Supporting Information

A Self-Assembled Nanotube for the Direct Aldol Reaction in Water

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Experimental Methods. *General Methods*. Fourier transform-infrared (FTIR) spectroscopy was performed using a Shimadzu IRAffinity-1S, FTIR spectrometer. Circular dichroic (CD) spectra were taken with a JASCO CD spectrometer. Atomic force microscopy (AFM) was conducted in tapping mode. All fluorescence spectroscopy were performed on a Shimadzu RF-6000 instrument using a cuvette with 1 mm or 1 cm pass length at 25°C. ESI or FAB mass spectra were recorded at the Bruker MicrOTOF MS instrument in The Ohio-State University Chemical Instrument Center-Chemistry. Transmission electron microscopy (TEM) was performed with a Technai G2 Spirit instrument operating at 80 kV. All reactions were performed under an argon or nitrogen atmosphere. ^{1}H NMR were recorded at 400 or 500 MHz and ^{13}C NMR spectra at 100 or 125 MHz on a Bruker DPX-400 or DPX-500 instrument as indicated. Dimethylformamide (DMF) was dried by distillation from MgSO4. Chromatographic separations were performed on silica gel 60 (230-400 mesh, 60 Å) using the indicated solvents. All water used for sample solutions was HPLC grade and passed through membrane filter (0.02 μm). Boc-Pro-OH and Boc-lys-OH was purchased from Novabiochem and used without further purification. Chromatographic separations were performed on silica gel 60 (230-400 mesh, 60 Å) using the indicated solvents. Peptide purity was assessed by analytical reverse-phase HPLC and identity confirmed using ESI mass spectrometry.

A. **Reaction Schemes:**

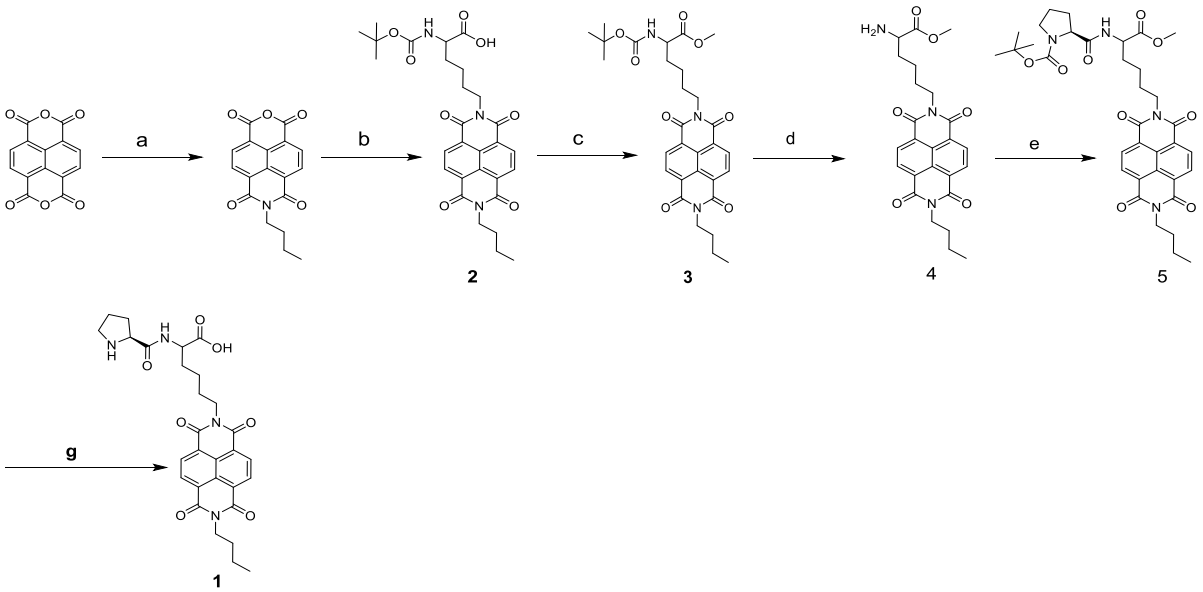


Figure S1: Reaction scheme of dipeptide 1; key (a) n-butylamine, DMF, 140°C (b) Boc-lys-OH, DMF, 120°C (c) MeI, K_2CO_3, acetone, reflux (d) TFA, CH_2Cl_2 (e) Boc-proline-OH, DIC, HOBt, DMAP, DMF/CH_2Cl_2 (f) 1)LiOH, MeOH/H_2O 2) TFA

Boc-lys(NDI)-OH (2) Boc-lys-OH (515 mg, 22.09 mmol) and monobutyl NDI (775.5 mg, 2.40 mmol) were dissolved in DMF (11 mL). The mixture was stirred at 50°C for 3 h and then heated to 110°C for 16 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (CH_2Cl_2 to 10/1 CH_2Cl_2/acetone) to afford Boc-lys(NDI)-OH as a pale yellow foamy solid (925 mg, 82.5 %). Rf 0.15 (10/1 CH_2Cl_2/acetone) MP..131-132°C (CH_2Cl_2/acetone); ^{1}H NMR(400 MHz, $CDCl_3$) 0.99 (t, J = 7.5 Hz, 3H), 1.35-1.55 (m, 13H), 1.68-1.79 (m, 5H), 1.97 (m, 1H), 4.20 (t, J = 7.5 Hz, 4H), 4.30 (m, 1H), 8.74 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ13.64, 19.83, 23.22, 27.00, 27.98, 28.19, 29.44, 30.60, 53.35, 77.93, 79.15,

125.27, 125.45, 130.19, 155.60, 161.84, 174.17; ESI-MS calcd. for $NaC_{29}H_{34}N_3O_8$ (M+Na) 574.2160, found 574.2031.

Boc-lys(NDI)-OMe (3) Boc-lys(NDI)-OH (272 mg, 0.494 mmol) and iodomethane (0.615 mL, 9.88 mmol) were dissolved in acetone (11 mL). Potassium carbonate (0.410 g, 2.97 mmol) was added to the mixture. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (CH_2Cl_2 to 10/1 CH_2Cl_2/acetone) to afford Boc-lys(NDI)-OMe as a pale yellow solid (218 mg, 78.3 %) MP..147-148°C (CH_2Cl_2/acetone). Rf 0.71 (10/1 CH_2Cl_2/acetone); ^{1}H NMR(400 MHz, $CDCl_3$) 0.920 (t, *J* = 7.2 Hz, 3H), 1.184 (s, 1H), 1.357 (s, 9H), 1.357-1.433 (m, 4H), 1.367-1.724 (m, 5H), 1.817-1.809 (m, 1H), 3.682 (s, 3H), 4.110(m, 4H), 4.110-4.234(m, 1H), 5.105(m, 1H), 8.637(s, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ13.67, 20.20, 22.69, 27.45, 28.19, 29.17, 29.55, 30.01, 31.62, 32.14, 40.21, 40.60, 52.15, 53.21, 53.77, 69.35, 76.35, 79.67, 126.32, 126.46, 130.82, 155.28, 162.56, 173.11, 210.56; ESI-MS calcd. for $NaC_{30}H_{35}N_3O_8$ (M+Na) 588.2316, found 588.2179.

Boc-Pro-lys(NDI)-OMe (5) Boc-lys(NDI)-OMe (2.7 g, 4.15 mmol) was dissolved in CH_2Cl_2 (20 mL). Then trifluoroacetic acid (40 mL) was added to the mixture. The solvent was removed in vacuo and cold diethyl ether was added. The precipitated residue was then dried under vacuum and redissolved in CH_2Cl_2/DMF 1:1. Then, 1,3-diisopropylcarbodiimide (DIC) (1.29 mL, 8.3 mmol, 4 equiv.), 1-hydroxybenzotriazole (HOBt) (1.27 g, 8.3 mmol), 4-dimethylaminopyridine (DMAP) (101 mg, 0.83 mmol), and hydroxybenzotriazole (HBTU) (1.57 g, 8.3 mmol) were added sequentially. The crude oil was purified by flash chromatography ($CHCl_3$ to 10/1 $CHCl_3$/acetone) to afford Boc-Pro-lys(NDI)-OMe as a yellow solid (265 mg, 46.3 %) MP..249-251°C ($CHCl_3$/acetone) . Rf 0.68 (10/1 CH_2Cl_2/acetone); ^{1}H NMR(400 MHz, $CDCl_3$) 0.901 (t, *J* = 7.2 Hz, 3H), 1.162 (m, 2H), 1.358-1.387 (m, 13H), 1.612-1.695 (m, 6H), 1.786-1.844 (m, 3H) 3.369 (s, broad, 2H), 3.658 (s, 3H), 4.089 (m, 5H), 4.493-4.544 (m, 1H), 8.624 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ13.62, 20.15, 22.43, 22.71, 27.20, 27.37, 28.15, 28.21, 29.50, 29.96, 30.94, 31.24, 36.30, 40.23, 40.53, 46.89, 52.47, 52.66, 126.43, 126.45, 130.68, 130.72, 162.35, 162.50, 162.55, 162.75, 171.05, 171.31, 172.40; ESI-MS calcd. for $NaC_{35}H_{42}N_4O_9$ (M+Na) 685.2844, found 685.2764.

Pro-lys(NDI)-OH (1) Boc-Pro-lys(NDI)-OMe (490 mg, 0.89 mmol) was dissolved in mixture of THF/MeOH/H_2O (3 mL/ 2 mL/ 2mL). LiOH (20 equiv, 426 mg, 17.8 mmol) was added to the solution at 0°C. The reaction mixture was stirred at rt for 12 h until reaction completion. Trifluoroacetic acid (40 mL) was added to mixture at 0°C. The reaction mixture was stirred at rt for 5 h. After stirring, the solvent was removed in vacuo and 50 mL cold diethyl ether was added. Evaporation of solvents under reduced pressure afforded an dark-yellowish green solid residue. The resultant precipitate was collected by centrifugation and dried by lyophilization. The crude residue was purified by reverse-phase HPLC (CH_3CN/H_2O) and dried with lyopholizer to yield product as bright yellow fluffy solid (340 mg, 91%) MP..194-195°C (acetonitrile/water). ^{1}H NMR (500 MHz,d-DMSO) 0.801-0.853 (m, 3H), 0.950 (t, *J* = 7.2 Hz, 3H),1.23 (m, 6H), 1.37-1.50 (m, 4H), 1.62-1.72 (m, 3H), 1.98-2.00 (m, 1H), 2.31 (d, *J* = 8.4 Hz, 1H), 3.22 (d, *J* = 24 Hz, 3H), 4.07-4.11(m, 4H), 4.238(dd, *J* = 3.6 Hz , *J* = 9 Hz, 2H) 8.57 (s, 5H), 8.74 (d, *J* = 7.2 Hz 1H), 9.40 (s, 1H); ^{13}C NMR (100 MHz, d-DMSO) δ 13.68, 19.79, 23.02, 23.37, 27.01, 29.48, 29.52, 30.43, 39.78, 45.95, 52.33, 58.79, 116.00 117.99, 1265.94, 1126.07, 126.11, 130.37, 158.03, 158.24, 162.43, 162.44, 168.35, 172.86; ESI-MS calcd for $NaC_{29}H_{32}N_4O_7$ [M+Na] 571.2163, found 571.2038.

B. **Circular Dichroism (CD) Spectroscopy Measurement.**

CD spectra were recorded on a JASCO CD spectrometer under a nitrogen atmosphere. Experiments were performed in a quartz cell with a 1 mm or 1 cm path length over the range of 190-450 nm at 25°C. CD spectra were taken routinely at peptide concentration of 1000 μM.

C. **Transmission Electron Microscopy (TEM) Measurement**

10 μL drops of peptide solutions were applied to carbon-coated copper grid (Ted Pella, Inc.) for 2 minutes after dilution from 10 mM to concentration ranging from 500-1000 μM. After removal the excess solution with filter paper, the grid was floated on 10 μL drops of 2 % wt uranyl acetate solution for negative stain for 2 min. The excess solution was removed by filter paper. The dried specimen was observed with Technai G2 Spirit instrument operating at 80 kV. The data were analyzed with Image pro software.

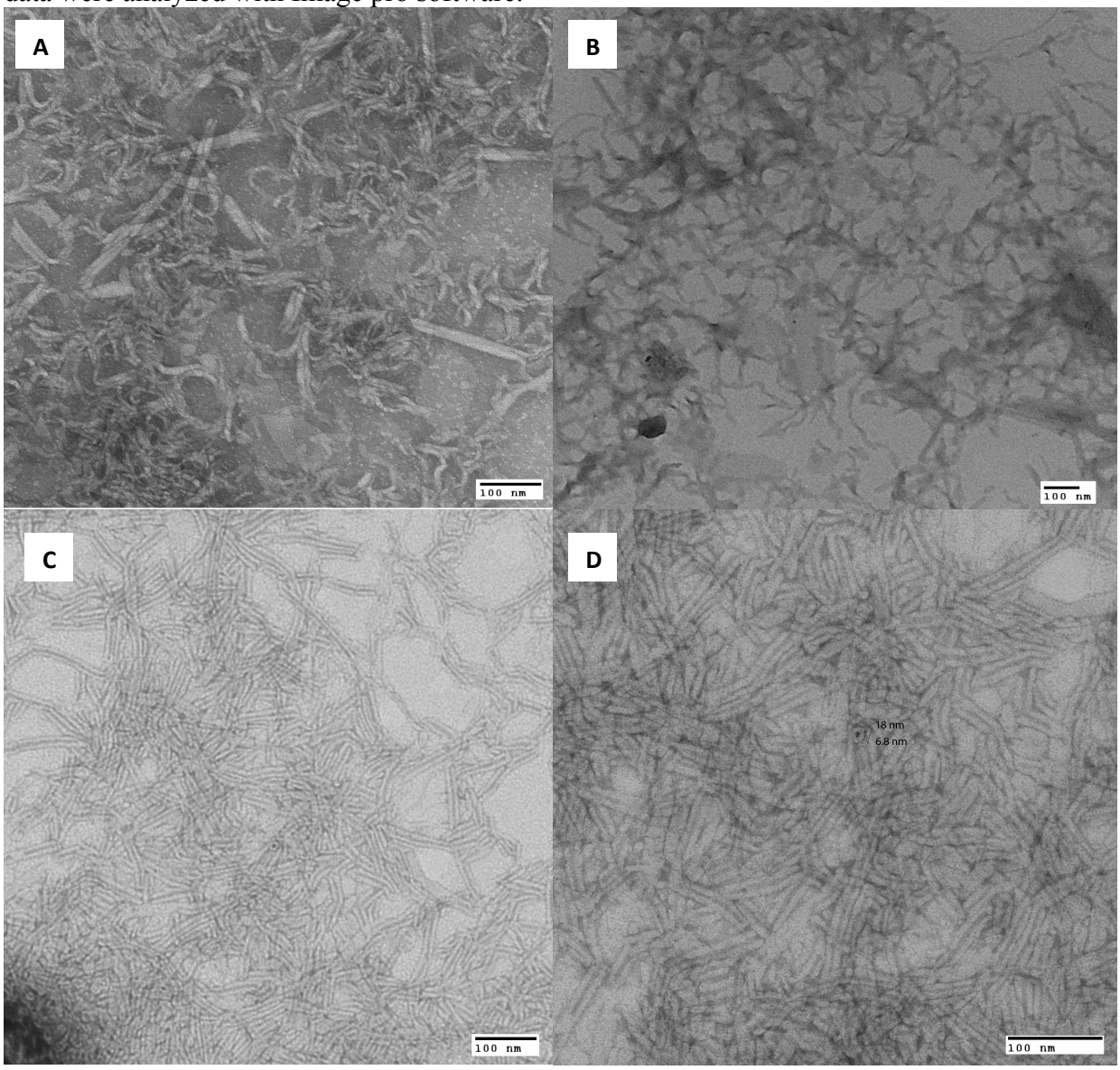


Figure S2: TEM images of 1 (A) in water, (B) 50 mM NaCl in water (C) in reaction mixture and (D) in reaction mixture with cross section image of nanotube

D. Fourier Transform Infrared (FTIR) Spectroscopy Measurement

All FTIR spectra were collected on a FTIR Shimadzu IFAffinity-1S spectrometer at ambient temperature. The instrument is operated in dry air. Interferograms were recorded between 1700 and 1600 cm^{-1} at a resolution of 4 cm^{-1}, and a total of 256 scans were averaged. Samples for FTIR were dissolved in D_2O (about 10 mg/mL) and analyzed in a transmission cell having CaF_2 windows and a 0.025 μm path length.

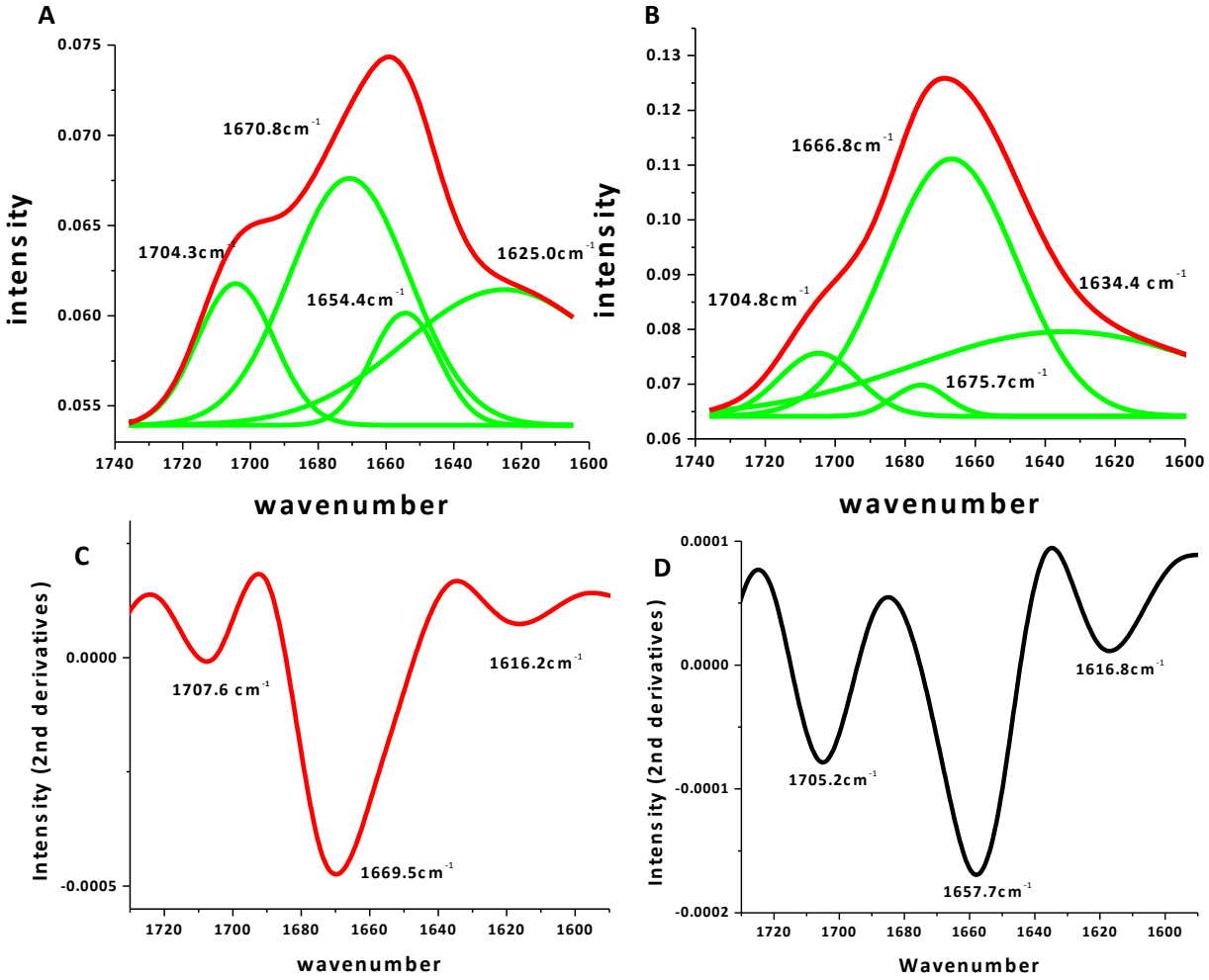


Figure S3: FTIR spectra of dipeptide **1** ranging from 1600 to 1750 cm^{-1} in (A) water (B) 50 mM NaCl solution; 2nd derivative of FTIR spectra of dipeptide 1 in (C) water (D) 50 mM NaCl solution

E. Atomic Force Microscopy (AFM)

The AFM images were collected on a Bruker NanoScope IIIa device at ambient temperature in tapping mode using silicon tips (NSC14/AIBS, MikroMasch). 10 μL of the sample solution (250 μM) was diluted 10-fold and placed on freshly cleaved mica. After adsorption for 30 minutes under moist conditions, excess solution was removed by absorption onto filter paper. The resultant substrates were rinsed with solvent (2 x 50 μL) to remove the loosely bound monomers and the samples were stored in a desiccator in vacuum for 1 h before imaging. The scanning

speed was at a line frequency of 1.0 Hz, and the original images were sampled at a resolution of 512 x 512 pixels.

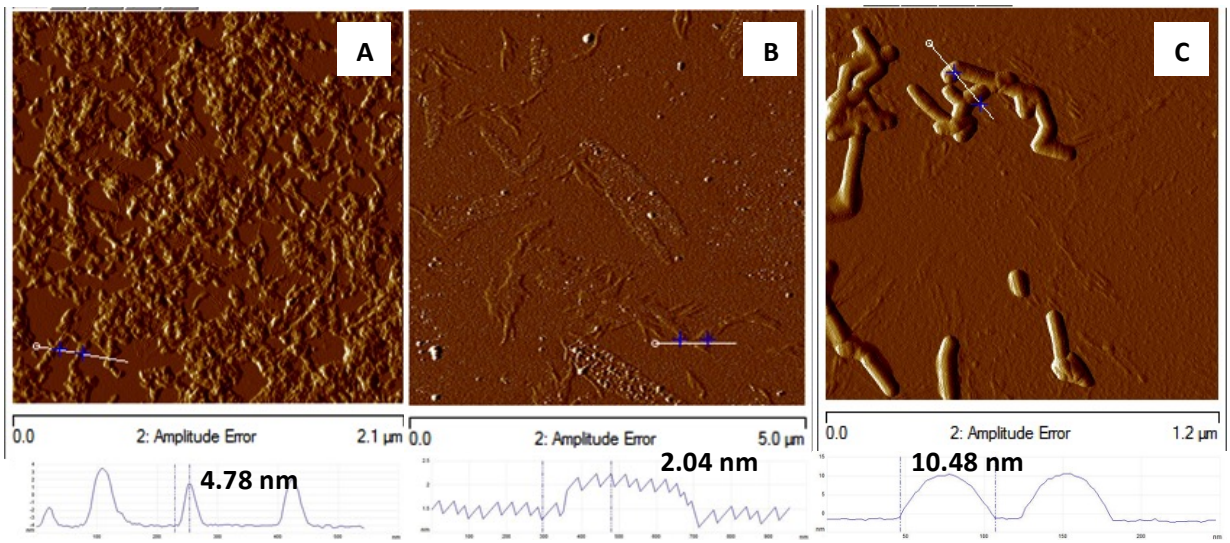


Figure S4: AFM image of dipeptide 1 in (A) water (B) 50 mM NaCl solution (C) reaction mixture

F. Fluorescence Spectroscopy Measurement

Nile Red Binding Assay: 50 µL of a 1.0 mg/mL stock solution of Nile Red in dichloromethane was added to an empty vial. The solvent was removed in vacuo for 2 h. Aqueous **Pro-lys(NDI)-OH** solutions (1 mL, 10 mM) was added to the vial. The solution was sonicated for 30 minutes and incubated for 24 h. The fluorescence emission spectra of Nile Red were measured with excitation at 540 nm.

In order to explore the internal regions of the **Pro-lys(NDI)-OH** assemblies, we performed encapsulation studies using 9-diethylamino-5-benzo[α]phenoxazinone (Nile Red) as a fluorescent probe. The fluorescence spectra of Nile Red in the presence of **Pro-lys(NDI)-OH** exhibited an intense peak at 607.0 nm in pure water and 608.8 nm in 50 mM NaCl solution. As compared with Nile red in water (665 nm), the emission maxima were ca. 60 nm blue-shifted, and the intensities increased.

Encapsulation efficiency of Nile Red in self-assembled **dipeptide 1 in water** and 50 mM NaCl solution. All the sample solutions contain the constant amount of dipeptide 1 (12.5 nmol) with the progressively increasing amount of Nile Red. The point of saturation of nile red encapsulation was calculated as the intercept of two straight-line fits extrapolating the data points from below and above the region in which a rapid change of slope is observed.[1]

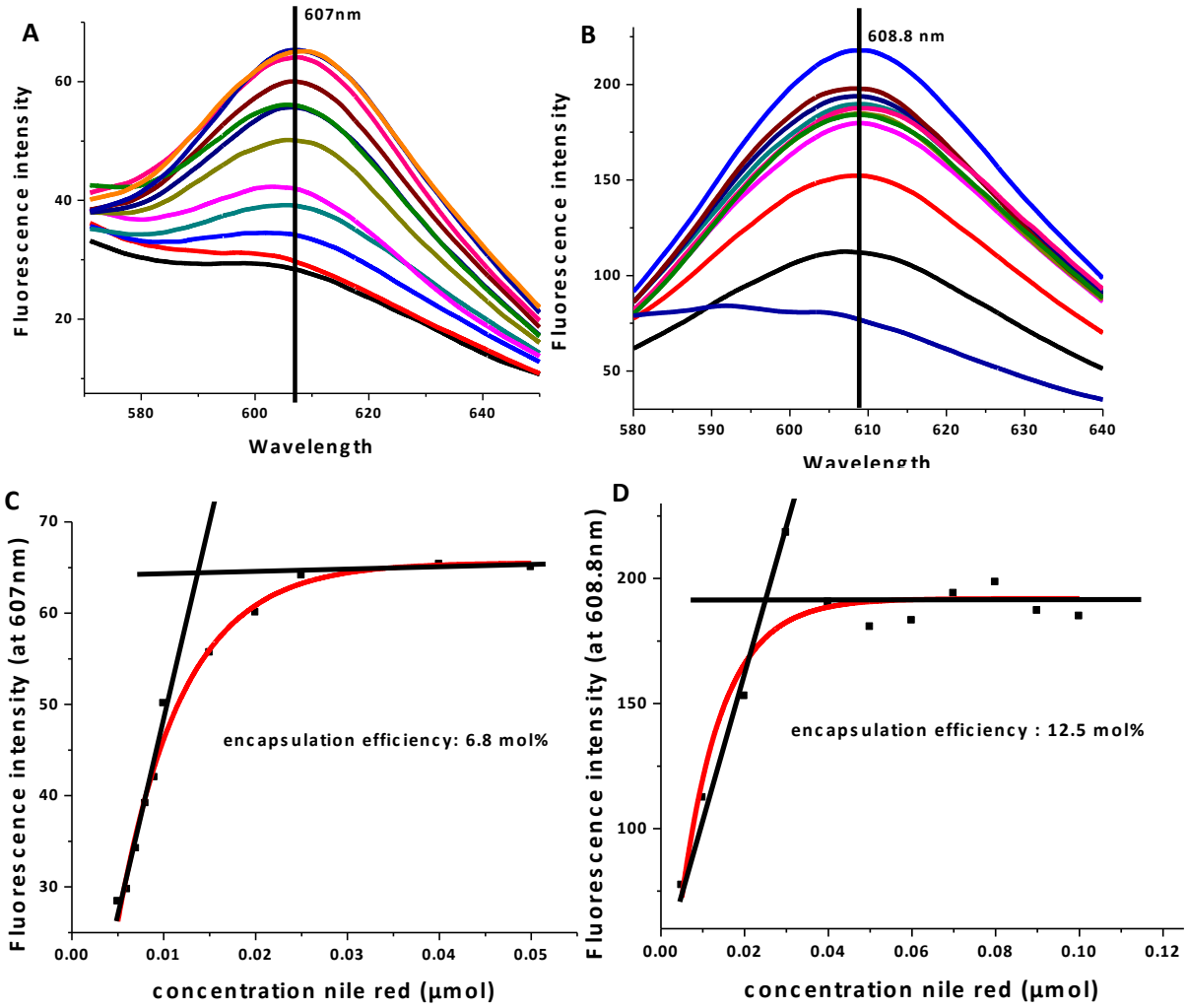


Figure S5: Fluorescence Spectra of dipeptide 1 ranging from 580 to 650 nm in (A) water (B) 50 mM NaCl solution. Encapsulation efficiency measurement of dipeptide 1 in (C) water (D) 50mM NaCl solution

G. Isolation of amphiphilic nanomaterial from aqueous solution

Ultra-centrifugation of the aqueous solution containing dipeptide **1** was performed on a Beckman Optima^{TM} TLX ultracentrifugation instrument at 100,000 rpm under vacuum for 35 mins. Experiments were performed in a polycarbonate centrifuge tube at 4°C

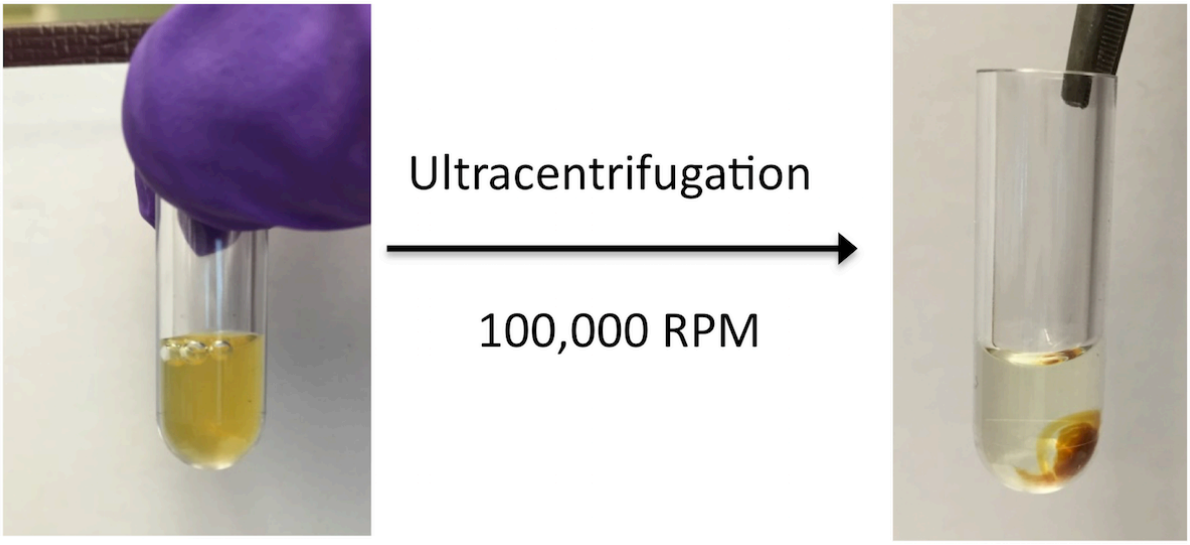


Figure S6: An aqueous solution of dipeptide **1** (10 mM) was prepared and incubated for 24 h at 25 °C. The solution was then transferred into a polycarbonate centrifuge tube (picture, left). The solution was then placed in the ultracentrifugation instrument where the temperature was lowered to 4 °C and vacuum was applied through the instrument. the sample was then centrifuged at the speed of 100,000 rpm for 35 mins. Completion of the centrifugation produce isolated assemblies of dipeptide **1** collected at the bottom of the tube, separated from the aqueous solution.

H. General Procedure for Aldol Reaction:

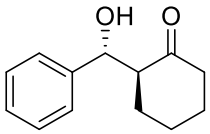
To a solution of catalyst (as indicated in table 1, mmol) in H_2O (0.5 mL) were added AcOH (1 eq. per prolinamide catalytic unit) and freshly distilled cyclohexanone (100 eq.). After stirring at rt for 15 min, 4-nitrobenzaldehyde (10 eq.) were added. The resulting mixture was stirred at rt for the indicated time. The reaction was treated with saturated aqueous ammonium chloride (1 mL). This mixture was diluted with water (20 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (20-50% EtOAc/hexane) to give pure aldol diasteromeric products. The diastereomeric ratios were calculated based on integrations of the diagnostic signals of the *syn* and *anti* diastereomers in the ^{1}H NMR spectra of the crude reaction mixture. The *enantioselectivitie*s were calculated from HPLC profiles of the reaction mixtures, see text (below); the *ee*s structure reported are for the major enantiomer.

I. Representative Procedure for Aldol Reaction between Cyclohexanone and 4-nitrobenzaldehyde Catalyzed by Pro-lys(NDI)-OH (1):

To a solution of Pro-lys(NDI)-OH (13 mg, 0.005 mmol) in water (0.5 mL) were added AcOH (2.3 µL, 0.04 mmol) and freshly distilled cyclohexanone (51 µL, 0.5 mmol). After stirring at rt for 15 min, 4-nitrobenzaldehyde (7.5 mg, 0.05 mmol) was added. The resulting mixture was stirred at rt for 120 h. The reaction was treated with saturated aqueous ammonium chloride (1 mL). This mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue

was purified by column chromatography on silica gel (20-40% EtOAc/pet ether) to give pure aldol products: 2-[hydroxy-(4-nitrophenyl)-methyl]-cyclohexanone (49.5 mg, 0.1985 mmol, 91.7%), as a white solid. The diastereoselectivity was determined by ^{1}H NMR analysis to be 11.1:1 (*anti:syn*). The enantioselectivity was determined by chiral HPLC Daicel Chiralpak AD-H, 20% *i*- PrOH/hexane, UV 254 nm, flow rate 0.5 mL/min. 79.9% ee for *anti* isomer (major, R-isomer) t_R 19.3 min, (minor, S-isomer) t_R 13.8 min. 10% ee for *syn* isomer (major), t_R 10.1 min, (minor) t_R 13.5 min.

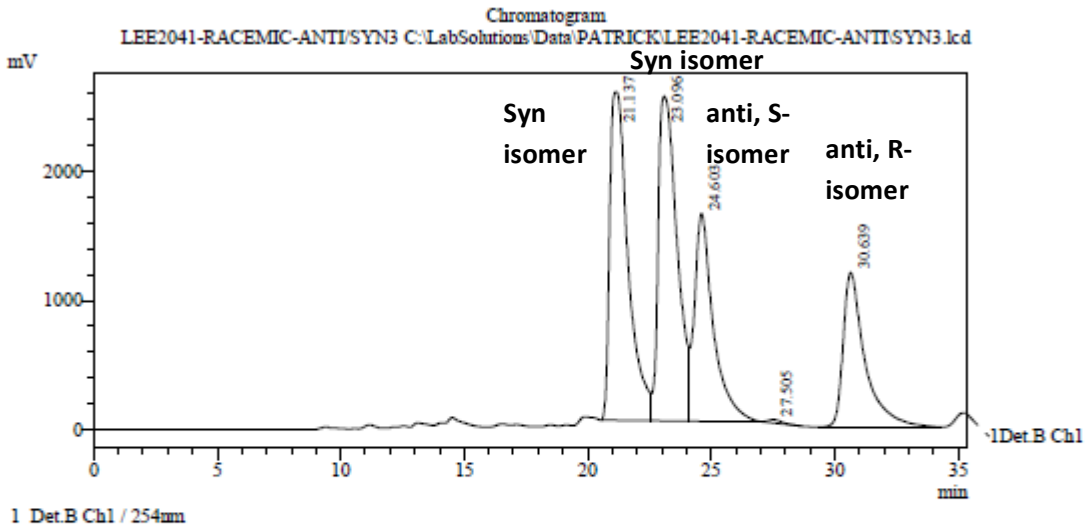
J. ^{1}H NMR and chiral HPLC data for aldol adducts.[2]



2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclohexanone (7): (*anti* isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.42 (m, 1H), 1.48-1.71 (m, 3H), 1.78-1.84 (m, 1H), 2.06-2.13 (m, 1H), 2.30-2.39 (m, 1H), 2.45-2.51 (m, 1H), 2.54-2.60 (m, 1H), 4.04 (s, 1H), 4.88 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 8.19 (d, J = 8.5 Hz, 2H); Chiral HPLC data: Daicel Chiralpak AD-H, 20% *i*-PrOH/hexane, UV 254 nm, flow rate 0.5 mL/min, Retention times: t_R 24.6 min and t_R 30.6 min; (*syn* isomer) ^{1}H NMR (400 MHz, $CDCl_3$) 1.4 4-1.77 (m, 4H), 1.84 (d, J = 11.5 Hz, 1H), 2.05-2.13 (m, 1H), 2.33-2.50 (m, 2H), 2.61 (dd, J = 12.9 Hz, 5.5 Hz, 1H), 3.14 (s, 1H), 5.46 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 8.9 Hz, 2H), 8.18 (d, J = 9.0 Hz, 2H); Chiral HPLC data: Daicel Chiralpak AD-H, 20% *i*-PrOH/hexane, UV 254 nm, Flow rate 0.5 mL/min, Retention times: *tR* 21.1 min and *tR* 23.1 min.

Figure S7: HPLC profile for racemic and entry 1 – 8, table 1 with enantiomeric excess value obtained from integration of peaks and diasteriomeric value obtained from NMR

HPLC profile for racemic product, (anti product). -14.6 %*ee*, 5 %*de*

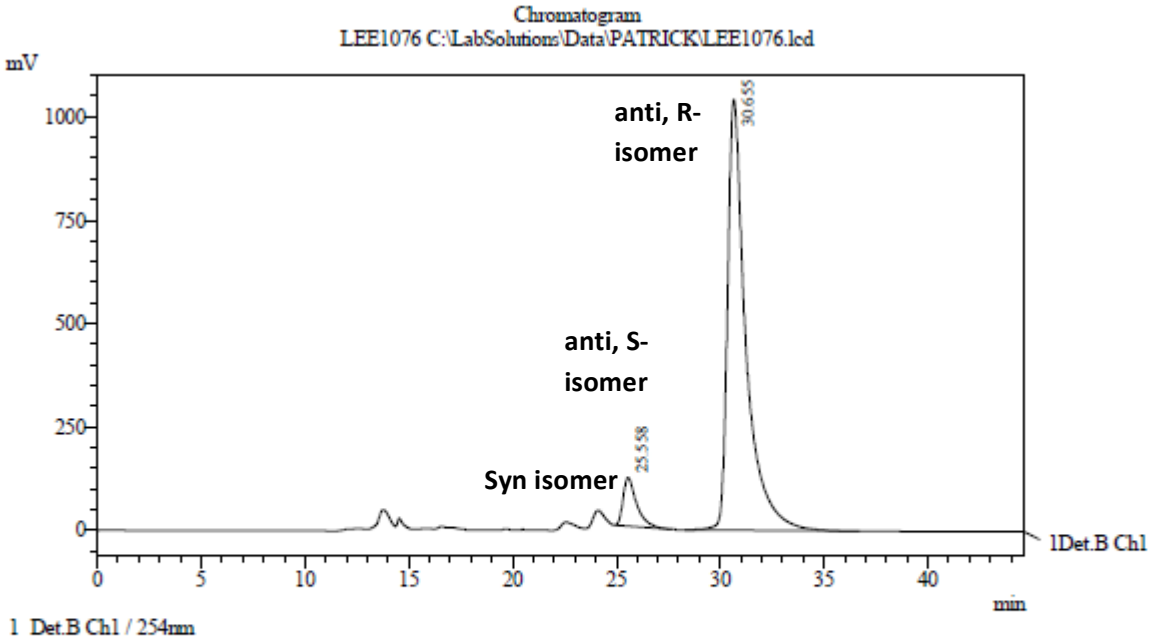


PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.137	132524118	2543269	31.073	32.265
2	23.096	133182581	2509129	31.227	31.831
3	24.603	85778889	1607514	20.113	20.393
4	27.505	1028611	25700	0.241	0.326
5	30.639	73979230	1196922	17.346	15.184
Total		426493429	7882534	100.000	100.000

HPLC profile for Entry 1, Table 1. 79.7 %ee, 83.5 %*de*



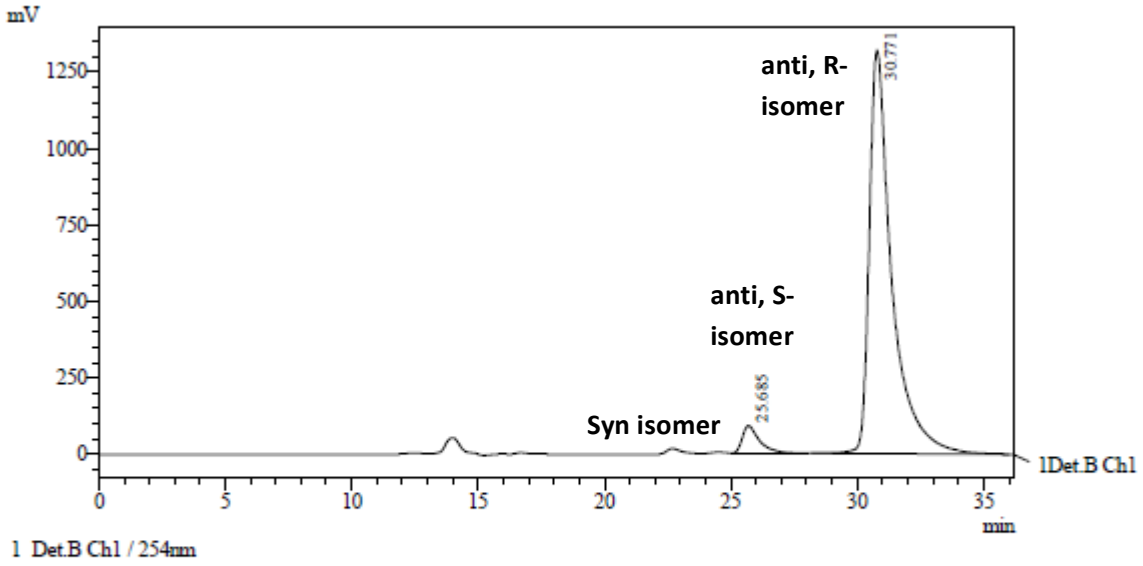
1 Det.B Ch1 / 254nm

PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.558	5327750	117661	7.639	10.140
2	30.655	64412110	1042756	92.361	89.860
Total		69739860	1160417	100.000	100.000

HPLC profile for Entry 2, Table 1. 87.3 %ee, 85.2 %*de*



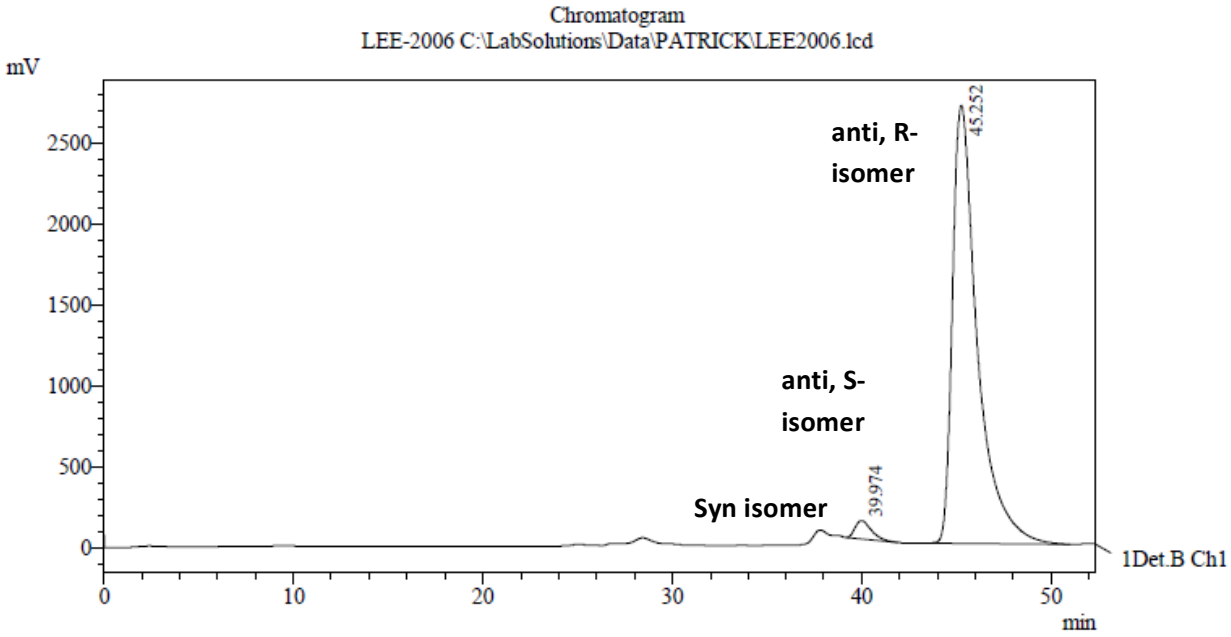
1 Det.B Ch1 / 254nm

PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.685	4233062	89015	4.926	6.333
2	30.771	81705686	1316662	95.074	93.667
Total		85938748	1405677	100.000	100.000

HPLC profile for Entry 3, Table 1. 91.9 %ee, 85.2 %*de*



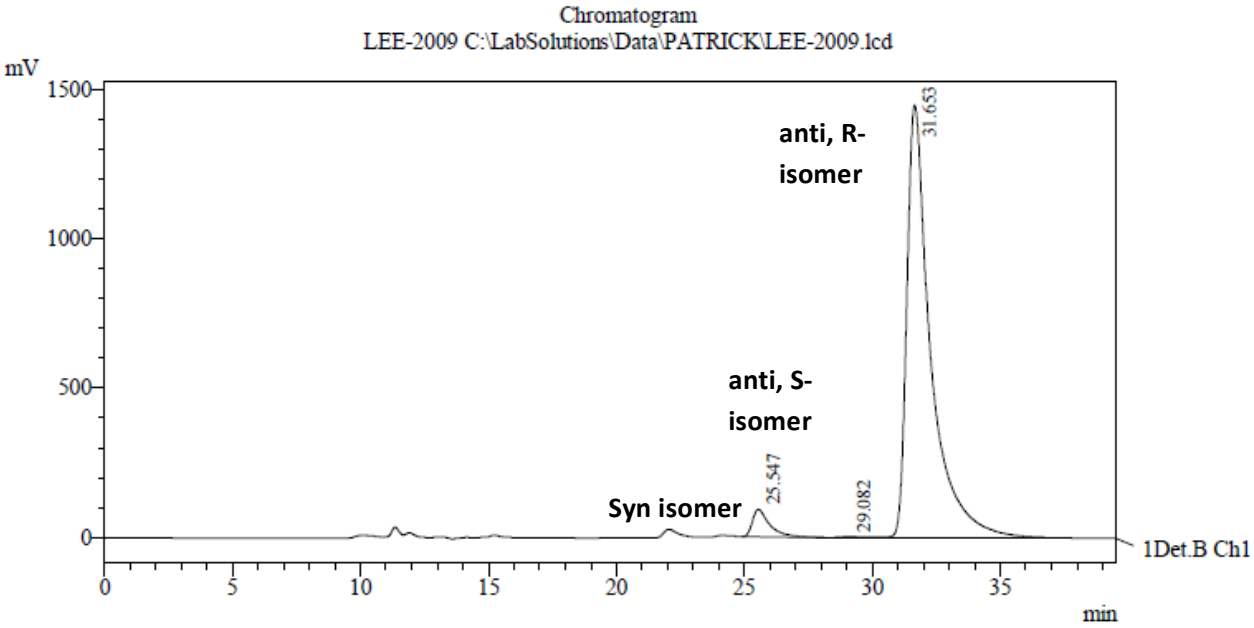
1 Det.B Ch1 / 254nm

PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.974	6802999	114096	2.667	4.046
2	45.252	248235716	2705776	97.333	95.954
Total		255038715	2819872	100.000	100.000

HPLC profile for Entry 4, Table 1. 88.0 %ee, 86.9 %*de*



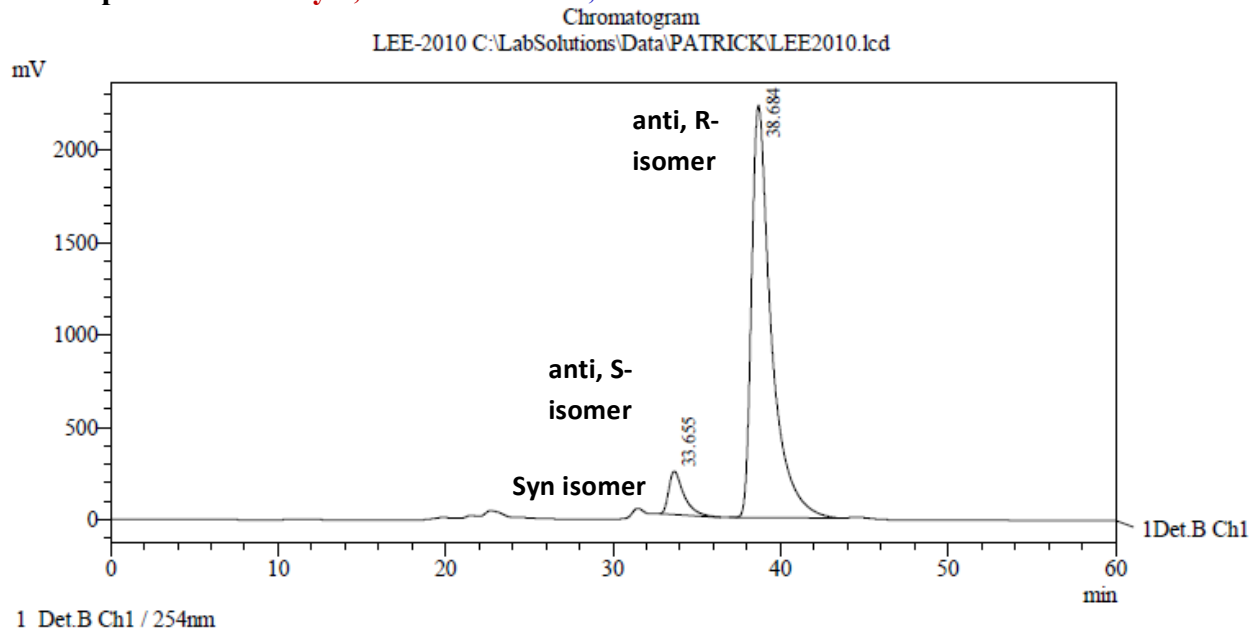
1 Det.B Ch1 / 254nm

PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.547	4350658	91847	4.427	5.963
2	29.082	179324	3243	0.182	0.211
3	31.653	93746356	1445227	95.391	93.827
Total		98276338	1540317	100.000	100.000

HPLC profile for Entry 5, Table 1. 81 %ee, 88.7 %*de*

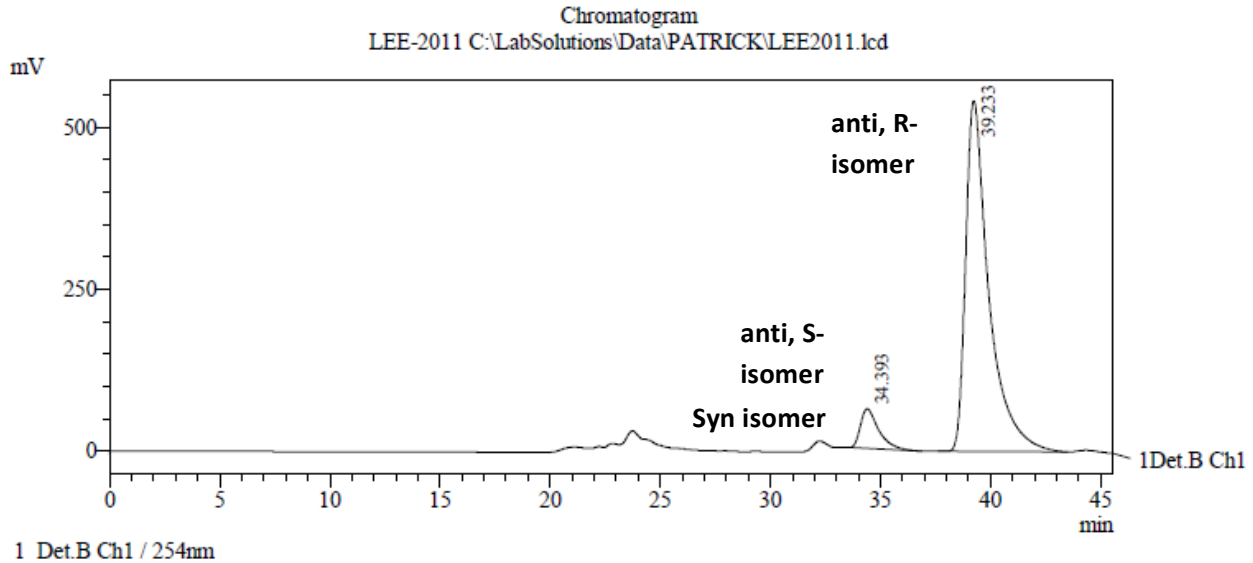


PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.655	14649268	234288	7.422	9.498
2	38.684	182733905	2232509	92.578	90.502
Total		197383173	2466797	100.000	100.000

HPLC profile for Entry 6, Table 1. 79.7 %ee, 86.9 %*de*

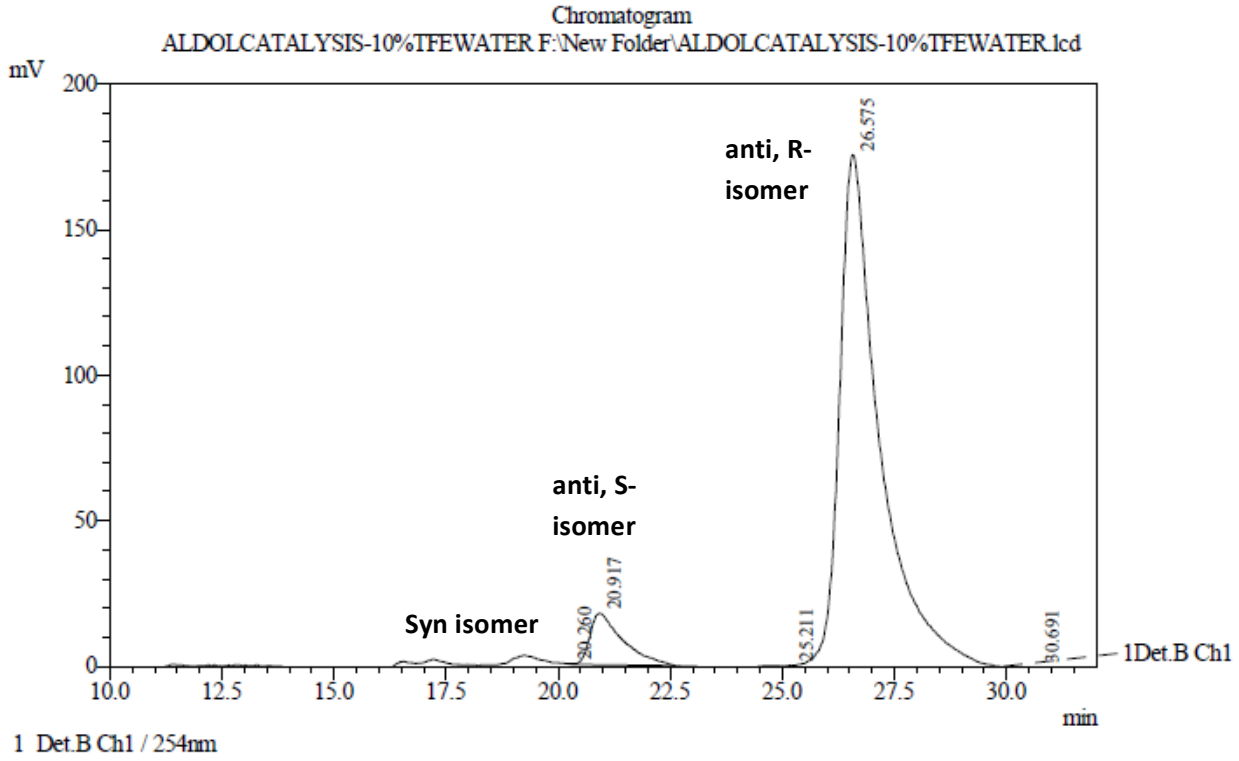


PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.393	3513419	61055	8.101	10.132
2	39.233	39858407	541555	91.899	89.868
Total		43371825	602610	100.000	100.000

HPLC profile for Entry 7, Table 1. 78.6 %ee, 84.7 %*de*



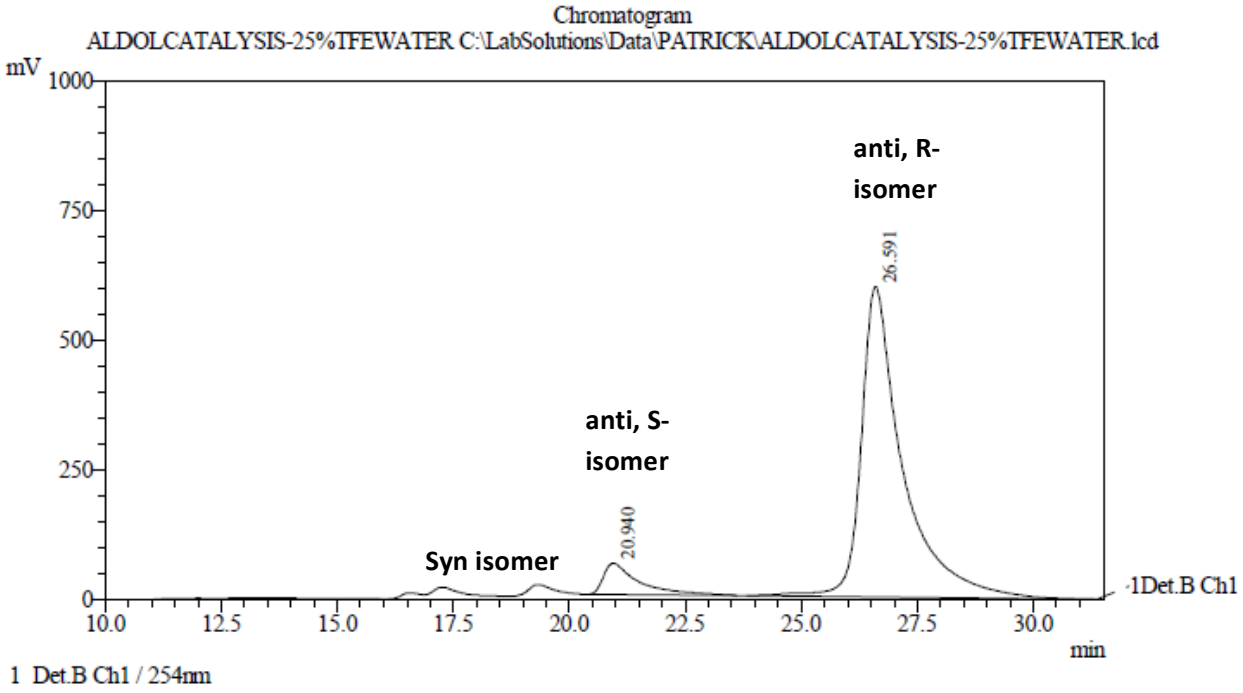
1 Det.B Ch1 / 254nm

PeakTable

Detector B Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.260	1017	159	0.009	0.082
2	20.917	890146	17610	7.445	9.065
3	25.211	1145	313	0.010	0.161
4	26.575	11058633	175915	92.488	90.549
5	30.691	5848	278	0.049	0.143
Total		11956790	194275	100.000	100.000

HPLC profile for Entry 8, Table 1. 75.4 %ee, 84.3 %*de*



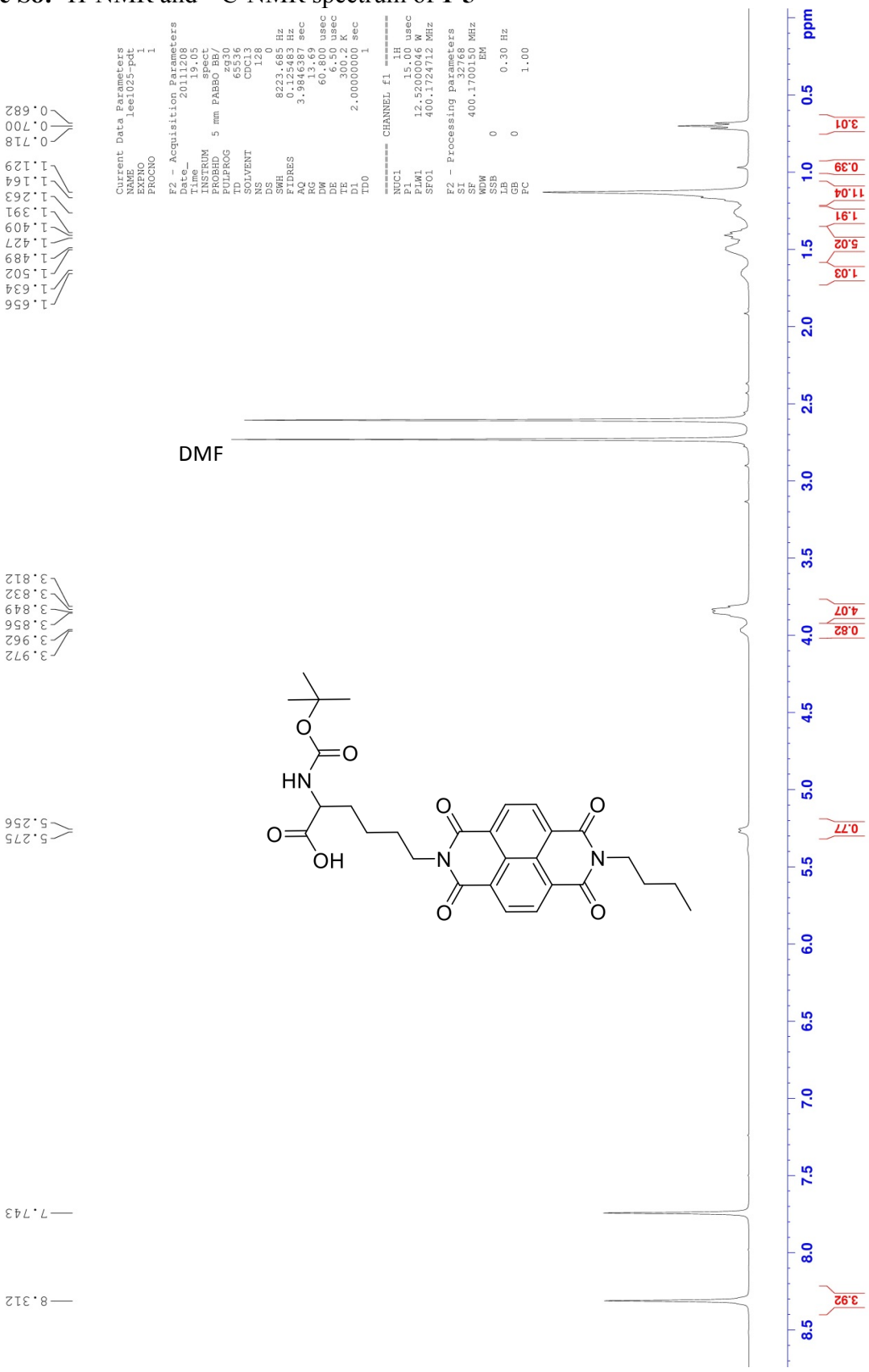
PeakTable

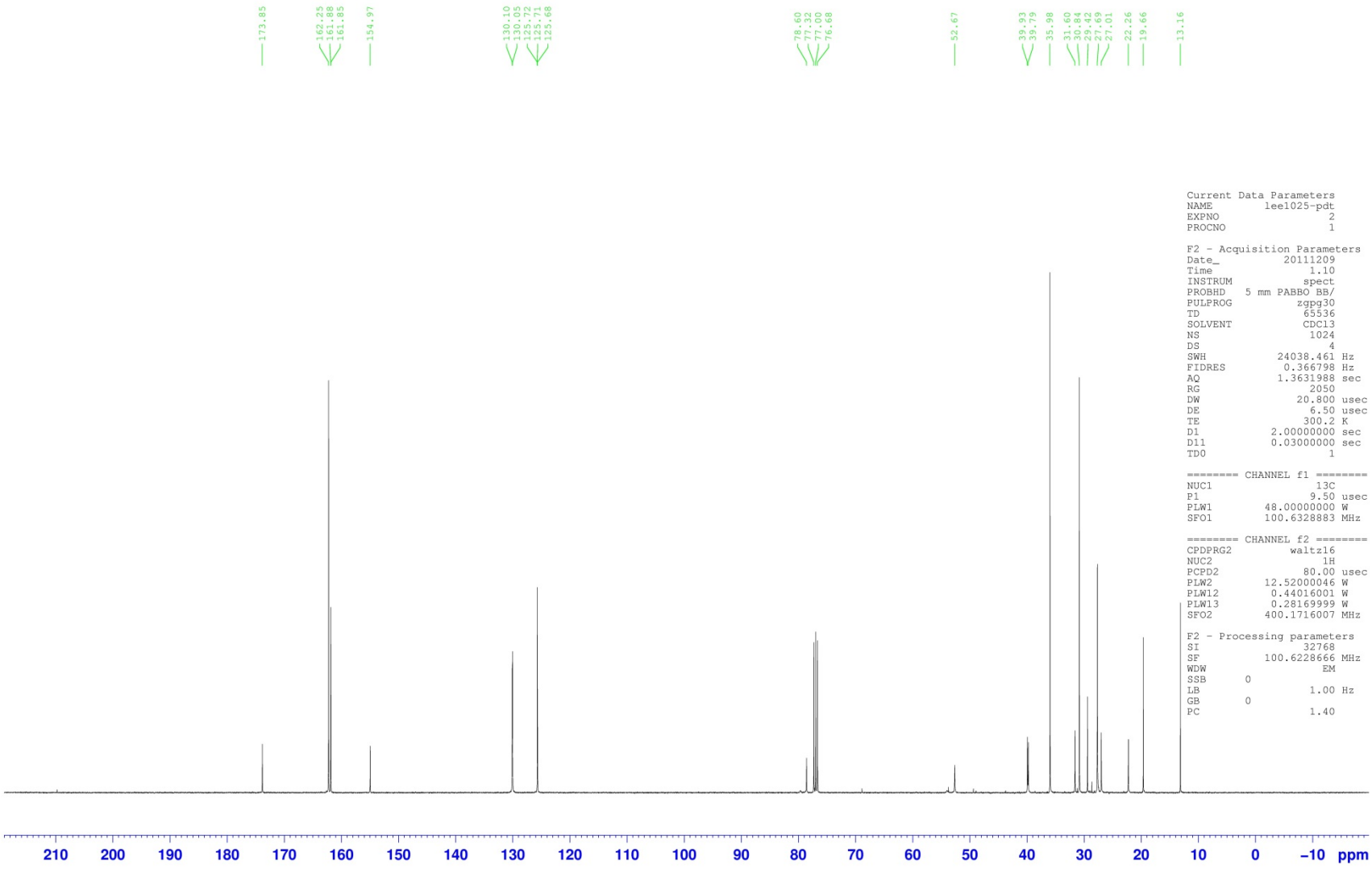
Detector B Ch1 254nm

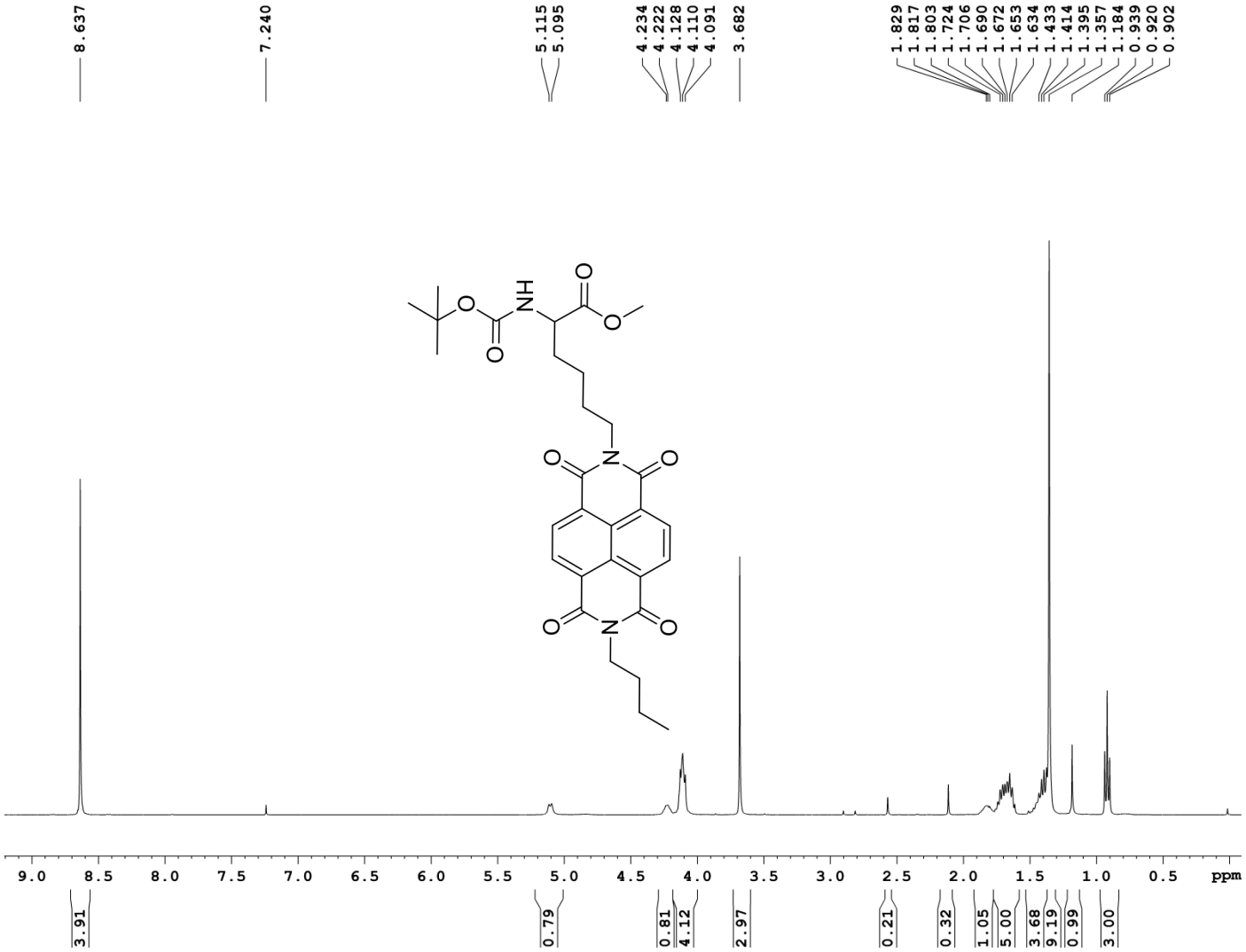
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.940	3198355	60957	7.860	9.229
2	26.591	37492561	599532	92.140	90.771
Total		40690916	660490	100.000	100.000

K. **^{1}H-NMR and ^{13}C-NMR SPECTRA of 1-5 and HRMS and HPLC chromatogram of 1**

Figure S8: ^{1}H-NMR and ^{13}C-NMR spectrum of **1-5**




173.85
162.25
161.88
161.85
154.97
130.10
130.05
125.72
125.71
125.68
78.60
77.32
77.00
76.68
52.67
39.93
39.79
35.98
31.60
30.84
29.42
29.09
27.01
22.26
19.66
13.16
Current Data Parameters
NAME lee1025-pdt
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111209
Time 1.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PLW1 48.00000000 W
SFO1 100.6328883 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 12.52000046 W
PLW12 0.44016001 W
PLW13 0.28169999 W
SFO2 400.1716007 MHz
F2 - Processing parameters
SI 32768
SF 100.6228666 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm




```
Current Data Parameters
NAME         lys-NDI-OMe
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130211
Time               15.28
INSTRUM            spect
PROBHD   5 mm BBI 1H-BB
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715922 sec
RG                  20.2
DW                60.600 usec
DE                 6.00 usec
TE                300.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               -2.65 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300164 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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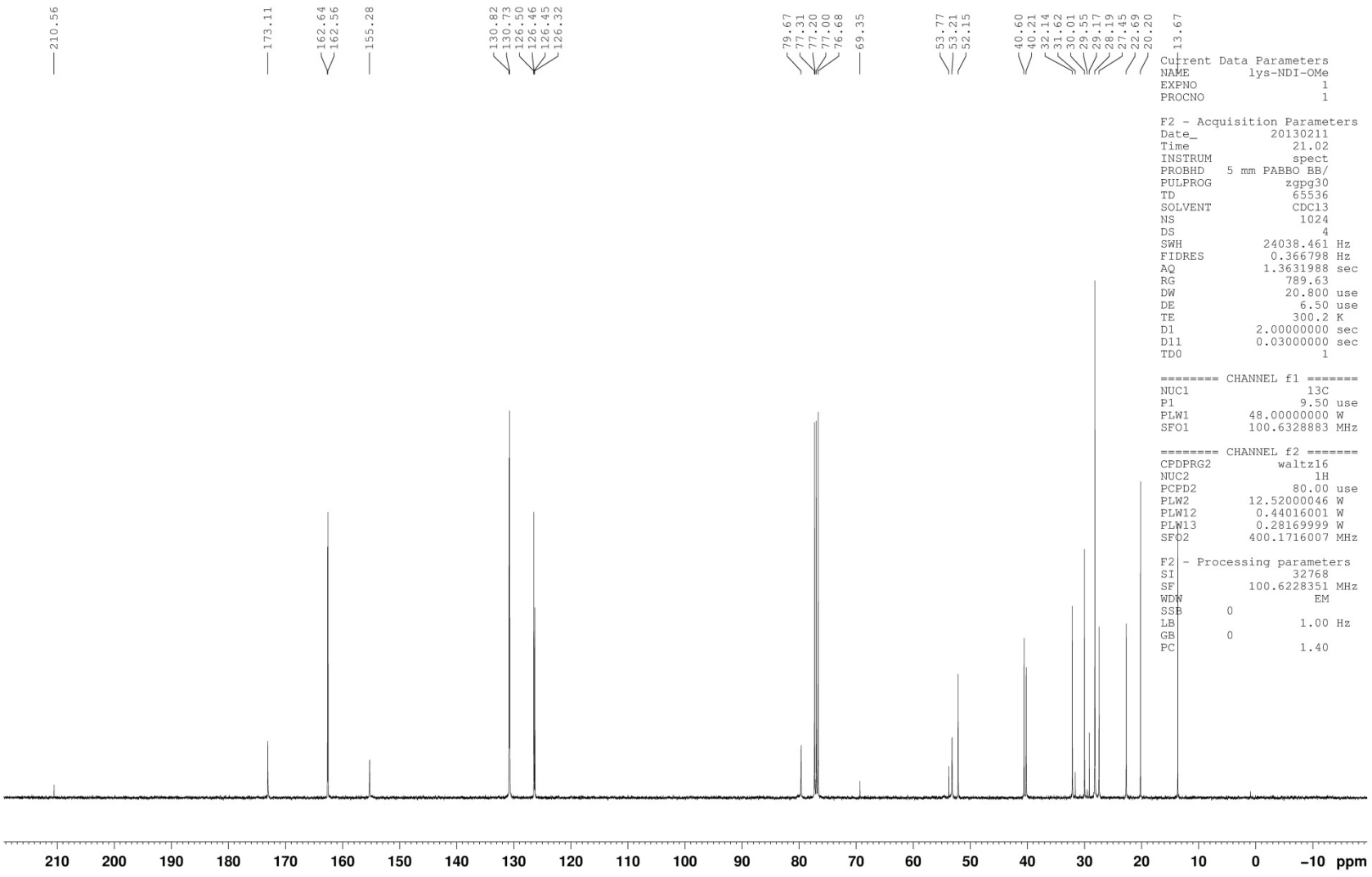
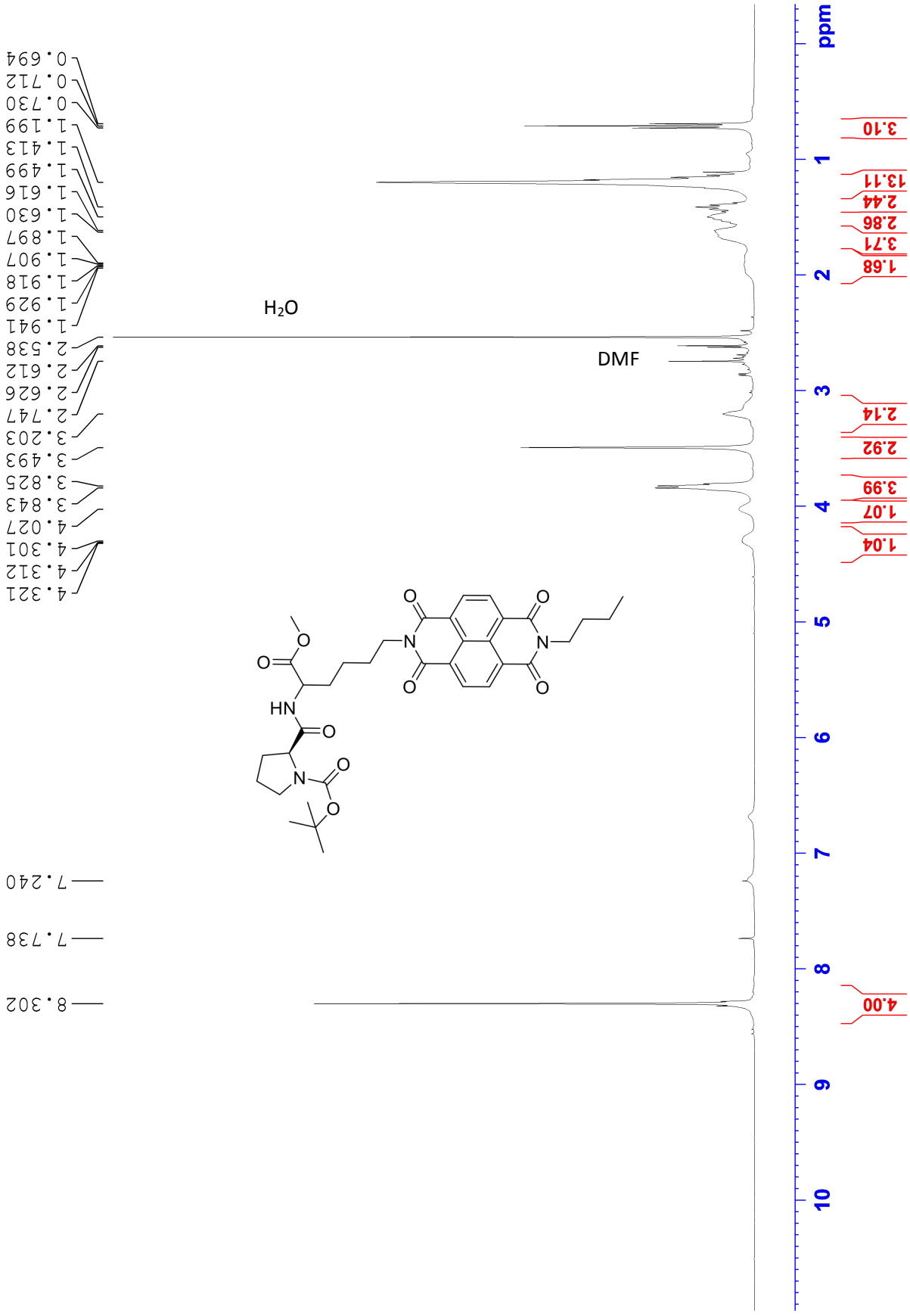
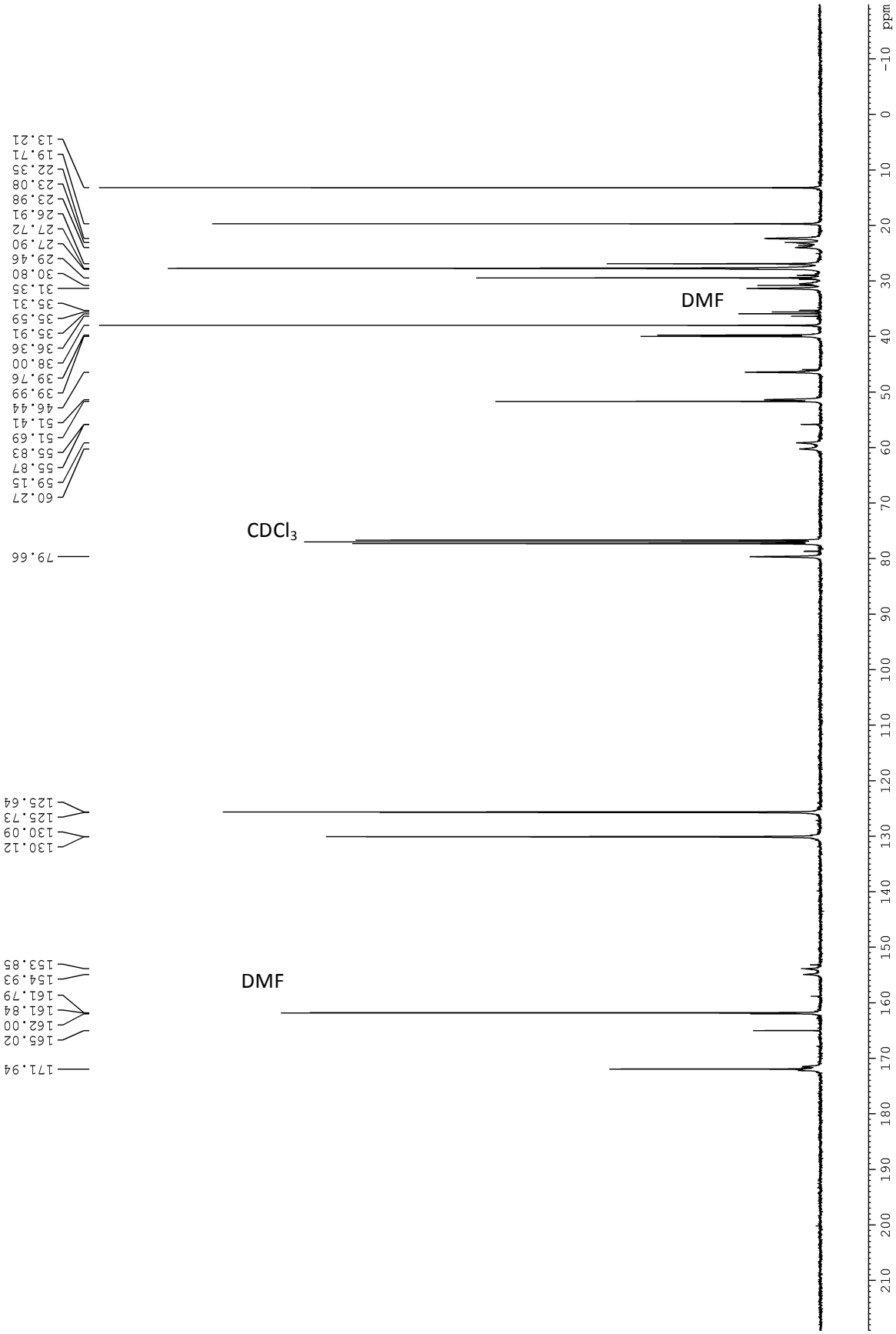
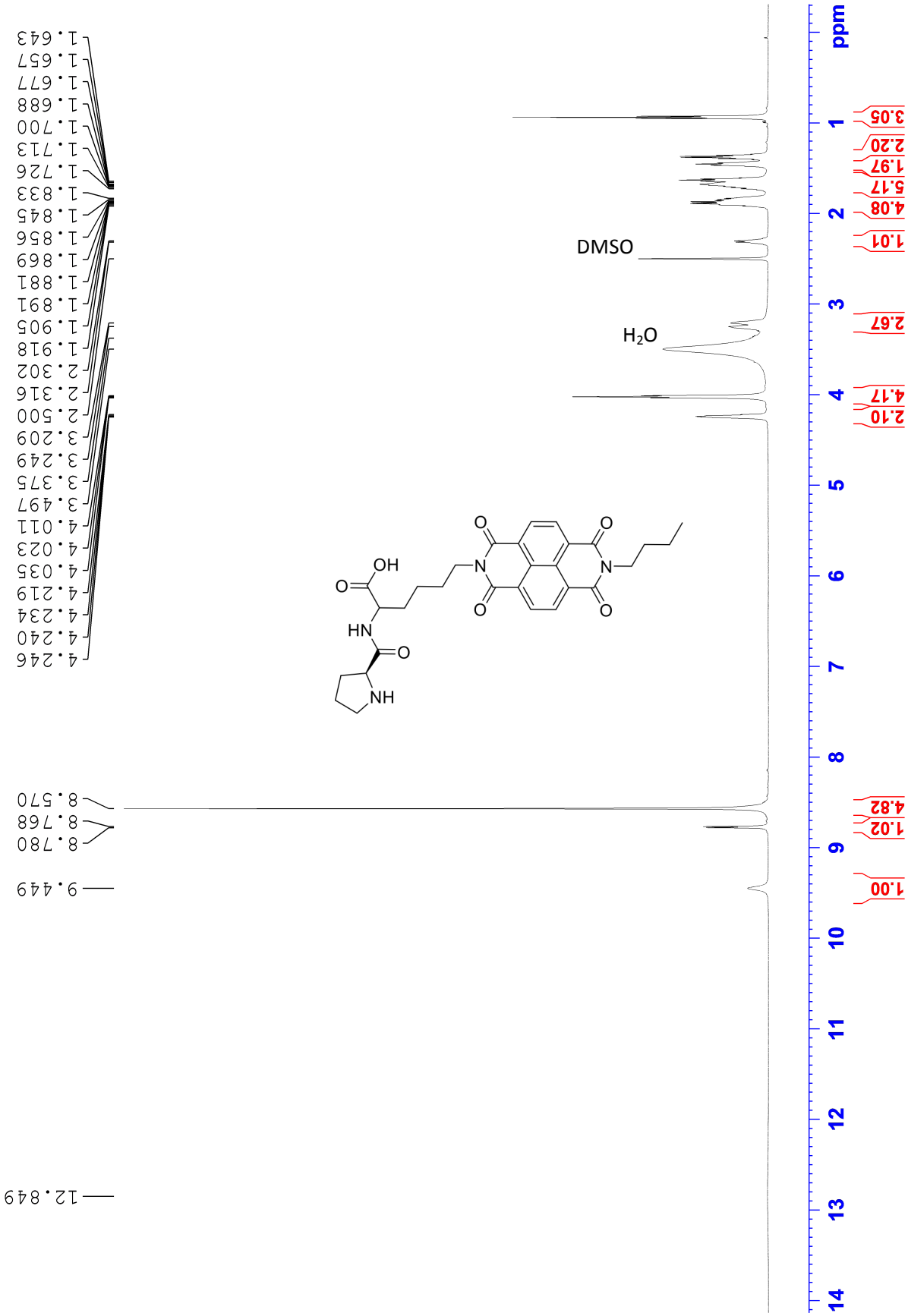

210.56
173.11
162.64
162.56
155.28
130.82
130.73
126.50
126.46
126.45
126.32
79.67
77.31
77.20
77.00
76.68
69.35
53.77
53.21
52.15
40.60
40.21
32.14
31.62
30.01
29.55
29.17
28.19
27.45
22.69
20.20
13.67
Current Data Parameters
NAME lys-NDI-OMe
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130211
Time 21.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 789.63
DW 20.800 use
DE 6.50 use
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 =======
NUC1 13C
P1 9.50 use
PLW1 48.00000000 W
SFO1 100.6328883 MHz
======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PLW2 12.52000046 W
PLW12 0.44016001 W
PLW13 0.28169999 W
SFO2 400.1716007 MHz
F2 - Processing parameters
SI 32768
SF 100.6228351 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


0.694
0.712
0.730
1.199
1.413
1.499
1.616
1.630
1.897
1.907
1.918
1.929
1.941
2.538
2.612
2.626
2.747
3.203
3.493
3.825
3.843
4.027
4.301
4.312
4.321
7.240
7.738
8.302
H2O
DMF
HN
N
O
ppm
1
2
3
4
5
6
7
8
9
10
3.10
13.11
2.44
2.86
3.71
1.68
2.14
2.92
3.99
1.07
1.04
4.00


13.21
19.71
22.35
23.08
23.98
26.91
27.72
27.90
29.46
30.80
31.35
35.31
35.59
35.91
36.36
38.00
39.76
39.99
46.44
51.41
51.69
55.83
55.87
59.15
60.27
79.66
130.12
130.09
125.73
125.64
153.85
154.93
161.79
161.84
162.00
165.02
171.94
DMF
CDCl3
DMF
ppm


DMSO
H2O
ppm

13.68
19.79
23.02
23.37
27.01
29.48
29.52
30.43
39.09
39.23
39.36
39.50
39.64
39.78
39.84
39.92
45.75
52.33
58.79
DMSO
116.00
117.99
125.94
126.07
126.11
130.37
158.03
158.24
162.43
162.44
168.35
172.86
ppm

Figure S9: High Resolution Mass Spectrum of **1**

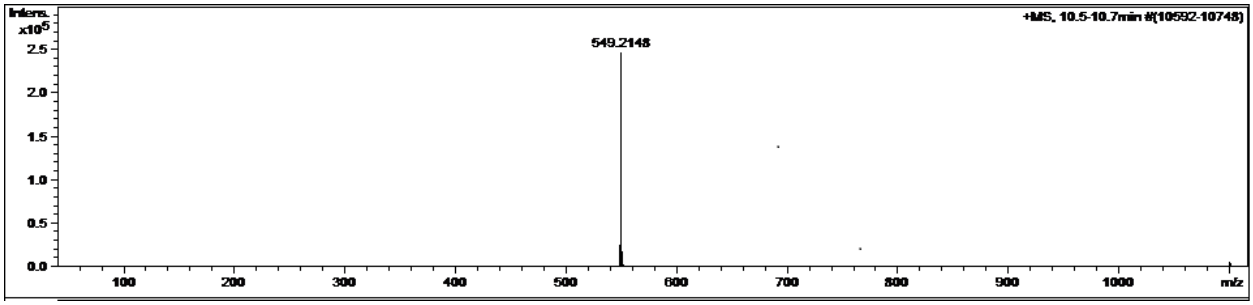
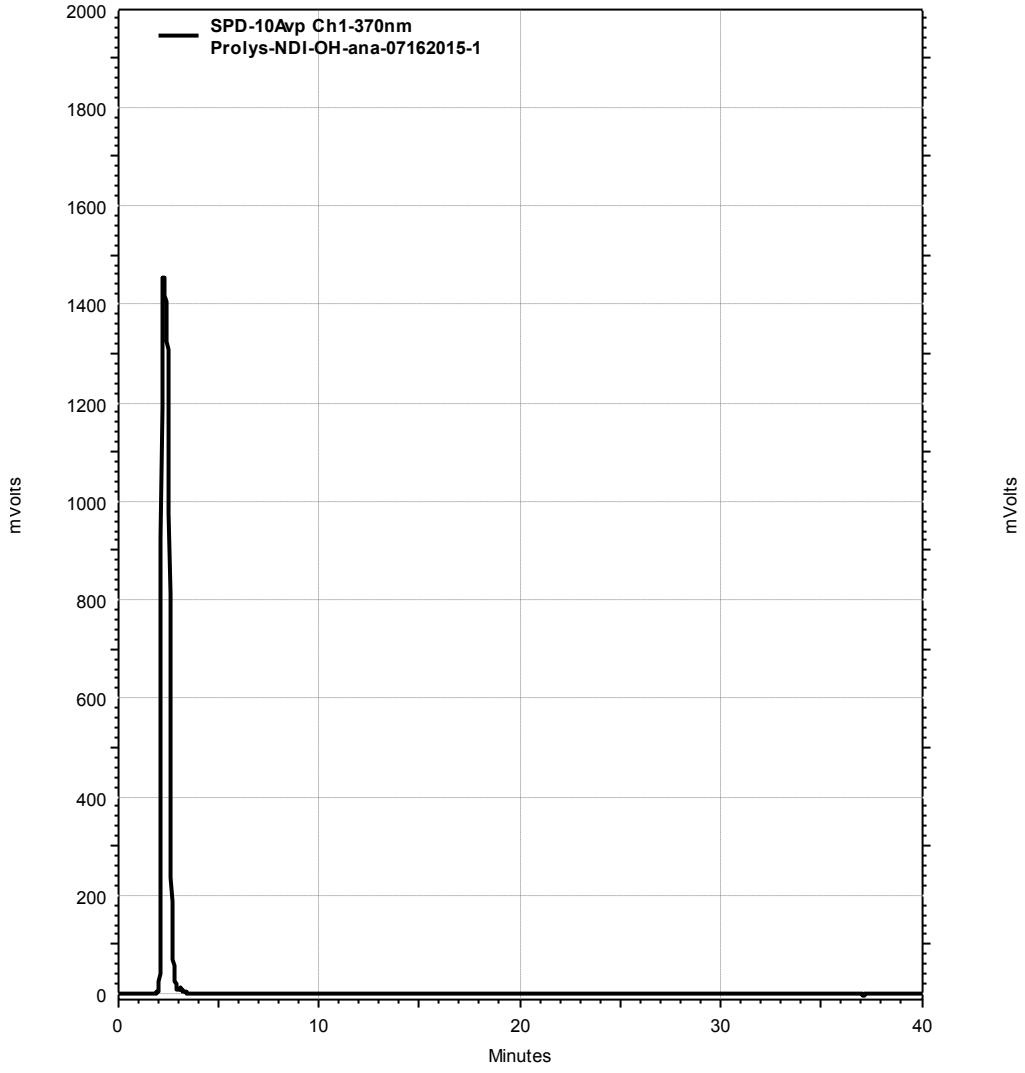


Figure S10: HPLC Chromatogram of **1**



L. References

1. (a) Lim, Y. B.; Lee, E.; Lee, M., Cell-penetrating-peptide-coated nanoribbons for intracellular nanocarriers. *Angew Chem Int Edit* **2007,** *46* (19), 3475-3478; (b) Ercelen, S.; Klymchenko, A. S.; Demchenko, A. P., Ultrasensitive fluorescent probe for the hydrophobic range of solvent polarities. *Anal Chim Acta* **2002,** *464* (2), 273-287.
2. (a) Moorthy, J. N.; Saha, S., Highly Diastereo- and Enantioselective Aldol Reactions in Common Organic Solvents Using N-Arylprolinamides as Organocatalysts with Enhanced Acidity. *Eur J Org Chem* **2009,** (5), 739-748; (b) Mitsui, K.; Hyatt, S. A.; Turner, D. A.; Hadad, C. M.; Parquette, J. R., Direct aldol reactions catalyzed by intramolecularly folded prolinamide dendrons: dendrimer effects on stereoselectivity. *Chem Commun* **2009,** (22), 3261-3263.