Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 384–385

Diene-transmissive hetero-Diels–Alder reaction of distyryl thioketone

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Experimental procedures

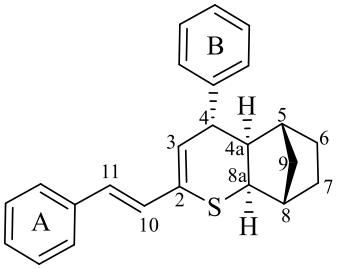
General information

All commercially available reagents and solvents were used as purchased. The stated yields are based on isolated material. Melting points were measured using an Electrothermal IA 9300 Series melting point apparatus. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance III 400 spectrometer (400 and 101 MHz, respectively) using residual solvent signals ($CDCl_3$: 7.25 ppm for ^{1}H and 77.0 ppm for ^{13}C nuclei; DMSO-d_6: 2.50 ppm for ^{1}H and 39.9 ppm for ^{13}C nuclei) as internal standard. High-resolution mass spectra recorded on a TripleTOF 5600+ mass spectrometer (electrospray ionization). Monitoring of the reaction progress was done by TLC on Sulifol 201S plates (eluent petroleum ether – EtOAc, 3:1).

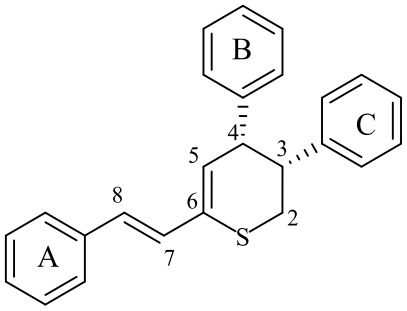
X-ray structural analysis of compound **3** was carried out at 100 K on a Bruker D8 QUEST (graphite monochromated MoKα radiation, ω-scanning) diffractometers according to the standard routine. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of solutions of compounds in CH_2Cl_2. The structures of compounds were solved by the direct method using the SHELXS[S1] and Superflip[S2] programs. The structures were refined using the SHELXL[S3] program included in the OLEX software package.[S4] The full set of X-ray structural data for compound **3** was deposited at the Cambridge Crystallographic Data Center (deposits CCDC 2123430).

General procedure for synthesis 2 and 3

The corresponding dienophile (4.3 mmol) and the Lawesson's reagent (2.3 mmol) were added to a solution of dibenzalacetone **1** (4.3 mmol) in anhydrous PhMe (20 ml). The resulting mixture was stirred at 75 °C for 8 h (80 ºC in water bath). The progress of the reaction was monitored by TLC. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on SiO_2, eluent CH_2Cl_2. After evaporation of the solvent, the residue was treated with Et_2O to afford a crystalline product.

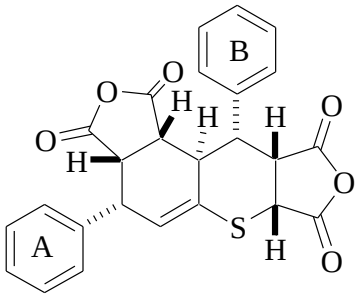


***rac*-(4*R*,4a*R*,5*R*,8*S*,8a*R*)-4-Phenyl-2-styryl-4a,5,6,7,8,8a-hexahydro-4*H*-5,8-methano-thiochromene (2)**[S5] was prepared according general method, using norbornene as dienophile, crystalline product was recrystallized from a EtOH. Yield: 0.59 g (40%), m. p. = 119-119.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51 – 7.12 (m, 10H, H Ar), 6.98 (d, *J*=15.7 Hz, 1H, 11-CH), 6.81 (d, *J*=15.7 Hz, 1H, 10-CH), 6.30 (d, *J*=4.3 Hz, 1H, 3-CH), 3.19 (dd, *J*=10.8, 4.3 Hz, 1H, 4-CH), 3.11 (dd, *J*=7.3, 1.5 Hz, 1H, 8a-CH), 2.35 (d, *J*=4.5 Hz, 1H, 5-CH), 2.43 – 2.22 (m, 1H, 9-CH_2), 2.10 (d, *J*=4.5 Hz, 1H, 8-CH), 1.97 (ddd, *J* = 10.8, 7.3, 1.4 Hz, 1H, 4a-CH), 1.65 (tt, *J*=12.0, 4.4 Hz, 1H, 7-CH_2), 1.46 (tt, *J*=12.0, 4.4 Hz, 1H, 6-CH_2), 1.35 – 1.23 (m, 1H, 7-CH_2), 1.25 – 1.15 (m, 1H, 9-CH_2), 1.14 – 0.99 (m, 1H, 6-CH_2). ^{13}C NMR(101 MHz, $CDCl_3$): δ (ppm) 144.9 (C, 2-C), 137.1 (C, C-1 Ph_A), 137.0 (C, C-1 Ph_B), 136.1 (CH, 3-C), 129.0 (2CH, C-3,5 Ph_A), 128.7 (2CH, C-2,6 Ph_B), 128.6 (CH, 11-C), 128.5 (3CH, 10-C, 2CH, C-3,5 Ph_B), 127.5 (CH, C-4 Ph_A), 126.6 (2CH, C-2,6 Ph_A), 126.5 (CH, C-4 Ph_B), 58.7 (CH, 4a-C), 50.8 (CH, 8a-C), 49.0 (CH, 4-C), 43.7 (CH, 5-C), 41.3 (CH, 8-C), 34.1 (CH_2, 9-C), 29.8 (CH_2, 6-C), 29.2 (CH_2, 7-C). HRMS (ESI+): Exact mass calculated for $C_{24}H_{22}S$ $[M+H]^+$: 345.1672, found 345.1671.



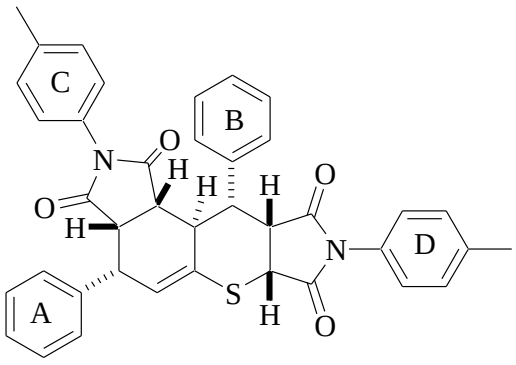
***cis*-3,4-Diphenyl-6-styryl-3,4-dihydro-2*H*-thiopyran (3)** was prepared according general method using styrene as dienophile, crystalline product was recrystallized from a EtOH. Yield: 0.71 g (47%), m. p. = 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53 – 7.44 (m, 2H, H-3,5 Ph_A), 7.38 – 7.32 (m, 2H, H-2,6 Ph_A), 7.30 – 7.22 (m, 1H, H-4, Ph_A), 7.22 – 7.07 (m, 6H, H-2,4,6Ph_B, H-3,4,5 Ph_C), 6.96 – 6.79 (m, 2H, 7-CH, 8-CH), 6.77 – 6.68 (m, 4H, H-2,6 Ph_C, H-3,5 Ph_B), 6.22 (d, *J* = 6.4 Hz, 1H, 5-CH), 3.87 (dd, *J* = 6.4, 4.7 Hz, 1H, 4-CH), 3.61 (ddd, *J*=12.3, 4.7, 2.4 Hz, 1H, 3-CH), 3.43 (t, *J* = 12.3 Hz, 1H, 2-CH_2), 2.85 (dt, *J* = 12.3, 1.9 Hz, 1H, 2-CH_2). ^{13}C NMR(101 MHz, $CDCl_3$): δ (ppm) 142.3 (C, C-1 Ph_C), 139.5 (C, C-1 Ph_B), 137.0 (C, C-1 Ph_A), 131.9 (CH, 6-C), 130.3 (2CH, C-3,5 Ph_B), 129.0 (CH, 8-C), 128.7(2CH, C-2,6 Ph_A), 128.5 (CH, 7-C), 127.9 (4CH, C-2,3,5,6 Ph_C), 127.7 (CH, C-4 Ph_A), 127.5 (2CH, C-2,6 Ph_B), 126.8 (2CH, 5-C, C-4 Ph_B), 126.6 (3CH, C-4 Ph_B, C-3,5 Ph_A), 47.3 (CH, 4-C), 44.3 (CH, 4-C), 25.3 (CH_2, 2-C). HRMS (ESI+): Exact mass calculated for $C_{25}H_{22}S$ $[M+H]^+$: 355.1515, found 355.1514.

General procedure for synthesis of 5a,b. The corresponding dienophile **4** (8.6 mmol) and the Lawesson's reagent (2.3 mmol) were added to a solution of dibenzalacetone **1** (4.3 mmol) in anhydrous PhMe (20 ml). The mixture was stirred at 75 °C for 3 h. The precipitate that formed after cooling was filtered off and recrystallized from the corresponding solvent.

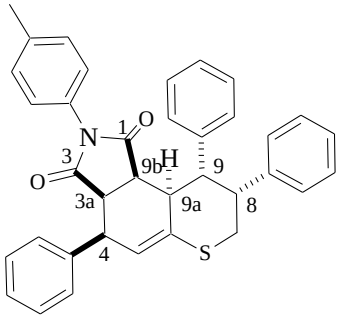


***rac*-(3a*S*,4*R*,6a*R*,9a*R*,10*S*,10a*R*,10b*S*)-4,10-Diphenyl-3a,6a,9a,10,10a,10b-hexahydro-3*H*-thiochromeno[2,3-*c*:5,6-*c'*]-difuran-1,3,7,9(4*H*)-tetraone (5a)** was prepared according general method, using maleic anhydride **4a** as dienophile. The product was recrystallized from a mixture of AcOH and Ac_2O in a 10:1 ratio. Yield: 1.37 g (72%), mp = 251-252 ºC. ^{1}H NMR (400 MHz, dmso-d_6): δ (ppm) 7.66 – 7.58 (m, 2H, H-2,6 Ph_B), 7.41 (t, *J*=7.6 Hz, 2H, H-3,5 Ph_B), 7.35 – 7.20 (m, 6H, H-2,3,4,5,6 Ph_A, H-4 Ph_B), 6.75 (dd, *J*=4.6, 2.3 Hz, 1H, 5-CH), 4.75 (d, *J*=10.2 Hz, 1H, 6a-CH), 4.25 (dd, *J*=12.8, 3.8 Hz, 1H, 10-CH), 4.15-4.21 (m, 1H, 4-CH), 4.02 (dd, *J*=10.2, 3.8 Hz, 1H, 9a-CH), 3.80 – 3.52 (m, 2H, 3a-CH, 10b-CH), 3.35 – 3.25 (m, 1H, 10a-CH). ^{13}C NMR (101 MHz, dmso-d_6): δ (ppm) 172.3 (7-C=O), 171.5 (1-C=O), 170.8 (3-C=O, 9-C=O), 138.1 (C, C-1 Ph_A), 138.0 (C, C-1 Ph_B), 132.3 (C, 5a-C), 132.0 (CH, 5-C), 130.1 (2CH, C-2,6 Ph_B), 128.9 (2CH, C-2,6 Ph_A), 128.7 (2CH, C-3,5 Ph_B), 128.6 (2CH, C-3,5 Ph_A), 127.8 (CH, C-4 Ph_B), 127.4 (CH, C-4 Ph_A), 48.7 (CH, 3a-C), 47.2 (CH, 9a-C), 45.6 (CH, 6a-C), 44.1 (CH, 10b-C), 42.2 (CH, 4-C), 40.7 (CH, 4-C), 37.7 (CH, 10a-C). HRMS (ESI+): Exact mass calculated for $C_{25}H_{18}O_6S$ $[M+H]^+$: 447.0897, found 447.0888.

***rac*-(3a*S*,4*R*,6a*R*,9a*R*,10*S*,10a*R*,10b*S*)-4,10-Diphenyl-2,8-di-*p*-tolyl-3a,6a,9a,10,10a,10b-hexahydro-1*H*-pyrrolo[3',4':5,6]thiopyrano[3,2-*e*]-isoindole-1,3,7,9(2*H*,4*H*,8*H*)-tetraone (5b)** was prepared according general method, using *N*-(*p*-tolyl)-maleimide **4b** as dienophile, product was recrystallized from a AcOH. Yield: 2.40 g (90%), mp = 290-291 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, *J*=7.8 Hz, 1H, H-2,6 Ph_B), 7.43 – 7.12 (m, 8H, H-2,3,4,5,6 Ph_A, H-3,4,5 Ph_B), 7.10 – 6.85 (m, 8H, H-2,3,5,6 Ph_C, H-2,3,5,6 Ph_D), 6.75 (dd, *J*=4.8, 1.9 Hz, 1H, 5-CH), 4.49 (d, *J*=9.3 Hz, 1H, 6a-CH), 4.41 (dd, *J*=12.0, 3.3 Hz, 1H, 10-CH), 4.10-4.18 (m, 1H, 4-CH), 3.84 (dd, *J*=9.3, 3.3 Hz, 1H, 9a-CH), 3.51 (t, *J*=7.4 Hz, 1H, 3a-CH), 3.47 – 3.34 (m, 2H, 10a-CH, 10b-CH). ^{13}C NMR(101 MHz, dmso-*d6*): δ (ppm) 176.1 (7-C=O), 175.5 (1-C=O), 175.4 (3-C=O, 9-C=O), 159.4 (2C, C-CH_3 Ph_C, C-CH_3 Ph_D), 139.8 (C, C-1 Ph_B), 139.5 (C, C-1 Ph_A), 132.5 (C, 5a-C), 131.0 (CH, 5-C), 130.5 (2CH, C-2,6 Ph_A), 129.1 (2CH, C-2,6 Ph_B), 128.7 (2CH, C-2,6 Ph_C), 128.6 (2CH, C-2,6 Ph_D), 128.3 (4CH, C-3,5 Ph_A, C-3,5 Ph_B), 127.1 (CH, C-4 Ph_A), 126.8 (CH, C-4 Ph_B), 125.2 (C, N-C Ph_C), 125.0 (C, N-C Ph_D), 114.7 (2CH, C-3,5 Ph_C), 114.5 (2CH, C-3,5 Ph_D), 55.8 ($2CH_3$), 47.8 (CH, 3a-C), 46.2



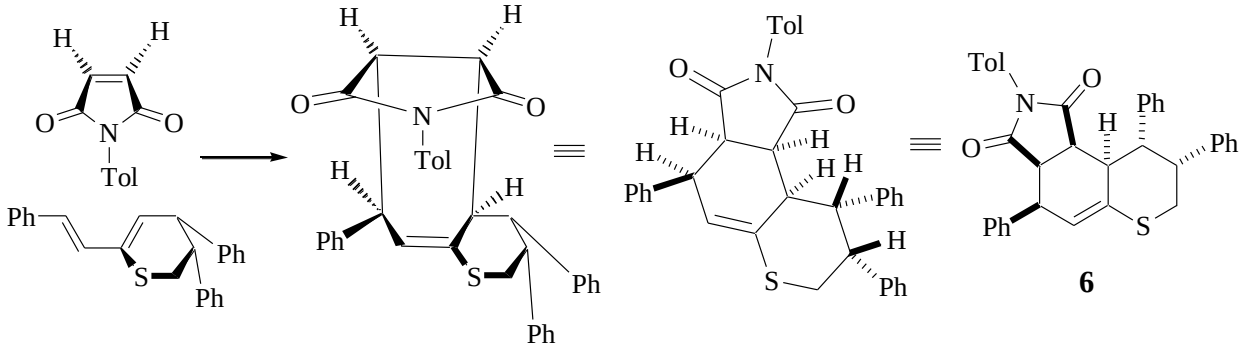
(CH, 9a-C), 45.7 (CH, 6a-C), 42.8 (CH, 4-C), 42.4 (CH, 10b-C), 41.2 (CH, 10-C), 38.8 (CH, 10a-C). HRMS (ESI+): Exact mass calculated for $C_{39}H_{32}N_2O_4S$ $[M+H]^+$: 625.2156, found 625.2150.



rac-(3a*R*,4*S*,8*R*,9*R*,9a*R*,9b*R*)-4,8,9-Triphenyl-2-(*p*-tolyl)-3a,7,8,9,9a,9b-hexahydrothiopyrano[3,2-*e*]isoindole-1,3(2*H*,4*H*)-dione* (6)

The adduct of the reaction with styrene **3** (1.0 g, 2.8 mmol) was added to a solution of *N*-(*p*-tolyl)maleimide **4b** (0.52 g, 2.8 mmol) in *o*-xylene (20 ml). The mixture was then refluxed for 12 h (TLC control). After cooling to room temperature, the solvent was evaporated under reduced pressure, the residue was treated with Et_2O to afford a crystalline product. Yield: 0.78 g (51%), mp = 233-234 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 – 7.06 (m, 14H), 6.80 – 6.68 (m, 4H), 6.57 (d, *J*=8.0 Hz, 2H), 4.63 (d, *J*=3.9 Hz, 1H), 3.64 – 3.52 (m, 2H), 3.46 (q, *J*=5.8, 5.7 Hz, 1H), 3.34 – 3.25 (m, 1H), 2.87 (d, *J*=12.3 Hz, 1H), 2.75 (dd, *J*=16.3, 4.2 Hz, 2H), 2.58 – 2.49 (m, 1H), 2.26 (s, 3H). ^{13}C NMR(101 MHz, dmso-d_6): δ (ppm) 175.6, 175.3, 142.2, 140.9, 138.7, 137.7, 129.8, 129.3, 129.1, 128.3, 128.2, 127.9, 127.8, 127.5, 127.0, 126.8, 126.7, 126.6, 120.9, 47.5, 44.4, 44.3, 43.3, 32.8, 25.0, 20.7. HRMS (ESI+): Exact mass calculated for $C_{36}H_{31}NO_2S$ $[M+H]^+$: 542.2148, found 542.2143.

*****The stereostructure of compound **6** is based on the preserve of the general stereo outcome in the Diels-Alder reaction.



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[S5] S. Motoki, Y. Terauchi and S. Kametani, *Chem. Lett.*, 1988, **17**, 717.

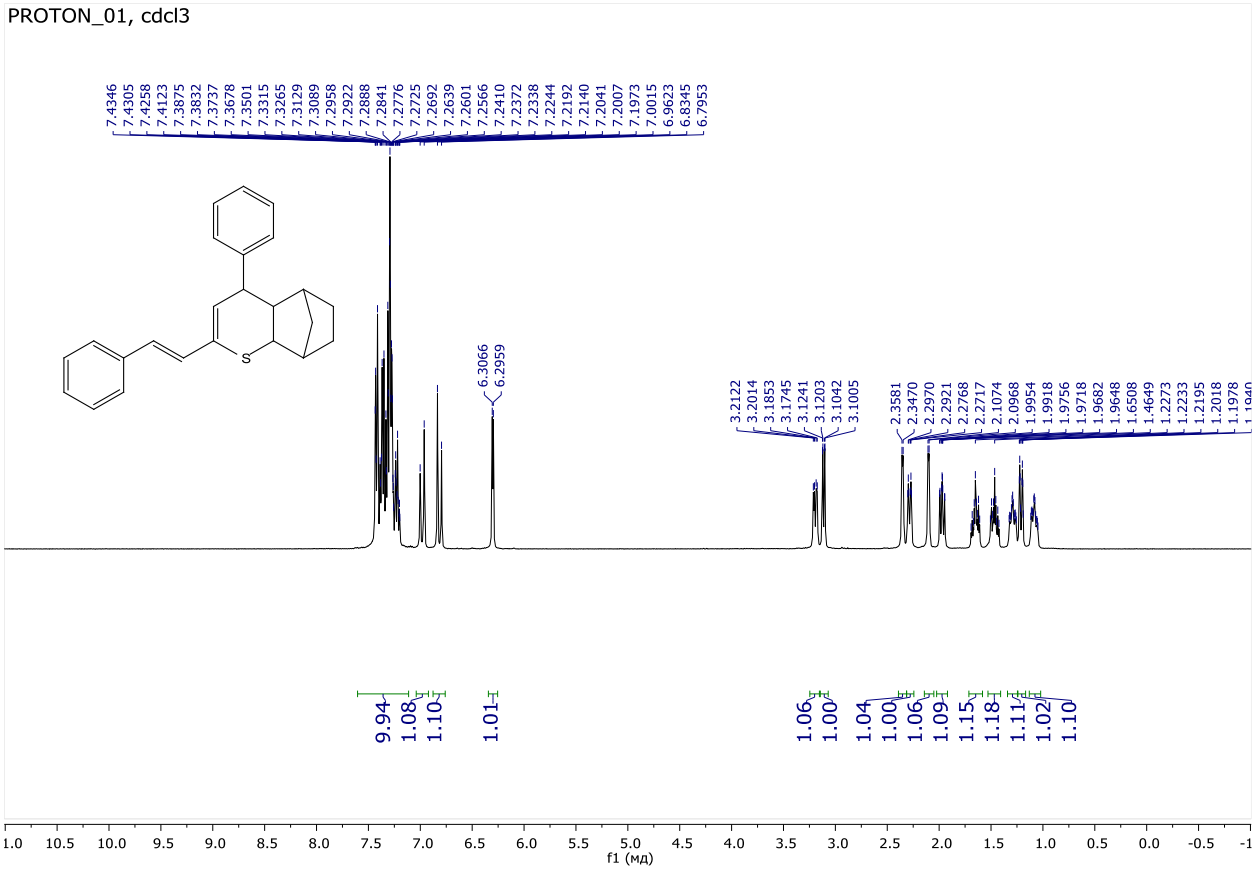

Figure S1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

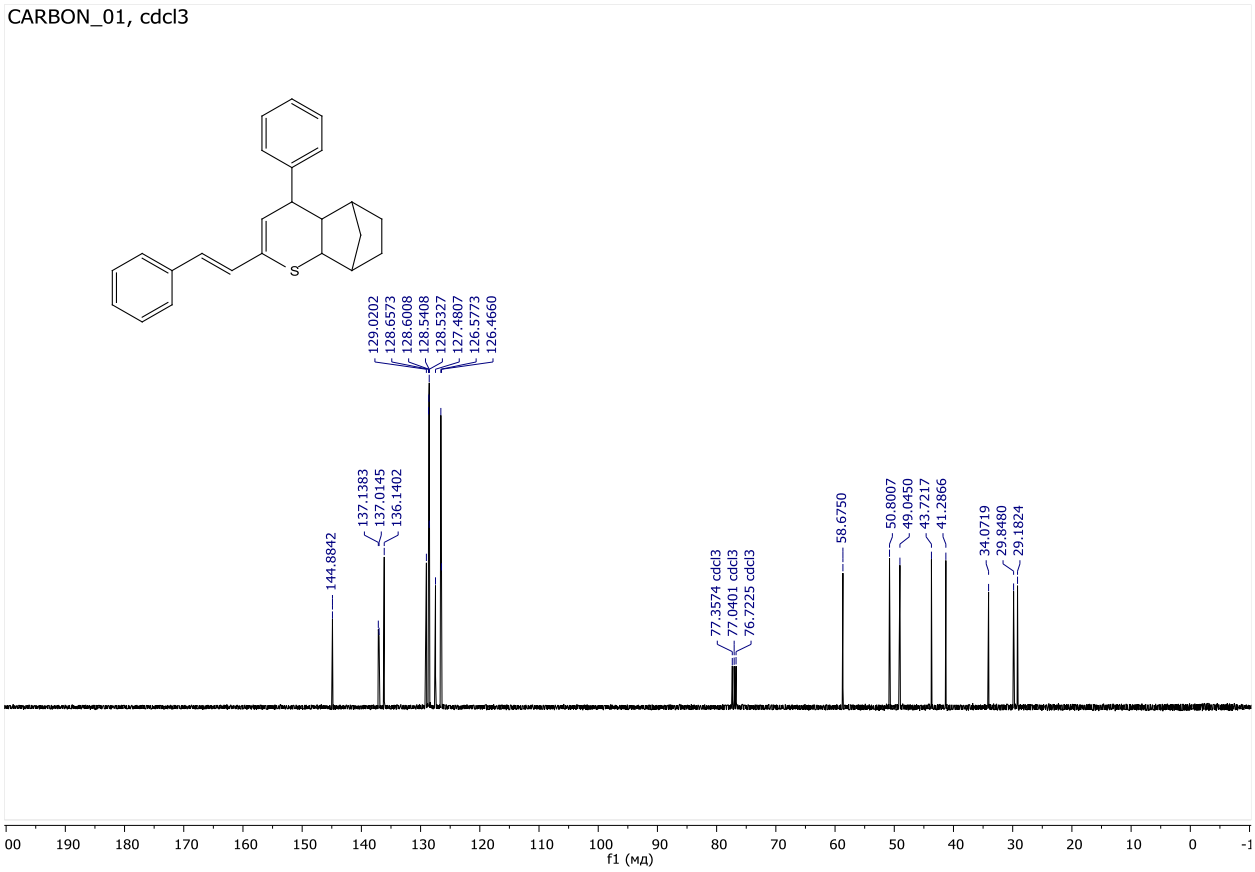

Figure S2. ^{13}C NMR spectrum of compound **2** in $CDCl_3$

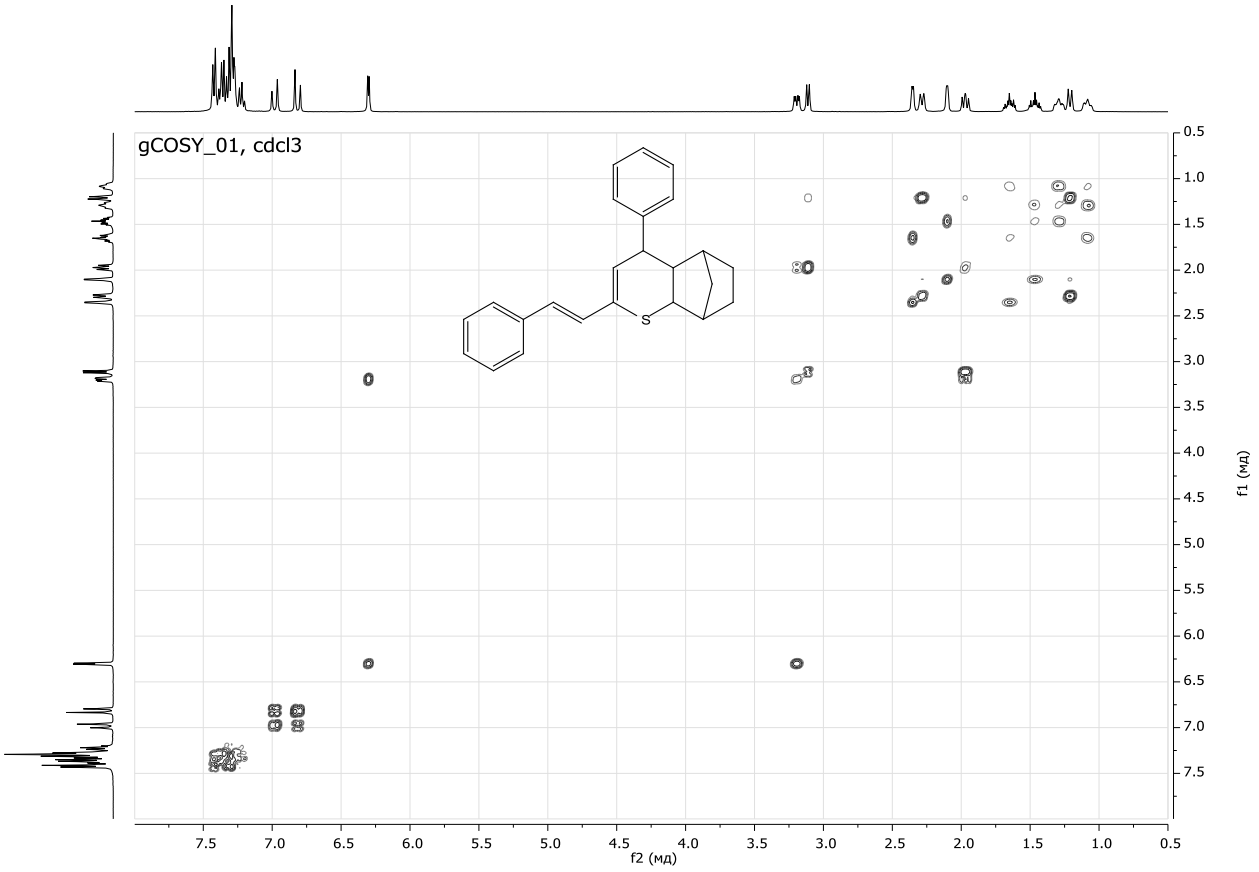

Figure S3. ^{1}H-^{1}H COSY spectrum of compound **2** in $CDCl_3$

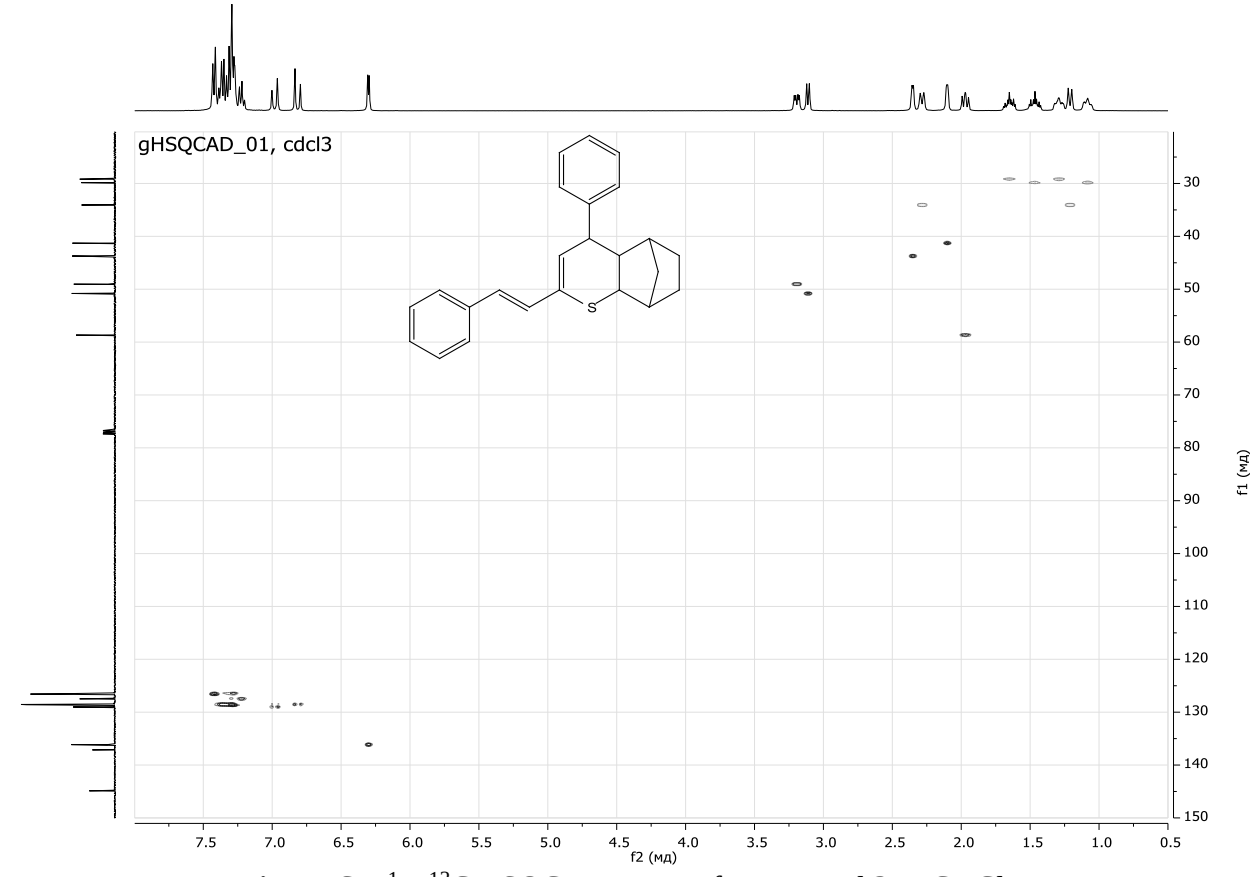

Figure S4. ^{1}H-^{13}C HSQC spectrum of compound **2** in $CDCl_3$

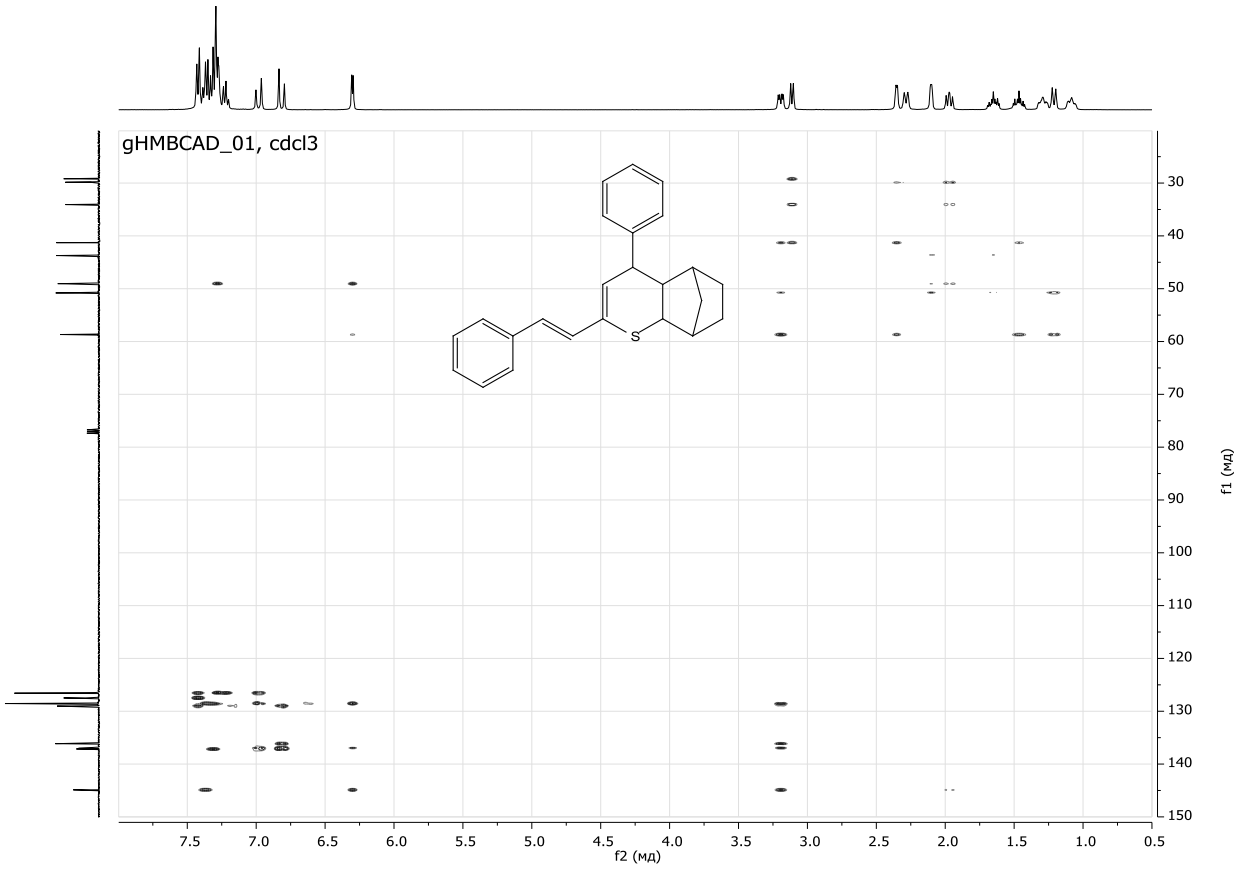

Figure S5. ^{1}H-^{13}C HMBC spectrum of compound **2** in $CDCl_3$

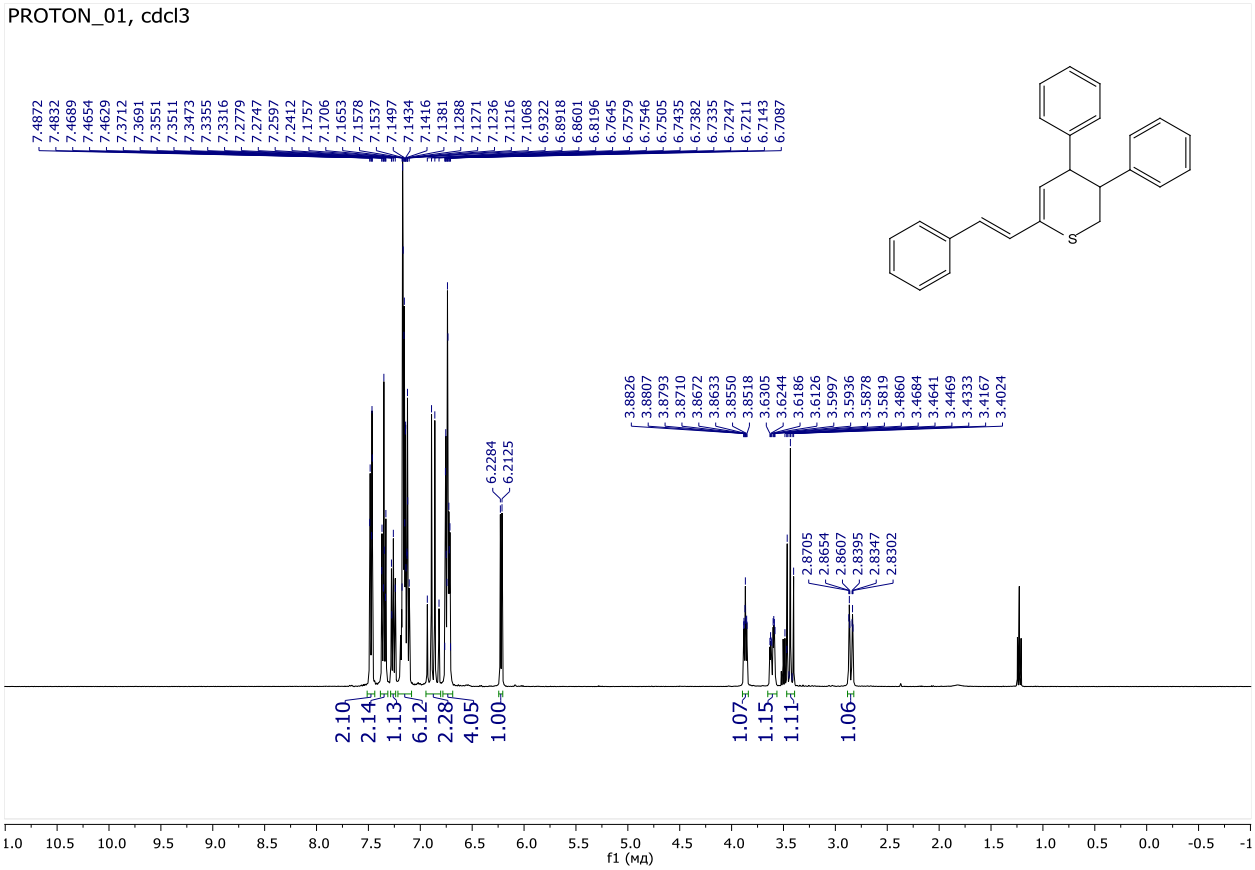

Figure S6. ^{1}H NMR spectrum of compound **3** in $CDCl_3$

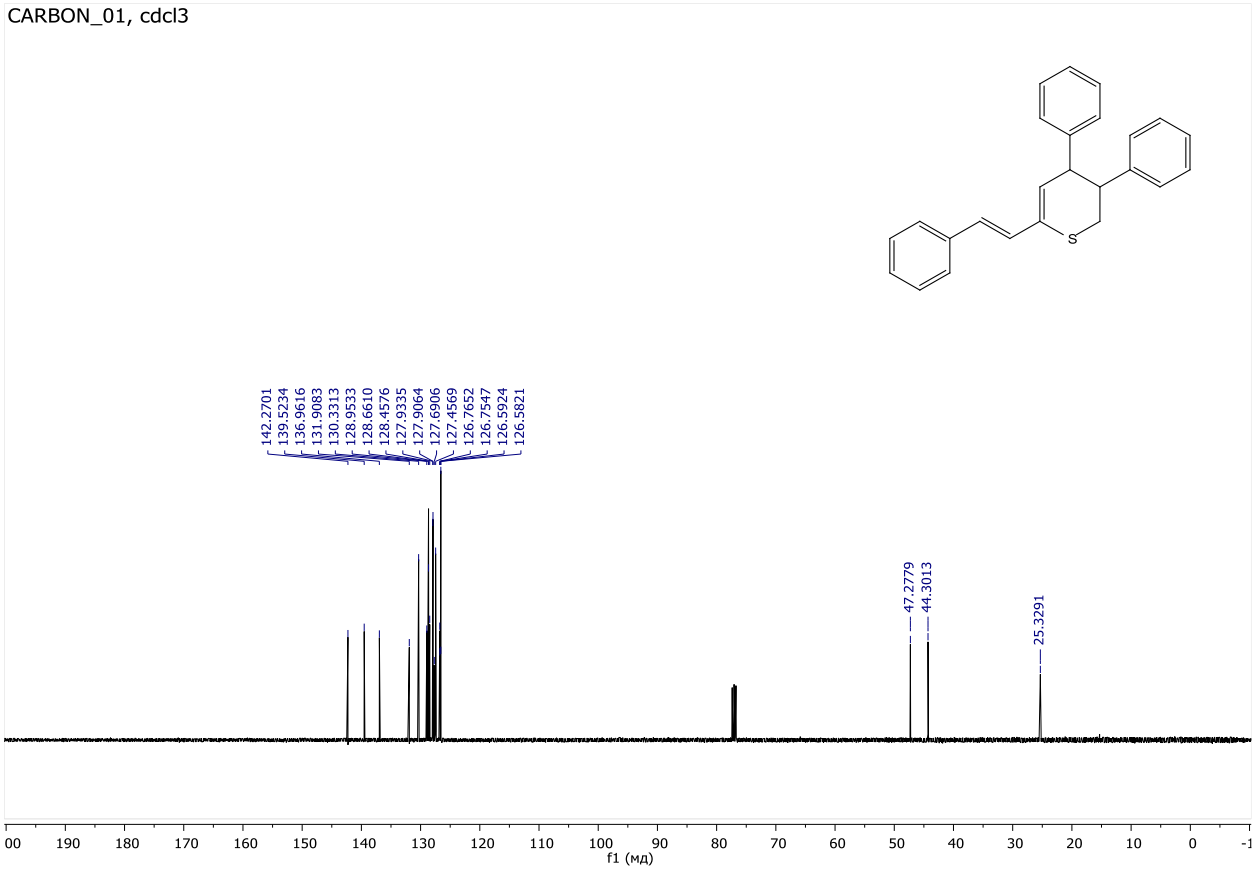

Figure S7. ^{13}C NMR spectrum of compound **3** in $CDCl_3$

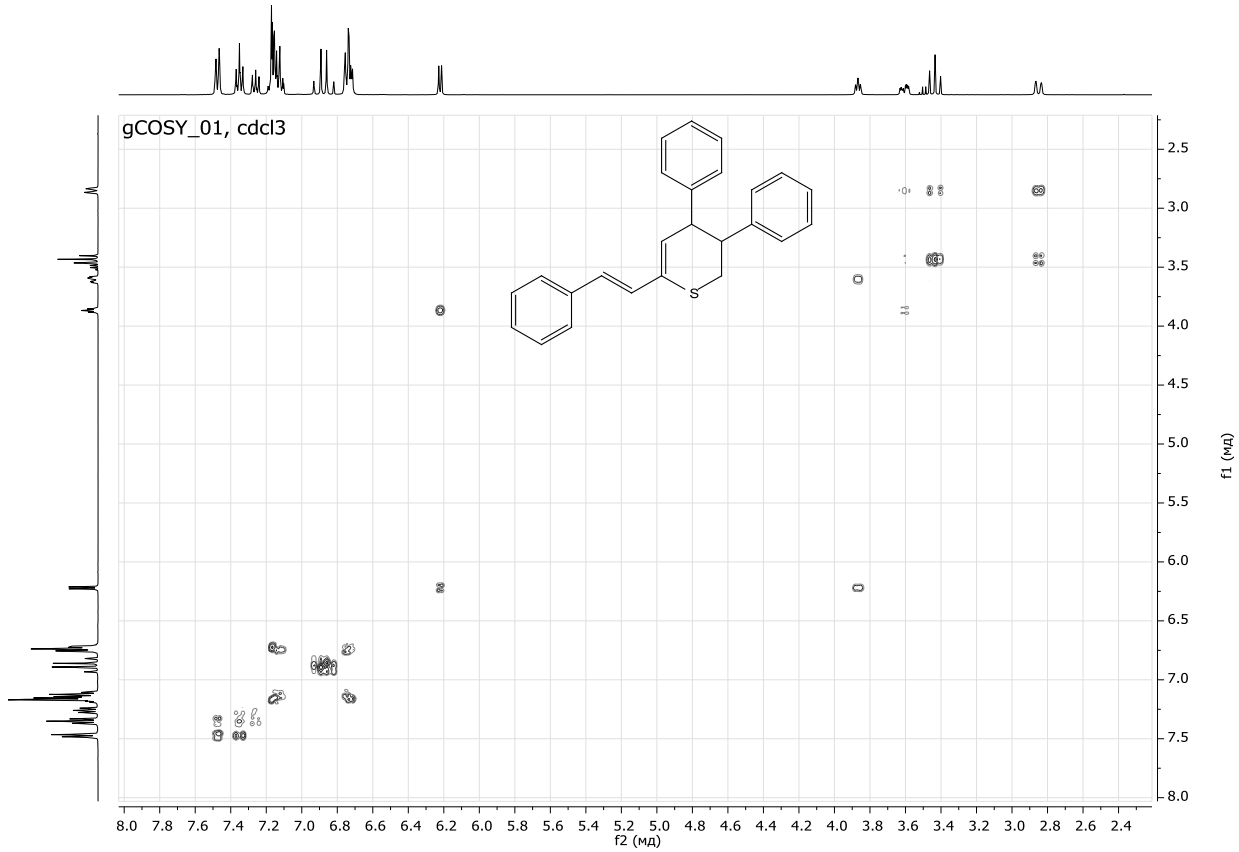

Figure S8. ^{1}H-^{1}H COSY spectrum of compound **3** in $CDCl_3$

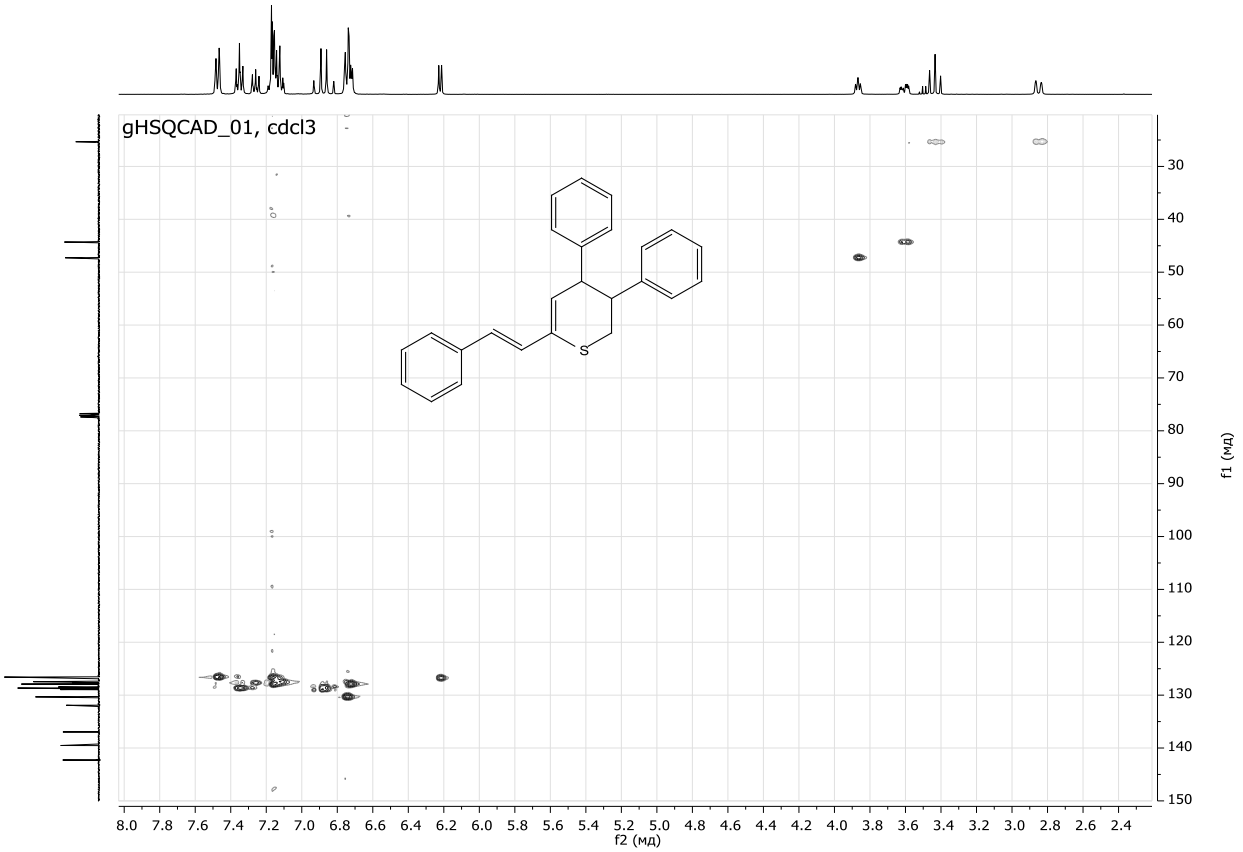

Figure S9. ^{1}H-^{13}C HSQC spectrum of compound **3** in $CDCl_3$

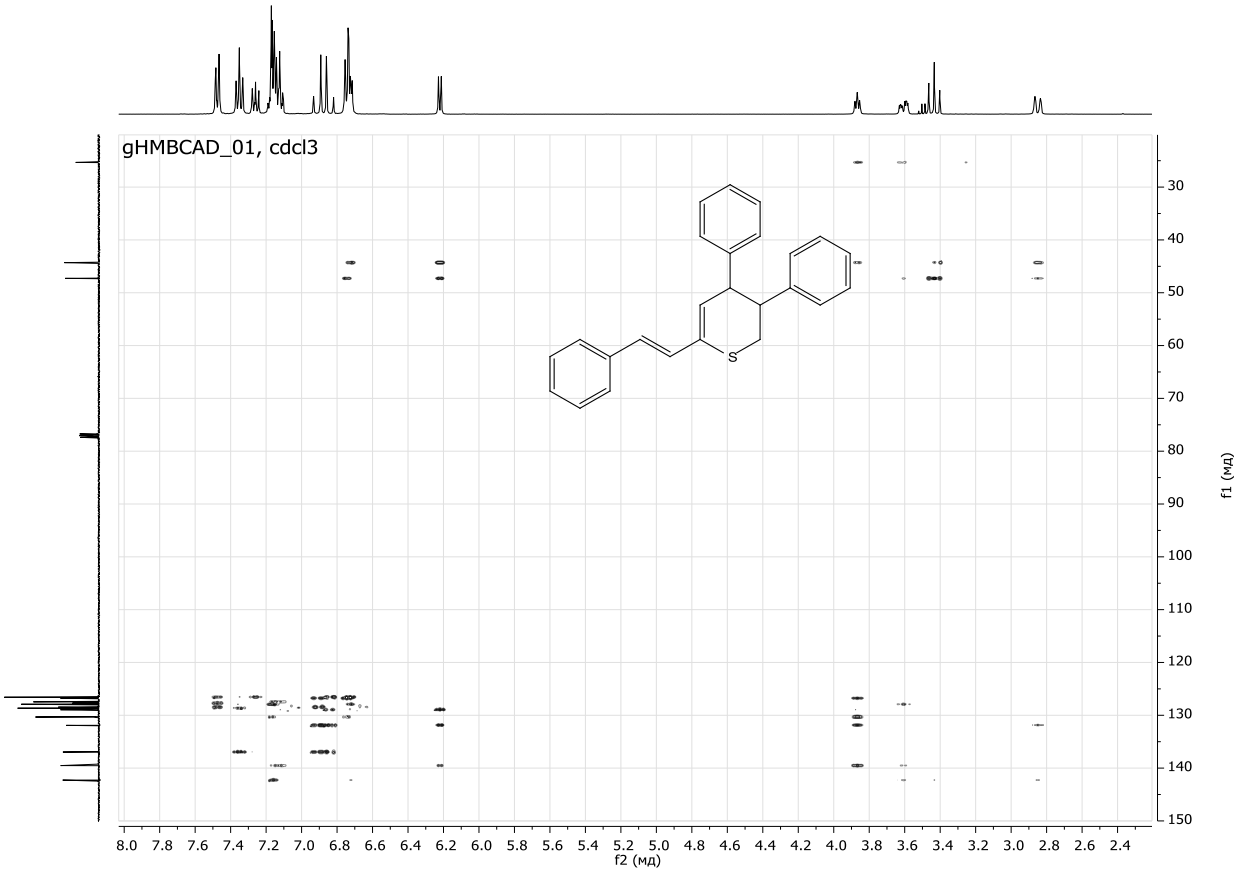

Figure S10. ^{1}H-^{13}C HMBC spectrum of compound **3** in $CDCl_3$

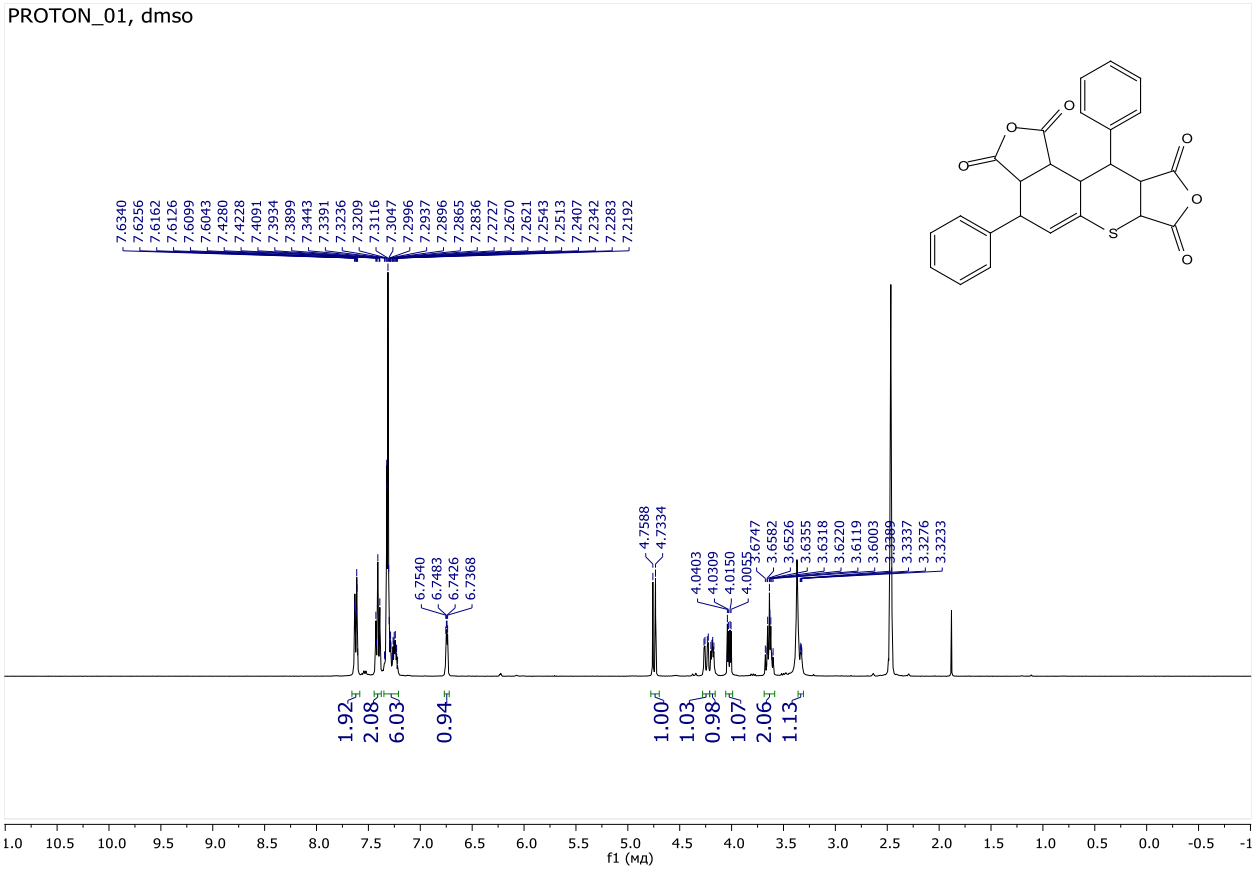

Figure S11. ^{1}H NMR spectrum of compound **5a** in DMSO

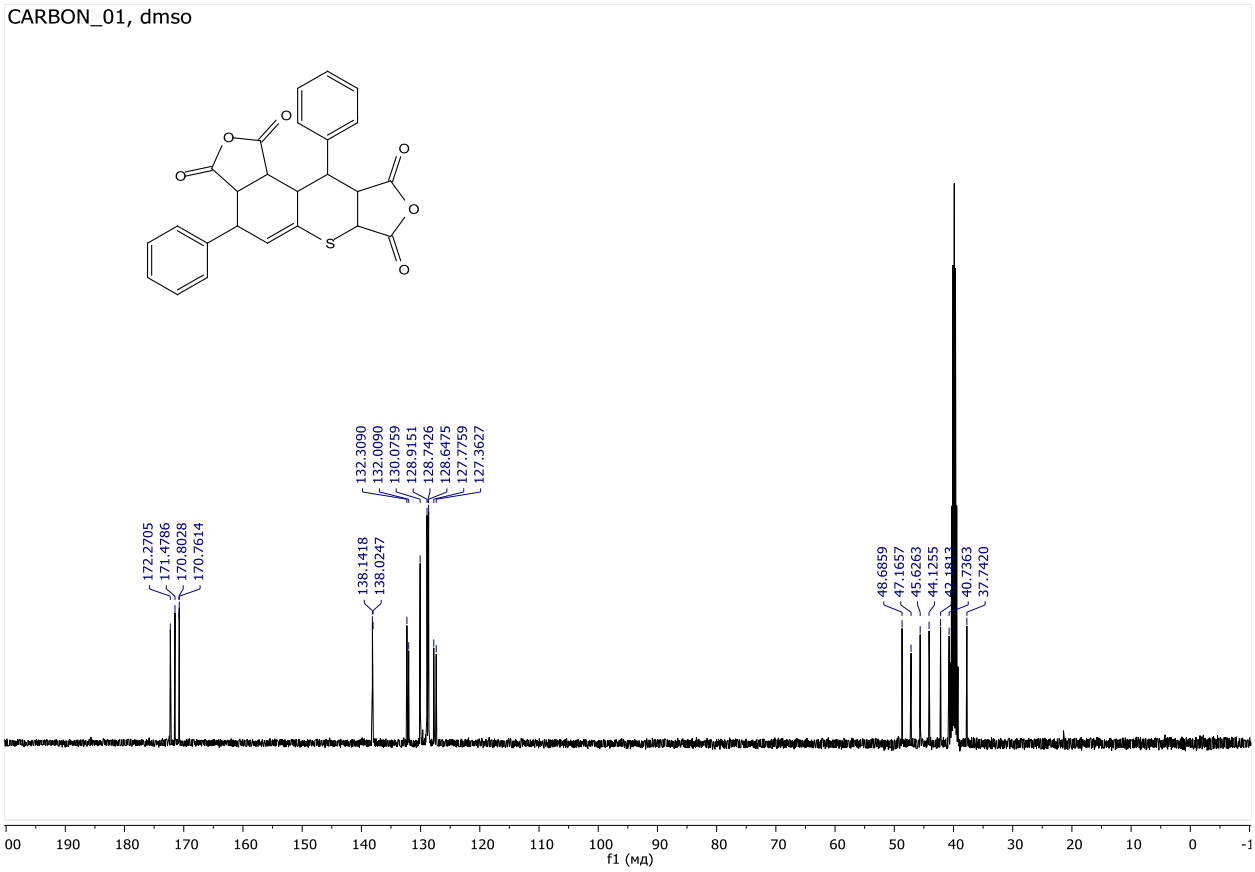

Figure S12. ^{13}C NMR spectrum of compound **5a** in DMSO

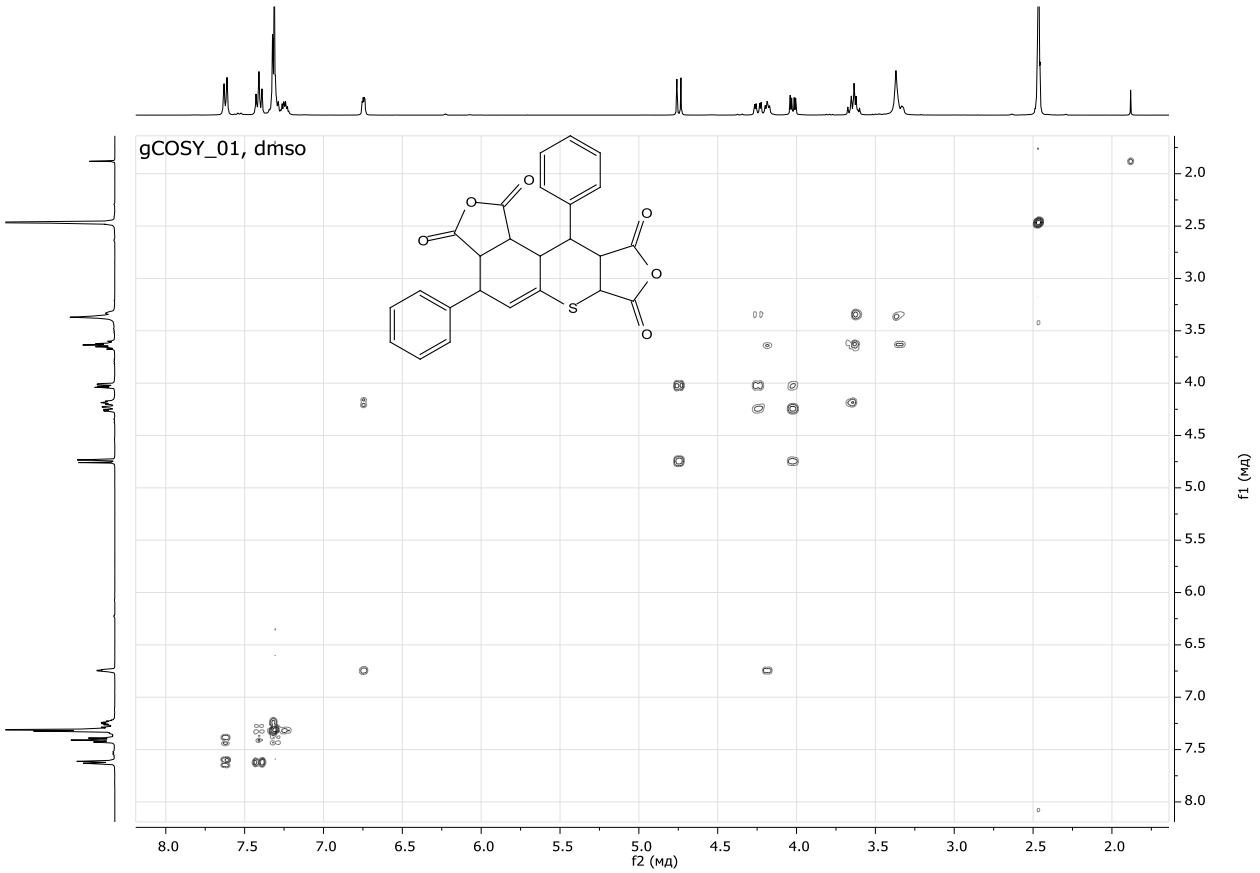

Figure S13. ^{1}H-^{1}H COSY spectrum of compound **5a** in DMSO

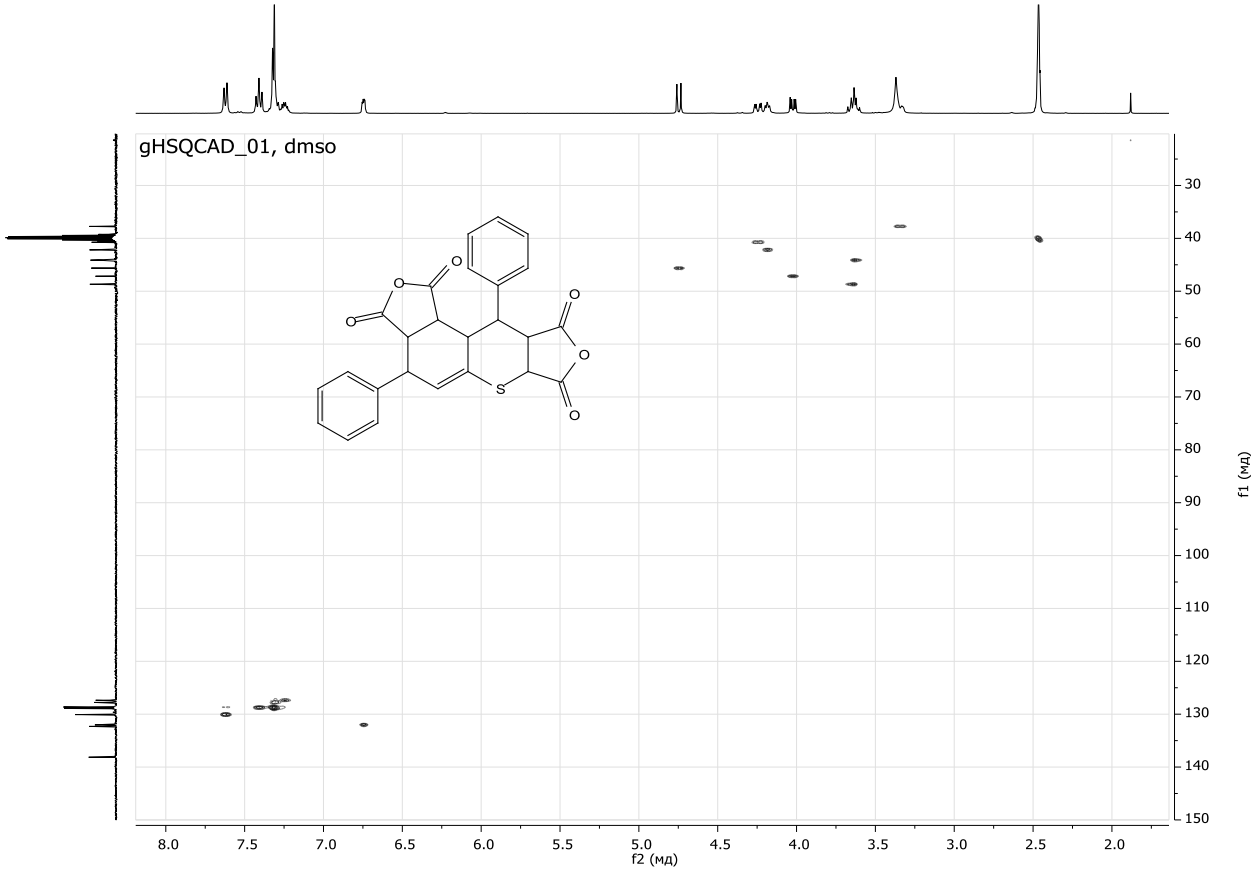

Figure S14. ^{1}H-^{13}C HSQC spectrum of compound **5a** in DMSO

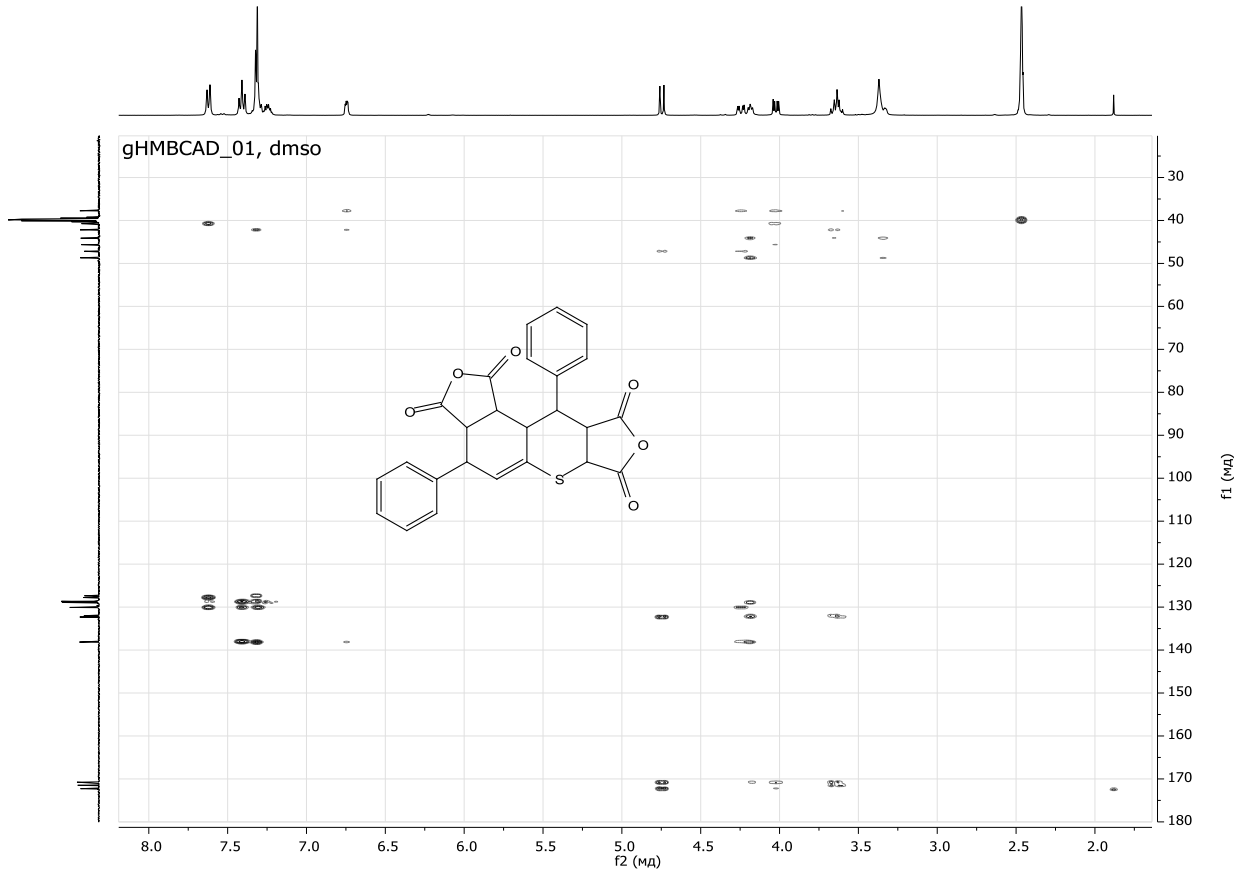

Figure S15. ^{1}H-^{13}C HMBC spectrum of compound **5a** in DMSO

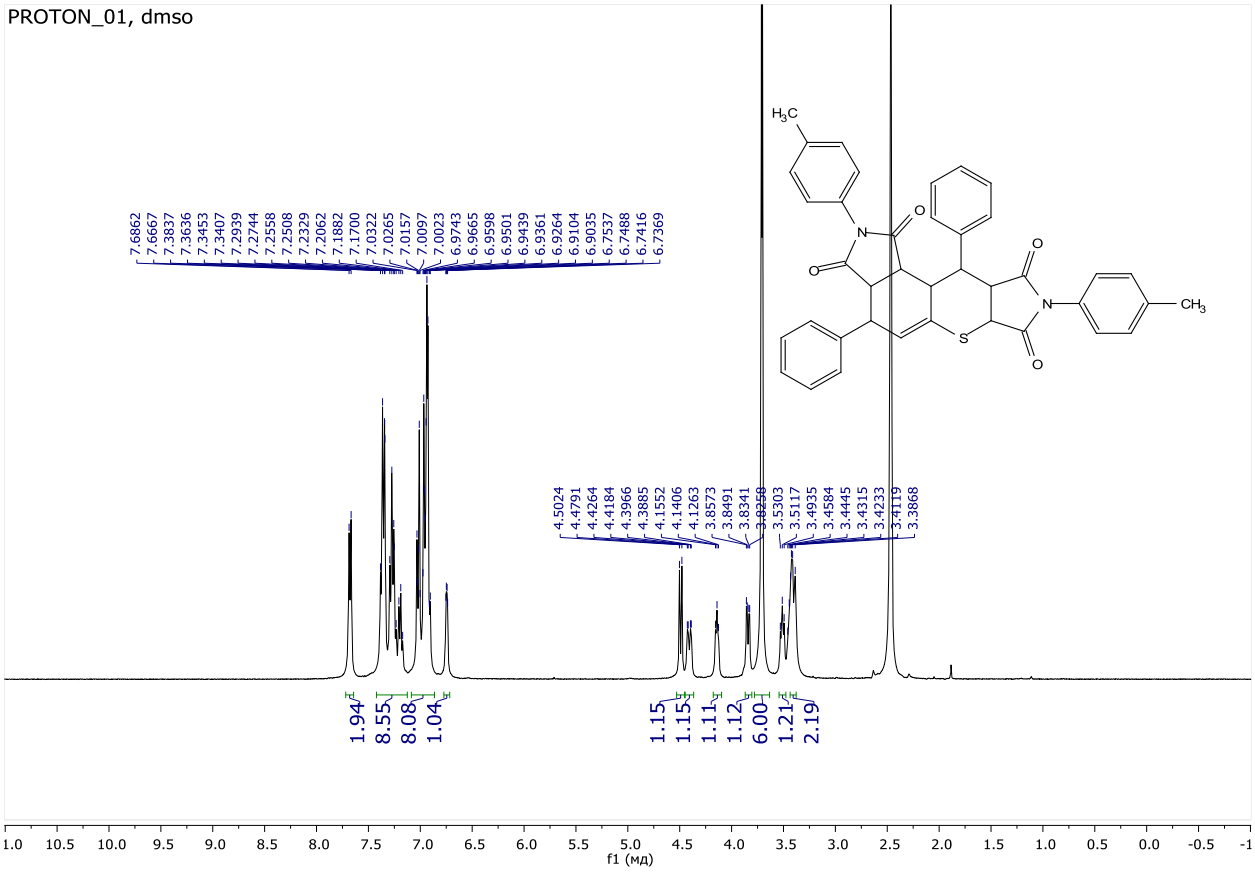

Figure S16. ^{1}H NMR spectrum of compound **5b** in DMSO

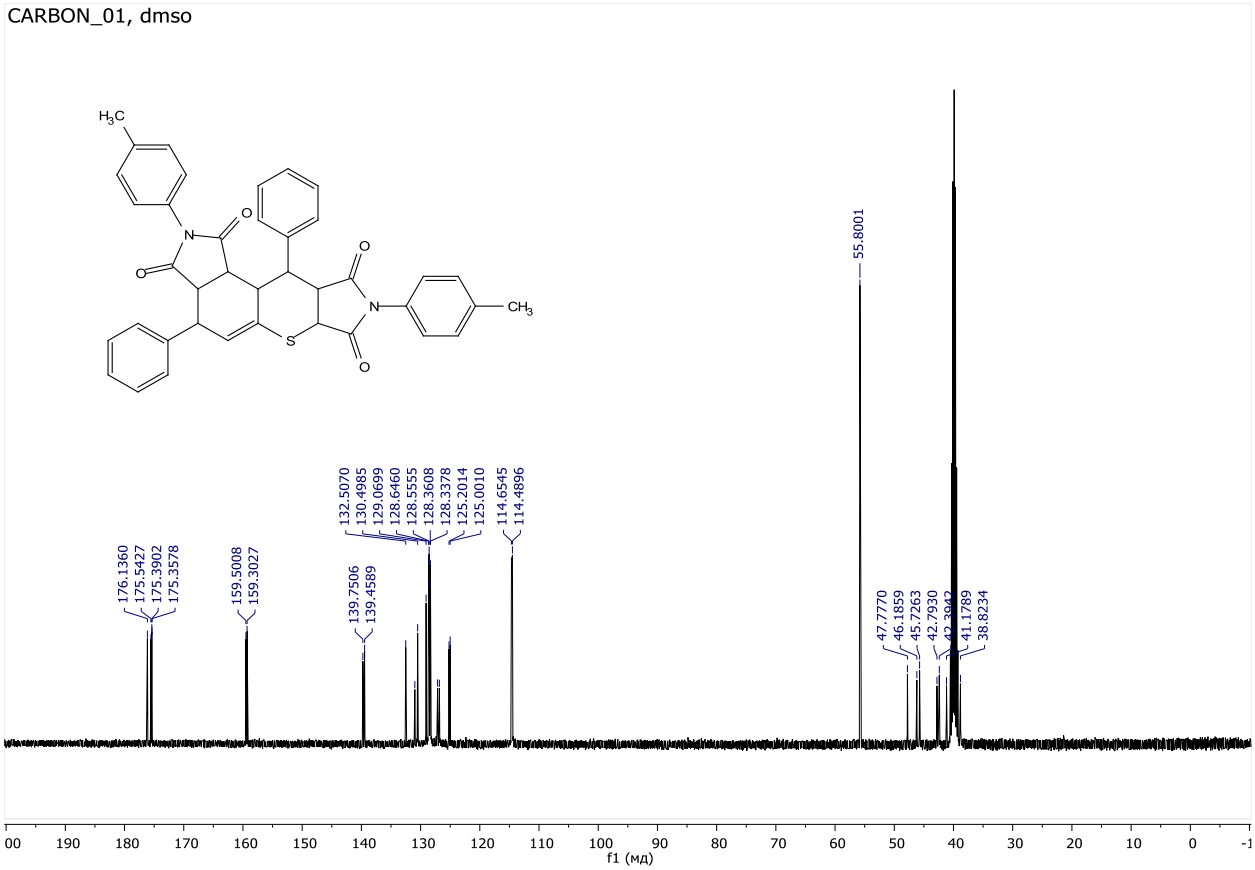

Figure S17. ^{13}C NMR spectrum of compound **5b** in DMSO

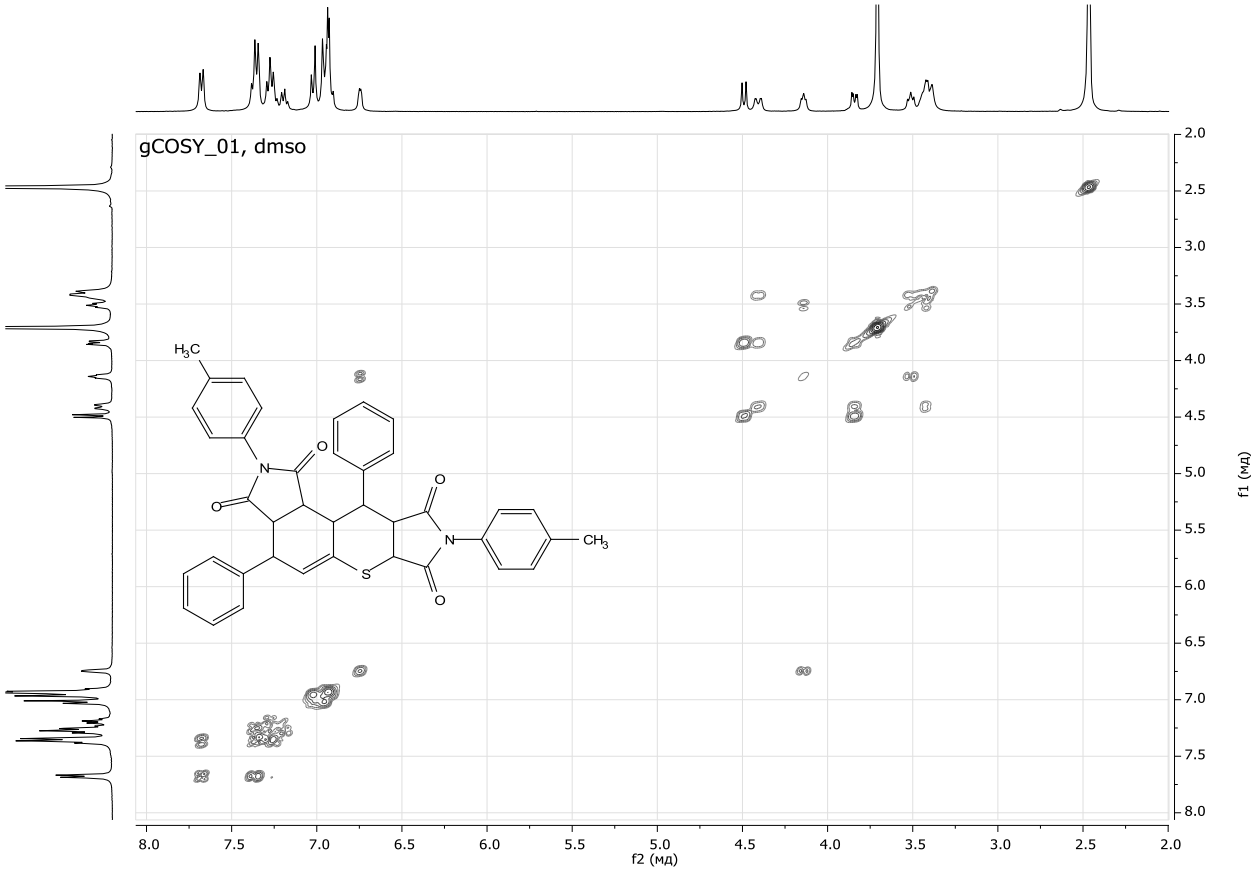

Figure S18. ^{1}H-^{1}H COSY spectrum of compound **5b** in DMSO

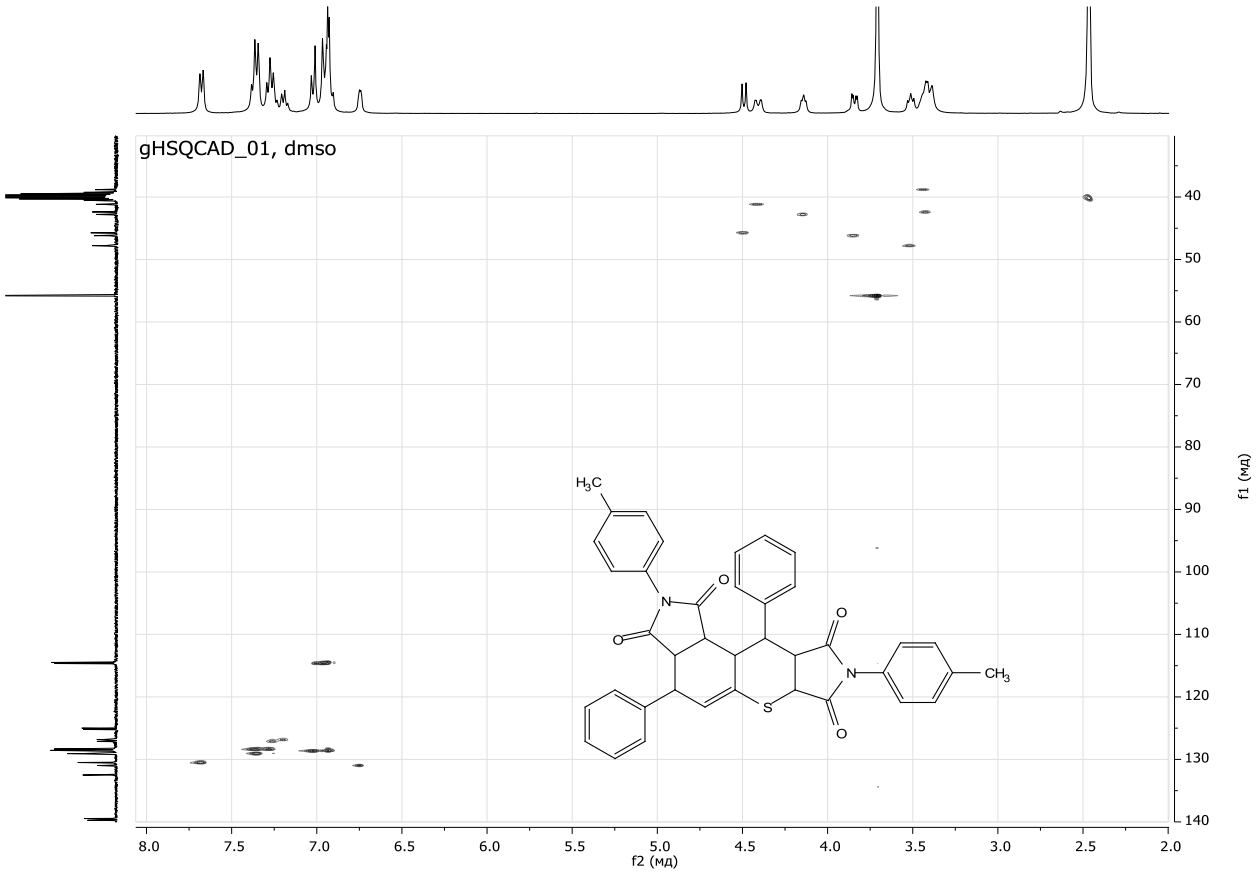

Figure S19. ^{1}H-^{13}C HSQC spectrum of compound **5b** in DMSO

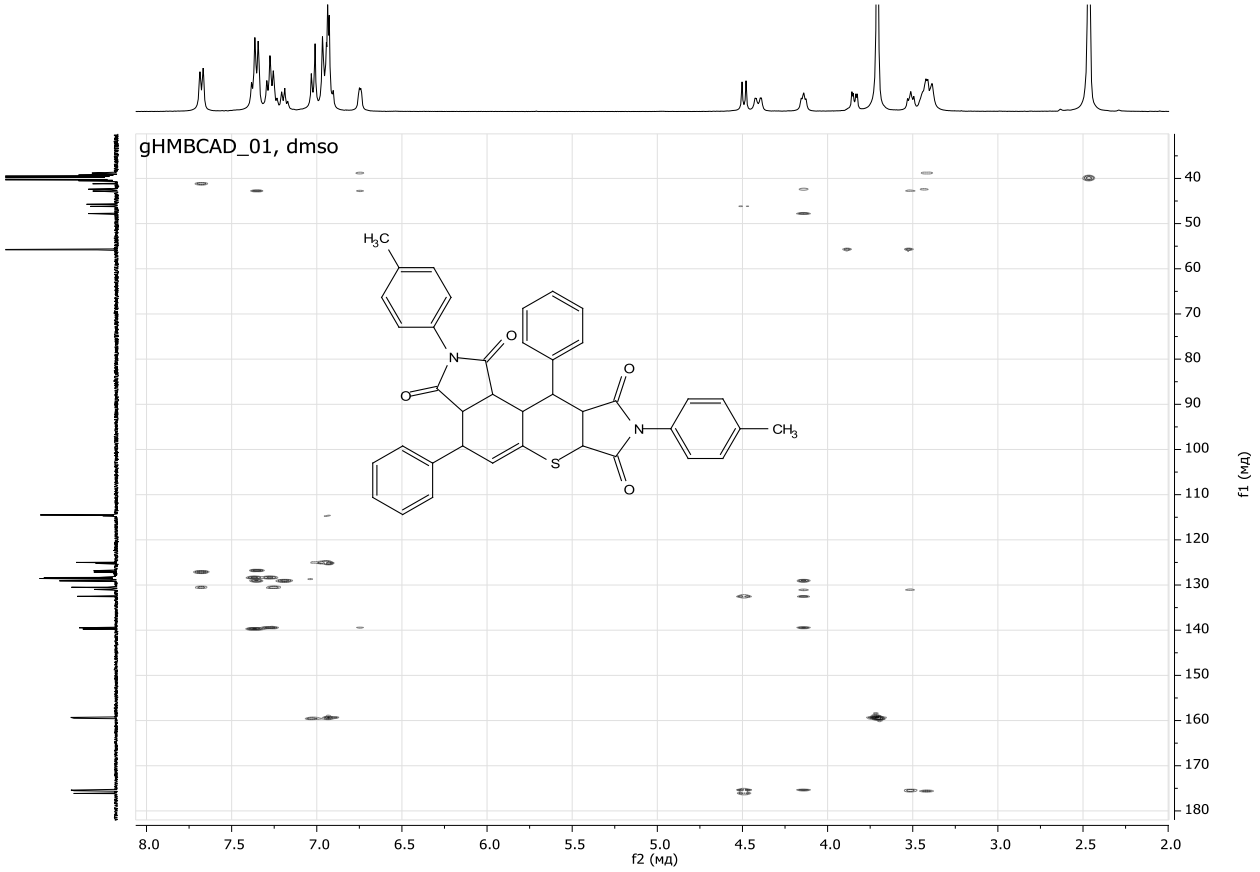

Figure S20. ^{1}H-^{13}C HMBC spectrum of compound **5b** in DMSO

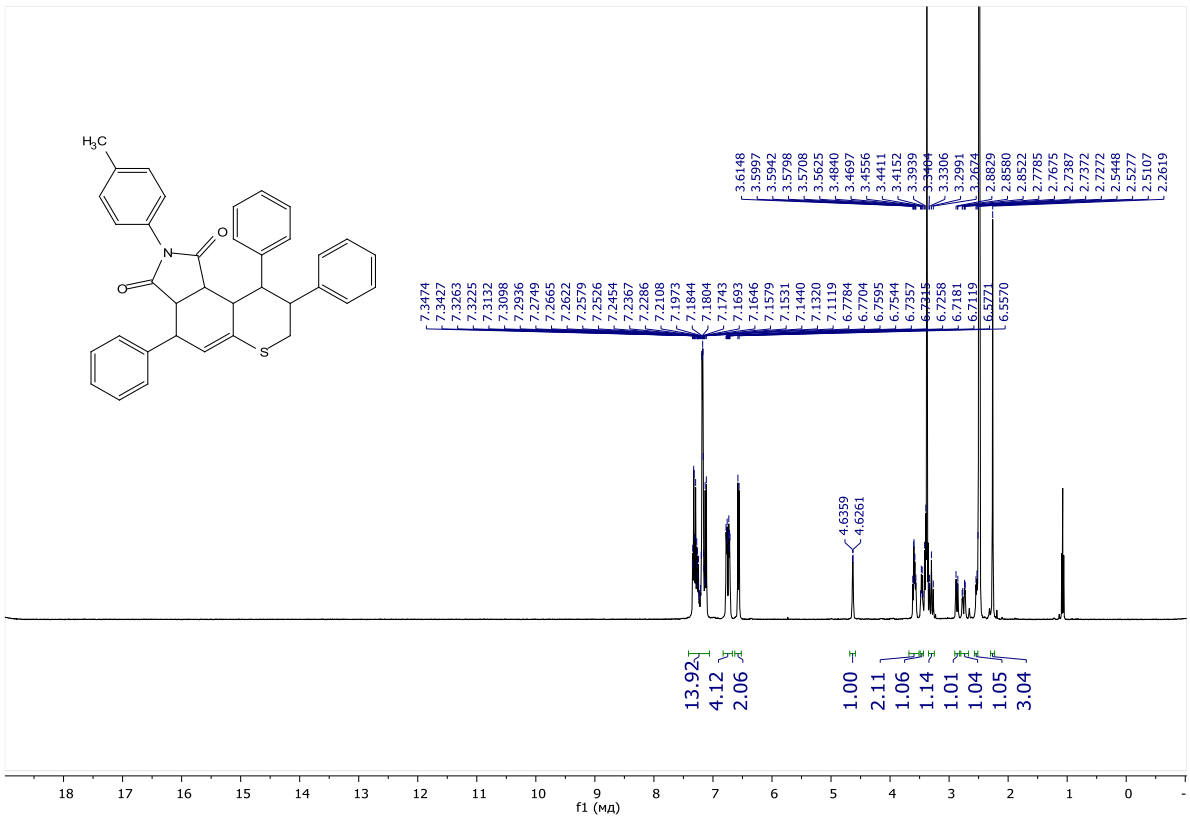

Figure S21. ^{1}H NMR spectrum of compound **6** in DMSO

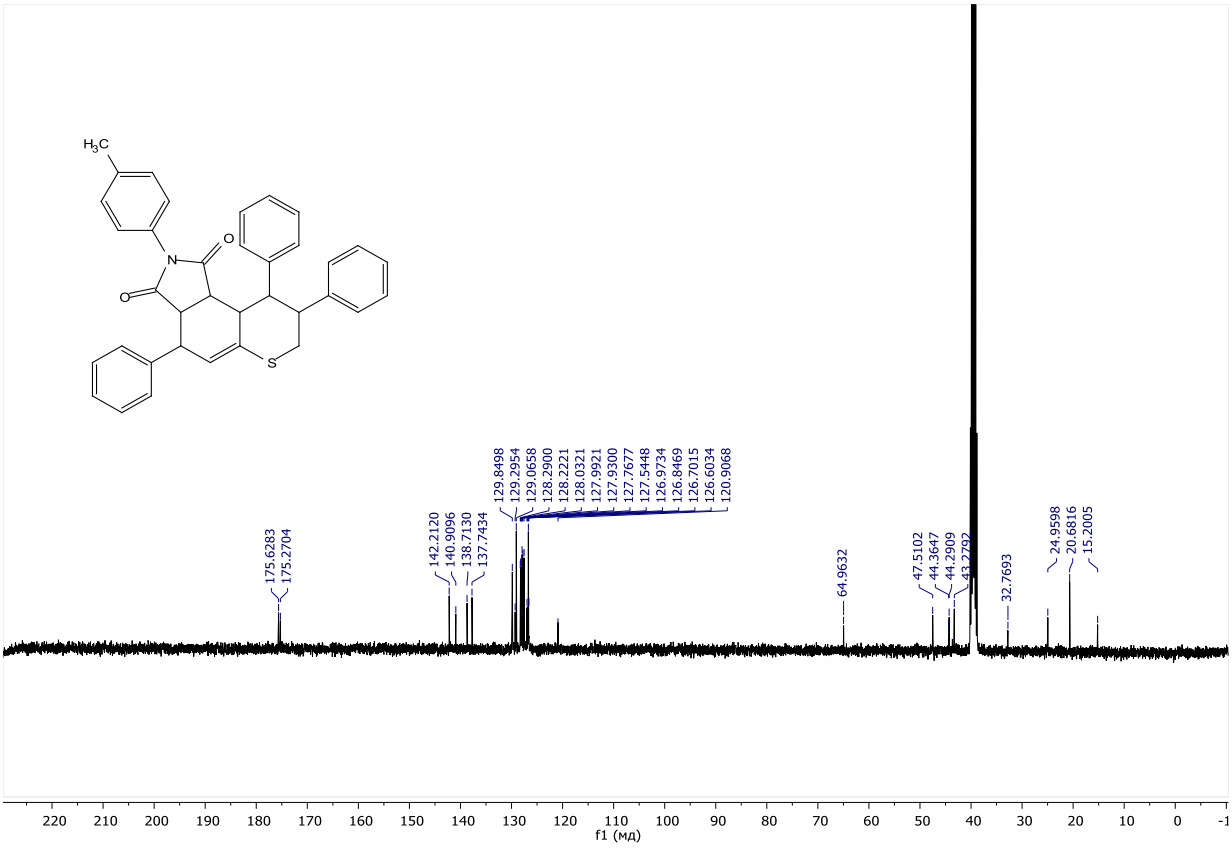

Figure S22. ^{13}C NMR spectrum of compound **6** in DMSO