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Supporting Information

Molecular engineering of pyrene carbazole dyes with a single bond and double bond as the mode of linkage

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 # Contributed equally

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List of content:

Scheme S1 Synthetic route of intermediate (**3**) and (**6**) and reference dye (**PC0**).

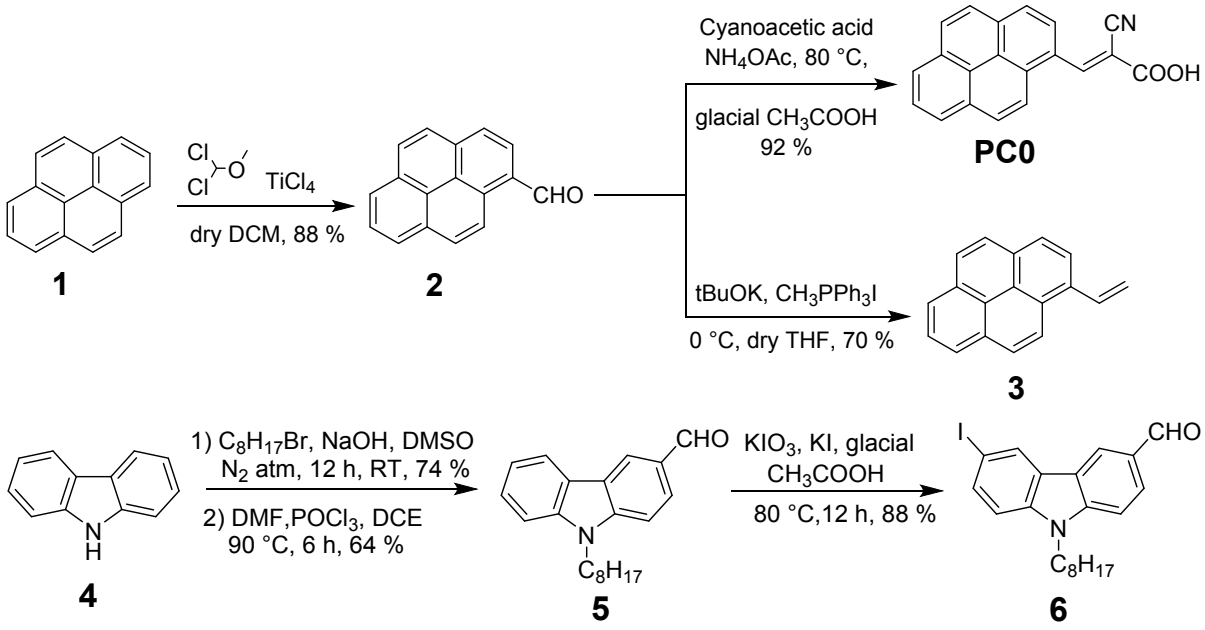
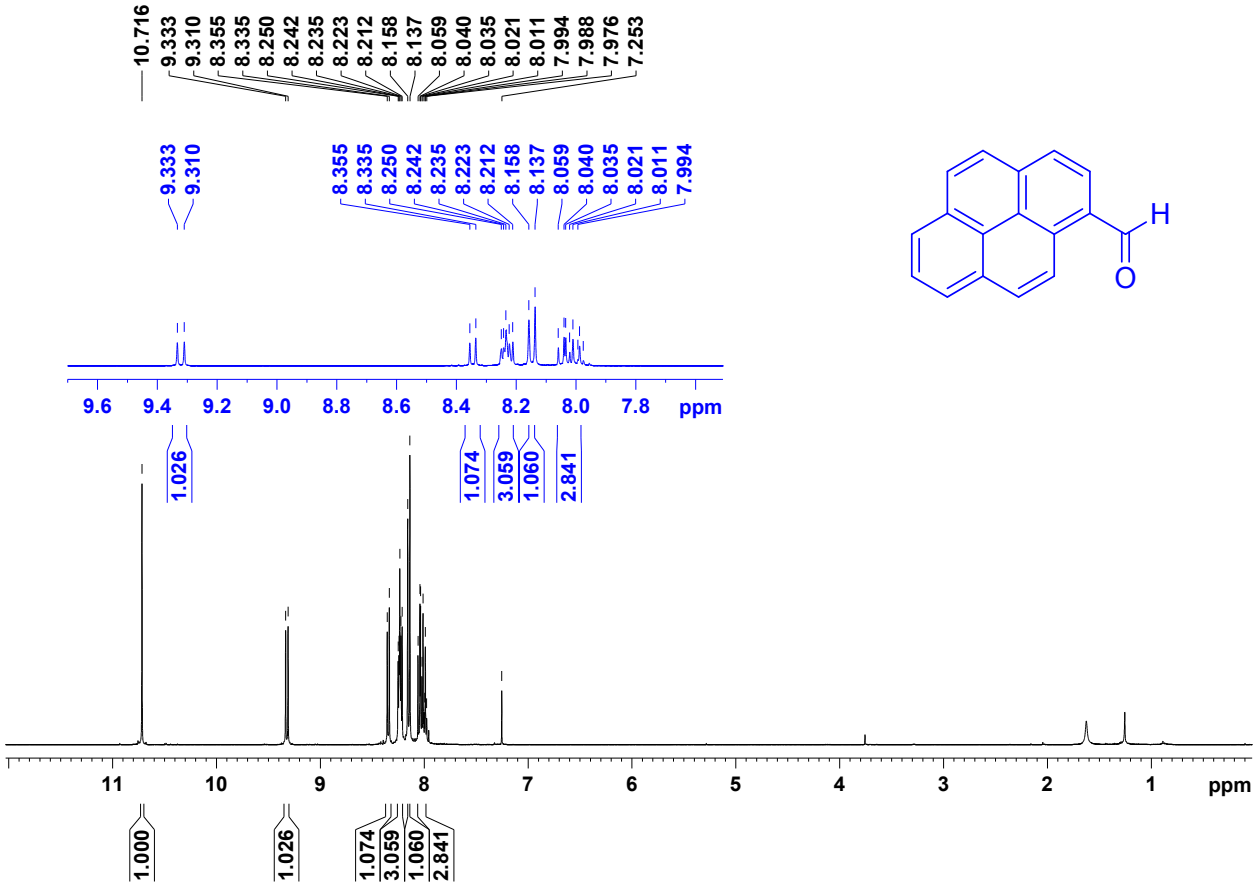
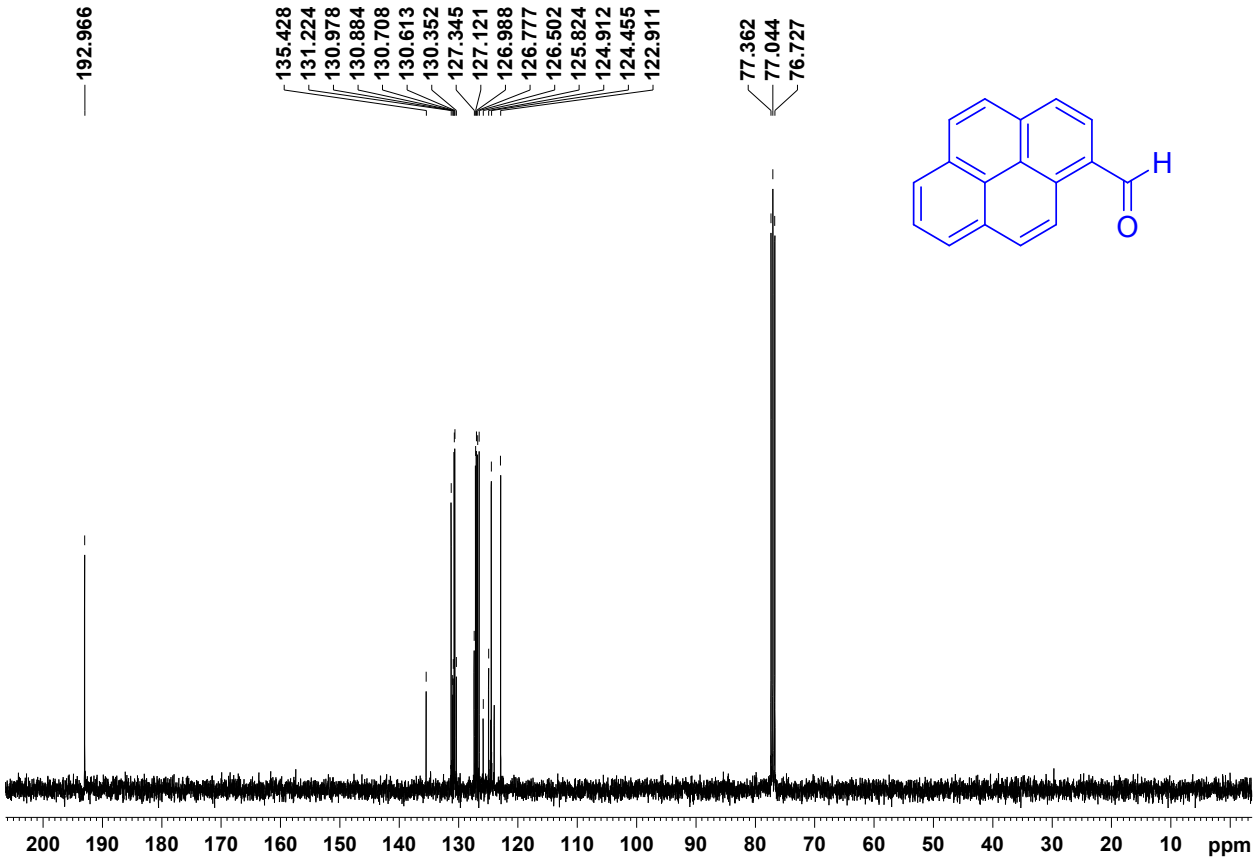


Fig. S1 [1] H, [13]C and Mass spectrum of intermediate (**2**).

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124.912
124.455
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77.362
77.044
76.727
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

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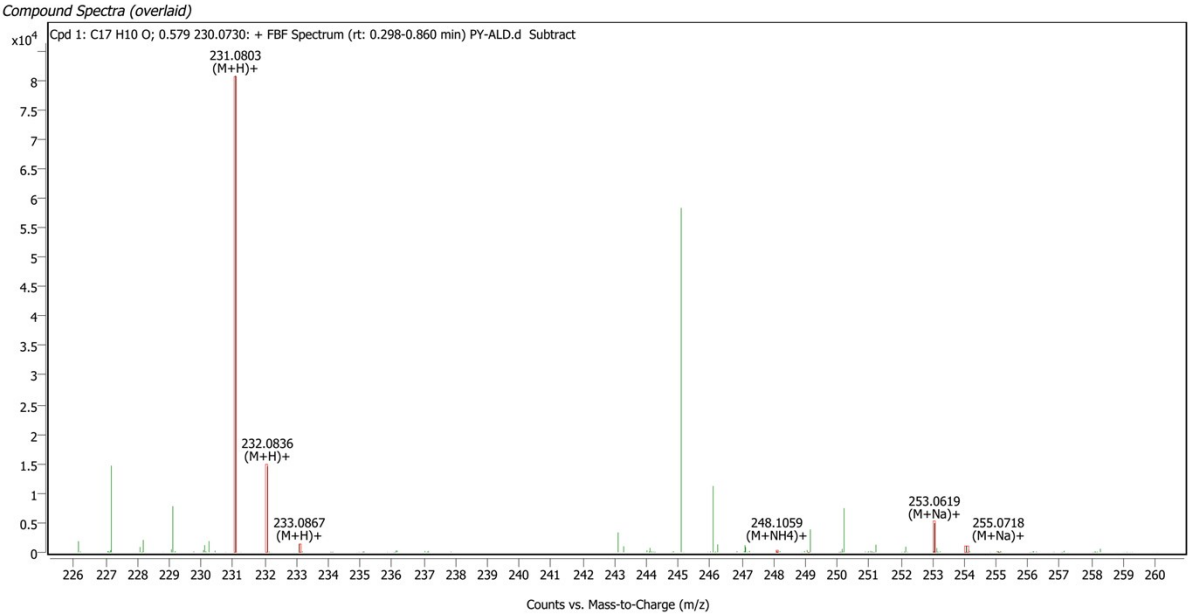
Name	241019-22-KRR-PY-ALD	**Data File Path**	D:\MassHunter\Data\2019\OCT-2019\KRR\PY-ALD.d
Sample ID		**Acq. Time (Local)**	24-10-2019 12:16:01 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)
Inj. Vol. (ul)	5	**IRM Status**	Success
Position	P1-B11	**Method Path (DA)**	D:\MassHunter\Methods\10.0\IIT-Target Screening_1.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C17 H10 O

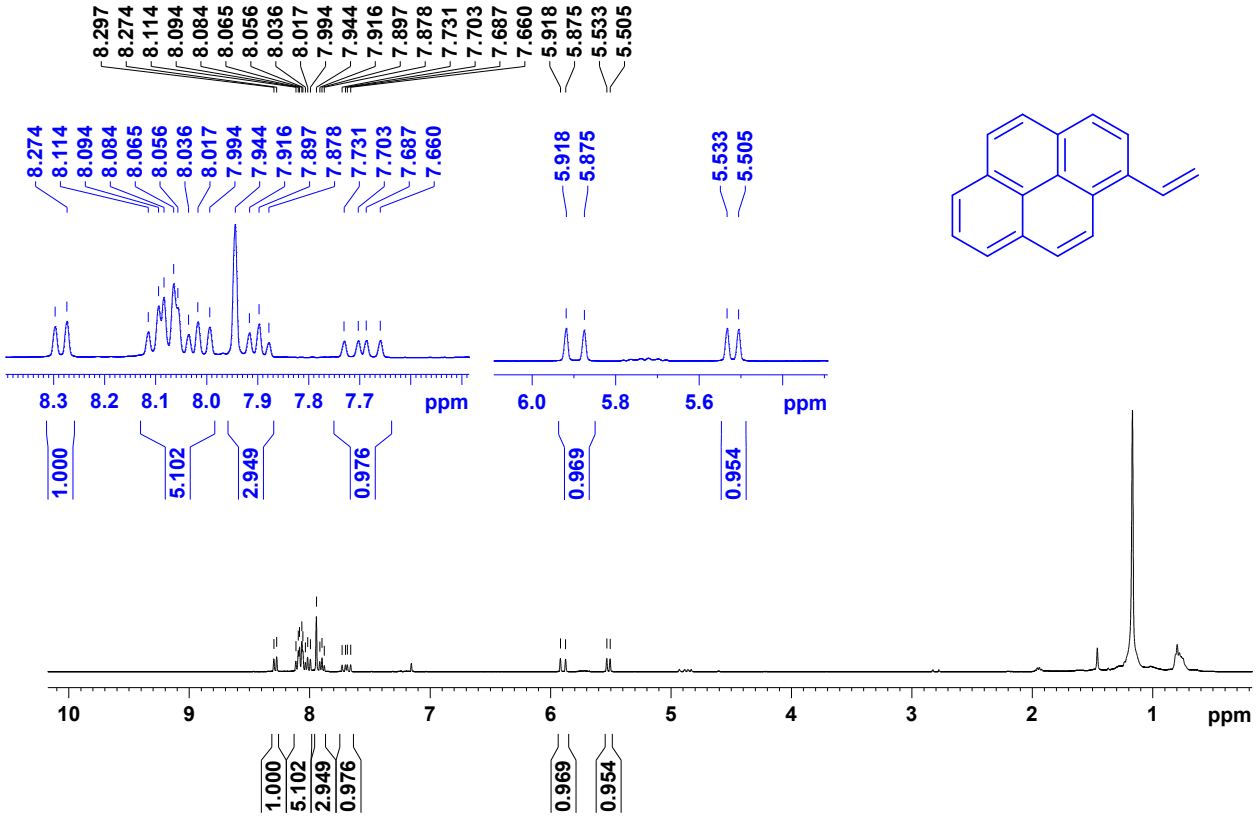
Compound Spectra (overlaid)

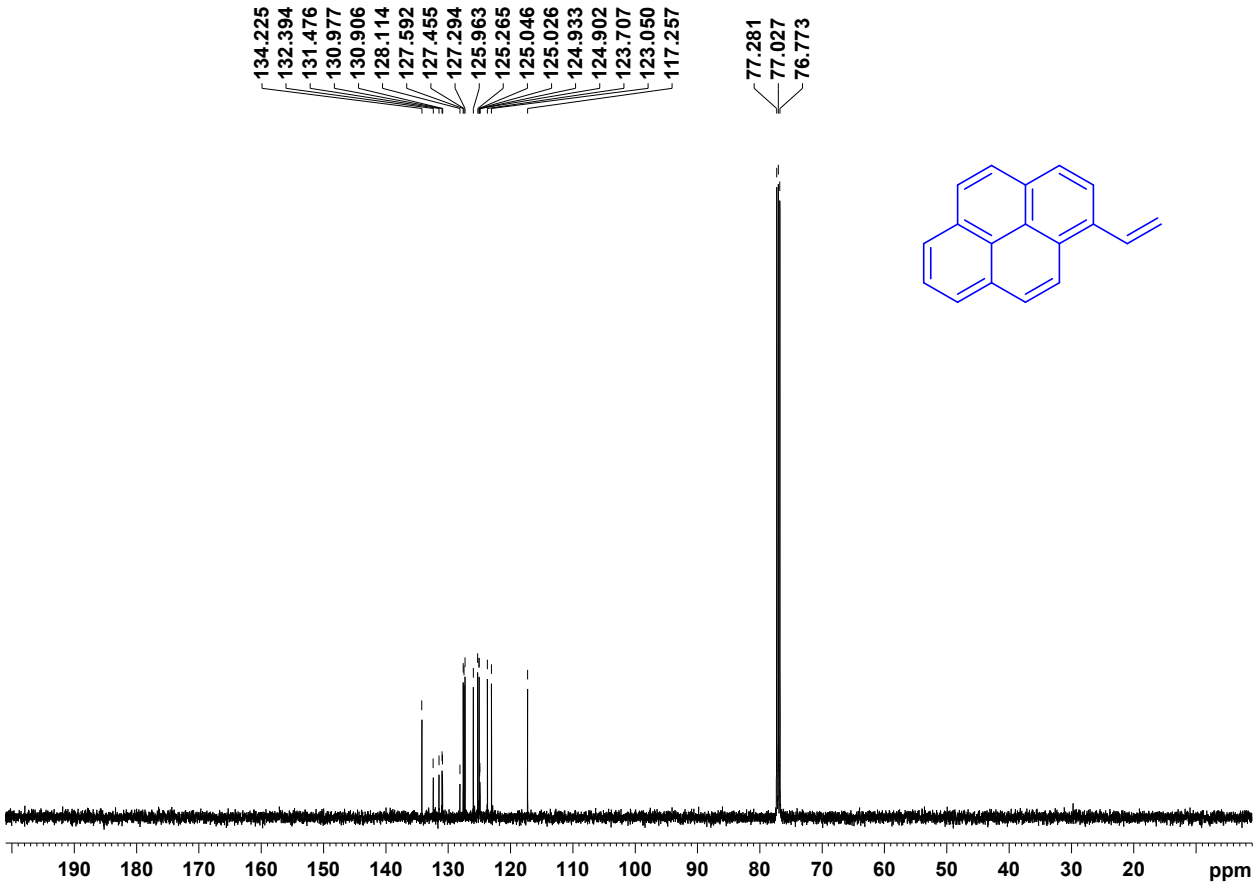


Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C17 H10 O	230.0732	230.0730	231.0803 248.1059 253.0619	(M+H)+ (M+NH4)+ (M+Na)+	-0.74	-0.17

Fig. S2 [1] H, [13]C and Mass spectrum of intermediate **(3)**.

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77.027
76.773
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180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

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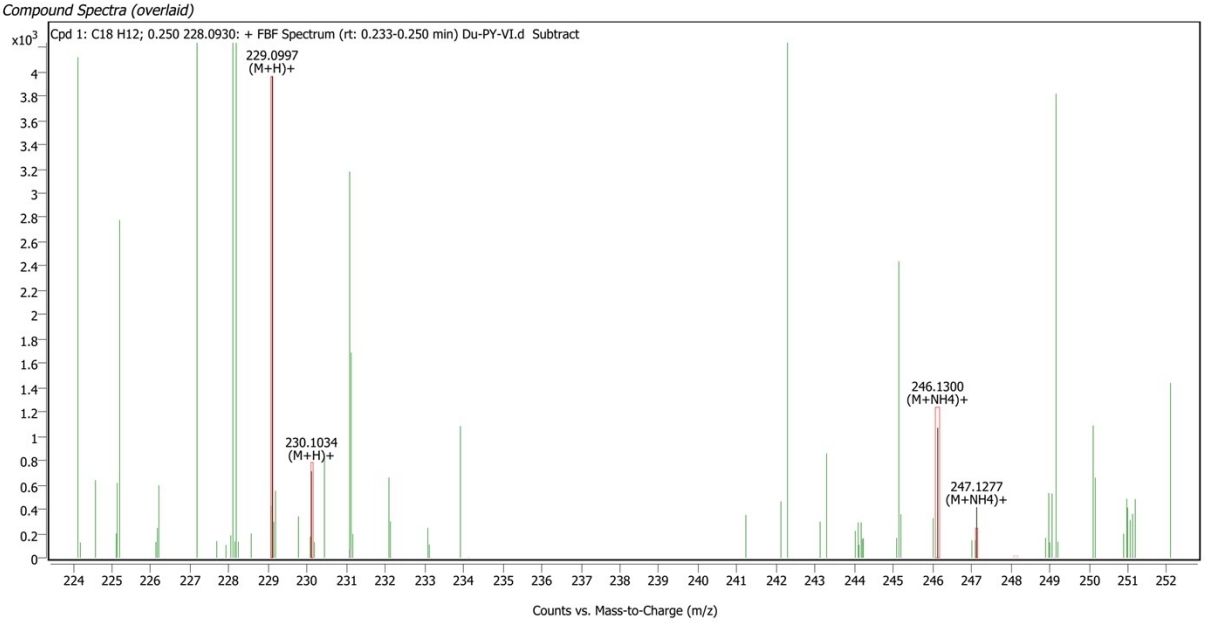
Name	060919-4-KRR-Du-PY-VI	**Data File Path**	D:\MassHunter\Data\2019\SEP-2019\KRR\Du-PY-VI.d
Sample ID		**Acq. Time (Local)**	06-09-2019 09:23:02 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)
Inj. Vol. (ul)	5	**IRM Status**	Success
Position	P2-D4	**Method Path (DA)**	D:\MassHunter\Methods\10.0\IIT-Target Screening_1.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C18 H12

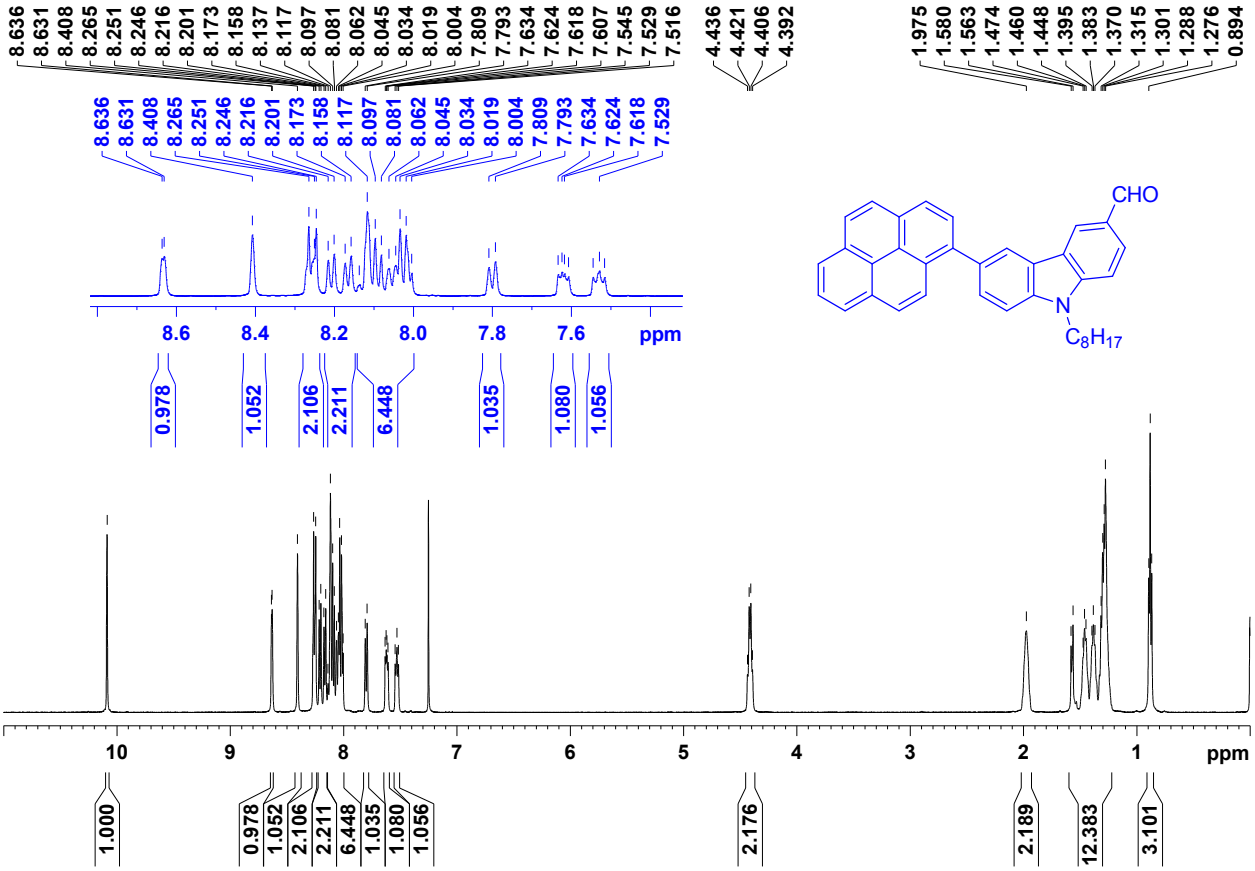
Compound Spectra (overlaid)

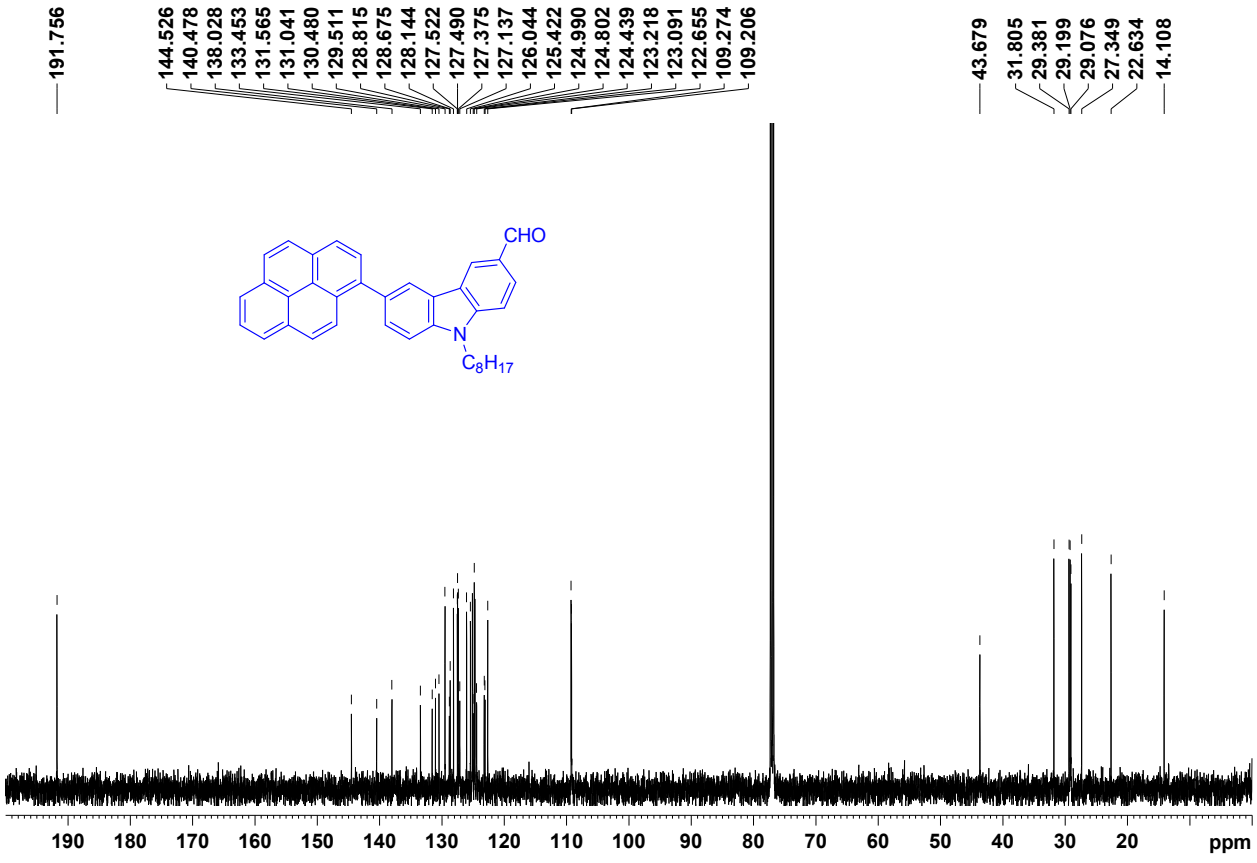


Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C18 H12	228.0939	228.0930	229.0997 246.1300	(M+H)+ (M+NH4)+	-3.97	-0.91

Fig. S3 [1] H, [13]C and Mass spectrum of intermediate (**8**).

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130
120
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100
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ppm

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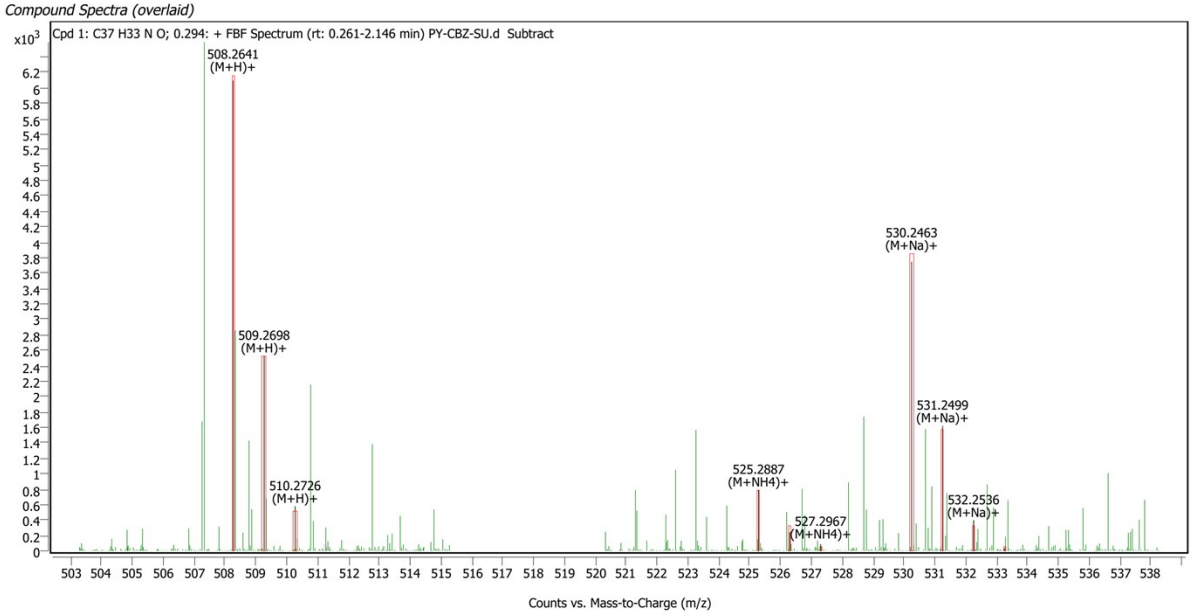
Name	14022020-KRR	**Data File Path**	D:\MassHunter\Data\2020\FEB-2020\KRR\PY-CBZ-SU.d
Sample ID		**Acq. Time (Local)**	14-02-2020 18:20:44 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF 10.1 (48.0)
Inj. Vol. (ul)	2	**IRM Status**	Success
Position	P1-E11	**Method Path (DA)**	D:\MassHunter\Methods\10.0\Default.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C37 H33 N O

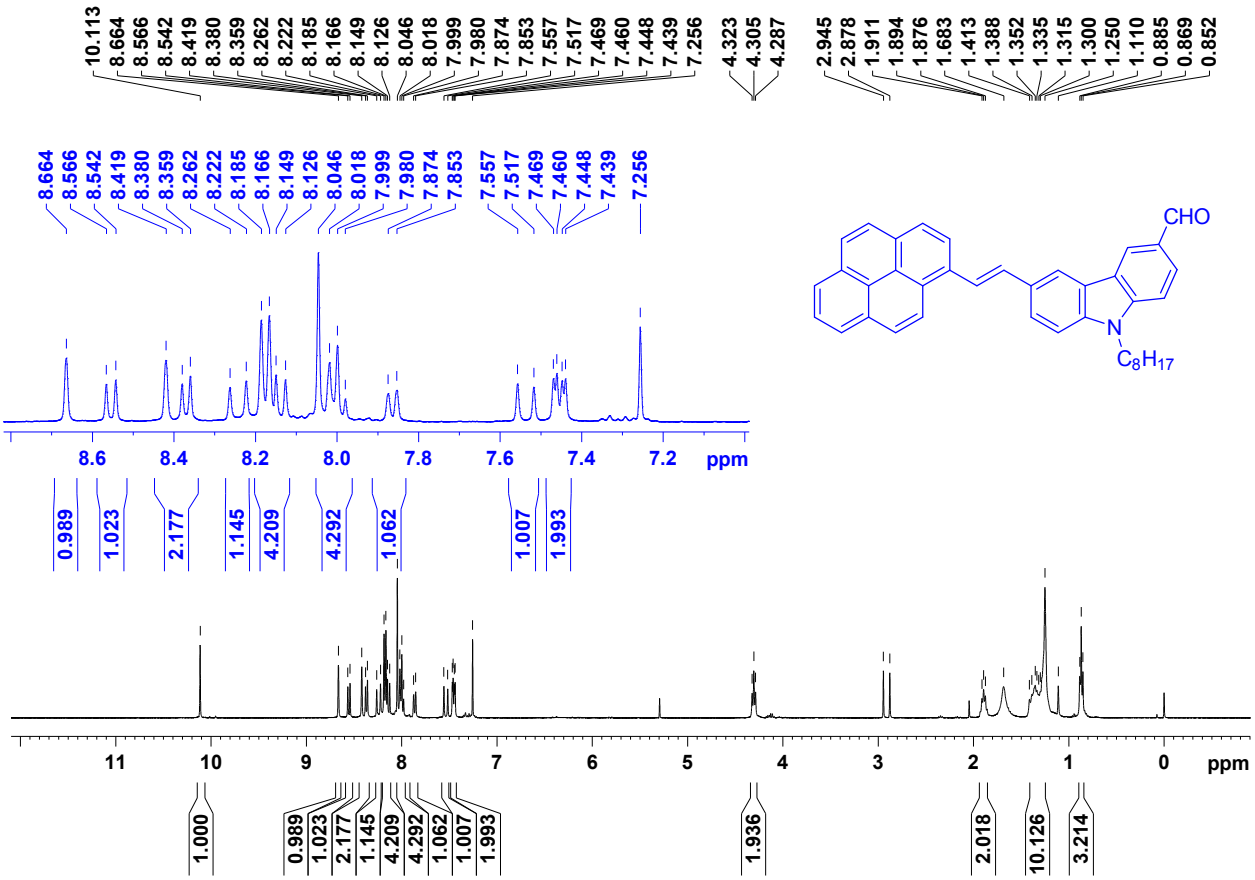
Compound Spectra (overlaid)

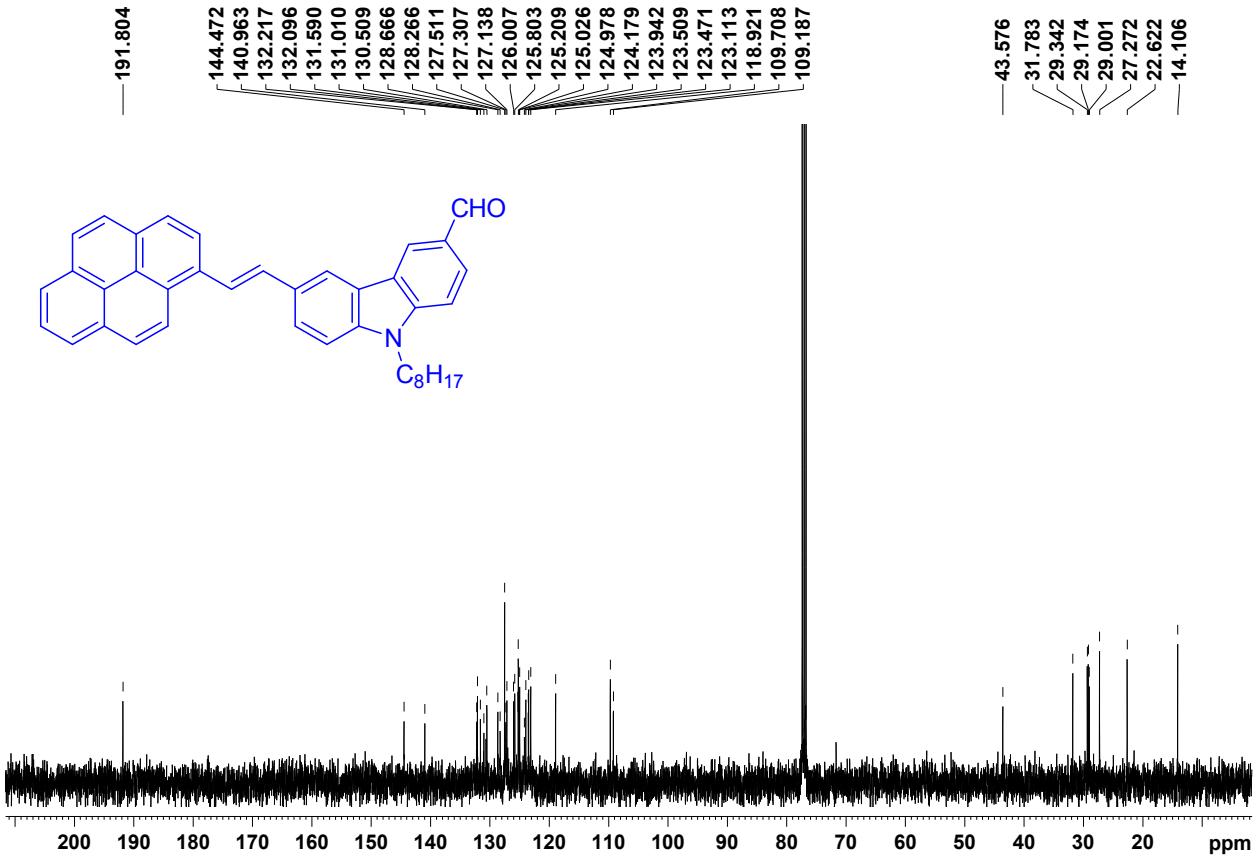


Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C37 H33 N O	507.2562	507.2573	508.2641 525.2887 530.2463	(M+H)+ (M+NH4)+ (M+Na)+	2.17	1.10

Fig. S4 [1] H, [13]C and Mass spectrum of intermediate **(9)**.

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ppm

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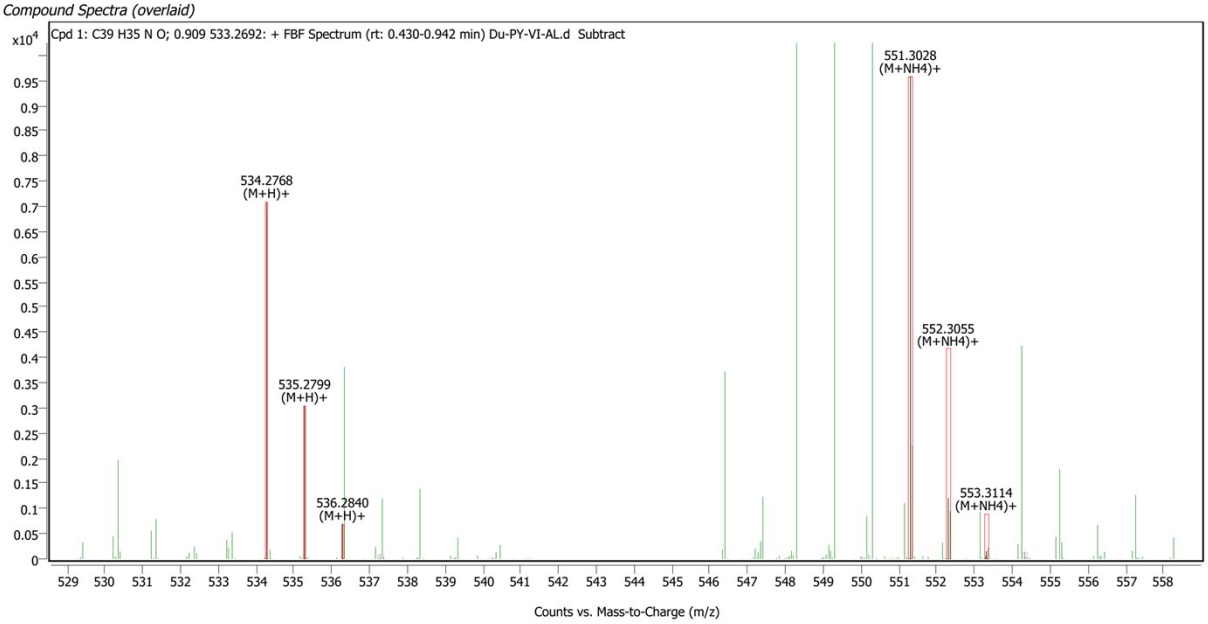
Name	160919-4-KRR-Du-PY-VI-AL	**Data File Path**	D:\MassHunter\Data\2019\SEP-2019\KRR\Du-PY-VI-AL.d
Sample ID		**Acq. Time (Local)**	16-09-2019 09:20:01 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)
Inj. Vol. (ul)	5	**IRM Status**	Success
Position	P2-D4	**Method Path (DA)**	D:\MassHunter\Methods\10.0\IIT-Target Screening_1.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C39 H35 N O

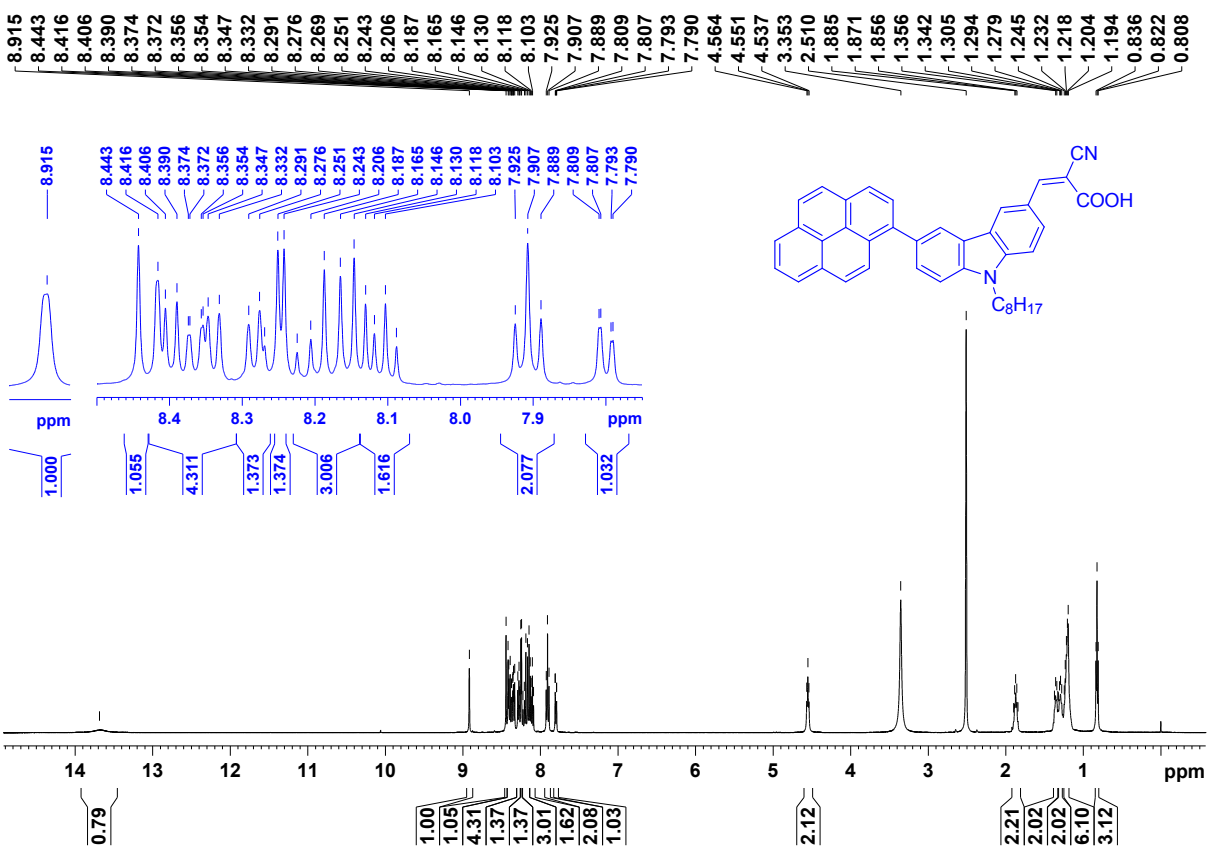
Compound Spectra (overlaid)

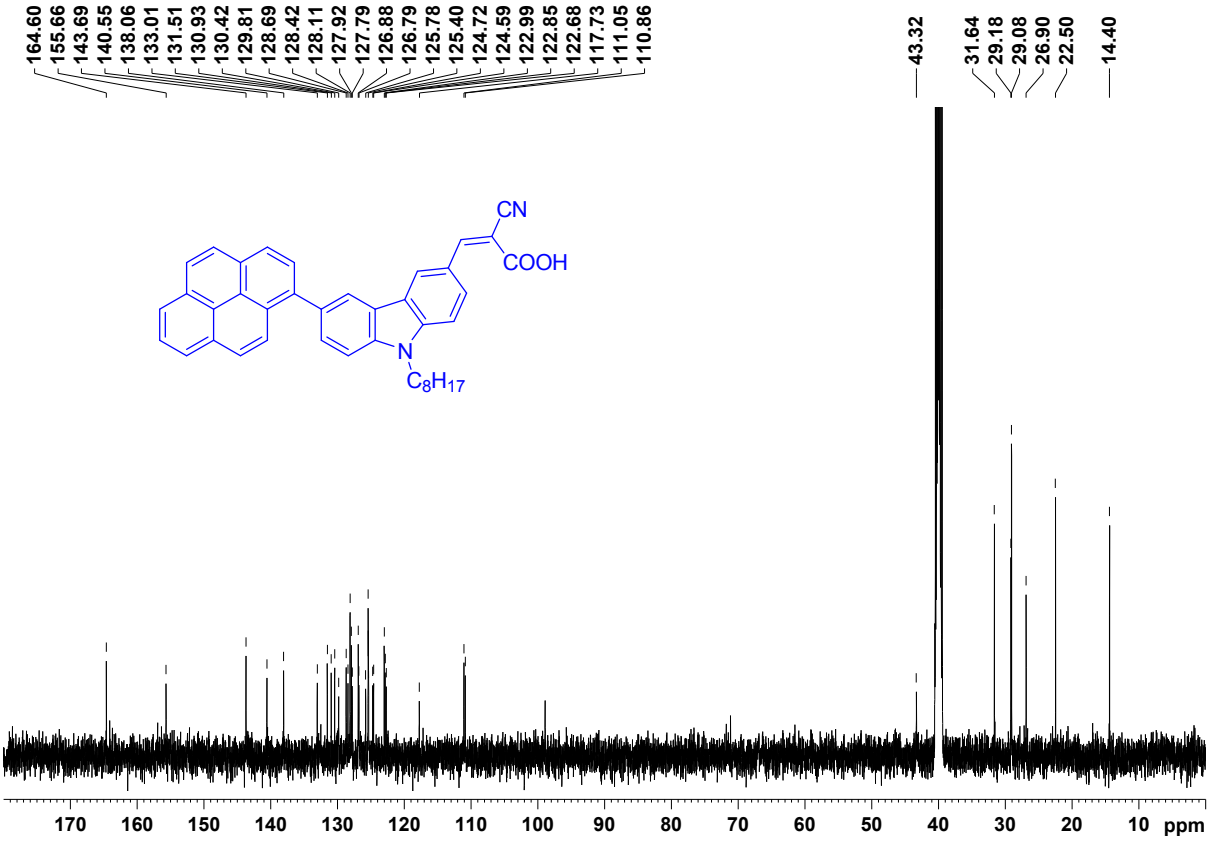


Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C39 H35 N O	533.2719	533.2692	534.2768 551.3028	(M+H)+ (M+NH4)+	-4.92	-2.62

Fig. S5 ^{1} H, ^{13}C and Mass spectrum of **PC1** dye.

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ppm

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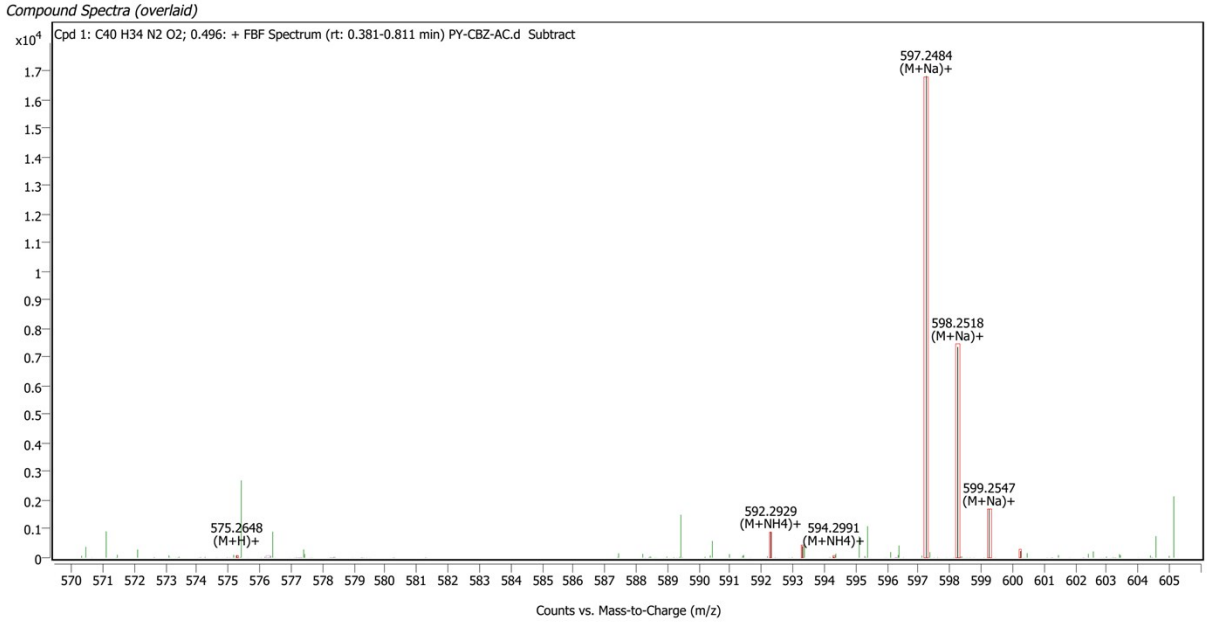
Name	10122019-16-KRR-PY-CBZ-AC	**Data File Path**	D:\MassHunter\Data\2019\NOV-2019\KRR\PY-CBZ-AC.d
Sample ID		**Acq. Time (Local)**	11-12-2019 10:32:42 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC-NEW.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)
Inj. Vol. (ul)	2	**IRM Status**	All ions missed
Position	P1-B5	**Method Path (DA)**	D:\MassHunter\Methods\10.0\Default.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C40 H34 N2 O2

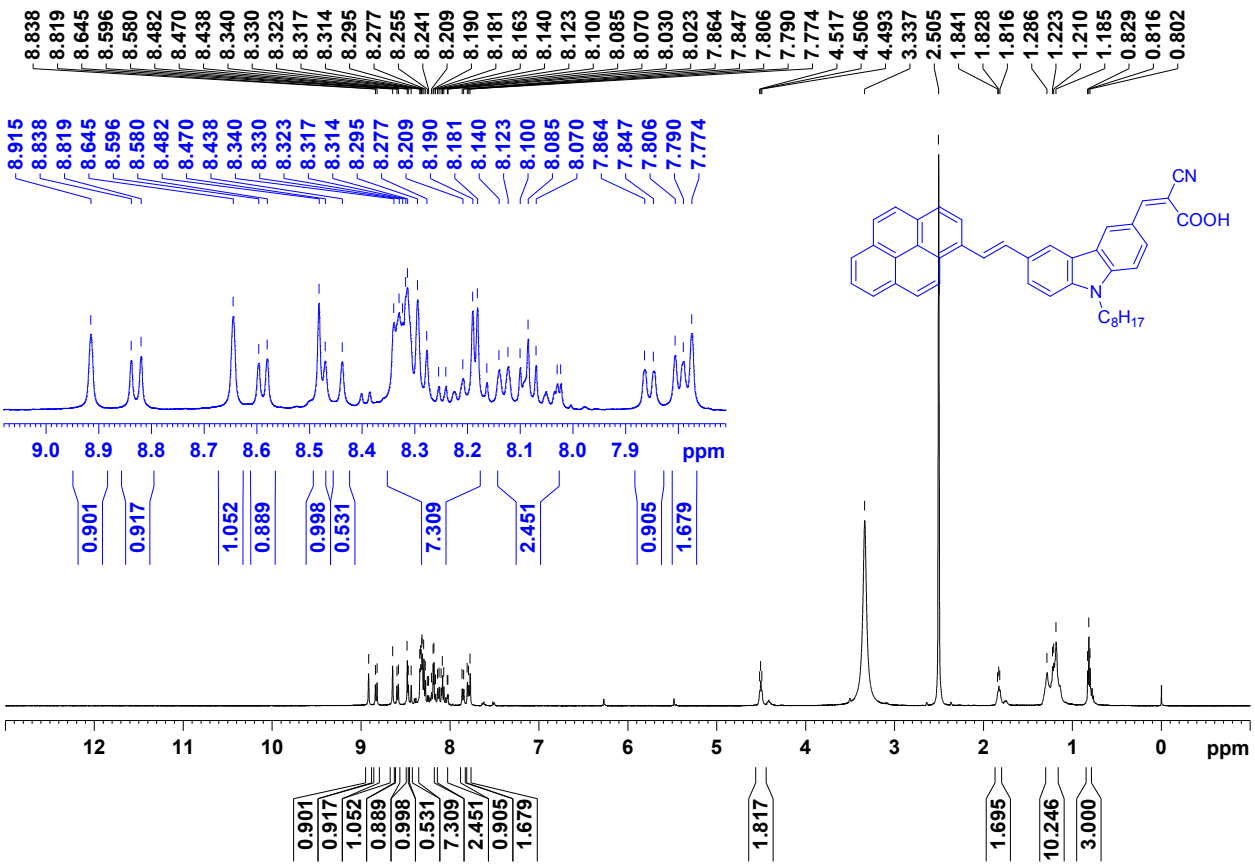
Compound Spectra (overlaid)

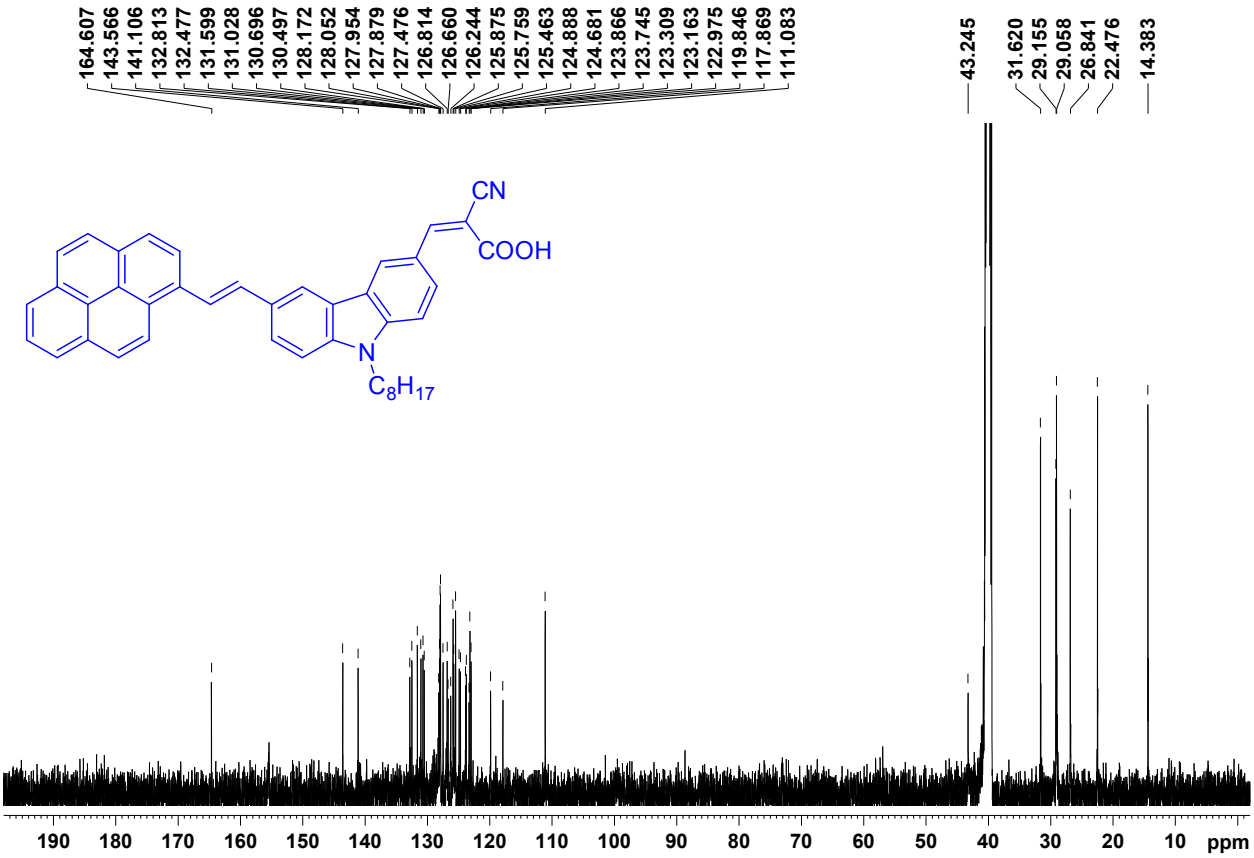


Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C40 H34 N2 O2	574.2620	574.2592	575.2648 592.2929 597.2484	(M+H)+ (M+NH4)+ (M+Na)+	-4.91	-2.82

Fig. S6 [1] H, [13]C and Mass spectrum of **PC2** dye.

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124.681
123.866
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123.309
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N
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ppm

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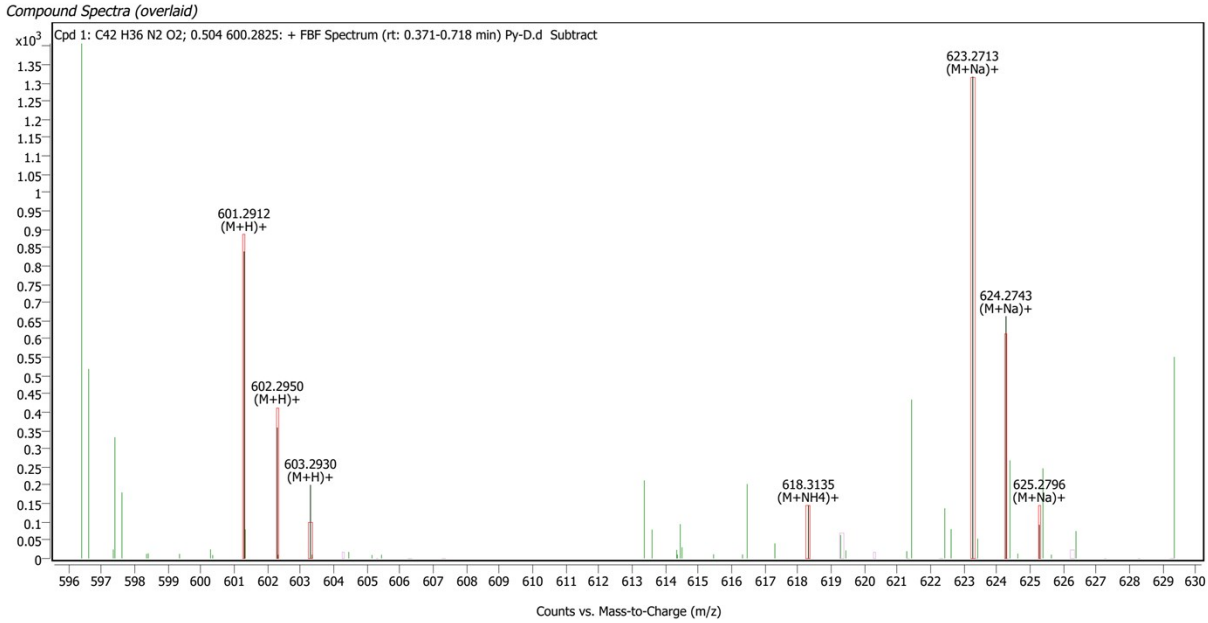
Name	031019-23-KRR-Py-D	**Data File Path**	D:\MassHunter\Data\2019\OCT-2019\KRR\Py-D.d
Sample ID		**Acq. Time (Local)**	03-10-2019 11:51:09 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)
Inj. Vol. (ul)	5	**IRM Status**	Success
Position	P1-C1	**Method Path (DA)**	D:\MassHunter\Methods\10.0\IIT-Target Screening_1.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C42 H36 N2 O2

Compound Spectra (overlaid)



Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C42 H36 N2 O2	600.2777	600.2825	601.2912 618.3135 623.2713	(M+H)+ (M+NH4)+ (M+Na)+	8.00	4.80

Fig. S7 Thickness of mesoporous TiO_2 coated on FTO plate measured using Nanomap Profilometer.

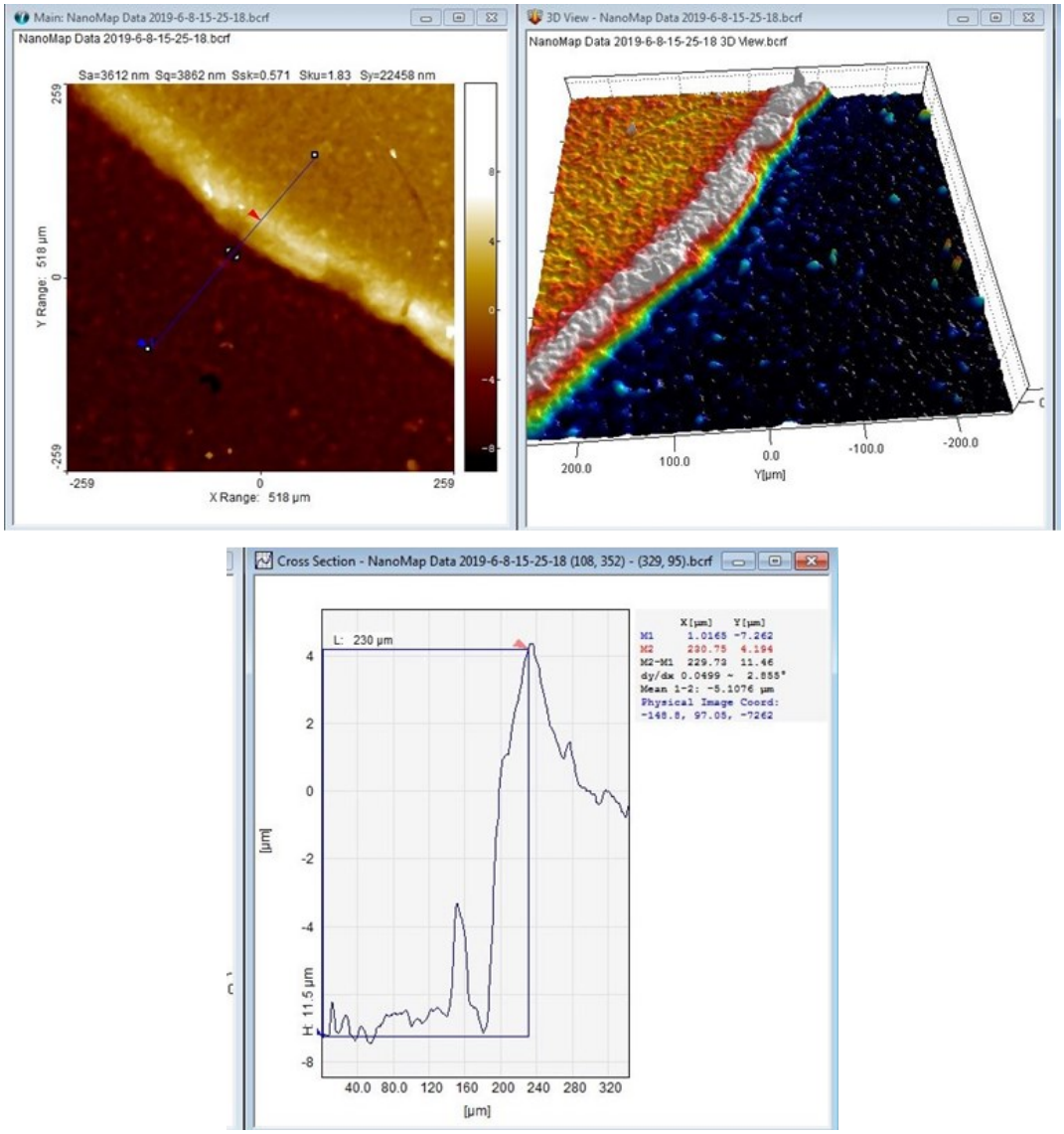


Fig. S8 *J-V* characteristics of devices sensitized with different solvents in without and with CDCA **PC0** (a, b) **PC1** (c, d) **PC2** (e, f) under one sun illumination (100 mWcm^{-2}).

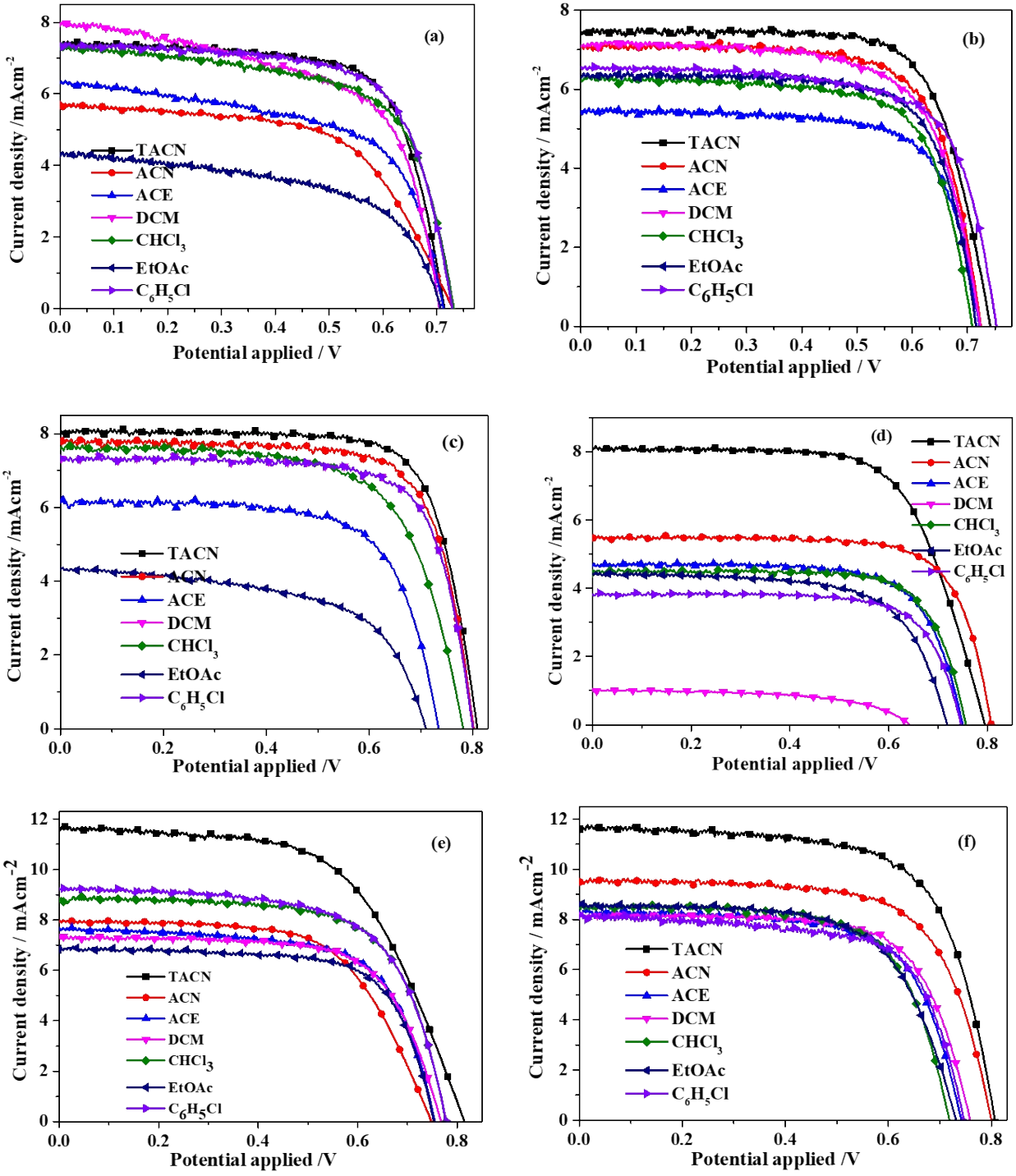


Table S1 HOMO, LUMO, calculated using B3LYP, CAM-B3LYP, M06, M06-2X, PBE1PBE, WB97XD/ 6-31G(d,p) method.

	B3LYP		**CAM-B3LYP**		**M06**		**M062X**		**PBE1PBE**		**WB97XD**	
Name of the Dye	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
PC0	-5.67	-2.65	-6.82	-1.39	-5.93	-2.51	-6.83	-1.76	-5.93	-2.58	-7.42	-0.86
PC1	-5.32	-2.22	-6.51	-1.14	-5.59	-2.21	-6.5	-1.49	-5.59	-2.27	-7.12	-0.64
PC2	-5.12	-2.37	-6.3	-1.17	-5.39	-2.24	-6.32	-1.53	-5.8	-2.3	-6.9	-0.68

Table S2 The projected density of states (PDOS) analysis of three dyes obtained using the B3LYP/6-31G(d,p) method.

Dye	**MO**	**Acceptor**	**Linker**	**Donor**
PC0	LUMO	56	NA	44
	HOMO	8	NA	92
PC1	LUMO	65	NA	35
	HOMO	1	NA	99
PC2	LUMO	62	2	36
	HOMO	1	15	84

Table S3 Optimization of solvents for **PC0** dye.

Solvents for **PC0** dye	V_{OC} **(V)** without/ with CDCA	J_{SC} **(mA cm^{-2})** without/ with CDCA	**FF** without/ with CDCA	η **(%)** without/ with CDCA
TACN	0.71/0.74	7.40/7.39	0.70/0.73	3.70/3.99
ACN	0.73/0.72	5.73/7.02	0.59/0.72	2.47/3.64
ACE	0.71/0.72	6.33/5.40	0.60/0.72	2.70/2.79
DCM	0.70/0.72	7.97/7.07	0.59/0.68	3.33/3.46
$CHCl_3$	0.73/0.70	7.30/6.22	0.64/0.72	3.41/3.13
EtOAc	0.71/0.72	4.28/6.32	0.56/0.73	1.68/3.32
C_6H_5Cl	0.73/0.75	7.33/6.52	0.68/0.69	3.64/3.37

Table S4 Optimization of solvents for **PC1** dye.

Solvents for **PC1** dye	V_{OC} *(V)* without/ with CDCA	J_{SC} *(mA cm^{-2})* without/ with CDCA	**FF** without/ with CDCA	**η (%)** without/ with CDCA
TACN	0.80/ 0.79	8.07/ 8.08	0.76/ 0.68	4.90/ 4.34
ACN	0.80/0.81	7.78/5.48)	0.74/0.74	4.60/3.27
ACE	0.73/0.75	6.12/4.64	0.69/0.72	3.08/2.50
DCM	0.79/0.64	7.27/1.0	0.75/0.57	4.32/0.36
$CHCl_3$	0.78/0.76	7.59/4.47	0.67/0.75	3.97/2.55
EtOAc	0.71/0.72	4.32/4.40	0.59/0.66	1.80/2.09
C_6H_5Cl	0.80/0.75	7.29/3.79	0.74/0.73	4.34/2.07

Table S5 Optimization of solvents for **PC2** dye.

Solvents for **PC2** dye	V_{OC} **(V)** without/ with CDCA	J_{SC} **(mA cm^{-2})** without/ with CDCA	**FF** without/ with CDCA	η **(%)** without/ with CDCA
TACN	0.81/0.80	11.57/11.59	0.60/0.68	5.57/6.30
ACN	0.75/0.79	7.95/9.49	0.62/0.69	3.69/5.17
ACE	0.75/0.74	7.61/8.28	0.66/0.67	3.77/4.10
DCM	0.77/0.76	7.24/8.13	0.68/0.69	3.79/4.27
$CHCl_3$	0.71/0.72	6.15/8.42	0.65/0.70	2.84/4.12
EtOAc	0.75/0.73	6.82/8.56	0.69/0.65	3.53/4.06
C_6H_5Cl	0.75/0.74	7.38/8.12	0.64/0.67	3.54/4.03