Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

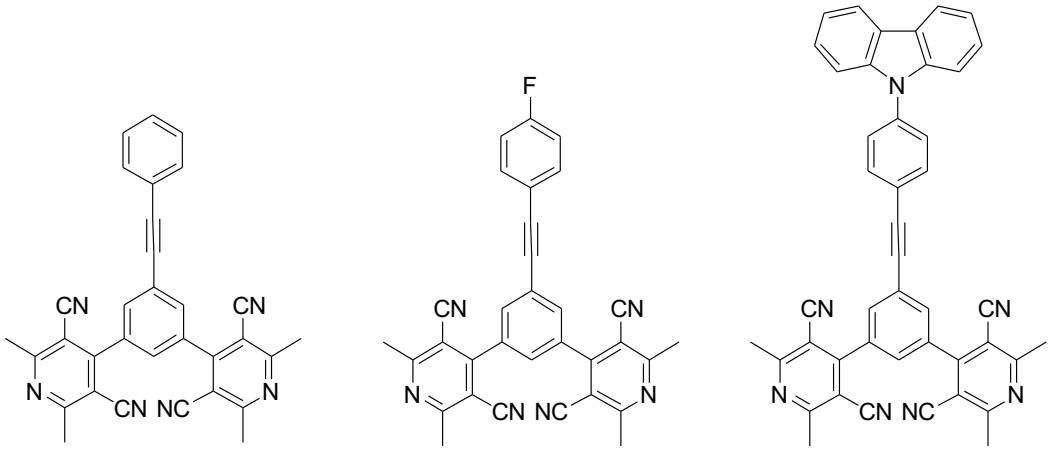
3,5-Dicyanopyridine motifs for electron-transporting semiconductors: from design and synthesis to efficient organic light-emitting diodes

Karolis Leitonas,[a] Brigita Vigante,[b] Dmytro Volyniuk,[a] Audrius Bucinskas,[a] Rasa Keruckiene[a], Pavels Dimitrijevs,[b] Tien-Lung Chiu[c], Juozas Vidas Grazulevicius,*[a] Pavel Arsenyan*[b]

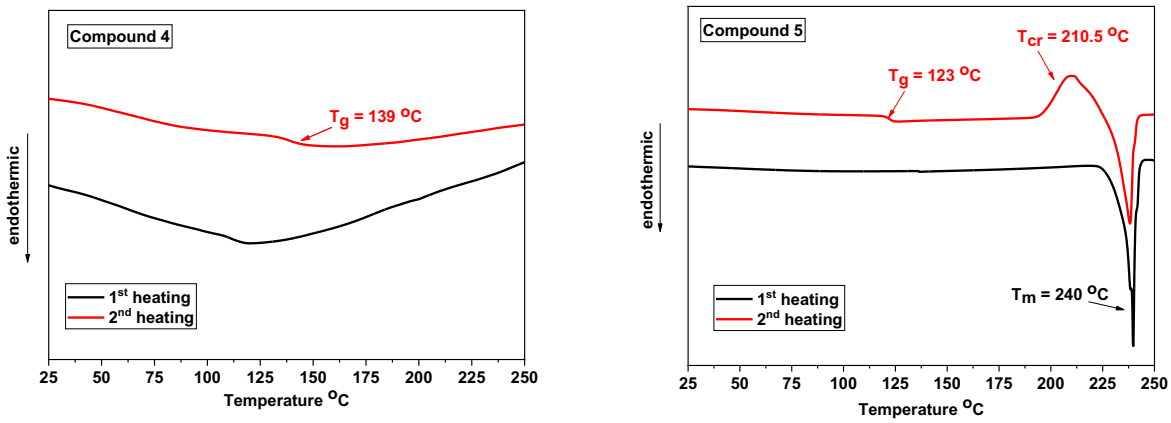
[a] *Department of Polymer Chemistry and Technology, Kaunas University of Technology, Baršausko Str. 59, LT-51423, Kaunas, Lithuania. e-mail: juozas.grazulevicius@ktu.lt*

[b] *Latvian Institute of Organic Synthesis, Aizkraukles 21, LV-1006, Riga, Latvia. e-mail: pavel@osi.lv*

[c] *Department of Electrical Engineering, Yuan Ze University, Taiwan. e-mail: tlchiu@saturn.yzu.edu.tw*

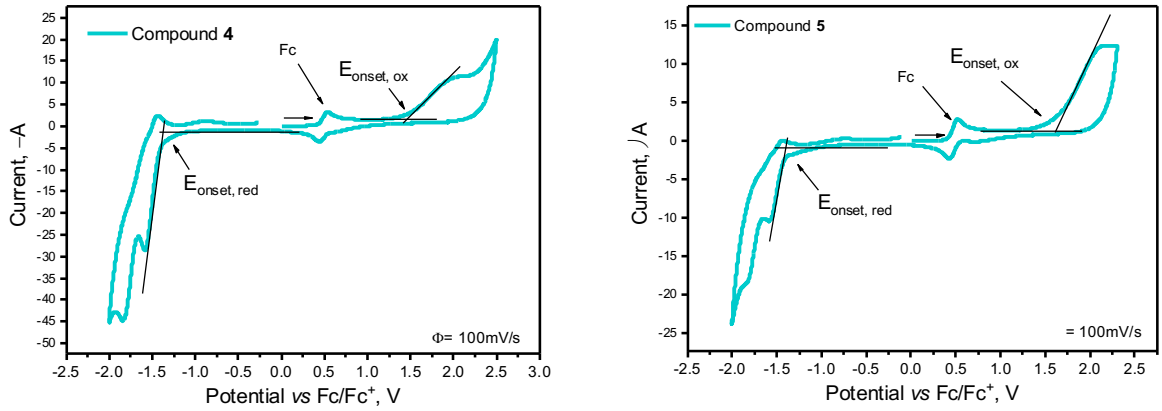


PPDD or **4** **FPDD** or **5** **CzPDD** or **6**



a b

Figure S1. DSC thermograms of compounds **4** (a) and **5** (b).



a b

Figure S2. CV curves of the DCM solutions of **4** (a) and **5** (b).

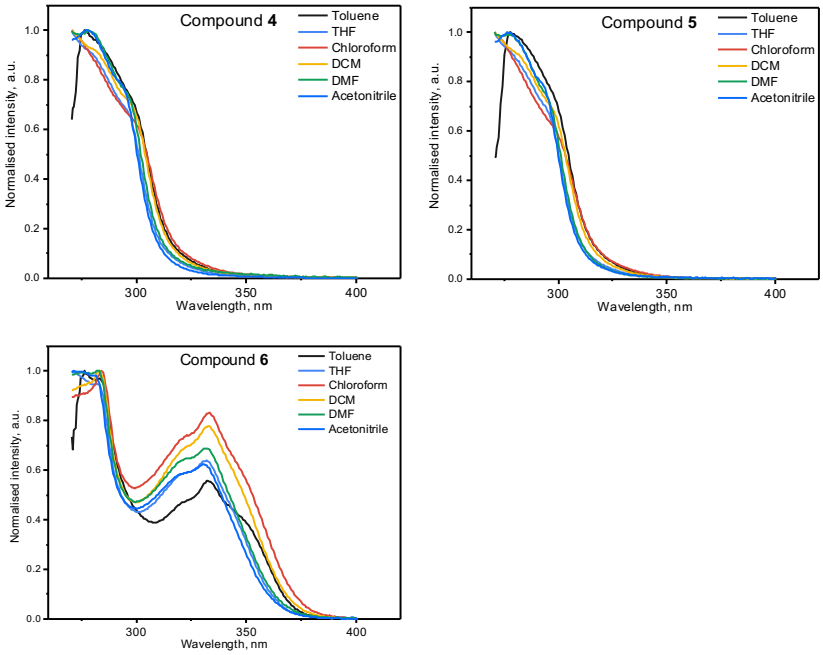


Figure S3. Normalised UV-VIS spectra of different polarity solutions of compounds **4**, **5** and **6**.

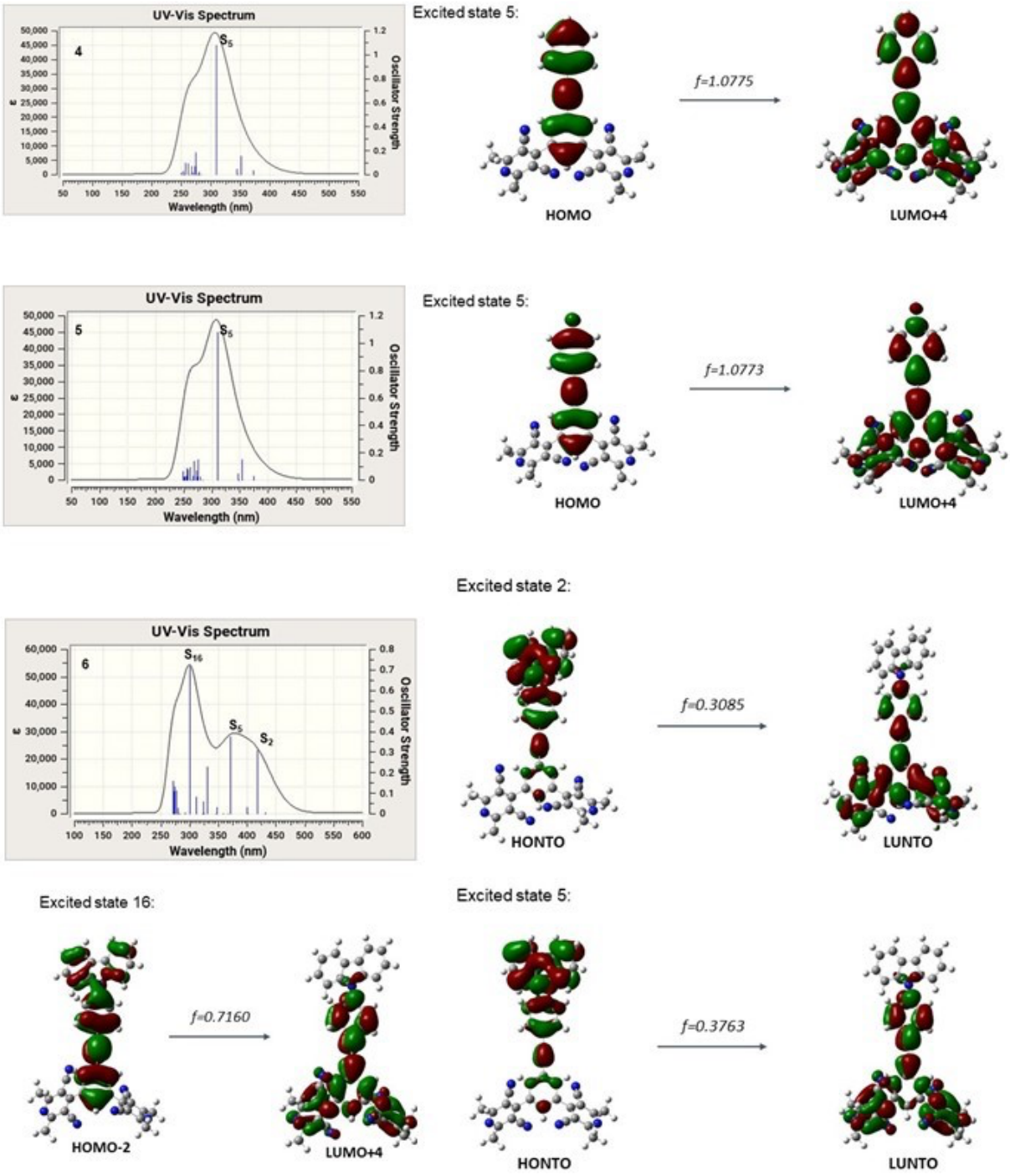


Figure S4. Theoretical UV spectra (in toluene) obtained from TD-DFT calculations of compounds **4**–**6**.

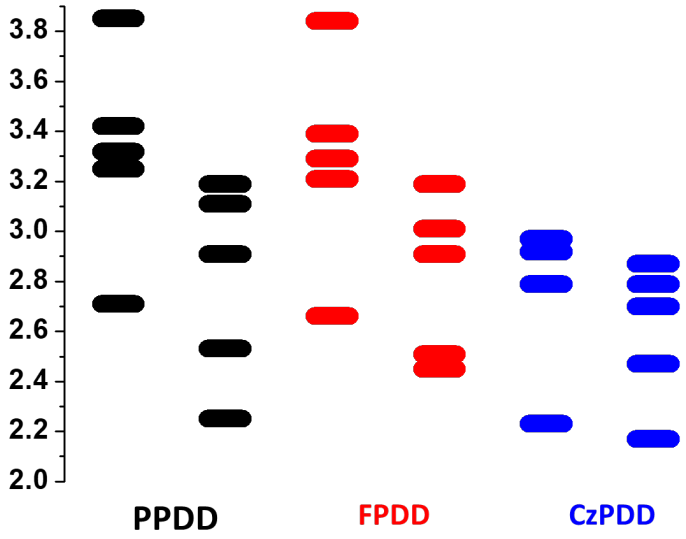


Figure S5. Energy diagrams of the first five singlet and triplet excited-states

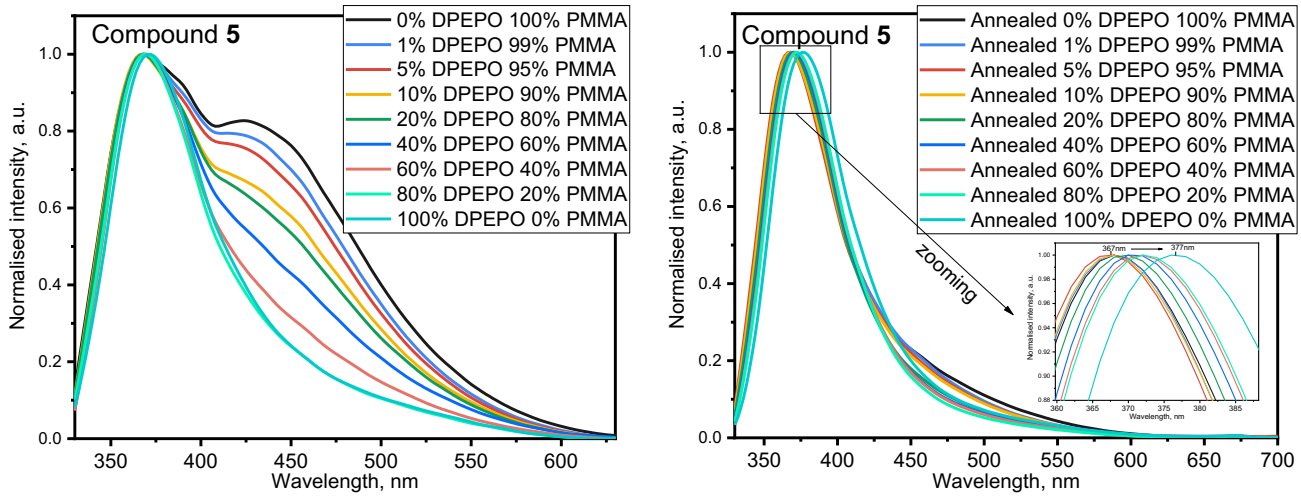
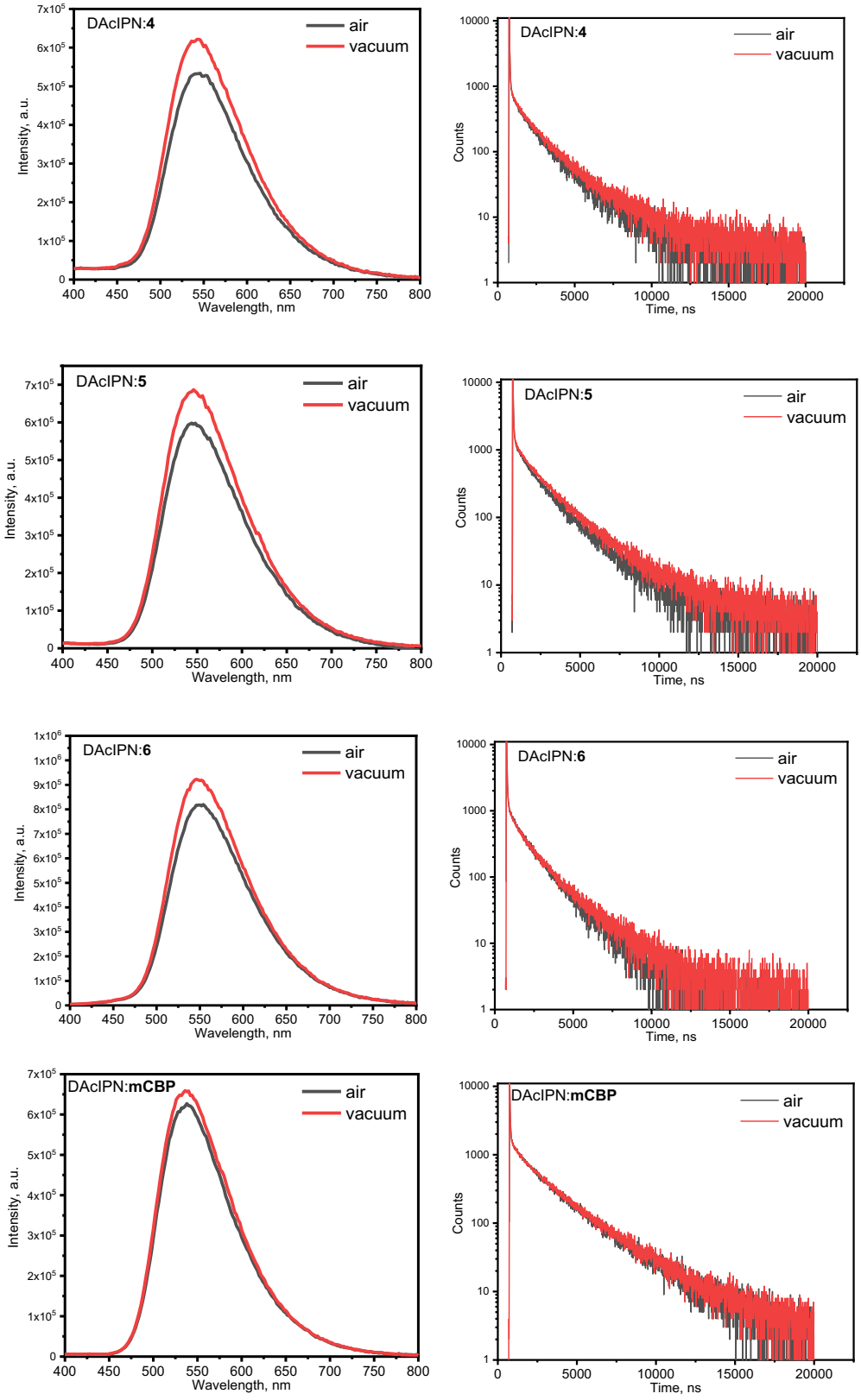


Figure S6. PL spectra of the dispersion of compound 5 in the host mixture of DPEPO and PMMA before and after annealing with the same concentration of the emitter and the different concentrations of the co-hosts DPEPO and PMMA.



a) b)

Figure S7. PL spectra (a) and PL decay curves (b) of DAclPN(10wt.%) in different hosts **4-6** and mCBP at air and vacuum.

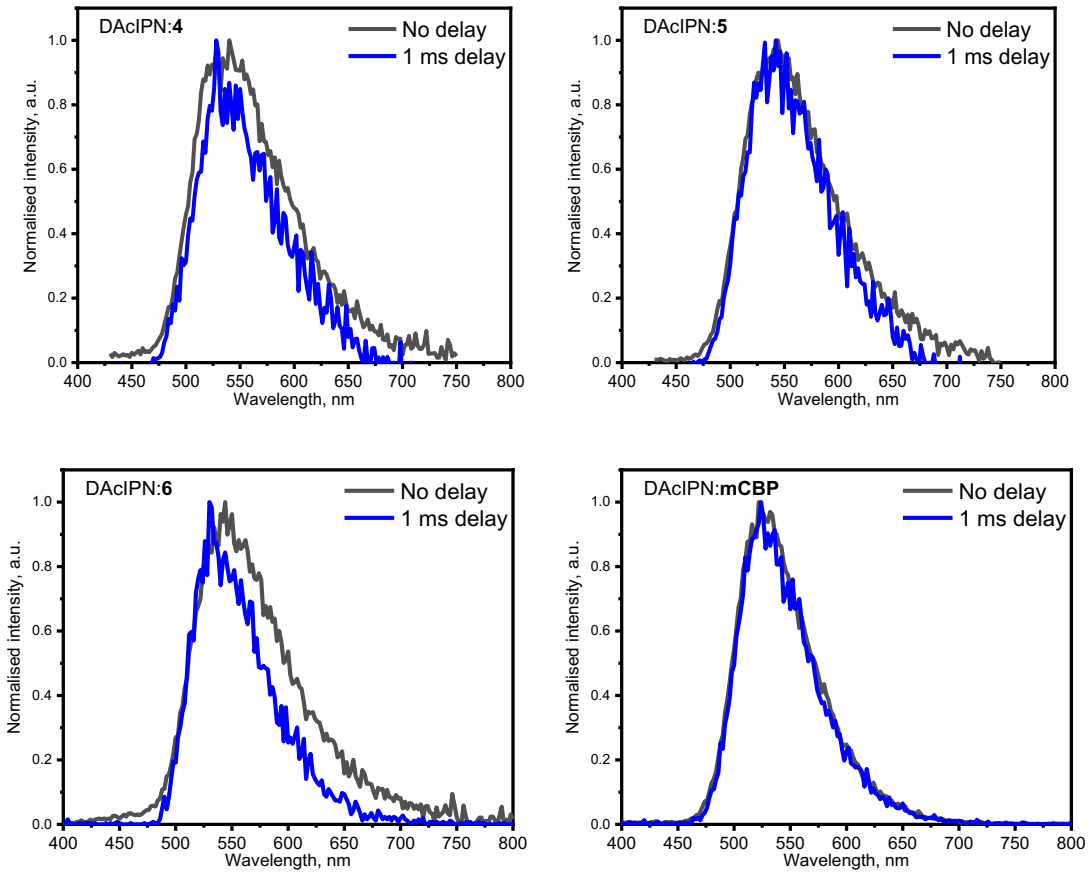
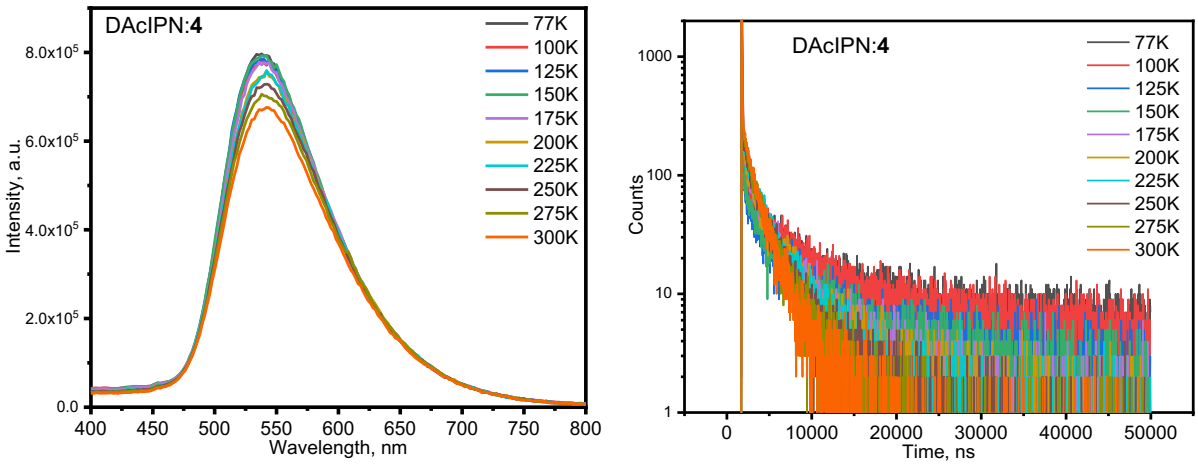


Figure S8. PL and phosphorescence spectra of DAcIPN(10wt.%) in different hosts **4-6** and mCBP at 77K respectively recorded without and with 1 ms delay after excitation.



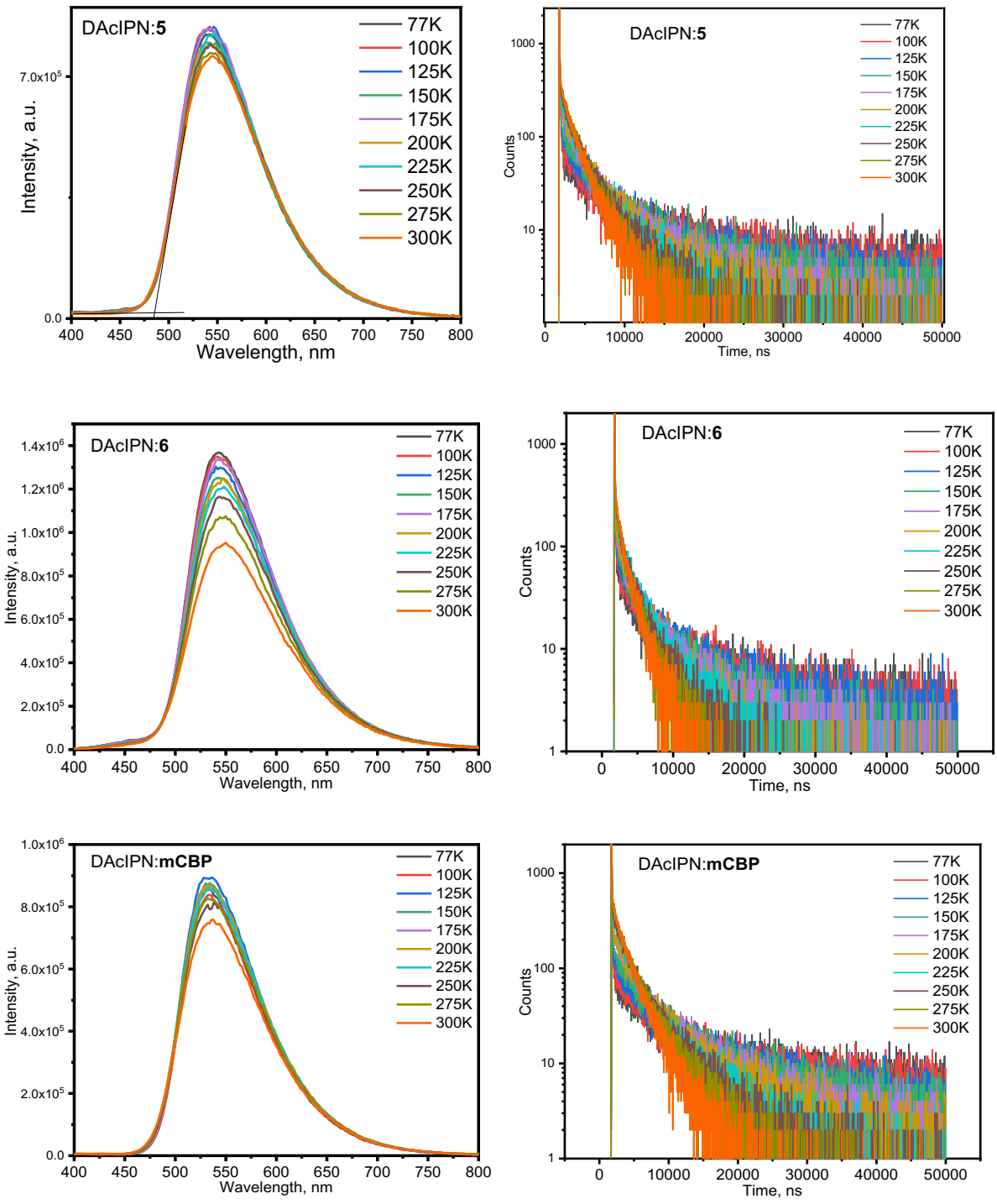


Figure S9. PL spectra (a) and PL decay curves (b) of DAclPN(10wt.%) in different hosts **4–6** and mCBP at different temperatures.

TADF parameters of DAcIPN(10wt.%) in different hosts 4–6 and mCBP at different temperatures

To investigate TADF features of the DAcIPN(10wt.%) in hosts **4–6** and mCBP, the fitting of their PL decays were provided (Table S1–S4). Using that fitting, the radiation transition rate of the doped films of the compounds 2–5 was calculated using the formula shown below[1]:

$$k_{PF} = \frac{\mathbf{\Phi PF}}{\tau_{PF}}; \quad (1)$$

$$k_{ISC} = \frac{\mathbf{\Phi DF}}{\mathbf{\Phi PF} + \mathbf{\Phi DF}} k_{PF} \quad (2)$$

$$k_{DF} = \frac{\mathbf{\Phi DF}}{\tau_{DF}} \quad (3)$$

$$k_{RISC} = \frac{\mathbf{\Phi DF}}{\mathbf{\Phi PF}} \cdot \frac{k_{PF}.k_{DF}}{k_{ISC}}; \quad (4)$$

where k_{PF}, k_{DF}, k_{ISC}, and k_{RISC} are rate constants of prompt and delayed components, intersystem crossing (ISC) and RISC processes, respectively; **ΦPF** and **c** are prompt and delayed PLQYs was distinguished from the total PLQY (**ΦN2**) by comparing the integrated intensity of the prompt and delayed components in the transient photoluminescence spectra (Table S1–S4). The obtained rate constants for **PHhA**:ZEONEX and **bPHhA**:ZEONEX are collected in Table S1–S4.

Table S1. The fitting parameters of PL decay curves of the film DAcIPN(10wt.%):**4** recorded at the different temperatures.

T, K	1/T	τPF, ns	τDF, ns	ΦN2, %	ΦPF, %	ΦDF, %	kPF, s^{-1}	kDF, s^{-1}	kISC, s^{-1}	kRISC, s^{-1}
300	0.0033	29.25	1382.93	18.64	10.66	7.98	3.64E+06	5.77E+04	1.56E+06	1.01E+05
275	0.0036	31.83	1577.83	18.22	10.27	7.94	3.23E+06	5.03E+04	1.41E+06	8.92E+04
250	0.0040	33.80	1746.32	17.02	9.69	7.32	2.87E+06	4.19E+04	1.23E+06	7.36E+04
225	0.0044	36.95	1962.61	17.64	9.73	7.91	2.63E+06	4.03E+04	1.18E+06	7.31E+04
200	0.0050	35.20	2131.49	15.86	9.42	6.44	2.68E+06	3.02E+04	1.09E+06	5.09E+04
175	0.0057	35.35	2118.69	15.69	9.39	6.30	2.66E+06	2.97E+04	1.07E+06	4.97E+04
150	0.0067	40.56	2577.92	10.62	7.12	3.50	1.75E+06	1.36E+04	5.79E+05	2.03E+04
125	0.0080	41.4513	2960.6785	9.66	6.70	2.95	1.62E+06	9.97E+03	4.94E+05	1.44E+04
100	0.0100	42.64526	2690.2848	7.37	5.49	1.88	1.29E+06	6.99E+03	3.29E+05	9.39E+03
77	0.0130	43.82709	2393.023	6.10	4.75	1.35	1.08E+06	5.65E+03	2.40E+05	7.27E+03

Table S2. The fitting parameters of PL decay curves of the film DAcIPN(10wt.%):**5** recorded at the different temperatures.

1/T	τPF, ns	τDF, ns	ΦN2, %	ΦPF, %	ΦDF, %	kPF, s^{-1}	kDF, s^{-1}	kISC, s^{-1}	kRISC, s^{-1}
0.0033	32.59	1518.02	37.91	6.13	31.77	1.88E+06	2.09E+05	1.58E+06	1.29E+06
0.0036	34.42	1702.64	37.91	6.57	31.34	1.91E+06	1.84E+05	1.58E+06	1.06E+06
0.0040	35.33	1930.60	36.08	6.79	29.29	1.92E+06	1.52E+05	1.56E+06	8.06E+05
0.0044	35.04	2089.62	33.22	6.90	26.32	1.97E+06	1.26E+05	1.56E+06	6.06E+05
0.0050	36.61	2445.03	32.58	7.49	25.09	2.05E+06	1.03E+05	1.58E+06	4.47E+05
0.0057	37.78	2683.15	30.03	7.71	22.32	2.04E+06	8.32E+04	1.52E+06	3.24E+05
0.0067	42.93	3128.68	24.65	7.52	17.13	1.75E+06	5.48E+04	1.22E+06	1.80E+05
0.0080	46.36367	3371.5696	21.30	7.19	14.11	1.55E+06	4.19E+04	1.03E+06	1.24E+05
0.0100	47.98664	3590.6633	16.58	6.84	9.74	1.43E+06	2.71E+04	8.37E+05	6.58E+04
0.0130	48.78793	3634.581	14.42	6.57	7.85	1.35E+06	2.16E+04	7.33E+05	4.74E+04

Table S3. The fitting parameters of PL decay curves of the film DAcIPN(10wt.%):**6** recorded at the different temperatures.

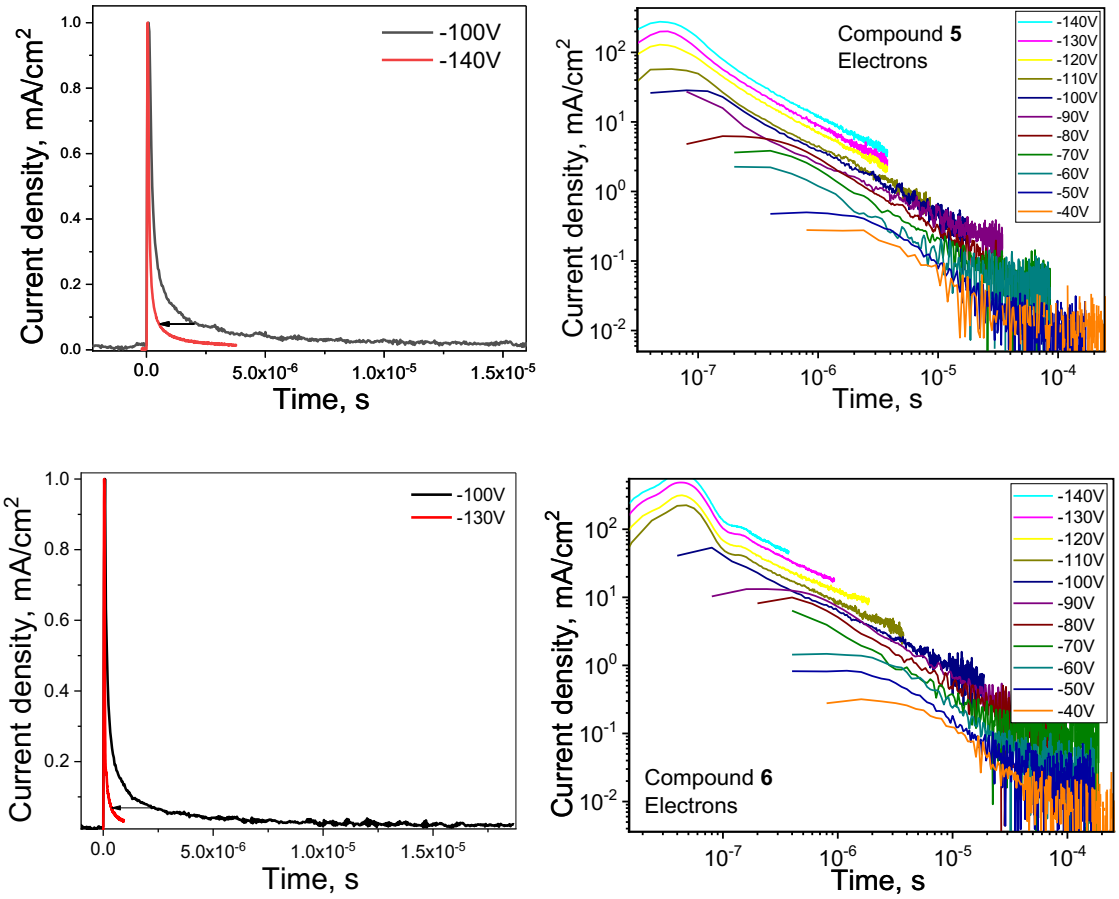
T, K	1/T	τPF, ns	τDF, ns	ΦN2, %	ΦPF, %	ΦDF, %	kPF, s^{-1}	kDF, s^{-1}	kISC, s^{-1}	kRISC, s^{-1}
300	0.0033	29.54	1080.23	21.39	5.30	16.09	1.79E+06	1.49E+05	1.35E+06	6.01E+05
275	0.0036	31.78	1205.07	20.74	5.24	15.50	1.65E+06	1.29E+05	1.23E+06	5.09E+05
250	0.0040	35.29	1449.34	20.64	5.75	14.89	1.63E+06	1.03E+05	1.18E+06	3.69E+05
225	0.0044	33.52	1743.79	22.48	6.22	16.27	1.85E+06	9.33E+04	1.34E+06	3.37E+05
200	0.0050	36.22	1841.63	21.11	6.30	14.82	1.74E+06	8.04E+04	1.22E+06	2.70E+05
175	0.0057	40.83	2207.95	17.45	6.17	11.28	1.51E+06	5.11E+04	9.77E+05	1.44E+05
150	0.0067	37.15	2111.91	15.74	6.11	9.64	1.64E+06	4.56E+04	1.01E+06	1.18E+05
125	0.0080	43.51603	2624.6172	14.03	6.00	8.03	1.38E+06	3.06E+04	7.89E+05	7.15E+04
100	0.0100	44.23426	2675.7764	12.31	5.80	6.51	1.31E+06	2.43E+04	6.93E+05	5.17E+04
77	0.0130	46.86233	2525.9469	9.64	5.17	4.47	1.10E+06	1.77E+04	5.12E+05	3.30E+04

Table S4. The fitting parameters of PL decay curves of the film DAcIPN(10wt.%):**mCBP** recorded at the different temperatures.

T, K	1/T	τPF, ns	τDF, ns	ΦN2, %	ΦPF, %	ΦDF, %	kPF, s^{-1}	kDF, s^{-1}	kISC, s^{-1}	kRISC, s^{-1}
300	0.0033	33.68	1826.92	35.74	3.63	32.11	1.08E+06	1.76E+05	9.68E+05	1.73E+06
275	0.0036	35.92	2130.32	35.56	4.10	31.46	1.14E+06	1.48E+05	1.01E+06	1.28E+06
250	0.0040	36.34	2434.04	33.99	4.37	29.61	1.20E+06	1.22E+05	1.05E+06	9.45E+05
225	0.0044	37.97	2561.12	32.08	4.43	27.65	1.17E+06	1.08E+05	1.01E+06	7.82E+05
200	0.0050	41.96	3162.64	28.35	4.74	23.60	1.13E+06	7.46E+04	9.42E+05	4.46E+05
175	0.0057	42.64	3347.65	26.86	4.84	22.02	1.13E+06	6.58E+04	9.30E+05	3.65E+05
150	0.0067	45.92	3952.84	21.65	5.01	16.64	1.09E+06	4.21E+04	8.38E+05	1.82E+05
125	0.0080	47.9508	4284.0919	17.91	4.58	13.33	9.54E+05	3.11E+04	7.11E+05	1.22E+05
100	0.0100	47.77659	4498.1135	14.17	4.77	9.40	9.98E+05	2.09E+04	6.62E+05	6.21E+04
77	0.0130	49.93294	4909.0628	12.64	4.54	8.10	9.10E+05	1.65E+04	5.83E+05	4.59E+04

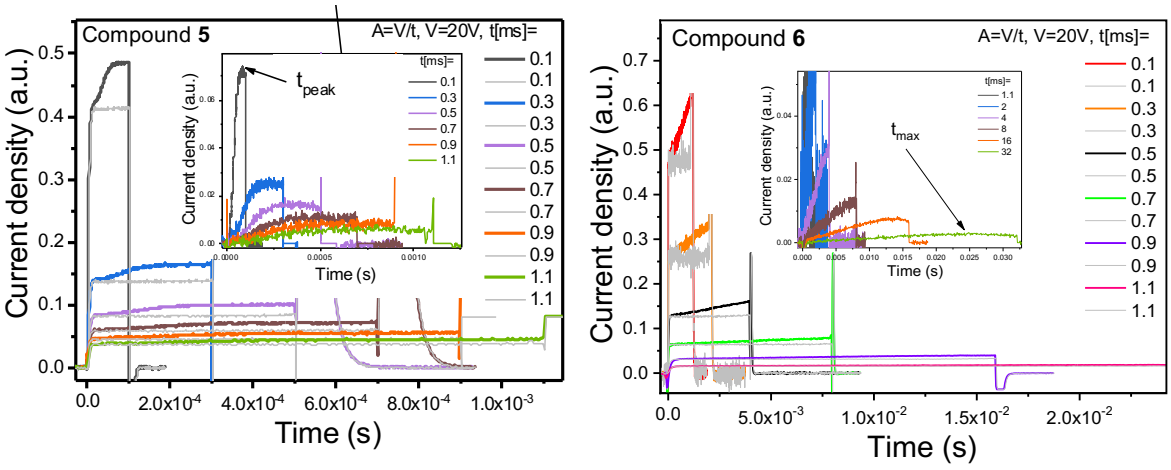
Table S5. The activation energy of ISC and RISC processes of DAcIPN(10wt.%) dispersed in different hosts.

	DAcIPN:**4**	DAcIPN:**5**	DAcIPN:**6**	DAcIPN:**mCBP**
ΔE_A^{RISC}, meV	26	31	27	34
ΔE_A^{ISC}, meV	18	8	9	6



a) b)

Figure S10. TOF signals at different voltages for electrons in films of **5** and **6** in linear (a) and log-log scales (b).



a) b)

Figure S11. Dark-CELIV (grey curves) and photo-CELIV (colour curves) signals at different voltages for electrons in films of **5** (a) and **6** (b). Insets: result of subtraction of dark-CELIV from photo-CELIV signals.

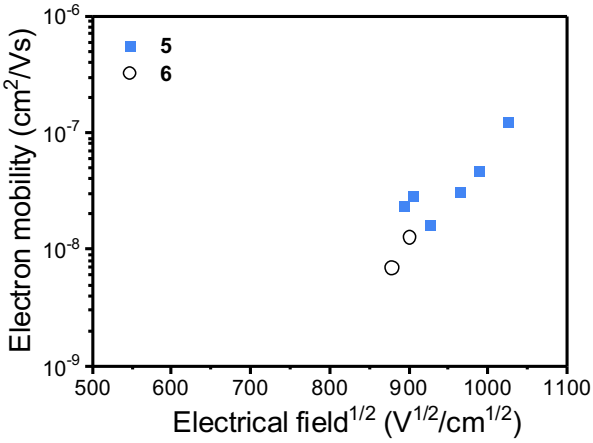
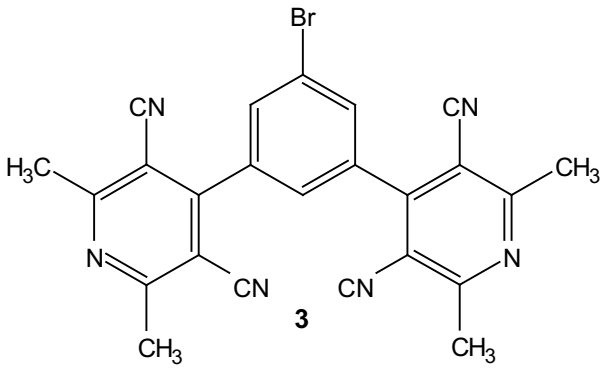


Figure S12. Dependences of electron drift mobilities versus electric field for compounds **5** and **6**

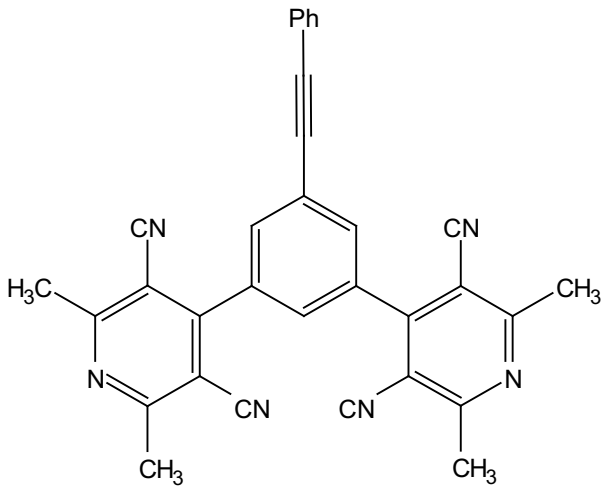
References:

1 C. Han, Z. Zhang, D. Ding and H. Xu, *Chem*, 2018, **4**, 2154–2167.


Br
CN
CN
H3C
CH3
N
N
CN
CN
CH3
CH3

3

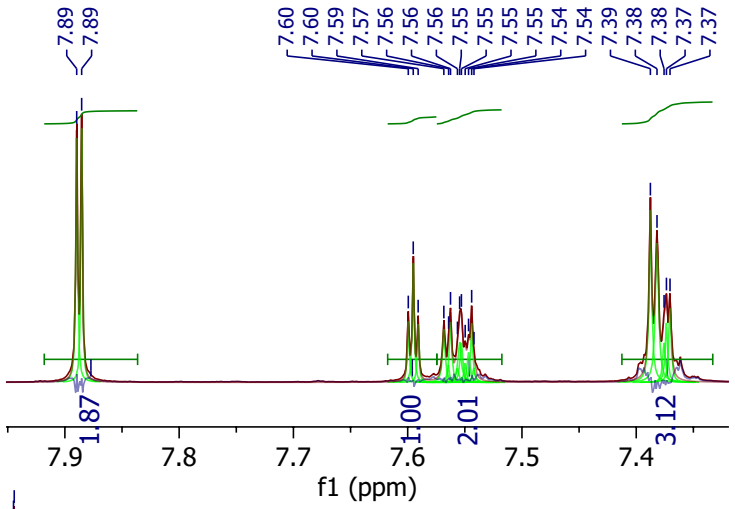
7.91
7.90
7.61
7.61
7.60
7.26
2.89
2.17
1.97
0.99
12.88
f1 (ppm)

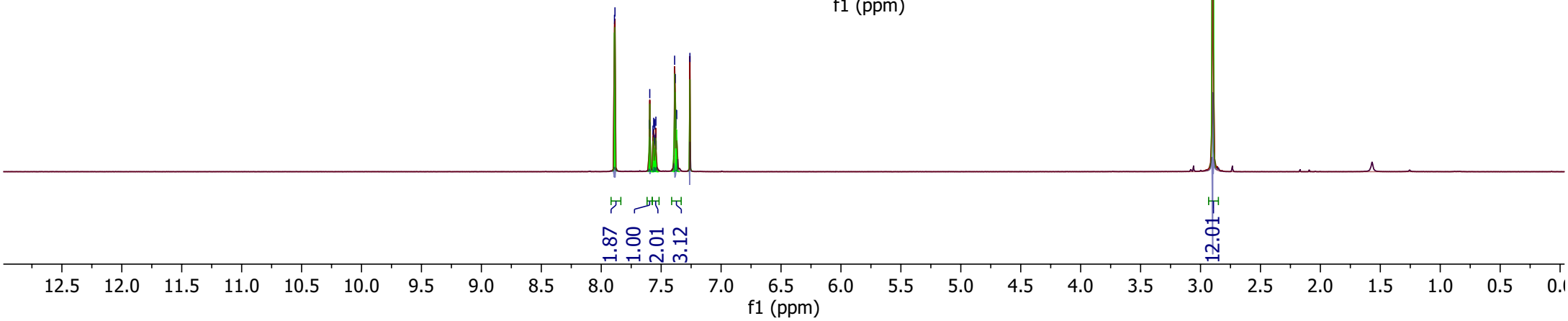

Ph
CN
CN
H_3C
CH_3
N
N
CN
CN
CN
CN
CH_3
CH_3

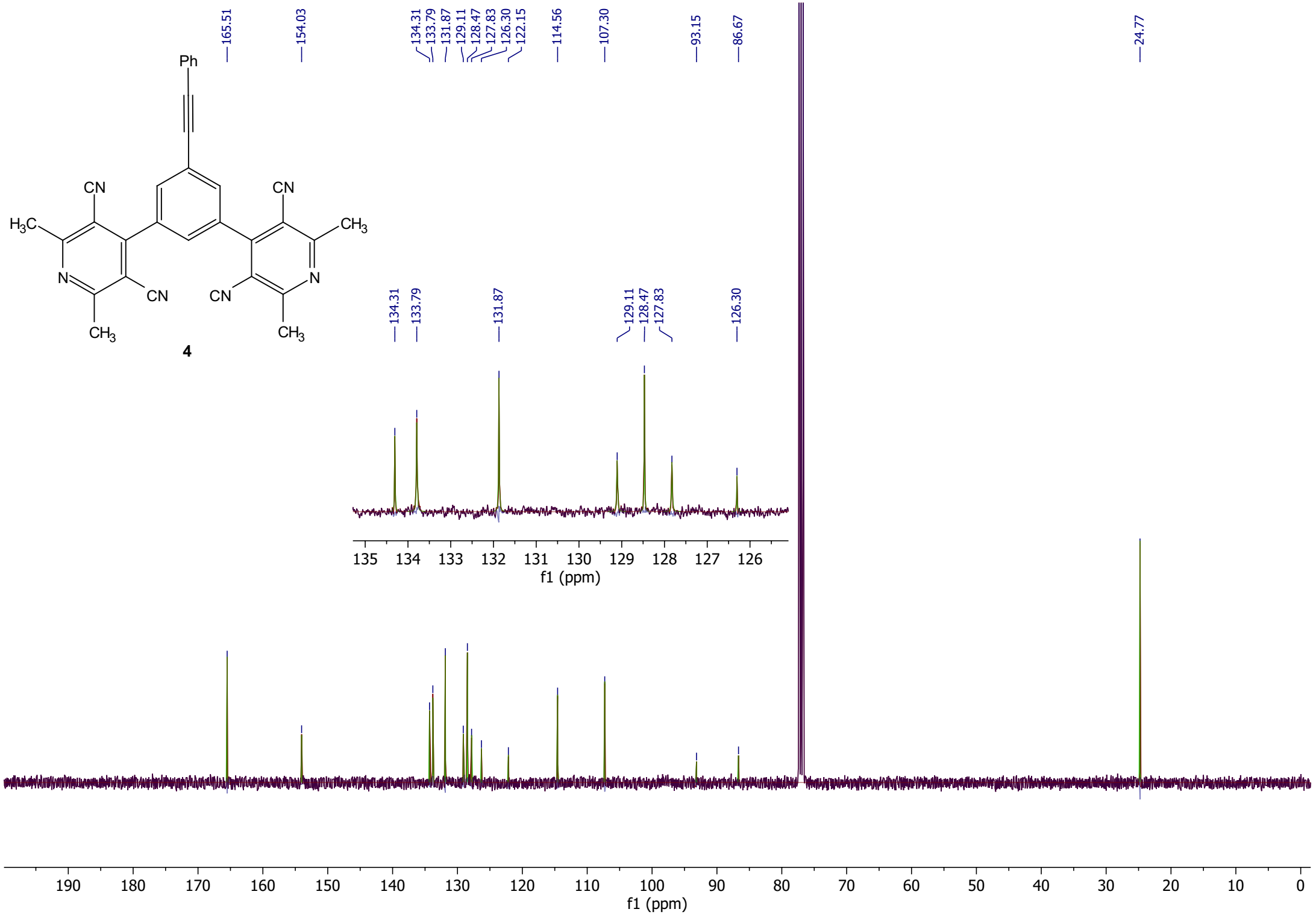
4

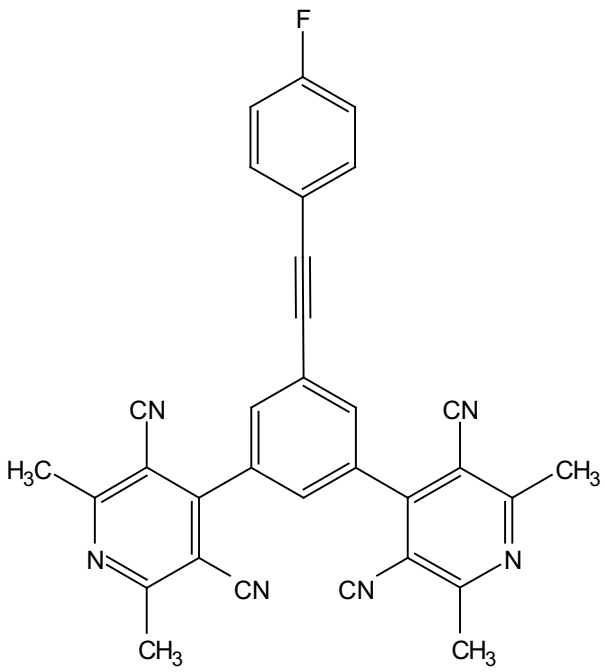

7.89
7.89
7.60
7.60
7.59
7.57
7.56
7.56
7.56
7.55
7.55
7.55
7.55
7.54
7.54
7.39
7.38
7.38
7.37
7.37
7.26


2.90


7.89
7.89
7.60
7.60
7.59
7.57
7.56
7.56
7.56
7.55
7.55
7.55
7.55
7.54
7.54
7.39
7.38
7.38
7.37
7.37
1.87
1.00
2.01
3.12
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)

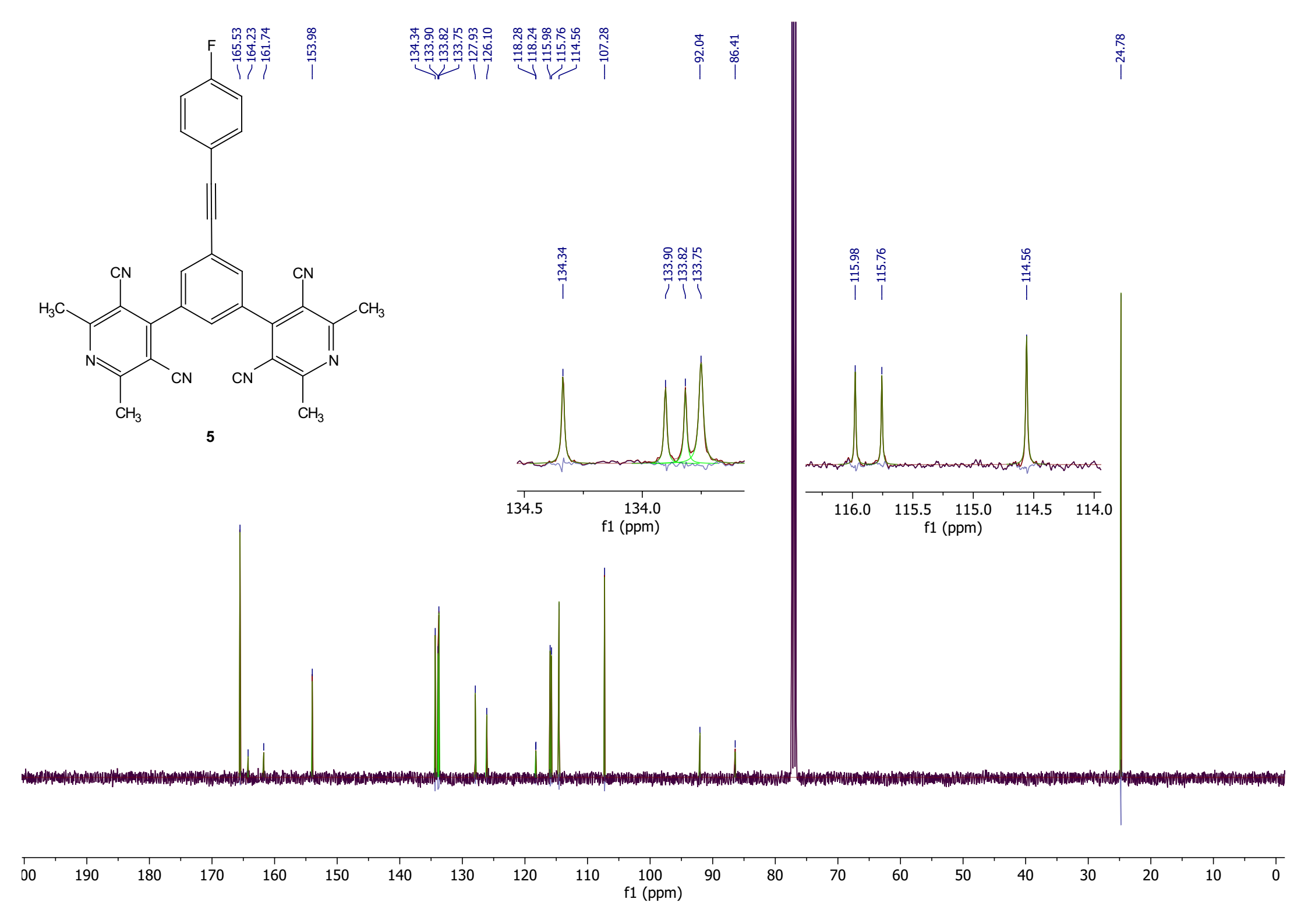

1.87
1.00
2.01
3.12
12.01
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

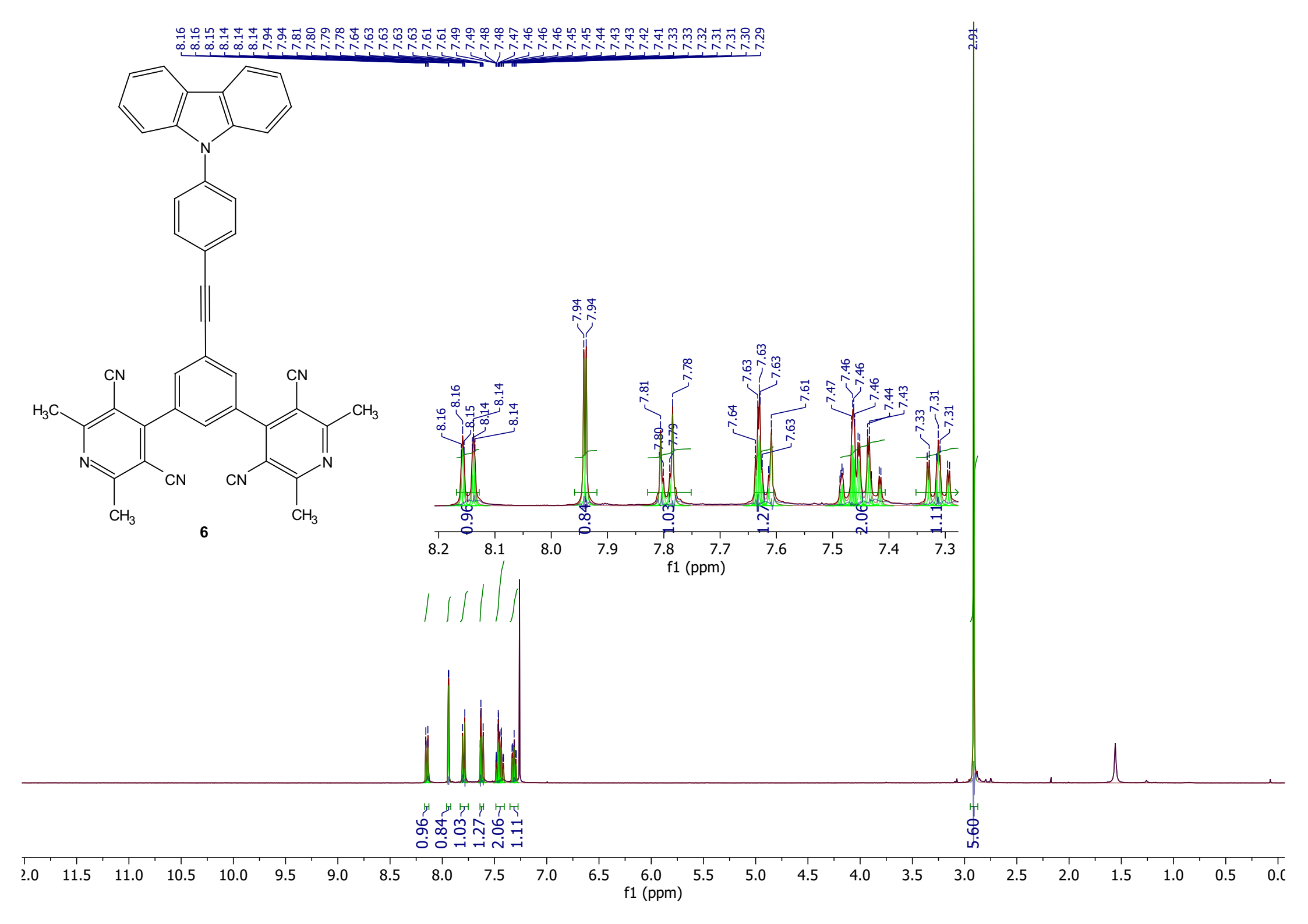

165.51
154.03
134.31
133.79
131.87
129.11
128.47
127.83
126.30
122.15
114.56
107.30
93.15
86.67
24.77
Ph
CN
CN
CN
CN
H3C
CH3
N
N
CH3
CH3
4
f1 (ppm)
f1 (ppm)

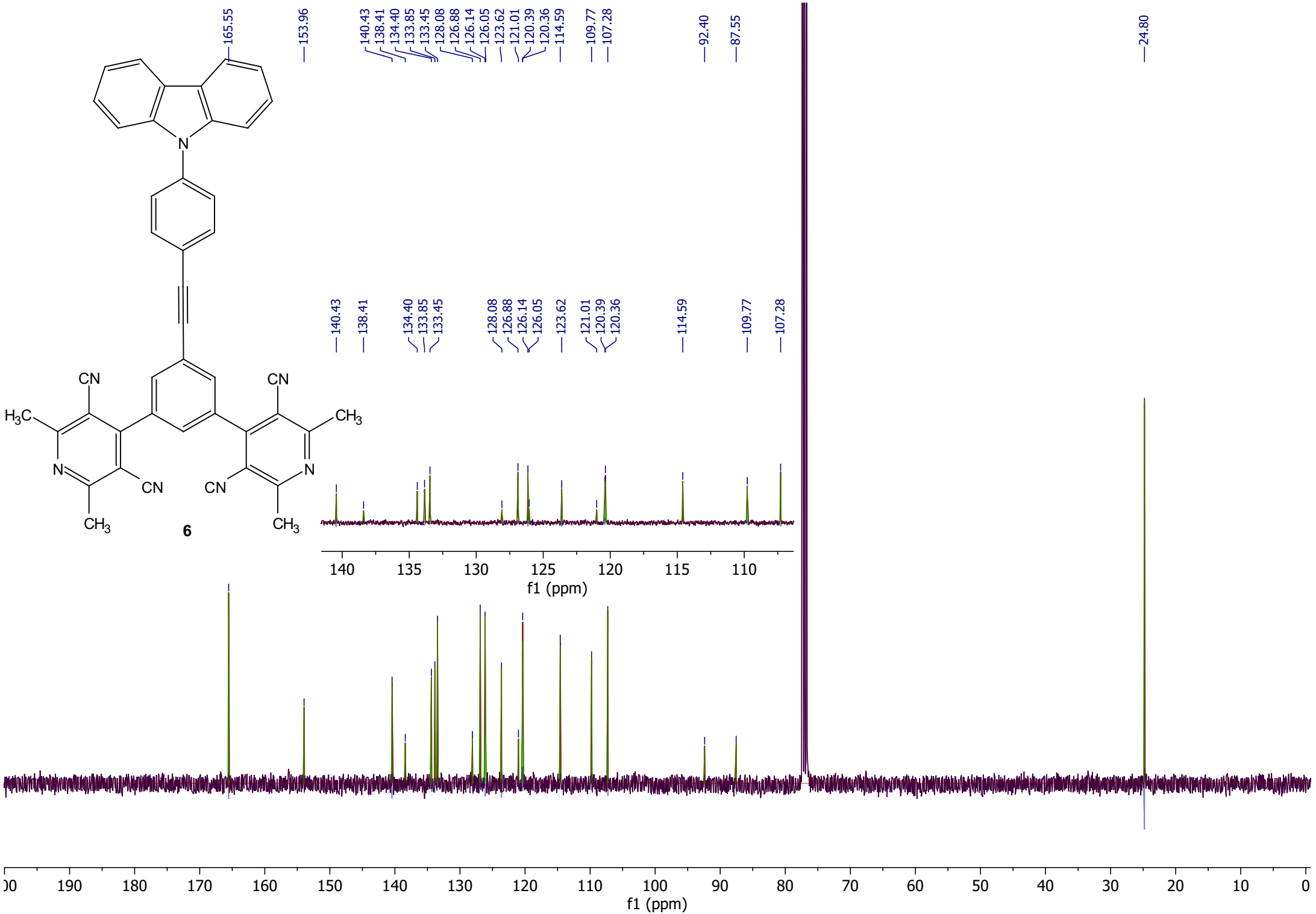

F
CN
CN
H3C
CH3
N
N
CN
CN
CH3
CH3

5

7.87
7.87
7.60
7.60
7.59
7.56
7.54
7.53
7.52
7.26
7.10
7.07
7.05
2.90
1.87
0.92
2.03
2.02
12.17
f1 (ppm)


F
CN
CN
CN
CN
H_3C
CH_3
CH_3
CH_3
N
N
5
165.53
164.23
161.74
153.98
134.34
133.90
133.82
133.75
127.93
126.10
118.28
118.24
115.98
115.76
114.56
107.28
92.04
86.41
24.78
134.5
134.0
f1 (ppm)
116.0
115.5
115.0
114.5
114.0
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.16 8.16 8.15 8.14 8.14 8.14 7.94 7.94 7.81 7.80 7.79 7.78 7.64 7.63 7.63 7.63 7.61 7.61 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.33 7.32 7.31 7.31 7.30 7.29
2.91
CN
CN
H3C
CH3
N
N
CN
CN
CH3
CH3
6
7.94 7.94
8.16 8.16 8.15 8.14 8.14 8.14
7.81 7.80 7.79 7.78
7.64 7.63 7.63 7.63 7.61
7.47 7.46 7.46 7.46 7.44 7.43
7.33 7.31 7.31
0.96 0.84 1.03 1.27 2.06 1.11
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
0.96 0.84 1.03 1.27 2.06 1.11 5.60
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.55
153.96
140.43
138.41
134.40
133.85
133.45
128.08
126.88
126.14
126.05
123.62
121.01
120.39
120.36
114.59
109.77
107.28
92.40
87.55
24.80
CN
CN
H3C
CH3
N
N
CN
CN
CH3
CH3
6
f1 (ppm)
f1 (ppm)