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Visible Light Mediated Organocatalytic Dehydrogenative Aza-coupling of 1,3-Diones Using ArylDiazonium Salts

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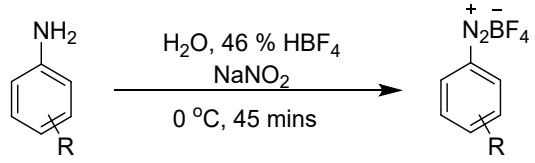
Supporting Information

1. General information

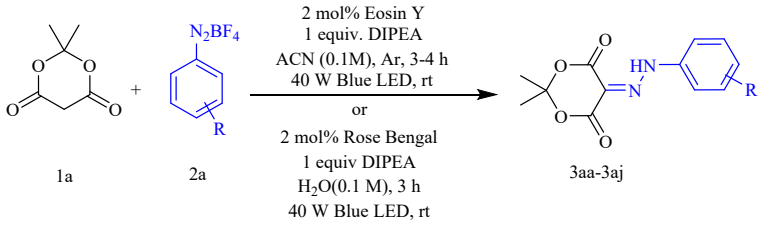
All the reagents are used as received without any further purification unless stated and the solvents used were distilled prior to use. The reactions were performed in an oven-dried 20 ml glass vial under argon atmosphere. The reactions were monitored by thin layer chromatography and visualized under UV light of 254 nm and charred in vanillin solution. ^{1}HNMR and ^{13}CNMR were recorded in a 400 MHz Bruker Avance III 400 spectrophotometer with $CDCl_3$ as a solvent and using TMS as the internal standard solvent (at 0 ppm). The chemical shifts are reported in parts per million(ppm) and all coupling constants in Hertz (Hz). The multiplicity denoted as s (singlet); d (doublet); t (triplet); q (quartet); p (pentate); m(multiplet), bs (broad singlet). The mass spectra were recorded in Waters ZQ-4000. Column chromatography was used to purify the mixture using 100-200 silica mesh size purchased from Sigma Aldrich; petroleum ether and ethyl acetate as eluent.

2. Preparation of aryldiazonium tetrafluoroborate salt[1,2]



To a stirred suspended solution of substituted aniline and H_2O, were added 46% HBF_4 and cooled the solution to 0 °C. A saturated aqueous solution of $NaNO_2$ was added and stirred for 45 mins. The mixture was then filtered off and the filtrate was dissolved in minimum amount of acetone and again diethyl ether was added to precipitate to obtain the desired aryldiazonium salt. The resulting precipitate was filtered and dried under a high vacuum.

3. General experimental procedure[3]



Method A: 0.2-0.3 mmol of 1,3- diones, 2 mol% of Eosin Y and 1.2 eq of aryldiazonium tetrafluoroborate were dissolved in 2 ml of acetonitrile in a 20 ml oven-dried glass vial and argon were purged through a needle to the solution for 5 mins. 1 eq. of diisopropyl ethyl amine was added slowly to the mixture and again argon was purged for another 5 mins and sealed with a cap. The glass vial was irradiated with a 40W Blue Led Kessil bulb with continuous stirring for 3-4 hours. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated under reduced pressure in a rotary evaporator without any workup

procedure. The resulting crude was purified in column chromatography using petroleum ether and ethyl acetate as eluent.

Method B: 0.2-0.3 mmol of 1,3- diones, 2 mol% of Rose Bengal and 1.2 eq of aryldiazonium tetrafluoroborate were dissolved in 2 ml of water in a 20 ml oven-dried glass vial. 1 eq. of diisopropyl ethyl amine was added slowly to the mixture and sealed with a cap. The glass vial was irradiated with a 40W Blue Led Kessil bulb with continuous stirring for 3-4 hours. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated under reduced pressure in a rotary evaporator without any workup procedure. The resulting crude was purified in column chromatography using petroleum ether and ethyl acetate as eluent.

4. UV-Visible spectroscopic analysis

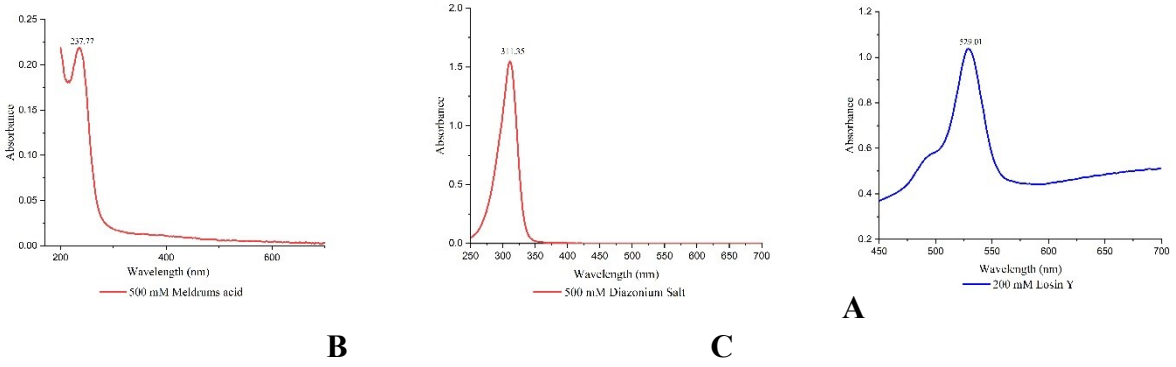


Fig S1: UV-Vis absorptions Spectrum of (A) Meldrums' acid (500 mM) at λ_{max} 237.77 nm, (B) *p*-methoxydiazonium salt (500 mM) at λ_{max} 310 nm, and (C) Eosin Y (200 mM) at λ_{max} 530 nm.

Interestingly, upon the mixing of A, B and C with diisopropyl ethyl amine, the gradual change of color to a yellow was observed within 15 to 20 mins which led to a bathochromic shift. Upon irradiation in the presence of Blue Led light, two new peaks were observed at 295nm and 390 nm (Fig S2) which confirms the formation of a new adduct. After purification, it was confirmed that the product was **3ac** by analyzing NMR and Mass Spectroscopy.

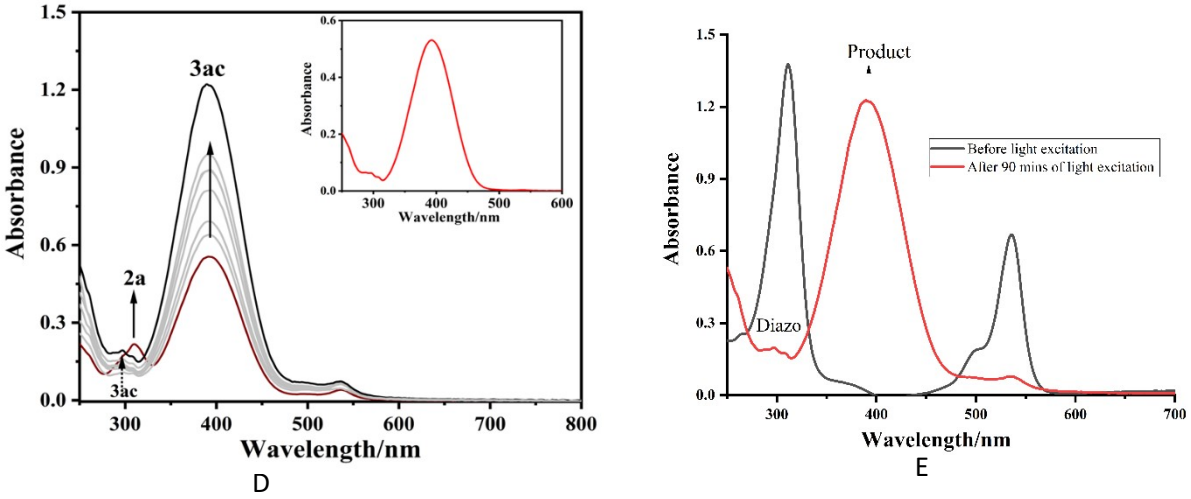
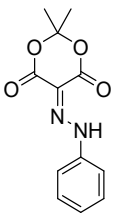


Fig S2: 0.2 mmol of Meldrums' acid, 0.24 mmol of p-methoxydiazonium salt, 0.004 mmol of Eosin Y and 0.2 mmol of DIPEA was dissolved in 2ml ACN and irradiated in the presence of Blue LED light. After 15 mins and interval of 15 mins, UV-Visible Spectroscopy was analyzed and depicted in D. An inset graph was also plotted after the purification of the reaction mixture. A comparison of the substrates and the product was also depicted in E.

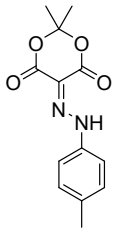
6. Characterization of new compounds[4-7]



3aa

2,2-dimethyl-5-(2-phenylhydrazineylidene)-1,3-dioxane-4,6-dione (3aa)

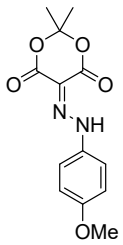
The diazenyl product was synthesized according to the general procedure as a a yellow solid in 92% (82%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.66(bs, 1H), 7.54(d, *J=8 Hz,* 2H), 7.44(d, *J=8 Hz,* 2H), 7.29(t, *J=8 Hz,* 1H), 1.81(s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 160.99, 159.24, 140.38, 129.79, 127.55, 117.19, 112.32, 105.82, 27.50. HRMS (ESI^+): calcd. for m/z $[C_{12}H_{12}N_2O_4+Na]^+$ 271.0695 found to be 271.0691.



3ab

2,2-dimethyl-5-(2-(p-tolyl)hydrazineylidene)-1,3-dioxane-4,6-dione (3ab)

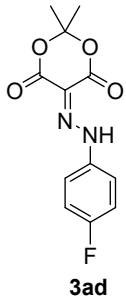
The diazenyl product was synthesized according to the general procedure as a yellow solid in 90% (90%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.64(bs, 1H), 7.38-7.34(m, 2H), 7.19-7.15(m, 2H), 2.3(s, 3H), 1.73(s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.25, 159.48, 138.25, 137.99, 130.45, 117.25, 111.84, 105.79, 27.54, 21.20. HRMS (ESI^+): calcd. for m/z $[C_{13}H_{14}N_2O_4+Na]^+$ 285.0851 found to be 285.0779.



3ac

5-(2-(4-methoxyphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ac)

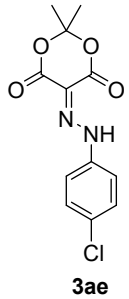
The diazenyl product was synthesized according to the general procedure as a yellow solid in 92% (85%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.82(bs, 1H), 7.51(d, *J=8 Hz,* 2H), 6.97(d, *J=8 Hz,* 2H), 3.85(s, 3H), 1.81(s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.35, 159.63, 159.28, 133.95, 118.75, 115.02, 111.19, 105.69, 55.66, 27.41. HRMS (ESI^+): calcd. for m/z $[C_{13}H_{14}N_2O_5+Na]^+$ 301.0800 found to be 301.0806.



3ad

5-(2-(4-fluorophenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ad)

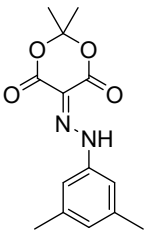
The diazenyl product was synthesized according to the general procedure as a yellow solid in 86% (78%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.63 (bs, 1H), 7.46 (m, 2H), 7.08(m, 2H), 1.74(s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 162.82, 161.08, 160.35, 159.18, 136.68, 118.86, 118.78, 116.96, 116.72, 112.33, 105.94, 27.51. HRMS (ESI^+): calcd. for m/z $[C_{12}H_{11}FN_2O_4+Na]^+$ 289.0601 found to be 289.0608.



3ae

5-(2-(4-chlorophenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ae)

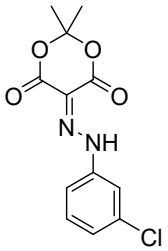
The diazenyl product was synthesized according to the general procedure as a yellow solid in 90% (80%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.54(bs, 1H), 7.39 (m, 2H), 7.32(m, 2H), 1.71(s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 160.98, 159.03, 138.99, 132.94, 129.98, 118.3, 112.78, 106.03, 27.56. HRMS (ESI$^+$): calcd. for m/z $[C_{12}H_{11}ClN_2O_4+Na]^+$ 305.0305 found to be 305.0314.



3af

5-(2-(3,5-dimethylphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3af)

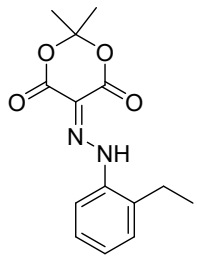
The diazenyl product was synthesized according to the general procedure as a yellow solid in 89% (81%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.63 (bs, 1H), 7.16 (s, 2H), 6.92 (s, 1H), 2.35 (s, 6H), 1.80 (s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.02, 159.40, 140.33, 139.82, 129.51, 114.98, 111.94, 105.68, 27.45, 21.23. HRMS (ESI$^+$): calcd. for m/z $[C_{14}H_{16}N_2O_4+Na]^+$ 299.1008 found to be 299.1105.



3ag

5-(2-(3-chlorophenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ag)

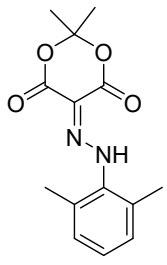
The diazenyl product was synthesized according to the general procedure as a yellow solid in 87% (79%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.55 (bs, 1H), 7.60 (s, 1H), 7.39–7.35 (m, 2H), 7.27–7.23 (m, 1H), 1.82 (s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 160.80, 158.80, 141.54, 135.92, 130.78, 127.32, 117.14, 115.37, 113.28, 106.04, 27.57. HRMS (ESI$^+$): calcd. For m/z $[C_{12}H_{11}ClN_2O_4+Na]^+$ 305.0305 found to be 305.0309.



3ah

5-(2-(2-ethylphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ah)

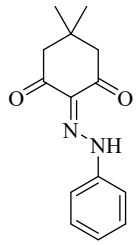
The diazenyl product was synthesized according to the general procedure as a yellow solid in 89% (83%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 14.02 (s, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.28 (m, 3H), 2.79 (q, J = 7.6 Hz, 2H), 1.83 (s, 6H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.36, 159.30, 137.99, 132.35, 129.36, 127.74, 127.57, 116.62, 112.79, 105.79, 27.49, 23.81, 14.07. HRMS (ESI$^+$): calcd. For m/z $[C_{14}H_{16}N_2O_4+Na]^+$ 299.1008 found to be 299.1013.



3ai

5-(2-(2,6-dimethylphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ai)

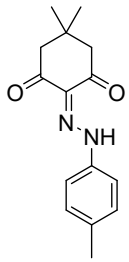
The diazenyl product was synthesized according to the general procedure as a yellow solid in 85% (78%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 13.71 (s, 1H), 7.12 (d, J = 1.5 Hz, 3H), 2.46 (s, 6H), 1.82 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.03, 159.28, 137.22, 130.45, 129.79, 127.64, 112.20, 105.62, 27.47, 19.14. HRMS (ESI$^+$): calcd. For m/z $[C_{14}H_{16}N_2O_4+Na]^+$ 299.1008 found to be 299.1024.



4aa

5,5-dimethyl-2-(2-phenylhydrazineylidene)cyclohexane-1,3-dione (4aa)

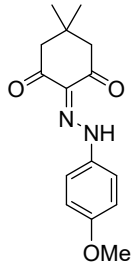
The diazenyl product was synthesized according to the general procedure as a yellow solid in 91% (85%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.43 (bs, 1H), 7.58 – 7.54 (m, 2H), 7.44 – 7.39 (m, 2H), 7.28 – 7.24 (m, 1H), 2.62 (s, 4H), 1.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.05, 193.36, 141.05, 130.29, 129.64, 127.19, 117.52, 52.59, 52.53, 30.75, 28.51. HRMS (ESI^+): calcd. for m/z $[C_{14}H_{16}N_2O_2+Na]^+$ 267.1109 found to be 267.1124.



4ab

5,5-dimethyl-2-(2-(p-tolyl)hydrazineylidene)cyclohexane-1,3-dione (4ab)

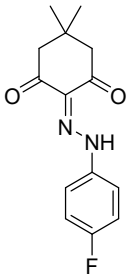
The diazenyl product was synthesized according to the general procedure as a yellow solid in 93% (87%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.46(bs, 1H), 7.53 (m, 2H), 6.95(m, 2H), 3.84(s, 3H), 2.59(s, 4H), 1.14(s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 197.10, 196.80, 193.35, 193.27, 162.66, 160.20, 138.71, 137.47, 137.34, 130.21, 129.97, 119.09, 119.01, 117.48, 116.74, 116.51, 52.54, 52.44, 30.74, 28.49, 21.11. HRMS (ESI^+): calcd. for m/z $[C_{15}H_{18}N_2O_2+Na]^+$ 281.1266 found to be 281.1352



4ac

2-(2-(4-methoxyphenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ac)

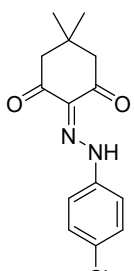
The diazenyl product was synthesized according to the general procedure as a yellow solid in 91% (89%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.71(s, 1H), 7.53 (m, 2H), 6.95(m, 2H), 3.84(s, 3H), 2.59(s, 4H), 1.14(s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 196.57, 193.39, 159.15, 134.49, 129.78, 119.09, 114.95, 55.60, 52.48, 52.32, 30.82, 28.51. HRMS (ESI^+): calcd. for m/z $[C_{15}H_{18}N_2O_3+Na]^+$ 297.1215 found to be 297.1224.



4ad

2-(2-(4-fluorophenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ad)

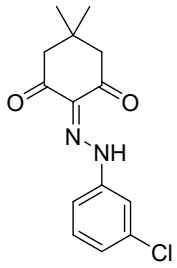
The diazenyl product was synthesized according to the general procedure as a yellow solid in 87% (80%)yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.46 (bs, 1H), 7.55 – 7.50 (m, 1H), 7.14 – 7.07 (m, 1H), 2.60 (s, 4H), 1.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.12, 193.37, 162.68, 160.22, 137.33, 130.24, 119.11, 119.03, 116.75, 116.73, 116.52, 52.53, 52.43, 30.75, 28.48. HRMS (ESI^+): calcd. for m/z $[C_{14}H_{15}FN_2O_2+Na]^+$ 285.1015 found to be 285.1027.



4ae

2-(2-(4-chlorophenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ae)

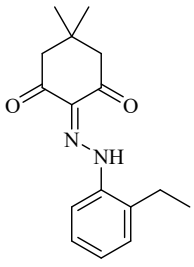
The diazenyl product was synthesized according to the general procedure as a yellow solid in 89% (85%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.28 (bs, 1H), 7.43 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 2.54 (s, 4H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 197.31, 193.23, 139.71, 132.47, 130.48, 129.80, 118.57, 52.60, 52.56, 30.72, 28.50. HRMS (ESI^+): calcd. for m/z $[C_{14}H_{15}ClN_2O_2+Na]^+$ 301.0720 found to be 301.0784.



4af

2-(2-(3-chlorophenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4af)

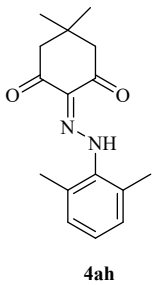
The diazenyl product was synthesized according to the general procedure as a yellow solid in 90% (83%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.25 (bs, 1H), 7.62 (t, *J* = 2.0 Hz, 1H), 7.39 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.21 (dt, *J* = 7.6, 1.6 Hz, 1H), 2.63 (s, 4H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.45, 193.27, 142.28, 135.76, 130.67, 130.61, 126.92, 117.35, 115.64, 52.62, 52.60, 30.71, 28.50. HRMS (ESI^+): calcd. for m/z $[C_{14}H_{15}ClN_2O_2+Na]^+$ 301.0720 found to be 301.0925.



4ag

2-(2-(2-ethylphenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ag)

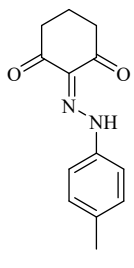
The diazenyl product was synthesized according to the general procedure as a yellow solid in 91% (86%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.77 (s, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.31 (m, 1H), 7.23 (m, 2H), 2.79 (q, *J* = 7.6 Hz, 2H), 2.63 (m, 4H), 1.34 (t, *J* = 7.5 Hz, 3H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.88, 193.38, 138.65, 132.66, 130.89, 129.14, 127.65, 127.34, 116.89, 52.58, 52.39, 30.81, 28.54, 24.00, 14.02. For m/z $[C_{16}H_{20}N_2O_2+Na]^+$ 295.1422 found to be 295.1437.



4ah

2-(2-(2,6-dimethylphenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ah)

The diazenyl product was synthesized according to the general procedure as a yellow solid in 85% (85%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 15.42 (s, 1H), 7.11 (s, 3H), 2.62 (dd, *J* = 7.7, 1.2 Hz, 4H), 2.47 (s, 6H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.47, 193.23, 137.77, 130.75, 130.65, 129.68, 127.30, 52.51, 52.39, 30.82, 28.56, 19.36. For m/z $[C_{16}H_{20}N_2O_2+Na]^+$ 295.1422 found to be 295.1437.

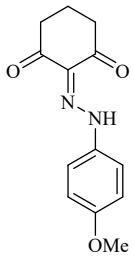


4bb

2-(2-(p-tolyl)hydrazineylidene)cyclohexane-1,3-dione (4bb)

The diazenyl product was synthesized according to the general procedure as a yellow solid in 92% (84%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.56 (bs, 1H), 7.48 – 7.43 (m, 2H), 7.21 (d, *J* = 8 Hz, 2H), 2.71 (td, *J* = 6.5, 4.1 Hz, 4H), 2.36 (s, 3H), 2.07 (p, *J* = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.38, 193.79, 138.73, 137.62, 131.06,

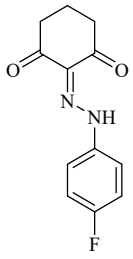
130.24, 117.58, 38.89, 38.85, 21.12, 18.76. HRMS (ESI$^+$): calcd. for m/z $[C_{13}H_{14}N_2O_2+Na]^+$ 253.0953 found to be 253.0972.



4bc

2-(2-(4-methoxyphenyl)hydrazineylidene)cyclohexane-1,3-dione (4bc)

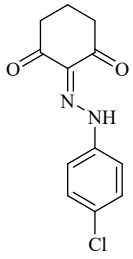
The diazenyl product was synthesized according to the general procedure as a yellow solid in 90% (85%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.74 (bs, 1H), 7.51 (td, *J* = 5.6, 2.5 Hz, 1H), 7.11 (tt, *J* = 5.4, 2.7 Hz, 1H), 6.94 (dtd, *J* = 11.5, 5.7, 2.6 Hz, 2H), 3.82 (m, 3H), 2.63 (m, 4H), 2.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.09, 159.27, 131.87, 119.17, 114.99, 114.87, 77.32, 77.00, 76.68, 55.60, 55.27, 38.79, 38.70, 20.44, 18.85. HRMS (ESI$^+$): calcd. for m/z $[C_{13}H_{14}N_2O_3+Na]^+$ 269.0902 found to be 269.1457



4bd

2-(2-(4-fluorophenyl)hydrazineylidene)cyclohexane-1,3-dione (4bd)

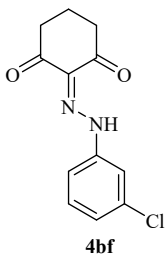
The diazenyl product was synthesized according to the general procedure as a yellow solid in 91% (90%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.50 (bs, 1H), 7.56 – 7.51 (m, 2H), 7.14 – 7.07 (m, 2H), 2.71 (m, 4H), 2.08 (p, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.66, 193.79, 162.75, 160.29, 137.33, 131.31, 119.19, 119.11, 116.78, 116.55, 38.89, 38.86, 18.64. HRMS (ESI$^+$): calcd. for m/z $[C_{12}H_{11}FN_2O_2+Na]^+$ 257.0702 found to be 257.0726.



4be

2-(2-(4-chlorophenyl)hydrazineylidene)cyclohexane-1,3-dione (4be)

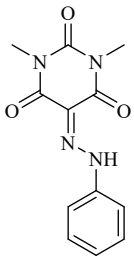
The diazenyl product was synthesized according to the general procedure as a yellow solid in 90% (87%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.41 (bs, 1H), 7.57– 7.49 (m, 2H), 7.42 – 7.32 (m, 2H), 2.72 (m, 4H), 2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.82, 193.78, 139.70, 130.38, 129.83, 129.66, 118.65, 38.94, 29.67, 18.57. HRMS (ESI$^+$): calcd. for m/z $[C_{12}H_{11}ClN_2O_2+Na]^+$ 273.0407 found to be 273.0529.



4bf

2-(2-(3-chlorophenyl)hydrazineylidene)cyclohexane-1,3-dione (4bf)

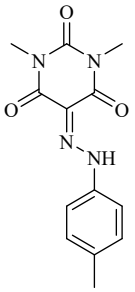
The diazenyl product was synthesized according to the general procedure as a yellow solid in 88% (89%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.55 (s, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.37(m, 2H), 7.25 (m, 1H), 2.75 (q, *J* = 6.0 Hz, 4H), 2.11 (p, *J* = 6.5 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 197.95, 193.60, 142.27, 135.78, 131.77, 130.63, 127.00, 117.42, 115.69, 39.04, 38.98, 18.50. HRMS (ESI$^+$): calcd. for m/z $[C_{12}H_{11}ClN_2O_2+Na]^+$ 273.0407 found to be 273.0471.



4ca

1,3-dimethyl-5-(2-phenylhydrazineylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (4ca)

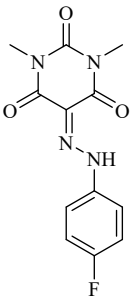
The diazenyl product was synthesized according to the general procedure as a yellow solid in 94% (87%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.66 (bs, 1H), 7.59 (dd, J = 8.5, 1.4 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.34 – 7.25 (m, 1H), 3.45 (s, 3H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.16, 159.15, 150.72, 140.75, 129.75, 127.26, 117.27, 116.33, 28.58, 27.49. HRMS (ESI$^+$): calcd. for m/z $[C_{12}H_{12}N_4O_3+Na]^+$ 283.0807 found to be 283.0815.



4cb

1,3-dimethyl-5-(2-(p-tolyl)hydrazineylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (4cb)

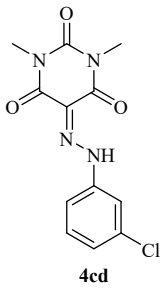
The diazenyl product was synthesized according to the general procedure as a yellow solid in 92% (89%) yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 14.69 (bs, 1H), 7.48 – 7.44 (m, 2H), 7.26 – 7.22 (m, 2H), 3.43 (s, 3H), 3.39 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.19, 159.25, 150.75, 138.47, 137.58, 130.31, 117.22, 115.85, 28.53, 27.43, 21.13. HRMS (ESI$^+$): calcd. for m/z $[C_{13}H_{14}N_4O_3+Na]^+$ 297.0964 found to be 297.0816.



4cc

5-(2-(4-fluorophenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cc)

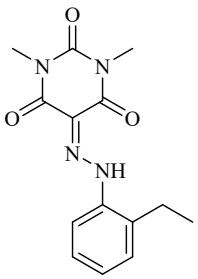
The diazenyl product was synthesized according to the general procedure as a yellow solid in 90% (84%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.66 (bs, 1H), 7.56 – 7.51 (m, 2H), 7.17 – 7.11 (m, 2H), 3.42 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.67, 161.18, 160.20, 159.07, 150.64, 137.06, 118.85, 118.77, 116.87, 116.64, 116.32, 28.58, 27.50. HRMS (ESI$^+$): calcd. for m/z $[C_{12}H_{11}FN_4O_3+Na]^+$ 301.0713 found to be 301.0572.



4cd

5-(2-(3-chlorophenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cd)

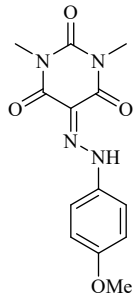
The diazenyl product was synthesized according to the general procedure as a yellow solid in 90% (85%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.49 (s, 1H), 7.60 (t, *J* = 2.0 Hz, 1H), 7.42 – 7.30 (m, 2H), 7.22 (dt, *J* = 7.3, 1.8 Hz, 1H), 3.42 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.04, 158.78, 150.52, 141.90, 135.86, 130.71, 126.95, 117.12, 117.05, 115.35, 28.62, 27.56. HRMS (ESI$^+$): calcd. for m/z $[C_{12}H_{11}ClN_4O_3+Na]^+$ 317.0417 found to be 317.0715.



4ce

5-(2-(2-ethylphenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4ce)

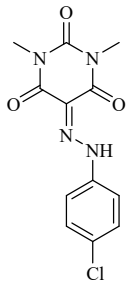
The diazenyl product was synthesized according to the general procedure as a yellow solid in 89% (91%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.49 (s, 1H), δ 7.33 (ddd, *J* = 8.6, 6.8, 2.1 Hz, 0H), 7.24 (dtd, *J* = 9.0, 7.7, 6.0 Hz, 1H), 3.43 (s, 1H), 3.40 (s, 1H), 2.80 (q, *J* = 7.6 Hz, 1H), 1.35 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.30, 159.19, 150.72, 138.37, 132.34, 129.18, 127.70, 127.26, 116.84, 116.66, 28.53, 27.50, 23.91, 14.02. HRMS (ESI^+): calcd. for m/z $[C_{14}H_{16}N_4O_3+Na]^+$ 311.1120 found to be 311.1128.



4cf

5-(2-(4-methoxyphenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cf)

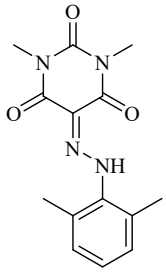
The diazenyl product was synthesized according to the general procedure as a yellow solid in 95% (83%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.81 (bs, 1H), 7.54 – 7.51 (m, 2H), 6.99 – 6.95 (m, 2H), 3.86 (s, 3H), 3.43 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.29, 159.33, 159.13, 150.80, 134.33, 118.78, 115.50, 115.02, 55.63, 28.48, 27.38. HRMS (ESI^+): calcd. for m/z $[C_{13}H_{14}N_4O_4+Na]^+$ 313.0913 found to be 313.0957.



4cg

5-(2-(4-chlorophenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cg)

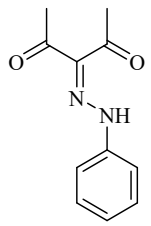
The diazenyl product was synthesized according to the general procedure as a yellow solid in 92% (85%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.53 (bs, 1H), 7.43 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 3.35 (s, 3H), 3.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.15, 158.94, 139.39, 132.59, 129.91, 118.33, 116.72, 29.68, 27.53. HRMS (ESI^+): calcd. for m/z $[C_{12}H_{11}ClN_4O_3+Na]^+$ 317.0417 found to be 317.0647.



4ch

5-(2-(2,6-dimethylphenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4ch)

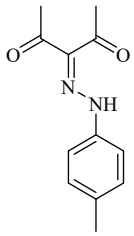
The diazenyl product was synthesized according to the general procedure as a yellow solid in 87% (91%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.61 (s, 1H), 7.11 (s, 3H), 3.41 (s, 3H), 3.39 (s, 3H), 2.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.07, 159.27, 150.83, 137.55, 130.41, 129.78, 127.37, 116.39, 28.43, 27.36, 19.30. HRMS (ESI^+): calcd. for m/z $[C_{14}H_{16}N_4O_3+Na]^+$ 311.1120 found to be 311.1128.



4da

3-(2-phenylhydrazineylidene)pentane-2,4-dione (4da)

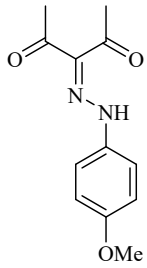
The diazenyl product was synthesized according to the general procedure as a yellow solid in 86% (78%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.71 (bs, 1H), 7.40 (d, *J* = 4.3 Hz, 4H), 7.19 (p, *J* = 4.3 Hz, 1H), 2.59 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.88, 197.03, 141.54, 133.21, 129.64, 125.87, 116.24, 31.63, 26.59. HRMS (ESI^+): calcd. for m/z $[C_{11}H_{12}N_2O_2+Na]^+$ 227.0796 found to be 227.0746.



4db

3-(2-(p-tolyl)hydrazineylidene)pentane-2,4-dione (4db)

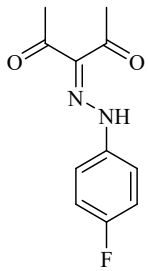
The diazenyl product was synthesized according to the general procedure as a yellow solid in 84% (76%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.83 (bs, 1H), 7.35 – 7.31 (m, 2H), 7.23 (d, *J* = 8 Hz, 2H), 2.62 (s, 3H), 2.51 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.78, 197.10, 139.27, 135.97, 132.95, 130.22, 129.62, 125.76, 116.27, 31.59, 26.61, 21.00. HRMS (ESI^+): calcd. for m/z $[C_{12}H_{14}N_2O_2+Na]^+$ 241.0953 found to be 241.0981.



4dc

3-(2-(4-methoxyphenyl)hydrazineylidene)pentane-2,4-dione (4dc)

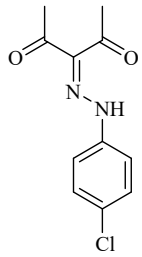
The diazenyl product was synthesized according to the general procedure as a yellow solid in 82% (86%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.95 (s, 1H), 7.35 (dd, *J* = 9.1, 1.2 Hz, 1H), 6.94 (m, 1H), 3.83 (s, 3H), 2.59 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.54, 196.92, 158.04, 135.10, 132.69, 117.63, 114.92, 55.57, 31.50, 26.57. HRMS (ESI^+): calcd. for m/z $[C_{12}H_{14}N_2O_3+Na]^+$ 257.0902 found to be 257.0947.



4de

3-(2-(4-fluorophenyl)hydrazineylidene)pentane-2,4-dione (4dd)

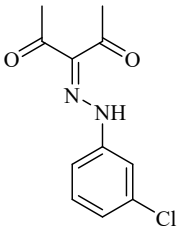
The diazenyl product was synthesized according to the general procedure as a yellow solid in 88% (84%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.80 (bs, 1H), 7.40 – 7.36 (m, 2H), 7.15 – 7.08 (m, 2H), 2.60 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.99, 196.90, 161.82, 159.38, 137.85, 133.24, 117.69, 117.61, 116.68, 116.45, 31.59, 26.56. HRMS (ESI^+): calcd. for m/z $[C_{11}H_{11}FN_2O_2+Na]^+$ 245.0702 found to be 245.0862.



4de

3-(2-(4-chlorophenyl)hydrazineylidene)pentane-2,4-dione (4de)

The diazenyl product was synthesized according to the general procedure as a yellow solid in 86% (80%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.67 (bs, 1H), 7.34 (m, 4H), 2.59 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.10, 196.84, 140.16, 133.41, 130.93, 129.73, 117.30, 31.67, 26.59. HRMS (ESI$^+$): calcd. for m/z $[C_{11}H_{11}ClN_2O_2+Na]^+$ 261.0407 found to be 261.0417.



4df

3-(2-(3-chlorophenyl)hydrazineylidene)pentane-2,4-dione (4df)

The diazenyl product was synthesized according to the general procedure as a yellow solid in 85% (83%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.58 (s, 1H), 7.43 (q, J = 2.1 Hz, 1H), 7.31 (tt, J = 7.7, 3.0 Hz, 1H), 7.22 (m, 1H), 7.15 (m, 1H), 2.61 (d, J = 1.9 Hz, 3H), 2.49 (d, J = 2.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.21, 196.92, 142.76, 135.67, 133.70, 130.65, 125.60, 116.10, 114.46, 31.68, 26.62. HRMS (ESI$^+$): calcd. for m/z $[C_{11}H_{11}ClN_2O_2+Na]^+$ 261.0407 found to be 261.0417.

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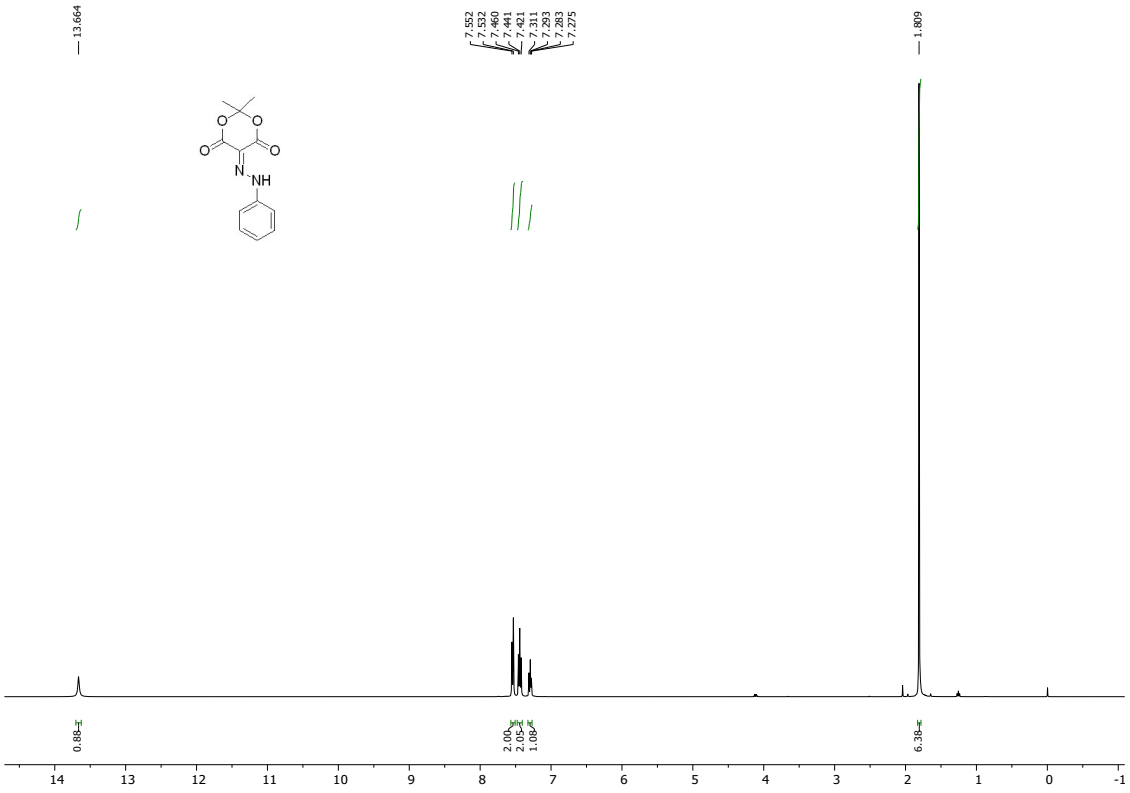
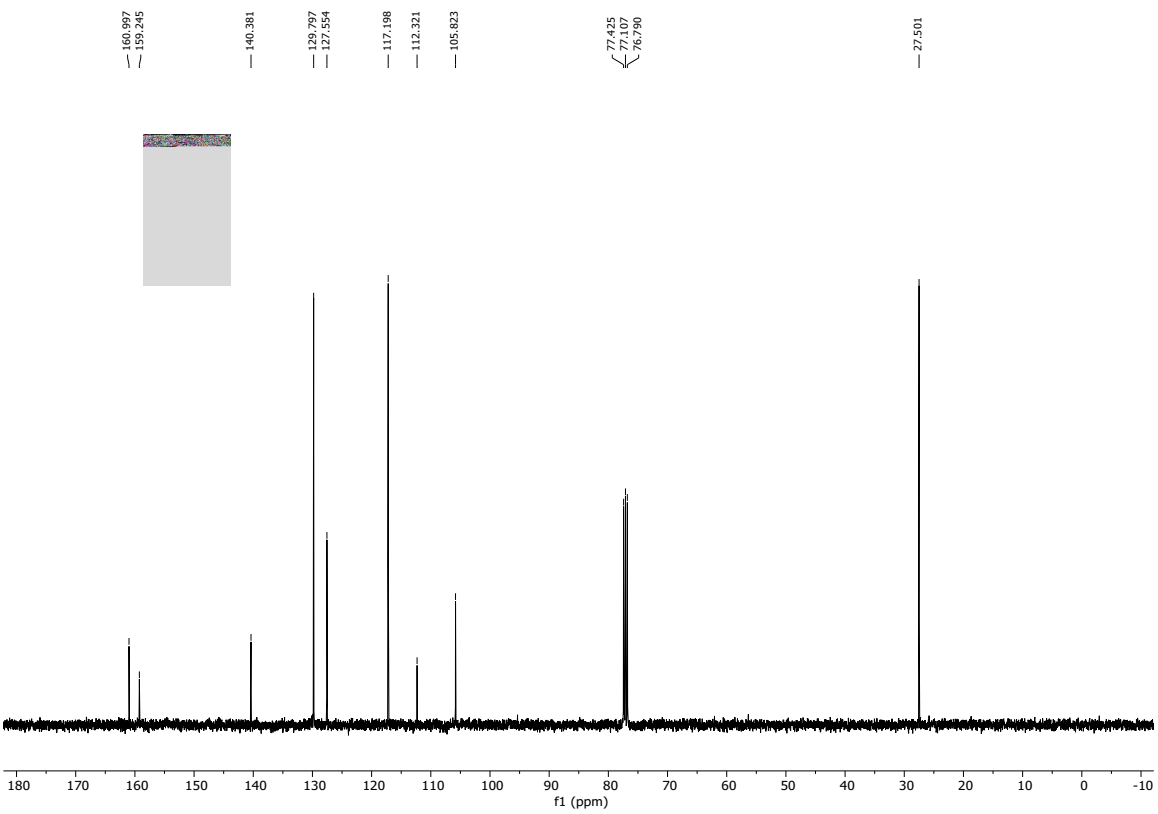
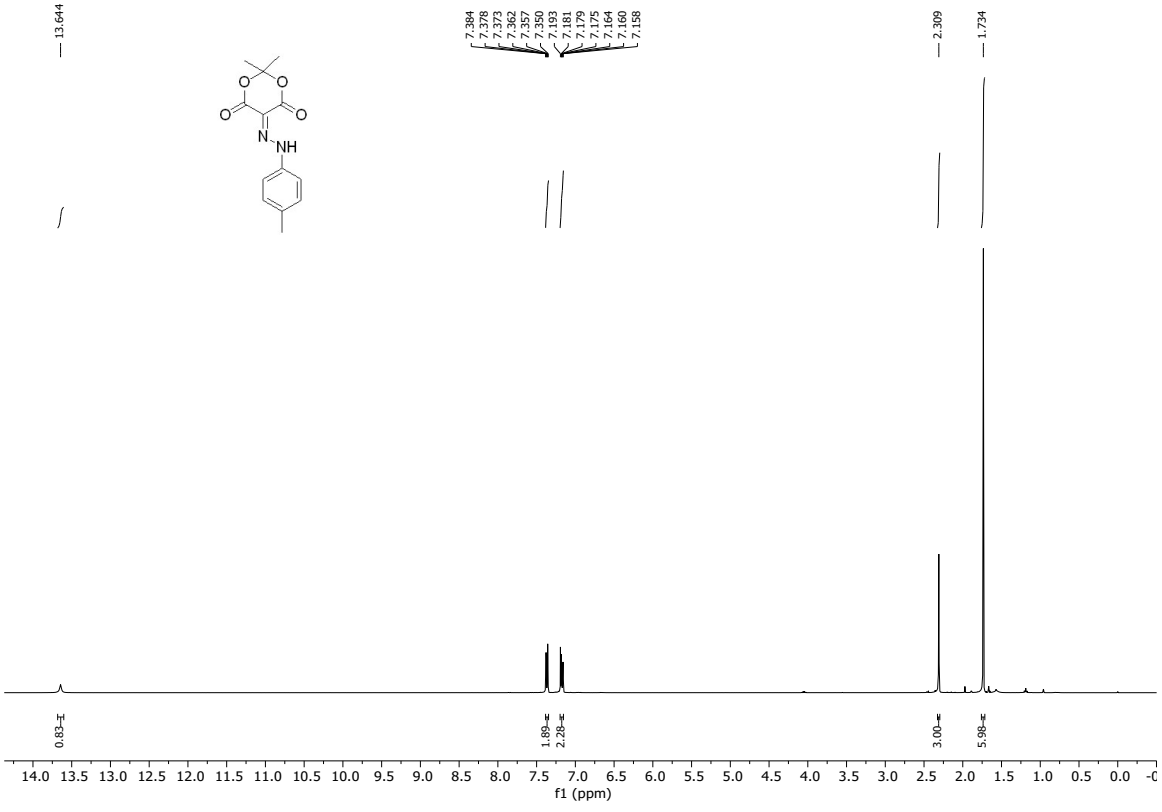
Spectra

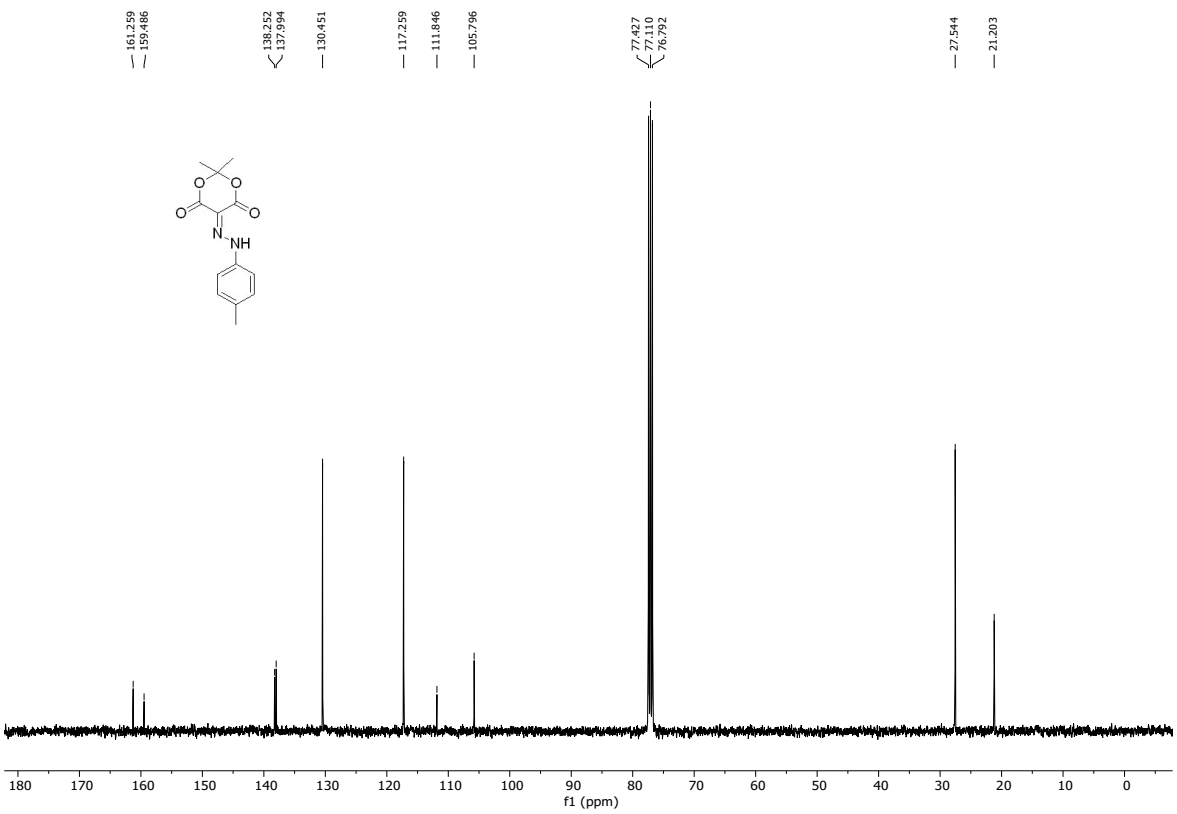
2,2-dimethyl-5-(2-phenylhydrazineylidene)-1,3-dioxane-4,6-dione (3aa)



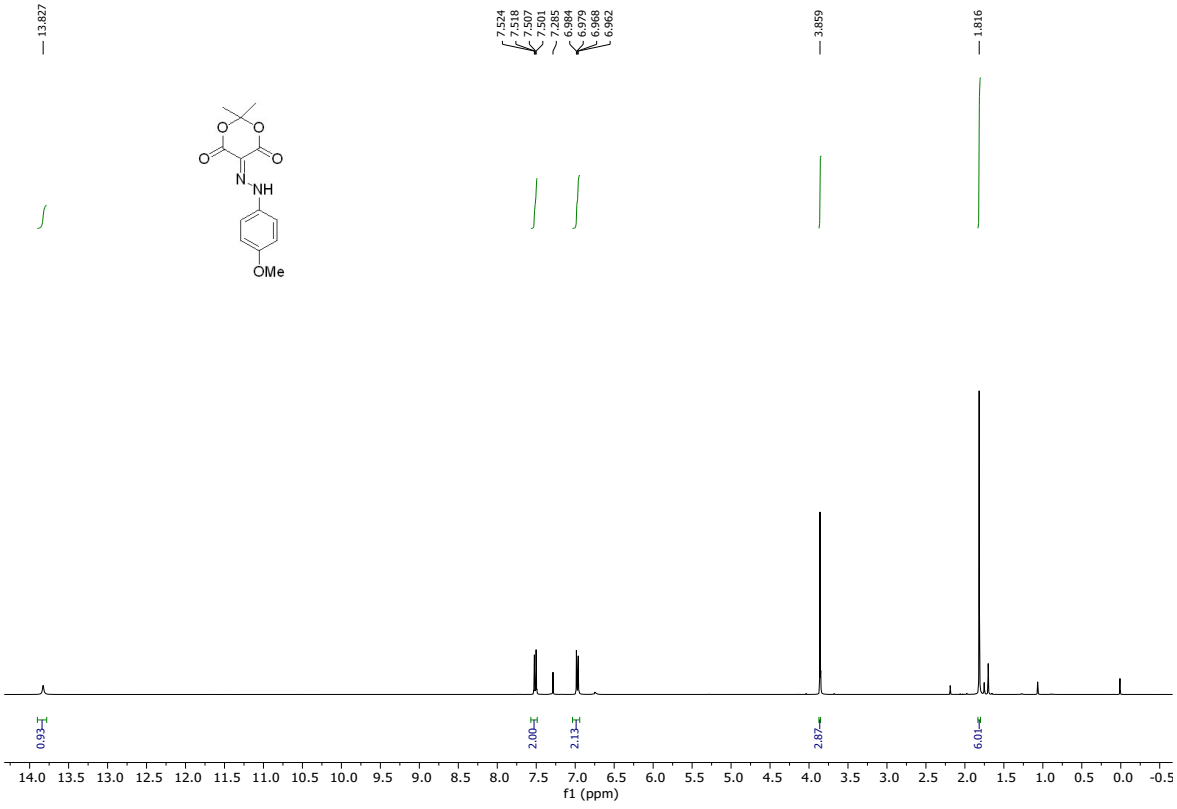


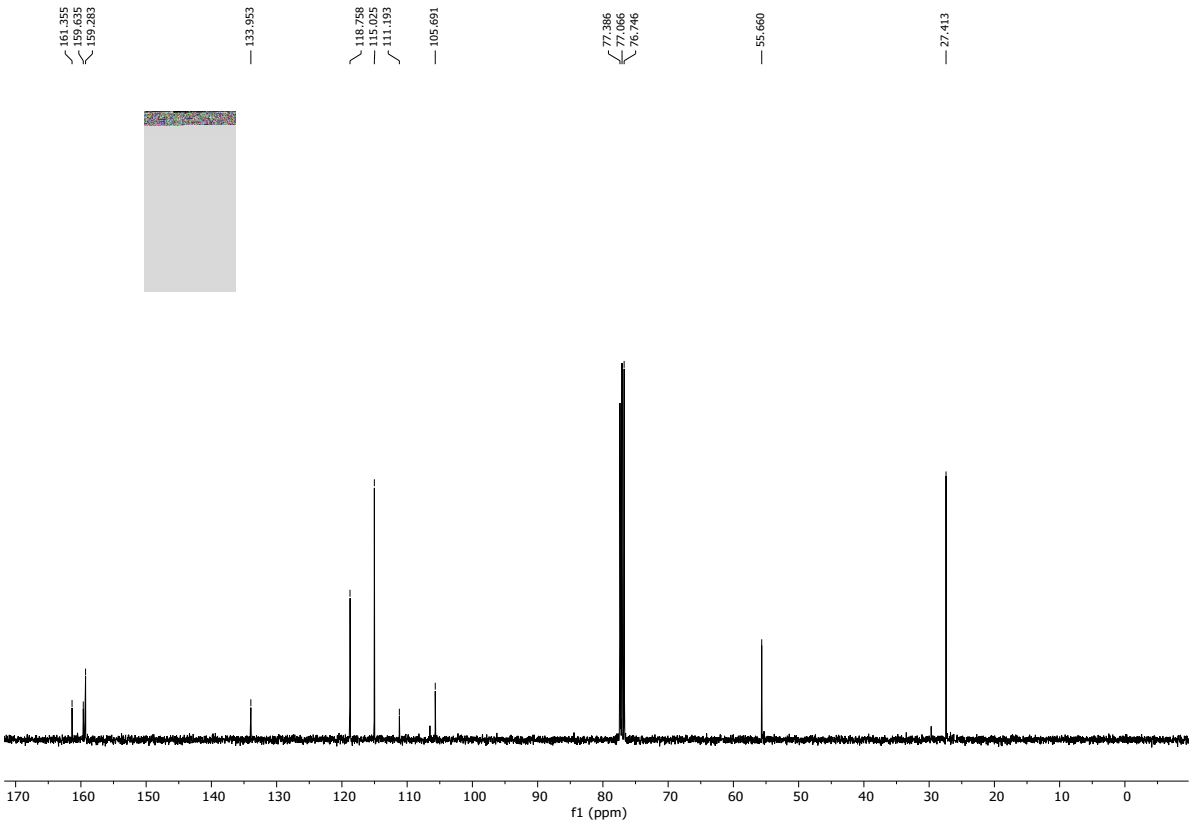
2,2-dimethyl-5-(2-(p-tolyl)hydrazineylidene)-1,3-dioxane-4,6-dione (3ab)



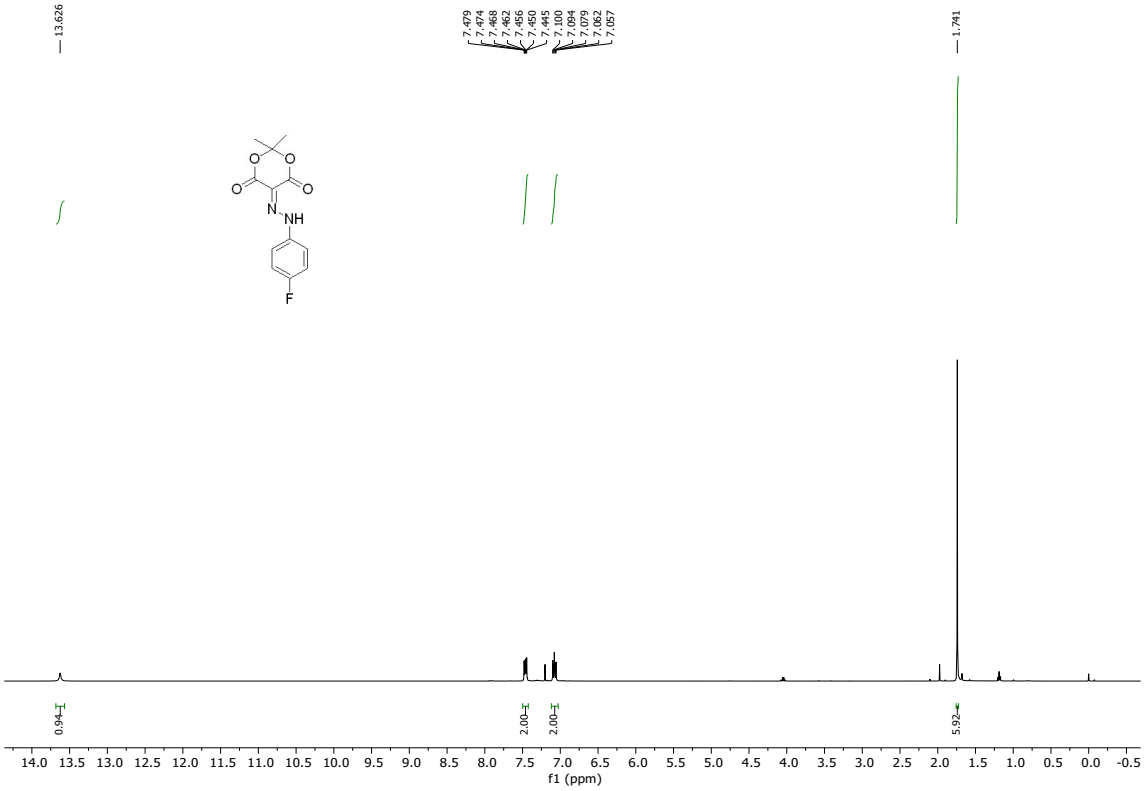


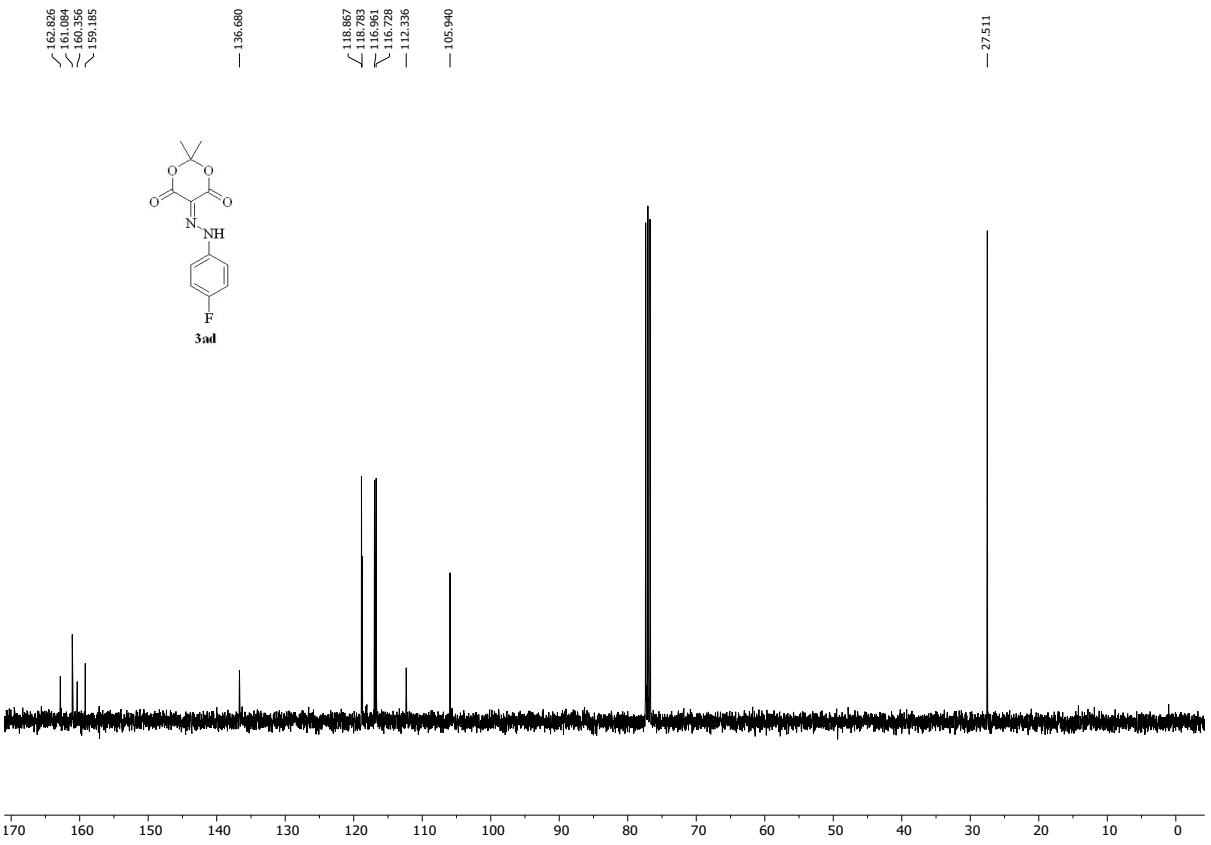
5-(2-(4-methoxyphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ac)



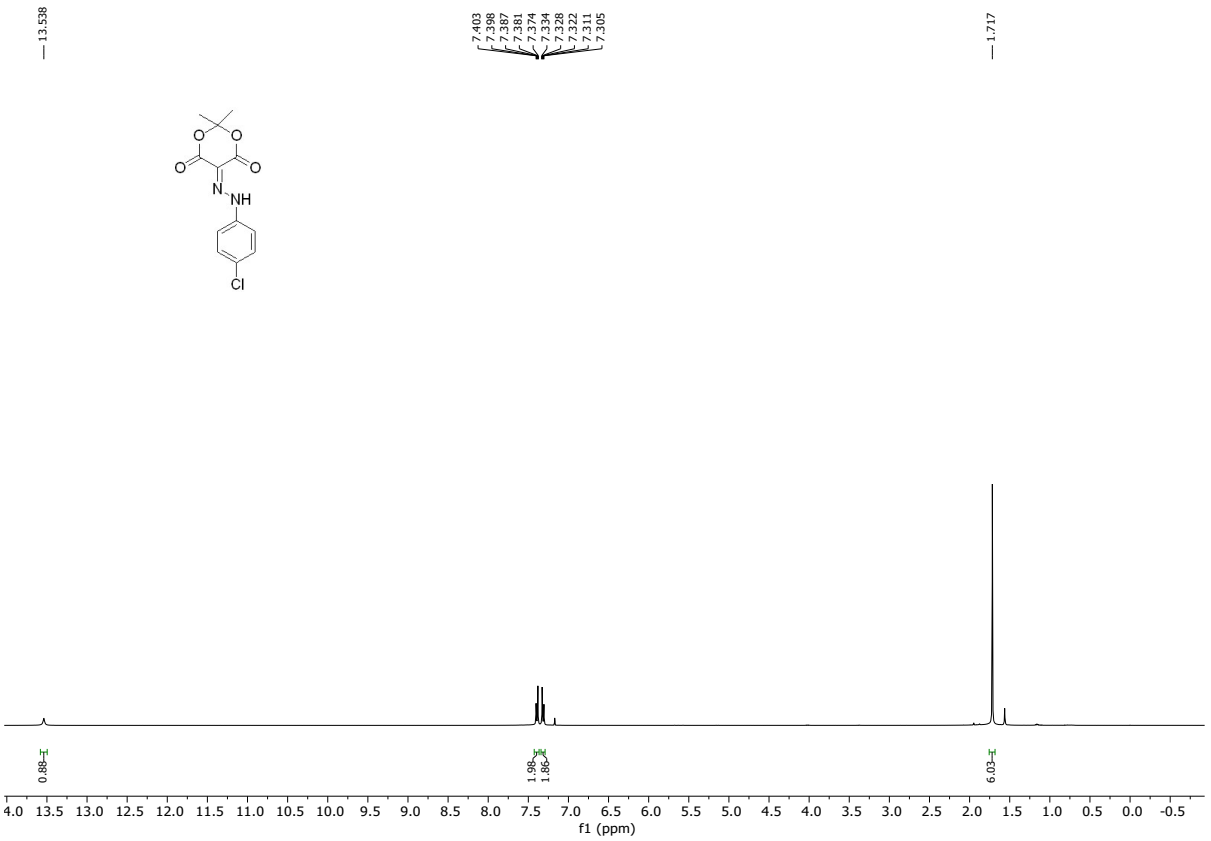


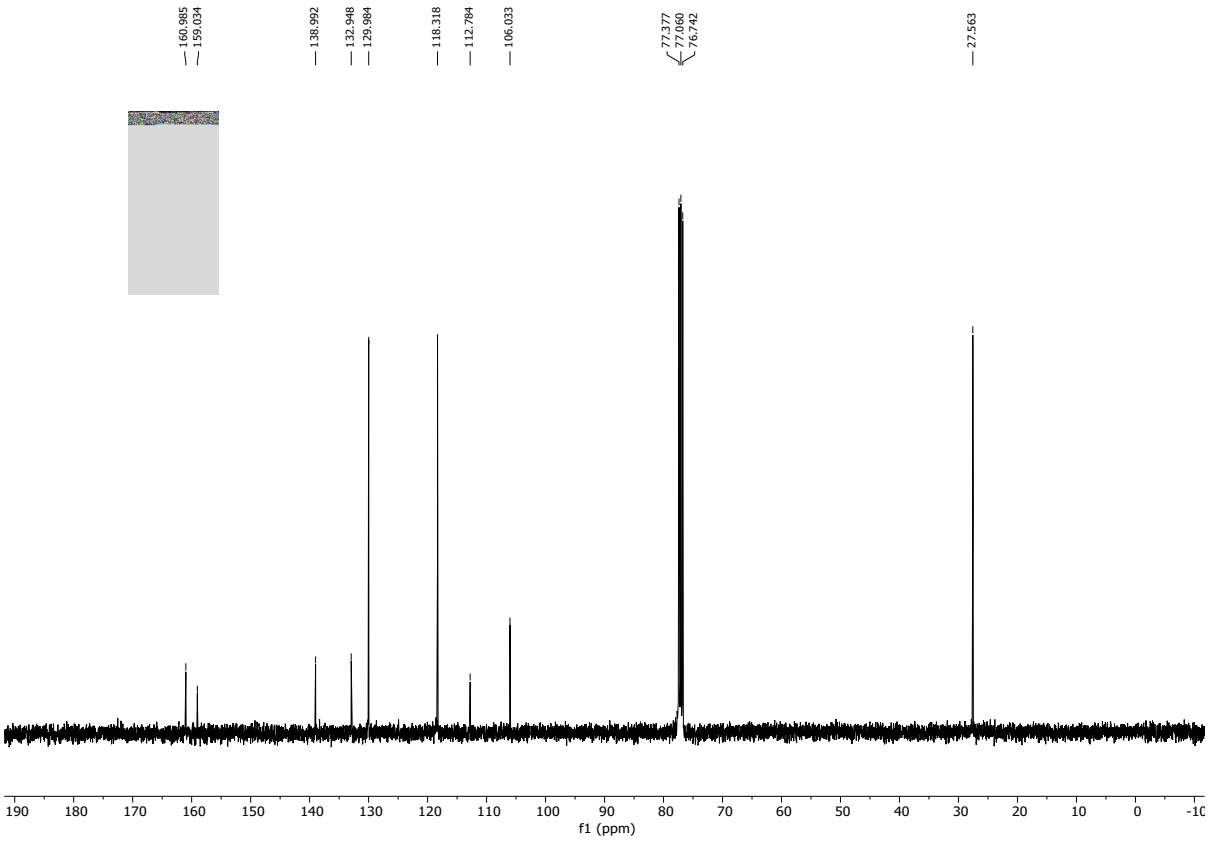
5-(2-(4-fluorophenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ad)



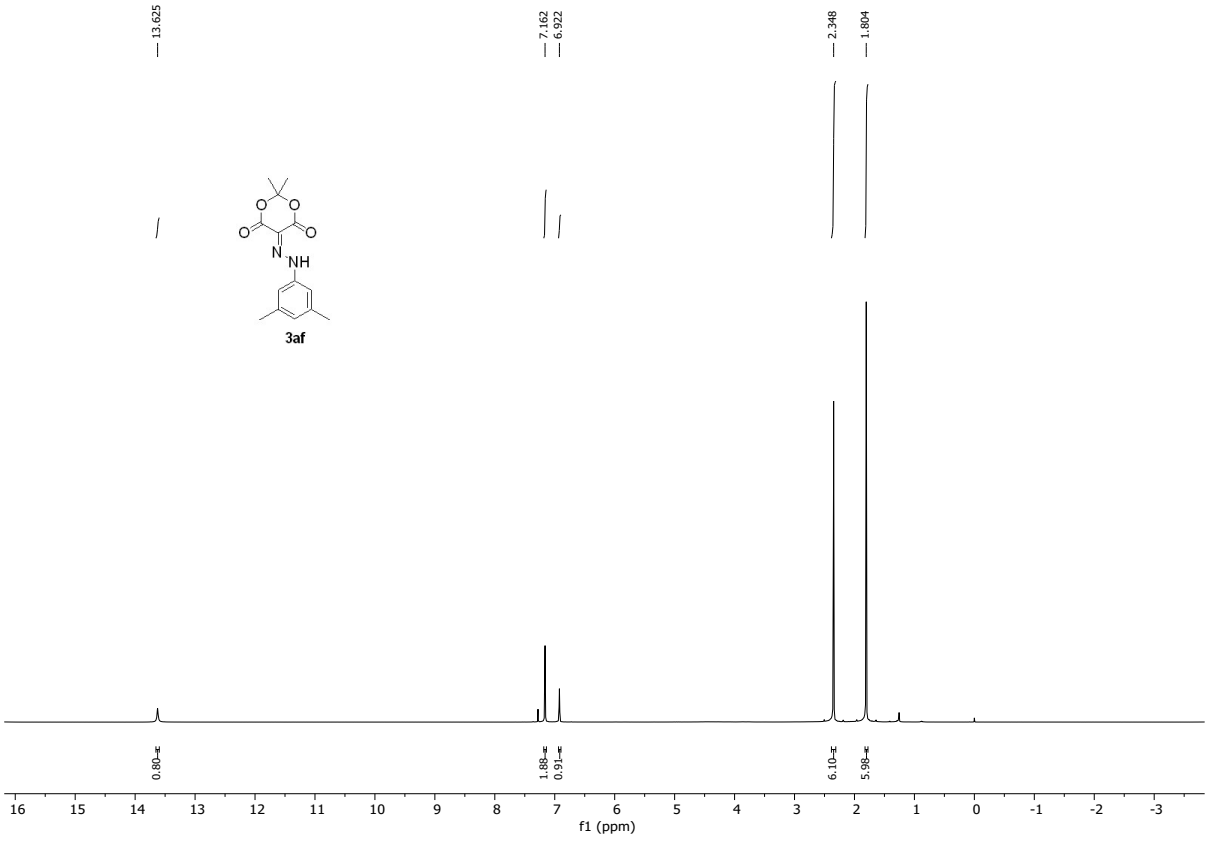


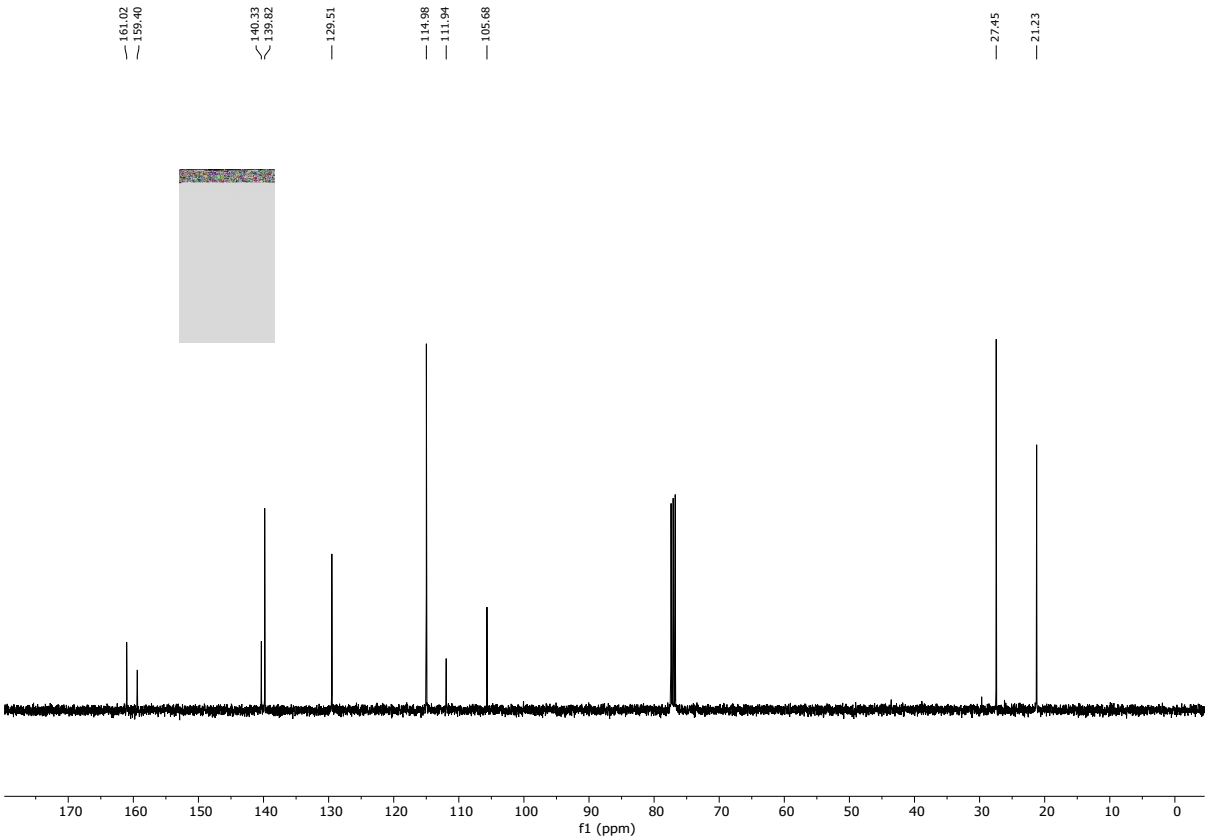
5-(2-(4-chlorophenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ae)



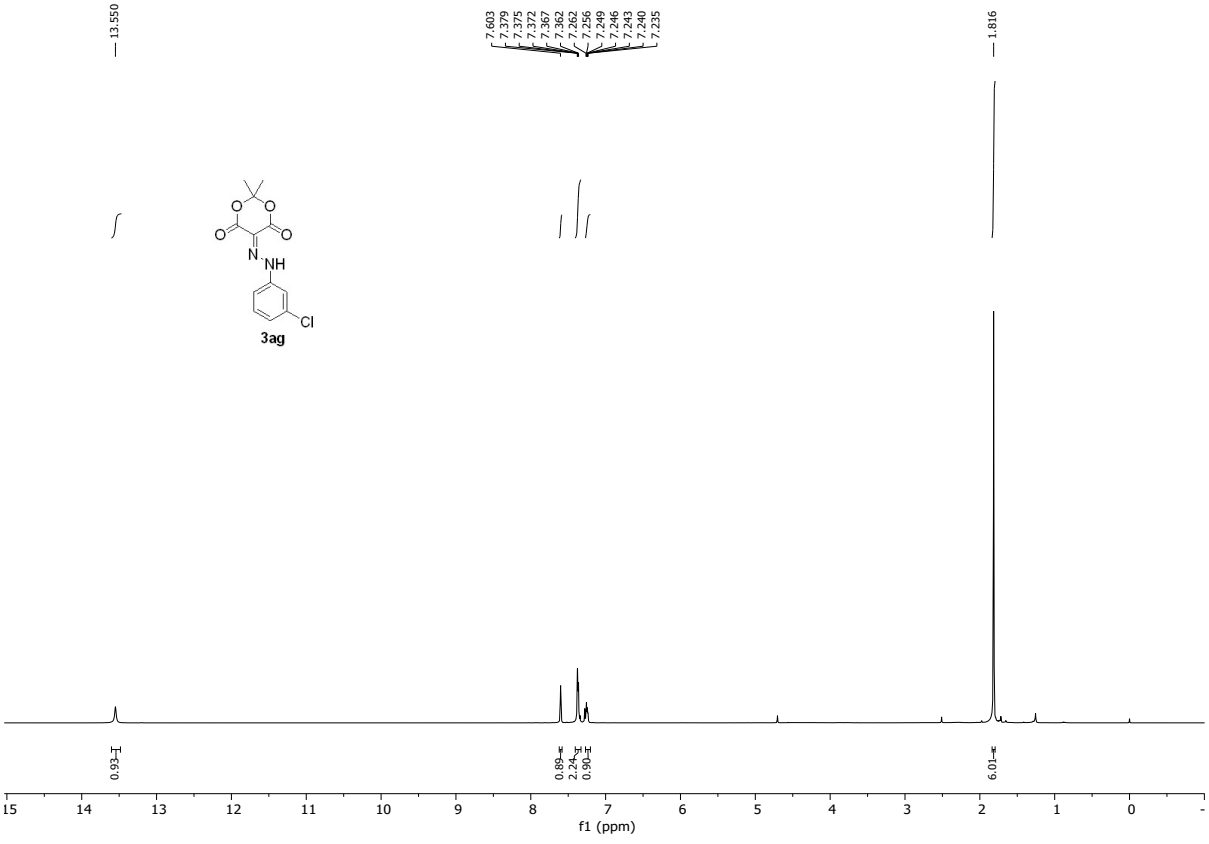


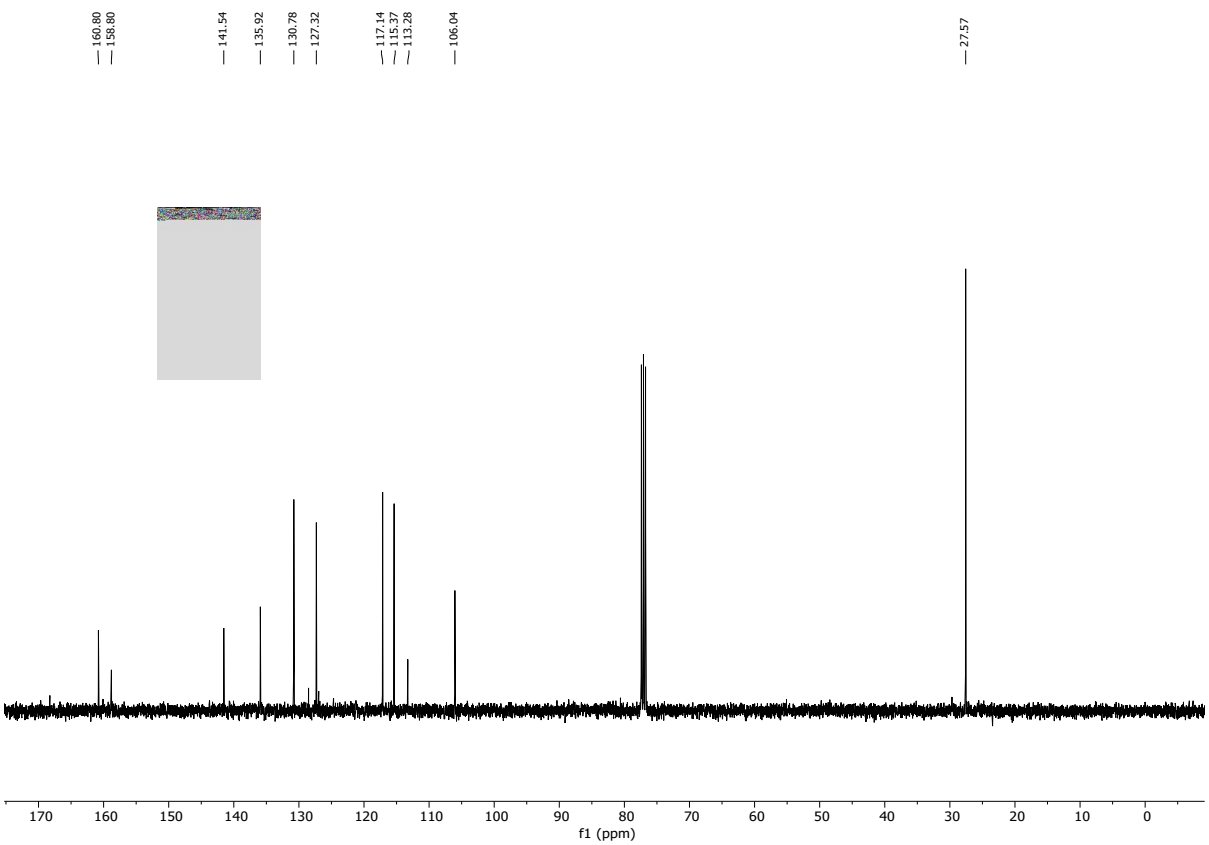
5-(2-(3,5-dimethylphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3af)



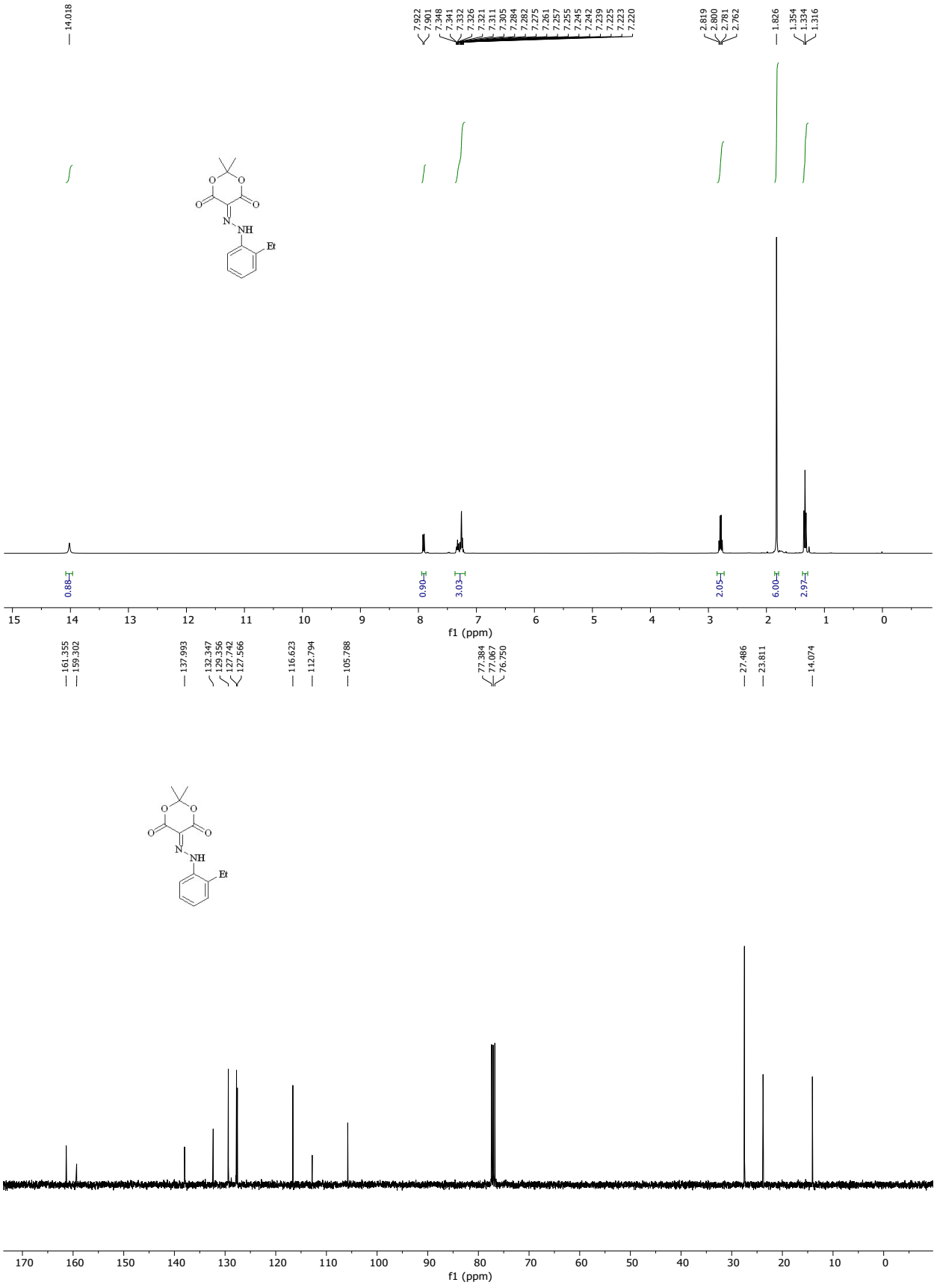


5-(2-(3-chlorophenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ag)

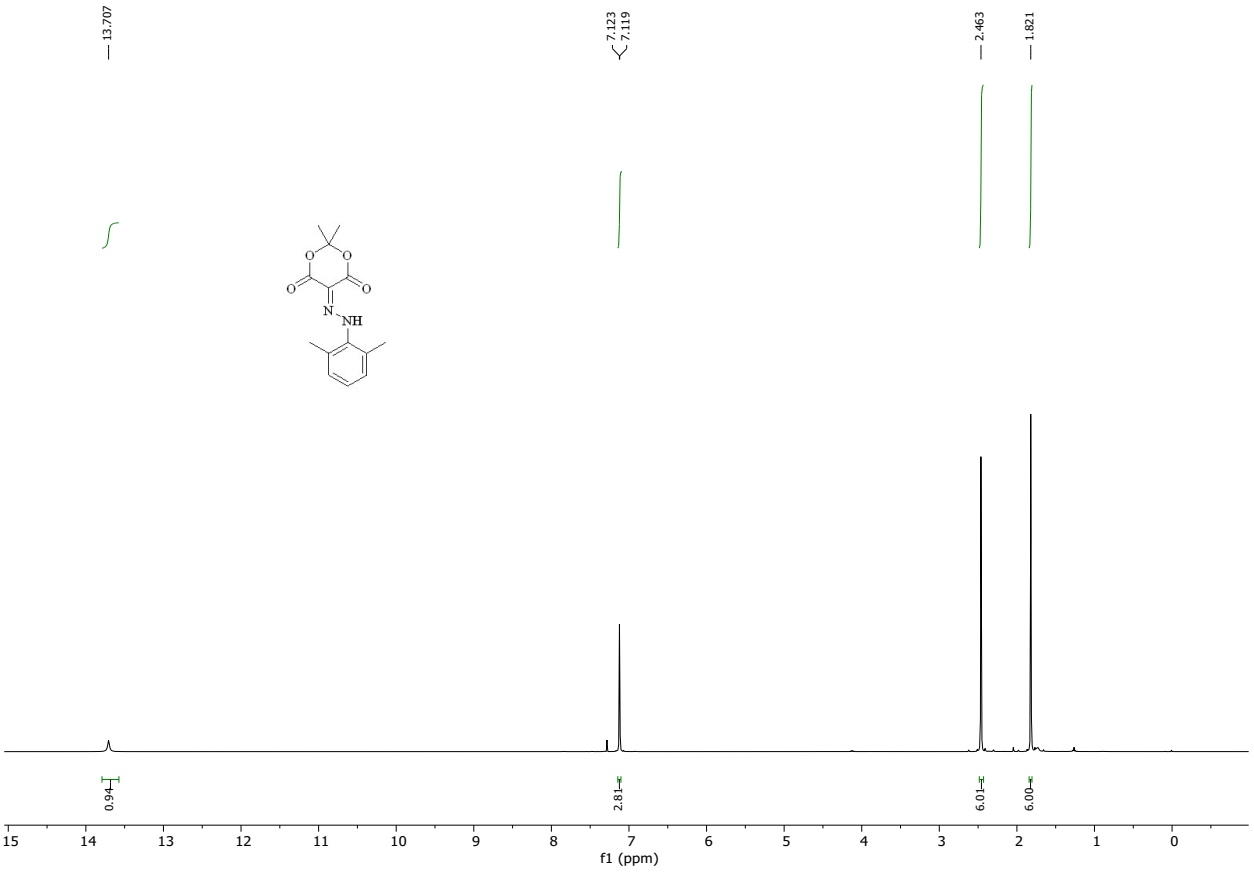


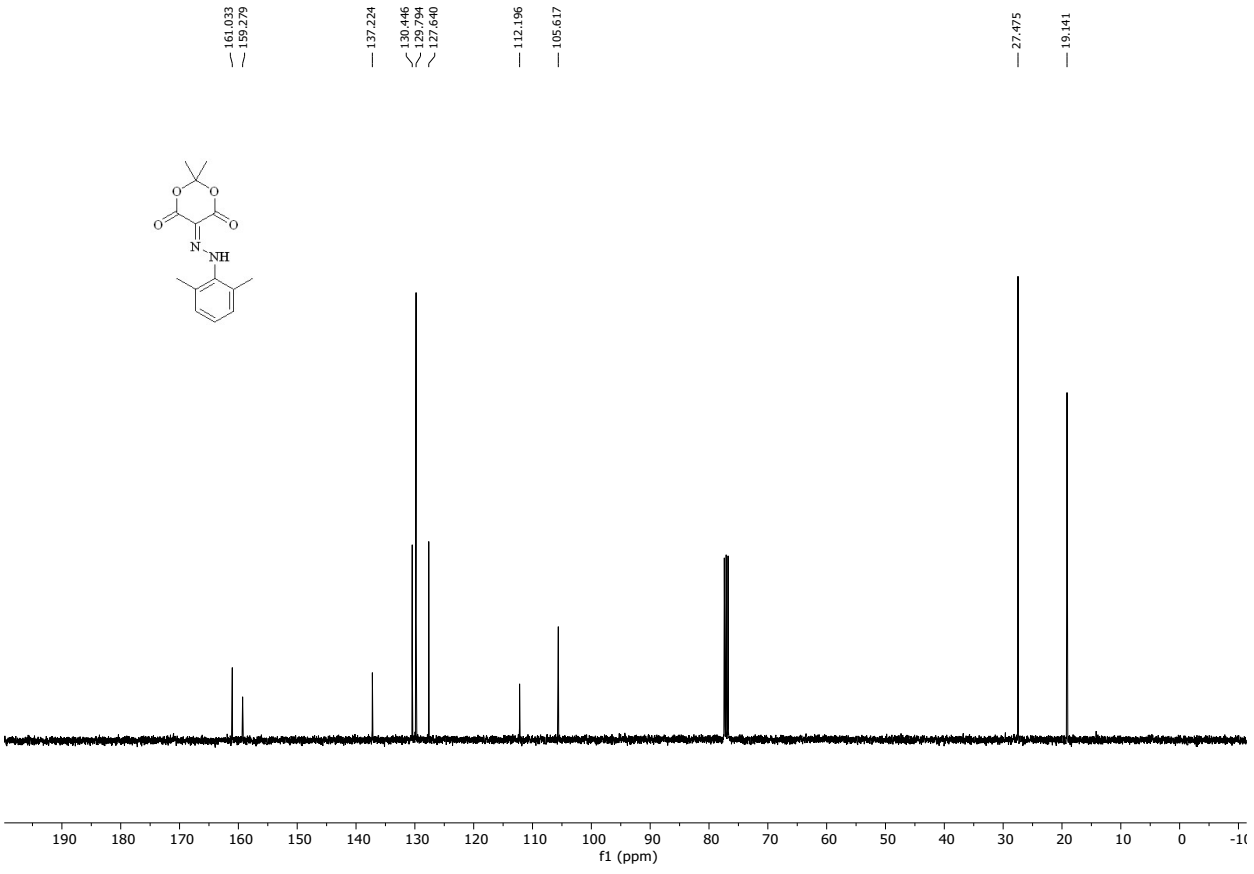


5-(2-(2-ethylphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ah)

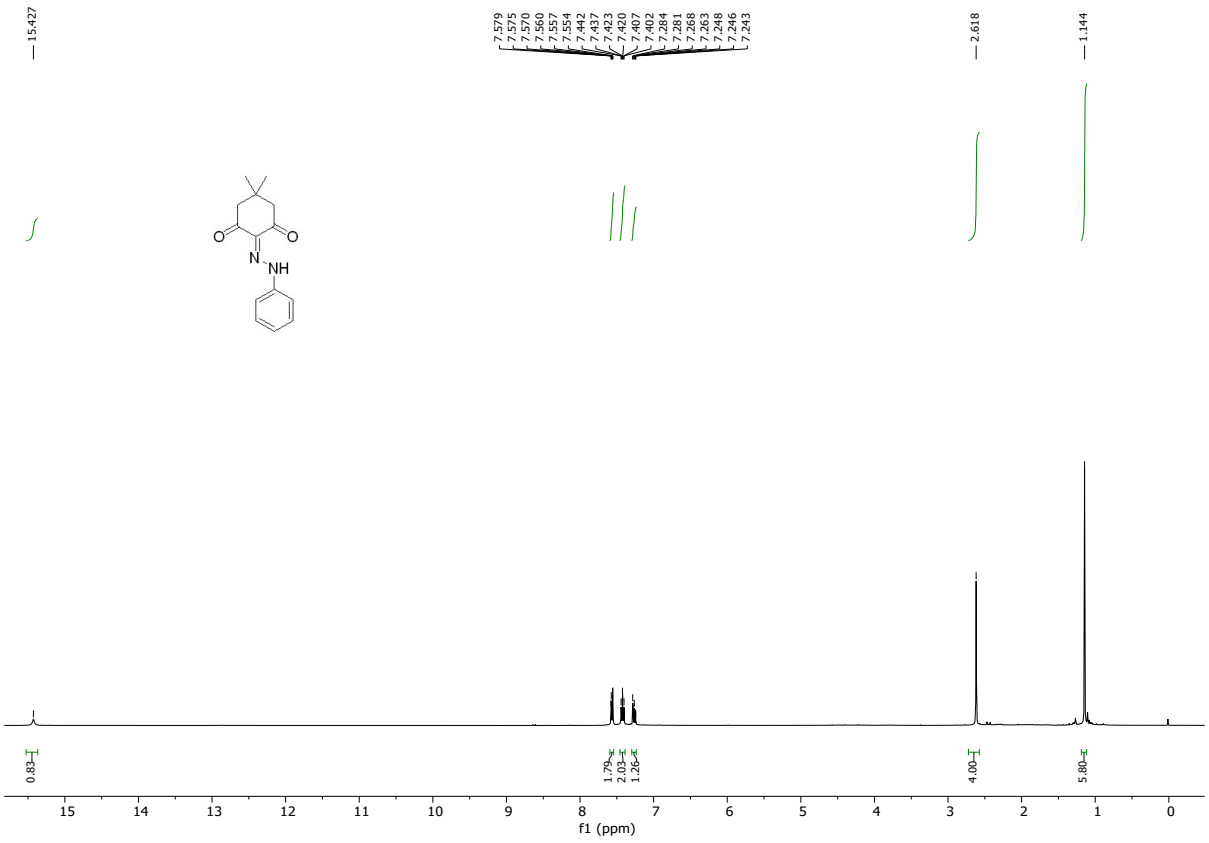


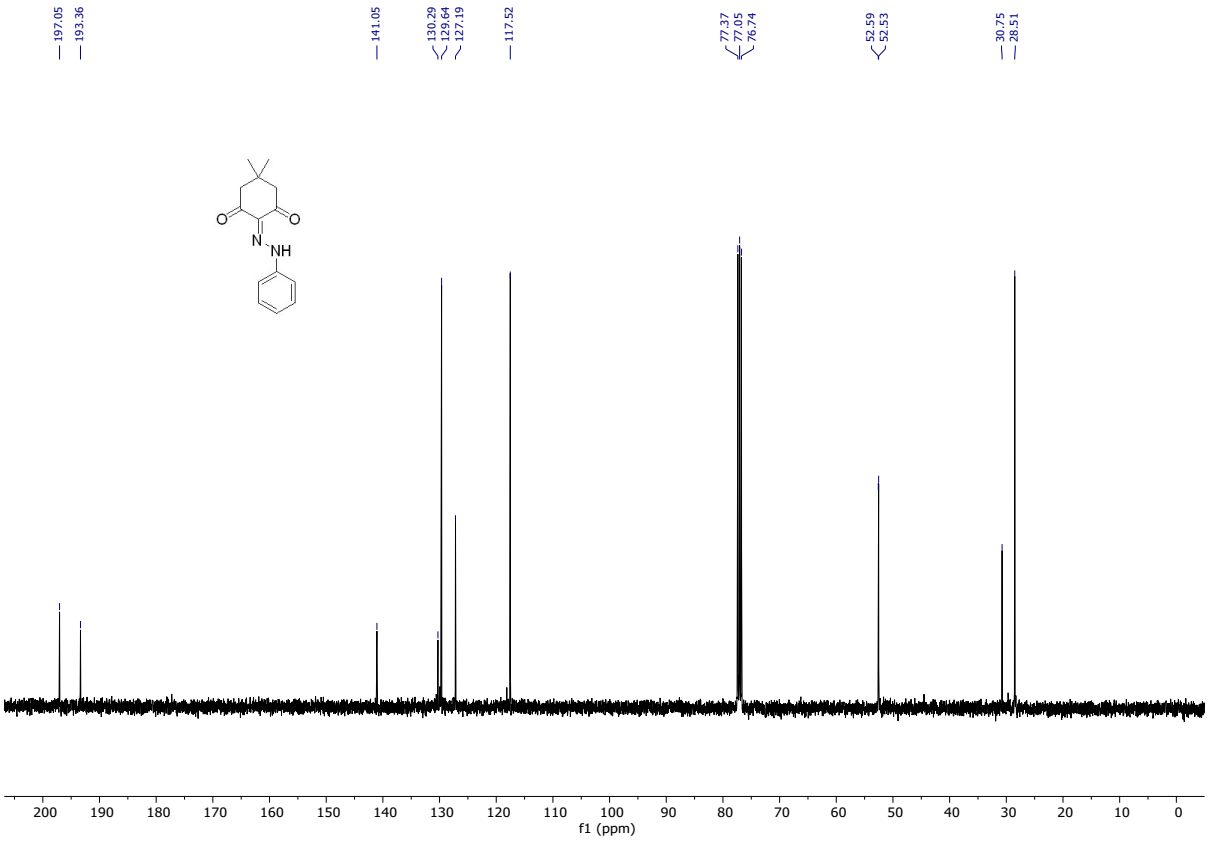
5-(2-(2,6-dimethylphenyl)hydrazineylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ai)



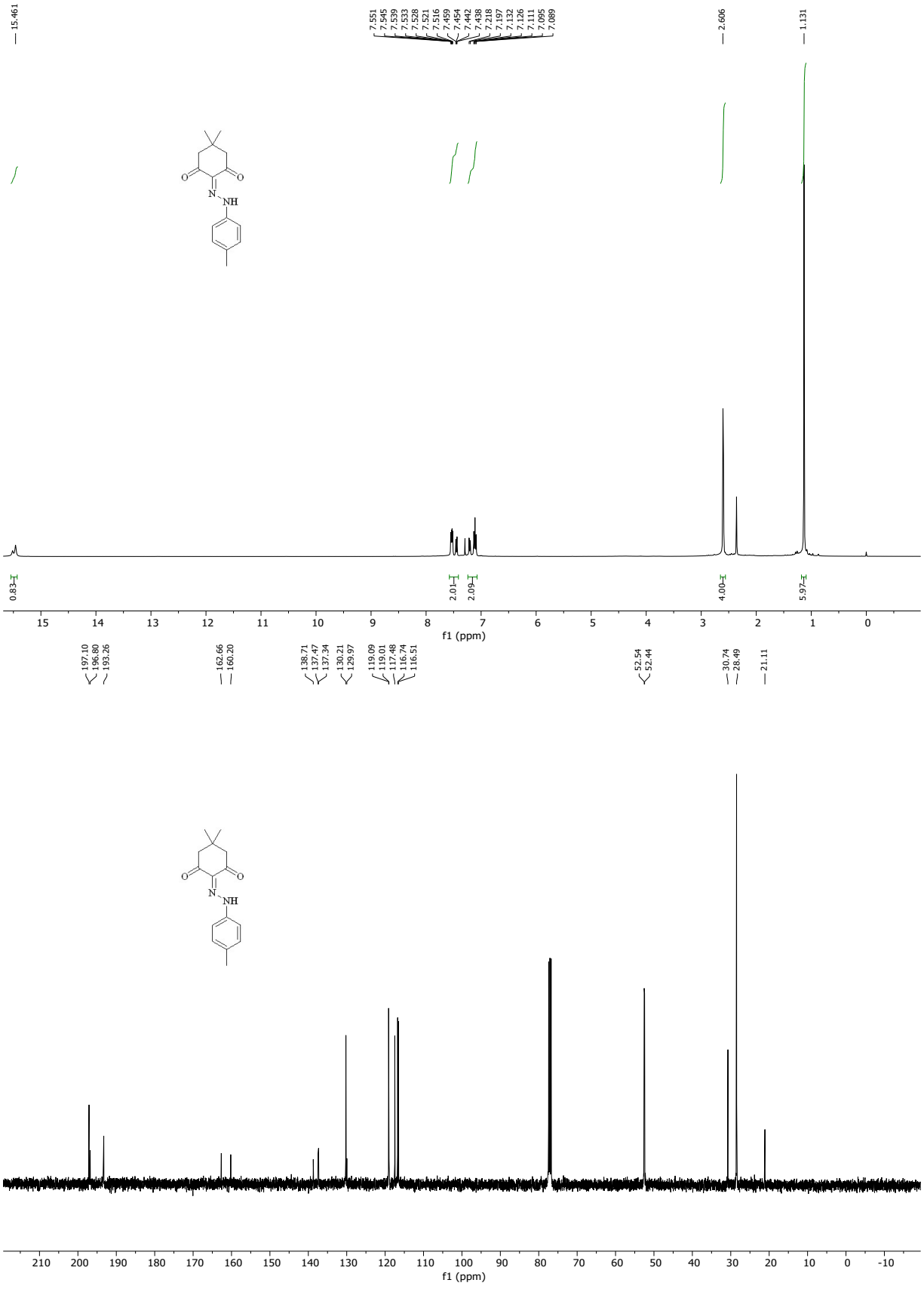


5,5-dimethyl-2-(2-phenylhydrazineylidene)cyclohexane-1,3-dione (4aa)

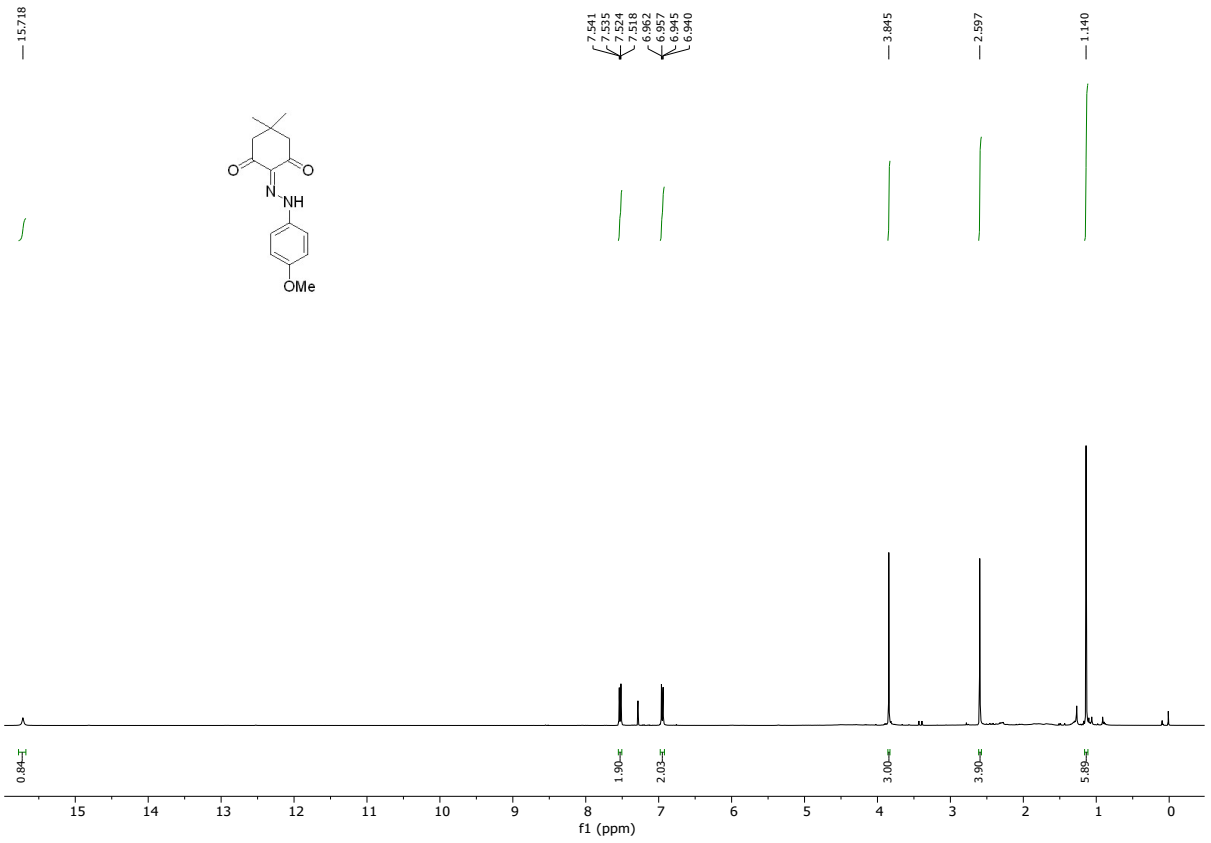


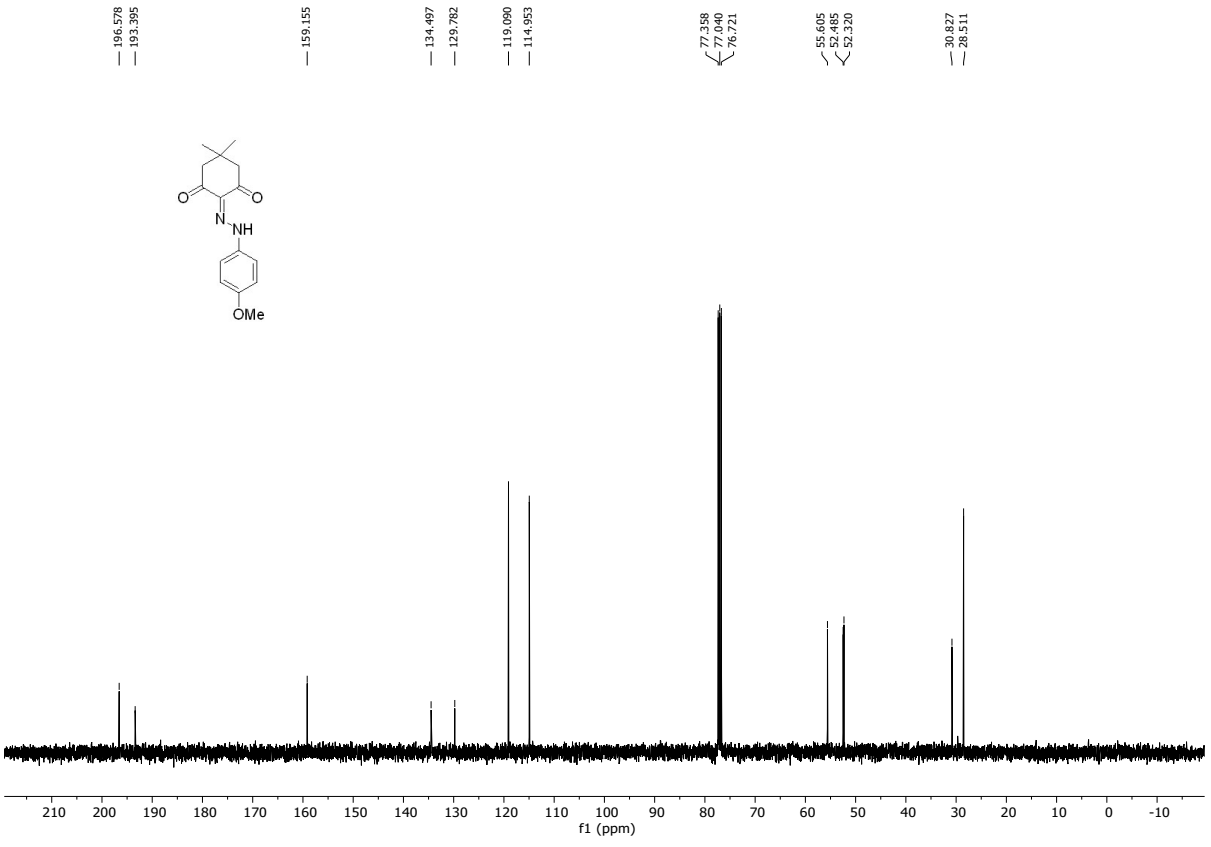


5,5-dimethyl-2-(2-(p-tolyl)hydrazineylidene)cyclohexane-1,3-dione (4ab)

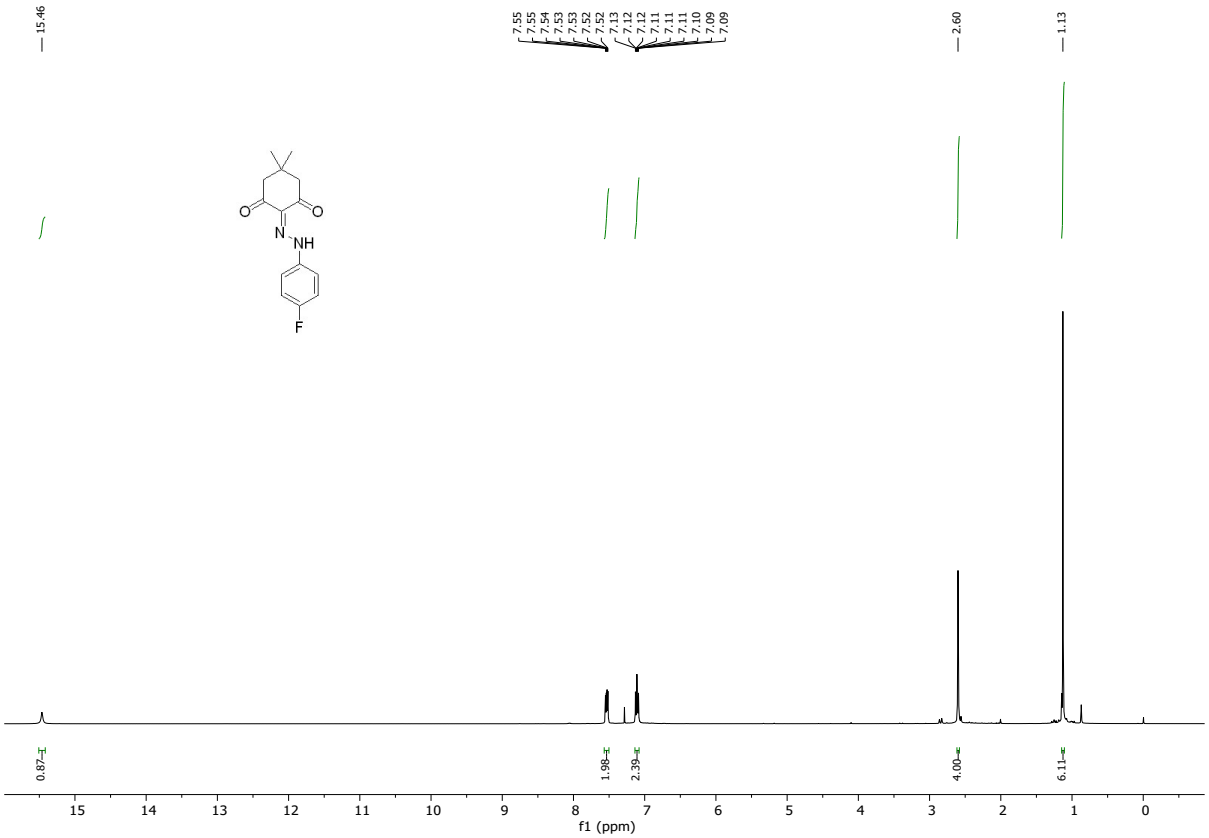


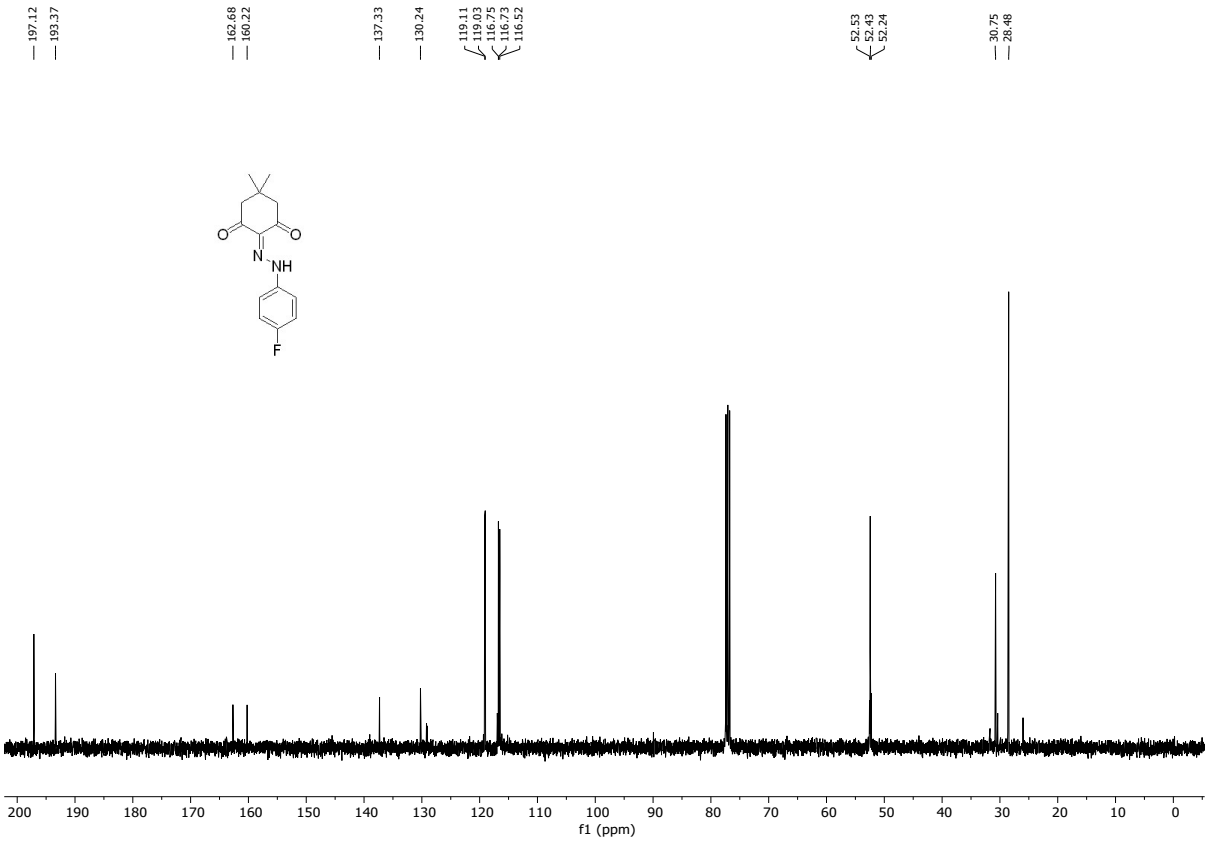
2-(2-(4-methoxyphenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ac)



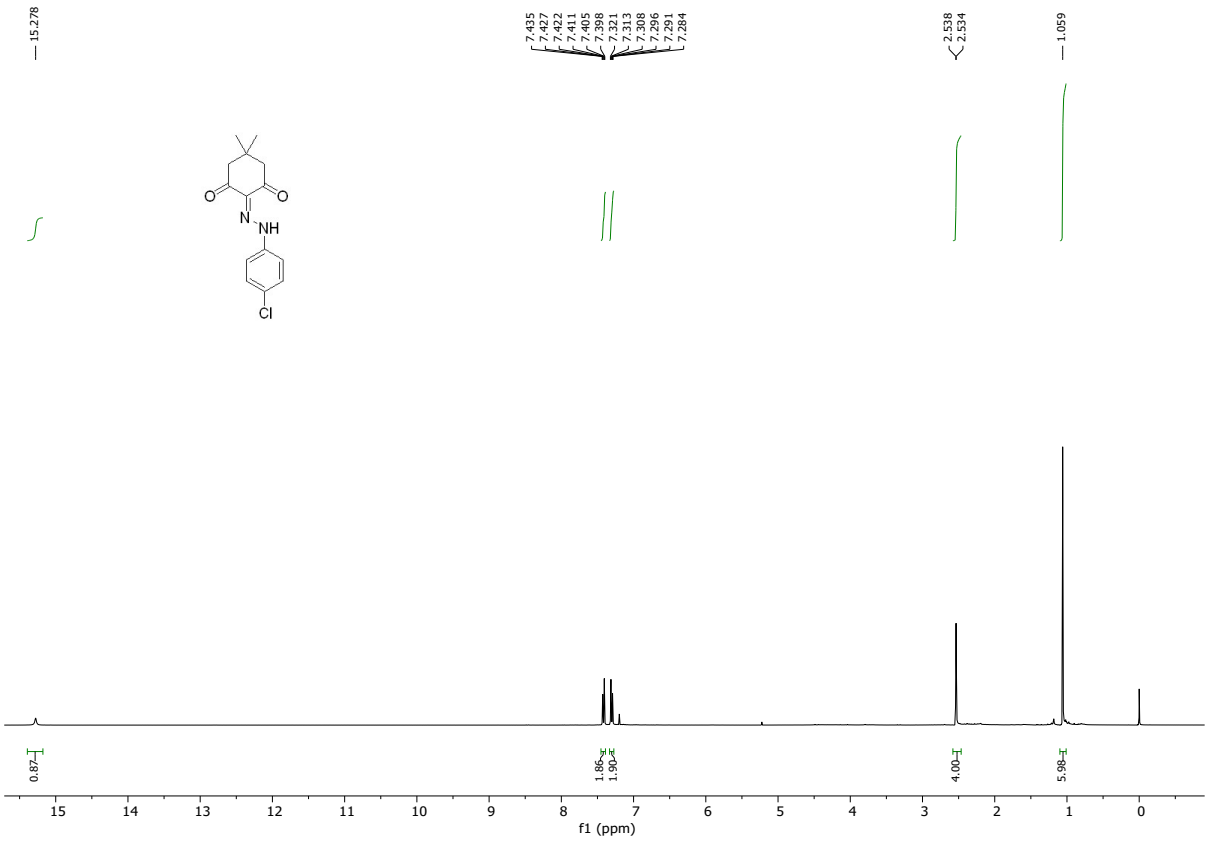


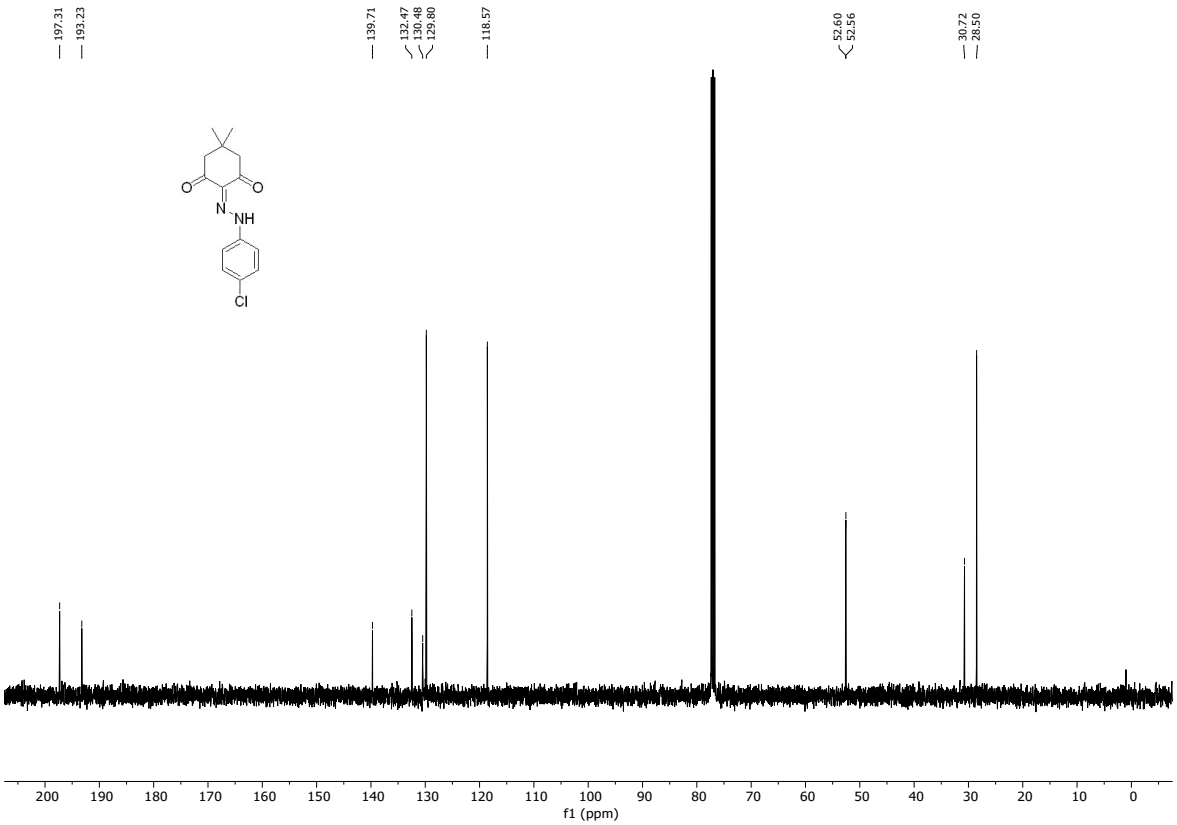
2-(2-(4-fluorophenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ad)



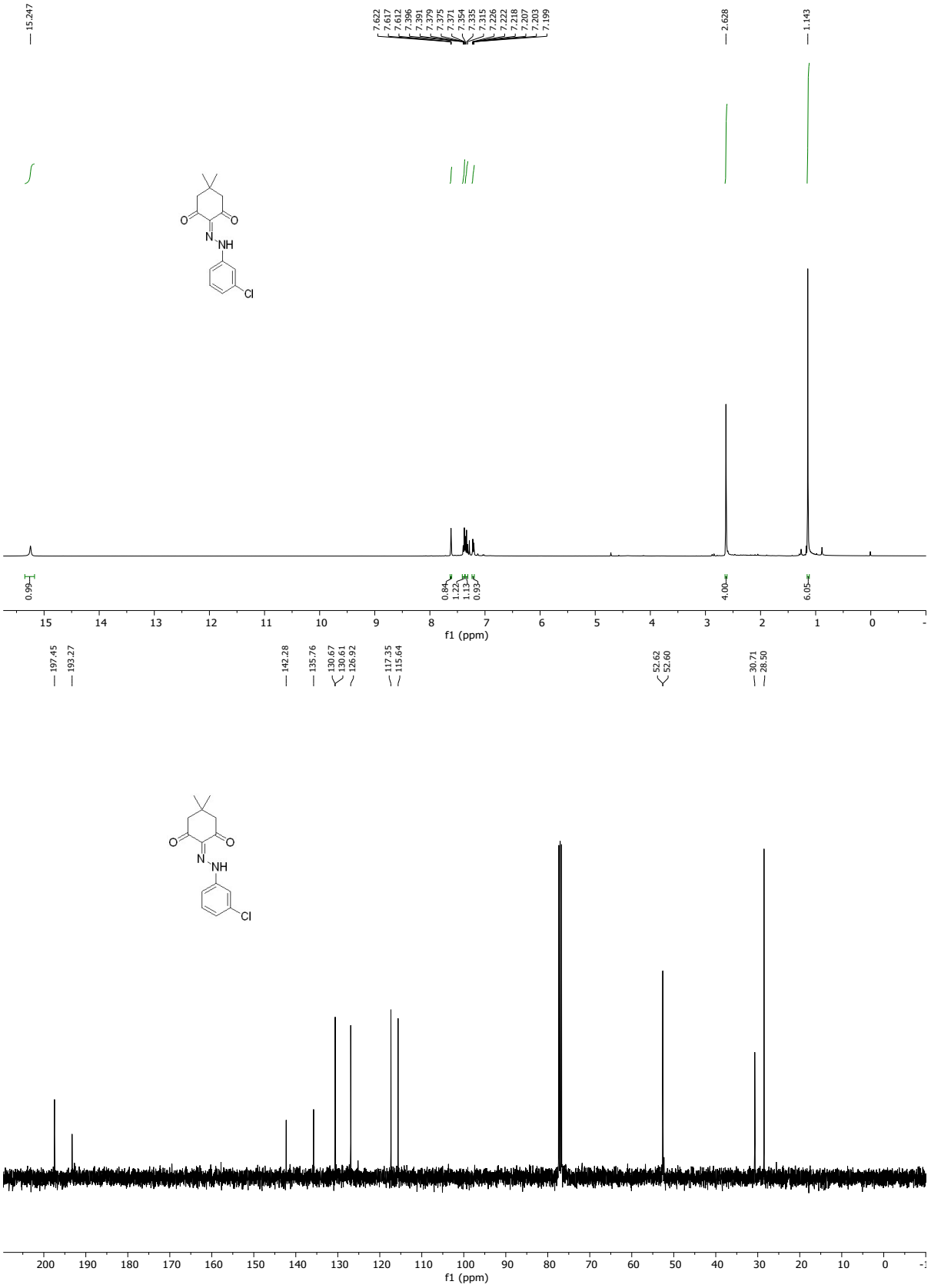


2-(2-(4-chlorophenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ae)

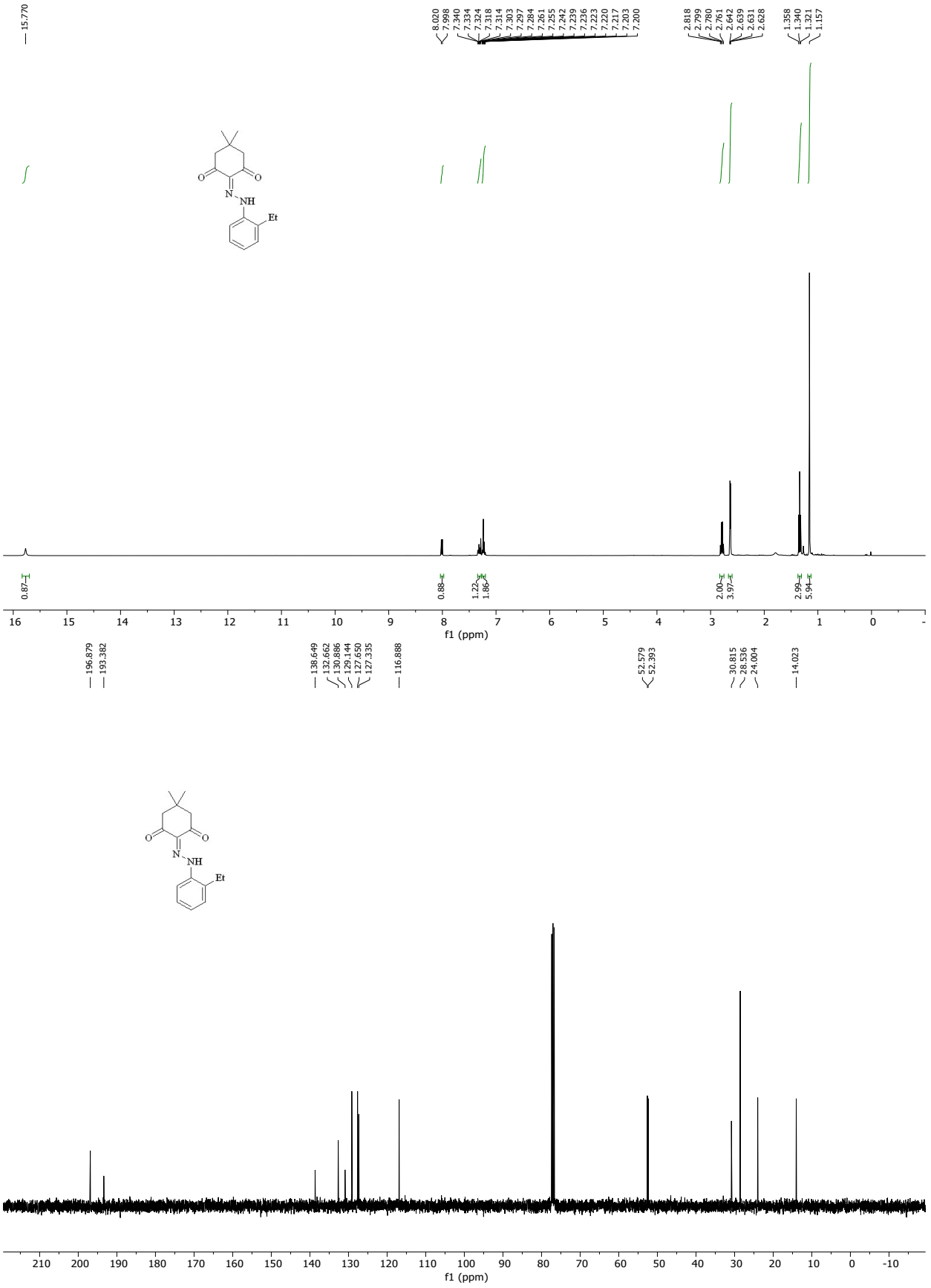




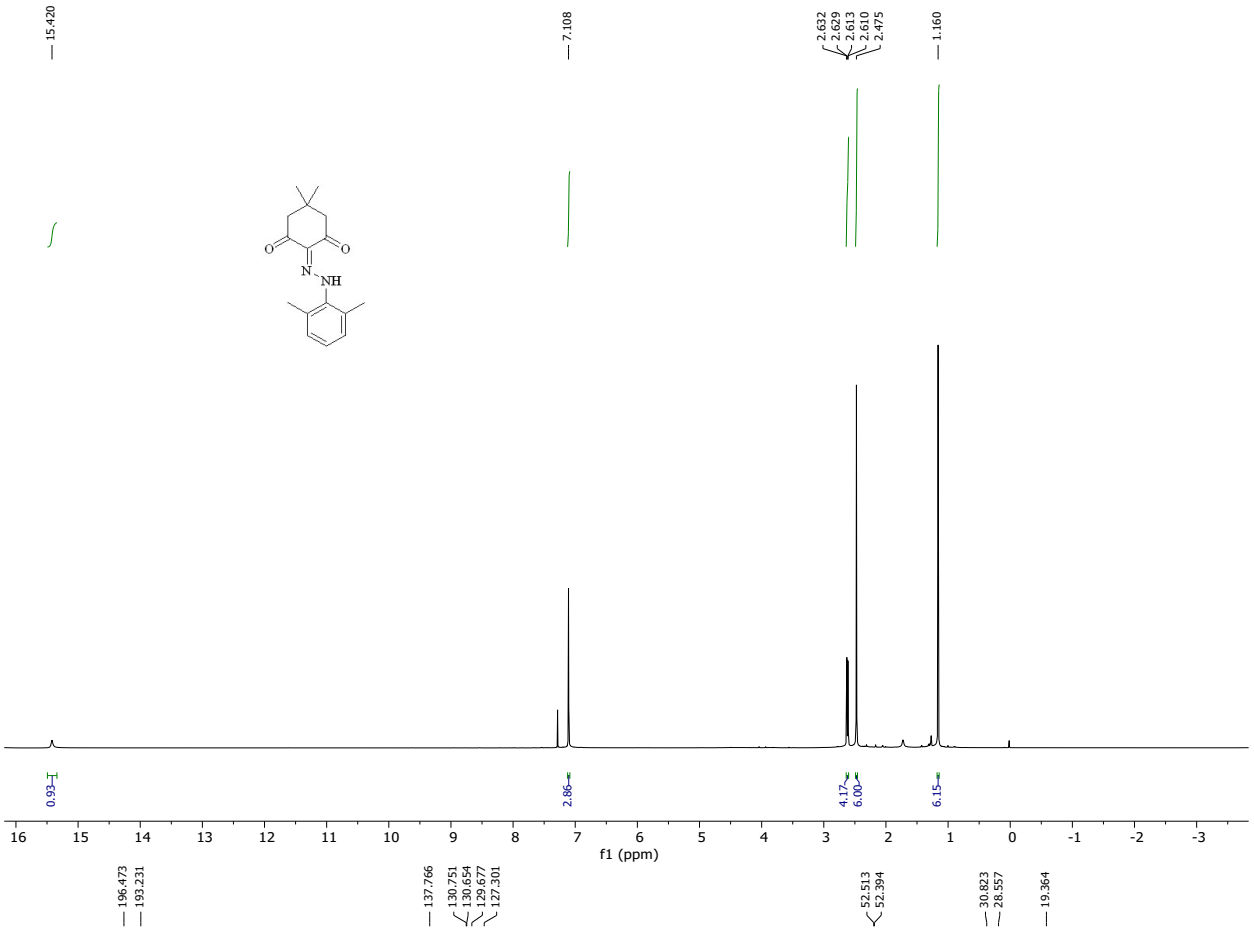
2-(2-(3-chlorophenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4af)

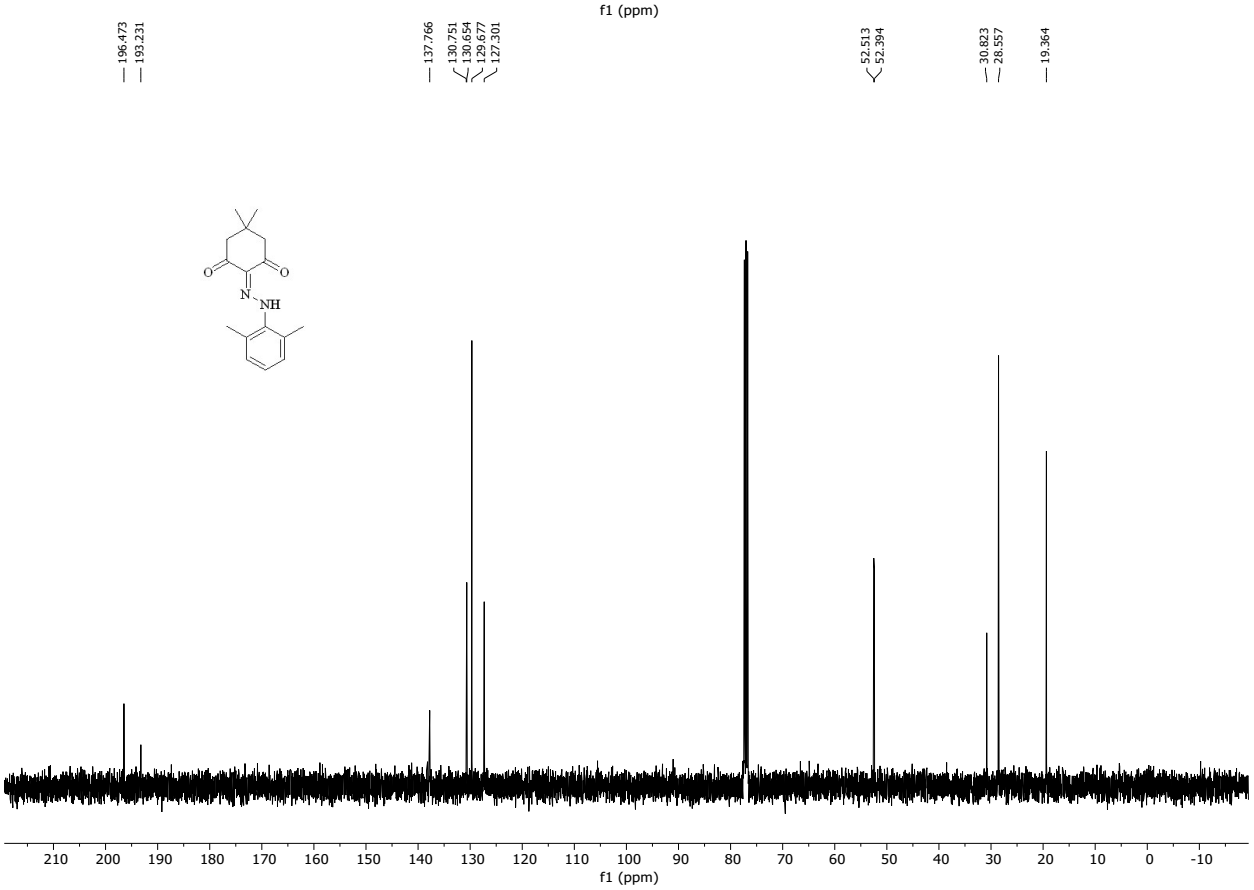


2-(2-(2-ethylphenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ag)

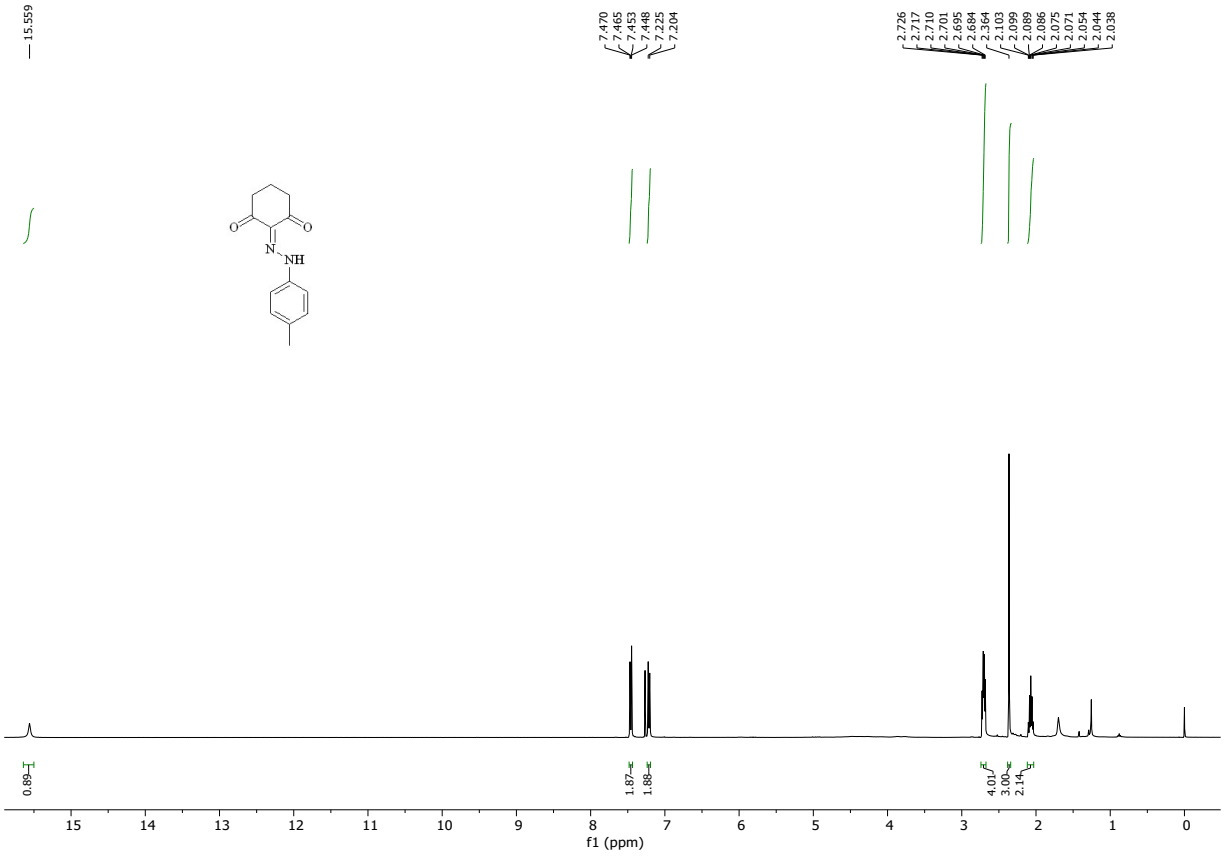


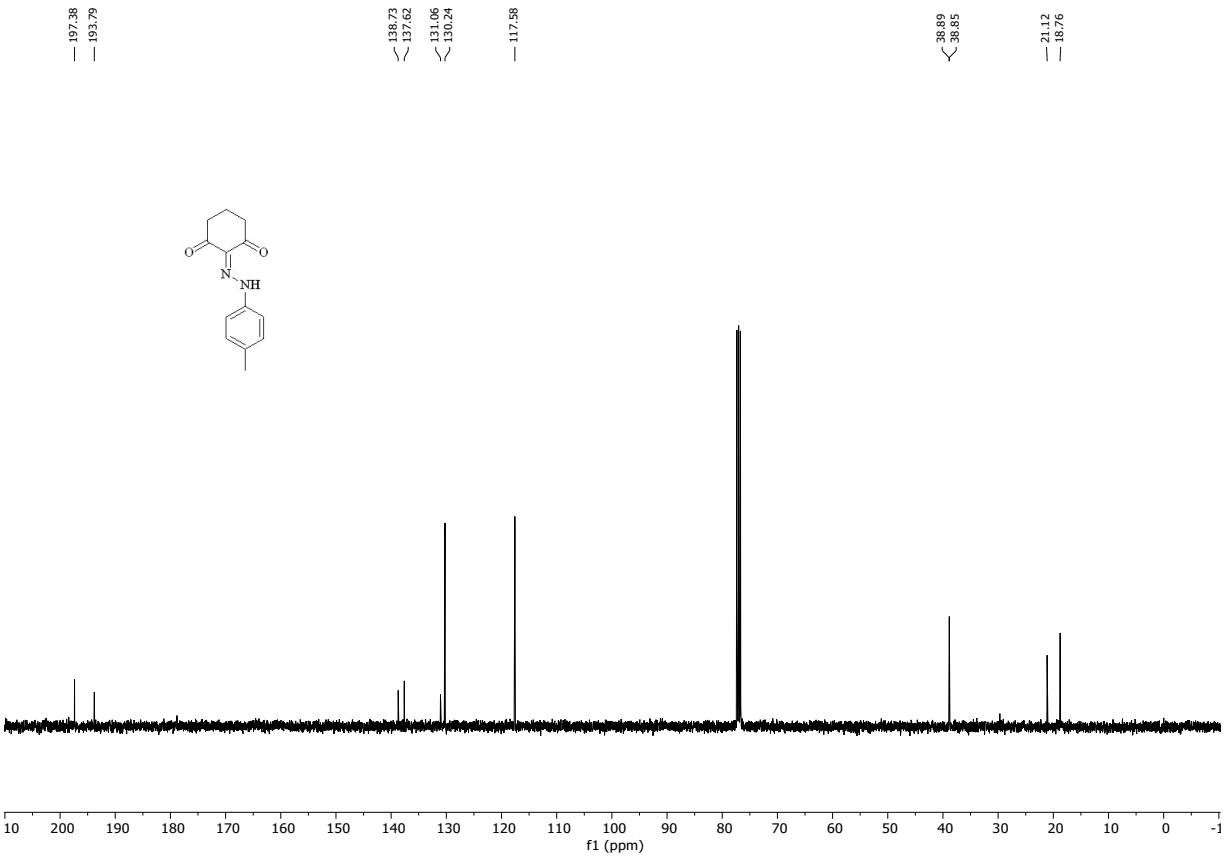
2-(2-(2,6-dimethylphenyl)hydrazineylidene)-5,5-dimethylcyclohexane-1,3-dione (4ah)



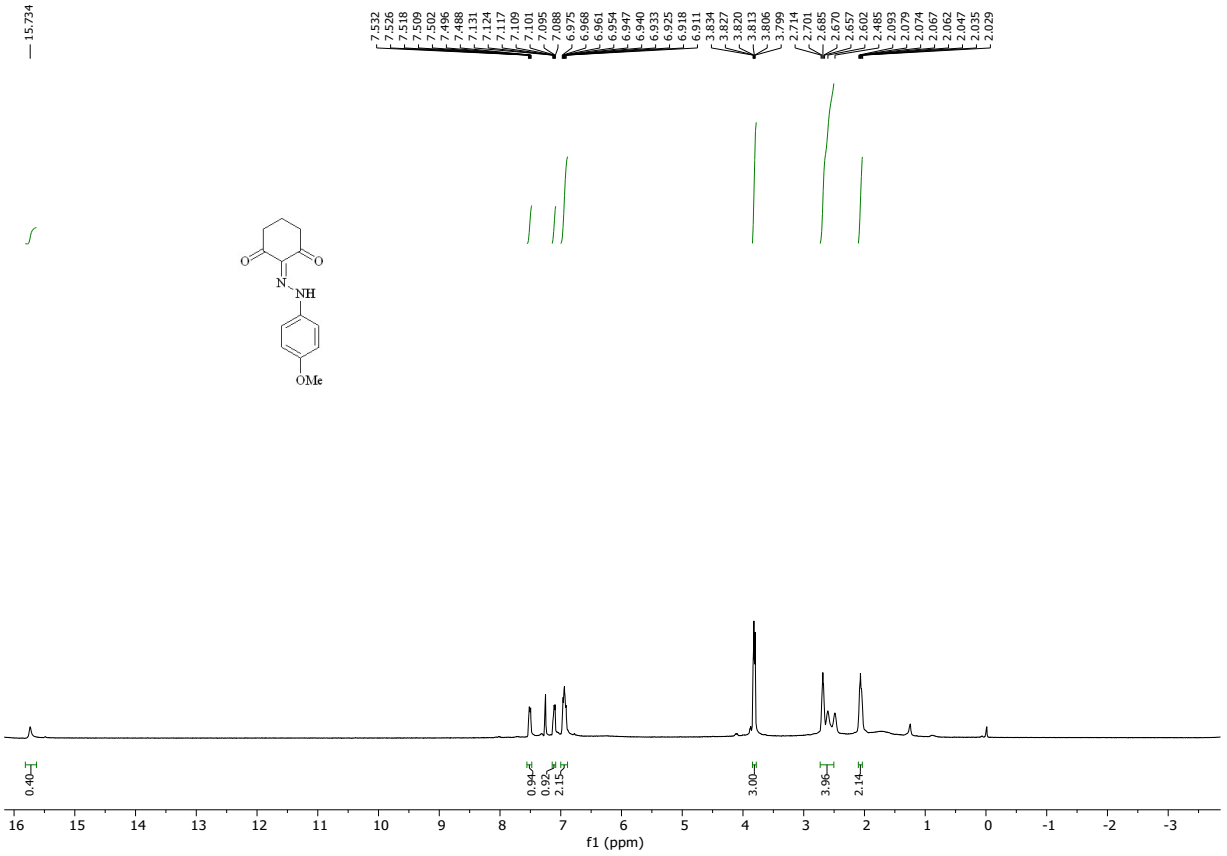


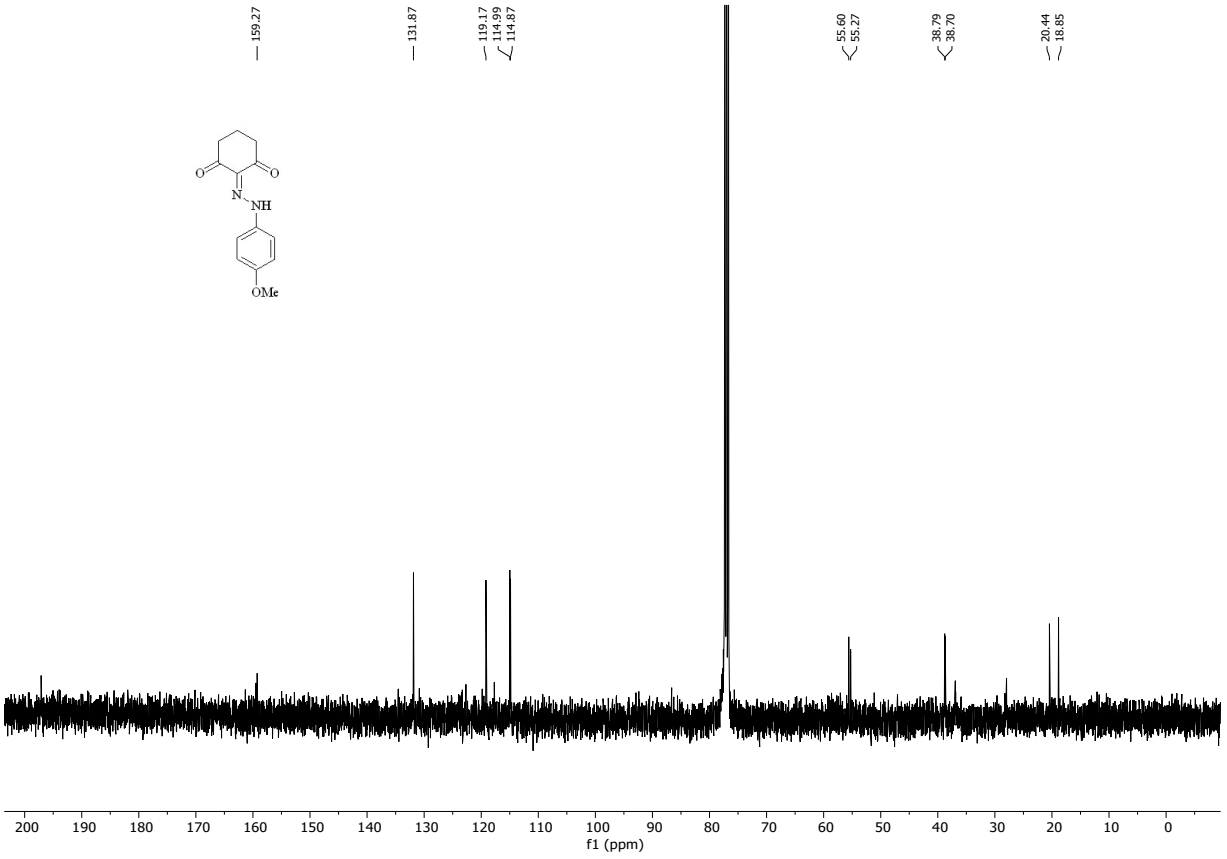
2-(2-(p-tolyl)hydrazineylidene)cyclohexane-1,3-dione (4bb)



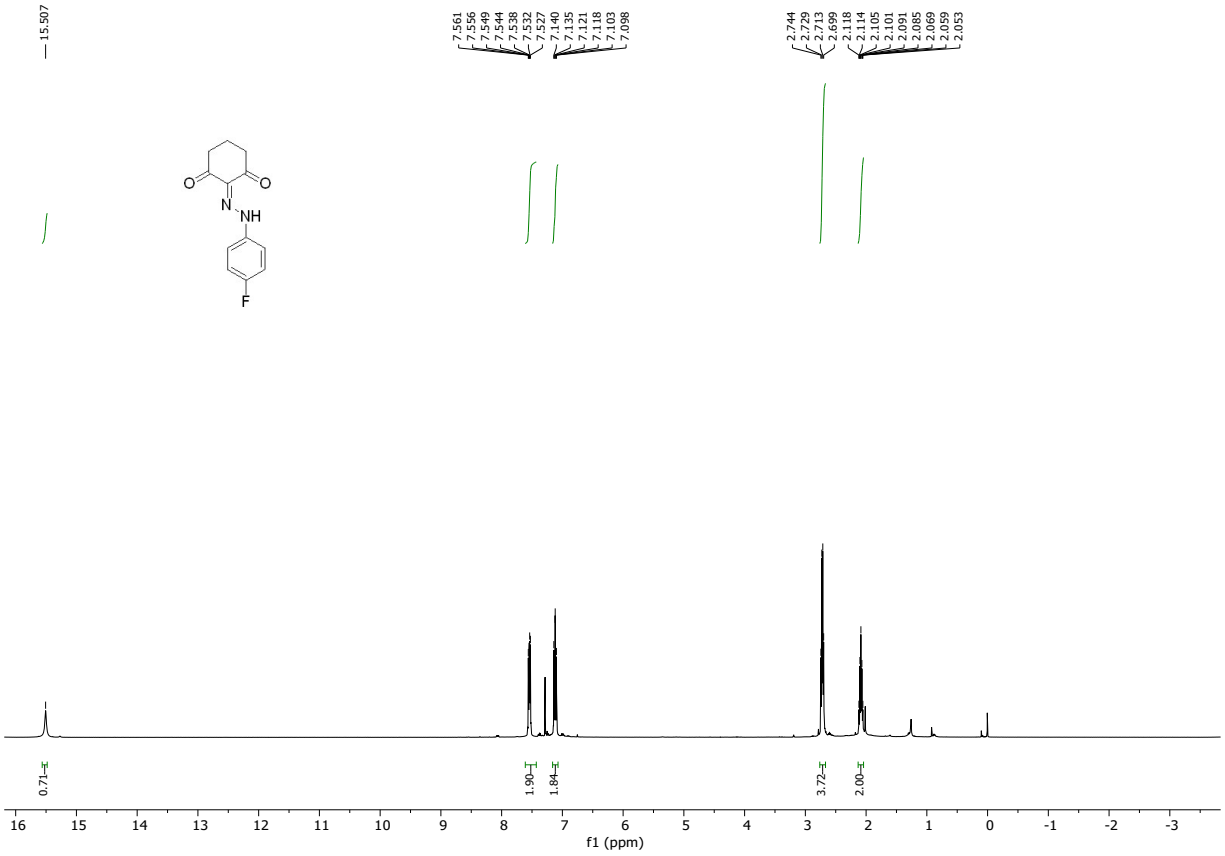


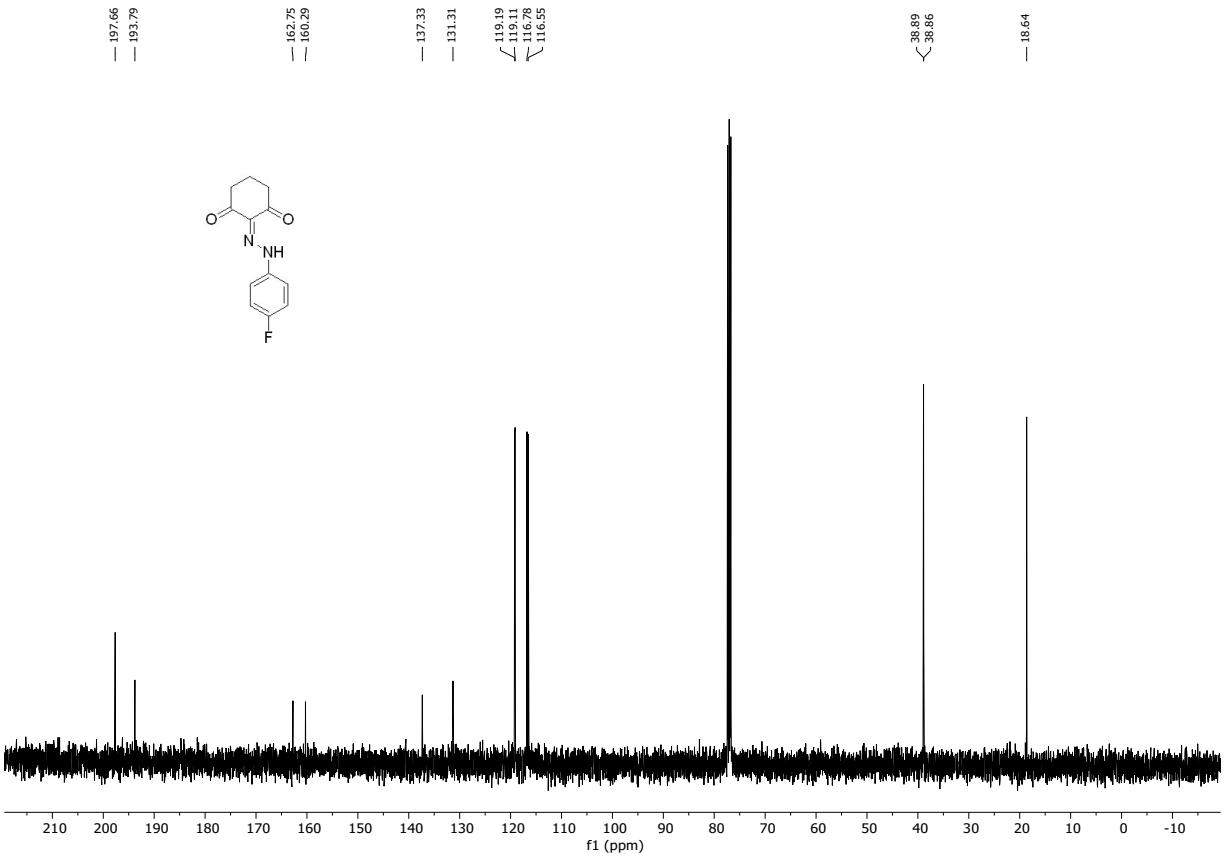
2-(2-(4-methoxyphenyl)hydrazineylidene)cyclohexane-1,3-dione (4bc)



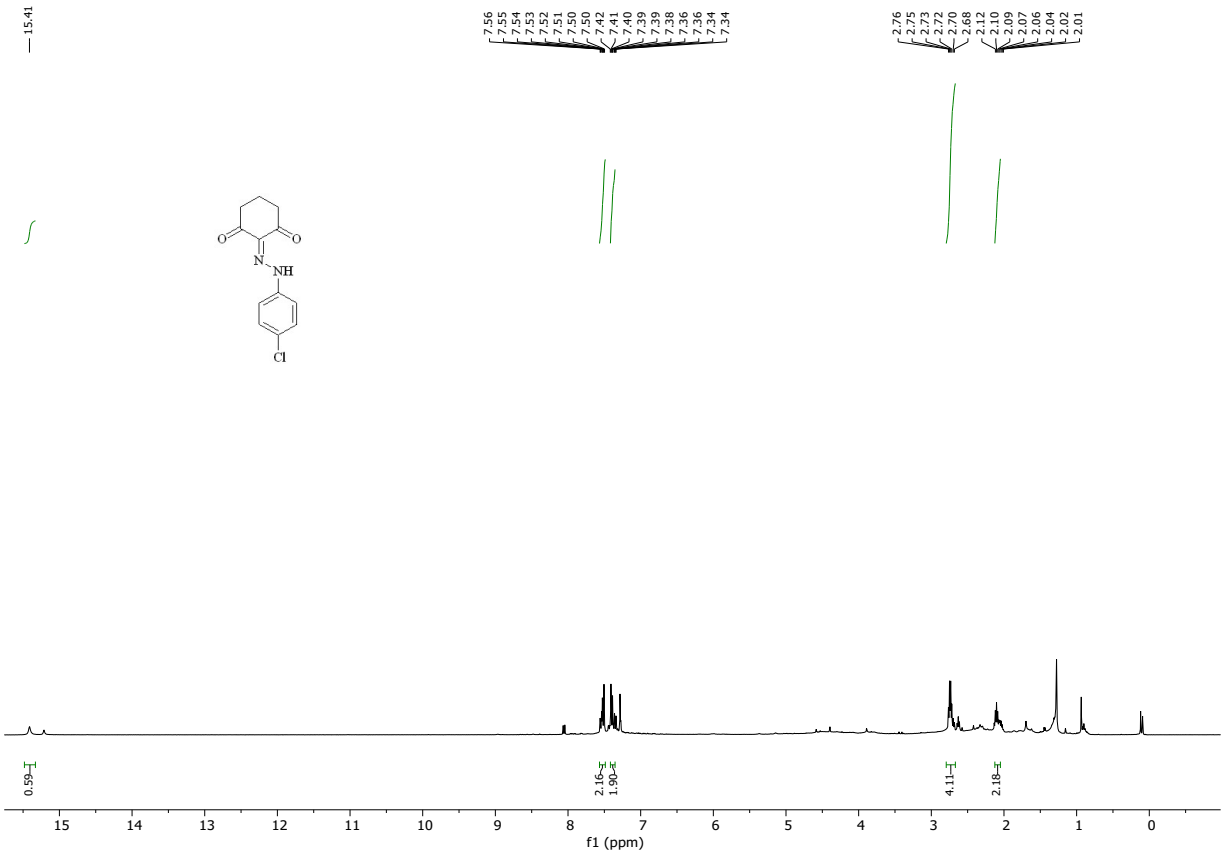


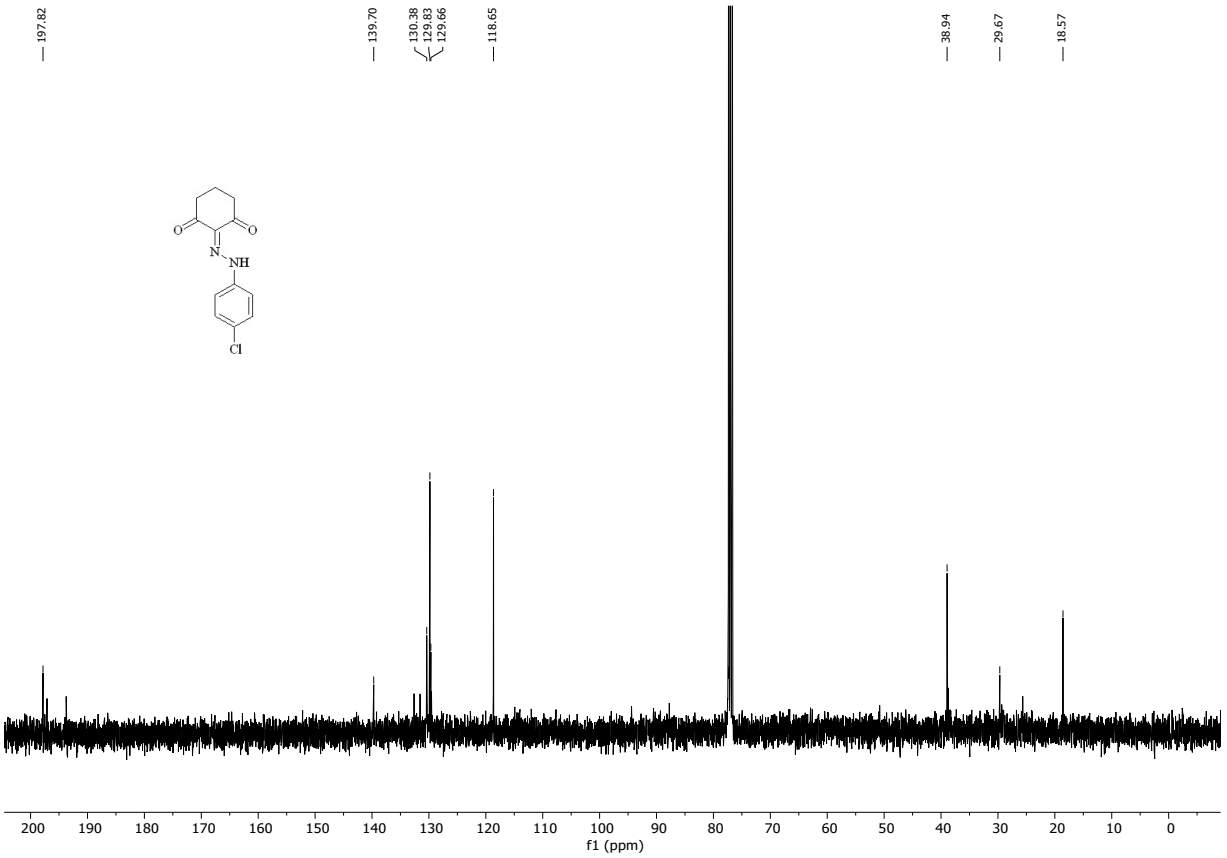
2-(2-(4-fluorophenyl)hydrazineylidene)cyclohexane-1,3-dione (4bd)



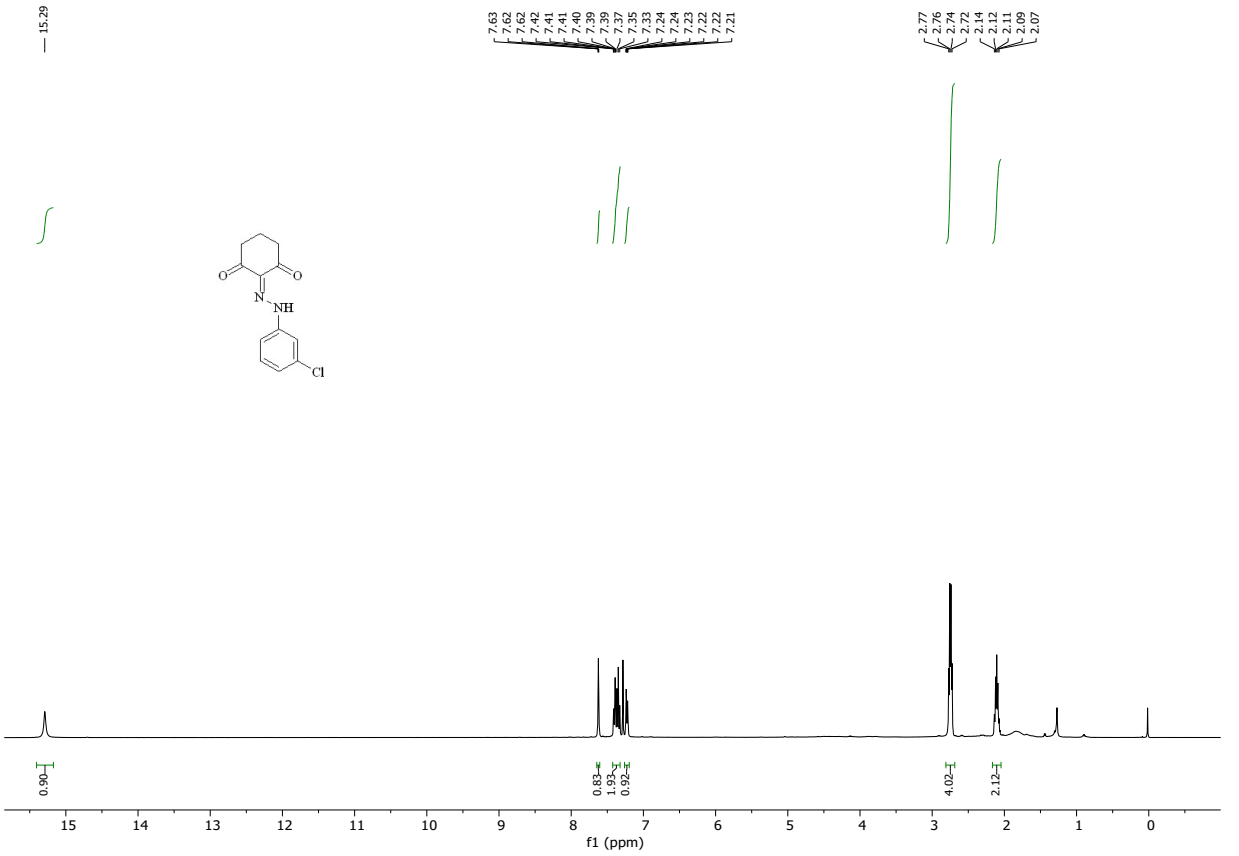


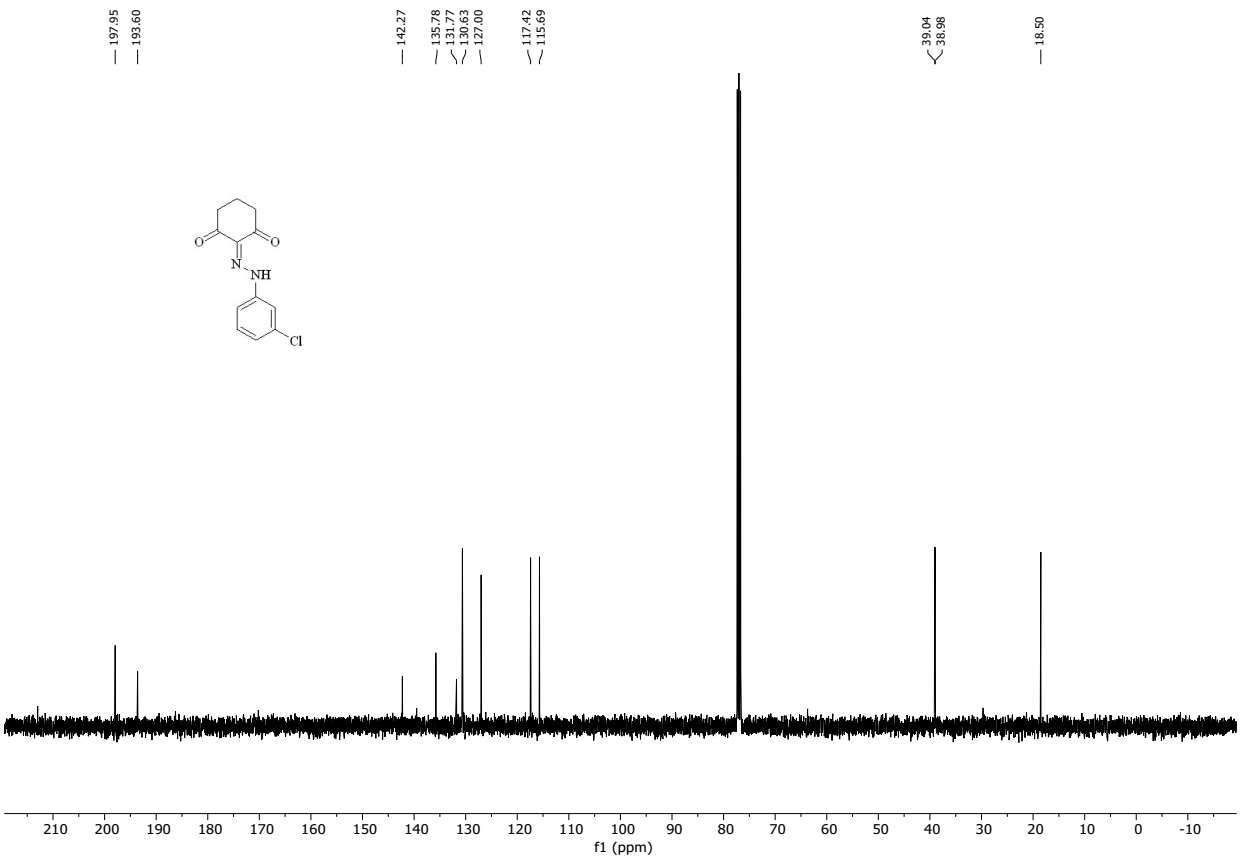
2-(2-(4-chlorophenyl)hydrazineylidene)cyclohexane-1,3-dione (4be)



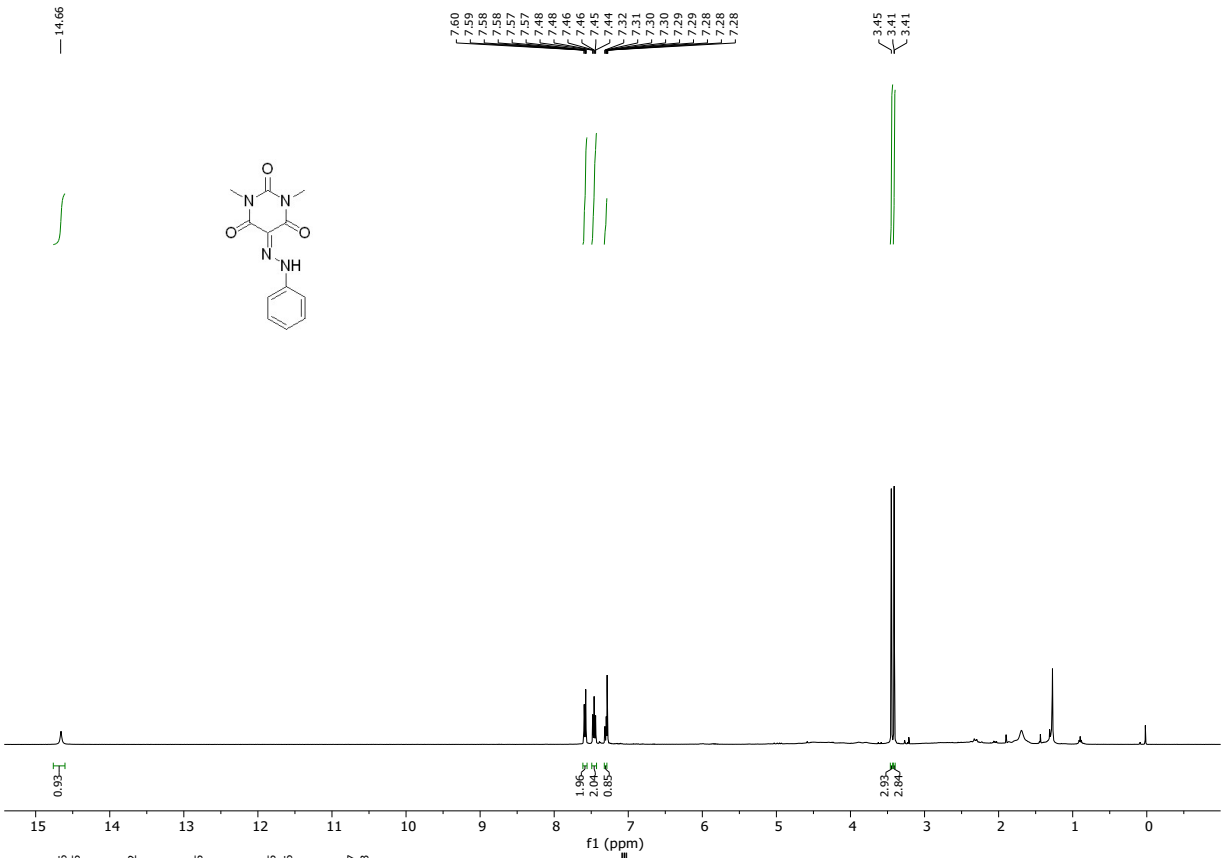


2-(2-(3-chlorophenyl)hydrazineylidene)cyclohexane-1,3-dione (4bf)





1,3-dimethyl-5-(2-phenylhydrazineylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (4ca)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7.60
7.59
7.58
7.58
7.57
7.57
7.48
7.48
7.46
7.46
7.45
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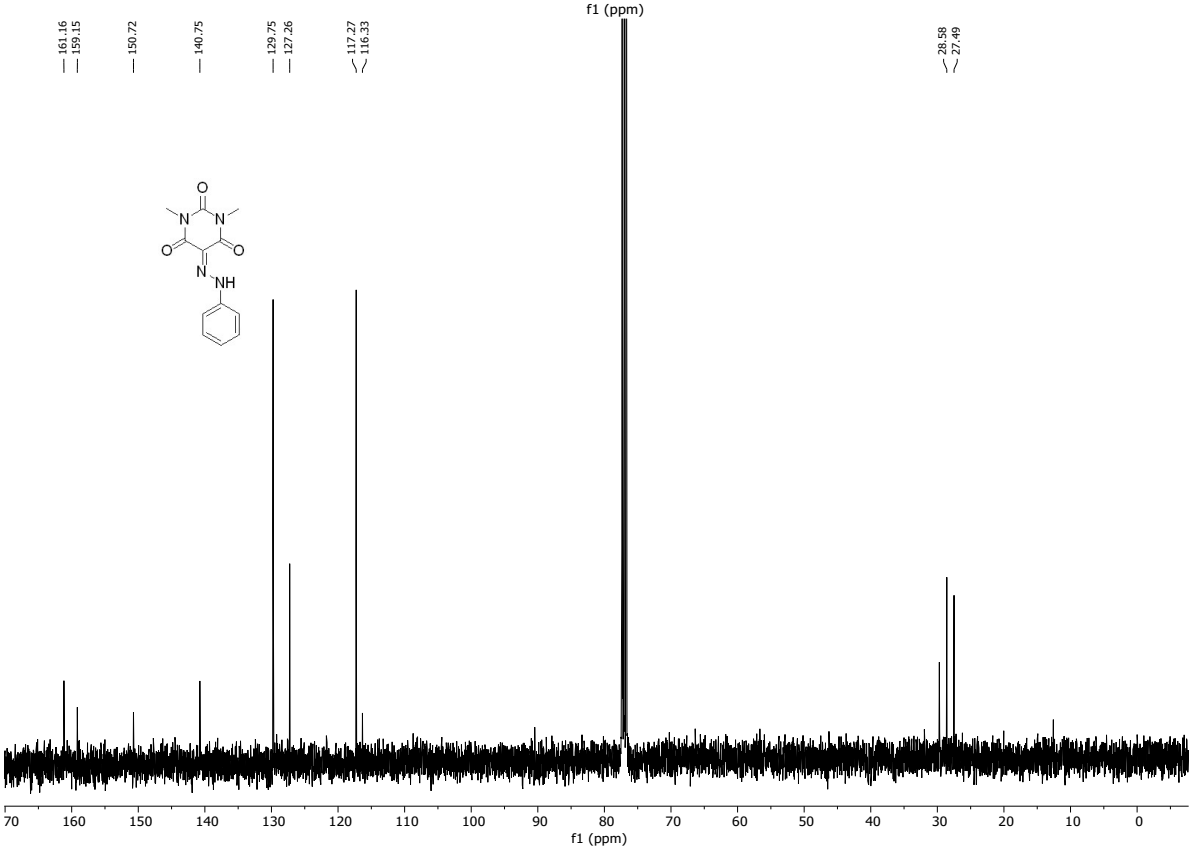
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.28
3.45
3.41
3.41
O
N
N
O
O
N
NH
0.93
1.96
2.04
0.85
2.93
2.84
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


161.16
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117.27
116.33
28.58
27.49
O
N
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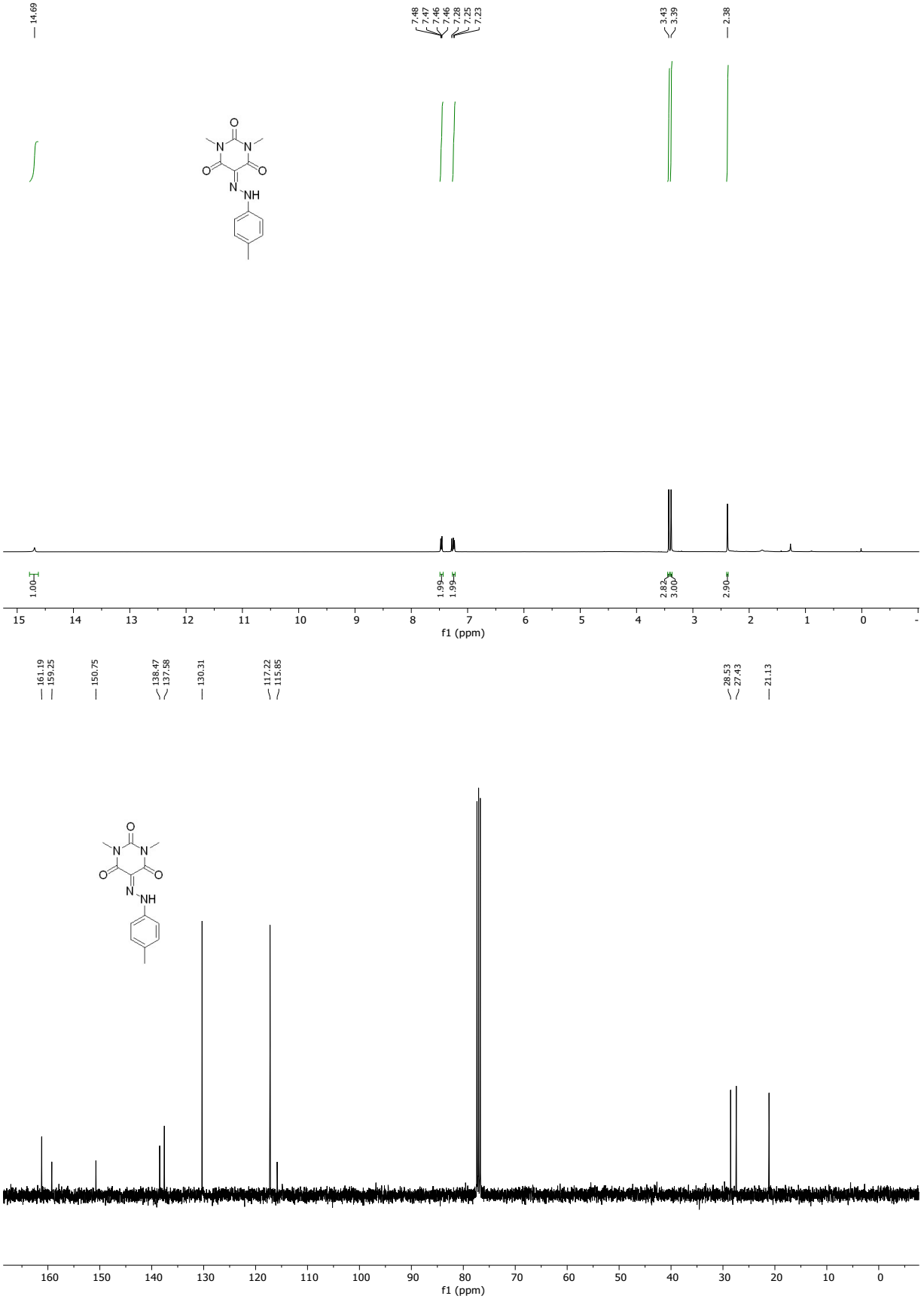
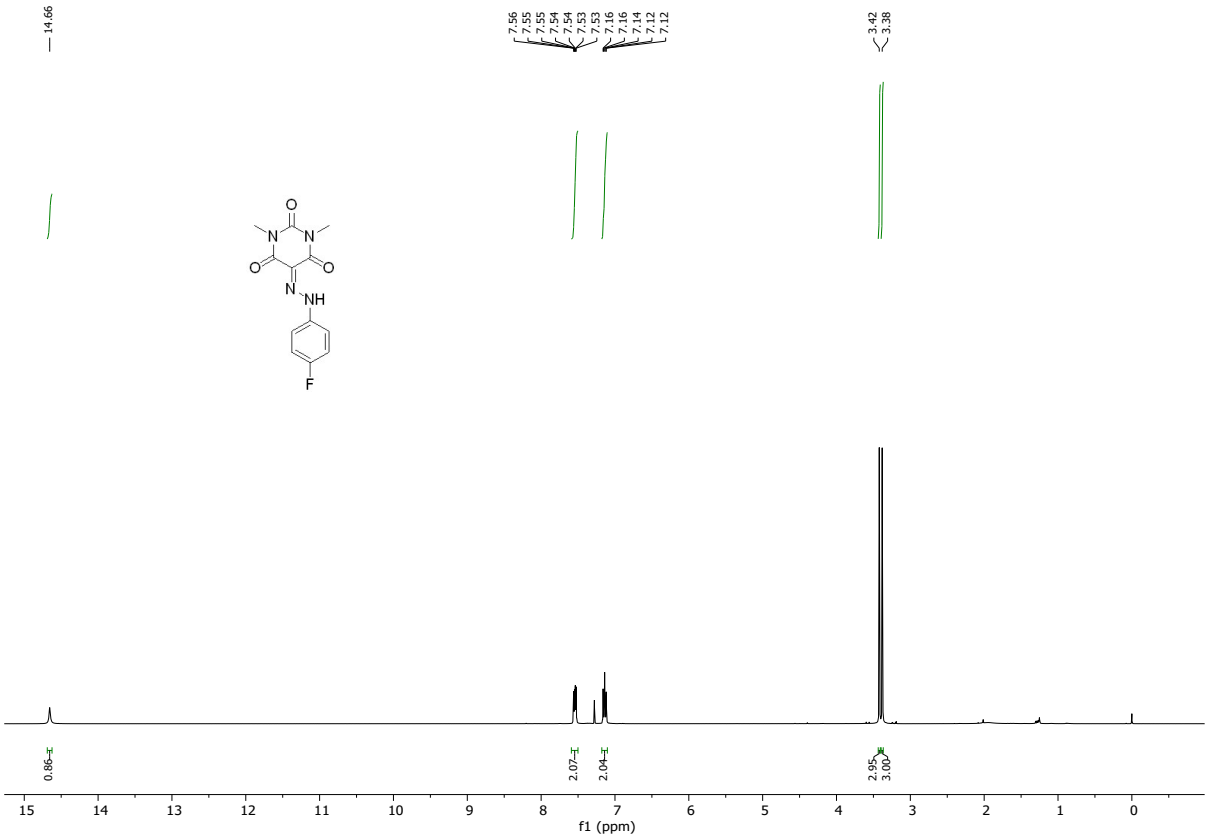
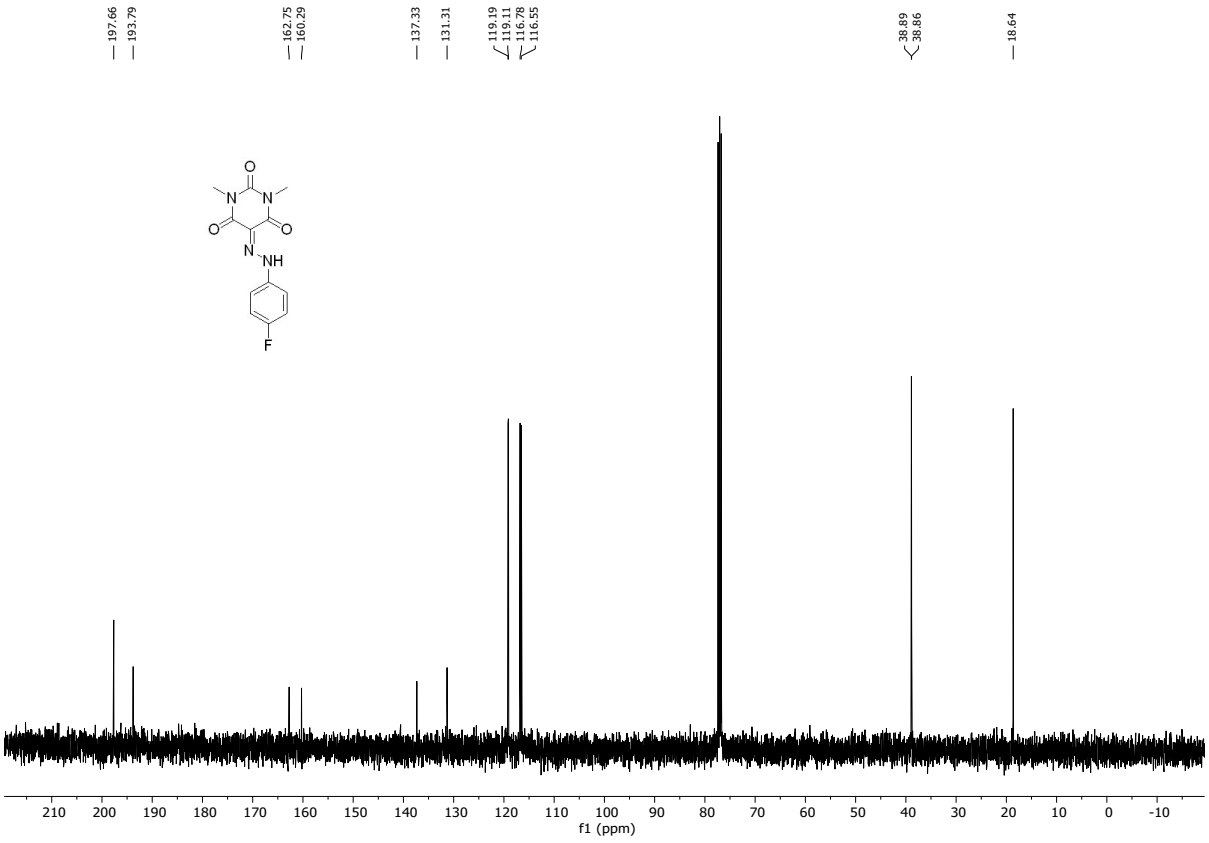
O
N
NH
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1,3-dimethyl-5-(2-(p-tolyl)hydrazineylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (4cb)

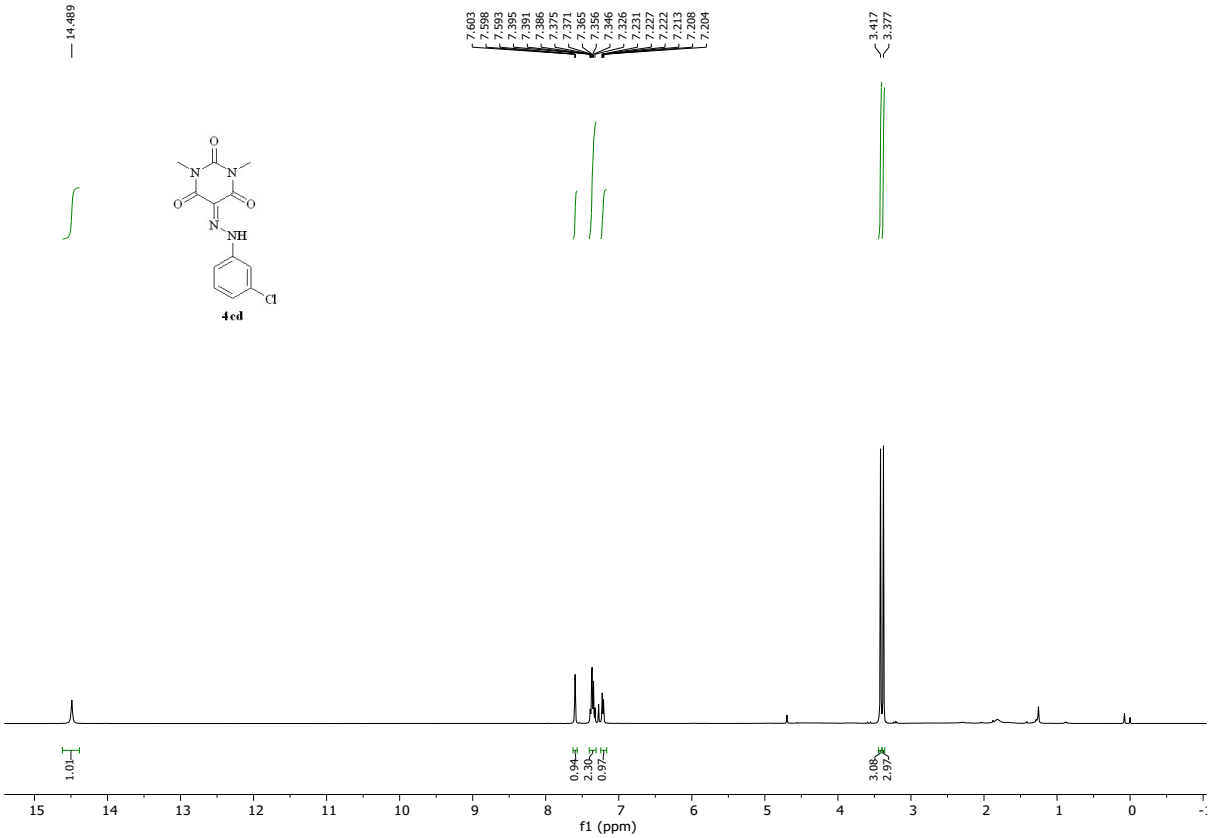


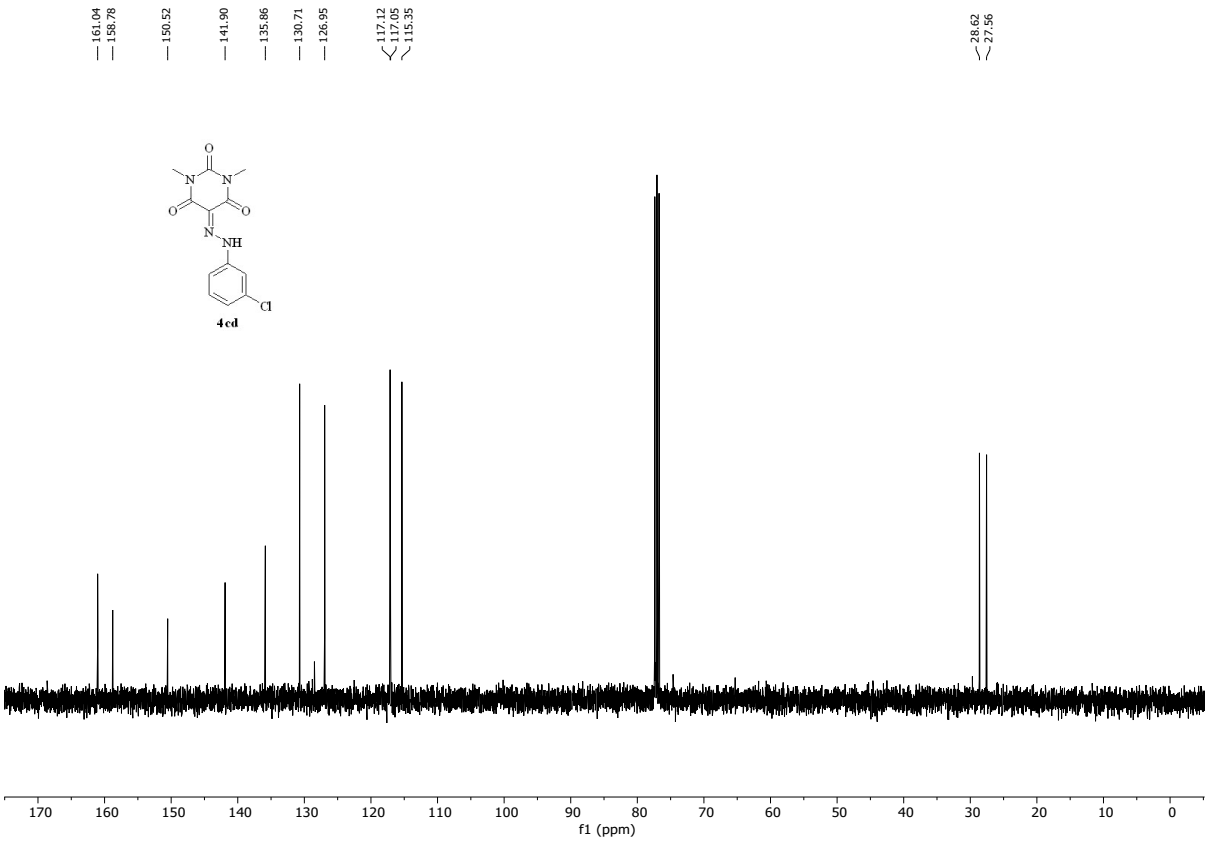
5-(2-(4-fluorophenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cc)



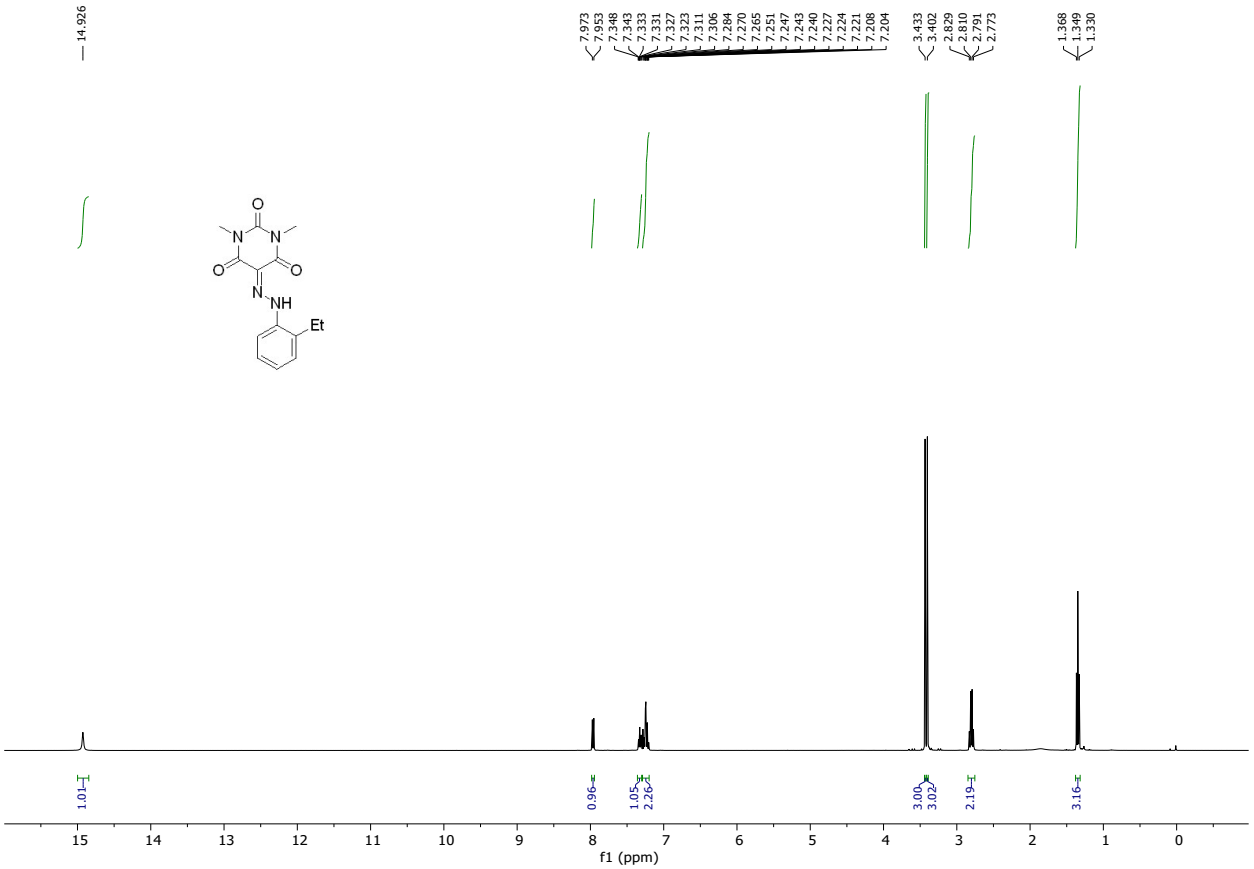


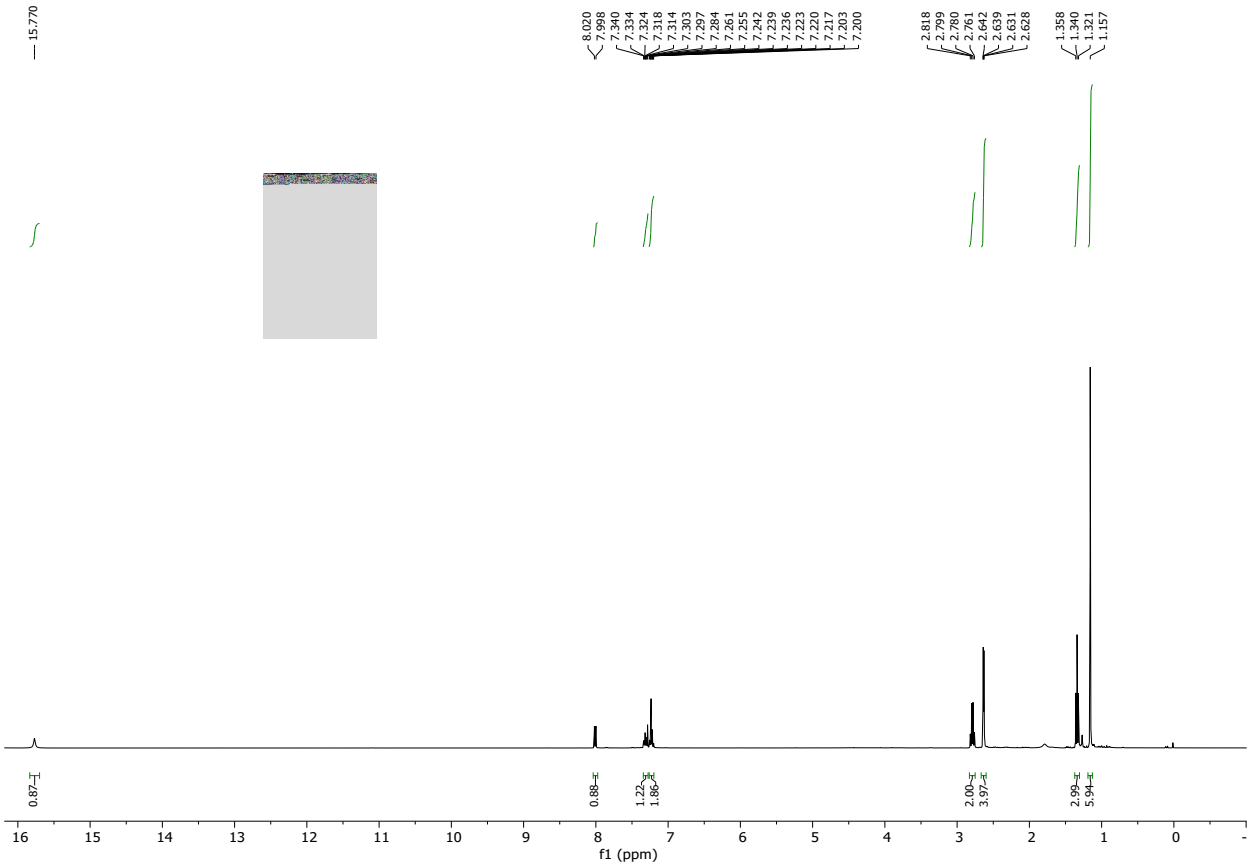
5-(2-(3-chlorophenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cd)



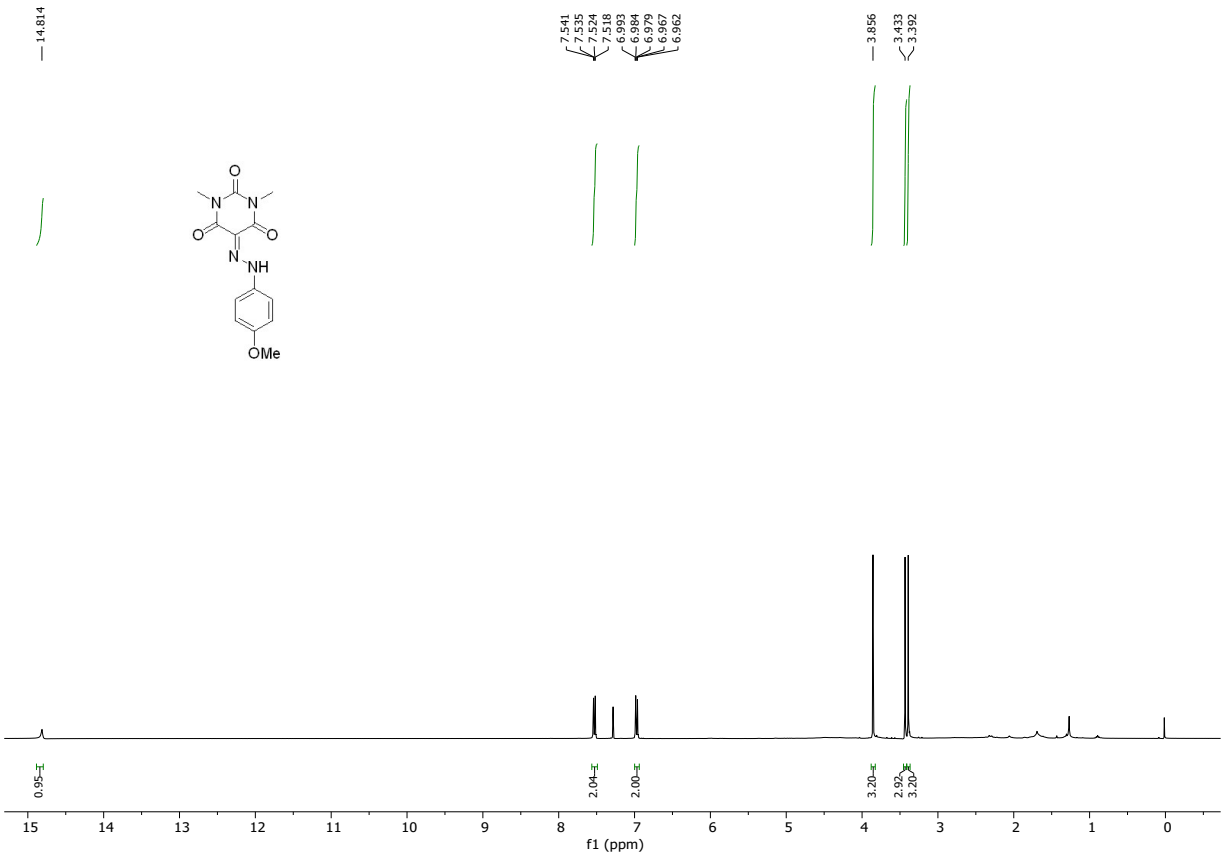


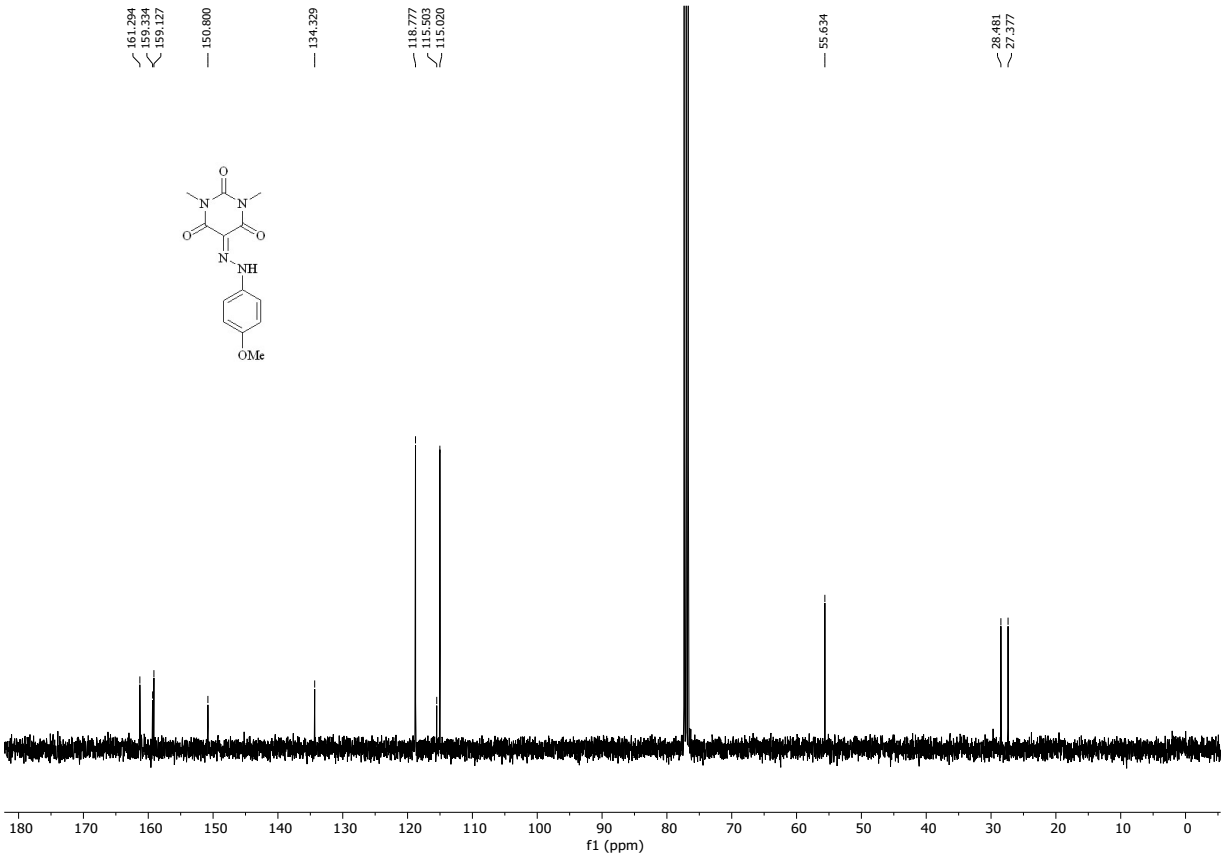
5-(2-(2-ethylphenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4ce)



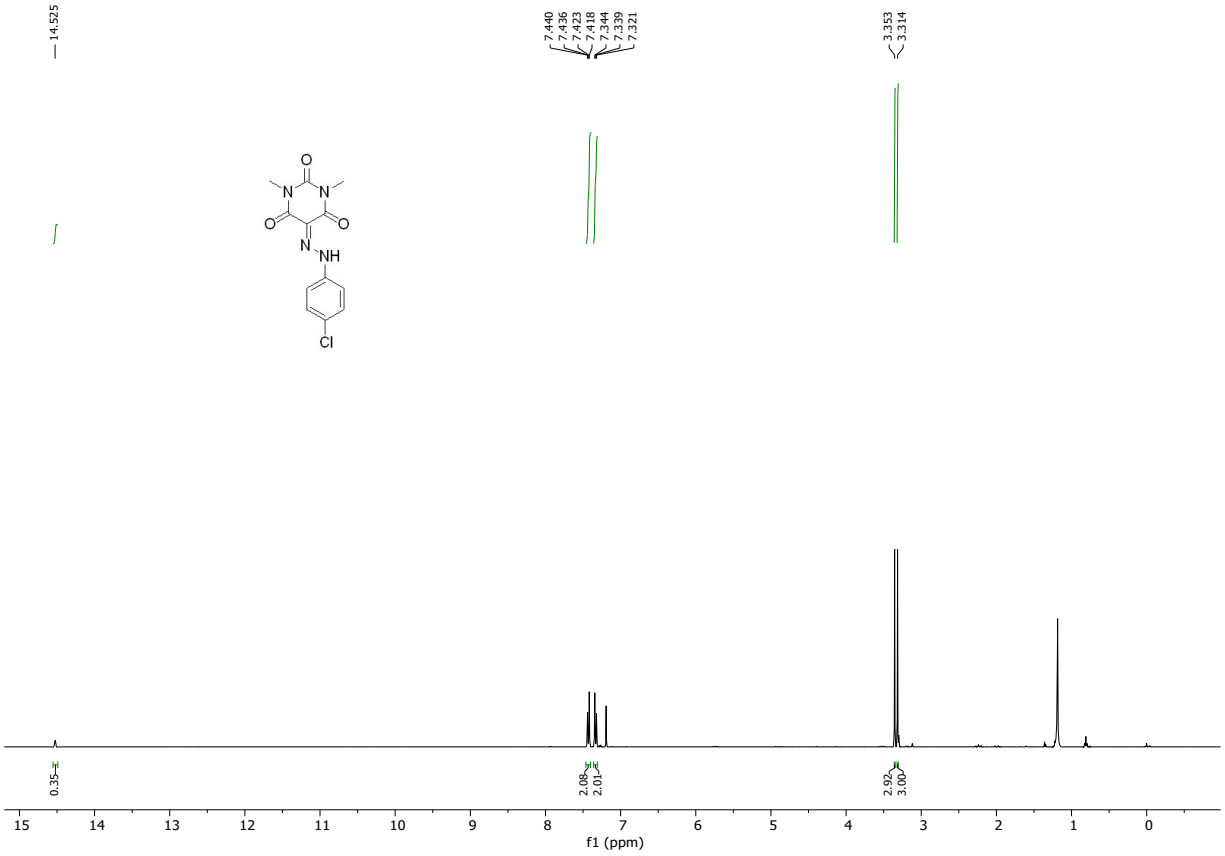


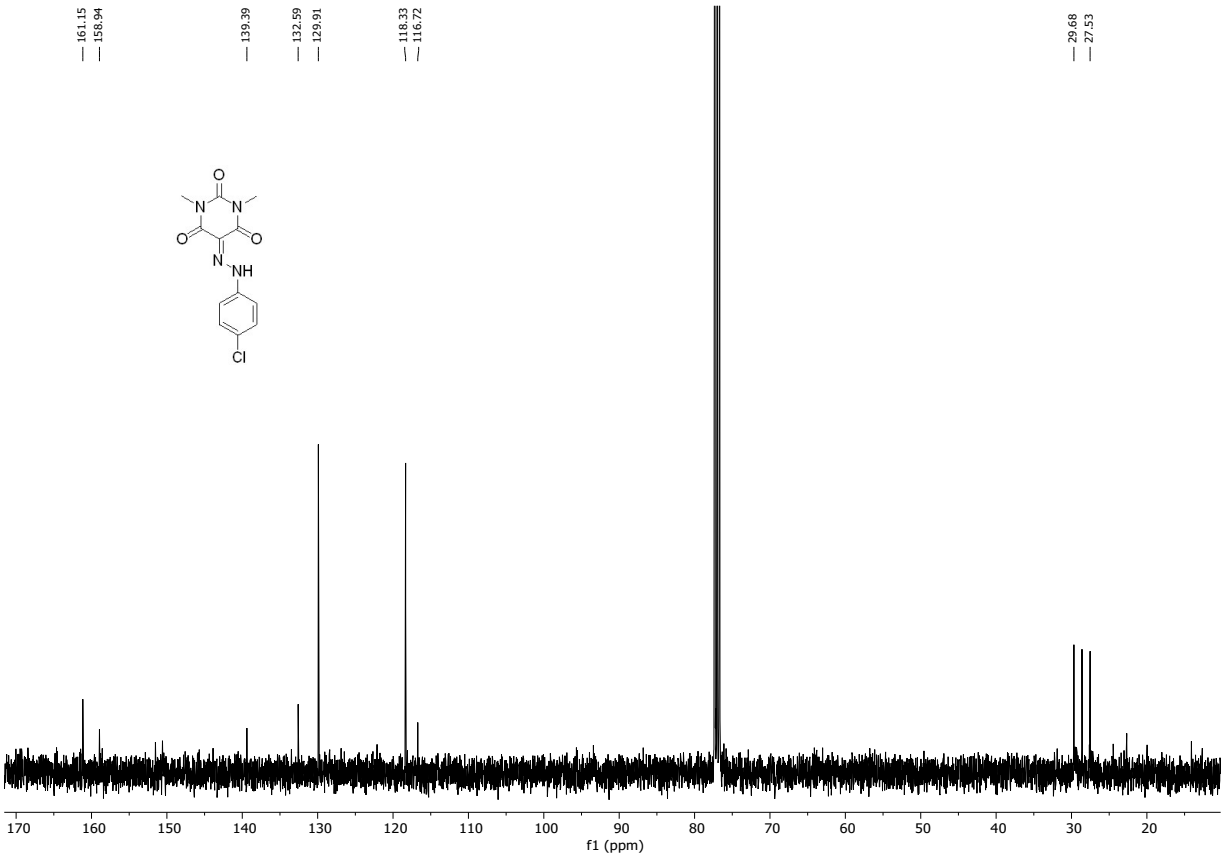
5-(2-(4-methoxyphenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cf)



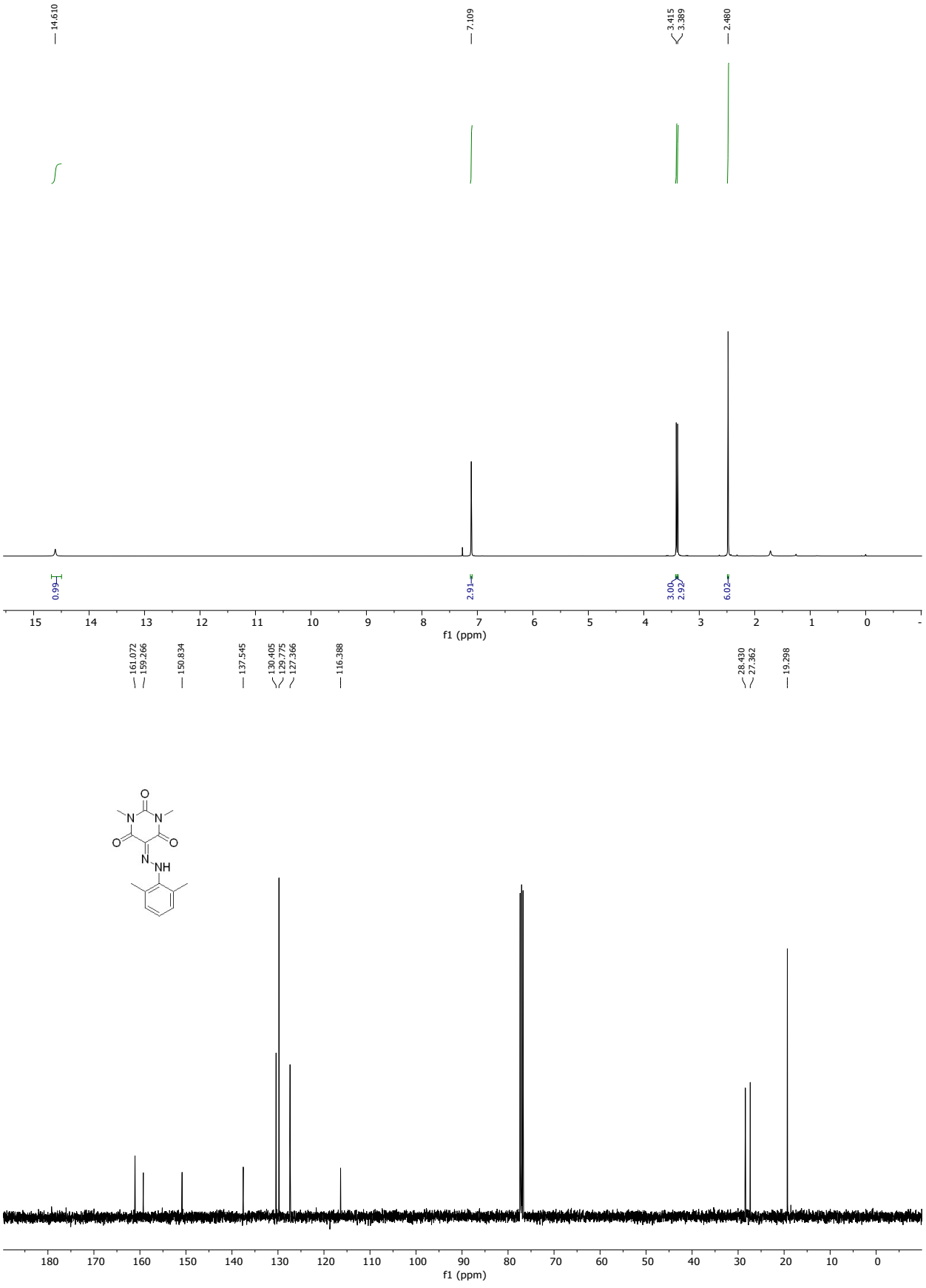


5-(2-(4-chlorophenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4cg)

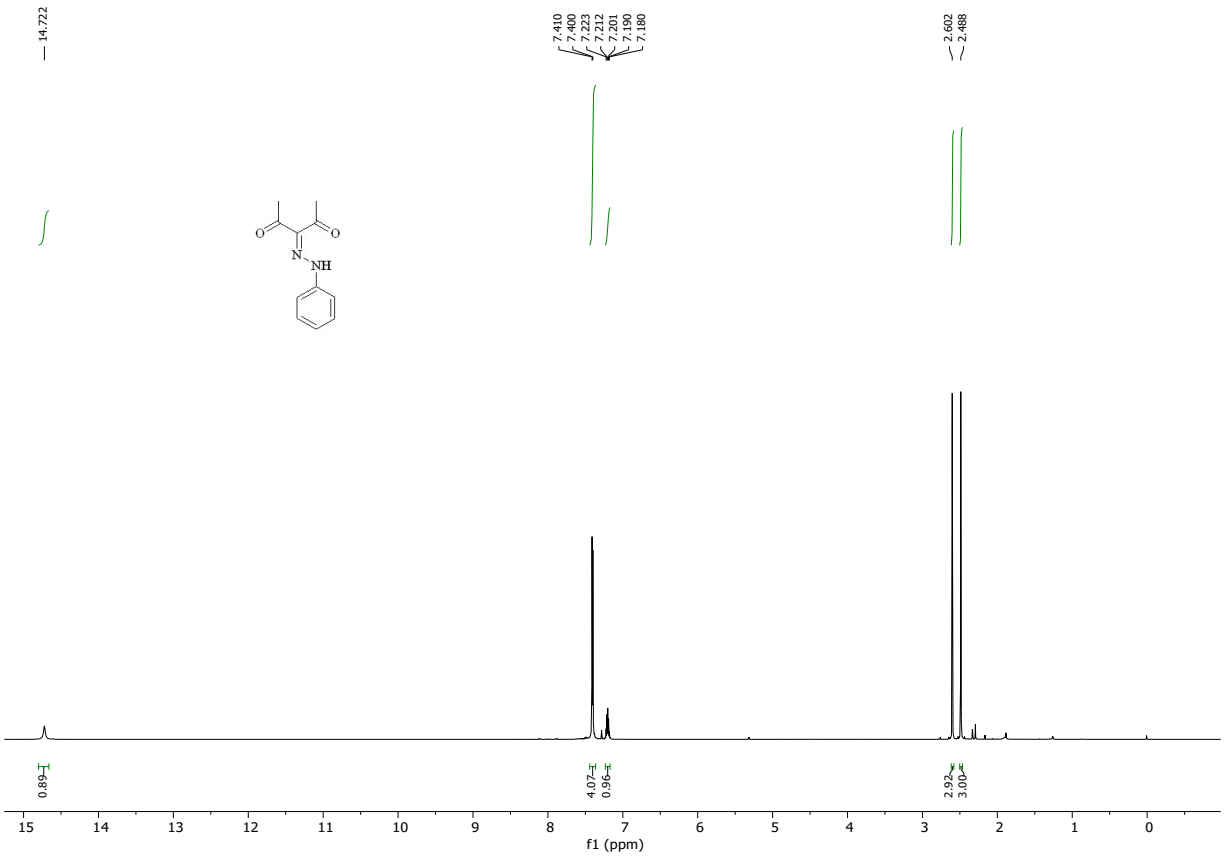


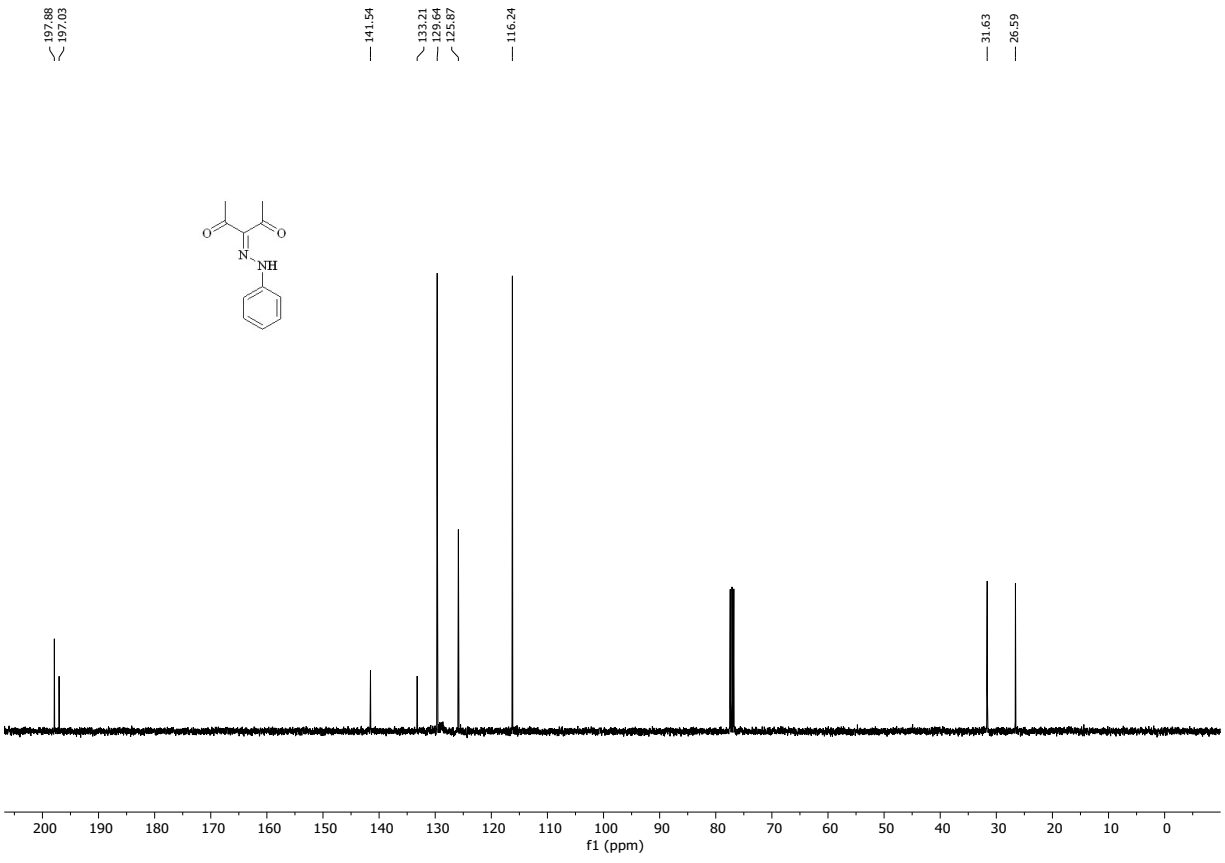


5-(2-(2,6-dimethylphenyl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4ch)

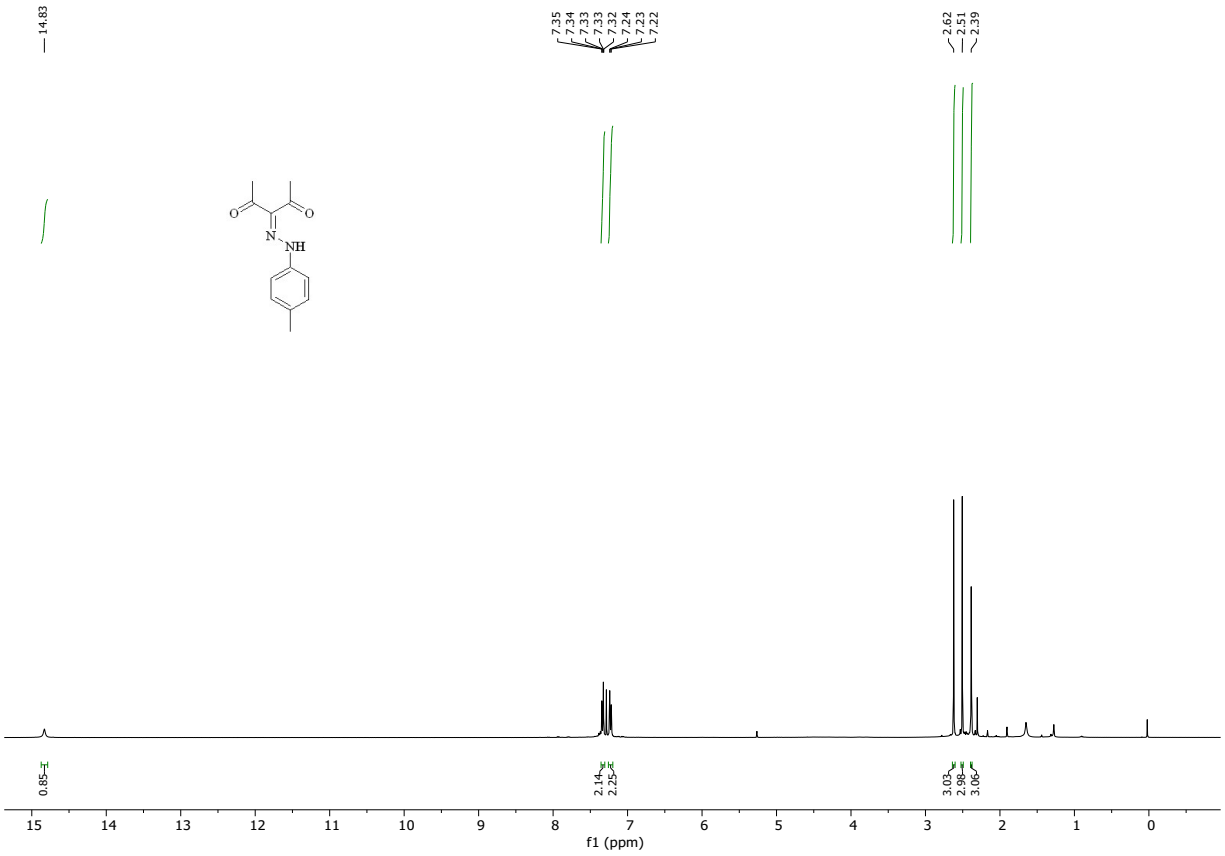


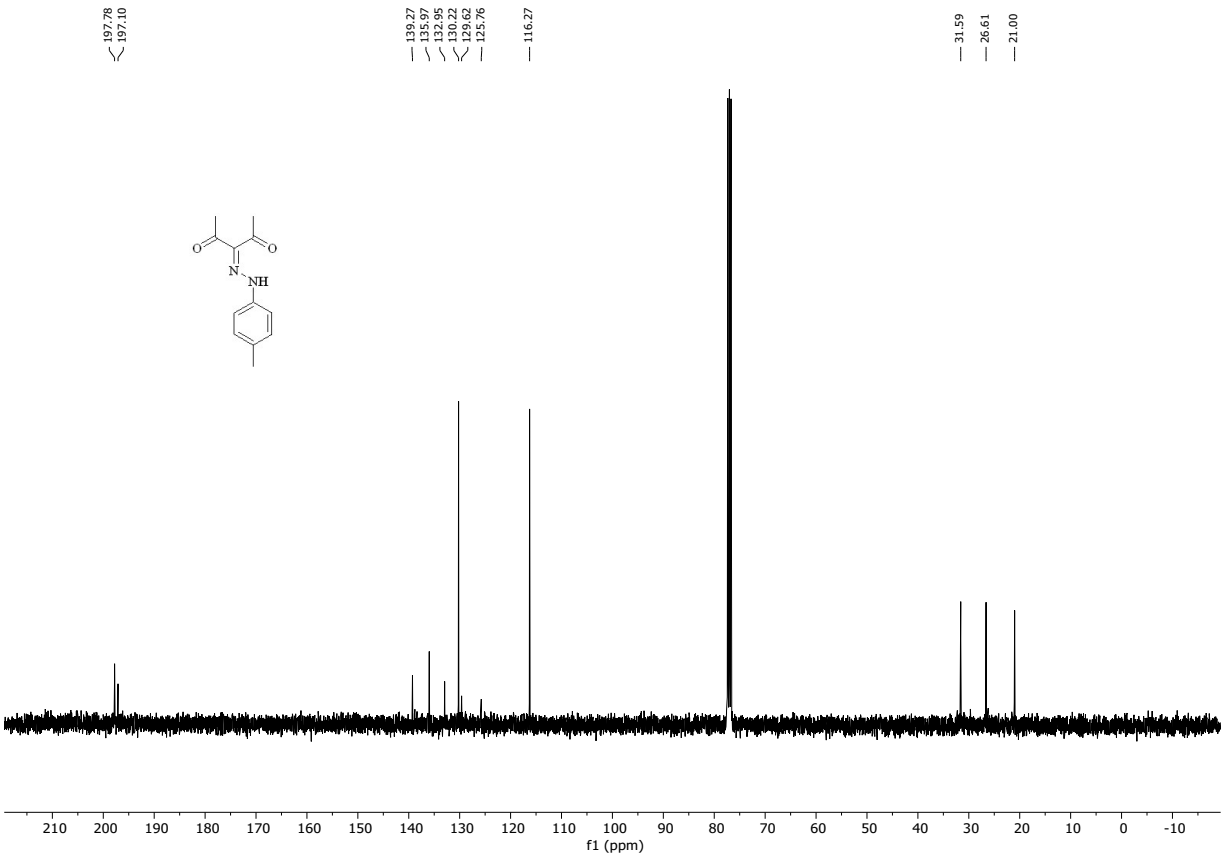
3-(2-phenylhydrazineylidene)pentane-2,4-dione (4da)



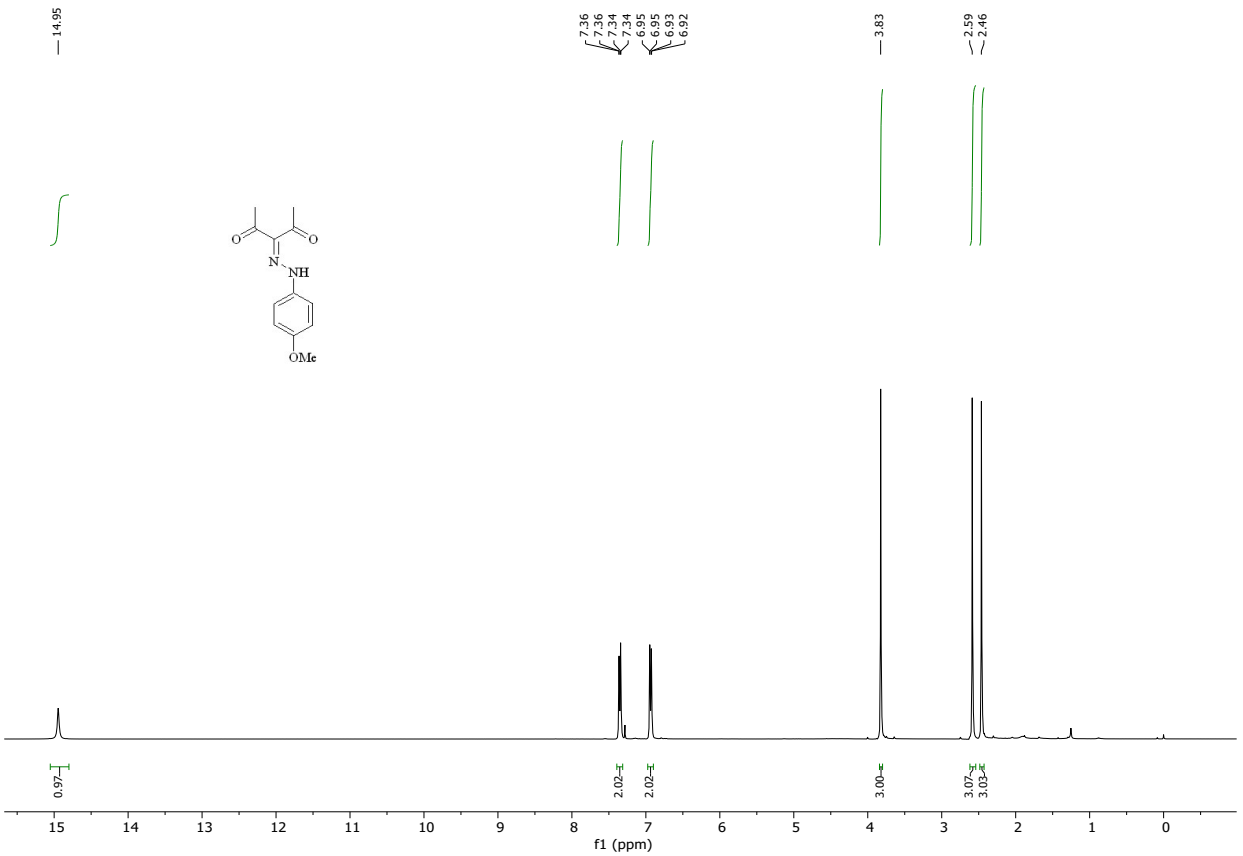


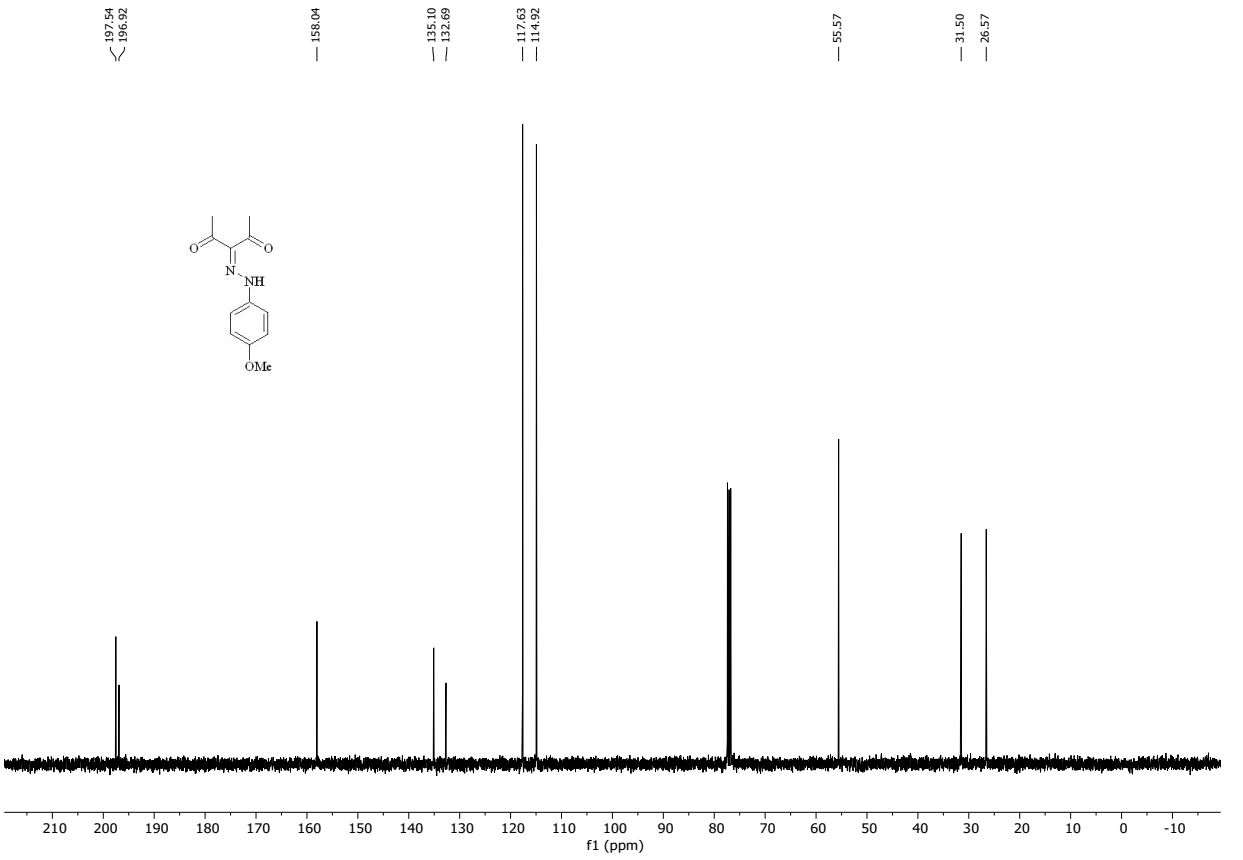
3-(2-(p-tolyl)hydrazineylidene)pentane-2,4-dione (4db)



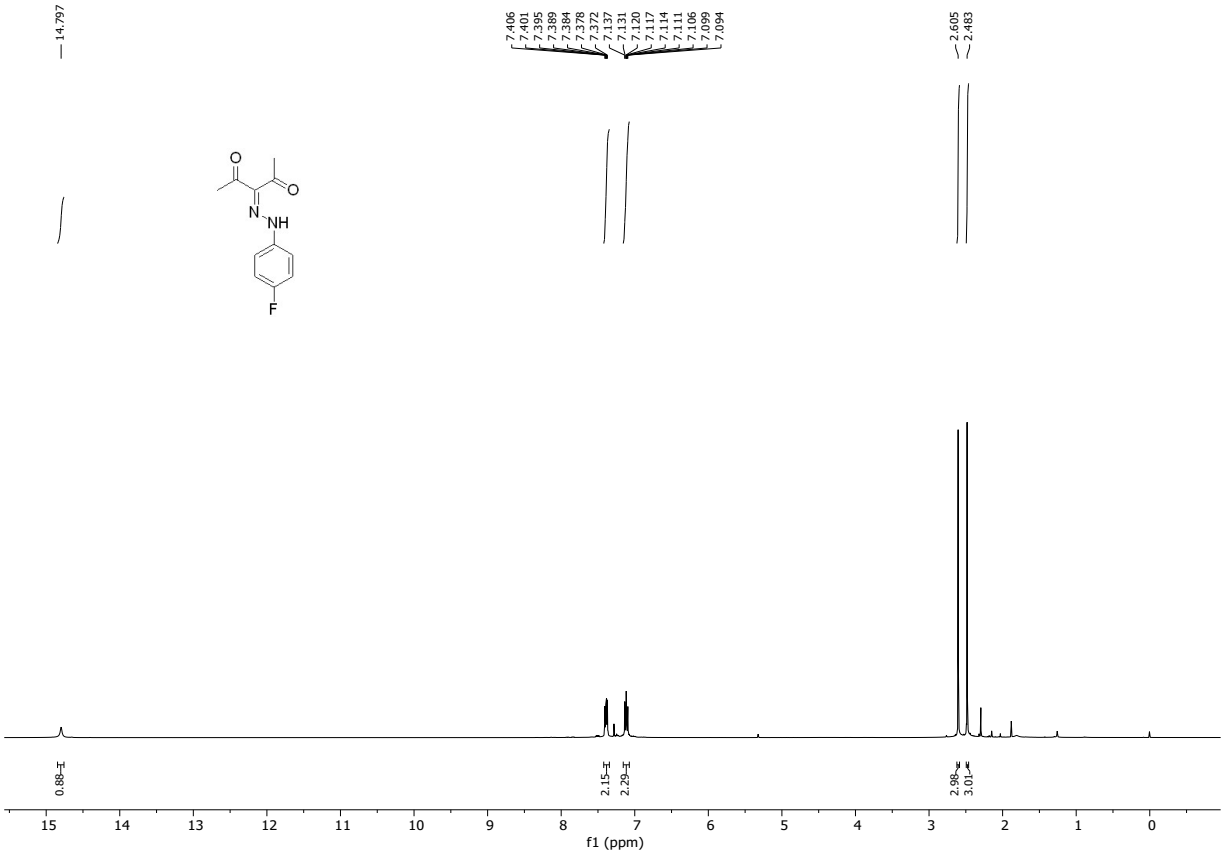


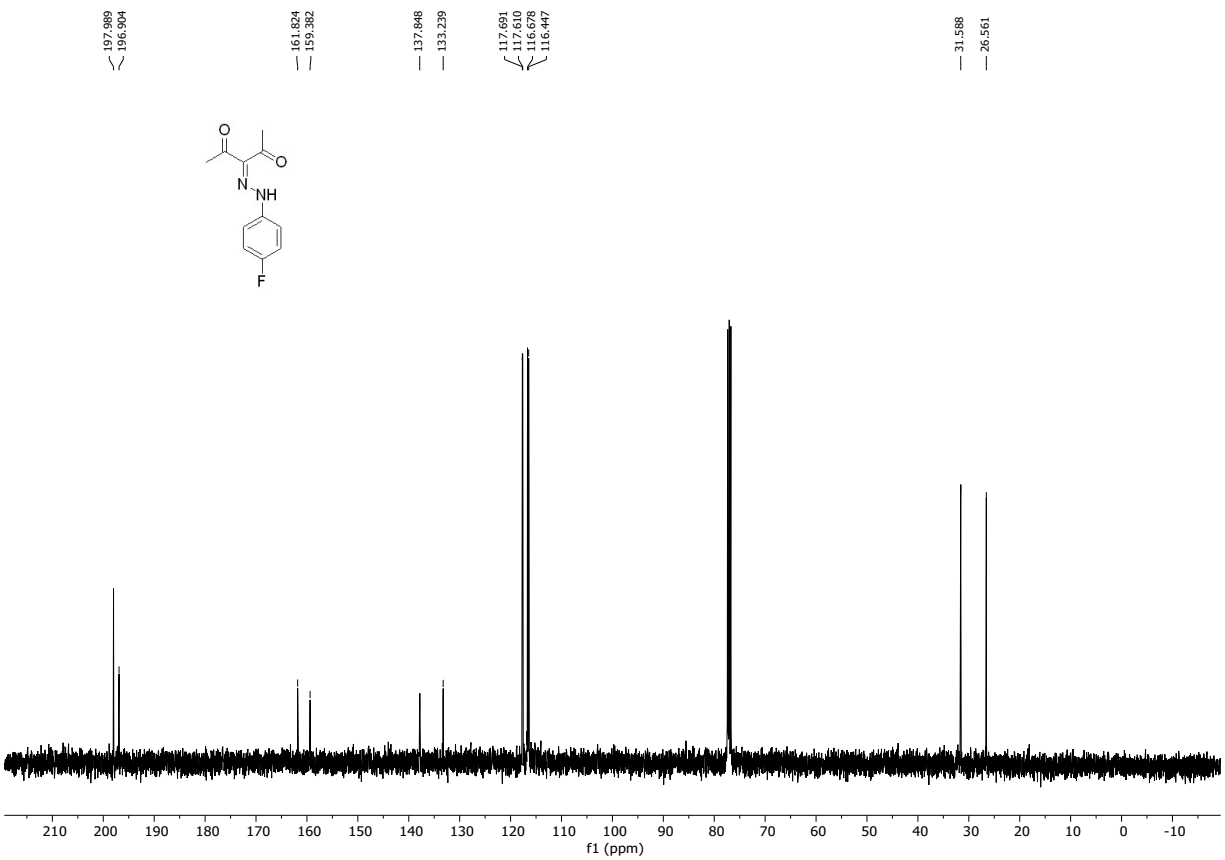
3-(2-(4-methoxyphenyl)hydrazineylidene)pentane-2,4-dione (4dc)



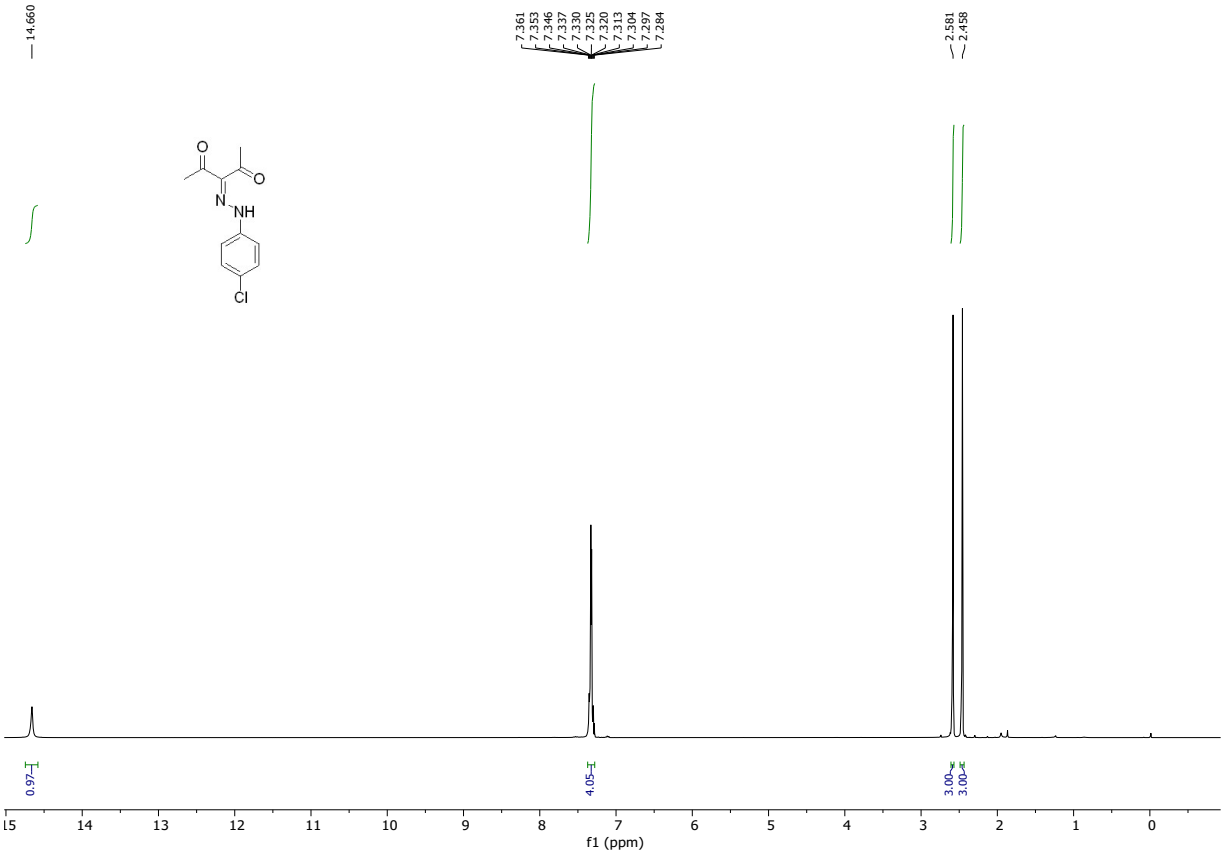


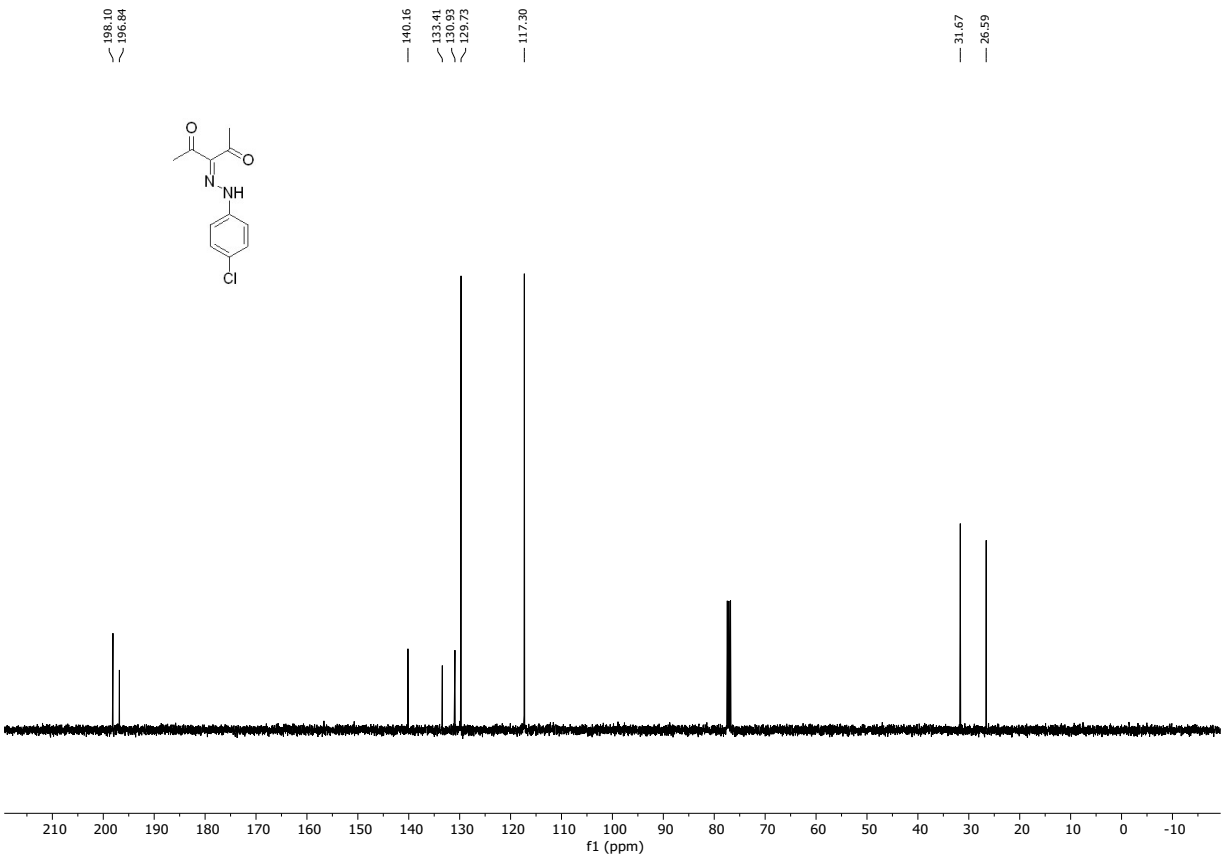
3-(2-(4-fluorophenyl)hydrazineylidene)pentane-2,4-dione (4dd)



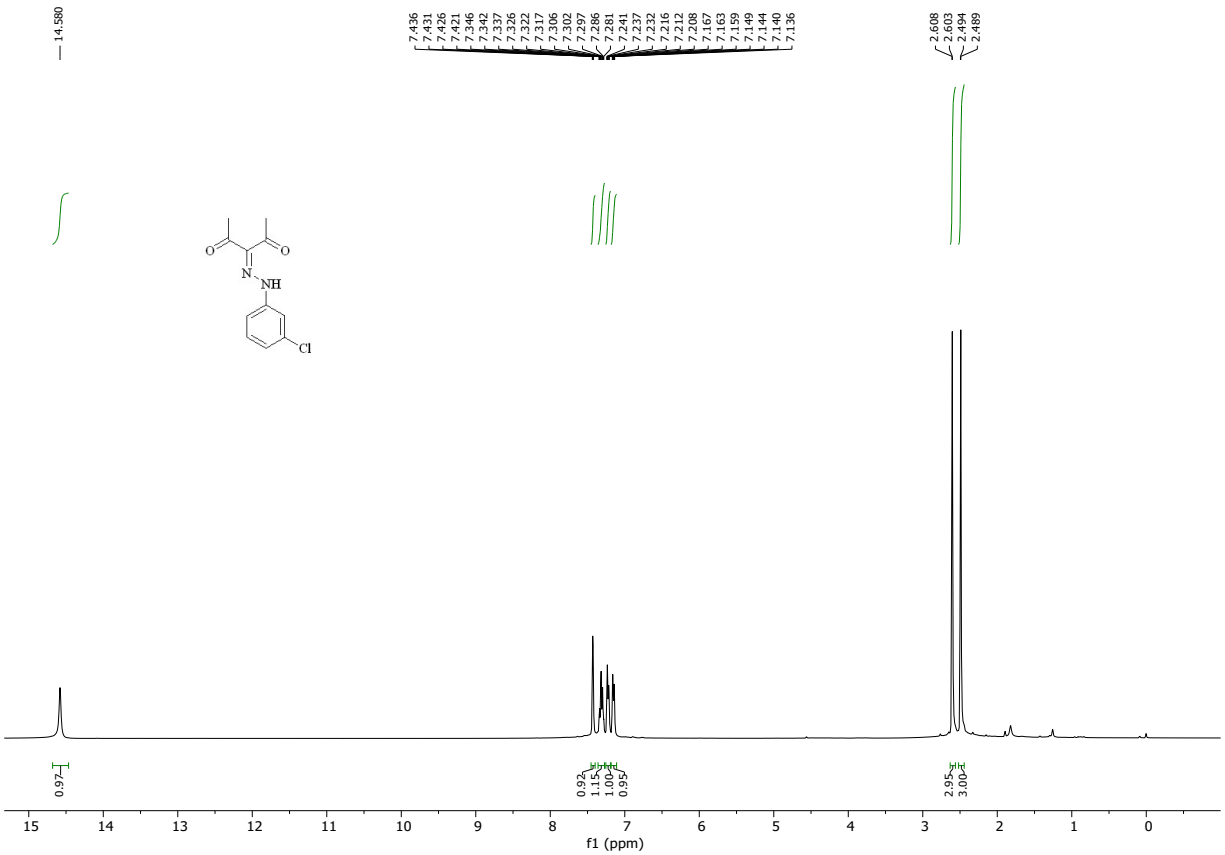


3-(2-(4-chlorophenyl)hydrazineylidene)pentane-2,4-dione (4de)





3-(2-(3-chlorophenyl)hydrazineylidene)pentane-2,4-dione (4df)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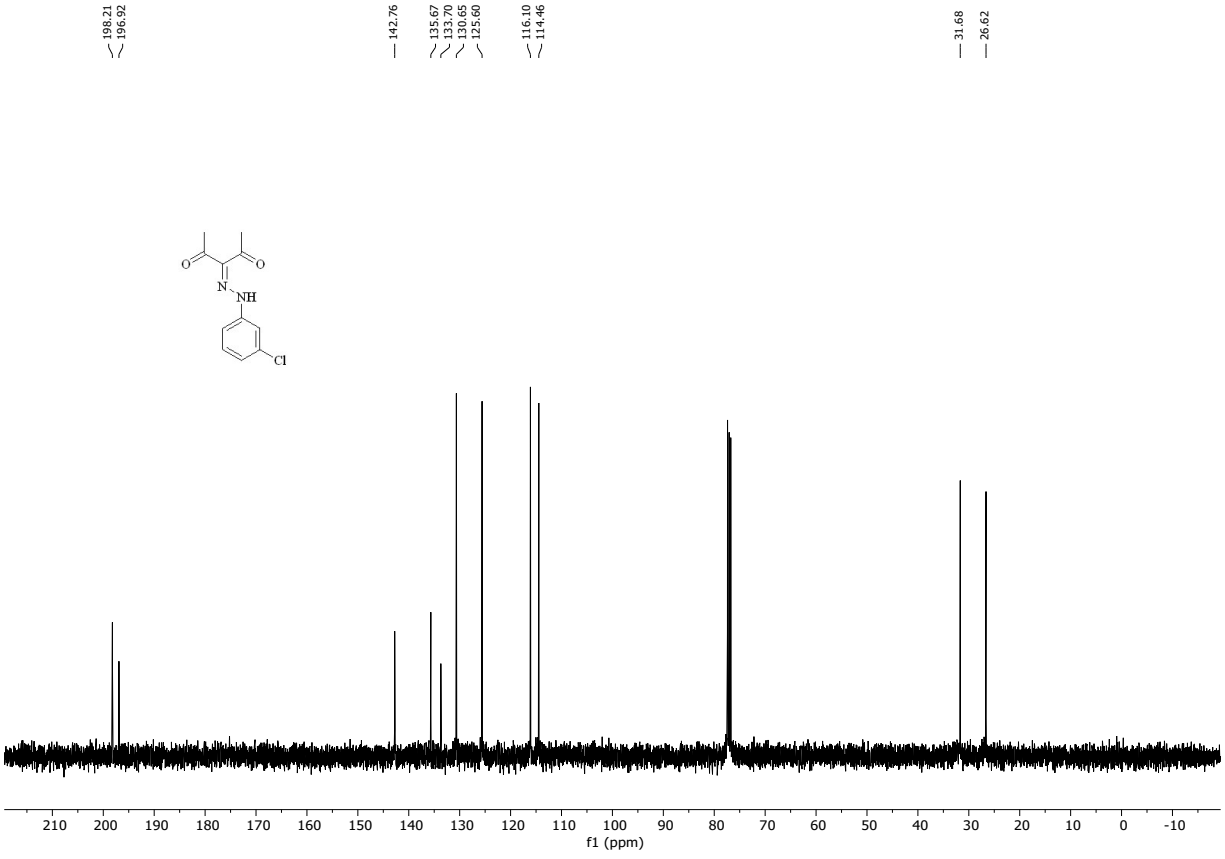
7.302
7.297
7.286
7.281
7.241
7.237
7.232
7.216
7.212
7.208
7.167
7.163
7.159
7.149
7.144
7.140
7.136
2.608
2.603
2.494
2.489
O
O
N
NH
Cl
0.97
0.92
1.15
1.00
0.95
2.95
3.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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116.10
114.46
31.68
26.62
O
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NH
Cl
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)