Light- and solvent-driven morphological transformations of self-assembled hydrogen-bonded nanostructures

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Supporting Information

General Experiments

All the starting materials and solvents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra of compounds were collected on a 400 MHz spectrometer at room temperature. IR data was obtained from a Perkin Elmer Spectrum 2000 FT-IR spectrometer. UV-visible absorption spectra were recorded on a spectrophotometer (HITACHI U2800A).

Scanning electron microscopy

Samples were prepared by drop-casting a solution of **1** (0.1 mM) onto a flat SiO_2/Si substrate as described above. The samples were imaged using a FEI Nova NanoSEM 200 in low-vacuum mode with no conductive overcoat. The chamber pressure was maintained at 0.45 Torr water using a differential pumping system. An immersion lens was employed and the secondary electrons amplified by gas vapor and collected by an electrode mounted on the pole piece.

Transmission electron microscopy

Samples were drop-casted onto a 200 mesh copper grid coated with formvar film stabilized with vacuum-evaporated carbon and dried under air. The samples were examined in electron microscopes operating at 75 kv (Hitachi H-7650) and at 200 kv (JEOL JEM-2100).

Grazing Incidence X-Ray Scattering (GIXS) Measurements

X-ray scattering experiments were performed at 298 K at Beamline 17A1 using a

GIXS apparatus at the National Synchrotron Radiation Research Center, Taiwan (NSRRC). The incident X-ray wavelength was 1.33146 Å, and the imaging plate was a Mar345 Imaging Plate Area Detector with a resolution factor of 3450 × 3450. To extract the structural information, the 2D SAXS patterns were converted to one-dimensional (1D) profiles as a function of the half the scattering angle by circularly averaging. The distance from the sample to the detector was 1000 mm, and the data accumulation time was 120 s for each sample.

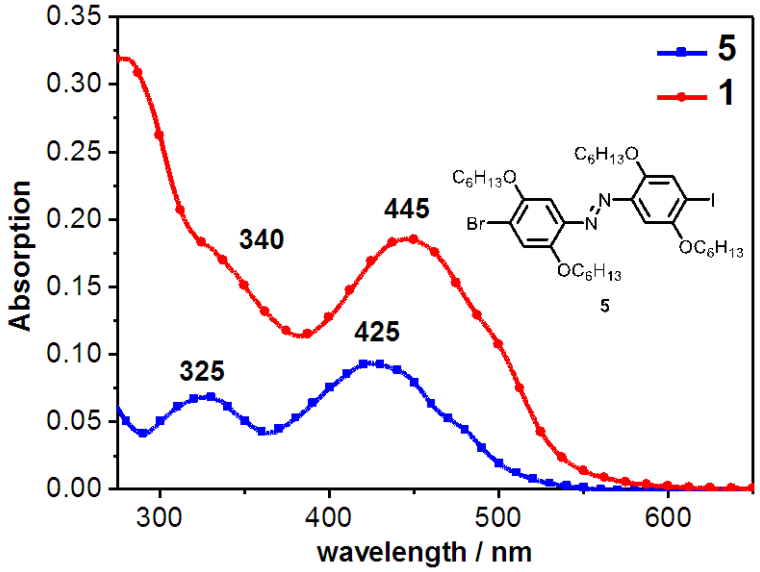


Figure S1. UV/Vis spectra of compounds **1** and **5** in THF solution (10^{-5} M).

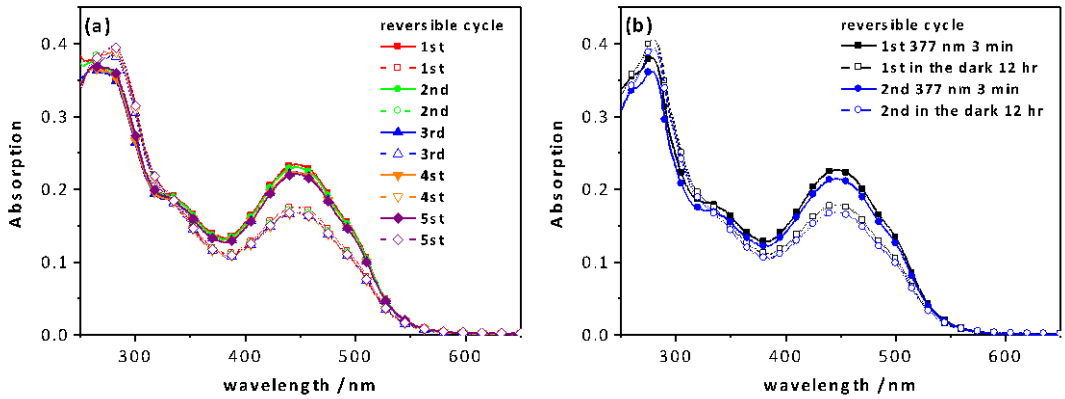


Figure S2. (a) The absorption spectra of compound *E*-**1** after excited at 377 nm for 2 minutes (solid symbol) and then excited at 450 nm for 2 minutes (empty symbol). (b) The absorption spectra of compound *E*-**1** after excited at 377 nm for 3 minutes (solid symbol) and stood for 12 hrs in the dark (empty symbol). A high power Xe lamp (1000 W) is used as the light source.

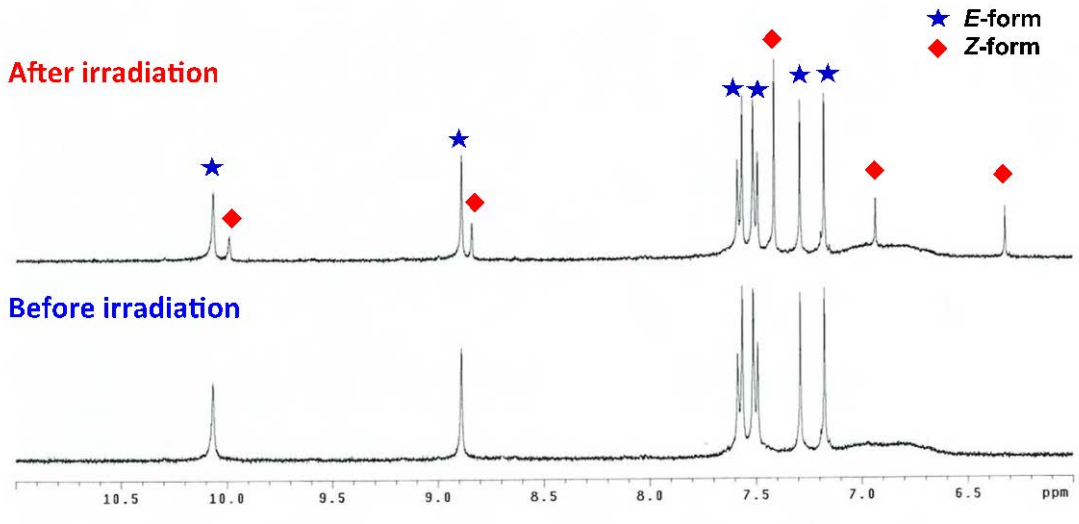


Figure S3. The NMR spectra of compound **1** before and after irradiation for 2 hr (1000 W).

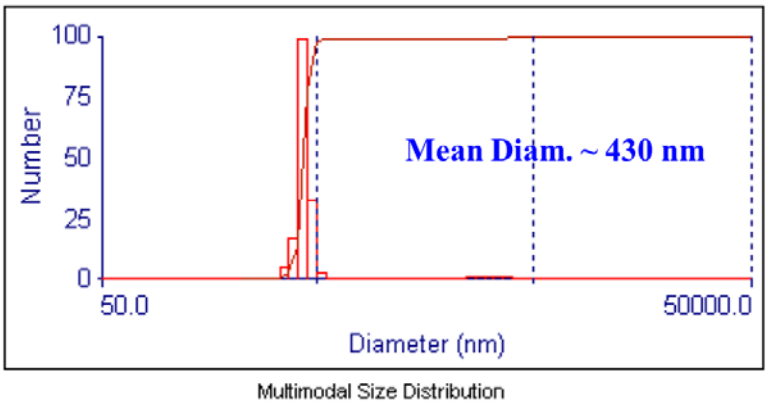


Figure S4. DLS measurement of phototreated (377 nm UV-light, 30 mins) compound **1** (10^{-4} M in THF).

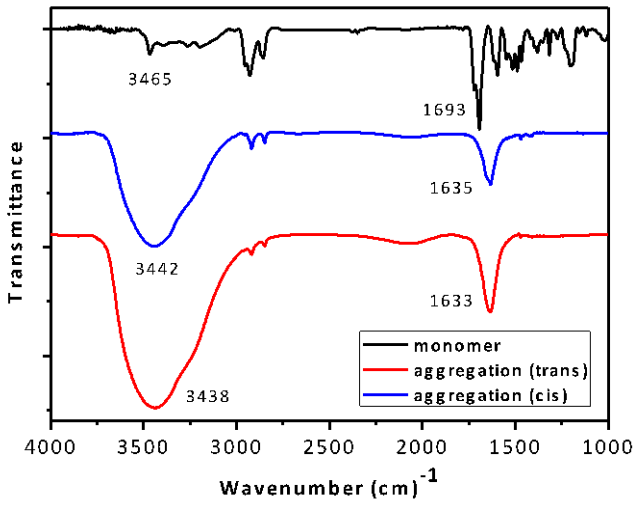


Figure S5. FT-IR spectra of compound **1** in monomer and aggregation states.

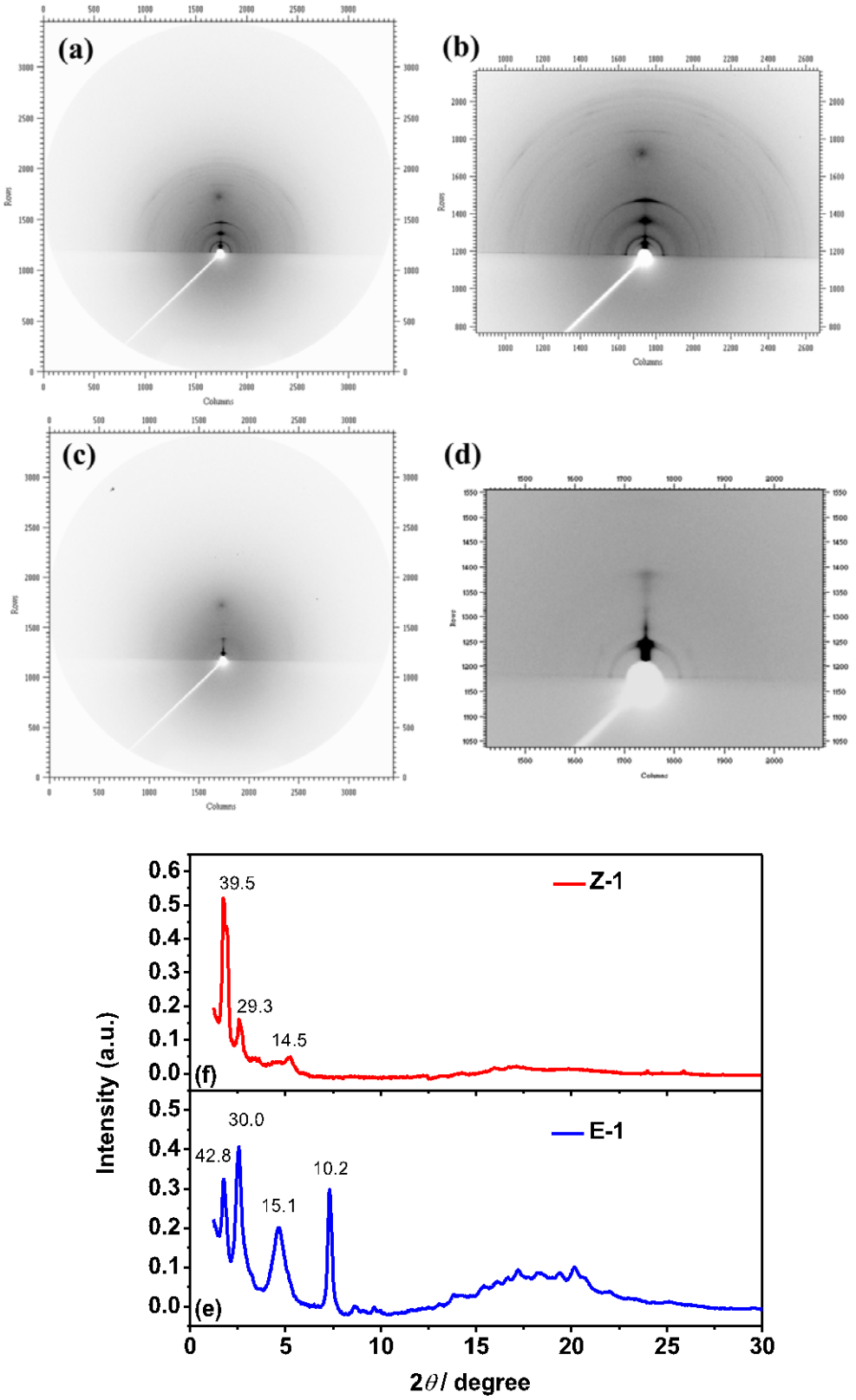


Figure S6. GIXS patterns of (a, b) *E*-**1** and (c, d) *Z*-**1** in self-assembled states. The magnification images are displayed in (b) and (d). XRD patterns of (e) *E*-**1** nanofribers, and (f) *Z*-**1** nanospheres.

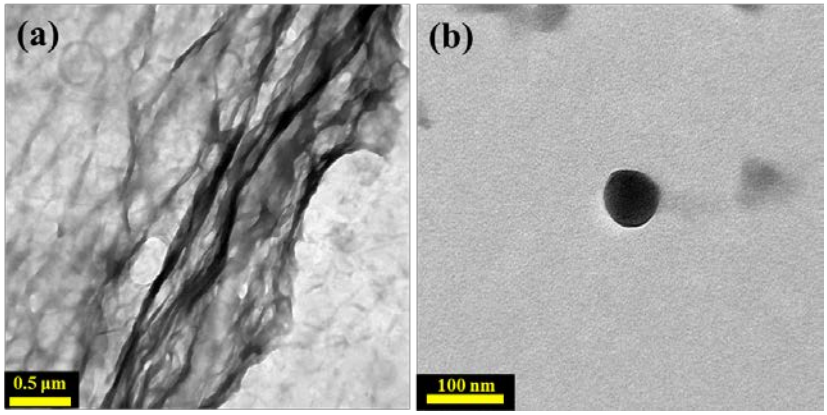


Figure S7. TEM images of compound **1** at 10^{-4} M in co-solvent systems of (a) THF/Hex = 1:5 (b) TEM of THF/H_2O system, V_{THF} / V_{water} = 1/20

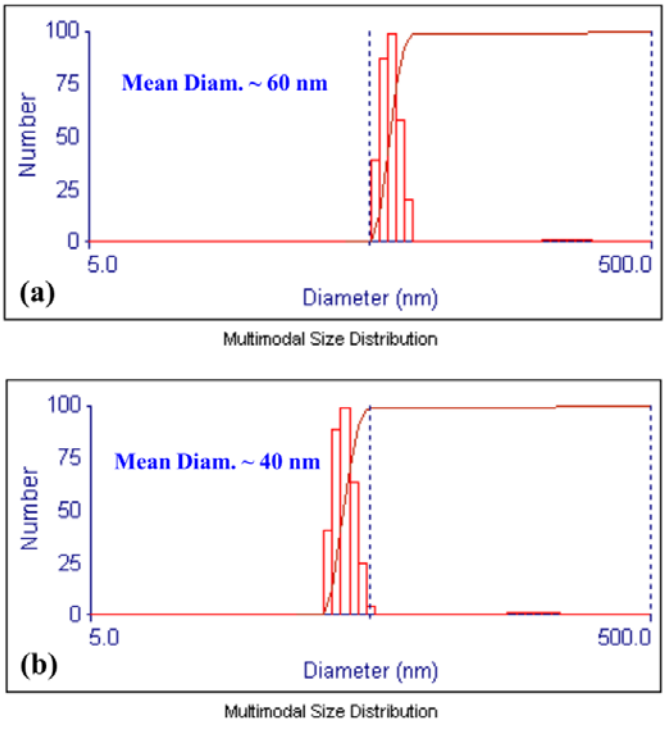


Figure S8. DLS measurement of compound **1** at THF/Water (a) 1:10 and (b) 1:20.

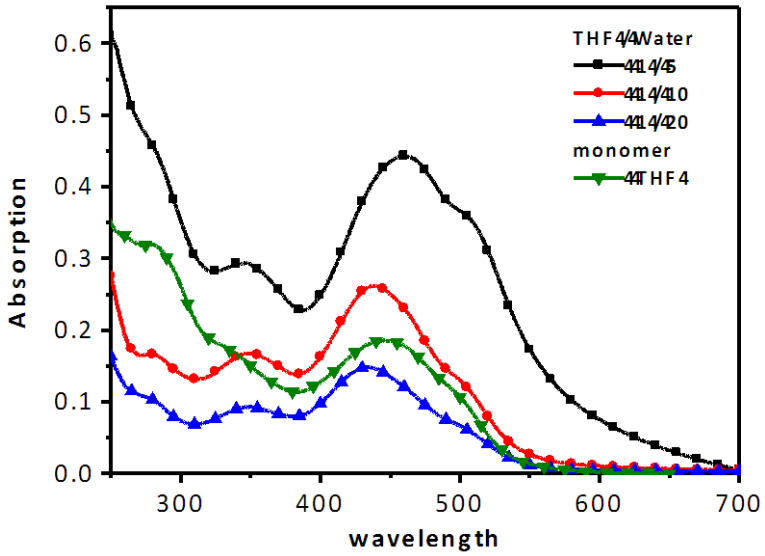


Figure S9. Absorption spectra of compound **1** in different volume ratio of THF/H_2O system from 1/5 to 1/20 compared with monomer in pure THF solution (10^{-5} M).

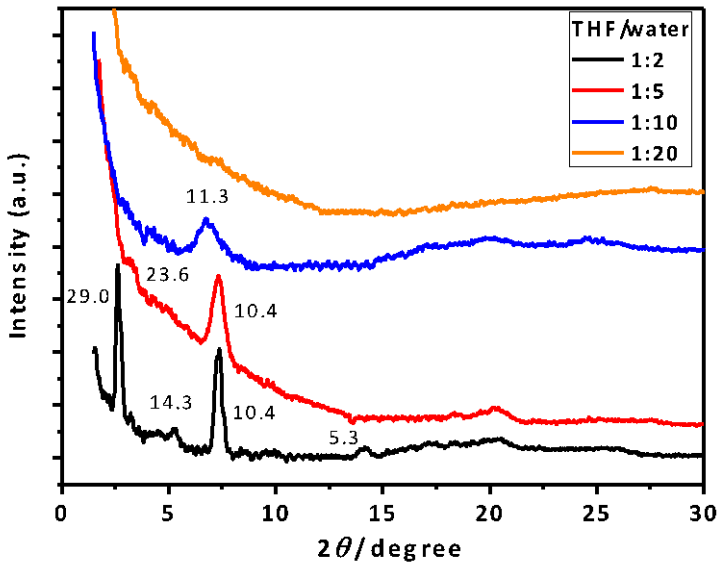


Figure S10. XRD patterns of compound **1** self-assembled in different volume ratio of THF/H_2O system from 1/2 to 1/20. Two strong peaks at 29.0 Å, 10.4 Å and two weak peaks at 14.3 Å, 5.3 Å in the small-angle region are attributed to a rectangular columnar arrangement.[1] Along with increasing composition of water, the peaks become weak and broad, then disappear finally.

[1] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hgele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, and M. Tosoni, *Angew. Chem., Int. Ed.* 2007, **46**, 4832.

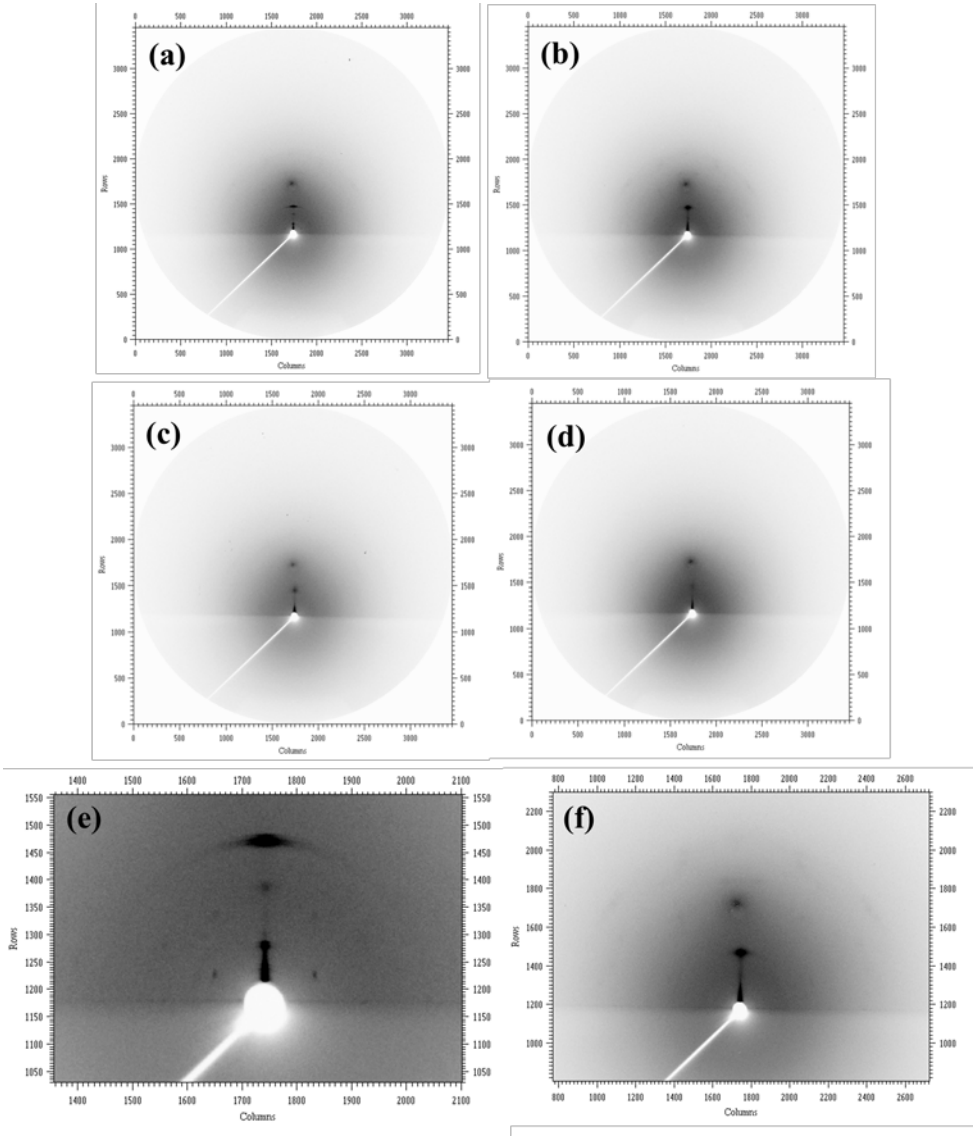
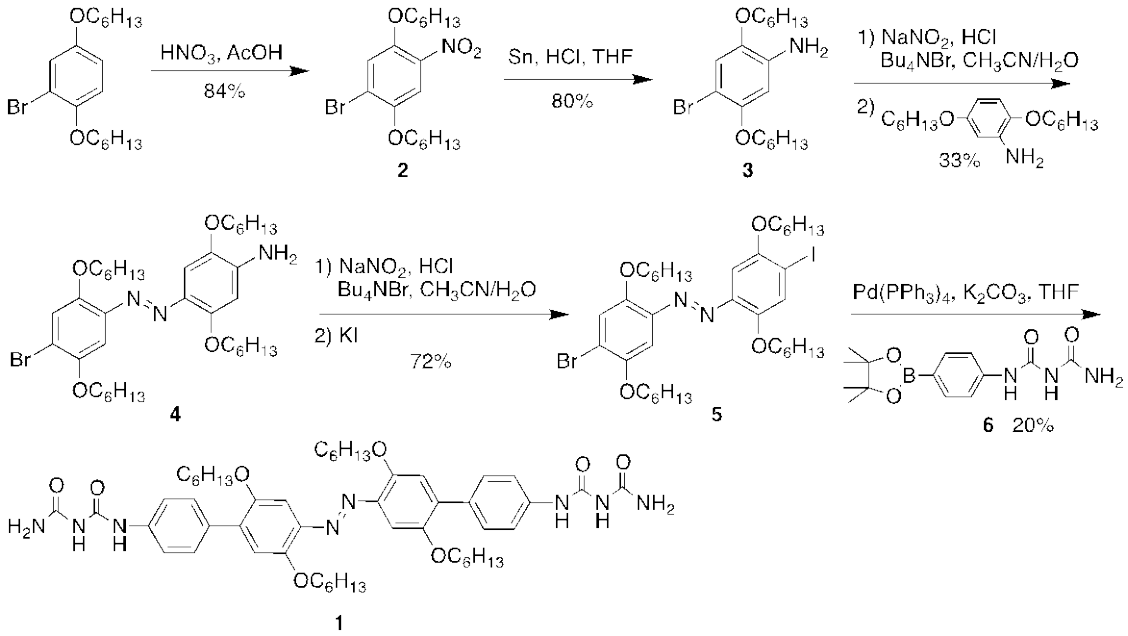


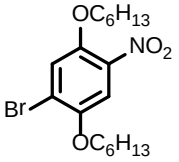
Figure S11. GIXS patterns of compound **1** self-assembled in different volume ratio of THF/H_2O system from (a) 1/2, (b) 1/5, (c) 1/10 and (d) 1/20. The magnification GIXS patterns of compound **1** in (e) 1/2, (f) 1/5 THF/H_2O system.

Syntheses

Nitration of 2-bromo-1,4-dihexyloxybenzene gave nitro compound **2**, which was reduced to give amino derivative **3**. Compound **3** was then treated with $NaNO_2$ in the presence of a phase-transfer catalyst to give a diazonium intermediate,[2] that was *in-situ* coupled with 2,5-dihexyloxyaniline to give diazo compound **4**. The amino group of **4** was then transformed via the Sandmeyer reaction[3] to compound **5**, which was then coupled to **6**[4] through Suzuki cross-coupling methodology to give the final compound **1**.



Detail procedures:



2

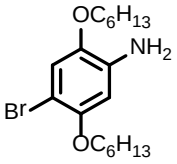
Synthesis of compound 2. HNO_3 (2.4 mL) was slowly added to a stirred solution of 2-bromo-1,4-dihexyloxybenzene (9.6 g, 26.9 mmol) in AcOH (25 mL) at room temperature. After 60 min, H_2O was added and the mixture was stirred for 10 min to give a yellow precipitate. The solid was filtered, washed with H_2O and air-dried. The crude product was extracted with ethyl acetate and concentrated to give solely nitro product **2** without further purification (9.1 g, 84%). m.p. 50-51 ^oC; IR (KBr) 3119,

[2] R. A. Tapia, L. Villalobos, C. Salas, *Synthesis* 2007, **24**, 3773.

[3] (a) J. K. Kochi, *J. Am. Chem. Soc.* 1957, **79**, 2942; (b) H. H. Hodgson, *Chem. Rev.* 1947, **40**, 251; (c) M. P. Doyle, B. Siegfried, J. F. Dellaria, *J. Org. Chem.* 1977, **42**, 2426.

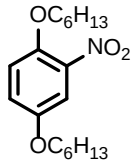
[4] (a) F.-C. Fang, C.-C. Chu, C.-H. Huang, G. Raffy, A. Del Guerzo, K.-T. Wong, D. M. Bassani, *Chem. Commun.* 2008, 6369

3092, 2950, 2932, 2856, 1618, 1562, 1465, 1380, 1339, 1271, 1125, 1016, 864, 801, 755, 727, 539 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 7.41 (s, 1H), 7.30 (s, 1H) 4.06-4.00 (m, 4H), 1.85-1.80 (m, 4H), 1.52-1.46 (m, 4H), 1.38-1.32 (m, 8H), 0.94-0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.1, 147.1, 138.5, 120.3, 119.0, 109.8, 71.0, 70.5, 31.8, 31.7, 29.3, 29.2, 25.9, 25.8, 23.0, 22.9, 14.4; MS (*m/z*, FAB^+) 401 (18), 402 (27), 403 (24), 404 (21); HRMS (*m/z*, FAB^+) Calcd for $C_{18}H_{28}{}^{79}BrNO_4$ 401.1202 found 401.1194, Cacld for $C_{18}H_{28}{}^{81}BrNO_4$ 403.1181, found 403.1184.



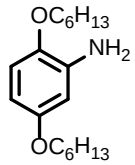
3

Synthesis of compound 3. Concentrated HCl (5.5 mL) and compound **2** (5.0 g, 12.5 mmol) were combined in a flask under 75 mL THF and cooled with an ice bath. Tin metal (3.0 g, 25.3 mmol) was added slowly to maintain a temperature of 0-5 ^oC and stirred for 30 min. After back to room temperature, the reaction was quenched with NaOH aqueous solution (PH ~ 10). The resulting mixture was extracted with ethyl acetate and brine then concentrated to generate the crude product, which was purified by column chromatography on silica gel with 1:12 ethyl acetate/Hexane as eluent to afford compound **3** (3.7 g, 80%). The amino product was used to the next reaction immediatedly. m.p. 38-39 ^oC; IR (KBr) 3356, 3189, 3004, 2919, 2849, 2360, 1658, 1632, 1504, 1469, 1422, 1215, 1137, 1017, 721, 646, 516 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 6.91 (s, 1H), 6.36 (s, 1H) 3.92 (t, *J* = 6.4 Hz, 4H), 3.81 (bs, 2H), 1.51-1.44 (m, 4H), 1.53-1.47 (m, 4H), 1.36-1.33 (m, 8H), 0.93-0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.4, 140.8, 136.0, 116.3, 101.9, 98.6, 70.2, 69.3, 31.9, 29.6, 29.5, 26.1, 26.0, 23.0, 14.5; MS (*m/z*, FAB^+) 371 (3), 373 (3); HRMS (*m/z*, FAB^+) Calcd for $C_{18}H_{30}{}^{79}BrNO_2$ 371.1460 found 371.1456, Cacld for $C_{18}H_{30}{}^{81}BrNO_2$ 373.1439, found 373.1426.



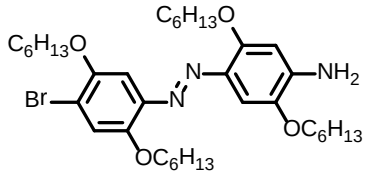
***p*-diOHex-NO$_2$**

Synthesis of *p*-diOHex-NO$_2$. HNO_3 (3.8 mL) was slowly added to a stirred solution of ***p*-diOHex** (11.5 mg, 41.3 mmol) in AcOH (50 mL) at room temperature. After 60 min, was added and the mixture was stirred for 10 min to give a yellow precipitate. The solid was filtered, washed with H_2O and air-dried. The crude product was extracted with ethyl acetate and concentrated to give solely liquid nitro product ***p*-diOHex-NO$_2$** without further purification (13.5 g, 99%). IR (KBr) 3087, 2931, 2859, 1740, 1500, 1468, 1391, 1351, 1277, 1220, 1149, 1018, 935, 853. 813, 727, 675 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 7.35 (d, *J* = 3.2 Hz, 1H), 7.06 (dd, *J* = 8.8 Hz, 3.2 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 1.82-1.76 (m, 4H), 1.47-1.42 (m, 4H), 1.36-1.32 (m, 8H), 0.94-0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 152.0, 146.4, 139.6, 121.0, 116.2, 110.2, 70.4, 68.9, 31.5, 31.4, 29.1, 29.0, 25.7, 25.5, 22.6, 22.5, 14.1; MS (*m/z*, FAB^+) 323 (100); HRMS (*m/z*, FAB^+) Calcd for $C_{18}H_{29}NO_4$ 323.2097 found 323.2095.



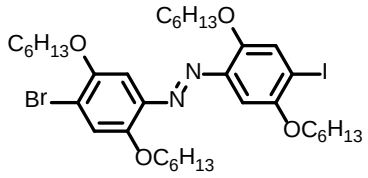
2,5-dihexyloxyaniline

Synthesis of 2,5-dihexyloxyaniline. Concentrated HCl (5.2 mL) and ***p*-diOHex-NO$_2$** (3.8 g, 11.7 mmol) were combined in a flask under 50 mL THF and cooled with an ice bath. Tin metal (2.8 g, 23.6 mmol) was added slowly to maintain a temperature of 0-5 ^{o}C and stirred for 30 min. After back to room temperature, the reaction was quenched with NaOH aqueous solution (PH ~ 10). The resulting mixture was extracted with ethyl acetate and brine then concentrated to generate the crude product, which was purified by column chromatography on silica gel with 1:12 ethyl acetate/Hexane as eluent to afford **2,5-dihexyloxyaniline** (2.7 g, 78%). The liquid amino product was used to the next reaction immediatedly. IR (KBr) 3382, 3476, 2930, 2859, 1622, 1514, 1469, 1390, 1292, 1218, 1144, 1033, 935. 838, 785, 725, 626, 567, 449 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) 6.67 (d, *J* = 8.8 Hz, 1H), 6.33 (d, *J* = 2.8 Hz, 1H), 6.22 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.80 (bs, 2H), 1.80-1.72 (m, 4H), 1.49-1.42 (m, 4H), 1.37-1.31 (m, 8H), 0.93-0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 153.6, 140.9, 137.2, 112.5, 102.8, 102.5, 69.1, 68.3, 31.7, 29.6, 29.4, 25.9, 25.8, 22.7, 14.1; MS (*m/z*, FAB^{+}) 293 (100); HRMS (*m/z*, FAB^{+}) Calcd for $C_{18}H_{31}NO_2$ 293.2355 found 293.2350.



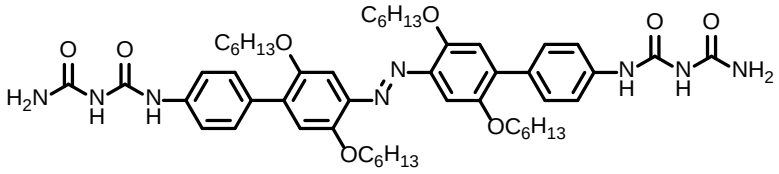
4

Synthesis of compound 4. Compound **3** (1.8g, 4.8 mmol), HCl (1.3 mL), acetonitrile (10 mL) and H_2O (10 mL) stirred in an ice bath. $NaNO_2$ (350 mg, 5.1 mmol) in 5 mL water was added slowly under 0~5 ^{o}C for 30 minutes. The diazonium salt was transferred to the prepared solution of 2,5-dihexyloxyaniline (1.4g, 4.8 mmol), acetonitrile (12 mL), H_2O (12 mL) and tetrabutylammoniumbromide (150 mg) and stirred over 30 minutes. The temperature was controlled at 0~5 ^{o}C on the whole process. The reaction was back to room temperature and stirred overnight. The resulting mixture was extracted with ethyl acetate and brine then concentrated to generate the crude product, which was purified by column chromatography on silica gel with 1:12 ethyl acetate/Hexane as eluent to afford compound **4** (1.1 g, 33%). m.p. 84-85 ^{o}C; IR (KBr) 3490, 3357, 3190, 2920, 2850, 2360, 1738, 1620, 1579, 1512, 1468, 1378, 1352, 1249. 1191, 1020, 800, 722, 643, 544 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) 7.32 (s, 1H), 7.28 (s, 2H), 6.38 (s, 1H), 4.44 (bs, 2H), 4.13-4.09 (m, 4H), 4.03-4.00 (m, 4H), 1.88-1.80 (m, 8H), 1.54-1.50 (m, 8H), 1.37-1.35 (m, 16H), 0.94-0.90 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) 154.8, 150.9, 150.7, 143.5, 143.1, 141.8, 134.8, 121.2, 113.7, 101.4, 100.5, 99.2, 72.0, 71.1, 70.1, 69.2, 32.3, 32.2, 32.1, 30.2, 30.1, 29.9, 29.8, 26.5, 26.4, 26.4, 23.3, 14.5, 14.4; MS (*m/z*, FAB^{+}) 675 (15), 676 (100), 677 (51), 678 (94). 679 (35); HRMS (*m/z*, FAB^{+}) Calcd for $C_{36}H_{58}{}^{79}BrN_3O_4$ 675.3611 found 675.3612, Cacld for $C_{36}H_{58}{}^{81}BrN_3O_4$ 677.3590, found 677.3592.



5

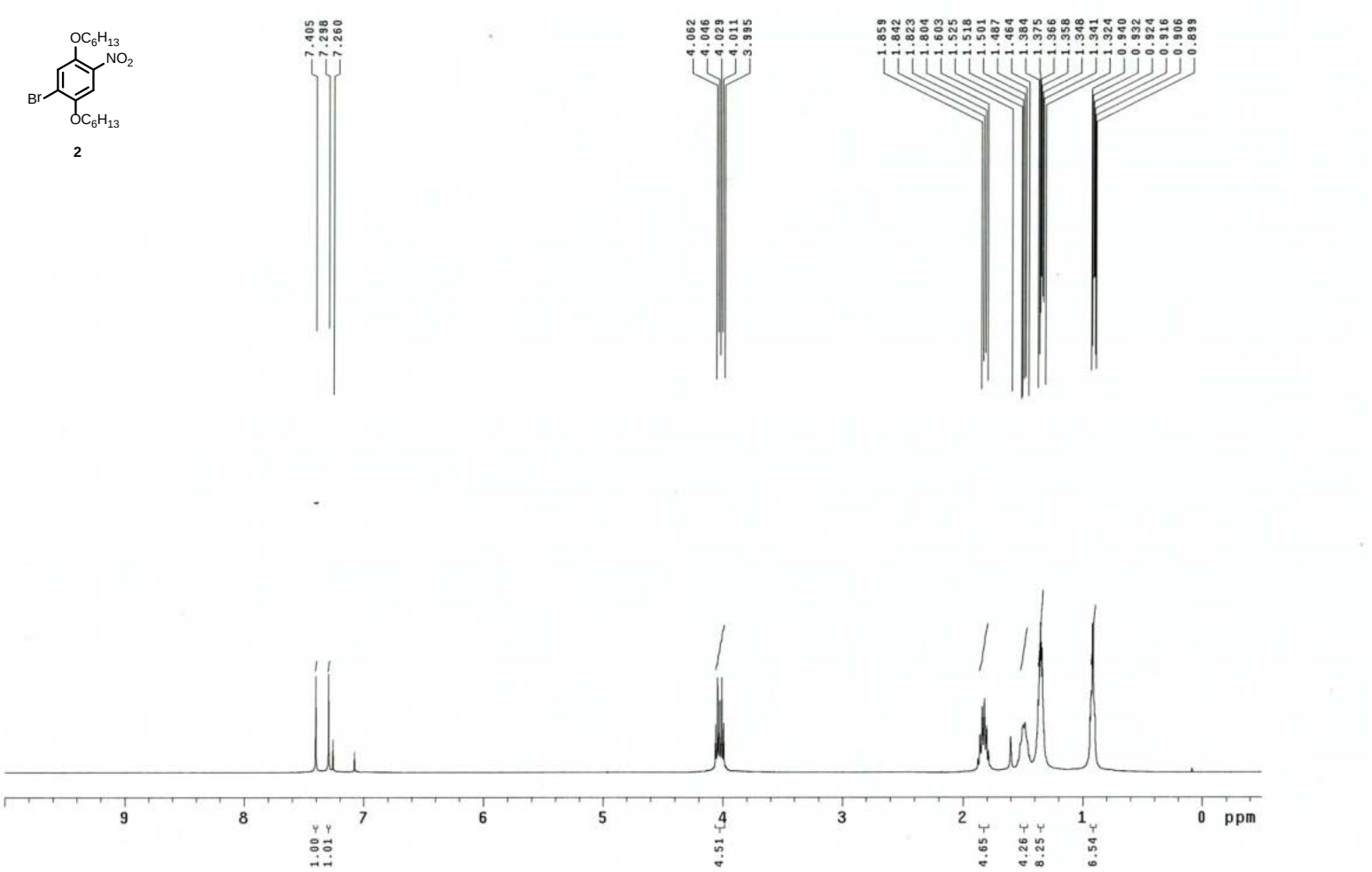
Synthesis of compound 5. Compound **4** (1.5 g, 2.3 mmol), HCl (1.1 mL), acetonitrile (30 mL), ethyl acetate (20 mL) and H_2O (30 mL) stirred in an ice bath. $NaNO_2$ (187 mg, 2.7 mmol) in 3 mL water was added slowly under 0~5 ^oC for 30 minutes, then an aqueous solution of KI (563 mg, 3.4 mmol) and 5 mL H_2O dropped to the diazonium salt above for over 30 minutes. The reaction was back to room temperature and stirred overnight. The resulting mixture was extracted with ethyl acetate and brine then concentrated to generate the crude product. Purification was performed with silica-gel column chromatography, eluting with 1:15 EA/Hex to give the oil product compound **5** (1.3 g, 72%). m.p. 96-97 ^oC; IR (KBr) 2953, 2925, 2866, 1562, 1486, 1462, 1378, 1261, 1216, 1158, 1028, 872, 821, 746, 575 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) 7.57 (s, 1H), 7.34 (s, 1H), 7.29 (s, 1H), 7.17 (s, 1H), 4.15-4.12 (m, 4H), 4.03-4.00 (m, 4H), 1.88-1.81 (m, 8H), 1.56-1.50 (m, 8H), 1.37-1.34 (m, 16H), 0.95-0.89 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) 153.0, 152.1, 152.0, 150.6, 143.5, 142.6, 127.2, 121.0, 116.9, 101.0, 99.5, 91.8, 71.7, 71.6, 70.3, 70.2, 32.2, 32.1, 30.1, 30.0, 29.7, 29.3, 26.4, 26.3, 23.3, 23.2, 14.5, 14.4; MS (*m/z*, FAB^+) 786 (8), 787 (36), 788 (18), 789 (29). 790 (10); HRMS (*m/z*, FAB^+) Calcd for $C_{36}H_{56}{}^{79}BrIN_2O_4$ 786.2468 found 786.2463, Cacld for $C_{36}H_{56}{}^{81}BrIN_2O_4$ 788.2448, found 788.2444.

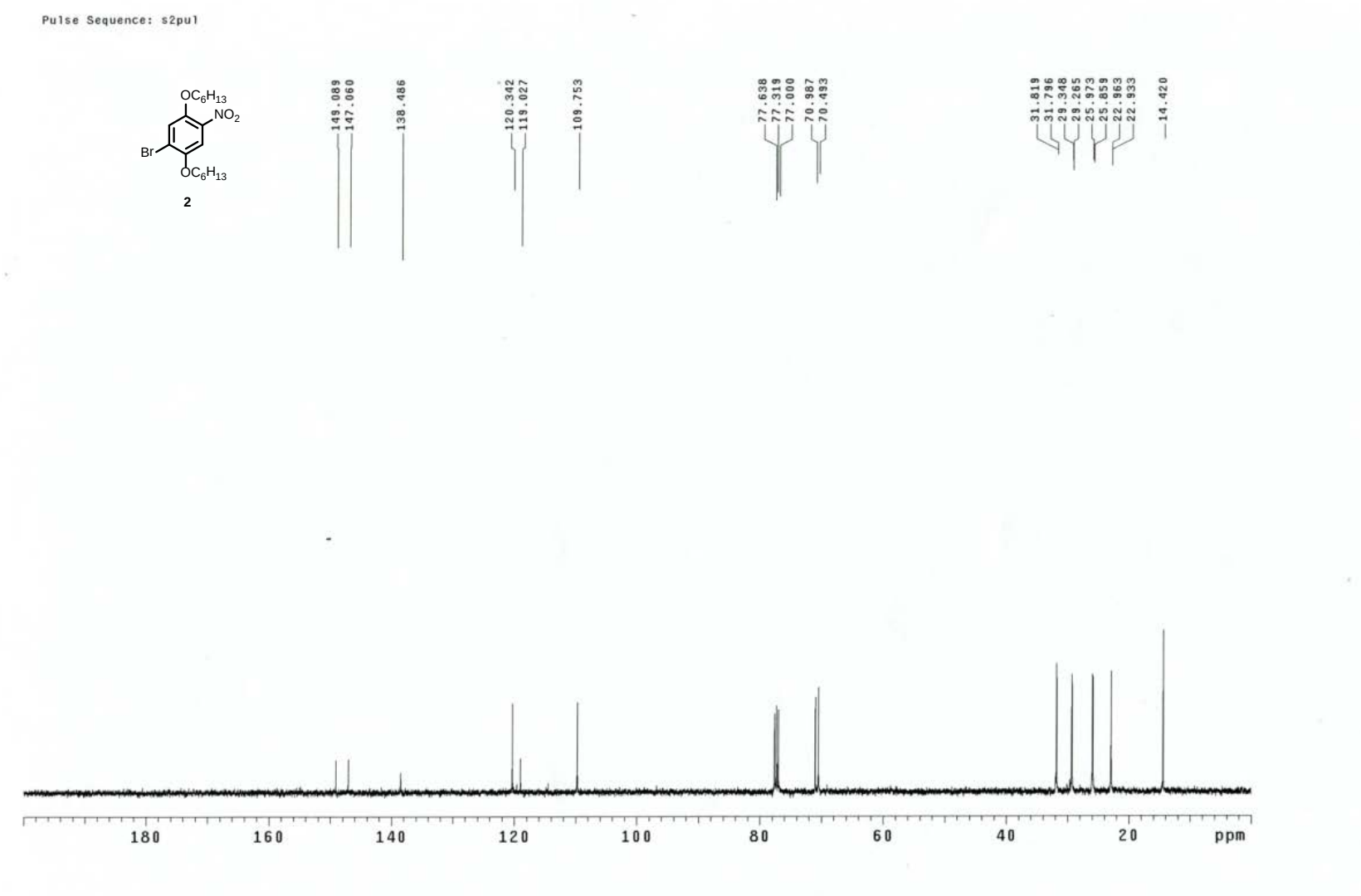


1

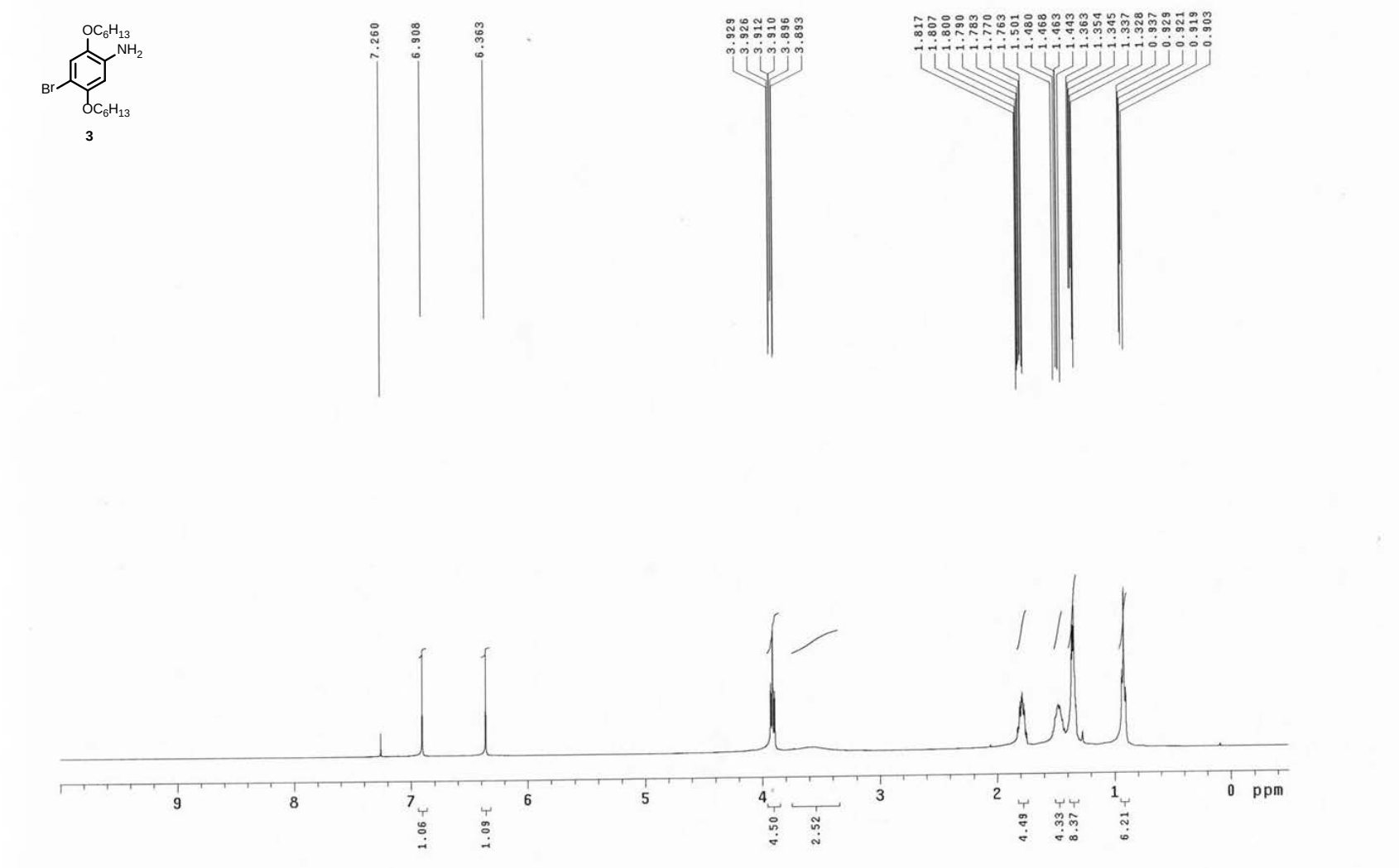
Synthesis of compound 1. A mixture of $Pd(PPh_3)_4$ (40 mg g, 0.03 mmol), K_2CO_3 (2 M, 1.5 mL), compound **5** (240 mg, 0.3 mmol), 4-pinacolatoboronic ester-benzenebiuret (compound **6**) (201 mg, 0.66 mmol) in degassed THF (20 mL) was refluxed for three days. The reaction was quenched by adding water and extracted with THF. The combined organic solution was washed with brine and dried over $MgSO_4$. Purification was performed with silica-gel column chromatography, eluting with 1:2 THF/CH_2Cl_2 to afford the desired molecule as orange solid compound **1** (60 mg, 20%). m.p. 230-231 ^oC; IR (KBr) 3367, 3262, 3197, 2929, 2856, 1693, 1596, 1547, 1489, 1316, 1274, 1203, 870, 834. 769, 678, 450 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) 10.7 (s, 2H), 8.89 (s, 2H), 7.29 (s, 2H), 7.57 (d, *J* = 8.4 Hz, 4H), 7.50 (d, *J* = 8.4 Hz, 4H), 7.29 (s, 2H), 7.17 (s, 2H), 6.90 (bs, 4H), 4.19 (t, *J* = 6.2 Hz, 4H), 3.91 (t, *J* = 6.2 Hz, 4H), 1.78 (t, *J* = 7.0 Hz, 4H), 1.65 (t, *J* = 6.8 Hz, 4H), 1.51 (t, *J* = 7.0 Hz, 4H), 1.35-1.25 (m, 24H), 0.84 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz) 155.9, 152.4, 151.9, 150.4, 141.8, 138.1, 134.3, 132.2, 130.3, 118.8, 118.3, 100.2, 70.7, 68.6, 31.5, 31.2, 29.5, 29.0, 25.8, 25.6, 22.5, 22.4, 14.3, 14.2; MS (*m/z*, FAB^+) 936 (5), 937 (11), 938 (7); HRMS (*m/z*, FAB^+) Calcd for $C_{52}H_{72}N_8O_8$ 936.5473 found 936.5462.

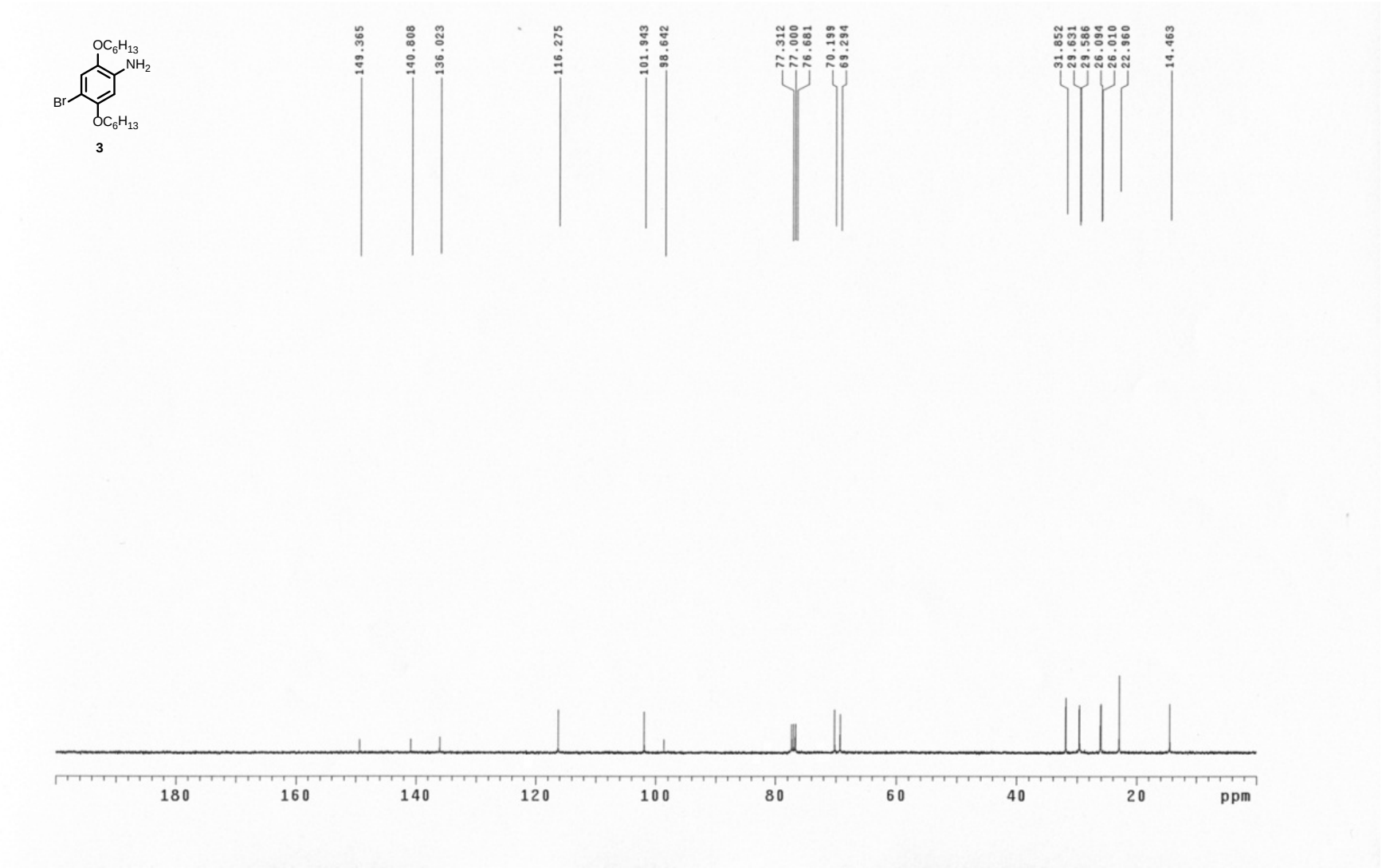
^{1}H and ^{13}C spectra of compound ***p*-diOHex-Br-NO$_2$**.



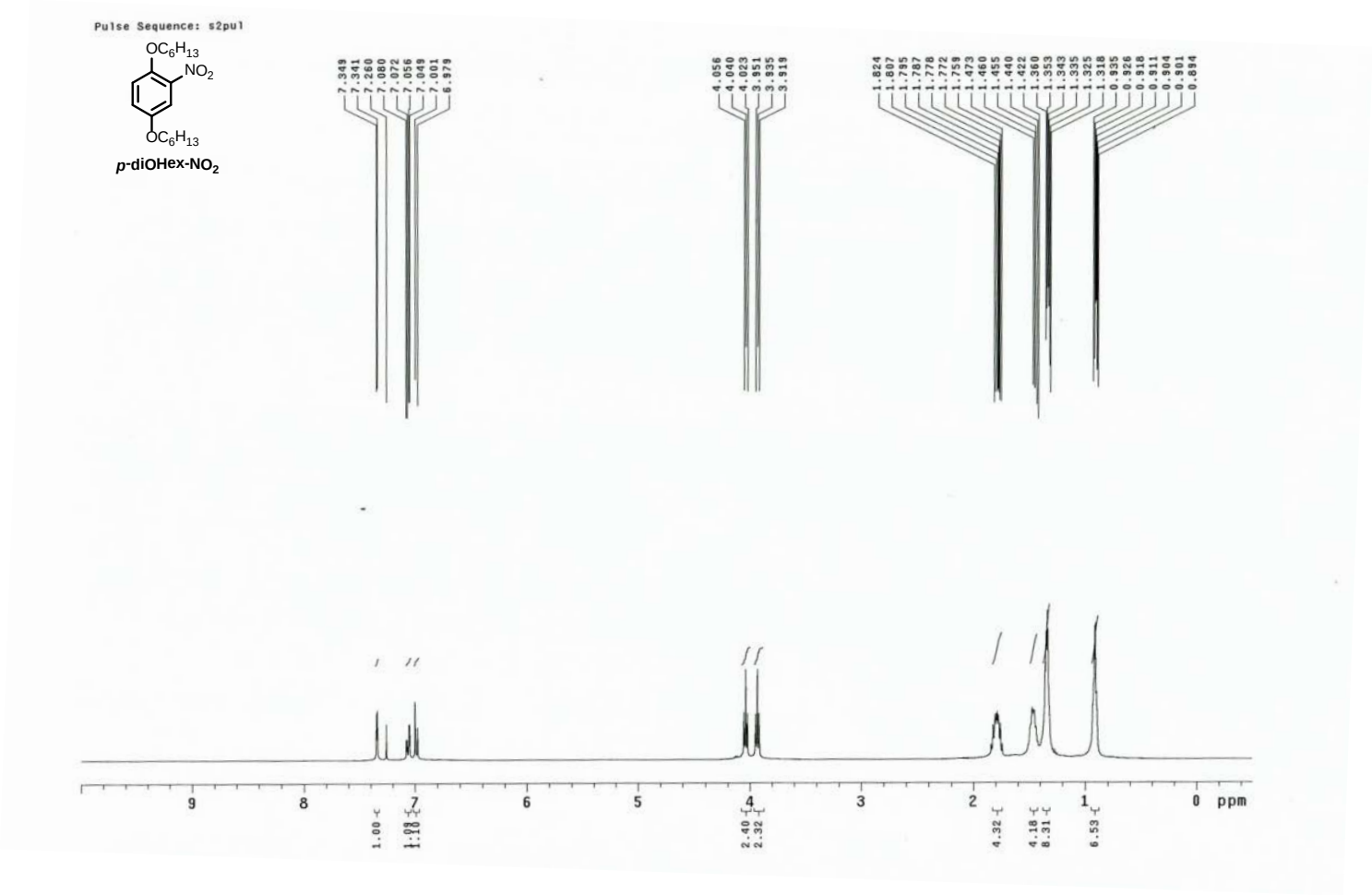


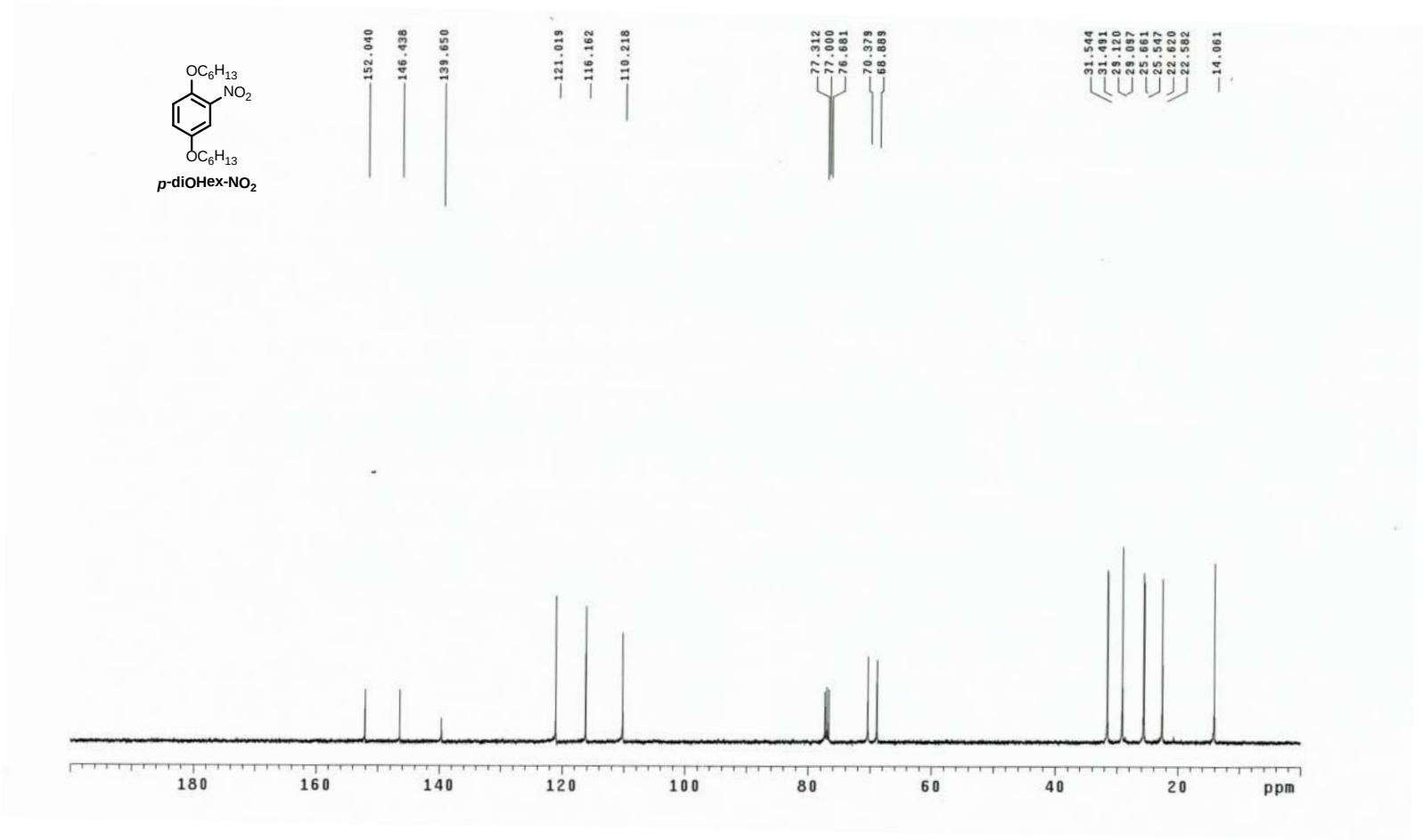
^{1}H and ^{13}C spectra of compound ***p*-diOHex-Br-NH$_2$**.



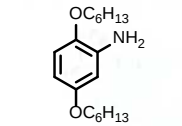


^{1}H and ^{13}C spectra of compound ***p*-diOHex- NO_2**.

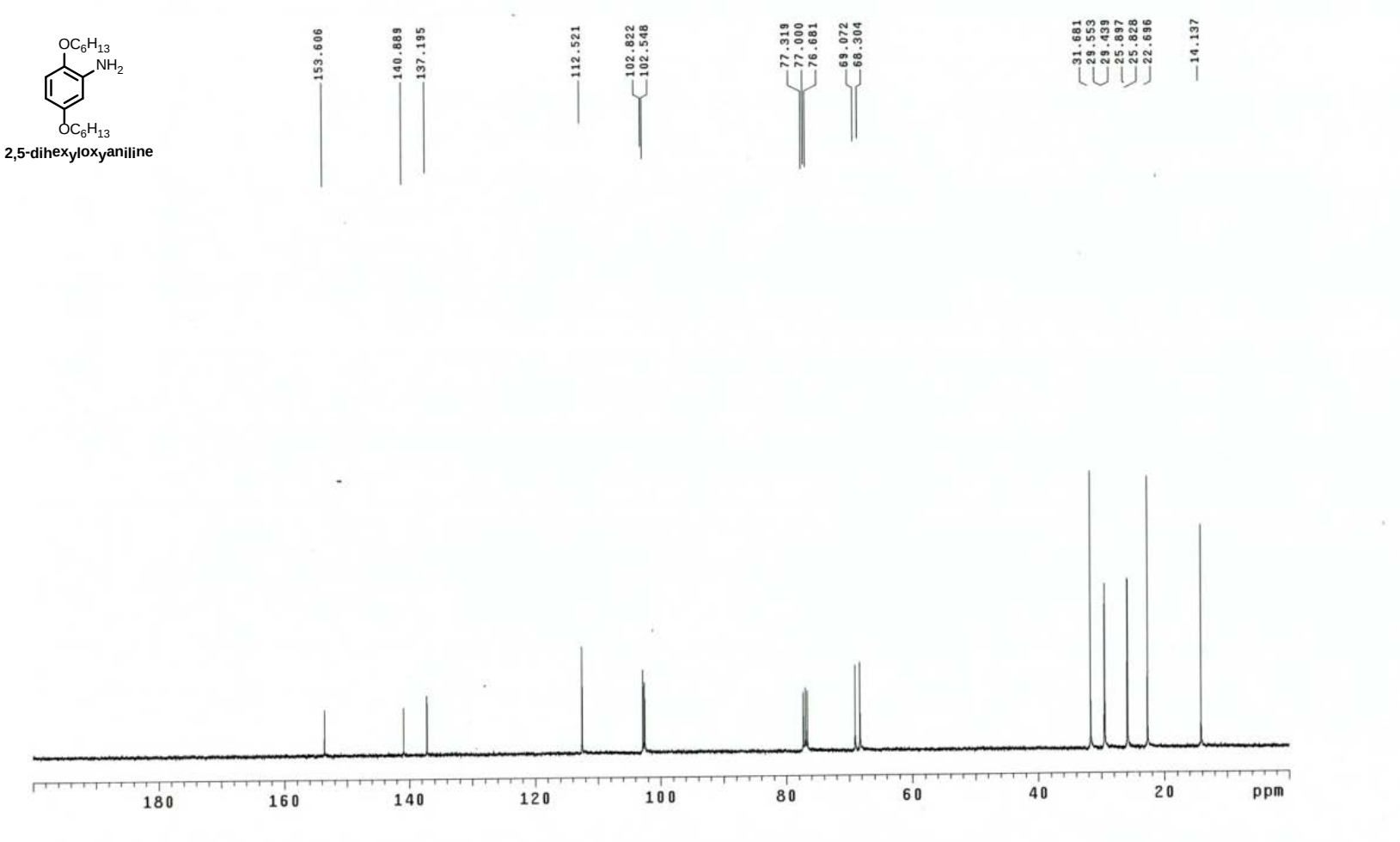




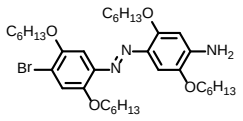
^{1}H and ^{13}C spectra of compound ***p*-diOHex- NH_2**.



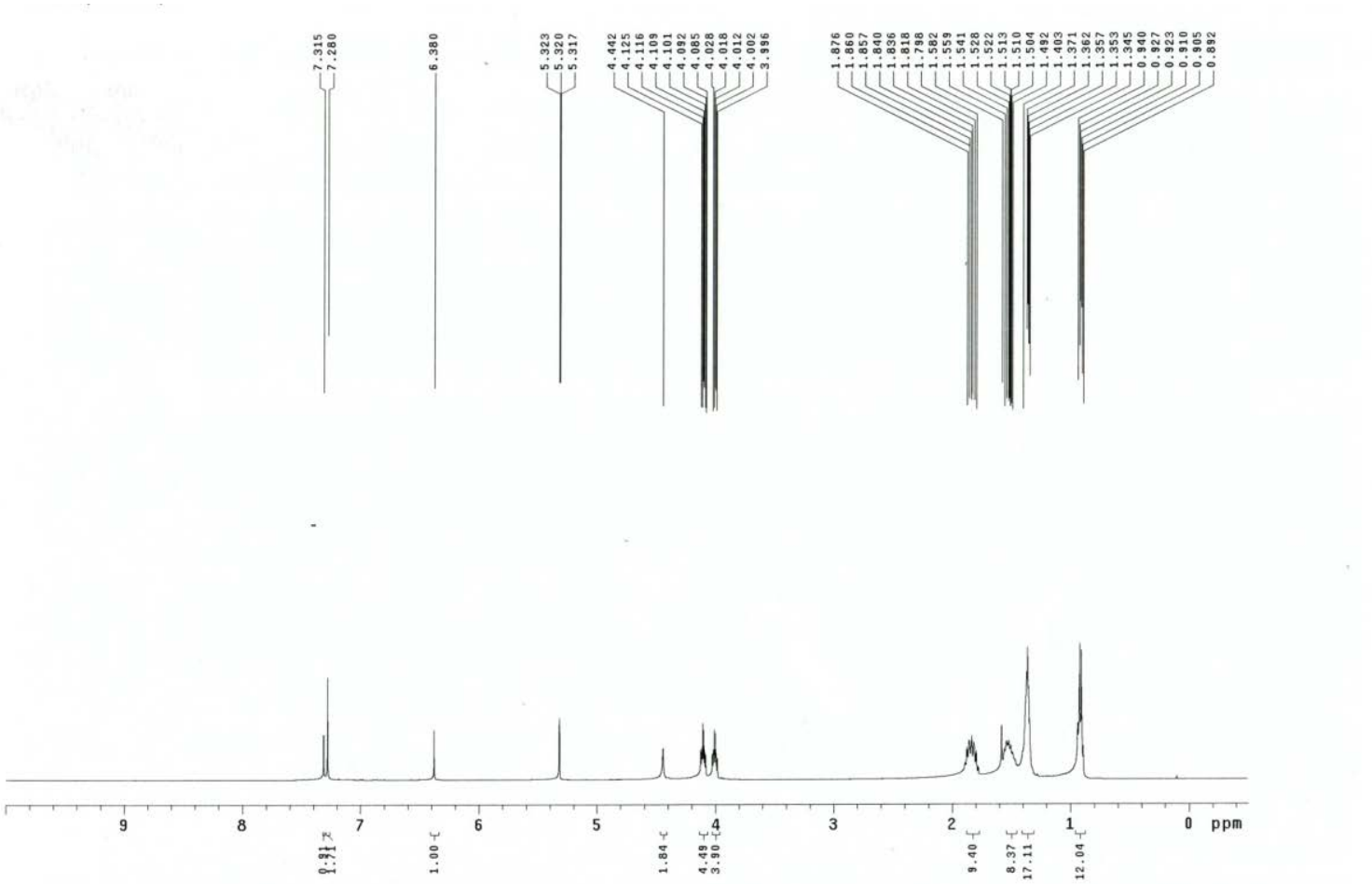
2,5-dihexyloxyaniline

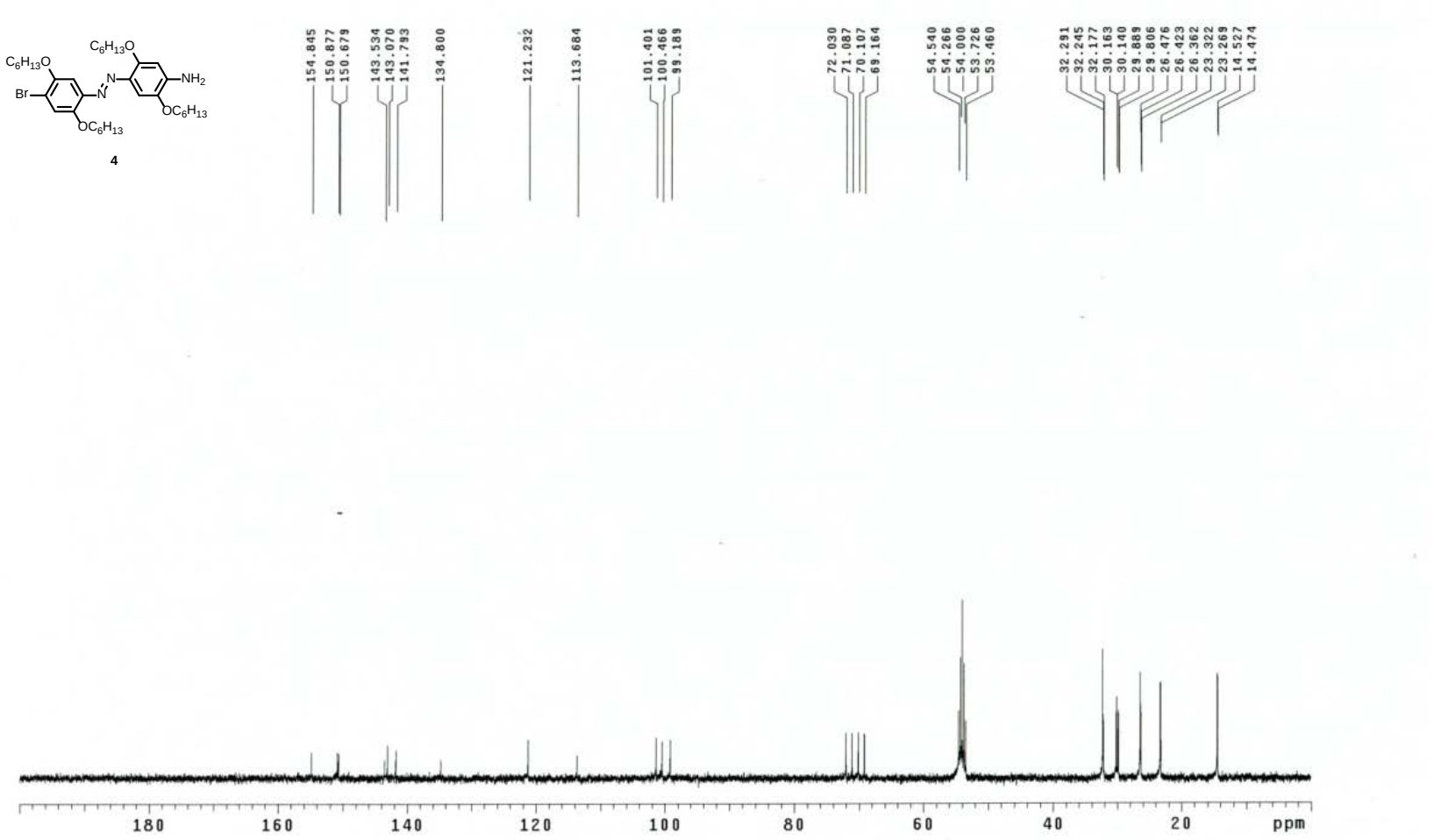


^{1}H and ^{13}C spectra of compound **4**.

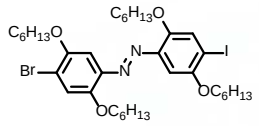


4





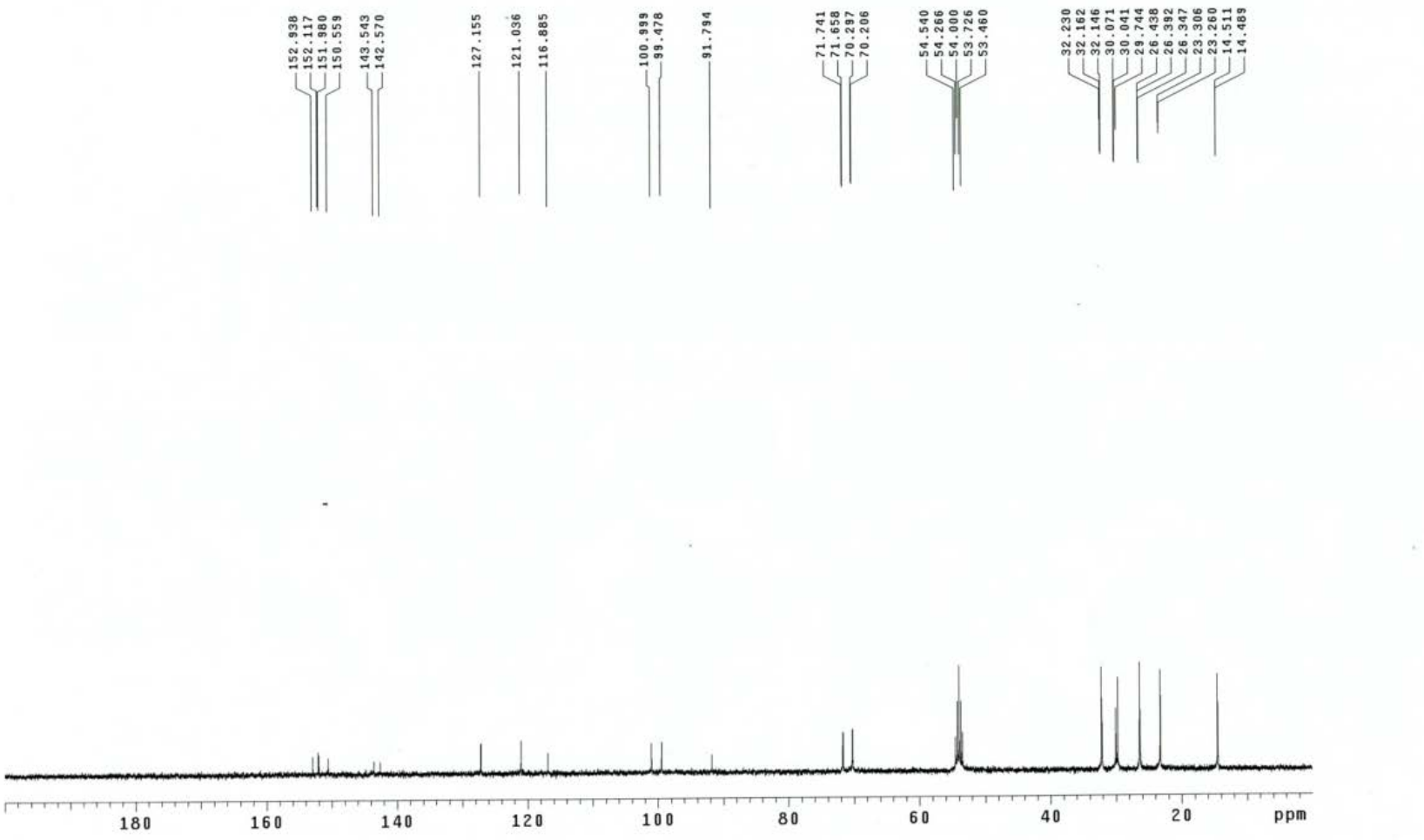
^{1}H and ^{13}C spectra of compound **5**.



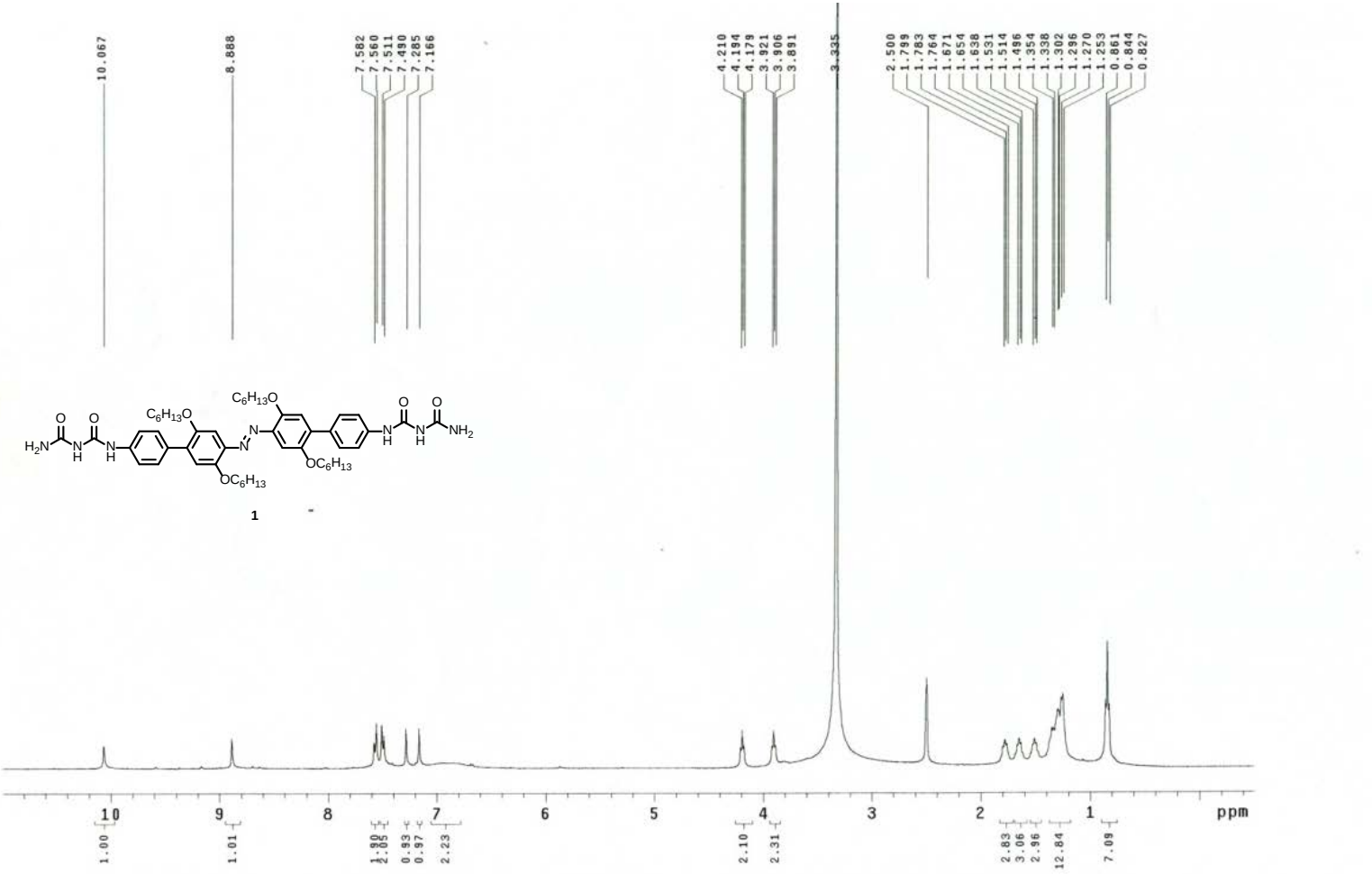
5

C6H13O
C6H13O
N
I
Br
OC6H13
OC6H13

5



^{1}H and ^{13}C spectra of compound **AzoBiuret**.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7.285
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4.210
4.194
4.179
3.921
3.906
3.891
3.335
2.500
1.799
1.783
1.764
1.671
1.654
1.638
1.531
1.514
1.496
1.354
1.338
1.302
1.296
1.270
1.253
0.861
0.844
0.827
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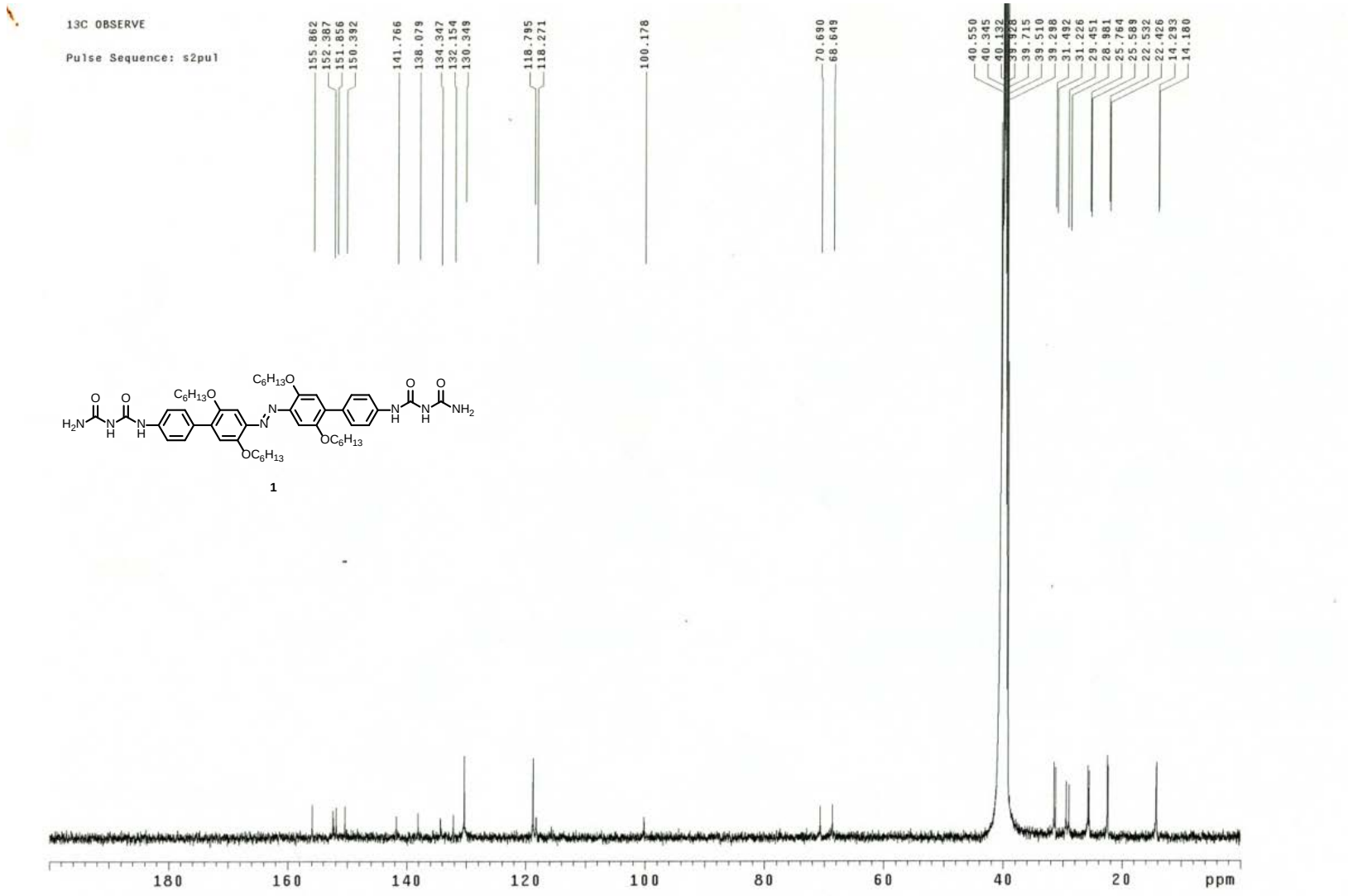
2.31
2.83
3.06
2.96
12.84
7.09
ppm

1


13C OBSERVE
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150.392
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138.079
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132.154
130.349
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118.271
100.178
70.690
68.649
40.550
40.345
40.132
39.928
39.715
39.510
39.298
31.492
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29.451
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25.764
25.589
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14.180
180
160
140
120
100
80
60
40
20
ppm

1