Photo-Triggered C-Arylation of Active-Methylene Compounds with Diazonium salts Via Electron Donor-Acceptor (EDA) Complex

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1.General consideration

All commercially available reagents and solvents were used directly without further purification. All reactions were conducted under an oxygen atmosphere and oven-dried glassware were used. All reactions were conducted using a blue light-emitting diode (LED) as the visible light source. The progress of reaction measured by thin-layer chromatography (TLC) and visualized using UV light. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. Perkin Elmer Micro analyzer was used for (C and H, All the 1H and 13C spectra were recorded through Bruker 500 MHz spectrometer (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz), in DMSO-d 6 and chemical shift was indicated in δ ppm, using TMS as an internal standard. HRMS (m/z) were recorded in an electron ionization or electrospray ionization (ESI) mode on Waters-Q-TOF Premier-HAB213 and Sciex X500R QTOF instruments.

2. Experimental procedure

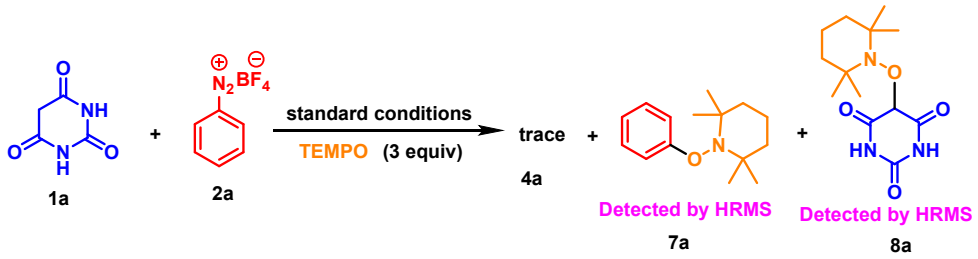
2.1 General procedure for the preparation compound 4a-4i, 4aa-4ak, 5a-5c and 6a-6d.

At first, the benzene diazonium tetrafluoroborate **2a** (1 mmol) was prepared from the amines and after that, added active methylene **1a** (1 mmol) compound in presence of pyridine and dry DMSO as a solvent in insitu condition. Then, the reaction-mixture was stirred at room-temperature and irradiated with blue LED strip at 40-45 min. and thus, the obtained precipitate was filtered and recrystallized.

3. Mechanistic investigation

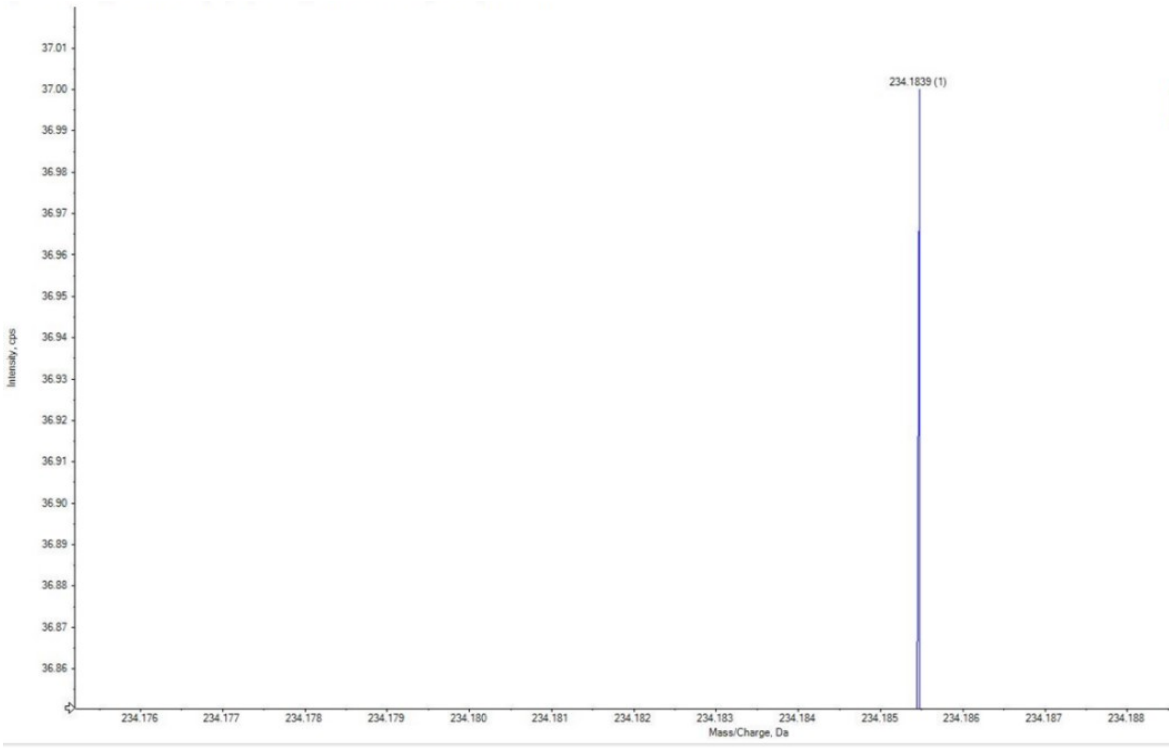
3.1 Radical trapping experiment

To find out the mechanism of the reaction, control experiments were done. Firstly, a radical scavenger TEMPO was added to the reaction- mixture and found that the compound **4a** was obtained in trace amount which showed that the radicals are involved in this reaction. The TEMPO adduct was confirmed from HRMS data.


standard conditions
TEMPO (3 equiv)
trace
4a
Detected by HRMS
7a
Detected by HRMS
8a

1a

2a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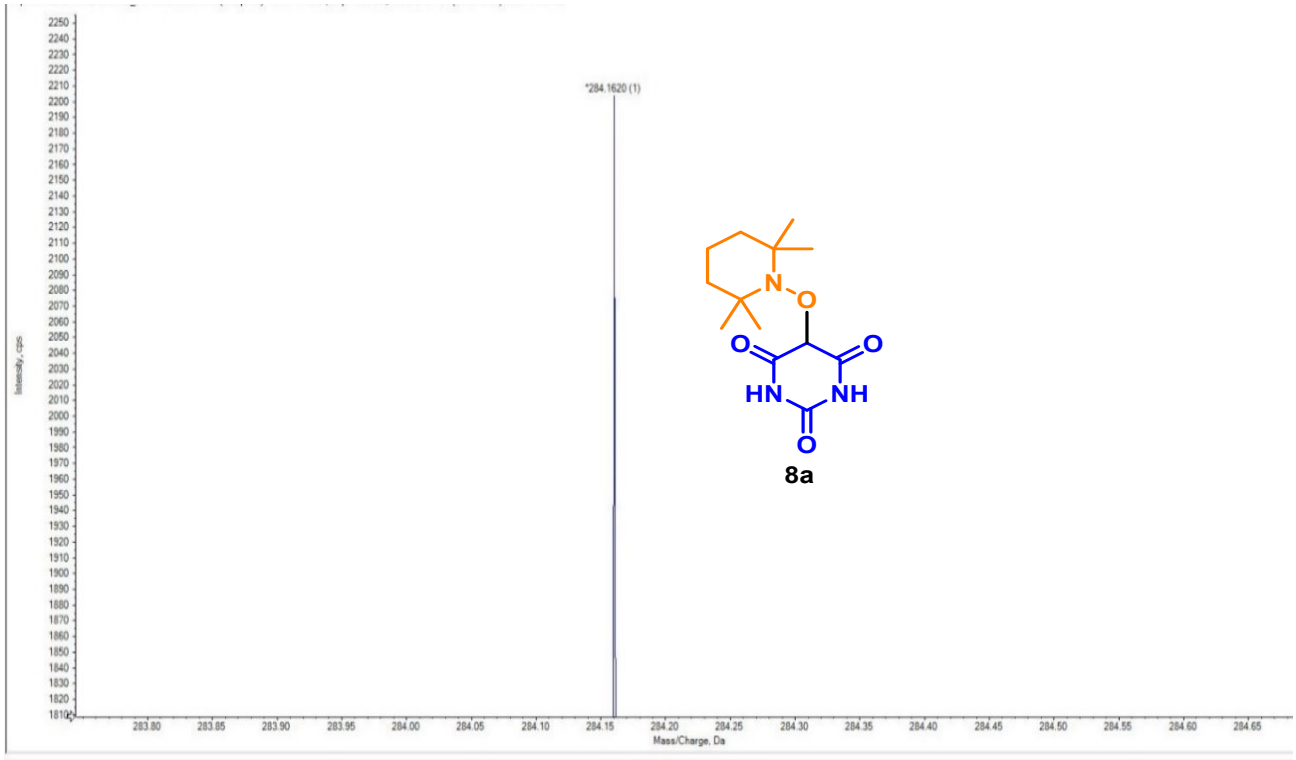
Intensity, cps
Mass/Charge, Da


*284.1620 (1)
Intensity, cps
Mass/Charge, Da

8a

3.2 UV-Vis absorption experiment

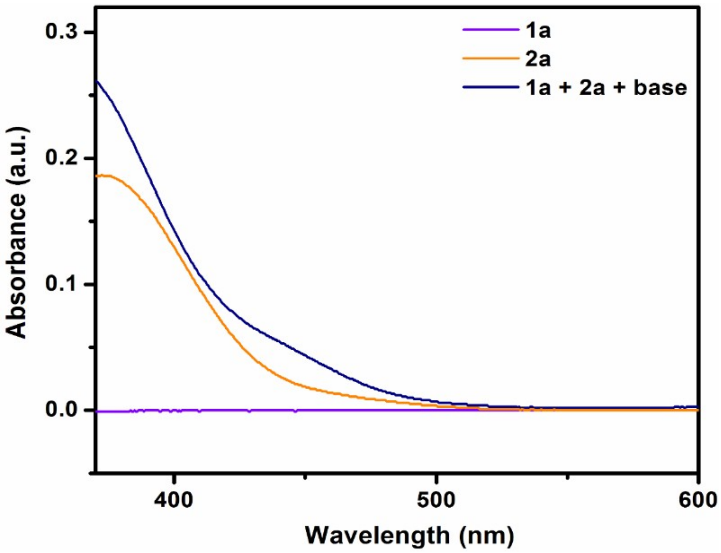


Figure S1. Absorption spectra of **1a**, **2a** and mixture of **1a+2a** and base (left) and photographs of the solutions of **1a, 2a** and mixture (right).

3.3 ON/OFF experiment

The on/off experiment was carried out to see the role of visible light in the reaction. For this, the reaction -mixture was subjected for stirring under visible-light irradiation followed by stirring in the absence of visible-light irradiation at particular time- intervals and we found that reaction proceeds when the mixture was allowed under visible-light and in absence of visible-light, reaction was suspended. Thus, this experiment showed the effect of visible light in the reaction.

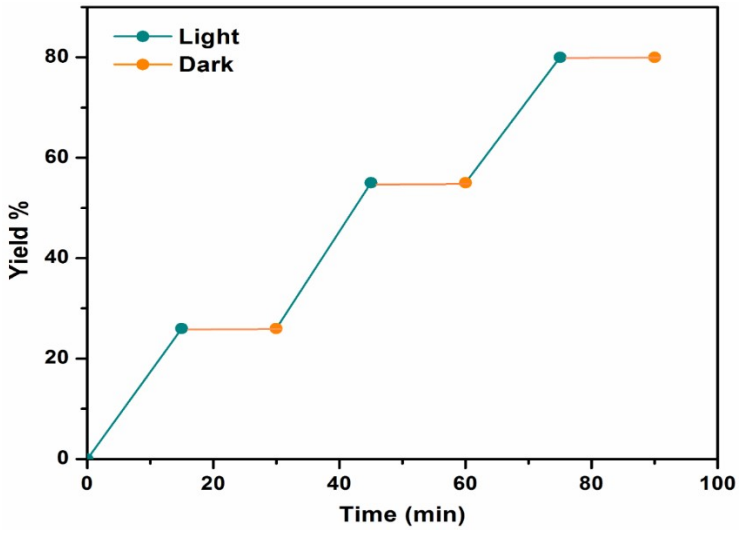


Figure S2. Light on/off experiment

3.4 Job's Plot

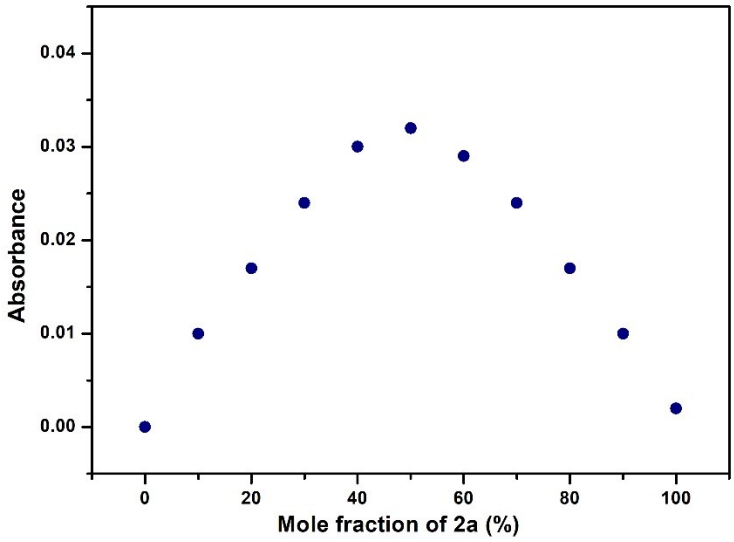
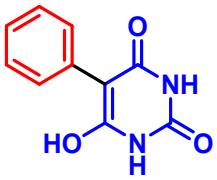


Figure S3. Job's Plot

The Job's plot approach was used for calculating the stoichiometry of the EDA complexes **1a** and **2a**. The Job's plot of the EDA complex between **1a** and **2a** was calculated determining the absorption of Acetonitrile solutions at 490 nm with different donor/acceptor ratios with constant concentration (0.02 M) of the two components. The molar fraction (%) of **2a** was plotted against the absorbance values. A Job's plot study of the EDA complex between **1a** and **2a** revealed a highest absorbance at 50% of 2a's molar fraction, indicating that the EDA complex in solution is 1:1 stoichiometric.

4. Characterization data of compounds



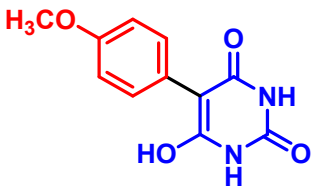
4a

6-hydroxy-5-phenylpyrimidine-2,4(1H,3H)-dione (4a): 84% yield. Yellow solid. m.p: 247-248 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.15 (s, 1H), 11.51 (s, 1H), 11.29 (s, 1H), 7.58 (d, J = 9.6 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.25 (t, J = 7.8 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.6, 160.3, 150.2, 141.8, 130.1, 126.5, 118.2, 117.1.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_9N_2O_3$ 205.0613; found: 205.0615.



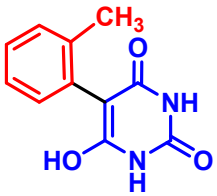
4b

6-hydroxy-5-(4-methoxyphenyl) pyrimidine-2,4(1H,3H)-dione (4b): 91% yield. Yellow solid. m.p: 236-237 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.29 (s, 1H), 11.43 (s, 1H), 11.21 (s, 1H), 7.56 (d, *J* = 9.1 Hz, 2H), 7.0 (d, *J* = 9.1 Hz, 2H), 3.79 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.7, 160.4, 158.3, 150.3, 135.2, 118.7, 115.4, 55.9.

HRMS (ESI) m/z: [M+H] + calculated for $C_{11}H_{11}N_2O_4$ 235.0718; found: 235.0716.



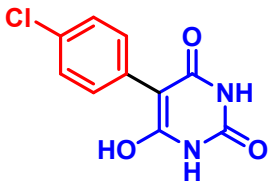
4c

6-hydroxy-5-(o-tolyl) pyrimidine-2,4(1H,3H)-dione (4c): 79% yield. Brownish solid. m.p: 229-230 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.50 (s, 1H), 11.60 (s, 1H), 11.34 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.21 – 7.14 (m, 1H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 163.3, 160.2, 150.2, 139.6, 131.6, 128.0, 126.3, 126.0, 118.9, 115.3, 16.7.

HRMS (ESI) m/z: [M+H] + calculated for $C_{11}H_{11}N_2O_3$ 219.0769; found: 219.0761.



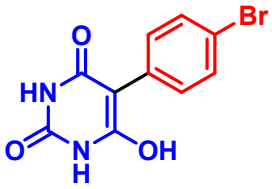
4d

5-(4-chlorophenyl)-6-hydroxypyrimidine-2,4(1H,3H)-dione(4d): 89% yield. Yellow solid. m.p: 217-218 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.04 (s, 1H), 11.53 (s, 1H), 11.32 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.3, 160.2, 150.2, 140.9, 130.1, 130.0, 118.7, 118.6.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_8ClN_2O_3$ 239.0223; found: 239.0224.



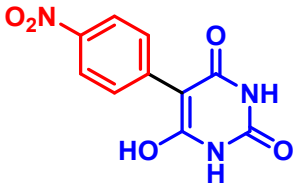
4e

5-(4-bromophenyl)-6-hydroxypyrimidine-2,4(1H,3H)-dione (4e): 81% yield. Yellow solid. m.p: 221-222 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.04 (s, 1H), 11.53 (s, 1H), 11.32 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.3, 160.2, 150.2, 140.9, 130.1, 130.0, 118.7, 118.6.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_8BrN_2O_3$ 282.9718; found: 282.9719.



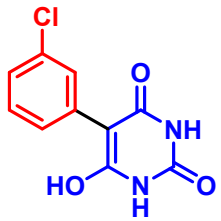
4f

6-hydroxy-5-(4-nitrophenyl) pyrimidine-2,4(1H,3H)-dione (4f): 78% yield. Yellow solid. m.p: 239-240 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 13.98 (s, 1H), 11.66 (s, 1H), 11.44 (s, 1H), 8.32 (d, *J* =9.2 Hz, 2H), 7.79 (d, *J* = 9.2 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.0, 159.9, 150.2, 147.4, 144.2, 126.0, 121.2, 117.1.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_8N_3O_5$ 250.0463; found; 250.0464.



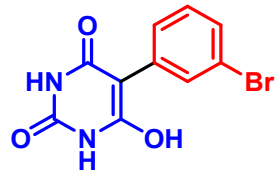
4g

5-(3-chlorophenyl)-6-hydroxypyrimidine-2,4(1H,3H)-dione (4g): 82% yield. Light yellow solid. m.p: 225-226°C

^{1}H NMR (500 MHz, DMSO-d_6) δ 13.96 (s, 1H), 11.56 (s, 1H), 11.35 (s, 1H), 7.67 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.2, 160.2, 150.2, 143.4, 134.5, 131.7, 125.7, 119.1, 116.6, 115.8.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_8ClN_2O_3$ 239.0223; found: 239.0236.



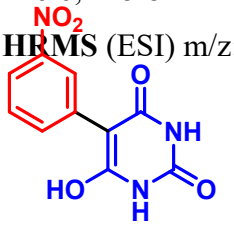
4h

5-(3-bromophenyl)-6-hydroxypyrimidine-2,4(1H,3H)-dione (4h): 75% yield. Yellow solid. m.p: 220-221 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 13.96 (s, 1H), 11.56 (s, 1H), 11.35 (s, 1H), 7.67 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.27 (dd, *J* = 8.2, 1.0 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.2, 160.2, 150.2, 143.4, 134.5, 131.7, 125.7, 119.1, 116.6, 115.8.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_8BrN_2O_3$ 282.9718; found: 282.9717.



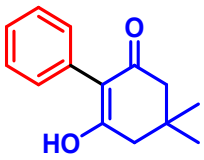
4i

6-hydroxy-5-(3-nitrophenyl) pyrimidine-2,4(1H,3H)-dione (4i): 73% yield. Yellow solid. m.p: 231 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.00 (s, 1H), 11.60 (s, 1H), 11.40 (s, 1H), 8.45 (s, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 8.03 (d, *J* = 2.1 Hz, 1H), 7.73 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 150.2, 149.1, 143.4, 131.4, 123.3, 120.1, 119.9, 111.4, 56.4, 19.0.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_8N_3O_5$ 250.0463; found: 250.0455.



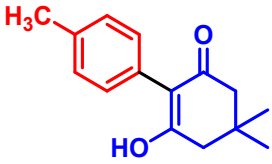
4aa

6-hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (4aa): 90% yield. Shiny red solid. m.p: 239-240 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.89 (s, 1H), 7.61 (d, *J* = 9.5 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 2.65 (s, 2H), 2.57 (s, 2H), 1.04 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.3, 193.1, 141.9, 130.5, 130.1, 126.9, 117.5, 52.4, 52.1, 30.7, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{14}H_{17}O_2$ 217.1228; found: 217.1229.



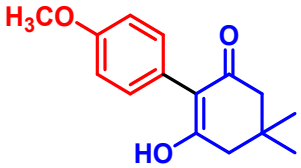
4ab

6-hydroxy-4,4,4'-trimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (4ab): 89% yield. Yellow solid. m.p: 219-220 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 15.00 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.63 (s, 2H), 2.55 (s, 2H), 2.32 (s, 3H), 1.03 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.2, 193.1, 139.5, 136.7, 130.6, 130.2, 117.5, 52.4, 52.0, 30.7, 28.4, 21.0.

HRMS (ESI) m/z: [M+H] + calculated for $C_{15}H_{19}O_2$ 231.1385; found: 231.1386.



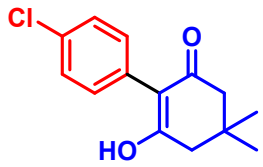
4ac

6-hydroxy-4'-methoxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (4ac) :92% yield. Brown solid. m.p: 246-247 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 15.15 (s, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 2.61 (s, 2H), 2.53 (s, 2H), 1.03 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 196.7, 192.9, 158.6, 135.2, 129.9, 119.1, 115.4, 55.9, 52.3, 51.9, 30.8, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{15}H_{19}O_3$ 247.1334; found: 247.1322.



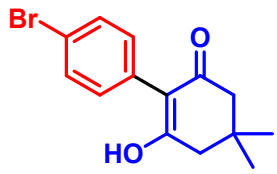
4ad

4'-chloro-6-hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (4ad): 88% yield. Yellow solid. m.p: 248 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.73 (s, 1H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 2.65 (s, 2H), 2.57 (s, 2H), 1.04 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.3, 193.2, 144.5, 144.3, 141.0, 130.0, 126.8, 119.2, 52.4, 52.2, 30.7, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{14}H_{16}ClO_2$ 251.0838; found: 251.0838.



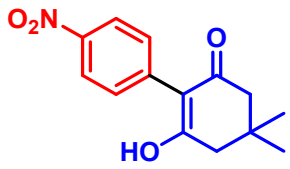
4ae

4'-bromo-6-hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (4ae): 83% yield. Yellow solid. m.p: 219 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.73 (s, 1H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 2.65 (s, 2H), 2.57 (s, 2H), 1.04 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.3, 193.2, 144.5, 144.3, 141.0, 130.0, 126.8, 119.2, 52.4, 52.2, 30.7, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{14}H_{16}BrO_2$ 295.0333; found: 295.0334.



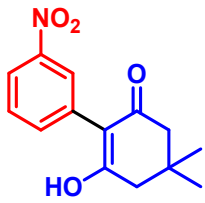
4af

6-hydroxy-4,4-dimethyl-4'-nitro-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one(4af): 79% yield. reddish solid. m.p: 247-248 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.49 (s, 1H), 8.32 (d, *J* = 9.2 Hz, 2H), 7.83 (d, *J* = 9.2 Hz, 2H), 2.71 (s, 2H), 2.63 (s, 2H), 1.05 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.8, 193.5, 147.6, 146.2, 144.6, 132.2, 126.1, 126.0, 52.5, 52.4, 30.6, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{14}H_{16}NO_4$ 262.1079; found: 262.1078.



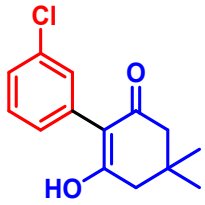
4ag

6-hydroxy-4,4-dimethyl-3'-nitro-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one(4ag): 77% yield. black solid. m.p: 219°C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.57 (s, 1H), 8.48 (s, 1H), 8.07 (d, *J* = 2.2 Hz, 1H), 8.05 (d, *J* = 2.2 Hz, 1H), 7.73 (t, *J* = 8.2 Hz, 1H), 2.69 (s, 2H), 2.62 (s, 2H), 1.05 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.4, 193.4, 149.1, 143.6, 131.4, 123.8, 120.5, 111.9, 52.5, 52.3, 30.6, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{14}H_{16}NO_4$ 262.1079; found: 262.1080.



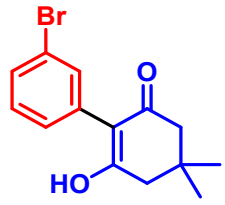
4ah

3'-chloro-6-hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one(4ah): 82% yellow solid. yield. m.p: 245-246 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.60 (s, 1H), 7.70 (s, 1H), 7.60 – 7.57 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 2.66 (s, 2H), 2.58 (s, 2H), 1.04 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.4, 193.2, 143.6, 134.5, 134.3, 131.7, 131.0, 126.1, 117.0, 116.2, 52.4, 52.2, 30.6, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{14}H_{16}ClO_2$ 251.0838; found: 251.0839.



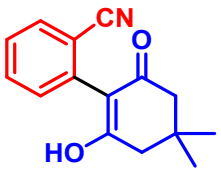
4ai

3'-bromo-6-hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one(4ai): 78% yield. yellow solid. m.p: 227-228 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.60 (s, 1H), 7.70 (s, 1H), 7.58 (d, *J* = 9.5 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 2.66 (s, 2H), 2.58 (s, 2H), 1.04 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.4, 193.2, 143.6, 134.5, 134.3, 131.7, 131.0, 126.1, 117.0, 116.2, 52.4, 52.2, 30.6, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{14}H_{16}BrO_2$ 295.0333; found: 295.0335.



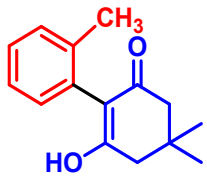
4aj

6'-hydroxy-4',4'-dimethyl-2'-oxo-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carbonitrile(4aj): 76% yield. reddish solid. m.p: 229 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 15.20 (s, 1H), 7.90 (dd, *J* = 13.2, 4.9 Hz, 2H), 7.82 (t, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 2.73 (s, 2H), 2.63 (s, 2H), 1.06 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 198.8, 193.2, 144.4, 135.5, 133.7, 132.3, 126.4, 116.4, 100.4, 52.4, 52.2, 30.6, 28.4.

HRMS (ESI) m/z: [M+H] + calculated for $C_{15}H_{16}NO_2$ 242.1181; found: 242.1182.



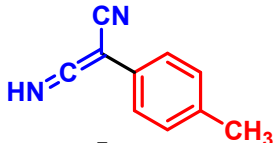
4ak

6-hydroxy-2',4,4-trimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (4ak): 78% yield. Black solid. m.p: 209 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 15.33 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 2.68 (s, 2H), 2.57 (s, 2H), 2.37 (s, 3H), 1.05 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.8, 193.1, 139.7, 131.6, 131.3, 128.1, 126.8, 126.6, 115.5, 52.4, 52.0, 30.8, 28.4, 16.8.

HRMS (ESI) m/z: [M+H] + calculated for $C_{15}H_{19}O_2$ 231.1385; found:231.1384.



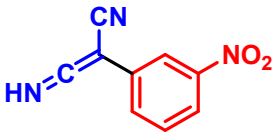
5a

3-imino-2-(p-tolyl) acrylonitrile(5a): 88% yield. Shiny yellow solid. m.p: 156-157 °C

^{1}H NMR (500 MHz, DMSO-d_6) 7.37 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 139.6, 135.8, 130.4, 116.9, 114.9, 110.5, 84.2, 20.9.

HRMS (ESI) m/z: [M+H] + calculated for $C_{10}H_9N_2$ 157.0765; found: 157.0764



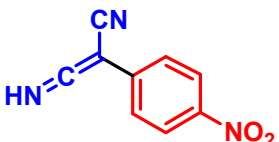
5b

3-imino-2-(3-nitrophenyl) acrylonitrile (5b): 77% yield. Brown solid. m.p: 163°C

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (s, 1H), 8.02 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.70 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 148.9, 143.4, 131.5, 122.8, 120.1, 114.5, 111.5, 110.2, 87.2.

HRMS (ESI) m/z: [M+H] + calculated for $C_9H_6N_3O_2$ 188.0460; found: 188.0461.



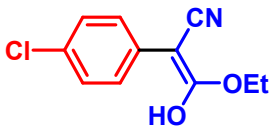
5c

3-imino-2-(4-nitrophenyl) acrylonitrile (5c): 88% yield. Shiny orange solid. m.p: 159 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28 (d, *J* = 9.3 Hz, 2H), 7.64 (d, *J* = 9.3 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 147.7, 144.3, 126.0, 117.2, 114.5, 110.1, 88.7.

HRMS (ESI) m/z: [M+H] + calculated for $C_9H_6N_3O_2$ 188.0460; found: 188.0462.



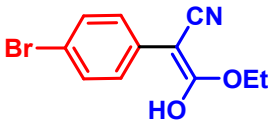
6a

(Z)-2-(4-chlorophenyl)-3-ethoxy-3-hydroxyacrylonitrile(6a): 83% yield. Yellow solid. m.p: 161-162°C

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 160.8, 140.7, 129.8, 118.4, 118.1, 116.1, 105.4, 62.4, 14.3.

HRMS (ESI) m/z: [M+H] + calculated for $C_{11}H_{11}ClNO_2$ 224.0478; found: 224.0479.



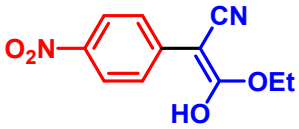
6b

(Z)-2-(4-bromophenyl)-3-ethoxy-3-hydroxyacrylonitrile (6b): 78% yield. Yellow solid. m.p: 136 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 160.8, 140.7, 129.8, 118.4, 118.1, 116.1, 105.4, 62.4, 14.3.

HRMS (ESI) m/z: [M+H] + calculated for $C_{11}H_{11}BrNO_2$ 267.9973; found: 267.9975.



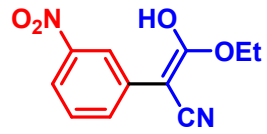
6c

(Z)-3-ethoxy-3-hydroxy-2-(4-nitrophenyl) acrylonitrile (6c): 79% yield. Yellow solid. m.p: 146-147 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.31 (d, *J* = 9.3 Hz, 2H), 7.65 (d, *J* = 9.3 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 160.7, 147.0, 143.7, 126.0, 116.6, 111.3, 108.2, 62.4, 14.5.

HRMS (ESI) m/z: [M+H] + calculated for $C_{11}H_{11}N_2O_4$ 235.0718; found: 235.0719.



6d

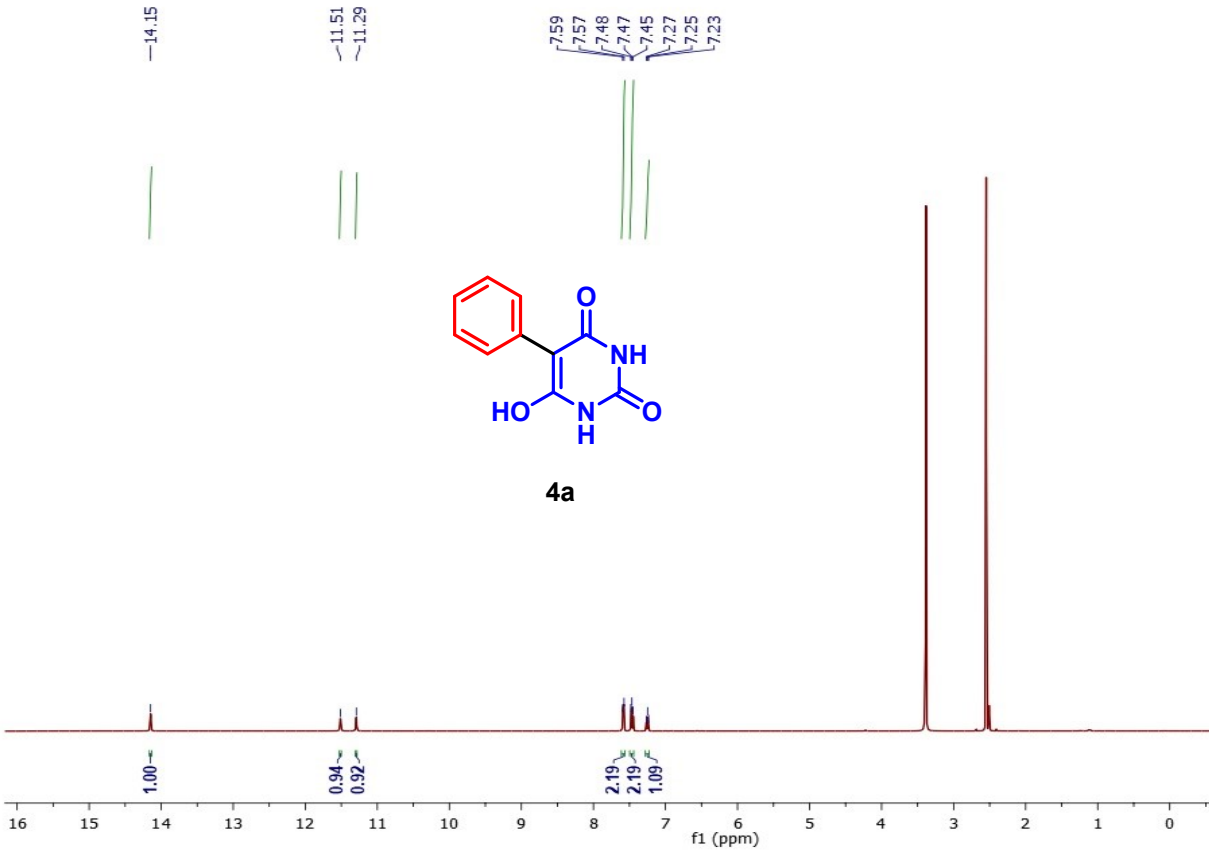
(Z)-3-ethoxy-3-hydroxy-2-(3-nitrophenyl) acrylonitrile (6d): 76% yield. Yellow solid. m.p: 137-138 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.50 (s, 1H), 8.26 (s, 1H), 7.96 -7.93 (m, 1H), 7.84 -7.81 (m, 1H), 7.68 (t, J = 8.2 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H).

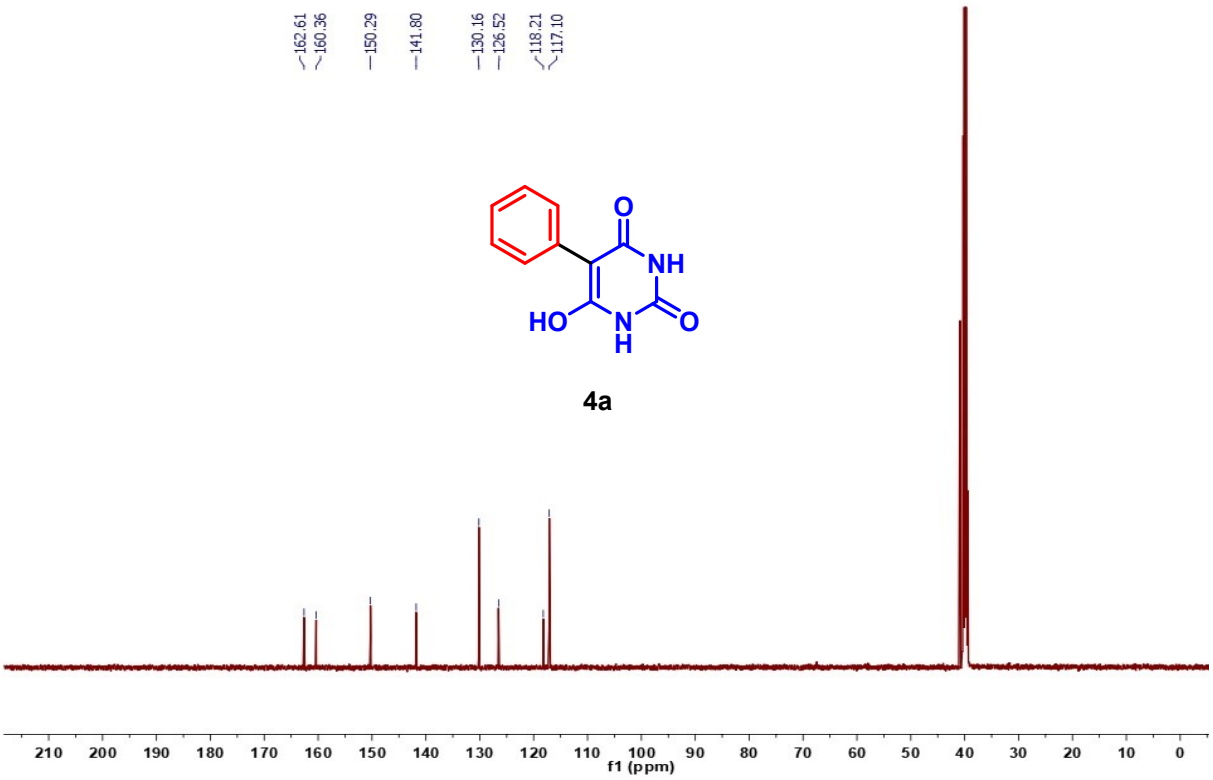
^{13}C NMR (126 MHz, DMSO-d_6) δ 160.8, 148.9, 143.5, 131.4, 122.3, 119.2, 111.4, 110.9, 106.5, 62.3, 14.5.

HRMS (ESI) m/z: [M+H] + calculated for $C_{11}H_{10}N_2O_4$ 234.0640; found: 234.0641.

5. Copies of NMR spectra



4a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141.80
130.16
126.52
118.21
117.10
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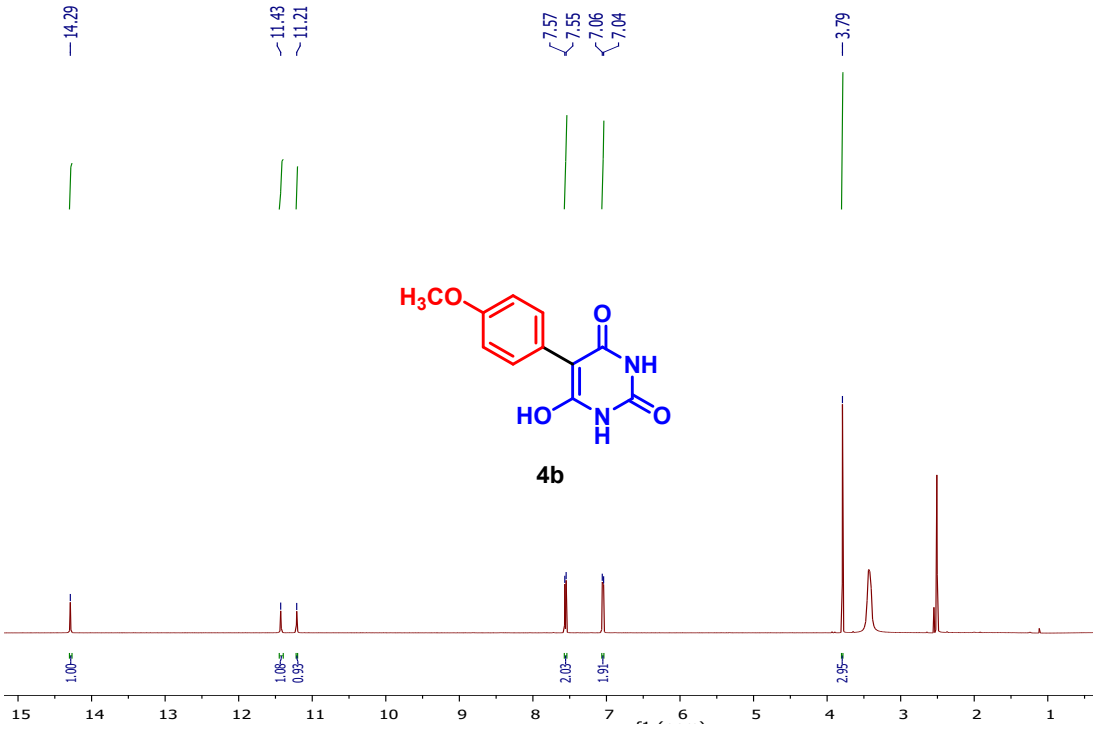
NH
HO
N
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4a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11.43
11.21
7.57
7.55
7.06
7.04
3.79
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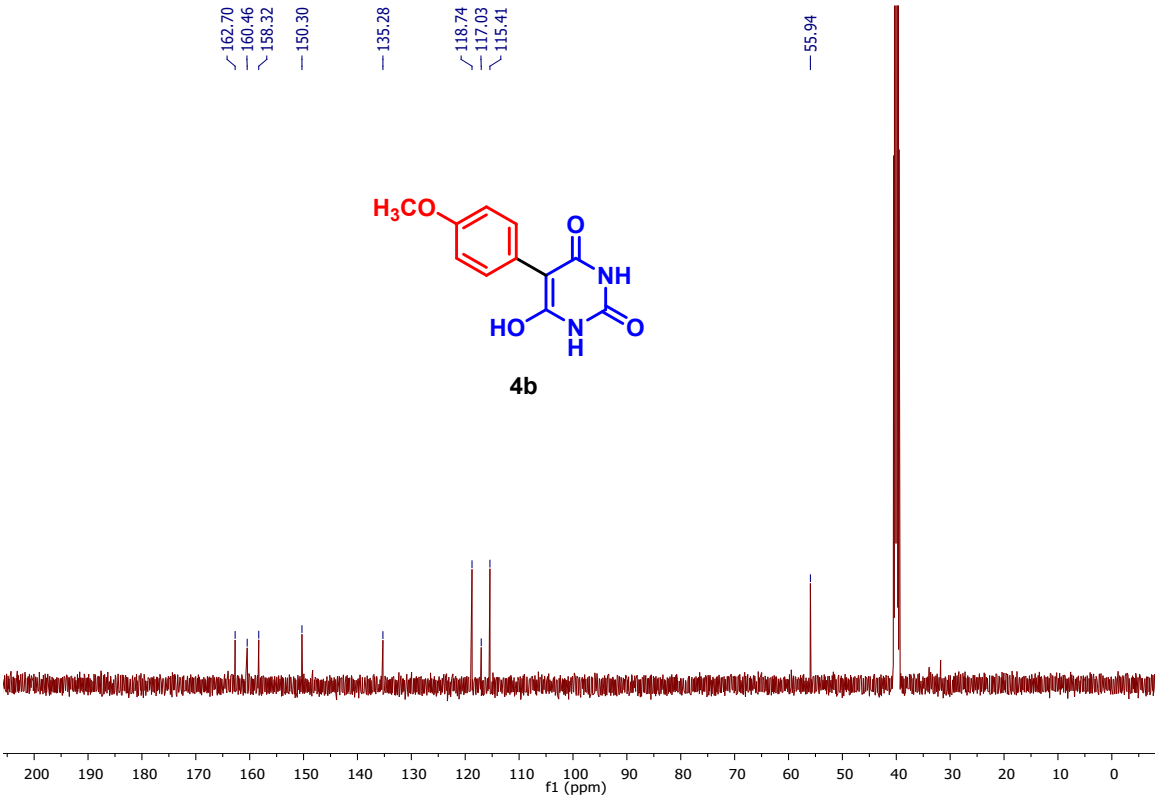
O
NH
HO
N
H
O
1.00
1.08
0.93
2.03
1.91
2.95
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

4b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160.46
158.32
150.30
135.28
118.74
117.03
115.41
55.94
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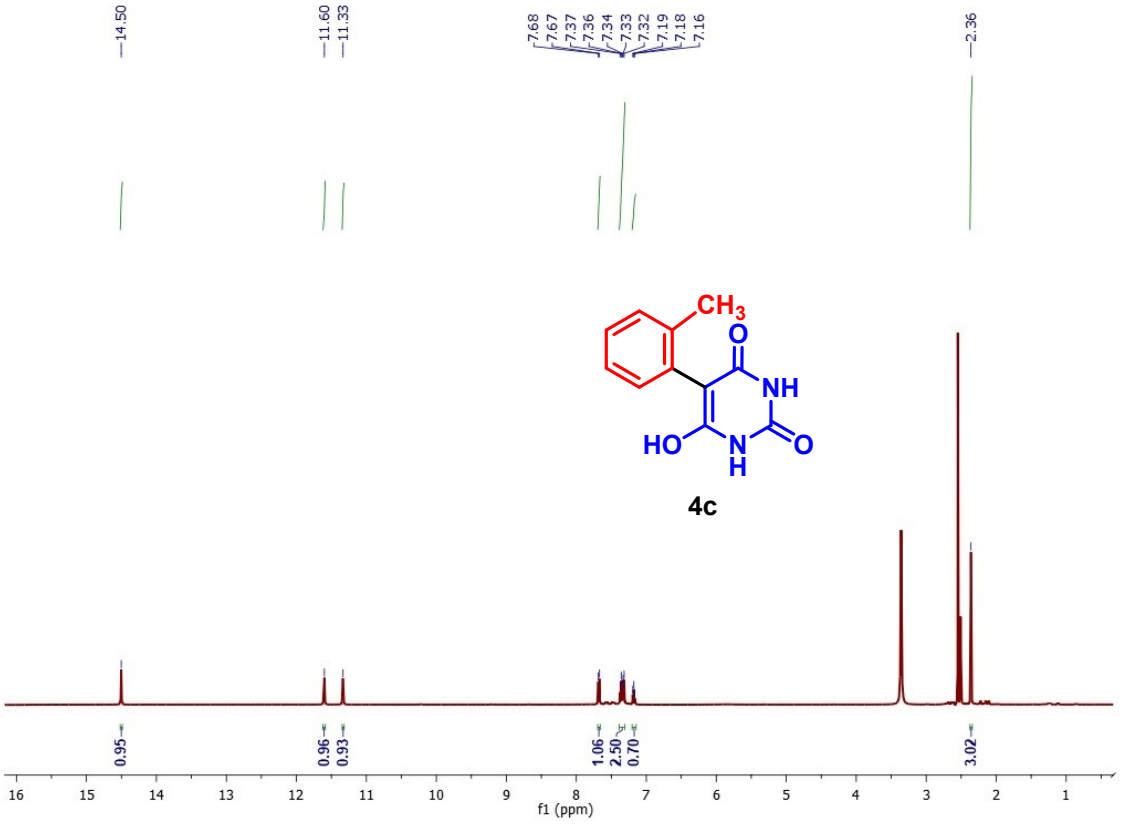
NH
HO
N
H
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4b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11.60
11.33
7.68
7.67
7.37
7.36
7.34
7.33
7.32
7.19
7.18
7.16
2.36
CH3
O
NH
HO
N
H
O
0.95
0.96
0.93
1.06
2.50
0.70
3.02
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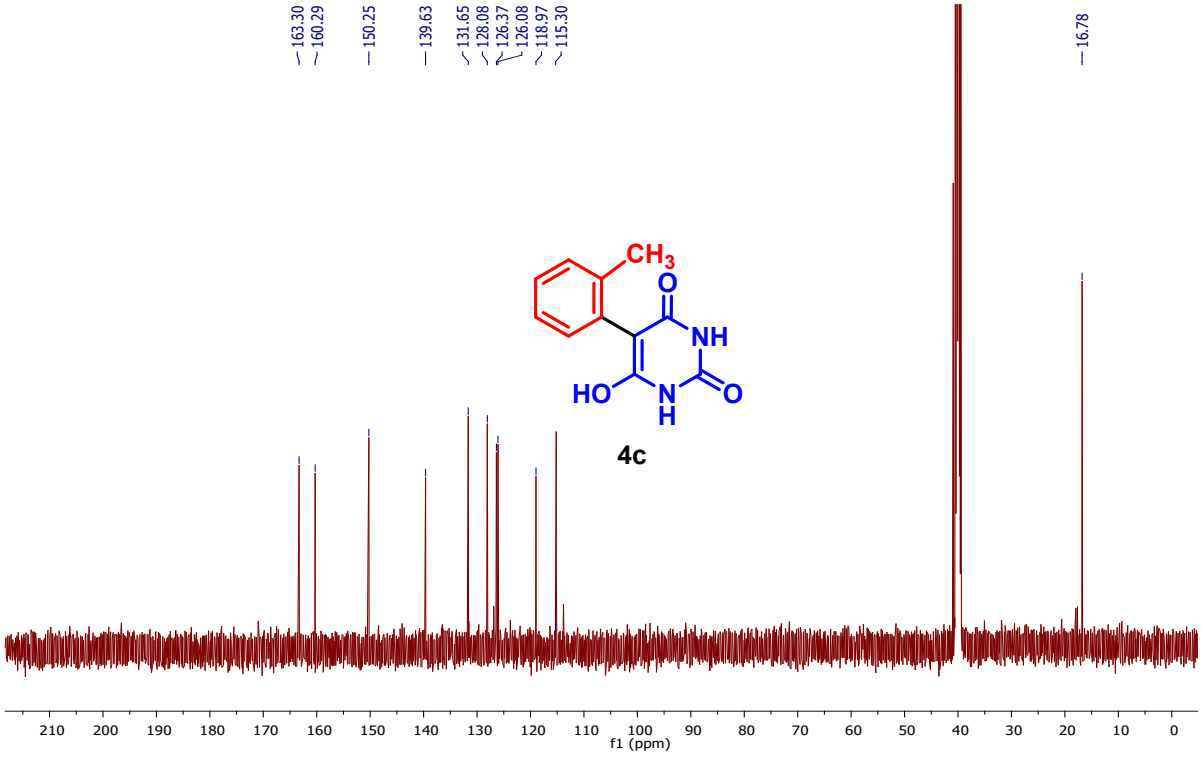
f1 (ppm)

4c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139.63
131.65
128.08
126.37
126.08
118.97
115.30
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NH
HO
N
H
O
4c
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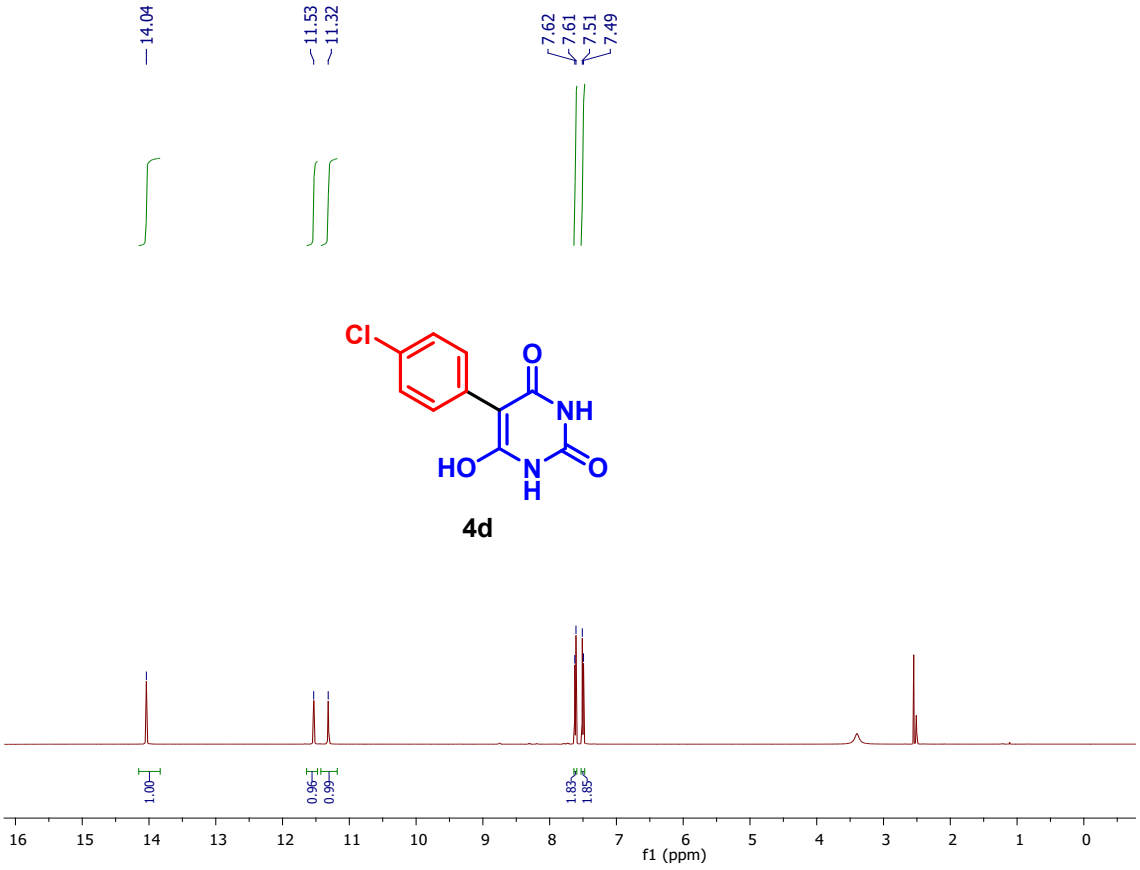
f1 (ppm)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11.32
7.62
7.61
7.51
7.49
Cl
O
NH
HO
N
H
O
4d
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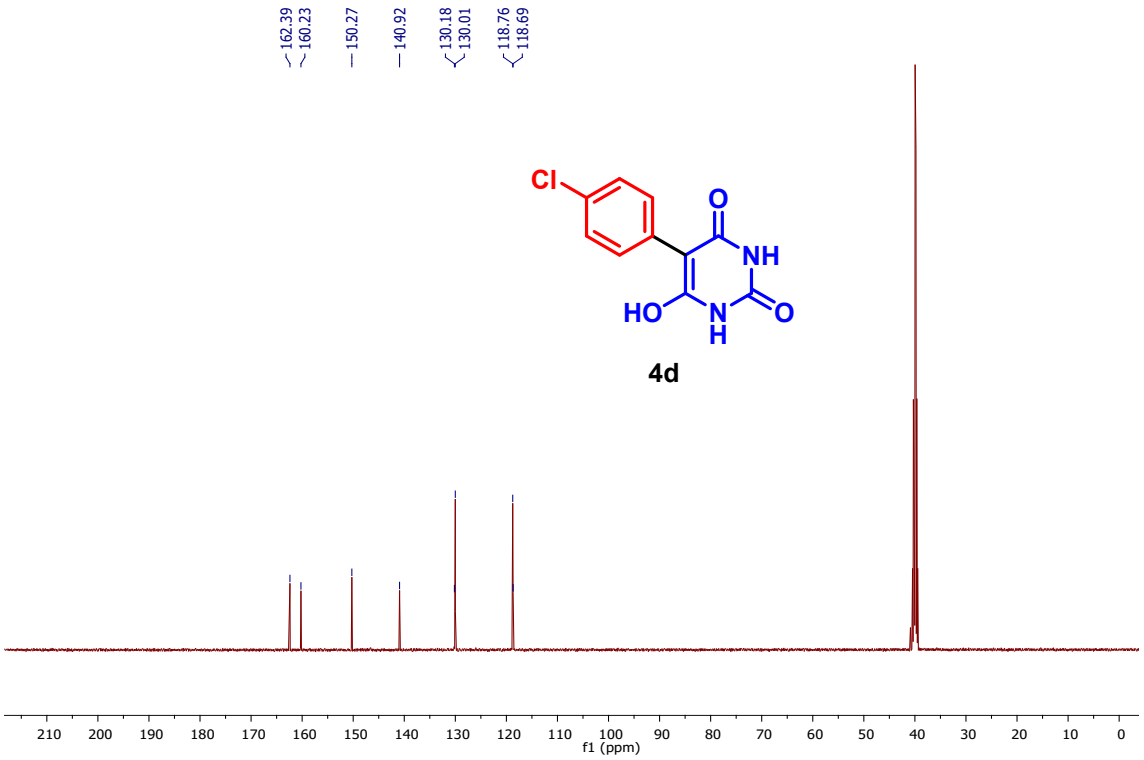
0.96
0.99
1.83
1.85
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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HO
N
H
O
4d
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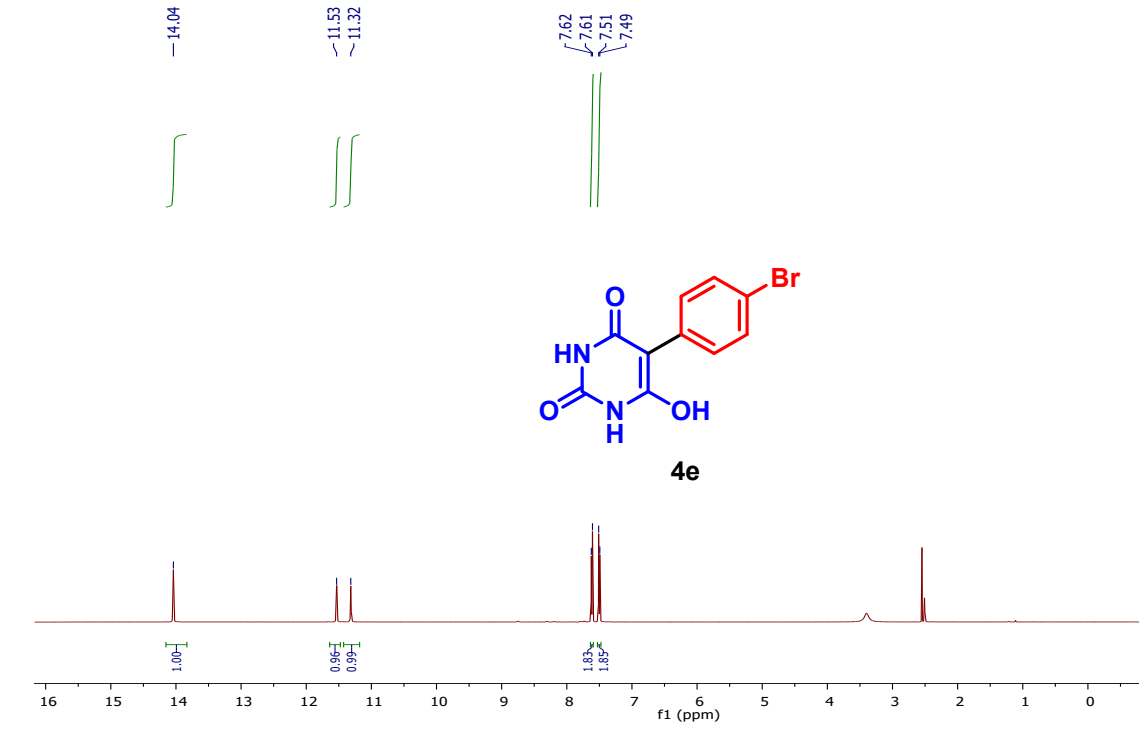
f1 (ppm)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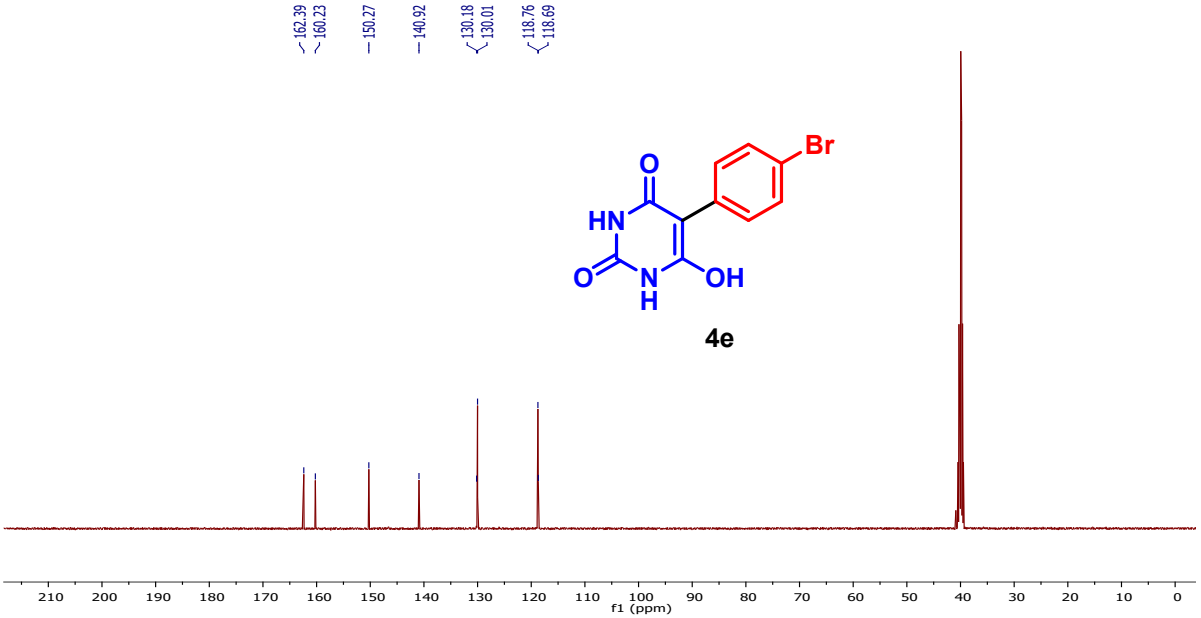
11.53
11.32
7.62
7.61
7.51
7.49
Br
O
HN
O
N
H
OH
4e
1.00
0.96
0.99
1.83
1.85
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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140.92
130.18
130.01
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HN
O
N
H
OH
4e
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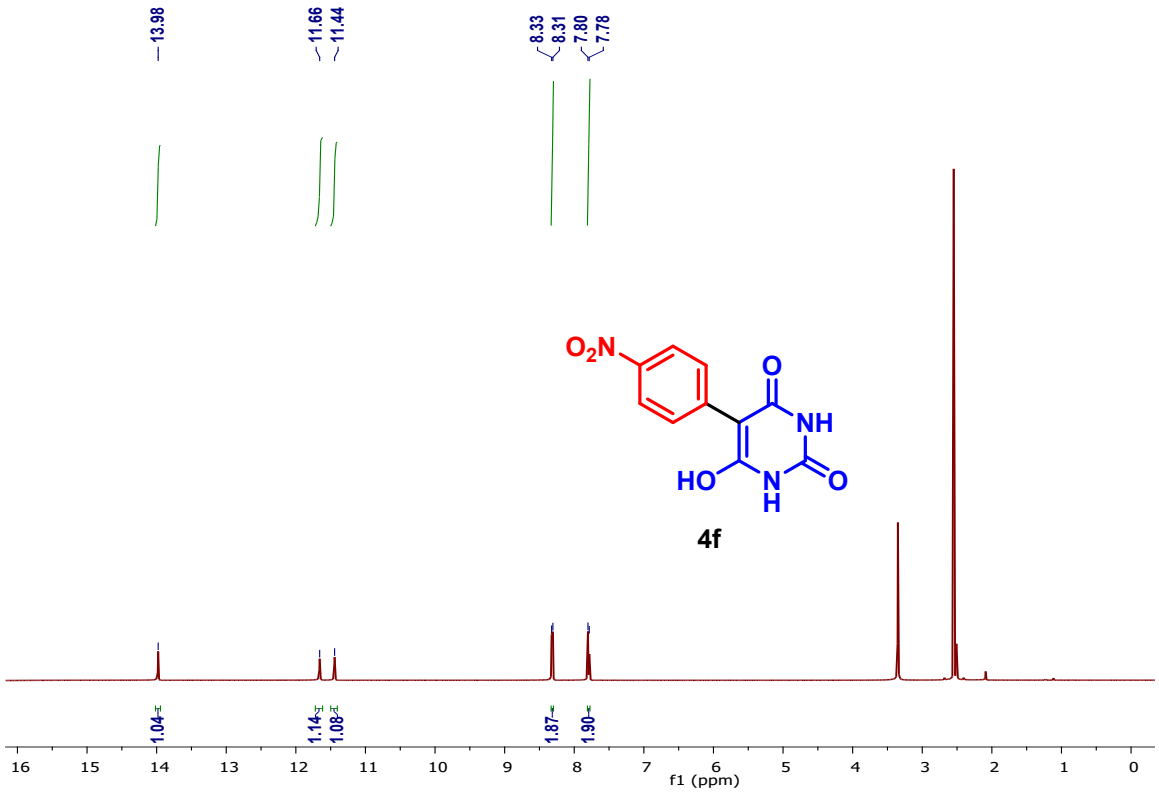
f1 (ppm)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8.31
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7.78
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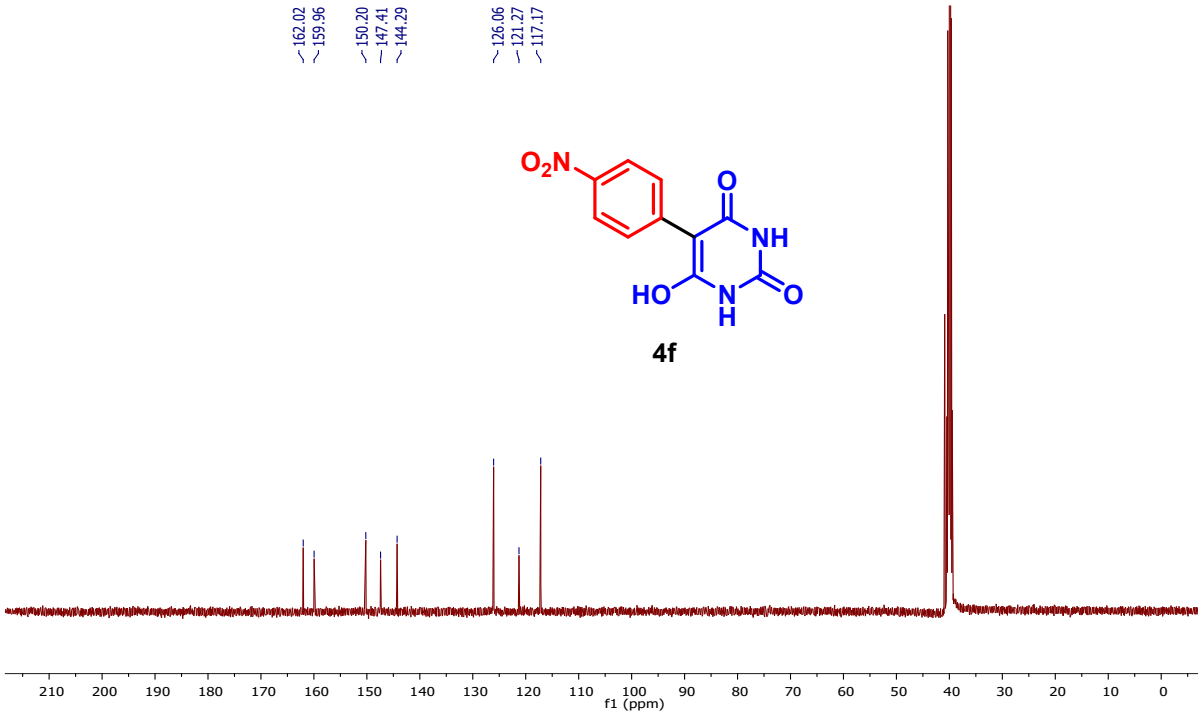
HO
N
H
O
4f
1.04
1.14
1.08
1.87
1.90
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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144.29
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121.27
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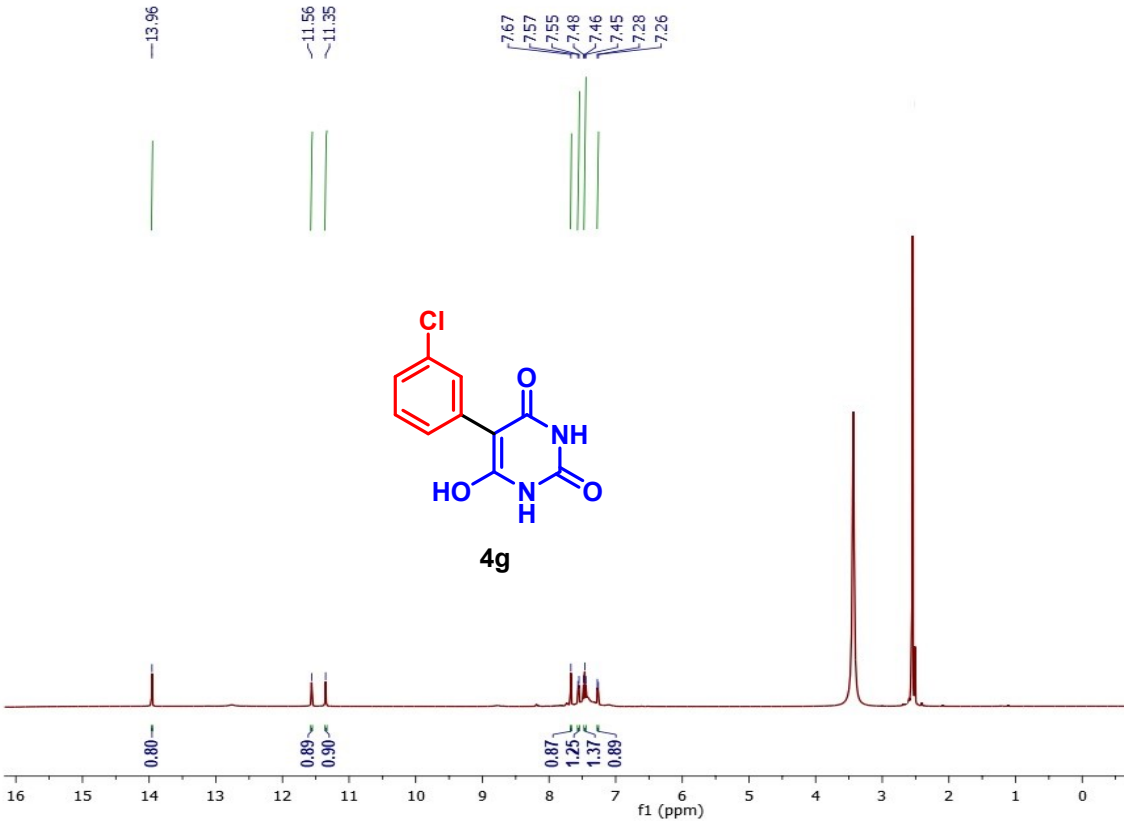
O
NH
HO
N
H
O
f1 (ppm)

4f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7.48
7.46
7.45
7.28
7.26
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NH
HO
N
H
O
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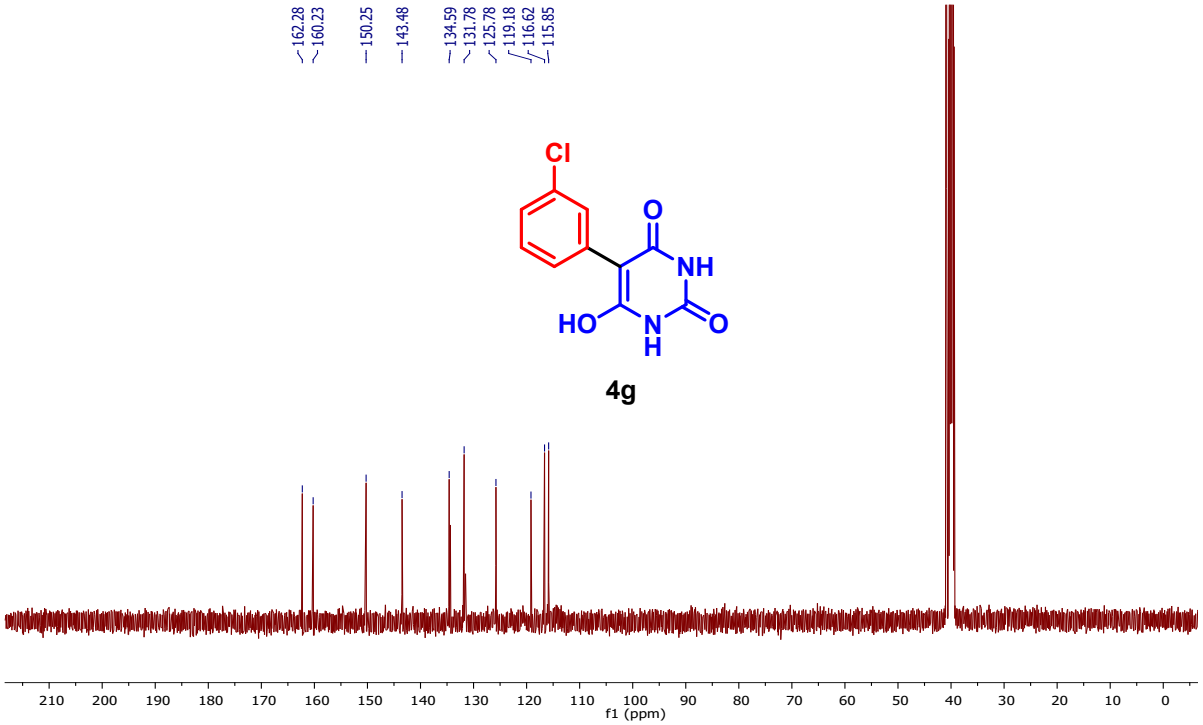
0.89
0.90
0.87
1.25
1.37
0.89
f1 (ppm)

4g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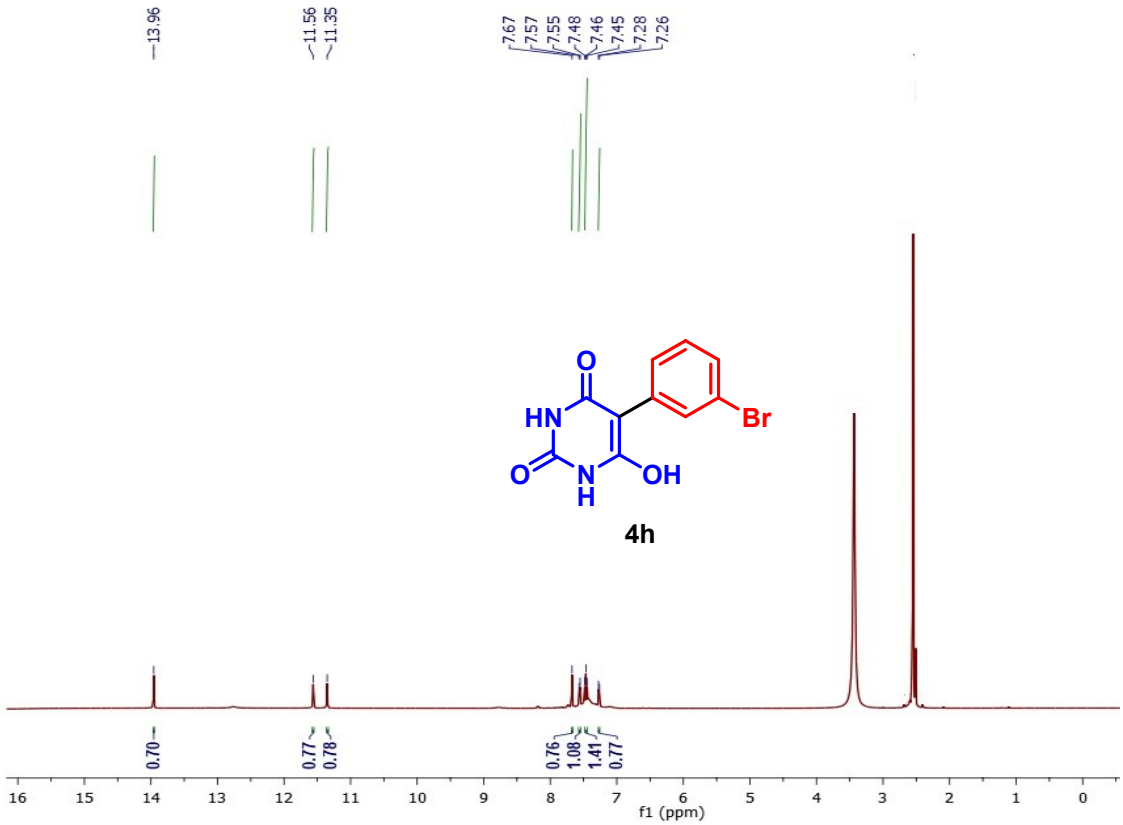
150.25
143.48
134.59
131.78
125.78
119.18
116.62
115.85
Cl
O
NH
HO
N
H
O
f1 (ppm)

4g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11.35
7.67
7.57
7.55
7.48
7.46
7.45
7.28
7.26
O
HN
Br
O
N
H
OH
0.70
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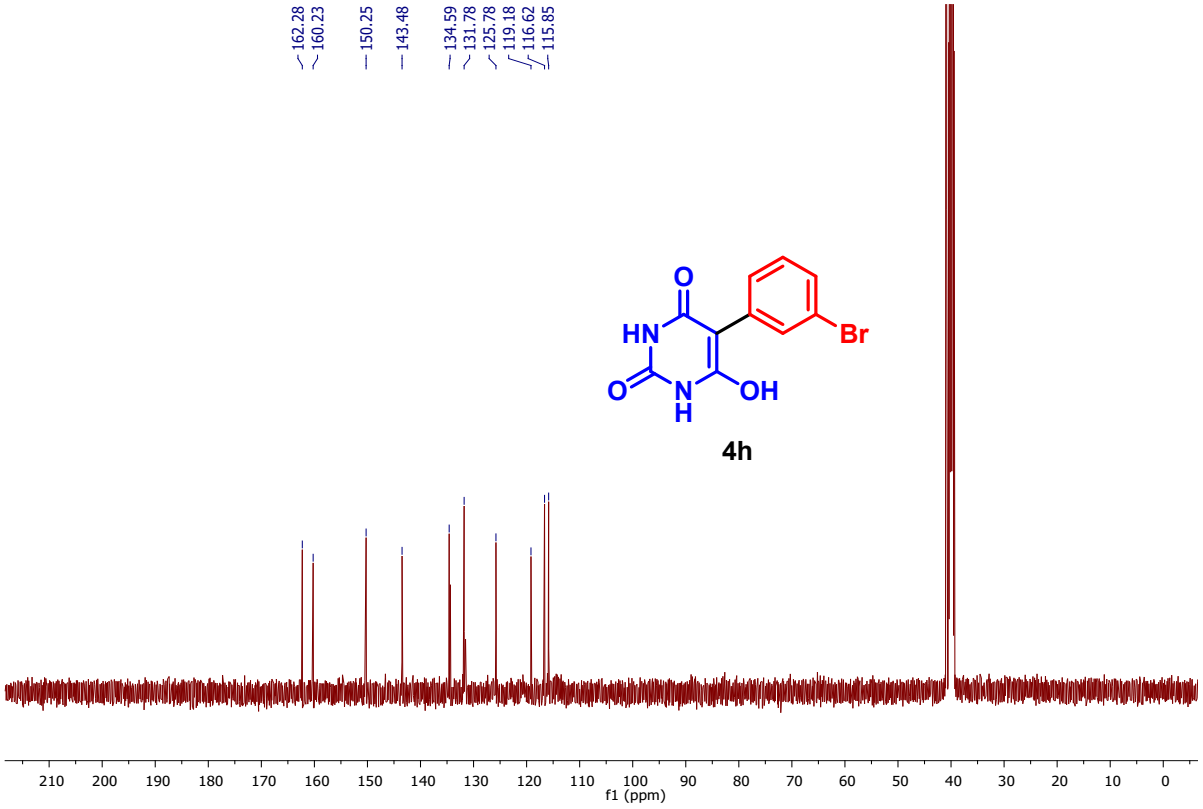
0.78
0.76
1.08
1.41
0.77
f1 (ppm)

4h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143.48
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Br
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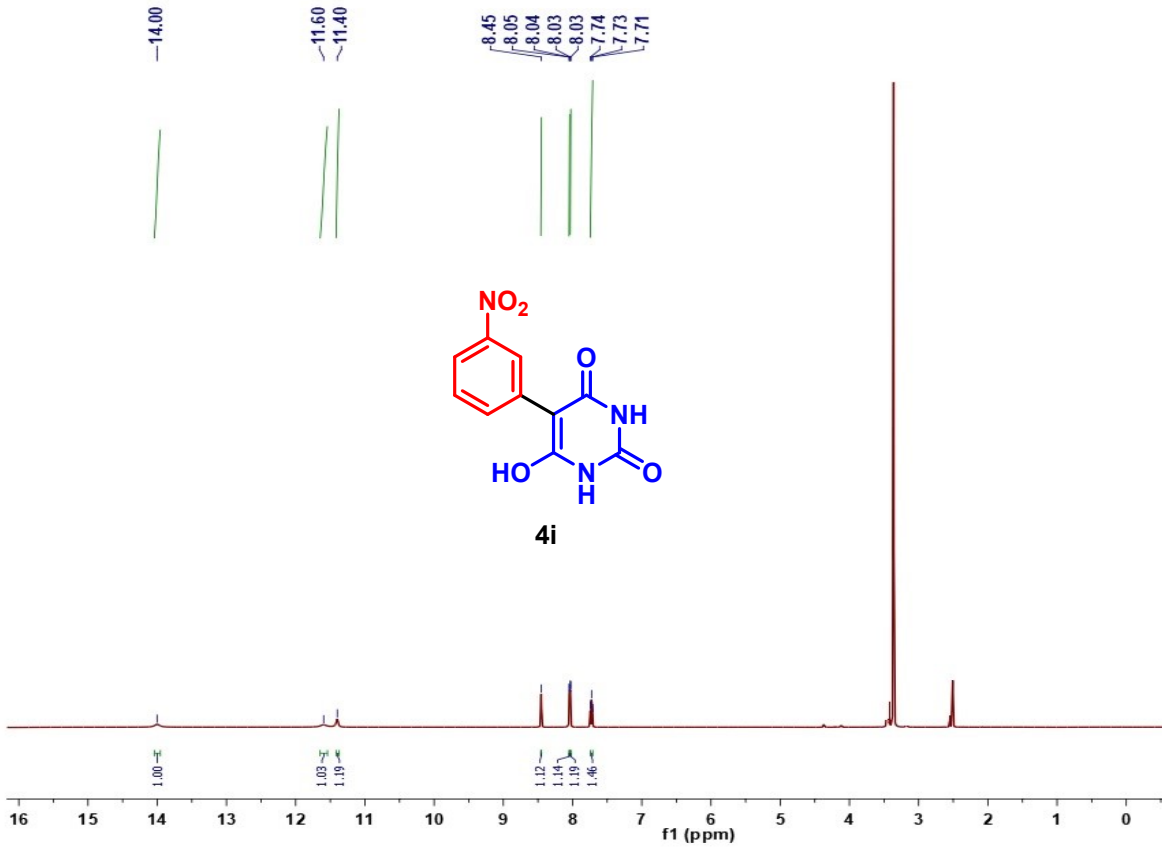
N
H
OH
4h
f1 (ppm)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8.05
8.04
8.03
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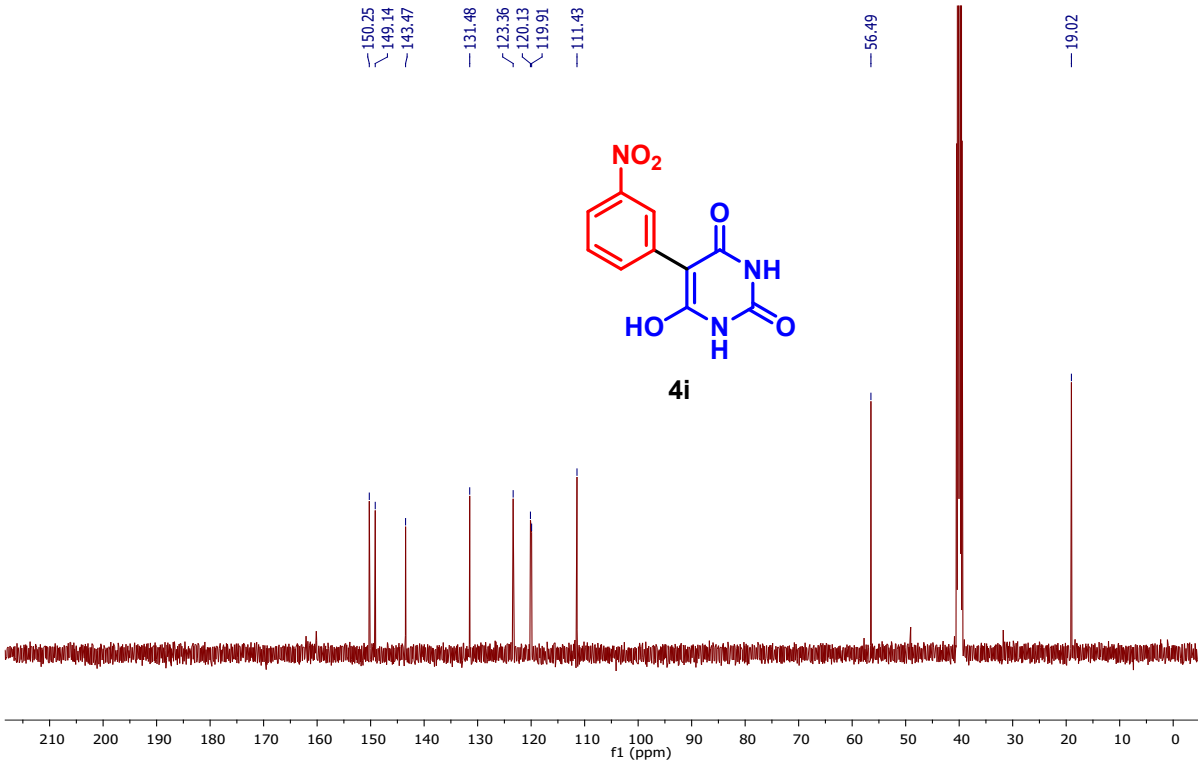
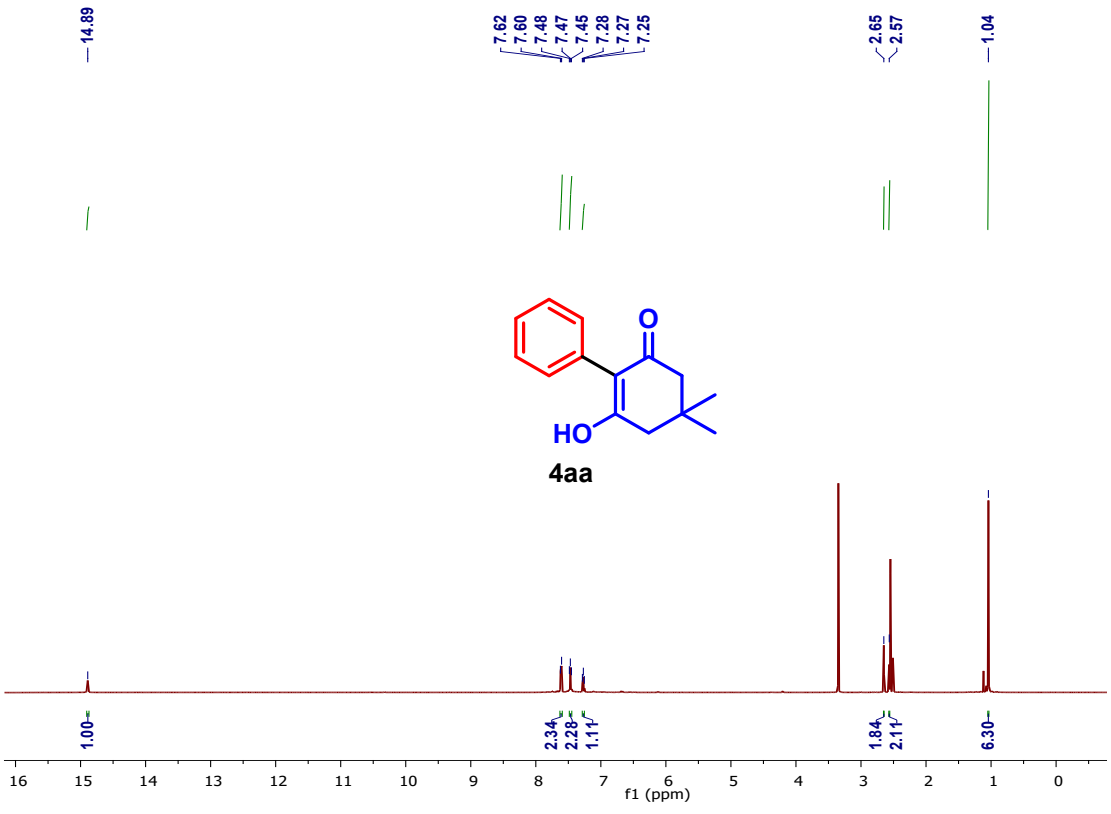
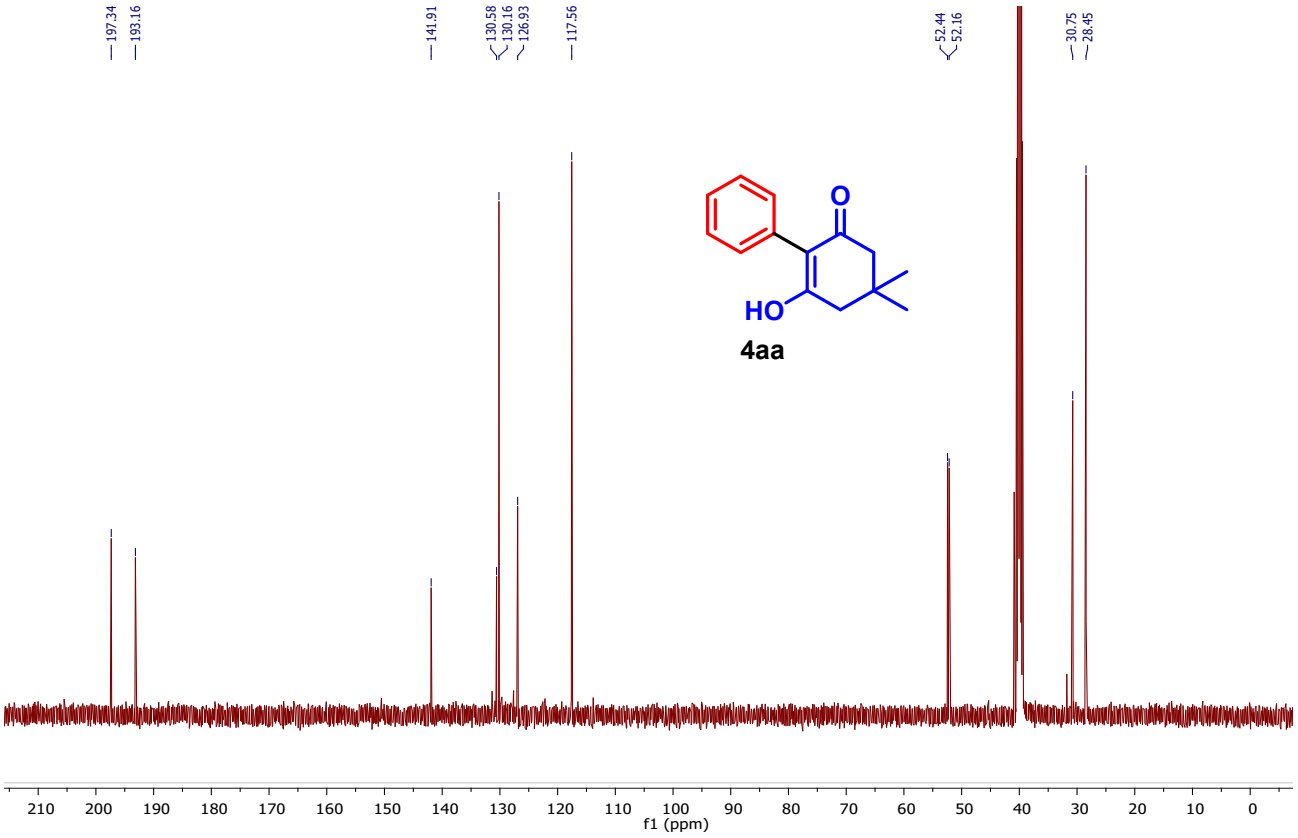
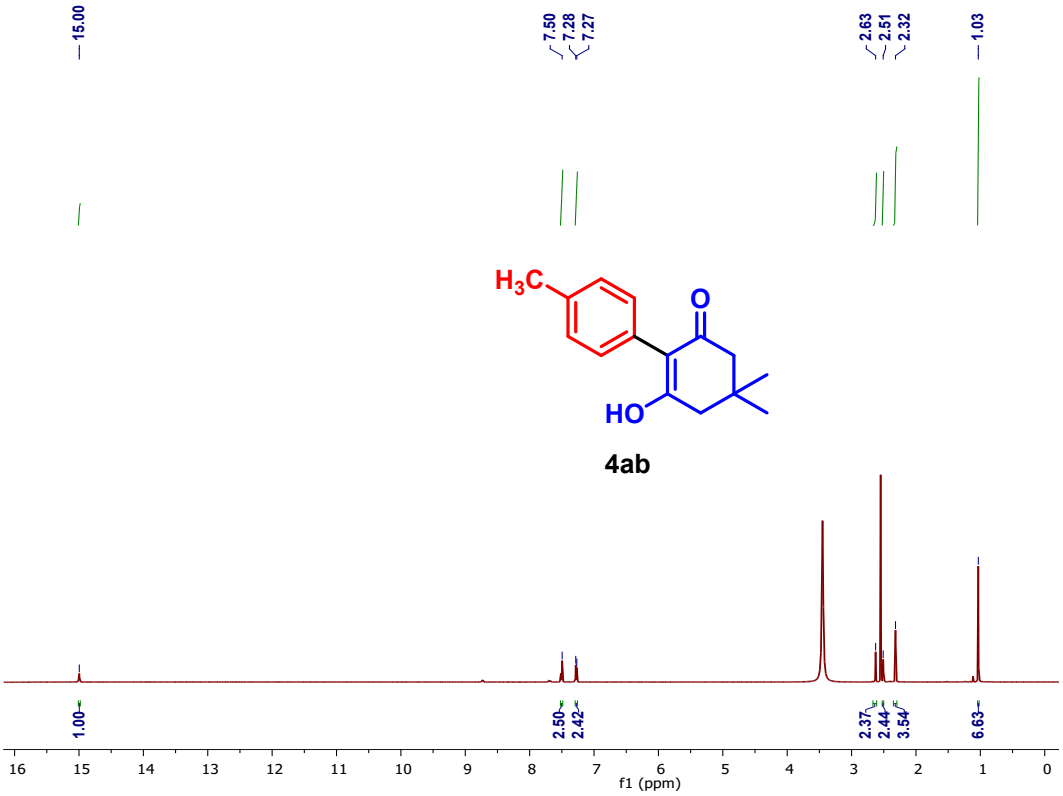
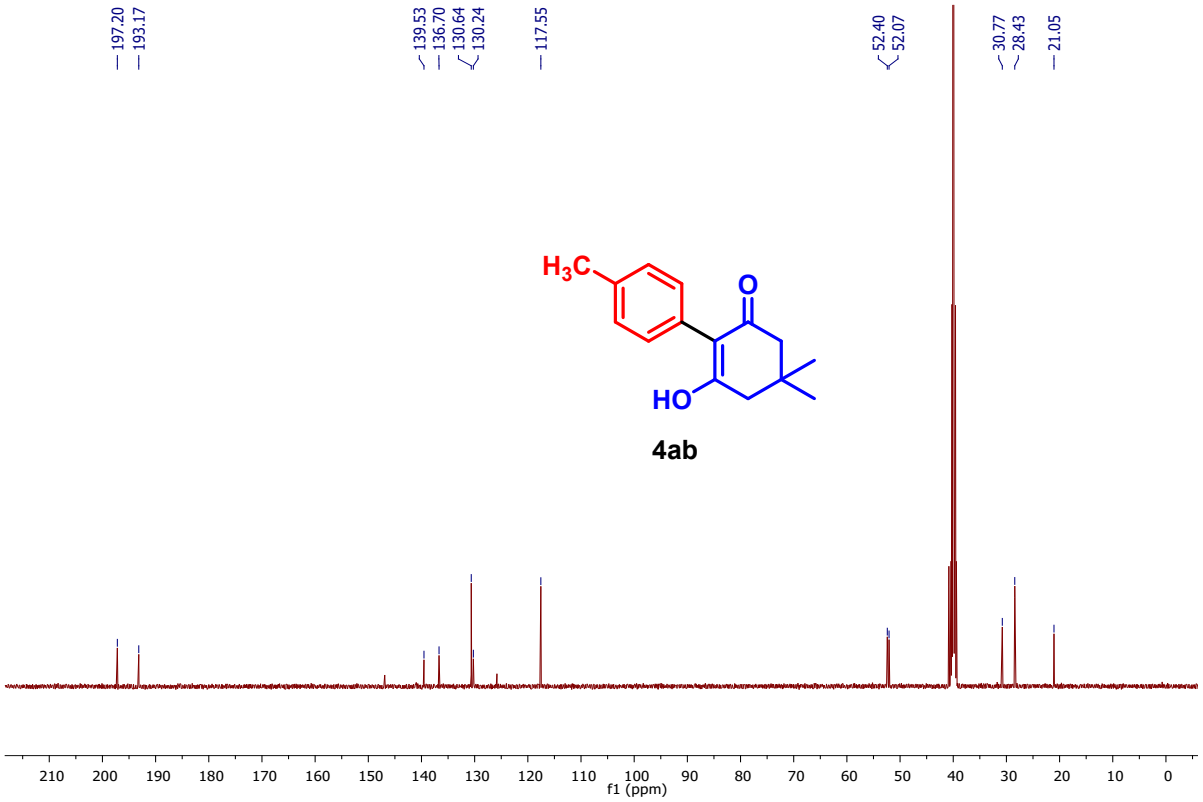
7.73
7.71
NO2
O
NH
HO
N
H
O
4i
1.00
1.03
1.19
1.12
1.14
1.19
1.46
f1 (ppm)

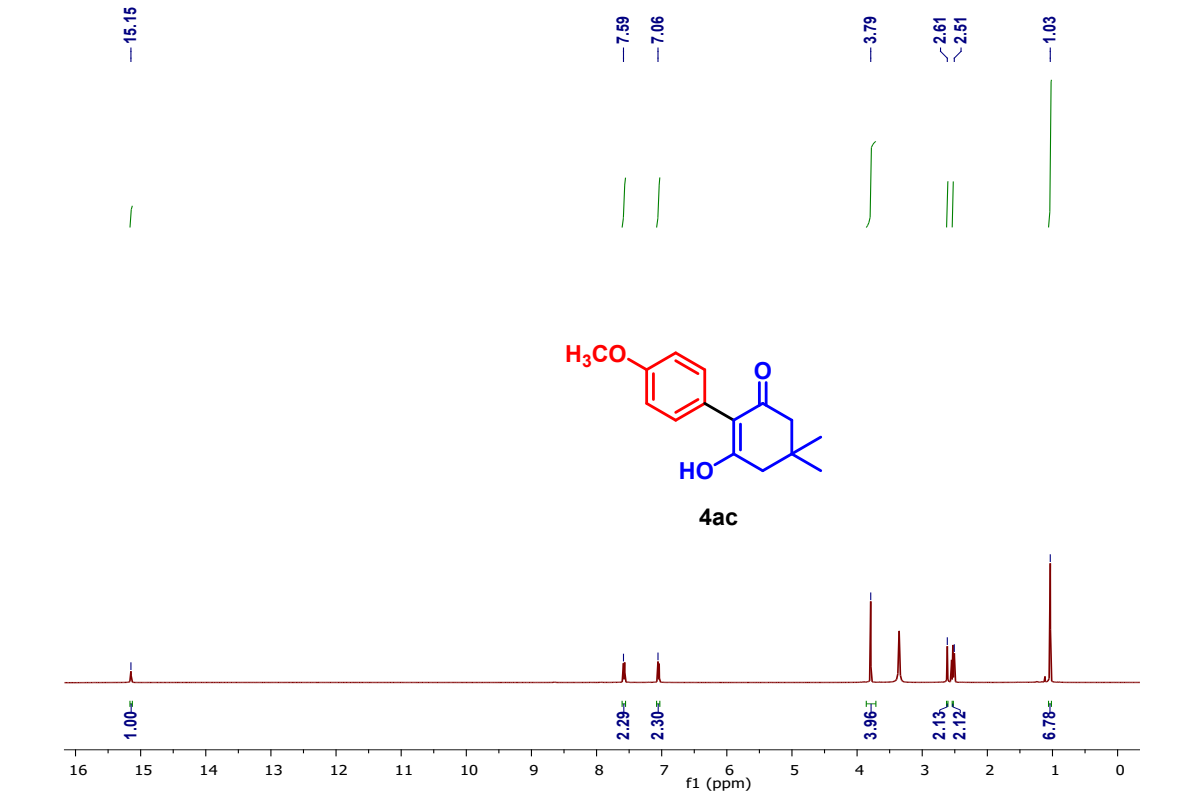

150.25
149.14
143.47
131.48
123.36
120.13
119.91
111.43
56.49
19.02
NO2
O
NH
HO
N
H
O
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

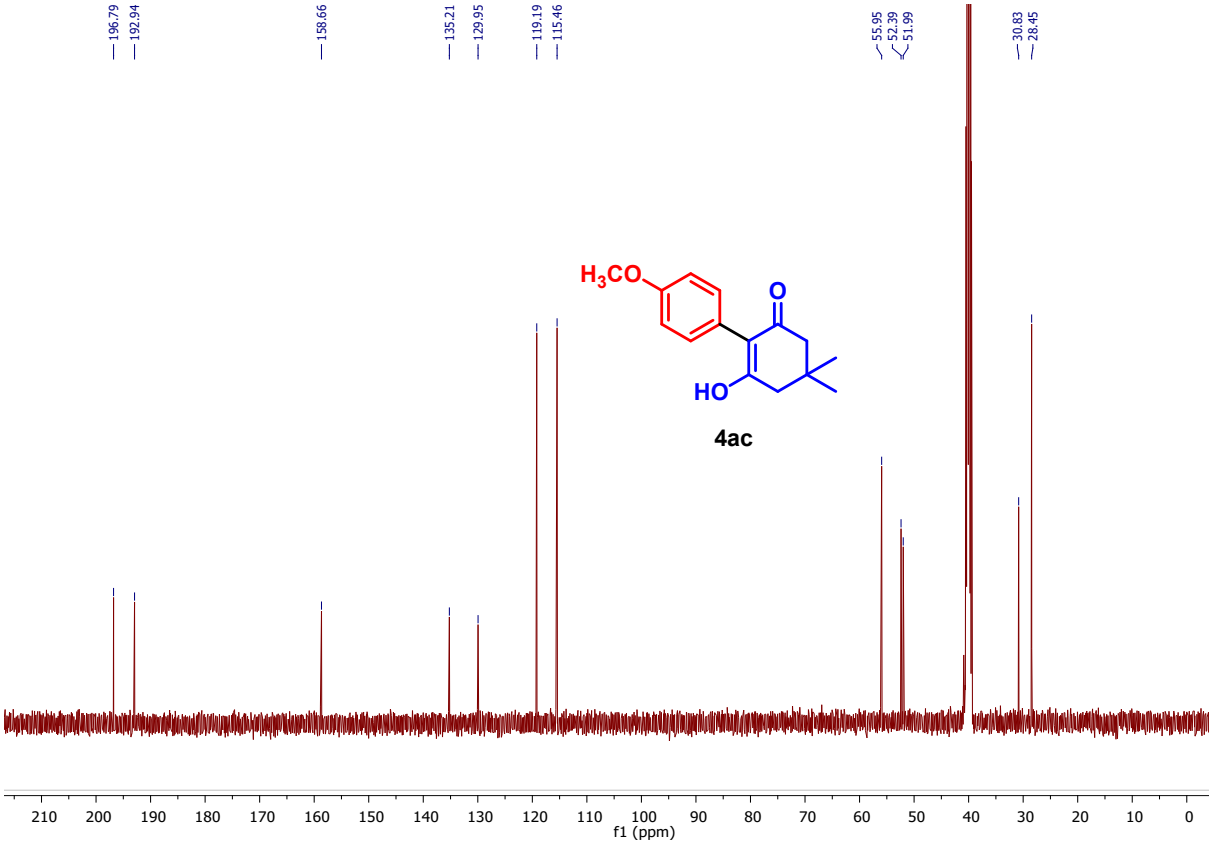

14.89
7.62
7.60
7.48
7.47
7.45
7.28
7.27
7.25
2.65
2.57
1.04
O
HO
4aa
1.00
2.34
2.28
1.11
1.84
2.11
6.30
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

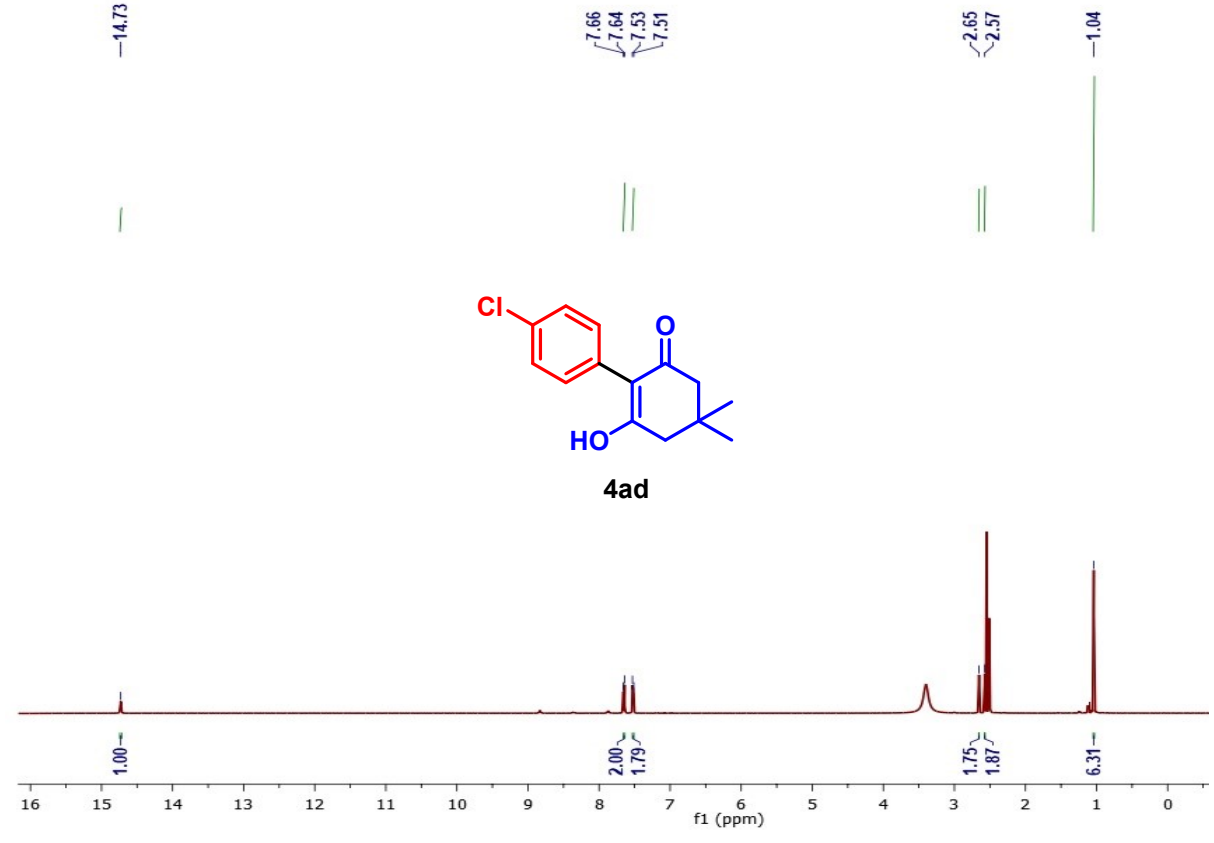

197.34
193.16
141.91
130.58
130.16
126.93
117.56
52.44
52.16
30.75
28.45
O
HO
4aa
f1 (ppm)


15.00
7.50
7.28
7.27
2.63
2.51
2.32
1.03
H3C
O
HO
4ab
1.00
2.50
2.42
2.37
2.44
3.54
6.63
f1 (ppm)


197.20
193.17
139.53
136.70
130.64
130.24
117.55
52.40
52.07
30.77
28.43
21.05
H3C
O
HO
4ab
f1 (ppm)


15.15
7.59
7.06
3.79
2.61
2.51
1.03
H3CO
O
HO
4ac
1.00
2.29
2.30
3.96
2.13
2.12
6.78
f1 (ppm)


196.79
192.94
158.66
135.21
129.95
119.19
115.46
55.95
52.39
51.99
30.83
28.45
H3CO
O
HO
4ac
f1 (ppm)


14.73
7.66
7.64
7.53
7.51
2.65
2.57
1.04
Cl
O
HO
4ad
1.00
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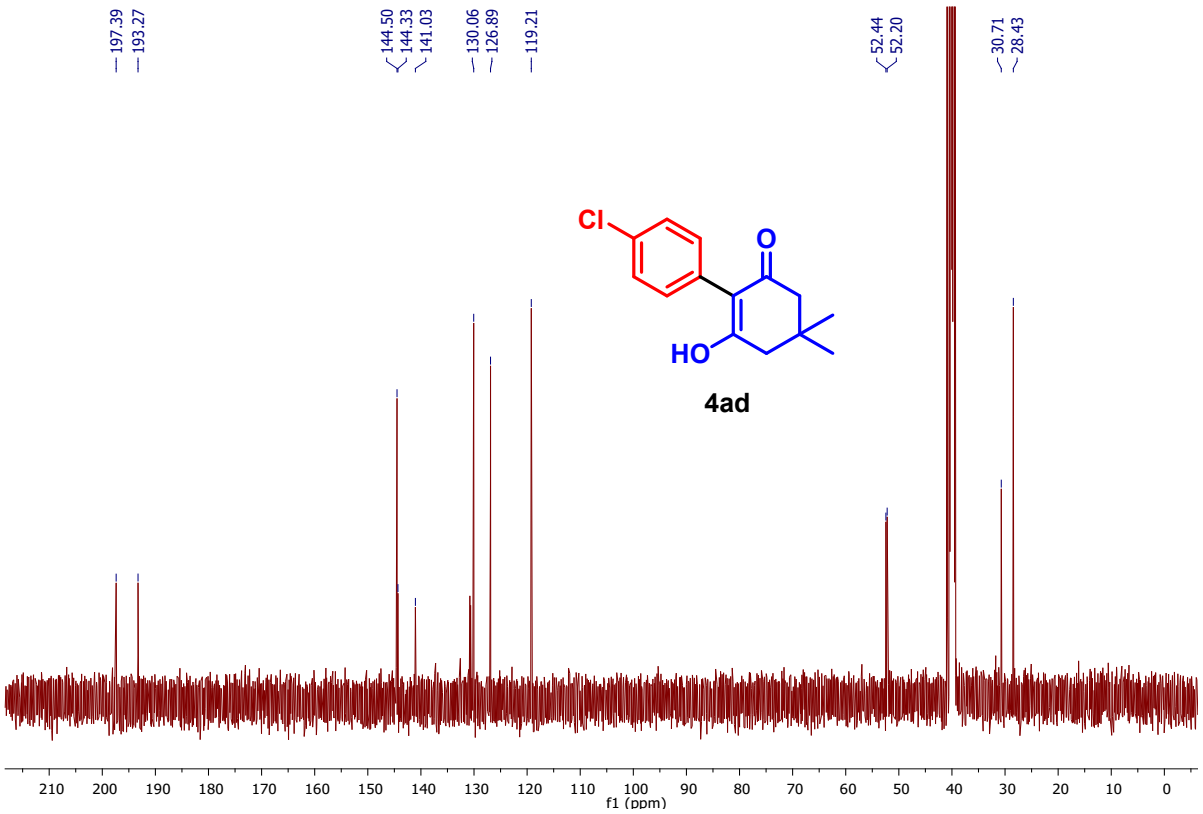
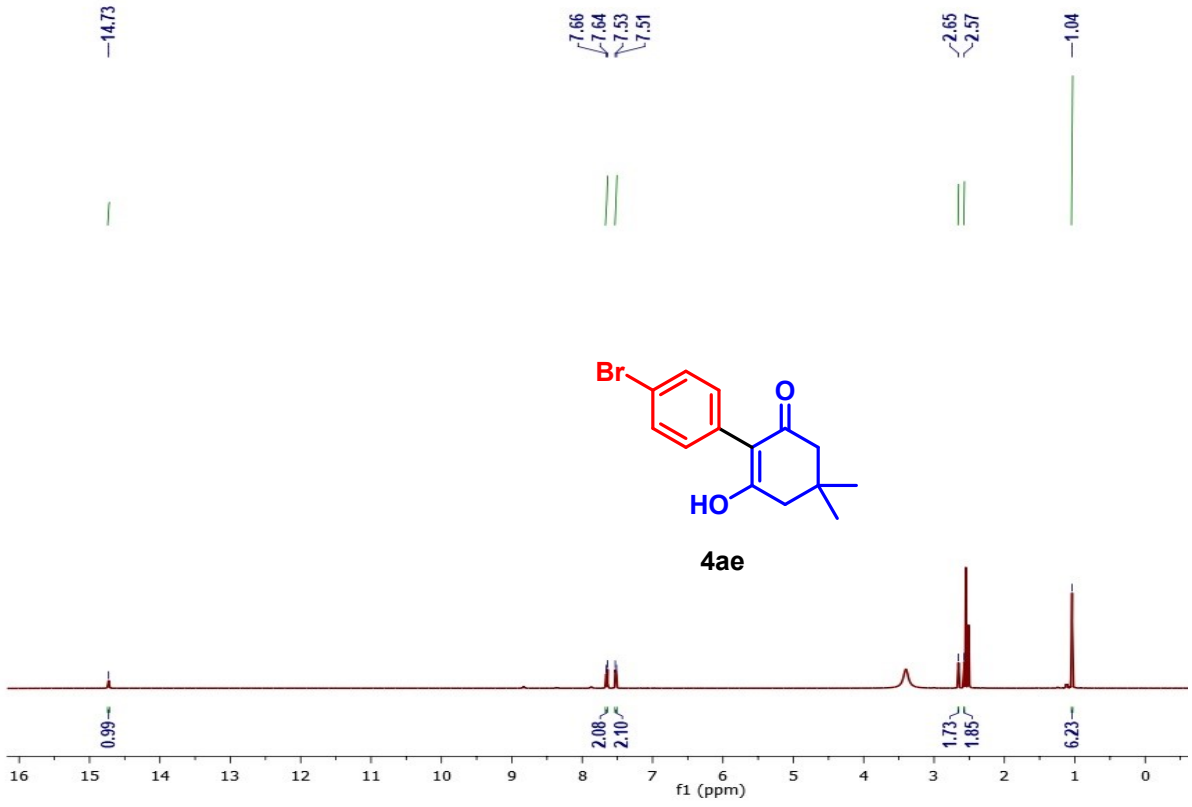
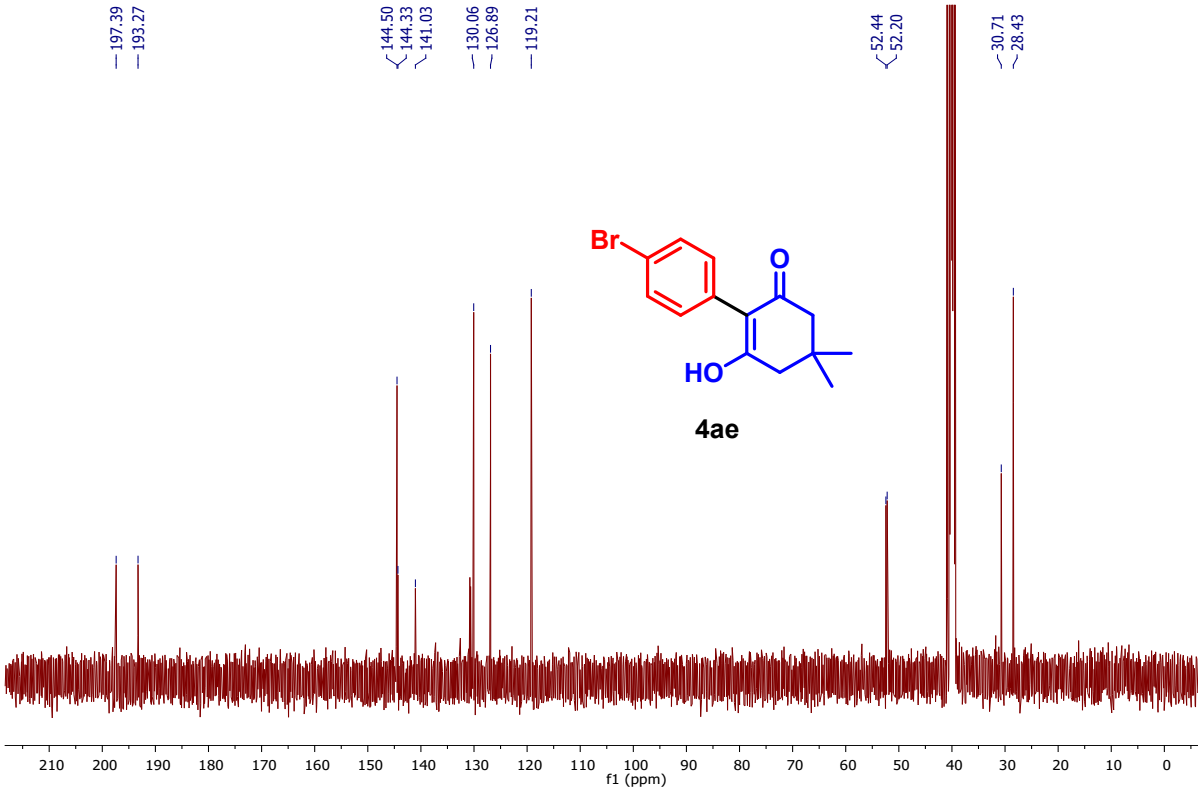
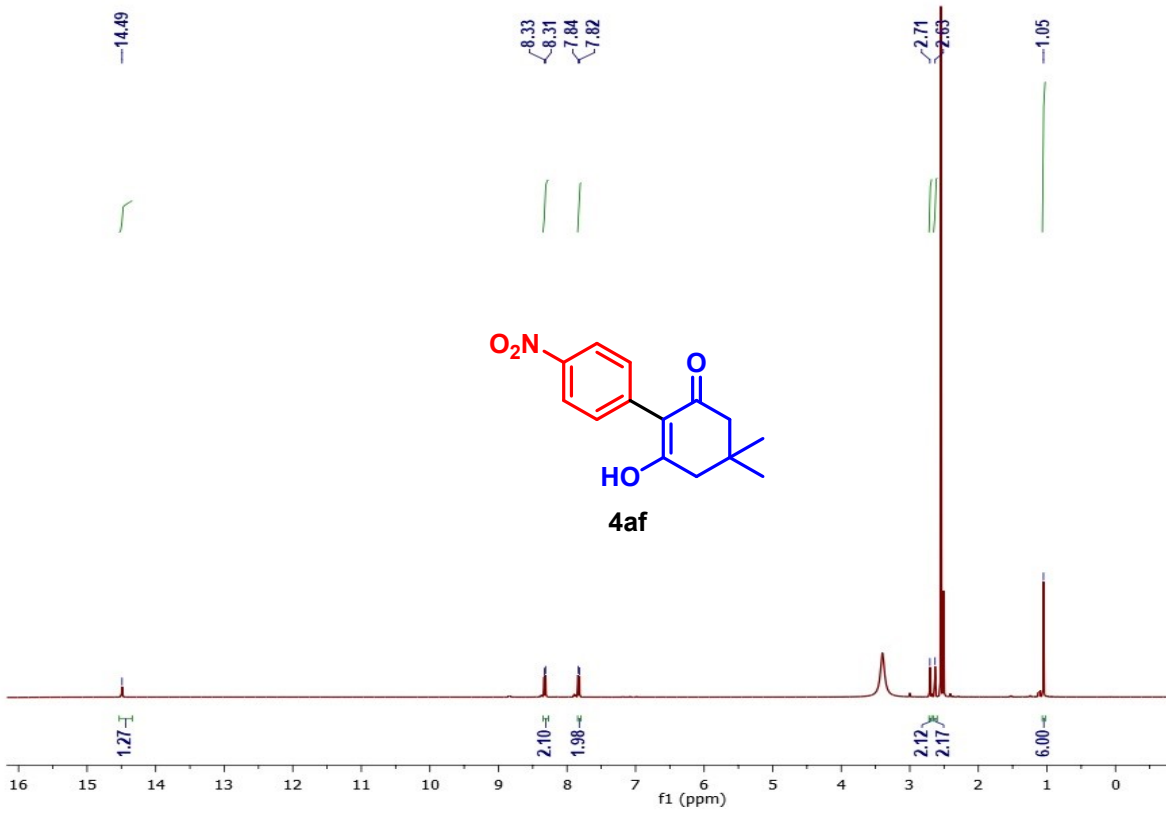
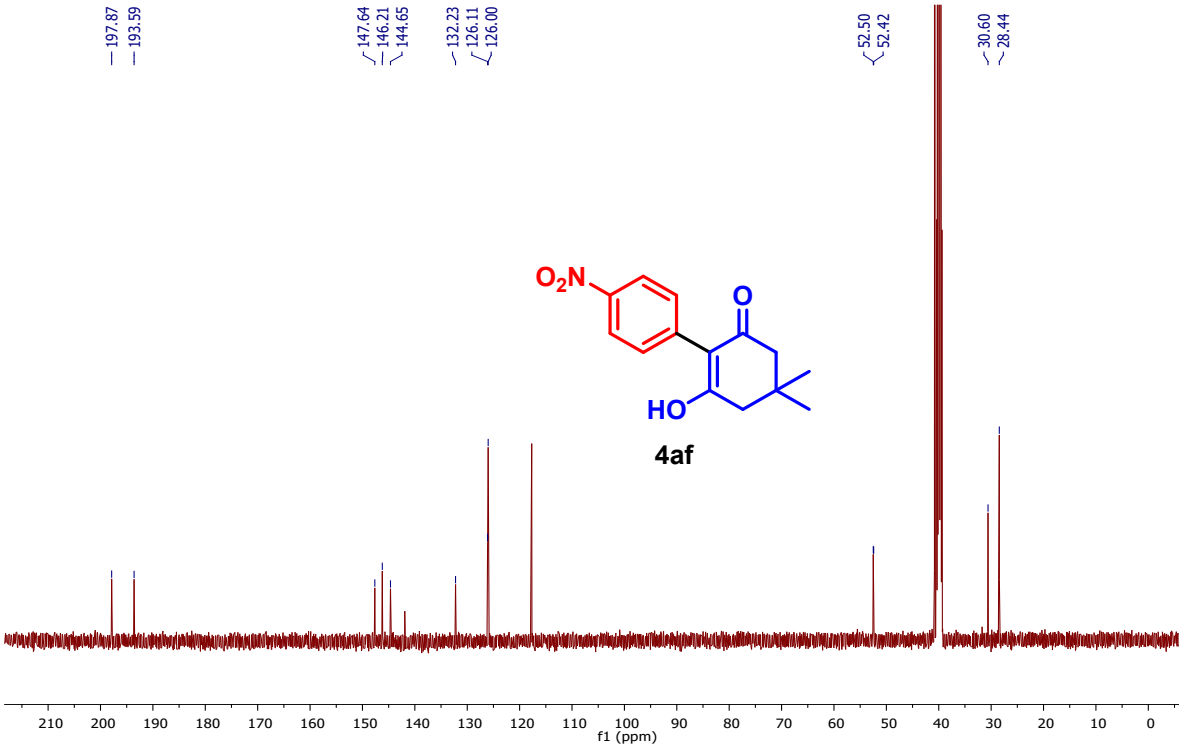
1.79
1.75
1.87
6.31
f1 (ppm)

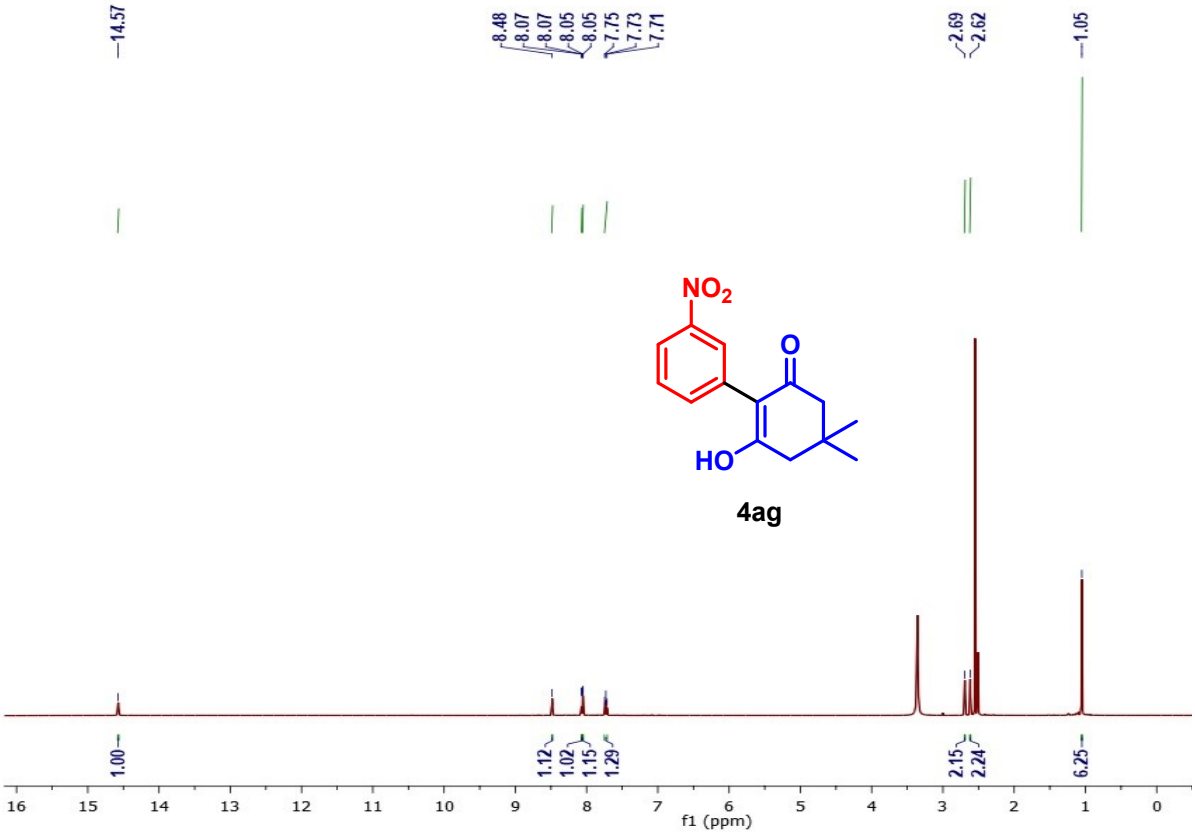

197.39
193.27
144.50
144.33
141.03
130.06
126.89
119.21
52.44
52.20
30.71
28.43
Cl
O
HO
4ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

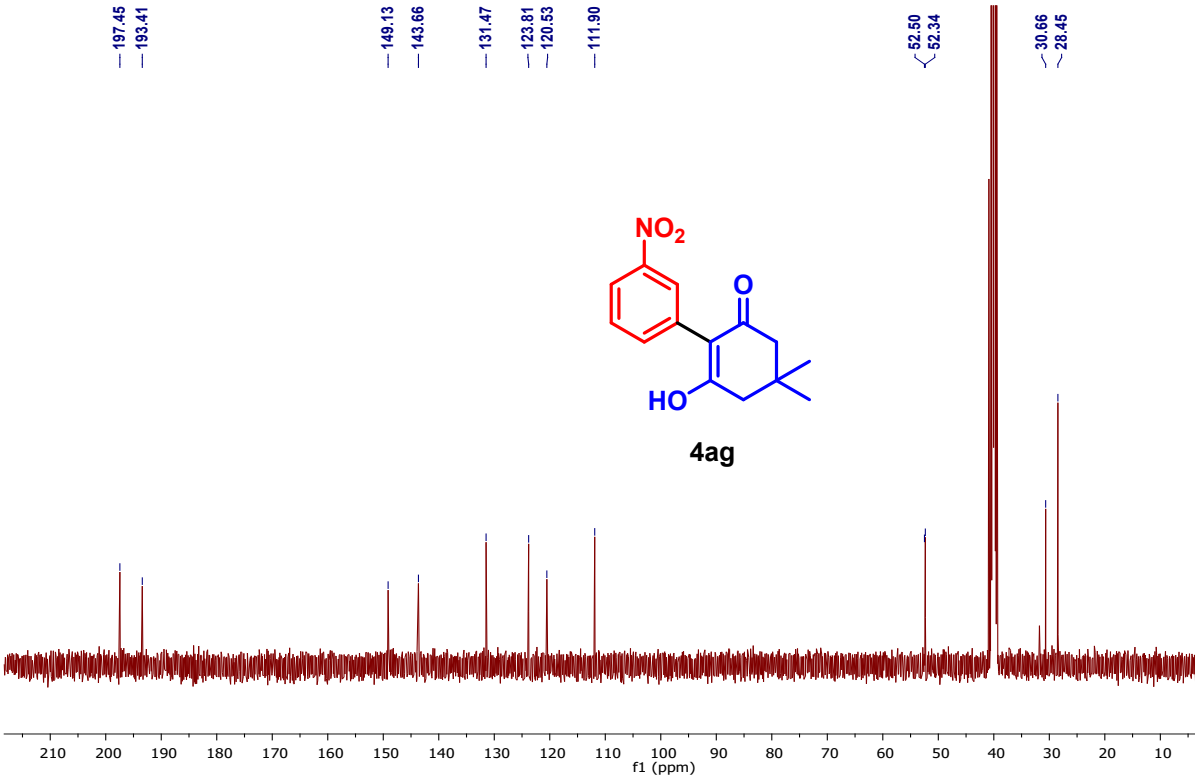

14.73
7.66
7.64
7.53
7.51
2.65
2.57
1.04
Br
O
HO
4ae
0.99
2.08
2.10
1.73
1.85
6.23
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

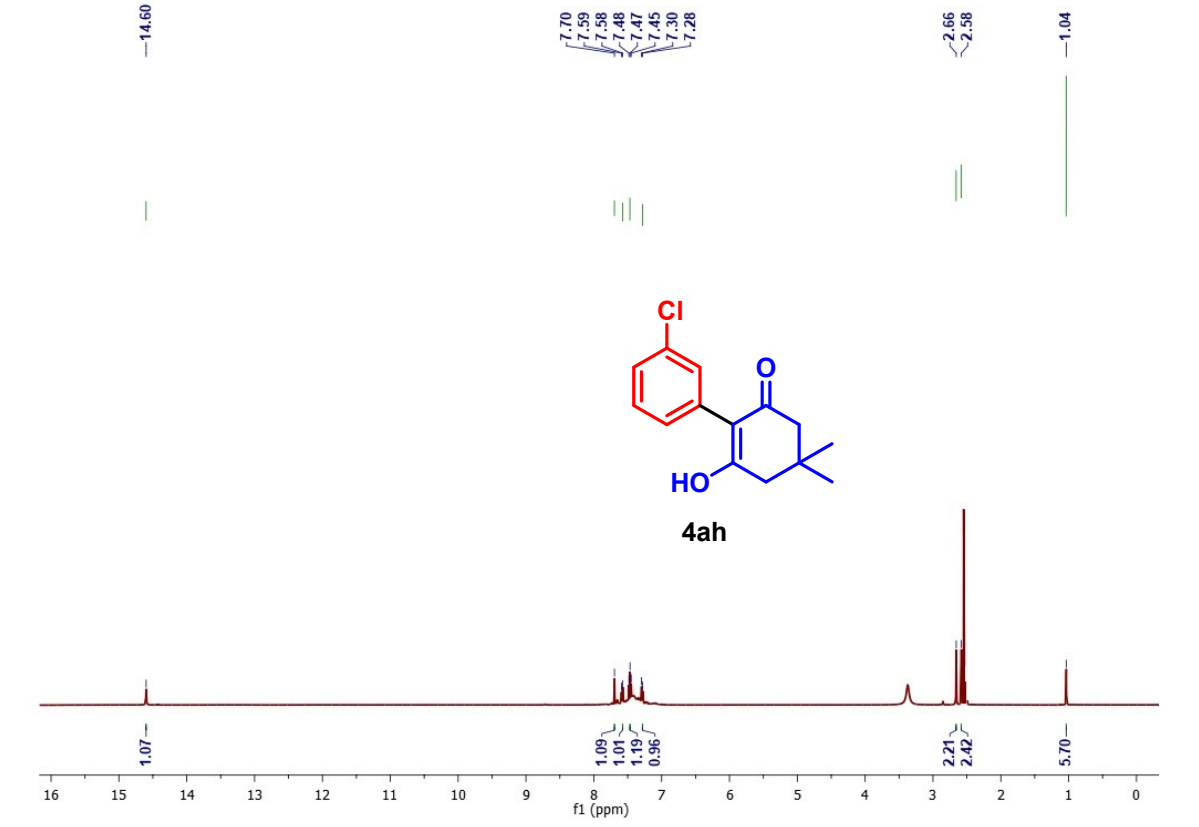

197.39
193.27
144.50
144.33
141.03
130.06
126.89
119.21
52.44
52.20
30.71
28.43
Br
O
HO
4ae
f1 (ppm)

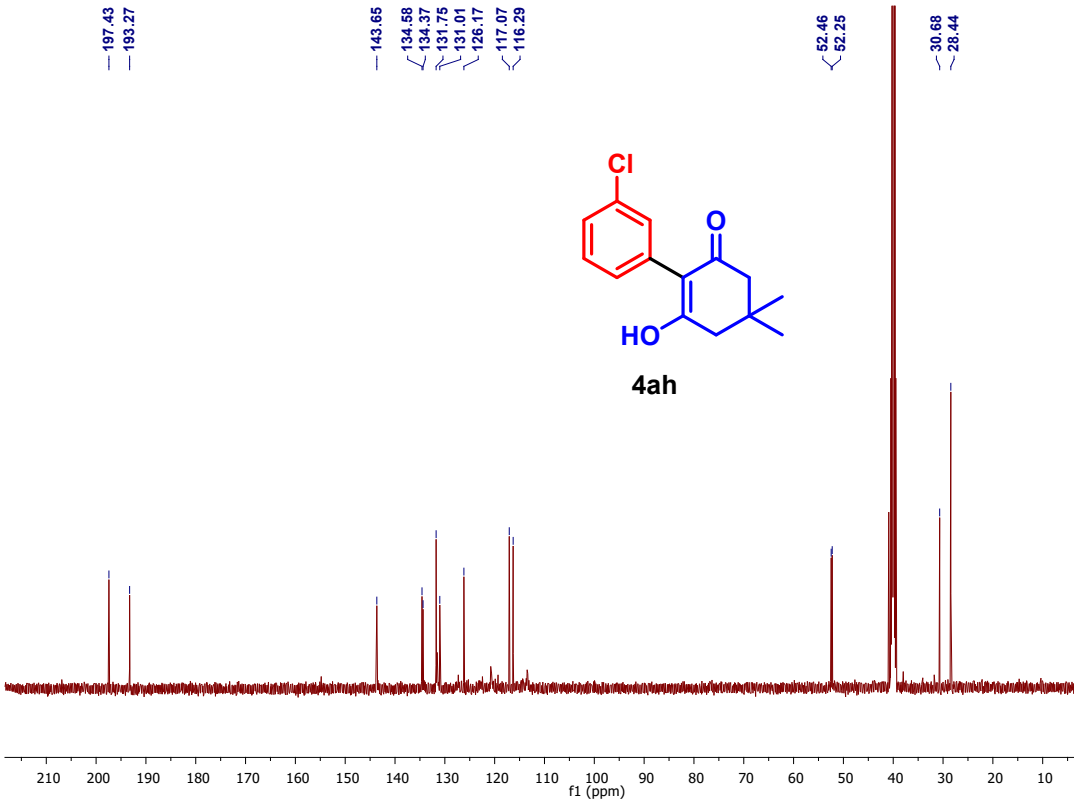

14.49
8.33
8.31
7.84
7.82
2.71
2.63
1.05
O2N
O
HO
4af
1.27
2.10
1.98
2.12
2.17
6.00
f1 (ppm)

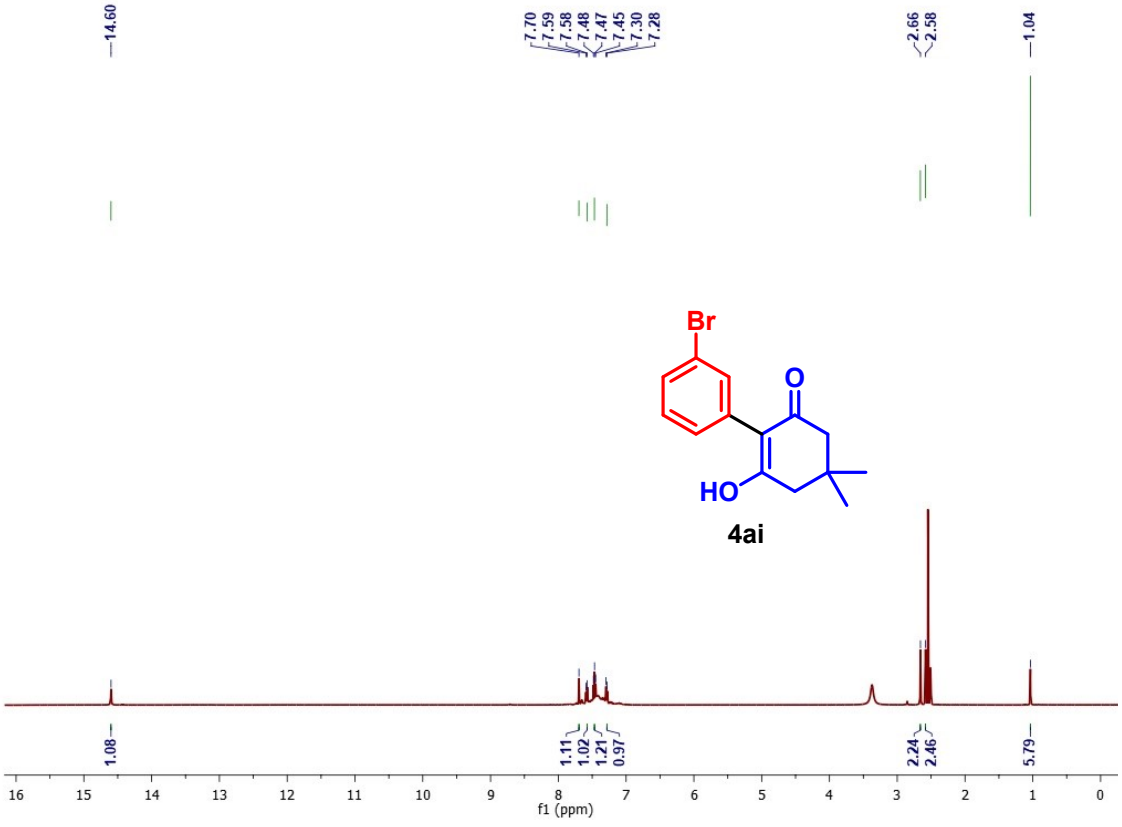

197.87
193.59
147.64
146.21
144.65
132.23
126.11
126.00
52.50
52.42
30.60
28.44
O2N
O
HO
4af
f1 (ppm)

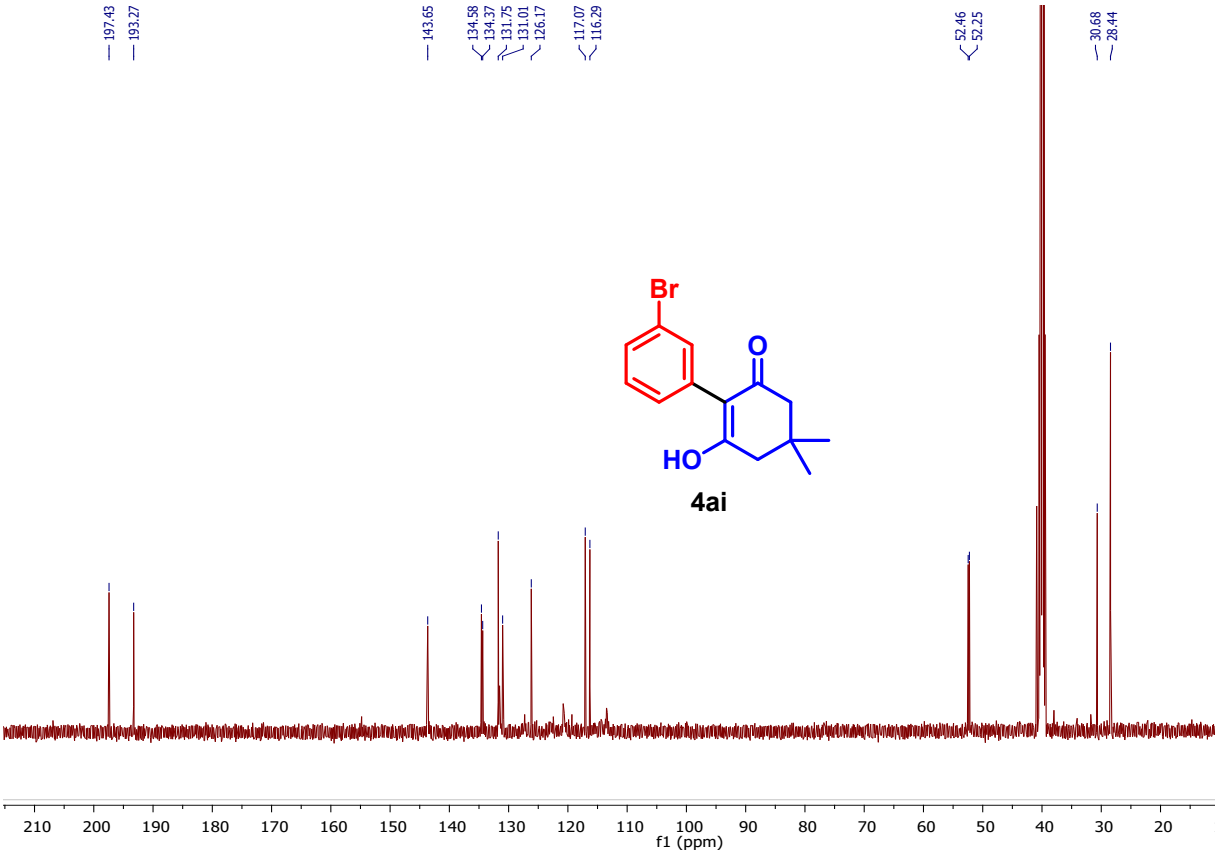

14.57
8.48
8.07
8.07
8.05
8.05
7.75
7.73
7.71
2.69
2.62
1.05
NO2
O
HO
4ag
1.00
1.12
1.02
1.15
1.29
2.15
2.24
6.25
f1 (ppm)

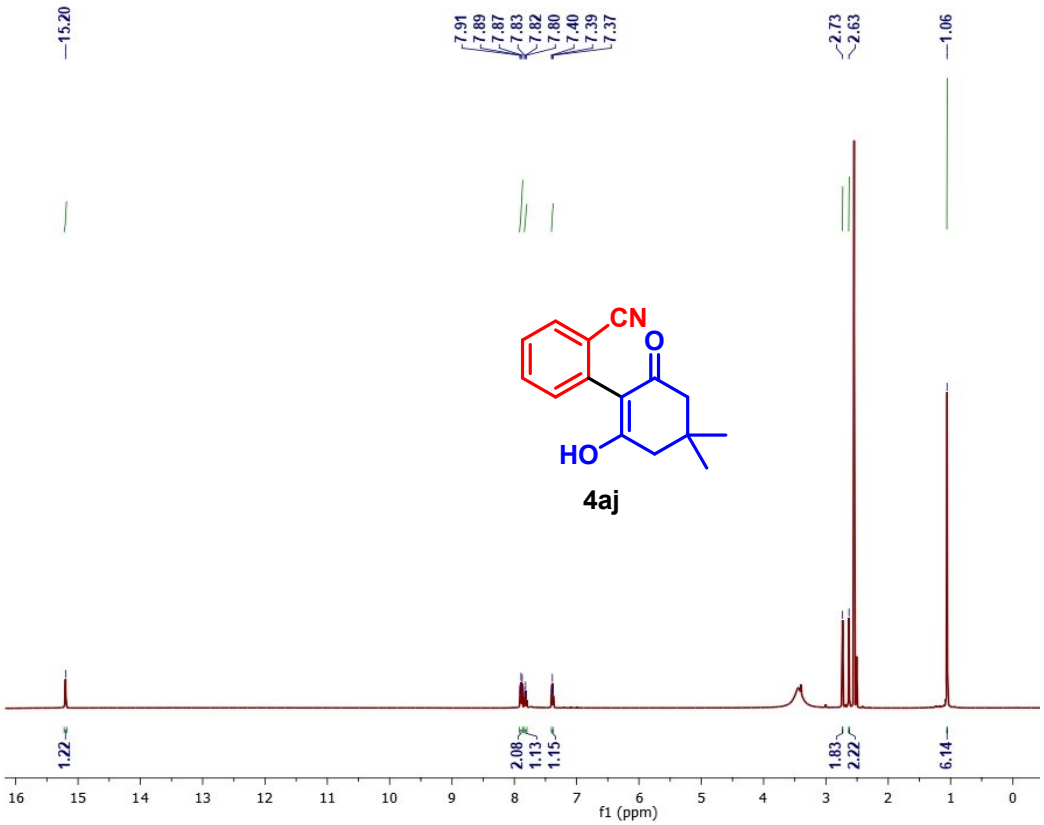

197.45
193.41
149.13
143.66
131.47
123.81
120.53
111.90
52.50
52.34
30.66
28.45
NO2
O
HO
4ag
f1 (ppm)

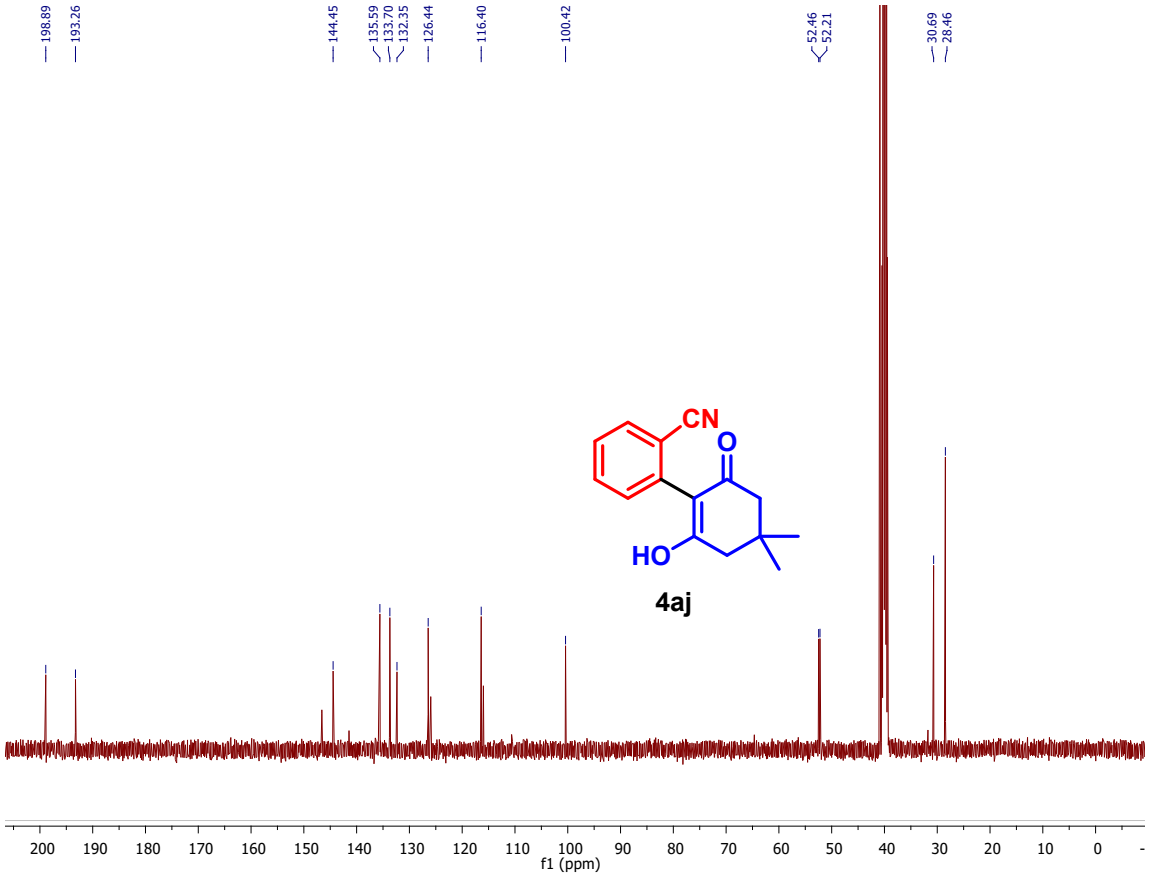

14.60
7.70
7.59
7.58
7.48
7.47
7.45
7.30
7.28
2.66
2.58
1.04
Cl
O
HO
4ah
1.07
1.09
1.01
1.19
0.96
2.21
2.42
5.70
f1 (ppm)

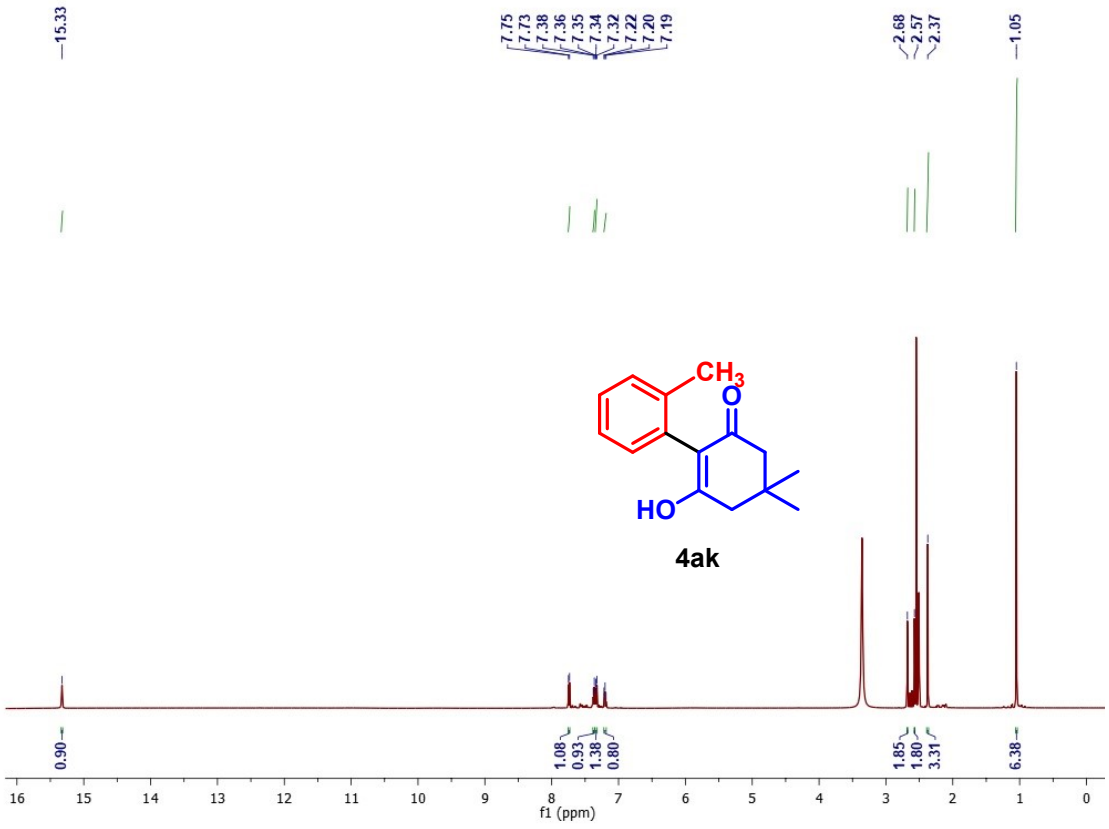

197.43
193.27
143.65
134.58
134.37
131.75
131.01
126.17
117.07
116.29
52.46
52.25
30.68
28.44
Cl
O
HO
4ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

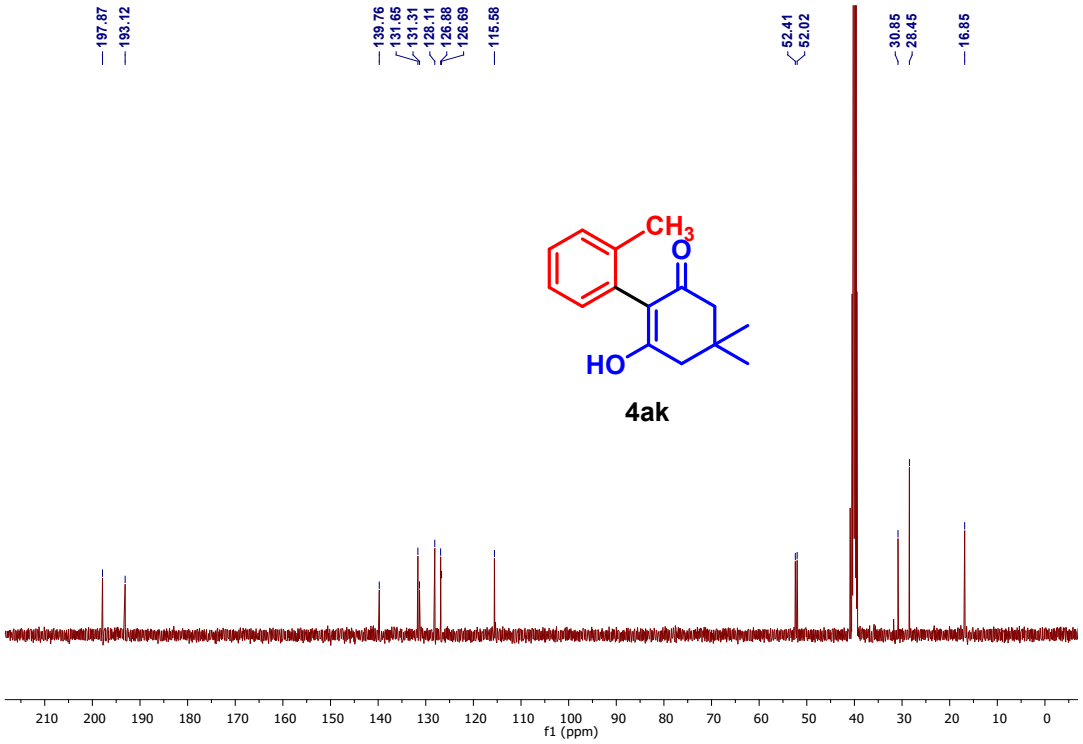

14.60
7.70
7.59
7.58
7.48
7.47
7.45
7.30
7.28
2.66
2.58
1.04
Br
O
HO
4ai
1.08
1.11
1.02
1.21
0.97
2.24
2.46
5.79
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


197.43
193.27
143.65
134.58
134.37
131.75
131.01
126.17
117.07
116.29
52.46
52.25
30.68
28.44
Br
O
HO
4ai
f1 (ppm)


15.20
7.91
7.89
7.87
7.83
7.82
7.80
7.40
7.39
7.37
2.73
2.63
1.06
CN
O
HO
4aj
1.22
2.08
1.13
1.15
1.83
2.22
6.14
f1 (ppm)


198.89
193.26
144.45
135.59
133.70
132.35
126.44
116.40
100.42
52.46
52.21
30.69
28.46
CN
O
HO
4aj
f1 (ppm)


15.33
7.75
7.73
7.38
7.36
7.35
7.34
7.32
7.22
7.20
7.19
2.68
2.57
2.37
1.05
CH3
O
HO
4ak
0.90
1.08
0.93
1.38
0.80
1.85
1.80
3.31
6.38
f1 (ppm)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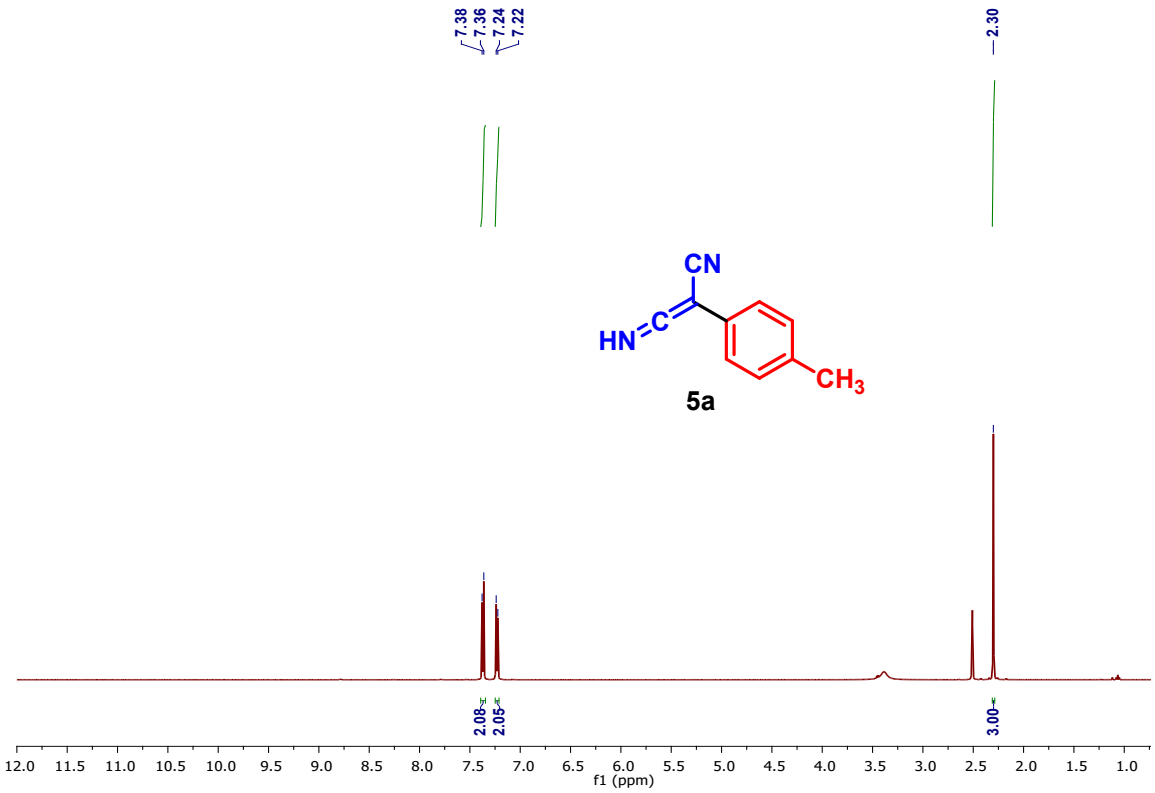
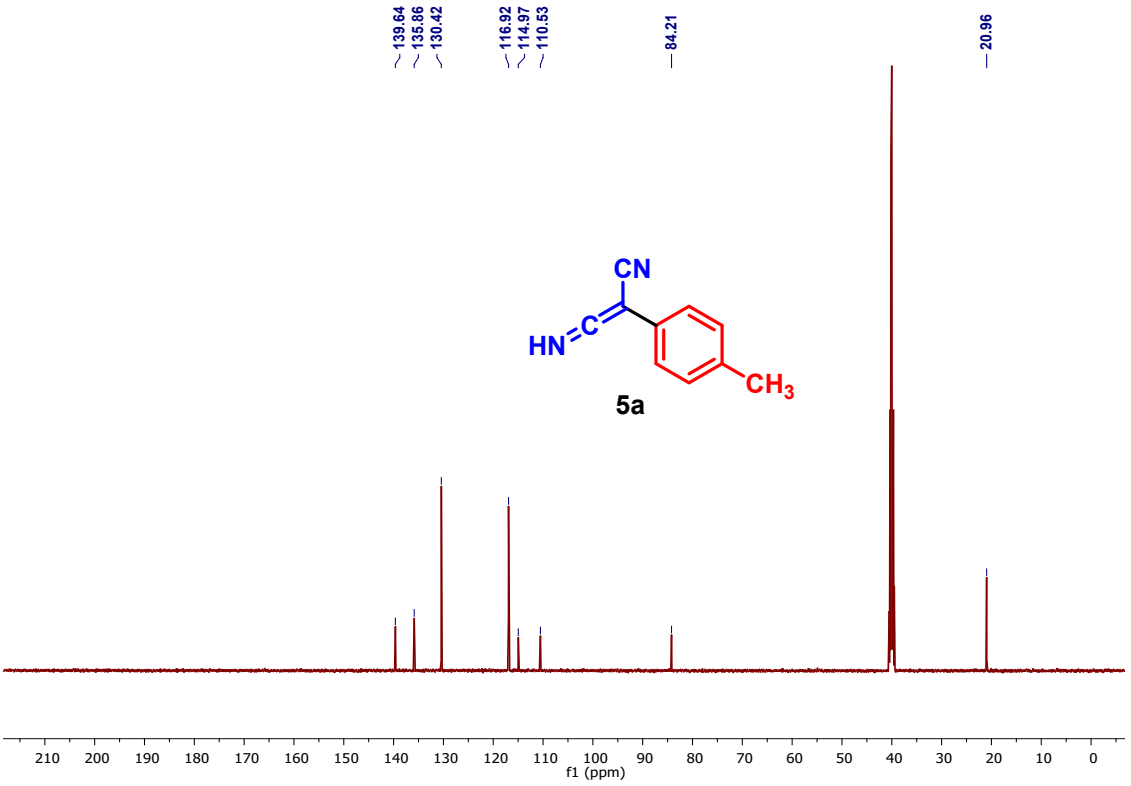
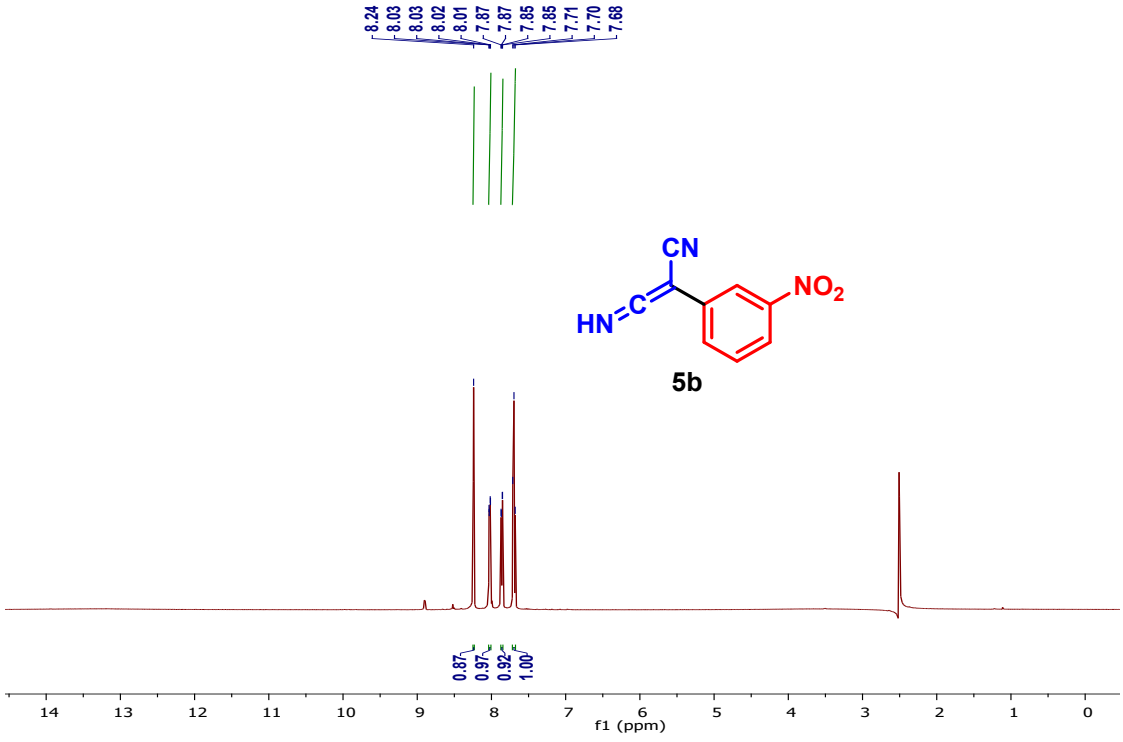
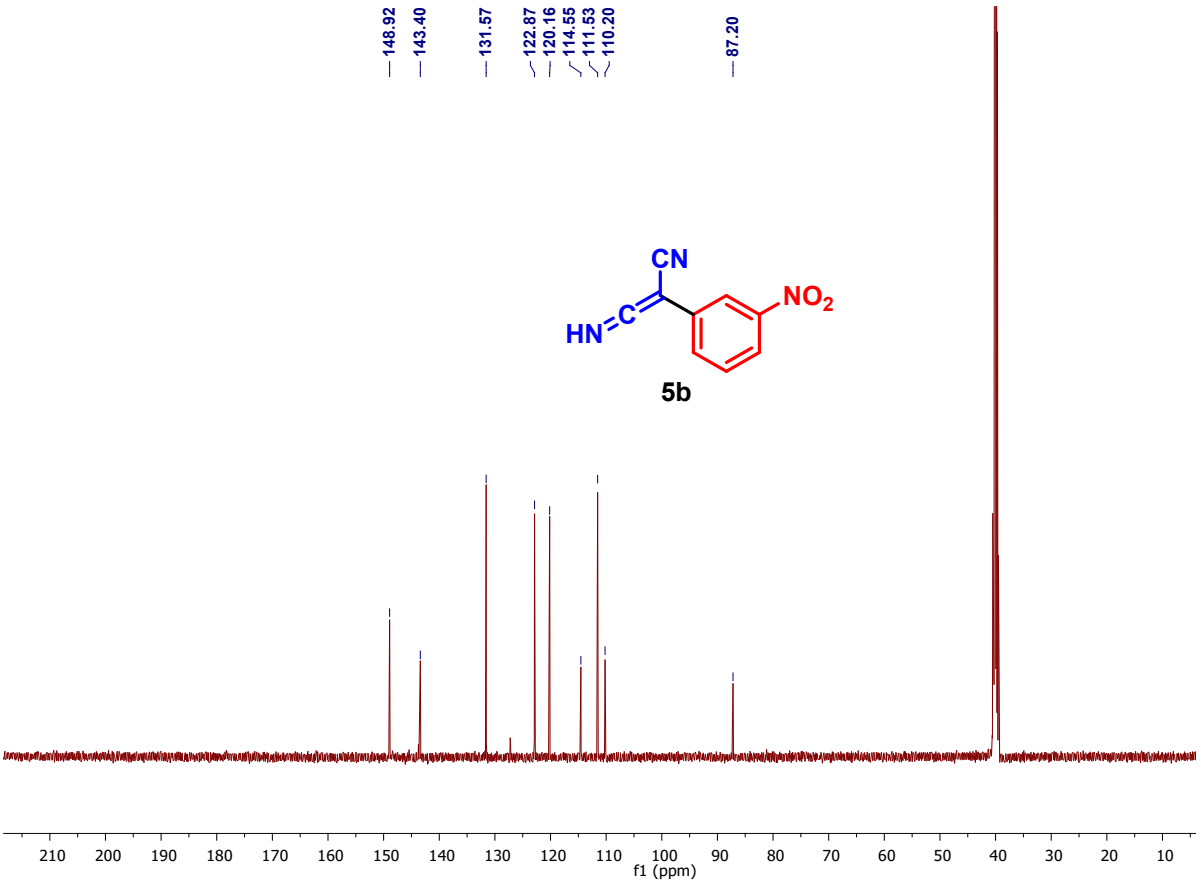
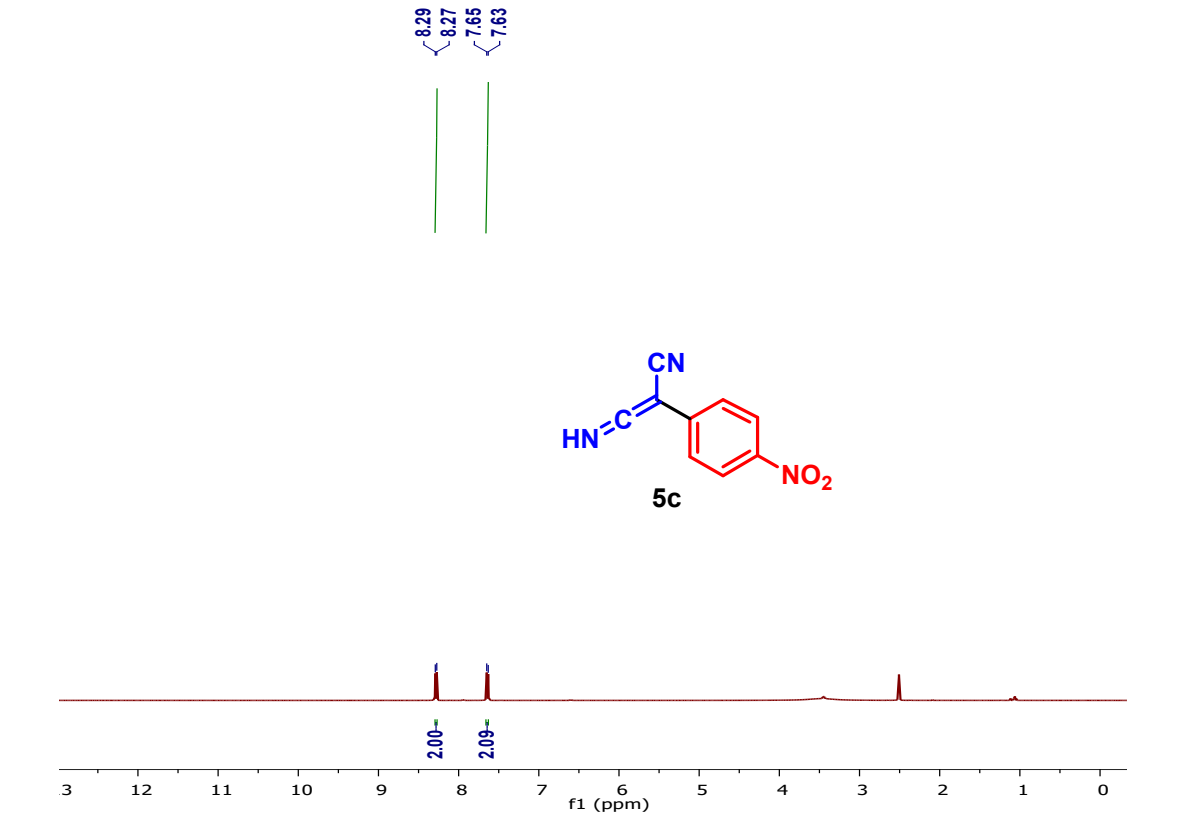
139.76
131.65
131.31
128.11
126.88
126.69
115.58
52.41
52.02
30.85
28.45
16.85
CH3
O
HO
4ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

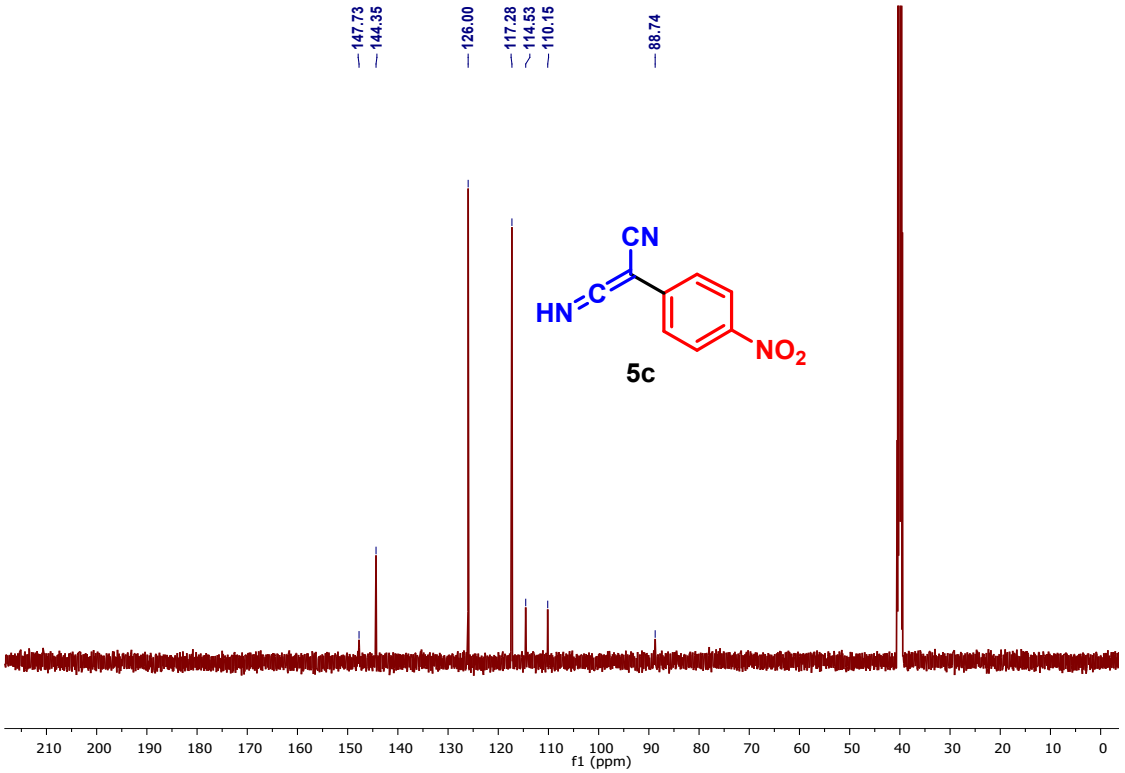

7.38
7.36
7.24
7.22
2.30
CN
HN
C
CH3
5a
2.08
2.05
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

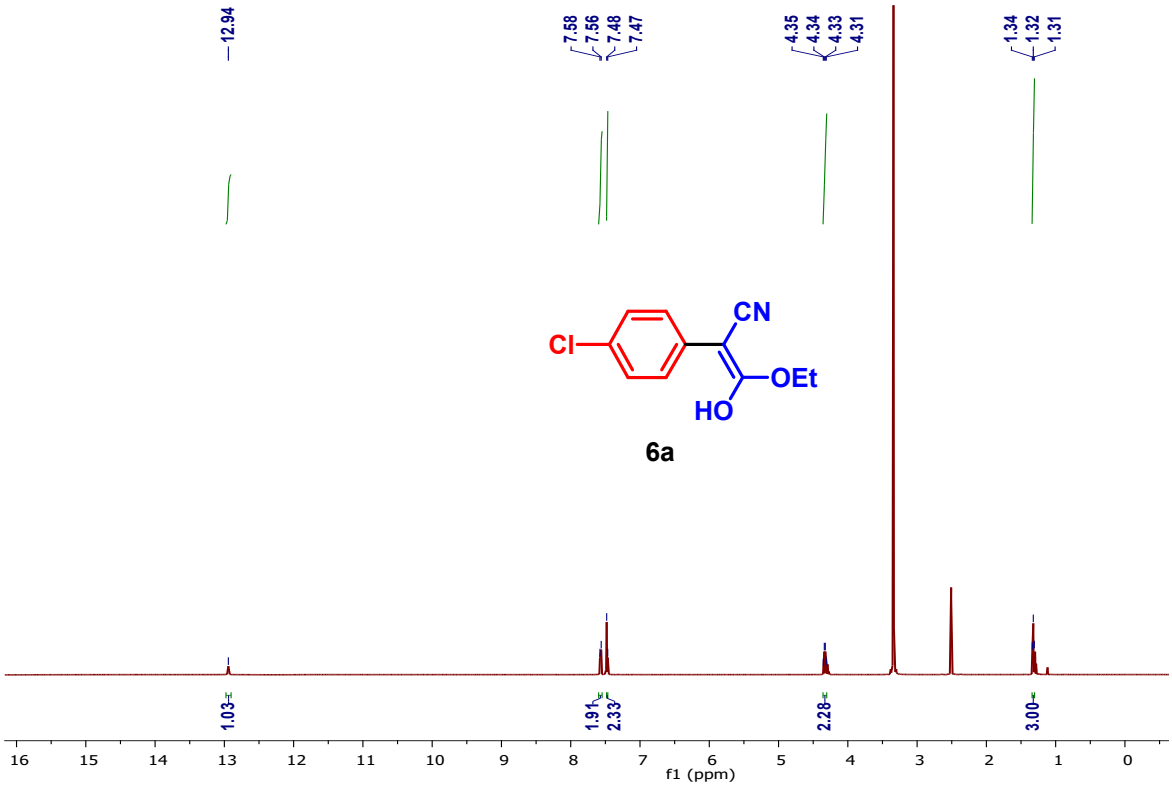

139.64
135.86
130.42
116.92
114.97
110.53
84.21
20.96
CN
HN=C
CH3
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.24
8.03
8.03
8.02
8.01
7.87
7.87
7.85
7.85
7.71
7.70
7.68
CN
HN=C
NO2
5b
0.87
0.97
0.92
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


148.92
143.40
131.57
122.87
120.16
114.55
111.53
110.20
87.20
CN
HN=C
NO2
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.29
8.27
7.65
7.63
CN
HN=C
NO2
5c
2.00
2.09
3 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


147.73
144.35
126.00
117.28
114.53
110.15
88.74
CN
HN
NO2
5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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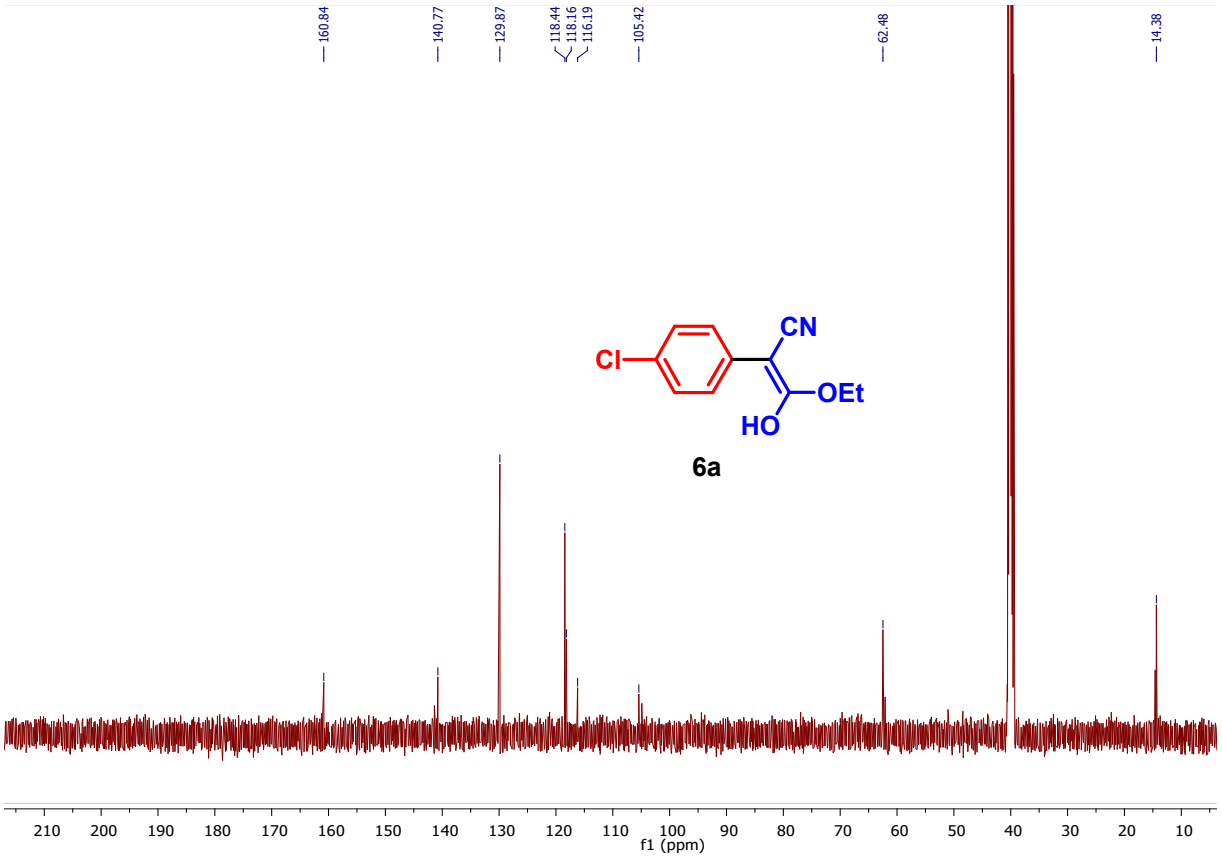
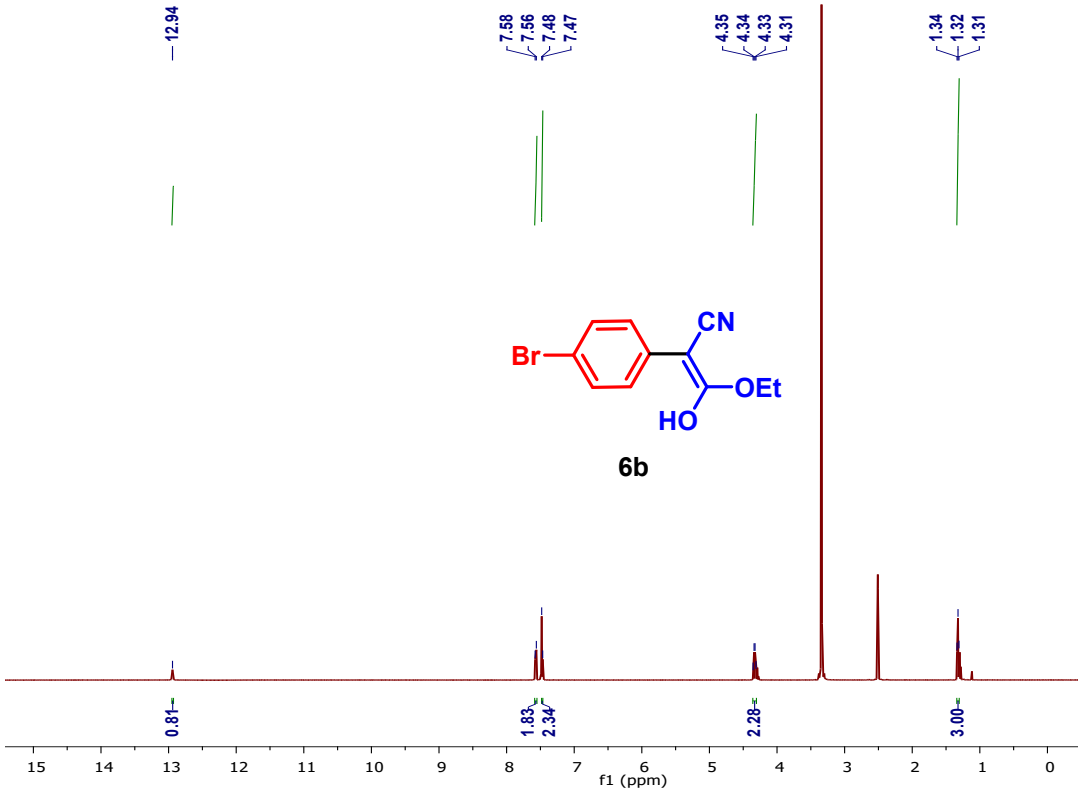
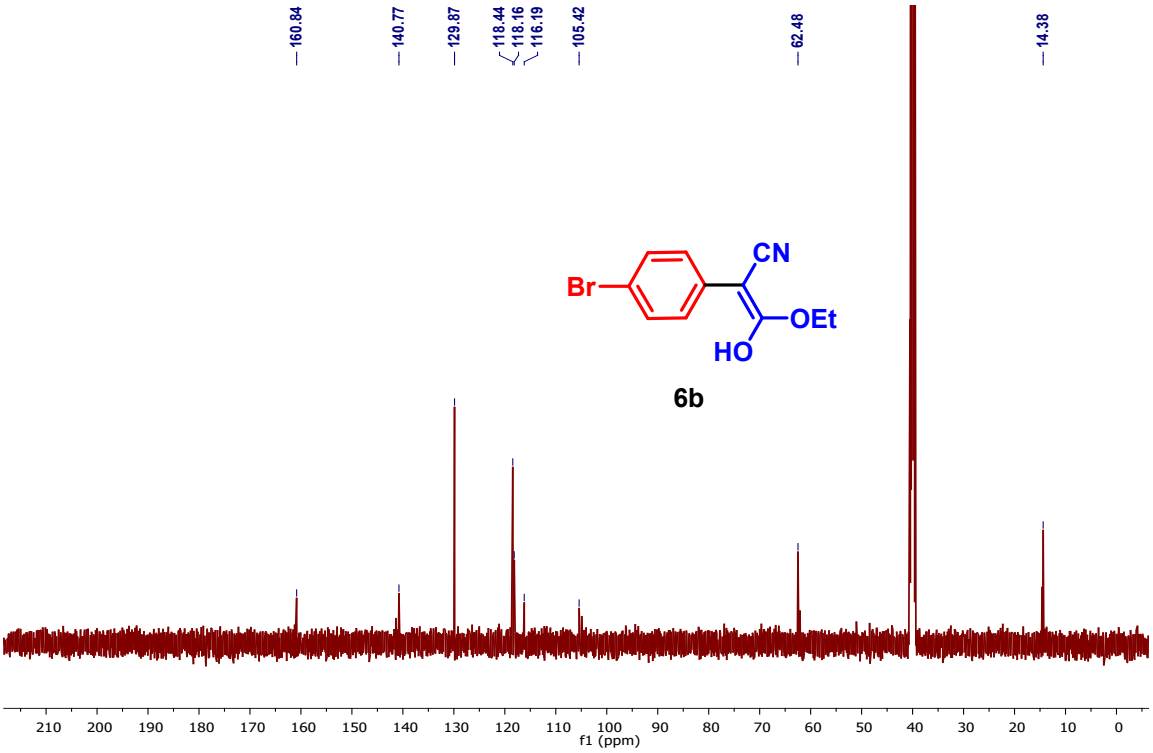
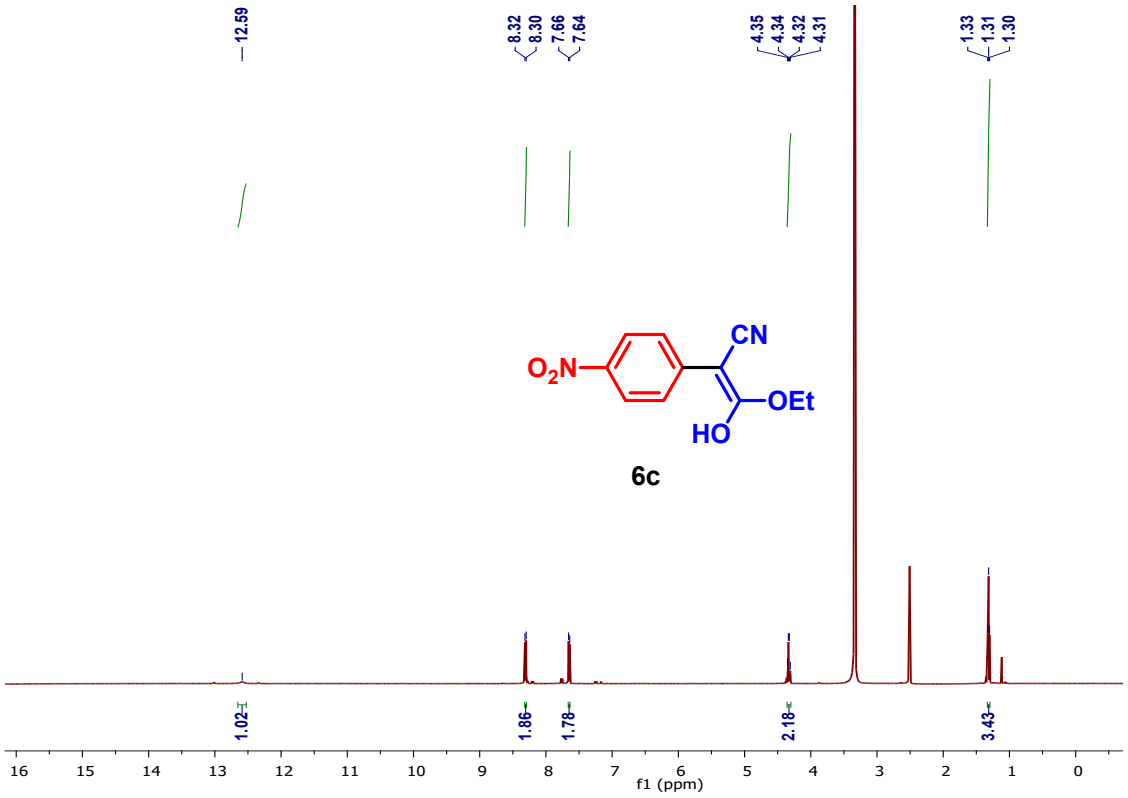
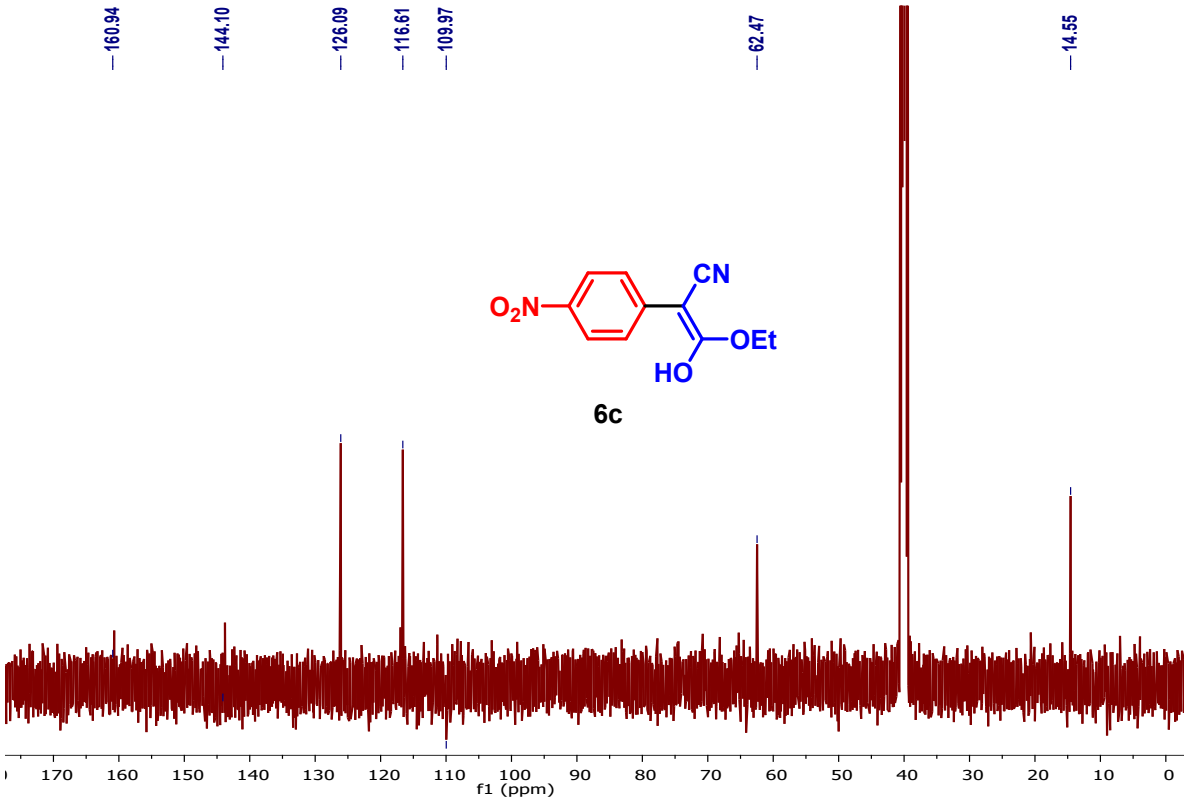
7.58
7.56
7.48
7.47
4.35
4.34
4.33
4.31
1.34
1.32
1.31
Cl
CN
OEt
HO
6a
1.03
1.91
2.33
2.28
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

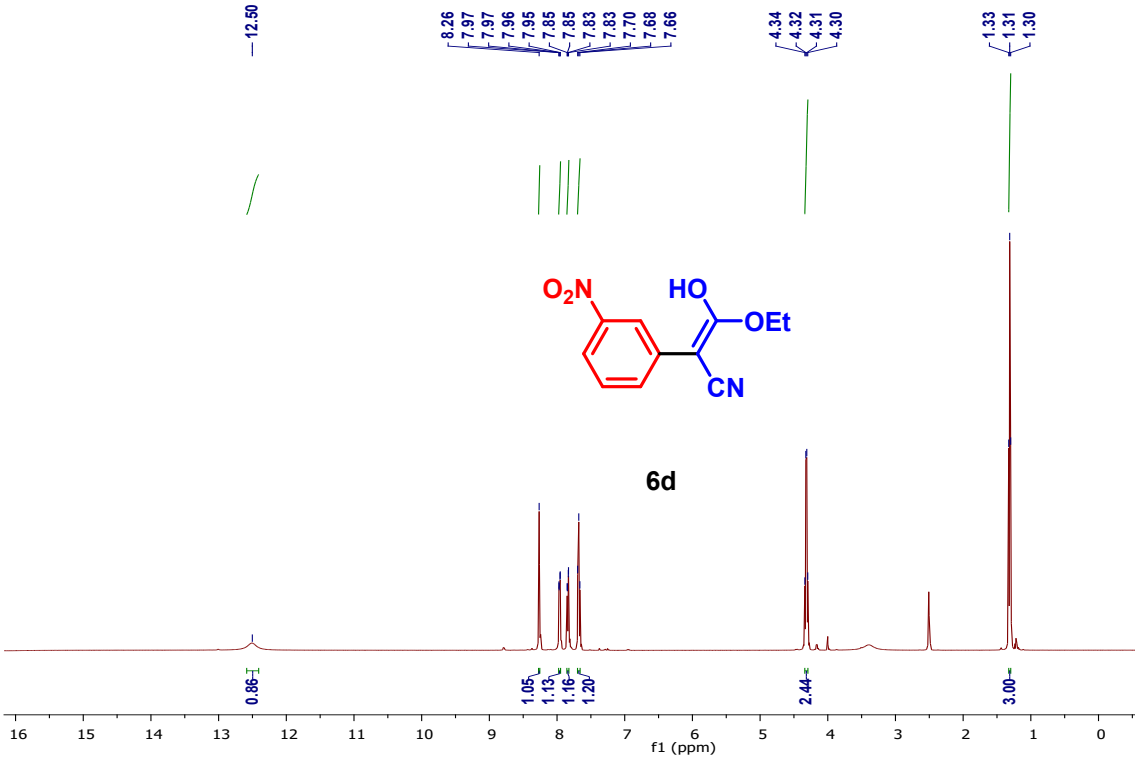

160.84
140.77
129.87
118.44
118.16
116.19
105.42
62.48
14.38
CN
Cl
OEt
HO
6a
f1 (ppm)

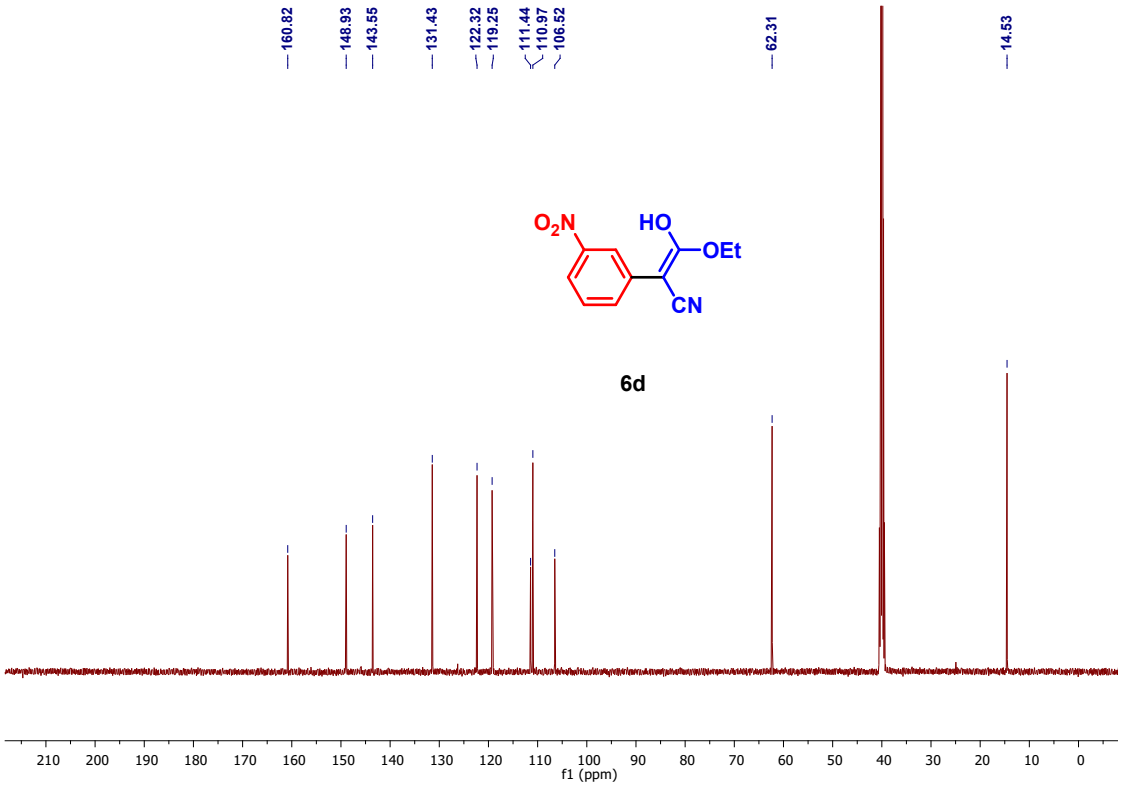

12.94
7.58
7.56
7.48
7.47
4.35
4.34
4.33
4.31
1.34
1.32
1.31
CN
Br
OEt
HO
6b
0.81
1.83
2.34
2.28
3.00
f1 (ppm)


160.84
140.77
129.87
118.44
118.16
116.19
105.42
62.48
14.38
CN
Br
OEt
HO
6b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.59
8.32
8.30
7.66
7.64
4.35
4.34
4.32
4.31
1.33
1.31
1.30
CN
O2N
OEt
HO
6c
1.02
1.86
1.78
2.18
3.43
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


160.94
144.10
126.09
116.61
109.97
62.47
14.55
CN
O_2N
OEt
HO
6c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.50
8.26
7.97
7.97
7.96
7.95
7.85
7.85
7.83
7.83
7.70
7.68
7.66
4.34
4.32
4.31
4.30
1.33
1.31
1.30
O_2N
HO
OEt
CN
6d
0.86
1.05
1.13
1.16
1.20
2.44
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)



6. HRMS Spectra

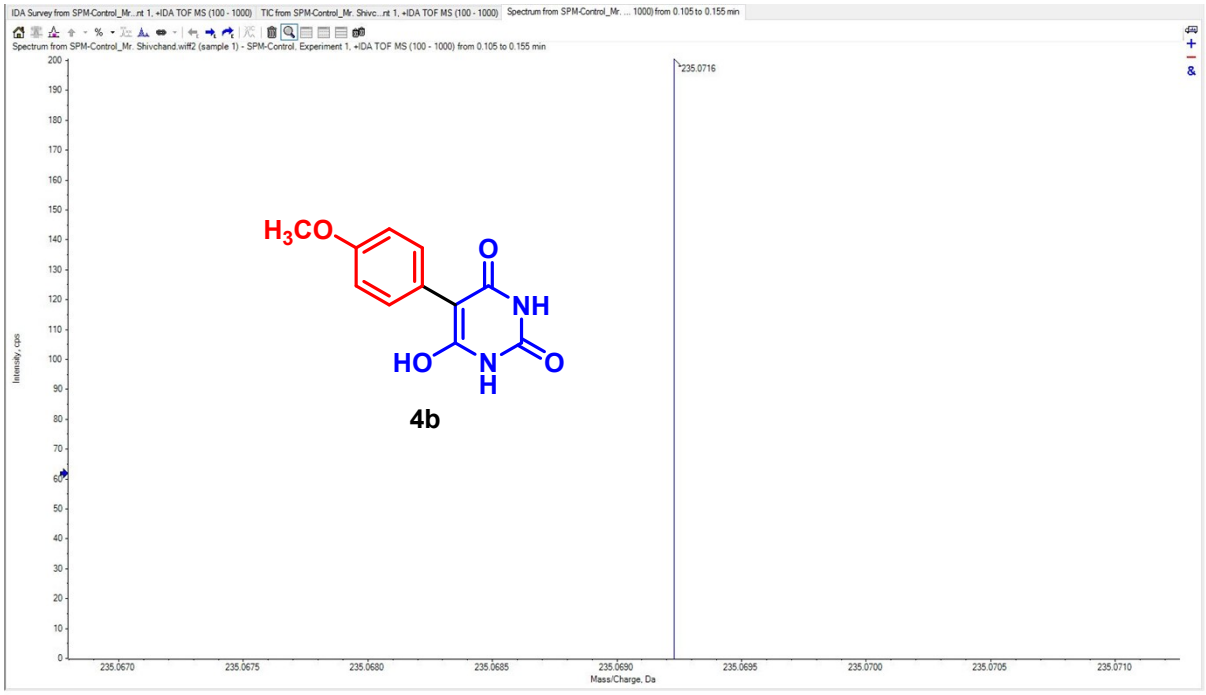


Figure S4

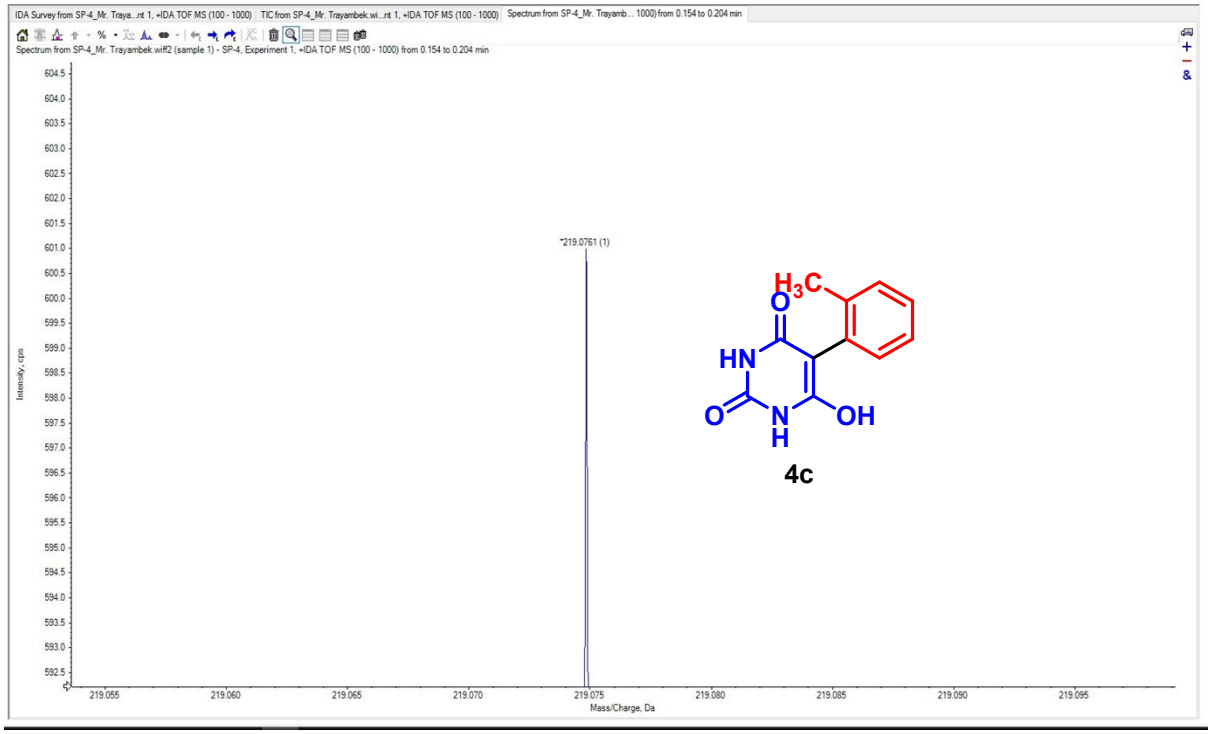


Figure S5

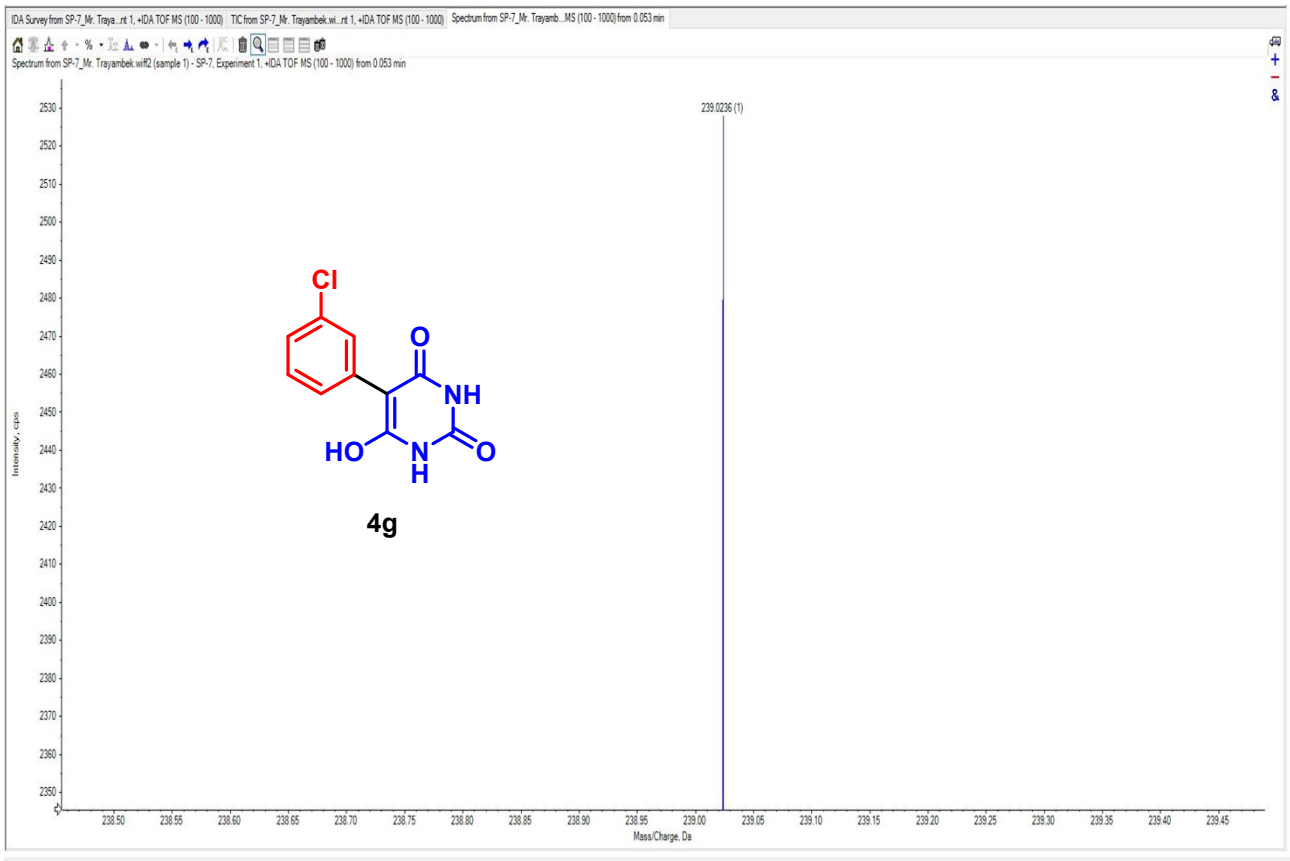


Figure S6

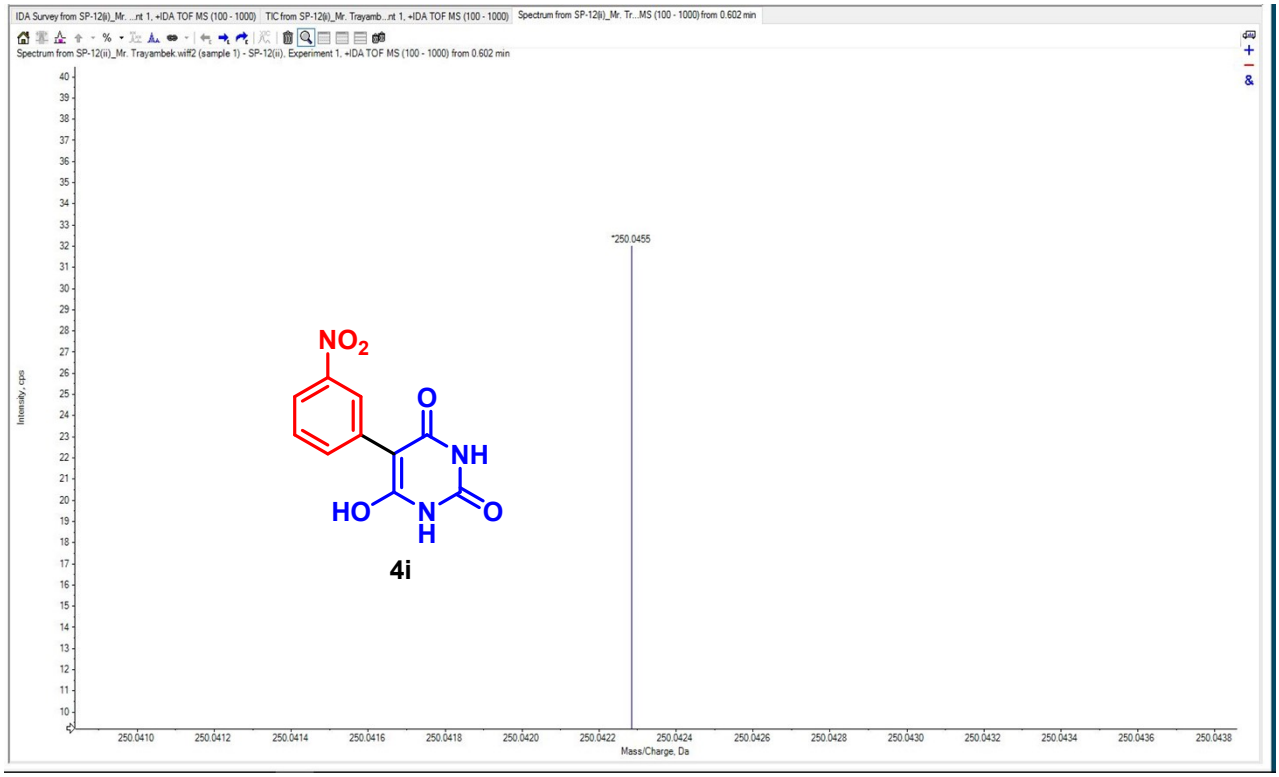


Figure S7

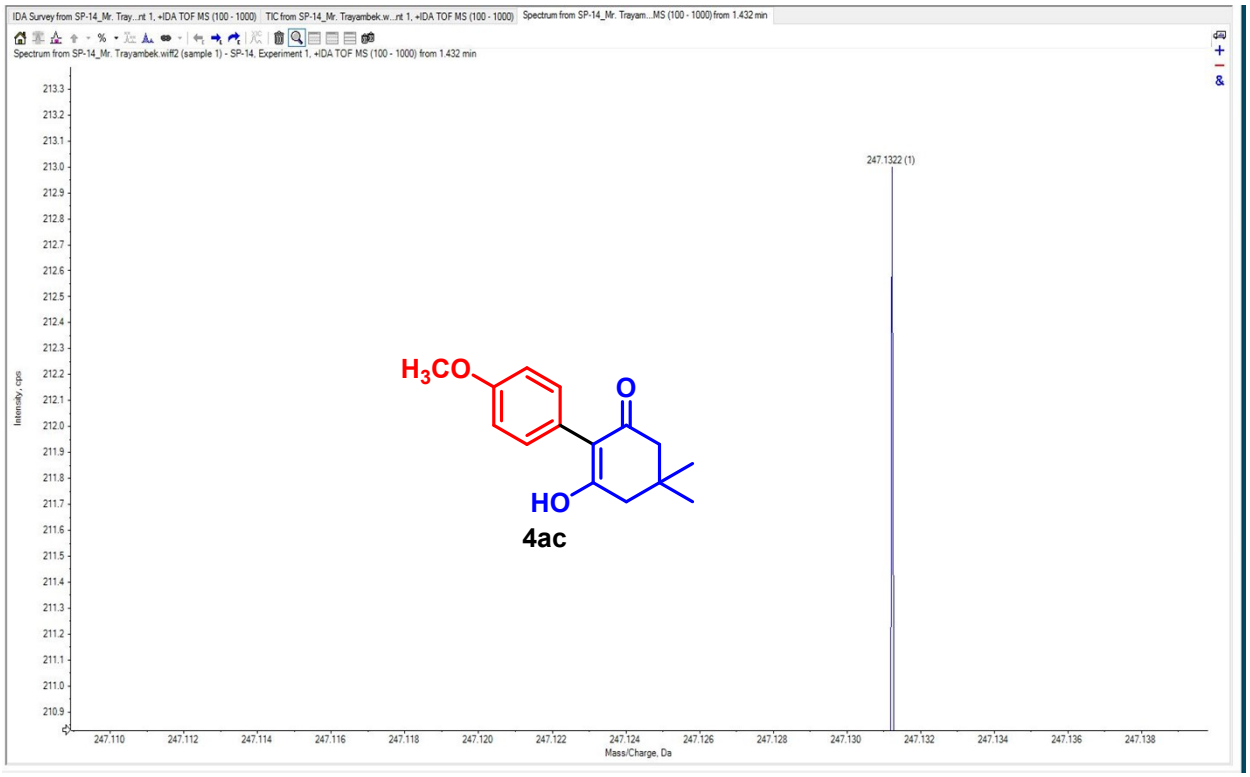


Figure S8

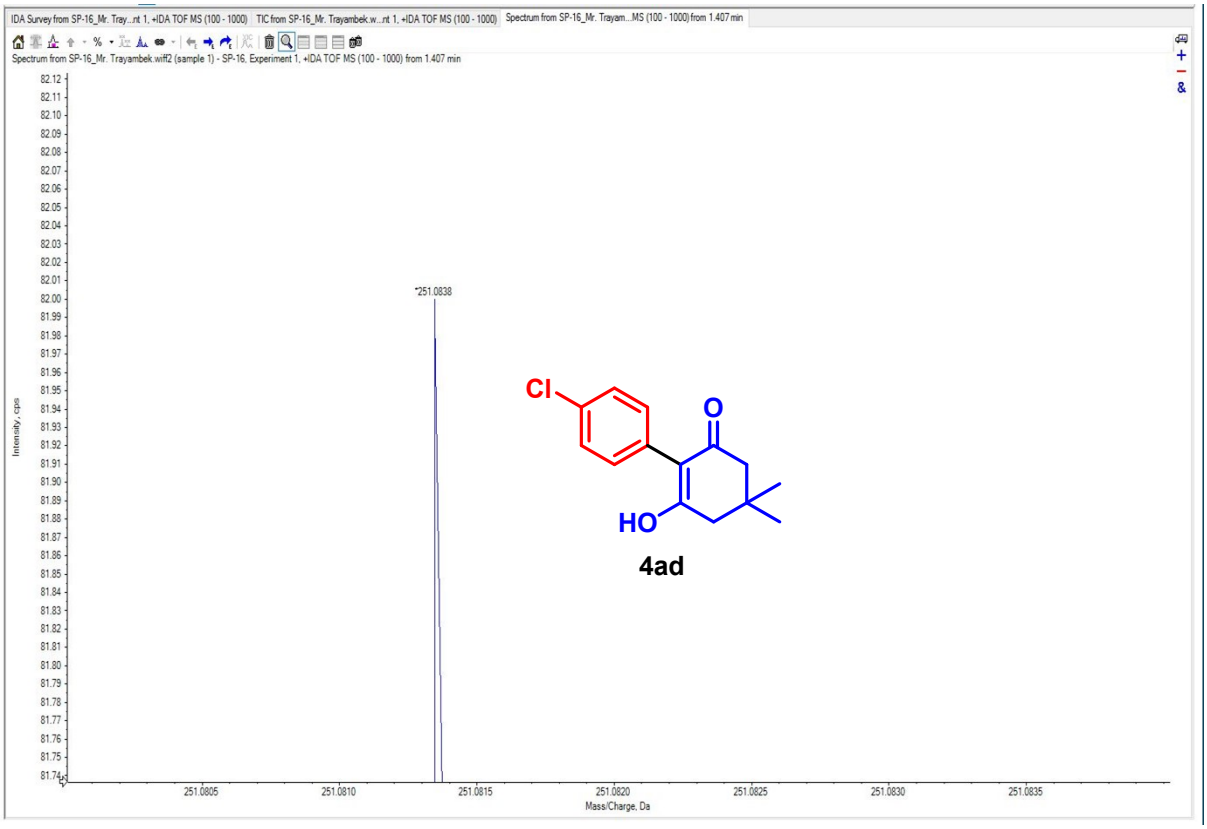


Figure S9

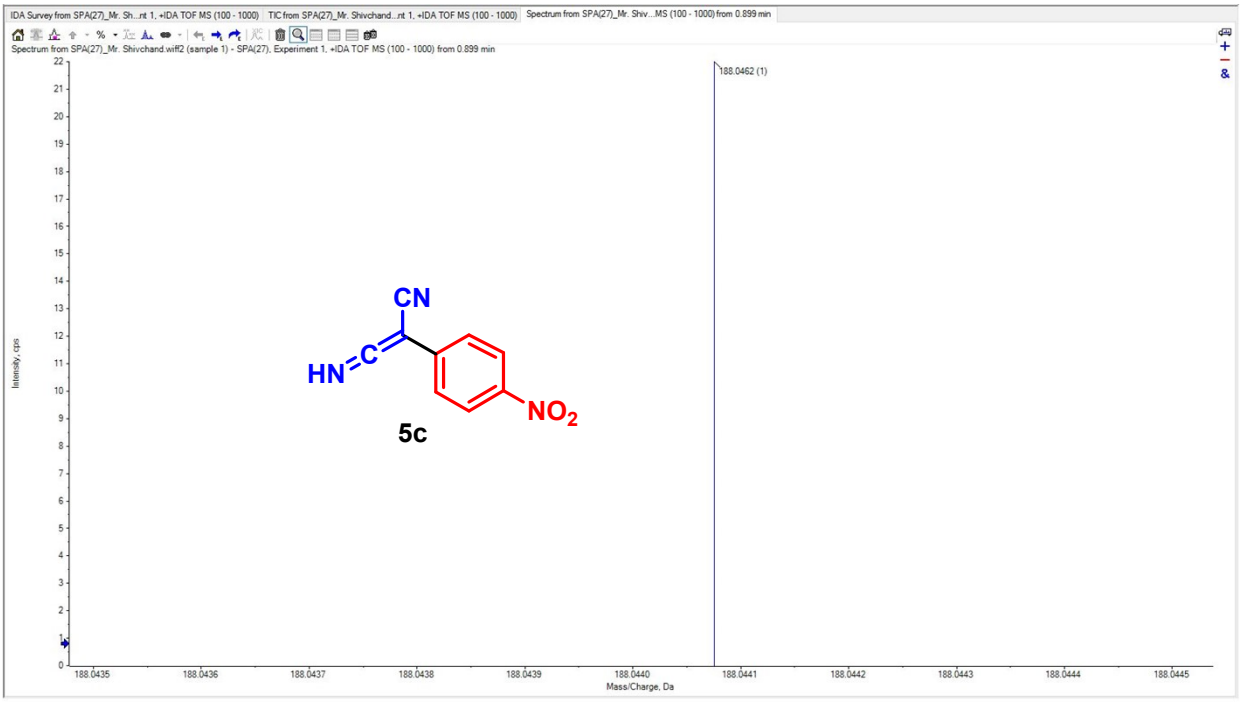


Figure S10

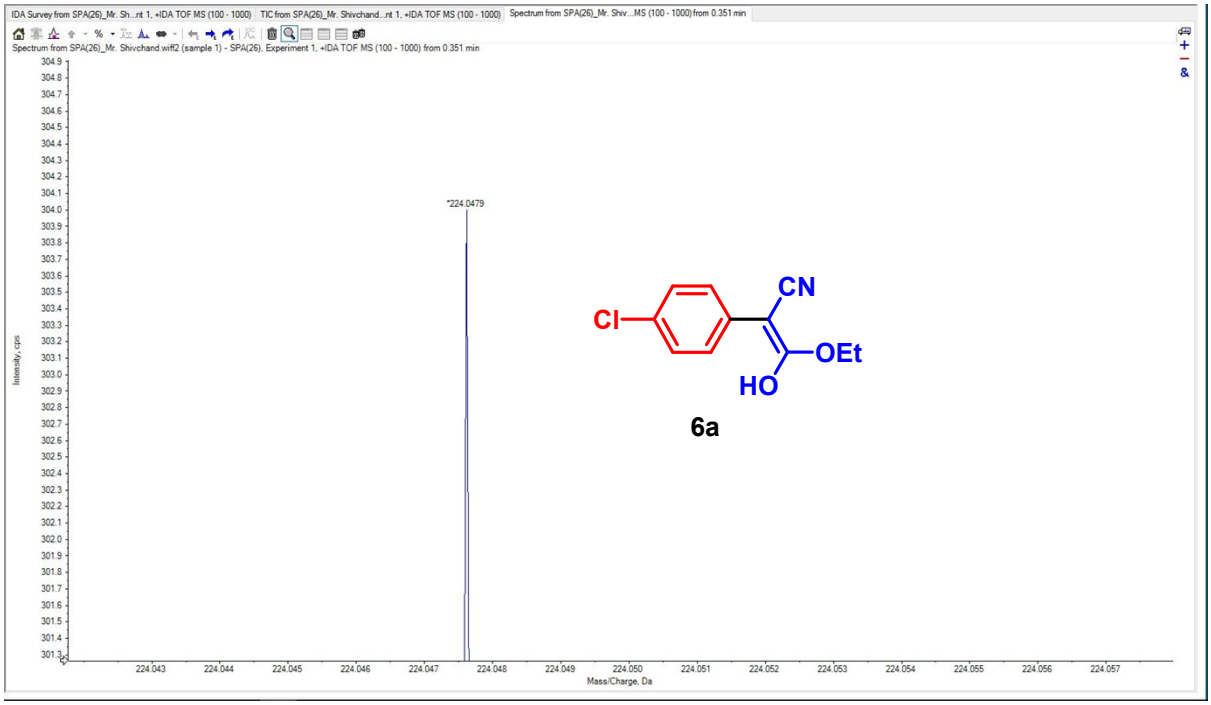
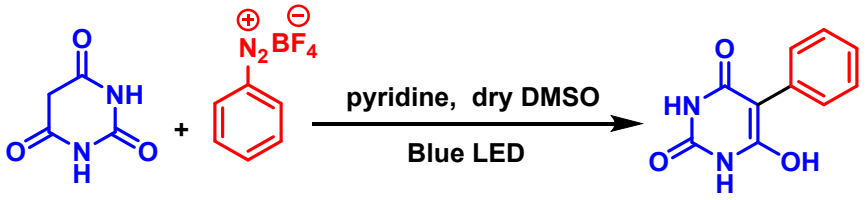

IDA Survey from SPA(26)_Mr. Sh...nt 1, +IDA TOF MS (100 - 1000)
TIC from SPA(26)_Mr. Shivchand...nt 1, +IDA TOF MS (100 - 1000)
Spectrum from SPA(26)_Mr. Shiv...MS (100 - 1000) from 0.351 min
Spectrum from SPA(26)_Mr. Shivchand.wiff2 (sample 1) - SPA(26), Experiment 1, +IDA TOF MS (100 - 1000) from 0.351 min
*224.0479
Intensity, cps
Mass/Charge, Da
Cl
CN
OEt
HO
6a

Figure S11

7. Optimization-Table

Table S1. Optimization of the reaction- conditions[a]



1a 2a 4a

Entry	Bases	Solvents	Yield[b](%)
1	Na_2CO_3	CH_3CN	19
2	Cs_2CO_3	CH_3CN	26
3	$NaHCO_3$	CH_3CN	21
4	K_2CO_3	acetone	49
5	DIPEA	DMSO	10
6	Pyridine	DMSO	80
7[C]	Pyridine	dry DMSO	92
8	Pyridine	DMF	71
9	Pyridine	H_2O	nr
10	Pyridine	CH_3CN	22
11	Pyridine	Ethanol	nr
12	Pyridine	DCM	trace
13	Pyridine	-	49
14	-	CH_3CN	nr
15[d]	Pyridine	dry DMSO	nr
16[e]	Pyridine	dry DMSO	36
17[f]	Pyridine	dry DMSO	79

[a]Reaction condition: **1a** (1.0 mmol), **2a** (1.0 mmol), Pyridine (3 equiv), solvents (5 mL) at room temperature, for 40-45 min, and irradiate under blue LED. [b] Isolated yield, [c]Blue LED, [d]In the dark, [e]a green LED, [f]White LED room temperature, reaction for 40-45 min. (nr = no reaction)

Table S2. Optimization of catalyst[a]

Entry	Catalysts(mol%)	Base	Solvent	Yield[b](%)
1	Eosin-Y (2)	Pyridine	dry DMSO	29
2	Rose-Bengal(5)	Pyridine	dry DMSO	36
3	Acridine-red(10)	Pyridine	dry DMSO	31
4	Rhodamine-B(15)	Pyridine	dry DMSO	19

[a]Reaction condition: **1a** (1.0 mmol), **2a** (1.0 mmol), Pyridine (3 equiv), catalysts (mol%), dry DMSO (5 mL) at room temperature, for 40-45 min, and irradiate under blue LED. [b] Isolated yield.

8. Comparison Table

Table S3. Advantages and disadvantages of methods used for C-arylation of active methylene compounds.[47-49.]

S.no.	Methods used	Advantages and disadvantages	Time
1.	*Iodobenzene + acetylacetone + Cs_2CO_3 at 80 °C in DMSO, in the presence of CuO-nanoparticles*	**Disadvantages:** • Use of CuO nanoparticles catalyst • High temperature • Long reaction time	8-10h
2.	*2-aryl-1,3-dicarbonyl+ aryl iodides and aryl bromides in DMSO at 40-50°C in the presence of Cs_2CO_3. by a CuI/L-proline-catalyzed compounds*	**Disadvantages:** • Use of proline and CuI catalyst • Long reaction time	4-24h
3.	*Sonochemical arylation of active methylene compounds and haloarene in DMSO + potassium carbonate heated at 100-150 ^0C*	**Disadvantages:** • High temperature • Energy-intensive	*30 min.*
4.	*Visible light mediated diazonium salt+ active-methylene compounds+dry DMSO (this study)*	**No such disadvantages** **Advantages:** • No metal catalyst • Dry DMSO used as solvent. • Greener approach as visible light • Easy work-up • Via EDA complex • Less-time	40-45 min.