Supporting Information

Aryl/Hetero-Arylethyne Bridged Dyes: The Effect of Planar π-Bridge on the Performance of Dye-Sensitized Solar Cells

Jun-Ling Song,[a] Pitchamuthu Amaladass,[a] Shu-Hao Wen,[b] Kalyan Kumar Pasunooti,[a] Yao-Lun Yu,[b] An Li,[a] Xin Wang,[b] Wei-Qiao Deng,*[c] and Xue-Wei Liu*[a]

[a] Division of Chemistry and Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore; [b] Division of Chemical and Biomolecular Engineering, School of Chemical and Biomedical Engineering, Nanyang technological University, Singapore 638798; [c] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China;

E-mail: *xuewei@ntu.edu.sg and dengwq@dicp.ac.cn*

Contents:

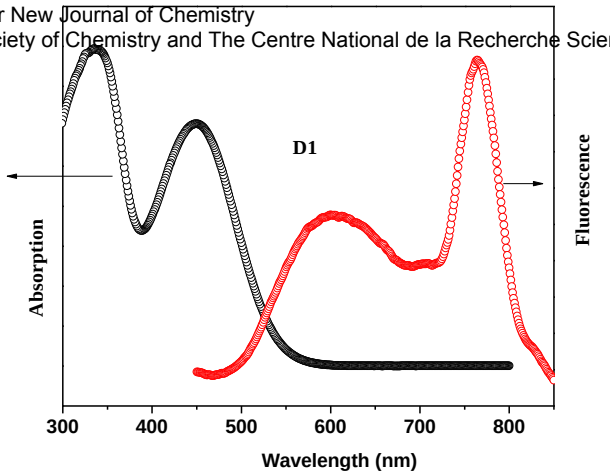
Table S1. Molecular orbital contribution (MOC) of the 5 highest occupied and 5 lowest unoccupied molecular orbitals of **D1**, **D2** and **D3** calculated at the B3LYP/6-31G* level in chloroform solution

	Energy, eV	Donor	Triple-bond	Bridge	Acceptor
D1					
HOMO-4	-6.983	99.9	0.0	0.0	0.0
HOMO-3	-6.850	67.3	3.1	15.2	14.5
HOMO-2	-6.291	99.8	0.1	0.0	0.0
HOMO-1	-6.041	53.3	17.4	19.1	10.2
HOMO	-4.904	88.9	5.1	3.7	2.2
LUMO	-2.737	7.9	6.3	29.7	56.1
LUMO+1	-1.002	52.3	13.2	15.2	19.3
LUMO+2	-0.524	99.9	0.0	0.1	0.0
LUMO+3	-0.308	0.3	0.0	99.1	0.6
LUMO+4	-0.136	98.9	0.7	0.2	0.2
D2					
HOMO-4	-7.010	96.1	0.5	1.5	1.9
HOMO-3	-6.762	66.3	2.6	15.0	16.0
HOMO-2	-6.310	99.8	0.2	0.0	0.0
HOMO-1	-5.926	42.4	14.2	26.8	16.7
HOMO	-4.926	85.4	5.3	5.7	3.5
LUMO	-2.749	9.3	7.3	37.9	45.5
LUMO+1	-1.099	43.1	11.4	24.6	20.9
LUMO+2	-0.552	99.9	0.0	0.1	0.0
LUMO+3	-0.159	97.4	0.8	1.2	0.5
LUMO+4	-0.067	66.7	1.8	20.6	10.9
D3					
HOMO-4	-6.936	81.1	3.5	9.6	5.8
HOMO-3	-6.430	54.9	6.5	24.9	13.7
HOMO-2	-6.297	99.8	0.1	0.0	0.0
HOMO-1	-5.618	33.3	9.1	46.6	11.1
HOMO	-4.824	80.4	6.2	11.4	2.0
LUMO	-2.819	3.9	3.1	53.2	39.8
LUMO+1	-1.587	20.1	9.7	52.0	18.2
LUMO+2	-0.550	46.8	5.3	38.2	9.7
LUMO+3	-0.499	100.0	0.0	0.0	0.0
LUMO+4	-0.119	99.1	0.8	0.1	0.0

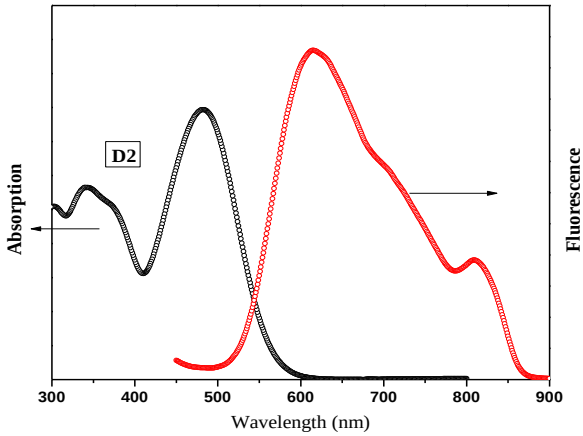
Table S2. Computed excited energies (eV), oscillator strengths (f) for **D1**, **D2**, and **D3** in chloroform calculated using TD-B3LYP/6-31G*//B3LYP/6-31G* using C-PCM framework

	nm	cm^{-1}•(1000)	eV	f	Assignment H=HOMO,L=LUMO,L+1=LUMO+1,etc.
D1					
	638.5	15.7	1.94	0.9358	H-0->L+0(+92%)
	410.6	24.4	3.02	0.9669	H-1->L+0(+87%)
	375.4	26.6	3.30	0.0107	H-2->L+0(+99%)
	353.6	28.3	3.51	0.3327	H-0->L+1(+83%),H-3->L+0(+6%)
D2					
	637.9	15.7	1.94	1.0566	H-0->L+0(+90%)
	424.9	23.5	2.92	0.8808	H-1->L+0(+84%)
	376.5	26.6	3.29	0.0125	H-2->L+0(+99%)
	359.3	27.8	3.45	0.2470	H-0->L+1(+82%),H-3->L+0(+9%)
D3					
	697.0	14.3	1.78	0.9931	H-0->L+0(+92%)
	487.3	20.5	2.54	1.0352	H-1->L+0(+83%)
	423.0	23.6	2.93	0.3406	H-0->L+1(+85%)
	379.3	26.4	3.27	0.0050	H-2->L+0(+99%)
	369.3	27.1	3.36	0.0830	H-3->L+0(+84%)

D1



D2



D3

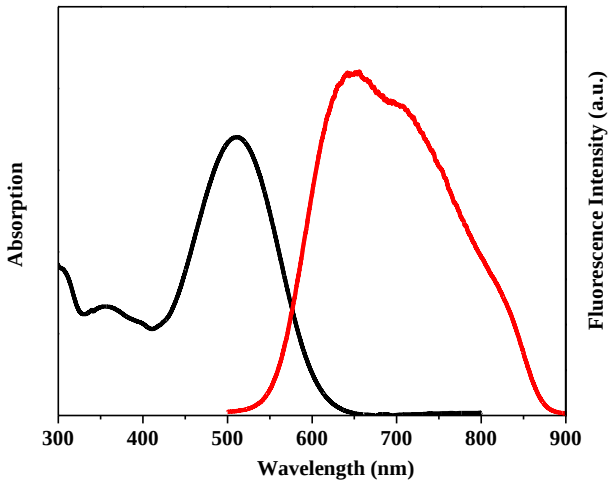


Figure S1. The UV-Vis absorption and fluorescence of dye sensitizers in this study.

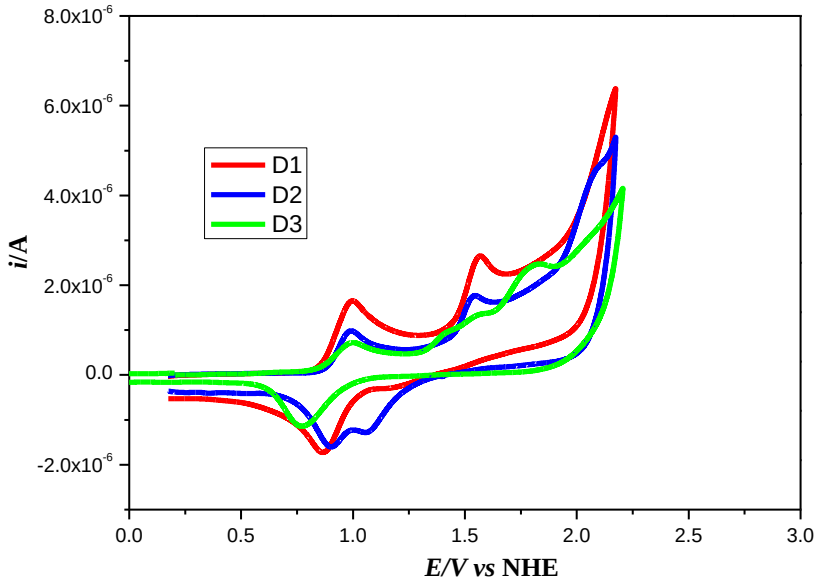


Figure S2. Cyclic voltammetry of **D1**, **D2** and **D3.**

Figure S3. ^{1}H NMR spectrum of 4-(2-(4-(Bis (4-methoxyphenyl) amino) phenyl) ethynylbenzaldehyde (7)

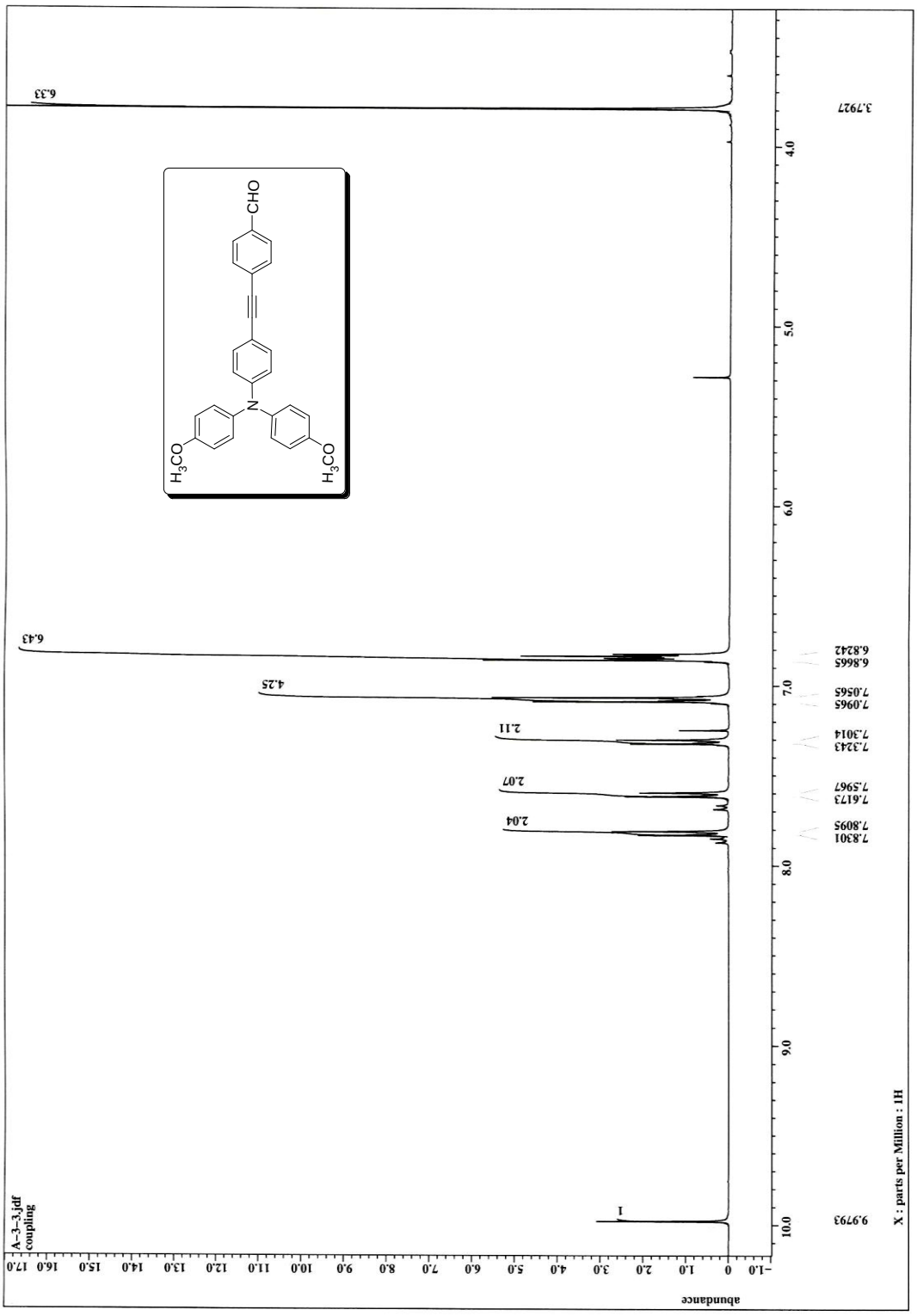


Figure S4. ^{13}C NMR spectrum of 4-(2-(4-(Bis (4-methoxyphenyl) amino) phenyl) ethynylbenzaldehyde (7)

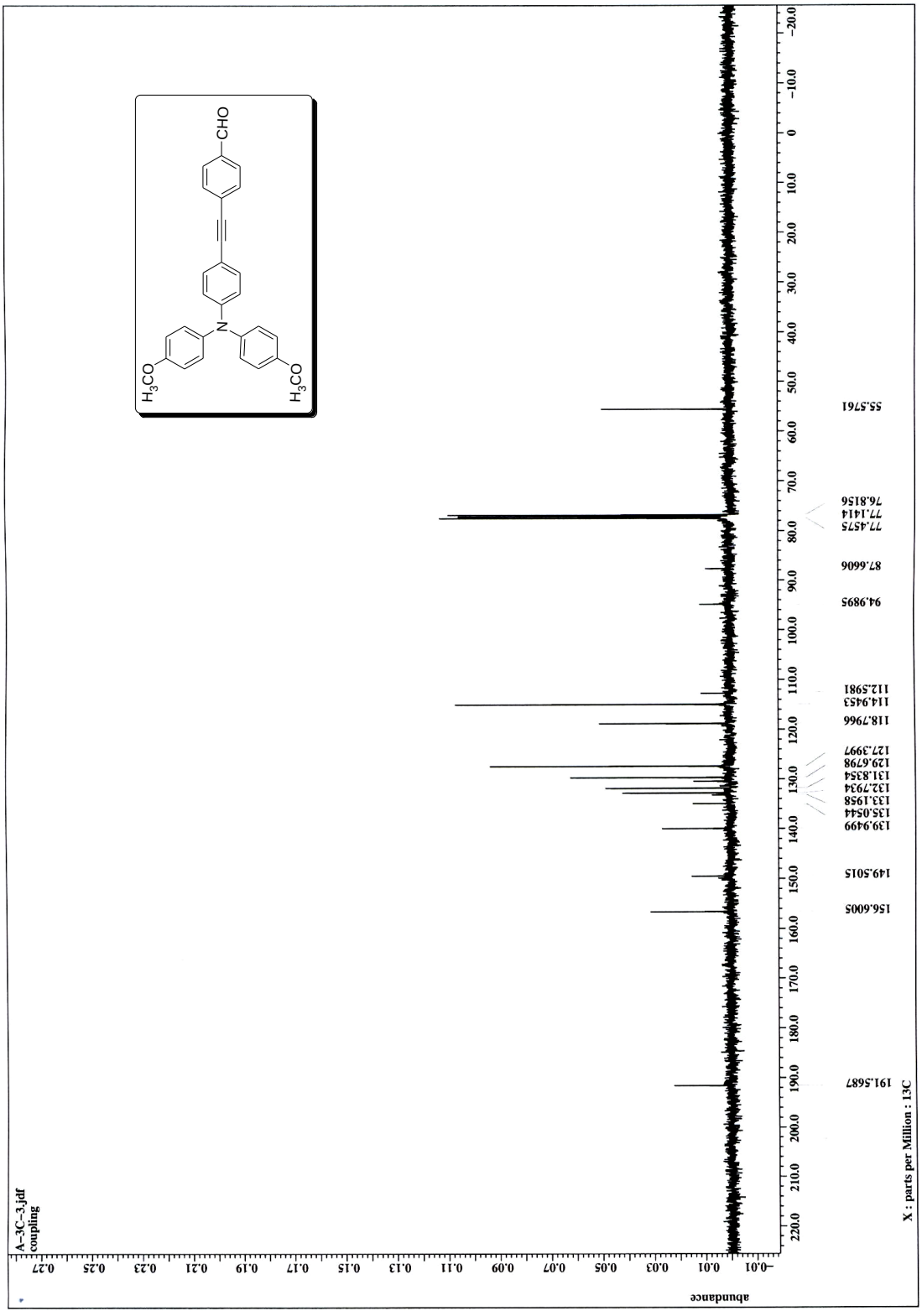


Figure S5. ^{1}H NMR spectrum of 5-(2-(4-(bis (4-methoxyphenyl) amino) phenyl) ethynyl) thiophene-2-carbaldehyde (11)

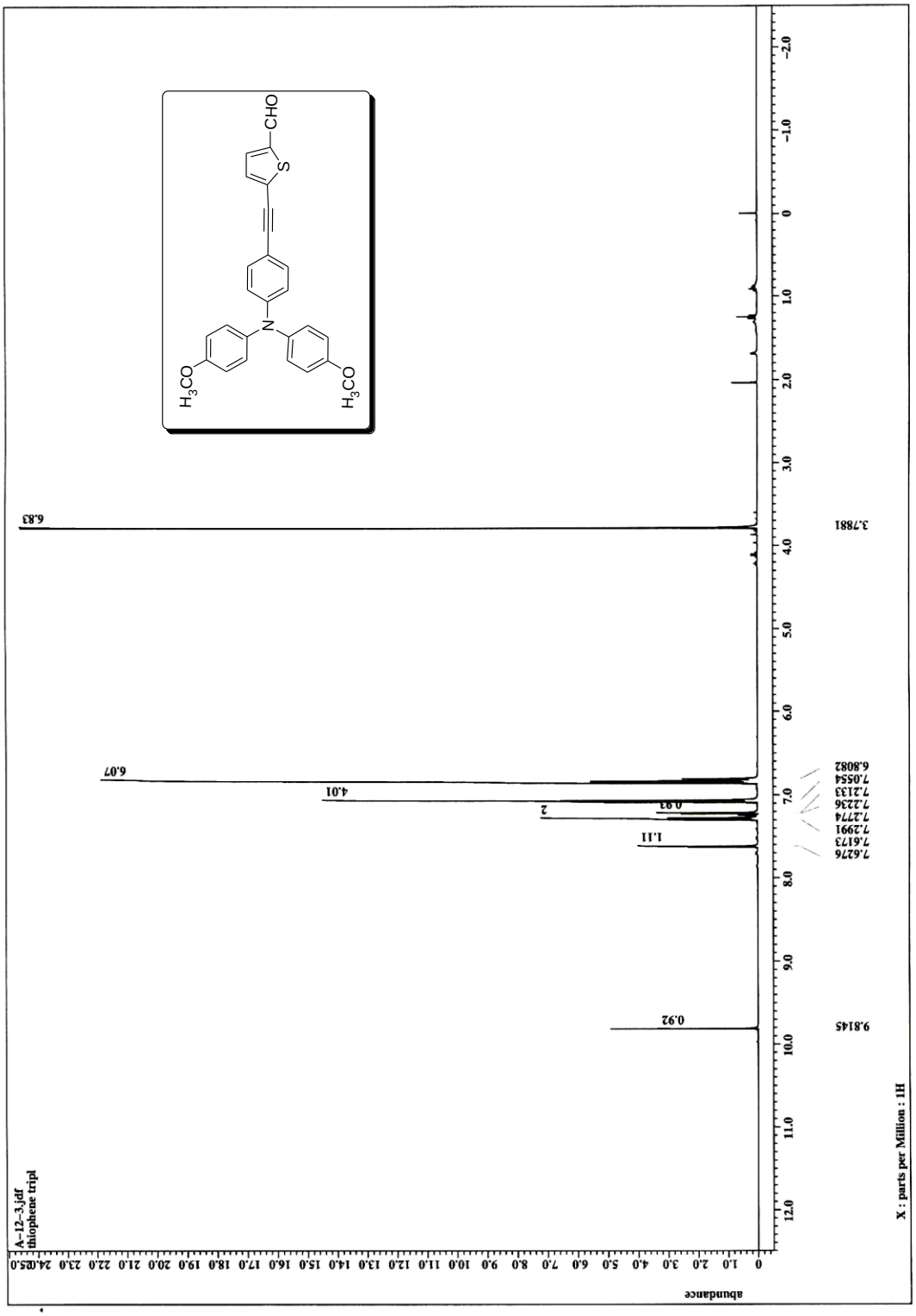


Figure S6. ^{13}C NMR spectrum of 5-(2-(4-(bis (4-methoxyphenyl) amino) phenyl) ethynyl) thiophene-2-carbaldehyde (11)

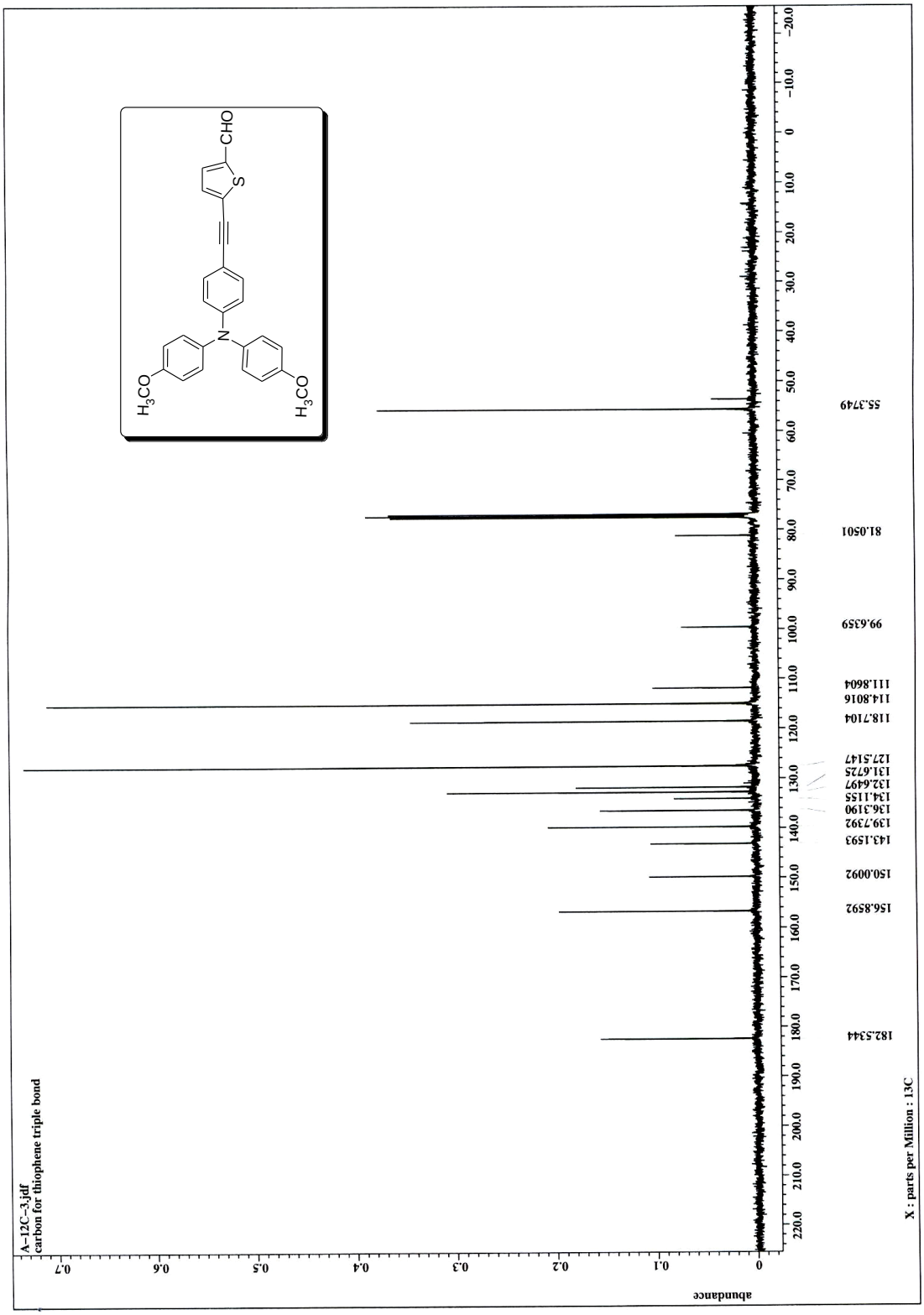


Figure S7. ^{1}H NMR spectrum of Dye D2

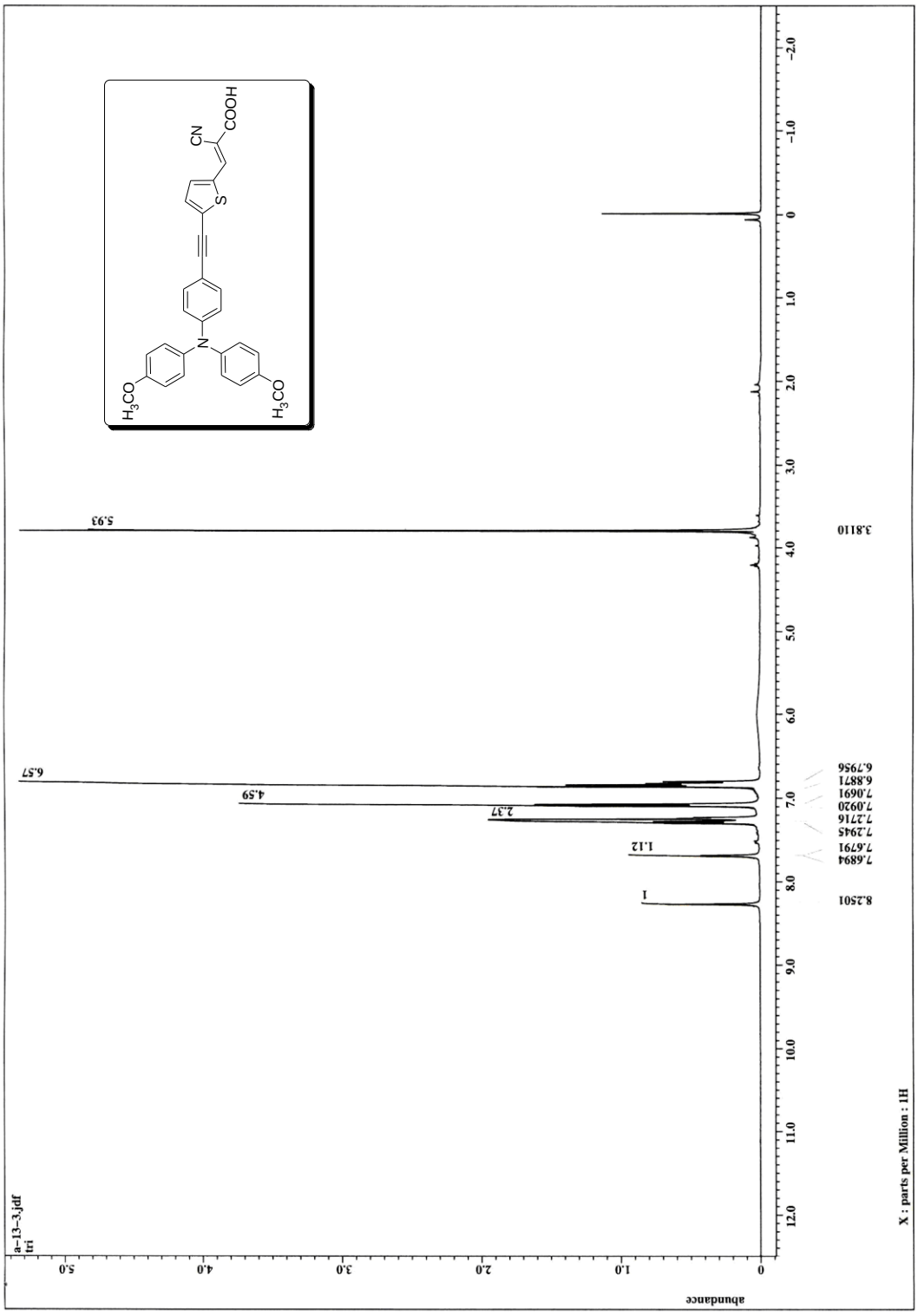


Figure S8. ^{13}C NMR spectrum of Dye D2

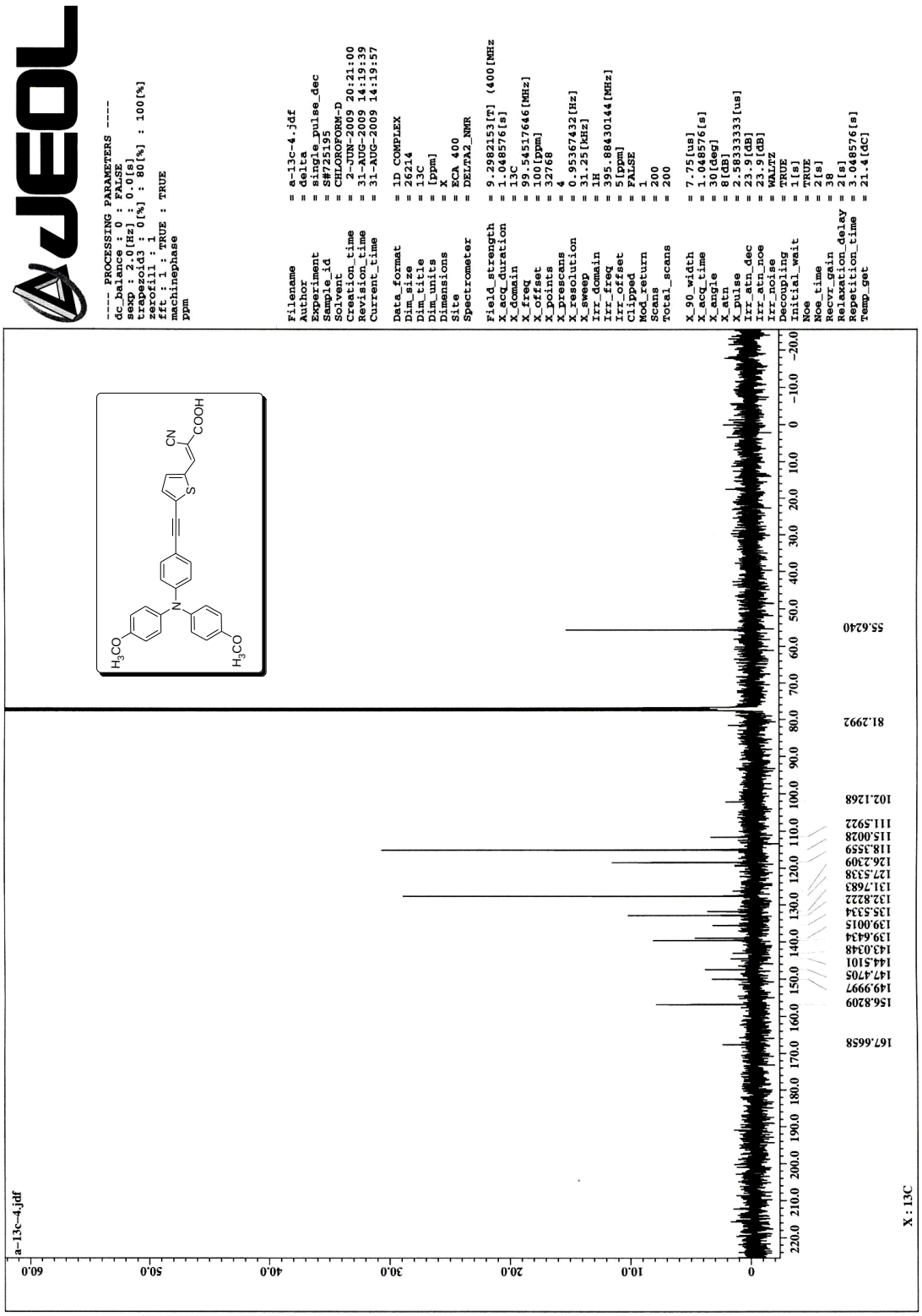
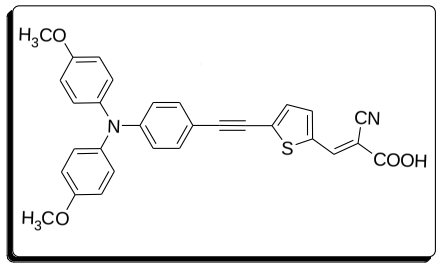


Figure S9. HRMS spectrum of Dye D2

Elemental Composition Report



Single Mass Analysis
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-23 N: 0-2 O: 0-4 P: 0-1 S: 0-1

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HAB333

09:47:16
06-Aug-2009
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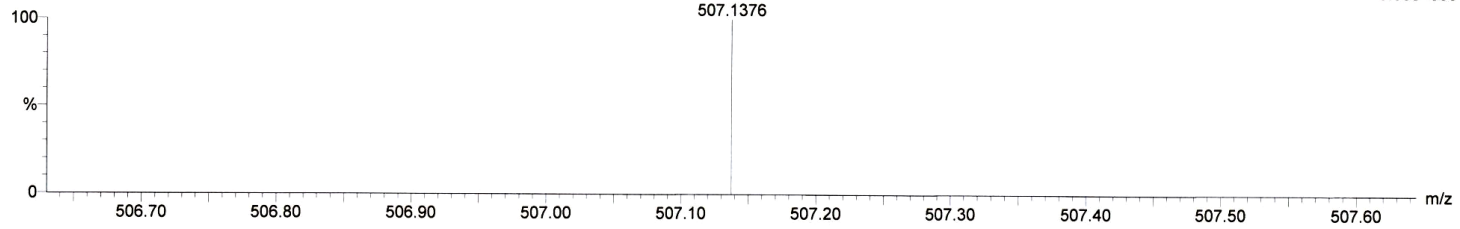
5.06e+000

A-1 11 (0.257)



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Maximum:		50.0	2.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
507.1376	507.1379	-0.3	-0.6	20.5	13.5	0.0	C30 H23 N2 O4 S

Figure S10. ^{1}H NMR spectrum of Dye D1

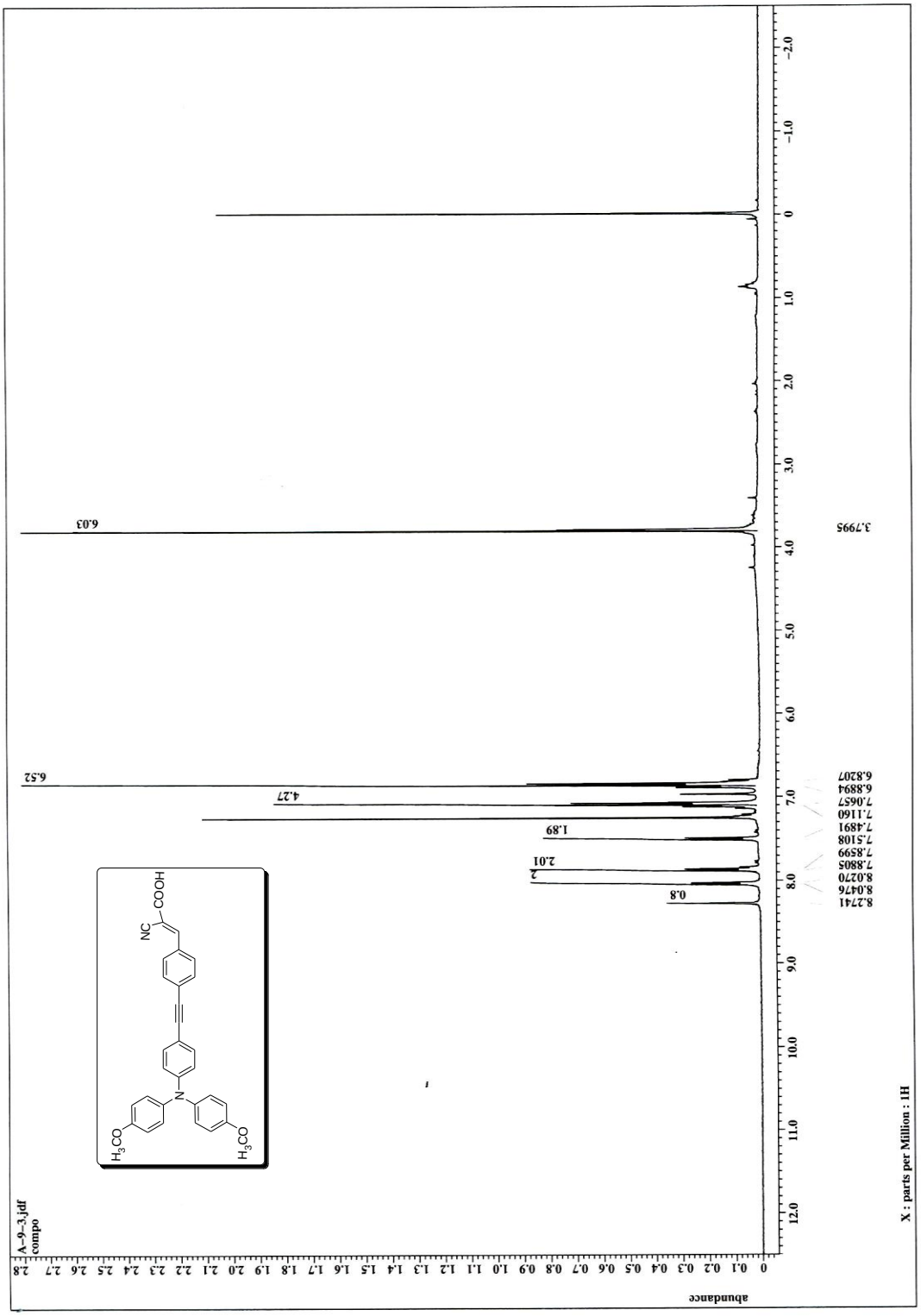

Figure S11. ^{13}C NMR spectrum of Dye D1

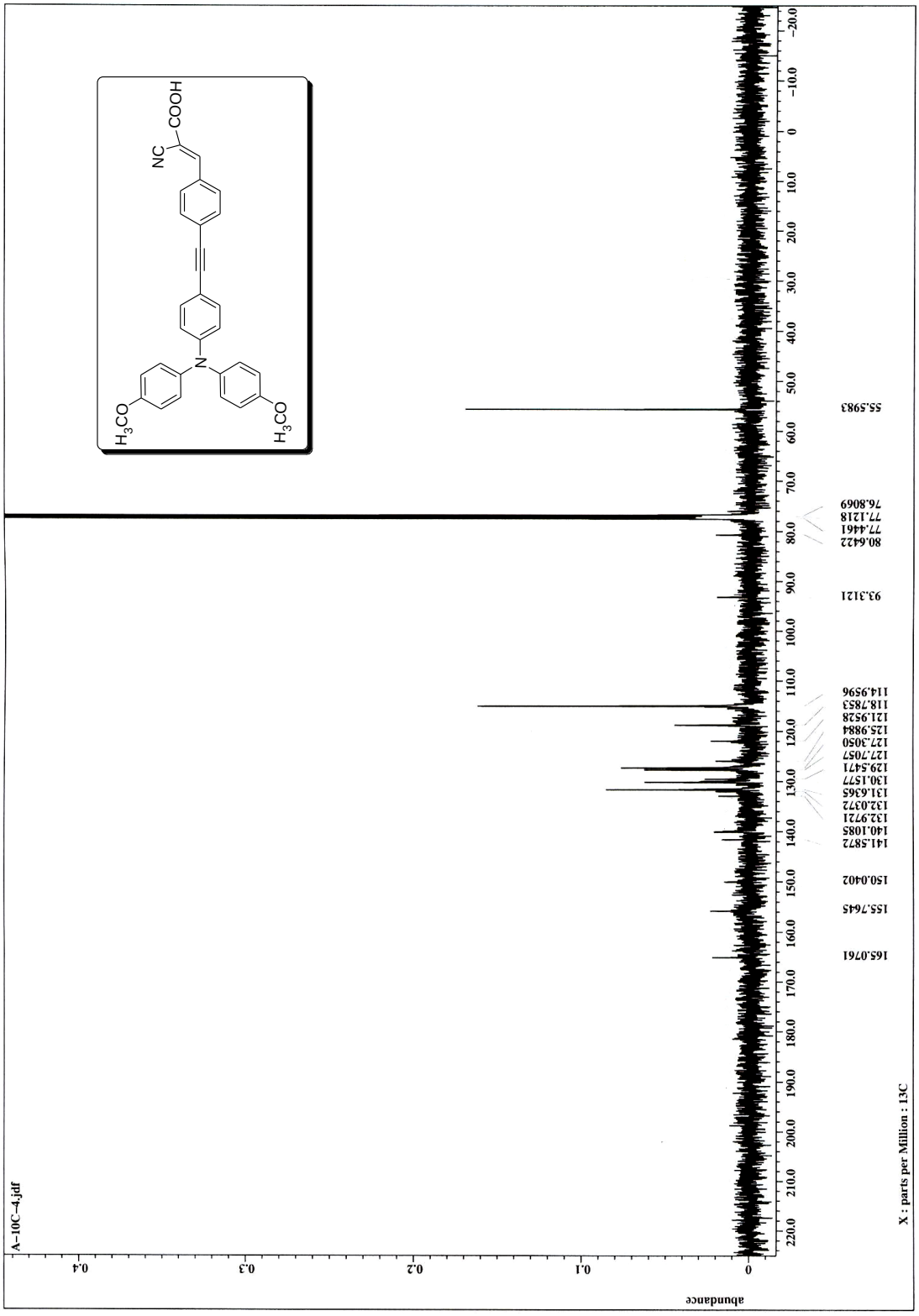

Figure S12.HRMS spectrum of Dye D1

Elemental Composition Report **Page 1**

Single Mass Analysis
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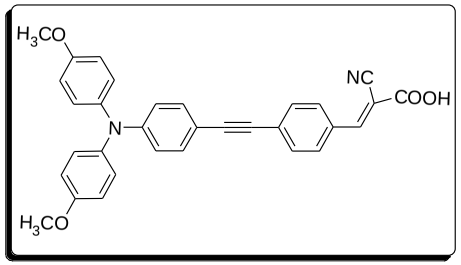
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
16 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-32 H: 0-25 N: 0-2 O: 0-4 P: 0-1



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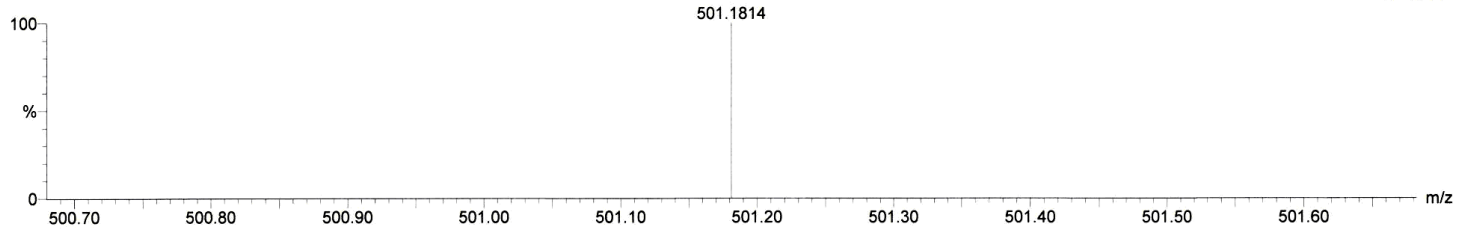
1.01e+001

A-2 4 (0.101) Cm (4:17)



Minimum:				-1.5			
Maximum:		50.0	2.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
501.1814	501.1814	0.0	0.0	21.5	14.2	0.0	C32 H25 N2 O4

Figure S13. ^{1}H NMR spectrum of 5-(5-(2-(4-(bis(4-methoxyphenyl)amino)ethynyl)thiophene-2-yl)thiophene -2-carbaldehyde (16)

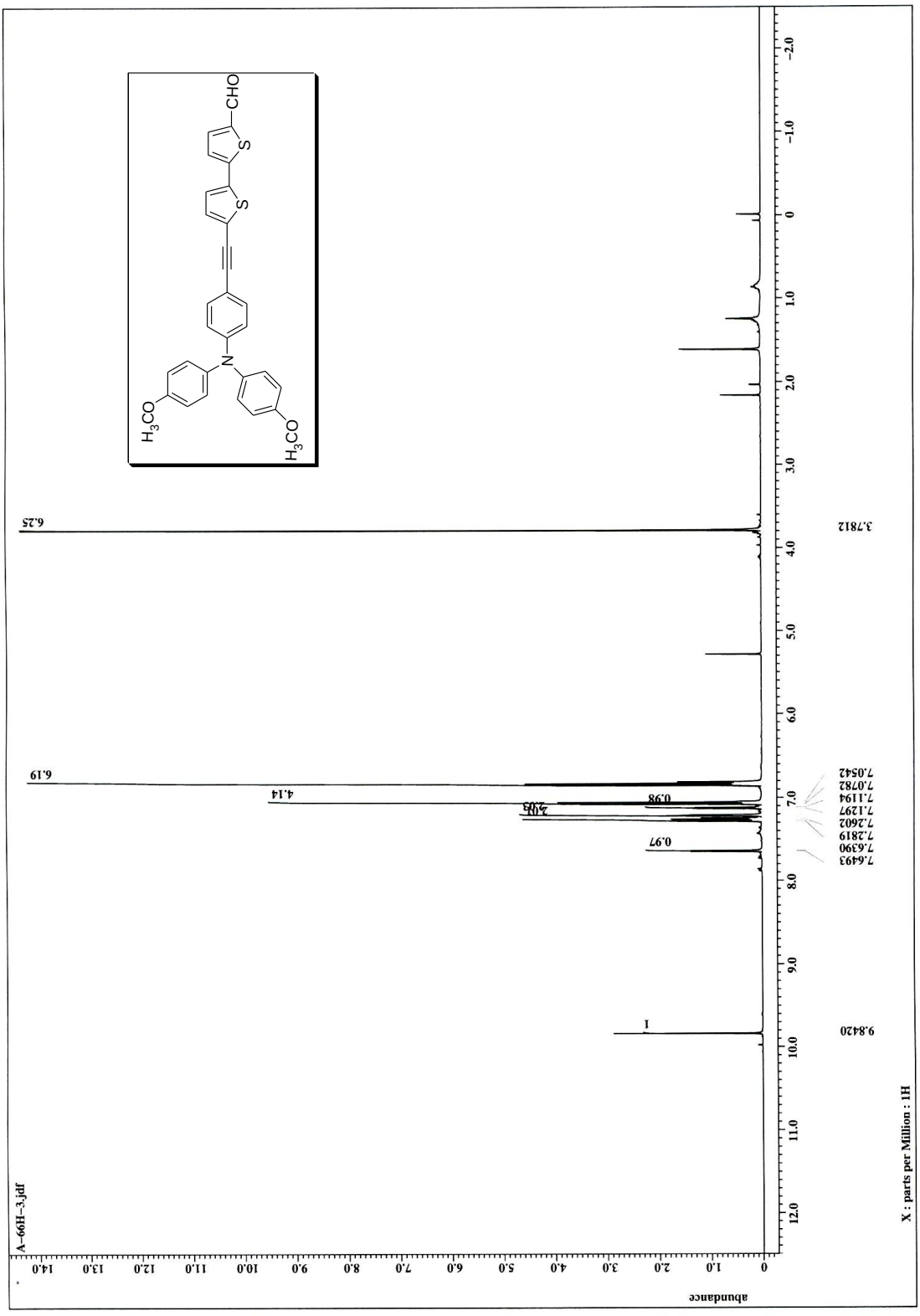


Figure S14. ^{13}C NMR spectrum of 5-(5-(2-(4-(bis(4-methoxyphenyl)amino)ethynyl)thiophene-2-yl)thiophene -2-carbaldehyde (16)

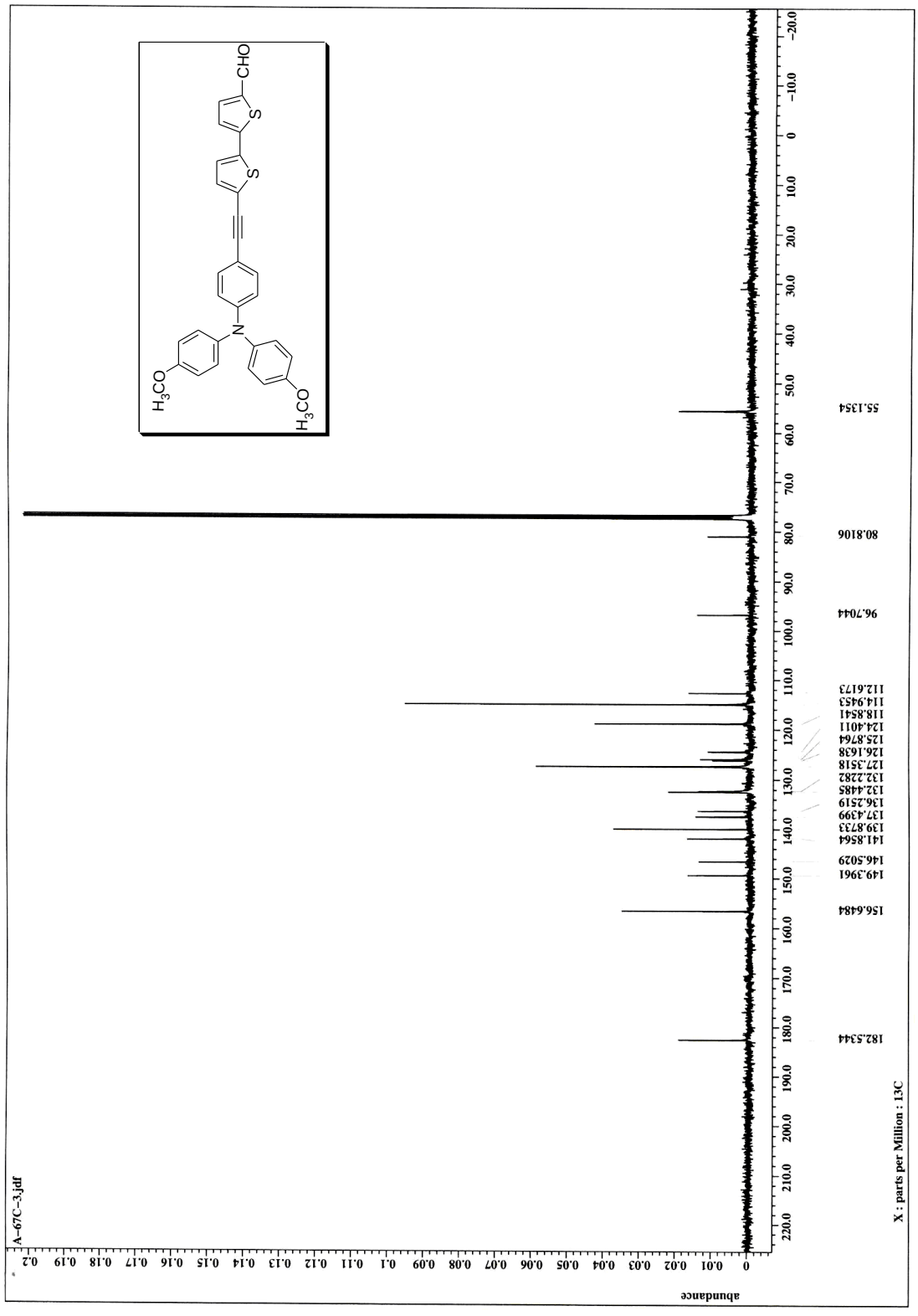


Figure S15. ^{1}H NMR spectrum of Dye D3

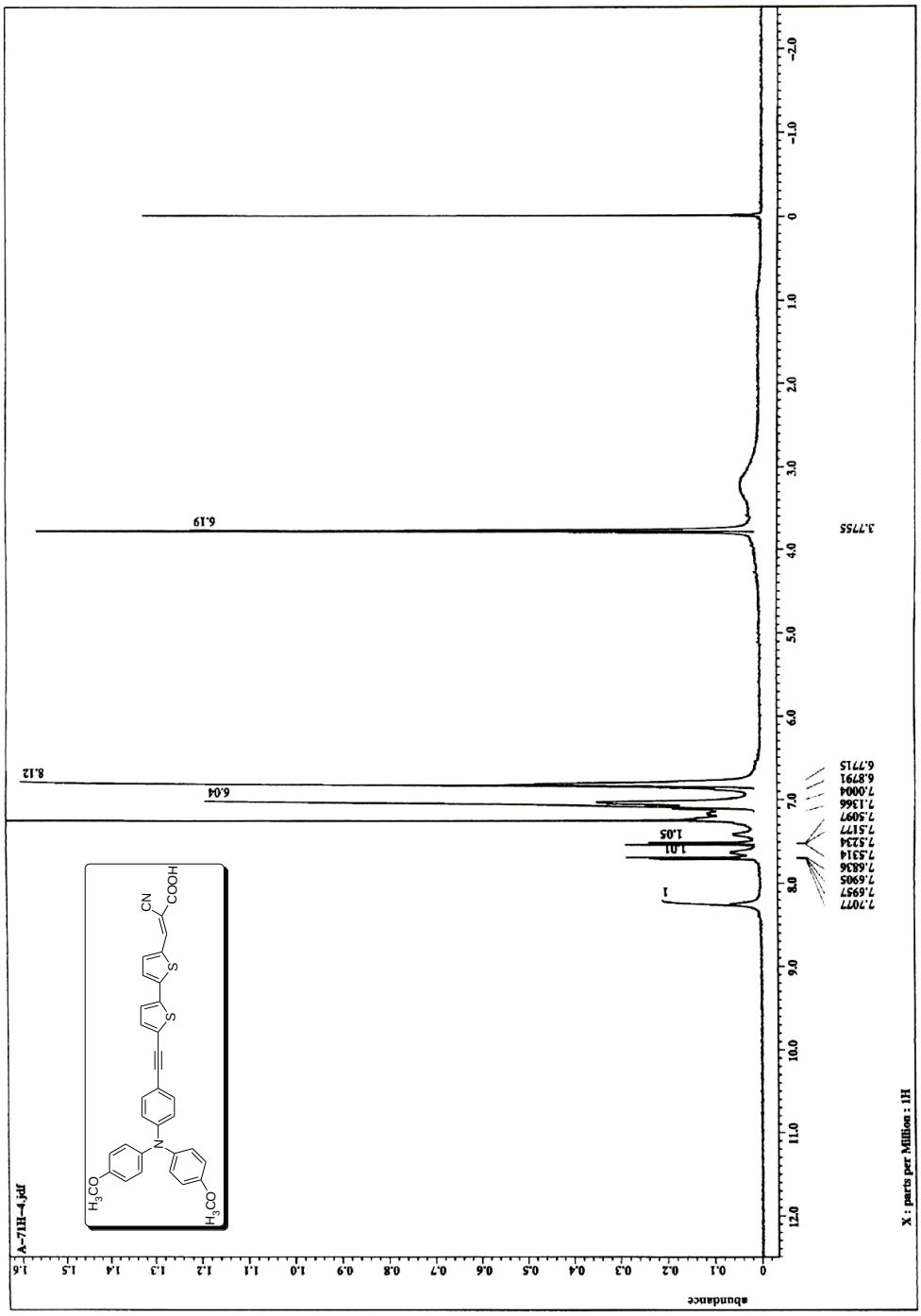


Figure S16. ^{13}C NMR spectrum of Dye D3

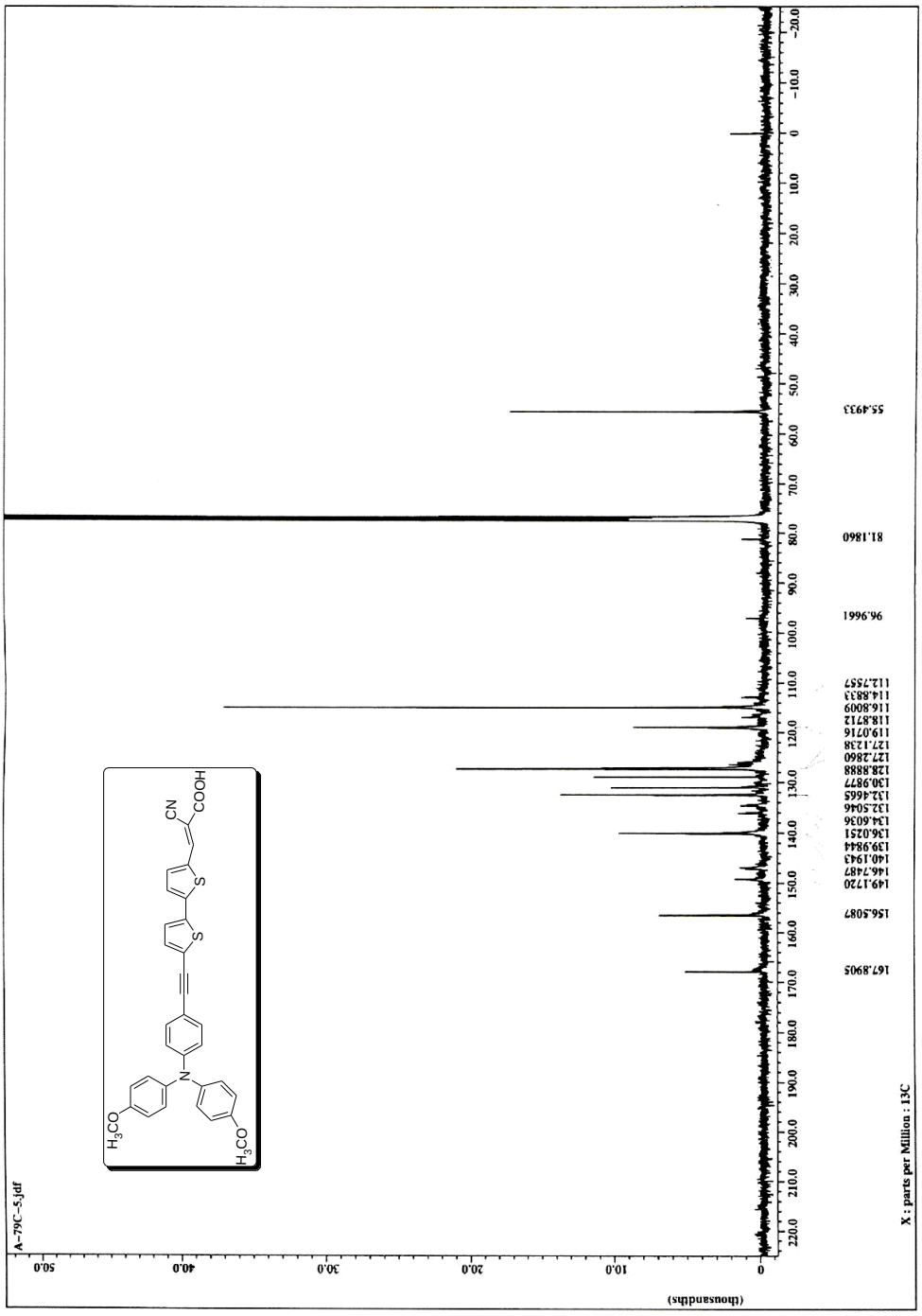
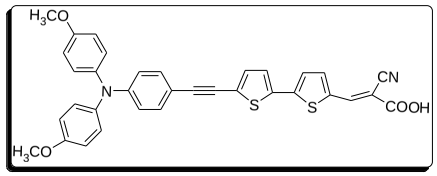


Figure S17. HRMS spectrum of Dye D3

Elemental Composition Report



Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 21-34 H: 24-25 N: 0-2 O: 3-4 S: 1-2

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07-Oct-2009
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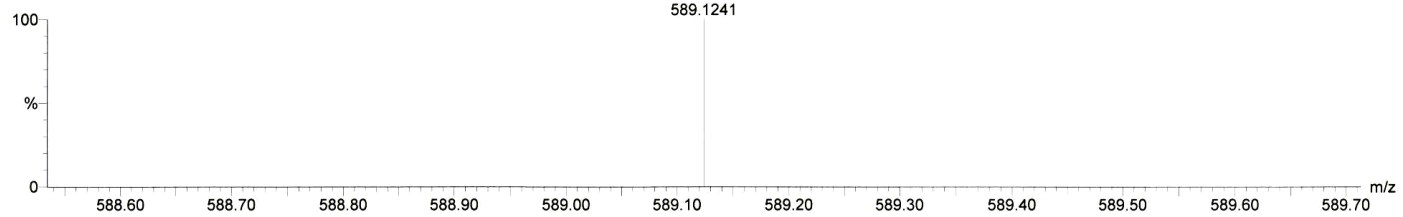

Minimum:				-1.5			
Maximum:		5.0	50.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
589.1241	589.1256	-1.5	-2.5	23.5	20.5	0.0	C34 H25 N2 O4 S2