Supporting information

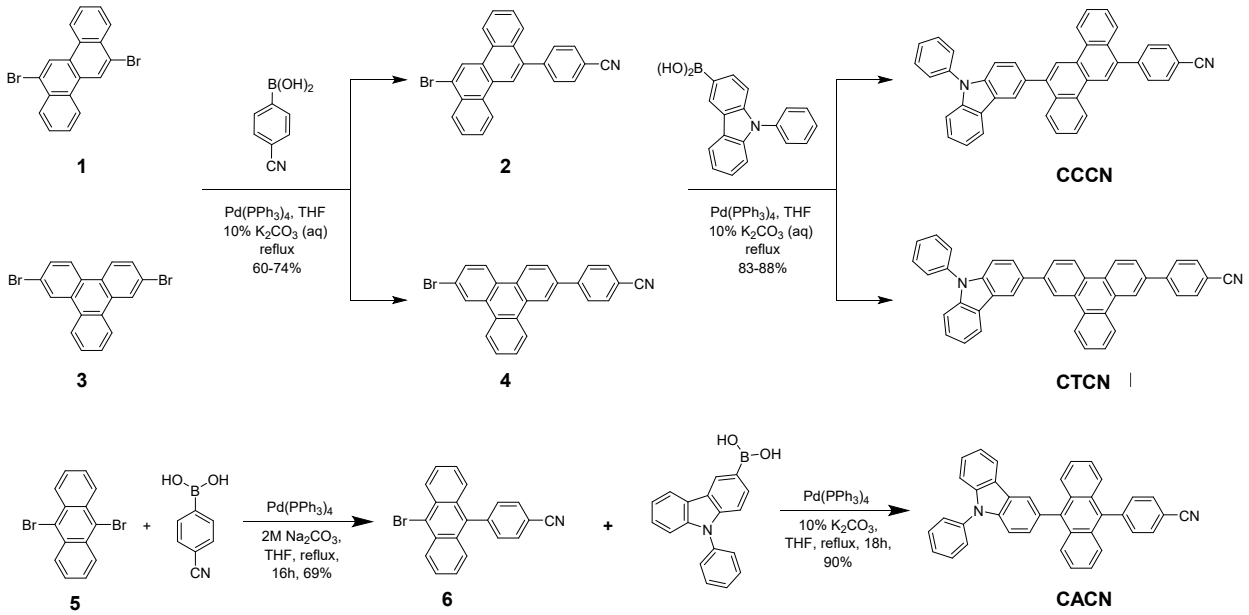
Observation of delayed fluorescence/room-temperature phosphorescence emissions in organic small-molecule emitters, their properties, and electroluminescent performance

Nuttapong Chantanop,[a] Phattananawee Nalaoh,[a] Wijitra Waengdongbung,[a] Rattanasiri Wannapakdee,[a] Patteera Funchien,[a] Suwapat Kongsabay,[a] Taweesak Sudyoadsuk[b] and Vinich Promarak[a]*

[a] Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Wangchan, Rayong 21210, Thailand.
*E-mail: vinich.p@vistec.ac.th.
[b] Frontier Research Center (FRC), Vidyasirimedhi Institute of Science and Technology, Wangchan, Rayong 21210, Thailand.

---

1. Materials synthesis



Scheme S1 The synthesis of the designed molecules.

4-(12-Bromochrysen-6-yl)benzonitrile (2)

A mixture of 6,12-dibromochrysene (700 mg, 1.80 mmol), 4-cyanophenylboronic acid (88 mg, 0.6 mmol), 10% K_2CO_3 (aq) (10 mL), and $Pd(PPh_3)_4$ (35 mg, 5 mol%) in dried THF (60 mL) was degassed with N_2 for 10 min. The reaction mixture was stirred at reflux under N_2 for 18 h. After being cooled to room temperature, the mixture was diluted with water (50 mL) and extracted with DCM (3 x 50 mL). The combined organic layer was washed with water (50 mL), brine (2 x 50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to dryness. The crude was purified by column chromatography on silica gel eluting with a gradient of dichloromethane/hexane mixture (0% to 50%) to obtain light yellow solids (147 mg, 60%). M.p. = 241–245 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.09 (1H, s, Ar-H), 8.80 (1H, d, J = 8.4 Hz, Ar-H), 8.78 – 8.73 (1H, m, Ar-H), 8.56 (1H, s, Ar-H), 8.50 – 8.45 (1H, m, Ar-H), 7.92 – 7.84 (m, 3H), 7.81 – 7.72 (m, 5H), 7.62 (1H, ddd, J = 8.1, 6.8, 1.2 Hz, Ar-H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 137.8, 132.3, 131.4, 130.9, 130.8, 130.4, 130.0, 128.7, 128.3, 127.8, 127.8,

127.3, 127.2, 127.1, 126.2, 125.3, 123.6, 123.5, 123.3, 122.3, 118.8, 111.6; HRMS APCI/Q-TOF (*m/z*): calcd 409.0289 for $C_{25}H_{14}BrN$; found 409.9745 [M^+].

4-(7-Bromotriphenylen-2-yl)benzonitrile (4)

It was synthesized similarly to compound **2** using 2,7-dibromotriphenylene and obtained as white solids (270 mg, 74%). M.p. = 287–290 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (1H, s, Ar-H), 8.79 (1H, d, *J* = 1.9 Hz, Ar-H), 8.73 – 8.70 (1H, m, Ar-H), 8.68 (1H, d, *J* = 8.5 Hz, Ar-H), 8.62 – 8.57 (1H, m, Ar-H), 8.52 (1H, d, *J* = 8.7 Hz, Ar-H), 7.90 – 7.87 (3H, m, Ar-H), 7.82 (1H, d, *J* = 8.0 Hz, Ar-H), 7.78 (1H, dd, *J* = 8.6, 1.9 Hz, Ar-H), 7.76 – 7.69 (2H, m, Ar-H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 138.1, 132.8, 131.8, 130.5, 129.8, 129.3, 129.0, 128.1, 128.0, 127.9, 126.4, 126.2, 125.2, 124.2, 123.6, 123.3, 122.2, 118.9, 111.3; HRMS APCI/Q-TOF (*m/z*): calcd 409.0289 for $C_{25}H_{14}BrN$; found 409.9523 [M^+].

4-(10-Bromoanthracen-9-yl)benzonitrile (6)

It was synthesized similarly to compound **2** using 9,10-dibromoanthracene and obtained as yellow solids (338 mg, 69%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.9 Hz, 2H), 7.92 – 7.88 (m, 2H), 7.63 – 7.60 (m, 2H), 7.57 – 7.52 (m, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.43 – 7.40 (m, 2H); ^{13}C NMR (151 MHz, CDCl3) δ 143.8, 135.1, 132.3, 132.1, 130.5, 130.2, 128.2, 127.1, 126.4, 126.3, 124.0, 118.7, 112.0. HRMS APCI/Q-TOF (*m/z*): calcd for $C_{25}H_{14}BrN$ 357.0153; found: 358.0198 [M + H]$^+$.

2. Single crystal XRD data

All crystallographic information (CIF) data, including CCDC numbers 1984569and 2012094 for **CCCN** and **CTCN**, were deposited and obtained with no cost at https://www.ccdc.cam.ac.uk/.

Table S1 Crystal structures information.

Compound	**CCCN**	**CTCN**
CCDC Deposit Number	1984569	2012094
Empirical formula	$C_{43}H_{26}N_2$	$C_{43}H_{26}N_2$
Formula weight	570.66	570.66
Temperature/K	110	195
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	*P21/n*
a/Å	17.234(2)	14.7177(4)
b/Å	9.2814(11)	8.9166(2)
c/Å	40.346(5)	22.1216(6)
α/°	90	90
β/°	98.618(4)	99.1280(10)
γ/°	90	90
Volume/Å^3	6380.7(13)	2866.29(13)
Z	8	4
ρ_{calc}g/cm^3	1.188	1.322
μ/mm^{-1}	0.069	0.590
F(000)	2384.0	1192.0
Crystal size/mm^3	0.38 × 0.30 × 0.08	0.58 × 0.12 × 0.05

Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.782 to 52.742	6.75 to 140.138
Index ranges	-21 ≤ h ≤ 21, -11 ≤ k ≤ 11, -50 ≤ l ≤ 50	-17 ≤ h ≤ 14, -10 ≤ k ≤ 10, -26 ≤ l ≤ 26
Reflections collected	70682	43547
Independent reflections	6531 [R_{int} = 0.0711, R_{sigma} = 0.0339]	5421 [R_{int} = 0.0570, R_{sigma} = 0.0284]
Data/restraints/parameters	6531/0/406	5421/0/407
Goodness-of-fit on F^2	1.100	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0563, wR_2 = 0.1296	R_1 = 0.0424, wR_2 = 0.1068
Final R indexes [all data]	R_1 = 0.0716, wR_2 = 0.1363	R_1 = 0.0542, wR_2 = 0.1141

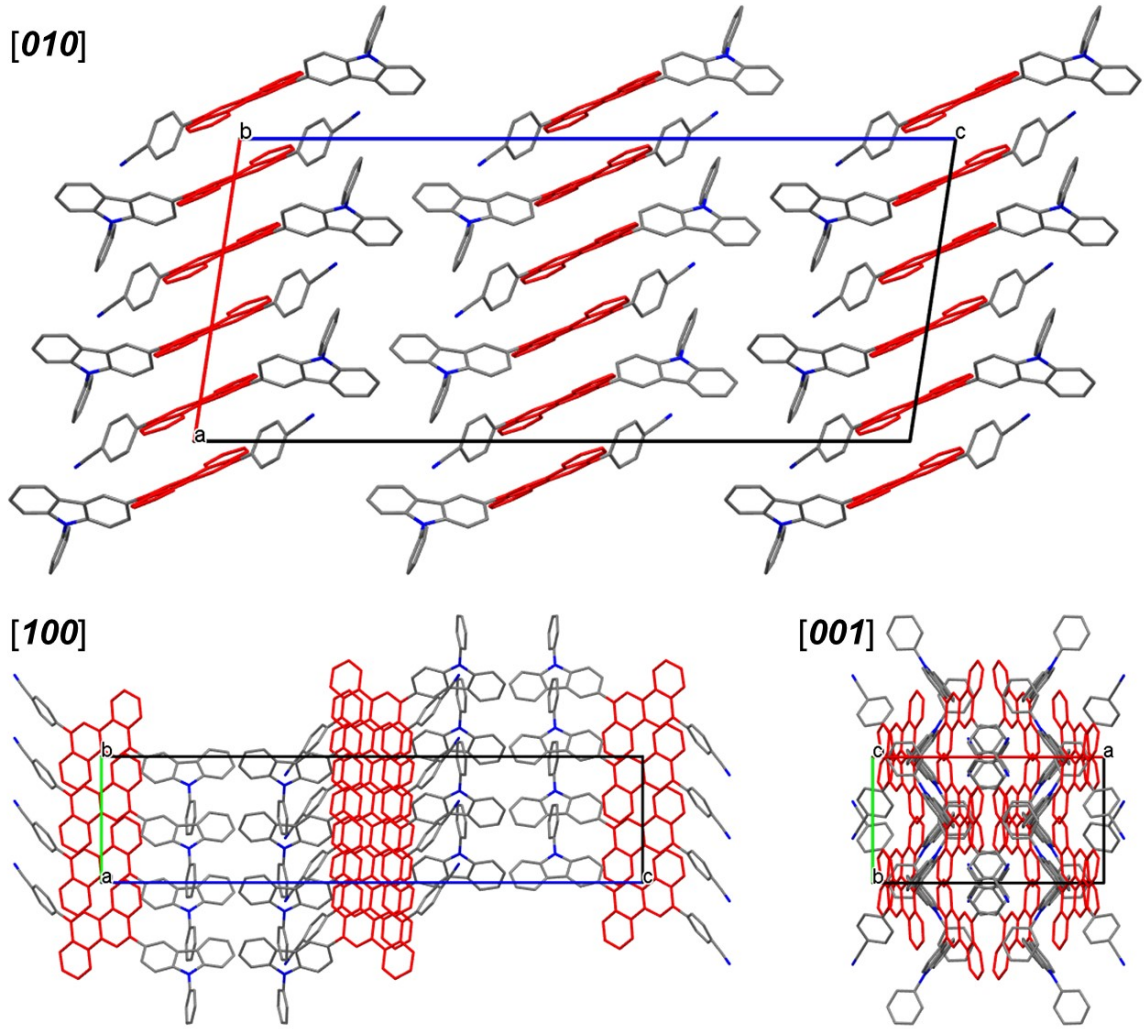


Fig. S1. Crystal packing of **CCCN** along [*100*], [*010*], and [*001*] directions with red-highlighted chrysene structure. All hydrogen atoms were omitted for clarity.

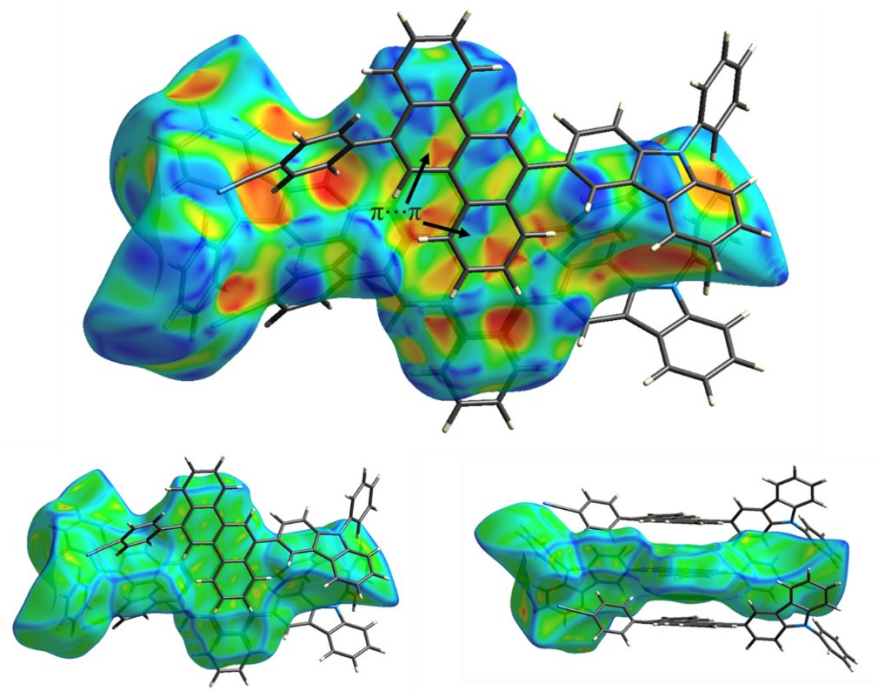


Fig. S2 Hirshfeld Surface Analysis of **3CzCsCN** displayed shape index (top) and curvedness (bottom-left: the top view, bottom-right: the side view). The blue and red triangles on the shape index surface indicated π–π interaction in the 6-membered-ring subunits of chrysene (highlighted with the arrow line). A flat green surface of curvedness indicated the intermolecular π–π interaction, while the blue-line edge crossed over the subunit of the chrysene moiety that presented no interplane π–stacking.

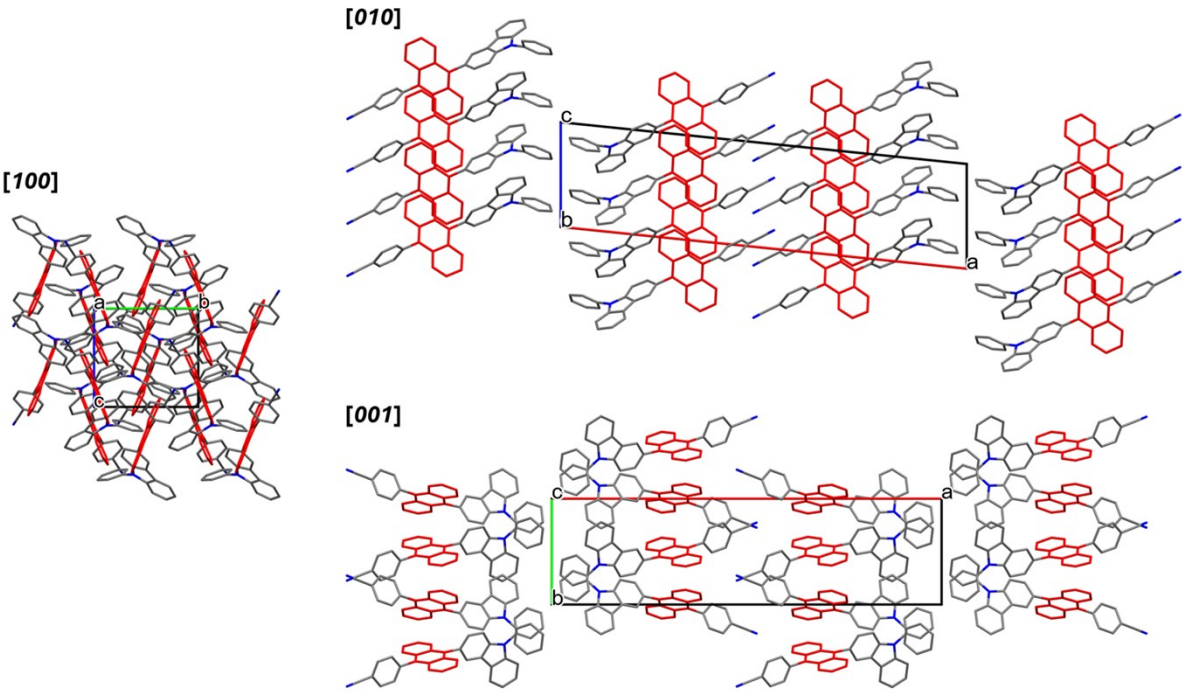


Fig. S3 Crystal packing of **CzAnthBN** from reference[1] along [*100*], [*010*], and [*001*] directions with red-highlighted anthracene structure. All hydrogen atoms were omitted for clarity.

[1]Journal of Materials Chemistry C, 2019, 7, 1014, DOI: 10.1039/C8TC05707A

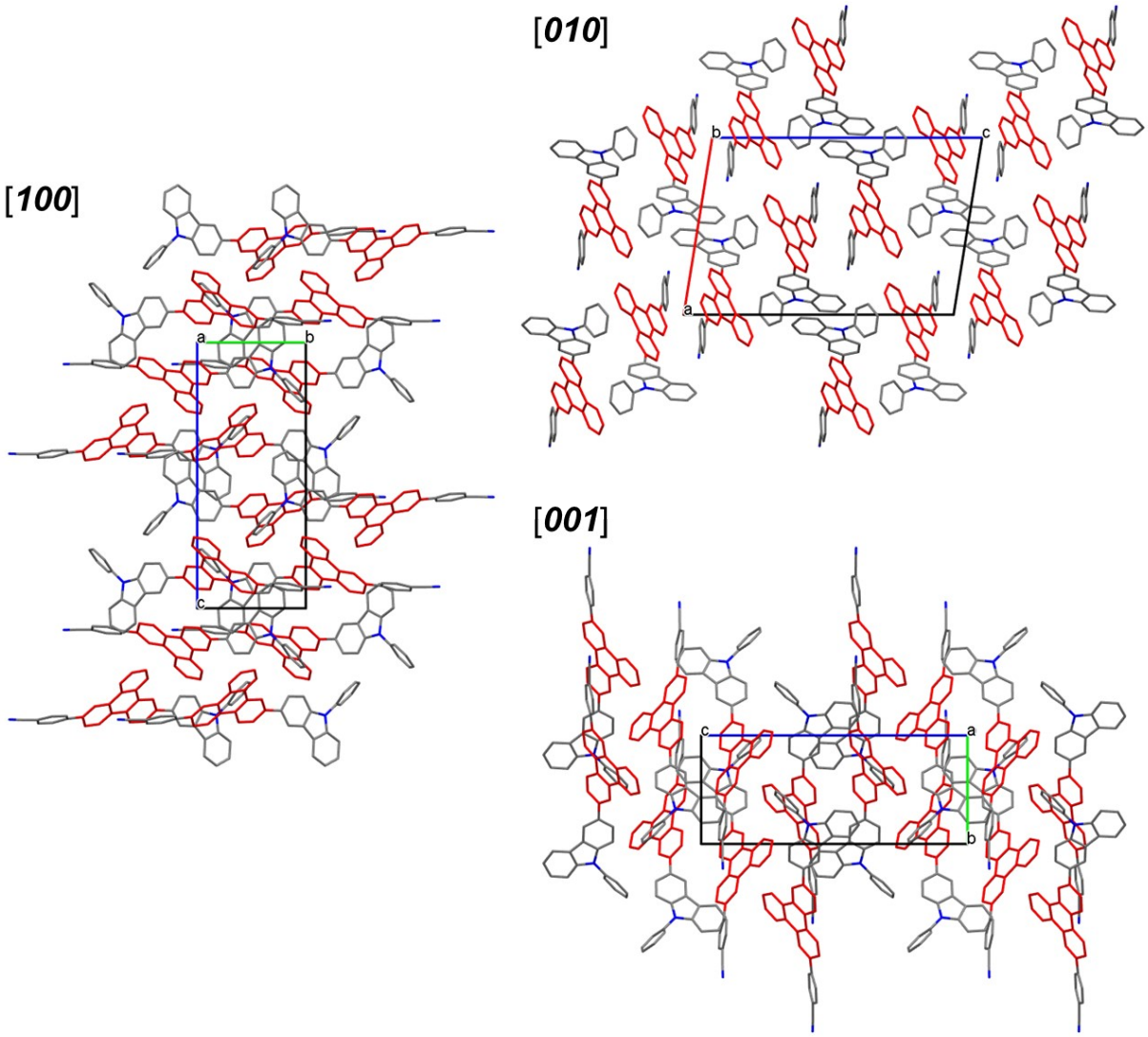
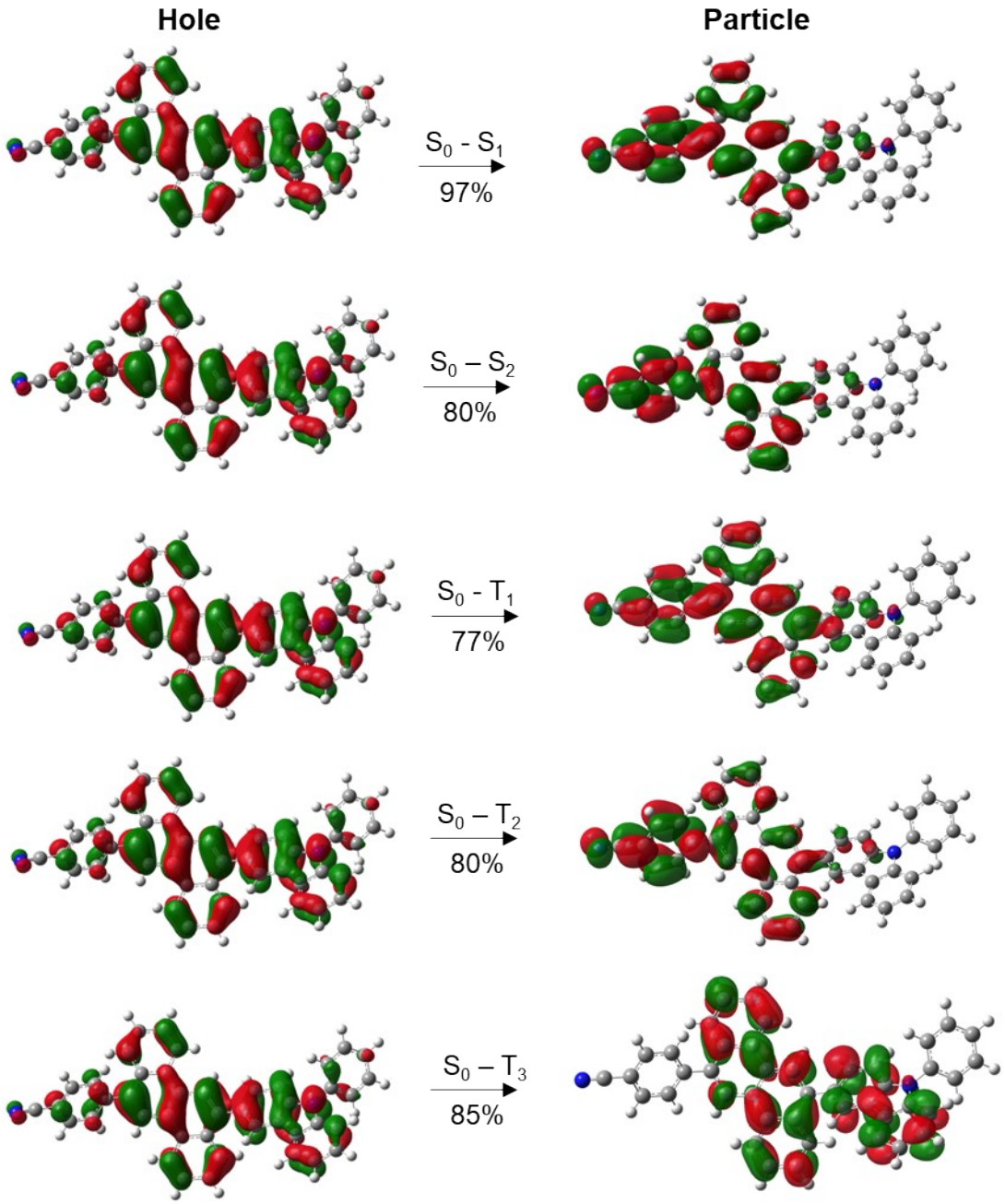


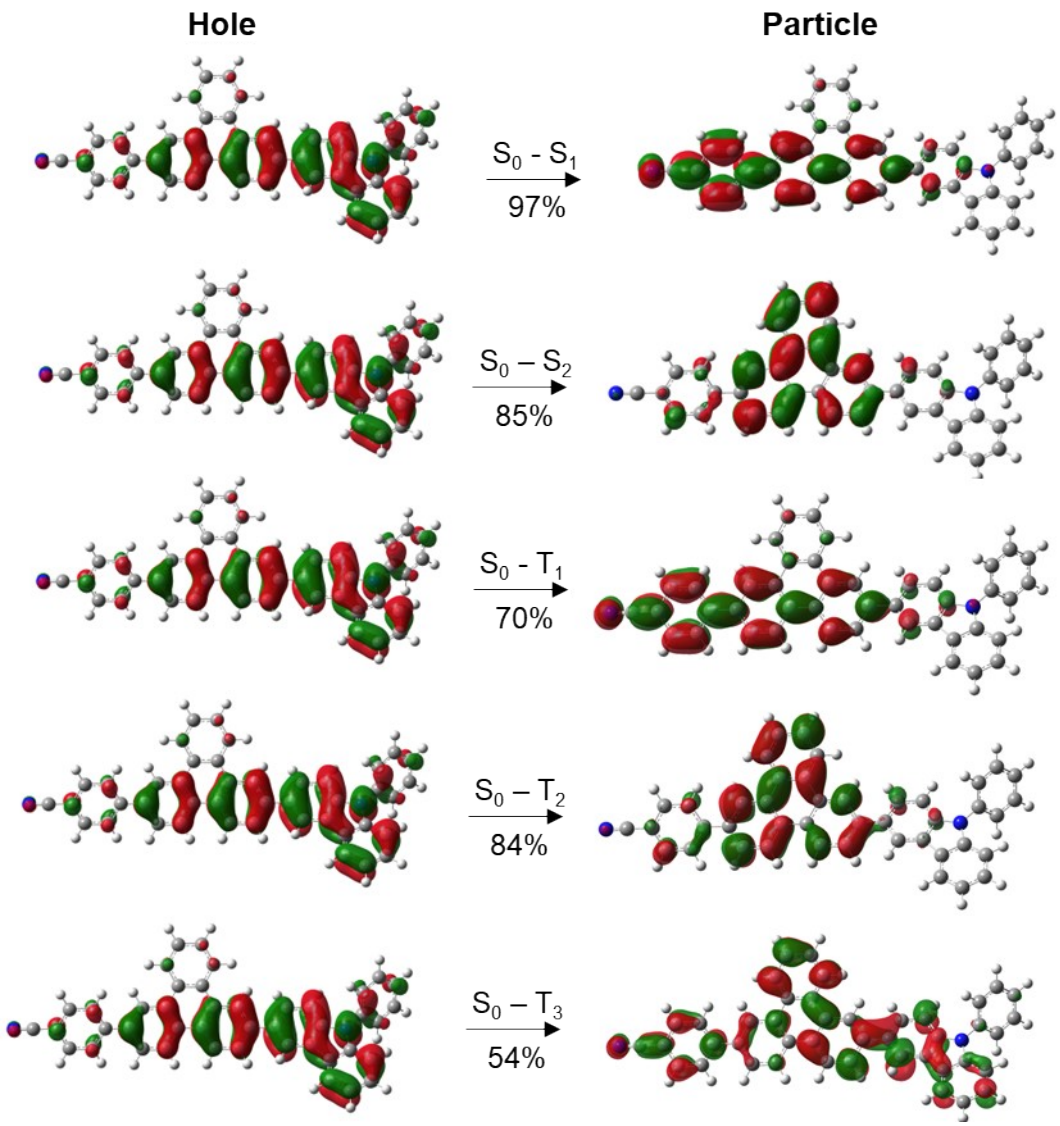
Fig. S4 Crystal packing of **CTCN** along [*100*], [*010*], and [*001*] directions with red-highlighted triphenylene structure. All hydrogen atoms were omitted for clarity.

3. DFT calculation results



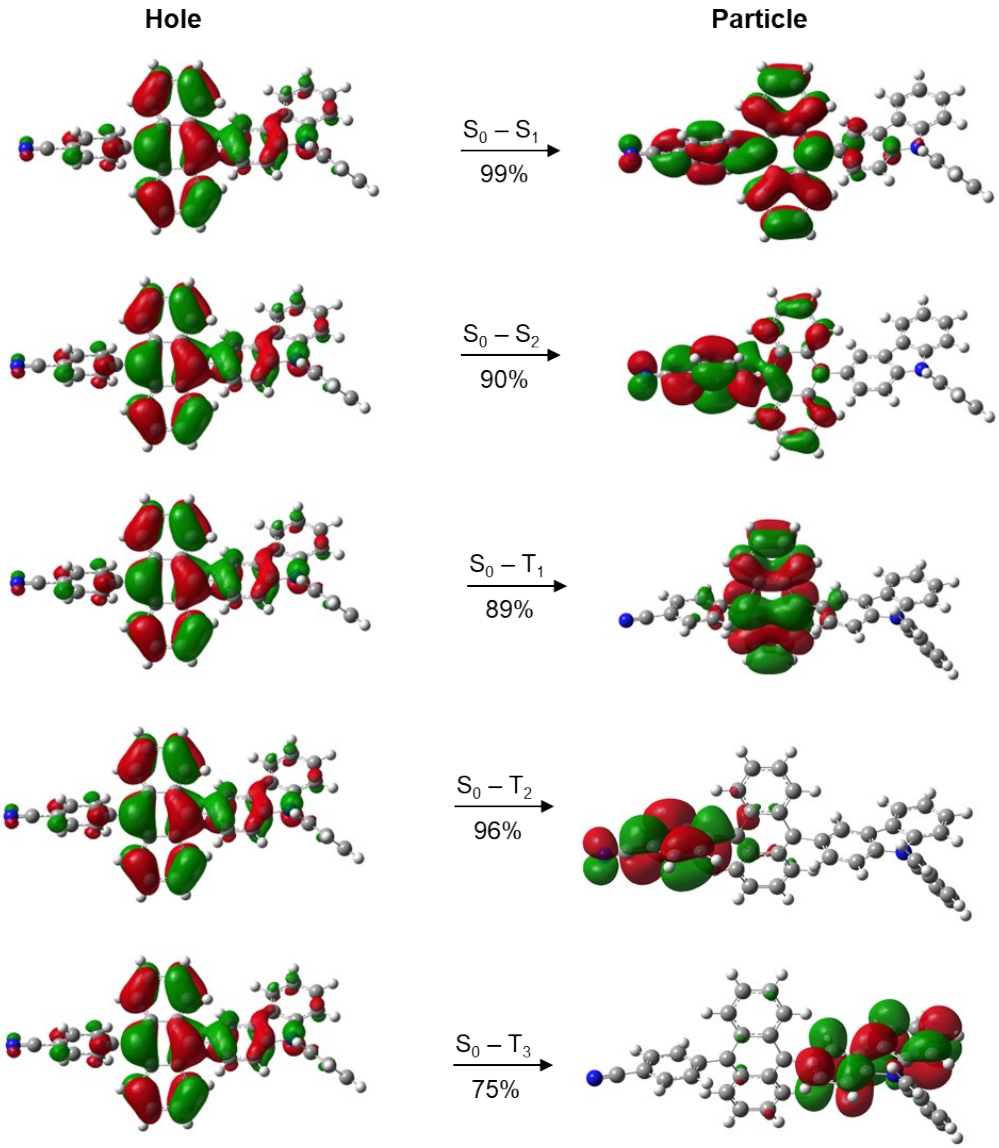
State	Energy (eV)	Osc. Strength	Transition character	Sm index
S1	2.69	0.5674	LE+CT	0.44675
S2	3.31	0.0248	LE+CT	0.31347
T1	1.48	-	LE+CT	0.61379
T2	2.72	-	LE+CT	0.46677
T3	2.88	-	LE+CT	0.36178

Fig. S5 NTOs and the excited states energies of CCCN calculated by the TD-B3LYP/6-31G(d,p) function.



State	Energy (eV)	Osc. Strength	Transition character	Sm index
S1	2.85	0.7212	LE+CT	0.25433
S2	3.41	0.0586	LE+CT	0.53270
T1	1.92	-	LE+CT	0.46628
T2	2.69	-	LE+CT	0.40238
T3	3.03	-	LE+CT	0.43569

Fig. S6 NTOs and the excited states energies of CTCN calculated by the TD-B3LYP/6-31G(d,p) function.



State	Energy (eV)	Osc. Strength	Transition character	Sm index
S1	3.05	0.4561	LE+CT	0.60781
S2	3.14	0.0019	LE+CT	0.21827
T1	1.73	-	LE+CT	0.71428
T2	2.97	-	LE+CT	0.27335
T3	3.23	-	LE+CT	0.42218

Fig. S7 NTOs and the excited states energies of CACN calculated by the TD-B3LYP/6-31G(d,p) function.

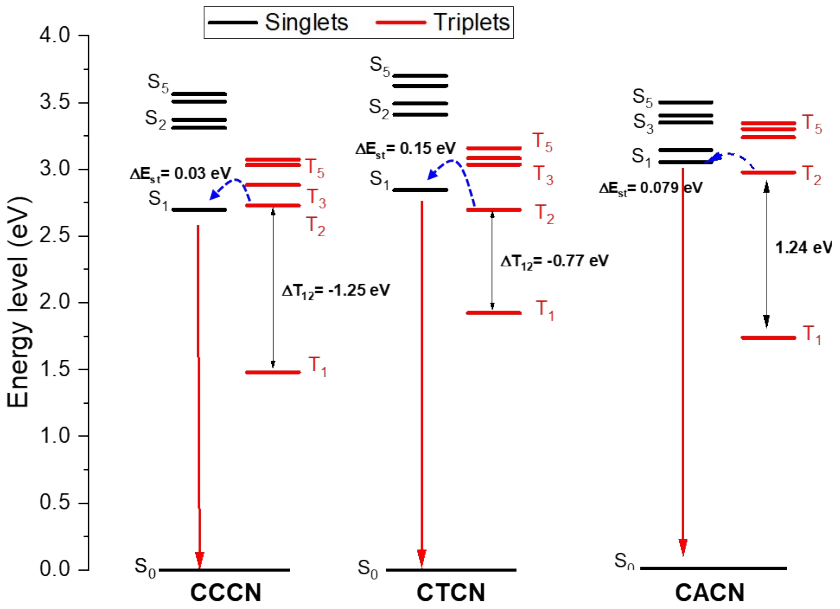


Fig. S8 The energy diagrams of single excited states and triplet excited states calculated by TD-DFT B3LYP/6-31G(d,p).

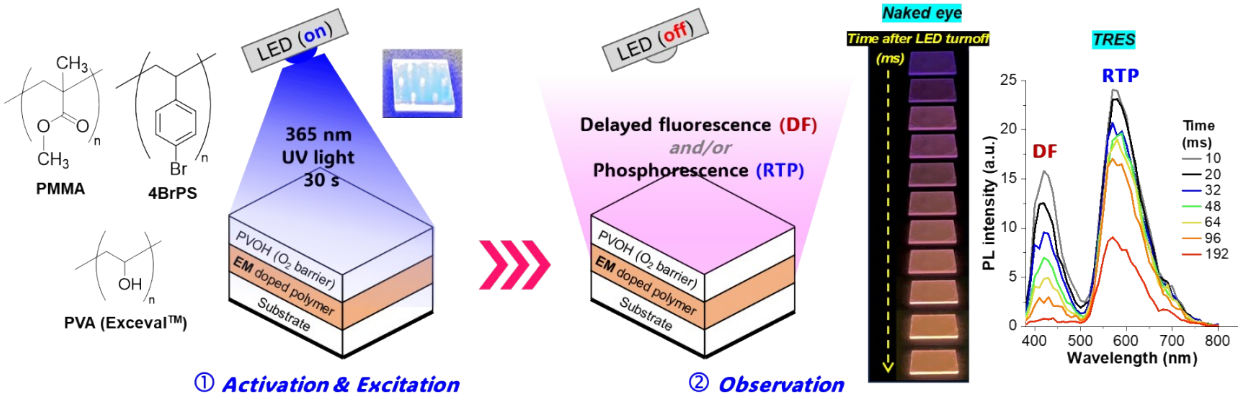


Fig. S9 Experimental scheme for the observation of delayed fluorescence (DF)/room-temperature phosphorescence (RTP) emissions in solid films at ambient conditions.

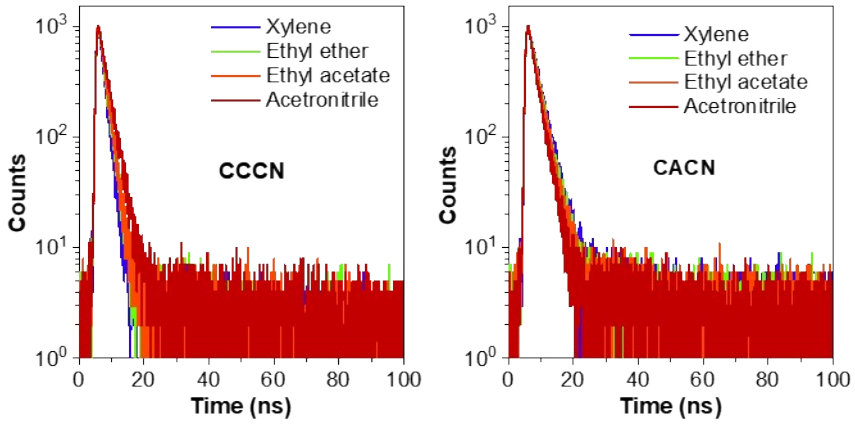


Fig. S10 Transient PL decay spectra of CCCN and CACN in various solvents.

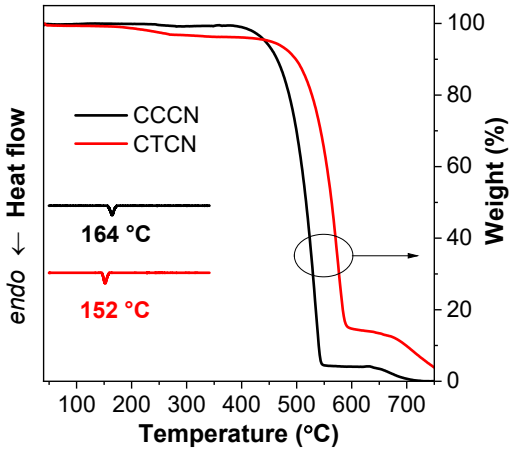


Fig. S11 DSC and TGA thermograms of CCCN and CTCN measured at a heating rate of 10 °C/min under N2 flow.

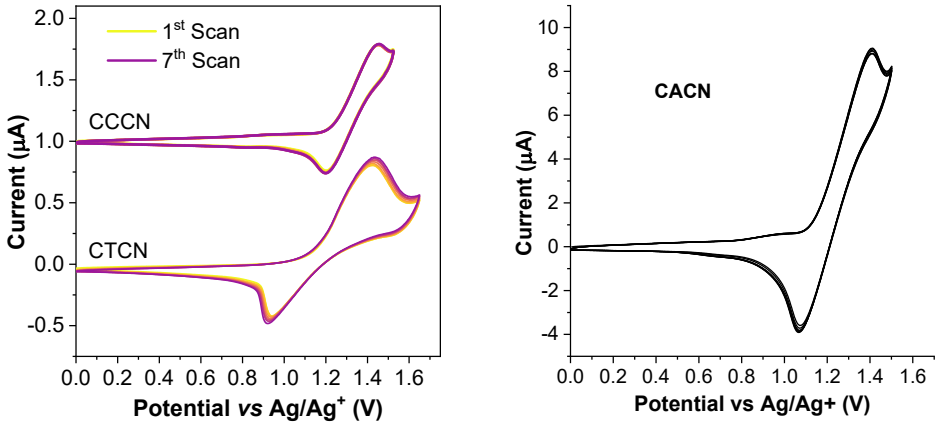


Fig. S12 CV voltammograms analyzed in dry DCM containing *n*-Bu_4NPF_6 as a supporting electrolyte at a scan rate of 50 mV s^{-1} under Ar atmosphere.

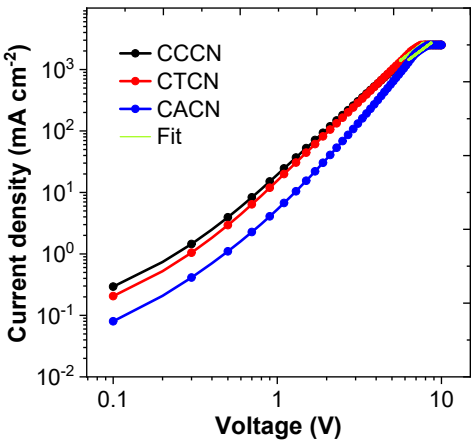


Fig. S13 *I-V* plots of the hole-only device (HOD).

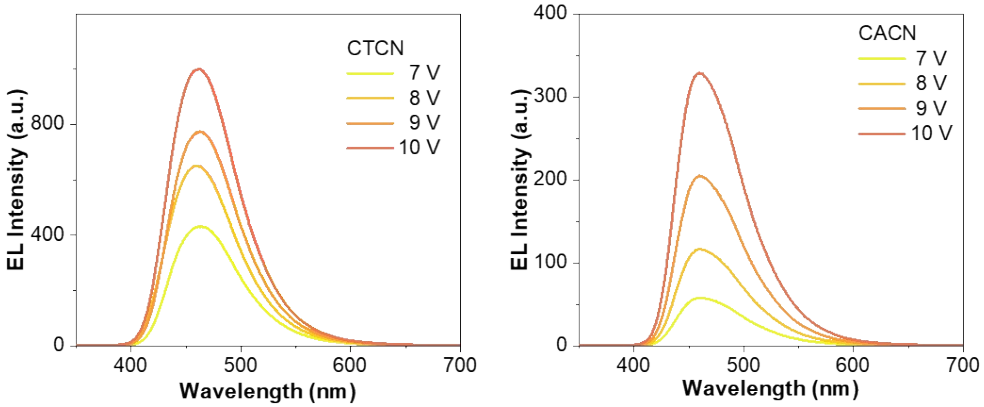


Fig. S14 EL spectra at different voltages of CTCN- and CACN-based OLEDs.

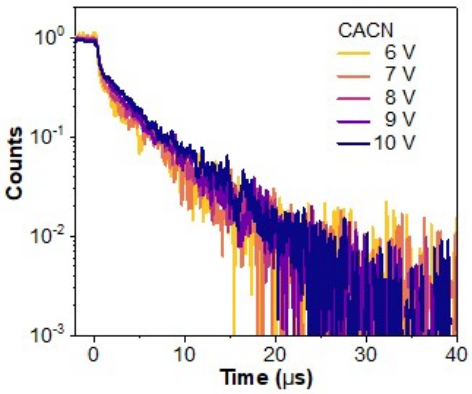
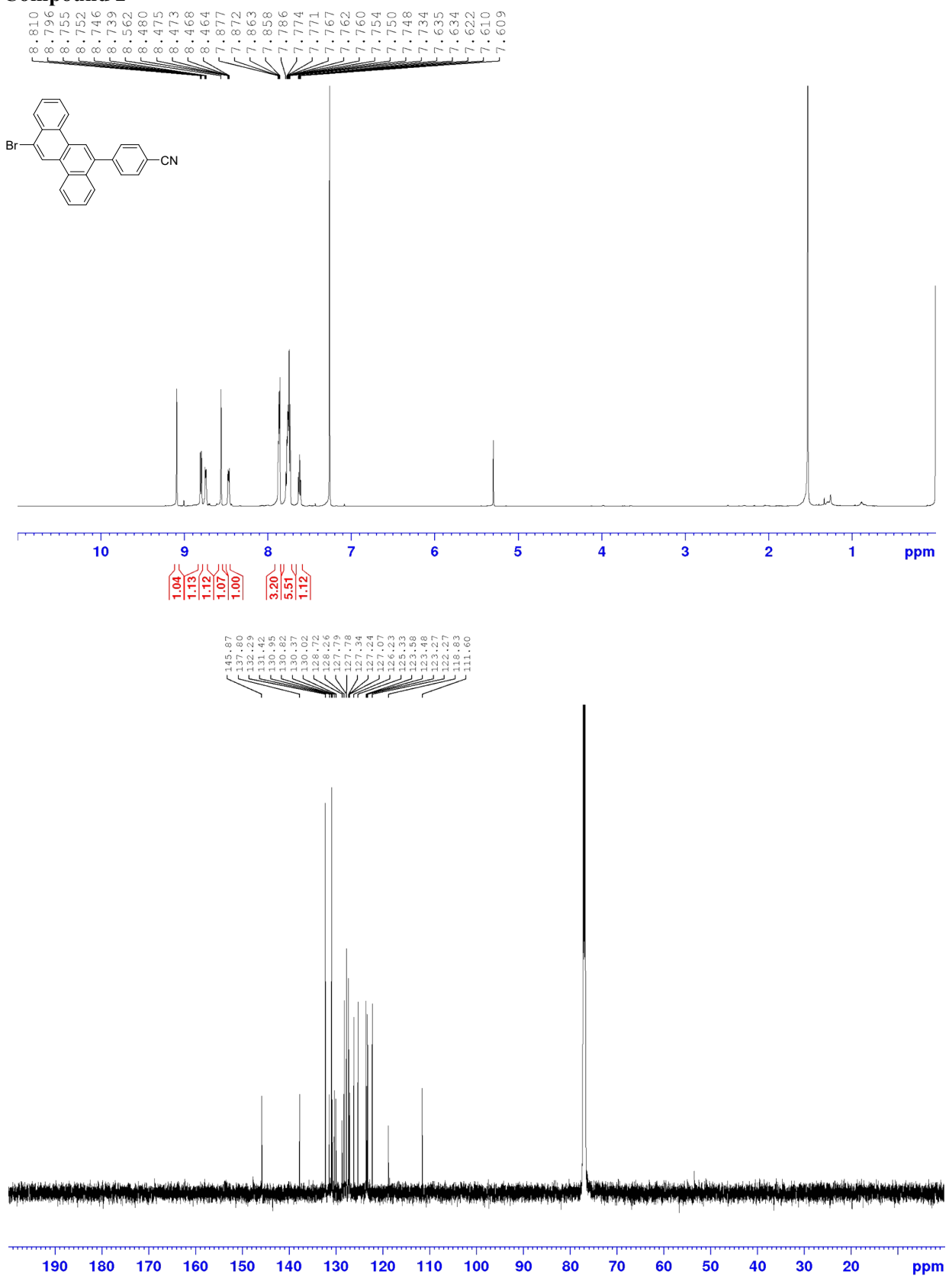
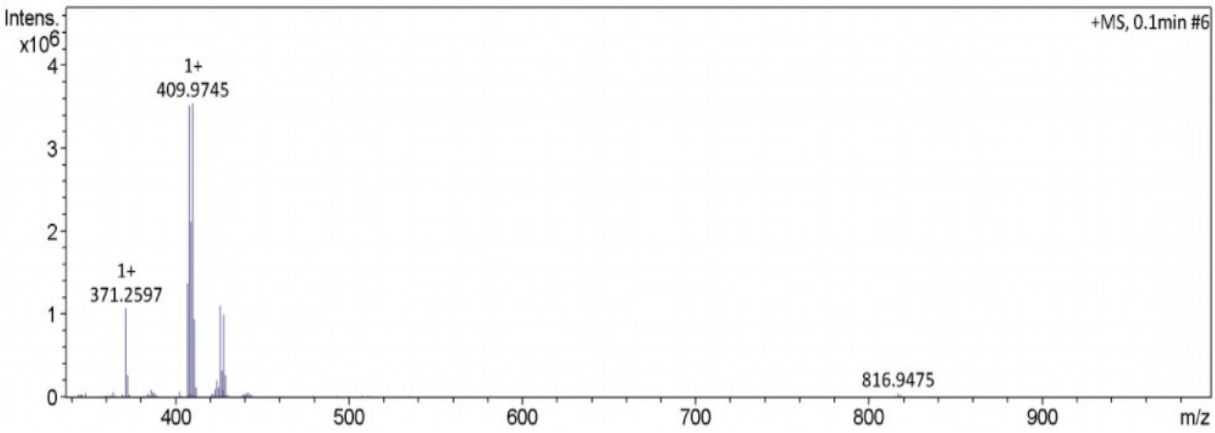


Fig. S15 Transient EL spectra at different voltage of CACN-based device.

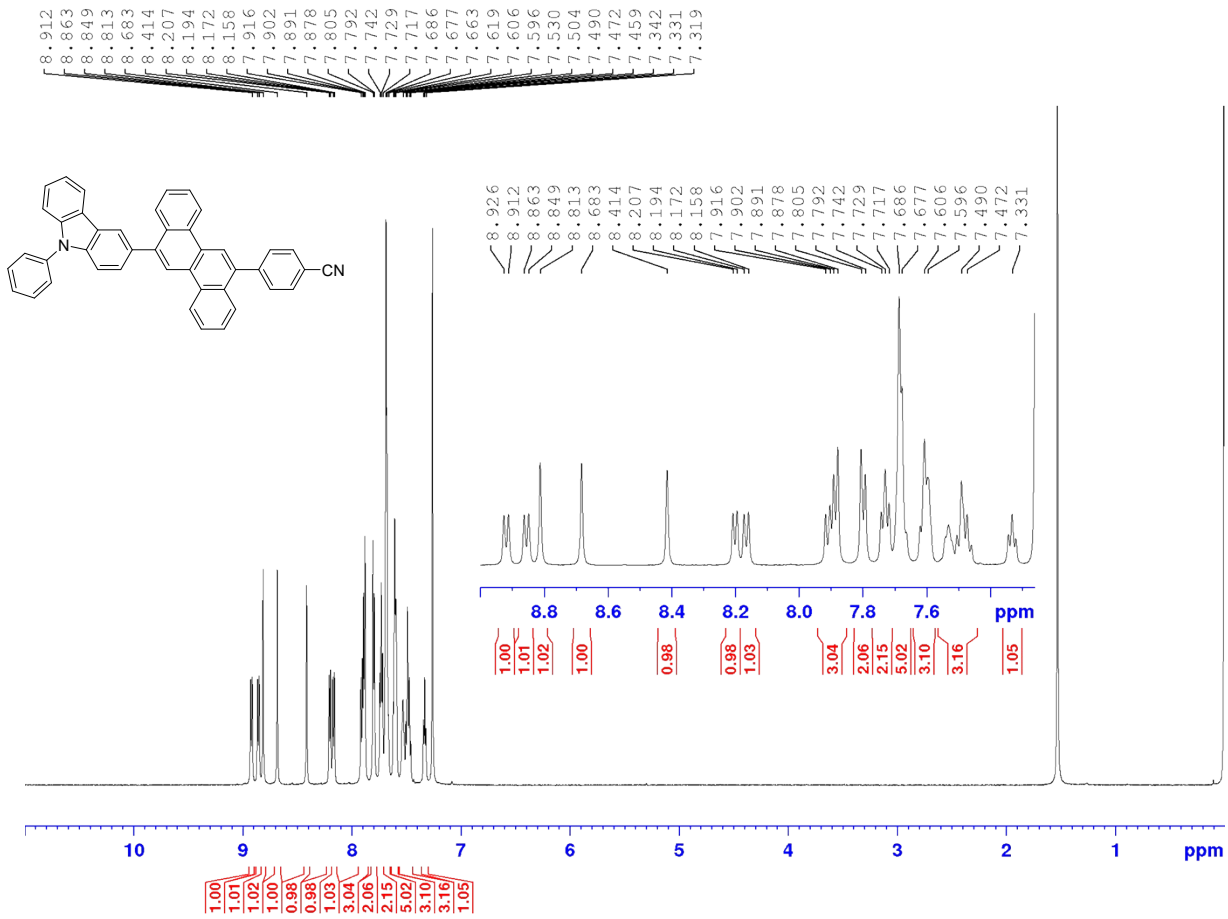
Fig. S16 Copies of 600 MHz NMR ($^{1}H/^{13}C$) spectra in $CDCl_3$ and HRMS mass spectra of the synthesized compounds.

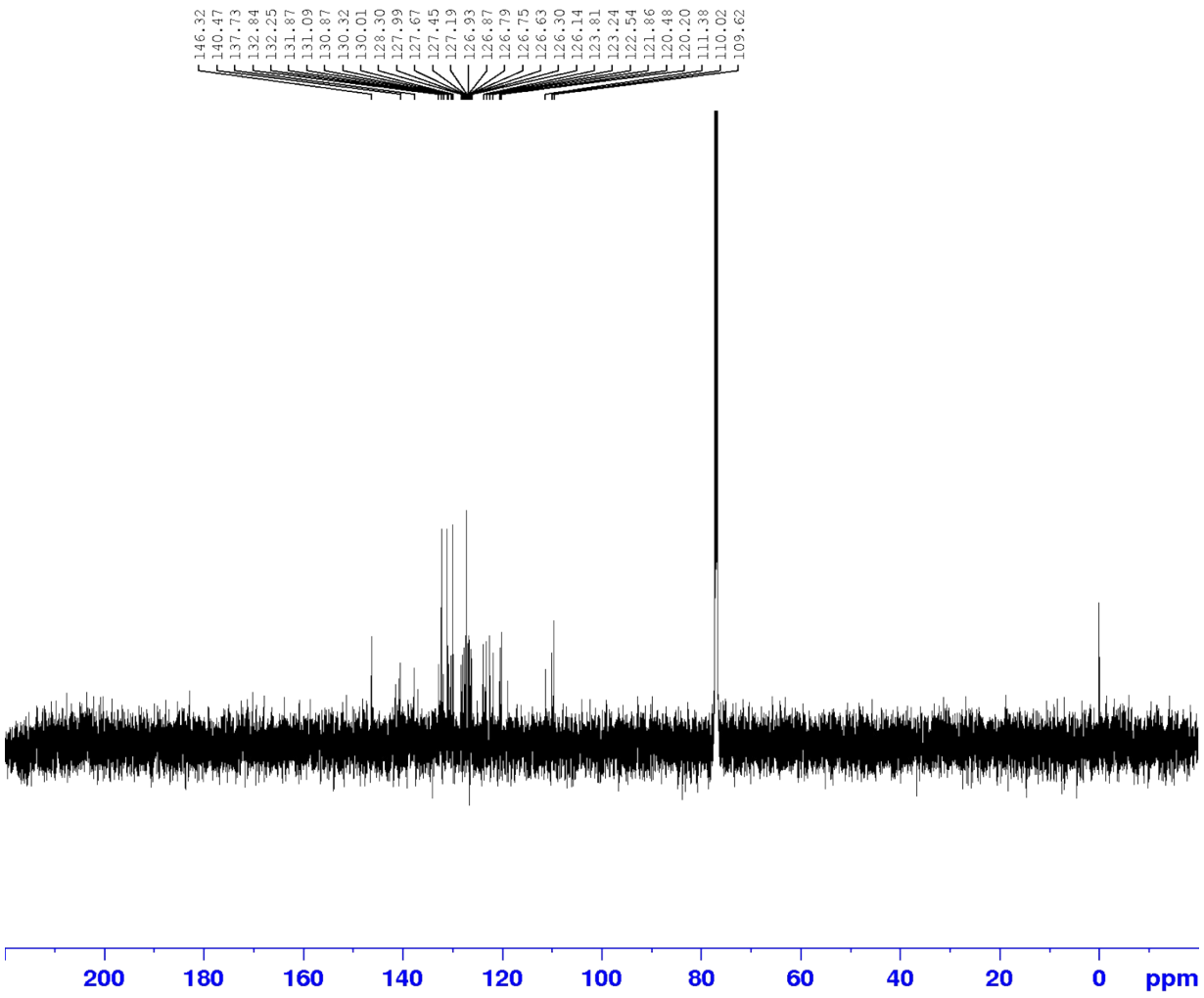
Compound 2

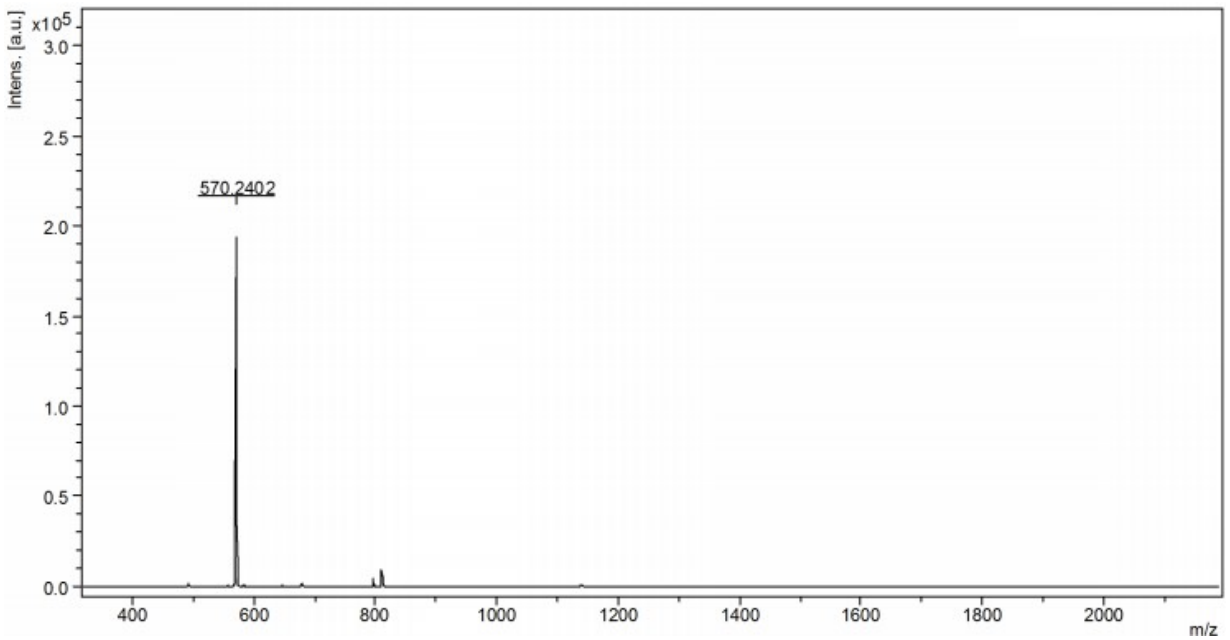




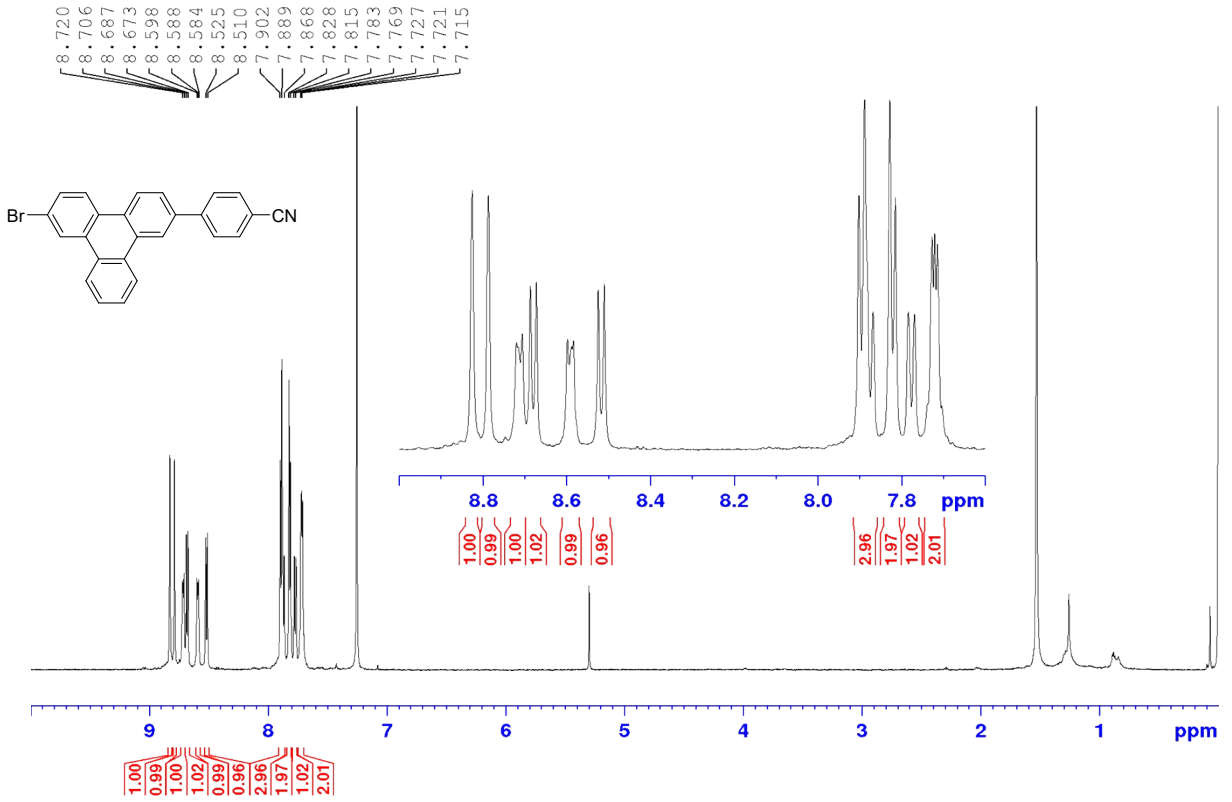
CCCN

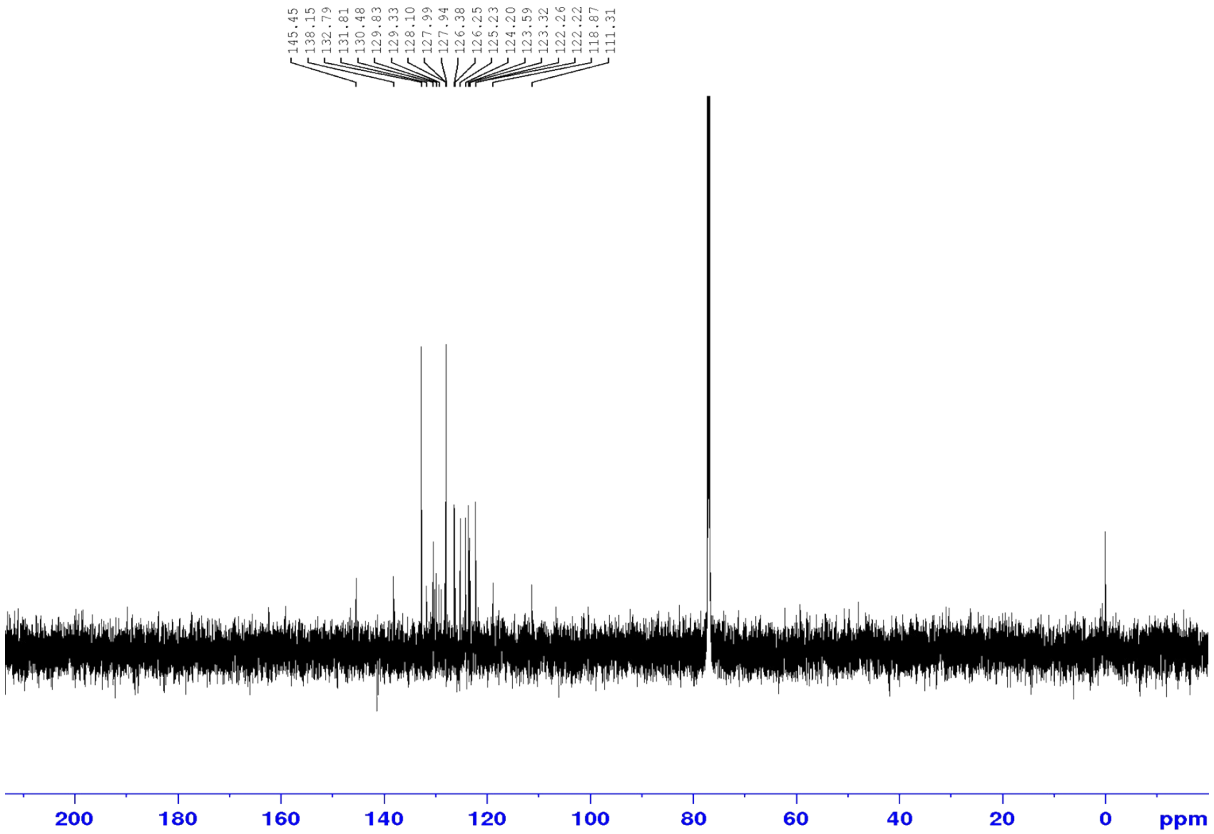


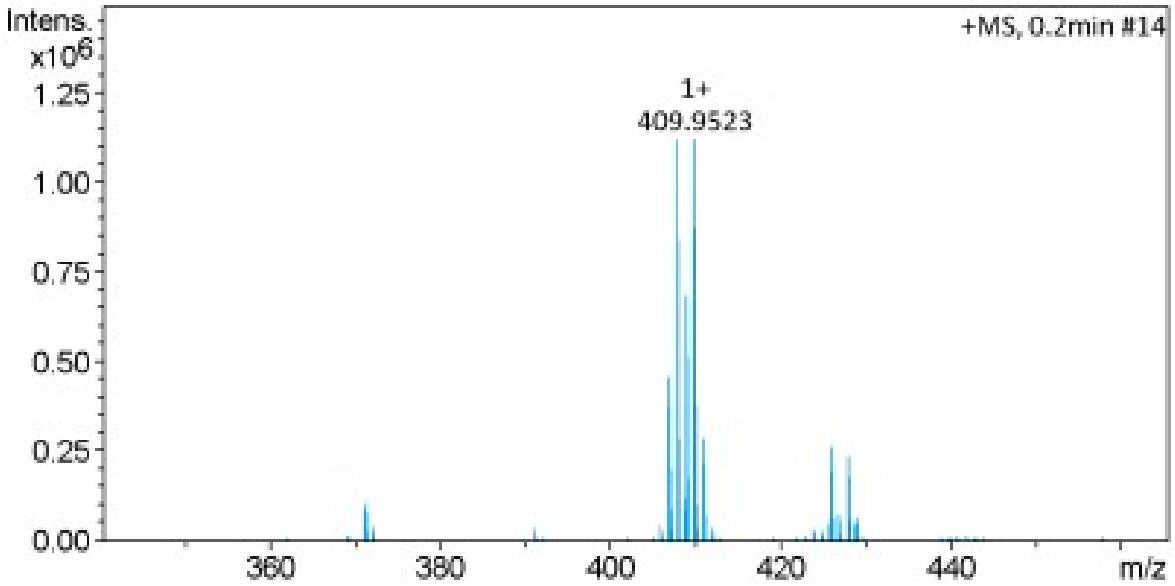

146.32
140.47
137.73
132.84
132.25
131.87
131.09
130.87
130.32
130.01
128.30
127.99
127.67
127.45
127.19
126.93
126.87
126.79
126.75
126.63
126.30
126.14
123.81
123.24
122.54
121.86
120.48
120.20
111.38
110.02
109.62
200
180
160
140
120
100
80
60
40
20
0
ppm


Intens. [a.u.]
x10^5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
570.2402
400
600
800
1000
1200
1400
1600
1800
2000
m/z

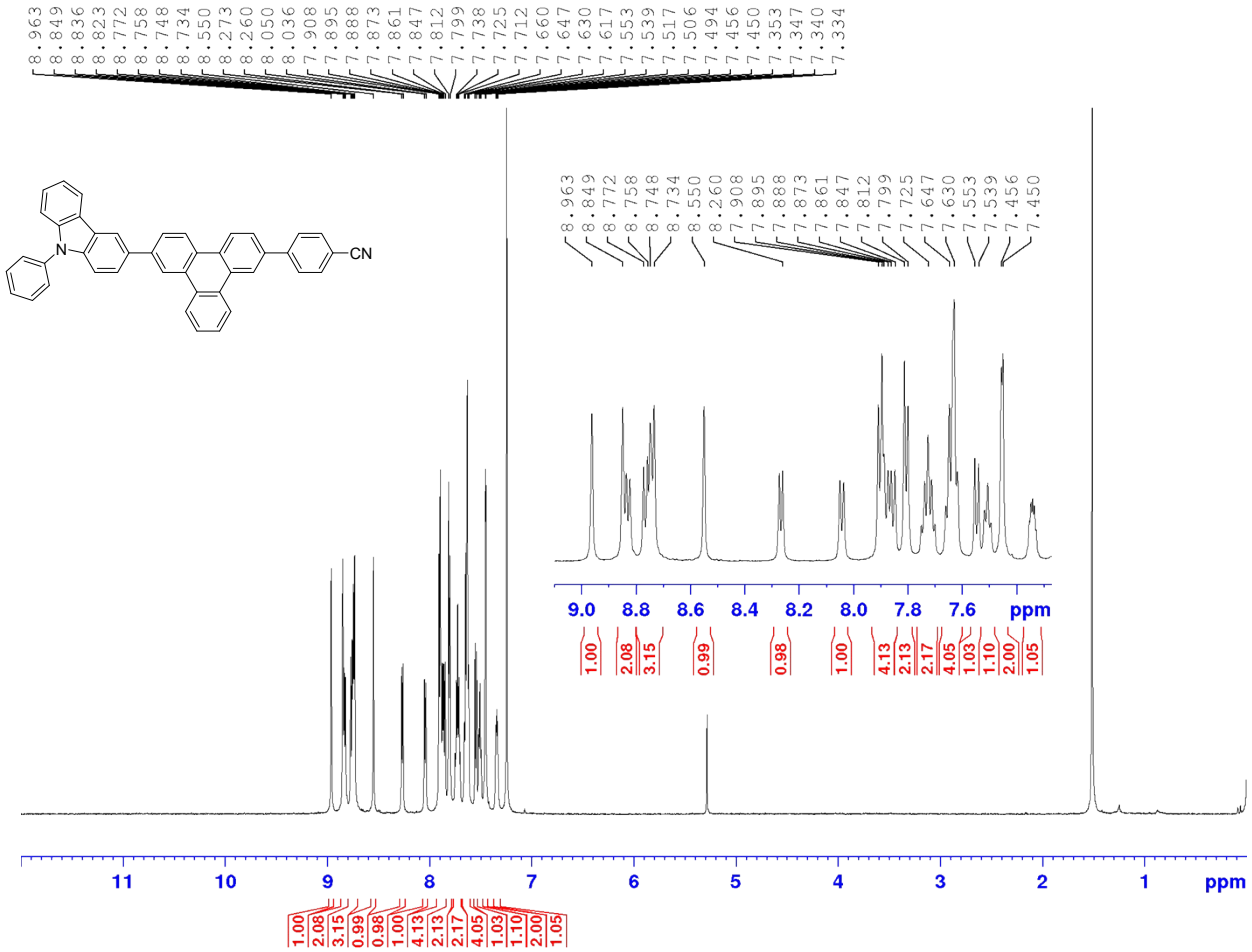
Compound 4

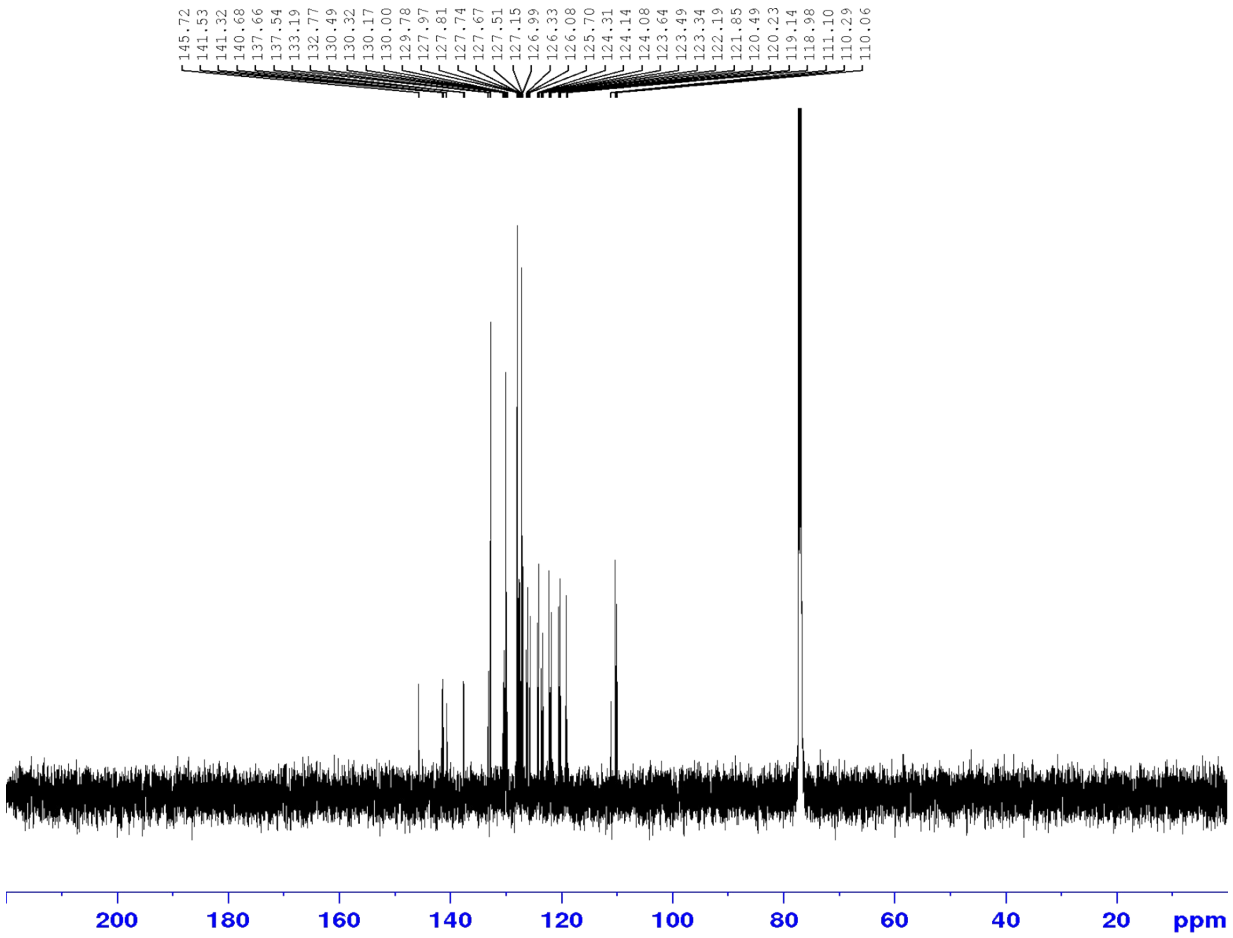

8.720
8.706
8.687
8.673
8.598
8.588
8.584
8.525
8.510
7.902
7.889
7.868
7.828
7.815
7.783
7.769
7.727
7.721
7.715
Br
CN
8.8
8.6
8.4
8.2
8.0
7.8
ppm
1.00
0.99
1.00
1.02
0.99
0.96
2.96
1.97
1.02
2.01
9
8
7
6
5
4
3
2
1
ppm

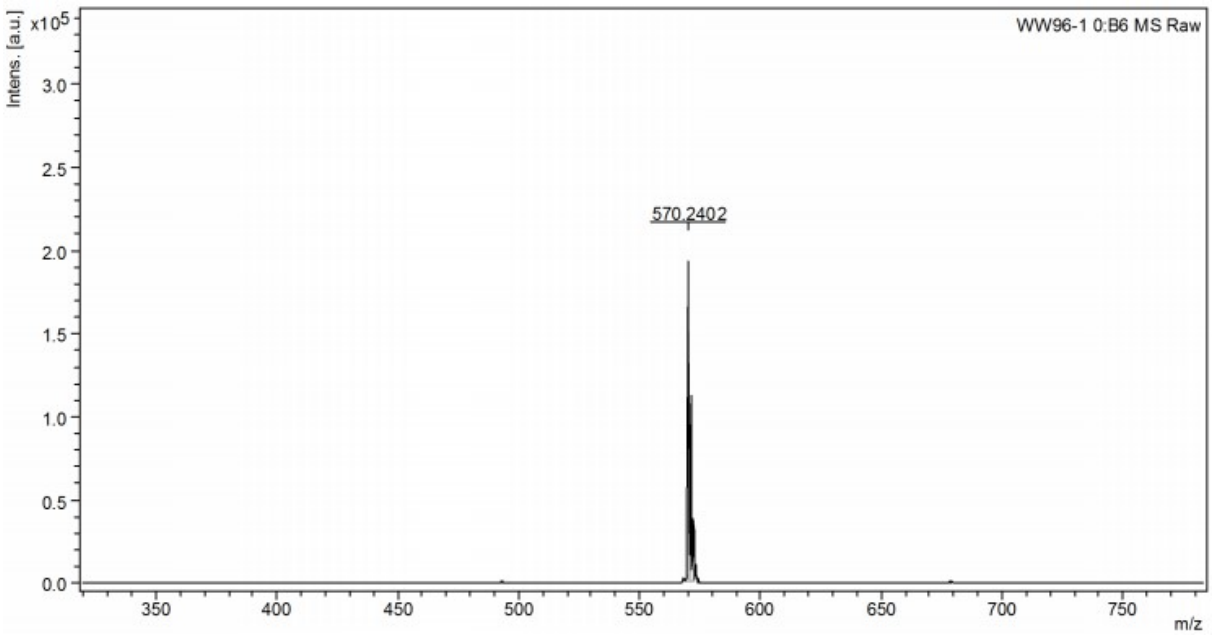

145.45
138.15
132.79
131.81
130.48
129.83
129.33
128.10
127.99
127.94
126.38
126.25
125.23
124.20
123.59
123.32
122.26
122.22
118.87
111.31
200
180
160
140
120
100
80
60
40
20
0
ppm


Intens.
x10^6
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.2min #14
1+
409.9523
360
380
400
420
440
m/z

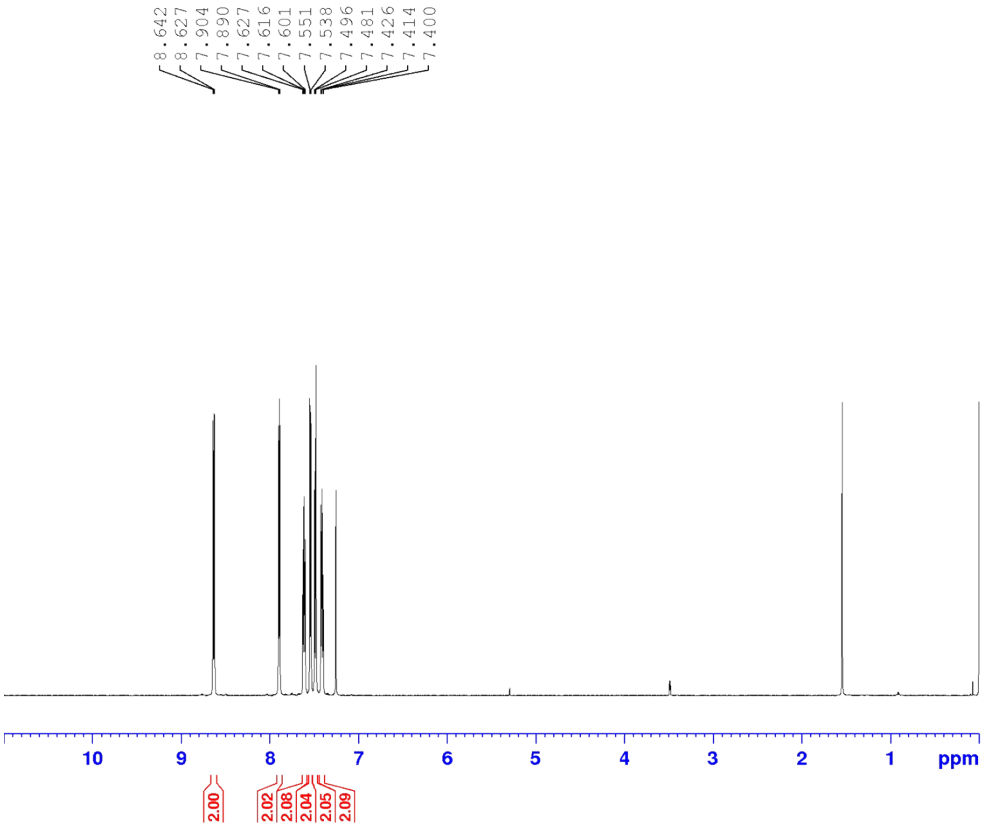
CTCN


8.963
8.849
8.836
8.823
8.772
8.758
8.748
8.734
8.550
8.273
8.260
8.050
8.036
7.908
7.895
7.888
7.873
7.861
7.847
7.812
7.799
7.738
7.725
7.712
7.660
7.647
7.630
7.617
7.553
7.539
7.517
7.506
7.494
7.456
7.450
7.353
7.347
7.340
7.334
CN
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
ppm
1.00
2.08
3.15
0.99
0.98
1.00
4.13
2.13
2.17
4.05
1.03
1.10
2.00
1.05
11
10
9
8
7
6
5
4
3
2
1
ppm

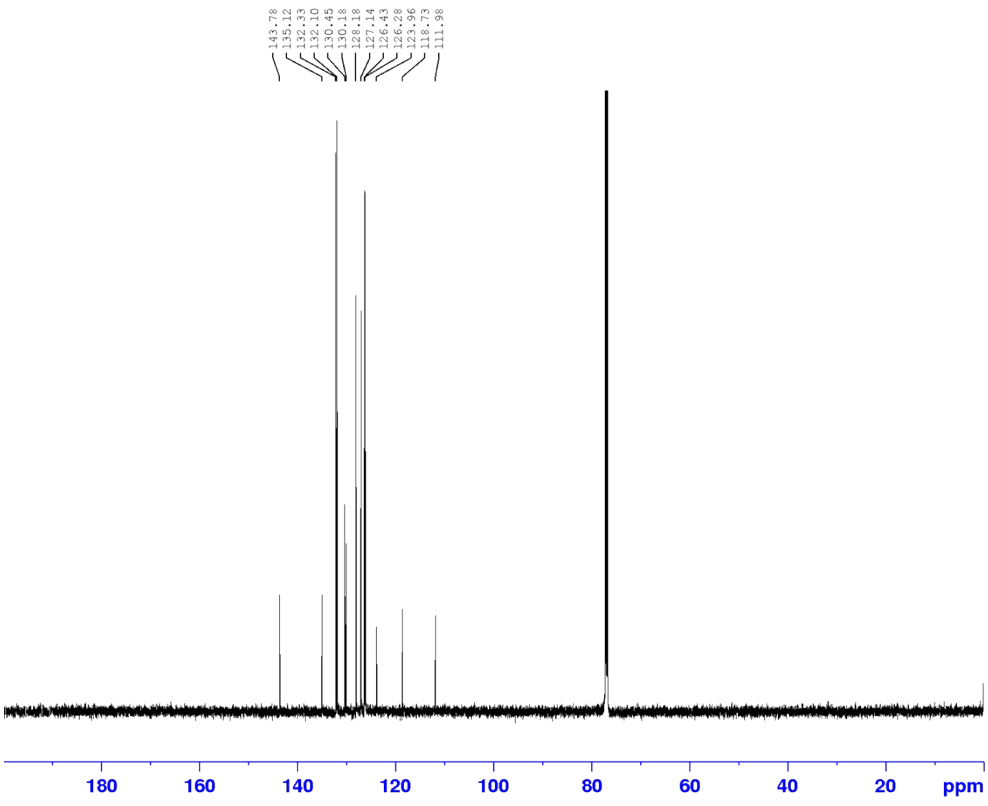

145.72
141.53
141.32
140.68
137.66
137.54
133.19
132.77
130.49
130.32
130.17
130.00
129.78
127.97
127.81
127.74
127.67
127.51
127.15
126.99
126.33
126.08
125.70
124.31
124.14
124.08
123.64
123.49
123.34
122.19
121.85
120.49
120.23
119.14
118.98
111.10
110.29
110.06
200
180
160
140
120
100
80
60
40
20
ppm


WW96-1 0:B6 MS Raw
Intens. [a.u.]
x10^5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
570.2402
350
400
450
500
550
600
650
700
750
m/z

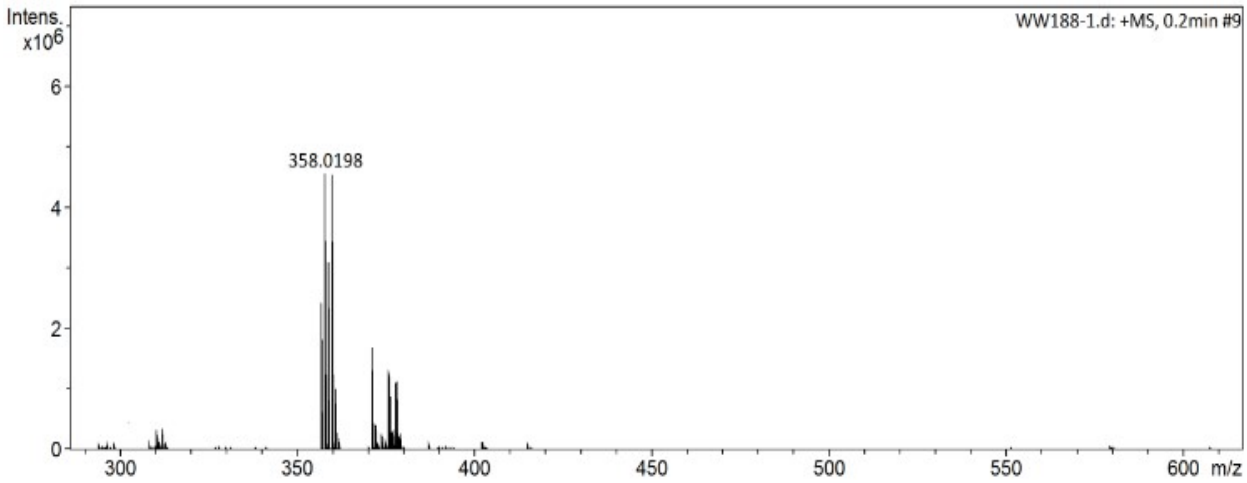
Compound 6



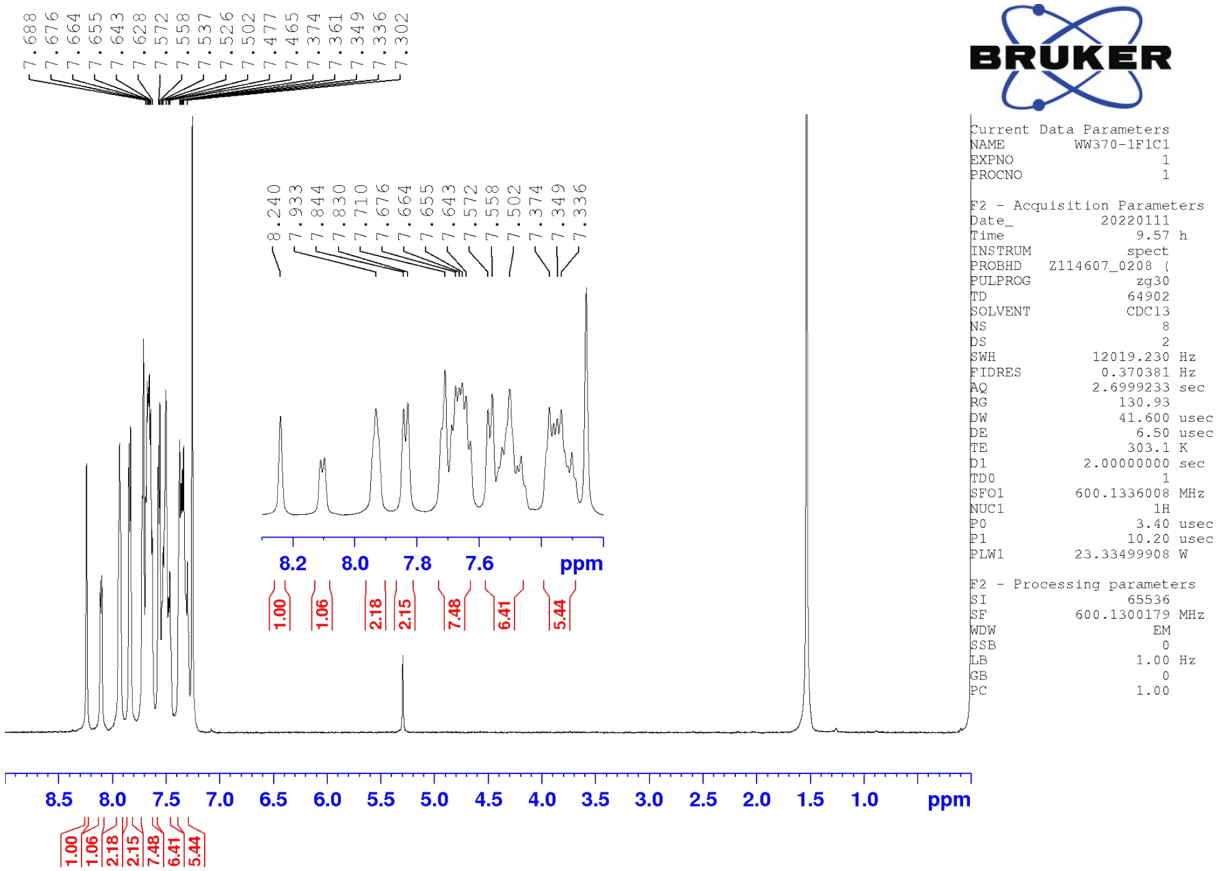

```
Current Data Parameters
NAME         WW188-1F3C1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200909
Time               14.46 h
INSTRUM             spect
PROBHD    Z856701_0011 (
PULPROG              zg30
TD                  64902
SOLVENT             CDC13
NS                      8
DS                      2
SWH            12019.230 Hz
FIDRES          0.370381 Hz
AQ             2.6999233 sec
RG                 191.96
DW                41.600 usec
DE                 6.50 usec
TE                    0 K
D1             2.00000000 sec
TD0                    1
SFO1          600.1336008 MHz
NUC1                  1H
P0                  4.33 usec
P1                 13.00 usec
PLW1          23.00000000 W

F2 - Processing parameters
SI                 65536
SF            600.1300170 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

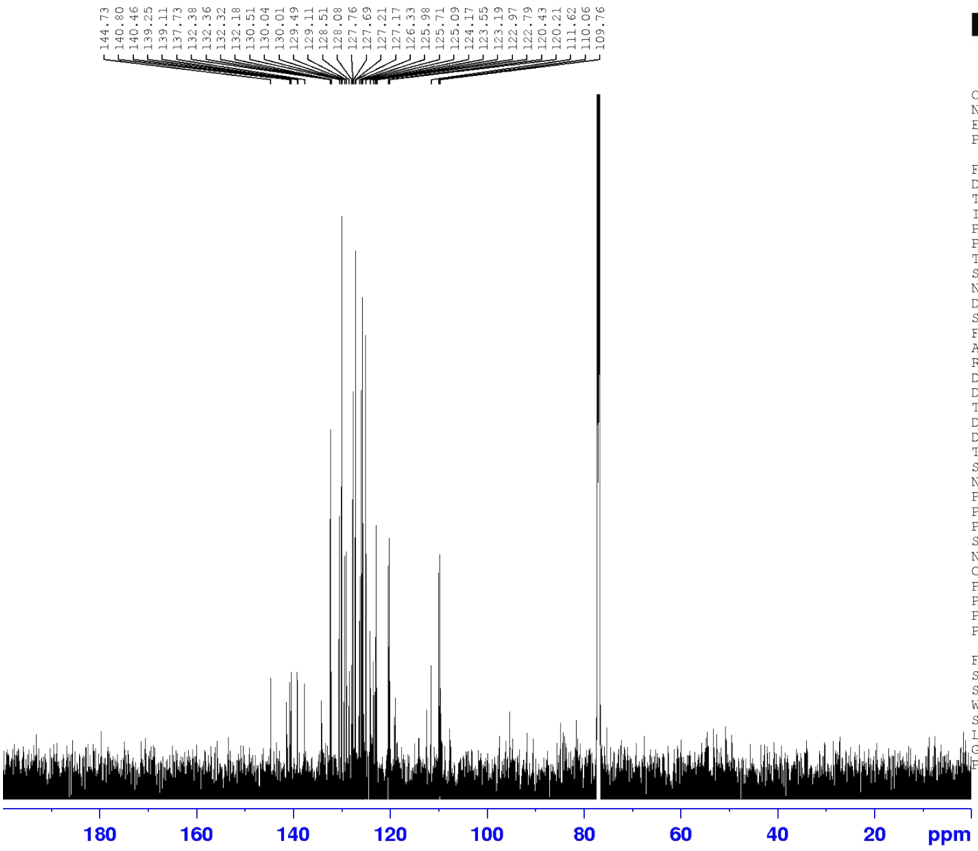



```
Current Data Parameters
NAME         WW188-1F3C1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200909
Time               22.47 h
INSTRUM             spect
PROBHD    Z856701_0011 (
PULPROG           zgpg30
TD                 65536
SOLVENT             CDC13
NS                  1024
DS                      2
SWH            36231.883 Hz
FIDRES          1.105709 Hz
AQ             0.9043968 sec
RG                 191.96
DW                13.800 usec
DE                 6.50 usec
TE                    0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          150.9178988 MHz
NUC1                  13C
P0                  3.33 usec
P1                 10.00 usec
PLW1          54.00000000 W
SFO2          600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              70.00 usec
PLW2          23.00000000 W
PLW12          0.79326999 W
PLW13          0.39901000 W

F2 - Processing parameters
SI                 32768
SF            150.9028094 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


Intens.
x10^6
WW188-1.d: +MS, 0.2min #9
358.0198
m/z

CACN


BRUKER
Current Data Parameters
NAME WW370-1F1C1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220111
Time 9.57 h
INSTRUM spect
PROBHD Z114607_0208 (
PULPROG zg30
TD 64902
SOLVENT CDCl3
NS 8
DS 2
SWH 12019.230 Hz
FIDRES 0.370381 Hz
AQ 2.6999233 sec
RG 130.93
DW 41.600 usec
DE 6.50 usec
TE 303.1 K
D1 2.00000000 sec
TD0 1
SFO1 600.1336008 MHz
NUC1 1H
P0 3.40 usec
P1 10.20 usec
PLW1 23.33499908 W
F2 - Processing parameters
SI 65536
SF 600.1300179 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
ppm



Current Data Parameters
NAME WW370-1F1C1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220114
Time 7.49 h
INSTRUM spect
PROBHD Z114607_0208 (
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 1024
DS 2
SWH 36231.883 Hz
FIDRES 1.105709 Hz
AQ 0.9043968 sec
RG 191.96
DW 13.800 usec
DE 6.50 usec
TE 303.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P0 3.67 usec
P1 11.00 usec
PLW1 91.30000305 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.33499908 W
PLW12 0.49546000 W
PLW13 0.24921000 W

F2 - Processing parameters
SI 32768
SF 150.9028085 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Comment 1
Comment 2