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Supplementary information for

Optical and Electrochemical Properties of Ethynylaniline Derivatives of Phenothiazine, Phenothiazine-5-oxide and Phenothiazine-5,5-dioxide

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1) Calculated geometries of ground and excited states
2) Cyclic voltammograms
3) Differential pulse voltammograms
4) FTIR spectra
5) ^{1}H and ^{13}C NMR spectra
6) Fluorescence Lifetime measurements
7) Solvatochromism
8) Multi-parameter solvent effect analysis

Figure S1: Calculated ground state and excited state geometries of **3a-3c**

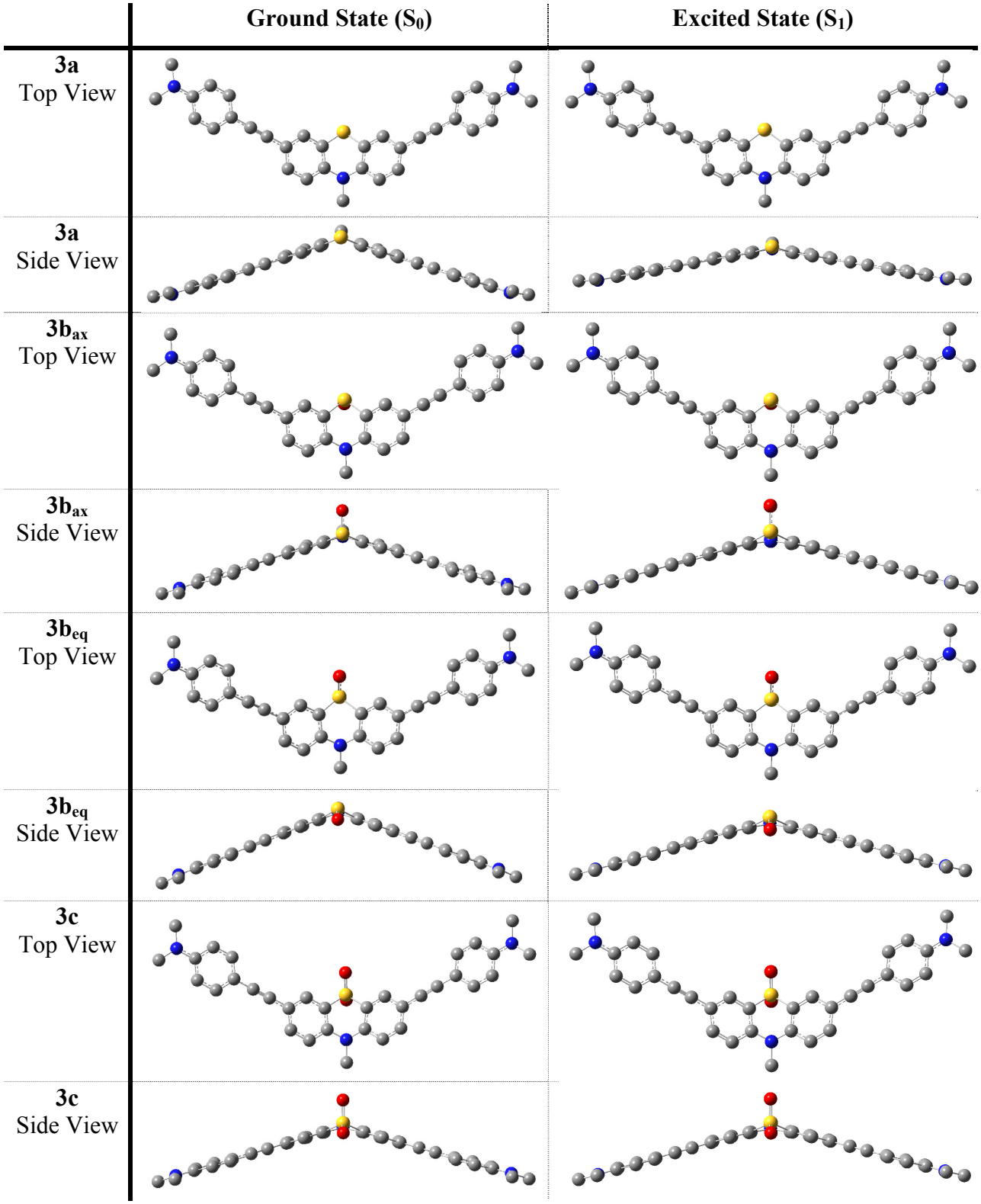


Figure S2: Cyclic Voltammograms in DMF of **3a** (blue), **3b** (green) and **3c** (black) vs. Fc/Fc^+

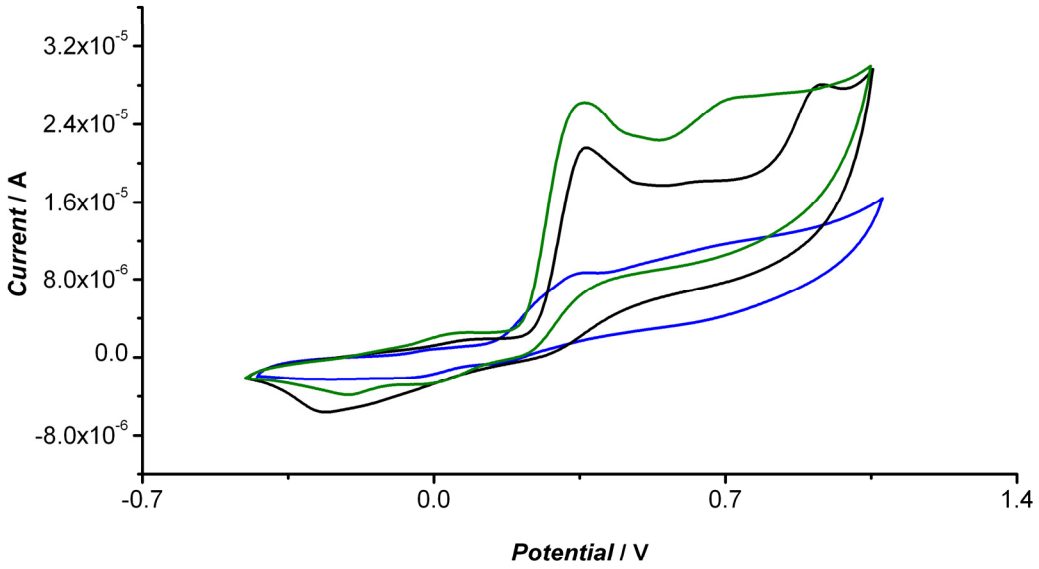


Figure S3: Differential Pulse Voltammograms in DMF of **3a** (blue), **3b** (green), **3c** (black) vs Fc/Fc^+.

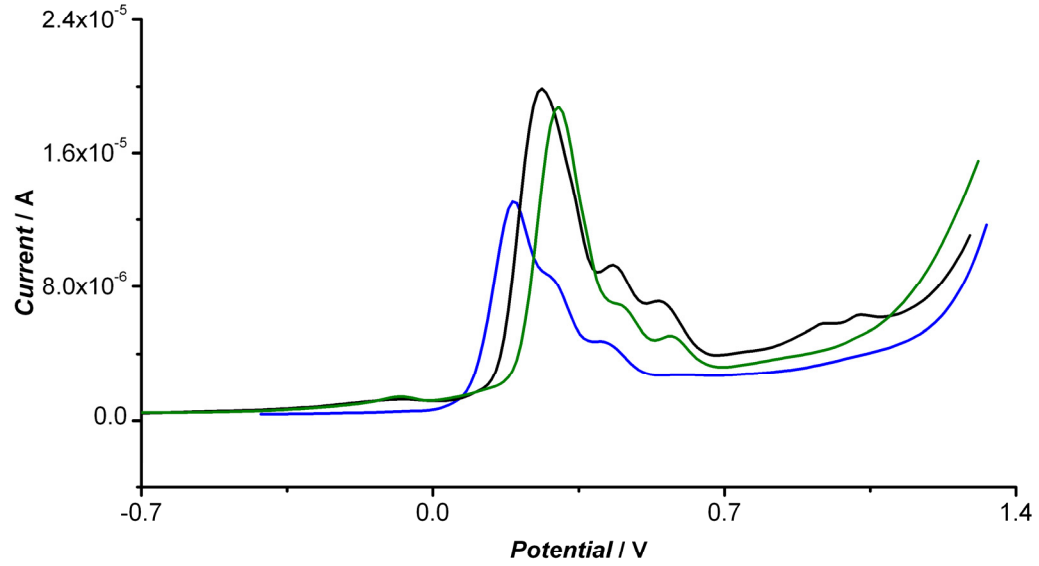


Figure S4: Normalized diffuse reflectance FTIR spectra in KBr of **3a**, **3b** and **3c**

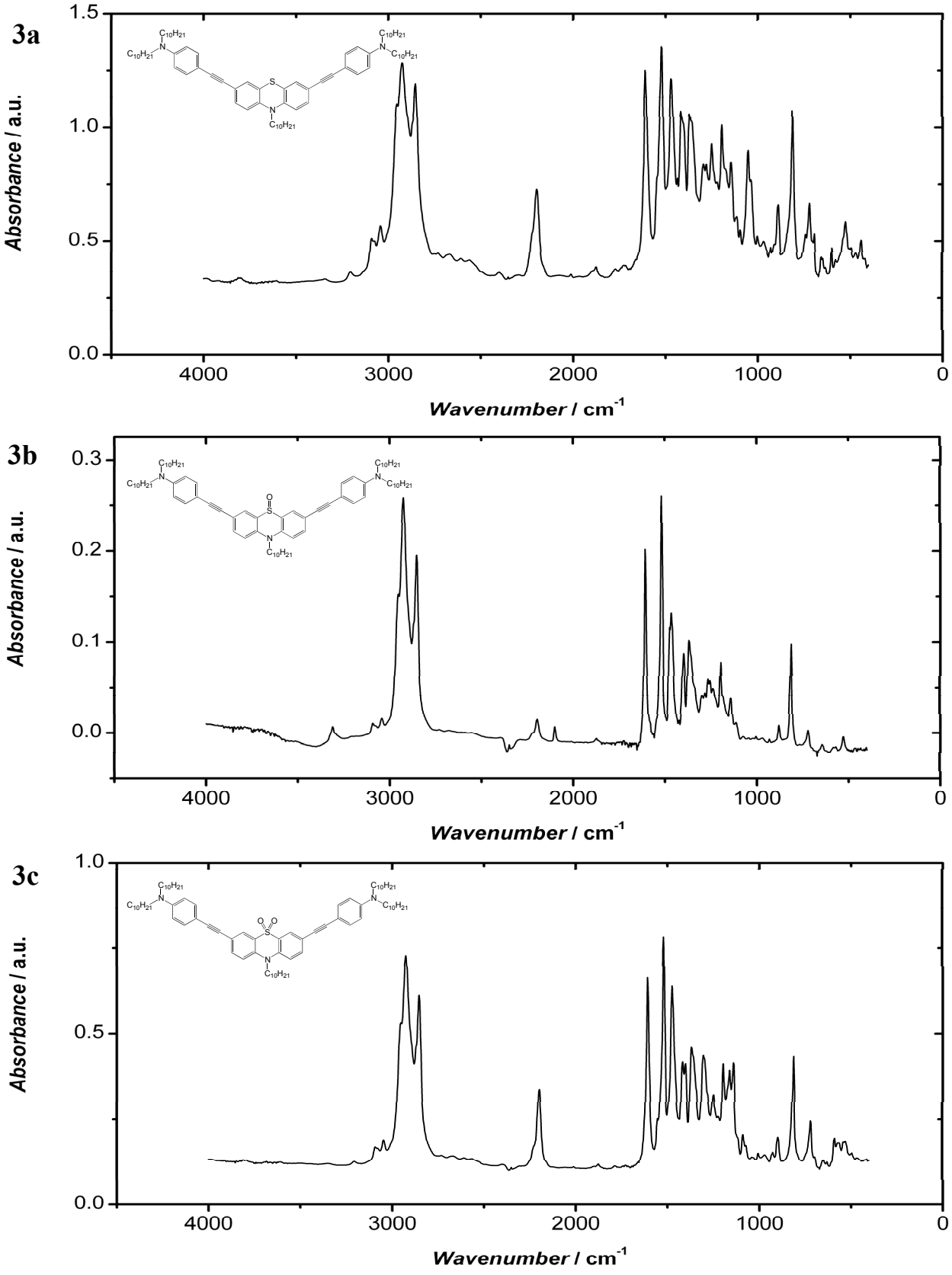
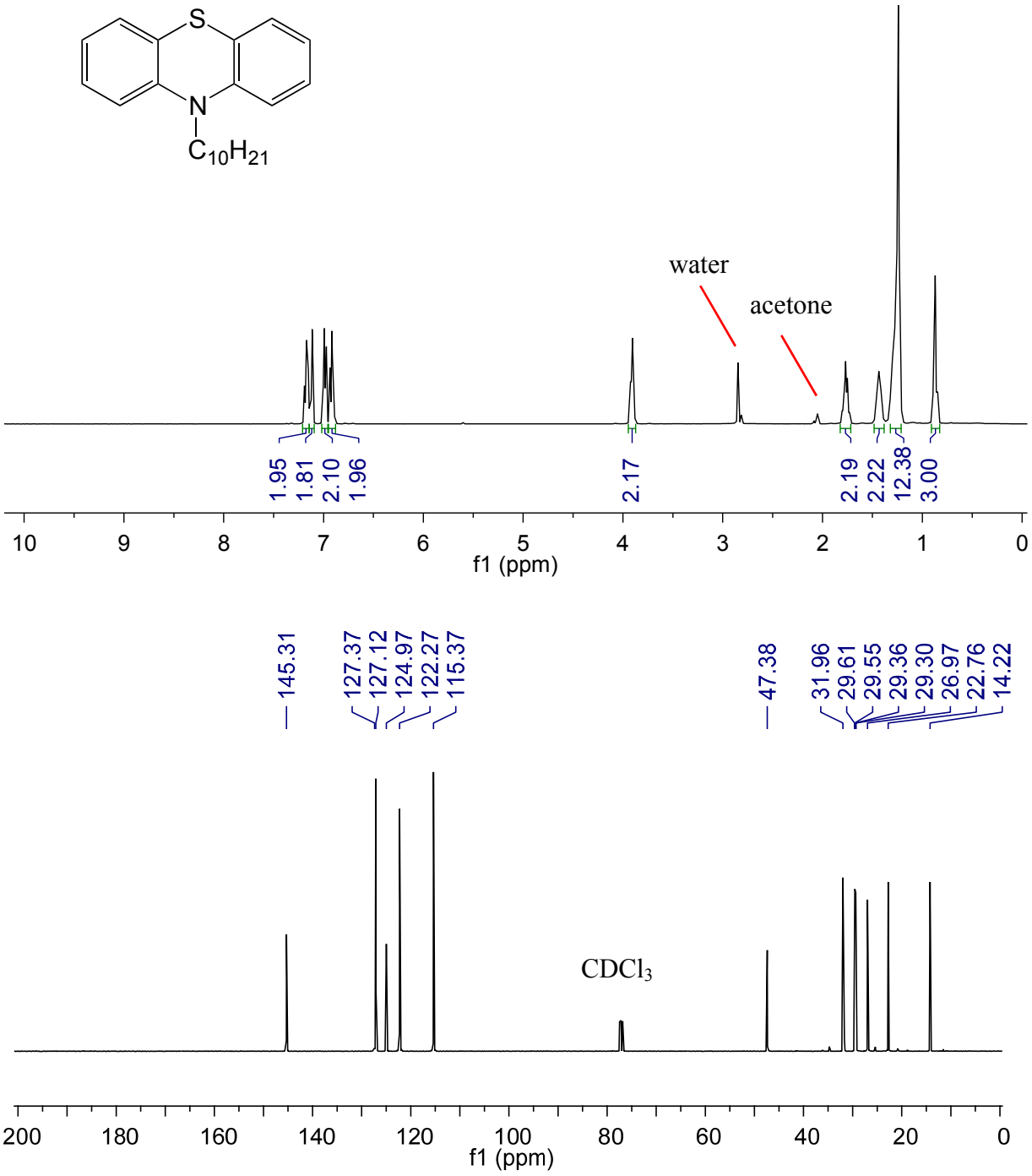
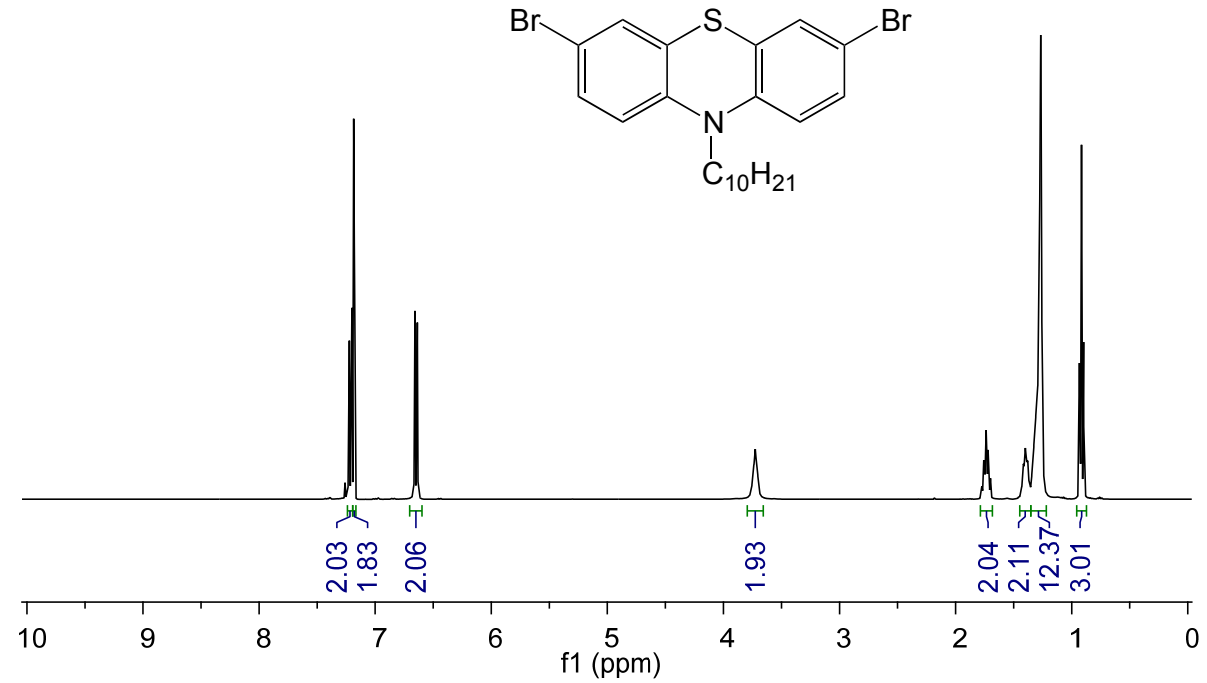


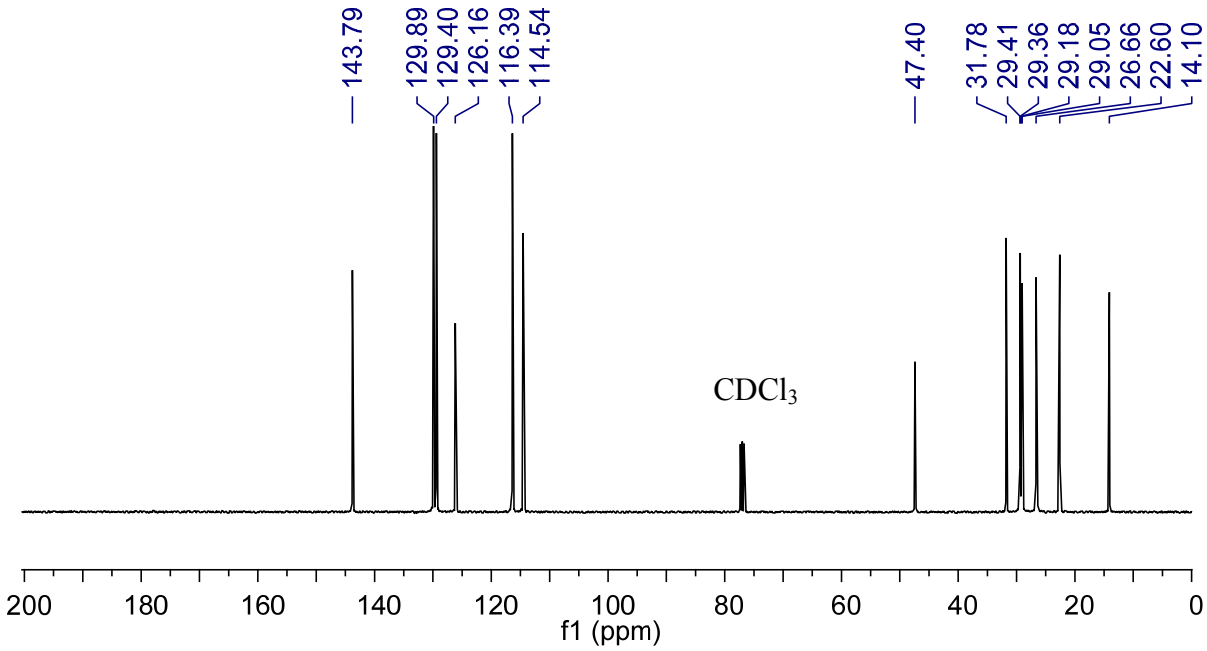
Figure S5: ^{1}H and ^{13}C NMR of all newly synthesized compounds.

1

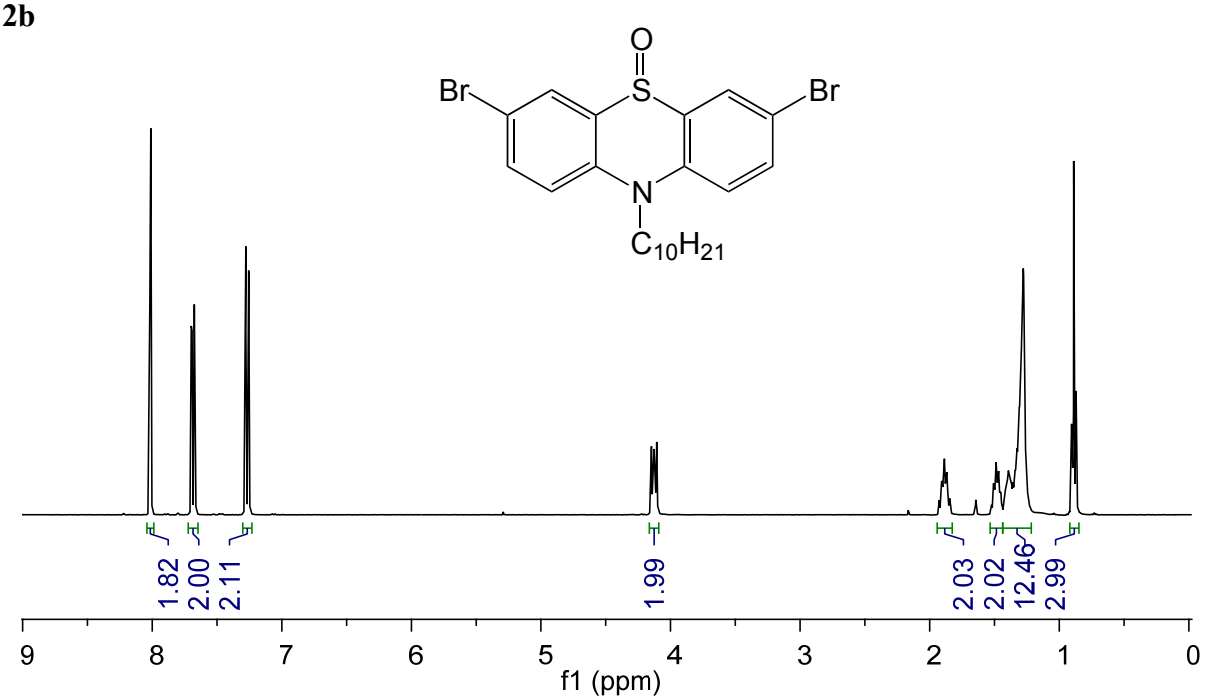


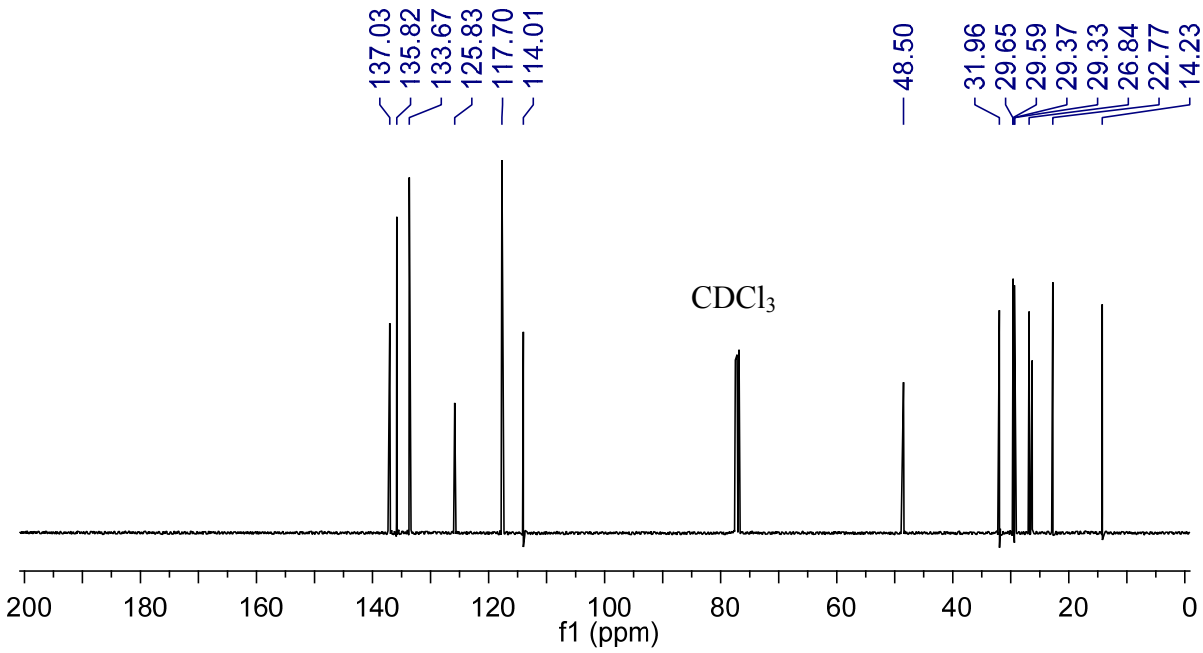
2a


Br
S
Br
N
$C_{10}H_{21}$
2.03
1.83
2.06
1.93
2.04
2.11
12.37
3.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

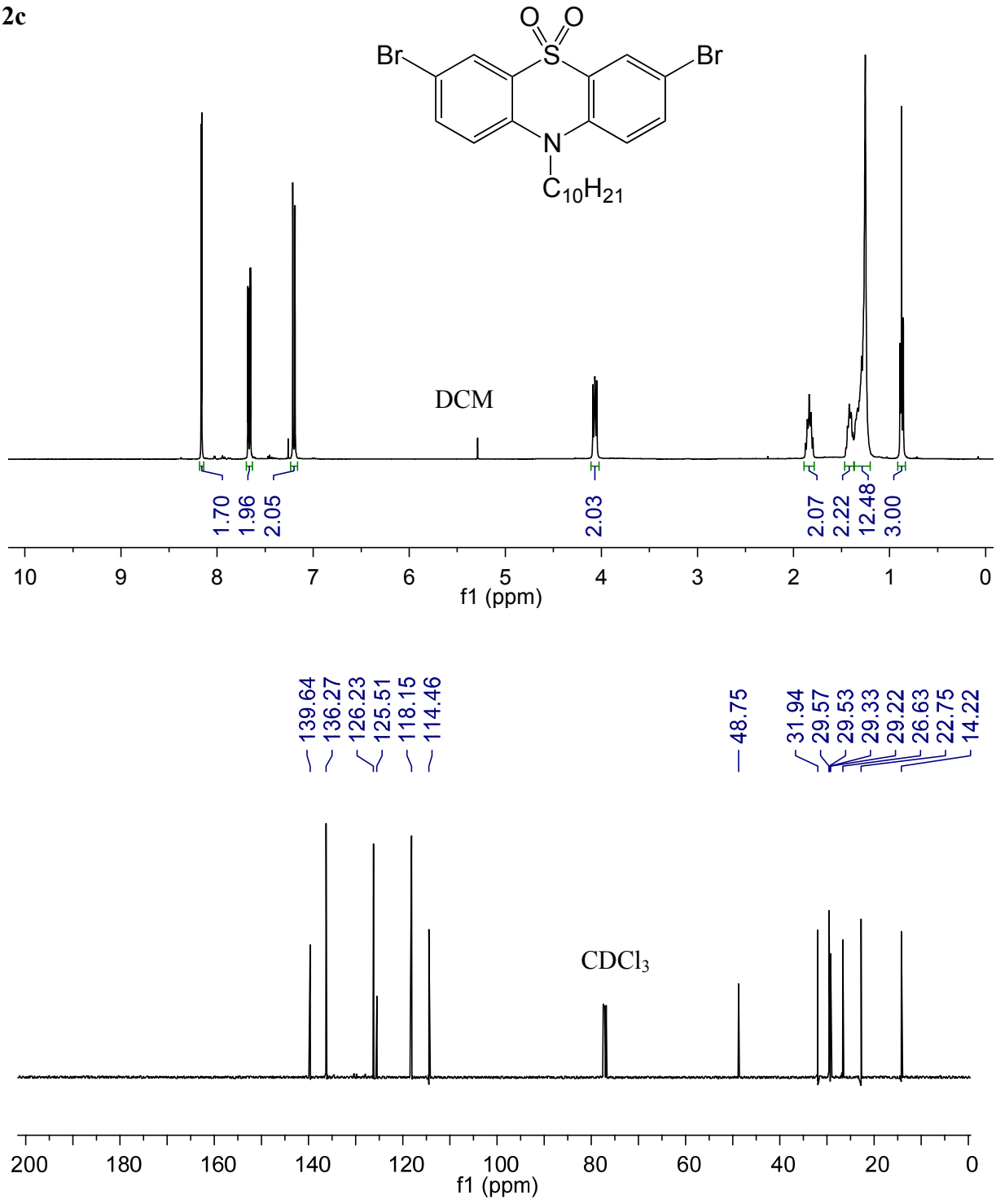

143.79
129.89
129.40
126.16
116.39
114.54
47.40
31.78
29.41
29.36
29.18
29.05
26.66
22.60
14.10
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

2b

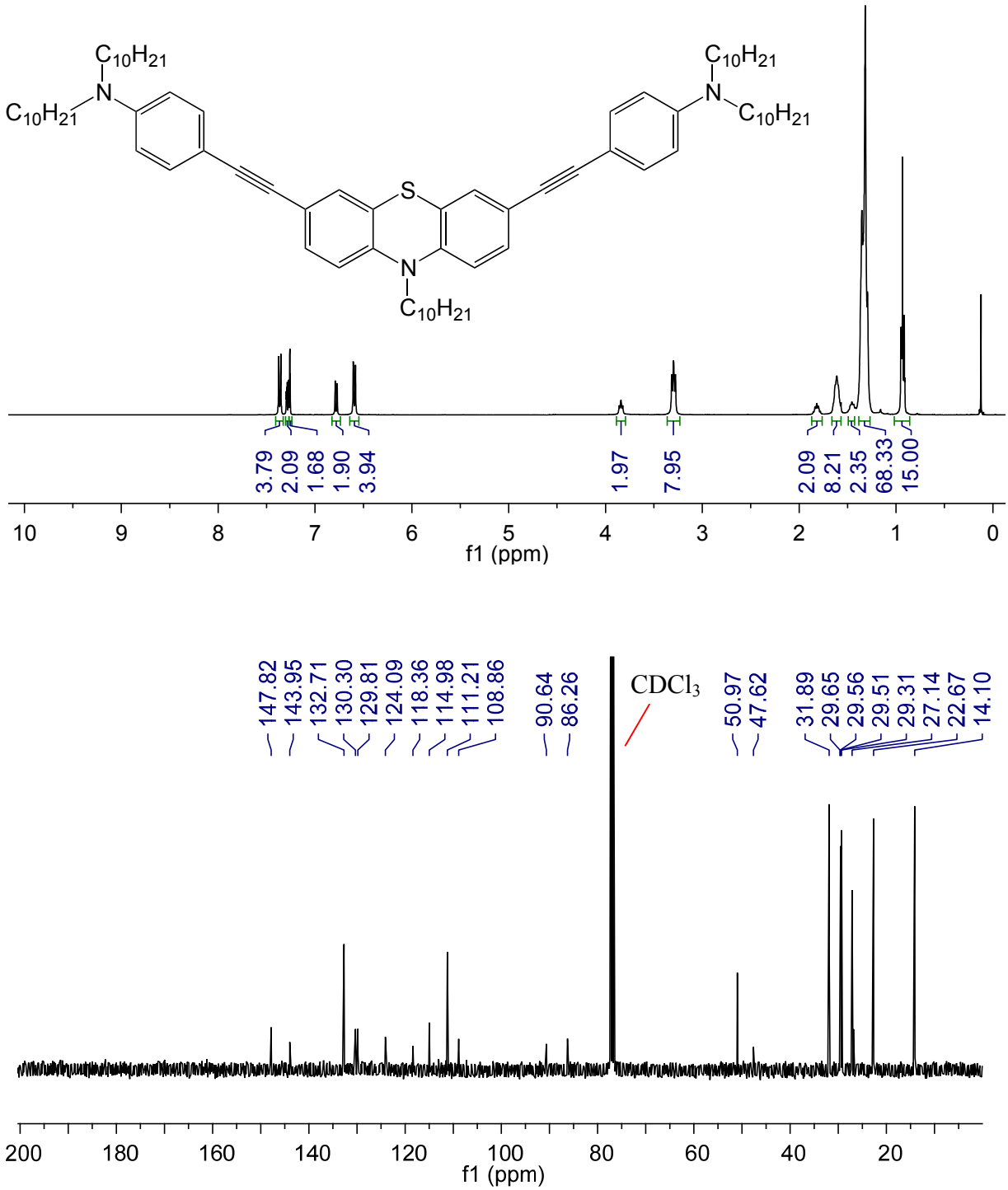

O
S
Br
Br
N
$C_{10}H_{21}$
1.82
2.00
2.11
1.99
2.03
2.02
12.46
2.99
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


137.03
135.82
133.67
125.83
117.70
114.01
48.50
31.96
29.65
29.59
29.37
29.33
26.84
22.77
14.23
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

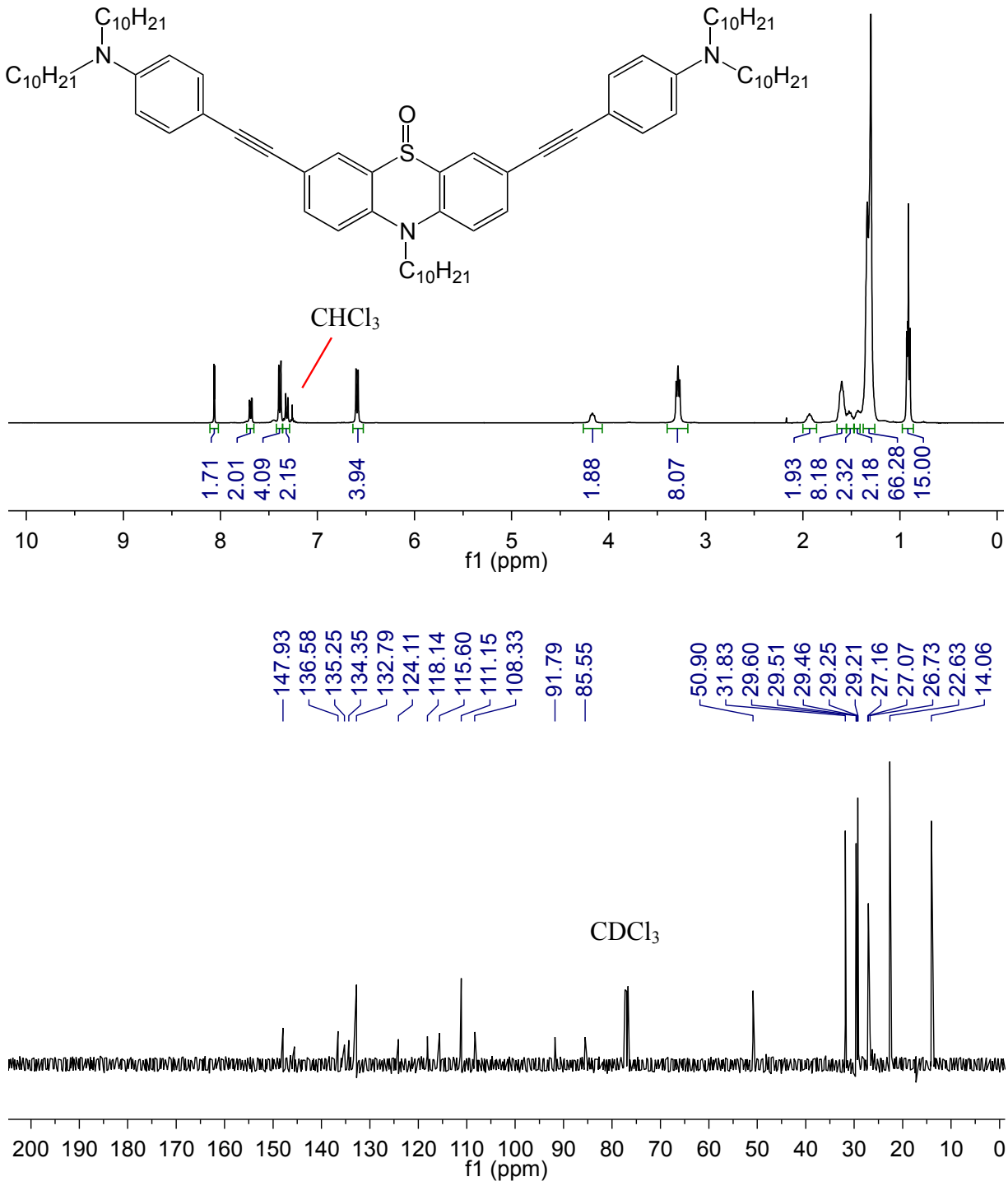
2c


O
O
S
Br
Br
N
$C_{10}H_{21}$
DCM
1.70
1.96
2.05
2.03
2.07
2.22
12.48
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
139.64
136.27
126.23
125.51
118.15
114.46
48.75
31.94
29.57
29.53
29.33
29.22
26.63
22.75
14.22
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

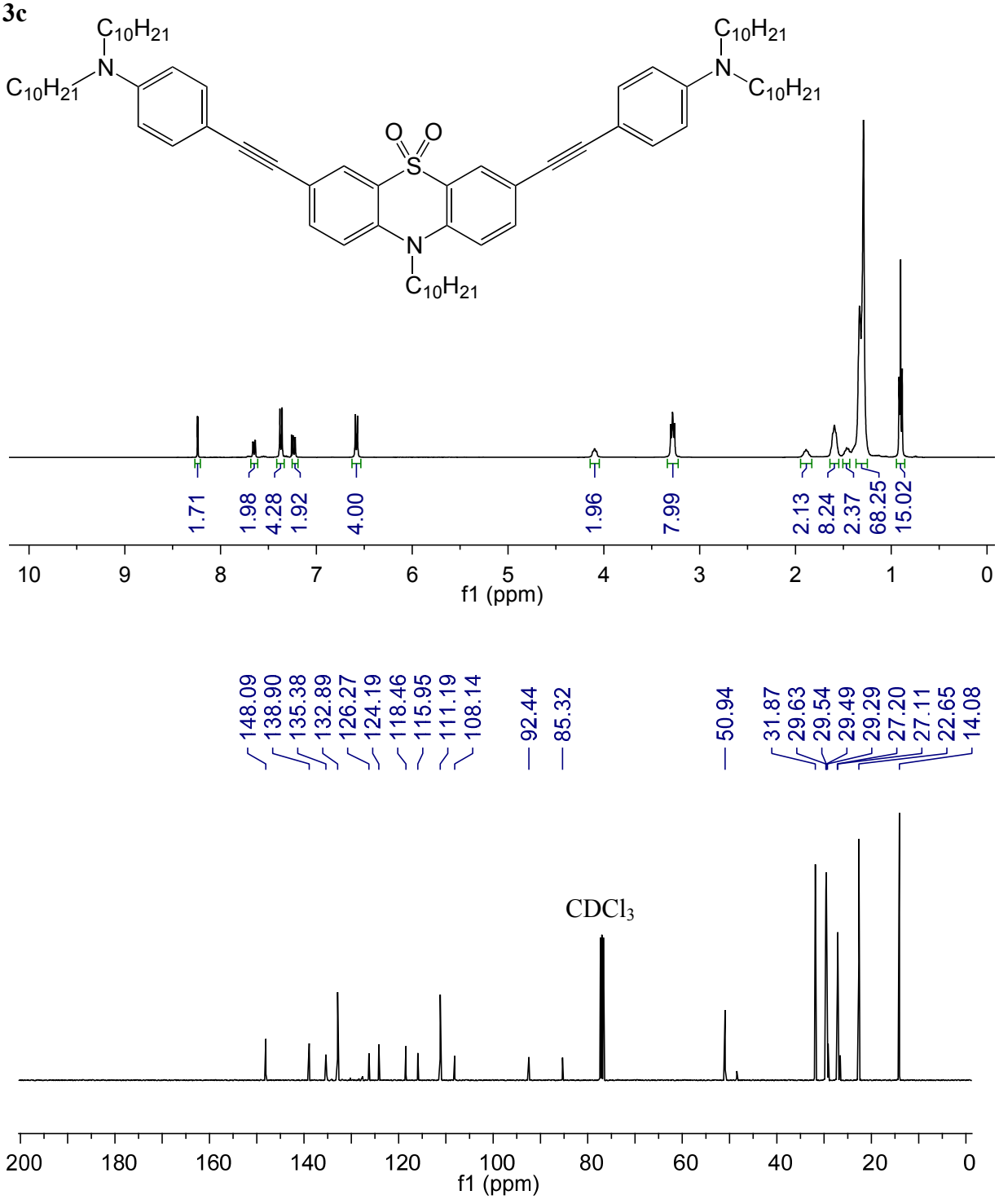
3a


C10H21
N
C10H21
S
N
C10H21
3.79
2.09
1.68
1.90
3.94
1.97
7.95
2.09
8.21
2.35
68.33
15.00
f1 (ppm)
147.82
143.95
132.71
130.30
129.81
124.09
118.36
114.98
111.21
108.86
90.64
86.26
CDCl3
50.97
47.62
31.89
29.65
29.56
29.51
29.31
27.14
22.67
14.10
f1 (ppm)

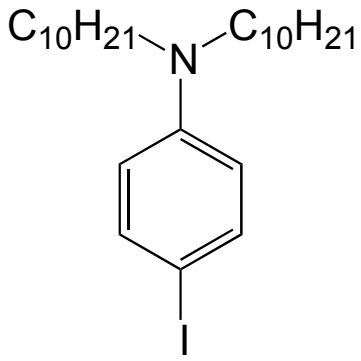
3b


C10H21
N
C10H21
C10H21
N
C10H21
O
S
N
C10H21
CHCl3
1.71
2.01
4.09
2.15
3.94
1.88
8.07
1.93
8.18
2.32
2.18
66.28
15.00
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
147.93
136.58
135.25
134.35
132.79
124.11
118.14
115.60
111.15
108.33
91.79
85.55
50.90
31.83
29.60
29.51
29.46
29.25
29.21
27.16
27.07
26.73
22.63
14.06
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

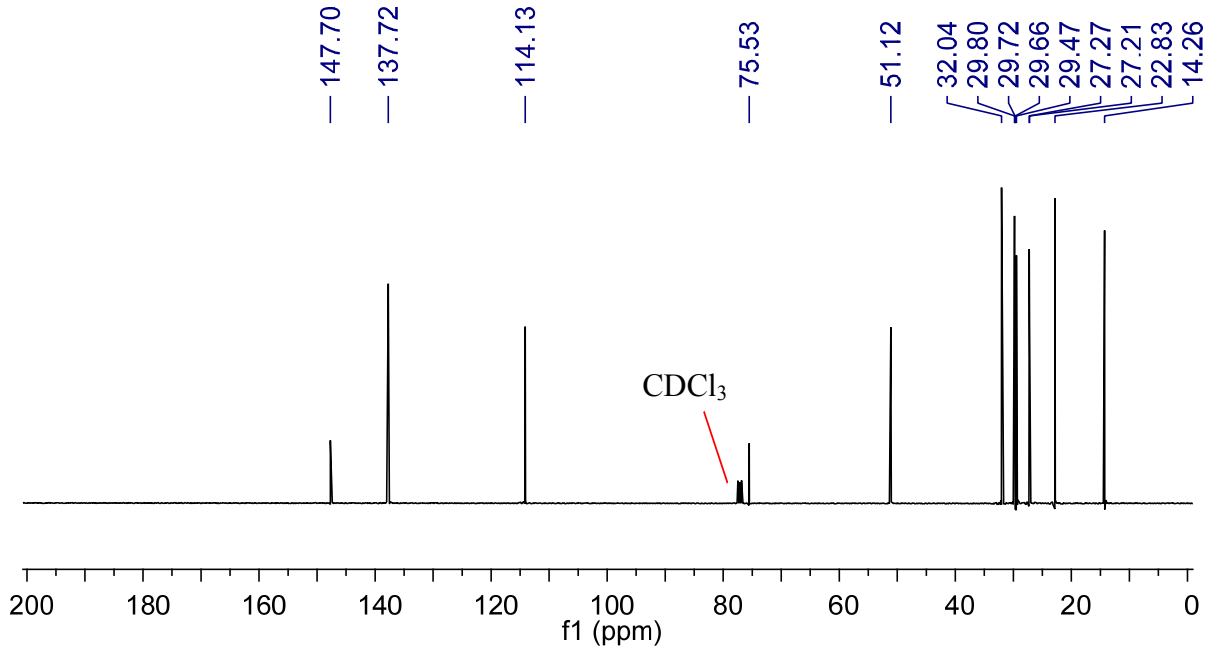
3c


C10H21
N
C10H21
C10H21
N
C10H21
O
O
S
N
C10H21
1.71
1.98
4.28
1.92
4.00
1.96
7.99
2.13
8.24
2.37
68.25
15.02
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
148.09
138.90
135.38
132.89
126.27
124.19
118.46
115.95
111.19
108.14
92.44
85.32
50.94
31.87
29.63
29.54
29.49
29.29
27.20
27.11
22.65
14.08
CDCl3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

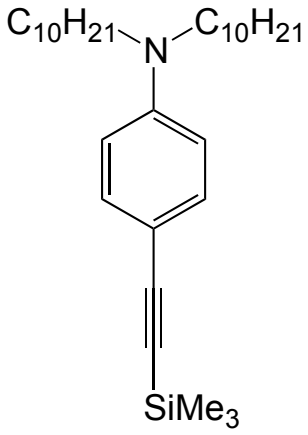
5


$C_{10}H_{21}$
N
$C_{10}H_{21}$
I

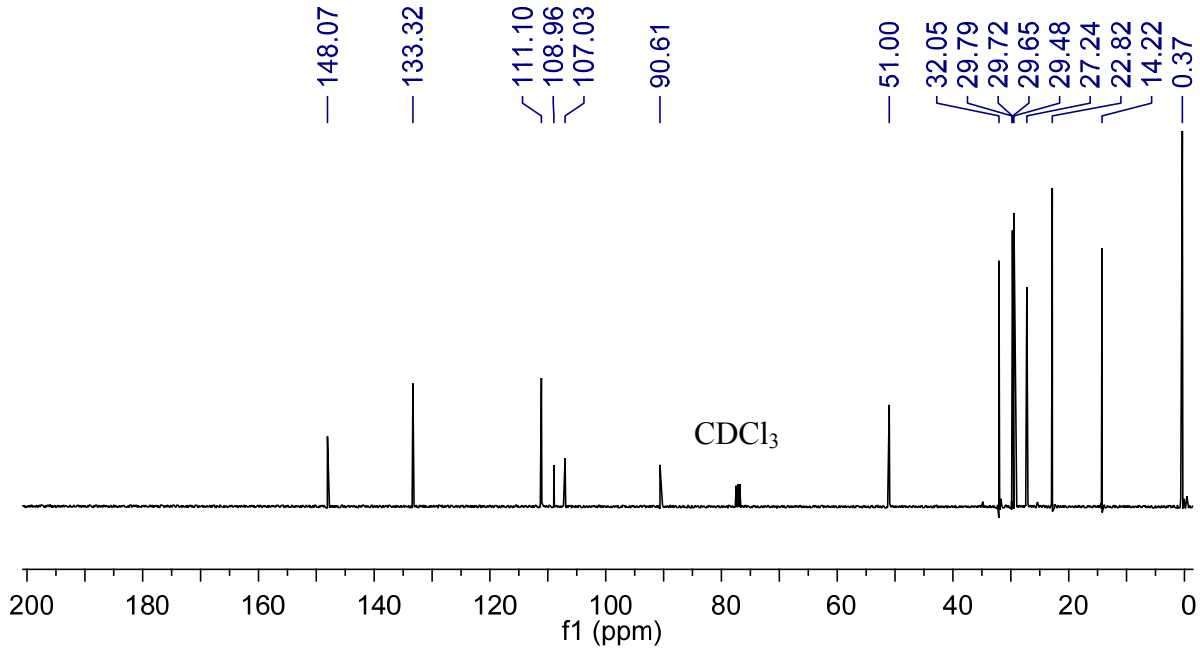
1.98
2.04
4.08
4.08
28.33
6.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


147.70
137.72
114.13
75.53
51.12
32.04
29.80
29.72
29.66
29.47
27.27
27.21
22.83
14.26
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

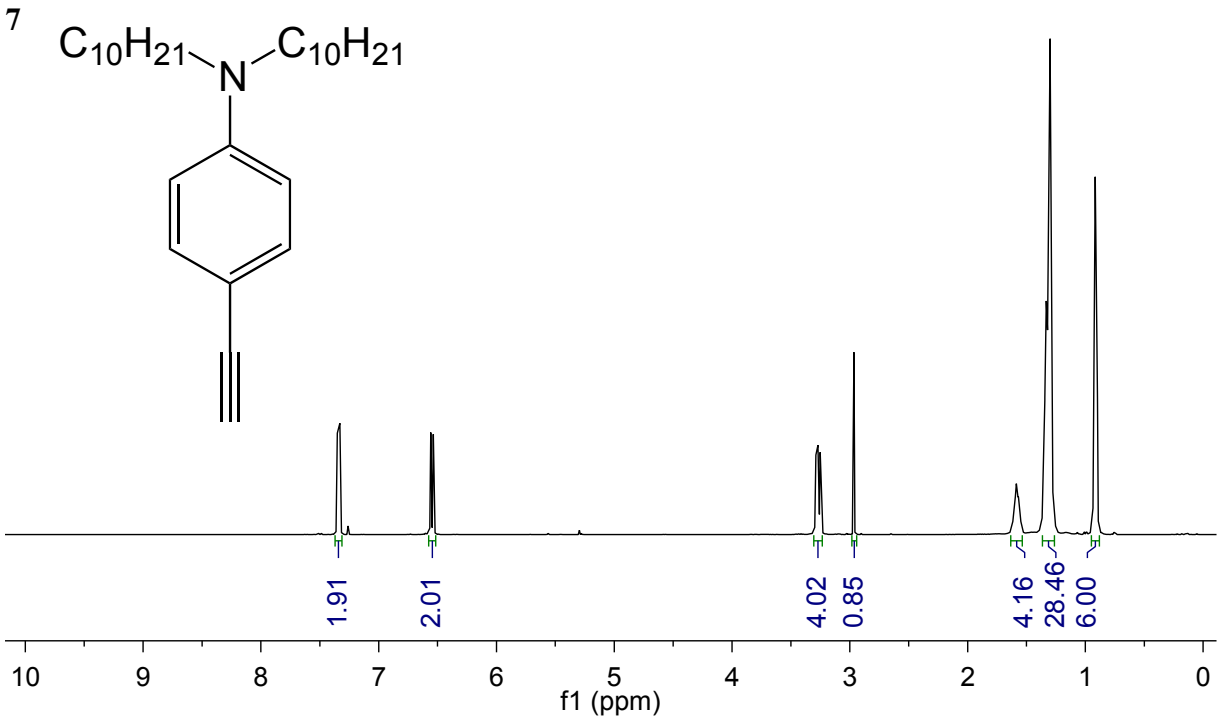
6


$C_{10}H_{21}$
N
$C_{10}H_{21}$
$SiMe_3$

2.00
2.02
4.04
4.18
28.39
6.16
8.97
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


148.07
133.32
111.10
108.96
107.03
90.61
51.00
32.05
29.79
29.72
29.65
29.48
27.24
22.82
14.22
0.37
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

7


C10H21
N
C10H21
1.91
2.01
4.02
0.85
4.16
28.46
6.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

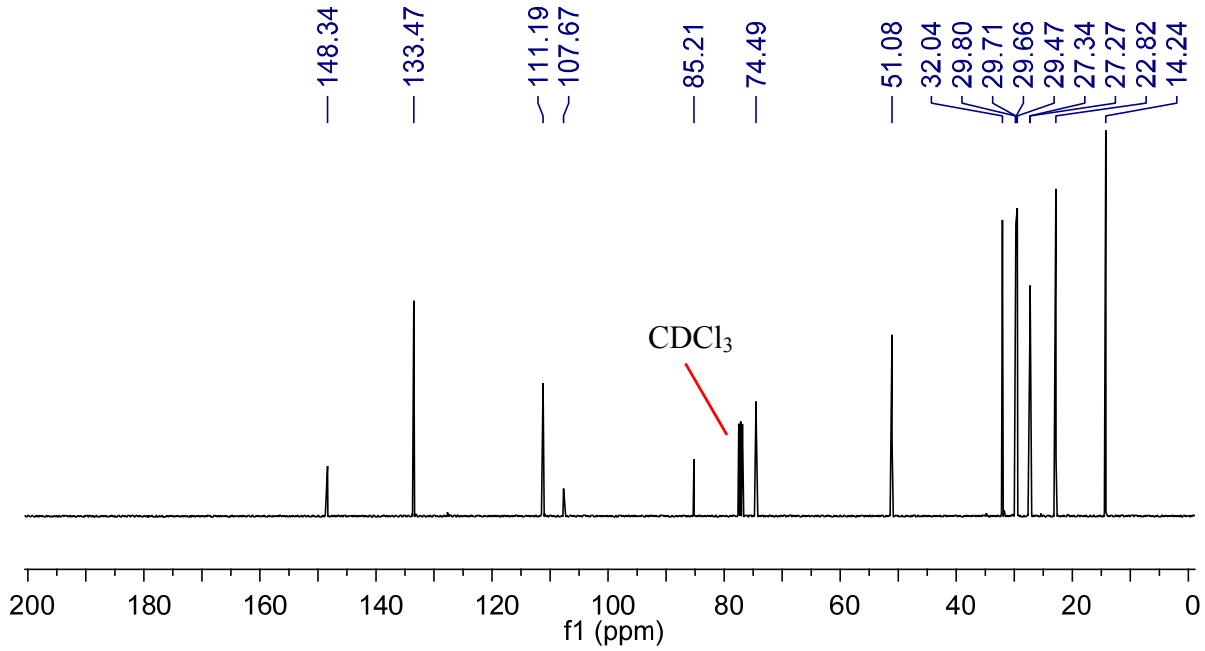
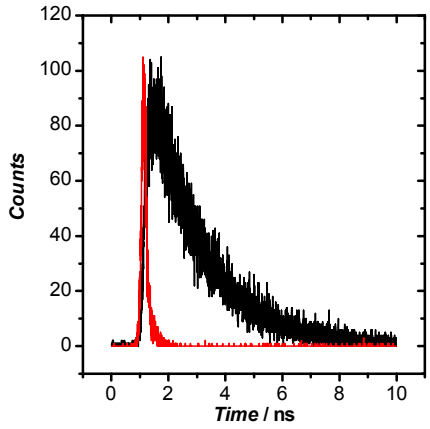
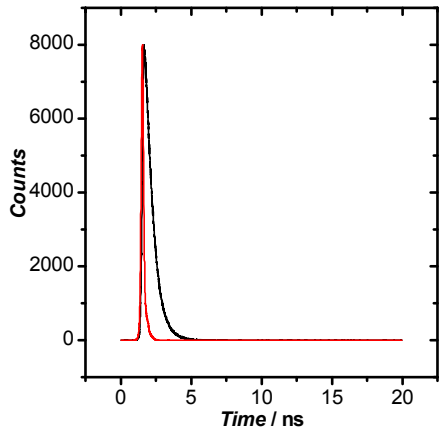

148.34
133.47
111.19
107.67
85.21
74.49
51.08
32.04
29.80
29.71
29.66
29.47
27.34
27.27
22.82
14.24
CDCl3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

Figure S6: Transient lifetime (Black) and instrument response (Red) of **3a**, **3b** and **3c**

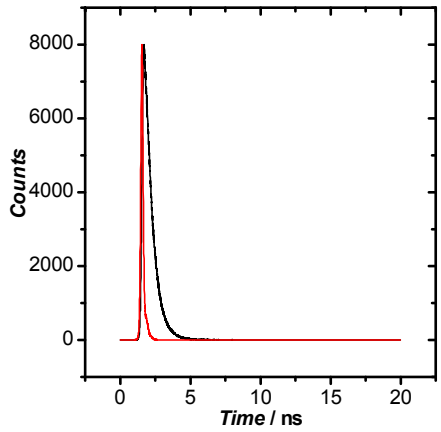
3a



3b



3c



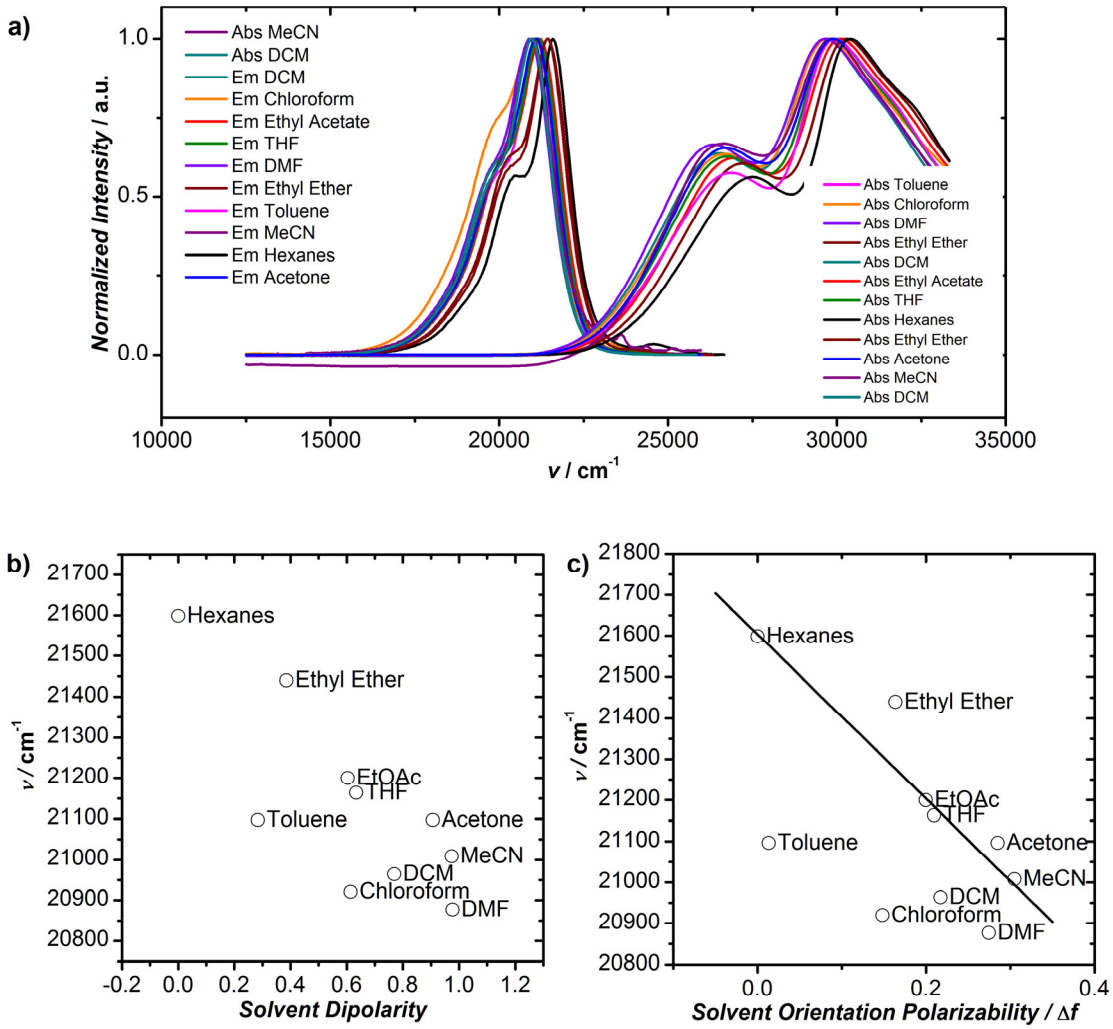


Fig S7a. a) Absorption and emission spectra of **3a** in different solvents. b) Emission peak wavenumber as a function of solvent dipolarity (SdP) c) Emission peak wavenumber as a function of orientation polarizability.

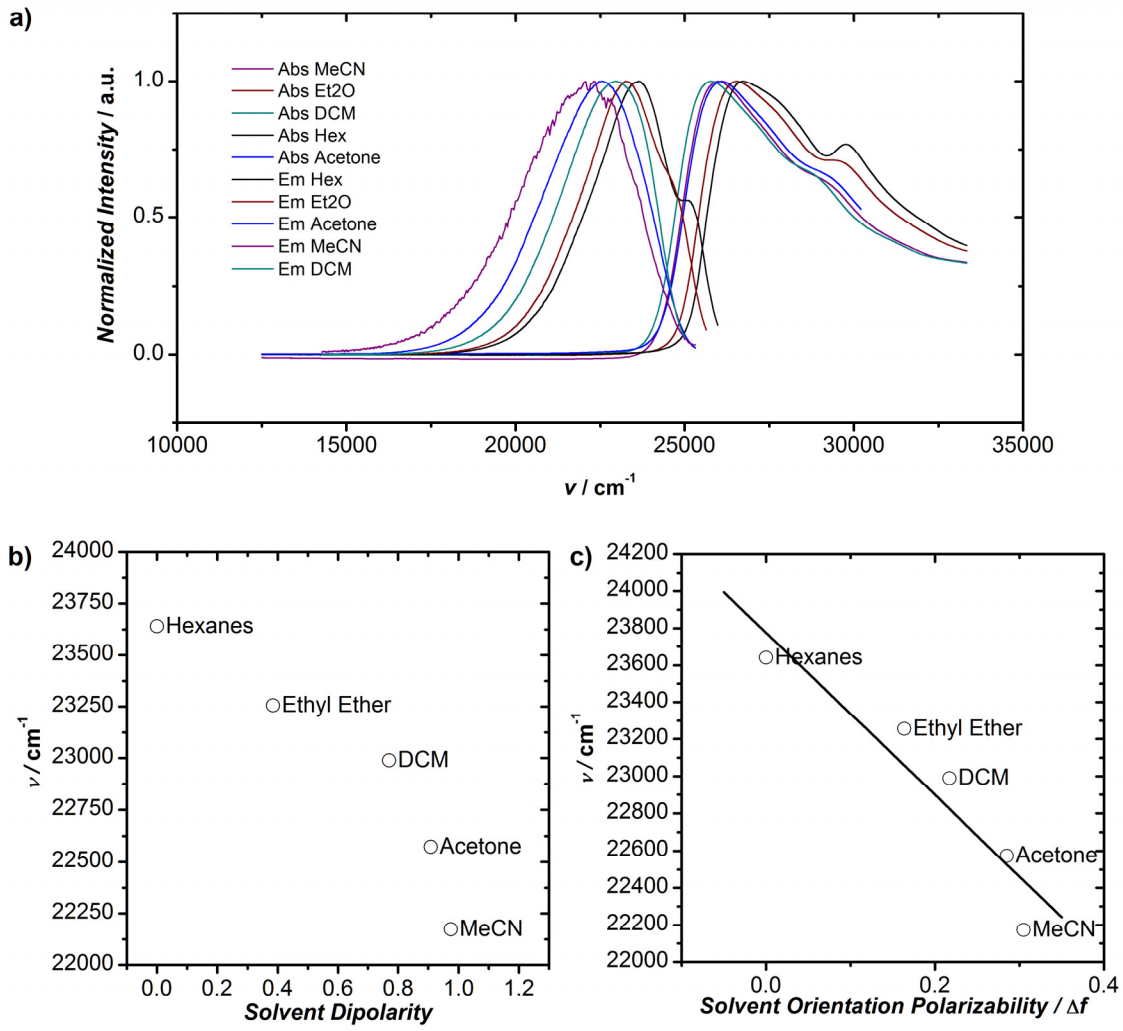


Fig S7b. a) Absorption and emission spectra of **3b** in different solvents. b) Emission peak wavenumber as a function of solvent dipolarity (SdP) c) Emission peak wavenumber as a function of orientation polarizability.

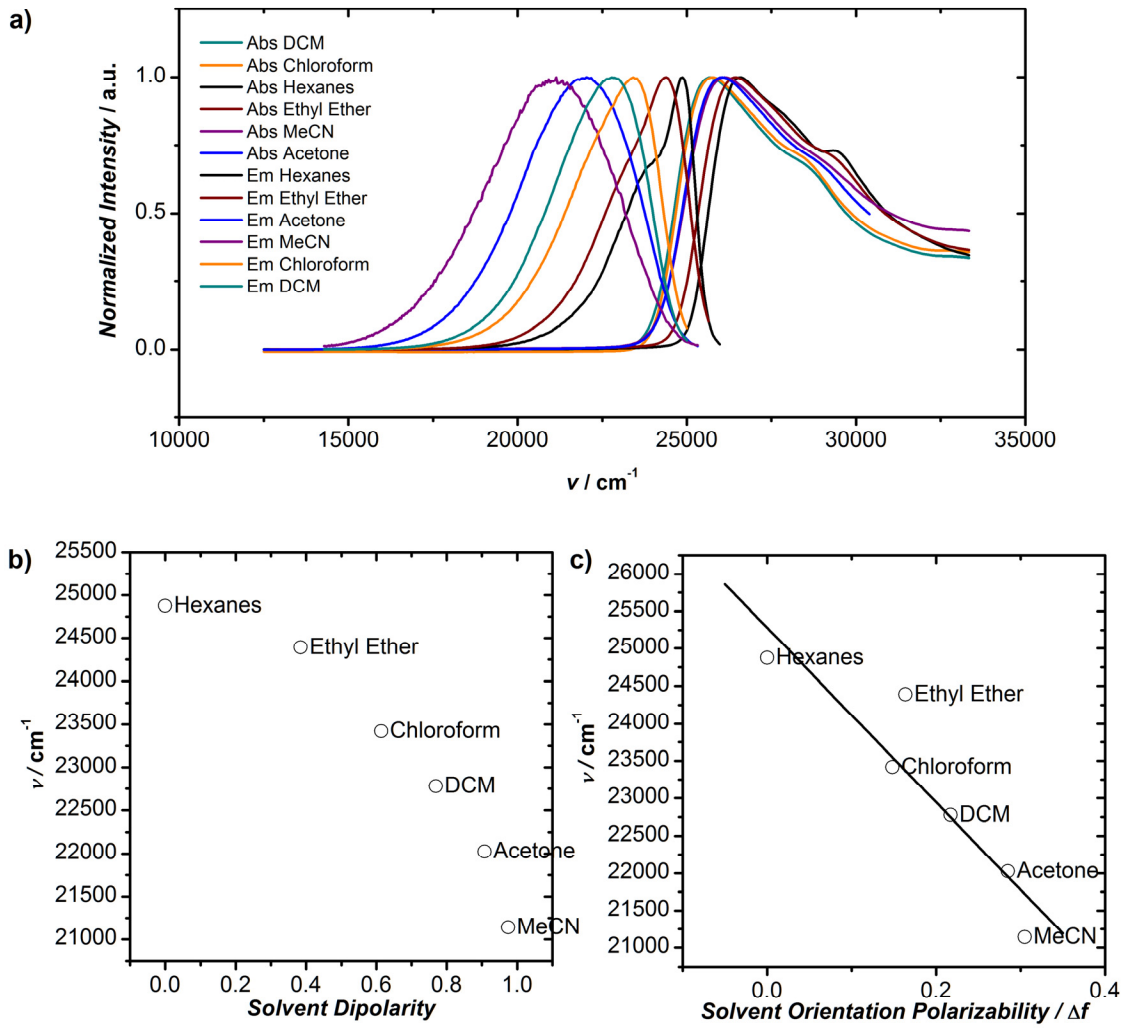


Fig S7c. a) Absorption and emission spectra of **3c** in different solvents. b) Emission peak wavenumber as a function of solvent dipolarity (SdP) c) Emission peak wavenumber as a function of orientation polarizability.

S8. Multi-parameter solvent effect analysis of **3a**, **3b** and **3c**

Using the approach described by Catalán[1] to determine a multi-parameter general scale for describing the optical response in different solvents using solvent scales based on two specific scales (solvent acidity, SA and solvent basicity, SB) and two general scales (solvent polarizability, SP and solvent dipolarizability, SdP). The linear combination of solvent scales results in the following formula:

$$\nu = bSA + cSB + dSP + eSdP + \nu_0$$

where ν is the optical property of interest (absorption or emission peak) in wavenumbers, ν_0 is the frequency of the transition in absence of solvent (gas phase), SA, SB, SP and SdP are solvent parameters to describe solute-solvent interactions and coefficients *b* to *e* are regressions coefficients that correlate to the sensitivity of the optical property to the different solute-solvent parameters.

The multi-parameter regression analysis resulted in the following fits to the absorption and emission peaks.

3a (PTZ-thioether)

$\nu_{abs} = (-2712 \pm 522)SP - (783 \pm 100)SdP + (29221 \pm 349)$
$n = 11$; $R^2 = 0.94$

$\nu_{em} = (142 \pm 72)SB - (1875 \pm 206)SP - (560 \pm 49)SdP + (22742 \pm 141)$
$n = 11$; $R^2 = 0.98$

3b (PTZ-sulfoxide)

$\nu_{abs} = (-3350 \pm 559)SP + (642 \pm 82)SdP + (28818 \pm 349)$
$n = 5$; $R^2 = 0.98$

$\nu_{em} = (669 \pm 403)SB + (4136 \pm 1380)SP - (1730 \pm 217)SdP + (21035 \pm 903)$
$n = 5$; $R^2 = 0.98$

3c (PTZ-sulfone)

$\nu_{abs} = (-3593 \pm 297)SP - (445 \pm 60)SdP + (28823 \pm 194)$
$n = 6$; $R^2 = 0.98$

$\nu_{em} = (2750 \pm 206)SB + (7936 \pm 547)SP - (4778 \pm 107)SdP + (19817 \pm 377)$
$n = 6$; $R^2 = 0.99$

1 J. Catalán, *The Journal of Physical Chemistry B*, 2009, **113**, 5951-5960.