Electronic Supporting Information

Expedient One-pot Route to *N*-Acyl Ureas: a Formal Four-Component Hydrolytic Reaction Involving Aminonitrones and Isocyanide Dibromides

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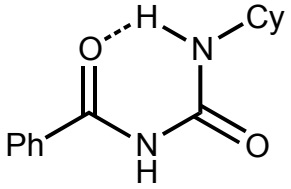
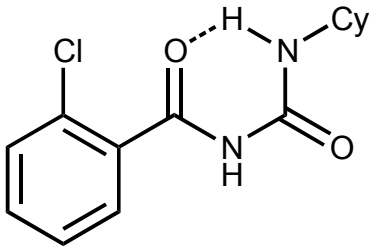
Synthesis and characterization of 1–12

A solution of Br_2 (1.2 mmol) in $CHCl_3$ (1 mL) was added dropwisely (1 min) to a stirred solution of an isocyanide (1.2 mmol) in $CHCl_3$ (1 mL) placed in 10-mL round-bottomed flask. The mixture was kept on stirring for 2 min at RT in air and then an aminonitrone (1.0 mmol) and Et_3N (1.0 mmol) were added to the reaction mixture. After 5 min a mixture of EtOH and H_2O (5:1, v/v) was added. The reaction mixture was left on stirring upon reflux for 24 h, whereupon the solvent was evaporated *in vacuo* at 40 °C and **1**–**12** were isolated by column chromatography (for each product eluent is specified in their characterization below).

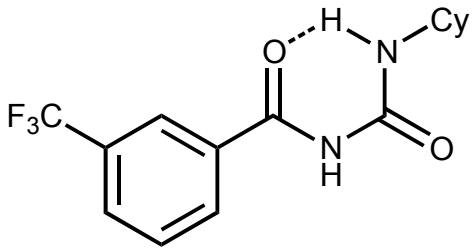


1. Yield: 92% (228 mg). Mp: 156–158 °C. R_f = 0.30 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 269.1265 ([M + Na]$^+$, calcd 269.1260). IR (KBr, selected bands, cm^{-1}): 3281 (m), 3226 (m) *ν*(N–H). 3071 (w–m), 2941 (m–s), 2853 (m) *ν*(C–H); 1692 (vs), 1667(s) *ν*(C=O). ^{1}H NMR ($CDCl_3$, *δ*): 9.18 (s, 1H, C(=O)–N*H*–C(=O)), 8.69 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C(=O)–N*H*–Cy), 7.97–7.95 (m, 2H, C*H*), 7.63–7.99 (m, 1H, C*H*), 7.52–7.48 (m, 2H, C*H*), 3.84–3.78 (m, 1H, NH–C*H*), 2.03–2.00 (m, 2H, CH_2), 1.81–1.76 (m, 2H, CH_2), 1.66–1.62 (m, 1H, CH_2), 1.48–1.24 (m, 5H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, *δ*): 168.02, 153.20 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy); 132.98, 132.58, 128.79, 127.65 (Ar); 48.93 (NH–*C*H); 32.87, 25.57, 24.68 (Cy).

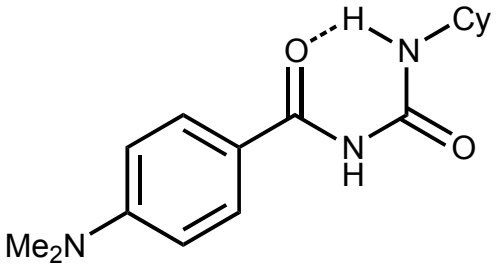


2. Yield: 51% (142 mg). Mp: 163–165 °C. R_f = 0.67 (EtOAc/Hexane, 1:1). High resolution ESI$^+$-MS (MeOH, *m/z*): 303.0884 ([M + Na]$^+$, calcd 303.0871). IR (KBr, selected bands, cm^{-1}): 3318 (s), 3215 (w–m) *ν*(N–H); 3083 (m), 2931 (s), 2855 (m–s) *ν*(C–H); 1676 (vs) *ν*(C=O). ^{1}H NMR

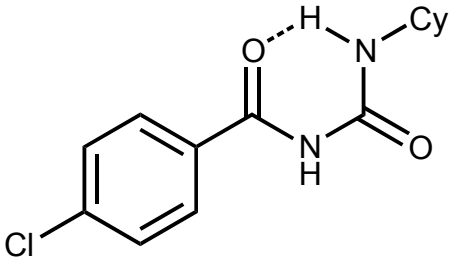
($CDCl_3$, δ): 8.94 + 8.83 (s, br, 1H, C(=O)–N*H*–C(=O)), 8.37 (d, $^3J_{HH}$ = 6.9 Hz, 1H, C(=O)–N*H*–Cy), 7.65 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C*H*), 7.48–7.43 (m, 2H, C*H*), 7.41–7.36 (m, 1H, C*H*), 3.75–3.67 (m, 1H, NH–C*H*), 1.98–1.95 (m, 2H, CH_2), 1.78–1.74 (m, 2H, CH_2), 1.64–1.61 (m, 1H, C*H*), 1.44–1.24 (m, 5H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.35, 152.33 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy); 133.38, 132.41, 131.19, 130.66, 129.89, 127.12 (Ar); 49.00 (NH–*C*H); 32.82, 25.52, 24.67 (Cy).



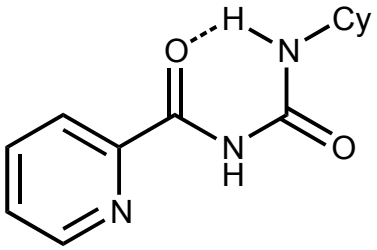
3. Yield: 95% (182 mg). Mp: 134–135 °C. R_f = 0.44 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 315.1318 ($[M + H]^+$, calcd 315.1315), 337.1143 ($[M + Na]^+$, calcd 337.1134), 353.0884 ($[M + Na]^+$, calcd 353.0874). IR (KBr, selected bands, cm^{-1}): 3280 (s), 3237 (s) ν(N–H); 3162 (m), 3131 (m), 2932 (s), 2860(m–s) ν(C–H); 1691 (vs) ν(C=O). ^1H NMR ($CDCl_3$, δ): 10.33 (s, 1H, C(=O)–N*H*–C(=O)), 8.79 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C(=O)–N*H*–Cy), 8.37 (s, 1H, C*H*), 8.26 (d, 1H, $^3J_{HH}$ = 7.8 Hz, C*H*), 7.87 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C*H*), 7.64 (t, $^3J_{HH}$ = 7.8 Hz, 1H, C*H*), 3.87–3.80 (m, 1H, NH–C*H*), 2.00–1.97 (m, 2H, CH_2), 1.78–1.75 (m, 2H, CH_2), 1.66–1.62 (m, 1H, CH_2), 1.48–1.28 (m, 5H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.20, 153.76 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy)); 133.54 (s), 131.50 (s), 131.44, 131.11 (q, $^2J_{CF}$ = 33.2 Hz), 129.38, 129.35 (q, $^3J_{CF}$ = 3.5 Hz), 129.17 (s), 125.17, 125.14 (q, $^3J_{CF}$ = 3.7 Hz) (Ar); 125.01, 122.31 (q, *C*F_3, $^1J_{CF}$ = 272.6 Hz), 48.65 (NH–*C*H); 32.84, 25.53, 24.51 (Cy).



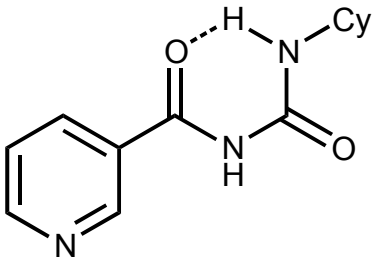
4. Yield: 45% (130 mg). Mp: 182–183 °C. R_f = 0.50 (EtOAc/Hexane, 1:1). High resolution ESI$^+$-MS (MeOH, *m/z*): 290.1873 ([M + H]$^+$, calcd 290.1863), 312.1700 ([M + Na]$^+$, calcd 312.1682). IR (KBr, selected bands, cm^{-1}): 3275 (m), 3119 (w–m) *ν*(N–H); 2929 (m–s), 2852 (m) *ν*(C–H); 1689 (vs), 1659 (s) *ν*(C=O). ^{1}H NMR (CDCl$_3$, *δ*): 8.72 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C(=O)–N*H*–Cy), 8.01 (s, 1H, C(=O)–N*H*–C(=O)), 7.74 (d, $^3J_{HH}$ = 8.9 Hz, 2H, C*H*), 6.70 (d, $^3J_{HH}$ = 8.9 Hz, 2H, C*H*), 3.85–3.78 (m, 1H, NH–C*H*), 3.08 (s, 6H, N(CH_3)$_2$), 2.02–1.99 (m, 2H, CH_2), 1.79–1.75 (m, 2H, CH_2), 1.62–1.58 (m, 1H, CH_2), 1.48–1.22 (m, 5H, CH_2). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 167.35, 153.38 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy); 129.18, 118.49, 111.06 (Ar); 48.68 (NH–*C*H); 40.01 (CH$_3$); 32.99, 25.60, 24.67 (Cy).



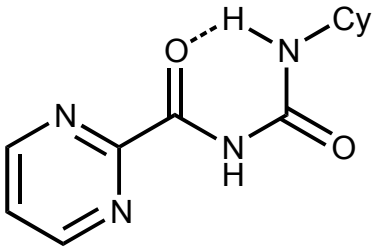
5. Yield: 96% (270 mg). Mp: 217–218 °C. R_f = 0.45 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 303.0861 ([M + Na]$^+$, calcd 303.0870). IR (KBr, selected bands, cm^{-1}): 3288 (m–s), 3225 (m–s) *ν*(N–H); 3131 (m), 2934 (m–s), 2851 (m) *ν*(C–H); 1691 (vs), 1672 (vs) *ν*(C=O). ^{1}H NMR (CDCl$_3$, *δ*): 10.14 (s, 1H, C(=O)–N*H*–C(=O)), 8.77 (d, , J_{HH}^3 = 6.5 Hz, 1H, C(=O)–N*H*–Cy), 8.02 (d, $^3J_{HH}$ = 8.5 Hz, 2H, C*H*), 7.46 (d, $^3J_{HH}$ = 8.6 Hz, 2H, C*H*), 3.85–3.75 (m, 1H, NH–C*H*), 2.01–1.98 (m, 2H, CH_2), 1.81–1.77 (m, 2H, CH_2), 1.68–1.65 (m, 1H, CH_2), 1.49–1.28 (m, 5H, CH_2). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 167.36, 153.85 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy); 139.41, 130.93, 129.52, 128.91 (Ar); 49.10 (NH–*C*H); 32.74, 25.55, 24.63 (Cy).



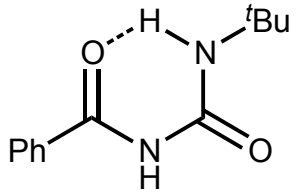
6. Yield: 47% (115 mg). Mp: 81–82 °C. R_f = 0.30 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 270.1212 ([M + Na]$^+$, calcd 270.1213), 286.0951 ([M + K]$^+$, calcd 286.0952). IR (KBr, selected bands, cm^{-1}): 3340 (s), 3281 (s) *ν*(N–H); 3072 (w–m), 2931 (s), 2853 (s) *ν*(C–H); 1689 (vs) *ν*(C=O). ^{1}H NMR (CDCl$_3$, *δ*): 9.88 (s, 1H, C(=O)–N*H*–C(=O)), 8.63 (d, $^3J_{HH}$ = 4.4 Hz , 1H, C*H*), 8.39 (d, $^3J_{HH}$ = 6.4 Hz, 1H, C(=O)–N*H*–Cy), 8.21 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C*H*), 7.92 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, C*H*), 7.55–7.52 (m, 1H, C*H*), 3.87–3.78 (m, 1H, NH–C*H*), 2.02–1.99 (m, 2H, CH_2), 1.78–1.74 (m, 2H, CH_2), 1.64–1.60 (m, 1H, CH_2), 1.48–1.22 (m, 5H, CH_2). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 164.69, 151.93 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy); 148.56, 147.91, 137.69, 127.46, 122.76 (Ar); 48.65 (NH–*C*H); 32.98, 25.56, 24.62 (Cy).



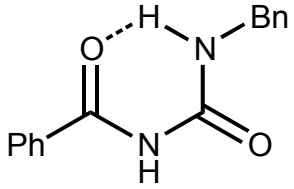
7. Yield: 78% (191 mg). Mp: 142–143 °C. R_f = 0.30 (EtOAc). High resolution ESI$^+$-MS (MeOH, *m/z*): 248.1388 ([M + H]$^+$, calcd 248.1394), 270.1210 ([M + Na]$^+$, calcd 270.1213). IR (KBr, selected bands, cm^{-1}): 3293 (m–s), 3223 (m–s) *ν*(N–H); 3143 (m), 3080 (m–w), 2925 (s), 2855 (m–s) *ν*(C–H); 1690 (vs) *ν*(C=O). ^{1}H NMR (CDCl$_3$, *δ*): 10.54 (s, 1H, C(=O)–N*H*–C(=O)), 9.28 (s, 1H, C(=O)–N*H*–Cy), 8.84 (d, $^3J_{HH}$ = 3.9 Hz, 1H, C*H*), 8.72 (d, $^3J_{HH}$ = 7.3 Hz, 1H, C*H*), 8.46 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*), 7.47 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, C*H*), 3.84–3.77 (m, 1H, NH–C*H*), 2.00–1.97 (m, 2H, CH_2), 1.79–1.75 (m, 2H, CH_2), 1.66–1.63 (m, 1H, CH_2), 1.49–1.25 (m, 5H, CH_2). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 166.65, 153.67 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy); 152.65, 149.09, 136.16, 128.73, 123.41 (Ar); 49.08 (NH–*C*H); 32.68, 25.52, 24.55 (Cy).



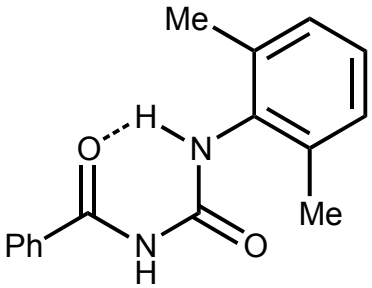
8. Yield: 77% (190 mg). Mp: 118–119 °C. R_f = 0.40 (EtOAc). High resolution ESI$^+$-MS (MeOH, *m/z*): 271.1163 ([M + Na]$^+$, calcd 271.1165), 287.0895 ([M + K]$^+$, calcd 287.0905). IR (KBr, selected bands, cm^{-1}): 3338 (s), 3052 (w–m) *ν*(N–H); 2933 (s), 2854 (m–s) *ν*(C–H); 1696 (s) *ν*(C=O). ^{1}H NMR (CDCl$_3$, *δ*): 9.77 (s, 1H, C(=O)–N*H*–C(=O)), 8.97 (d, $^3J_{HH}$ = 4.9 Hz, 2H, C*H*), 8.43 (d, $^3J_{HH}$ =6.8 Hz, 1H, C(=O)–N*H*–CH), 7.55 (t, $^3J_{HH}$ = 4.9 Hz, 1H, C*H*), 3.89–3.80 (m, 1H, C*H*), 2.02–1.99 (m, 2H, CH_2), 1.80–1.75 (m, 2H, CH_2), 1.65–1.61 (m, 1H, CH_2), 1.49–1.23 (m, 5H, CH_2). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 162.28, 157.85 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Cy); 156.20, 151.55, 123.42 (Ar); 48.79 (NH–*C*H); 32.82, 25.51, 24.50 (Cy).



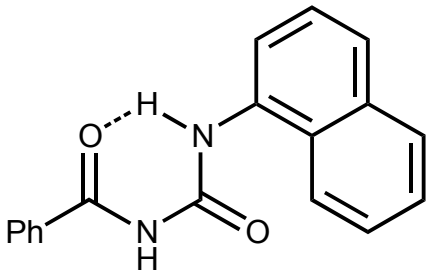
9. Yield: 71% (156 mg). Mp: 111–112 °C. R_f = 0.61 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 243.1118 ([M + Na]$^+$, calcd 243.1104) 259.0848 ([M + K]$^+$, calcd 259.0843). IR (KBr, selected bands, cm^{-1}): 3263 (s), 3132 (m–s) *ν*(N–H); 3062 (m), 2974 (m–s) *ν*(C–H); 1696 (vs), 1664(s) *ν*(C=O). ^{1}H NMR (CDCl$_3$, *δ*): 9.96 (s, 1H, C(=O)–N*H*–C(=O)), 8.90 (s, 1H, C(=O)–N*H*–^{t}Bu), 8.08 (d, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*), 7.61–7.58 (m, 1H, C*H*), 7.51–7.47 (m, 2H, C*H*), 1.47 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 168.52, 153.32 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–^{t}Bu), 132.82, 132.67, 128.65, 127.94 (Ar); 50.98 (NH–*C*); 28.89 (*C*H$_3$).



10. Yield: 44% (110 mg). Mp: 164–165 °C. R_f = 0.30 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 277.0939 ([M + Na]$^+$, calcd 277.0947). IR (KBr, selected bands, cm^{-1}): 3378 (m), 3304 (m–s) *v*(N–H); 3064 (w–m), 3032 (w–m), 2948 (m–w) *v*(C–H); 1693 (vs), 1667(vs) *v*(C=O).^{1}H NMR (CDCl$_3$, *δ*): 9.93 (s, 1H, C(=O)–N*H*–C(=O)), 9.24 (s, 1H, C(O=)–N*H*–CH$_2$), 8.03–8.00 (m, 2H, C*H*), 7.61–7.57 (m, 1H, C*H*), 7.48–7.44 (m, 2H, C*H*), 7.40–7.35 (m, 4H, C*H*), 7.33–7.31 (m, 1H, C*H*), 4.60 (d, $^3J_{HH}$ = 5.9 Hz, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 168.37, 154.71 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–CH$_2$); 138.14, 133.03, 132.39, 128.70, 127.93, 127.52, 127.45 (Ar); 43.80 (NH–*C*H$_2$).



11. Yield: 32% (84 mg). Mp: 237–238 °C. R_f = 0.48 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 291.1107 ([M + Na]$^+$, calcd 291.1104), 307.0843 ([M + K]$^+$, calcd 307.0843). IR (KBr, selected bands, cm^{-1}): 3266 (m–s), 3128 (m) *v*(N–H); 2966 (w–m), 2923 (w–m) *v*(C–H); 1690 (vs), 1664(vs) *v*(C=O). ^{1}H NMR (CDCl$_3$, *δ*): 10.23 (s, 1H, C(=O)–N*H*–C(=O)), 9.74 (s, 1H, C(=O)–N*H*–Xyl), 8.02 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*), 7.62–7.58 (m, 1H, C*H*), 7.45–7.41 (m, 2H, C*H*), 7.21– 7.14 (m, 3H, C*H*), 2.34 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 168.45, 152.59 (*C*(=O)–NH–C(=O) and *C*(=O)–NH– Xyl), 135.50, 133.32, 133.25, 131.99, 128.81, 128.15, 127.90, 127.34 (Ar); 18.53 (*C*H$_3$).



12. Yield: 31% (90 mg). Mp: 214–215 °C. R_f = 0.40 (EtOAc/Hexane, 2:8). High resolution ESI$^+$-MS (MeOH, *m/z*): 313.0962 ([M + Na]$^+$, calcd 313.0947). IR (KBr, selected bands, cm^{-1}): 3202 (m), 3130 (m) *v*(N–H); 3069 (m) *v*(C–H); 1710 (vs), 1671 (s) *v*(C=O). ^{1}H NMR ((CD$_3$,)$_2$SO *δ*): 11.11 (s, 1H, C(=O)–N*H*–C(=O)), 11.05 (s, 1H, C(=O)–N*H*–Nh), 8.24 (d, $^4J_{HH}$ = 1.3 Hz, 1H, C*H*), 8.07 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*), 7.94–7.87 (m, 3H, C*H*), 7.70–7.66 (m, 2H, C*H*), 7.59–7.42 (m, 5H, C*H*). ^{13}C{^{1}H} NMR ((CD$_3$,)$_2$SO, *δ*): 169.28, 151.70 (*C*(=O)–NH–C(=O) and *C*(=O)–NH–Nh), 135.73, 133.91, 133.54, 132.79, 130.47, 129.17, 129.05, 128.80, 127.98, 127.79, 127.04, 125.31, 120.89, 116.35 (Ar).

Crystal data for 3 and 10

Identification code	**3**	**10**
Empirical formula	$C_{15}H_{17}F_3N_2O_2$	$C_{15}H_{14}N_2O_2$
Formula weight	314.30	254.28
Temperature/K	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	5.1066(12)	5.3129(5)
b/Å	11.5568(13)	9.3886(7)
c/Å	12.7664(13)	12.8335(8)
α/°	100.531(9)	86.747(5)
β/°	94.646(14)	88.785(7)
γ/°	100.547(15)	75.123(8)
Volume/Å^3	723.1(2)	617.68(9)
Z	2	2
ρ_{calc}g/cm^3	1.444	1.367
μ/mm^1	0.122	0.092
F(000)	328.0	268.0
Crystal size/mm^3	0.2 × 0.2 × 0.15	0.25 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.538 to 54.994	5.366 to 54.964
Index ranges	$-6 \le h \le 6$, $-15 \le k \le 14$, $-15 \le l \le 16$	$-6 \le h \le 6$, $-12 \le k \le 12$, $-16 \le l \le 13$
Reflections collected	6124	5736
Independent reflections	3326 [R_{int} = 0.0338, R_{sigma} = 0.0486]	2821 [R_{int} = 0.0269, R_{sigma} = 0.0459]
Data/restraints/parameters	3326/0/199	2821/0/172
Goodness-of-fit on F^2	1.064	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0464, wR_2 = 0.1157	R_1 = 0.0419, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0619, wR_2 = 0.1328	R_1 = 0.0580, wR_2 = 0.1036
Largest diff. peak/hole / e Å^{-3}	0.31/-0.33	0.25/-0.28
CCDC number	**1938714**	**1938715**

Spectra of 1−12

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

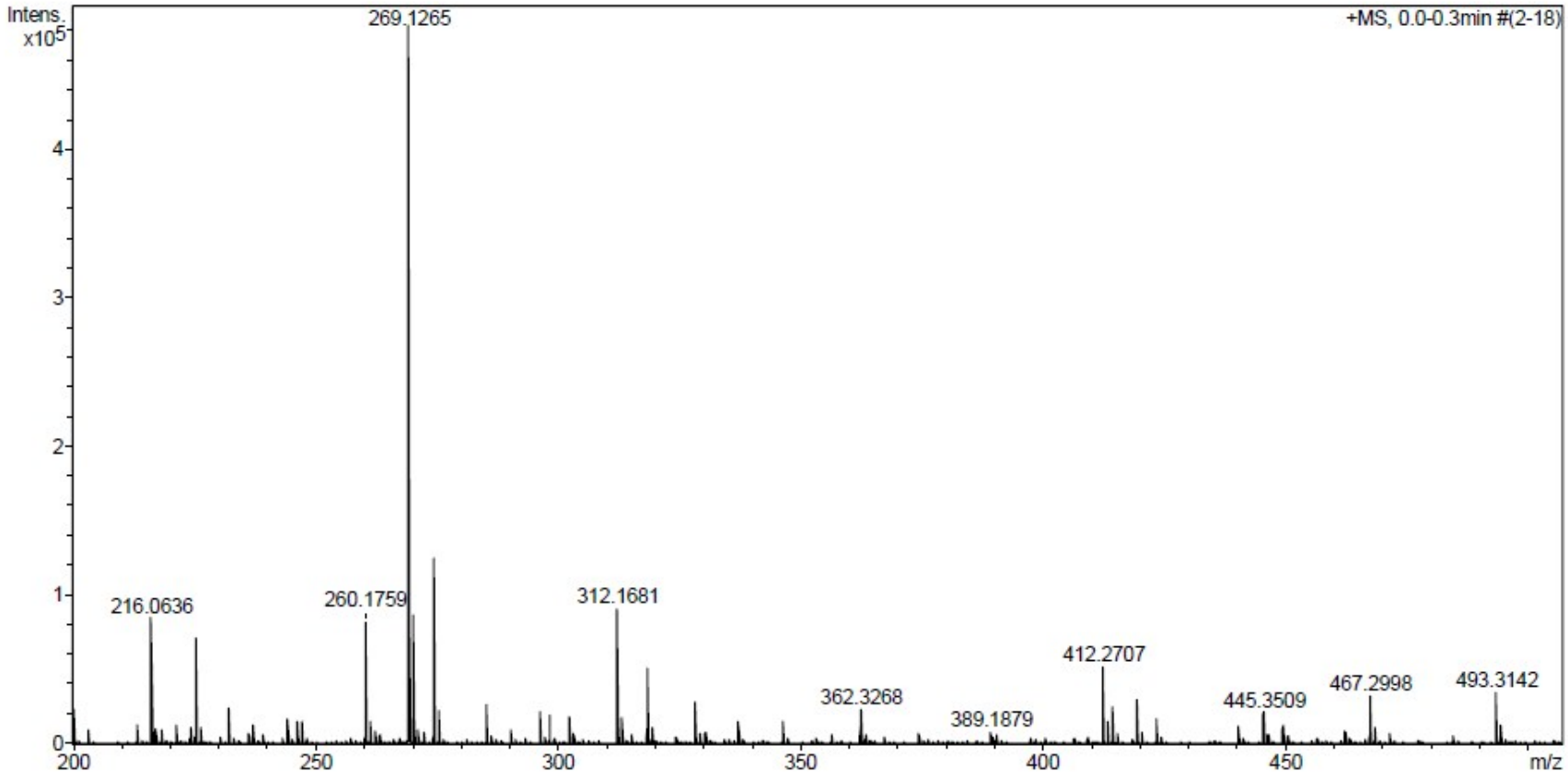


Figure 33S. HRESI^{+}-MS of **1**.

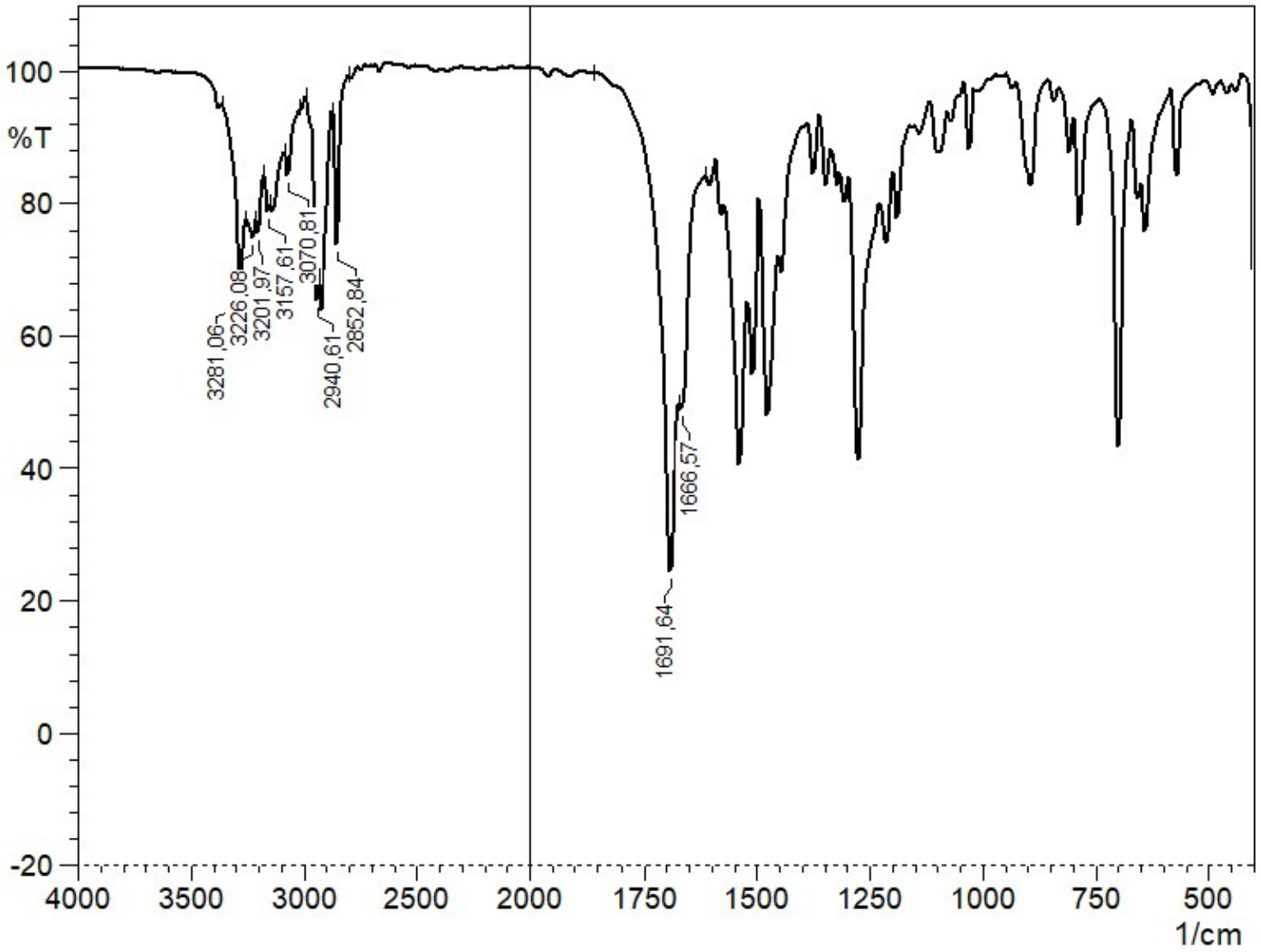


Figure 34S. IR spectrum of **1**.

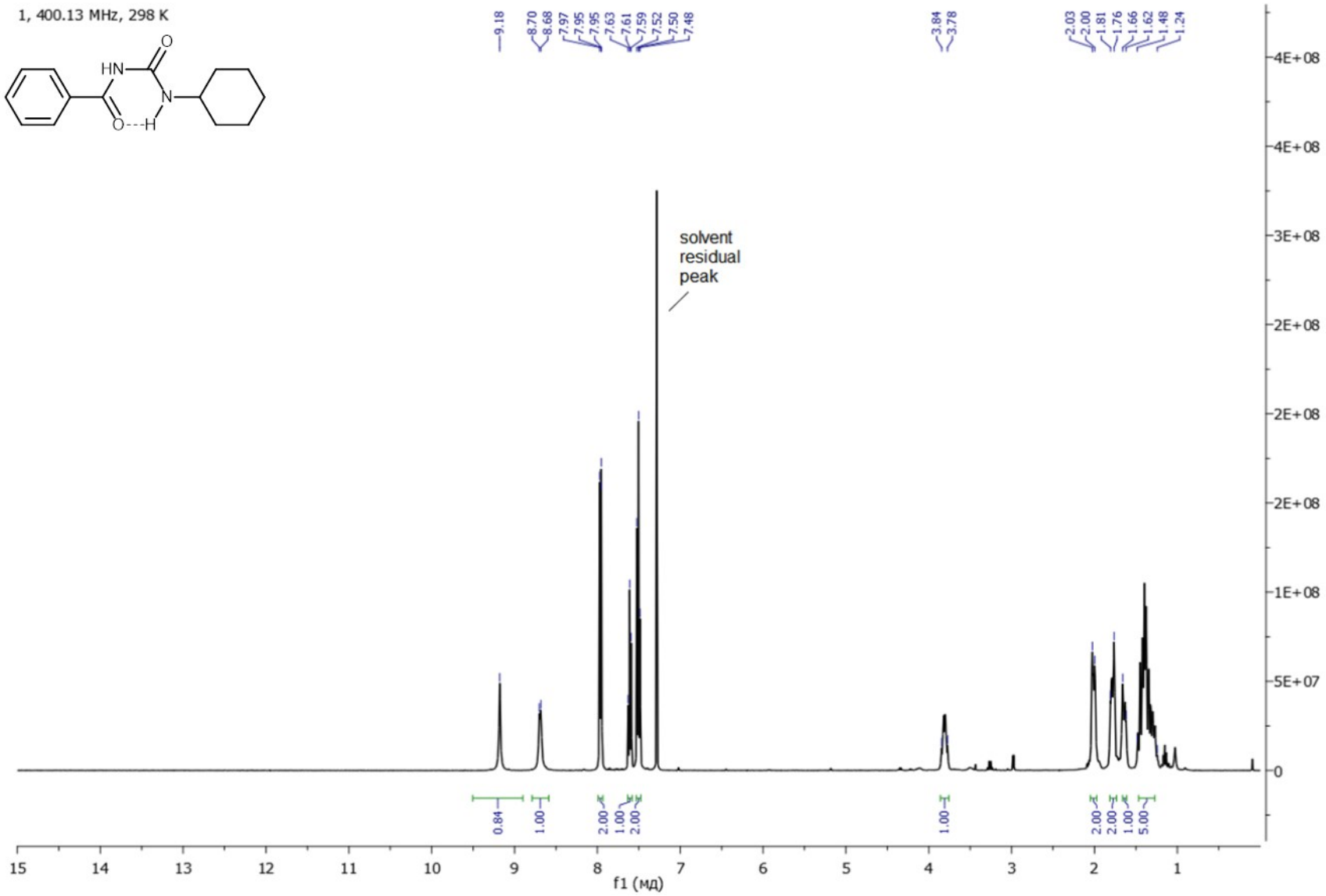


Figure 35S. ^{1}H NMR spectrum of **1**.

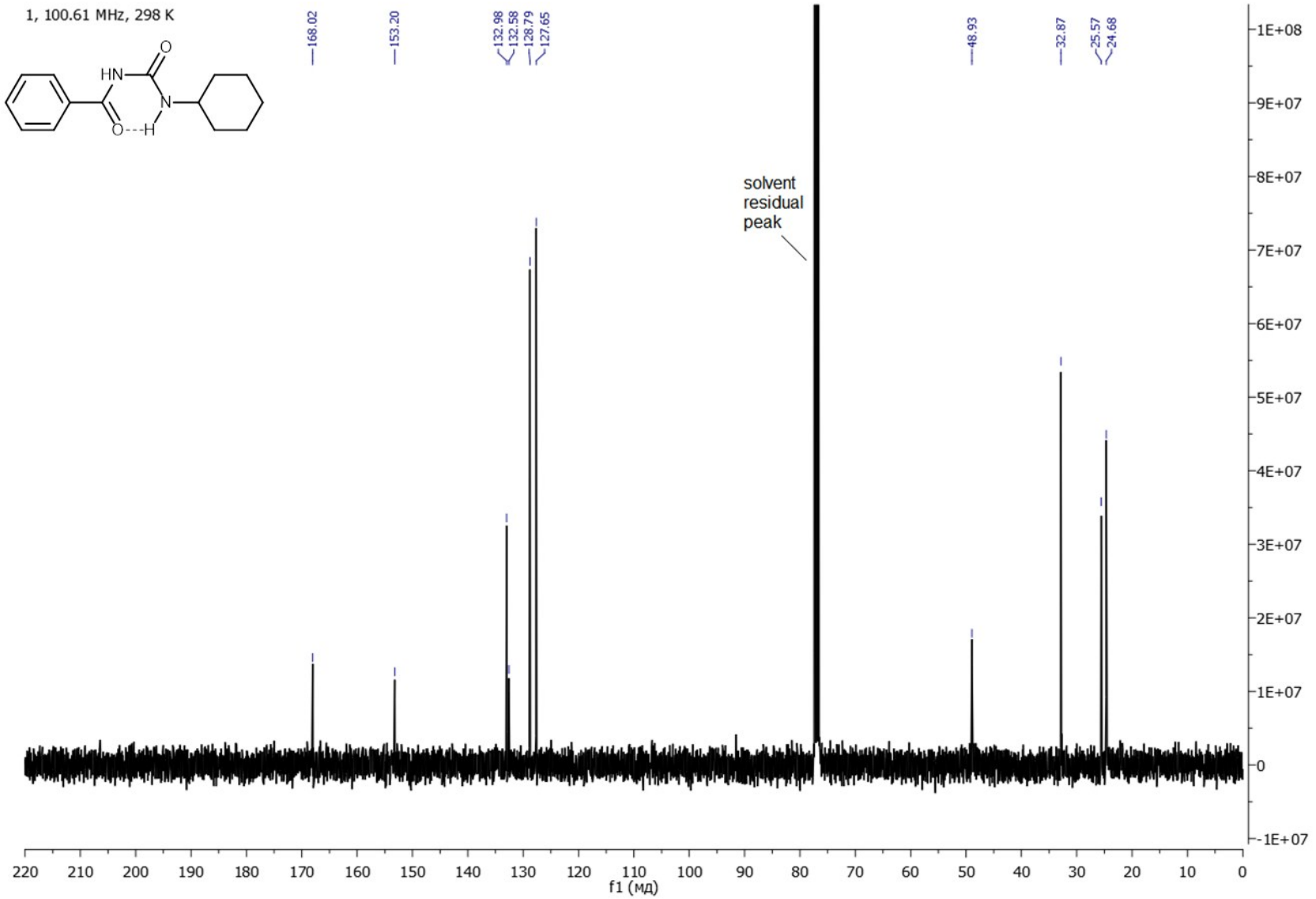


Figure 36S. $^{13}C\{^{1}H\}$ NMR spectrum of **1**.

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

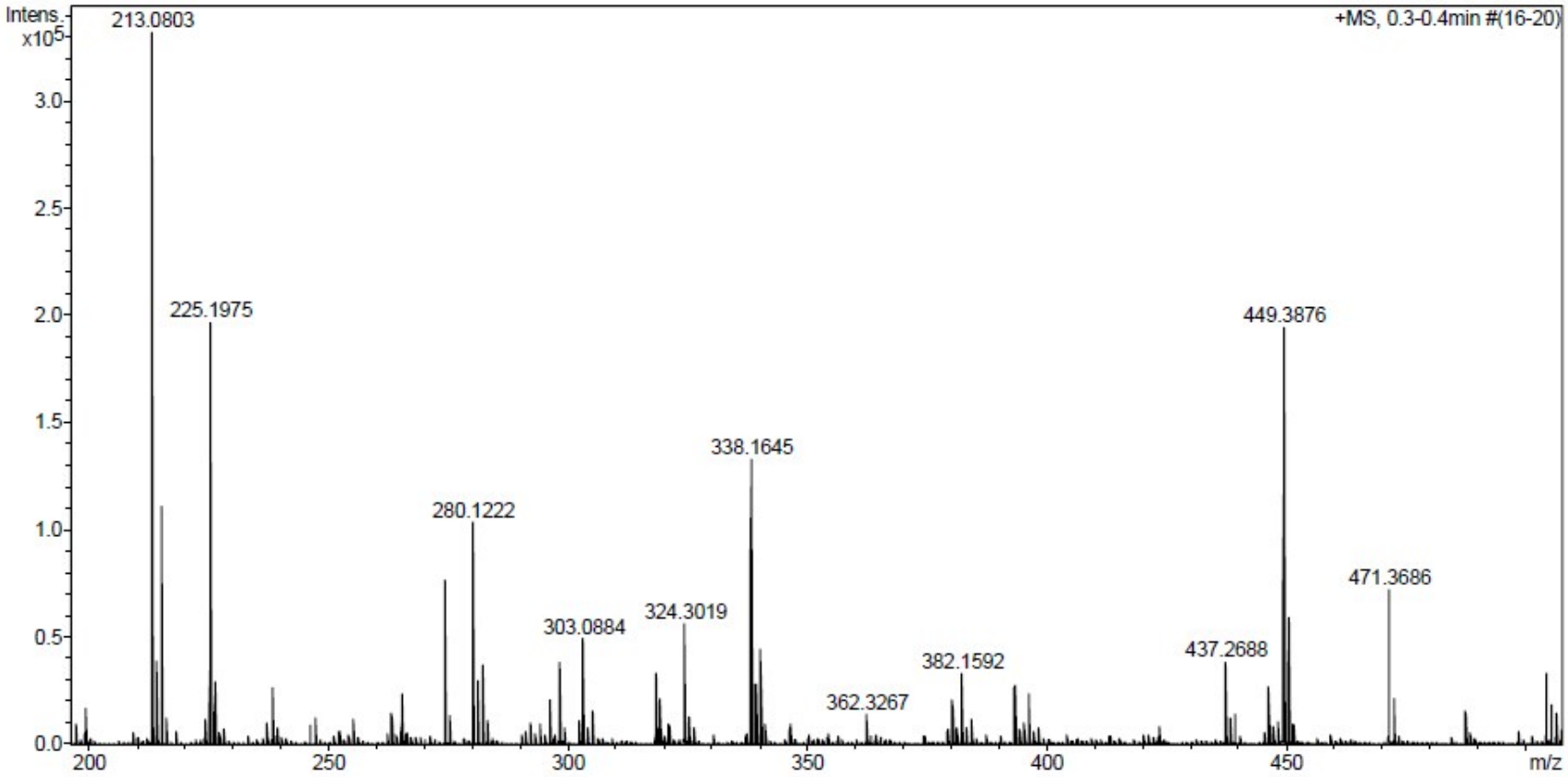


Figure 37S. HRESI^{+}-MS of **2**.

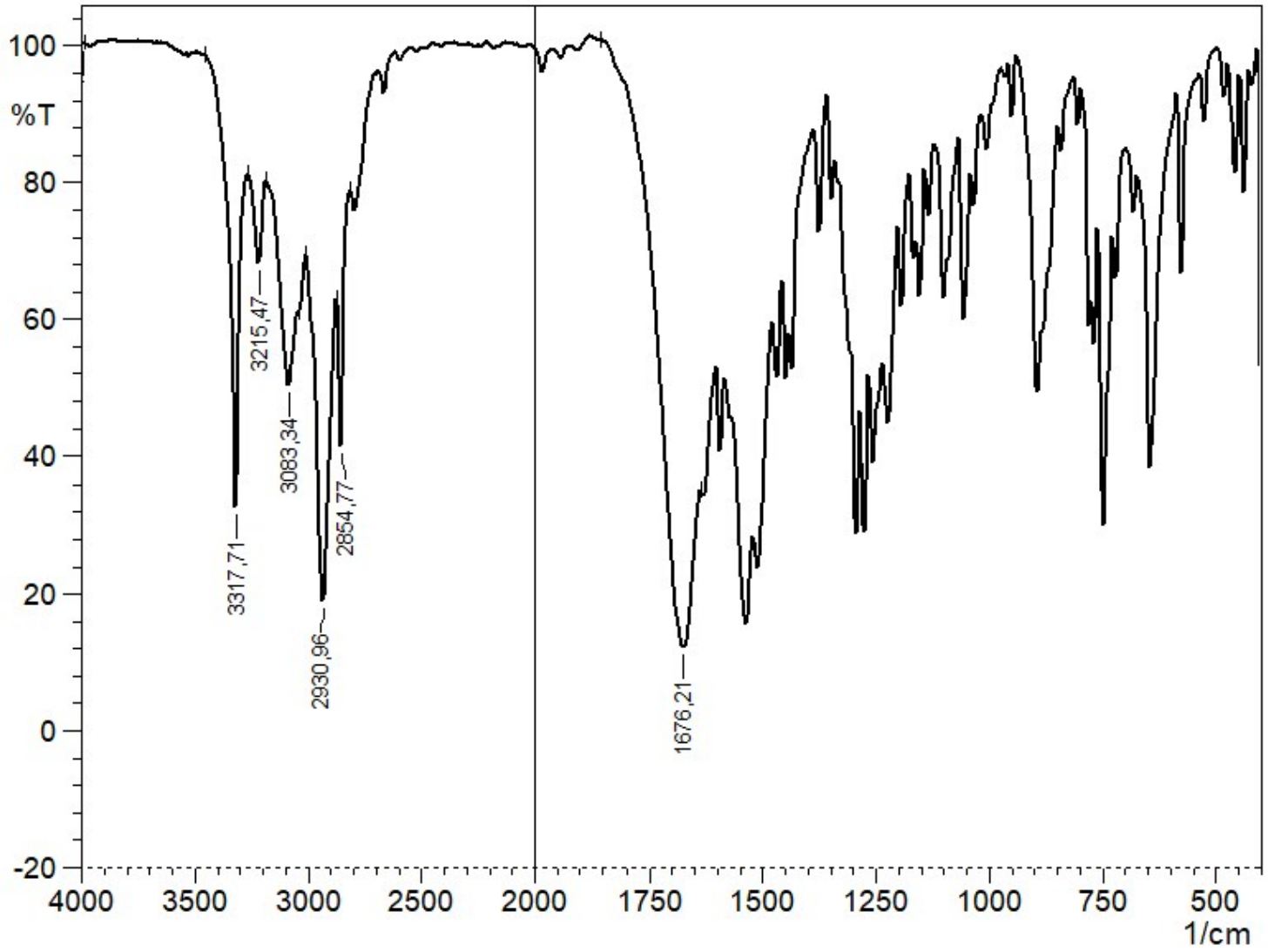


Figure 38S. IR spectrum of **2**.

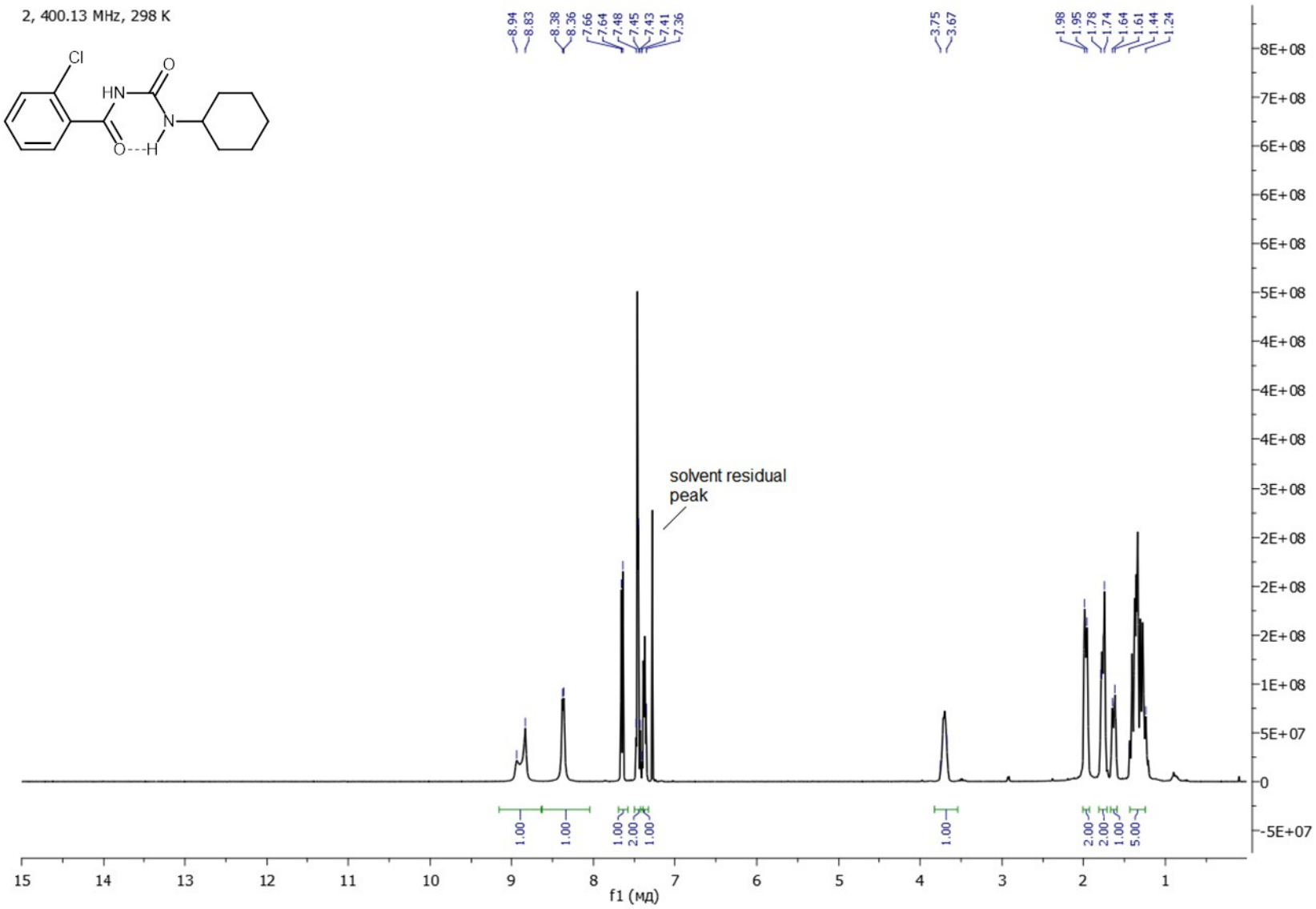


Figure 39S.[1]H NMR spectrum of **2**.

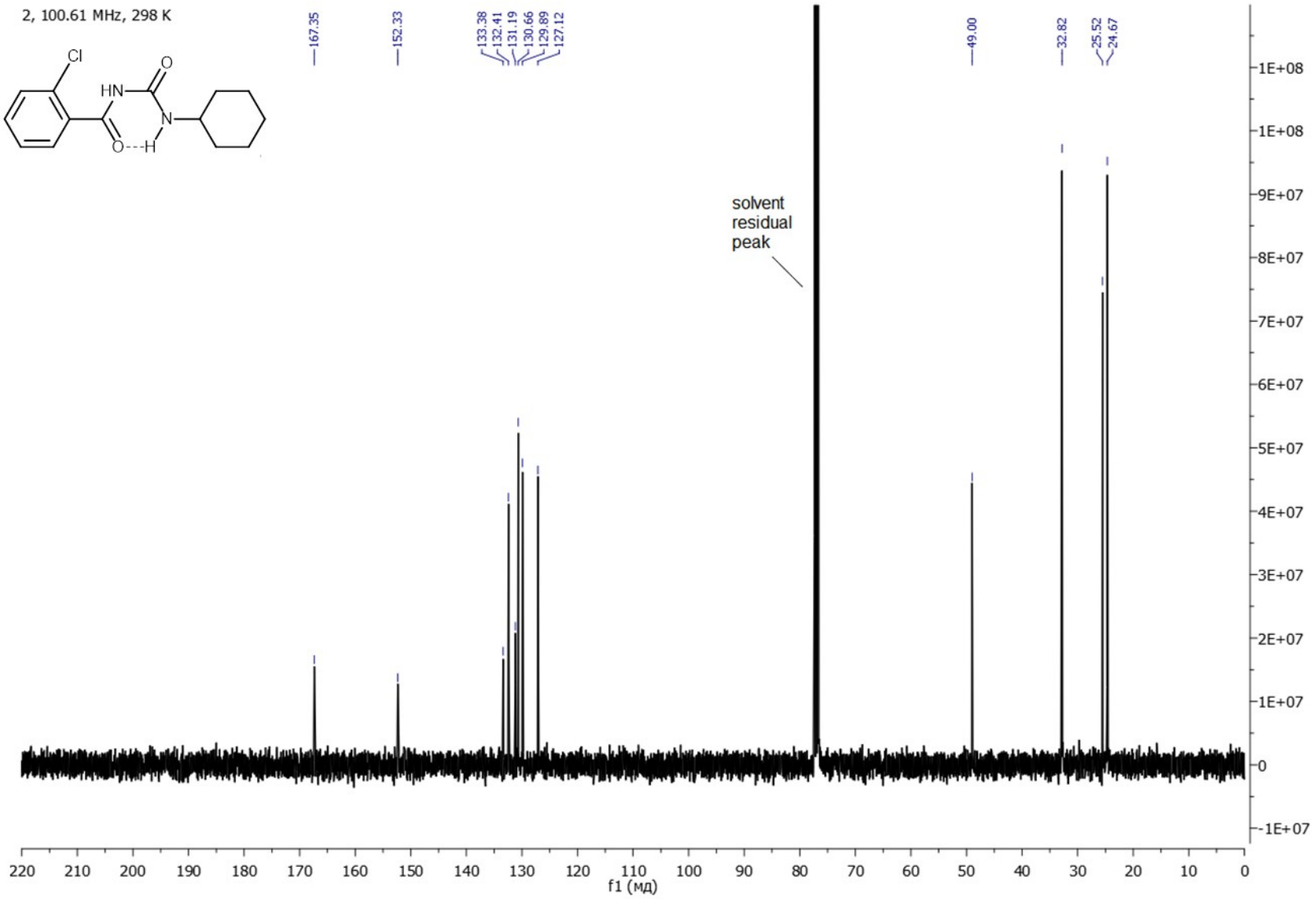


Figure 40S. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

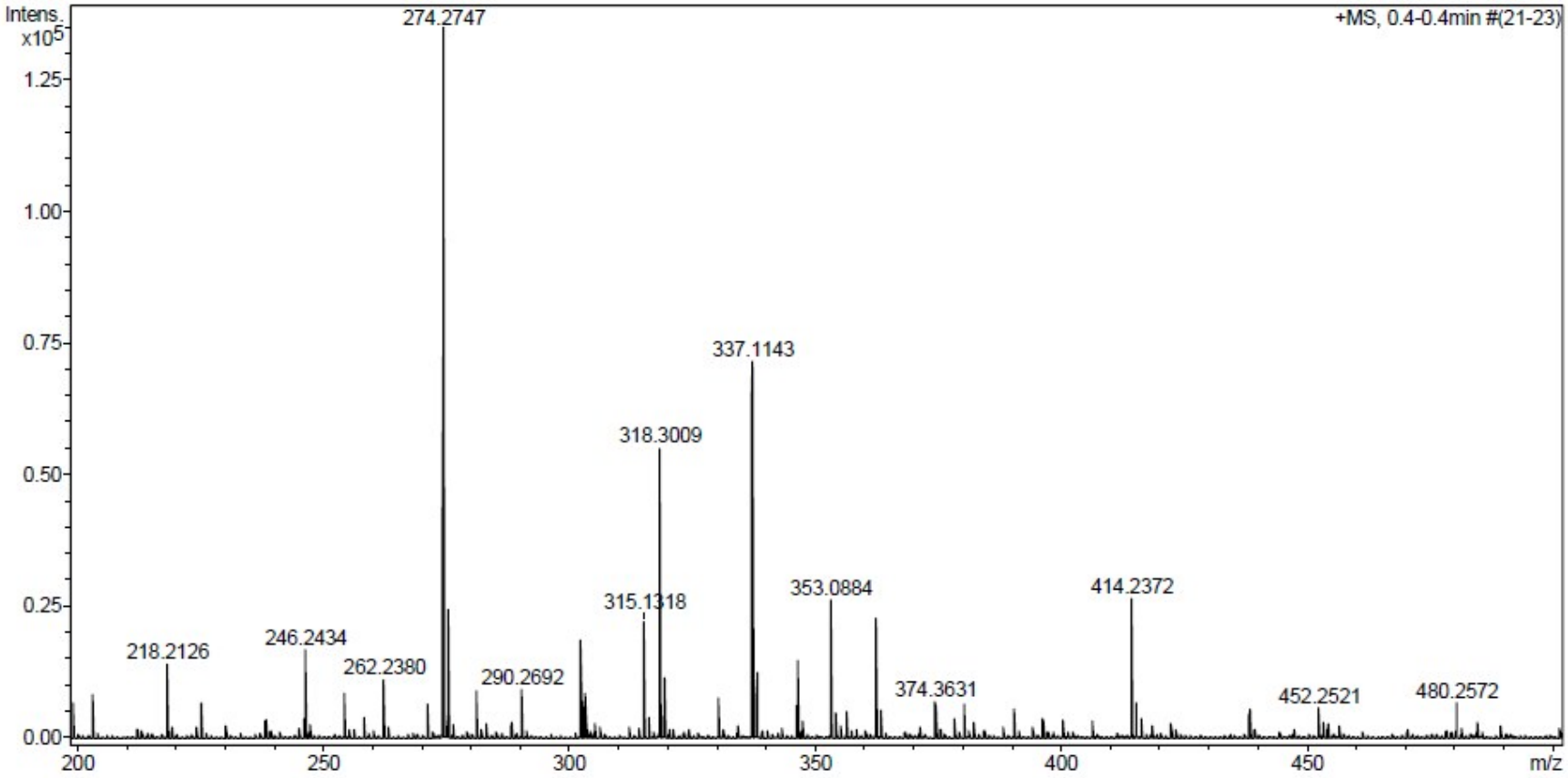


Figure 41S. HRESI^{+}-MS of **3**.

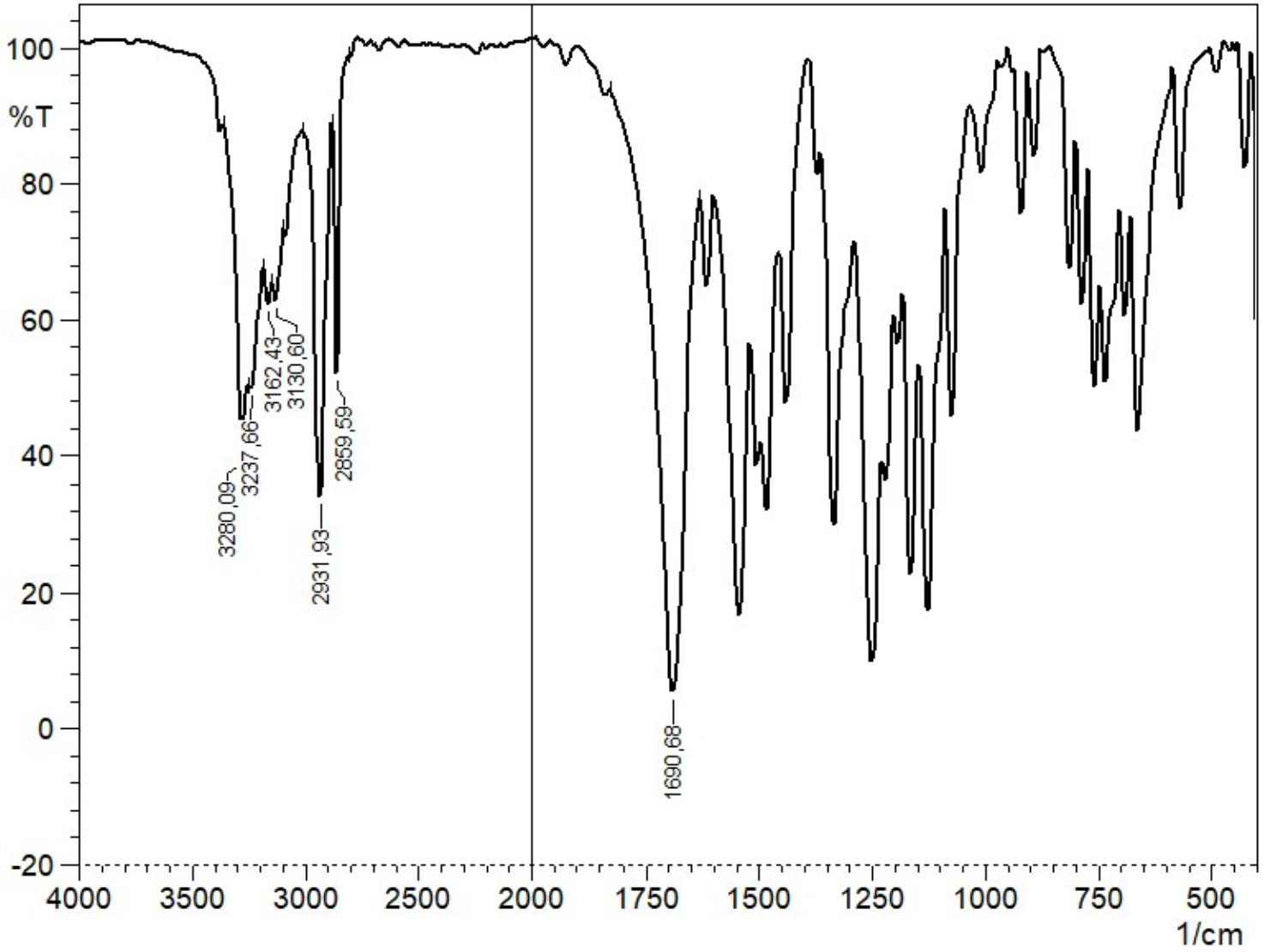


Figure 42S. IR spectrum of **3**.

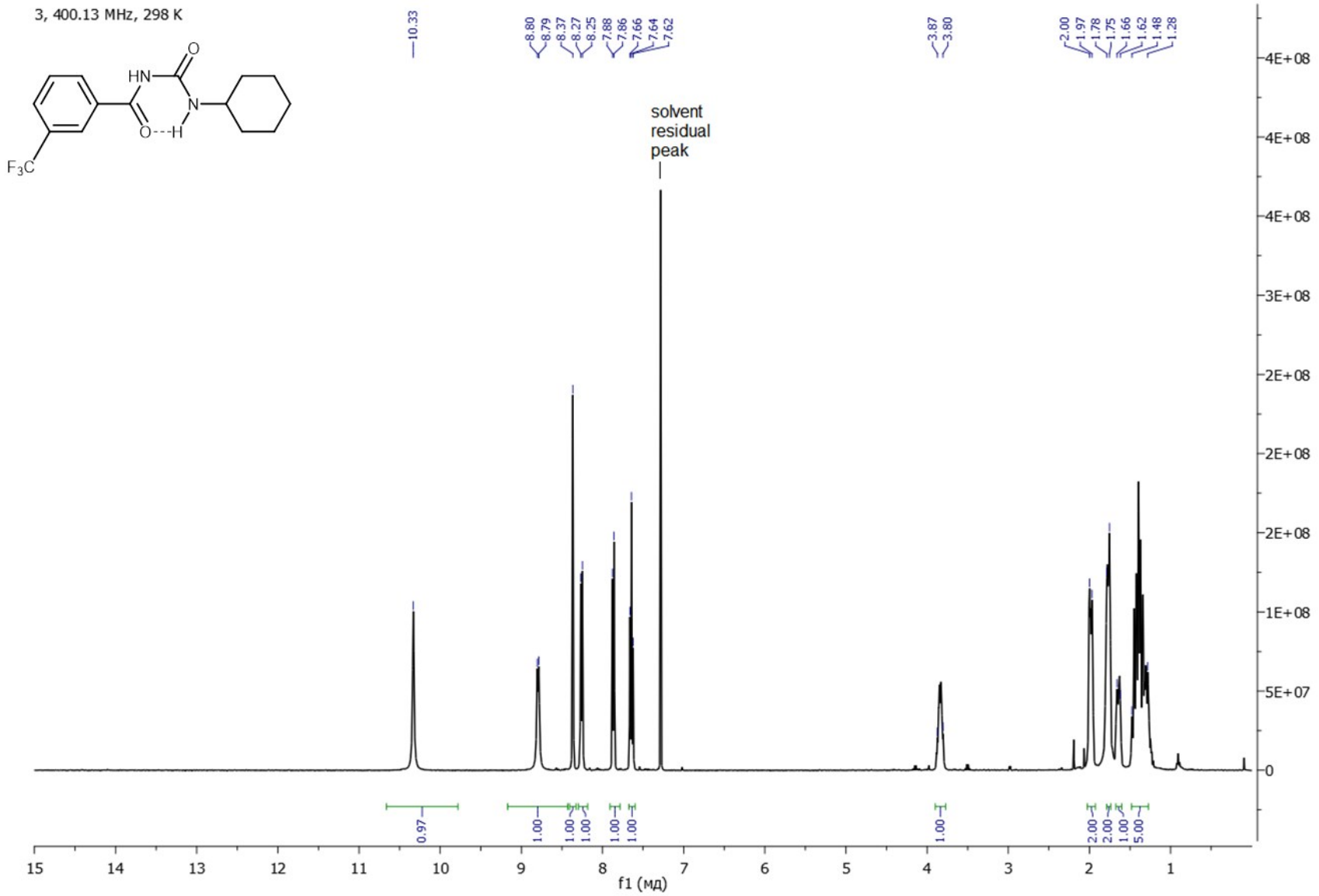


Figure 43S. [1]H NMR spectrum of **3**.

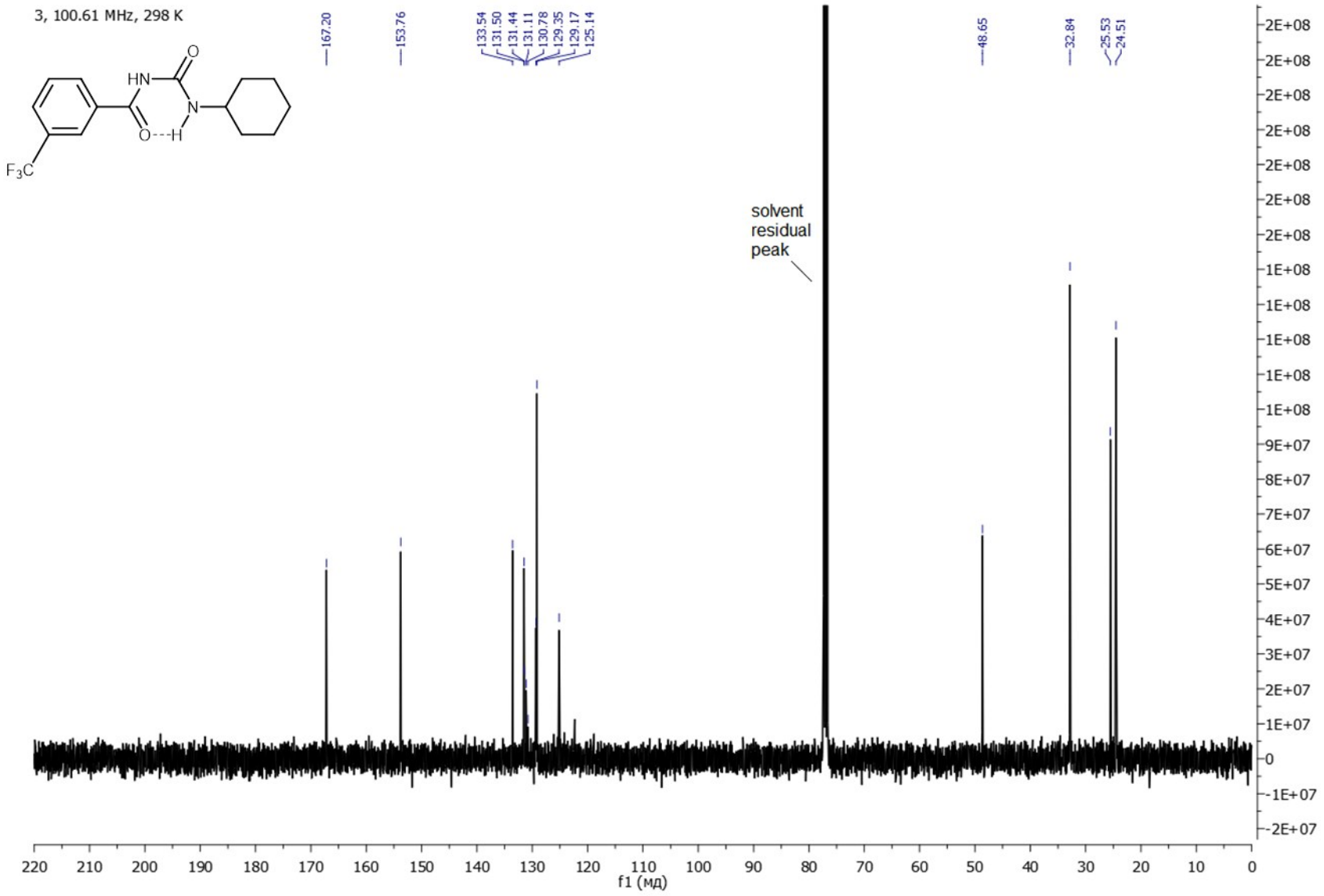


Figure 44S. $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

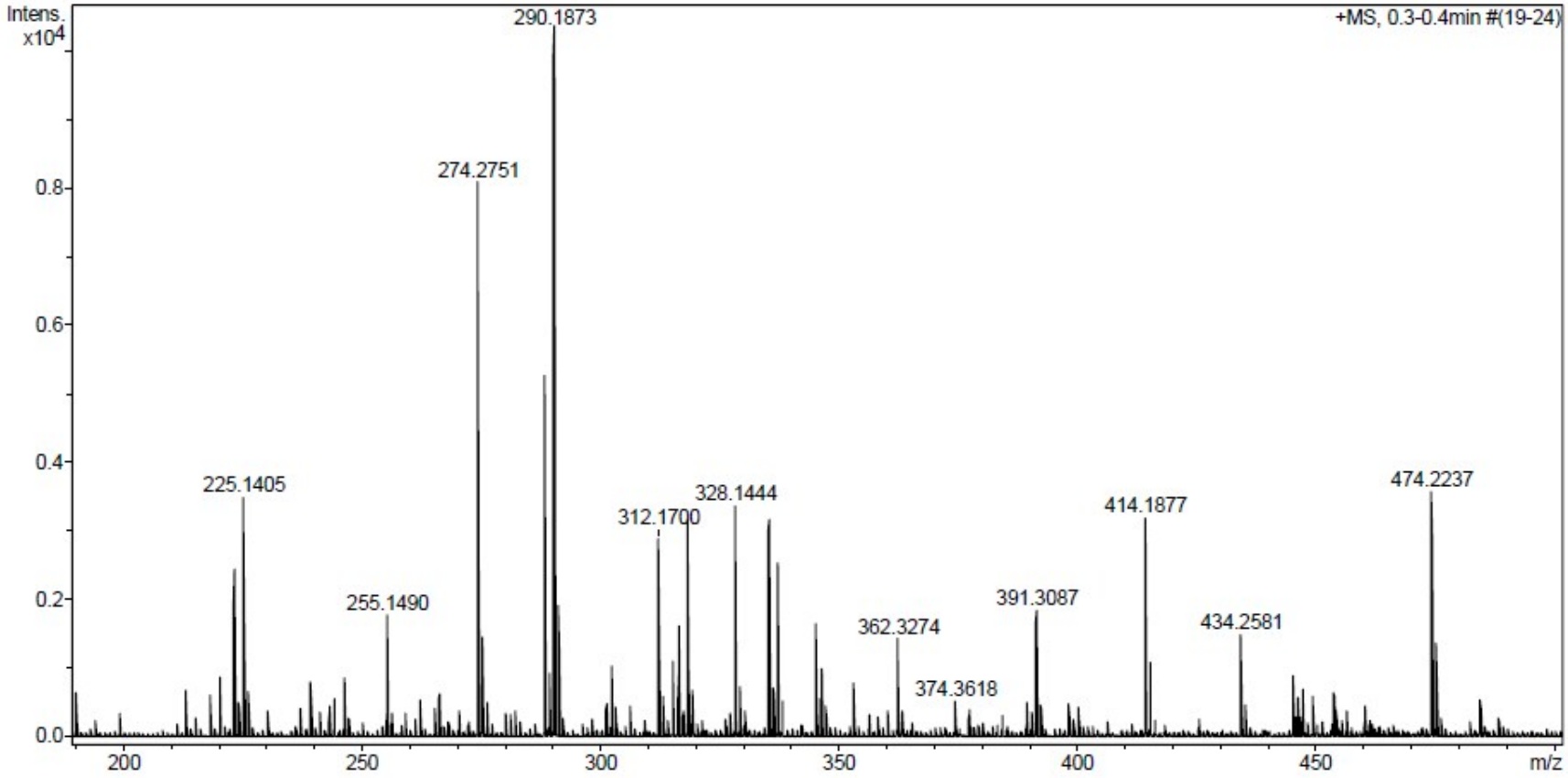


Figure 45S. HRESI^{+}-MS of **4**.

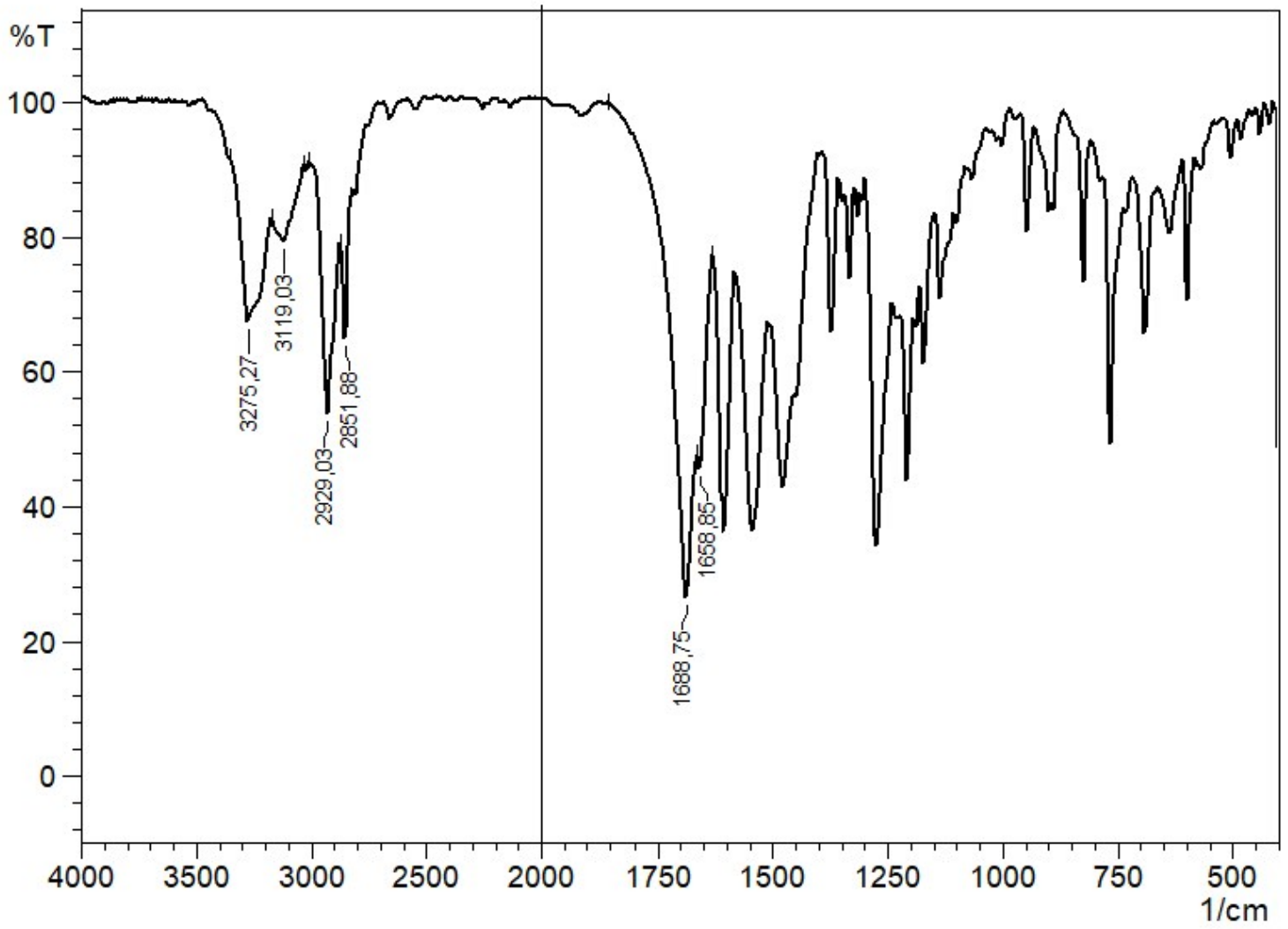


Figure 46S. IR spectrum of **4**.

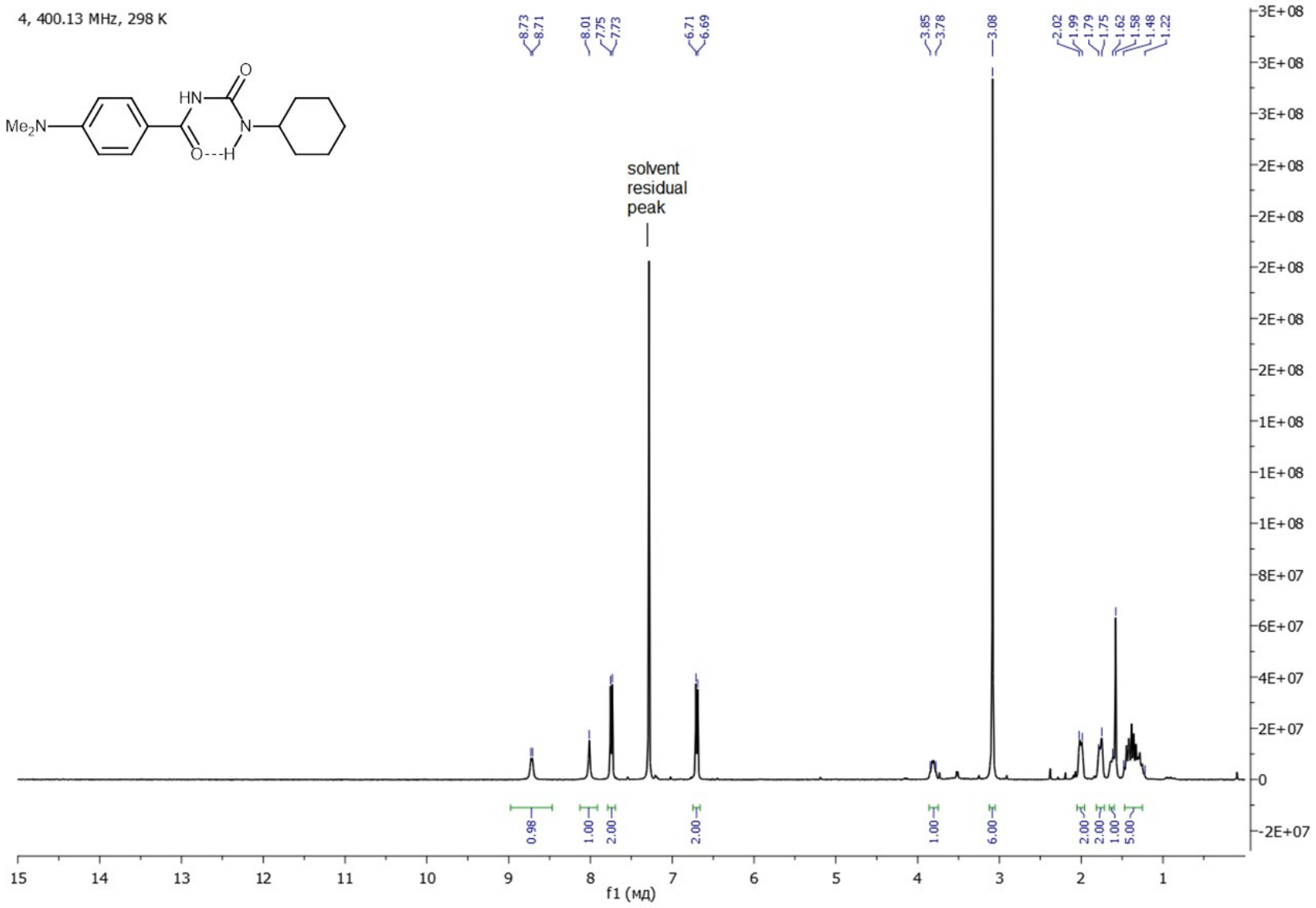


Figure 47S. ^{1}H NMR spectrum of **4**.

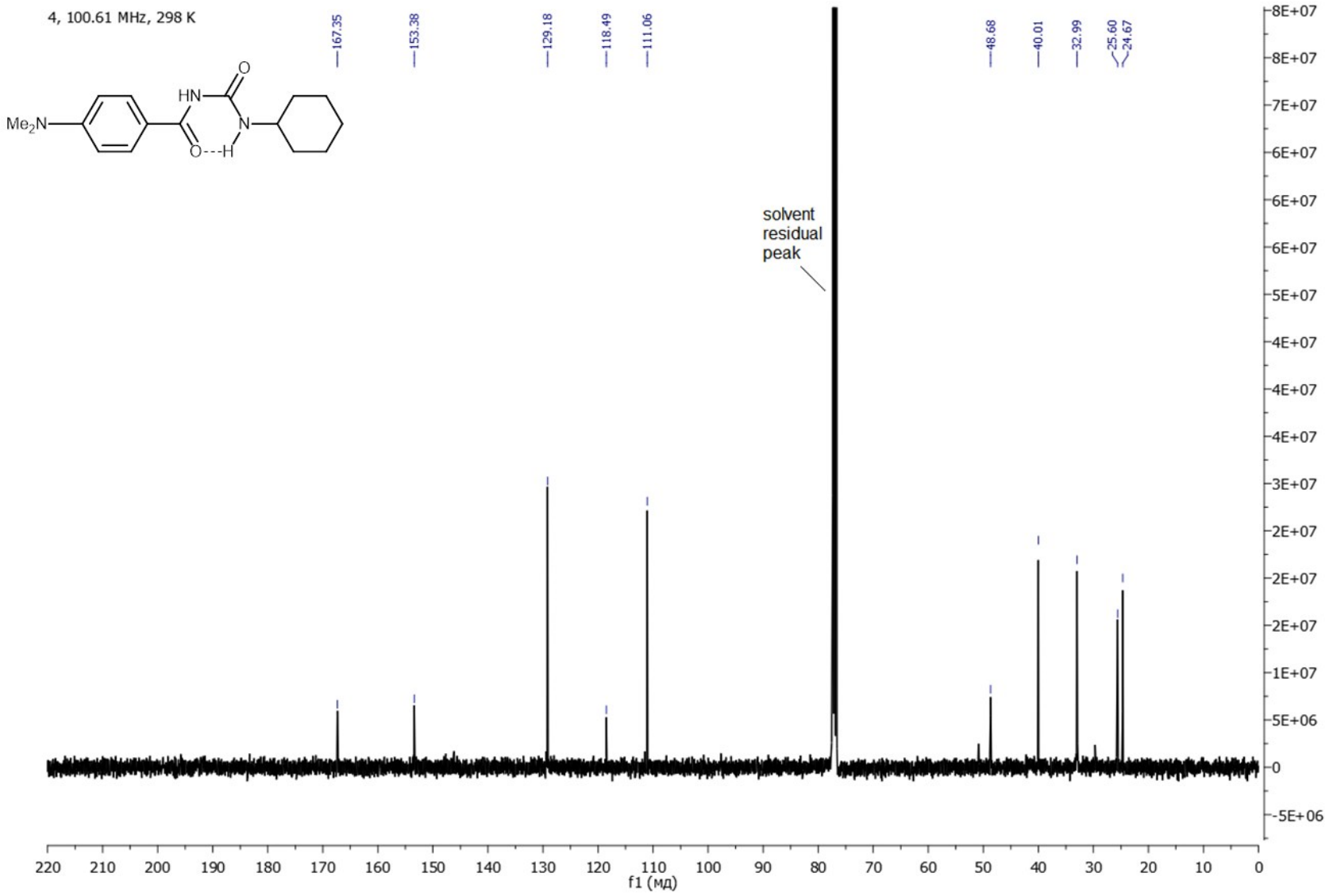


Figure 48S. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

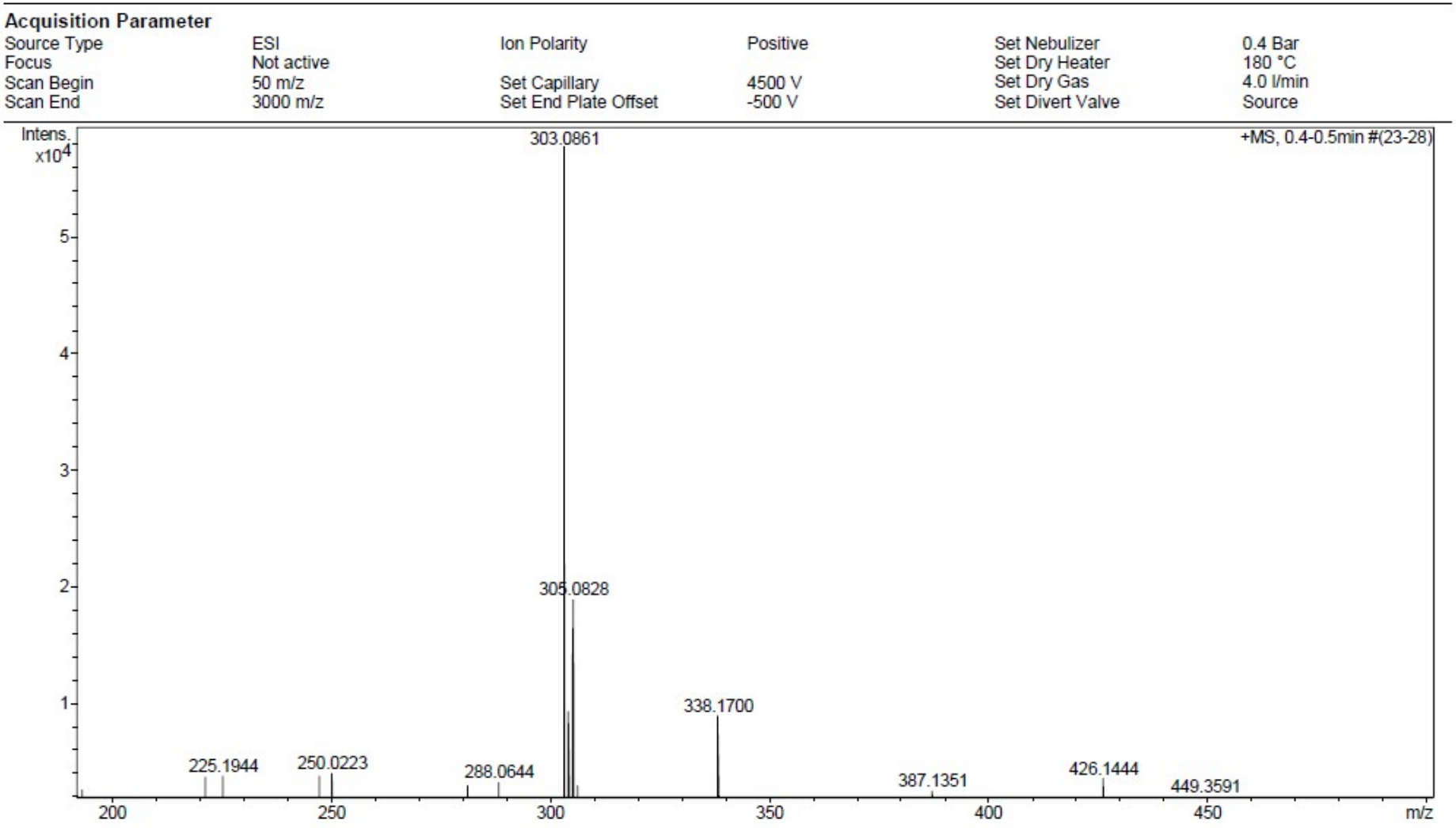


Figure 49S. HRESI^{+}-MS of **5**.

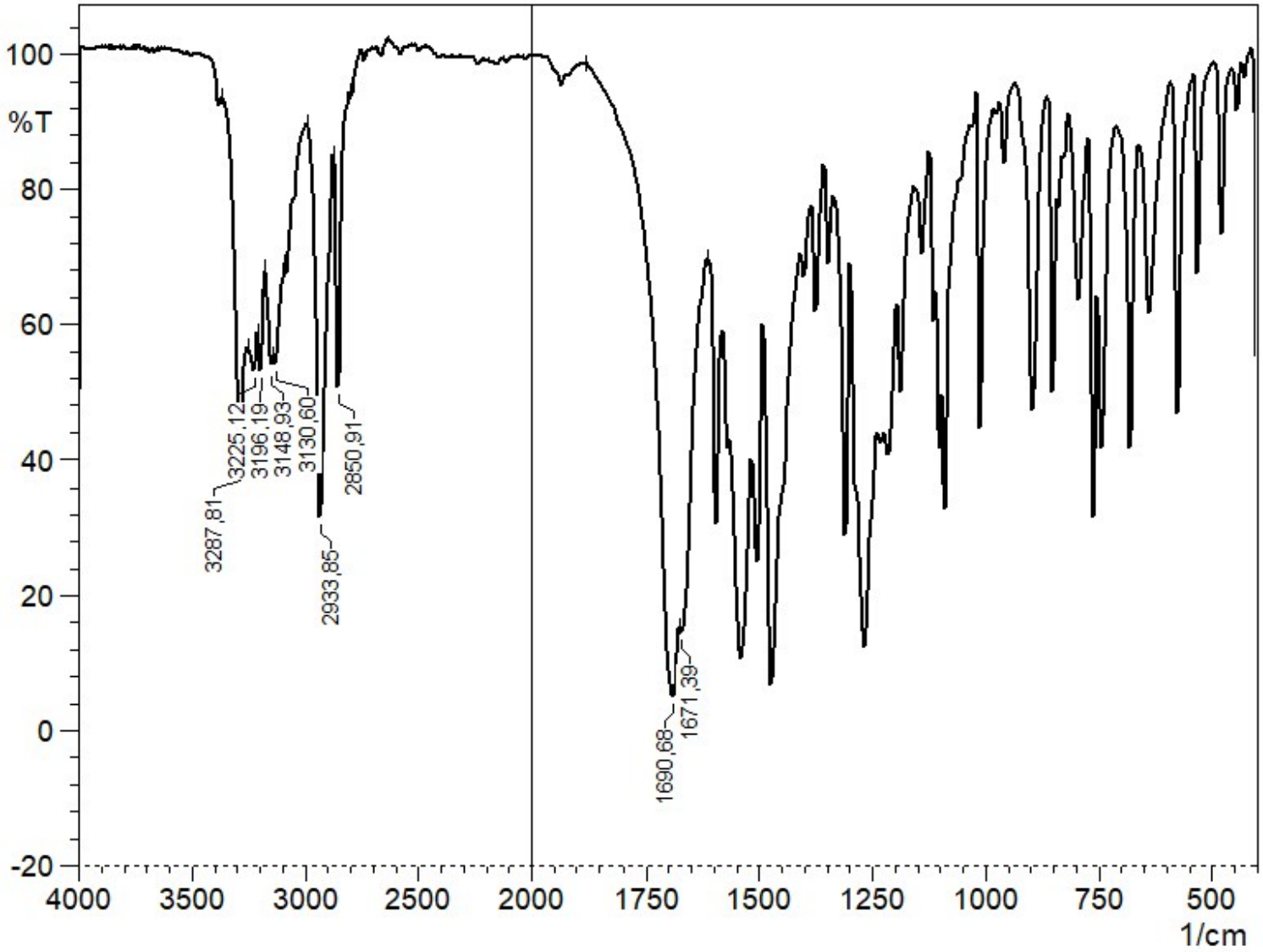


Figure 50S. IR spectrum of **5**.

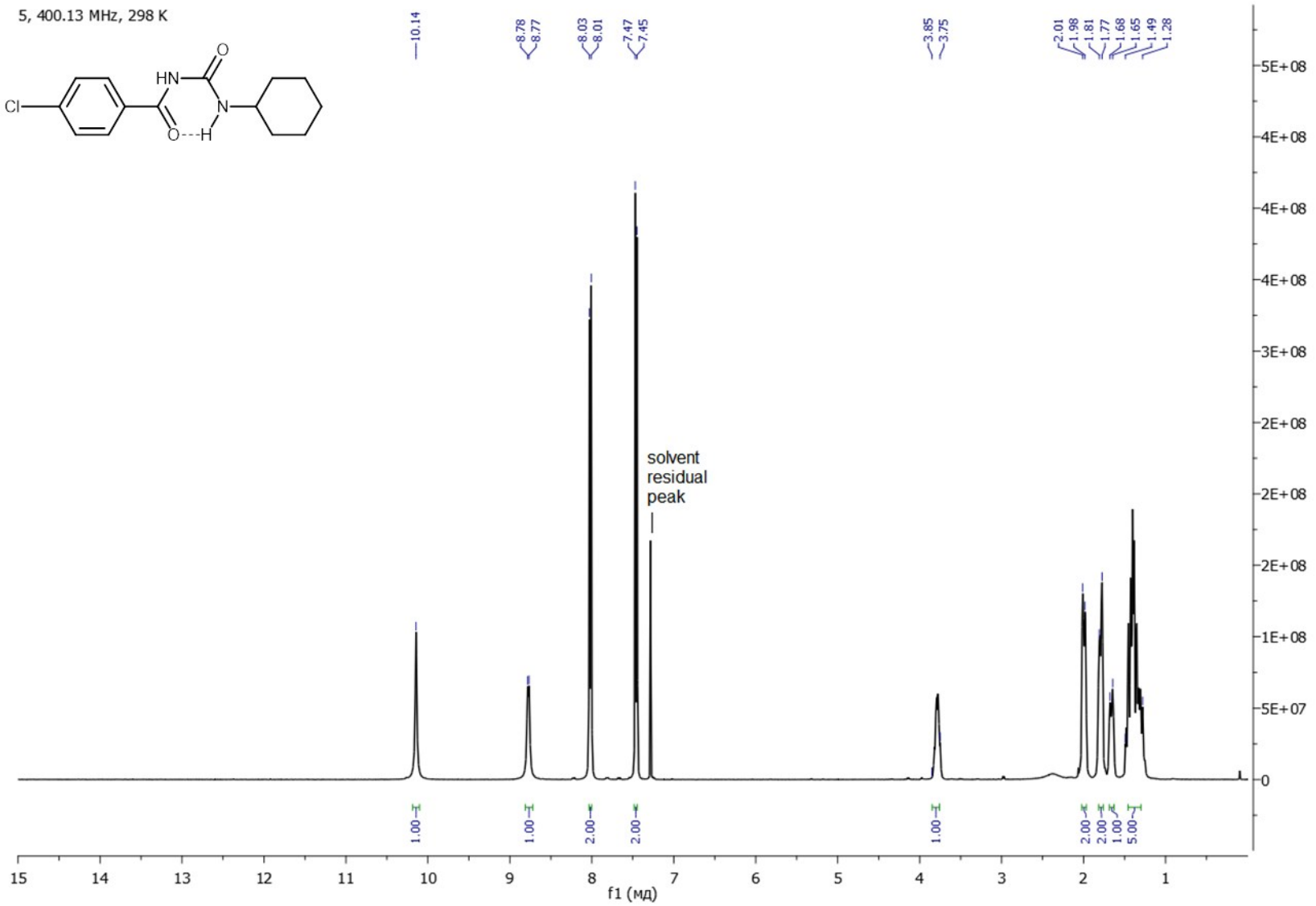


Figure 51S. ^{1}H NMR spectrum of **5**.

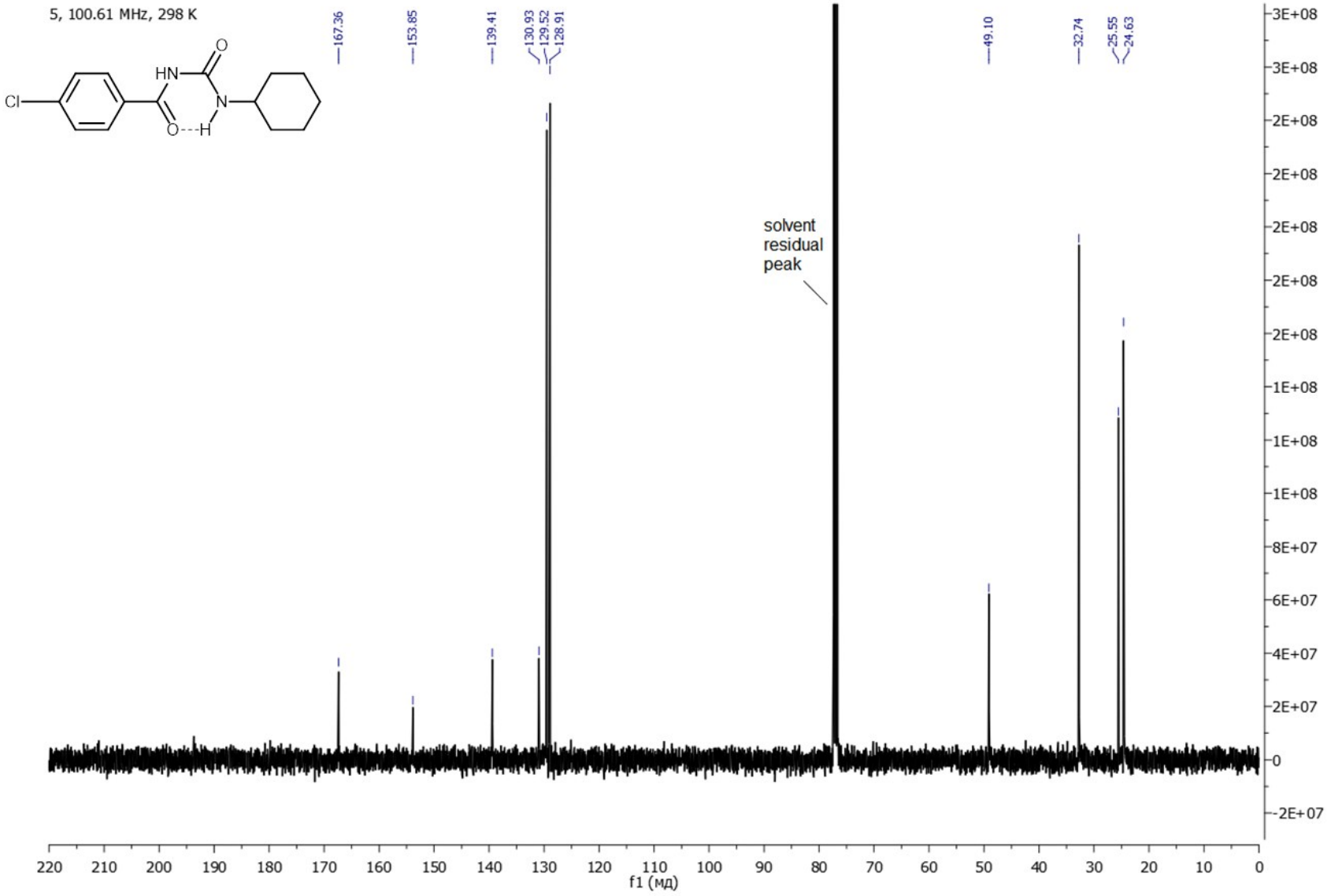


Figure 52S. $^{13}C\{^{1}H\}$ NMR spectrum of **5**.

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

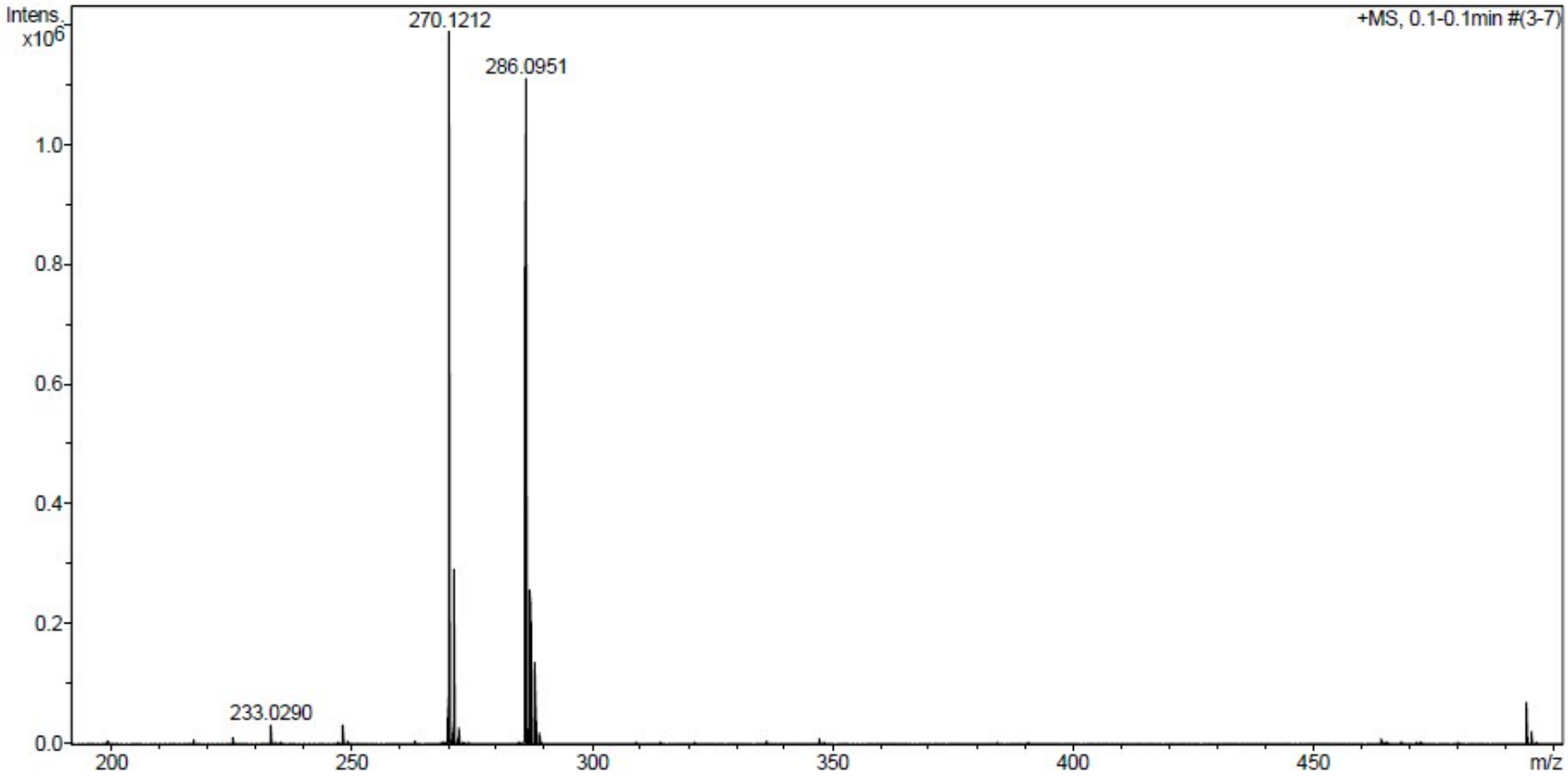


Figure 53S. HRESI^{+}-MS of **6**.

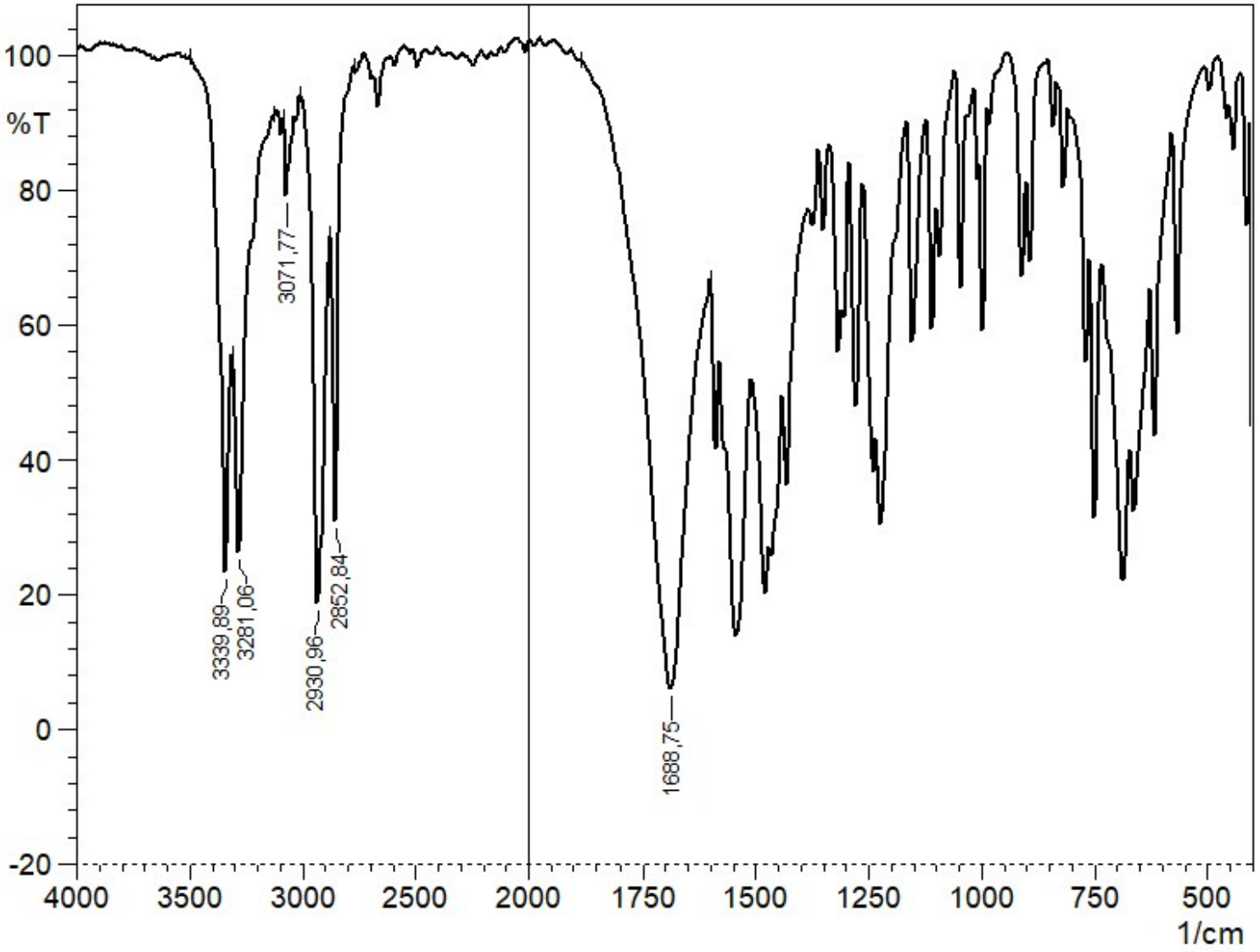


Figure 54S. IR spectrum of **6**.

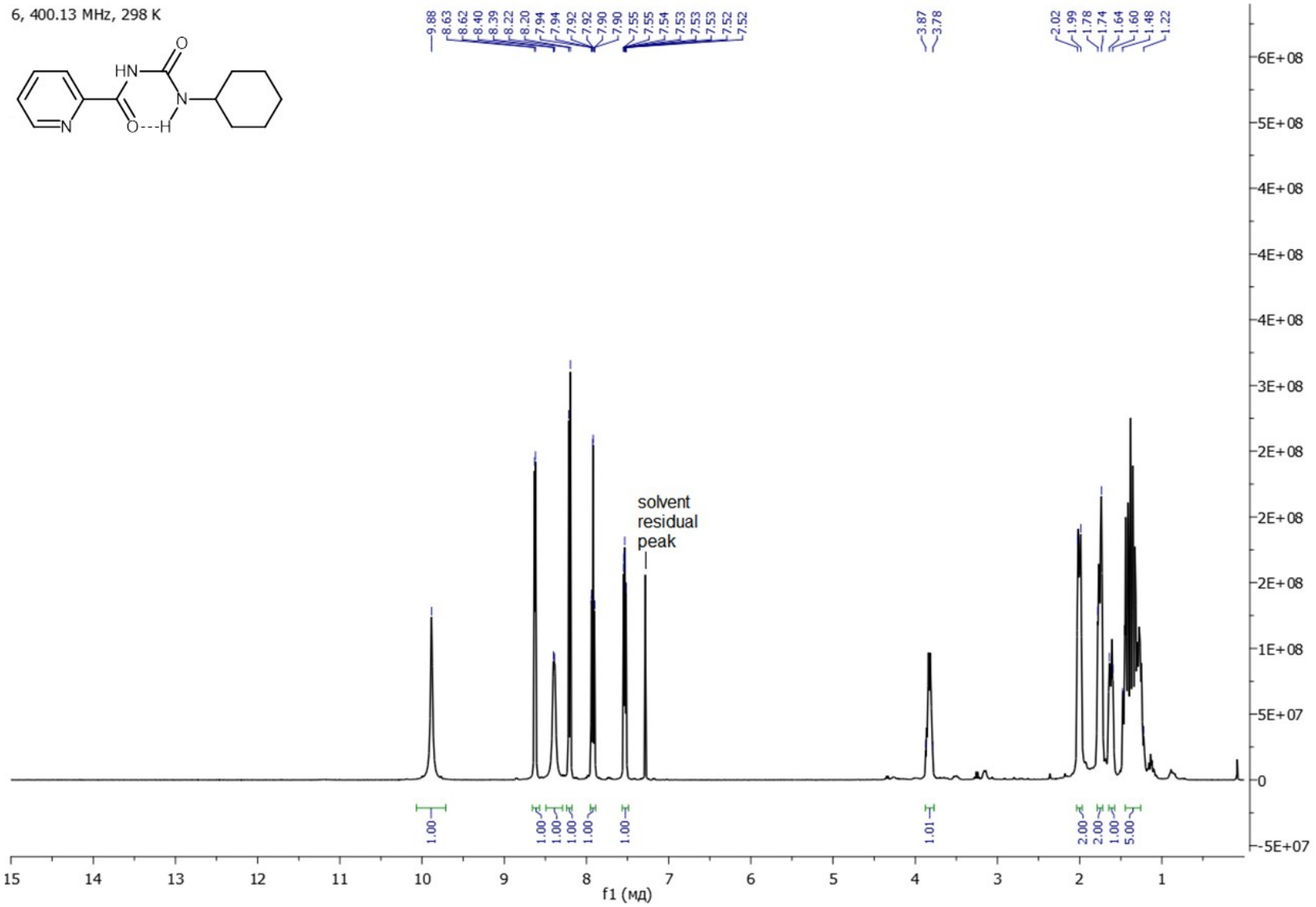


Figure 55S. ^{1}H NMR spectrum of **6**.

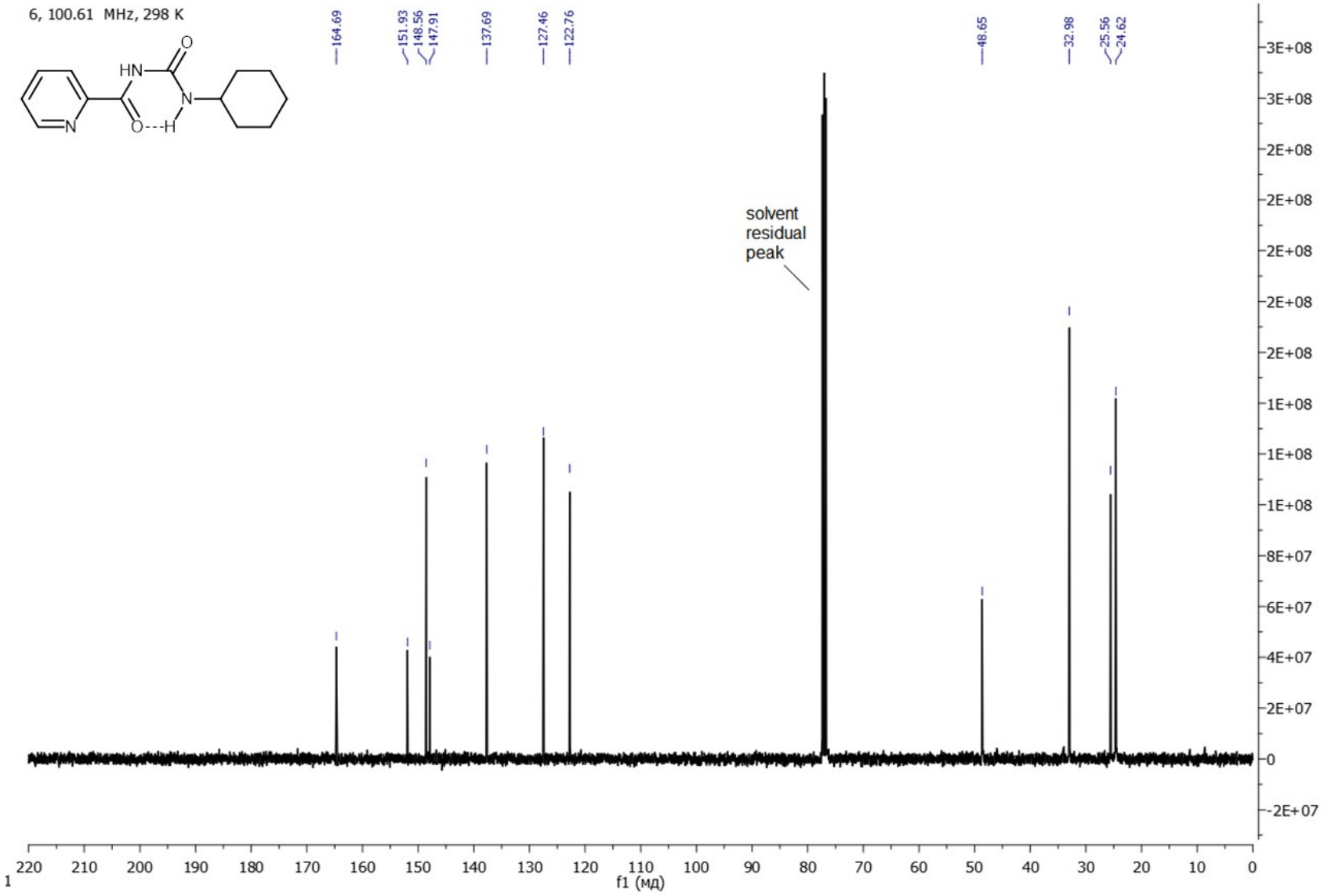


Figure 56S. $^{13}C\{^{1}H\}$ NMR spectrum of **6**.

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

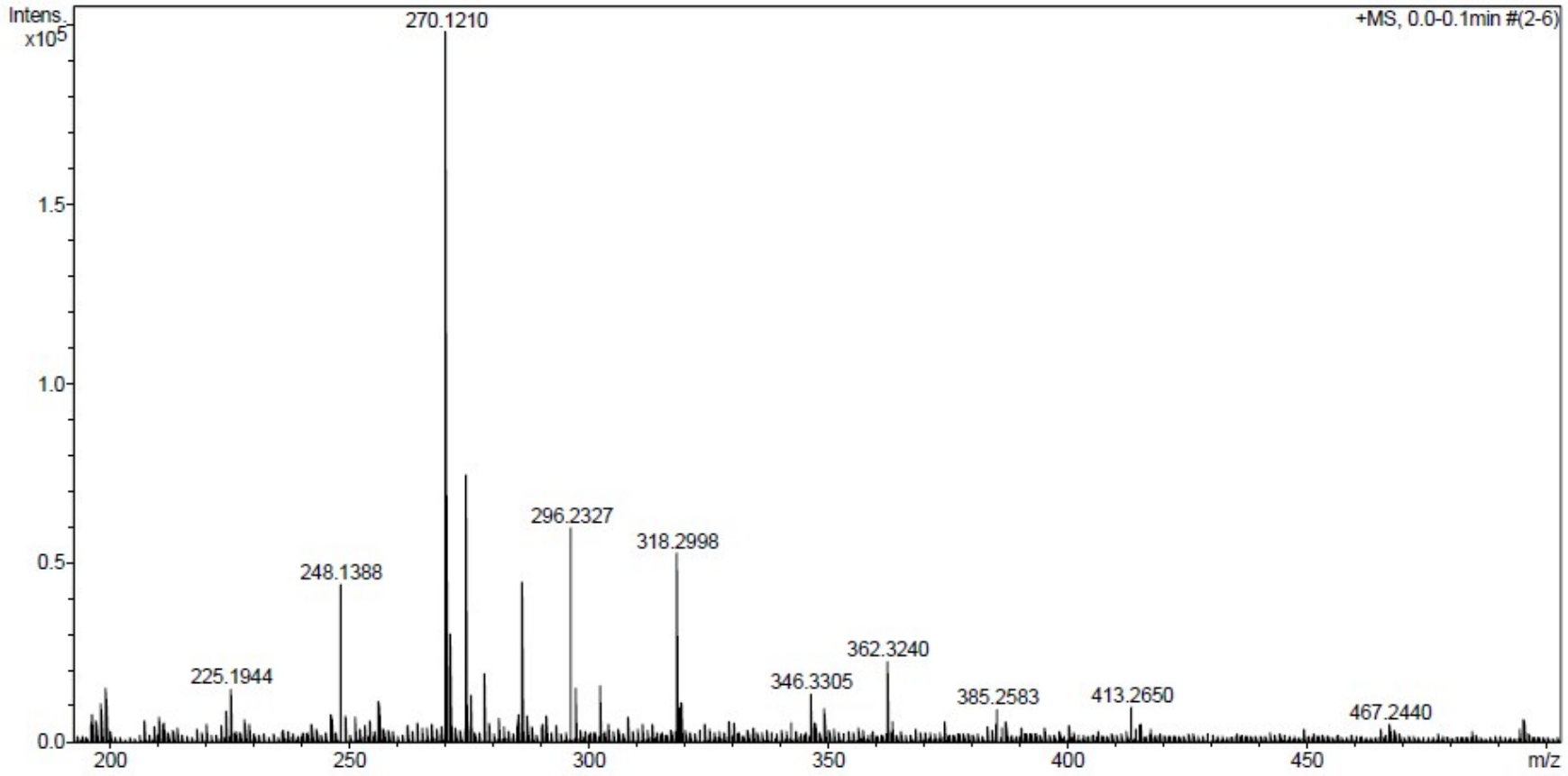


Figure 57S. HRESI^{+}-MS of **7**.

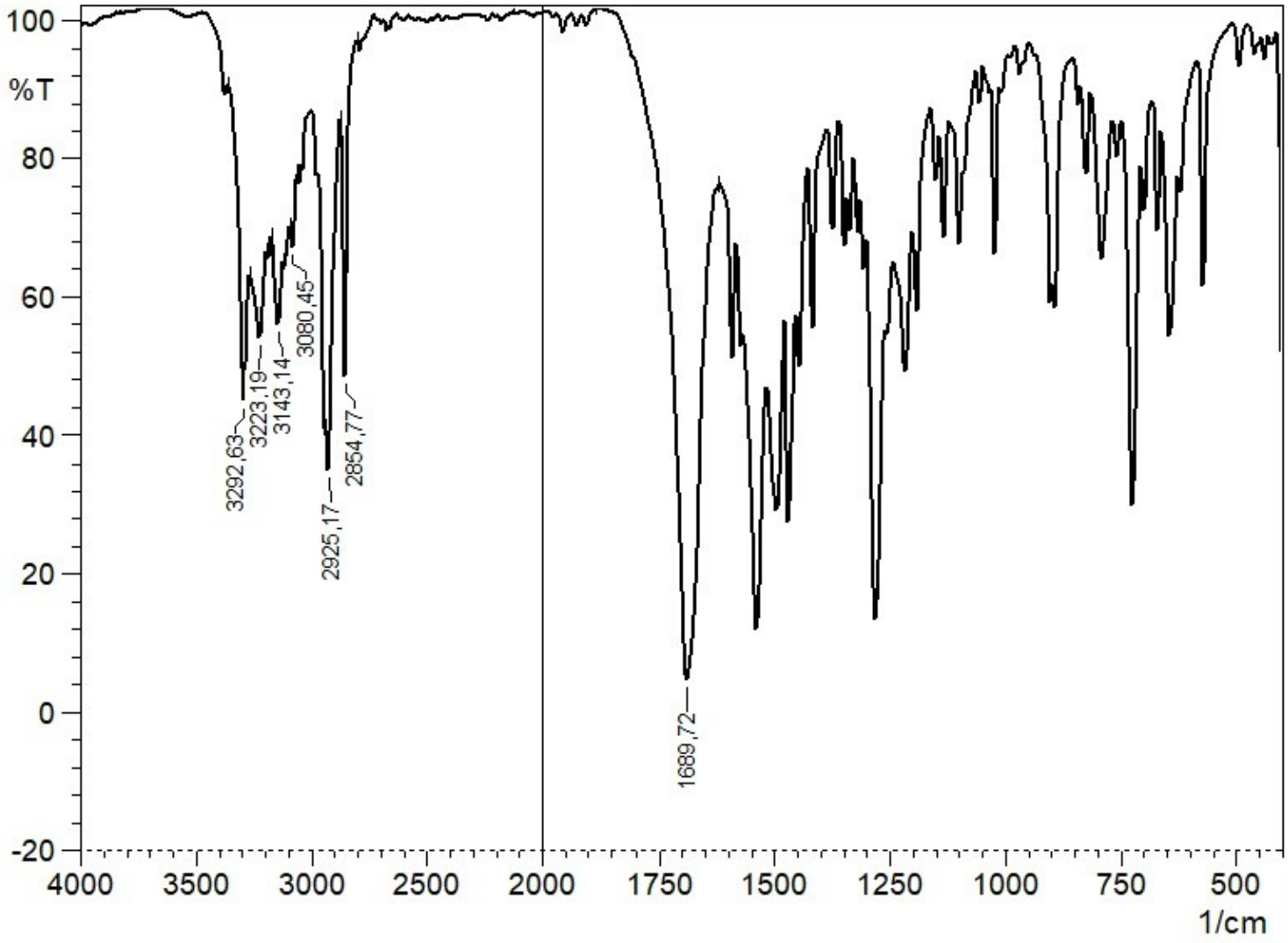


Figure 58S. IR spectrum of **7**.

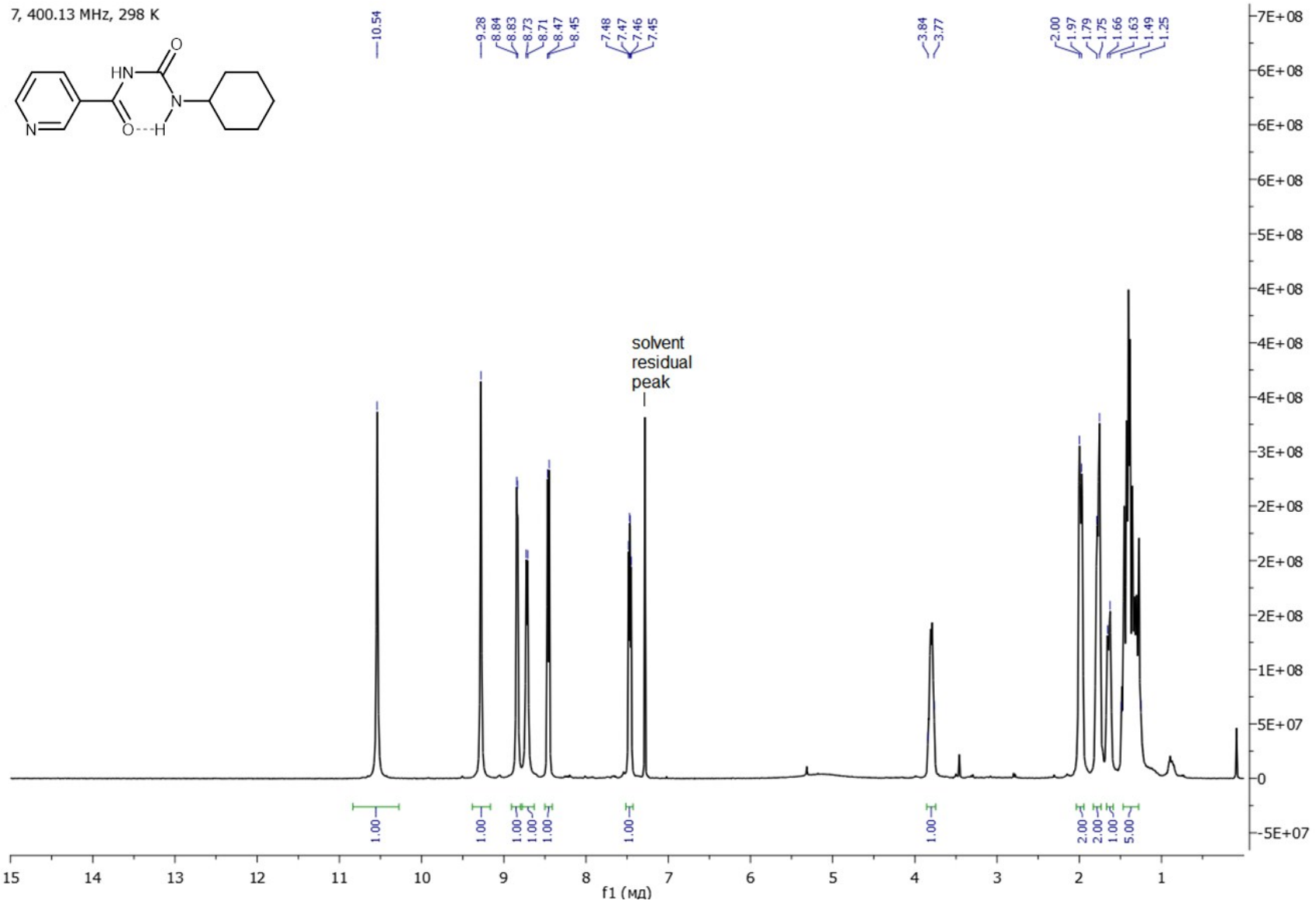


Figure 59S. ^{1}H NMR spectrum of **7**.

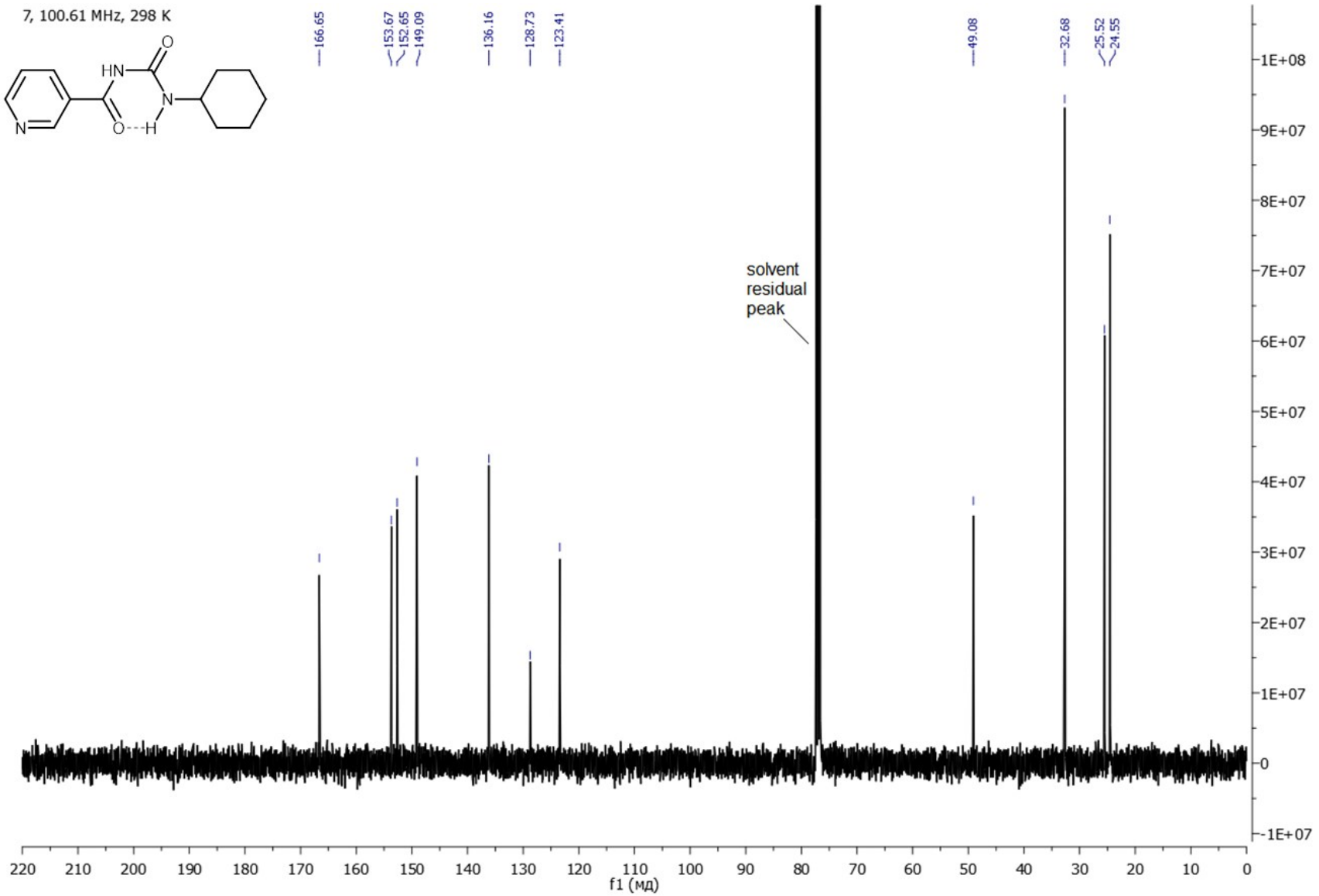


Figure 60S. $^{13}C\{^{1}H\}$ NMR spectrum of **7**.

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

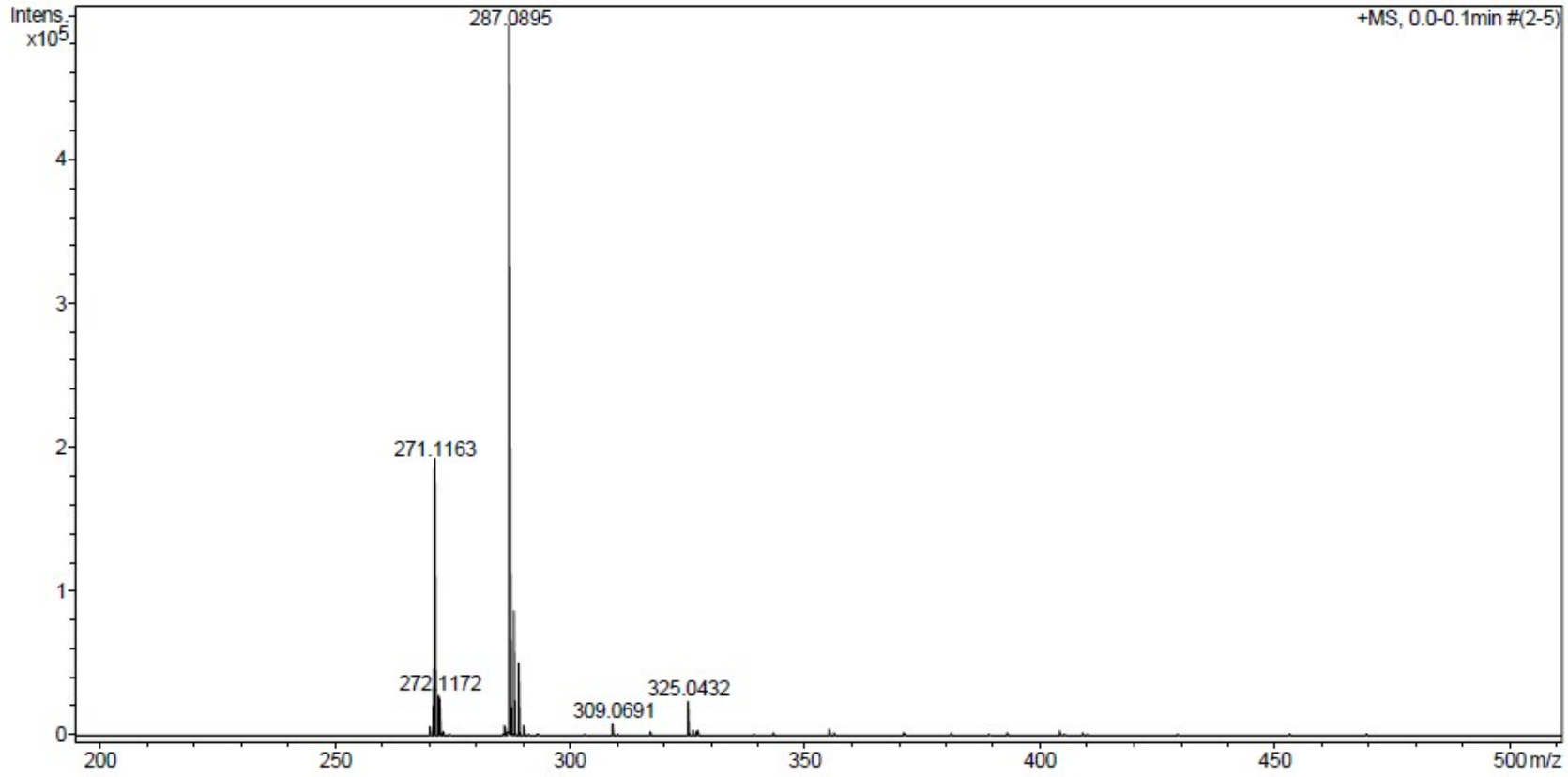


Figure 61S. HRESI^{+}-MS of **8**.

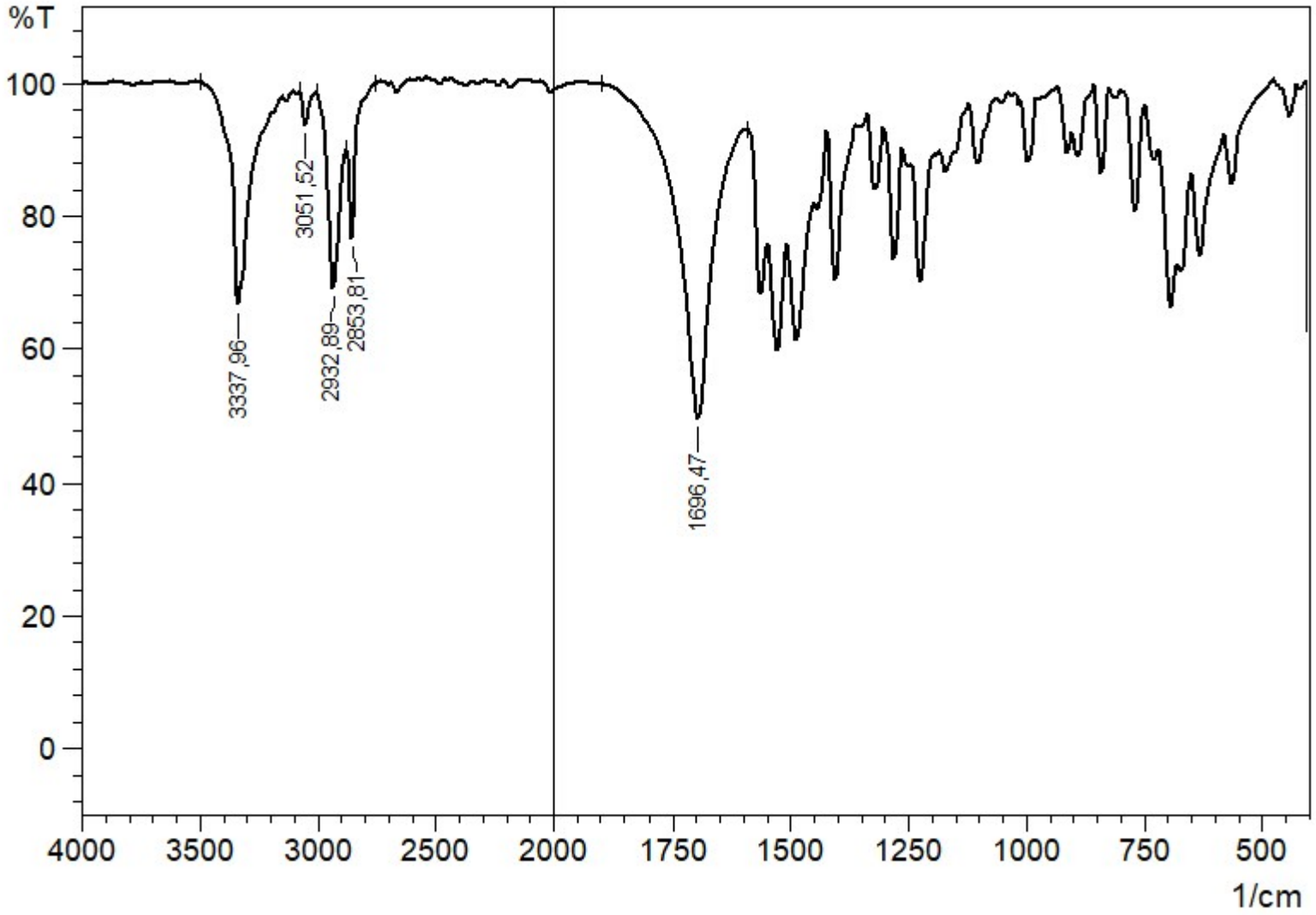


Figure 62S. IR spectrum of **8**.

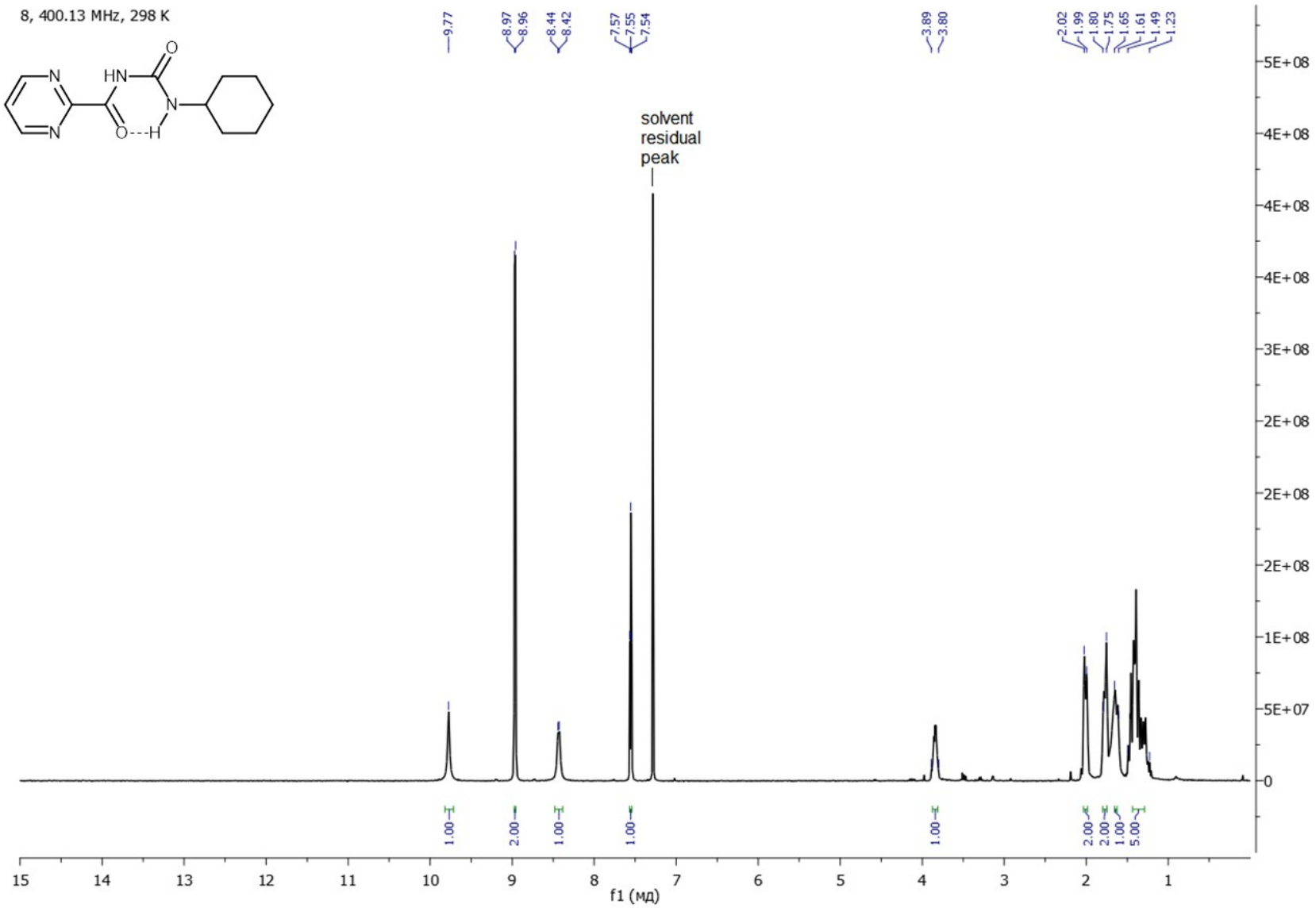


Figure 63S. ^{1}H NMR spectrum of **8**.

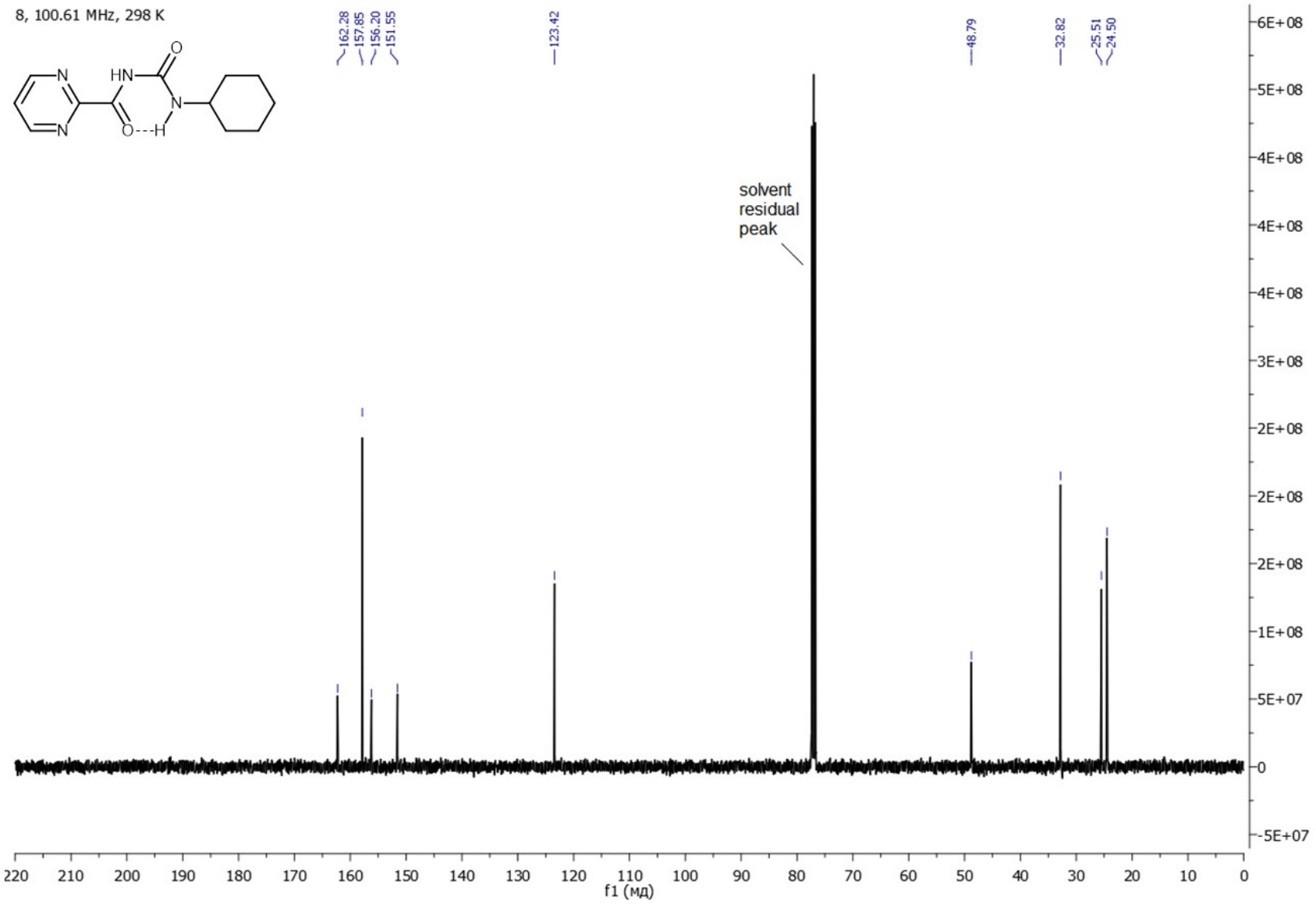


Figure 64S. $^{13}C\{^{1}H\}$ NMR spectrum of **8**.

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

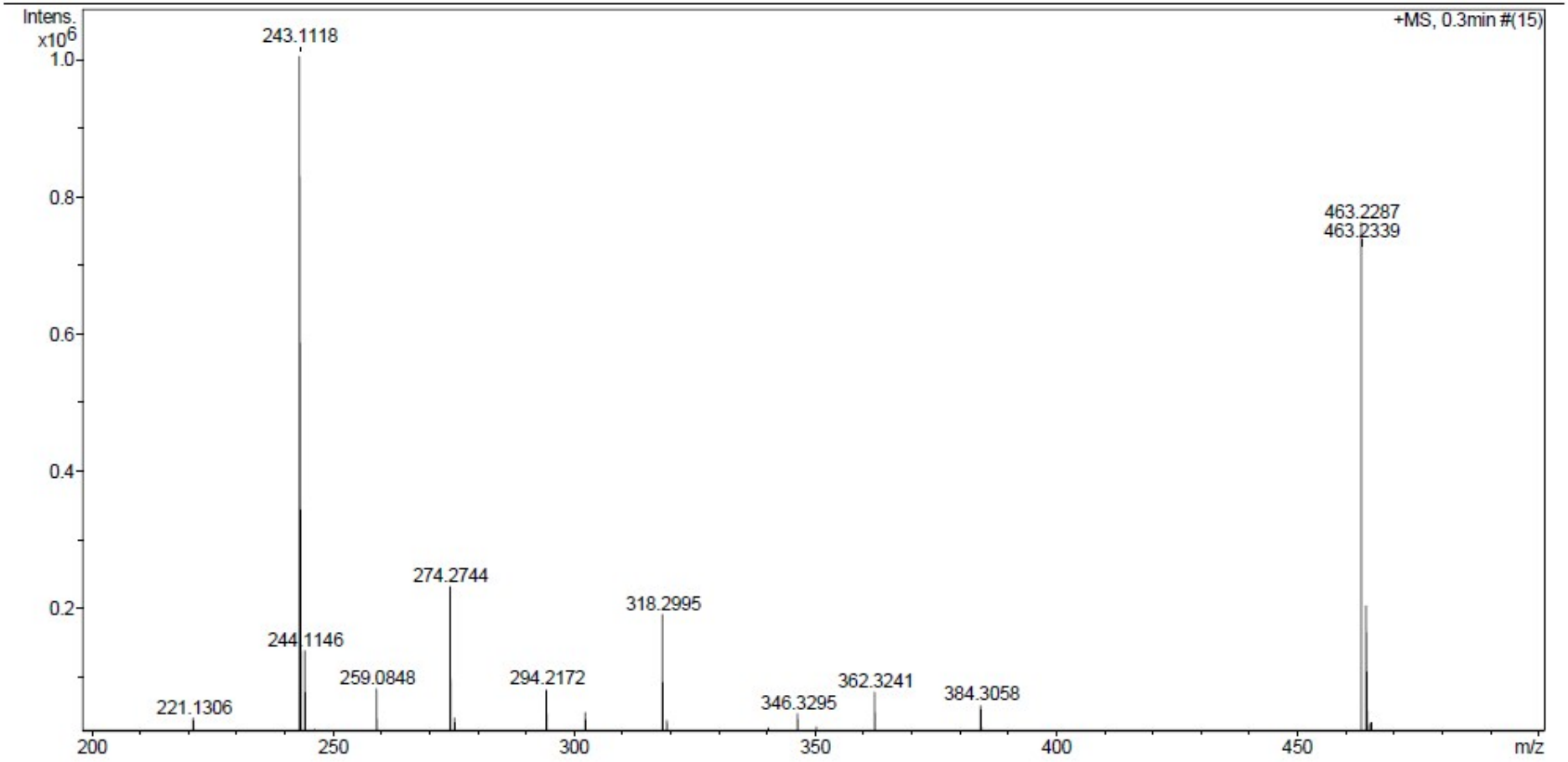


Figure 65S. HRESI^{+}-MS of **9**.

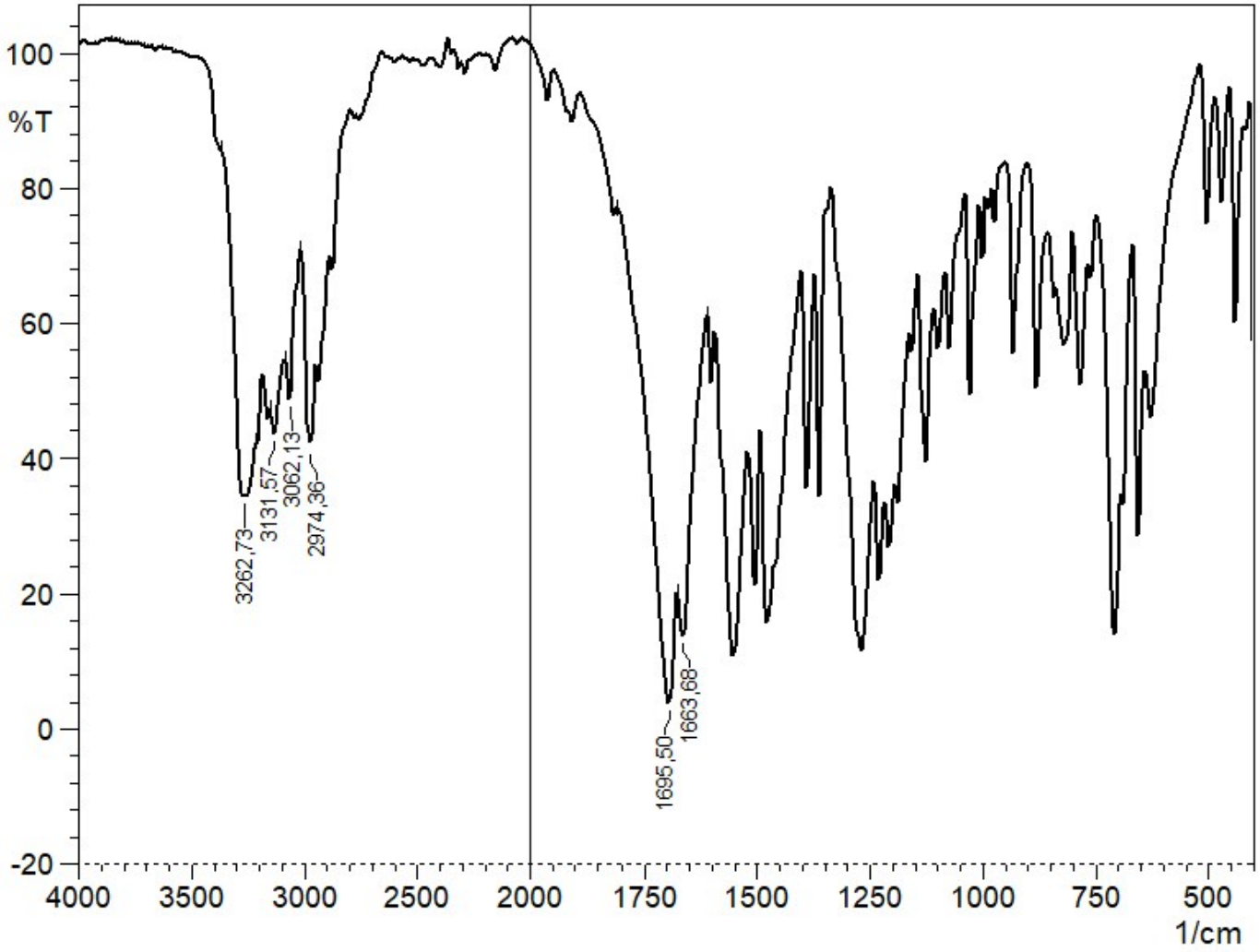


Figure 66S. IR spectrum of **9**.

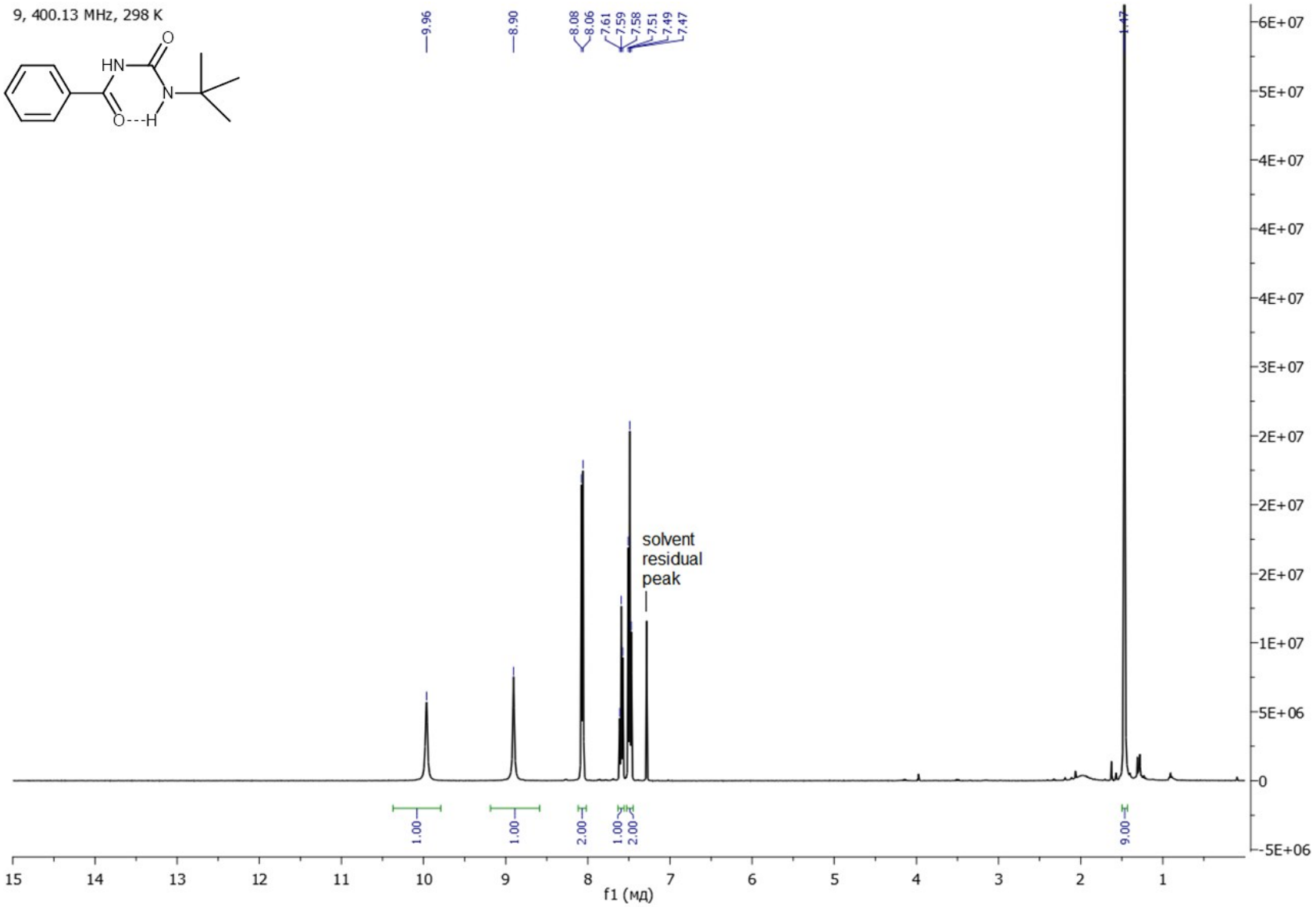


Figure 67S. ^{1}H NMR spectrum of **9**.

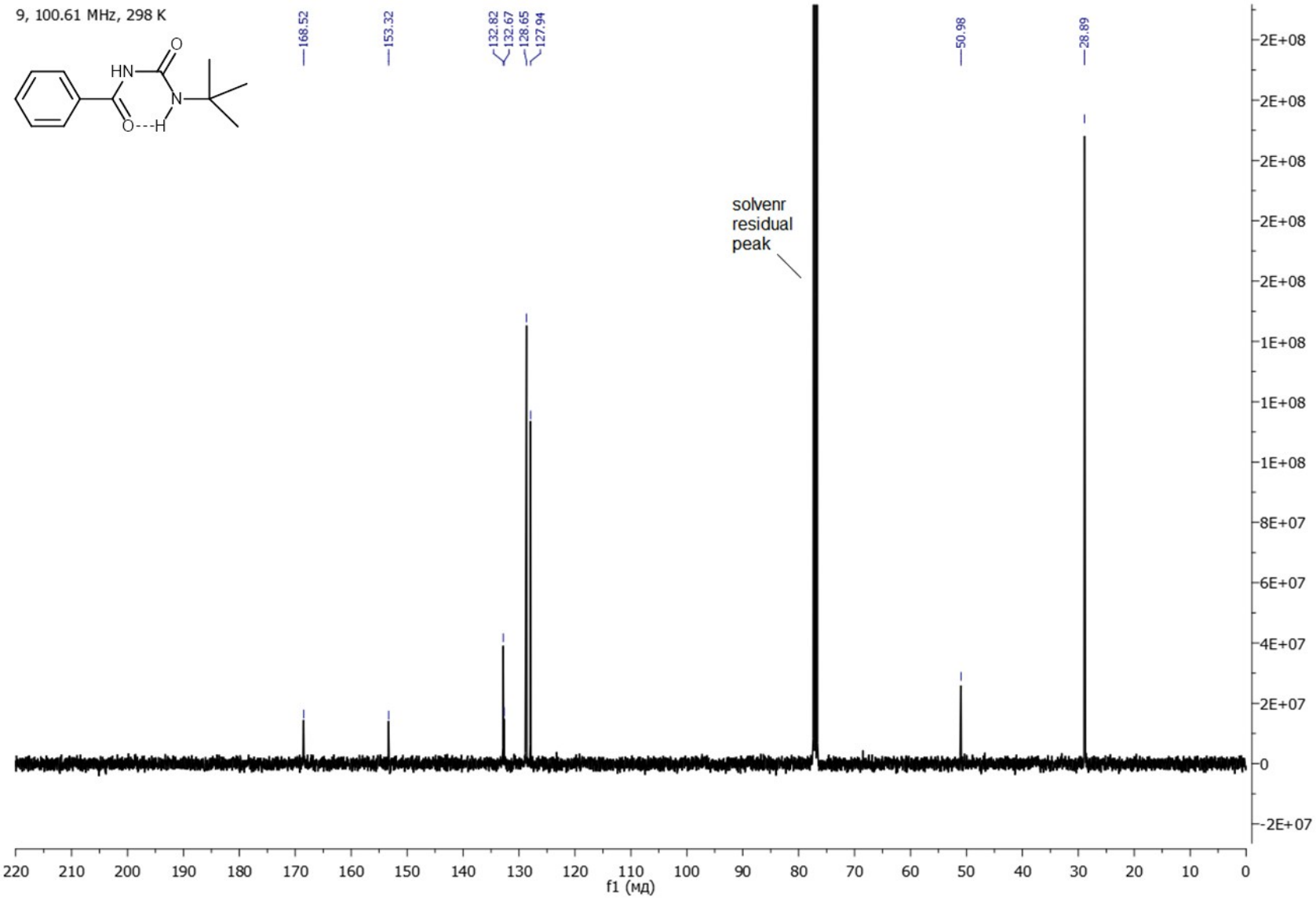


Figure 68S. $^{13}C\{^{1}H\}$ NMR spectrum of **9**.

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

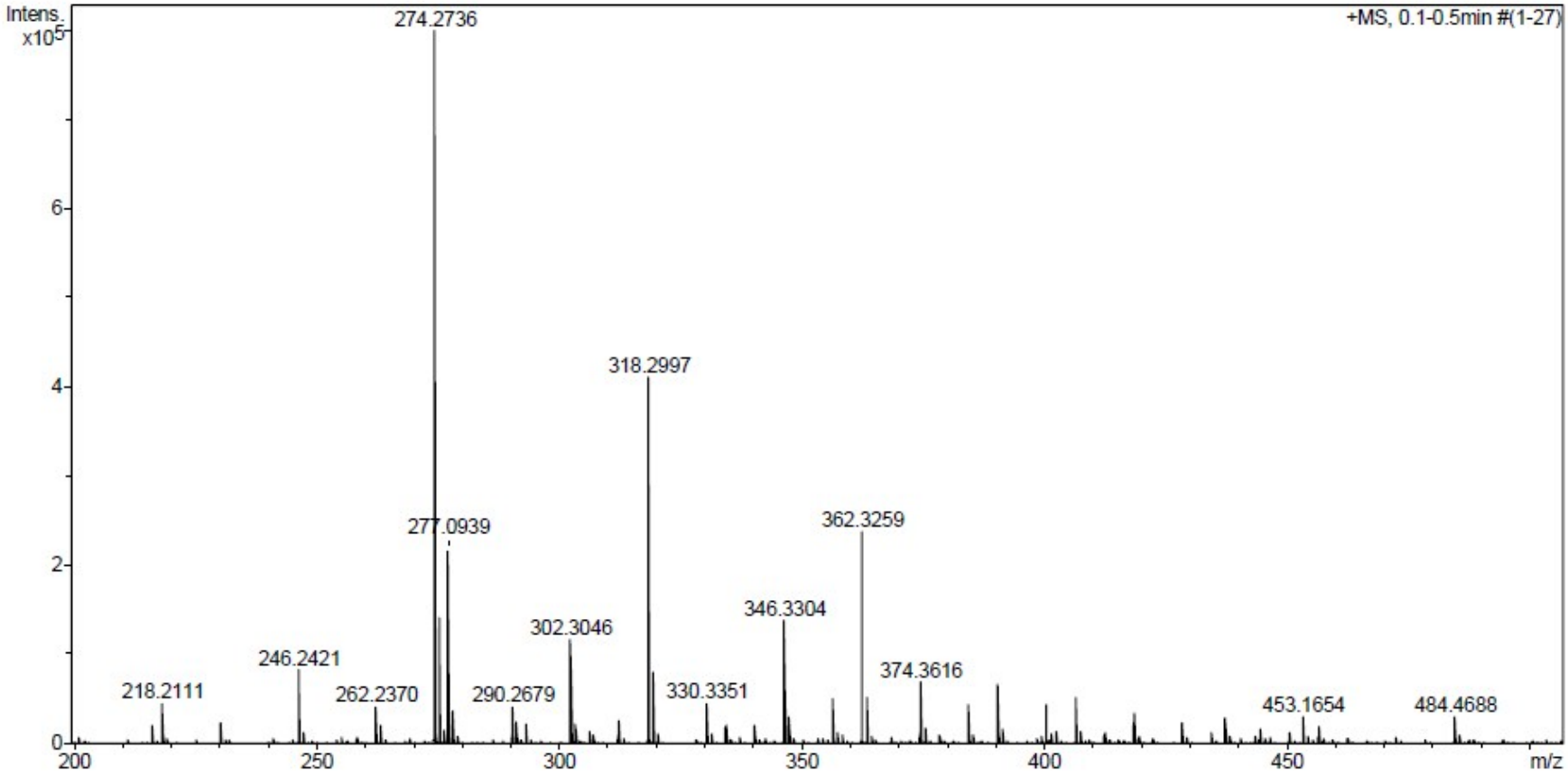


Figure 69S. HRESI^{+}-MS of **10**.

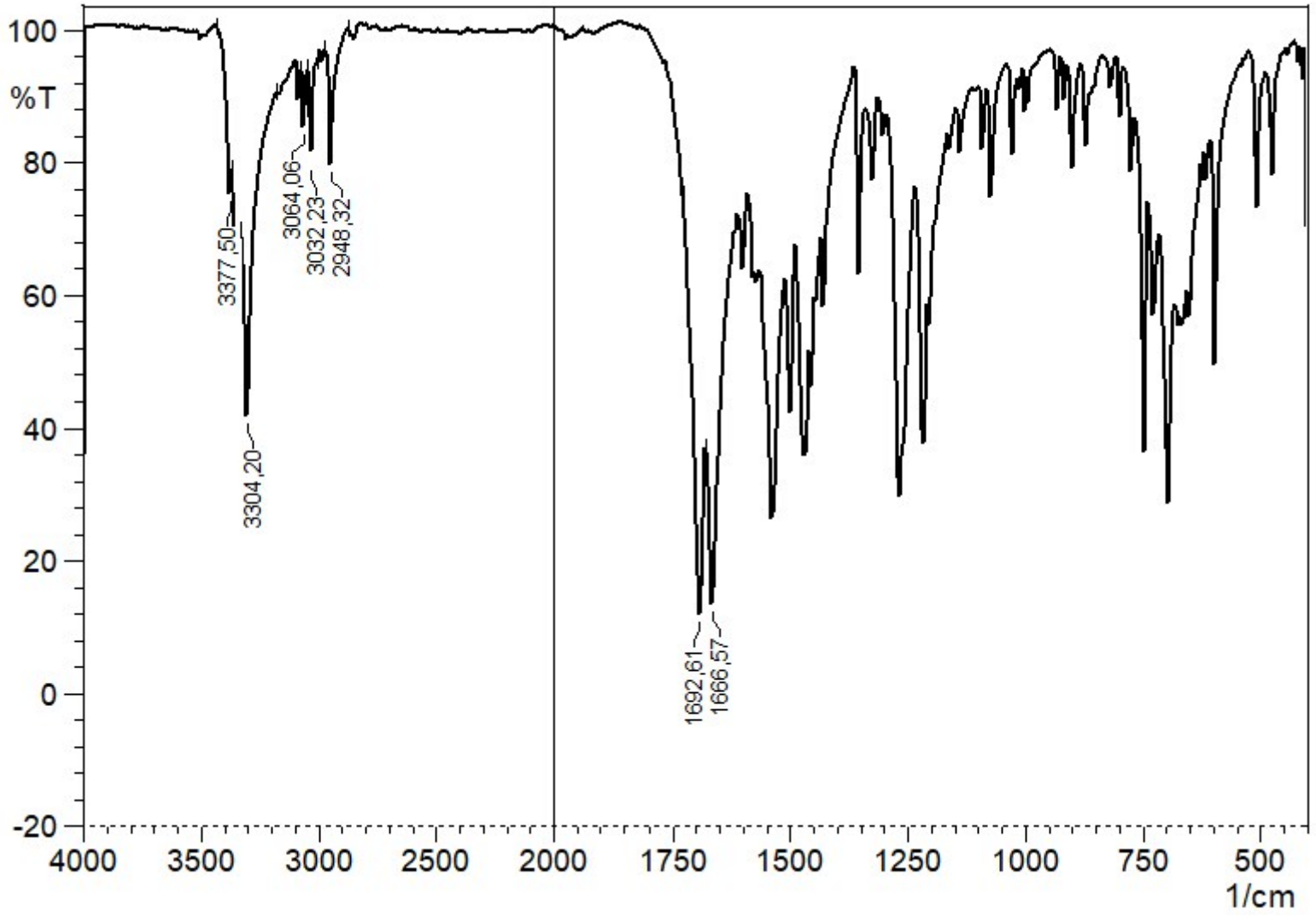


Figure 70S. IR spectrum of **10**.

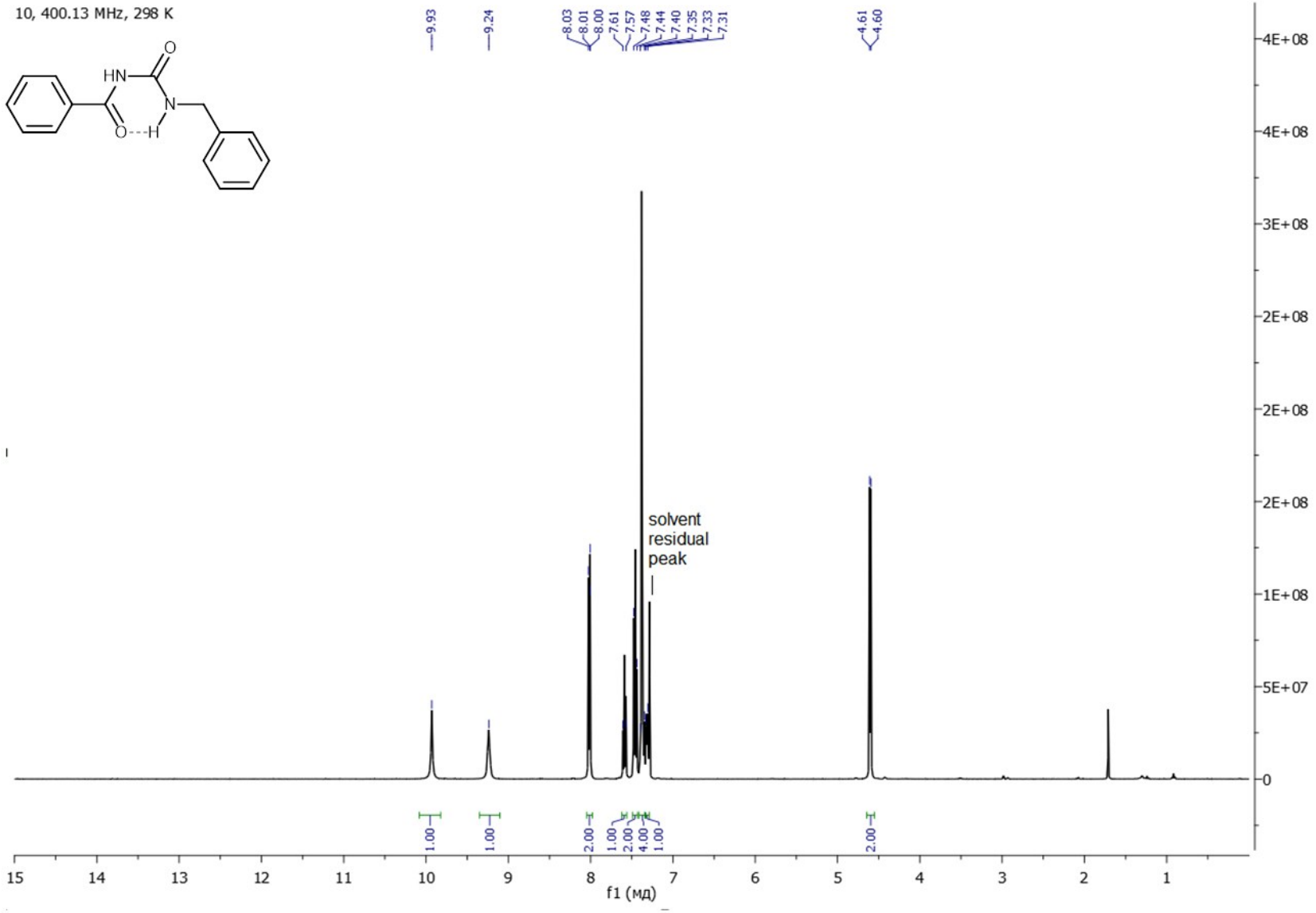


Figure 71S. $^{13}C\{^{1}H\}$ NMR spectrum of **10**.

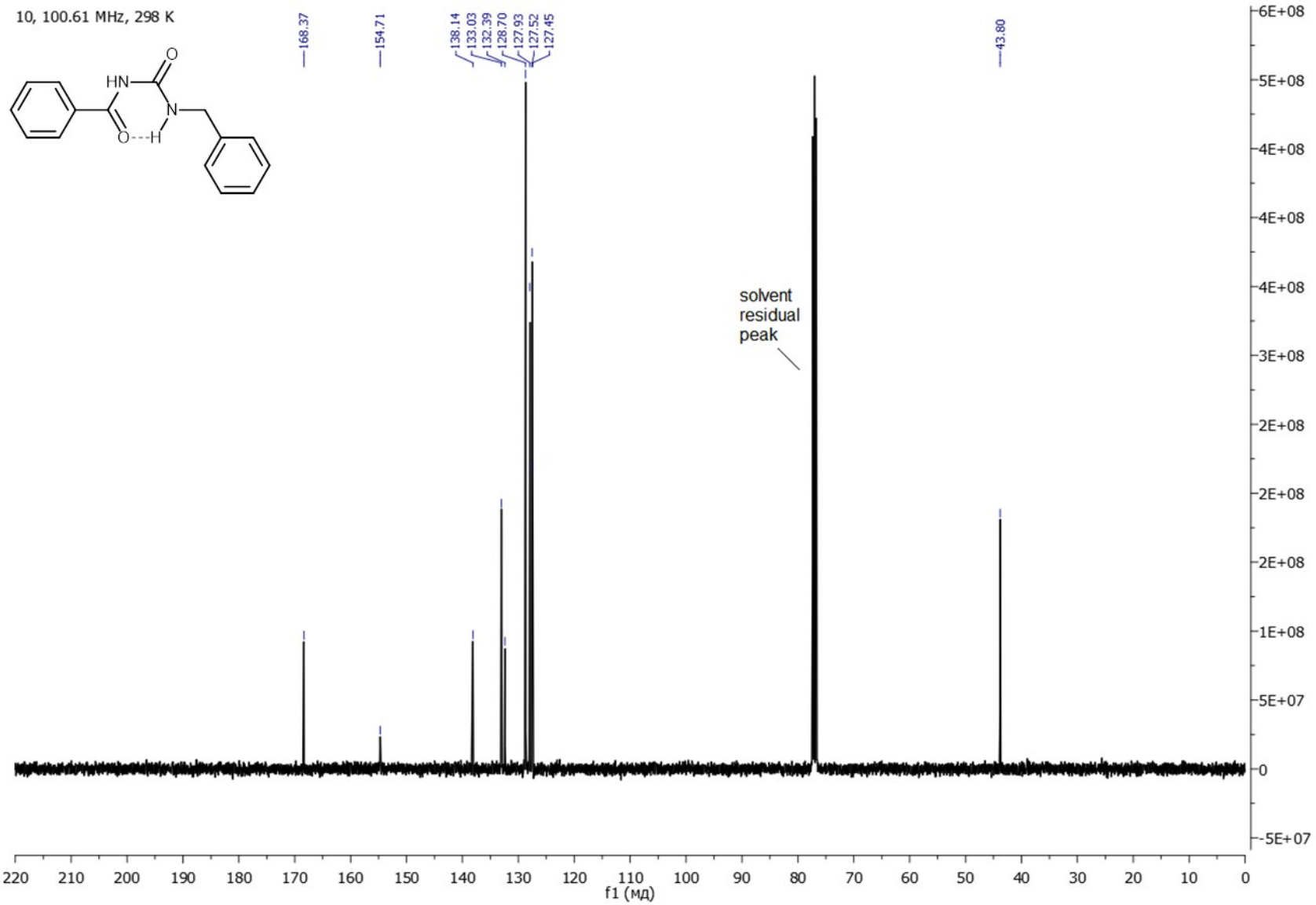


Figure 72S. $^{13}C\{^{1}H\}$ NMR spectrum of **10**.

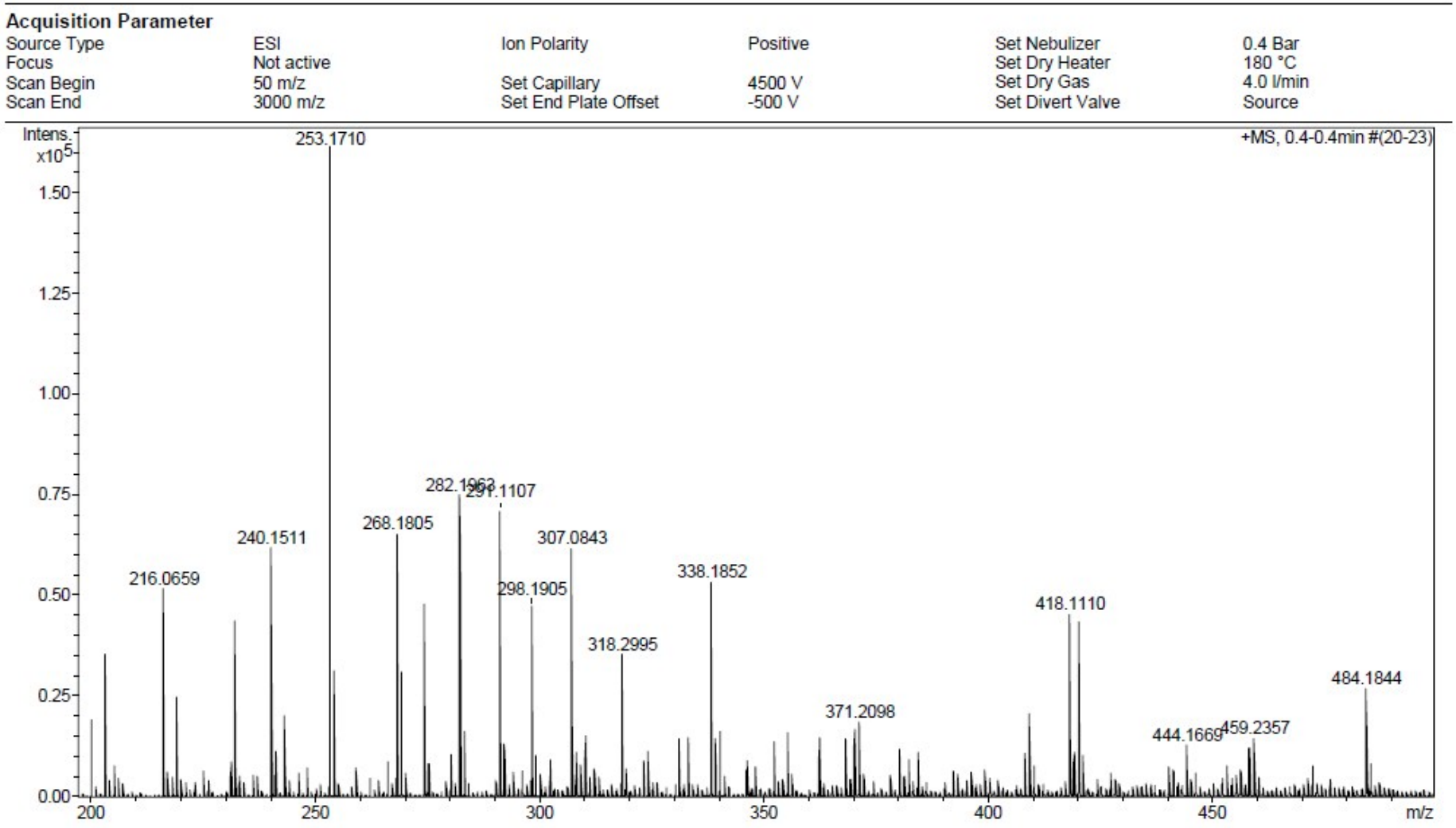


Figure 73S. HRESI^{+}-MS of **11**.

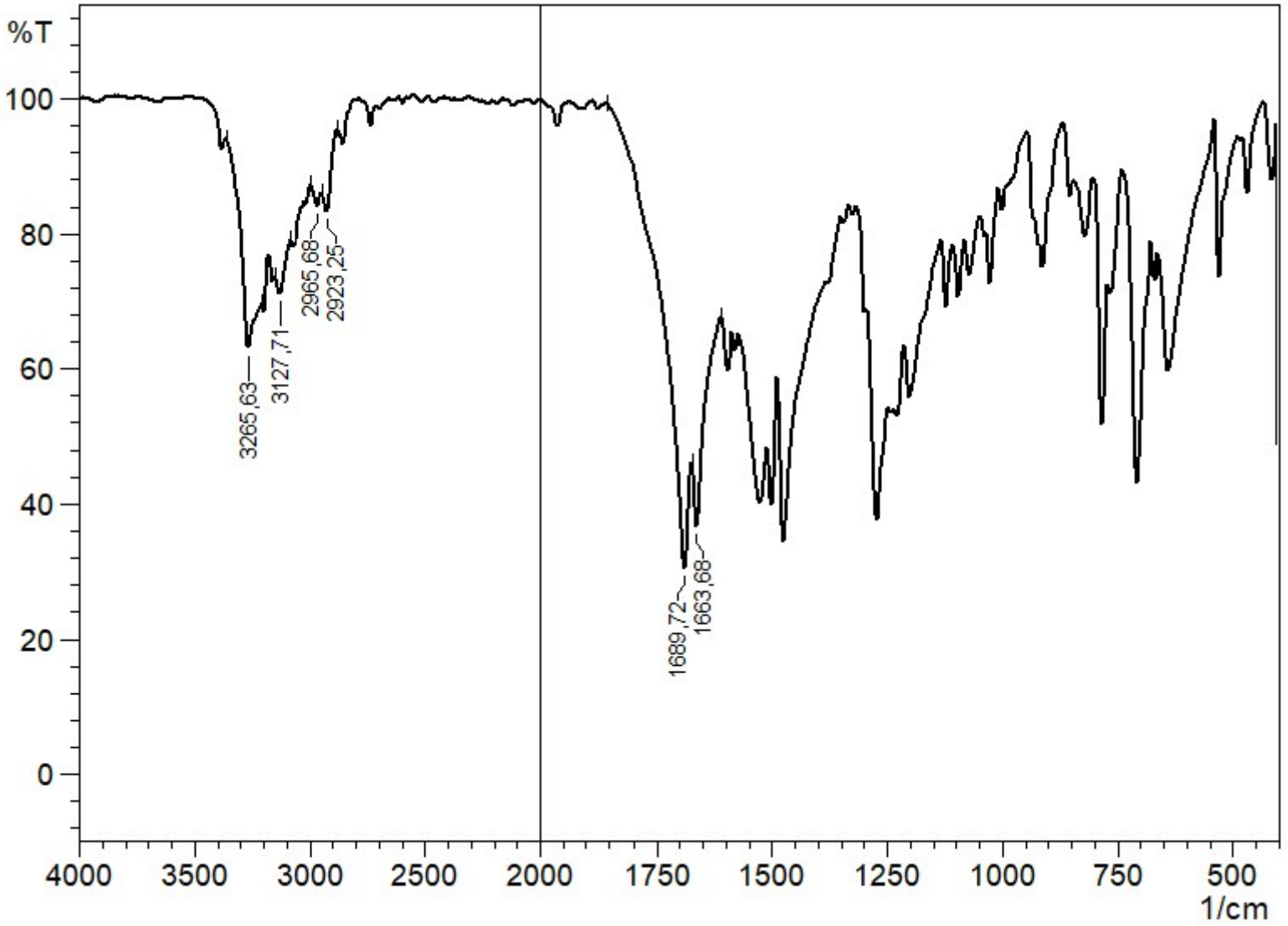


Figure 74S. IR spectrum of **11**.

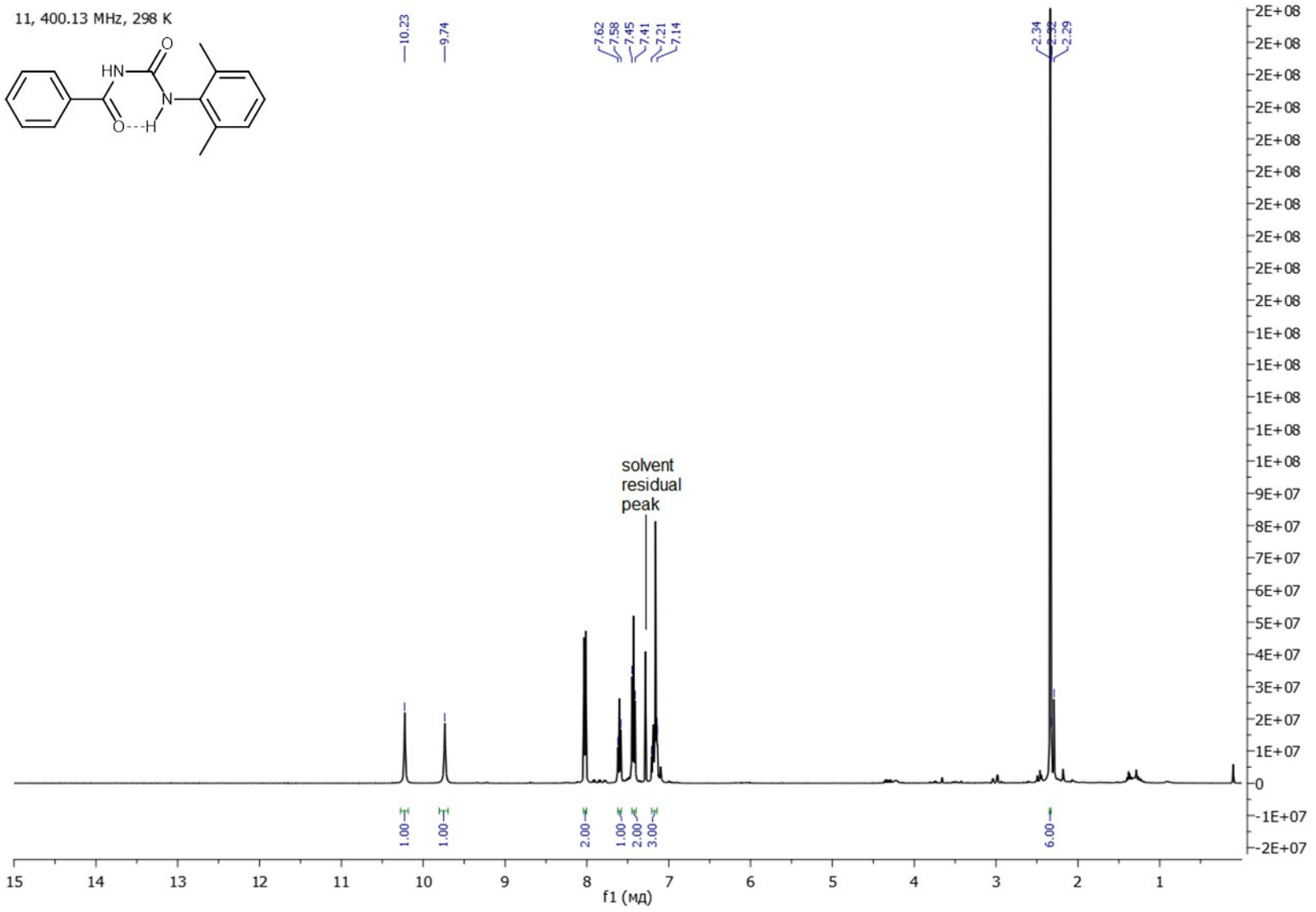


Figure 75S. $^{13}C\{^{1}H\}$ NMR spectrum of **11**.

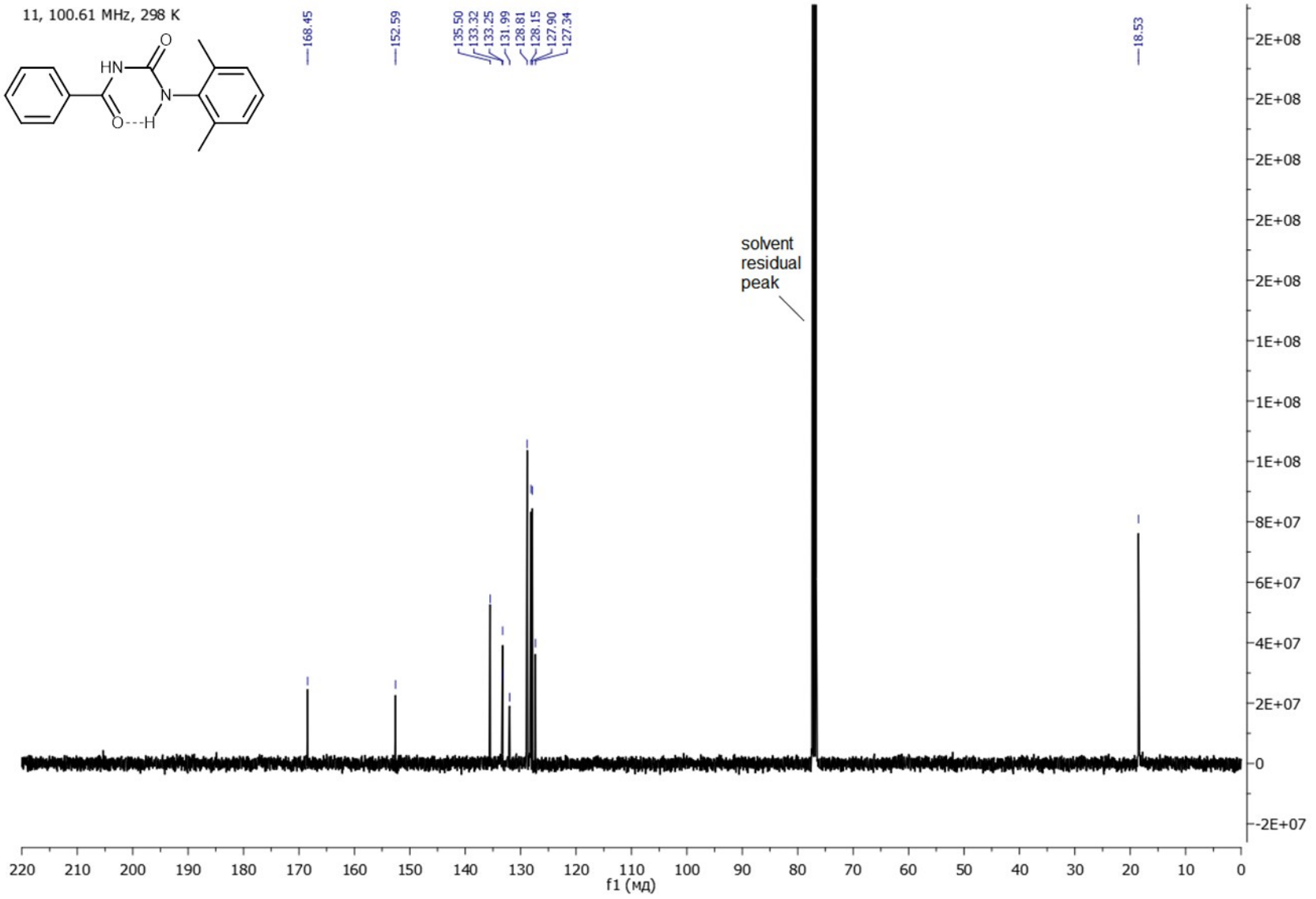


Figure 76S. $^{13}C\{^{1}H\}$ NMR spectrum of **11**.

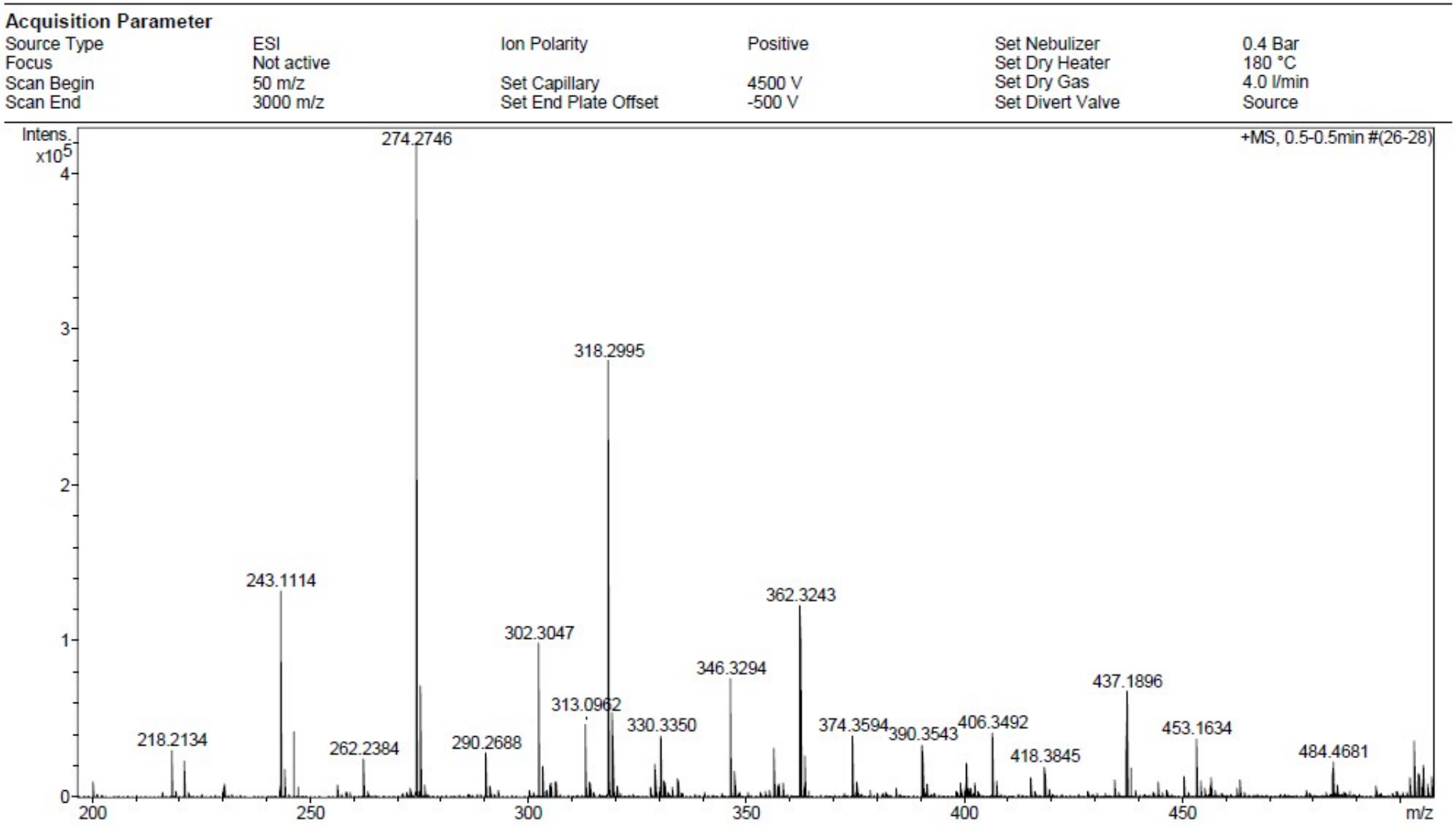


Figure 77S. HRESI^{+}-MS of **12**.

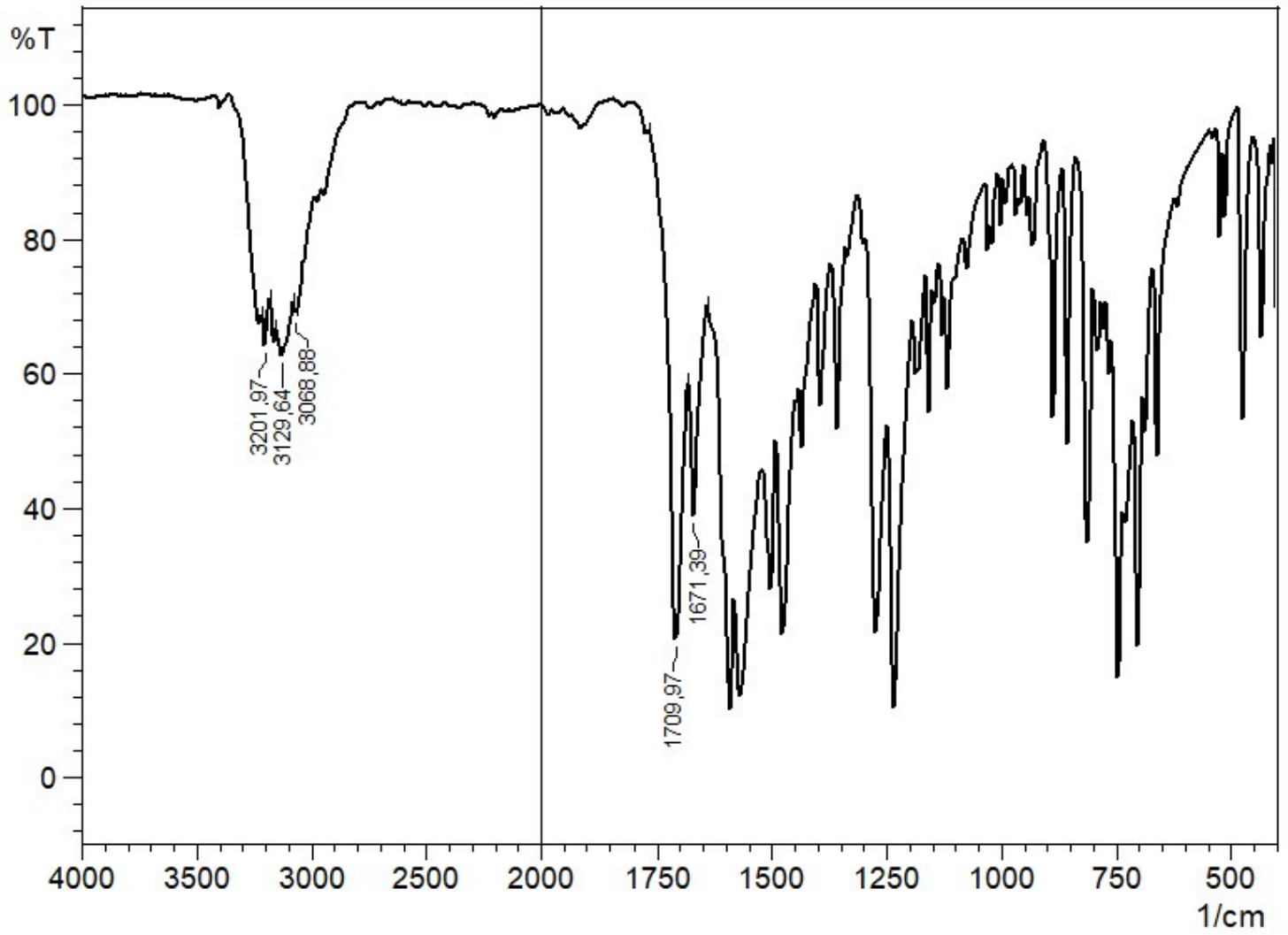


Figure 78S. IR spectrum of **12**.

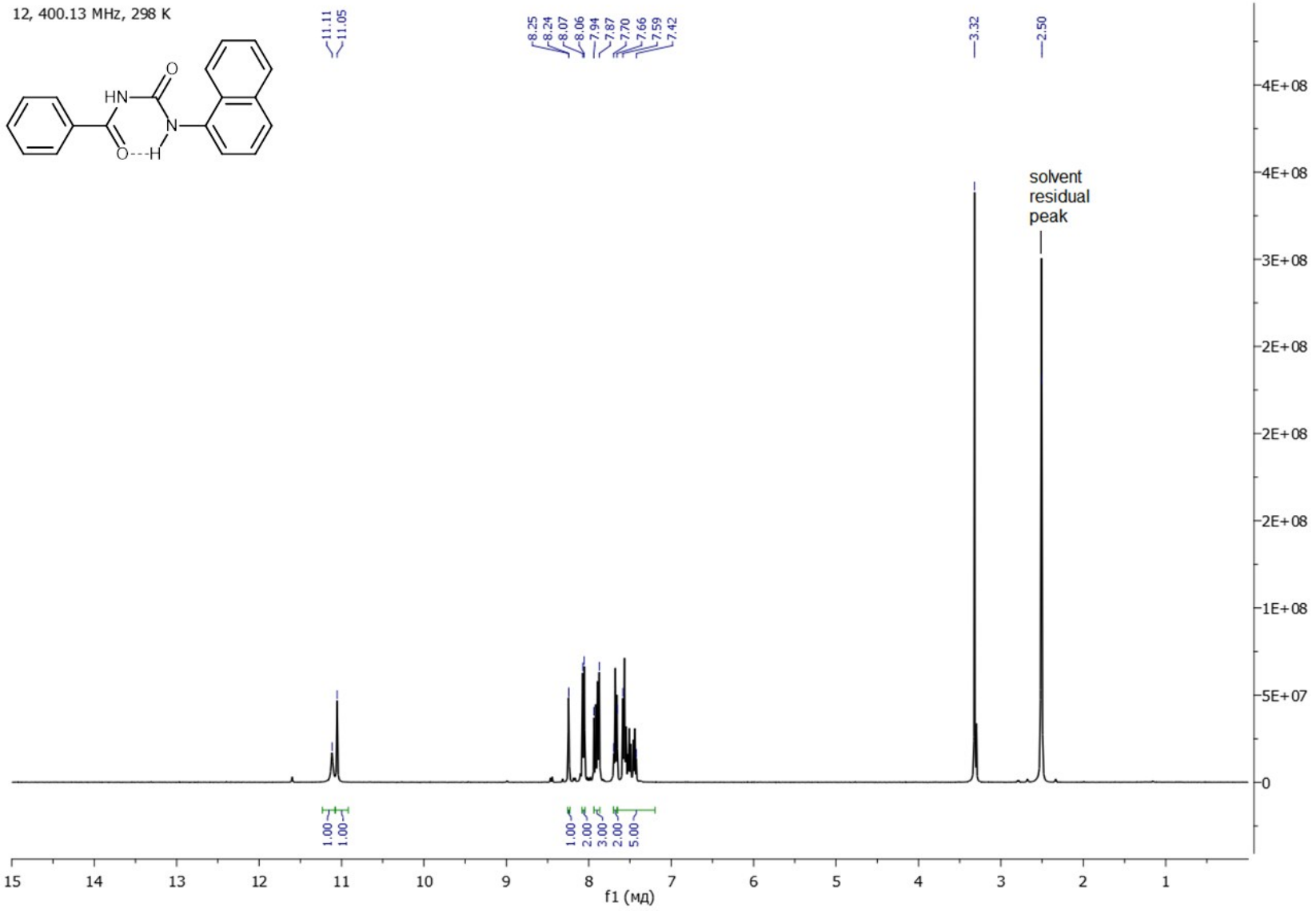


Figure 79S. ^{1}H NMR spectrum of **12**.

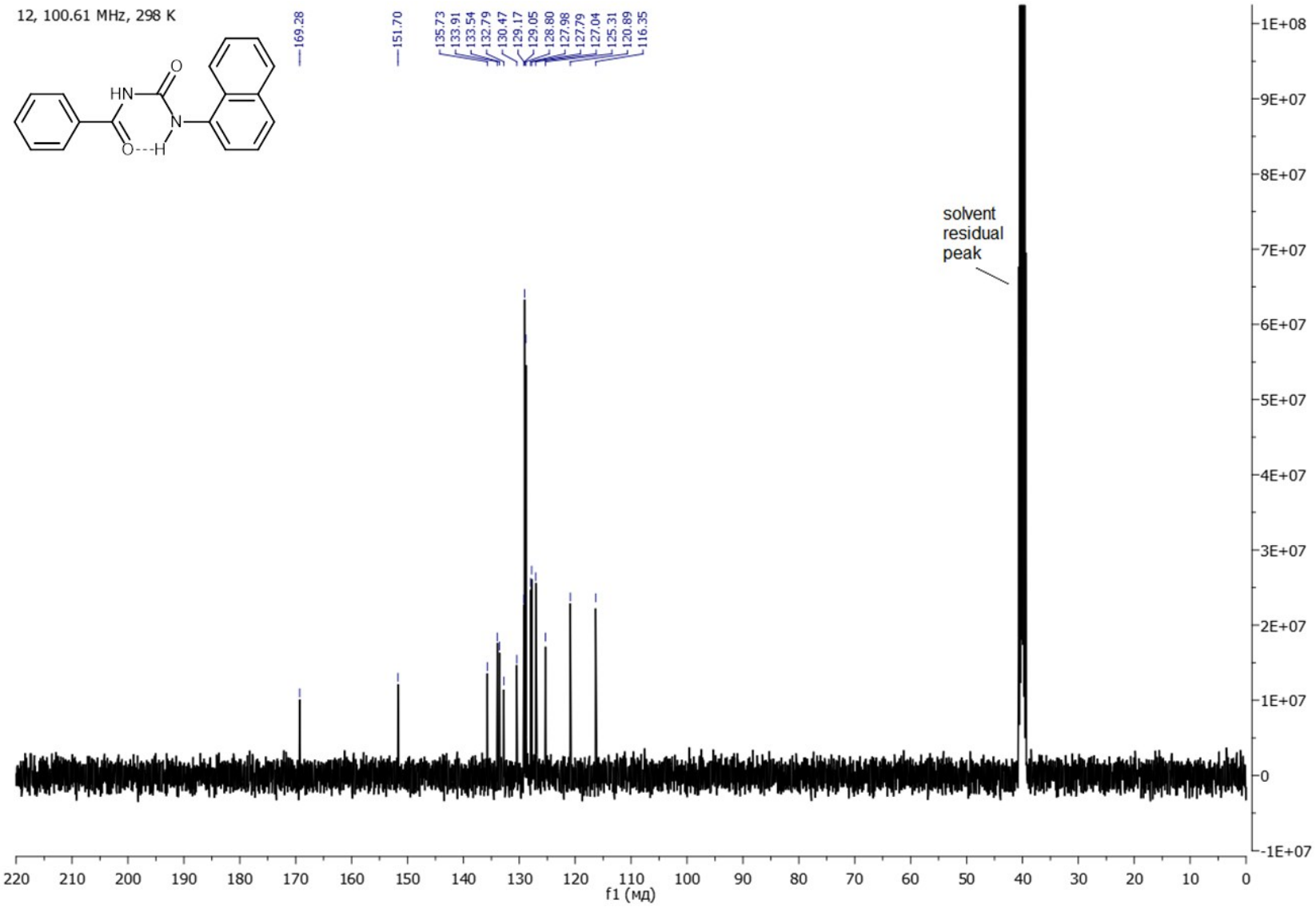


Figure 80S. $^{13}C\{^{1}H\}$ NMR spectrum of **12**.

Computational Details

Hirshfeld surface analysis

The molecular Hirshfeld surface (visualization of short interatomic contacts using sums of appropriate vdW radii) represents an area where molecules come into contacts, and its analysis gives the possibility of an additional insight into the nature of intermolecular interactions in the crystal state. We carried out the Hirshfeld surface analysis for the X-ray structures of **3** and **10** to understand what kind of intermolecular contacts gives the largest contributions in crystal packing (**Table 3**). For the visualization, we have used a mapping of the normalized contact distance (d_{norm}); its negative value enables identification of molecular regions of substantial importance for detection of short contacts. **Figure 3** depicts the Hirshfeld surfaces for **3** and **10**. In these Hirshfeld surfaces, the regions of shortest intermolecular contacts N–H···O and C–H···O visualized by red circle areas. The Hirshfeld surface analysis for the X-ray structures of **3** and **10** reveals that in both cases the intermolecular contacts involving hydrogen atoms (viz. H–H, F–H, C–H, and O–H) give the largest contribution in the crystal packing.

NOS	Contributions of different intermolecular contacts to the molecular Hirshfeld surface
3	H–H 39.7%, F–H 25.9%, O–H 13.3%, C–H 7.5%, C–C 3.1%, F–C 3.1%, F–O 1.6%, N–C 1.6%, O–C 1.4%, N–H 1.3%, F–F 1.3%, O–N 0.2%
10	H–H 47.1%, C–H 26.0%, O–H 17.7%, C–C 4.2%, N–H 1.9%, N–C 1.7%, O–C 0.9%, O–N 0.5%

Table S1. Calculated total electronic energies, enthalpies, Gibbs free energies (Hartree), and entropies (cal/mol•K) for optimized equilibrium model structures (E, H, G, and S, respectively), M06-2X/6-31G* level of theory.

Model structure	E	H	G	S
H_2O	-76.3733781405	-76.348061	-76.369495	45.112
A	-822.527483125	-822.168380	-822.232494	134.939
TS_{AB}	-975.275074078	-974.865498	-974.933197	142.484
TS_{AC}	-975.271690804	-974.860784	-974.931302	148.417
B	-898.912884387	-898.524885	-898.589933	136.904
C	-898.907819798	-898.520327	-898.588103	142.647
D	-782.865707243	-782.549657	-782.609628	126.221
TS_{DE}	-935.576570724	-935.211994	-935.277991	138.904
TS_{DF}	-935.590881517	-935.224398	-935.291924	142.122
E	-859.229474358	-858.884346	-858.948071	134.121
F	-859.232575226	-858.888258	-858.951049	132.156

Table S2. Calculated values of Gibbs free energies of activation ($\Delta G^{\neq}$) and reaction (ΔG) in kcal/mol, M06-2X/6-31G* level of theory.

Transformation	$\Delta G^{\neq}$	ΔG
A + $2H_2O$ → **B** + H_2O	24.0	7.6
A + $2H_2O$ → **C** + H_2O	25.2	8.7
D + $2H_2O$ → **E** + H_2O	44.3	19.5
D + $2H_2O$ → **F** + H_2O	35.6	17.6

Table S3. Cartesian atomic coordinates for optimized equilibrium model structures (M06-2X/6-31G* level of theory).

Atomic charge	X	Y	Z
H_2O			
8	0.000000	0.000000	0.118471
1	0.000000	-0.762395	-0.473883
1	0.000000	0.762395	-0.473883
A			
7	-1.028929	1.099882	0.413669
6	-1.656241	-0.028086	0.050729
7	-0.785722	-1.009094	-0.196946
6	0.402402	-0.460372	0.031375
8	0.330613	0.834334	0.410936
6	-3.103377	-0.151890	-0.072352
7	1.585865	-1.013191	-0.075494
6	2.870902	-0.321002	0.155941
6	-3.901065	0.939582	-0.441936
6	-5.274299	0.772562	-0.557593
6	-5.847539	-0.473373	-0.305312
6	-5.049886	-1.562858	0.043443
6	-3.674556	-1.410526	0.152103
6	3.292101	0.486533	-1.074428
6	4.642117	1.165560	-0.824041
6	5.710717	0.140983	-0.437266
6	5.275747	-0.674361	0.782006
6	3.925248	-1.356281	0.542329

6	-1.408827	2.300332	1.141038
1	1.589470	-1.971967	-0.408998
1	2.710385	0.358858	1.002681
1	-3.450400	1.897710	-0.685293
1	-5.895974	1.609457	-0.856192
1	-6.921752	-0.599083	-0.394901
1	-5.500952	-2.532380	0.224579
1	-3.036964	-2.248721	0.413438
1	3.371678	-0.198204	-1.929280
1	2.521189	1.226883	-1.317526
1	4.942326	1.719623	-1.717990
1	4.532503	1.903032	-0.017290
1	5.887996	-0.536302	-1.283464
1	6.659410	0.645552	-0.232262
1	6.024968	-1.432223	1.027767
1	5.195282	-0.013963	1.655684
1	4.025137	-2.080508	-0.279707
1	3.601294	-1.906819	1.431909
1	-0.817402	2.347978	2.057082
1	-2.465473	2.206957	1.390625
1	-1.236782	3.185457	0.526824
TS_{AB}			
7	0.795468	-1.074125	0.848085
6	1.505529	0.103534	0.439113
7	0.581055	0.830562	-0.358270
6	-0.598055	0.367835	-0.010959
8	-0.582589	-0.669151	0.817007
6	2.858520	-0.173774	-0.176154
7	-1.773704	0.830179	-0.395812
6	-3.069719	0.213292	-0.029412
6	3.955983	-0.544812	0.607012
6	5.181101	-0.809747	0.014874
6	5.328312	-0.700428	-1.371771
6	4.236706	-0.334782	-2.153872
6	2.997510	-0.075586	-1.554969
6	-3.355846	-1.065644	-0.839469
6	-4.710349	-1.662841	-0.441468
6	-5.835186	-0.638649	-0.611766
6	-5.538729	0.652054	0.168560
6	-4.172532	1.252457	-0.218588
6	1.064397	-1.671095	2.146183
1	-1.774648	1.605838	-1.042786
1	-3.008248	-0.044375	1.046100
1	3.876657	-0.659109	1.693802
1	6.031709	-1.105702	0.625175
1	6.281062	-0.913310	-1.837679
1	4.338681	-0.255816	-3.237185
1	2.142059	0.202989	-2.162564
1	-3.358604	-0.805315	-1.916849
1	-2.546752	-1.797477	-0.686869

1	-4.915135	-2.564464	-1.035517
1	-4.672223	-1.981828	0.614065
1	-5.940538	-0.396633	-1.682663
1	-6.795884	-1.069998	-0.287697
1	-6.316303	1.408138	0.003940
1	-5.542609	0.431729	1.257744
1	-4.188945	1.548921	-1.284255
1	-3.955397	2.150322	0.377587
1	0.391537	-2.526473	2.259624
1	0.914802	-0.973443	2.973984
1	2.085445	-2.049280	2.120002
8	1.750202	1.046115	1.669012
1	1.828057	2.189120	1.141627
1	2.582382	0.813718	2.124346
8	1.659074	3.047946	0.366788
1	2.482321	3.359783	-0.058857
1	1.141502	2.456182	-0.289444
TS_{AC}			
7	-1.151190	-1.275695	-0.772010
6	-1.689233	-0.183568	-0.141257
7	-0.834877	0.773198	0.065652
6	0.427235	0.314267	-0.431426
8	0.241419	-1.031912	-0.835240
6	-3.119143	-0.105356	0.176296
7	1.498006	0.621653	0.394717
6	2.859282	0.167194	0.048353
6	-4.069888	-0.734797	-0.635735
6	-5.419587	-0.618142	-0.326878
6	-5.818932	0.118560	0.787153
6	-4.871377	0.750312	1.591379
6	-3.520410	0.646059	1.285711
6	3.159444	-1.256840	0.529337
6	4.598495	-1.656815	0.188512
6	5.604054	-0.660113	0.768448
6	5.302130	0.761089	0.288949
6	3.865250	1.164434	0.625141
6	-1.386699	-2.658509	-0.357517
1	1.256248	0.461682	1.368871
1	2.927010	0.197233	-1.046352
1	-3.756600	-1.283717	-1.519476
1	-6.160584	-1.095527	-0.959130
1	-6.873846	0.203838	1.027104
1	-5.185596	1.321852	2.458166
1	-2.770040	1.125901	1.906353
1	3.022806	-1.290234	1.621032
1	2.445693	-1.962125	0.090765
1	4.798510	-2.666761	0.559554
1	4.711791	-1.693570	-0.903706
1	5.552420	-0.691686	1.865340
1	6.623301	-0.945916	0.490987

1	6.001354	1.475349	0.734072
1	5.446026	0.814909	-0.798975
1	3.739151	1.193743	1.717679
1	3.635535	2.166716	0.249016
1	-0.844574	-2.872622	0.568151
1	-1.046889	-3.320080	-1.153815
1	-2.457449	-2.788750	-0.205287
8	0.730803	1.051994	-1.703995
1	0.257262	0.622950	-2.440393
1	0.385477	2.238954	-1.422583
8	-0.047306	3.140146	-0.822962
1	-0.602429	3.752598	-1.336267
1	-0.611230	2.632685	-0.170838
B			
7	0.993987	0.670069	0.965149
6	1.668625	0.560940	-0.340264
7	0.675034	-0.316723	-0.994427
6	-0.527537	-0.006992	-0.499827
8	-0.428680	0.683283	0.609197
6	3.028225	-0.080931	-0.182274
7	-1.709246	-0.308632	-0.977308
6	-2.982739	0.013727	-0.284216
6	4.172747	0.718511	-0.187473
6	5.425622	0.134891	-0.017190
6	5.533989	-1.240145	0.163512
6	4.388281	-2.034705	0.187591
6	3.135227	-1.457432	0.021834
6	-3.299725	-1.024537	0.792420
6	-4.633034	-0.687994	1.467886
6	-5.761977	-0.588231	0.439528
6	-5.427100	0.436488	-0.646194
6	-4.093775	0.110386	-1.327086
6	1.255241	1.902278	1.700735
8	1.696359	1.790243	-0.984610
1	0.811468	-0.635999	-1.946019
1	-1.758610	-0.836455	-1.841653
1	-2.838174	0.995806	0.180440
1	4.097117	1.797228	-0.298047
1	6.313580	0.757819	-0.021228
1	6.510719	-1.694262	0.293874
1	4.471896	-3.105651	0.339540
1	2.239982	-2.070413	0.057245
1	-3.363864	-2.012771	0.317159
1	-2.486423	-1.061132	1.525622
1	-4.860478	-1.447693	2.221021
1	-4.537258	0.267407	2.000917
1	-5.919157	-1.571339	-0.023746
1	-6.699351	-0.317434	0.933950
1	-6.218024	0.476228	-1.400397
1	-5.364929	1.437467	-0.199398

1	-4.179073	-0.857177	-1.844357
1	-3.842418	0.869213	-2.076039
1	0.694680	1.859243	2.634287
1	1.005322	2.797903	1.127807
1	2.323221	1.888712	1.931921
1	2.447499	1.824573	-1.597392
C			
7	-1.148988	1.274452	-0.212778
6	-1.731196	0.149161	0.136482
7	-0.817851	-0.667637	0.658346
6	0.519866	-0.055116	0.748292
8	0.202472	1.250406	0.079803
6	-3.151011	-0.165644	-0.022603
7	1.471042	-0.836707	0.121442
6	2.906562	-0.531556	0.291140
6	-4.124592	0.803403	0.248436
6	-5.467203	0.474958	0.112458
6	-5.833950	-0.808090	-0.291725
6	-4.862174	-1.772775	-0.554144
6	-3.516480	-1.458485	-0.415129
6	3.282759	0.883826	-0.155551
6	4.788146	1.119560	-0.001862
6	5.591788	0.069877	-0.771763
6	5.208599	-1.343955	-0.329682
6	3.703985	-1.582834	-0.479656
6	-1.549228	2.351827	-1.100400
8	0.917654	0.210076	2.022050
1	-1.032432	-1.512989	1.172879
1	1.215538	-1.044259	-0.839367
1	3.122279	-0.641011	1.359485
1	-3.834407	1.791284	0.595033
1	-6.227821	1.217136	0.329138
1	-6.884309	-1.058760	-0.398269
1	-5.153061	-2.768826	-0.869362
1	-2.754260	-2.200600	-0.635465
1	2.993198	1.007541	-1.209737
1	2.717917	1.622757	0.424941
1	5.042885	2.127771	-0.342609
1	5.051892	1.069609	1.063250
1	5.395661	0.179814	-1.847202
1	6.664122	0.232967	-0.627023
1	5.759157	-2.092114	-0.907854
1	5.491108	-1.485845	0.721948
1	3.435232	-1.519894	-1.545775
1	3.426234	-2.582951	-0.130891
1	-0.850711	2.372809	-1.939172
1	-1.515018	3.300031	-0.561695
1	-2.559097	2.147174	-1.453992
1	0.410246	0.958784	2.372095
D			

7	-1.109318	-1.226830	-0.643642
6	-1.695305	-0.135550	-0.228776
7	-0.855388	0.922539	0.022858
6	0.304348	0.406248	-0.277579
8	0.245195	-0.868089	-0.676696
6	-3.152430	-0.053661	-0.039870
7	1.511296	1.010734	-0.268204
6	2.756713	0.245727	-0.296484
6	-3.969465	-1.147462	-0.340769
6	-5.342652	-1.056034	-0.153515
6	-5.906866	0.122530	0.333690
6	-5.092427	1.211661	0.632346
6	-3.716338	1.126590	0.445849
6	3.010882	-0.512576	1.011084
6	4.333014	-1.281069	0.948521
6	5.497960	-0.343337	0.624759
6	5.240438	0.420716	-0.676319
6	3.915735	1.185954	-0.620558
1	1.516270	1.902763	0.210366
1	2.657525	-0.482039	-1.111757
1	-3.518592	-2.059159	-0.720036
1	-5.975717	-1.905843	-0.389337
1	-6.980777	0.190560	0.479138
1	-5.528774	2.130494	1.011733
1	-3.066310	1.965334	0.672601
1	3.045132	0.216963	1.833215
1	2.174007	-1.191129	1.209057
1	4.508880	-1.800866	1.895882
1	4.262499	-2.054808	0.171648
1	5.621548	0.375906	1.446429
1	6.434038	-0.907176	0.553133
1	6.061221	1.114800	-0.884563
1	5.206804	-0.290755	-1.512653
1	3.975654	1.955977	0.164084
1	3.717262	1.700166	-1.566744
TS_{DE}			
7	0.903675	0.807236	0.832098
6	1.506343	0.156917	-0.226813
7	0.573205	-0.545227	-0.966262
6	-0.559624	-0.062585	-0.539418
8	-0.480356	0.819337	0.460383
6	2.880513	-0.367993	-0.016342
7	-1.783631	-0.339248	-1.016636
6	-3.013166	-0.007276	-0.298134
6	3.832936	0.417518	0.636276
6	5.104537	-0.093799	0.859312
6	5.428531	-1.381513	0.431125
6	4.477667	-2.156721	-0.224441
6	3.199455	-1.650879	-0.449752
6	-3.199957	-0.855050	0.964879

6	-4.509245	-0.494203	1.670029
6	-5.703525	-0.652800	0.726978
6	-5.513536	0.183705	-0.540985
6	-4.200409	-0.164351	-1.246082
1	-1.805091	-1.090170	-1.694691
1	-2.933950	1.047743	-0.005523
1	3.579849	1.429758	0.943719
1	5.848794	0.515096	1.363087
1	6.424649	-1.777143	0.605735
1	4.729113	-3.157478	-0.562158
1	2.443294	-2.238550	-0.959672
1	-3.215704	-1.914252	0.671290
1	-2.343325	-0.711430	1.631737
1	-4.636817	-1.116796	2.561405
1	-4.456670	0.546903	2.017205
1	-5.805896	-1.711143	0.449468
1	-6.631099	-0.365886	1.233297
1	-6.352553	0.038834	-1.229159
1	-5.503729	1.248835	-0.272649
1	-4.239763	-1.209700	-1.588721
1	-4.051109	0.463410	-2.131280
8	2.020227	1.560758	-1.399238
1	1.948915	2.477952	-0.625070
1	1.308775	1.592846	-2.056228
8	1.834458	3.059322	0.435661
1	1.205153	3.791000	0.382292
1	1.256676	1.939688	0.867290
TS_{DF}			
7	1.206297	-1.610759	0.340459
6	1.788682	-0.545090	-0.108014
7	0.903095	0.364391	-0.640097
6	-0.319941	-0.131265	-0.294344
8	-0.172062	-1.381666	0.130864
6	3.241270	-0.339283	-0.077801
7	-1.477256	0.288962	-0.819283
6	-2.722957	-0.129952	-0.147138
6	4.048929	-1.210389	0.659664
6	5.422588	-1.012520	0.692239
6	5.994015	0.052230	-0.004159
6	5.189025	0.918636	-0.738211
6	3.812062	0.724771	-0.778085
6	-3.513215	-1.095575	-1.027954
6	-4.822214	-1.497235	-0.344157
6	-5.655393	-0.263654	0.014732
6	-4.854099	0.704704	0.889131
6	-3.541044	1.107386	0.215000
1	-1.414061	1.290942	-1.013026
1	-2.434820	-0.627008	0.787099
1	3.587359	-2.029860	1.201284
1	6.049970	-1.686383	1.266775

1	7.068186	0.205821	0.026670
1	5.632948	1.745282	-1.283452
1	3.184190	1.389679	-1.363997
1	-3.729034	-0.600183	-1.984772
1	-2.897876	-1.974193	-1.251134
1	-5.393220	-2.171748	-0.990882
1	-4.593038	-2.056210	0.573682
1	-5.955739	0.249208	-0.909826
1	-6.577061	-0.562468	0.525985
1	-5.446121	1.597311	1.117352
1	-4.626818	0.221724	1.849163
1	-3.759808	1.669476	-0.705971
1	-2.932813	1.743420	0.866226
8	-0.552352	0.880731	1.491290
1	0.135657	0.659836	2.135572
1	-0.255606	1.932881	0.858373
8	0.012247	2.634886	-0.033604
1	0.282187	3.508739	0.270795
1	0.941658	1.427374	-0.557278
E			
7	-1.013006	-0.549252	1.470297
6	-1.744702	-0.977563	0.236954
7	-0.756699	-0.881589	-0.813312
6	0.376013	-0.842252	-0.208948
8	0.373982	-0.772056	1.138857
6	-2.934735	-0.056766	0.030310
7	1.603357	-0.898177	-0.780183
6	2.791265	-0.368095	-0.109732
6	-4.203248	-0.565202	-0.229717
6	-5.271407	0.303112	-0.450787
6	-5.073938	1.678974	-0.413749
6	-3.802384	2.189097	-0.152535
6	-2.738205	1.324436	0.069531
6	2.739831	1.153066	0.066321
6	4.013981	1.669665	0.738661
6	5.257889	1.254937	-0.050576
6	5.307281	-0.263906	-0.232952
6	4.031454	-0.786928	-0.897381
8	-2.185346	-2.313542	0.370837
1	-1.192840	-1.266049	2.176261
1	1.566746	-0.801080	-1.787919
1	2.831615	-0.836527	0.881403
1	-4.347531	-1.639062	-0.252220
1	-6.259776	-0.100227	-0.650339
1	-5.906280	2.355066	-0.585571
1	-3.642747	3.262682	-0.119727
1	-1.746039	1.711056	0.283550
1	2.632000	1.613513	-0.926492
1	1.852575	1.421062	0.650294
1	3.968463	2.758687	0.842208

1	4.077196	1.257970	1.755475
1	5.235845	1.736776	-1.038072
1	6.165013	1.604864	0.453584
1	6.180735	-0.552583	-0.826647
1	5.420496	-0.741447	0.749929
1	3.957641	-0.372192	-1.914584
1	4.054526	-1.877678	-0.992674
1	-1.686862	-2.822367	-0.286016
F			
7	-1.272345	1.077697	1.053992
6	-1.801568	0.136053	0.362347
7	-0.909421	-0.867854	-0.023462
6	0.369981	-0.471440	0.549755
8	0.060968	0.716857	1.284005
6	-3.220495	0.104228	-0.014565
7	1.291189	-0.184918	-0.487668
6	2.672421	0.099678	-0.092847
6	-4.142521	0.911056	0.659977
6	-5.483707	0.872604	0.303722
6	-5.915131	0.026175	-0.717920
6	-4.998416	-0.777330	-1.389110
6	-3.651365	-0.737867	-1.041653
6	3.259999	1.157848	-1.029479
6	4.702723	1.503792	-0.653804
6	5.584497	0.252976	-0.629832
6	5.004838	-0.802387	0.314181
6	3.561828	-1.149081	-0.062073
8	0.866295	-1.414427	1.457927
1	-1.183493	-1.816990	0.214826
1	1.220329	-0.881768	-1.223636
1	2.625324	0.523976	0.919289
1	-3.791745	1.557500	1.458109
1	-6.198024	1.499785	0.827838
1	-6.965702	-0.004217	-0.990031
1	-5.329605	-1.430935	-2.189964
1	-2.925661	-1.341631	-1.578445
1	3.232414	0.765012	-2.057086
1	2.618057	2.043893	-1.010108
1	5.106929	2.245287	-1.351438
1	4.713023	1.968721	0.342186
1	5.643711	-0.165707	-1.644449
1	6.606998	0.511703	-0.333049
1	5.624258	-1.706007	0.308528
1	5.022957	-0.413851	1.342194
1	3.551085	-1.601286	-1.066778
1	3.137329	-1.880757	0.631125
1	0.449239	-1.224477	2.313202

Table S4. Cartesian atomic coordinates for optimized equilibrium model structures (ωB97XD/6-31++G** level of theory).

Atomic charge	X	Y	Z
3			
9	-5.000429	-1.690751	-1.220295
9	-4.902625	-2.038911	0.912114
9	-6.355325	-0.645282	0.109747
8	2.484256	2.214896	-1.103344
8	0.031095	-0.812385	0.331443
7	0.519732	1.265832	-0.485280
1	0.139518	2.132863	-0.836593
7	2.534690	0.078755	-0.285099
1	1.945525	-0.664943	0.076356
6	3.981729	-0.079178	-0.351115
1	4.320172	0.423050	-1.265498
6	1.933594	1.222930	-0.648689
6	-1.772029	0.718597	0.110935
6	4.322196	-1.567455	-0.442106
1	3.840293	-2.002806	-1.324374
1	3.911100	-2.081318	0.439209
6	-4.080499	0.027295	0.114067
6	-2.728864	-0.289356	0.015609
1	-2.402479	-1.313332	-0.133301
6	-0.331992	0.310935	0.004194
6	-2.175711	2.038689	0.334400
1	-1.441769	2.829687	0.457647
6	5.837204	-1.785247	-0.492416
1	6.054951	-2.858121	-0.520194
1	6.231510	-1.359317	-1.425118
6	4.678450	0.577669	0.846707
1	4.275762	0.135132	1.768529
1	4.437848	1.645104	0.861247
6	-4.485544	1.342286	0.328961
1	-5.539679	1.579712	0.411866
6	6.193317	0.362979	0.787375
1	6.667658	0.814163	1.665236
1	6.598288	0.883345	-0.091342
6	-3.527120	2.345164	0.446879
1	-3.835686	3.368041	0.632801
6	-5.090478	-1.083453	-0.019569
6	6.540246	-1.125649	0.697685
1	7.624166	-1.260322	0.615105
1	6.227484	-1.625873	1.624699
10			
8	1.097136	0.895974	1.218238
8	-0.718935	-2.421119	-0.477672
7	-1.058788	-0.742045	1.042072
1	-0.644629	0.113674	1.399711
7	0.995208	-0.999088	-0.055303
1	1.464383	-1.554260	-0.756184
6	-0.336037	-1.441979	0.147734
6	1.645545	0.088273	0.477491

6	3.082227	0.239377	0.084251
6	-3.393252	-0.213609	0.419997
6	-2.462551	-1.042920	1.279451
1	-2.665990	-0.864124	2.339010
1	-2.606203	-2.107380	1.082251
6	-4.072484	0.880749	0.955847
1	-3.950899	1.125213	2.008413
6	-3.559925	-0.521673	-0.934279
1	-3.032005	-1.374369	-1.352701
6	3.894677	-0.849385	-0.246873
1	3.508662	-1.863976	-0.206030
6	-4.903416	1.662888	0.154887
1	-5.424834	2.512656	0.584578
6	3.619845	1.529017	0.086826
1	2.982063	2.360641	0.366643
6	-4.388375	0.258289	-1.735481
1	-4.513040	0.010720	-2.785226
6	5.755499	0.644047	-0.601574
1	6.795766	0.801801	-0.867929
6	-5.061614	1.353112	-1.193020
1	-5.707992	1.960074	-1.819364
6	5.229087	-0.645509	-0.585964
1	5.858640	-1.494834	-0.830349
6	4.949877	1.730707	-0.263444
1	5.360919	2.734946	-0.269834
Supramolecular dimeric associate **3**			
9	-4.644934	-6.202262	2.919877
9	-5.802576	-4.460683	3.473773
9	-6.343043	-5.607189	1.714856
8	0.871997	0.524505	1.266403
8	-1.692052	-1.790677	3.479130
7	-0.859521	-0.916615	1.544470
1	-0.906070	-0.846206	0.521684
7	0.298277	-0.022609	3.388087
1	-0.339547	-0.581689	3.948827
6	1.369630	0.754241	3.999612
1	2.284579	0.561636	3.423730
6	0.151266	-0.093642	2.060944
6	-2.625436	-2.627293	1.467407
6	1.577898	0.272136	5.436128
1	1.802900	-0.800145	5.436882
1	0.640521	0.407644	5.994525
6	-4.391615	-4.269216	1.583296
6	-3.506633	-3.406566	2.219207
1	-3.484531	-3.323173	3.300044
6	-1.695375	-1.745136	2.251733
6	-2.637797	-2.724456	0.072144
1	-1.977485	-2.128484	-0.547552
6	2.697874	1.057742	6.123774
1	2.802193	0.721694	7.160529

1	3.651382	0.837628	5.624570
6	1.088077	2.261210	3.959858
1	0.140291	2.454376	4.480241
1	0.959192	2.579699	2.921047
6	-4.402311	-4.372120	0.193470
1	-5.092939	-5.048258	-0.297873
6	2.220169	3.040693	4.634501
1	2.000844	4.113383	4.612420
1	3.149962	2.896190	4.065233
6	-3.524178	-3.595392	-0.554476
1	-3.526058	-3.667900	-1.637149
6	-5.299188	-5.131244	2.420363
6	2.440057	2.566739	6.073934
1	3.277076	3.106411	6.529661
1	1.547634	2.802061	6.669960
9	4.644934	6.202262	-2.919877
9	5.802576	4.460683	-3.473773
9	6.343043	5.607189	-1.714856
8	-0.871997	-0.524505	-1.266403
8	1.692052	1.790677	-3.479130
7	0.859521	0.916615	-1.544470
1	0.906070	0.846206	-0.521684
7	-0.298277	0.022609	-3.388087
1	0.339547	0.581689	-3.948827
6	-1.369630	-0.754241	-3.999612
1	-2.284579	-0.561636	-3.423730
6	-0.151266	0.093642	-2.060944
6	2.625436	2.627293	-1.467407
6	-1.577898	-0.272136	-5.436128
1	-1.802900	0.800145	-5.436882
1	-0.640521	-0.407644	-5.994525
6	4.391615	4.269216	-1.583296
6	3.506633	3.406566	-2.219207
1	3.484531	3.323173	-3.300044
6	1.695375	1.745136	-2.251733
6	2.637797	2.724456	-0.072144
1	1.977485	2.128484	0.547552
6	-2.697874	-1.057742	-6.123774
1	-2.802193	-0.721694	-7.160529
1	-3.651382	-0.837628	-5.624570
6	-1.088077	-2.261210	-3.959858
1	-0.140291	-2.454376	-4.480241
1	-0.959192	-2.579699	-2.921047
6	4.402311	4.372120	-0.193470
1	5.092939	5.048258	0.297873
6	-2.220169	-3.040693	-4.634501
1	-2.000844	-4.113383	-4.612420
1	-3.149962	-2.896190	-4.065233
6	3.524178	3.595392	0.554476
1	3.526058	3.667900	1.637149

6	5.299188	5.131244	-2.420363
6	-2.440057	-2.566739	-6.073934
1	-3.277076	-3.106411	-6.529661
1	-1.547634	-2.802061	-6.669960
Supramolecular dimeric associate **10**			
8	1.404719	0.786367	-0.139387
8	-0.169316	4.441847	-1.276650
7	-0.656603	2.208990	-1.286604
1	-0.360463	1.278054	-1.005133
7	1.437082	3.022247	-0.555496
1	1.932873	3.889436	-0.403264
6	0.125408	3.274445	-1.064269
6	2.003249	1.860325	-0.127493
6	3.408088	1.952299	0.377764
6	-2.925272	2.689646	-0.443583
6	-2.054848	2.393425	-1.647948
1	-2.371257	1.463668	-2.125023
1	-2.122796	3.204492	-2.376309
6	-3.120820	1.704928	0.529734
1	-2.660056	0.728826	0.398762
6	-3.516020	3.941402	-0.273786
1	-3.346190	4.716217	-1.015984
6	4.330710	2.873079	-0.128798
1	4.052181	3.554701	-0.927557
6	-3.898881	1.969768	1.652570
1	-4.044805	1.194576	2.399273
6	3.801352	1.048646	1.367578
1	3.084610	0.320586	1.731839
6	-4.299965	4.207023	0.848349
1	-4.753643	5.185803	0.971353
6	6.015030	2.004672	1.364743
1	7.028756	2.028159	1.752146
6	-4.492379	3.221895	1.813899
1	-5.098414	3.429250	2.690862
6	5.632854	2.894254	0.362104
1	6.349246	3.603055	-0.040069
6	5.098408	1.082345	1.866197
1	5.396055	0.380077	2.637720
8	0.790170	-4.154661	-0.438515
8	-1.293682	-0.658368	-1.179414
7	-1.490896	-2.926606	-1.182715
1	-1.003057	-3.787681	-0.955370
7	0.539732	-1.888371	-0.644005
1	0.969856	-0.980067	-0.477249
6	-0.813947	-1.778256	-1.011946
6	1.276740	-3.027433	-0.434519
6	2.739374	-2.813293	-0.196402
6	-3.840010	-2.639789	-0.419046
6	-2.893056	-2.916533	-1.568994
1	-3.105847	-3.895425	-2.007252

1	-3.028819	-2.163342	-2.349597
6	-4.052239	-3.604657	0.569792
1	-3.539431	-4.561690	0.507014
6	-4.504252	-1.417576	-0.325249
1	-4.328028	-0.653870	-1.077245
6	3.435506	-1.730597	-0.740887
1	2.922469	-0.993578	-1.349248
6	-4.913130	-3.350578	1.633121
1	-5.070625	-4.108433	2.394504
6	3.423608	-3.766570	0.563029
1	2.874851	-4.614159	0.959512
6	-5.370820	-1.160040	0.735620
1	-5.870844	-0.198671	0.797912
6	5.476450	-2.535543	0.260105
1	6.541170	-2.424127	0.440756
6	-5.576308	-2.126038	1.716843
1	-6.251478	-1.927653	2.543662
6	4.801817	-1.595673	-0.514446
1	5.334514	-0.749975	-0.937170
6	4.786131	-3.621527	0.798700
1	5.312161	-4.357822	1.397907