Electronic Supplementary Information

Enantiopure versus Racemic Naphthalene Diimide-Based n-Type Organic Semiconductors: Effect on Charge Transport

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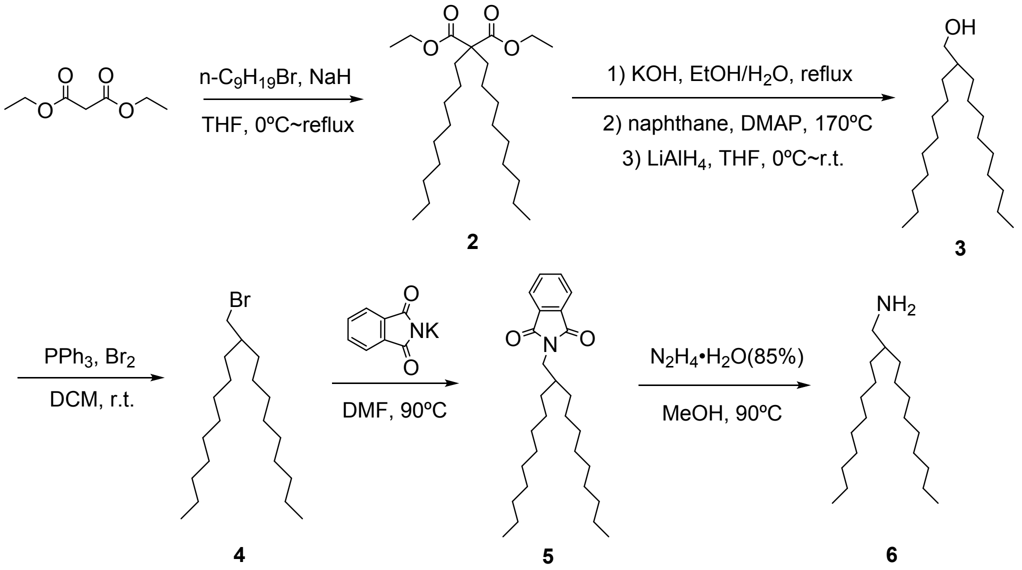
1. Synthesis and characterization.



Scheme S1

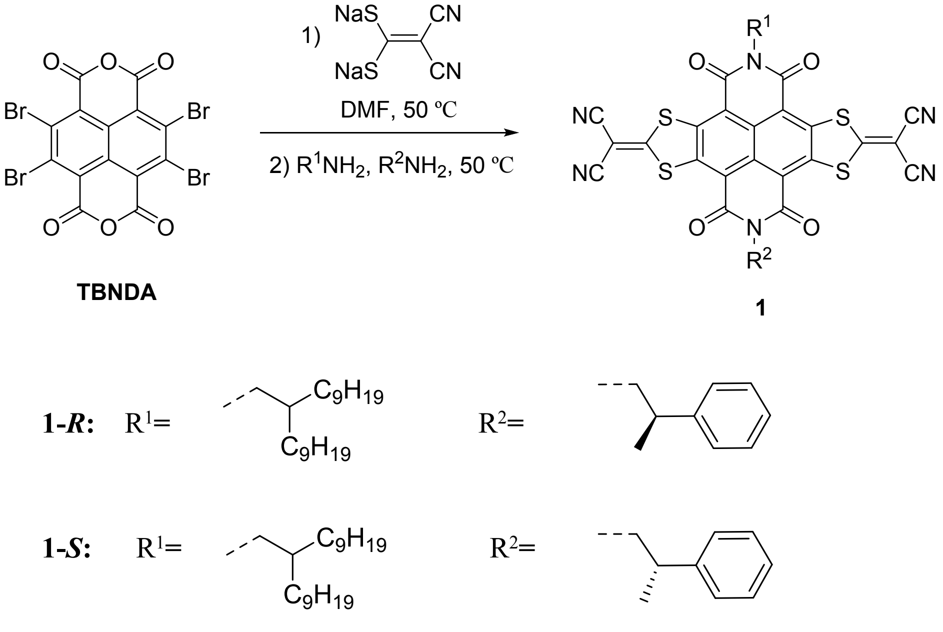
Diethyl 2,2-dinonylmalonate (2). Under a nitrogen atmosphere, to a solution of 1-Bromononane (60 mL, 0.34 mol) and NaH (16 g, 0.40 mol) in redistilled tetrahydrofuran (200 mL), diethyl malonate (17.2 mL, 0.114 mol) was added dropwise over 0.5 hour at 0 °C. The resulting mixture was warmed to room temperature and then refluxed for 12 h. Quenched the reaction by adding water dropwise at 0 °C and the mixture was poured into Saturated brine (300 mL) and extracted with ether for three times. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was then removed by rotary evaporation and the residue was purified by silica gel chromatography with ethyl acetate/petroleum ether (v/v= 1:50) as eluent to give compound **2** as a light yellow oil (36 g, yield 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.17 (q, *J* = 7.1 Hz, 4H), 1.89 – 1.81 (m, 4H), 1.14 – 1.3 (m, 34H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$**)** δ (ppm): 172.07, 60.92, 57.59, 32.14, 31.94, 29.89, 29.54, 29.38, 29.33, 23.93, 22.72, 14.15, 14.12. MS (ESI) m/z: 413.3 $(M+H)^+$. HRMS (ESI) (m/z): $(M+H)^+$ Calcd. for $C_{25}H_{49}O_4$: 413.3625; Found: 413.3625.

2-nonylundecan-1-ol (3). To a solutioin of Compound **2** (36 g, 0.087 mol) in ethanol (100 mL), 200 mL aqueous KOH (6 M) was added. The mixture was stirred and refluxed for 48 hours. After cooled to room temperature, con. HCl was added slowly at 0 °C to yield a white solid, which was filtered and then dissolved with ether. The organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo to give the crude product as a white solid that was re-dissolved in naphthane. DAMP (0.5 g, 4.1 mmol) was added to the solution and heated to 170°C for 24 h, then naphthane and water were removed by vacuum distillation. The residue that was re-dissolved in redistilled tetrahydrofuran (50 mL) was added to a solution of $LiAlH_4$ (10.0 g, 0.256 mol) in redistilled tetrahydrofuran (200 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred overnight at room temperature, which was quenched by water and dropped with aqueous HCl (3 M) to a transparent solution that was extracted with ether (200 mL) for three times and washed with water and brine, dried over Na_2SO_4. The solvent was then removed by rotary evaporation and the residue was purified by silica gel chromatography with ethyl acetate/petroleum ether (v/v= 1:5) as eluent to give compound **3** as a light yellow oil (14.2 g, yield 54.6% for 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.53 (d, *J* = 5.5 Hz, 2H), 1.45 (br, 1H), 1.27 (br, 32H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$**)** δ (ppm): 65.82, 40.62, 31.99, 31.02, 30.16, 29.74, 29.72, 29.43, 26.98, 22.77, 14.18. MS (ESI) m/z: 321.3 $(M+Na)^+$. HRMS (ESI) (m/z): $(M+NH_4)^+$ Calcd. for $C_{20}H_{46}ON$: 316.3574; Found: 316.3574.

10-(bromomethyl)nonadecane (4). To a solution of triphenylphosphine (12.6 g, 0.048 mol) in dichloromethane (60 mL), a solution of liquid bromine (2.9 ml, 0.057 mol) in dichloromethane (5 mL) was added dropwise over 0.5 h at 0 °C under anitrogen atmosphere. Then a solution of compound **2** (14.2 g, 0.048 mol) in dichloromethane (10 mL) was dropped in the mixture over 20 minutes and stirred for 24 h at room temperature. The reaction mixture was purified by silica gel column chromatography with petroleum ether as eluent and compound **4** was obtained as a transparent oil (10.0 g, yield 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.44 (d, *J* = 4.8 Hz, 2H), 1.59 (br, 1H), 1.25 – 1.41 (m, 32H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$**)** δ (ppm): 39.66, 39.65, 39.60, 32.66, 32.01, 29.89, 29.70, 29.43, 26.66, 22.78, 14.18. MS (EI) m/z: 360 M^+. HRMS (EI) (m/z): M^+ Calcd. for $C_{20}H_{41}Br$: 360.2392; Found: 360.2383.

2-(2-nonylundecyl)isoindoline-1,3-dione (5). Under a nitrogen atmosphere, a solution of compound 3 (10 g, 0.028 mol) and potassium phthalimide (6.2 g, 0.033 mol) in DMF (20 mL) was stirred for 24 h at 90 °C. After cooled to room temperature, the reaction mixture was poured into 200 mL of water. Dichloromethane was used to extract the product, and the combined organic solution was washed with aqueous KOH (0.2 M), water, brine and dried over anhydride Na_2SO_4. The solvent was removed by rotary evaporation, and the residue was purified by silica gel chromatography with ethyl acetate/petroleum ether (v/v = 1/10) as eluent. Compound **5** was obtained as a transparent oil (11 g, yield 93%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.57 (d, *J* = 7.3 Hz, 2H), 1.88 (br, 1H), 1.22 – 1.37 (m, 32H), 0.87 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$**)** δ (ppm): 168.77, 133.87, 132.20, 123.21, 42.38, 37.09, 31.98, 31.54, 30.03, 29.67, 29.41, 26.36, 22.76, 14.19. MS (ESI) m/z: 428.3 (M+H)$^+$. HRMS (ESI) (m/z): (M+H)$^+$ Calcd. for $C_{28}H_{46}O_2N$: 428.3523; Found: 428.3523.

2-nonylundecan-1-amine (6). Compound **5** (11 g, 0.026 mol), hydrazine hydrate (hydrazine, 80 %) (4 g, 0.08 mol) and 100 mL methanol were mixed and refluxed for 12 hours. The methanol was removed by rotary evaporation, and the residue was added to dichloromethane (100 mL). The resulting clear solvent was collected by filtration, and washed with 10 % KOH, water and dried over anhydride Na_2SO_4. The solvent was removed by rotary evaporation and afforded a light yellow oil as product **6** which was used in the next synthesis without further purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.60 (d, *J* = 4.0 Hz, 2H), 1.21 – 1.34 (m, 33H), 1.06 (s, 2H), 0.88 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$**)** δ (ppm): 45.32, 41.02, 31.99, 31.62, 30.18, 29.76, 29.72, 29.43, 26.88, 22.76, 14.17. MS (ESI) m/z: 298.3 (M+H)$^+$. HRMS (ESI) (m/z): (M+H)$^+$ Calcd. for $C_{20}H_{44}N$: 298.3468; Found: 298.3469.



Scheme S2. Synthesis of **1-*R*** and **1-*S***

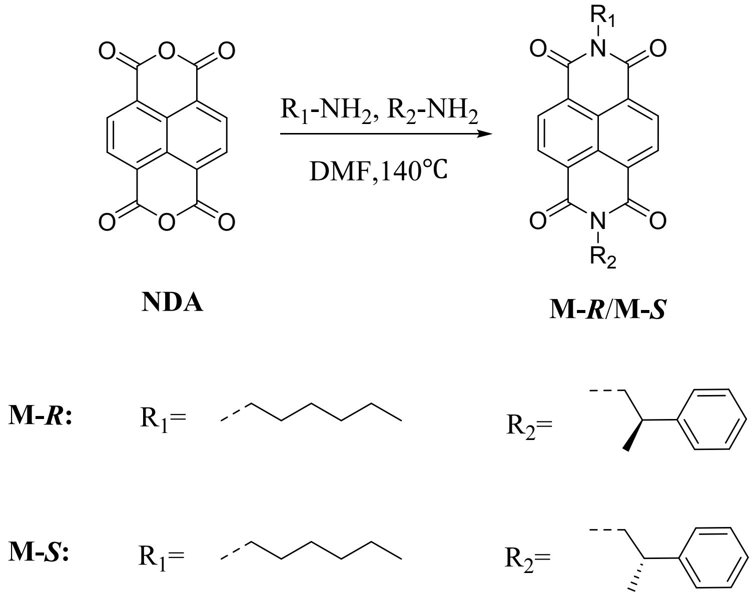
1-*R* and **1-*S*** were synthesized according to the present procedures of our group.

(*R*)-2,2'-(2-(2-nonylundecyl)-1,3,7,9-tetraoxo-8-(2-phenylpropyl)-1,2,3,7,8,9-hexahydro-

[1,3]dithiolo[4',5':5,6]benzo[1,2,3,4-lmn][1,3]dithiolo[4,5-f][3,8]phenanthroline-5,11-diylidene)dimalononitrile (1-*R*). A solution of TBNDA (500 mg, 0.856 mmol) and sodium 1,1-dicyanoethene-2,2-dithiolate (480 mg, 2.6 mmol) in DMF (45 mL) was stirred at 50 ºC for 1.5 hour. Then compound **6** (306 mg, 1.03 mmol) and (R)-2-phenylpropan-1-amine (197 mg, 1.45 mmol) were added to the reaction mixture. The resulting purple black solution was stirred at 55 ºC for 10 hours, and water (300 mL) was added to quench the reaction. The product was extracted with CH_2Cl_2 (3 × 150 mL), and the combined organic solution was washed with water, brine, and dried over anhydrous Na_2SO_4. After the solvent was removed by rotary evaporation, the crude product was purified by silica gel column chromatography with CH_2Cl_2 as eluent. Compound **1-*R*** was obtained as a brownish red solid (85 mg, yield 11%). M.p. > 300 ºC. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.26 – 7.08 (m, 5H), 4.45 – 4.33 (m, 2H), 4.14 (d, J = 7.3 Hz, 2H), 3.45 – 3.35 (m, 1H), 1.94 (br, 1H), 1.55 – 1.12 (m, 35H), 0.79 (t, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) δ (ppm): 182.75, 162.04, 161.76, 145.25, 142.43, 128.85, 127.59, 127.38, 125.16, 117.95, 117.64, 112.12, 70.92, 48.69, 46.66, 38.05, 36.66, 32.10, 31.57, 30.23, 29.92, 29.85, 29.80, 29.57, 26.41, 22.95, 18.74, 14.47. Anal. Calcd. For $C_{51}H_{52}N_6O_4S_4$: C, 65.08; H, 5.57; N, 8.93; S, 13.62. Found: C, 65.34; H, 5.65; N, 8.66; S, 13.58.

(*S*)-2,2'-(2-(2-nonylundecyl)-1,3,7,9-tetraoxo-8-(2-phenylpropyl)-1,2,3,7,8,9-hexahydro-[1,3]dithiolo[4',5':5,6]benzo[1,2,3,4-lmn][1,3]dithiolo[4,5-f][3,8]phenanthroline-5,11-diylidene)dimalononitrile (1-*S*). A solution of TBNDA (500 mg, 0.856 mmol) and sodium 1,1-dicyanoethene-2,2-dithiolate (480 mg, 2.6 mmol) in DMF (45 mL) was stirred at 50 ºC for 1.5 hour. Then compound **6** (306 mg, 1.03 mmol) and (S)-2-phenylpropan-1-amine (197 mg, 1.45 mmol) were added to the reaction mixture. The resulting purple black solution was stirred at 55 ºC for 10 hours, and water (300 mL) was added to quench the reaction. The product was extracted with CH_2Cl_2 (3 × 150 mL), and the combined organic solution was washed with water, brine, and dried over anhydrous Na_2SO_4. After the solvent was removed by rotary evaporation, the crude product was purified by silica gel column chromatography with CH_2Cl_2 as eluent. Compound **1-*S*** was obtained as a brownish red solid (90 mg, yield 12%). M.p. > 300 ºC. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm): 7.26 – 7.08 (m, 5H), 4.45 – 4.33 (m, 2H), 4.14 (d, J = 7.3 Hz, 2H), 3.45 – 3.35 (m, 1H), 1.94 (br, 1H), 1.55 – 1.12 (m, 35H), 0.79 (t, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) δ (ppm):

182.75, 162.04, 161.76, 145.25, 142.43, 128.85, 127.59, 127.38, 125.16, 117.95, 117.64, 112.12, 70.92, 48.69, 46.66, 38.05, 36.66, 32.10, 31.57, 30.23, 29.92, 29.85, 29.80, 29.57, 26.41, 22.95, 18.74, 14.47. Anal. Calcd. For $C_{51}H_{52}N_6O_4S_4$: C, 65.08; H, 5.57; N, 8.93; S, 13.62. Found: C, 65.35; H, 5.79; N, 8.60; S, 13.46.



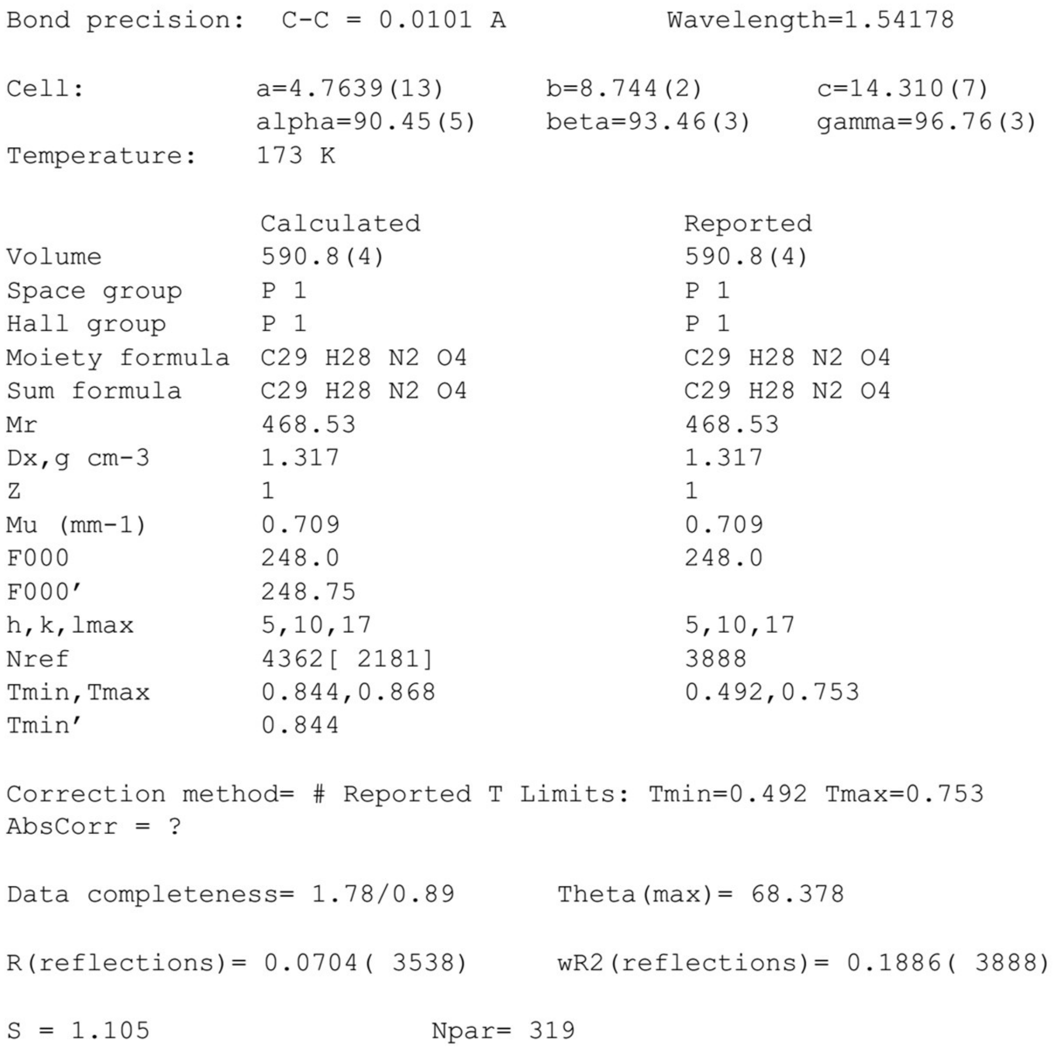
Scheme S3. Synthesis of **M-*R*** and **M-*S***

(*R*)-2-hexyl-7-(2-phenylpropyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (M-*R*). n-hexylamine (240 mg, 2.25 mmol) and (R)-2-phenylpropan-1-amine (315 mg, 2.25 mmol) were added to the solution of NDA (500 mg, 0.856 mmol) in DMF (20 mL) under a nitrogen atmosphere. The mixture was stirred at 140 ºC overnight. Water (100 mL) was added to quench the reaction and the product was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic solution was washed with water, brine, and dried over anhydrous Na_2SO_4. After the solvent was removed by rotary evaporation, the crude product was purified by silica gel column chromatography with CH_2Cl_2:PE = 3:1 as eluent. Compound **M-*R*** was obtained as a pink solid (200 mg, yield 23%). M.p. = 228 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.71 (q, J = 7.6 Hz, 4H), 7.38 – 7.07 (m, 5H), 4.37 (d, J = 7.9 Hz, 2H), 4.23 – 4.13 (t, J = 7.6 Hz, 2H), 3.44 (m, 1H), 1.73 (p, J = 8.0, 7.5 Hz, 2H), 1.39 (br, 9H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.99, 162.87, 143.52, 131.06, 130.98, 128.49, 127.52, 126.81, 126.73, 126.72, 126.71, 126.45, 47.28, 41.05, 38.14, 31.57, 28.10, 26.82, 22.63, 18.72, 14.14. Anal. Calcd. For $C_{51}H_{52}N_6O_4S_4$: C, 65.08; H, 5.57; N, 8.93; S, 13.62. Found: C, 65.35; H, 5.79; N, 8.60; S, 13.46. MS (MALDI) m/z: 469.2 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M)^+$ Calcd. for $C_{29}H_{28}N_2O_4$: 468.2044; Found: 468.2032.

(*S*)-2-hexyl-7-(2-phenylpropyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (M-*S*). n-hexylamine (240 mg, 2.25 mmol) and (S)-2-phenylpropan-1-amine (315 mg, 2.25 mmol) were added to the solution of NDA (500 mg, 0.856 mmol) in DMF (20 mL) under a nitrogen atmosphere. The mixture was stirred at 140 ºC overnight. Water (100 mL) was added to quench the reaction and the product was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic solution was washed with water, brine, and dried over anhydrous Na_2SO_4. After the solvent was removed by rotary evaporation, the crude product was purified by silica gel column chromatography with CH_2Cl_2:PE = 3:1 as eluent. Compound **M-*S*** was obtained as a pink solid (200 mg, yield 23%). M.p. = 228 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70 (q, *J* = 7.6 Hz, 4H), 7.35 – 7.09 (m, 5H), 4.36 (d, *J* = 7.8 Hz, 2H), 4.23 – 4.11 (t, *J* = 7.6 Hz, 2H), 3.43 (m, 1H), 1.72 (p, *J* = 8.0, 7.6 Hz, 2H), 1.49 – 1.26 (br, 9H), 0.95 – 0.82 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.01, 162.89, 143.53, 131.06, 130.99, 128.49, 127.52, 126.81, 126.75, 126.74, 126.73, 126.47, 47.28, 41.06, 38.15, 31.57, 28.11, 26.82, 22.63, 18.73, 14.13. MS (MALDI) m/z: 469.1 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M)^+$ Calcd. for $C_{29}H_{28}N_2O_4$: 468.2044; Found: 468.2056.

2. X-ray Crystallographic data

Table S1. Crystal data and structure refinement for **M-*S***.



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Bond precision:  C-C = 0.0101 A          Wavelength=1.54178

Cell:            a=4.7639(13)      b=8.744(2)       c=14.310(7)
                 alpha=90.45(5)    beta=93.46(3)    gamma=96.76(3)
Temperature:     173 K

                 Calculated                    Reported
Volume           590.8(4)                      590.8(4)
Space group      P 1                           P 1
Hall group       P 1                           P 1
Moiety formula   C29 H28 N2 O4                 C29 H28 N2 O4
Sum formula      C29 H28 N2 O4                 C29 H28 N2 O4
Mr               468.53                        468.53
Dx,g cm-3        1.317                         1.317
Z                1                             1
Mu (mm-1)        0.709                         0.709
F000             248.0                         248.0
F000’            248.75
h,k,lmax         5,10,17                       5,10,17
Nref             4362[ 2181]                   3888
Tmin,Tmax        0.844,0.868                   0.492,0.753
Tmin’            0.844

Correction method= # Reported T Limits: Tmin=0.492 Tmax=0.753
AbsCorr = ?

Data completeness= 1.78/0.89      Theta(max)= 68.378

R(reflections)= 0.0704( 3538)     wR2(reflections)= 0.1886( 3888)

S = 1.105                  Npar= 319
```

Table 2. Crystal data and structure refinement for **M-*R***

Empirical formula	C29 H28 N2 O4	
Formula weight	468.53	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 4.8296(2) Å	a= 89.9140(10)°
	b = 8.7435(3) Å	b= 86.0960(10)°
	c = 14.4477(5) Å	g = 82.5490(10)°
Volume	603.52(4) Å^3	
Z	1	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.694 mm^{-1}	
F(000)	248	
Crystal size	0.190 x 0.150 x 0.100 mm^3	
Theta range for data collection	5.102 to 66.493°.	
Index ranges	-5<=h<=5, -10<=k<=10, -17<=l<=17	
Reflections collected	17553	
Independent reflections	4116 [R(int) = 0.0349]	
Completeness to theta = 67.679°	95.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5986	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4116 / 20 / 332	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1536	
R indices (all data)	R1 = 0.0541, wR2 = 0.1564	
Absolute structure parameter	-0.05(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.184 and -0.168 e.Å^{-3}	

3. Thermodynamic data of 1-*R*, 1-*S* and 1-*rac*.

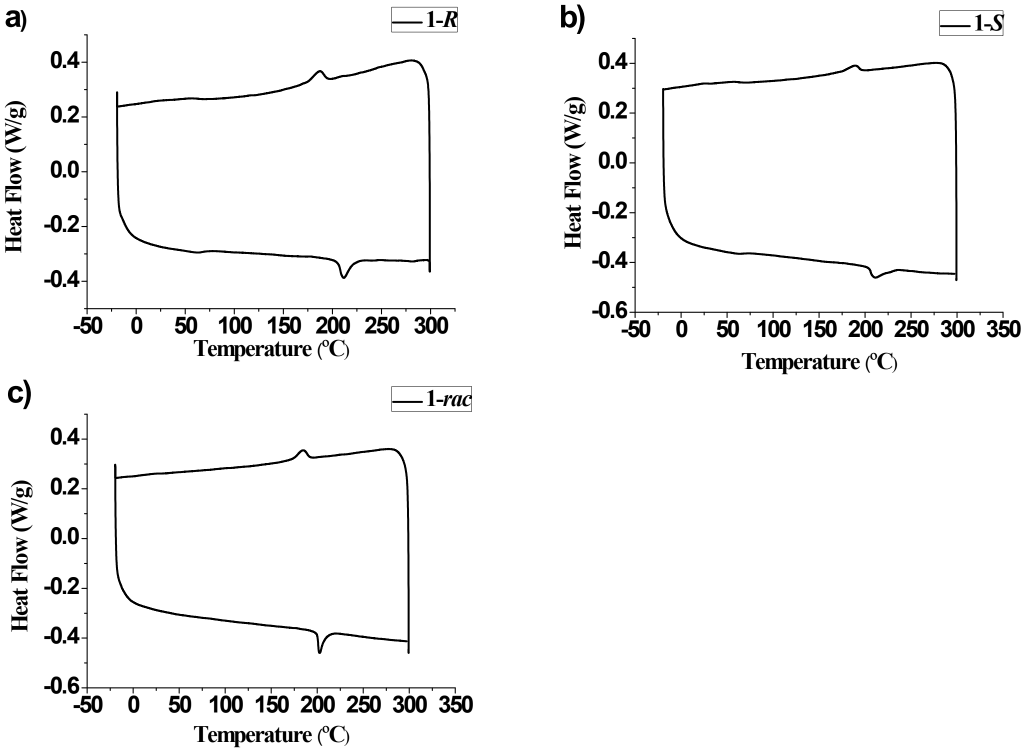


Fig. S1 a)-c) DSC measurements for **1-*R***, **1-*S*** and **1-*rac***.

4. Characteristics of OFET devices of 1-*R*, 1-*S* and 1-*rac*.

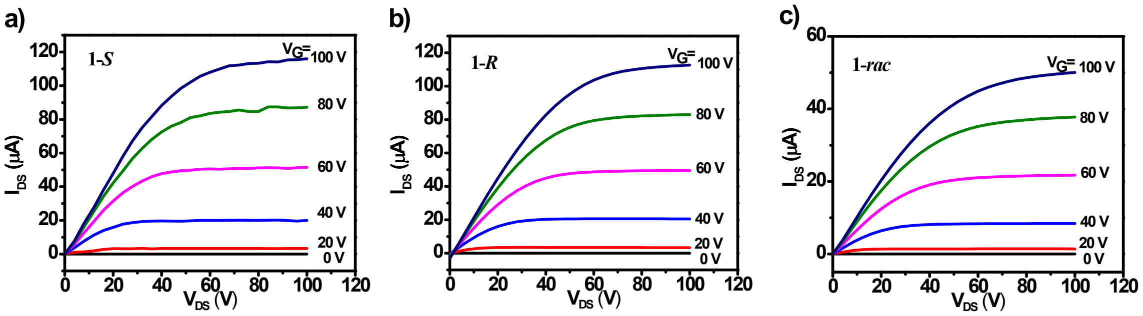


Fig. S2 a)-c) output characteristics for **1-*S***, **1-*R*** and **1-*rac*** of OFETs fabricated by as-cast films.

Table S3. Average (Maximum) electron mobilites (μ_e), current on/off ratios (I_{on}/I_{off}), and threshold voltages (V_T) for thin films of **1-*R***, **1-*S*** and **1-*rac*** fabricated by spin coating on OTS-treated Si/SiO$_2$ substrates.

	As-cast			**annealed at 80 °C**			**annealed at 160 °C**		
	μ_e^a(cm^2 V^{-1} s^{-1})	$I_{on}/I_{off}{}^a$	V_T^a (V)	μ_e^a(cm^2 V^{-1} s^{-1})	$I_{on}/I_{off}{}^a$	V_T^a (V)	μ_e^a(cm^2 V^{-1} s^{-1})	$I_{on}/I_{off}{}^a$	V_T^a (V)
1-*R*	0.54 (0.61)	10^5-10^6	9.2-10.8	0.75 (0.85)	10^5-10^6	9.1-9.5	0.97 (1.07)	10^5-10^6	4.5-5.3
1-*S*	0.60 (0.67)	10^5-10^6	8.4-9.6	0.80 (0.90)	10^5-10^6	7.6-8.2	0.98 (1.01)	10^5-10^6	4.2-5.2
1-*rac*	0.15 (0.19)	10^4-10^5	6.5-9.2	0.25 (0.27)	10^4-10^5	5.9-7.0	0.42 (0.46)	10^4-10^5	3.8-4.6

[a] The average values for every material were obtained from at least 18 devices and all devices were measured in nitrogen.

5. GIWAXS data of 1-*R*, 1-*S* and 1-*rac*.

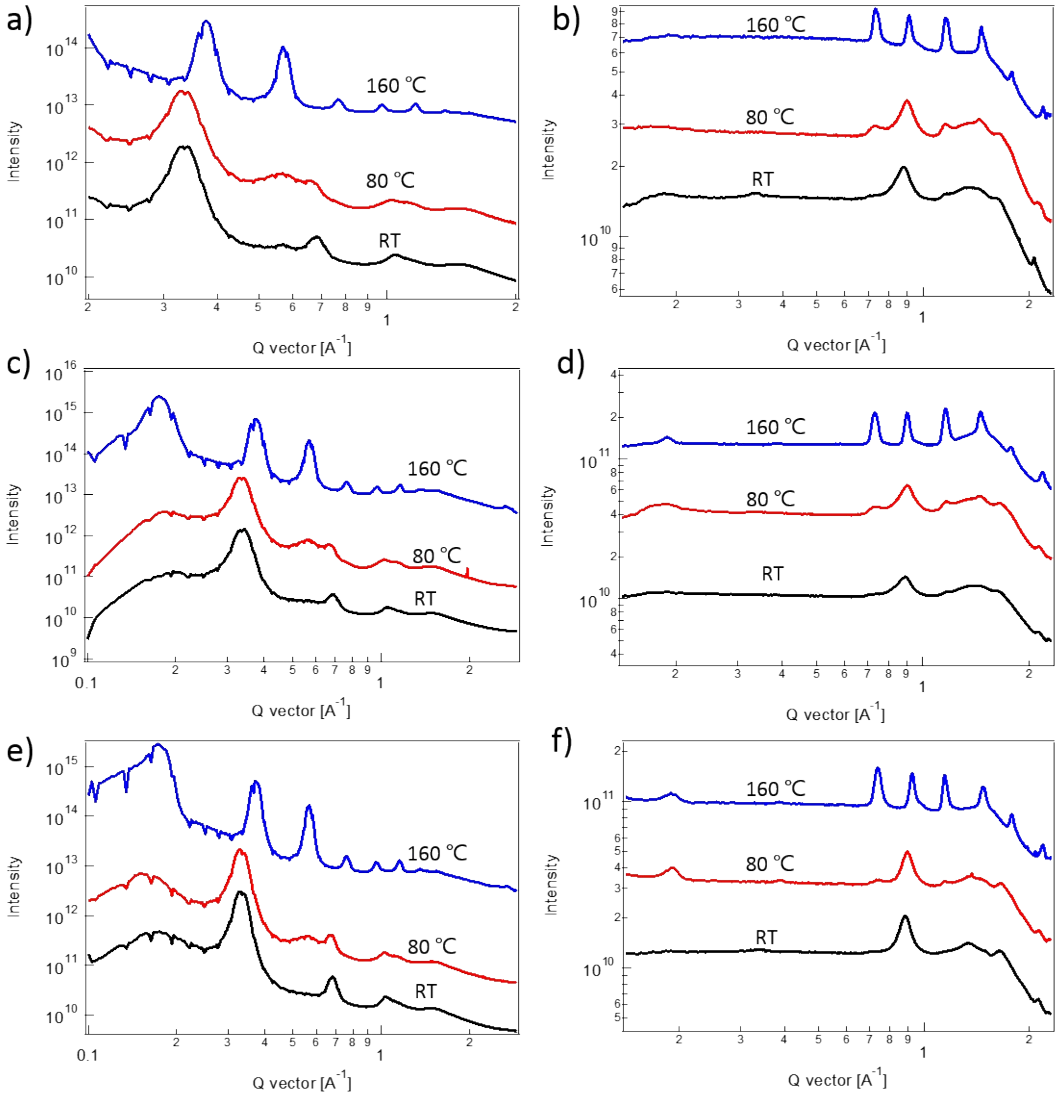


Fig. S3 1D-GIXRD integrated cake slices from 2D GIWAXS diffraction pattern. a)-b) Out-of-plane and In-plane diffractogram profiles of **1-*R***. c)-d) Out-of-plane and In-plane diffractogram profiles of **1-*S***. e)-f) Out-of-plane and In-plane diffractogram profiles of **1-*rac*.**

6. NMR, IR and MS spectra

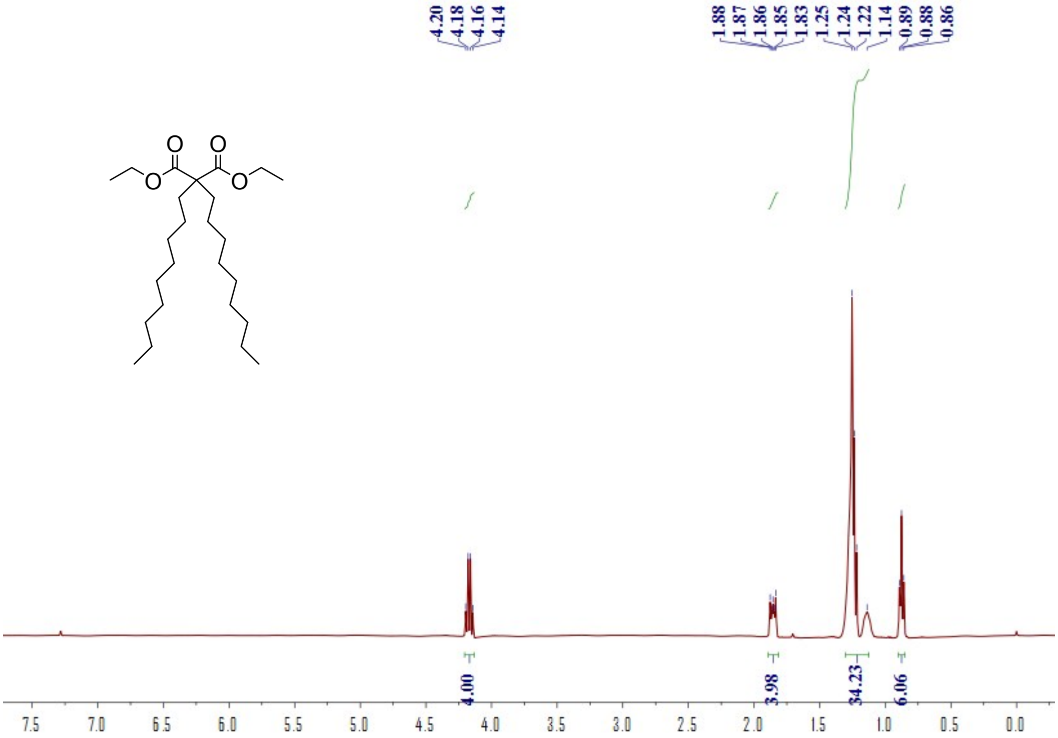


Figure S5. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

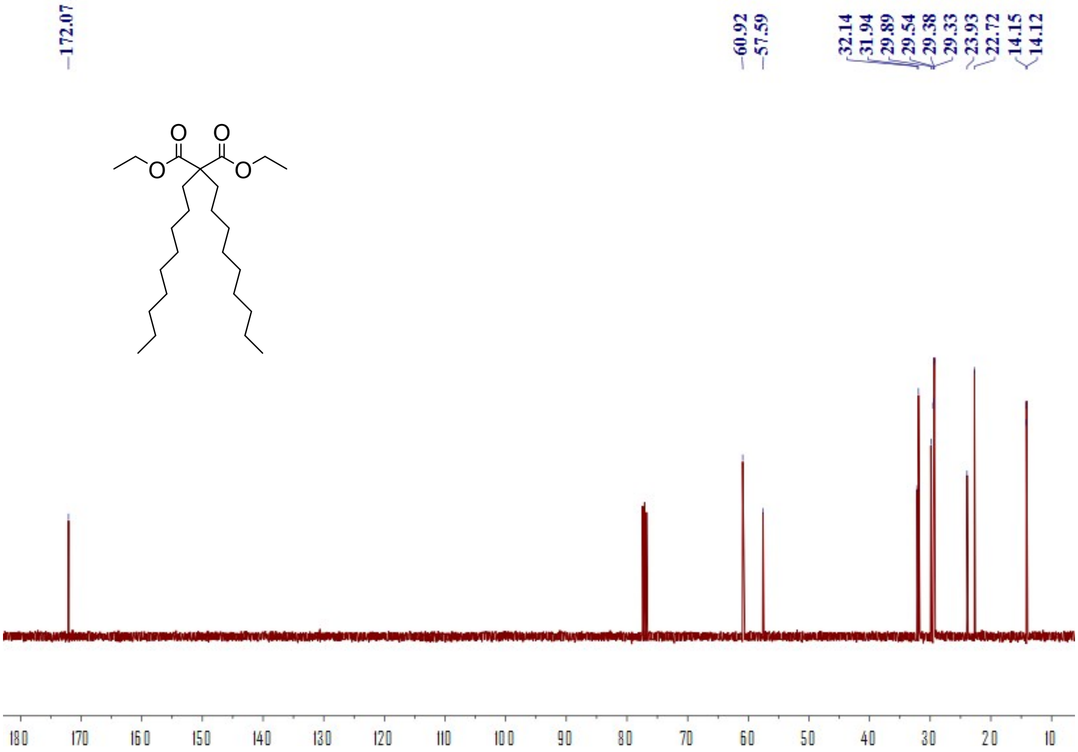


Figure S6. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$).

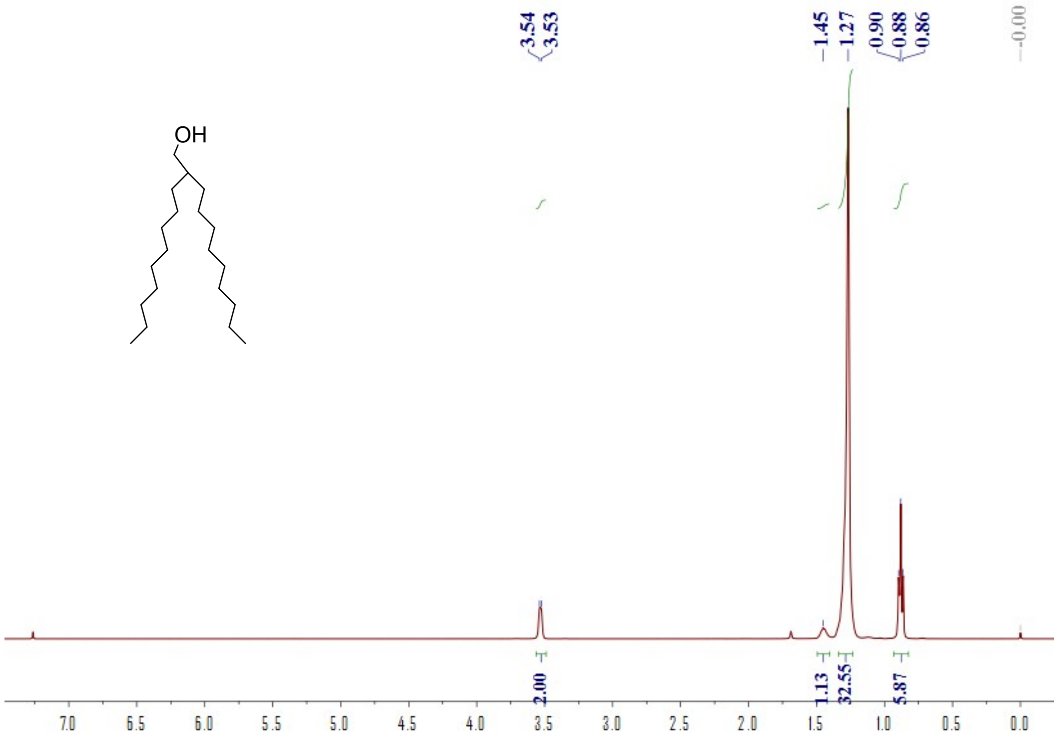


Figure S7. ^{1}H NMR spectrum of **3** (400 MHz, CDCl$_3$).

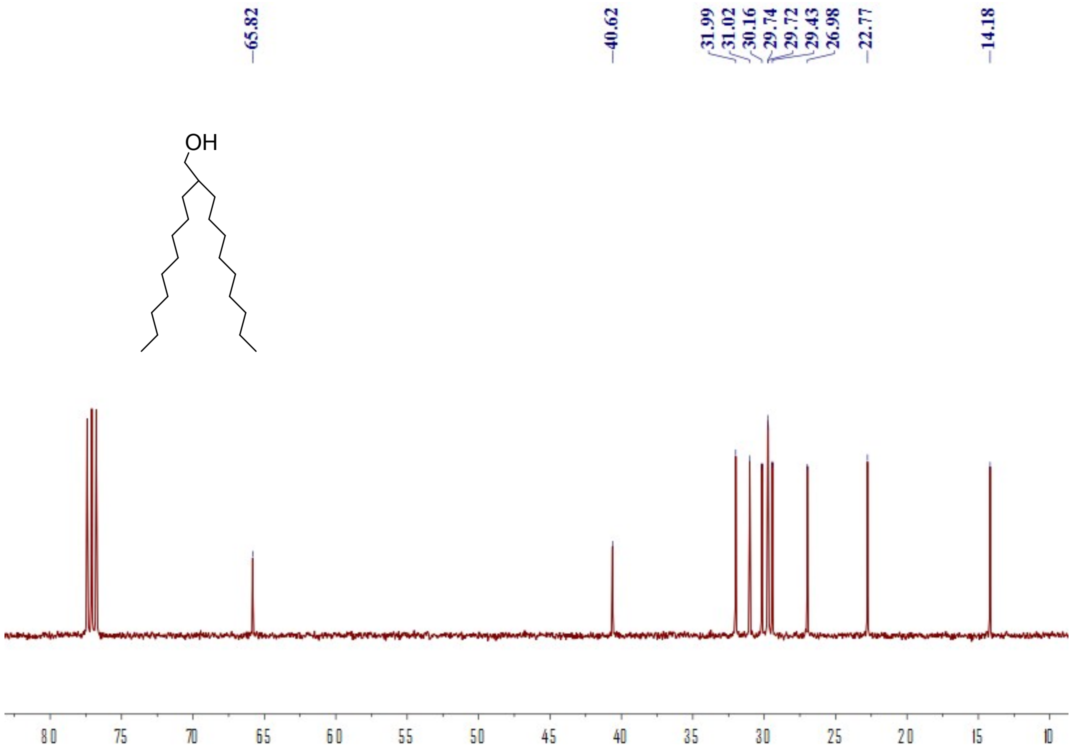


Figure S8. ^{13}C NMR spectrum of **3** (100 MHz, CDCl$_3$).

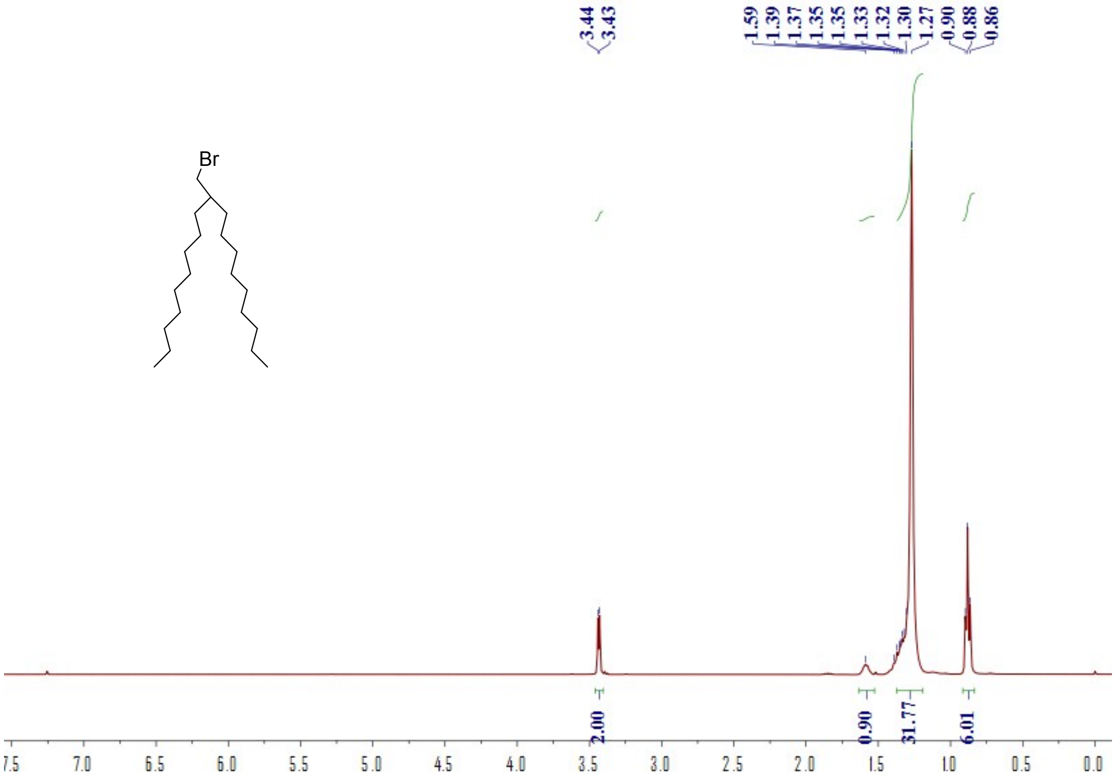


Figure S9. ${}^{1}H$ NMR spectrum of **4** (400 MHz, $CDCl_3$).

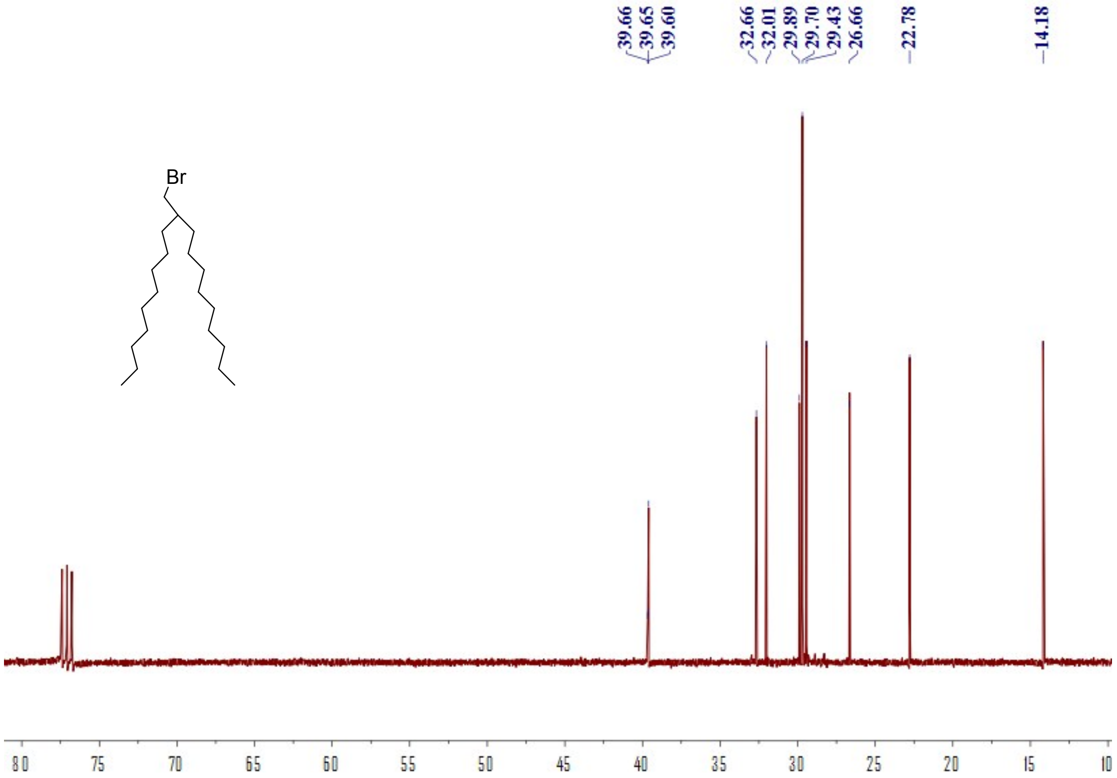


Figure S10. ${}^{13}C$ NMR spectrum of **4** (100 MHz, $CDCl_3$).

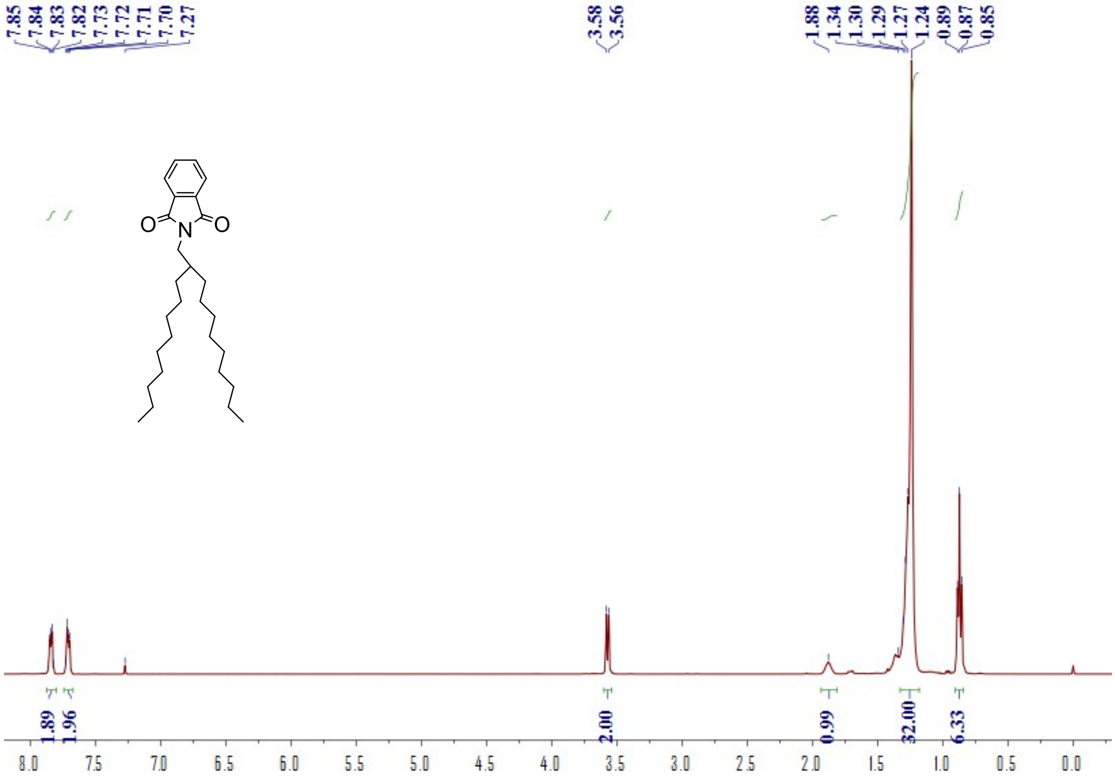


Figure S11. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

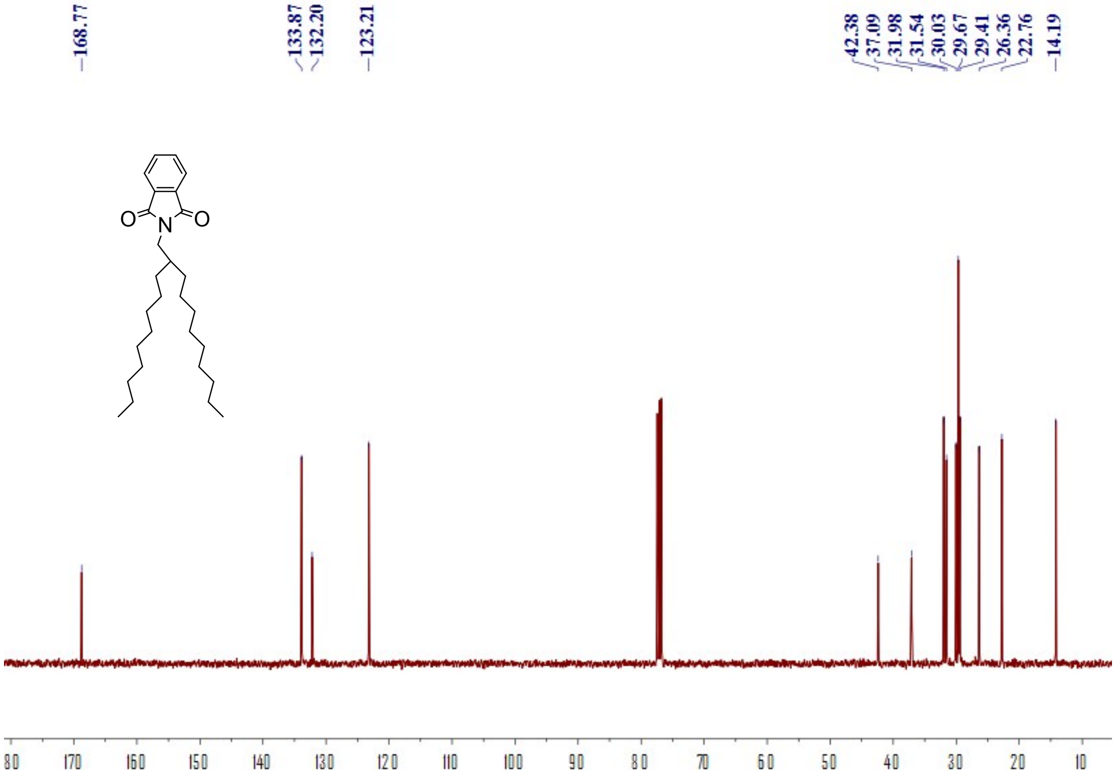


Figure S12. ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$).

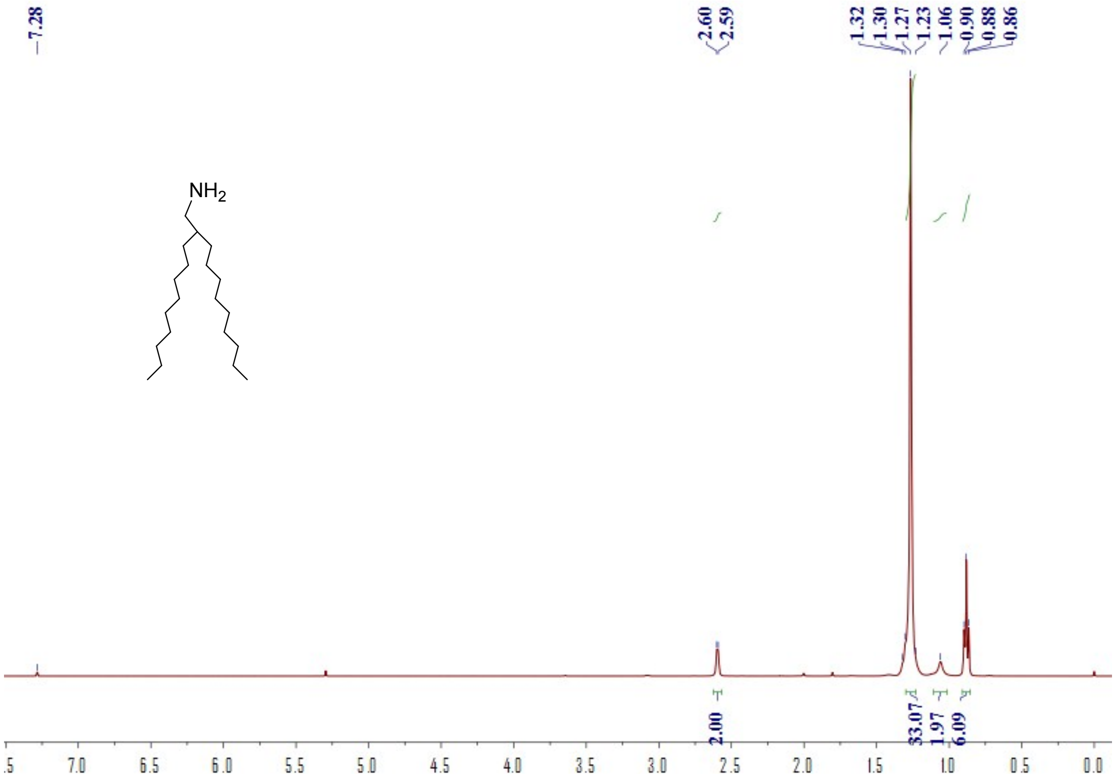


Figure S13. ^{1}H NMR spectrum of **6** (400 MHz, CDCl$_3$).

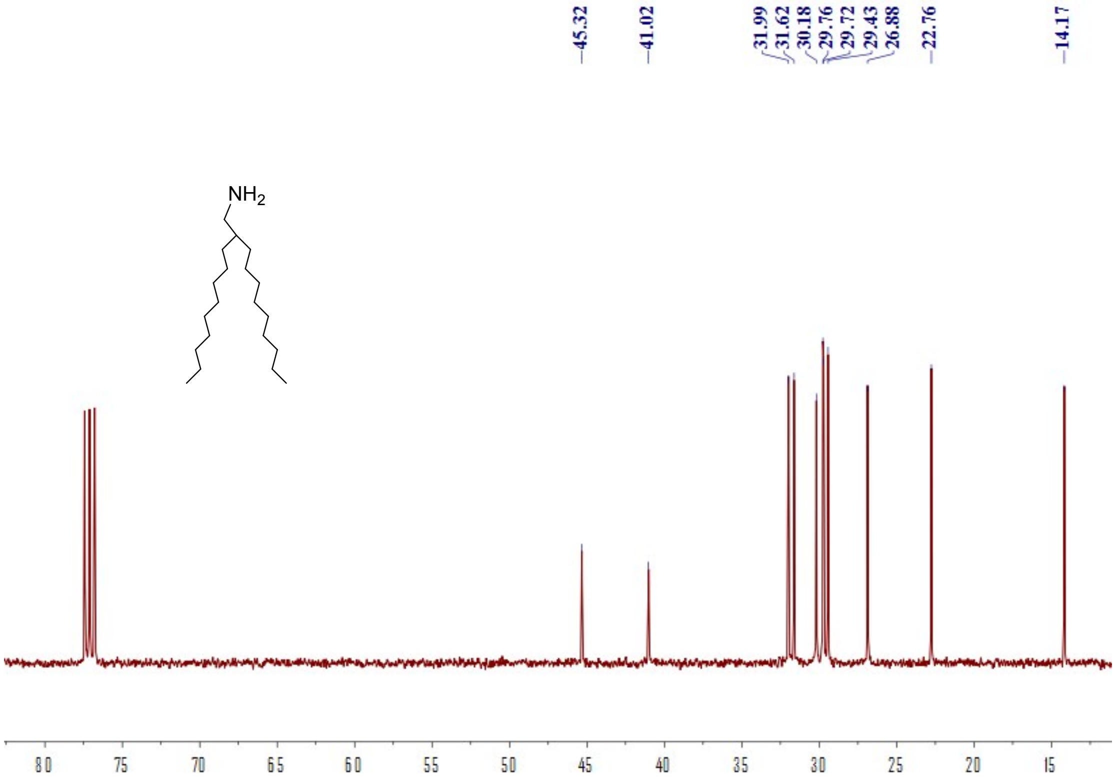


Figure S14. ^{13}C NMR spectrum of **6** (100 MHz, CDCl$_3$).

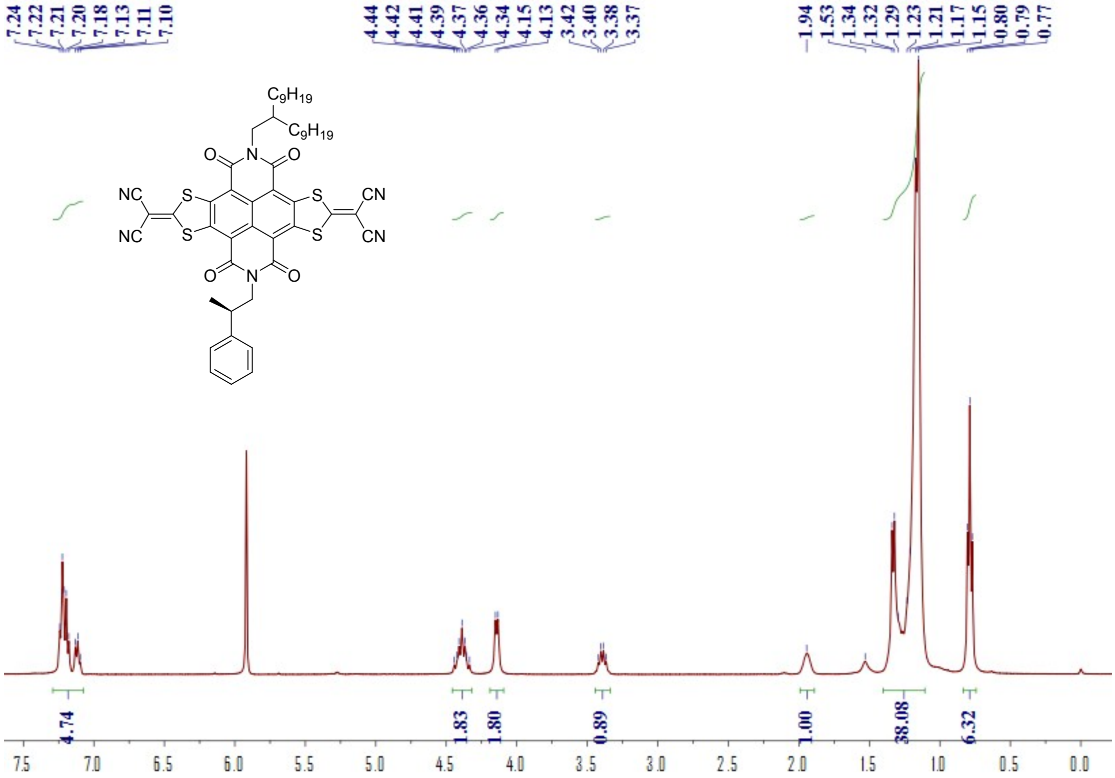


Figure S15. ^{1}H NMR spectrum of **1-*R*** (400 MHz, $C_2D_2Cl_4$).

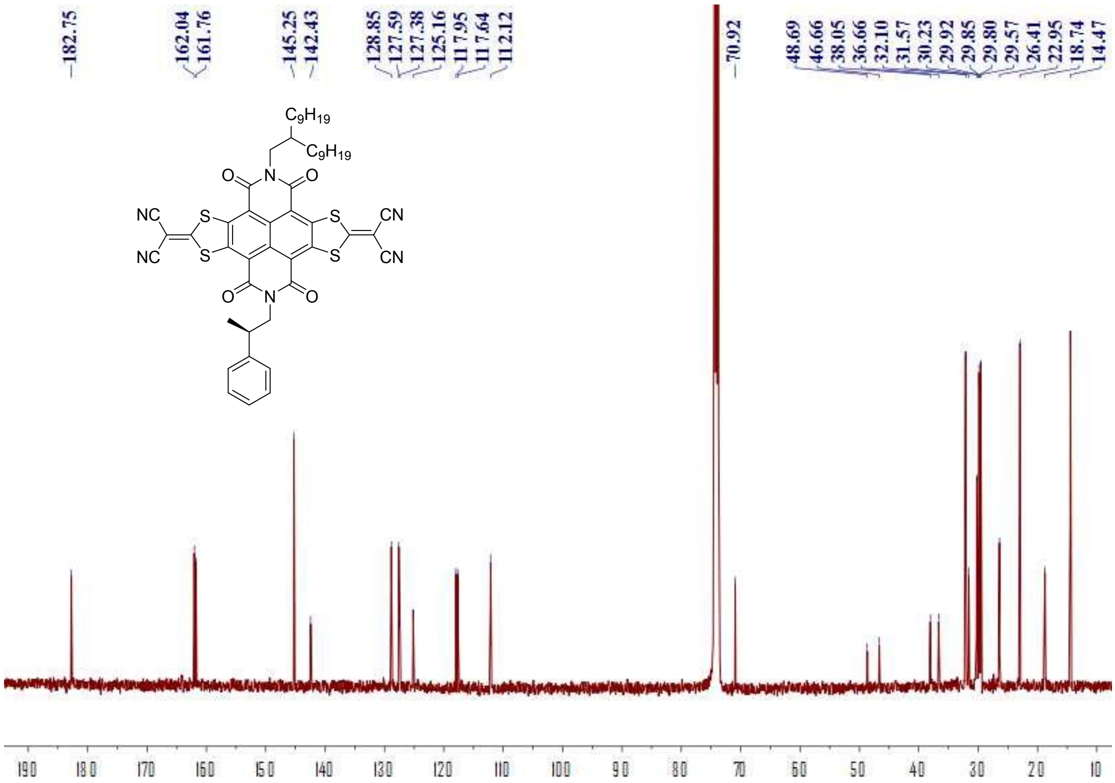


Figure S16. ^{13}C NMR spectrum of **1-*R*** (100 MHz, $C_2D_2Cl_4$).

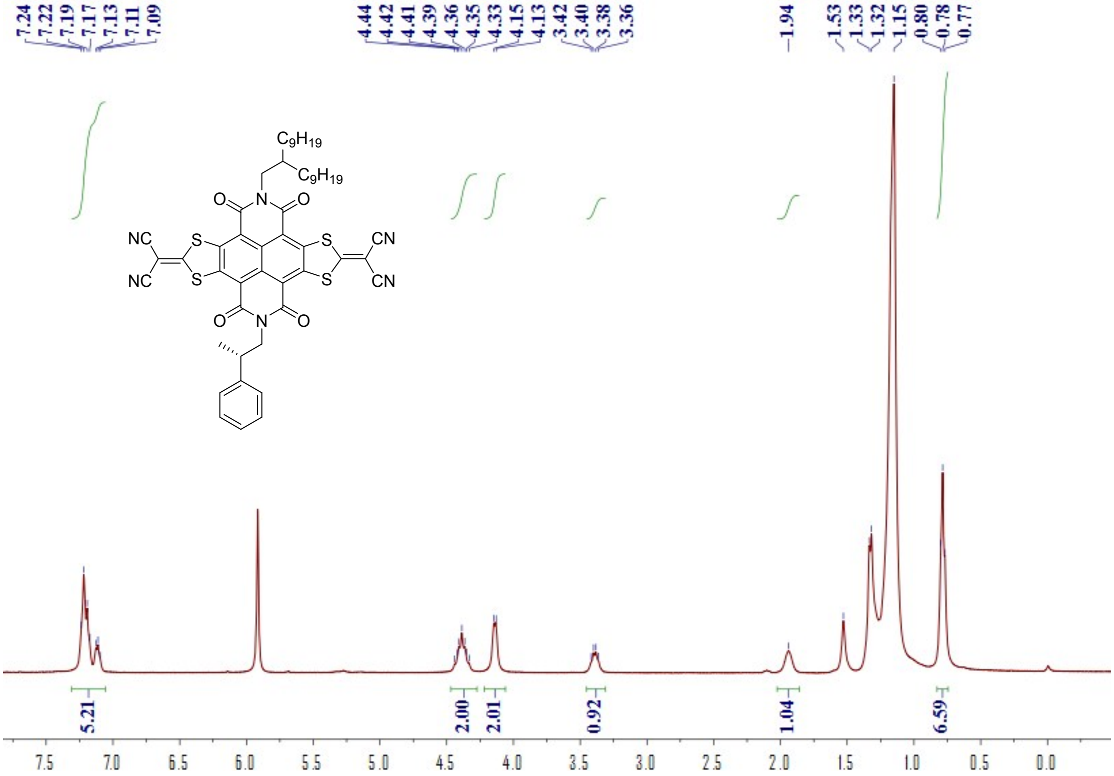


Figure S17. ^{1}H NMR spectrum of **1-*S*** (400 MHz, $C_2D_2Cl_4$).

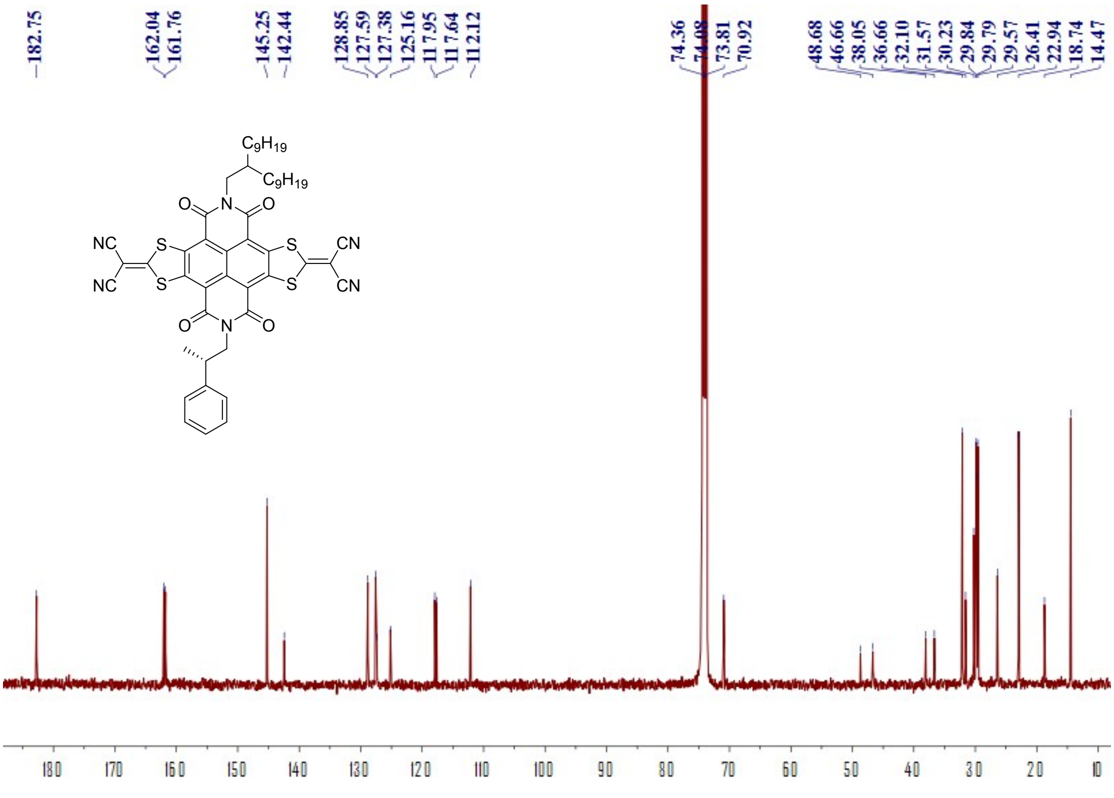


Figure S18. ^{13}C NMR spectrum of **1-*S*** (100 MHz, $C_2D_2Cl_4$).

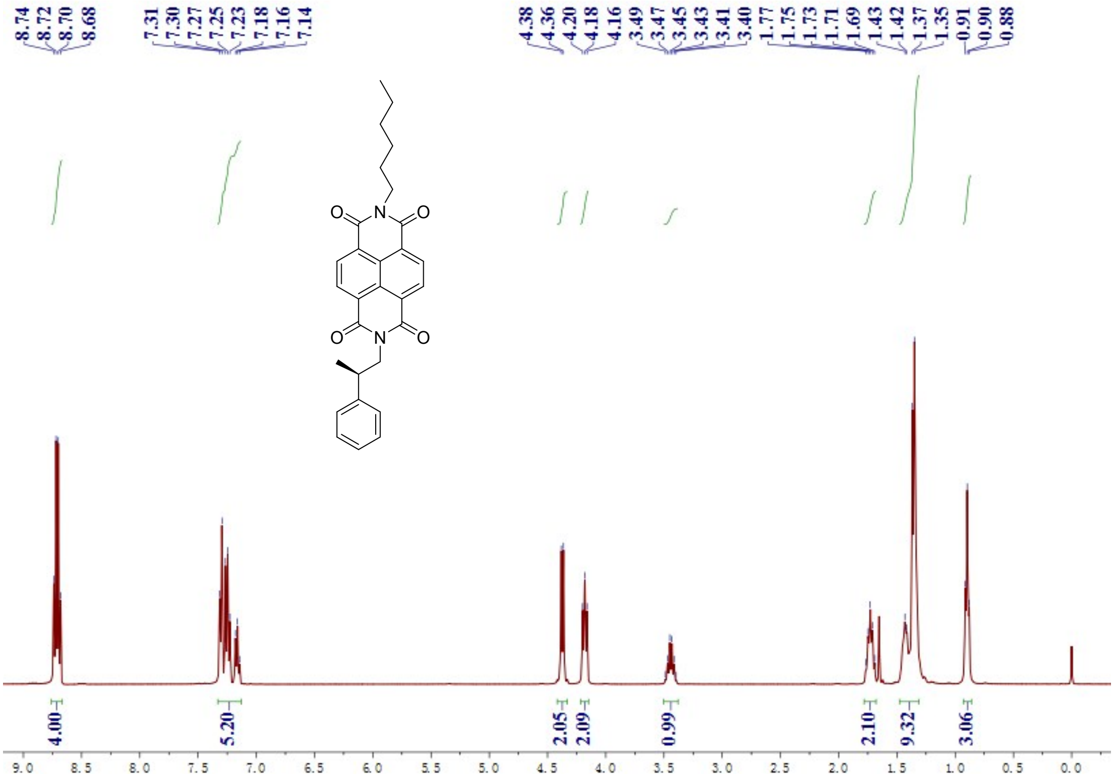


Figure S19. ^{1}H NMR spectrum of **M-*R*** (400 MHz, $CDCl_3$).

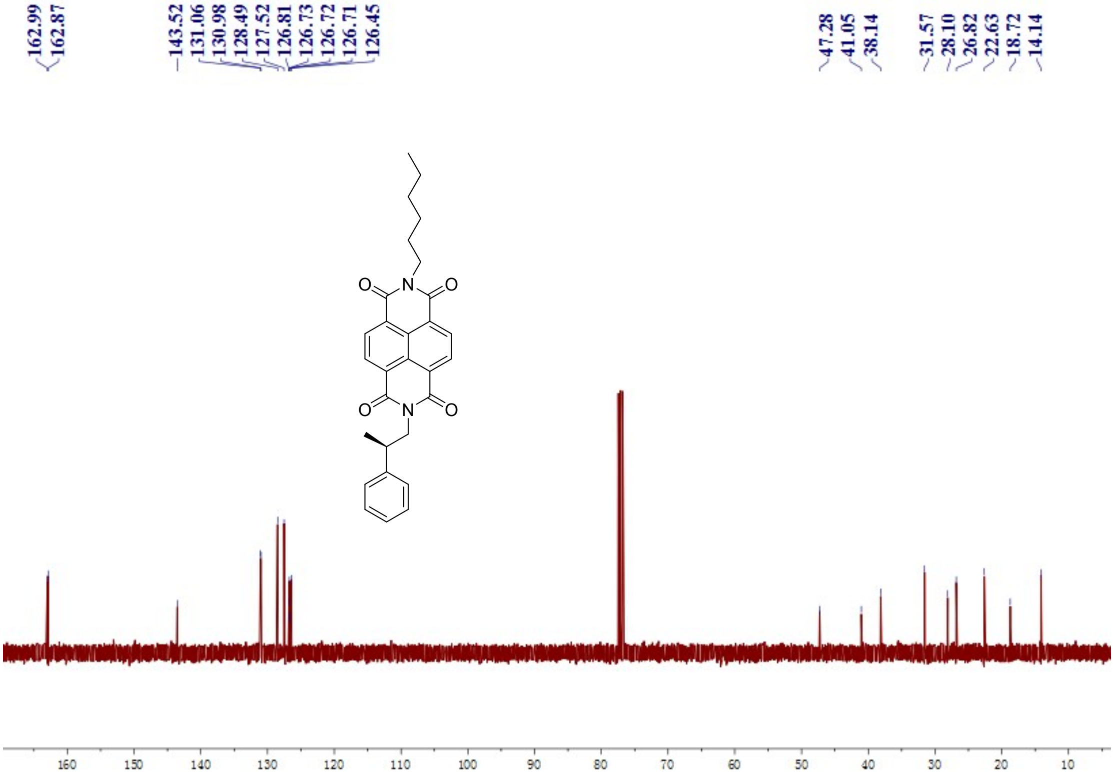


Figure S20. ^{13}C NMR spectrum of **M-*R*** (100 MHz, $CDCl_3$).

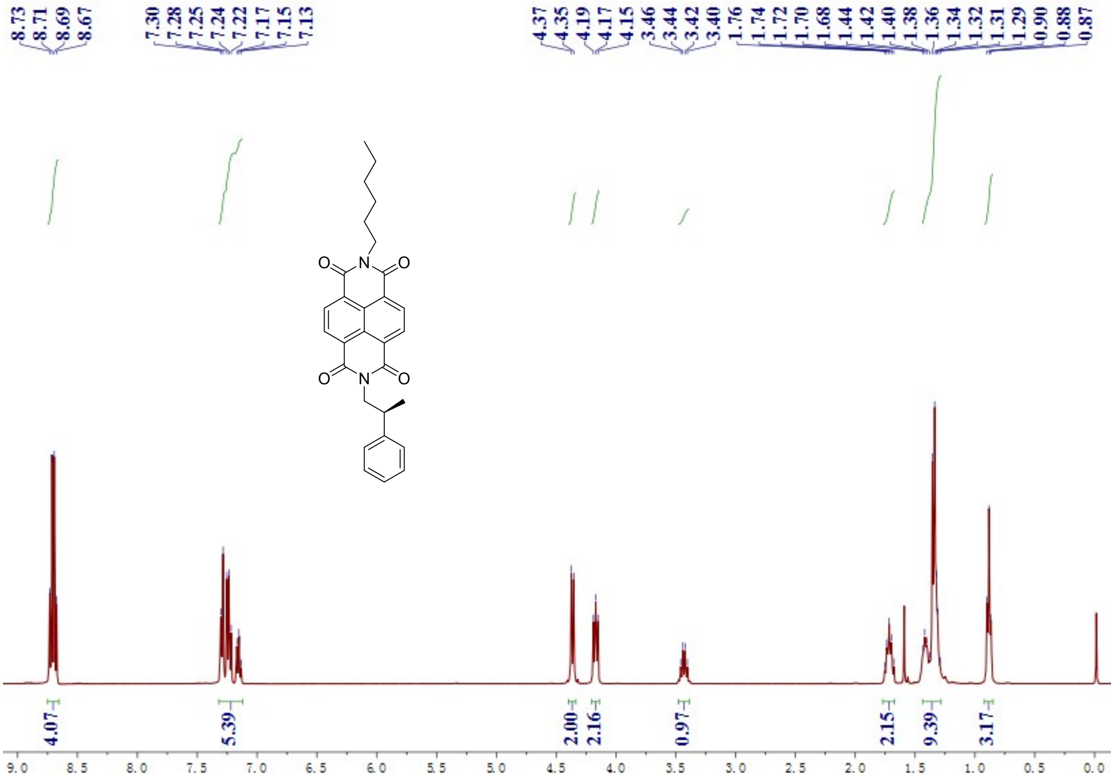


Figure S31. ^{1}H NMR spectrum of **M-*S*** (400 MHz, CDCl$_3$).

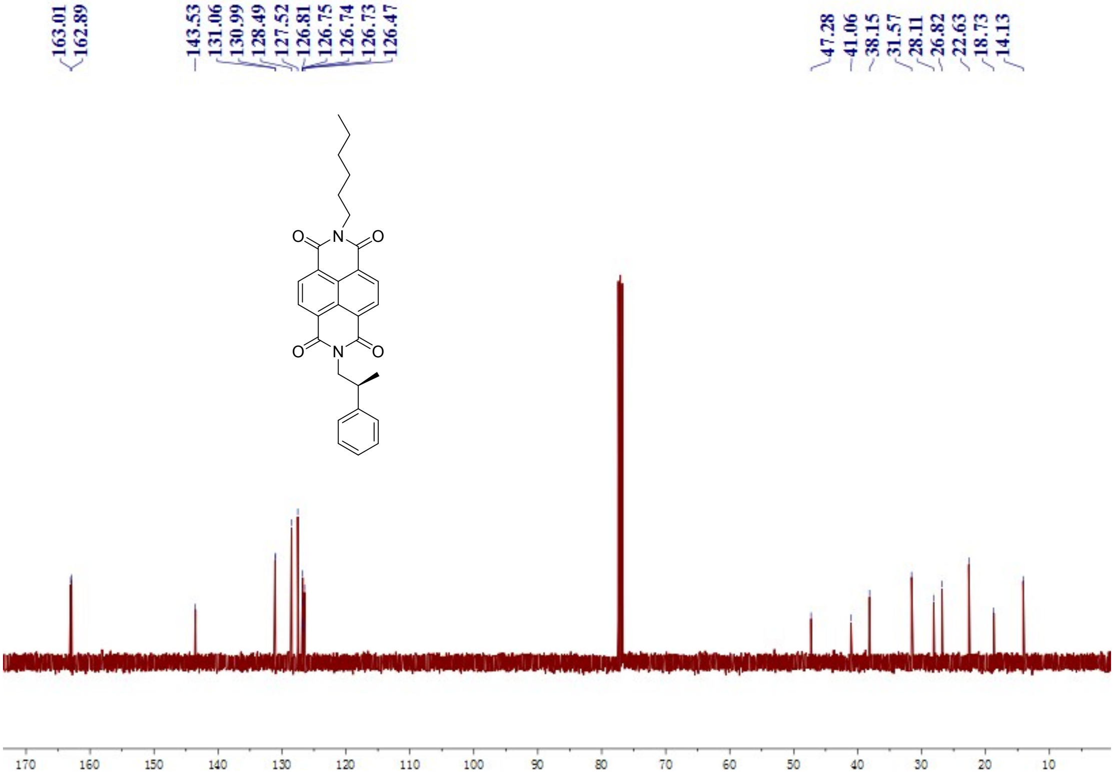


Figure S22. ^{13}C NMR spectrum of **M-*S*** (100 MHz, CDCl$_3$).

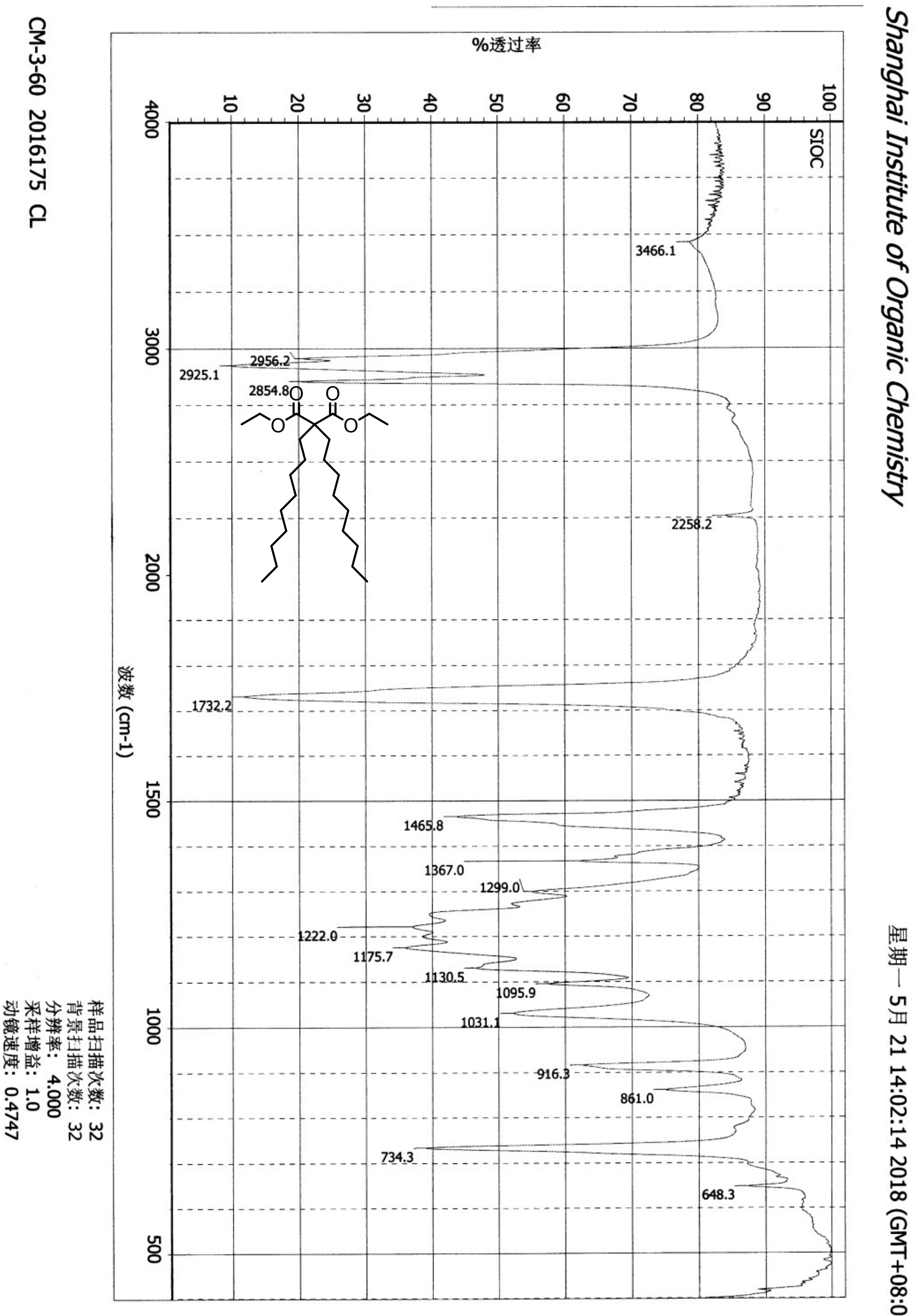


Figure S23. IR spectrum of **2**

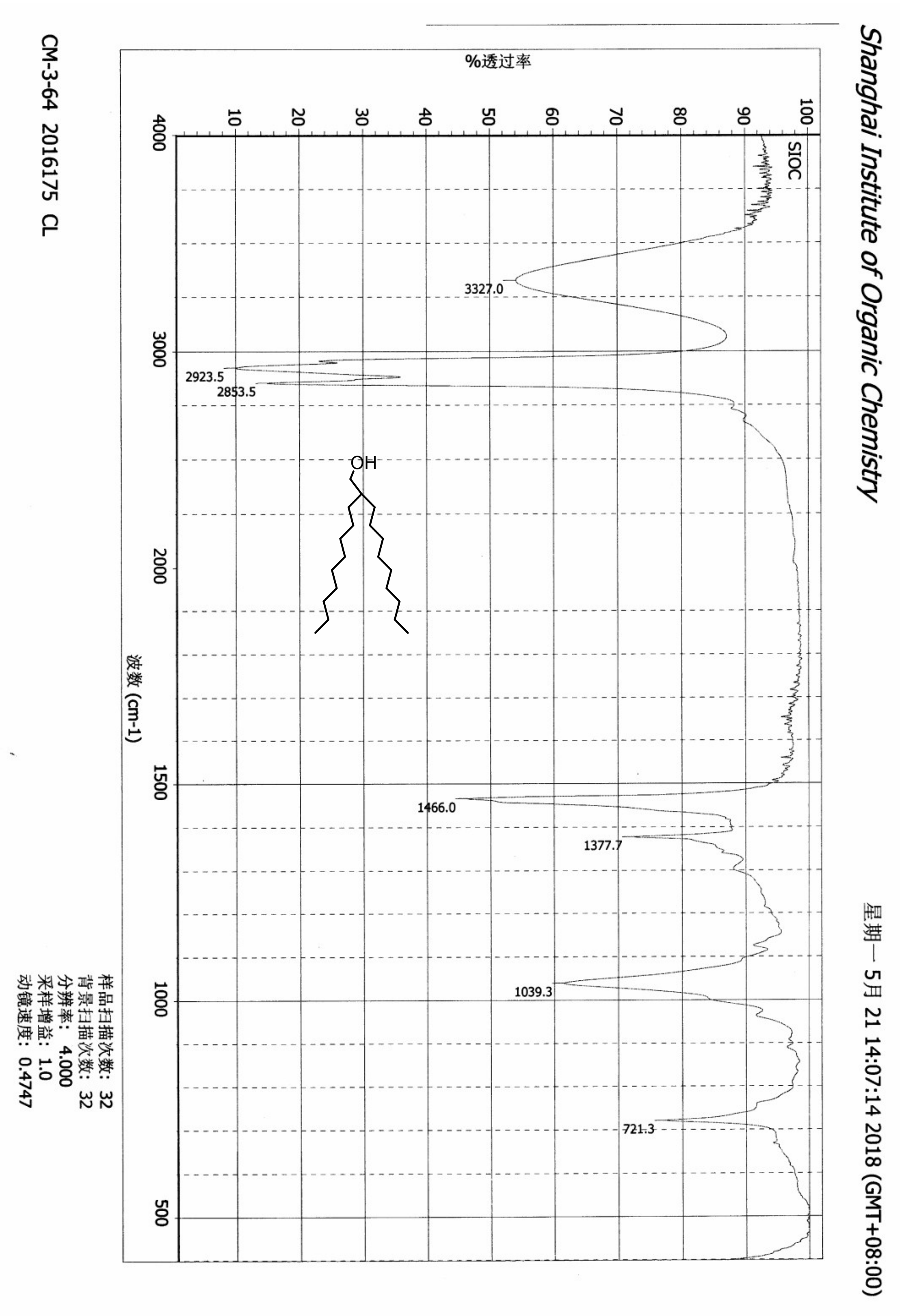


Figure S24. IR spectrum of **3**

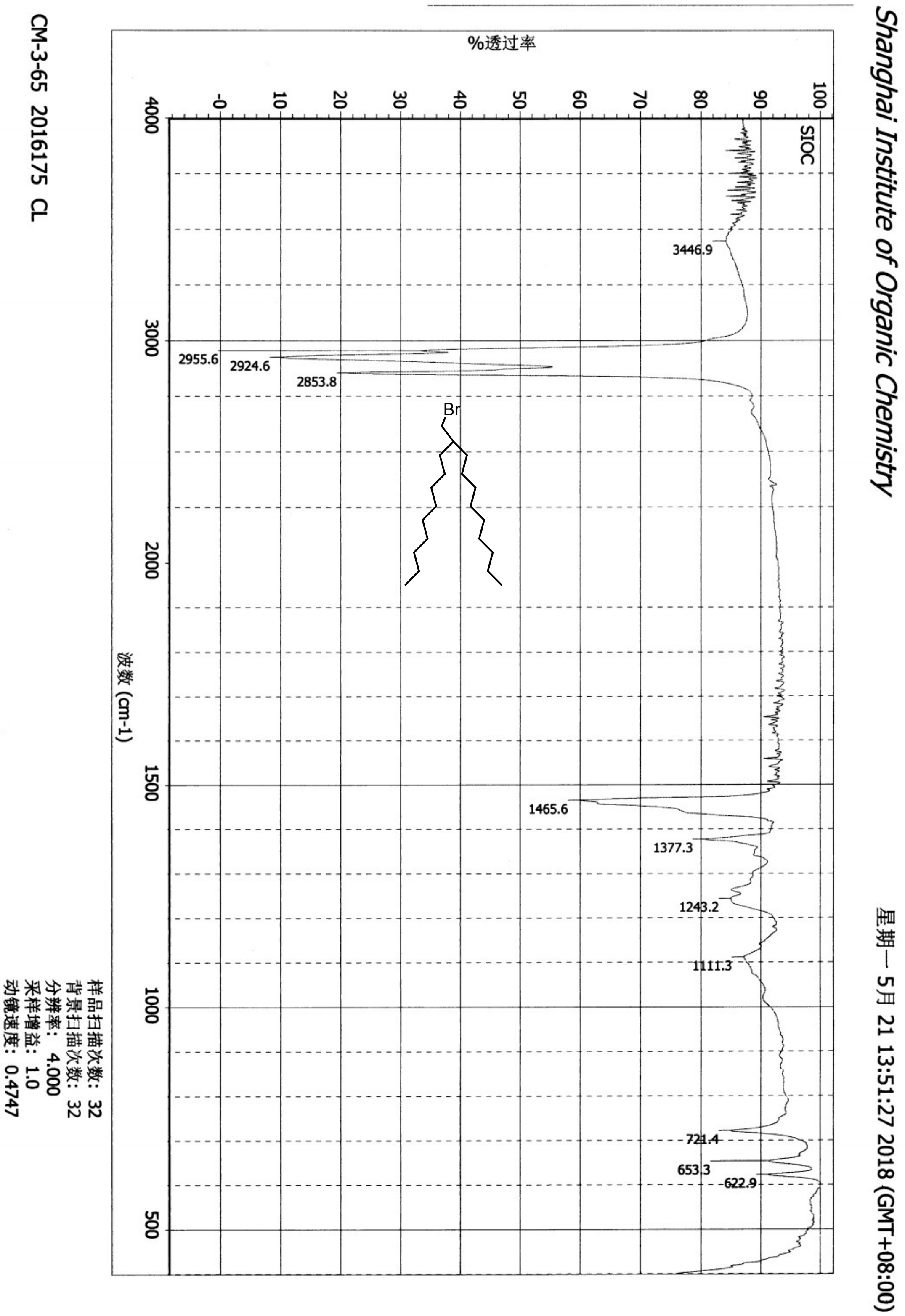


Figure S25. IR spectrum of **4**

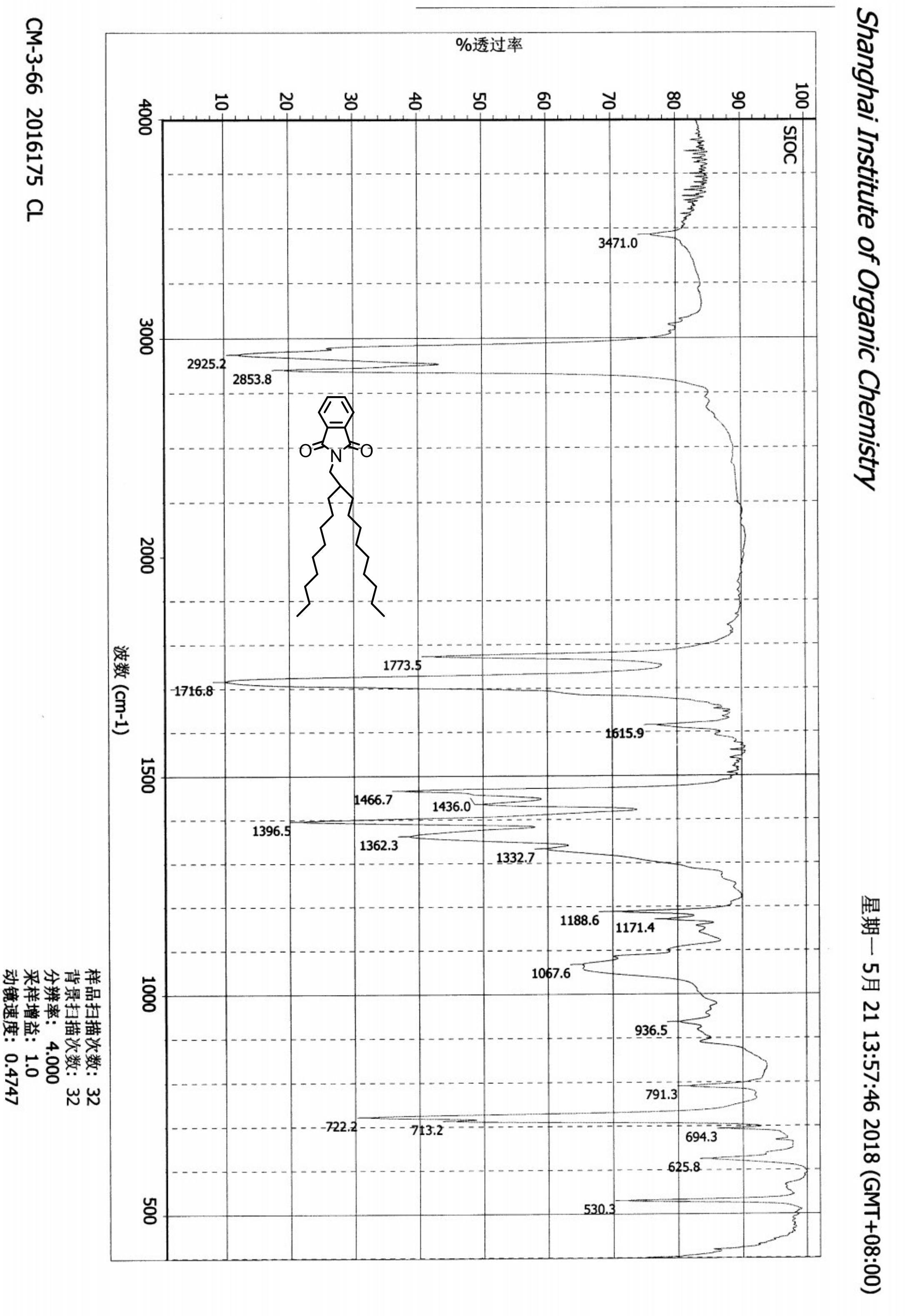


Figure S26. IR spectrum of **5**

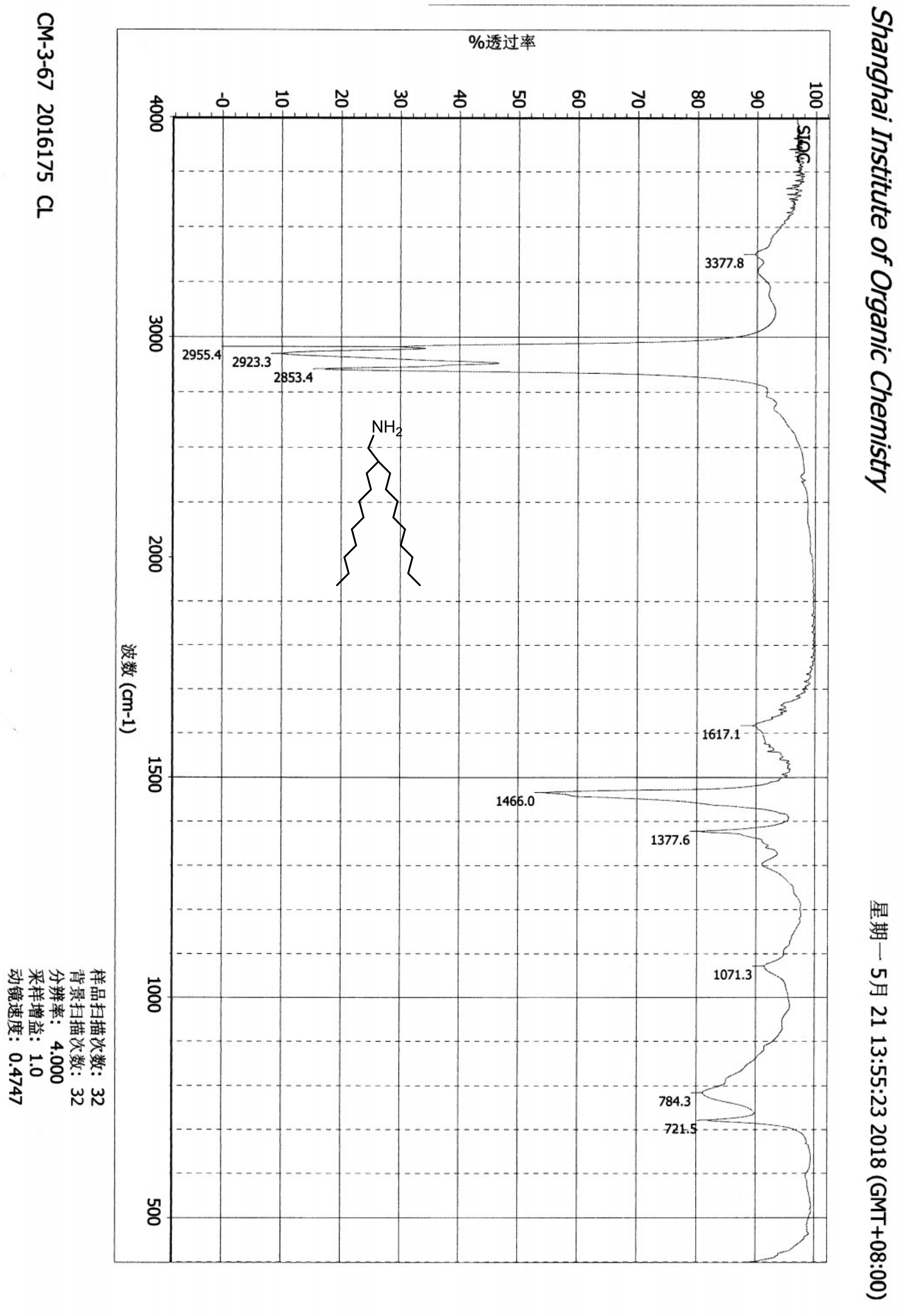
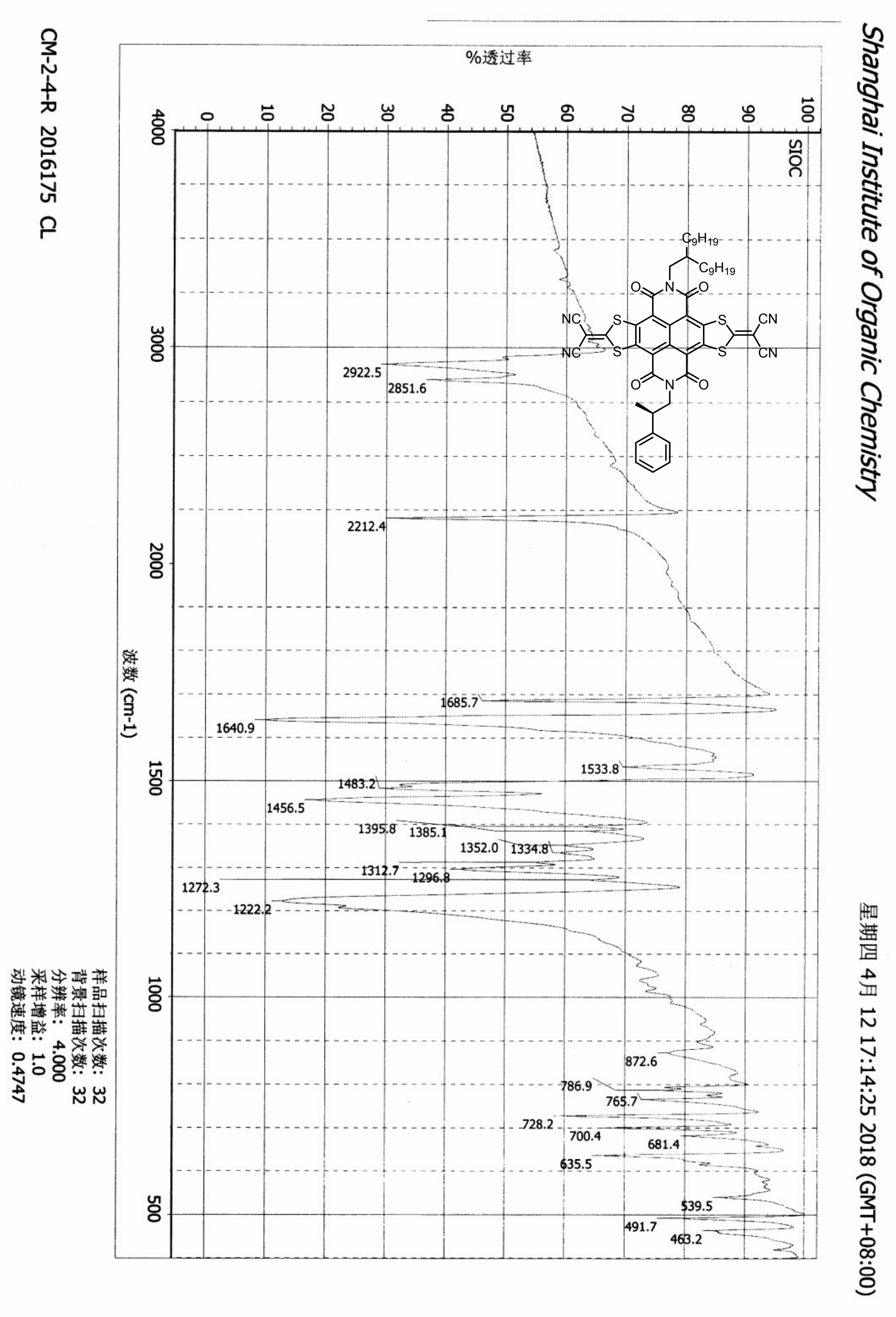


Figure S27. IR spectrum of **6**



样品扫描次数: 32
背景扫描次数: 32
分辨率: 4.000
采样增益: 1.0
动镜速度: 0.4747

Figure S28. IR spectrum of **1-(*R*)**

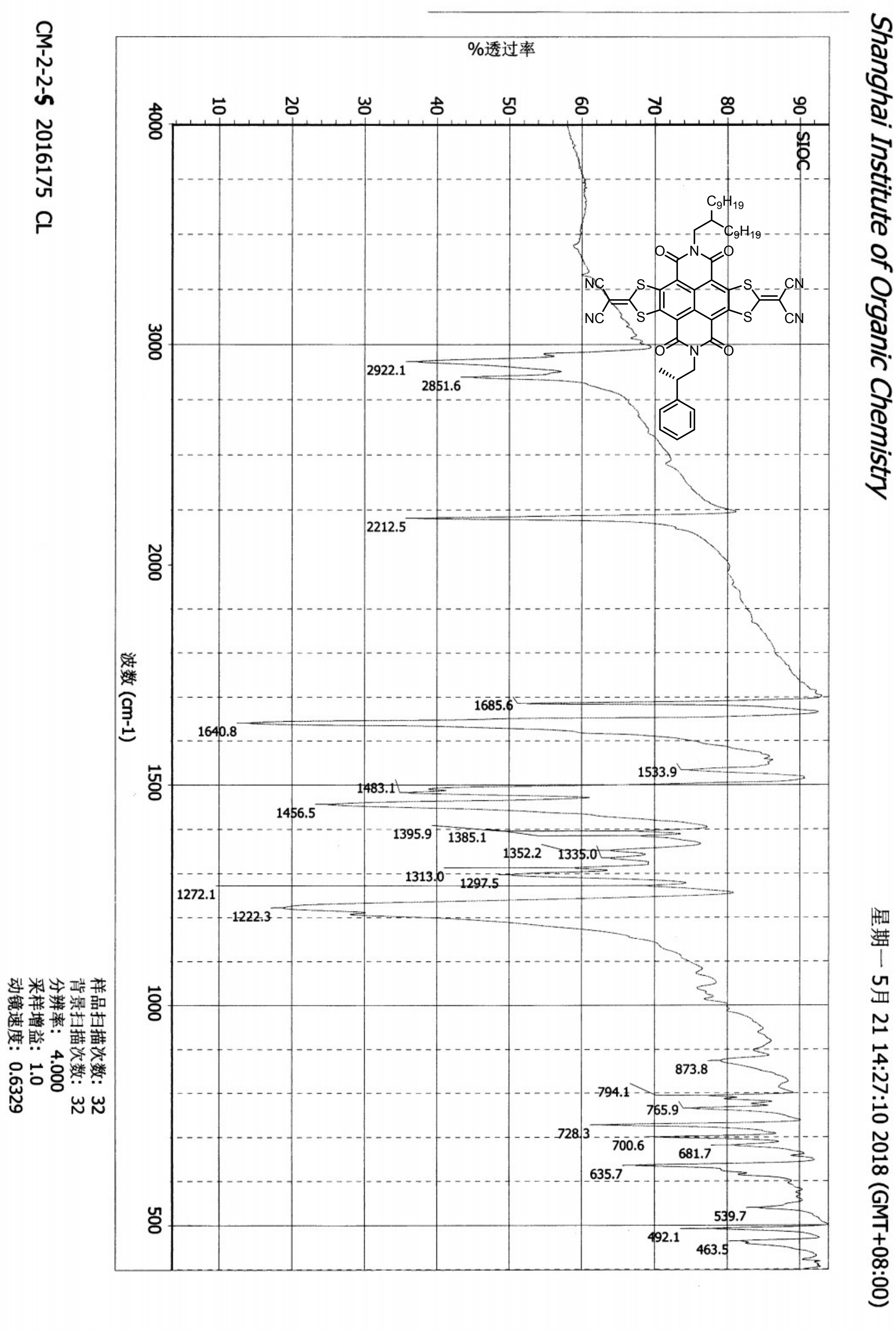
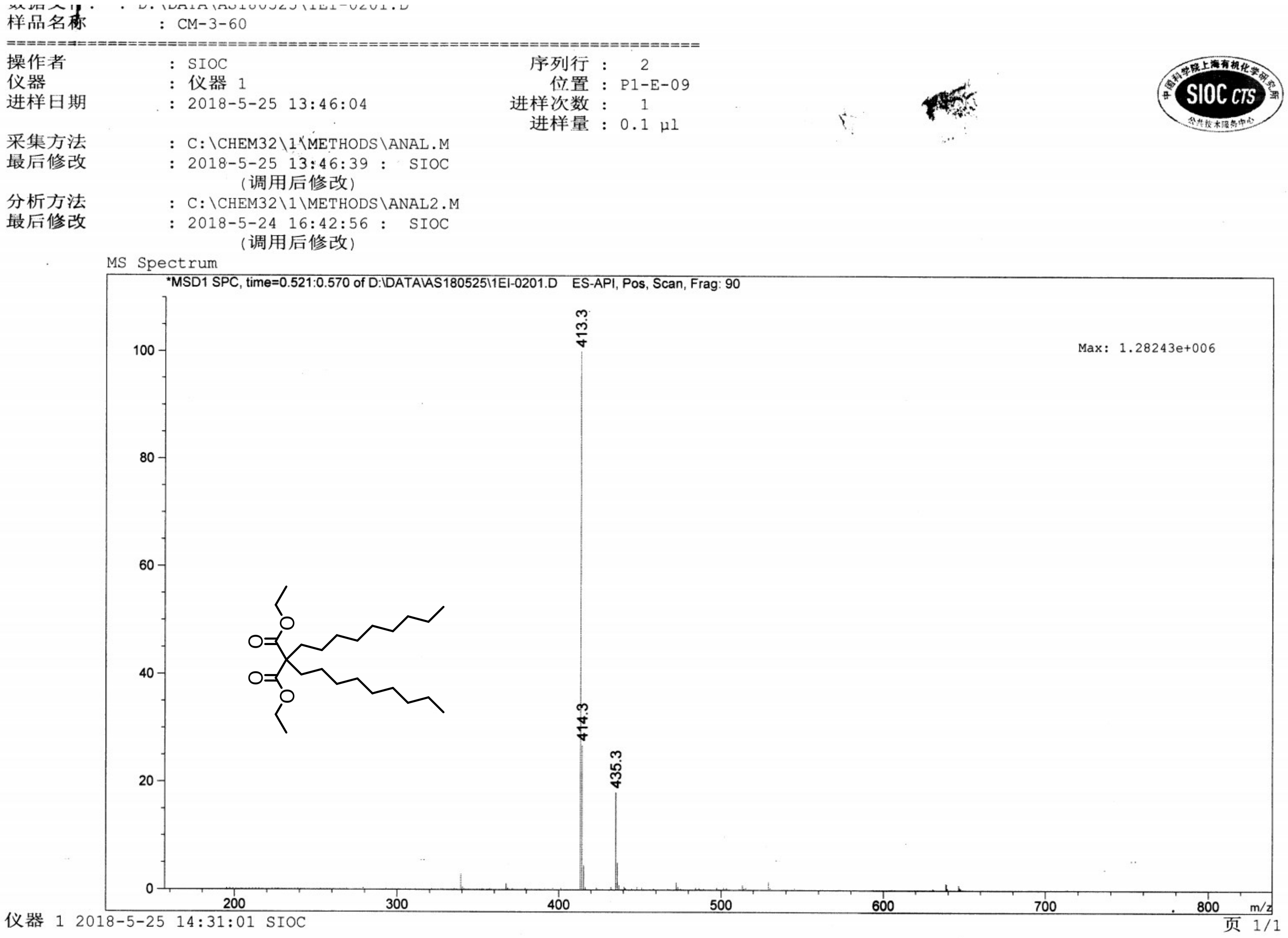


Figure S29. IR spectrum of **1-(*S*)**



样品名称 : CM-3-60

操作者 : SIOC
仪器 : 仪器 1
进样日期 : 2018-5-25 13:46:04

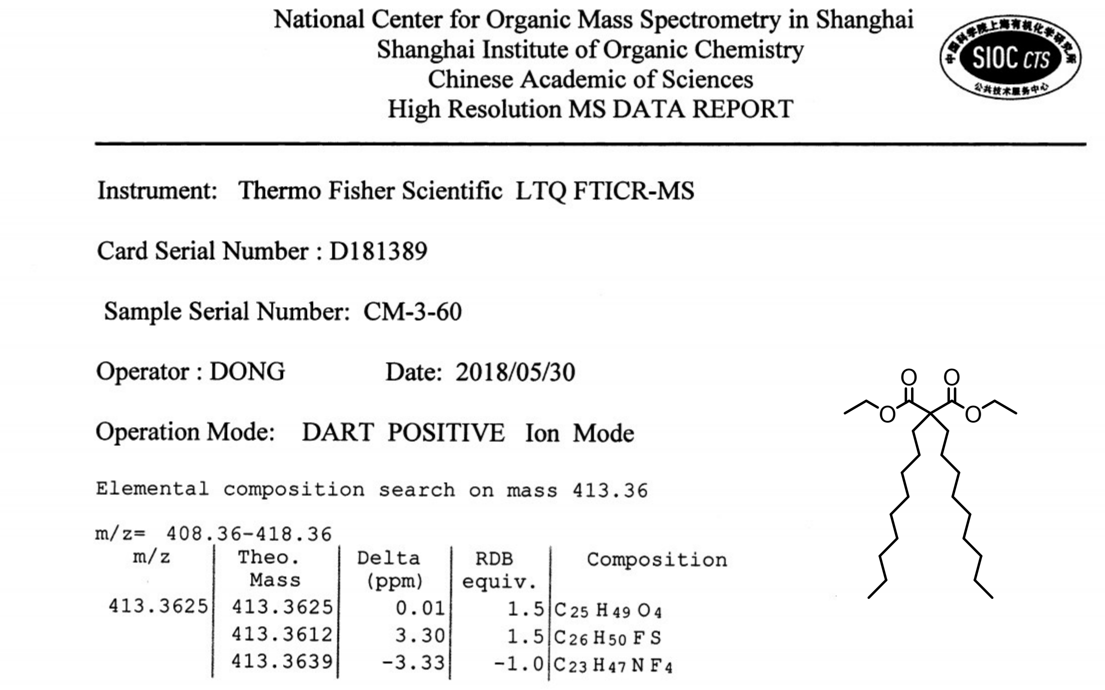
序列行 : 2
位置 : P1-E-09
进样次数 : 1
进样量 : 0.1 µl

采集方法 : C:\CHEM32\1\METHODS\ANAL.M
最后修改 : 2018-5-25 13:46:39 : SIOC
(调用后修改)

分析方法 : C:\CHEM32\1\METHODS\ANAL2.M
最后修改 : 2018-5-24 16:42:56 : SIOC
(调用后修改)

仪器 1 2018-5-25 14:31:01 SIOC
页 1/1

Figure S30. MS spectrum of **2**



National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D181389

Sample Serial Number: CM-3-60

Operator : DONG Date: 2018/05/30

Operation Mode: DART POSITIVE Ion Mode

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Elemental composition search on mass 413.36

m/z= 408.36-418.36
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          |   Mass    |  (ppm)   | equiv. |
 413.3625 | 413.3625  |     0.01 |    1.5 |C25 H49 O4
          | 413.3612  |     3.30 |    1.5 |C26 H50 F S
          | 413.3639  |    -3.33 |   -1.0 |C23 H47 N F4
```
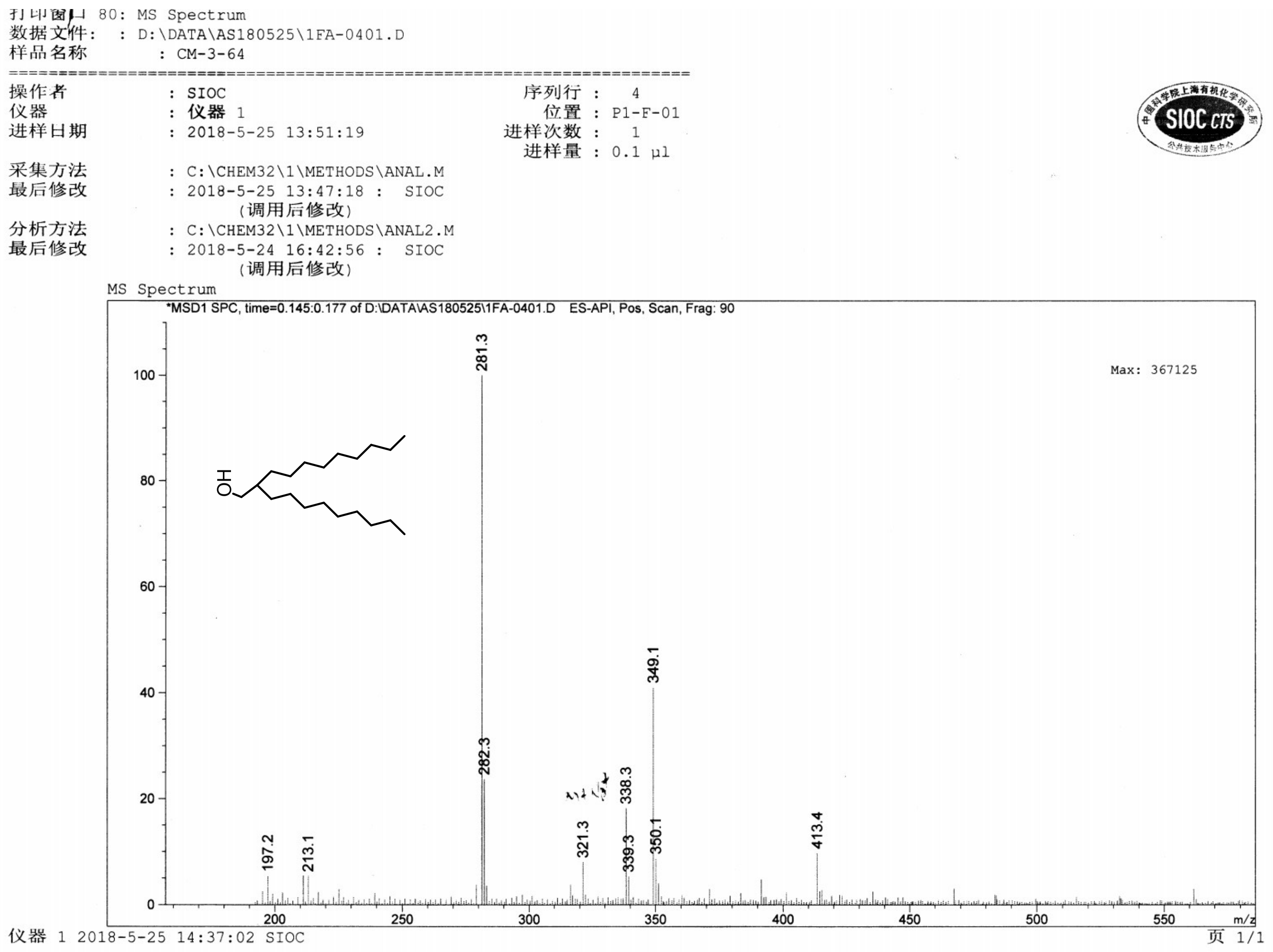

Figure S31. HRMS spectrum of **2**



打印窗口 80: MS Spectrum
数据文件: : D:\DATA\AS180525\1FA-0401.D
样品名称 : CM-3-64

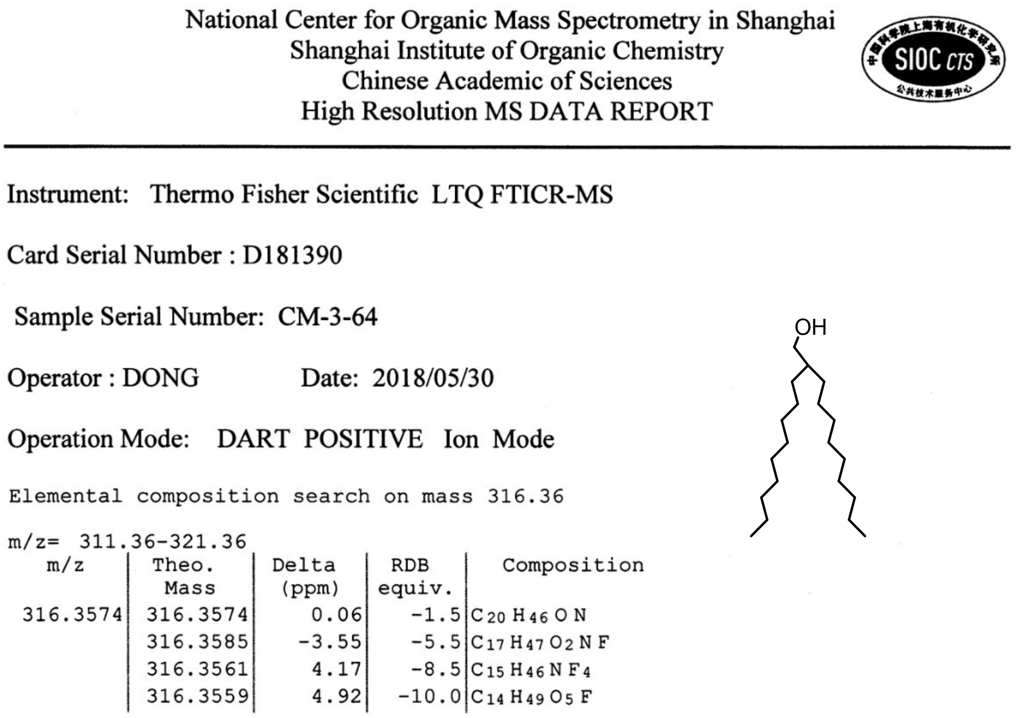
操作者 : SIOC
仪器 : 仪器 1
进样日期 : 2018-5-25 13:51:19

序列行 : 4
位置 : P1-F-01
进样次数 : 1
进样量 : 0.1 µl

采集方法 : C:\CHEM32\1\METHODS\ANAL.M
最后修改 : 2018-5-25 13:47:18 : SIOC
(调用后修改)
分析方法 : C:\CHEM32\1\METHODS\ANAL2.M
最后修改 : 2018-5-24 16:42:56 : SIOC
(调用后修改)

仪器 1 2018-5-25 14:37:02 SIOC
页 1/1

Figure S32. MS spectrum of **3**



National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D181390

Sample Serial Number: CM-3-64

Operator : DONG Date: 2018/05/30

Operation Mode: DART POSITIVE Ion Mode

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Elemental composition search on mass 316.36

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          |  Mass    |  (ppm)  | equiv. |
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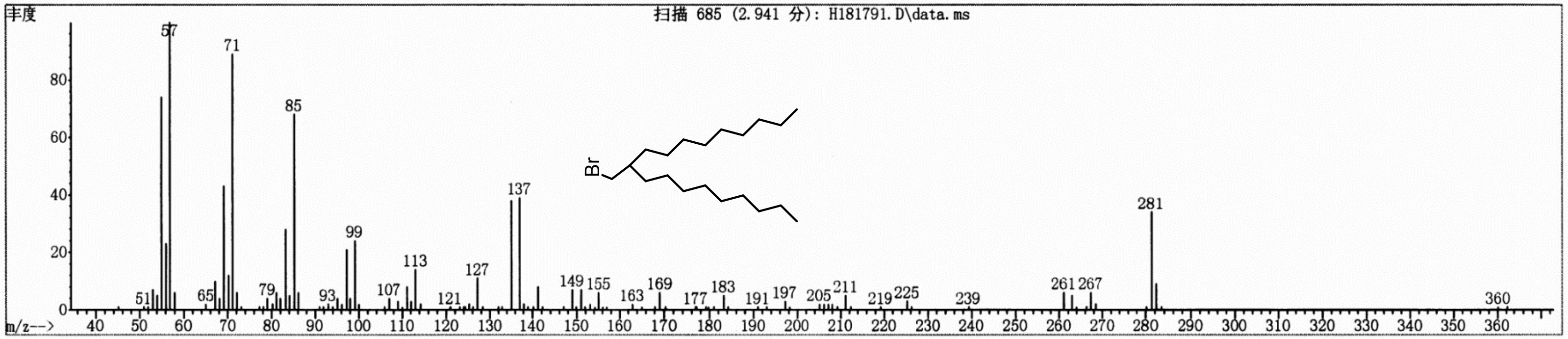
          | 316.3585 |   -3.55 |   -5.5 |C17 H47 O2 N F
          | 316.3561 |    4.17 |   -8.5 |C15 H46 N F4
          | 316.3559 |    4.92 |  -10.0 |C14 H49 O5 F
```

Figure S33. HRMS spectrum of **3**

File : E:\5973N date\2018\201805\20180528\H181791.D
Acquired : 28 May 2018 10:28
Sample Name : CM-3-65
Instrument : Agilent Technologies 5973N
: National Center for Organic Mass Spectrometry in Shanghai, Shanghai Institute of Organic Chemistry

Base m/z:57.1 Inten:30016

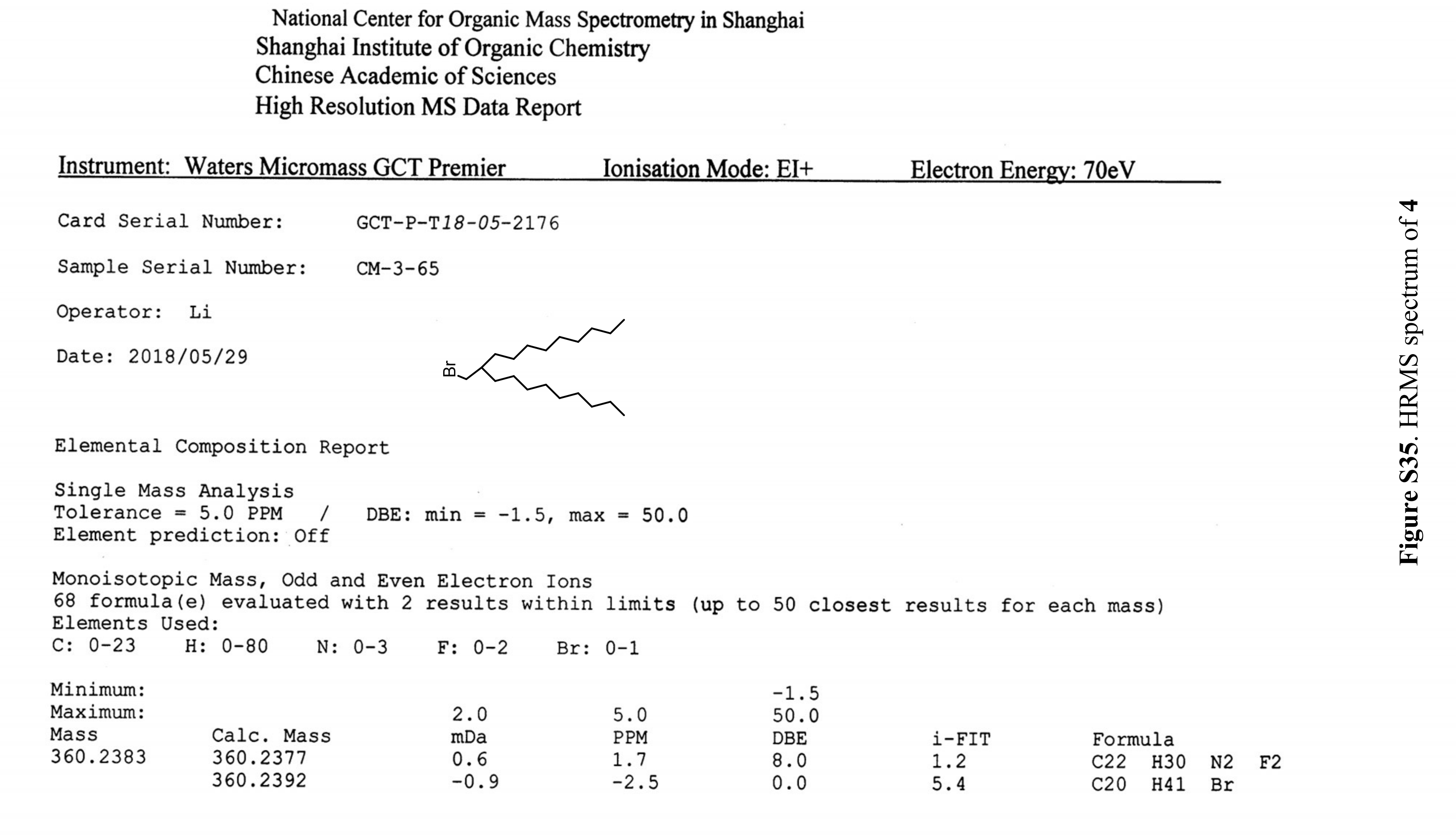


m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
45	0.53	51	0.71	52	0.84	53	6.51	54	4.64	55	73.77	56	22.96	57	100	58	5.76
65	1.52	67	10.45	68	3.63	69	43.28	70	12.31	71	88.83	72	5.95	73	0.9	77	1.06
78	0.92	79	3.56	80	1.82	81	6.01	82	3.7	83	27.75	84	5.46	85	67.59	86	5.52
91	1.35	92	0.76	93	1.54	94	0.59	95	4.41	96	2.26	97	20.56	98	4.44	99	24.04
100	1.92	106	1.1	107	3.57	109	2.94	110	0.85	111	8.06	112	3.18	113	13.77	114	1.71
121	0.75	121	0.76	123	1.37	124	0.71	124	0.64	125	2.41	126	1.3	127	11.17	128	0.84
132	0.6	133	0.94	135	37.57	137	39.43	138	2.17	139	0.61	140	1.28	141	8.2	142	0.85
147	0.61	149	6.59	150	0.58	151	6.68	152	1.1	153	1.68	154	1.22	155	6.47	156	0.59
157	0.51	163	1.57	165	1.43	168	0.61	169	6.48	170	0.58	177	0.99	177	0.96	179	1.33
180	0.81	181	0.55	183	5.12	184	0.85	191	1.24	193	0.96	197	3.47	198	1.07	205	1.72
206	1.77	207	1.6	208	2.3	209	1.09	211	5.14	212	0.96	219	0.7	225	2.71	226	0.78
239	0.96	261	5.95	263	4.78	264	0.53	266	0.59	267	5.83	268	1.56	280	0.72	281	33.65
282	9.01	283	0.87	360	0.97	362	0.96										

8 Peak Value:

57	100	71	88.83	55	73.77	85	67.59	69	43.28	137	39.43	135	37.57	281	33.65

Figure S34. MS spectrum of **4**



National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier **Ionisation Mode: EI+** **Electron Energy: 70eV**

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Card Serial Number:      GCT-P-T18-05-2176

Sample Serial Number:    CM-3-65

Operator:  Li

Date: 2018/05/29


Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
68 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23    H: 0-80    N: 0-3    F: 0-2    Br: 0-1

Minimum:                                          -1.5
Maximum:                   2.0         5.0        50.0
Mass       Calc. Mass      mDa         PPM        DBE         i-FIT       Formula
360.2383   360.2377        0.6         1.7        8.0         1.2         C22  H30  N2  F2
           360.2392        -0.9        -2.5       0.0         5.4         C20  H41  Br
```
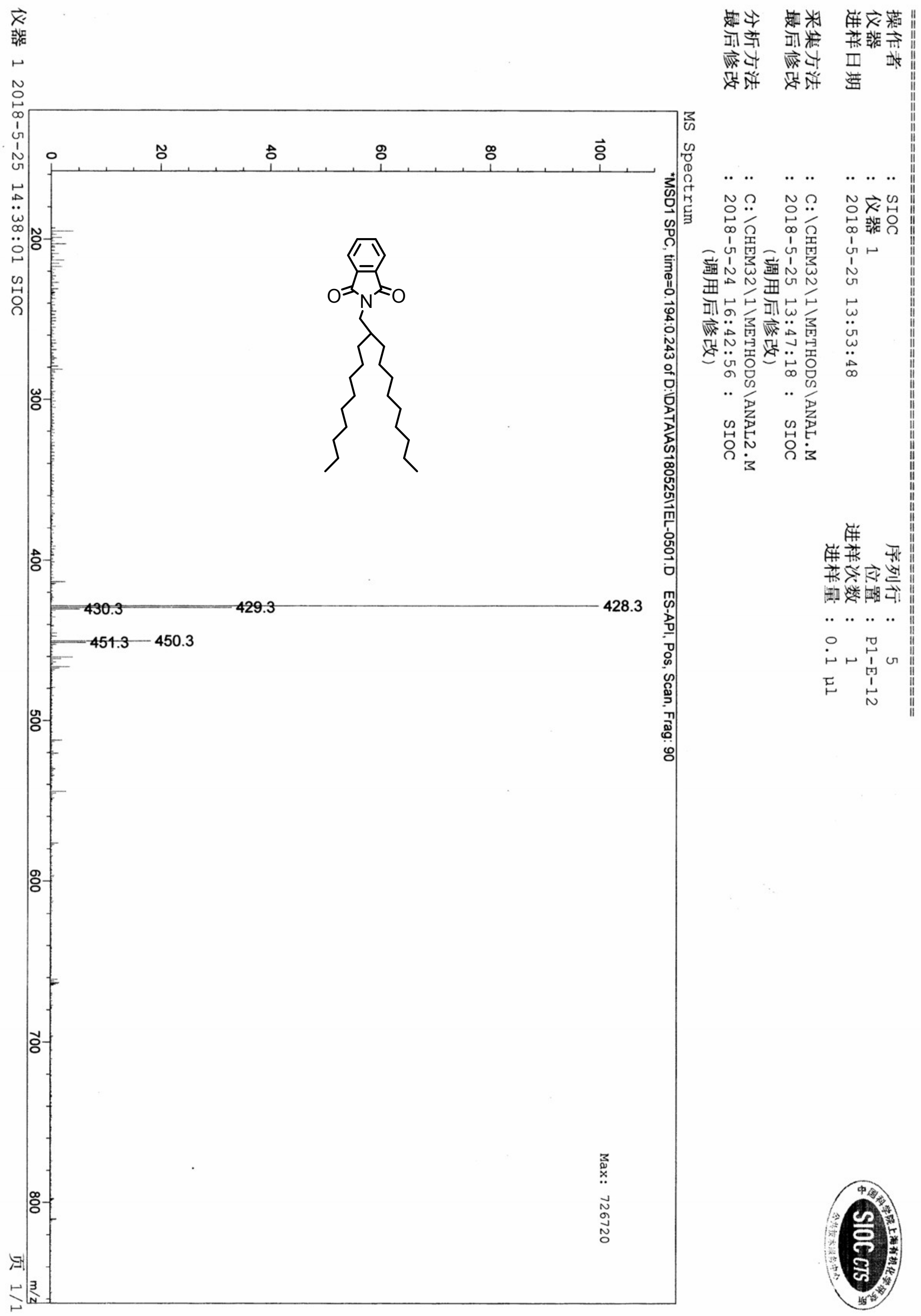

Figure S35. HRMS spectrum of **4**



打印窗口 80: MS Spectrum
数据文件: : D:\DATA\AS180525\1EL-0501.D
样品名称 : CM-3-66

操作者 : SIOC
仪器 : 仪器 1
进样日期 : 2018-5-25 13:53:48

序列行 : 5
位置 : P1-E-12
进样次数 : 1
进样量 : 0.1 µl

采集方法 : C:\CHEM32\1\METHODS\ANAL.M
最后修改 : 2018-5-25 13:47:18 : SIOC
(调用后修改)
分析方法 : C:\CHEM32\1\METHODS\ANAL2.M
最后修改 : 2018-5-24 16:42:56 : SIOC
(调用后修改)

MS Spectrum

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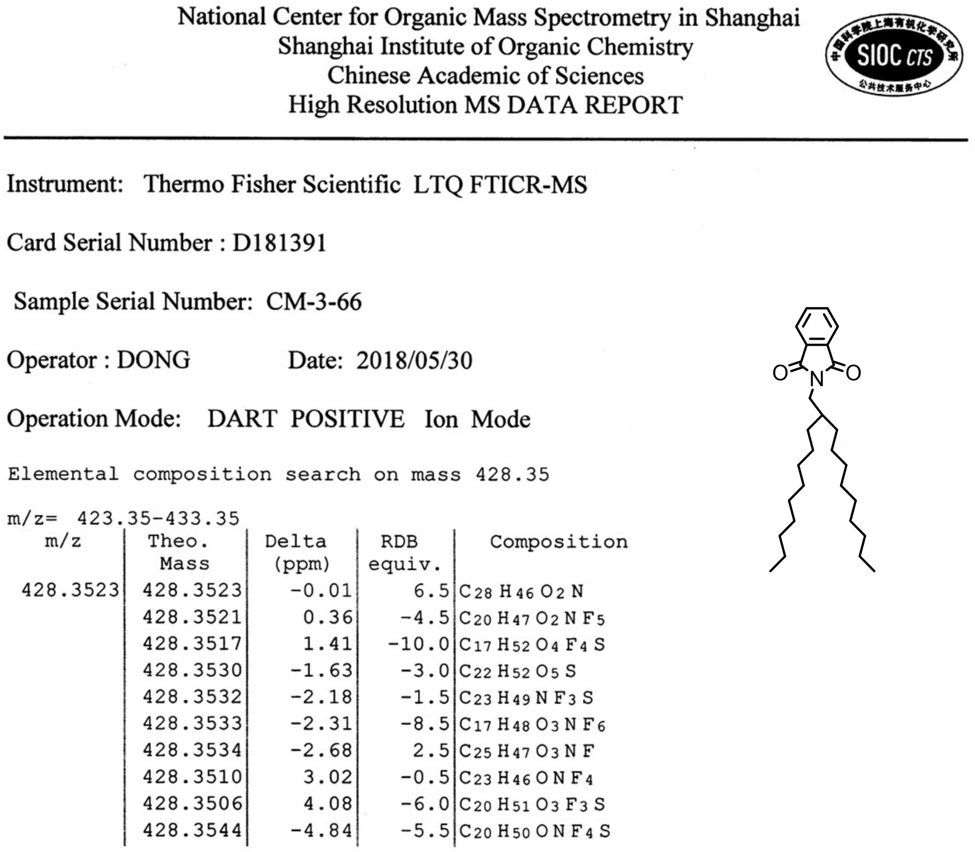
仪器 1 2018-5-25 14:38:01 SIOC
页 1/1

Figure S36. MS spectrum of **5**



National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D181391

Sample Serial Number: CM-3-66

Operator : DONG Date: 2018/05/30

Operation Mode: DART POSITIVE Ion Mode

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Elemental composition search on mass 428.35

m/z= 423.35-433.35
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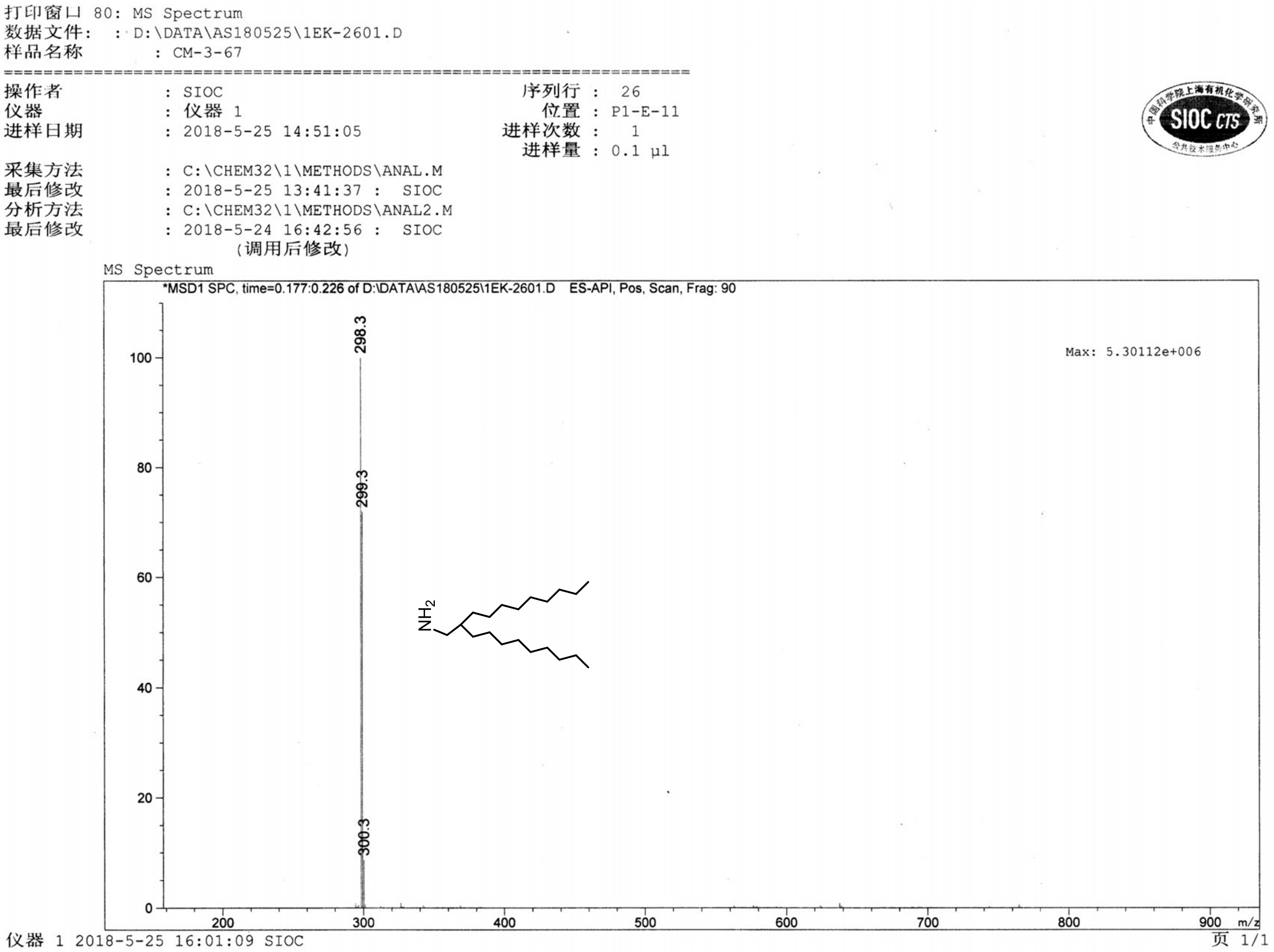
          |  Mass    |  (ppm)  | equiv.  |
 428.3523 | 428.3523 |   -0.01 |     6.5 | C28 H46 O2 N
          | 428.3521 |    0.36 |    -4.5 | C20 H47 O2 N F5
          | 428.3517 |    1.41 |   -10.0 | C17 H52 O4 F4 S
          | 428.3530 |   -1.63 |    -3.0 | C22 H52 O5 S
          | 428.3532 |   -2.18 |    -1.5 | C23 H49 N F3 S
          | 428.3533 |   -2.31 |    -8.5 | C17 H48 O3 N F6
          | 428.3534 |   -2.68 |     2.5 | C25 H47 O3 N F
          | 428.3510 |    3.02 |    -0.5 | C23 H46 O N F4
          | 428.3506 |    4.08 |    -6.0 | C20 H51 O3 F3 S
          | 428.3544 |   -4.84 |    -5.5 | C20 H50 O N F4 S
```

Figure S37. HRMS spectrum of **5**



打印窗口 80: MS Spectrum
数据文件: : D:\DATA\AS180525\1EK-2601.D
样品名称 : CM-3-67

操作者 : SIOC
仪器 : 仪器 1
进样日期 : 2018-5-25 14:51:05

序列行 : 26
位置 : P1-E-11
进样次数 : 1
进样量 : 0.1 µl

采集方法 : C:\CHEM32\1\METHODS\ANAL.M
最后修改 : 2018-5-25 13:41:37 : SIOC
分析方法 : C:\CHEM32\1\METHODS\ANAL2.M
最后修改 : 2018-5-24 16:42:56 : SIOC
（调用后修改）

MS Spectrum

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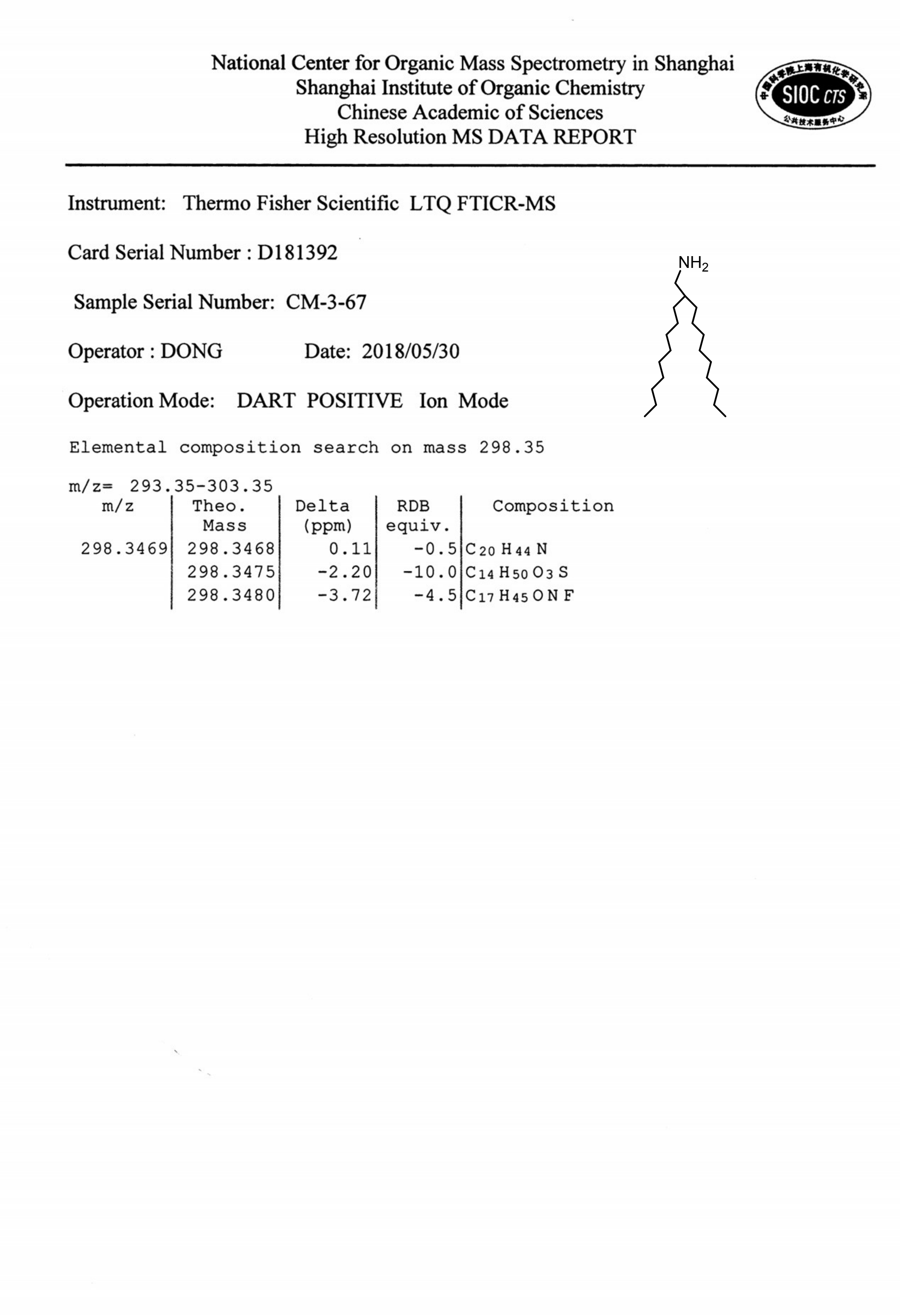
Max: 5.30112e+006

仪器 1 2018-5-25 16:01:09 SIOC

页 1/1

Figure S38. MS spectrum of **6**



National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D181392

Sample Serial Number: CM-3-67

Operator : DONG Date: 2018/05/30

Operation Mode: DART POSITIVE Ion Mode

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Elemental composition search on mass 298.35

m/z= 293.35-303.35
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          |  Mass    |  (ppm)   | equiv. |
 298.3469 | 298.3468 |    0.11  |   -0.5 | C20 H44 N
          | 298.3475 |   -2.20  |  -10.0 | C14 H50 O3 S
          | 298.3480 |   -3.72  |   -4.5 | C17 H45 O N F
```

Figure S39. HRMS spectrum of **6**

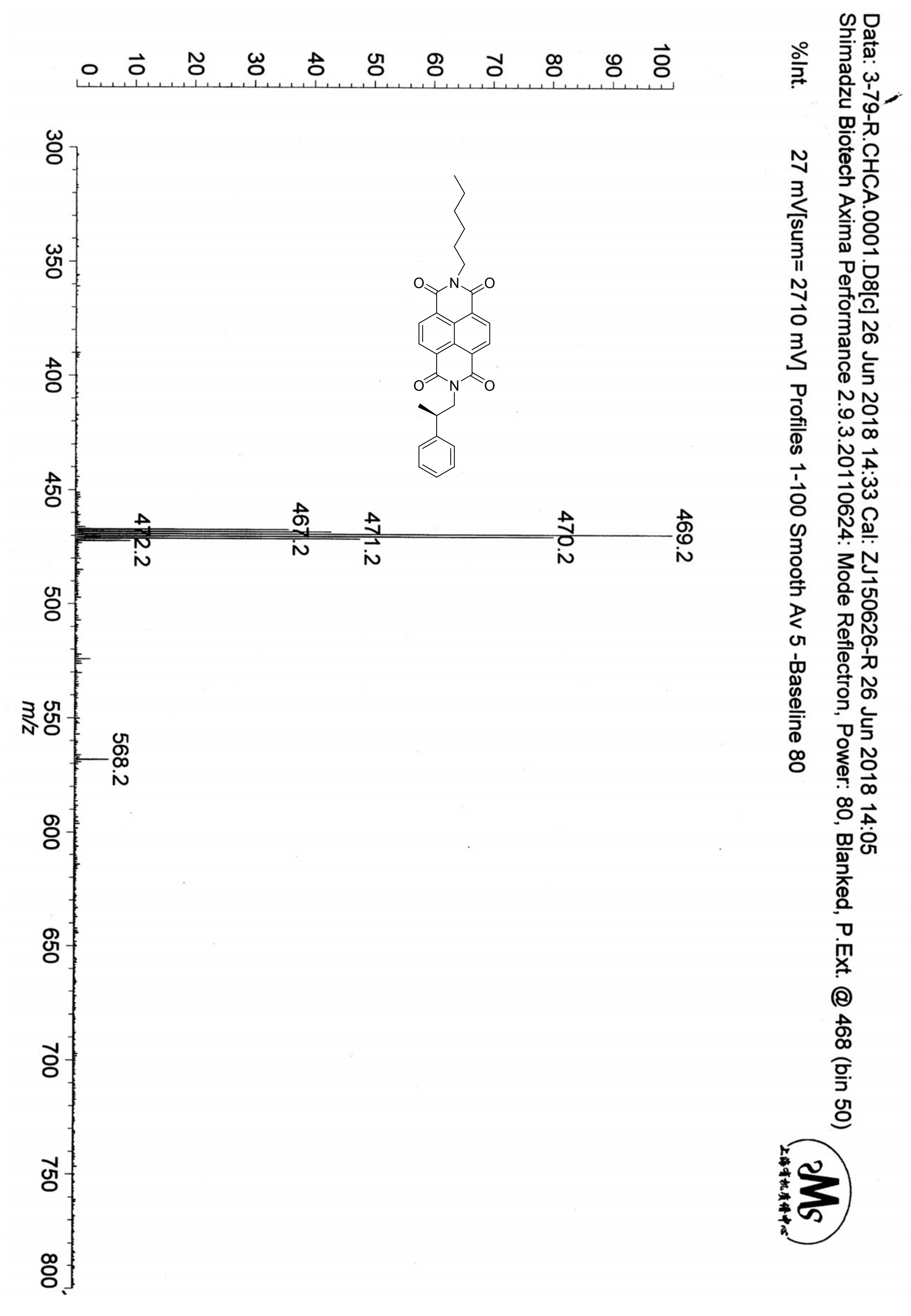
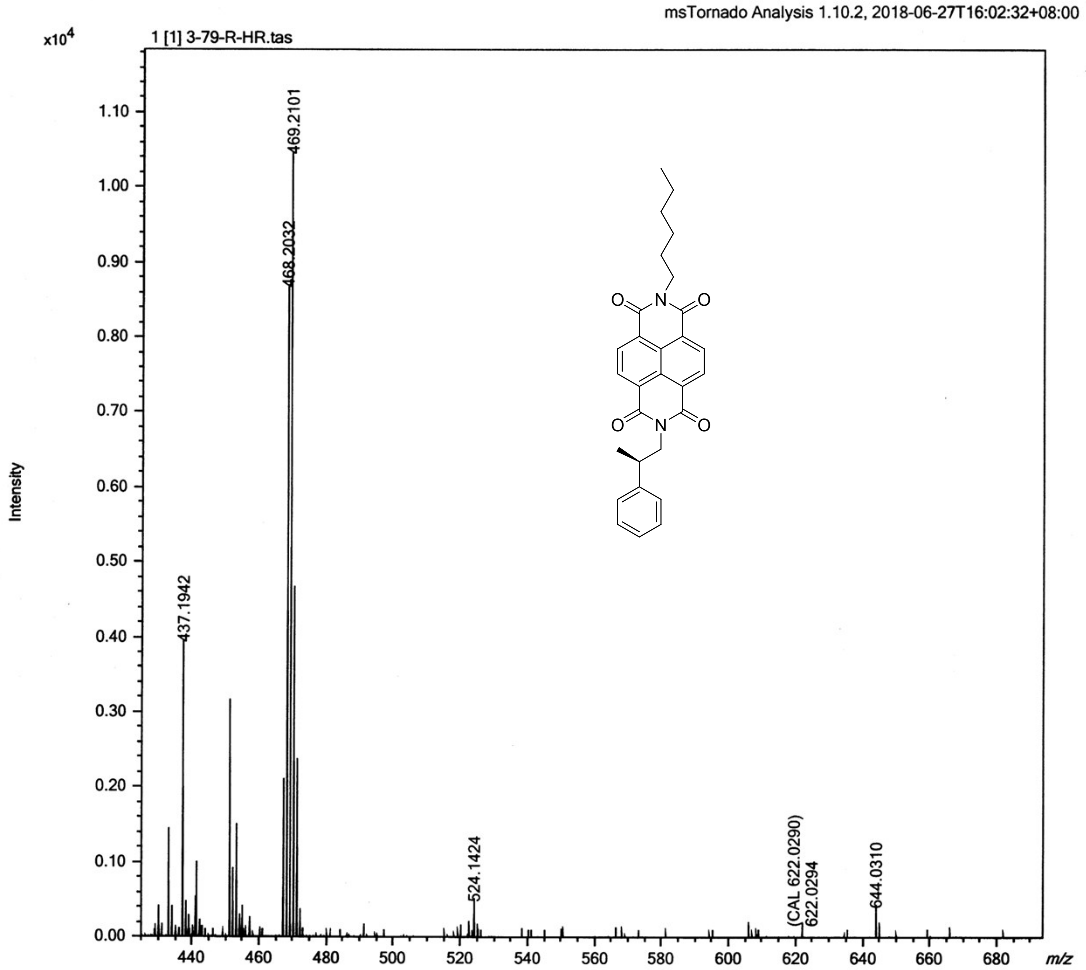


Figure S40. MS spectrum of **M-*R***



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
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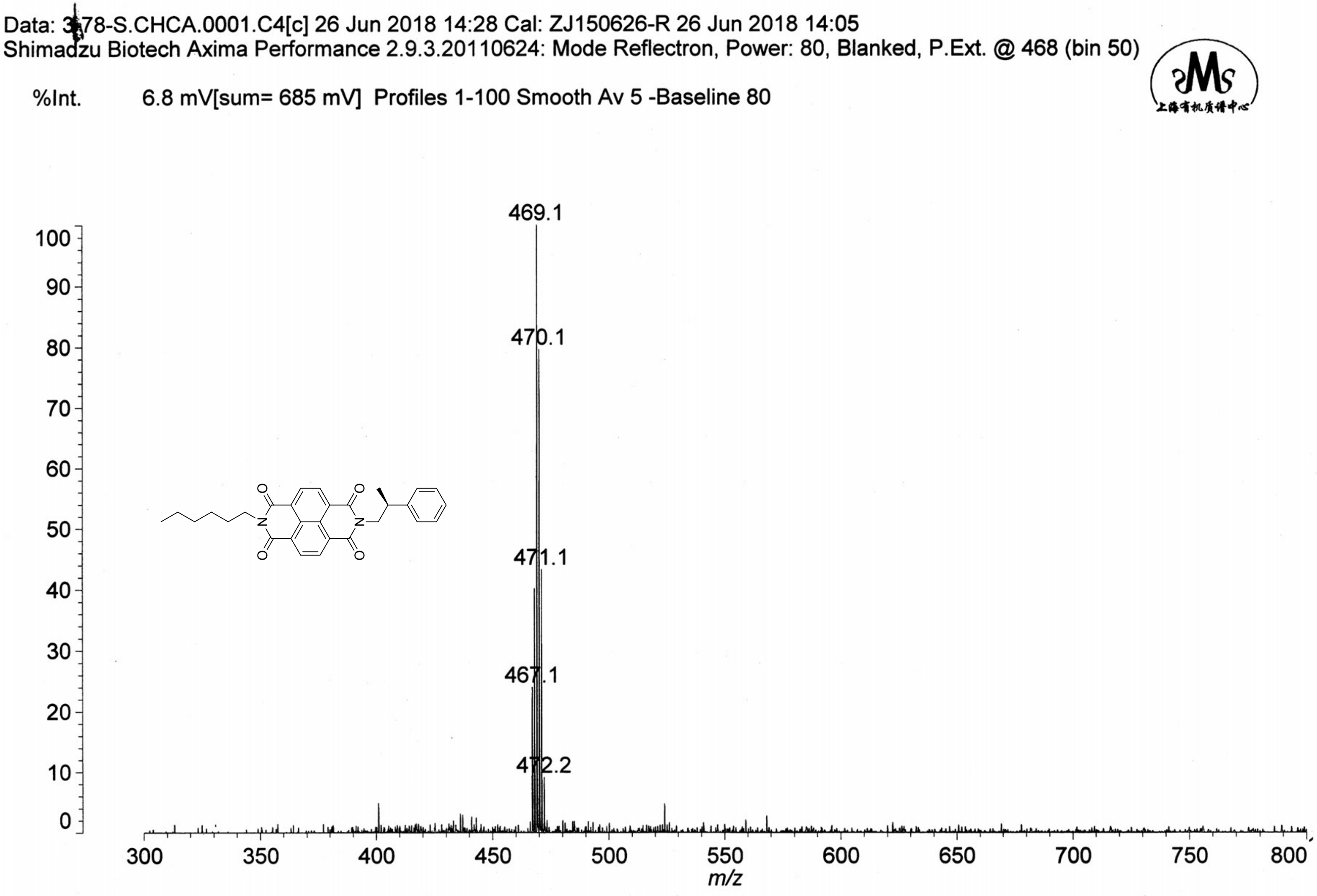
Elements

C 0 - 32 H 0 - 30 P 0 - 0 O 0 - 4 N 0 - 2 Na 0 - 1

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C27 H29 N2 O4 Na	468.20195	14.0	0.00120	0.00120	2.56
2	C29 H28 N2 O4	468.20436	17.0	0.00121	-0.00121	-2.58

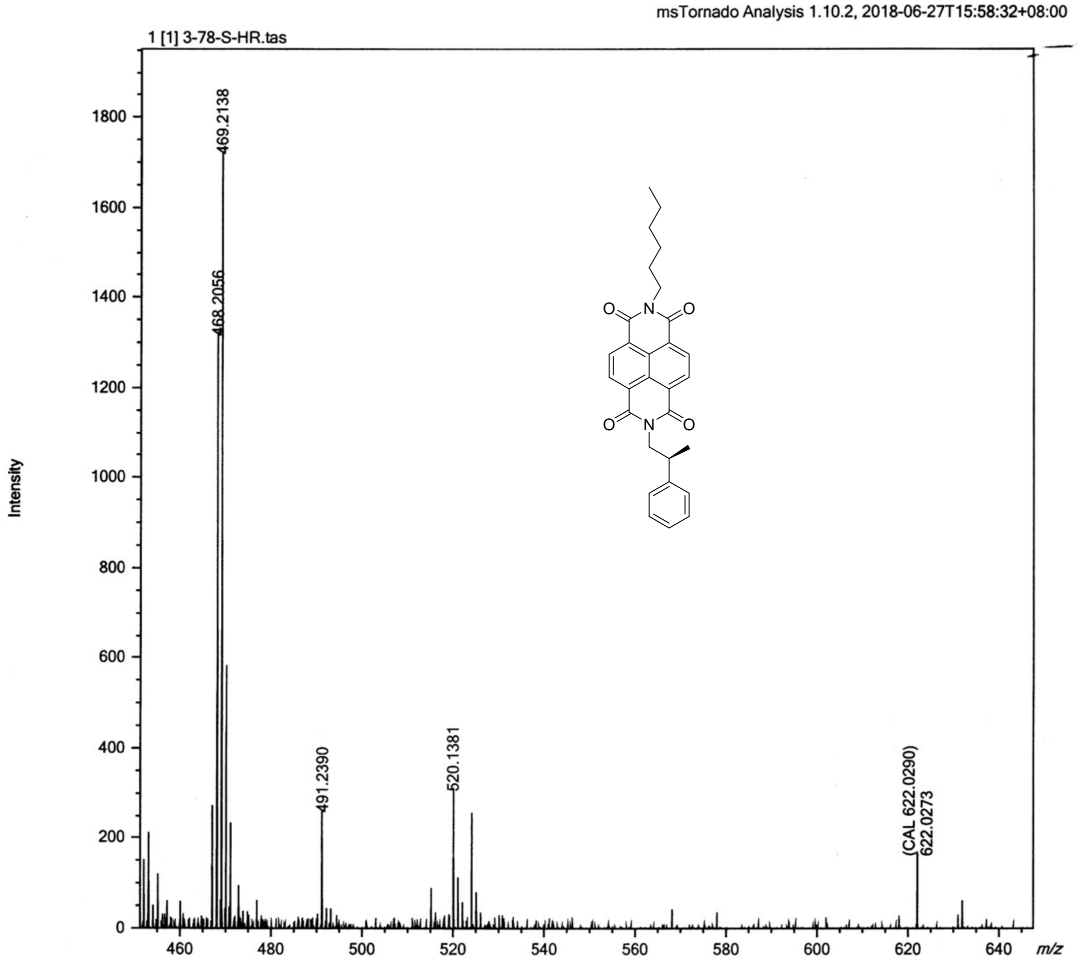
Figure S41. HRMS spectrum of **M-*R***



Data: 3[illegible]78-S.CHCA.0001.C4[c] 26 Jun 2018 14:28 Cal: ZJ150626-R 26 Jun 2018 14:05
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron, Power: 80, Blanked, P.Ext. @ 468 (bin 50)

%Int. 6.8 mV[sum= 685 mV] Profiles 1-100 Smooth Av 5 -Baseline 80

Figure S42. MS spectrum of **M-*S***



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
468.20558 ± 0.00234	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 30 H 0 - 30 P 0 - 0 O 0 - 4 N 0 - 2 Na 0 - 1

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C29 H28 N2 O4	468.20436	17.0	0.00122	0.00122	2.61

Figure S43. HRMS spectrum of **M-*S***