SUPPORTING INFORMATION

N-Methylmelamines – Synthesis, Characterization, and Physical Properties

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Table S1. Crystal data and data collection and structure refinement details.

	2	**3**	**4**	**6**	**8**	**9**
Empirical formula	$C_4H_8N_6$	$C_5H_{10}N_6$	$C_5H_{10}N_6$	$C_6H_{12}N_6$	$C_7H_{14}N_6$	$C_8H_{16}N_6$
Molecular weight	140.16	154.19	154.19	168.22	185.27	196.27
Size, mm^3	0.47×0.35×0.35	0.42×0.40×0.32	0.51×0.36×0.35	0.40×0.08×0.05	0.92×0.91×0.40	0.50×0.50×0.20
Crystal system	orthorhombic	tetragonal	trigonal	monoclinic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P4_32_12$	R-3c	$P2_1/n$	$P2_12_12_1$	$C2/c$
a, Å	7.2421(16)	7.398(1)	20.343(5)	7.4349(13)	7.0830(7)	14.8994(9)
b, Å	7.2490(16)	7.398(1)	20.343(5)	9.2666(14)	11.3665(14)	10.3474(7)
c, Å	12.642(3)	13.714(2)	9.880(3)	12.249(2)	12.0396(15)	28.420(2)
α, deg	90	90	90	90	90	90
β, deg	90	90	90	103.723(6)	90	90.814(2)
γ, deg	90	90	120	90	90	90
V, $Å^3$	663.7(2)	750.49(18)	3540.9(16)	819.8(2)	969.30(19)	4381.1(5)
$\rho_{calcd.}$, g cm^{-1}	1.403	1.365	1.302	1.363	1.270	1.190
Z	4	4	18	4	4	16
μ(MoK□), mm^{-1}	0.10	0.10	0.09	0.10	0.09	0.08
T, K	300	230	233	205	300	300
θ_{max}, deg	23.6	25.0	24.9	22.8	24.4	25.0
Measured reflections	5031	4497	19278	4229	5911	13760
Independent reflections	21	437	688	1100	1571	3855
Reflections with $I > 2\sigma(I)$)	595	407	541	822	1247	2942
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan

T_{min}/T_{max}	0.72, 0.97	0.94, 0.98	0.43, 0.97	0.95, 0.97	0.93, 0.97	0.96, 0.98
Restraints/refined param.	0/94	0/54	0/54	0/113	0/131	0/264
R_1 ($I \geq 2\sigma(I)$)	0.037	0.029	0.044	0.047	0.043	0.053
wR_2	0.096	0.084	0.133	0.133	0.124	0.156
$\Delta\sigma_{fin}$ (max/min), e Å^{-3}	0.16/-0.16	0.12/-0.15	0.23/-0.15	0.23/-0.20	0.16/-0.14	0.24/-0.22
CCDC no.	1048857	1048858	1048859	1048860	1048861	1048862

Table S2. Bond lengths and angles of 2–4, 6, 8, 9, melamine, and hexamethyl-melamine determined by single-crystal X-ray diffraction (for clarity, no esd are given).

compound	**melamine** [55]	**2**	**3**	**4**	**6**	**8**	**9** (two molecules in unit cell)		**hexamethyl-melamine** [49]
inner-cycle bond lengths and angles									
C–N	1.349 1.350 1.354 1.344 1.341 1.353	1.340 1.340 1.345 1.338 1.348 1.357	1.353 1.342 1.346	1.342 1.343 1.344	1.342 1.341 1.356 1.341 1.353 1.353	1.340 1.342 1.355 1.343 1.341 1.352	1.342 1.337 1.347 1.351 1.333 1.347	1.342 1.344 1.340 1.337 1.348 1.351	1.342 1.334
C–N–C	114.68 114.62 114.28	113.79 115.09 113.58	114.02 114.24	114.02 114.33	114.58 113.49 114.04	114.60 113.64 114.12	114.29 113.49 113.66	113.54 114.30 113.61	112.67
N–C–N	125.43 124.90 125.96	126.46 125.71 125.27	125.45 125.80	125.87 125.47	125.42 126.16 126.30	125.49 125.74 126.34	126.00 125.89 126.52	126.26 126.31 125.89	127.33
N_{in}–C–NH_2	116.86/117.70 116.95/118.14 116.42/117.60	116.26/118.02 116.36/118.37	116.99/117.21	117.27	-	116.93/116.74	-	-	-
N_{in}–C–$NH_{2-n}Me_n$ (n = 1, 2)	-	115.85/117.68	117.28/117.28	116.46/117.66	117.17/117.40 115.94/117.76 116.34/117.50	117.13/117.38 117.10/117.16	115.89/117.62 116.88/117.11 116.40/117.71	116.07/117.66 116.47/117.21 116.31/117.80	115.79/116.88
outer-cycle bond lengths and angles									

C–NH_2	1.343 1.340 1.364	1.336 1.339	1.339	1.332	-	1.341	-	-	-
C–$NH_{2-n}Me_n$ (n = 1, 2)	-	1.341	1.342	1.334	1.338 1.346 1.344	1.354 1.357	1.353 1.357 1.349	1.341 1.355 1.358	1.359
C_{in}–NH_{2-n}–$C_{Me,n}$ (n = 1, 2)	-	124.41	121.28	124.23	122.56 124.46 121.82	120.31/121.98 120.36/122.15	123.00 120.45/121.64 120.75/122.26	123.76 120.96/120.94 120.26/122.0	121.09/121.35

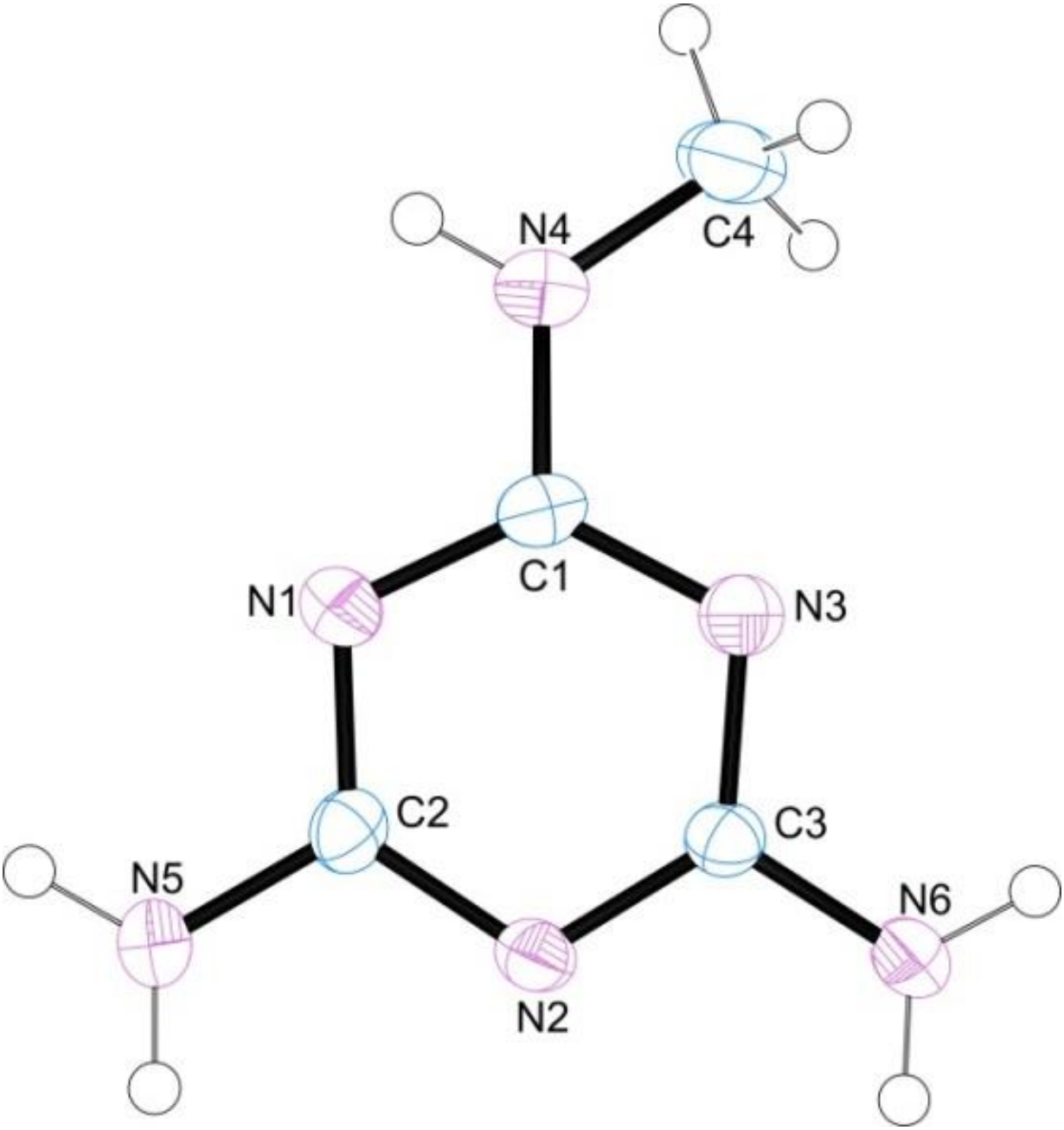

Figure S3. Molecular structure of compound **2** (ellipsoids drawn at the 50% probability level).

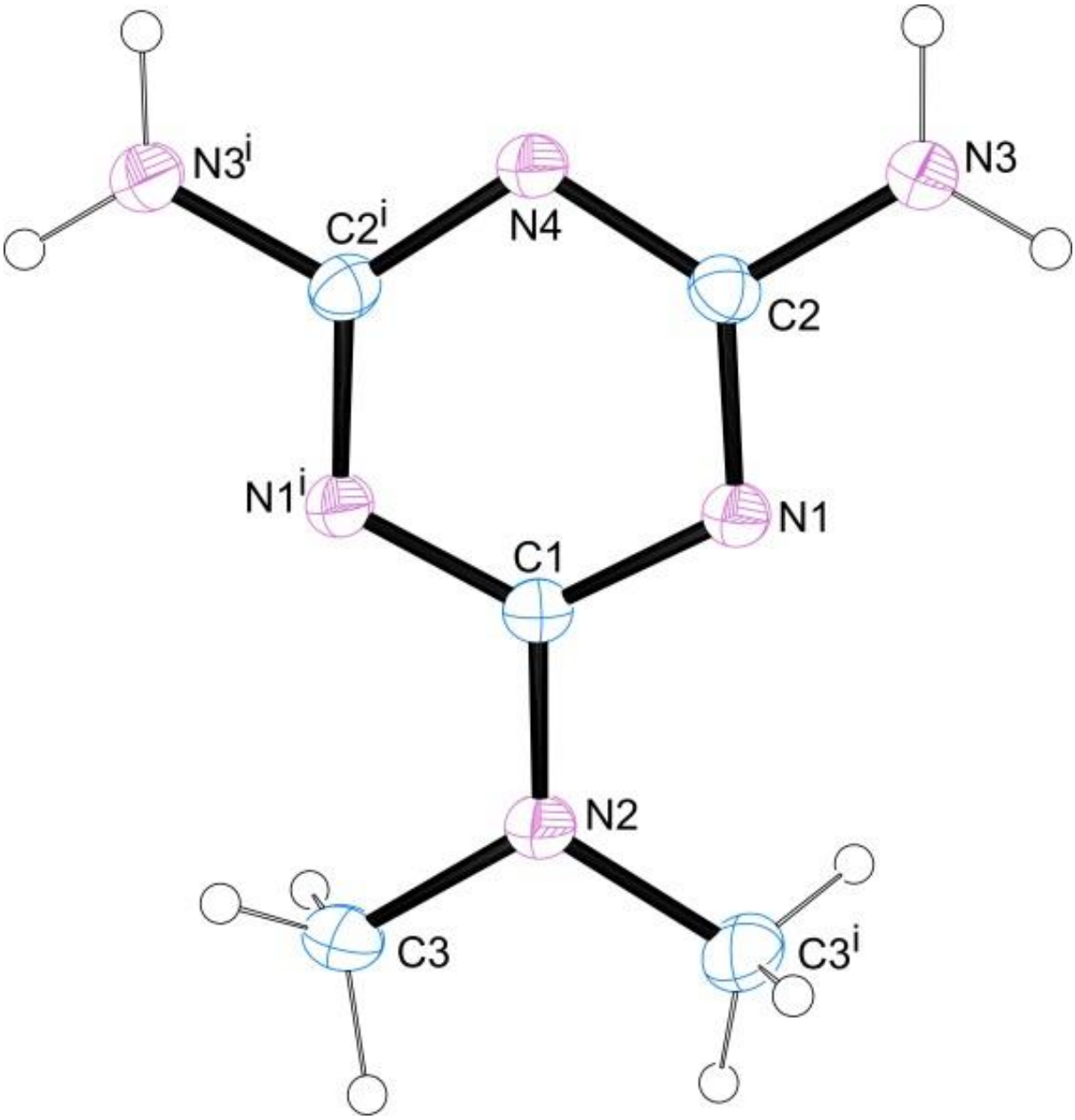

Figure S4. Molecular structure of compound **3** (ellipsoids drawn at the 50% probability level).

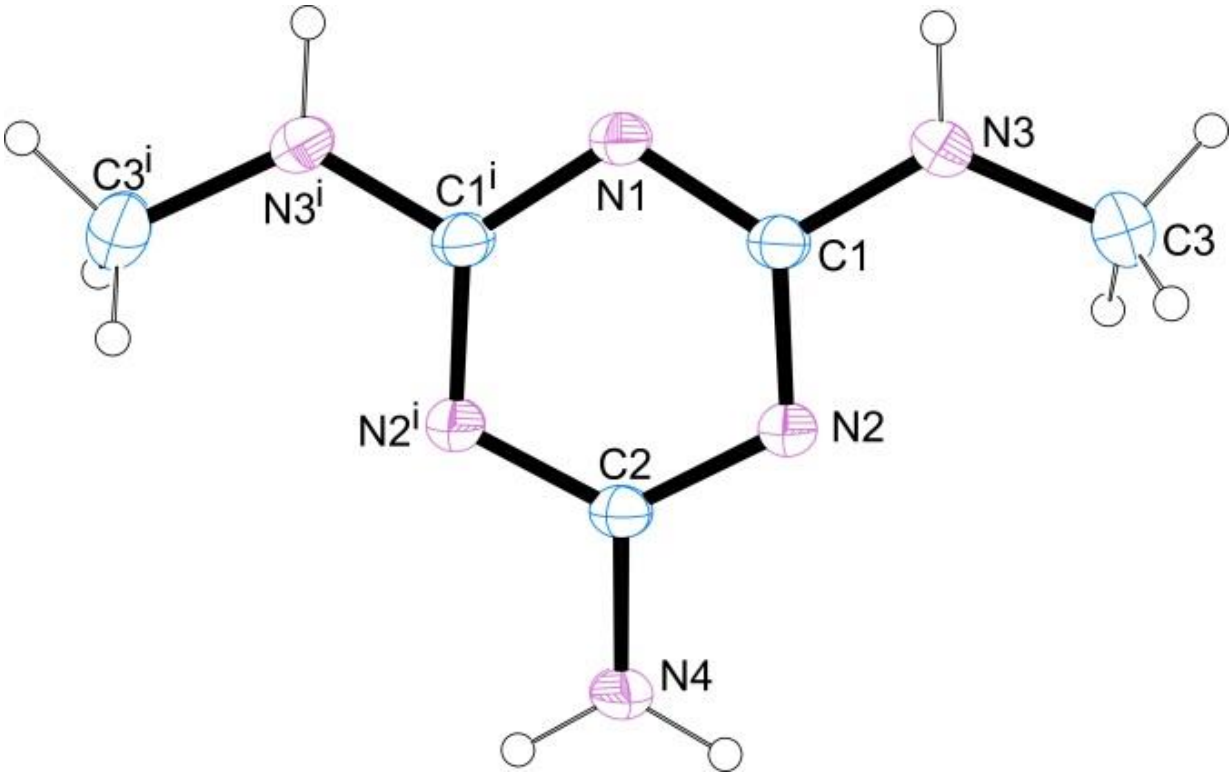

Figure S5. Molecular structure of compound **4** (ellipsoids drawn at the 50% probability level).

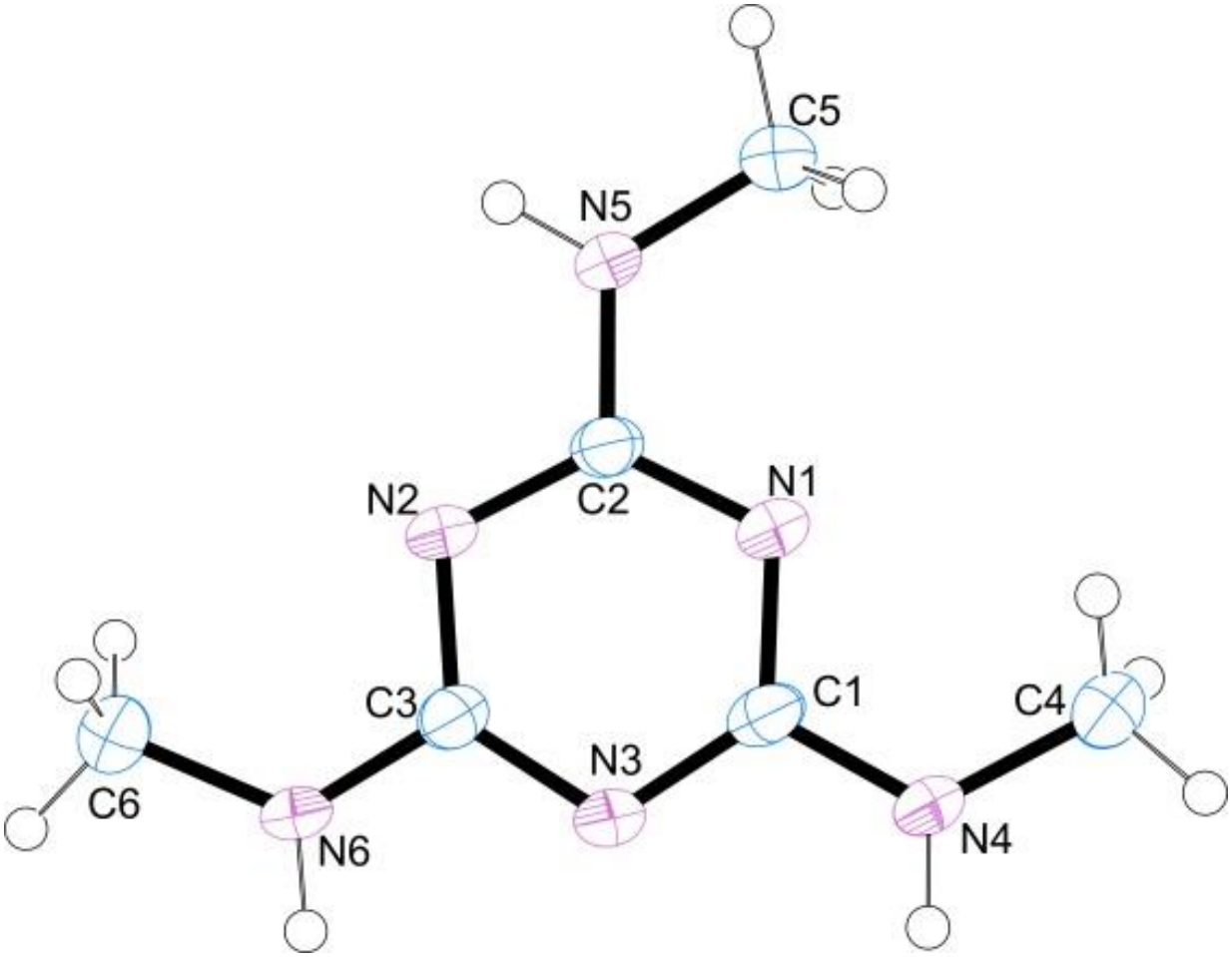

Figure S6. Molecular structure of compound **6** (ellipsoids drawn at the 50% probability level).

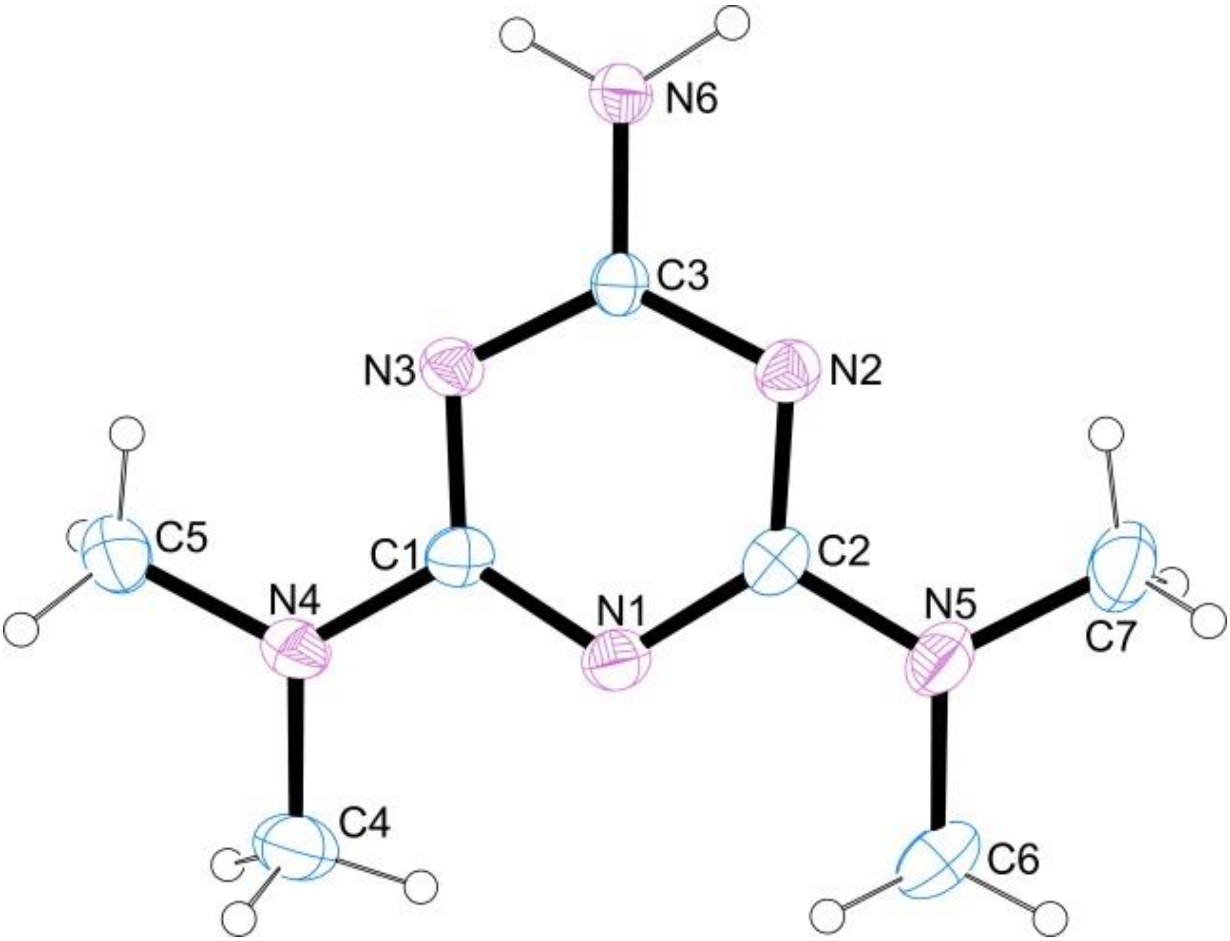

Figure S7. Molecular structure of compound **8** (ellipsoids drawn at the 50% probability level).

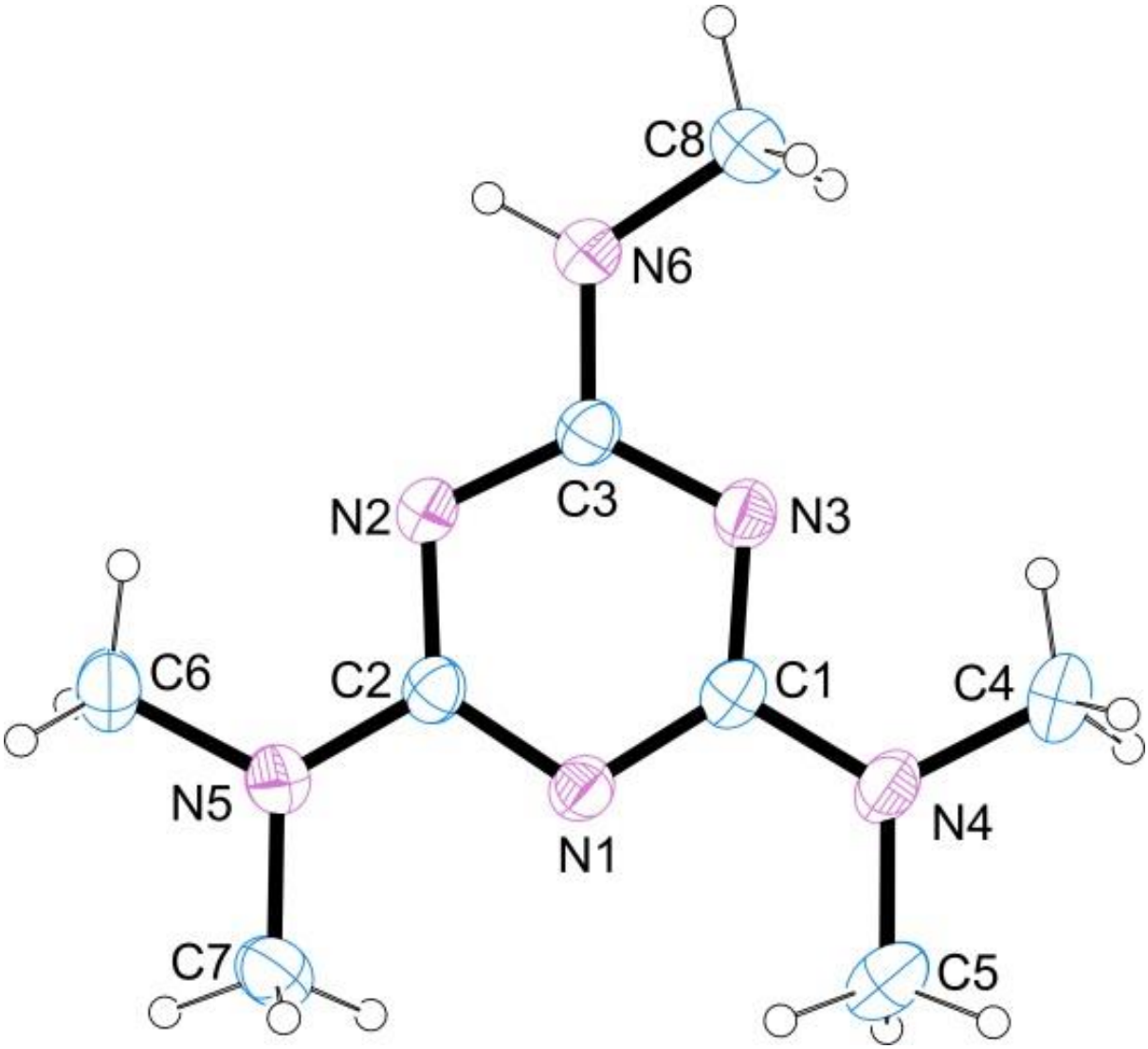

Figure S8. Molecular structure of compound **9** (ellipsoids drawn at the 50% probability level).

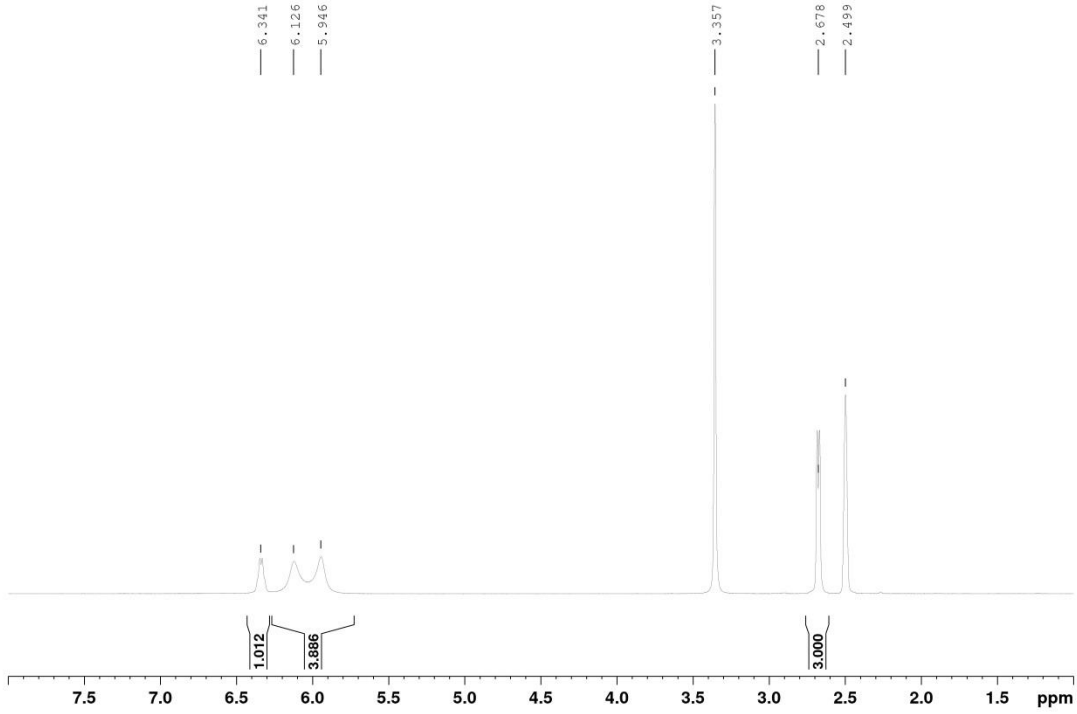

Figure S9. ^{1}H-NMR of compound **2** in DMSO-*d6* (3.35 ppm water in solvent)

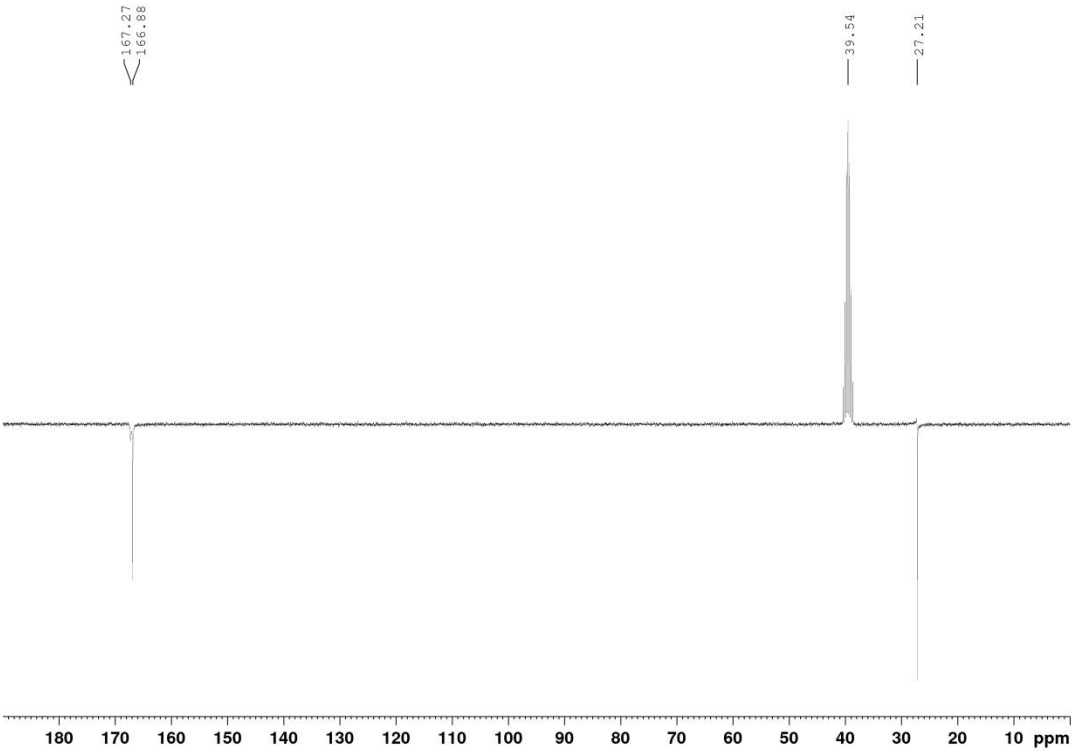

Figure S10. ^{13}C-NMR of compound **2** in DMSO-*d6*

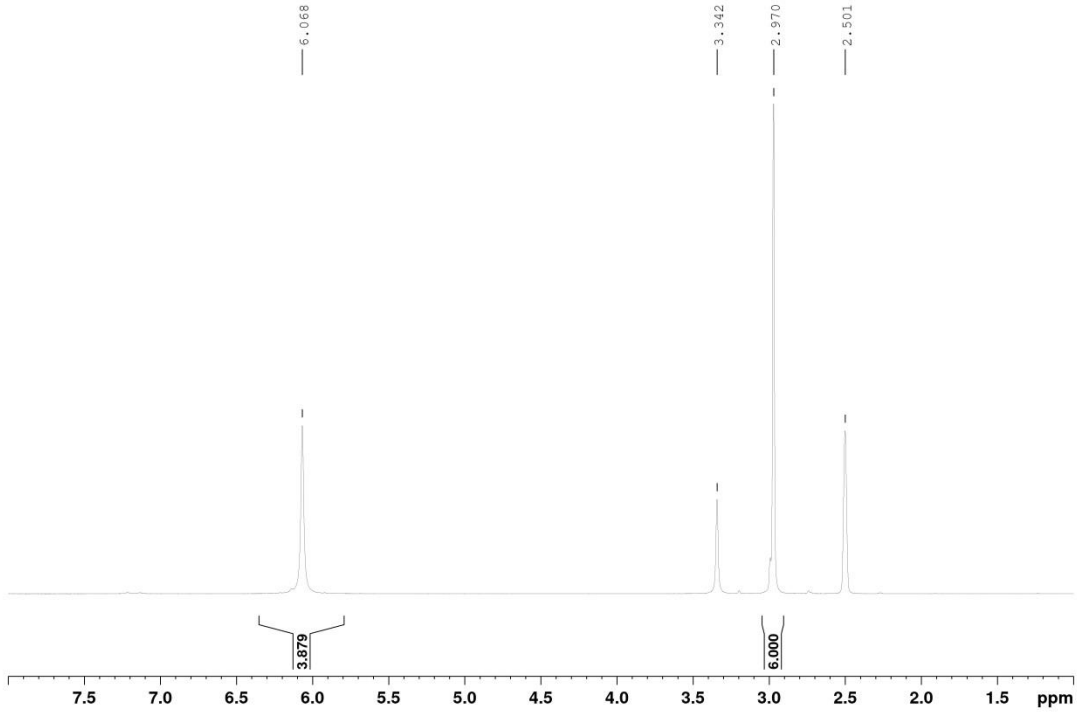

Figure S11. [1]H-NMR of compound **3** in DMSO-*d6* (3.34 ppm water in solvent)

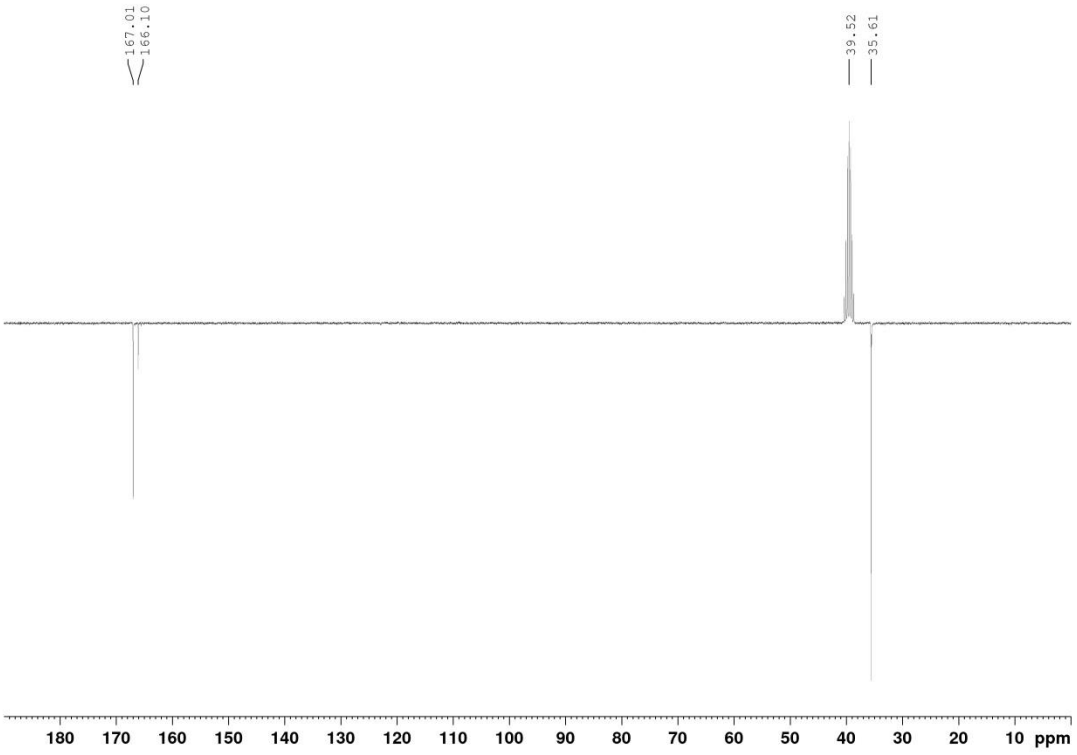

Figure S12. [13]C-NMR of compound **3** in DMSO-*d6*

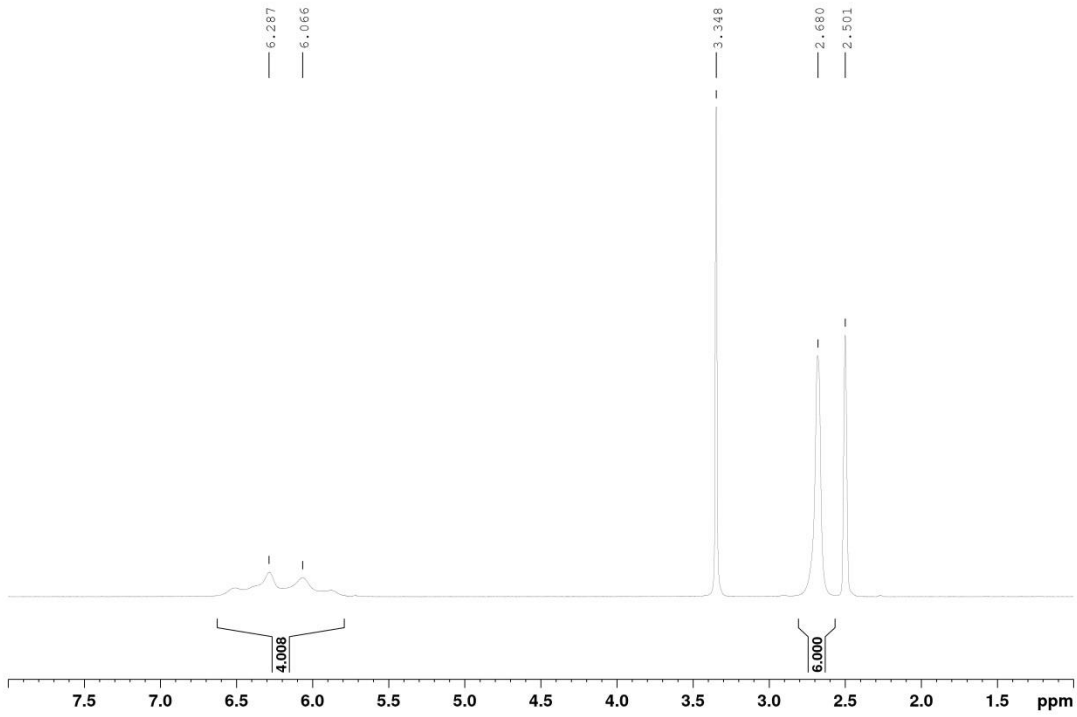

Figure S13. [1]H-NMR of compound **4** in DMSO-*d6* (3.34 ppm water in solvent)

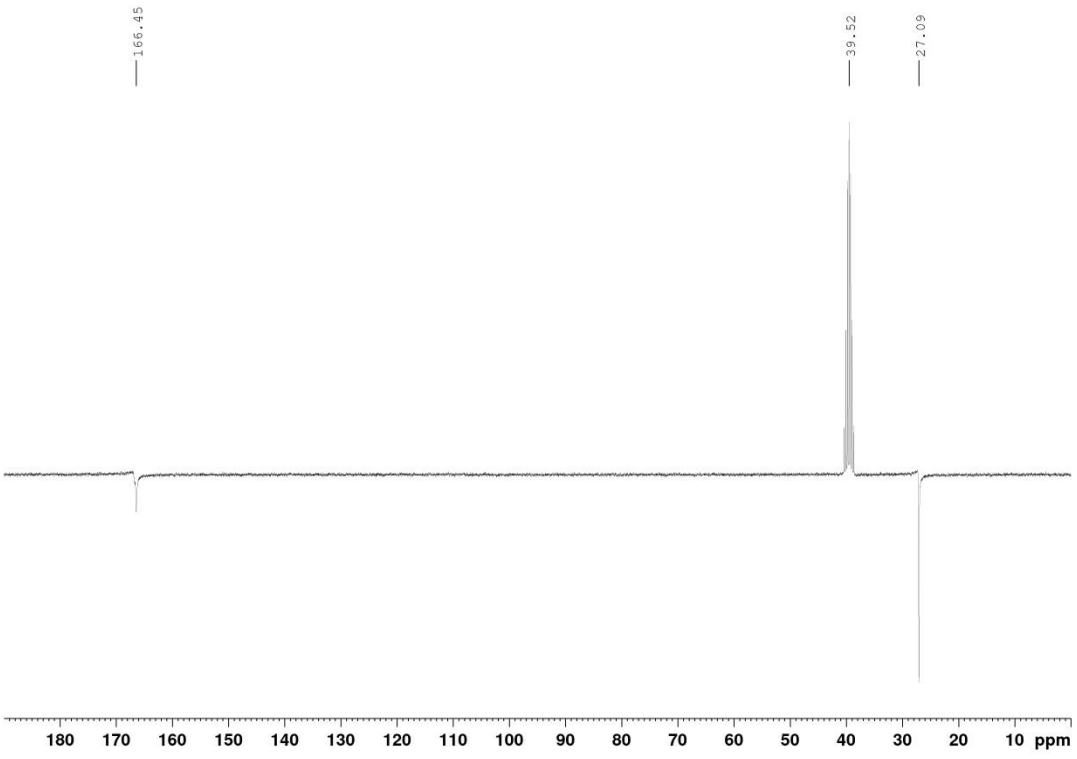

Figure S14. [13]C-NMR of compound **4** in DMSO-*d6*

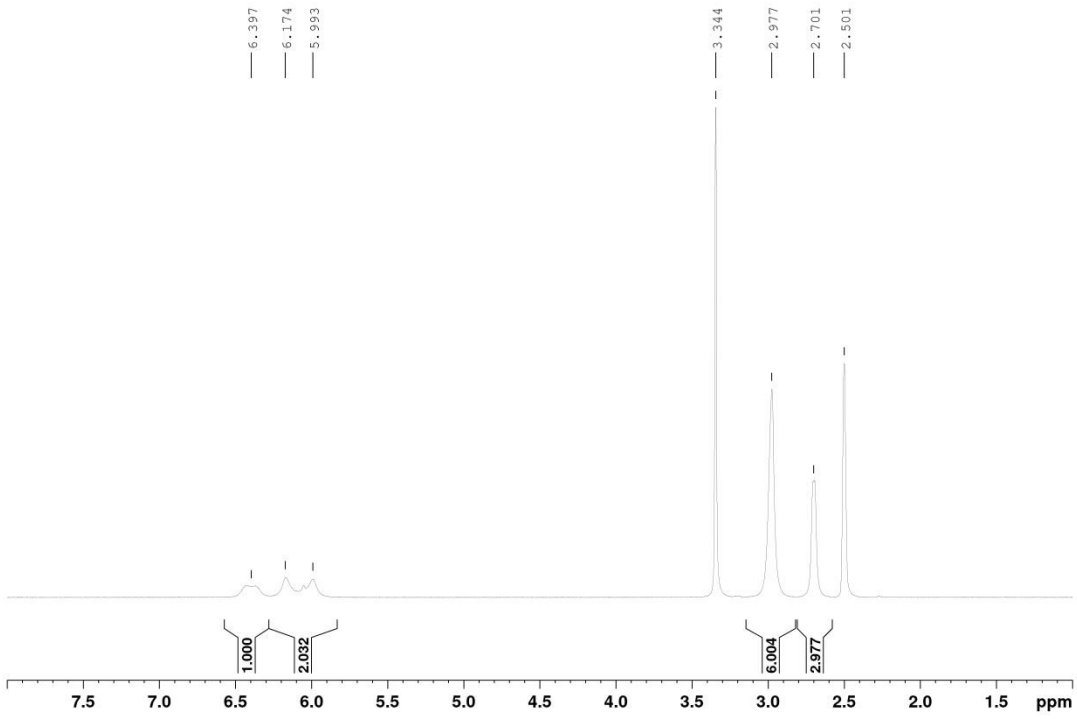

Figure S15. [1]H-NMR of compound **5** in DMSO-*d6* (3.34 ppm water in solvent)

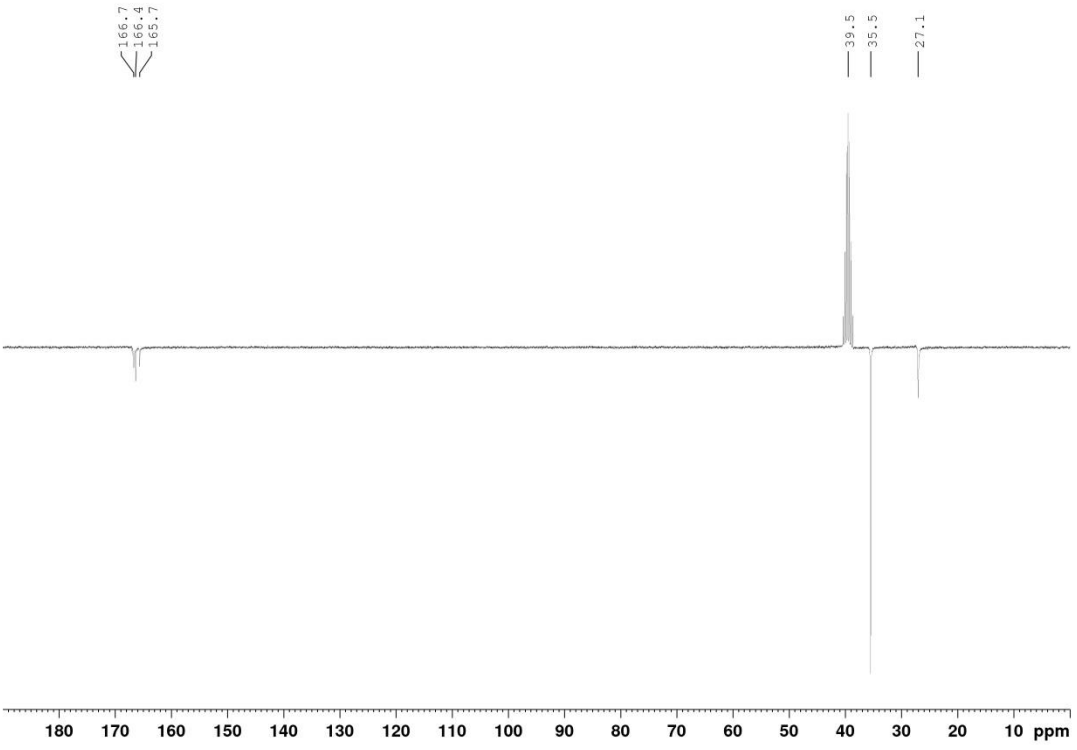

Figure S16. [13]C-NMR of compound **5** in DMSO-*d6*

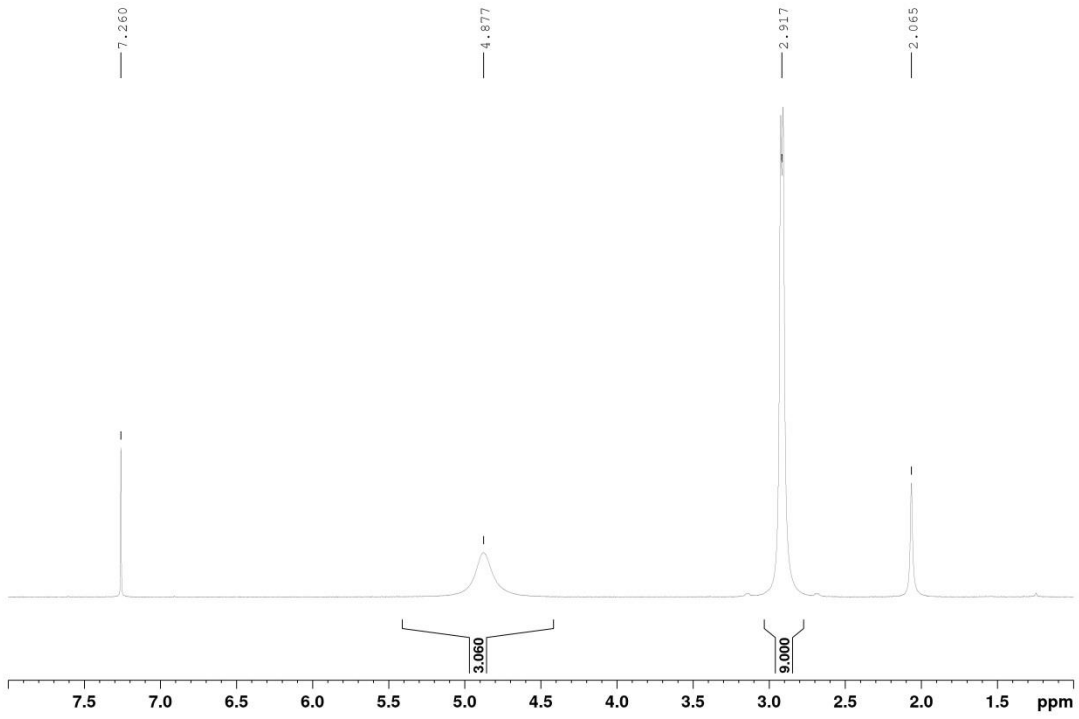

Figure S17. ^{1}H-NMR of compound **6** in $CDCl_3$ (2.07 ppm water)

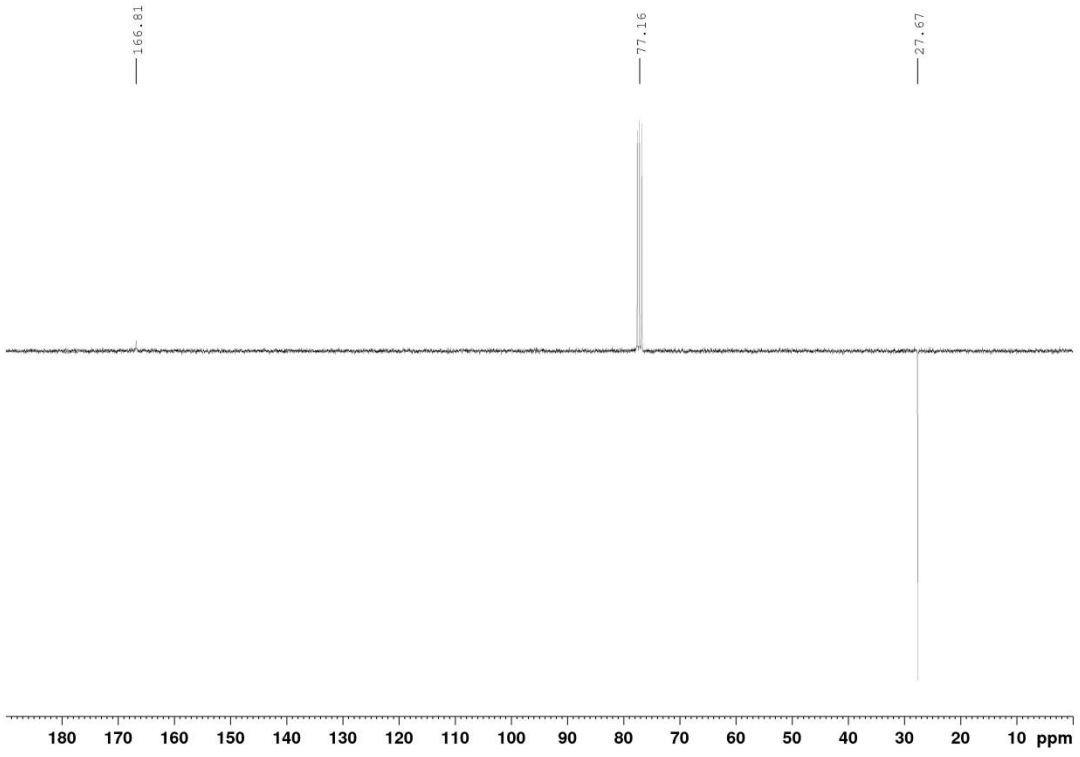

Figure S18. ^{13}C-NMR of compound **6** in $CDCl_3$

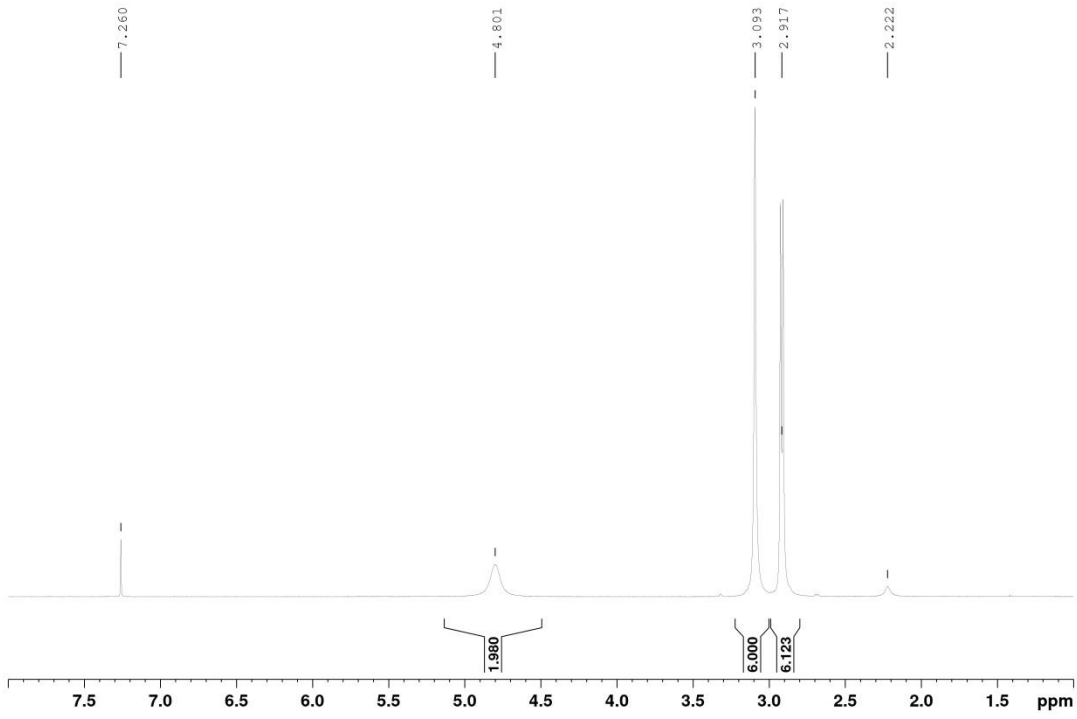

Figure S19. ^{1}H-NMR of compound **7** in $CDCl_3$

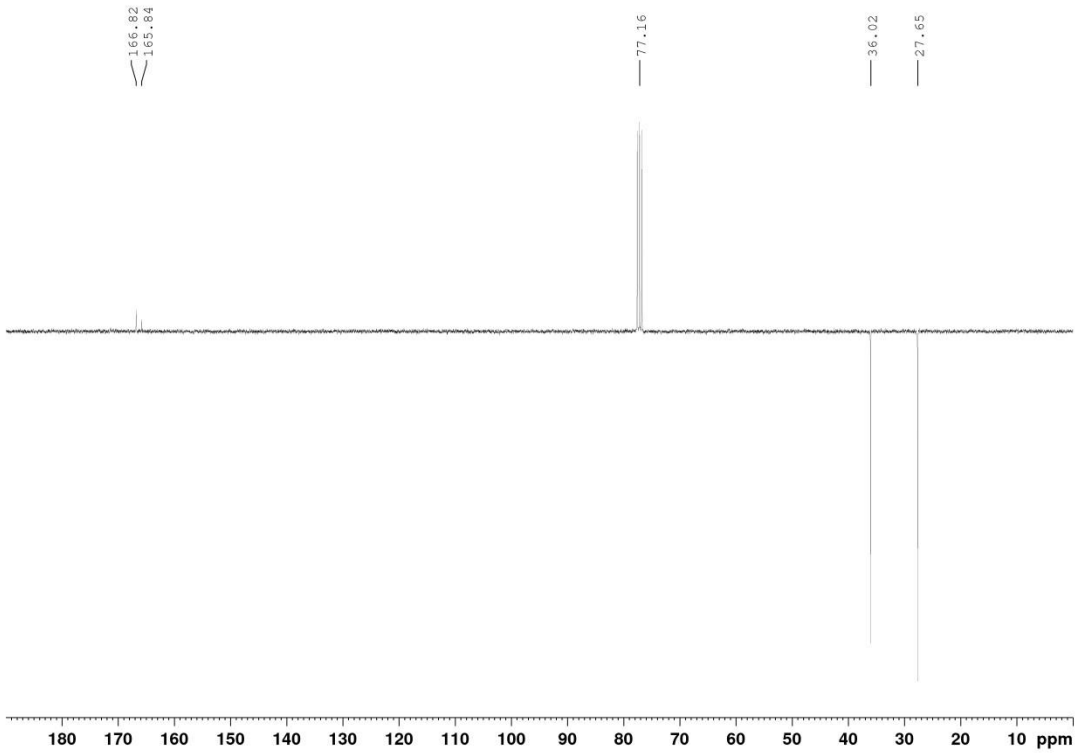

Figure S20. ^{13}C-NMR of compound **7** in $CDCl_3$

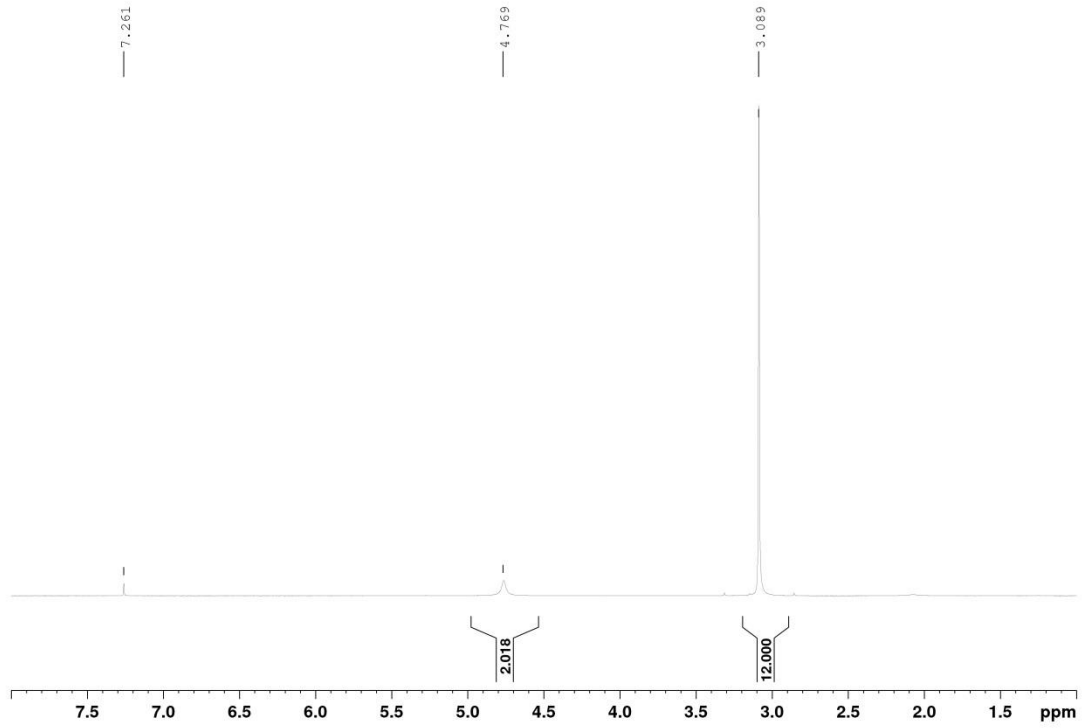

Figure S21. ^{1}H-NMR of compound **8** in $CDCl_3$

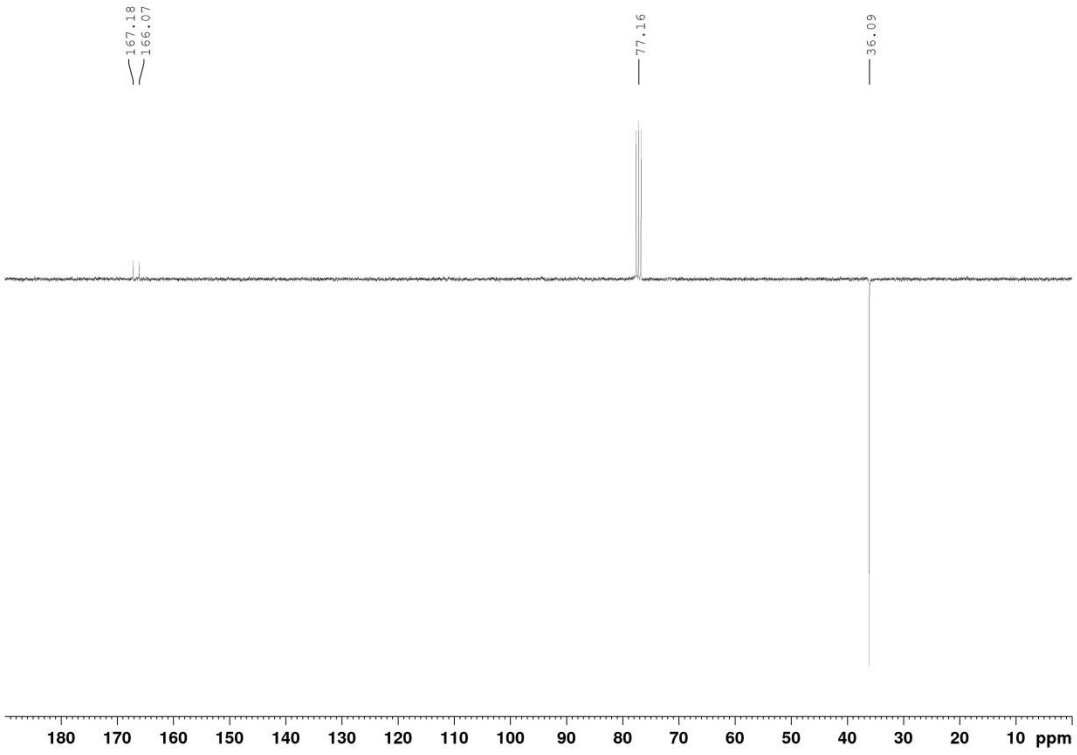

Figure S22. ^{13}C-NMR of compound **8** in $CDCl_3$

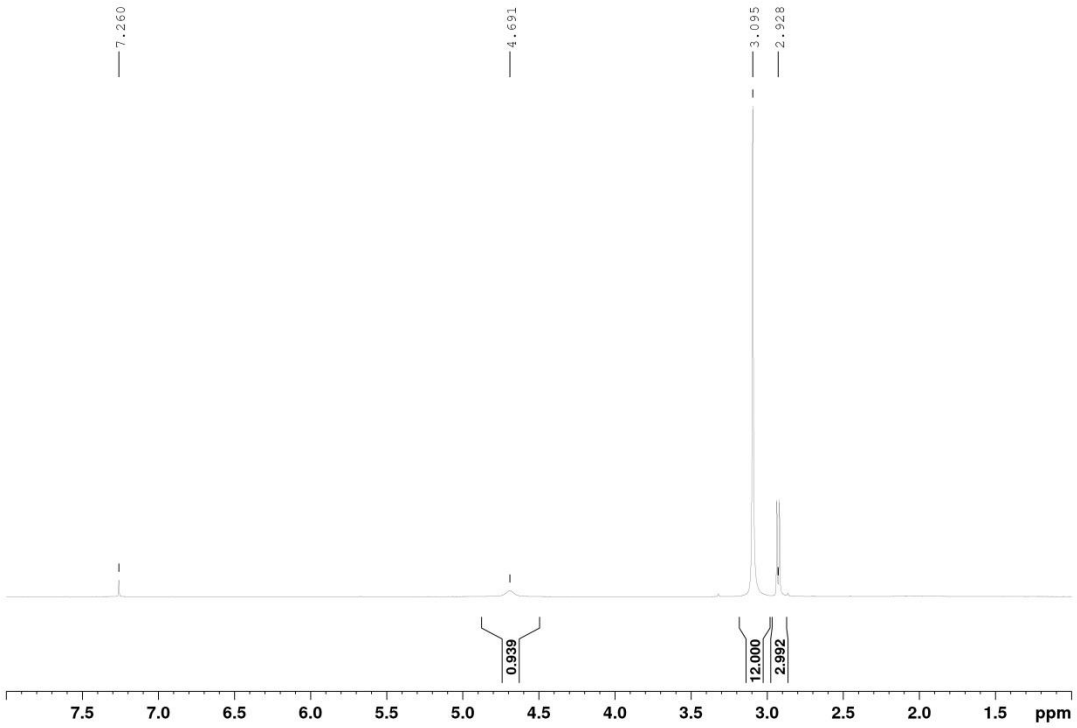

Figure S23. ^{1}H-NMR of compound **9** in $CDCl_3$

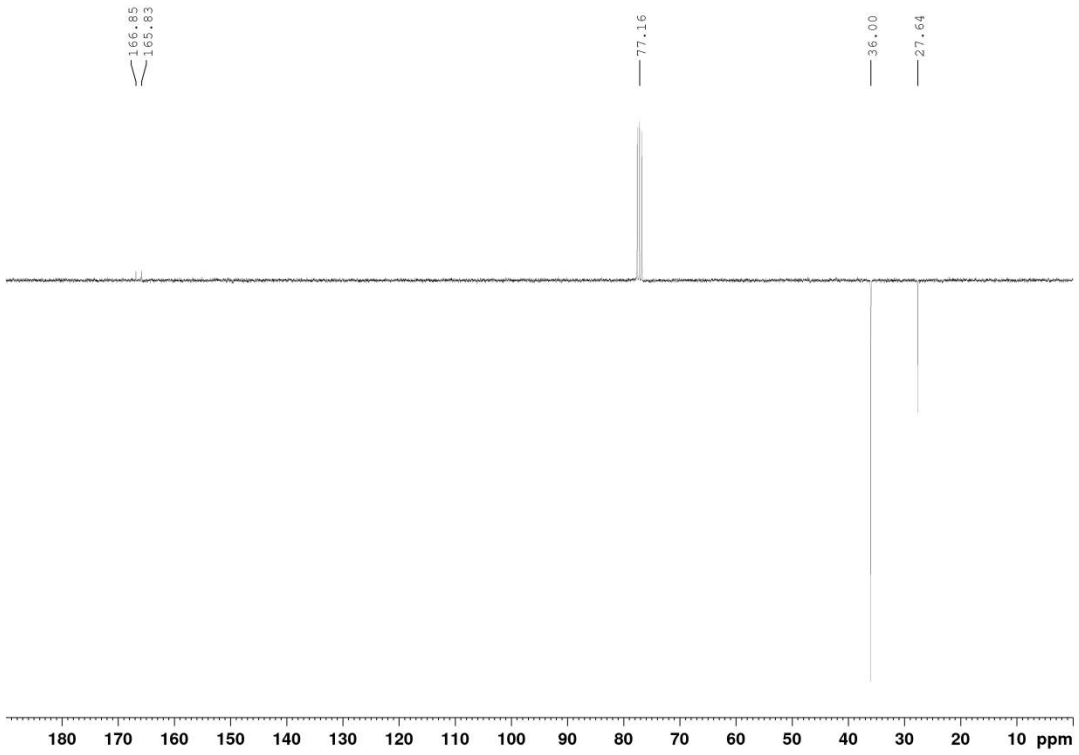

Figure S24. ^{13}C-NMR of compound **9** in $CDCl_3$

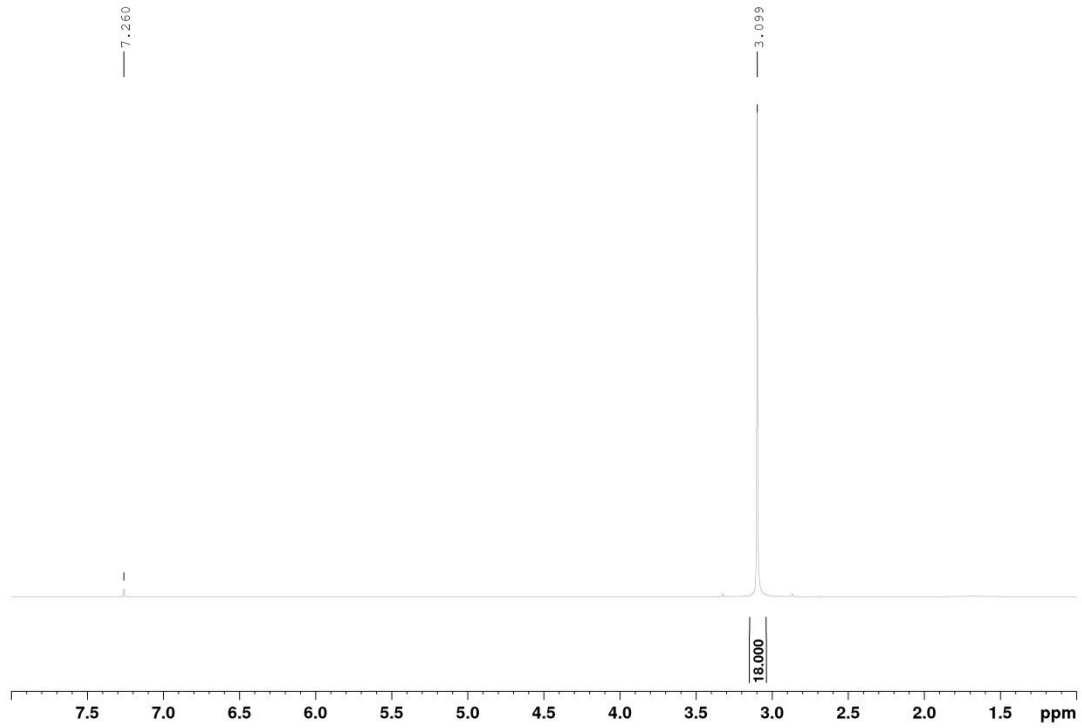

Figure S25. ^{1}H-NMR of compound **10** in $CDCl_3$

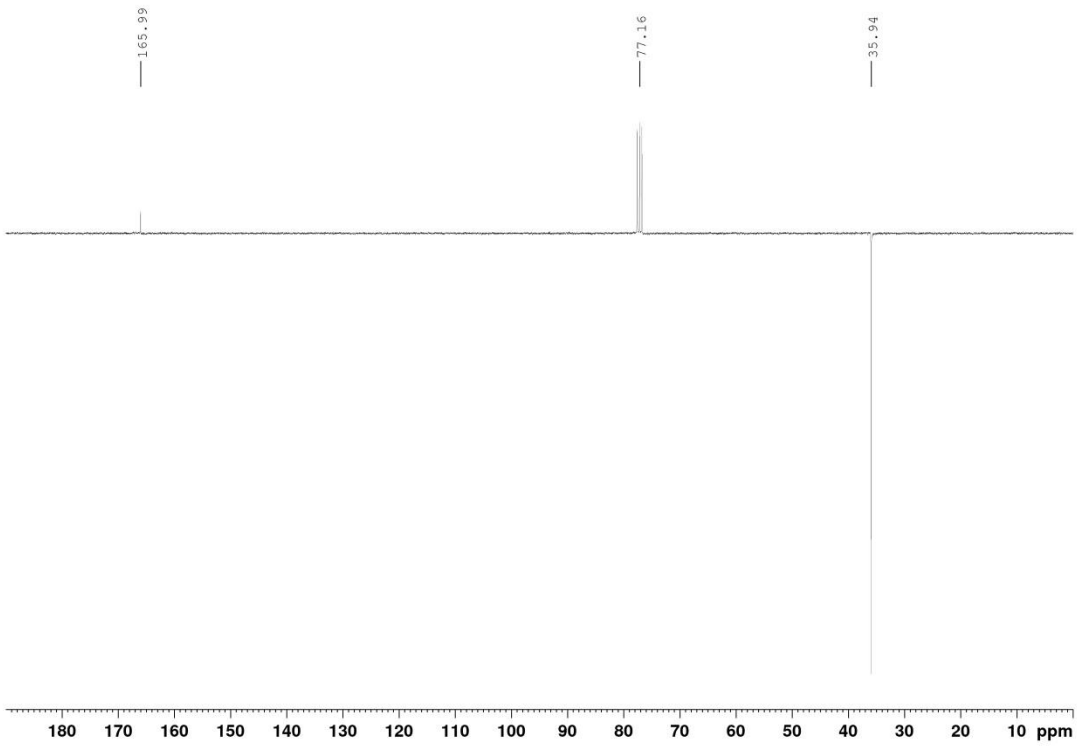

Figure S26. ^{13}C-NMR of compound **10** in $CDCl_3$