Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Strategy towards large two-photon absorption cross-sections for diketopyrrolopyrroles

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S1. Stability of the compounds in various solvents.

Stability of the compounds in three different solvents (chloroform (CLF), DCM, and THF) was checked under air saturated condition at Room temperature (23 ºC) by UV-vis absorption spectral measurements (Fig. S1.1). Considerable spectral change was found for **4** in spectroscopic grade CLF after 1 day stored in dirk. The first one-photon absorption (OPA) peak (@625 nm) was reduced and a new peak appeared red-side (670 nm). The similar change was also observed for **4** in THF and **5** in CLF but less significant even after 3 days. For other solutions, negligible change was observed.

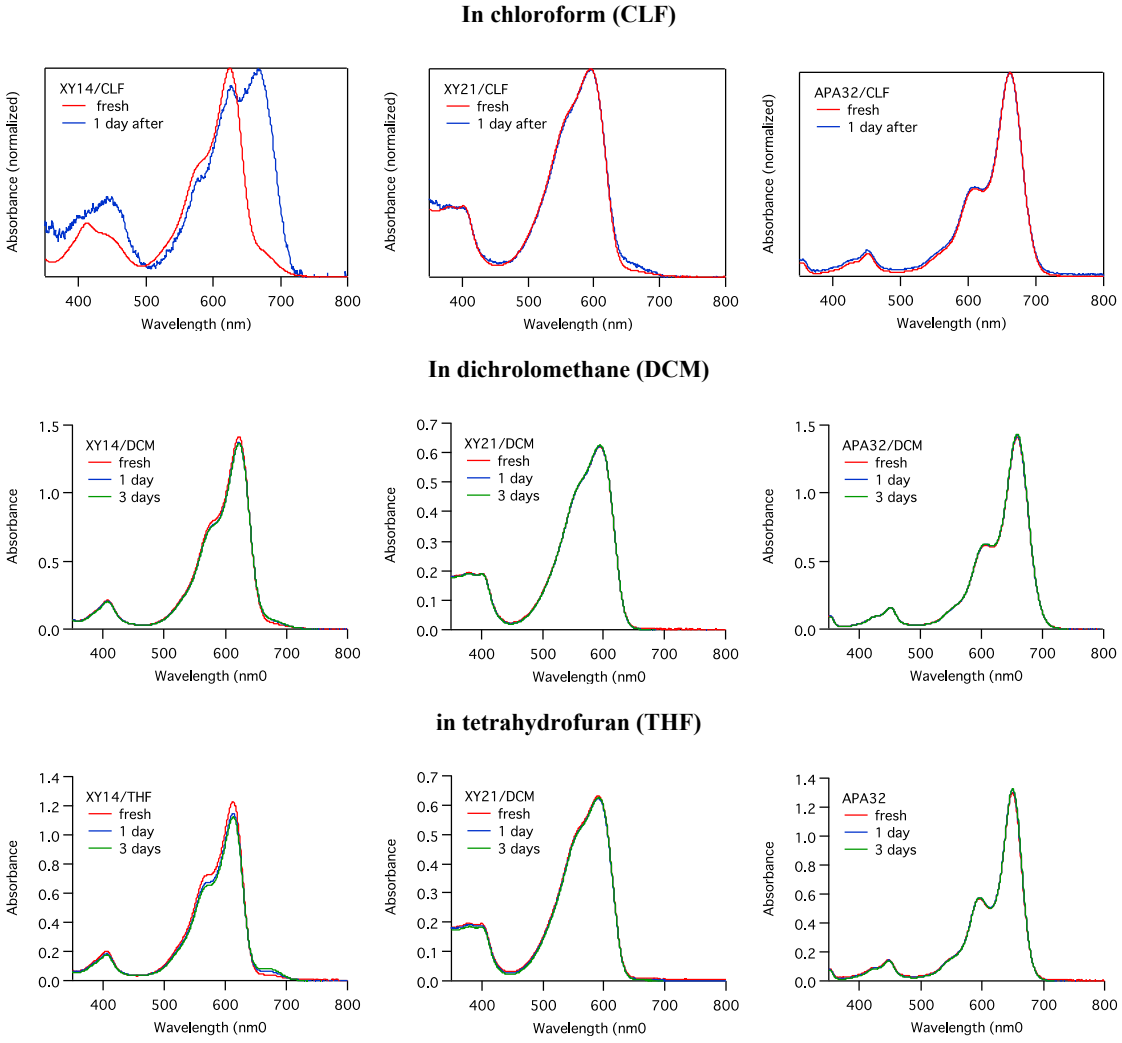


Fig. S1.1. Spectral change of the sample solutions after preparation in various solvents. From left to right, compound **4**, **5**, and **9**,

S2. TPA measurements

S2.1. Open-aperture Z-scan traces

The open-aperture Z-scan measurements were performed with the irradiation power of 0.3 mW or less with siring the sample solution (see section S2.3) by changing the incident wavelength. CH_2Cl_2 was selected because its solutions are the most stable among the tested (section S1). Typical open-aperture Z-scan traces with theoretical fitting curves are shown in Figs. S2.1-S2.4. Normal open-aperture signals (i.e., a symmetrical dip to the focal point) were observed for all samples and wavelengths (as in Figs. S2.1-S2.4), except the cases of solution of **4** at short wavelengths. The data were well reproduced by the theoretical equation of transmittance through a two-photon absorptive media for the spatially and temporally Gaussian pulsed with correction for the linear absorption if it is not negligible.[1] The data shown in Fig. S2.4 corresponds to the data poit that gives the large TPA cross section of 19,000 GM for **9** as in the text. For the solution of **4** at wavelengths shorter than 740 nm, a bump was observed which is a characteristic feature of saturable absorption (SA) as shown in Fig. S2.4. Such data were analyzed with theoretical equation considering both TPA and SA [2] by curve fitting (also shown in Fig. S2.4).

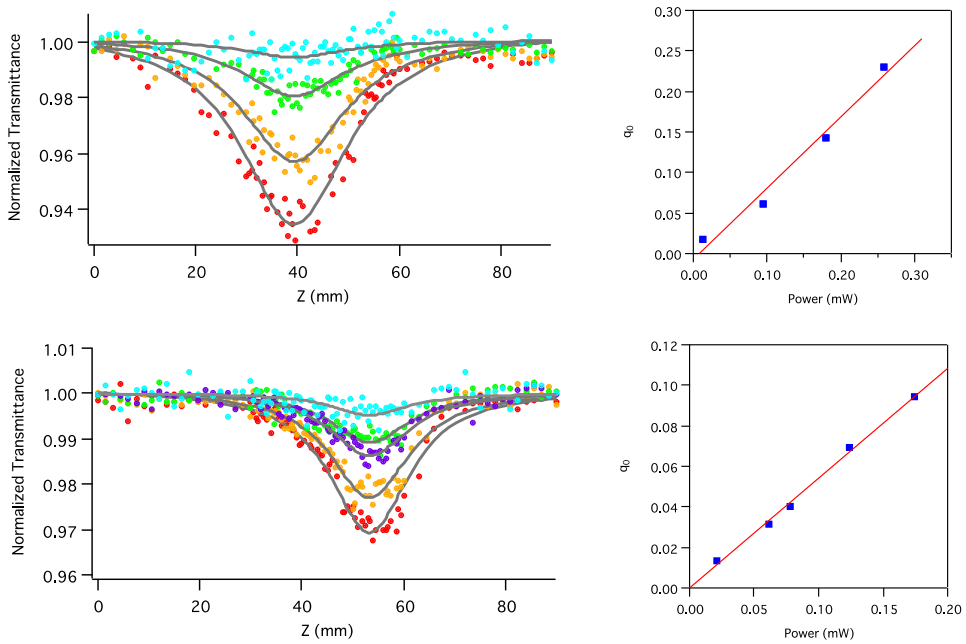
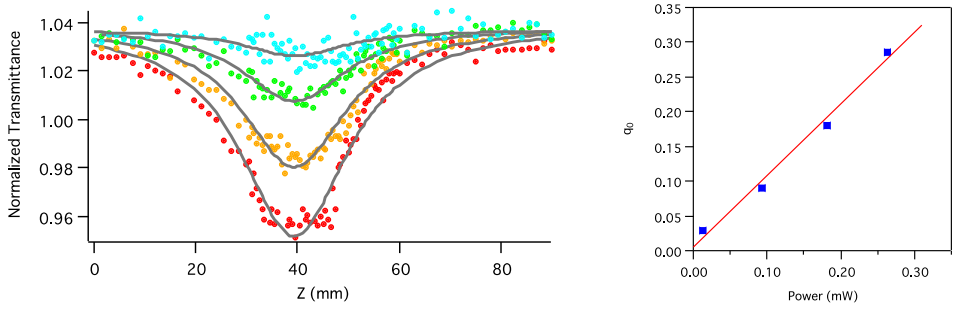


Fig. S2.1. Open-aperture Z-scan traces of **4** in CH_2Cl_2 with various incident powers (circles) with the best fit of the theoretical curves (left) and the corresponding plot of two-photon absorbance q_0 versus the incident power (right). At 762 nm with concentration of 0.53 mM (top row) and at 860 nm with 2.0 mM (bottom row).



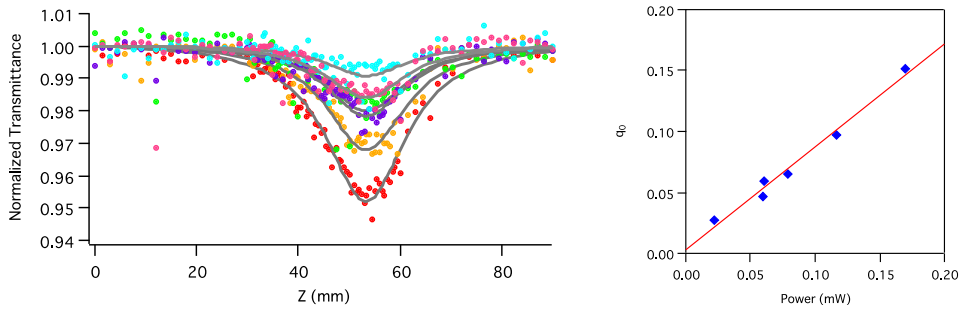


Fig. S2.2. Open-aperture Z-scan traces of **5** in CH_2Cl_2 with various incident powers (circles) with the best fit of the theoretical curves (left) and the corresponding plot of two-photon absorbance q_0 versus the incident power (right). At 762 nm with concentration of 1.9 mM (top row) and at 860 nm with 2.1 mM (bottom row).

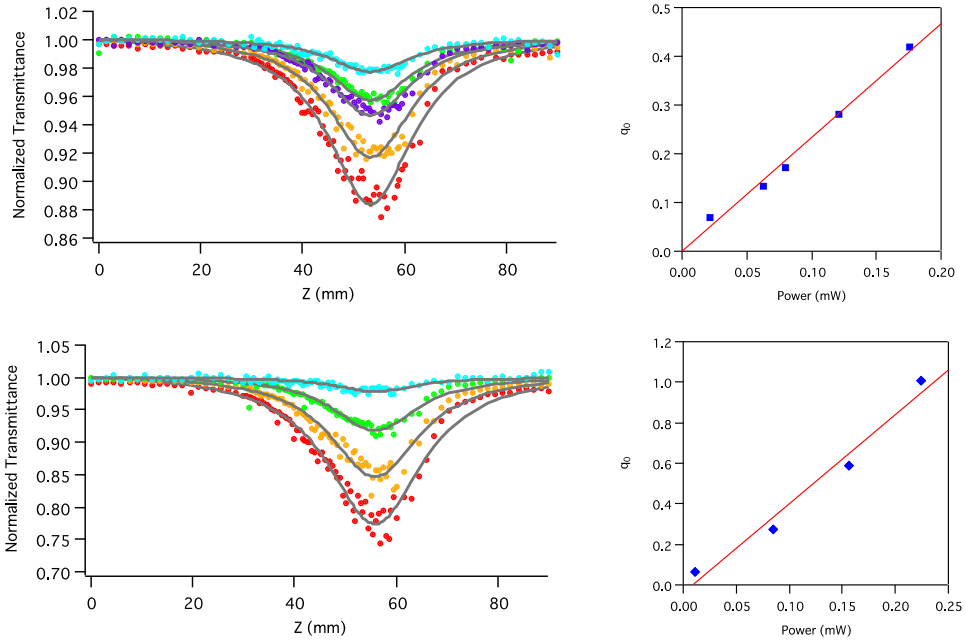


Fig. S2.3. Open-aperture Z-scan traces of **9** in CH_2Cl_2 with various incident powers (circles) with the best fit of the theoretical curves (left) and the corresponding plot of q_0 versus the incident power (right). At 860 nm with concentration of 0.5 mM (top row) and at 944 nm with 2.0 mM (bottom row).

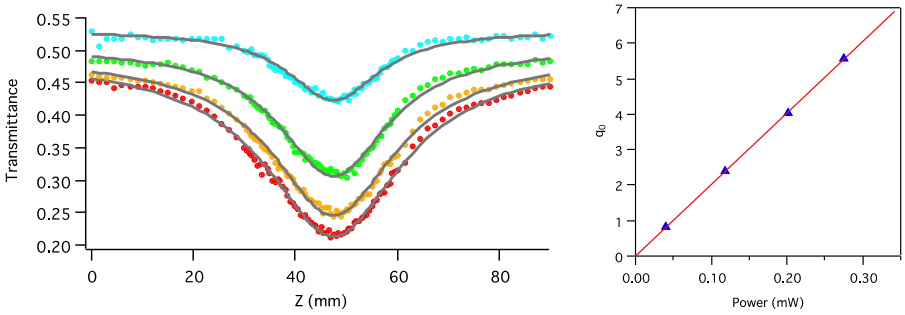


Fig. S2.4. Open-aperture Z-scan traces of **9** in CH_2Cl_2 with various incident powers (circles) with the best fit of the theoretical curves (left) and the corresponding plot of q_0 versus the incident power (right). The data were measured at 721 nm with concentration of 2.0 mM. In the open-aperture Z-scan traces, vertical axis is shown in transmittance (not normalized) to show the magnitude of linear absorption. The drift of the baseline due to the linear absorption was included in the curve fitting analysis.

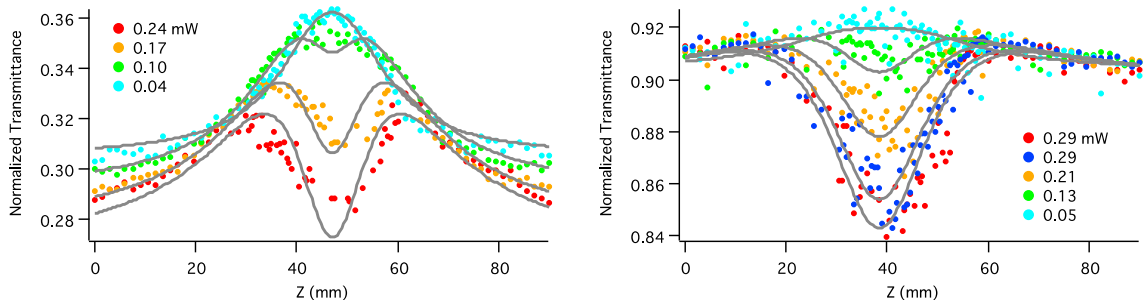


Fig. S2.5. Open-aperture Z-scan traces of **4** in CH_2Cl_2 (2.0 m) with various incident powers (circles) at 699 nm (left) and at 739 nm (right). The gray lines are the best fit by the theoretical curves considering both TPA and SA.

S2.2. TPA spectrum of compounds

TPA spectrum of the solution of compound **4**, **5**, and **9** in CH_2Cl_2, obtained from the data repeatedly measured by changing the incident wavelength as mentioned in section S2.1, was show in Fig. S2.6 for whole the spectral range measured.

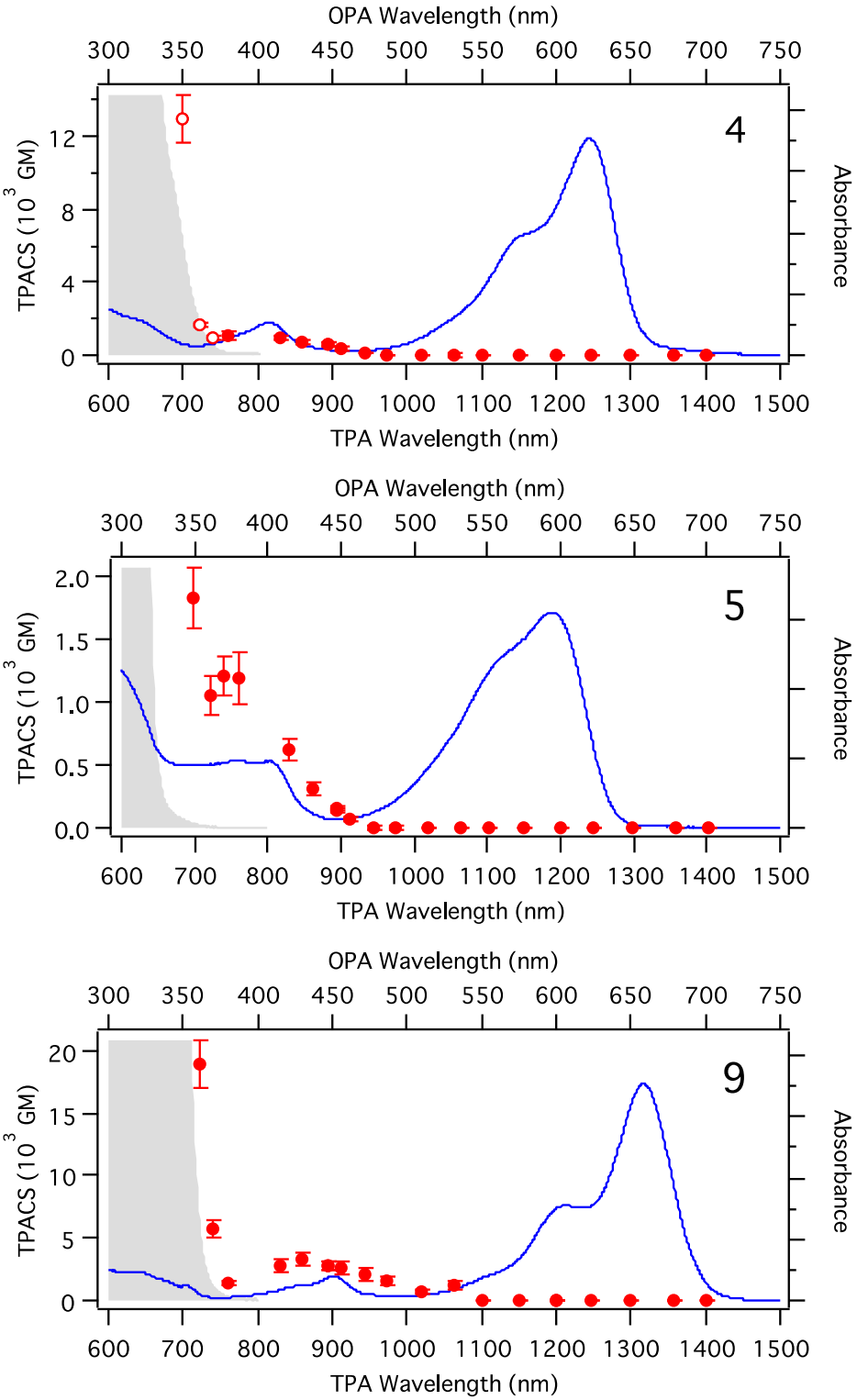


Fig. S2.6. TPA spectrum of compounds **4**, **5**, and **9** in CH_2Cl_2 (filled circle) with OPA spectrum of the same sample (gray area, against the bottom wavelength scale; the full scale of vertical axis is 1.0 in absorbance). Compound **4** showed saturable absorption (SA) at the three shortest wavelengths. These data were analyzed by taking also SA into account (see section S2.1) and is plotted with open circles. The OPA spectra of diluted solutions are also shown by solid curve against the top wavelength scale, which is the half of the bottom scale so that the transition energies matches between the TPA and OPA spectra.

S2.3. Stirring the sample solution during the Z-scan measurement

Normally, open-aperture Z-scan signal is symmetric against the focal point irrespective of the scanning directions. However, deformed traces (with asymmetric and wider dip, or square or double-well shapes for significant cases) were observed for **4** and **9**. The deformation can originates from saturation of TPA and/or generation of photo-induced product. When the direction of scan was changed, it was found that the asymmetric shape was reversed according to the scanning directions (Fig. S2.7 left). This suggests that TPA excitation generate new species that absorb the incident light more because the dip always has tails after crossing the focal point. To remove the accumulated product from the volume monitored, the sample solution was stirred during the measurements by putting a micro stirring bar into the cuvette (*ISIS Co. Ltd., remote and micro magnetic stirrer HP40107*). Stirring significantly reduced the asymmetric deformation (Fig. S2.7 right). Thus, the sample solution was stirred during the measurement for all compounds presented in the TPA spectra.

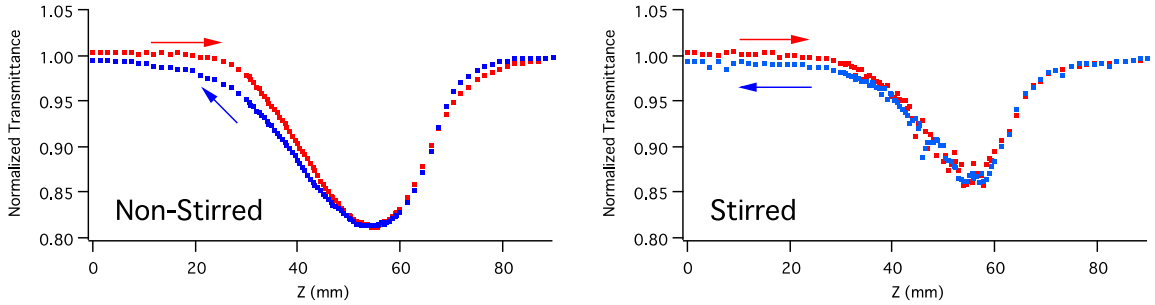


Fig. S2.7. Example of the Z-scan traces by changing the scanning directions (shown by arrows) at 890 nm with incident power of 0.34 mW. Sample solution (**9** in CH_2Cl_2, 2.0 mM) was not stirred (left) and stirred (right) during the measurement.

S2.4. Spectral change before and after Z-scan measurements

OPA (UV-vis) spectrum of the samples was measured both before and after the laser experiments for every time. No spectral change was observed (less than 0.004 in absorbance for 2-mm cubette) for all samples in DCM. However, the solution of **9** showed spectral change after the Z-scan measurements at 720–760 nm, where the laser light strongly absorbed by OPA. The difference spectra between before and after the measurements are shown in Fig. S2.8.

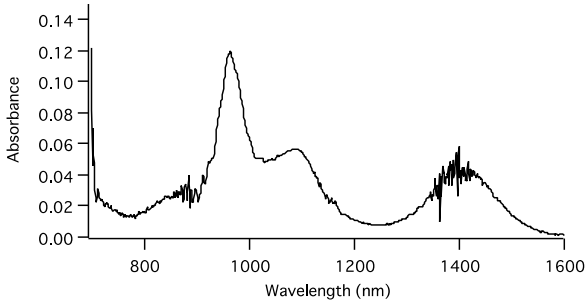
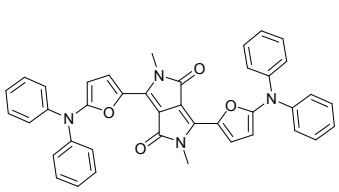


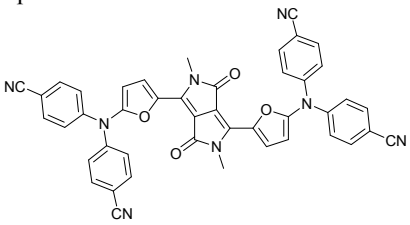
Fig. S2.8. Difference UV-vis-NIR spectrum of the solution of **9** before and after the Z-scan measurements at the wavelengths of 720–760 nm, where the laser light absorpbed strongly by OPA.

S3 Quantum chemical calculation of model molecules

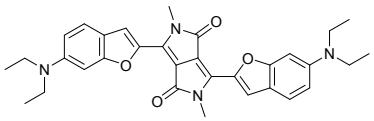
Quantum chemical calculations were performed for the model molecules as follows:



4-m



5-m



9-m

The geometry optimization and TD-DFT calculation were performed at the level of CAM-B3LYP//6-31+G(d) for all molecules in gas phase by using Gaussian 09 package.[3] The first four excited states of **5-m** is summarized in Table S3.1 and the map of the related molecular orbital is shown in Fig. S3.1.

==== Optimized coodinate for **4-m** ====

C	-0.6962230000	3.4980840000	-0.7865390000
N	-0.4489750000	2.0736300000	-0.7748370000
C	-1.3885060000	1.0493810000	-0.7015410000
C	-2.7957100000	1.3044820000	-0.7561280000
C	-3.5738940000	2.2684730000	-1.3408640000
C	-4.9263870000	1.9163350000	-1.1241080000
C	-4.8945980000	0.7537520000	-0.3846160000
N	-5.9105950000	0.0182410000	0.1698010000
C	-7.2237910000	0.5885210000	0.1002000000
C	-7.5300570000	1.7366610000	0.8274550000
C	-8.8081770000	2.2813700000	0.7554190000
C	-9.7840640000	1.6751140000	-0.0320030000
C	-9.4761510000	0.5234200000	-0.7519140000
C	-8.1960730000	-0.0176800000	-0.6918490000
C	-5.7556470000	-1.2829400000	0.7378680000
C	-6.5950690000	-1.6539840000	1.7930260000
C	-6.4925970000	-2.9205920000	2.3549900000
C	-5.5438060000	-3.8250670000	1.8858520000
C	-4.7033540000	-3.4462270000	0.8440360000
C	-4.8091120000	-2.1887250000	0.2595670000
O	-3.6256500000	0.3716100000	-0.1629930000
C	-0.7018880000	-0.1397260000	-0.5885650000
C	0.7018910000	0.1397150000	-0.5885680000
C	1.3885090000	-1.0493920000	-0.7015270000
C	2.7957140000	-1.3044920000	-0.7561130000
C	3.5738990000	-2.2684810000	-1.3408510000
C	4.9263910000	-1.9163400000	-1.1240990000
C	4.8946000000	-0.7537560000	-0.3846070000
N	5.9105960000	-0.0182410000	0.1698070000
C	7.2237940000	-0.5885160000	0.1002070000
C	7.5300650000	-1.7366520000	0.8274660000
C	8.8081860000	-2.2813570000	0.7554300000
C	9.7840690000	-1.6751020000	-0.0319970000
C	9.4761520000	-0.5234130000	-0.7519120000
C	8.1960720000	0.0176840000	-0.6918470000
C	5.7556420000	1.2829440000	0.7378640000
C	6.5950700000	1.6540040000	1.7930120000
C	6.4925910000	2.9206160000	2.3549660000
C	5.5437870000	3.8250780000	1.8858290000
C	4.7033300000	3.4462220000	0.8440240000
C	4.8090950000	2.1887160000	0.2595640000
O	3.6256530000	-0.3716180000	-0.1629800000
N	0.4489800000	-2.0736400000	-0.7748420000
C	0.6962300000	-3.4980930000	-0.7865760000
C	-0.8804360000	-1.5683210000	-0.7275580000
O	-1.8622010000	-2.2940200000	-0.8077380000
C	0.8804400000	1.5683080000	-0.7275830000
O	1.8622060000	2.2940100000	-0.8077240000
H	-1.4686130000	3.7603170000	-0.0594120000
H	-0.9969480000	3.8506810000	-1.7788660000

H	0.2423950000	3.9866090000	-0.5217340000
H	-3.2187320000	3.1199350000	-1.9018810000
H	-5.8064180000	2.4444220000	-1.4550500000
H	-6.7643470000	2.1956320000	1.4452800000
H	-9.0441930000	3.1757590000	1.3243070000
H	-10.7827650000	2.0982190000	-0.0827090000
H	-10.2326260000	0.0468580000	-1.3681220000
H	-7.9433720000	-0.9144550000	-1.2489700000
H	-7.3295420000	-0.9519420000	2.1727640000
H	-7.1536100000	-3.1941340000	3.1723340000
H	-5.4583980000	-4.8114510000	2.3317430000
H	-3.9460510000	-4.1268560000	0.4675940000
H	-4.1217860000	-1.9240140000	-0.5324350000
H	3.2187370000	-3.1199440000	-1.9018680000
H	5.8064240000	-2.4444240000	-1.4550430000
H	6.7643560000	-2.1956220000	1.4452940000
H	9.0442050000	-3.1757430000	1.3243220000
H	10.7827710000	-2.0982050000	-0.0827030000
H	10.2326240000	-0.0468510000	-1.3681240000
H	7.9433680000	0.9144560000	-1.2489720000
H	7.3295520000	0.9519720000	2.1727500000
H	7.1536080000	3.1941710000	3.1723030000
H	5.4583740000	4.8114650000	2.3317130000
H	3.9460170000	4.1268410000	0.4675830000
H	4.1217640000	1.9239910000	-0.5324290000
H	1.4686340000	-3.7603360000	-0.0594670000
H	0.9969370000	-3.8506740000	-1.7789140000
H	-0.2423830000	-3.9866240000	-0.5217610000

==== End of Optimized coodinate for **4-m** ====

==== Optimized coodinate for **5-m** ====

C	-0.5055390000	3.5589940000	-1.5582100000
N	-0.3455730000	2.1619590000	-1.2209740000
C	-1.3403080000	1.2401050000	-0.9141220000
C	-2.7406600000	1.5460440000	-0.9504840000
C	-3.5197970000	2.5588750000	-1.4505870000
C	-4.8728250000	2.1944350000	-1.2226050000
C	-4.8312080000	0.9896890000	-0.5747770000
N	-5.8117290000	0.1548080000	-0.0702930000
C	-6.9926780000	0.7133850000	0.4757070000
C	-6.9283450000	1.8459060000	1.2941470000
C	-8.0858020000	2.3934120000	1.8219500000
C	-9.3283180000	1.8107740000	1.5501190000
C	-9.3927360000	0.6742480000	0.7383250000
C	-8.2353480000	0.1340350000	0.2009060000
C	-5.6629440000	-1.2546340000	-0.2076390000
C	-6.0028030000	-2.0940030000	0.8549560000
C	-5.8474680000	-3.4644800000	0.7336300000
C	-5.3364110000	-4.0093340000	-0.4490910000
C	-4.9907560000	-3.1666260000	-1.5079020000
C	-5.1599940000	-1.7970410000	-1.3892210000
O	-3.5559690000	0.5951050000	-0.3949200000
C	-0.7297310000	0.0494990000	-0.5960530000
C	0.6845980000	0.2197290000	-0.7042230000
C	1.2891550000	-1.0061140000	-0.5298850000
C	2.6797160000	-1.3577410000	-0.5454330000
C	3.3789740000	-2.4824080000	-0.8897930000
C	4.7578300000	-2.1705180000	-0.7937710000
C	4.8143890000	-0.8678100000	-0.3628510000
N	5.8915710000	-0.0827480000	-0.0072230000
C	7.1401640000	-0.7603240000	0.1622280000
C	7.3002140000	-1.6713410000	1.2002130000
C	8.5214620000	-2.3311590000	1.3549630000
C	9.5838290000	-2.0699100000	0.4836840000
C	9.4133860000	-1.1516880000	-0.5446680000
C	8.1945060000	-0.5027150000	-0.7123560000
C	5.8539270000	1.3329710000	0.0951110000
C	6.7611350000	1.9708440000	0.9510290000

C	6.7635420000	3.3504740000	1.0672490000
C	5.8469330000	4.1179710000	0.3415120000
C	4.9343410000	3.4780530000	-0.5010150000
C	4.9428070000	2.0989210000	-0.6346000000
O	3.5772630000	-0.3634650000	-0.2132210000
N	0.2926400000	-1.9491050000	-0.3188970000
C	0.4534430000	-3.3474400000	0.0192730000
C	-1.0042370000	-1.3536310000	-0.3451060000
O	-2.0273670000	-1.9943230000	-0.1785650000
C	0.9479050000	1.5773160000	-1.1307840000
O	1.9708470000	2.1928900000	-1.3971570000
H	-1.1084360000	4.0769430000	-0.8072910000
H	-0.9588270000	3.6853960000	-2.5466430000
H	0.4946250000	3.9932240000	-1.5792810000
H	-3.1784480000	3.4474540000	-1.9578580000
H	-5.7595980000	2.7429980000	-1.5032720000
H	-5.9663740000	2.2922070000	1.5208560000
H	-8.0300760000	3.2683730000	2.4608740000
H	-10.3545780000	0.2229500000	0.5191900000
H	-8.2921960000	-0.7407360000	-0.4373280000
H	-6.3772170000	-1.6688120000	1.7799630000
H	-6.1042570000	-4.1172520000	1.5610240000
C	-5.1584890000	-5.4283170000	-0.5710370000
H	-4.5881990000	-3.5876250000	-2.4225740000
H	-4.8870760000	-1.1444640000	-2.2114900000
H	2.9585630000	-3.4215680000	-1.2164410000
H	5.5938710000	-2.8186810000	-1.0051010000
H	6.4805560000	-1.8671730000	1.8830410000
C	8.6860790000	-3.2771370000	2.4247570000
H	10.5288720000	-2.5848810000	0.6175890000
H	10.2321950000	-0.9458140000	-1.2262560000
H	8.0540590000	0.2116220000	-1.5174080000
H	7.4641060000	1.3864310000	1.5335150000
H	7.4683380000	3.8365510000	1.7334650000
C	5.8401800000	5.5471740000	0.4686600000
H	4.2044090000	4.0545250000	-1.0583980000
H	4.2015860000	1.6424930000	-1.2750020000
H	1.2330050000	-3.4748780000	0.7741430000
H	0.6949200000	-3.9521340000	-0.8607690000
H	-0.5028390000	-3.6901670000	0.4164670000
C	-10.5270050000	2.3754010000	2.1007890000
N	-11.4936060000	2.8319910000	2.5443690000
N	-5.0163300000	-6.5727080000	-0.6707840000
N	5.8369360000	6.7002890000	0.5712670000
N	8.8189680000	-4.0404770000	3.2836670000

==== End of Optimized coodinate for **5-m** ====

==== Optimized coodinate for **9-m** ====

C	-0.8338690000	3.4778810000	0.0297130000
N	-0.5361690000	2.0646510000	0.0166530000
C	-1.4278170000	1.0003980000	-0.0020260000
C	-2.8549360000	1.1570120000	-0.0123900000
C	-3.7153260000	2.2215840000	-0.0118240000
C	-5.0366430000	1.6747400000	-0.0265890000
C	-6.3471730000	2.1723370000	-0.0274460000
C	-7.4046350000	1.2863550000	-0.0410370000
C	-7.2125930000	-0.1281910000	-0.0604060000
N	-8.3008400000	-0.9797990000	-0.0996750000
C	-8.0818090000	-2.4038340000	0.0484540000
C	-9.6337080000	-0.4600060000	0.1295700000
C	-5.9034780000	-0.6342130000	-0.0456930000
C	-4.8697000000	0.2856260000	-0.0351880000
O	-3.5532740000	-0.0276760000	-0.0260190000
C	-0.6946100000	-0.1662190000	-0.0076910000
C	0.6946100000	0.1662210000	0.0076120000
C	1.4278160000	-1.0003960000	0.0019730000
C	2.8549360000	-1.1570110000	0.0123630000

C	3.7153250000	-2.2215840000	0.0118200000
C	5.0366420000	-1.6747400000	0.0266010000
C	6.3471710000	-2.1723370000	0.0274850000
C	7.4046340000	-1.2863560000	0.0410860000
C	7.2125920000	0.1281900000	0.0604390000
N	8.3008380000	0.9797970000	0.0997150000
C	8.0818120000	2.4038340000	-0.0484050000
C	9.6337150000	0.4599990000	-0.1294610000
C	5.9034780000	0.6342140000	0.0457010000
C	4.8696990000	-0.2856260000	0.0351860000
O	3.5532730000	0.0276770000	0.0259930000
N	0.5361690000	-2.0646490000	-0.0167030000
C	0.8338680000	-3.4778800000	-0.0297290000
C	-0.8191120000	-1.6143930000	-0.0238910000
O	-1.7632550000	-2.3845230000	-0.0402560000
C	0.8191120000	1.6143950000	0.0237940000
O	1.7632550000	2.3845250000	0.0401970000
H	-1.3837760000	3.7783820000	-0.8674280000
H	0.1269560000	3.9942620000	0.0459270000
H	-1.4030950000	3.7575550000	0.9214920000
H	-3.4531870000	3.2671940000	-0.0024960000
H	-6.5394000000	3.2411630000	-0.0144710000
H	-8.4095700000	1.6873750000	-0.0394270000
H	-7.4268590000	-2.7830710000	-0.7430690000
H	-9.0366920000	-2.9236590000	-0.0365160000
H	-7.6307460000	-2.6616510000	1.0188280000
H	-9.9141370000	0.2696740000	-0.6376480000
H	-9.7369950000	0.0185560000	1.1150550000
H	-10.3483480000	-1.2817550000	0.0738350000
H	-5.6772520000	-1.6912970000	-0.0429140000
H	3.4531850000	-3.2671930000	0.0024960000
H	6.5393980000	-3.2411640000	0.0145230000
H	8.4095690000	-1.6873760000	0.0394960000
H	7.6307440000	2.6616560000	-1.0187750000
H	9.0366980000	2.9236540000	0.0365610000
H	7.4268680000	2.7830700000	0.7431240000
H	9.9141170000	-0.2696530000	0.6377940000
H	10.3483520000	1.2817500000	-0.0737320000
H	9.7370390000	-0.0186000000	-1.1149240000
H	5.6772530000	1.6912970000	0.0429110000
H	1.3837540000	-3.7783640000	0.8674320000
H	1.4031150000	-3.7575700000	-0.9214890000
H	-0.1269560000	-3.9942610000	-0.0459560000

==== End of Optimized coodinate for **9-m** ====

Table S3.1. Symmetry (approximate), orbital contribution, transition energy, and oscillator strength of the model molecules of **5-m**.

State	Symmetry nature, Major orbital component	Transition energy (wavelength), Oscillator strength
S_1	*Au*-like, HOMO(*g*)→LUMO(*u*)	2.4860 eV (498.72 nm) f=0.7005
S_2	*Ag*-like , HOMO-1 (*u*)→(HOMO(*g*))→LUMO(*u*)	3.5695 eV (347.34 nm) f=0.0225
S_3	*Ag*-like, HOMO-3 (*u*)→(HOMO(*g*))→LUMO(*u*)	3.7016 eV (334.95 nm) f=0.0260
S_4	*Au*-like , HOMO-2(*g*)→LUMO(*u*)	3.8092 eV (325.48 nm) f=0.6585

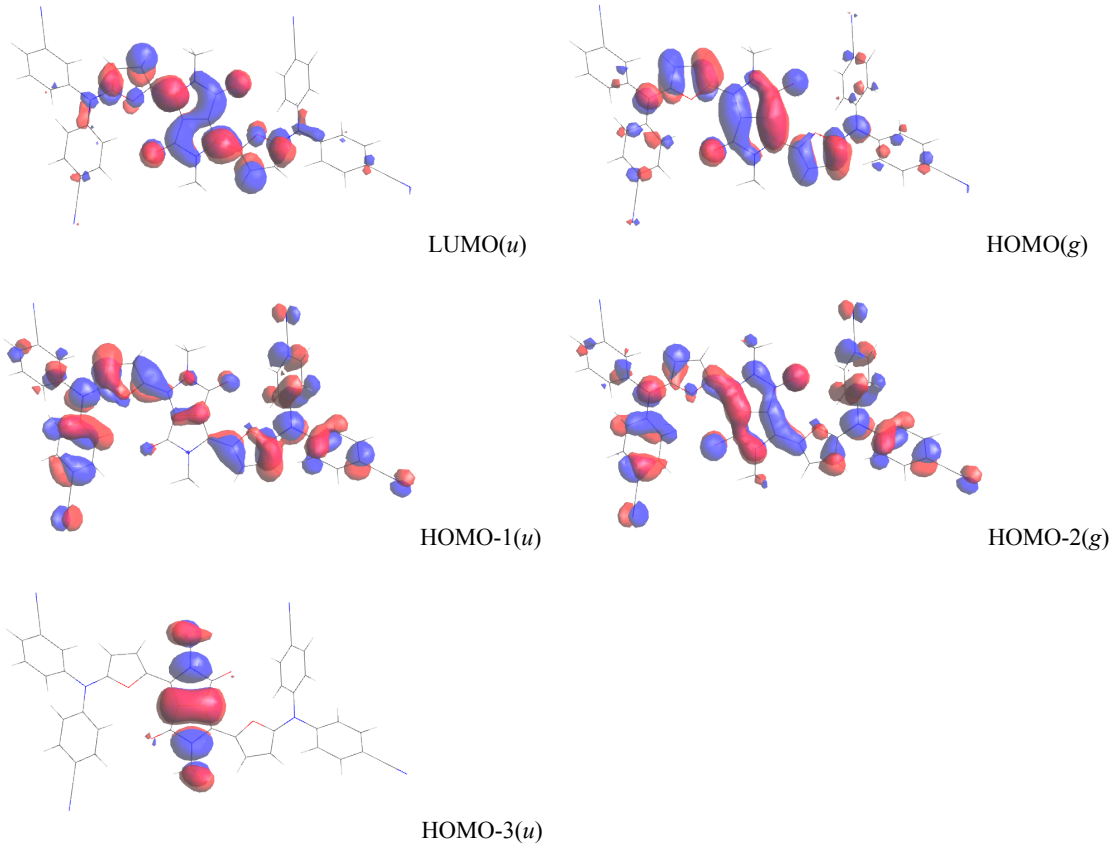


Fig. S3.1. Map of the molecular orbitals related to the lowest four excited states (Table S3.1) of **5-m**. The symmetry assignments (*g* and *u*) are approximate ones determined form the orbital patterns.

S4. Optical properties in THF and DCM

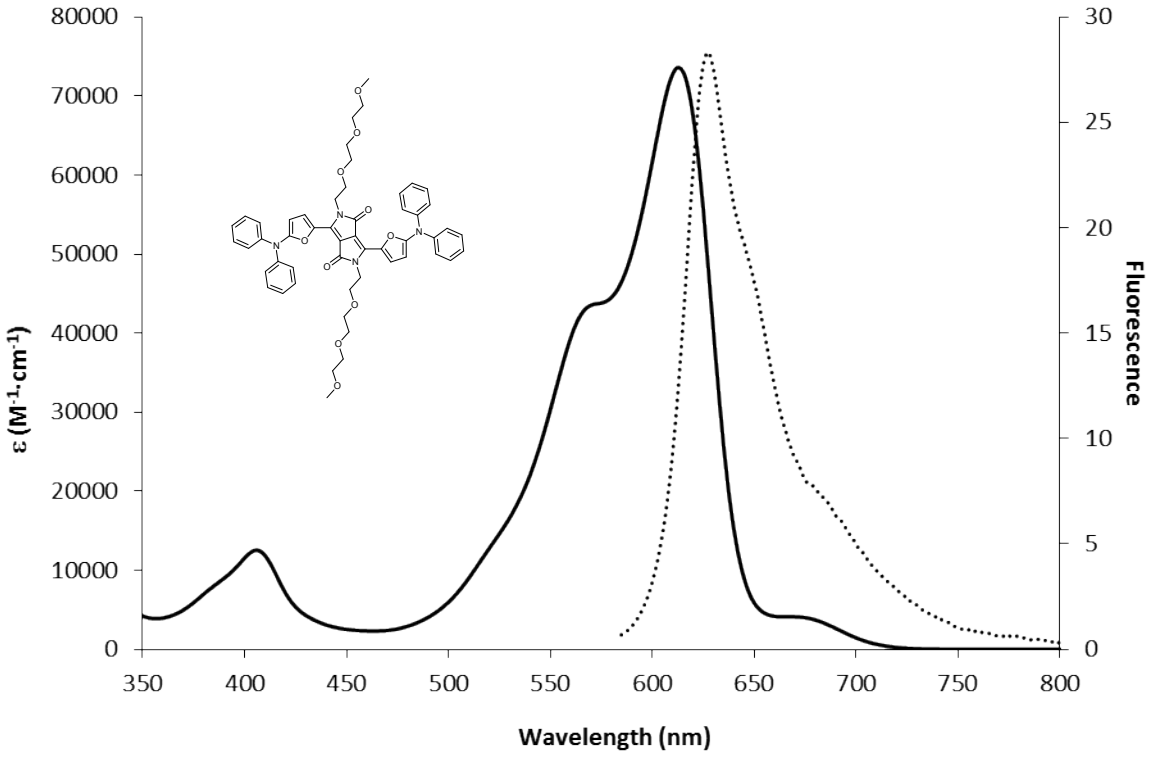


Fig. S4.1 Absorption (solid lines) and fluorescence (dotted lines) **4** in THF.

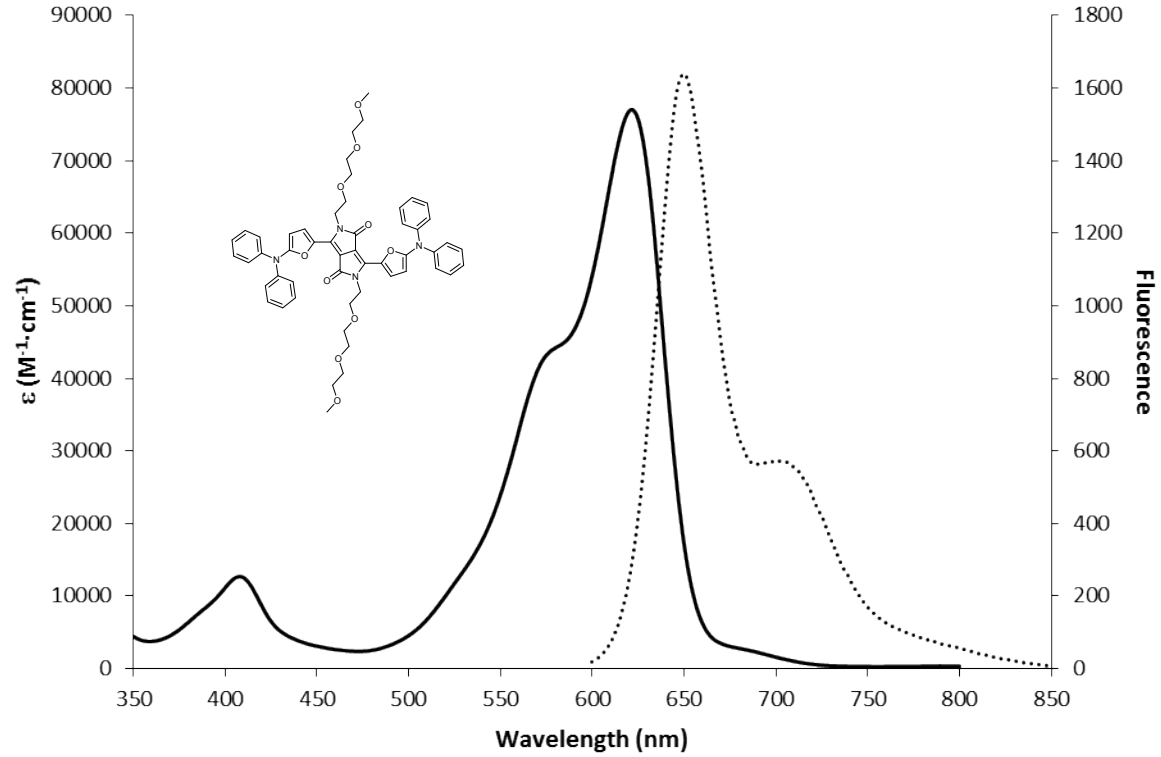


Fig. S4.2 Absorption (solid lines) and fluorescence (dotted lines) **4** in DCM.

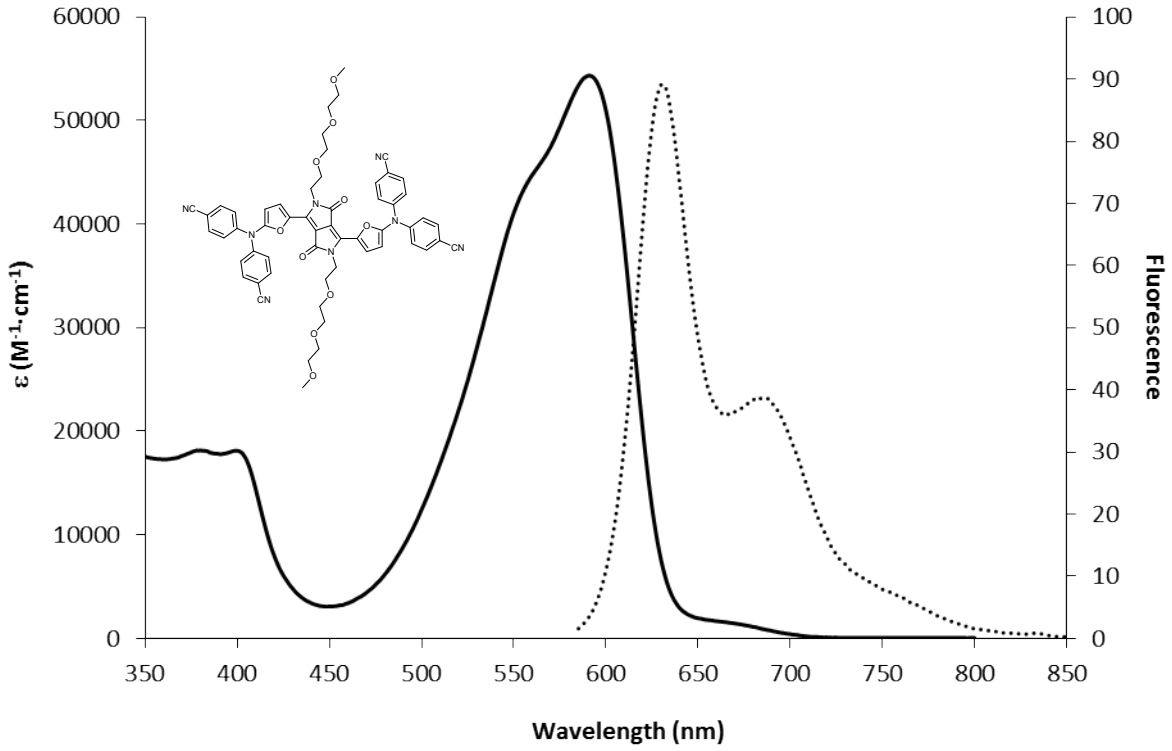


Fig. S4.3 Absorption (solid lines) and fluorescence (dotted lines) **5** in THF.

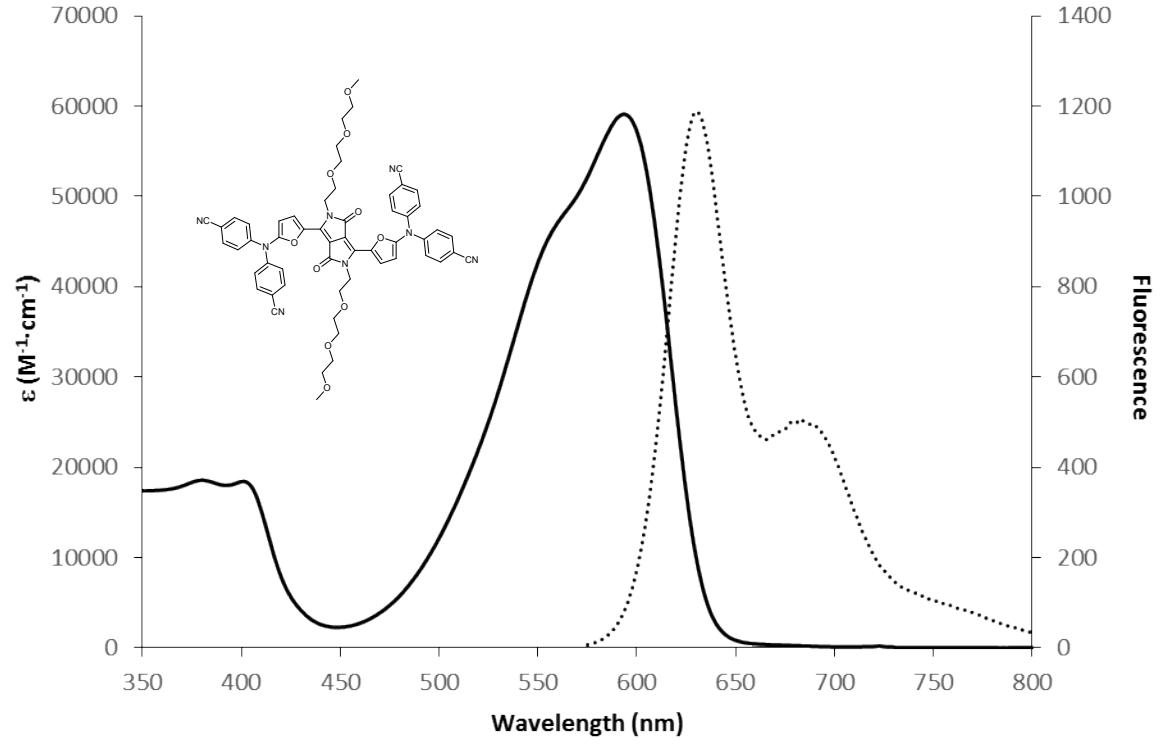


Fig. S4.4 Absorption (solid lines) and fluorescence (dotted lines) **5** in DCM.

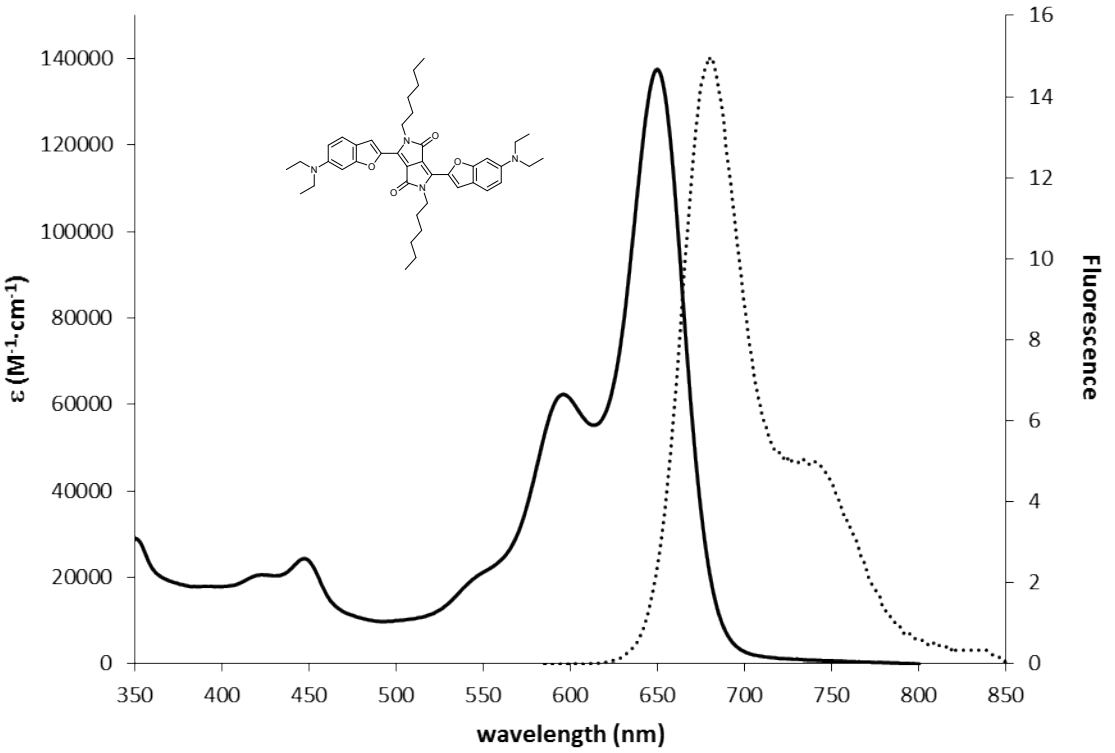


Fig. S4.5 Absorption (solid lines) and fluorescence (dotted lines) **9** in THF.

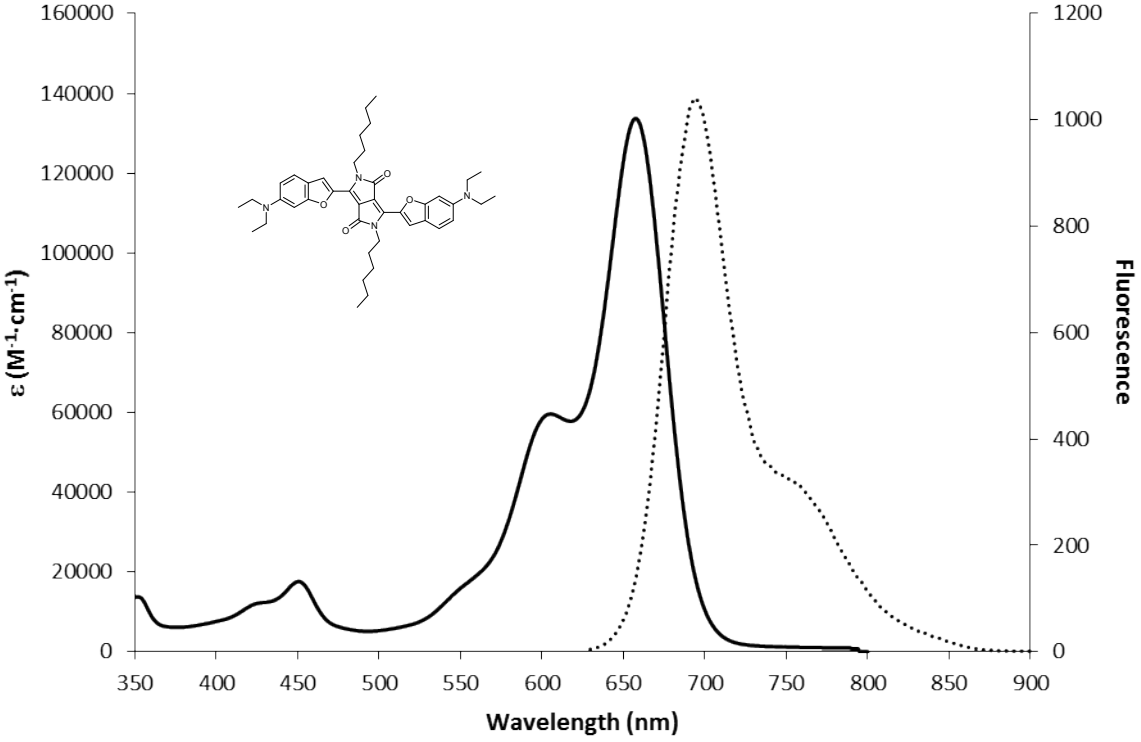
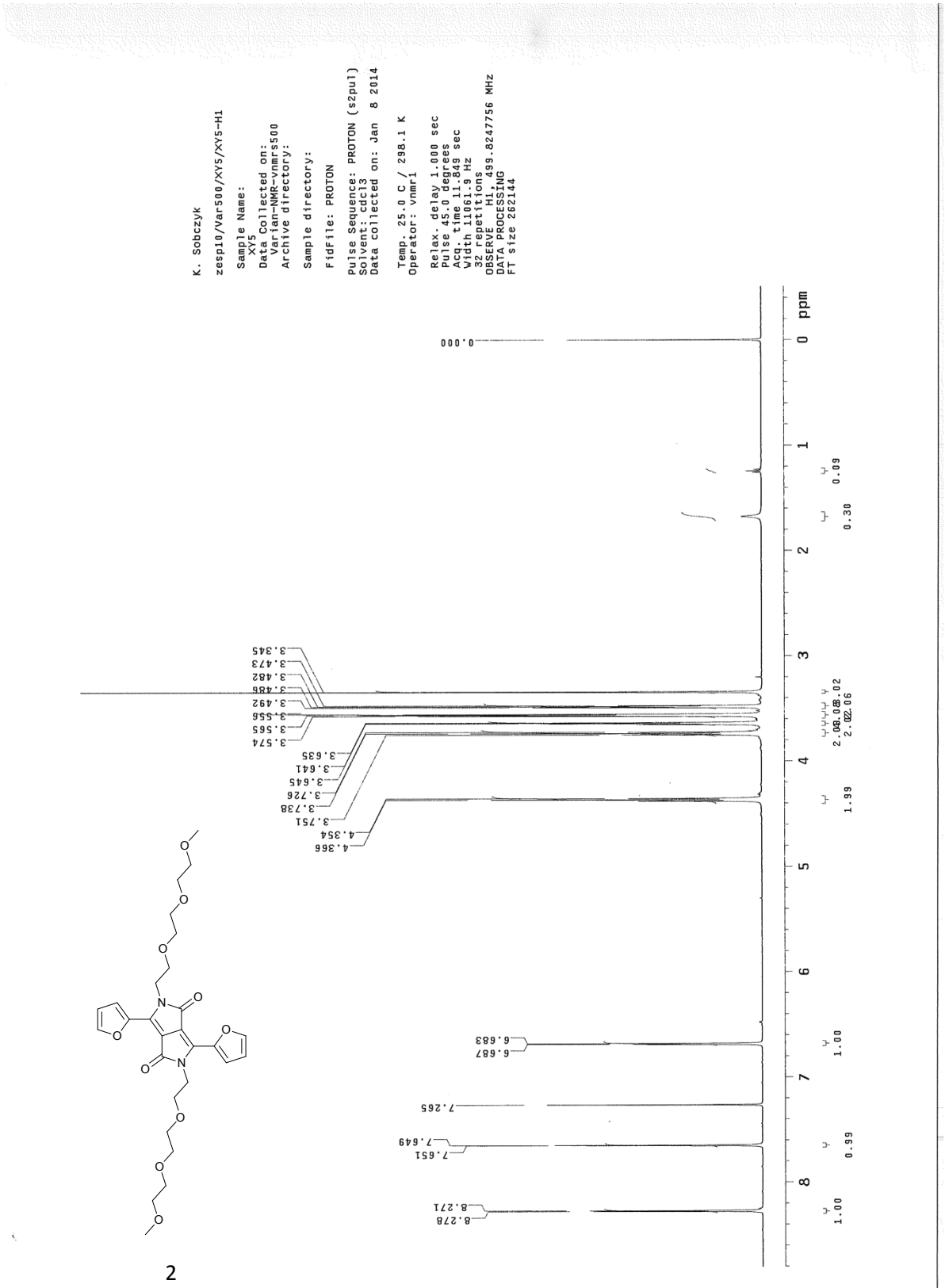
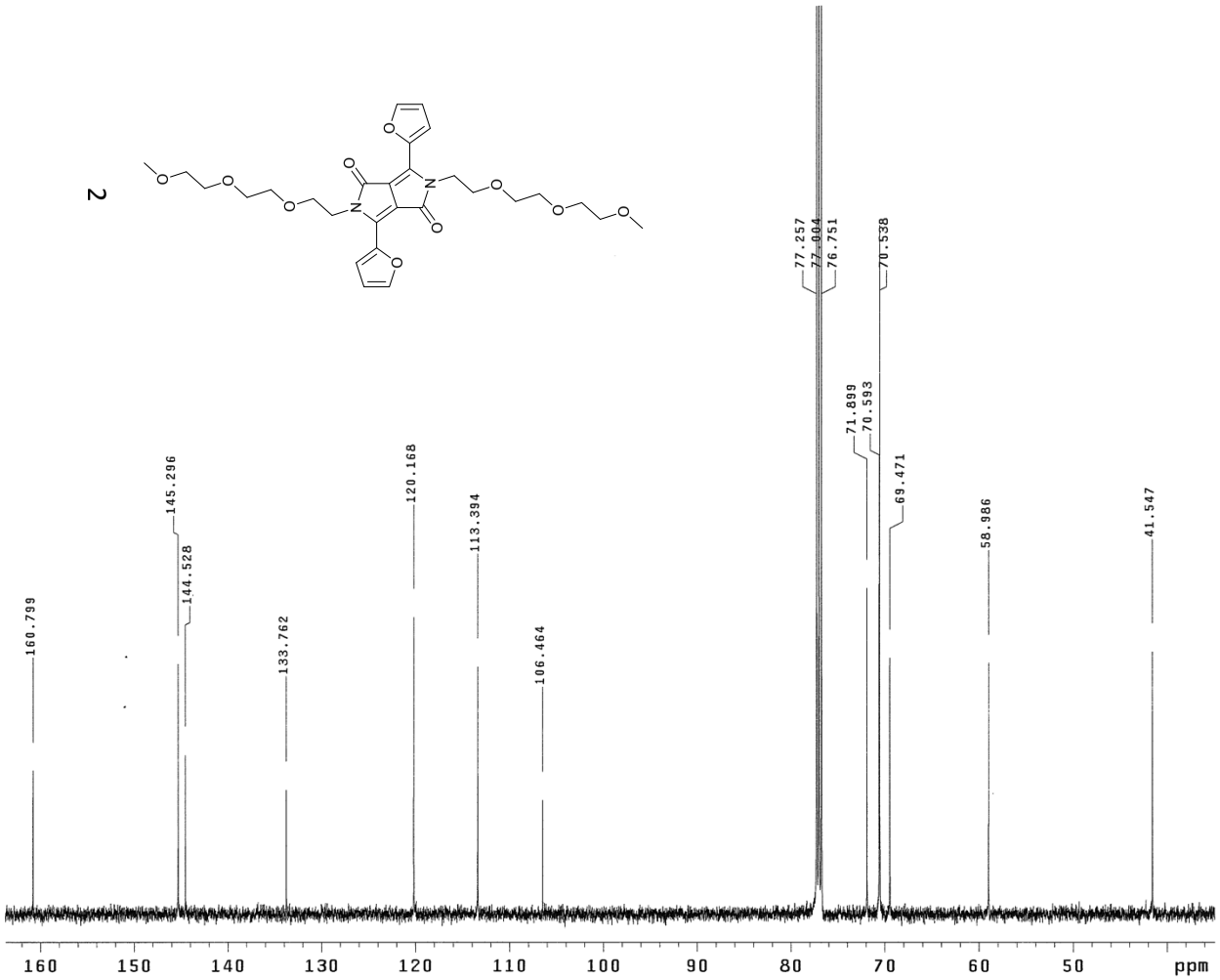


Fig. S4.6 Absorption (solid lines) and fluorescence (dotted lines) **9** in DCM.

S5. Spectra 1H and 13C NMR for dyes synthesized



2



K. Sobczyk
zesp10/Var500/XY5/XY5-C13

Sample Name:
XY5
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

Sample directory:

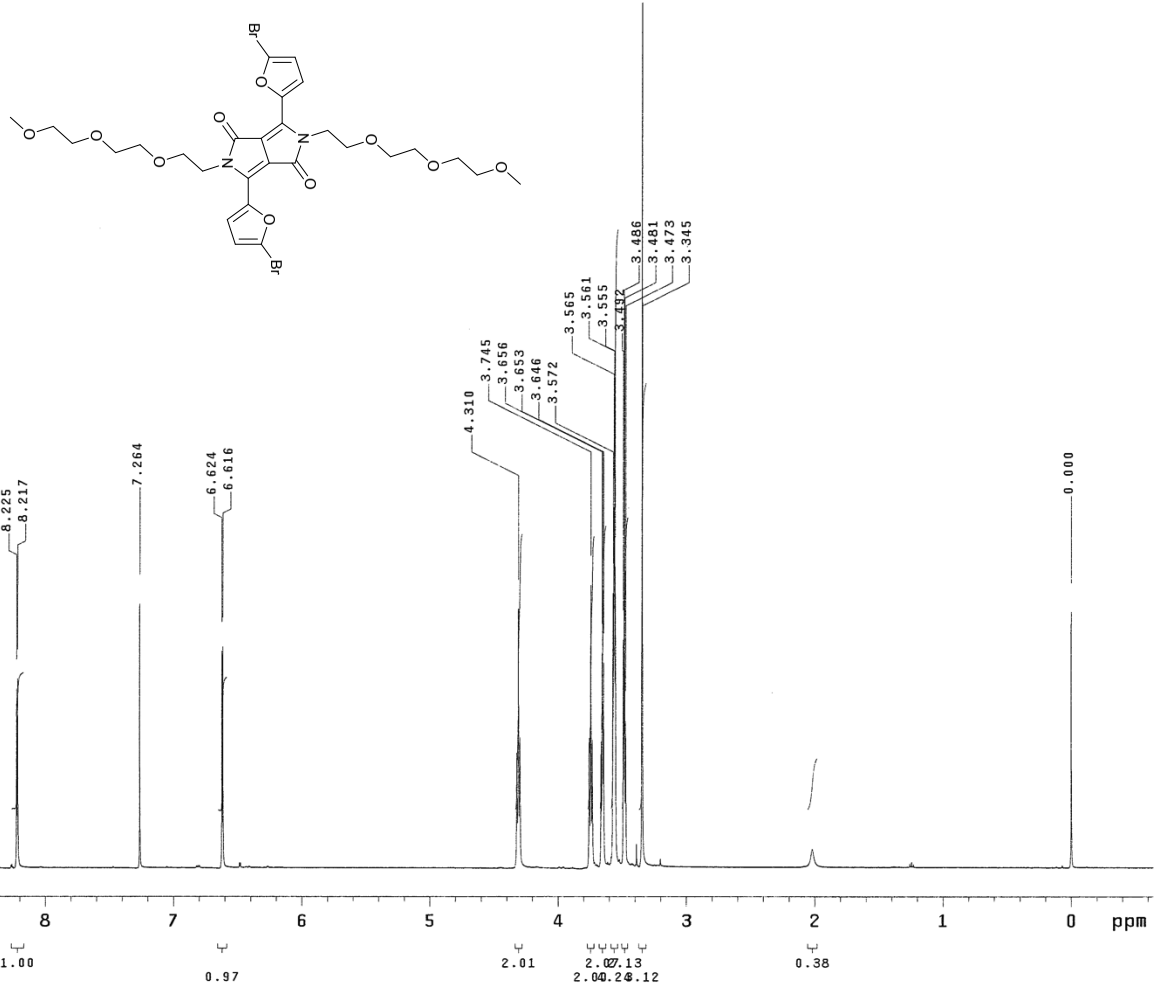
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 8 2014

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 0.500 sec
Pulse 30.0 degrees
Acq. time 1.200 sec
Width 37878.8 Hz
992 repetitions
OBSERVE C13, 125.6810405 MHz
DECOUPLE H1, 499.8272777 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072

3



K. Sobczyk

Sample Name:
XY7
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

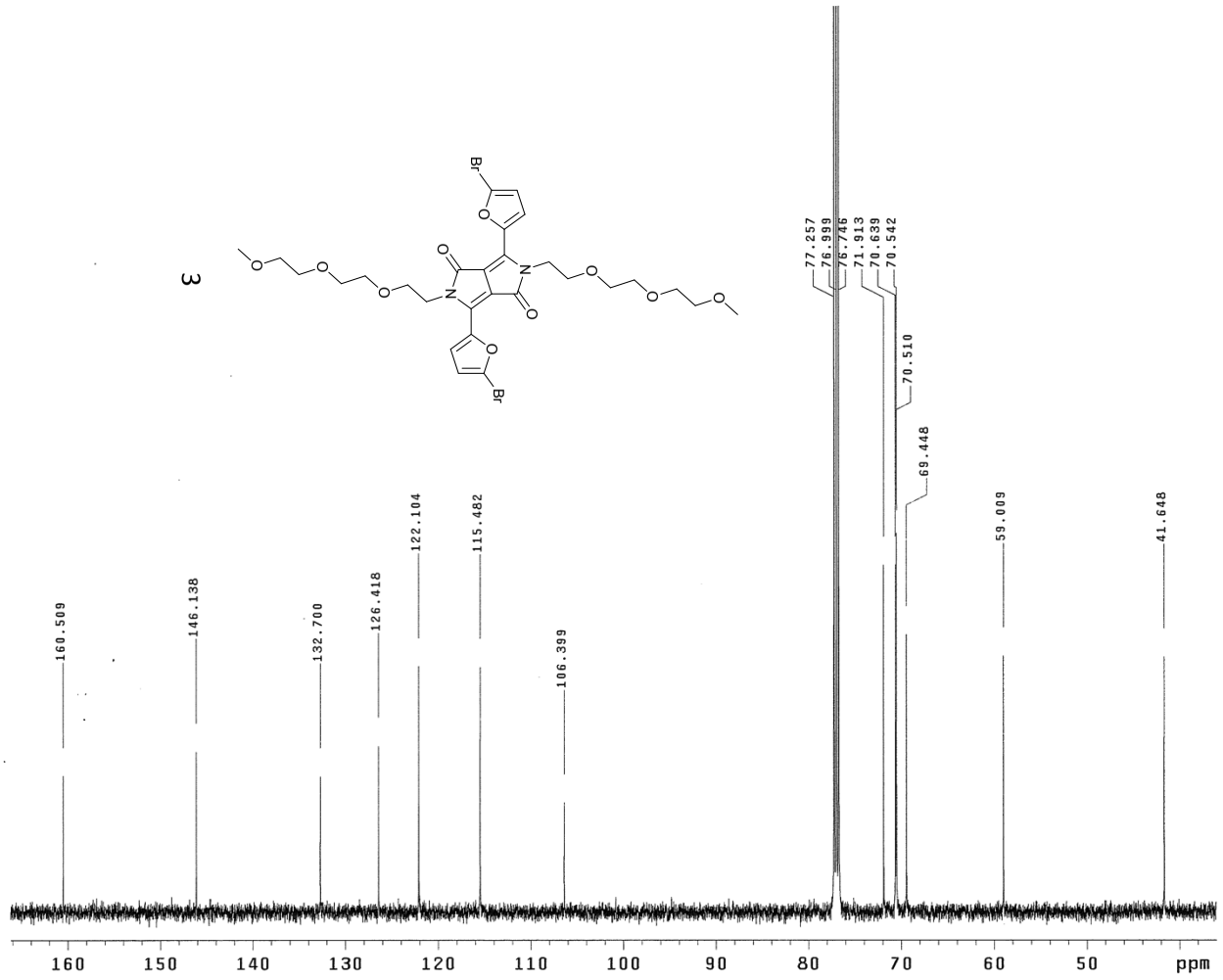
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 8 2014

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 11061.9 Hz
32 repetitions
OBSERVE H1, 499.8247764 MHz
DATA PROCESSING
FT size 131072



K. Sobczyk

zesp10/Var500/XY7/XY7-C13

Sample Name:
XY7
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

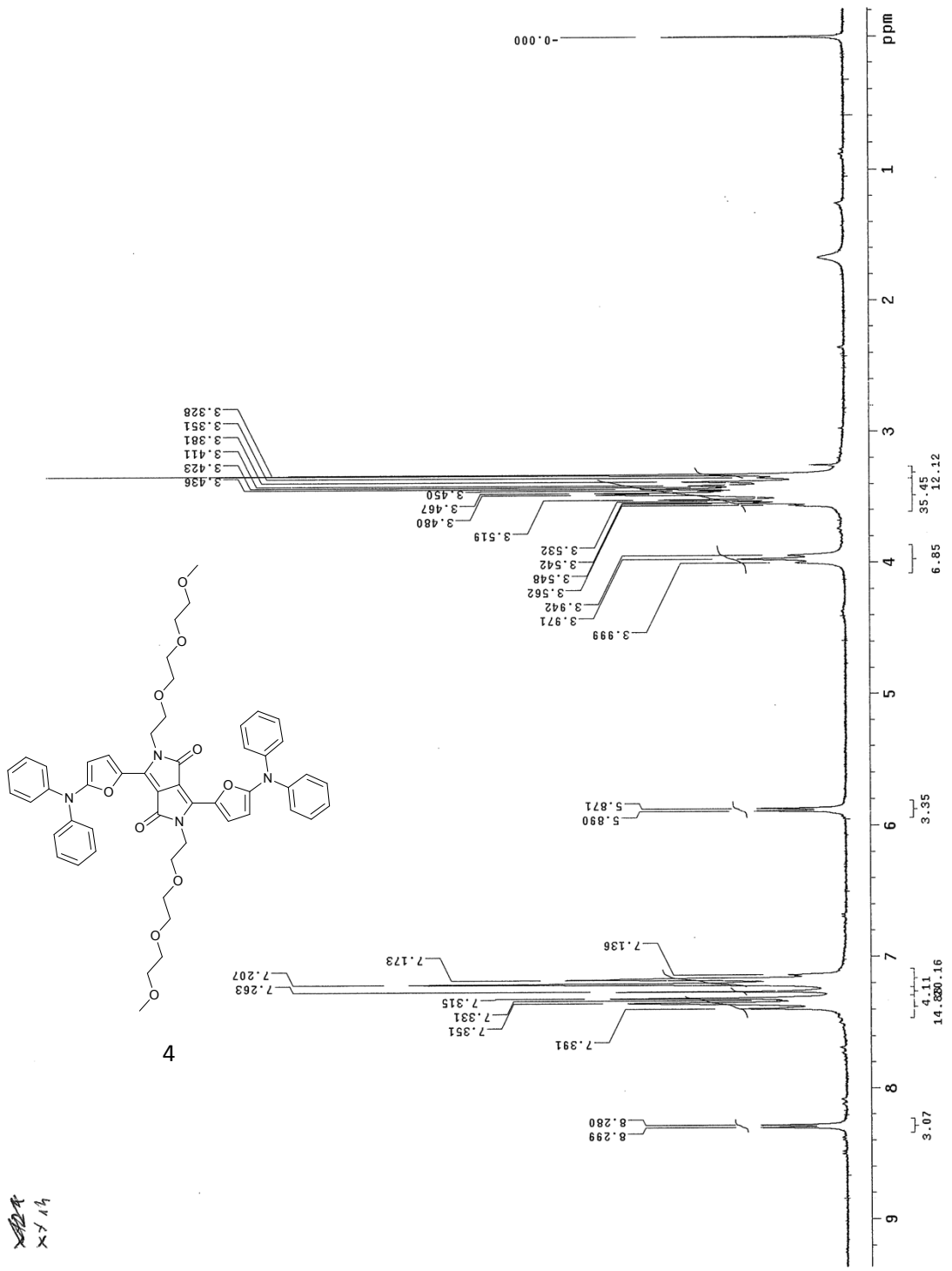
Sample directory:

FidFile: CARBON

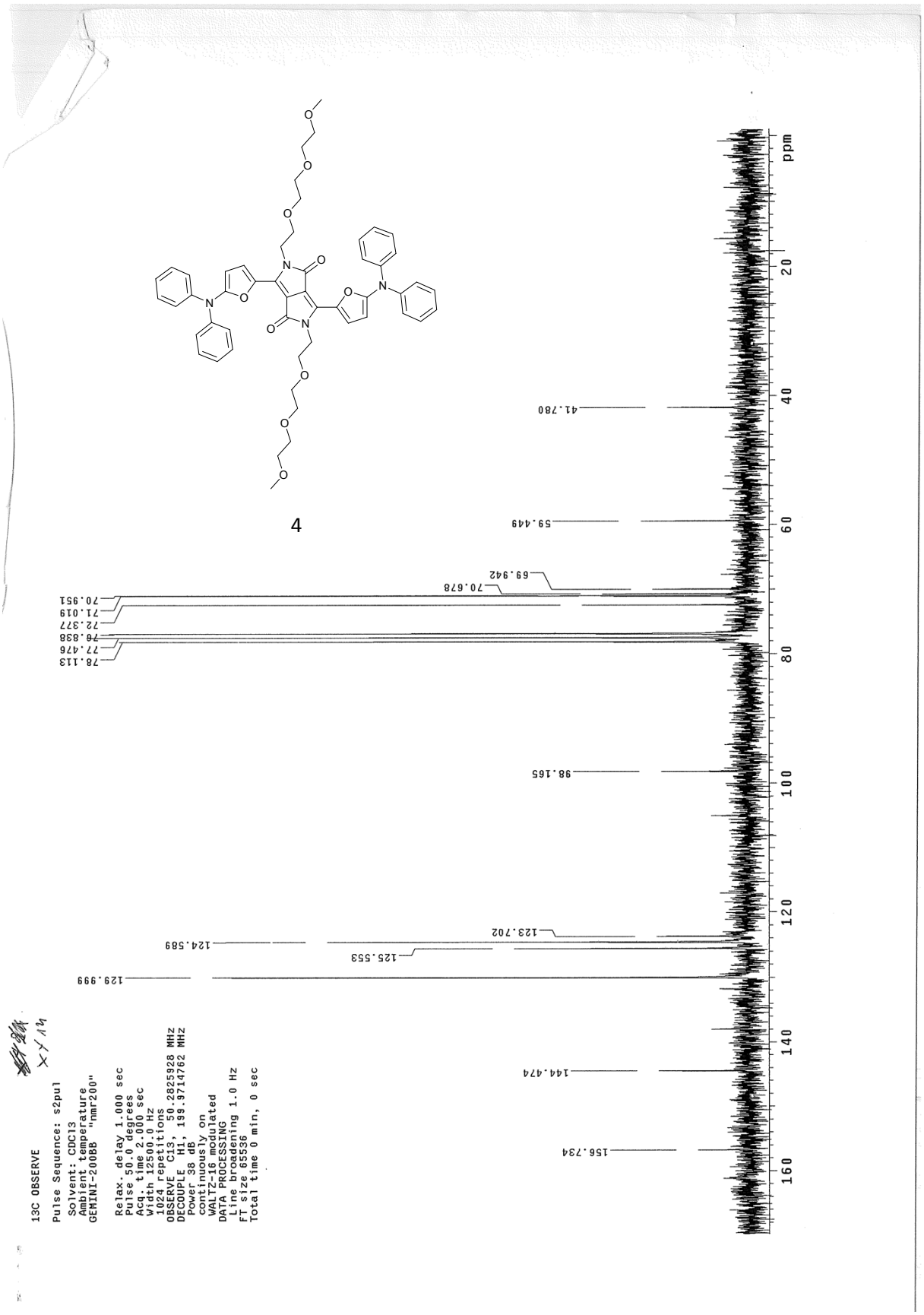
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 8 2014

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 0.500 sec
Pulse 30.0 degrees
Acq. time 1.200 sec
Width 37878.8 Hz
1136 repetitions
OBSERVE C13, 125.6810405 MHz
DECOUPLE H1, 499.8272777 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072


-0.000
8.299
8.280
7.391
7.351
7.331
7.315
7.263
7.207
7.173
7.136
5.890
5.871
3.999
3.971
3.942
3.562
3.548
3.542
3.532
3.519
3.480
3.467
3.450
3.436
3.423
3.411
3.381
3.351
3.328
ppm
3.07
4.11
14.83
60.16
3.35
6.85
35.45
12.12

4


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "nmr200"
Relax. delay 1.000 sec
Pulse 50.0 degrees
Acq. time 2.000 sec
Width 12500.0 Hz
1024 repetitions
OBSERVE C13, 50.2825928 MHz
DECOUPLE H1, 199.9714762 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 0 min, 0 sec
78.113
77.476
76.838
72.377
71.019
70.951
70.678
69.942
59.449
41.780
129.999
124.589
125.553
123.702
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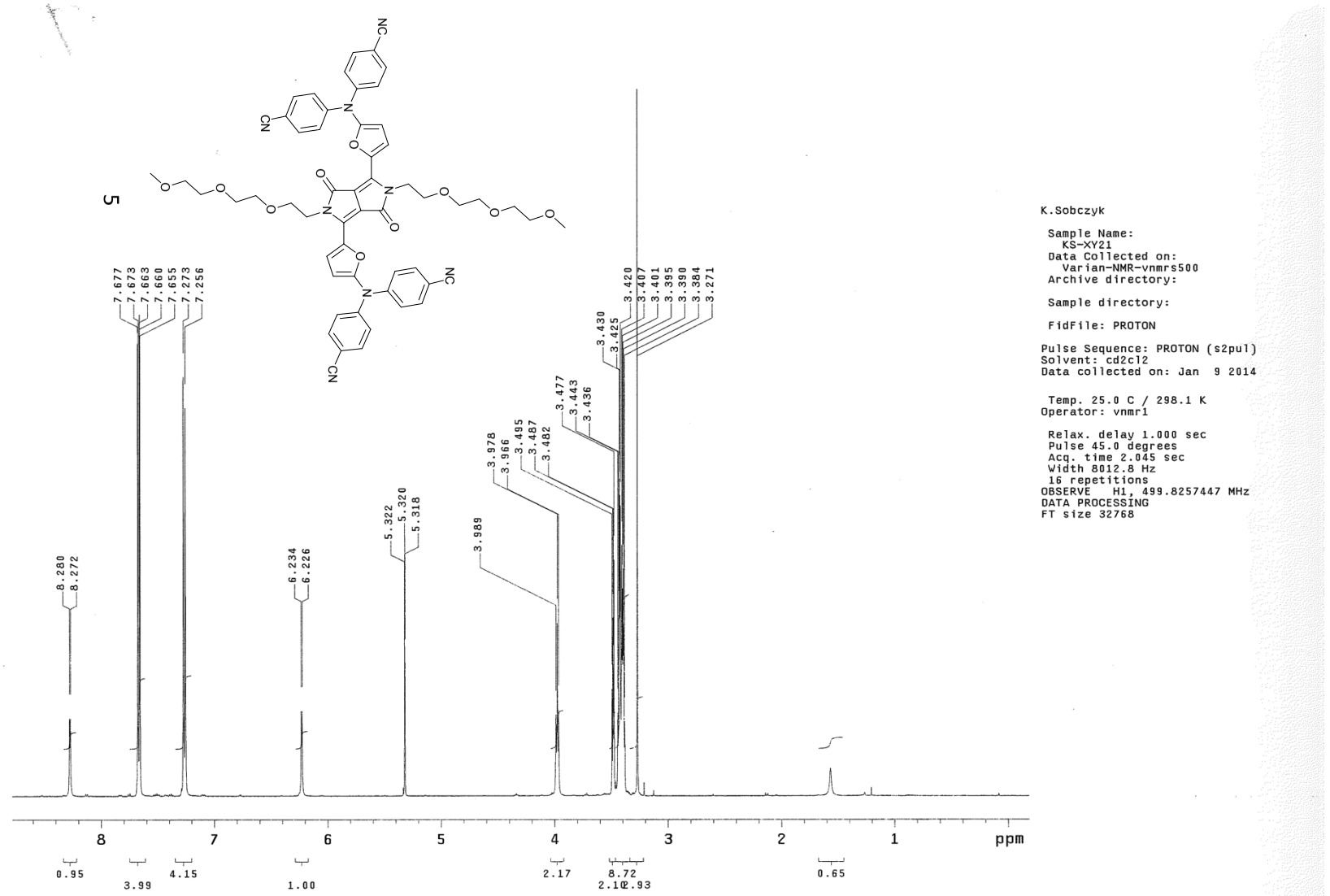
ppm
20
40
60
80
100
120
140
160

4



K.Sobczyk

Sample Name:
KS-XY21
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

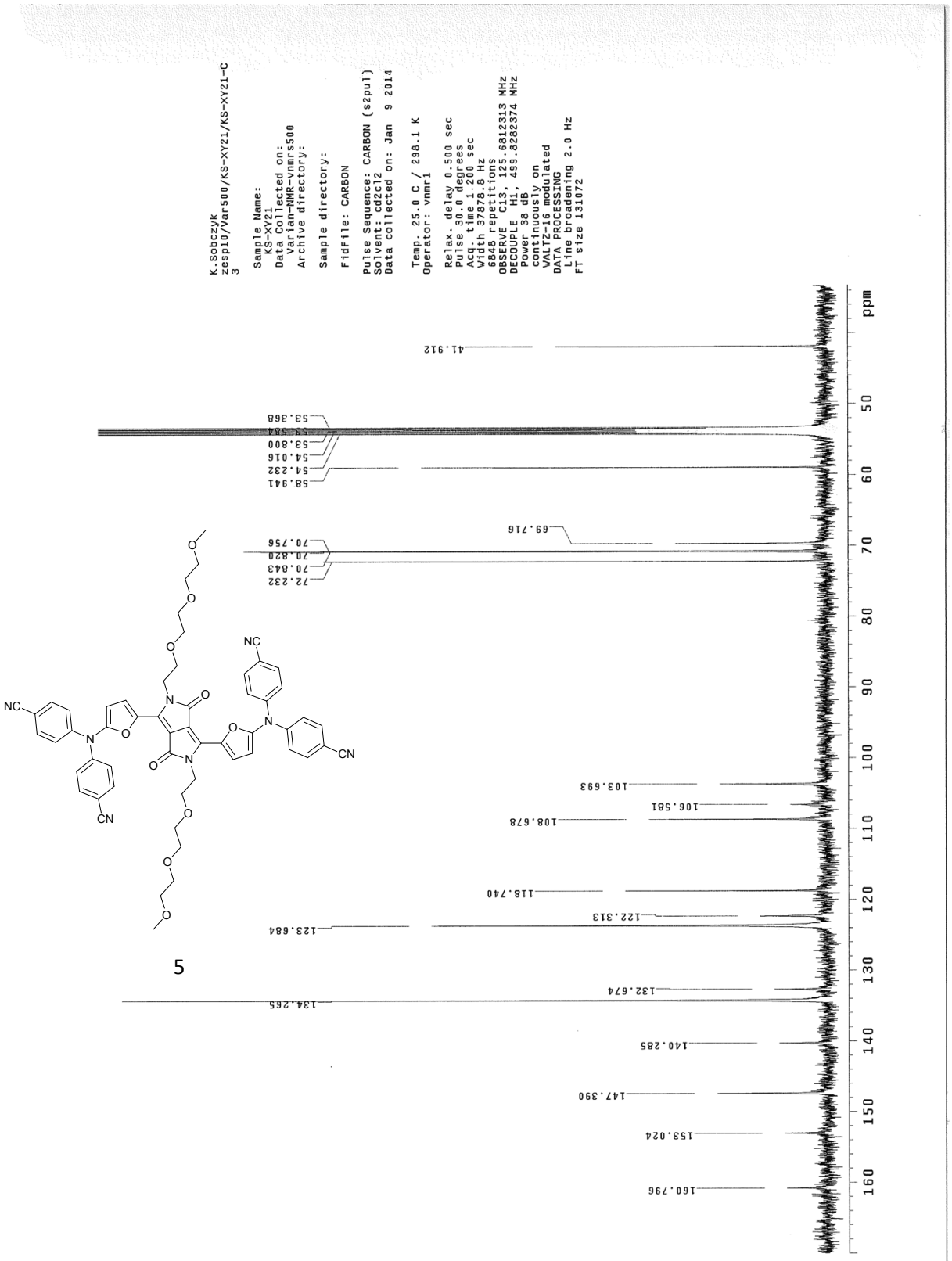
Sample directory:

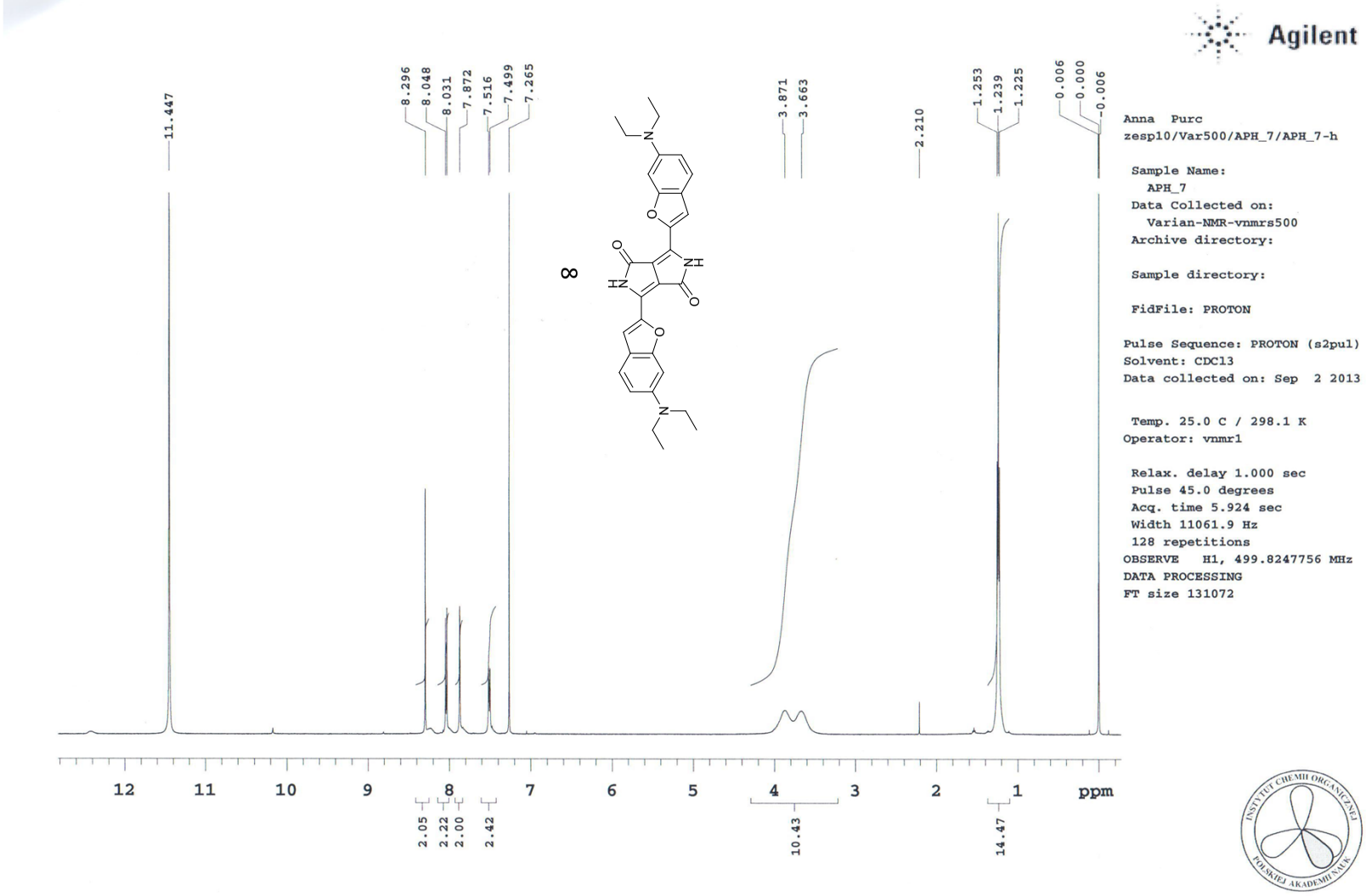
FidFile: PROTON

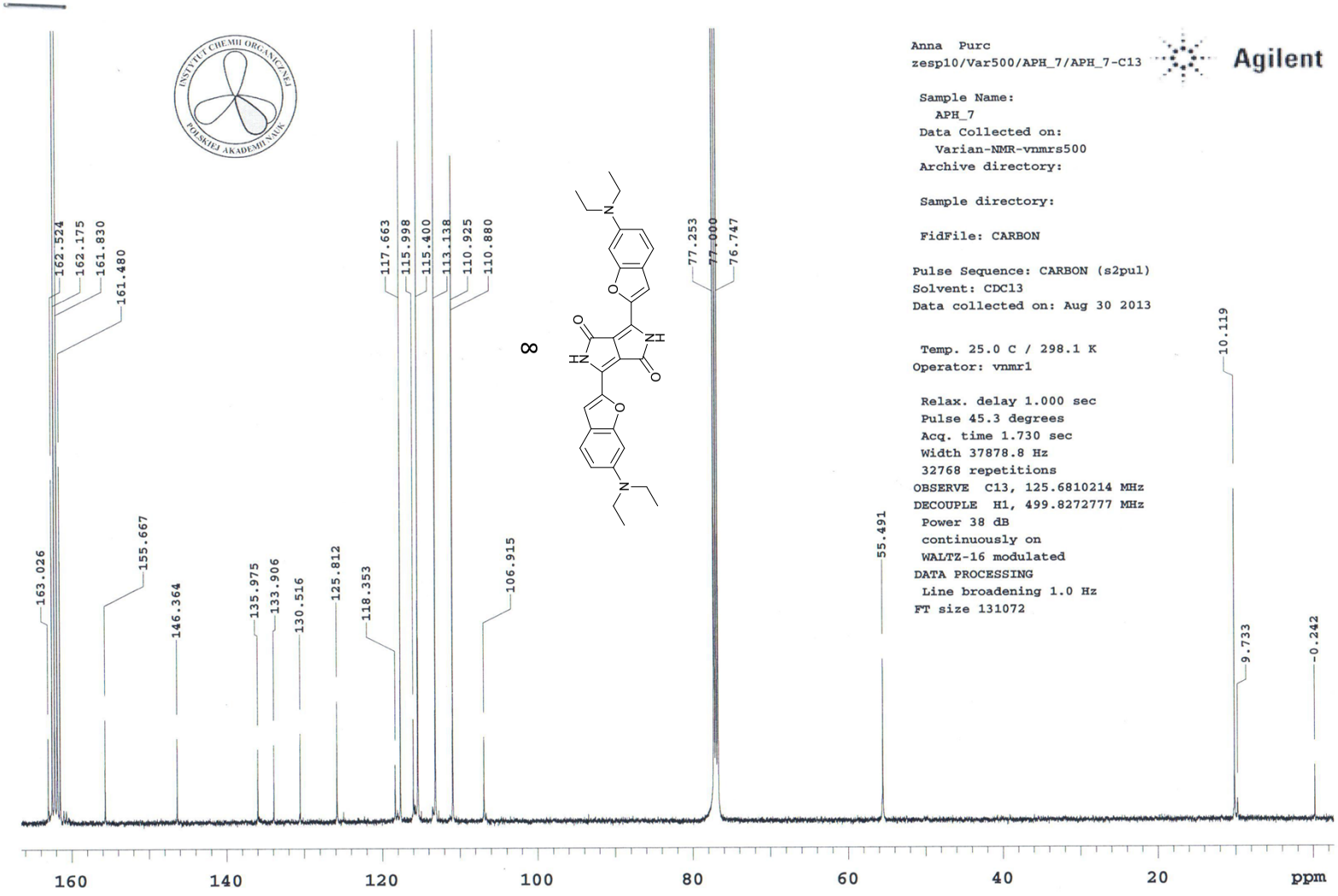
Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: Jan 9 2014

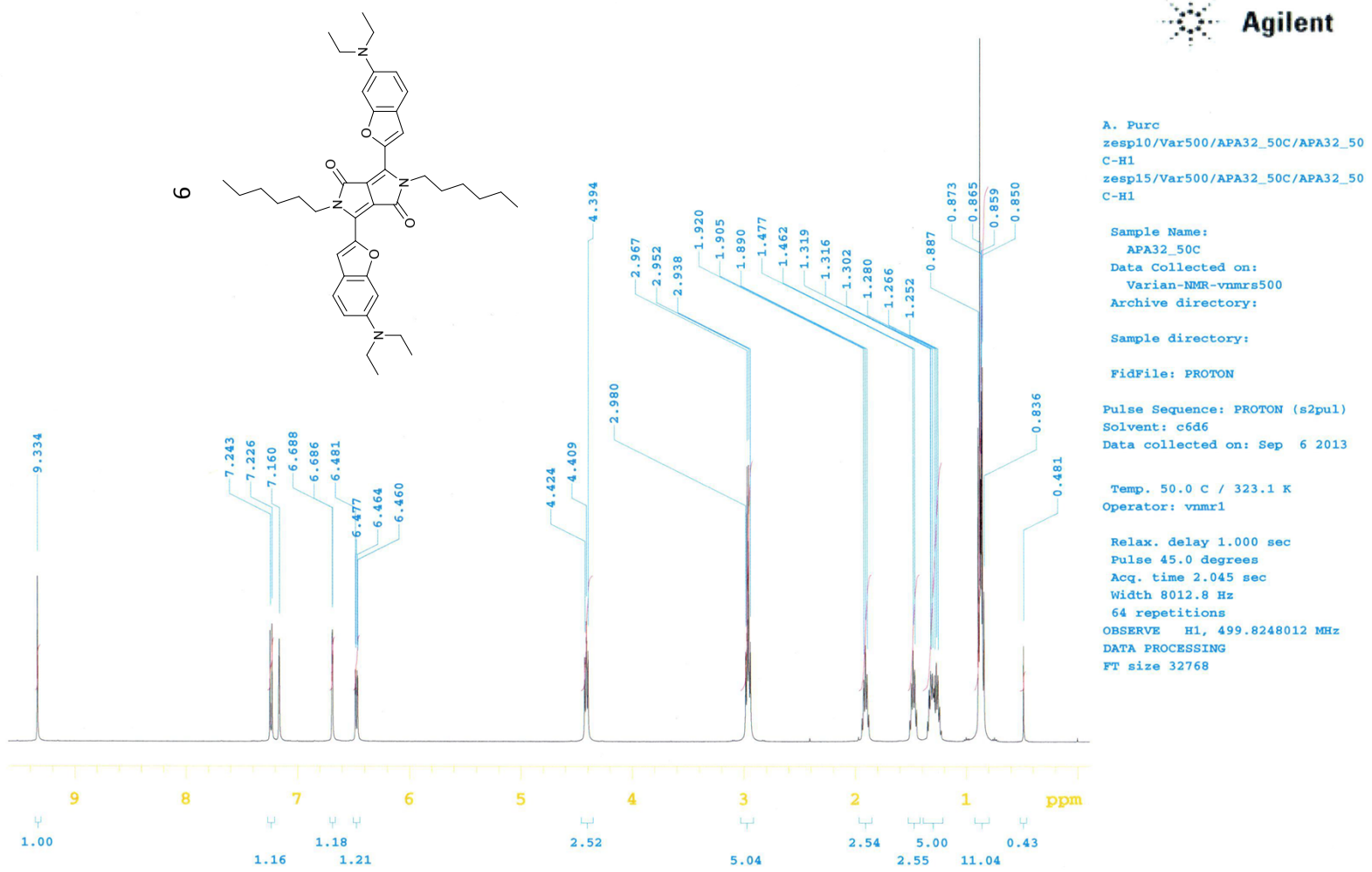
Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 499.8257447 MHz
DATA PROCESSING
FT size 32768


K.SobczyK
zesp10/Var500/KS-XY21/KS-XY21-C
3
Sample Name:
KS-XY21
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jan 9 2014
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 0.500 sec
Pulse 30.0 degrees
Acq. time 1.200 sec
Width 37878.8 Hz
6848 repetitions
OBSERVE C13, 125.6812313 MHz
DECOUPLE H1, 499.8282374 MHz
Power 38 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
41.912
53.368
53.584
53.800
54.016
54.232
58.941
69.716
70.756
70.820
70.843
72.232
103.693
106.581
108.678
118.740
122.313
123.684
132.674
134.265
140.285
147.390
153.024
160.796
ppm
NC
CN
5


Agilent
11.447
8.296
8.048
8.031
7.872
7.516
7.499
7.265
3.871
3.663
2.210
1.253
1.239
1.225
0.006
0.000
-0.006
8
Anna Purc
zesp10/Var500/APH_7/APH_7-h
Sample Name:
APH_7
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: CDCl3
Data collected on: Sep 2 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.924 sec
Width 11061.9 Hz
128 repetitions
OBSERVE H1, 499.8247756 MHz
DATA PROCESSING
FT size 131072
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.05
2.22
2.00
2.42
10.43
14.47
INSTYTUT CHEMII ORGANICZNEJ
POLSKIEJ AKADEMII NAUK


INSTYTUT CHEMII ORGANICZNEJ
POLSKIEJ AKADEMII NAUK
Anna Purc
zesp10/Var500/APH_7/APH_7-C13
Agilent
Sample Name:
APH_7
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Aug 30 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 1.730 sec
Width 37878.8 Hz
32768 repetitions
OBSERVE C13, 125.6810214 MHz
DECOUPLE H1, 499.8272777 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
8
163.026
162.524
162.175
161.830
161.480
155.667
146.364
135.975
133.906
130.516
125.812
118.353
117.663
115.998
115.400
113.138
110.925
110.880
106.915
77.253
77.000
76.747
55.491
10.119
9.733
-0.242
160
140
120
100
80
60
40
20
ppm



Agilent

A. Purc
zesp10/Var500/APA32_50C/APA32_50C-H1
zesp15/Var500/APA32_50C/APA32_50C-H1

Sample Name:
APA32_50C
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

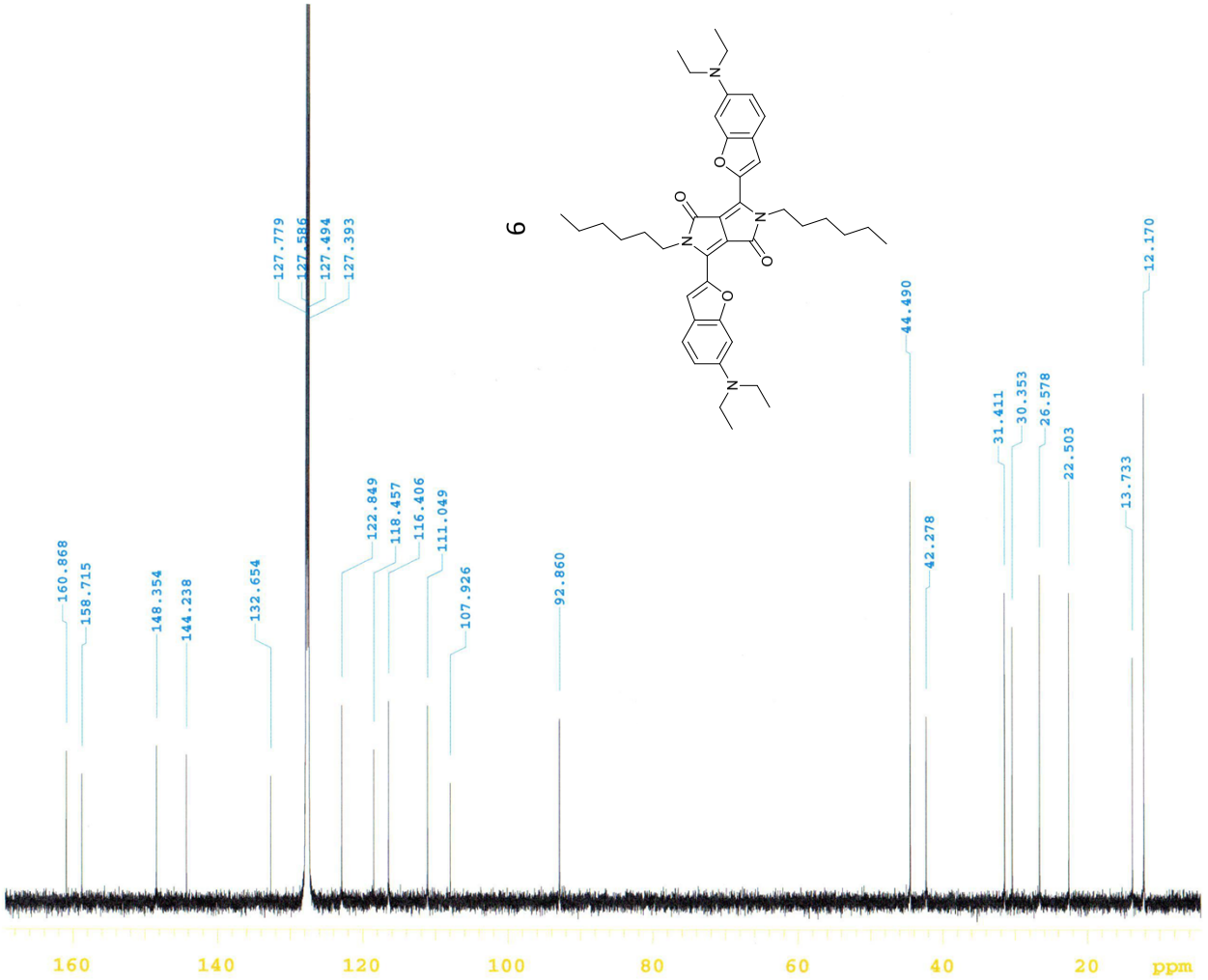
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: c6d6
Data collected on: Sep 6 2013

Temp. 50.0 C / 323.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 8012.8 Hz
64 repetitions
OBSERVE H1, 499.8248012 MHz
DATA PROCESSING
FT size 32768



Agilent

A. Purc
zesp10/Var500/APA32_50C/APA32_50
C-C13
zesp15/Var500/APA32_50C/APA32_50
C-C13

Sample Name:
APA32_50C
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Sep 6 2013

Temp. 50.0 C / 323.1 K
Operator: vnmr1

Relax. delay 0.500 sec
Pulse 30.0 degrees
Acq. time 1.200 sec
Width 37878.8 Hz
1936 repetitions
OBSERVE C13, 125.6810519 MHz
DECOUPLE H1, 499.8273227 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072

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[1] R. L. Sutherland, "Handbook of Nonlinear Optics", 2nd Ed., (Mercel Dekker Inc., 2003, New York) p. 629.

[2] Supporting information of K. Kamada, K. Ohta, T. Kubo, A. Shimizu, Y. Morita, K. Nakasuji, R. Kishi, S. Ohta, S. Furukawa, H. Takahashi, M. Nakano, *Angew. Chem. Int. Ed.* 2007, **46**, 3544.

[3] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, 2009.