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Experimental

Synthesis

All reagents were purchased from Aldrich, Merck and Fluka and were used without any further purification. The deuterated solvents were purchased from Deutero GmbH. Fluka silica gel (TLC-cards 60778 with fluorescent indicator 254 nm) were used for TLC chromatography and R_f-values determination. Merck Silica gel 60 (0.040-0.063 mm) was used for flash chromatography purification of the products. The melting points were determined in capillary tubes on SRS MPA100 OptiMelt (Sunnyvale, CA, USA) automated melting point system. UV spectra were measured on Varian Cary 100 spectrophotometer in acetone. The NMR spectra were recorded on a Bruker Avance II+ 600 spectrometer (Rheinstetten, Germany), ^{1}H at 600 MHz and ^{13}C at 151 MHz, in $CDCl_3$ or DMSO-d_6; the chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as an internal standard and the coupling constants were calculated in Hz. The spectra were processed with Topspin 2.1 program. For simplicity, naphthyl ring nuclei are depicted as Ar, azo-dye pyridyl unit as Py, NH-connected pyridyl moiety as Py', aryl or heteroaryl substituent at methyne bridge as Ar', and methylene or methyne bridge as CH_2 and CH, respectively. In some cases the spectra of slightly impure samples were recorded and analysed due to the much lower solubility of the pure products. The compounds purities after final recrystallization were proved by TLC and melting points determination. The turbo spray mass spectra were taken on API 150EX (AB/MAS Sciex).

*Starting azo-dye **1***

To 3-amino pyridine (10 mmol) ice, conc. HCl (3 ml), and $NaNO_2$ (11 mmol) were subsequently added and the mixture was stirred at 0^{o}C for 5 min to form a diazonium salt. To a solution of naphthalene-1-ol (10 mmol) in 10 % aq. NaOH (10 ml) the solution of the diazonium salt was added at 0^{o}C. The residue formed was filtered off, washed with water and dried in air to give 4-(3-pyridyldiazenyl)naphthalen-1-ol **1**, which was further used without purification. A sample for analyses was purified by flash chromatography on silica gel by using mobile phase with a gradient of polarity from CH_2Cl_2 to 2 % MeOH in CH_2Cl_2 (2 % MeOH/CH_2Cl_2): m. p. 209.5-210 °C; R_f 0.38 (5 % MeOH/DCM); UV λ_{max} 415 nm; ^{1}H NMR (DMSO-d_6) 7.046 (d, 1H, J 8.4, C*H*-2 Ar), 7.613 (m, 2H, C*H*-5 Py and C*H*-7 Ar), 7.721 (ddd, 1H, J 8.4, 6.8, 1.3, C*H*-6 Ar), 7.935 (d, 1H, J 8.4, C*H*-3 Ar), 8.248 (d, 1H, J 8.3, C*H*-8 Ar), 8.292 (ddd, 1H, J 8.2, 1.9, 1.1, C*H*-6 Py), 8.699 (dd, 1H, J 4.3, 1.1, C*H*-4 Py), 8.920 (d, 1H, J 8.4, C*H*-5 Ar), 9.162 (d, 1H, J 1.9, C*H*-2 Py), 11.339 (s, 1H, O*H*); ^{13}C NMR 108.93 (*C*H-2 Ar), 114.87 (*C*H-3 Ar), 122.90 (*C*H-8 Ar), 123.07 (*C*H-5 Ar), 124.78 (C_{quat}-8a Ar), 125.05 (*C*H-5

Py), 126.08 (*C*H-7 Ar), 127.25 (*C*H-6 Py), 128.56 (*C*H-6 Ar), 133.27 (C_{quat}-4a Ar), 140.13 (C_{quat}-4 Ar), 146.70 (*C*H-2 Py), 148.60 (C_{quat}-1 Py), 151.48 (*C*H-4 Py), 158.99 (C_{quat}-1 Ar).

*Methylation of **1***

To a solution of crude **1** (1 mmol) in THF (5 ml) KOH (2 mmol) and after 15 min CH_3I (5 mmol) was added and the suspension was stirred at room temperature for 2 h. The solid phase was filtered off and washed with THF. The solvent was removed in *vacuo* and the residue formed was purified by flash chromatography on silica gel by using mobile phase with a gradient of polarity from CH_2Cl_2 to 15 % acetone/CH_2Cl_2 to give: compound **1-OMe**: R_f 0.70 (5 % MeOH/DCM); 15 % yield; m. p. 126.5-127 °C; UV λ_{max} 401 nm; ^{1}H NMR ($CDCl_3$) 4.098 (s, 3H, C*H*$_3$), 6.921 (d, 1H, J 8.5, C*H*-2 Ar), 7.484 (dd, 1H, J 8.1, 4.8, C*H*-5 Py), 7.593 (ddd, 1H, J 8.4, 6.8, 1.4, C*H*-7 Ar), 7.694 (ddd, 1H, J 8.3, 6.8, 1.4, C*H*-6 Ar), 7.976 (d, 1H, J 8.5, C*H*-3), 8.259 (ddd, 1H, J 8.2, 2.2, 1.6, C*H*-6 Py), 8.329 (ddd, 1H, J 8.3, 1.4, 0.7, C*H*-8 Ar), 8.689 (d, 1H, J 4.2, C*H*-4 Py), 8.943 (ddd, 1H, J 8.4, 1.4, 0.7, C*H*-5 Ar), 9.258 (bs, 1H, C*H*-2 Py); ^{13}C NMR 55.98 (*C*H$_3$), 103.73 (*C*H-2 Ar), 113.59 (*C*H-3 Ar), 122.24 (*C*H-8 Ar), 122.96 (*C*H-5 Ar), 124.12 (*C*H-5 Py), 125.59 (C_{quat}-8a Ar), 126.03 (*C*H-7 Ar), 127.38 (*C*H-6 Py), 127.90 (*C*H-6 Ar), 132.79 (C_{quat}-4a Ar), 141.67 (C_{quat}-4 Ar), 146.86 (*C*H-2 Py), 148.65 (C_{quat}-1 Py), 150.56 (*C*H-4 Py), 159.25 (C_{quat}-1 Ar); ESI (TIS)-Q m/z 264.16 $[M+1]^+$, $C_{16}H_{13}N_3O$; and compound **1-NMe**: R_f 0.51 (5 % MeOH/DCM); 4 % yield; UV λ_{max} 443 nm; ^{1}H NMR ($CDCl_3$) 3.790 (s, 3H, C*H*$_3$), 6.749 (d, 1H, J 10.4, C*H*-2 Ar), 7.557 (d, 1H, J 10.4, C*H*-3 Ar), 7.615 (overlapped signals, C*H*-5 Py), 7.630 (ddd, 1H, J 7.9, 7.3, 0.8, C*H*-7 Ar), 7.714 (ddd, 1H, J 8.0, 7.3, 1.1, C*H*-6 Ar), 7.973 (dd, 1H, J 8.4, 1.3, C*H*-6 Py), 8.215 (dd, 1H, J 7.9, 1.1, C*H*-8 Ar), 8.362 (d, 1H, J 4.8, C*H*-4 Py), 8.404 (dd, 1H, J 8.0, 0.8, C*H*-5 Ar), 8.711 (bs, 1H, C*H*-2 Py); ^{13}C NMR 45.62 (*C*H$_3$), 124.21 (*C*H-5 Ar), 125.28 (*C*H -5 Py), 126.40 (*C*H-8 Ar), 127.41 (*C*H-6 Py), 128.67 (*C*H-3 Ar), 130.09 (*C*H-7 Ar), 130.82 (C_{quat}-8a Ar), 131.05 (*C*H-2 Ar), 132.46 (*C*H-2 Py), 132.89 (*C*H-6 Ar), 133.76 (C_{quat}-4a Ar), 137.61 (*C*H-4 Py), 144.89 (C_{quat}-4 Ar), 146.91 (C_{quat}-1 Py), 184.54 (C_{quat}-1 Ar); ESI (TIS)-Q m/z 264.22 $[M+1]^+$, $C_{16}H_{13}N_3O$.

Compounds with methylene bridged side chain (Mannich reaction)

General procedure: To a solution of piperidine or 3-aminopyridine (1.5 mmol) in benzene (5-6 ml) paraformaldehyde (1.5 mmol), *p*-toluenesulfonic acid (10 mg), and then crude **1** (1 mmol) were added and the mixture was refluxed with stirring for 3 h. The products were purified by flash chromatography on silica gel.

*Compound **2**:* 70 % overall yield; R_f 0.33 (5 % MeOH/DCM); m. p. 114-115 °C; UV λ_{max} 422 nm; ^{1}H NMR ($CDCl_3$) 1.699 (bs, 6H, C*H*$_2$-3, C*H*$_2$-4 and C*H*$_2$-5 piperidine), 2.227 (bs, 2H, ½ of

CH_2-2 and CH_2-6 piperidine), 3.063 (bs, 2H, ½ of CH_2-2 and CH_2-6 piperidine), 3.910 (s, 2H, CH_2), 7.434 (dd, 1H, J 8.1, 4.6, C*H*-5 Py), 7.550 (ddd, 1H, J 8.3, 6.8, 1.0, C*H*-7 Ar), 7.640 (ddd, 1H, J 8.4, 6.8, 1.2, C*H*-6 Ar), 7.762 (s, 1H, C*H*-3 Ar), 8.207 (ddd, 1H, J 8.1, 2.0, 1.6, C*H*-6 Py), 8.309 (d, 1H, J 8.3, C*H*-8 Ar), 8.646 (dd, 1H, J 4.6, 1.3, C*H*-4 Py), 8.911 (d, 1H, J 8.4, C*H*-5 Ar), 9.220 (d, 1H, J 2.0, C*H*-2 Py), 10.737 (bs, 1H, O*H*); ^{13}C NMR 23.79 (*C*H_2-4 piperidine), 25.72 (*C*H_2-3 and *C*H_2-5 piperidine), 53.88 (*C*H_2-2 and *C*H_2-6 piperidine), 62.01 (*C*H_2), 113.88 (*C*H-3 Ar), 114.06 (C_q-2 Ar), 122.44 (*C*H-8 Ar), 122.71 (*C*H-5 Ar), 123.99 (*C*H-5 Py), 125.05 (C_{quat}-8a Ar), 125.51 (*C*H-7 Ar), 126.67 (*C*H-6 Py), 127.65 (*C*H-6 Ar), 132.79 (C_{quat}-4a Ar), 139.76 (C_{quat}-4 Ar), 147.15 (*C*H-2 Py), 148.66 (C_{quat}-1 Py), 150.51 (*C*H-4 Py), 160.08 (C_{quat}-1 Ar); ESI (TIS)-Q m/z 347.31 $[M+1]^+$ $C_{21}H_{22}N_4O$.

*Compound **3**:* 36 % overall yield; R_f 0.36 (5 % MeOH/DCM + 0.5% NH_4OH); m. p. 161-162 °C (at 140.5-141 °C became very dark); UV λ_{max} 451 nm; The product is not enough soluble in DMSO-d_6 to record proper ^{13}C spectrum at reasonable time-scale; a part of the signals were extracted from HSQC and HMBC experiments, another are missing. The extra pyridyl unit is depicted as Py"; ^{1}H NMR (DMSO-d_6) 3.40 (bs, N*H*-C_q-1 Py', overlapped with H_2O in DMSO-d_6), 4.259 (bs, 2H, CH_2), 5.092 (s, 2H, N-CH_2-NH), 6.271 (bs, 1H, N*H*-C_q-1 Py"), 6.949 (dd, 1H, J 8.1, 1.3, C*H*-6 Py'), 7.084 (dd, 1H, J 8.1, 4.5, C*H*-5 Py'), 7.143 (dd, 1H, J 8.3, 4.5, C*H*-5 Py"), 7.415 (bs, 1H, C*H*-5 Py), 7.481 (dd, 1H, J 8.3, 1.6, C*H*-6 Py"), 7.560 (t, 1H, J 7.4, C*H*-7 Ar), 7.715 (t, 1H, J 7.4, C*H*-6 Ar), 7.787 (d, 1H, J 4.0, C*H*-4 Py'), 7.918 (bs, 1H, C*H*-4 Py), 7.978 (d, 1H, J 4.3, C*H*-4 Py"), 8.057 (d, 1H, J 1.9, C*H*-2 Py'), 8.112 (bs, 1H, C*H*-8 Ar), 8.216 (bs, 1H, C*H*-3 Ar), 8.271 (bs, 1H, C*H*-6 Py), 8.422 (d, 1H, J 2.3, C*H*-2 Py"), 8.496 (bs, 1H, C*H*-5 Ar), 8.772 (bs, 1H, C*H*-2 Py); ^{13}C NMR 42.36 (*C*H_2-NH-C_q-1 Py'), 66.34 (*C*H_2- NH-C_q-1 Py"), 117.98 (*C*H-6 Py'), 122.90 (*C*H-5 Ar), 123.46 (*C*H-5 Py"), 123.79 (*C*H-5 Py'), 123.87 (*C*H-6 Py"), 124.31 (*C*H-5 Py), 125.64 (*C*H-8 Ar), 127.75 (*C*H-7 Ar), 129.63 (C_{quat}-8a Ar), 131.97 (*C*H-6 Ar), 135.40 (C_{quat}-4a Ar), 135.70 (*C*H-2 Py'), 136.24 (*C*H-4 Py), 137.28 (*C*H-4 Py'), 139.33 (*C*H-2 Py"), 141.14 (*C*H-4 Py"), 144.13 (C_{quat}-1 Py"), 144.83 (C_{quat}-1 Py'), 144.97 (C_{quat}-1 Py); ESI (TIS)-Q m/z 462.29 $[M+1]^+$, $C_{27}H_{23}N_7O$.

*Compound **4**:* A solution of 3-aminopyridine (1.5 mmol) and paraformaldehyde (1.5 mmol) in DMSO (1 ml) was stirred at 85 °C for 1.5 h. The mixture was cooled to room temperature, the crude **1** (1 mmol) was added, and the solution was kept at room temperature for 3 h. The reaction mixture was poured in water and the solid phase formed was filtered off. The product was purified by flash chromatography on silica gel to give **4**: 56 % overall yield; R_f 0.17 (5 % MeOH/DCM); m. p. 168-169 °C; UV λ_{max} 450 nm; ^{1}H NMR (DMSO-d_6) 4.258 (s, 2H, CH_2), 6.273 (bs, 1H, N*H*-CH_2), 6.948 (ddd, 1H, J 8.3, 2.9, 1.4, C*H*-6 Py'), 7.083 (ddd, 1H, J 8.3, 4.6, 0.5, C*H*-5 Py'), 7.418 (bm, 1H, C*H*-5 Py), 7.561 (ddd, 1H, J 8.6, 7.1, 1.0, C*H*-7 Ar), 7.716

(ddd, 1H, J 8.3, 7.1, 1.4, C*H*-6 Ar), 7.788 (dd, 1H, J 4.6, 1.2, C*H*-4 Py'), 7.919 (bs, 1H, C*H*-4 Py), 8.059 (d, 1H, J 2.7, C*H*-2 Py'), 8.108 (bs, 1H, C*H*-8 Ar), 8.224 (bs, 1H, C*H*-3 Ar), 8.269 (bs, 1H, C*H*-6 Py), 8.496 (bs, 1H, C*H*-5 Ar), 8.779 (bs, 1H, C*H*-2 Py), 11.702 (bs, 1H, N*H*-N); ESI (TIS)-Q m/z 356.18 $[M+1]^+$, $C_{21}H_{17}N_5O$.

Compounds with aryl-methyne bridged side chain (Betti condensation)

General procedure: A solution of crude **1** (1 mmol), 3-aminopyridine (1.5 mmol) and aldehyde (1.5 mmol) in DMSO (1 ml) was kept at room temperature for 4-6 days. The reaction mixture was poured in water and the solid phase formed was filtered off. The product was purified by flash chromatography on silica gel.

*Compound **5a**:* Reaction time: 4 days; 54 % overall yield; R_f 0.28 (5 % MeOH/DCM); m. p. 176-177 °C; UV λ_{max} 453 nm; Compound **5a** is not enough soluble even in DMSO-d_6 to record proper ^{13}C spectrum at reasonable time-scale; a part of the signals were extracted from HSQC and HMBC experiments, another are missing; ^{1}H NMR (DMSO-d_6, 343K) 5.957 (bs, 1H, C*H*), 6.300 (bs, 1H, N*H*-CH), 6.964 (ddd, 1H, J 8.3, 2.8, 1.4, C*H*-6 Py'), 7.052 (ddd, 1H, J 8.3, 4.6, 0.4, C*H*-5 Py'), 7.261 (tt, 1H, J 1.3, 7.3, C*H*-4 Ar'), 7.356 (ddt, 2H, J 7.7, 7.3, 1.5, C*H*-3 and C*H*-5 Ar'), 7.436 (dd, 1H, J 8.3, 4.7, C*H*-5 Py'), 7.538 (dt, 2H, J 7.7, 1.3, C*H*-2 and C*H*-6 Ar'), 7.559 (dd, 1H, J 8.3, 1.2, C*H*-7 Ar), 7.702 (ddd, 1H, J 8.3, 7.1, 1.4, C*H*-6 Ar), 7.810 (dd, 1H, J 4.6, 1.4, C*H*-4 Py'), 7.953 (dd, 1H, J 8.3, 2.1, C*H*-4 Py), 8.112 (d, 1H, J 2.8, C*H*-2 Py'), 8.141 (bd, 1H, J 8.1, C*H*-8 Ar), 8.321 (bs, 1H, C*H*-3 Ar), 8.351 (bd, 1H, J 4.5, C*H*-6 Py), 8.546 (bd, 1H, J 7.9, C*H*-5 Ar), 8.838 (d, 1H, J 1.9, C*H*-2 Py), 11.449 (bs, 1H, N*H*-N); ^{13}C NMR 55.68 (*C*H), 118.63 (*C*H-6 Py'), 119.63 (*C*H-6 Py), 122.19 (*C*H-5 Ar), 122.41 (*C*H-2 Py), 123.08 (*C*H-5 Py'), 123.74 (*C*H-5 Py), 124.50 (*C*H-8 Ar), 126.86 (*C*H-4 Ar'), 126.99 (*C*H-7 Ar), 127.16 (*C*H-2 and *C*H-6 Ar'), 128.08 (*C*H-3 and *C*H-5 Ar'), 130.87 (*C*H-6 Ar), 134.07 (C_{quat}-8a Ar), 135.03 (C_{quat}-4a Ar), 136.10 (*C*H-2 Py'), 136.68 (*C*H-4 Py), 137.54 (*C*H-4 Py'), 140.98 (C_{quat}-1 Ar'), 143.47 (C_{quat}-1 Py'), 146.93 (C_{quat}-1 Py). The signals for C*H*-3 Ar and C*H*-6 Py changing their places at 302K: 8.302 (bm, 1H, C*H*-6 Py), 8.368 (bs, 1H, C*H*-3 Ar); C*H*-3 Ar shows NOESY cross peaks with CH-2 and CH-6 Ar' and with CH-6 Py'; ESI (TIS)-Q m/z 432.23 $[M+1]^+$, $C_{27}H_{21}N_5O$.

*Compound **5b**:* Reaction time: 4 days; 53 % overall yield; R_f 0.26 (5 % MeOH/DCM); m. p. 156-157 °C; UV λ_{max} 455 nm; ^{1}H NMR (DMSO-d_6) 5.981 (bs, 1H, C*H*), 6.543 (bs, 1H, N*H*-CH), 6.894 (bd, 1H, J 7.9, C*H*-6 Py'), 7.051 (dd, 1H, J 8.3, 4.6, C*H*-5 Py'), 7.233 (d, 1H, J 4.4, C*H*-4 Ar'), 7.440 (m, 1H, C*H*-5 Py), 7.466 (bs, 1H, C*H*-2 Ar'), 7.561 (dd, 1H, J 5.0, 2.9, C*H*-5 Ar'), 7.553 (t, 1H, J 7.6, C*H*-7 Ar), 7.704 (td, 1H, J 7.6, 1.0, C*H*-6 Ar), 7.778 (dd, 1H, J 4.4, 0.9, C*H*-4 Py'), 7.958 (bs, 1H, C*H*-4 Py), 8.069 (d, 1H, J 2.8, C*H*-2 Py'), 8.131 (bs, 1H, C*H*-8

Ar), 8.329 (bs, 1H, C*H*-3 Ar), 8.362 (bs, 1H, C*H*-6 Py), 8.541 (bs, 1H, C*H*-5 Ar), 8.817 (bs, 1H, C*H*-2 Py), 11.756 (bs, 1H, N*H*-N); ESI (TIS)-Q m/z 438.19 $[M+1]^+$, $C_{25}H_{19}N_5OS$.

*Compound **5c**:* Reaction time: 4 days; 56 % overall yield; R_f 0.15 (5 % MeOH/DCM); m. p. 136-137 °C; UV λ_{max} 459 nm; ^{1}H NMR (DMSO-d_6, 373K) 6.029 (bs, 1H, C*H*), 6.958 (bd, 1H, J 8.2, C*H*-5 Py'), 7.025 (bd, 1H, J 8.2, C*H*-6 Py'), 7.345 (dd, 1H, J 7.7, 4.6, C*H*-5 Py or Ar'), 7.437 (dd, 1H, J 7.8, 4.6, C*H*-5 Py or Ar'), 7.549 (dd, 1H, J 8.1, 0.9, C*H*-7 Ar), 7.702 (dd, 1H, J 8.2, 1.2, C*H*-6 Ar), 7.805 (dt, 1H, J 7.9, 1.6, C*H*-4 Py or Py'), 7.884 (dt, 1H, J 7.9, 1.6, C*H*-4 Py or Py'), 7.950 (bd, 1H, J 7.6, C*H*-4 Ar'), 8.075 (bs, 1H, C*H*-2 Py'), 8.153 (bd, 1H, J 8.0, C*H*-8 Ar), 8.311 (bs, 1H, C*H*-6 Py), 8.371 (bs, 1H, C*H*-3 Ar), 8.468 (bs, 2H, J 1.3, 7.7, C*H*-6 Ar'), 8.554 (bd, 1H, J 8.2, C*H*-5 Ar), 8.766 (bs, 1H, C*H*-2 Py or Ar'), 8.850 (bs, 1H, C*H*-2 Py or Ar'); ^{13}C NMR 54.88 (*C*H), 119.81 (*C*H-6 Py'), 120.72 (*C*H-5 Py'), 121.31 (*C*H-6 Py), 123.24 (*C*H-4 Ar'), 123.31 (*C*H-5 Ar), 124.08 (*C*H-5 Py or Ar'), 124.62 (*C*H-5 Py or Ar'), 125.28 (*C*H-2 Py'), 125.32 (*C*H-8 Ar), 127.76 (*C*H-7 Ar), 131.66 (*C*H-6 Ar), 134.65 (*C*H-4 Py or Py'), 135.46 (*C*H-4 Py or Py'), 148.84 (*C*H-6 Ar'), 149.51 (*C*H-2 Py or Ar'), 130.69 (C_{quat}-8a Ar), 137.08 (C_{quat}-4a Ar), 138.79 (C_{quat}-1 Ar'), 141.28 (C_{quat}-1 Py'), 145.16 (C_{quat}-1 Py); ESI (TIS)-Q m/z 433.22 $[M+1]^+$, $C_{26}H_{20}N_6O$.

*Compound **5d**:* Reaction time: 4 days; 35 % overall yield; R_f 0.30 (5 % MeOH/DCM); m. p. 214-215 °C; UV λ_{max} 455 nm; ^{1}H NMR (DMSO-d_6) 2.286 (s, 3H, CH_3), 5.776 (bs, 1H, C*H*), 6.483 (bs, 1H, N*H*-CH), 6.087 (bd, 1H, J 7.7, C*H*-6 Py'), 7.056 (dd, 1H, J 8.3, 4.6, C*H*-5 Py'), 7.080 (d, 1H, J 7.5, C*H*-4 Ar'), 7.240 (t, 1H, J 7.6, C*H*-5 Ar'), 7.321 (bd, 1H, J 7.5, C*H*-6 Ar'), 7.344 (bs, 1H, C*H*-2 Ar'), 7.431 (bs, 1H, C*H*-5 Py), 7.546 (bt, 1H, J 7.2, C*H*-7 Ar), 7.706 (ddd, 1H, J 8.2, 7.2, 1.3, C*H*-6 Ar), 7.784 (dd, 1H, J 4.6, 0.9, C*H*-4 Py'), 7.937 (bs, 1H, C*H*-4 Py), 8.059 (d, 1H, J 2.8, C*H*-2 Py'), 8.083 (bs, 1H, C*H*-8 Ar), 8.282 (bs, 1H, C*H*-6 Py), 8.400 (bs, 1H, C*H*-3 Ar), 8.482 (bs, 1H, C*H*-5 Ar), 8.794 (bs, 1H, C*H*-2 Py), 11.819 (bs, 1H, N*H*-N); ^{13}C NMR 21.18 (*C*H_3), 56.50 (*C*H), 118.70 (*C*H), 119.97 (*C*H), 122.90 (*C*H), 123.69 (*C*H), 123.78 (C_{quat}), 124.35 (*C*H), 124.90 (*C*H), 128.15 (*C*H), 128.20 (*C*H), 128.31 (*C*H), 128.51 (*C*H), 136.10 (C_{quat}), 136.28 (*C*H), 136.71 (C_{quat}), 137.37 (C_{quat}), 137.63 (*C*H), 137.73 (C_{quat}), 143.93 (C_{quat}); ESI (TIS)-Q m/z 446.32 $[M+1]^+$, $C_{28}H_{23}N_5O$.

*Compound **5e**:* Reaction time: 6 days; 17 % overall yield; R_f 0.29 (5 % MeOH/DCM); m. p. 212-213 °C; UV λ_{max} 456 nm; ^{1}H NMR (DMSO-d_6) 3.707 (s, 3H, OCH_3), 3.749 (s, 3H, OCH_3), 5.782 (bs, 1H, C*H*), 6.446 (bs, 1H, N*H*-CH), 6.870 (bd, 1H, J 7.2, C*H*-6 Py'), 6.915 (d, 1H, J 8.5, C*H*-5 Ar'), 7.008 (bm, 1H, C*H*-6 Ar'), 7.055 (dd, 1H, J 8.3, 4.6, C*H*-5 Py'), 7.141 (d, 1H, J 1.9, C*H*-2 Ar'), 7.426 (bs, 1H, C*H*-5 Py), 7.550 (bt, 1H, J 7.2, C*H*-7 Ar), 7.709 (ddd, 1H, J 8.2, 7.2, 1.3, C*H*-6 Ar), 7.783 (d, 1H, J 4.2, C*H*-4 Py'), 7.919 (bs, 1H, C*H*-4 Py), 8.051 (d, 1H, J 2.7, C*H*-2 Py'), 8.081 (bs, 1H, C*H*-8 Ar), 8.267 (bs, 1H, C*H*-6 Py), 8.375 (bs, 1H,

C*H*-3 Ar), 8.476 (bs, 1H, C*H*-5 Ar), 8.784 (bs, 1H, C*H*-2 Py), 11.801 (bs, 1H, N*H*-N); ^{13}C NMR 54.98 (*C*H), 55.59 (O*C*H$_3$), 55.70 (O*C*H$_3$), 111.79 (*C*H-5 Ar'), 111.78 (*C*H-2 Ar'), 118.73 (*C*H-6 Py'), 119.82 (*C*H-6 Ar'), 119.88 (C_{quat}), 122.90 (*C*H-5 Ar), 123.66 (*C*H-5 Py'), 123.74 (*C*H-6 Py), 124.35 (*C*H-5 Py), 125.62 (*C*H-8 Ar), 128.05 (*C*H-7 Ar), 132.45 (*C*H-6 Ar), 136.23 (*C*H-4 Py), 136.348 (*C*H-2 Py'), 136.34 (C_{quat}), 137.64 (*C*H-4 Py'), 143.98 (C_{quat}), 148.24 (C_{quat}), 148.80 (C_{quat}); ESI (TIS)-Q m/z 492.28 $[M+1]^+$, $C_{29}H_{25}N_5O_3$.

*Reaction between **5b** and acetaldehyde*

Version 1. To a solution of **5b** (0.2 mmol) in DMF (6 ml; 3x10^{-2} M) acetaldehyde (1 mmol) was added and was kept at room temperature for 6 days. The reaction mixture was poured in water and the solid phase formed was filtered off. The product was purified by flash chromatography on silica gel.

*Compound **7**:* 51 % yield; R_f 0.51 (5 % MeOH/DCM); m. p. 116-117 °C decomp.; UV λ_{max} 408 nm; ^{1}H NMR ($CDCl_3$) 2.349 (ddd, 1H, J 13.4, 8.4, 2.4, ½ C*H*$_2$), 2.421 (ddd, 1H, J 13.4, 11.0, 5.6, ½ C*H*$_2$), 4.633 (dd, 1H, J 8.3, 5.8, C*H*-Ar'), 5.849 (dd, 1H, J 5.1, 2.3, C*H*-OH), 6.941 (dd, 1H, J 5.0, 1.3, C*H*-4 Ar'), 6.996 (ddd, 1H, J 2.9, 1.3, 0.6, C*H*-2 Ar'), 7.305 (dd, 1H, J 5.0, 3.0, C*H*-5 Ar'), 7.413 (ddd, 1H, J 8.1, 4.7, 0.7, C*H*-5 Py), 7.510 (ddd, 1H, J 8.1, 6.8, 1.2, C*H*-7 Ar), 7.588-7.616 (ddd, 1H, J 1., C*H*-6 Ar, overlapped with C*H*-3 Ar), 7.602 (d, 1H, J 0.5, C*H*-3 Ar), 8.156 (ddd, 1H, J 8.2, 2.3, 1.6, C*H*-4 Py), 8.281 (dt, 1H, J 8.1, 0.8, C*H*-8 Ar), 8.622 (dd, 1H, J 4.7, 1.6, C*H*-6 Py), 8.851 (dt, 1H, J 8.2, 0.6, C*H*-5 Ar), 9.126 (d, 1H, J 2.0, C*H*-2 Py); ^{13}C NMR 33.80 (*C*H-Ar'), 36.02 (*C*H-OH), 114.51 (*C*H-3 Ar), 118.47 (C_{quat}-2 Ar), 122.02 (*C*H-8 Ar), 122.70 (*C*H-2 Ar'), 122.98 (*C*H-5 Ar), 124.09 (*C*H-5 Py), 125.33 (C_{quat}-4 Ar), 126.13 (*C*H-7 Ar), 126.51 (*C*H-5 Ar'), 127.22 (*C*H-4 Ar'), 127.46 (*C*H-6 Ar), 127.73 (*C*H-4 Py), 131.95 (C_{quat}-4a Ar), 141.30 (C_{quat}-8a Ar), 144.66 (C_{quat}-1 Ar'), 146.44 (*C*H-2 Py), 148.53 (C_{quat}-1 Py), 150.36 (*C*H-6 Py), 151.68 (C_{quat}-1 Ar); ESI (TIS)-Q m/z 388.58 $[M+1]^+$, $C_{22}H_{17}N_3O_2S$.

Version 2. To a suspension of **5b** (0.1 mmol) in ethanol (20 ml) acetaldehyde (1 mmol) was added and the mixture was stirred at room temperature for 4 days. Complete dissolution was reached at the end of the reaction; followed by TLC. The solvent was evaporated and the product was purified by flash chromatography on silica gel followed by preparative TLC.

*Compound **6**:* 67 % yield; R_f 0.49 (5 % MeOH/DCM); m. p. 188-189 °C; UV λ_{max} 450 nm; ^{1}H NMR ($CDCl_3$) 1.377 (t, 3H, J 7.0, C*H*$_3$), 3.762 (q, 2H, J 7.0, C*H*$_2$), 5.826 (bs, 1H, C*H*-Ar'), 7.109 (dd, 1H, J 5.1, 1.0, C*H*-4 Ar'), 7.208 (dd, 1H, J 2.6, 0.8, C*H*-2 Ar'), 7.29 (dd, 1H, J 5.1, 3.1, C*H*-5 Ar'), 7.470 (dd, 1H, J 8.1, 4.7, C*H*-5 Py), 7.606 (ddd, 1H, J 8.2, 6.9, 1.3, C*H*-7 Ar), 7.693 (ddd, 1H, J 8.4, 6.8, 1.3, C*H*-6 Ar), 7.737 (s, 1H, C*H*-3 Ar), 8.226 (ddd, 1H, J 8.1, 2.0,

1.8, C*H*-4 Py), 8.366 (dd, 1H, J 8.2, 0.8, C*H*-8 Ar), 8.679 (dd, 1H, J 4.6, 1.3, C*H*-6 Py), 8.925 (dd, 1H, J 8.4, 0.8, C*H*-5 Ar), 9.223 (d, 1H, J 1.9, C*H*-2 Py), 9.676 (bs, 0.8, N*H*); ^{13}C NMR 15.18 (*C*H$_3$), 65.76 (*C*H$_2$), 81.53 (*C*H-Ar'), 113.23 (*C*H-3 Ar), 117.92 (C_{quat}-2 Ar), 122.55 (*C*H-8 Ar), 122.78 (*C*H-5 Ar), 123.26 (*C*H-2 Ar'), 124.06 (*C*H-5 Py), 125.80 (C_{quat}-4 Ar), 126.03 (*C*H-7 Ar), 126.53 (*C*H-4 Ar'), 126.79 (*C*H-5 Ar'), 127.05 (*C*H-4 Py), 128.05 (*C*H-6 Ar), 132.66 (C_{quat}-4a Ar), 140.67 (C_{quat}-8a Ar), 141.16 (C_{quat}-1 Ar'), 147.05 (*C*H-2 Py), 148.54 (C_{quat}-1 Py), 150.72 (*C*H-6 Py), 155.89 (C_{quat}-1 Ar); ESI (TIS)-Q m/z 389.54 $[M+1]^+$, $C_{22}H_{20}N_4OS$.

Crystallography

The crystals of **4** perchlorate, **6** and **7** were mounted on a glass capillary and all geometric and intensity data were taken from these crystals. Diffraction data were taken on an Agilent SupernovaDual diffractometer equipped with an Atlas CCD detector using micro-focus Mo Kα radiation (λ = 0.71073 Å) at room temperature. The determination of the unit cell parameters, data collection and reduction were performed with Crysalispro software [S1]. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 with ShelxS and ShelxL 2018/1 programs [S2]. All non-hydrogen atoms, including solvent molecules, were located successfully from Fourier maps and were refined anisotropically. The H atoms were placed in idealized positions (C—H = 0.86 to 0.93 Å) and were constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl}). The most important crystallographic and refinement indicators are listed on Table S1.

References

[S1] Rigaku Oxford Diffraction, CrysAlisPro Software system, version 1.171.37.35, Rigaku Corporation, Oxford, UK **2018**.

[S2] G. M. Sheldrick, *Acta Cryst. A* **2008**, *64*, 112–122.

Table S1. Crystal data and the most important structure refinement indicators for compounds **4** as perchlorate, **6** and **7**.

Identification code	Compound **4** perchlorate	Compound **6**	Compound **7**
Empirical formula	$C_{23}H_{22}Cl_2N_6O_9$	C22 H20 N4 O S, H2 O	C22 H17 N3 O2 S, 0.5(C6 H6)
Formula weight	597.36	406.5	426.50
Temperature/K	290	290	290
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a/Å	8.6004(13)	15.582(2)	5.0282(8)
b/Å	10.5677(13)	5.5480(9)	19.643(3)
c/Å	14.8352(17)	23.037(3)	22.121(3)
α/°	107.404(11)	90	90
β/°	95.633(11)	90.669	91.341(13)
γ/°	92.707(11)	90	90
Unit cell volume /Å^3	1276.2(3)	1991.3(5)	2151.3(6)
Z	2	4	4
ρ_{calc}g/cm^3	1.555	1.356	1.317
μ/mm^{-1}	0.320	0.189	0.178
F(000)	616.0	856	892
Crystal size/mm^3	0.25 × 0.15 × 0.10	0.25 × 0.15 × 0.15	0.3 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Θ range for data collection/°	2.9 to 28.4	3.1 to 27.1	2.8 to 29.1
Index ranges	-7 ≤ h ≤ 10, -12 ≤ k ≤ 14, -17 ≤ l ≤ 18	-18 ≤ *h* ≤ 16, -6 ≤ *k* ≤ 7, -29 ≤ *l* ≤ 28	-6 ≤ *h* ≤ 5, -25 ≤ *k* ≤ 25, -20 ≤ *l* ≤ 30
Reflections collected/independent/ $I > 2\sigma(I)$	8992 / 5212/ 2556	9766 /3585/ 1324	11756/4981/ 1470
R_{int} / R_{sigma}	0.063 / 0.0328	0.095 / 0.1909	0.1005 / 0.133
Data/restraints/parameters	5212/48/391	3585/0/286	4981/ 14/ 300
Goodness-of-fit on F^2	1.032	1.030	0.948
R_1, wR_2 indexes, I>=2σ (I)	0.01029, 0.2525	0.095/0.150	0.0907 /0.2416
R_1, wR_2 indexes, all data	0.1954, 0. 3107	0.259/0.209	0.2472 / 0.3569
Largest diff. peak/hole / e Å^{-3}	0.0.8/-0.6	0.26/-0.30	0.27 / -0.27
CCDC number	1854785	1873276	1873277

I) NMR spectra of starting azo-dye **1**

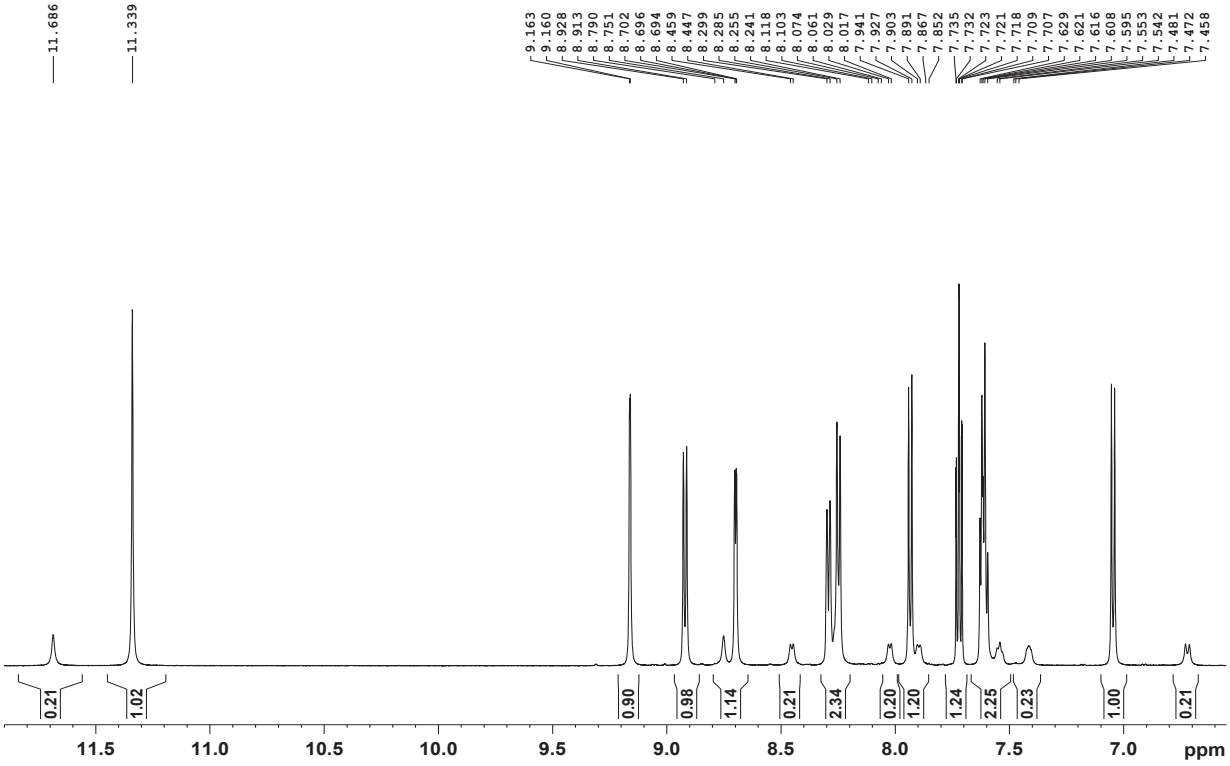

Figure S1. ^{1}H spectrum of **1** in DMSO-d_6.

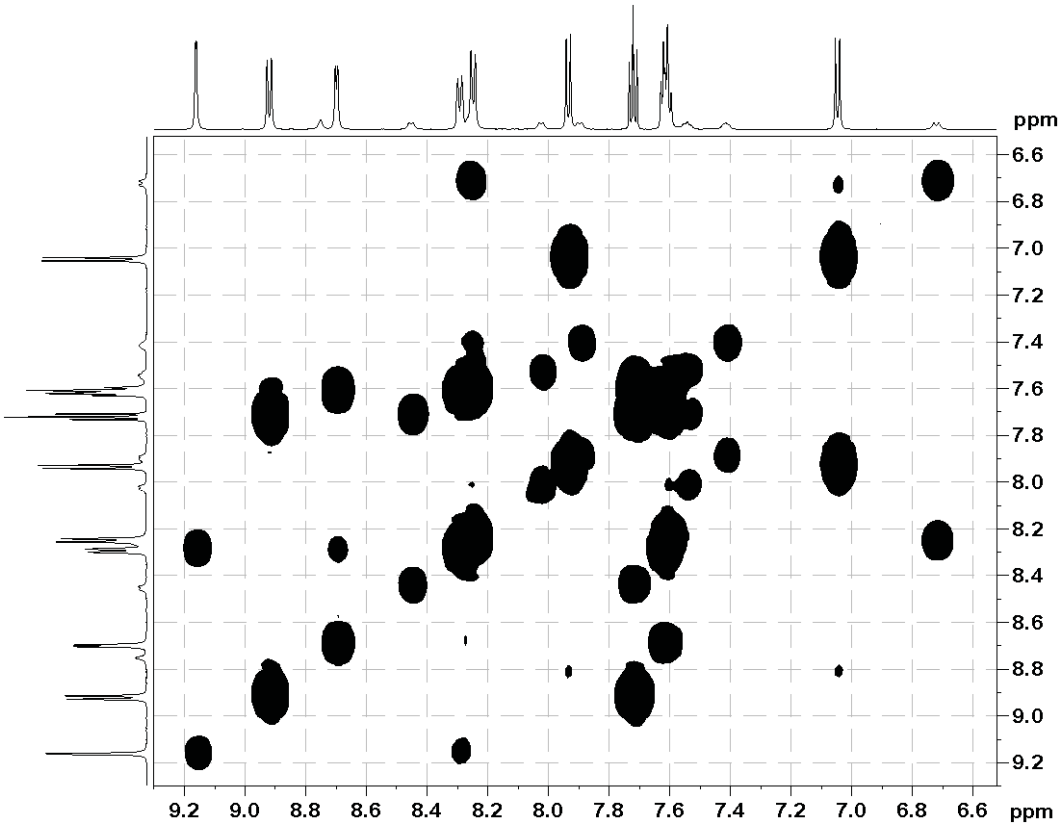

Figure S2. ^{1}H-^{1}H COSY spectrum of **1** in DMSO-d_6.

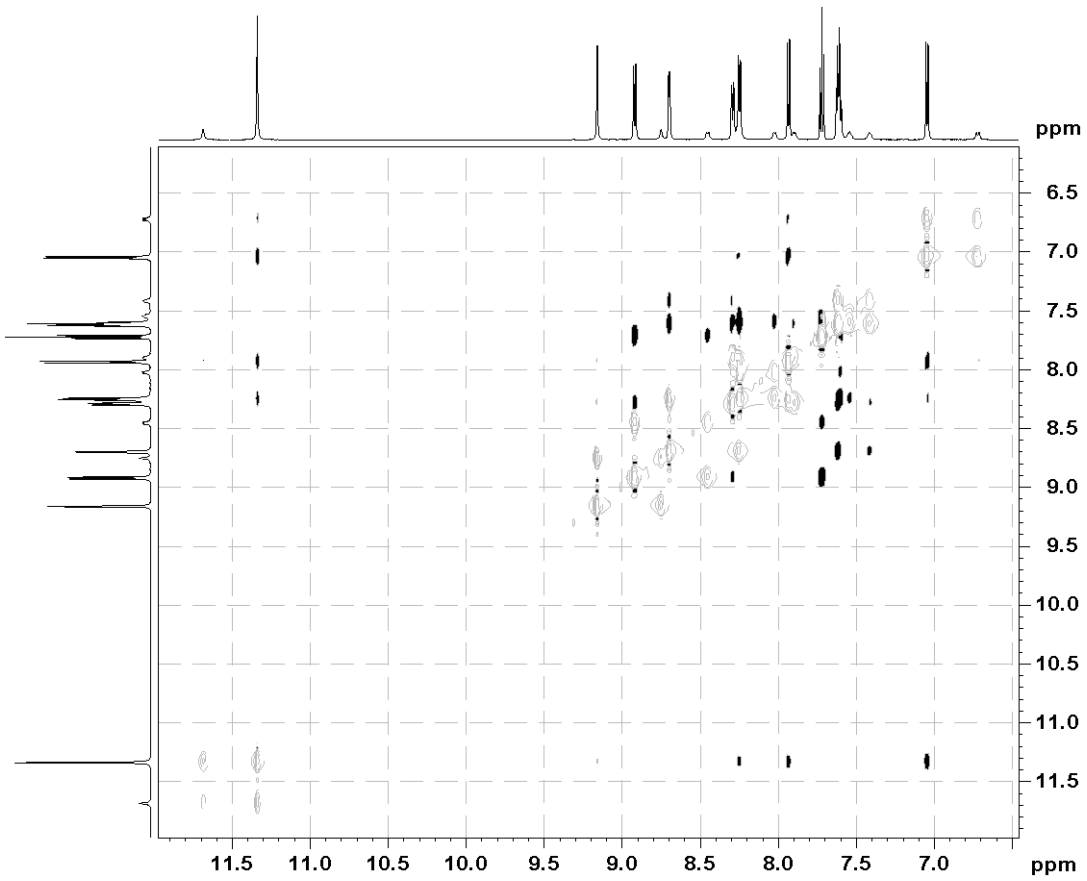

Figure S3. ^{1}H-^{1}H NOESY spectrum of **1** in DMSO-d_6.

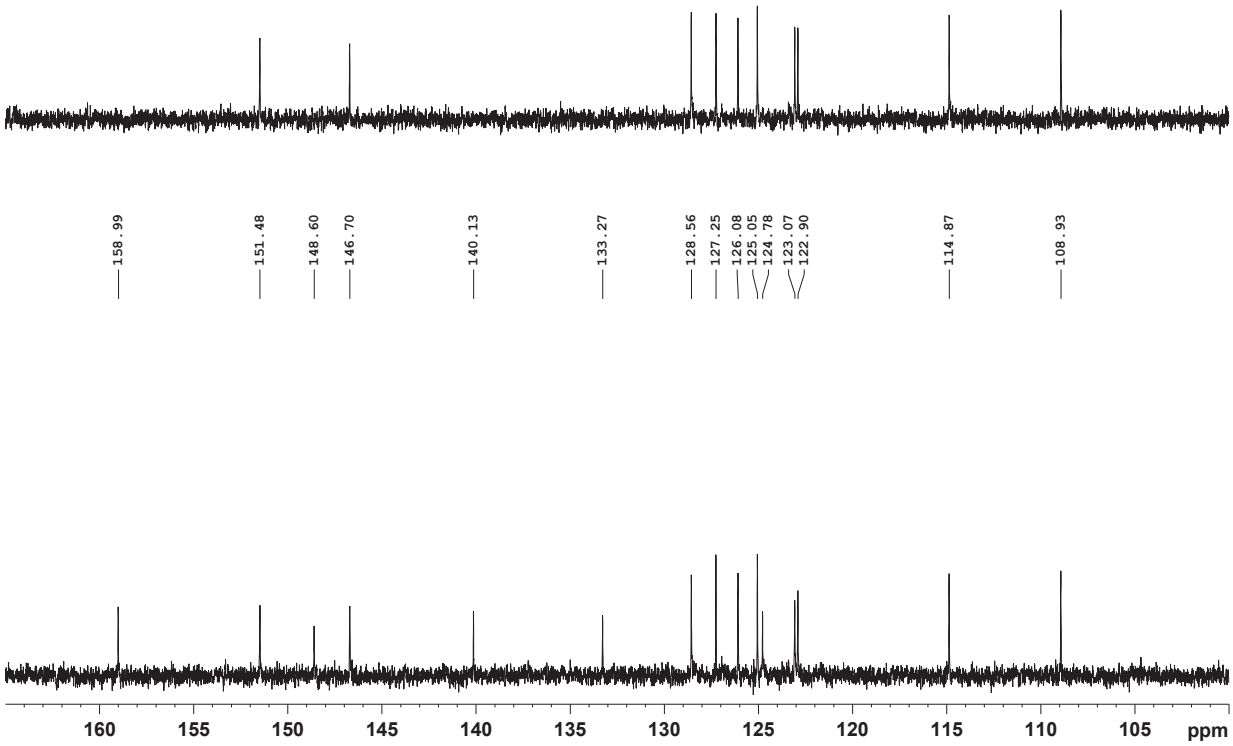

Figure S4. ^{13}C (down) and DEPT (up) spectra of **1** in DMSO-d_6.

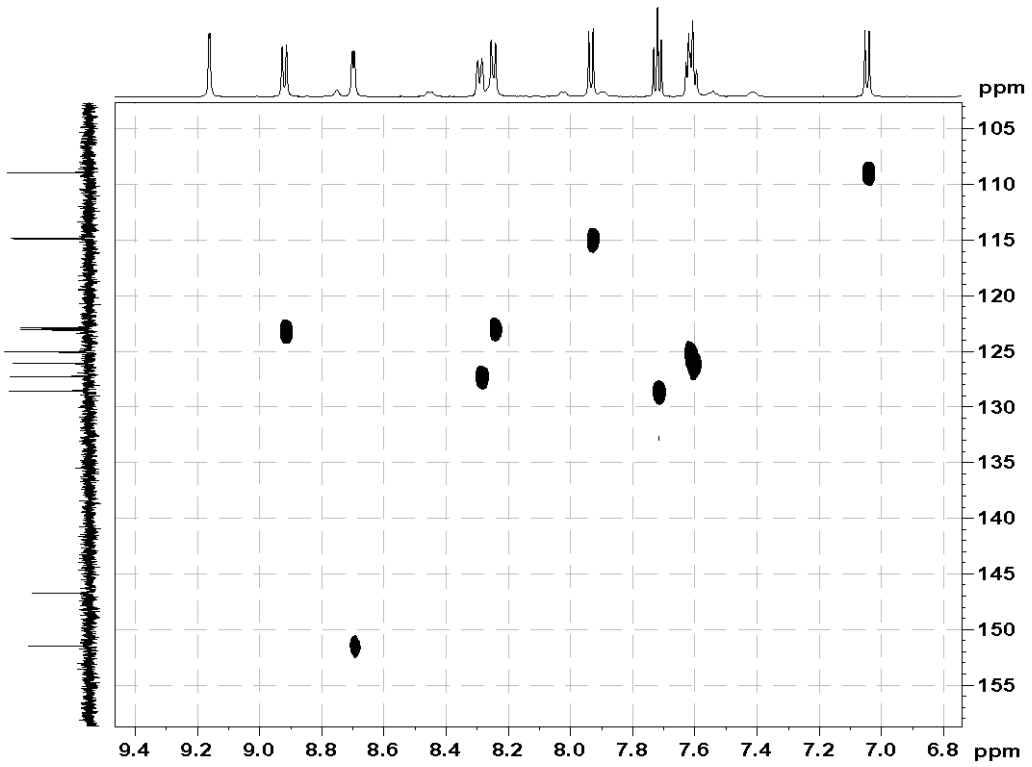

Figure S5. ^{1}H-^{13}C HSQC spectrum of **1** in DMSO-d_6.

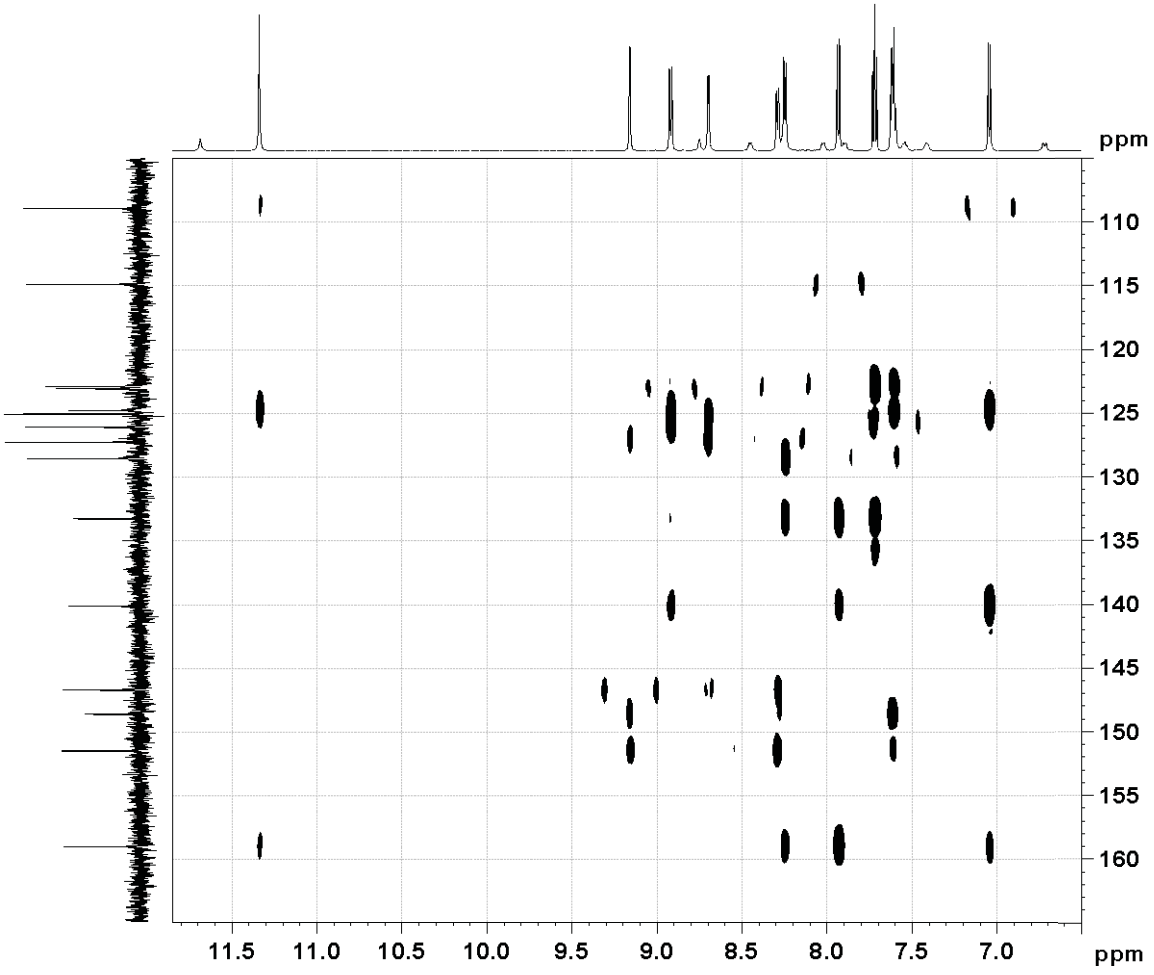

Figure S6. ^{1}H-^{13}C HMBC spectrum of **1** in DMSO-d_6.

II) NMR spectra of **1-OMe**

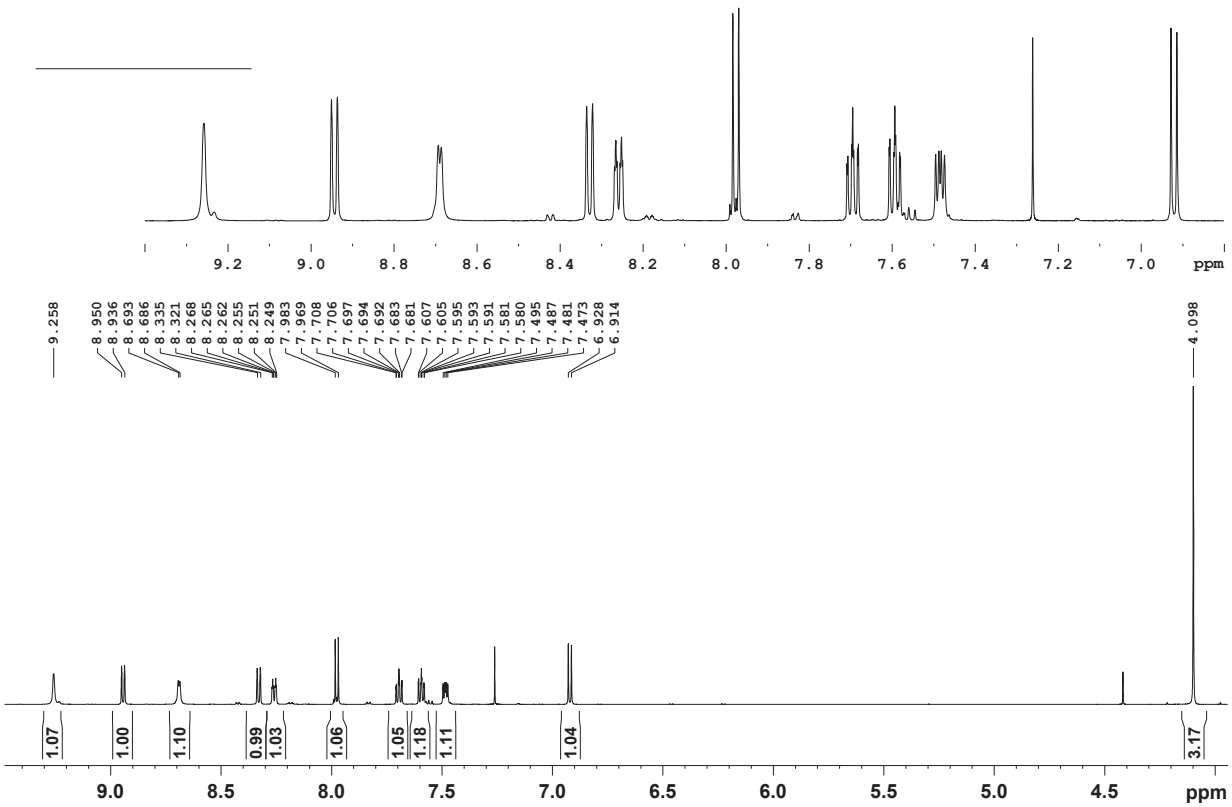

Figure S7. ^{1}H spectrum of **1-OMe** in $CDCl_3$.

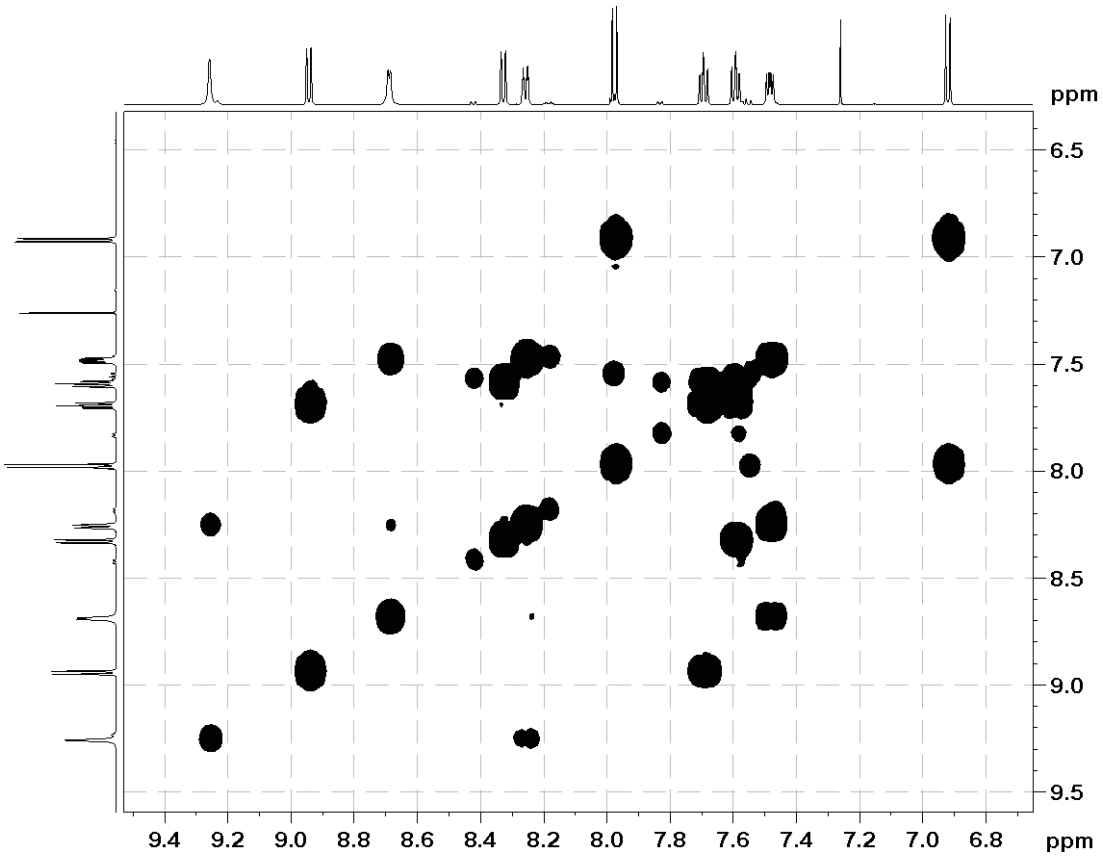

Figure S8. ^{1}H-^{1}H COSY spectrum of **1-OMe** in $CDCl_3$.

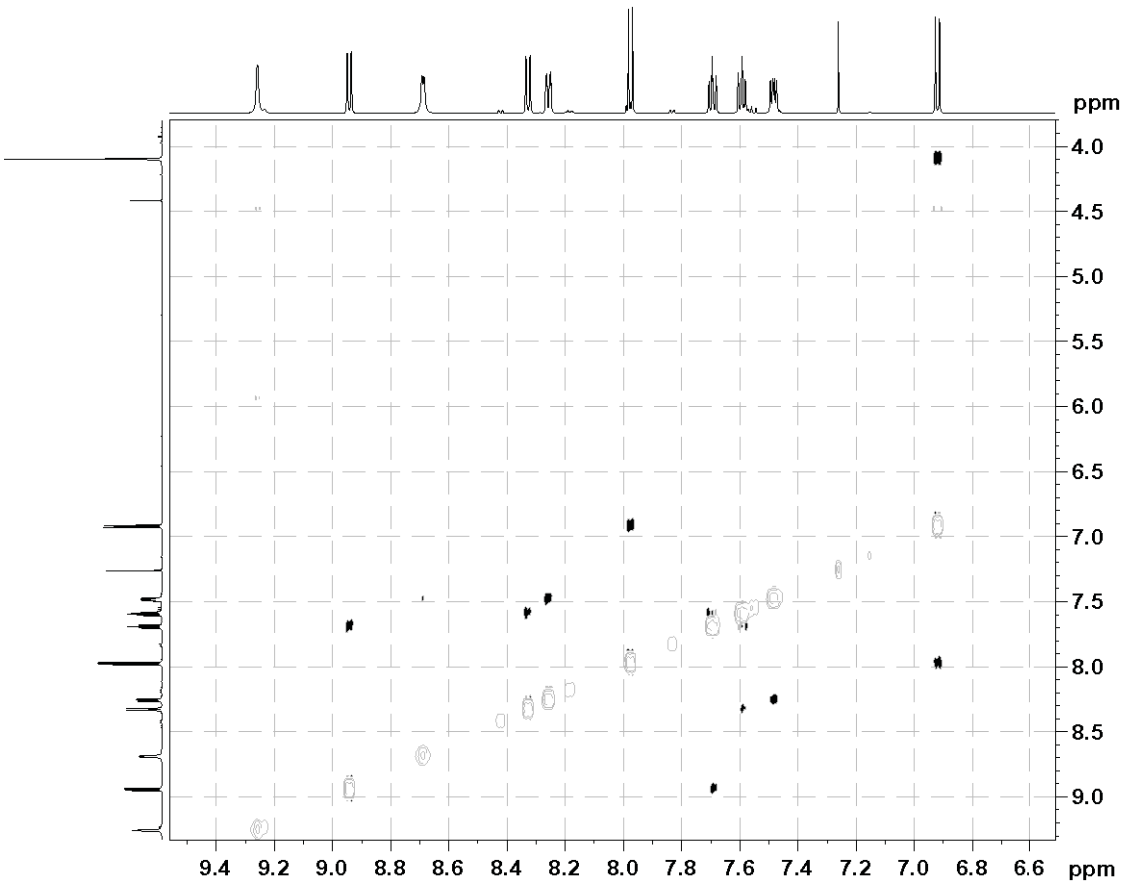

Figure S9. ^{1}H-^{1}H NOESY spectrum of **1-OMe** in $CDCl_3$.

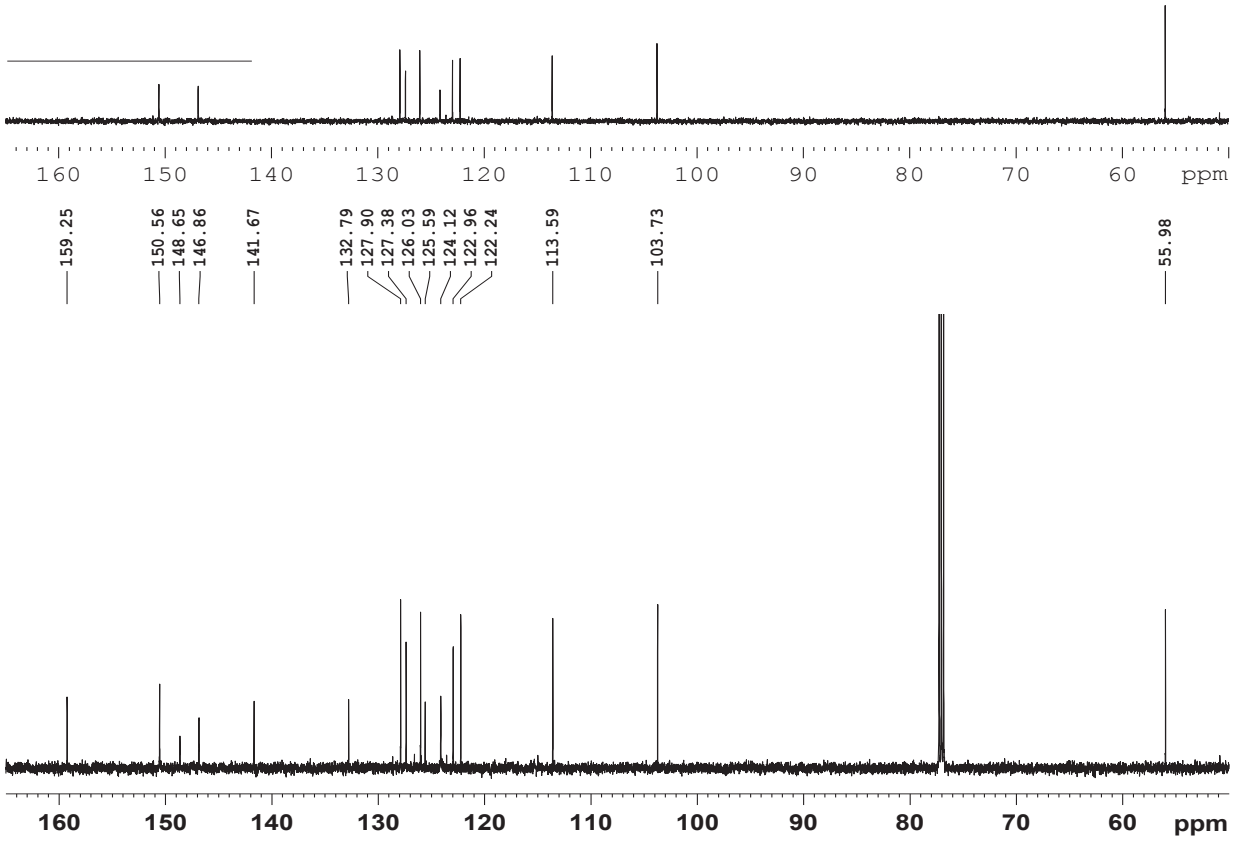

Figure S10. ^{13}C (down) and DEPT (up) spectra of **1-OMe** in $CDCl_3$.

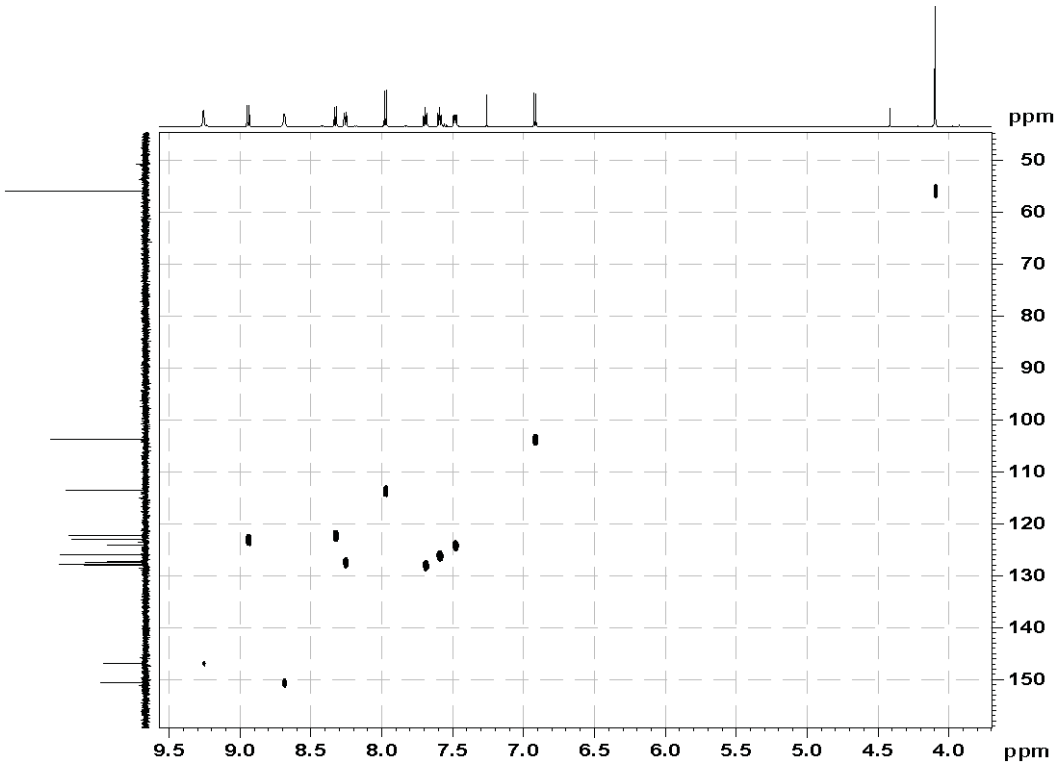

Figure S11. ^{1}H-^{13}C HSQC spectrum of **1-OMe** in $CDCl_3$.

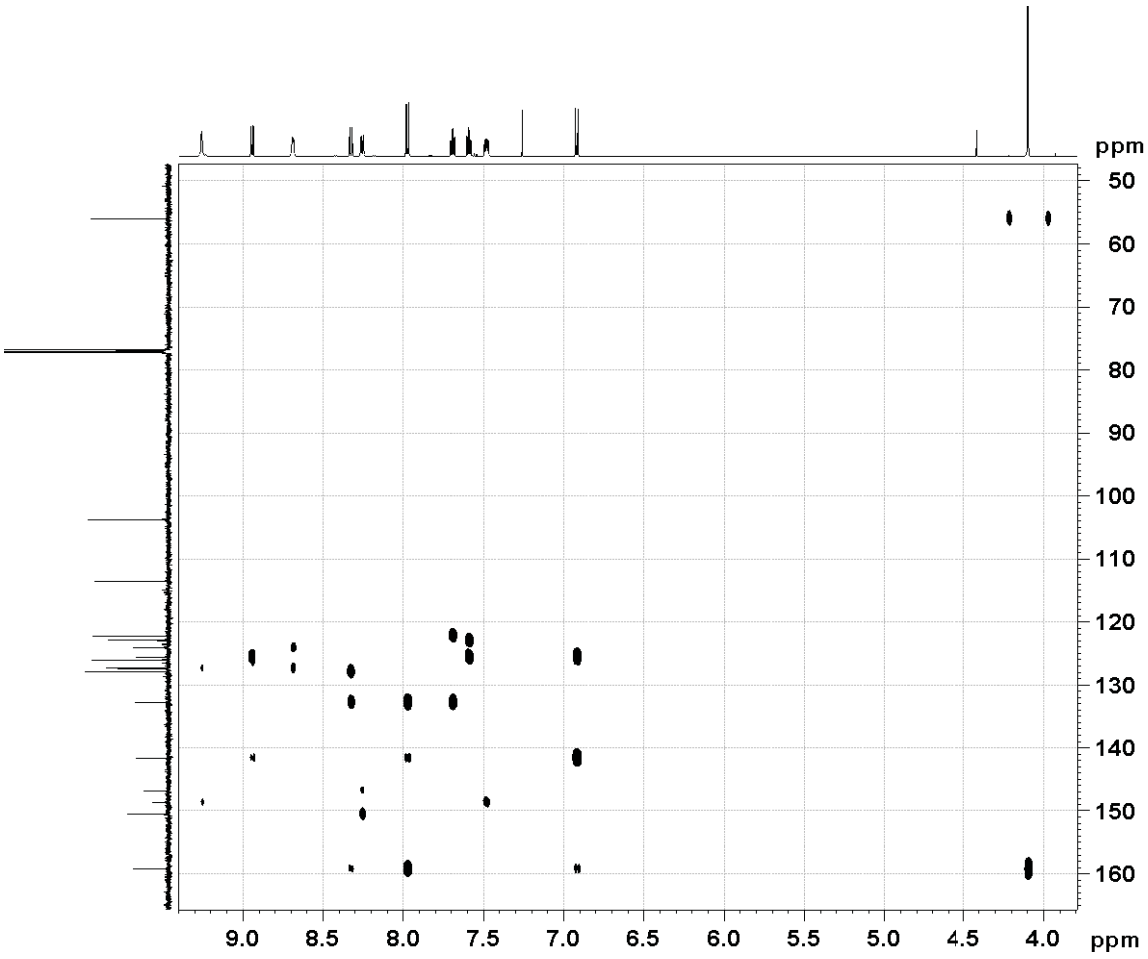

Figure S12. ^{1}H-^{13}C HMBC spectrum of **1-OMe** in $CDCl_3$.

III) NMR spectra of **1-NMe**

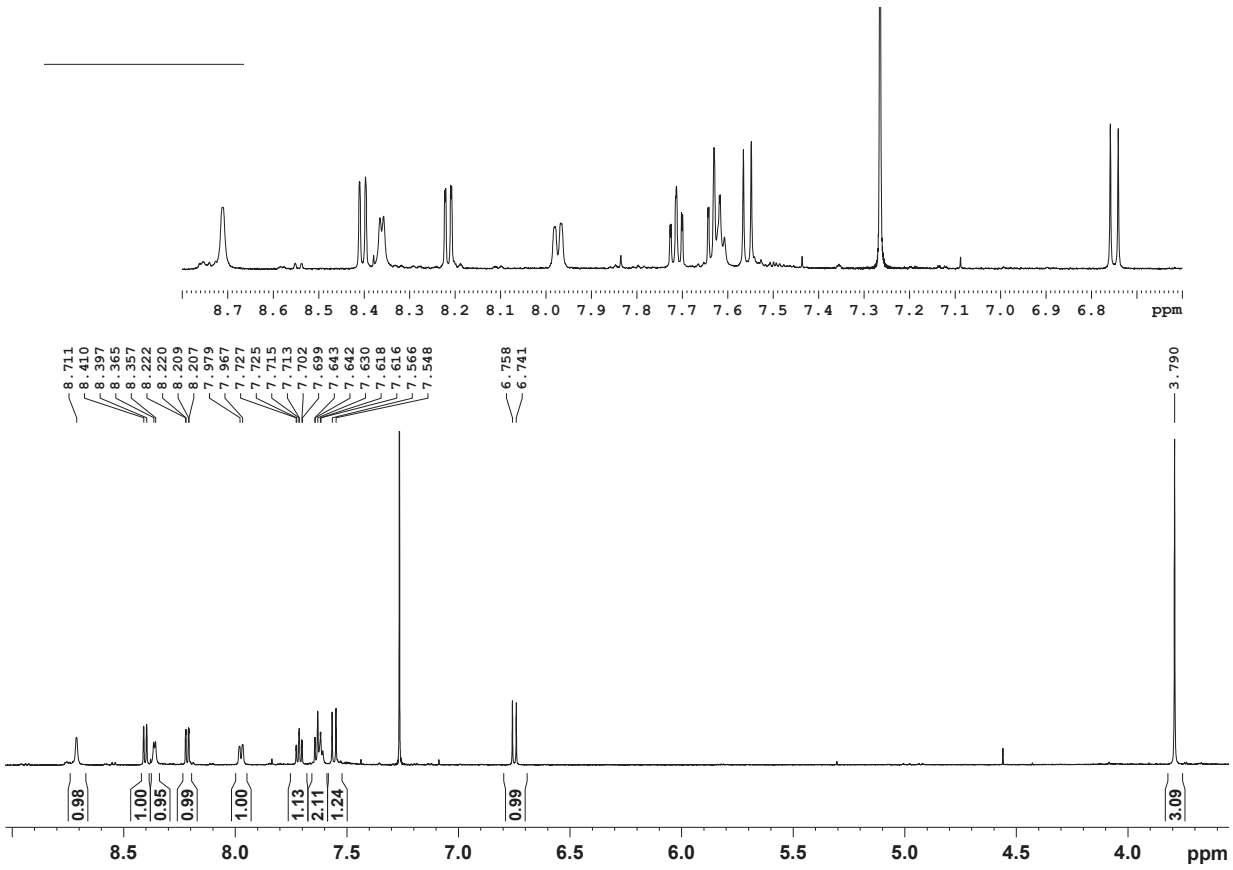

Figure S13. ^{1}H spectrum of **1-NMe** in $CDCl_3$.

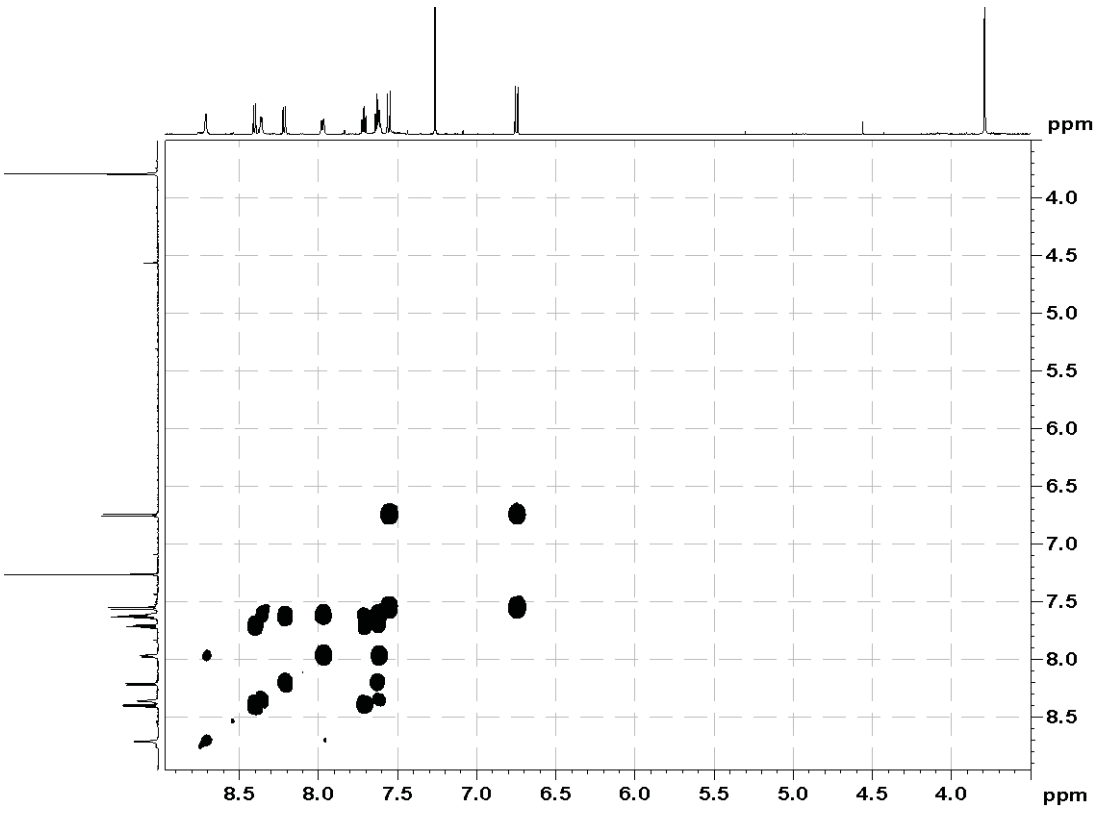

Figure S14. ^{1}H-^{1}H COSY spectrum of **1-NMe** in $CDCl_3$.

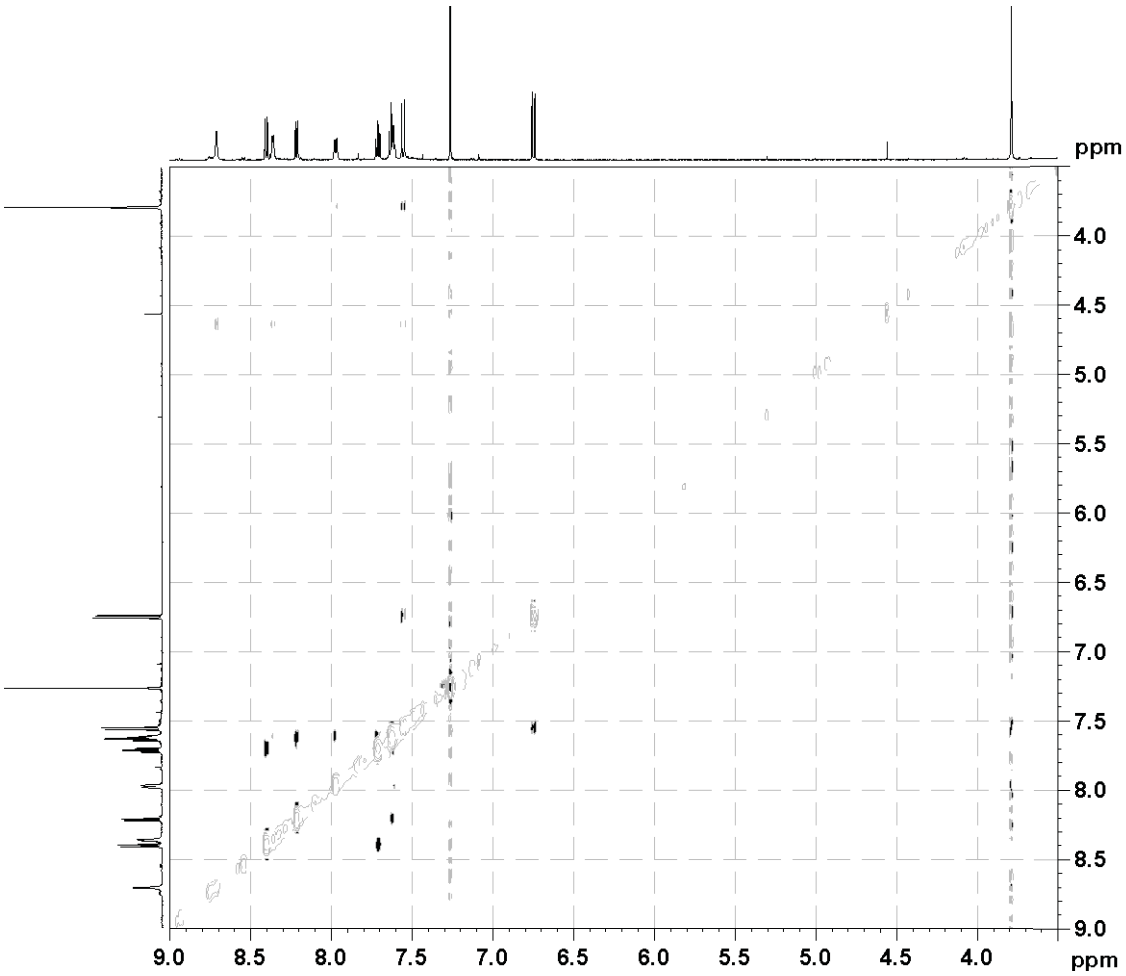

Figure S15. ^{1}H-^{1}H NOESY spectrum of **1-NMe** in $CDCl_3$.

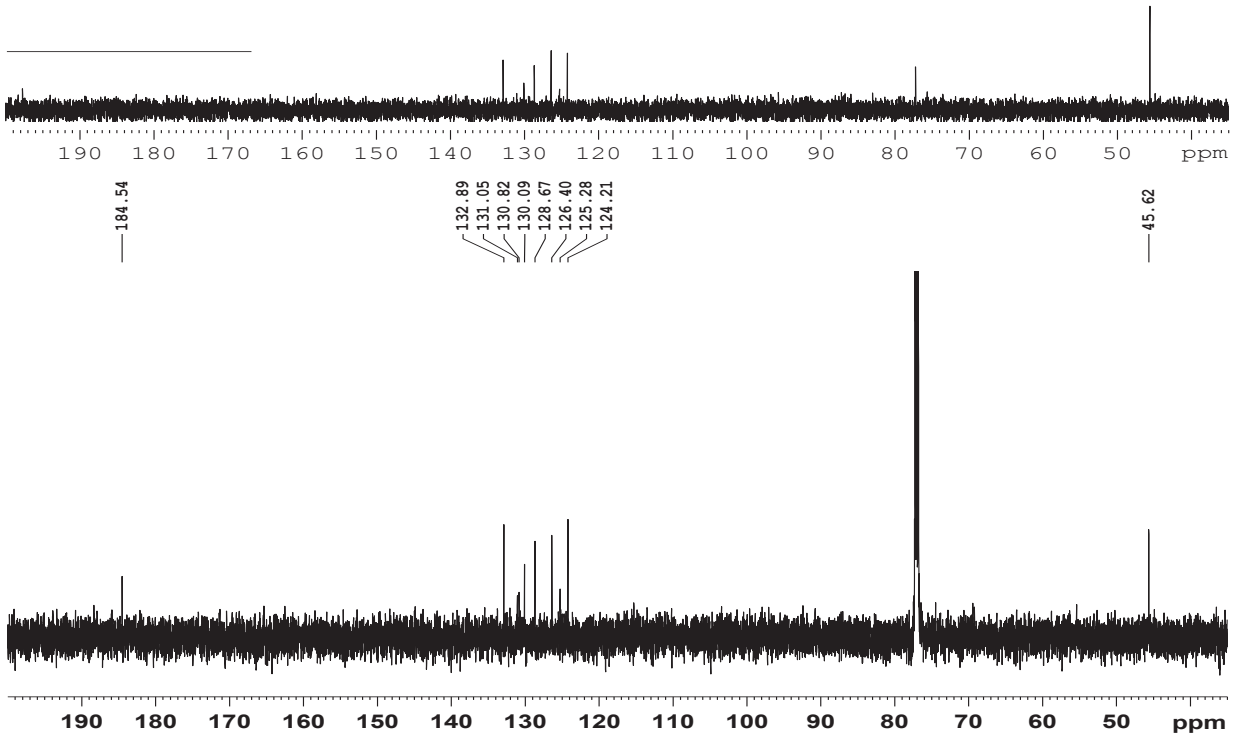

Figure S16. ^{13}C (down) and DEPT (up) spectra of **1-NMe** in $CDCl_3$.

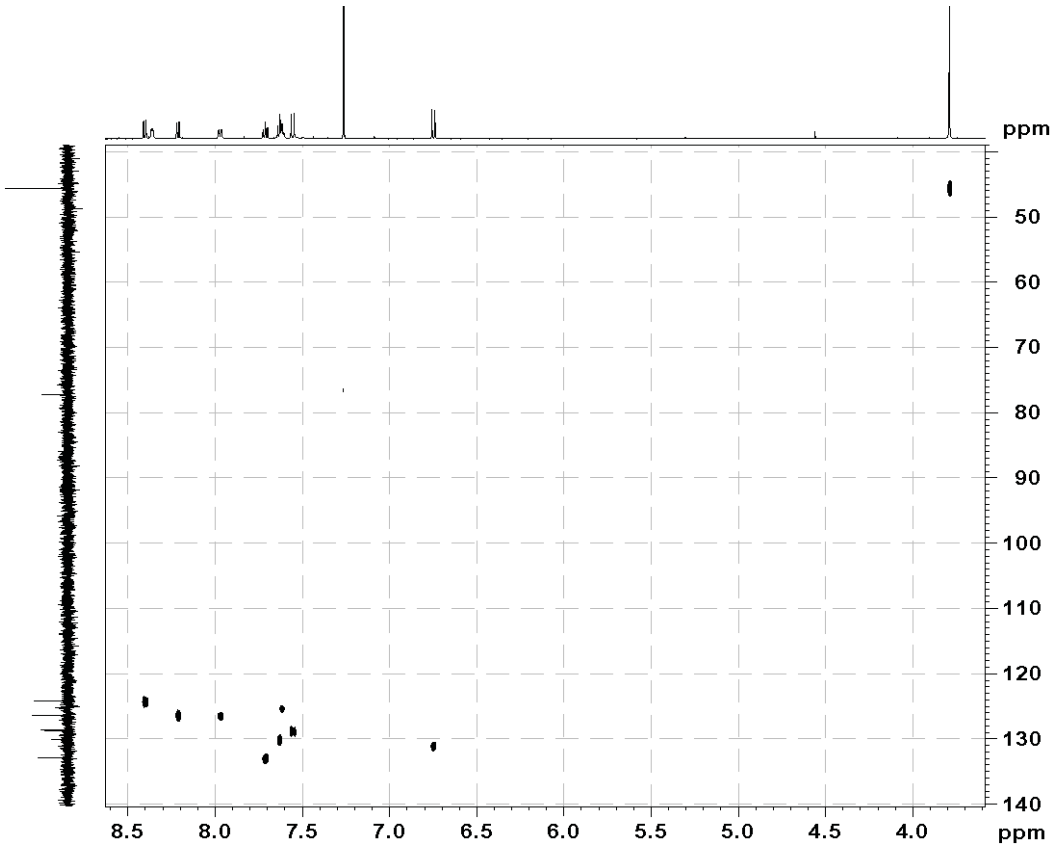

Figure S17. ^{1}H-^{13}C HSQC spectrum of **1-NMe** in $CDCl_3$.

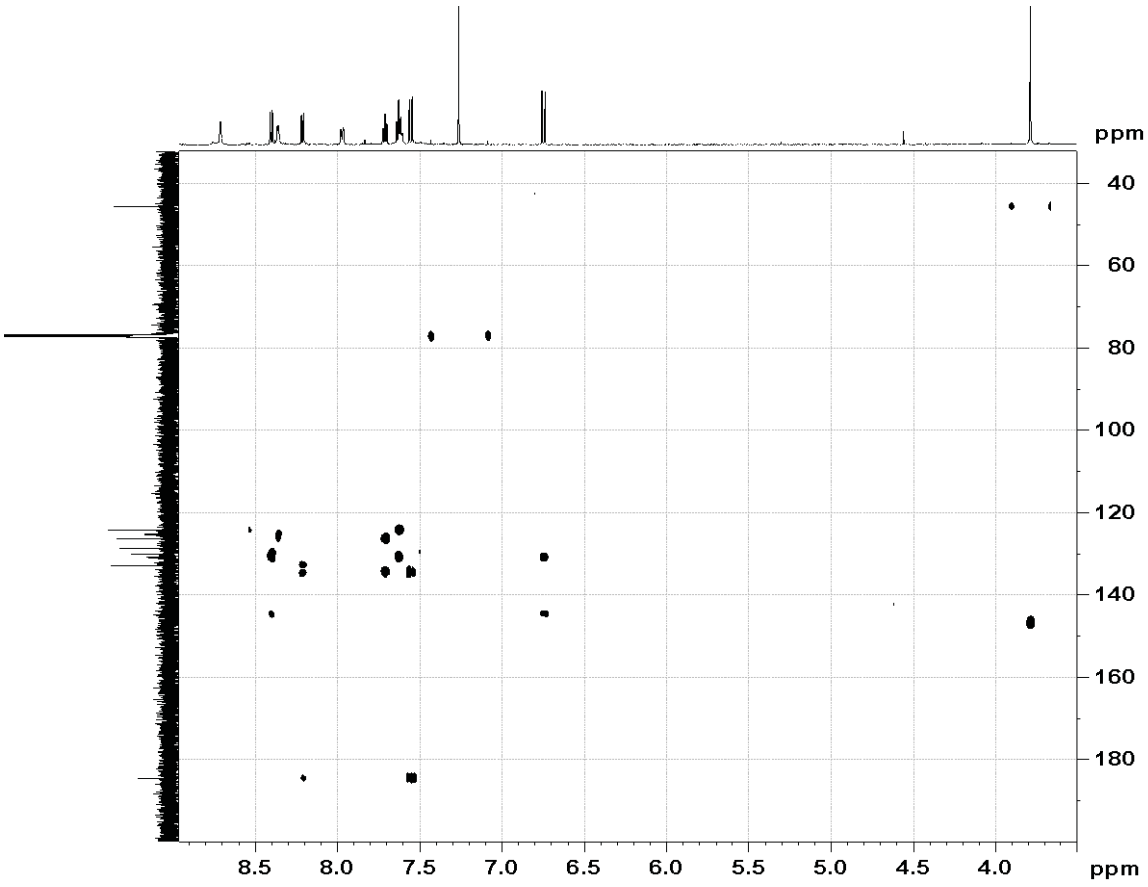

Figure S18. ^{1}H-^{13}C HMBC spectrum of **1-NMe** in $CDCl_3$.

IV) Comparison between ^{1}H and ^{13}C NMR spectra of compounds **1**, **1-OMe** and **1-NMe**

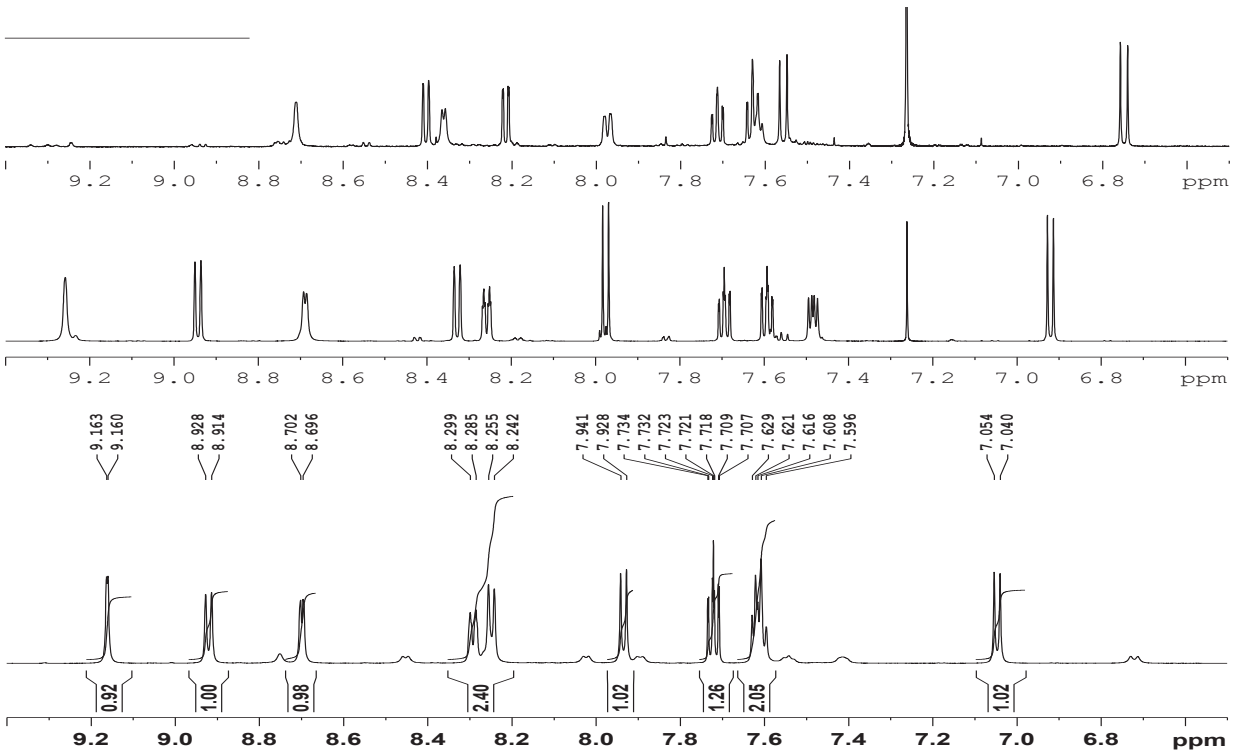

Figure S19. ^{1}H NMR spectra of 4-(pyridin-3-yldiazenyl)naphthalen-1-ol (**1**) in DMSO-d_6 (down), **1-OMe** in $CDCl_3$ (middle), and **1-NMe** $CDCl_3$ (up).

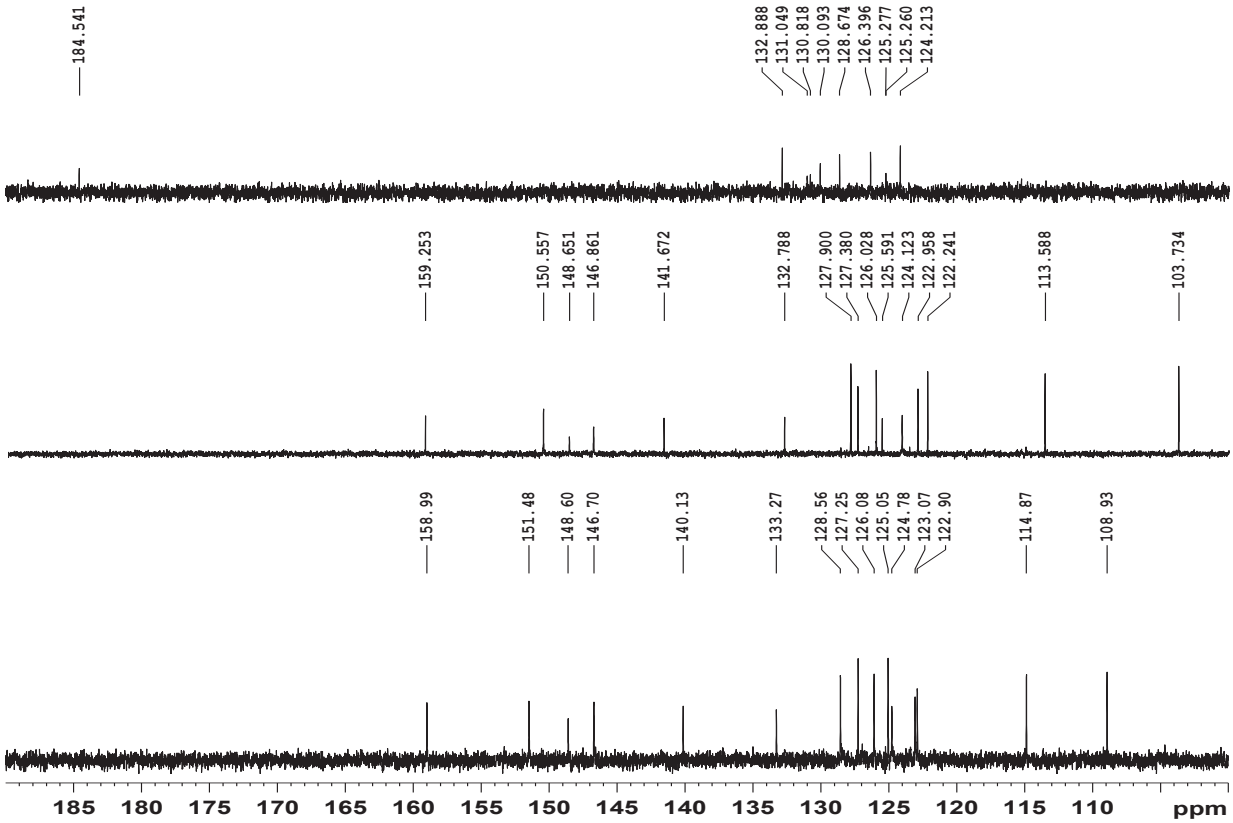

Figure S20. ^{13}C NMR spectra of 4-(pyridin-3-yldiazenyl)naphthalen-1-ol (**1**) in DMSO-d_6 (down), **1-OMe** in $CDCl_3$ (middle), and **1-NMe** $CDCl_3$ (up).

V) NMR spectra of compound **2**

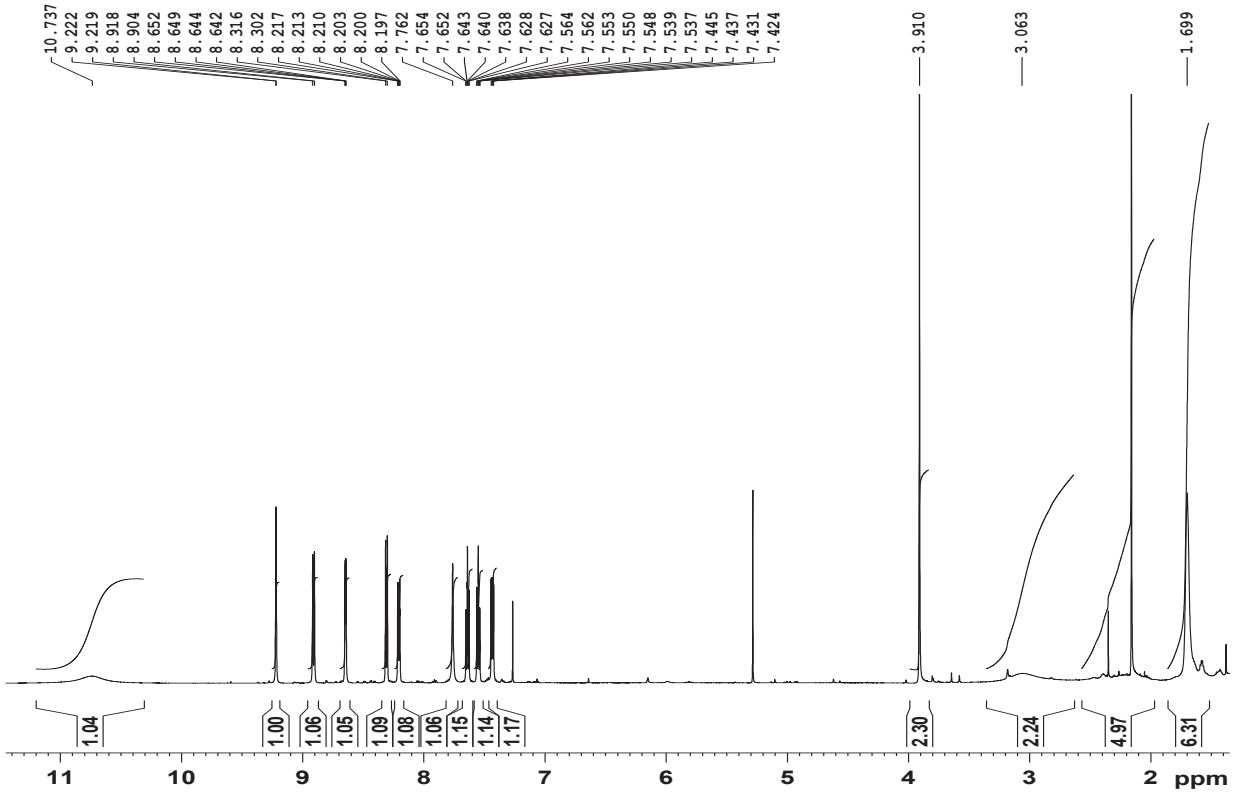

Figure S21. ^{1}H spectrum of **2** in $CDCl_3$.

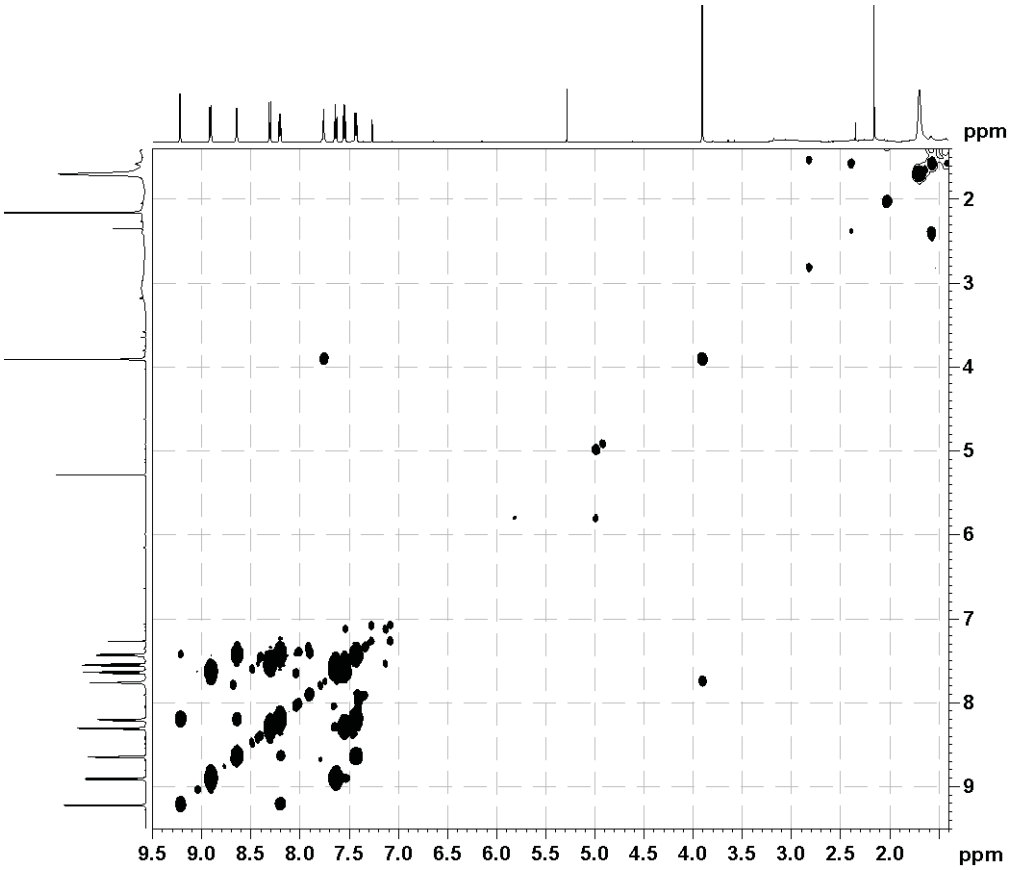

Figure S22. ^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$.

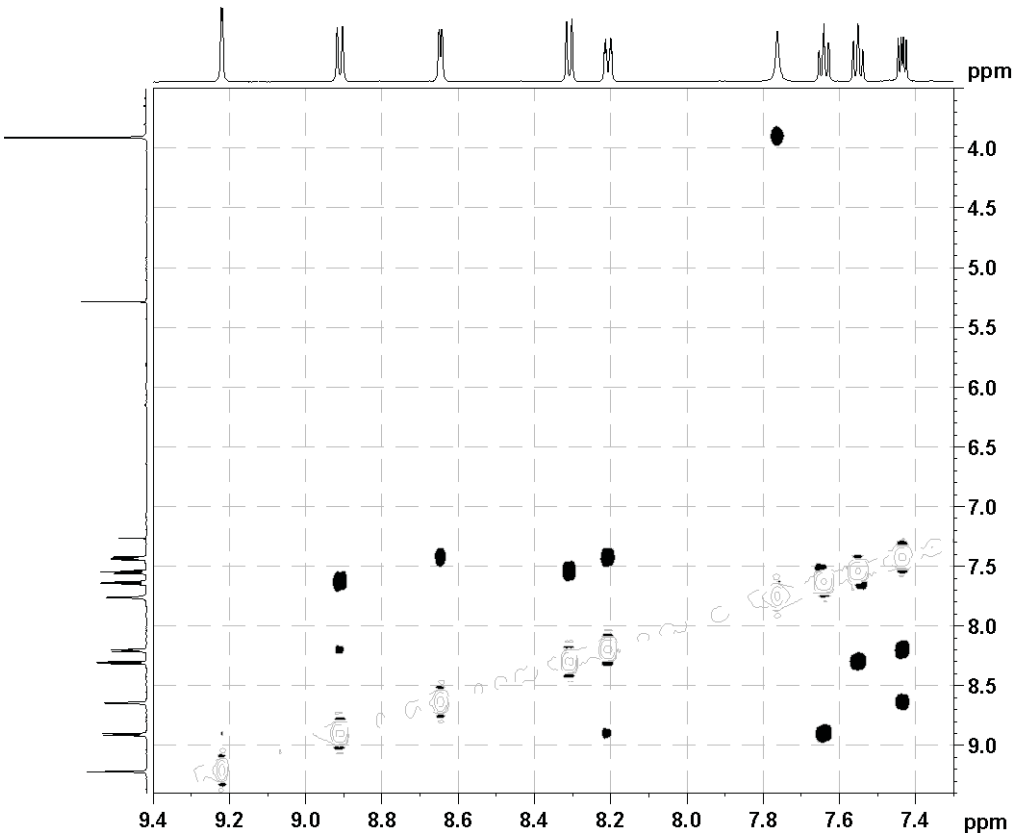

Figure S23. ^{1}H-^{1}H NOESY spectrum of **2** in $CDCl_3$.

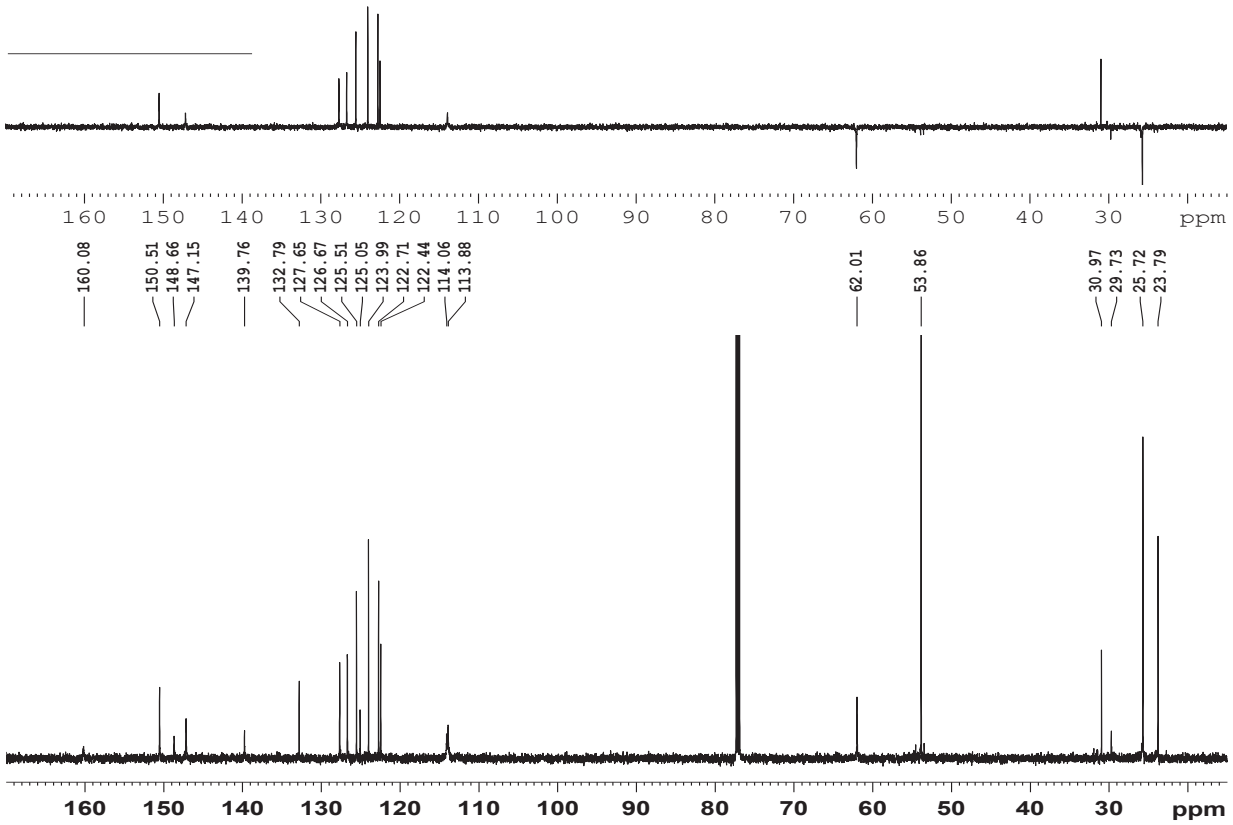

Figure S24. ^{13}C (down) and DEPT (up) spectra of **2** in $CDCl_3$.

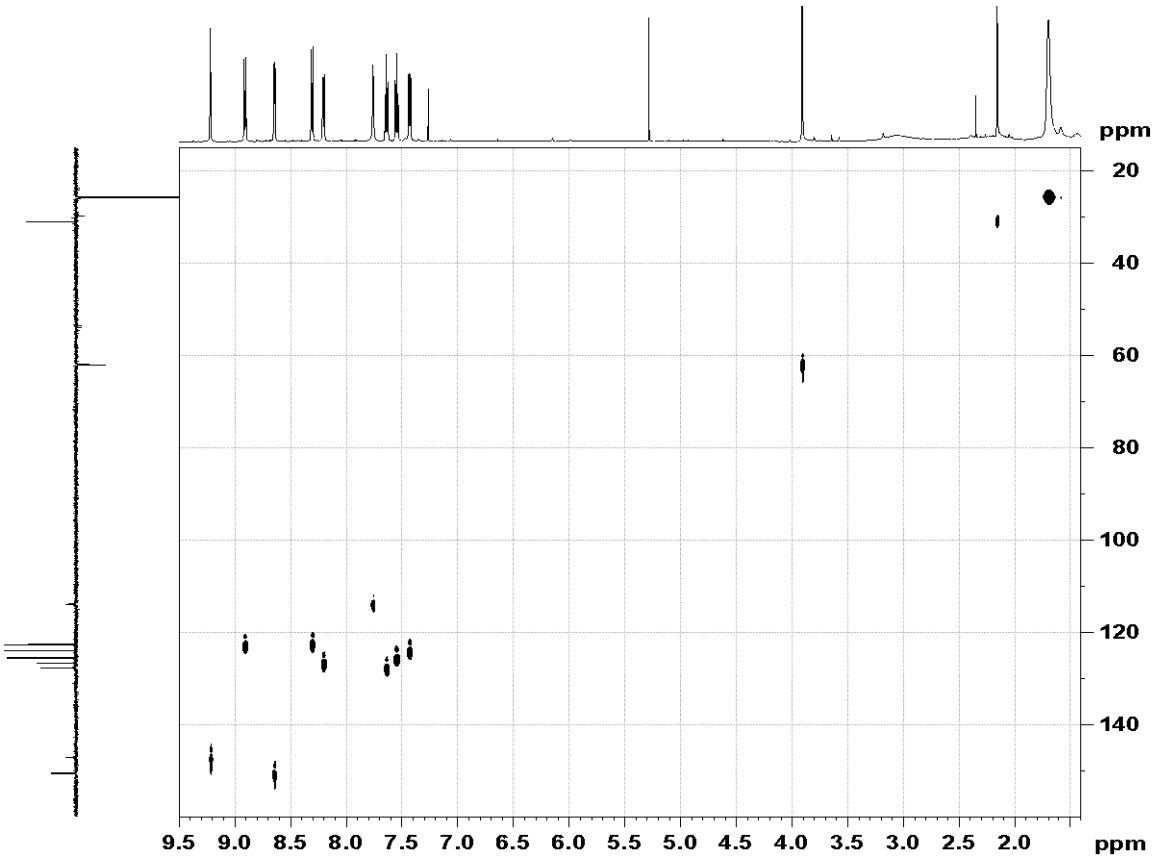

Figure S25. ^{1}H-^{13}C HSQC spectrum of **2** in $CDCl_3$.

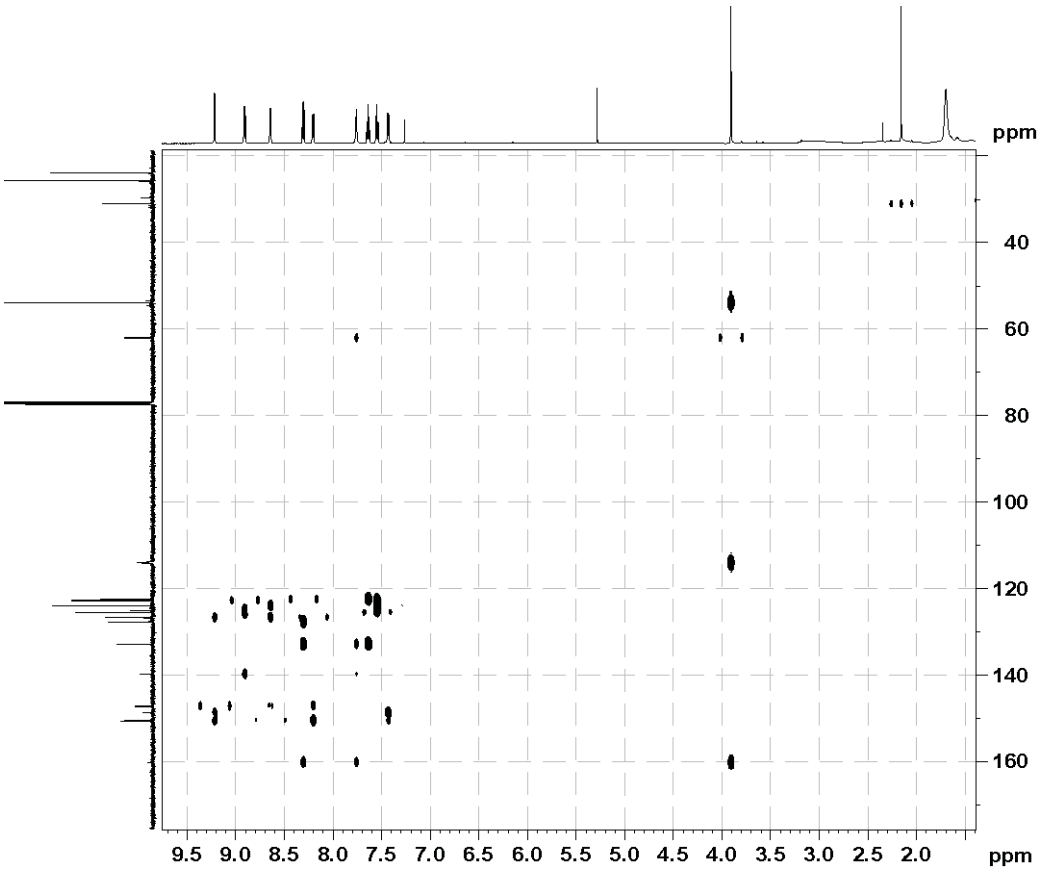

Figure S26. ^{1}H-^{13}C HMBC spectrum of **2** in $CDCl_3$.

VI) NMR spectra of compound **3**

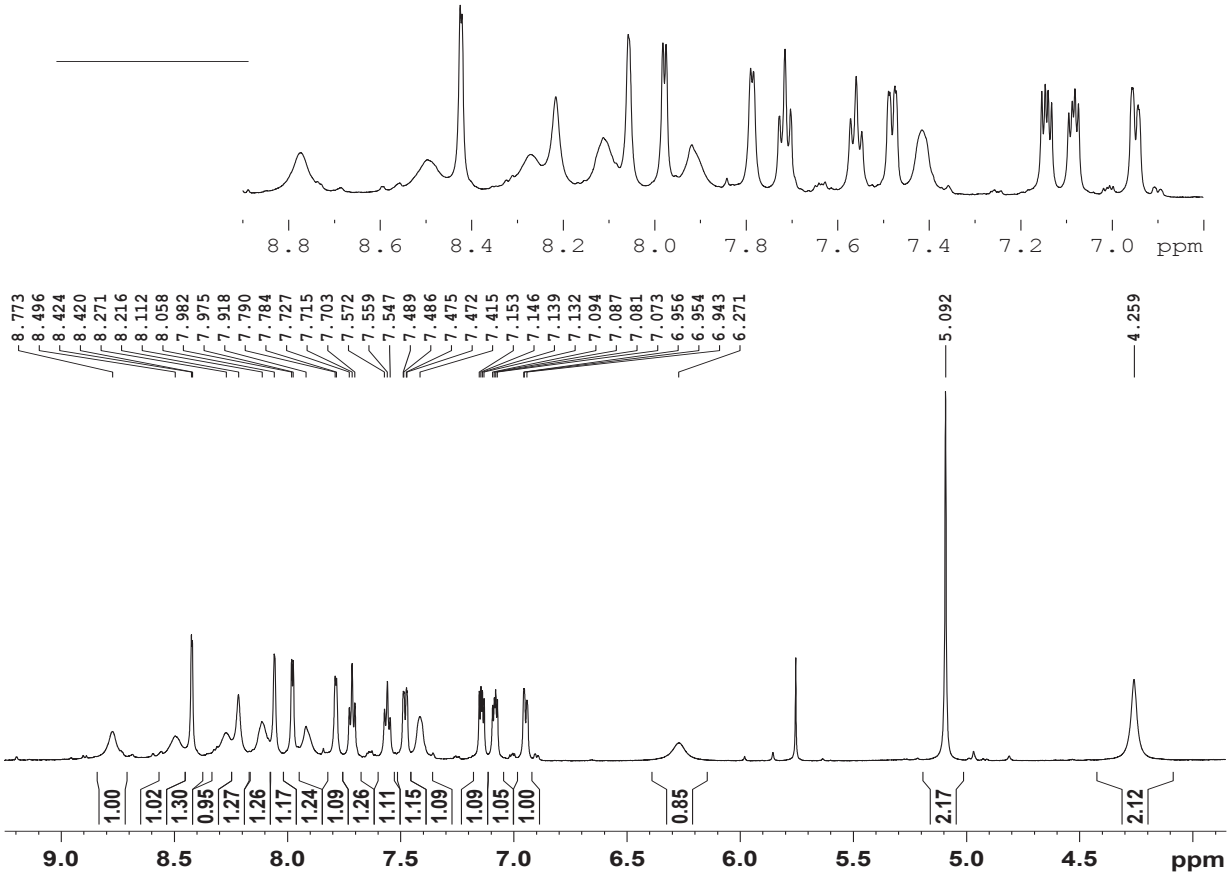

Figure S27. ^{1}H spectrum of **3** in DMSO-d_6.

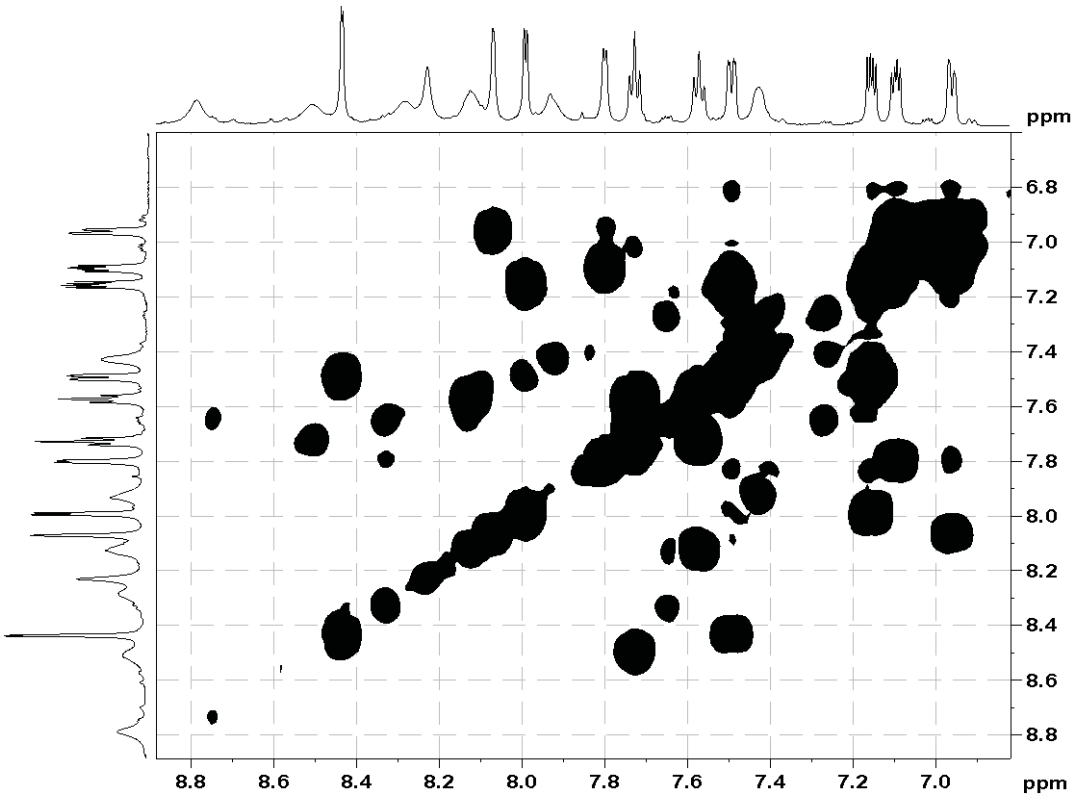

Figure S28. ^{1}H-^{1}H COSY spectrum of **3** in DMSO-d_6.

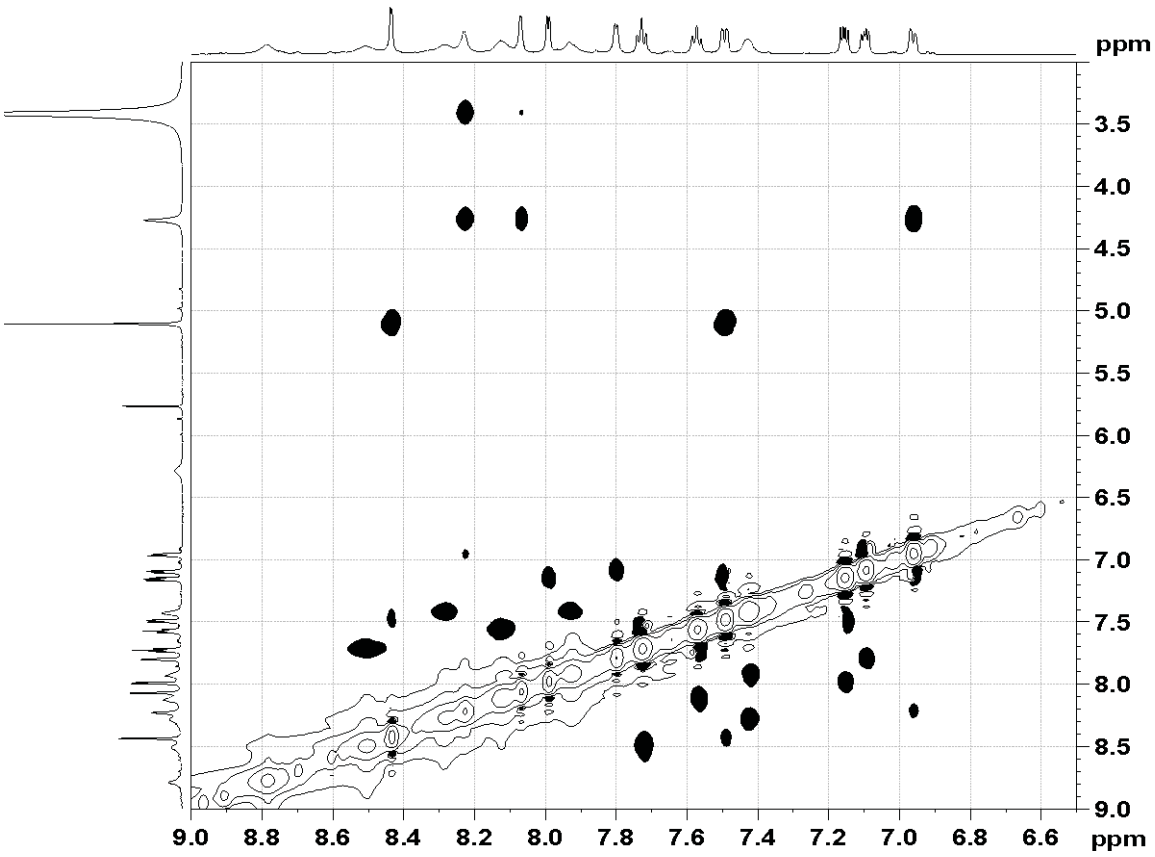

Figure S29. ^{1}H-^{1}H ROESY spectrum of **3** in DMSO-d_6.

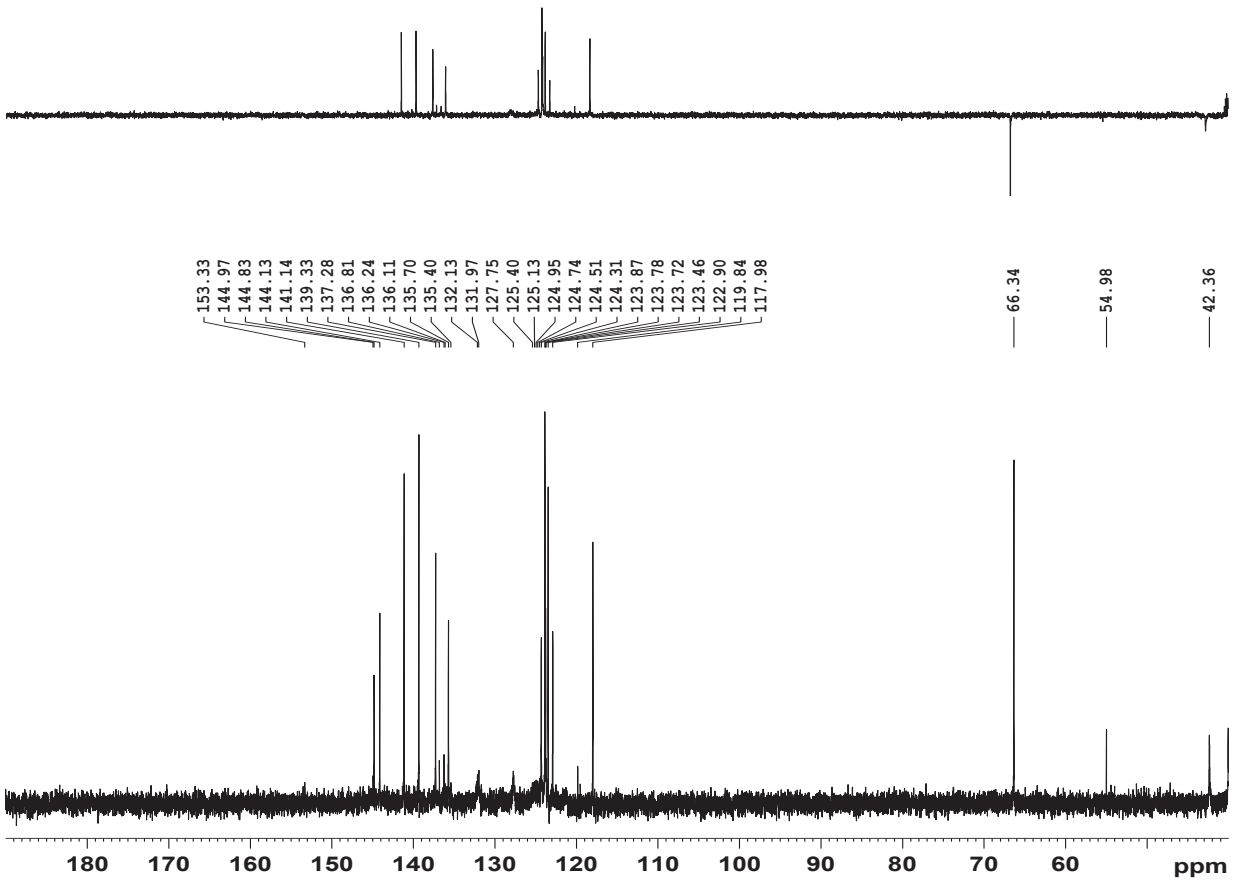

Figure S30. ^{13}C (down) and DEPT (up) spectra of **3** in DMSO-d_6.

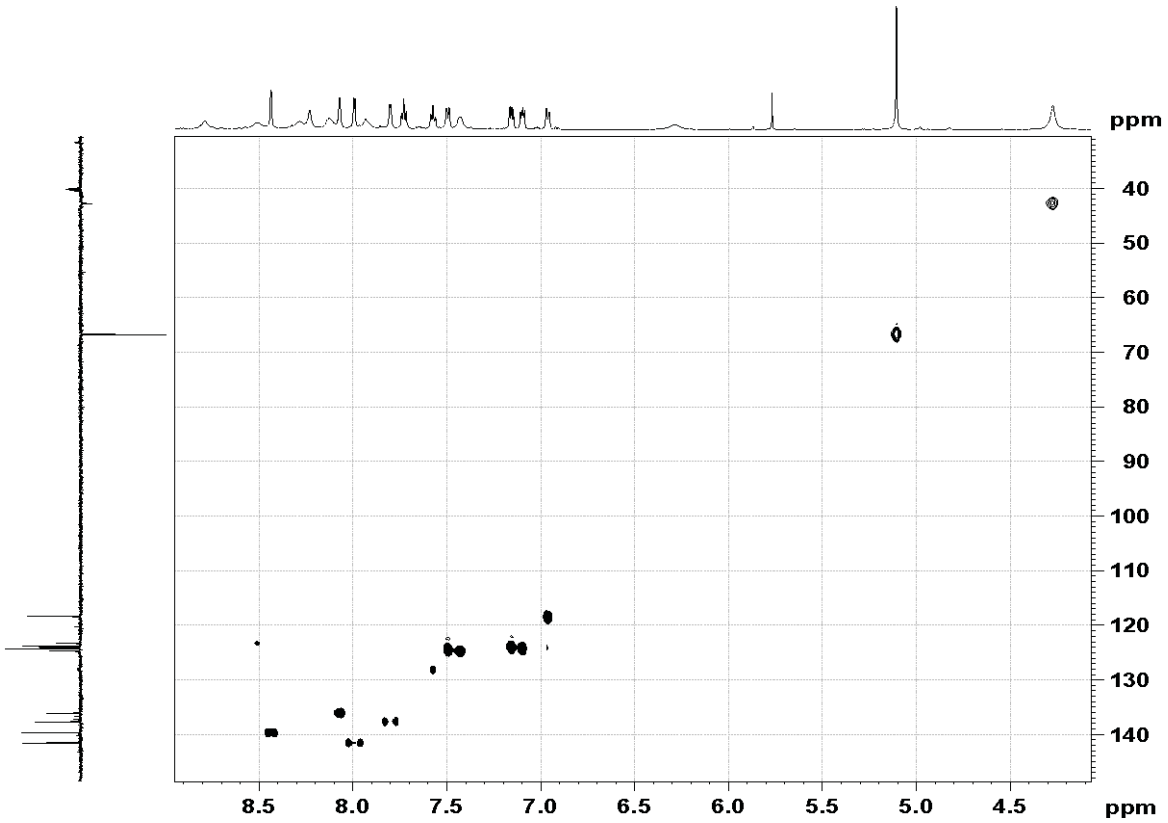

Figure S31. ^{1}H-^{13}C HSQC spectrum of **3** in DMSO-d_6.

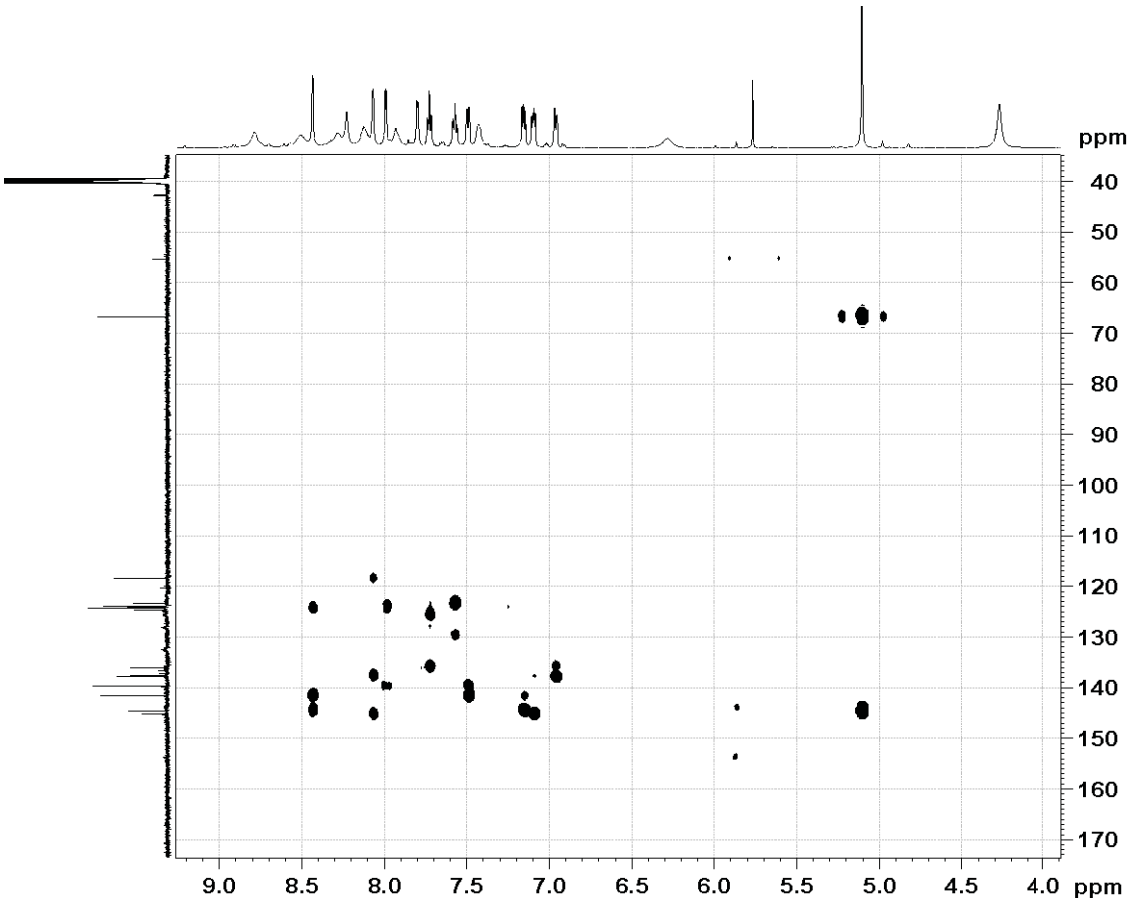

Figure S32. ^{1}H-^{13}C HMBC spectrum of **3** in DMSO-d_6.

VII) NMR spectra of compound **4**

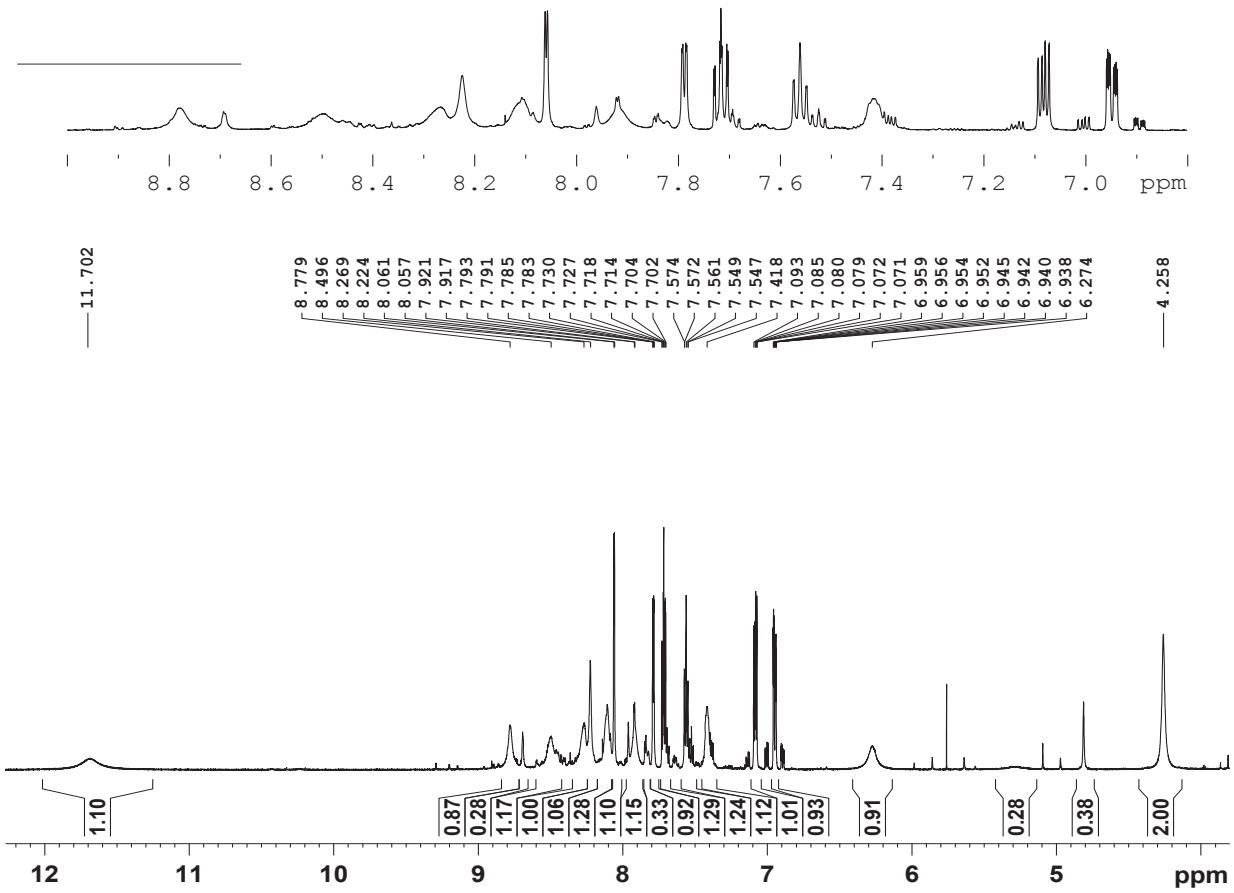

Figure S33. ^{1}H spectrum of **4** in $CDCl_3$.

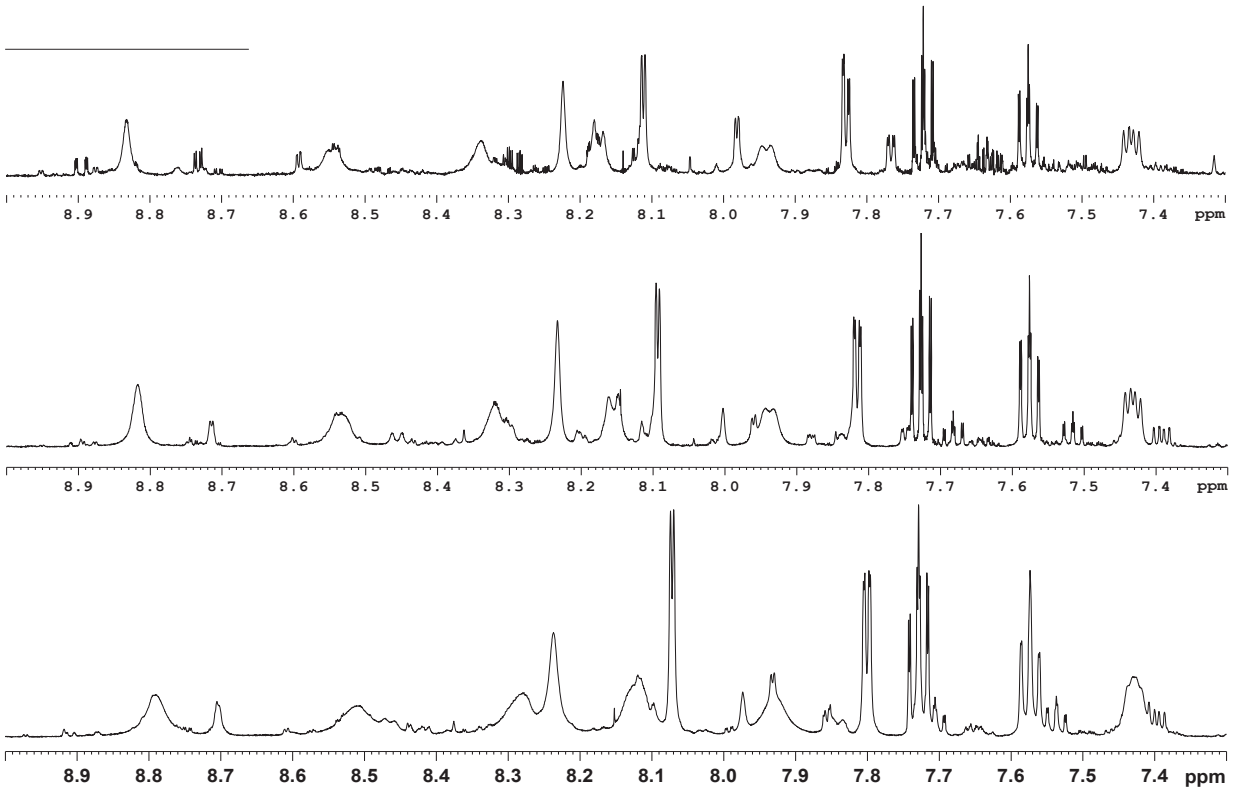

Figure 34. ^{1}H spectra of **4** at 300K (down), 328K (middle) and 358K (up) in DMSO-d_6.

VIII) NMR spectra of compound **5a**

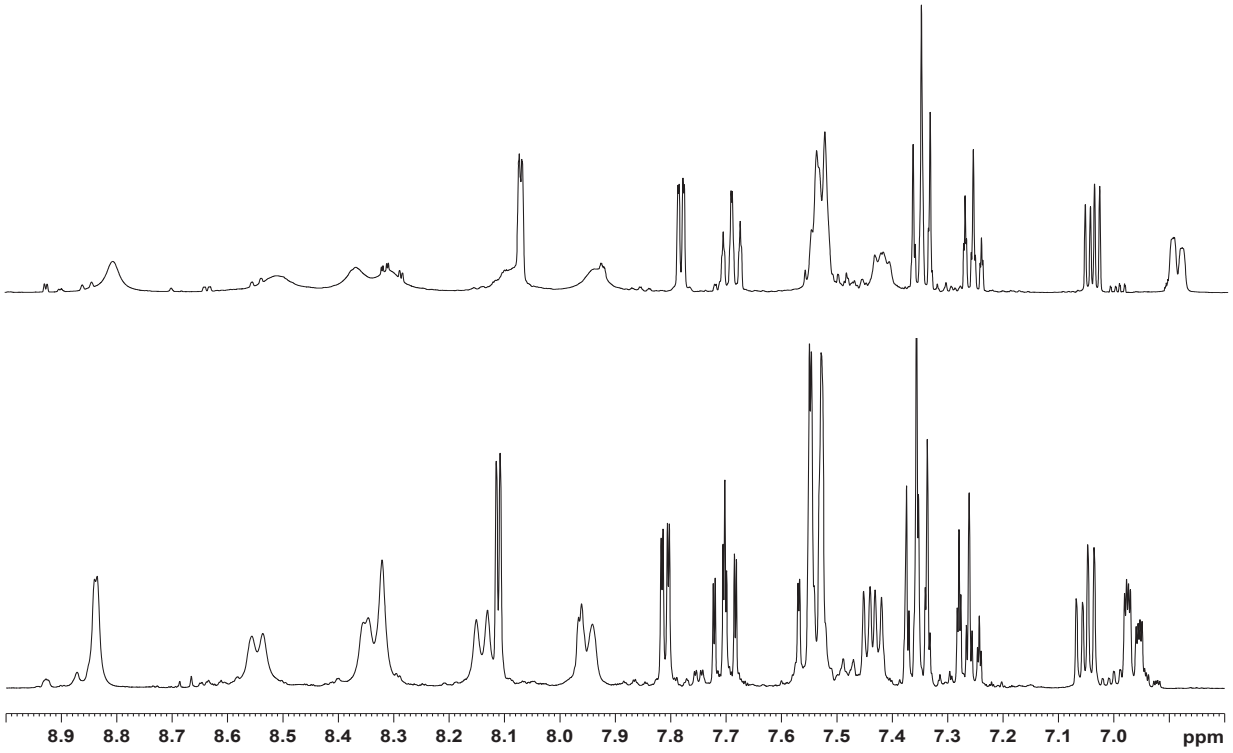

Figure S35. ^{1}H spectrum of **5a** in DMSO-d_6 at 343K (down) and at 302K (up)

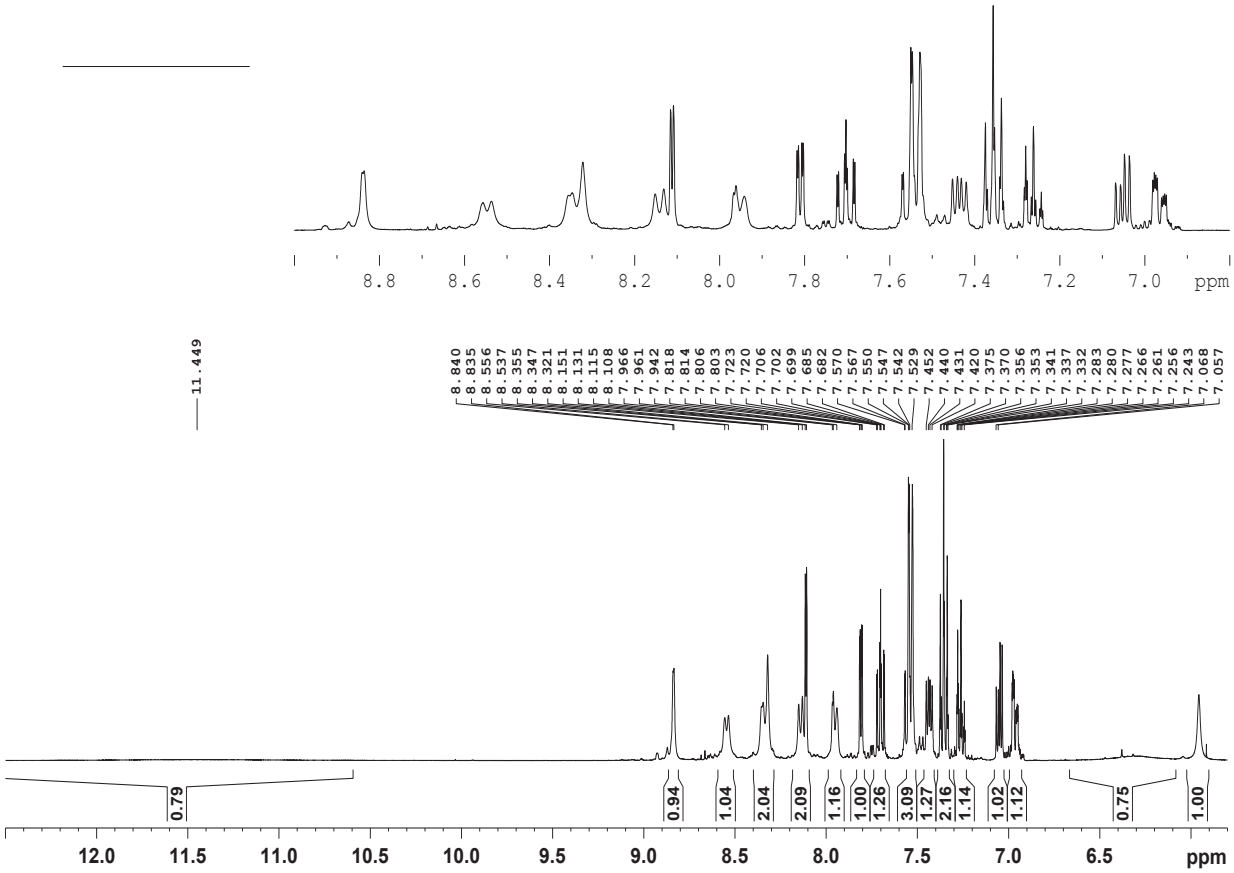

Figure S36. ^{1}H spectrum of **5a** in DMSO-d_6 at 343K.

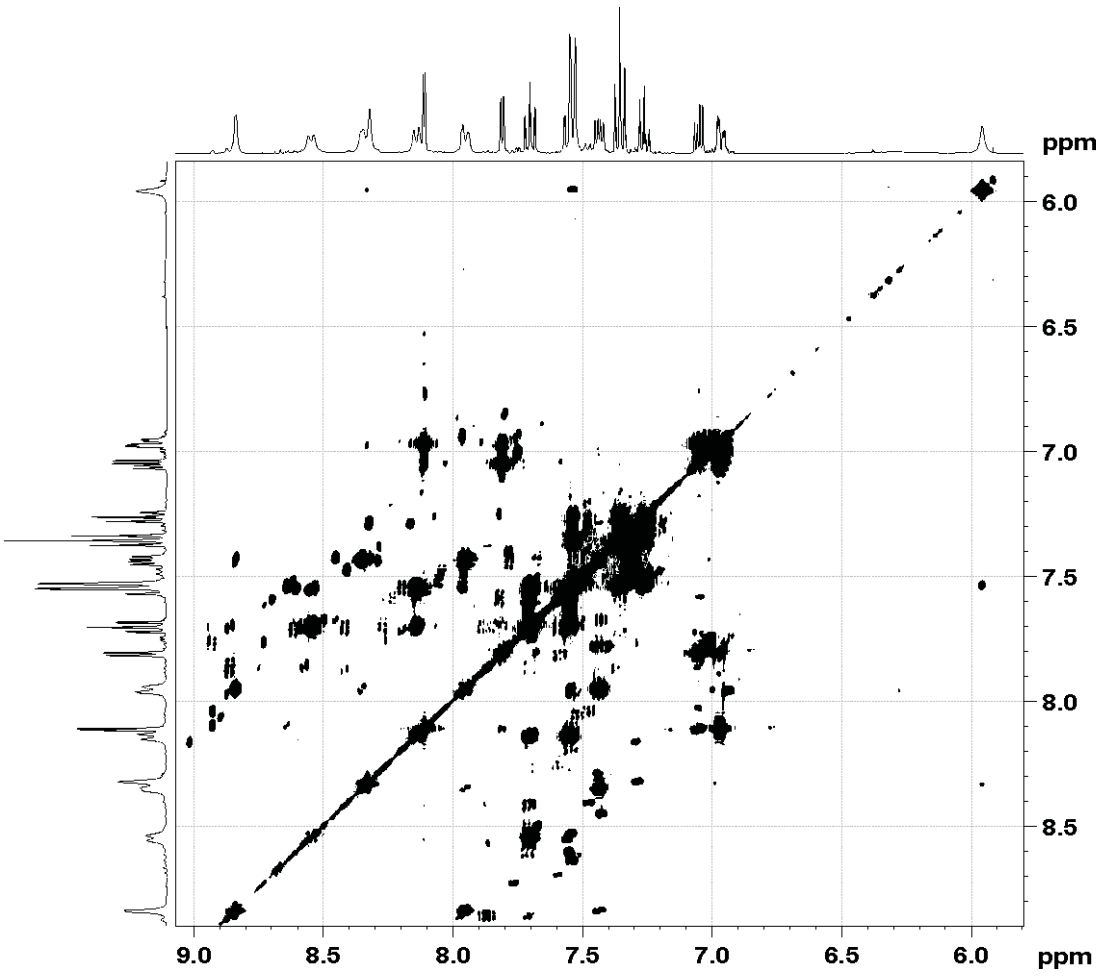

Figure S37. ^{1}H-^{1}H COSY spectrum of **5a** in DMSO-d_6 at 343K.

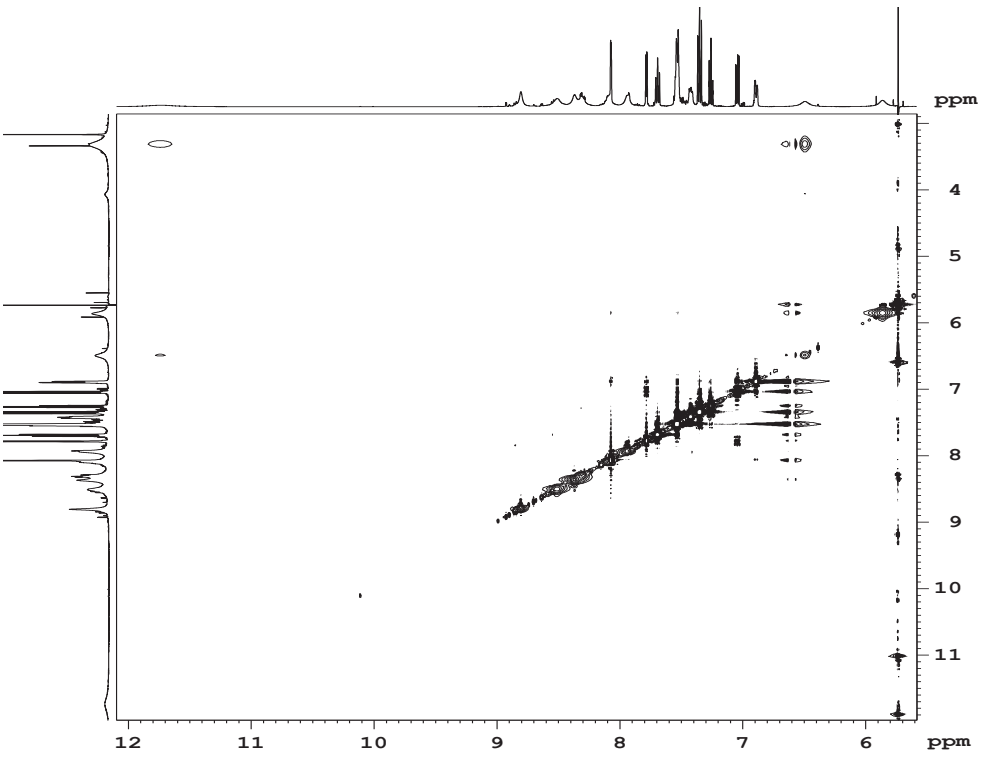

Figure S38. ^{1}H-^{1}H NOESY spectrum of **5a** in DMSO-d_6 at 343K.

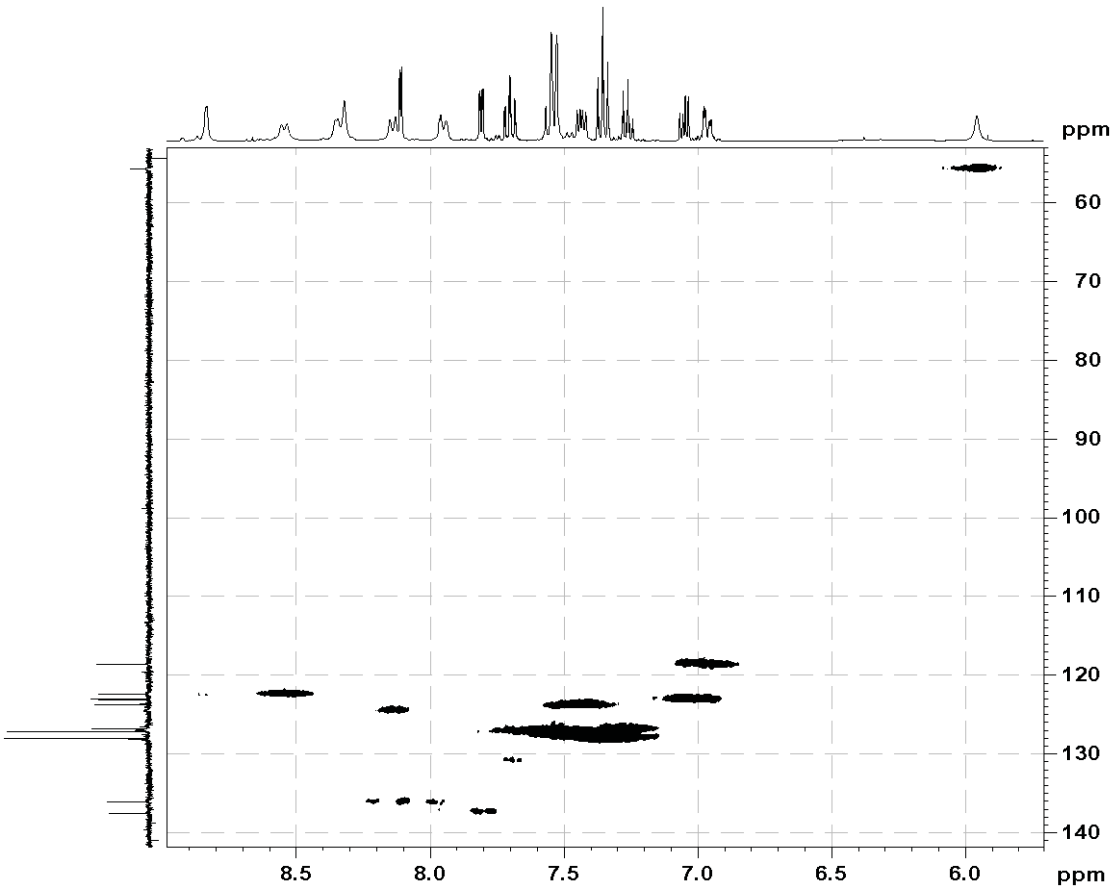

Figure S39. ^{1}H-^{13}C HSQC spectrum of **5a** in DMSO-d_6 at 343K.

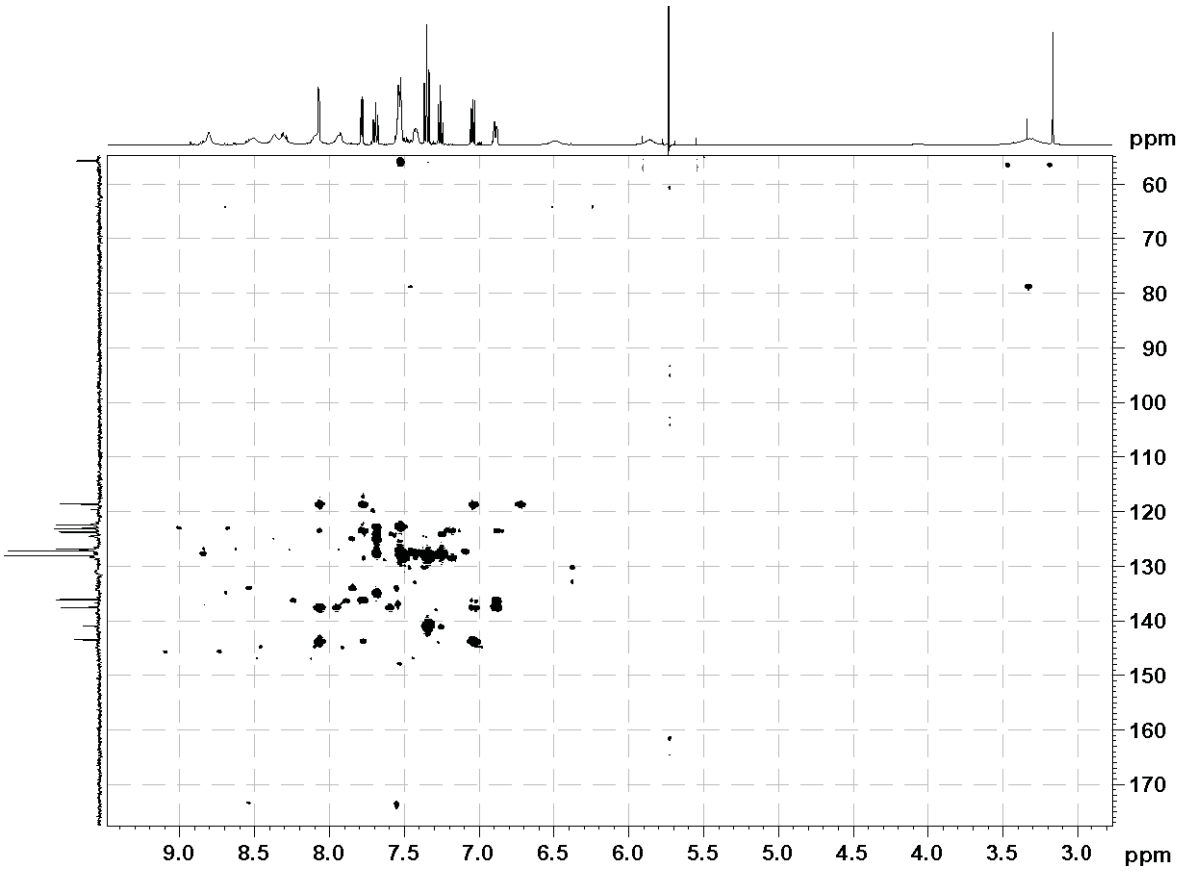

Figure S40. ^{1}H-^{13}C HMBC spectrum of **5a** in DMSO-d_6 at 343K.

selective NOE experiments at 298K

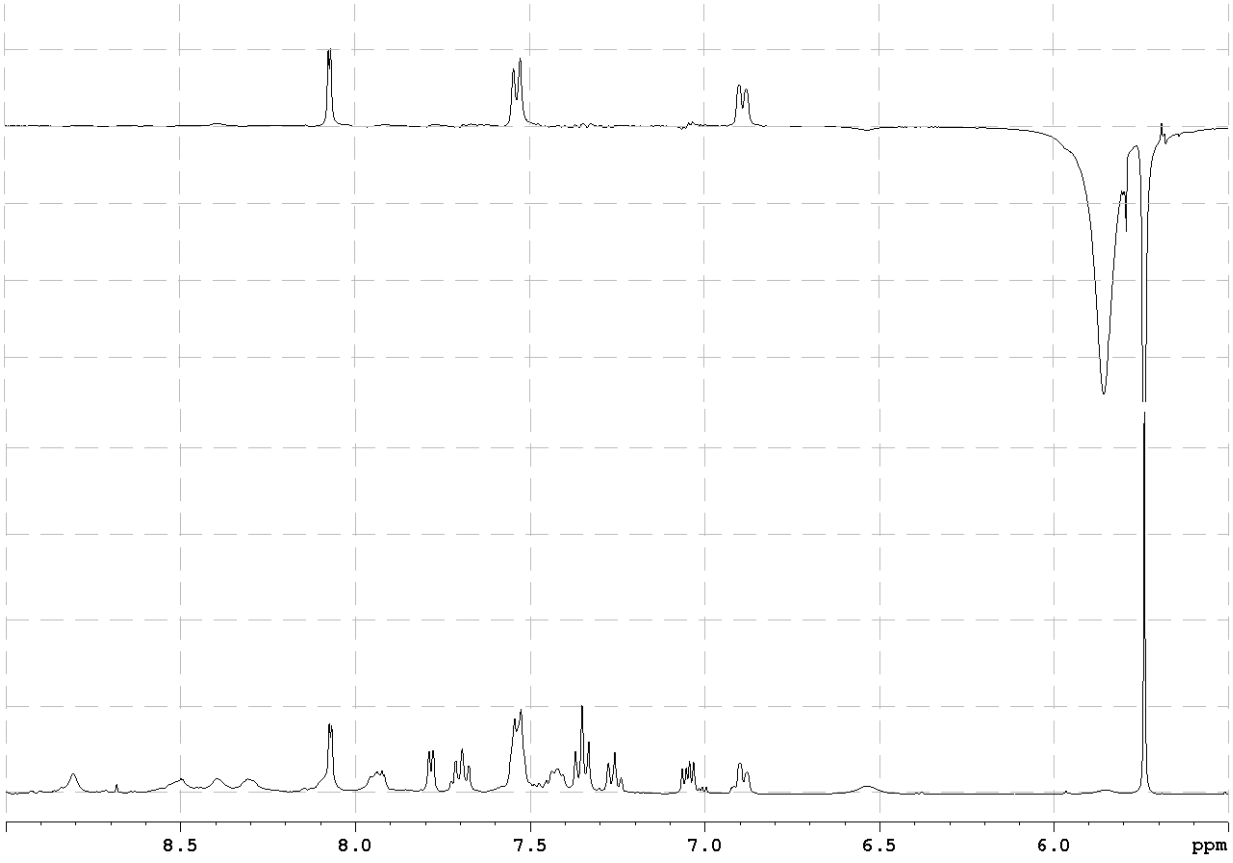

Figure S41. Irradiation at 5.86 ppm.

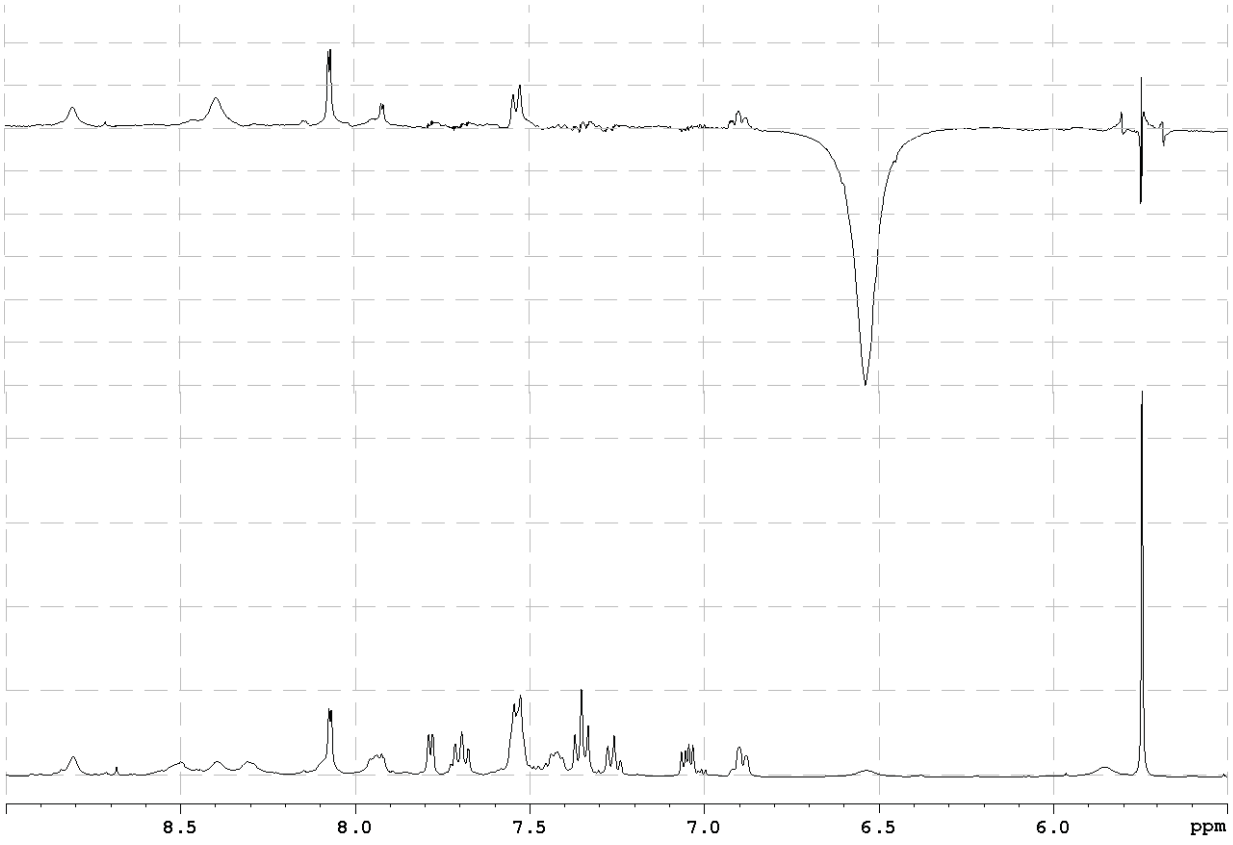

Figure S42. Irradiation at 6.54 ppm.

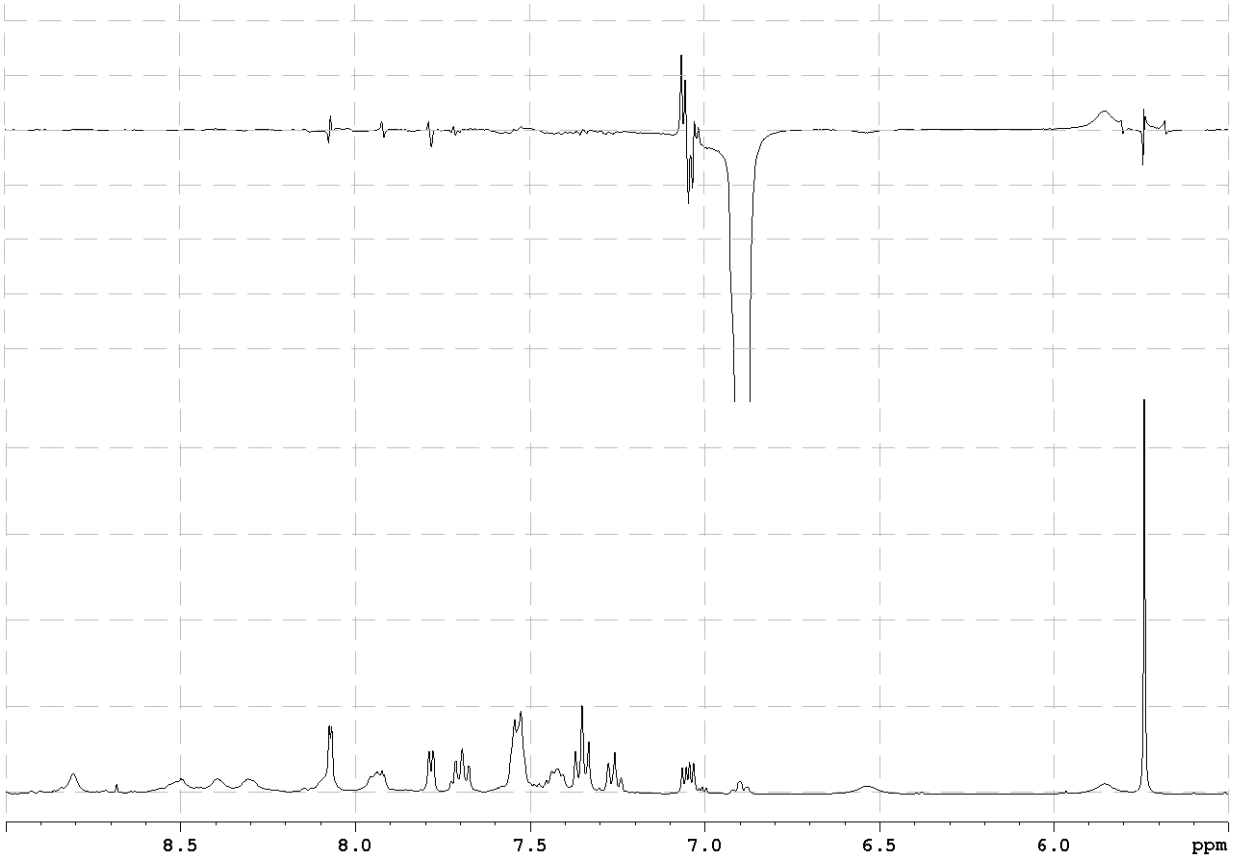

Figure S43. Irradiation at 6.90 ppm.

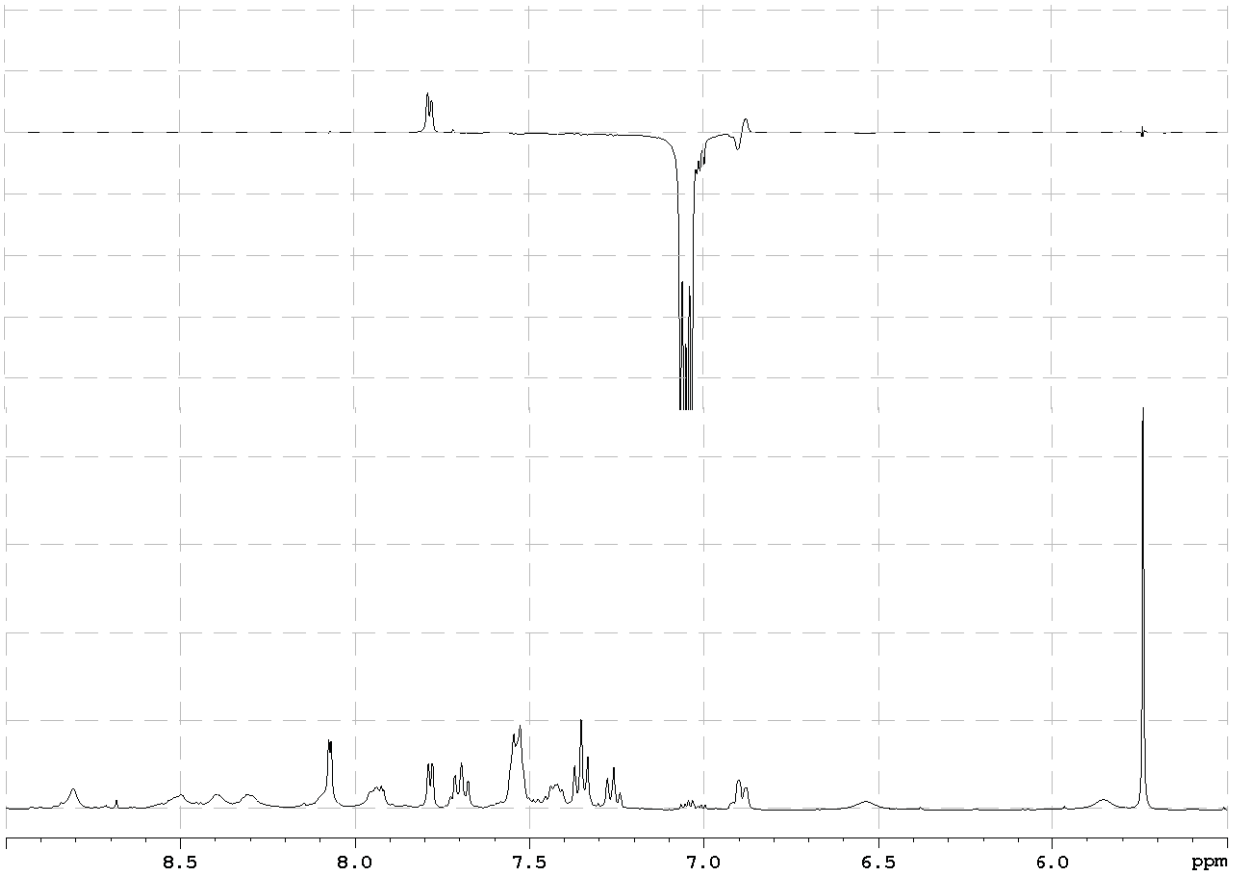

Figure S44. Irradiation at 7.06 ppm.

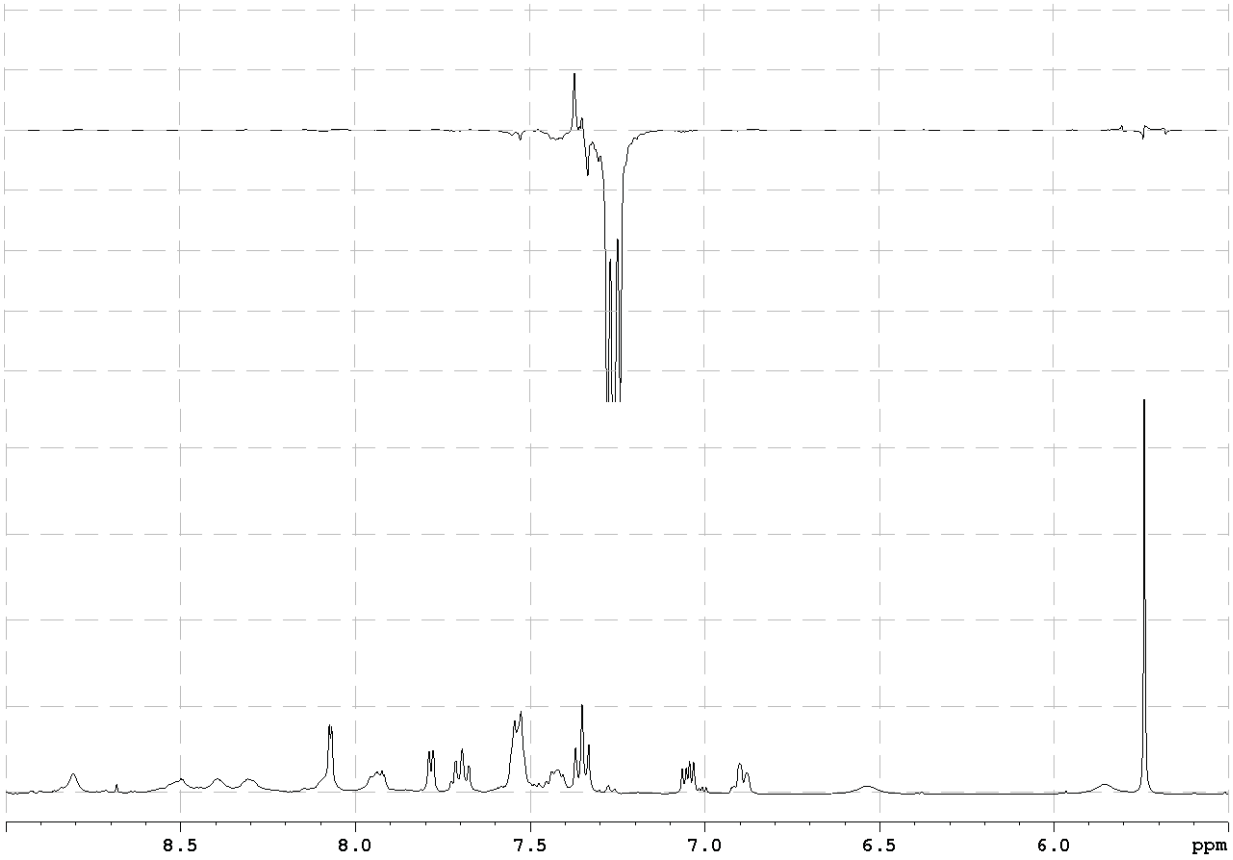

Figure S45. Irradiation at 7.26 ppm.

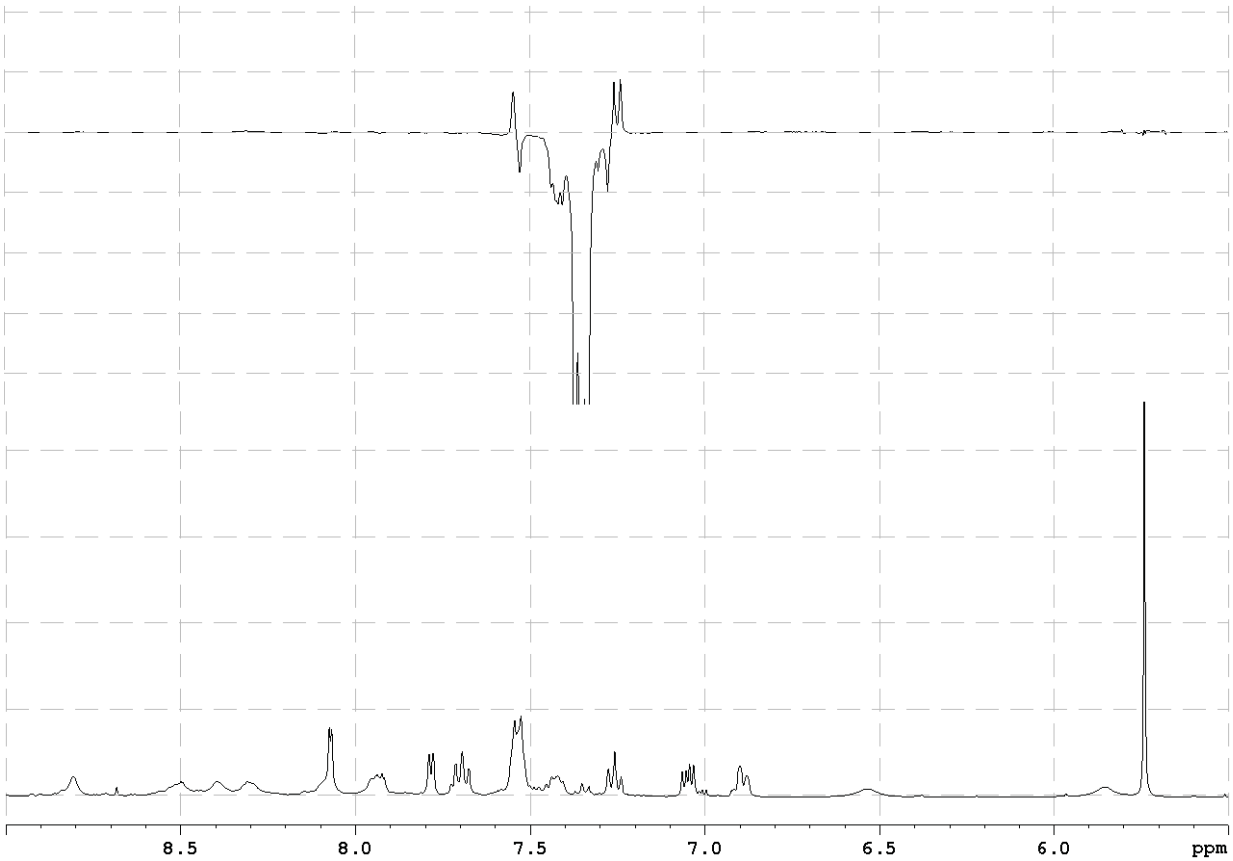

Figure S46. Irradiation at 7.35 ppm.

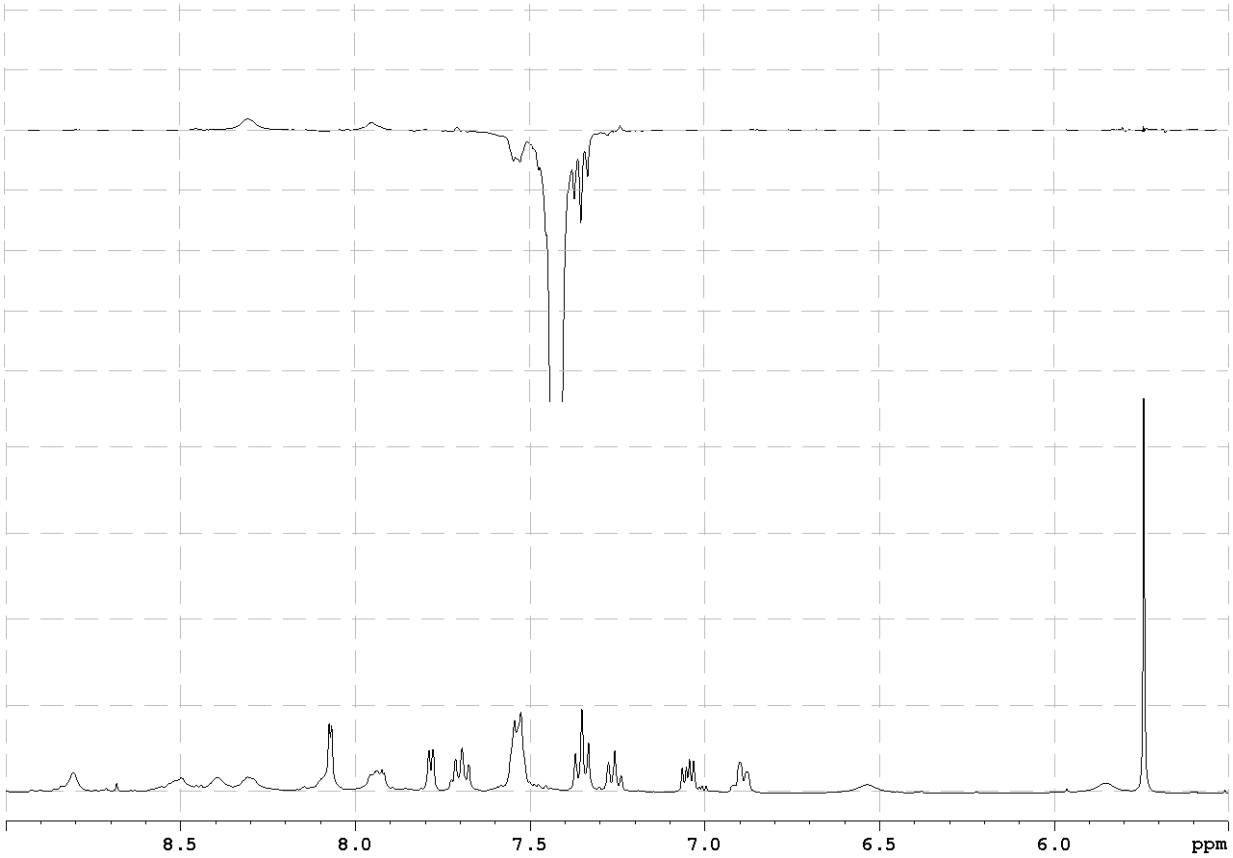

Figure S47. Irradiation at 7.43 ppm.

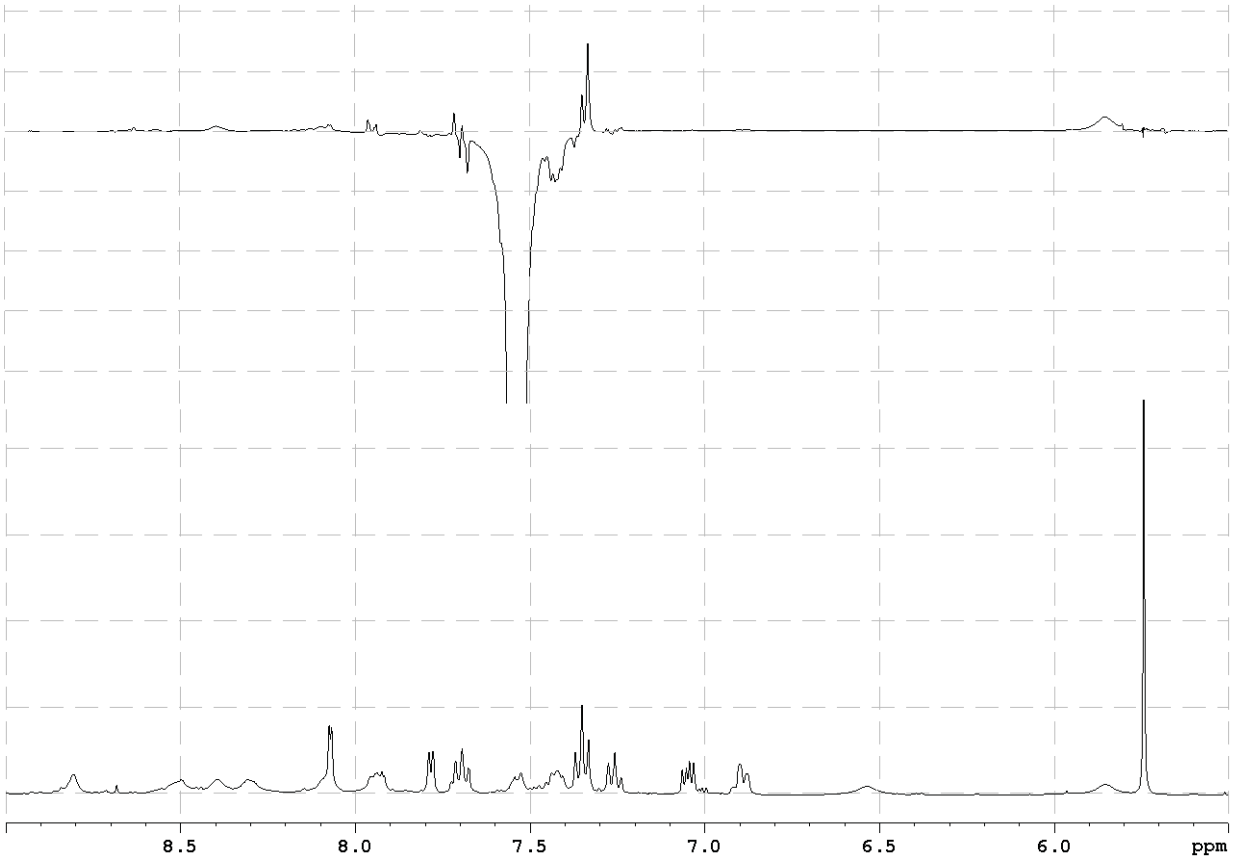

Figure S48. Irradiation at 7.54 ppm.

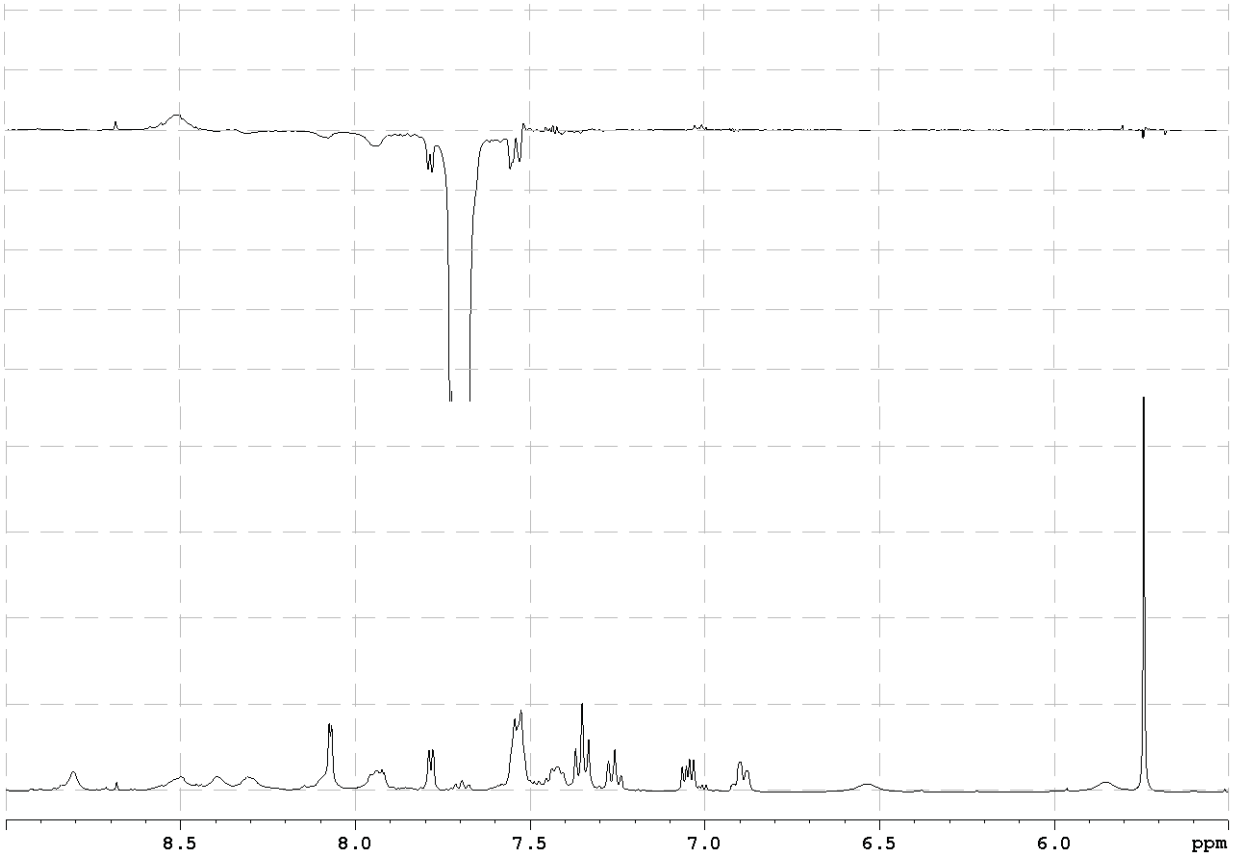

Figure S49. Irradiation at 7.70 ppm.

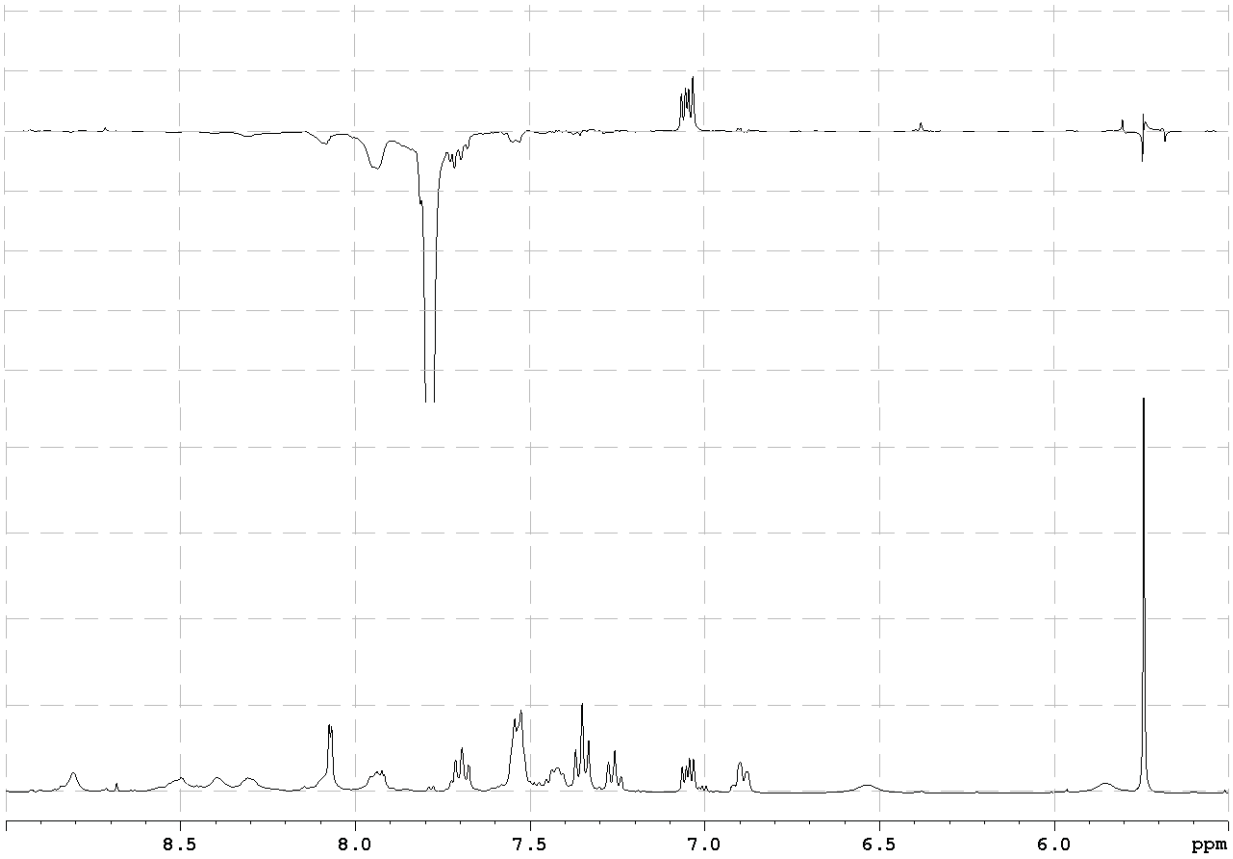

Figure S50. Irradiation at 7.78 ppm.

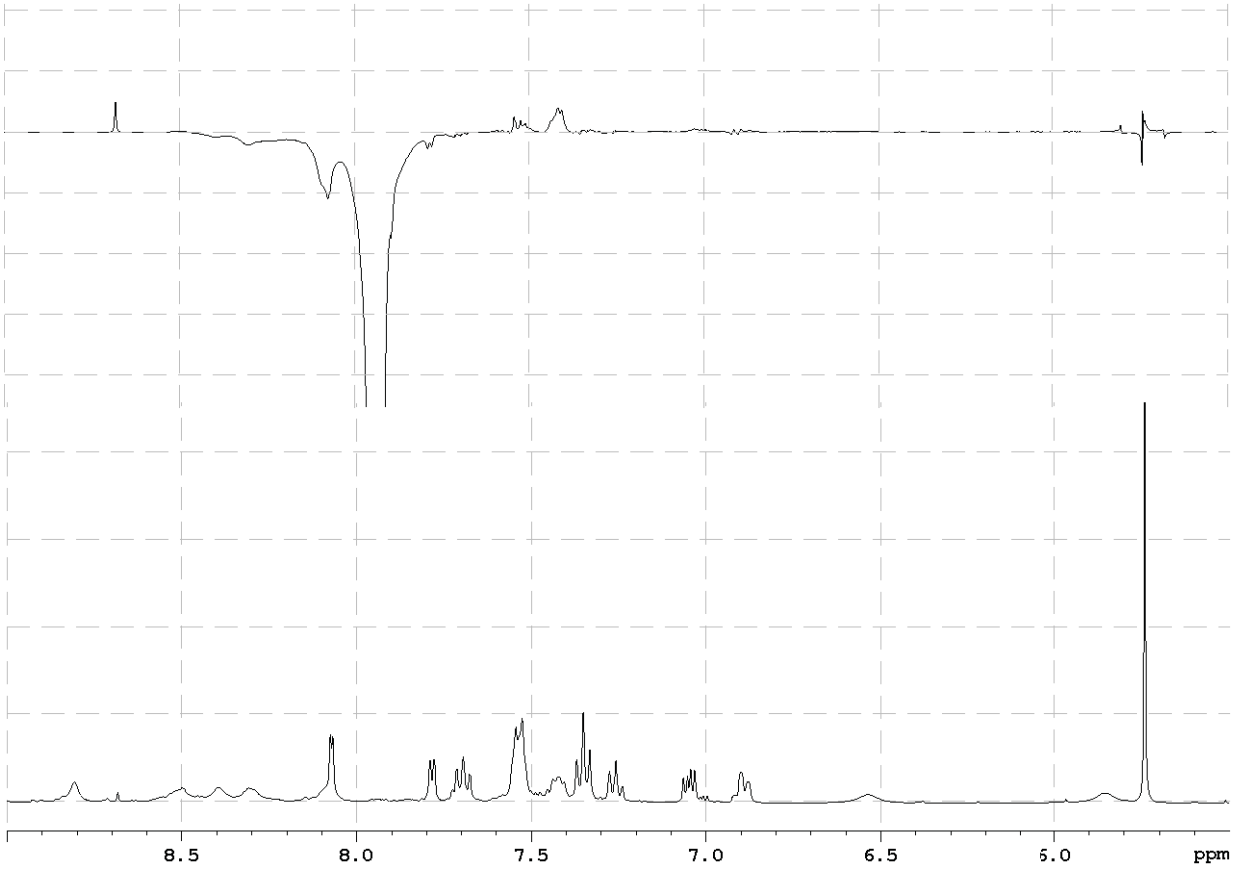

Figure S51. Irradiation at 7.94 ppm.

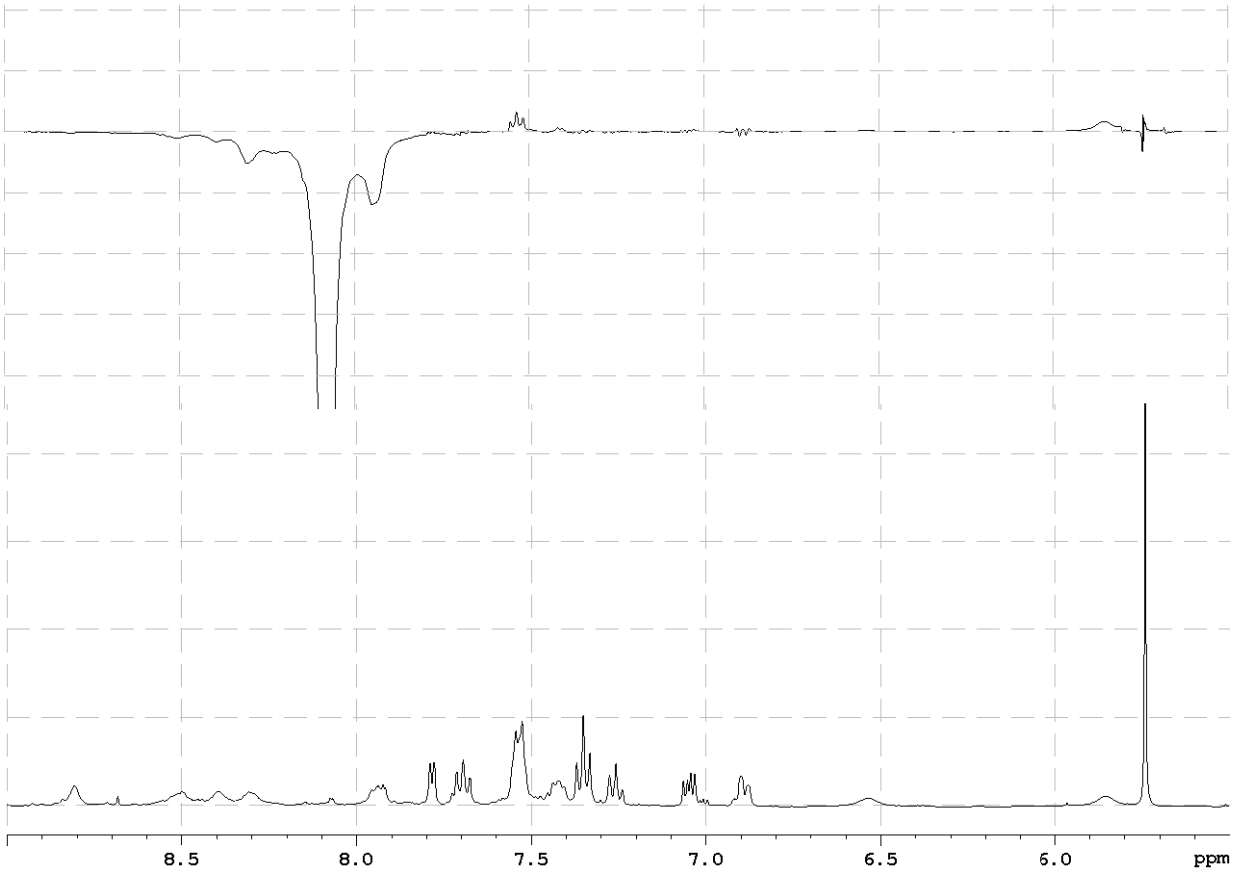

Figure S52. Irradiation at 8.07 ppm.

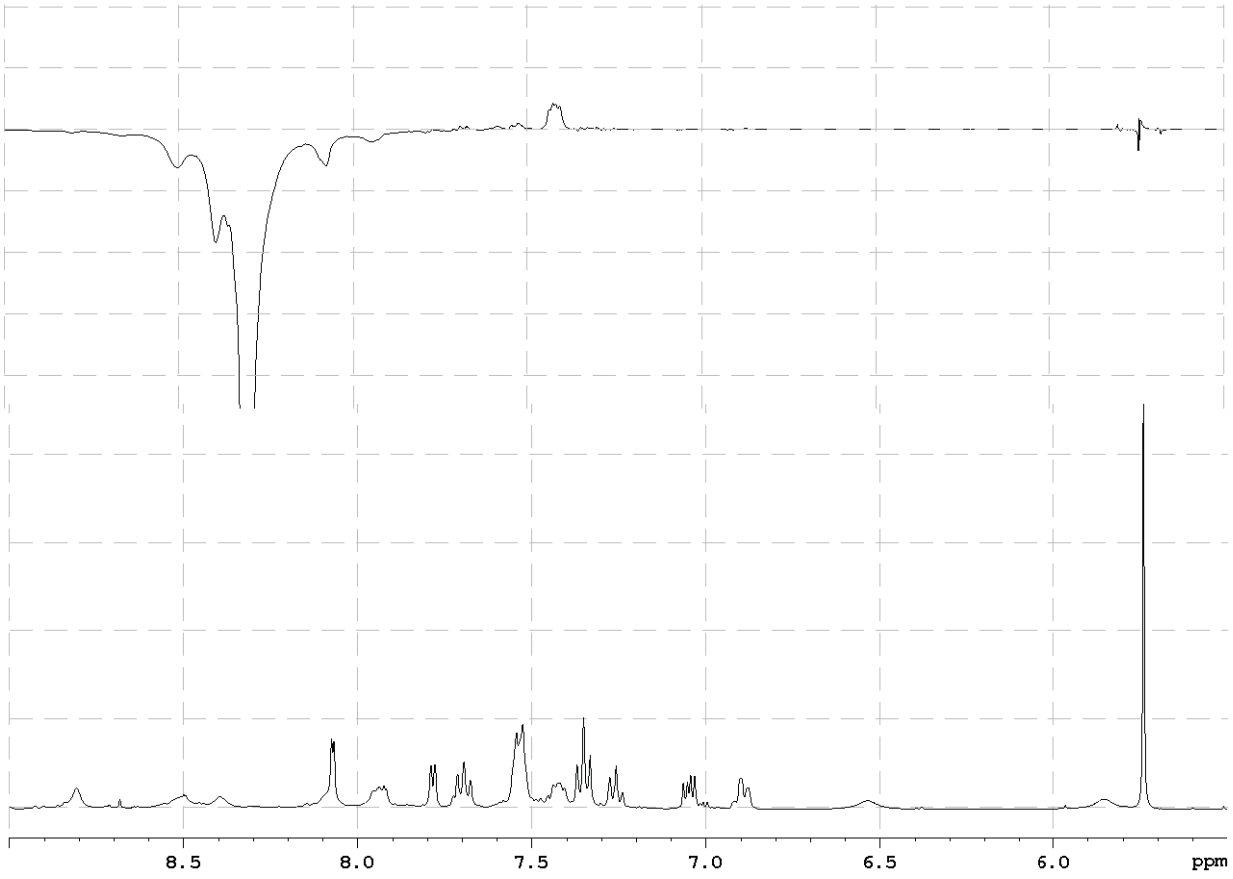

Figure S53. Irradiation at 8.30 ppm.

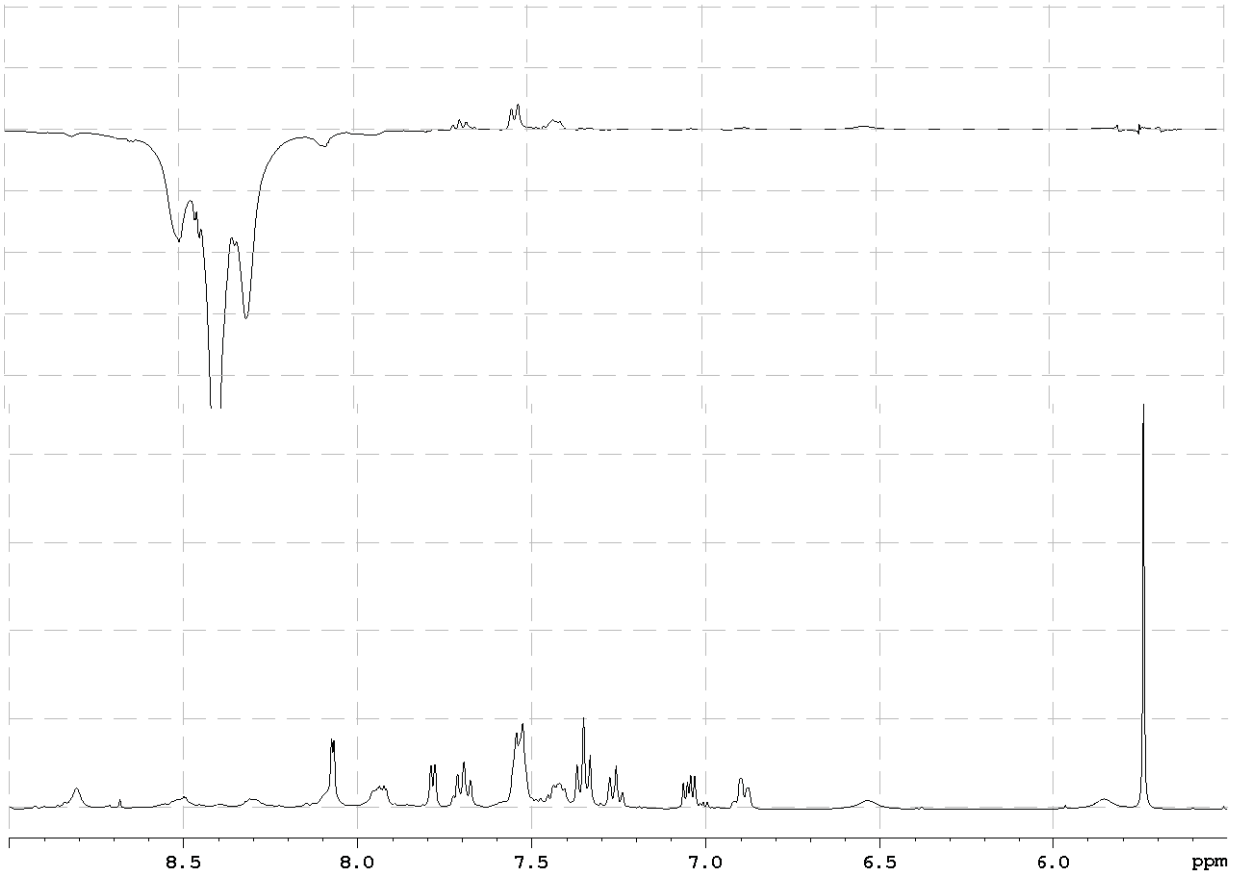

Figure S54. Irradiation at 8.40 ppm.

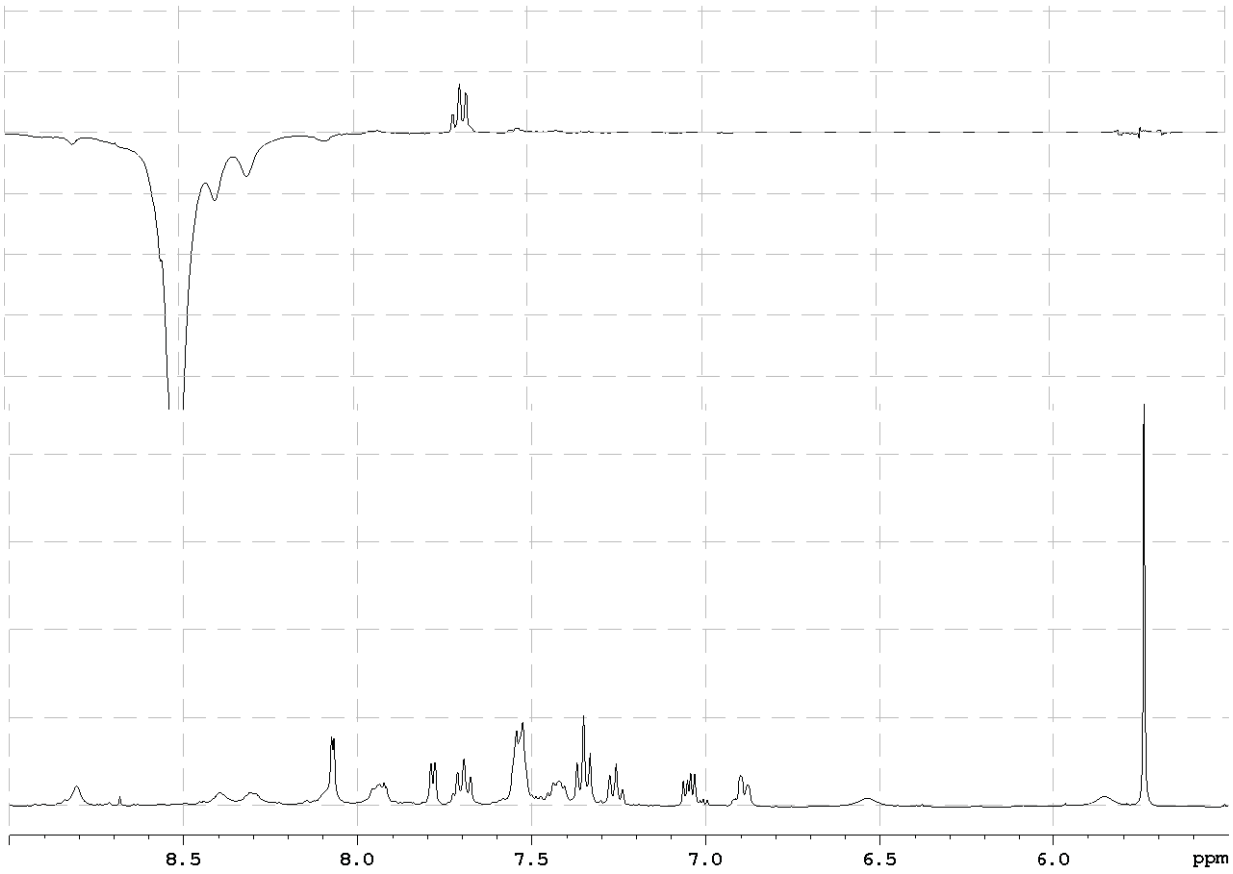

Figure S55. Irradiation at 8.51 ppm.

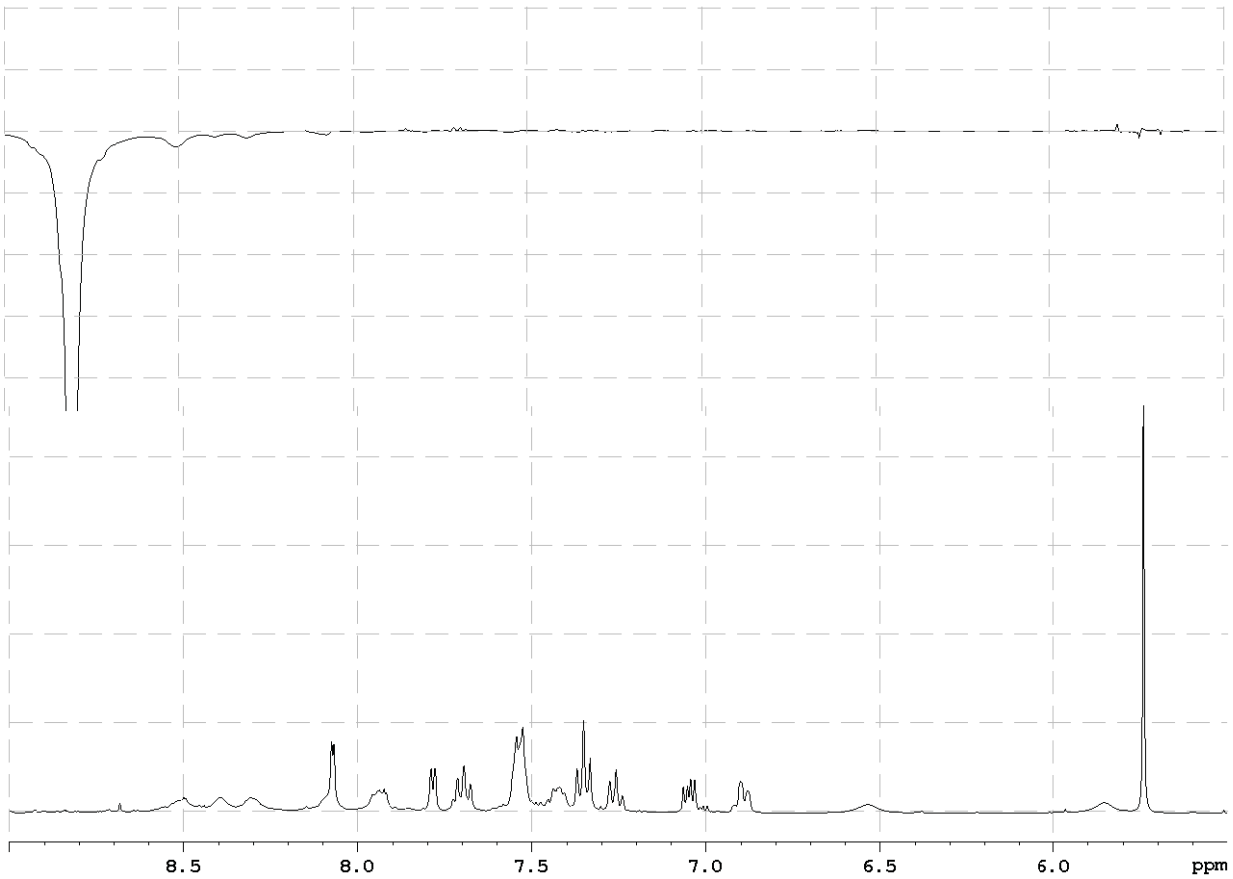

Figure S56. Irradiation at 8.81 ppm.

IX) NMR spectra of compound **5b**

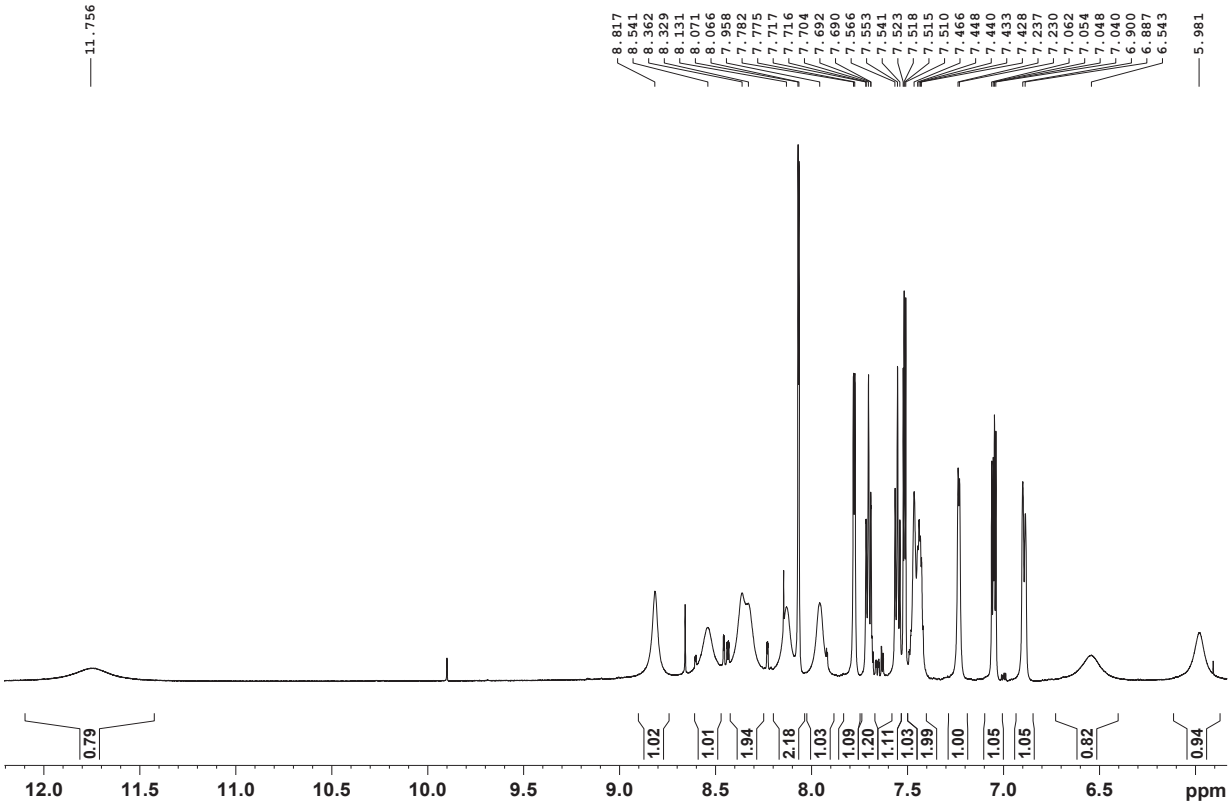

Figure S57. ^{1}H spectrum of **5b** in DMSO-d_6.

X) NMR spectra of compound **5c**

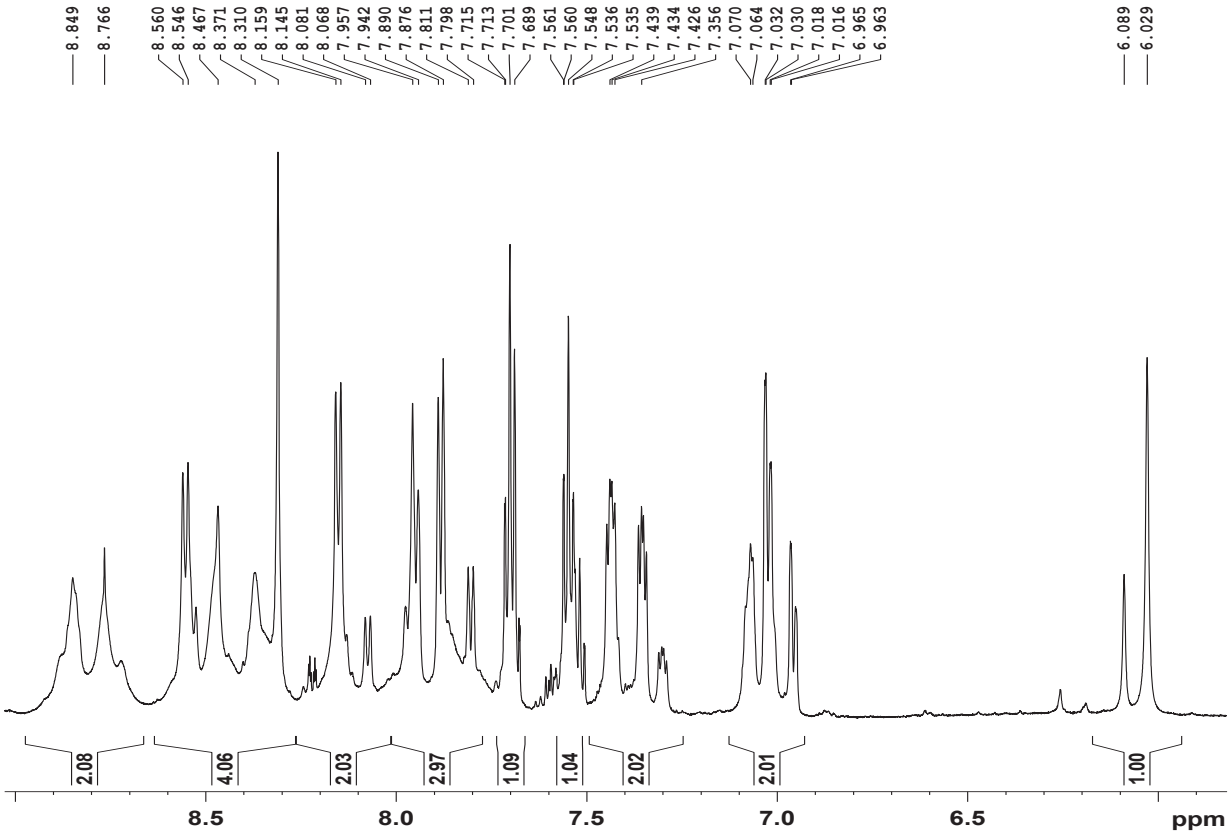

Figure S58. ^{1}H spectrum of **5c** in DMSO-d_6 at 373K.

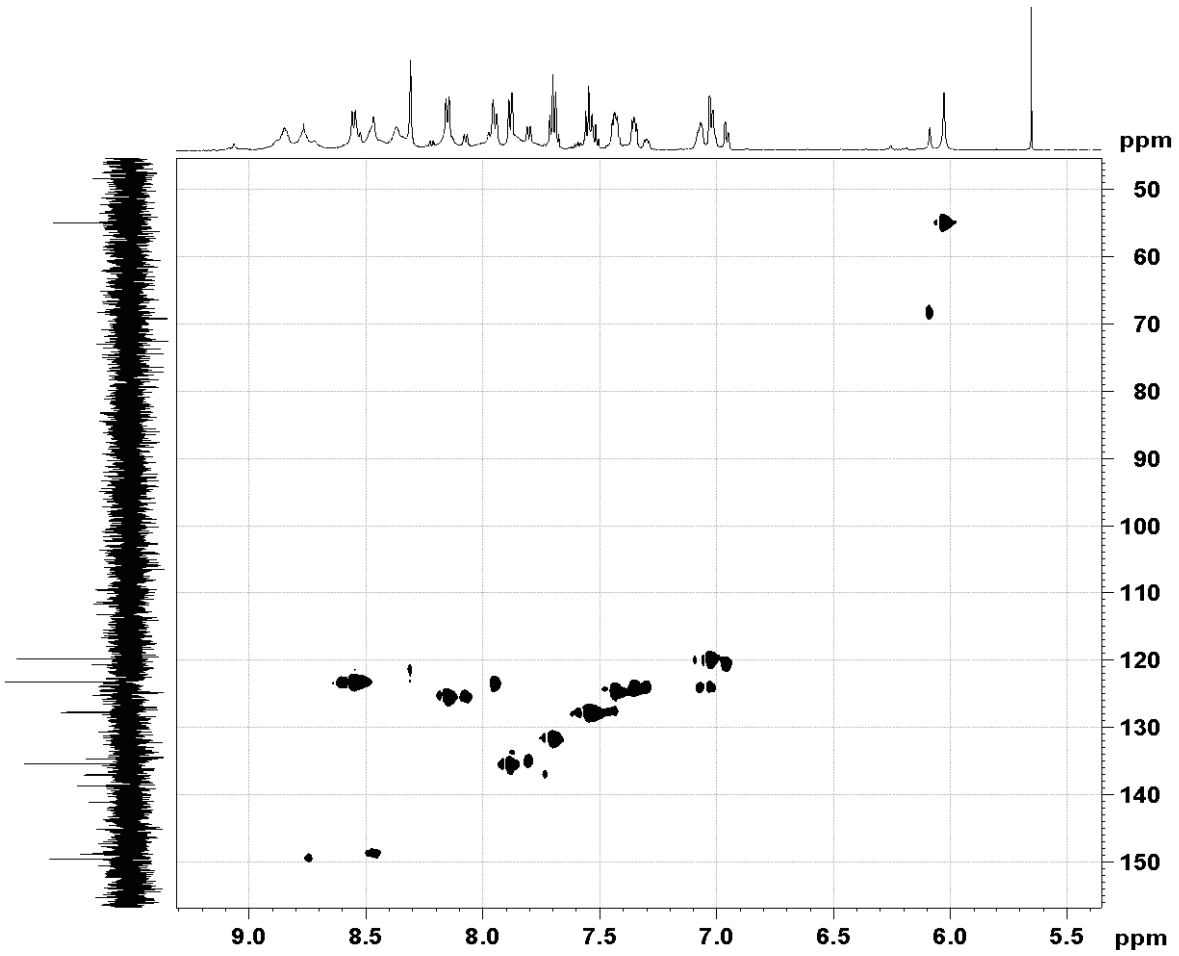

Figure S59. ^{1}H-^{13}C HSQC spectrum of **5c** in DMSO-d_6 at 373K.

XI) NMR spectra of compound **5d**

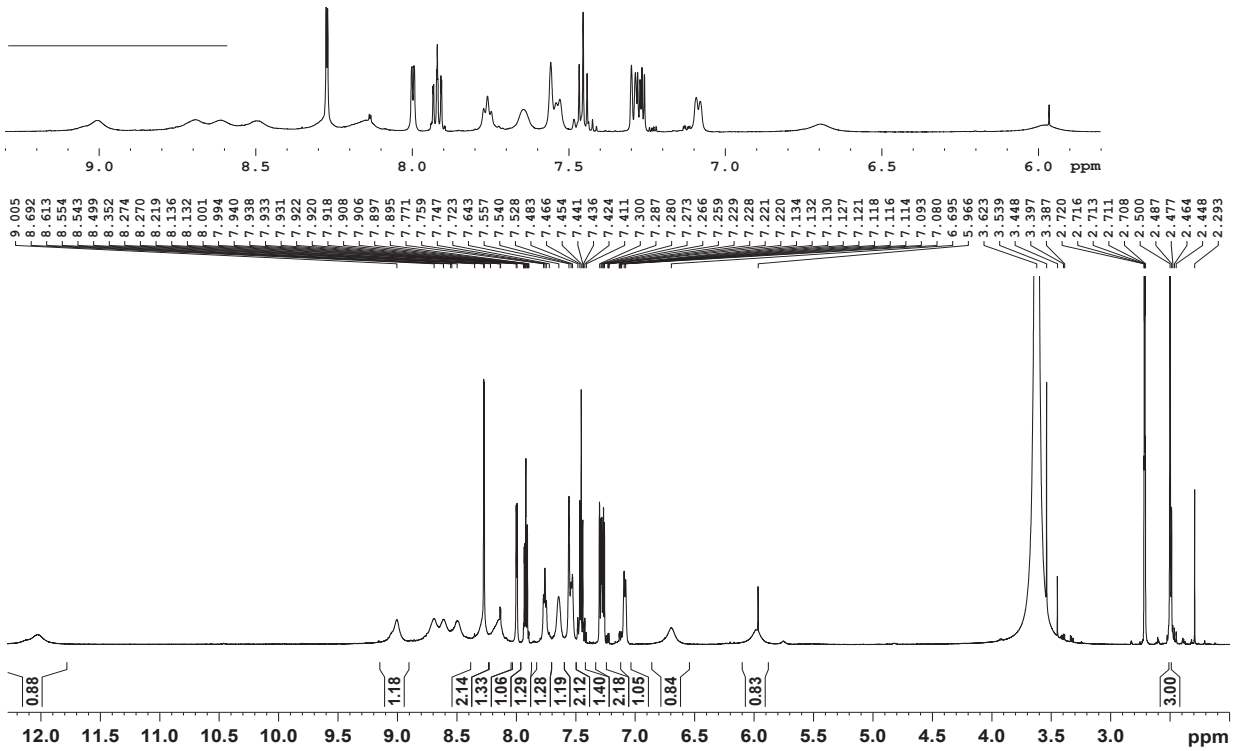

Figure S60. ^{1}H spectrum of **5d** in DMSO-d_6.

XII) NMR spectra of compound **5e**

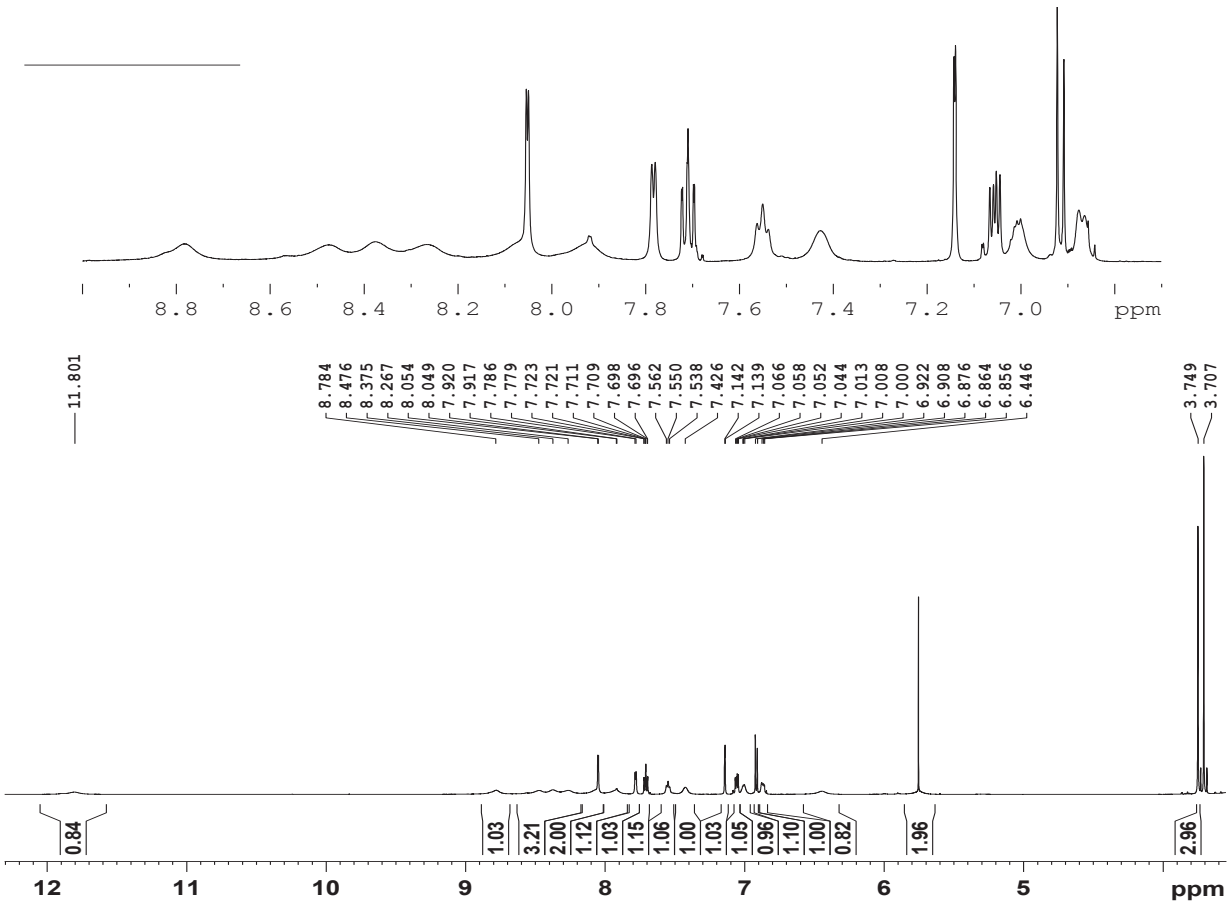

Figure S61. ^{1}H spectrum of **5e** in DMSO-d_6.

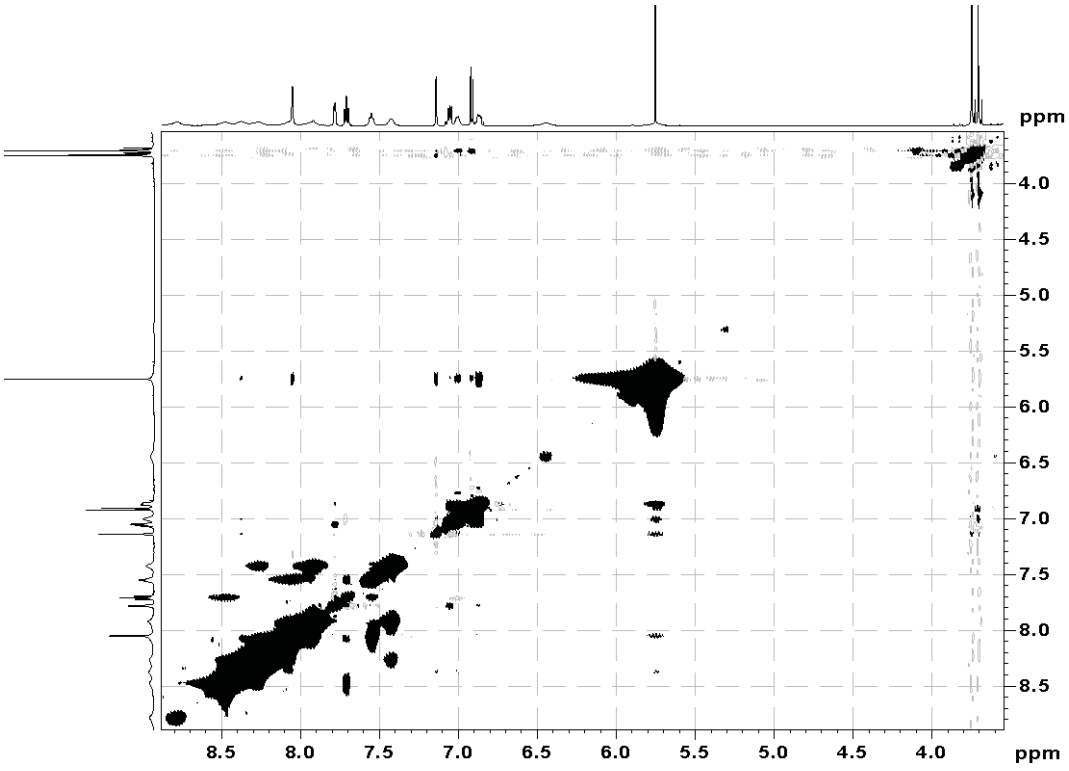

Figure S62. ^{1}H-^{1}H NOESY spectrum of **5e** in DMSO-d_6.

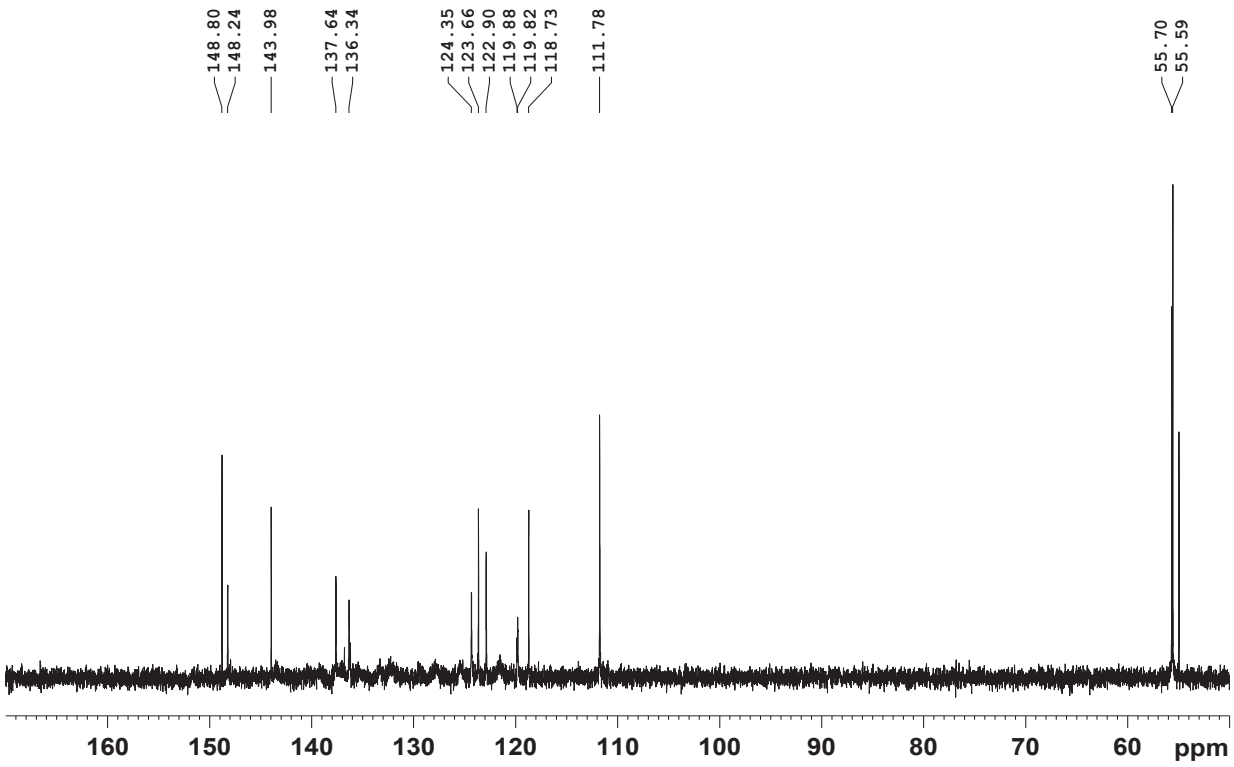

Figure S63. ^{13}C spectrum of **5e** in DMSO-d_6.

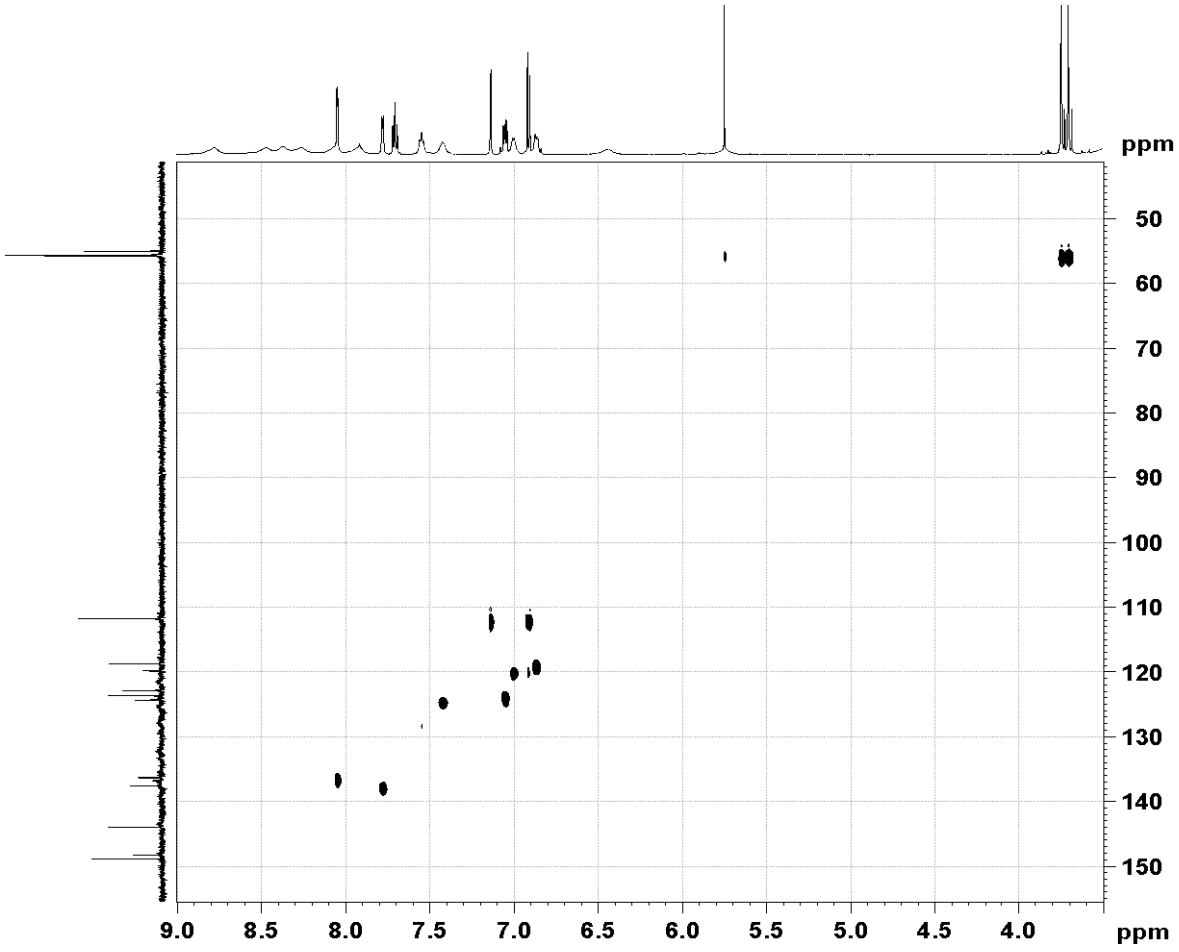

Figure S64. ^{1}H-^{13}C HSQC spectrum of **5e** in DMSO-d_6.

XIII) NMR spectra of compound **7**

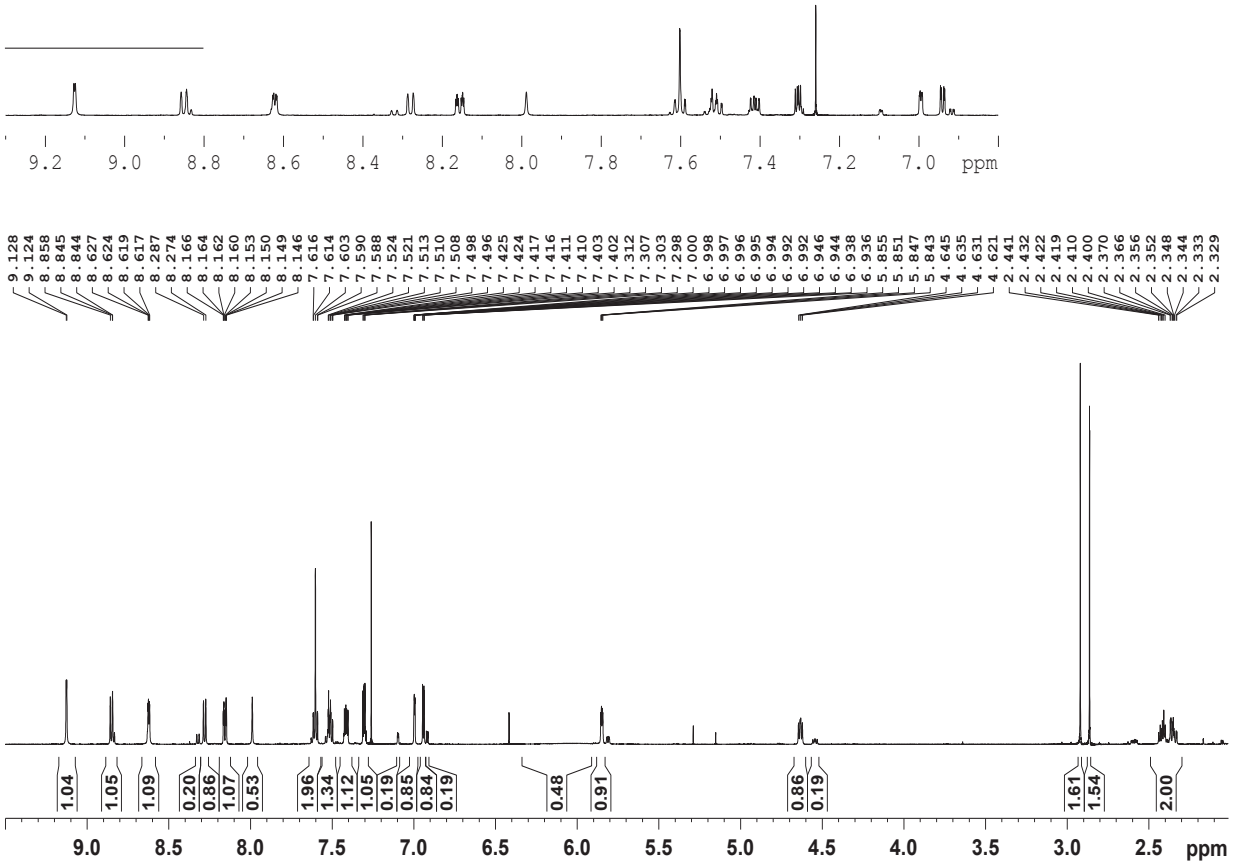

Figure S65. ^{1}H spectrum of **7** in $CDCl_3$.

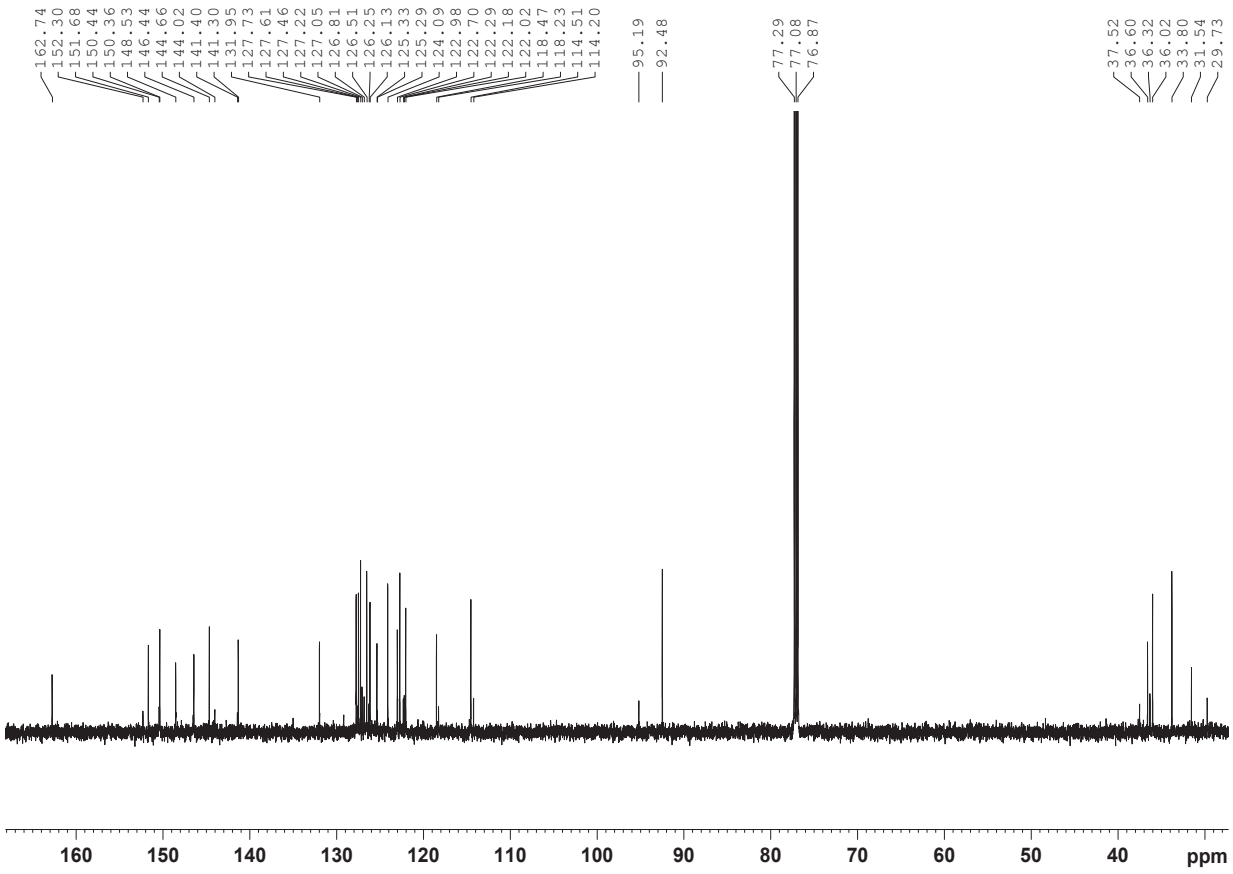

Figure S66. ^{13}C spectrum of **7** in $CDCl_3$.

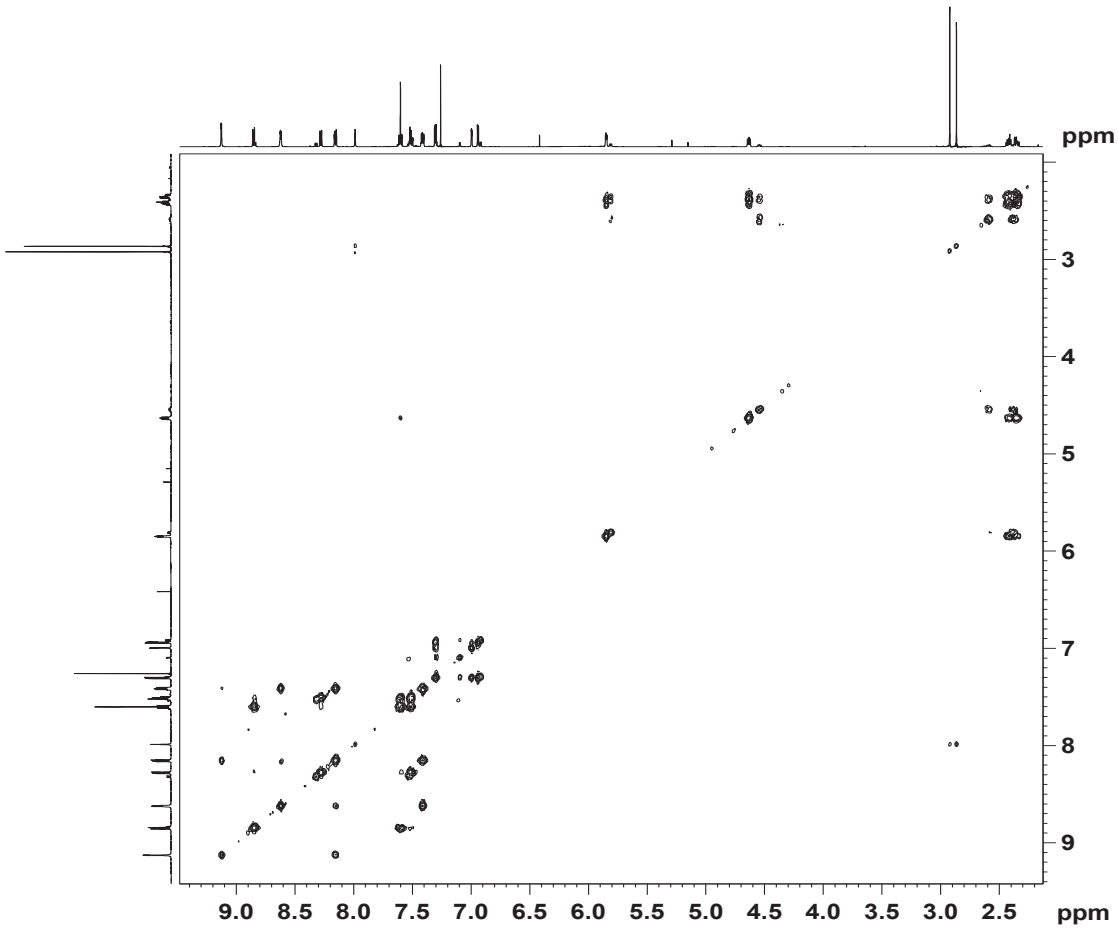

Figure S67. ^{1}H-^{1}H COSY spectrum of **7** in $CDCl_3$.

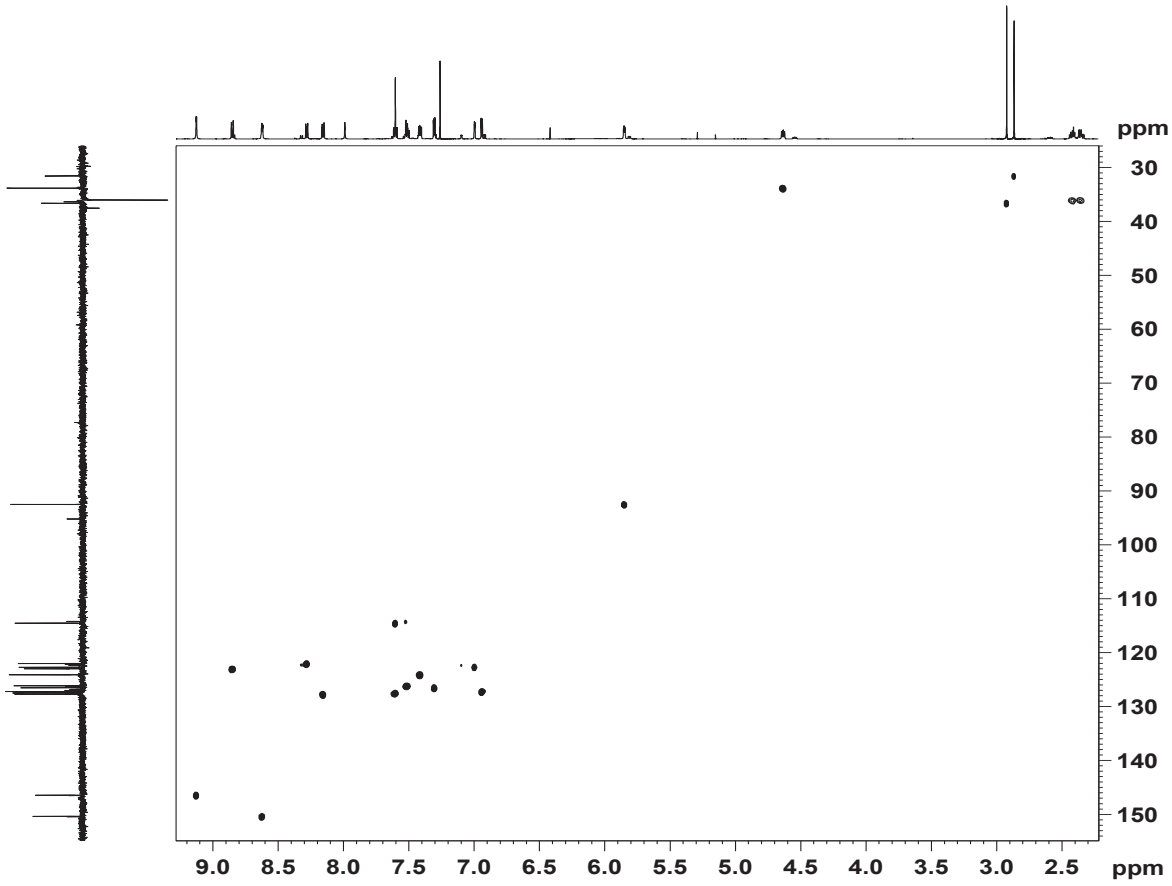

Figure S68. ^{1}H-^{13}C HSQC spectrum of **7** in $CDCl_3$.

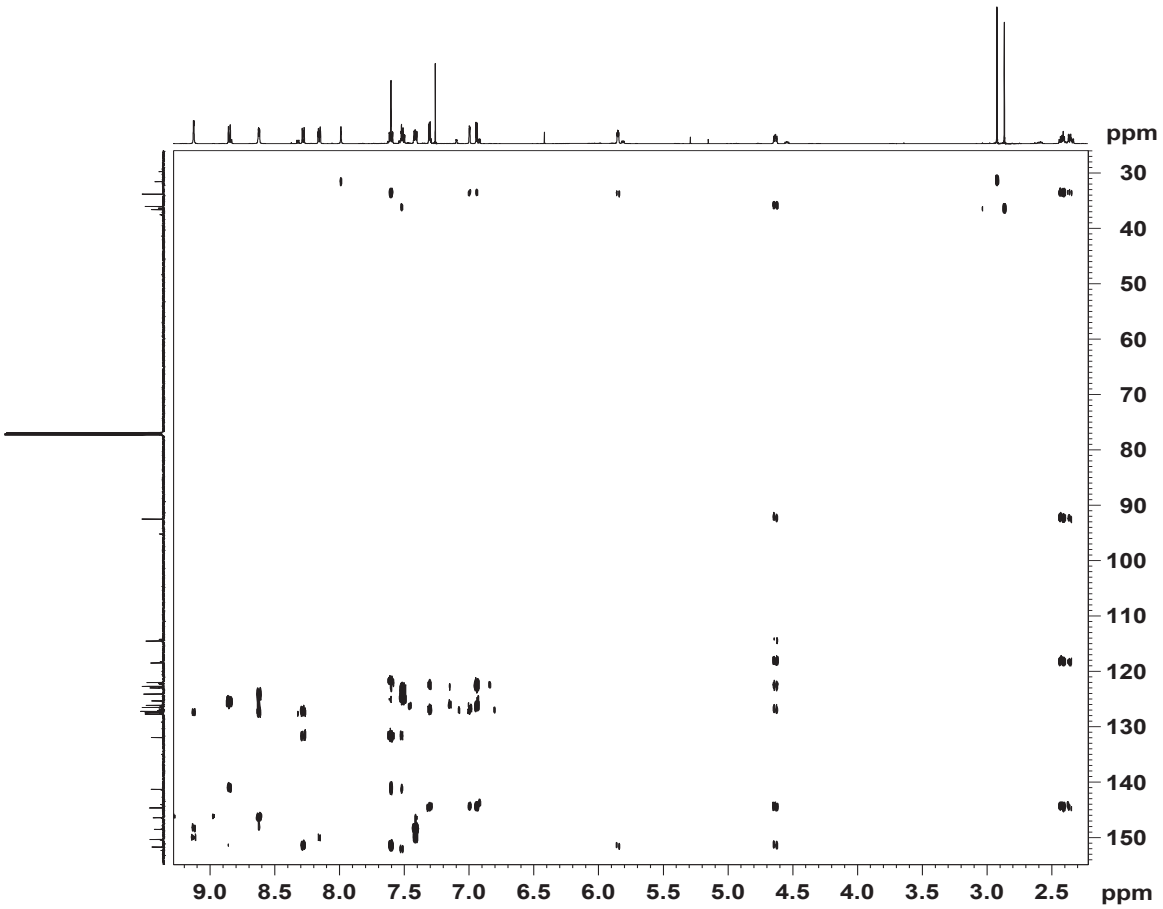

Figure S69. ^{1}H-^{13}C HMBC spectrum of **7** in $CDCl_3$.

XIV) NMR spectra of compound **6**

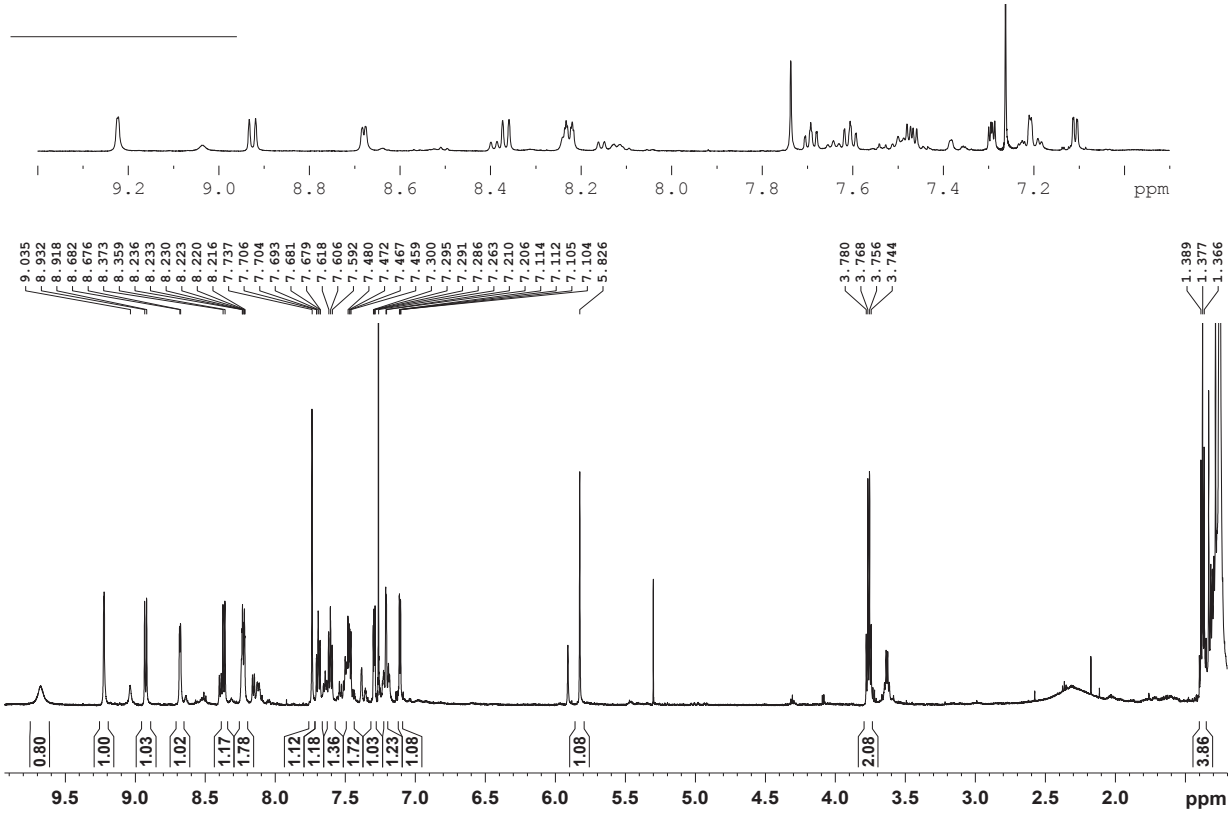

Figure S70. ^{1}H spectrum of **6** in $CDCl_3$.

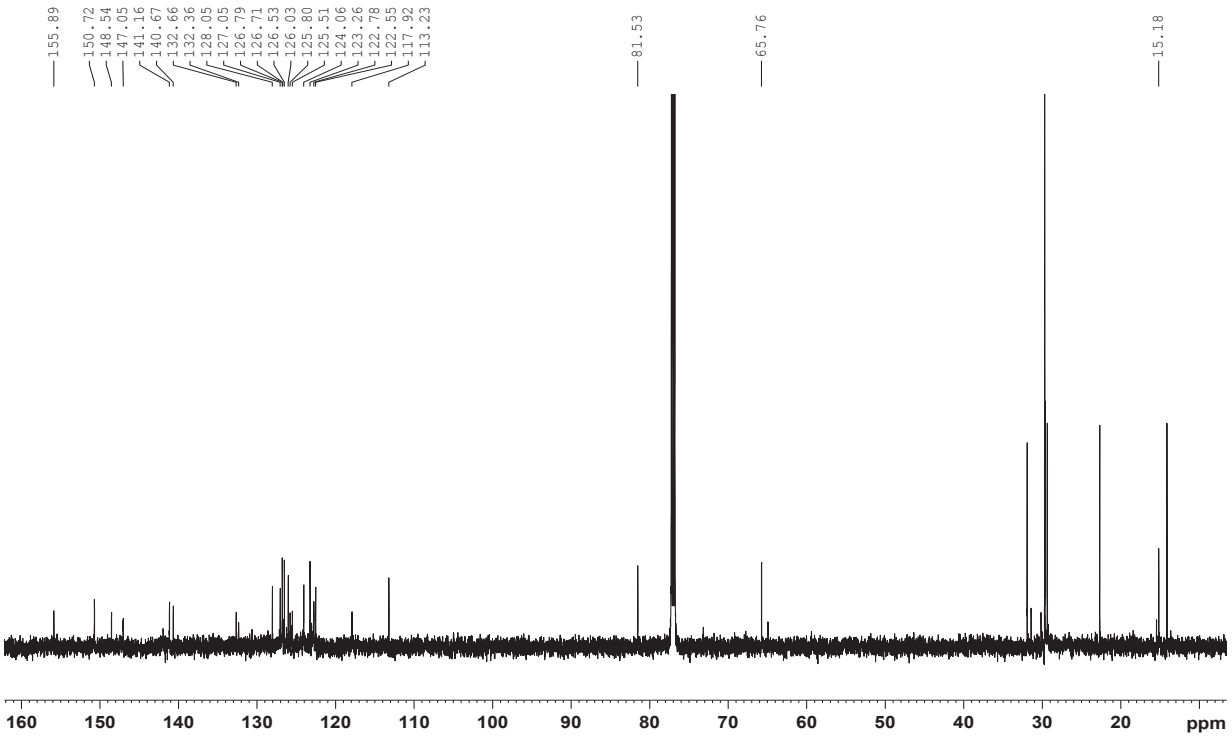

Figure S71. ^{13}C spectrum of **6** in $CDCl_3$.

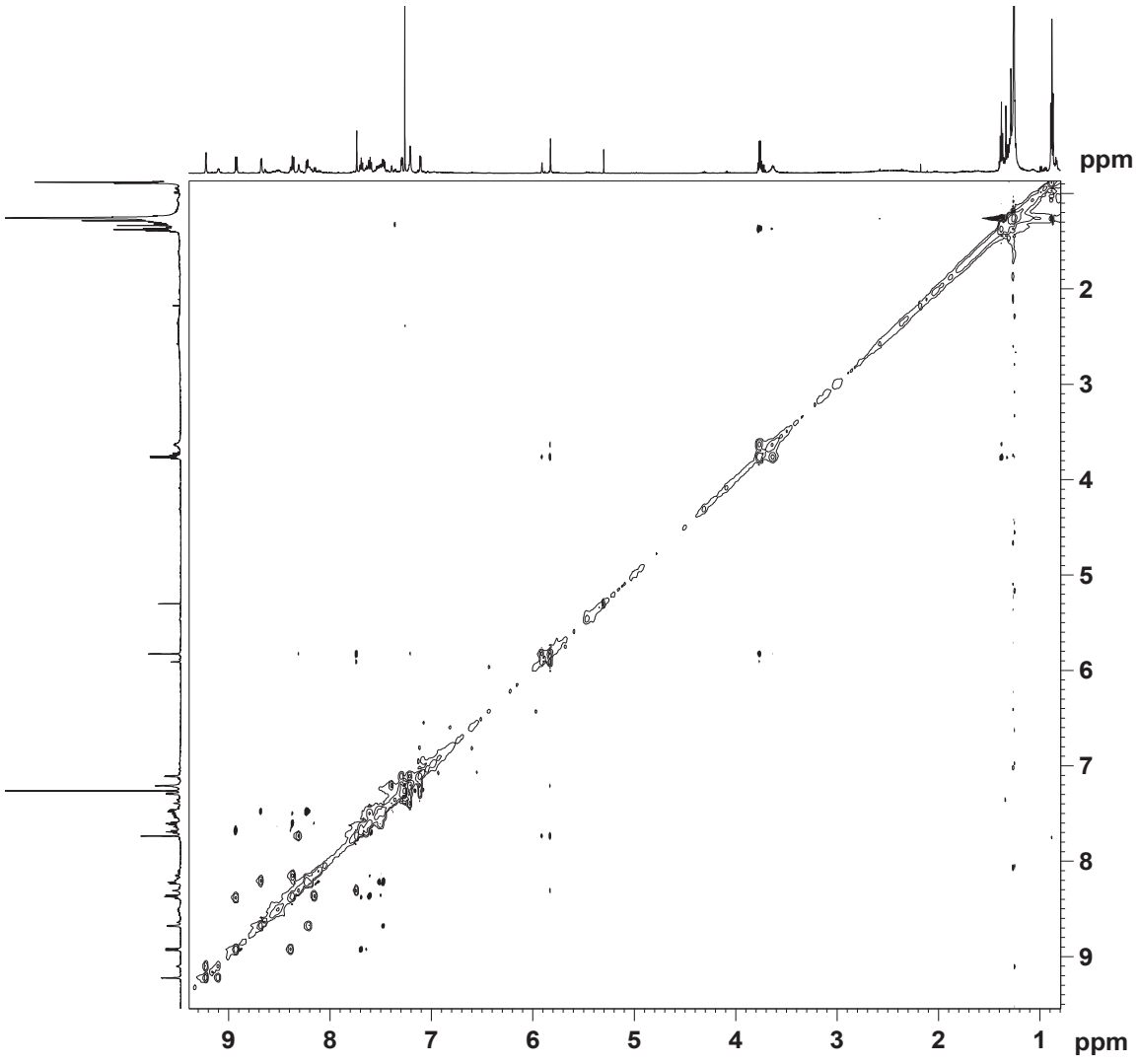

Figure S72. ^{1}H-^{1}H NOESY spectrum of **6** in $CDCl_3$.

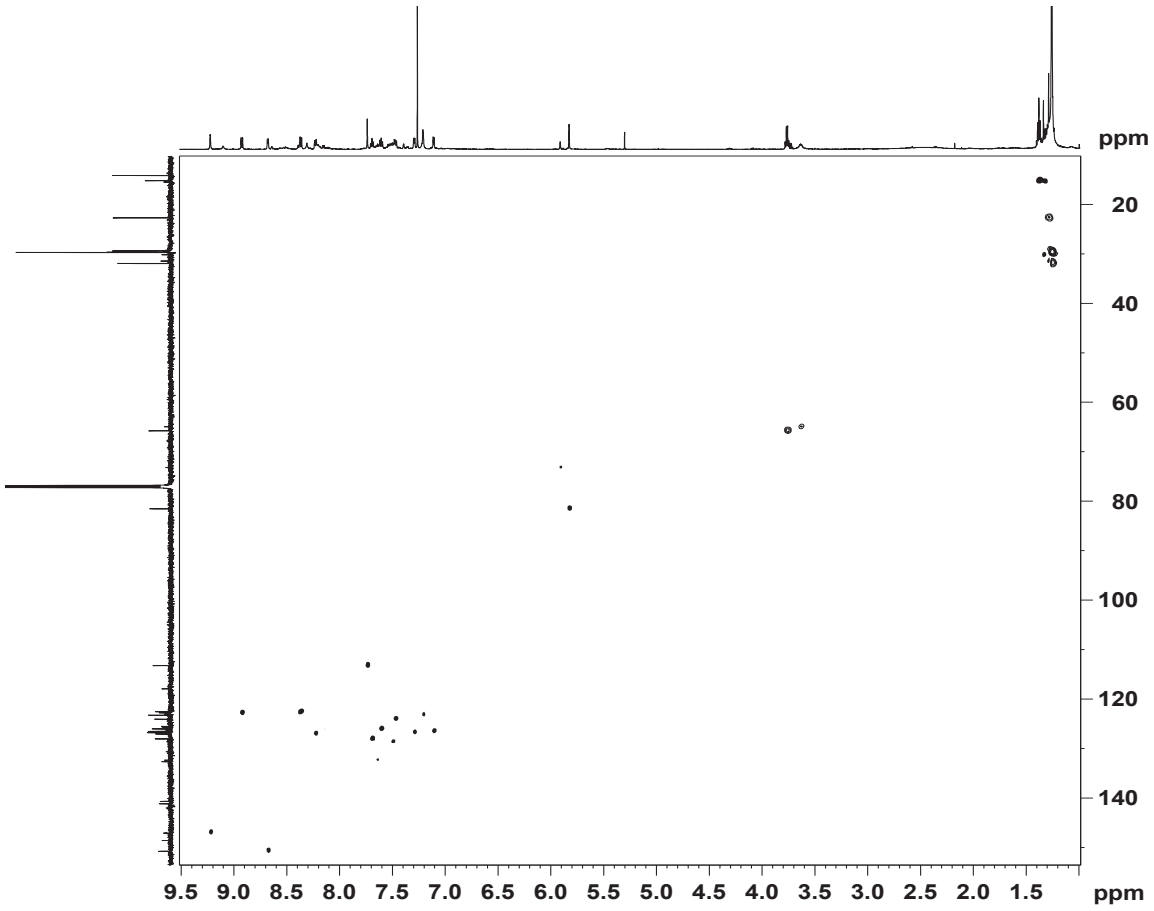

Figure S73. ^{1}H-^{13}C HSQC spectrum of **6** in $CDCl_3$.

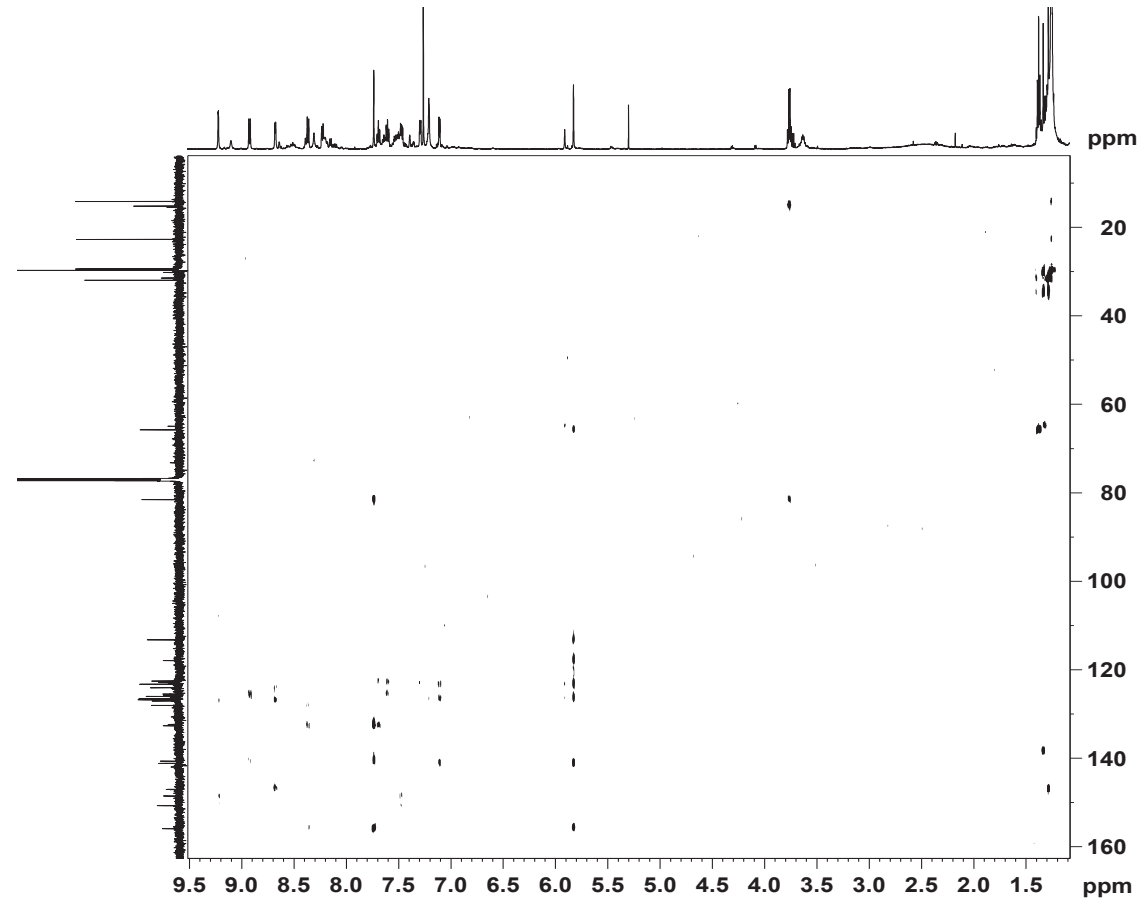

Figure S74. ^{1}H-^{13}C HMBC spectrum of **6** in $CDCl_3$.

XV) UV spectra

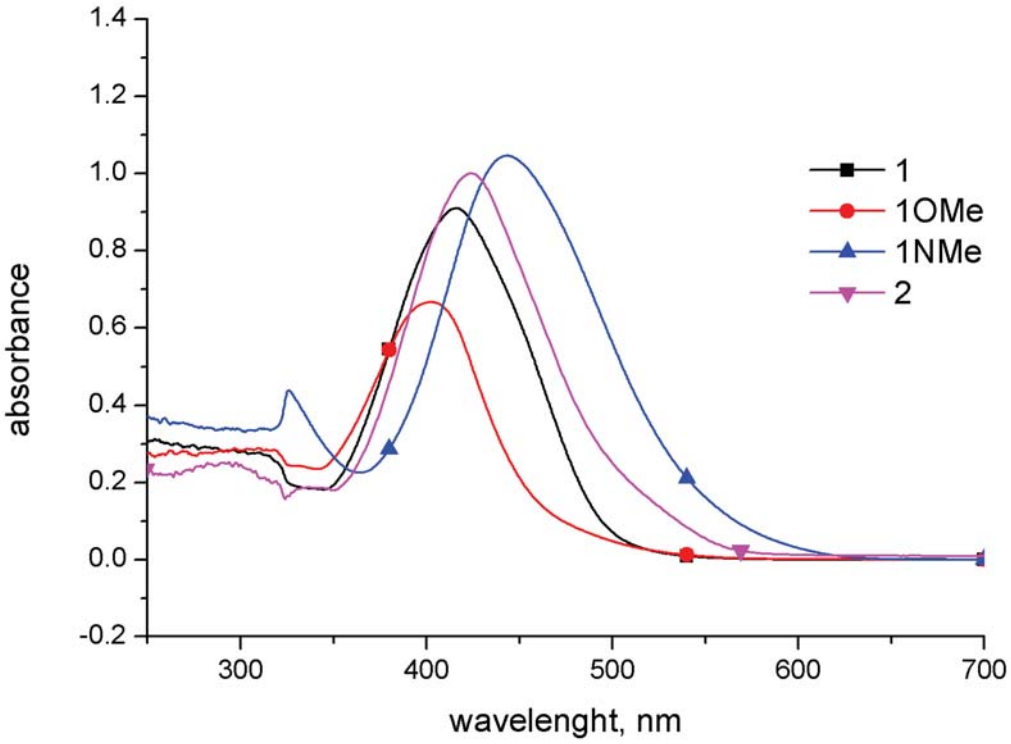

Figure S75. UV spectra of compounds **1**, **1-OMe**, **1-NMe**, and **2** in acetone.

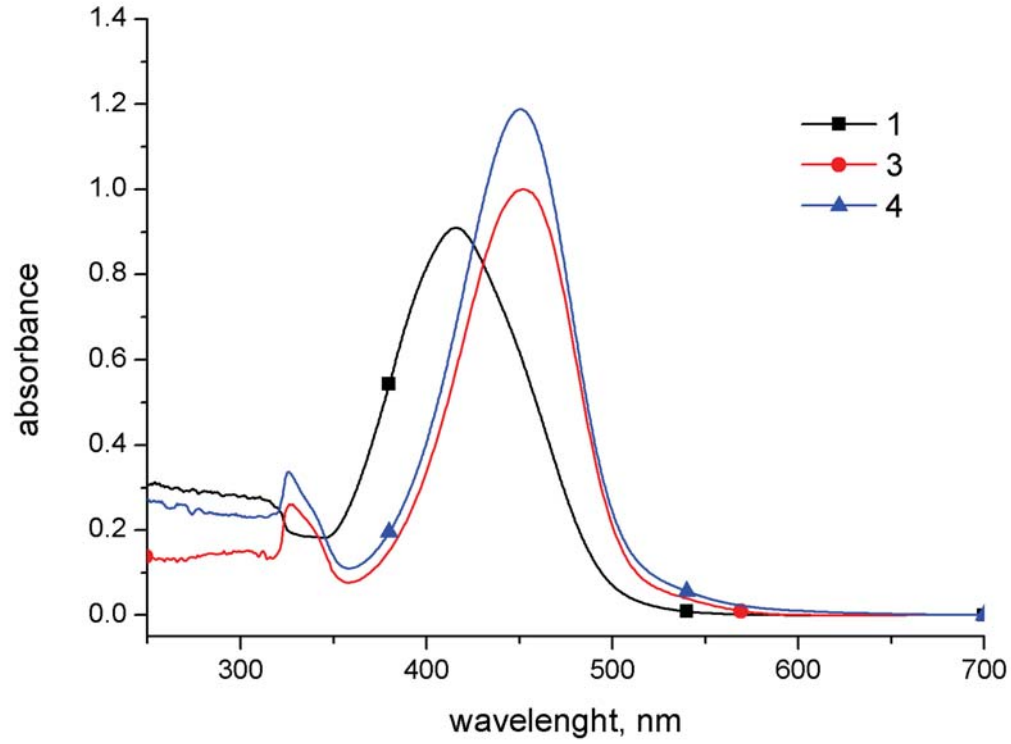

Figure S76. UV spectra of compounds **1**, **3**, and **4** in acetone.

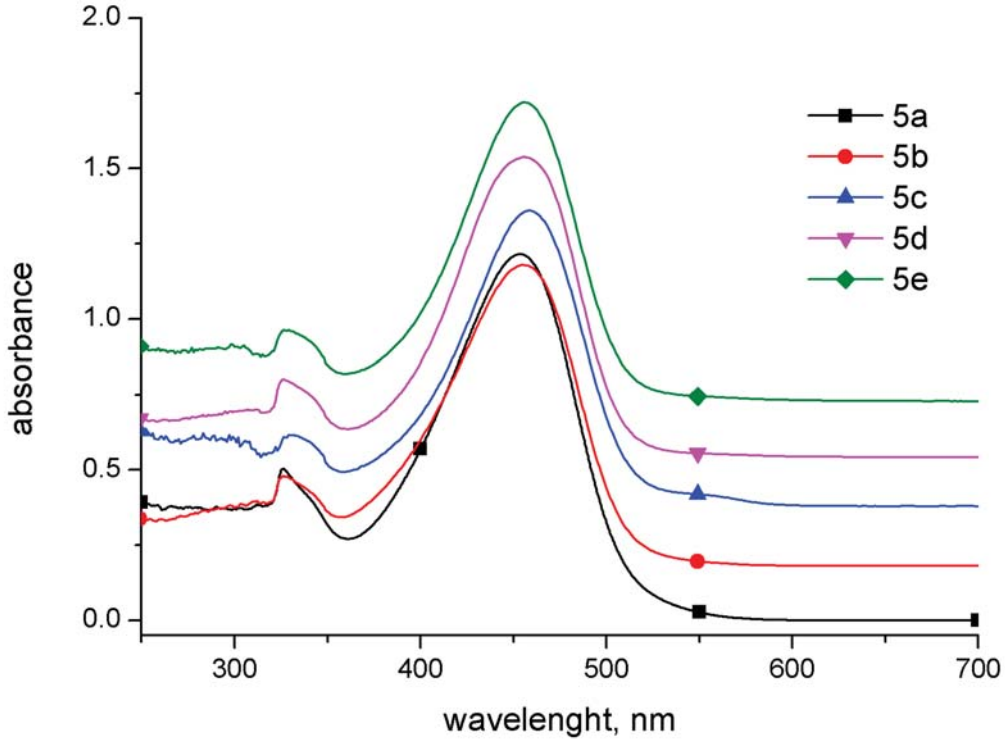

Figure S77. UV spectra of compounds **5a-5e** in acetone.

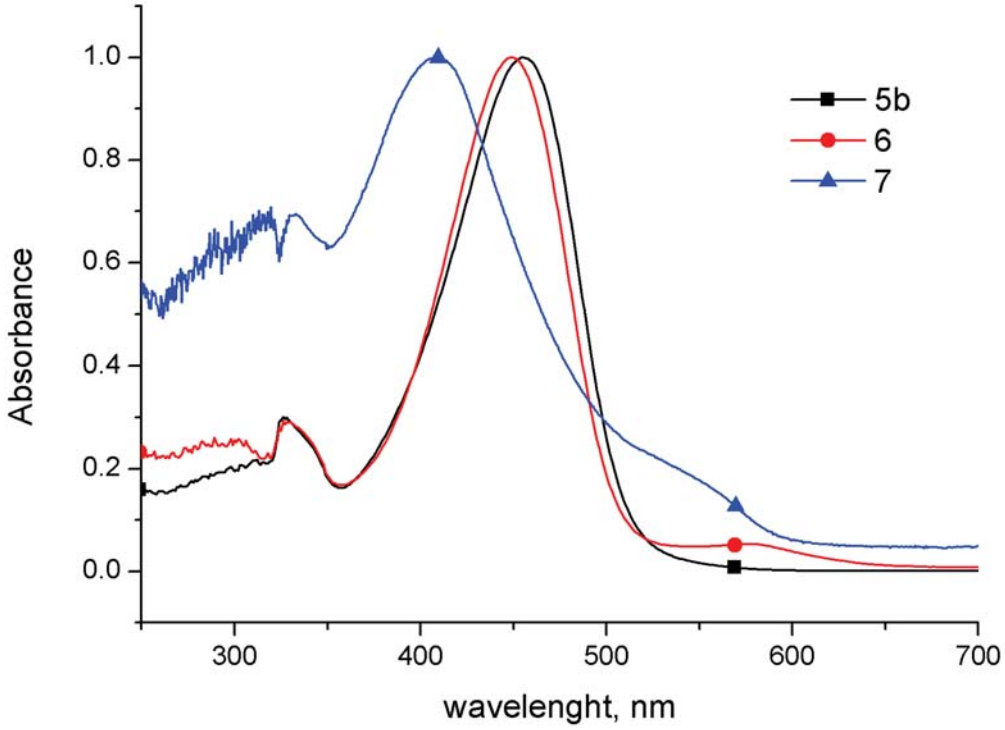

Figure S78. UV spectra of compounds **5b**, **6**, and **7** in acetone.