤ 4.65] for assignments of non-aromatic protons (δH2A, δH3A/H3B, δH10A and δH10B). Panels (**B**) – (**E**) show the selective ^{1}H decoupled [δH2A: Panel (**B**), δH10A: Panel (**C**), δH10B: Panel (**D**), δH3A/H3B: Panel (**E**)] proton

spectra for **1a** and Panel (**A**) shows similar region of the un-decoupled spectra for comparison.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pyridinium moiety
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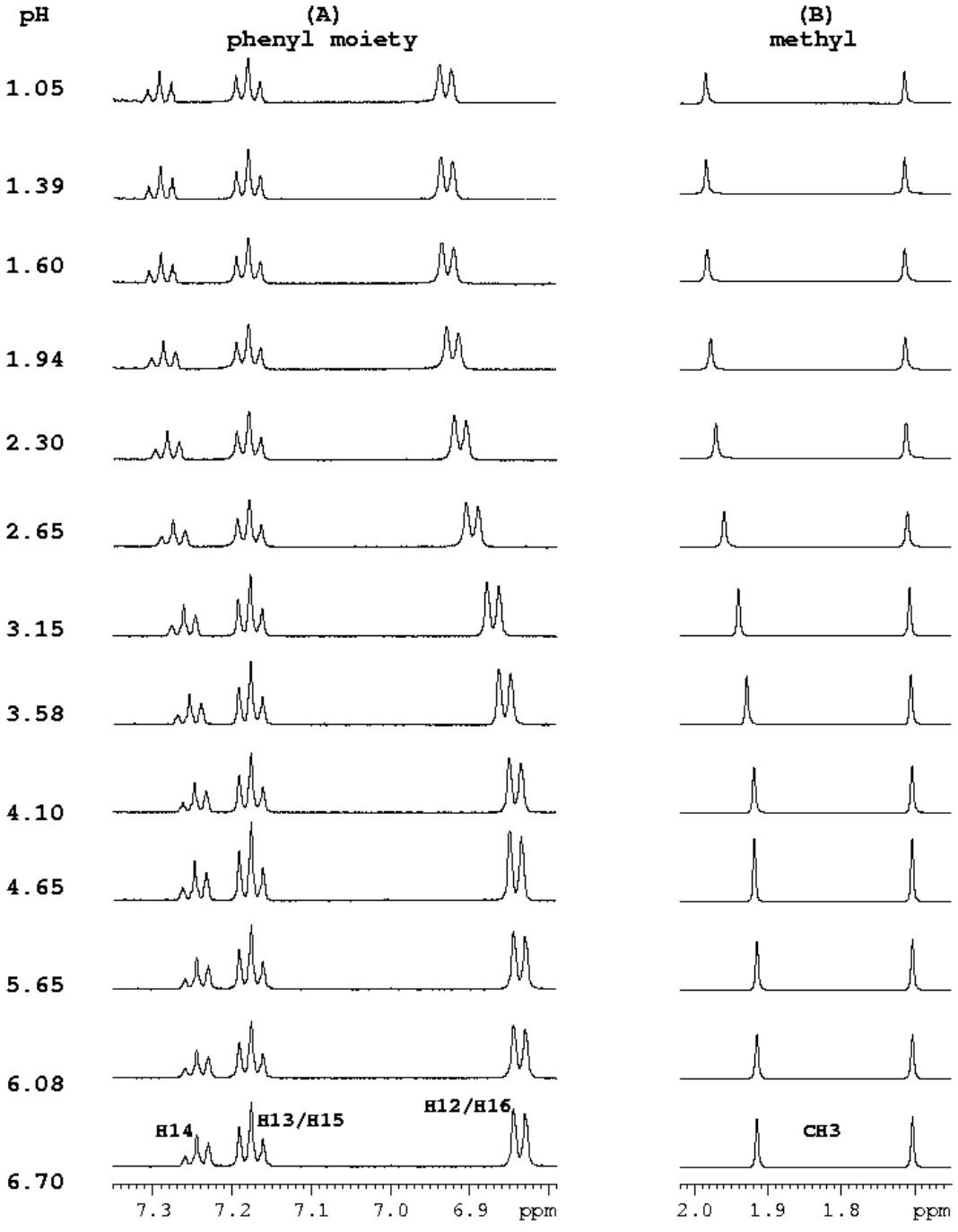
1.39
1.60
1.94
2.30
2.65
3.15
3.58
4.10
4.65
5.65
6.08
6.70
H9
H5
H7
H8
8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 ppm

Figure S1A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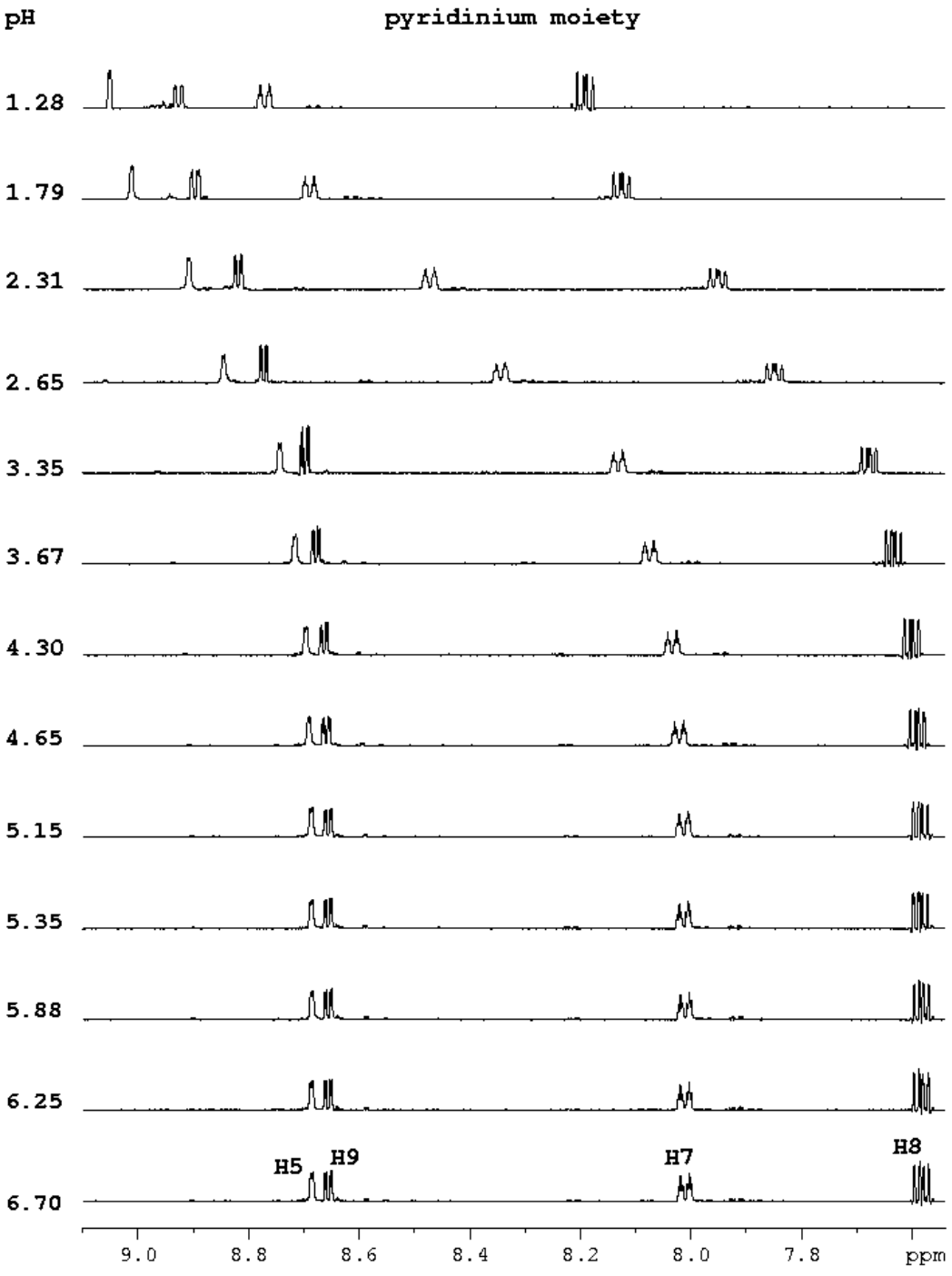
(A)
phenyl moiety
(B)
methyl
1.05
1.39
1.60
1.94
2.30
2.65
3.15
3.58
4.10
4.65
5.65
6.08
6.70
H14
H13/H15
H12/H16
CH3
7.3
7.2
7.1
7.0
6.9
ppm
2.0
1.9
1.8
ppm

Figure S1B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2.65
3.35
3.67
4.30
4.65
5.15
5.35
5.88
6.25
6.70
H5
H9
H7
H8
9.0
8.8
8.6
8.4
8.2
8.0
7.8
ppm

Figure S2

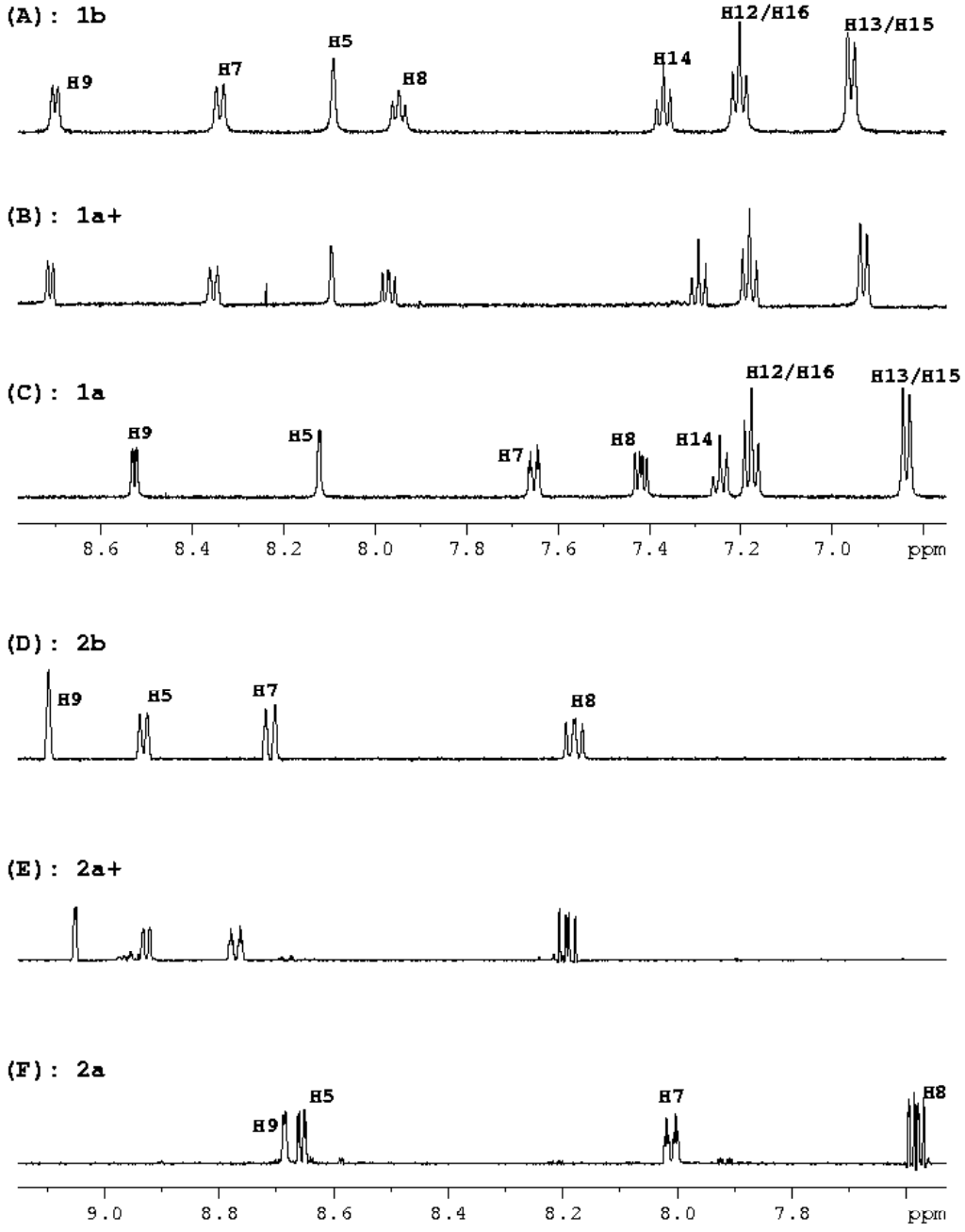
(A): 1b
H9
H7
H5
H8
H14
H12/H16
H13/H15
(B): 1a+
(C): 1a
H9
H5
H7
H8
H14
H12/H16
H13/H15
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
(D): 2b
H9
H5
H7
H8
(E): 2a+
(F): 2a
H9
H5
H7
H8
9.0
8.8
8.6
8.4
8.2
8.0
7.8
ppm

Figure S3A

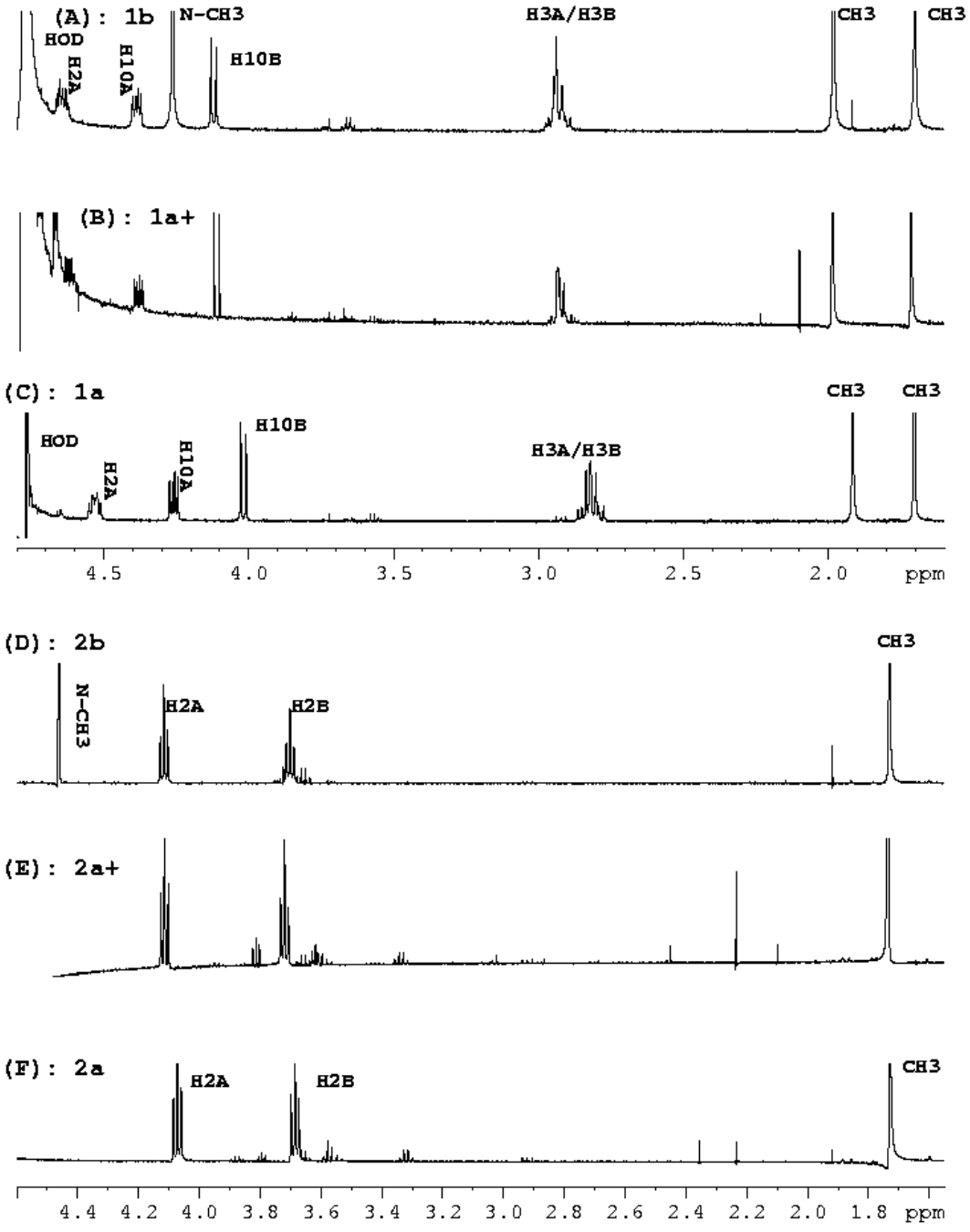
(A) : 1b
HOD
H2A
H10A
N-CH3
H10B
H3A/H3B
CH3
CH3
(B) : 1a+
(C) : 1a
HOD
H2A
H10A
H10B
H3A/H3B
CH3
CH3
4.5
4.0
3.5
3.0
2.5
2.0
ppm
(D) : 2b
N-CH3
H2A
H2B
CH3
(E) : 2a+
(F) : 2a
H2A
H2B
CH3
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
ppm

Figure S3B

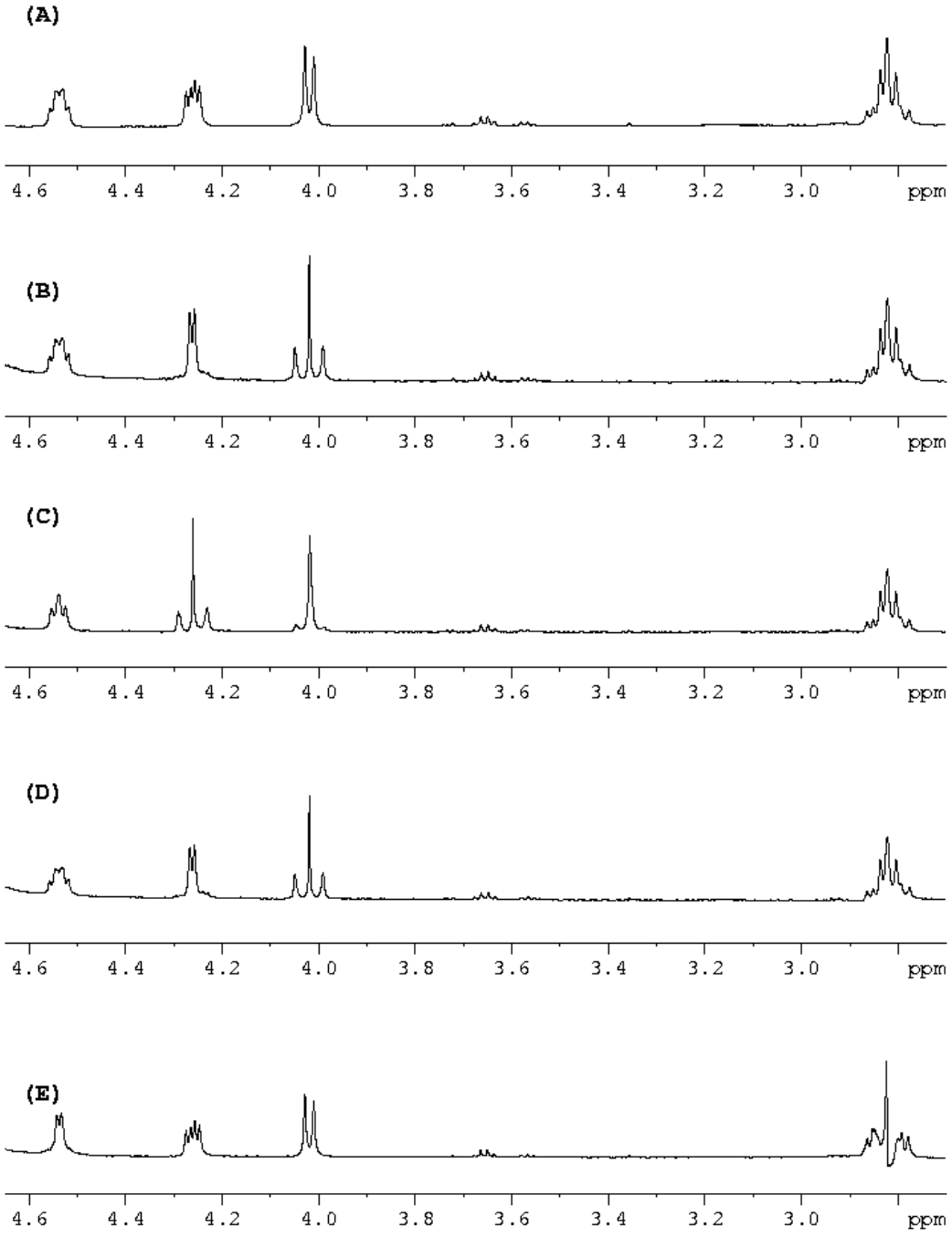
(A)
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 ppm
(B)
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 ppm
(C)
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 ppm
(D)
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 ppm
(E)
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 ppm

Figure S4

Table 1: Coordinates of Compound 1a (PDB format)

```
HEADER
REMARK   6-31G** Hartree-Fork optimized geometry structure of 1a
HETATM    1  C15        1      0.000   0.000   0.000
HETATM    2  C16        1      0.000   0.000   1.385
HETATM    3  C14        1      1.199   0.000  -0.695
HETATM    4  H15        1     -0.934   0.008  -0.534
HETATM    5  C11        1      1.191  -0.006   2.105
HETATM    6  C13        1      2.392   0.011   0.008
HETATM    7  H16        1     -0.937   0.017   1.916
HETATM    8  H14        1      1.202   0.002  -1.770
HETATM    9  C12        1      2.386   0.013   1.393
HETATM   10  C10        1      1.163  -0.008   3.618
HETATM   11  H13        1      3.328   0.024  -0.521
HETATM   12  C2         1      1.293  -1.378   4.313
HETATM   13 1H10        1      0.232   0.431   3.956
HETATM   14 2H10        1      1.959   0.625   4.004
HETATM   15  H12        1      3.323   0.038   1.921
HETATM   16  N1         1      0.359  -2.386   3.796
HETATM   17  C3         1      2.632  -2.091   4.149
HETATM   18  H2         1      1.086  -1.212   5.361
HETATM   19  C1         1      1.107  -3.547   3.232
HETATM   20  O1         1      2.415  -3.054   3.161
HETATM   21  C4         1     -0.910  -2.346   4.286
HETATM   22 1H3         1      3.432  -1.444   3.821
HETATM   23 2H3         1      2.936  -2.559   5.082
HETATM   24  O2         1     -1.239  -1.532   5.112
HETATM   25  C17        1      1.063  -4.753   4.172
HETATM   26  C18        1      0.746  -3.936   1.806
HETATM   27  C6         1     -1.963  -3.288   3.773
HETATM   28  C7         1     -2.695  -4.045   4.678
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HETATM   30 1H17        1      1.733  -5.519   3.798
HETATM   31 2H17        1      0.067  -5.172   4.234
HETATM   32 3H17        1      1.382  -4.478   5.171
HETATM   33 1H18        1      1.545  -4.564   1.428
HETATM   34 2H18        1     -0.176  -4.496   1.752
HETATM   35 3H18        1      0.680  -3.055   1.182
HETATM   36  C8         1     -3.731  -4.827   4.212
HETATM   37  N2         1     -3.366  -4.038   1.994
HETATM   38  H7         1     -2.452  -4.012   5.725
HETATM   39  H5         1     -1.854  -2.700   1.719
HETATM   40  C9         1     -4.023  -4.788   2.857
HETATM   41  H8         1     -4.311  -5.441   4.876
HETATM   42  H9         1     -4.829  -5.379   2.458
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CONECT    9    5    6   15
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CONECT   20   17   19
CONECT   21   16   24   27
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CONECT   23   17
CONECT   24   21
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CONECT   26   19   33   34   35
CONECT   27   21   28   29
CONECT   28   27   36   38
CONECT   29   27   37   39
CONECT   30   25
CONECT   31   25
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CONECT   37   29   40
CONECT   38   28
CONECT   39   29
CONECT   40   36   37   42
CONECT   41   36
CONECT   42   40
END
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Table 2: Coordinates of Compound **1a**$^{+}$ (PDB format)

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HEADER
REMARK 6-31G** Hartree-Fork optimized geometry structure
REMARK of protonated 1a (1a+)
HETATM    1  C15       1      -0.335   3.390  -0.838
HETATM    2  C16       1       0.326   2.691   0.162
HETATM    3  C11       1       1.532   2.043  -0.091
HETATM    4  C12       1       2.068   2.130  -1.371
HETATM    5  C13       1       1.409   2.823  -2.374
HETATM    6  C14       1       0.202   3.452  -2.113
HETATM    7  C10       1       2.226   1.287   1.024
HETATM    8  C2        1       2.134  -0.254   0.964
HETATM    9  N1        1       0.808  -0.731   0.529
HETATM   10  C1        1       0.934  -1.573  -0.702
HETATM   11  O1        1       2.220  -1.267  -1.131
HETATM   12  C3        1       3.047  -0.954  -0.043
HETATM   13  C4        1      -0.183  -0.683   1.433
HETATM   14  O2        1      -0.039  -0.368   2.583
HETATM   15  C17       1       0.821  -3.058  -0.355
HETATM   16  C18       1       0.021  -1.196  -1.861
HETATM   17  C6        1      -1.616  -0.944   1.012
HETATM   18  C7        1      -2.385  -1.874   1.705
HETATM   19  C8        1      -3.740  -2.018   1.433
HETATM   20  C9        1      -4.314  -1.187   0.509
HETATM   21  N2        1      -3.561  -0.270  -0.109
HETATM   22  C5        1      -2.250  -0.127   0.110
HETATM   23  H7        1      -1.920  -2.480   2.461
HETATM   24  H8        1      -4.340  -2.745   1.944
HETATM   25  H5        1      -1.750   0.656  -0.426
HETATM   26  H9        1      -5.354  -1.215   0.248
HETATM   27  H2        1       2.333  -0.624   1.961
HETATM   28 2H3        1       3.852  -0.331  -0.401
HETATM   29 1H3        1       3.476  -1.855   0.383
HETATM   30 1H10       1       1.805   1.602   1.970
HETATM   31 2H10       1       3.280   1.549   1.057
HETATM   32  H12       1       3.009   1.661  -1.594
HETATM   33  H16       1      -0.083   2.674   1.159
HETATM   34  H13       1       1.845   2.882  -3.355
HETATM   35  H14       1      -0.299   4.005  -2.888
HETATM   36  H15       1      -1.250   3.911  -0.611
HETATM   37 1H17       1       1.043  -3.650  -1.235
HETATM   38 2H17       1      -0.180  -3.312  -0.021
HETATM   39 3H17       1       1.519  -3.331   0.427
HETATM   40 1H18       1       0.415  -1.673  -2.750
HETATM   41 2H18       1      -0.992  -1.552  -1.725
HETATM   42 3H18       1       0.034  -0.126  -2.021
HETATM   43  HN2       1      -4.001   0.347  -0.763
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CONECT    3   2   4   7
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CONECT    5   4   6  34
CONECT    6   1   5  35
CONECT    7   3   8  30  31
CONECT    8   7   9  12  27
CONECT    9   8  10  13
CONECT   10   9  11  15  16
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CONECT   13    9   14   17
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CONECT   15   10   37   38   39
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CONECT   21   20   22   43
CONECT   22   17   21   25
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CONECT   24   19
CONECT   25   22
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CONECT   27    8
CONECT   28   12
CONECT   29   12
CONECT   30    7
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CONECT   32    4
CONECT   33    2
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CONECT   35    6
CONECT   36    1
CONECT   37   15
CONECT   38   15
CONECT   39   15
CONECT   40   16
CONECT   41   16
CONECT   42   16
CONECT   43   21
END
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Table 3: Coordinates of Compound 2a (PDB format)

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HEADER
REMARK 6-31G** Hartree-Fock optimized geometry of 2a
HETATM    1 1H2         1      0.000   0.000   0.000
HETATM    2  C2         1      0.000   0.000   1.085
HETATM    3  N1         1      1.374   0.000   1.589
HETATM    4  C3         1     -0.528   1.306   1.639
HETATM    5  H2         1     -0.533  -0.869   1.435
HETATM    6  C1         1      1.750   1.382   2.003
HETATM    7  O1         1      0.606   2.126   1.668
HETATM    8  C4         1      1.896  -1.193   1.995
HETATM    9 2H3         1     -1.273   1.778   1.013
HETATM   10 1H3         1     -0.941   1.176   2.637
HETATM   11  O2         1      1.241  -2.203   2.005
HETATM   12  C17        1      1.994   1.496   3.507
HETATM   13  C18        1      2.885   1.999   1.197
HETATM   14  C6         1      3.342  -1.288   2.389
HETATM   15  C7         1      3.683  -1.901   3.588
HETATM   16  C5         1      4.370  -0.942   1.526
HETATM   17 1H17        1      2.101   2.544   3.761
HETATM   18 2H17        1      2.892   0.977   3.813
HETATM   19 3H17        1      1.154   1.094   4.063
HETATM   20 1H18        1      2.873   3.070   1.360
HETATM   21 2H18        1      3.853   1.622   1.496
HETATM   22 3H18        1      2.734   1.812   0.141
HETATM   23  C8         1      5.018  -2.070   3.894
HETATM   24  N2         1      5.650  -1.120   1.802
HETATM   25  H7         1      2.912  -2.234   4.258
HETATM   26  H5         1      4.148  -0.522   0.562
HETATM   27  C9         1      5.961  -1.658   2.965
HETATM   28  H8         1      5.325  -2.523   4.818
HETATM   29  H9         1      7.012  -1.780   3.167
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CONECT    2    1    3    4    5
CONECT    3    2    6    8
CONECT    4    2    7    9   10
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CONECT    6    3    7   12   13
CONECT    7    4    6
CONECT    8    3   11   14
CONECT    9    4
CONECT   10    4
CONECT   11    8
CONECT   12    6   17   18   19
CONECT   13    6   20   21   22
CONECT   14    8   15   16
CONECT   15   14   23   25
CONECT   16   14   24   26
CONECT   17   12
CONECT   18   12
CONECT   19   12
CONECT   20   13
CONECT   21   13
CONECT   22   13
CONECT   23   15   27   28
CONECT   24   16   27
CONECT   25   15
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CONECT   26   16
CONECT   27   23   24   29
CONECT   28   23
CONECT   29   27
END
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Table 4: Coordinates of Compound **2a**$^{+}$ (PDB format)

```
HEADER
REMARK  6-31G** Hartree-Fock optimized geometry of
REMARK  of the protonated 2a (2a+)
HETATM    1 1H2         1      0.000   0.000   0.000
HETATM    2  C2         1      0.000   0.000   1.083
HETATM    3  N1         1      1.388   0.000   1.576
HETATM    4  C3         1     -0.527   1.304   1.649
HETATM    5  H2         1     -0.529  -0.871   1.435
HETATM    6  C1         1      1.732   1.366   2.093
HETATM    7  O1         1      0.619   2.113   1.721
HETATM    8  C4         1      1.930  -1.192   1.885
HETATM    9 2H3         1     -1.246   1.795   1.010
HETATM   10 1H3         1     -0.966   1.167   2.632
HETATM   11  O2         1      1.348  -2.240   1.841
HETATM   12  C17        1      1.884   1.374   3.614
HETATM   13  C18        1      2.916   2.026   1.398
HETATM   14  C6         1      3.401  -1.301   2.243
HETATM   15  C7         1      3.769  -2.039   3.369
HETATM   16  C5         1      4.393  -0.904   1.386
HETATM   17 1H17        1      1.987   2.399   3.949
HETATM   18 2H17        1      2.761   0.826   3.938
HETATM   19 3H17        1      1.012   0.945   4.093
HETATM   20 1H18        1      2.881   3.087   1.613
HETATM   21 2H18        1      3.868   1.653   1.756
HETATM   22 3H18        1      2.843   1.897   0.325
HETATM   23  C8         1      5.104  -2.294   3.645
HETATM   24  N2         1      5.672  -1.191   1.664
HETATM   25  H7         1      3.001  -2.416   4.019
HETATM   26  H5         1      4.207  -0.382   0.469
HETATM   27  C9         1      6.053  -1.855   2.758
HETATM   28  H8         1      5.401  -2.842   4.518
HETATM   29  H9         1      6.374  -0.902   1.012
HETATM   30  HN2        1      7.105  -2.023   2.881
CONECT    1    2
CONECT    2    1    3    4    5
CONECT    3    2    6    8
CONECT    4    2    7    9   10
CONECT    5    2
CONECT    6    3    7   12   13
CONECT    7    4    6
CONECT    8    3   11   14
CONECT    9    4
CONECT   10    4
CONECT   11    8
CONECT   12    6   17   18   19
CONECT   13    6   20   21   22
CONECT   14    8   15   16
CONECT   15   14   23   25
CONECT   16   14   24   26
CONECT   17   12
CONECT   18   12
CONECT   19   12
CONECT   20   13
CONECT   21   13
CONECT   22   13
CONECT   23   15   27   28
```

```
CONECT   24   16   27   29
CONECT   25   15
CONECT   26   16
CONECT   27   23   24   30
CONECT   28   23
CONECT   29   24
CONECT   30   27
END
```