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SUPPORTING INFORMATION

Title: Unusual Reactions Between Aromatic Carbon Supernucleophiles and 1,2-Diazabuta-1,3-dienes: Useful Routes to New Pyrazolone and Cinnoline Derivatives

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Ref. No.: O200800445

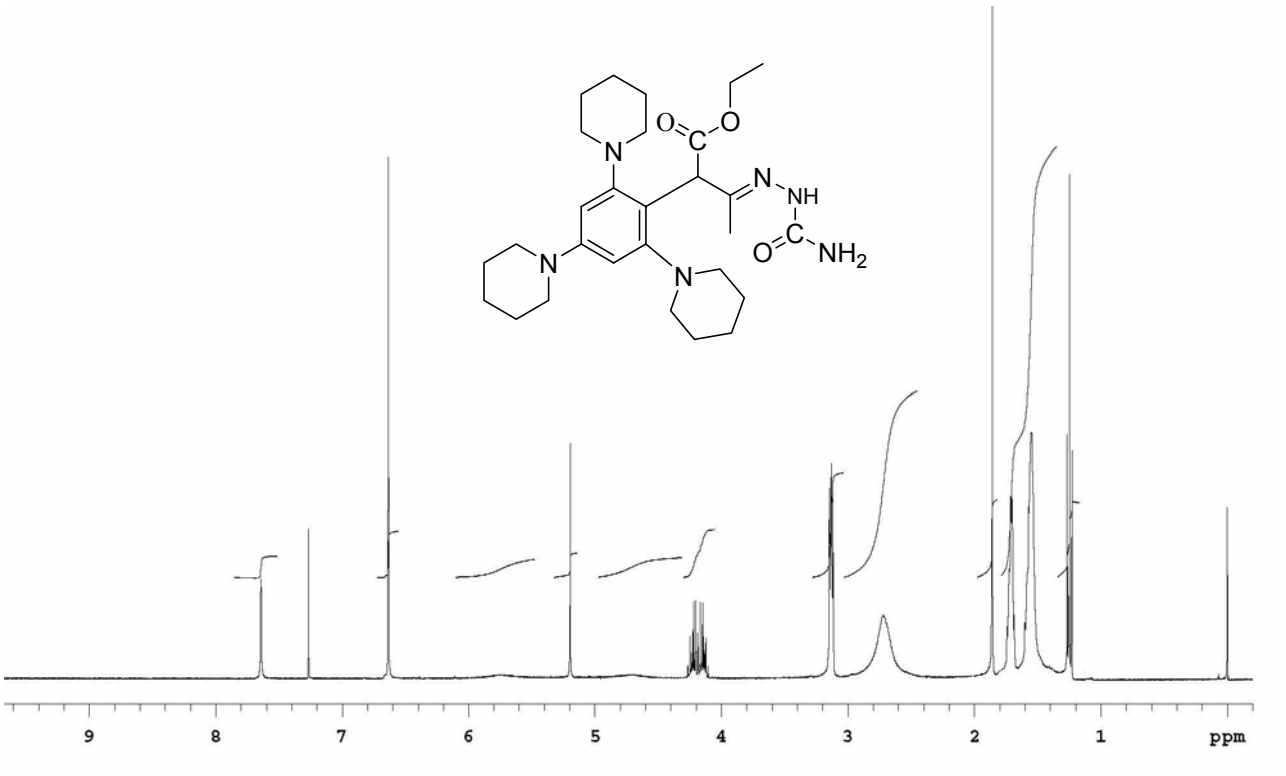
Characterization data of **DBD 5–7** and NMR spectra of all new compounds.

Methyl 3-[(aminocarbonyl)diazenyl]pent-2-enoate (5): m.p.: 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=1.03 (t, 3H, *J*=7.6 Hz), 2.88 (q, 2H, *J*=7.6 Hz), 3.84 (s, 3H), 6.35 (br.s, 1H, exch.), 6.51 (br.s, 1H, exch.), 6.86 ppm (s, 1H); ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ=12.3, 18.1, 52.0, 131.0, 161.7, 165.8, 168.1 ppm; IR (CD_2Cl_2): ν= 3511, 3399, 1742, 1642, 1578, 1436, 1210, 896 cm^{-1}; ES^{+}: (m/z) = 186 $[M + H]^{+}$, 208 [M + Na]; elemental analysis calcd (%) for $C_7H_{11}N_3O_3$ (185.2): C 45.40, H 5.99; N, 22.69; found: C 45.37, H 6.01; N, 22.67.

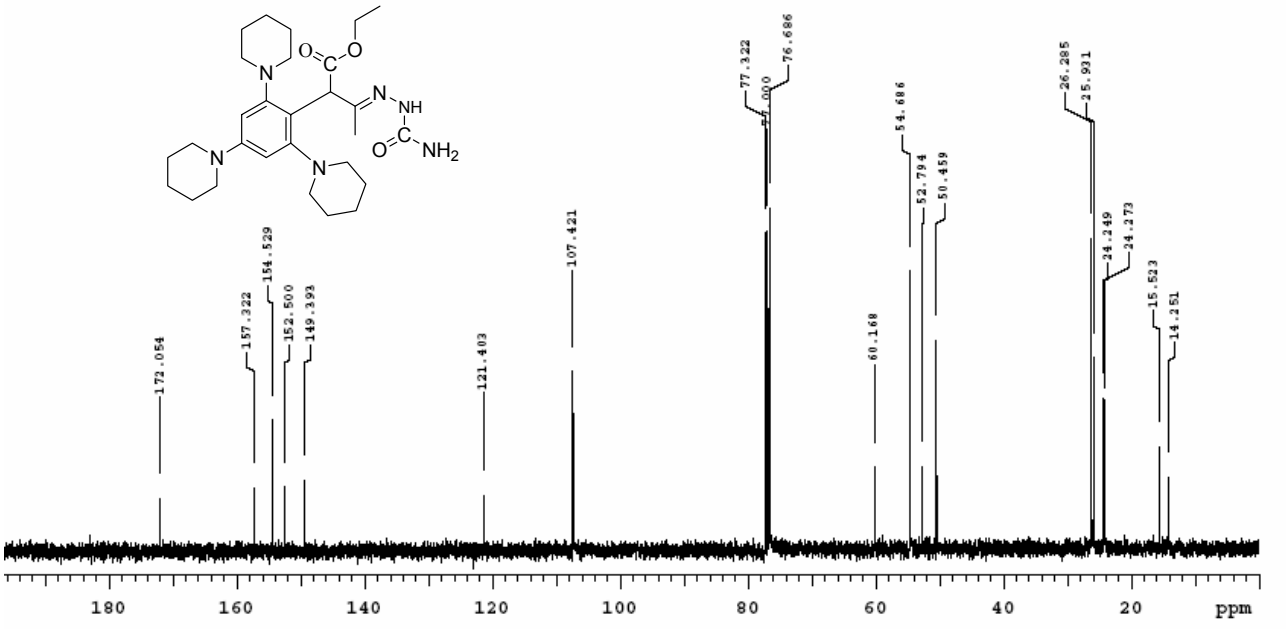
2-[3-(Dimethylamino)-1-ethyl-3-oxoprop-1-en-1-yl]diazenecarboxamide (6): m.p.: 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=1.98 (s, 3H), 3.02 (s, 3H), 3.06 (s, 3H), 6.62 (br.s., 1H, exch.), 6.86 (br.s., 1H, exch.), 7.32 ppm (s, 1H); ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ=11.3, 34.7, 37.5, 137.9, 157.5, 162.3, 165.8 ppm; IR ($CDCl_3$): ν= 3944, 3690, 3513, 3400, 1737, 1648, 1630, 1421, 1262, 896 cm^{-1}; ES^{+}: (m/z) = 185 $[M + H]^{+}$, 207 [M + Na]; elemental analysis calcd (%) for $C_7H_{12}N_4O_2$ (184.2): C 45.64, H 6.57; N, 30.42; found: C 45.59, H 6.59; N, 30.40.

2-[3-(Dimethylamino)-1-ethyl-3-oxoprop-1-en-1-yl]-*N*-phenyldiazenecarboxamide (7): m.p.: 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=2.07 (s, 3H), 3.07 (s, 3H), 3.09 (s, 3H), 7.19 (t_{app}, 1H, *J*=7.2 Hz), 7.37 (s, 1H), 7.40 (d, 2H, *J*=8.4 Hz), 7.73 (d, 2H, *J*=8.4 Hz), 8.68 ppm (br.s., 1H, exch.); ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ=11.5, 34.8, 37.5, 119.6, 125.2, 129.2, 136.8, 138.2, 157.4, 157.8, 165.8 ppm; IR ($CDCl_3$): ν= 3620, 1730, 1648, 1627, 1526, 1480, 1213, 1046, 929 cm^{-1}; ES^{+}:

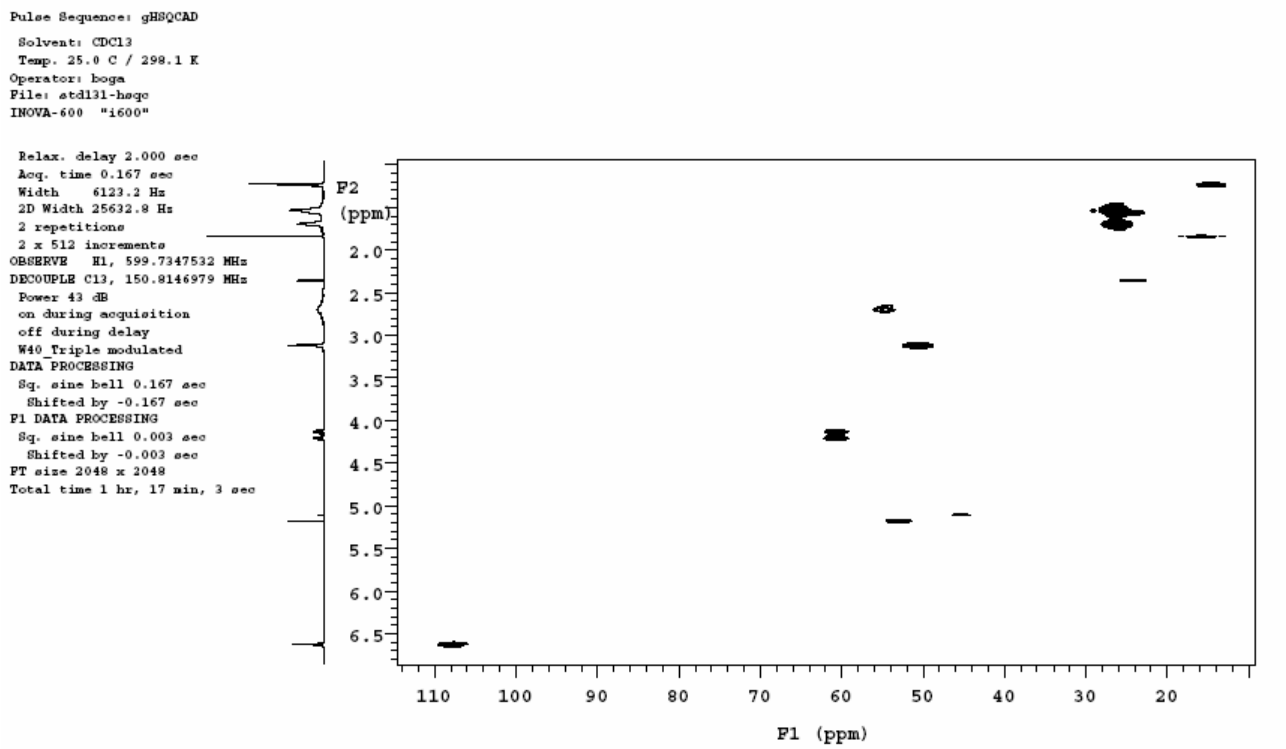
(m/z) = 283 [M + Na]; elemental analysis calcd (%) for $C_{13}H_{16}N_4O_2$ (260.3): C 59.99, H 6.20; N, 21.52; found: C 59.95, H 6.21; N, 21.49.



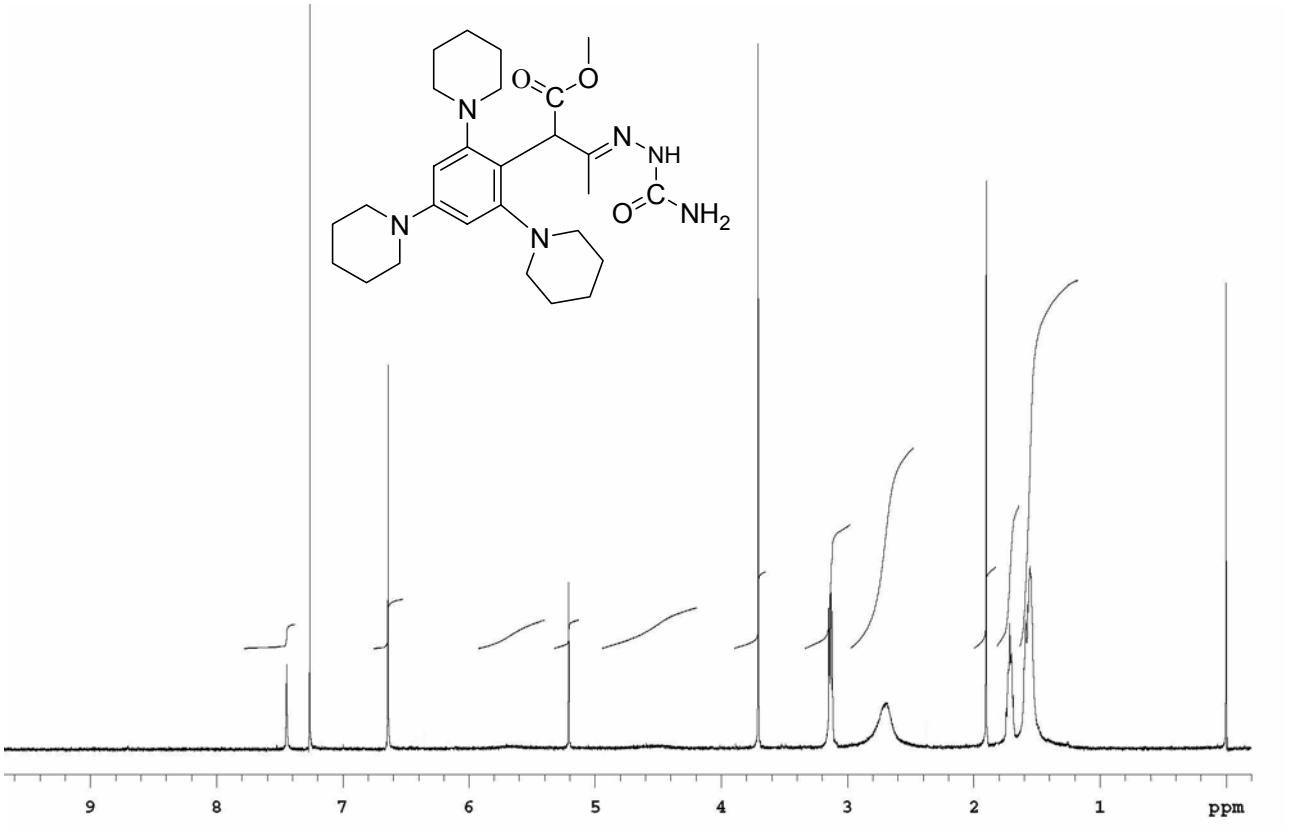
^{1}H NMR spectrum in $CDCl_3$ of compound **8**.



^{13}C NMR spectrum in $CDCl_3$ of compound **8**.

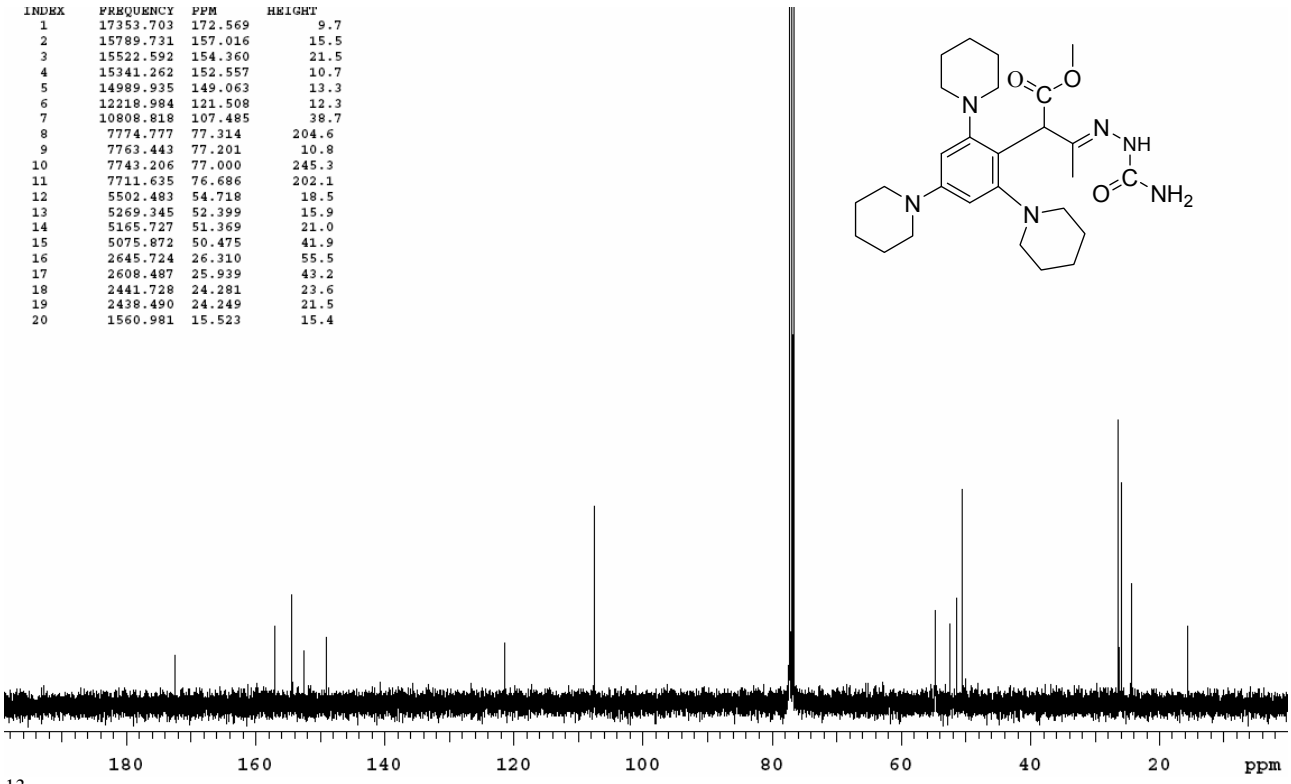


gHSQC spectrum of compound **8a** and its isomeric form showing that the singlet at 5.1 ppm of this latter belongs to a C-H bond.

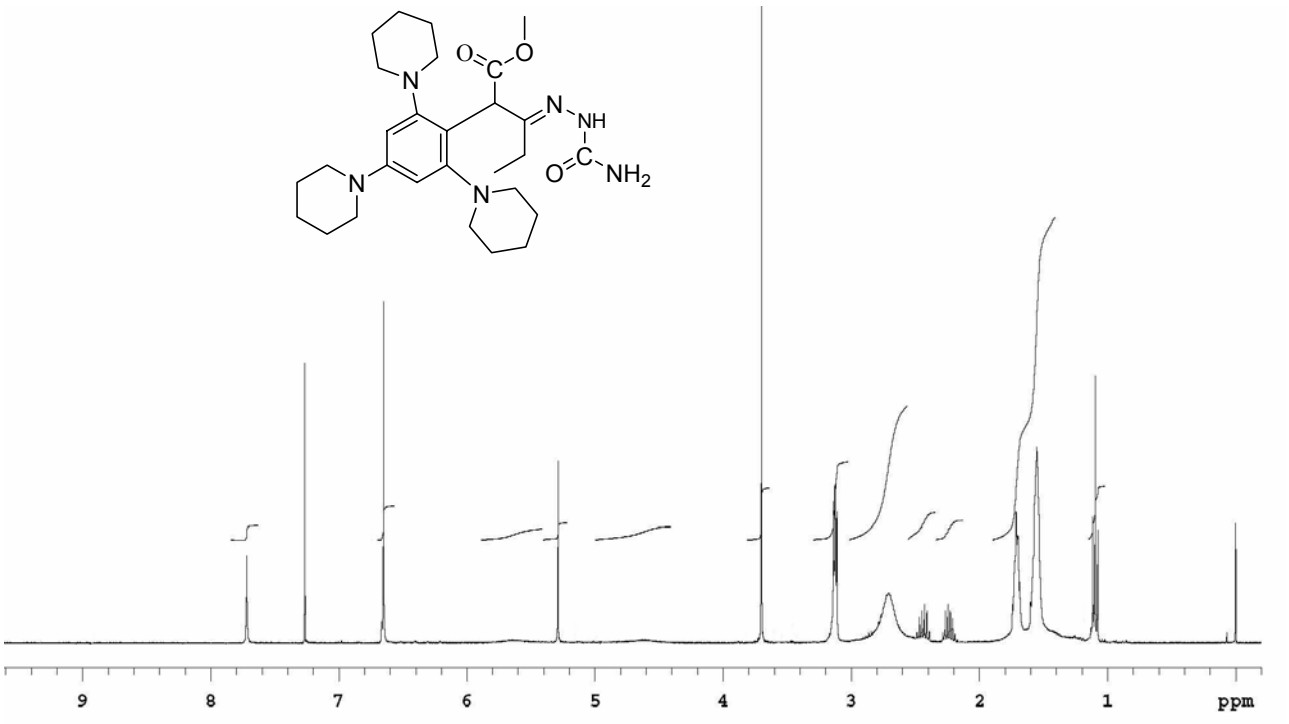


^{1}H NMR spectrum in $CDCl_3$ of compound **9**.

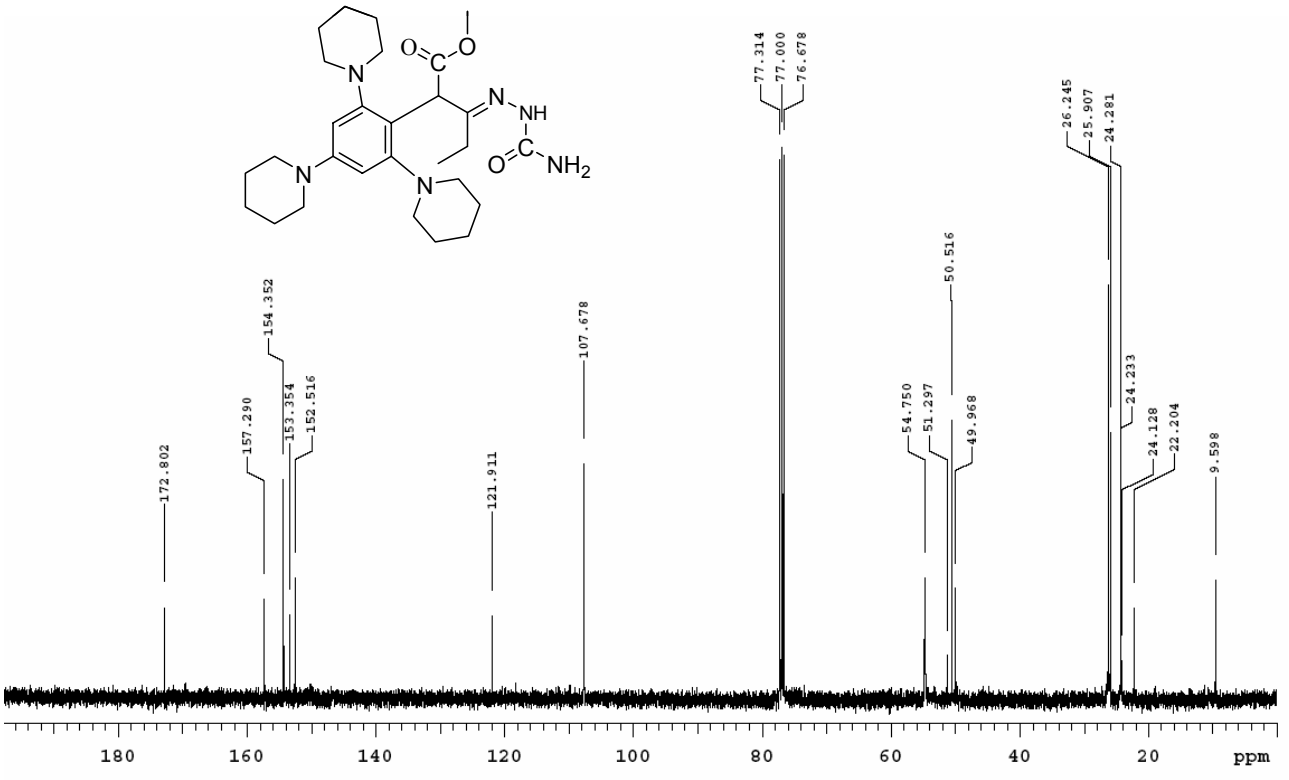
INDEX	FREQUENCY	PPM	HEIGHT
1	17353.703	172.569	9.7
2	15789.731	157.016	15.5
3	15522.592	154.360	21.5
4	15341.262	152.557	10.7
5	14989.935	149.063	13.3
6	12218.984	121.508	12.3
7	10808.818	107.485	38.7
8	7774.777	77.314	204.6
9	7763.443	77.201	10.8
10	7743.206	77.000	245.3
11	7711.635	76.686	202.1
12	5502.483	54.718	18.5
13	5269.345	52.399	15.9
14	5165.727	51.369	21.0
15	5075.872	50.475	41.9
16	2645.724	26.310	55.5
17	2608.487	25.939	43.2
18	2441.728	24.281	23.6
19	2438.490	24.249	21.5
20	1560.981	15.523	15.4



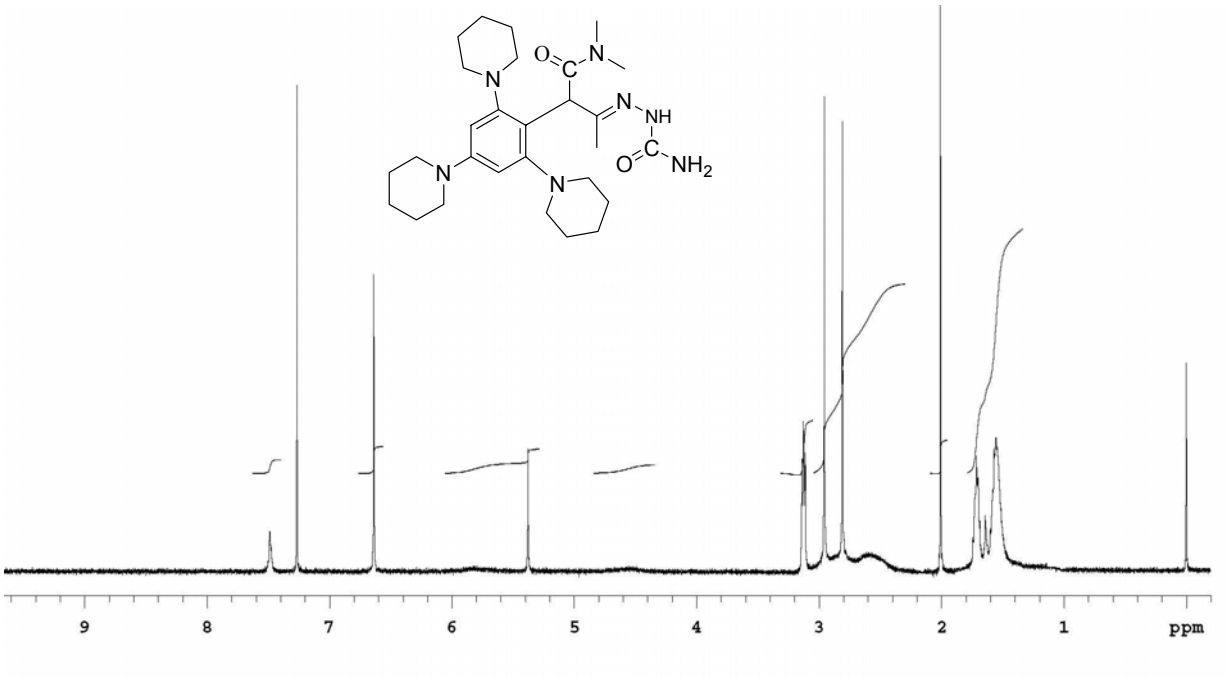
^{13}C NMR spectrum in $CDCl_3$ of compound **9**.



^{1}H NMR spectrum in $CDCl_3$ of compound **10**.

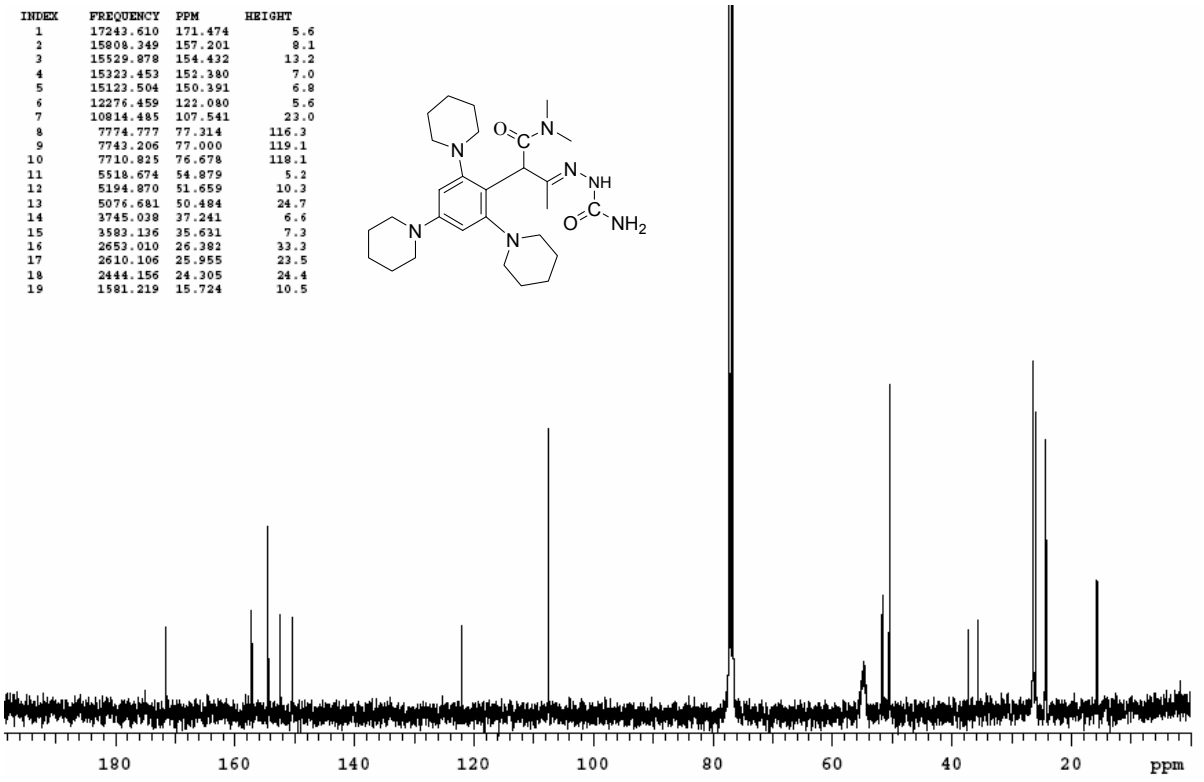


^{13}C NMR spectrum in $CDCl_3$ of compound **10**.

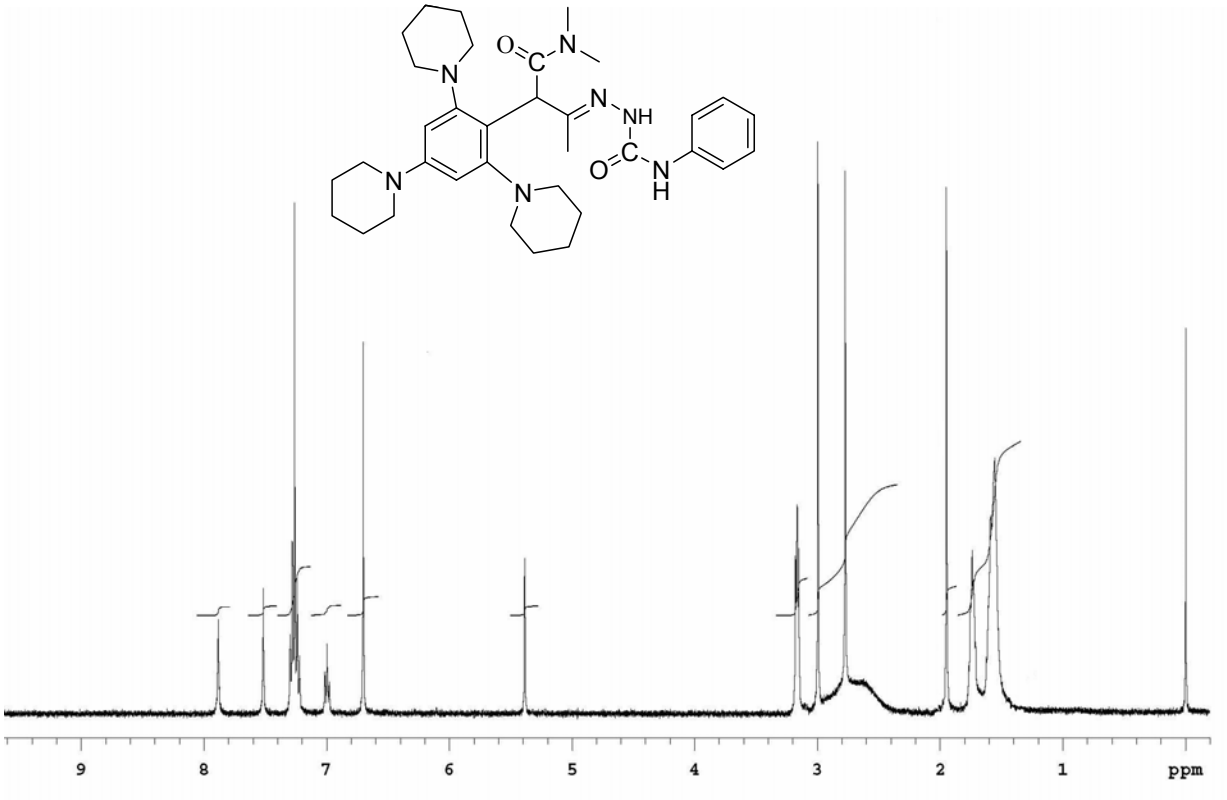


^{1}H NMR spectrum in $CDCl_3$ of compound **11**.

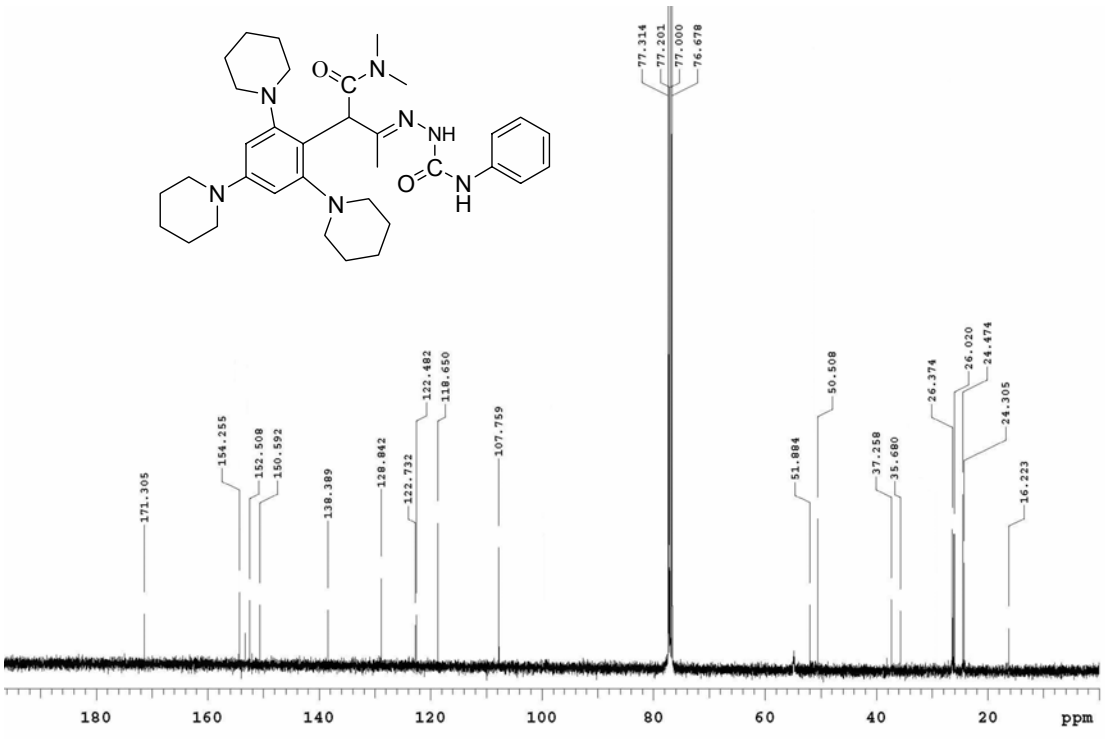
INDEX	FREQUENCY	PPM	HEIGHT
1	17243.610	171.474	5.6
2	15808.349	157.201	8.1
3	15529.878	154.432	13.2
4	15323.453	152.380	7.0
5	15123.504	150.391	6.8
6	12276.459	122.080	5.6
7	10814.485	107.541	23.0
8	7774.777	77.314	116.3
9	7743.206	77.000	119.1
10	7710.825	76.678	118.1
11	5518.674	54.879	5.2
12	5194.870	51.659	10.3
13	5076.681	50.484	24.7
14	3745.038	37.241	6.6
15	3583.136	35.631	7.3
16	2653.010	26.382	33.3
17	2610.106	25.955	23.5
18	2444.156	24.305	24.4
19	1581.219	15.724	10.5



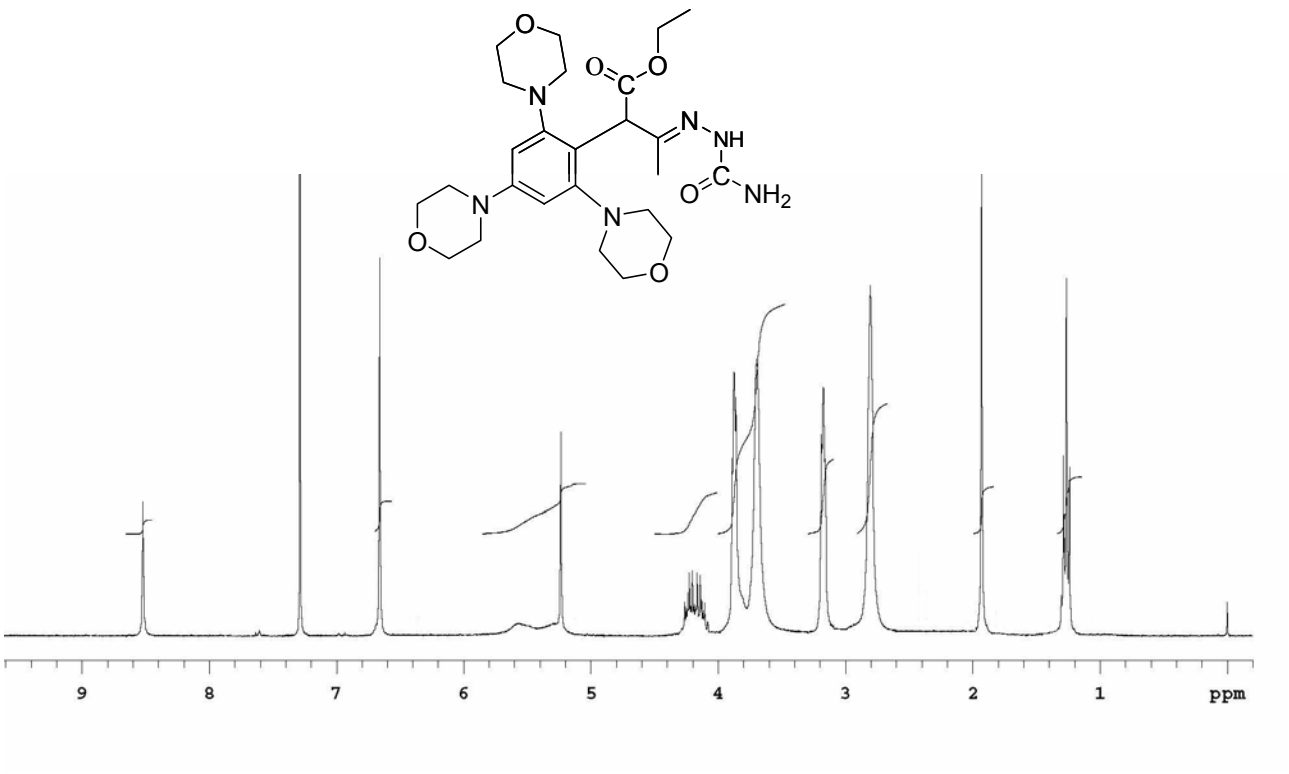
^{13}C NMR spectrum in $CDCl_3$ of compound **11**.



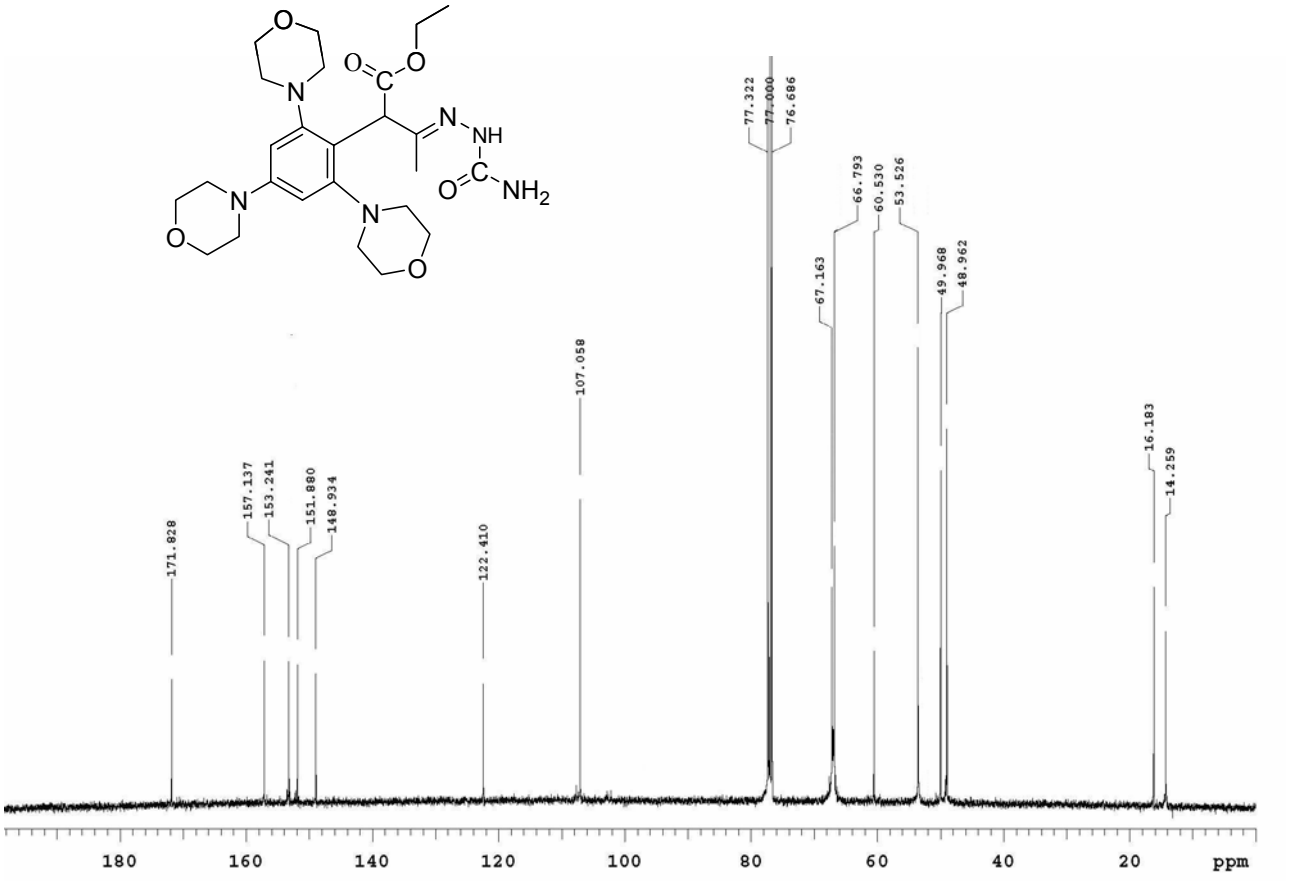
^{1}H NMR spectrum in $CDCl_3$ of compound **12**.



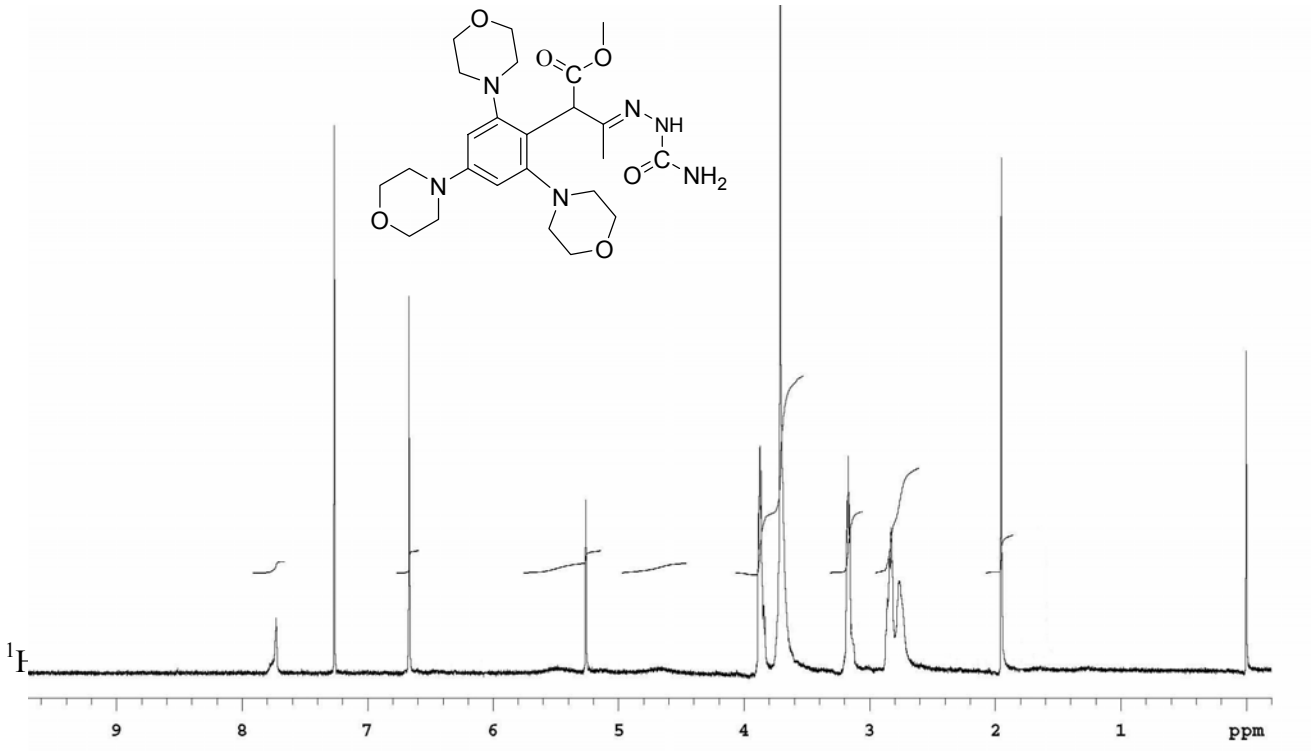
^{13}C NMR spectrum in $CDCl_3$ of compound **12**.



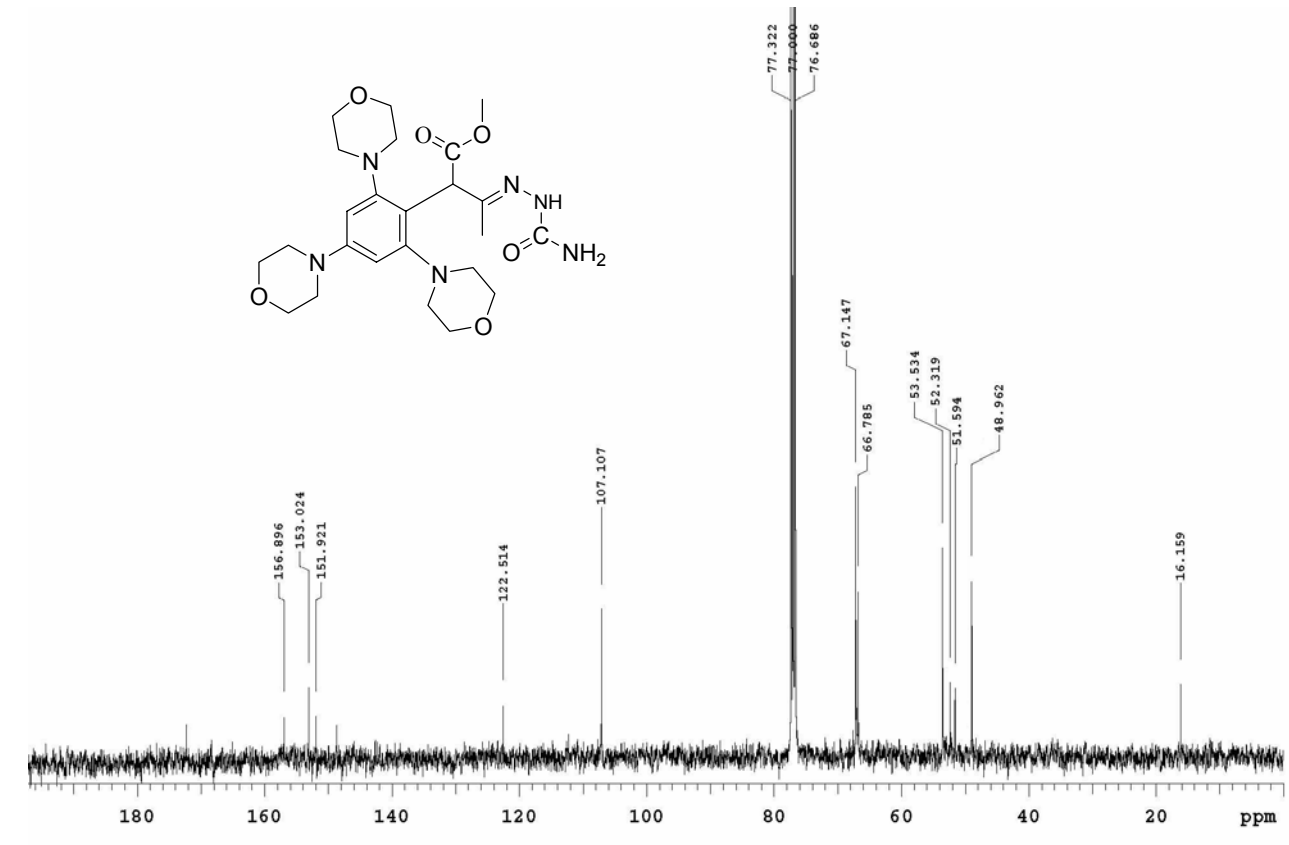
^{1}H NMR spectrum in $CDCl_3$ of compound **13.**



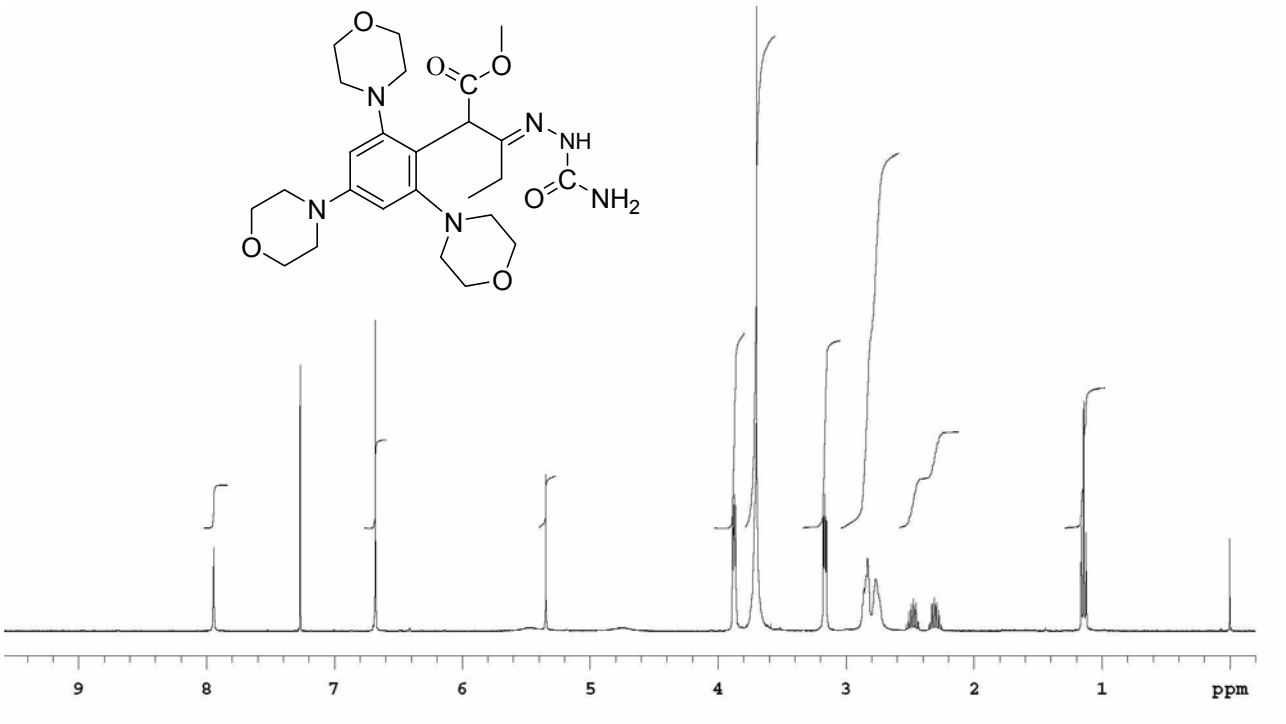
^{13}C NMR spectrum in $CDCl_3$ of compound **13**.



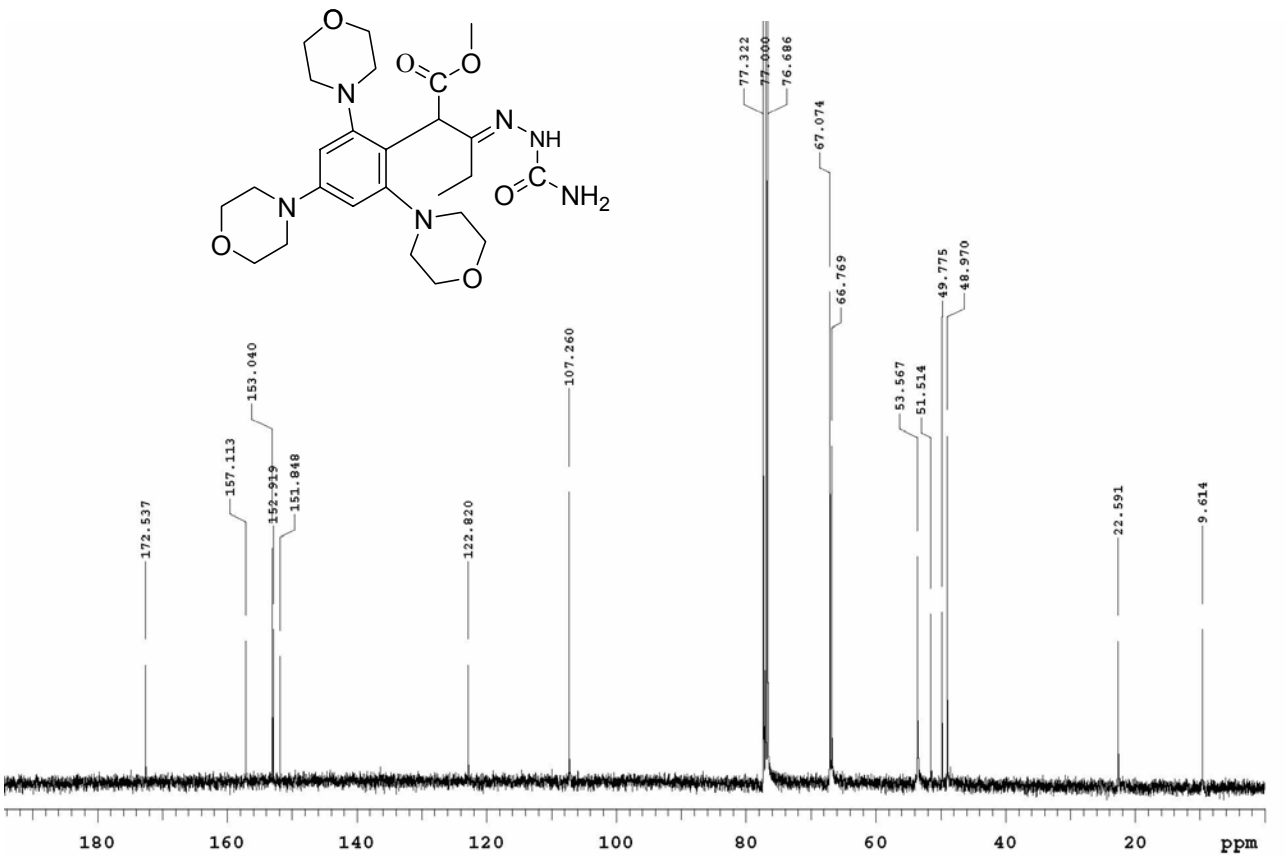
^{1}H NMR spectrum in $CDCl_3$ of compound **14.**



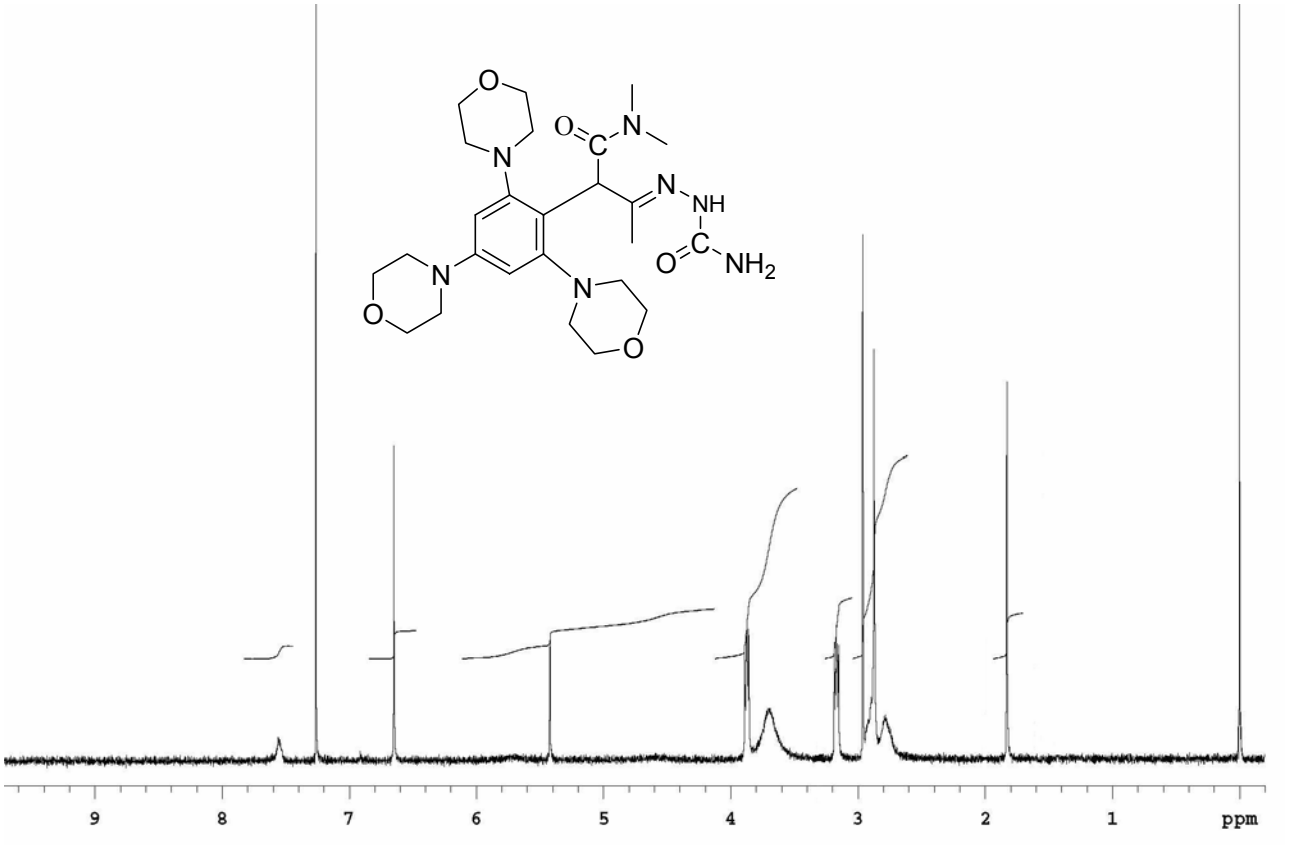
^{13}C NMR spectrum in $CDCl_3$ of compound **14**.



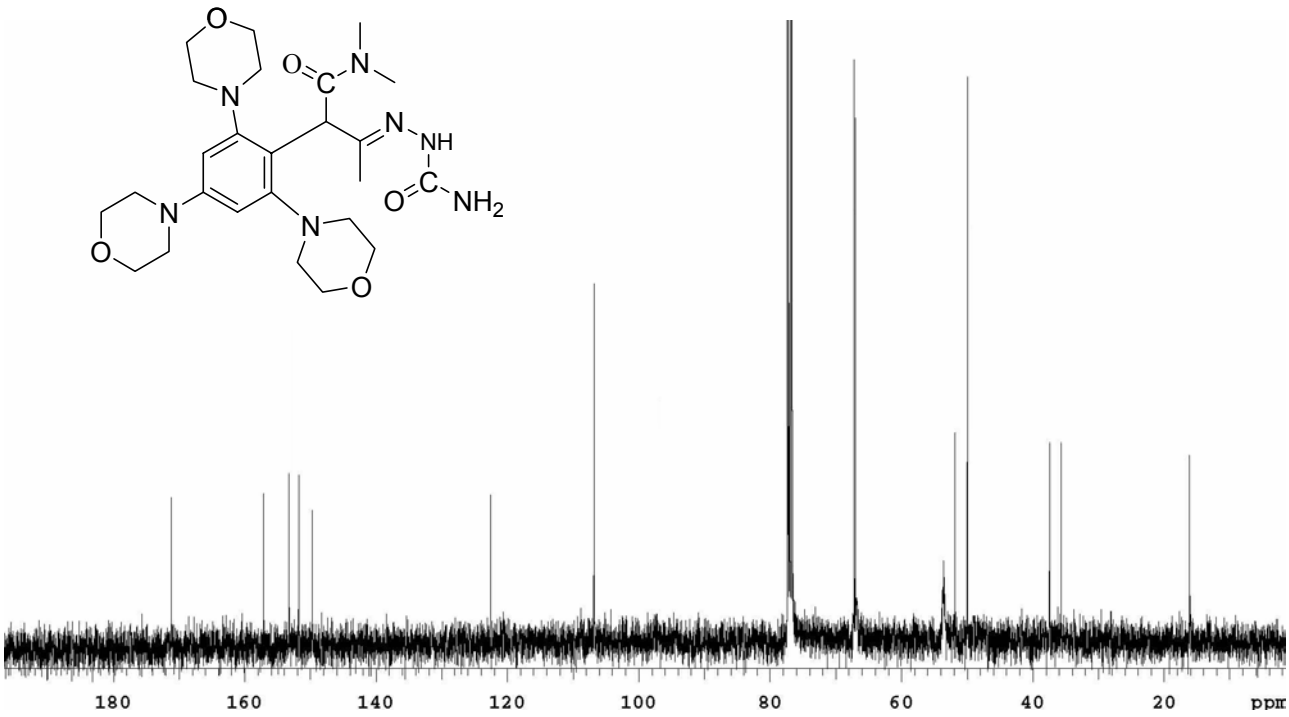
^{1}H NMR spectrum in $CDCl_3$ of compound **15.**



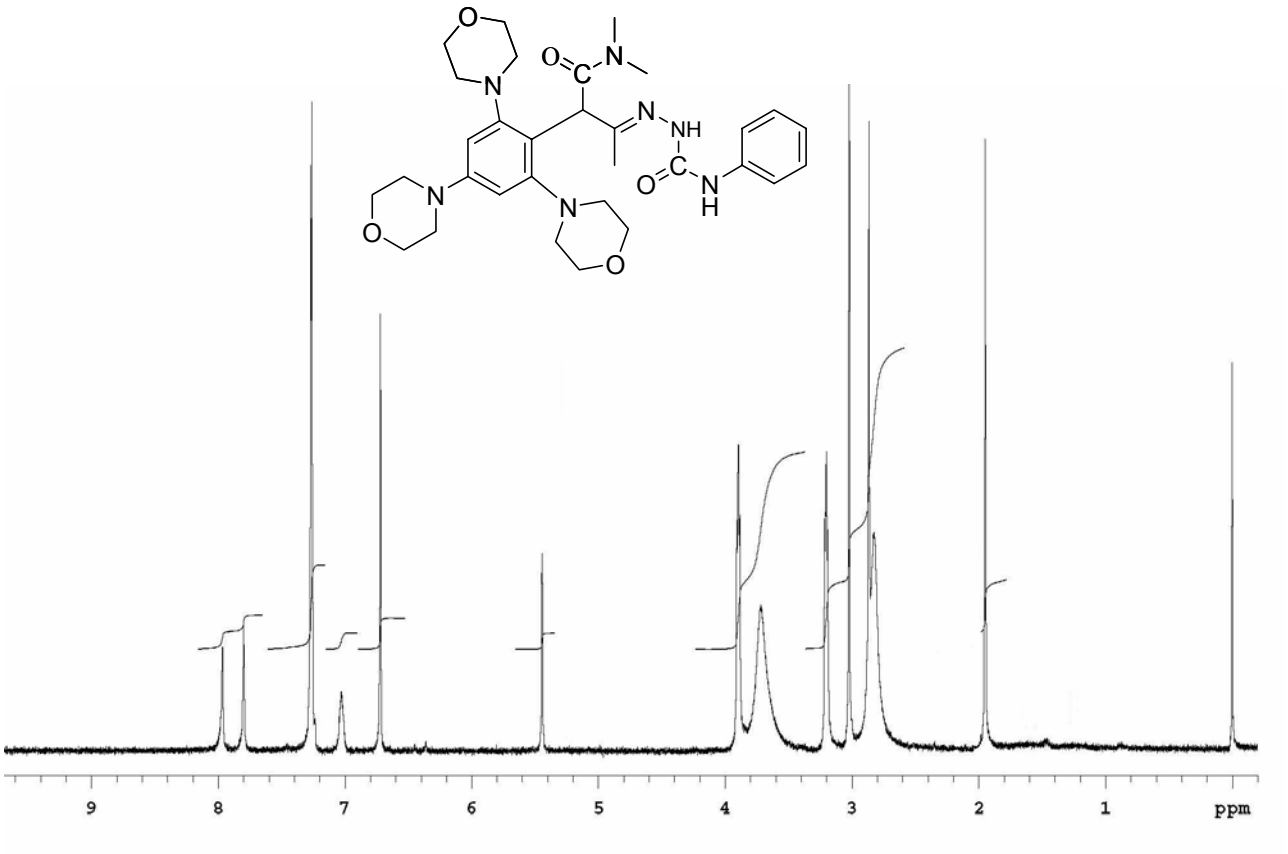
^{13}C NMR spectrum in $CDCl_3$ of compound **15**.



^{1}H NMR spectrum in $CDCl_3$ of compound **16**.

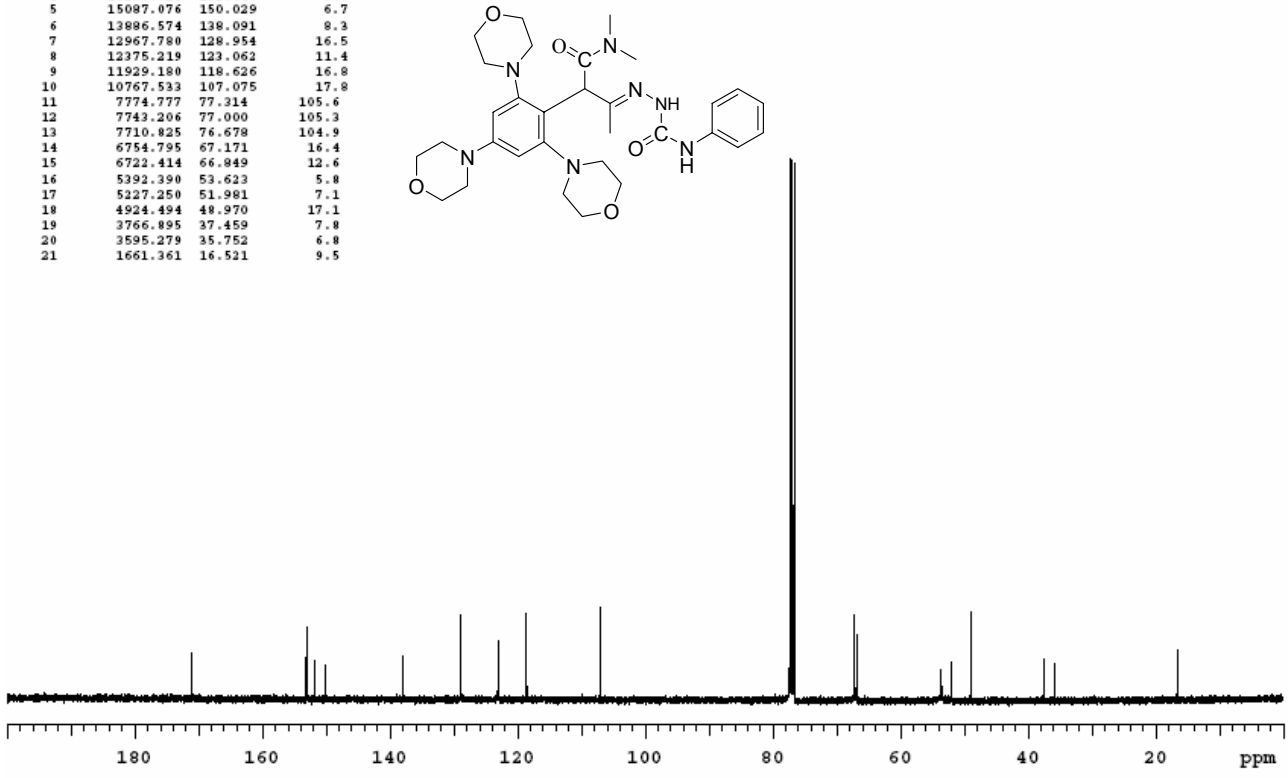


^{13}C NMR spectrum in $CDCl_3$ of compound **16**.

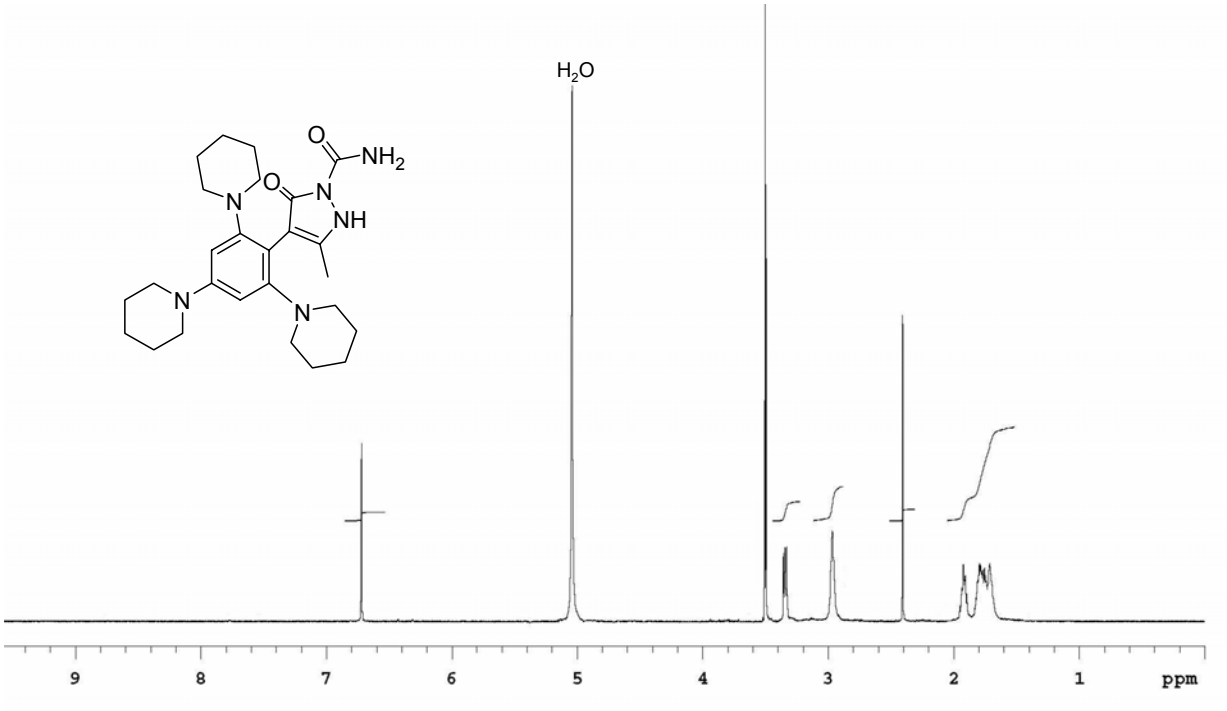


^{1}H NMR spectrum in $CDCl_3$ of compound **17**.

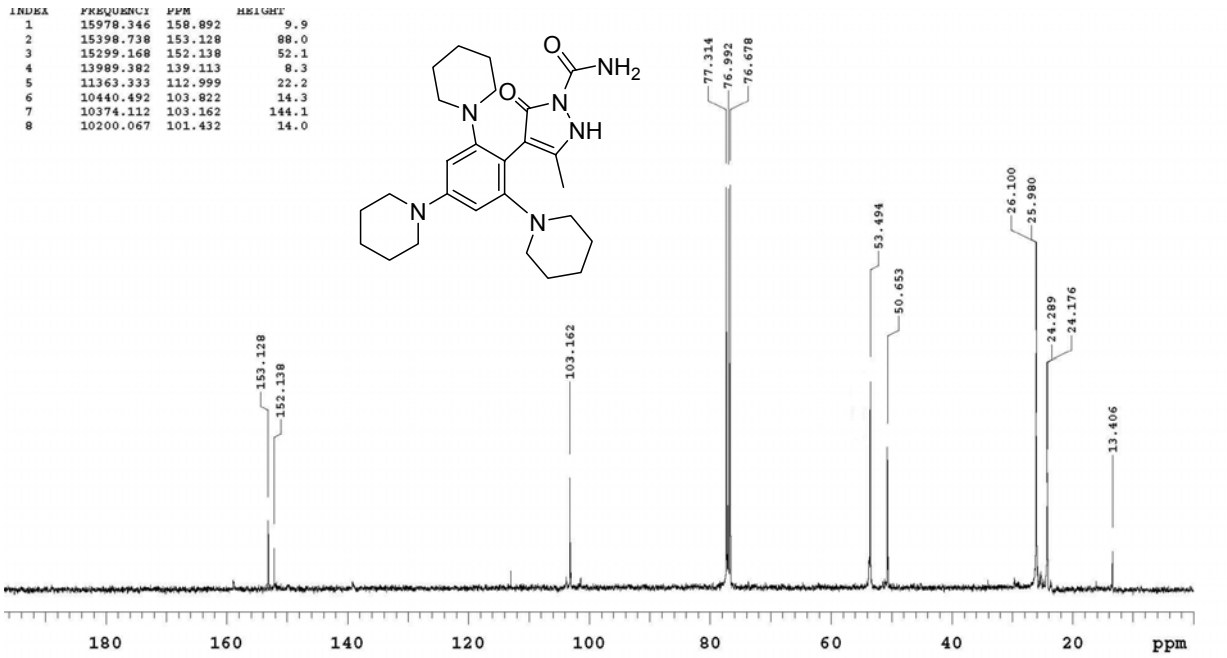
1	17195.849	170.999	9.1
2	15405.214	153.193	8.0
3	15391.452	153.056	14.0
4	15270.025	151.848	7.6
5	15087.076	150.029	6.7
6	13886.574	138.091	8.3
7	12967.780	128.954	16.5
8	12375.219	123.062	11.4
9	11929.180	118.626	16.8
10	10767.533	107.075	17.8
11	7774.777	77.314	105.6
12	7743.206	77.000	105.3
13	7710.825	76.678	104.9
14	6754.795	67.171	16.4
15	6722.414	66.849	12.6
16	5392.390	53.623	5.8
17	5227.250	51.981	7.1
18	4924.494	48.970	17.1
19	3766.895	37.459	7.8
20	3595.279	35.752	6.8
21	1661.361	16.521	9.5



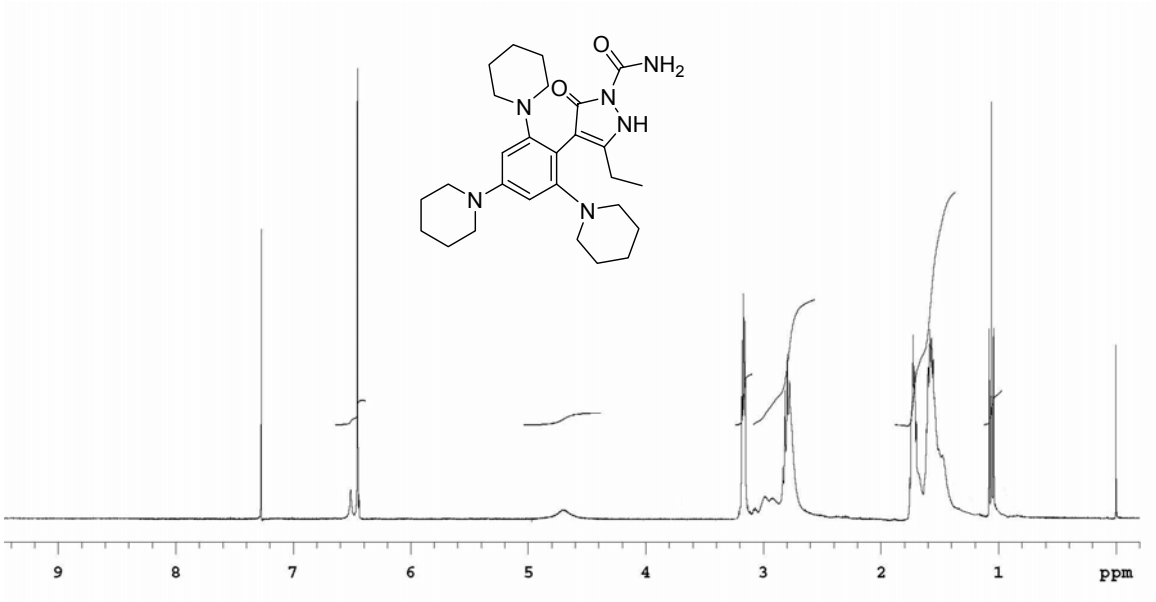
^{13}C NMR spectrum in $CDCl_3$ of compound **17**.



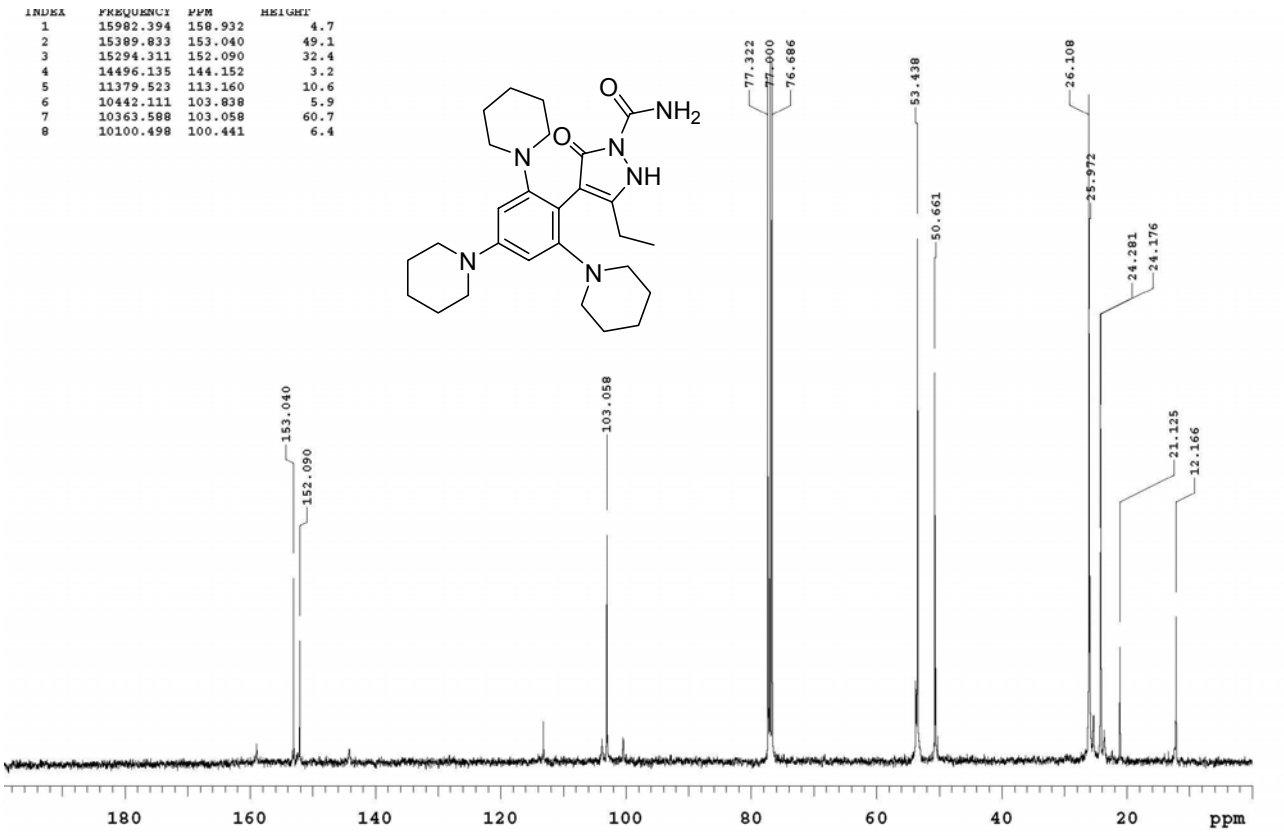
^{1}H NMR spectrum in CD_3OD of compound **20**.



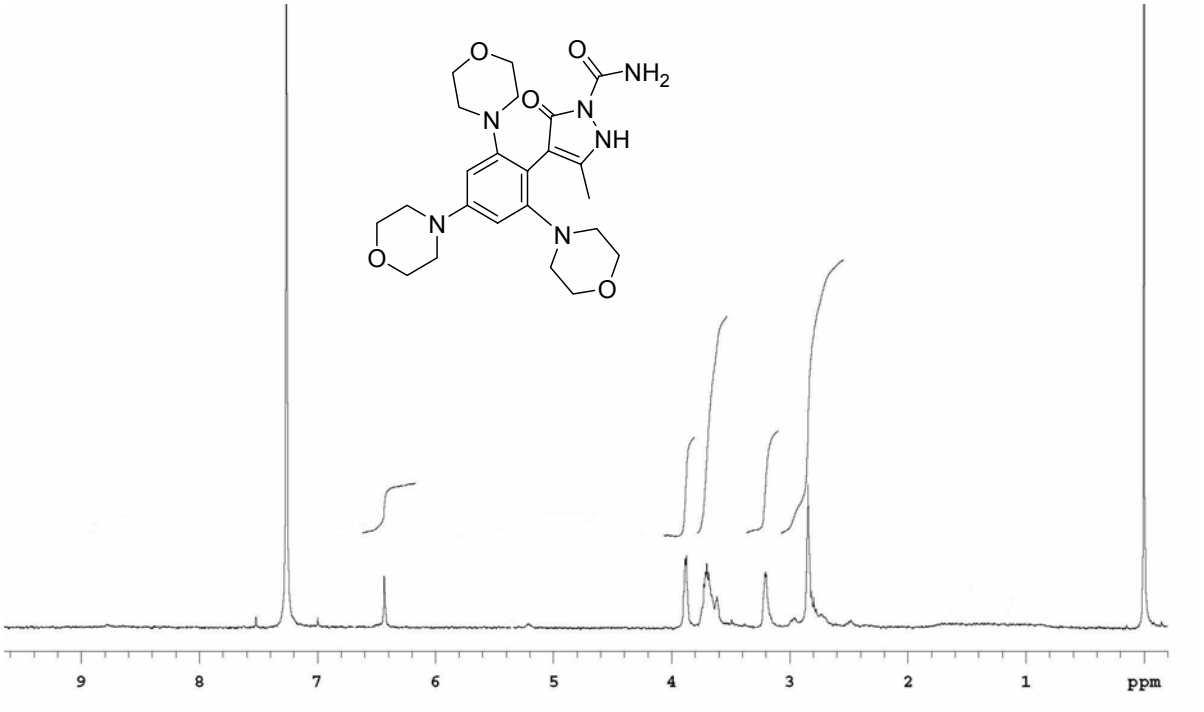
^{13}C NMR spectrum in $CDCl_3$ of compound **20**.



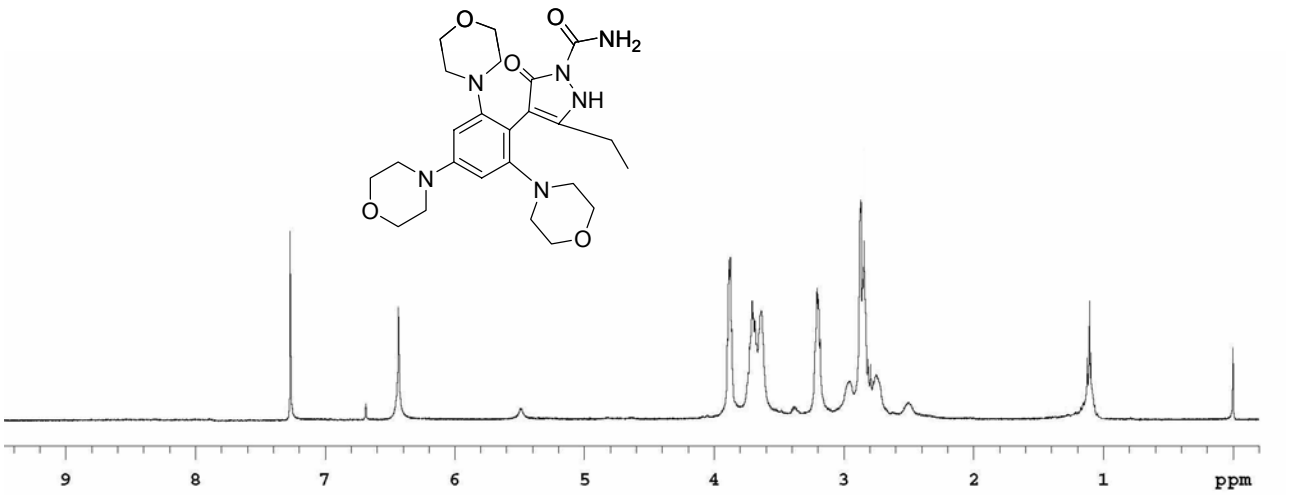
^{1}H NMR spectrum in $CDCl_3$ of compound **21**.



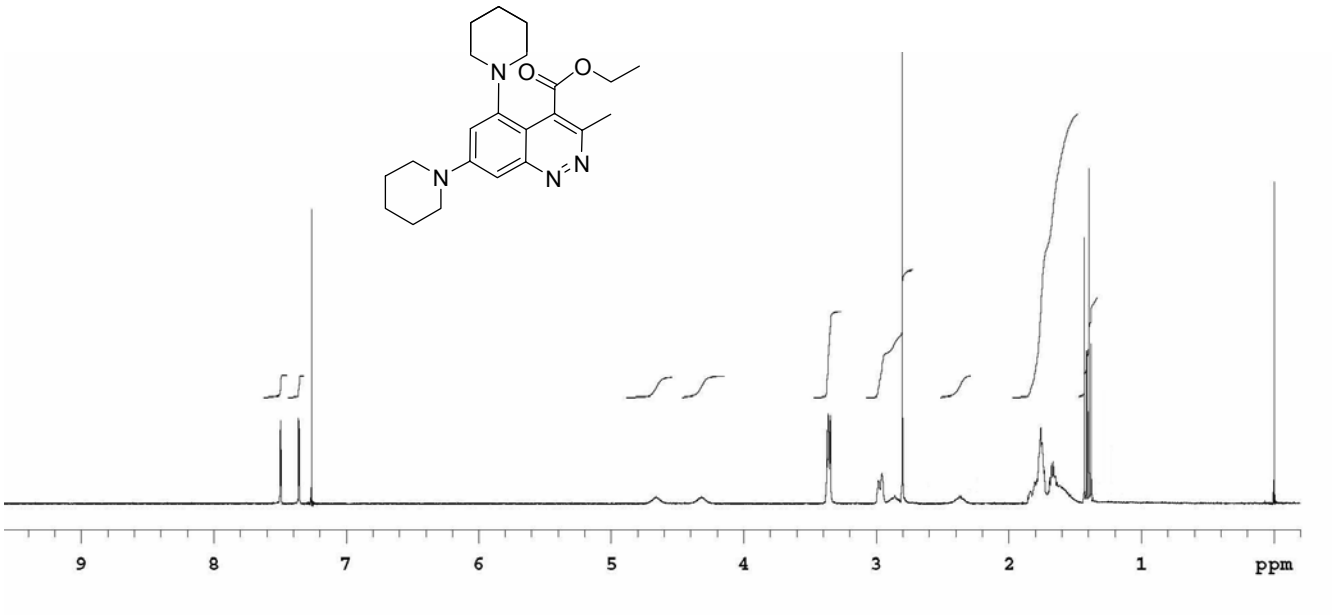
^{13}C NMR spectrum in $CDCl_3$ of compound **21**.



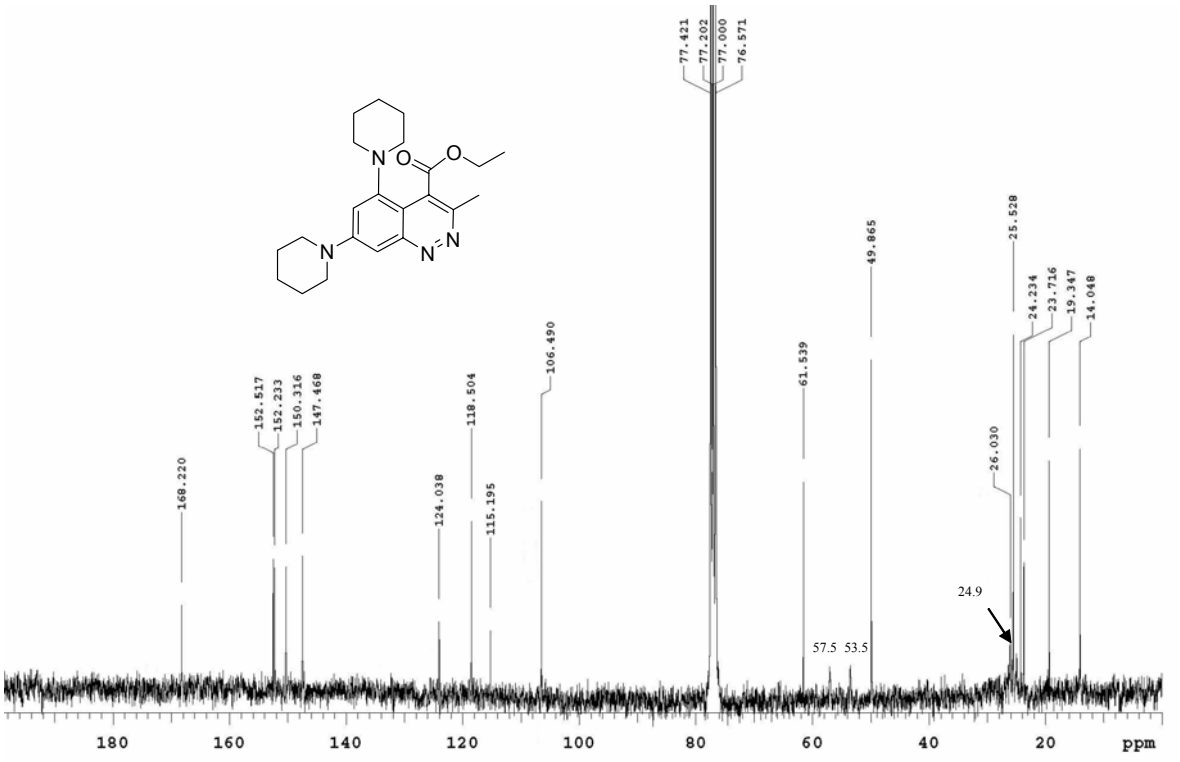
^{1}H NMR spectrum in $CDCl_3$ of compound **22**.



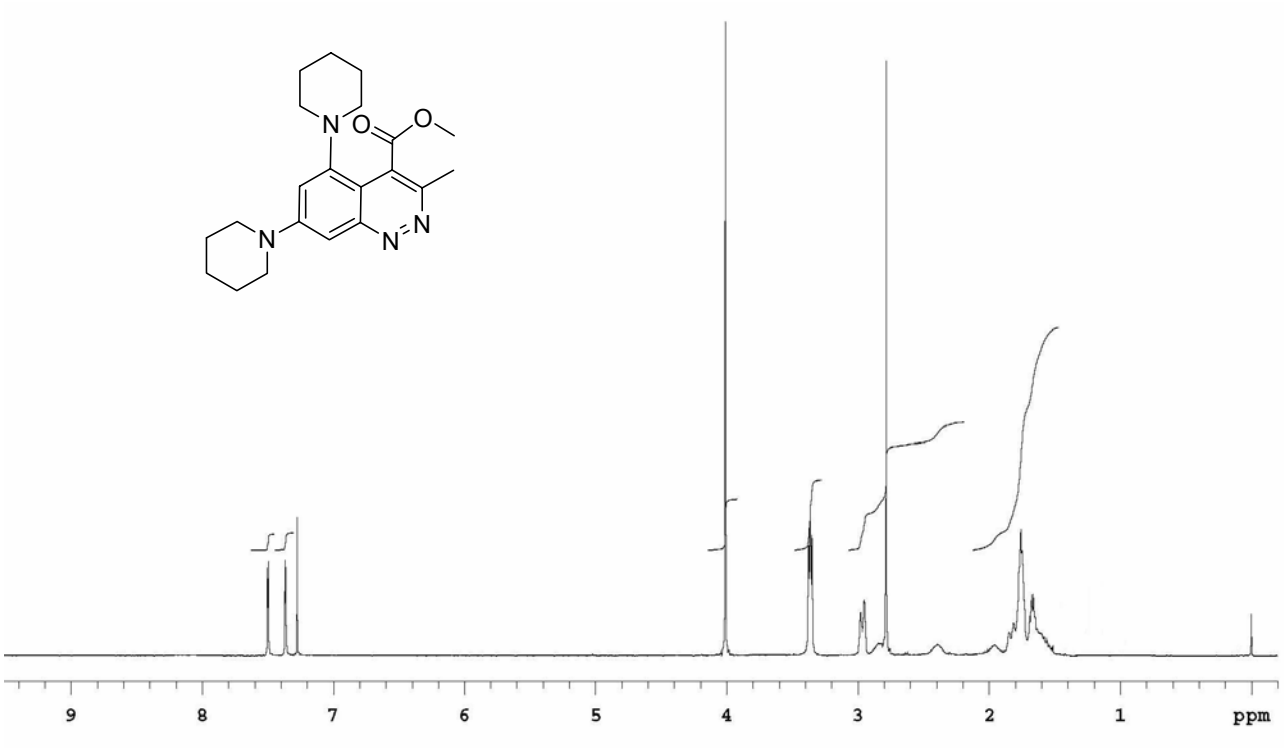
^{1}H NMR spectrum in $CDCl_3$ of compound **23**.



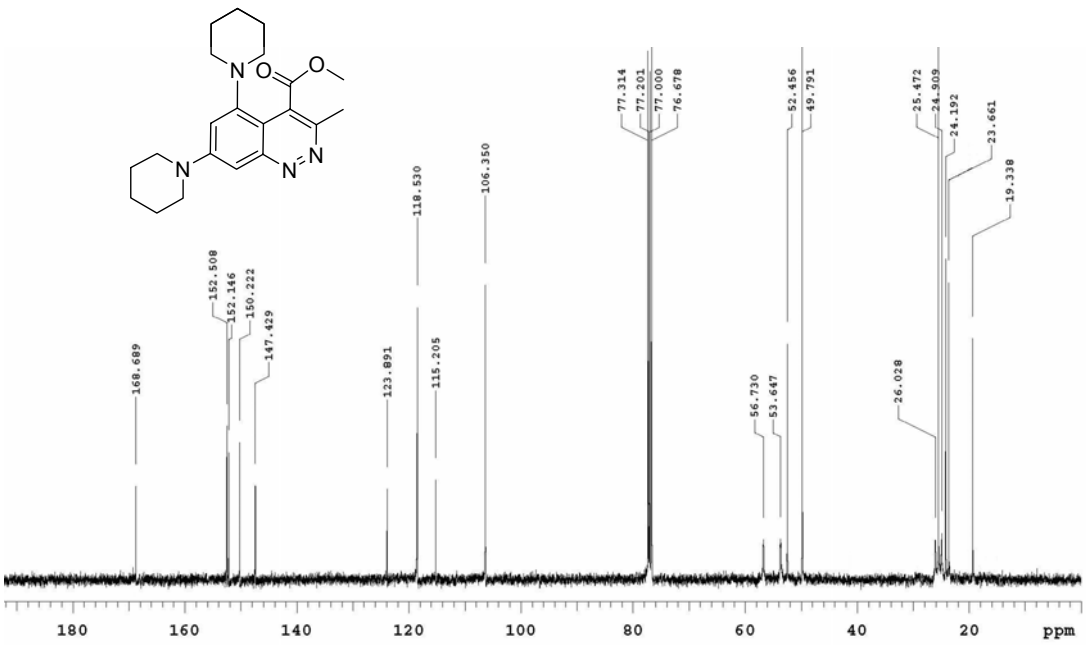
^{1}H NMR spectrum in $CDCl_3$ of compound **24**.



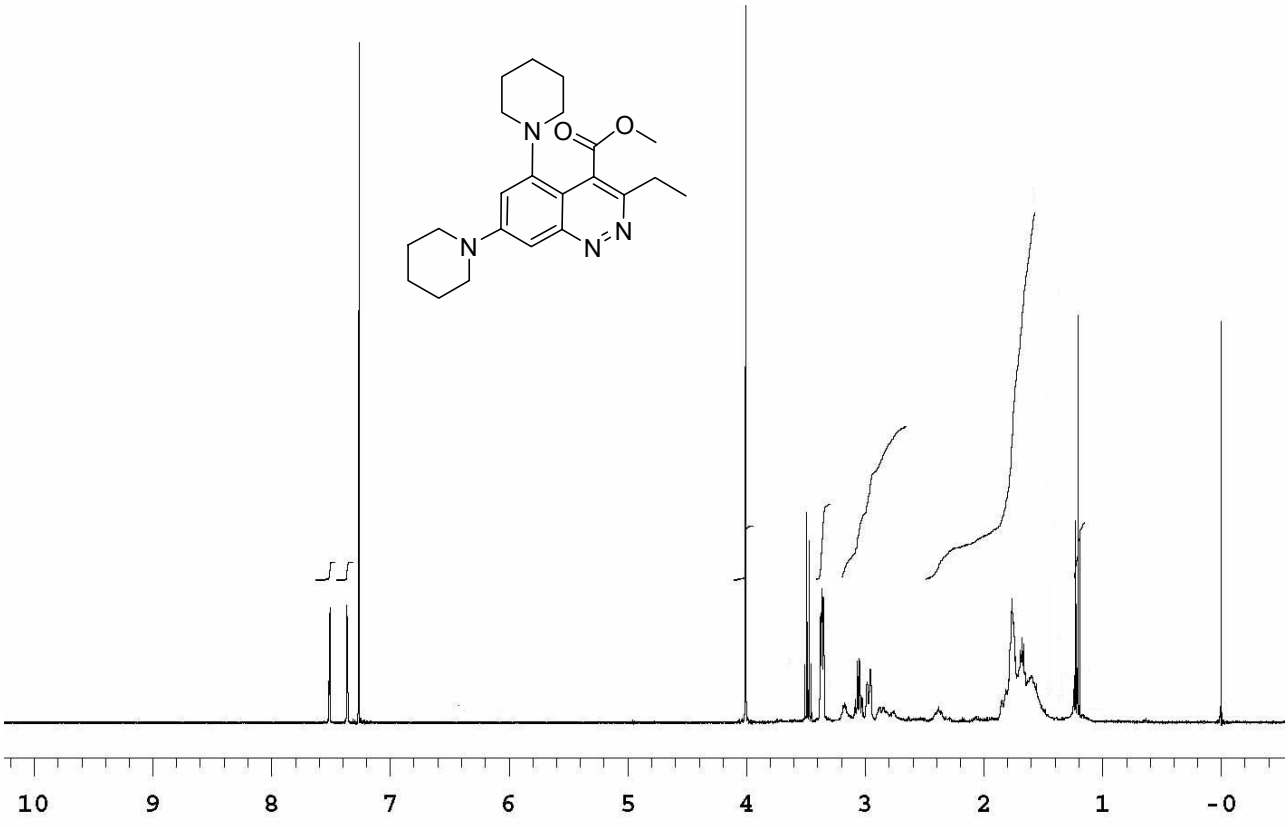
^{13}C NMR spectrum in $CDCl_3$ of compound **24**.



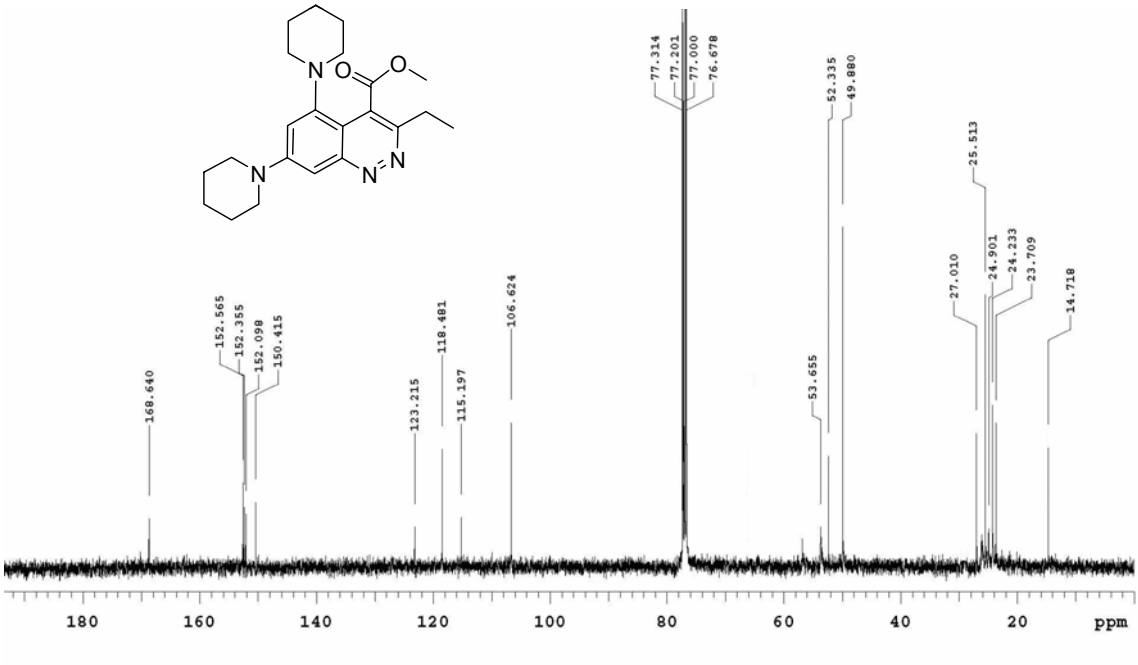
^{1}H NMR spectrum in $CDCl_3$ of compound **25**.



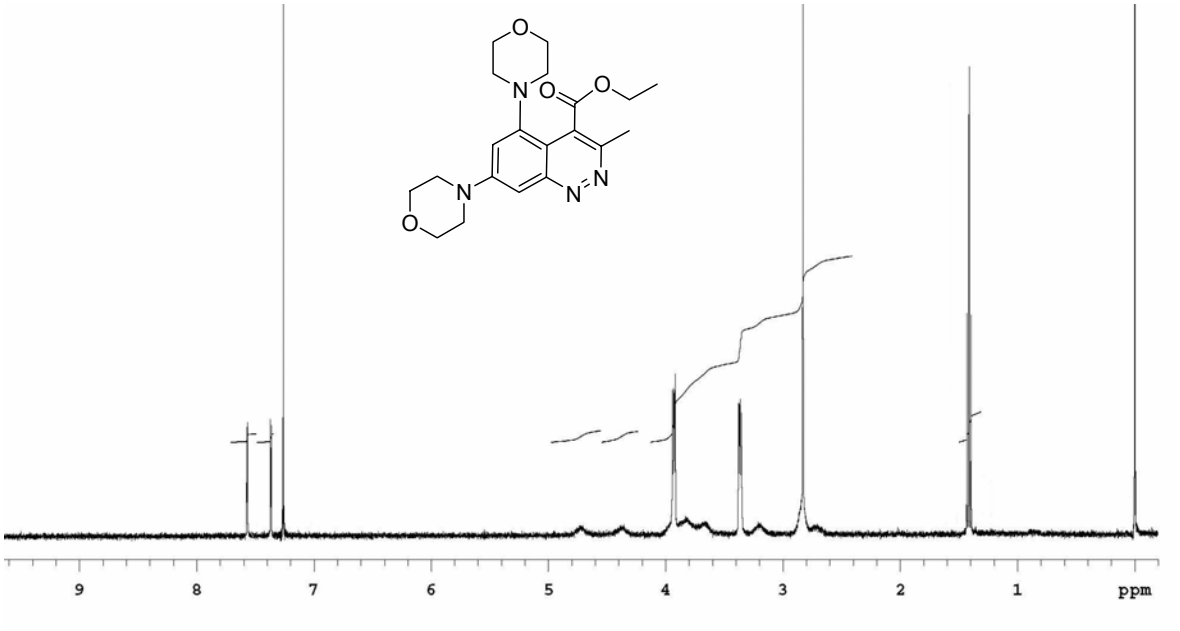
^{13}C NMR spectrum in $CDCl_3$ of compound **25**.



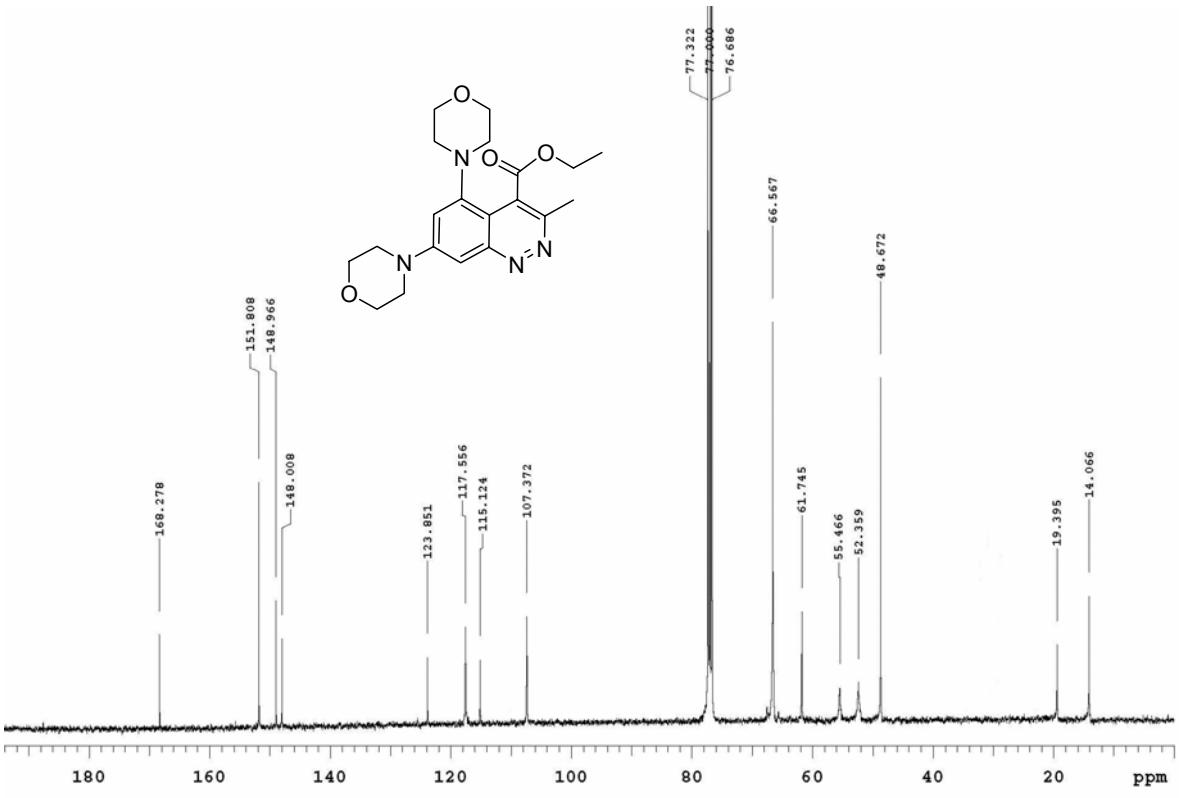
^{1}H NMR spectrum in $CDCl_3$ of compound **26**.



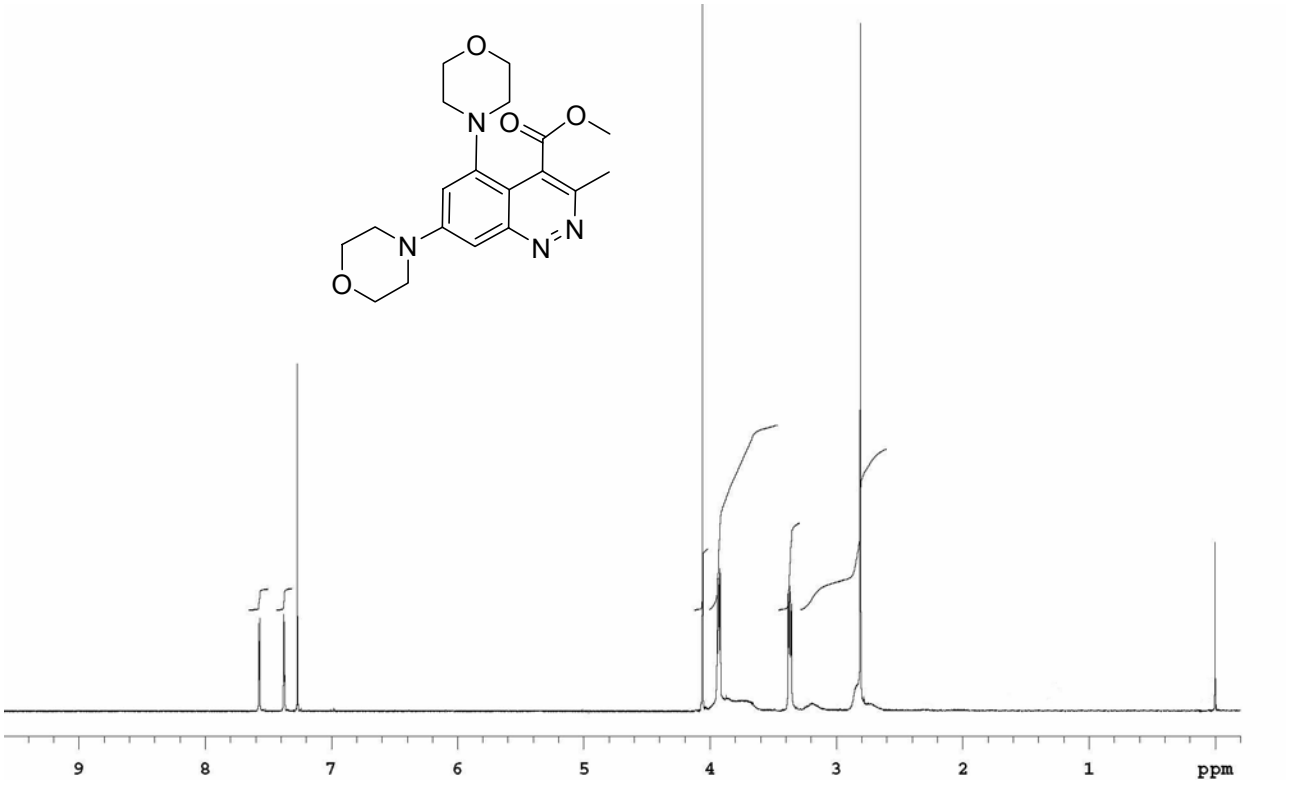
^{13}C NMR spectrum in $CDCl_3$ of compound **26**.



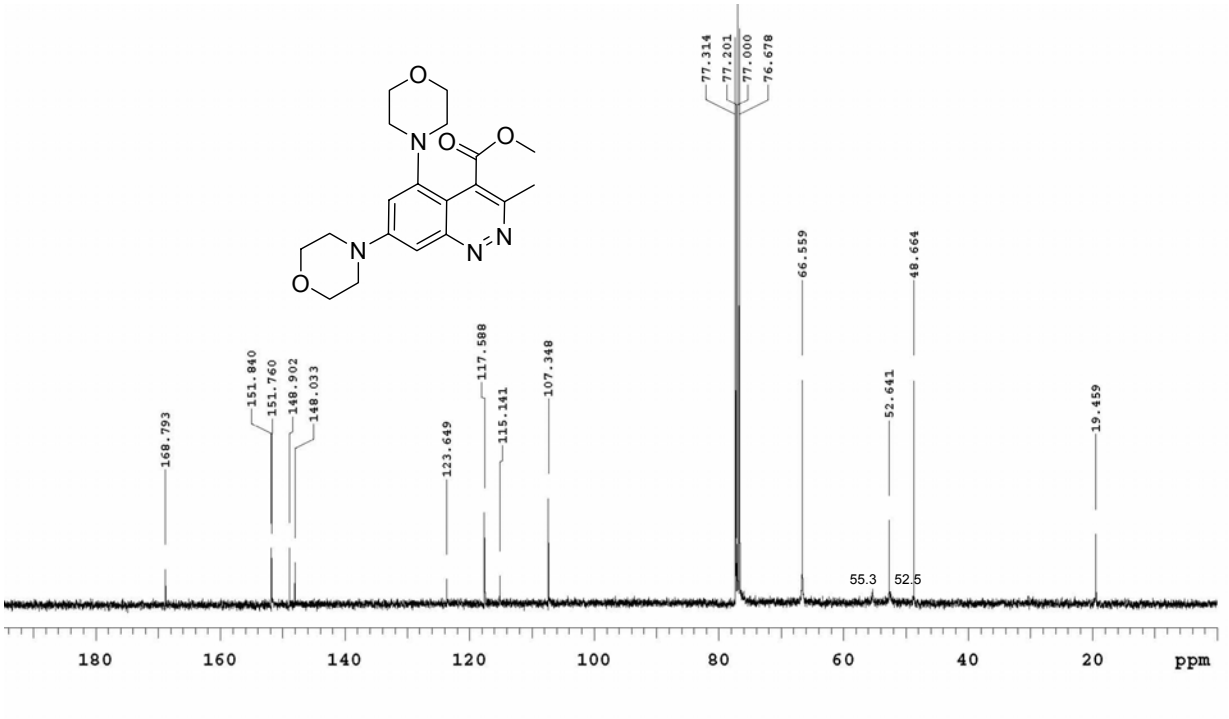
^{1}H NMR spectrum in $CDCl_3$ of compound **27**.



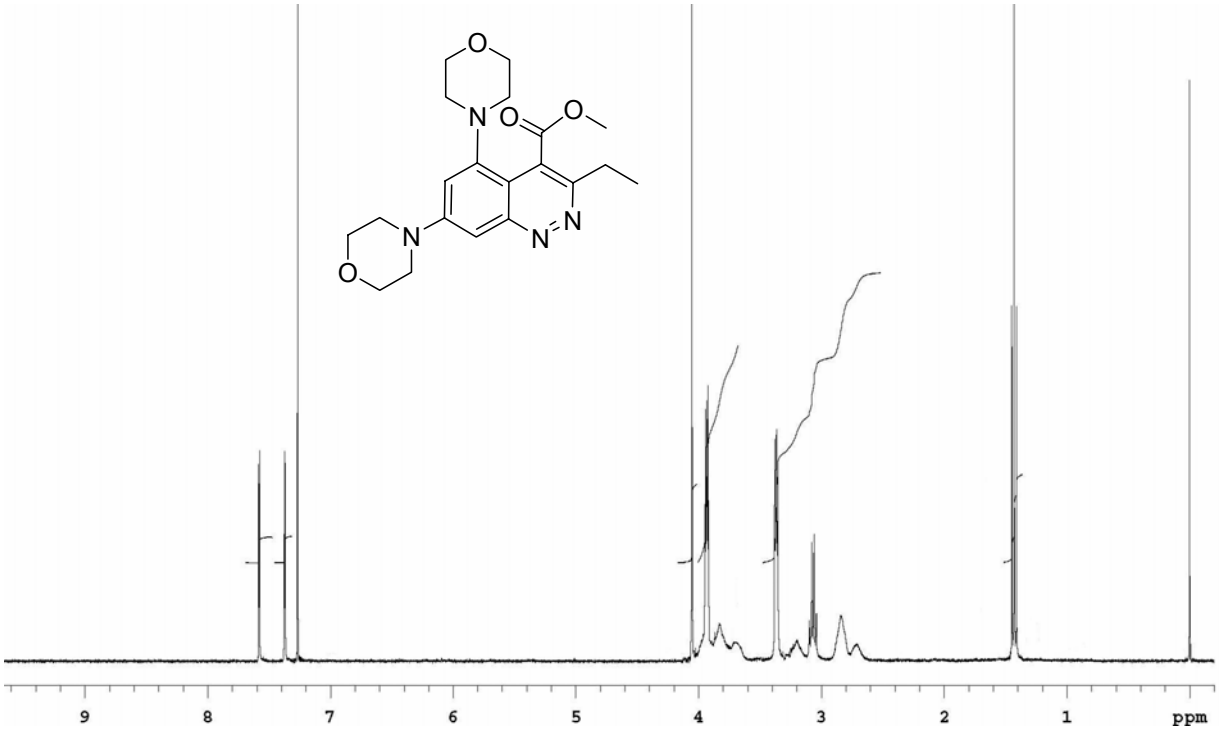
^{13}C NMR spectrum in $CDCl_3$ of compound **27**.



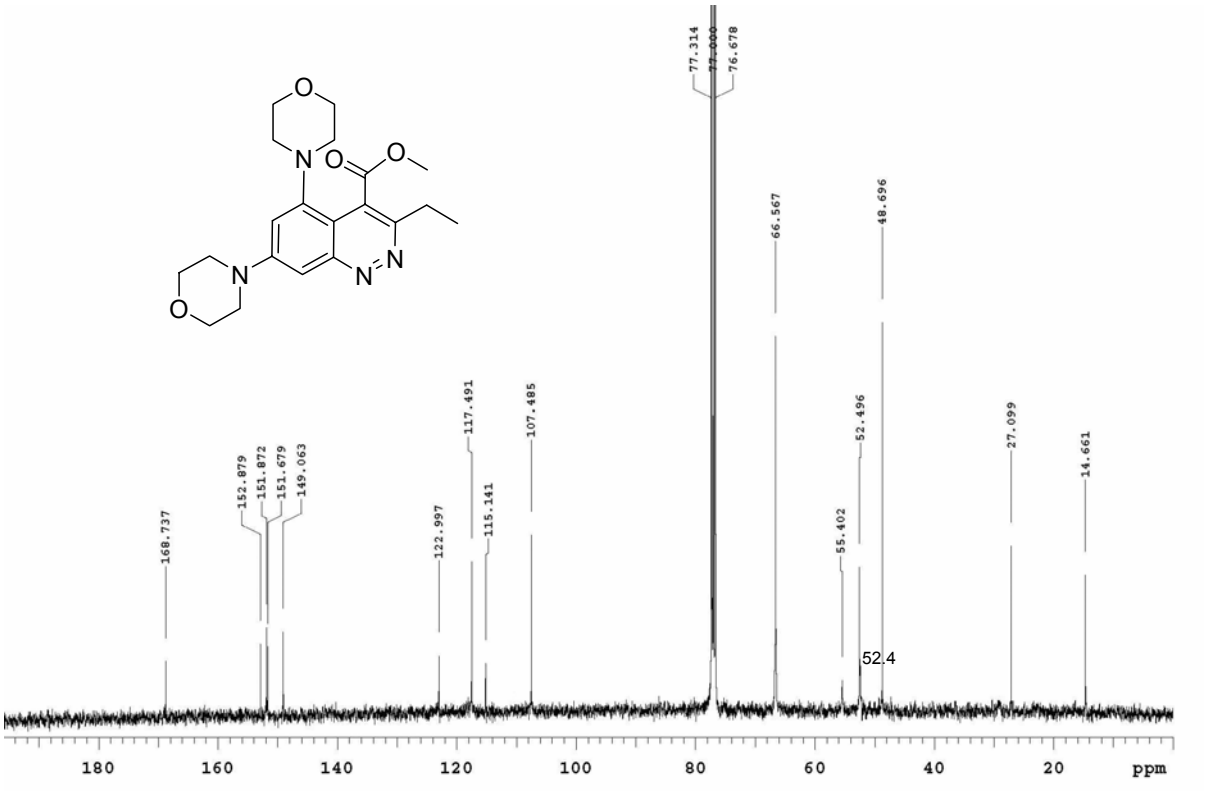
^{1}H NMR spectrum in $CDCl_3$ of compound **28**.



^{13}C NMR spectrum in $CDCl_3$ of compound **28**.



^{1}H NMR spectrum in $CDCl_3$ of compound **29**.



^{13}C NMR spectrum in $CDCl_3$ of compound **29**.