

Electronic Supplementary Information

Switching between ring closed and open N-incorporated heterocycles with tuneable charges and modular reactivity based upon 5-(2-bromoethyl)phenanthridinium bromide

Roslyn Eadie,^a Craig Richmond,^a Samantha Moreton^a and Leroy Cronin^{a*}

Table of Contents:

¹H NMR spectra (in D₆-DMSO)

1-Benzothiazol-6-yl-1,2,3,12 <i>b</i> -tetrahydroimidazo[1,2- <i>f</i>]phenanthridine (1)	S3
1-Benzothiazol-6-yl-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (2)	S3
1-(1 <i>H</i> -Benzoimidazol-5-yl)-1,2,3,12 <i>b</i> -tetrahydroimidazo[1,2- <i>f</i>]phenanthridine (3)	S4
1-(1 <i>H</i> -Benzoimidazol-5-yl)-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (4)	S4
1-[3-(2-Methyl-thiazol-4-yl)-phenyl]-1,2,3,12 <i>b</i> -tetrahydroimidazo[1,2- <i>f</i>]phenanthridine (5)	S5
1-[3-(2-Methyl-thiazol-4-yl)-phenyl]-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (6)	S5
5-[2-([1,10]Phenanthrolin-5-ylamino)-ethyl]phenanthridinium bromide (7)	S6
1-(9 <i>H</i> -Fluoren-2-yl)-1,2,3,12 <i>b</i> -tetrahydroimidazo[1,2- <i>f</i>]phenanthridine (8)	S6
5-[2-(Fluoranthren-3-ylamino)-ethyl]phenanthridinium bromide (9)	S7
1-(2-Ethynyl-phenyl)-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (10)	S7
1-(5-Chloro-pyridin-2-yl)-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (11)	S8
1-(6-Chloro-pyridin-3-yl)-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (12)	S8
1-Pyridin-2-yl-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (13)	S9
1-(2-Hydroxy-phenyl)-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (14)	S9
1-(4-Hydroxy-pyridin-3-yl)-2,3-dihydro-1 <i>H</i> -imidazo[1,2- <i>f</i>]phenanthridin-4-ylum bromide (15)	S10
5-[2-(3-Hydroxy-pyridin-2-ylamino)-ethyl]phenanthridinium bromide (16)	S10

5-[2-(2-Hydroxy-pyridin-3-ylamino)-ethyl]phenanthridinium bromide (**17**) S11
¹H NMR reaction spectrum

Pseudo base formation for failed reactions (in CD₃OD) S12

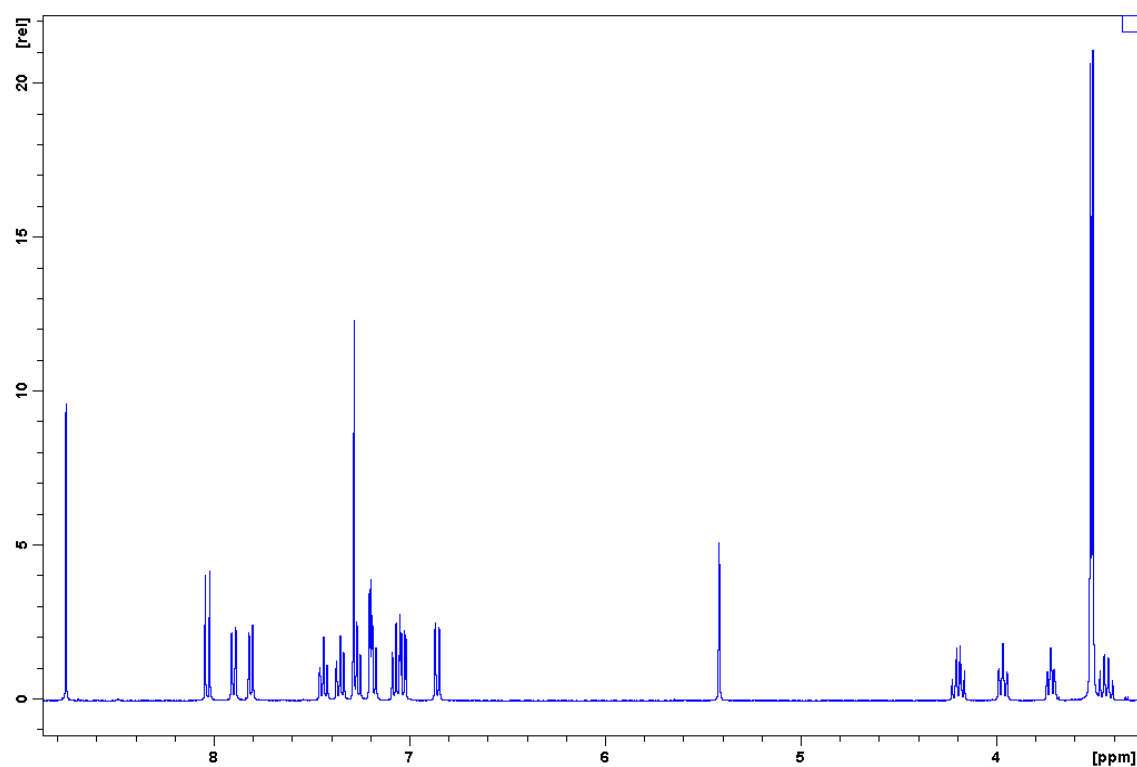
UV-vis reaction spectra

1-(9H-Fluoren-2-yl)-1,2,3,12*b*-tetrahydroimidazo[1,2-*f*]phenanthridine (**8**) S13

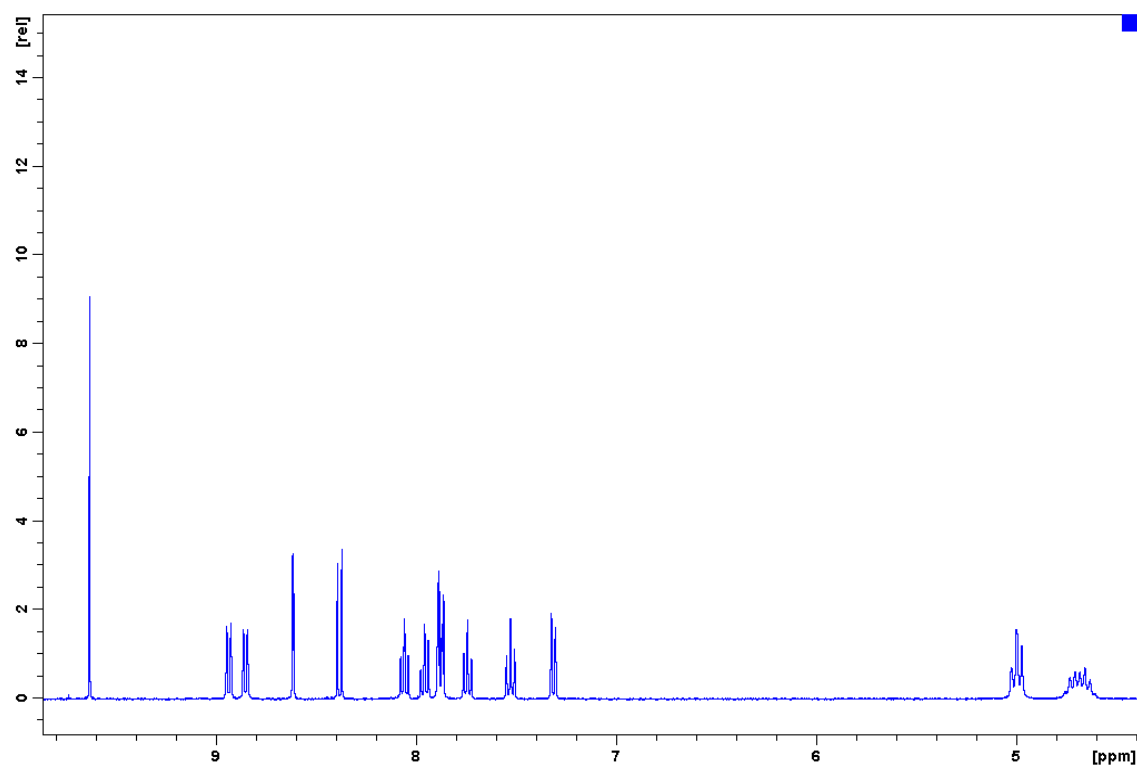
5-[2-(Fluoranthren-3-ylamino)-ethyl]phenanthridinium bromide (**9**) S14

1-(2-Ethynyl-phenyl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (**10**) S15

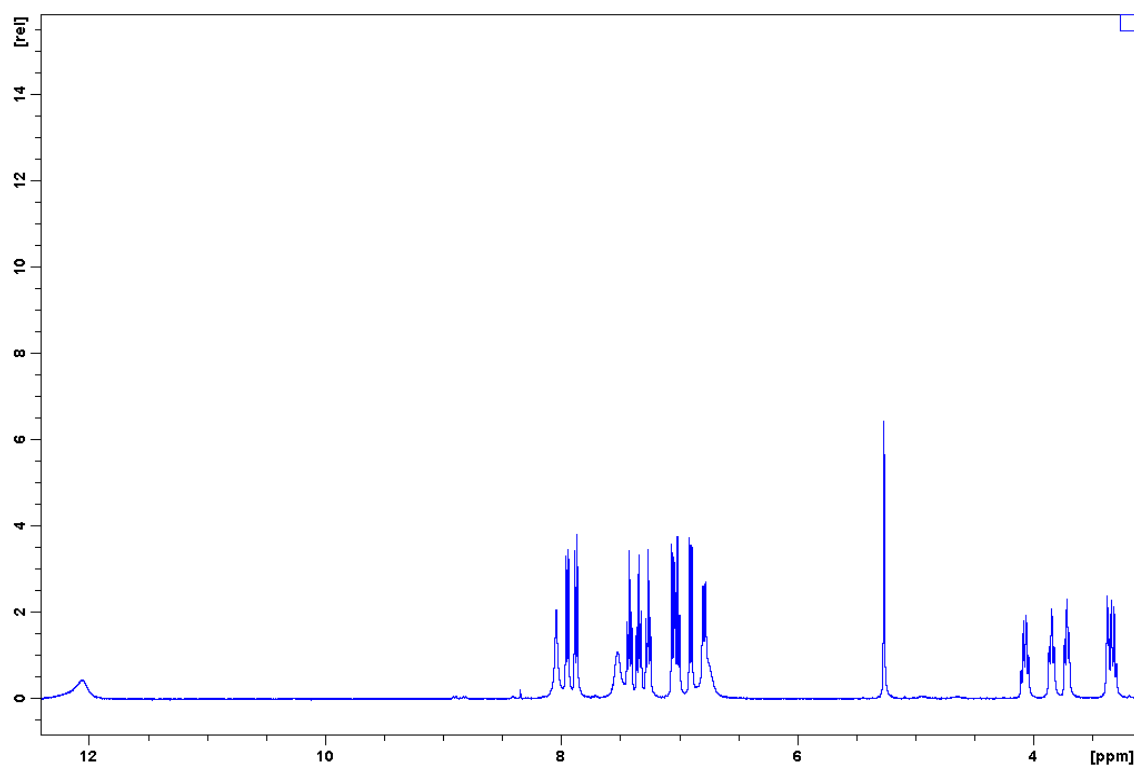
1-Benzothiazol-6-yl-1,2,3,12*b*-tetrahydroimidazo[1,2-*f*]phenanthridine (in D₆-DMSO) (**1**)



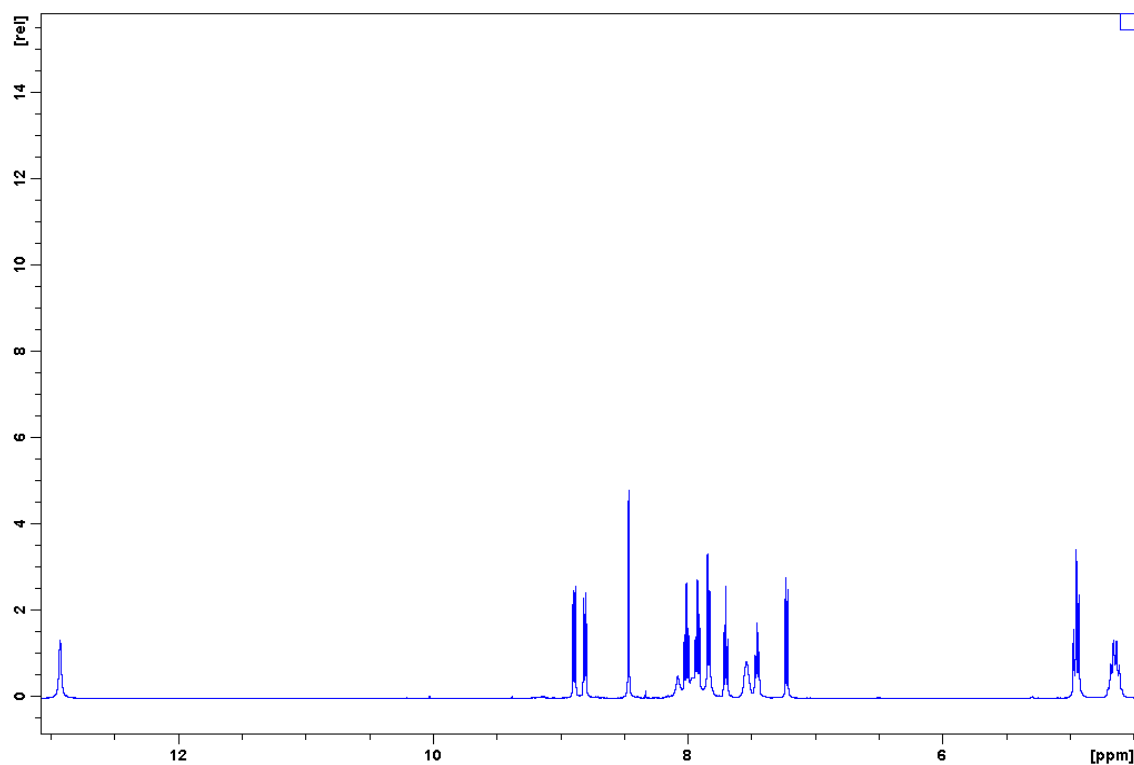
1-Benzothiazol-6-yl-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (in D₆-DMSO) (**2**)



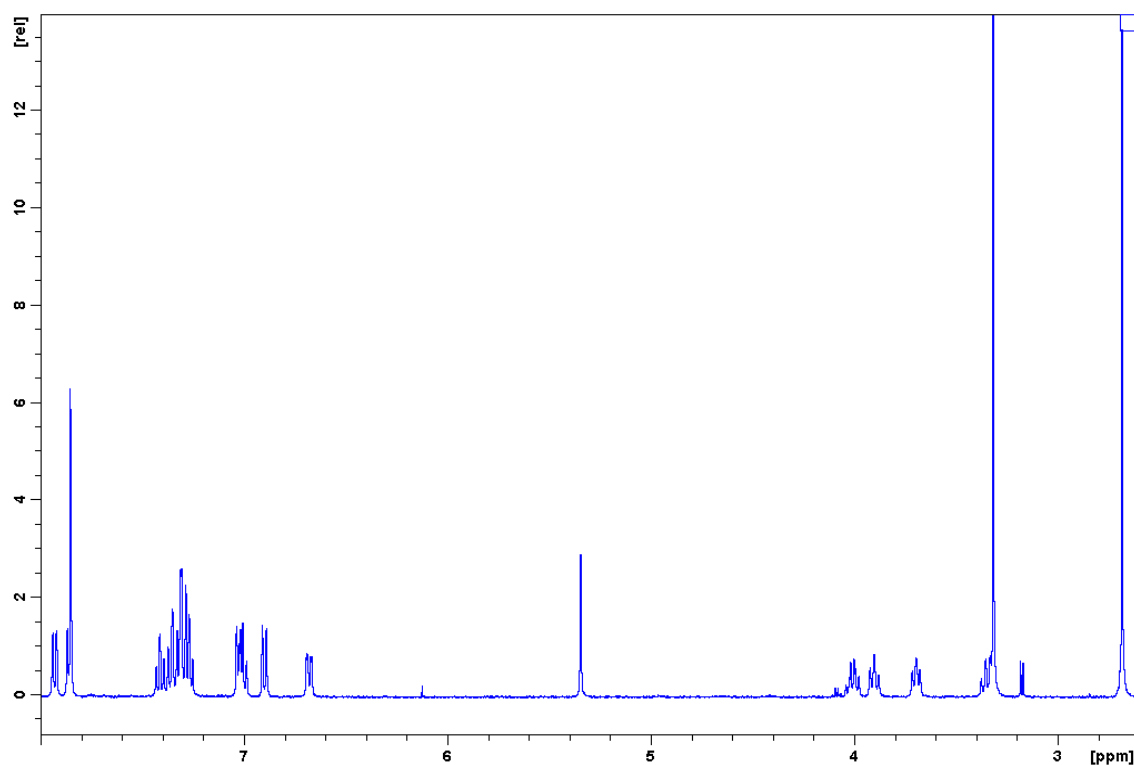
1-(1H-Benzoimidazol-5-yl)-1,2,3,12*b*-tetrahydroimidazo[1,2-*f*]phenanthridine (in D₆-DMSO)
(3)



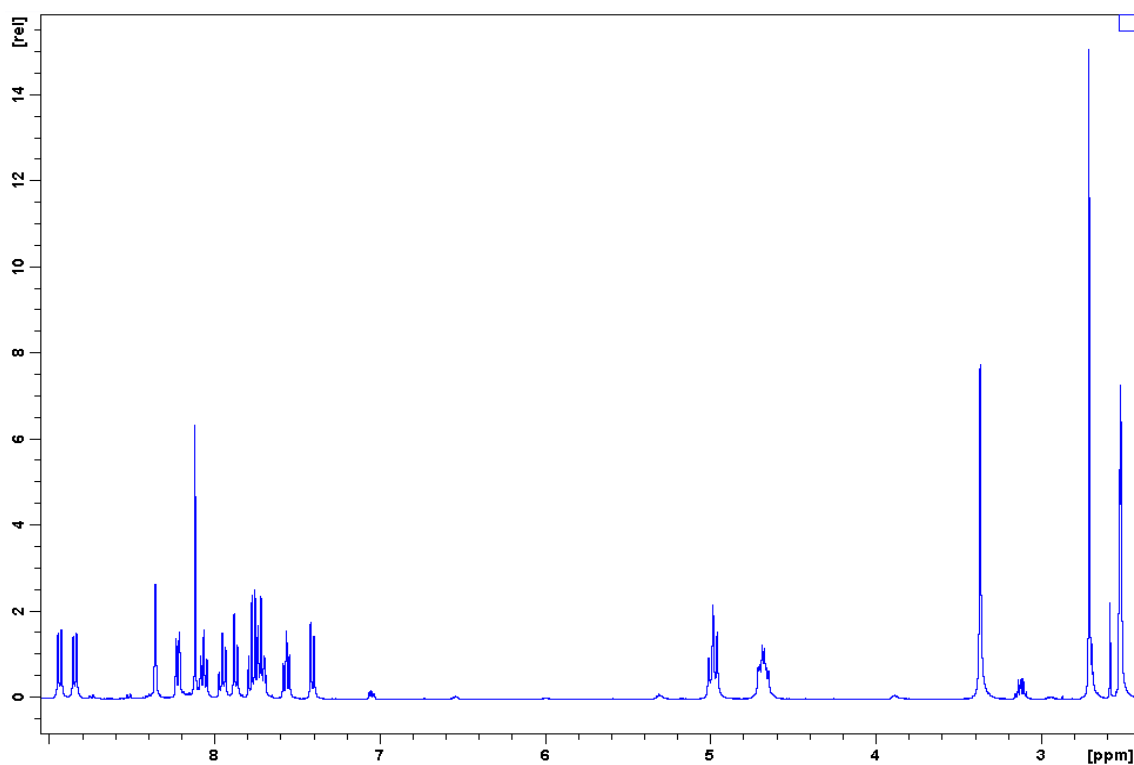
1-(1H-Benzoimidazol-5-yl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide
(in D₆-DMSO) **(4)**



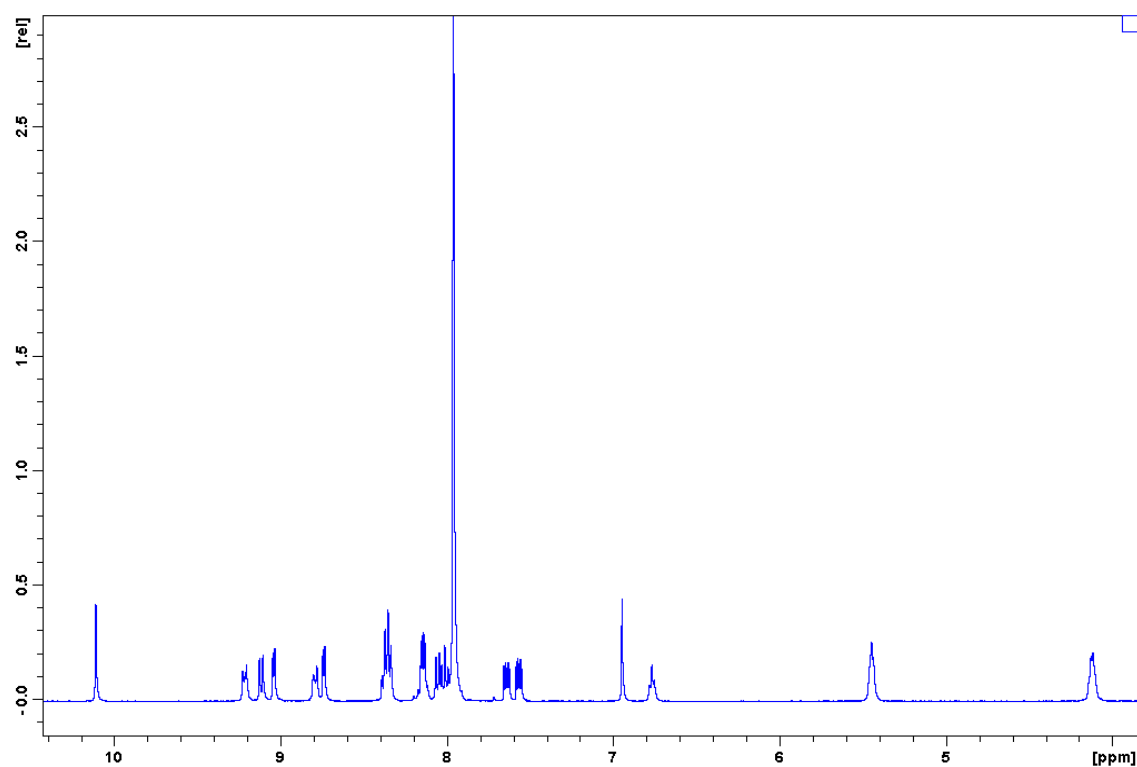
1-[3-(2-Methyl-thiazol-4-yl)-phenyl]-1,2,3,12*b*-tetrahydroimidazo[1,2-*f*]phenanthridine (in D₆-DMSO) (**5**)



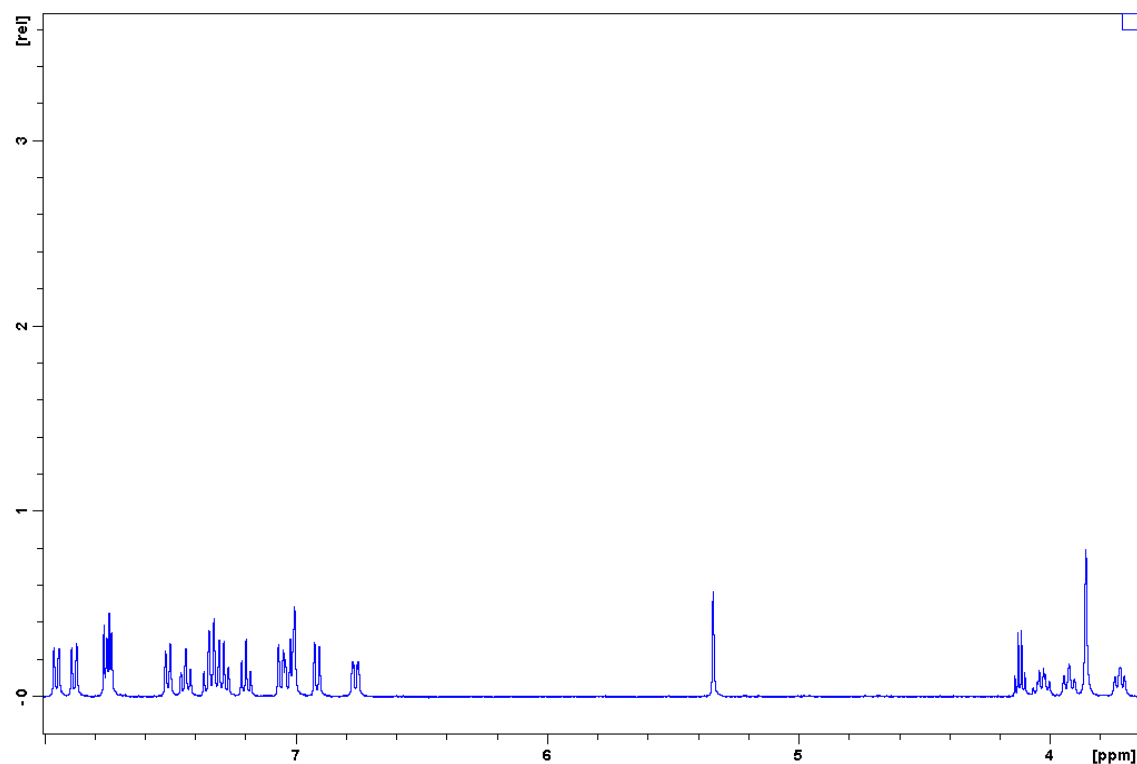
1-[3-(2-Methyl-thiazol-4-yl)-phenyl]-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (in D₆-DMSO) (**6**)



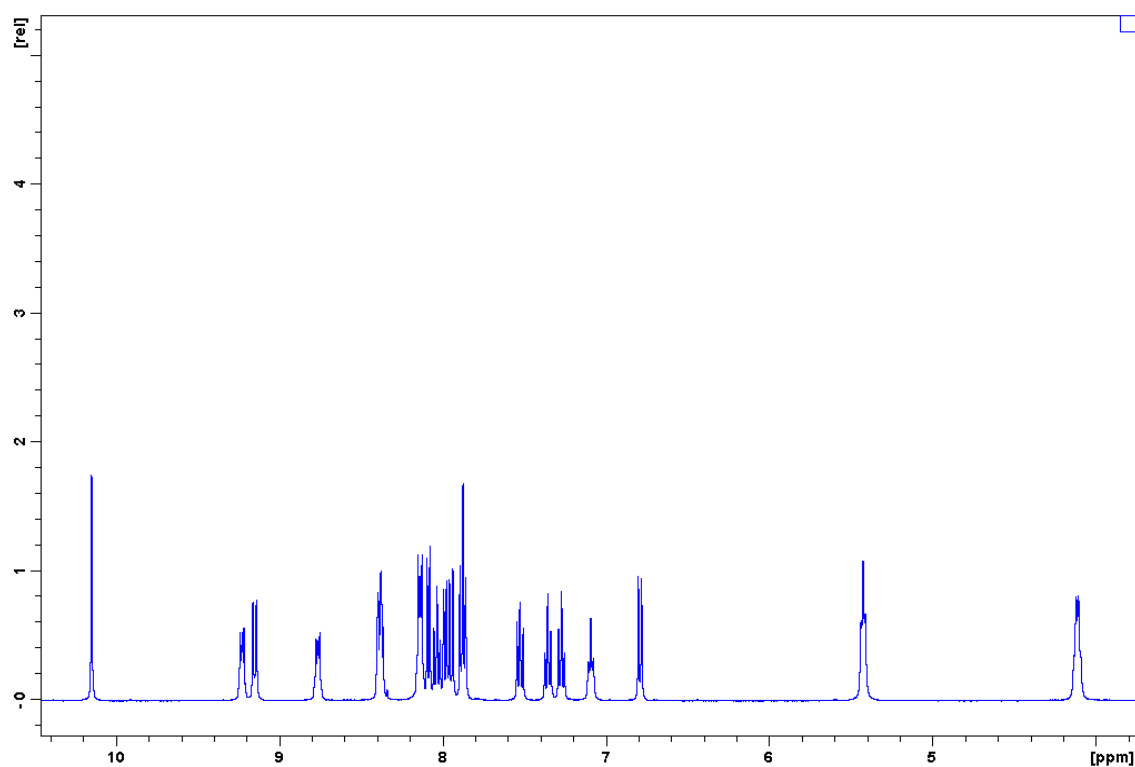
5-[2-([1,10]Phenanthroline-5-ylamino)-ethyl]phenanthridinium bromide (in D₆-DMSO) (**7**)



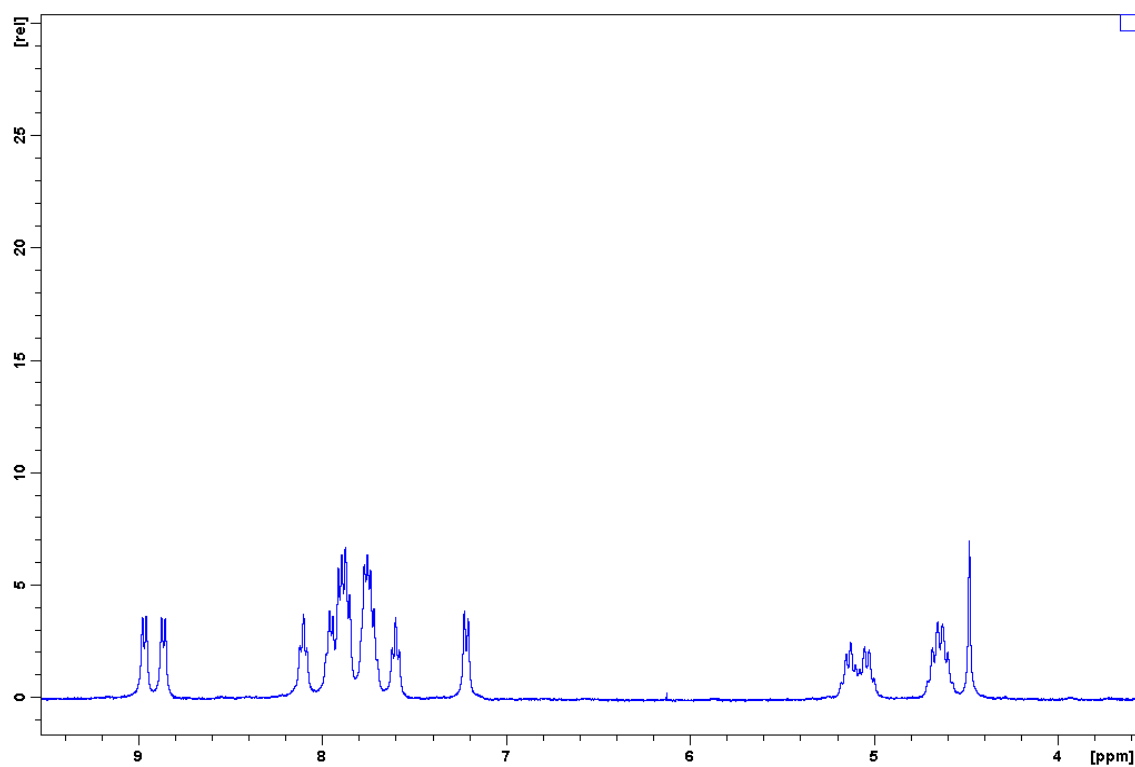
1-(9H-Fluoren-2-yl)-1,2,3,12*b*-tetrahydroimidazo[1,2-*f*]phenanthridine (in D₆-DMSO) (**8**)



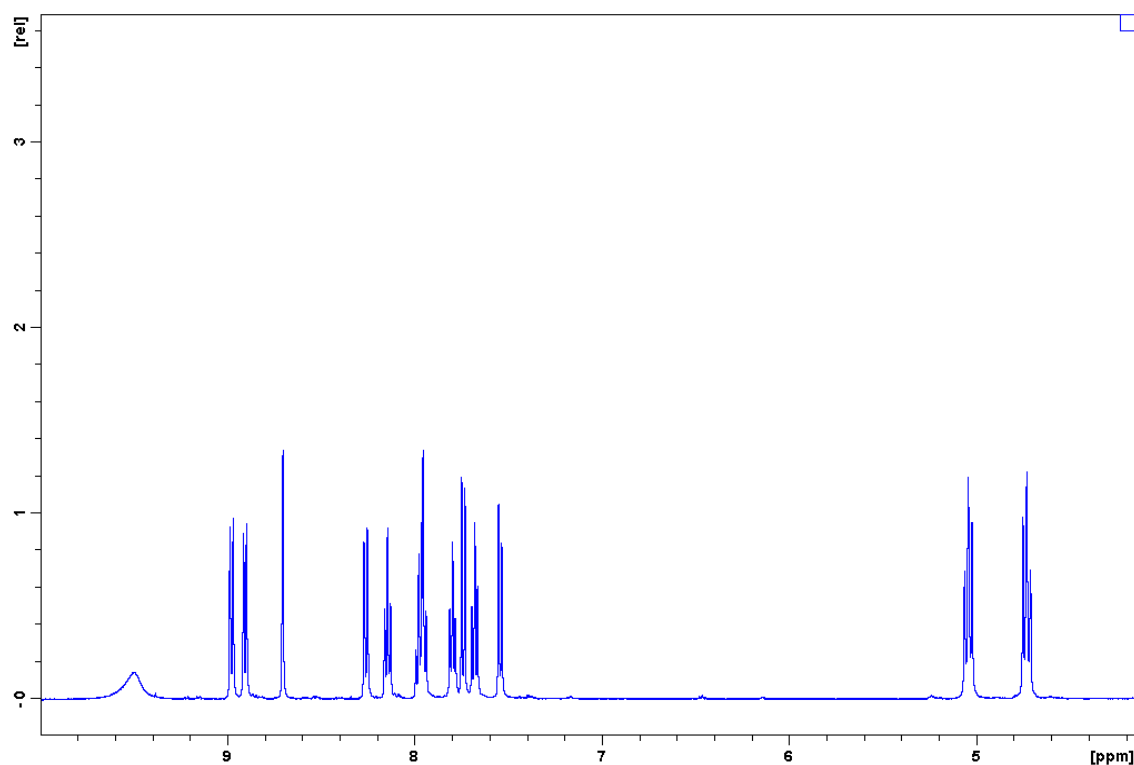
5-[2-(Fluoranthen-3-ylamino)-ethyl]phenanthridinium bromide (in D₆-DMSO) (**9**)



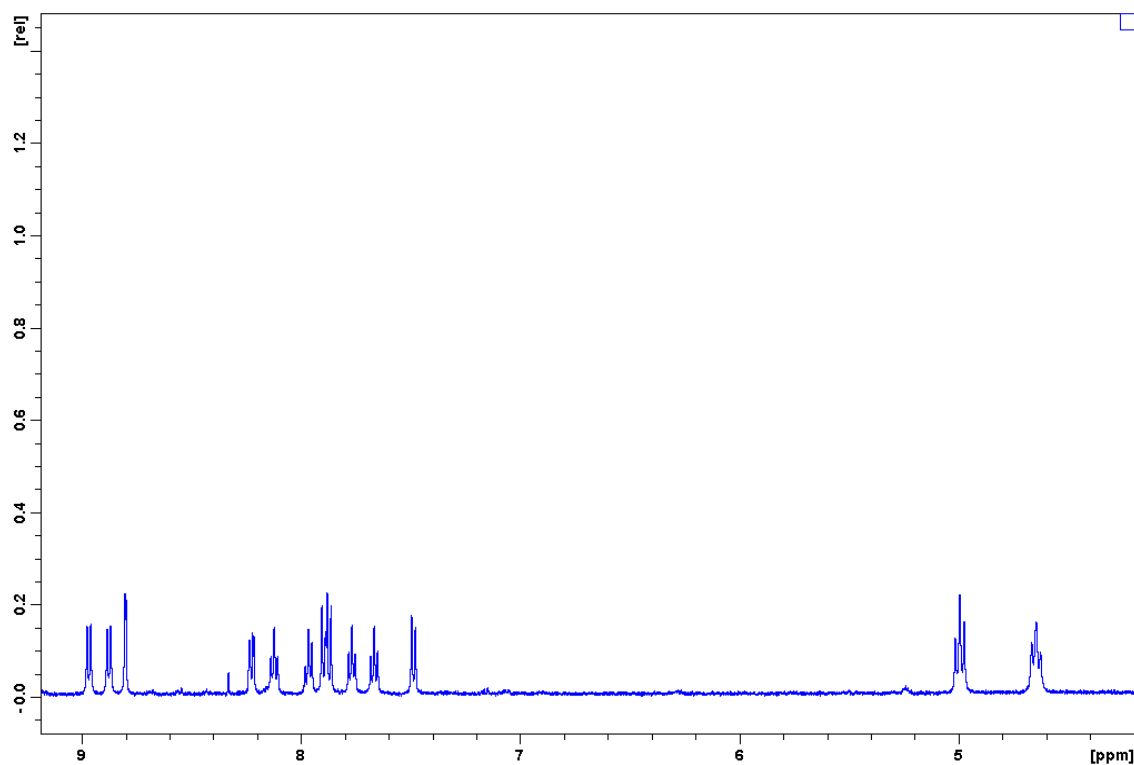
1-(2-Ethynyl-phenyl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (in D₆-DMSO) (**10**)



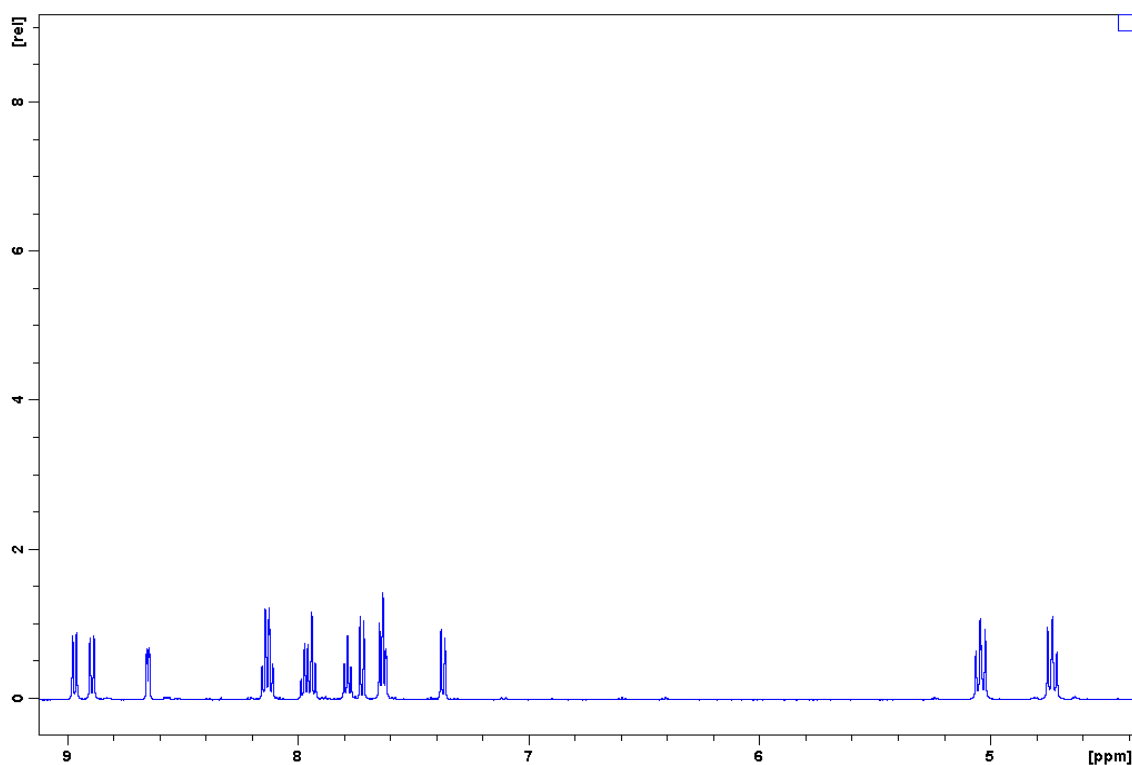
1-(5-Chloro-pyridin-2-yl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (in D₆-DMSO) (**11**)



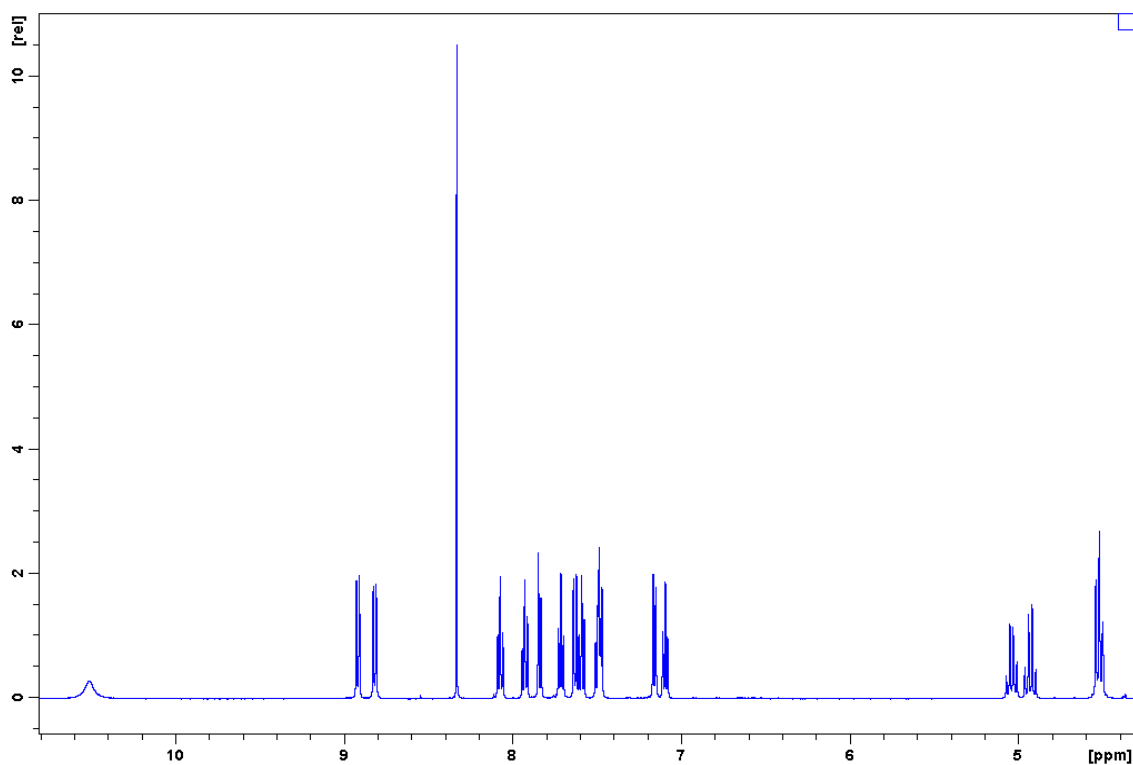
1-(6-Chloro-pyridin-3-yl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (in D₆-DMSO) (**12**)



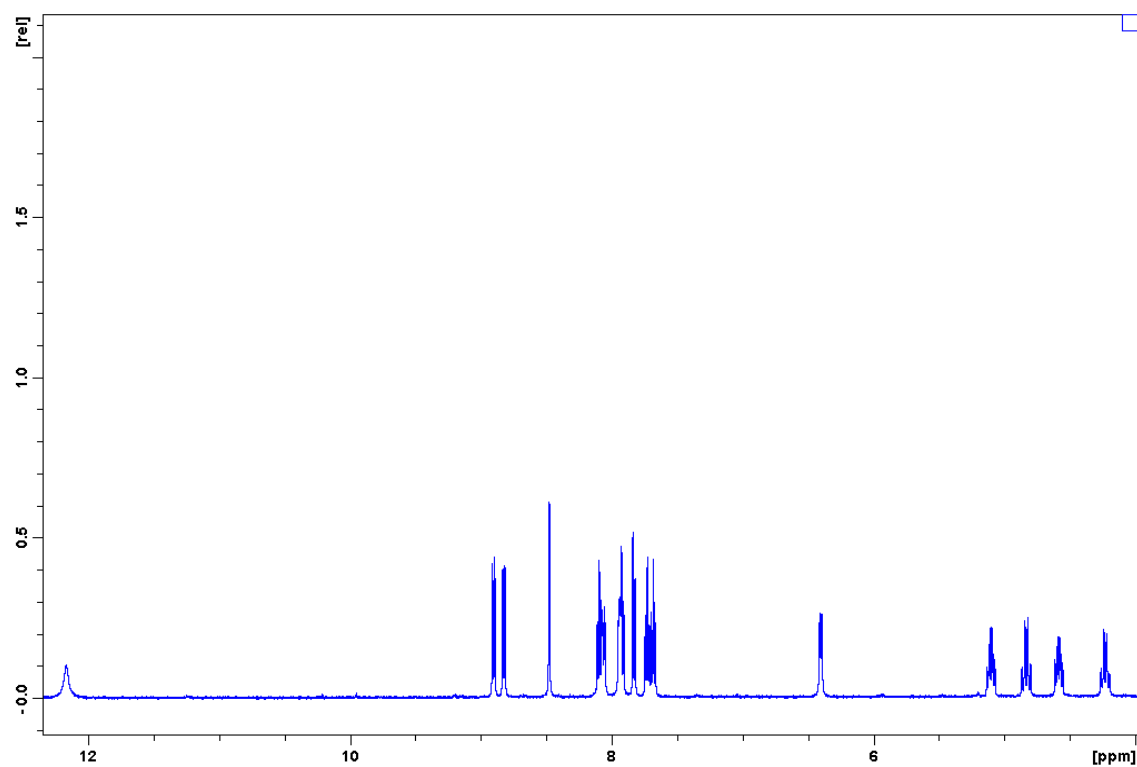
1-Pyridin-2-yl-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (in D₆-DMSO)
(13)



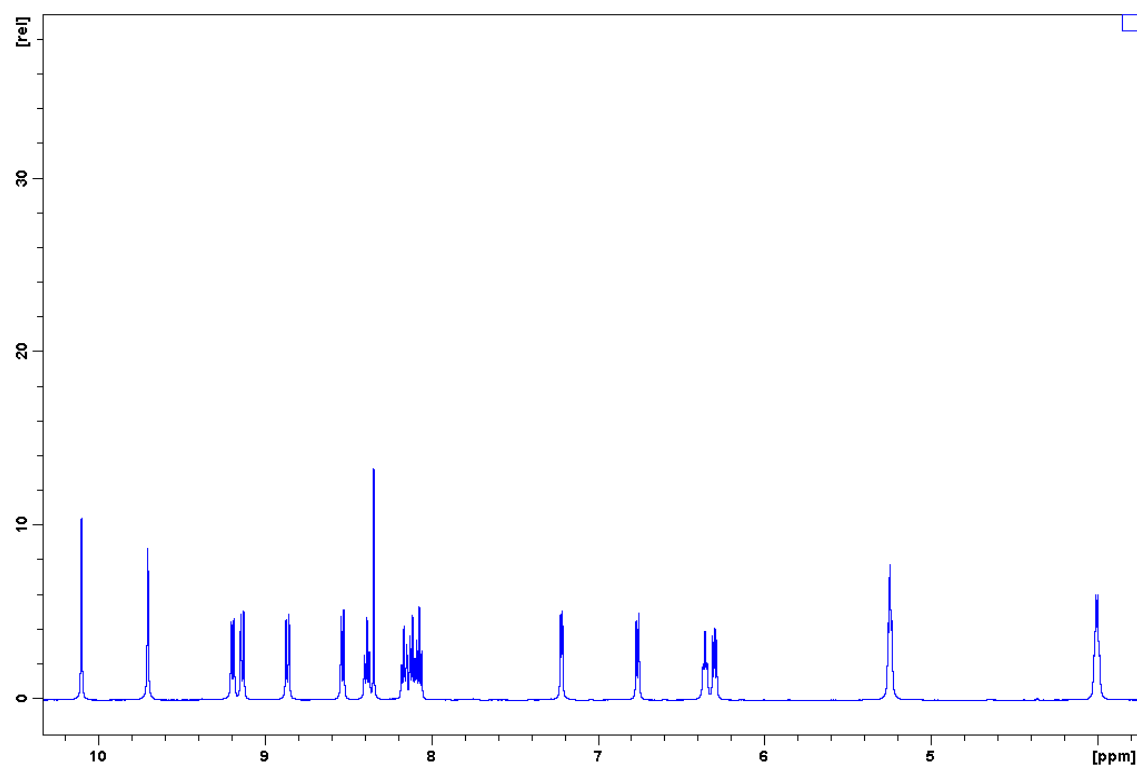
1-(2-Hydroxy-phenyl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (in D₆-DMSO)
(14)



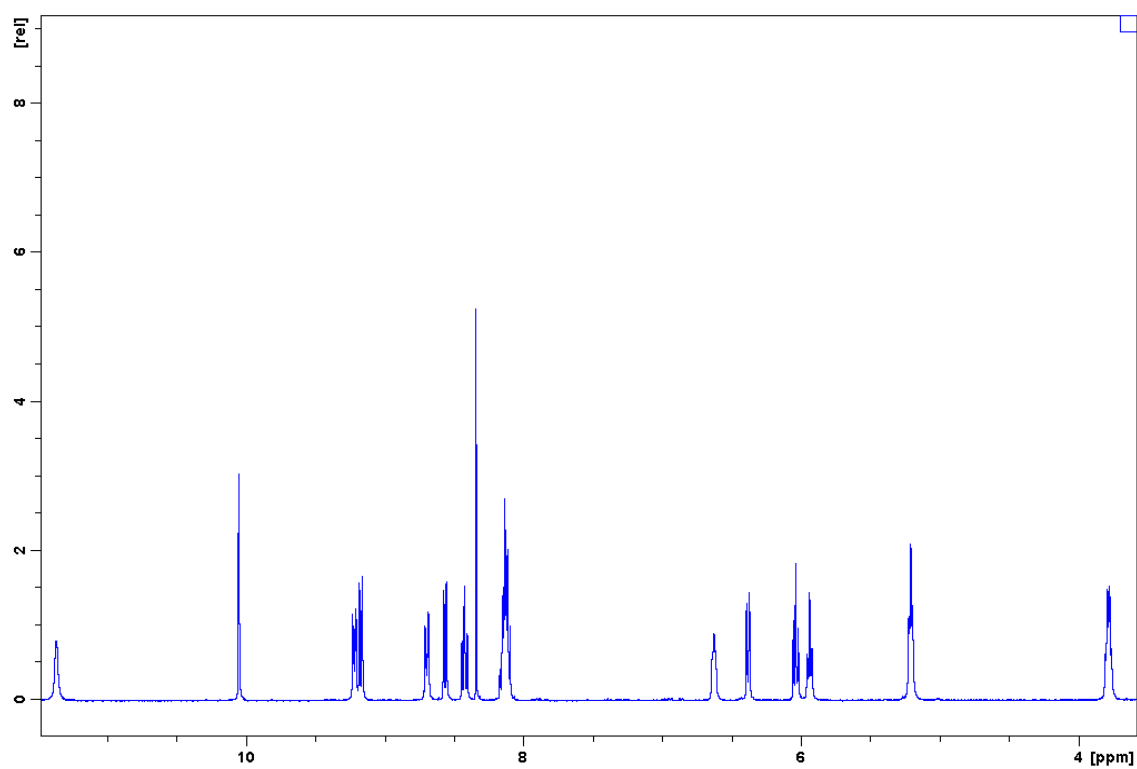
1-(4-Hydroxy-pyridin-3-yl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide
(in D₆-DMSO) (**15**)



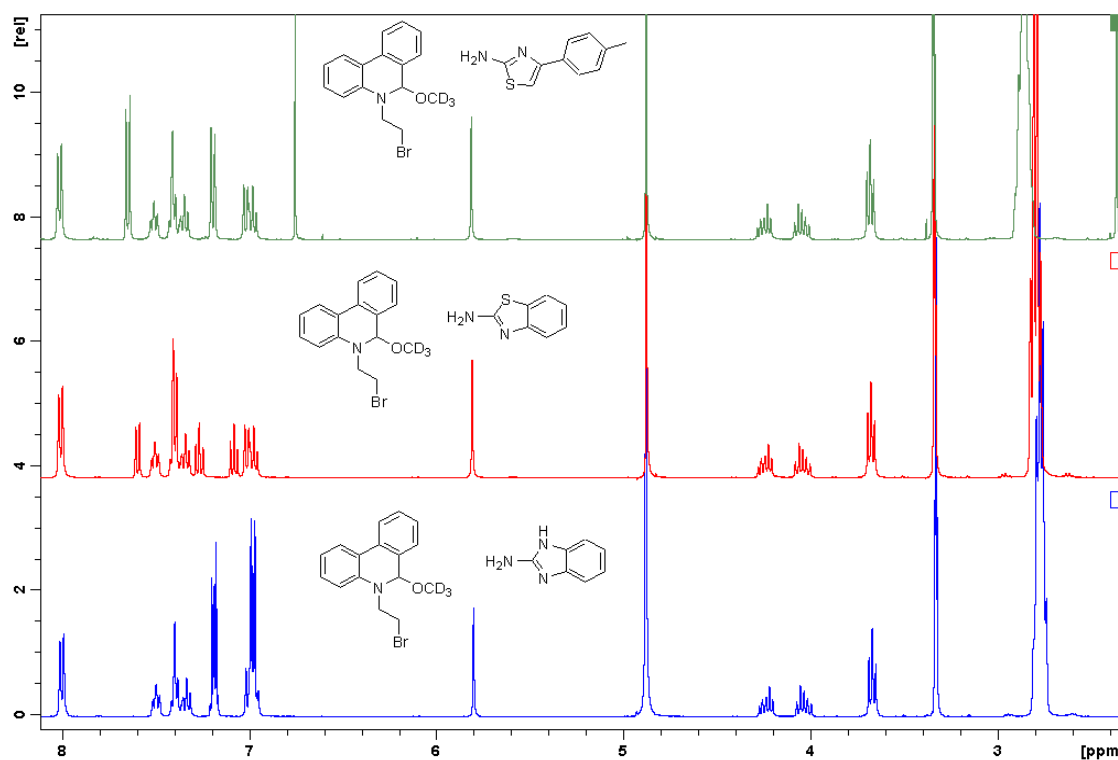
5-[2-(3-Hydroxy-pyridin-2-ylamino)-ethyl]phenanthridinium bromide (in D₆-DMSO) (**16**)



5-[2-(2-Hydroxy-pyridin-3-ylamino)-ethyl]phenanthridinium bromide (D₆-DMSO) (**17**)



Pseudo base formation reaction for failed reactions (in CH₃OD)

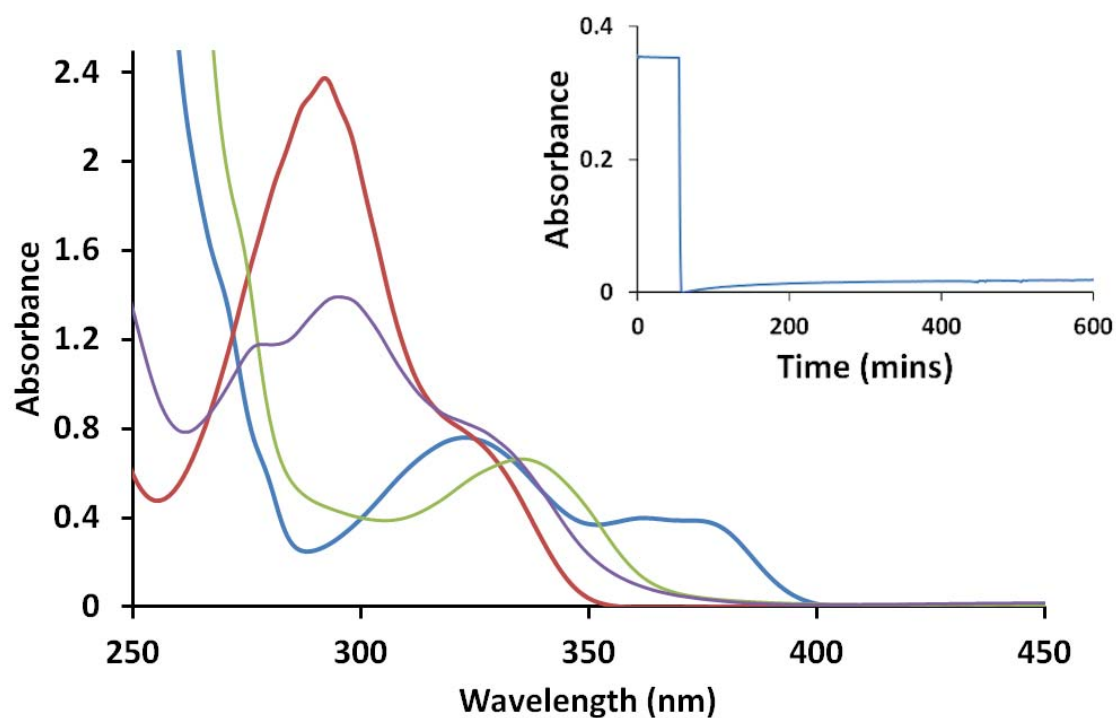


¹H NMR spectrum in green (top) from reaction of BEP (1eq.), 2-amino-4(p-tolyl)thiazole (1eq.) and triethylamine (3eq.) in CH₃OD.

¹H NMR spectrum in red (middle) from reaction of BEP (1eq.), 2-benzothiazoleamine (1eq.) and triethylamine (3eq.) in CH₃OD.

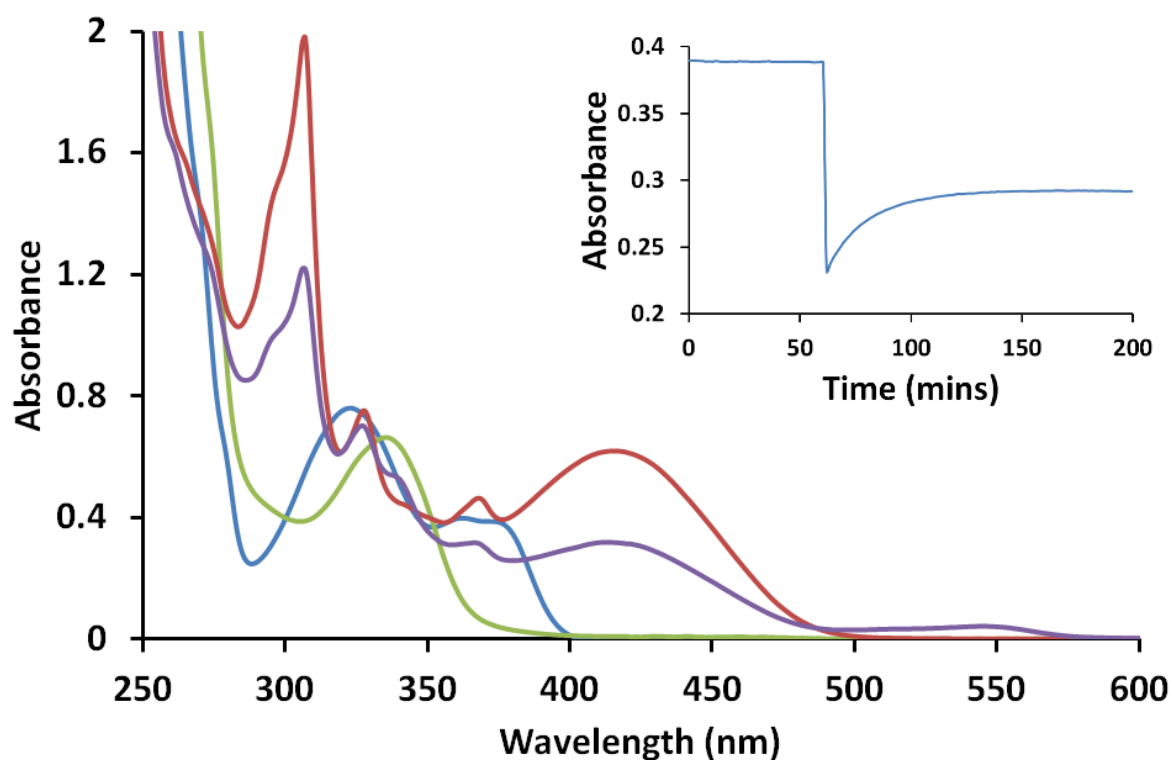
¹H NMR spectrum in blue (bottom) from reaction of BEP (1eq.), 2-aminobenzimidazole (1eq.) and triethylamine (3eq.) in CH₃OD.

1-(9H-Fluoren-2-yl)-1,2,3,12*b*-tetrahydroimidazo[1,2-*f*]phenanthridine (**8**)



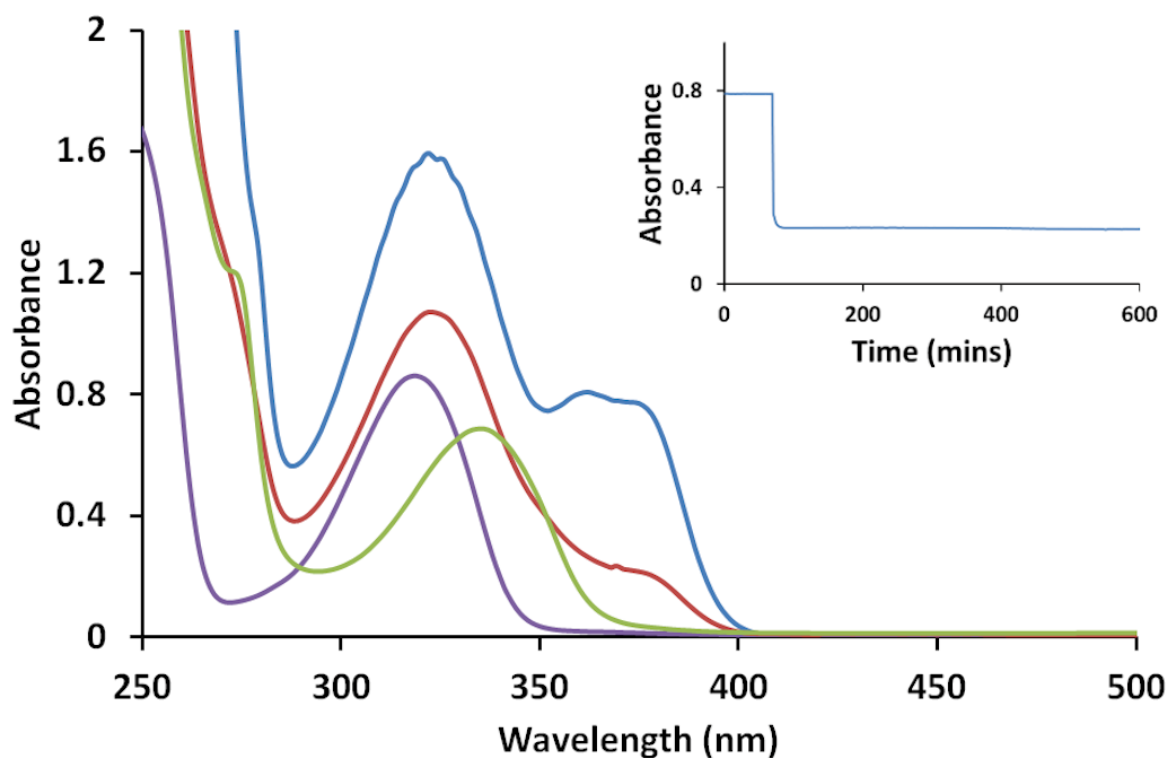
Spectrum for the products, reactants and reaction mixture for the reaction between 0.1mM BEP solution (2mL, 1 eq.) and 0.1mM 2-aminofluorene and triethylamine solution (2mL, 1 and 3 eq. respectively) (i) 0.1mM BEP, blue curve; (ii) 0.1mM 2-aminofluorene, red curve; (iii) product solution after 10hours, purple curve; (iv) 0.05mM pseudo base, green curve. (Inset) Plot of absorbance changes at 373nm against time.

5-[2-(Fluoranthen-3-ylamino)-ethyl]phenanthridinium bromide (**9**)



Spectrum for the products, reactants and reaction mixture for the reaction between 0.1mM BEP solution (2mL, 1 eq.) and 0.1mM 3-aminofluoranthene and triethylamine solution (2mL, 1 and 3 eq. respectively) (i) 0.1mM BEP, blue curve; (ii) 0.1mM 3-aminofluoranthene, red curve; (iii) product solution after 10hours, purple curve; (iv) 0.05mM pseudo base, green curve. (Inset) Plot of absorbance changes at 373nm against time.

1-(2-Ethynyl-phenyl)-2,3-dihydro-1*H*-imidazo[1,2-*f*]phenanthridin-4-ylum bromide (**10**)



Spectrum for the products, reactants and reaction mixture for the reaction between 0.2mM BEP solution (2mL, 1 eq.) and 0.2mM 2-ethynylamine and triethylamine solution (2mL, 1 and 3 eq. respectively) (i) 0.2mM BEP, blue curve; (ii) 0.2mM 2-ethynylamine, red curve; (iii) product solution after 10hours, purple curve; (iv) 0.01mM pseudo base, green curve. (Inset) Plot of absorbance changes at 373nm against time.