Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Optical-switchable energy transfer controlled by multiple-responsive turn-on fluorescence via metal-ligand and host-guest interactions in diarylethene-based [2]pseudo-rotaxane polymers

Ravinder Singh,[a] Chi-Chong Xiao,[a] Chong-Lun Wei,[a] Feng-Cheng Ho,[a] Trang Manh Khang,[a] Chinmayananda Gouda,[a] Tung-Kung Wu,[b,c] Yaw-Kuen Li,[b,c] Kung-Hwa Wei[a,c] and Hong-Cheu Lin*[a,c]

[a] Department of Materials Science & Engineering, National Chiao Tung University, Hsinchu 300, Taiwan.

[b] Department of Biological Science & Technology, National Chiao Tung University, Hsinchu 300, Taiwan.

[c] Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 300,

Taiwan.

*E-mail: linhc@mail.nctu.edu.tw

List of contents:

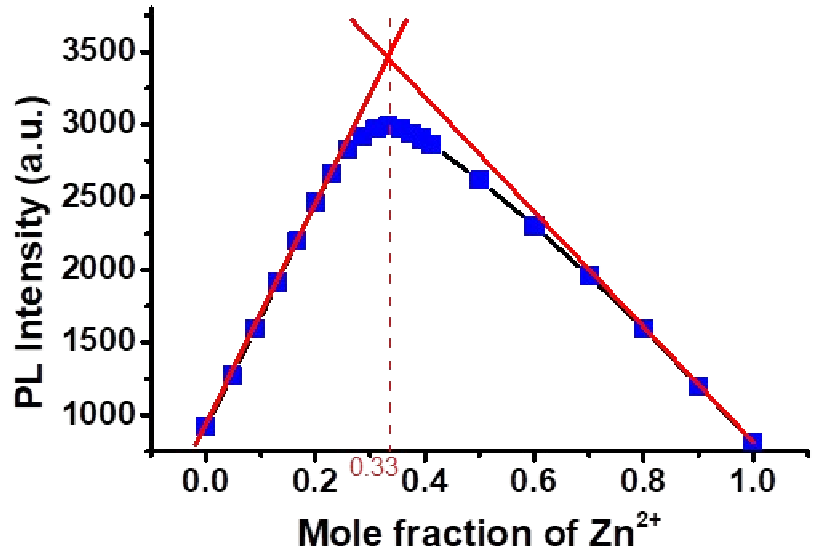


Fig. S1 Job's plot of metal-ligand complex **Zn^{2+}-TC_2** (1:2). (λex = 300 nm for PL exp.)

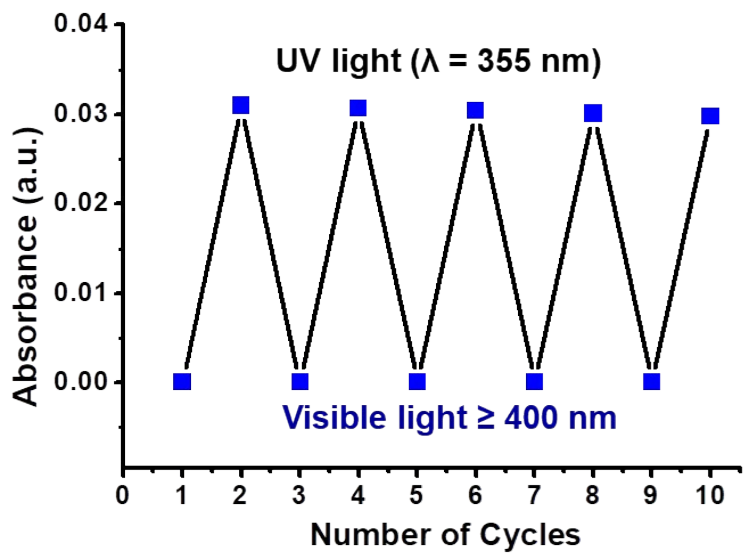


Fig. S2 Reversible absorption behavior between **DS(O)** and **DS(C)** at λ = 425 nm.

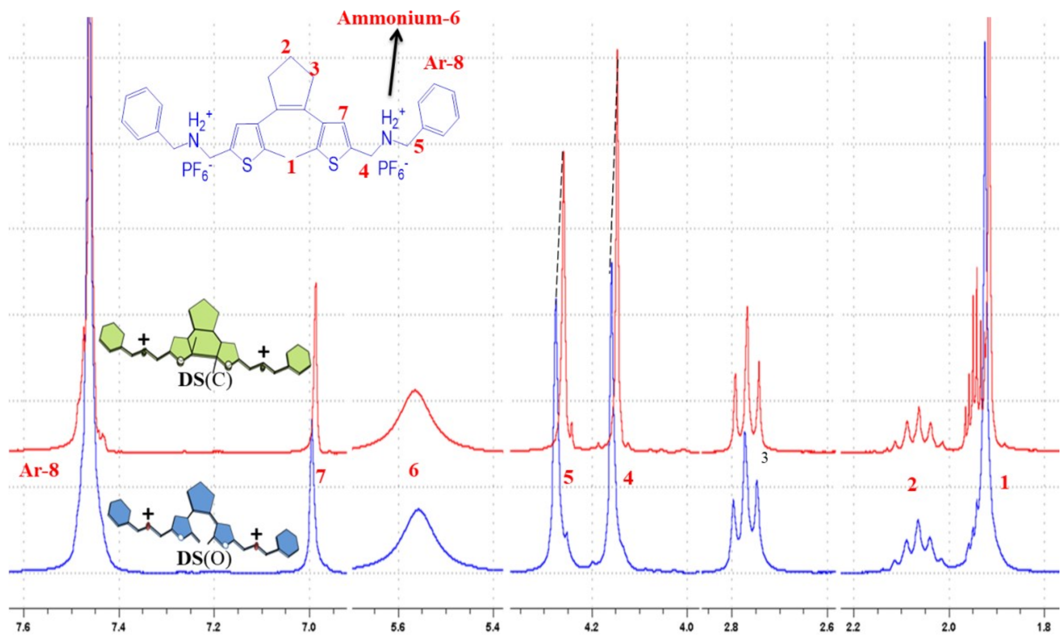
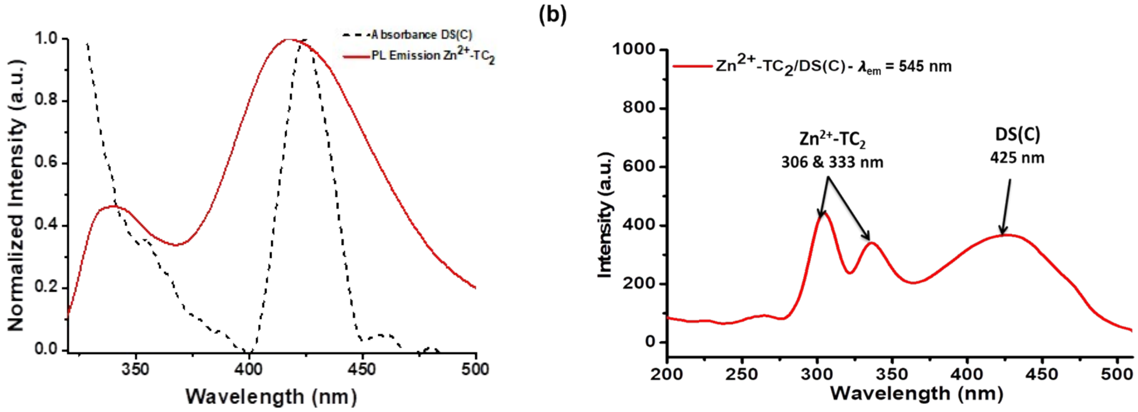


Fig. S3 ^{1}H-NMR (300 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 298K) of **DS** guest (6 mg in $CHCl_3/CH_3CN$ (1/1, v/v)) before and after UV-irradiation (at λ = 355 nm for 15 min).

(a)

(b)



Absorbance DS(C)
PL Emission Zn^{2+}-TC_2
Normalized Intensity (a.u.)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
350
400
450
500
Zn^{2+}-TC_2/DS(C)- λ_{em} = 545 nm
Zn^{2+}-TC_2
306 & 333 nm
DS(C)
425 nm
Intensity (a.u.)
Wavelength (nm)
1000
800
600
400
200
0
200
250
300
350
400
450
500

Fig. S4 (a) Spectral overlaps of the emission of **Zn^{2+}-TC_2** host and absorption of **DS(C)** guest in $CHCl_3/CH_3CN$ (1/1, v/v), (λ_{ex} = 300 nm for PL exp.), (b) PL excitation spectrum of supramolecular polymer **Zn^{2+}-TC_2/DS(C)** in $CHCl_3/CH_3CN$ (1/1, v/v) solution (1 mM) for emission at 545 nm.

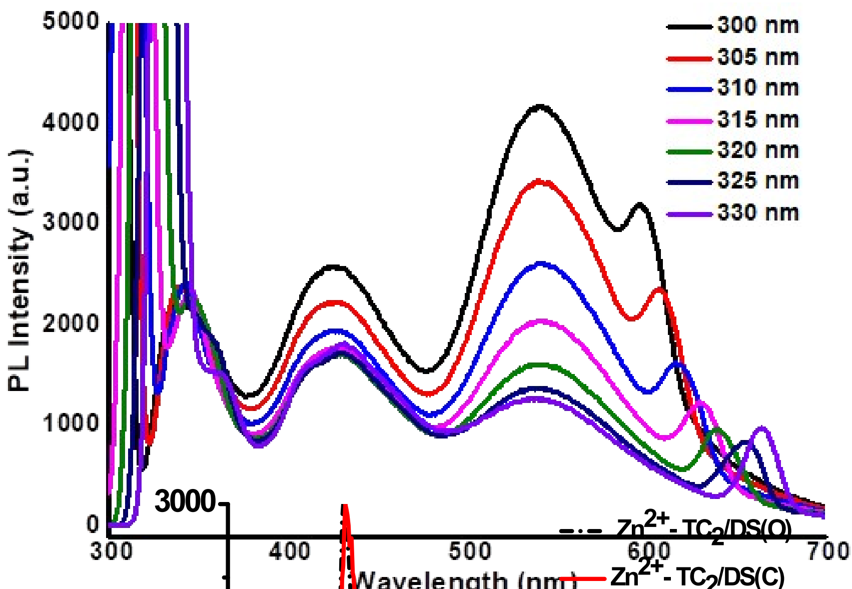


Fig. S5 PL emission spectra of supramolecular polymer **Zn^{2+}-TC_2/DS(C)** in $CHCl_3/CH_3CN$ (1/1, v/v) solutions (1 mM) at different excitation wavelengths from 300 nm to 330 nm. (λex = 300 nm.)

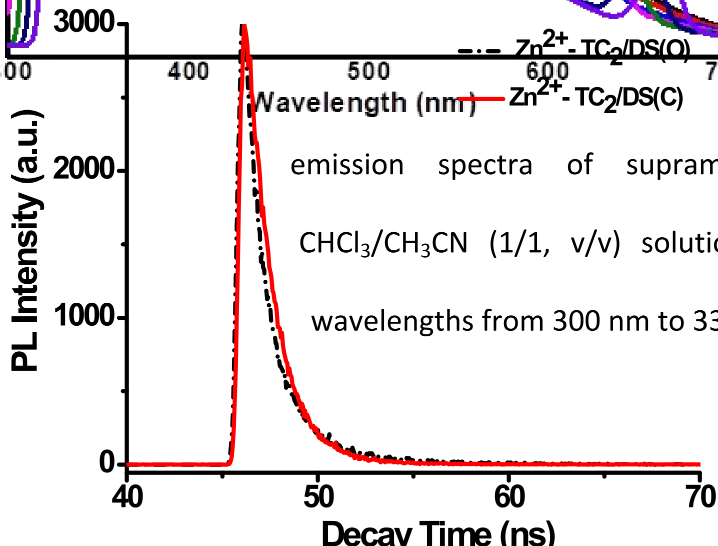


Fig. S6 Time-resolved fluorescence measurement of **Zn^{2+}-TC_2** host emissions (at λ_{max} = 417 nm) in supramolecular polymer **Zn^{2+}-TC_2/DS(O & C)** in $CHCl_3$/CH_3CN (1/1, v/v) before and after UV-irradiation.

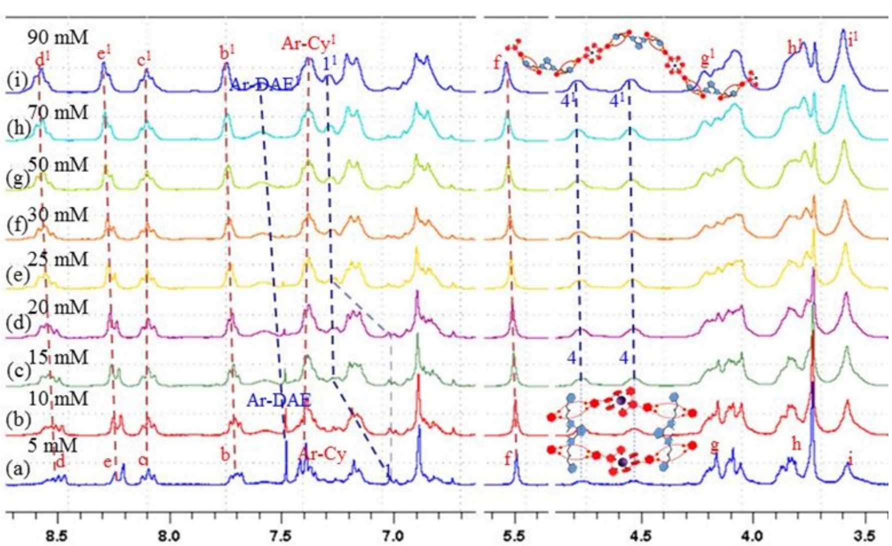


Fig. S7 ^{1}H-NMR spectra (300 MHz, $CDCl_3$/CD_3CN (1/1, v/v), 298K) of supramolecular polymer **Zn^{2+}-TC_2/DS(O)** at various concentrations: (a) 5; (b) 10; (c) 15; (d) 20; (e) 25; (f) 30; (g) 50; (h) 70; (i) 90 mM.

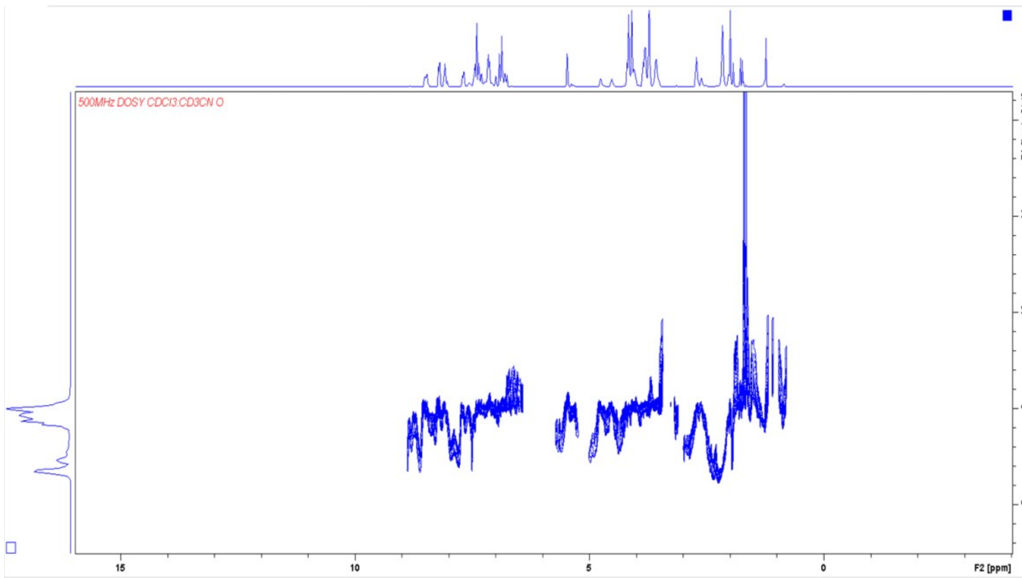


Fig. S8 Two-dimensional diffusion-ordered NMR (DOSY) spectra (500 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 298K) of supramolecular polymer **Zn^{2+}-TC_2/DS(O)** at concentration 10 mM.

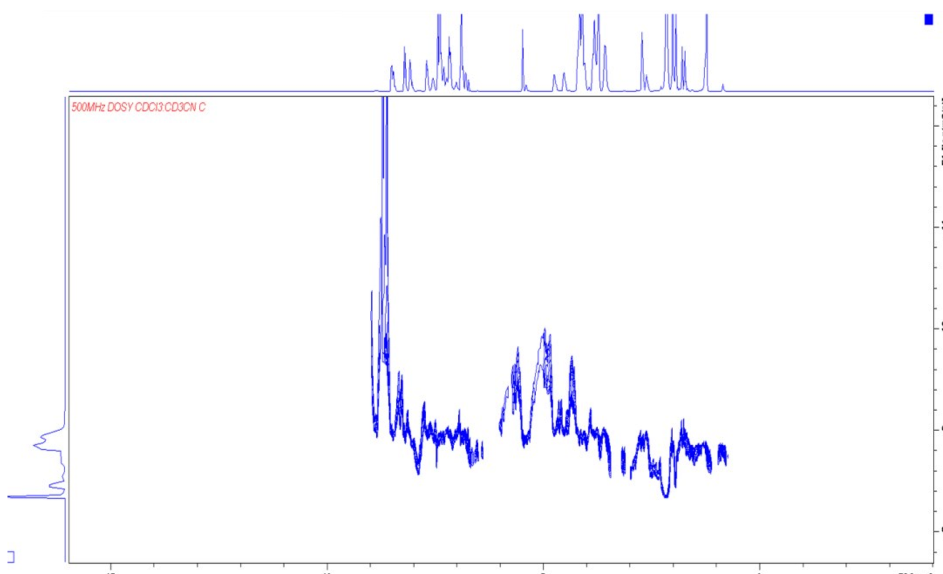


Fig. S9 Two-dimensional diffusion-ordered NMR (DOSY) spectra (500 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 298K) of supramolecular polymer **Zn^{2+}-TC_2/DS(C)** at concentration 10 mM.

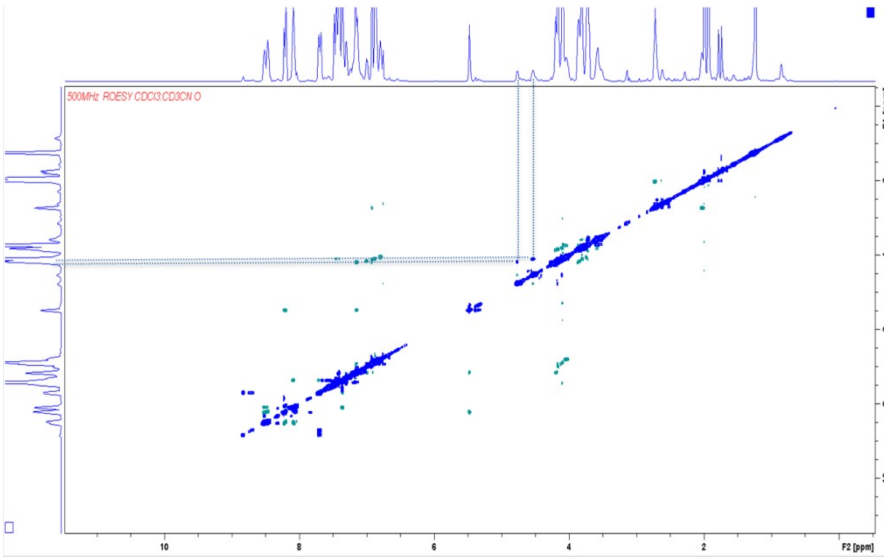


Fig. S10 Rotating-frame nuclear overhauser effect NMR (ROESY) spectra (500 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 298K) of supramolecular polymer **Zn^{2+}-TC_2/DS(O)** at concentration 10 mM.

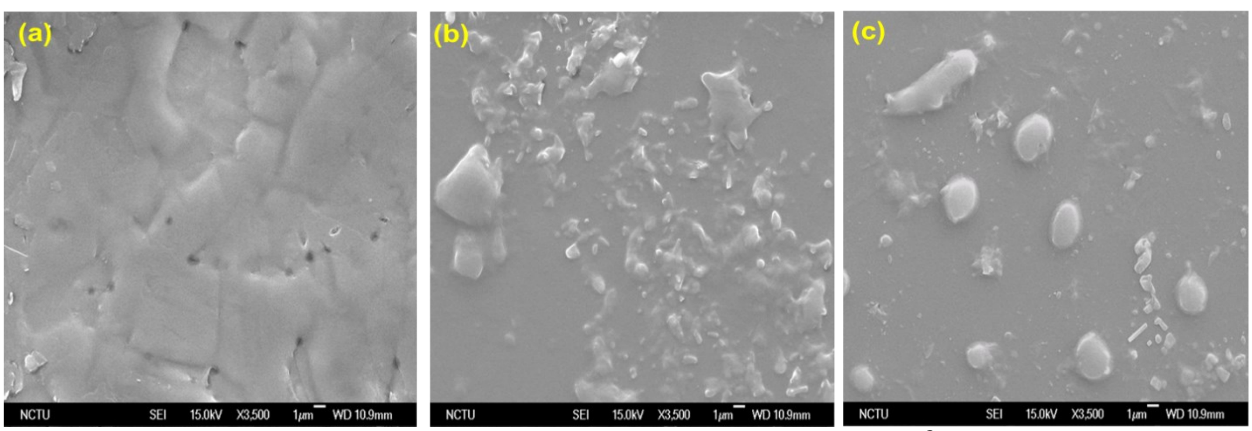


Fig. S11 Morphological SEM images of (a) metal-coordinated **Zn^{2+}-TC_2** host along with supramolecular polymers (b) **Zn^{2+}-TC_2/DS(O)** and (c) **Zn^{2+}-TC_2/DS(C)** prepared from $CHCl_3/CH_3CN$ (1/1, v/v) solutions (1 mM).

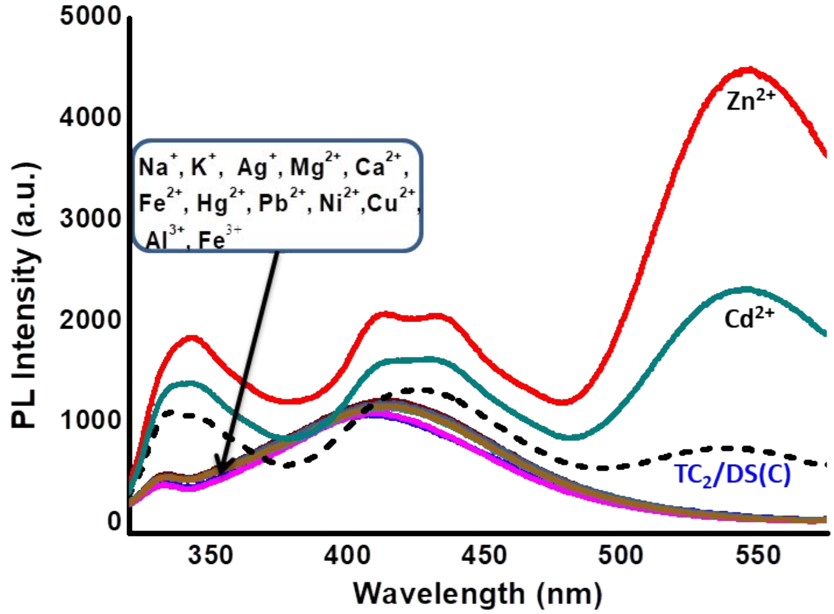
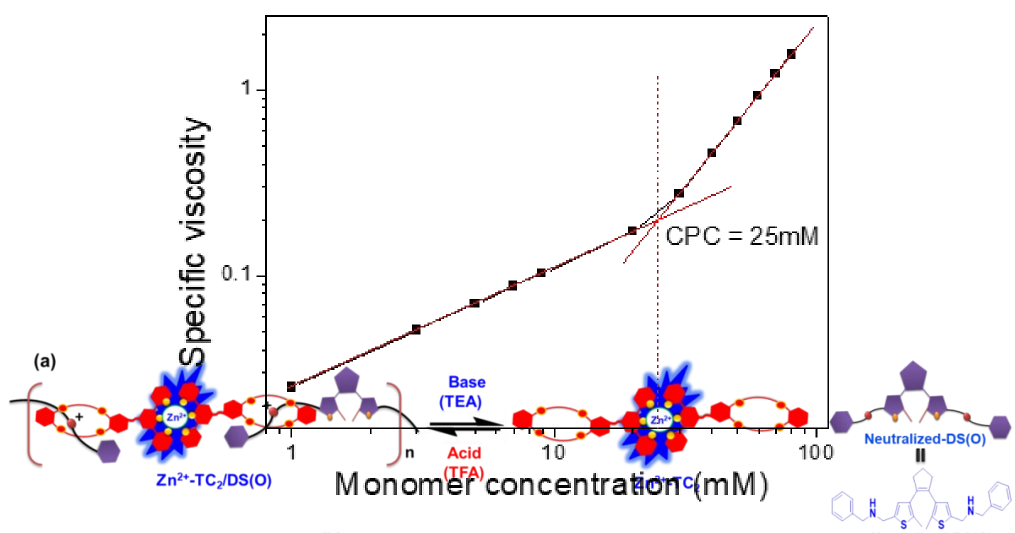


Fig. S7 PL spectra of dis-metaled component **TC$_2$/DS(C)** in $CHCl_3/CH_3CN$ (1/1, v/v) solutions (1 mM) after chelation with various metal ions (i.e., 0.5 equiv.). (λex = 300 nm.)



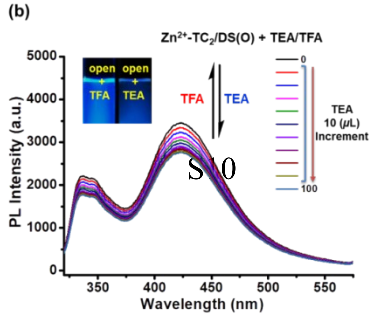
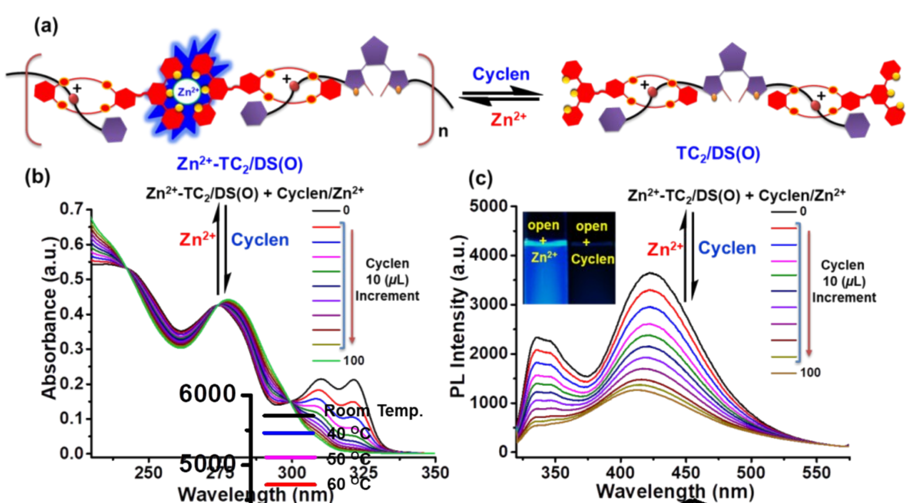


Fig. S13 Specific viscosity measurement of supramolecular polymer **Zn^{2+}-TC_2/DS(O)** in $CHCl_3/CH_3CN$ (1:1, v/v, 298 K).

Fig. S14 (a) Pictorial demonstration of the dis-assembly/re-assembly in supramolecular polymer **Zn^{2+}-TC_2/DS(O)** (1:1) by means of interaction with base/acid in $CHCl_3/CH_3CN$ (1/1, v/v). (b) PL spectral changes of **Zn^{2+}-TC_2/DS(O)** upon the addition of TEA (0 to 100 μL) and TFA (0 to 100 μL) in $CHCl_3/CH_3CN$ (1/1, v/v). Insets: photoimages of **Zn^{2+}-TC_2/DS(O)** with acid/base in $CHCl_3/CH_3CN$ (1/1, v/v). (λex = 300 nm for PL exp.)



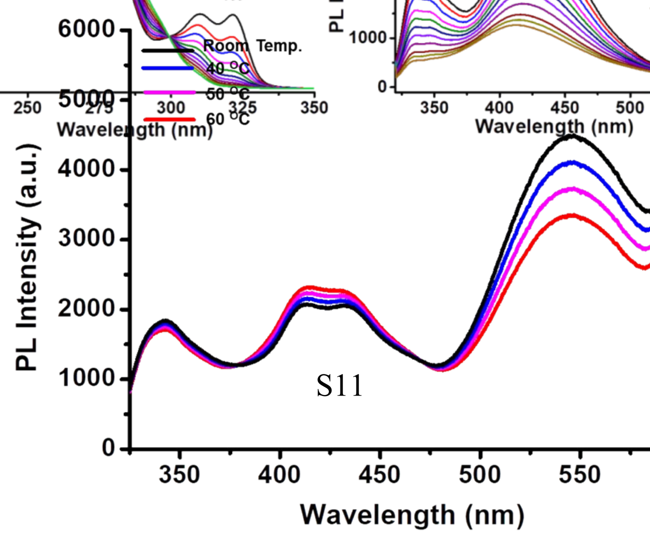


Fig. S15 (a) Pictorial demonstration of the dis-assembly/re-assembly in supramolecular polymer **Zn^{2+}-TC_2/DS(O)** (1:1) by means of interaction of Cyclen/Zn^{2+} in $CHCl_3$/CH_3CN (1/1, v/v). (b) UV/Vis spectral changes of **Zn^{2+}-TC_2/DS(O)** upon the addition of cyclen (0 to 100 μL) and $Zn(OTf)_2$ in $CHCl_3$/CH_3CN (1/1, v/v). (c) PL spectral changes of **Zn^{2+}-TC_2/DS(O)** upon the addition of cyclen (0 to 100 μL) and $Zn(OTf)_2$ in $CHCl_3$/CH_3CN (1/1, v/v). Insets: photoimages of **Zn^{2+}-TC_2/DS(O)** in the absence and presence of cyclen (0 and 100 μL). (λex = 300 nm for PL exp.)

Fig. S16 Temperature dependent PL spectra of supramolecular polymer **Zn^{2+}-TC_2/DS(C)** in $CHCl_3$/CH_3CN (1/1, v/v) solution (1 mM) within the temperature range of 40-60 °C. (λex = 300 nm.)

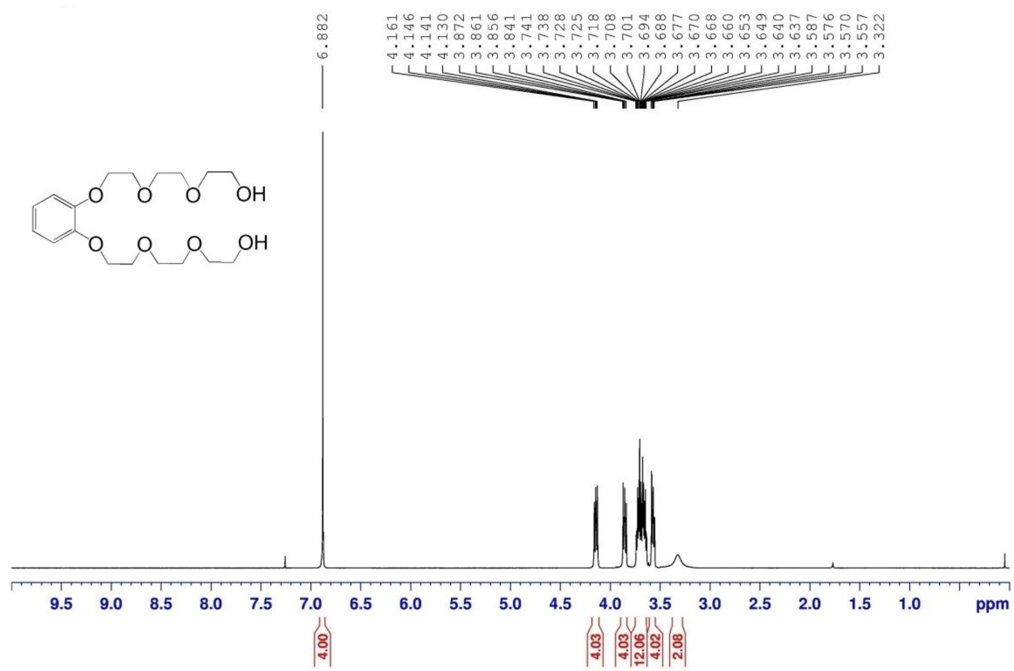


Fig. S17.1 ^{1}H-NMR of intermediate **1**.

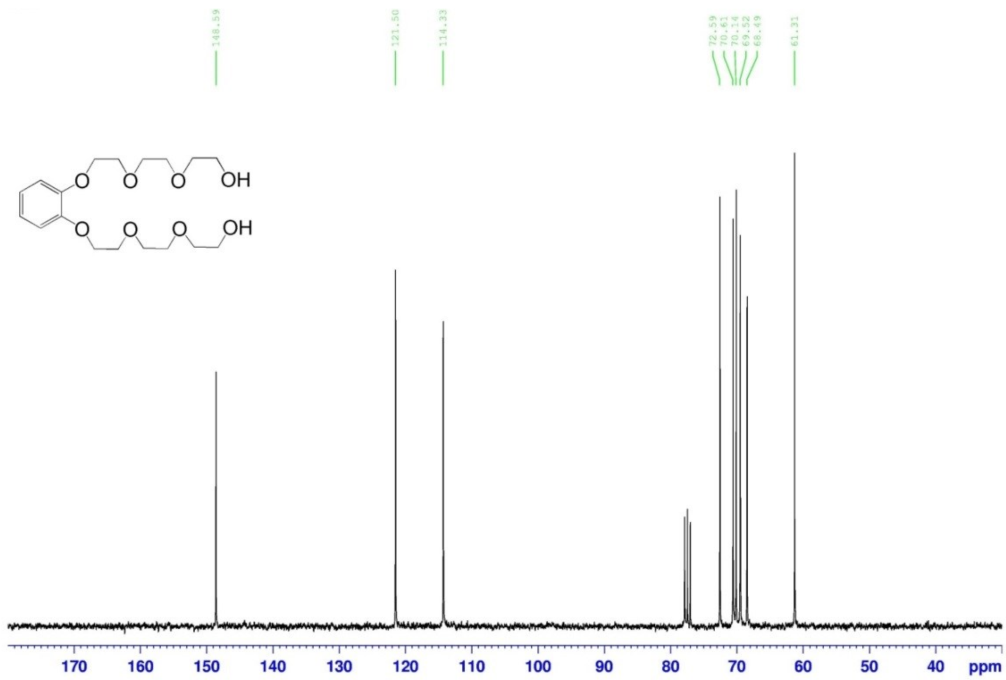


Fig. S17.2 ^{13}C-NMR of intermediate **1**.

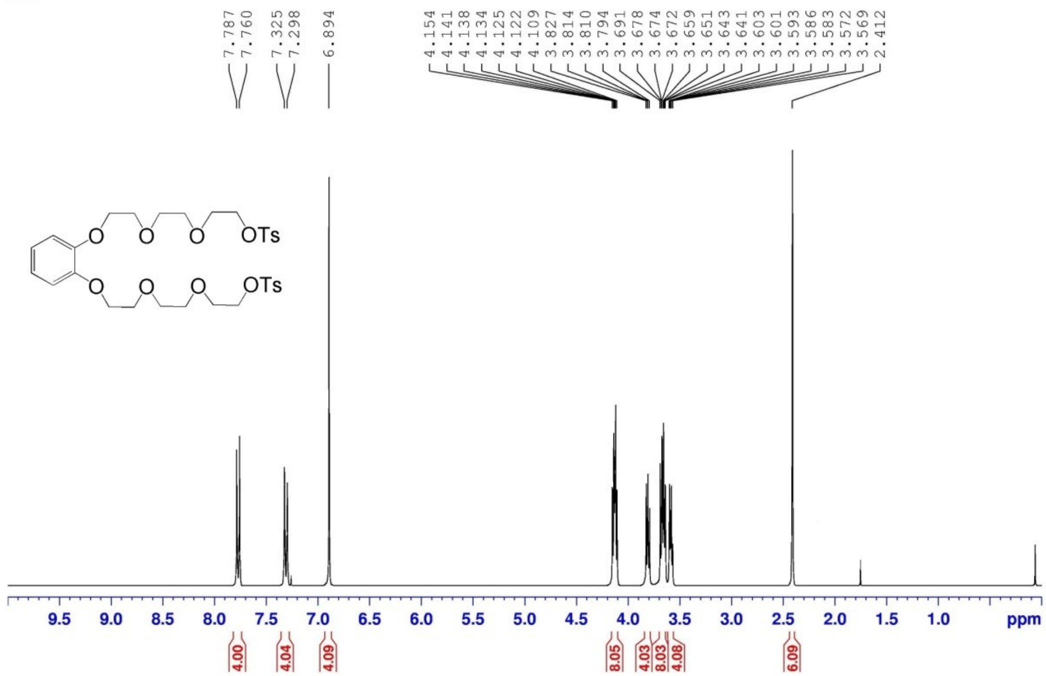


Fig. S18.1 ^{1}H-NMR of intermediate **2**.

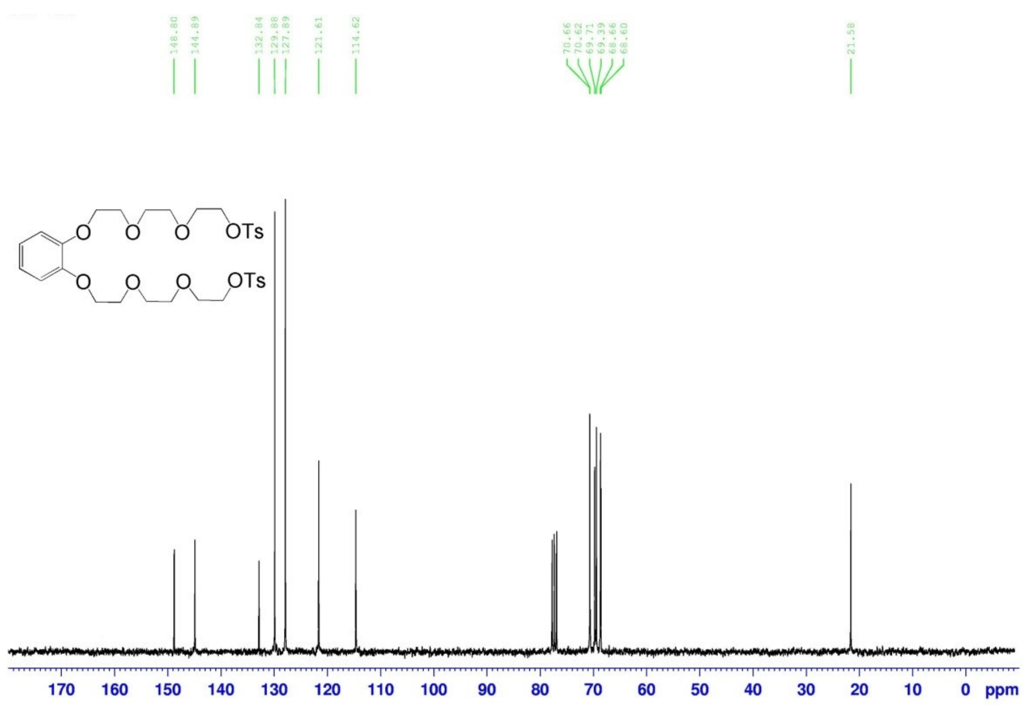


Fig. S18.2 ^{13}C-NMR of intermediate **2**.

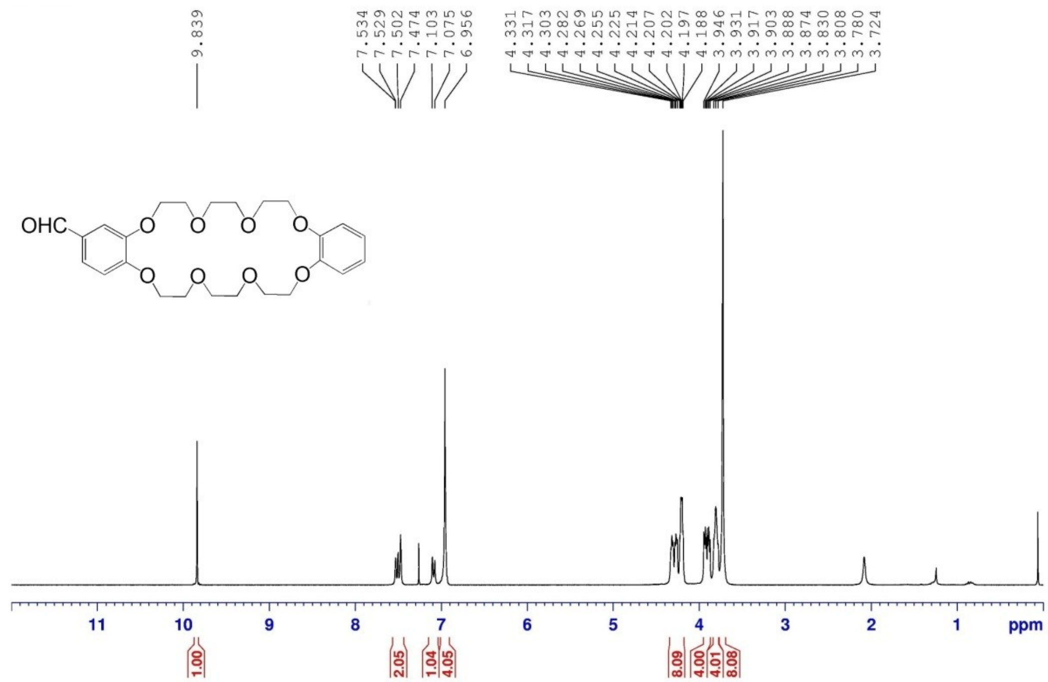


Fig. S19.1 ^{1}H-NMR of intermediate **3**.

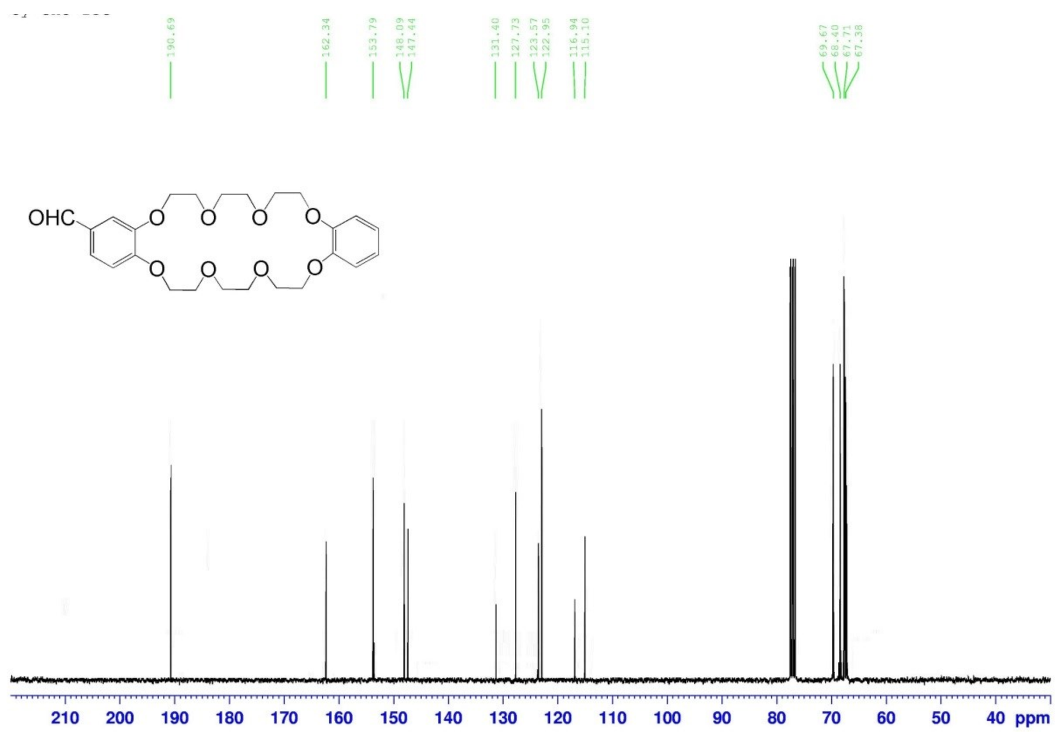


Fig. S19.2 ^{13}C-NMR of intermediate **3**.

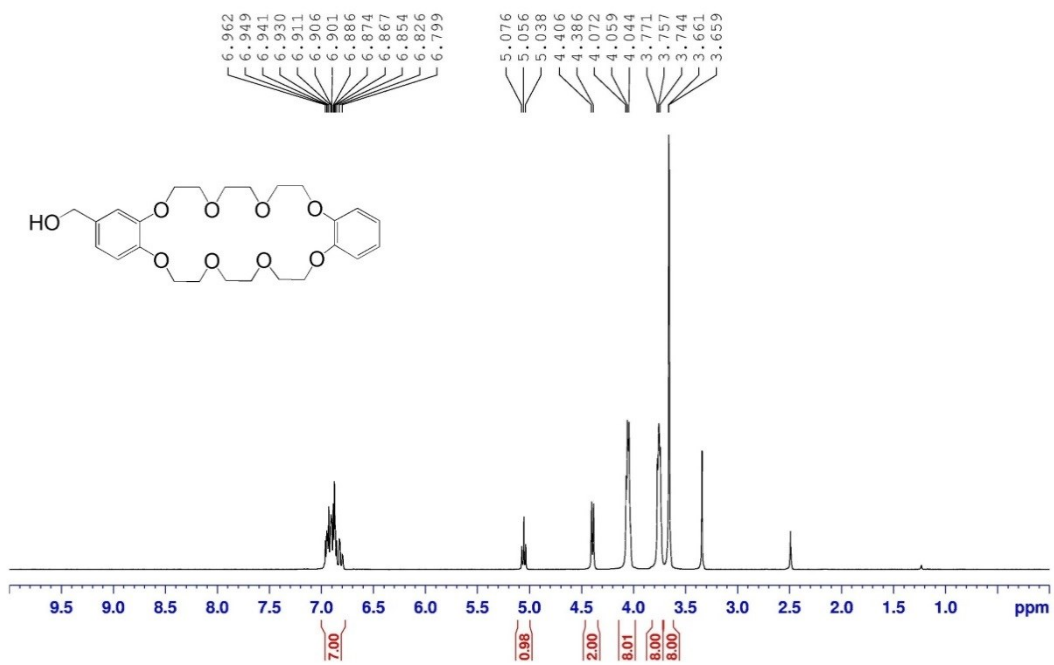


Fig. S20.1 ^{1}H-NMR of intermediate **4**.

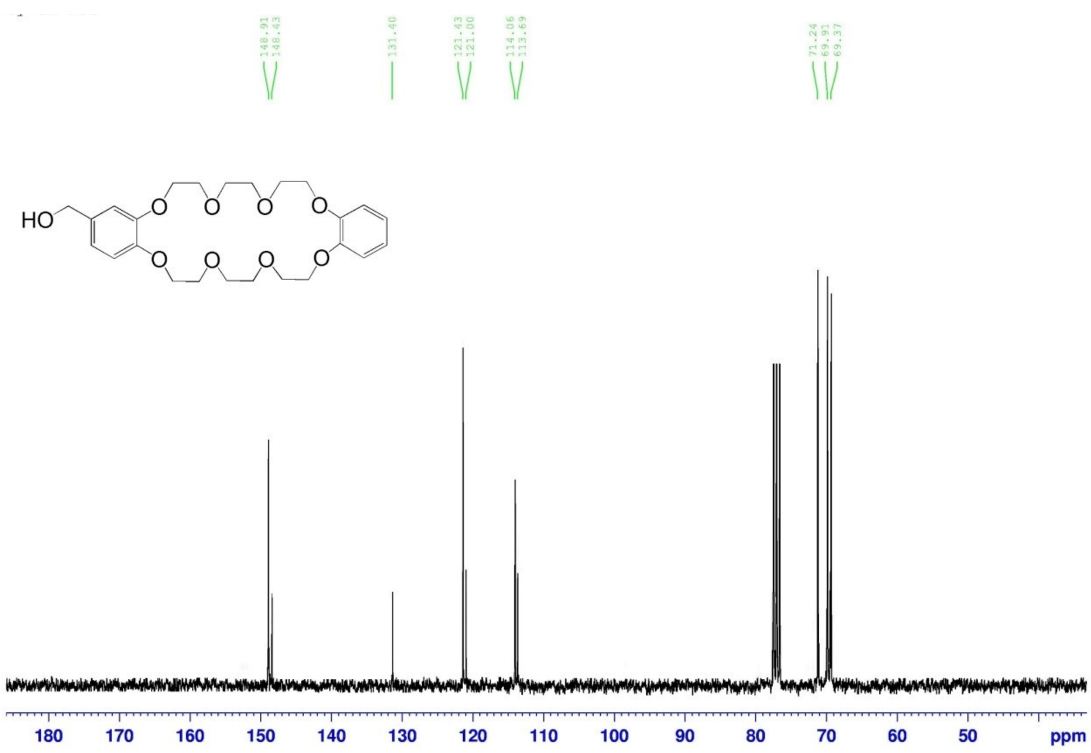


Fig. S20.2 ^{13}C-NMR of intermediate **4**.

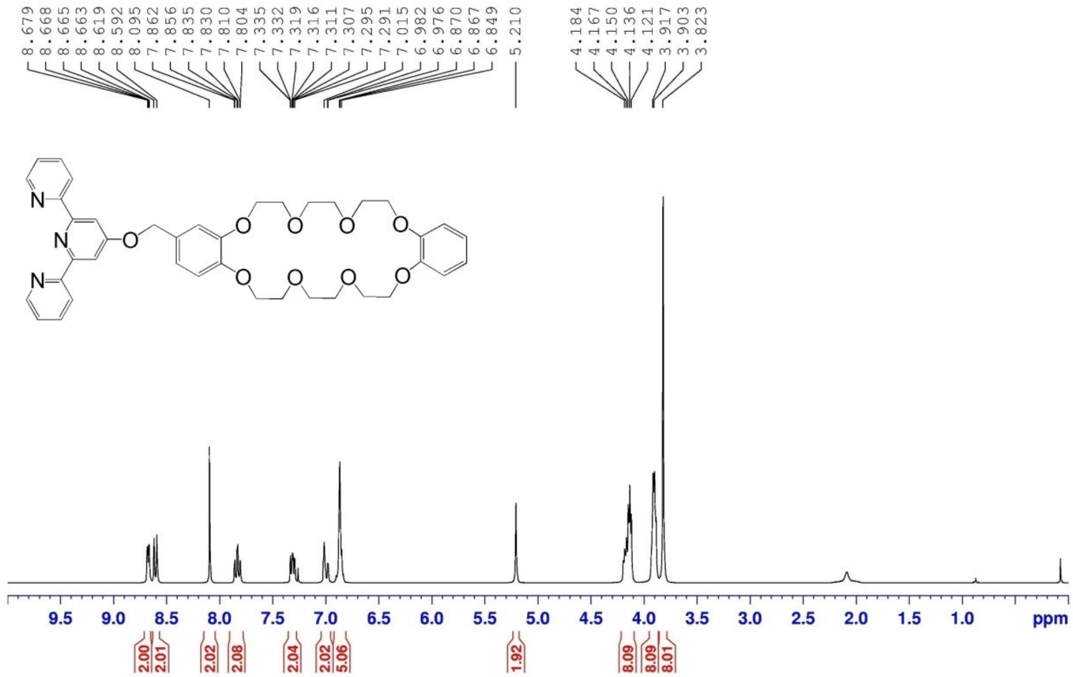


Fig. S21.1 ^{1}H-NMR of intermediate **TC**.

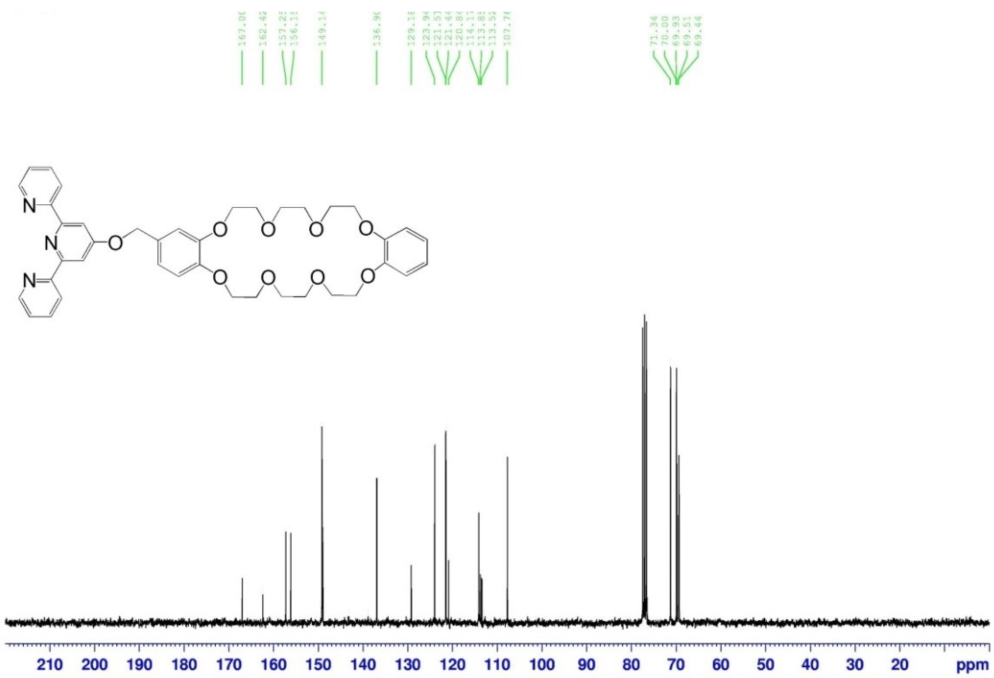


Fig. S21.2 ^{13}C-NMR of intermediate **TC**.

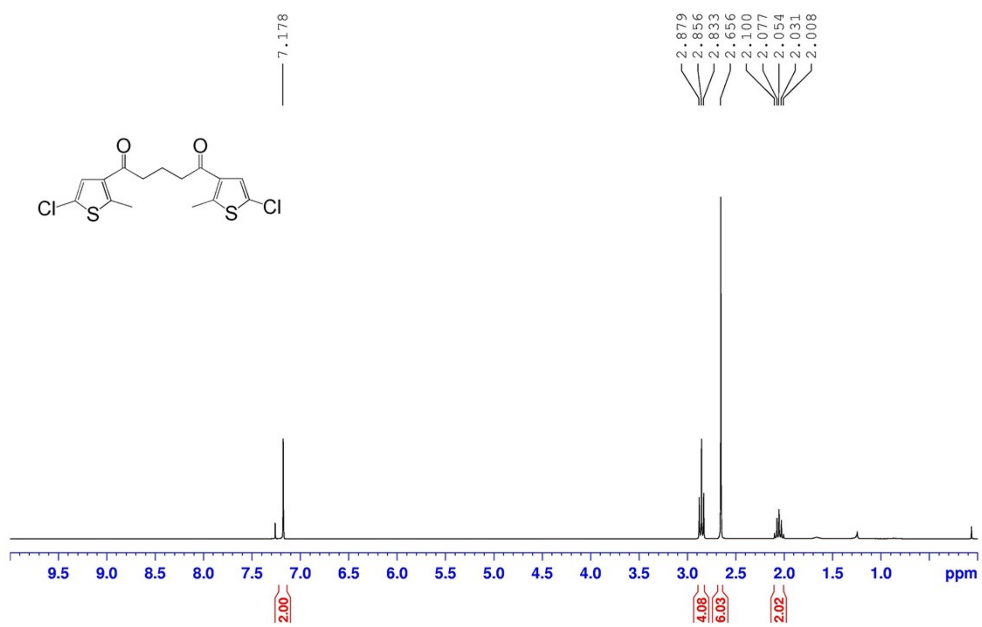


Fig. S22.1 ^{1}H-NMR of intermediate **5**.

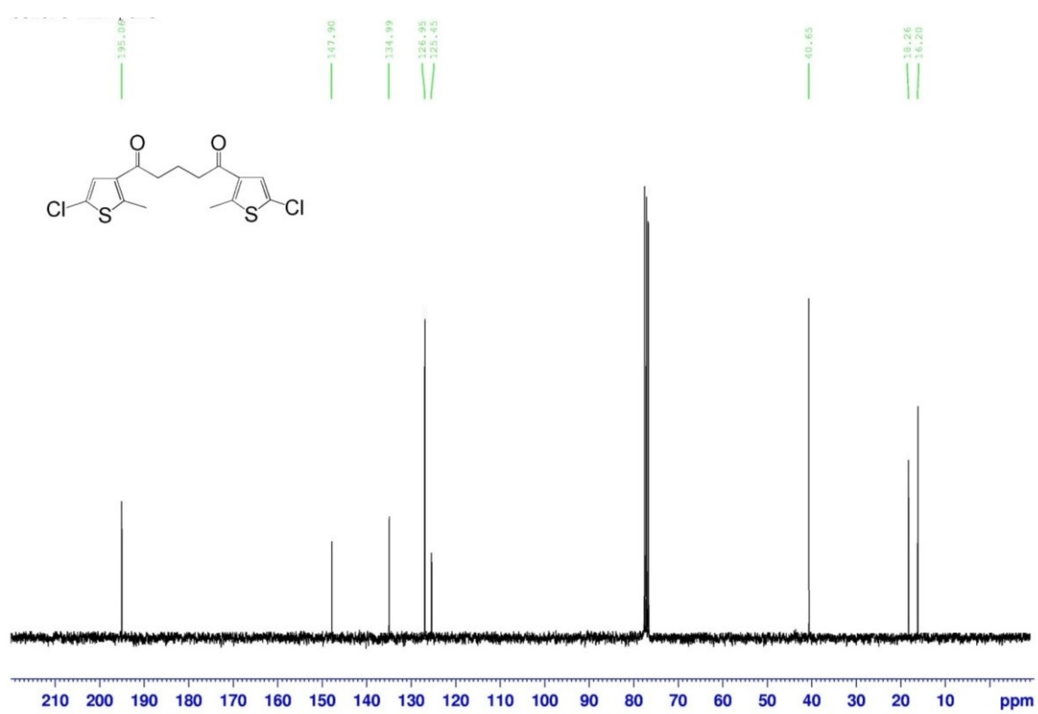


Fig. S22.2 ^{13}C-NMR of intermediate **5**.

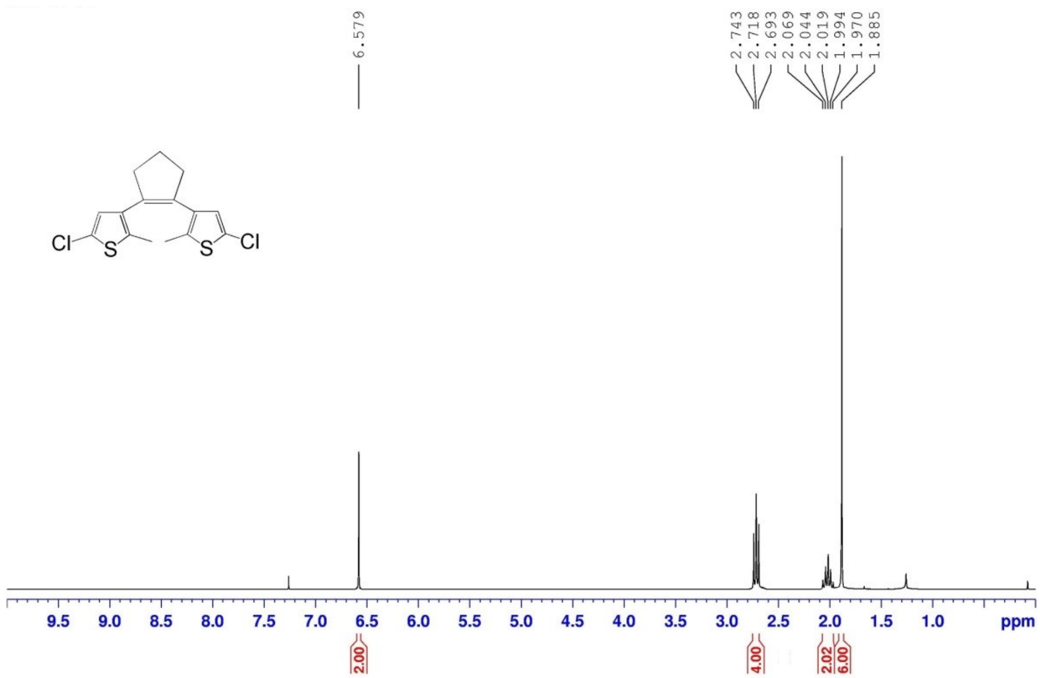


Fig. S23.1 ^{1}H-NMR of intermediate **6**.

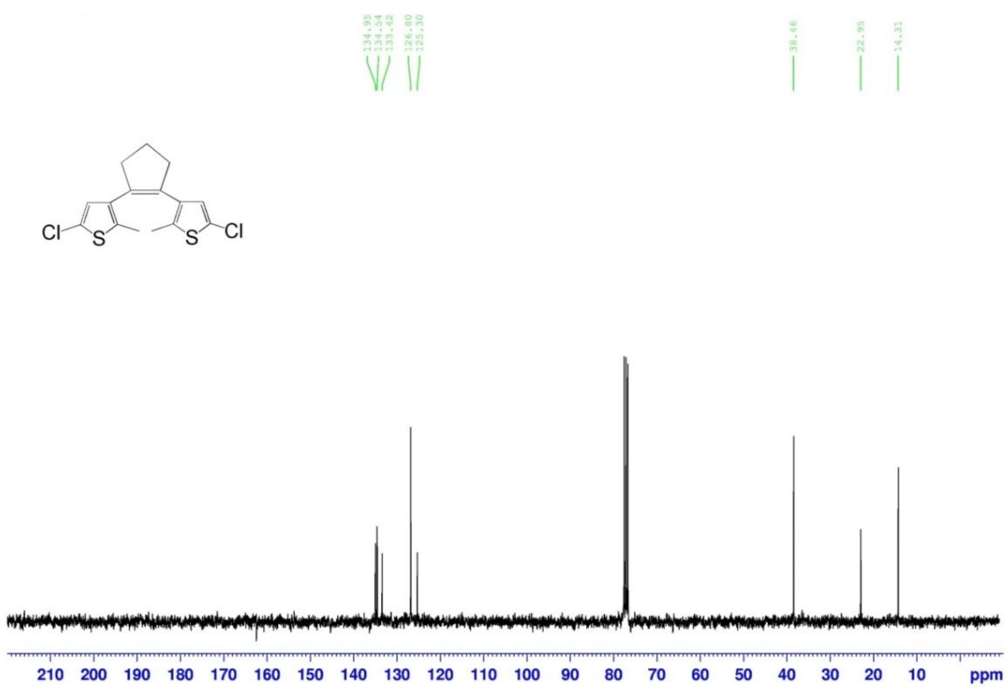


Fig. S23.2 ^{13}C-NMR of intermediate **6**.

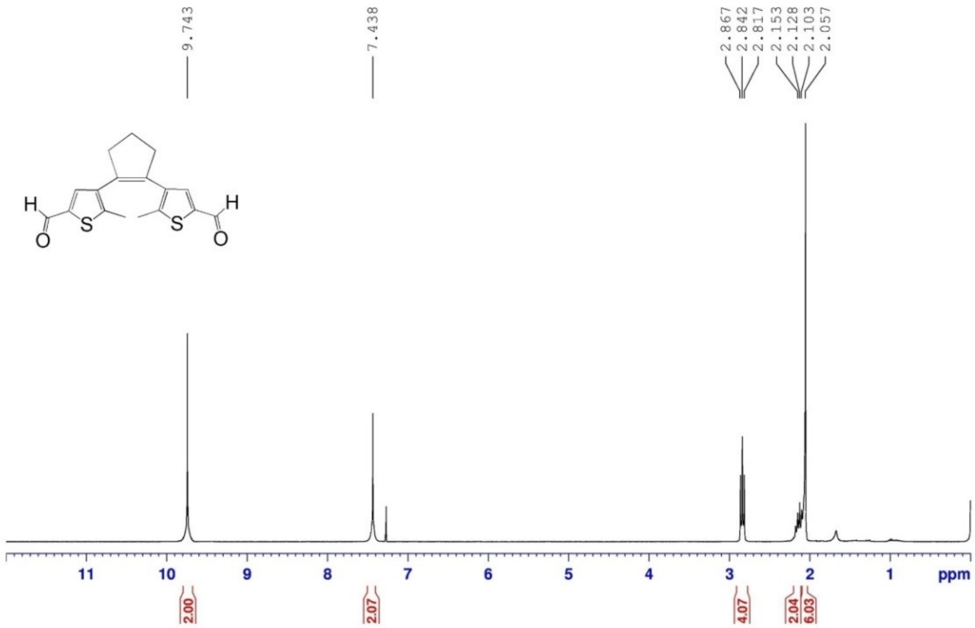


Fig. S24.1 ^{1}H-NMR of intermediate **7**.

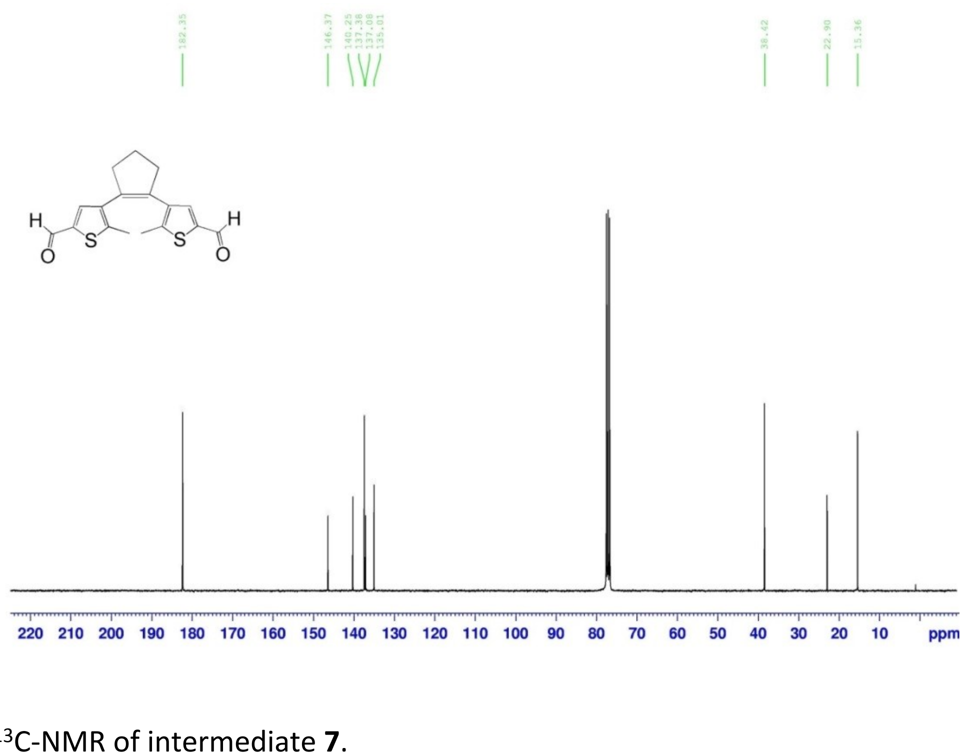


Fig. S24.2 ^{13}C-NMR of intermediate **7**.

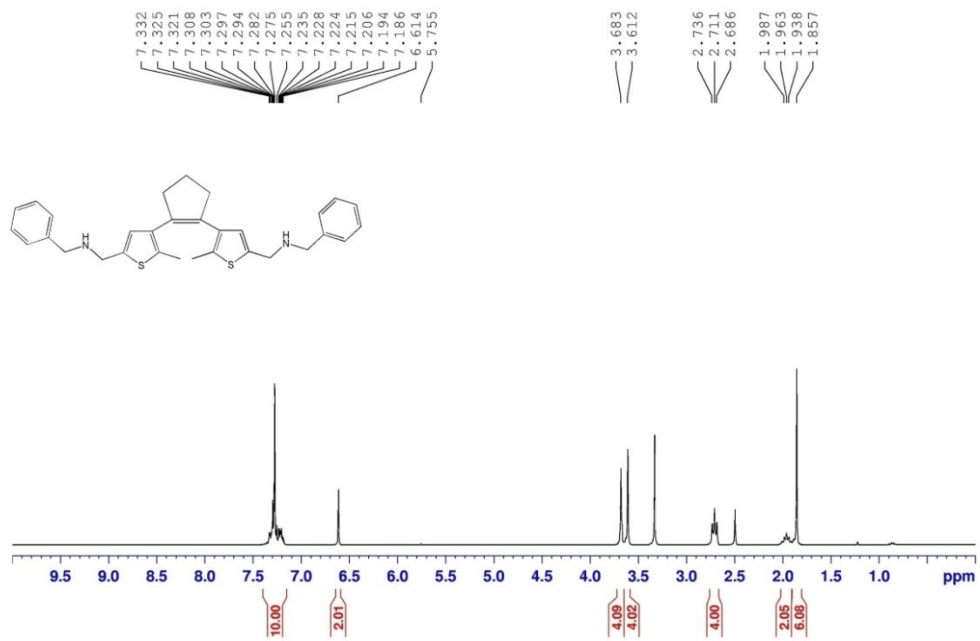


Fig. S25.1 ^{1}H-NMR of intermediate **8**.

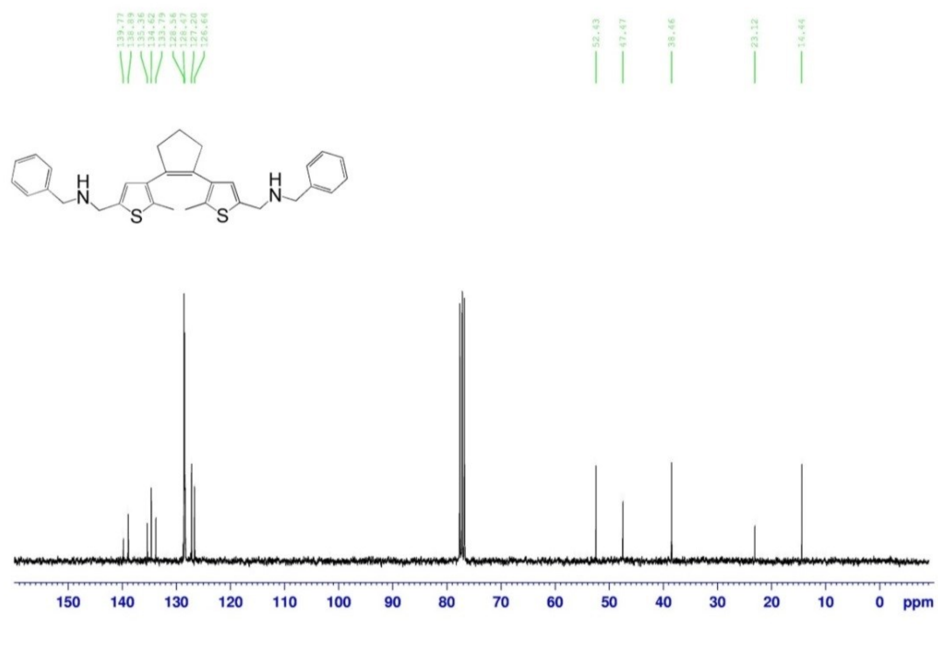


Fig. S25.2 ^{13}C-NMR of intermediate **8**.

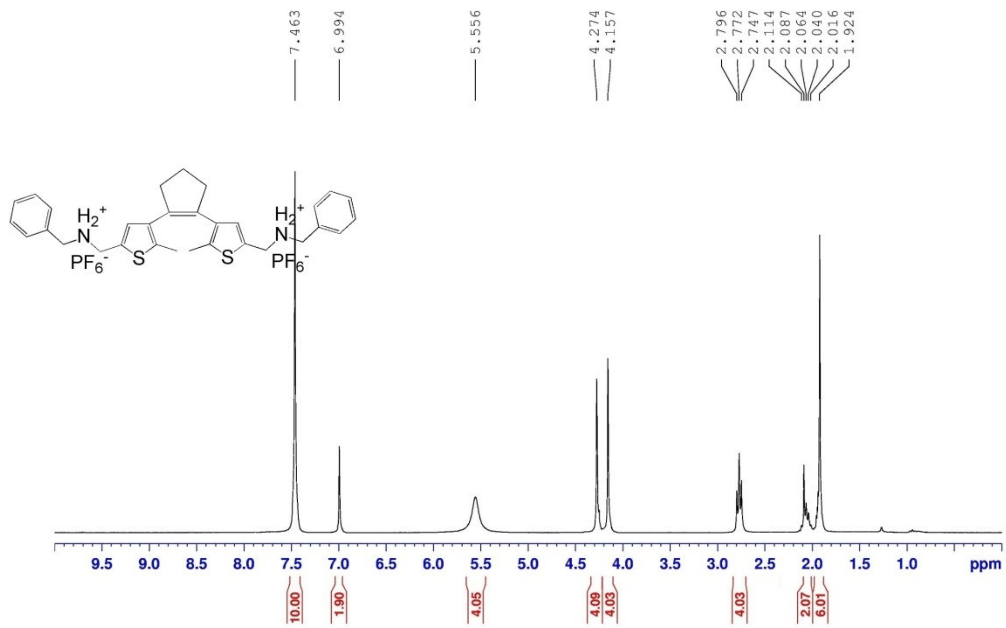


Fig. S26.1 ^{1}H-NMR of intermediate **DS**.

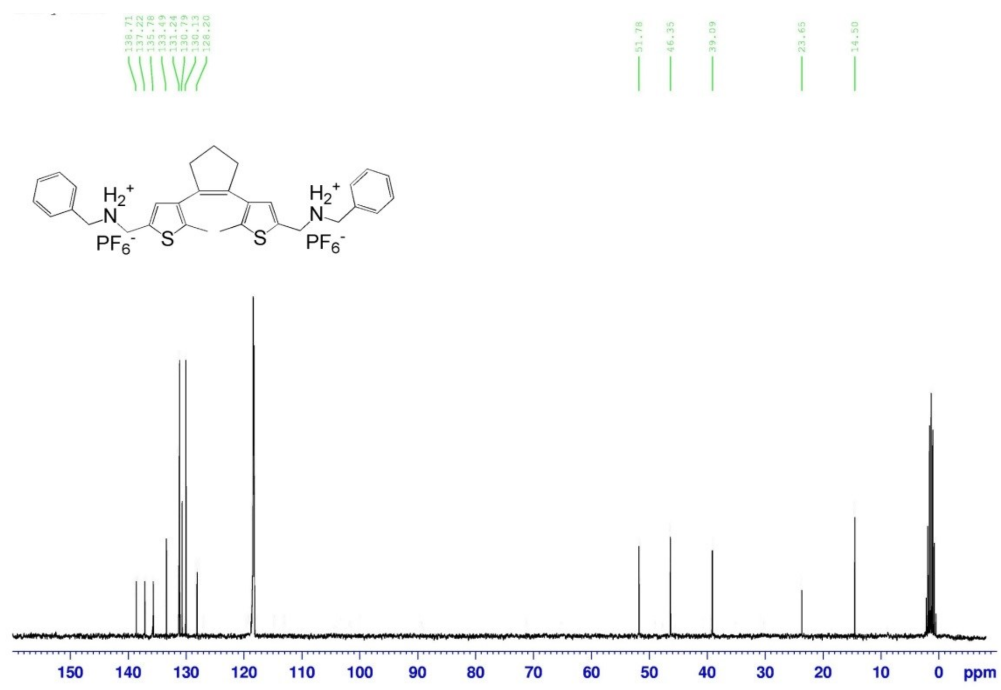


Fig. S26.2 ^{13}C-NMR of intermediate **DS**.

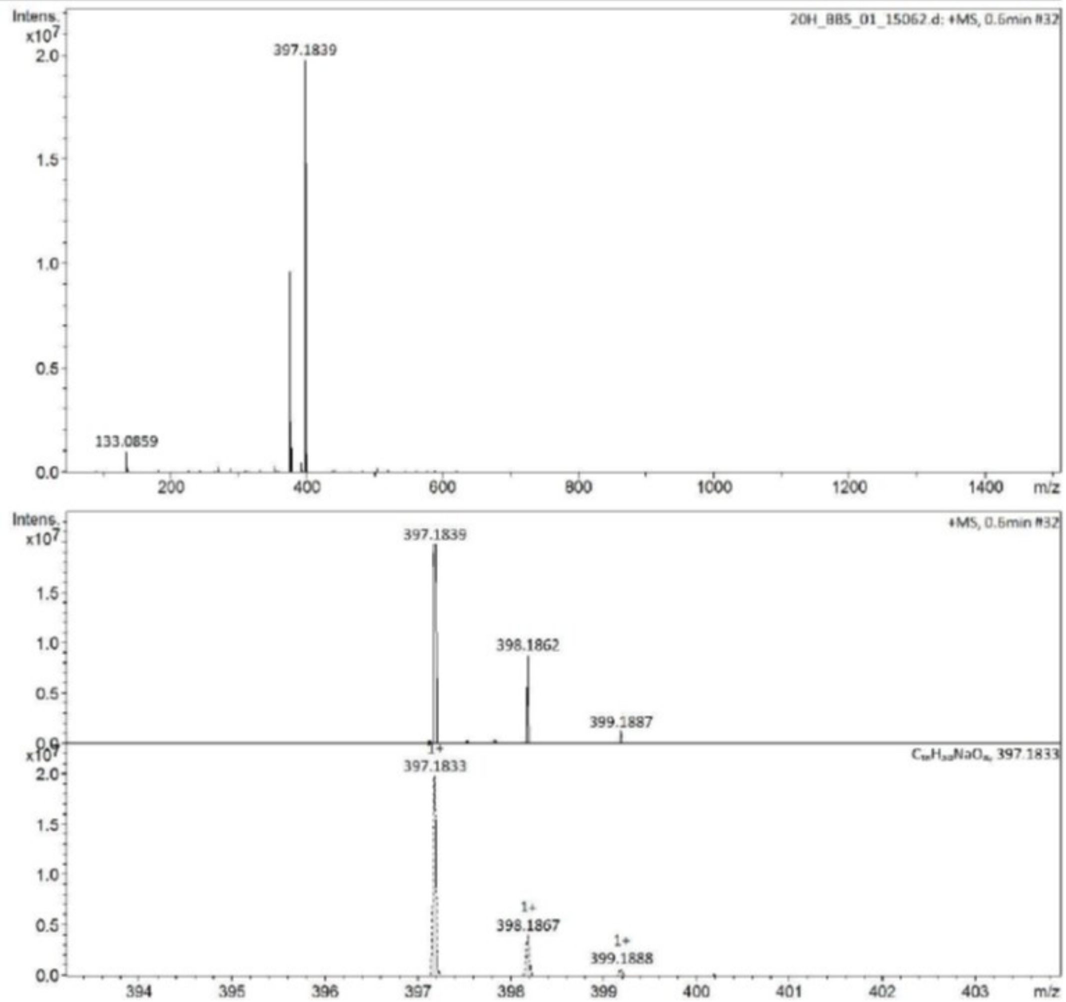
Display Report

Analysis Info

Analysis Name	D:\Data\nctu service\data\2017\20170808\20H_BB5_01_15062.d	Acquisition Date	8/8/2017 10:44:40 AM
Method	Small molecule.m	Operator	NCTU
Sample Name	20H	Instrument	impact HD 1819696.00164
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
397.1839	1	C18H30NaO8	397.1833	-1.6	121.9	1	100.00	3.5	even	ok	M+Na

Fig. S27 HRMS (ESI) data of intermediate **1**.

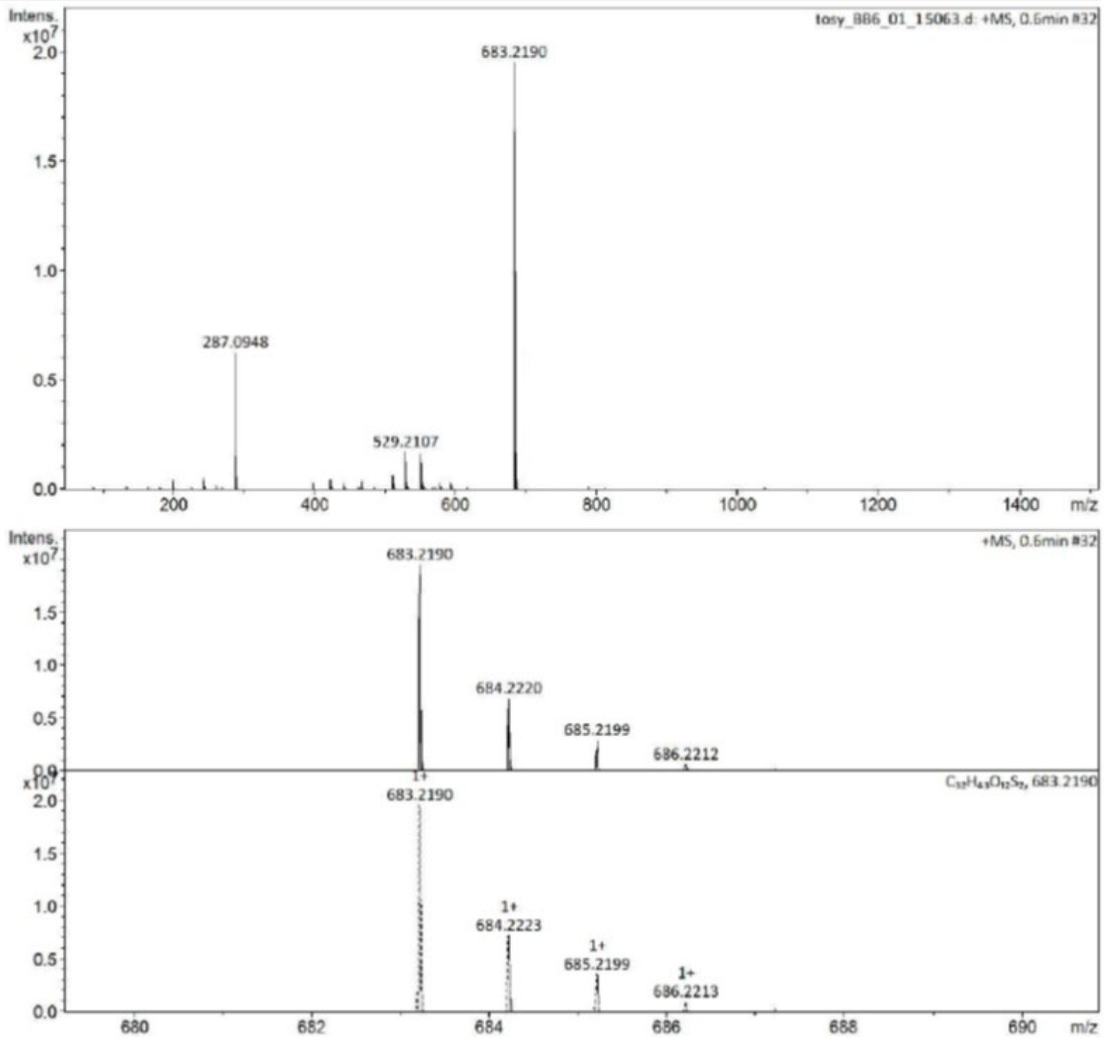
Display Report

Analysis Info

Analysis Name	D:\Data\nctu service\data\2017\20170808\tosy_BB6_01_15063.d	Acquisition Date	8/8/2017 10:48:57 AM
Method	Small molecule.m	Operator	NCTU
Sample Name	tosy	Instrument	impact HD 1819696.00164
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule	Adduct
683.2190	1	C32H43O12S2	683.2190	0.1	20.1	1	100.00	11.5	even	ok	M+H

Fig. S28 HRMS (ESI) data of intermediate **2**.

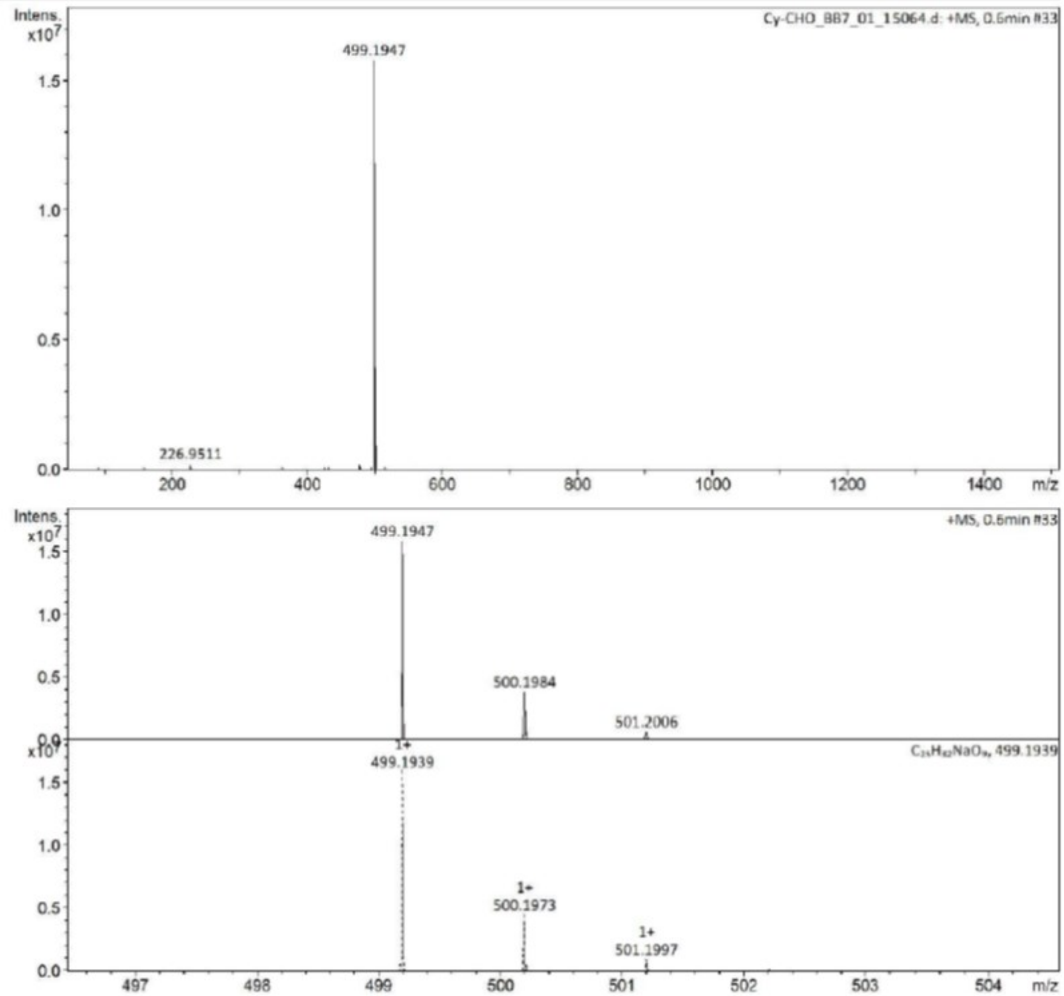
Display Report

Analysis Info

Analysis Name	D:\Data\nctu service\data\2017\20170808\Cy-CHO_BB7_01_15064.d	Acquisition Date	8/8/2017 10:53:12 AM
Method	Small molecule.m	Operator	NCTU
Sample Name	Cy-CHO	Instrument	impact HD 1819696.00164
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
499.1947	1	C25H32NaO9	499.1939	1.7	19.7	1	100.00	9.5	even	ok	M+Na

Fig. S29 HRMS (ESI) data of intermediate **3**.

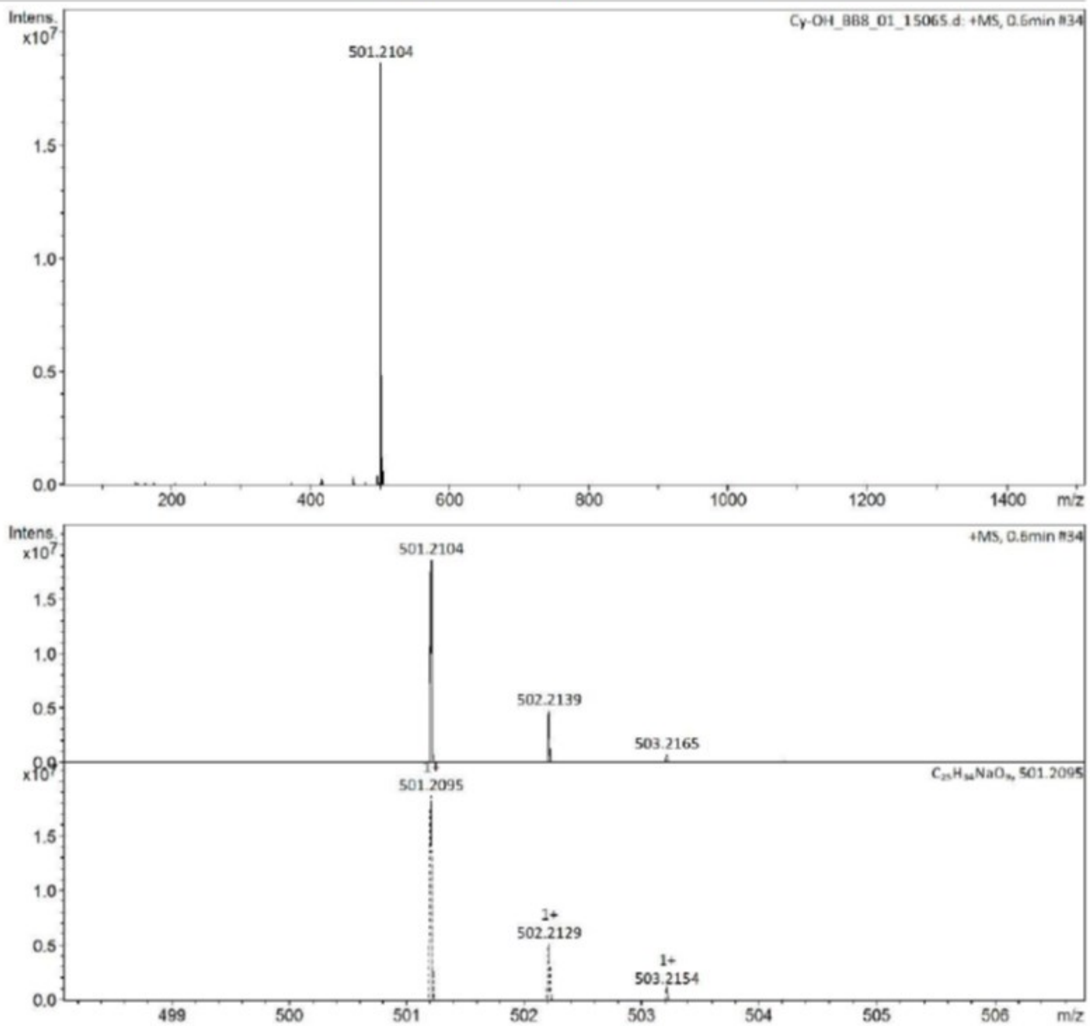
Display Report

Analysis Info

Analysis Name	D:\Data\nctu service\data\2017\20170808\Cy-OH_BB8_01_15065.d	Acquisition Date	8/8/2017 10:57:28 AM
Method	Small molecule.m	Operator	NCTU
Sample Name	Cy-OH	Instrument	impact HD 1819696.00164
Comment			

Acquisition Parameter

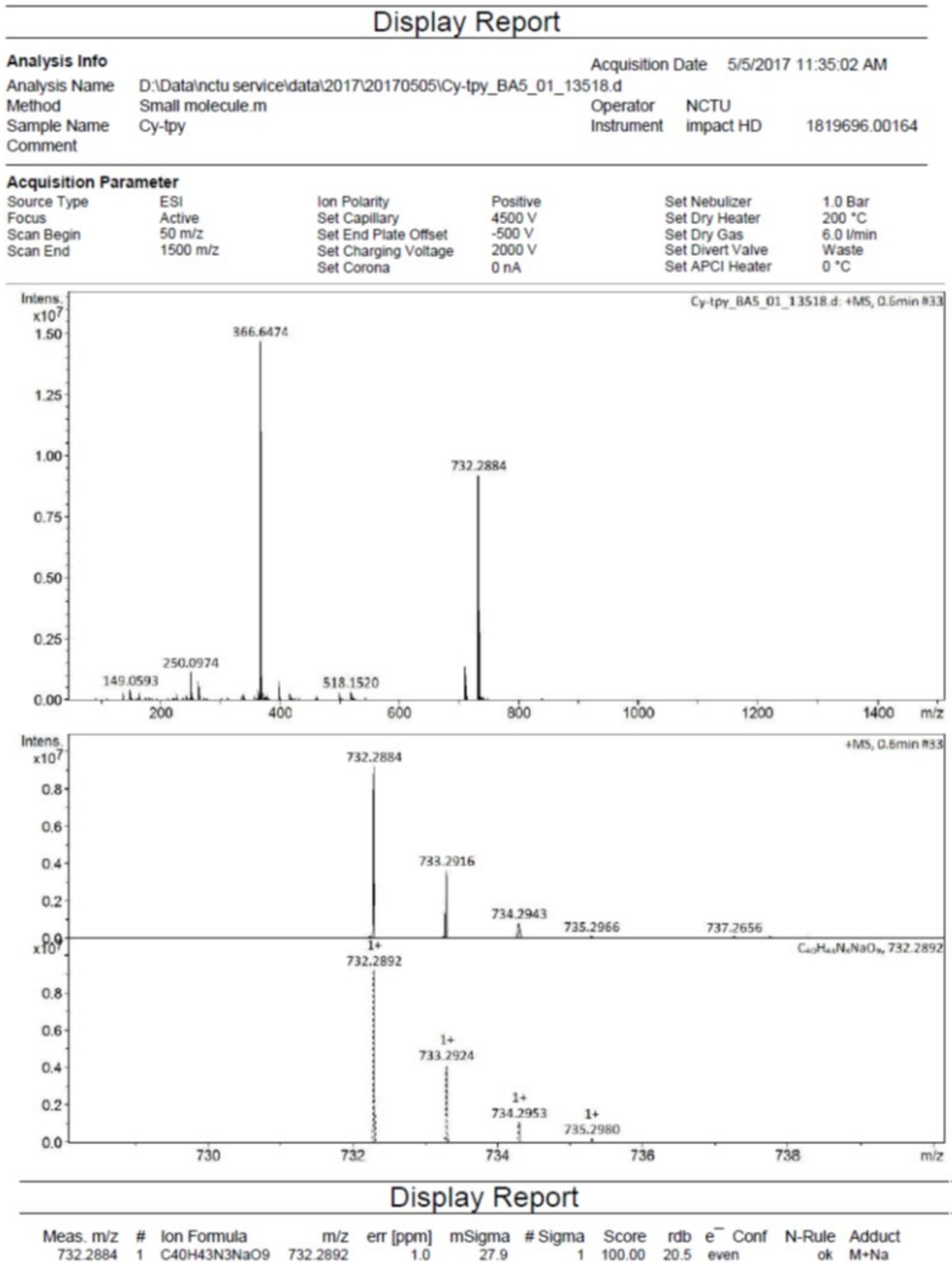
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
501.2104	1	C25H34NaO9	501.2095	1.8	10.8	1	100.00	8.5	even	ok	M+Na

Fig. S30 HRMS (ESI) data of intermediate **4**.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
732.2884	1	C40H43N3NaO9	732.2892	1.0	27.9	1	100.00	20.5	even	ok	M+Na

Fig. S31 HRMS (ESI) data of intermediate **TC**.

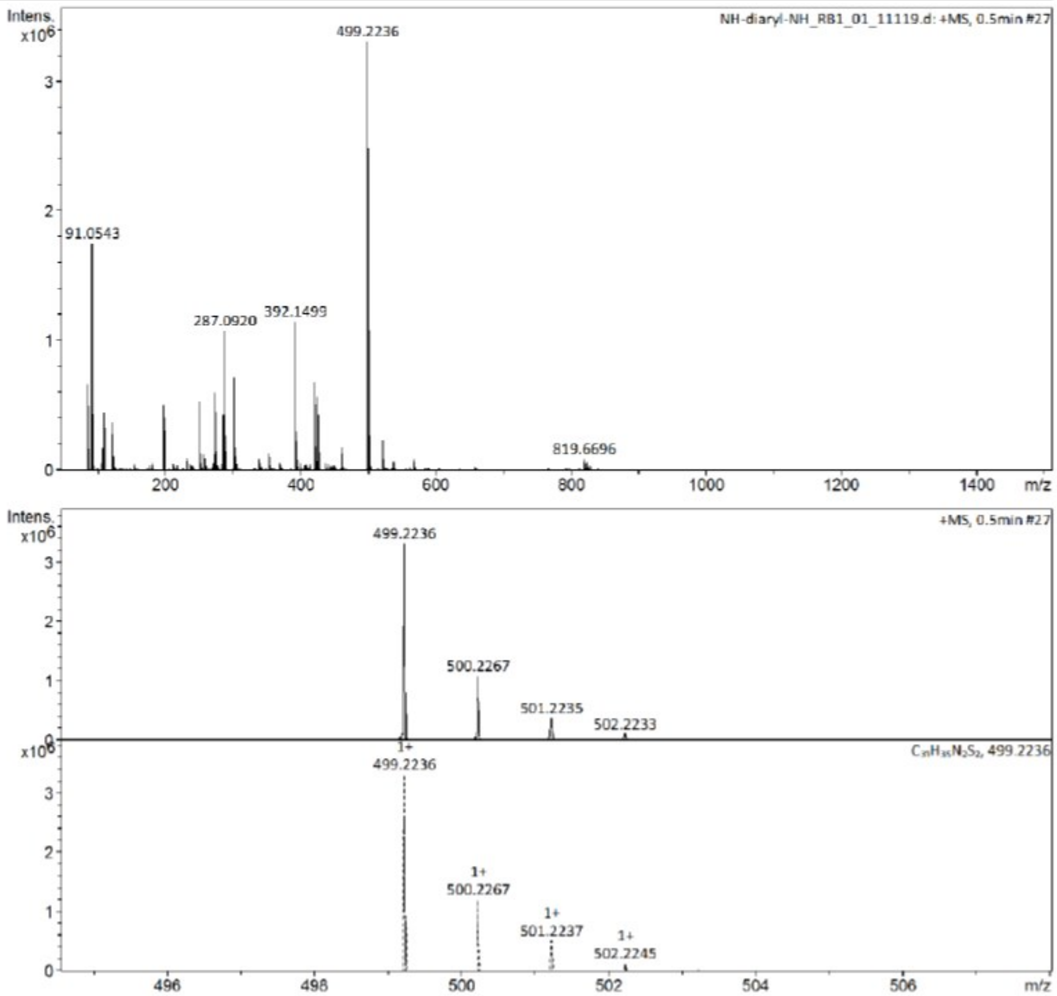
Display Report

Analysis Info

Analysis Name	D:\Data\nctu service\data\2016\20160923\NH-diaryl-NH_RB1_01_11119.d	Acquisition Date	9/23/2016 9:52:44 AM
Method	Small molecule.m	Operator	NCTU
Sample Name	NH-diaryl-NH	Instrument	impact HD 1819696.00164
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
499.2236	1	C31H35N2S2	499.2236	0.0	24.9	2	100.00	15.5	even	ok	M+H

Fig. S32 HRMS (ESI) data of intermediate **8**.

國立中興大學研發處貴重儀器使用中心
元素分析儀服務報告書

說明：

1. 本實驗數據為檢測結果，不得用於商業廣告、認證及法律証據使用。(This result is for academic use only, not to be used for any judicial or commercial advertising purpose.)
2. 儀器負責人： 鄭政峯 教授 檢測技術員： 陳宜絹。 (Instrument Director : Prof. Jen-Fon Jen Operator : I-Chuan Chen)

樣品資訊：

Web NO	SEA0001002017040171		
Department :	交大材料所		DATE
Supervisor :	林宏洲	收件日：	2017.07.21
User name :	蕭智中	分析日：	2017.08.04（NCH）
			2017.08.04（O）
			2017.08.04（S）

分析結果：

Sample code	*Weight(mg)*	*N %*	*C %*	*H %*	*O %*	*S %*	*Repeat*	*Charge*
2OH	2.023		57.70	8.08	34.22		1	$ 3,000
	2.075		57.79	8.11	34.10			
推測值			57.74	8.08	34.18			
Tosy	2.285		56.31	6.20	28.15	9.34	1	$ 3,000
	2.309		56.33	6.19	28.08	9.40		
推測值			56.29	6.20	28.12	9.39		
Cy-CHO	2.403		62.79	6.79	30.24		1	$ 3,000
	2.414		63.05	6.75	30.20			
推測值			63.01	6.77	30.22			
Cy-OH	2.678		62.80	7.14	30.06		1	$ 3,000
	2.691		62.73	7.17	30.10			
推測值			62.75	7.16	30.09			

備註：

使用儀器：Elementar vario CUBE(CHN-OS Rapid, German), Accuracy: 0.1%, Precision: 0.2%

	標準品	*N %*	*C %*	*H %*	*O %*	*S %*
★	*Acetanilid*	*10.36*	*71.09*	*6.71*		
★	*Benzoic acid*				*26.20*	
★	*Sulfanilic acid*	*8.09*	*41.60*	*4.07*		*18.50*
	Daily standard	*10.40*	*71.13*	*6.73*		
	Daily standard				*26.21*	
	Daily standard	*8.11*	*41.62*	*4.11*		*18.43*

Fig. S33 Elementary analysis (EA) data of intermediates **1**, **2**, **3**, and **4**.

國立中興大學研發處貴重儀器使用中心
元素分析儀服務報告書

說明：

1.本實驗數據為檢測結果，不得用於商業廣告、認證及法律証據使用。(This result is for academic use only, not to be used for any judicial or commercial advertising purpose.)

2.儀器負責人： 鄭政峯 教授 檢測技術員： 陳宜絹。

(Instrument Director : Prof. Jen-Fon Jen Operator : I-Chuan Chen)

樣品資訊：

Web NO	SEA0001002017040230		
Department :	交大材料所		DATE
Supervisor :	林宏洲	收件日：	2017.08.10
User name :	蕭智中	分析日：	2017.08.14（NCH）
			2017.08.14（O）
			2017.08.14（S）

分析結果：

Sample code	*Weight(mg)*	*N %*	*C %*	*H %*	*O %*	*S %*	*Repeat*	*Charge*
Diary-amine	2.410		74.66	6.88	5.59	12.87	1	$ 3,000
	2.423		74.66	6.90	5.59	12.85		
推測值			74.65	6.87	5.62	12.86		

備註:

使用儀器: Elementar vario CUBE(CHN-OS Rapid, German), Accuracy: 0.1%, Precision: 0.2%

	標準品	*N %*	*C %*	*H %*	*O %*	*S %*
★	*Acetanilid*	*10.36*	*71.09*	*6.71*		
★	*Benzoic acid*				*26.20*	
★	*Sulfanilic acid*	*8.09*	*41.60*	*4.07*		*18.50*
	Daily standard	*10.40*	*71.13*	*6.73*		
	Daily standard				*26.21*	
	Daily standard	*8.11*	*41.62*	*4.11*		*18.43*

Fig. S34 Elementary analysis (EA) data of intermediate **8**.

國立中興大學研發處貴重儀器使用中心
元素分析儀服務報告書

說明：

1.本實驗數據為檢測結果，不得用於商業廣告、認證及法律証據使用。(This result is for academic use only, not to be used for any judicial or commercial advertising purpose.)

2.儀器負責人： 鄭政峯 教授 檢測技術員： 陳宜絹。

(Instrument Director : Prof. Jen-Fon Jen Operator : I-Chuan Chen)

樣品資訊 ：

Web NO SEA0001002017040129

Department : 交大材料所

Supervisor : 林宏洲

User name : 蕭智中

DATE

收件日 ： 2017.05.03

分析日 ： 2017.05.04（NCH）
2017.05.05（O）
2017.05.12（S）

分析結果 :

Sample code	*Weight(mg)*	*N %*	*C %*	*H %*	*O %*	*S %*	*Repeat*	*Charge*
Diary-salt	2.019	3.55	47.10	4.60		8.11	1	$ 3,000
	2.025	3.53	47.08	4.61		8.12		
推測值		3.54	47.09	4.59		8.11		
Cy-tpy	2.345	5.92	67.64	6.13	20.31		1	$ 3,000
	2.339	5.94	67.64	6.10	20.32			
推測值		5.92	67.69	6.11	20.29			

備註:

使用儀器 : Elementar vario CUBE(CHN-OS Rapid, German), Accuracy: 0.1%, Precision: 0.2%

	標準品	*N %*	*C %*	*H %*	*O %*	*S %*
★	*Acetanilid*	*10.36*	*71.09*	*6.71*		
★	*Benzoic acid*				*26.20*	
★	*Sulfanilic acid*	*8.09*	*41.60*	*4.07*		*18.50*
	Daily standard	*10.40*	*71.13*	*6.73*		
	Daily standard				*26.21*	
	Daily standard	*8.11*	*41.62*	*4.11*		*18.43*

Fig. S35 Elementary analysis (EA) data of intermediates **DS** and **TC**.