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Indacenodithienothiophene based chromophore with cyclopentadienylidenehydrazine acceptor moieties

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Contents

1. Experimental Section

1.1 Materials and characterization

^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ with tetramethylsilane as an internal reference standard or at 500 and 125 MHz in DMSO-d_6. High resolution mass spectra (HRMS) were recorded using an ESI-TOF spectrometer. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet probe). Column chromatography was performed with SiO_2 (230−400 mesh).

Sodium 1-amino-2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienide[S1] and IDTT[S2] were synthesized according to the literature procedures, other reagents were obtained from commercial suppliers and used without additional purification. Absorption profiles were recorded with a multifunctional spectrometer ALS01M. Measurement in a solution was carried out at room temperature in chloroform (2.5×10^{-5} M). Films were cast from chloroform solutions on quartz substrates.

Cyclic voltammetry measurements were performed in 1:4 MeCN:*o*-$C_6H_4Cl_2$ solution using 0.1 M Bu_4NPF_6 as supporting electrolyte and using IPC-Pro M potentiostate. The scan rate was 200 mV s^{-1}. The glassy carbon electrode was used as a work electrode. Potentials were measured relative to a saturated calomel electrode (SCE). The HOMO and LUMO energy levels were calculated using the first standard formal oxidation and reduction potentials obtained from the CV experiment according to the following equations: LUMO=e(φ_{red}+4.40) (eV) and HOMO=-e(φ_{ox}+4.40) (eV).[S3,S4]

1.2 Synthesis

2,8-Bis{2-[2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopenta-2,4-dien-1-ylidene]hydrazino}-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-*d*:2′,3′-*d*′]-*s*-indaceno-[1,2-*b*:5,6-*b*']dithiophene 1. A 2 M solution of *n*-BuLi in cyclohexane (2.6 mmol, 1.3 ml) was added to a solution of IDTT **2** (1.0 mmol, 1.02 g) in absolute THF (10 ml) at 0°C under inert atmosphere. The mixture was allowed to warm up to an ambient temperature and was stirred for 30 min. The resulting solution of organolithium compound was syringed dropwise within 15 min to a solution of dimethyl 2-diazo-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate **3** (3.0 mmol, 1,08 g) in 10 ml of absolute THF at –78°C under inert atmosphere. After warming up to a room temperature, trifluoroacetic acid (0.3 ml) was added. The resulting mixture was treated with brine and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, the solvent was removed *in vacuo*, and the residue was subjected to chromatography to give the desired product (1.18 g, 68%). HRMS (m/z): $[M + H]^+$ calcd for $C_{110}H_{106}N_4O_8S_4$, 1740.6998, Found, 1740.6987. mp: 220–225°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ[ppm] 15.41 (s, 2H, NH), 7.51 (s, 2H), 7.28 –7.22 (m, 12H), 7.20 – 7.13 (m, 12H), 7.08 (s, 2H),7.06 – 7.00 (m, 8H), 3.84 (s, 6H), 3.57 (s, 6H), 2.61 (t, *J* = 7.8 Hz, 8H), 1.69 – 1.59 (m, 8H), 1.41 – 1.31 (m, 24H), 0.91 (t, *J* = 6.7 Hz, 12H).^{13}C NMR(75.5 MHz, $CDCl_3$) δ [ppm] 168.6 (2 CO_2Me), 166.0(2 CO_2Me), 154.5, 153.6, 149.3, 147.0, 142.1, 141.9, 141.3, 140.9, 140.1, 140.1, 136.1, 135.9, 134.1, 129.8, 129.5, 129.5, 129.4, 128.6, 128.0, 127.7, 127.6, 127.4, 127.1, 116.7, 109.9, 105.8, 62.9, 52.1, 51.9, 35.6, 31.7, 31.3, 29.2, 22.6, 14.1.

Tetramethyl 5-amino-3-methoxycyclopenta-1,4-diene-1,2,3,4-tetracarboxylate 7. Sodium 1-amino-2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienide **5** (0.60 mmol, 0.20 g) and TFA (1.8 mmol, 135 μl) were added to absolute MeOH (3 ml). The solution was cooled to 0 °C, and isoamyl nitrite (0.90 mmol, 120 μl) was added. The mixture was allowed to warm up to an ambient temperature and was stirred for 2 h. The resulted mixture was treated with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, the solvent was removed *in vacuo*, and the residue was subjected to column chromatography (CH_2Cl_2) to give the desired product **7** (0.15 g, 70%). HRMS: calcd for $C_{14}H_{17}NO_9$ $[M + Na]^+$ 366.0796, found: *m/z* 366.800; mp: 178–179°C. MS (m/z (relintens, %)) 343 (67%, M^+), ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] 7.40 (br. s, 1H, NH), 6.85 (br. s, 1H, NH), 3.88 (s, 3H), 3.86 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ [ppm] 167.6, 165.5, 163.1, 162.0, 158.6, 152.0, 129.9, 93.5, 89.6, 53.1, 53.0, 52.9, 52.0, 50.9.

2. Supporting figures

2.1 NMR and HRMS spectra.

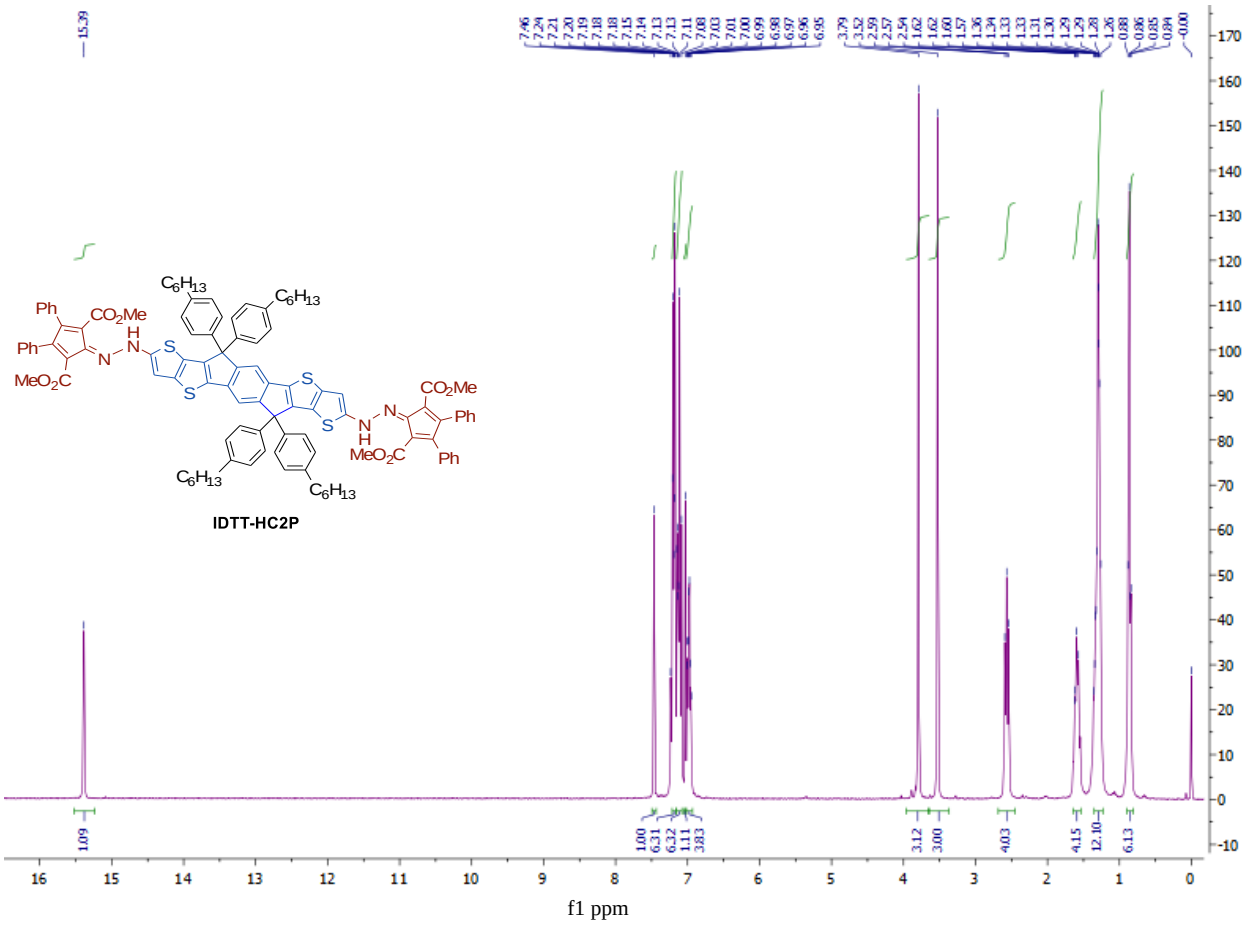

Figure S1. ^{1}H NMR spectrum of compound **1** (**IDTT-HC2P)** (300 MHz, $CDCl_3$).

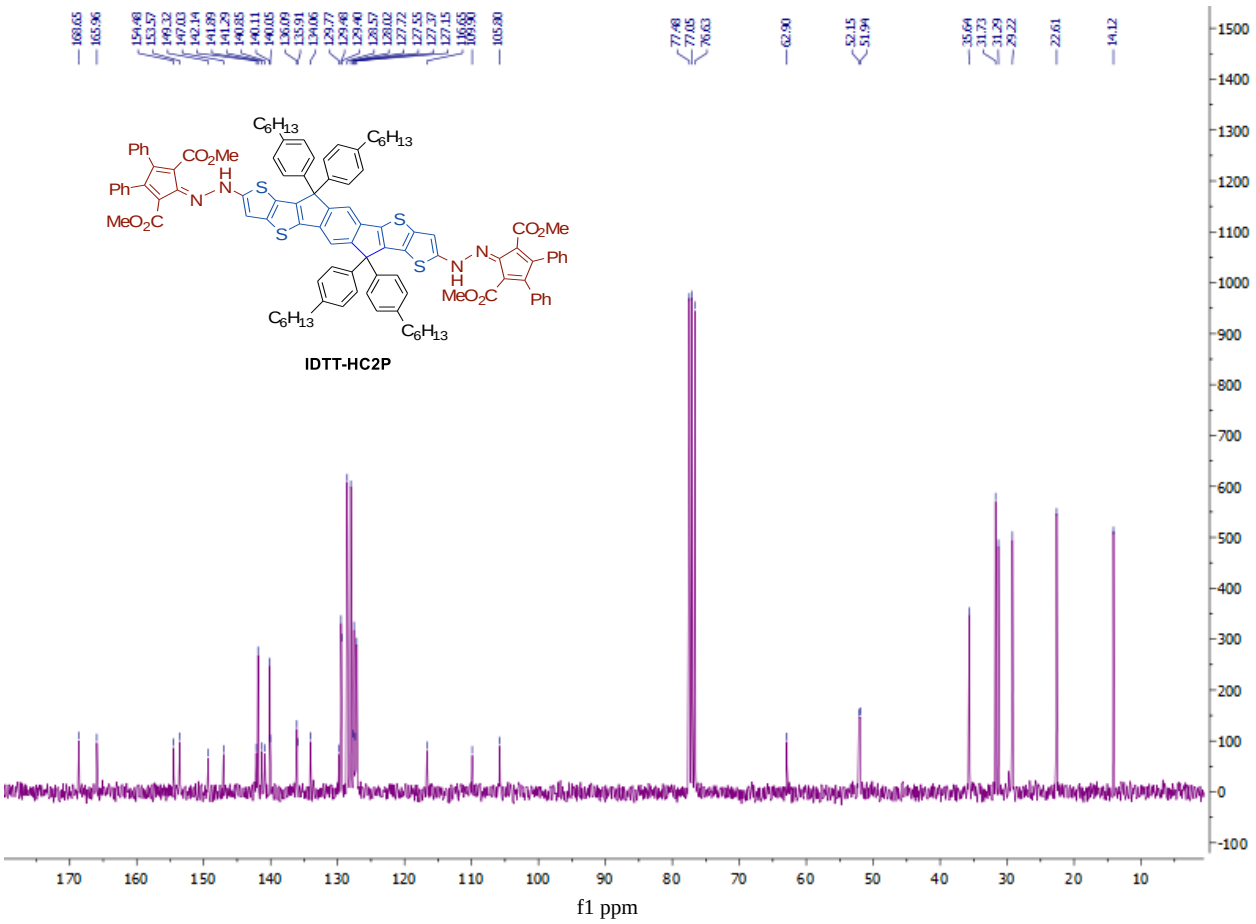

Figure S2. ^{13}C NMR spectrum of compound **1** (**IDTT-HC2P)** (75.5 MHz, $CDCl_3$).

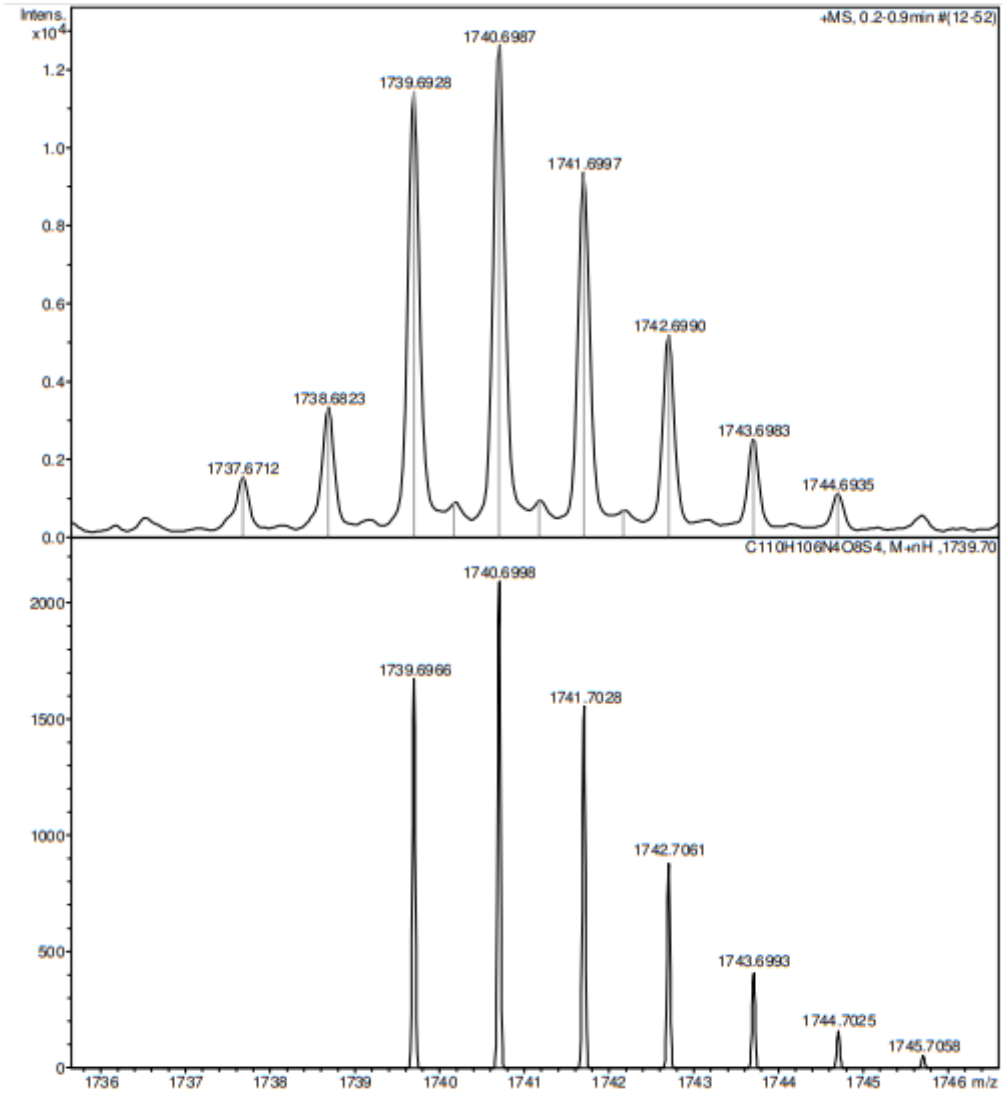

Figure S3. HRMS spectrum of compound **1 (IDTT-HC2P)**

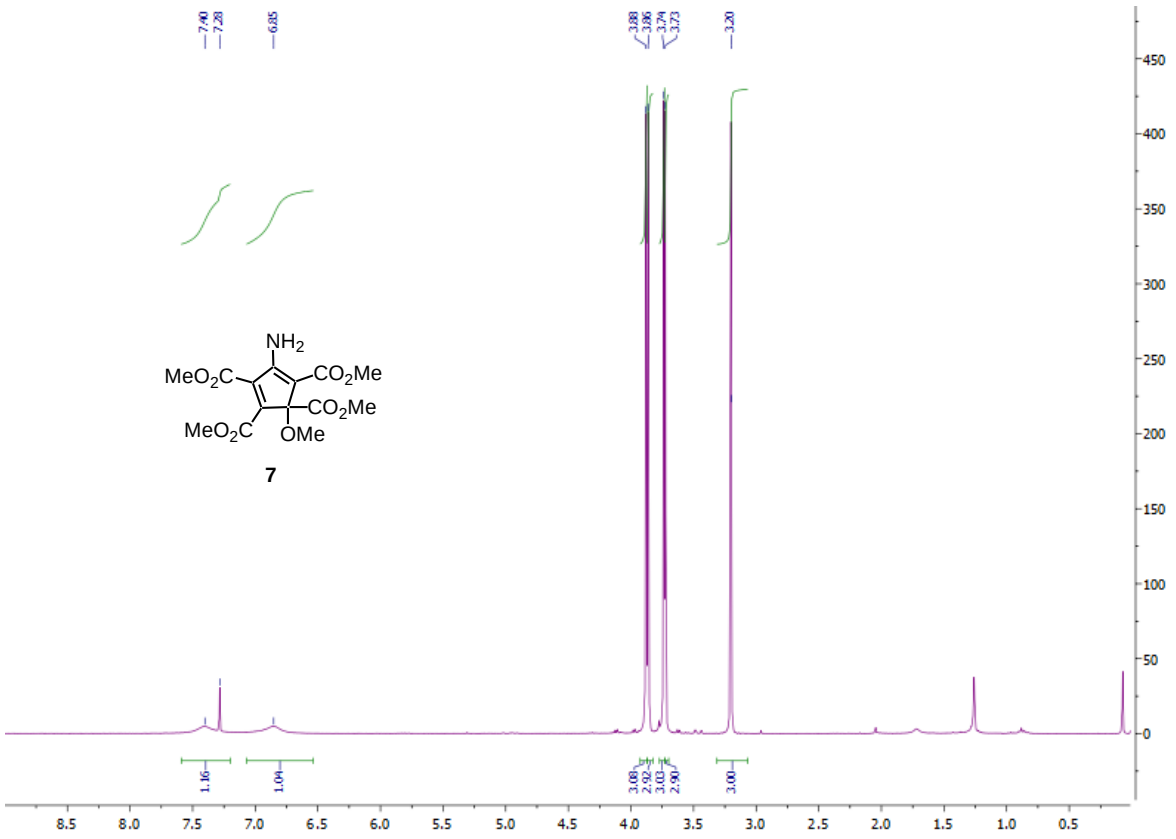

Figure S4. ^{1}H NMR spectrum of compound **7** (300 MHz, $CDCl_3$).

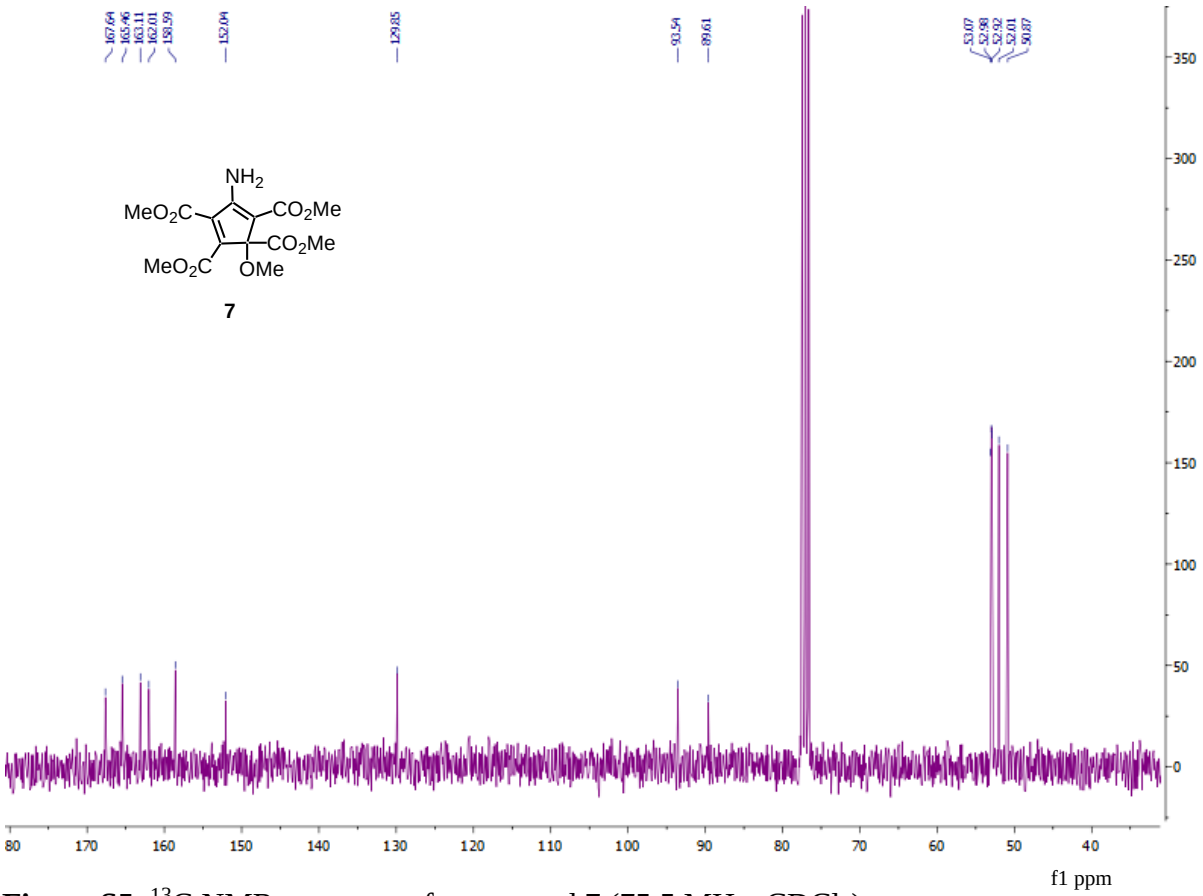

Figure S5. ^{13}C NMR spectrum of compound **7** (75.5 MHz, $CDCl_3$).

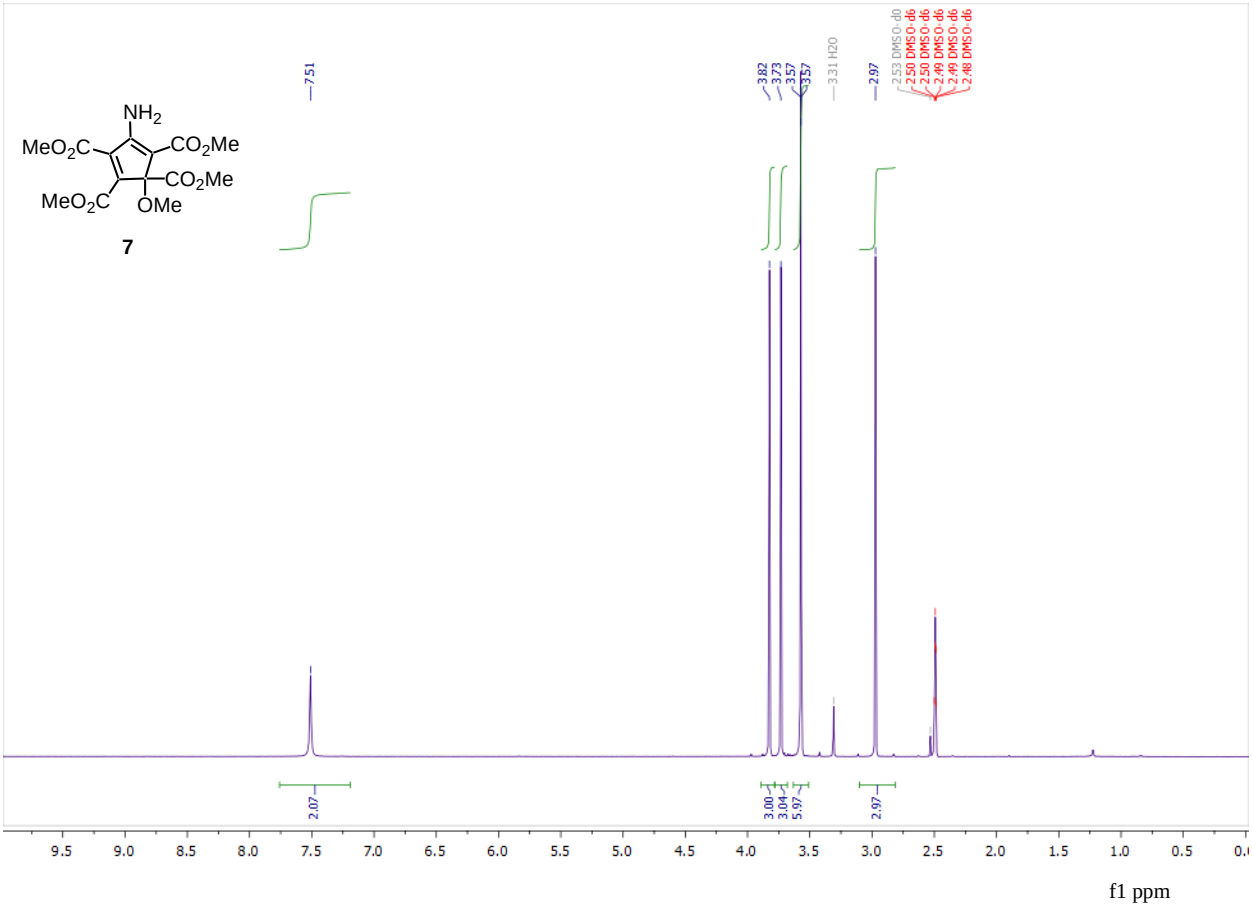

Figure S6. ^{1}H NMR spectrum of compound **7** (500 MHz, DMSO–d_6).

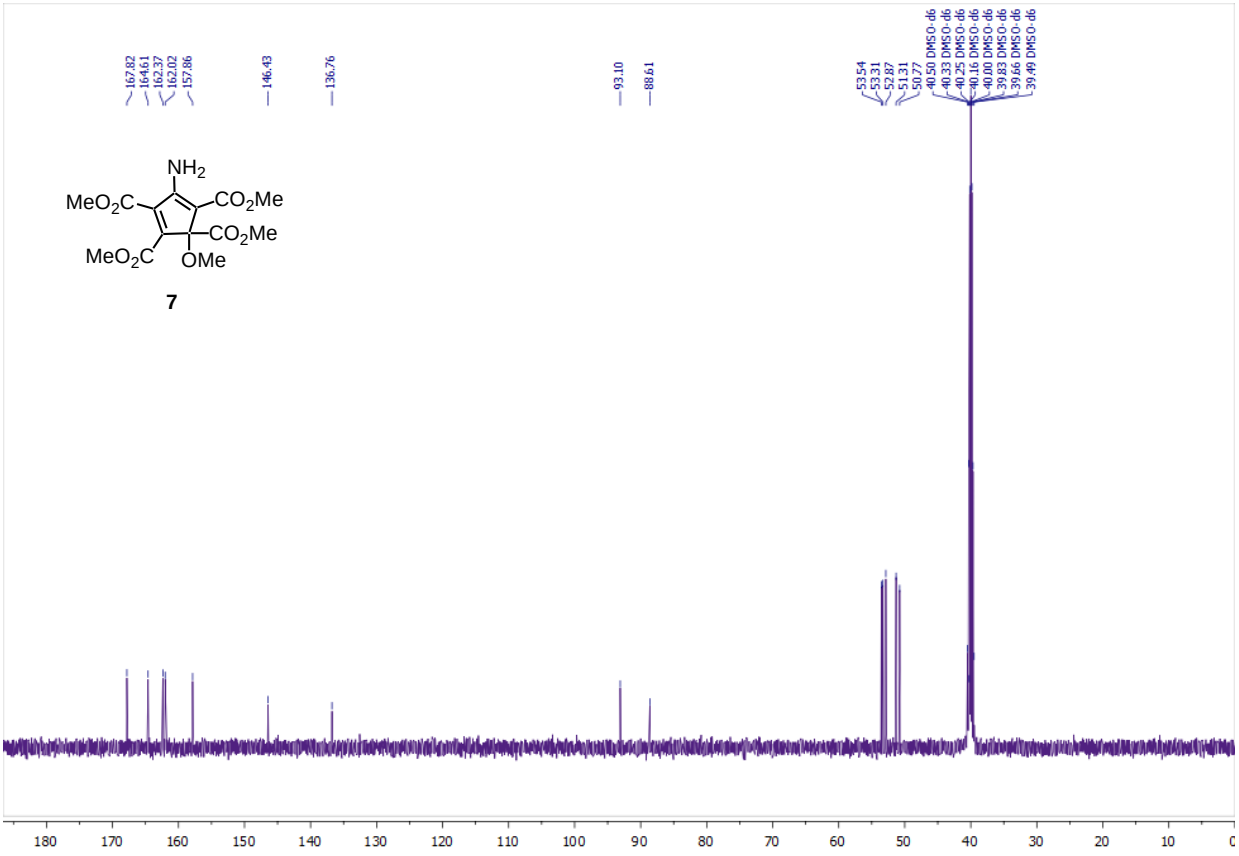

Figure S7. ^{13}C NMR spectrum of compound **7** (125 MHz, DMSO–d_6).

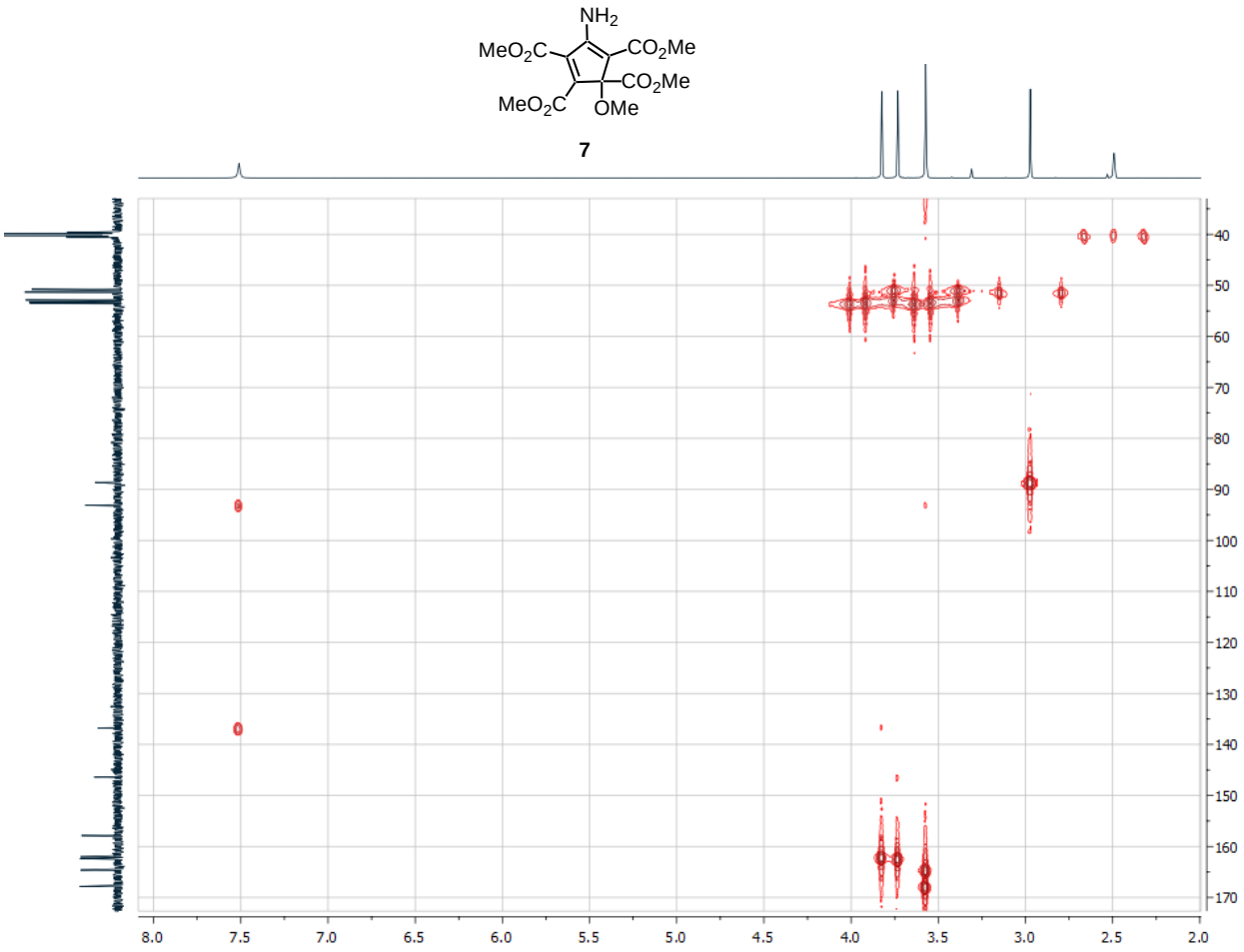

Figure S8. $^{1}H–^{13}C$ HMBC NMR correlation spectrum of compound **7**

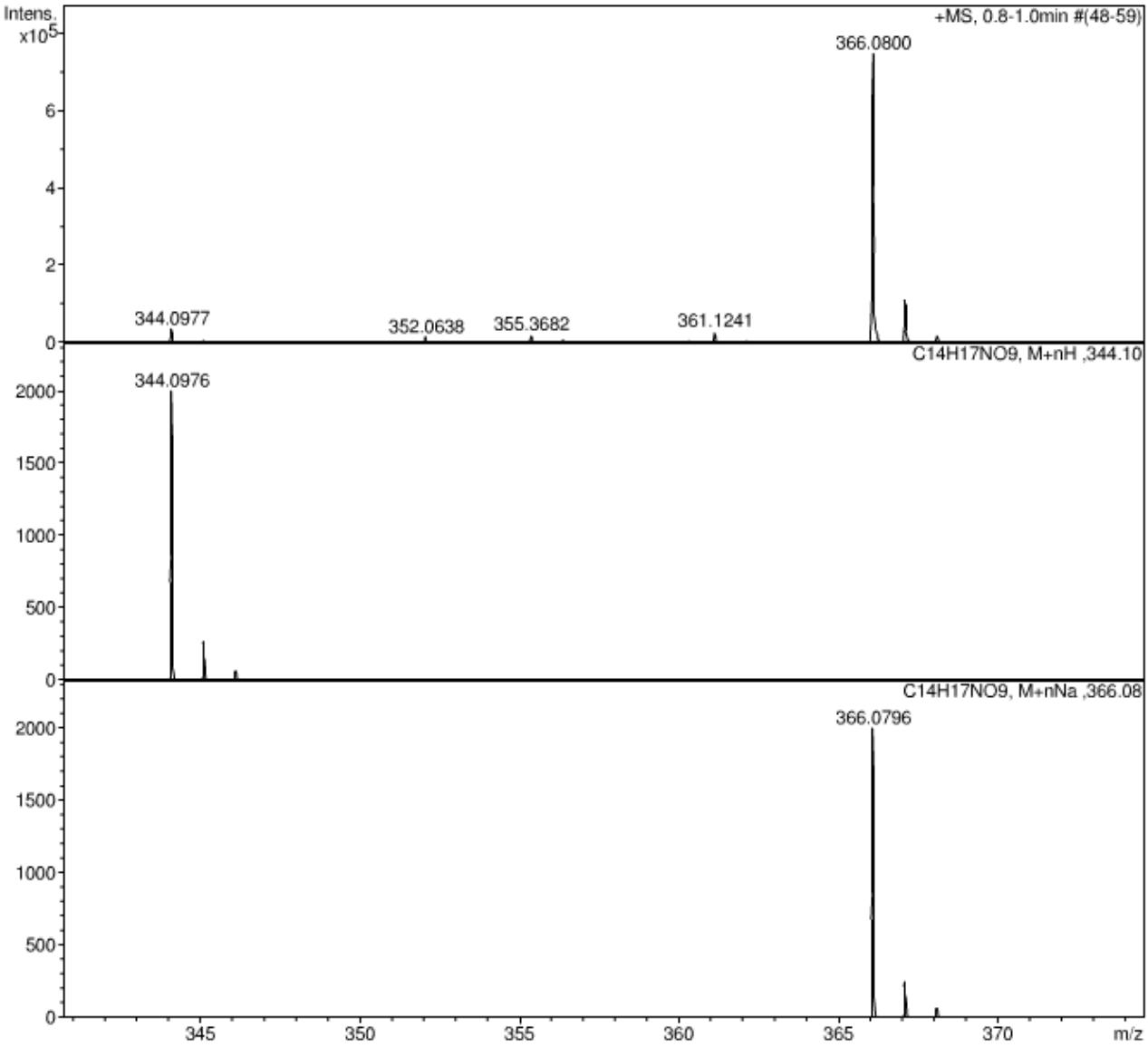

Figure S9. HRMS spectrum of compound **7**

3. References

S1. R. W. Hoffmann and J. Backes, *Chem. Ber.*, 1976, **109**, 1928

S2. Y.-X. Xu, C.-C. Chueh, H.-L. Yip, F.-Z. Ding, Y.-X. Li, C.-Z. Li, X. Li, W.-C. Chen and A. K.-Y. Jen, *Adv. Mater*., 2012, **24**, 6356.

S3. S. A. Ponomarenko, S. Kirchmeyer, A. Elschner, N. M. Alpatova, M. Halik, H. Klauk, U. Zschieschang and G. Schmid, *Chem. Mater*., 2006, **18**, 579.

S4. S. A. Ponomarenko, N. N. Rasulova, Y. N. Luponosov, N. M. Surin, M. I. Buzin, I. Leshchiner, S. M. Peregudova, and A. M. Muzafarov, *Macromolecules*, 2012, **45**, 2014.