

Supplementary Information

Highly fluorescent complexes with 3-isocyanoperylene and *N*-(2,5-di-*tert*-butylphenyl)-9-isocyano-perylene-3,4-dicarboximide

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Fig. S1 Absorption spectra of PMI-NC and their complexes **5a**, **9a-12a**, recorded in CHCl₃ solution ($\sim 10^{-5}$ M) at room temperature

Fig. S2 Absorption spectra of Per-NC and their complexes **5b-11b**, recorded in CHCl₃ solution ($\sim 10^{-5}$ M) at room temperature

Fig. S3 Emission spectra of **11b** in different solvents (ca. 10^{-5} M) at room temperature.

Fig. S4 Schematic representation of main expected transition in the absorption spectra of PMIH and perylene.

Table S1 Calculated absorption parameters (wavelengths in nm and their intensities) for R-X (R = PMI and Per) compounds in gas phase and chloroform solution.

Table S2 Calculated absorption peaks for [M(CO)₅(CNR)] (M = Cr, Mo, W; R = PMI, Per).

Fig. S5 ¹H and ¹⁹F NMR spectra

Fig. S6 IR spectra

Fig. S7 Fluorescence decays in dichloromethane, at room temperature

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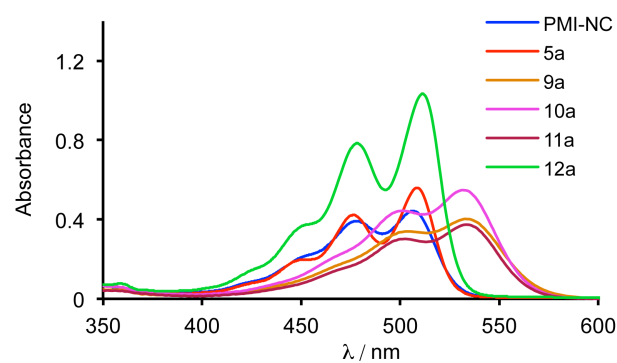


Figure S1. Absorption spectra of PMI-NC and their complexes **5a**, **9a-12a**, recorded in CHCl_3 solution ($\sim 10^{-5}$ M) at room temperature

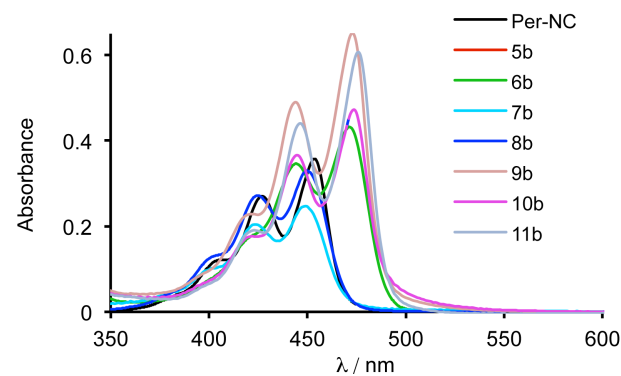


Figure S2. Absorption spectra of Per-NC and their complexes **5b-11b**, recorded in CHCl_3 solution ($\sim 10^{-5}$ M) at room temperature

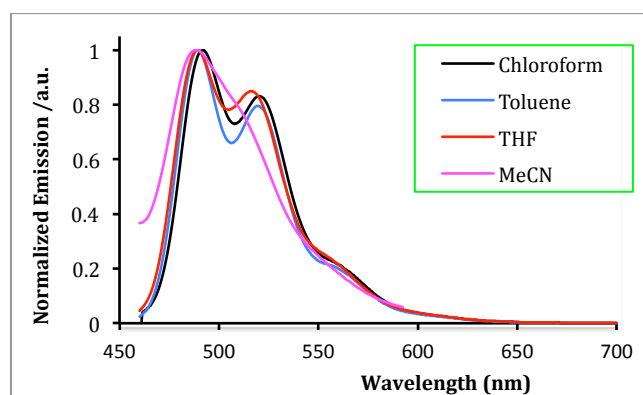


Fig. S3 Emission spectra of **11b** in different solvents (ca. 10^{-5} M) at room temperature.

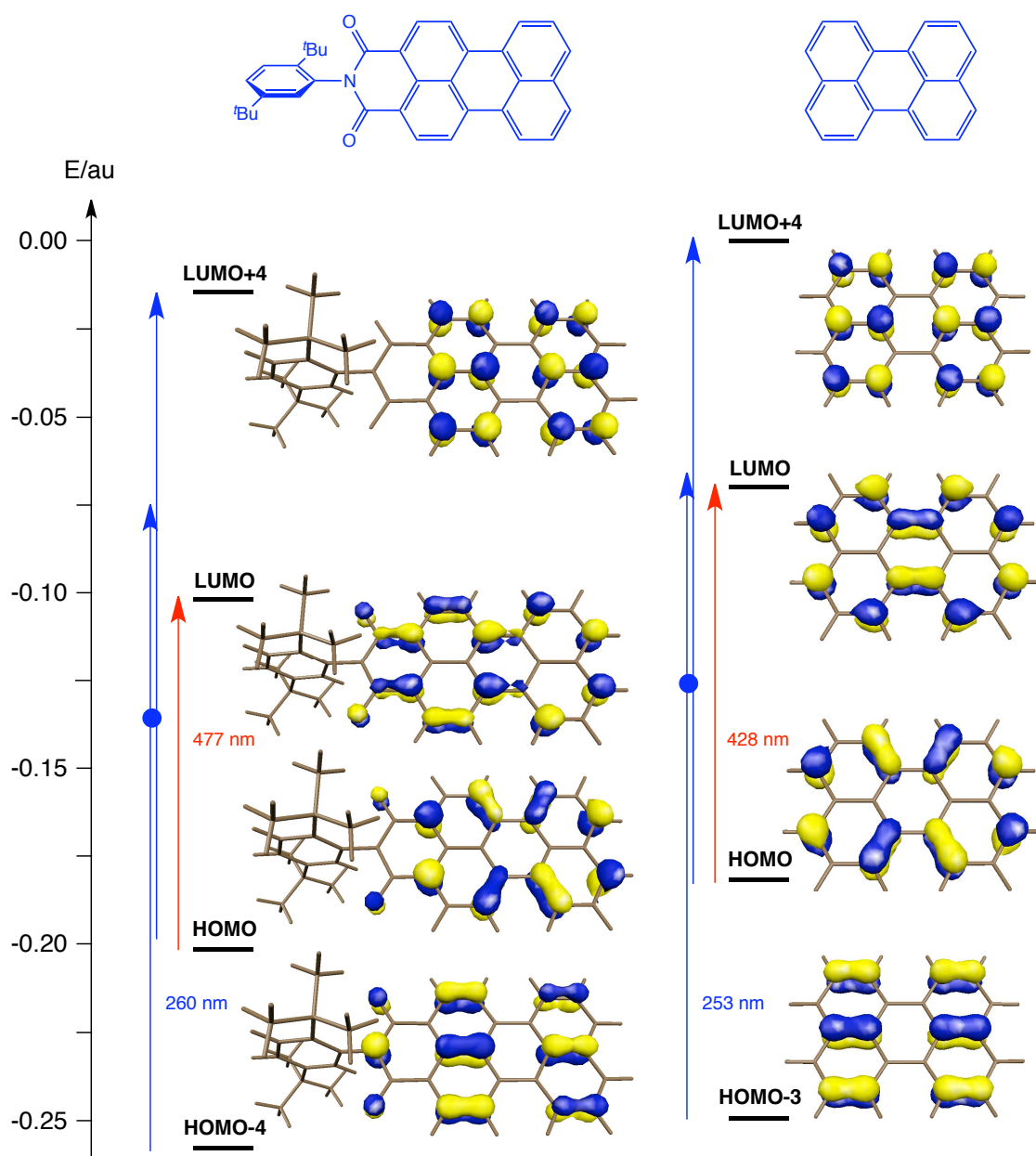


Fig. S4 Schematic representation of main expected transition in the absorption spectra of PMIH and perylene.

Table S1. Calculated absorption parameters (wavelengths in nm, oscillator strength (f), and coefficients of the main contributions of the orbitals [in brackets]) for R-X (R = PMI and Per) compounds in gas phase and chloroform solution.

(a) Organics

λ (f)	Solvent	H	NC
PMI-X	Gas phase	477 (0.61) [0.62]	490 (0.69) [0.61]
		260 (0.09), 259 (0.11) [0.48, 0.38],[0.44,0.40]	261 (0.19) [0.55,0.23]
	CHCl ₃	500 (0.77) [0.63]	512 (0.86) [0.63]
		262 (0.26) [0.55,0.15]	263 (0.22) [0.51,0.30]
Per-X	Gas phase	428 (0.36) [0.62]	446 (0.44) [0.62]
		253 (0.30) [0.48,0.36]	257 (0.28) [0.48,0.25]
	CHCl ₃	442 (0.48) [0.63]	465 (0.58) [0.63]
		257 (0.51) [0.50,0.38]	260 (0.44) [0.51,0.22]

^a Coefficients are [$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$] for first transition in all cases, and [$\pi_{HOMO} \rightarrow \pi^*$, $\pi \rightarrow \pi^*_{LUMO}$] for second band of perylene systems.

(b) Chromium complexes

λ (f)	[(PMI-NC)Cr(CO) ₅]	[(PerNC)Cr(CO) ₅]
Gas phase	518 (0.97)	468 (0.70)
	$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})_L$ [0.70]	$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})_L$ [0.70]
	281 (0.08)	259 (0.15)
	$\pi(\text{CO}) + \pi d \rightarrow \pi^*(\text{CO})_{eq}$ [0.52]	$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per})$ [0.42]
	$\pi(\text{CO}) \rightarrow \pi^*(\text{PMI-NC})$ [0.33]	$\pi d \rightarrow \pi^*(\text{Per})$ [0.26]
	266 (0.09)	
CHCl ₃	$\pi(\text{CO}) + \pi d \rightarrow \pi^*(\text{PMI-NC})$ [0.54]	
	$\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI})$ [0.24]	
	536 (1.14)	482 (0.84)
	$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})_L$ [0.70]	$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})_L$ [0.70]
	282 (0.10)	265 (0.19)
	$\pi(\text{CO}) + \pi d \rightarrow \pi^*(\text{CO})_{eq}$ [0.54]	$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per})$ [0.35]
	$\pi(\text{CO}) + \pi d \rightarrow \pi^*(\text{PMI-NC})$ [0.31]	$\pi d \rightarrow \pi^*(\text{CO})_{eq}$ [0.31]
	264 (0.12)	$\pi d \rightarrow \pi^*(\text{CO})_{eq}$ [0.24]
	$\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI})$ [0.38]	262 (0.22)
	$\pi(\text{CO}) + \pi d \rightarrow \pi^*(\text{CO})_{eq}$ [0.35]	$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per})$ [0.37]
		$\pi d \rightarrow \pi^*(\text{CO})_{eq}$ [0.28]
		$\pi d \rightarrow \pi^*(\text{NC})$ [0.23]

Annotation for the involved orbitals:

- $\pi(\text{PMI})$ and $\pi(\text{Per})$ indicate generic occupied orbitals as well as $\pi^*(\text{PMI})$, and $\pi^*(\text{Per})$ are empty ones. Since all of these orbitals are of type π , only H and L are emphasized. Orbital contribution on the nitrile group included when remarkable.
- $\pi(\text{Ph})$ and $\pi^*(\text{Ph})$ are occupied and empty orbitals centered in the phenylic diimido substituent.
- Other fragments such as C₆F₅ or CO are also used to designate centered π orbitals.
- Other d -orbitals are generally written as πd .

(c) Gold complexes

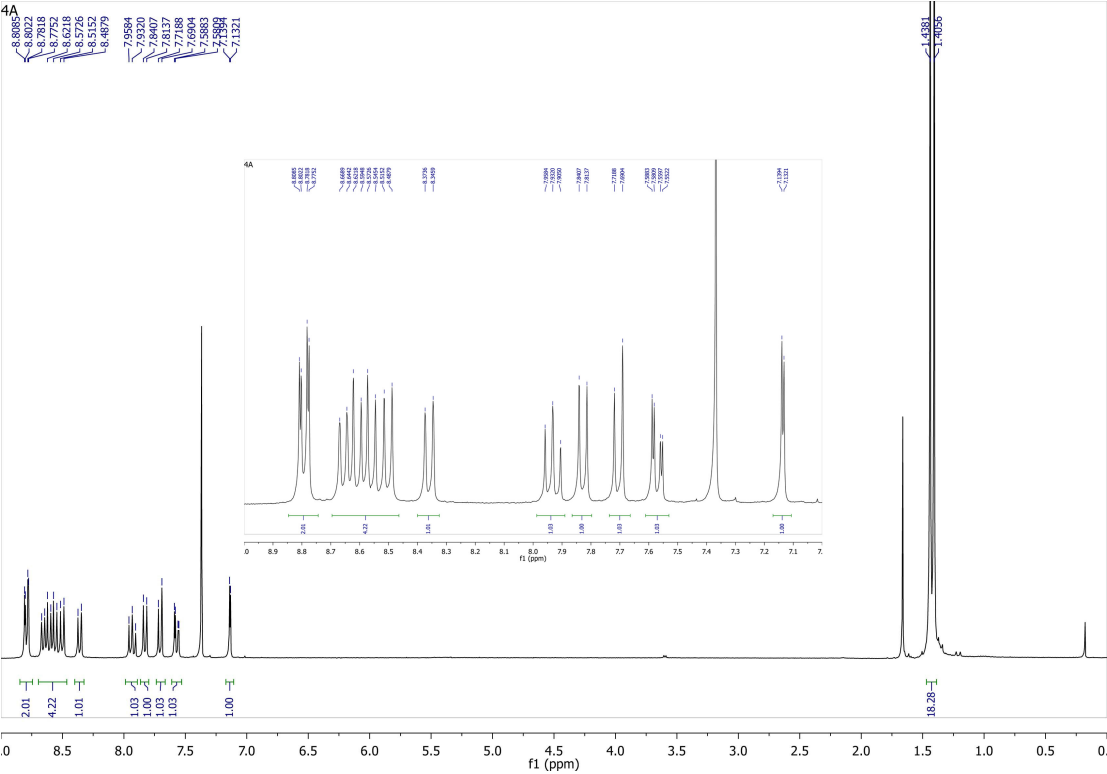
λ (f)	$[(\text{PMI-NC})\text{Au}(\text{C}_6\text{F}_5)]$	$[(\text{PerNC})\text{Au}(\text{C}_6\text{F}_5)]$
Gas phase	519 (0.79) $\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})_L$ [0.68] 481 (0.15) $\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.64] 325 (0.12) $\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{PMI-NC})$ [0.63] 269 (0.10) $\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})$ [0.64] 264 (0.12) $\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI})$ [0.48] $\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI-NC})$ [0.30]	474 (0.69) $\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})_L$ [0.70] 296 (0.25) $\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{Per-NC})$ [0.53] 262 (0.19) $\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})$ [0.49] $\pi(\text{Per}) \rightarrow \pi^*(\text{Per-NC})_L$ [0.26]
CHCl_3	527 (1.08) $\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})_L$ [0.71] 332 (0.08) $\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.46] $\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.37] 292 (0.16) $\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI})$ [0.40] $\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.37] 288 (0.10) $\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.59] $\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI})$ [0.27] 264 (0.15) $\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})$ [0.53] $\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.34]	493 (0.79) $\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})_L$ [0.70] 297 (0.14) $\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{Per-NC})$ [0.49] 266 (0.30) $\pi(\text{Per}) \rightarrow \pi^*(\text{Per-NC})_L$ [0.44] $\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})$ [0.39] 262 (0.23) $\pi(\text{Per}) \rightarrow \pi^*(\text{Per-NC})_L$ [0.52] $\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})$ [0.33]

Table S2. Calculated absorption peaks for [M(CO)₅(CNR)] (M = Cr, Mo, W; R = PMI, Per).

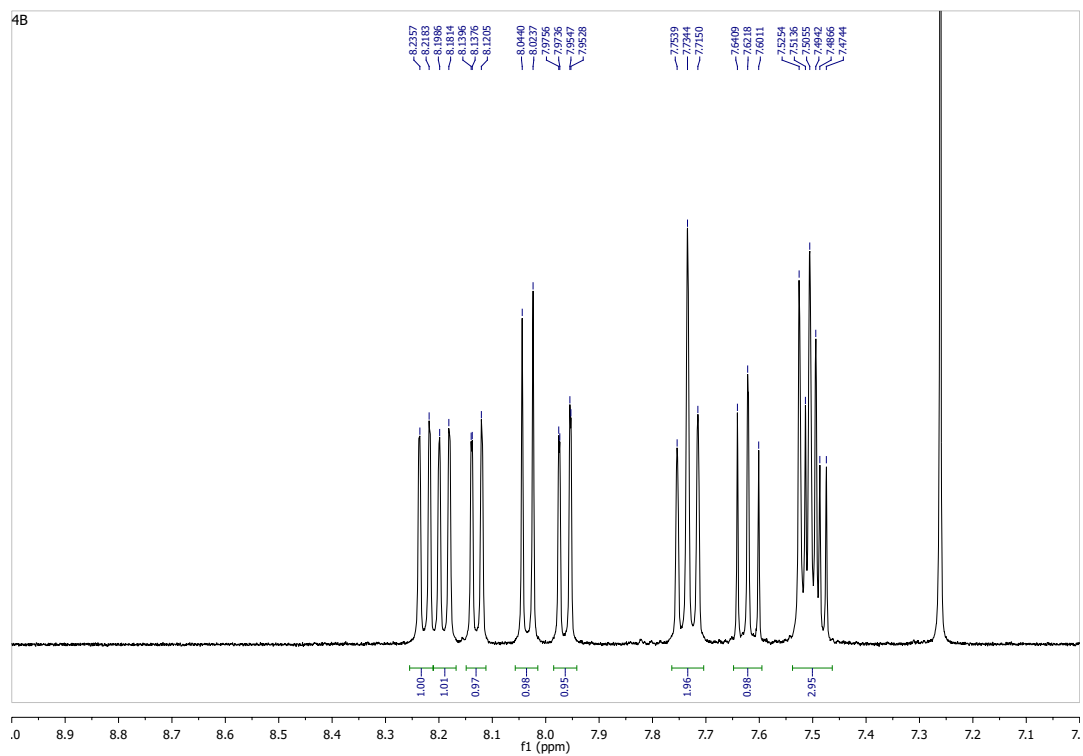
R-X	Cr(CO) ₅		Mo(CO) ₅		W(CO) ₅	
	Gas phase	CHCl ₃	Gas phase	CHCl ₃	Gas phase	CHCl ₃
PMI-NC-X λ (f)	518 (0.97)	536 (1.14)	526 (0.99)	542 (1.19)	530 (1.02)	547 (1.22)
	281 (0.08)	282 (0.10)	299 (0.16)	300 (0.16)	303 (0.12)	305 (0.14)
	266 (0.09)	264 (0.12)	266 (0.07)	282 (0.07)	269 (0.12)	268 (0.20)
			264 (0.06)	267 (0.11)	265 (0.07)	266 (0.10)
				266 (0.13)		
Per-NC-X λ (f)	468 (0.70)	482 (0.84)	474 (0.75)	487 (0.90)	477 (0.78)	492 (0.93)
	259 (0.15)	265 (0.19)	285 (0.11)	286 (0.10)	286 (0.10)	287 (0.09)
		262 (0.22)	261 (0.24)	264 (0.37)	262 (0.22)	265 (0.34)
			256 (0.08)	259 (0.05)	259 (0.07)	

Fig. S5 ¹H and ¹⁹F NMR spectra

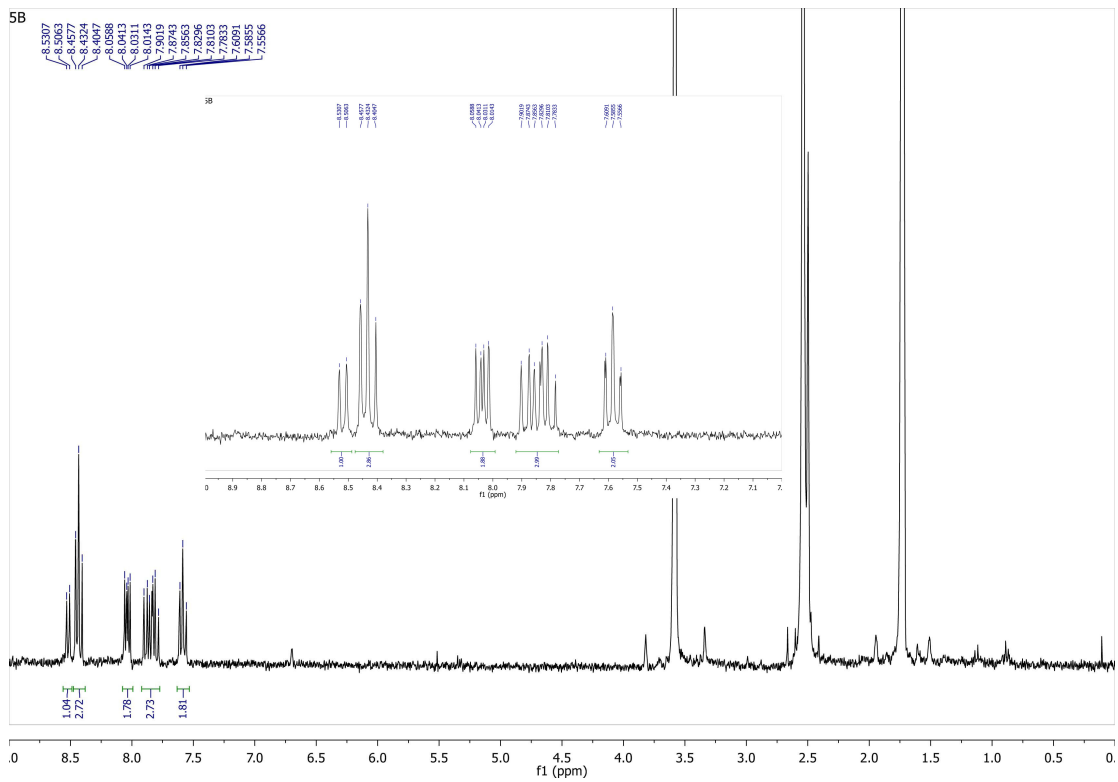
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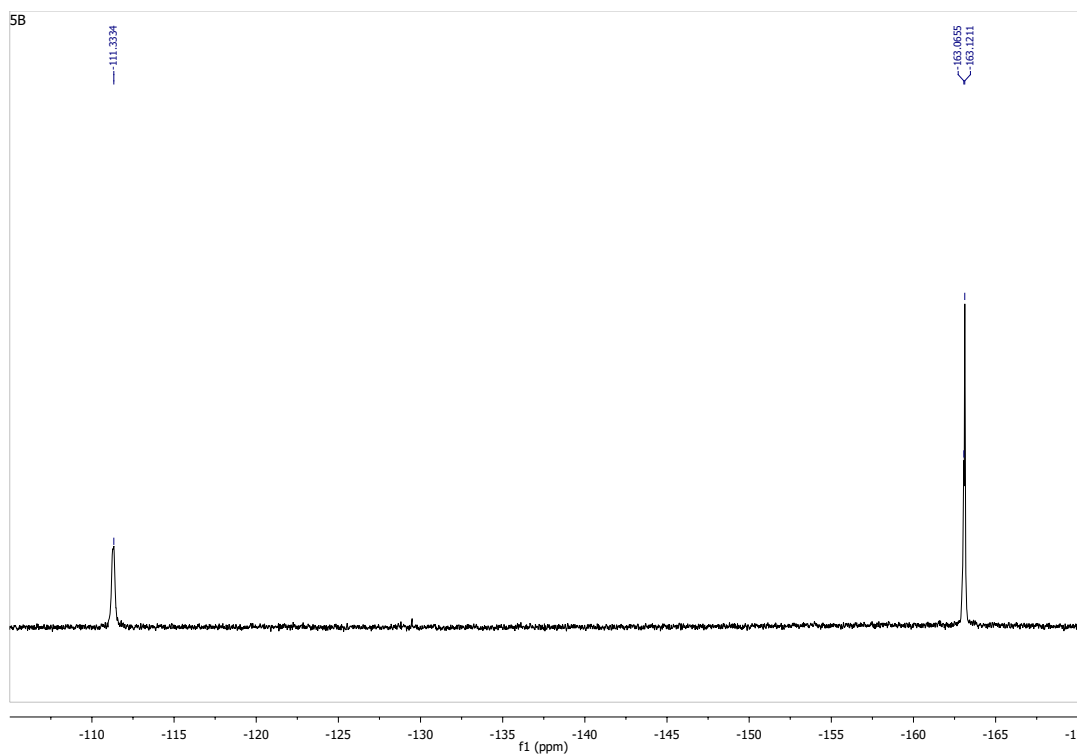


4b

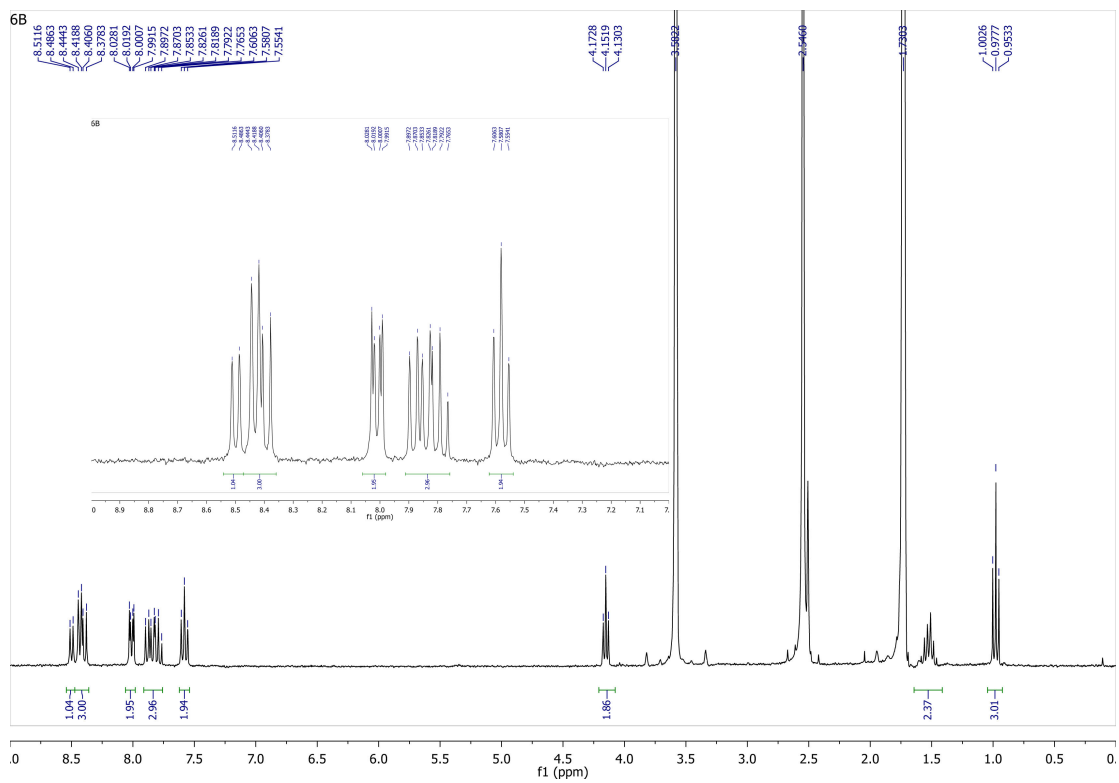


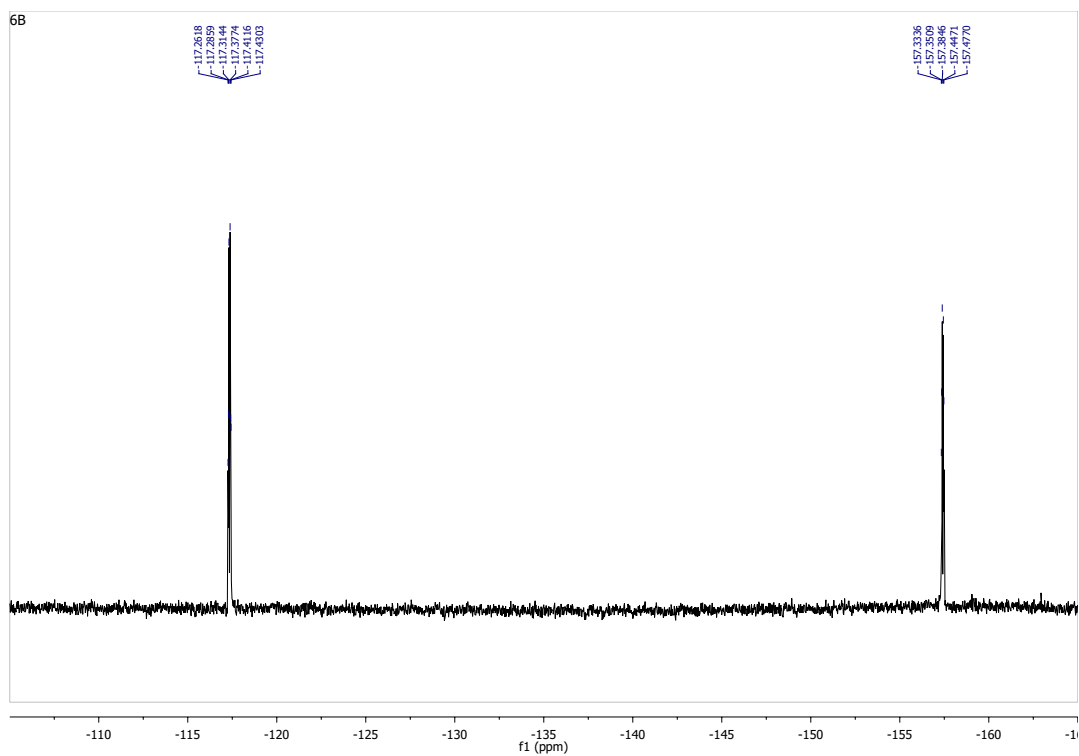
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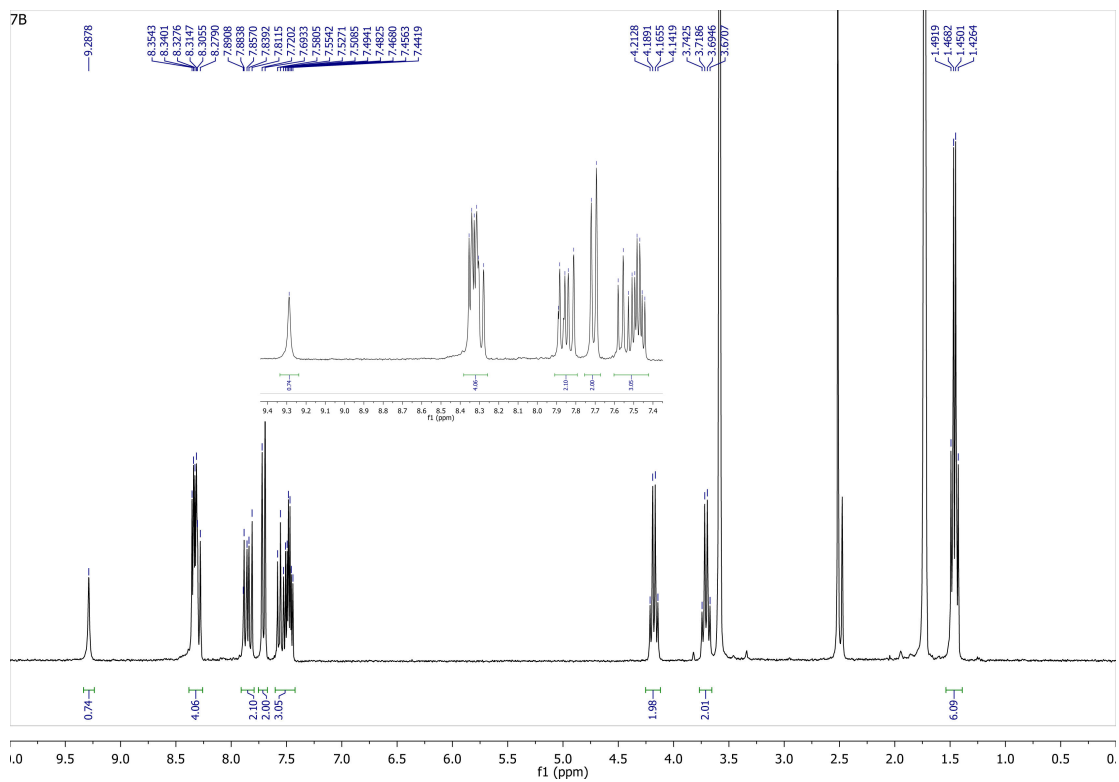


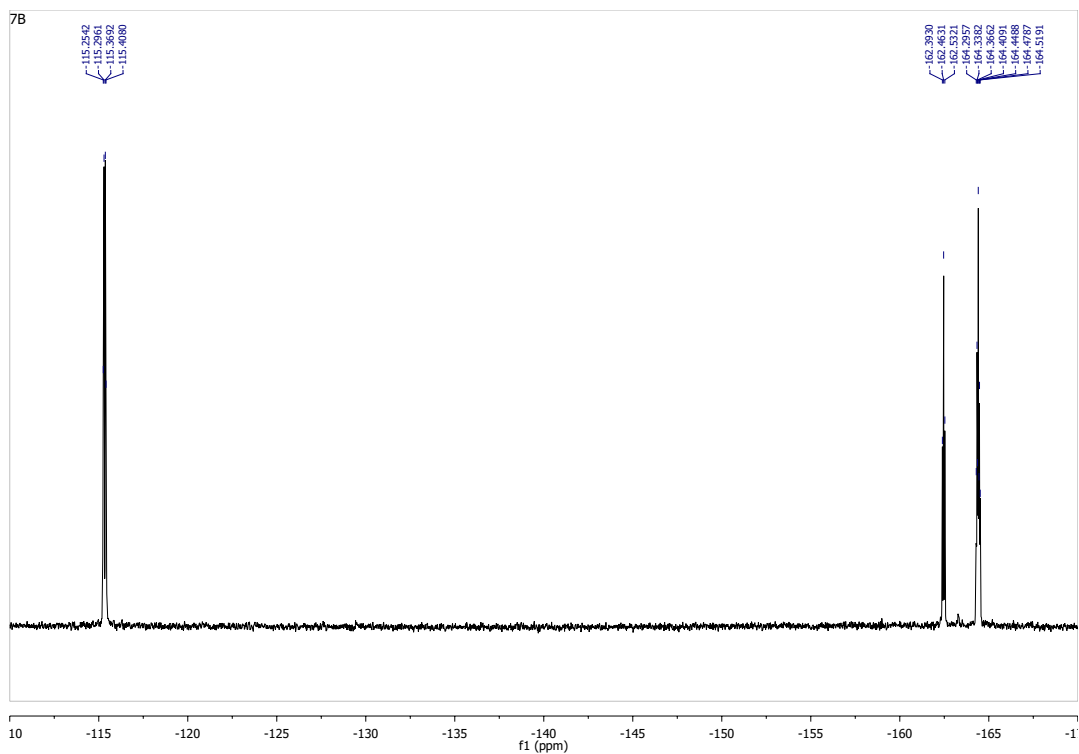
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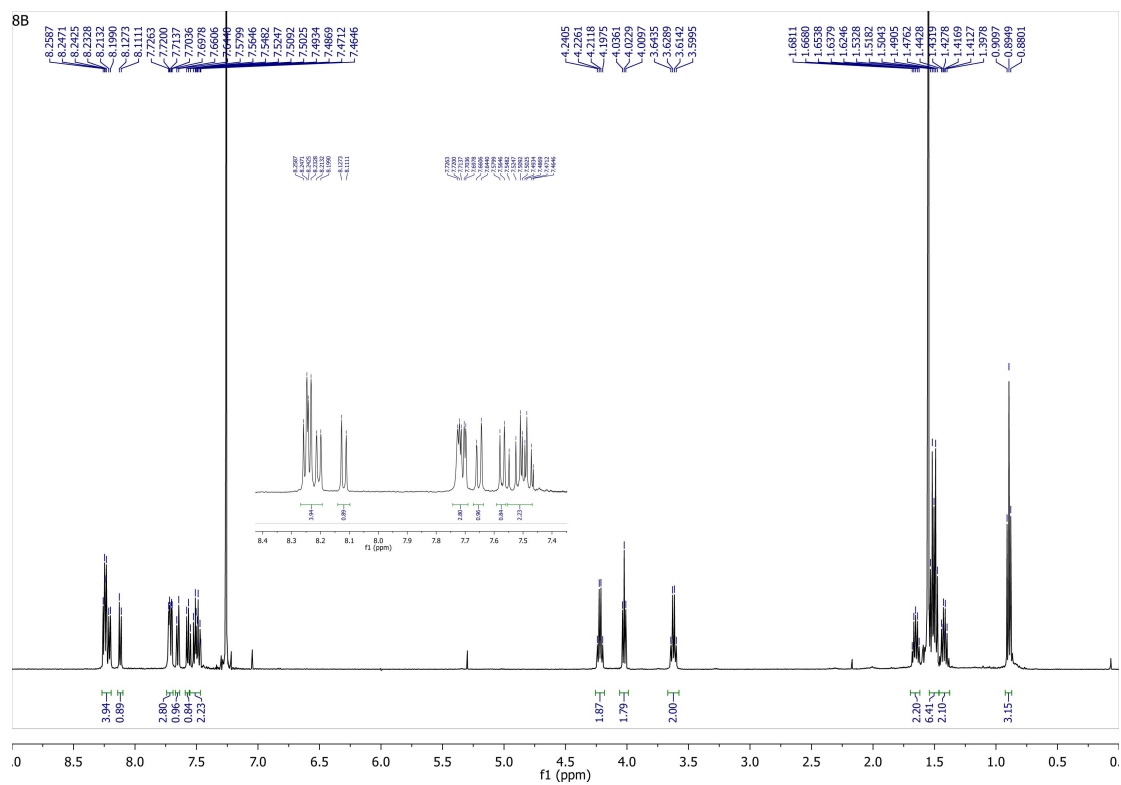


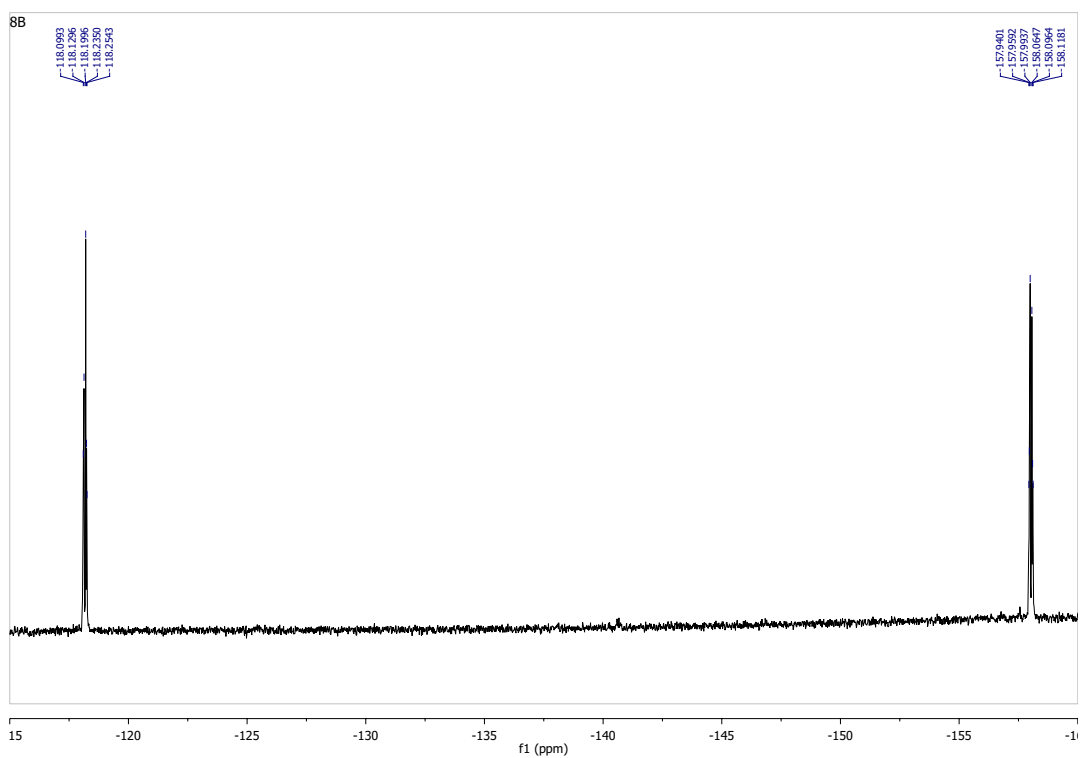
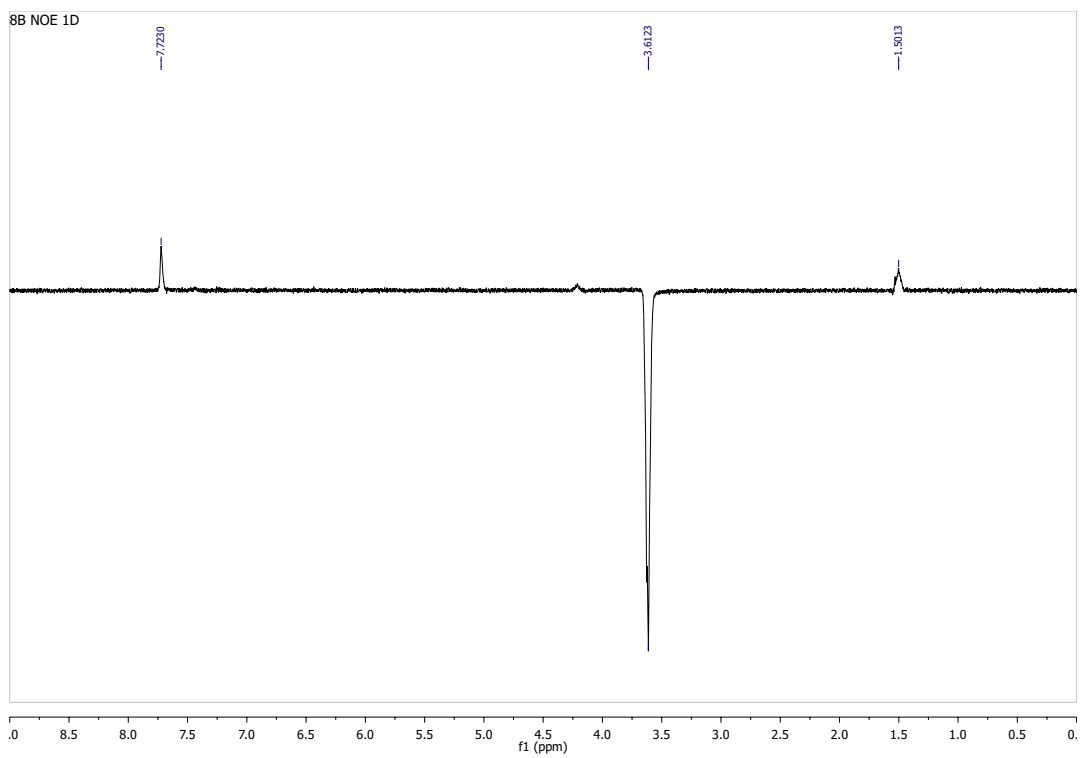
7b



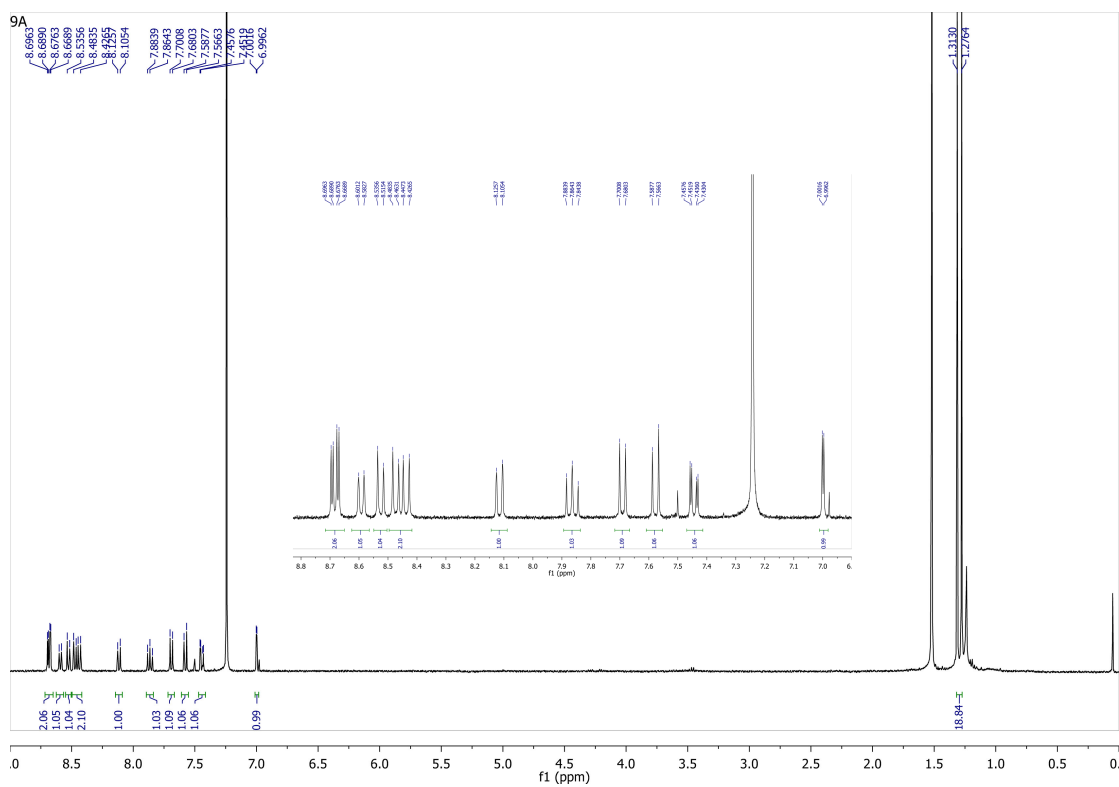


8b

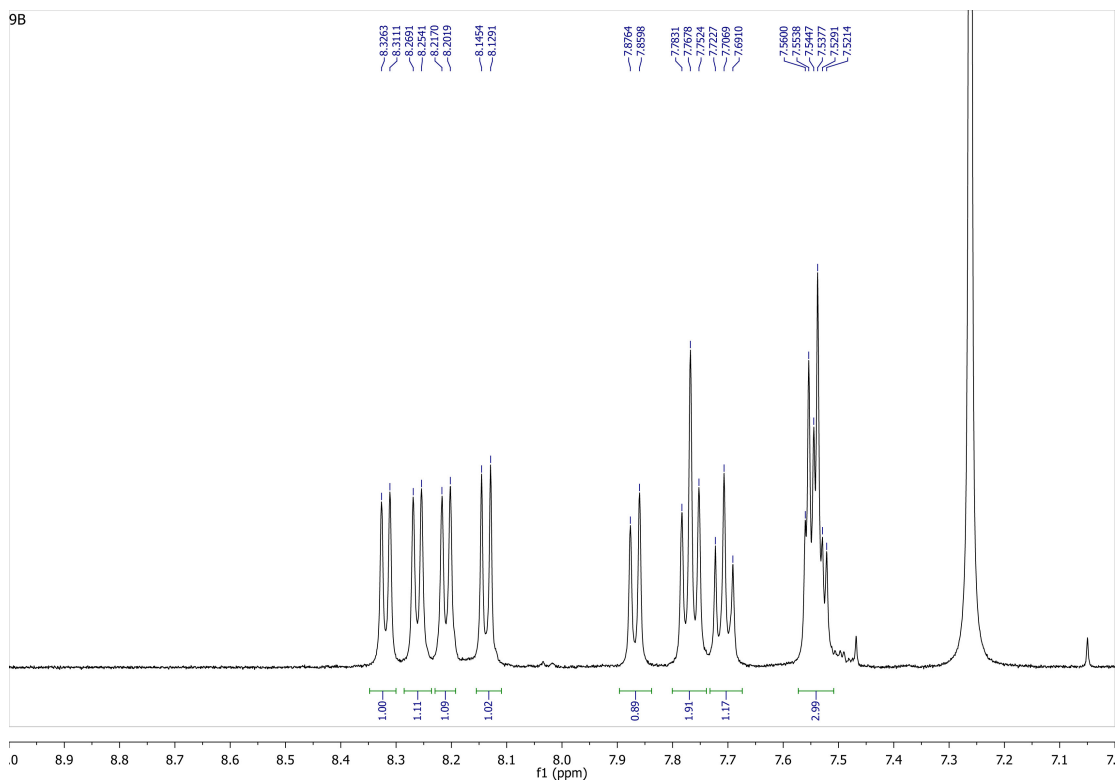




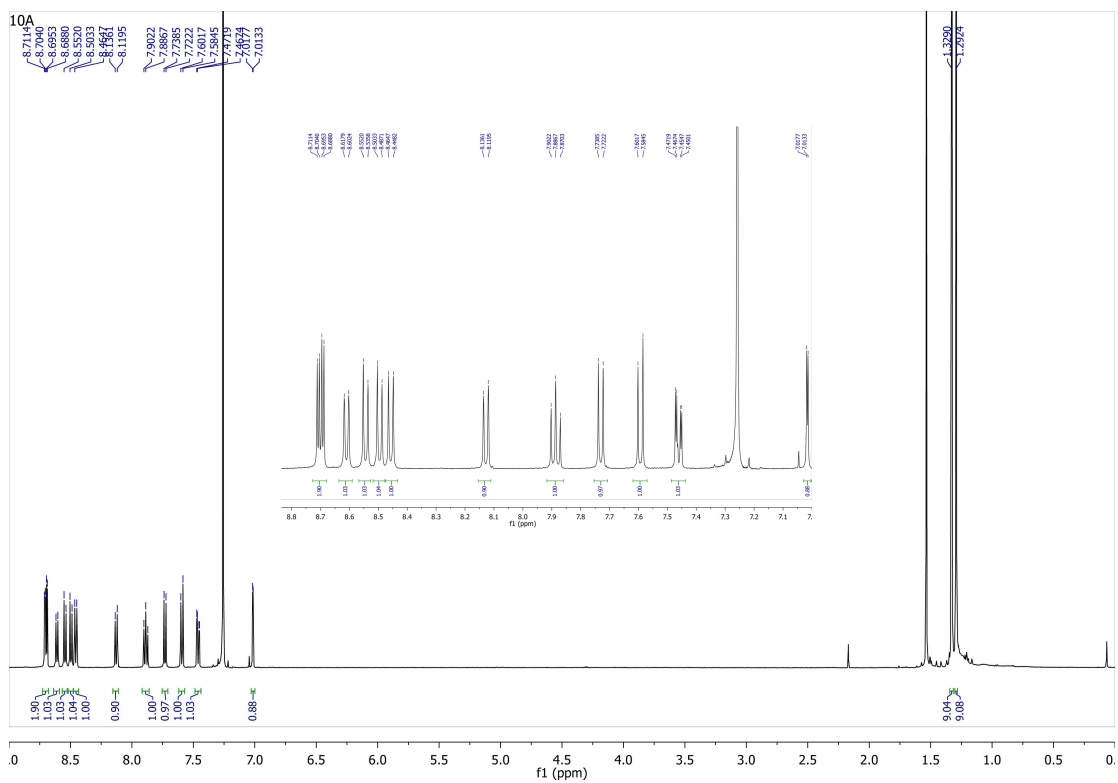
9a



9b



10a



9b

¹H NMR spectrum (CDCl₃) of compound **9b**. The x-axis represents the chemical shift in ppm, ranging from 7.0 to 9.0. The spectrum shows several multiplets in the aromatic region and a reference peak at 7.26 ppm.

Chemical shifts (ppm) and integration values are listed below the spectrum:

Chemical Shift (ppm)	Integration
8.3263	1.00
8.3111	1.11
8.2691	1.09
8.2541	1.02
8.2170	
8.2015	
8.1454	
8.1291	
7.8764	0.89
7.8598	
7.7831	1.91
7.7685	
7.7594	
7.7227	1.17
7.7069	
7.6910	
7.5690	2.99
7.5598	
7.5447	
7.5377	
7.5291	
7.5214	
7.26	

11A

¹H NMR spectrum (CDCl₃) of compound 11A. The spectrum shows peaks from 0 to 10 ppm. An inset shows a zoomed-in view of the aromatic region from 7.0 to 8.8 ppm. Integration values are provided below the peaks.

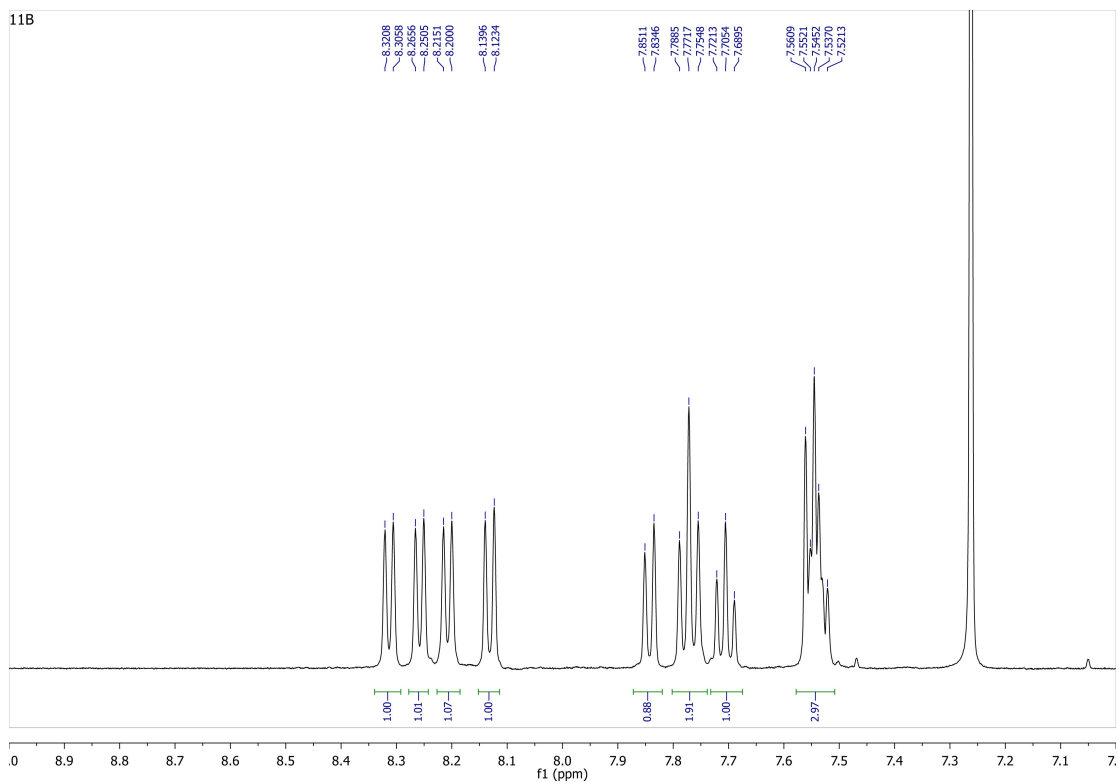
Peak Data (ppm):

- 8.71058, 8.7031, 8.6950, 8.6872, 8.5905, 8.5900, 8.5825, 8.1095, 7.9011, 7.8850, 7.7321, 7.7255, 7.6025, 7.5852, 7.4730, 7.4605, 7.0162, 7.0147
- 7.3289, 7.2931

Integration Values:

- 2.00, 1.05, 1.10, 1.10, 0.98, 1.06, 1.04, 1.05, 1.05, 0.94, 18.80

11b



12a

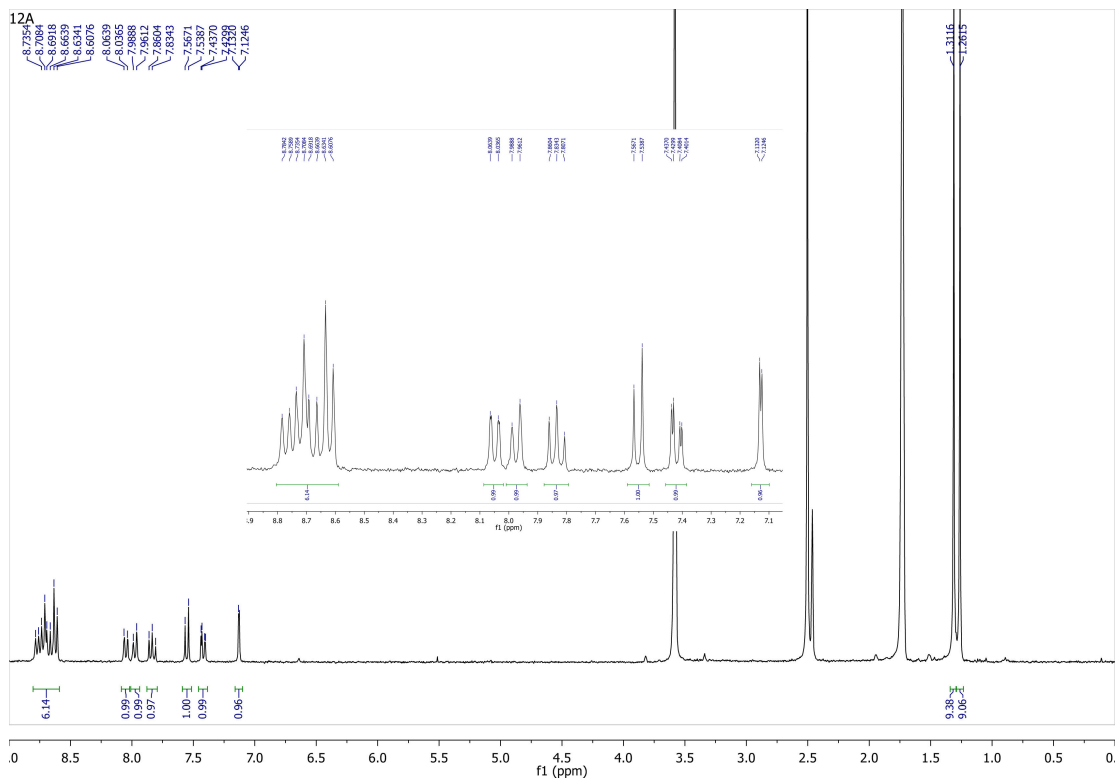
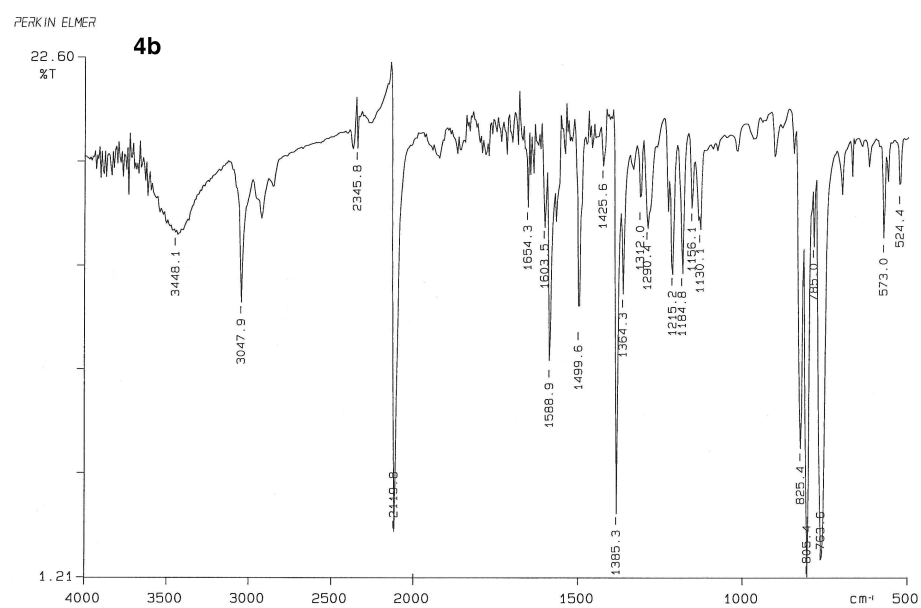
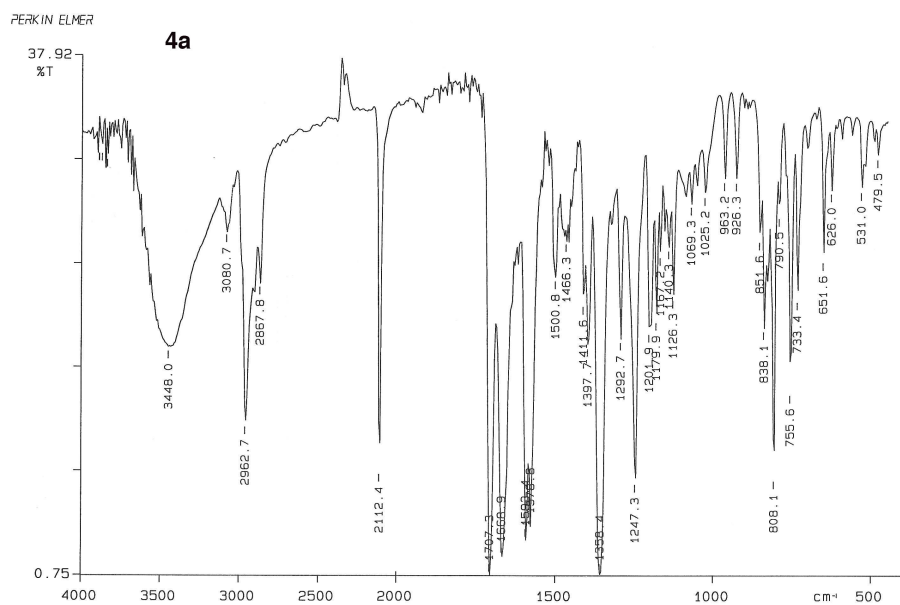
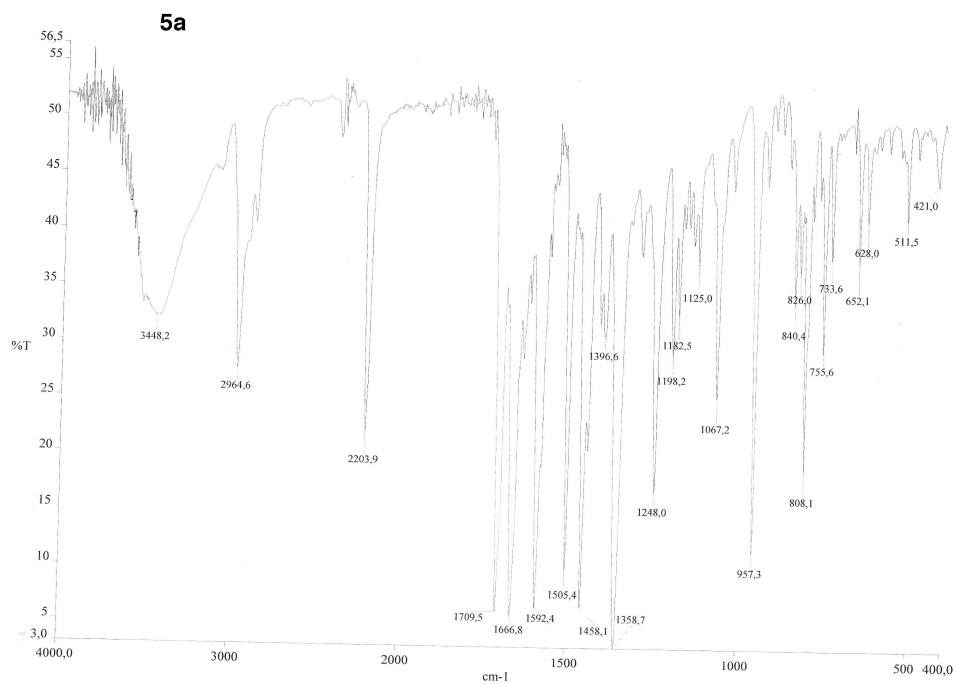
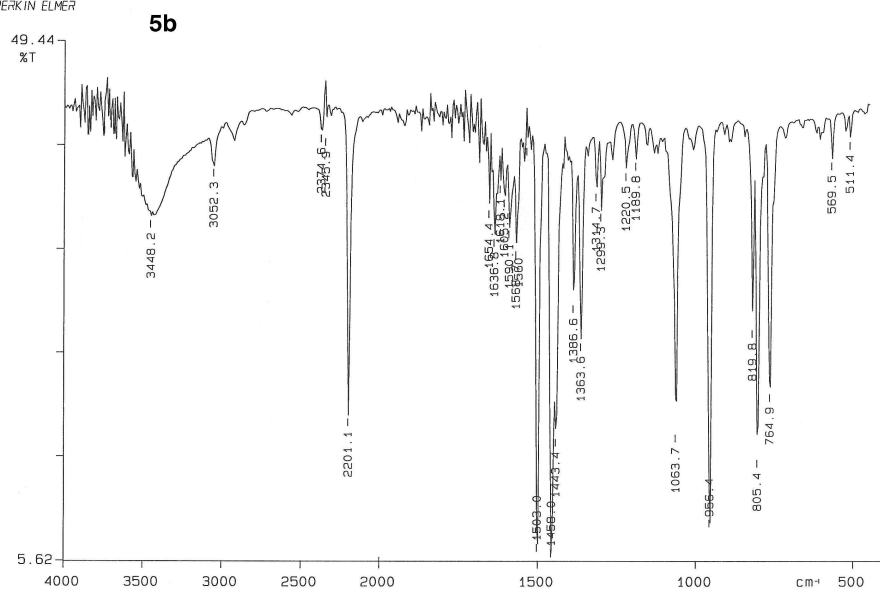


Fig. S6. IR spectra

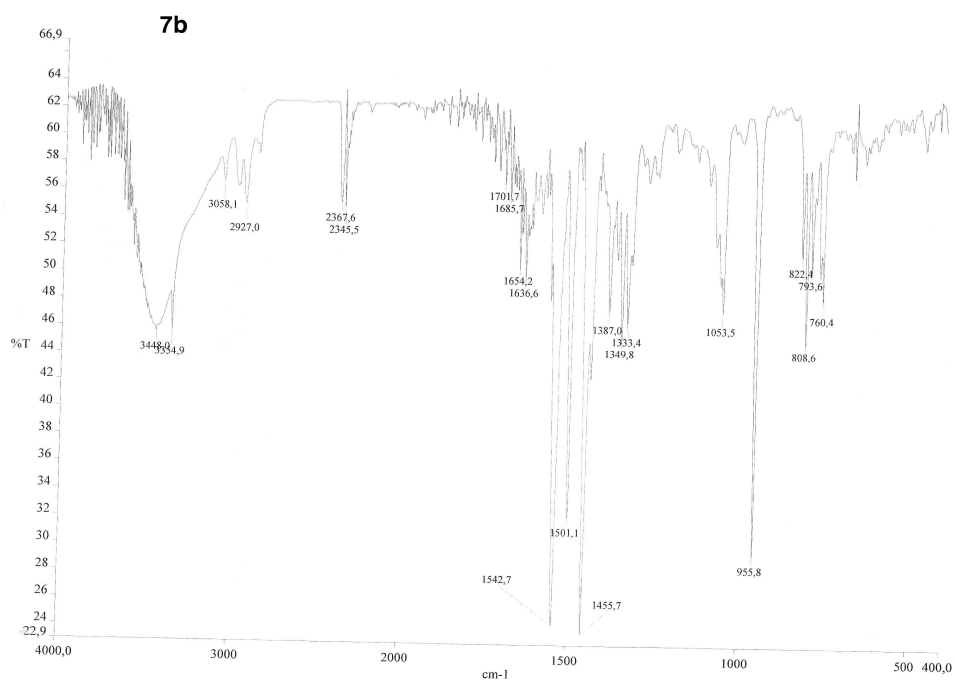
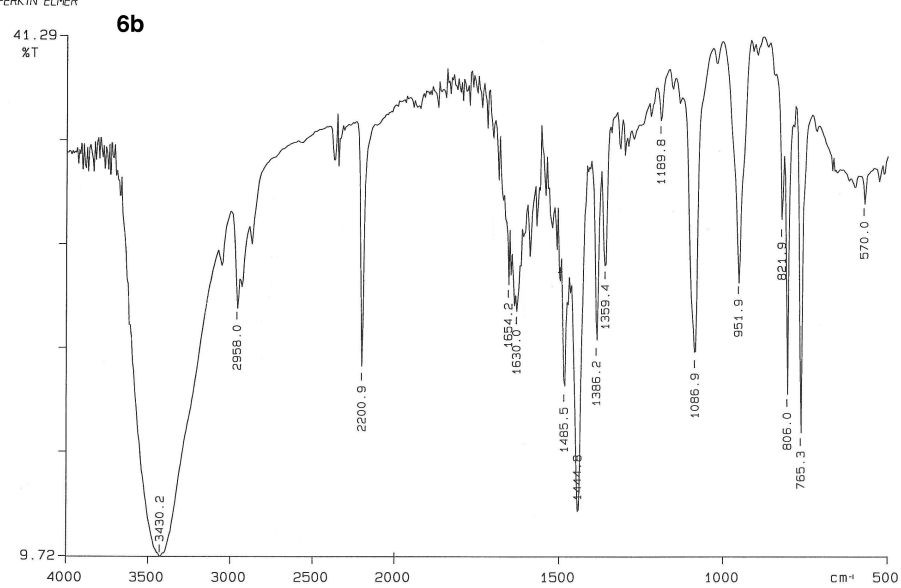




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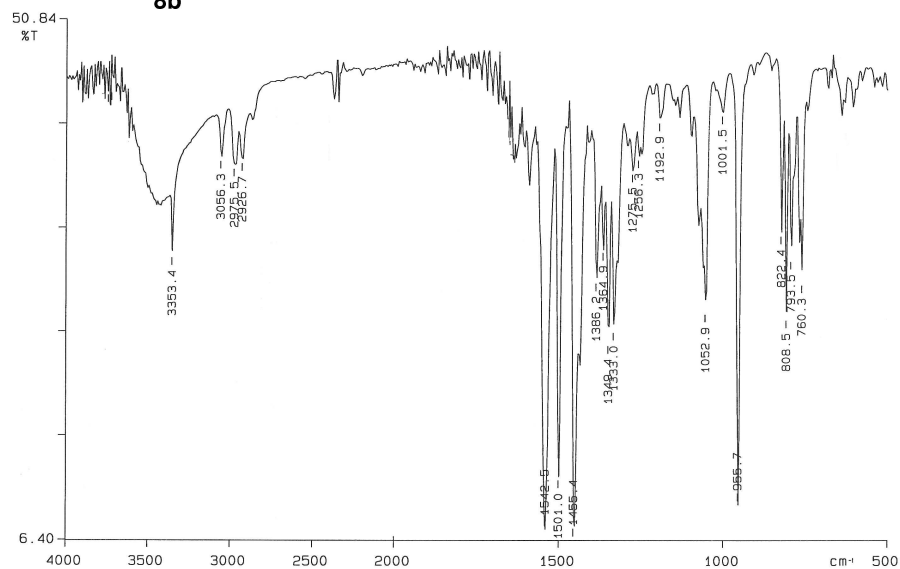


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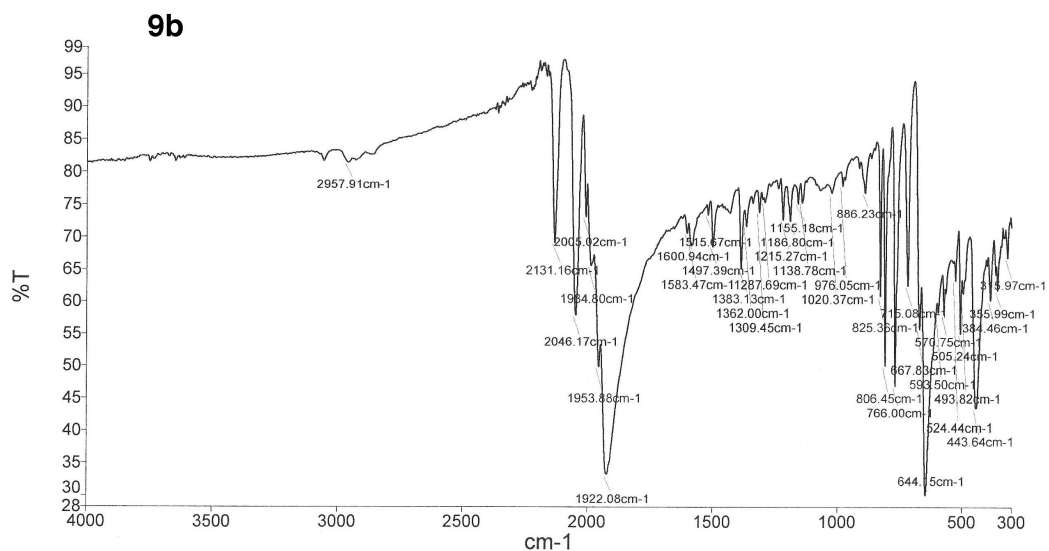


PERKIN ELMER

8b

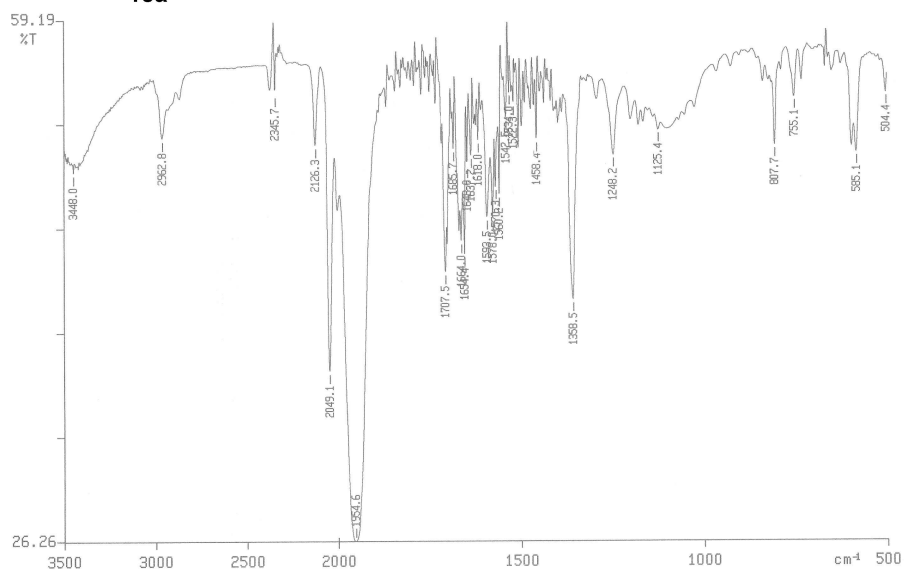


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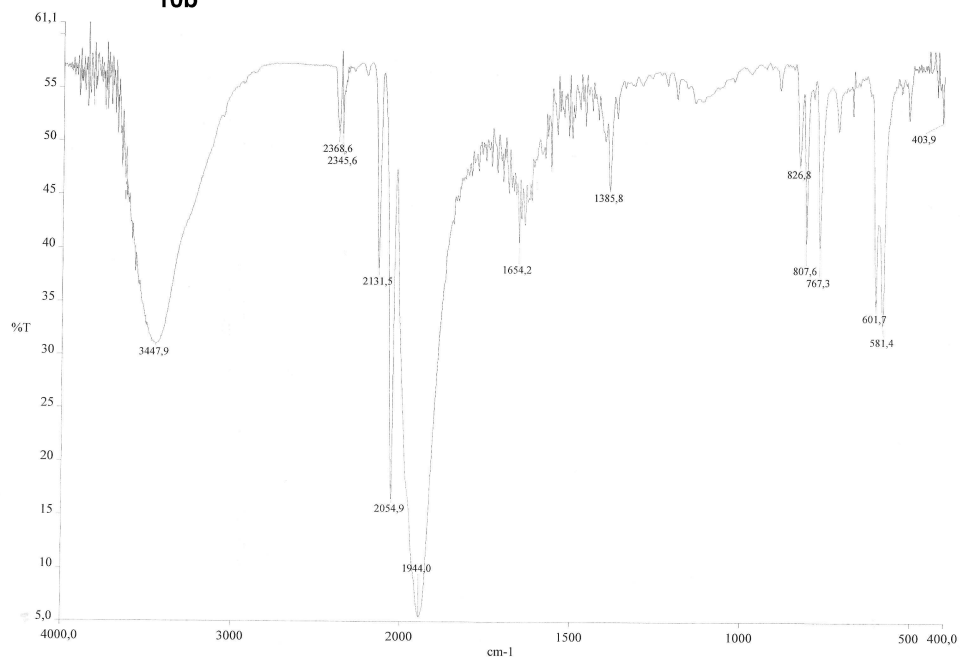


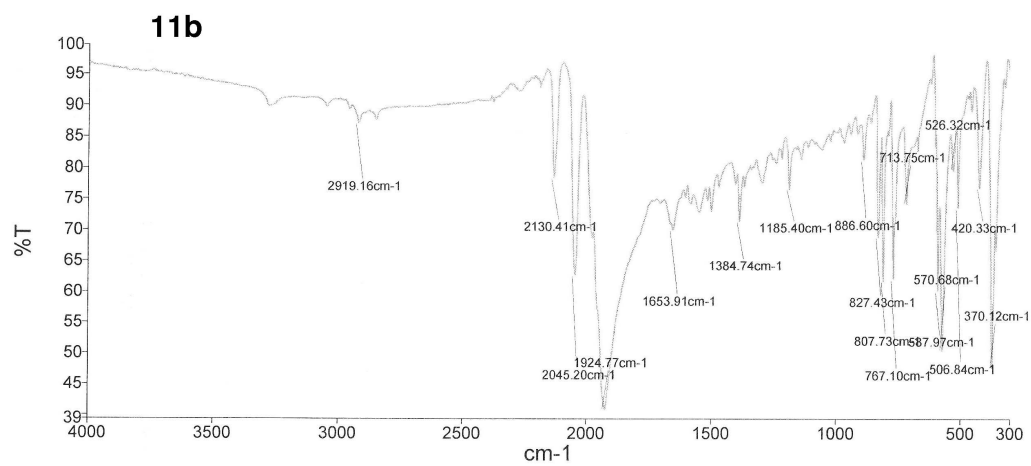
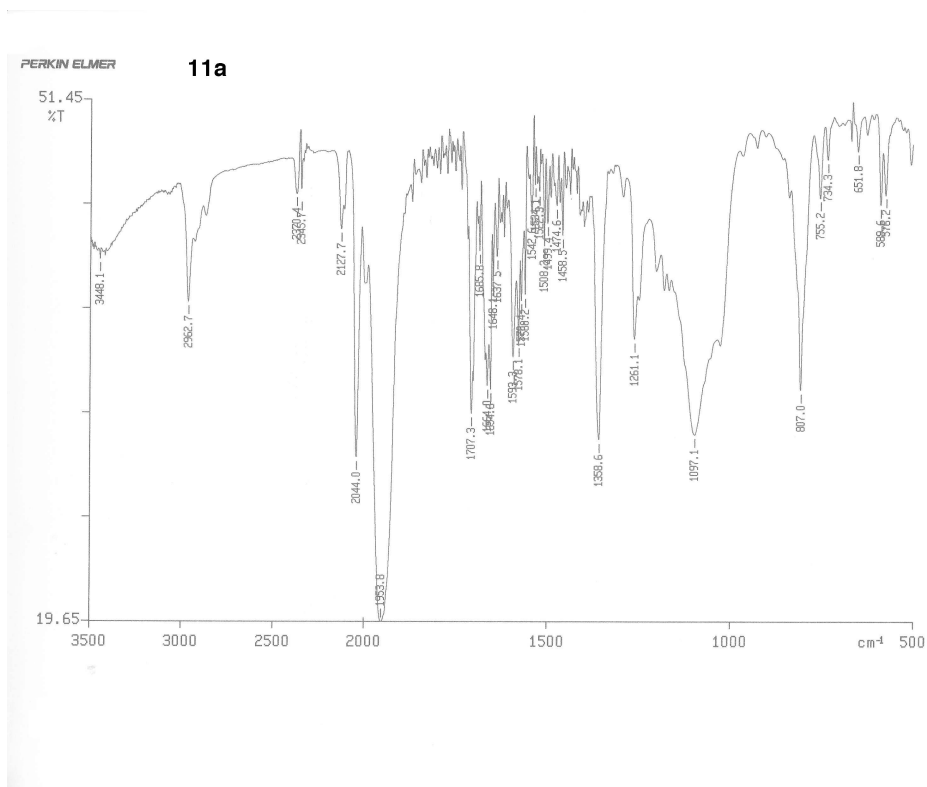
PERKIN ELMER

10a



10b





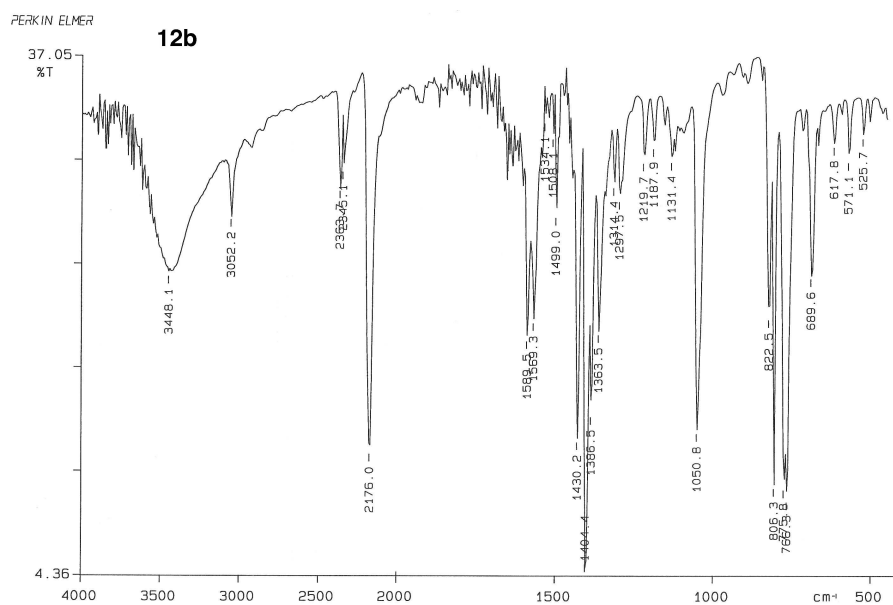
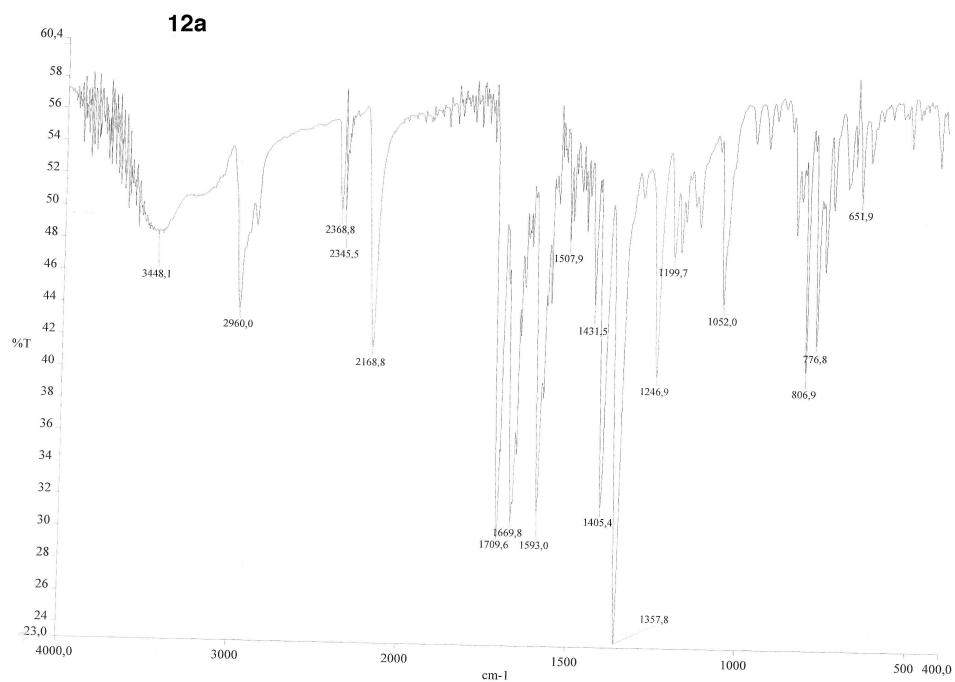


Fig. S7. Fluorescence decays in dichloromethane, at room temperature

Mono-exponential and bi-exponential fluorescence decay models were fitted to each decay. Eqn (1) describes the mono-exponential decay model:

$$I(t) = I_0 \cdot \exp(-t/\tau) \quad (1)$$

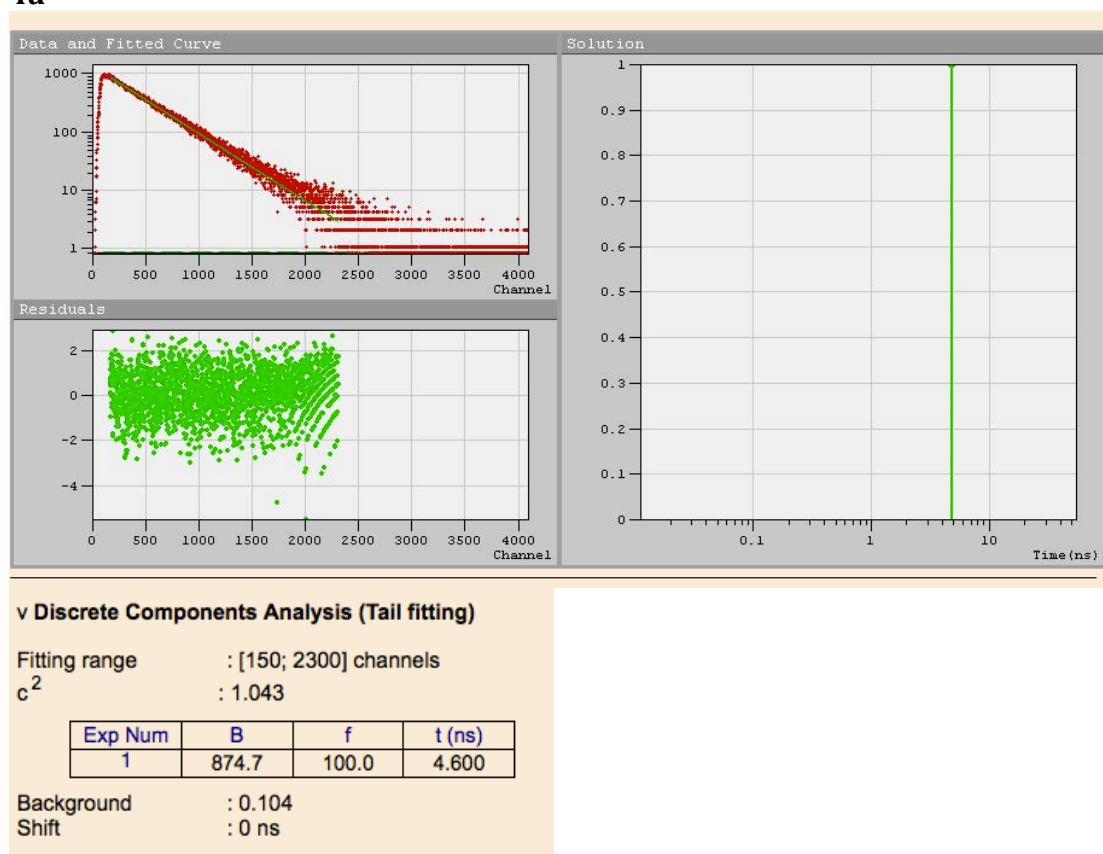
where I_0 is the relative intensity, t is the time and τ is the fluorescence lifetime, both expressed in ns. The bi-exponential decay model is expressed by Equation (2) as:

$$I(t) = A + B_1 \cdot \exp(-t/\tau_1) + B_2 \cdot \exp(-t/\tau_2) \quad (2)$$

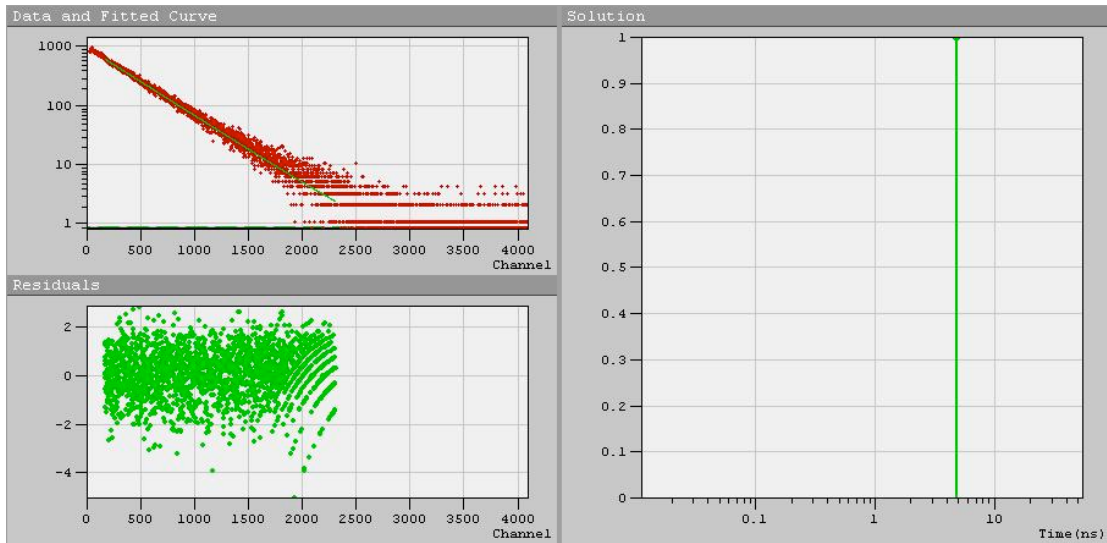
where B_1 and B_2 are the relative intensities associated with two lifetimes, τ_1 and τ_2 , respectively.

Mono-exponential models are normally used to fit fluorescence decay. Bi-exponential fits may be more appropriate for samples containing non-linear decays. Fitting was done using FAST software from Edinburgh Instruments by a least-squares algorithm using a reconvolution approach. In this method, convolution of Equation (1) or (2) with the instrumental response function (IRF) is done prior to evaluating the goodness of fit with a weighted χ^2 parameter.

4a



4b



v Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2300] channels

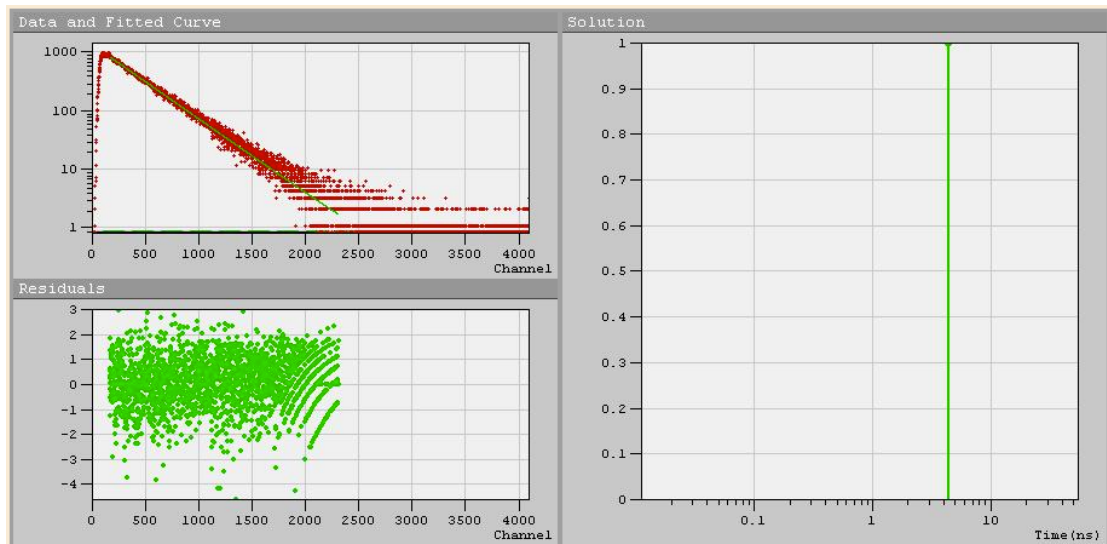
c^2 : 1.013

Exp Num	B	f	t (ns)
1	618.6	100.0	4.626

Background : 0.288

Shift : 0 ns

5a



v Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2300] channels

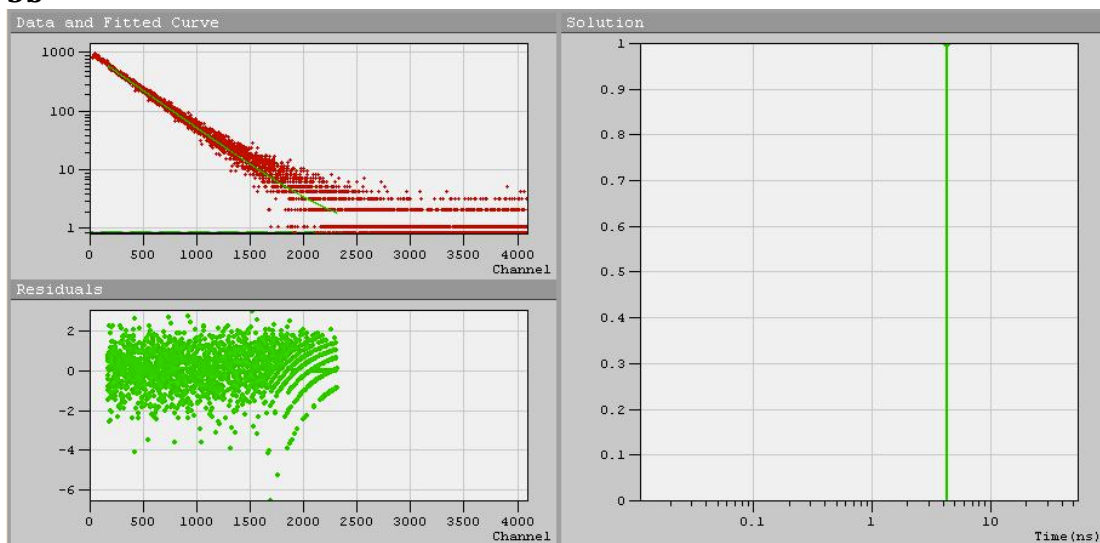
c^2 : 1.027

Exp Num	B	f	t (ns)
1	834.6	100.0	4.188

Background : 0.138

Shift : 0 ns

5b



v Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2300] channels

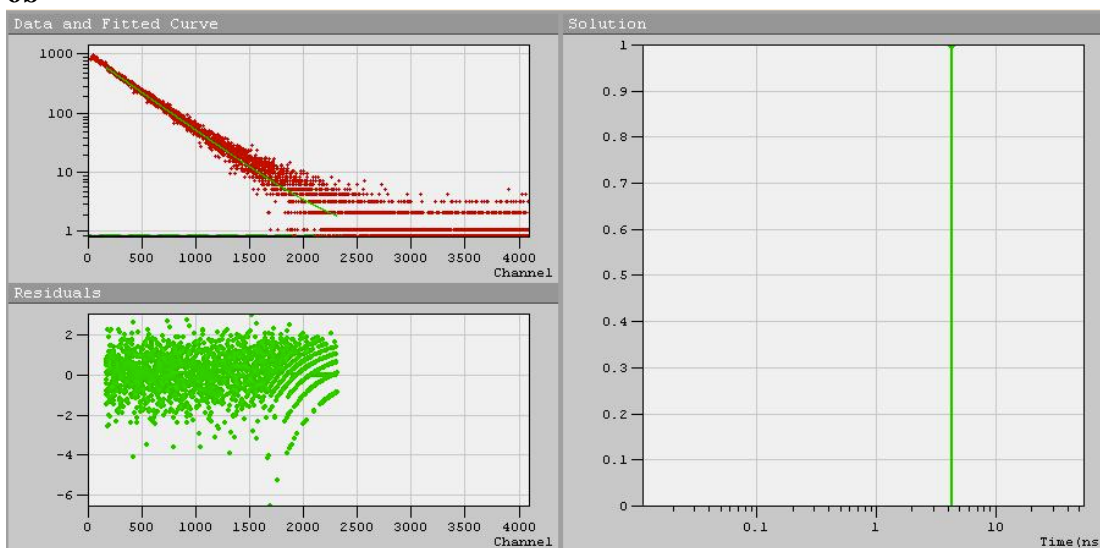
c^2 : 1.039

Exp Num	B	f	t (ns)
1	604.5	100.0	4.149

Background : 0.791

Shift : 0 ns

6b



v Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2300] channels

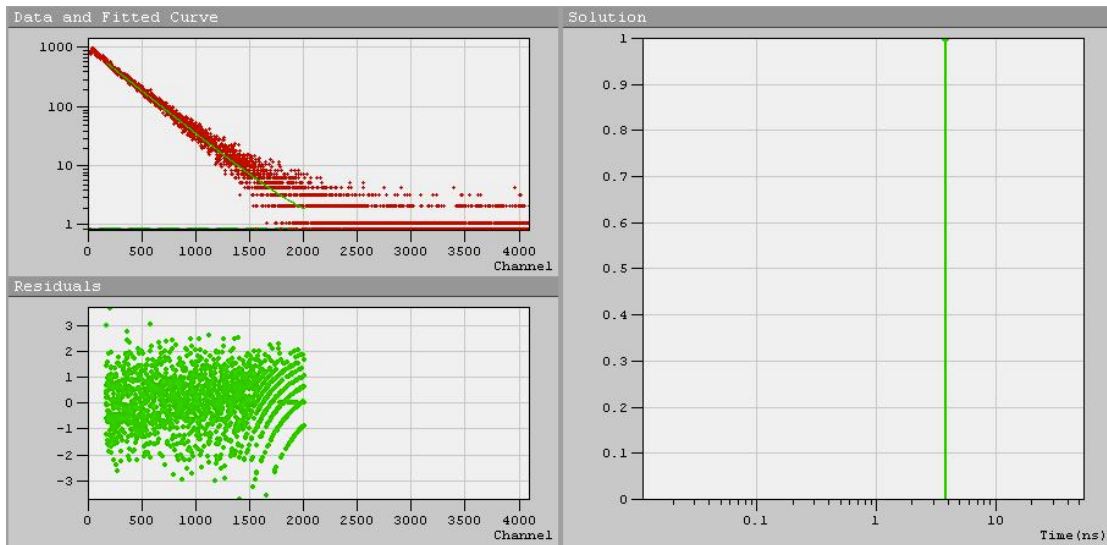
c^2 : 1.039

Exp Num	B	f	t (ns)
1	604.5	100.0	4.149

Background : 0.791

Shift : 0 ns

7b



v Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2000] channels

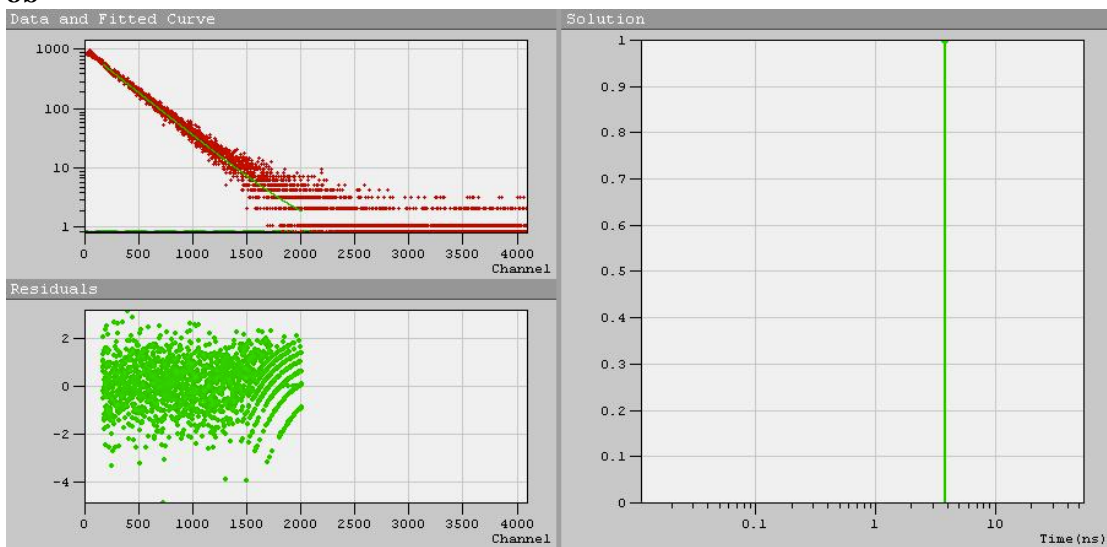
c^2 : 1.032

Exp Num	B	f	t (ns)
1	562.8	100.0	3.670

Background : 0.669

Shift : 0 ns

8b



v Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2000] channels

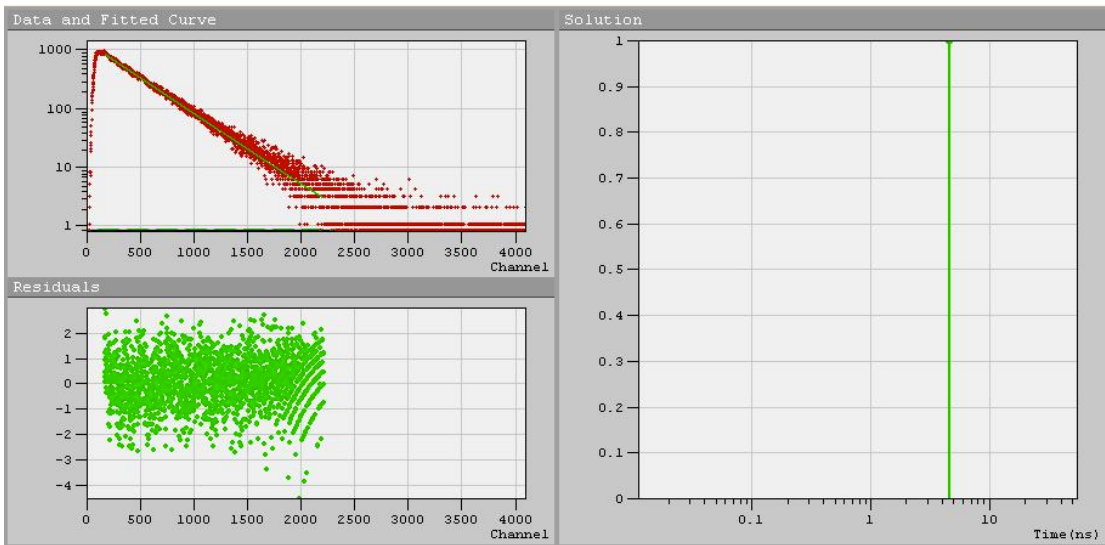
c^2 : 1.032

Exp Num	B	f	t (ns)
1	562.8	100.0	3.670

Background : 0.669

Shift : 0 ns

9a



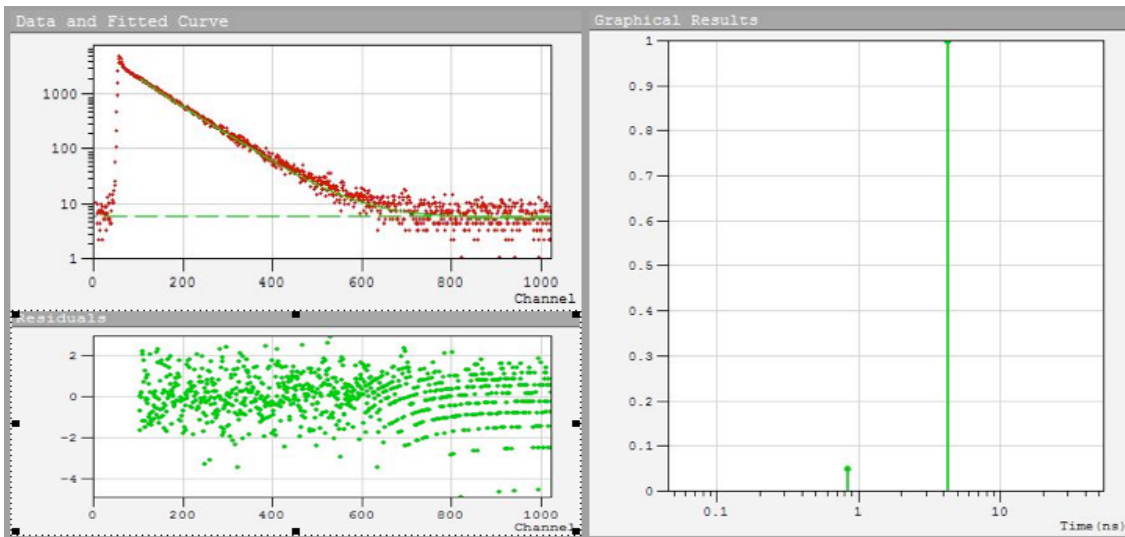
v Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2200] channels
 c^2 : 1.013

Exp Num	B	f	t (ns)
1	848.4	100.0	4.388

Background : 0.206
 Shift : 0 ns

9b



❖ Exponential Components Analysis (Tail Fitting)

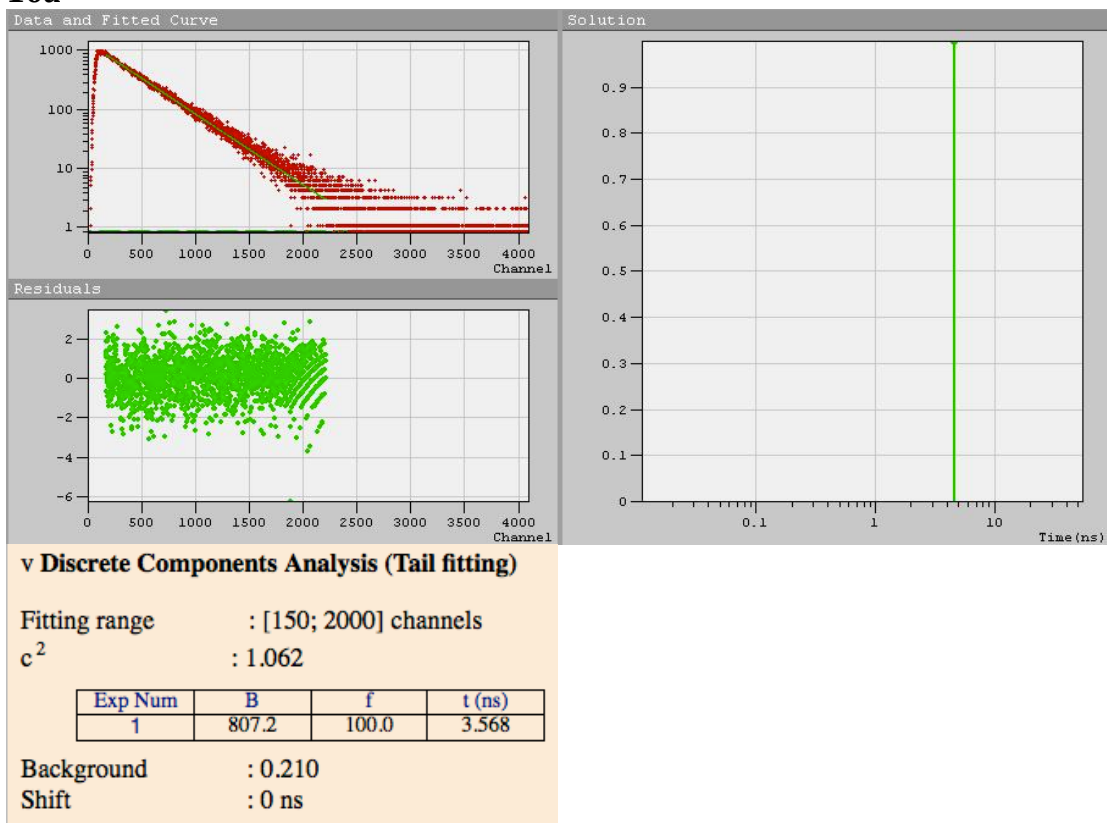
Fitting range : [100; 1024] channels
 χ^2 : 1.201

	B_i	f_i	t_i (ns)
1	88.5537	0.921	0.810
2	1855.0070	99.079	4.161

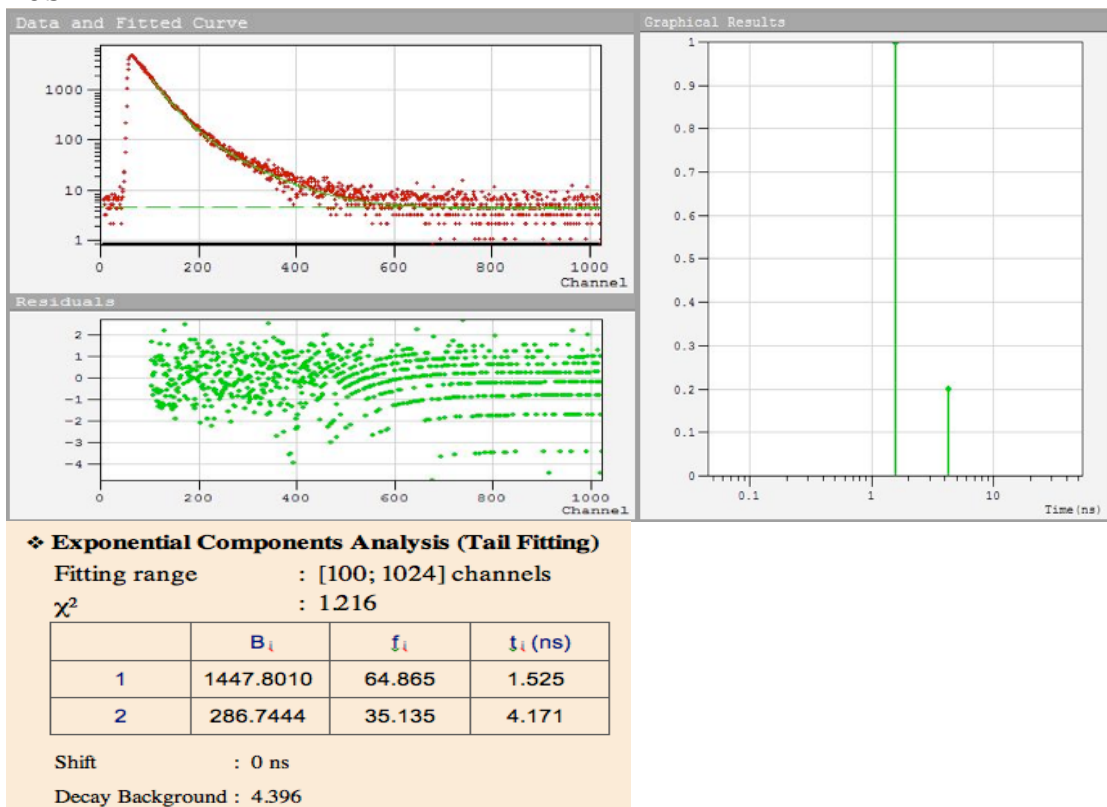
Shift : 0 ns

Decay Background : 5.529

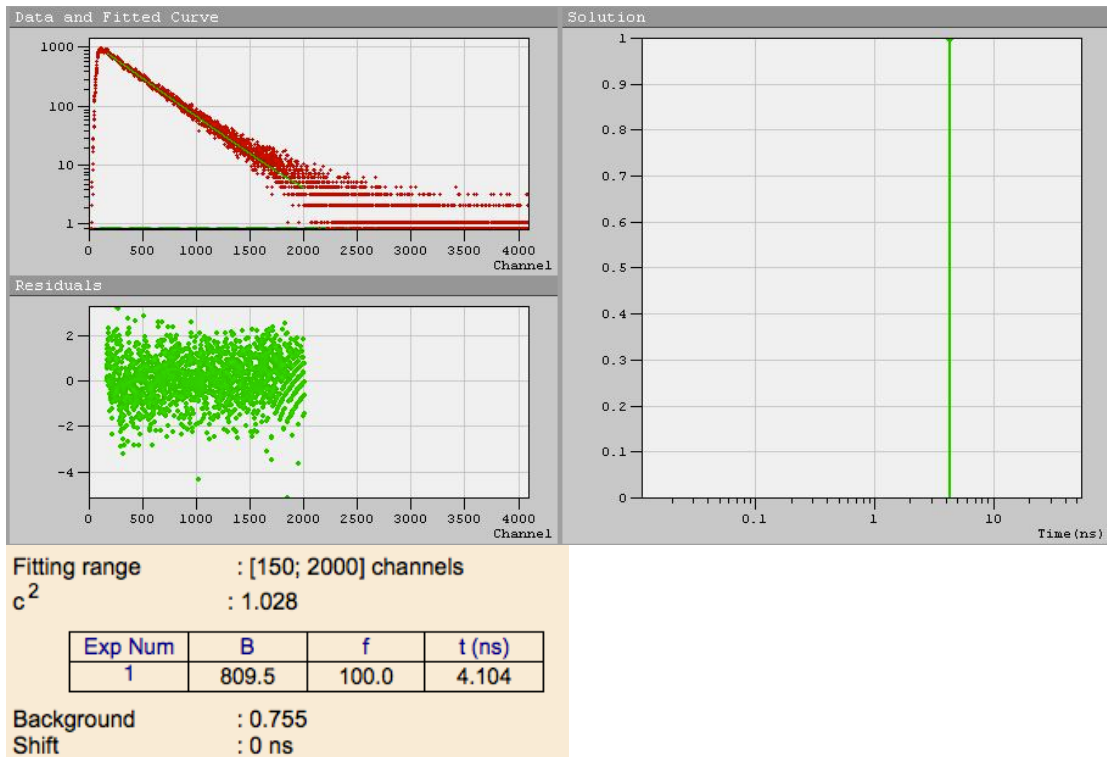
10a



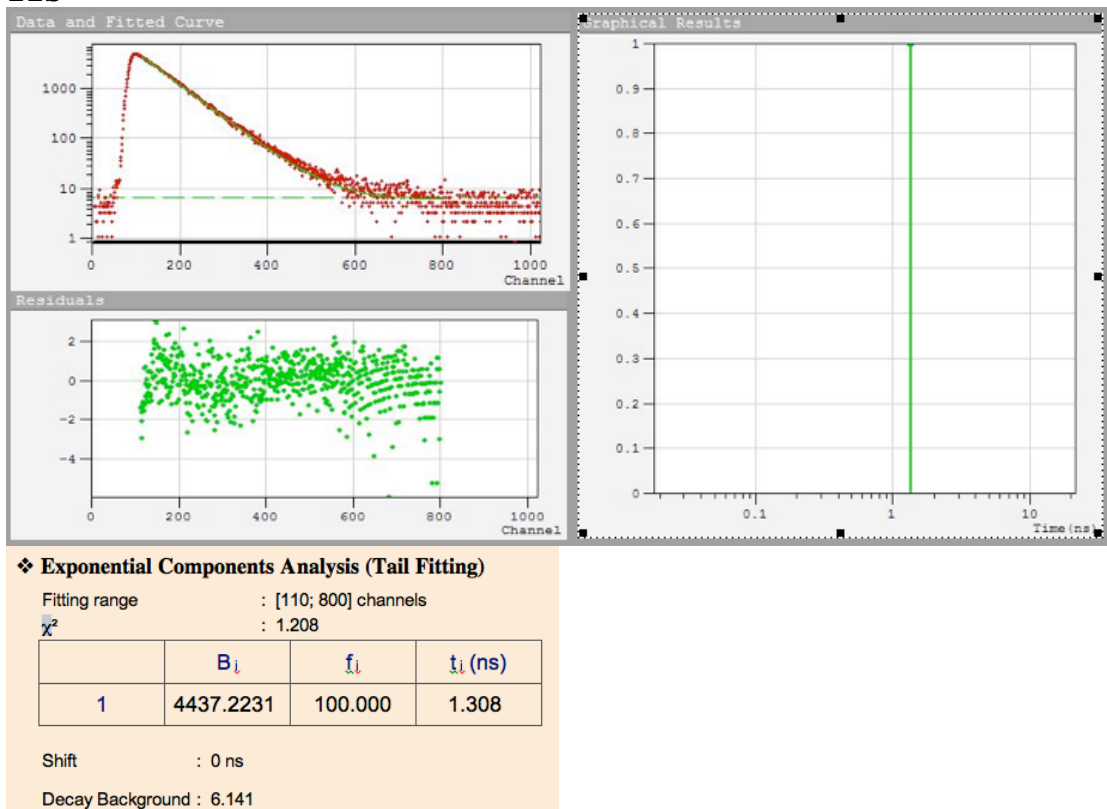
10b



11a



11b



12a

