Electronic Supplementary Information

Effect of an Auxiliary Acceptor on D-A-π-A Sensitizers for Highly Efficient and Stable Dye-Sensitized Solar Cells

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1. DTF simulation of the three compounds

The molecular structures were optimised in vacuum, using the software Avogadro[1] to enter the starting geometry. Then the structure was optimised in dichloromethane, using the optimised structure from vacuum. All calculations were carried out using the Gaussian 09 program[2] with the hybrid B3LYP functional[3] and the standard 6-31G(d) basis set. In the calculations, the long alkyl chains were replaced by methyl groups to reduce computational costs without affecting the nature of frontier molecular orbitals. Time-dependent DFT calculations (TD-DFT) were performed using Gaussian 09 program with a dichloromethane polarisable continuum model (PCM)[4], using the range-separated CAM-B3LYP functional[5] and the triple-zeta TZVP basis set[6]. The 20 lowest singlet electronic transitions were calculated and processed with the GaussSum software package.[7]

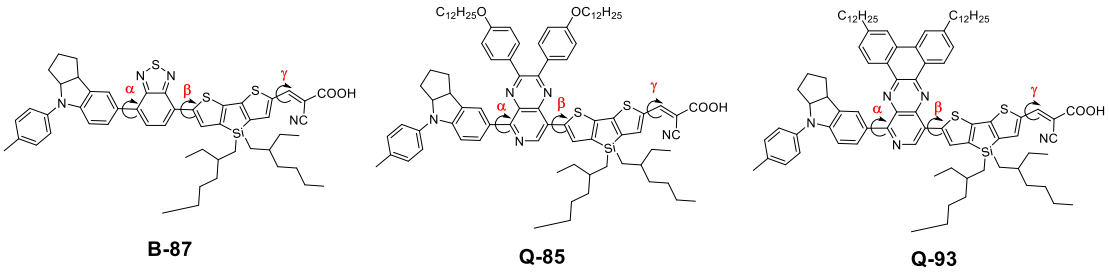
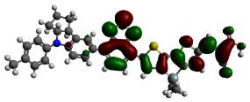
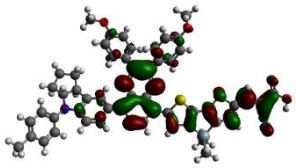
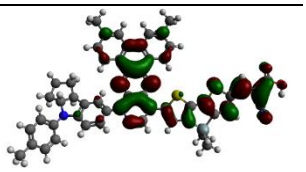
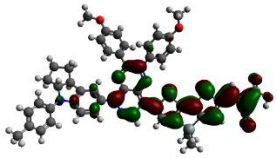
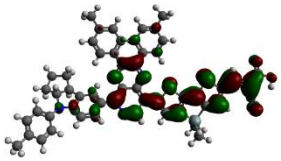


Fig. S1 Chemical structures of dyes **B-87**, **Q-85** and **Q-93.**

Table S1. Molecular orbital distributions and energy optimized in DCM (isodensity=0.020 a.u.).

	B-87	Q-85	Q-93
LUMO+1	 -2.42 eV	 -2.34 eV	 -2.52 eV
LUMO	 -2.85 eV		

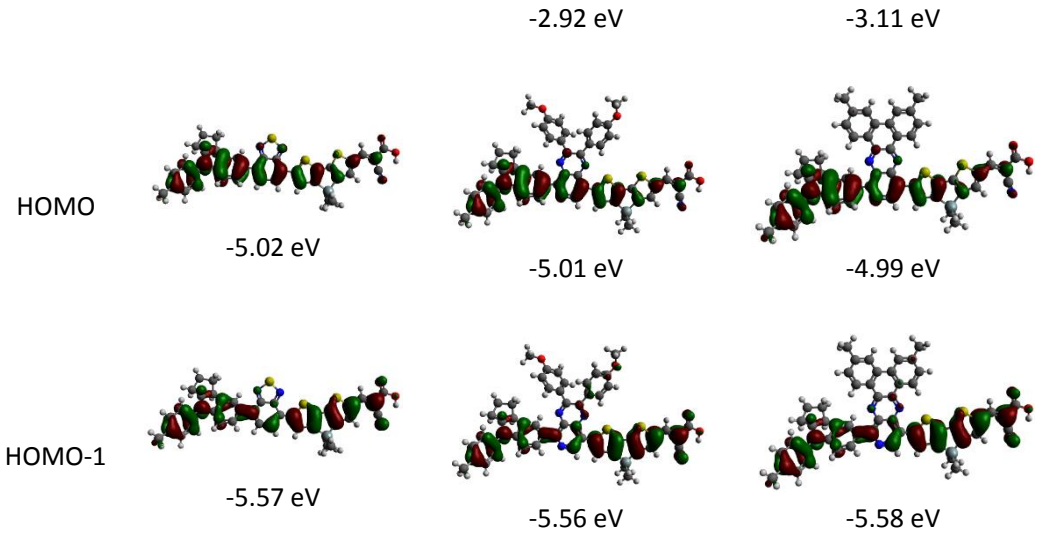


Table S2. Dihedral angles and dipole moments of **B-87**, **Q-85** and **Q-93**

Dyes	α	β	γ	Dipole moment
B-87	33.6°	-5.6°	-0.1°	13.03
Q-85	24.7°	17.4°	0°	13.43
Q-93	29.3°	20.4°	0°	12.17

2. Optimized process of photoelectrode in DSSCs.

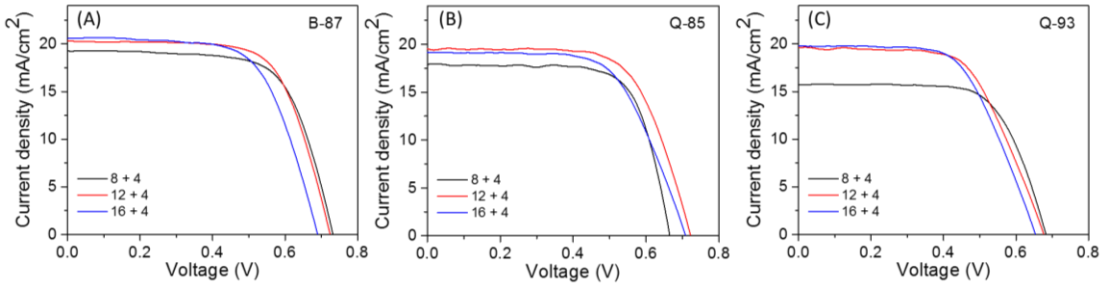


Fig. S2 *J-V* curves for DSSCs based on the dyes B-87, Q-85 and Q-93 with different thickness of TiO_2 layer under illumination of AM 1.5 G simulated sunlight (100 mW cm^{-2}).

Table S3. Photovoltaic performance of the DSSCs based on dyes B-87, Q-85 and Q-93 with different thickness of TiO_2 layer.

Dye	TiO_2 Thickness[a] (μm)	V_{oc} (mV)	J_{sc} (mA cm^{-2})	*FF* (%)	PCE (%)
B-87	8 + 4	732	18.52	67.97	9.22
	12 + 4	724	20.28	68.26	10.02
	16 + 4	689	20.63	64.63	9.19
Q-85	8 + 4	664	17.91	71.67	8.53
	12 + 4	722	19.55	66.64	9.41
	16 + 4	708	19.18	63.46	8.62
Q-93	8 + 4	682	15.74	68.08	7.31
	12 + 4	676	19.53	61.83	8.17
	16 + 4	653	19.80	61.14	7.90

[a]Thick commercial colloidal paste TiO_2 film layer + scattering TiO_2 film layer.

3. Optimized process of CDCA concentration in DSSCs.

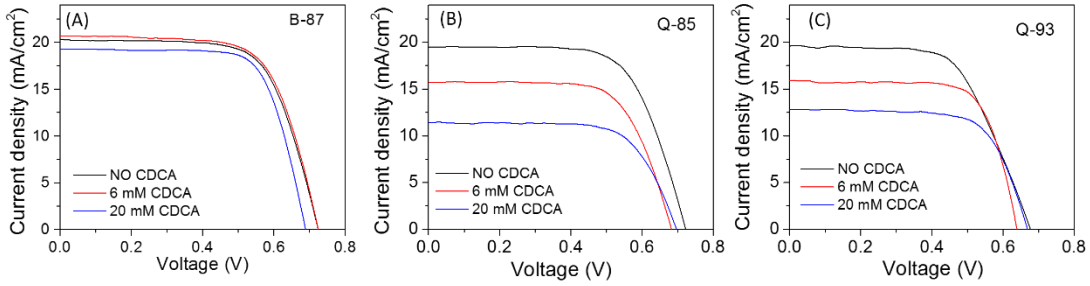


Fig. S3 *J-V* curves for DSSCs based on the dyes B-87, Q-85 and Q-93 with different concentration of CDCA under illumination of AM 1.5 G simulated sunlight (100 mW cm^{-2}) in iodide electrolyte.

Table S4 Photovoltaic performance of the DSSC based on dyes B-87, Q-85 and Q-93 with different concentration of CDCA.

Dye	CDCA	V_{oc} (mV)	J_{sc} (mA cm^{-2})	*FF*	PCE (%)
B-87	0	724	20.28	68.26	10.02
	6 mM	724	20.78	67.77	10.20
	20 mM	708	18.75	65.64	8.71
Q-85	0	722	19.55	66.64	9.41
	6 mM	682	15.74	68.08	7.31
	20 mM	696	11.40	69.00	5.48
Q-93	0	676	19.53	61.83	8.17
	6 mM	638	15.83	72.67	7.35
	20 mM	668	12.83	69.20	5.93

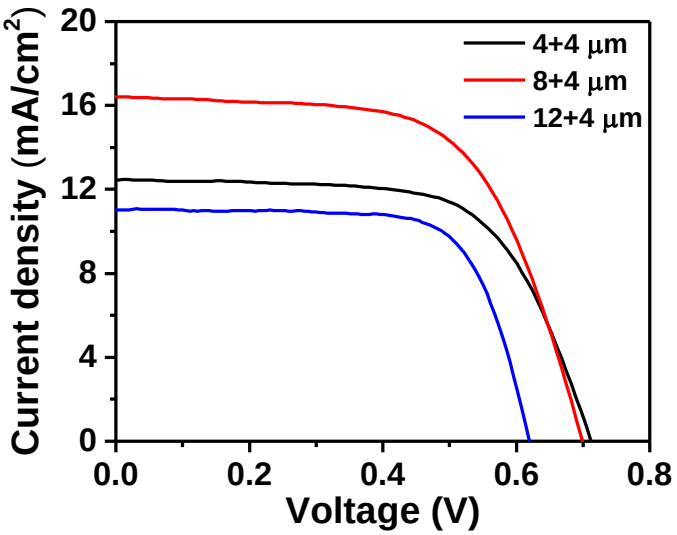


Fig. S4 *J-V* curves for **B-87** based DSSCs with different thickness of the photoelectrode by using ionic liquid electrolyte under illumination of AM 1.5 G simulated sunlight (100 mW cm^{-2}).

4. Characterization of compounds **B-87**, **Q-85** and **Q-93**

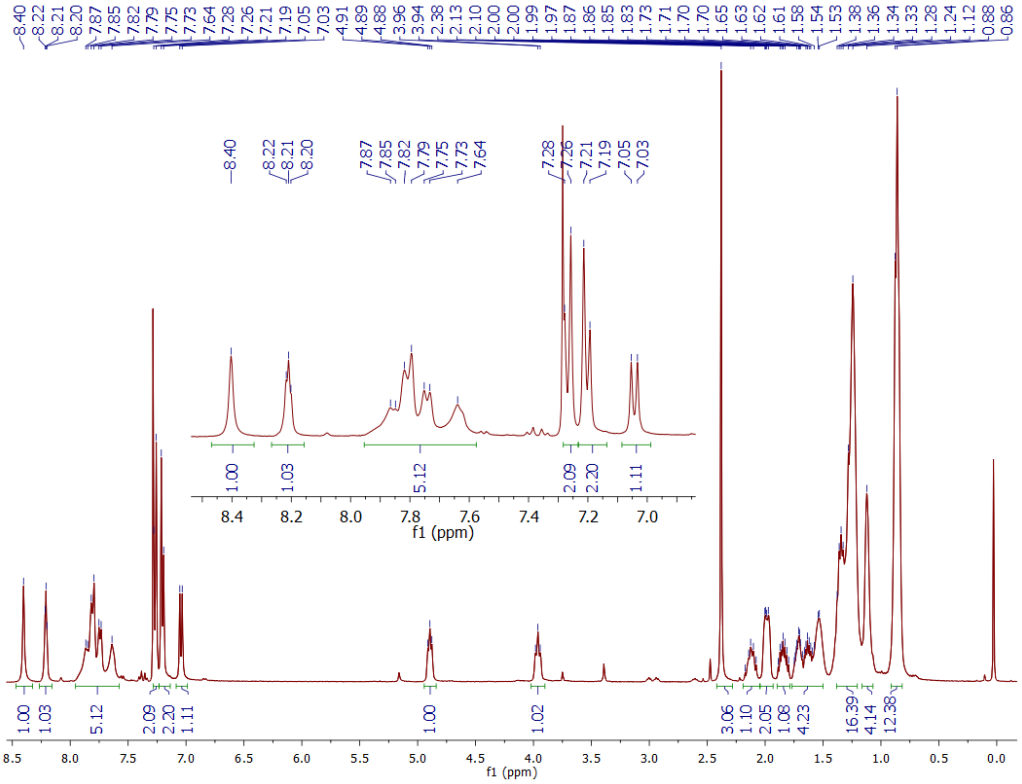


Fig. S5 ^{1}H NMR spectrum of compound **B-87** in $CDCl_3$

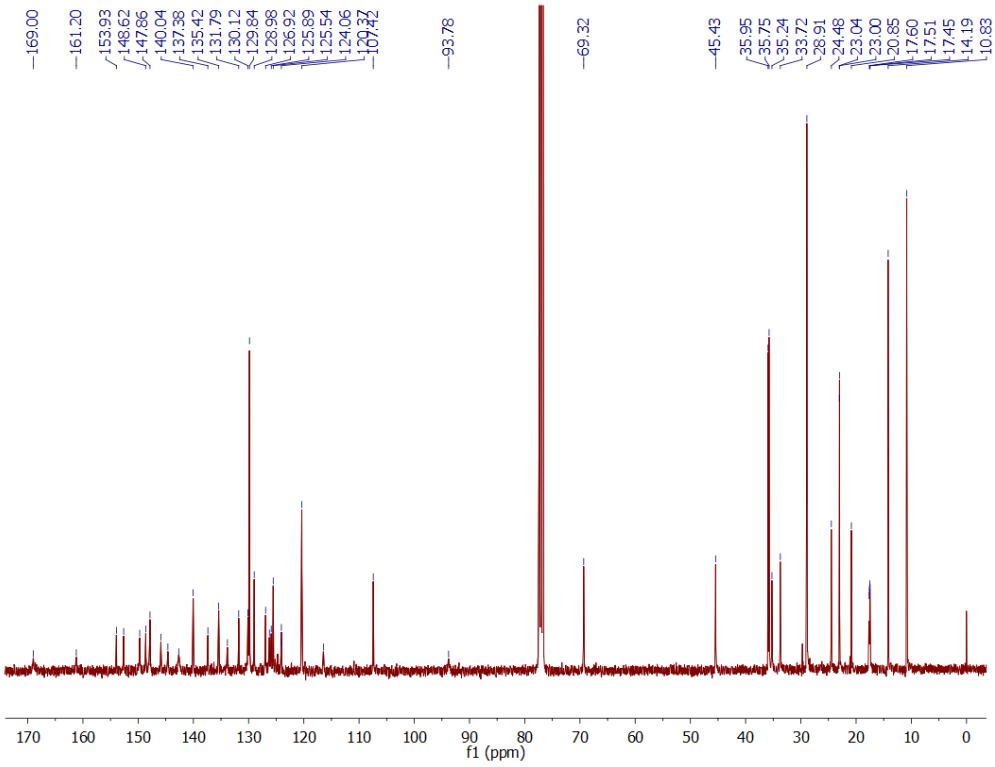


Fig. S6 ^{13}C NMR spectrum of compound **B-87** in $CDCl_3$

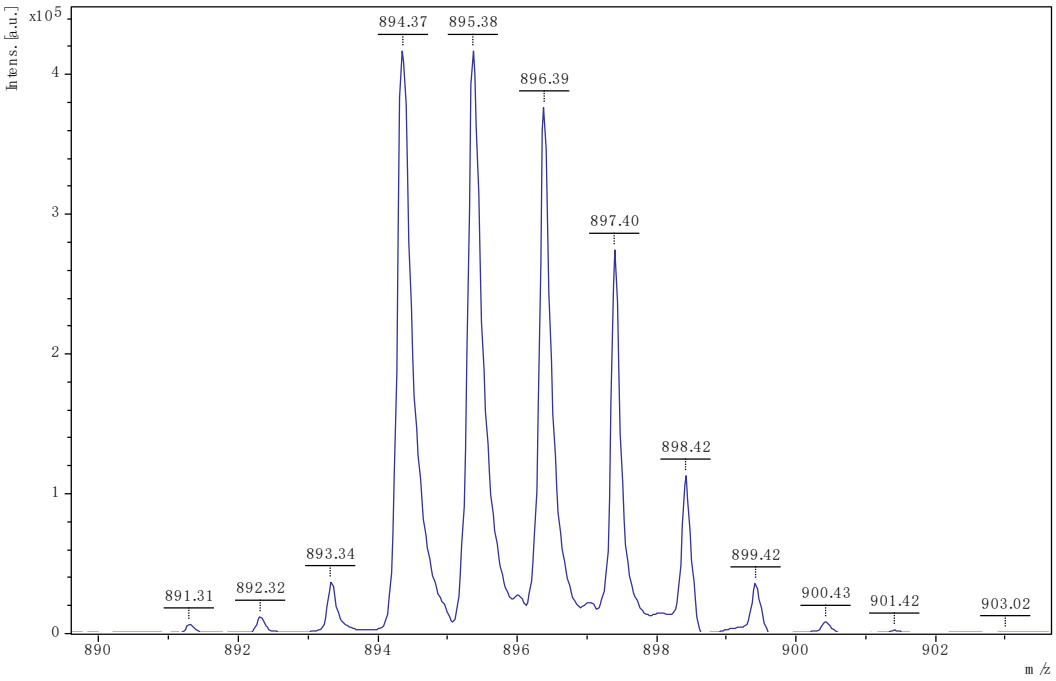


Fig. S7 MALDI-TOF spectrum of compound **B-87**

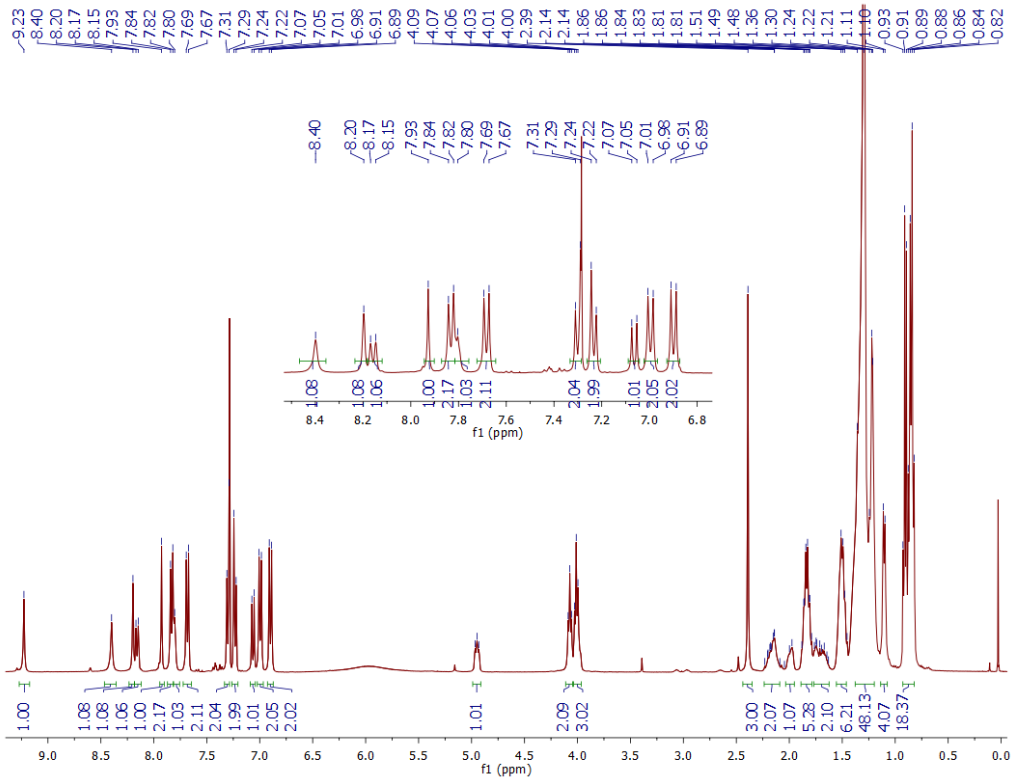


Fig. S8 ^{1}H NMR spectrum of compound **Q-85** in $CDCl_3$

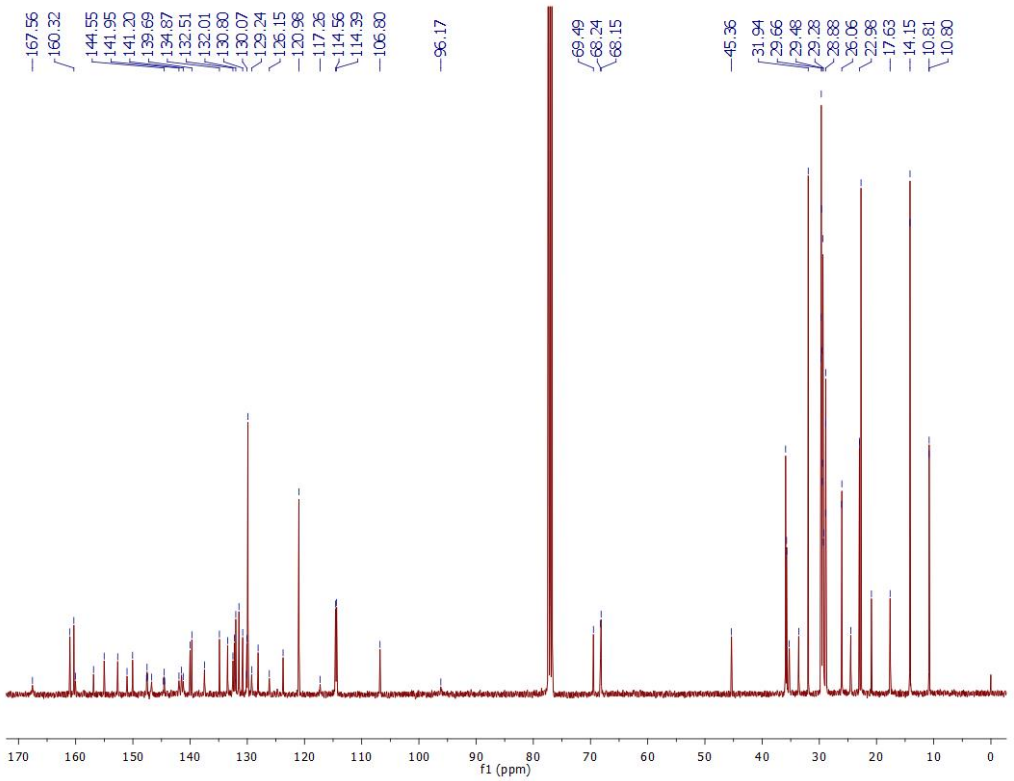


Fig. S9 ^{13}C NMR spectrum of compound **Q-85** in $CDCl_3$

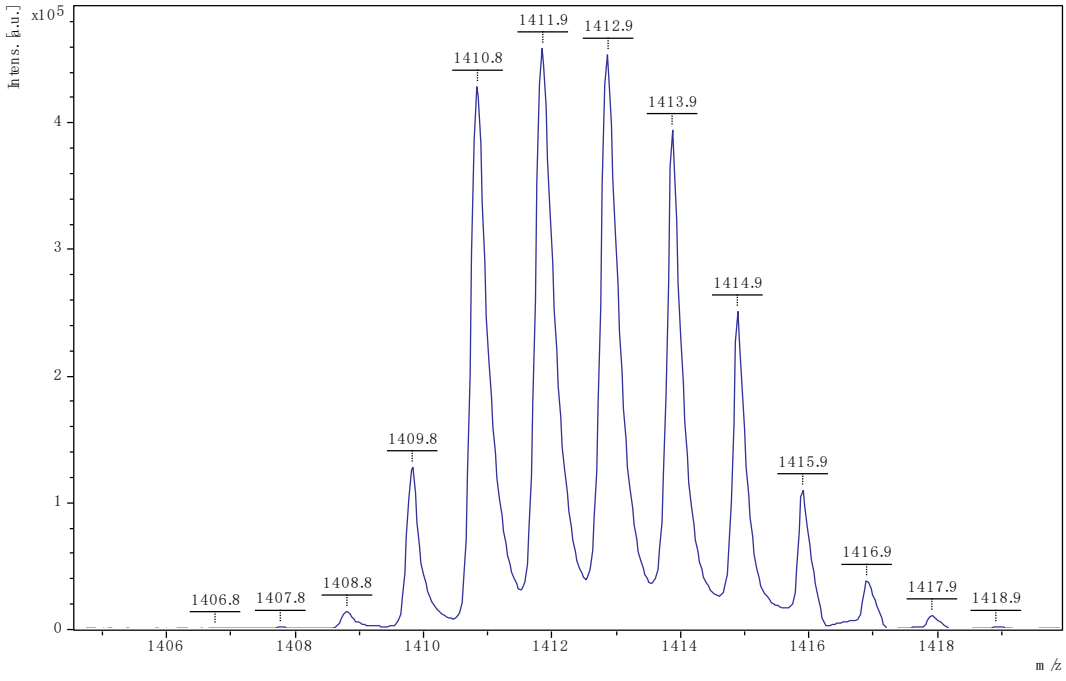


Fig. S10 MALDI-TOF spectrum of compound **Q-85**

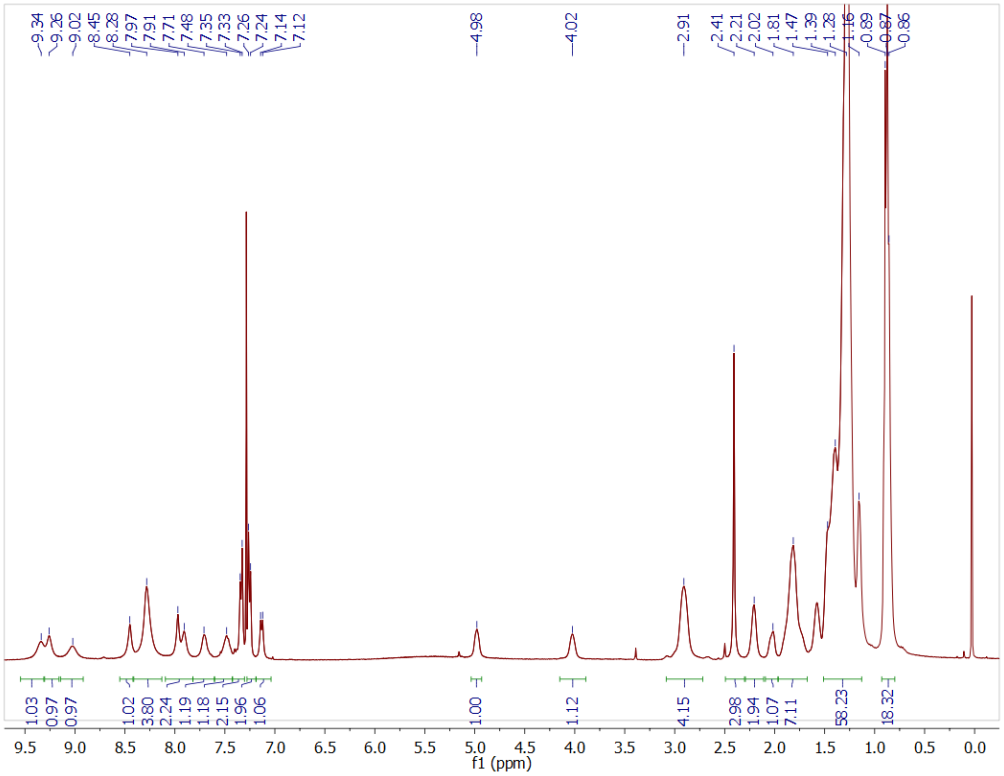


Fig. S11 MALDI-TOF spectrum of compound **Q-93**

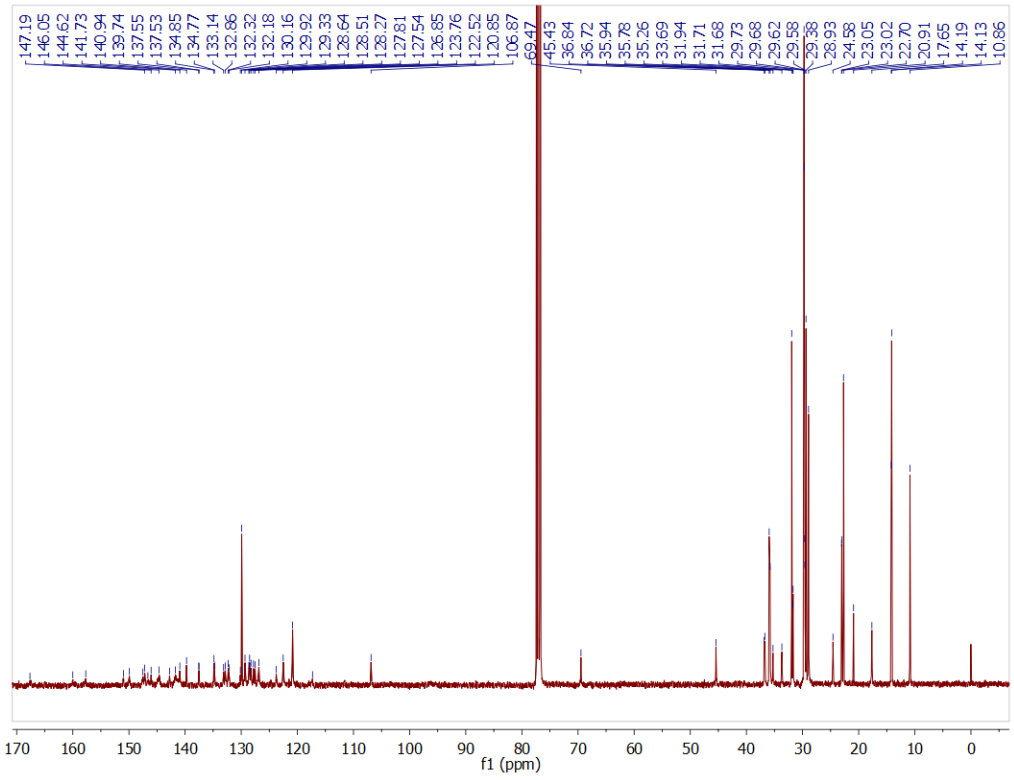


Fig. S12 ^{13}C NMR spectrum of compound **Q-93** in $CDCl_3$

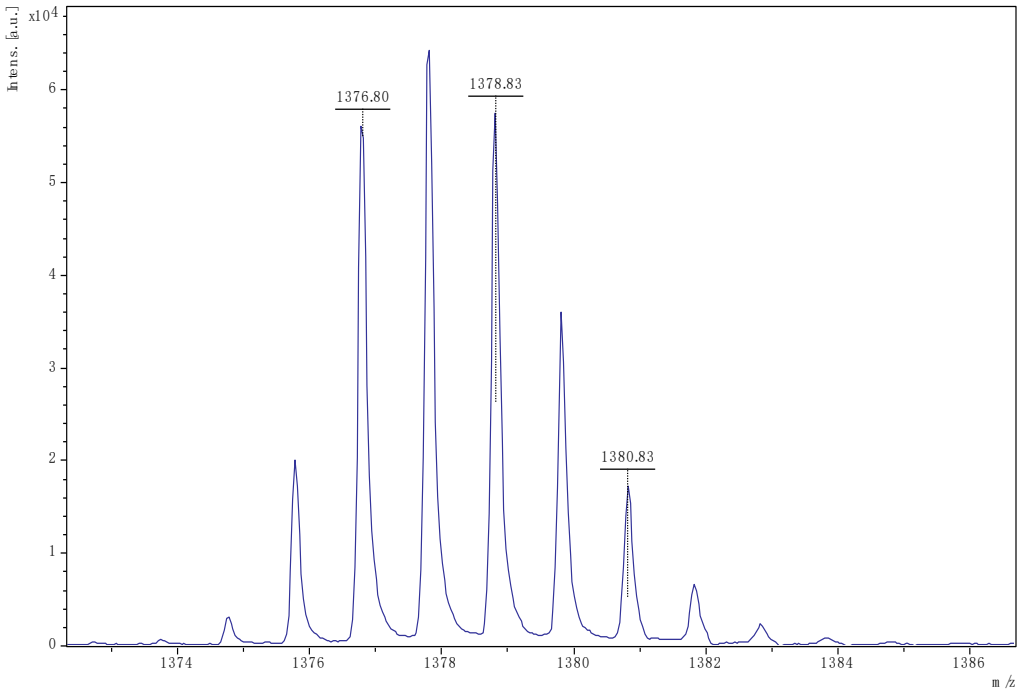


Fig. S13 MALDI-TOF spectrum of compound **Q-93**

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