Supporting Information

for

Elemental Step Thermodynamics of Dihydropyrimidine: a New Class of Organic Hydride Donors

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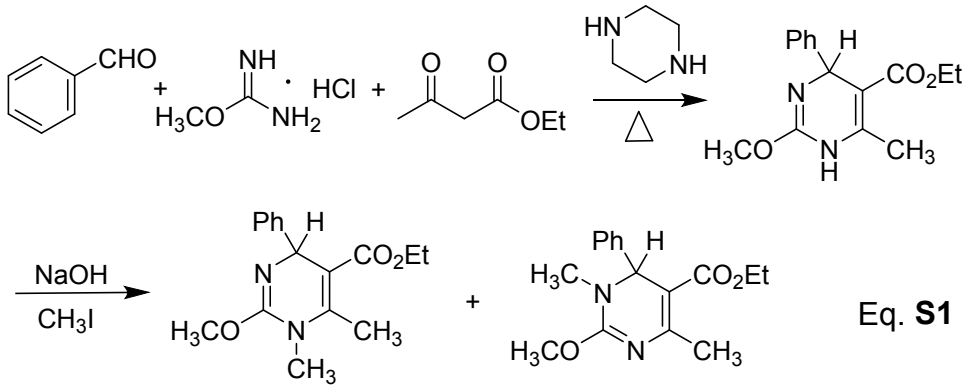
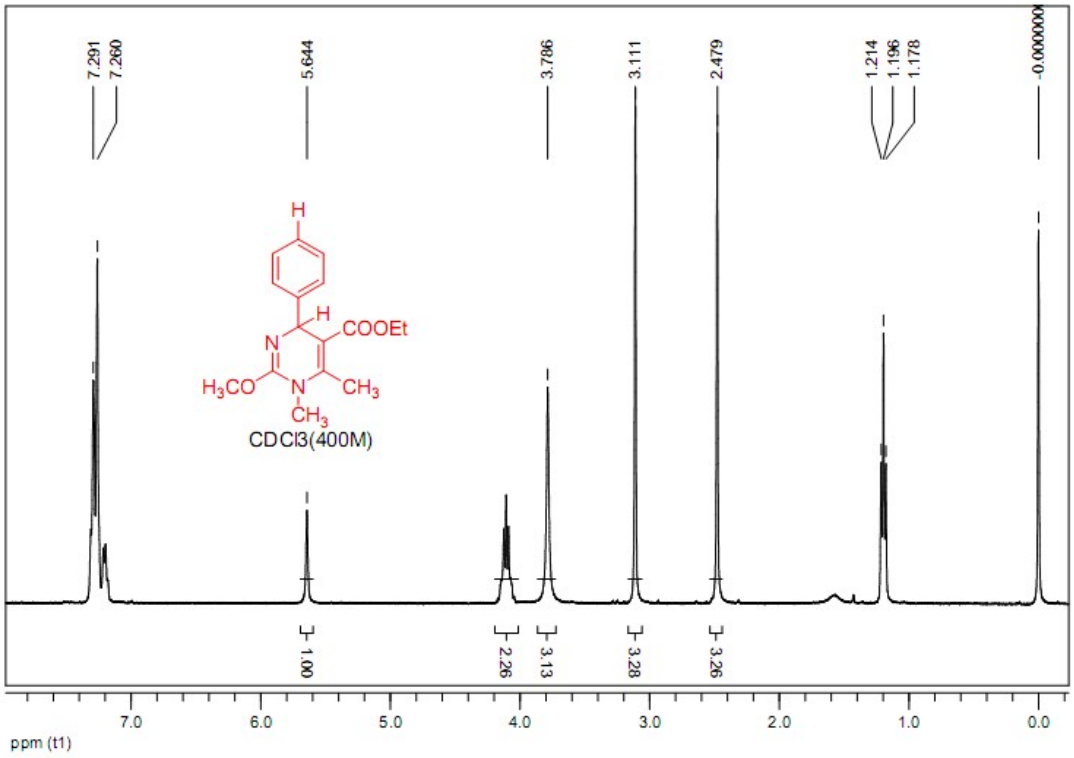
Synthesis of dihydropyrimidines by the Biginelli reaction.

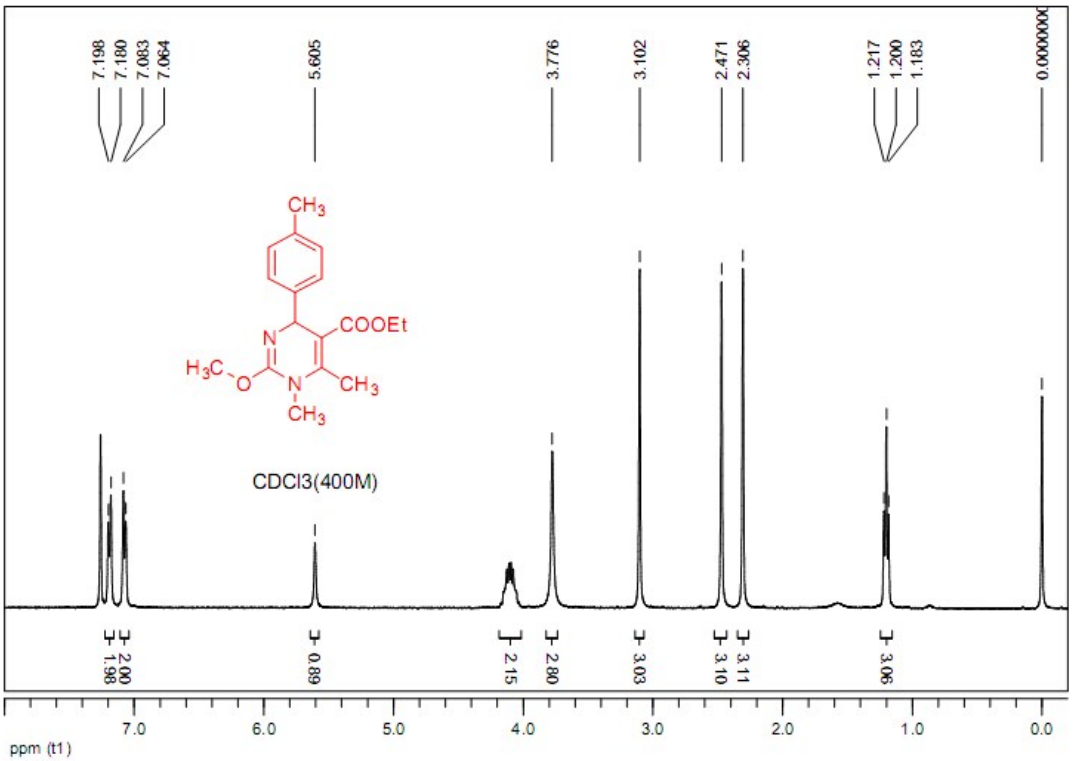


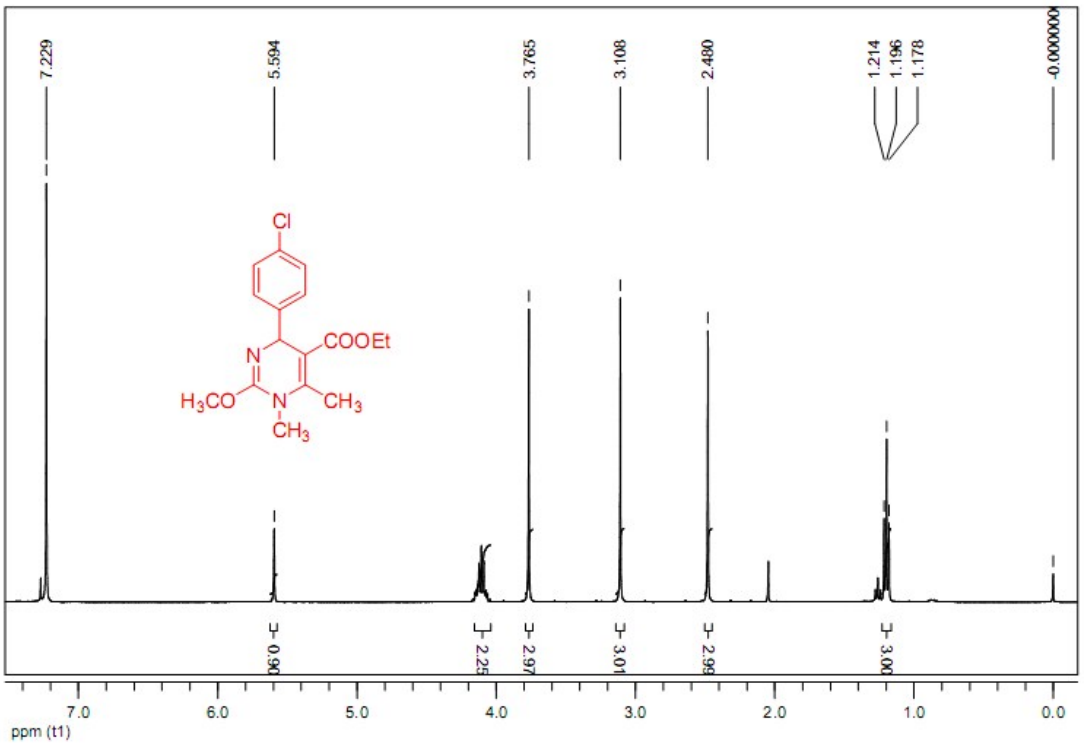
Eq. **S1**

A mixture of aldehyde (20 mmol), ethyl acetoacetate (22 mmol), O-Methylisourea hemisulfate (15 mmol mmol), acetic acid (3 mmol) and piperazine (catalytic amount) was stirred in 50 ml toluene. The resulting mixture was refluxed for 3 h. After completion (as followed by TLC), excess toluene was evaporated under reduced pressure. The residues were treated with excess cold water (200 ml). The crude product thus was extracted by CH_2Cl_2, concentrated and isolated through column chromatography to afford 1, 4-dihydropyrimidine. The obtained compounds were methylated by CH_3I, and isolated through column chromatography to afford 1, 2-dihydro- and 1, 4-dihydro-isomers, respectively.

Copies of the Typical ^{1}H NMR Spectra of XH.



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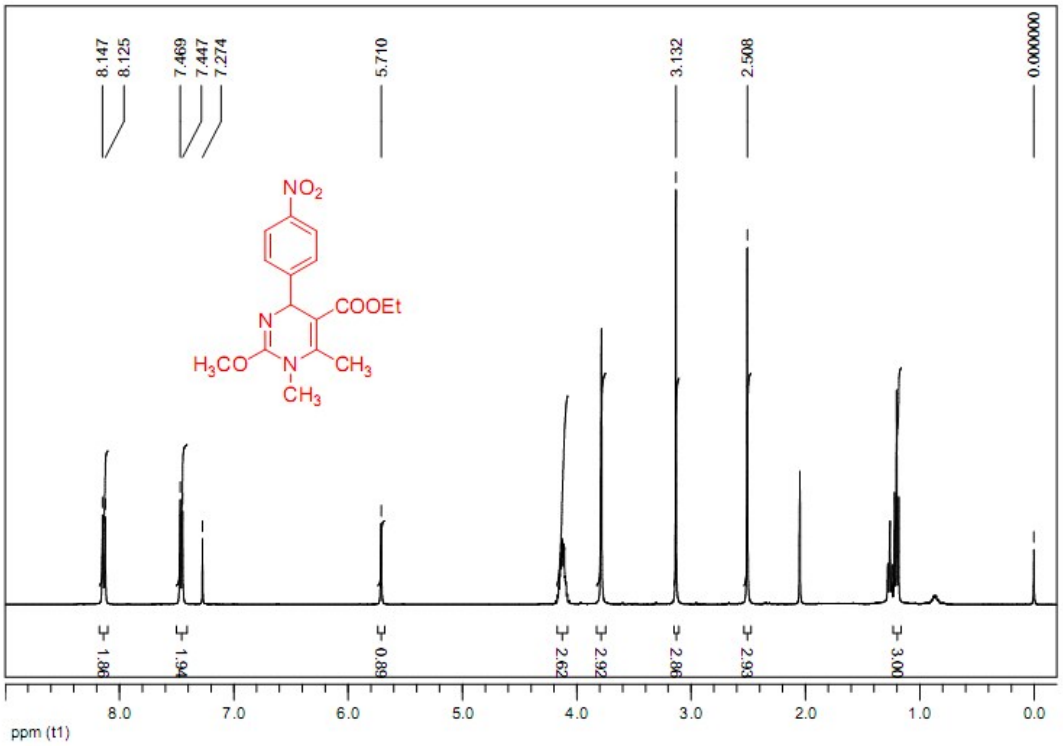
5.594
3.765
3.108
2.480
1.214
1.196
1.178
-0.000000
Cl
COOEt
N
H3CO
N
CH3
CH3
0.90
2.25
2.97
3.01
2.99
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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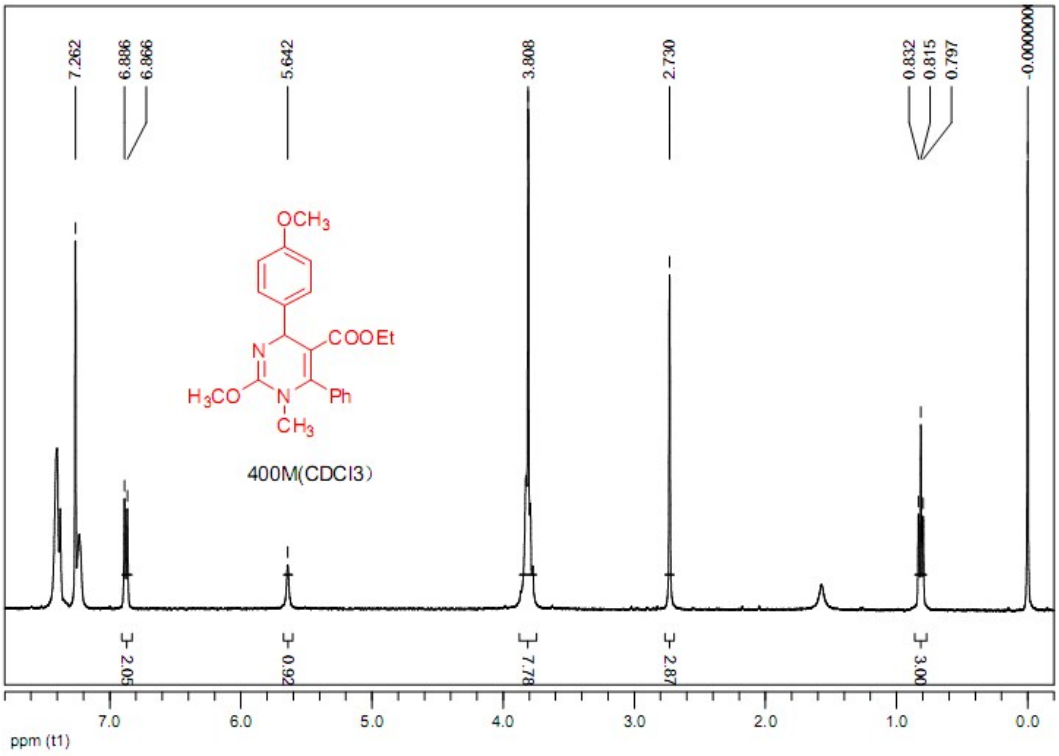
7.469
7.447
7.274
5.710
3.132
2.508
0.000000
NO2
COOEt
N
H3CO
N
CH3
CH3
1.86
1.94
0.89
2.62
2.92
2.86
2.93
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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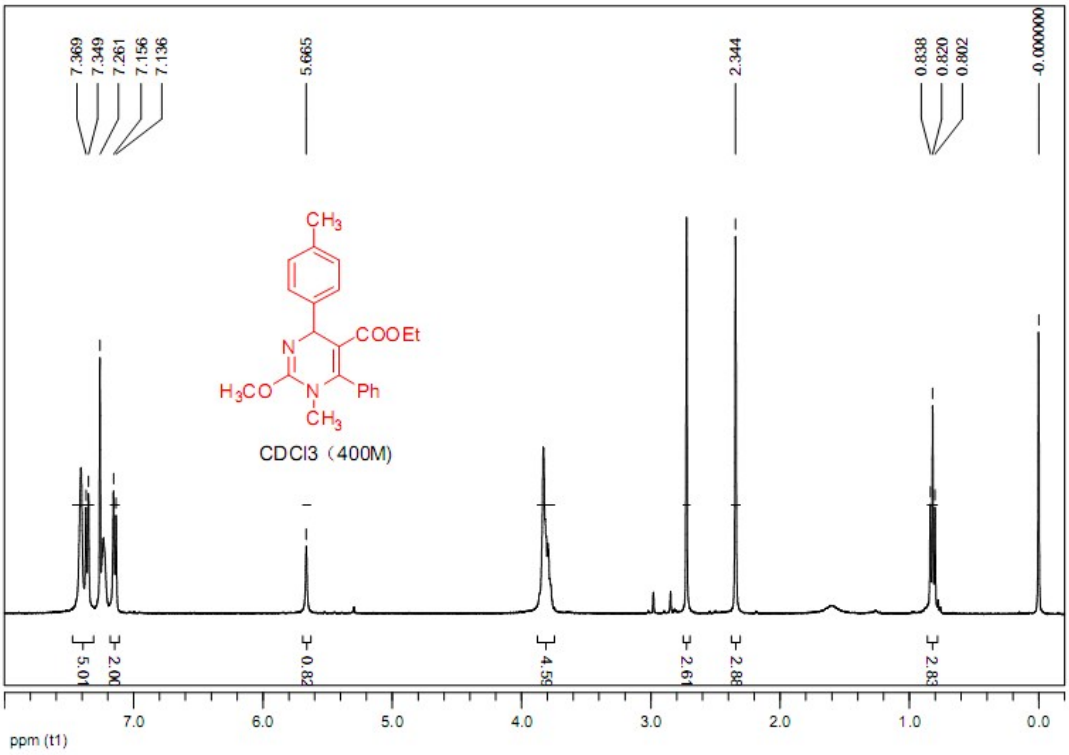
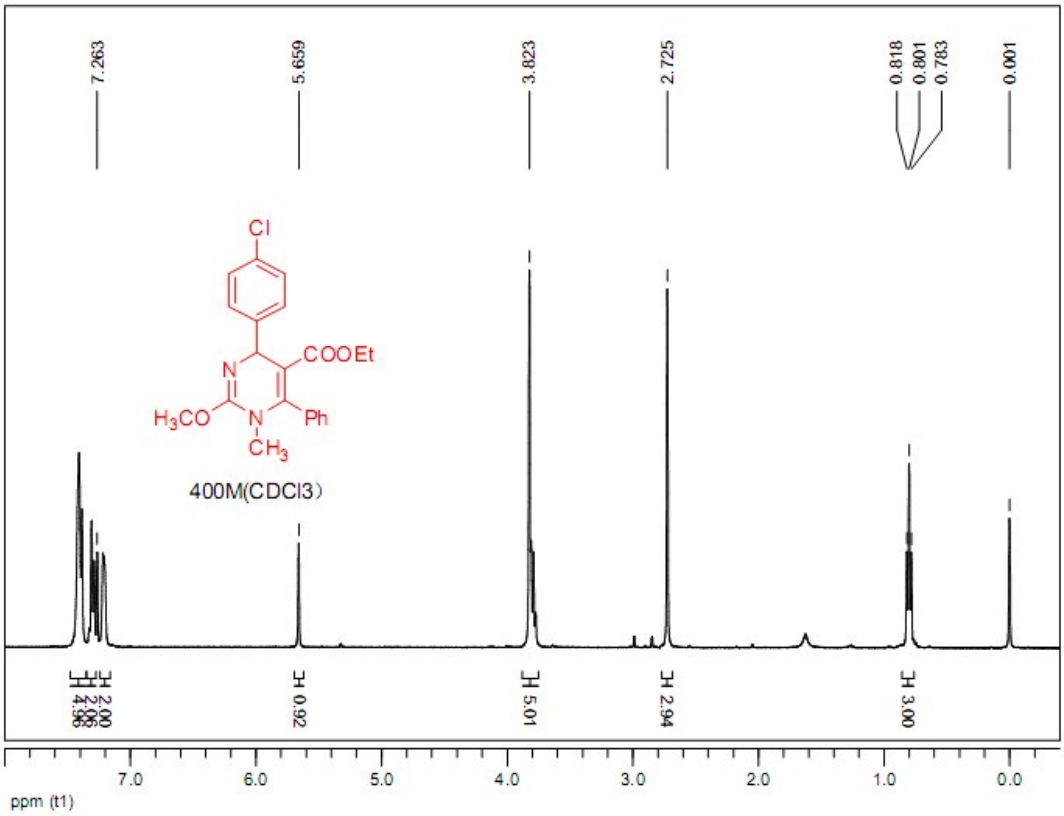
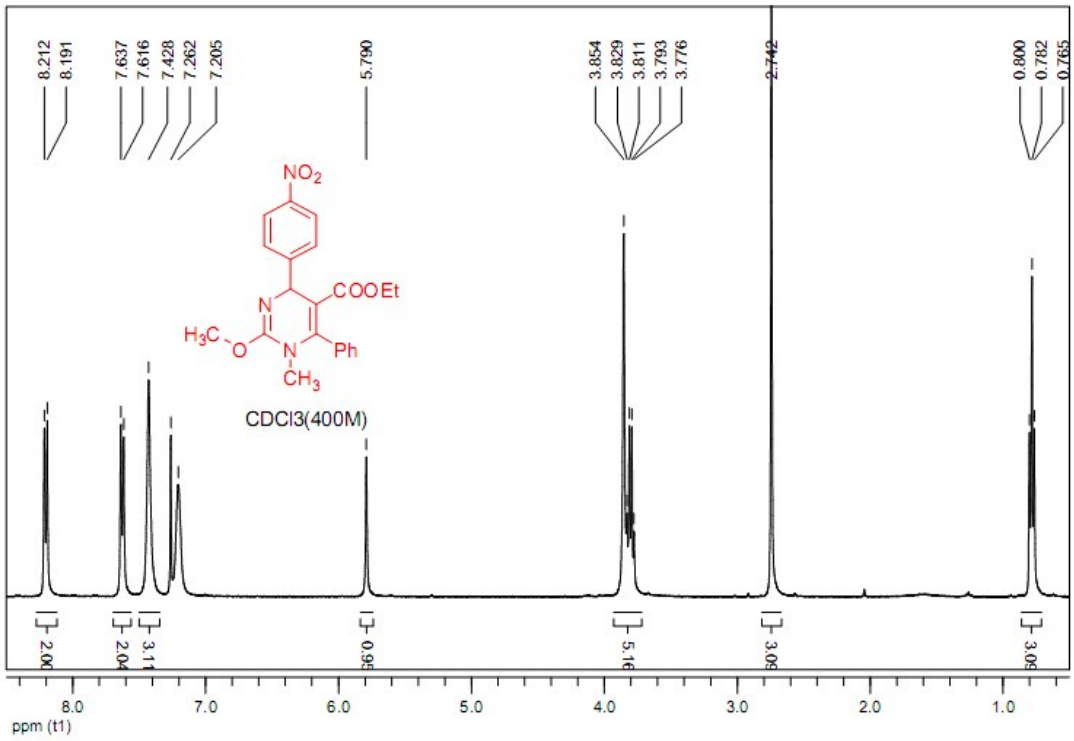
6.886
6.866
5.642
3.808
2.730
0.832
0.815
0.797
0.000000
OCH3
COOEt
N
H3CO
N
Ph
CH3
400M(CDCl3)
2.05
0.93
7.78
2.87
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.369
7.349
7.261
7.156
7.136
5.665
2.344
0.838
0.820
0.802
0.000000
CH3
COOEt
N
H3CO
N
Ph
CH3
CDCl3（400M)
5.01
2.00
0.82
4.59
2.61
2.86
2.83
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.263
5.659
3.823
2.725
0.818
0.801
0.783
0.001
Cl
COOEt
N
H3CO
N
Ph
CH3
400M(CDCl3)
H 2.00
H 0.92
H 5.01
H 2.94
H 3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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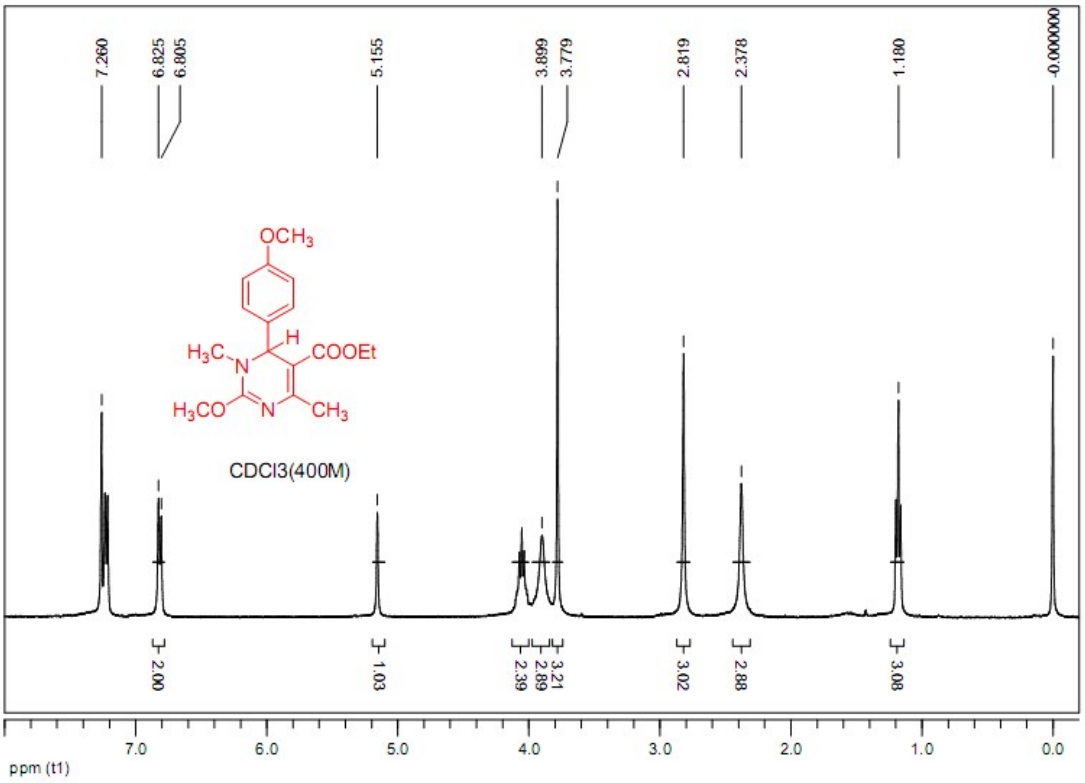
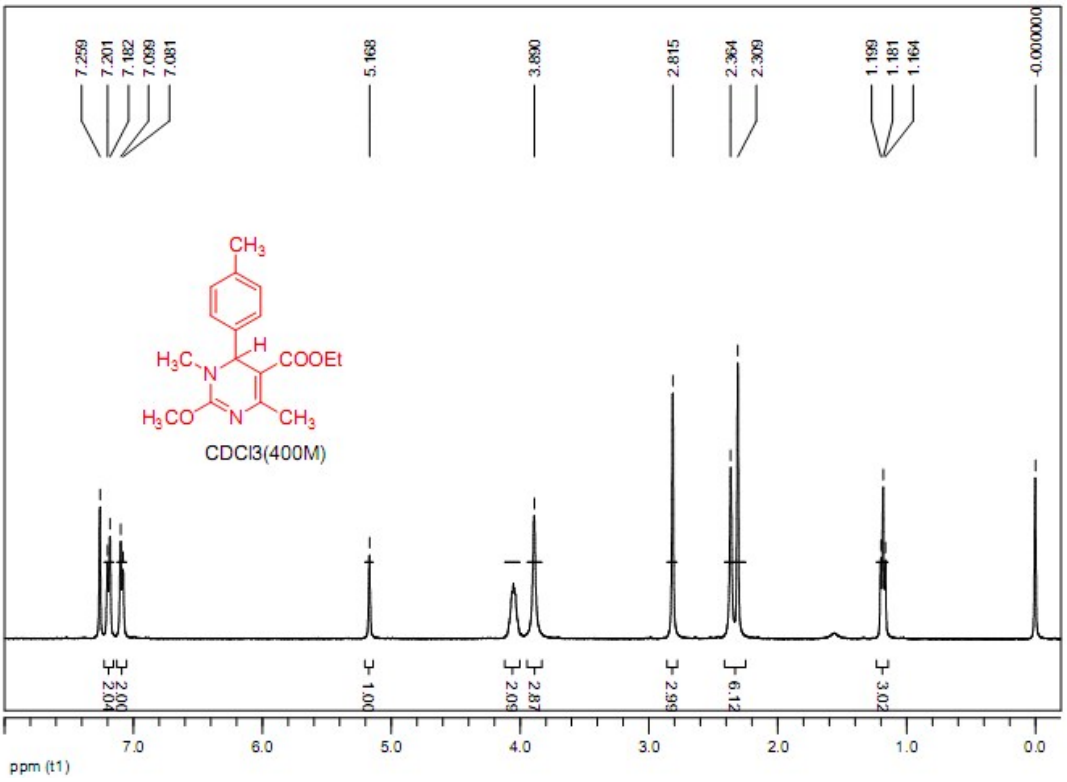
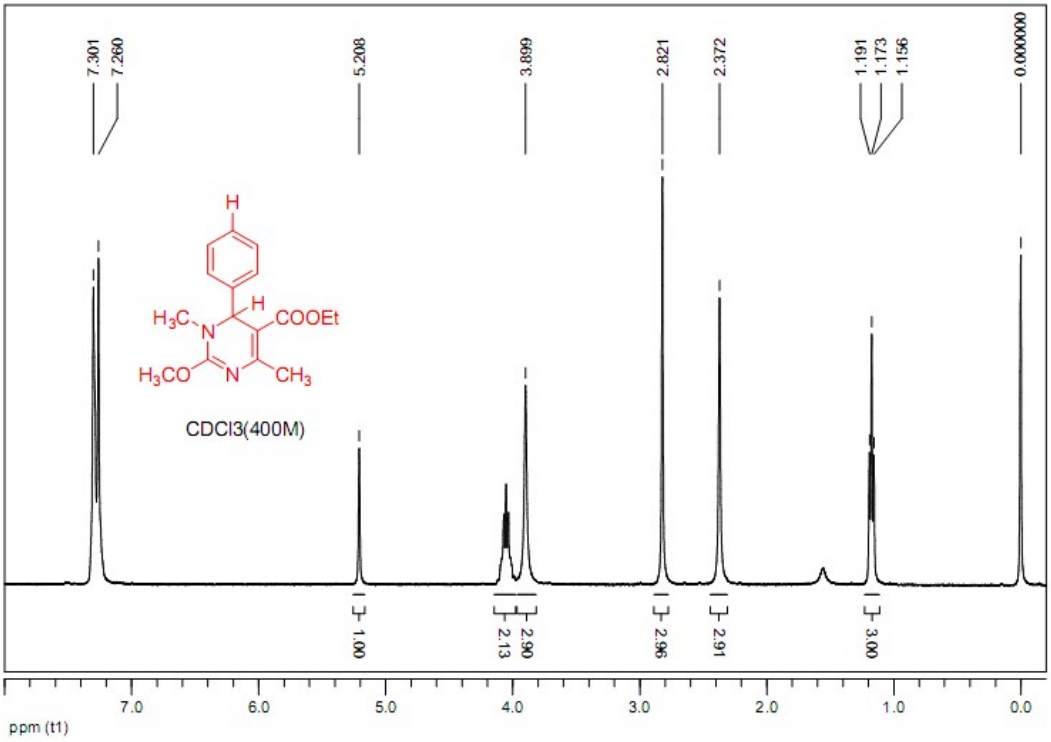
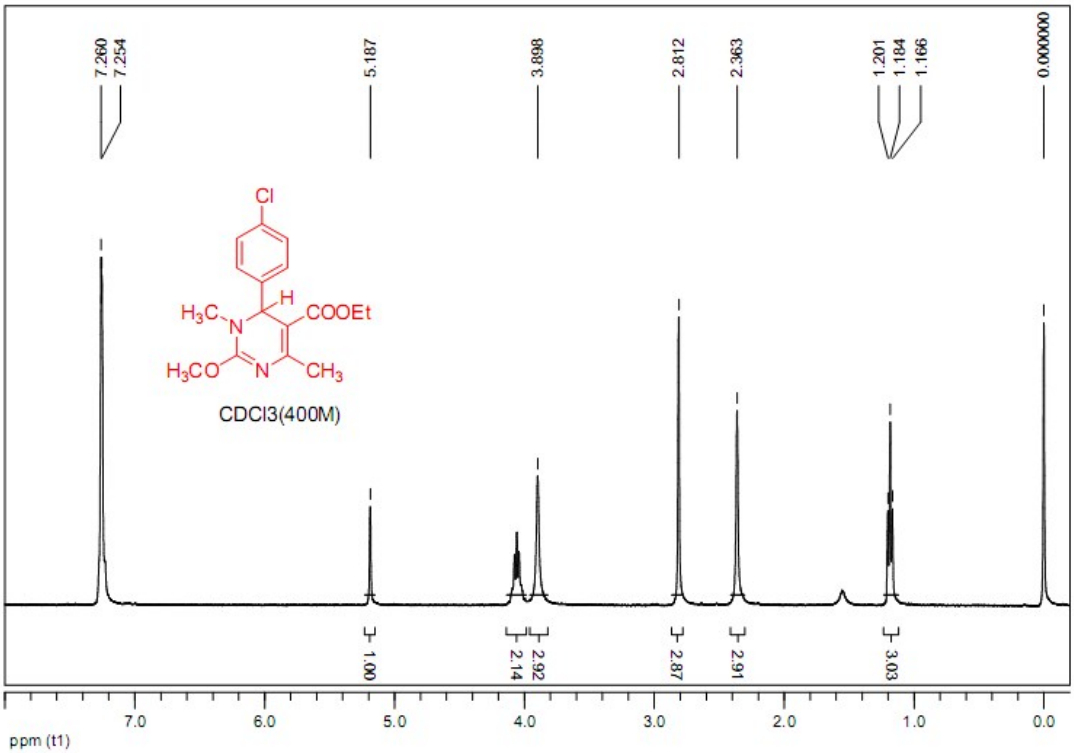
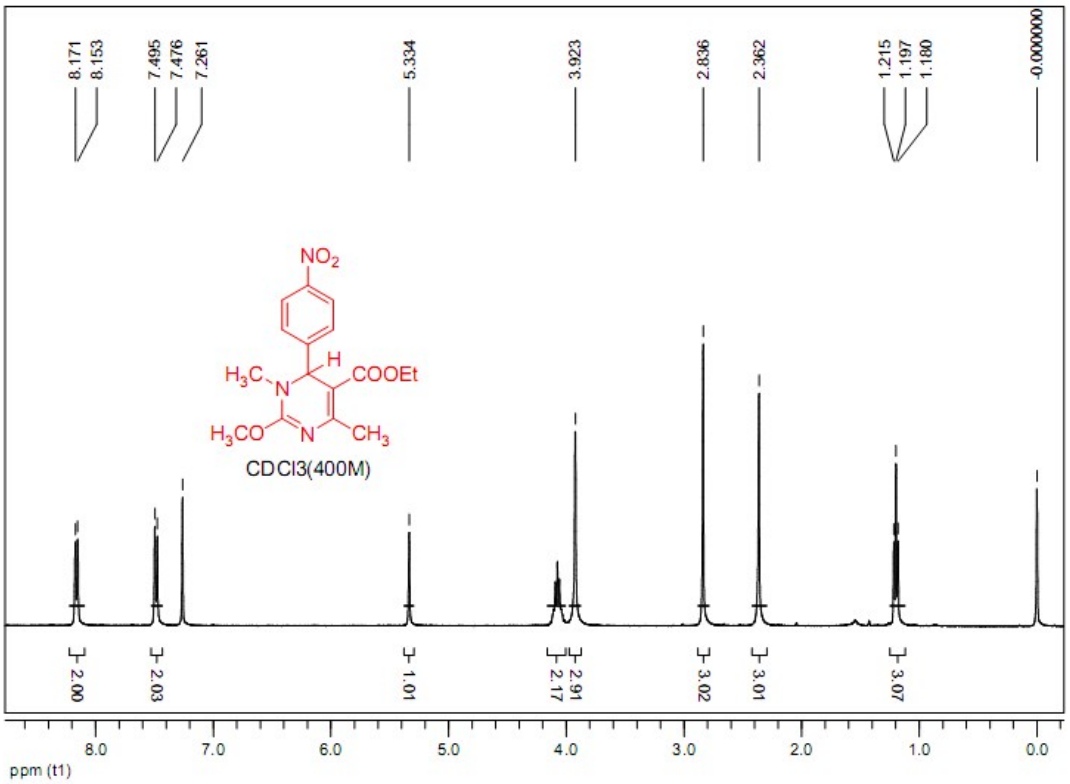
8.191
7.637
7.616
7.428
7.262
7.205
5.790
3.854
3.829
3.811
3.793
3.776
2.742
0.800
0.782
0.765
NO2
COOEt
N
H3C
O
N
Ph
CH3
CDCl3(400M)
2.00
2.04
3.11
0.95
5.16
3.09
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


7.260
6.825
6.805
5.155
3.899
3.779
2.819
2.378
1.180
-0.000000
OCH3
H3C
N
H
COOEt
H3CO
N
CH3
CDCl3(400M)
2.00
1.03
2.39
2.89
3.21
3.02
2.88
3.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.259
7.201
7.182
7.099
7.081
5.168
3.890
2.815
2.364
2.309
1.199
1.181
1.164
-0.000000
CH3
H3C
N
H
COOEt
H3CO
N
CH3
CDCl3(400M)
2.04
2.00
1.00
2.09
2.87
2.99
6.12
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.301
7.260
5.208
3.899
2.821
2.372
1.191
1.173
1.156
0.000000
H
H3C
N
H
COOEt
H3CO
N
CH3
CDCl3(400M)
1.00
2.13
2.90
2.96
2.91
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.260
7.254
5.187
3.898
2.812
2.363
1.201
1.184
1.166
0.000000
Cl
H3C
N
H
COOEt
H3CO
N
CH3
CDCl3(400M)
1.00
2.14
2.92
2.87
2.91
3.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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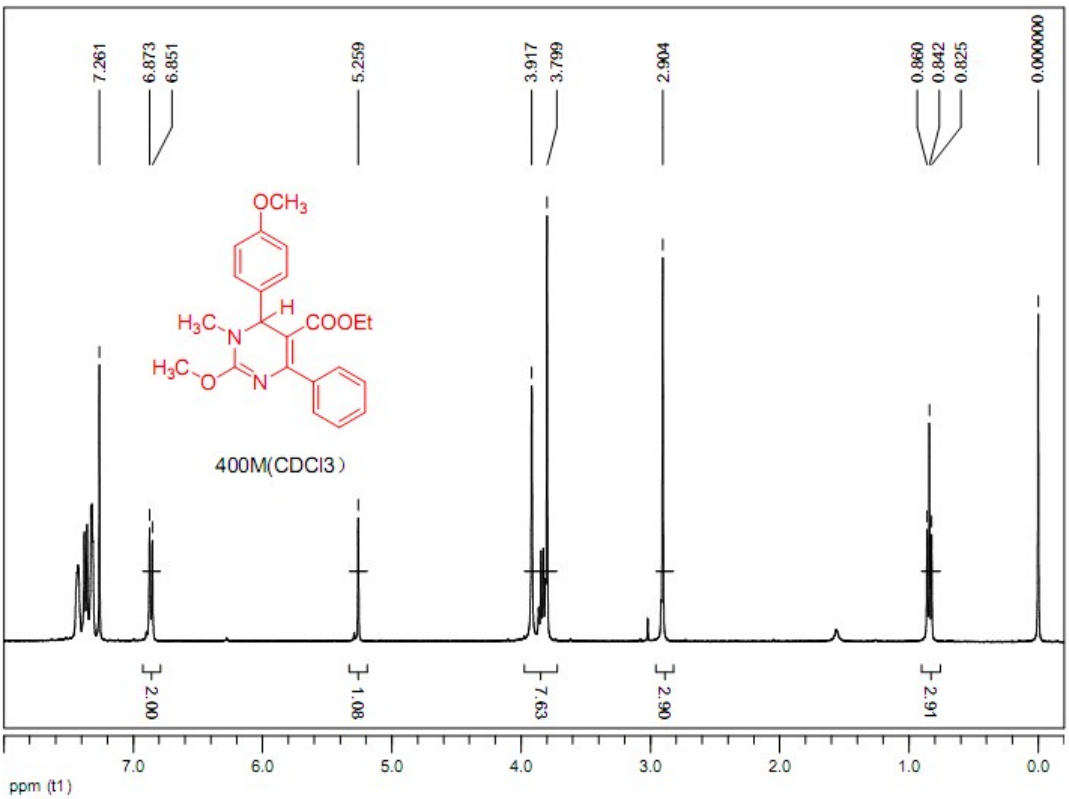
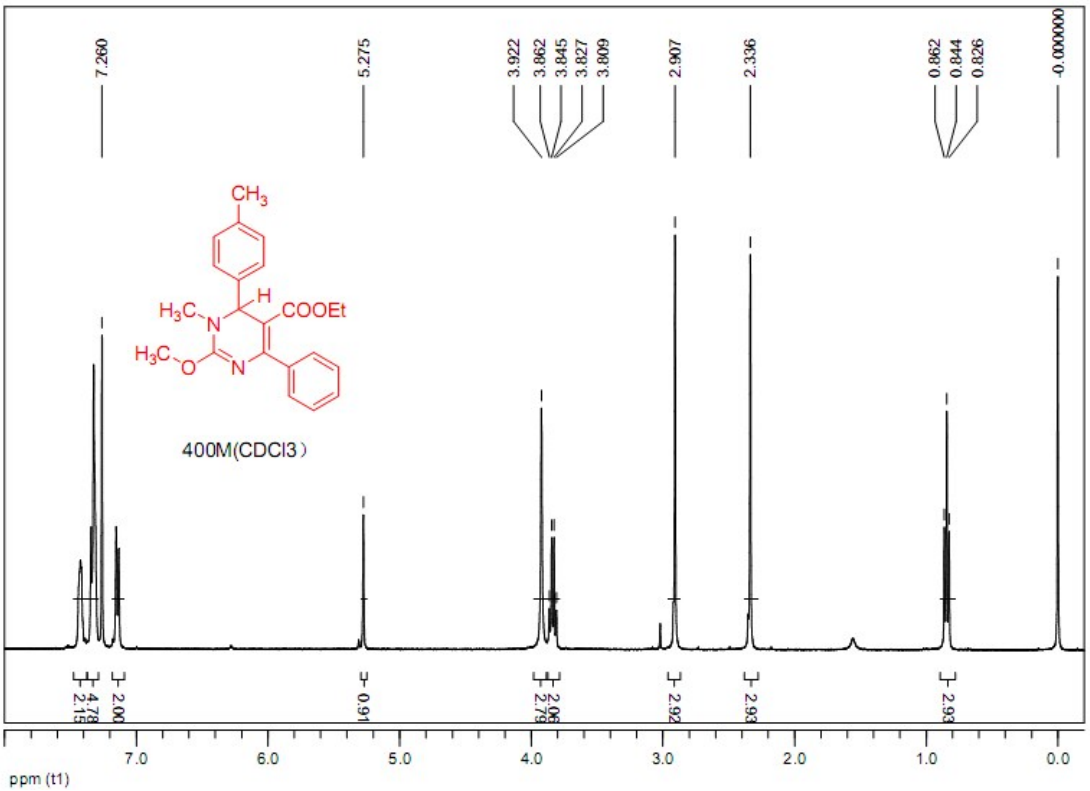
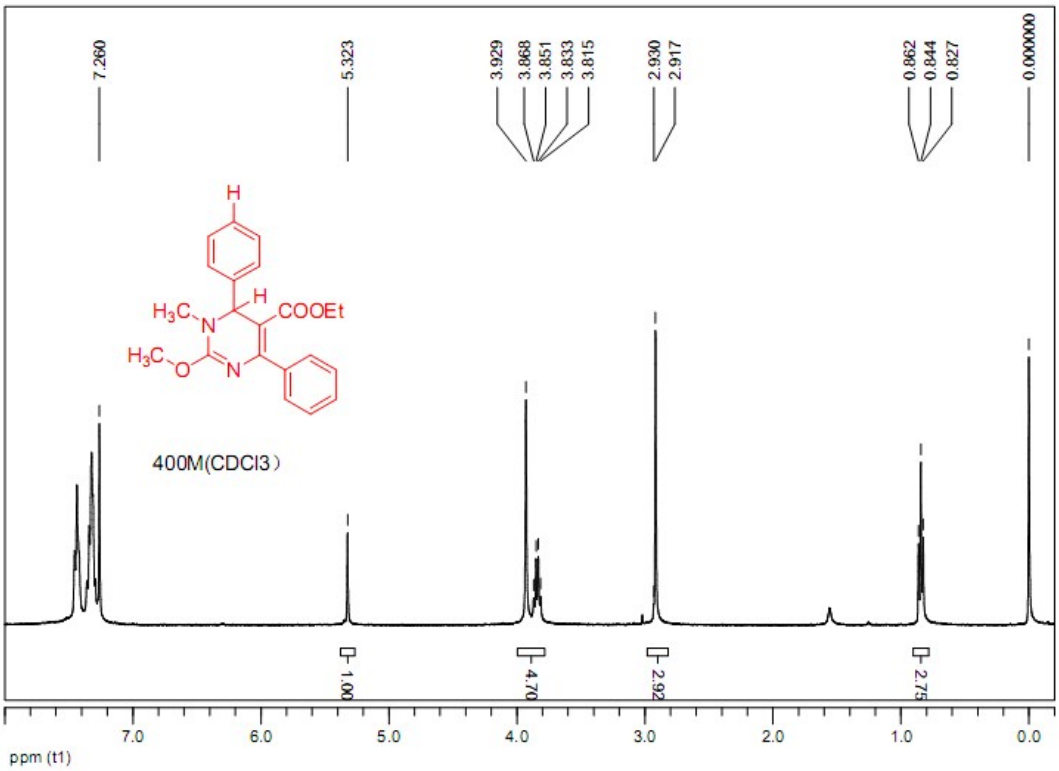
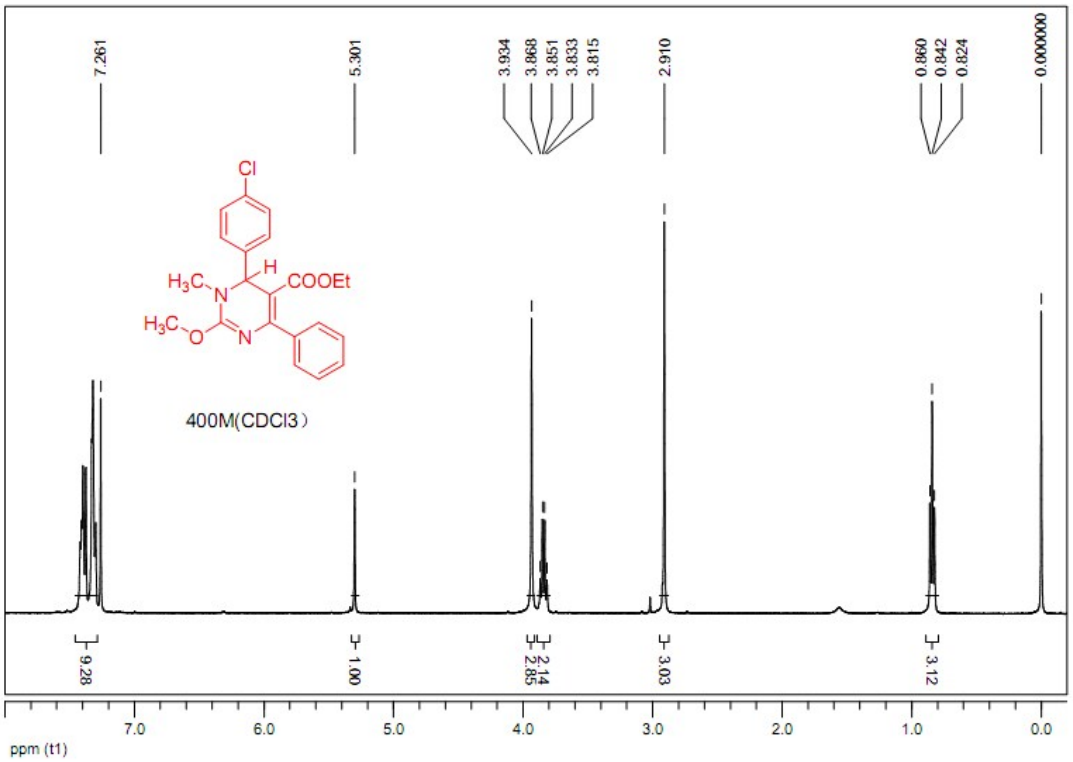
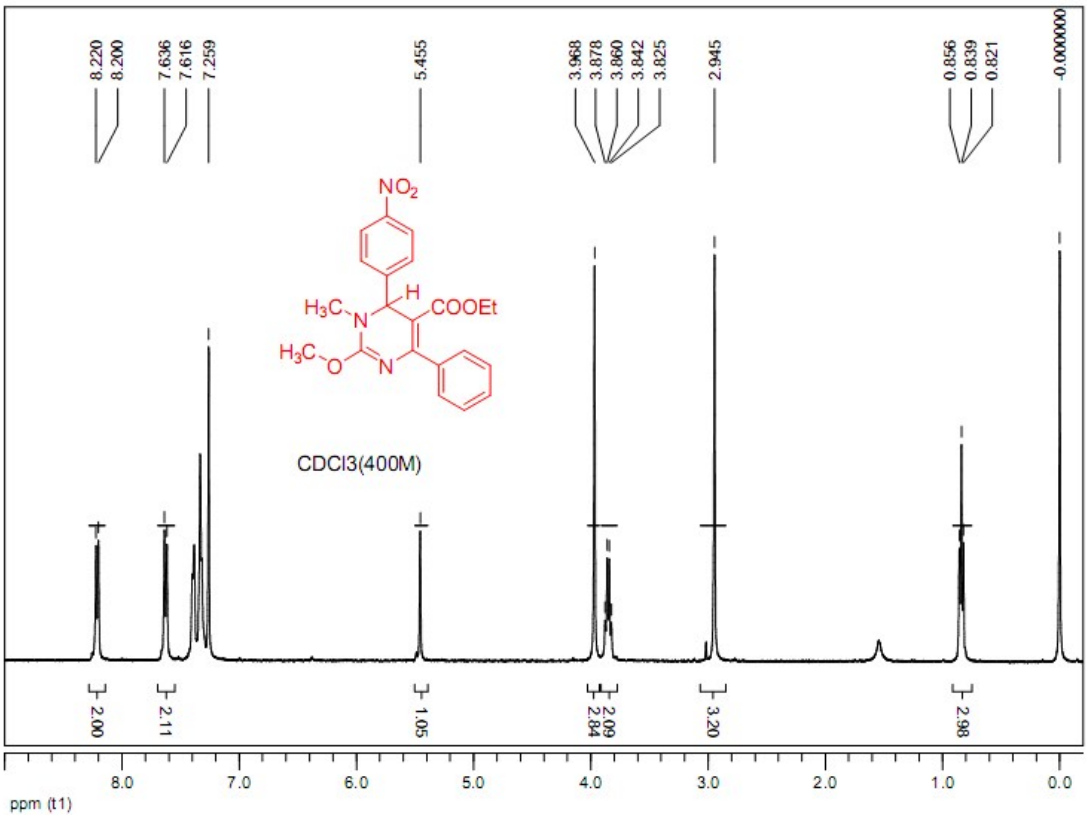
8.153
7.495
7.476
7.261
5.334
3.923
2.836
2.362
1.215
1.197
1.180
-0.000000
NO2
H3C
N
H
COOEt
H3CO
N
CH3
CDCl3(400M)
2.00
2.03
1.01
2.17
2.91
3.02
3.01
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.261
6.873
6.851
5.259
3.917
3.799
2.904
0.860
0.842
0.825
0.000000
OCH3
H3C
N
H
COOEt
H3C
O
N
400M(CDCl3)
2.00
1.08
7.63
2.90
2.91
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.260
5.275
3.922
3.862
3.845
3.827
3.809
2.907
2.336
0.862
0.844
0.826
-0.000000
CH3
H
H3C
N
COOEt
H3C
O
N
400M(CDCl3)
2.15
4.78
2.00
0.91
2.79
2.06
2.92
2.93
2.93
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.260
5.323
3.929
3.868
3.851
3.833
3.815
2.930
2.917
0.862
0.844
0.827
0.000000
H
H
H3C
N
COOEt
H3C
O
N
400M(CDCl3)
1.00
4.70
2.92
2.75
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.261
5.301
3.934
3.868
3.851
3.833
3.815
2.910
0.860
0.842
0.824
0.000000
Cl
H
COOEt
H_3C
N
H_3C
O
N
400M(CDCl3）
9.28
1.00
2.14
2.85
3.03
3.12
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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7.636
7.616
7.259
5.455
3.968
3.878
3.860
3.842
3.825
2.945
0.856
0.839
0.821
0.000000
NO_2
H
COOEt
H_3C
N
H_3C
O
N
CDCl3(400M)
2.00
2.11
1.05
2.84
2.09
3.20
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5.0
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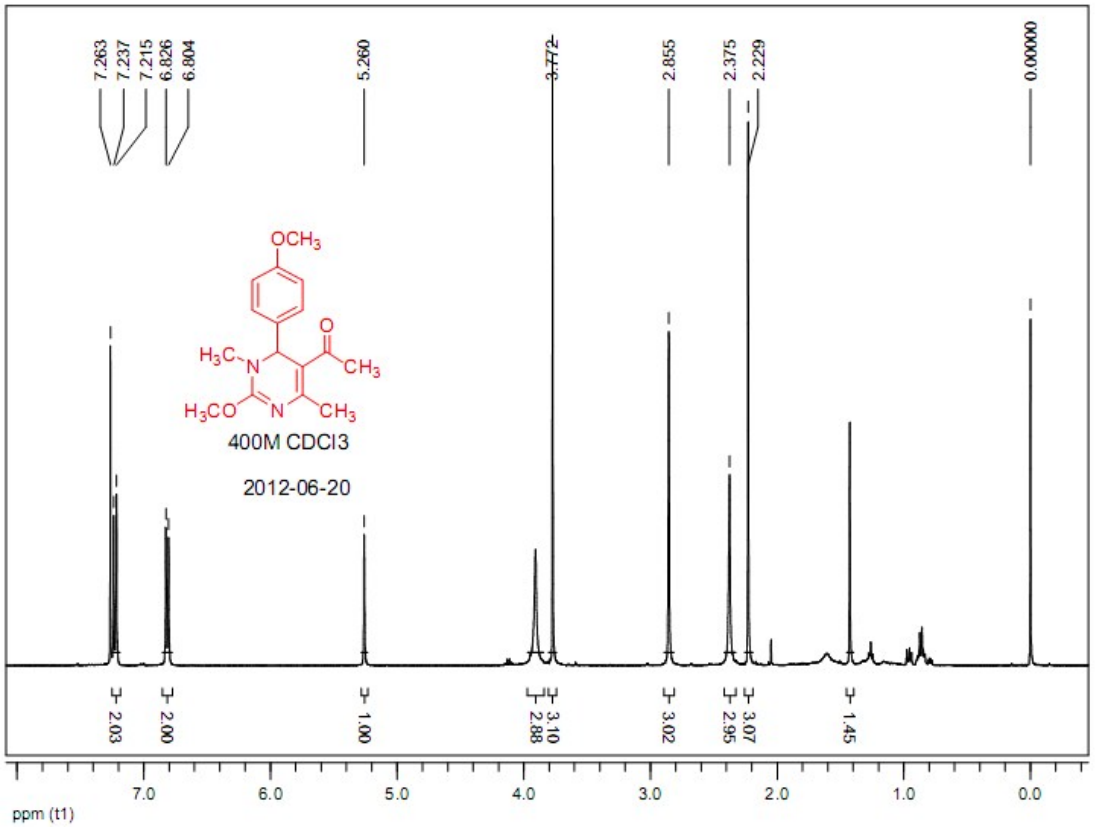
ppm (t1)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6.826
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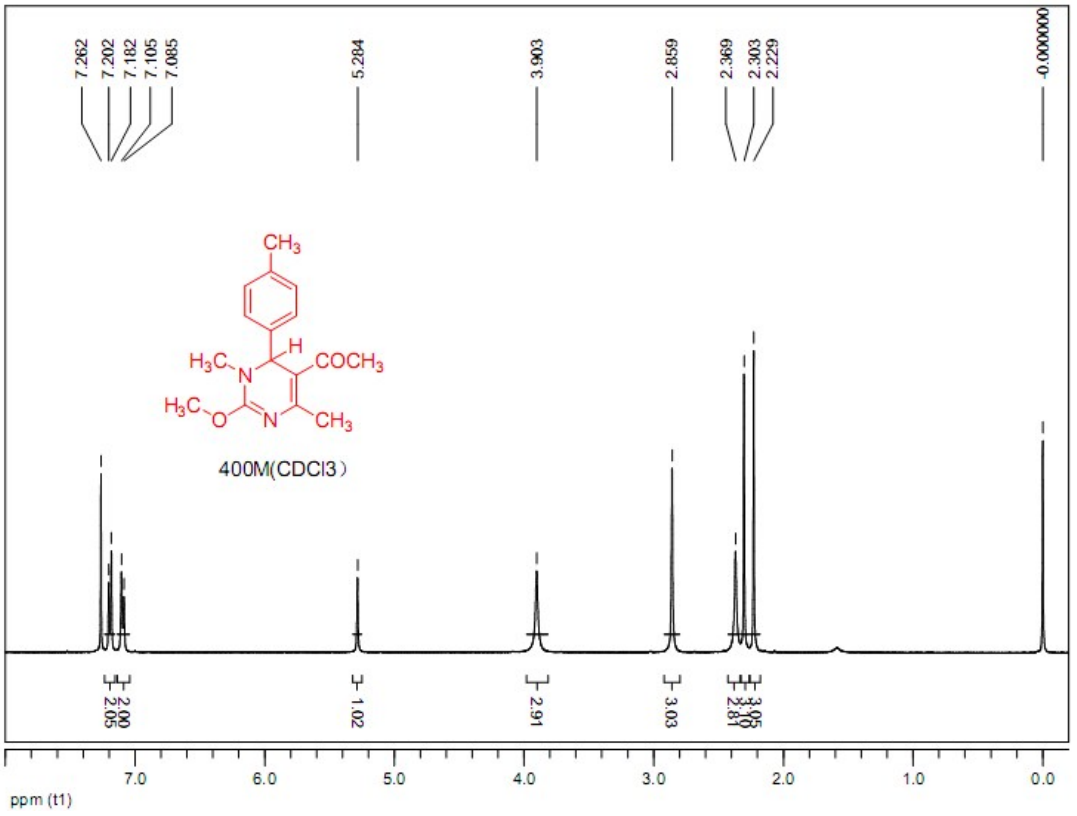
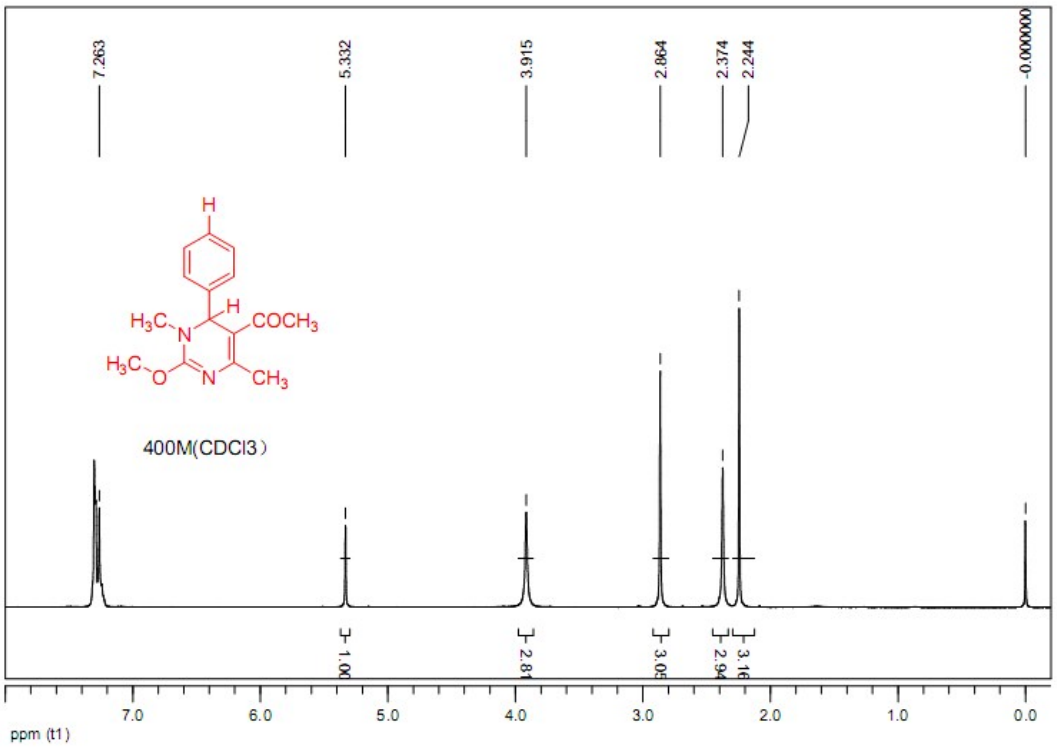
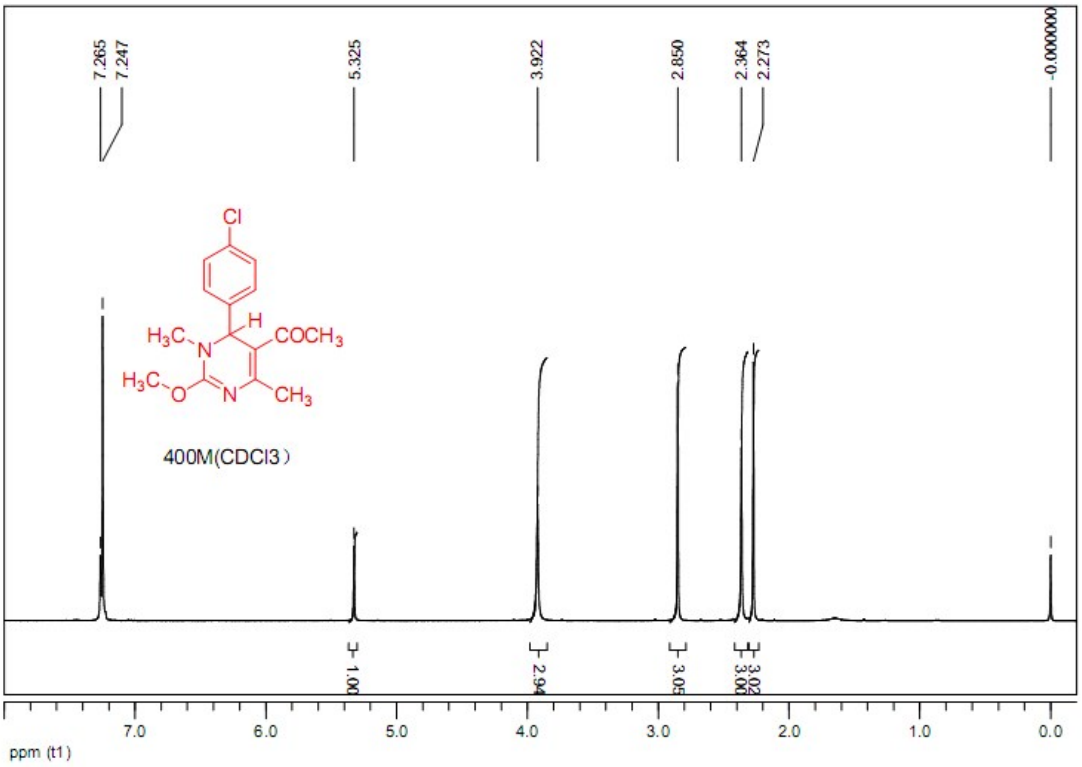
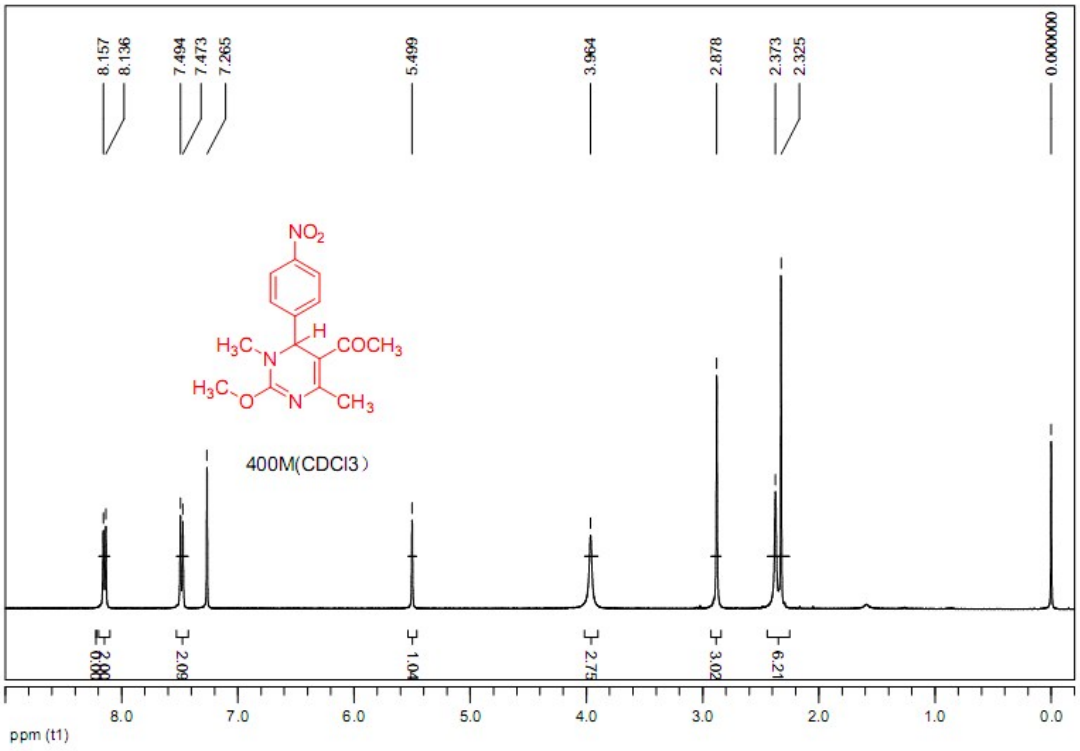
5.260
3.772
2.855
2.375
2.229
0.00000
OCH3
O
H3C
N
CH3
H3CO
N
CH3
400M CDCl3
2012-06-20
2.03
2.00
1.00
2.88
3.10
3.02
2.95
3.07
1.45
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.262
7.202
7.182
7.105
7.085
5.284
3.903
2.859
2.369
2.303
2.229
-0.000000
CH3
H
H3C
N
COCH3
H3C
O
N
CH3
400M(CDCl3)
2.05
2.00
1.02
2.91
3.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.263
5.332
3.915
2.864
2.374
2.244
-0.000000
H
H
H3C
N
COCH3
H3C
O
N
CH3
400M(CDCl3)
1.00
2.81
3.05
2.94
3.16
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.265
7.247
5.325
3.922
2.850
2.364
2.273
-0.000000
Cl
H
H3C
N
COCH3
H3C
O
N
CH3
400M(CDCl3)
1.00
2.94
3.05
3.02
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


8.157
8.136
7.494
7.473
7.265
5.499
3.964
2.878
2.373
2.325
0.000000
NO2
H
H3C
N
COCH3
H3C
O
N
CH3
400M(CDCl3)
2.08
2.00
1.04
2.75
3.02
6.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

Typical Electrochemical Spectra

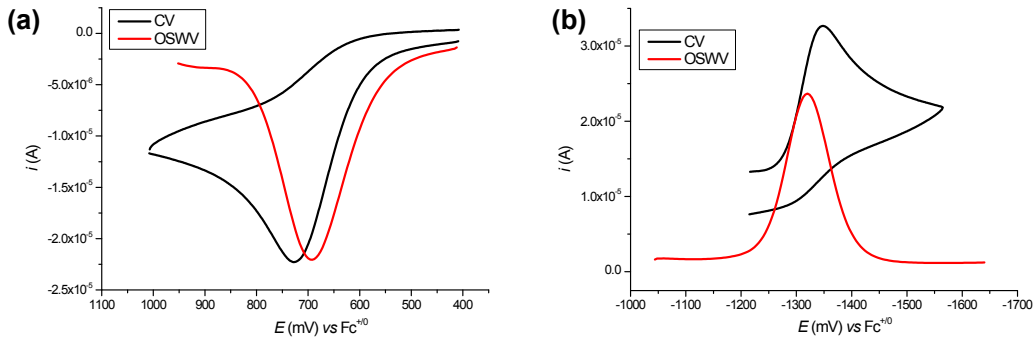


Figure s1. CV and OSWV for the oxidation of **1H**($R = CH_3$) (a) and reduction of $\mathbf{1}^+$($R = CH_3$) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

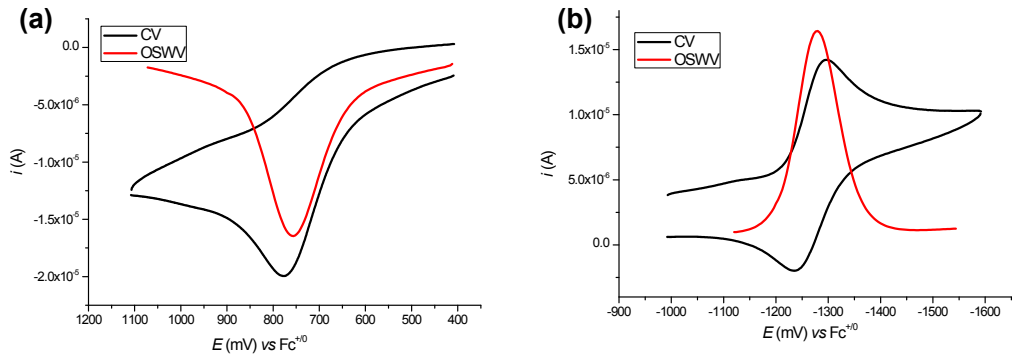


Figure s2. CV and OSWV for the oxidation of **2H**($R = OCH_3$) (a) and reduction of $\mathbf{2}^+$($R = OCH_3$) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

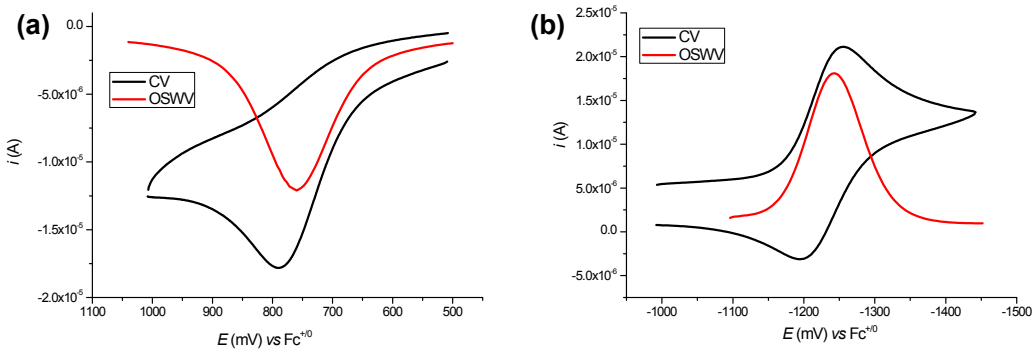


Figure s3. CV and OSWV for the oxidation of **2H**($R = CH_3$) (a) and reduction of $\mathbf{2}^+$($R = CH_3$) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

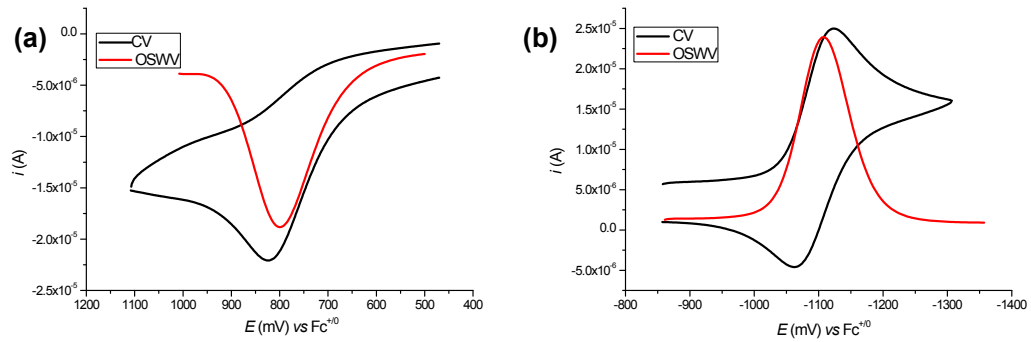


Figure s4. CV and OSWV for the oxidation of **2H**(R = Cl) (a) and reduction of $\mathbf{2}^{+}$(R = Cl) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

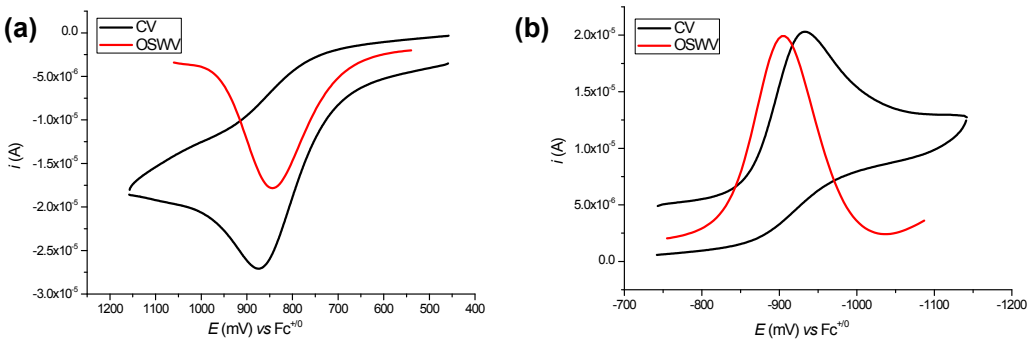


Figure s5. CV and OSWV for the oxidation of **2H**(R = NO_2) (a) and reduction of $\mathbf{2}^{+}$(R = NO_2) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

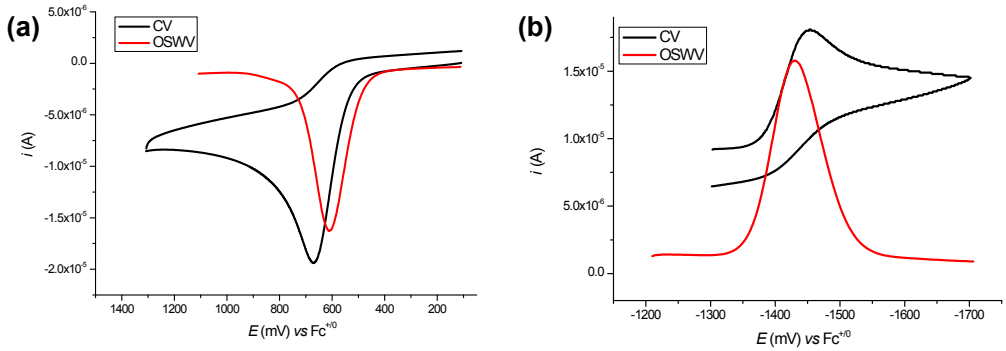


Figure s6. CV and OSWV for the oxidation of **3H**(R = OCH_3) (a) and reduction of $\mathbf{3}^{+}$(R = OCH_3) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

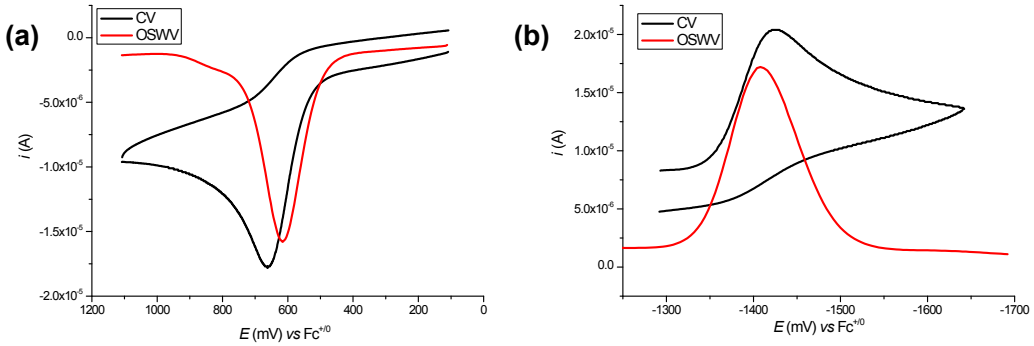


Figure s7. CV and OSWV for the oxidation of **3H**(R = CH_3) (a) and reduction of $\mathbf{3}^+$(R = CH_3) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

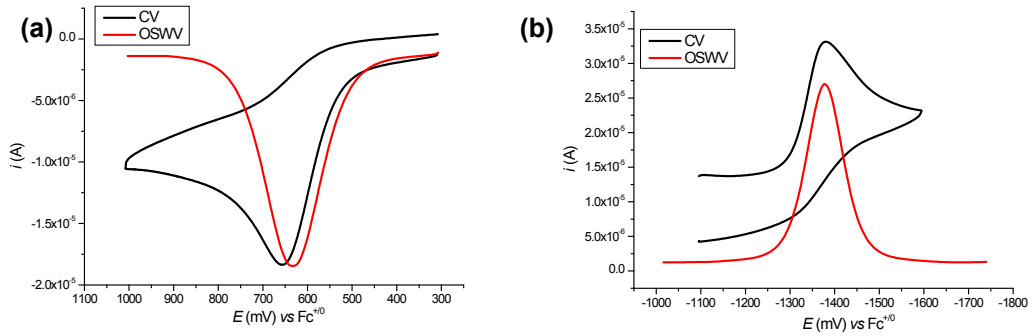


Figure s8. CV and OSWV for the oxidation of **3H**(R = H) (a) and reduction of $\mathbf{3}^+$(R = H) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

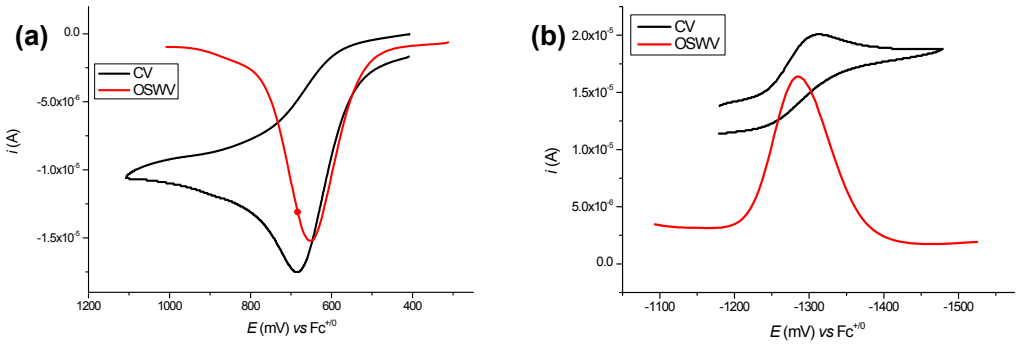


Figure s9. CV and OSWV for the oxidation of **3H**(R = Cl) (a) and reduction of $\mathbf{3}^+$(R = Cl) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

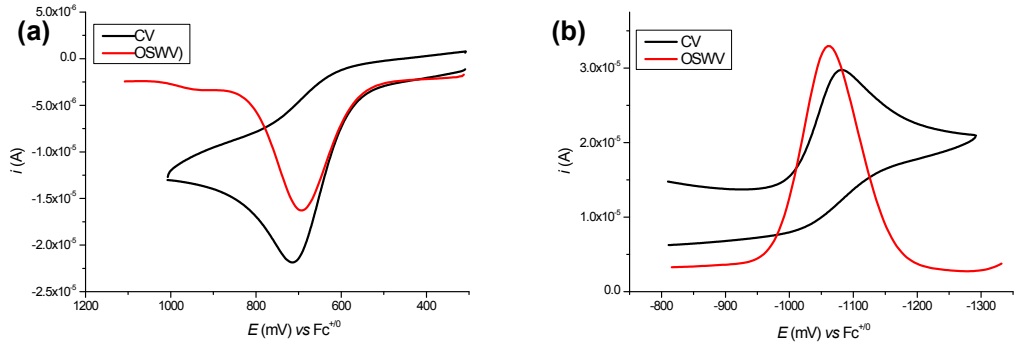


Figure s10. CV and OSWV for the oxidation of **3H**(R = NO_2) (a) and reduction of **3**$^+$(R = NO_2) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

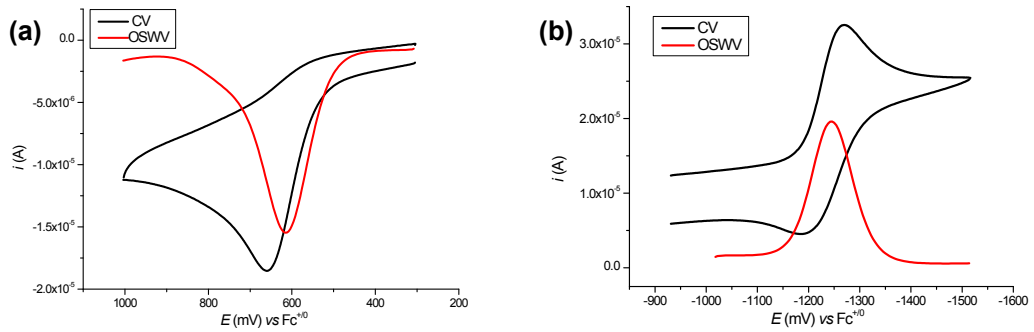


Figure s11. CV and OSWV for the oxidation of **4H**(R = OCH_3) (a) and reduction of **4**$^+$(R = OCH_3) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

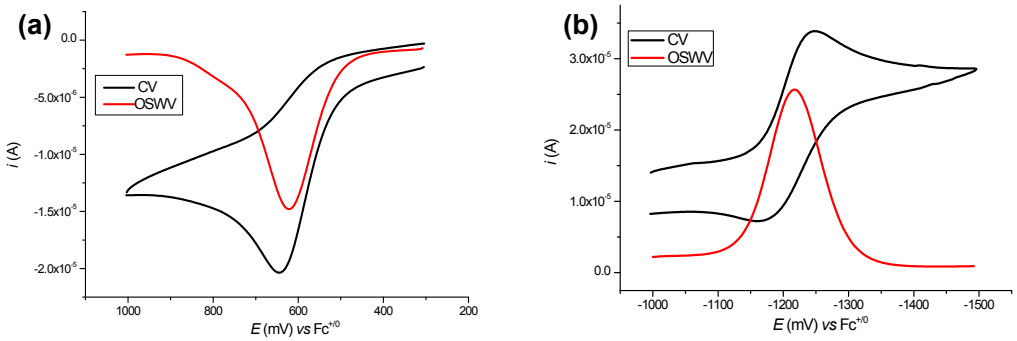


Figure s12. CV and OSWV for the oxidation of **4H**(R = CH_3) (a) and reduction of **4**$^+$(R = CH_3) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

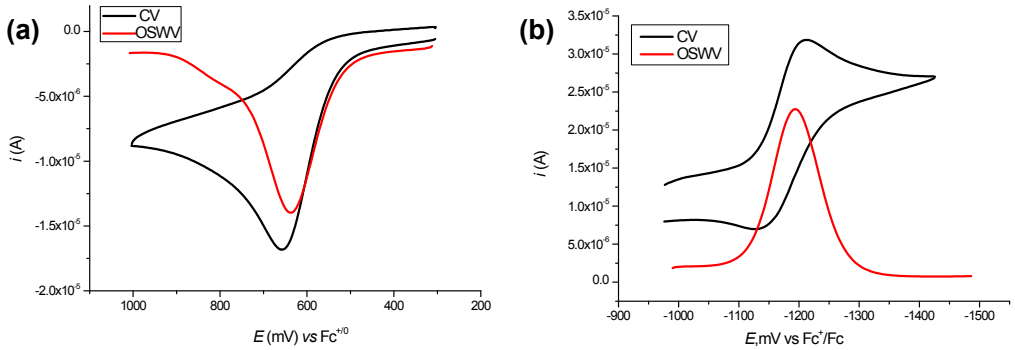


Figure s13. CV and OSWV for the oxidation of **4H**(R = H) (a) and reduction of **4**$^{+}$(R = H) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

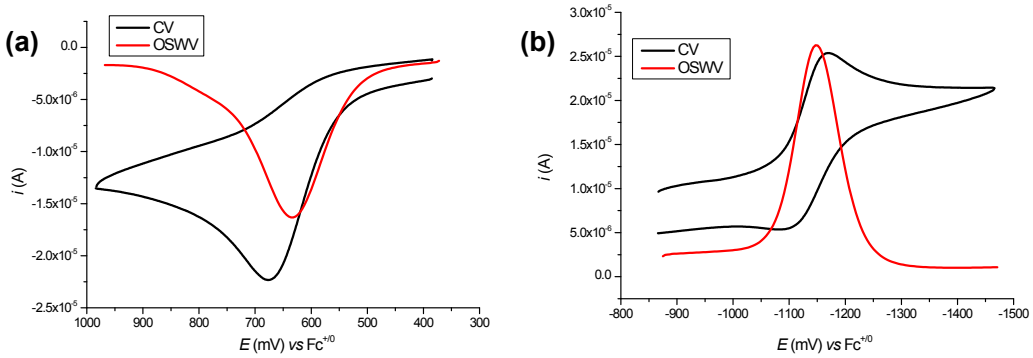


Figure s14. CV and OSWV for the oxidation of **4H**(R = Cl) (a) and reduction of **4**$^{+}$(R = Cl) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

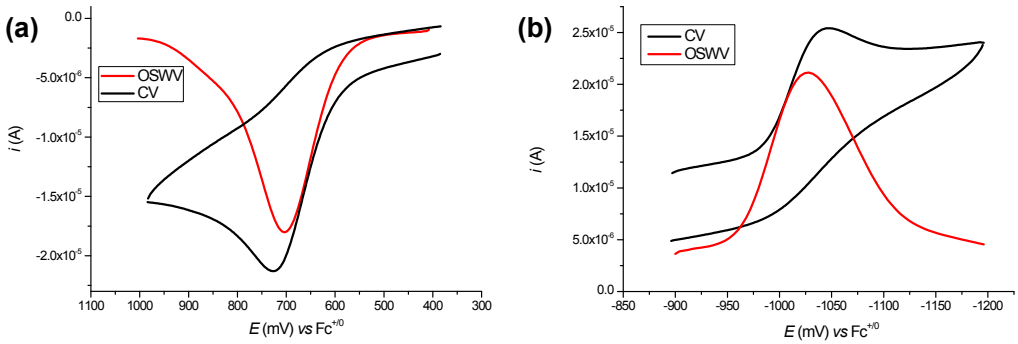


Figure s15. CV and OSWV for the oxidation of **4H**(R = NO_2) (a) and reduction of **4**$^{+}$(R = NO_2) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

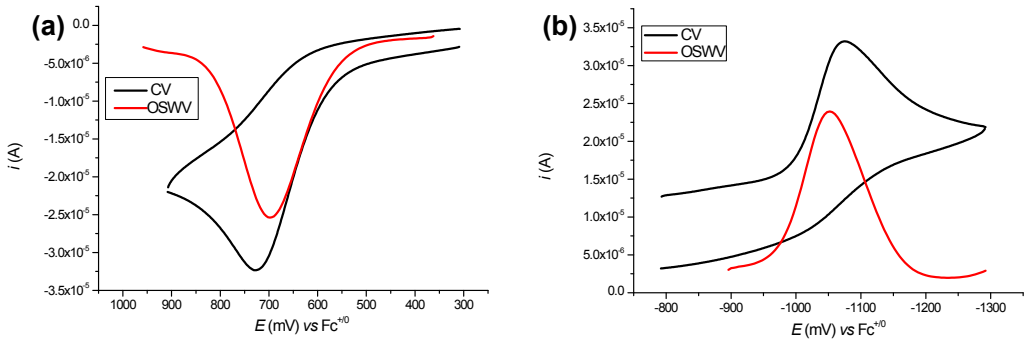


Figure s16. CV and OSWV for the oxidation of **5H**(R = NO_2) (a) and reduction of **5**$^+$(R = NO_2) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

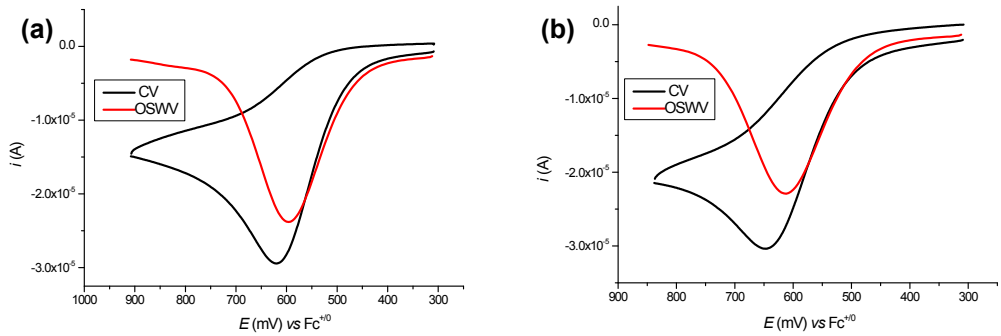


Figure s17. CV and OSWV for the oxidation of **5H**(R = CH_3) (a) and **5H**(R = H) (b) in deaerated acetonitrile containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte.

Typical ITC Spectra

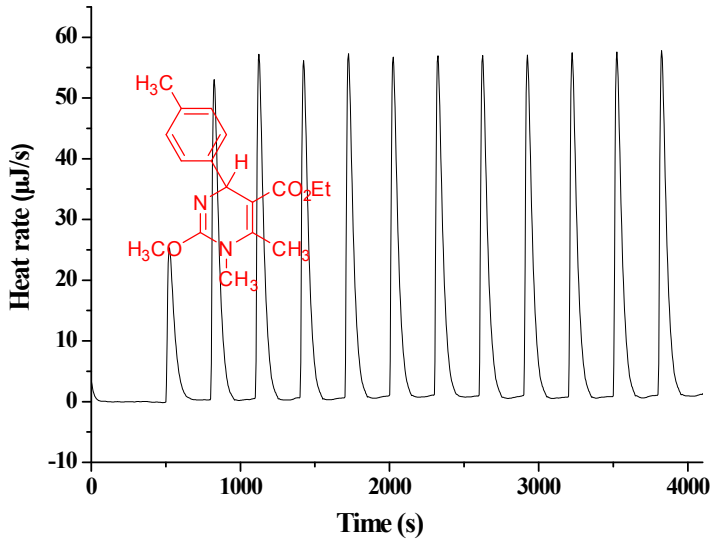


Figure s18. Isothermal titration calorimetry (ITC) for the reaction heat of **1H**(R = CH_3) with 9-phenylxanthylium perclorate ($PhXn^+ClO_4^-$) in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **1H**(R = CH_3) (2.87 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

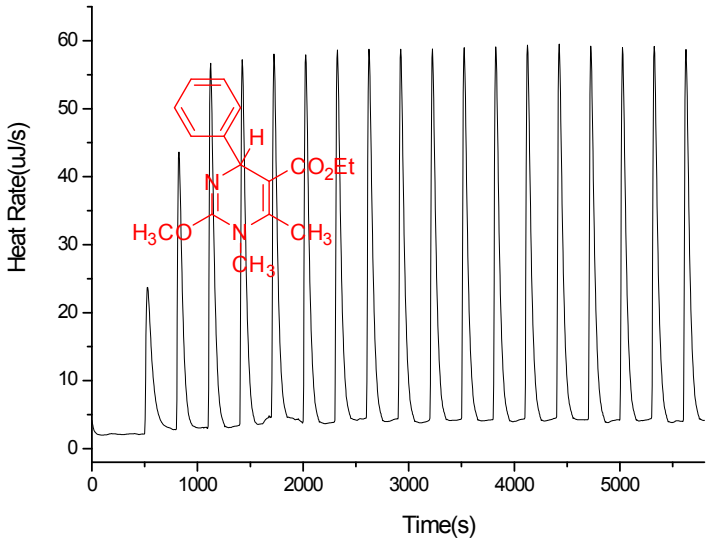


Figure s19. ITC for the reaction heat of **1H**(R = H) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **1H**(R = H) (2.97 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

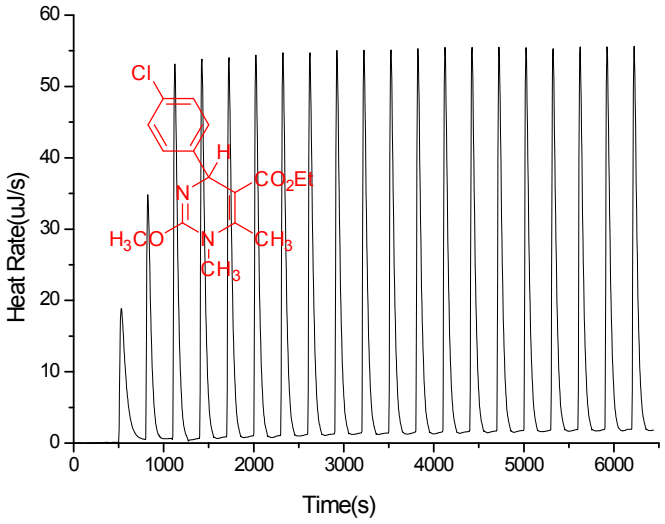


Figure s20. ITC for the reaction heat of **1H**(R = Cl) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **1H**(R = Cl) (3.03 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

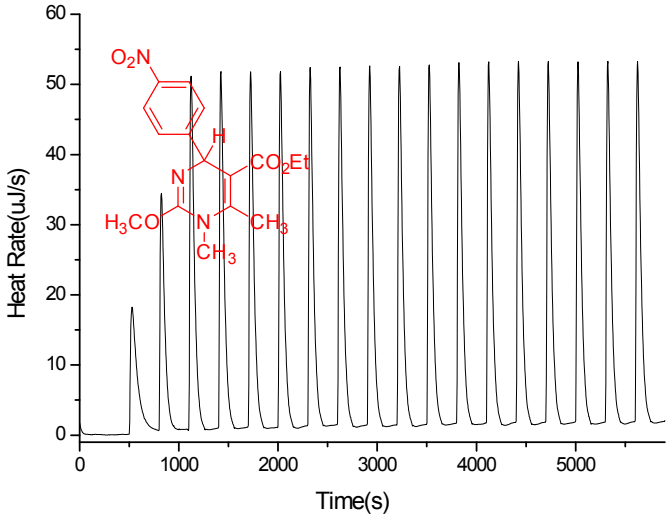


Figure s21. ITC for the reaction heat of **1H**(R = NO_2) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **1H**(R = NO_2) (3.01 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

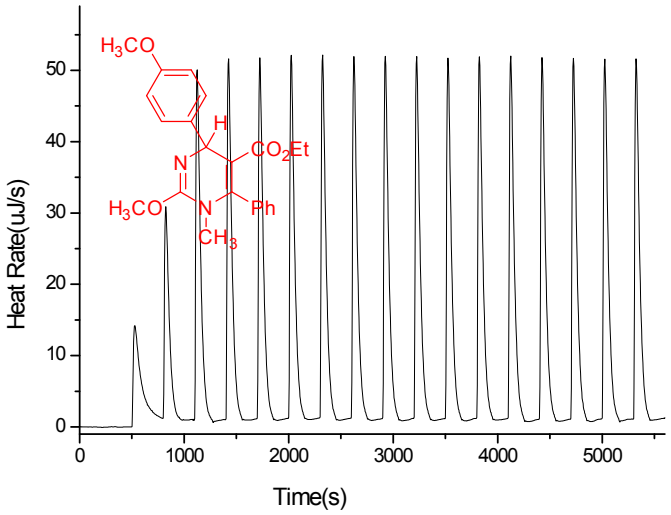


Figure s22. ITC for the reaction heat of **2H**(R = OCH_3) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **2H**(R = OCH_3) (2.98 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

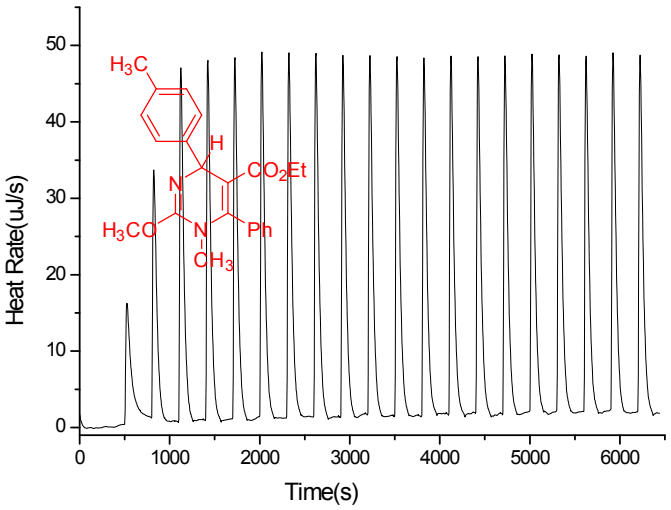


Figure s23. ITC for the reaction heat of **2H**(R = CH_3) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **2H**(R = CH_3) (2.89 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

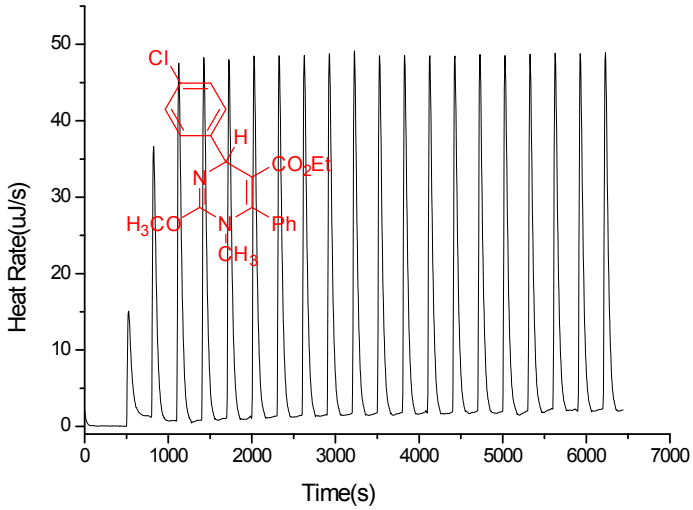


Figure s24. ITC for the reaction heat of **2H**(R = Cl) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **2H**(R = Cl) (3.04 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

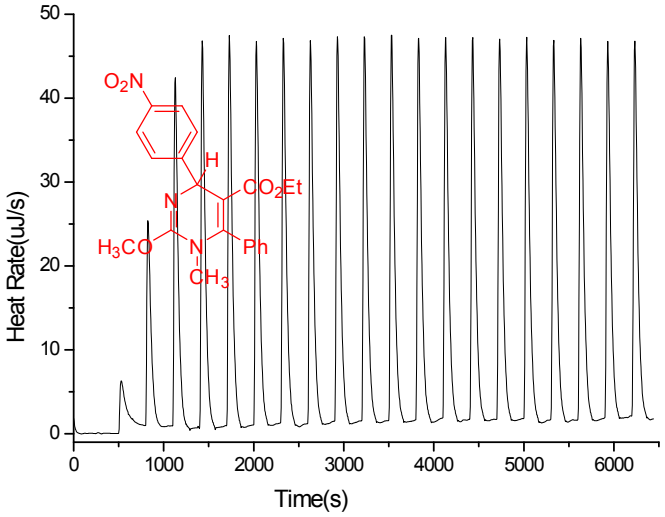


Figure s25. ITC for the reaction heat of **2H**(R = NO_2) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **2H**(R = NO_2) (2.98 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

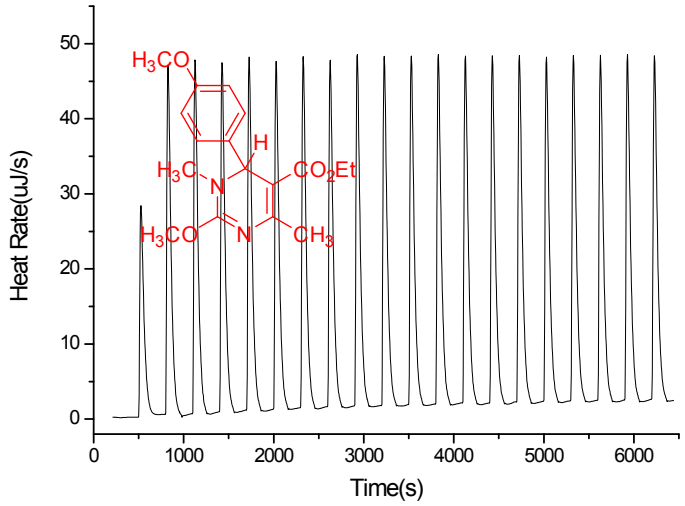


Figure s26. ITC for the reaction heat of **3H**(R = OCH_3) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **3H**(R = OCH_3) (2.98 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

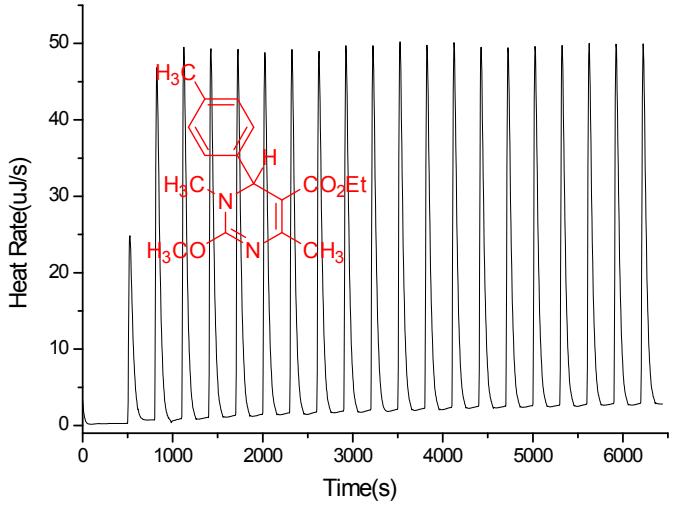


Figure s27. ITC for the reaction heat of **3H**(R = CH_3) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **3H**(R = CH_3) (3.03 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

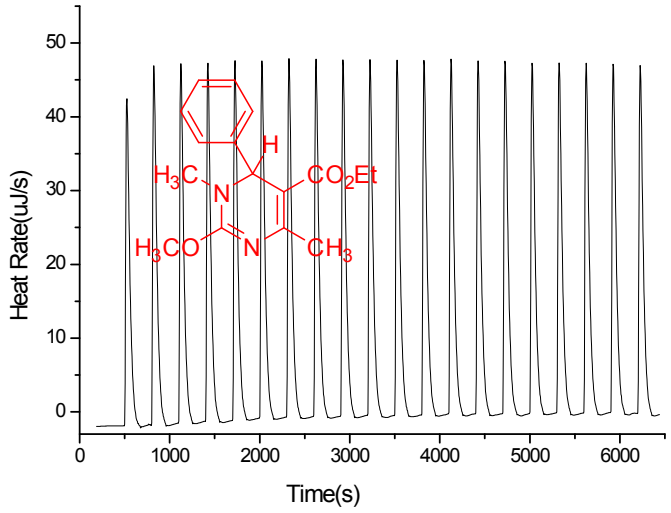


Figure s28. ITC for the reaction heat of **3H**(R = H) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **3H**(R = H) (2.99 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

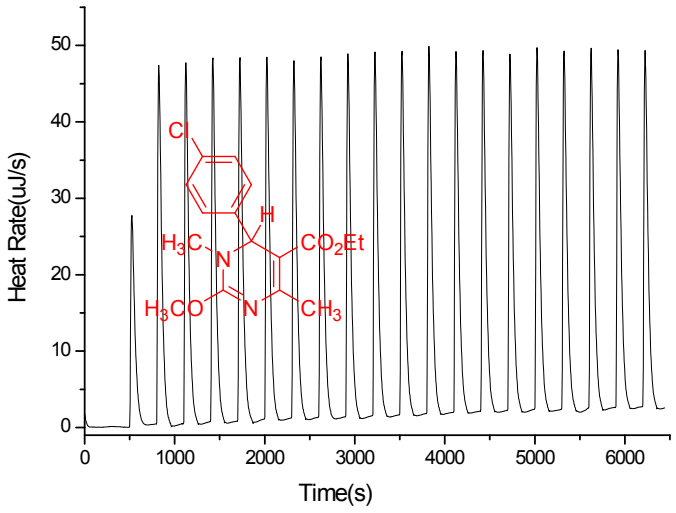


Figure s29. ITC for the reaction heat of **3H**(R = Cl) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **3H**(R = Cl) (3.02 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

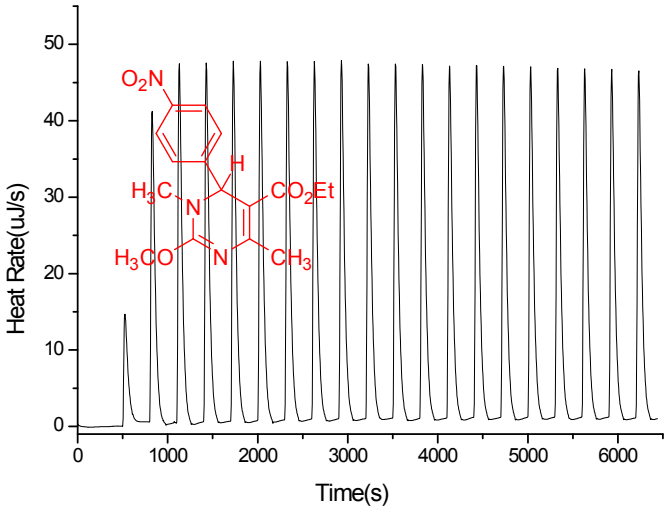


Figure s30. ITC for the reaction heat of **3H**(R = NO_2) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **3H**(R = NO_2) (3.03 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

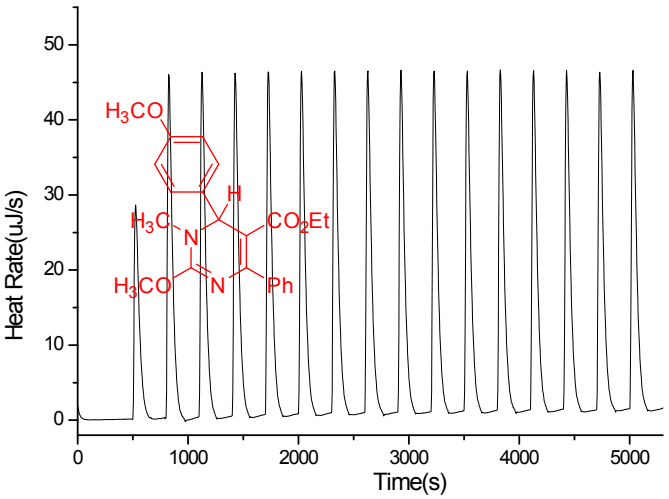


Figure s31. ITC for the reaction heat of **4H**(R = OCH_3) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **4H**(R = OCH_3) (3.00 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

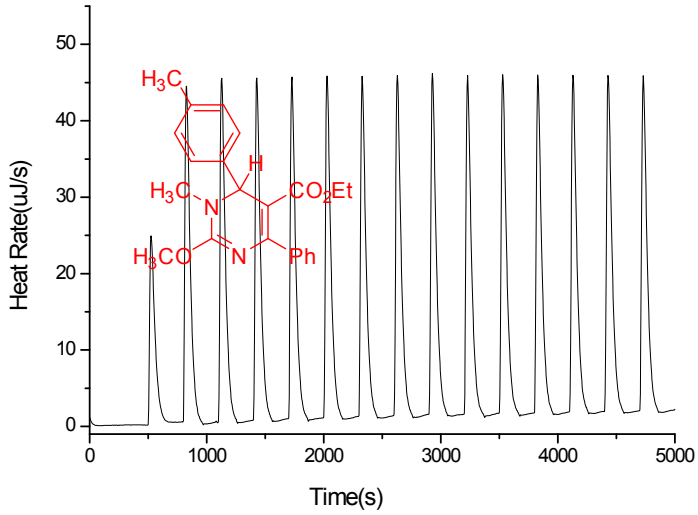


Figure s32. ITC for the reaction heat of **4H**(R = CH_3) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **4H**(R = CH_3) (3.01 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

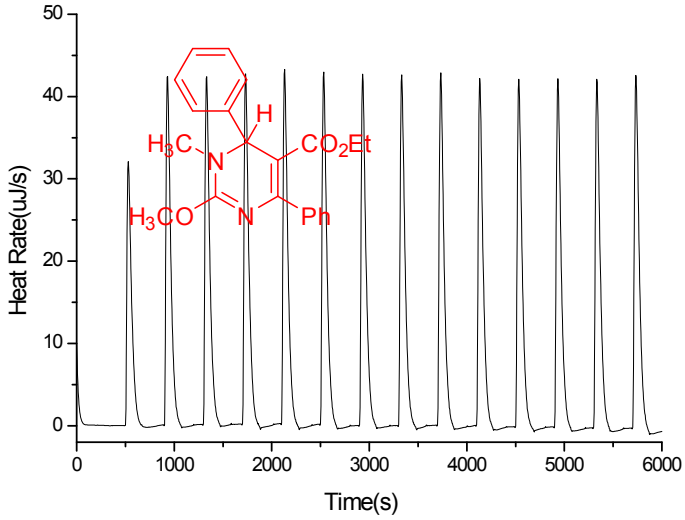


Figure s33. ITC for the reaction heat of **4H**(R = H) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **4H**(R = H) (2.95 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

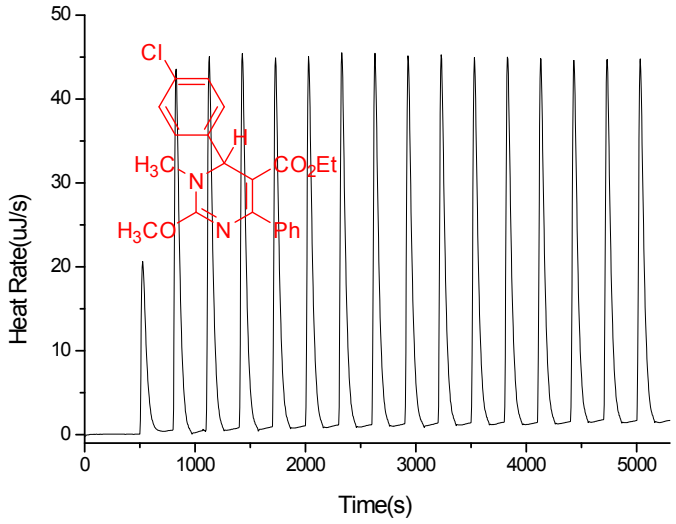


Figure s34. ITC for the reaction heat of **4H**(R = Cl) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **4H**(R = Cl) (3.15 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

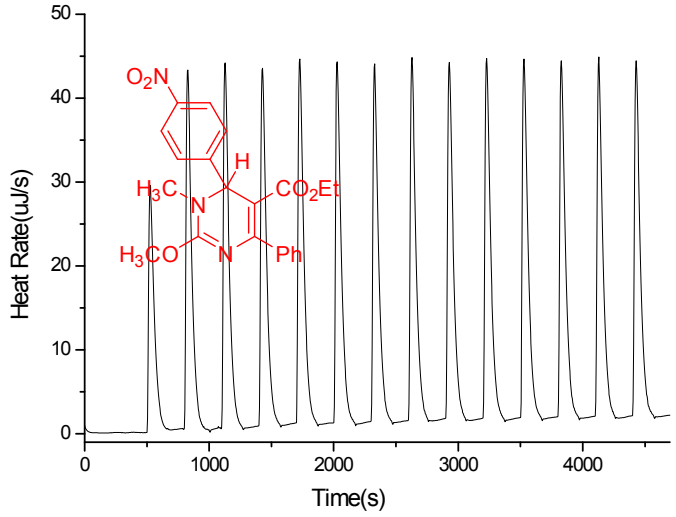


Figure s35. ITC for the reaction heat of **4H**(R = NO_2) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **4H**(R = NO_2) (3.09 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

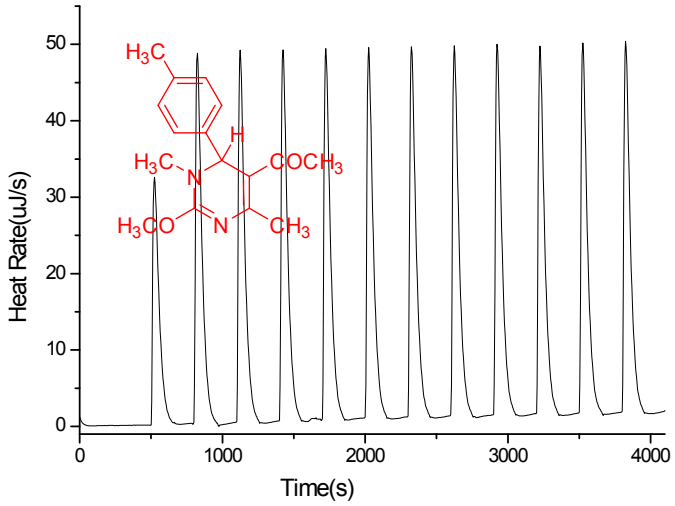


Figure s36. ITC for the reaction heat of **5H**(R = CH_3) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **5H**(R = CH_3) (3.07 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

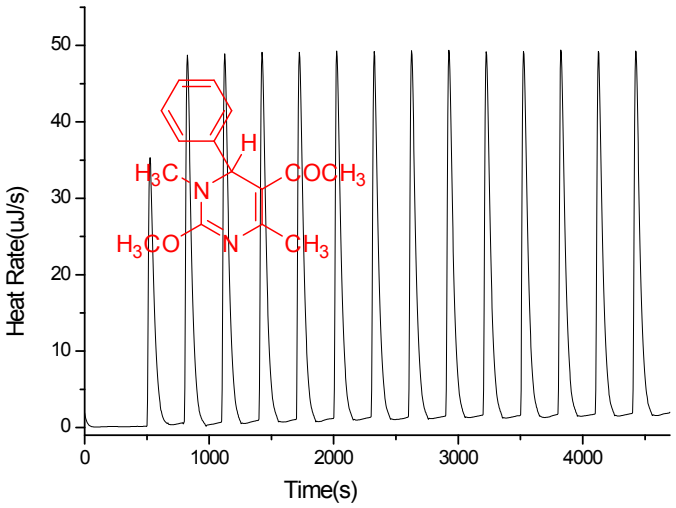


Figure s37. ITC for the reaction heat of **5H**(R = H) with $PhXn^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **5H**(R = H) (3.09 mM) every 300 s into the acetonitrile containing $PhXn^+ClO_4^-$ (ca. 30 mM).

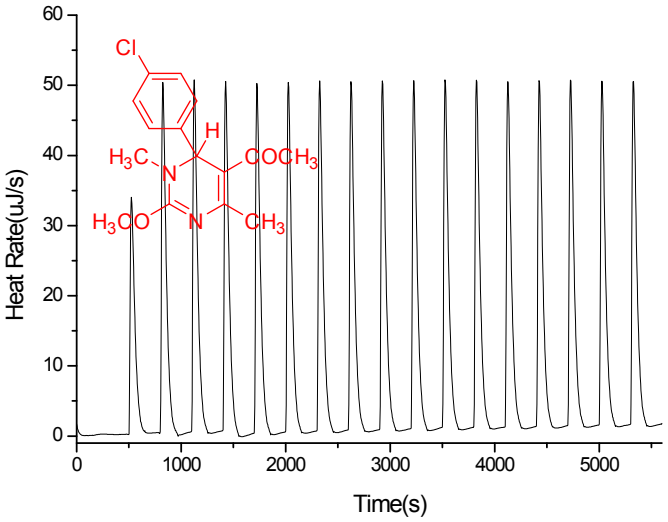


Figure s38. ITC for the reaction heat of **5H**(R = Cl) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **5H**(R = Cl) (3.15 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

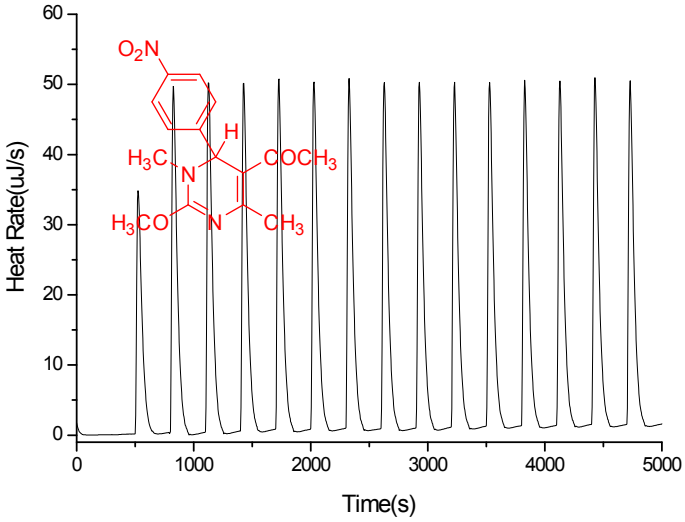


Figure s39. ITC for the reaction heat of **5H**(R = NO_2) with $PhXn^{+}ClO_4^{-}$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of **5H**(R = NO_2) (3.21 mM) every 300 s into the acetonitrile containing $PhXn^{+}ClO_4^{-}$ (ca. 30 mM).

Typical Hammett Plots for Thermodynamic Parameters.

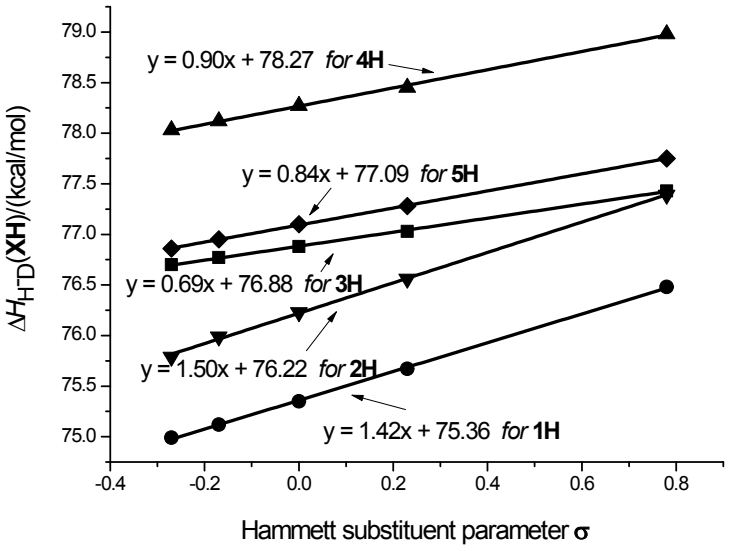


Figure s40. Plot of $\Delta H_{H\text{-}D}$(**XH**) against Hammett substituent parameter (σ).

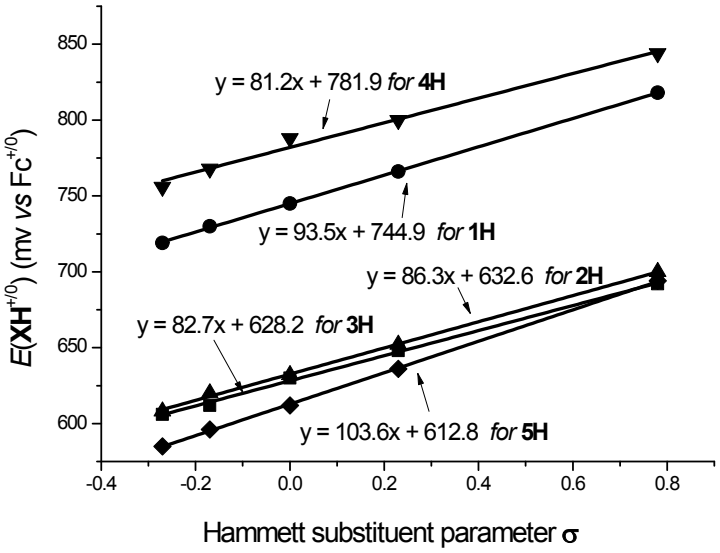


Figure s41. Plot of E(**XH**$^{+/0}$) against Hammett substituent parameter (σ).