Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Quantitive and Highly Selective Sensing of Sodium Houttuyfonate via Long-aliphatic chains Hydrophobic Assemble and Aggregation-Induced Emission

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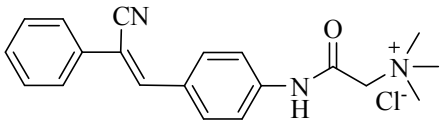
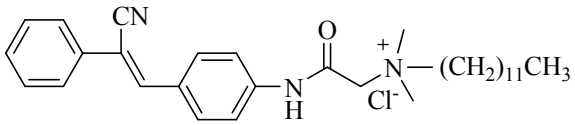
S1. The structure of the quaternary ammonium salts of cyano-distyrylbenzene derivatives **CDB 1-5** and **CDB-DMA12**



CDB-1



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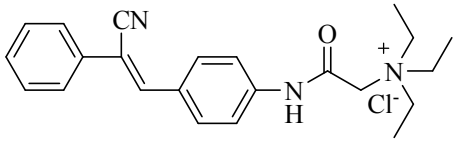

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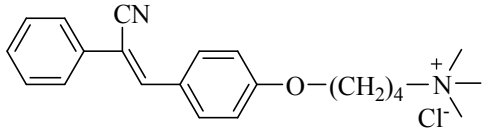
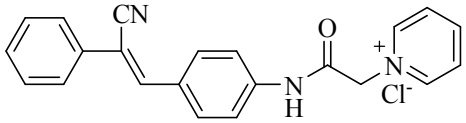
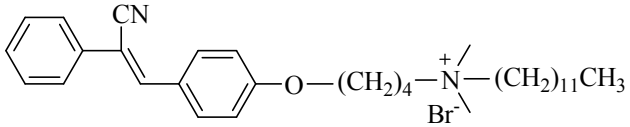


CDB-5

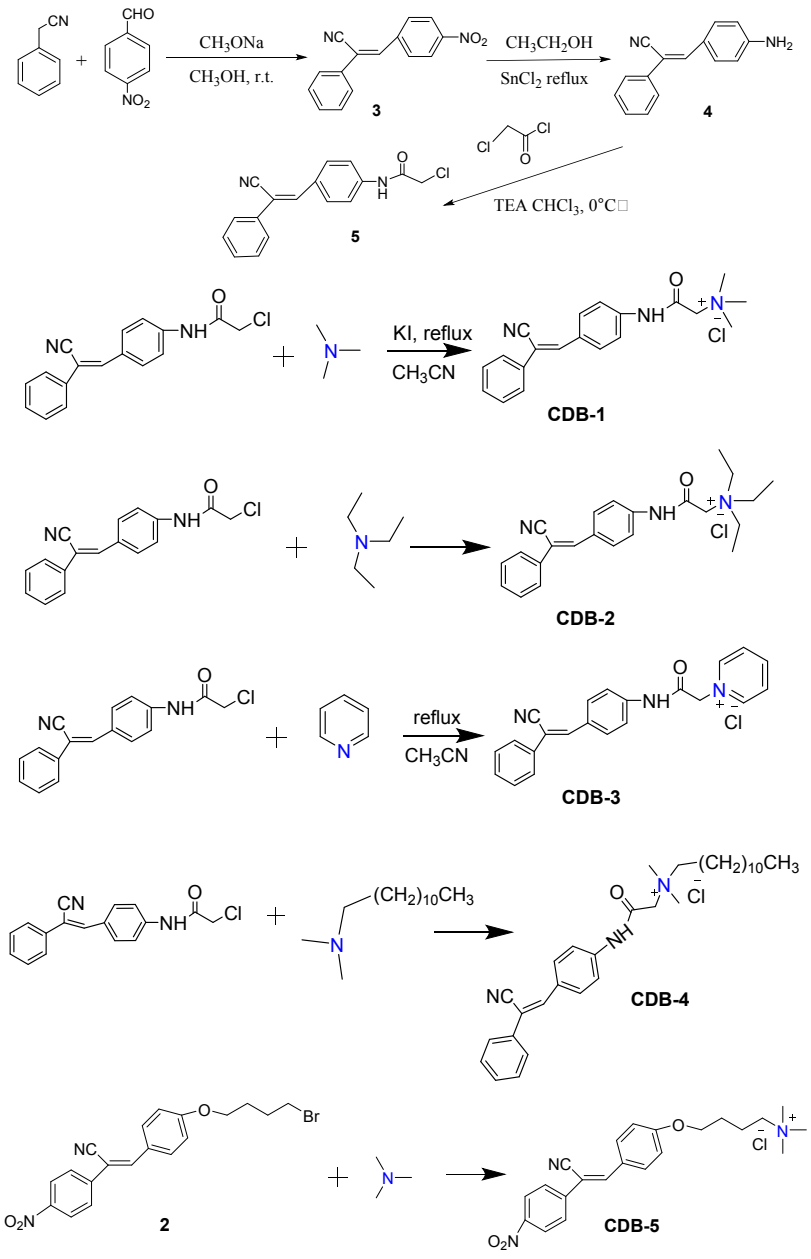


CDB-3



CDB-DMA12

S2. The synthetic routes and the synthetic details of the quaternary ammonium salts of cyano-distyrylbenzene derivatives CDB1-5.



Compound **3**、**4**、**5** were synthesize according to the reported procedure (Y. S. Zheng, Y. J. Hu, D. M. Li, Y. C. Chen, Enantiomer analysis of chiral carboxylic acids by AIE molecules bearing optically pure aminol groups. *Talanta,* 2010, **80**(3), 1470-1474.).

The synthetic details of the quaternary ammonium salts of cyano-distyrylbenzene derivatives **CDB1-5** were described below:

S2-1 Synthesis of CDB-1

To a three-necked flask, compound **5** (2 g, 6.75 mmol), trimethylamine in alcohol (1.6 mL, 6.75 mmol) and acetonitrile (30mL) were added under stirred. KI was added as catalytic. Then, the mixture was refluxed for about 3h until one of the reactants disappeared (monitored by TLC; ethyl acetate : methanol = 4:1). The reaction mixture was cooled to iced temperature and a resultant yellow precipitate was collected by filtering. The residue was washed with acetone to give a yellow powder (2.16 g, 83%). IR (KBr, cm^{-1}) υ：3305, 3279, 3184, 3106, 3050, 2954, 2223, 1690, 1601, 1536, 840, 820, 756, 712; ^1H NMR (400MHz, D_2O): δ 8.37 (s, 1H, -NH), 7.94~7.92 (d, *J* =8.4 Hz, 2H), 7.71~7.67 (t, *J*=7.6Hz,4H), 7.40~7.50 (m, 4H), 4.36 (s, 2H), 3.41 (s, 9H); MS (MALDI-TOF): calcd. for $C_{20}H_{22}N_3O^+$ (m/z): 320.18; found: 320.09.

S2-2 Synthesis of CDB-2

To a three-necked flask, compound **5** (2 g, 6.75 mmol) and acetonitrile (30mL), triethylamine (1.0 mL, 6.75 mmol) were added under stirred. KI was added as catalytic. Then, the mixture was refluxed for about 4h until one of the reactants disappeared (monitored by TLC; eluent : ethyl acetate). The reaction mixture was cooled to iced temperature and a resultant yellow precipitate was collected by filtering. The residue was washed with diethyl ether to give a yellow powder (1.74 g, 70%). IR (KBr, cm^{-1}) υ：3305, 3279, 3184, 3106, 3050, 2954, 2223, 1690, 1601, 1536, 840, 820, 756, 712; ^1H NMR (400MHz，CD_3OH): δ 8.37 (s，1H，-NH)，7.94~7.92 (d，*J*=8.4Hz，2H)，7.71~7.67 (t，*J*=7.6Hz，4H)，7.40~7.50 (m, 4H)，4.23 (s，2H)，3.69~3.67 (q，6H)，1.41~1.37（t，*J*=7.2Hz，9H); MS (MALDI-TOF): calcd. for $C_{23}H_{28}N_3O^+$ (m/z): 362.22; found: 362.19.

S2-3 Synthesis of CDB-3

To a three-necked flask, compound **5** (2 g, 6.75 mmol) and acetone (30mL), pyridine (1.3 mL, 6.75 mmol) were added under stirred. KI was added as catalytic. Then, the mixture was refluxed for about 6h until one of the reactants disappeared (monitored by TLC; eluant : ethyl acetate). The reaction mixture was cooled to iced temperature and a resultant yellow precipitate was collected

by filtering. The residue was washed with diethyl ether to give a yellow powder (1.91 g, 75.3%). IR (KBr，cm^{-1}) υ：3305, 3279, 3184, 3106, 3050, 2954, 2223, 1690, 1601, 1536, 840, 820, 756, 712。^{1}H NMR (400MHz，CD_3OH): δ 9.00~8.98 (d，*J*=4，2H)，8.73~8.69（t，*J*=8，1H), 8.21~8.18（t，*J*=8，2H）, 7.94~7.92 (d，*J*=8.4Hz，2H)，7.71~7.67 (t，*J*=7.6Hz，4H)，7.40~7.50 (m, 4H)，5.68 (s，2H); MS (MALDI-TOF): calcd. for $C_{22}H_{18}N_3O^+$ (m/z): 340.14; found: 340.09.

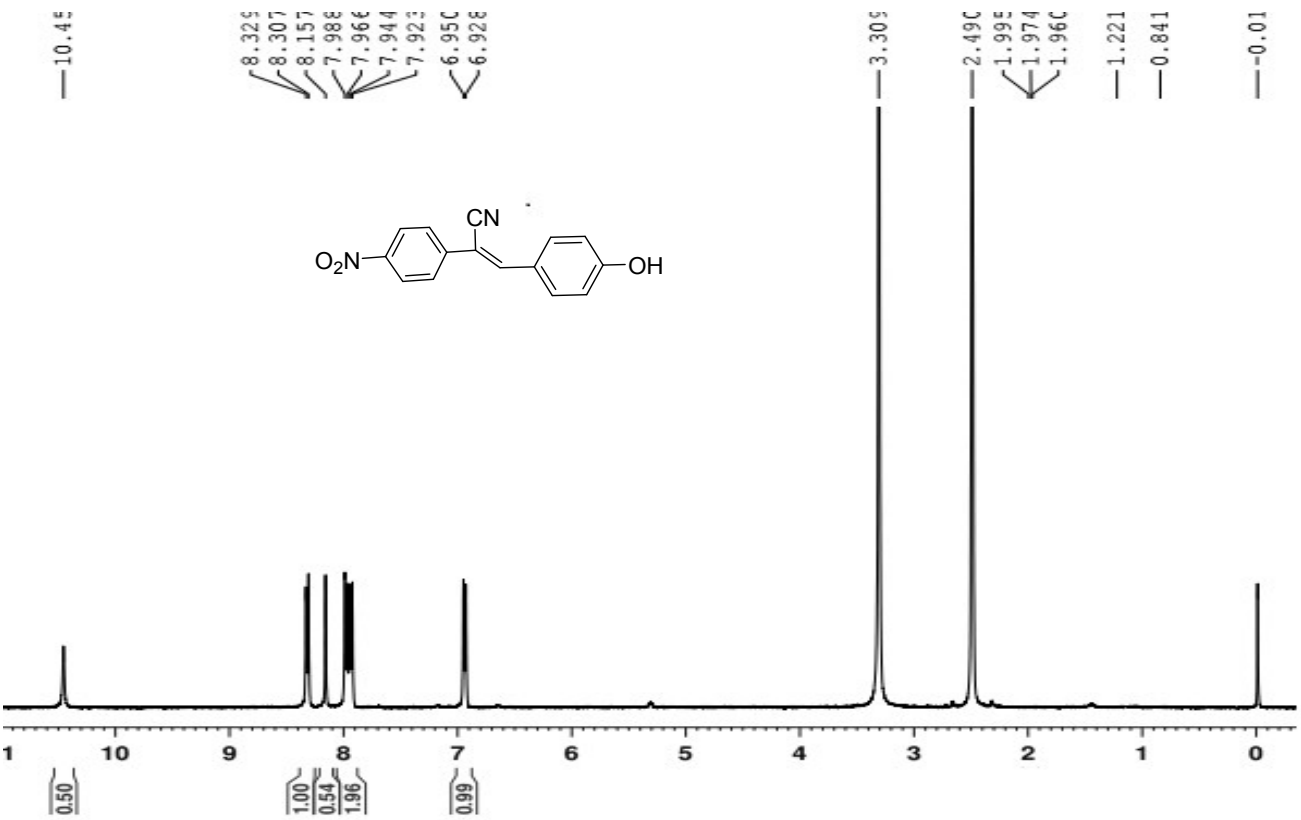
S2-4 Synthesis of CDB-4

To a three-necked flask, compound **5** (2 g, 6.75 mmol) and acetonitrile (30mL), N, N-dimethyldodecylamine (1.8 mL, 6.75 mmol) were added under stirred. KI was added as catalytic. Then, the mixture was refluxed for about 6h until one of the reactants disappeared (monitored by TLC; eluant : ethyl acetate). The reaction mixture was cooled to iced temperature and a resultant yellow precipitate was collected by filtering. The residue was washed with diethyl ether to give a yellow powder (2.73 g, 79.2%). IR (KBr, cm^{-1}) υ：3305, 3279, 3184, 3106, 3050, 2954, 2223, 1690, 1601, 1536, 840, 820, 756, 712; ^{1}H-NMR (400MHz，CD_3OH): δ 7.94~7.92 (d，*J*=8.4Hz，2H)，7.71~7.67 (t, *J*=7.6Hz, 4H), 7.40~7.50 (m, 4H), 4.62 (s, 2H), 4.29（s, 2H）, 3.64~3.60 (m, 2H), 3.36（s, 6H), 1.84（s, 2H), 1.39（s, 4H), 1.25~1.02（t，*J*=7.2，14H), 0.88~0.85（t，*J*=7.2, 3H); MS (MALDI-TOF): calcd. for $C_{31}H_{44}N_3O^+$ (m/z): 474.35; found:474.30.

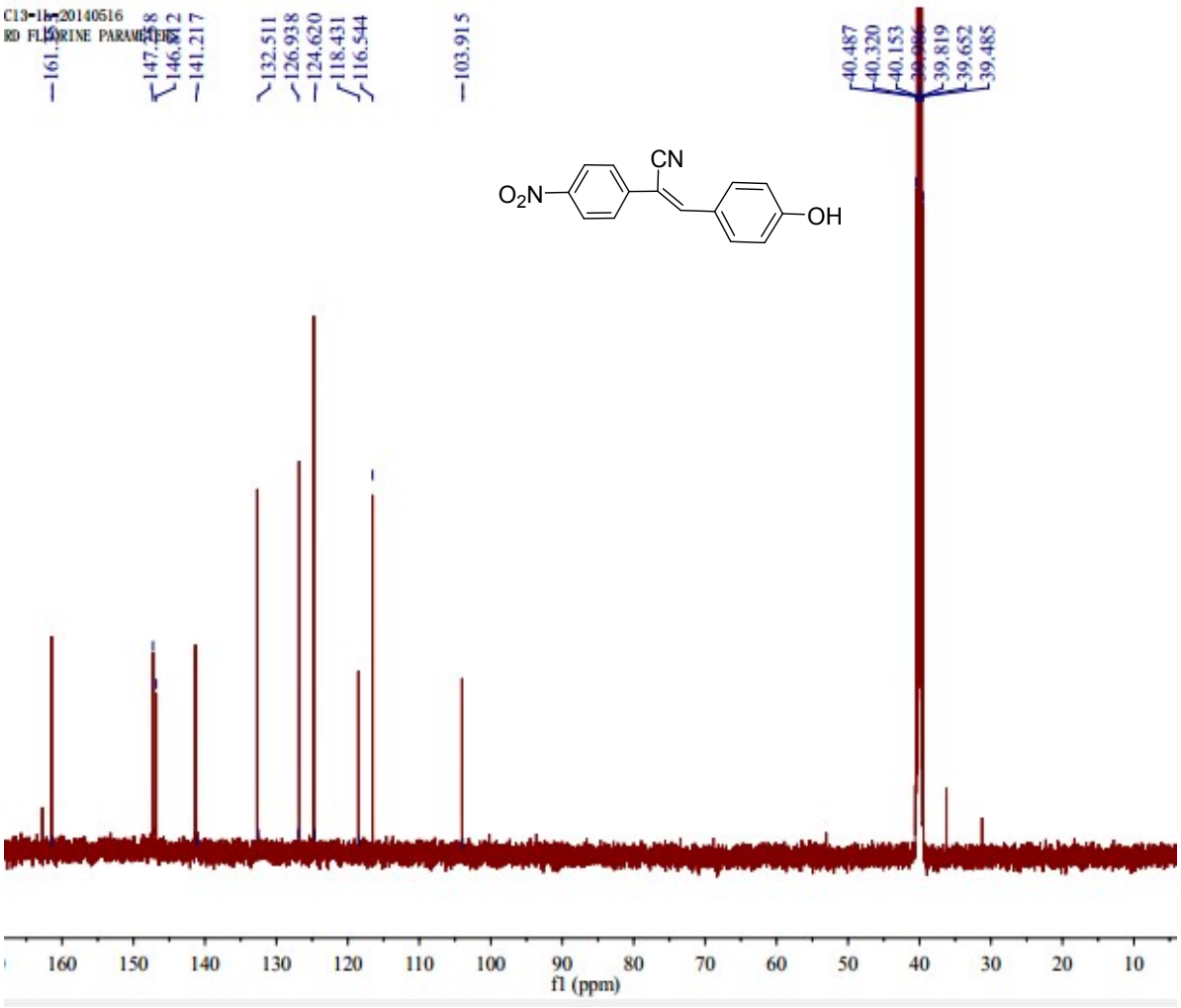
S2-5 Synthesis of CDB-5

To a three-necked flask, compound **2** (2.7 g, 6.75 mmol) and acetonitrile (30mL), trimethylamine in alcohol (1.6 mL, 6.75 mmol) were added under stirred. KI was added as catalytic. Then, the mixture was refluxed for about 6h until one of the reactants disappeared (monitored by TLC; eluant : ethyl acetate : methanol = 4:1). The reaction mixture was cooled to iced temperature and a resultant yellow precipitate was collected by filtering. The residue was washed with diethyl ether to give a yellow powder (2.59 g, 83.4%). IR (KBr, cm^{-1}) *v* 3103, 3069, 2210, 1577, 1509, 1460, 1421, 1372, 1337, 1309 ; ^{1}H NMR (400 MHz , $CDCl_3$) *δ* 8.28 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.63 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.09 (t, *J* = 6.0 Hz, 2H), 3.50 (t, *J* = 6.4 Hz, 2H), 2.11 (m, 2H), 2.00 (m, 2H); MS (MALDI-TOF): calcd. for $C_{22}H_{26}N_3O_3^+$ (m/z): 380.20; found: 380.19.

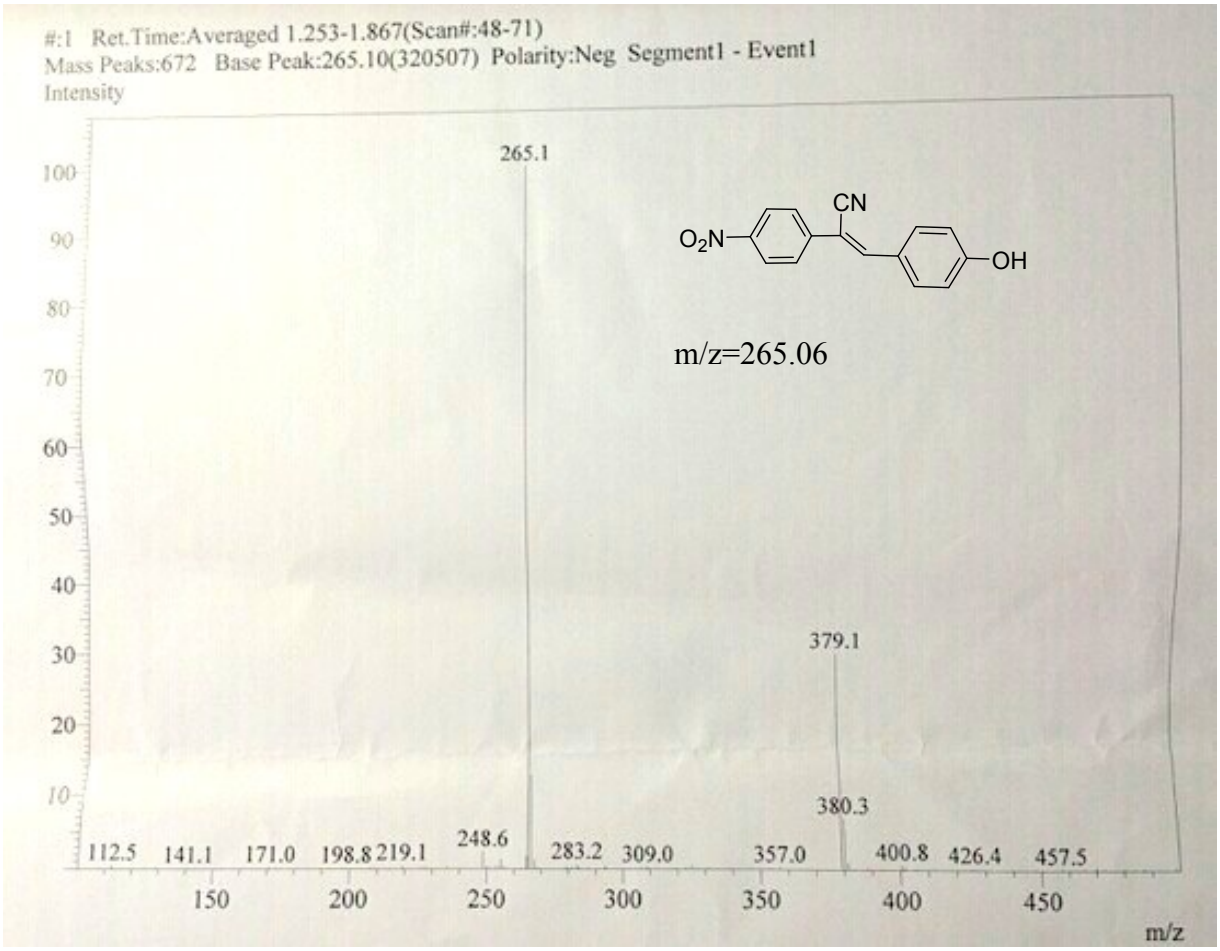
S3. The characterization of products



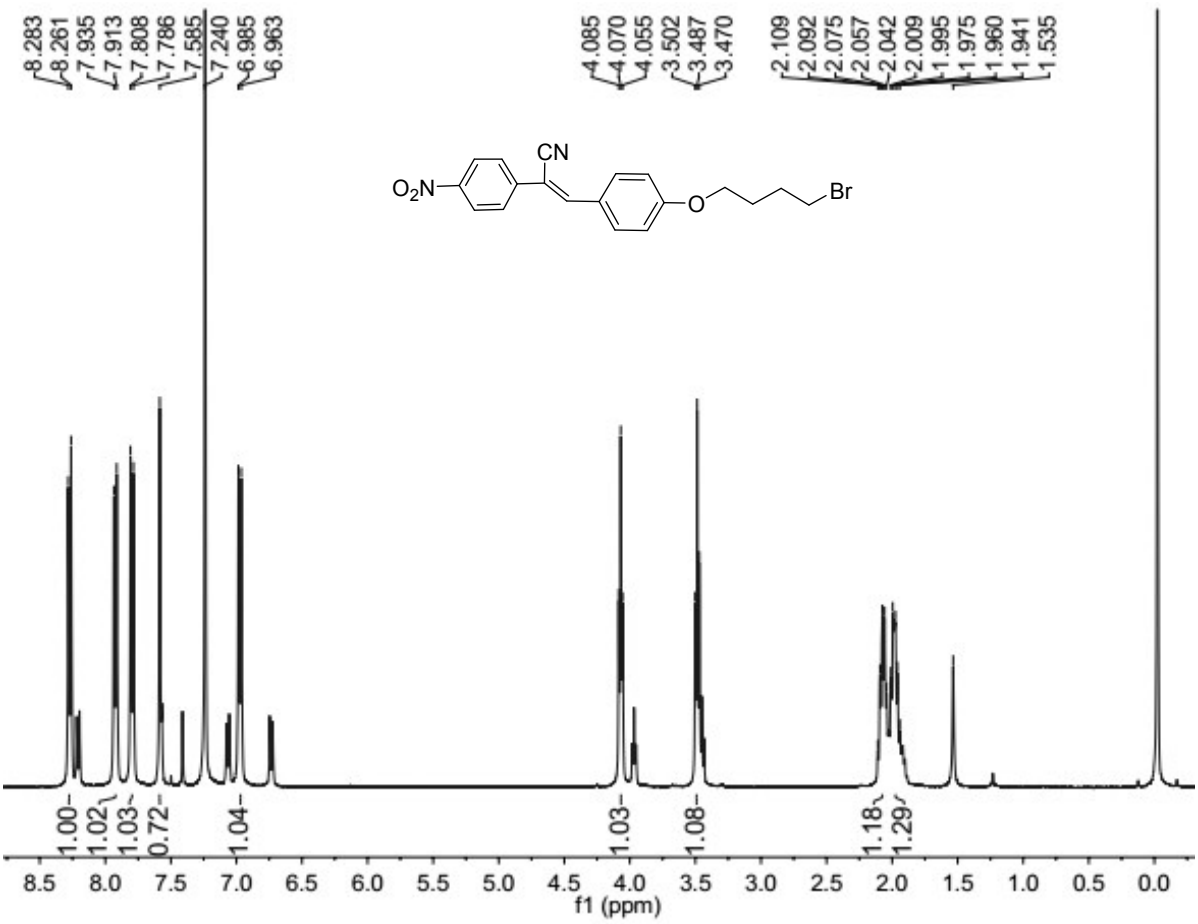
S3-1a The ^{1}H NMR spectrum of intermediate **1**



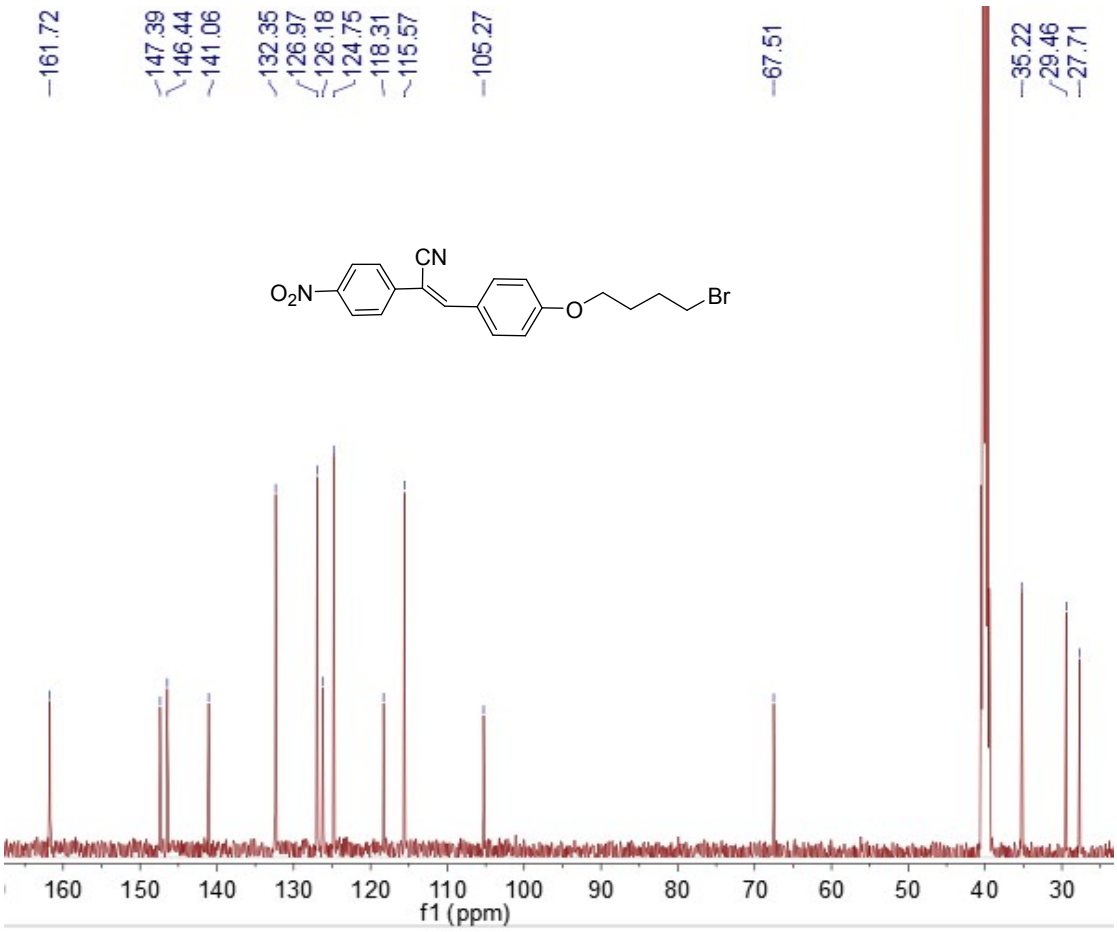
S3-1b The ^{13}C NMR spectrum of intermediate **1**



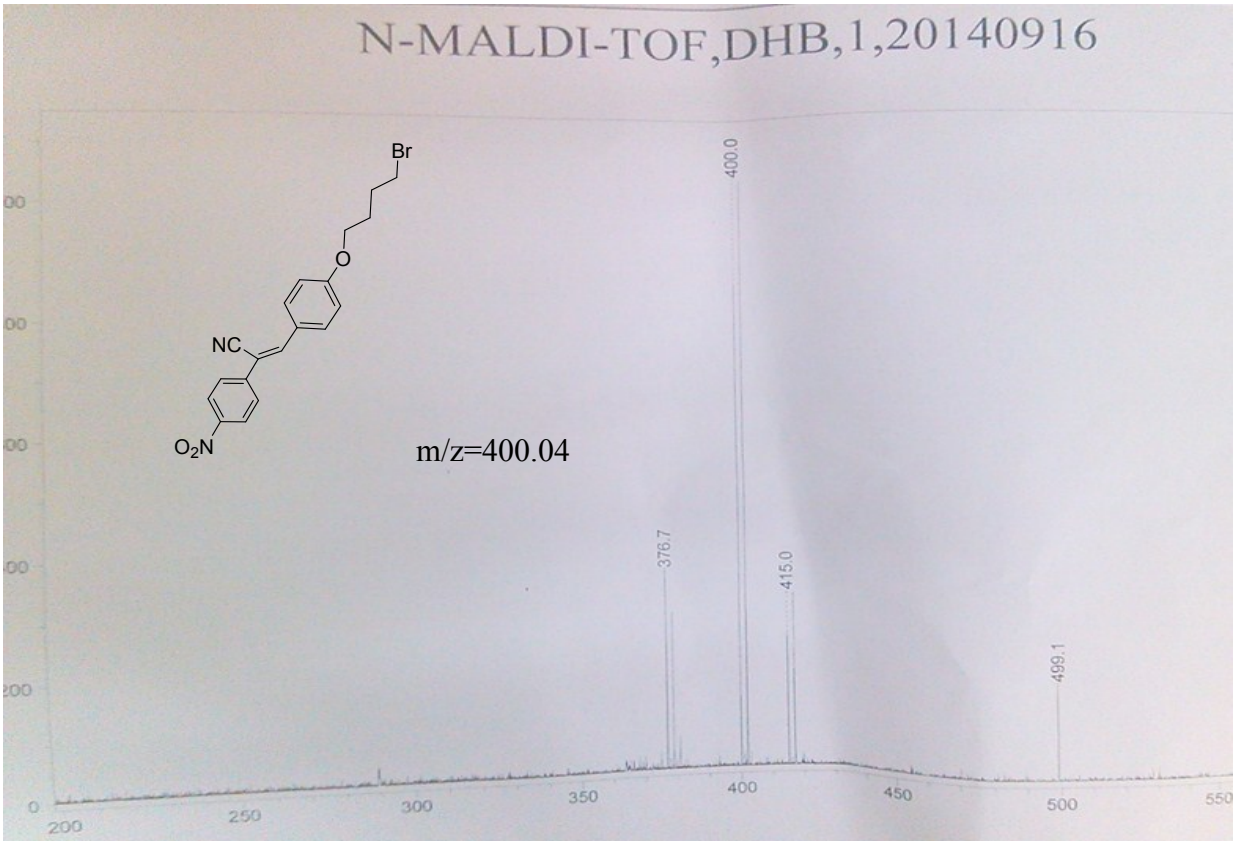
S3-1c The mass spectrum of intermediate **1**



S3-2a The ^{1}H NMR spectrum of intermediate **2**



S3-2b The ^{13}C NMR spectrum of intermediate **2**



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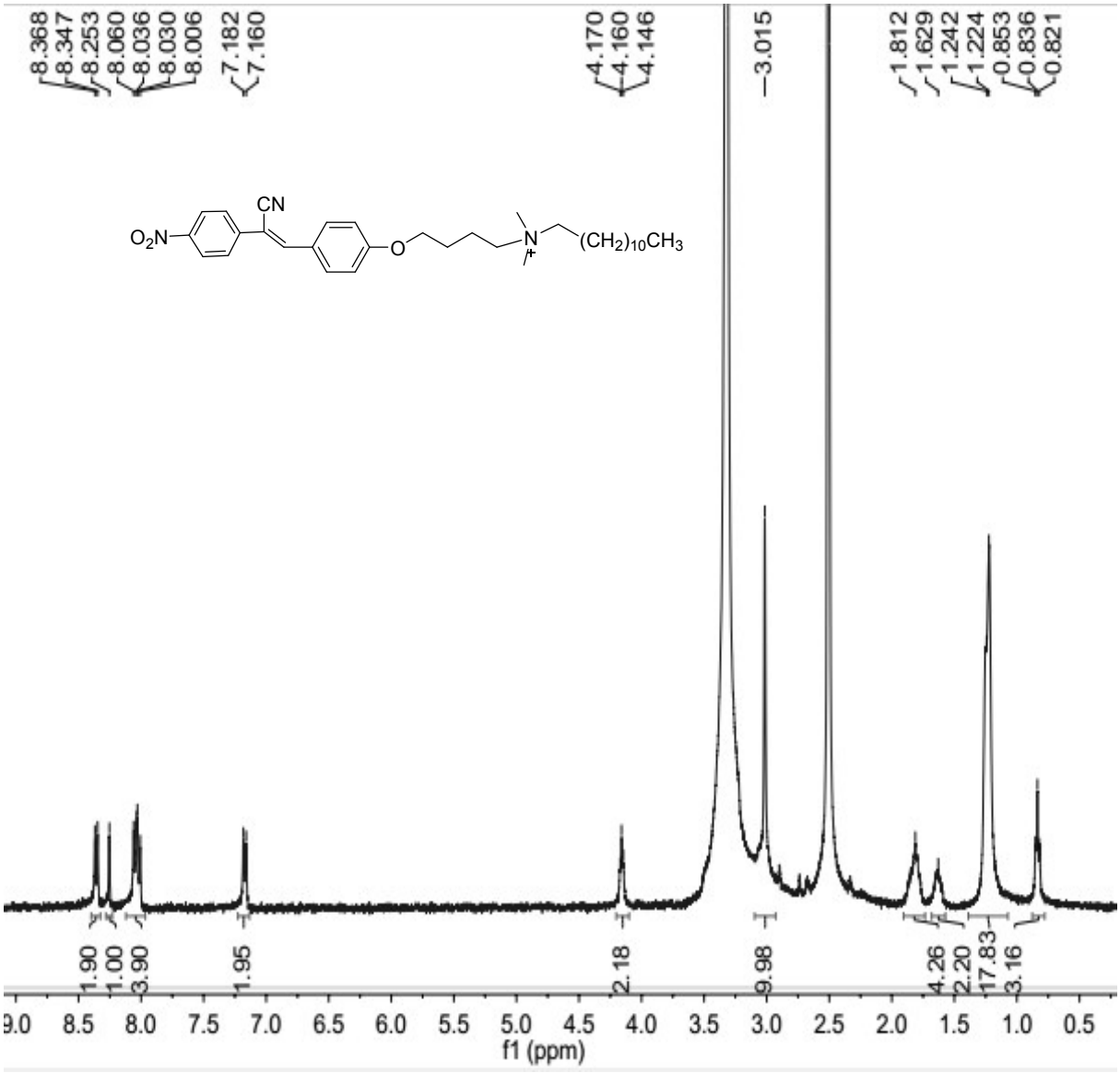
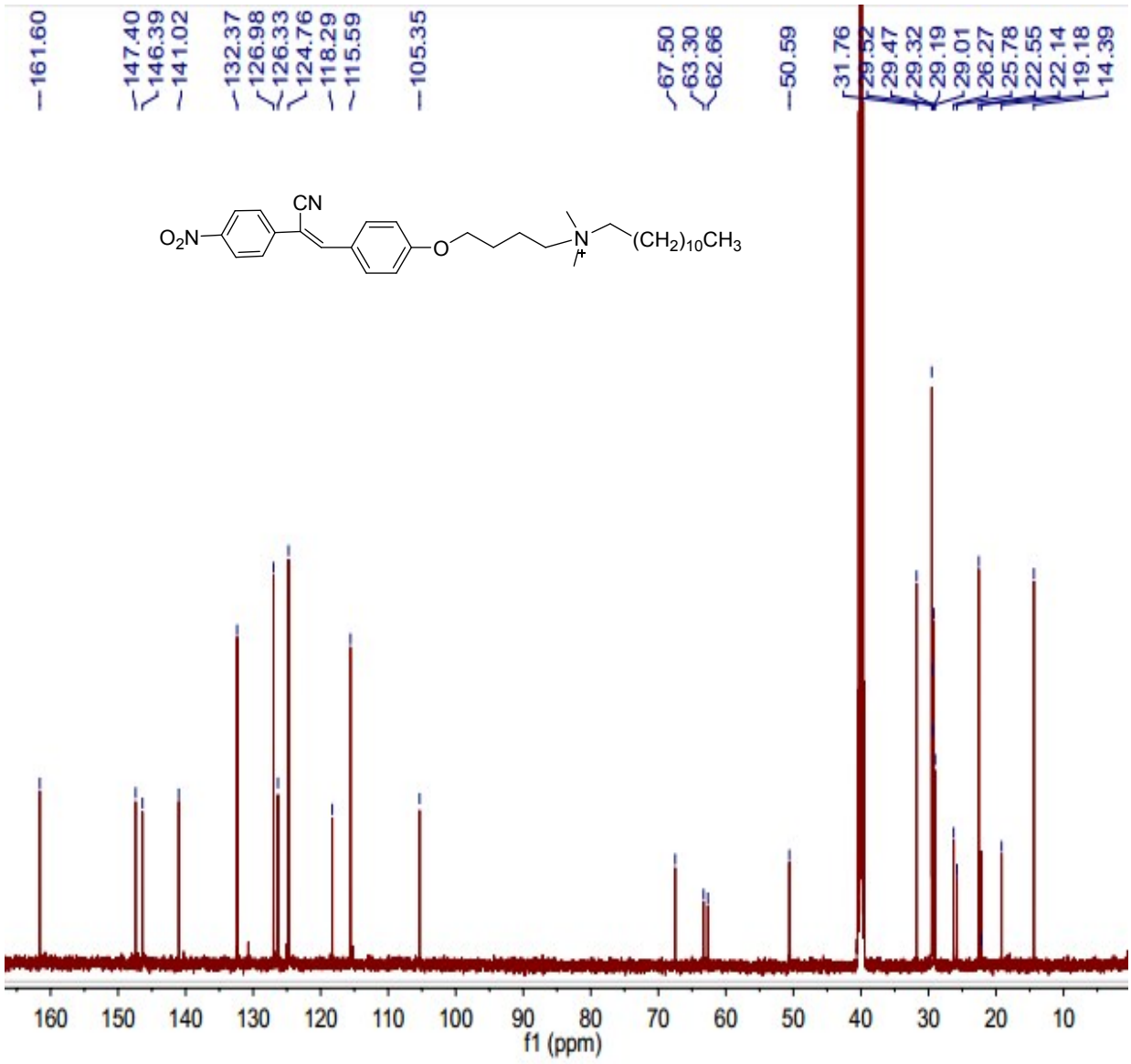
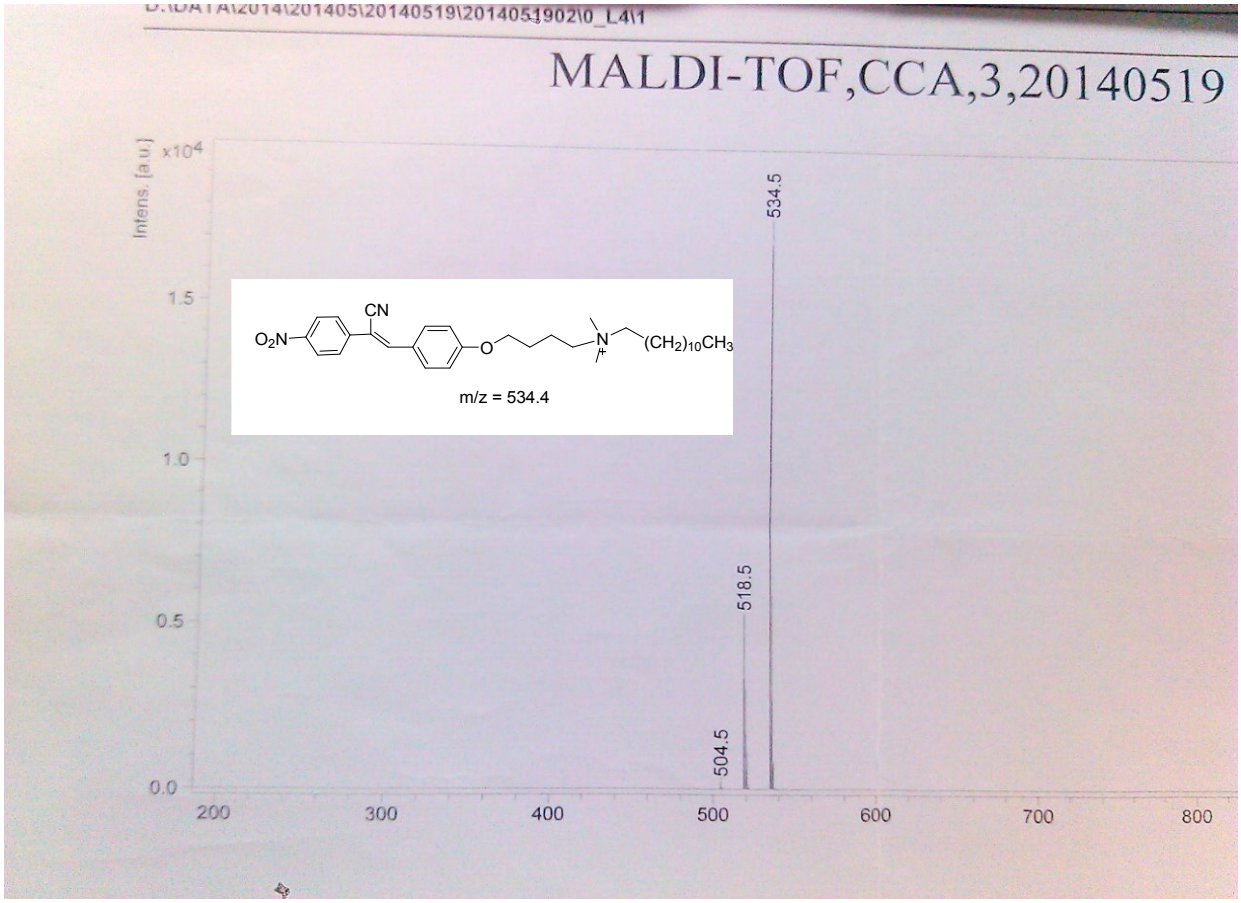


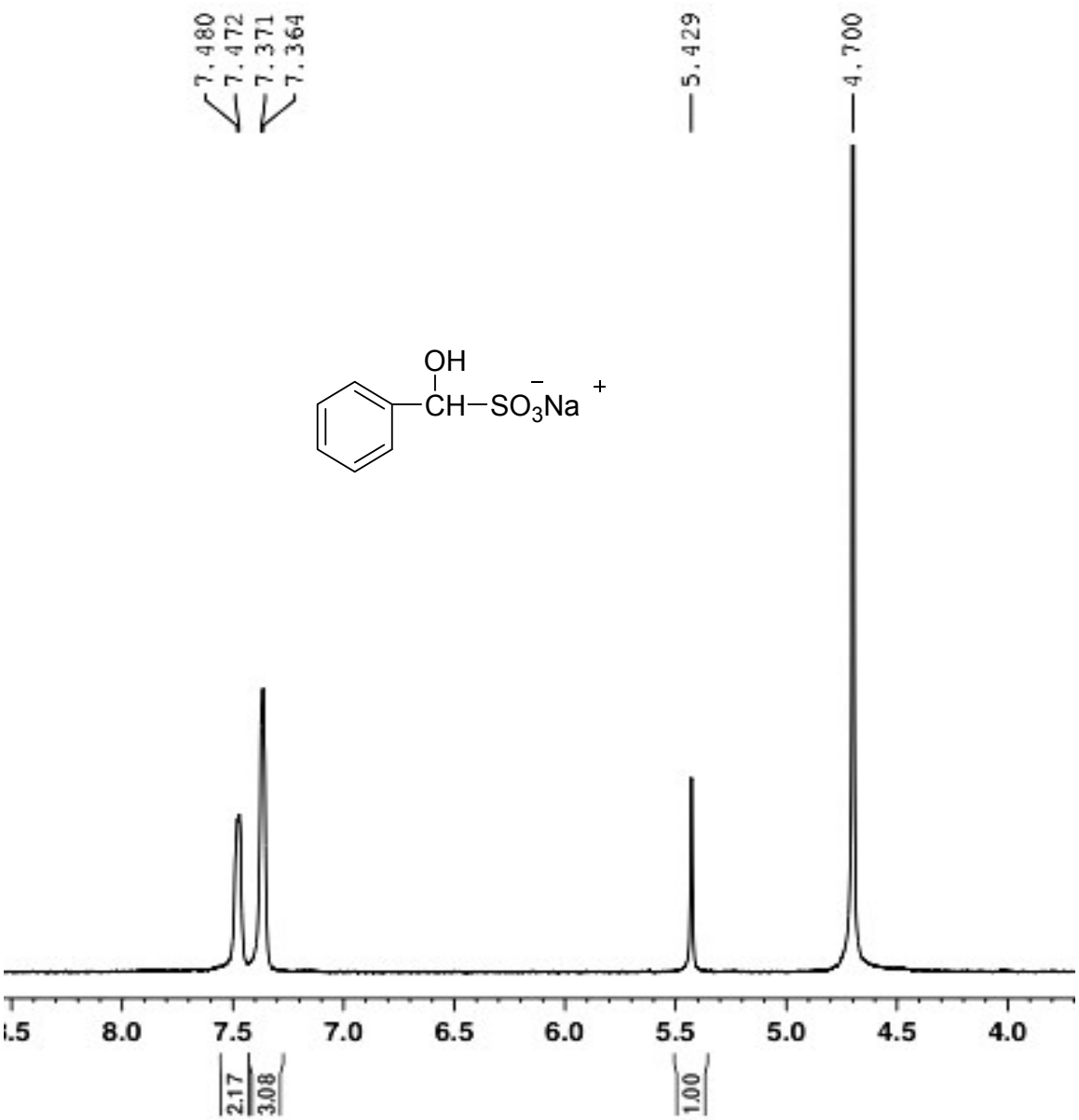
S3-3a The ^{1}H NMR spectrum of **CDB-DMA12**



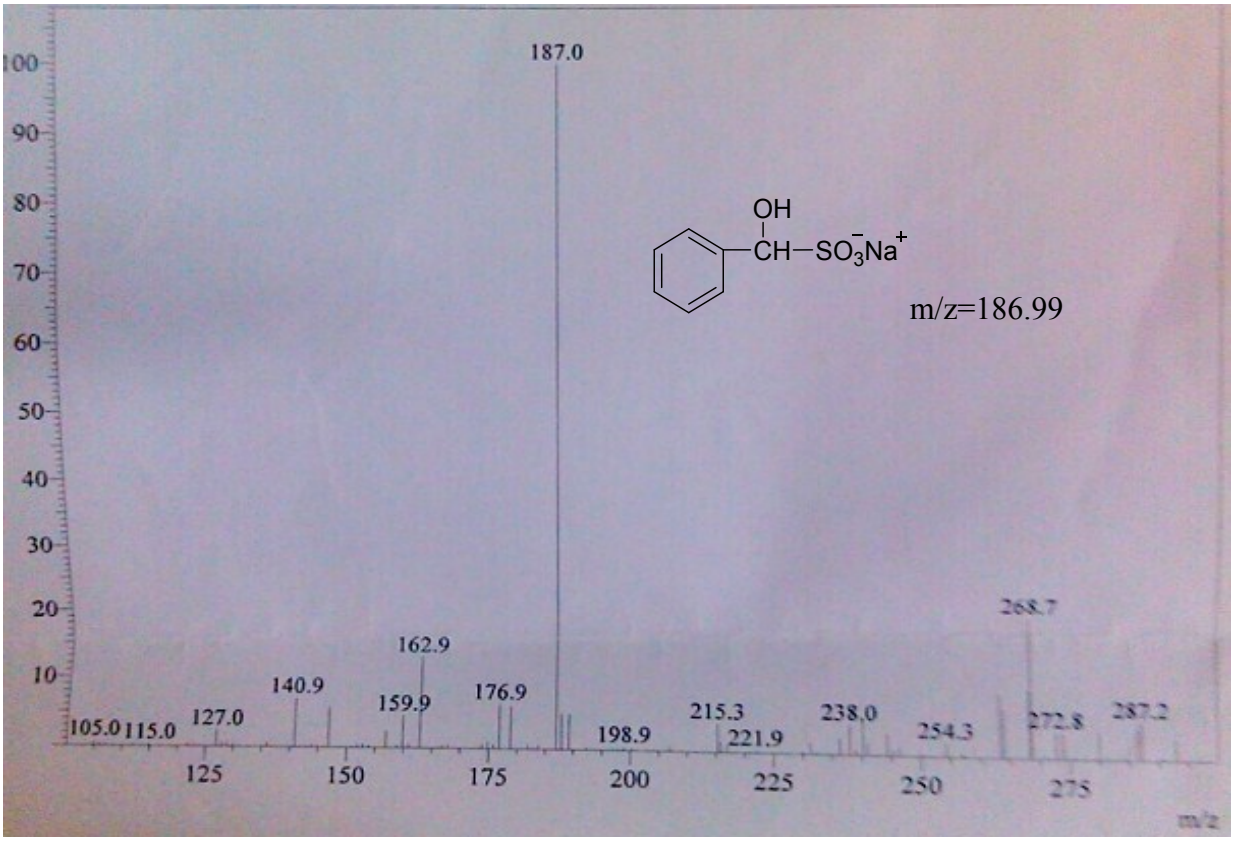
S3-3b The ^{13}C NMR spectrum of **CDB-DMA12**



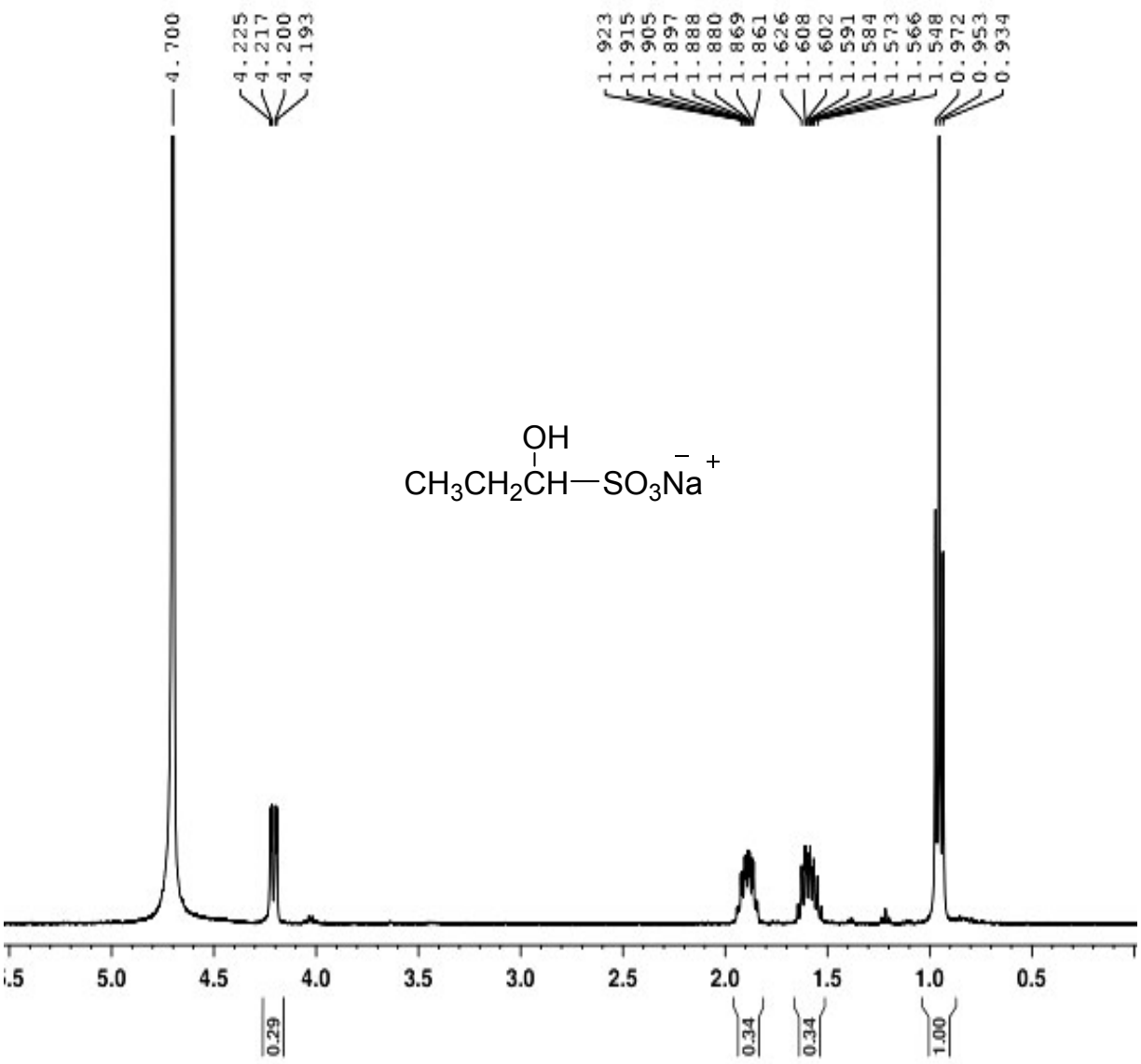
S3-3c The mass spectrum of **CDB-DMA12**



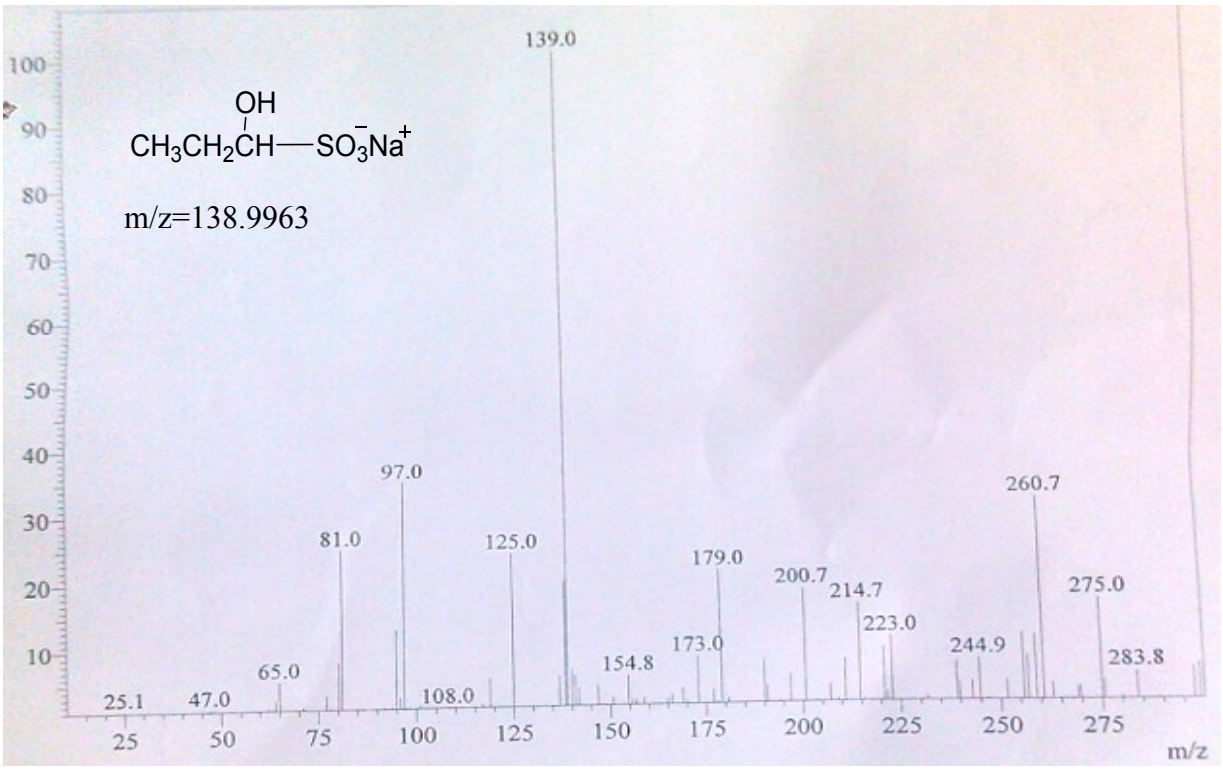
S3-4a The ^{1}H NMR spectrum of **Model 1**



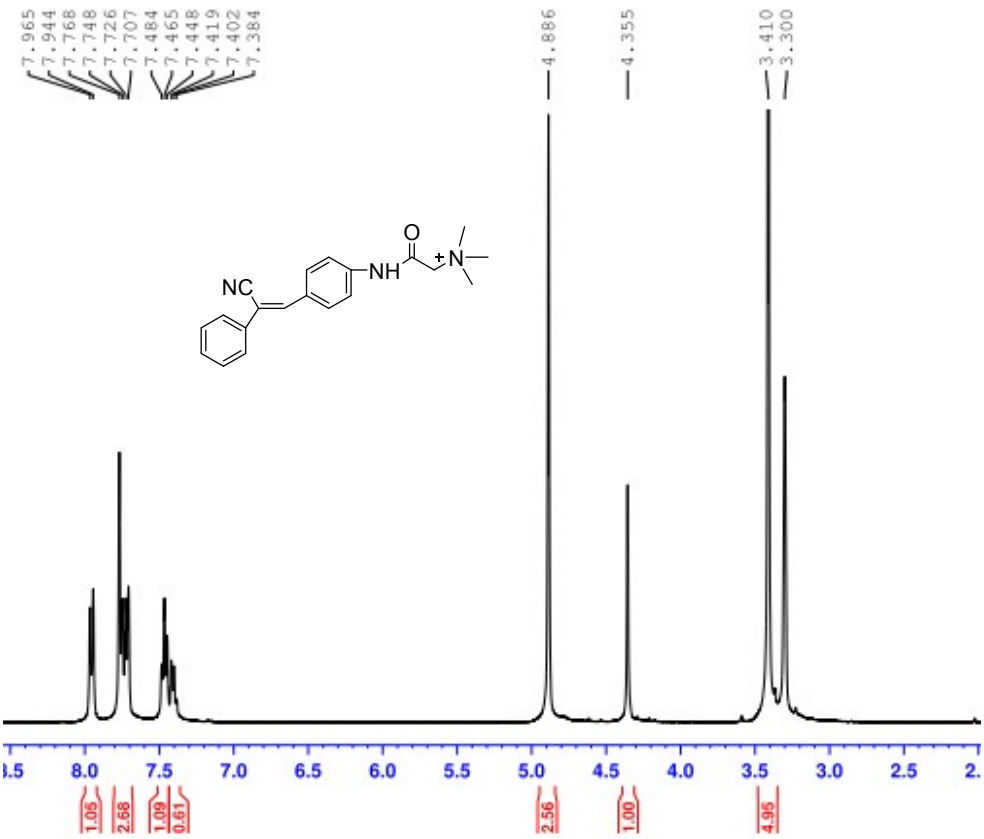
S3-4b The mass spectrum of **Model 1**



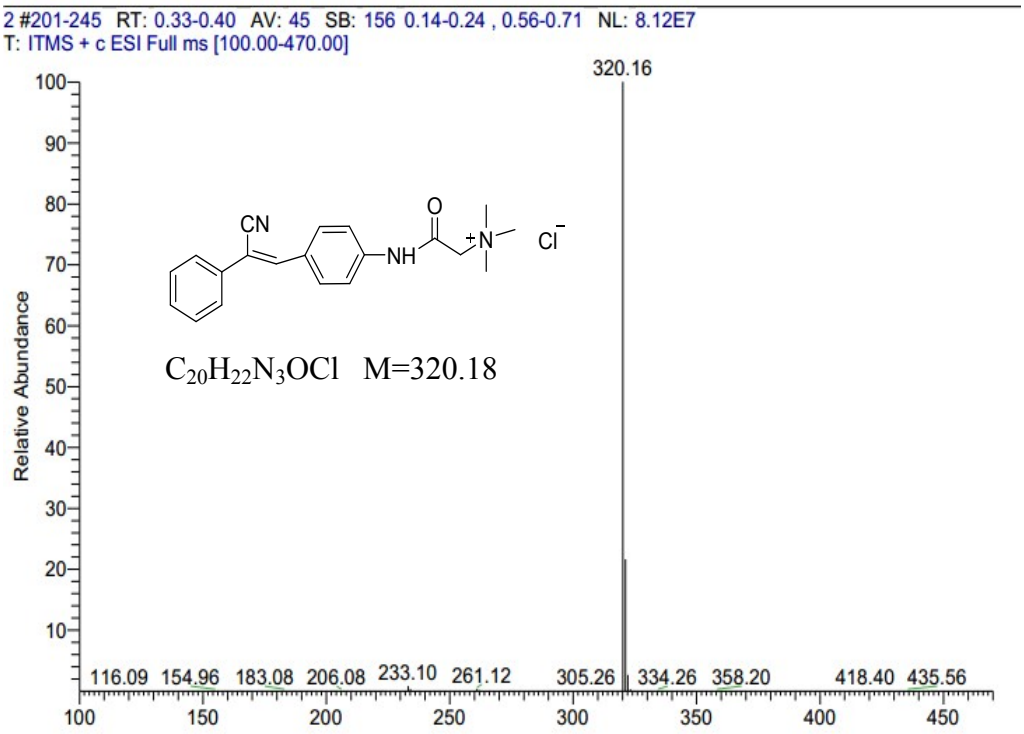
S3-5a The ^{1}H NMR spectrum of **Model 2**



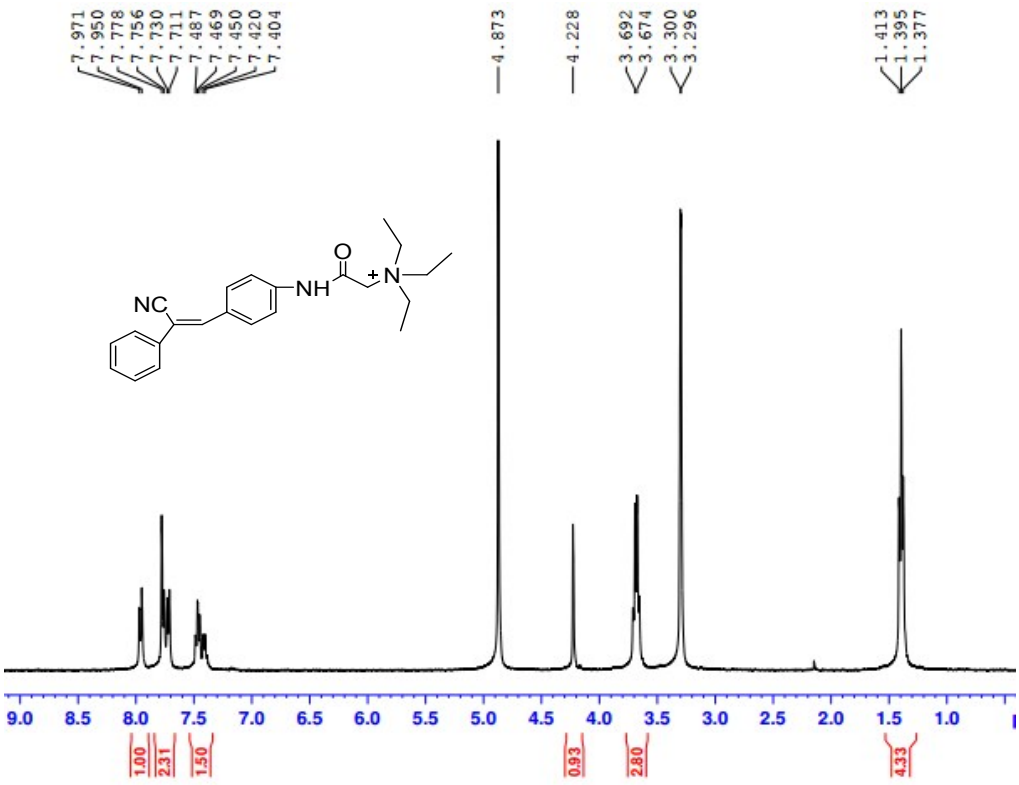
S3-5b The mass spectrum of **Model 2**



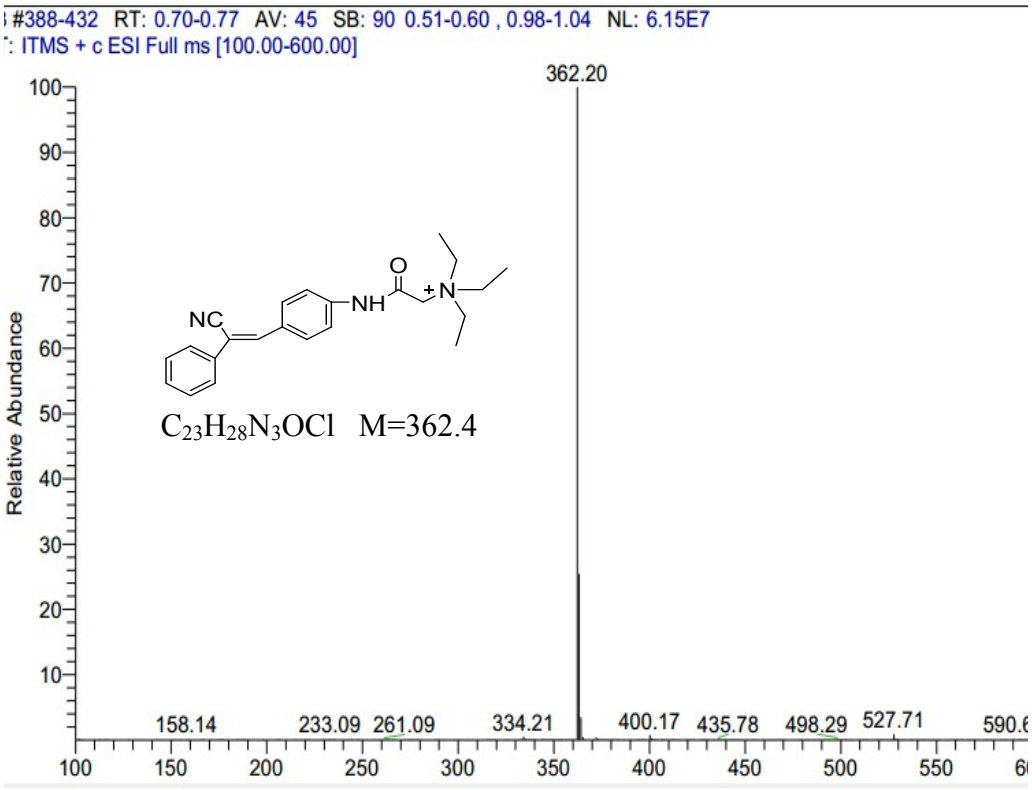
S3-6a The ^{1}H NMR spectrum of **CDB-1**



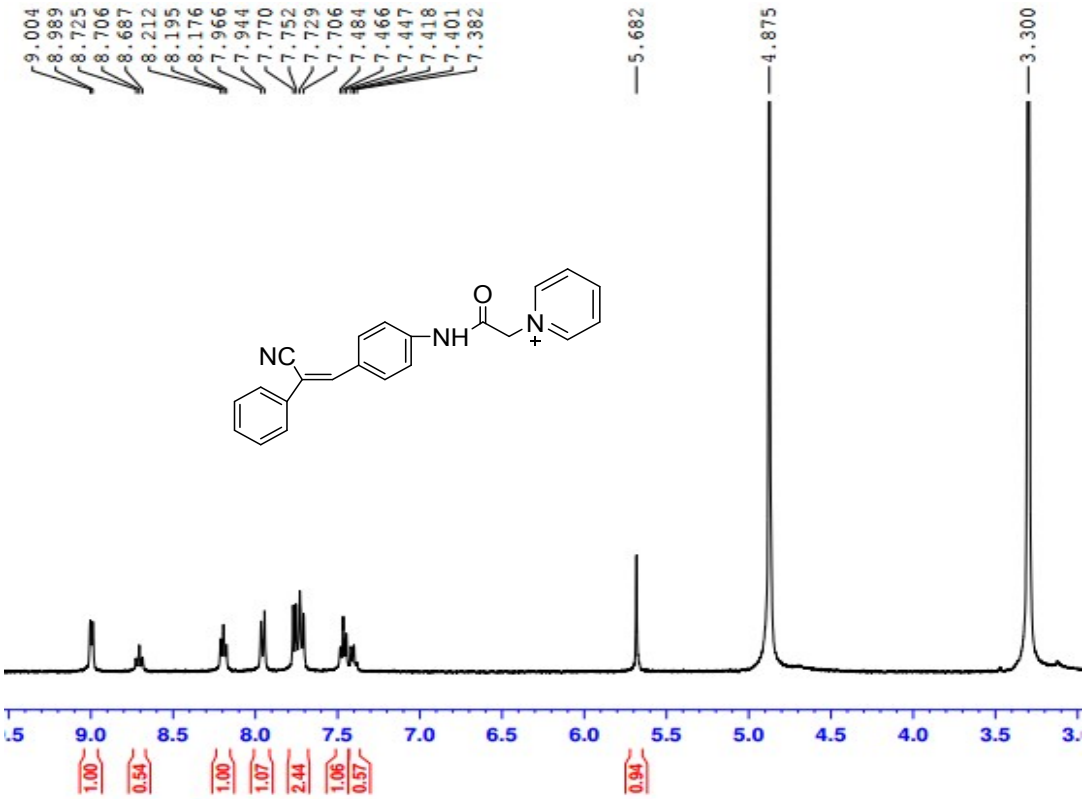
S3-6b The mass spectrum of **CDB-1**



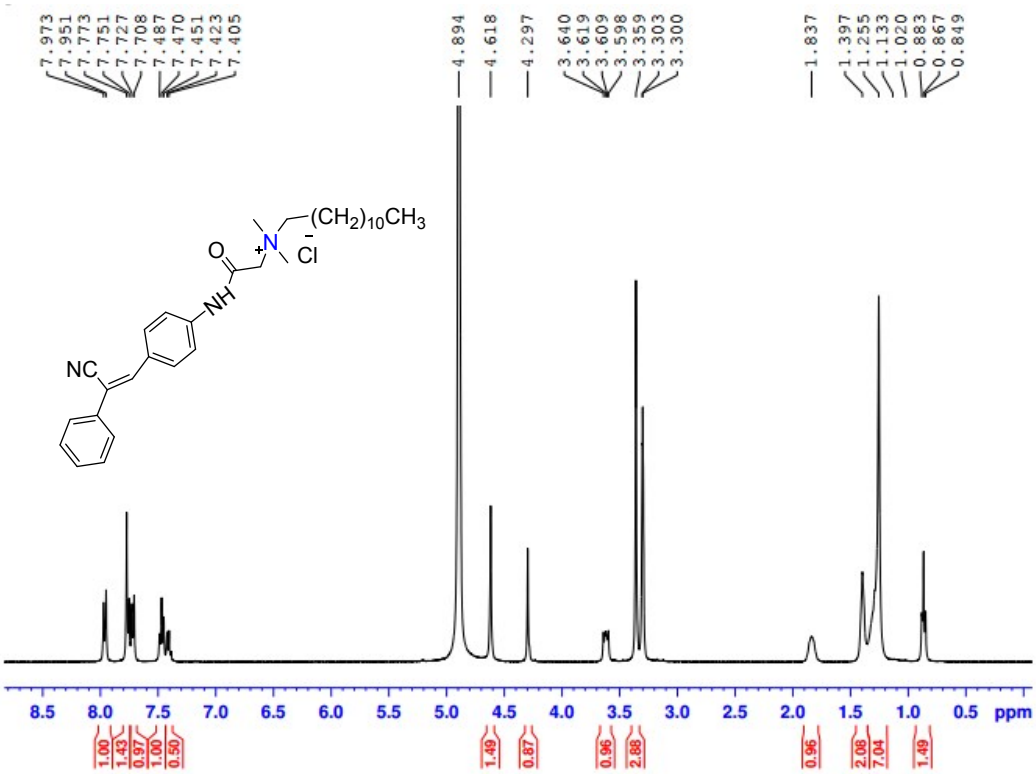
S3-7a The ^{1}H NMR spectrum of **CDB-2**



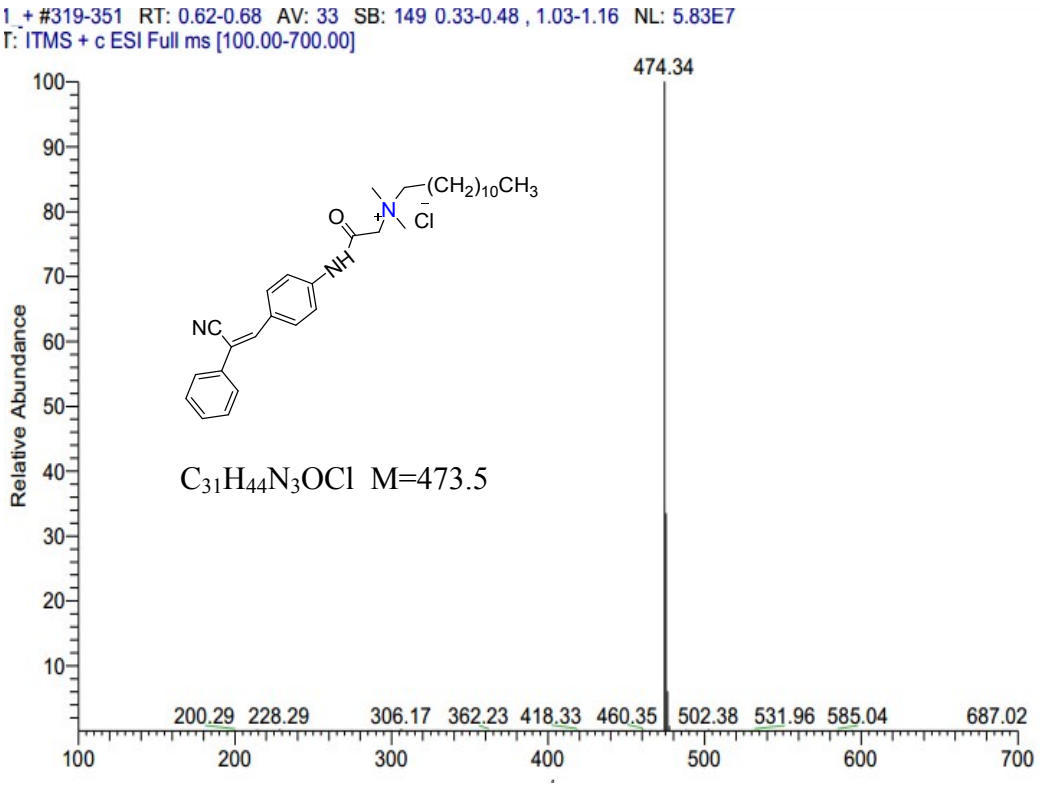
S3-7b The mass spectrum of **CDB-2**



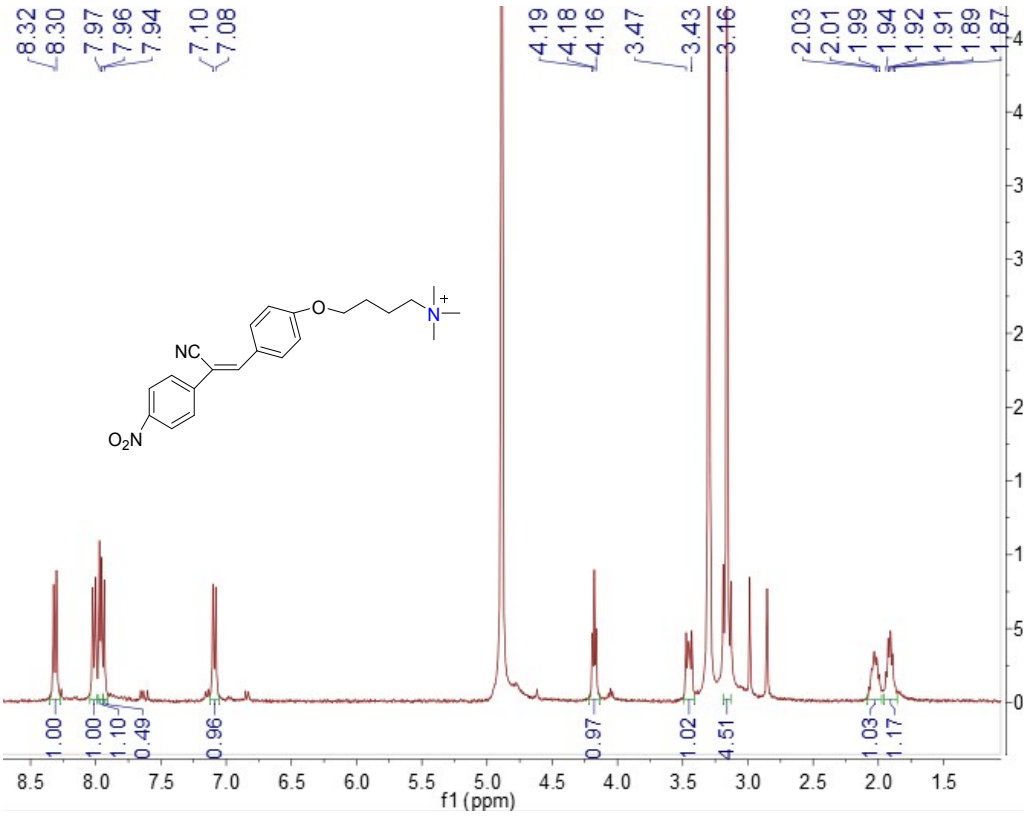
S3-8 ^{1}H NMR spectrum of **CDB-3**



S3-9a The ^{1}H NMR spectrum of **CDB-4**



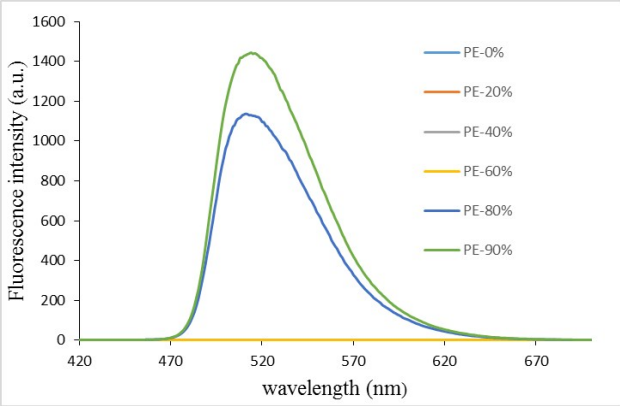
S3-9b The mass spectrum of **CDB-4**



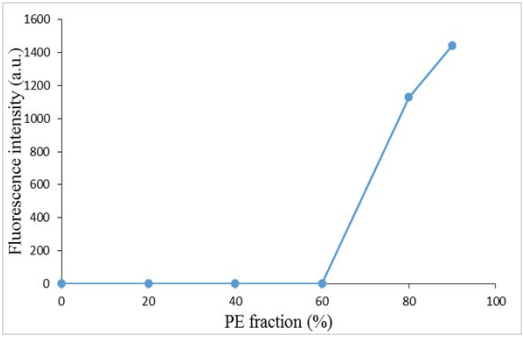
S3-10 The ^{1}H NMR spectrum of **CDB-5**

S4. The AIE behavior of CDB-DMA12 itself and UV absorption spectra of CDB-DMA12 (35.0μM) with the addition of different amount of SH

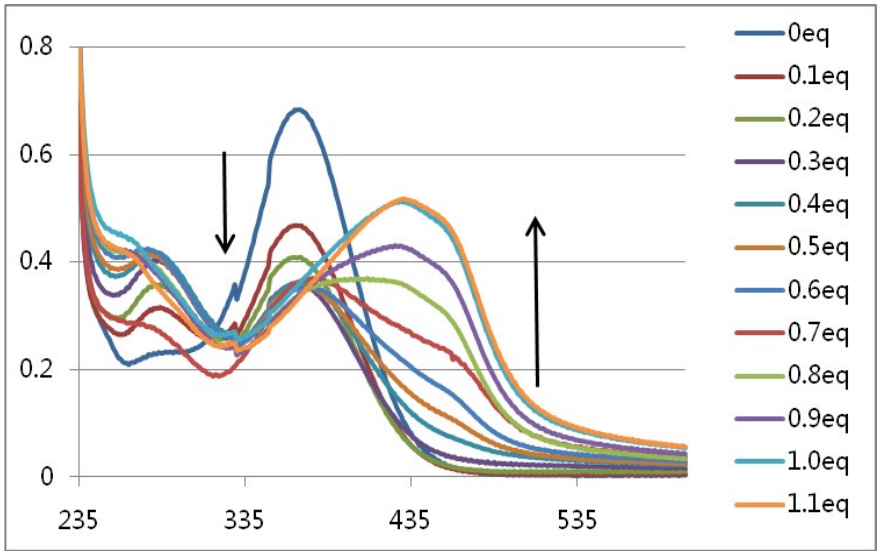
The AIE behavior of **CDB-DMA12** was investigated in mixture $CHCl_3$/petroleum with petroleum from 0 to 90%. As expected, **CDB-DMA12** is virtually nonluminescent when molecularly dissolved in $CHCl_3$ (but showed strong fluorescence of its solid), which was indicated by the photographs and fluorescence spectrum. However, when a large amount of petroleum was added into the solution, the emission of **CDB-DMA12** turned on and showed red fluorescence. The fluorescence intensity of **CDB-DMA12** exhibited higher enhancement when petroleum content reached to 90%. Clearly, the emission of **CDB-DMA12** is induced by aggregate formation.



S4-a. PL spectra of **CDB-DMA12** (3.5×10^{-5} M) in mixture $CHCl_3$/Petroleum with Petroleum from 0 to 90%.

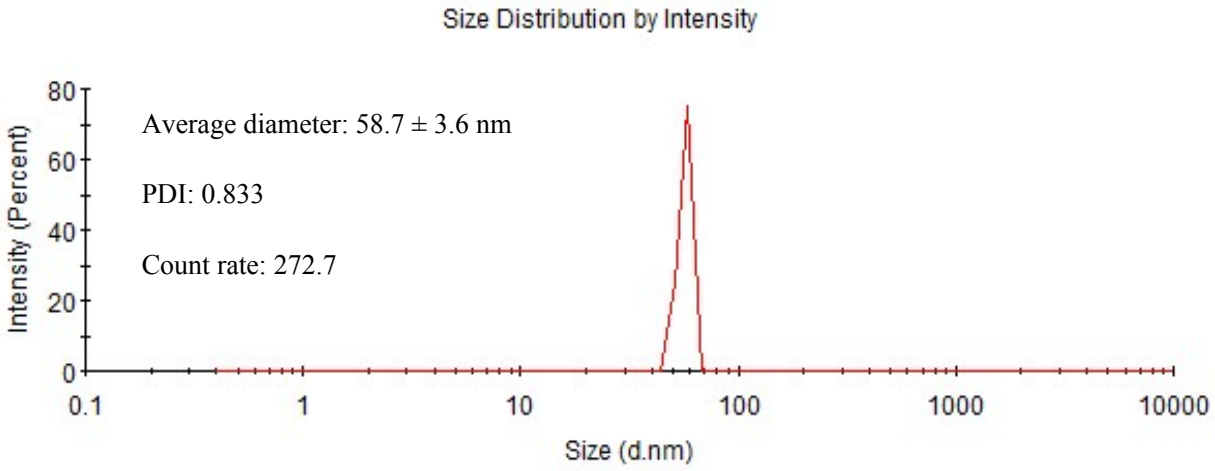


S4-b. Fluorescence intensity of **CDB-DMA12** (3.5×10^{-5} M) in λ_{em}=520nm vs. composition of $CHCl_3$/Petroleum mixtures; λ_{ex}=400nm.

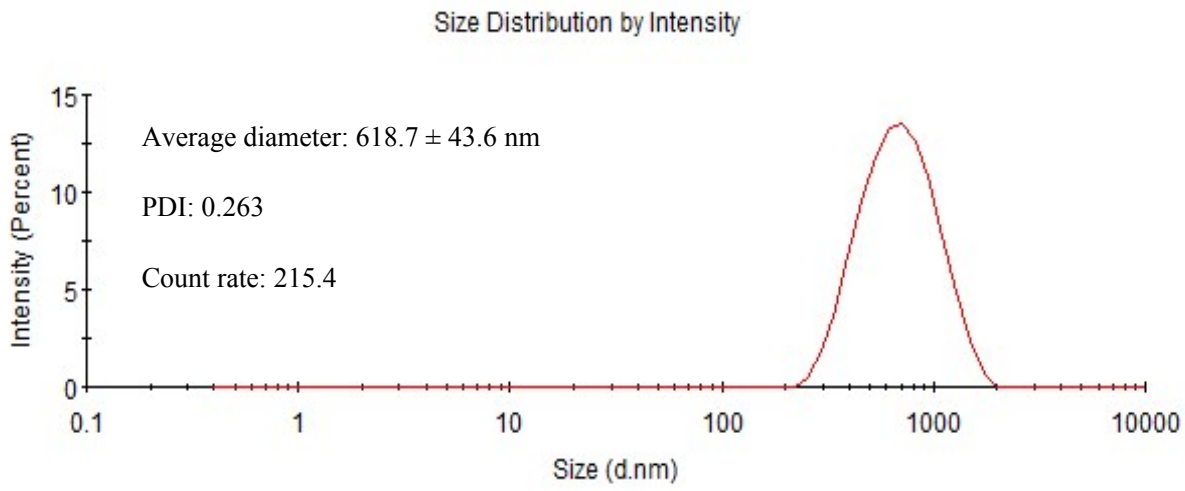


S4-c. UV absorption spectra of **CDB-DMA12** (35.0 μM) in H_2O/DMSO (993:7,v/v) with the addition of different amount of **SH** (0.0, 7.0, 14.0, 21.0, 28.0, 35.0, 42.0, 49.0, 56.0, 63.0, 70.0, 77.0 μM).

S5. The dynamic light scattering results



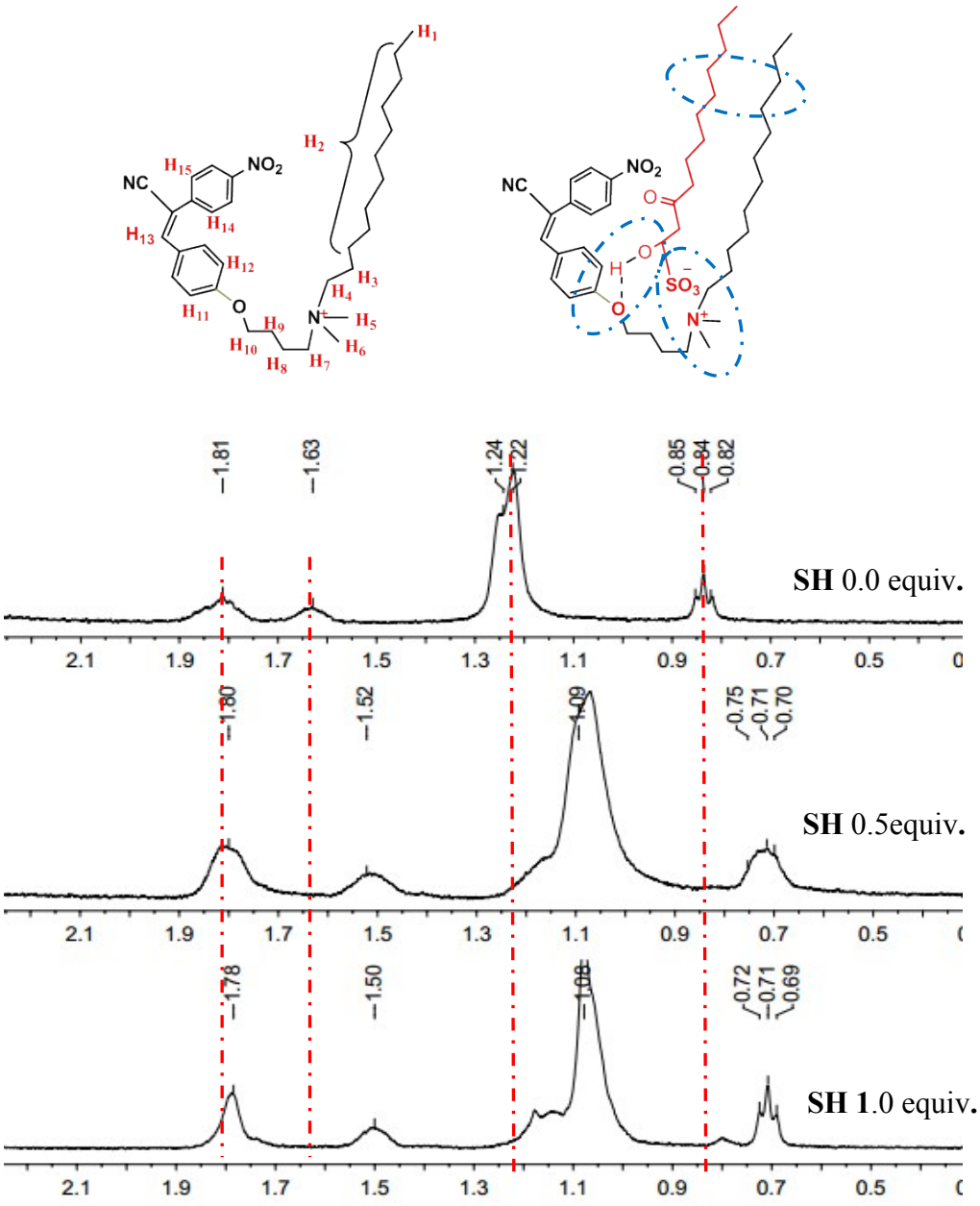
(a)

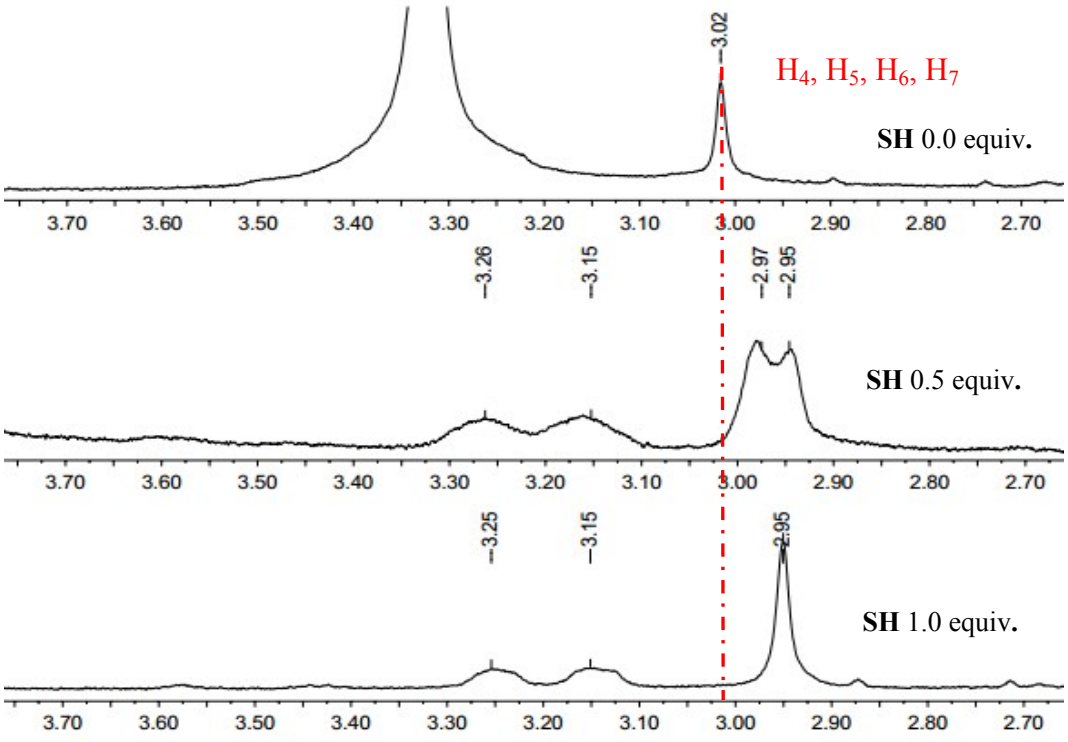


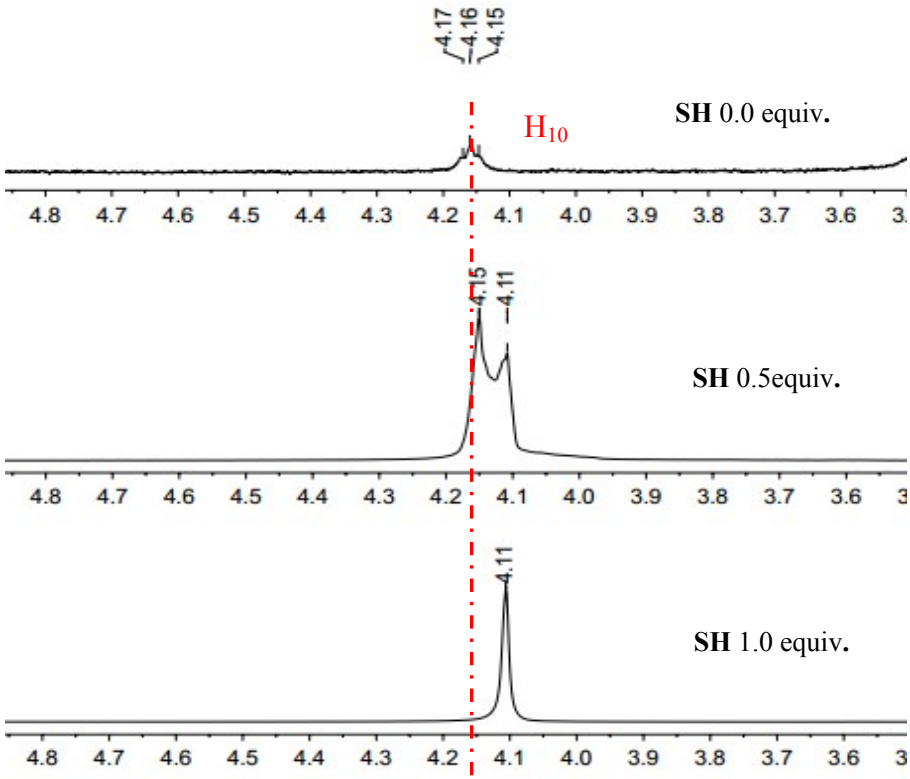
(b)

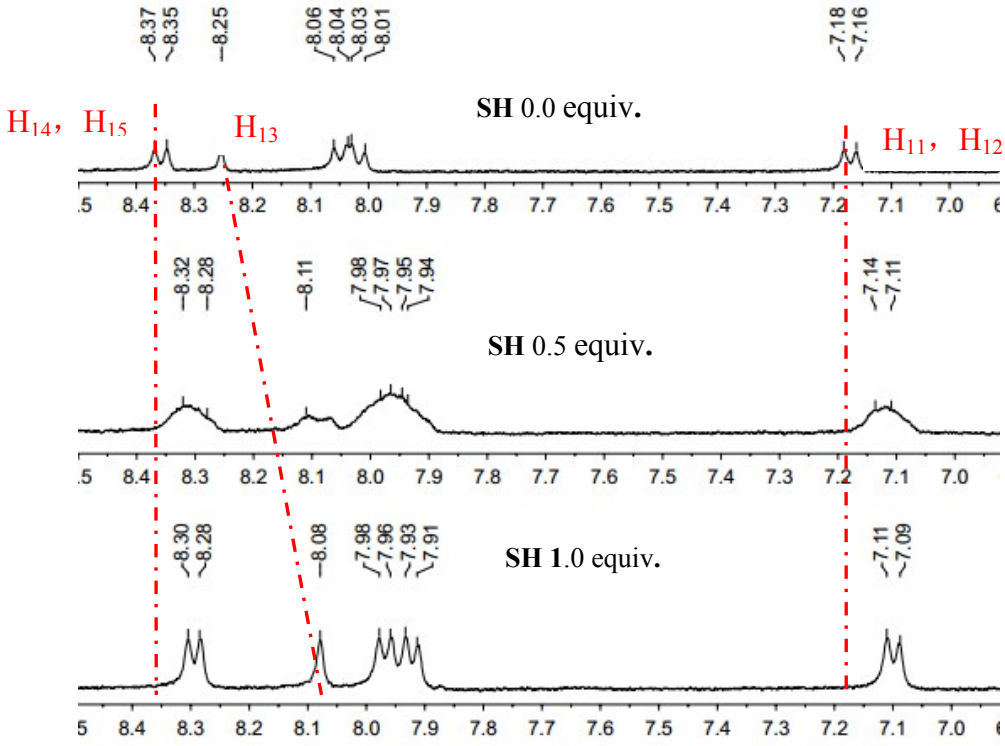
S5. The dynamic light scattering results for the solution of (a) **CDB-DMA12** itself (35.0 μM) and in the presence of **SH** (35.0 μM) (b) in water and DMSO (993:7, v/v)

S6a. ^{1}H NMR titration of CDB-DMA12 with the addition of SH




3.02
H4, H5, H6, H7
SH 0.0 equiv.
3.26
3.15
2.97
2.95
SH 0.5 equiv.
3.25
3.15
2.95
SH 1.0 equiv.
3.70 3.60 3.50 3.40 3.30 3.20 3.10 3.00 2.90 2.80 2.70

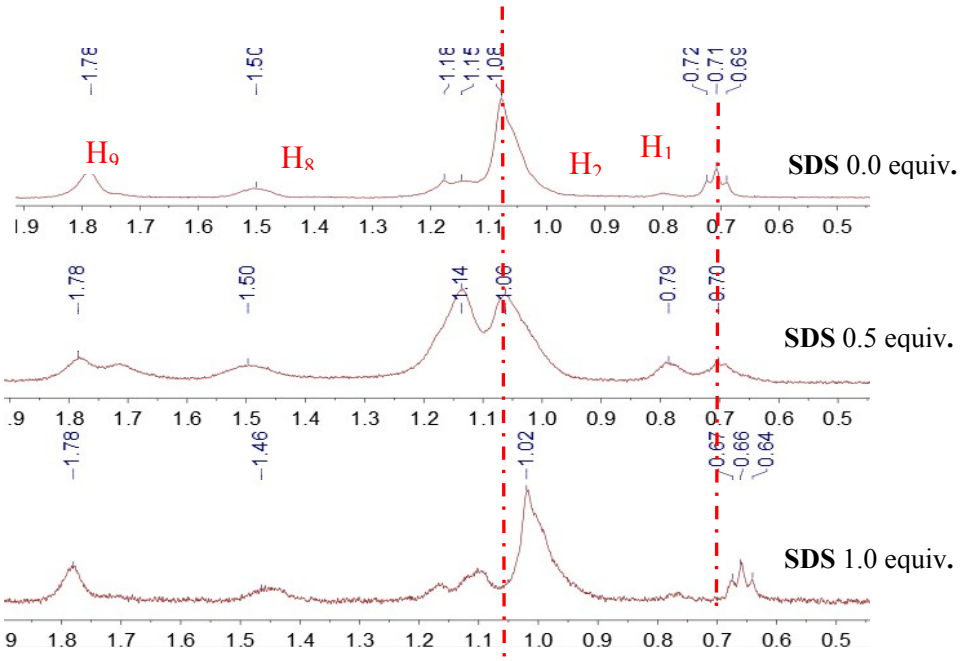

4.17
4.16
4.15
H10
SH 0.0 equiv.
4.15
4.11
SH 0.5equiv.
4.11
SH 1.0 equiv.
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6

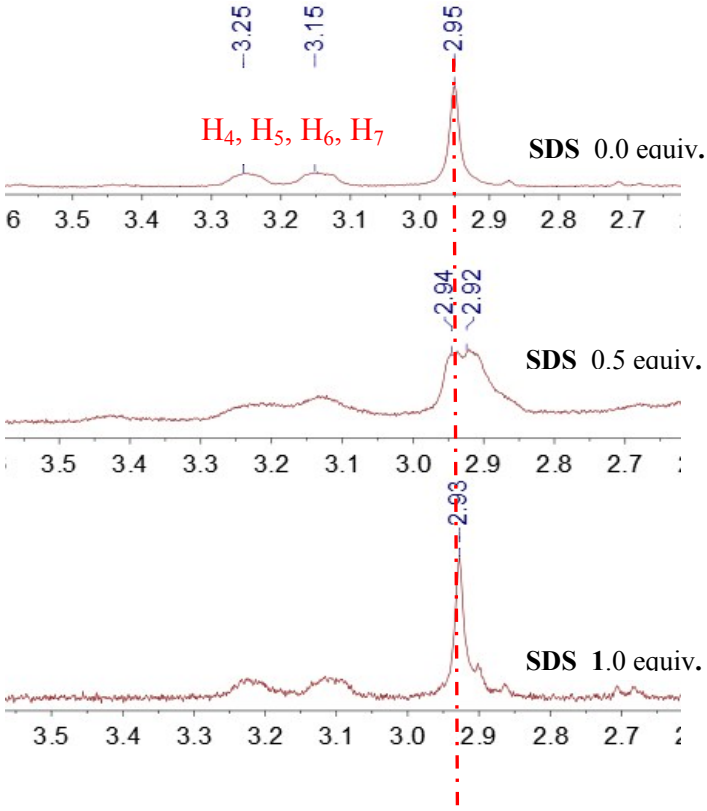


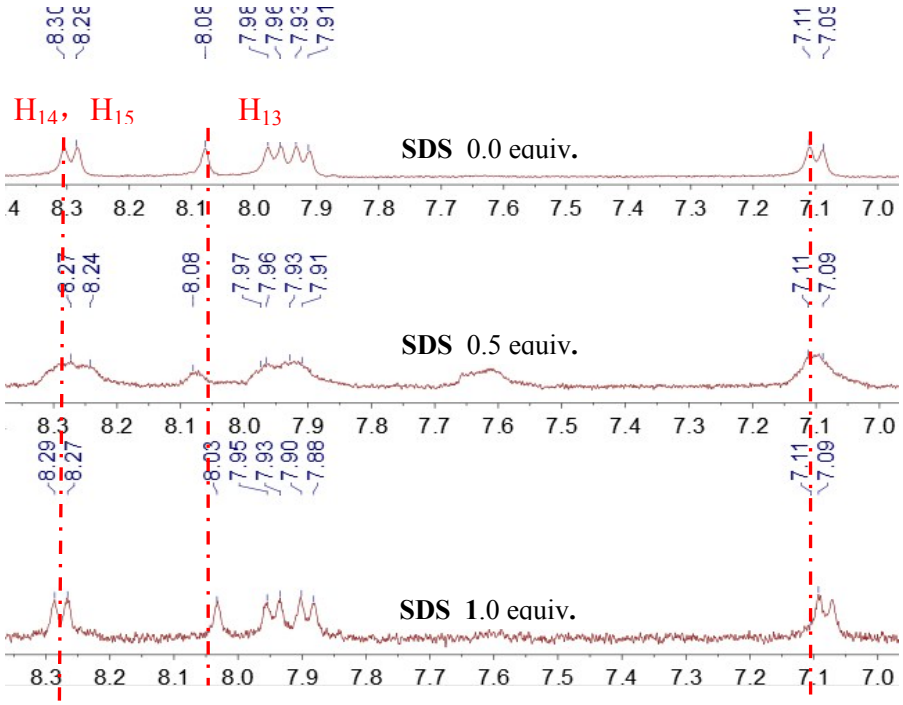
S6a. ^{1}H NMR titration of **CDB-DMA12** with the addition of **SH.**

It could be seen from the ^{1}H NMR titration of **CDB-DMA12** with the addition of **SH** that the protons on the **CDB-DMA12** are upfield-shifted, which indicate the formation of **CDB-DMA12/SH** complexes via electrostatic forces of the opposite charges, the hydrogen bindings and hydrophobic interactions.

S6b. ^{1}H NMR titration of CDB-DMA12 with the addition of SDS







S6b. ^{1}H NMR titration of **CDB-DMA12** with the addition of **SDS**.

It could be seen from the ^{1}H NMR titration of **CDB-DMA12** with the addition of **SDS** that the protons shifts on the **CDB-DMA12** are almost no change, which indicate there are no form of **CDB-DMA12**/**SDS** complexes via electrostatic forces of the opposite charges, the hydrogen bindings and hydrophobic interactions.