Supporting Information

Influence of Alkyl Chains on Photovoltaic Properties of 3D Rylene Propeller Electron Acceptors

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1. Measurements.

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in deuterated solvents on a Bruker ADVANCE 500 NMR Spectrometer. *J* values are expressed in Hz and quoted chemical shifts are in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. The signals have been designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), sd (singlet doublet), dd (doublet doublet) and m (multiplets). High resolution mass spectra (HRMS) were determined on IonSpec 4.7 Tesla Fourier Transform Mass Spectrometer. UV-vis absorption spectra were acquired with Hitachi (Model U-3010) UV-vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammogram (CV) measurement were carried out on a Zahner IM6e electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode at a scanning rate of 100 mVs-1under a nitrogen atmosphere. 0.1 M tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) dissolved in CH_2Cl_2 or acetonitrile (HPLC grade) was employed as the supporting electrolyte, which was calibrated by the ferrocene/ferroncenium (Fc/Fc^+) as the redox couple.

2. Thermal gravimetric analysis and DSC thermograms.

Table S1 Thermal properties date of TPH-4-TPH-7 molecules

Molecules	TPH-4	TPH-5	TPH-6	TPH-7
T_d[a] (°C)	374	391	351	363
T_m[b] (°C)	163	165	164	162
T_c [c] (°C)	123	123	123	123
ΔH[d] (J g^{-1})	-1.54	-1.54	-1.58	-0.71

[a]Thermal decomposition temperature corresponding to 5% weight loss in nitrogen measured by TGA; [b]Melting temperature determined from DSC; [c]Crystallization temperature determined from DSC; [d]Crystallization heat determined from DSC.

3. The chemical structure and optical properties of PDBT-T1.

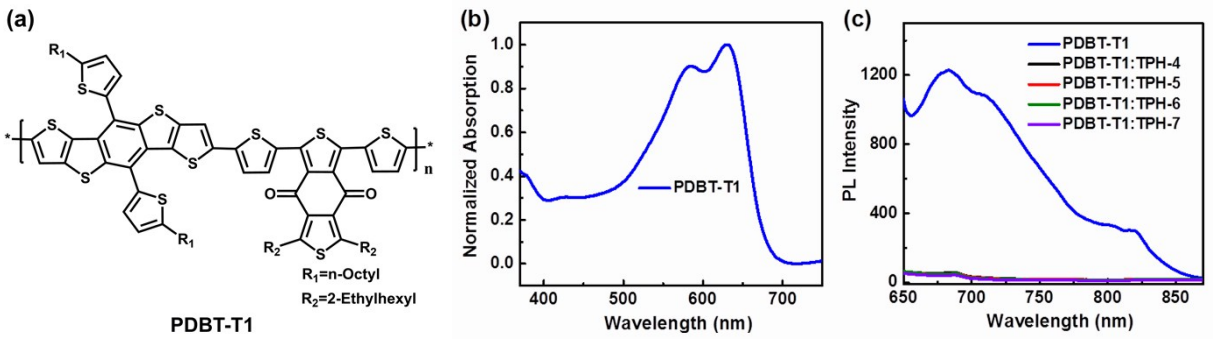


Fig. S1 (a) Chemical structure of PDBT-T1; (b) UV-vis absorption spectrum of neat PDBT-T1 film; (c) Photoluminescent spectra of neat PDBT-T1 film and PDBT-T1:TPH blend films (excitation at 630nm).

4. Cyclic voltammograms.

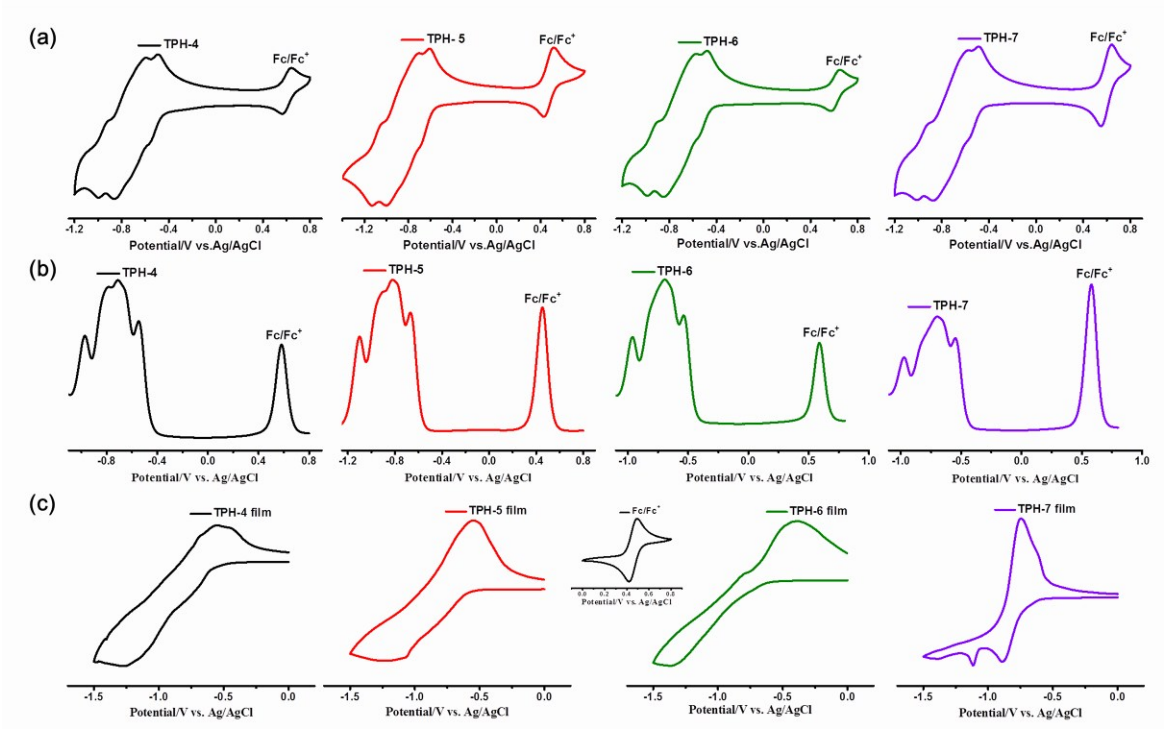


Fig. S2 Cyclic voltammograms (a) and differential pulse voltammetry (DPV) profiles (b) of TPH-4-TPH-7 in CH_2Cl_2 solution; (c) Cyclic voltammograms of TPH-4-TPH-7 in film and ferrocene in solution.

5. Photovoltaic performance.

Table S2 Summary of device parameters of solar cells based on PDBT-T1: TPHs with different D/A weight ratios

Active Layer	D:A Ratio	Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%] [a)]	PCE_{max} [%]
PDBT-T1 :TPH-4	1.3:1	111	0.983±0.004	11.98±0.11	60.1±0.7	7.07±0.08	7.26
	1:1	104	0.975±0.005	12.08±0.23	62.2±1.2	7.33±0.09	7.41
	1:1.3	103	0.994±0.002	11.64±0.13	59.6±0.9	6.89±0.14	6.99
PDBT-T1 :TPH-5	1.3:1	102	0.993±0.003	11.99±0.21	59.6±0.7	7.10±0.08	7.22
	1:1	107	0.982±0.003	12.06±0.13	61.6±1.3	7.30±0.11	7.38
	1:1.3	106	0.993±0.001	11.72±0.26	58.1±1.4	6.82±0.07	6.89
PDBT-T1 :TPH-6	1.3:1	108	0.979±0.002	11.95±0.20	61.3±0.8	7.17±0.06	7.32
	1:1	104	0.978±0.007	12.04±0.12	62.9±0.2	7.40 ±0.07	7.49
	1:1.3	113	0.988±0.003	11.58±0.05	60.6±0.4	6.94±0.10	7.08
PDBT-T1 :TPH-7	1.3:1	101	0.981±0.003	12.35±0.12	59.9±0.5	7.26±0.15	7.42
	1:1	105	0.982±0.004	12.33±0.34	64.8±1.4	7.83 ±0.17	8.04
	1:1.3	95	0.993±0.001	11.72±0.11	61.9±0.4	7.20±0.07	7.30

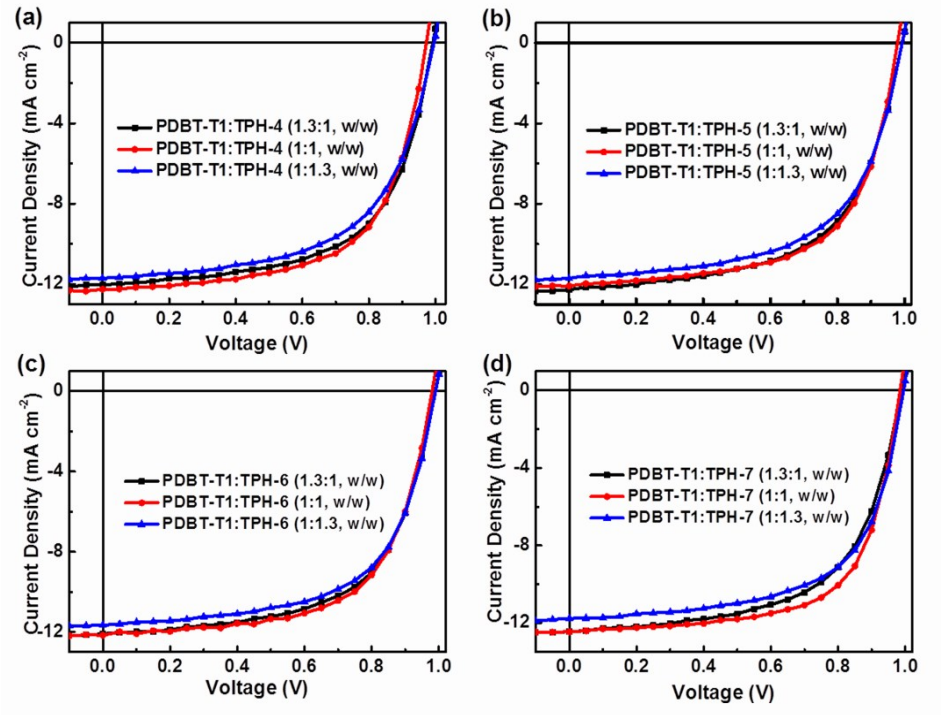


Fig. S3 The characteristic current density-voltage (*J-V*) curves for the devices based on PDBT-T1: TPHs with different D/A weight ratios.

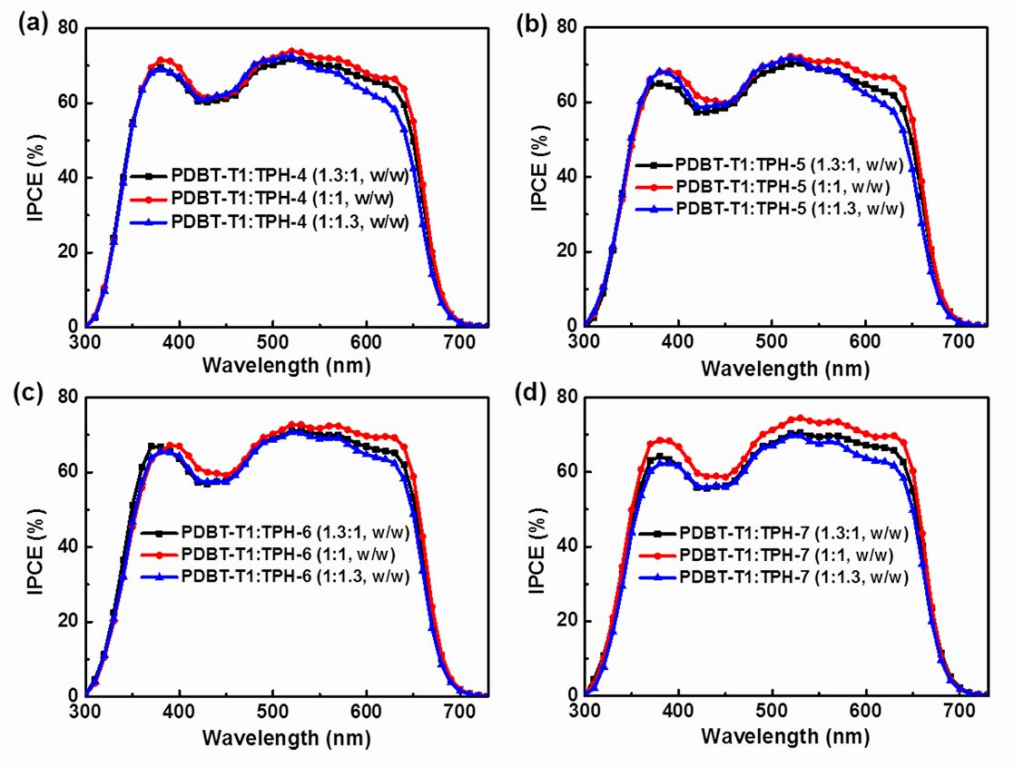


Fig. S4 The IPCE spectra for the devices based on PDBT-T1: TPHs with different D/A weight ratios.

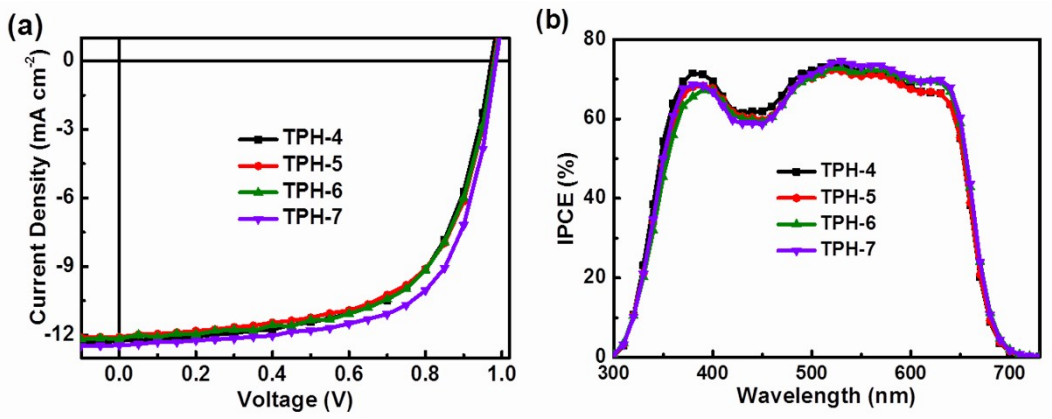


Fig. S5 (a) Characteristic current density-voltage (*J-V*) curves for the optimal devices without DIO under simulated AM 1.5G irradiation (100 mW cm^{-2}) and the corresponding IPCE spectra.

6. Carrier Mobility Measurements.

Carrier mobility was measured using the space-charge-limit current (SCLC) method. The electron mobility for pure TPH films was measured with the device architecture of ITO/Al/TPHs/Al. For the blend films, the electron mobility was measured with the device architecture of ITO/Al/PDBT-T1:TPHs/Al and the hole mobility was measured with the device architecture of ITO/MoO_x/PDBT-T1:TPHs/ MoO_x/Al. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, described by the Equation:

$$J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3 \quad (1)$$

where J is the current density, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant of the transport medium, μ is the charge mobility and L is the thickness of the acceptor. $V=V_{app}$ - V_{bi}, where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here). The electron mobility can be calculated from the slope of the $J^{0.5}$~V curves.

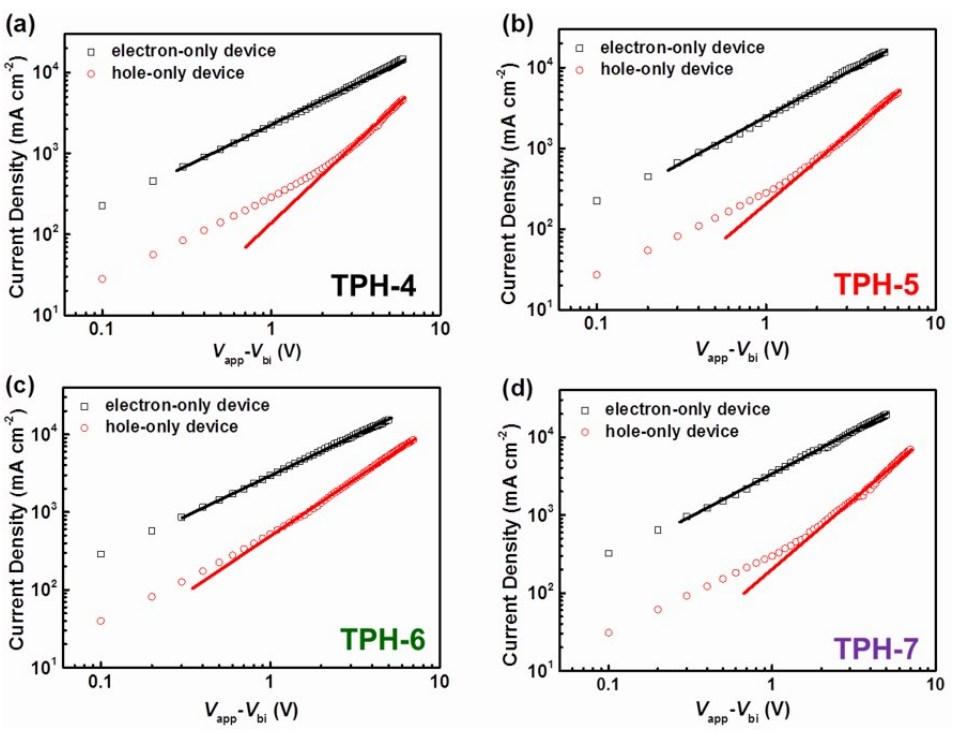


Fig. S6 The experimental current density-applied voltage (J-V) characteristics for the hole-only devices, and electron-only devices for (a) PDBT-T1:TPH-4, (b) PDBT-T1:TPH-5 (c) PDBT-T1:TPH-6 and (d) PDBT-T1:TPH-7 blend films.

Table S3 The electron and hole mobilities results measured by SCLC method based on PDBT-T1:TPHs blend films

Blend (0.25% DIO)	μ_e [10^{-3} cm^2 V^{-1} s^{-1}]	μ_e [10^{-3} cm^2 V^{-1} s^{-1}]	μ_e/μ_h
PDBT-T1:TPH-4	1.21 ± 0.22	0.73 ± 0.05	1.7
PDBT-T1:TPH-5	1.44 ± 0.13	0.85 ± 0.12	1.7
PDBT-T1:TPH-6	1.15 ± 0.14	0.75 ± 0.10	1.5
PDBT-T1:TPH-7	1.55 ± 0.16	1.08 ± 0.05	1.4

7. Morphology analysis.

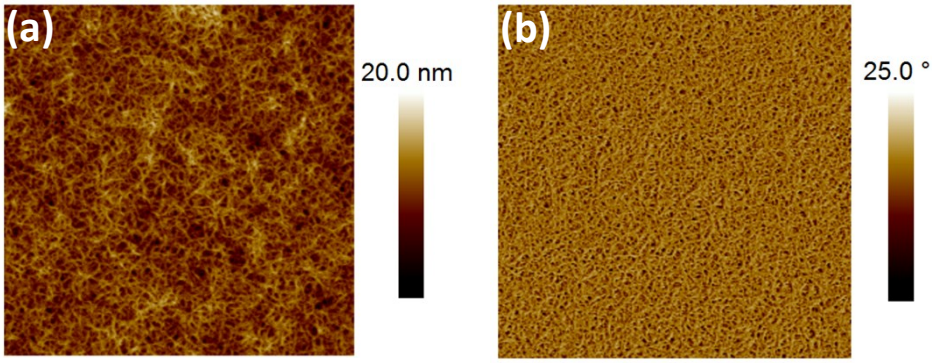


Fig. S7 AFM height (a) and phase (b) images of the neat PDBT-T1 film.

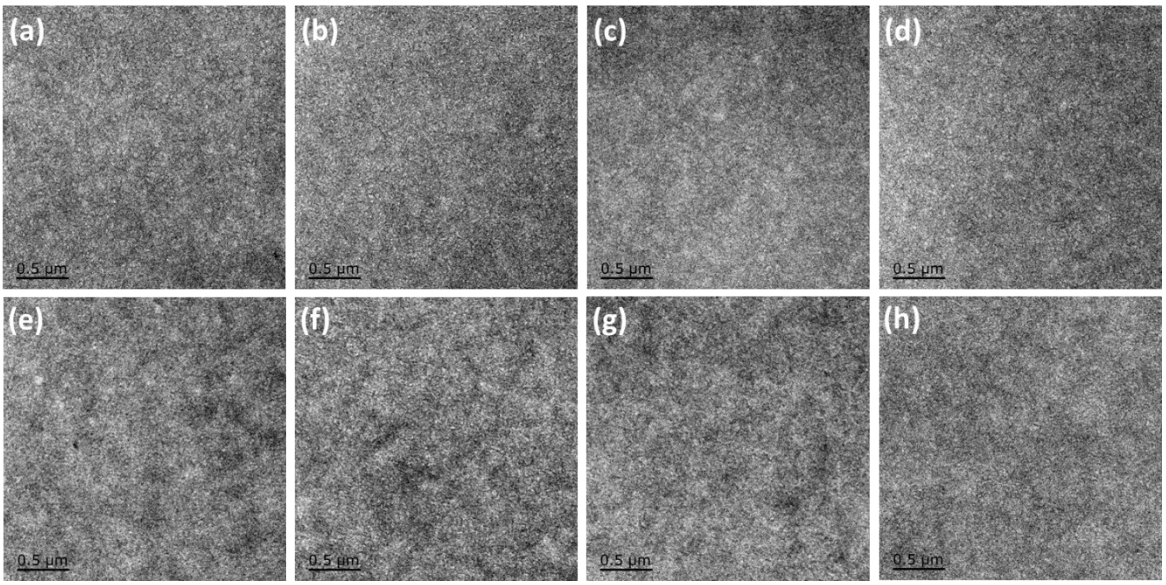


Fig. S8 TEM images of blend films based on (a, e) PDBT-T1:TPH-4, (b, f) PDBT-T1:TPH-5, (c, g) PDBT-T1:TPH-6, and (d, h) PDBT-T1:TPH-7 (a, b, c, d) without and (e, f, g, h) with 0.25% DIO.

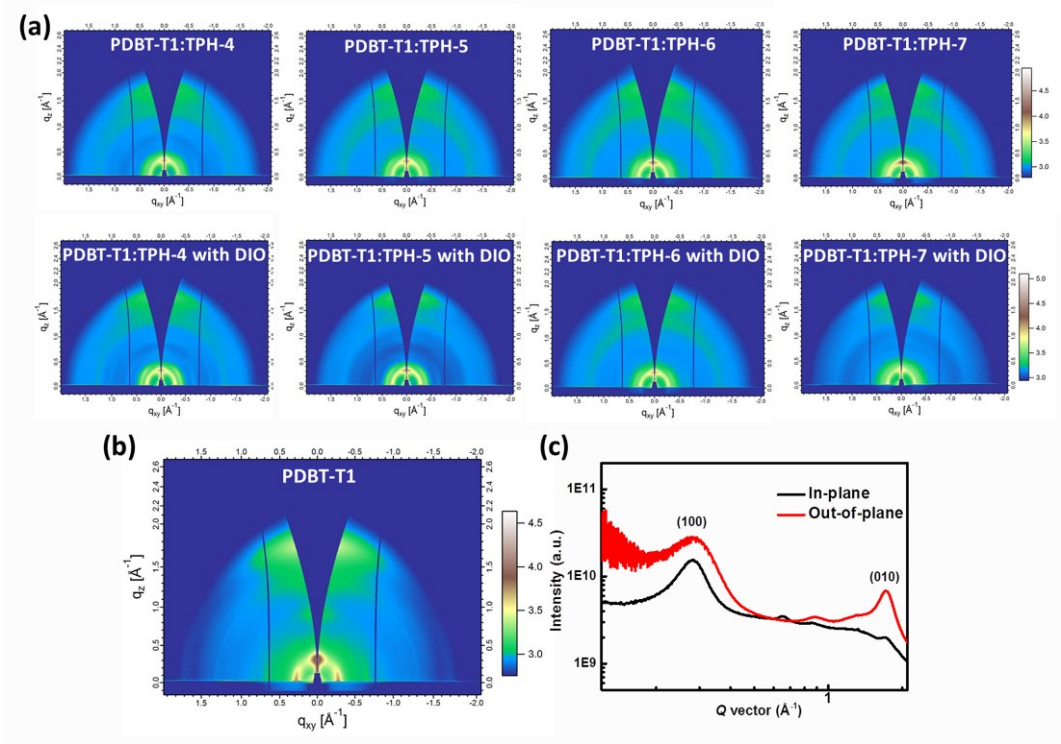


Fig. S9 (a) 2D GIWAXS patterns for the blend films without and with DIO. (b) 2D GIWAXS patterns for PDBT-T1 neat film and (c) scattering profiles of in-plane and out-of-plane for PDBT-T1neat film.

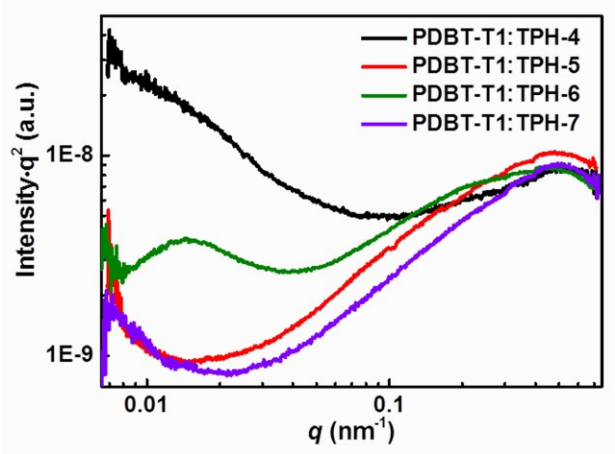
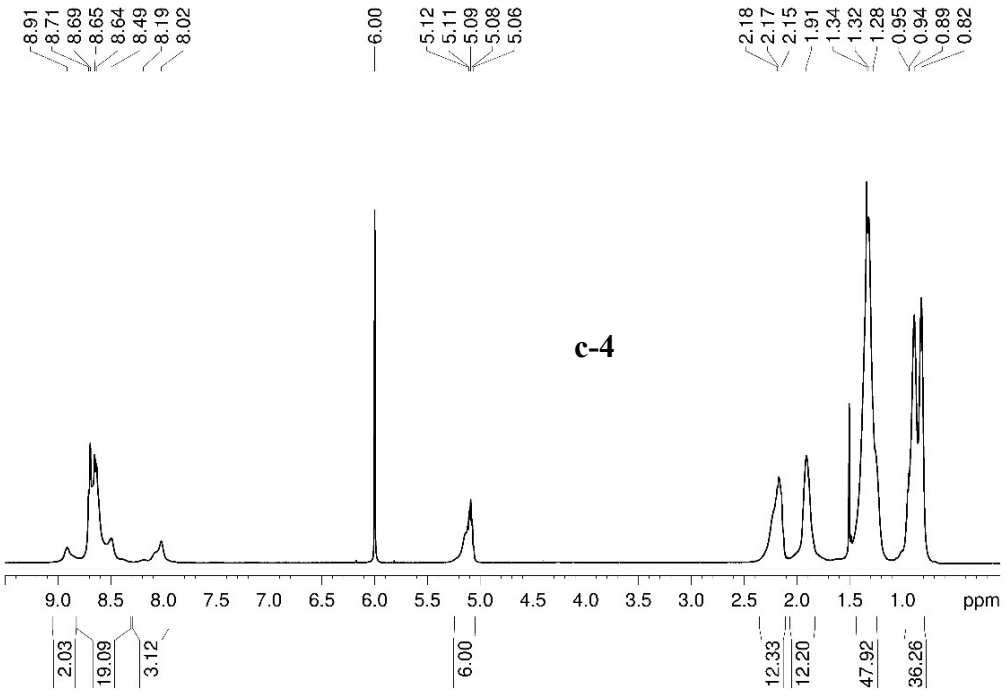
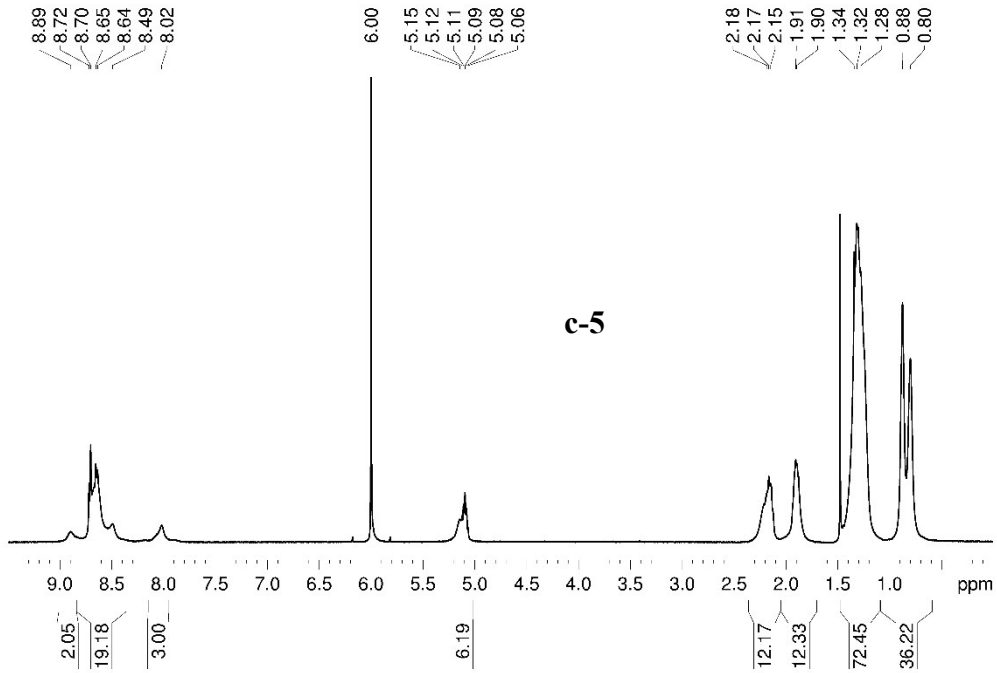


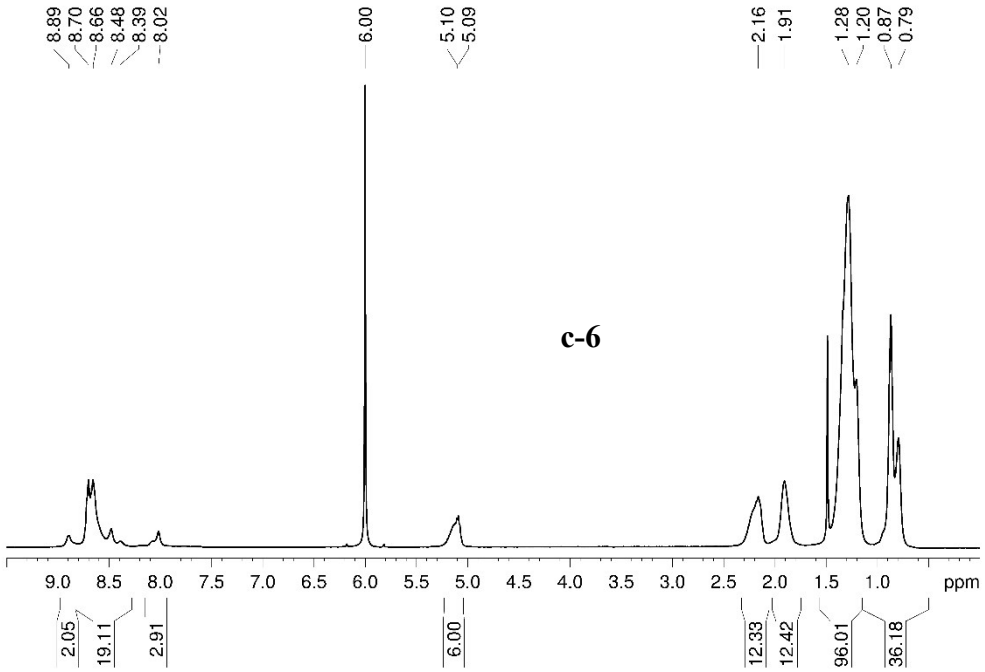
Fig. S10 R-SoXS profiles for the blend films.

8. ^{1}H NMR Spectra and ^{13}C NMR Spectra.

^{1}H NMR Spectra of c-4-c-5 and TPH-4-TPH-5 (500 MHz, $C_2D_2Cl_4$, 373.2 K)



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8.48
8.39
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5.10
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0.87
0.79
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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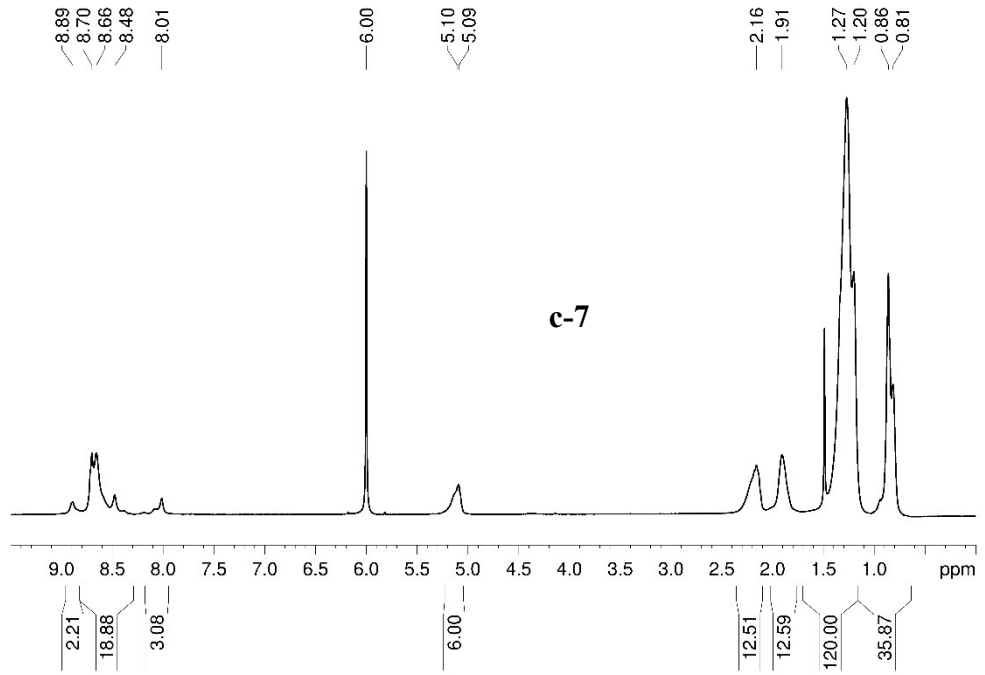
c-6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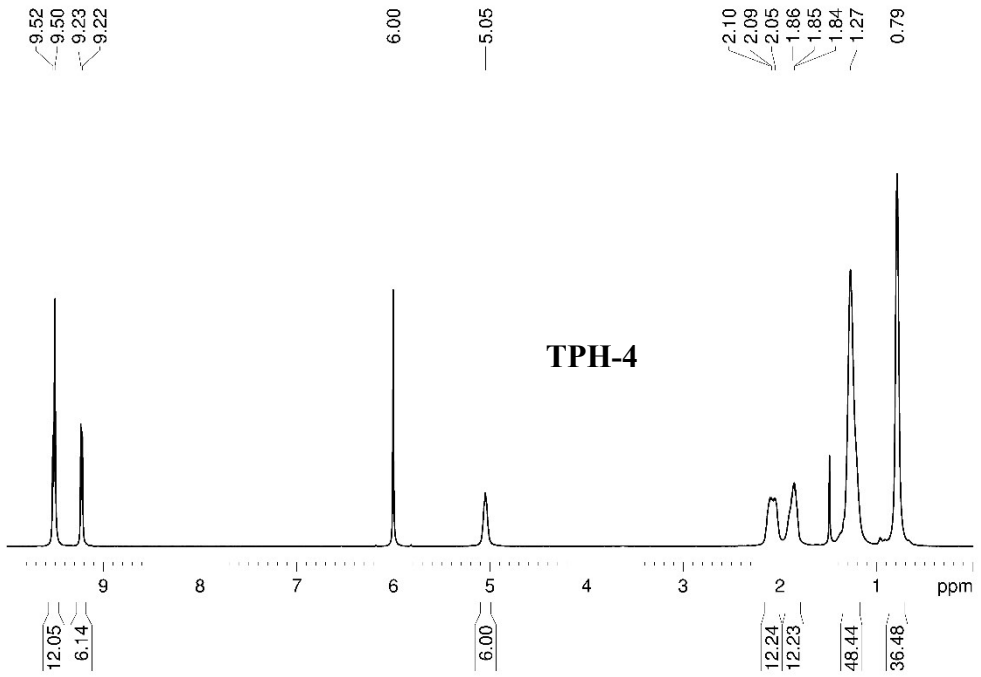
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TPH-4
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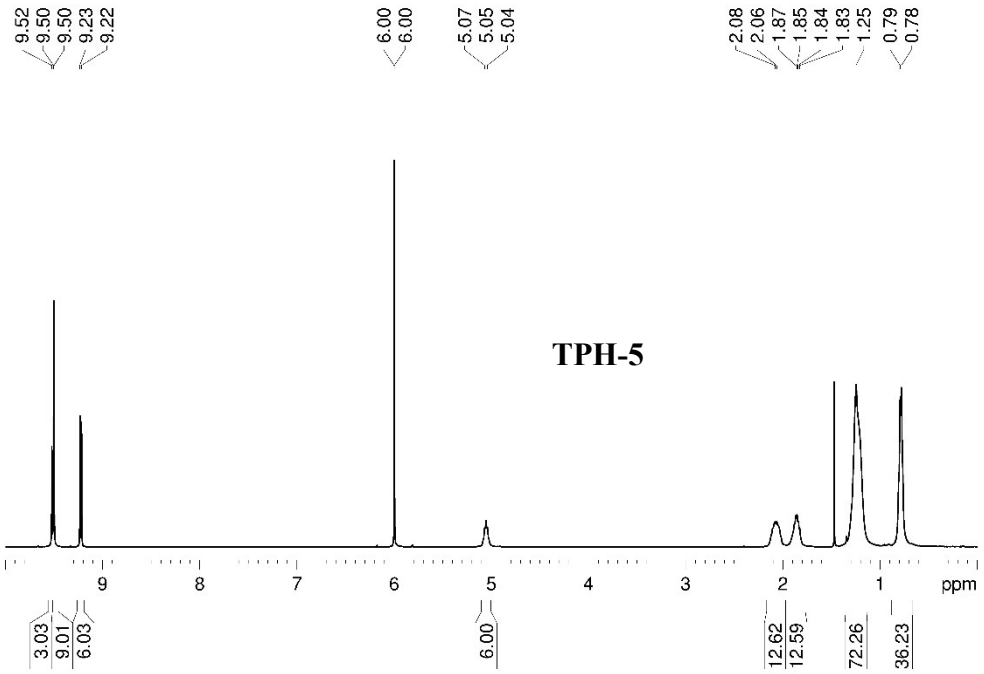
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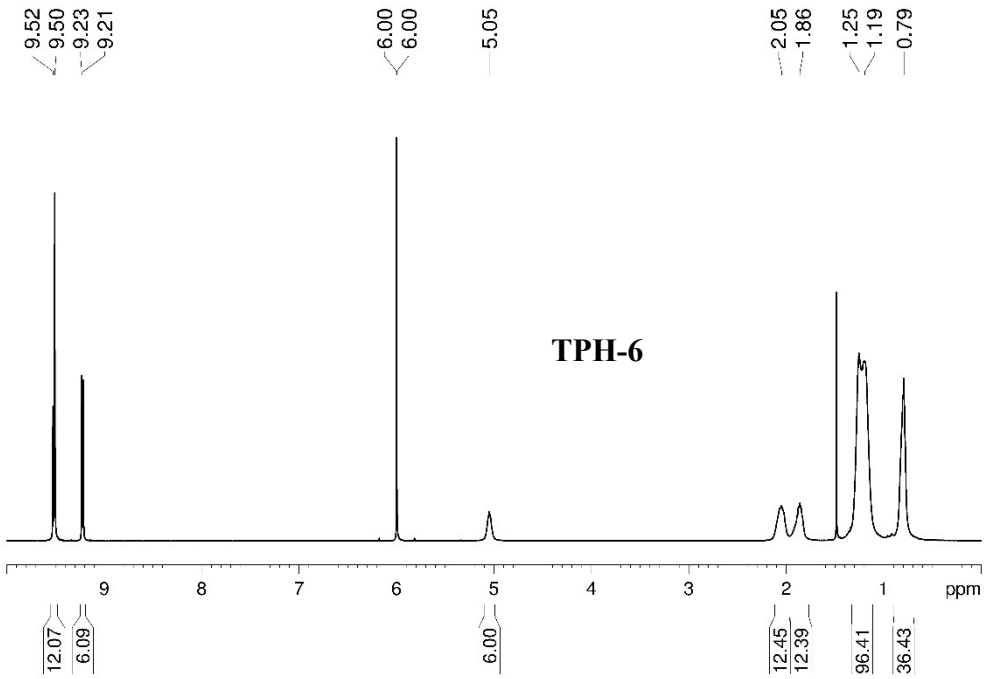
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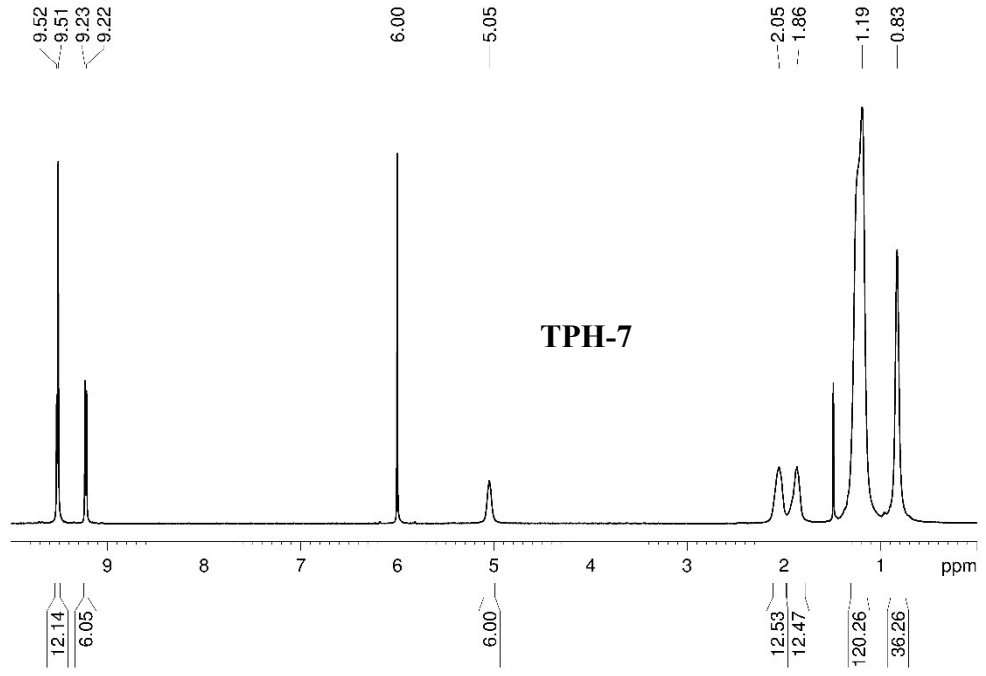
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7
6
5
4
3
2
1
ppm
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6.00
12.53
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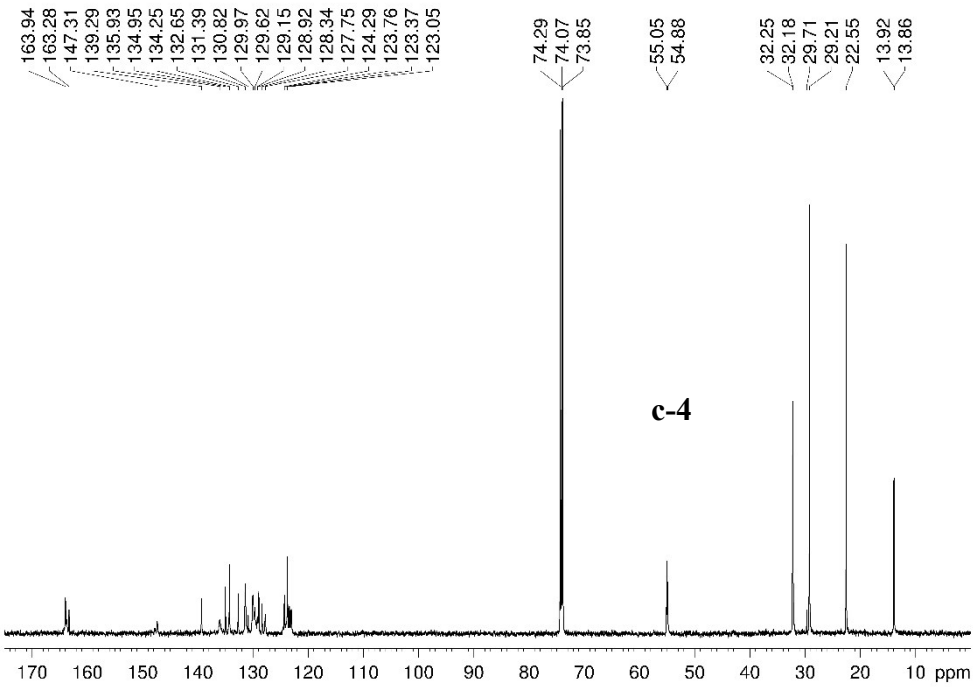
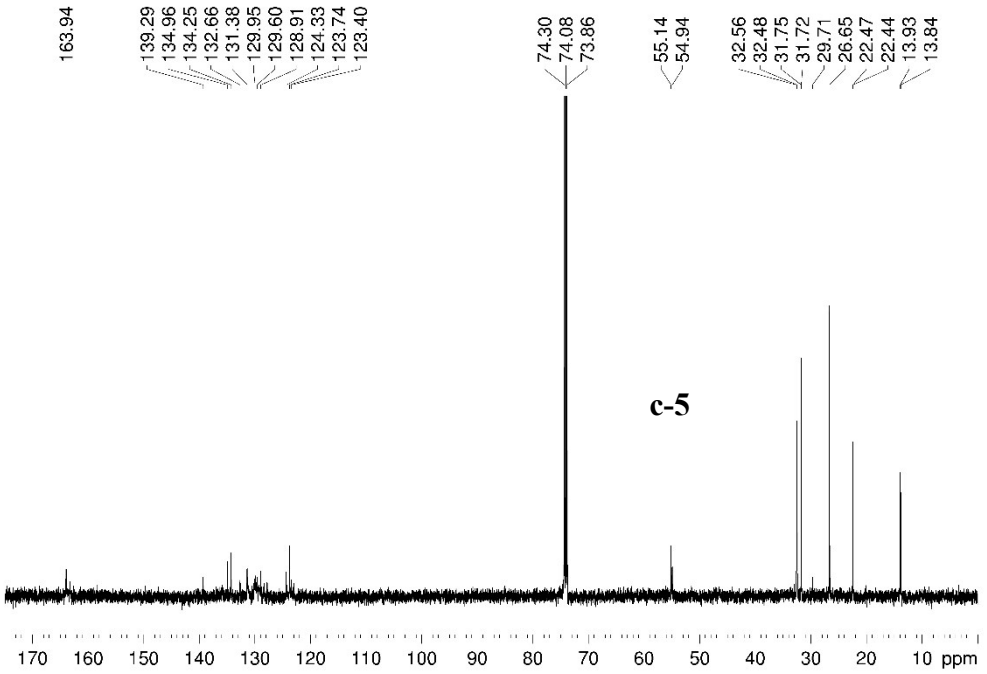
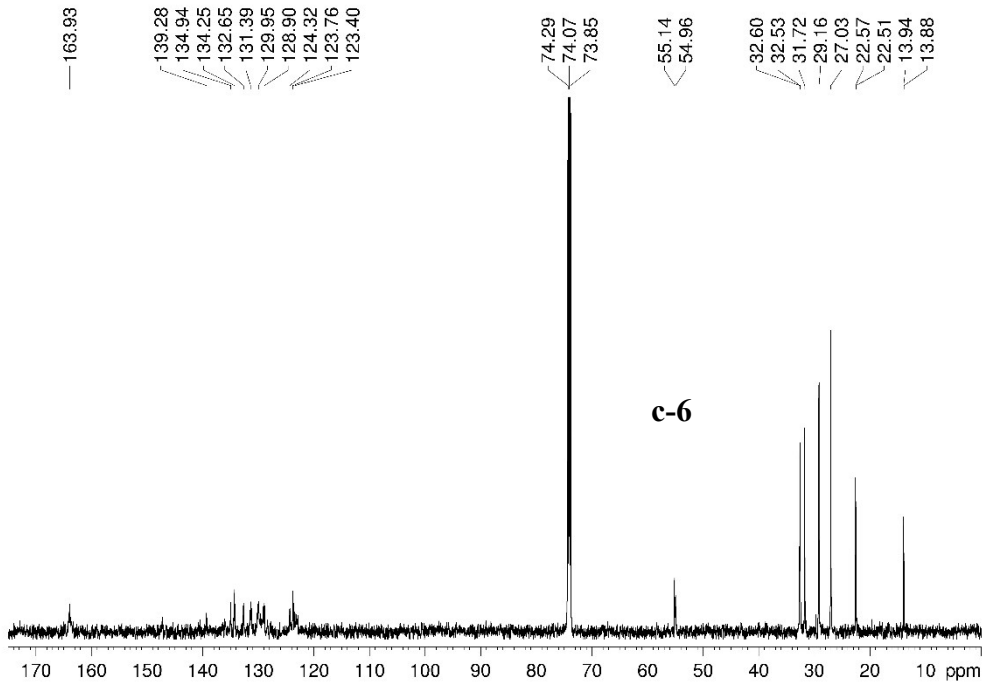
^{13}C NMR Spectra of c-4-c-7 and TPH-4-TPH-7(500 MHz, $C_2D_2Cl_4$, 373.2 K)



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55.14
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32.60
32.53
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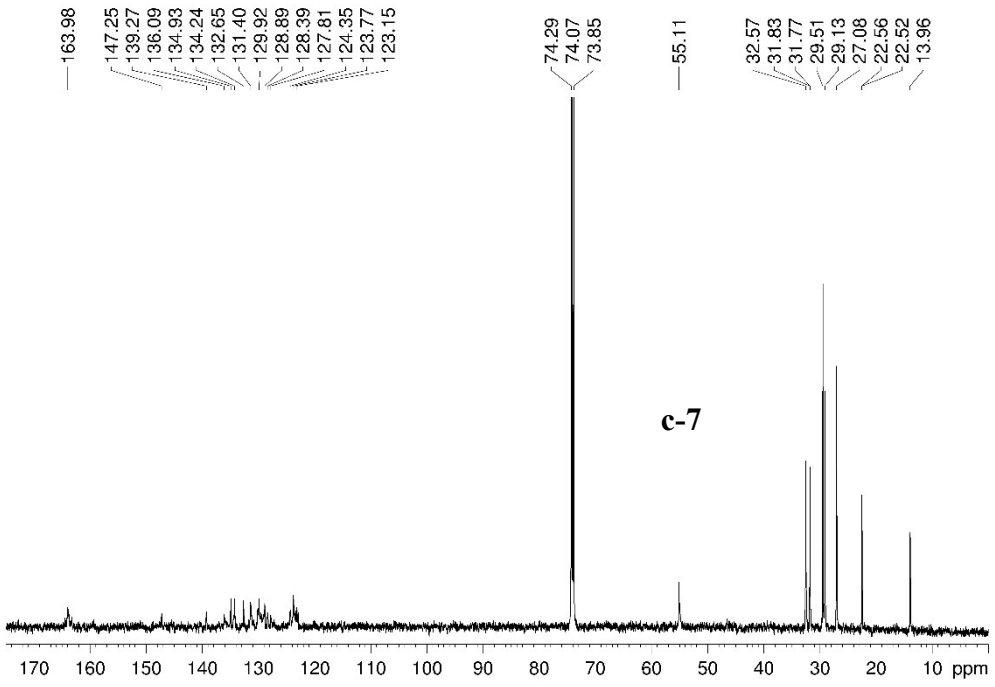
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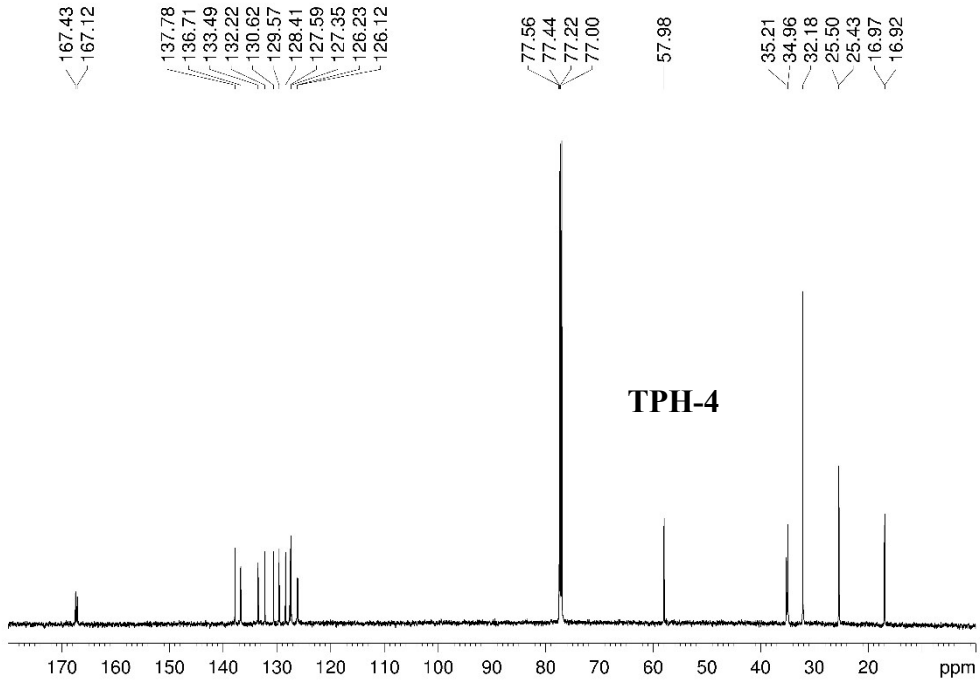
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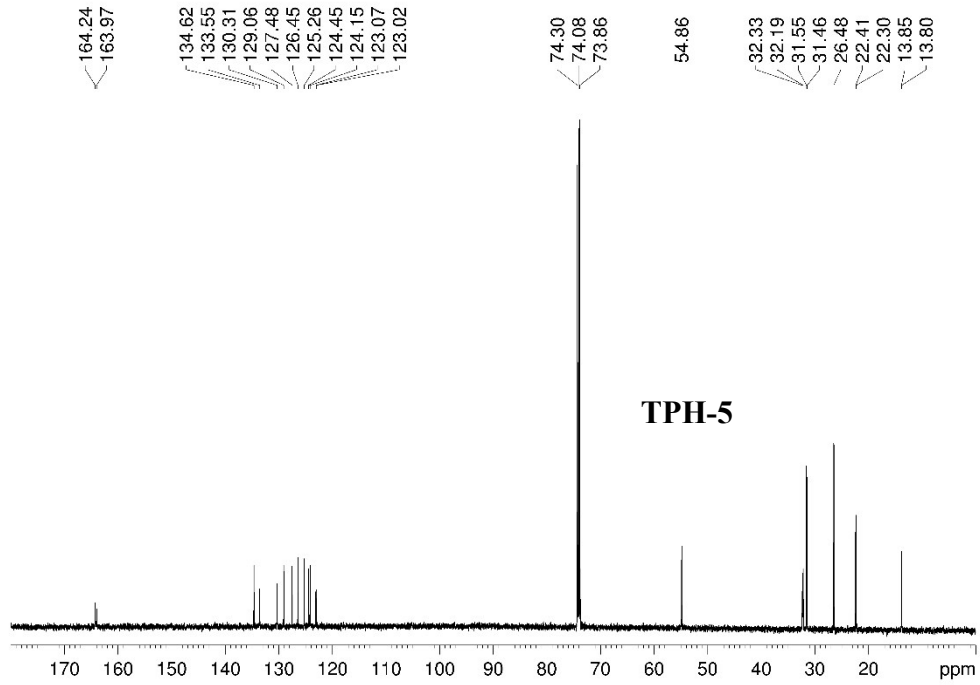
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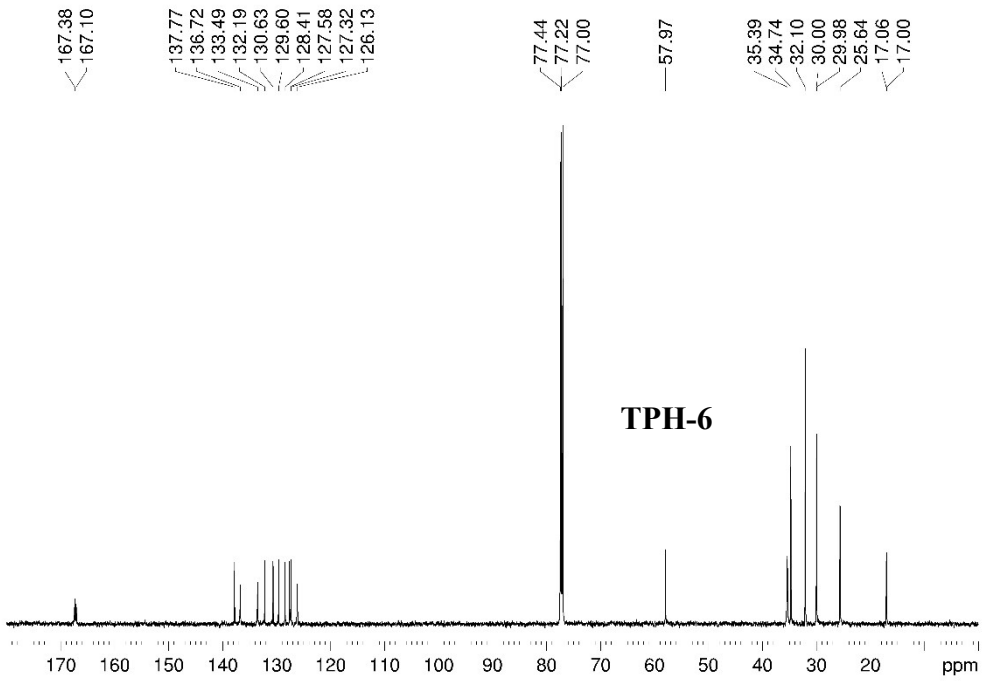
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TPH-6
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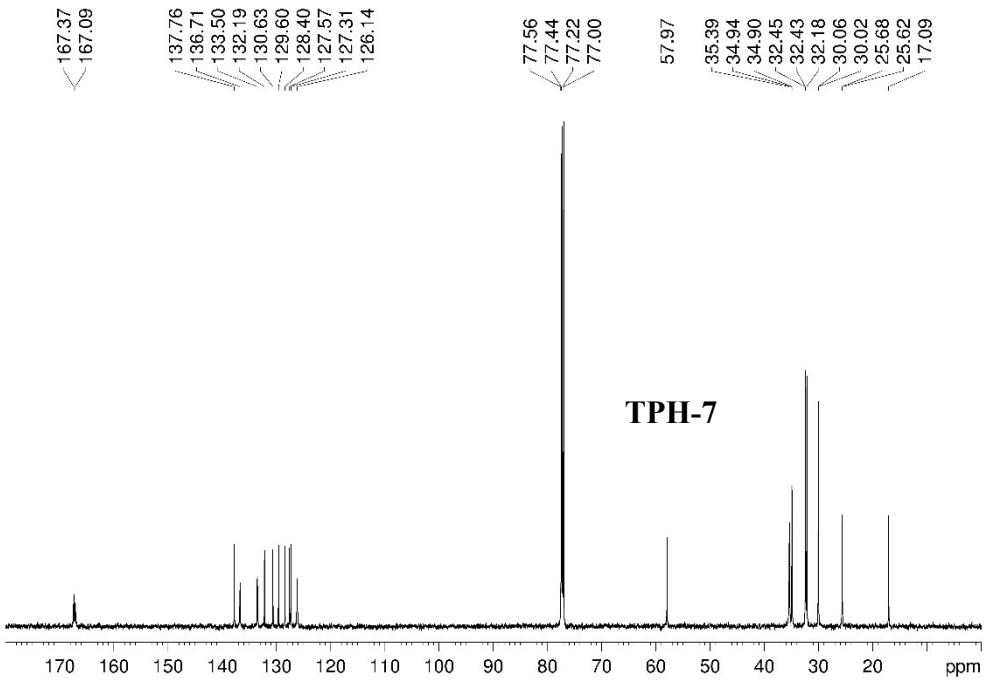
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32.45
32.43
32.18
30.06
30.02
25.68
25.62
17.09
TPH-7
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

9. HRMS Spectra of c-4-c-7 and TPH-4-TPH-7

Analysis Info

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Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

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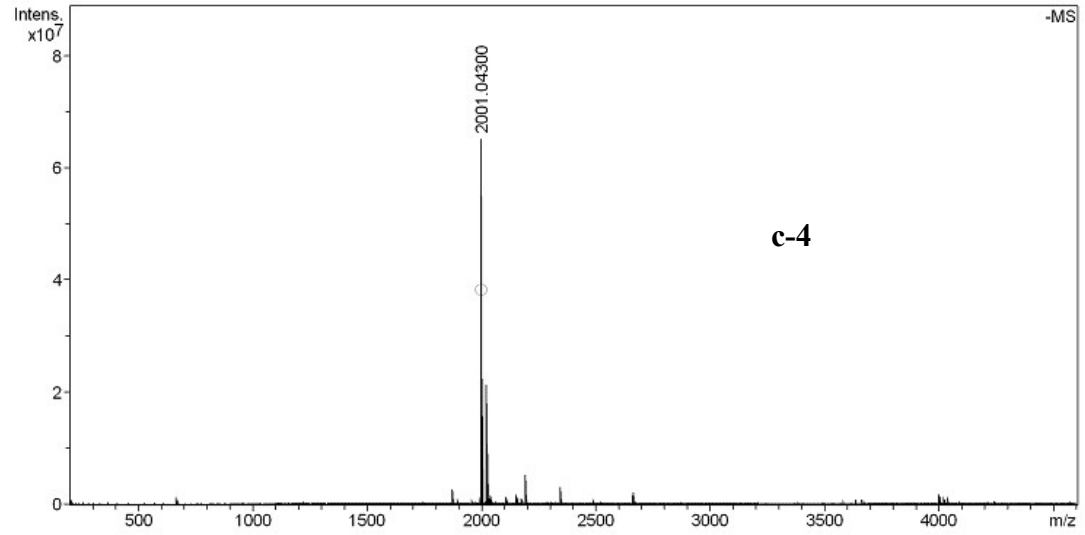
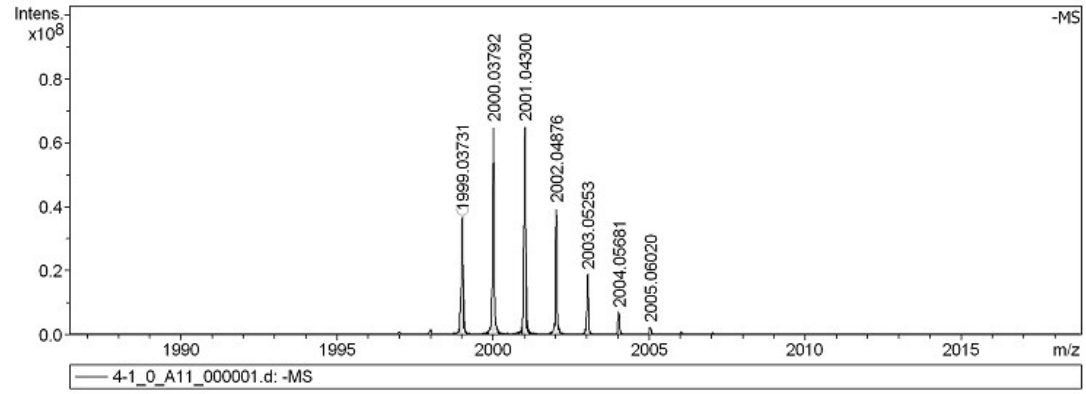
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	4600.0 m/z	Laser Power	29.4 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				





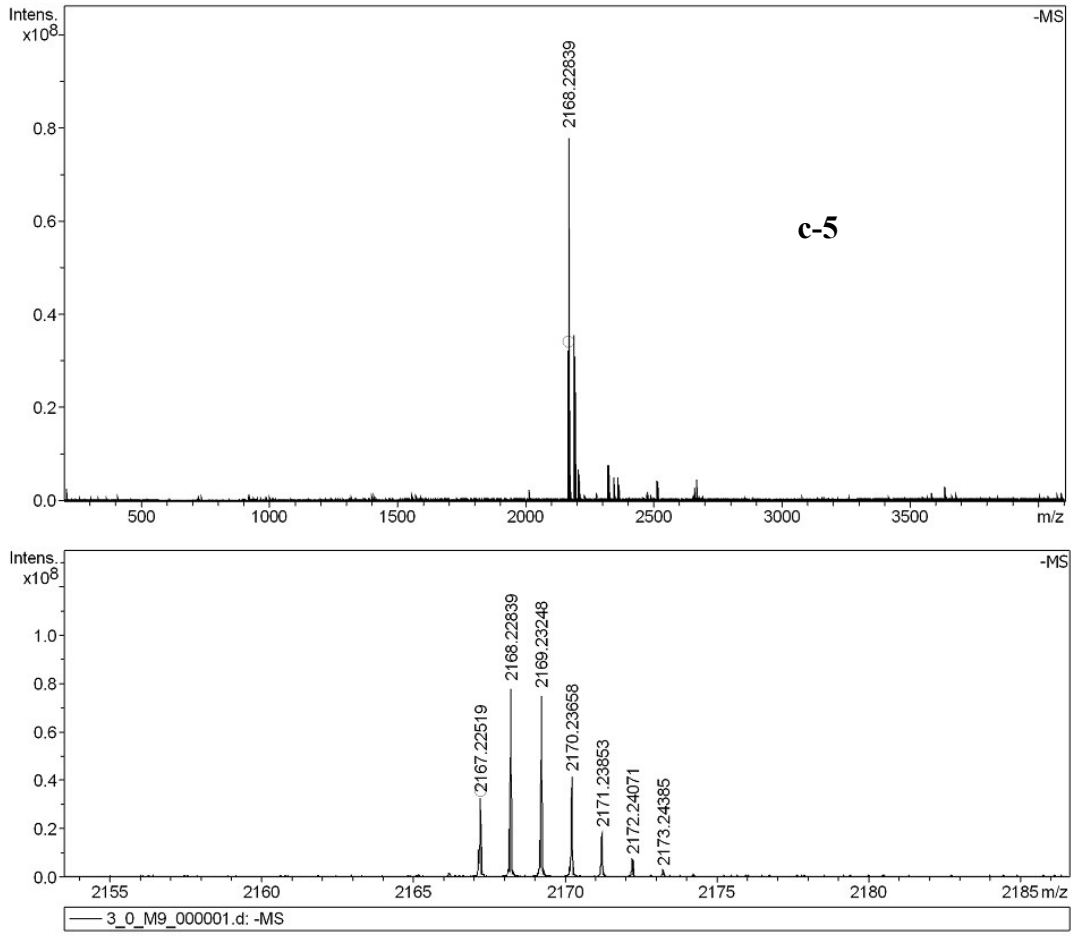
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1999.037313	1	C132H138N6O12	100.00	1999.037822	-0.3	0.4	148.7	67.0	odd	ok

Analysis Info

Analysis Name	D:\Data\MALDI\2015\1027\3_0_M9_000001.d	Acquisition Date	10/27/2015 4:31:51 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	14	Calibration Date	Tue Oct 27 03:43:13
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	4100.0 m/z	Laser Power	27.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



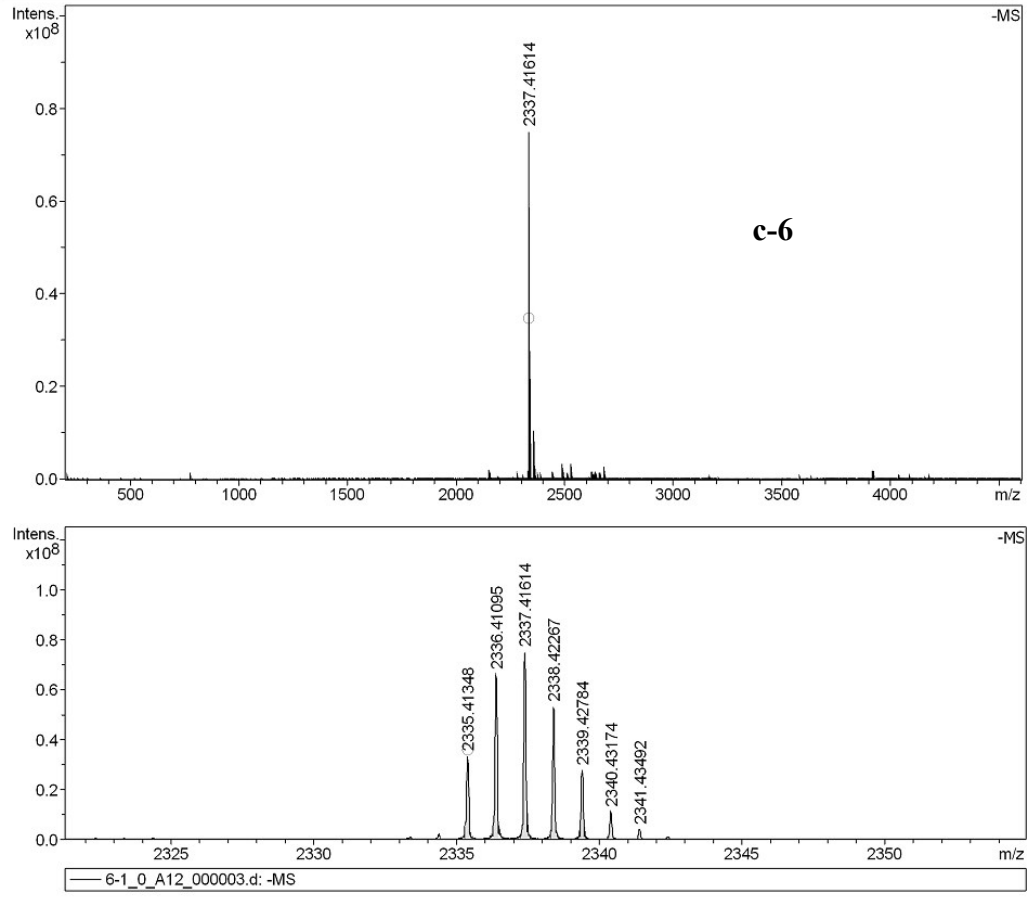
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
2167.225193	1	C144H162N6O12	100.00	2167.225623	0.2	0.0	97.9	67.0	odd	ok

Analysis Info

Analysis Name	D:\Data\MALDI\2015\1119\6-1_0_A12_000003.d	Acquisition Date	11/19/2015 3:45:52 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	6	Calibration Date	Thu Nov 19 03:32:21
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	4600.0 m/z	Laser Power	34.2 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



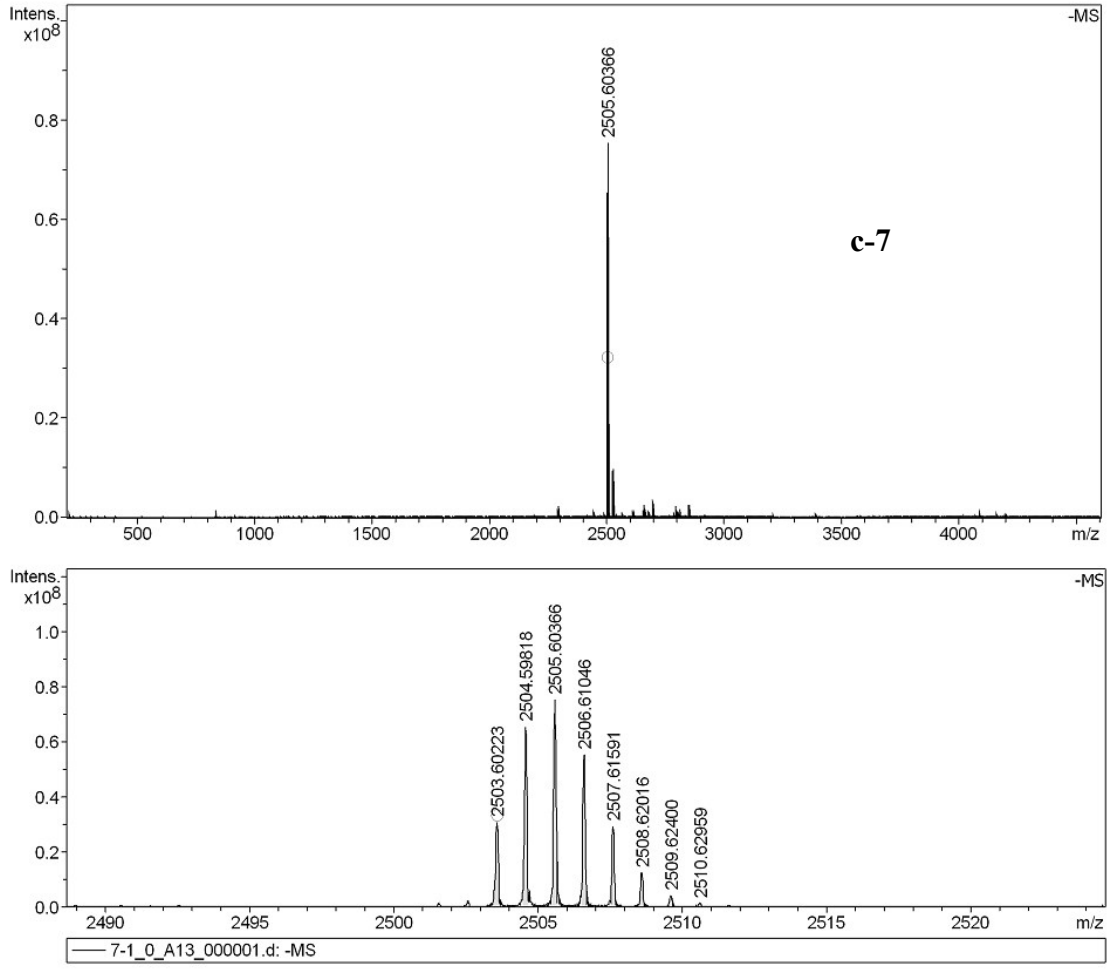
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2335.413482	1	C156H186N6O12	100.00	2335.413424	-0.0	1.0	116.3	67.0	odd	ok

Analysis Info

Analysis Name	D:\Data\MALDI\2015\1119\7-1_0_A13_000001.d	Acquisition Date	11/19/2015 3:47:44 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	6	Calibration Date	Thu Nov 19 03:32:21
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	4600.0 m/z	Laser Power	35.2 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



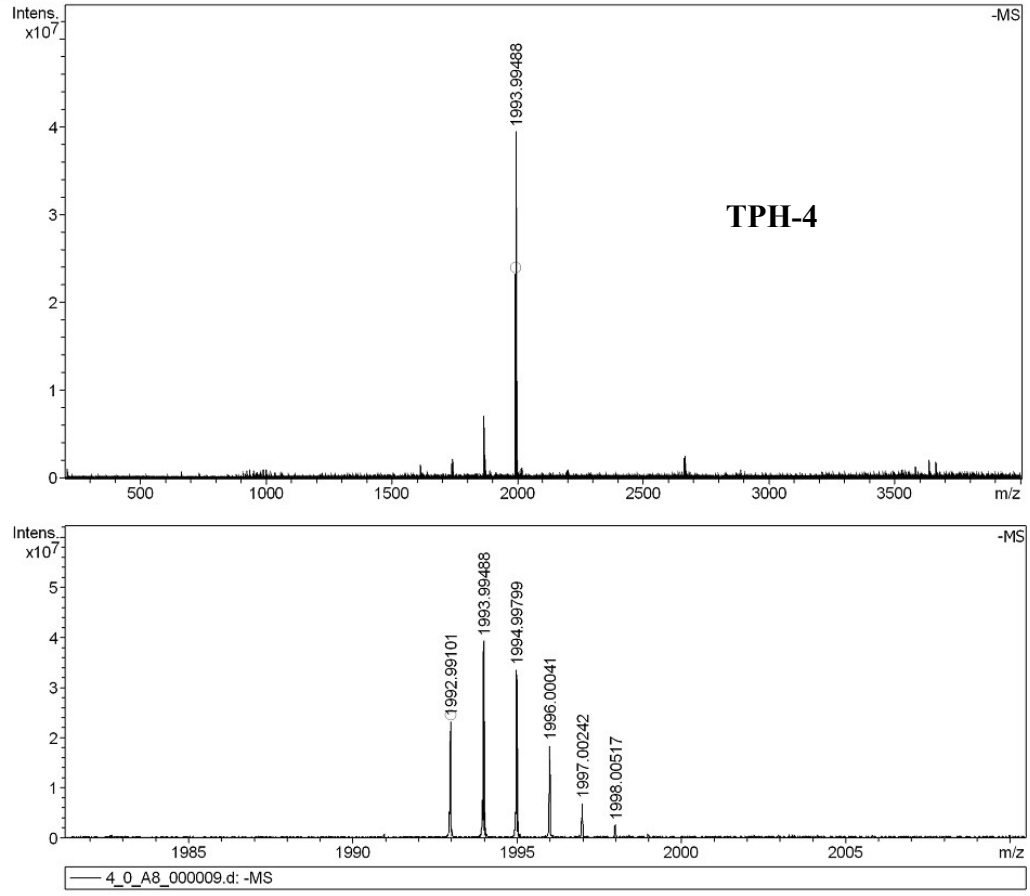
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2503.602227	1	C168H210N6O12	100.00	2503.601225	0.4	0.9	93.8	67.0	odd	ok

Analysis Info

Analysis Name	D:\Data\MALDI\2015\1119\4_0_A8_000009.d	Acquisition Date	11/19/2015 3:20:10 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	10	Calibration Date	Wed Nov 18 04:39:25
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	4000.0 m/z	Laser Power	20.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



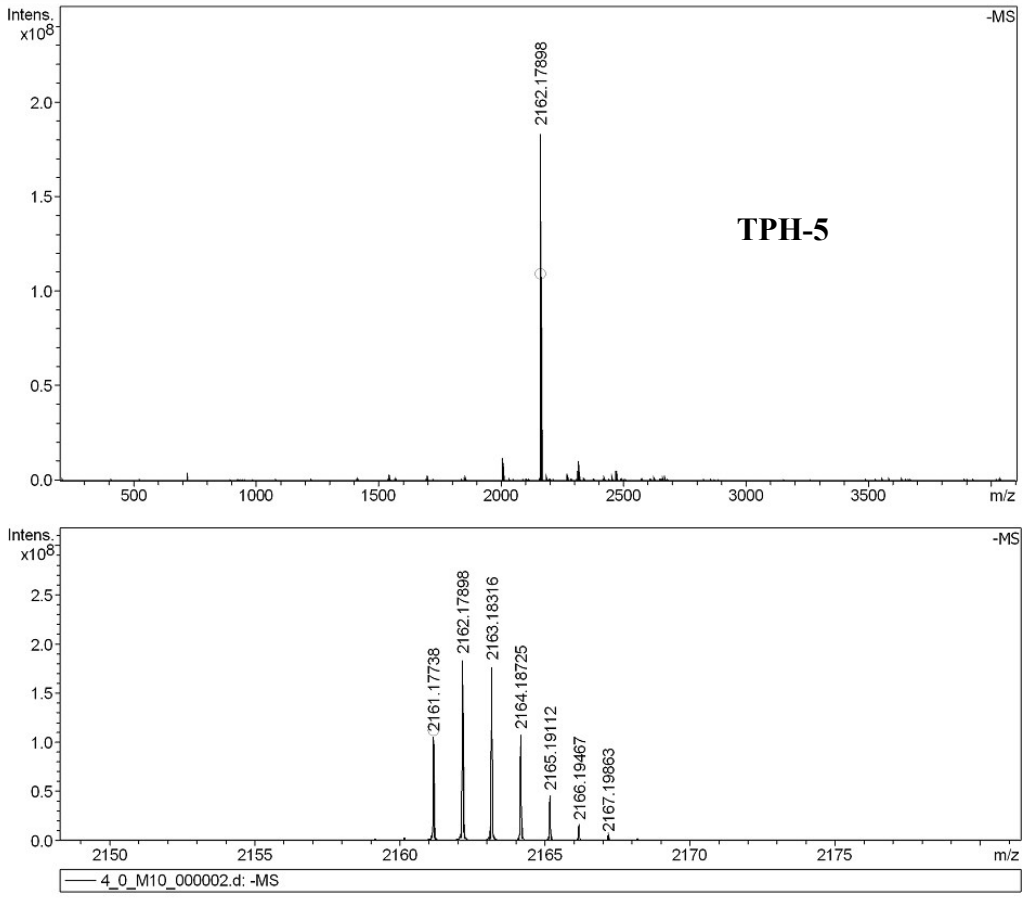
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1992.991008	1	C132H132N6O12	100.00	1992.990872	-0.1	-0.1	65.1	70.0	odd	ok

Analysis Info

Analysis Name	D:\Data\MALDI\2015\1027\4_0_M10_000002.d	Acquisition Date	10/27/2015 4:35:02 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	5	Calibration Date	Tue Oct 27 03:43:13
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	4100.0 m/z	Laser Power	25.4 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



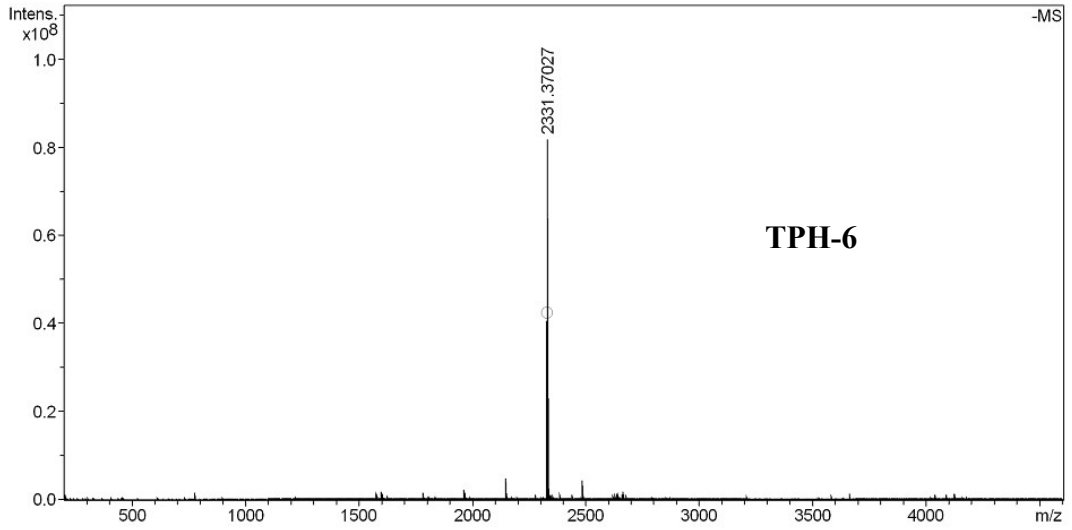
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2161.177381	1	C144H156N6O12	100.00	2161.178673	0.6	0.9	80.3	70.0	odd	ok

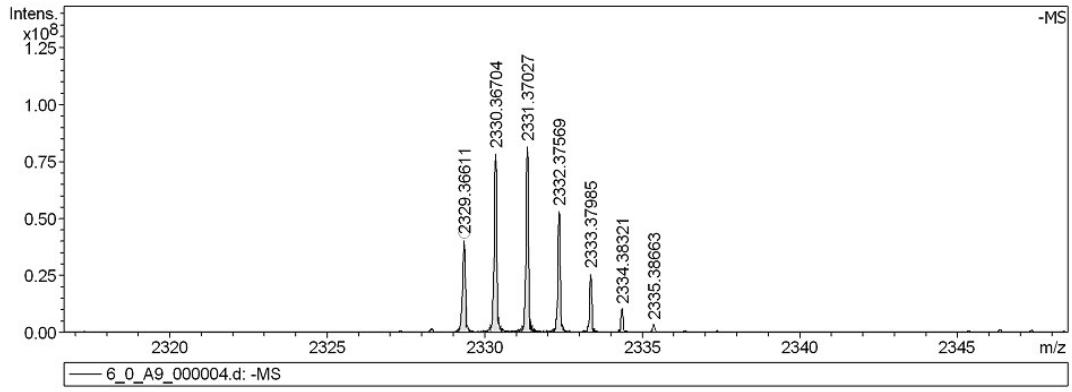
Analysis Info

Analysis Name	D:\Data\MALDI\2015\1119\6_0_A9_000004.d	Acquisition Date	11/19/2015 3:34:51 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	10	Calibration Date	Thu Nov 19 03:32:21
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	4600.0 m/z	Laser Power	28.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				





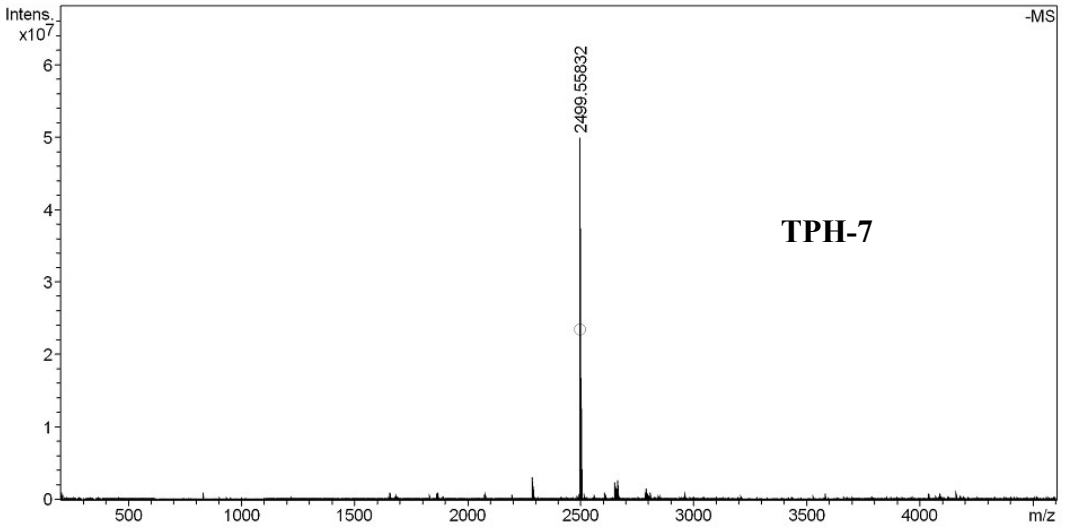
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
2329.366113	1	C156H180N6O12	100.00	2329.366474	-0.2	0.7	79.3	70.0	odd	ok

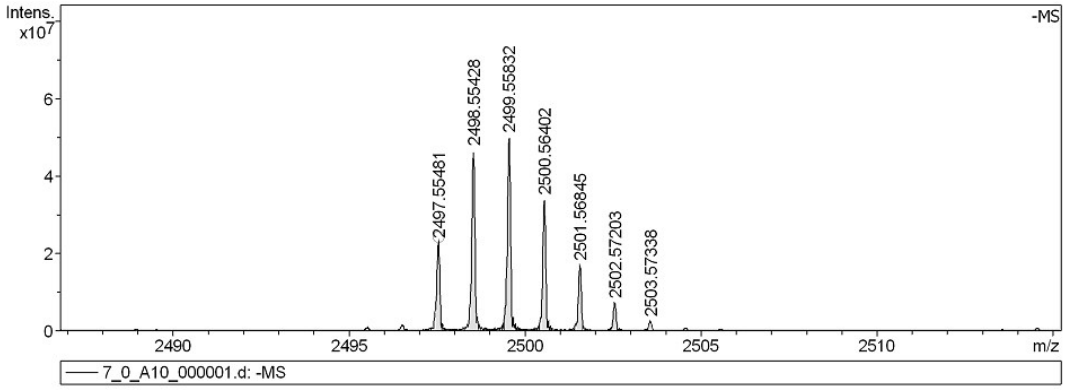
Analysis Info

Analysis Name	D:\Data\MALDI\2015\1119\7_0_A10_000001.d	Acquisition Date	11/19/2015 3:37:07 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	6	Calibration Date	Thu Nov 19 03:32:21
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	4600.0 m/z	Laser Power	32.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				





Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2497.554808	1	C168H204N6O12	100.00	2497.554275	0.2	0.5	57.0	70.0	odd	ok