SUPPORTING INFORMATION

Synthesis, structural characterization and reactivity of new trisubstituted N^1-acylamidrazones: solid state and solution studies

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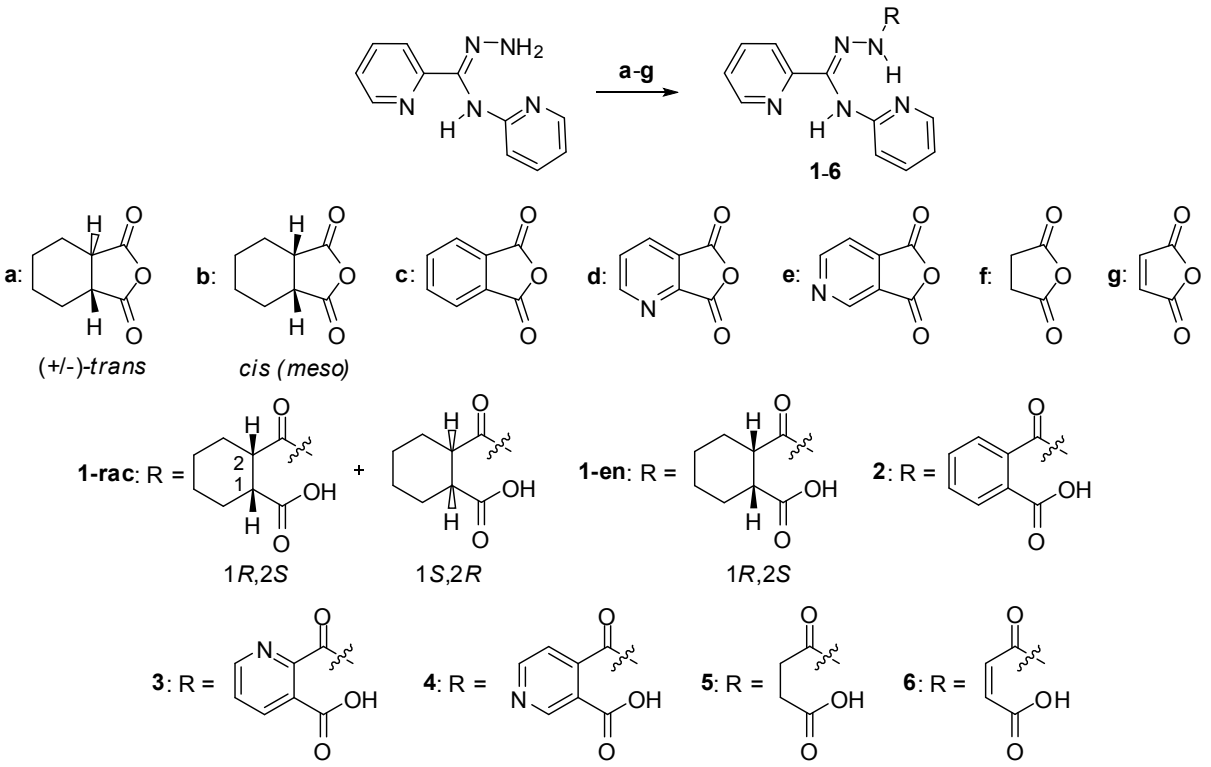
1. Synthetic, physicochemical and spectral characteristics of the studied forms

N^3-(2-pyridin-2-yl)-picolylamidrazone was prepared according to the established procedure. The appropriate anhydride **a-f** (10 mM) was dissolved in anhydrous diethyl ether (150 mL) and added to anhydrous diethyl ether solution (150 mL) of N^3-(2-pyridin-2-yl)-picolylamidrazone (2.13 g, 10 mM). The mixture was stirred at room temperature for 48 hours. The yellow precipitate of **1-en** and **2** - **5** was filtered off, dried, washed with diethyl ether and chloroform, than purified by crystallization from ethanol. The crude solid of **1-rac** obtained in the reaction with racemic *trans*-1,2-cyclohexanedicarboxylic anhydride was washed with diethyl ether, then dissolved in hot

chloroform and filtered off. The solution was evaporated, and the obtained product was purified by crystallization from ethanol. Derivative **6** was obtained in the reaction of N^3-(2-pyridin-2-yl)-picolylamidrazone and maleic anhydride (**g**) (Scheme 3). The substrates were dissolved in toluene at the molar ratio of 1:1, the reaction was carried out at ambient temperature for 10 minutes. The obtained precipitate of **6** was collected by filtration and washed with anhydrous toluene.



Scheme S1. Synthesis of the amidrazone derivatives **1 – 6.**

(**1-rac**) *(1R*,2S*)-{2-[pyridin-2-yl(pyridin-2-ylamino)methylidene]hydrazinecarbonyl}cyclohexane-carboxylic acid.* Yield: 83.13%. M.p. 172 - 176 °C; elemental analysis calc. for $C_{19}H_{21}N_5O_3$: C, 62.13; H, 5.72; N, 19.07%; found: C, 62.37; H, 5.83; N, 18.91%; IR (ν_{max}, cm^{-1}): 3161, 3049, 2927, 2858, 1738, 1656, 1601, 1568, 1519, 1464, 1434, 1428, 1379, 1347, 1328, 1289, 1224, 1156, 1095, 1044, 1002, 950; ^{1}H NMR (DMSO-d_6, 500 MHz) *Z-trans* 1.28-2.59 (m, 9H, CH), 2.85 (m, 1H, CH), 6.86 (t, 1H, CH), 6.98 (d, 1H, CH), 7.40 (t, 1H, CH), 7.64 (t, 1H, CH), 7.88 (t, 1H, CH), 8.04 (d, 1H, CH), 8.08 (d, 1H, CH), 8.49 (d, 1H, CH), 9.27 (bs, 1H, NH), 11.41 (bs, 1H, NH), 11.99 (bs, 1H, COOH); *Z-cis* 1.28-2.59 (m, 9H, CH), 3.73 (m, 1H, CH), 6.81 (t, 1H, CH), 6.94 (d, 1H, CH), 7.38 (t, 1H, CH), 7.61 (t, 1H, CH), 7.88 (t, 1H, CH), 7.94 (d, 1H, CH), 7.99 (d, 1H, CH), 8.46 (d, 1H, CH), 9.22 (bs, 1H, NH), 10.62 (bs, 1H, NH), 11.99 (bs, 1H, COOH); ^{13}C NMR (DMSO-d_6, 125 MHz) *Z-trans/cis*

22.2, 22.4, 23.7, 24.4, 25.0, 25.5, 26.6, 27.1, 38.2, 41.3, 42.0 (2x), 112.2, 112.4, 116.0, 116.2, 121.6, 121.9, 124.0, 124.2, 137.0 (2x), 137.7, 138.1, 138.4, 140.0, 146.8 (2x), 147.9 (2x), 152.1 (2x), 153.9 (2x), 169.7 (2x), 174.9, 175.1.

(**1-en**)*(1R,2S)-{2-[pyridin-2-yl(pyridin-2-ylamino)methylidene]hydrazinecarbonyl}cyclohexane-carboxylic acid.* Yield: 88%. M.p. 170 - 173 °C; IR (ν_{max}, cm^{-1}): 3252, 3097, 2935, 2859, 1716, 1641, 1622, 1602, 1587, 1566, 1558, 1519, 1476, 1462, 1435, 1396, 1343, 1323, 1266, 1220, 1209, 1189, 1127, 1100, 1062, 1043, 998, 983; ^{13}C NMR (DMSO-d_6, 100 MHz) *Z-trans/cis* 22.7, 23.2, 24.3, 24.9, 25.5, 26.0, 27.2, 27.7, 38.7, 41.8, 42.5 (2x), 112.7, 112.9, 116.5, 116.6, 122.1, 122.4, 122.5, 124.7, 137.5 (2x), 138.2, 138.6, 138.9, 140.5, 147.3 (2x), 148.5 (2x), 152.6, 152.7, 154.4 (2x), 170.2, 175.4, 175.5, 175.6.

(**2**) *2-{2-[pyridin-2-yl(pyridin-2-ylamino)methylidene]hydrazinecarbonyl}benzoic acid.*

Yield: 85.29%. M.p. 177 – 179 °C; elemental analysis calc. for $C_{19}H_{15}N_5O_3$: C, 63.16; H, 4.16; N, 19.39%; found: C, 63.02; H, 3.98; N, 19.21%; IR (ν_{max}, cm^{-1}): 3322, 3208, 3074, 2743, 2586, 2471, 1711, 1656, 1647, 1587, 1566, 1521, 1466, 1435, 1423, 1358, 1325, 1298, 1256, 1238, 1173, 1143, 1113, 1078, 1049, 999, 964; ^{1}H NMR (DMSO-d_6, 500 MHz); *Z-trans* 6.83 (t, 1H, CH), 7.10 (d, 1H, CH), 7.58 (t, 1H, CH), 7.61 (t, 1H, CH), 7.64 (t, 1H, CH), 7.65 (t, 1H, CH), 7.83 (d, 1H, CH), 7.84 (d, 1H, CH), 7.89 (d, 1H, CH), 7.94 (t, 1H, CH), 8.09 (d, 1H, CH), 8.62 (d, 1H, CH), 9.42 (bs, 1H, NH), 12.27 (bs, 1H, NH), 13.04 (bs, 1H, COOH); *Z-cis* 6.85 (t, 1H, CH), 6.96 (d, 1H, CH), 7.30 (t, 1H, CH), 7.41 (d, 1H, CH), 7.44 (d, 1H, CH), 7.64 (t, 1H, CH), 7.65 (t, 1H, CH), 7.70 (t, 1H, CH), 7.74 (t, 1H, CH), 7.91 (d, 1H, CH), 8.05 (d, 1H, CH), 8.38 (d, 1H, CH), 9.24 (bs, 1H, NH), 11.55 (bs, 1H, NH), 13.04 (bs, 1H, COOH).

(**3**) *2-{2-[pyridin-2-yl(pyridin-2-ylamino)methylidene]hydrazinecarbonyl}nicotinic acid.*

Yield: 79.05%. M.p. 174 – 176 °C; elemental analysis calc. for $C_{18}H_{14}N_6O_3$: C, 59.67; H, 3.87; N, 23.20%; found: C, 59.09; H, 3.61; N, 22.69%; IR (ν_{max}, cm^{-1}): 3235, 3066, 3038, 2532, 1704, 1638, 1600, 1585, 1529, 1497, 1460, 1435, 1419, 1337, 1281, 1270, 1233, 1167, 1149, 1126, 1107, 1097, 1042, 1000, 991; ^{1}H NMR (DMSO-d_6, 500 MHz) *Z-trans* 6.96 (t, 1H, CH), 7.26 (d, 1H, CH), 7.52 (t, 1H, CH), 7.66 (t, 1H, CH), 8.05 (d, 1H, CH), 8.22 (d, 1H, CH), 8.22 (d, 1H, CH), 8.60 (d, 1H, CH), 8.72 (t, 1H, CH), 8.72 (d, 1H, CH), 8.96 (t, 1H, CH), 9.75 (bs, 1H, NH), 13.57 (bs, 1H, NH), 13.00 (bs, 1H, COOH); ^{13}C NMR (DMSO-d_6, 125 MHz) *Z-trans* 112.8, 116.6, 122.0, 124.7, 125.8, 130.5, 136.7, 137.3, 139.1, 140.8, 146.8, 147.9, 148.4, 149.5, 151.5, 153.2, 160.3, 168.3.

(**4**) *4-{2-[pyridin-2-yl(pyridin-2-ylamino)methylidene]hydrazinecarbonyl}nicotinic acid.*

Yield: 89.26%. M.p. 179 – 180 °C; elemental analysis calc. for $C_{18}H_{14}N_6O_3$: C, 59.67; H, 3.87; N, 23.20%; found: C, 59.47; H, 3.63; N, 22.91%; IR (ν_{max}, cm^{-1}): 3234, 3065, 3015, 2759, 2610, 2499, 1733, 1723, 1652, 1622, 1601, 1581, 1567, 1533, 1510, 1473, 1464, 1435, 1402, 1343, 1314, 1260, 1235, 1166, 1151, 1125, 1048, 1034, 999, 969; ^{1}H NMR (DMSO-d_6, 400 MHz) *Z-trans/cis* 6.87 (m, 1H, CH), 6.99 (m, 1H, CH), 7.33 (m, 1H, CH), 7.42 (m, 1H, CH), 7.71 (m, 3H, CH), 7.92 (m,

1H, CH), 8.07 (d, 1H, CH), 8.47 (d, 1H, CH), 8.78 (m, 2H, CH), 9.38 (bs, 1H, NH), 11.92, 12.31 (s, 1H, NH), 13.70 (bs, 1H, COOH); ^{13}C NMR (DMSO-d_6, 100 MHz) *Z-trans/cis* 113.0, 113.4, 116.9, 117.0, 121.8, 121.9, 122.5, 123.0, 123.1, 124.6, 125.0, 131.1, 131.6, 137.4 (2x), 137.6, 138.9, 139.0, 139.2, 146.9, 147.2, 148.3, 148.5, 149.3, 151.4, 152.0, 153.3, 153.4, 153.8, 153.9, 154.0, 154.1, 166.5, 166.9, 168.6, 169.0.

(**5**) *4-oxo-4-{2-[pyridin-2-yl(pyridin-2-ylamino)methylidene]hydrazinyl}butanoic acid.* Yield: 80%. M.p. 143 – 145 °C; elemental analysis: calc. for $C_{15}H_{15}N_5O_3$: C, 57.50; H, 4.83; N, 22.35%; found: C, 57,34; H, 4,71; N, 22,40%. IR (ν_{max}, cm^{-1}): 3325, 3187, 3092, 2616, 1683, 1656, 1595, 1578, 1537, 1510, 1477, 1433, 1419, 1393, 1371, 1320, 1292, 1283, 1244, 1221, 1193, 1162, 1147, 1098, 1017, 987, 963; ^{1}H NMR (DMSO-d_6, 400 MHz) *Z-trans/cis* 2.91 (m, 1H, CH_2), 3.17 (d, 2H, CH_2), 4.09 (m, 1H, CH_2), 6.87 (m, 2H, CH), 7.40 (m, 1H, CH), 7.62 (m, 1H, CH), 7.94 (m, 3H, CH), 8.44 (m, 1H, CH), 9.17 (bs, 1H, NH), 10.80, 11.21 (s, 1H, NH), 12.11 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, 175 MHz) *Z-trans/cis* 27.5, 28.2, 29.0, 29.3, 40.0, 112.3 (2x), 116.1 (2x), 121.9, 122.5, 124.1, 124.2, 137.0, 137.1, 138.1, 138.2, 138.6, 147.0 (2x), 148.1 (2x), 152.3, 152.5, 152.6, 154.1 (2x), 167.7, 173.2, 173.8, 174.0.

(**5-metol**) M.p. 180 °C; IR (ν_{max}, cm^{-1}): 3586, 3322, 3188, 3067, 2920, 2713, 2620, 1732, 1672, 1657, 1636, 1593, 1530, 1473, 1477, 1465, 1437, 1423, 1403, 1361, 1340, 1320, 1293, 1246, 1230, 1174, 1162, 1150, 1099, 1074, 1047, 1029, 1024, 1028, 1008.

(**6**) *(Z)-4-oxo-4-{2-[pyridin-2-yl(pyridin-2-ylamino)methylidene]hydrazinyl}but-2-enoic acid.* Yield: 85%. M.p. 150 – 151 °C; elemental analysis calc. for $C_{15}H_{15}N_5O_3$: C, 57.51; H, 4.79; N, 22.36%; found: C, 57.81; H, 3.99; N, 22.39%; IR (ν_{max}, cm^{-1}): 3252, 3057, 2505, 1707, 1640, 1587, 1544, 1505, 1468, 1435, 1411, 1341, 1311, 1296, 1271, 1233, 1214, 1162, 1151, 1135, 1098, 1061, 1008; ^{1}H NMR (DMF-d_7, 500 MHz, -40°C) *ylide* 6.13 (d, 1H, CH), 6.43 (d, 1H, CH), 7.42 (t, 1H, CH), 7.75-7.81 (m, 2H, CH), 8.12 (t, 1H, CH), 8.18 (m, 1H, CH), 8.63 (d, 1H, CH), 8.69 (d, 1H, CH), 8.90 (d, 1H, CH), 12.08 (bs, 1H, NH), 15.84 (bs, 1H, NH), 19.05 (bs, 1H, COOH); *Z-trans* 6.51 (d, 1H, CH), 6.71 (d, 1H, CH), 6.90 (m, 1H, CH), 7.25 (d, 1H, CH), 7.54 (m, 1H, CH), 7.68 (m, 1H, CH), 7.98 (m, 1H, CH), 8.20 (m, 2H, CH), 8.54 (d, 1H, CH), 10.00 (bs, 1H, NH), 13.51 (bs, 1H, NH), 15.55 (bs, 1H, COOH); *Z-cis* 6.50 (d, 1H, CH), 6.60 (m, 1H, CH), 7.25 (m, 2H, CH), 7.54 (m, 1H, CH), 7.68 (m, 1H, CH), 7.98 (m, 1H, CH), 8.20 (m, 2H, CH), 8.54 (d, 1H, CH), 9.78 (bs, 1H, NH), 12.60 (bs, 1H, NH), 14.15 (bs, 1H, COOH).

2. X-ray crystallography

Table S1. Geometries of hydrogen bonds and selected short contacts.

Comp.	*Interaction*	$d_{D\text{-}H}$ / Å	$d_{H\cdots A}$ / Å	$d_{D\cdots A}$ / Å	<D-H…A / °	*Symmetry code*
1-rac	N1–H1n···N4	0.92(3)	1.83(3)	2.695(3)	156(2)	
	N3–H3n···N5	0.85(2)	2.08(2)	2.597(3)	119(2)	
	O2–H2o···O1	0.96(3)	1.69(3)	2.647(3)	178(2)	-*x*+3/2, *y*+1/2, -*z*+1/2
	C9–H9···O2	0.93	2.75	3.535(3)	142	-*x*+3/2, *y*-1/2, -*z*+1/2
	C5–H5···N2	0.93	2.61	3.523(3)	166	*x*-1/2, -*y*+3/2, *z*-1/2
	C6–H6···O1	0.93	2.62	3.172(3)	119	
	C6–H6···O3	0.93	2.53	3.398(3)	156	-*x*+1, -*y*+2, -*z*
	C11–H11···N4	0.93	2.72	3.376(3)	128	-*x*+1/2, *y*-1/2, -*z*+1/2
	C11–H11···O3	0.93	2.55	3.386(3)	150	
	C12–H12···O1	0.93	2.68	3.582(3)	165	*x*-1, *y*, *z*
1-en	N1–H1n···N4	0.98	1.87	2.706	141	
	N3–H3n···N5	0.98	2.01	2.608	117	
	N1a–H1a···N4a	0.86(3)	1.93(3)	2.725(4)	154(2)	
	N3a–H3a···N5a	0.95(4)	2.08(4)	2.607(4)	113(3)	
	O2–H2o···O1	0.93(4)	1.69(4)	2.612(5)	170(3)	-*x*+1, *y*-1/2, -*z*+1
	O2a–H2a···O1a	0.82	1.81	2.630	175	-*x*+2, *y*+1/2, -*z*+2
	C9–H9···O2	0.93	2.44	3.350(4)	167	-*x*+1, *y*+1/2, -*z*+1
	C9a–H9a···O2a	0.93	2.46	3.333(4)	156	-*x*+2, *y*-1/2, -*z*+2
	C5–H5···O3a	0.93	2.69	3.294(4)	124	*x*, *y*, *z*-1
	C6–H6···O2a	0.93	2.72	3.353(4)	127	-*x*+2, *y*-1/2, -*z*+1
	C11–H11···O3	0.93	2.47	3.180(4)	133	-*x*+2, *y*+1/2, -*z*+1
	C6a–H6a···O3	0.93	2.54	3.366(4)	148	-*x*+1, *y*+1/2, -*z*+1
	C11a–H11a···O3a	0.93	2.62	3.273(4)	128	-*x*+1, *y*-1/2, -*z*+2
	C13a–H13a···N5	0.93	2.73	3.583(4)	145	-*x*+2, *y*-1/2, -*z*+1
2	N1–H1n···N4	0.96(3)	1.73(3)	2.676(3)	169(2)	
	N3–H3n···N5	0.90(4)	2.03(3)	2.564(3)	117(2)	
	O2–H2o···O1	0.91(4)	1.71(4)	2.615(4)	172(3)	-*x*+1/2, *y*-1/2, -*z*+1/2
	C9–H9···O2	0.93	2.55	3.480(5)	176	-*x*+1/2, *y*+1/2, -*z*+1/2
	C5–H5···O1	0.93	2.65	3.368(5)	134	*x*+1/2, -*y*+3/2, z-1/2
	C5–H5···O3	0.93	2.55	3.344(5)	143	
	C12–H12···O3	0.93	2.68	3.468(4)	143	-*x*+3/2, *y*+1/2, -*z*+1/2
	C15–H15···O2	0.93	2.61	3.339(4)	136	-*x*, -*y*+1, -*z*
	C16–H16···O3	0.93	2.67	3.251(4)	121	*x*-1/2, -*y*+3/2, *z*-1/2
	C17–H17···O3	0.93	2.56	3.201(4)	126	
3	O2–H2o···O1	1.04(2)	1.39(2)	2.431(2)	178(1)	
	N1–H1n···N4	0.95(2)	1.76(2)	2.653(2)	156(1)	

	N3–H3n···N5	0.90(2)	2.02(2)	2.589(2)	120(1)	
	C5–H5···O1	0.93	2.68	3.149(2)	112	*x*-1/2, -*y*+3/2, *z*-1/2
	C6–H6···O3	0.93	2.54	3.250(2)	134	*x*-1/2, -*y*+1/2, *z*-1/2
	C10–H10···O2	0.93	2.49	3.321(2)	149	-*x*+5/2, *y*+1/2, -*z*+1/2
4	O2–H2o···O1	1.00(3)	1.63(3)	2.700(2)	169(1)	-*x*+3/2, *y*+1/2, -*z*+1/2
	O2–H2o···N2	1.00(3)	2.68(3)	3.234(2)	115(1)	
	N1–H1n···N4	0.92(2)	1.83(2)	2.700(2)	157(1)	
	N3–H3n···N5	0.88(2)	2.05(2)	2.604(2)	120(1)	
	C10–H10···O1	0.93	2.64	3.318(3)	130	-*x*+3/2, *y*-1/2, -*z*+1/2
	C11–H11···N6	0.93	2.60	3.422(3)	147	*x*+1, *y*-1, *z*
	C12–H12···O3	0.93	2.52	3.442(2)	170	2-*x*, -*y*, -*z*
5	O2–H2o···O2a	0.97(4)	1.63(4)	2.589(3)	171(2)	
	N1–H1a···O1	0.98(3)	1.99(3)	2.947(3)	166(2)	-*x*+3/2, *y*+1/2, -*z*+1/2
	N1–H1n···O1a	0.89(3)	2.06(3)	2.935(4)	166(2)	-*x*+3/2, *y*-1/2, -*z*+1/2
	N3a–H3a···O3a	0.97(3)	1.77(3)	2.723(3)	168(2)	
	N4a–H4n···O2a	0.98(3)	1.70(3)	2.664(3)	168(2)	*x*-1/2, -*y*+3/2, *z*-1/2
	N4–H4n···O3a	0.98(3)	2.66(3)	3.418(3)	135(2)	
	N3–H3n···O3	0.88(3)	2.22(3)	3.080(3)	167(2)	*x*-1/2, -*y*+1/2, *z*-1/2
	C4–H4···O2	0.93	2.48	3.249(4)	140	-*x*+3/2, *y*-1/2, -*z*+1/2
	C9–H9···O3a	0.93	2.41	3.152(4)	137	-*x*+1, -*y*+1, -*z*+1
	C7a–H7a···O3	0.93	2.47	3.351(3)	158	*x*-1/2, -*y*+3/2, *z*-1/2
	C7a–H7a···N5	0.93	2.72	3.216(3)	115	
	C10a–H10a···O1a	0.93	2.53	3.084(4)	119	*x*-1, *y*, *z*
	C14a–H14c···O2a	0.93	2.64	3.596(4)	171	-*x*+1, -*y*+1, -*z*+1
5-metol	O2–H2o···O4	0.99(3)	1.62(3)	2.606(2)	173(2)	
	N1–H1n···N4	0.88(2)	1.86(2)	2.710(3)	163(1)	
	N3–H3n···N5	0.86(2)	1.95(2)	2.557(3)	126(1)	
	O4–H4o···O1	0.90(2)	1.86(2)	2.723(2)	160(1)	-*x*+1/2, *y*, *z*-1/2
	O4–H4o···N2	0.90(2)	2.63(2)	3.246(2)	127(1)	
	C9–H9···O4	0.93	2.52	3.394(3)	157	-*x*+1/2, *y*, *z*+1/2
	C10–H10···O2	0.93	2.61	3.434(3)	148	-*x*+1/2, *y*-1, *z*+1/2
	C5–H5···O1	0.93	2.59	3.309(3)	134	*x*-1/2, -*y*+2, *z*
	C12–H12···O3	0.93	2.37	3.259(3)	159	-*x*, -*y*+1, *z*+1/2
	C13–H13b···O1	0.97	2.55	3.496(3)	166	*x*, *y*+1, *z*
	C14–H14a···O3	0.97	2.67	3.456(3)	139	

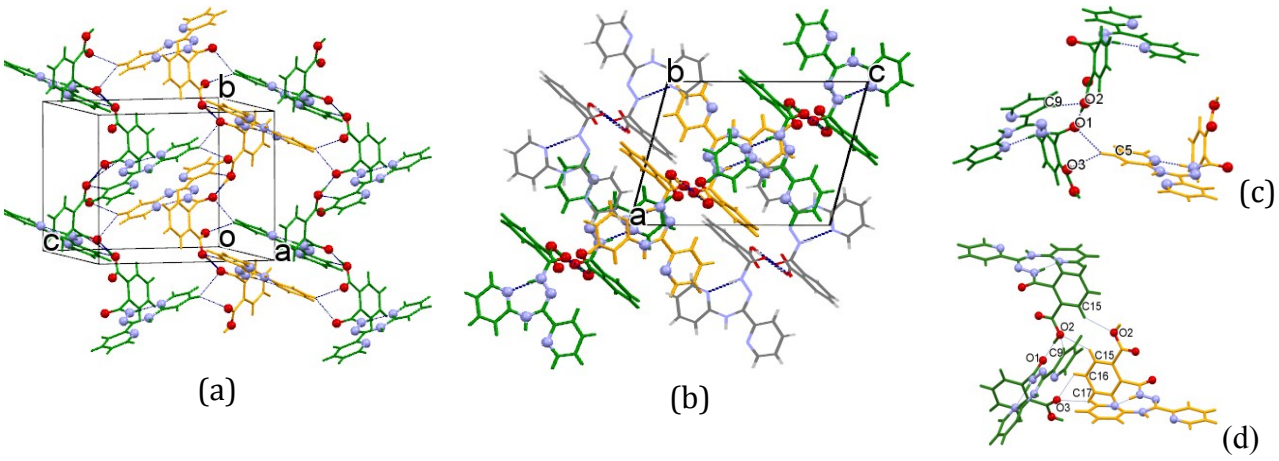


Figure S1. Crystal structure **2**: (*a*) hydrogen-bonded helical chains assembled via C–H···O and π···π interactions into the 3D supramolecular network; (b) crystal packing in view along the *Y* axis; (c) and (d) molecular dimers stabilized by strong O–H···O and weak C–H···O intermolecular interactions.

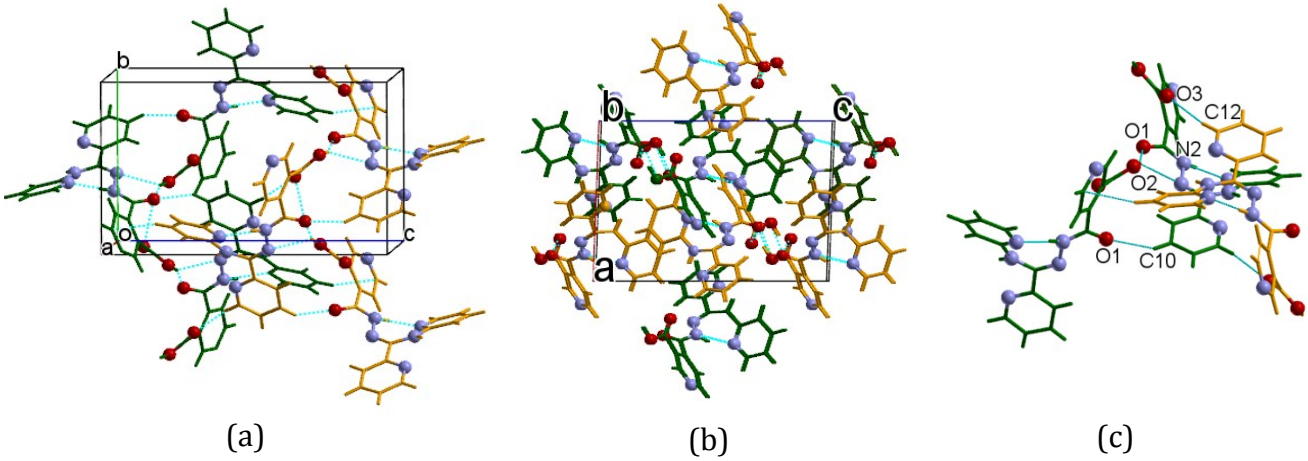


Figure S2. Part of the crystal structure of **4** showing: (*a*) hydrogen-bonded helical chains; (b) crystal packing in view along the *Y* axis; (c) molecular dimers stabilized by strong O–H···O and weak C–H···O hydrogen bonds.

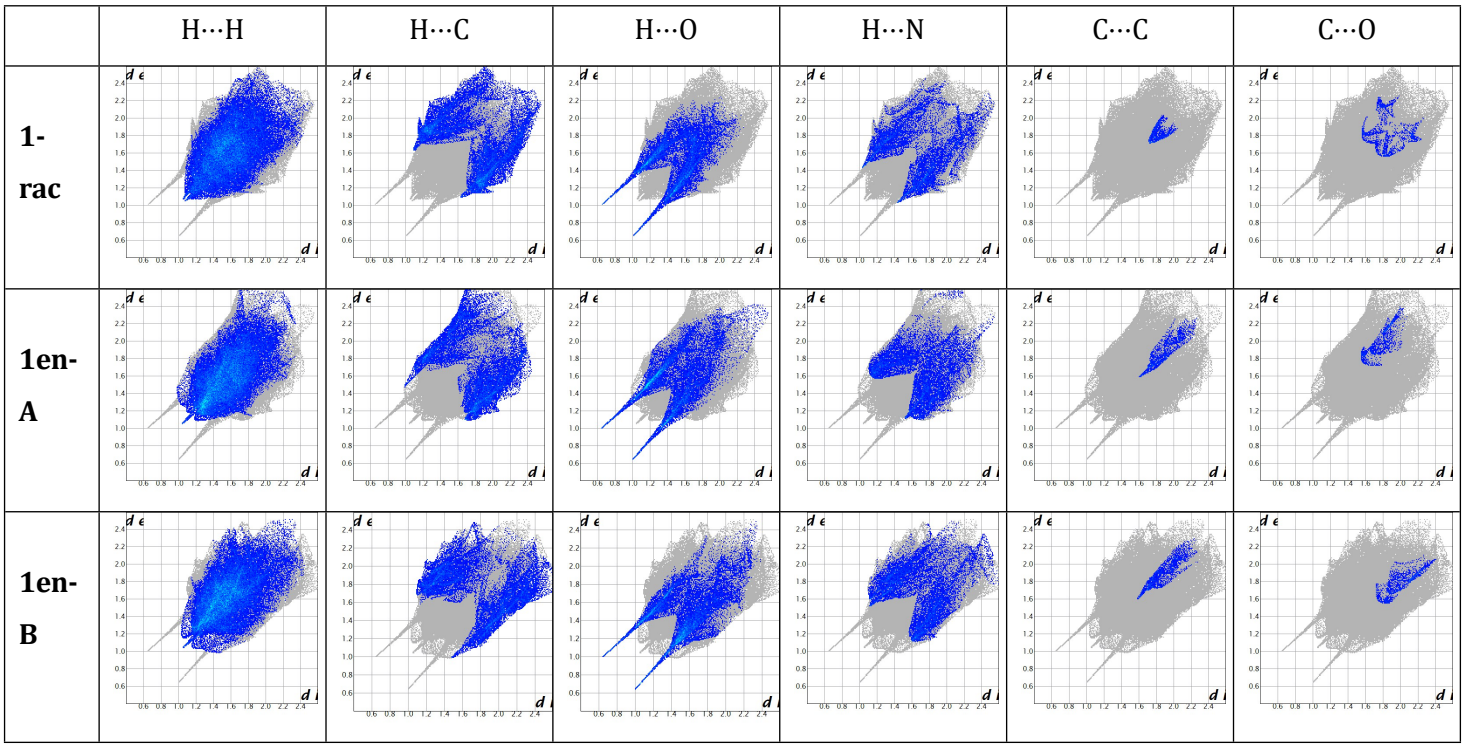


Figure S3. Hirshfeld surface fingerprint plots for **1-rac** and **1-en** (**1en-A** and **1en-B** represent the two crystallographically independent molecules in crystal **1-en**).

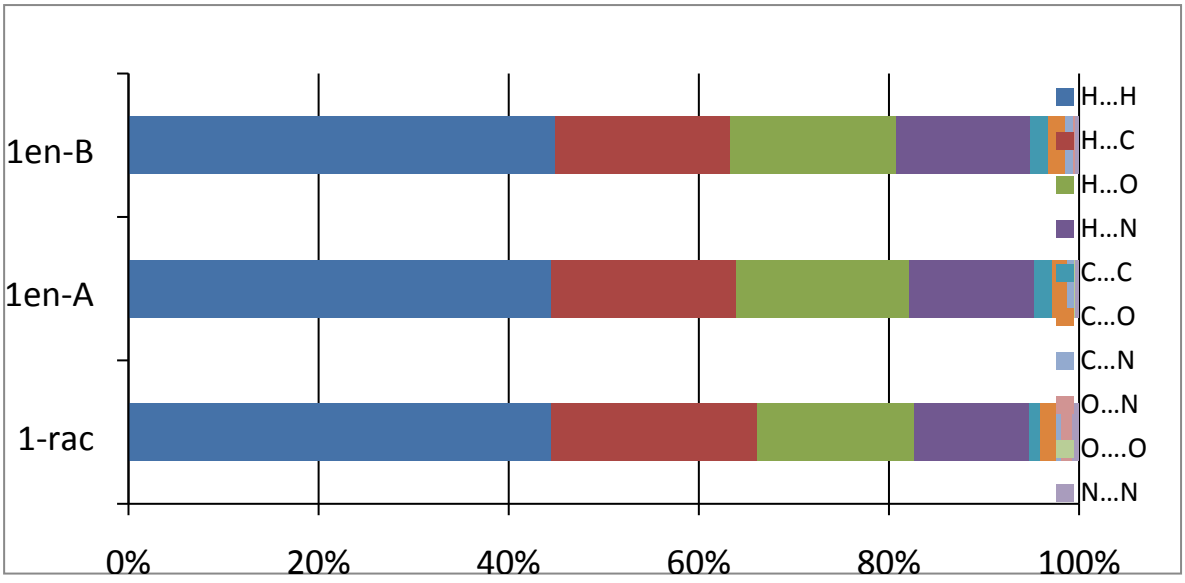


Figure S4. Percentage contributions to the Hirshfeld surface for close intermolecular contacts for the molecules in crystals **1-en** and **1-rac**.

3. Thermal stability studies

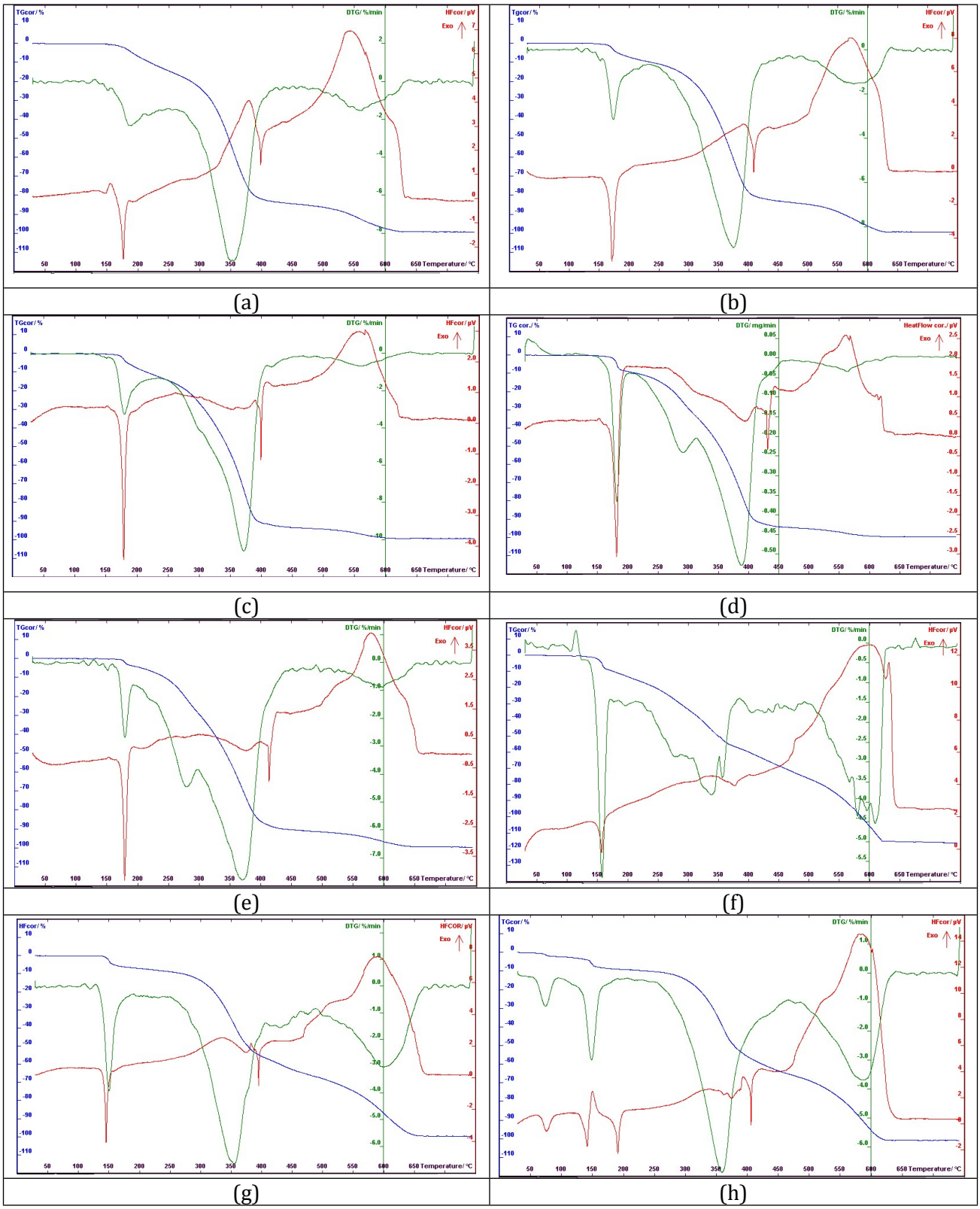
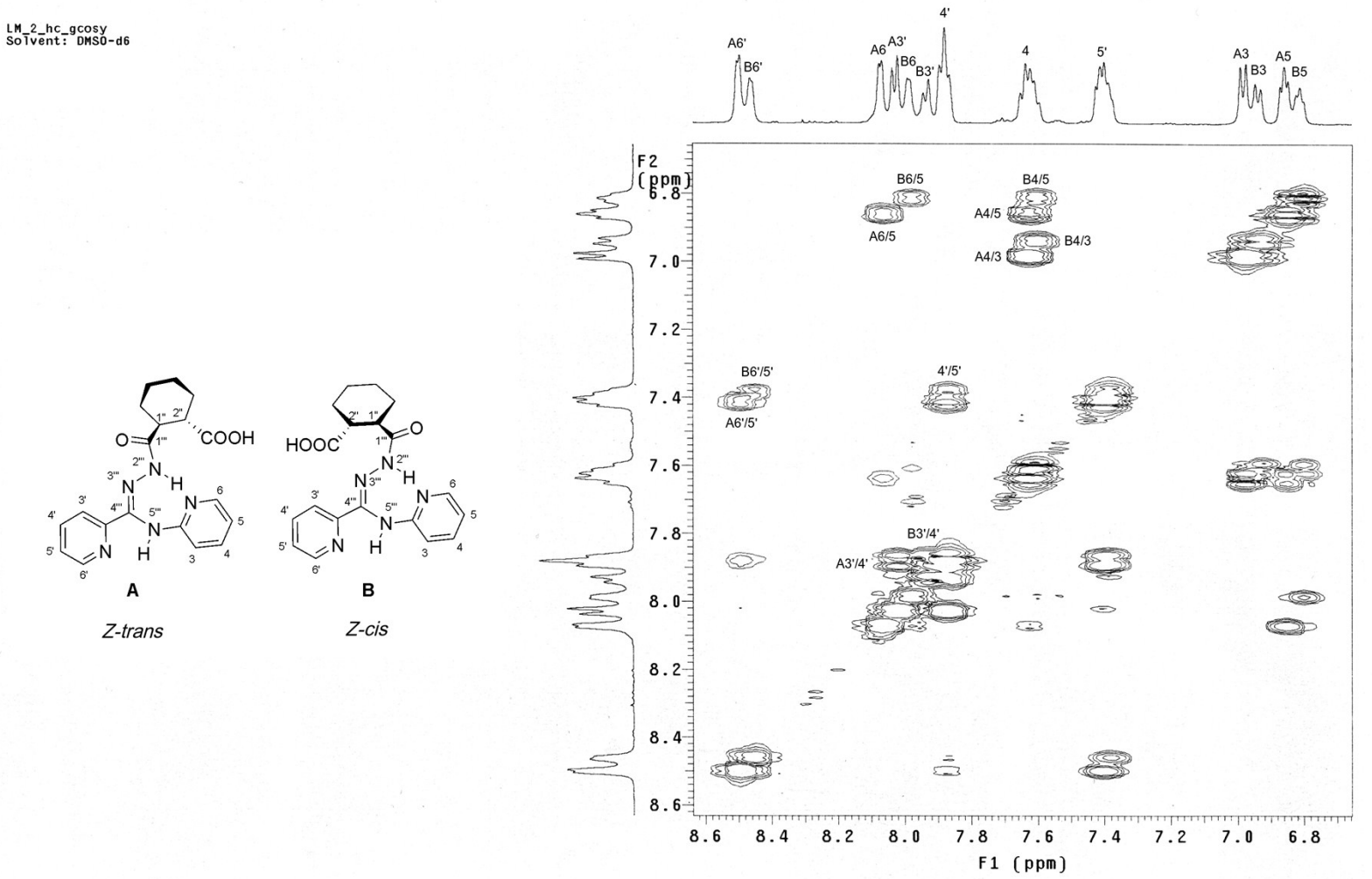
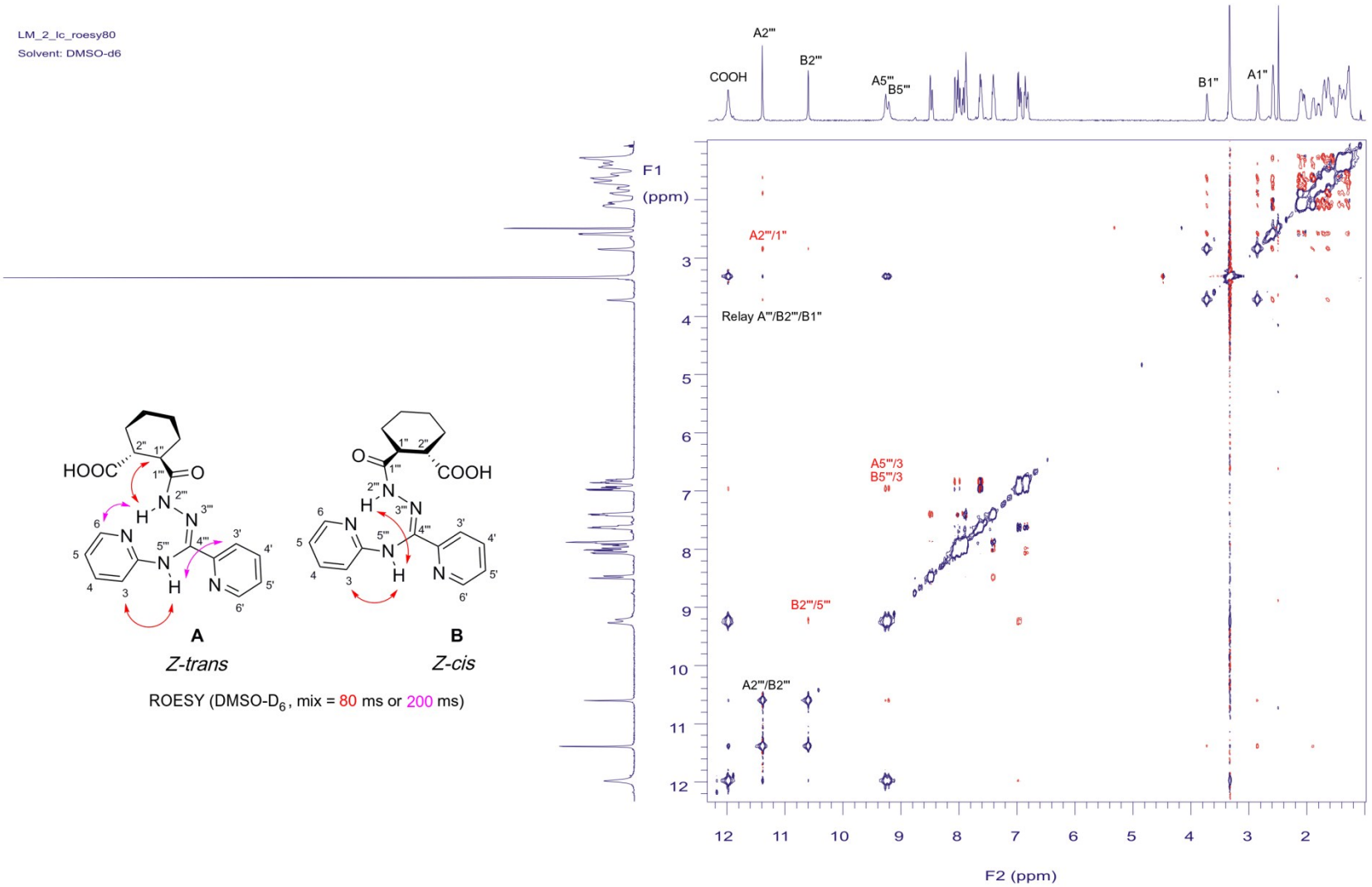


Figure S5. DSC (red solid line), TG (blue solid line) and DTG (green solid line) plots for (a) **1-rac**, (b) **1-en**, (c) **2**, (d) **3**, (e) **4,** (f) **6,** (g) **5** and (h) **5-metol.**

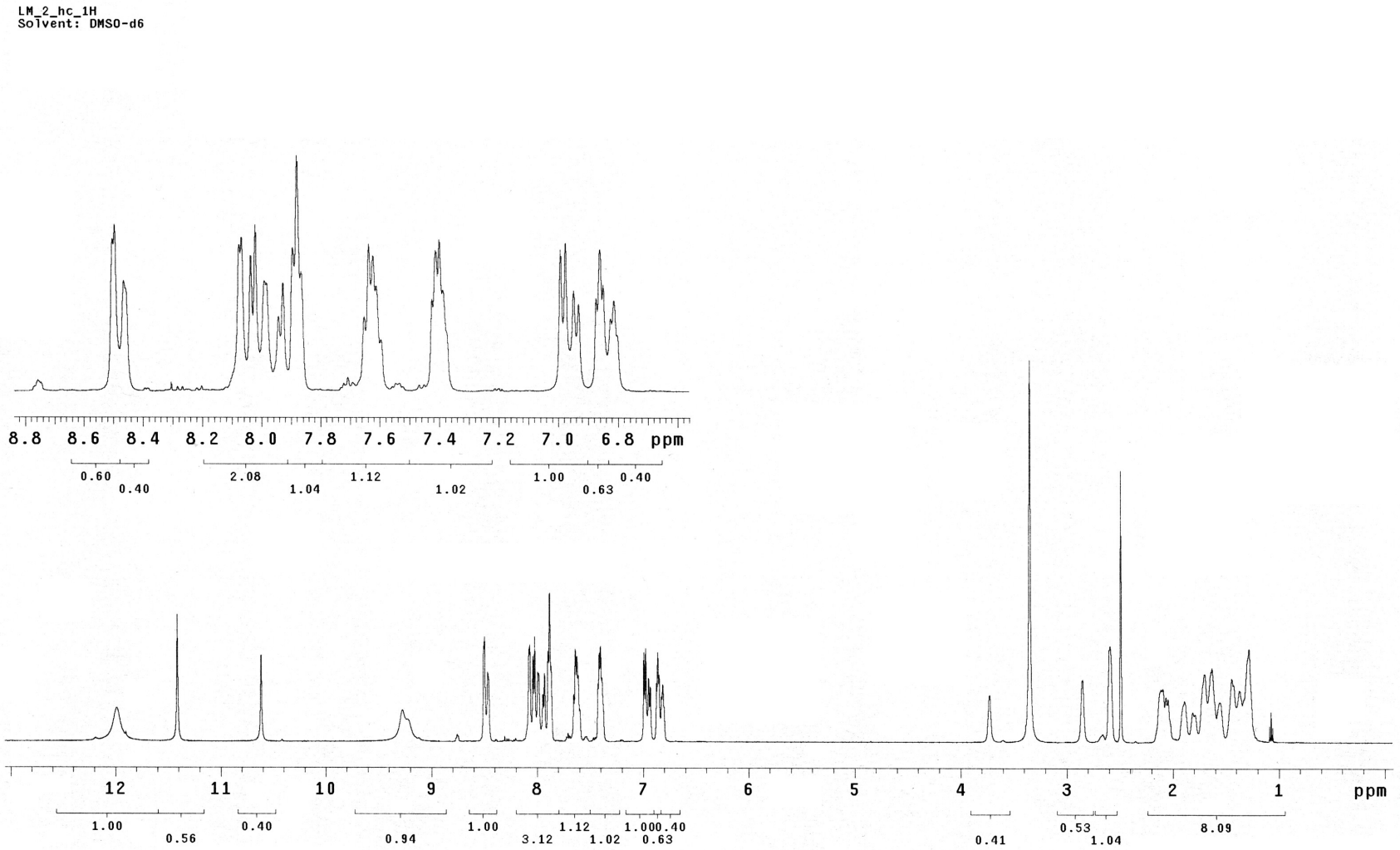
4. NMR studies



The fragment of gCOSY spectrum of compound **1-rac**.



The ROESY spectrum of compound **1-rac**.



^{1}H-NMR spectrum of compound **1-rac**.

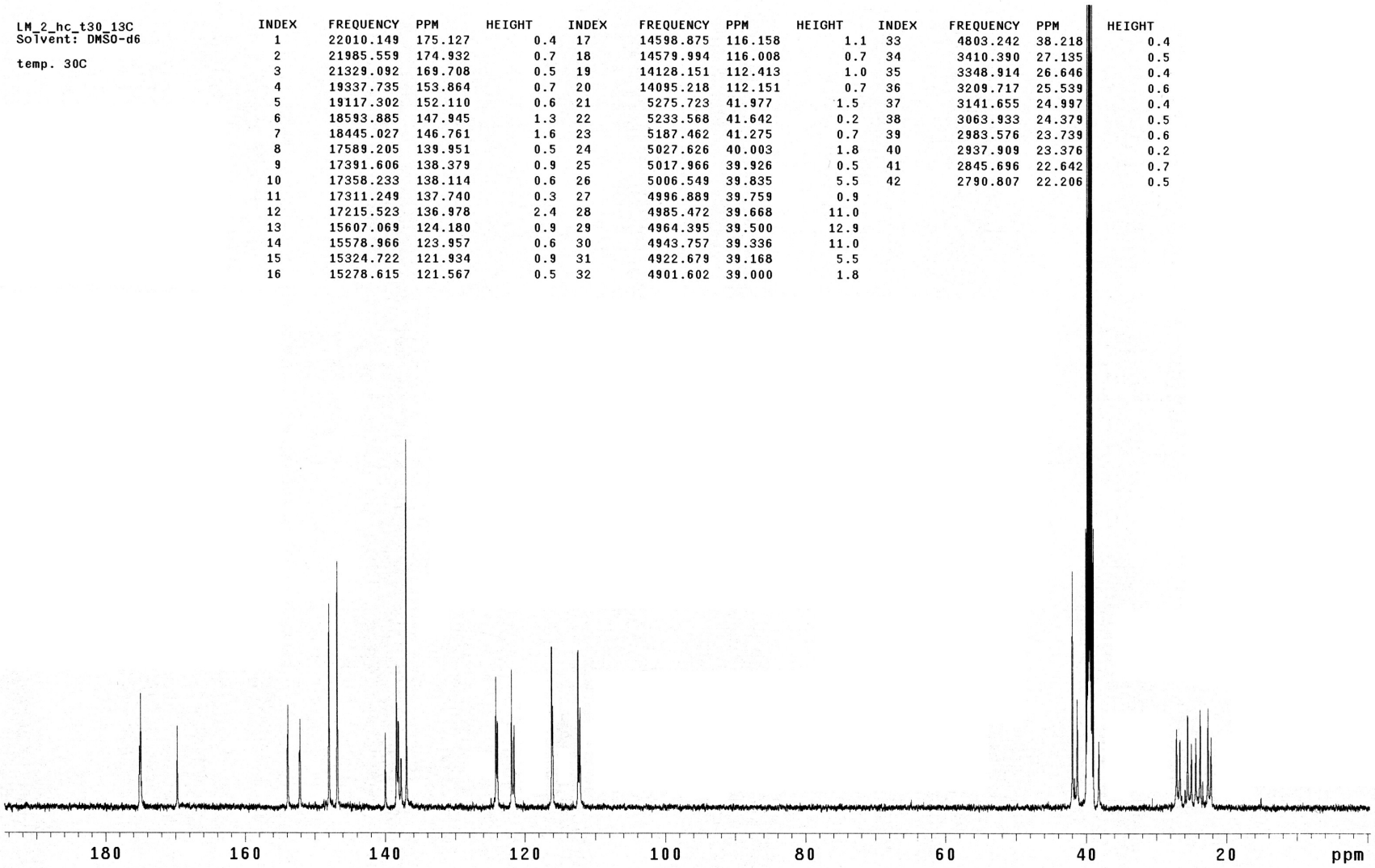
LM_2_hc_1H
Solvent: DMSO-d6

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	5991.400	11.987	1.6	28	3796.441	7.596	1.6	55	905.640	1.812	1.4
2	5947.452	11.899	0.5	29	3710.987	7.425	2.8	56	894.897	1.790	1.3
3	5703.784	11.412	6.1	30	3704.639	7.412	4.3	57	850.461	1.702	3.3
4	5305.811	10.615	4.2	31	3698.779	7.400	4.6	58	819.209	1.639	3.4
5	4634.871	9.273	1.5	32	3692.431	7.387	3.1	59	814.814	1.630	3.6
6	4376.555	8.756	0.3	33	3494.665	6.992	4.3	60	777.702	1.556	1.9
7	4250.571	8.504	4.6	34	3486.364	6.975	4.5	61	721.058	1.443	3.1
8	4246.664	8.496	5.1	35	3472.691	6.948	3.1	62	712.757	1.426	2.8
9	4231.038	8.465	3.4	36	3464.390	6.931	2.7	63	685.900	1.372	2.5
10	4150.955	8.305	0.3	37	3435.091	6.873	2.8	64	640.487	1.281	4.5
11	4036.202	8.075	4.4	38	3428.743	6.860	4.3	65	543.313	1.087	0.8
12	4032.784	8.068	4.7	39	3423.372	6.849	3.2	66	536.477	1.073	1.5
13	4017.158	8.037	4.1	40	3410.676	6.824	2.2	67	529.152	1.059	0.7
14	4008.857	8.021	5.1	41	3405.304	6.813	2.8				
15	3993.719	7.990	3.4	42	1861.753	3.725	2.3				
16	3990.301	7.983	3.3	43	1691.332	3.384	0.9				
17	3969.792	7.942	2.3	44	1684.496	3.370	2.5				
18	3961.979	7.927	3.3	45	1673.753	3.349	18.4				
19	3945.865	7.895	4.4	46	1423.738	2.848	3.0				
20	3938.540	7.880	7.2	47	1328.029	2.657	0.4				
21	3931.215	7.865	3.6	48	1294.336	2.590	4.6				
22	3852.109	7.707	0.4	49	1244.528	2.490	13.1				
23	3844.296	7.691	0.3	50	1055.063	2.111	2.5				
24	3824.763	7.652	2.3	51	1046.274	2.093	2.6				
25	3816.950	7.637	4.5	52	1031.624	2.064	2.2				
26	3810.114	7.623	4.1	53	1022.346	2.045	2.1				
27	3804.254	7.611	3.2	54	944.705	1.890	2.0				

LM_2_hc_t30_13C
Solvent: DMSO-d6

temp. 30C

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	22010.149	175.127	0.4	17	14598.875	116.158	1.1	33	4803.242	38.218	0.4
2	21985.559	174.932	0.7	18	14579.994	116.008	0.7	34	3410.390	27.135	0.5
3	21329.092	169.708	0.5	19	14128.151	112.413	1.0	35	3348.914	26.646	0.4
4	19337.735	153.864	0.7	20	14095.218	112.151	0.7	36	3209.717	25.539	0.6
5	19117.302	152.110	0.6	21	5275.723	41.977	1.5	37	3141.655	24.997	0.4
6	18593.885	147.945	1.3	22	5233.568	41.642	0.2	38	3063.933	24.379	0.5
7	18445.027	146.761	1.6	23	5187.462	41.275	0.7	39	2983.576	23.739	0.6
8	17589.205	139.951	0.5	24	5027.626	40.003	1.8	40	2937.909	23.376	0.2
9	17391.606	138.379	0.9	25	5017.966	39.926	0.5	41	2845.696	22.642	0.7
10	17358.233	138.114	0.6	26	5006.549	39.835	5.5	42	2790.807	22.206	0.5
11	17311.249	137.740	0.3	27	4996.889	39.759	0.9				
12	17215.523	136.978	2.4	28	4985.472	39.668	11.0				
13	15607.069	124.180	0.9	29	4964.395	39.500	12.9				
14	15578.966	123.957	0.6	30	4943.757	39.336	11.0				
15	15324.722	121.934	0.9	31	4922.679	39.168	5.5				
16	15278.615	121.567	0.5	32	4901.602	39.000	1.8				

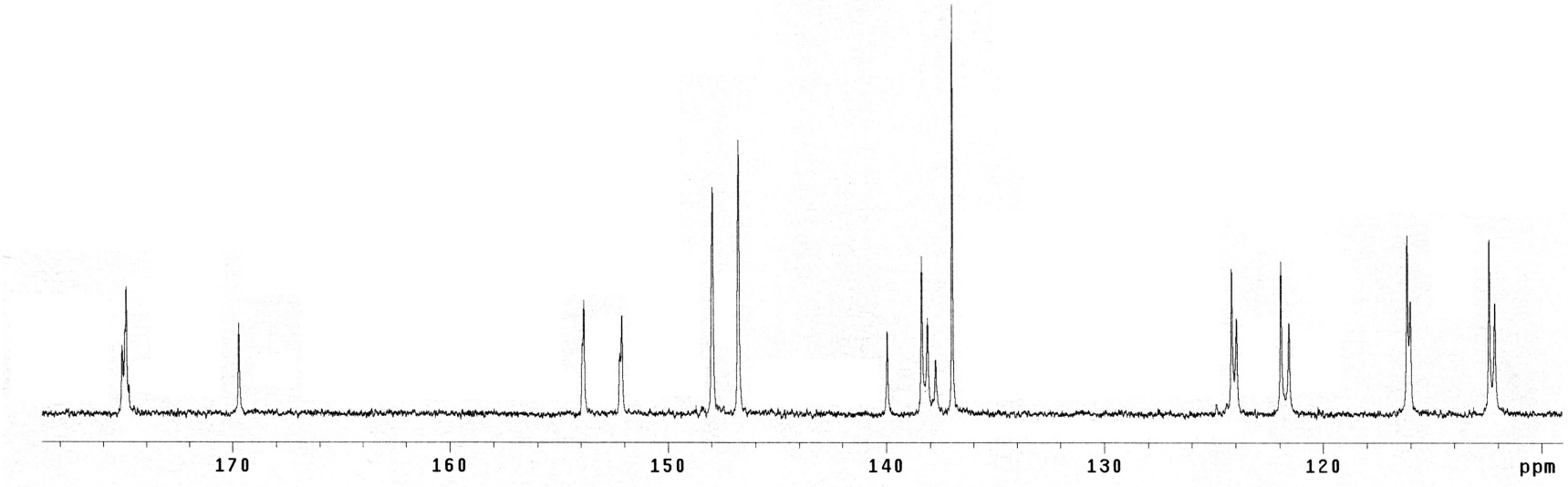


^{13}C-NMR spectrum of **1-rac**.

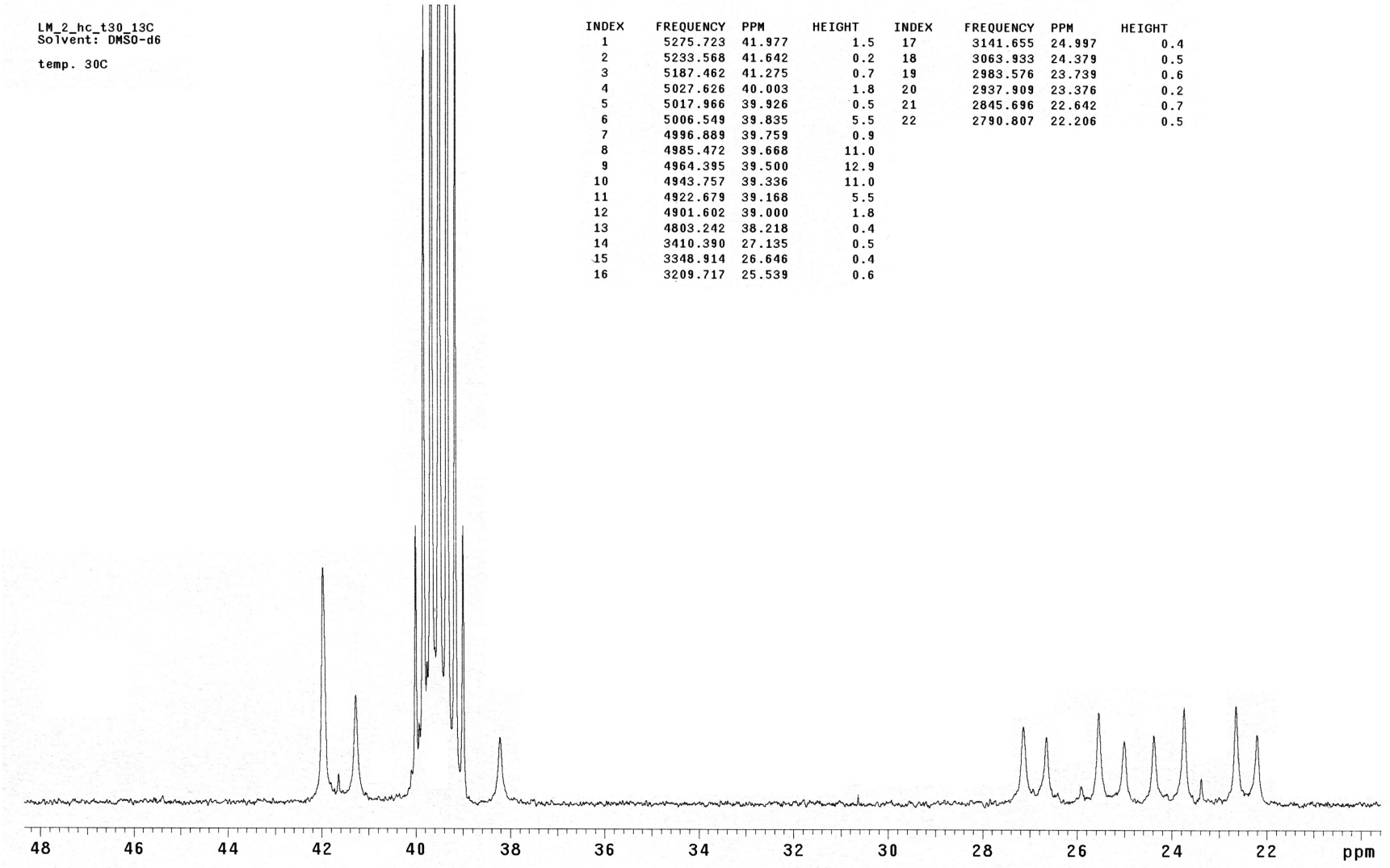
LM_2_hc_t30_13C
Solvent: DMSO-d6

temp. 30C

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	22010.149	175.127	0.4	17	14598.875	116.158	1.1
2	21985.559	174.932	0.7	18	14579.994	116.008	0.7
3	21329.092	169.708	0.5	19	14128.151	112.413	1.0
4	19337.735	153.864	0.7	20	14095.218	112.151	0.7
5	19117.302	152.110	0.6				
6	18593.885	147.945	1.3				
7	18445.027	146.761	1.6				
8	17589.205	139.951	0.5				
9	17391.606	138.379	0.9				
10	17358.233	138.114	0.6				
11	17311.249	137.740	0.3				
12	17215.523	136.978	2.4				
13	15607.069	124.180	0.9				
14	15578.966	123.957	0.6				
15	15324.722	121.934	0.9				
16	15278.615	121.567	0.5				

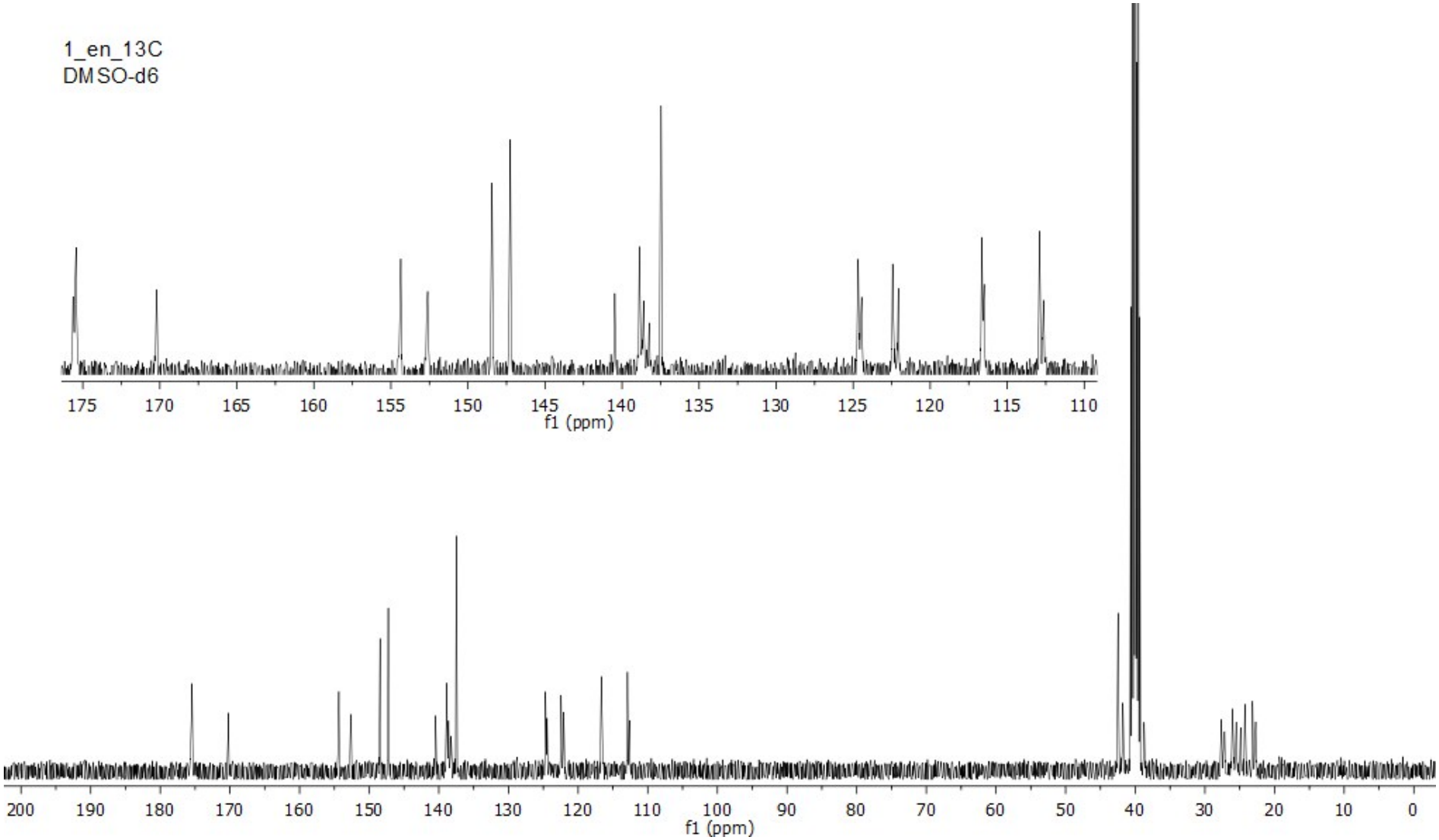


The fragment of ^{13}C-NMR spectrum of **1-rac**.



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	5275.723	41.977	1.5	17	3141.655	24.997	0.4
2	5233.568	41.642	0.2	18	3063.933	24.379	0.5
3	5187.462	41.275	0.7	19	2983.576	23.739	0.6
4	5027.626	40.003	1.8	20	2937.909	23.376	0.2
5	5017.966	39.926	0.5	21	2845.696	22.642	0.7
6	5006.549	39.835	5.5	22	2790.807	22.206	0.5
7	4996.889	39.759	0.9				
8	4985.472	39.668	11.0				
9	4964.395	39.500	12.9				
10	4943.757	39.336	11.0				
11	4922.679	39.168	5.5				
12	4901.602	39.000	1.8				
13	4803.242	38.218	0.4				
14	3410.390	27.135	0.5				
15	3348.914	26.646	0.4				
16	3209.717	25.539	0.6				

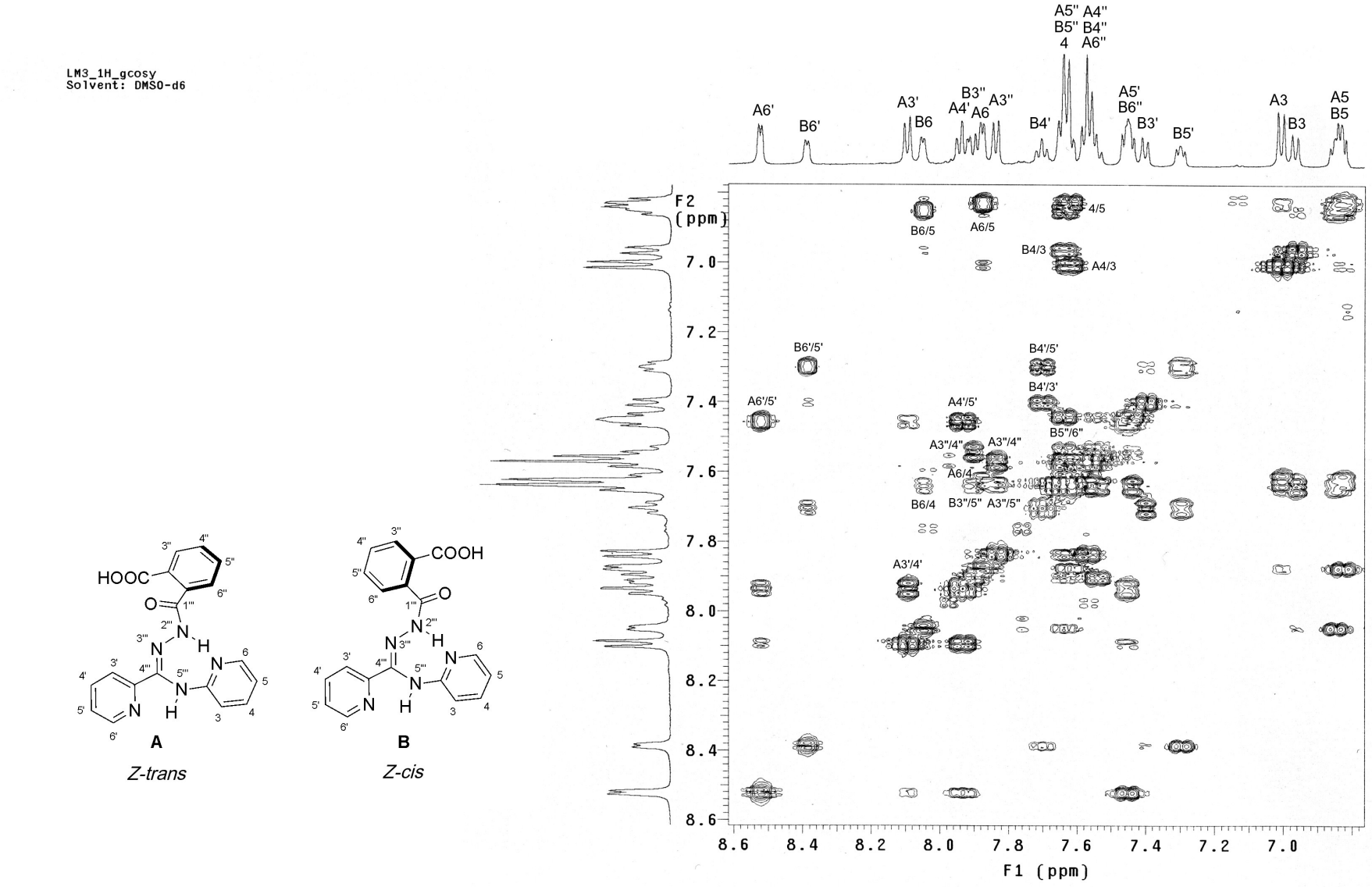
The fragment of ^{13}C-NMR spectrum of **1-rac**.



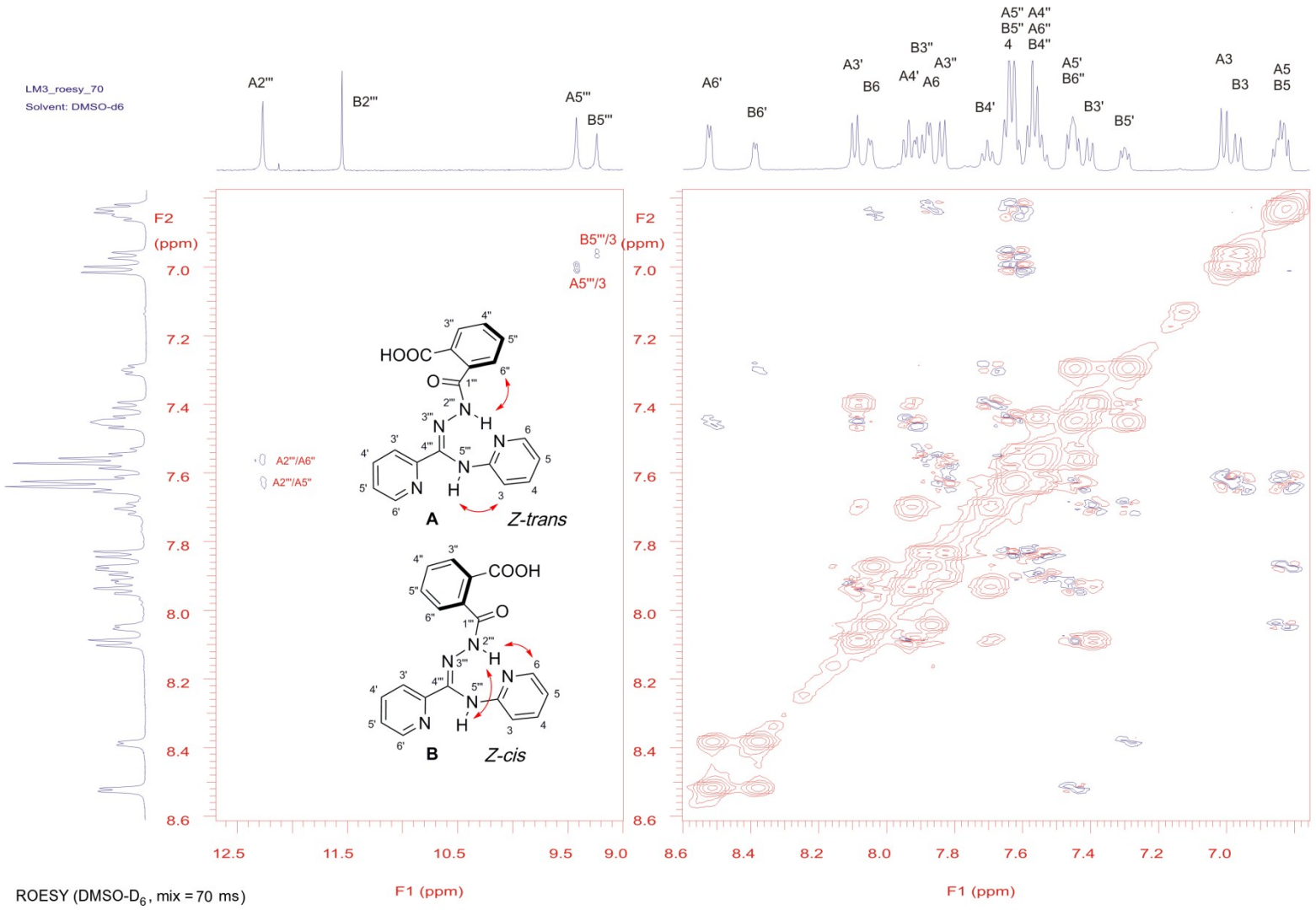
^{13}C-NMR spectrum of compound **1-en**.

1_en_13C
DMSO-d6

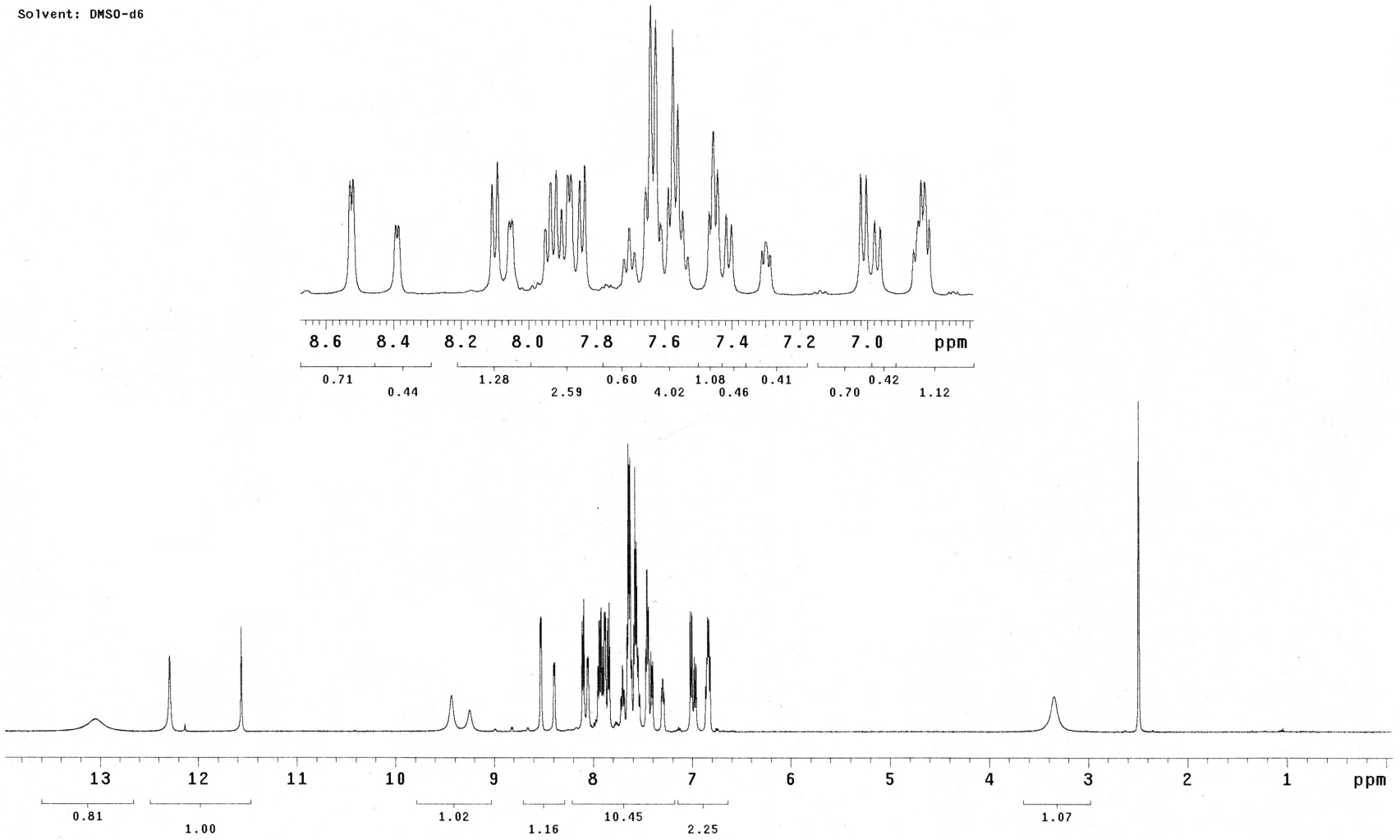
Index	ppm	Hz	Intensity	Index	ppm	Hz	Intensity
1	175.63	17672.3	1299.2	21	42.47	4273.3	4042.4
2	175.44	17653.5	2173.5	22	41.76	4202.5	1699.1
3	170.21	17127.6	1455.4	23	40.61	4086.7	12158.0
4	154.37	15533.4	1826.2	24	40.41	4065.8	36358.2
5	152.61	15356.5	1431.3	25	40.20	4044.8	73435.4
6	148.45	14937.8	3397.4	26	39.99	4023.7	87041.3
7	147.26	14818.1	4174.8	27	39.88	4013.3	1005.7
8	140.47	14134.8	1371.2	28	39.78	4002.8	72890.5
9	138.87	13973.8	2180.3	29	39.57	3981.7	36953.6
10	138.61	13947.7	1234.3	30	39.36	3960.7	12195.8
11	138.24	13910.1	793.2	31	38.71	3895.5	1250.5
12	137.48	13833.6	6088.4	32	27.65	2781.9	1291.7
13	124.68	12545.8	1971.2	33	27.17	2733.8	943.4
14	124.47	12524.2	1235.9	34	26.04	2620.1	1502.9
15	122.44	12320.3	1979.2	35	25.50	2566.4	1154.4
16	122.07	12283.5	1444.6	36	24.88	2503.5	1045.8
17	116.65	11738.1	2243.8	37	24.25	2440.1	1665.9
18	116.51	11724.1	1431.3	38	23.15	2329.2	1700.2
19	112.91	11361.2	2510.6	39	22.70	2284.4	1146.0
20	112.65	11335.0	1218.6				



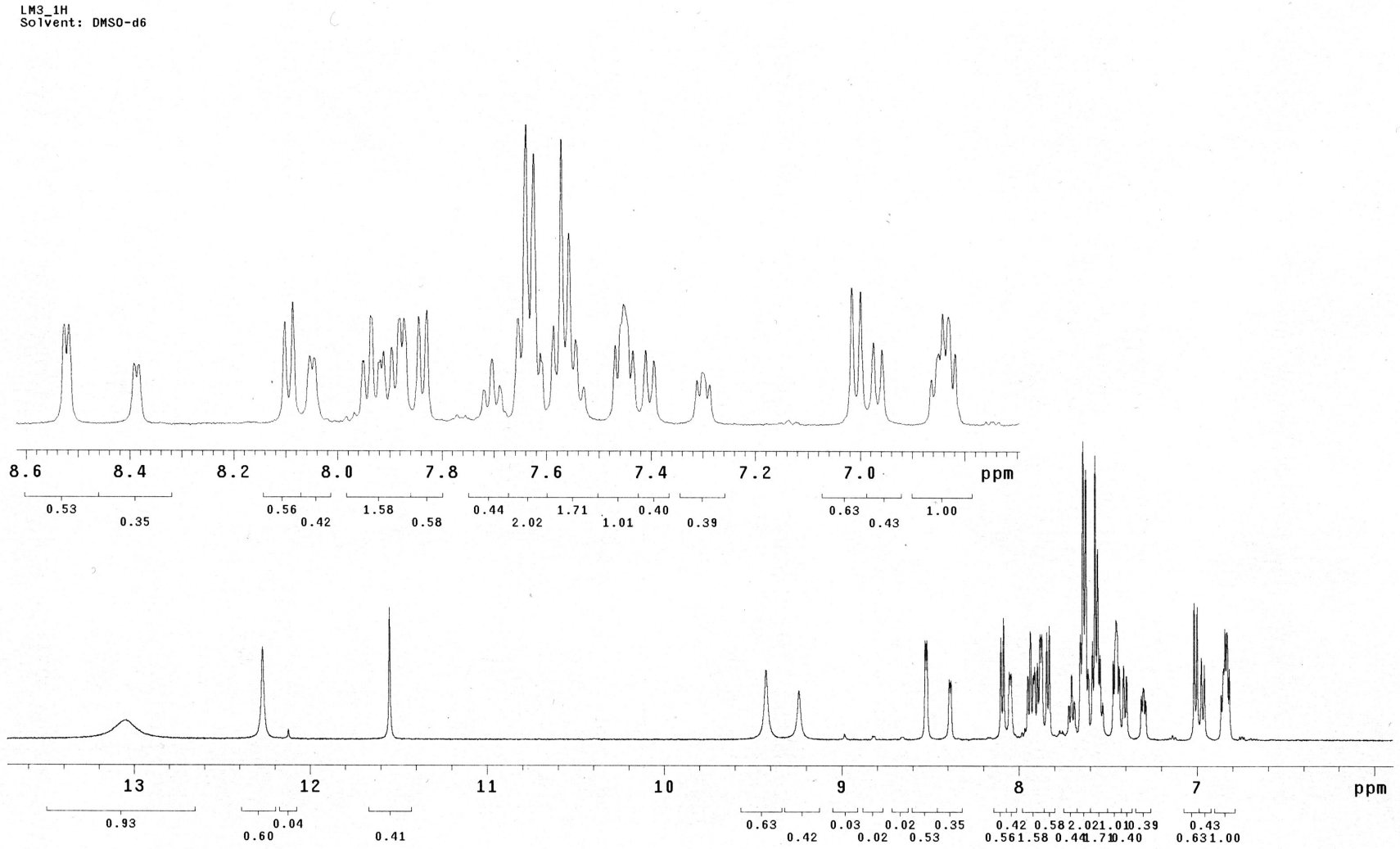
The gCOSY spectrum of compound **2**.



The ROESY spectrum of compound **2**.



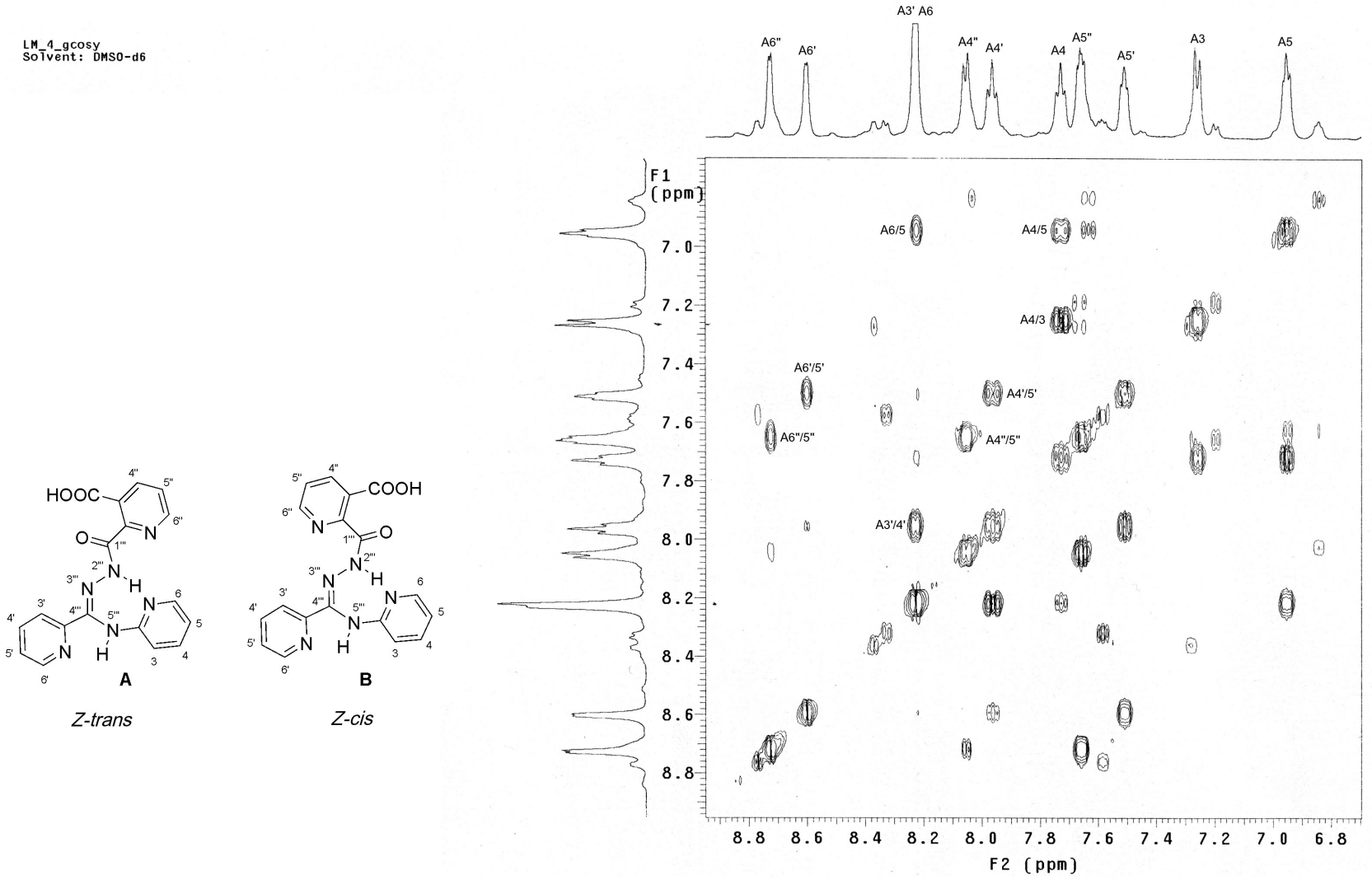
[1]H-NMR spectrum of compound **2**.



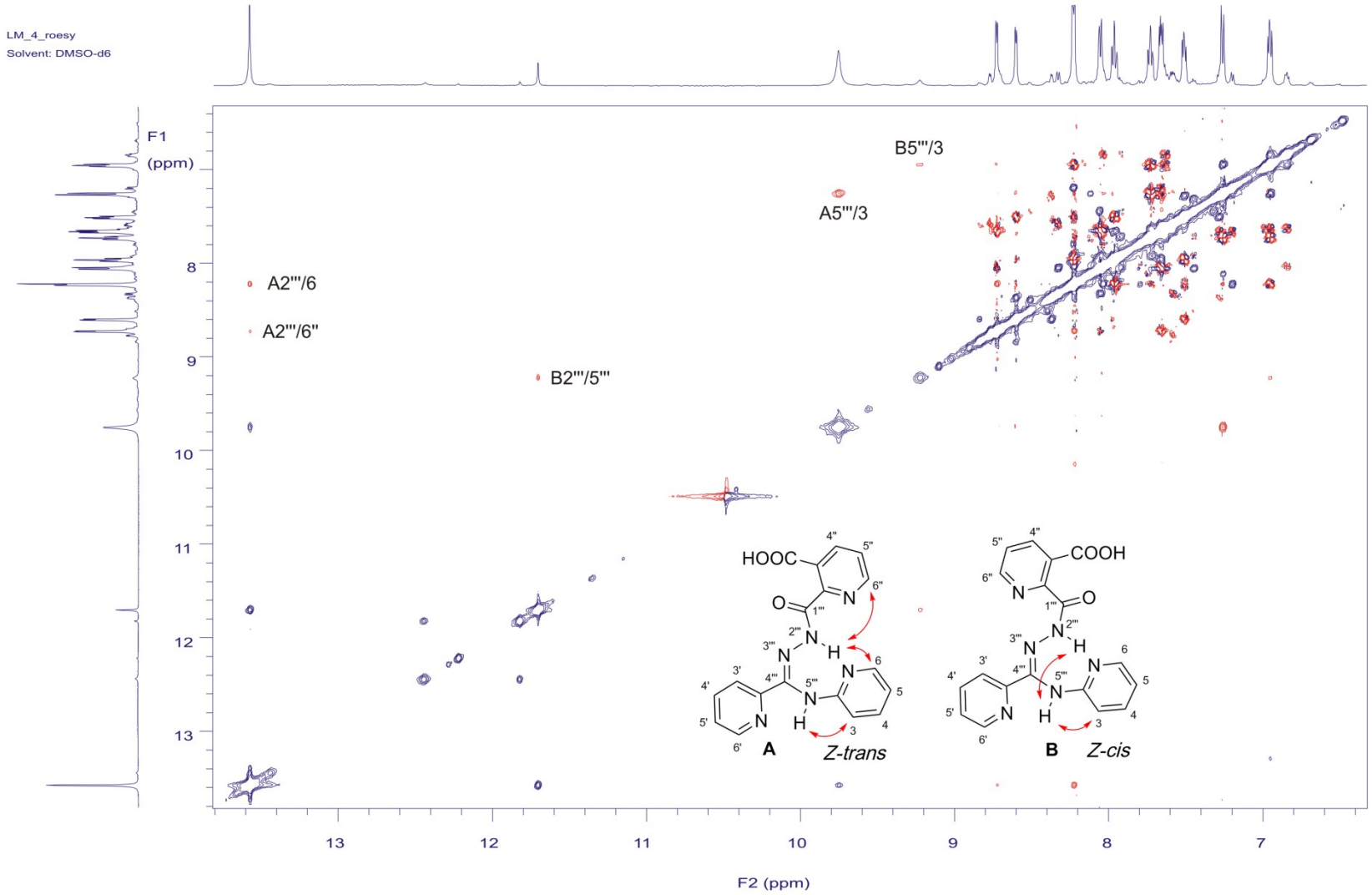
^{1}H-NMR spectrum of compound **2**.

LM3_1H
Solvent: DMSO-d6

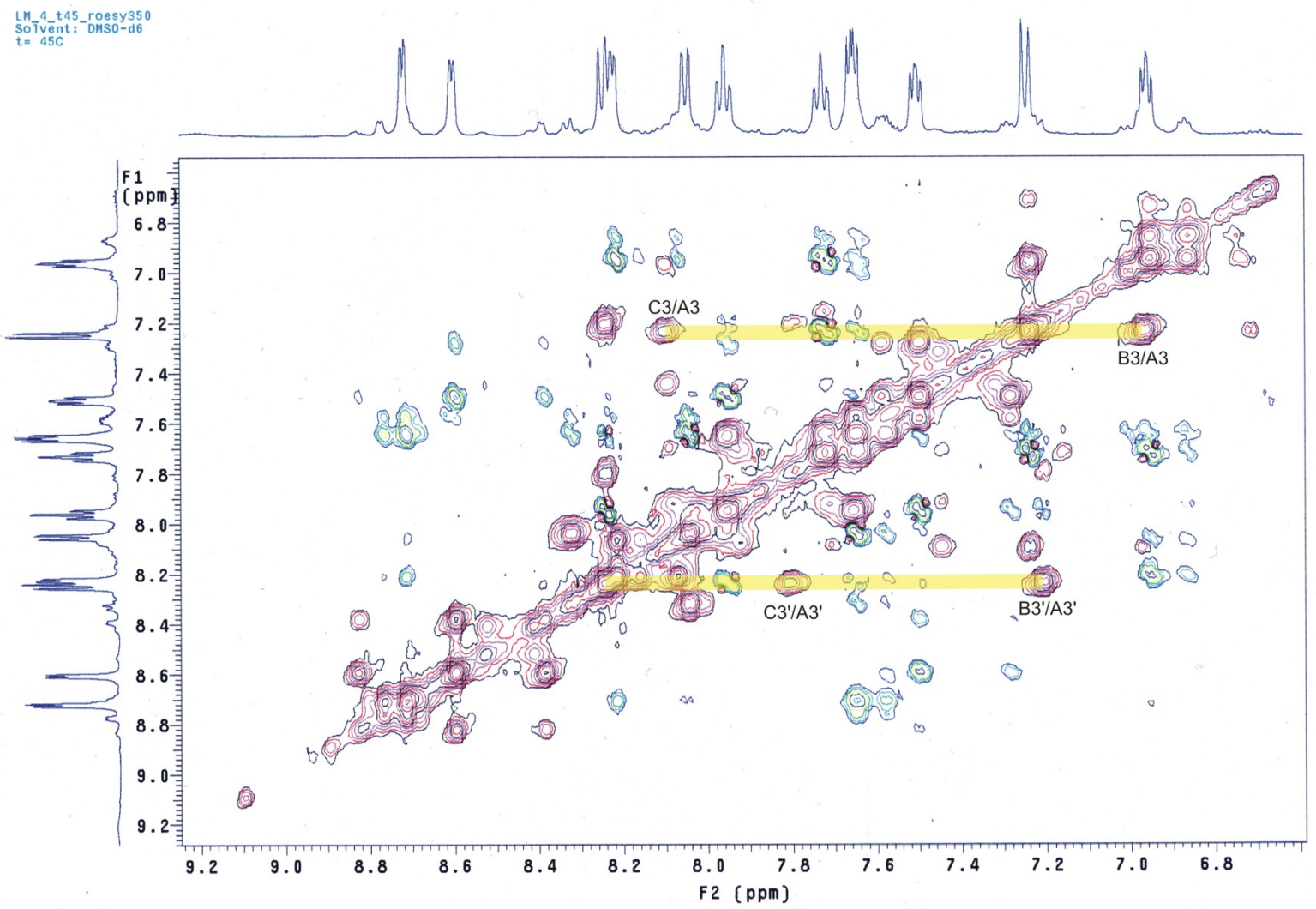
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	6519.264	13.043	1.2	28	3876.036	7.755	0.6	55	3419.465	6.841	6.7
2	6133.010	12.270	5.6	29	3857.969	7.719	2.1	56	3414.094	6.831	6.5
3	6059.763	12.124	0.6	30	3850.644	7.704	4.0	57	3407.746	6.818	4.3
4	5772.636	11.549	8.0	31	3843.319	7.689	2.4	58	1663.987	3.329	21.7
5	4710.071	9.423	4.2	32	3825.252	7.653	6.4	59	1245.993	2.493	15.9
6	4618.269	9.240	3.0	33	3817.927	7.639	18.1	60	1244.528	2.490	20.8
7	4490.331	8.984	0.3	34	3810.602	7.624	16.3				
8	4261.802	8.527	6.0	35	3804.254	7.611	4.3				
9	4257.407	8.518	6.0	36	3791.558	7.586	6.0				
10	4194.415	8.392	3.7	37	3784.234	7.571	17.2				
11	4190.020	8.383	3.6	38	3776.909	7.556	11.6				
12	4049.387	8.102	6.2	39	3770.561	7.544	5.1				
13	4041.574	8.086	7.4	40	3762.748	7.528	2.3				
14	4025.459	8.054	4.1	41	3732.961	7.469	4.8				
15	4021.064	8.045	4.0	42	3724.660	7.452	7.3				
16	3990.301	7.983	0.5	43	3715.870	7.434	4.5				
17	3982.000	7.967	0.7	44	3703.662	7.410	4.5				
18	3973.210	7.949	3.8	45	3695.361	7.393	3.9				
19	3966.374	7.936	6.6	46	3654.343	7.311	2.7				
20	3957.584	7.918	3.9	47	3648.971	7.301	3.2				
21	3954.166	7.911	4.4	48	3642.135	7.287	2.4				
22	3946.353	7.895	4.7	49	3506.385	7.015	8.3				
23	3938.540	7.880	6.4	50	3498.083	6.999	8.1				
24	3934.633	7.872	6.4	51	3485.876	6.974	5.0				
25	3920.472	7.844	6.5	52	3477.574	6.958	4.5				
26	3912.659	7.828	6.9	53	3430.208	6.863	2.8				
27	3883.849	7.770	0.6	54	3423.372	6.849	4.3				



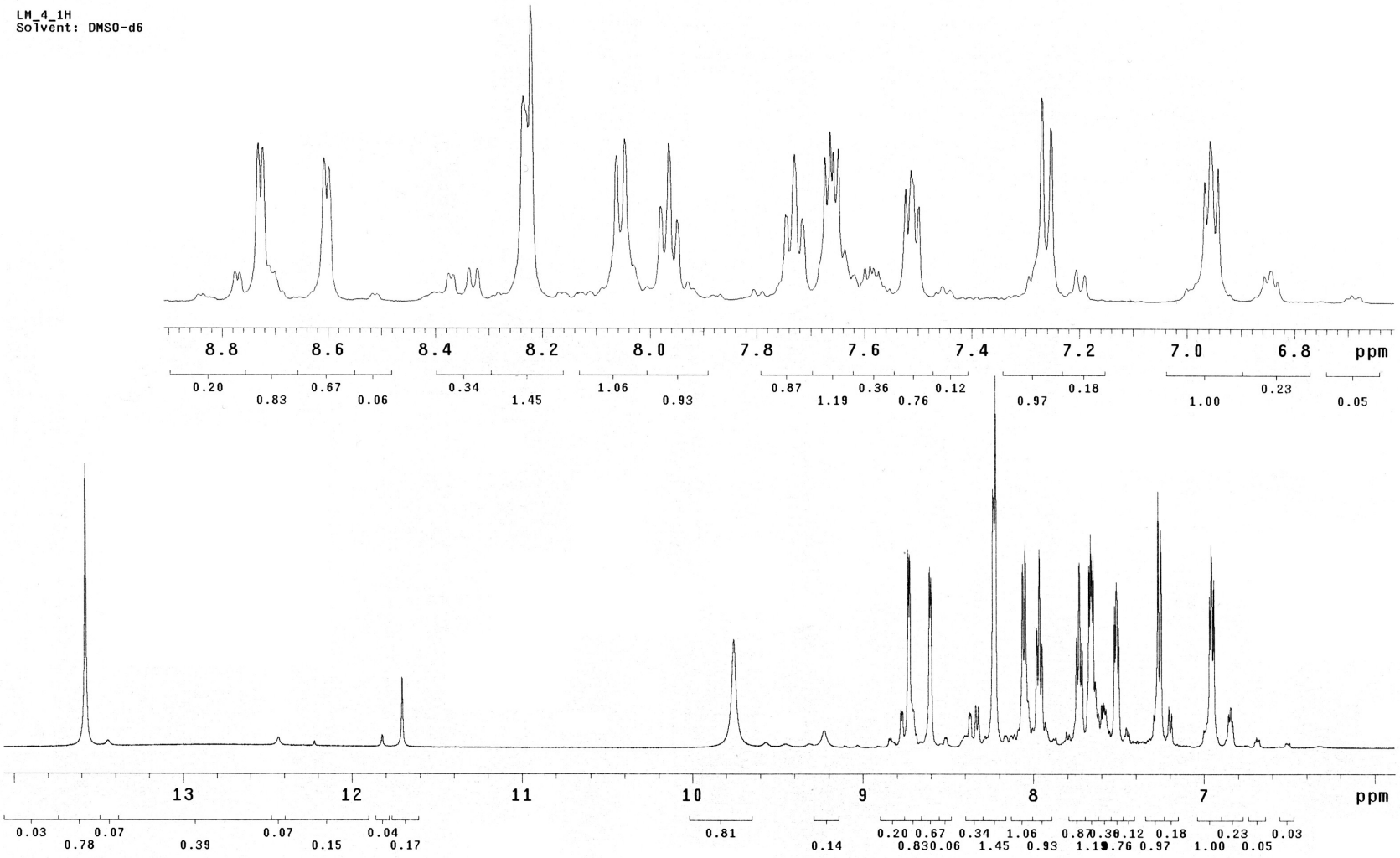
The gCOSY spectrum of compound **3**.



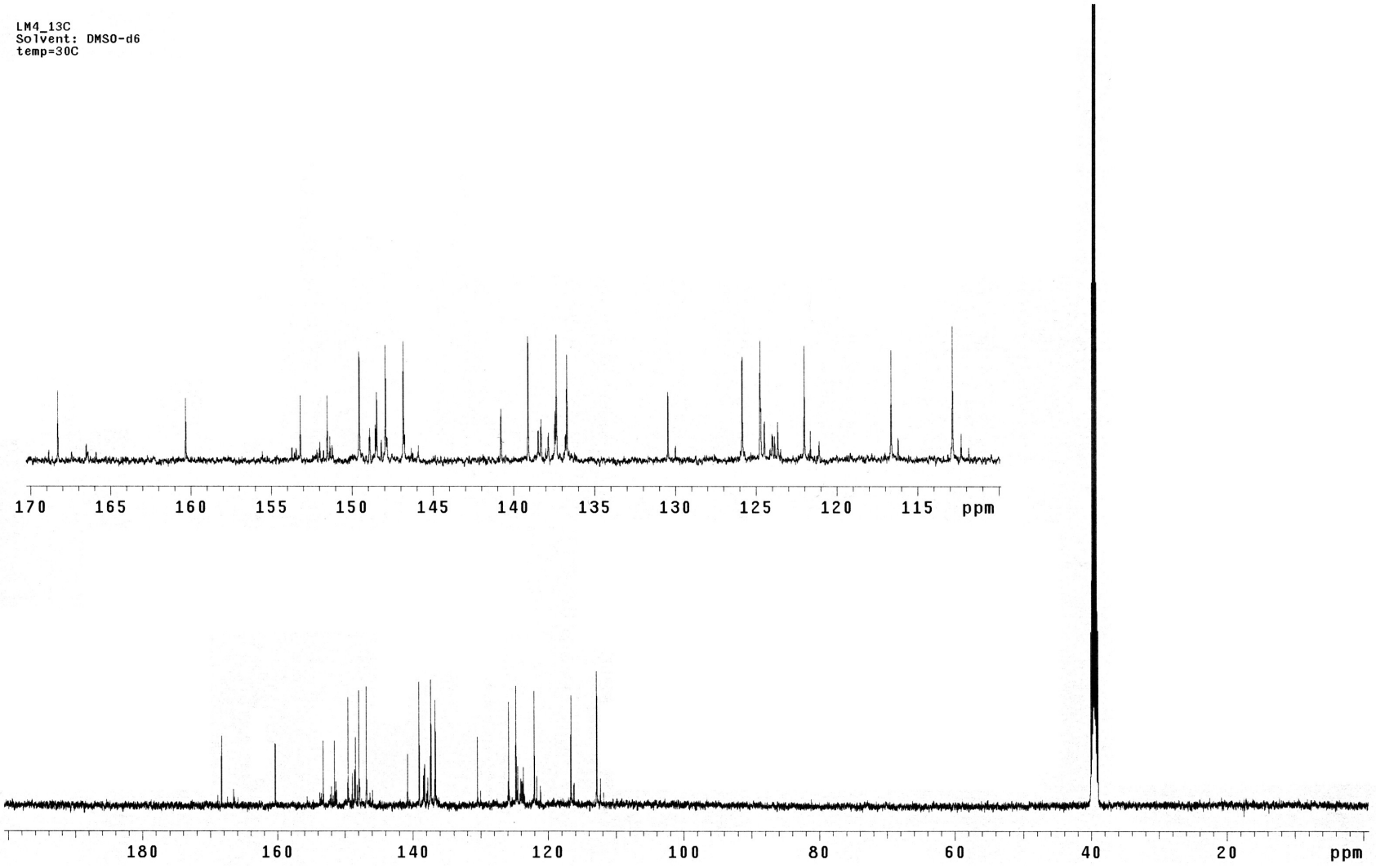
The ROESY spectrum of compound **3**.



The fragment of ROESY spectrum of compound **3**.



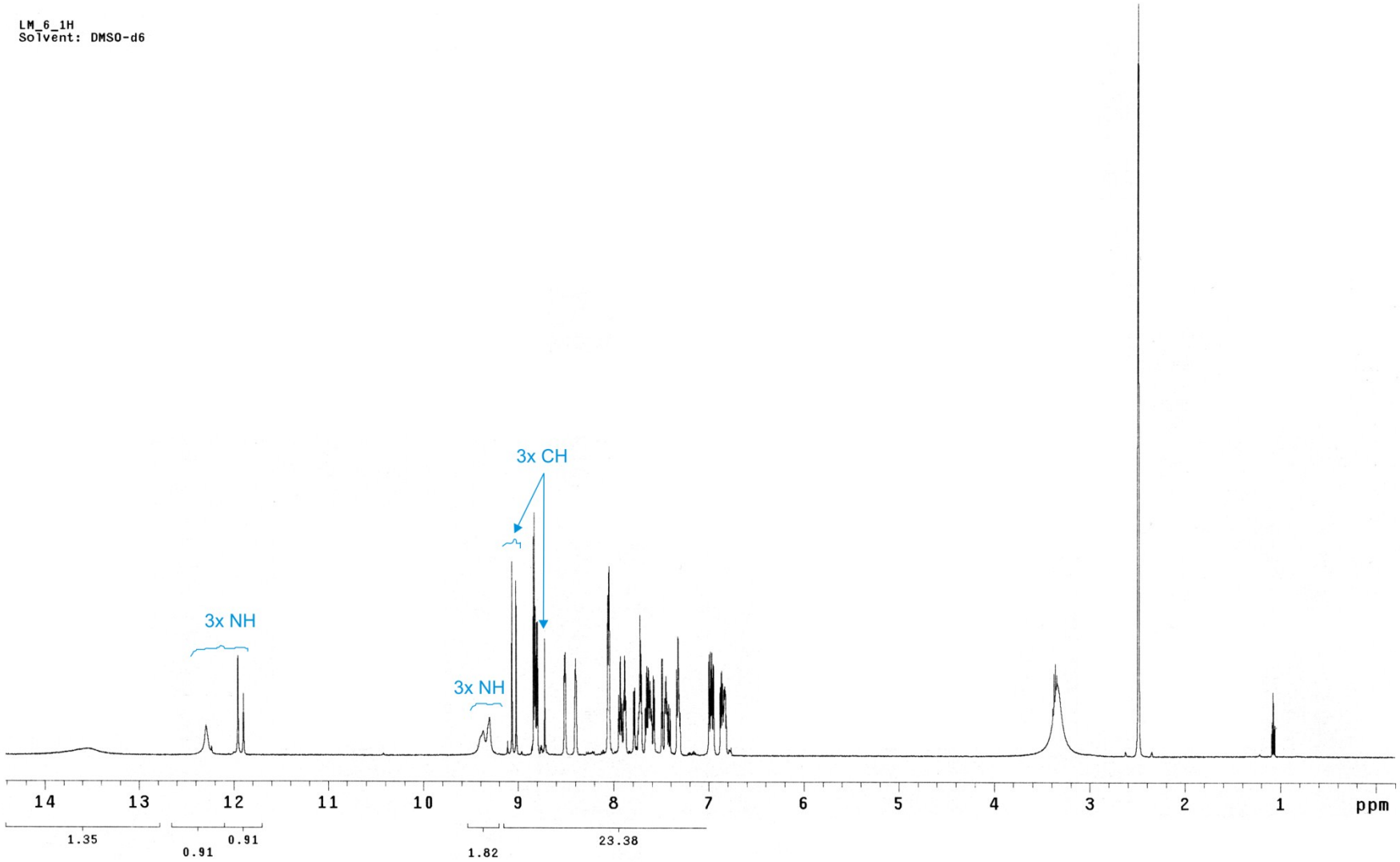
[1]H-NMR spectrum of compound **3**.



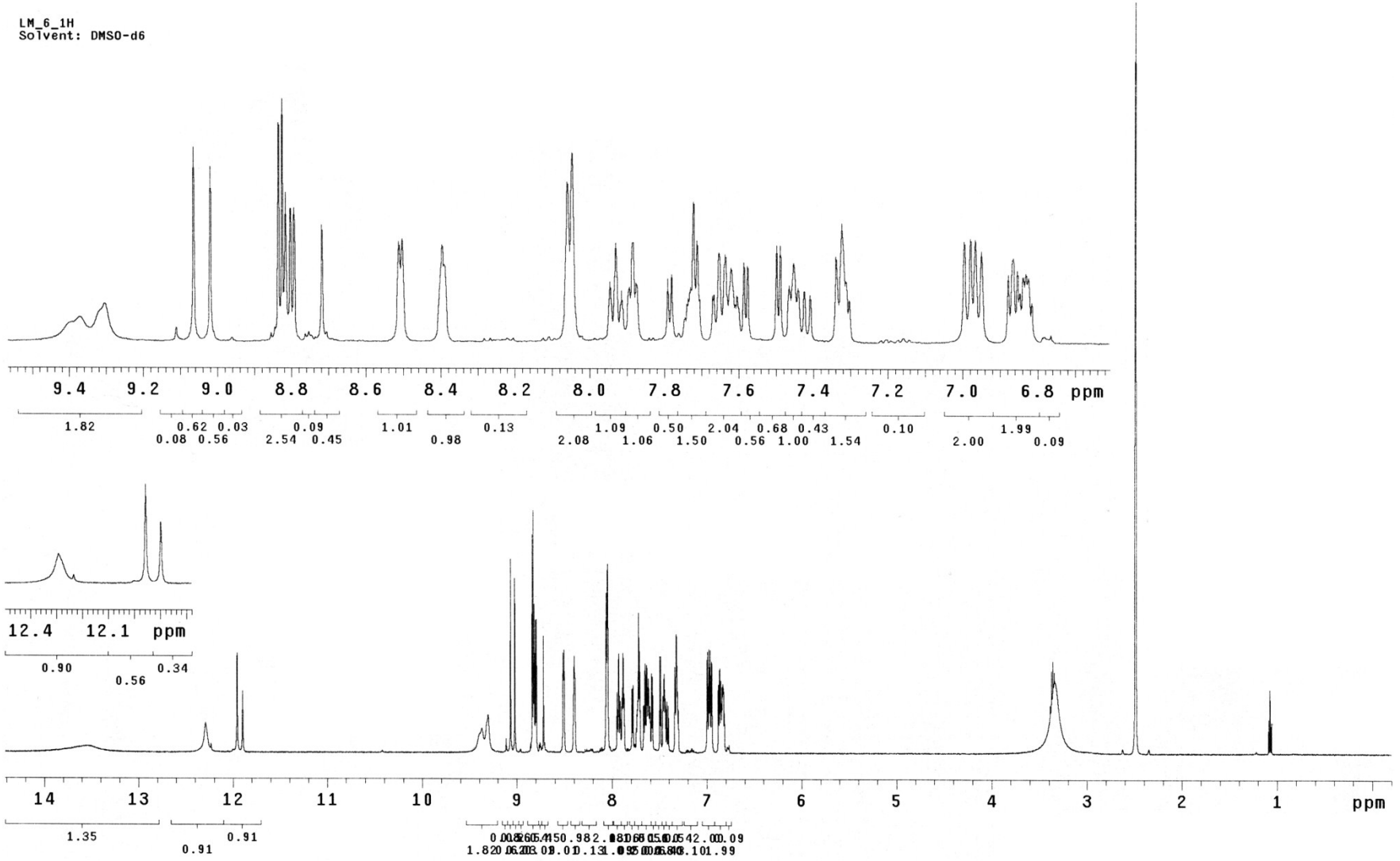
^{13}C-NMR spectrum of compound **3**.

LM4_13C
Solvent: DMSO-d6
temp=30C

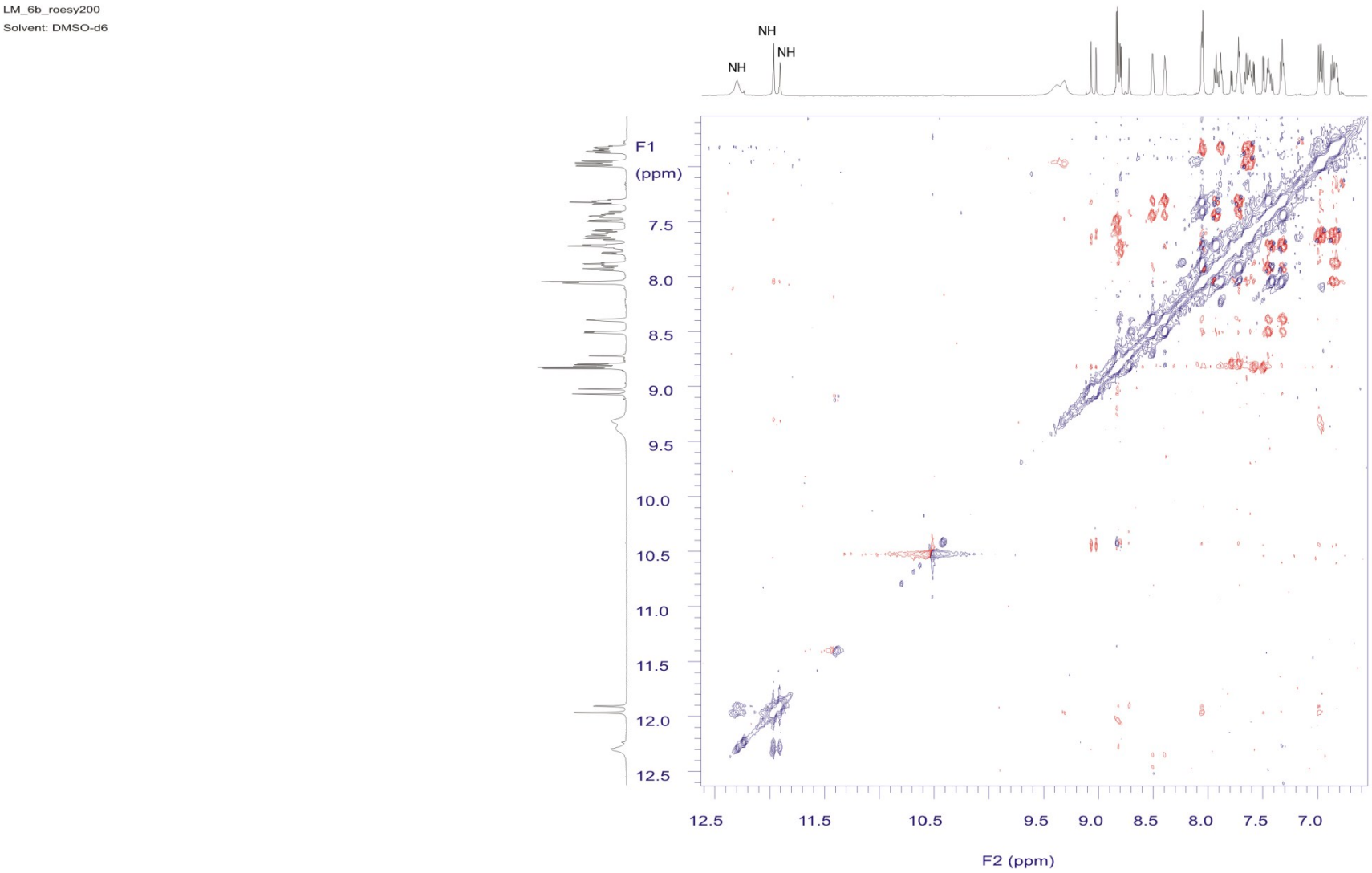
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	21151.692	168.297	0.4	28	16395.268	130.452	0.4
2	20928.625	166.522	0.1	29	16336.867	129.987	0.1
3	20148.768	160.317	0.4	30	15813.889	125.826	0.6
4	19318.853	153.714	0.1	31	15677.326	124.739	0.7
5	19252.987	153.189	0.4	32	15643.954	124.474	0.2
6	19100.616	151.977	0.1	33	15583.796	123.995	0.2
7	19042.215	151.512	0.4	34	15563.597	123.834	0.1
8	19021.577	151.348	0.1	35	15540.763	123.653	0.2
9	19003.573	151.205	0.1	36	15333.504	122.003	0.7
10	18792.801	149.528	0.7	37	15286.080	121.626	0.2
11	18713.761	148.899	0.2	38	15219.336	121.095	0.1
12	18667.216	148.529	0.2	39	14658.155	116.630	0.7
13	18657.116	148.448	0.4	40	14601.949	116.183	0.1
14	18621.549	148.165	0.1	41	14182.161	112.843	0.8
15	18589.933	147.914	0.7	42	14114.978	112.308	0.2
16	18452.492	146.820	0.7	43	14056.137	111.840	0.1
17	18389.699	146.321	0.1	44	5027.626	40.003	1.0
18	18336.567	145.898	0.1	45	5006.549	39.835	3.1
19	17691.517	140.765	0.3	46	4985.472	39.668	6.2
20	17478.549	139.071	0.7	47	4964.395	39.500	7.4
21	17399.949	138.445	0.2	48	4943.318	39.332	6.3
22	17378.872	138.278	0.2	49	4922.679	39.168	3.1
23	17321.348	137.820	0.2	50	4901.602	39.000	1.0
24	17269.973	137.411	0.3	51	2203.280	17.531	-0.1
25	17259.434	137.327	0.8				
26	17189.177	136.768	0.2				
27	17178.199	136.681	0.6				



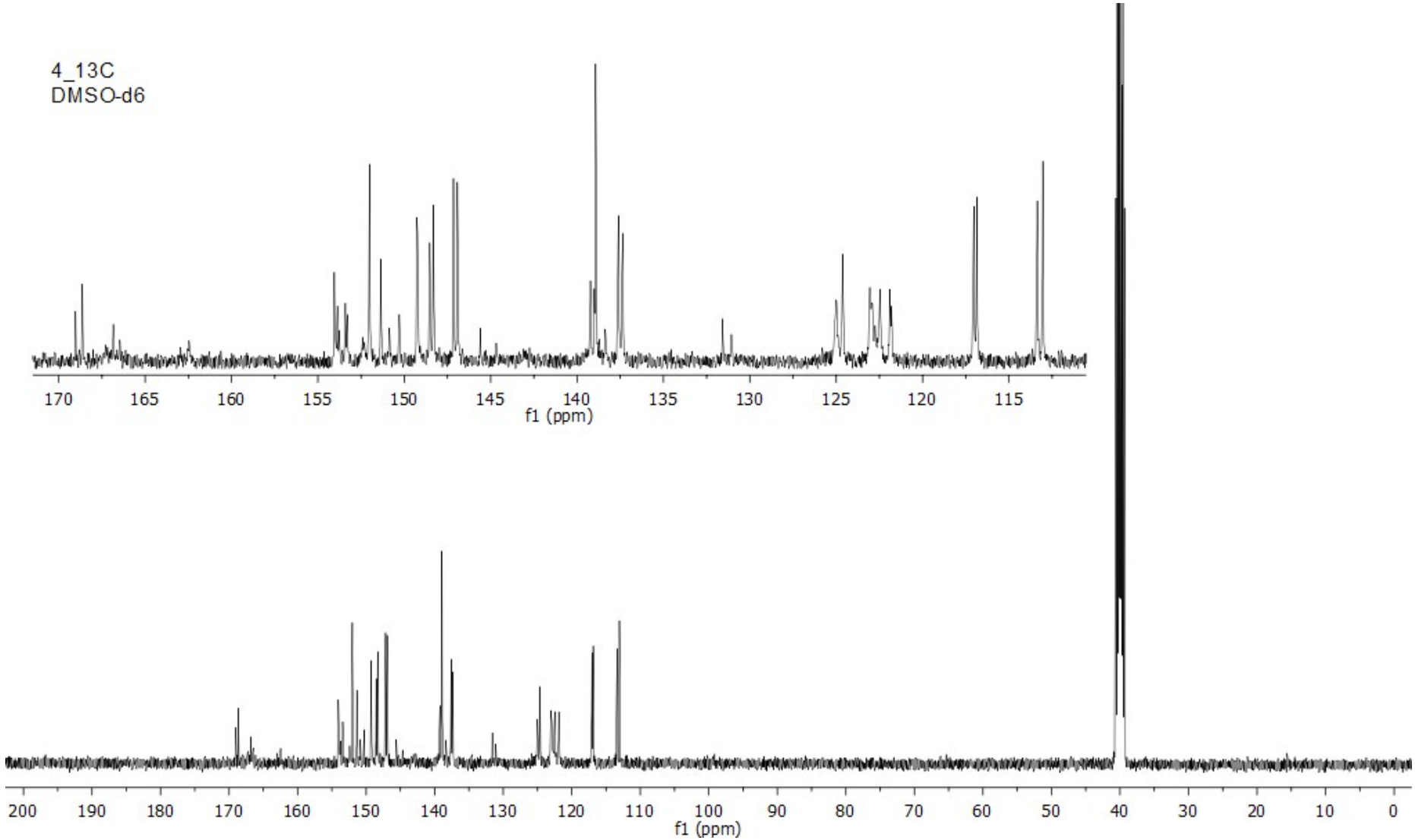
^{1}H-NMR spectrum of compound **4**.



[1]H-NMR spectrum of compound **4**.



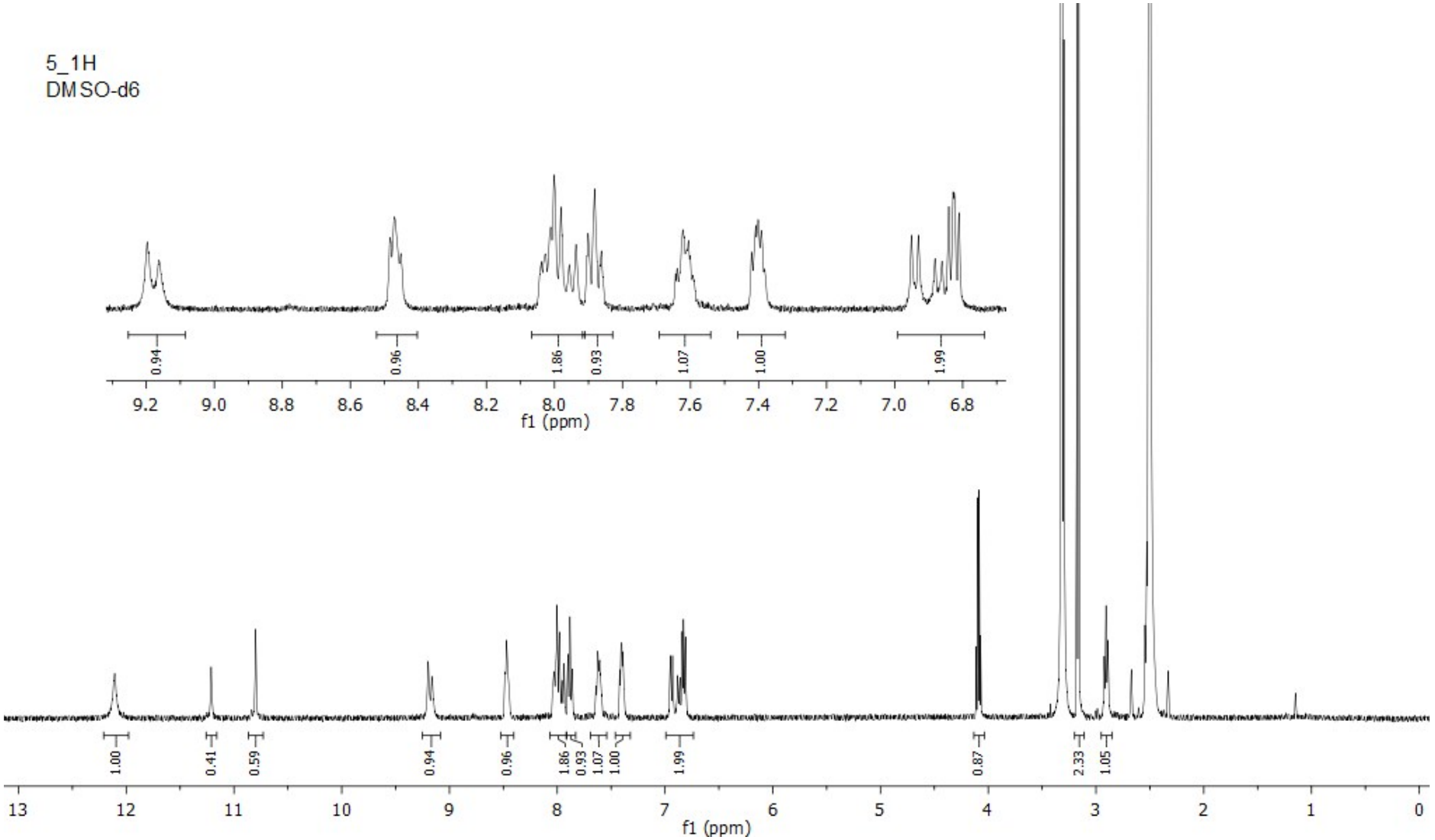
The ROESY spectrum of compound **4**.



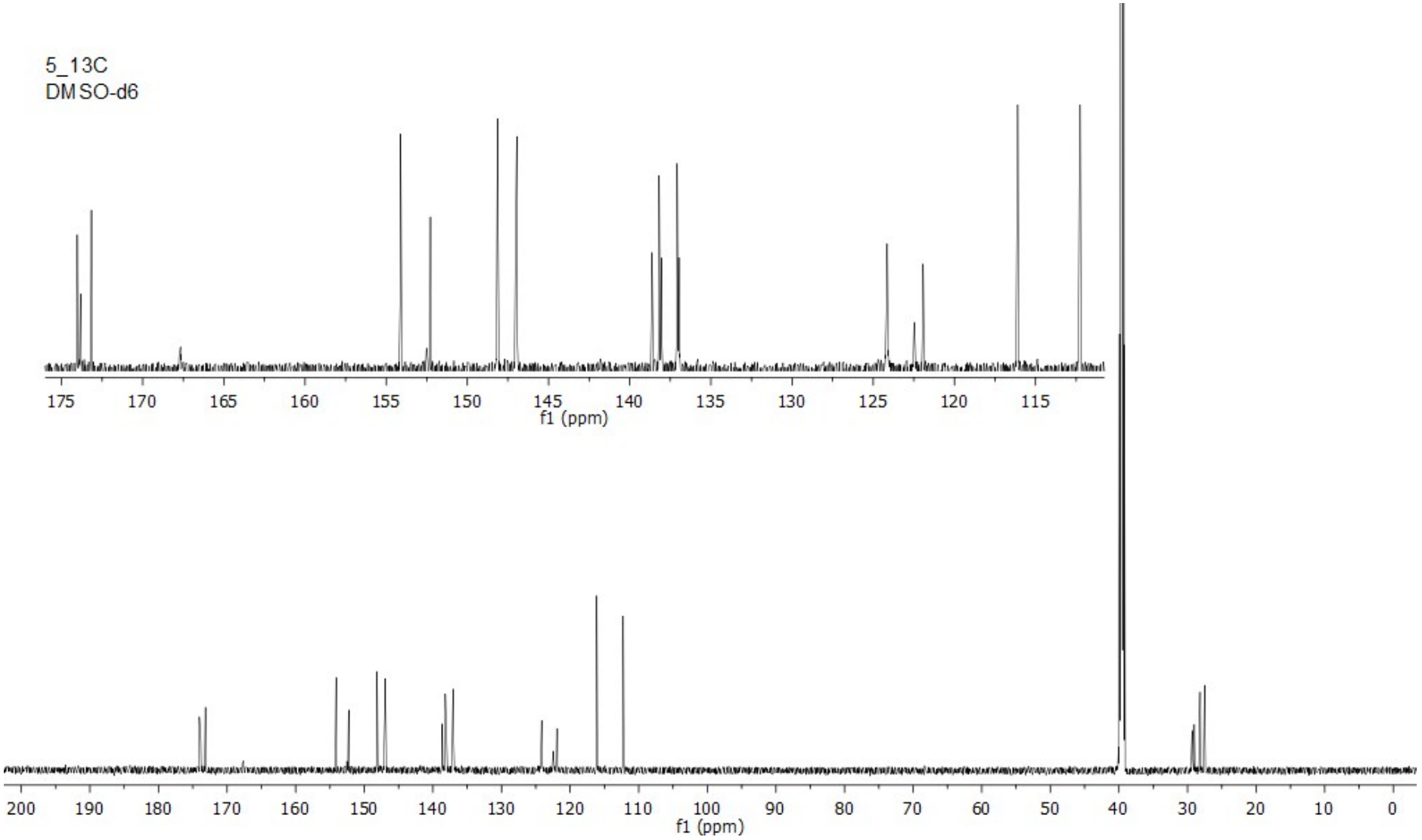
^{13}C-NMR spectrum of compound **4**.

4_13C
DMSO-d6

Index	ppm	Hz	Intensity	Index	ppm	Hz	Intensity
1	169.03	17008.0	1974.2	26	137.64	13849.8	2351.5
2	168.63	16968.3	3221.4	27	137.60	13846.2	5673.6
3	166.84	16788.2	1194.4	28	137.41	13826.8	3035.6
4	162.47	16348.6	789.5	29	137.35	13820.7	5034.5
5	154.05	15501.0	3607.0	30	131.58	13240.2	1774.2
6	153.99	15494.7	2223.4	31	131.06	13188.3	1114.1
7	153.87	15483.3	2206.8	32	125.00	12578.5	2418.1
8	153.76	15471.6	1228.9	33	124.62	12540.1	4474.5
9	153.41	15436.4	2381.2	34	123.05	12381.9	2573.4
10	153.30	15425.7	1867.9	35	122.46	12322.7	2476.9
11	152.38	15333.5	1000.7	36	121.89	12265.3	2840.2
12	152.01	15296.0	8061.6	37	121.80	12255.9	1766.7
13	151.36	15230.3	4345.8	38	117.03	11776.3	6056.8
14	150.87	15181.3	1251.6	39	116.86	11759.1	6687.3
15	150.29	15122.6	1901.6	40	113.37	11407.4	6787.2
16	149.26	15019.4	5314.5	41	113.04	11374.6	8162.2
17	148.53	14945.3	4886.1	42	40.60	4084.9	33381.0
18	148.31	14923.5	6433.2	43	40.39	4063.9	100828.1
19	147.15	14807.2	7432.5	44	40.18	4042.8	203715.7
20	146.93	14784.3	7260.5	45	39.97	4021.9	235783.7
21	145.60	14650.6	1421.9	46	39.76	4000.8	201924.6
22	139.22	14009.2	3171.3	47	39.63	3988.2	3219.9
23	139.00	13986.9	2193.8	48	39.55	3979.9	101736.9
24	138.92	13978.8	11894.9	49	39.34	3959.0	32579.8
25	138.37	13922.8	1113.9				



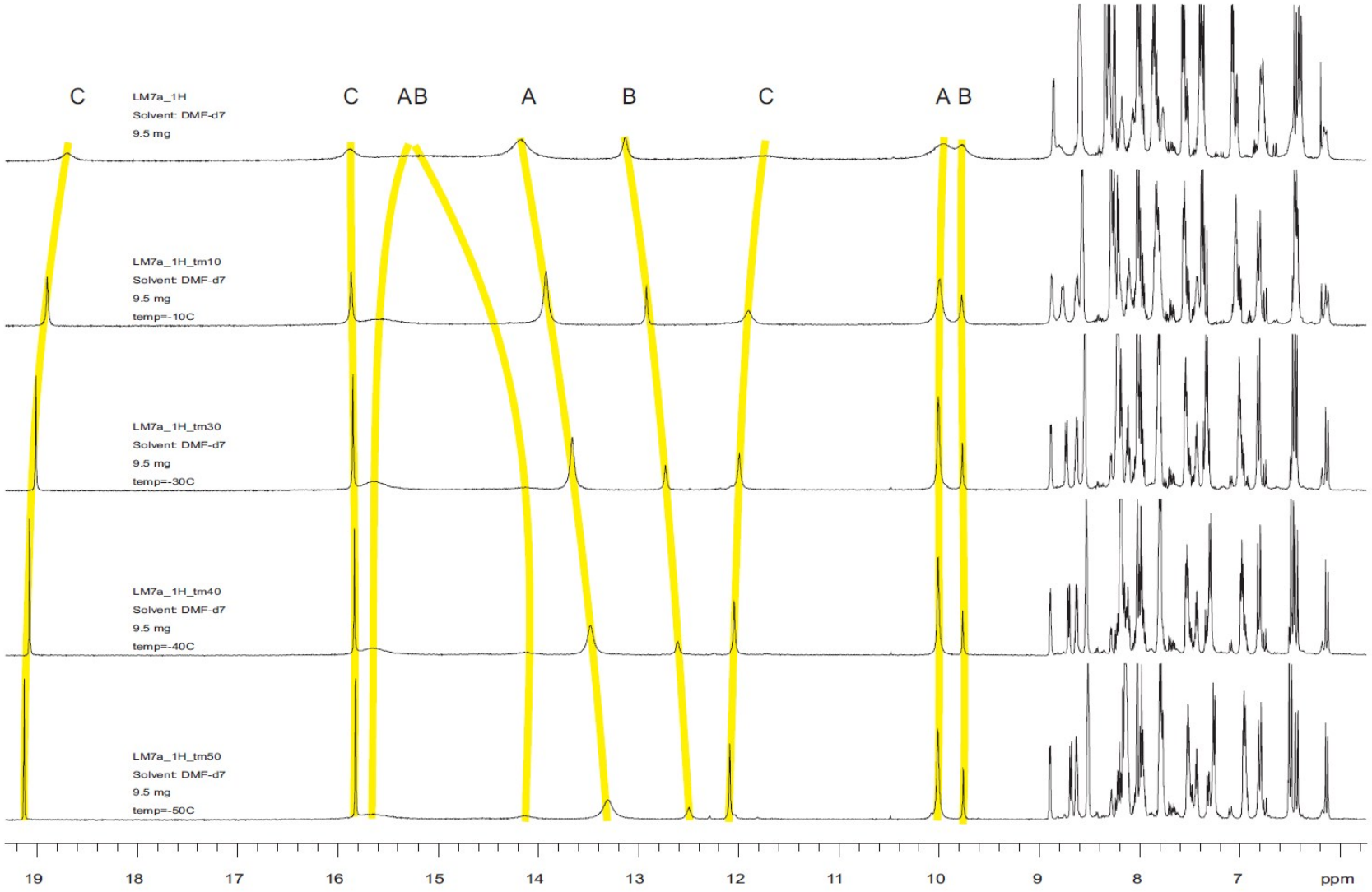
[1]H-NMR spectrum of compound **5**.



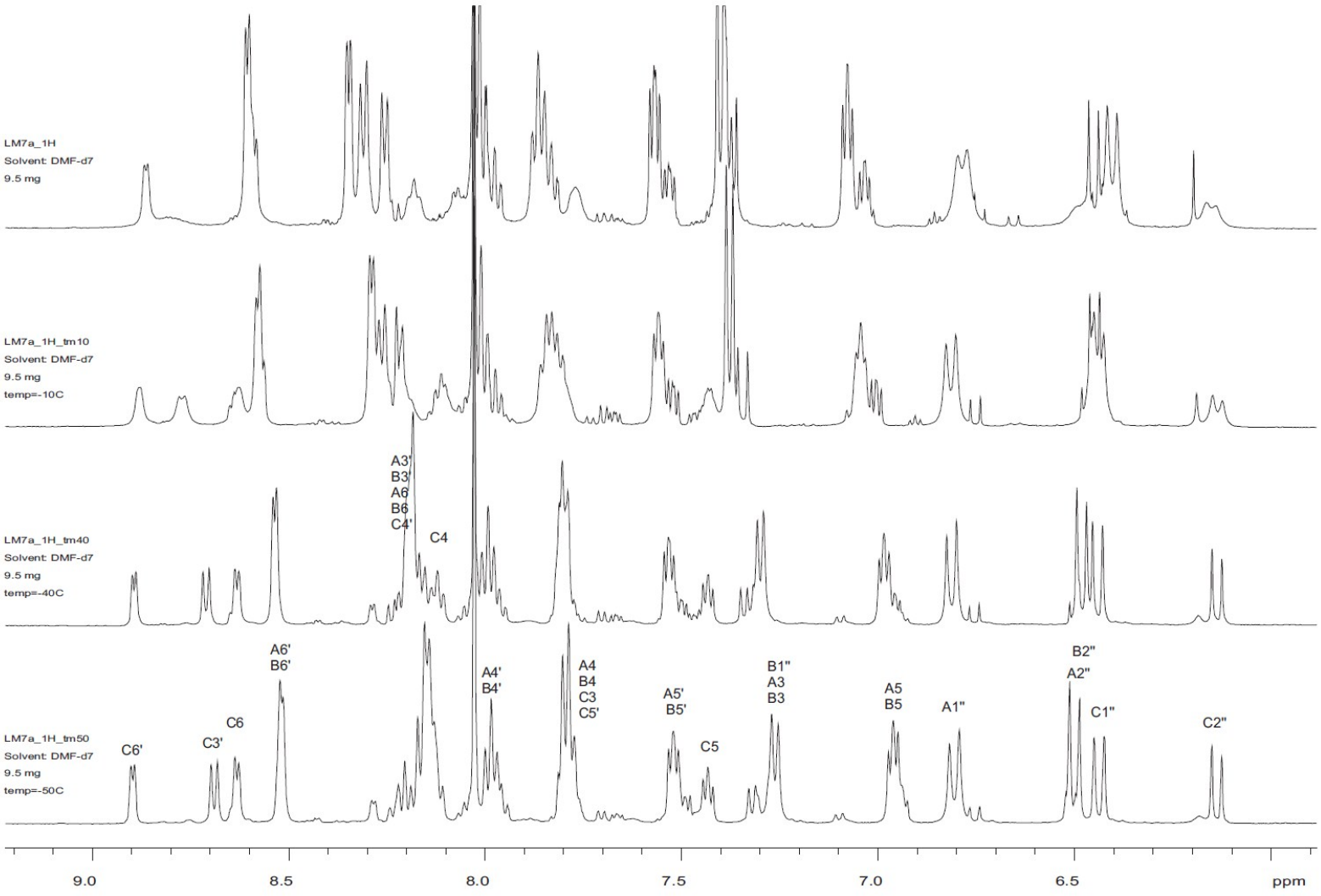
^{13}C-NMR spectrum of compound **5**.

5_13C
DMSO-d6

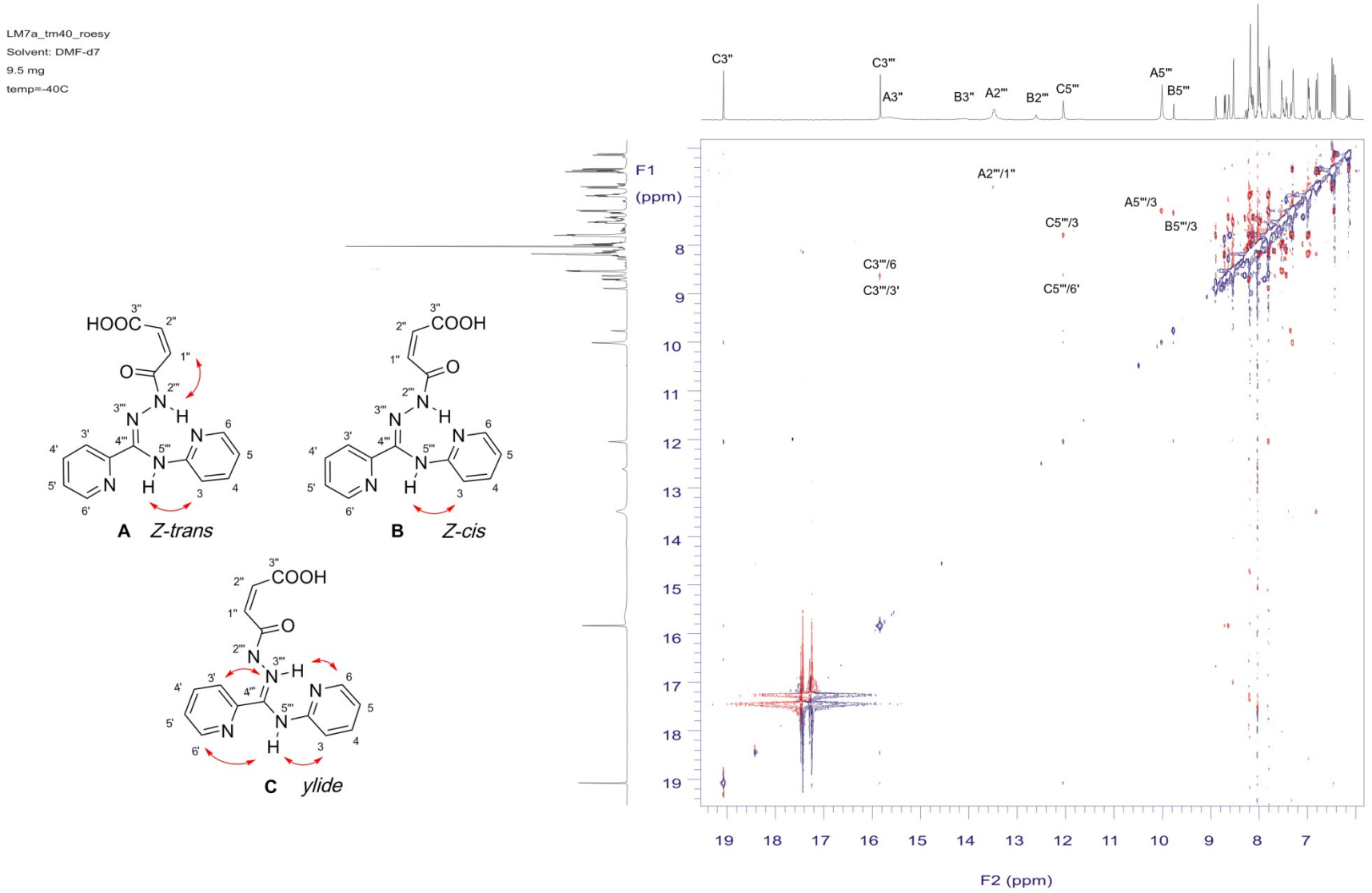
Index	ppm	Hz	Intensity	Index	ppm	Hz	Intensity
1	174.03	30646.9	1322.5	17	121.92	21470.5	1048.2
2	173.83	30611.1	721.7	18	116.12	20448.0	4214.9
3	173.16	30493.9	1546.8	19	112.27	19770.1	3770.7
4	167.68	29527.9	199.3	20	40.05	7053.4	559.9
5	154.11	27138.8	2212.7	21	39.92	7029.2	10648.4
6	152.28	26816.8	1485.2	22	39.80	7008.1	33293.3
7	148.14	26087.3	2429.8	23	39.68	6987.1	65072.8
8	147.02	25890.6	1240.3	24	39.56	6966.1	76127.6
9	146.96	25879.2	2219.6	25	39.44	6945.1	64891.0
10	138.62	24411.7	1136.3	26	39.32	6924.1	32715.2
11	138.18	24334.3	1862.2	27	39.20	6903.1	10813.2
12	138.05	24311.2	1070.4	28	29.34	5167.5	986.1
13	137.07	24138.1	1899.7	29	29.02	5110.7	1128.0
14	136.96	24119.1	1045.5	30	28.19	4963.6	1959.7
15	124.14	21861.5	1139.2	31	27.50	4843.6	2122.5
16	122.46	21566.1	442.3				



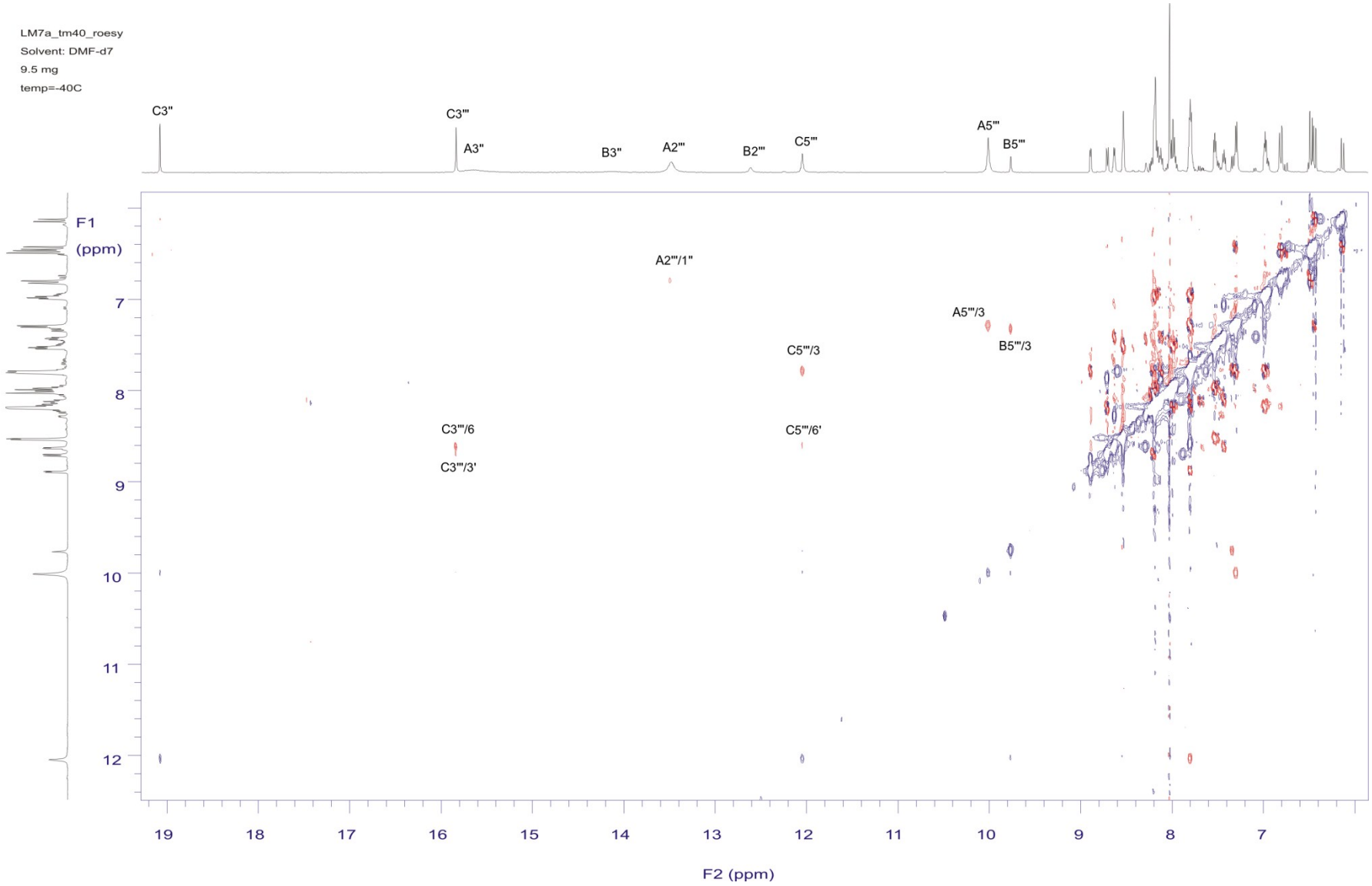
^{1}H-NMR spectrum of compound **6** acquired at various temperatures.



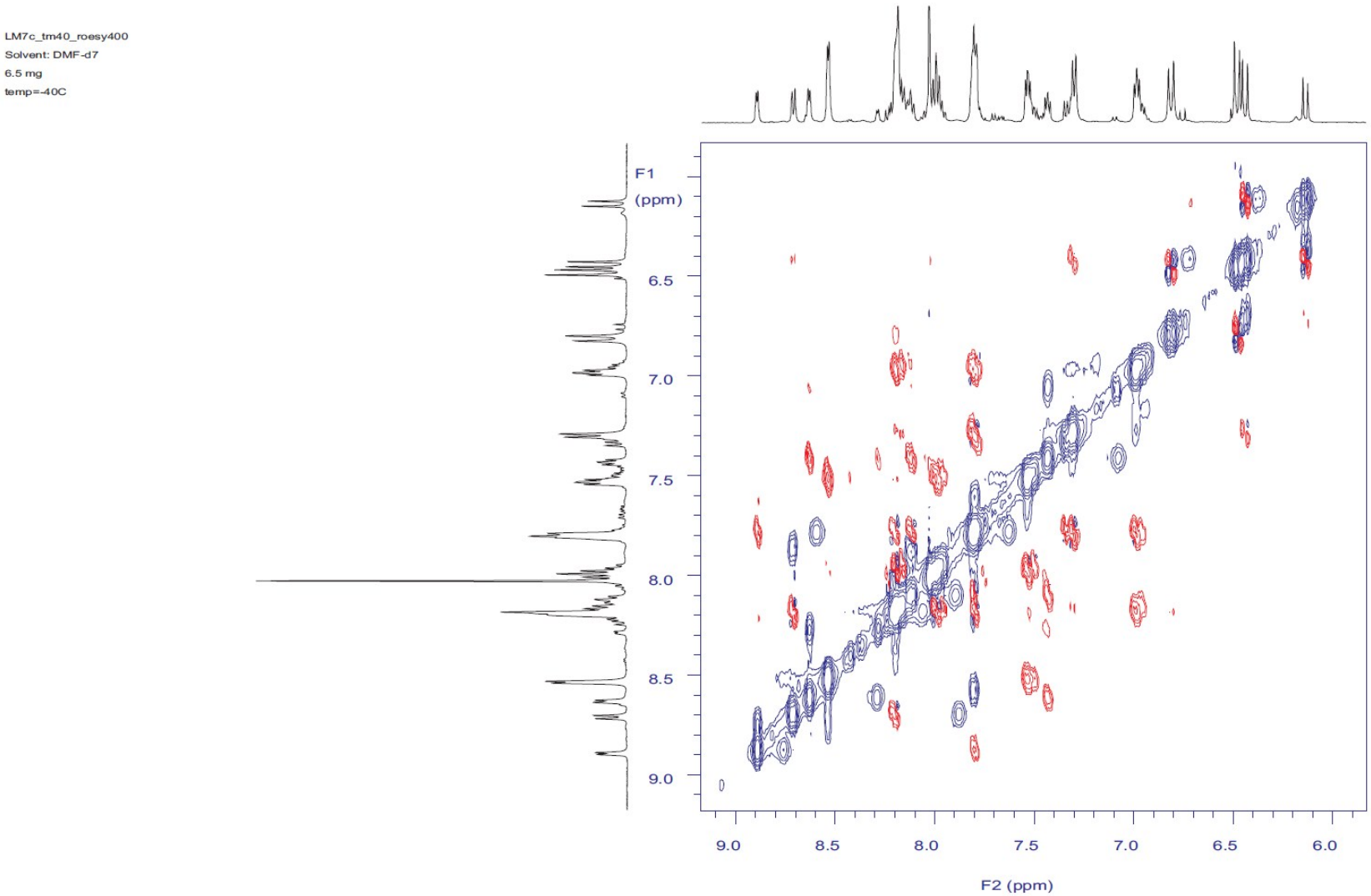
^{1}H-NMR spectrum of compound **6** acquired at various temperatures.



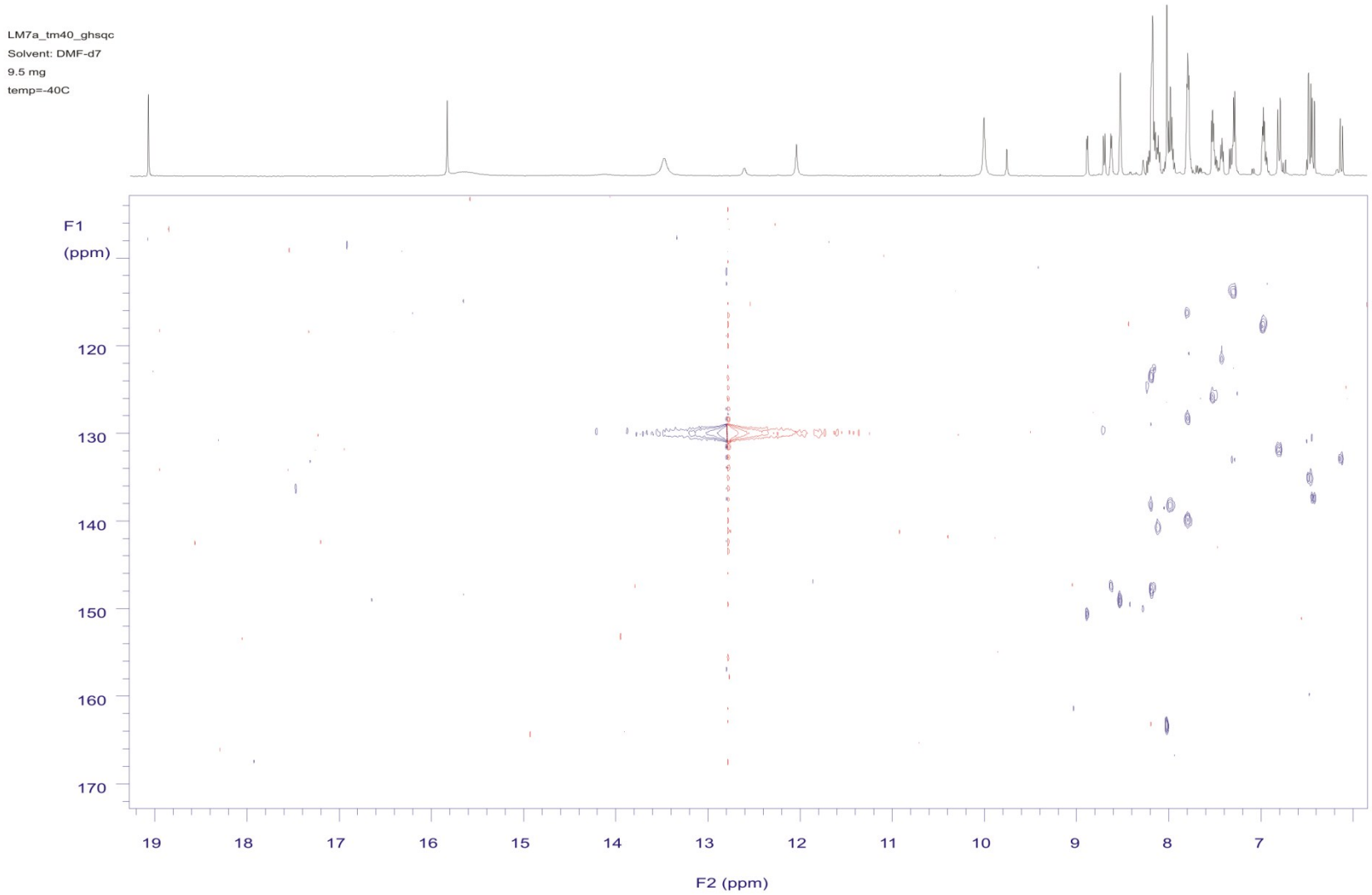
The ROESY spectrum of compound **6**.



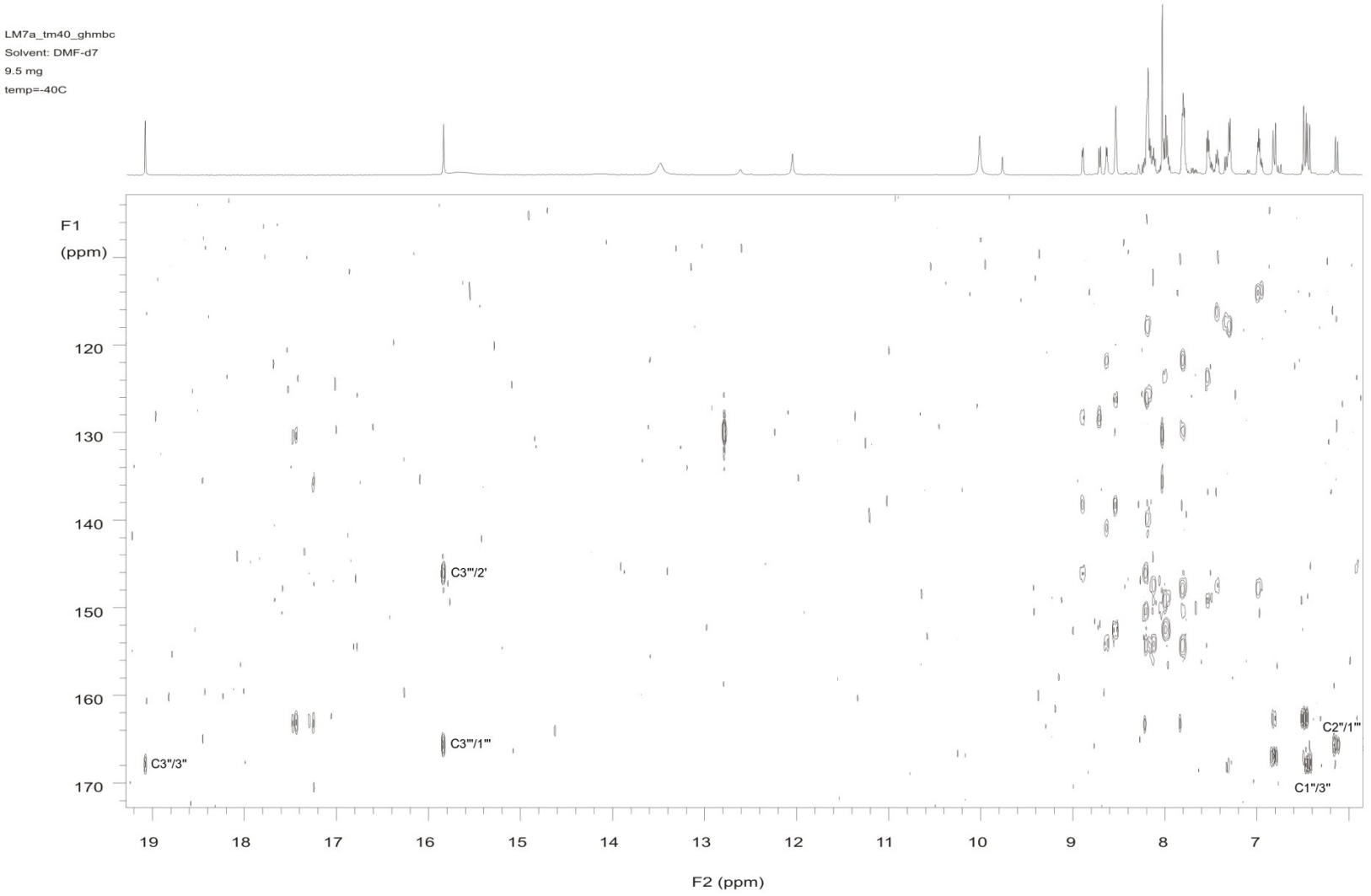
The fragment of ROESY spectrum of compound **6**.



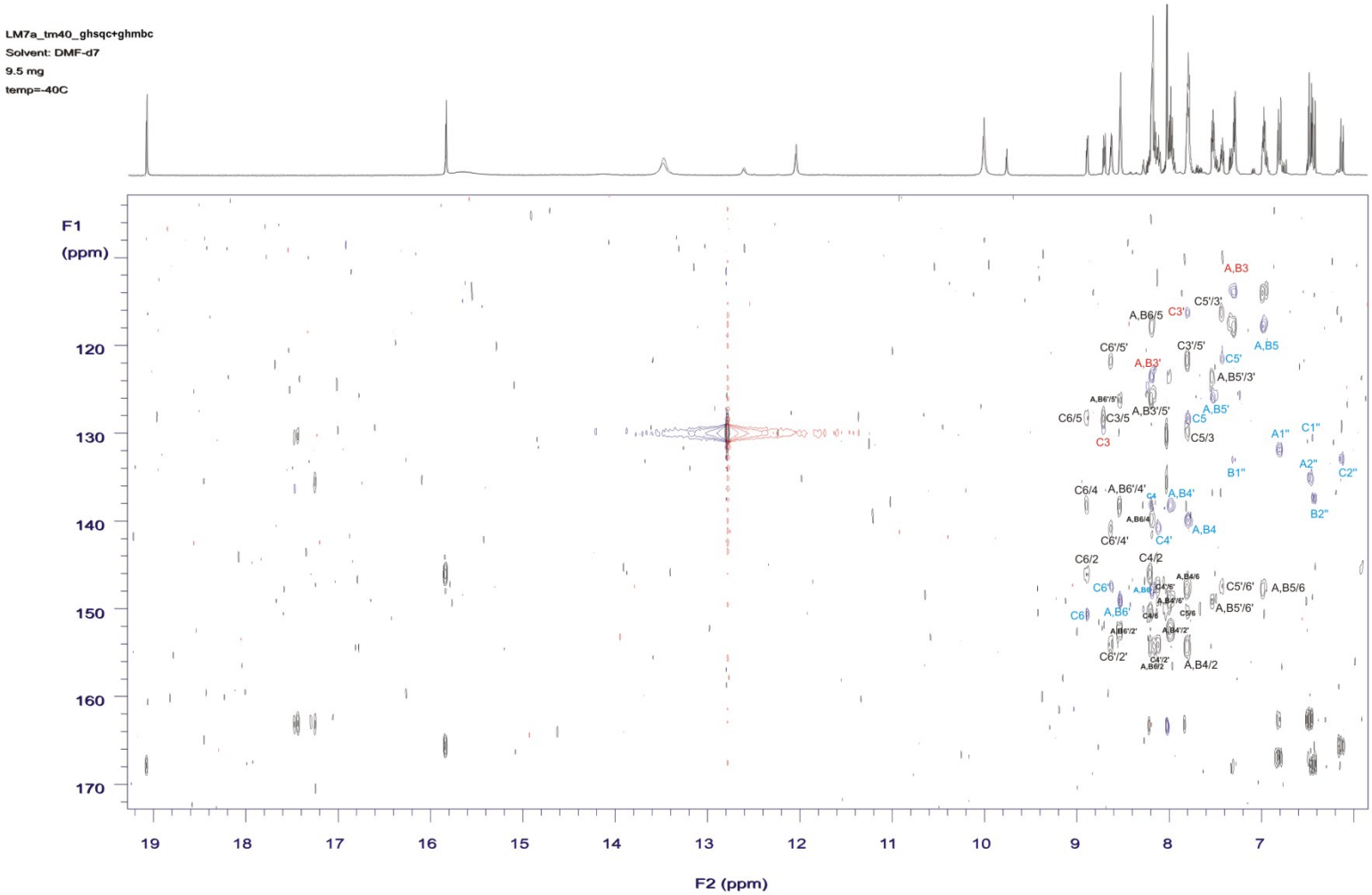
The fragment of ROESY spectrum of compound **6**.



The gHSQC spectrum of compound **6**.



The gHMBC spectrum of compound **6**.



The superimposed gHSQC and gHMBC spectra of compound **6**.