

Supplementary Information

Table S1. ^{13}C NMR data of prepared compounds (DMSO- d_6 , 30 °C).

Atom #	2		3		4		5		6		7		8	
	δ_{C}	m [#]	δ_{C}	m [#]	δ_{C}	m [#]	δ_{C}	m [#]	δ_{C}	m [#]	δ_{C}	m [#]	δ_{C}	m [#]
2	83.12	d	79.81	d	79.52	d	79.52	d	79.64	d	79.86	d	79.59	d
3	71.73	d	72.82	d	72.78	d	71.99	d	72.00	d	72.82	d	72.78	d
4	197.53	s	185.69	s	184.44	s	190.83	s	191.32	s	185.71	s	184.50	s
4a	100.34	s	110.46	s	105.19	s	100.32	s	100.64	s	110.46	s	105.28	s
5	163.36	s	150.81	s	151.92	s	163.30	s	163.28	s	150.81	s	151.92	s
6	96.17	d	111.51	d	105.84	d	96.79	d	96.60	d	111.50	d	105.80	d
7	167.28	s	156.27	s	165.06	–	168.2 *	–	167.40	s	156.27	s	164.91	s
8	95.15	d	109.25	d	101.04	d	95.76	d	95.53	d	109.25	d	101.04	d
8a	162.53	s	162.25	s	163.12	s	162.19	s	162.29	s	162.27	s	163.13	s
10	87.49	d	87.68	d	87.64	d	87.69	d	88.47	d	88.46	d	88.42	d
11	49.56	d	49.72	d	49.76	d	49.74	d	49.47	d	49.43	d	49.48	d
11a	127.76	s	129.29	s	129.18	s	129.22	s	129.66	s	129.71	s	129.61	s
12	115.10	d	122.21	d	122.03	d	122.03	d	121.91	d	122.07	d	121.90	d
13	130.47	s	128.72	s	129.12	s	129.11	s	128.66	s	128.37	s	128.76	s
14	116.24	d	123.07	d	122.95	d	122.89	d	122.84	d	123.00	d	122.88	d
15	140.93	s	133.10	s	133.06	s	133.09	s	133.08	s	133.07	s	133.04	s
15a	147.06	s	151.15	s	151.01	s	151.02	s	151.12	s	151.21	s	151.09	s
16	131.46	s	139.37	s	139.43	s	139.42	s	131.06	s	131.01	s	131.07	s
17	110.62	d	110.31	d	110.29	d	110.31	d	110.27	d	110.27	d	110.25	d
18	147.65	s	150.97	s	150.97	s	150.97	s	147.70	s	147.69	s	147.69	s
19	146.69	s	139.18	s	139.17	s	139.18	s	146.82	s	146.82	s	146.80	s
20	115.37	d	123.07	d	123.07	d	123.08	d	115.45	d	115.43	d	115.44	d
21	119.08	d	117.83	d	117.79	d	117.82	d	118.74	d	118.75	d	118.71	d
22	65.11	t	64.87	t	64.90	t	64.90	t	64.77	t	64.74	t	64.76	t
18-OMe	55.72	q	55.81	q	55.81	q	55.82	q	55.64	q	55.63	q	55.63	q
3-CO	–	–	168.54	s	168.62	s	168.74	s	168.73	s	168.55	s	168.63	s

Table S1. *Cont.*

Atom #	2		3		4		5		6		7		8	
	δ_C	m [#]	δ_C	m [#]	δ_C	m [#]	δ_C	m [#]	δ_C	m [#]	δ_C	m [#]	δ_C	m [#]
5-CO	–	–	168.53	s	168.55	–	–	–	–	–	168.53	s	168.55	S
7-CO	–	–	168.21	s	–	–	–	–	–	–	168.21	s	–	–
15-CO	–	–	168.26	s	168.26	s	168.28	s	168.24	s	168.21	s	168.22	s
19-CO	–	–	168.53	s	168.52	s	168.54	s	–	–	–	–	–	–
22-CO	170.39	s	170.31	s	170.31	s	170.33	s	170.33	s	170.32	s	170.32	s
3-Ac	–	–	20.05	q	20.11	q	20.11	q	20.09	q	20.06	q	20.12	q
5-Ac	–	–	20.73	q	20.85	q	–	–	–	–	20.73	q	20.85	q
7-Ac	–	–	20.91	q	–	–	–	–	–	–	20.91	q	–	–
15-Ac	–	–	20.35	q	20.35	q	20.37	q	20.38	q	20.36	q	20.37	q
19-Ac	–	–	20.40	q	20.40	q	20.41	q	–	–	–	–	–	–
22-Ac	20.62	q	20.52	q	20.51	q	20.54	q	20.53	q	20.52	q	20.52	q

* HMBC (Heteronuclear Multiple Bond Correlation) readout.

Table S2. ¹H NMR data of prepared compounds (DMSO-*d*₆, 30 °C).

Atom #	2		3		4		5		6		7		8								
	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]
2	5.020	d	11.2	5.720	d	12.4	5.544	d	12.1	5.546	d	11.8	5.560	d	11.9	5.714	d	12.4	5.540	d	12.1
3	4.517	dd	6.1, 11.2	5.971	d	12.4	5.757	d	11.1	5.924	d	11.8	5.943	d	11.9	5.968	d	12.4	5.757	d	12.1
6	5.896	d	2.0	6.790	d	2.2	6.259	d	2.2	5.922	d	2.0	5.967	d	2.1	6.786	d	2.2	6.265	d	2.2
8	5.848	d	2.0	6.904	d	2.2	6.314	d	2.2	5.901	d	2.0	5.944	d	2.1	6.907	d	2.2	6.322	d	2.2
10	5.439	d	7.7	5.717	d	6.6	5.714	d	6.4	5.715	d	6.4	5.571	d	6.8	5.568	d	6.9	5.566	d	6.8
11	3.764	dddd	0.6, 5.8, 7.4, 7.7	3.844	dddd	0.9, 5.9, 6.6, 6.7	3.843	m	–	3.844	dddd	0.8, 5.7, 6.4, 6.9	3.809	dddd	0.7, 5.8, 6.7, 6.8	3.808	dddd	0.8, 6.1, 6.8, 6.9	3.801	dddd	0.8, 6.0, 6.6, 6.8
12	6.892	dd	0.6, 1.7	7.475	dd	0.9, 1.7	7.442	dd	0.6, 1.6	7.424	dd	0.8, 1.7	7.408	dd	0.7, 1.6	7.453	dd	0.8, 1.7	7.420	dd	0.8, 1.7
14	6.865	d	1.7	7.272	d	1.7	7.244	d	1.6	7.228	d	1.7	7.212	d	1.6	7.249	d	1.7	7.221	d	1.7
17	6.984	d	2.0	7.159	d	2.0	7.156	d	1.9	7.155	d	2.0	6.949	d	1.8	6.950	d	1.9	6.947	d	1.8
20	6.780	d	8.1	7.105	d	8.2	7.105	d	8.2	7.105	d	8.2	6.772	d	8.0	6.770	d	8.0	6.770	d	8.1
21	6.823	dd	2.0, 8.1	6.970	dd	2.0, 8.2	6.967	dd	1.9, 8.2	6.967	dd	2.0, 8.2	6.793	dd	1.8, 8.0	6.794	dd	2.0, 8.0	6.790	dd	1.8, 8.1
22 α	4.375	dd	5.8, 11.0	4.371	dd	5.9, 11.0	4.380	dd	5.6, 11.2	4.377	dd	5.7, 11.1	4.337	dd	5.8, 11.0	4.327	dd	6.1, 11.2	4.327	dd	6.0, 11.1
22 β	4.249	dd	7.4, 11.0	4.344	dd	6.7, 11.0	4.347	dd	7.0, 11.2	4.345	dd	6.9, 11.1	4.311	dd	6.7, 11.0	4.304	dd	6.8, 11.2	4.305	dd	6.6, 11.1
3-OH	5.744	d	6.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
5-OH	11.898	s	–	–	–	–	–	–	–	11.451	s	–	11.426	s	–	–	–	–	–	–	–
7-OH	10.859	br.s.	–	–	–	–	11.119	br.s.	–	n.d.	–	–	11.021	br.s.	–	–	–	–	11.129	br.s.	–
15-OH	9.412	s	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
18-OMe	3.769	s	–	3.768	s	–	3.769	s	–	3.768	s	–	3.752	s	–	3.750	s	–	3.751	s	–

Table S2. *Cont.*

Atom #	2			3			4			5			6			7			8			
	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m ^{##}	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	δ_{H}	m [#]	$J_{\text{H-H}}$ [Hz]	
19-OH	9.047	s	–	–	–	–	–	–	–	–	–	–	9.064	s	–	9.064	s	–	9.061	s	–	–
3-Ac	–	–	–	1.942	s	–	1.927	s	–	1.954	s	–	1.963	s	–	1.948	s	–	1.933	s	–	–
5-Ac	–	–	–	2.300	s	–	2.260	s	–	–	–	–	–	–	–	2.300	s	–	2.261	s	–	–
7-Ac	–	–	–	2.281	s	–	–	–	–	–	–	–	–	–	–	2.282	s	–	–	–	–	–
15-Ac	–	–	–	2.293	s	–	2.292	s	–	2.292	s	–	2.272	s	–	2.272	s	–	2.270	s	–	–
19-Ac	–	–	–	2.252	s	–	2.252	s	–	2.251	s	–	–	–	–	–	–	–	–	–	–	–
22-AC	1.974	s	–	1.993	s	–	1.992	s	–	1.996	s	–	1.983	s	–	1.978	s	–	1.978	s	–	–

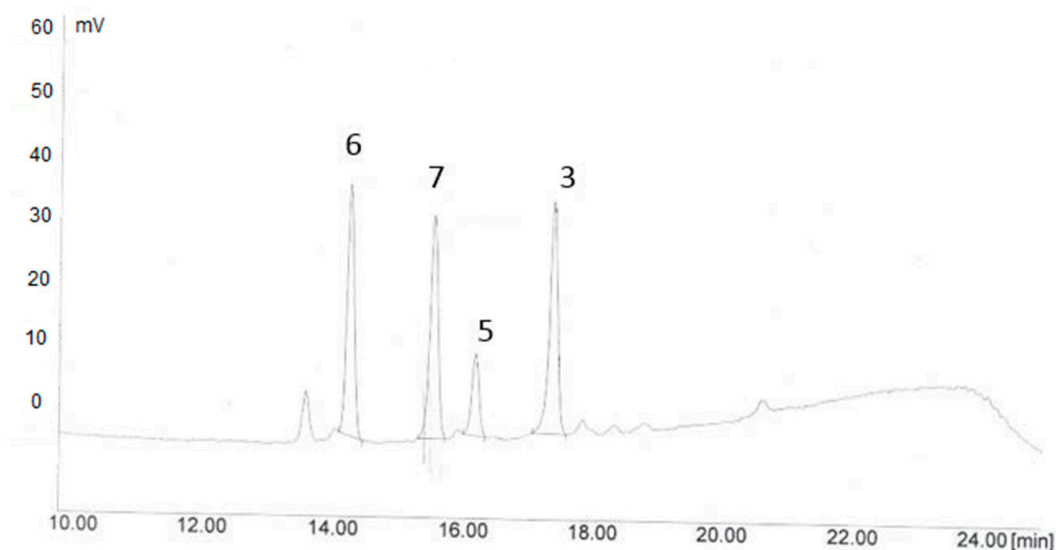


Figure S1. HPLC chromatogram of compounds **3**, **5**, **6**, **7**. Method: Jasco 880-PU (Jasco Europe, Cremella, Italy) pump equipped with a Jasco 875-UV/V detector; RP-18e (5 μ m) column (Purosphere STAR, 100 mm \times 3 mm, Merck, Germany); solvent system A: MeCN/H₂O/HCO₂H (5/95/0.1 v/v/v) and B: MeCN/HCO₂H (100/0.1 v/v). Gradient 0–1 min 30% B, 1–20 min 30%–80% B, 20–22 min 80% B, 22–24 min 30% B. Flow rate was 1.1 mL/min. The data were acquired at 285 nm. (Method B).

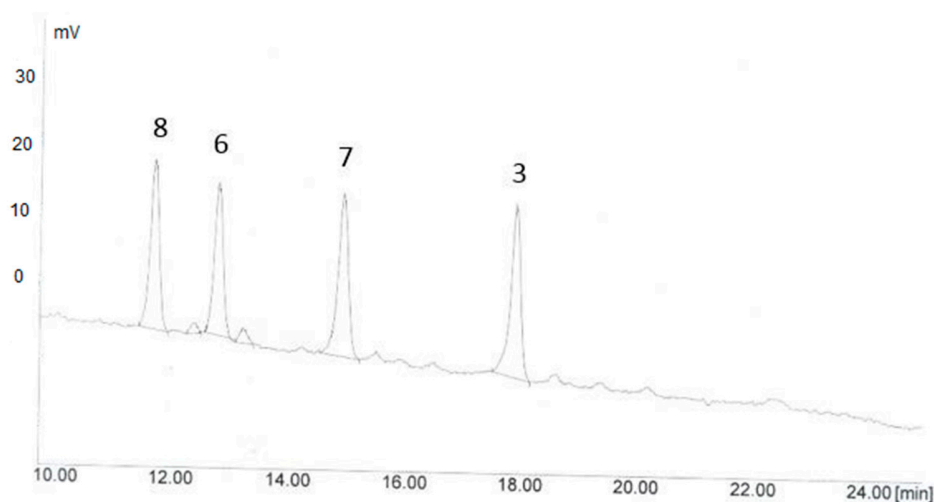


Figure S2. HPLC chromatogram of compounds **3**, **6**, **7**, **8**. Method: Jasco 880-PU (Jasco Europe, Cremella, Italy) pump equipped with a Jasco 875-UV/V detector; RP-18e (5 μ m) column (Purosphere STAR, 100 mm \times 3 mm, Merck, Germany); solvent system A: MeCN/H₂O/HCO₂H (5/95/0.1, v/v/v) and B: MeCN/HCO₂H (100/0.1, v/v). Gradient 0–1 min 40% B, 1–20 min 40%–70% B, 20–22 min 70% B, 22–24 min 40% B. Flow rate was 1.1 mL/min. The data were acquired at 285 nm. (Method B).

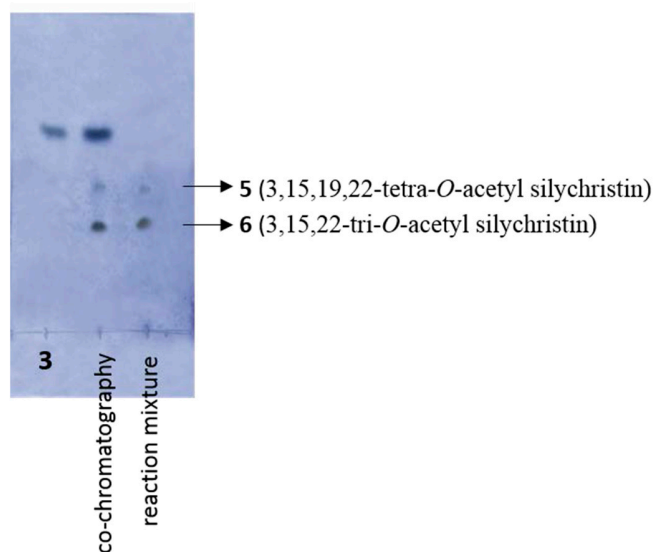


Figure S3. TLC (Thin layer chromatography) of the reaction mixture catalyzed by lipase PS after 100 h. Compound **3** (3,5,7,15,19,22-hexa-*O*-acetyl silychristin) was a starting material for the alcoholysis catalyzed by lipase PS. Co-chromatography was performed with **3** and reaction mixture. CHCl_3 /toluene/acetone/ HCO_2H , 12/2/2/0.1 was used as mobile phase. TLC plate was developed with Pancaldi reagent ($(\text{NH}_4)_6\text{MoO}_4$ 42 g, $\text{Ce}(\text{SO}_4)_2$ 2 g, H_2SO_4 62 mL, H_2O 1 L).

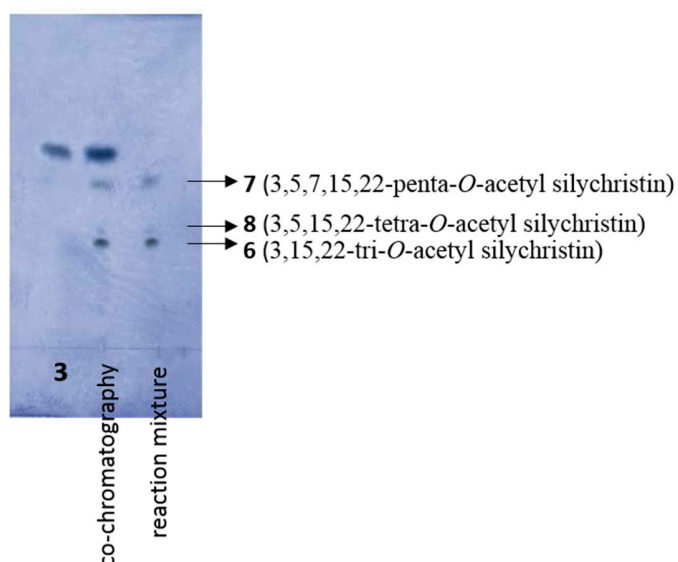


Figure S4. TLC of the reaction mixture catalyzed by Novozym 435 after 52 h. Compound **3** (3,5,7,15,19,22-hexa-*O*-acetyl silychristin) was a starting material for the alcoholysis catalyzed by Novozym 435. Co-chromatography was performed with **3** and reaction mixture. CHCl_3 /toluene/acetone/ HCO_2H 12/2/2/0.1 was used as mobile phase. TLC plate was developed with Pancaldi reagent ($(\text{NH}_4)_6\text{MoO}_4$ 42 g, $\text{Ce}(\text{SO}_4)_2$ 2 g, H_2SO_4 62 mL, H_2O 1 L).

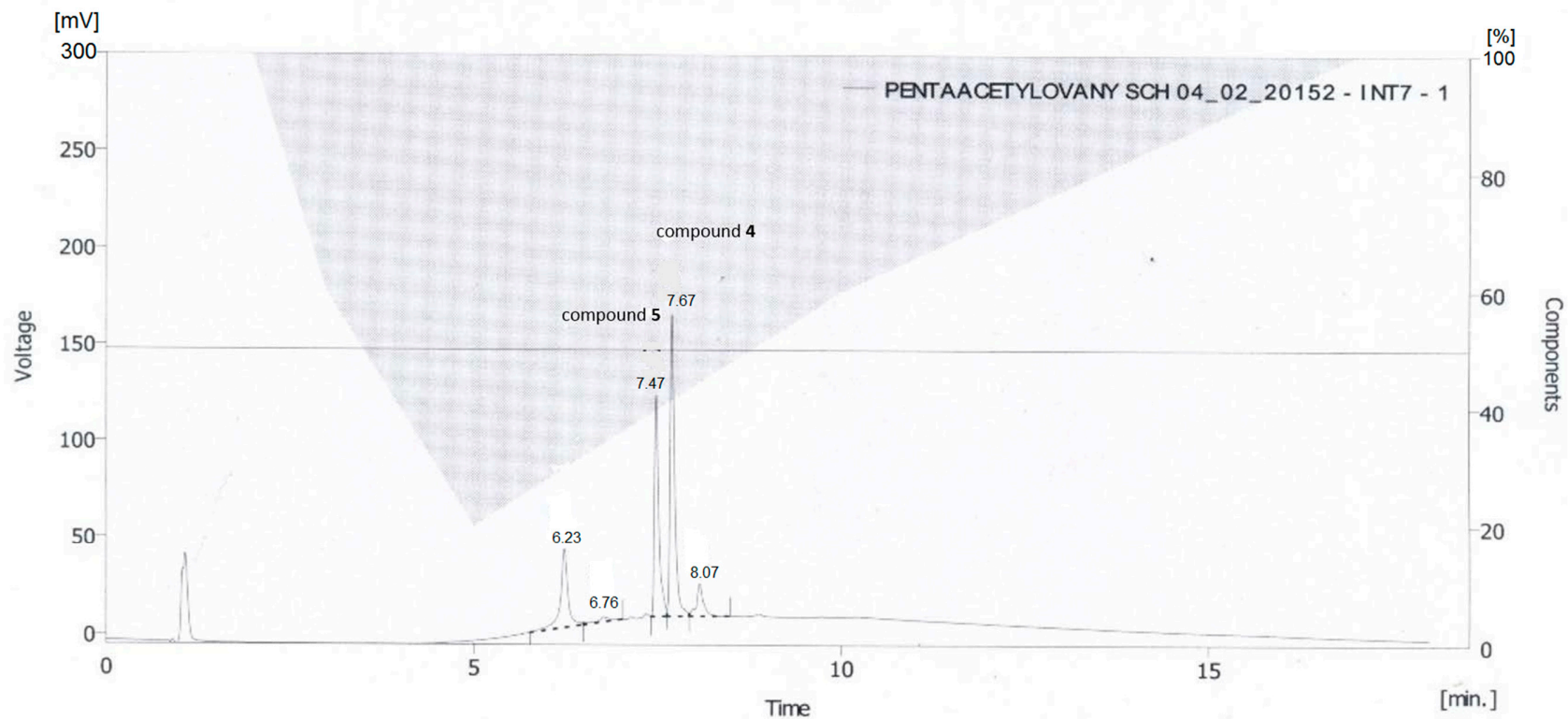


Figure S5. HPLC chromatogram of the inseparable mixture of two products 3,5,15,19,22-penta-*O*-acetyl-silychristin (**4**) and 3,15,19,22-tetra-*O*-acetyl silychristin (**5**). Twin Watrex (Prague, Czech Republic) Deltachrom SDS (030) pumps equipped with Thermo Separation Spectra 100 UV/V detector; RP-18e Chromolith[®] SpeedRod (50 mm × 4.6 mm, Merck, Darmstadt, Germany); solvent system A: MeOH/H₂O/HCO₂H (20/80/0.1, v/v/v) and B: MeOH/HCO₂H (100/0.1, v/v). Gradient: 0–2 min 100% A, 2–3 min 100%–60% A, 3–5 min 60%–20% A, 5–10 min 20%–60% A, 10–17 min 60%–100% A. (gradient depicted by the grey graph); flow rate 0.9 mL/min; signal at 285 nm was acquired. (Method C).

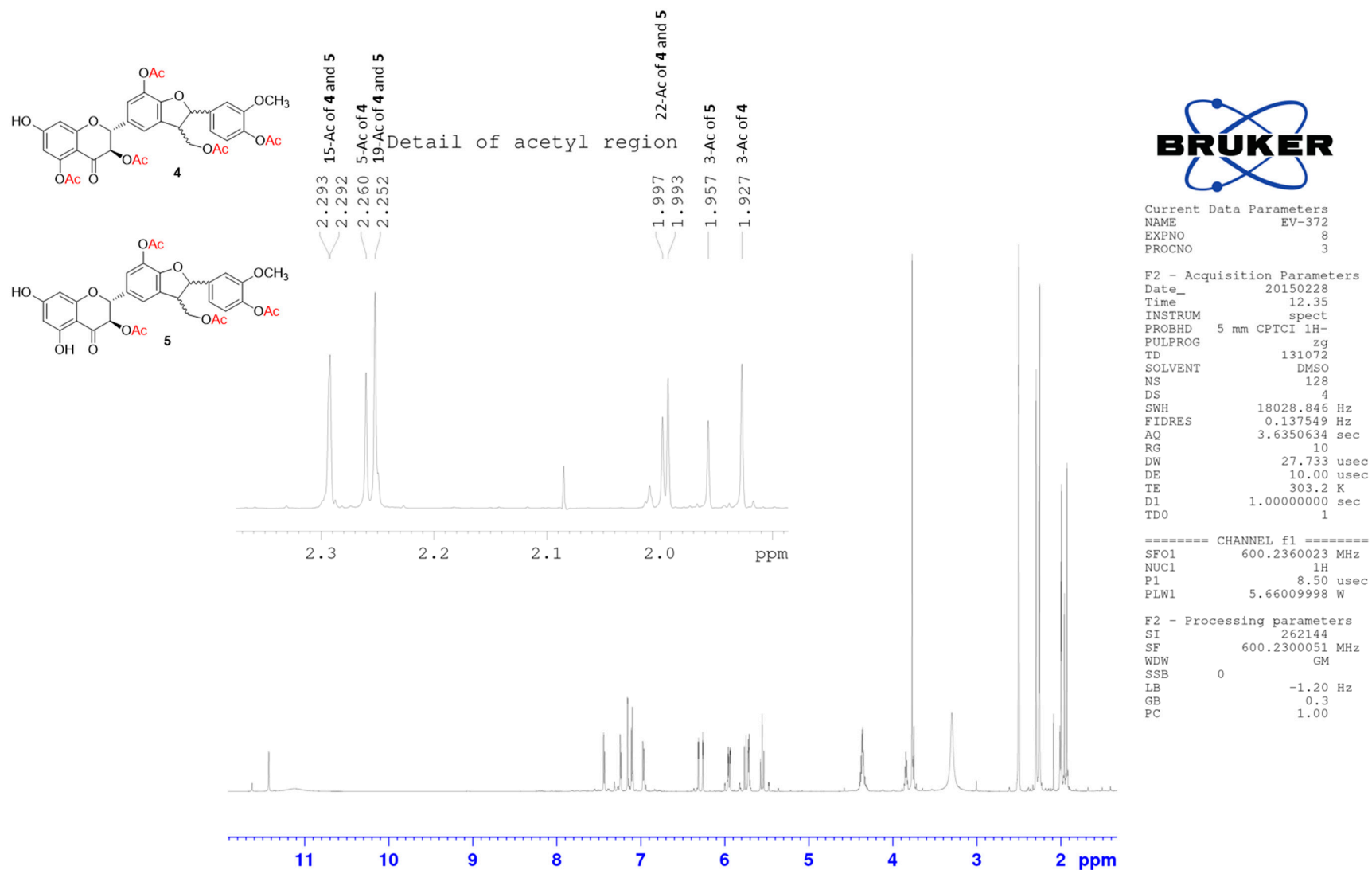


Figure S6. ^1H NMR spectrum of the mixture of compounds 4 and 5. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (600.23 MHz for ^1H 30 $^\circ\text{C}$) in $\text{DMSO-}d_6$.

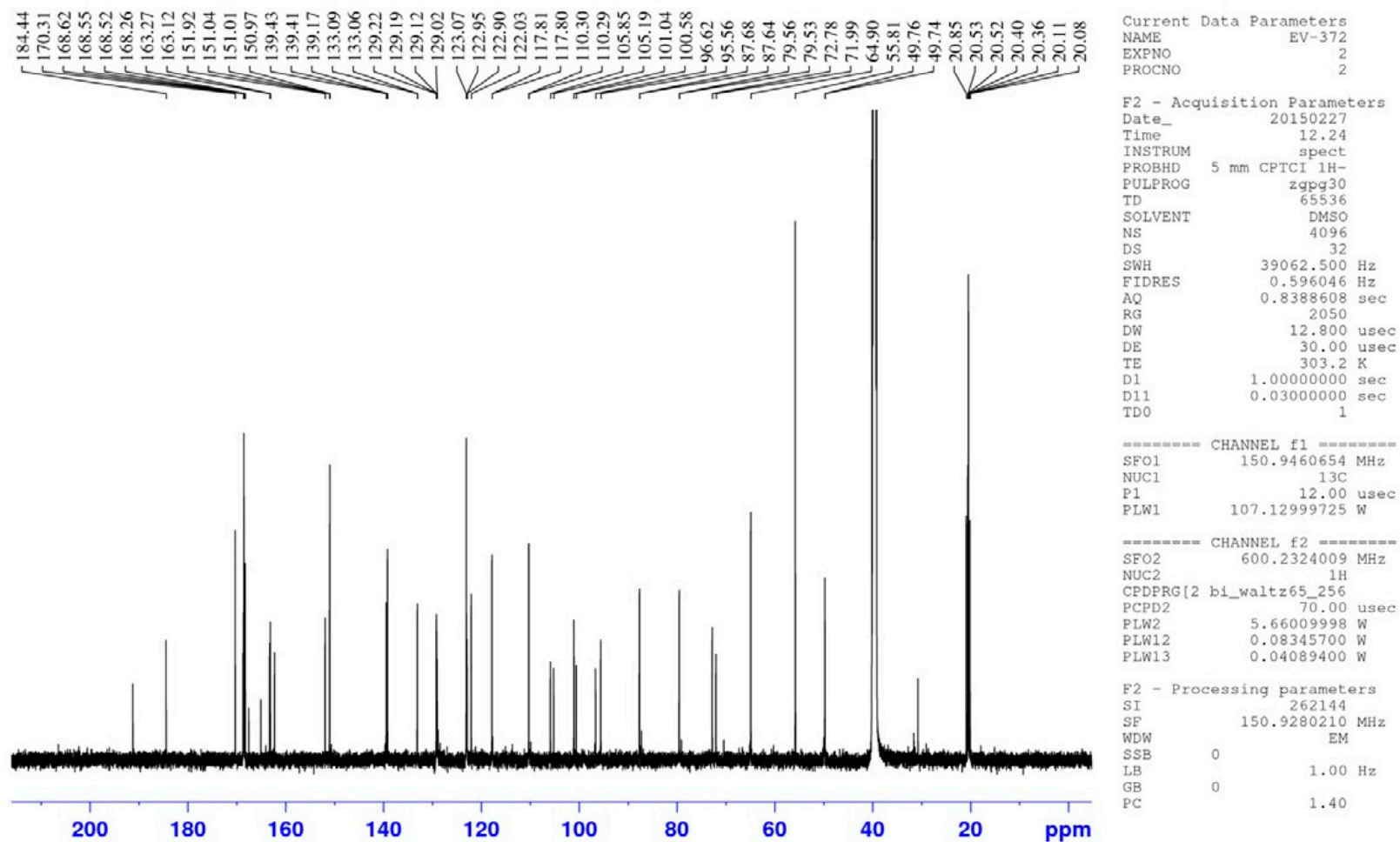


Figure S7. ^{13}C NMR spectrum of the mixture of compounds **4** and **5**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (150.93 MHz for ^{13}C at 30 °C) in DMSO- d_6 .

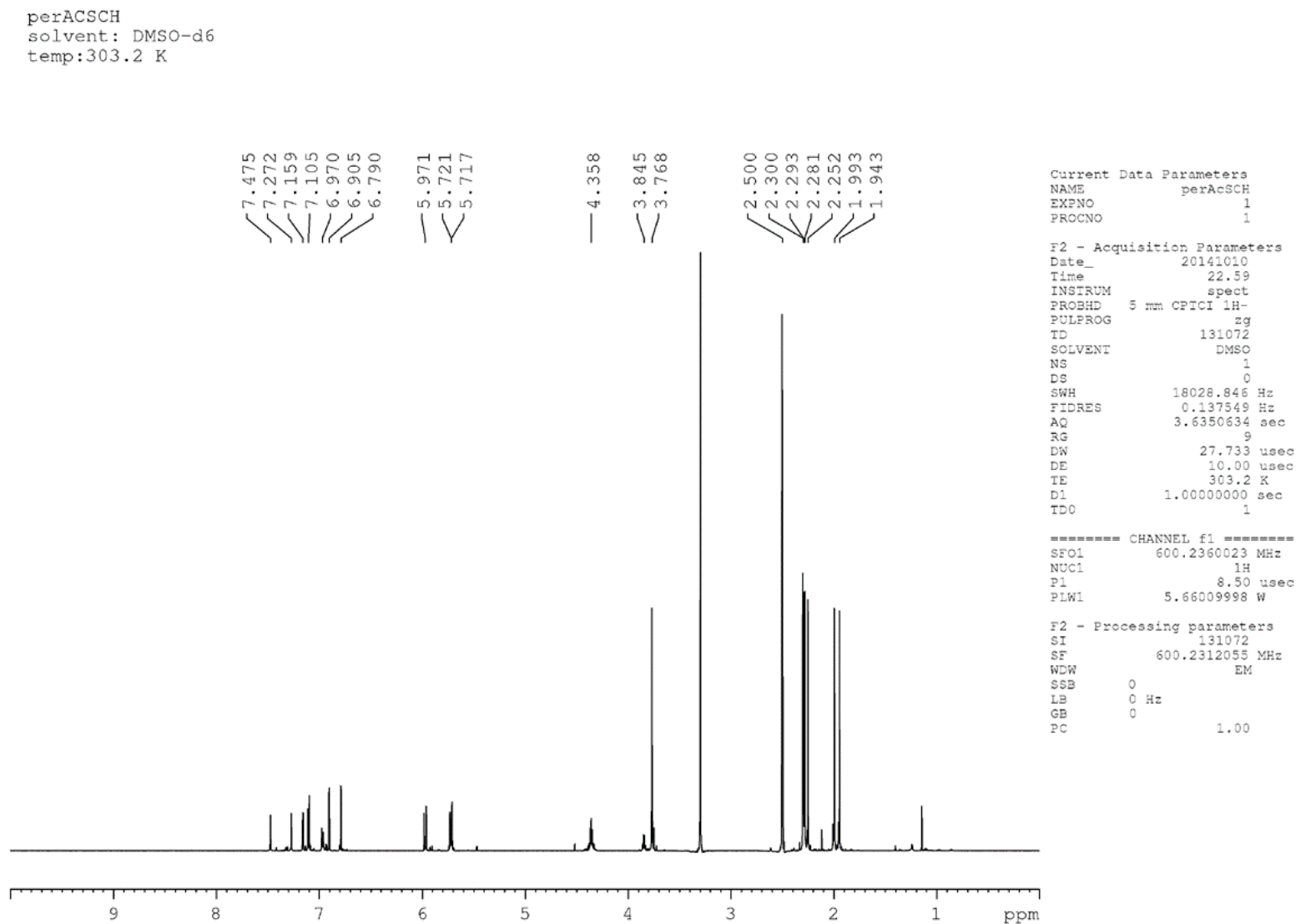


Figure S8. ^1H NMR spectrum of the compound **3**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (600.23 MHz for ^1H 30 °C) in DMSO- d_6 .

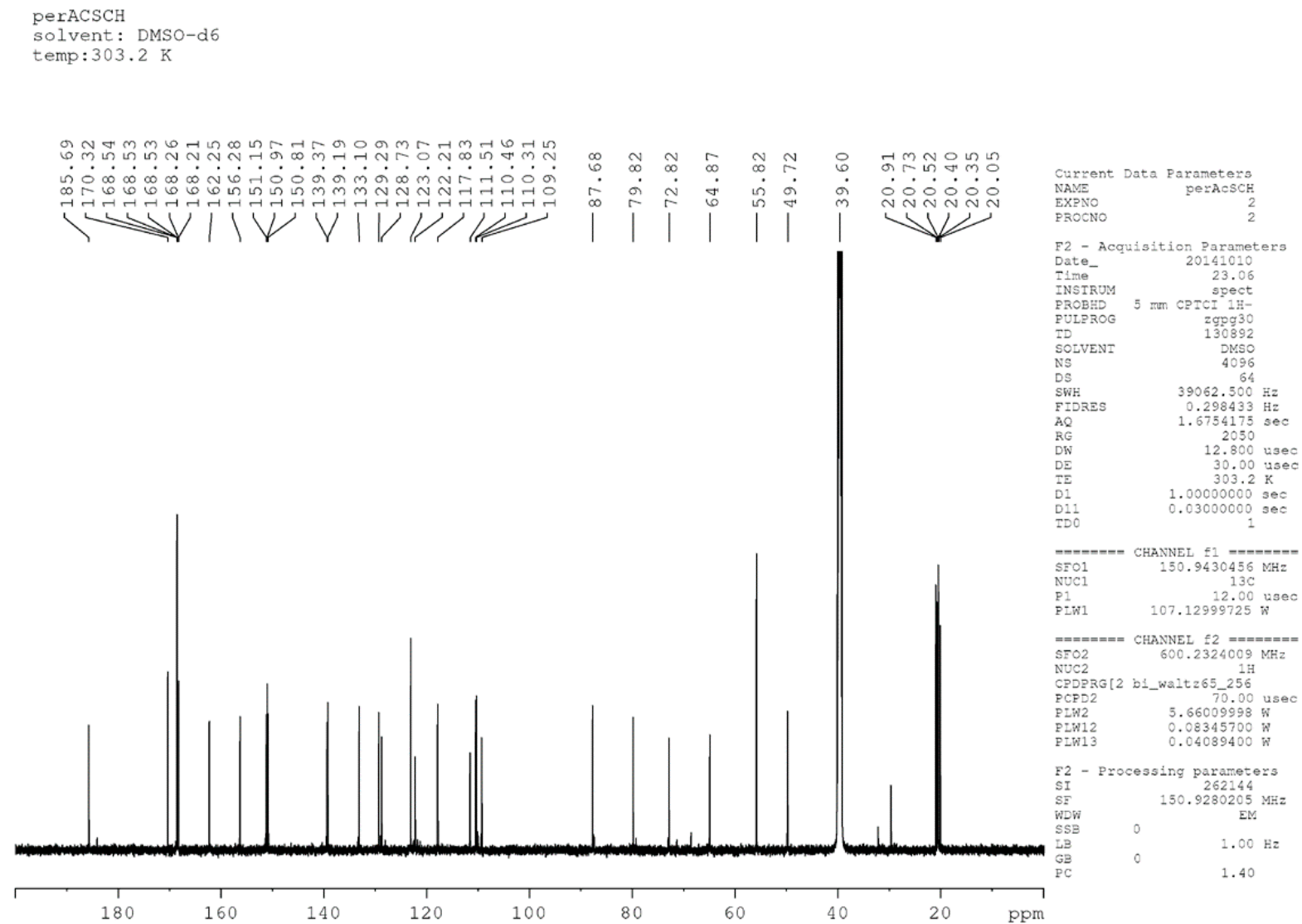


Figure S9. ^{13}C NMR spectrum of the compound **3**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (150.93 MHz for ^{13}C at 30 °C) in DMSO- d_6 .

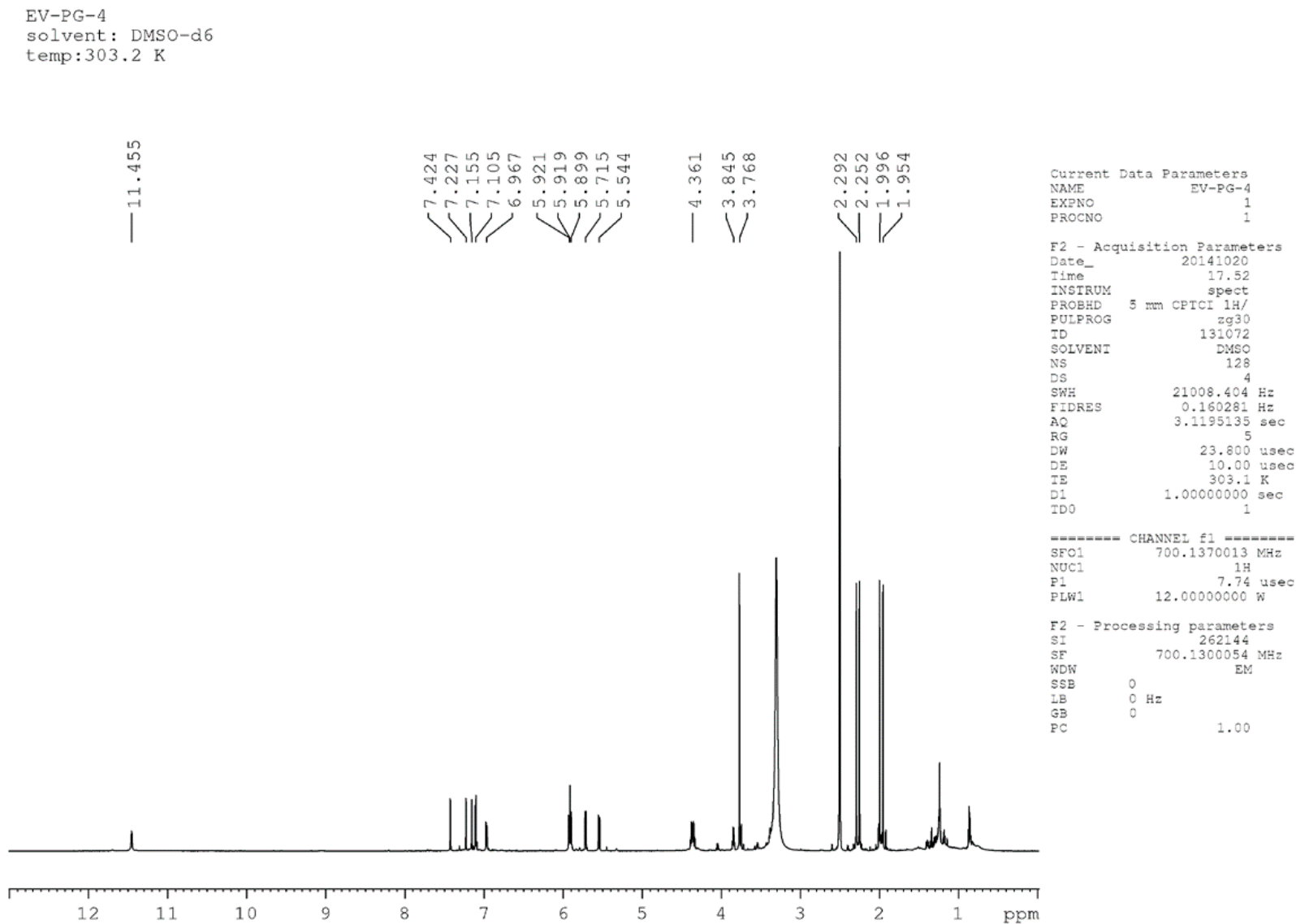


Figure S10. ^1H NMR spectrum of the compound **5**. NMR spectrum was recorded on a Bruker Avance III 700 MHz spectrometer (700.13 MHz for ^1H 30 °C) in DMSO- d_6 .

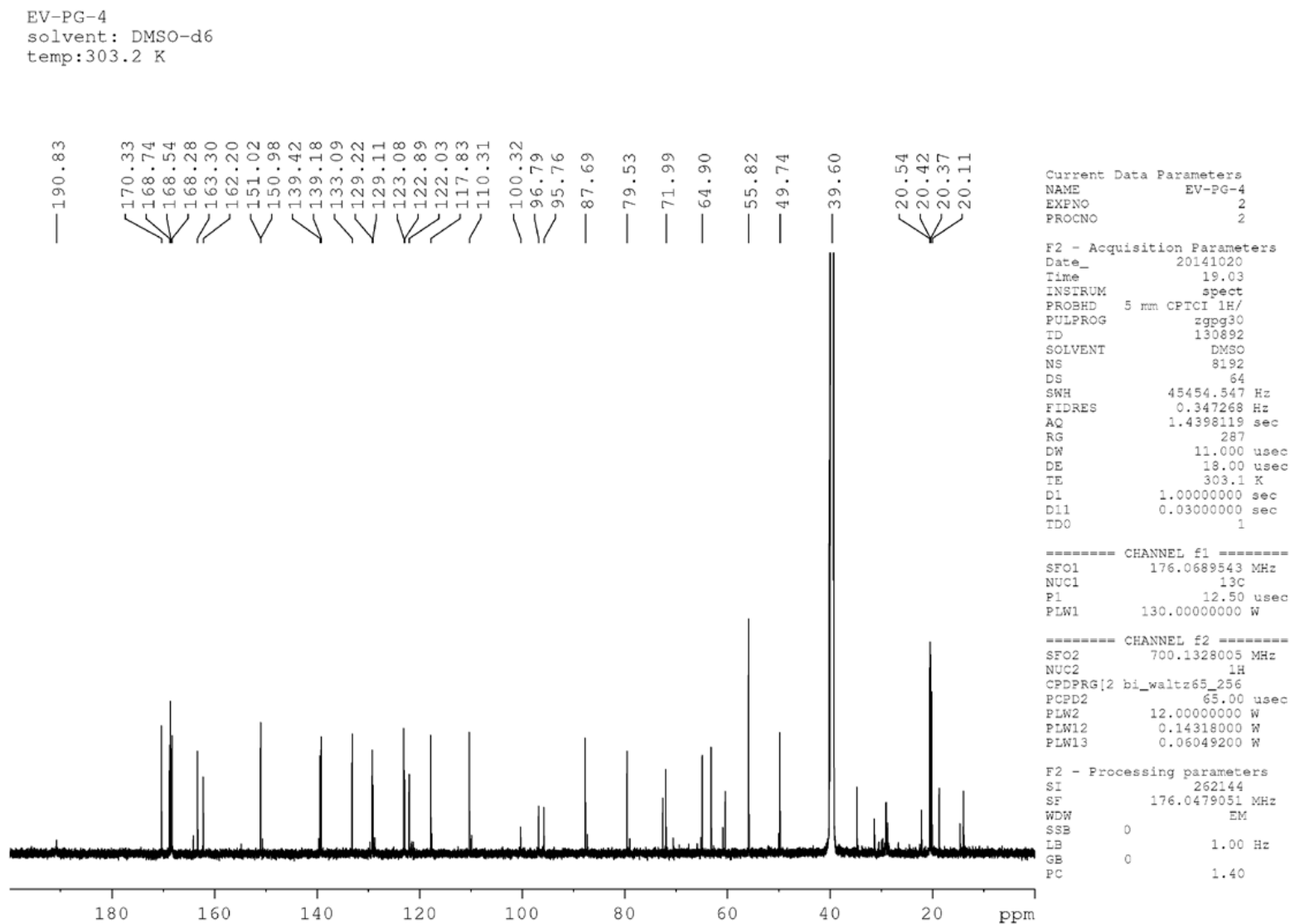


Figure S11. ^{13}C NMR spectrum of the compound **5**. NMR spectrum was recorded on a Bruker Avance III 700 MHz spectrometer (176.07 MHz for ^{13}C at 30 °C) in DMSO- d_6 .

EV-PG-3
 solvent: DMSO-d6
 temp:303.2 K

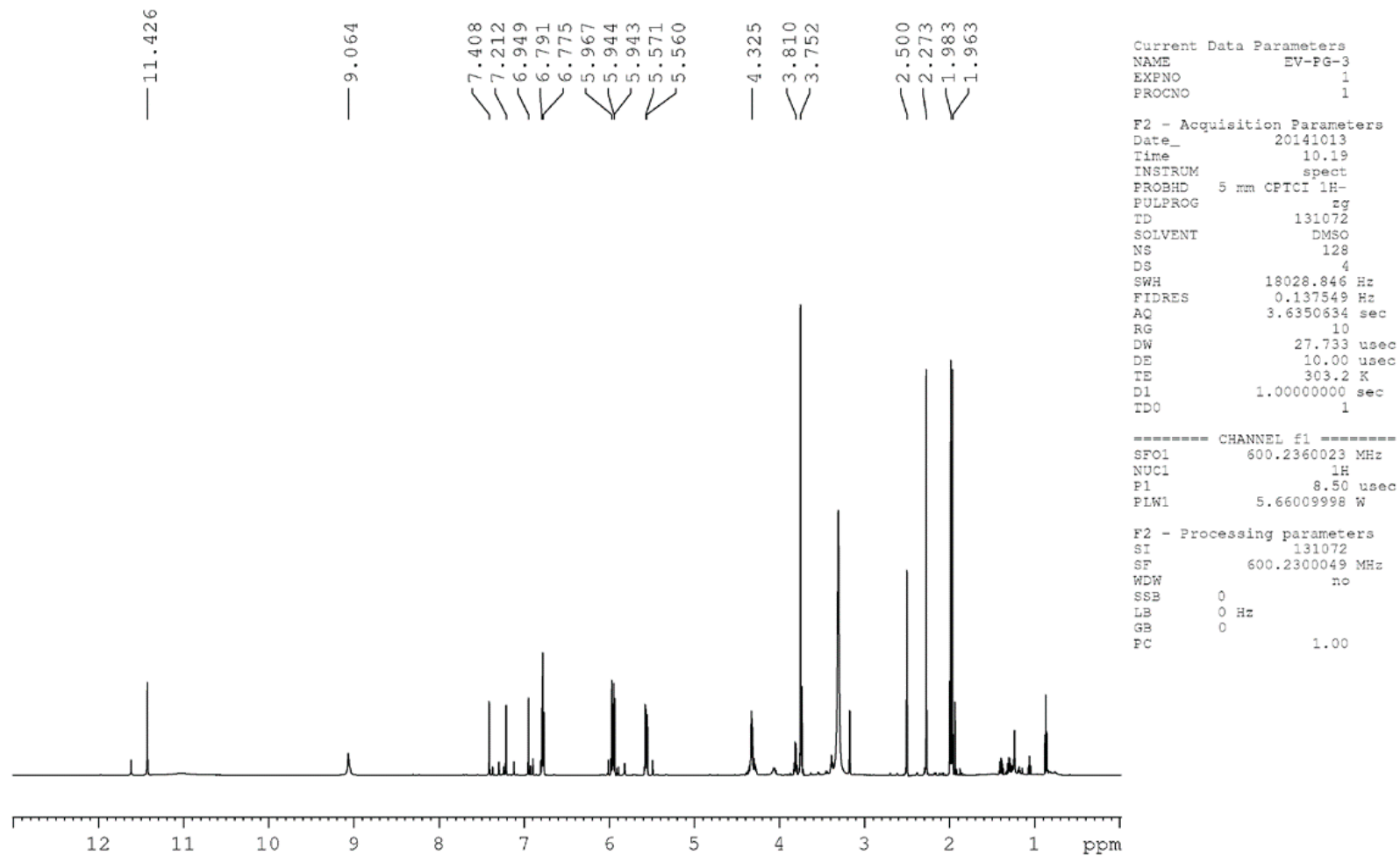


Figure S12. ^1H NMR spectrum of the compound **6**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (600.23 MHz for ^1H 30 °C) in DMSO- d_6 .

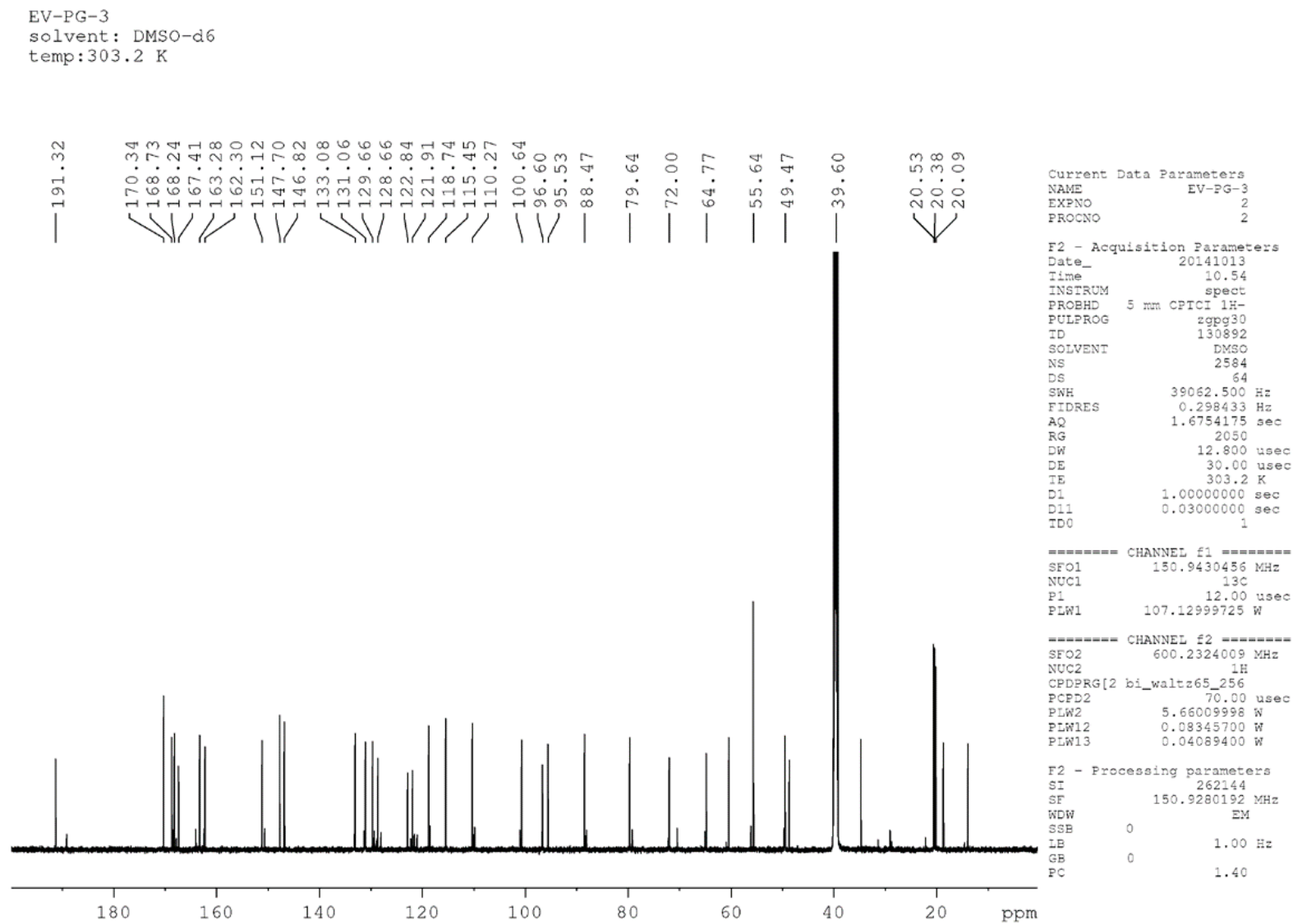


Figure S13. ^{13}C NMR spectrum of the compound **6**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (150.94 MHz for ^{13}C at 30 °C) in DMSO- d_6 .

EV-PG-1
solvent: DMSO-d6
temp:303.2 K

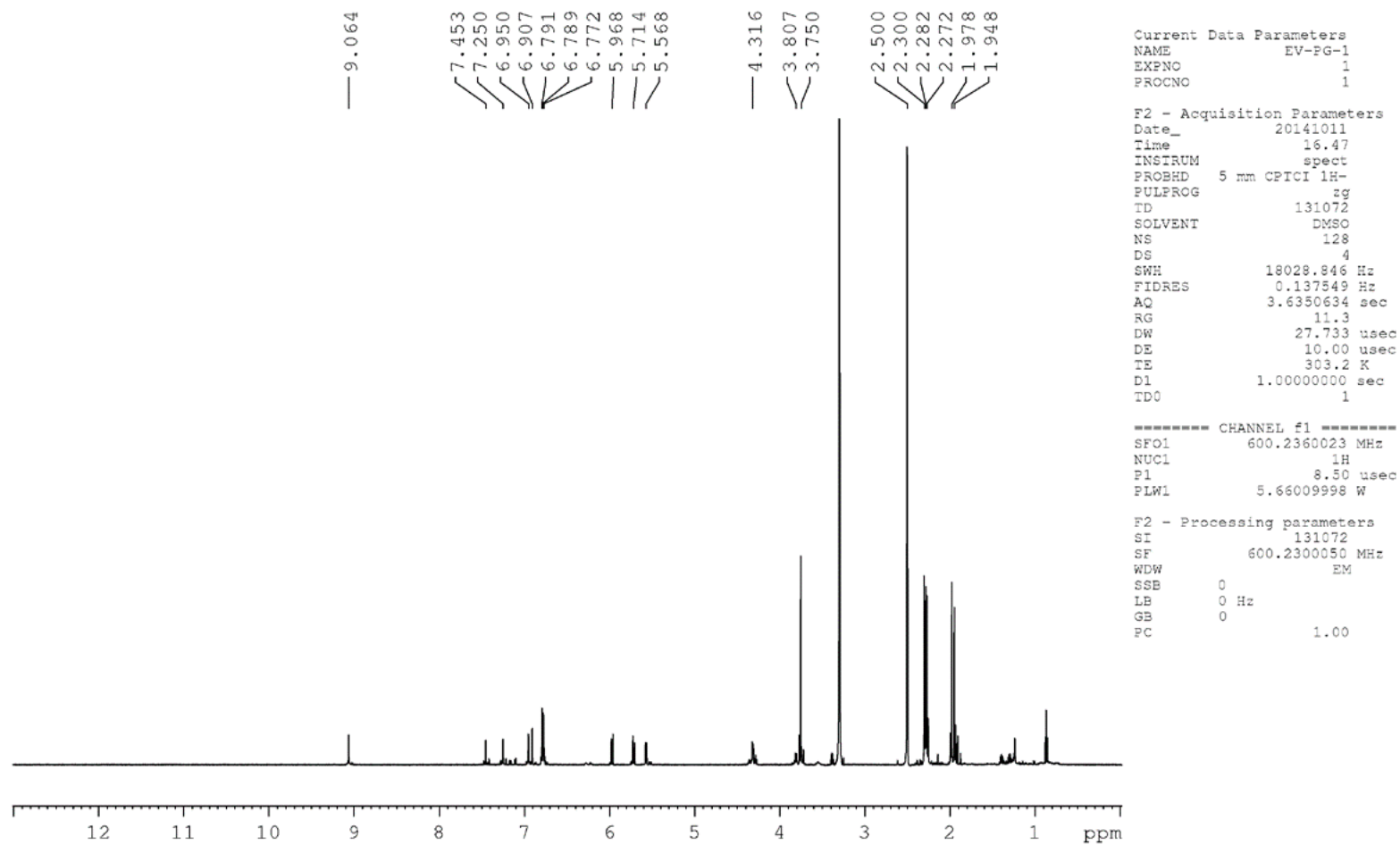


Figure S14. ^1H NMR spectrum of the compound 7. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (600.23 MHz for ^1H 30 °C) in DMSO- d_6 .

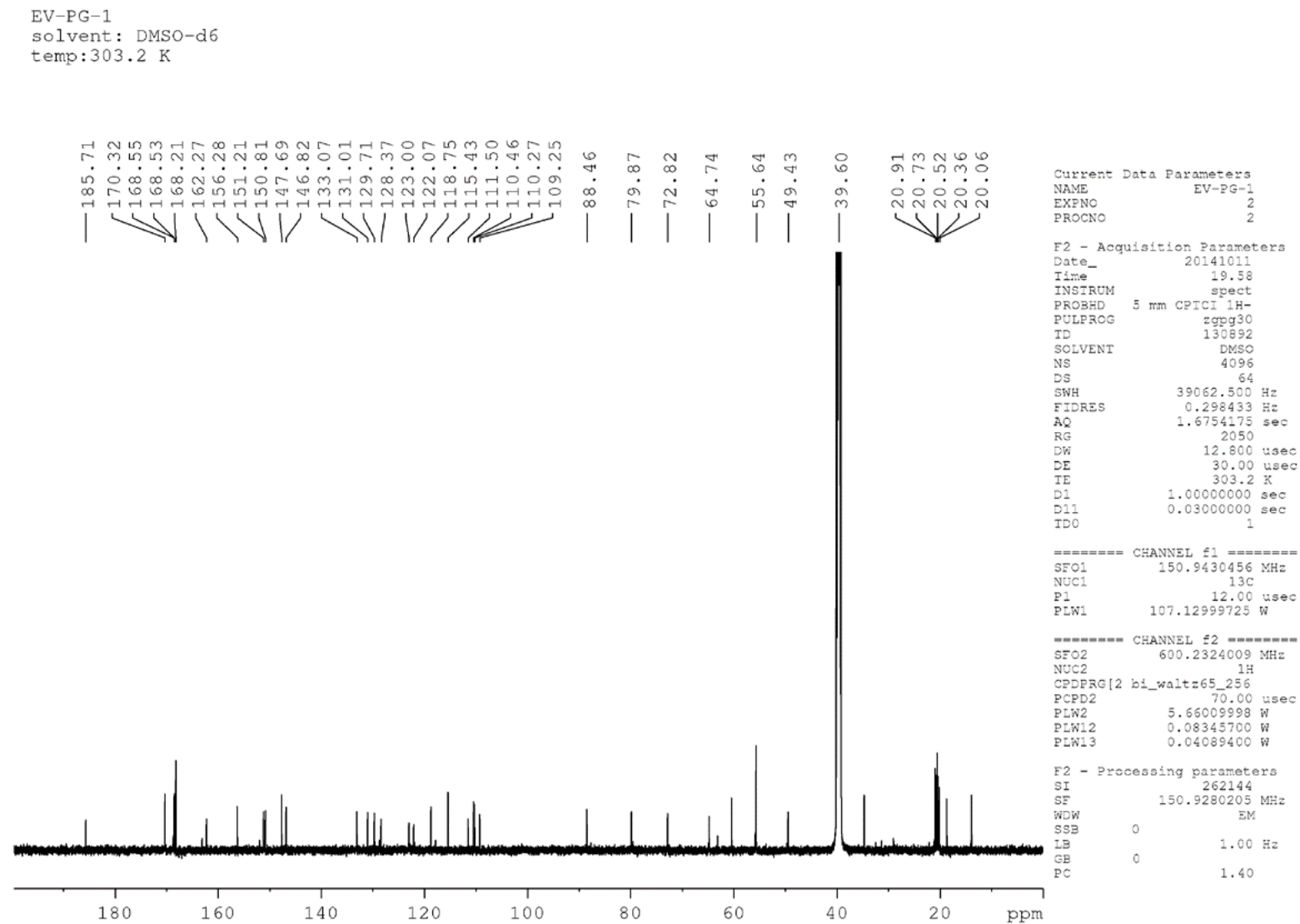


Figure S15. ^{13}C NMR spectrum of the compound **7**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (150.94 MHz for ^{13}C at 30 °C) in DMSO- d_6 .

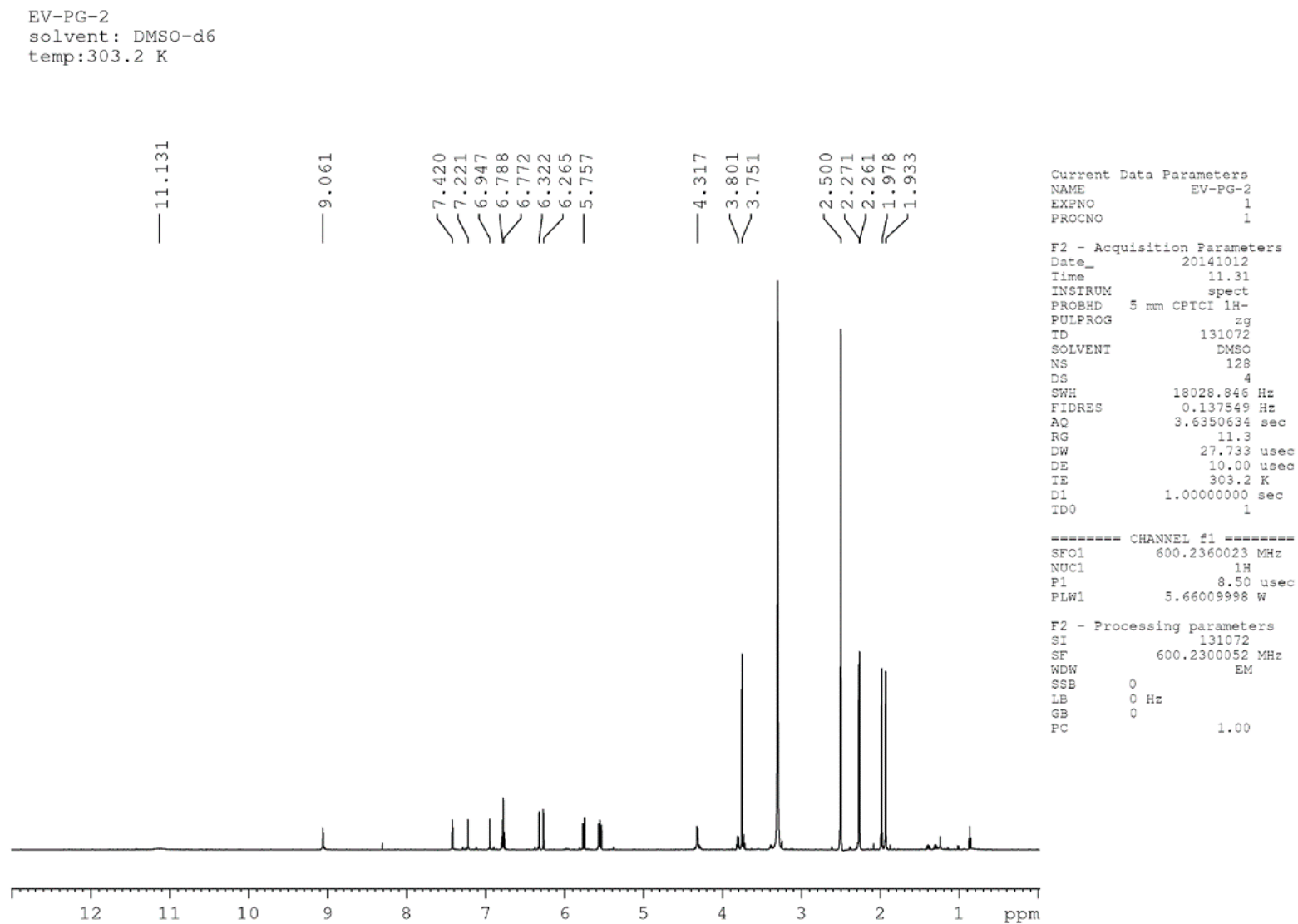


Figure S16. ^1H NMR spectrum of the compound **8**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (600.23 MHz for ^1H 30 $^\circ\text{C}$) in $\text{DMSO-}d_6$.

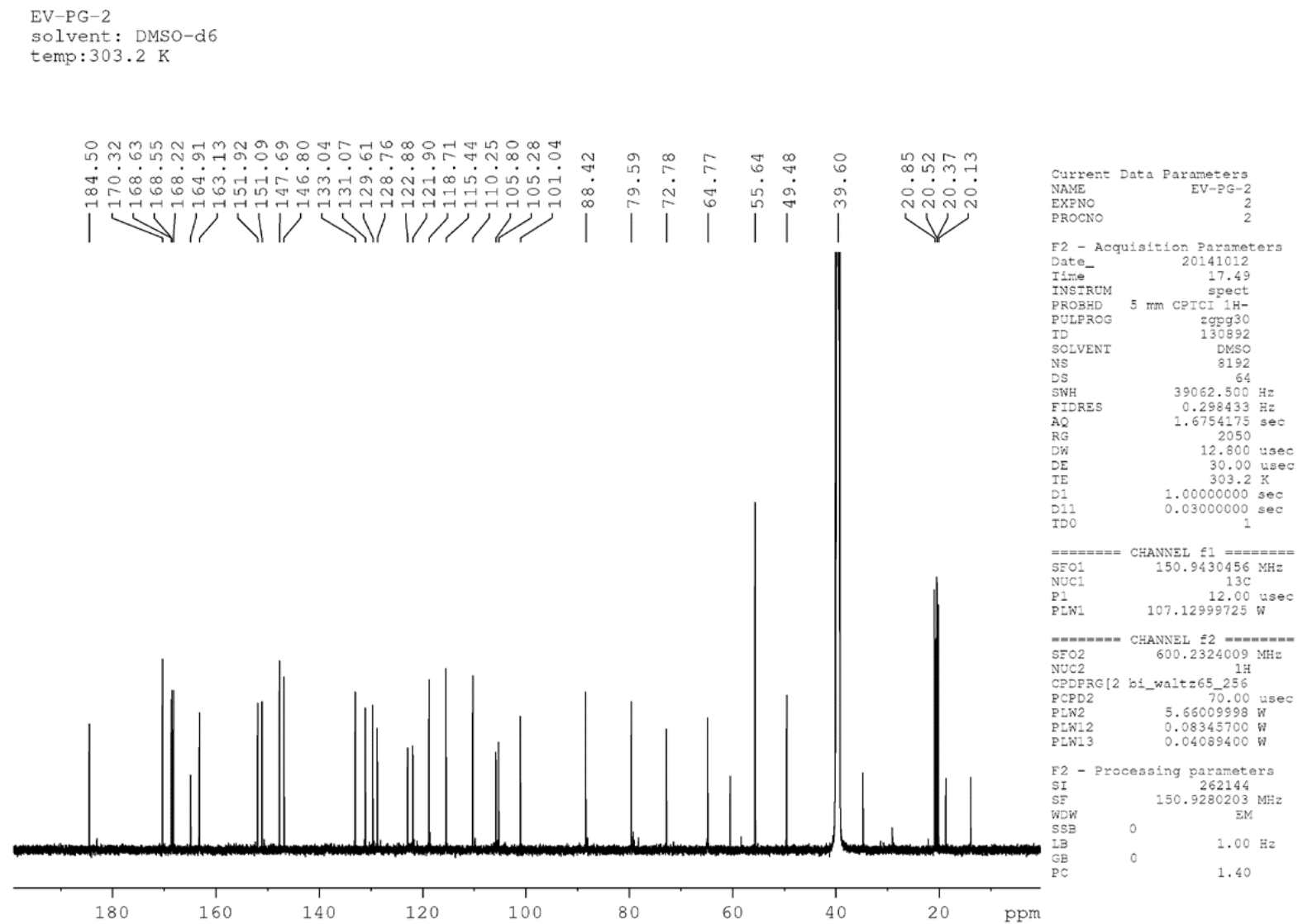


Figure S17. ^{13}C NMR spectrum of the compound **8**. NMR spectrum was recorded on a Bruker Avance III 600 MHz spectrometer (150.94 MHz for ^{13}C at 30 °C) in DMSO- d_6 .