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Synthesis and Characterization of Semiaromatic Polyamides Comprising Benzofurobenzofuran Repeating Units

Electronic Supplementary Information

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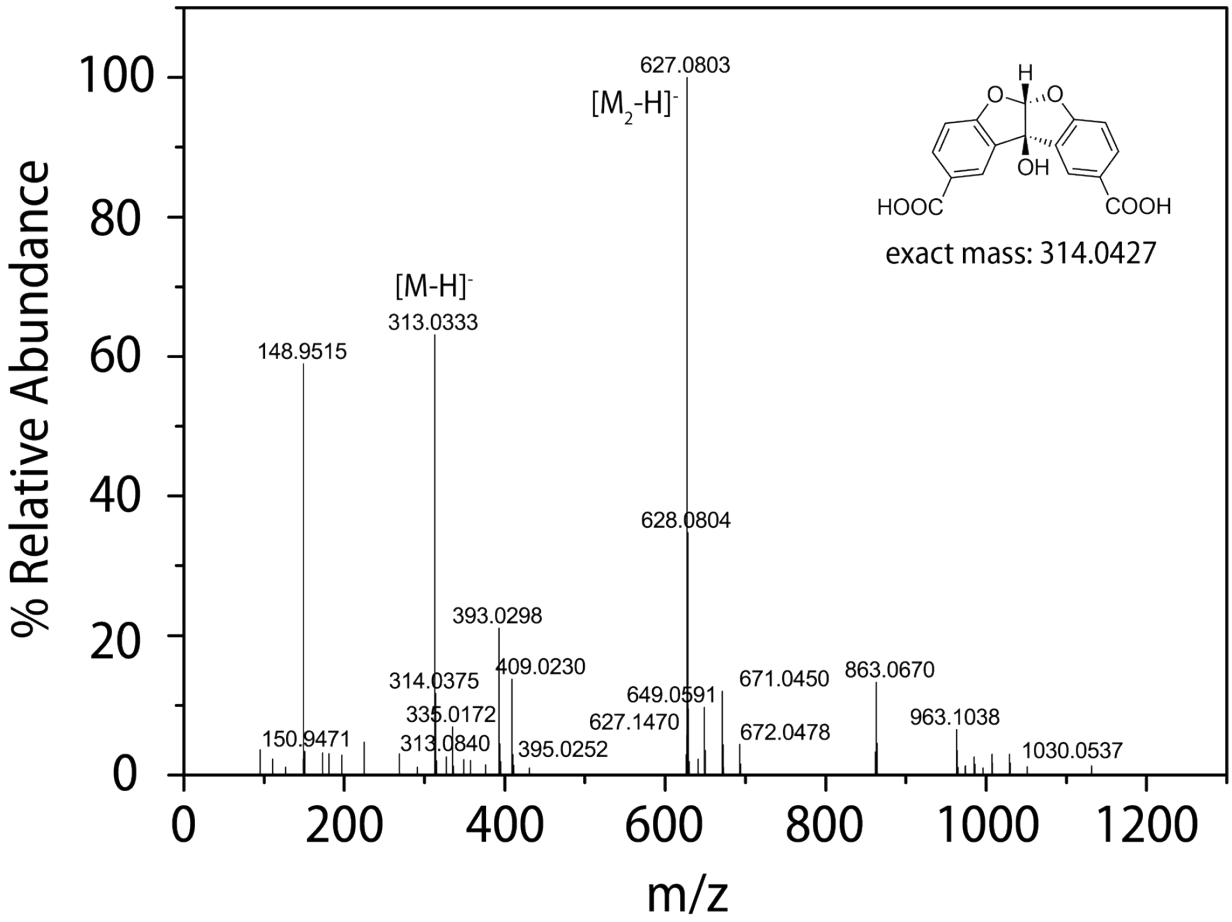
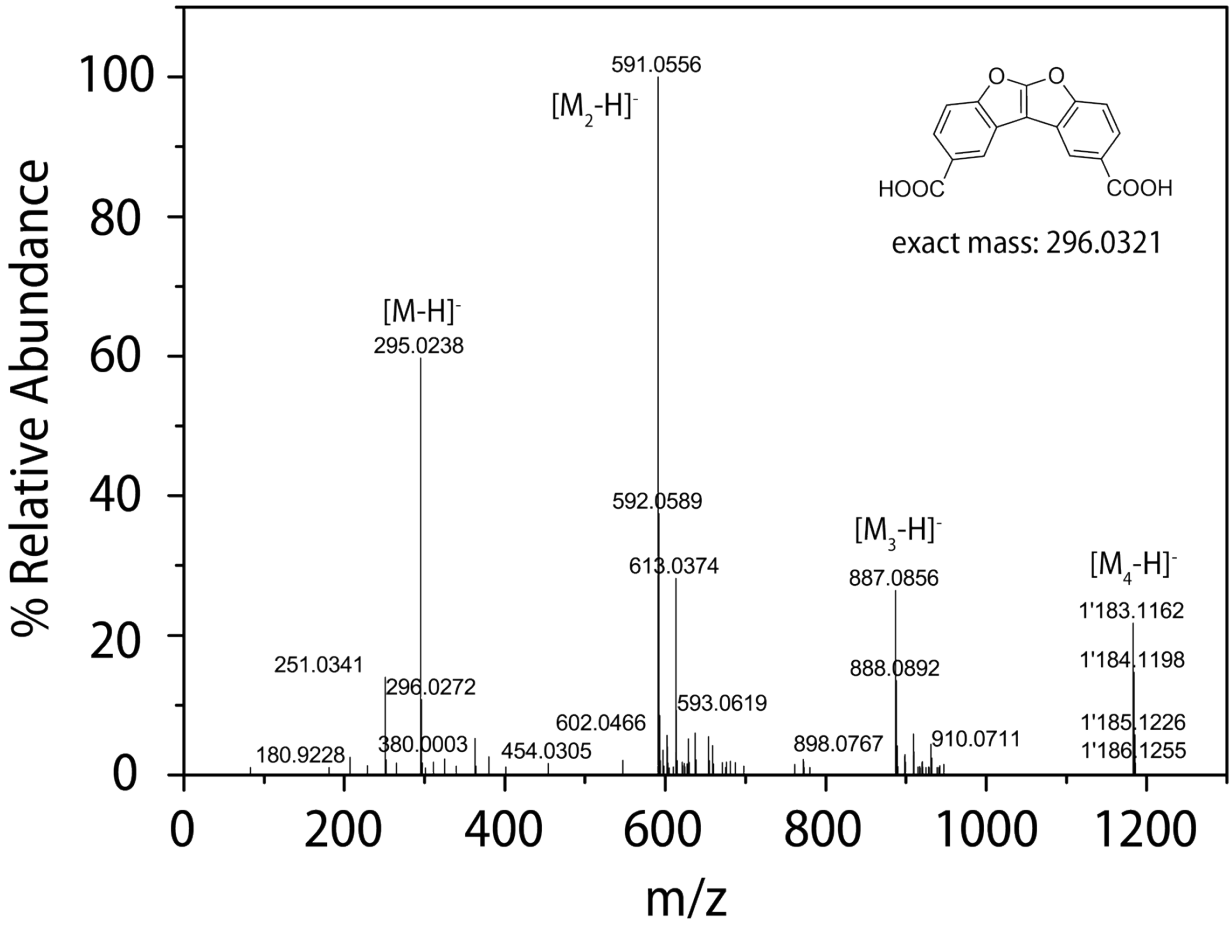
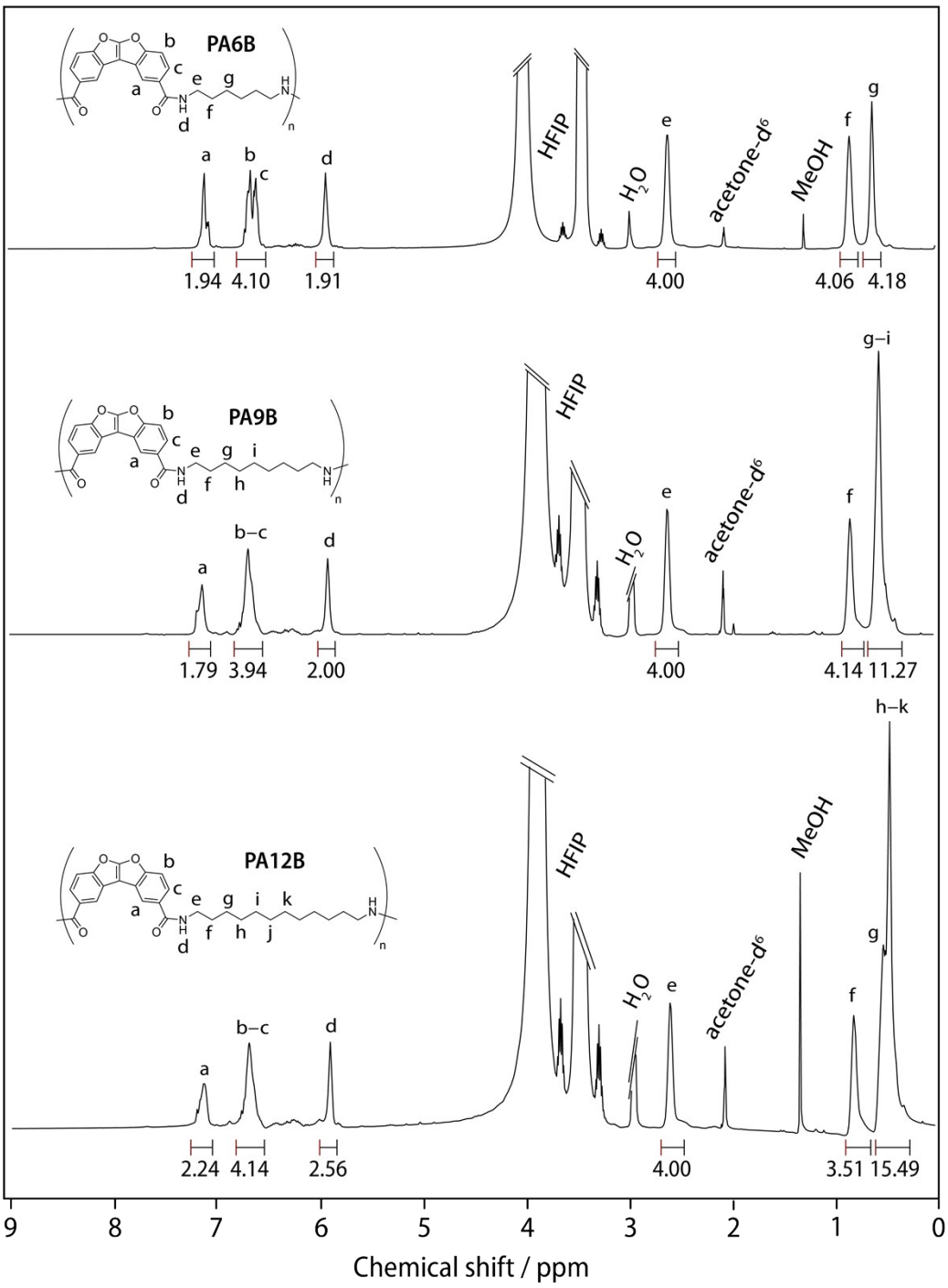
1. Supplementary Figures S1–S6



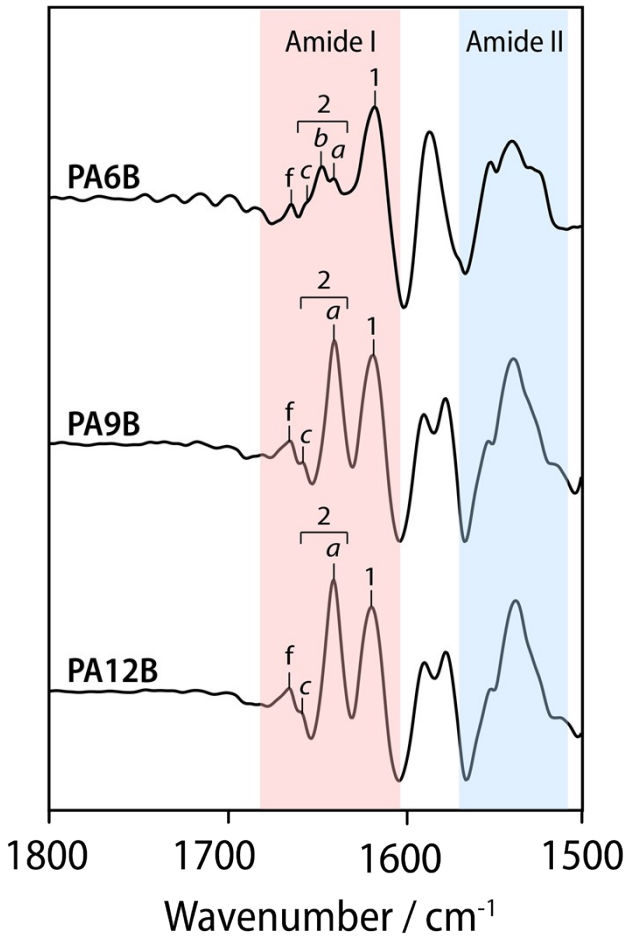
Supplementary Figure S1. High-resolution mass spectrum (MALDI-ToF, negative-mode) of *cis*-5a-hydro-10b-hydrobenzofuro[2,3-*b*]benzofuran-2,9-dicarboxylic acid **3**.



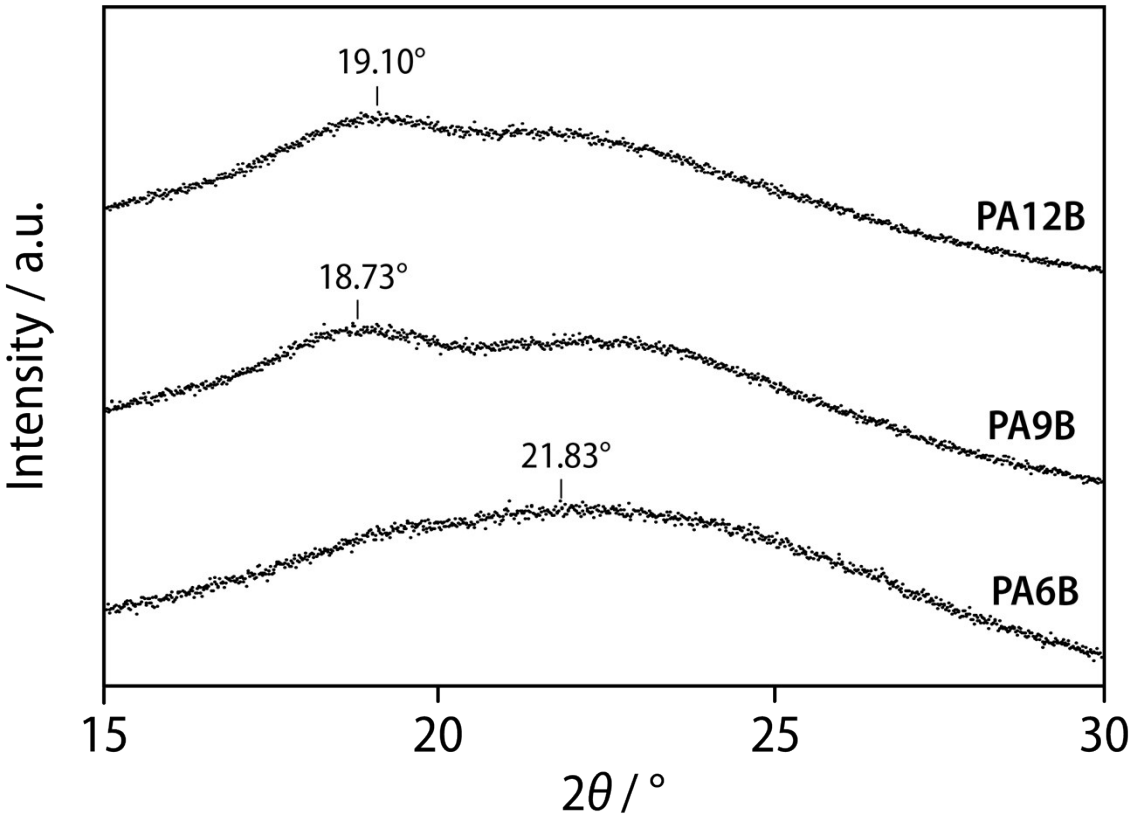
Supplementary Figure S2. High-resolution mass spectrum (MALDI-ToF, negative-mode) of benzofuro[2,3-*b*]benzofuran-2,9-dicarboxylic acid **2**.



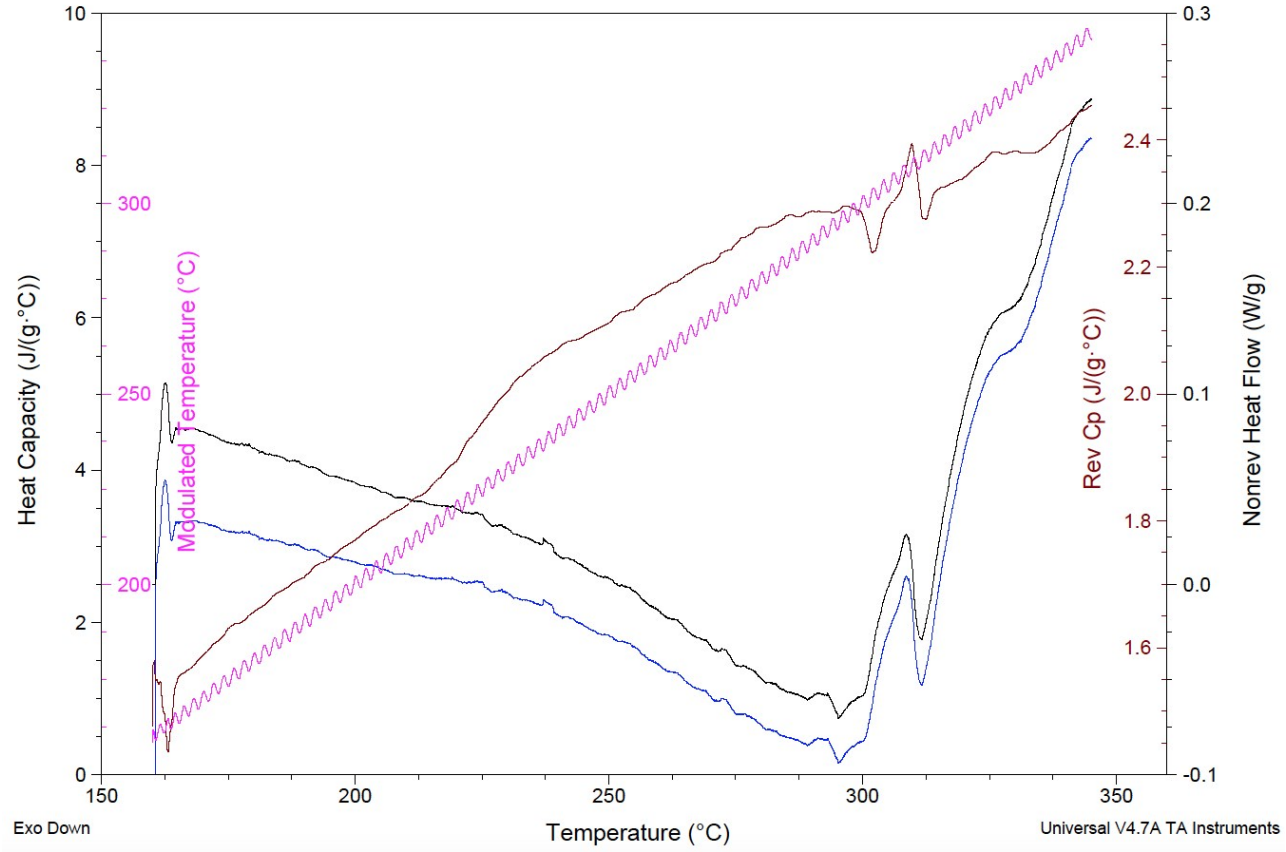
Supplementary Figure S3. ^{1}H-NMR spectra of the polyamides **PA6B**, **PA9B** and **PA12B** recorded in HFIP/acetone-d^6. The amide protons of the repeating unit are visible at 5.90–5.92 ppm. The *b* and *c* protons of the heterocyclic benzofurobenzofuran core can only be differentiated in the case of **PA6B**.



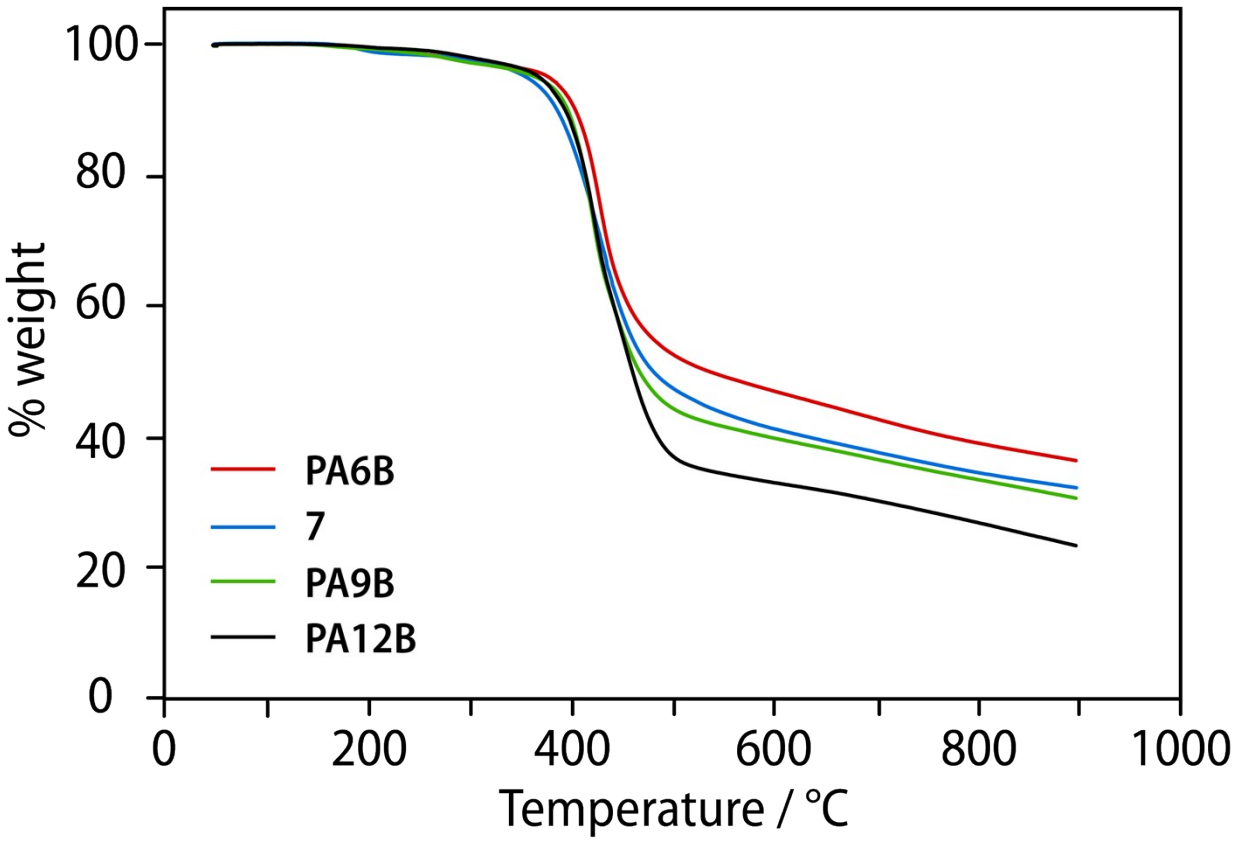
Supplementary Figure S4. Second derivative analysis of the IR spectra of the amide I and amide II regions of the polyamides **PA6B**, **PA9B** and **PA12B**.



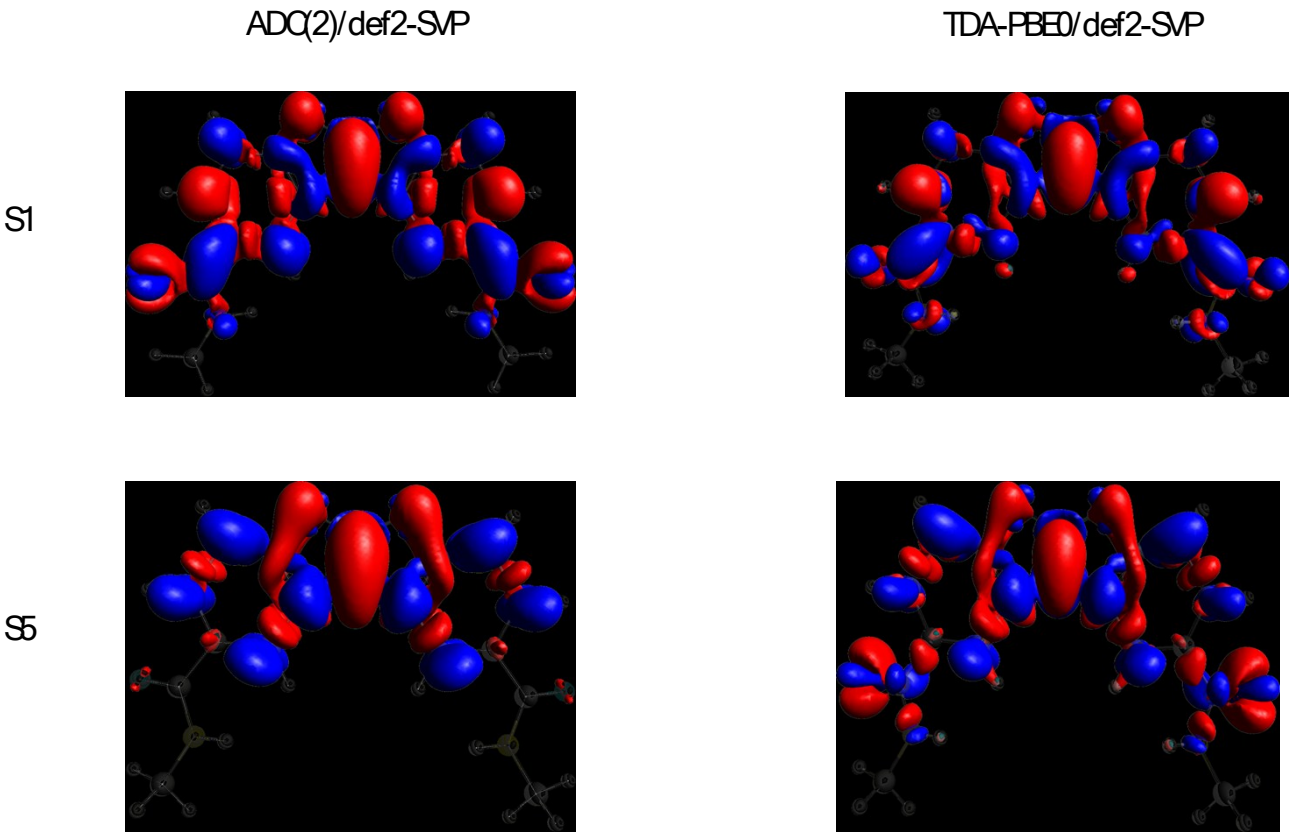
Supplementary Figure S5. Wide-angle X-ray scattering (WAXS) of the polyamides **PA6B**, **PA9B** and **PA12B**. **PA6B** shows an amorphous halo centered at 2θ = 21.83 °, as well as a broad diffraction peak at 2θ = 18.73 ° and 19.10 ° for **PA9B** and **PA12B**, respectively.



Supplementary Figure S6. Modulated differential scanning calorimetry (M-DSC) of benzofuro[2,3-*b*]benzofuran-2,9-dicarboxylic acid **2**. The observed T_g (220°C) is higher than the one measured with the conventional DSC due to the lower heating rate (1°C/min for M-DSC versus 10°C/min for conventional DSC).



Supplementary Figure S7. TGA of the polyamides **PA6B**, **PA9B** and **PA12B** and the model compound **7** in nitrogen.



Supplementary Figure S8. Density differences of the brightest transitions (S_0-S_1 and S_0-S_5) of dimethyl benzofurobenzofurane dicarboxylate **9** computed at both the ADC(2) level (isodensities = -0.0005 (red) and +0.0005 (blue)) and TDA-PBE0 level (isodensities = -0.0008 (red) and +0.0008 (blue)).

2. Supplementary Tables S1–S2

Table S1. Excitation energies for **9** at the TDA-PBE0/def2-SVP and the ADC(2)/def2-SVP level. Oscillator strengths are reported in parentheses. Note the quantitative agreement between the vertical excitation energies computed at the TDA-PBE0 and ADC(2) levels. To ensure the correct attribution of the character of the brightest states, the relaxed density differences computed at the TDA-PBE0 level are compared to the density differences from the ADC(2) computations (see Supplementary Figure S6).

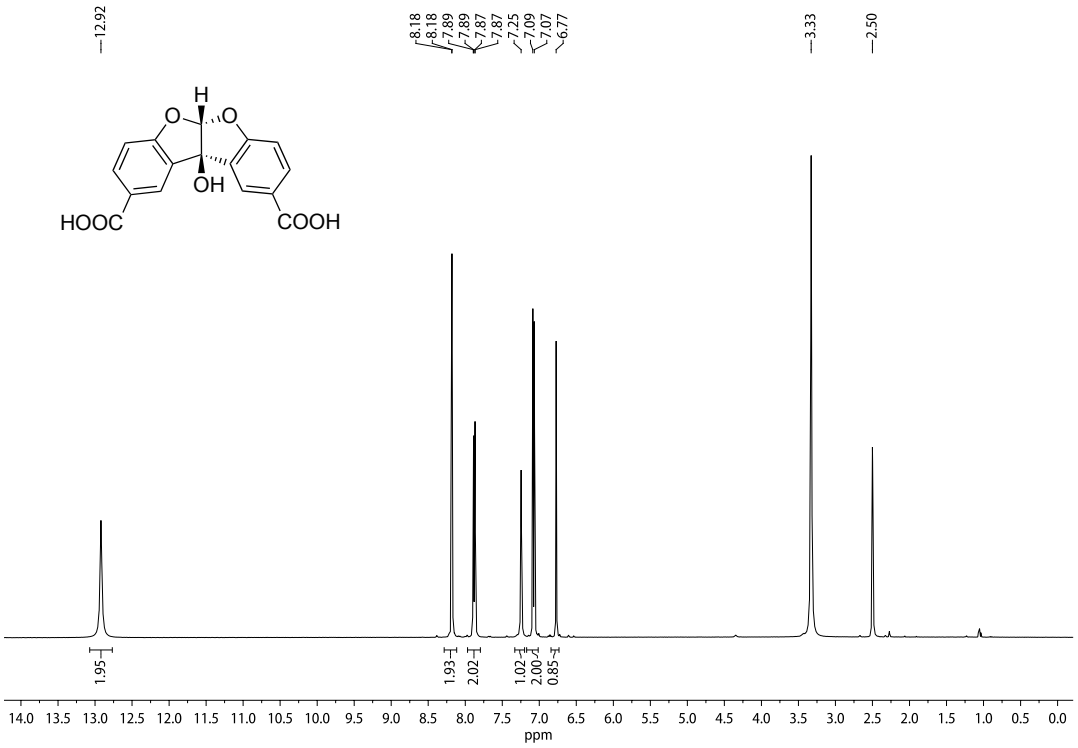
excitation	PBE0	ADC(2)
S_1 (vertical)	4.34 eV (0.031)	4.54 eV (0.032)
S_2 (vertical)	4.46 eV (0.002)	4.61 eV (0.008)
S_3 (vertical)	4.73 eV (0.009)	4.77 eV (0.001)
S_4 (vertical)	4.74 eV (0.004)	4.79 eV (0.002)
S_5 (vertical)	4.80 eV (0.345)	5.11 eV (0.604)

Table S2. Crystallographic and refinement data of compounds **6** and **8**.

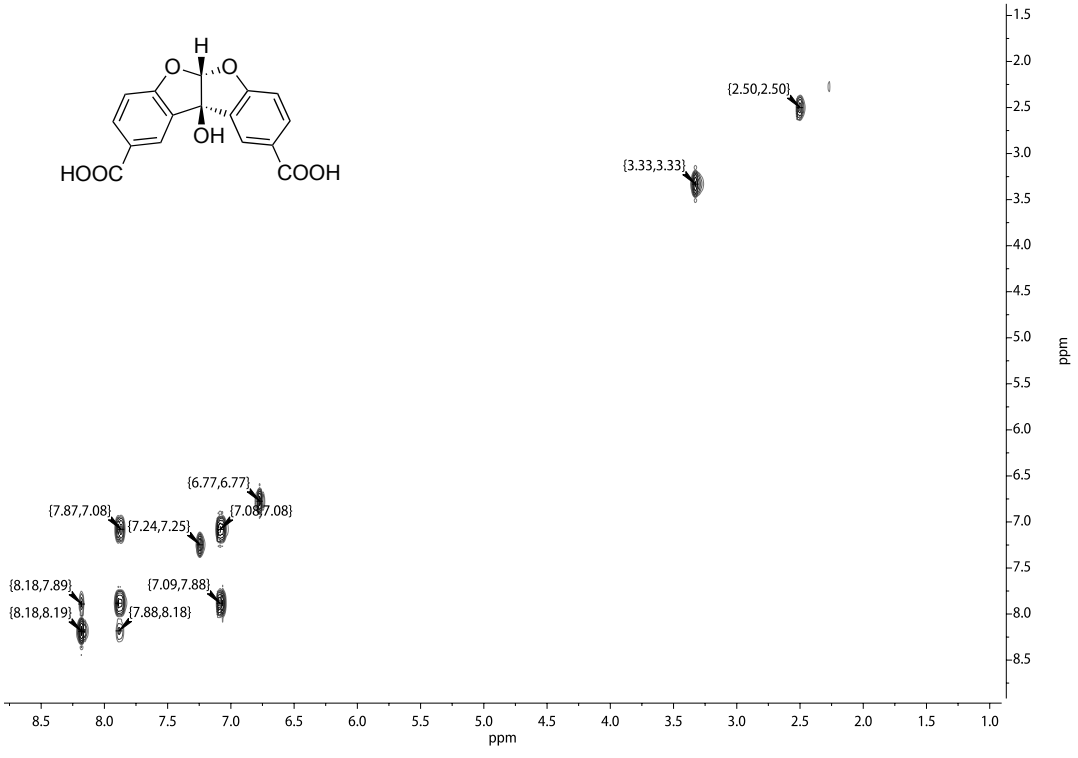
Identification code	**6**	**8**
Empirical formula	$2(C_{22}H_{24}N_2O_5), 3(C_2H_6O)$	$C_{22}H_{20}O_6$
Formula weight (g/mol)	931.06	380.38
Temperature (K)	140.00(10)	100.01(10)
Wavelength (Å)	1.54184	1.54184
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.1910(3)	8.7557(4)
b (Å)	13.7072(3)	10.3822(4)
c (Å)	19.0724(5)	11.1677(5)
α (°)	90.789(2)	63.052(4)
β (°)	103.313(3)	82.840(4)
γ (°)	109.953(2)	86.270(4)
Volume (Å^3)	2424.57(12)	897.85(8)
Z	2	2
Density (calculated) (Mg/m^3)	1.275	1.407
Absorption coefficient (mm^{-1})	0.757	0.850
F(000)	996	400
Crystal size (mm^3)	0.545 x 0.445 x 0.360	0.309 x 0.214 x 0.135
Theta range for data collection (°)	3.448 to 76.154	4.467 to 76.788
Index ranges	$-12 \le h \le 12$	$-10 \le h \le 10$
	$-9 \le k \le 17$	$-10 \le k \le 13$
	$-23 \le l \le 23$	$-14 \le l \le 14$
Reflections collected	17613	7574
Independent reflections	9787 [$R_{(int)}$ = 0.0198]	3705 [$R_{(int)}$ = 0.0129]
Data completeness	99.9 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Gaussian
Max. and min. transmission	1.00000 and 0.30076	0.916 and 0.843
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9787 / 40 / 664	3705 / 0 / 333
Goodness-of-fit on F^2	1.036	1.041
Final R indices [I>2sigma(I)]	R_1 = 0.0444, wR_2 = 0.1265	R_1 = 0.0356, wR_2 = 0.0915
R indices (all data)	R_1 = 0.0496, wR_2 = 0.1322	R_1 = 0.0371, wR_2 = 0.0927
Largest diff. peak and hole (e.Å^{-3})	0.366 and -0.245	0.299 and -0.193

3. NMR Spectra

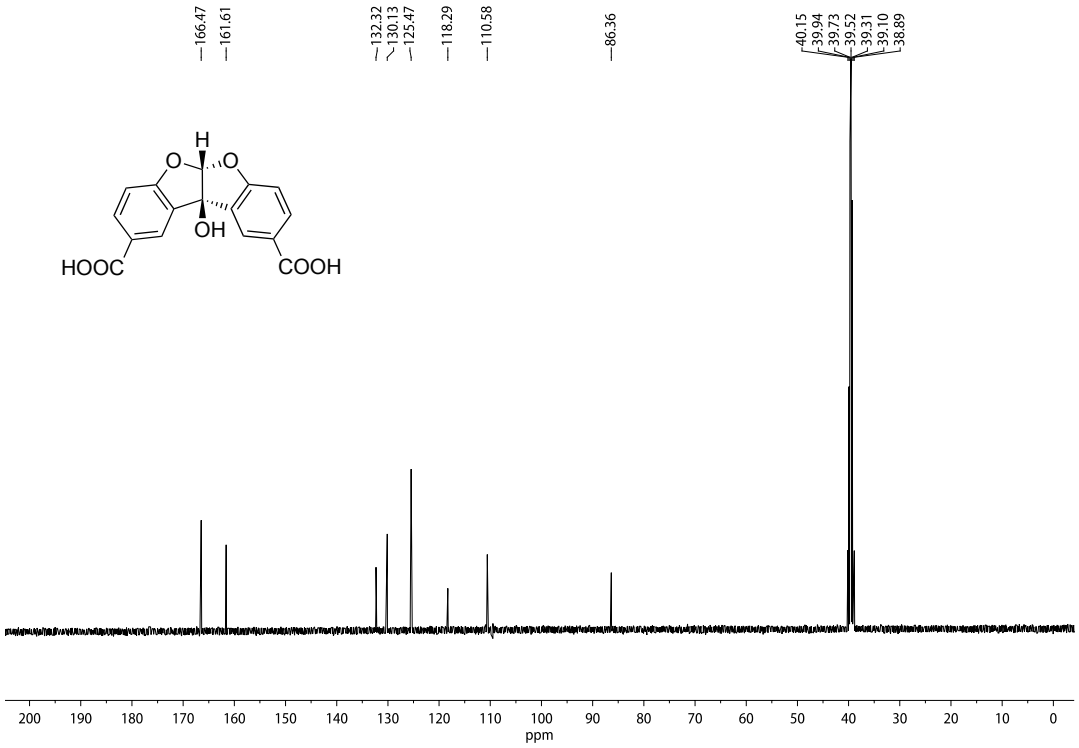
^{1}H NMR spectrum (DMSO-d^6, 400 MHz) of **3**



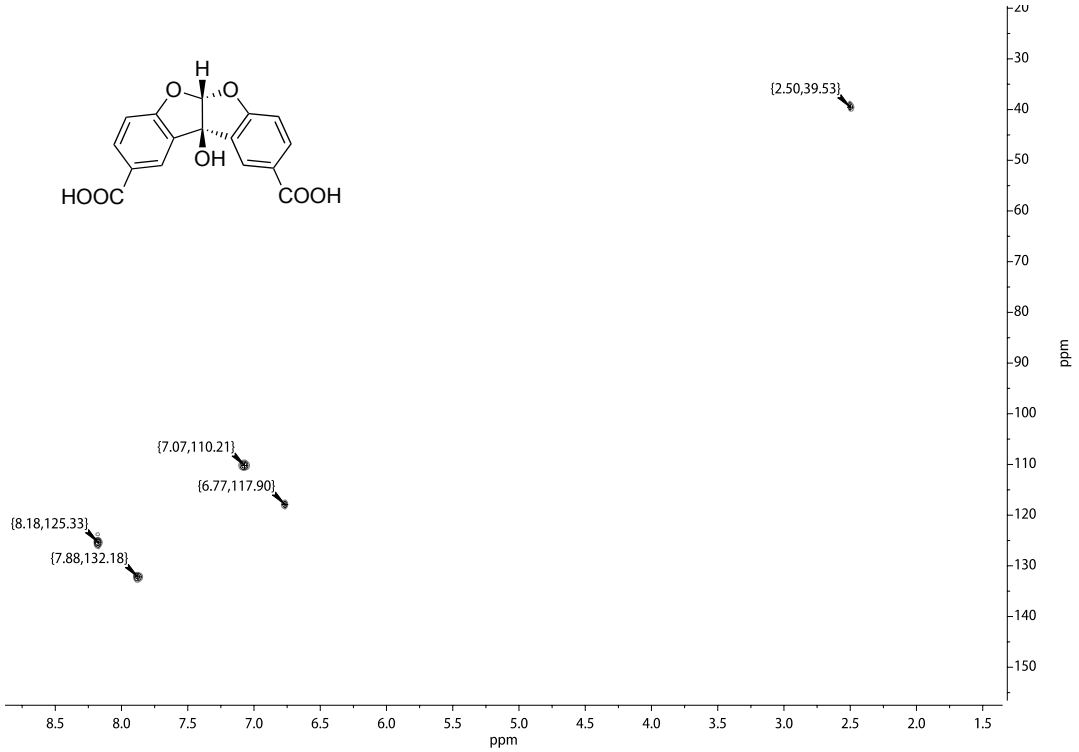
^{1}H-^{1}H COSY NMR spectrum (DMSO-d^6) of **3**



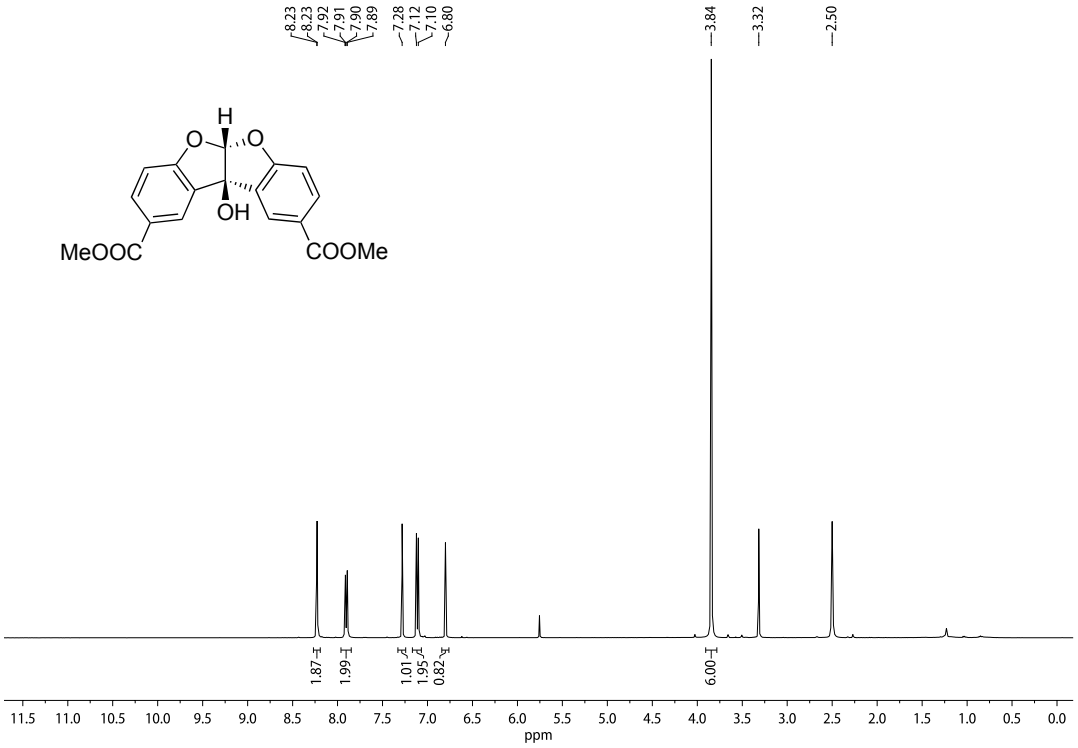
^{13}C NMR spectrum (DMSO-d^6, 101 MHz) of **3**



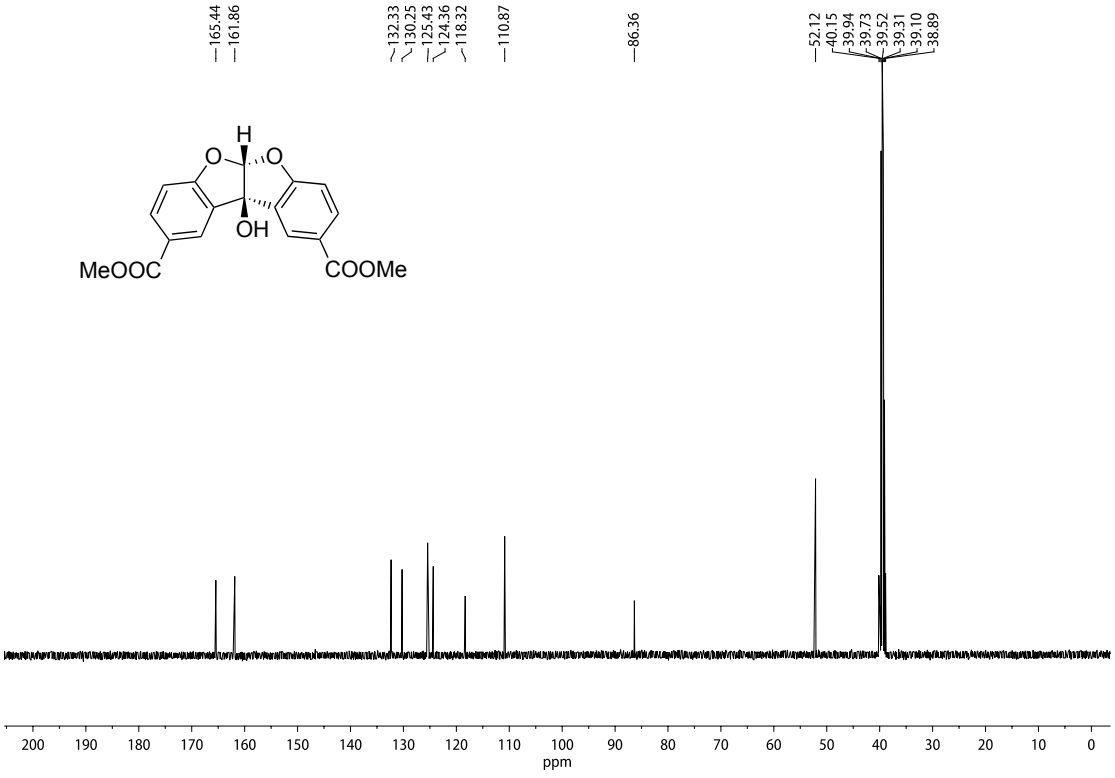
^{1}H-^{13}C HSQC NMR spectrum (DMSO-d^6) of **3**



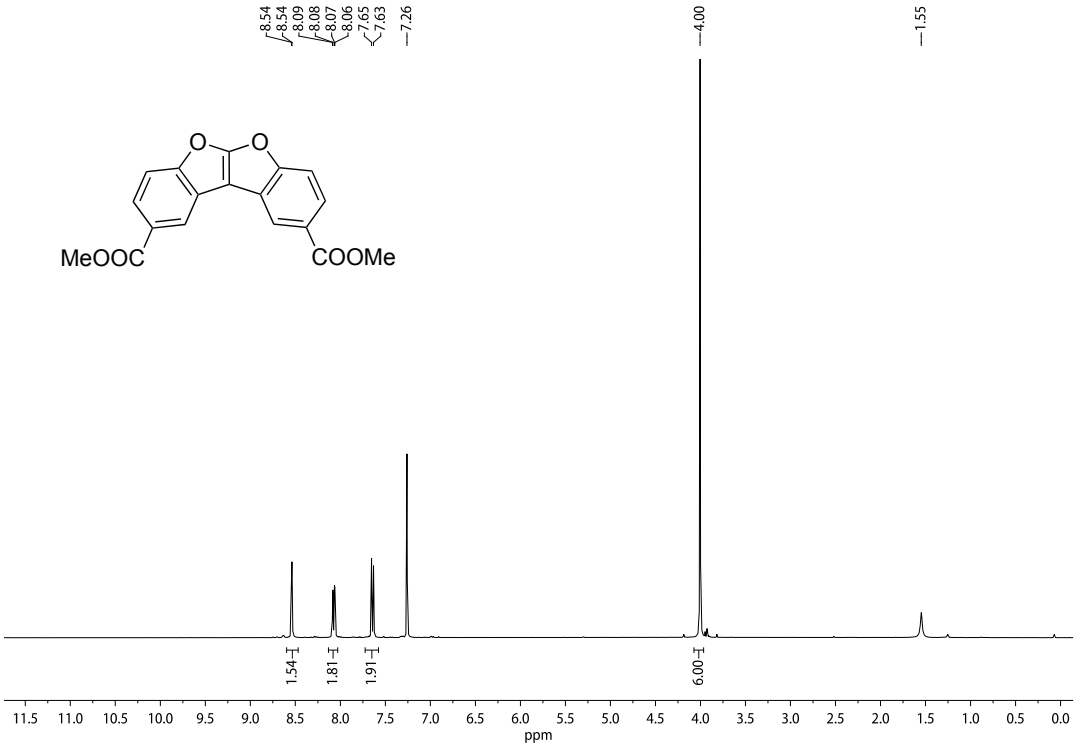
^{1}H NMR spectrum (DMSO-d^6, 400 MHz) of **4**



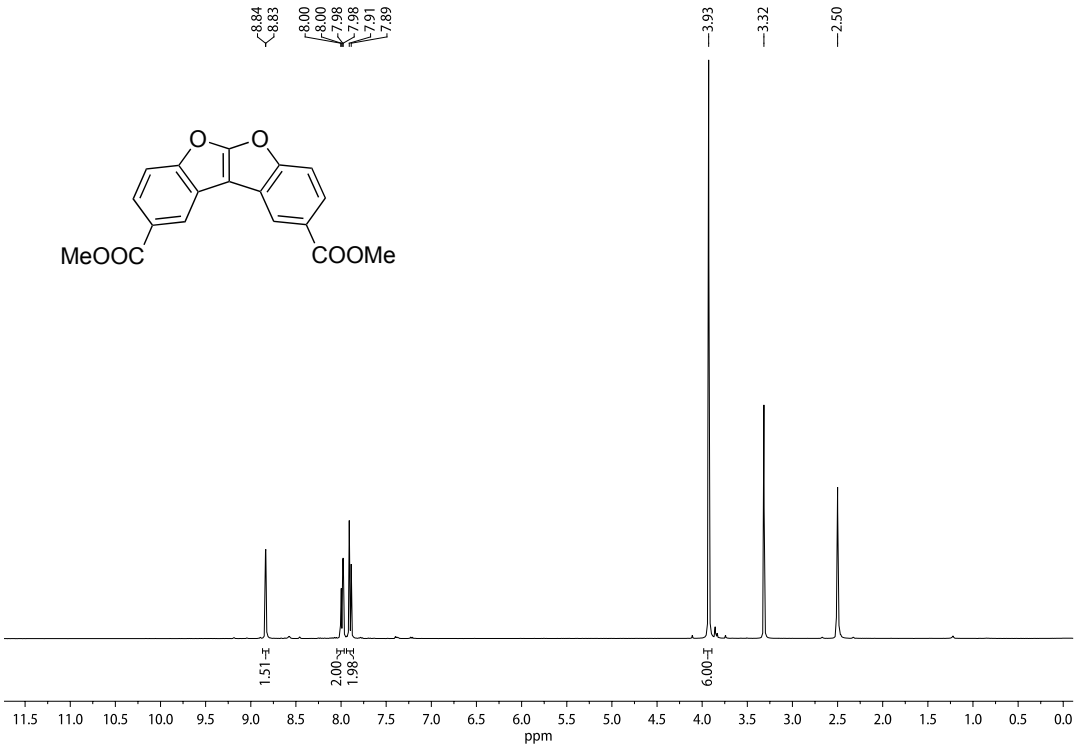
^{13}C NMR spectrum (DMSO-d^6, 101 MHz) of **4**



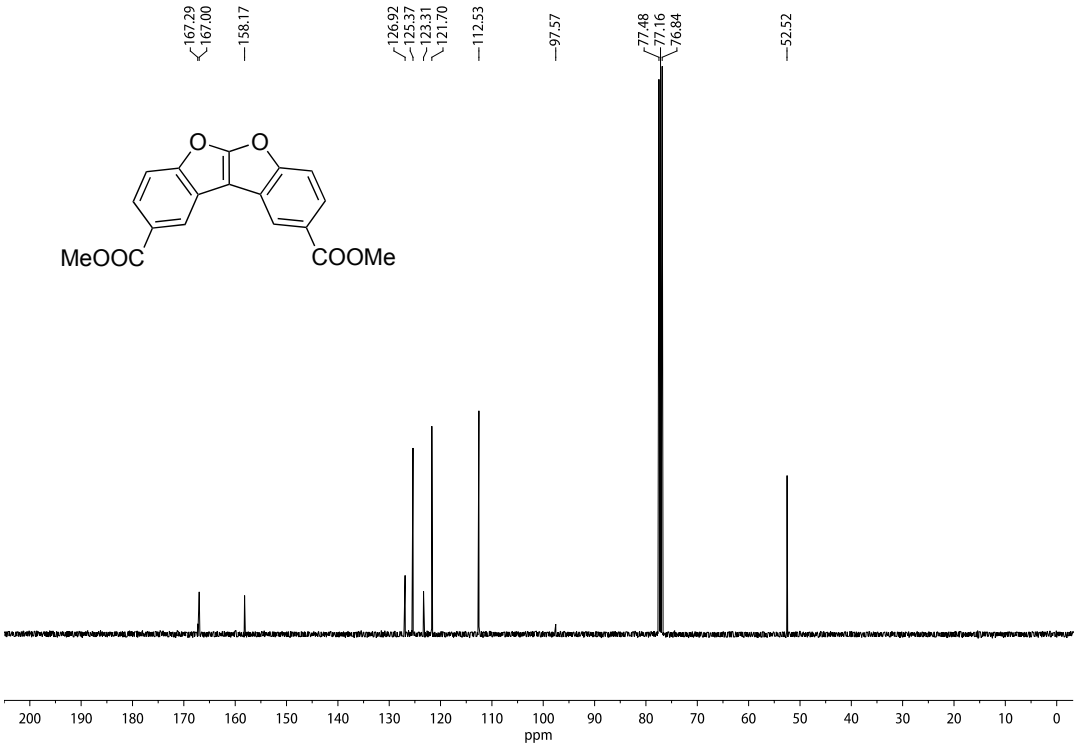
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5**



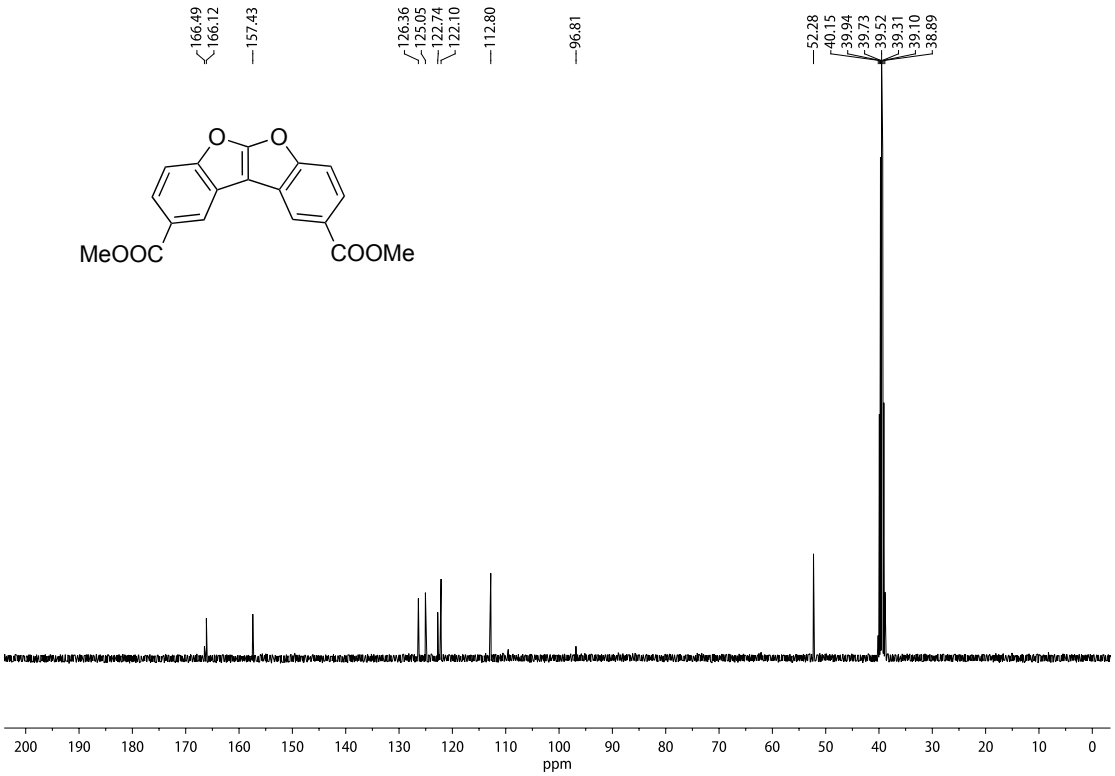
^{1}H NMR spectrum (DMSO-d^6, 400 MHz) of **5**



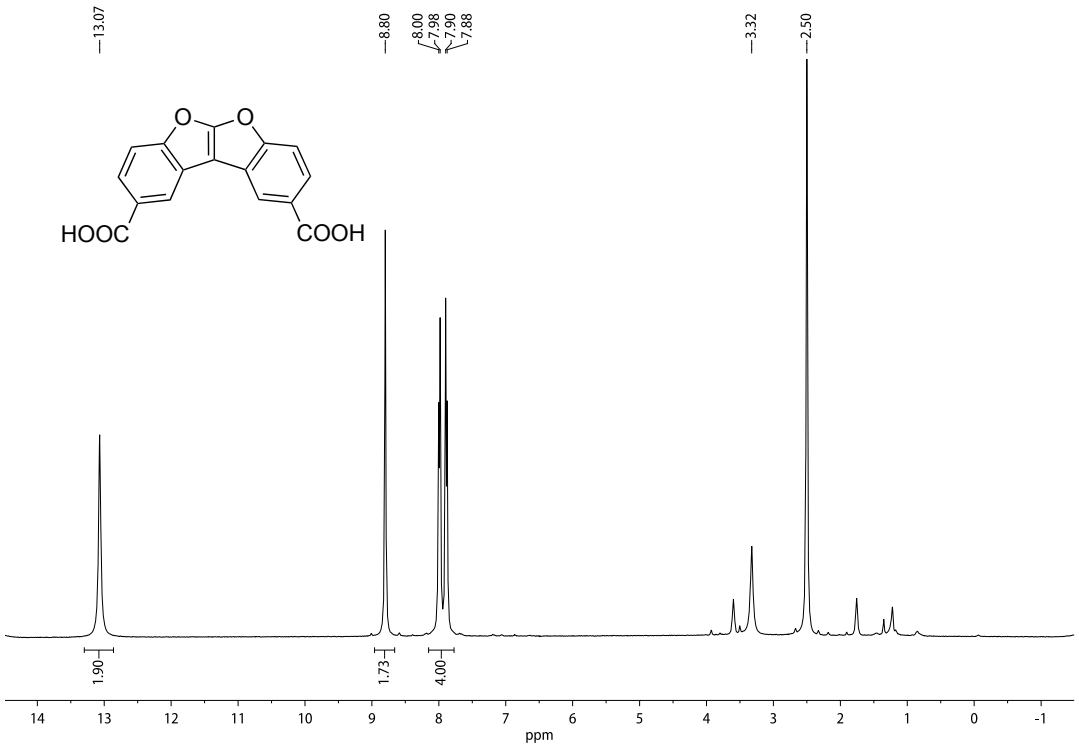
^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **5**



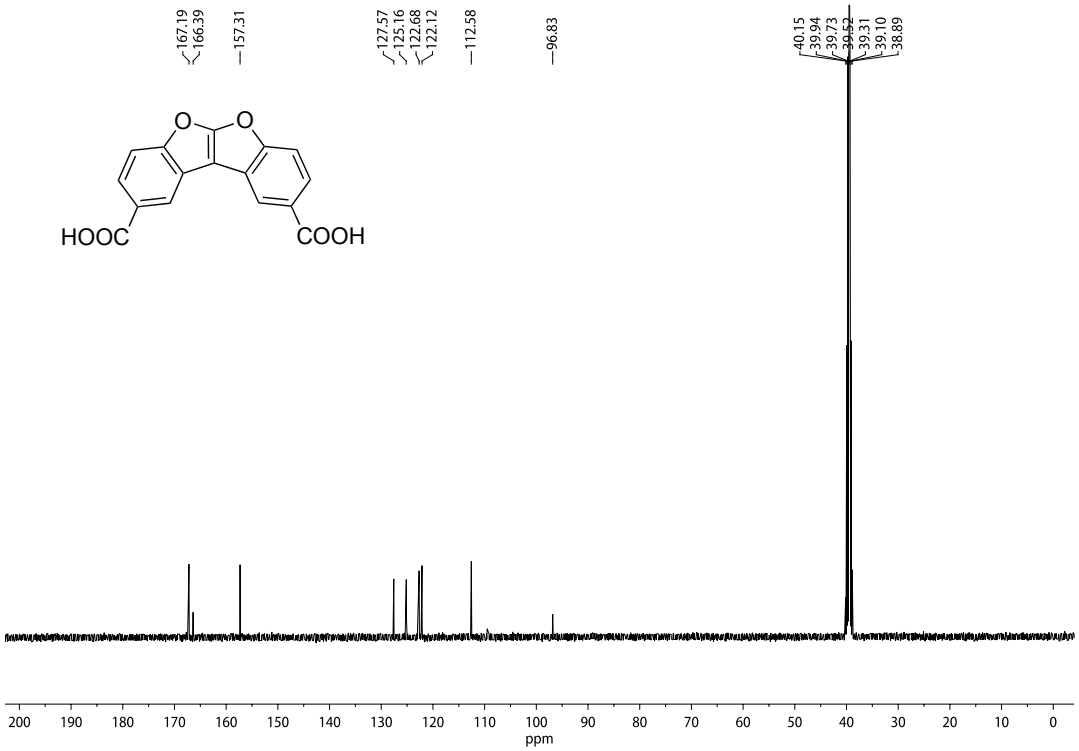
^{13}C NMR spectrum (DMSO-d^6, 101 MHz) of **5**



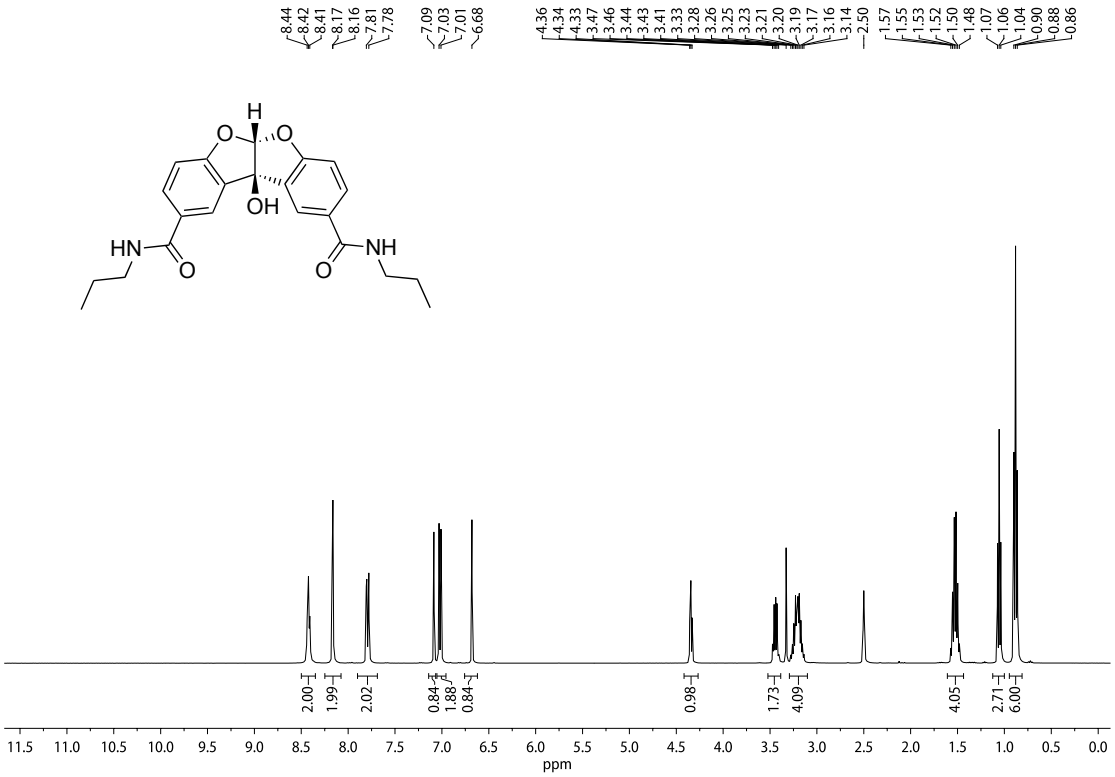
^{1}H NMR spectrum (DMSO-d^{6}, 400 MHz) of **2**



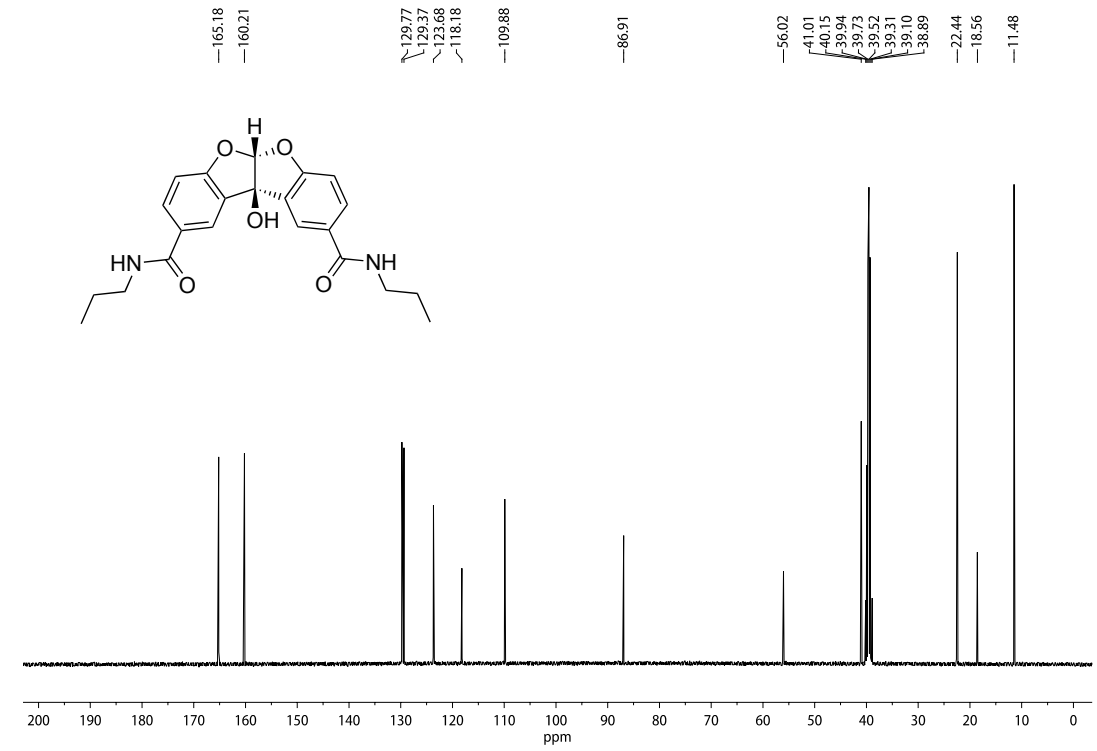
^{13}C NMR spectrum (DMSO-d^{6}, 101 MHz) of **2**



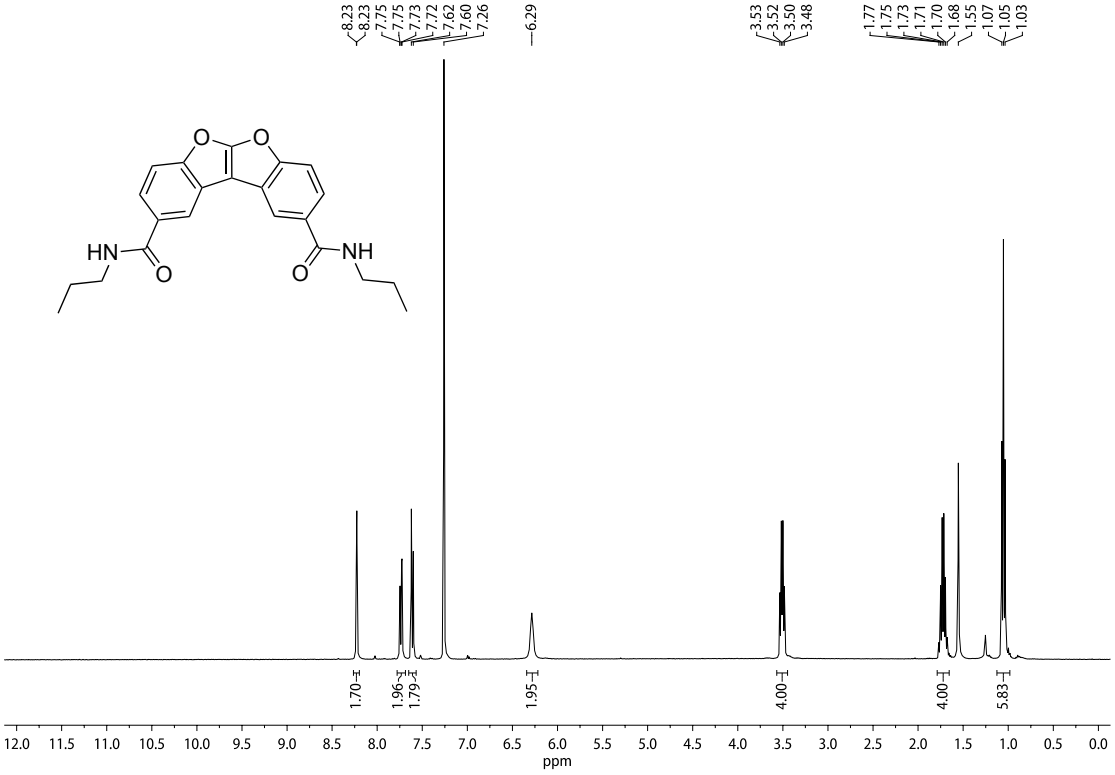
^{1}H NMR spectrum (DMSO-d^{6}, 400 MHz) of model compound **6** (co-crystals with EtOH)



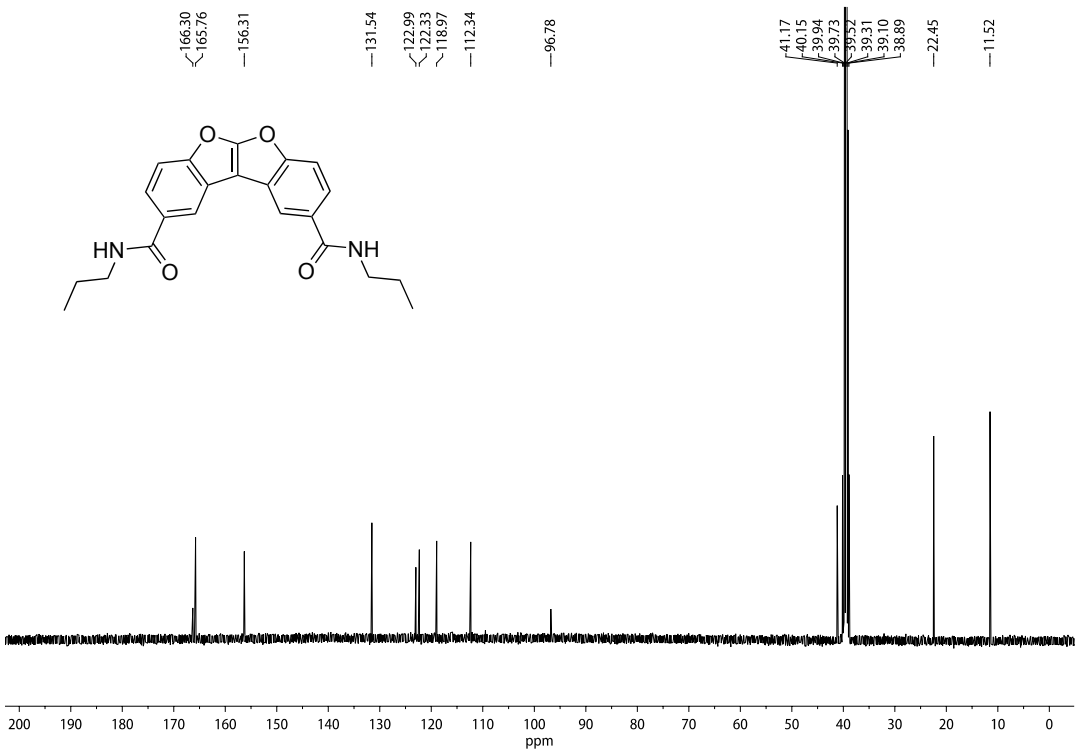
^{13}C NMR spectrum (DMSO-d^{6}, 101 MHz) of model compound **6** (co-crystals with EtOH)



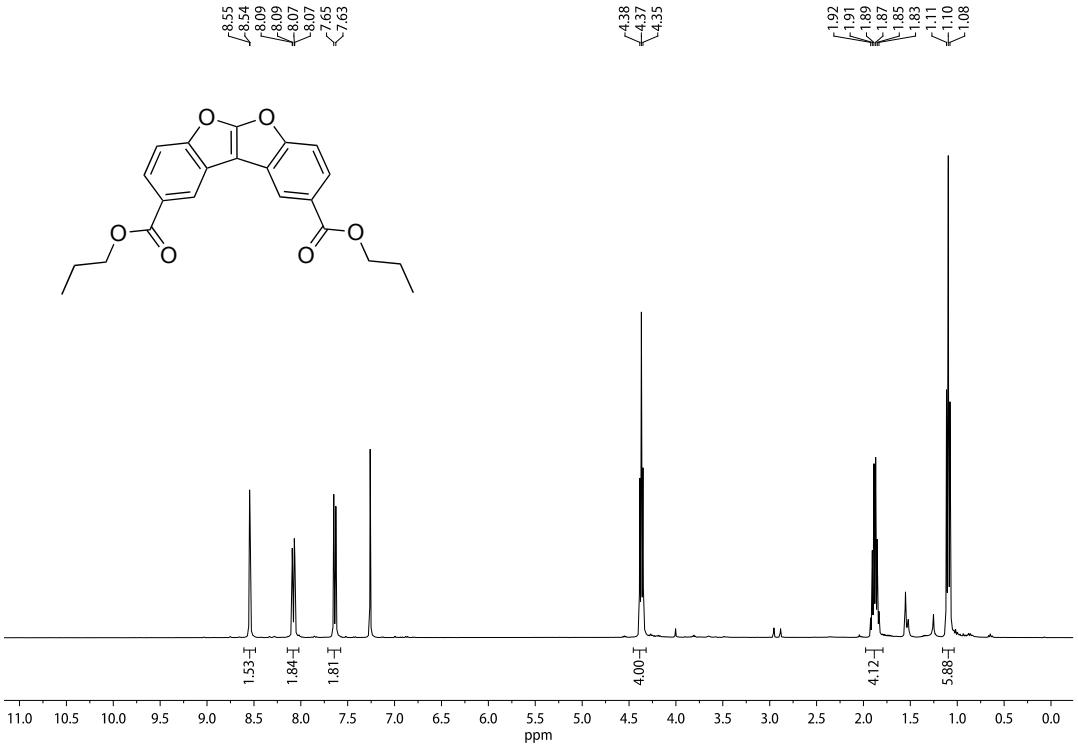
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of model compound **7**



^{13}C NMR spectrum (DMSO-d^6, 101 MHz) of model compound **7**



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of model compound **8**



^{13}C NMR spectrum (DMSO-d^6, 101 MHz) of model compound **8**