

## Supplementary Information

### **Molecularly engineered host materials for high performance inkjet-printed thermally activated delayed fluorescent organic light-emitting diodes**

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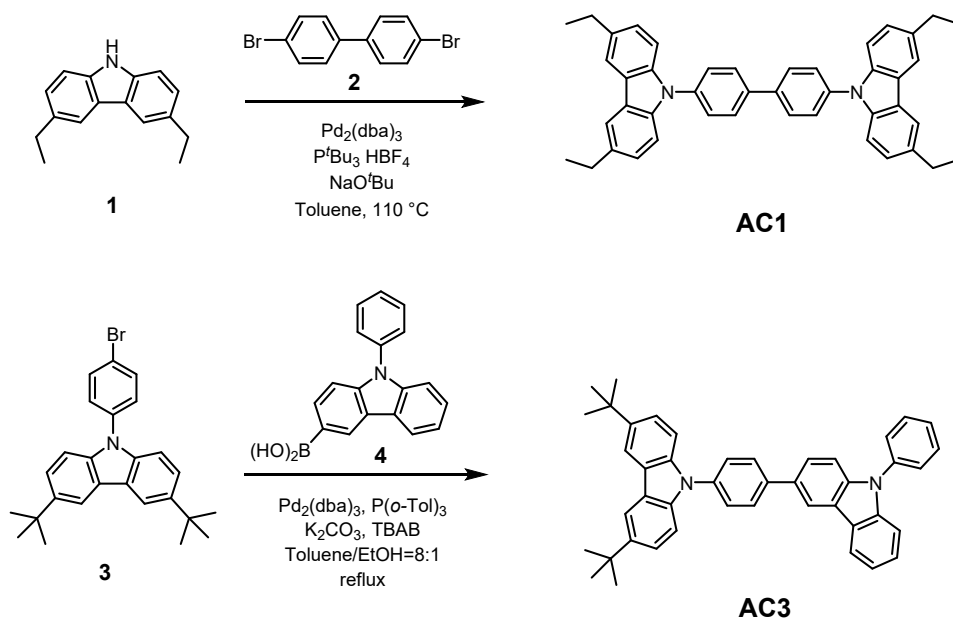
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## General synthetic procedures for AC1/AC3 compounds

Compound 1, 3, 4 were purchased from Puyang Huicheng Electronic Material Co., Ltd



### AC1:

To a 100 mL round bottle was added with compound 1 (11.1 mmol, 2.47 g) and compound 2 (4.8 mmol, 1.50 g), followed by the addition of Pd<sub>2</sub>(dba)<sub>3</sub> (0.10 mmol, 0.44 g), P(*t*Bu)<sub>3</sub>HBF<sub>4</sub> (0.2 mmol, 0.28 g) and NaO<sup>t</sup>Bu (14.4 mmol, 1.39 g). Then, anhydrous toluene was added into the mixture. The reaction was conducted under N<sub>2</sub> atmosphere overnight at a temperature of 110 °C. After completion and cooling to the room temperature, the reaction mixture was added into ice water and extracted with DCM three times, and then washed with saturated aqueous NaCl. The organic residue was dried by anhydrous MgSO<sub>4</sub> and then was filtered. Then, the crude product was purified by chromatography (the eluent solvent (hexane:dichloromethane)) on silica gel as a light-yellow solid (3.96 g, 59.6% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 4H), 7.91 – 7.86 (m, 4H), 7.71 – 7.65 (m, 4H), 7.42 (d, *J* = 8.6 Hz, 4H), 7.27 (dd, *J* = 8.4, 1.6 Hz, 3H), 2.86 (q, *J* = 7.6 Hz, 8H), 1.37 (t, *J* = 7.6, 1.4 Hz, 12H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 139.44, 138.88, 137.62, 135.98, 128.36, 127.13, 126.11, 123.61, 119.00, 109.56, 28.96, 16.54.

Elemental Analysis: calc.: C, 88.55; H, 6.76; N, 4.69; experiment: C, 87.75; H, 6.88;

N, 5.37.

**AC2:**

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.17 (td, *J* = 3.5, 1.1 Hz, 4H), 7.89 (t, *J* = 8.6 Hz, 4H), 7.69 (dd, *J* = 8.3, 1.6 Hz, 4H), 7.58 – 7.40 (m, 8H), 7.31 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 2H), 1.48 (s, 18 H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 143.01, 140.82, 139.37, 139.15, 138.70, 137.75, 137.12, 128.46, 128.38, 127.45, 127.04, 126.01, 123.67, 123.48, 120.36, 120.05, 116.30, 109.83, 109.26, 34.76, 32.03.

**AC3:**

To a 100 mL round bottle was added with compound 3 (6.0 mmol, 2.60g) and compound 4 (7.2 mmol, 2.1 g), followed by the addition of Pd<sub>2</sub>(dba)<sub>3</sub> (0.06 mmol, 0.06g), P(*o*-Tol)<sub>3</sub> (0.12 mmol, 0.04 g), K<sub>2</sub>CO<sub>3</sub> (12.0 mmol, 1.65 g) and a small portion of TBAB. Then, anhydrous toluene and EtOH was added into the mixture. The reaction was conducted under N<sub>2</sub> atmosphere overnight at a temperature of 110 °C. After completion and cooling to the room temperature, the reaction mixture was added into ice water and extracted with DCM three times, and then washed with saturated aqueous NaCl. The organic residue was dried by anhydrous MgSO<sub>4</sub> and then was filtered. Then, the crude product was purified by chromatography (the eluent solvent (hexane:dichloromethane)) on silica gel as a light-yellow solid (2.20 g, 62.0% yield).

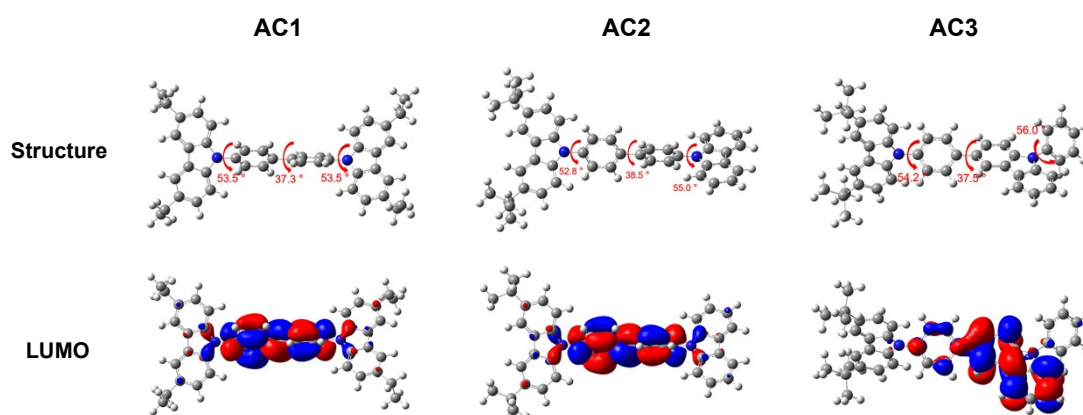
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.22 (td, *J* = 3.5, 1.1 Hz, 4H), 7.94 (t, *J* = 8.6 Hz, 4H), 7.74 (dd, *J* = 8.3, 1.6 Hz, 4H), 7.63 – 7.45 (m, 8H), 7.36 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 2H), 1.53 (s, 18H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.01, 140.82, 139.37, 139.15, 138.70, 137.75, 137.12, 128.46, 128.38, 127.45, 127.04, 126.01, 123.67, 123.48, 120.36, 120.05, 116.30, 109.83, 109.26, 34.76, 32.03.

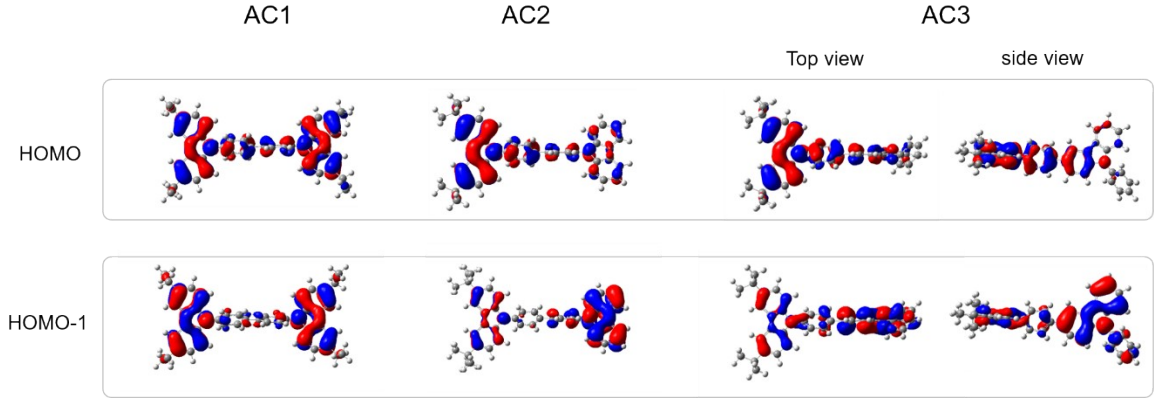
Elemental Analysis: calc.: C, 88.55; H, 6.76; N, 4.69; experiment: C, 89.03; H, 6.53; N, 4.44.

**Table S1.** Summary of EML inkjet-printed OLEDs.

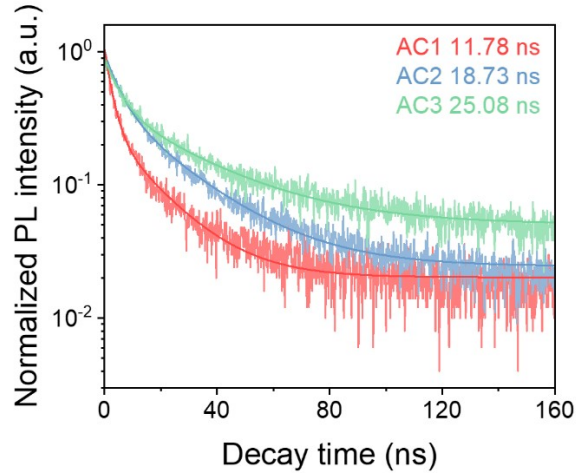
Inkjet-printed EML	Solvent	$EQE_{\max}$ (%)	$CE_{\max}$ ( $cd\ A^{-1}$ )	References
CBP + phosphorescent emitter	chlorobenzene	11.7	40.0	Thin Solid Films 520 (2012) 6954–6958
TCTA/3CzPFP + phosphorescent emitter	Chlorobenzene/ cyclohexanone	9.0	29.0	ACS Appl. Mater. Interfaces 2019, 11, 24, 21784–21794
CDBP + phosphorescent emitter	butyl benzoate	7.2	23.8	J. Mater. Chem. C, 2019,7, 4178-4184
t-BuCz-m-NPBI+ phosphorescent emitter	o-dichlorobenzene	-	17.89	J. Mater. Chem. C, 2020,8, 6906-6913
mCP/TPBi + phosphorescent emitter	butyl benzoate	6.7	23.0	Sci Rep 2019, 9, 6845
TAPC/TPBi + phosphorescent emitter	butyl benzoate /chlorobenzene	3.0	9.8	J. Phys. D: Appl. Phys. 2020, 53 (35).
Self-hosted Phosphorescent dendrimer emitter	Cyclohexanone/ 1-N-methyl pyrrolidinone	-	14.99	ACS Appl. Mater. Interfaces 2019, 11, 29, 26174–26184
$Cu^I$ -complex TADF self-hosted emitter	indane/mesitylene	4.7±0.6	15.2±1.4	Chem.Eur.J.2016,22,16400–16405
$Cu^I$ -complex TADF self-hosted emitter	decalin	13.9±1.9	45	Appl. Phys. A 2016, 122, 191
Self-hosted TADF dendrimer	toluene/tertralinal	-	18.0	Organic Electronics 74 (2019) 218–227
Self-hosted TADF Polymer	Anisole/ Propylene carbonate	1.58	1.58	Adv. Mater. Technol. 2022, 2200648
Small molecule (AC2) + organic TADF emitter	butyl benzoate	11.0	33.7	This work



**Figure S1.** The structure and LUMO distribution of AC1, AC2, AC3.



**Figure S2.** The comparison between HOMO and HOMO-1 distribution of AC1, AC2, AC3.



**Figure S3.** The transient PL spectra of AC1/AC2/AC3: 8 wt% 4CzIPN films: **prompt fluorescence component.**

The fitting for decay curves is carried out based on a double-exponential function:

$$I = A_1 \cdot \exp[-(\tau_1 - t_0)/t] + A_2 \cdot \exp[-(\tau_2 - t_0)/t] + I_0$$

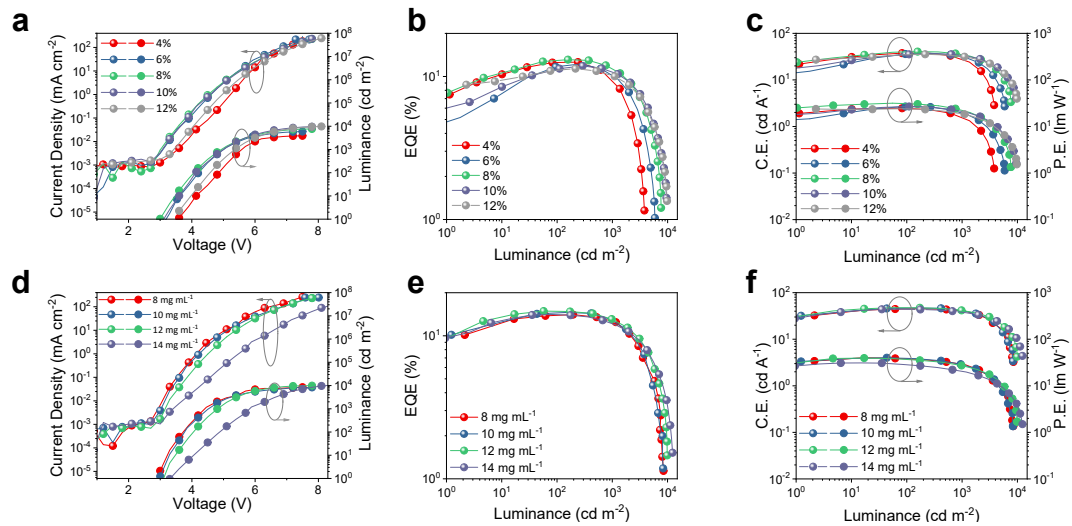
where  $\tau_1$  and  $\tau_2$  represent the decay time constants, and  $A_1$  and  $A_2$  represent the normalized amplitudes of each component. Therefore, the average lifetime of the decay is calculated by equation 1:

$$\tau_{ave} = \frac{A_1 * \tau_1^2 + A_2 * \tau_2^2}{A_1 * \tau_1 + A_2 * \tau_2}$$

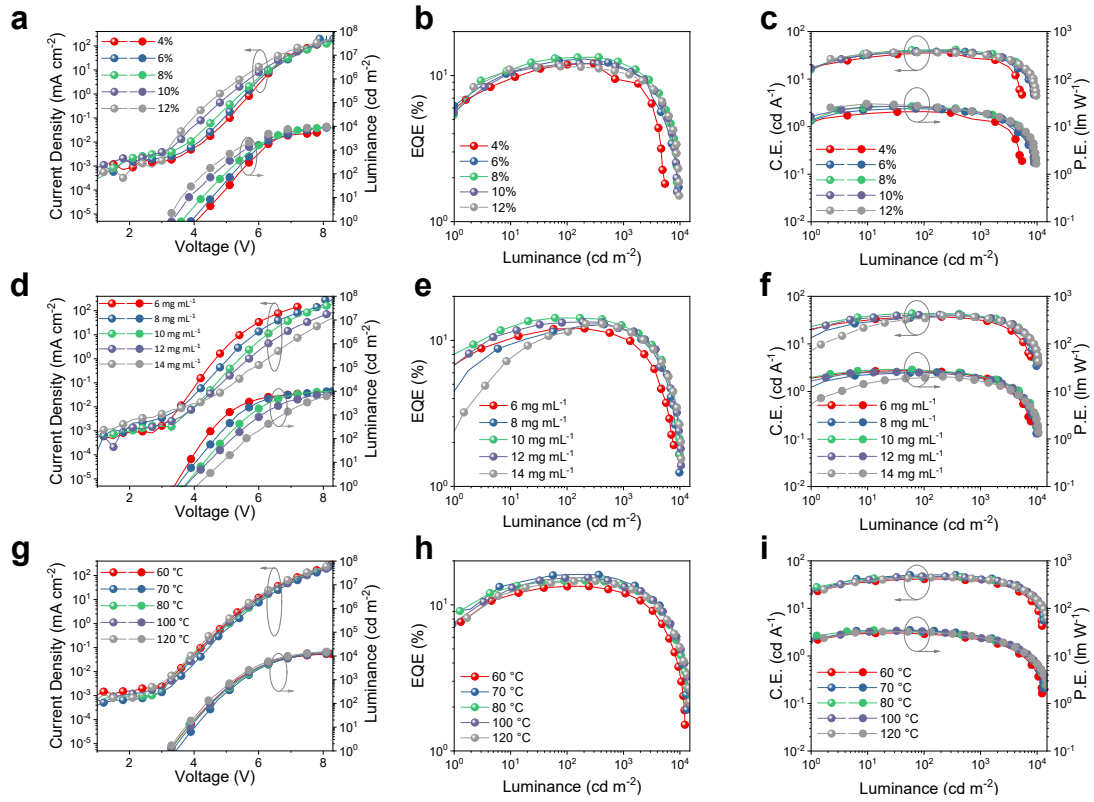
**Table S2.** Fitting parameters for the TRPL spectra.

Host	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\tau_{\text{ave}}$ (ns)	$R^2$ <sup>a</sup>
AC1	1.01	2.60	0.26	16.33	11.78	0.987
AC2	0.63	5.11	0.39	23.16	18.73	0.995
AC3	0.51	5.04	0.34	30.11	25.08	0.983

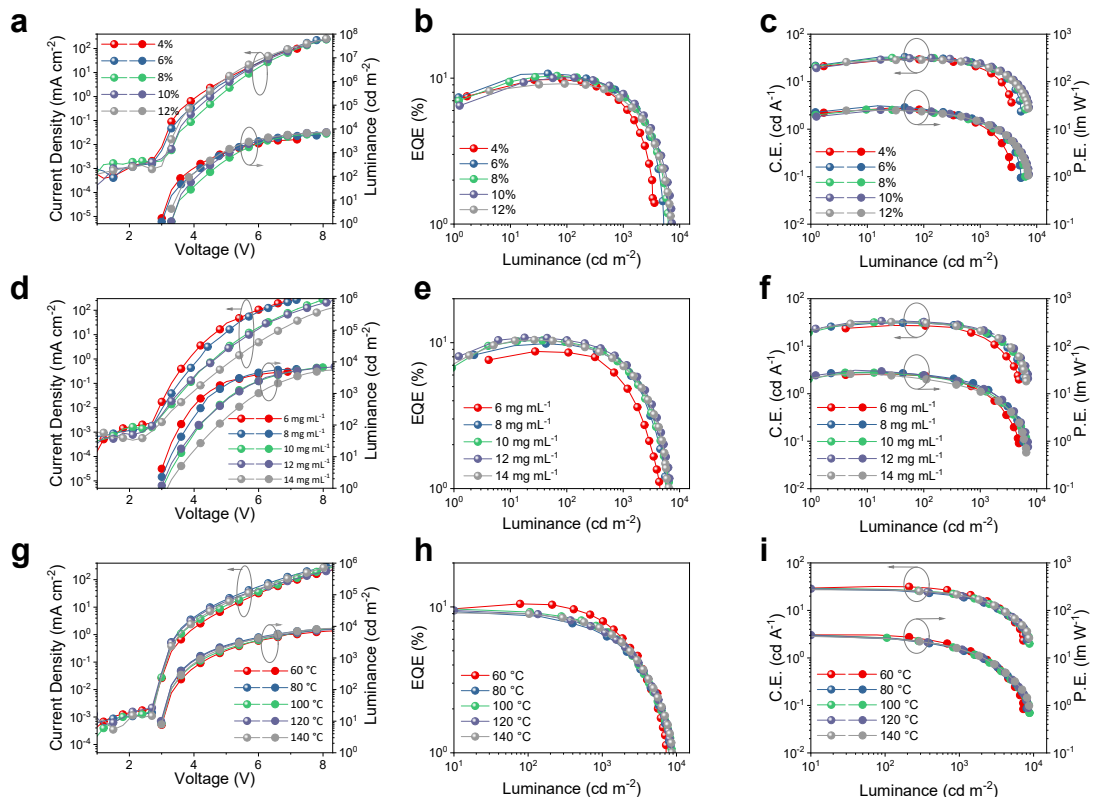
(a) R: Residuals of the bi-exponential fittings.



**Figure S4.** The EL properties of AC1-based OLEDs with different (a)(b)(c)doping concentration and (d)(e)(f)thickness of EML.



**Figure S5.** The EL properties of AC2-based OLEDs with different (a)(b)(c)doping concentration, (d)(e)(f)thickness and (g)(h)(i)annealing temperature of EML.



**Figure S6.** The EL properties of AC3-based OLEDs with different (a)(b)(c)doping

concentration, (d)(e)(f)thickness and (g)(h)(i)annealing temperature of EML.



**Table S3.** EL characteristic parameters of spin-coated AC1-based OLEDs with different doping concentration and thickness of EML.

Device (X)	EQE (%) <sup>a</sup>	PE (lm W <sup>-1</sup> ) <sup>a</sup>	CE (cd A <sup>-1</sup> ) <sup>a</sup>	$L_{\max}$ (cd m <sup>-2</sup> ) <sup>b</sup>	$V_T$ (V) <sup>c</sup>	$V_D$ (V) @10 <sup>2</sup> , 10 <sup>3</sup> , 10 <sup>4</sup> cd m <sup>-2</sup>	CIE (x, y) <sup>d</sup>					
<b>X wt% 4CzIPN:AC1 (chlorobenzene , 10 mg mL<sup>-1</sup>) ; annealing in 60°C ◦</b>												
4%	12.59	9.6	24.6	16	37.7	29	3859	3.6	4.9	5.6	-	(0.29,0.54)
6%	12.23	10.0	26.9	20	37.5	31	5882	3.3	4.2	5.0	-	(0.30,0.55)
8%	13.10	11.4	31.6	22	40.5	34	7624	3.0	4.1	5.0	-	(0.31,0.55)
10%	11.86	10.8	26.9	21	36.9	33	9532	3.1	4.1	5.0	-	(0.32,0.55)
12%	11.34	10.1	24.0	19	35.6	32	9770	3.4	4.6	5.3	-	(0.32,0.55)
<b>8 wt% 4CzIPN:AC1 (chlorobenzene , X mg mL<sup>-1</sup>) ; annealing in 60°C ◦</b>												
8	14.1	12.8	40.1	29.1	45.3	41.2	8472	2.9	3.8	4.4	-	(0.31,0.57)
10	14.56	13.0	40.0	29	46.9	41	8329	3.0	3.8	4.6	-	(0.31,0.57)
12	14.88	13.0	39.4	27	47.6	41	9868	3.1	4.1	4.9	-	(0.32,0.56)
14	14.09	12.0	31.0	20	44.1	28	12340	3.4	4.9	5.9	8.4	(0.32,0.55)

(a) Data at maximum and 1000 cd m<sup>-2</sup> from left to right. (b) Maximum luminance. (c) voltage in 1 cd m<sup>-2</sup>. (d) CIE: Commission Internationale de l'Eclairage at 1,000 cd m<sup>-2</sup>.

**Table S4.** EL characteristic parameters of spin-coated AC2-based OLEDs with different doping concentration, thickness and annealing temperature of EML.

Device (X)	EQE (%) <sup>a</sup>		PE (lm W <sup>-1</sup> ) <sup>a</sup>		CE (cd A <sup>-1</sup> ) <sup>a</sup>		$L_{\max}$ (cd m <sup>-2</sup> ) <sup>b</sup>	$V_T$ (V) <sup>c</sup>	$V_D$ (V) @10 <sup>2</sup> , 10 <sup>3</sup> , 10 <sup>4</sup> cd m <sup>-2</sup>			CIE (x, y) <sup>d</sup>
<b>X wt% 4CzIPN:AC2 (chlorobenzene , 10 mg mL<sup>-1</sup>) ; annealing in 60°C °</b>												
4%	12.1	9.0	20.7	13	35.6	27	5410	4.1	5.4	6.1	-	(0.26,0.53)
6%	13.0	11.5	24.0	19	39.7	35	9409	3.9	5.2	5.9	-	(0.26,0.55)
8%	13.4	12.0	26.7	20	41.5	37	8550	3.6	5.0	5.8	-	(0.28,0.55)
10%	12.1	11.0	26.6	20	37.7	34	8847	3.3	4.7	5.6	-	(0.29,0.56)
12%	11.5	10.5	30.3	20	36.6	33	9673	3.3	4.3	5.3	-	(0.29,0.56)
<b>8 wt% 4CzIPN:AC2 (chlorobenzene , X mg mL<sup>-1</sup>) ; annealing in 60°C °</b>												
6	12.1	10.5	27.7	20	37.2	32	7792	3.4	4.4	5.0	-	(0.28,0.55)
8	12.9	12.0	25.2	21	39.5	36	9780	3.4	4.7	5.3	-	(0.28,0.55)
10	14.2	12.5	29.1	21	43.8	38	9936	3.7	5.0	5.7	-	(0.28,0.55)
12	13.4	12.0	24.0	19	40.9	36	10460	3.8	5.2	6.1	8.9	(0.28,0.55)
14	13.0	11.5	20.5	16	39.2	35	10510	4.1	5.6	6.8	9.2	(0.27,0.54)
<b>8 wt% 4CzIPN:AC2 (chlorobenzene , 10 mg mL<sup>-1</sup>) ; annealing in X °C</b>												
60 °C	13.4	12.0	30.4	22	41.4	37	12250	3.3	4.5	5.3	7.3	(0.29,0.55)
70 °C	16.2	14.0	35.0	26	50.8	45	13150	3.4	4.7	5.5	7.3	(0.29,0.56)
80 °C	14.7	13.5	34.6	24	46.1	42	14260	3.3	4.6	5.5	7.2	(0.29,0.56)
100 °C	15.3	13.0	33.8	24	47.0	40	14960	3.3	4.6	5.4	7.1	(0.29,0.55)
120 °C	14.6	13.5	32.5	24	44.8	41	15020	3.3	4.4	5.3	6.9	(0.29,0.55)

(a) Data at maximum and 1000 cd m<sup>-2</sup> from left to right. (b) Maximum luminance. (c) voltage in 1 cd m<sup>-2</sup>. (d) CIE:

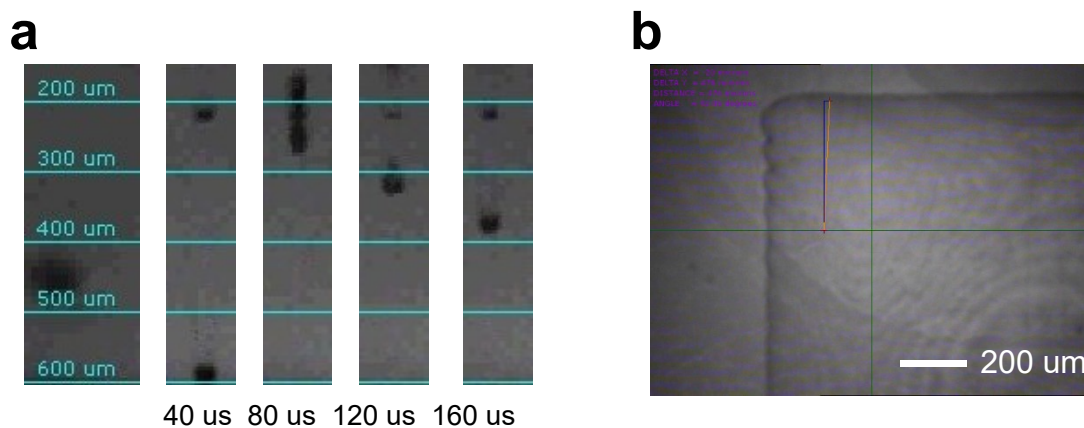
Commission Internationale de l'Eclairage at 1,000 cd m<sup>-2</sup>.

**Table S5.** EL characteristic parameters of spin-coated AC3-based OLEDs with different doping concentration, thickness and annealing temperature of EML.

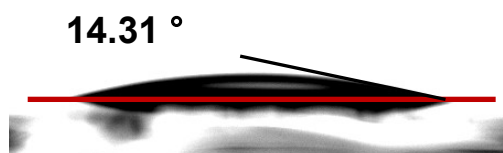
Device (X)	EQE (%) <sup>a</sup>	PE (lm W <sup>-1</sup> ) <sup>a</sup>	CE (cd A <sup>-1</sup> ) <sup>a</sup>	$L_{\max}$ (cd m <sup>-2</sup> ) <sup>b</sup>	$V_T$ (V) <sup>c</sup>	$V_D$ (V) @10 <sup>2</sup> , 10 <sup>3</sup> , 10 <sup>4</sup> cd m <sup>-2</sup>	CIE (x, y) <sup>d</sup>					
<b>X wt% 4CzIPN:AC3 (chlorobenzene , 10 mg mL<sup>-1</sup>) ; annealing in 60°C °</b>												
4%	9.79	6.5	27.8	12	29.4	19	3721	3.0	3.7	5.0	-	(0.29,0.54)
6%	10.7	7.5	31.0	14	33.4	23.3	5265	3.0	3.9	5.0	-	(0.30,0.55)
8%	10.36	7.5	25.8	13	32.2	23	6313	3.3	4.4	5.4	-	(0.31,0.55)
10%	10.07	8.0	25.4	15	31.5	24	7274	3.3	4.1	5.1	-	(0.32,0.55)
12%	9.17	7.0	24.9	14	28.9	21	7092	3.2	3.9	4.9	-	(0.33,0.56)
<b>8 wt% 4CzIPN:AC3 (chlorobenzene , X mg mL<sup>-1</sup>) ; annealing in 60°C °</b>												
6	8.70	5.5	26.1	12	27.4	17	4847	2.9	3.6	4.4	-	(0.30,0.56)
8	9.84	6.5	28.7	14	31.0	21	5877	3.0	3.8	4.6	-	(0.31,0.56)
10	10.36	7.0	27.7	13	32.2	21	6653	3.0	4.2	5.3	-	(0.32,0.55)
12	10.82	7.5	31.2	13	33.9	23	7014	3.0	4.1	5.3	-	(0.31,0.55)
14	10.44	7.0	26.0	11	32.3	21	6526	3.3	4.8	6.0	-	(0.31,0.55)
<b>8 wt% 4CzIPN:AC3 (chlorobenzene , 10 mg mL<sup>-1</sup>) ; annealing in X °C</b>												
60 °C	10.49	8.0	30.6	17	32.0	24	7238	2.9	3.4	4.5	-	(0.31,0.54)
80 °C	9.30	6.5	29.5	15	29.1	19	8092	2.9	3.3	4.1	-	(0.31,0.54)
100 °C	9.72	7.0	30.8	16	29.3	21	8812	2.9	3.3	4.4	-	(0.31,0.54)
120 °C	9.46	6.5	30.2	15	28.7	20	8415	2.9	3.3	4.2	-	(0.31,0.54)
140 °C	9.11	7.0	28.7	16	27.3	22	8703	2.9	3.3	4.3	-	(0.31,0.54)

(a) Data at maximum and 1000 cd m<sup>-2</sup> from left to right. (b) Maximum luminance. (c) voltage in 1 cd m<sup>-2</sup>. (d) CIE:

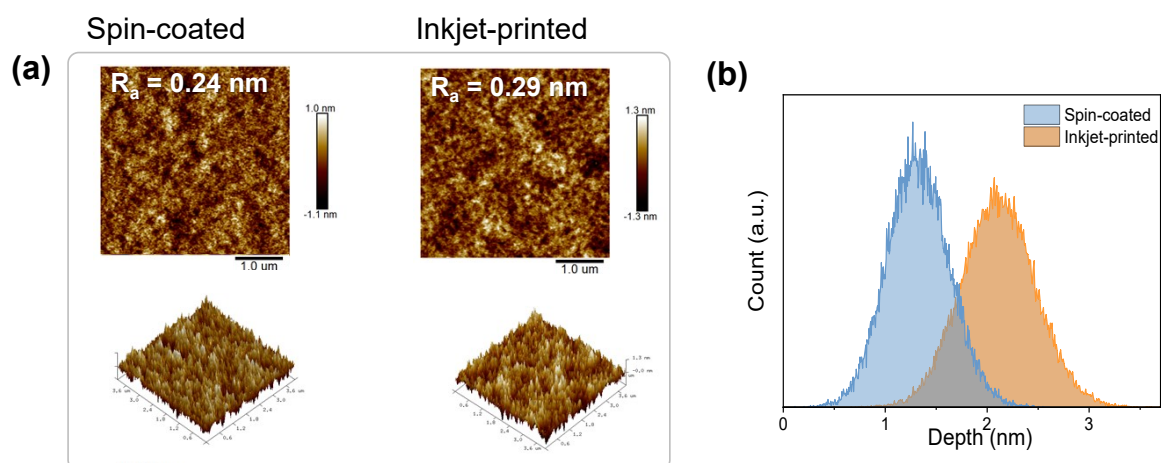
Commission Internationale de l'Eclairage at 1,000 cd m<sup>-2</sup>.



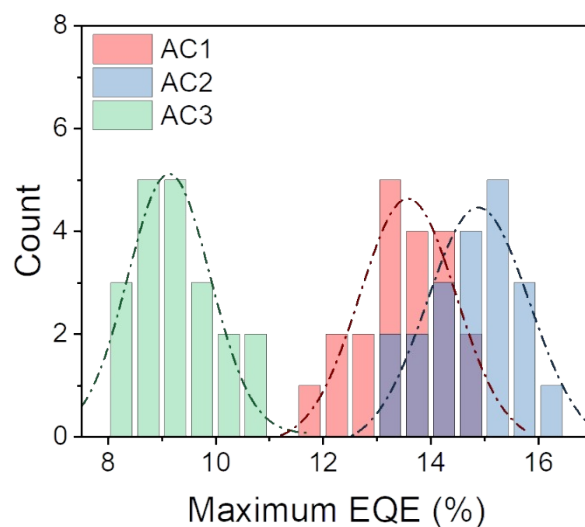
**Figure S7.** (a) drop formation, (b)optical inkjet-printed EML ink.



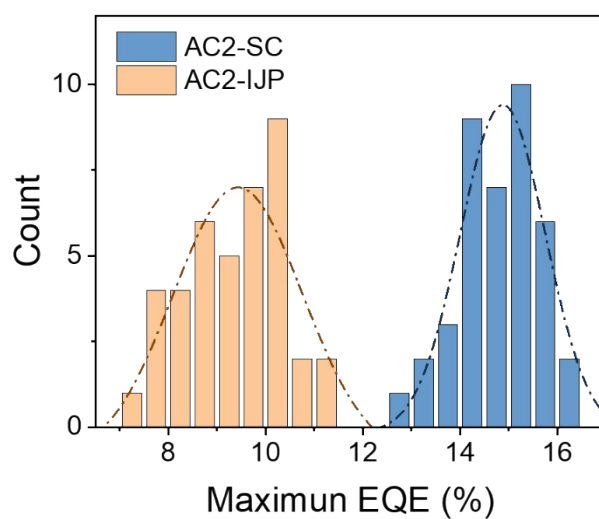
**Figure S8.** Contact angle of AC2 based ink on PEDOT:PSS layer.



**Figure S9.** (a) AFM topographic images and three-dimensional images ( $4 \times 4 \mu\text{m}$ ) of spin-coated EML and inkjet-printed EML films. (c) Surface depth histograms of spin-coated EML and inkjet-printed EML films.

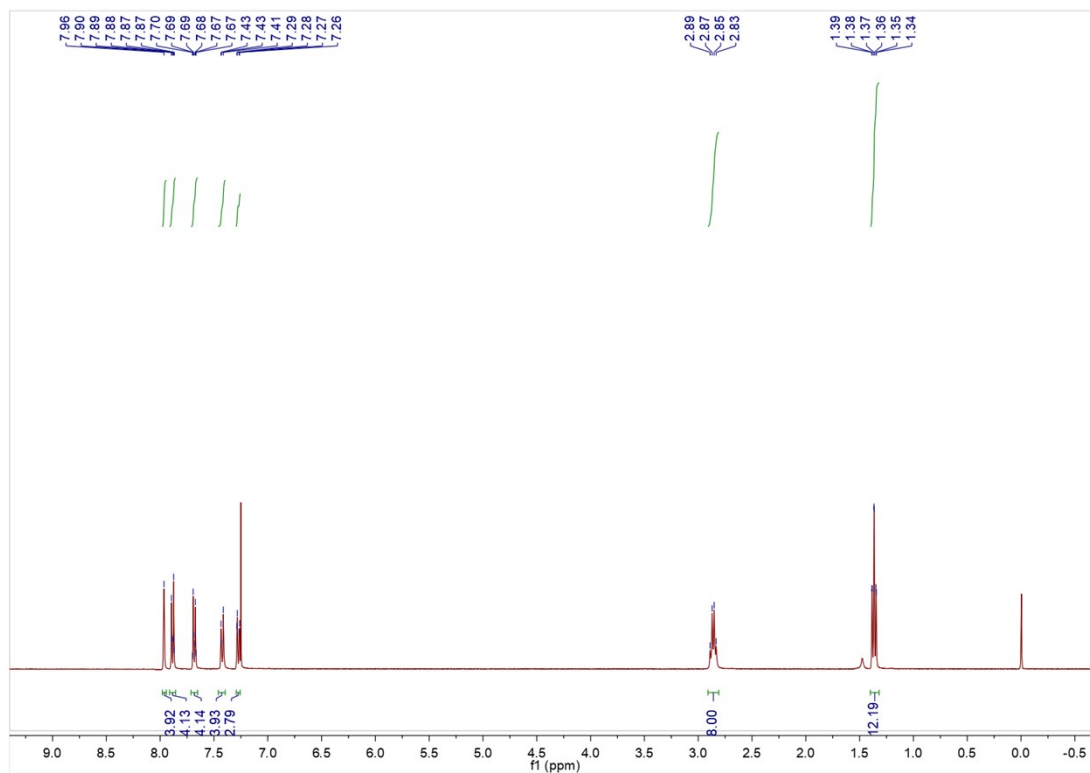


**Figure S10.** The histogram of maximum EQEs measured from 20 spin-coating devices based on AC1, AC2, AC3. The standard deviations of these values are calculated to be 0.79, 0.80, 0.88% for AC1, AC2, AC3, respectively.

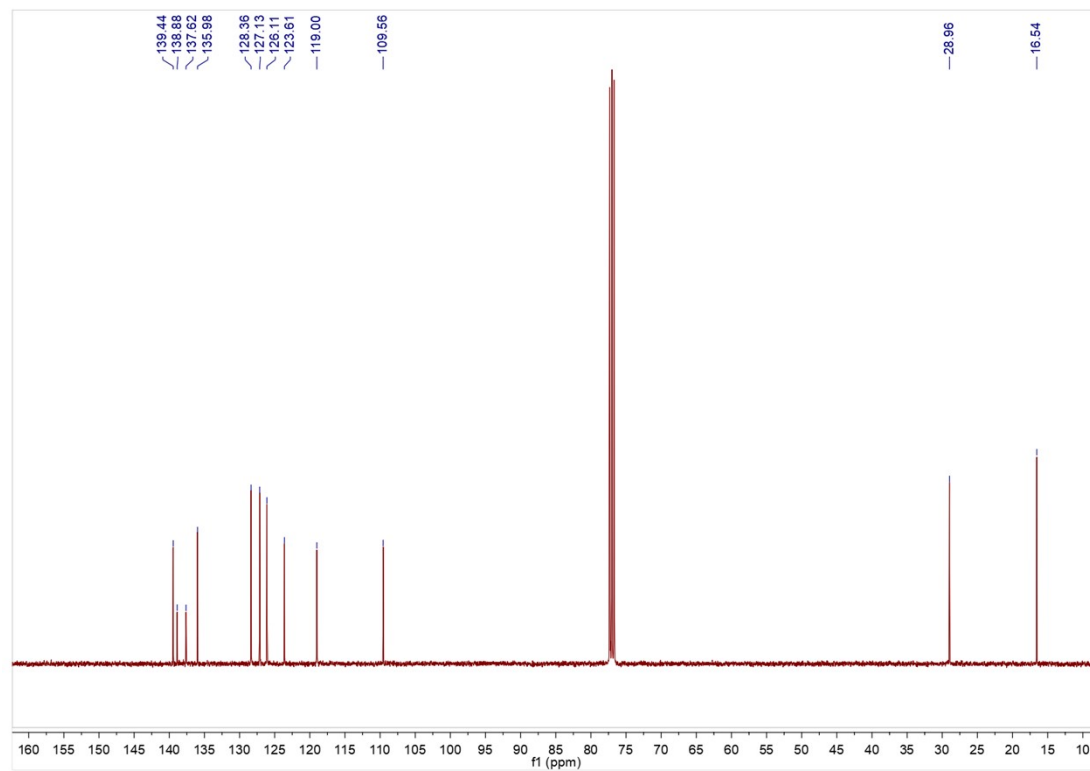


**Figure S11.** The histogram of maximum EQEs measured from 40 spin-coating and inkjet-printing devices based on AC2. The standard deviations of these values are calculated to be 0.84, 1.04% for spin-coating and inkjet printing devices, respectively.

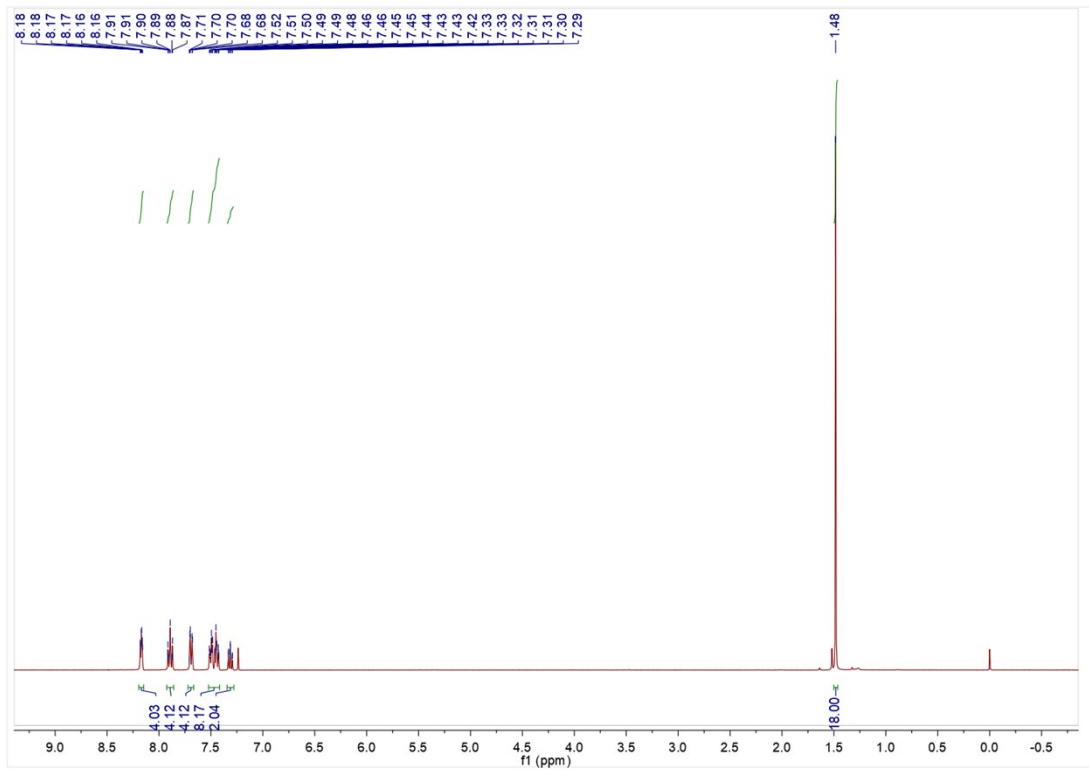
### <sup>1</sup>H NMR of AC1



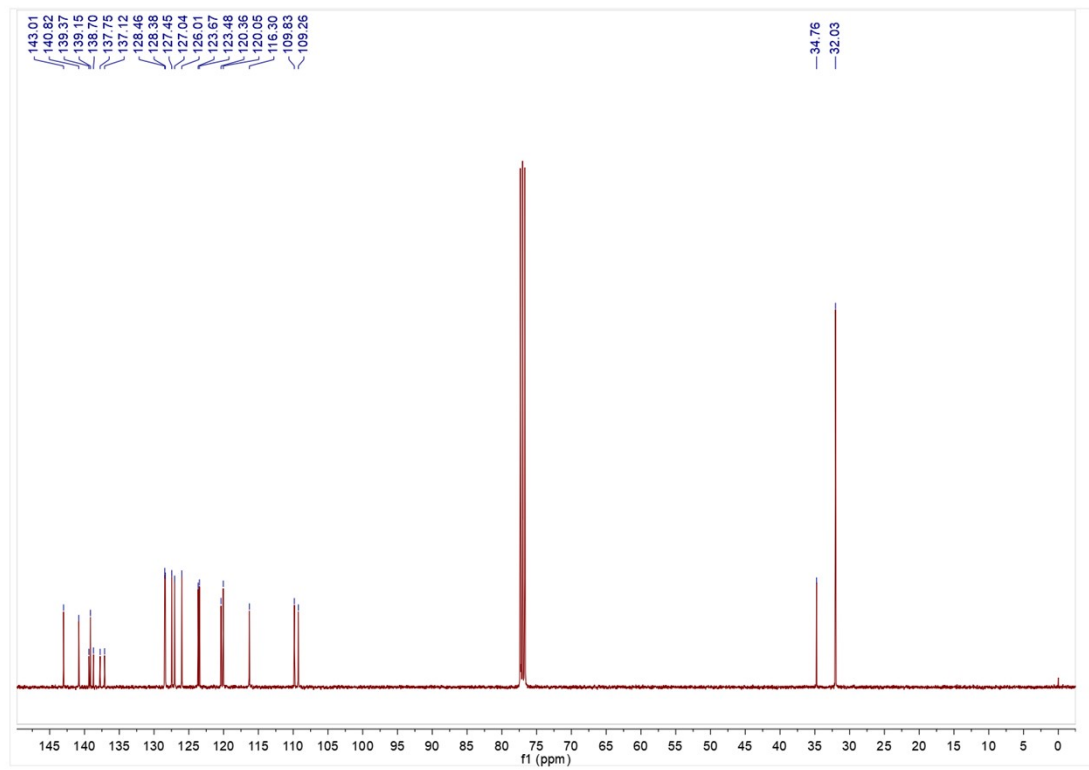
### <sup>13</sup>C NMR of AC1



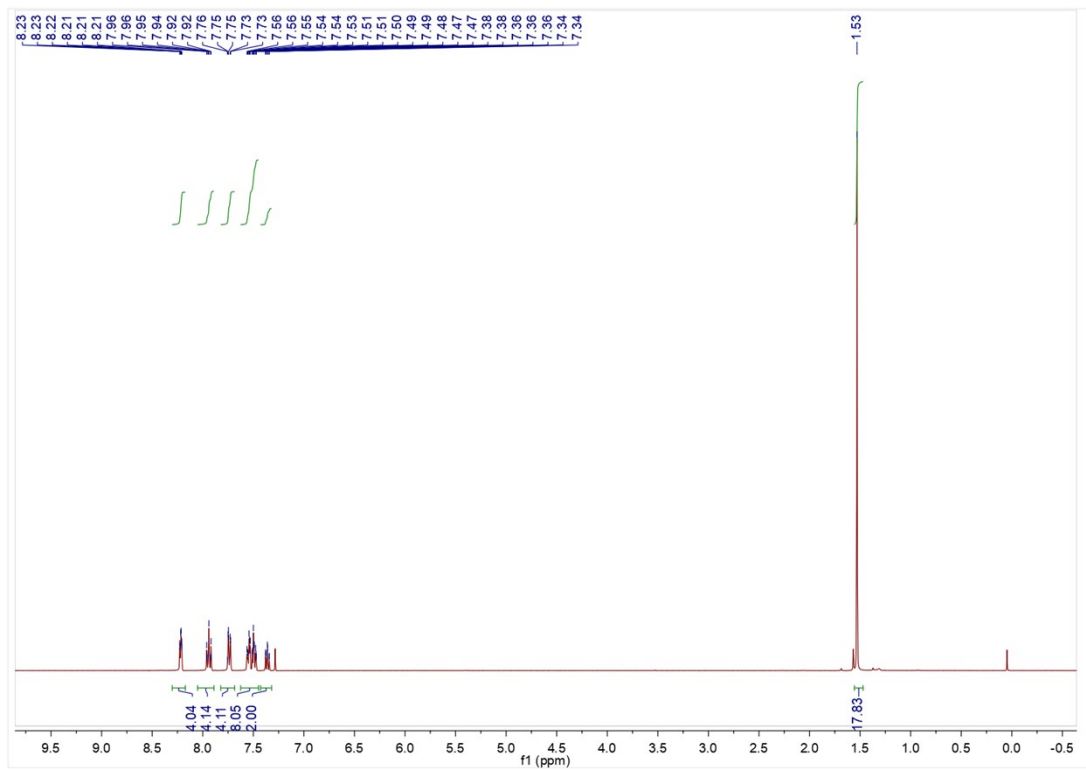
### <sup>1</sup>H NMR of AC2



### <sup>13</sup>C NMR of AC2



### <sup>1</sup>H NMR of AC3



### <sup>13</sup>C NMR of AC3

