Electronic Supplementary Information (ESI)

Molecular Conformational Twist Dependent Wide Fluorescence Tuning and White Light Emission in a Single Fluorophore via Halochormism

Parthasarathy Gayathri,[a] Probal Nag,[b] Neethu Anand,[b] Sivaranjana Reddy Vennapusa,[b] Mehboobali Pannipara,[c,d] Abdullah G. Al-Sehemi,[c,d] Dohyun Moon*[e] Savarimuthu Philip Anthony*[a]

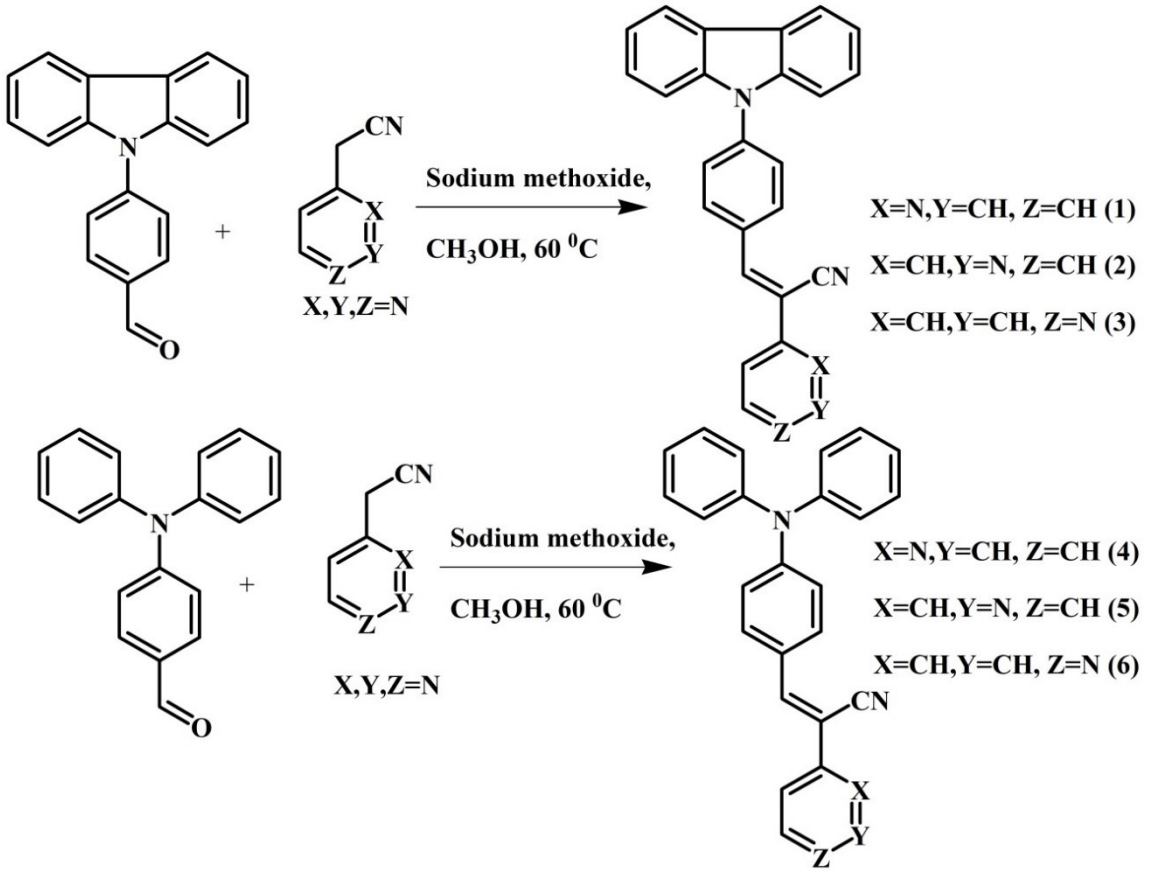
[a)]School of Chemical & Biotechnology, SASTRA Deemed University, Thanjavur-613401, Tamil Nadu, India. Fax: +914362264120; Tel: +914362264101; E-mail: philip@biotech.sastra.edu

[b)]School of chemistry, Indian Institute of Science Education and Research, Thiruvananthapuram, Kerala-695551, India

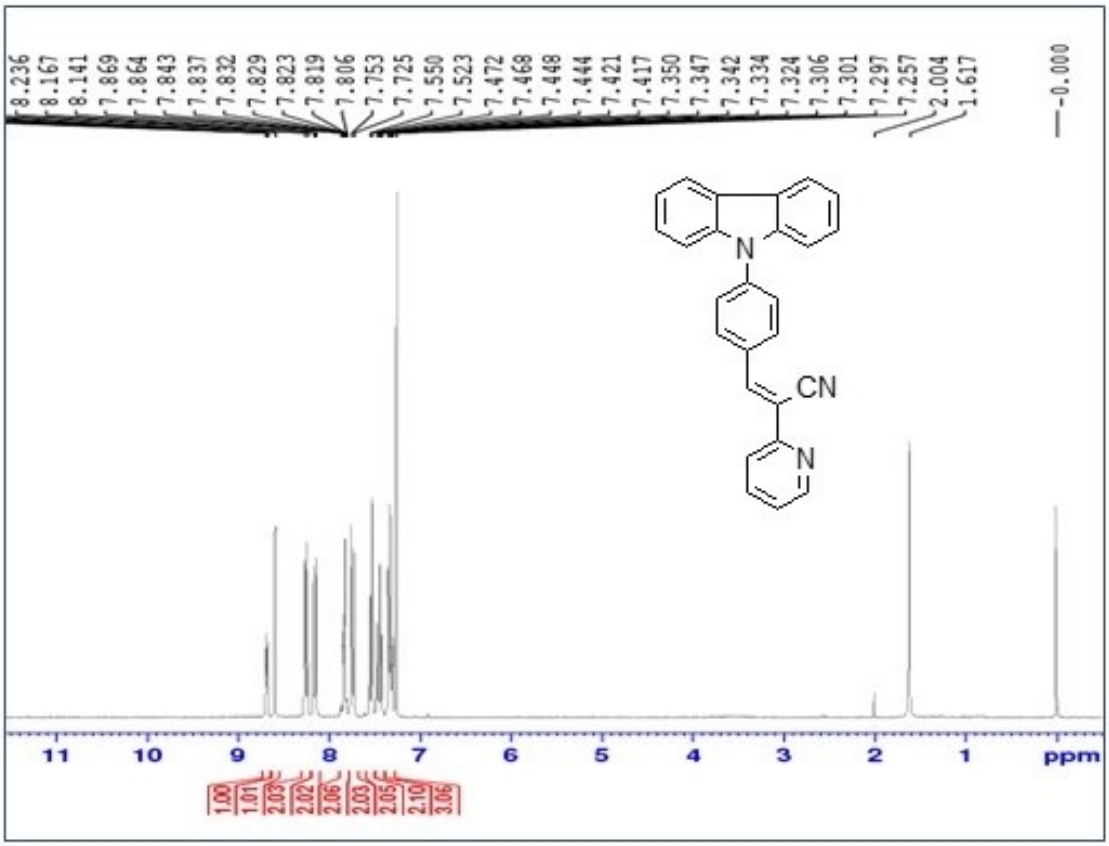
[b)]Department of chemistry, King Khalid University, Abha 61413, Saudi Arabia.

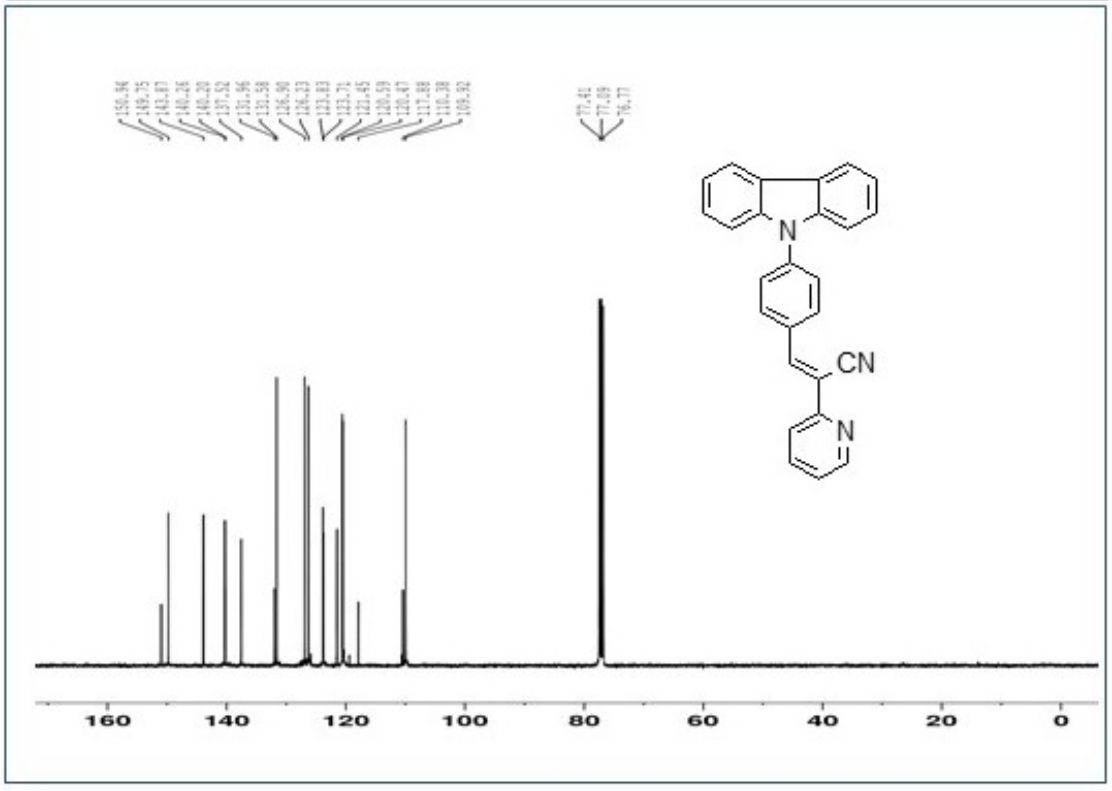
[c)]Research center for Advanced Materials Science, King Khalid University, Abha 61413, Saudi Arabia.

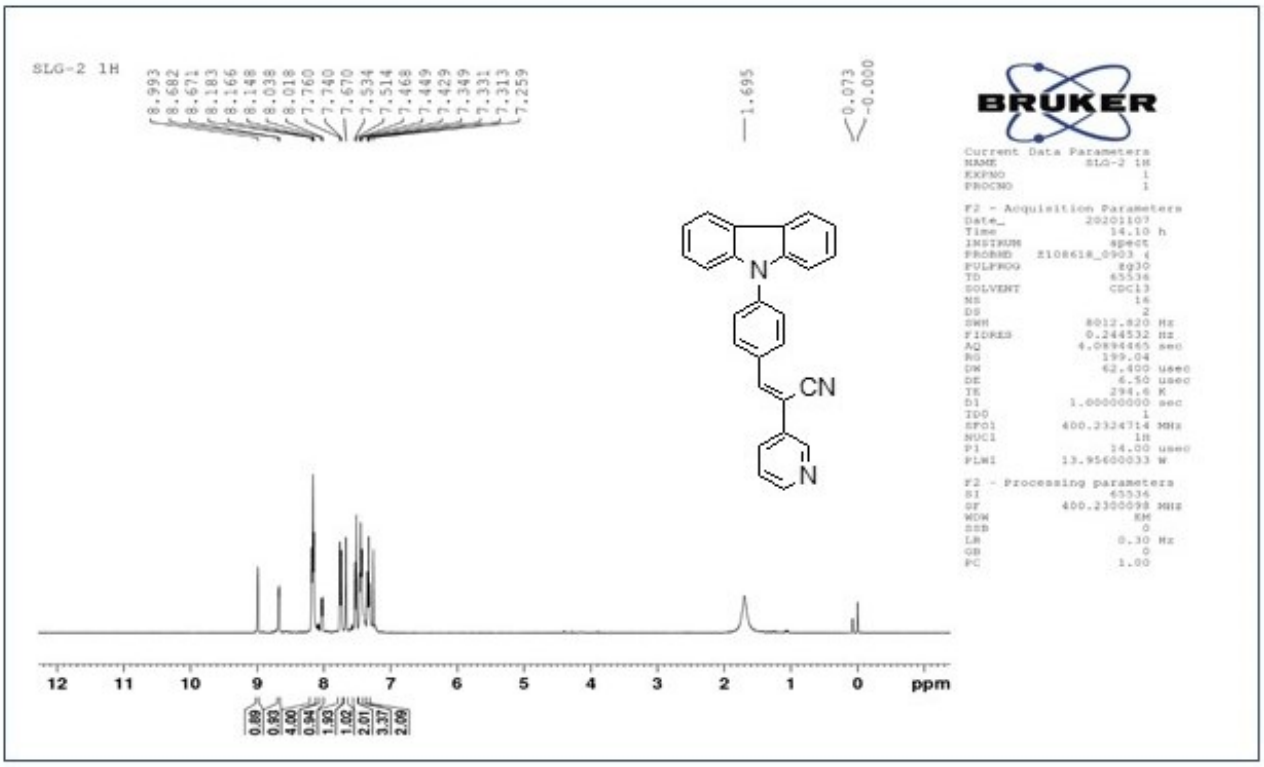
[b)]Beamline Department, Pohang Accelerator Laboratory, 80 Jigokro-127beongil, Nam-gu, Pohang, Gyeongbuk, Korea, Email: dmoon@postech.ac.kr

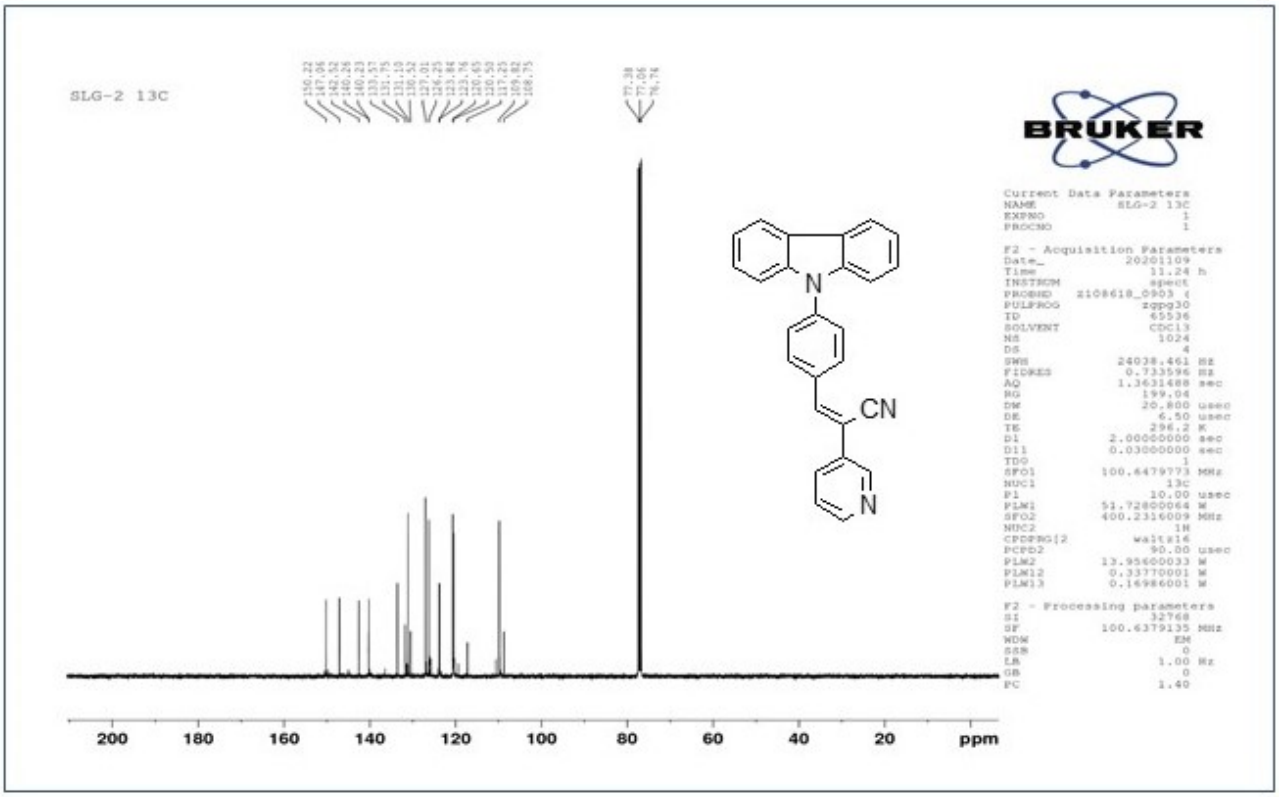


Scheme S1. Synthesis of carbazole and triphenylamine based isomers (**1-6**).

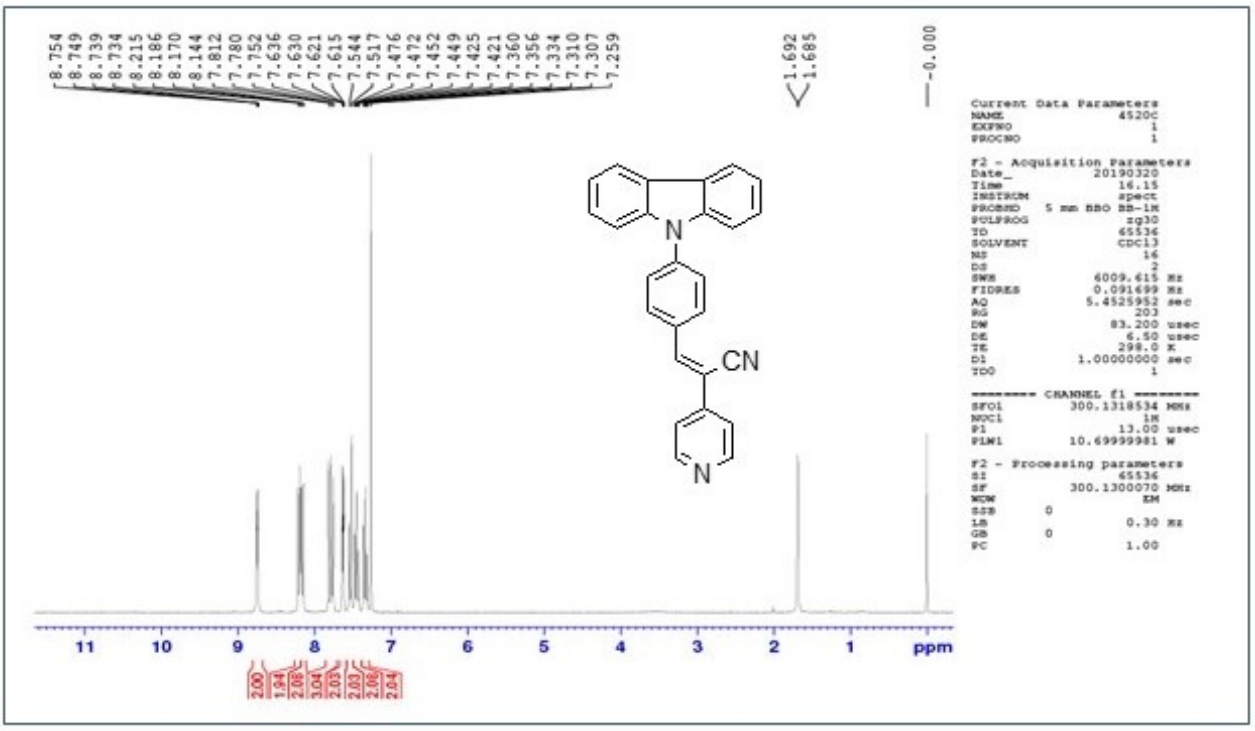

8.236
8.167
8.141
7.869
7.864
7.843
7.837
7.832
7.829
7.823
7.819
7.806
7.753
7.725
7.550
7.523
7.472
7.468
7.448
7.444
7.421
7.417
7.350
7.347
7.342
7.334
7.324
7.306
7.301
7.297
7.257
2.004
1.617
-0.000
N
CN
N
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
2.03
2.02
2.06
2.03
2.05
2.10
3.06

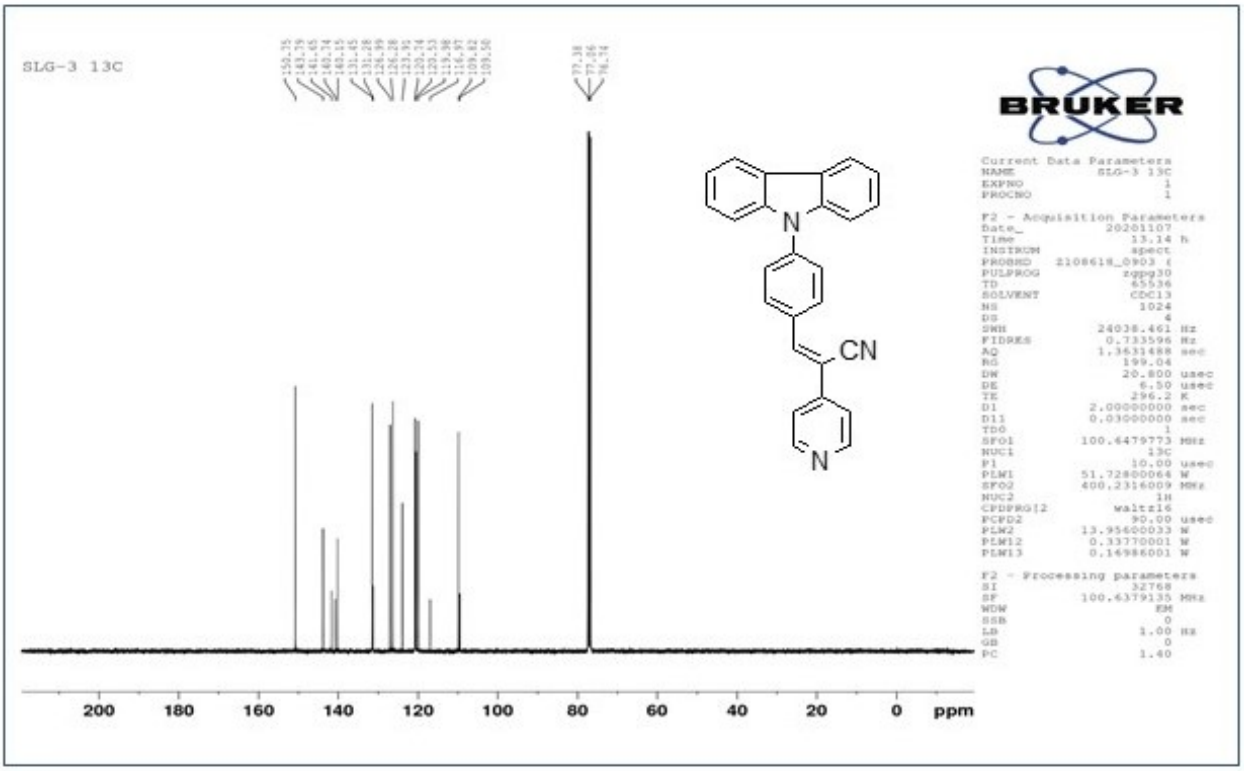

150.94
149.75
143.87
140.26
140.20
137.52
131.96
131.58
126.90
126.33
123.83
123.71
123.45
120.59
120.47
117.88
110.38
109.92
77.41
77.09
76.77
N
CN
N
160
140
120
100
80
60
40
20
0


SLG-2 1H
8.993
8.682
8.671
8.183
8.166
8.148
8.038
8.018
7.760
7.740
7.670
7.534
7.514
7.468
7.449
7.429
7.349
7.331
7.313
7.259
1.695
0.073
-0.000
N
CN
N
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.89
0.93
4.00
0.94
1.93
1.02
2.01
3.37
2.09
BRUKER
Current Data Parameters
NAME SLG-2 1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201107
Time 14.10 h
INSTRUM spect
PROBHD Z108618_0903 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 199.04
DW 62.400 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
IPO 1
SFO1 400.2324714 MHz
NUC1 1H
P1 14.00 usec
PLW1 13.95600033 W
F2 - Processing parameters
SI 65536
SF 400.2300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

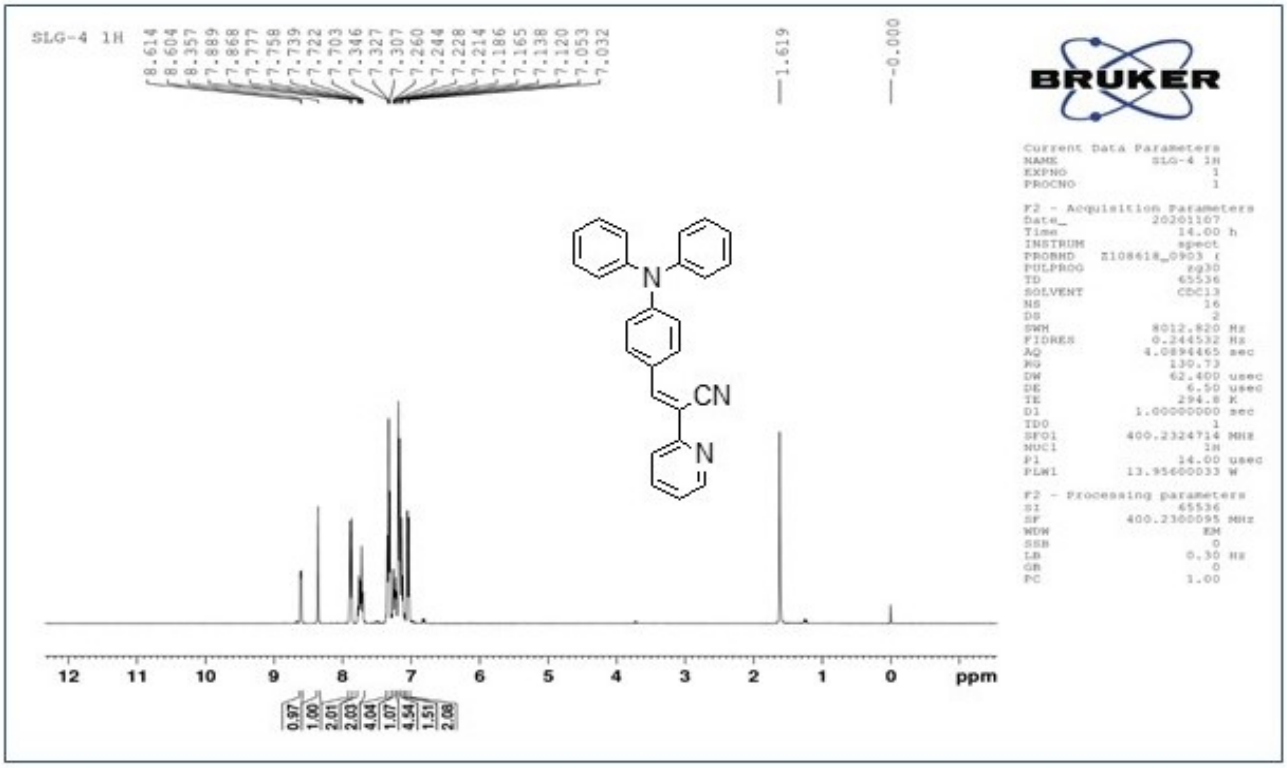

SLG-2 13C
150.22
147.06
142.52
140.26
140.23
133.57
131.75
131.10
130.52
127.01
124.21
123.84
123.76
120.65
120.50
117.25
109.82
108.75
77.38
77.06
76.74
N
CN
N
200
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME SLG-2 13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201109
Time 11.24 h
INSTRUM spect
PROBHD Z108618_0903 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 199.04
DW 20.800 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6479773 MHz
NUC1 13C
P1 10.00 usec
PLW1 51.72800064 W
SFO2 400.2316009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.95600033 W
PLW12 0.33770001 W
PLW13 0.16986001 W
F2 - Processing parameters
SI 32768
SF 100.6379135 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

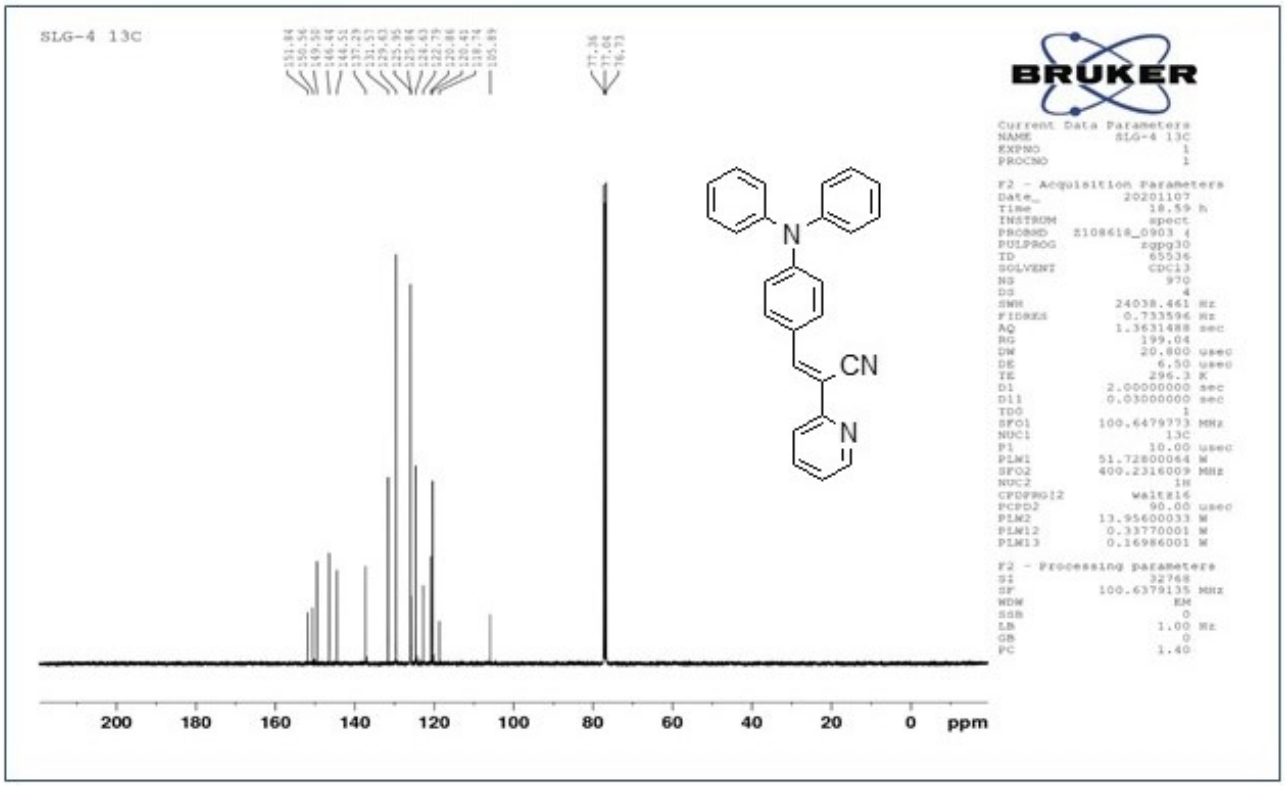
^{1}H and ^{13}C NMR of ***2.***


8.754
8.749
8.739
8.734
8.215
8.186
8.170
8.144
7.812
7.780
7.752
7.636
7.630
7.621
7.615
7.544
7.517
7.476
7.472
7.452
7.449
7.425
7.421
7.360
7.356
7.334
7.310
7.307
7.259
1.692
1.685
-0.000
N
CN
N
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.84
2.05
3.04
2.03
2.03
2.06
2.04
Current Data Parameters
NAME 4520C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190320
Time 16.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.091699 Hz
AQ 5.4525952 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.1318534 MHz
NUC1 1H
P1 13.00 usec
PLW1 10.69999981 W
F2 - Processing parameters
SI 65536
SF 300.1300070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

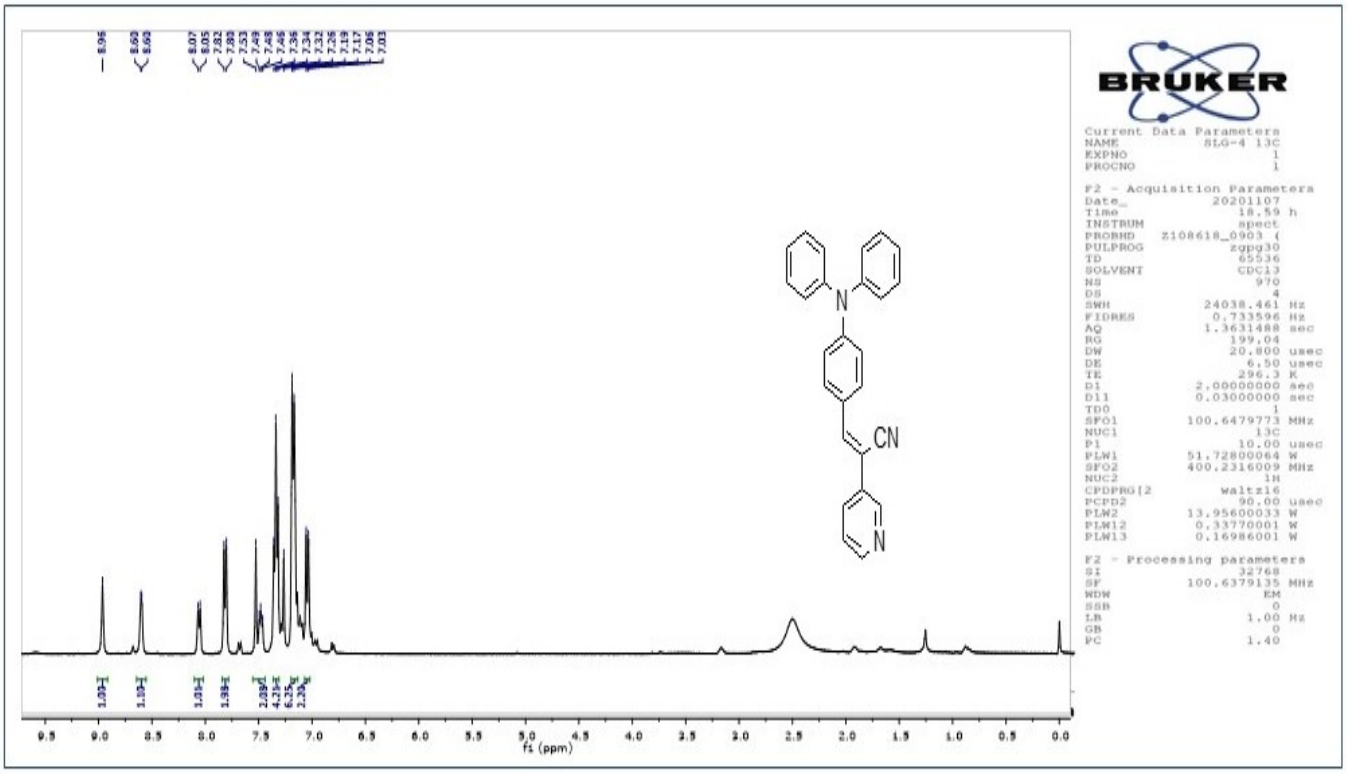

SLG-3 13C
150.35
143.59
141.65
140.34
140.15
131.45
131.28
126.99
126.28
123.76
123.24
120.53
119.98
114.97
109.82
109.58
77.38
77.06
76.74
N
CN
N
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME SLG-3 13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201107
Time 13.14 h
INSTRUM spect
PROBHD 2108618_0903 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 199.04
DW 20.800 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6479773 MHz
NUC1 13C
P1 10.00 usec
PLW1 51.72800064 W
SFO2 400.2316009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.95600033 W
PLW12 0.33770001 W
PLW13 0.16986001 W
F2 - Processing parameters
SI 32768
SF 100.6379135 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

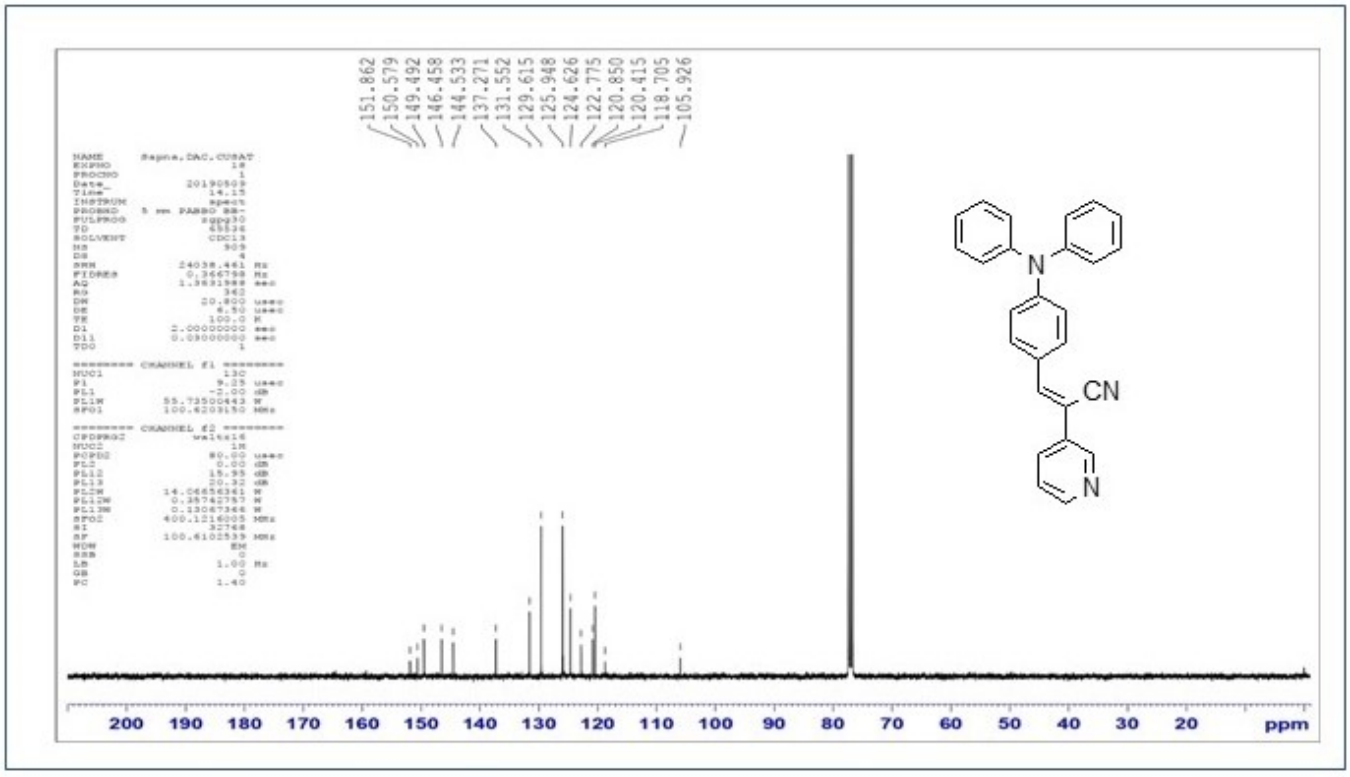
^{1}H and ^{13}C NMR of ***3.***


SLG-4 1H
8.614
8.604
8.357
7.889
7.868
7.777
7.758
7.739
7.722
7.703
7.346
7.327
7.307
7.260
7.244
7.228
7.214
7.186
7.165
7.138
7.120
7.053
7.032
1.619
0.000
BRUKER
Current Data Parameters
NAME SLG-4 1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201107
Time 14.00 h
INSTRUM spect
PROBHD Z108618_0903 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 130.73
DW 62.400 usec
DE 6.50 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1
SFO1 400.2324714 MHz
NUC1 1H
P1 14.00 usec
PLW1 13.95600033 W
F2 - Processing parameters
SI 65536
SF 400.2300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
N
CN
N
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.97 1.00 2.01 2.03 4.04 1.07 4.54 1.51 2.08

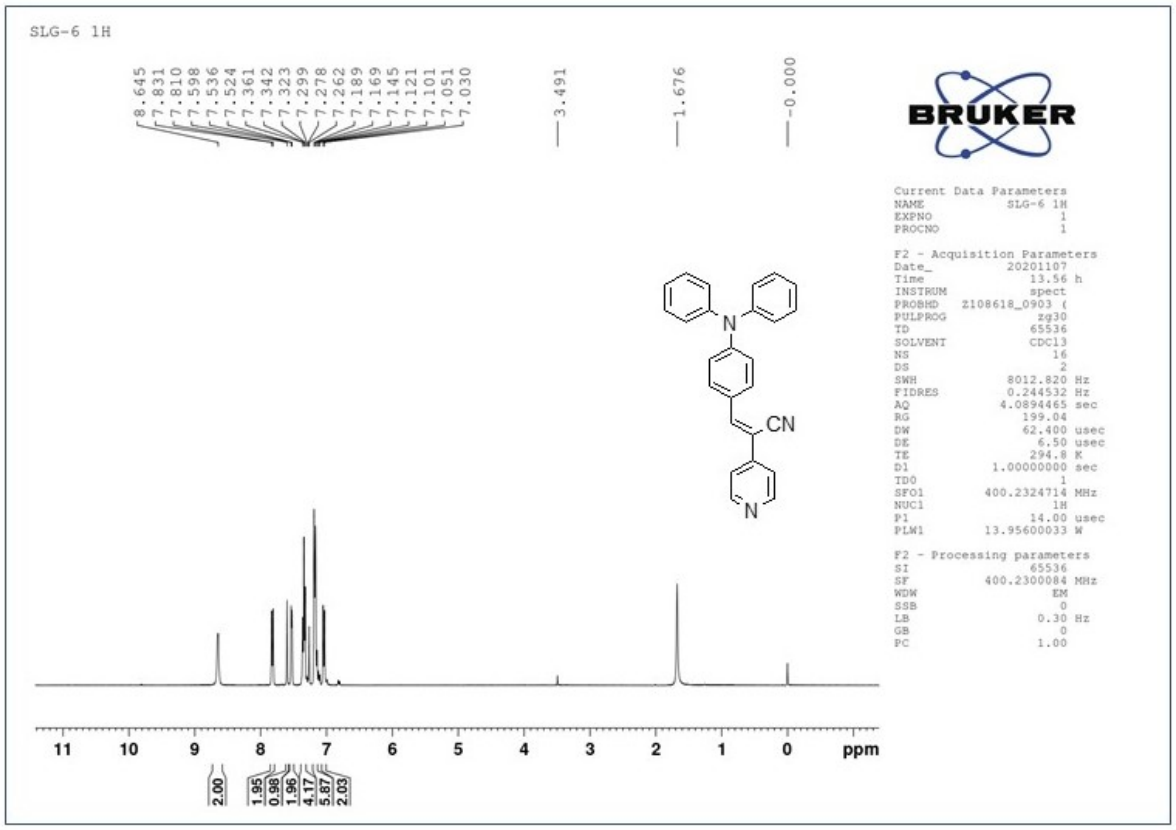

SLG-4 13C
151.84
150.56
149.30
146.44
144.51
137.29
131.53
129.63
125.95
125.84
124.63
122.79
120.86
120.41
118.74
105.89
77.36
77.04
76.73
BRUKER
Current Data Parameters
NAME SLG-4 13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201107
Time 18.59 h
INSTRUM spect
PROBHD Z108618_0903 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 970
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 199.04
DW 20.800 usec
DE 6.50 usec
TE 296.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6479773 MHz
NUC1 13C
P1 10.00 usec
PLW1 51.72800064 W
SFO2 400.2316009 MHz
NUC2 1H
CPDPRG12 waltz16
PCPD2 90.00 usec
PLW2 13.95600033 W
PLW12 0.33770001 W
PLW13 0.16986001 W
F2 - Processing parameters
SI 32768
SF 100.6379135 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CN
N
200 180 160 140 120 100 80 60 40 20 0 ppm

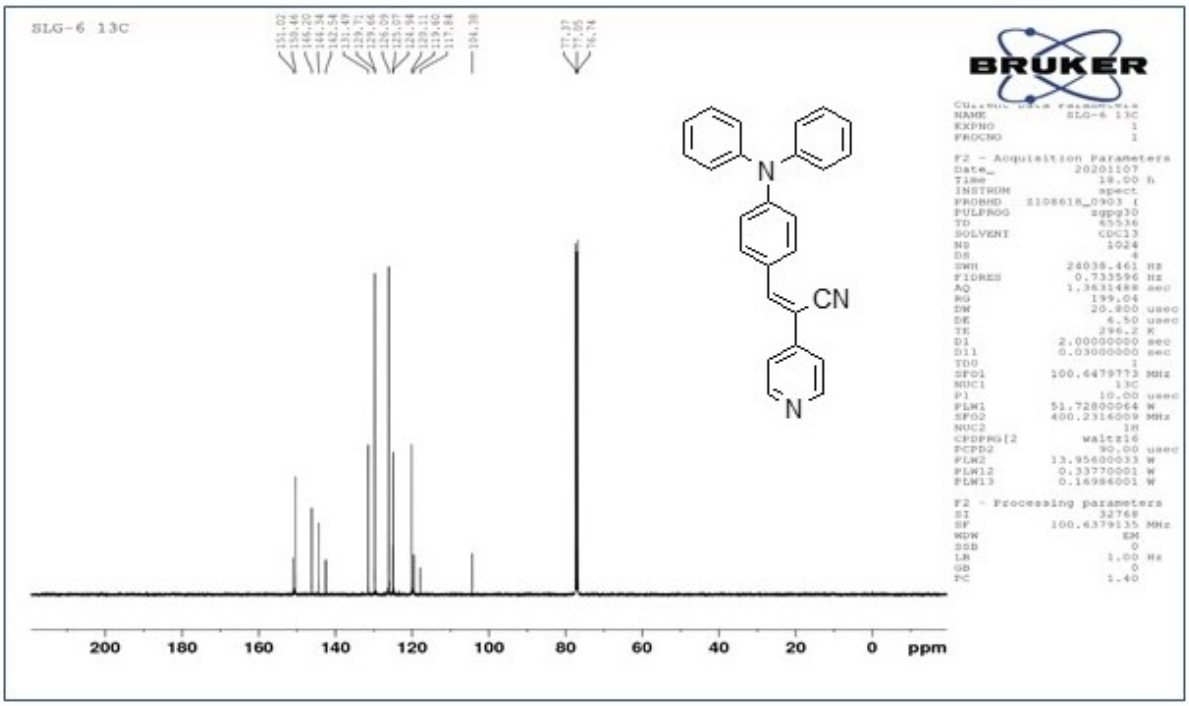
^{1}H and ^{13}C NMR of ***4.***


BRUKER
f1 (ppm)
CN
N

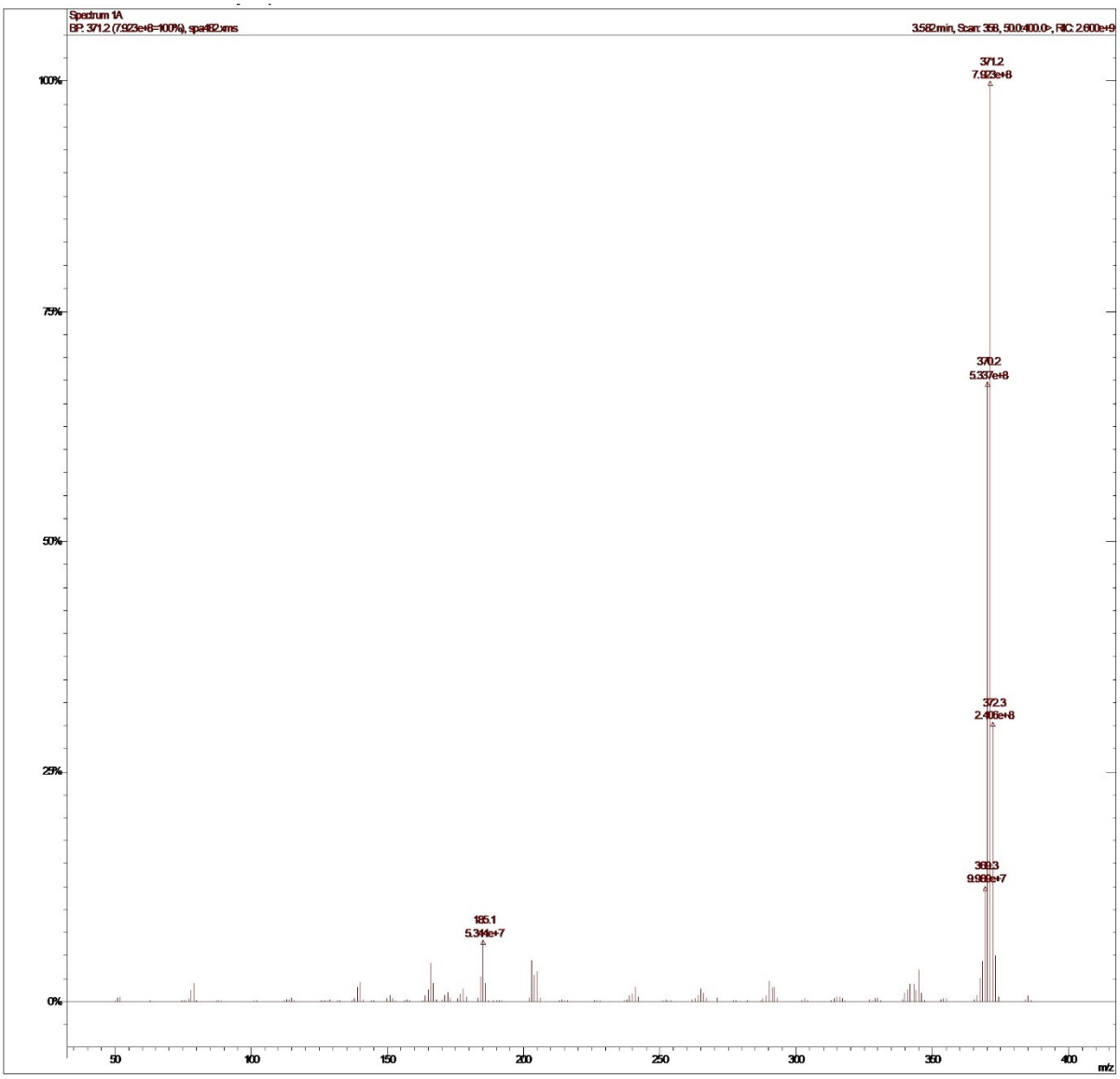

151.862
150.579
149.492
146.458
144.533
137.271
131.552
129.615
125.948
124.626
122.775
120.850
120.415
118.705
105.926
CN
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

^{1}H and ^{13}C NMR of ***5.***

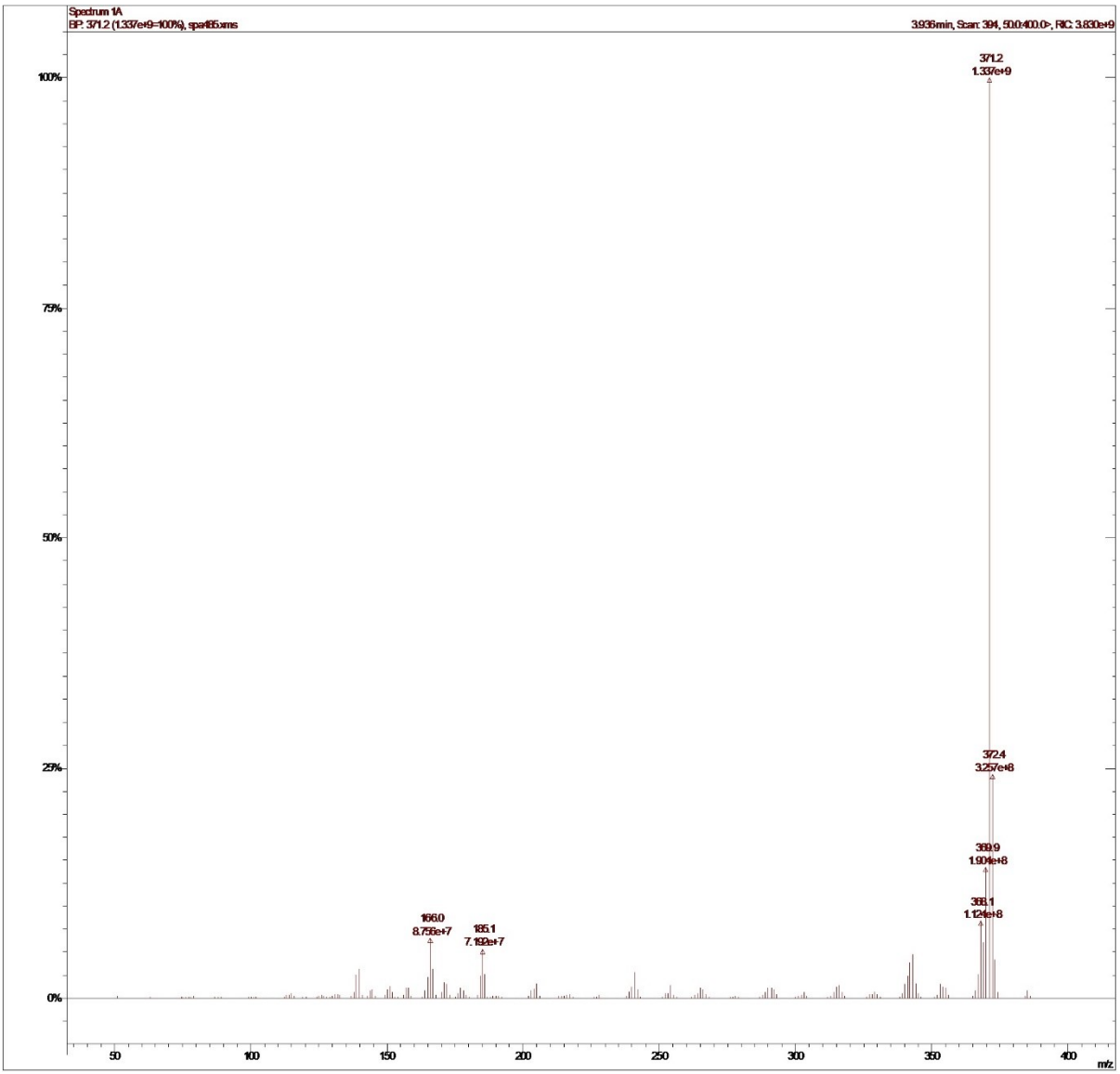

SLG-6 1H
8.645
7.831
7.810
7.598
7.536
7.524
7.361
7.342
7.323
7.299
7.278
7.262
7.189
7.169
7.145
7.121
7.101
7.051
7.030
3.491
1.676
0.000
BRUKER
Current Data Parameters
NAME SLG-6 1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201107
Time 13.56 h
INSTRUM spect
PROBHD Z108618_0903 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 199.04
DW 62.400 usec
DE 6.50 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1
SFO1 400.2324714 MHz
NUC1 1H
P1 14.00 usec
PLW1 13.95600033 W
F2 - Processing parameters
SI 65536
SF 400.2300084 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
N
CN
N
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
1.95
0.98
1.96
4.17
5.87
2.03


SLG-6 13C
151.02
150.46
146.20
144.34
142.54
131.49
129.71
129.66
126.09
125.07
124.94
120.11
119.40
117.84
104.38
77.27
77.05
76.74
BRUKER
NAME SLG-6 13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201107
Time 18.00 h
INSTRUM spect
PROBHD Z108618_0903 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 199.04
DW 20.800 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6479773 MHz
NUC1 13C
P1 10.00 usec
PLW1 51.72800064 W
SFO2 400.2314009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.95600033 W
PLW12 0.33770001 W
PLW13 0.16986001 W
F2 - Processing parameters
SI 32768
SF 100.6379135 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CN
N
200 180 160 140 120 100 80 60 40 20 0 ppm

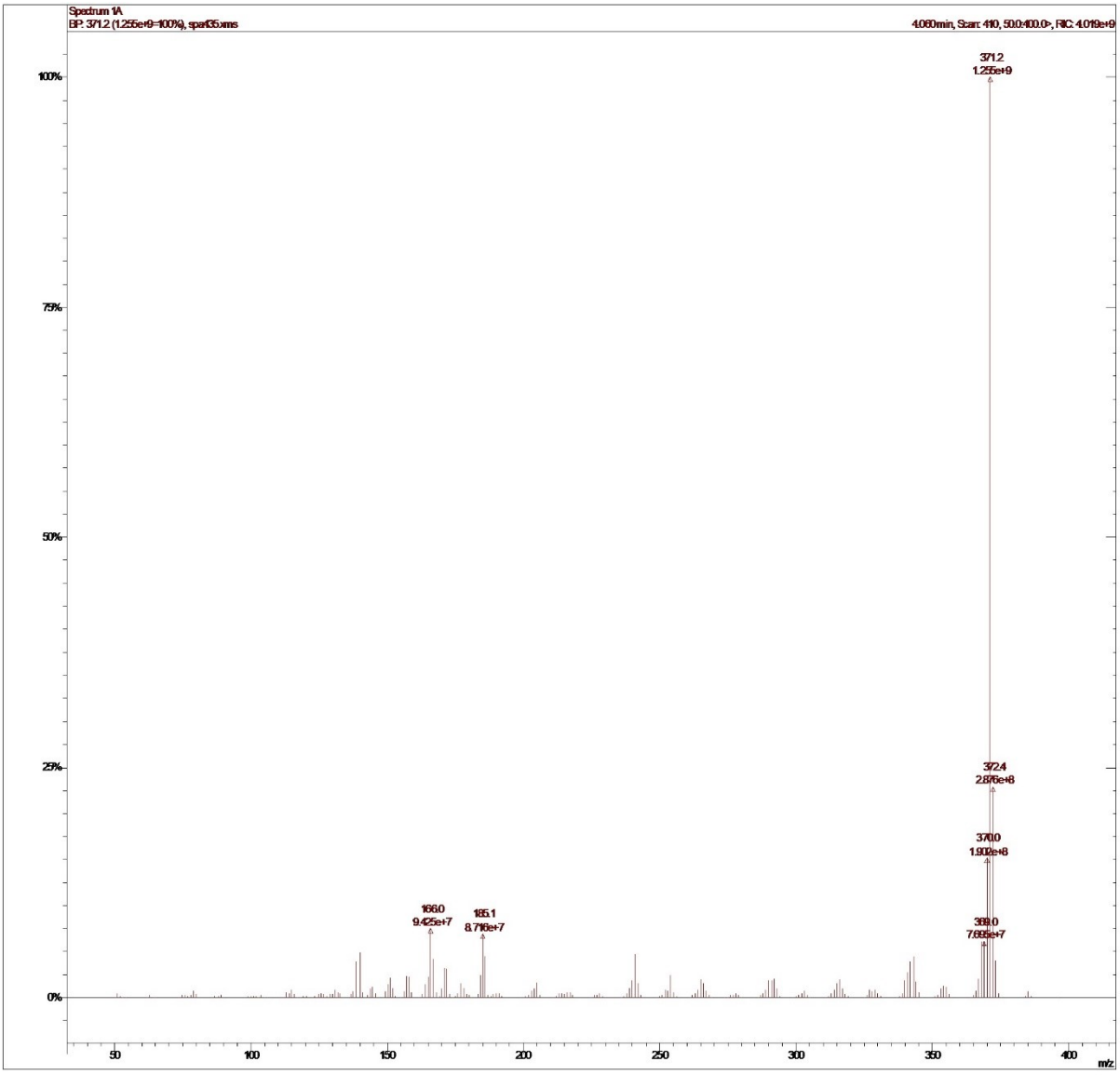
^{1}H and ^{13}C NMR of ***6.***



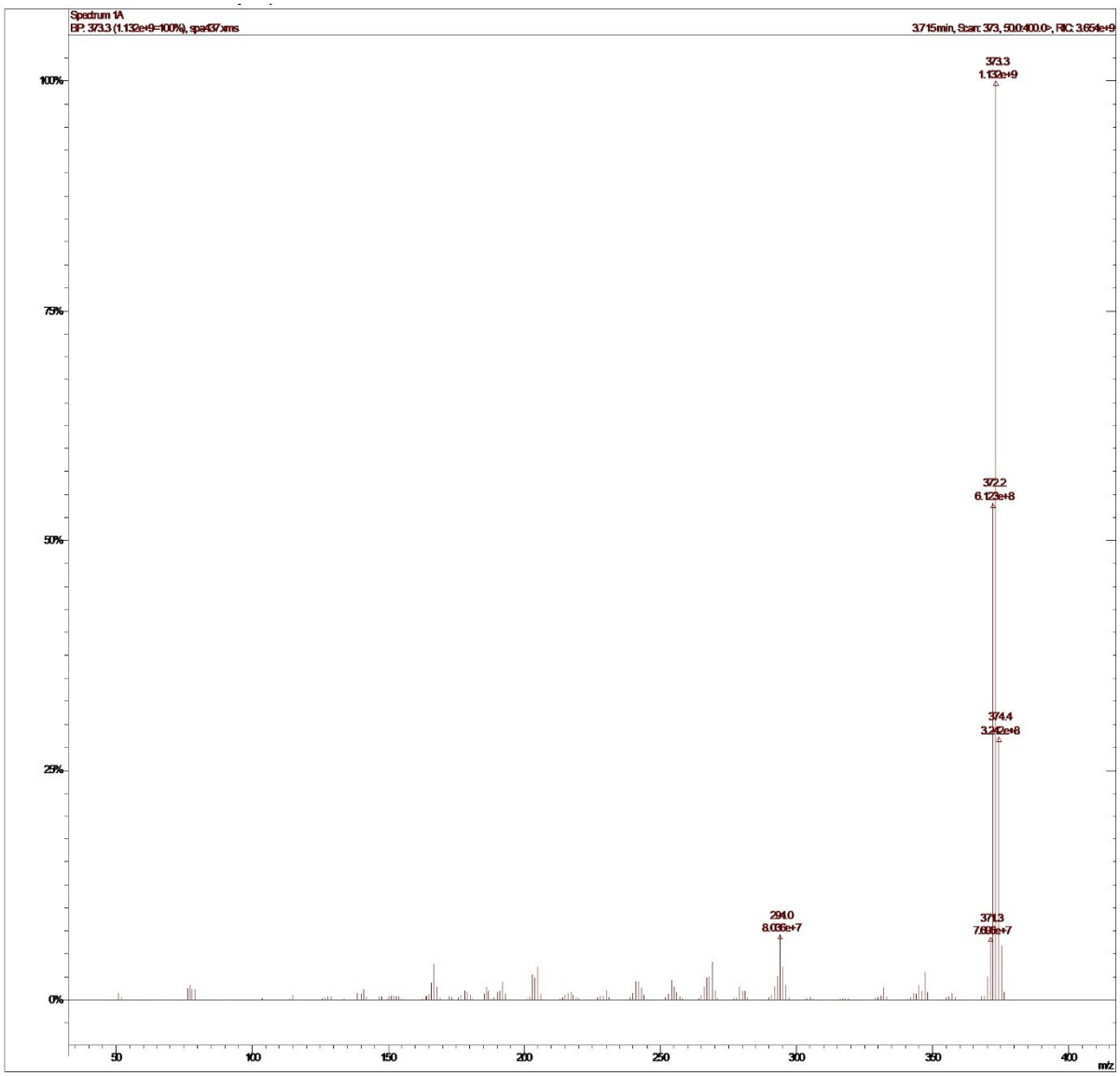
1: m/z calculated for $C_{26}H_{17}N_3$ (M + H): 371.14, found: 371.2



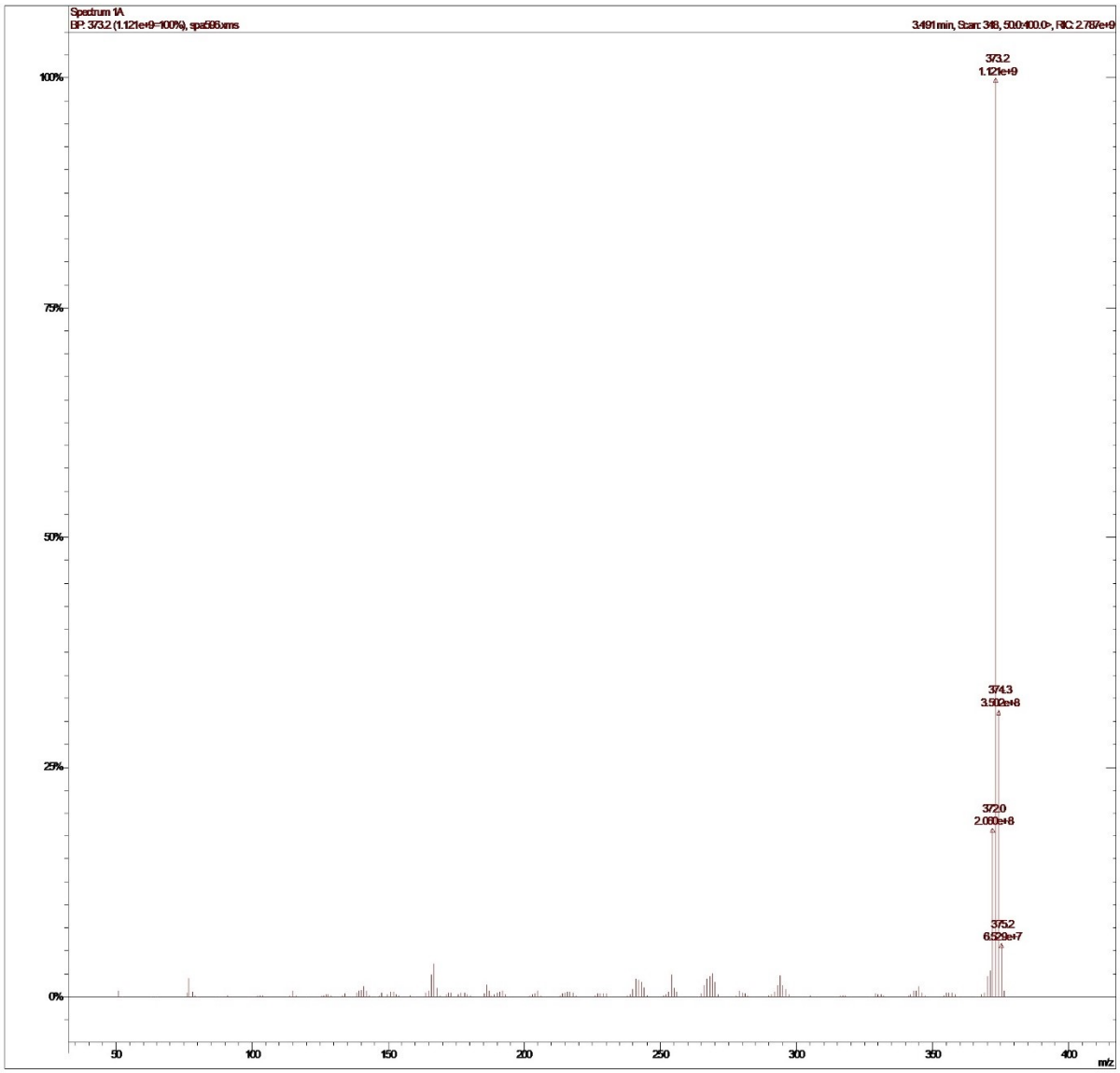
2: m/z calculated for $C_{26}H_{17}N_3$ (M + H): 371.14, found: 371.2



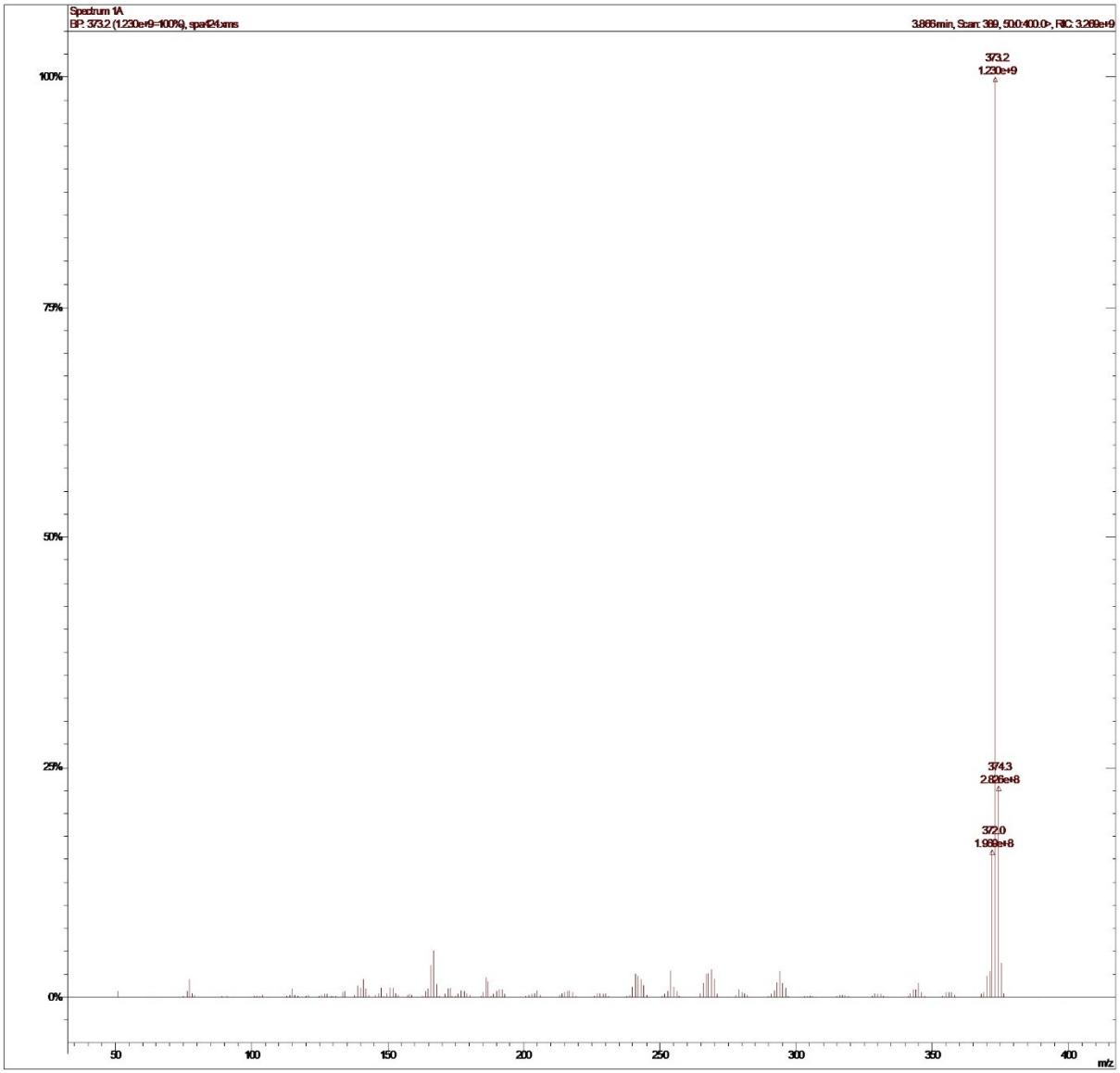
3: m/z calculated for $C_{26}H_{17}N_3$ (M + H): 371.14, found: 371.2



4: m/z calculated for $C_{26}H_{19}N_3$ (M + H): 373.16, found: 373.3



5: m/z calculated for $C_{26}H_{19}N_3$ (M + H): 373.16, found: 373.2



6: m/z calculated for $C_{26}H_{19}N_3$ (M + H): 373.16, found: 373.2

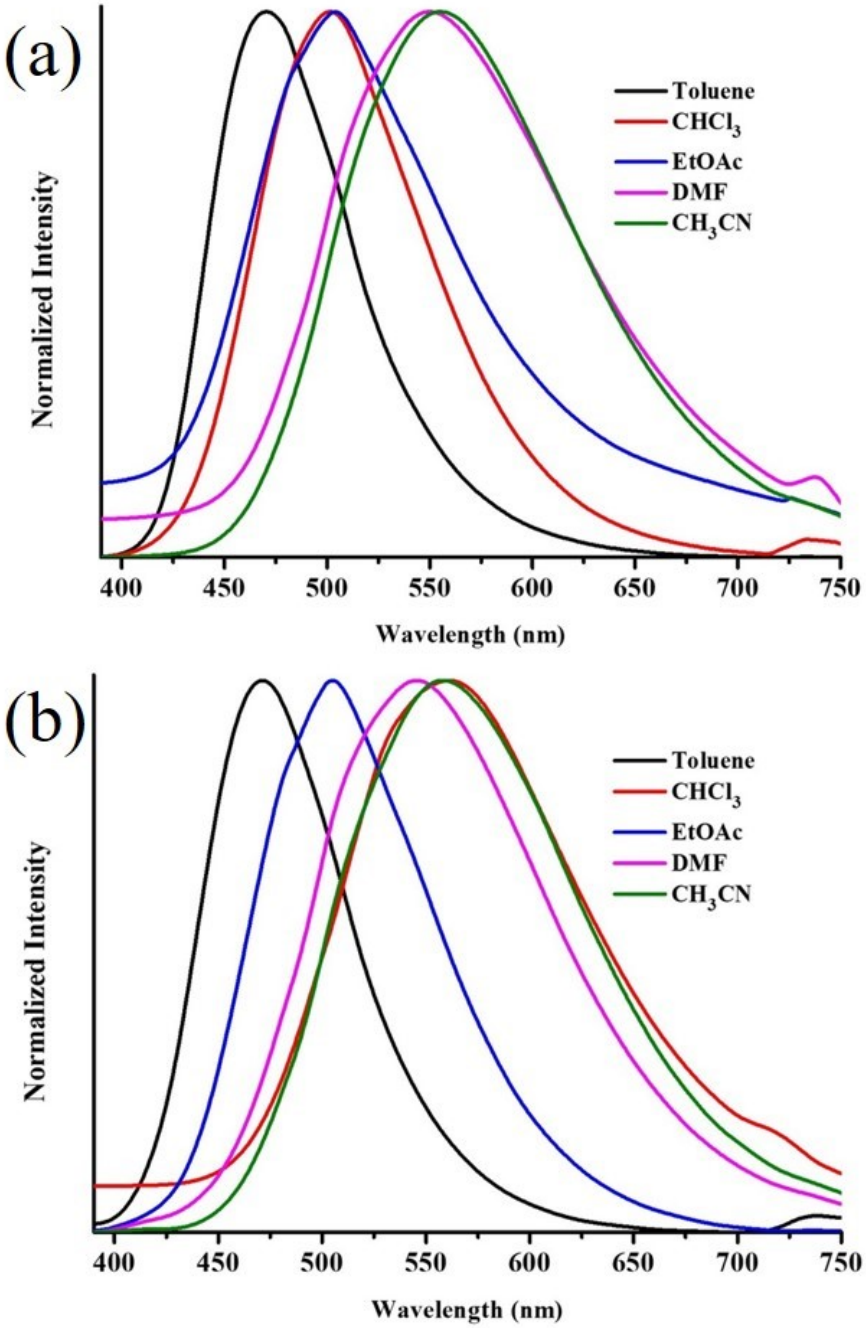


Fig. S1. Fluorescence spectra of (a) **1** and (b) **2** in different solvents (10^{-4} M).

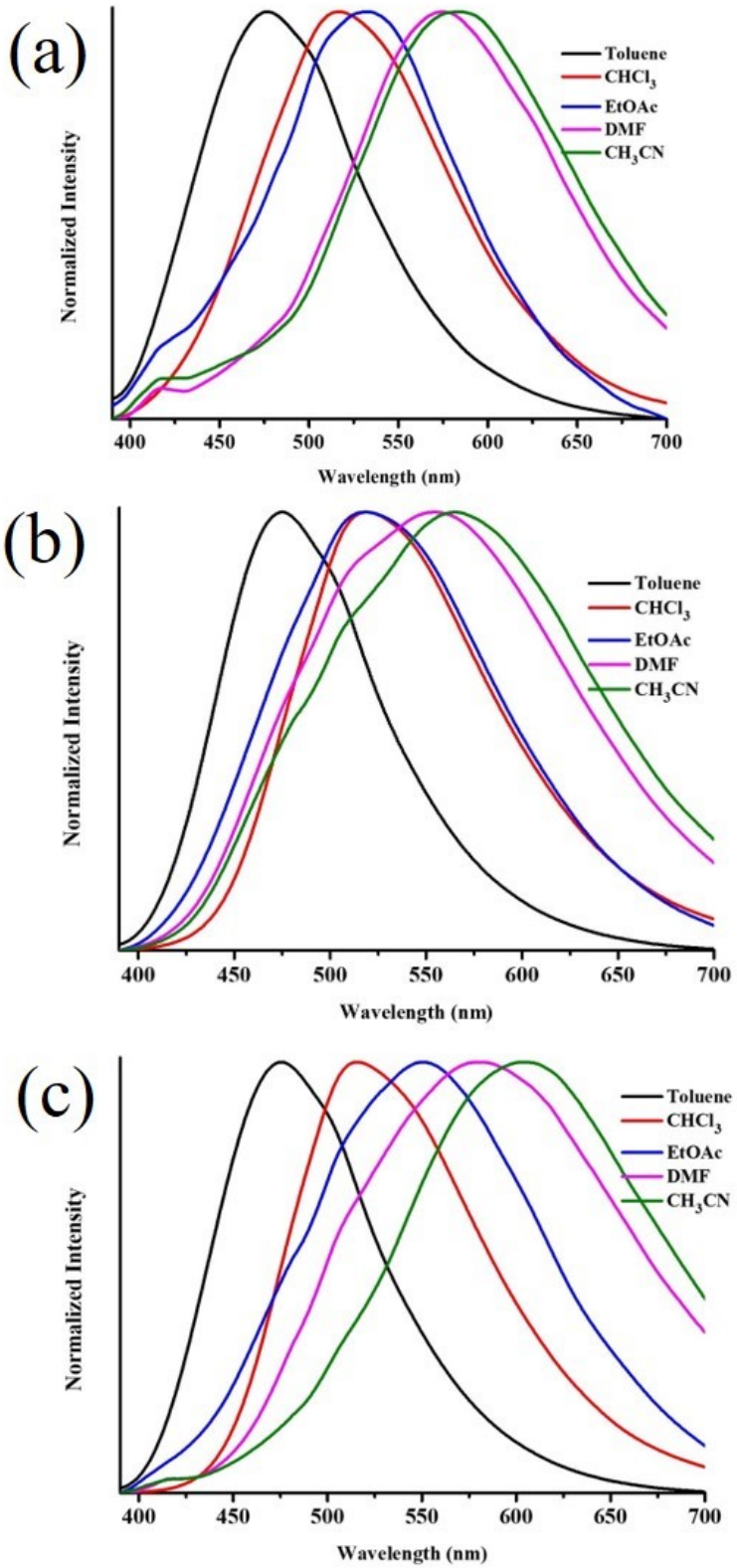


Fig. S2. Fluorescence spectra of (a) **4**, (b) **5** and (c) **6** in different solvents (10^{-4} M).

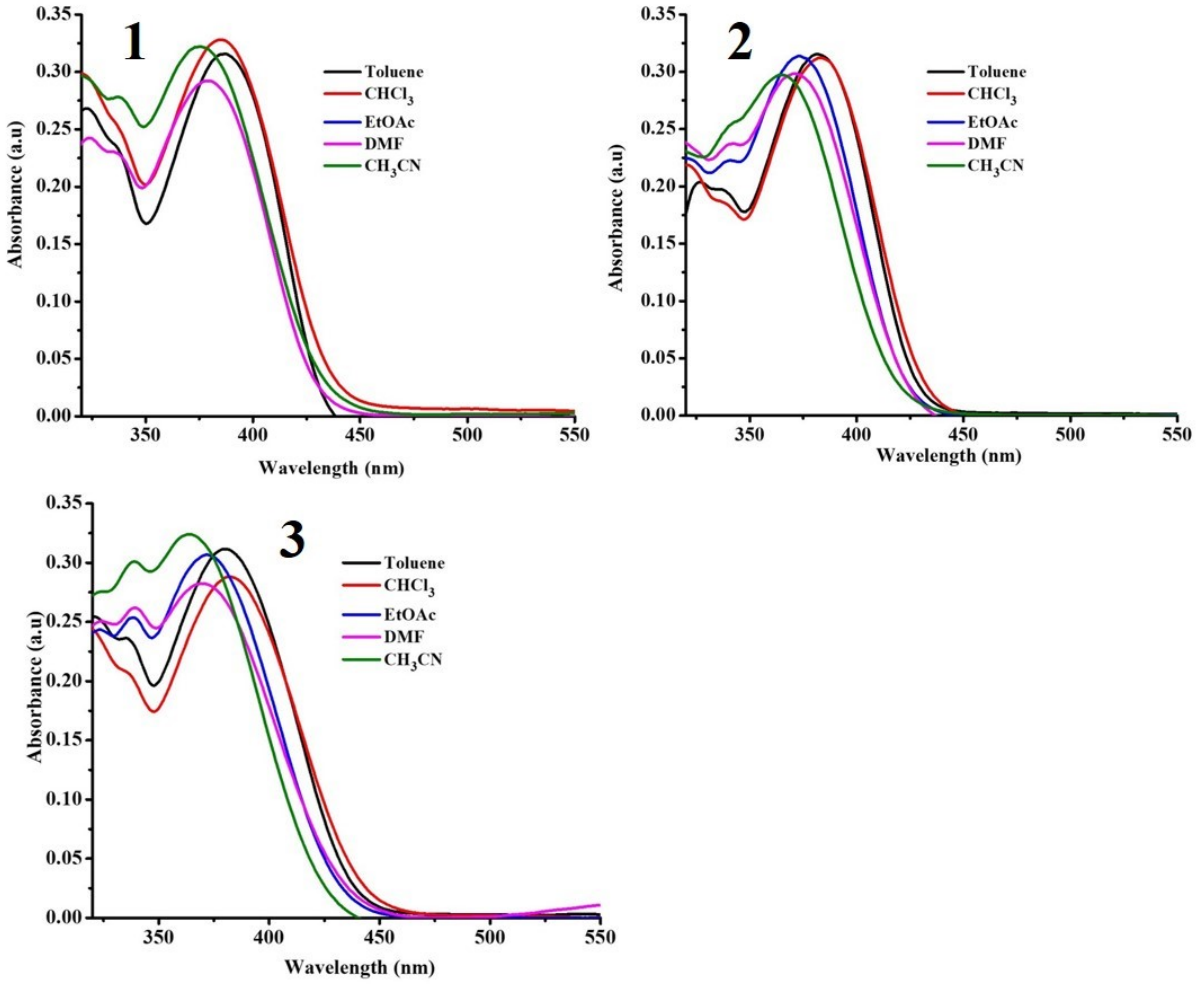


Fig. S3. Absorption spectra of **1**-**3** in different solvents (10^{-4} M).

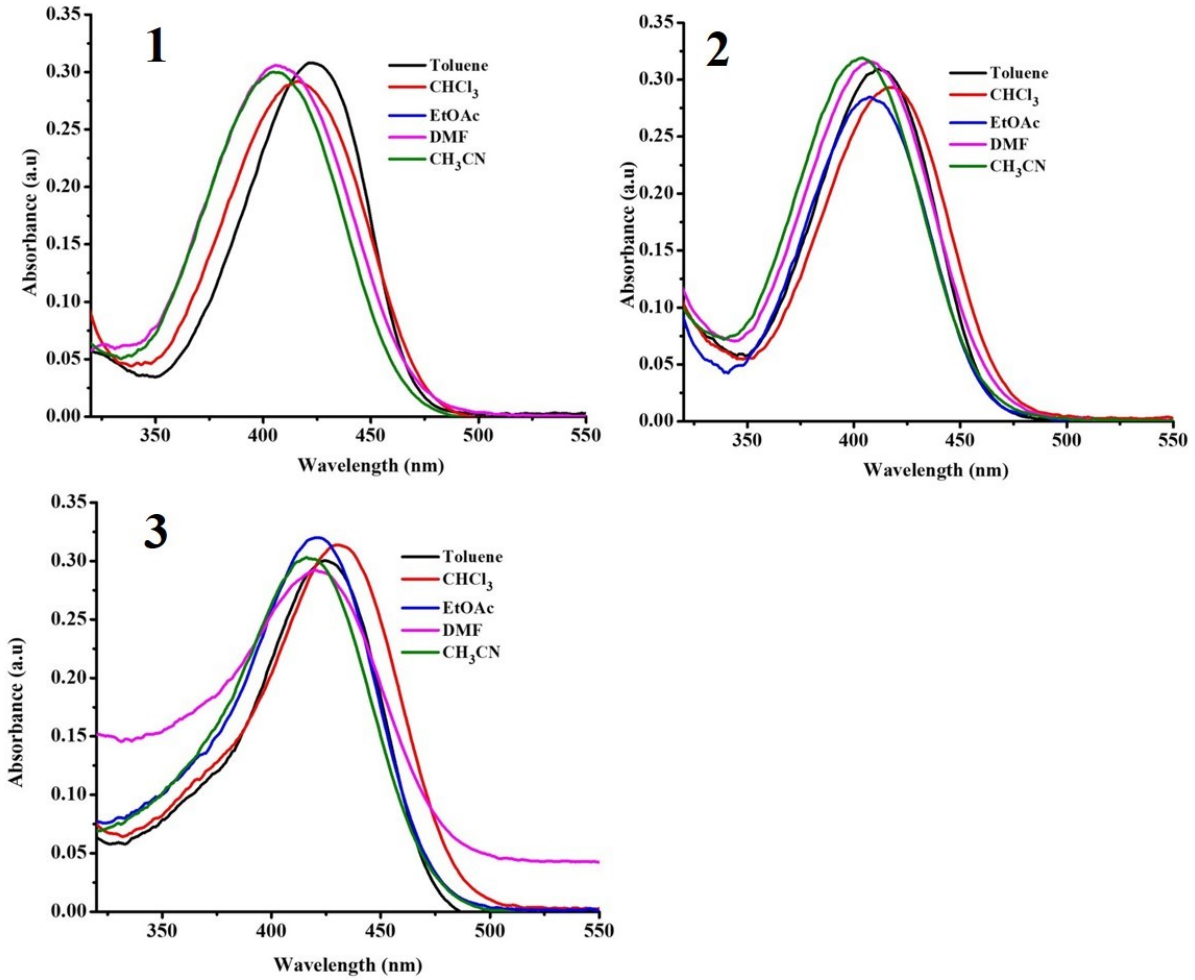


Fig. S4. Absorption spectra of **4-6** in different solvents (10^{-4} M).

Table S1. Fluorescence efficiency of **1-6** compared to quinine sulfate in different solvent polarity.

Solvents	Quantum Yield (Φ_f)					
	1	**2**	**3**	**4**	**5**	**6**
Toluene	0.142	0.28	0.095	0.036	0.21	0.085
$CHCl_3$	0.116	0.09	0.068	0.035	0.096	0.051
Ethyl acetate	0.132	0.25	0.088	0.033	0.023	0.031
DMF	0.160	0.163	0.13	0.030	0.059	0.036
CH_3CN	0.051	0.16	0.098	0.025	0.085	0.015

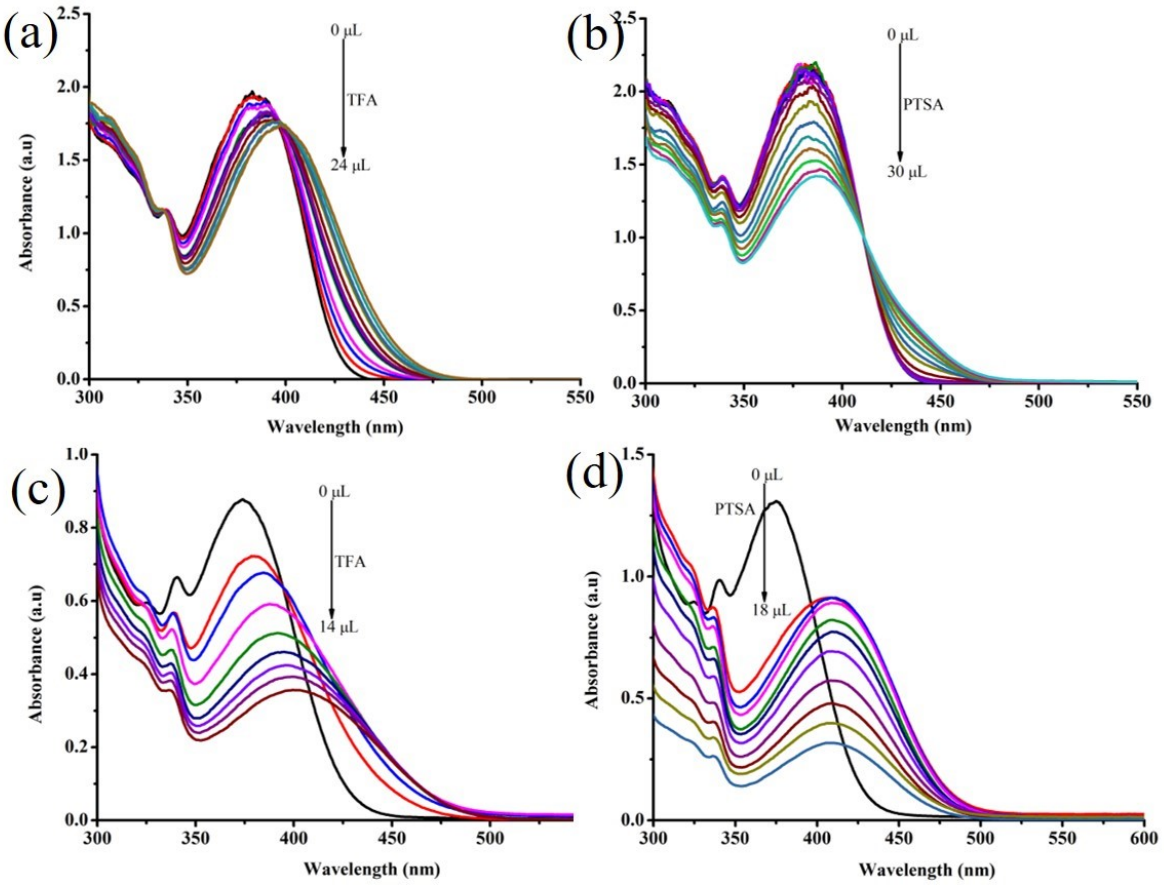


Fig. S5. Absorption changes of **2** (10^{-4} M) upon addition of (a, c) TFA (10^{-2} M) and (b, d) PTSA (10^{-2} M) in (a, b) toluene and (c, d) $CHCl_3$.

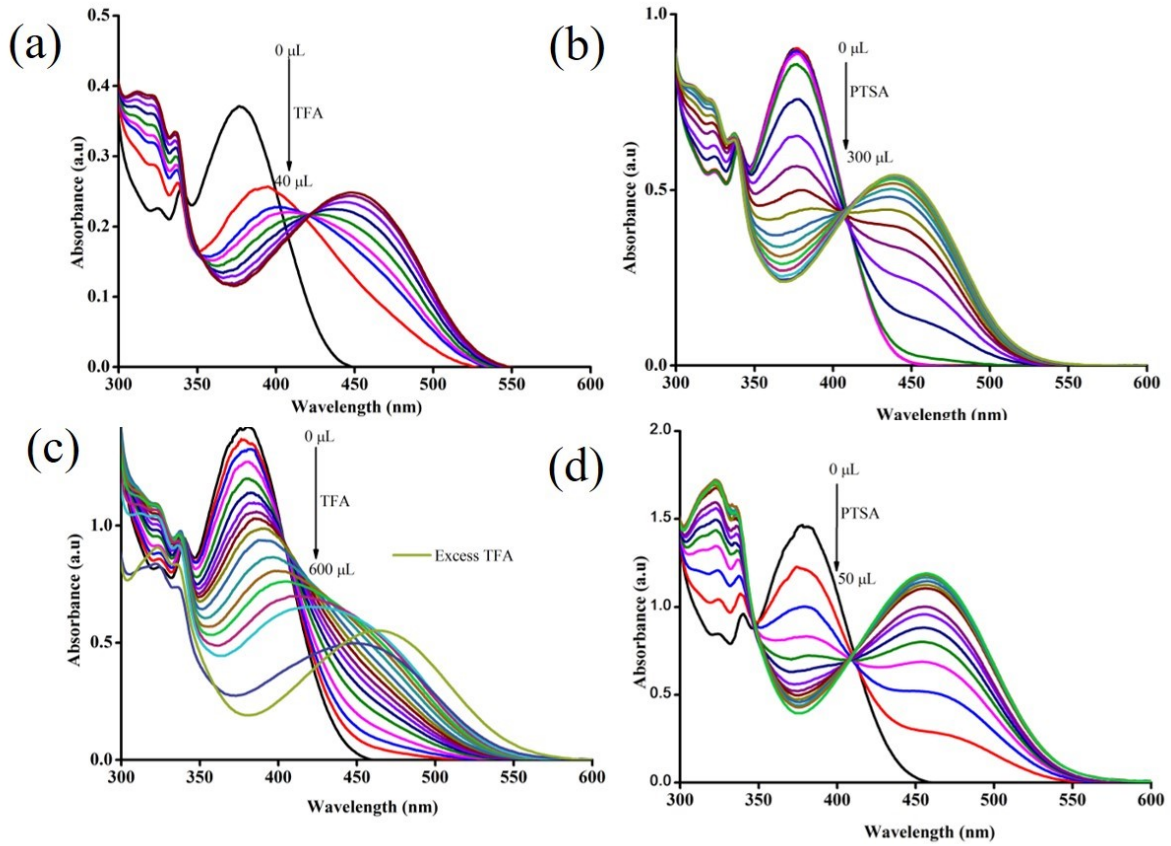


Fig. S6. Absorption changes of **3** (10^{-4} M) upon addition of (a, c) TFA (10^{-2} M) and (b, d) PTSA (10^{-2} M) in (a, b) toluene and (c, d) $CHCl_3$..

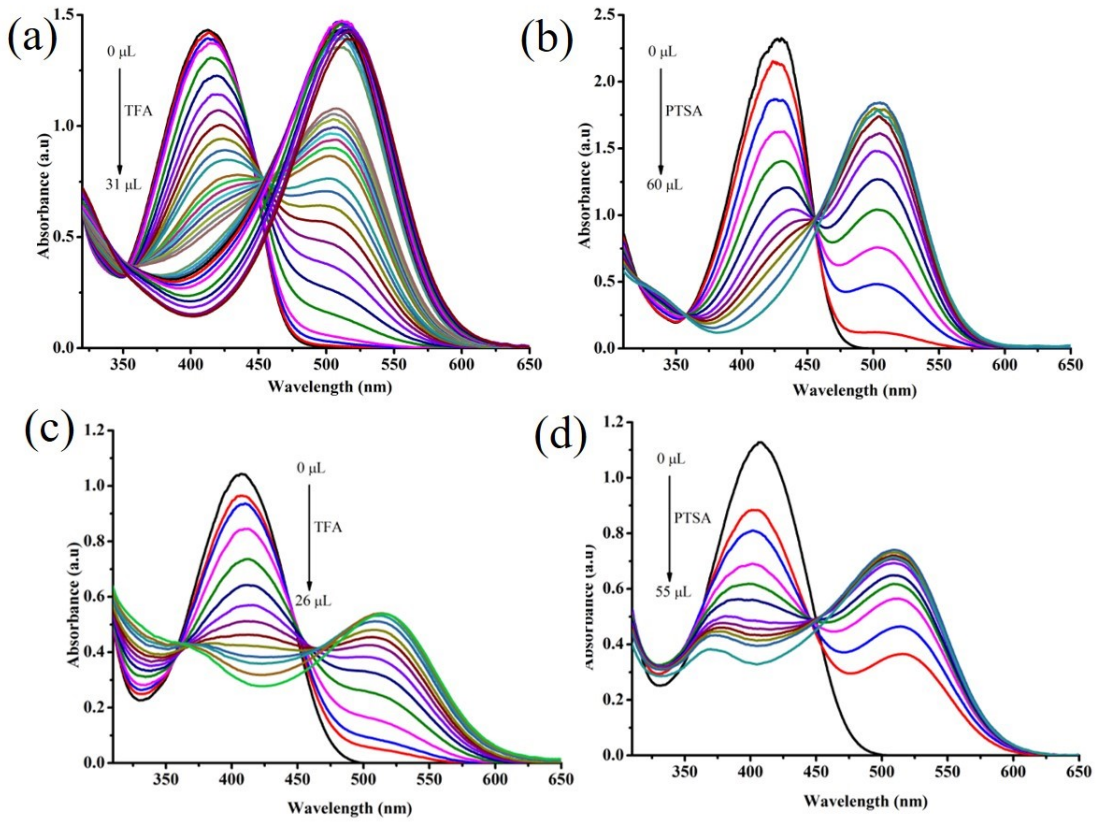


Fig. S7. Absorption changes of **4** (10^{-4} M) upon addition of (a, c) TFA (10^{-2} M) and (b, d) PTSA (10^{-2} M) in (a, b) toluene and (c, d) $CHCl_3$..

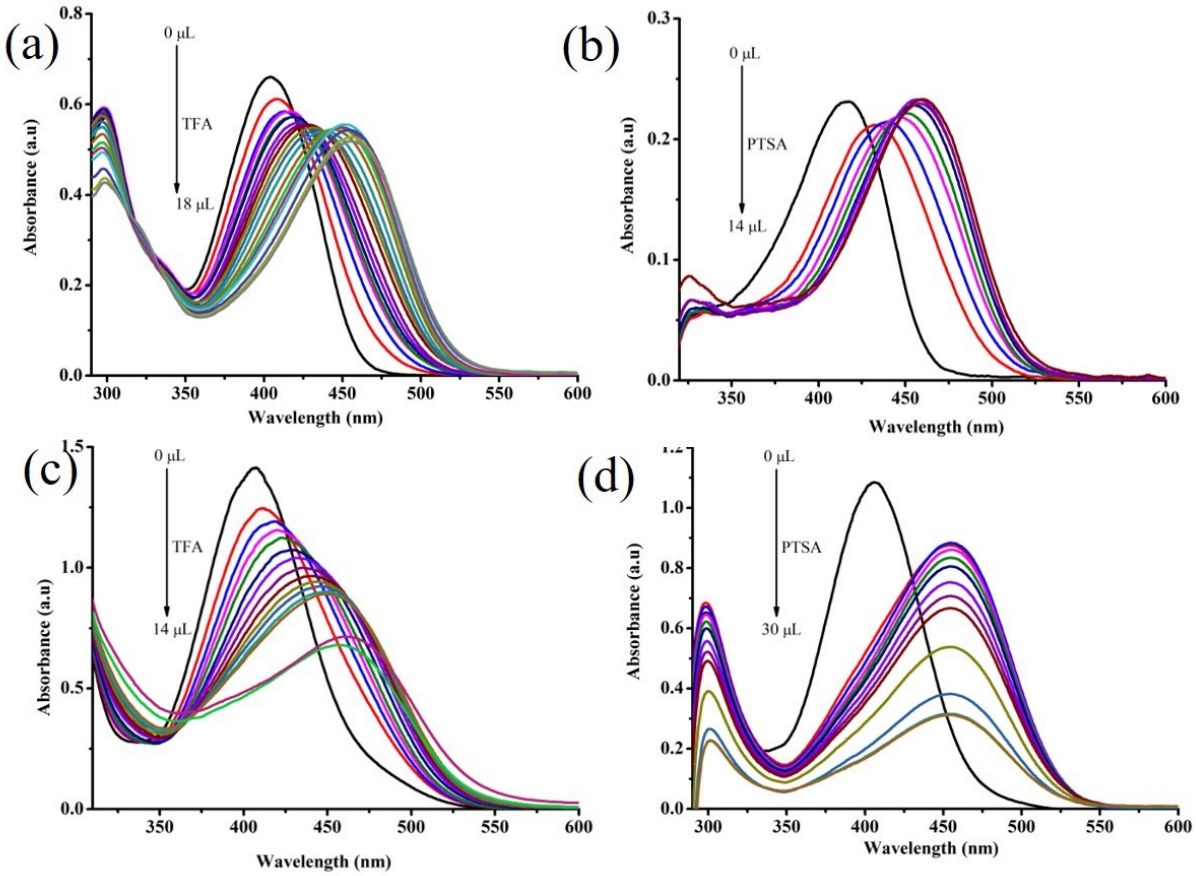


Fig. S8. Absorption changes of **5** (10^{-4} M) upon addition of (a, c) TFA (10^{-2} M) and (b, d) PTSA (10^{-2} M) in (a, b) toluene and (c, d) $CHCl_3$..

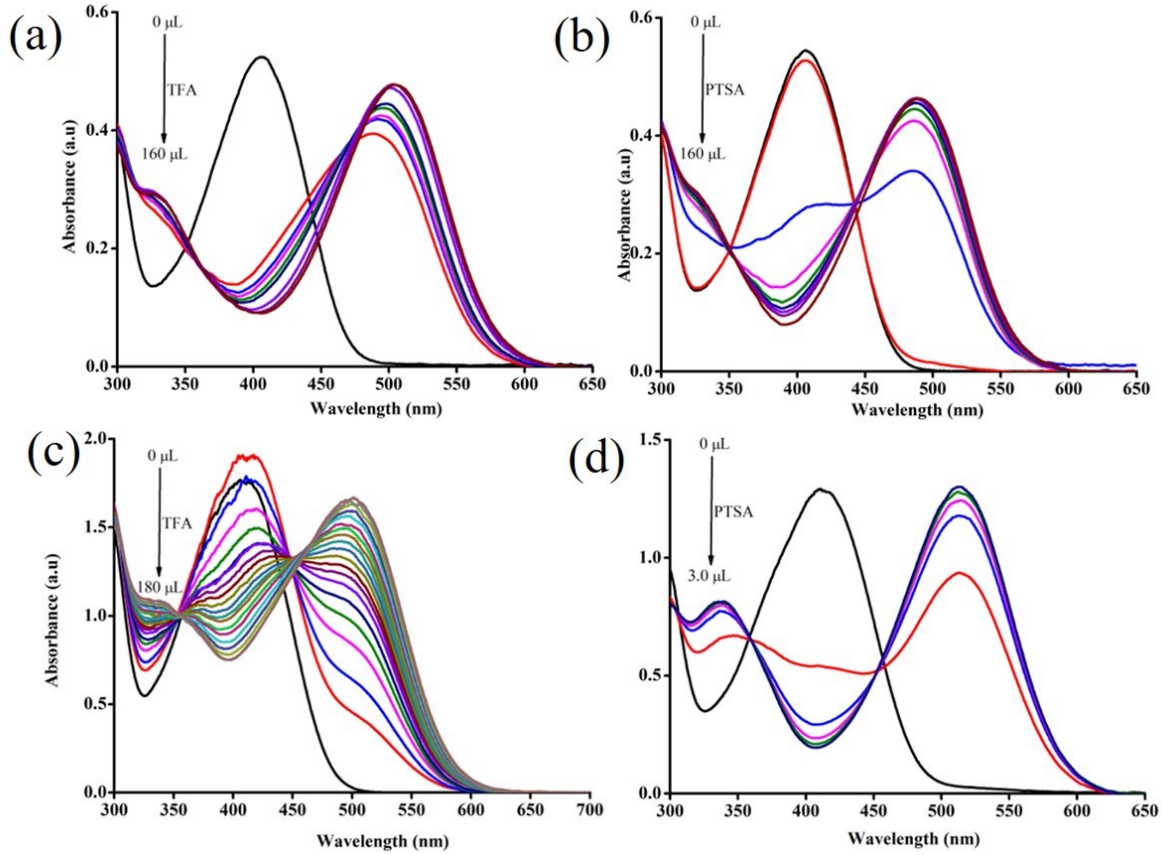


Fig. S9. Absorption changes of **6** (10^{-4} M) upon addition of (a, c) TFA (10^{-2} M) and (b, d) PTSA (10^{-2} M) in (a, b) toluene and (c, d) $CHCl_3$..

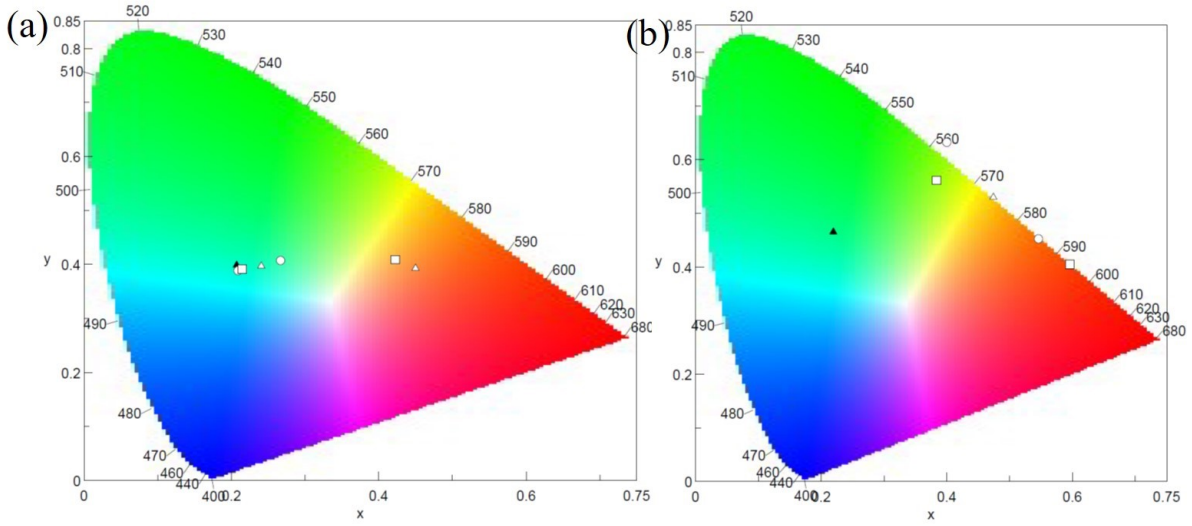


Fig. S10. CIE 1931 chromaticity plot with emission color coordinates of **1** in $CHCl_3$ by adding (a) TFA and (b) PTSA (10^{-2} M).

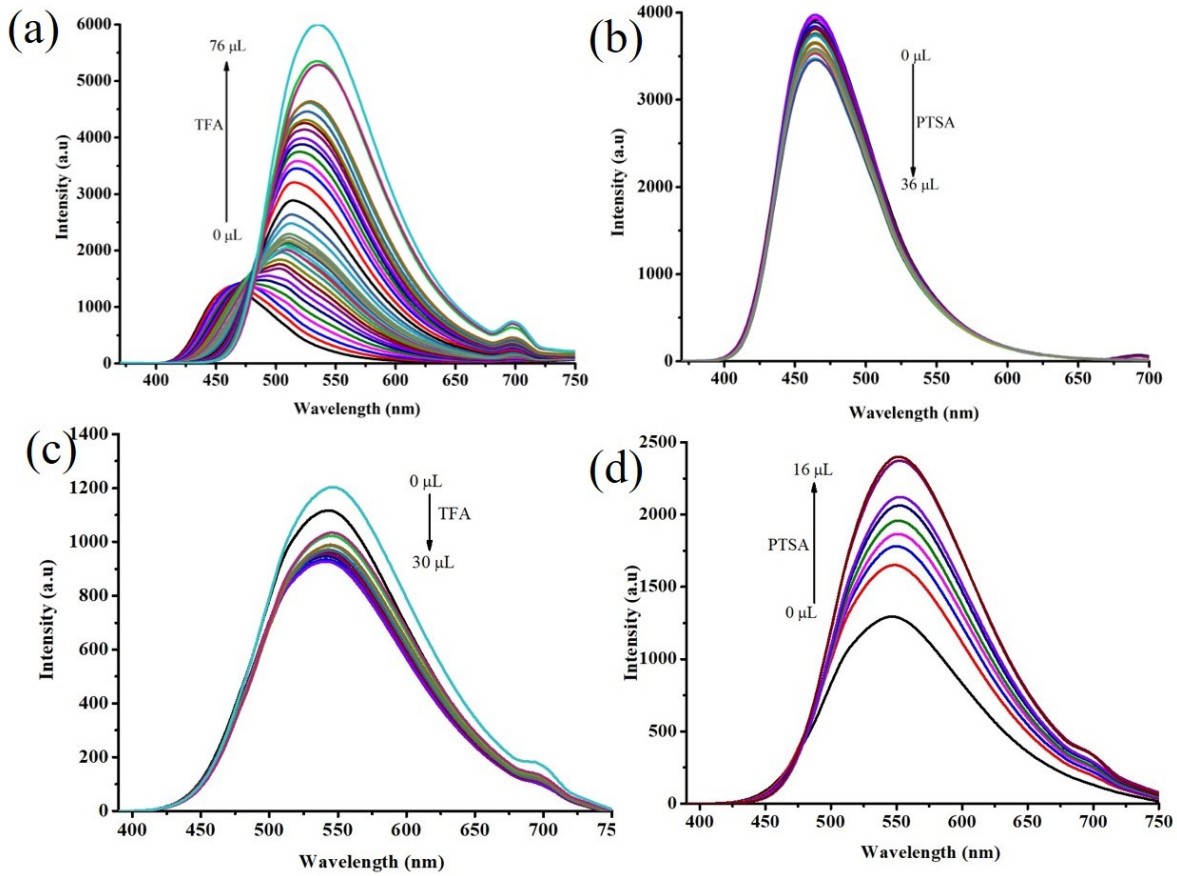


Fig. S11. Fluorescence spectra of **2** (10^{-4} M) upon addition of (a, c) TFA (10^{-2} M) and (b, d) PTSA (10^{-2} M) in (a, b) toluene and (c, d) $CHCl_3$. λ_{exc} = 370 nm.

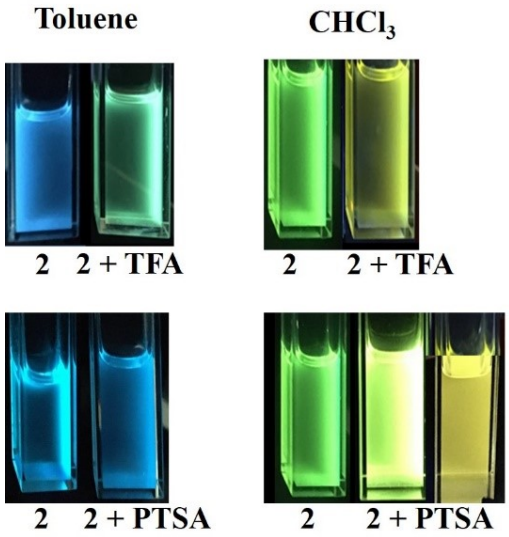


Fig. S12. Digital fluorescence images of **2** (10^{-4} M) upon addition of TFA (10^{-2} M) and PTSA (10^{-2} M) in toluene and $CHCl_3$. λ_{exc} = 365 nm.

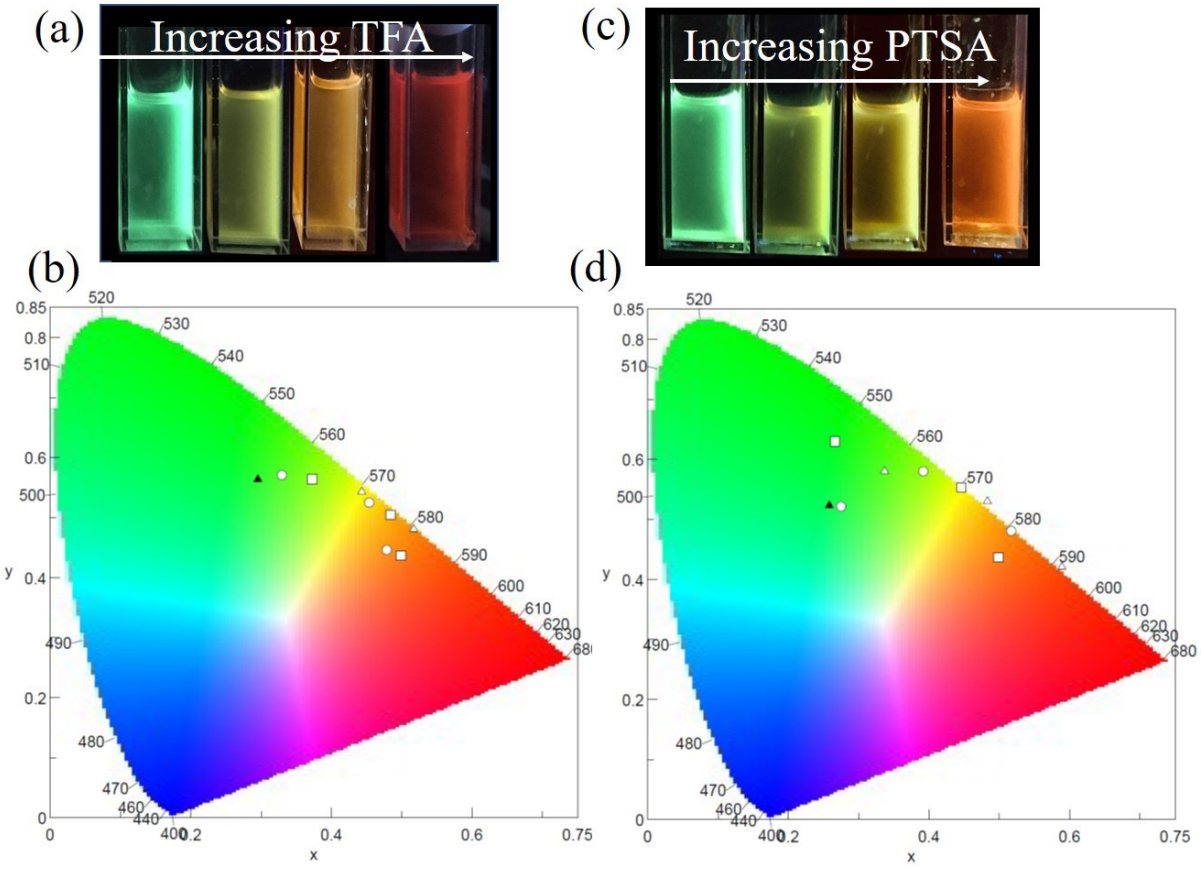


Fig. S13. (a, c) Digital fluorescence images and (b, d) CIE 1931 chromaticity plot with emission colour coordinates of **3** (10^{-4} M) upon adding (a, b) TFA (10^{-2} M) and (c, d) PTSA (10^{-2} M) in $CHCl_3$. λ_{exc} = 365 nm (for digital images) and 370 nm (for spectra)..

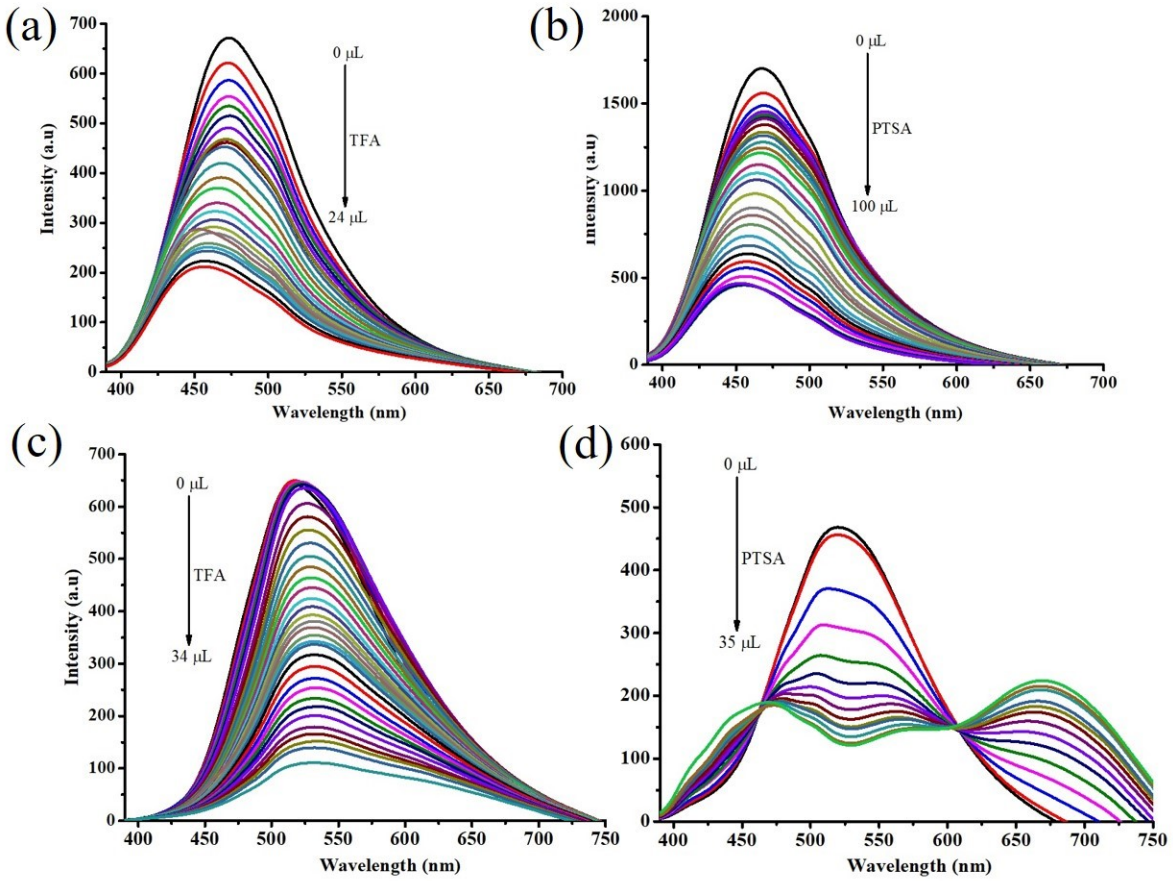


Fig. S14. Fluorescence spectra of **5** (10^{-4} M) upon addition of (a, c) TFA (10^{-2} M) and (b, d) PTSA (10^{-2} M) in (a, b) toluene and (c, d) $CHCl_3$. λ_{exc} = 370 nm.

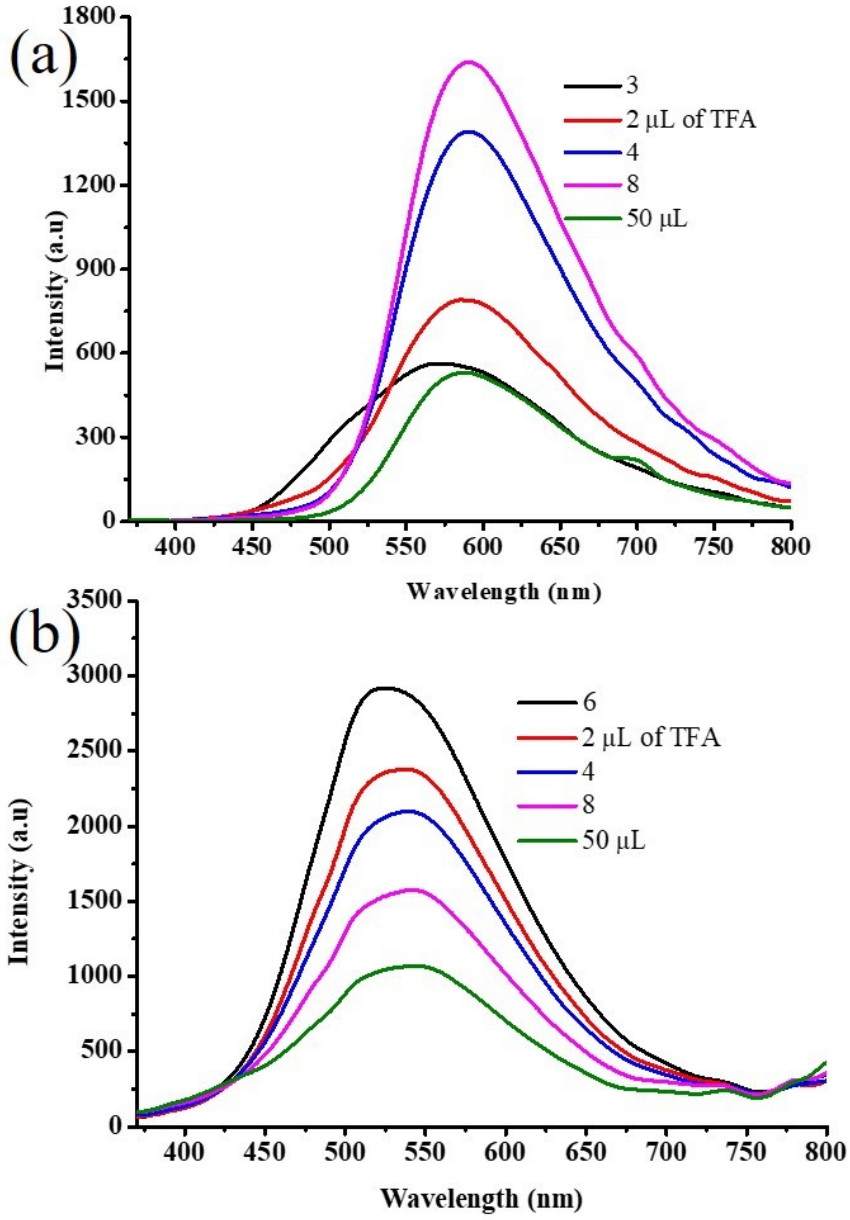


Fig. S15. Fluorescence spectra of (a) **3** (10^{-4} M) and (b) **6** (10^{-4} M) upon addition of TFA (10^{-2} M) in DMF. λ_{exc} = 370 nm..

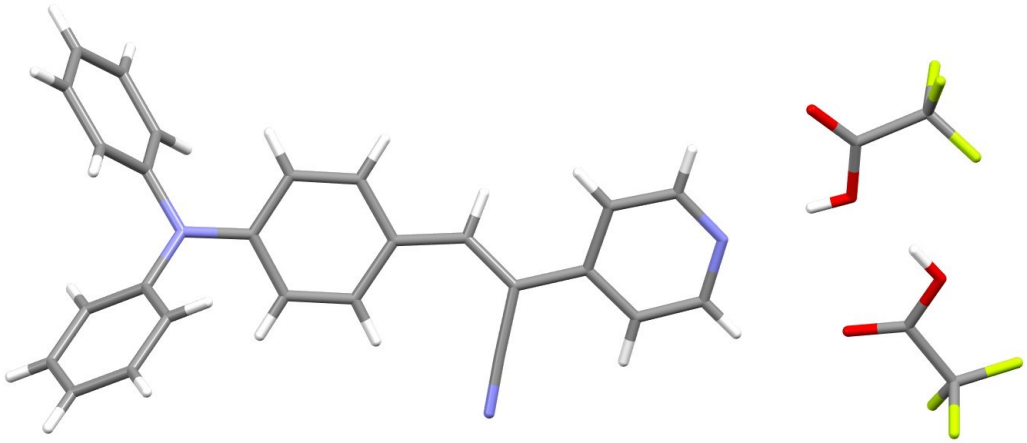


Fig. S16. Molecular structure of 6-TFA in the crystal lattice.

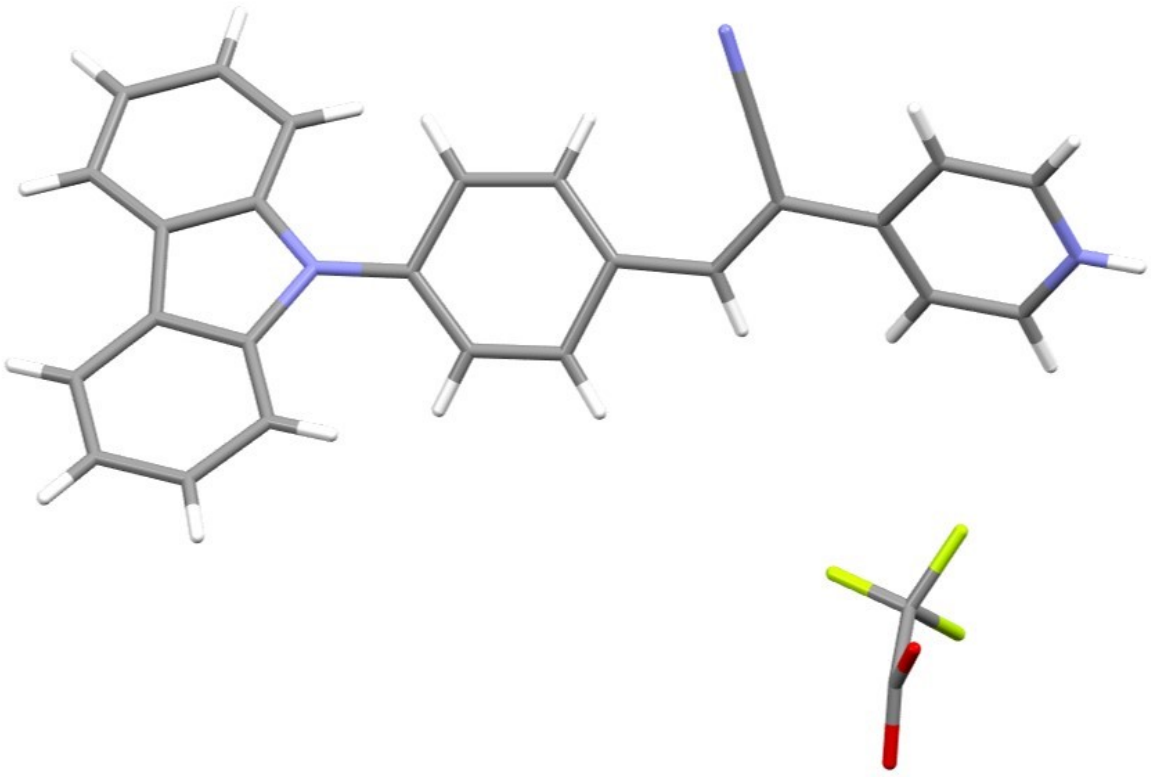
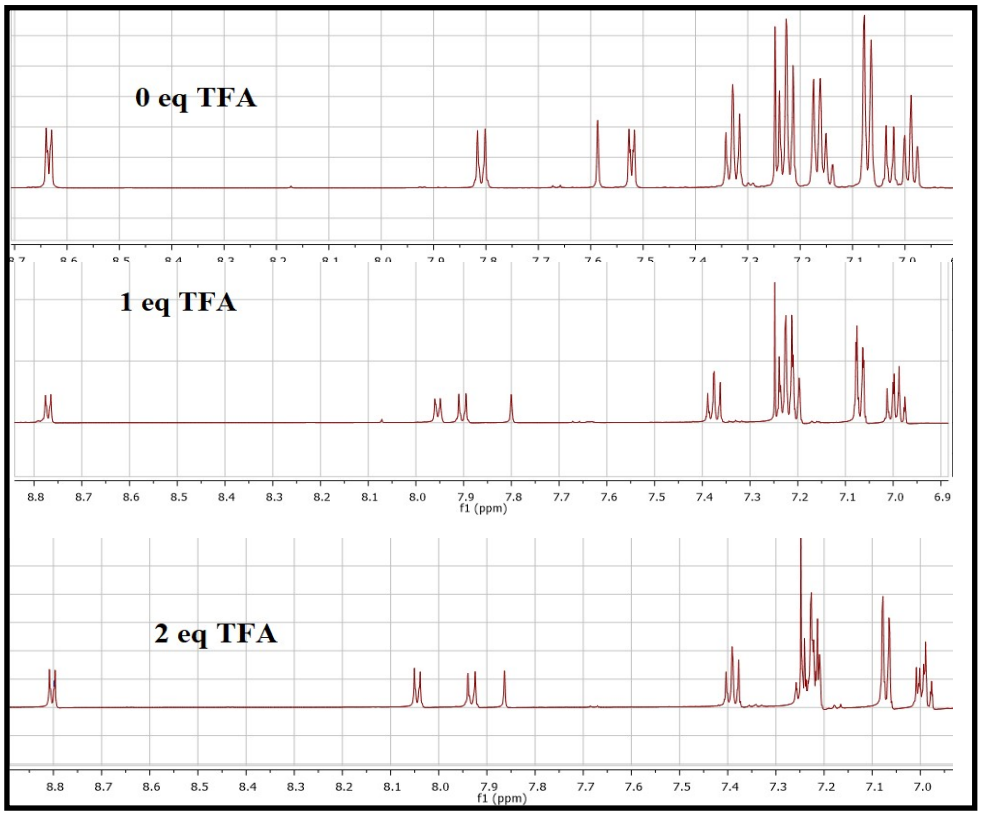


Fig. S17. Molecular structure of 3-TFA in the crystal lattice.

(a)



(b)

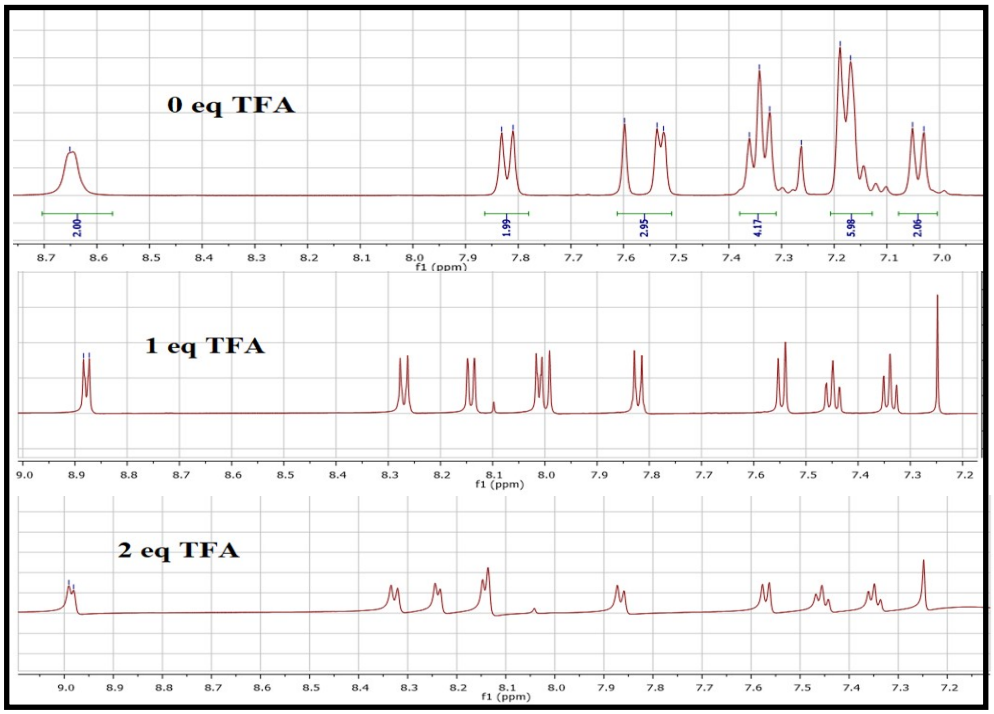


Fig. S18. NMR spectra of (a) 3 and 3-TFA and (b) 6 and 6-TFA.

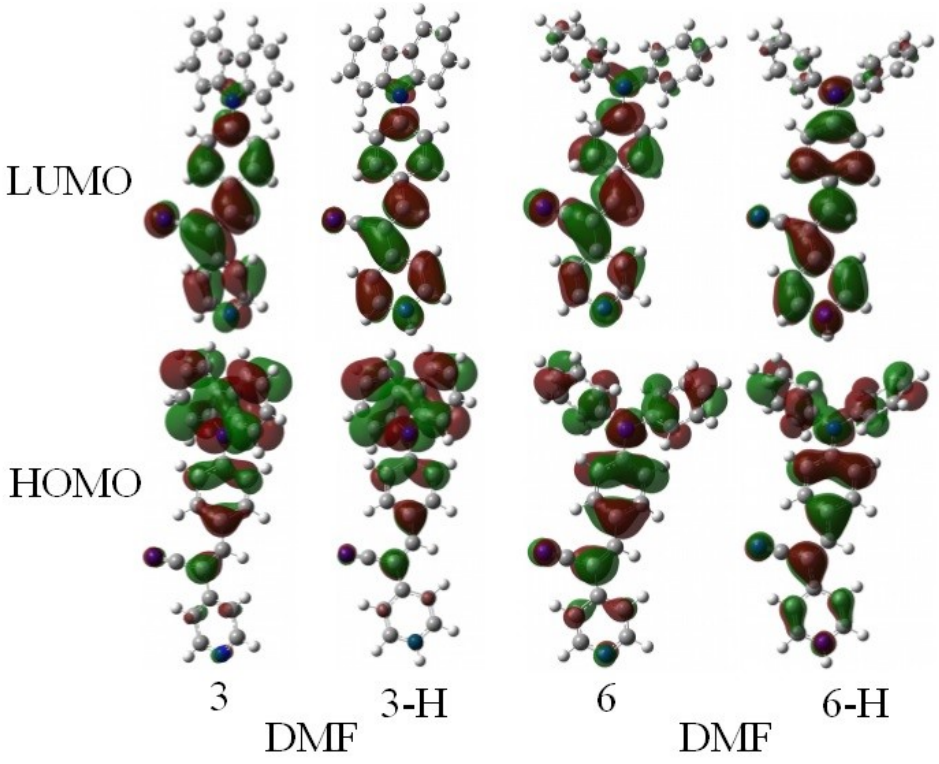


Fig. S19. Calculated frontier orbital for **3**, **3-H, 6** and **6-H** in DMF.

Table S2. Calculated energy level of HOMO, LUMO and optical band gap.

		HOMO (eV)	LUMO (eV)	Band gap (eV)
3	Toluene	-5.57	-2.49	-3.08
	$CHCl_3$	-5.57	-2.48	-3.09
	DMF	-5.58	-2.47	-3. 11
3-H	Toluene	-6.49	-4.50	-1.99
	$CHCl_3$	-6.07	-3.89	-2.18
	DMF	-5.74	-3.32	-2.42
6	Toluene	-5.29	-2.21	-3.08
	$CHCl_3$	-5.29	-2.23	-3.06
	DMF	-5.29	-2.25	-3.04
6-H	Toluene	-6.50	-4.15	-2.35
	$CHCl_3$	-6.02	-3.59	-2.43
	DMF	-5.62	-3.08	-2.54

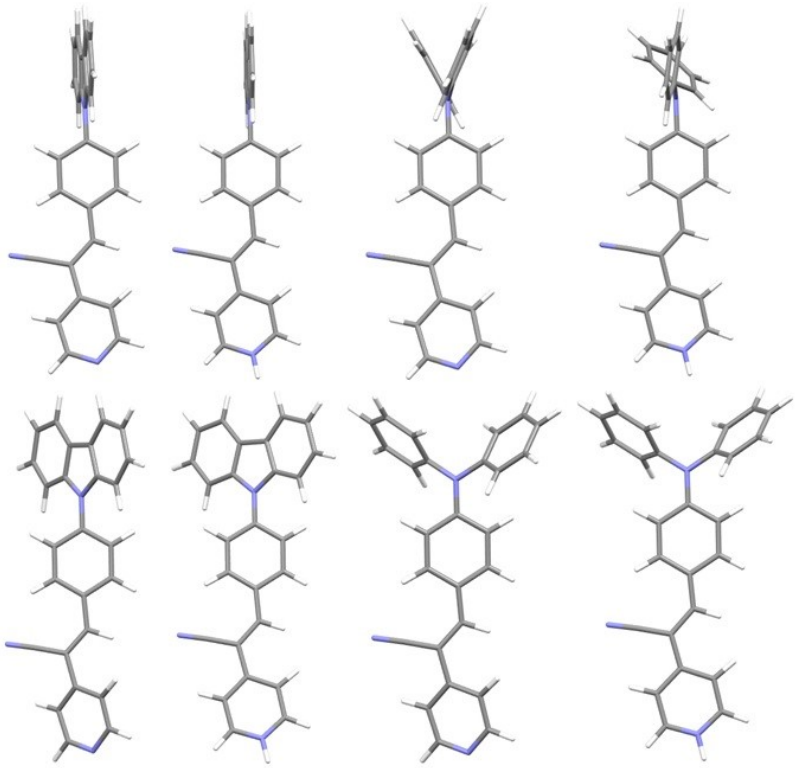


Fig. S20. Calculated ground and excited state (S1) molecular conformation of (a) **3** and **3-H** and (b) **6** and **6-H** in toluene.

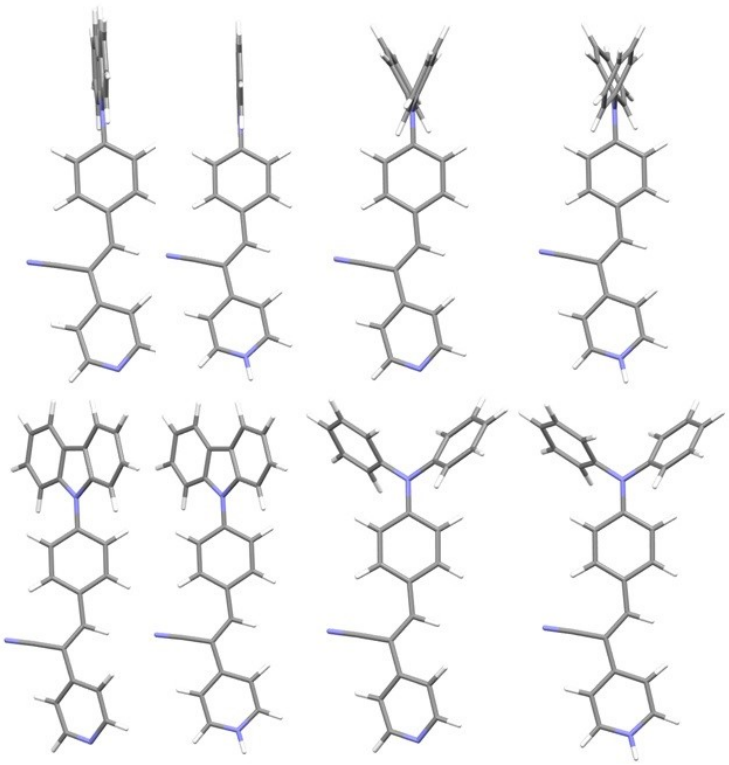


Fig. S21. Calculated ground and excited state (S1) molecular conformation of (a) **3** and **3-H** and (b) **6** and **6-H** in $CHCl_3$.

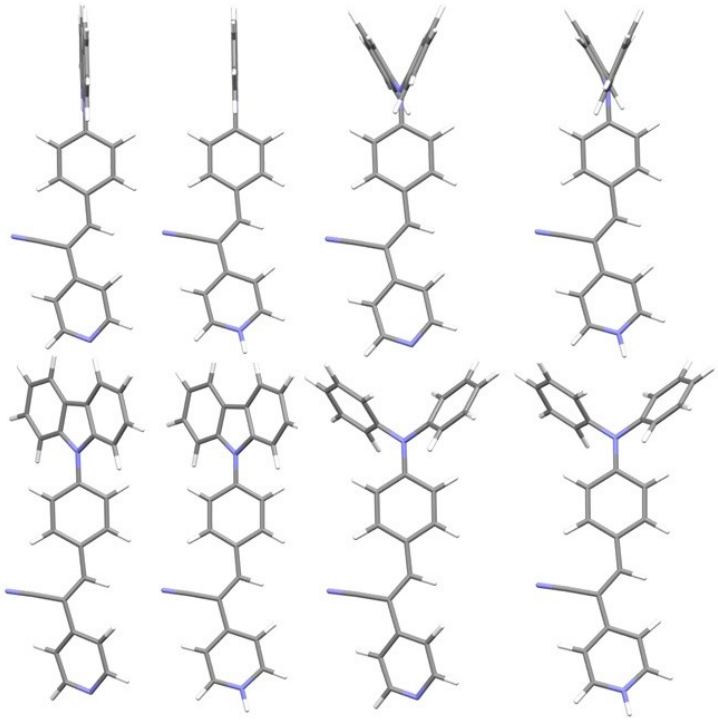
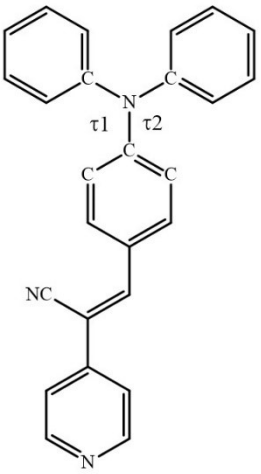


Fig. S22. Calculated ground and excited state (S1) molecular conformation of (a) **3** and **3-H** and (b) **6** and **6-H** in DMF.

Table S3. Comparison of torsion angle of ground/excited state **3** and **6** (protonated/deprotonated) in different sovlents.



		Ground state		Excited state (S1)	
		Torsion angle (τ1)	Torsion angle (τ2)	Torsion angle (τ1)	Torsion angle (τ2)
3	Toluene	49.69	49.36	89.48	89.49
	$CHCl_3$	49.85	49.55	89.28	89.14
	DMF	50.10	49.84	85.40	85.34
3-H	Toluene	42.20	42.13	89.69	90.38
	$CHCl_3$	43.94	43.58	89.99	90.51
	DMF	46.19	46.08	90.24	90.13
6	Toluene	27.96	27.69	84.71	85.15
	$CHCl_3$	27.16	26.56	81.21	81.44
	DMF	26.18	25.52	72.87	72.94
6-H	Toluene	18.86	18.26	81.22	96.60
	$CHCl_3$	19.45	18.97	91.87	91.40
	DMF	20.67	20.06	85.44	85.30