Electronic Supplementary Material (ESI) for Chemical Communications.

Visible-light-Absorbing, Photocatalysed C-N cross-coupling for synthesis of Hydrazones involving C(sp2)-H/C(sp3)-H functionalization

Ambuj Kumar Kushwaha, Suresh Kumar Maury, Arsala Kamal, Himanshu Kumar Singh, Shikha Pandey and Sundaram Singh*

Department of Chemistry, Indian Institute of Technology (BHU), Varanasi-221005

* Address for Correspondence

Dr. Sundaram Singh, Department of Chemistry, Indian Institute of Technology (BHU), Varanasi– 221 005, U.P., India,

ORCID: https://orcid.org/0000-0001-7931-9652

E-mail: sundaram.apc@iitbhu.ac.in, Tel: +919451658650.

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1. General considerations

All the starting materials like Indole, Phenyl hydrazine, Toluene etc. were purchased from Sigma-Aldrich and were directly used without any further purification. All reactions were conducted under open air 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 was monitored 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. All the ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded through Bruker 500 MHz spectrometer (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz and ^{19}F NMR at 126 MHz), in DMSO-d_6 and $CDCl_3$ 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 Procedures

2.1 General procedure for the preparation of compounds 4a-4o and 5a-5o.

A 25 mL RB flask equipped with a magnetic stirring bar was charged with Indole derivatives **1** (0.25 mmol), Eosin Y (3 mol%) and solvent (5 mL). The mixture was then stirred at room temperature and irradiated with blue LEDs lights strips for 6 h under open air. After that Phenyl hydrazine derivatives **2** (0.25 mmol) were added to the reaction mixture. The progress of the reaction was monitored via TLC. The precipitate obtained was filtered and washed with ethanol after the completion of the reaction. The desired product was obtained in good yields after recrystallization using ethanol.

2.2 General procedure for the preparation of compounds 6a-6t.

A 25 mL RB flask equipped with a magnetic stirring bar was charged with methylarenes **3** (0.25 mmol), Eosin Y (3 mol%) and solvent (5 mL). The mixture was then stirred at room temperature and irradiated with blue LEDs lights strips for 6 h under open air. After that Phenyl hydrazine derivatives **2** (0.25 mmol) were added to the reaction mixture. The progress of the reaction was monitored via TLC. The precipitate obtained was filtered and washed with ethanol after the completion of the reaction. The desired product was obtained in good yields after recrystallization using ethanol.

3. Mechanistic Studies

3.1 Radical trapping experiments by TEMPO/ HRMS data

Several mechanistic investigations were performed to investigate the mechanism of the visible-light photoredox C(sp2)-H/C(sp3)-H functionalization. At first 2, 2, 6, 6-tetramethylpiperidinooxy (TEMPO) (radical scavengers) (3 equiv.) was added to the reaction system, and the trace amount of the 4a and 6a was formed and TEMPO adducts 7a, 8a and 9a were detected in HRMS data from the crude reaction mixture (**Fig.1, 2 and 3**). These results suggested that the reaction passes through radical pathway.

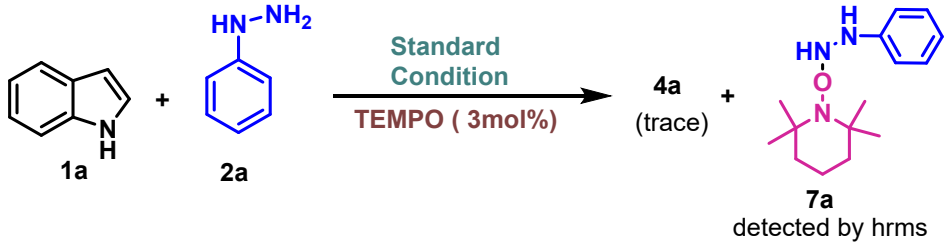
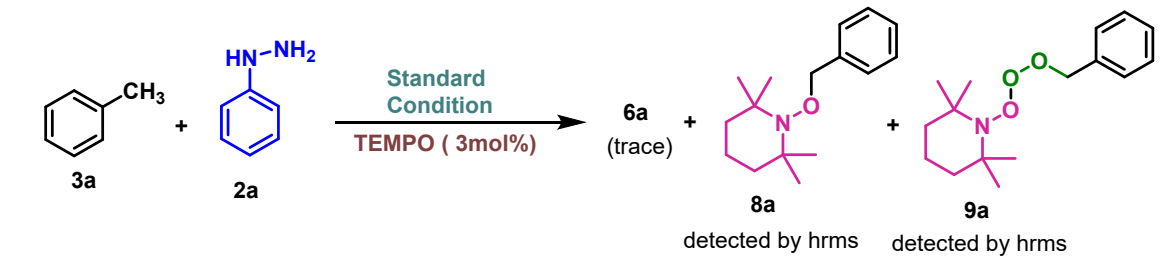


Fig 1: HRMS of adduct 7a



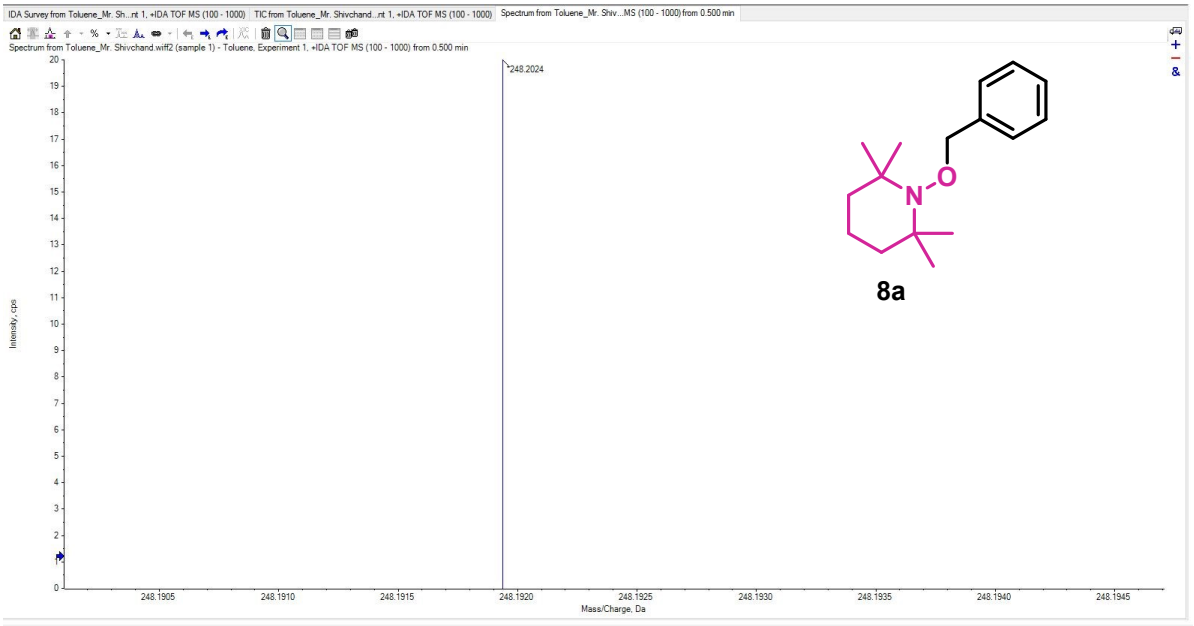
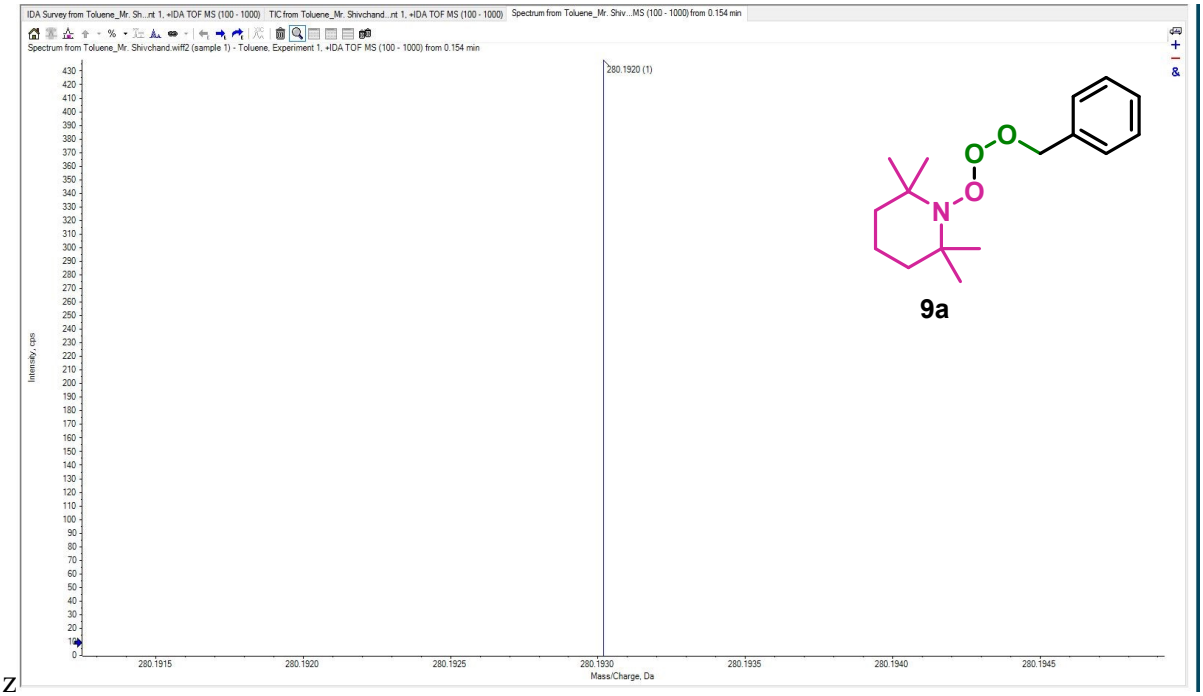


Fig 2: HRMS of adduct 8a



Z

Fig 3: HRMS of adduct 9a

3.2 UV/Vis absorption spectrometry

SHIMADZU UV-1800 UV-visible spectrophotometer was used to record UV- visible spectroscopy of reactants and reaction mixture. The sample was prepared by mixing of 1a, 2a and mixture (1a+2a) (**Fig 1A**) and 3a, 2a and mixture (2a+3a) (**Fig 1B**) in methanol solvent [Conc. reaction mixture = 1.25×10-4mol/L] in a light path quartz UV cuvette.

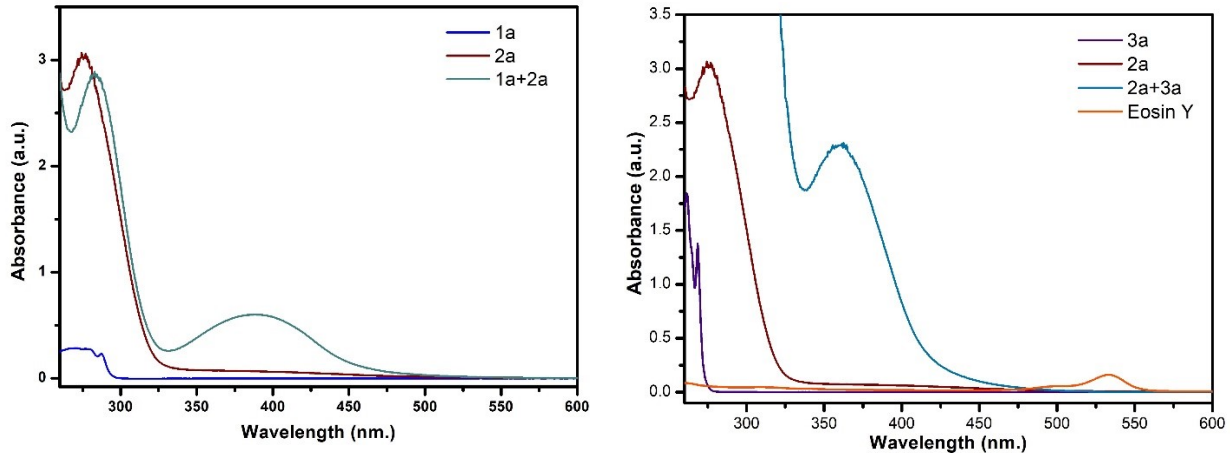


Fig 4- (A) UV-vis absorption spectra of (1a+2a), **(B)** UV-vis absorption spectra (2a+3a)

3.3 Stern- Volmer Fluorescence plots and quenching experiments

In a Fluorescence experiment, the solution of **2a** in ethanol was added to the appropriate amount of **1a**. The addition of **1a** was repeated 7 consecutive times. We recorded the emission spectra after each addition. All the solutions were excited at **275nm** and the emission was acquired from 0 nm to 450 nm. The result shown in **Fig 5** indicates that **2a** quenches the excited state of **1a** and its emission.

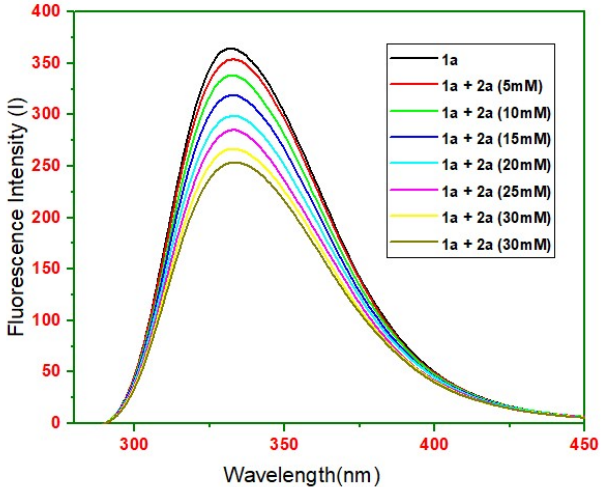


Fig 5: The fluorescence emission spectra of 1a with different concentration of quencher 2

The stern-volmer plot (**Fig 6**) indicated a linear relationship between the concentration of 1 and the ratio I_0/I. The stern-volmer constant K_{SV} was calculated using **equation 1**.

$$I_0/I = 1 + K_{SV}[Q] \qquad \text{…….Eq. 1}$$

Where, I_0 = the intensity of fluorescence of 2a, without quencher 1

I = the intensity of fluorescence of 2a, with quencher 1

[Q] = concentration of the quencher 1

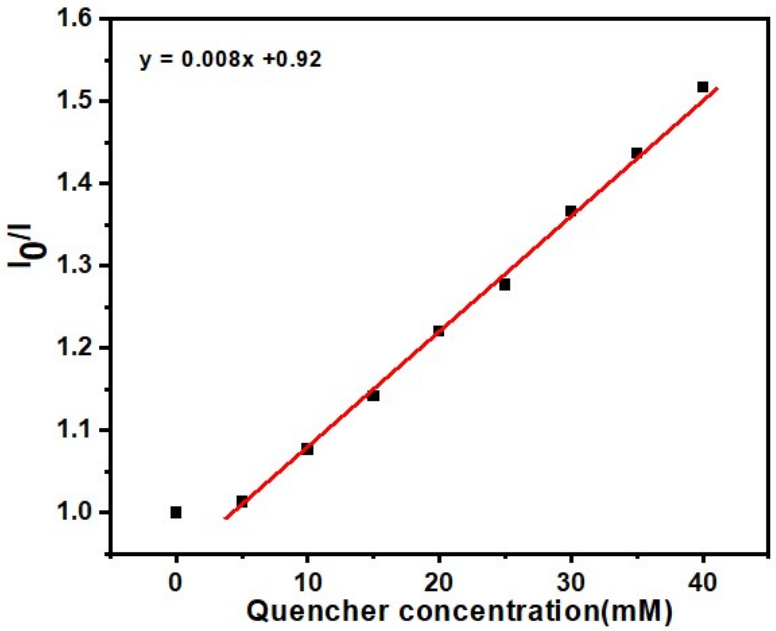


Fig 6: Stern-Volmer fluorescence quenching plot

3.4 Quantum Yield

The Quantum yield was recorded on a PerkinElmer LS 55 Fluorescence spectrometer 1.0 mM stock solution of 4a was prepared and diluted with ethanol. The solution was placed in a screw top 1.cm quartz cuvette and emission spectra of the sample was collected. The excitation wavelength was fixed at 395nm (**Fig 7**).

Estimation of Quantum Yields: The quantum yield of probe ***DPA*** and ***DPA***+N_2H_4 with respect to Quinine sulfate ($\Phi = 0.54$, 1M H_2SO_4) as an internal standard was estimated by using equation

$$\mathbf{Q = Q_R.\ \mathit{I}/\mathit{I}_R.\ OD_R/OD.\ n^2/n^2_R}$$

Where Q is the quantum yield, *I* stand for integrated area of fluorescence intensities, OD is optical densities and *n* is the refractive indexes of solution. The subscript *R* refers to the reference fluorophore of known quantum yield.

Quantum Yields Φ =0.0074

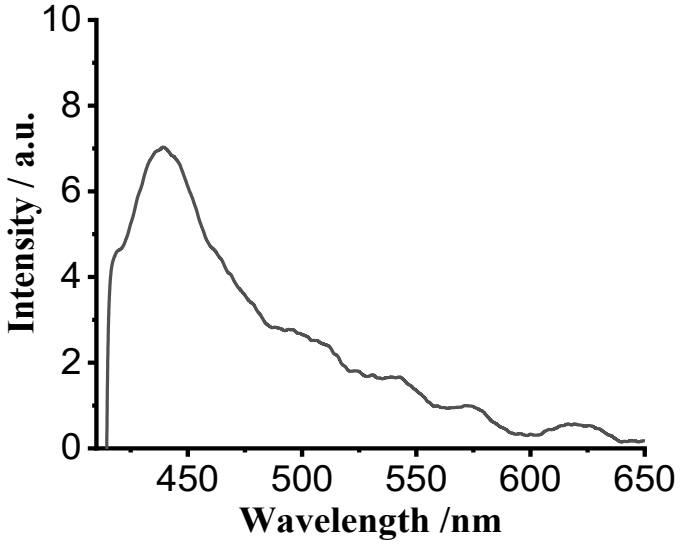


Fig 7: Quantum yield

3.5 Light-Dark cycle experiment

The reaction between **1b** and **2a** was conducted under the standard conditions on a 0.25 mmol scale. The reaction mixture was subjected to sequential periods of stirring under visible light irradiation (blue LED) followed by stirring in the absence of light. At each time point, one reaction system was suspended, which was then purified with column chromatography to give the corresponding products **3a**. The yield of **3a** was measured by weight of the product (**Fig 8**).

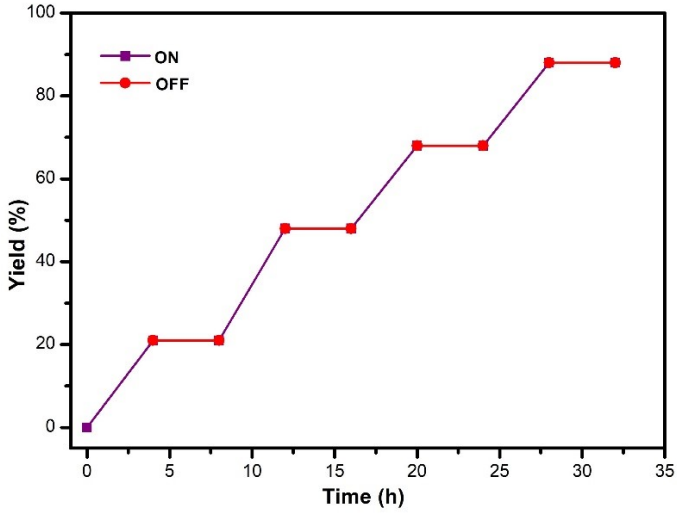


Fig 8: Light-Dark cycle experiment

4. Characterization data of desired compounds

4.1 HRMS spectra of products

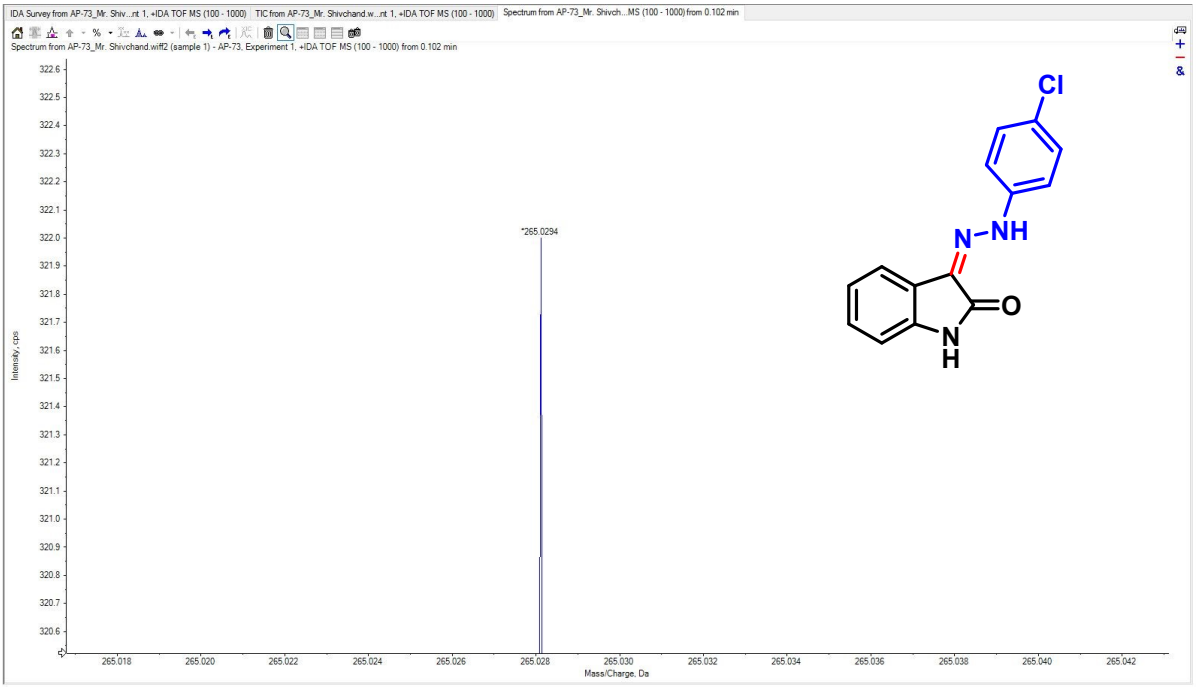


Fig 9: HRMS of compound 5c

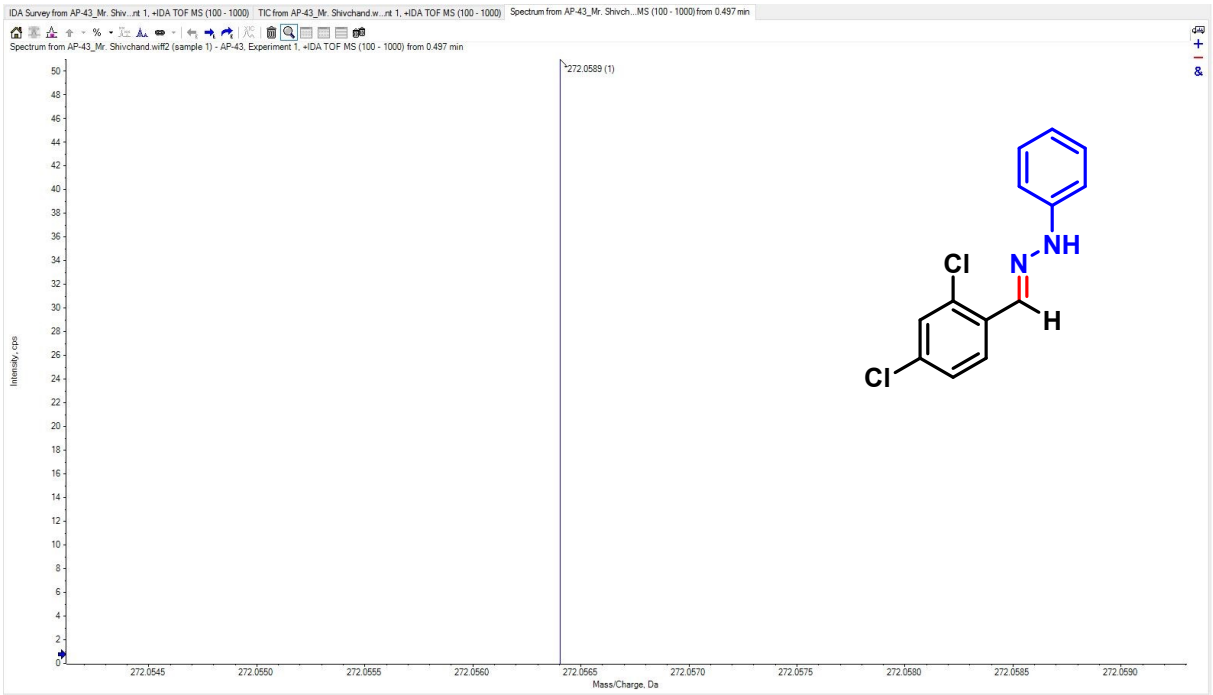
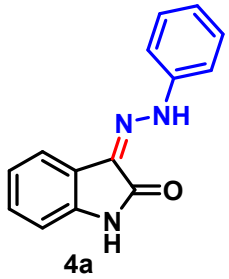


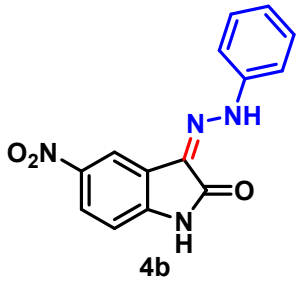
Fig 10: HRMS of compound 6c

4.2 ^{1}H and ^{13}C NMR data

3-(2-phenylhydrazineylidene)indolin-2-one (4a)



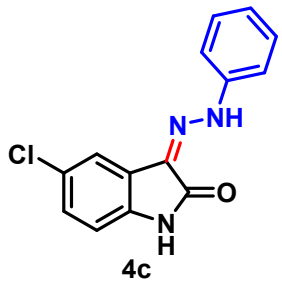
88% yield. Dark yellow solid. m.p.: 218-219 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.75 (s, 1H), 11.03 (s, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.08 – 7.04 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.65, 142.98, 140.28, 129.97, 128.99, 128.16, 123.39, 122.36, 121.63, 119.10, 114.55, 110.99. **HRMS** (ESI) m/z: [M+H] + calculated for C14H11N3O 238.0902; found: 238.0900.



5-nitro-3-(2-phenylhydrazineylidene)indolin-2-one (4b)

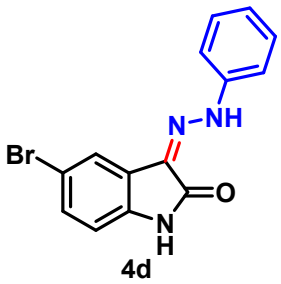
92% yield. Yellowish brown. m.p.: 280-281°C. **^{1}H NMR** (500 MHz, DMSO) δ 12.75 (s, 1H), 11.67 (s, 1H), 8.33 (d, *J* = 2.3 Hz, 1H), 8.18 (m, *J* = 8.6 Hz, 1H), 7.57 (m, *J* = 8.6 Hz, 2H), 7.41 (m, *J* = 7.8 Hz, 2H), 7.12 (m, *J* = 8.2 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 163.77, 145.13, 142.90, 142.57, 129.98, 126.06, 124.77, 124.39, 122.45, 115.39, 114.02, 111.05. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10N4O3 283.0753; found: 283.0757.

5-chloro-3-(2-phenylhydrazineylidene)indolin-2-one (4c)



89% yield. Yellow solid. m.p.: 270-271 °C **^{1}H NMR** (500 MHz, DMSO) δ 12.75 (s, 1H), 11.15 (s, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.39 (m, *J* = 7.8 Hz, 2H), 7.28 (m, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.42, 142.76, 138.80, 129.95, 128.23, 126.95, 126.58, 123.88, 123.46, 118.66, 114.96, 112.40. **HRMS** (ESI) m/z: [M+H] + calculated for C14H11N3O 238.0902; found: 238.0900.

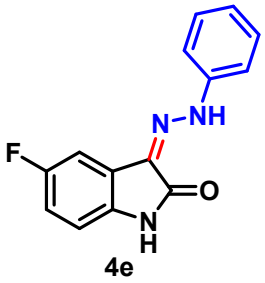
5-bromo-3-(2-phenylhydrazineylidene)indolin-2-one (4d)



4d

91% yield. Brown solid. m.p.: 265-267 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.75 (s, 1H), 11.15 (s, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.27 (m, *J* = 8.3 Hz, 1H), 7.08 (s, 1H), 6.93 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.42, 142.76, 138.81, 129.94, 128.23, 126.96, 126.58, 123.87, 123.46, 118.66, 114.96, 112.39. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10N3BrO 316.0007; found: 316.0006.

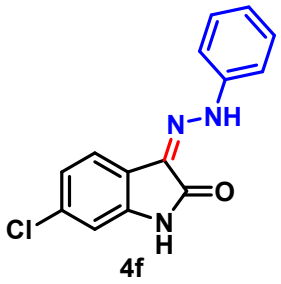
5-fluoro-3-(2-phenylhydrazineylidene)indolin-2-one (4e)



4e

86% yield. Reddish solid. m.p.: 251-253 °C. ^{1}H NMR (500 MHz, DMSO) δ 12.77 (s, 1H), 11.12 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.9 Hz, 3H), 7.46 – 7.42 (m, 1H), 7.15 – 7.09 (m, 1H), 6.92 (dd, *J* = 8.5, 4.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 163.43, 159.69, 146.69, 137.41, 134.25, 130.59, 122.55, 119.75, 116.41, 116.22, 115.28, 112.10, 107.10, 106.90, 104.69. ^{19}F NMR (471 MHz, DMSO) δ -121.15, -121.16. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10FN3O 256.0808; found: 256.0809.

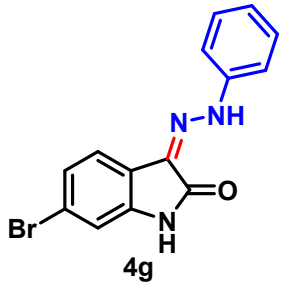
6-chloro-3-(2-phenylhydrazineylidene)indolin-2-one (4f)



4f

91% yield. Yellowish solid. m.p.: 264-265 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.80 (s, 1H), 11.09 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.24 (m, *J* = 8.3 Hz, 1H), 6.99 – 6.97 (m, 2H), 6.92 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.44, 156.39, 138.29, 136.38, 127.60, 126.43, 125.57, 123.67, 118.22, 116.37, 115.24, 112.24. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10ClN3O 272.0512; found: 272.0514.

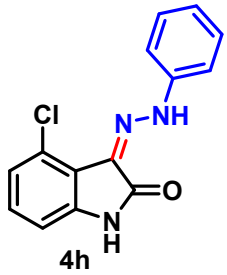
6-bromo-3-(2-phenylhydrazineylidene)indolin-2-one (4g)



4g

92% yield. Yellowish solid. m.p.: 270-272 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.79 (s, 1H), 11.09 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.41 (m, 3H), 7.37 (m, *J* = 8.3 Hz, 1H), 6.99 – 6.96 (m, 2H), 6.88 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.27, 156.40, 138.65, 136.39, 130.38, 125.40, 124.11, 120.98, 116.40, 115.13, 114.13, 112.74. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10BrN3O 316.0007; found: 316.0009.

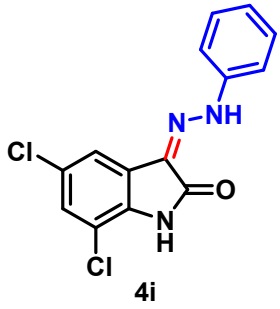
Chloro-3-(2-phenylhydrazineylidene)indolin-2-one (4h)



4h

85% yield. Yellowish solid. m.p.: 263-264 °C. **^{1}H NMR** (500 MHz, DMSO) δ 13.11 (s, 1H), 11.17 (s, 1H), 7.82 (m, *J* = 8.2 Hz, 1H), 7.61 (m, *J* = 7.5 Hz, 1H), 7.51 (m, *J* = 8.0 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.31 (m, *J* = 7.7 Hz, 1H), 7.11 – 7.04 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.83, 140.96, 139.25, 130.09, 129.87, 129.06, 123.76, 122.57, 119.71, 118.64, 114.60, 111.26. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10ClN3O 272.0512; found: 272.0514.

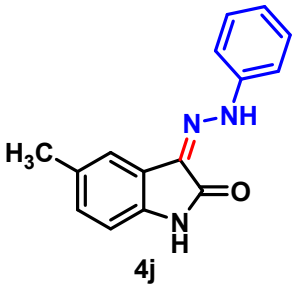
5,7-dichloro-3-(2-phenylhydrazineylidene)indolin-2-one (4i)



4i

84% yield. Dark brown solid. m.p.: 258-259 °C. **^{1}H NMR** (500 MHz, DMSO) δ 13.09 (s, 1H), 11.20 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.49 (m, *J* = 8.8 Hz, 1H), 7.32 (m, *J* = 7.7 Hz, 1H), 7.09 (m, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.84, 141.17, 138.52, 131.61, 130.16, 129.43, 126.50, 122.66, 120.85, 119.90, 115.68, 111.34. **HRMS** (ESI) m/z: [M+H] + calculated for C14H9Cl2N3O 306.0123; found: 306.0124.

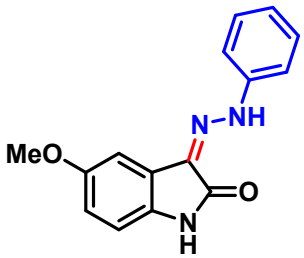
5-methyl-3-(2-phenylhydrazineylidene)indolin-2-one (4j)



4j

86% yield. Yellow solid. m.p.: 251-252 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.73 (s, 1H), 10.92 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.05 (m, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 7.9 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 163.77, 143.04, 138.11, 131.28, 129.95, 129.49, 128.31, 123.28, 121.67, 119.54, 114.49, 110.74, 21.19. **HRMS** (ESI) m/z: [M+H] + calculated for C15H13N3O 252.1059; found: 252.1057.

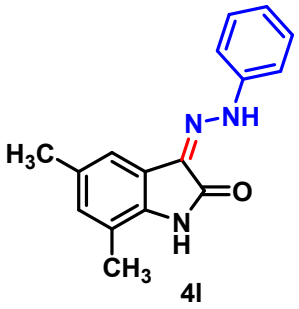
5-methoxy-3-(2-phenylhydrazineylidene)indolin-2-one (4k)



4k

85% yield. Dark brown solid. m.p.: 245-247°C. **^{1}H NMR** (500 MHz, DMSO) δ 12.79 (s, 1H), 10.85 (s, 1H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.15 (s, 1H), 7.05 (s, 1H), 6.84 (d, *J* = 7.1 Hz, 2H), 3.78 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 163.87, 155.56, 142.95, 134.06, 129.94, 128.49, 123.39, 122.44, 115.27, 114.60, 111.69, 104.34, 56.01. **HRMS** (ESI) m/z: [M+H] + calculated for C15H13N3O2 268.1008; found: 268.1009.

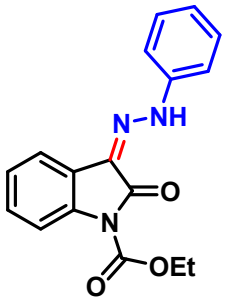
5,7-dimethyl-3-(2-phenylhydrazineylidene)indolin-2-one (4l)



4l

84% yield. White solid. m.p.: 256-258 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.95 (s, 1H), 11.07 (s, 1H), 7.61 – 7.55 (m, 2H), 7.25 (m, *J* = 7.7 Hz, 1H), 7.12 – 7.04 (m, 3H), 6.95 (d, *J* = 7.8 Hz, 1H), 2.26 (d, *J* = 5.2 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 164.05, 140.01, 138.51, 132.10, 131.78, 128.75, 128.28, 122.89, 122.34, 118.95, 112.89, 111.05, 20.83, 16.77. **HRMS** (ESI) m/z: [M+H] + calculated for C16H15N3O 266.1215; found: 266.1217.

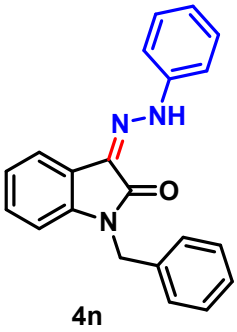
Ethyl-2-oxo-3-(2-phenylhydrazineylidene)indoline-1-carboxylate (4m)



4m

86% yield. Pale yellow solid. m.p.: 284-285 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.58 (s, 1H), 7.66 – 7.63 (m, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.16 (m, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 4.20 (s, 3H), 1.23 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 168.54, 154.11, 145.74, 142.85, 134.26, 131.50, 129.97, 126.64, 123.14, 114.88, 110.01, 61.74, 14.52. **HRMS** (ESI) m/z: [M+H] + calculated for C17H15N3O3 310.1113; found: 310.1114.

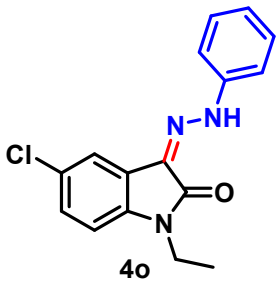
1-benzyl-3-(2-phenylhydrazineylidene)indolin-2-one (4n)



4n

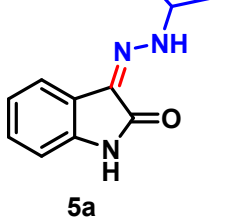
83% yield. Light brown solid. m.p.: 277-278 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.73 (s, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.33 (m, 6H), 7.30 – 7.25 (m, 2H), 7.12 – 7.07 (m, 2H), 5.04 (s, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 161.63, 142.91, 140.55, 136.84, 129.98, 129.19, 128.84, 128.00, 127.86, 123.66, 123.00, 121.05, 118.99, 114.80, 110.28, 42.80. **HRMS** (ESI) m/z: [M+H] + calculated for C21H17N3O 328.1372; found: 328.1374.

5-chloro-1-ethyl-3-(2-phenylhydrazineylidene)indolin-2-one (4o)



4o

86% yield. Yellow solid. m.p.: 280-281°C **^{1}H NMR** (500 MHz, DMSO) δ 12.70 (s, 1H), 7.85 – 7.76 (m, 3H), 7.69 – 7.66 (m, 3H), 7.40 (m, J = 8.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 3.82 (d, J = 7.2 Hz, 2H), 1.21 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 160.74, 146.62, 139.97, 134.22, 129.24, 129.01, 127.29, 122.37, 119.72, 119.44, 115.47, 111.49, 104.90, 31.77, 13.23. **HRMS** (ESI) m/z: [M+H] + calculated for C16H14ClN3O 299.0825; found: 299.0823.



5a

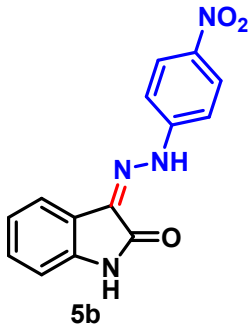
4-(2-(2-oxoindolin-3-ylidene)hydrazineyl)benzonitrile (5a)

93% yield. White solid. m.p.: 241-243°C. **^{1}H NMR** (500 MHz, DMSO) δ 12.76 (s, 1H), 11.12 (s, 1H), 7.82 – 7.78 (m, 2H), 7.61 – 7.57 (m, 3H), 7.32 – 7.28 (m, 1H), 7.08 (m, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 163.33, 146.86, 141.26, 134.27, 131.15, 130.16, 122.59, 121.15, 119.91, 119.82, 114.95, 111.19, 104.24.

HRMS (ESI) m/z: [M+H] + calculated for C15H10N4O 263.0855; found: 263.0854.

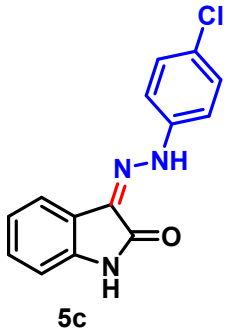
3-(2-(4-nitrophenyl)hydrazineylidene)indolin-2-one (5b)



5b

92% yield. Reddish solid. m.p.: 247-249 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.72 (s, 1H), 11.01 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.49 (m, *J* = 9.1 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.06 (m, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.53, 140.30, 128.97, 128.12, 122.32, 121.65, 119.08, 116.66, 116.48, 116.16, 116.09, 110.96. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10N4O3 283.0753; found: 283.0754.

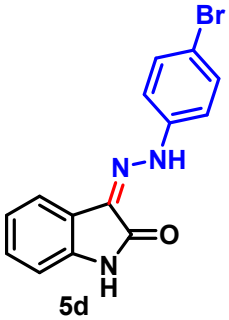
3-(2-(4-chlorophenyl)hydrazineylidene)indolin-2-one (5c)



5c

88% yield. White solid. m.p.: 255-256°C. **^{1}H NMR** (500 MHz, DMSO) δ 12.70 (s, 1H), 11.05 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.47 (m, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.26 (td, *J* = 7.7Hz, 1H), 7.06 (td, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.52, 142.09, 140.53, 129.75, 129.30, 128.86, 126.81, 122.42, 121.48, 119.30, 116.20, 111.05. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10ClN3O 272.0512; found: 272.0513.

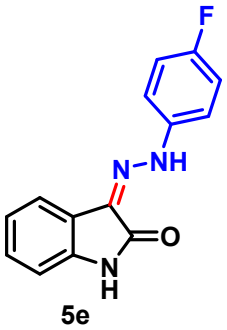
3-(2-(4-bromophenyl)hydrazineylidene)indolin-2-one (5d)



5d

89% yield. Yellowish solid. m.p.: 259-260 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.71 (s, 1H), 11.05 (s, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.41 (m, *J* = 9.1 Hz, 2H), 7.26 (m, *J* = 7.7 Hz, 1H), 7.06 (m, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.51, 142.11, 140.54, 129.75, 129.30, 128.86, 126.81, 122.41, 121.49, 119.30, 116.20, 111.05. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10BrN3O ;316.0007 found: 316.0009.

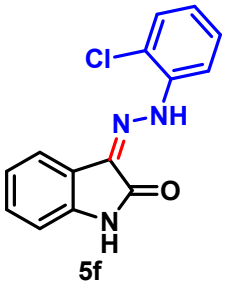
3-(2-(4-fluorophenyl)hydrazineylidene)indolin-2-one (5e)



5e

85% yield. White solid. m.p.: 248-249 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.72 (s, 1H), 11.01 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.27 – 7.20 (m, 3H), 7.06 (td, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.53, 140.30, 139.71, 128.97, 122.32, 121.65, 119.08, 116.66, 116.48, 116.16, 116.09, 110.96. ^{19}F NMR (471 MHz, DMSO) δ -120.75. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10FN3O 256.0808; found: 256.0809.

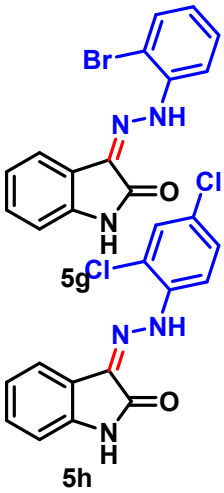
3-(2-(2-chlorophenyl)hydrazineylidene)indolin-2-one (5f)



5f

86% yield. White solid. m.p.: 257-258 °C. **^{1}H NMR** (500 MHz, DMSO) δ 13.11 (s, 1H), 11.17 (s, 1H), 7.82 (m, *J* = 8.2 Hz, 1H), 7.61 (m, *J* = 7.5 Hz, 1H), 7.51 (m, *J* = 8.0 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.31 (m, *J* = 7.7 Hz, 1H), 7.11 – 7.04 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.83, 140.96, 139.25, 130.94, 130.09, 129.87, 129.06, 123.76, 122.57, 121.03, 119.71, 118.64, 114.60, 111.26. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10ClN3O 272.0512; found: 272.0514.

3-(2-(2-bromophenyl)hydrazineylidene)indolin-2-one (5g)

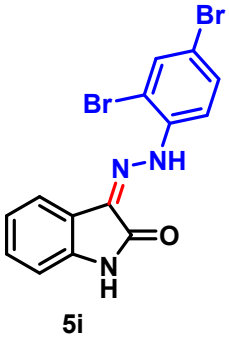


86% yield. Yellowish solid. m.p.: 264-265 °C. **^{1}H NMR** (500 MHz, DMSO) δ 13.11 (s, 1H), 11.17 (s, 1H), 7.82 (m, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.51 (m, *J* = 8.0Hz, 1H), 7.45 – 7.40 (m, 1H), 7.31 (m, *J* = 7.7 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.84, 140.97, 139.27, 130.95, 130.10, 129.88, 129.08, 123.78, 122.58, 121.04, 119.72, 118.65, 114.61, 111.27. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10BrN3O 316.0007; found: 316.0008.

3-(2-(2,4-dichlorophenyl)hydrazineylidene)indolin-2-one (5h)

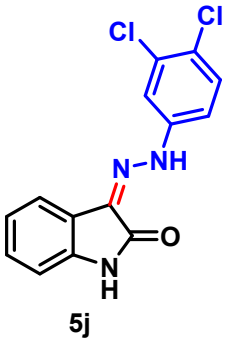
83% yield. White solid. m.p.: 248-249 °C. **^{1}H NMR** (500 MHz, DMSO) δ 13.09 (s, 1H), 11.20 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.49 (m, *J* = 8.8 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.09 (m, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.84, 141.17, 138.52, 131.61, 130.16, 129.43, 129.19, 126.50, 122.66, 120.85, 119.90, 119.19, 115.68, 111.34. **HRMS** (ESI) m/z: [M+H] + calculated for C14H9Cl2N3O 306.0123; found: 306.0125.

3-(2-(2,4-dibromophenyl)hydrazineylidene)indolin-2-one (5i)



82% yield. White solid. m.p.: 237-238 °C. **^{1}H NMR** (500 MHz, DMSO) δ 13.09 (s, 1H), 11.20 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 2.3 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.49 (m, *J* = 8.8 Hz, 1H), 7.32 (m, *J* = 7.7 Hz, 1H), 7.09 (m, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.84, 141.17, 138.53, 131.61, 130.17, 129.43, 129.19, 126.51, 122.66, 120.85, 119.90, 119.20, 115.69, 111.35. **HRMS** (ESI) m/z: [M+H] + calculated for C14H9Br2N3O 393.9112; found: 393.9114.

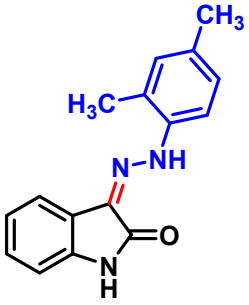
3-(2-(3,4-dichlorophenyl)hydrazineylidene)indolin-2-one (5j)



5j

86% yield. White solid. m.p.: 238-239 °C. **^{1}H NMR** (500 MHz, DMSO) δ 13.09 (s, 1H), 11.20 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 2.3 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.49 (m, *J* = 8.8 Hz, 1H), 7.32 (m, *J* = 7.7 Hz, 1H), 7.09 (m, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.84, 141.17, 138.53, 131.61, 130.17, 129.43, 129.19, 126.51, 122.66, 120.85, 119.90, 119.20, 115.69, 111.35. **HRMS** (ESI) m/z: [M+H] + calculated for C14H9Cl2N3O 306.0123; found: 306.0124.

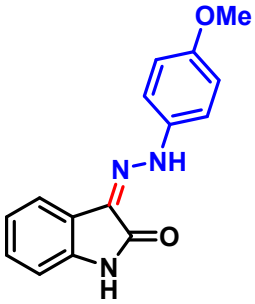
3-(2-(2,4-dimethylphenyl)hydrazineylidene)indolin-2-one (5k)



5k

85% yield. Reddish solid. m.p.: 229-230 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.95 (s, 1H), 11.07 (s, 1H), 7.61 – 7.55 (m, 2H), 7.25 (m, *J* = 7.7 Hz, 1H), 7.12 – 7.04 (m, 3H), 6.95 (d, *J* = 7.8 Hz, 1H), 2.26 (d, *J* = 5.2 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 164.05, 140.01, 138.51, 132.10, 131.78, 128.75, 128.33, 128.28, 122.89, 122.34, 121.52, 118.95, 112.89, 111.05, 20.83, 16.77. **HRMS** (ESI) m/z: [M+H] + calculated for C16H15N3O 266.1215; found: 266.1216.

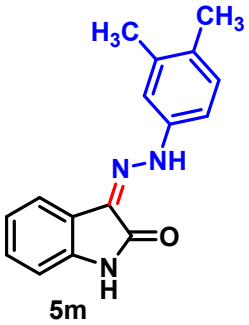
3-(2-(4-methoxyphenyl)hydrazineylidene)indolin-2-one (5l)



5l

86% yield. Brick red solid. m.p.: 227-229 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.78 (s, 1H), 10.96 (s, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.22 (t, *J* = 8.3 Hz, 1H), 7.04 (m, *J* = 9.3 Hz, 1H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 163.66, 156.03, 139.81, 136.65, 128.39, 126.82, 122.18, 121.86, 118.70, 115.93, 115.28, 110.86, 55.81. **HRMS** (ESI) m/z: [M+H] + calculated for C15H13N3O2 268.1008; found: 268.1009.

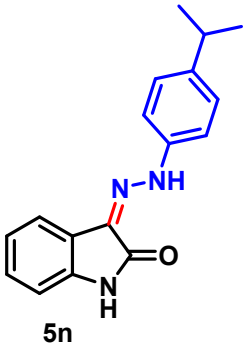
3-(2-(3,4-dimethylphenyl)hydrazineylidene)indolin-2-one (5m)



5m

86% yield. White solid. m.p.: 238-239 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.95 (s, 1H), 11.07 (s, 1H), 7.60 – 7.55 (m, 2H), 7.25 (m, *J* = 7.7 Hz, 1H), 7.09 (m, *J* = 7.1 Hz, 1H), 7.06 (m, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 2.26 (d, *J* = 5.2 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 164.05, 140.01, 138.51, 132.10, 131.78, 128.75, 128.33, 128.28, 122.89, 122.34, 121.52, 118.95, 112.89, 111.05, 20.83, 16.78. **HRMS** (ESI) m/z: [M+H] + calculated for C16H15N3O 266.1215; found: 266.1217.

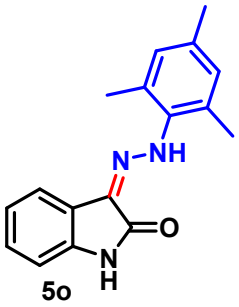
3-(2-(4-isopropylphenyl)hydrazineylidene)indolin-2-one (5n)



5n

88% yield. White solid. m.p.: 228-229°C. **^{1}H NMR** (500 MHz, DMSO) δ 12.78 (s, 1H), 11.13 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.26 (m, *J* = 8.6 Hz, 4H), 6.93 (d, *J* = 8.3 Hz, 1H), 2.91 – 2.85 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 163.47, 144.23, 140.71, 138.56, 127.95, 127.74, 126.51, 126.30, 123.54, 118.43, 115.02, 112.33, 33.34, 24.42. **HRMS** (ESI) m/z: [M+H] + calculated for C16H15N3O 279.1372; found: 279.1374.

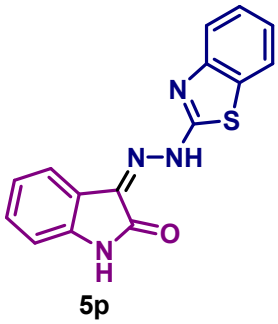
3-(2-mesitylhydrazineylidene)indolin-2-one (5o)



5o

82% yield. White solid. m.p.: 231-232 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.76 (s, 1H), 11.02 (s, 1H), 7.24 (m, J = 8.4 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.95 – 6.90 (m, 3H), 2.36 (s, 6H), 2.24 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 163.51, 138.06, 136.50, 134.15, 130.42, 128.50, 127.54, 126.43, 125.87, 123.72, 117.80, 112.33, 20.82, 19.37. **HRMS** (ESI) m/z: [M+H] + calculated for C17H17N3O 279.1372; found: 279.1375.

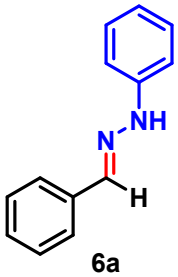
3-(2-(benzo[d]thiazol-2-yl)hydrazineylidene)indolin-2-one (5p)



5p

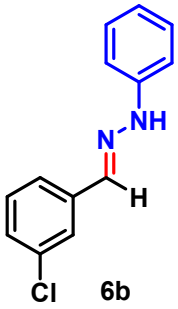
83% yield. Brick red solid. m.p.: 270-272 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.13 (s, 1H), 11.04 (s, 1H), 7.59 (m, *J* = 7.7 Hz, 2H), 7.51 (m, *J* = 7.4 Hz, 2H), 7.07 (m, *J* = 7.4 Hz, 2H), 6.91 (m, *J* = 7.9 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 184.86, 159.83, 151.19, 138.84, 136.28, 127.58, 125.16, 123.23, 118.30, 112.67.

1-benzylidene-2-phenylhydrazine (6a)



6a

86% yield. White solid. m.p.: 210-212 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.34 (s, 1H), 7.86 (s, 1H), 7.67 – 7.63 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (m, *J* =7.4 Hz, 2H), 7.08 (d, *J* = 1.0 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 145.75, 136.87, 136.30, 129.59, 129.12, 128.38, 126.08, 119.21, 112.44. **HRMS** (ESI) m/z: [M+H] + calculated for C13H12N2 197.1000; found: 197.1002.

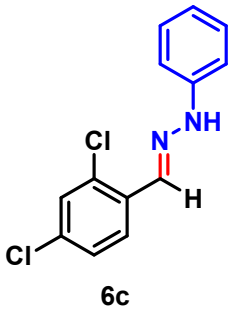


6b

1-(3-chlorobenzylidene)-2-phenylhydrazine (6b)

90% yield. Light brown. m.p.: 215-216 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.52 (s, 1H), 7.83 (s, 1H), 7.70 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 5.8 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 145.42, 138.65, 135.03, 134.01, 130.97, 129.63, 127.87, 124.68, 112.63. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11ClN2 231.0611; found: 231.0613.

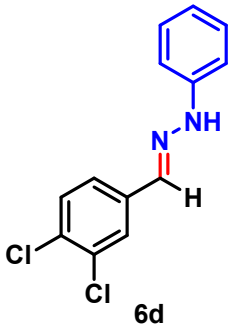
1-(2,4-dichlorobenzylidene)-2-phenylhydrazine (6c)



6c

87% yield. Cream solid. m.p.: 219-221 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.80 (s, 1H), 8.14 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 145.08, 132.09, 131.24, 129.69, 129.56, 128.18, 127.40, 120.02, 112.74. **HRMS** (ESI) m/z: [M+H] + calculated for C13H10Cl2N2 265.0221; found: 265.0222.

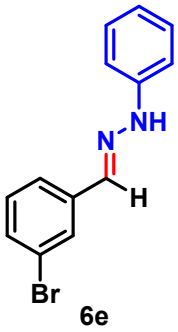
1-(3,4-dichlorobenzylidene)-2-phenylhydrazine (6d)



6d

87% yield. White solid. m.p.: 216-218 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.81 (s, 1H), 8.14 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.44 (m, *J* = 8.6 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 145.07, 132.88, 132.54, 132.09, 131.23, 129.70, 129.57, 128.20, 127.40, 120.02, 112.73. **HRMS** (ESI) m/z: [M+H] + calculated for C13H10Cl2N2 265.0221; found: 265.0223.

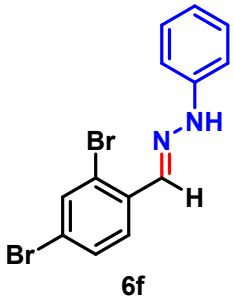
1-(3-bromobenzylidene)-2-phenylhydrazine (6e)



6e

92% yield. White solid. m.p.: 213-215 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.53 (s, 1H), 7.83 (s, 1H), 7.71 – 7.69 (m, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.33 (m, *J* = 7.9 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.09 (m, *J* = 8.6 Hz, 2H), 6.78 (m, *J* = 13.5 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 145.40, 138.63, 135.01, 133.99, 130.96, 129.62, 127.86, 125.24, 124.67, 119.59, 112.61. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11BrN2 275.0106; found: 275.0107.

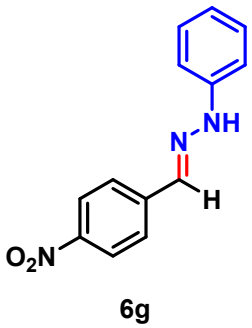
1-(2,4-dibromobenzylidene)-2-phenylhydrazine (6f)



6f

88% yield. White solid. m.p.: 217-219 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.81 (s, 1H), 8.14 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.44 (m, *J* = 8.6 Hz, 1H), 7.25 (m, *J* = 7.4 Hz, 2H), 7.12 – 7.08 (m, 2H), 6.81 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 145.05, 132.88, 132.53, 132.08, 131.22, 129.68, 129.56, 128.18, 127.39, 120.02, 112.72. **HRMS** (ESI) m/z: [M+H] + calculated for C13H10Br2N2 352.9211; found: 352.9210.

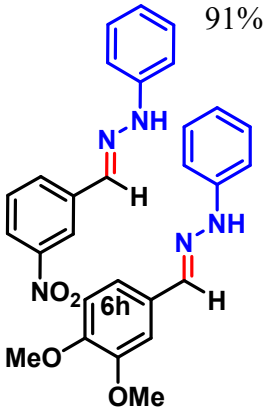
1-(4-nitrobenzylidene)-2-phenylhydrazine (6g)



6g

93% yield. Reddish brown solid. m.p.: 205-207 °C. **^{1}H NMR** (500 MHz, DMSO) δ 11.38 (s, 1H), 8.28 – 8.23 (m, 2H), 8.05 (s, 1H), 7.96 (d, *J* = 9.4 Hz, 2H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 148.46, 147.29, 142.20, 137.68, 134.24, 127.31, 124.40, 120.32, 113.08. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11N3O2 242.0851; found: 242.0853.

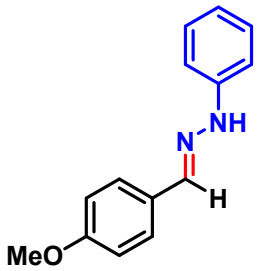
1-(3-nitrobenzylidene)-2-phenylhydrazine (6h)



6i

91% yield. Red solid. m.p.: 208-209 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.69 (s, 1H), 8.45 – 8.43 (m, 1H), 8.12 – 8.08 (m, 2H), 7.97 (s, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 148.78, 145.21, 138.33, 134.21, 130.60, 129.67, 122.41, 119.96, 119.90, 112.74. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11N3O2 242.0851; found: 242.0853.

1-(3,4-dimethoxybenzylidene)-2-phenylhydrazine (6i)



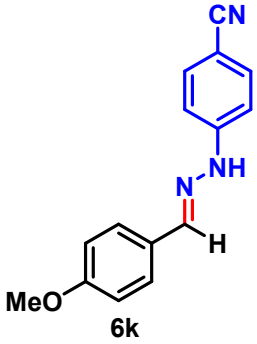
6j

85% yield. White solid. m.p.: 198-200 °C. **^{1}H NMR** (500 MHz, DMSO) δ 9.88 (s, 1H), 7.92 – 7.86 (m, 4H), 7.16 – 7.11 (m, 3H), 7.02 (d, *J* = 9.0 Hz, 1H), 3.85 (d, *J* = 21.8 Hz, 6H).**^{13}C NMR** (126 MHz, DMSO) δ 167.48, 164.70, 163.30, 132.27, 131.80, 130.14, 123.48, 114.98, 114.27, 56.15, 55.89. **HRMS** (ESI) m/z: [M+H] + calculated for C15H16N2O2 257.1212; found: 257.1215.

1-(4-methoxybenzylidene)-2-phenylhydrazine (6j)

86% yield. Cream solid. m.p.: 201-203 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.81 (s, 1H), 7.93 (s, 1H), 7.65 (d, *J* = 6.8 Hz, 2H), 7.61 (s, 2H), 7.13 (s, 2H), 7.00 (d, *J* = 4.7 Hz, 2H), 3.80 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 160.35, 149.18, 140.65, 133.51, 127.95, 120.79, 114.69, 112.27, 55.78. **HRMS** (ESI) m/z: [M+H] + calculated for C14H14N2O 227.1106; found: 227.1108.

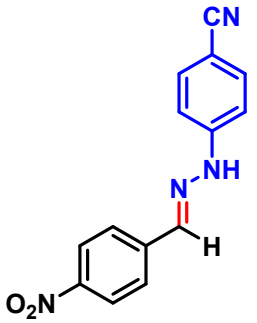
4-(2-(4-methoxybenzylidene)hydrazineyl)benzonitrile (6k)



6k

89% yield. Whitish brown solid. m.p.: 231-232 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.81 (s, 1H), 7.93 (s, 1H), 7.66 – 7.64 (m, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.00 – 6.97 (m, 2H), 3.80 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 160.45, 149.26, 140.65, 134.10, 128.21, 128.09, 120.67, 114.73, 112.34, 99.23, 55.72. **HRMS** (ESI) m/z: [M+H] + calculated for C15H13N3O 252.1059; found: 252.1057.

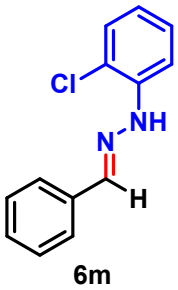
4-(2-(4-nitrobenzylidene)hydrazineyl)benzonitrile (6l)



6l

90% yield. Dark orange solid. m.p.: 224-225 °C .**^{1}H NMR** (500 MHz, DMSO) δ 11.38 (s, 1H), 8.25 (d, *J* = 8.9 Hz, 2H), 8.05 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 148.46, 147.23, 142.08, 137.83, 134.24, 127.31, 124.53, 120.32, 113.20, 101.07. **HRMS** (ESI) m/z: [M+H] + calculated for C14H10N4O2 267.0804; found: 267.0807.

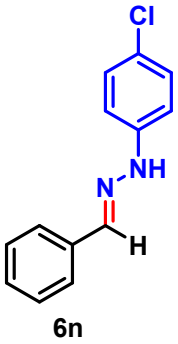
1-benzylidene-2-(2-chlorophenyl)hydrazine (6m)



6m

85% yield. White solid. m.p.: 213-215 °C. **^{1}H NMR** (500 MHz, DMSO) δ 9.90 (s, 1H), 8.30 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 6.6 Hz, 2H), 7.27 (t, *J* = 8.2 Hz, 1H), 6.82 – 6.78 (m, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 141.88, 140.85, 135.91, 129.83, 129.21, 129.03, 128.53, 126.50, 120.10, 116.65, 114.52. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11ClN2 231.0611; found: 231.0614.

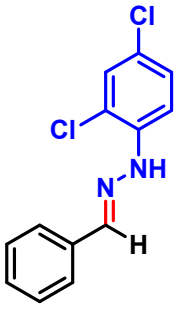
1-benzylidene-2-(4-chlorophenyl)hydrazine (6n)



6n

86% yield. White solid. m.p.: 217-218 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.47 (s, 1H), 7.88 (s, 1H), 7.67 – 7.64 (m, 2H), 7.40 (m, *J* = 7.6 Hz, 2H), 7.32 (m, *J* = 8.1 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.10 – 7.06 (m, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 144.70, 137.79, 136.04, 129.39, 129.13, 128.64, 126.23, 122.43, 113.88. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11ClN2 231.0611; found: 231.0608.

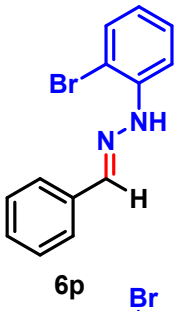
1-benzylidene-2-(2,4-dichlorophenyl)hydrazine (6o)



6o

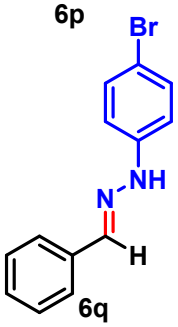
84% yield. White solid. m.p.:223-224 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.05 (s, 1H), 8.31 (s, 1H), 7.70 – 7.66 (m, 2H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.30 (m, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 141.61, 141.11, 135.68, 129.24, 129.22, 129.06, 128.54, 126.62, 122.67, 117.11, 115.52. **HRMS** (ESI) m/z: [M+H] + calculated for C13H10Cl2N2 265.0221; found: 265.0224.

1-benzylidene-2-(2-bromophenyl)hydrazine (6p)



6p

86% yield. White solid. m.p.: 218-219 °C. **^{1}H NMR** (500 MHz, DMSO) δ 9.89 (s, 1H), 8.30 (s, 1H), 7.68 (d, *J* = 9.3 Hz, 2H), 7.60 – 7.57 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 1H), 6.83 – 6.77 (m, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 141.95, 140.85, 135.91, 129.75, 129.28, 129.03, 128.53, 126.50, 120.10, 116.75, 114.64. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11BrN2 275.0106; found: 275.0108.

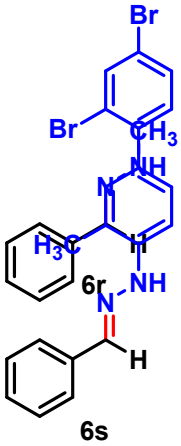


6q

1-benzylidene-2-(4-bromophenyl)hydrazine (6q)

89% yield. White solid. m.p.: 227-228 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.47 (s, 1H), 7.88 (s, 1H), 7.68 – 7.63 (m, 2H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 144.68, 137.79, 136.04, 129.39, 129.06, 128.55, 126.23, 122.36, 113.95. **HRMS** (ESI) m/z: [M+H] + calculated for C13H11BrN2 275.0106; found: 275.0107.

1-benzylidene-2-(2,4-dibromophenyl)hydrazine (6r)

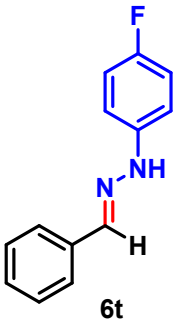


87% yield. White solid. m.p.: 228-229 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.05 (s, 1H), 8.31 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.47 (s, 1H), 7.44 – 7.40 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 141.61, 141.11, 135.78, 129.24, 128.99, 128.45, 126.74, 122.61, 117.19, 115.52. **HRMS** (ESI) m/z: [M+H] + calculated for C13H10Br2N2 352.9211; found: 352.9210.

1-benzylidene-2-(2,4-dimethylphenyl)hydrazine (6s)

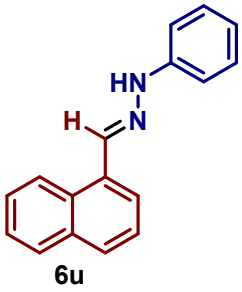
86% yield. Cream solid. m.p.: 216-218 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.38 (d, *J* = 8.0 Hz, 1H), 7.93 (m, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.12 (d, *J* = 3.0 Hz, 1H), 6.87 – 6.81 (m, 2H), 6.63 (d, *J* = 8.1 Hz, 1H), 2.18 (d, *J* = 11.9 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 166.59, 145.01, 133.54, 132.05, 131.18, 128.95, 127.83, 127.72, 127.16, 122.63, 111.97, 20.57, 17.67. **HRMS** (ESI) m/z: [M+H] + calculated for C15H16N2 225.1313; found: 225.1315.

1-benzylidene-2-(4-fluorophenyl)hydrazine (6t)



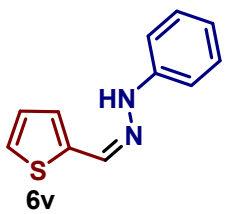
80% yield. White solid. m.p.: 210-211 °C**. ^{1}H NMR** (500 MHz, DMSO) δ 10.47 (s, 1H), 7.88 (s, 1H), 7.68 – 7.64 (m, 2H), 7.40 (m, *J* = 7.6 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.28 – 7.24 (m, 2H), 7.10 – 7.05 (m, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 144.63, 137.79, 136.04, 129.45, 129.26, 128.64, 126.23, 122.43, 113.98. 19F NMR (471 MHz, DMSO) δ -121.65, -121.66.

1-(naphthalen-1-ylmethylene)-2-phenylhydrazine (6u)



81% yield. Brown solid. m.p.: 79-80 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.41 (s, 1H), 9.17 (d, *J* = 8.5 Hz, 2H), 8.27 (d, *J* = 8.2 Hz, 2H), 8.18 (d, *J* = 7.1 Hz, 2H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.78 – 7.69 (m, 4H), 7.65 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 152.30, 137.22, 135.71, 133.79, 131.34, 130.25, 129.48, 129.18, 127.38, 125.84, 124.60.

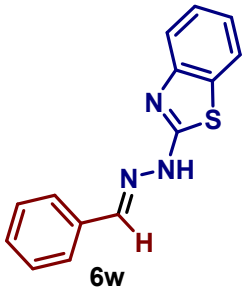
1-phenyl-2-(thiophen-2-ylmethylene)hydrazine(6v)



78% yield. White solid. m.p.: 145-147 °C. **^{1}H NMR** (500 MHz, DMSO) δ 10.30 (s, 1H), 8.06 (s, 1H), 7.46 (d, *J* = 5.0 Hz, 1H), 7.21 (s, 3H), 7.06 (m, *J* =

7.9 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 145.52, 141.39, 132.47, 129.60, 128.05, 127.04, 126.21, 119.23, 112.34.

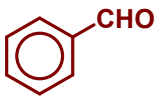
2-(2-benzylidenehydrazineyl)benzo[d]thiazole (6w)



6w

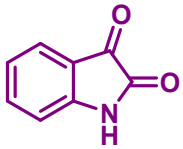
83% yield. Brown solid. m.p.: 190-191 °C. **^{1}H NMR** (500 MHz, DMSO) δ 12.49 (s, 1H), 8.44 (s, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.36 (m, *J* = 7.9 Hz, 2H), 7.21 (m, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 161.36, 151.06, 145.30, 138.70, 130.06, 128.73, 125.96, 123.54, 111.81.

Intermediate E (benzaldehyde)



^{1}H NMR (500 MHz, DMSO) δ 8.73 (s, 1H), 7.92 – 7.88 (m, 2H), 7.53 (m, J = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 161.97, 134.27, 131.86, 129.41, 128.84.

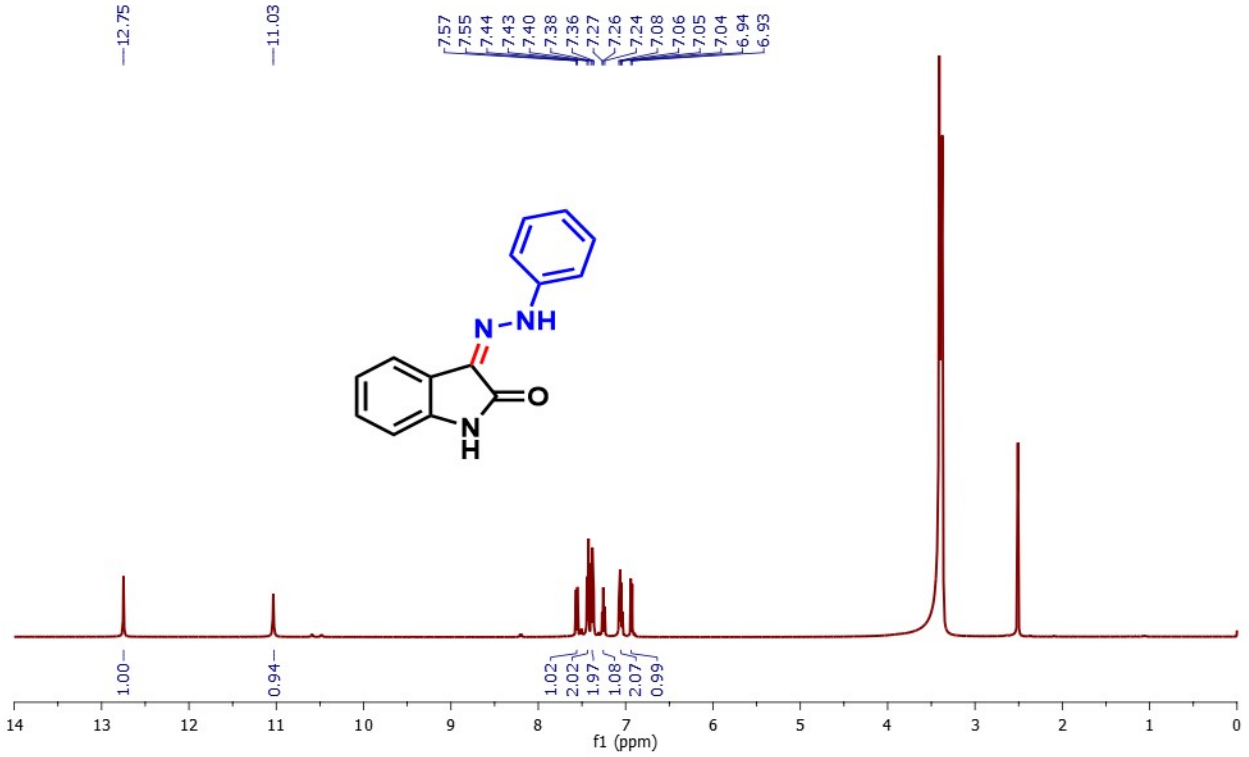
Intermediate VI (indoline-2,3-dione)

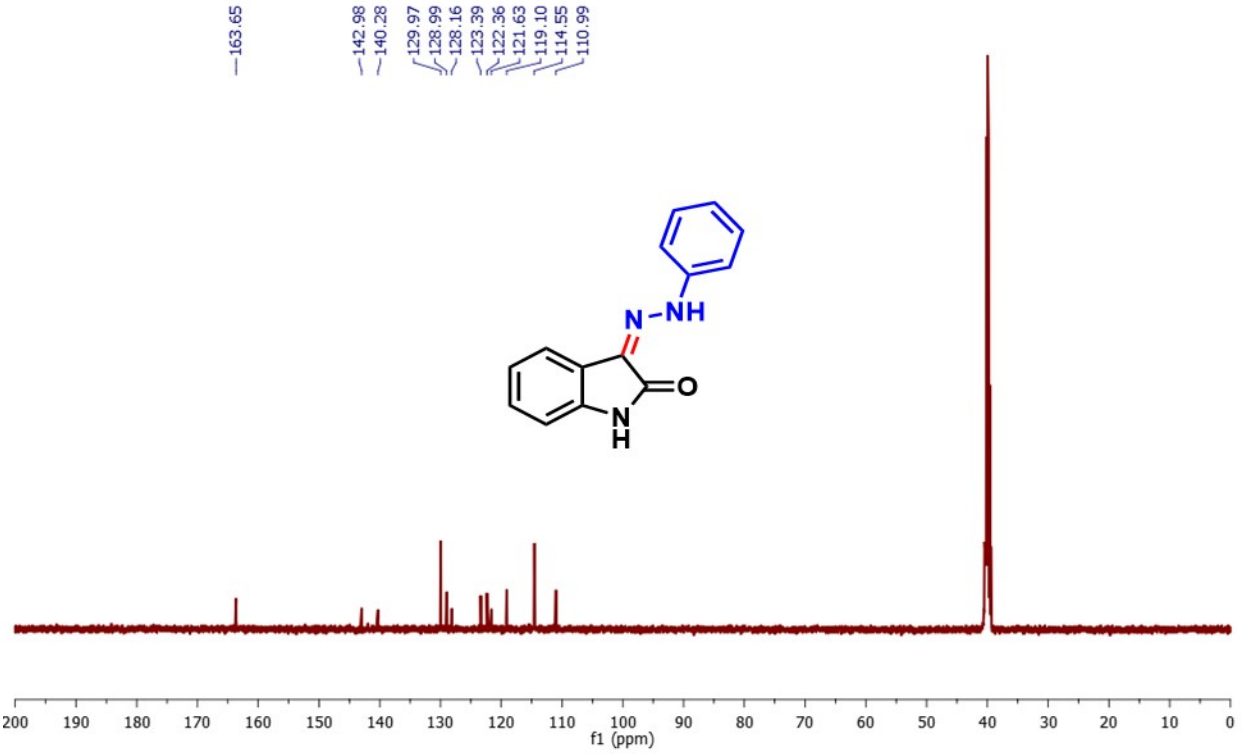


^{1}H NMR (500 MHz, DMSO) δ 11.22 (s, 1H), 7.88 (s, 1H), 7.59 – 7.51 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 182.16, 164.21, 151.08, 146.87, 138.05, 126.28, 123.61.

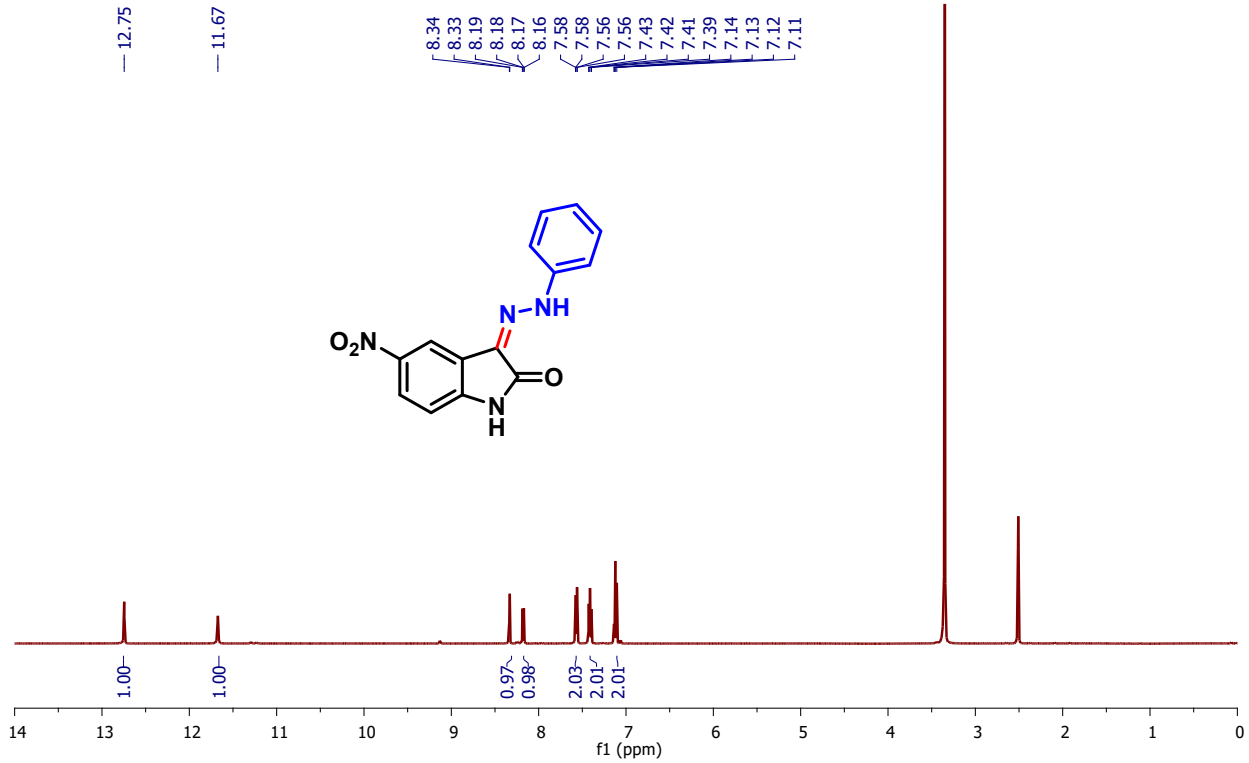
4.3 ^{1}H and ^{13}C NMR spectra

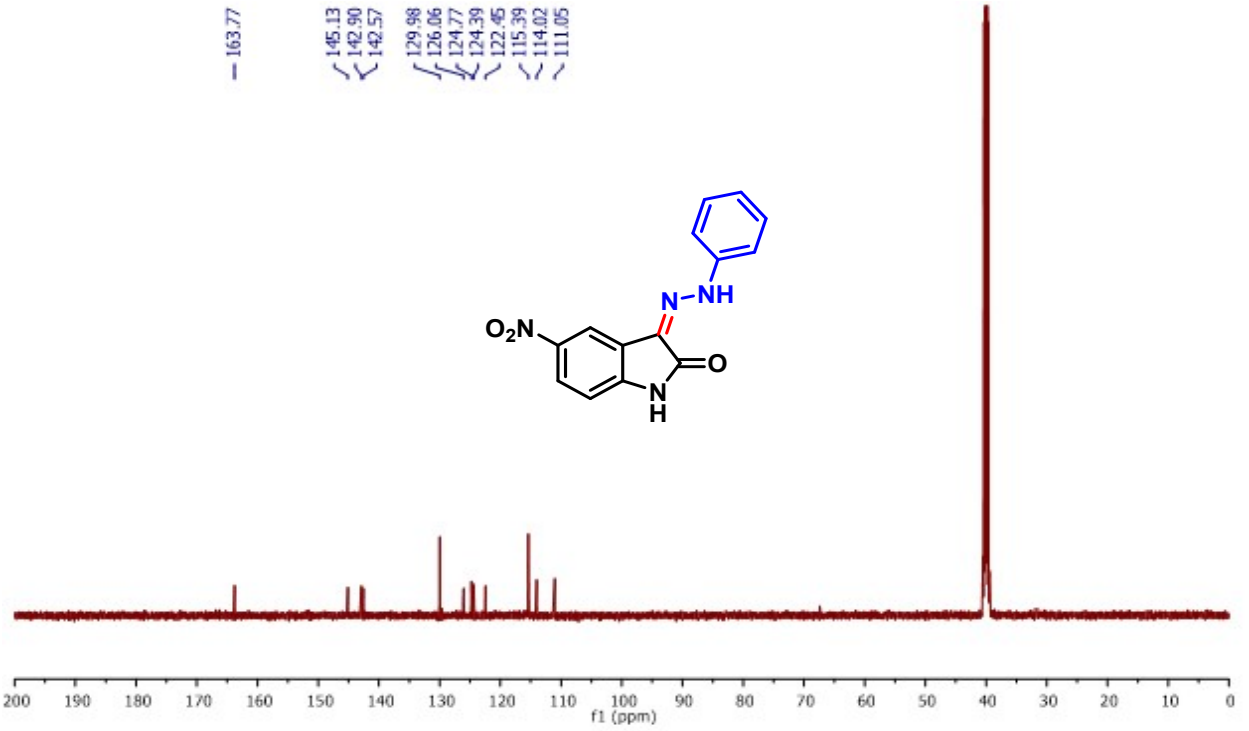
3-(2-phenylhydrazineylidene)indolin-2-one (4a)



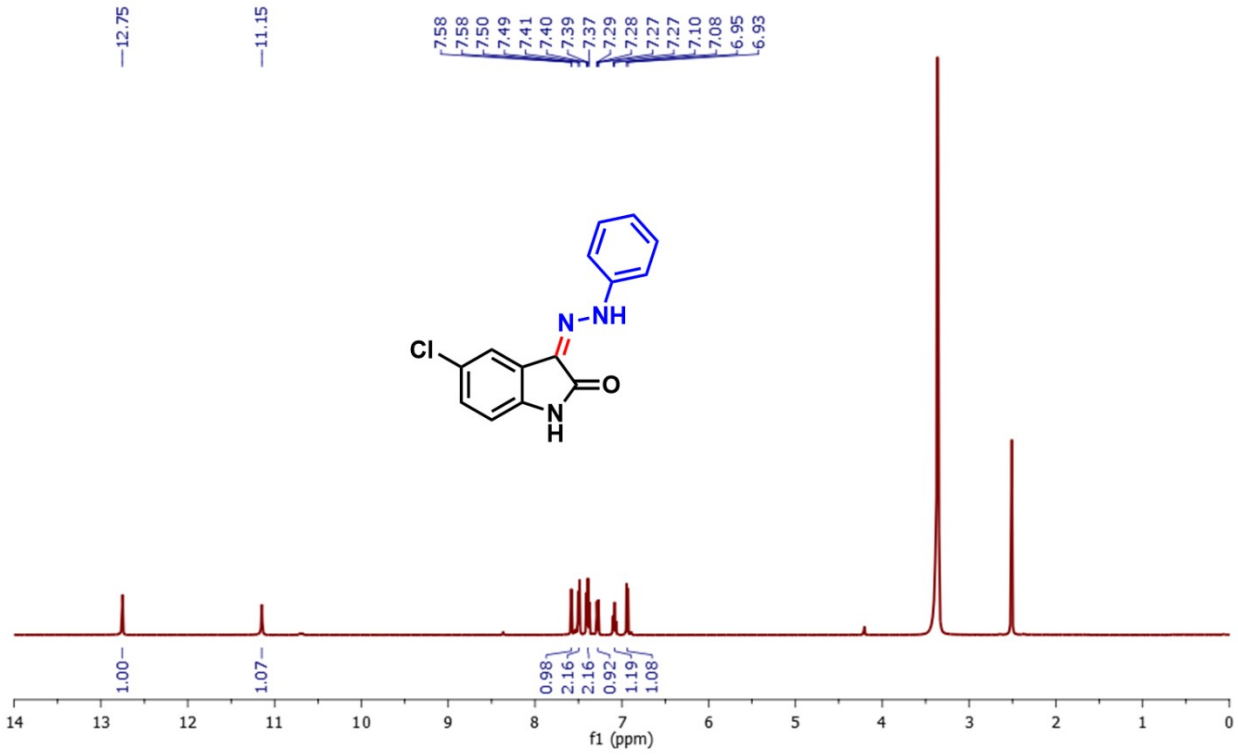


5-nitro-3-(2-phenylhydrazineylidene)indolin-2-one (4b)





5-chloro-3-(2-phenylhydrazineylidene)indolin-2-one (4c)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11.15
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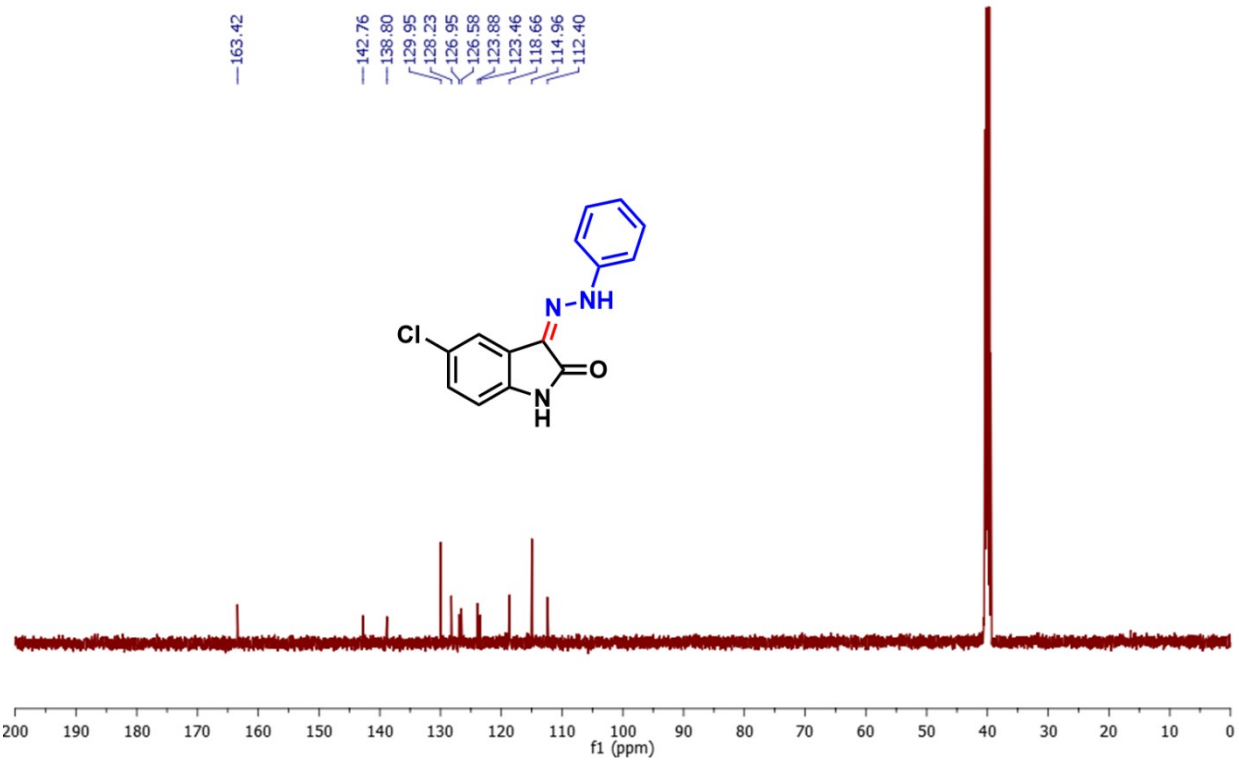
7.58
7.50
7.49
7.41
7.40
7.39
7.37
7.29
7.28
7.27
7.27
7.10
7.08
6.95
6.93
N-NH
Cl
O
N
H
1.00
1.07
0.98
2.16
2.16
0.92
1.19
1.08
f1 (ppm)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138.80
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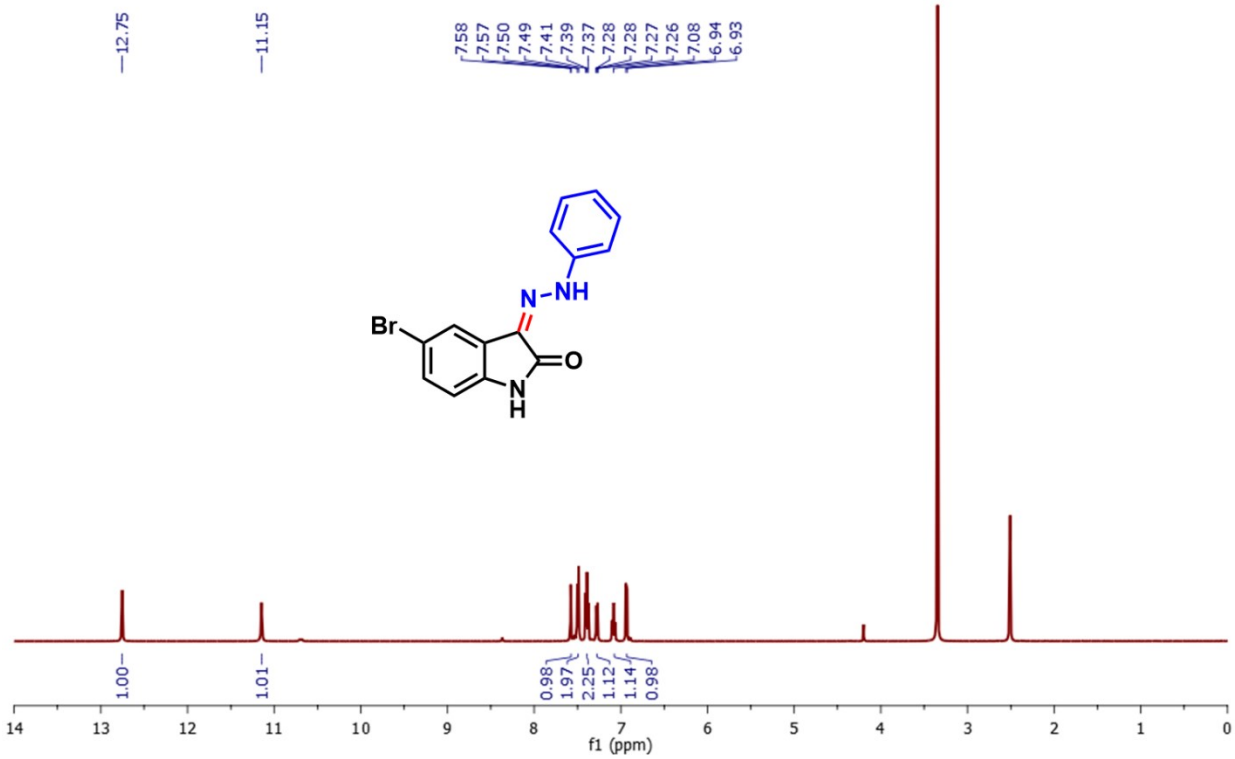
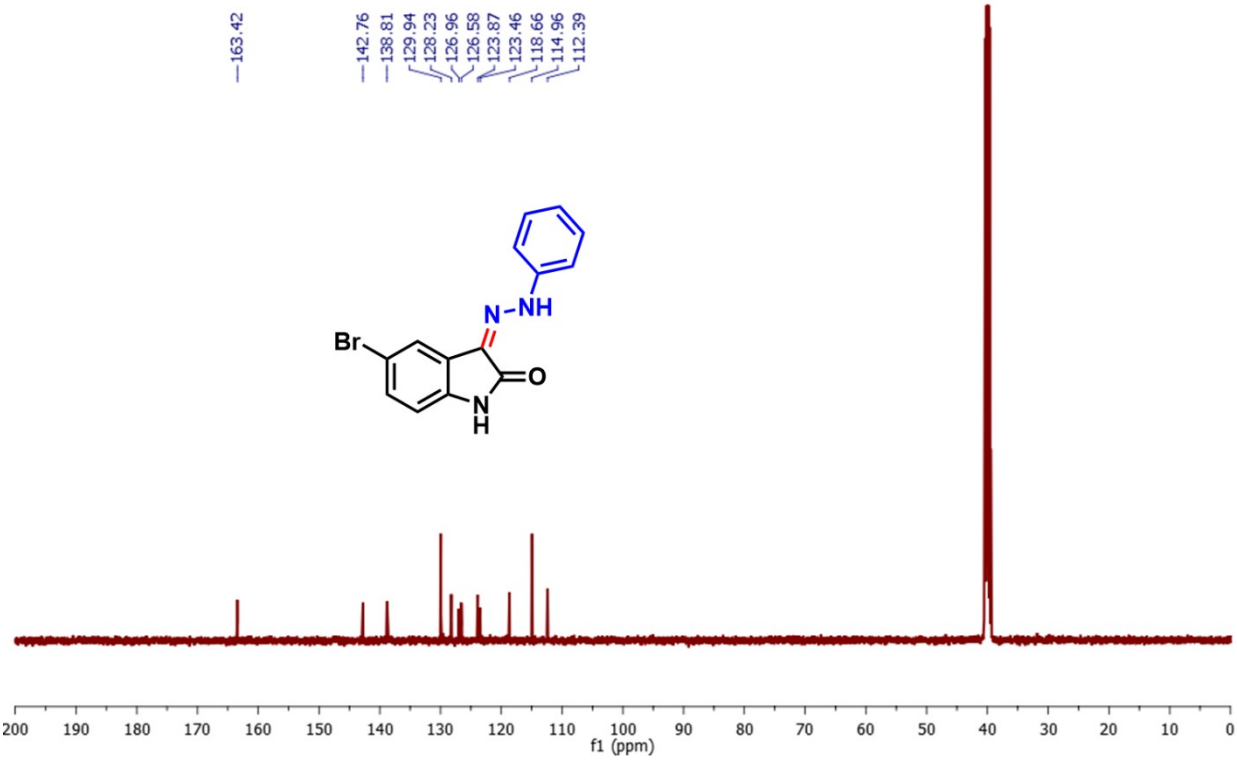
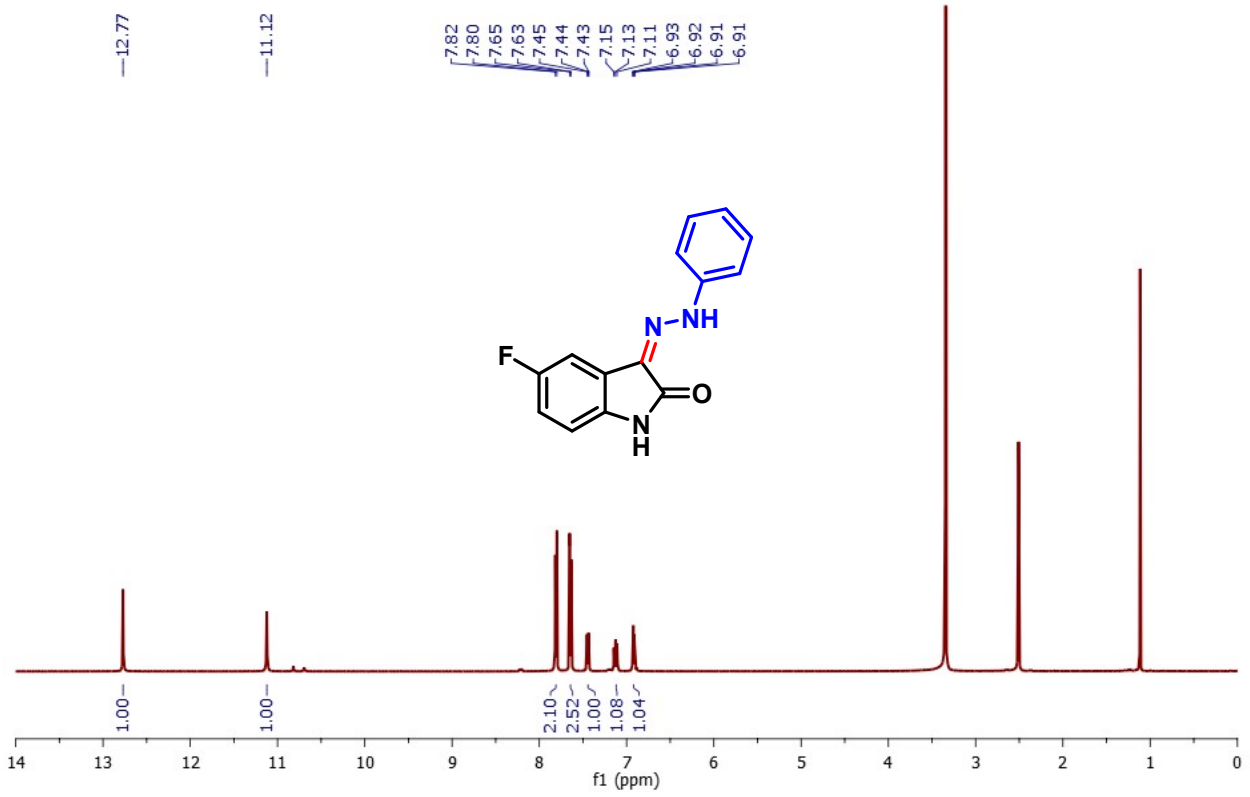
128.23
126.95
126.58
123.88
123.46
118.66
114.96
112.40
N-NH
Cl
O
N
H
f1 (ppm)

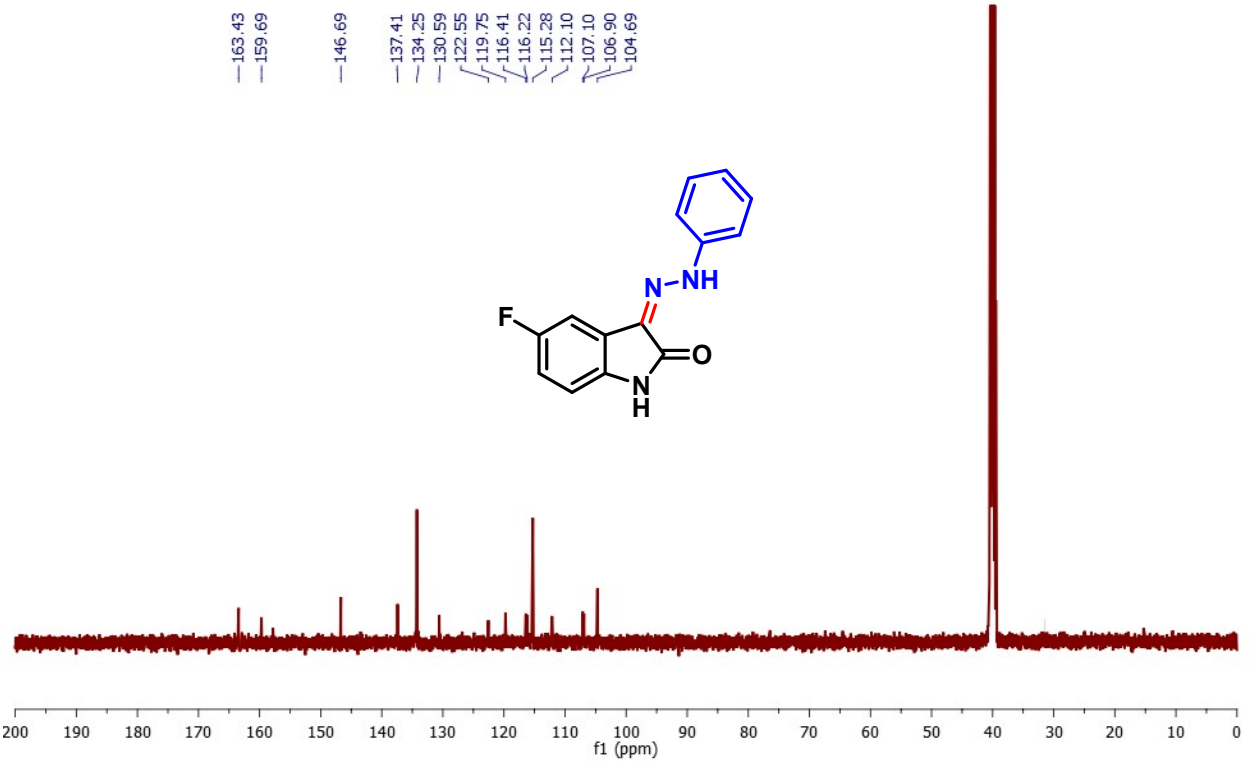
5-bromo-3-(2-phenylhydrazineylidene)indolin-2-one (4d)

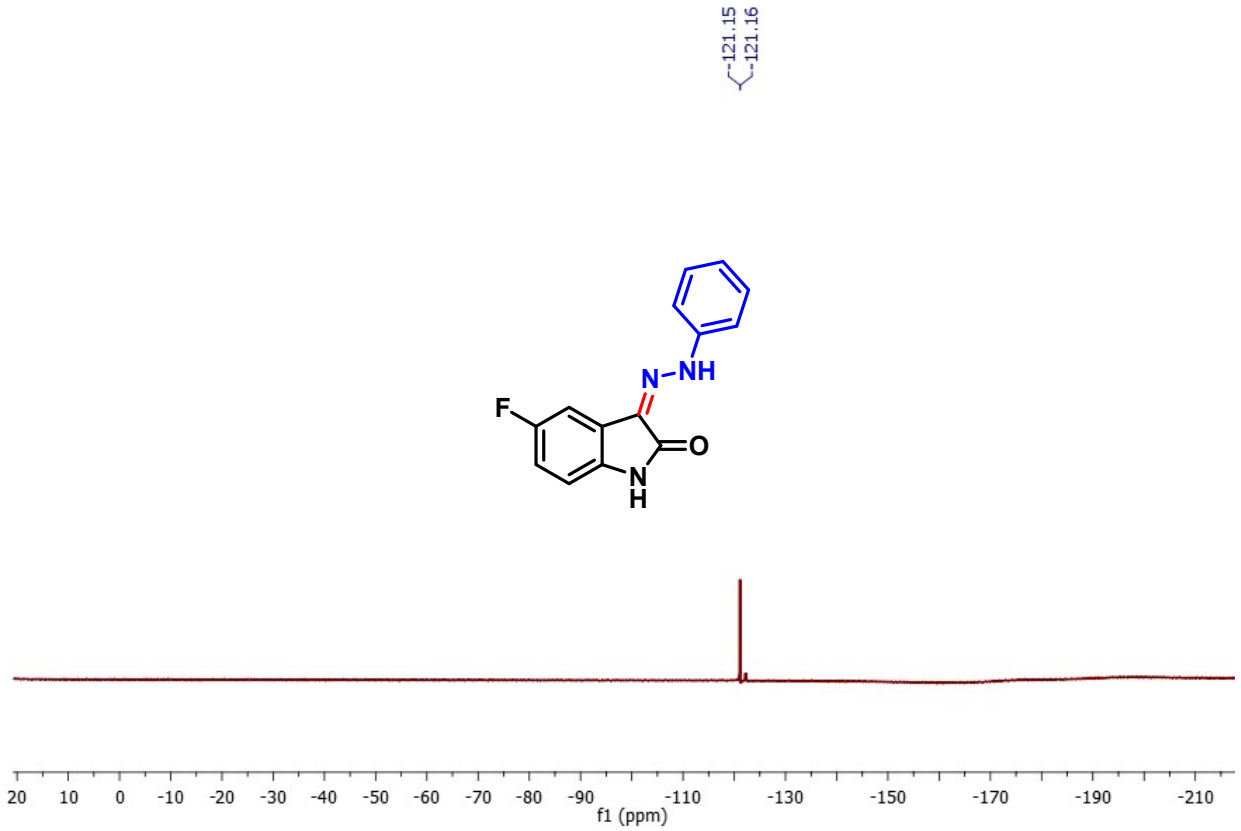




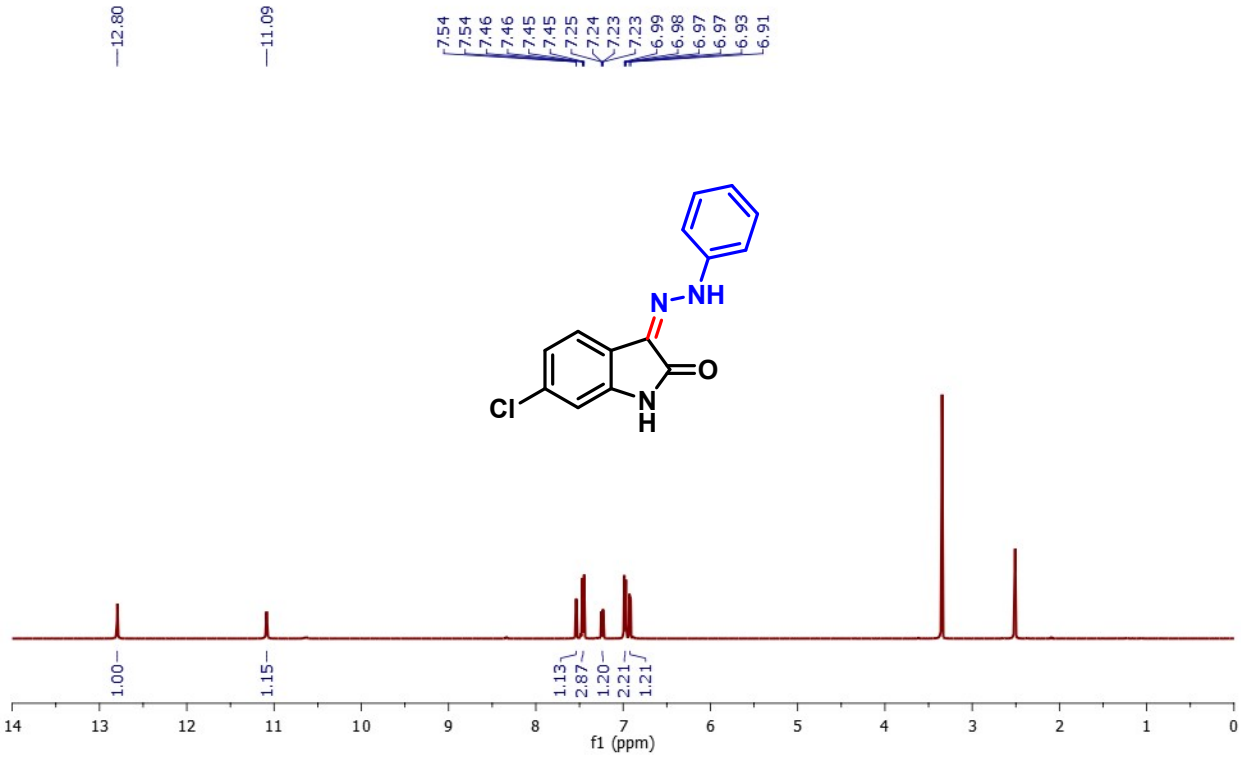
5-fluoro-3-(2-phenylhydrazineylidene)indolin-2-one (4e)

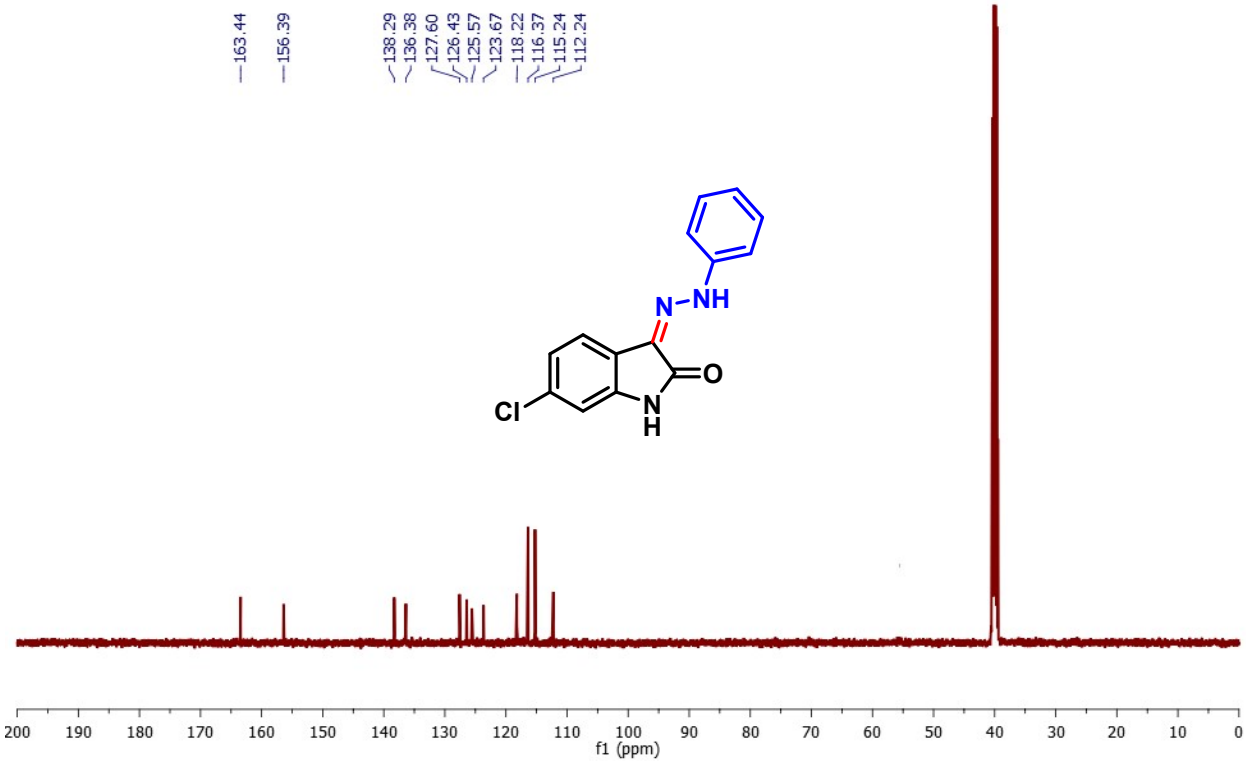




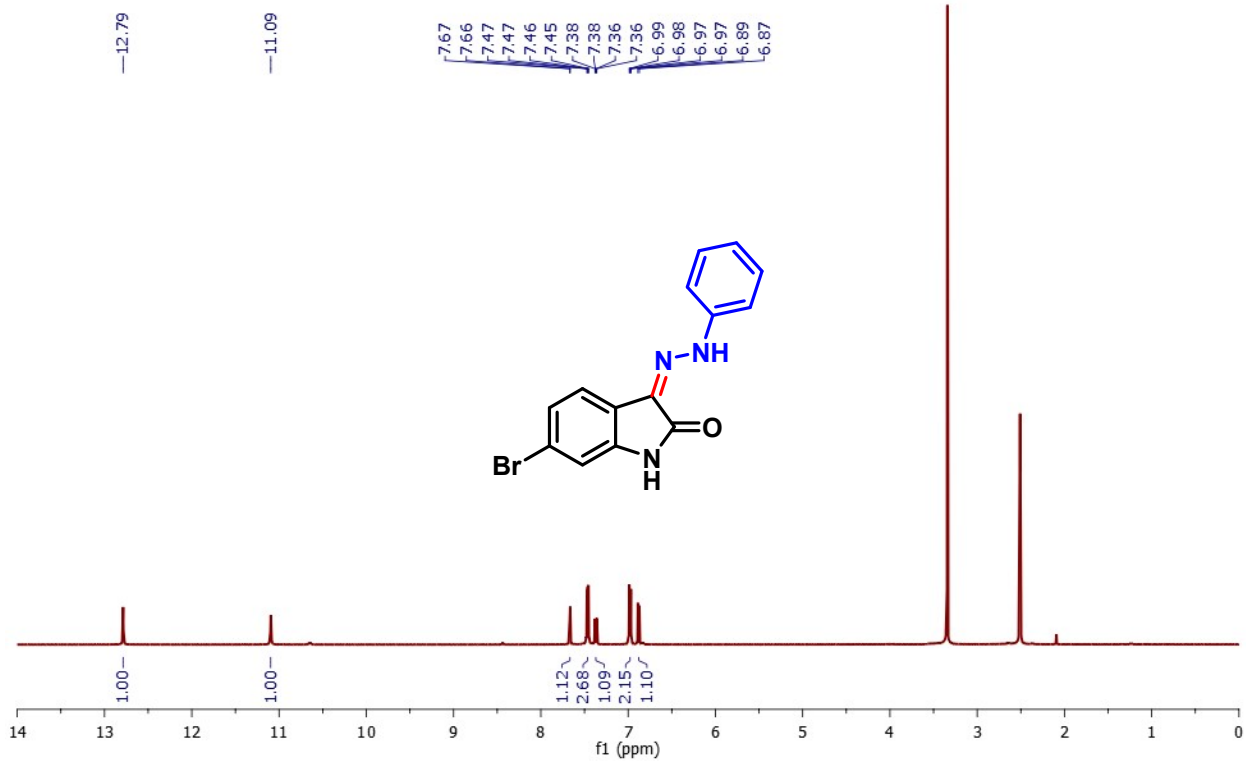


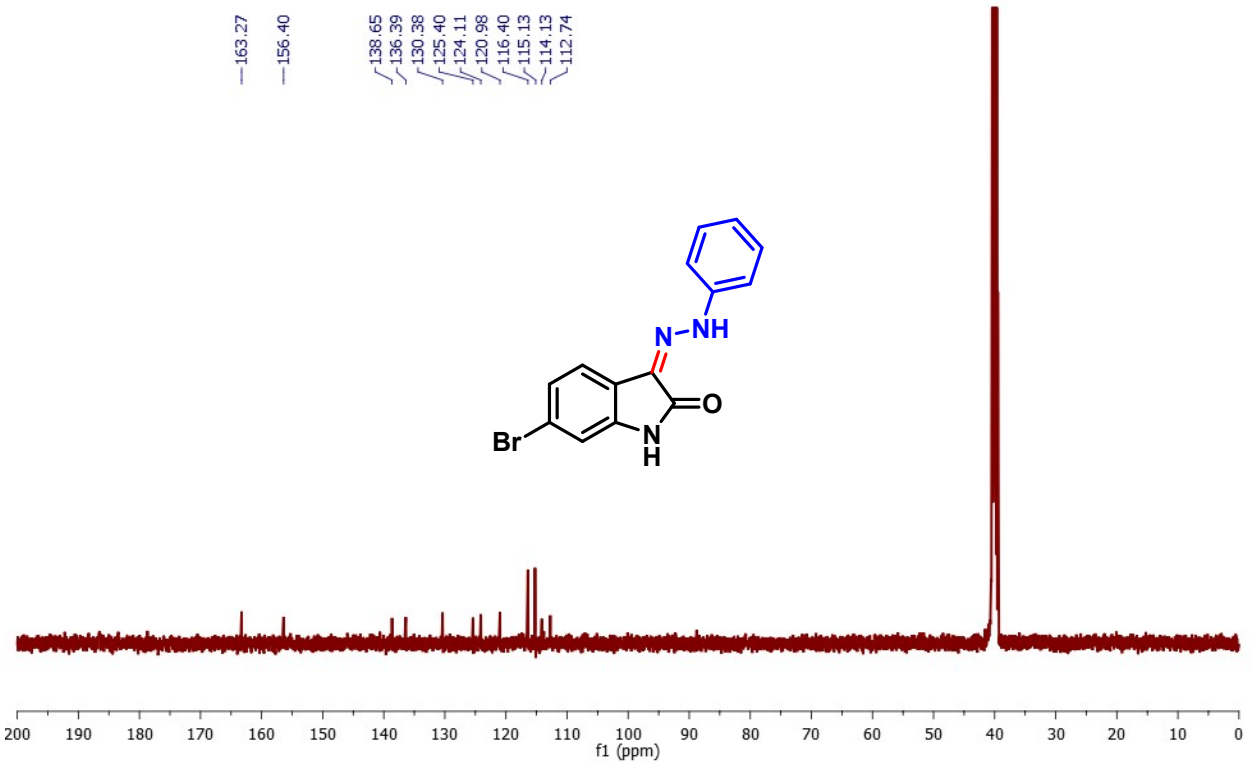
6-chloro-3-(2-phenylhydrazineylidene)indolin-2-one (4f)



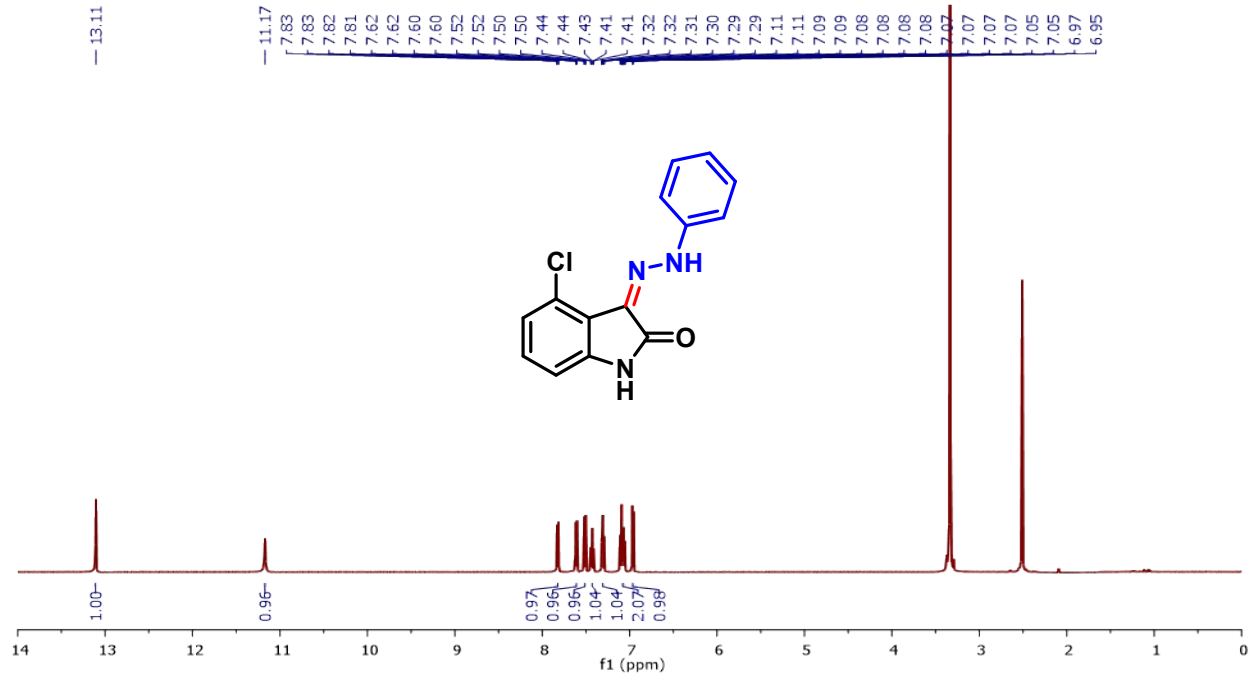


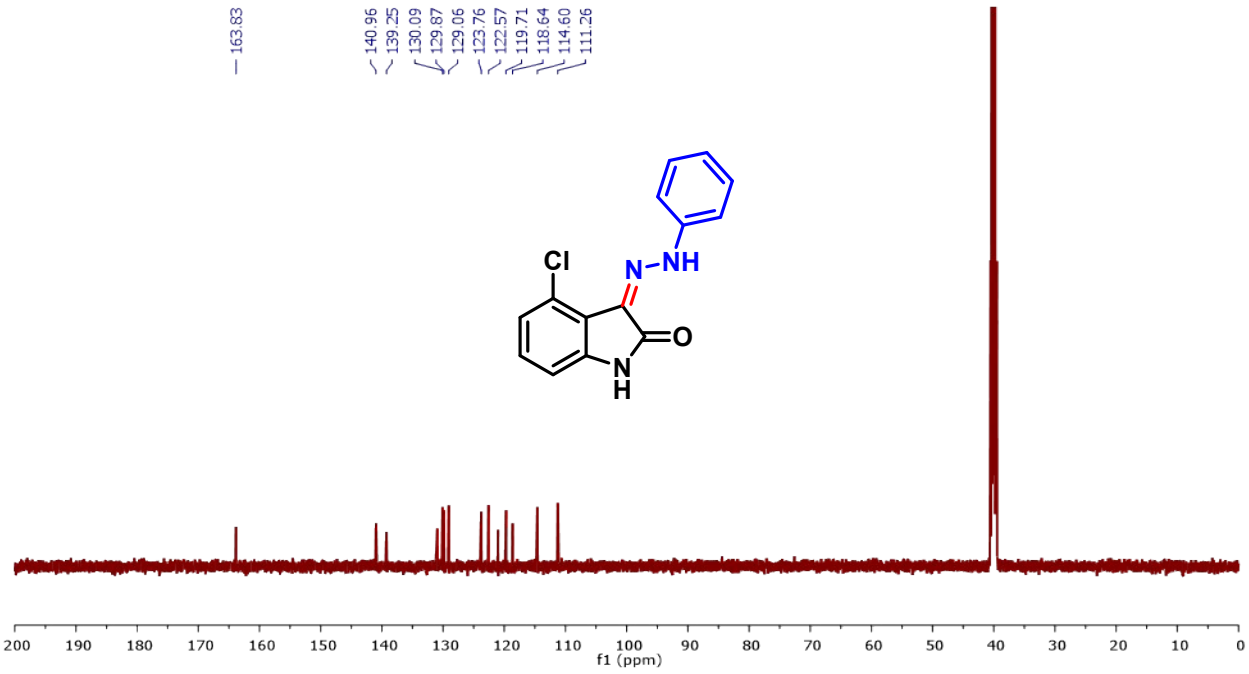
6-bromo-3-(2-phenylhydrazineylidene)indolin-2-one (4g)



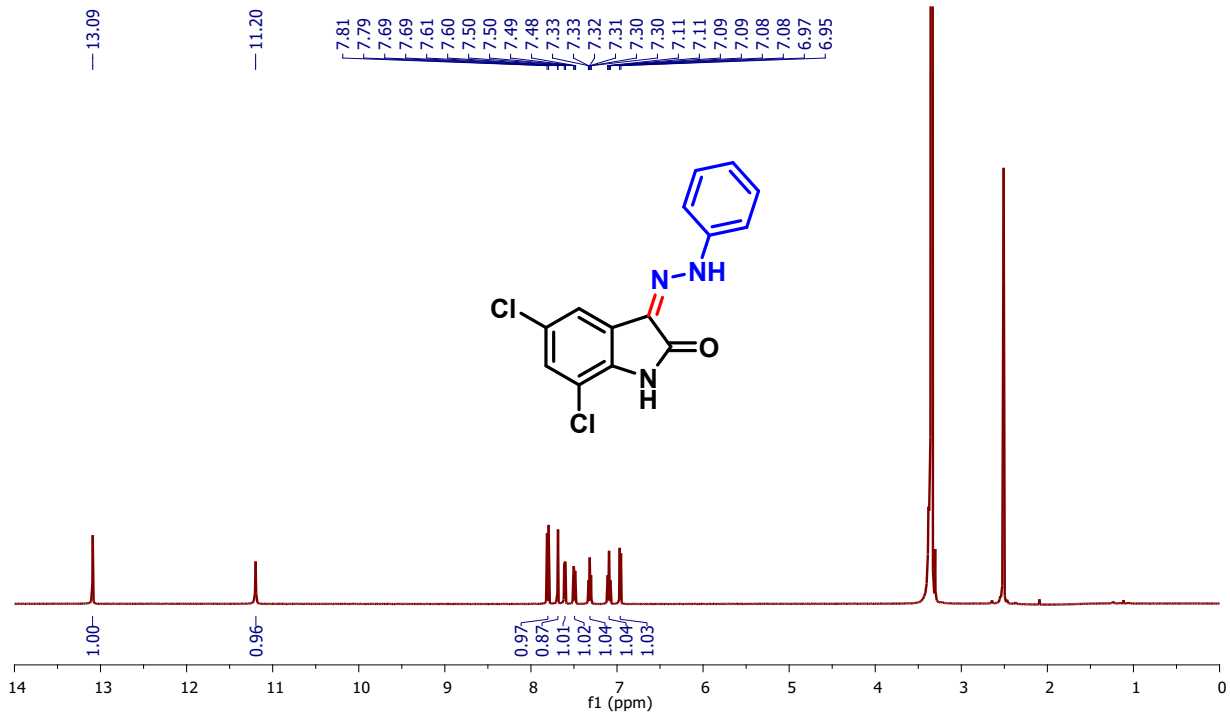


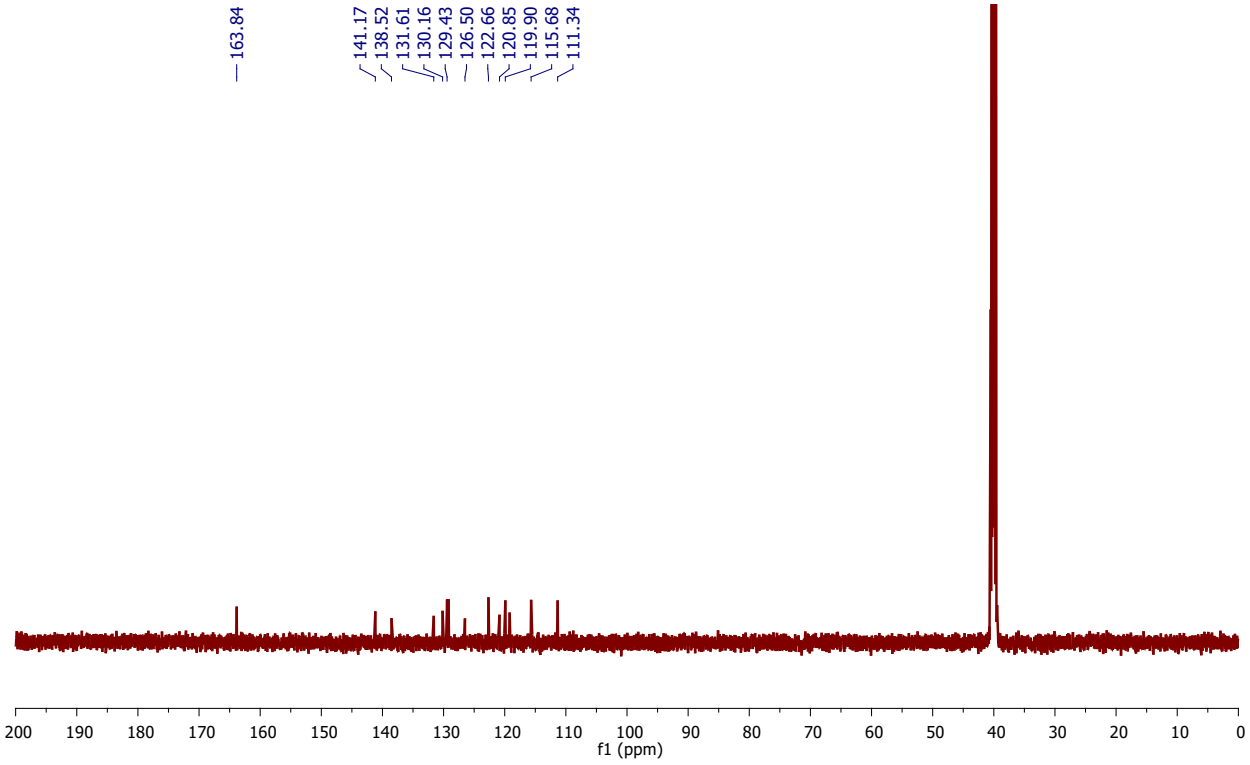
4-chloro-3-(2-phenylhydrazineylidene)indolin-2-one (4h)



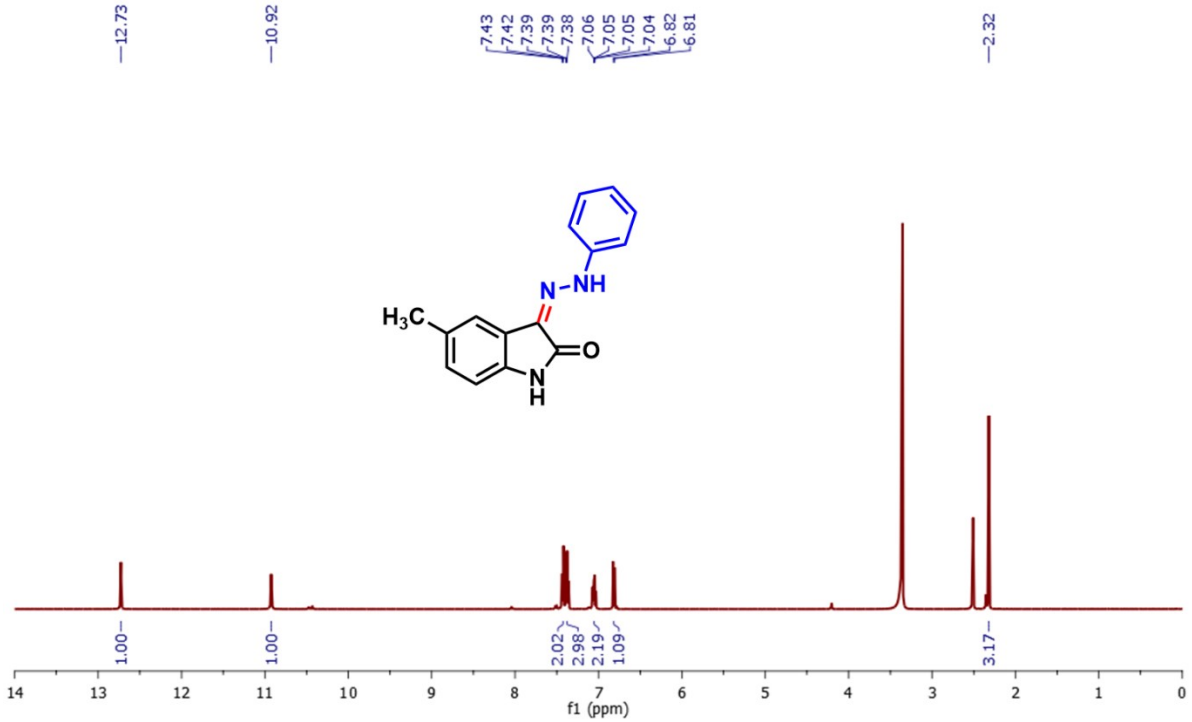


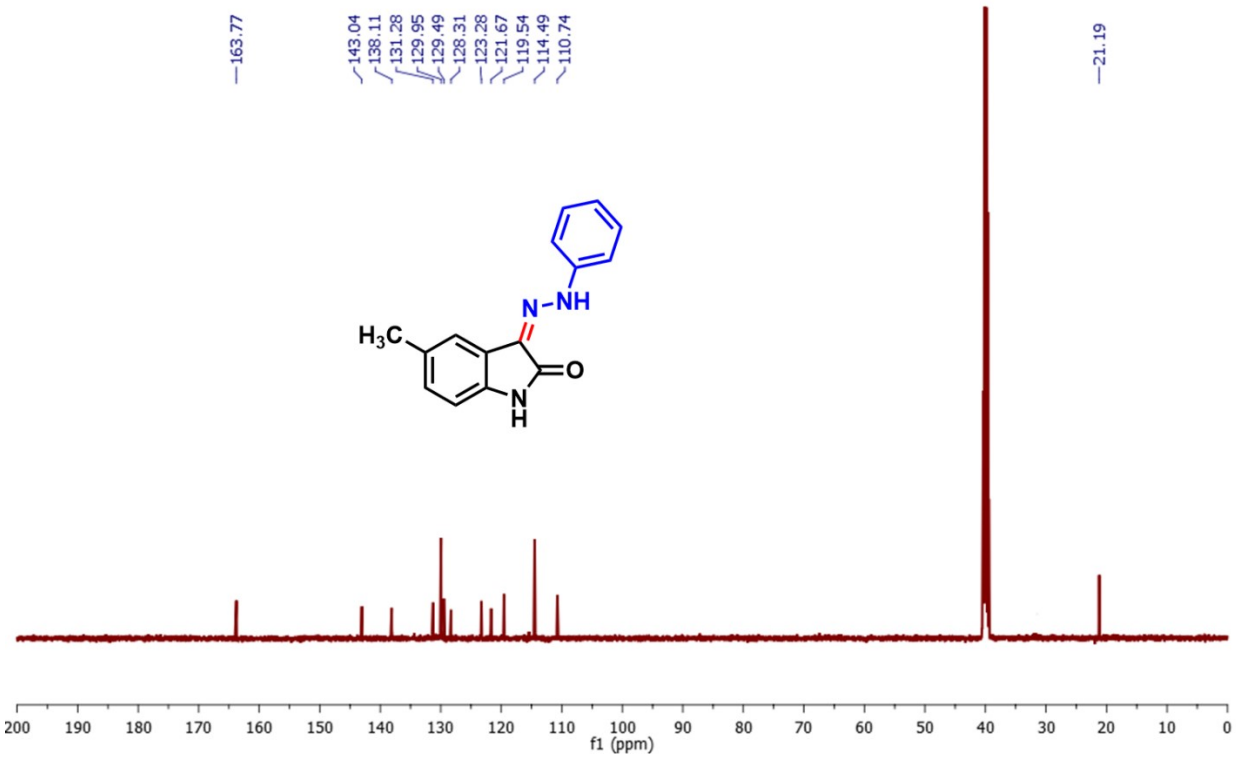
5,7-dichloro-3-(2-phenylhydrazineylidene)indolin-2-one (4i)



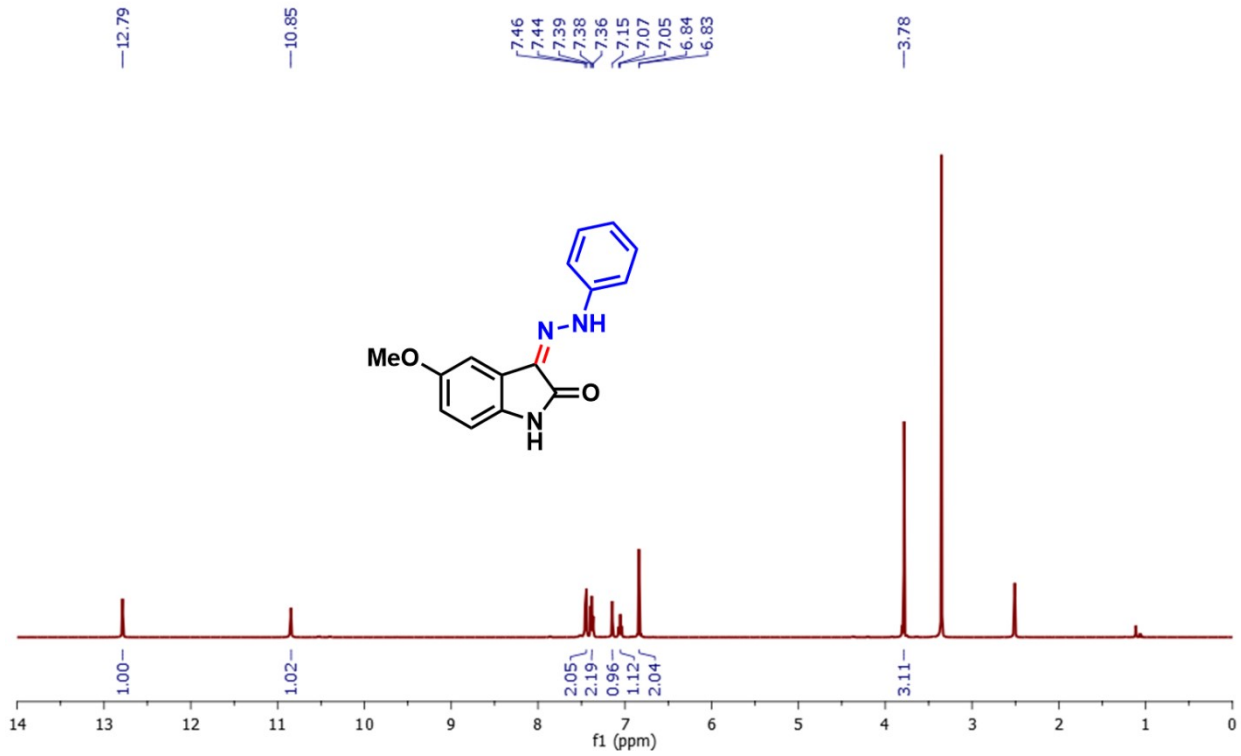


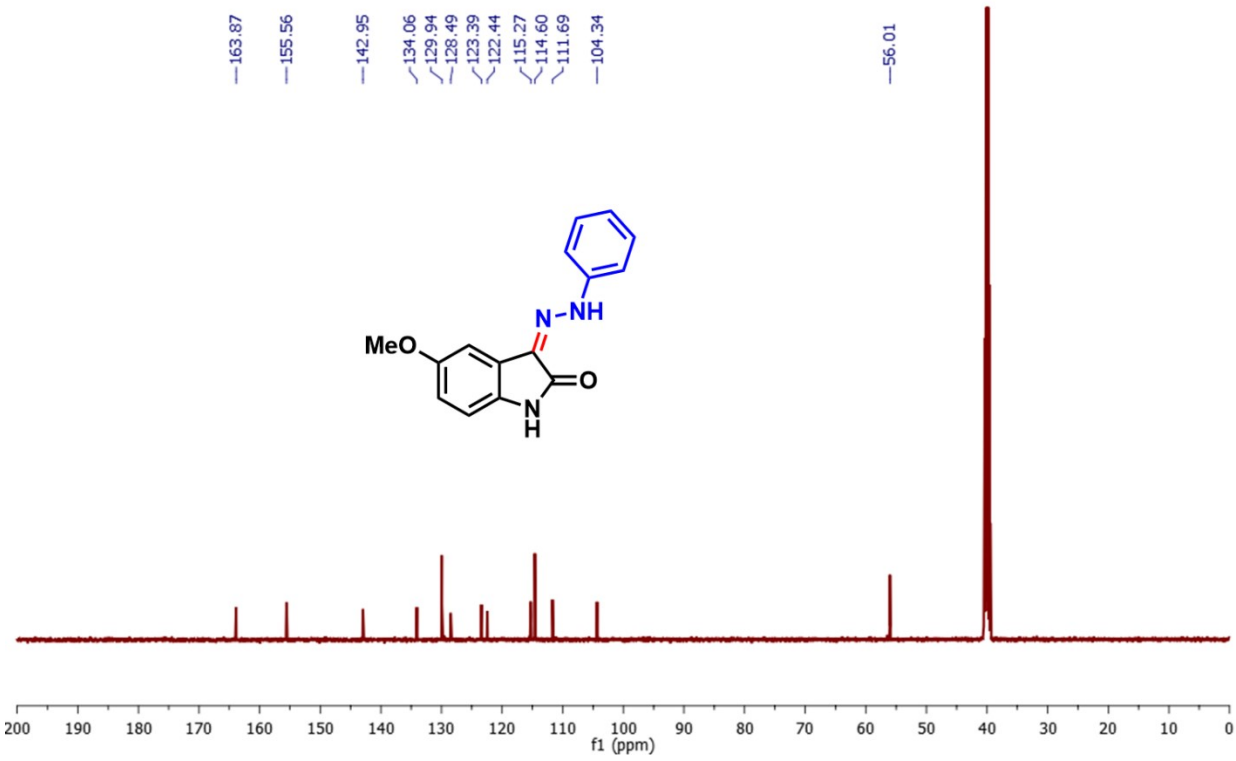
5-methyl-3-(2-phenylhydrazineylidene)indolin-2-one (4j)



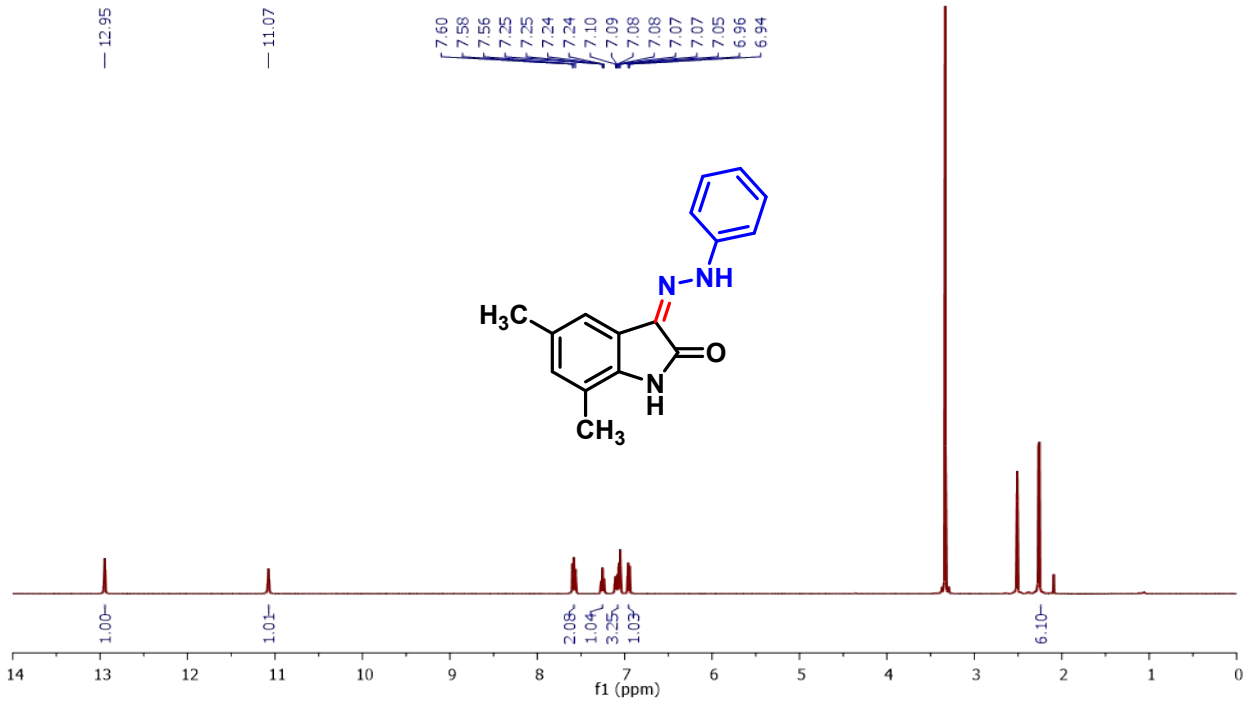


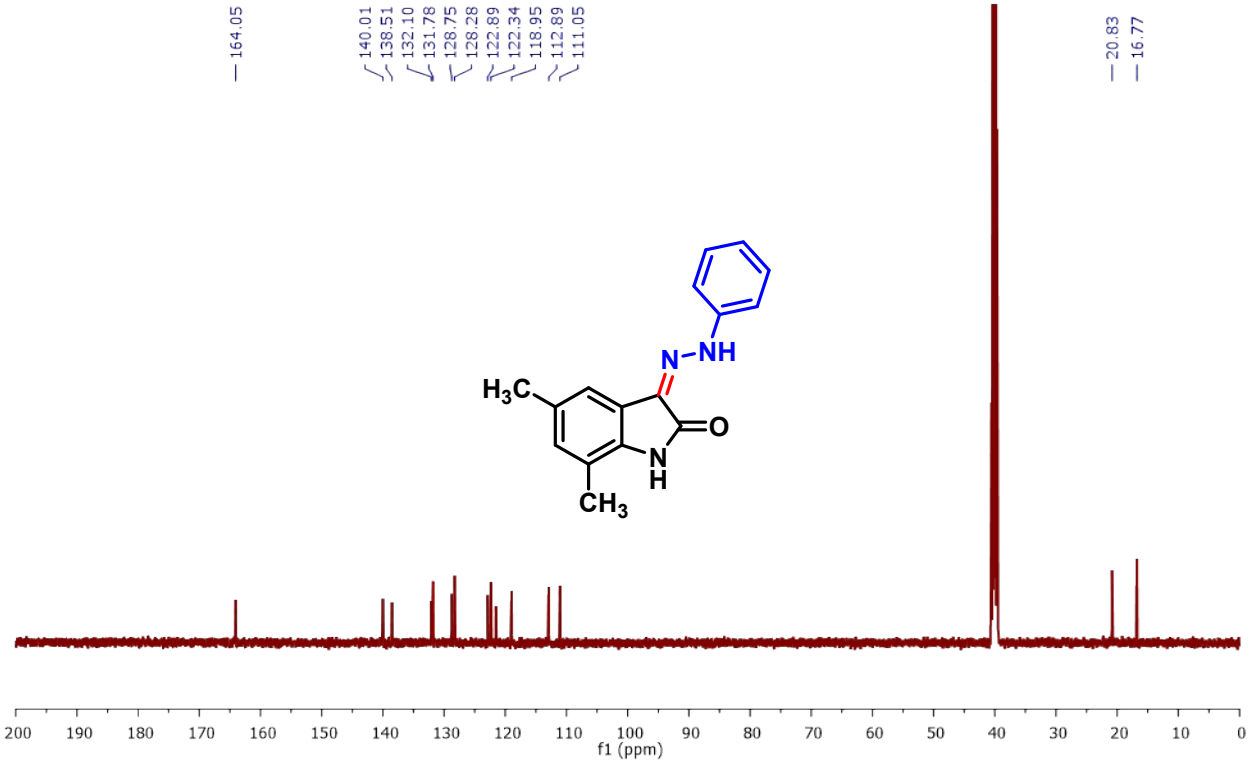
5-methoxy-3-(2-phenylhydrazineylidene)indolin-2-one (4k)



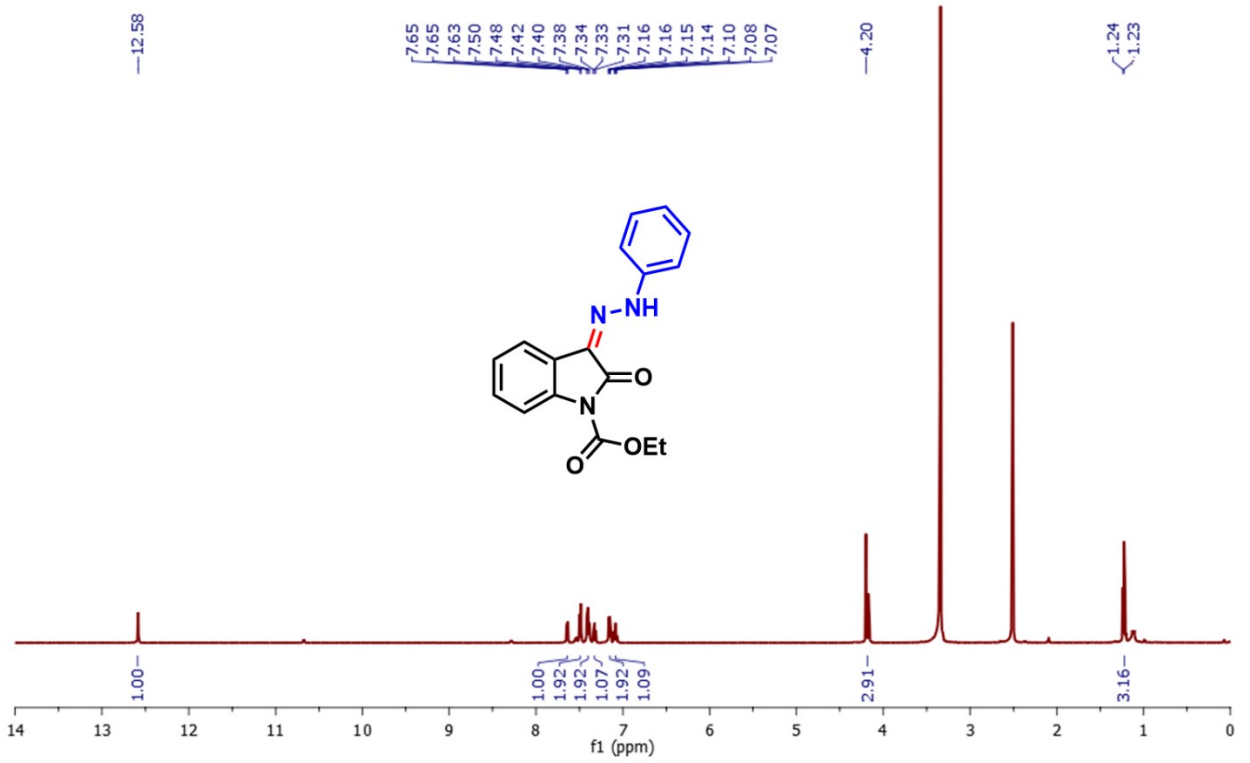


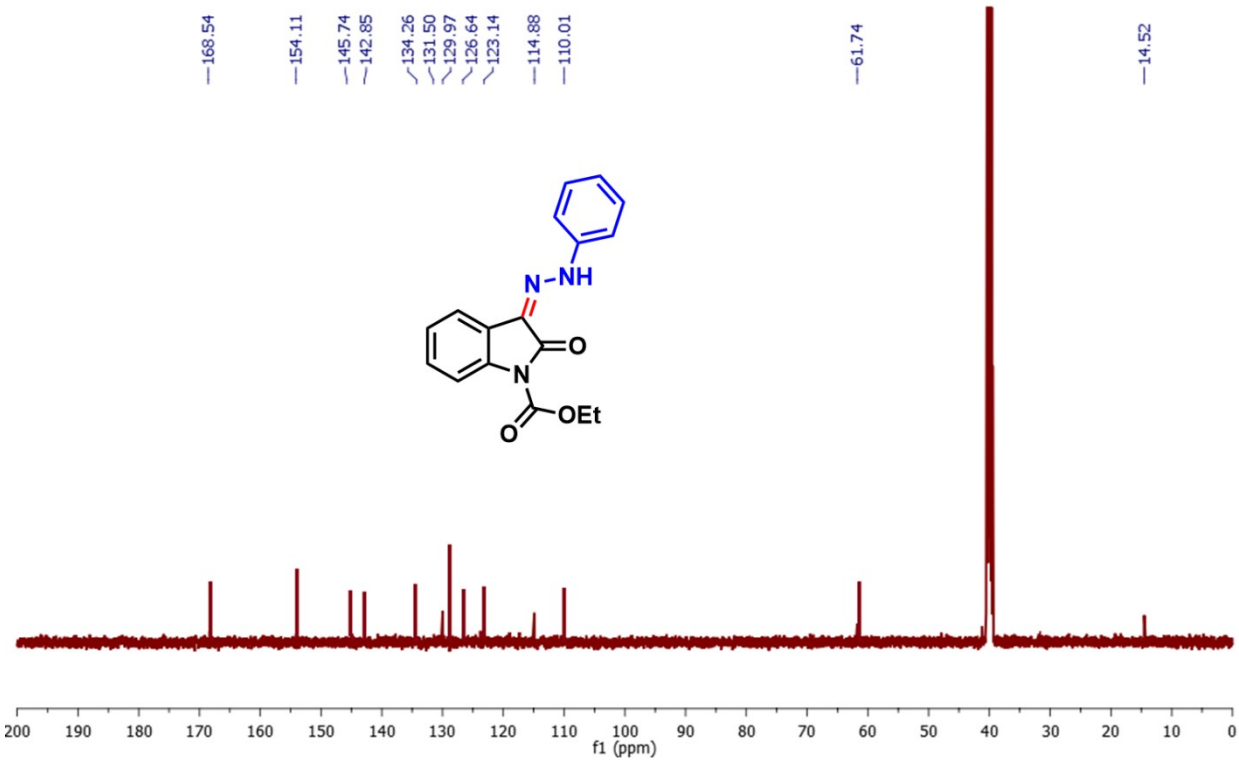
5,7-dimethyl-3-(2-phenylhydrazineylidene)indolin-2-one (4l)



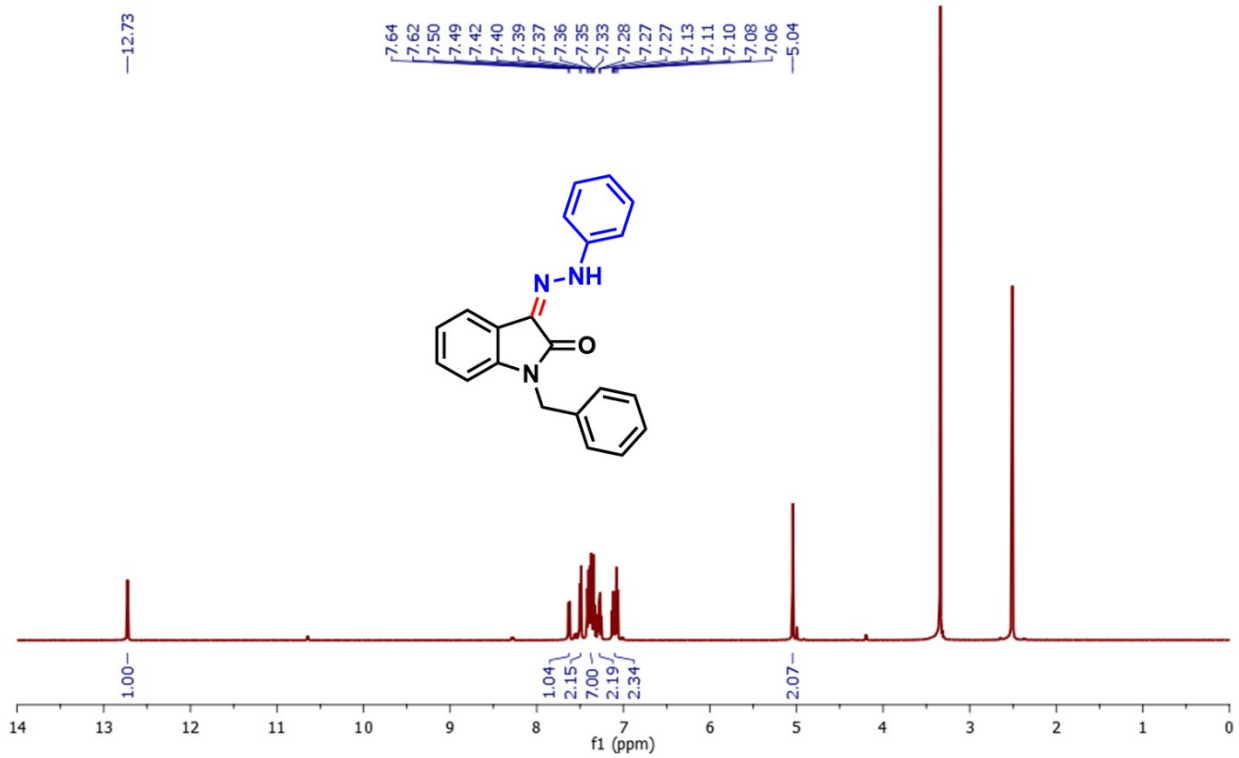


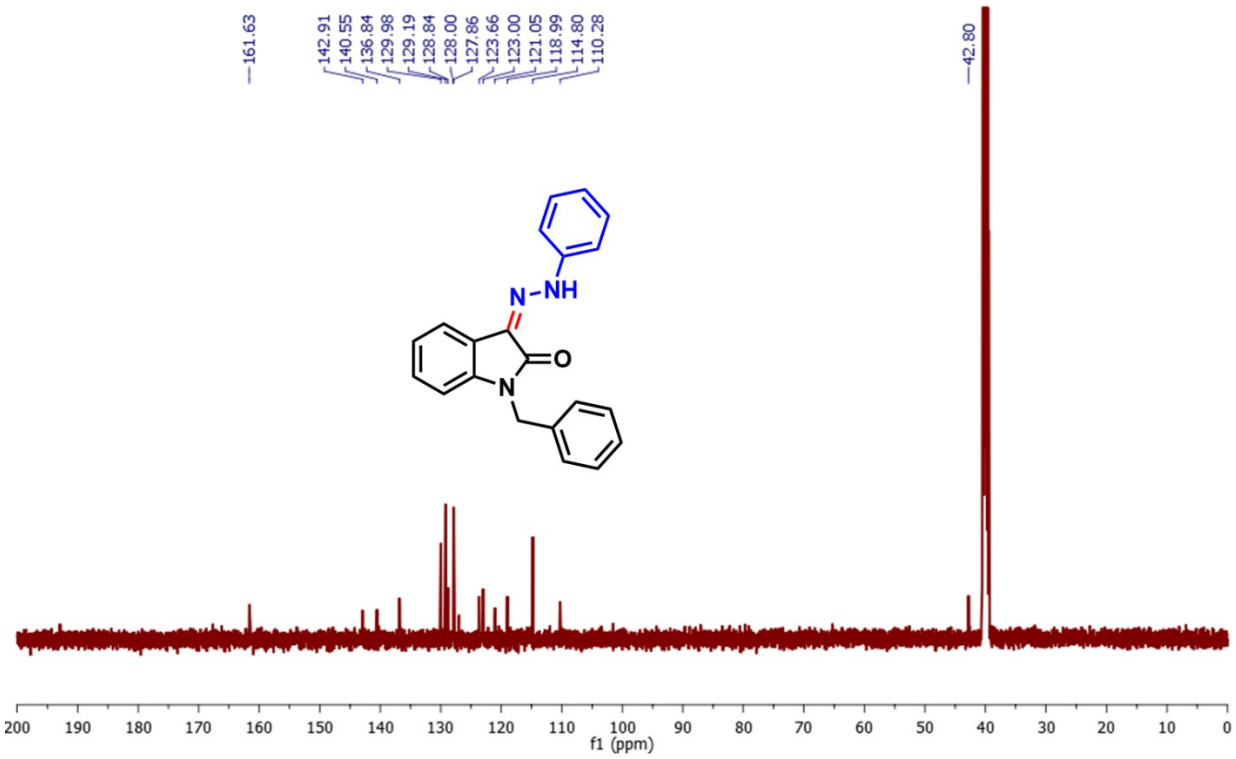
Ethyl-2-oxo-3-(2-phenylhydrazineylidene)indoline-1-carboxylate (4m)



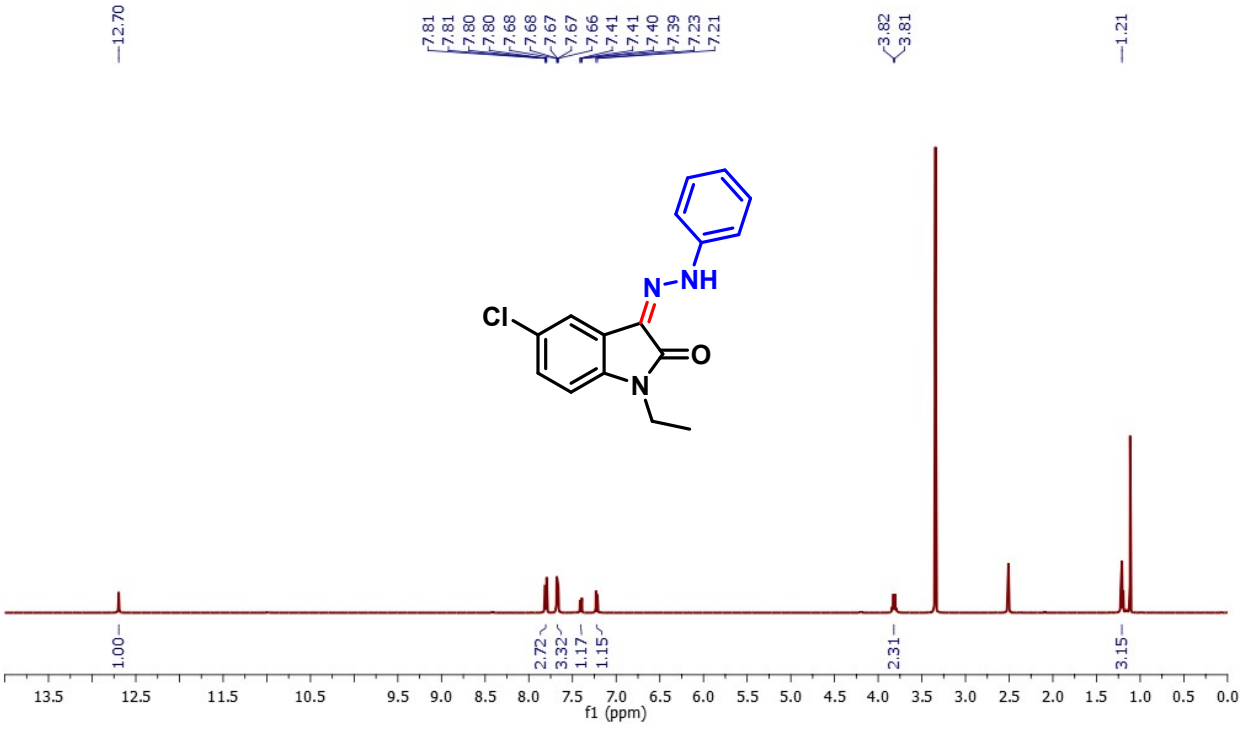


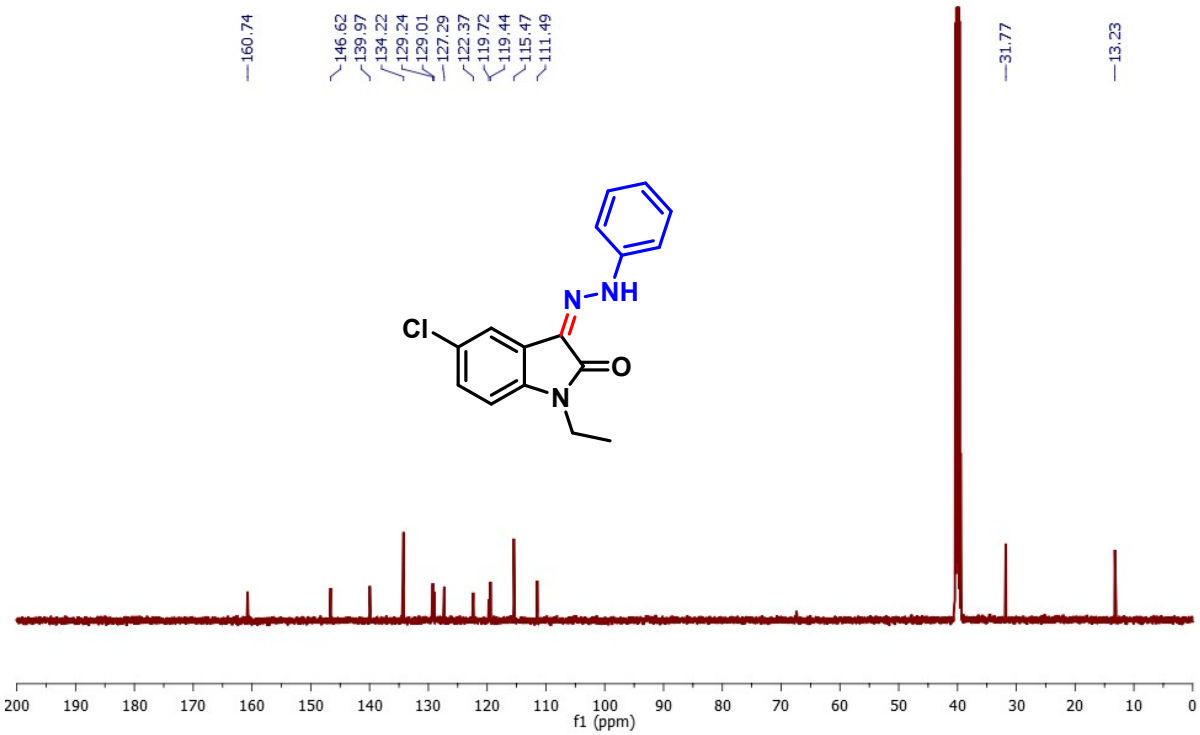
1-benzyl-3-(2-phenylhydrazineylidene)indolin-2-one (4n)



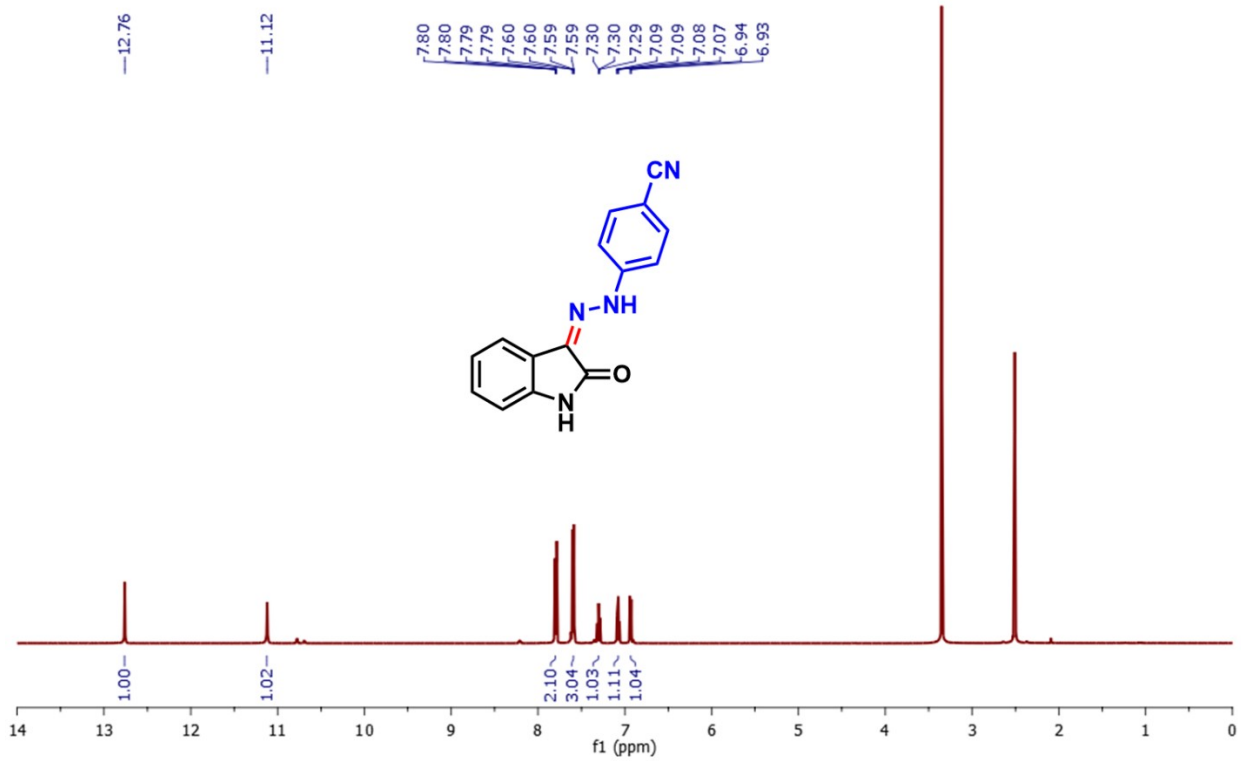


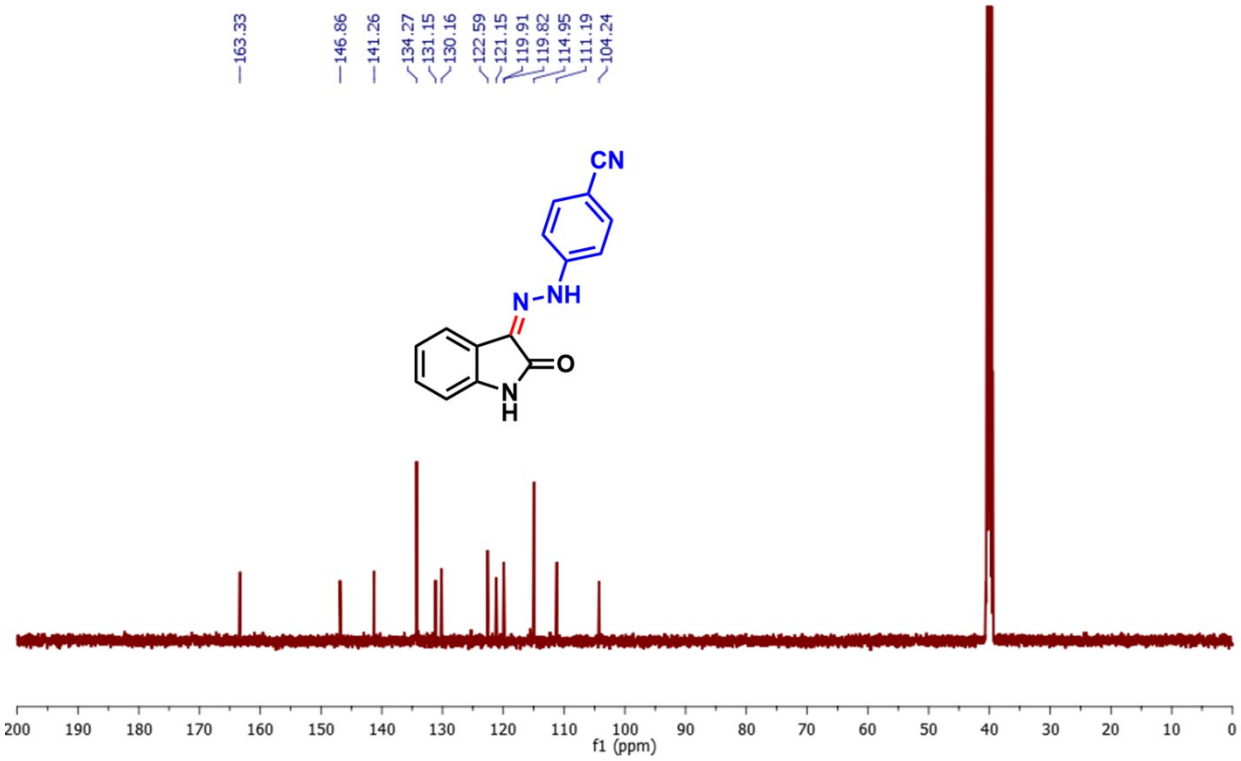
5-chloro-1-ethyl-3-(2-phenylhydrazineylidene)indolin-2-one(4o)



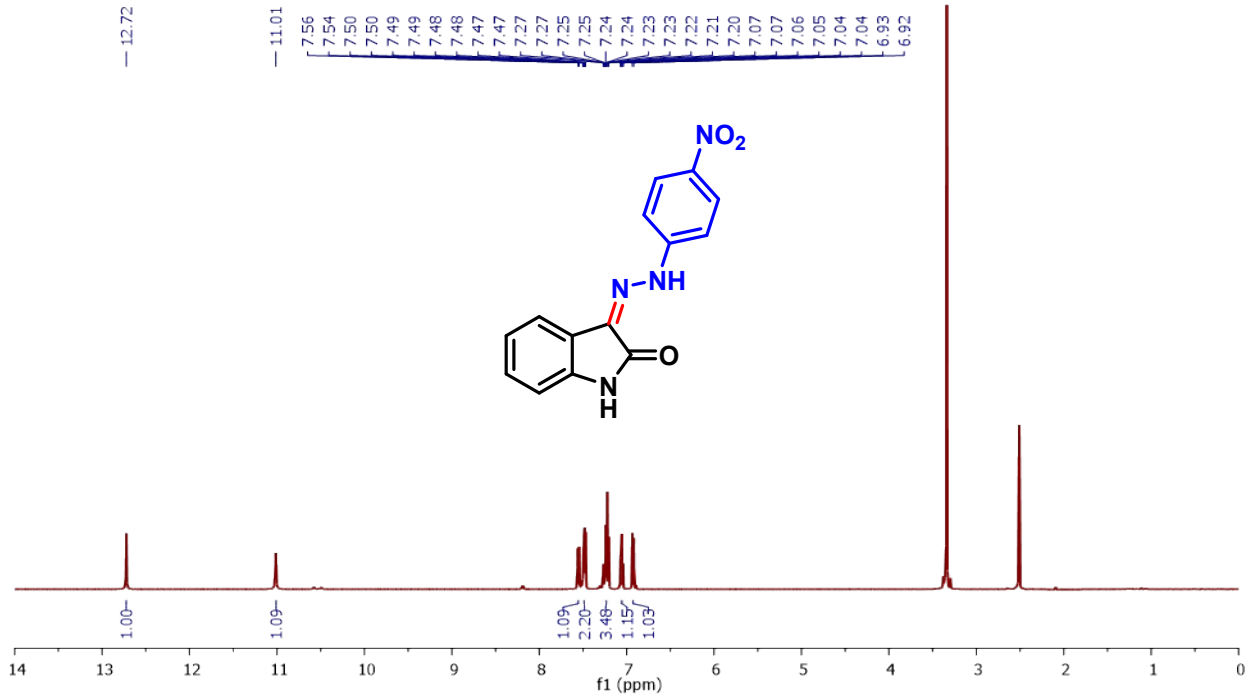


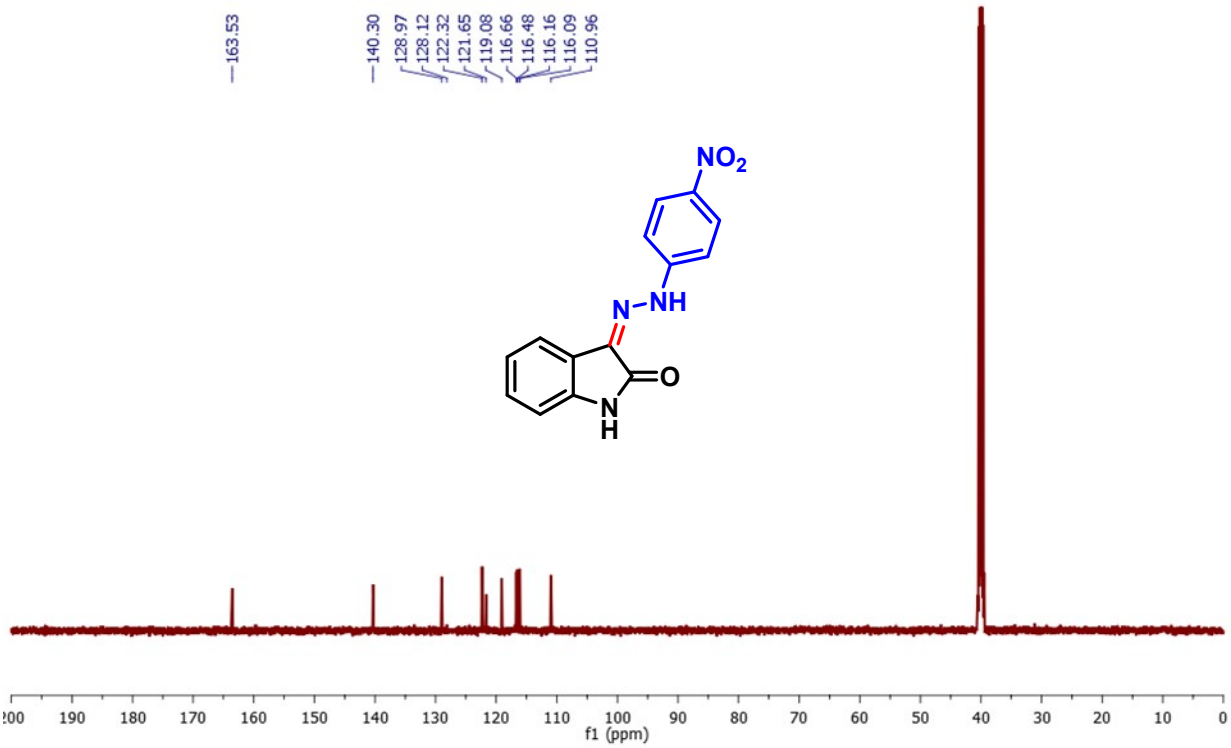
4-(2-(2-oxoindolin-3-ylidene)hydrazineyl)benzonitrile (5a)



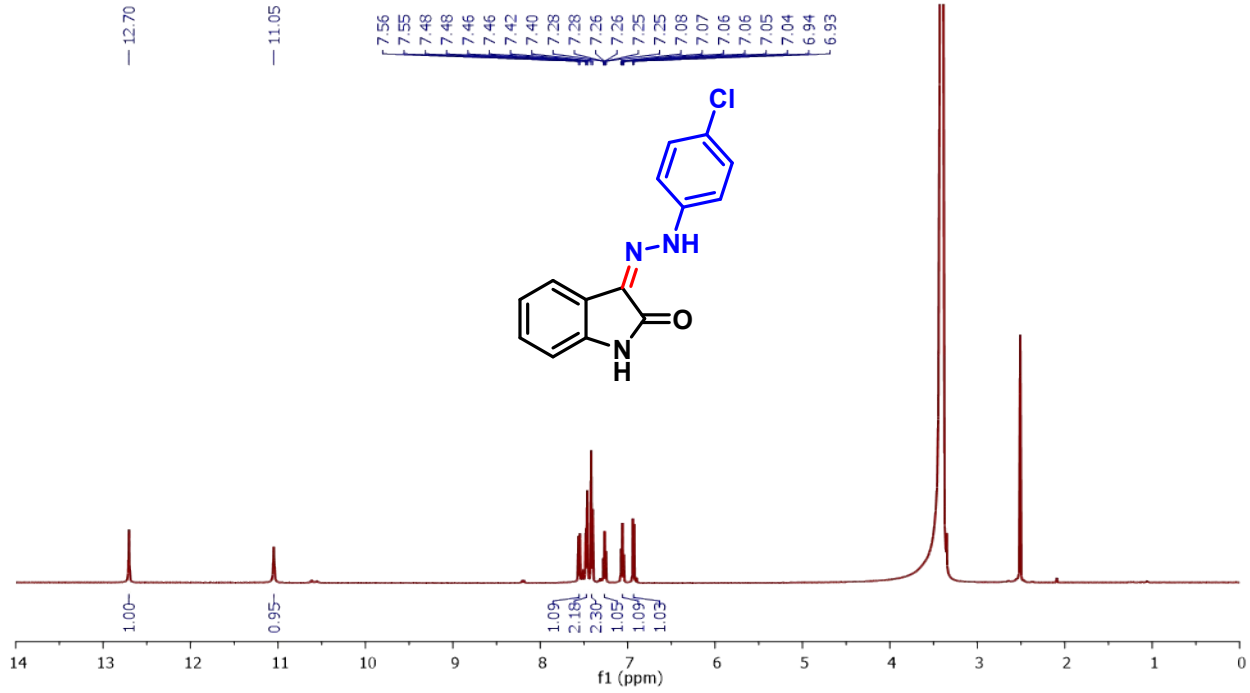


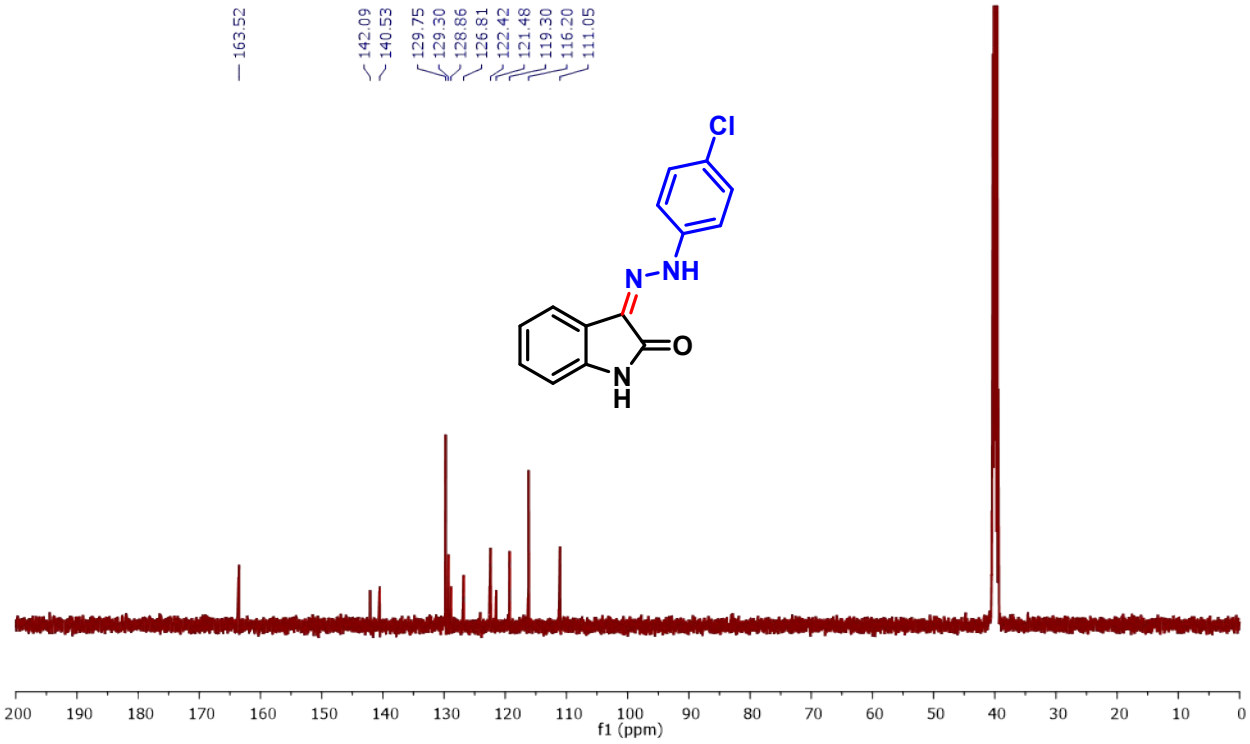
3-(2-(4-nitrophenyl)hydrazineylidene)indolin-2-one (5b)



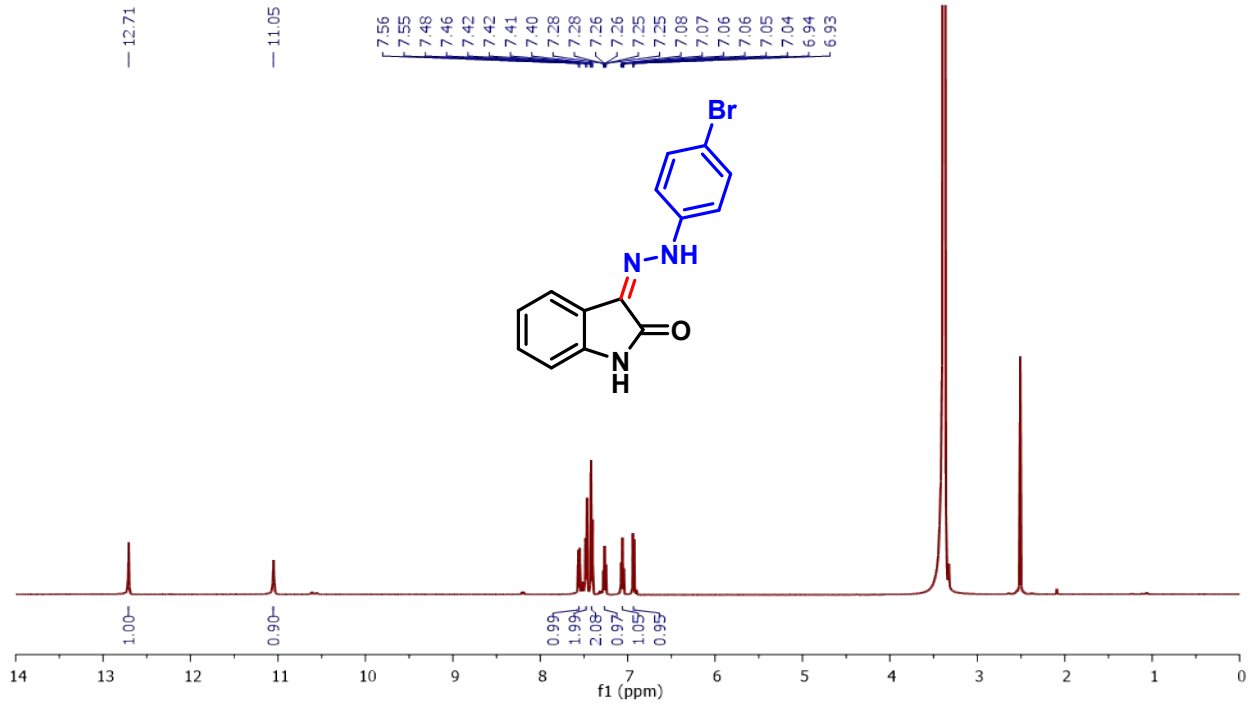


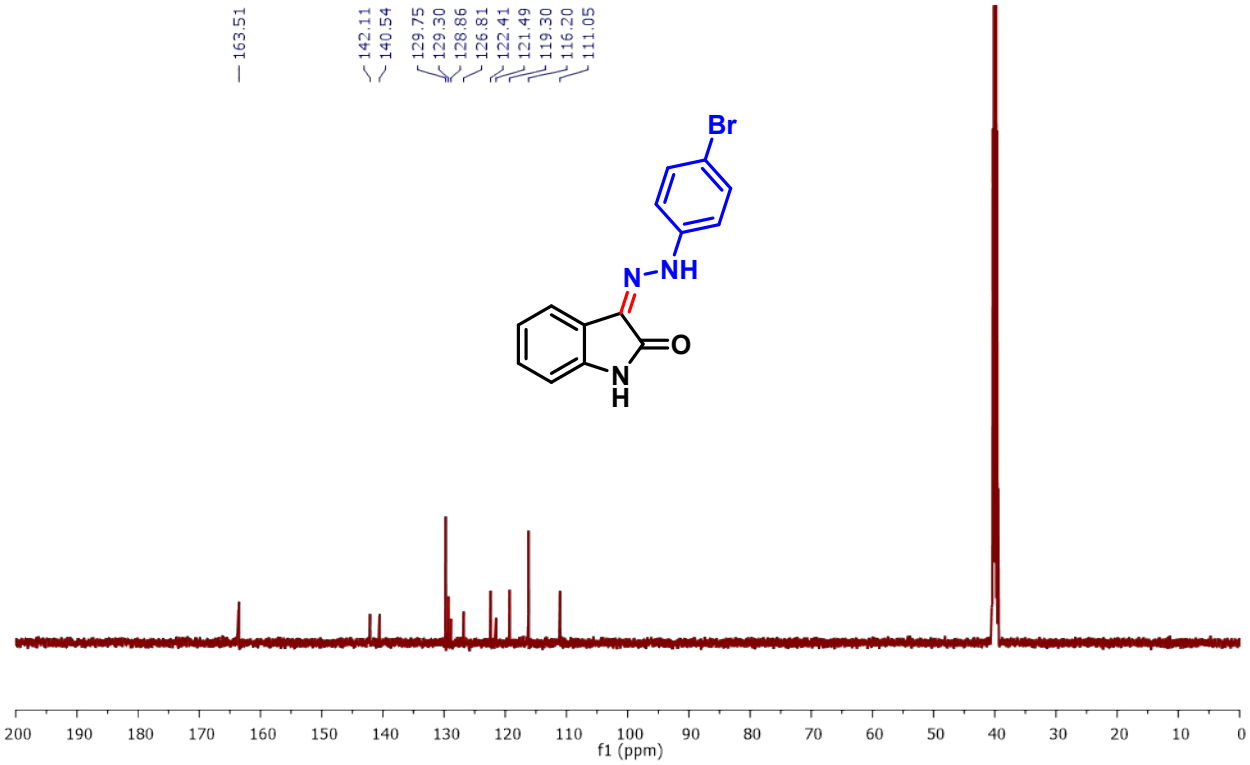
3-(2-(4-chlorophenyl)hydrazineylidene)indolin-2-one (5c)



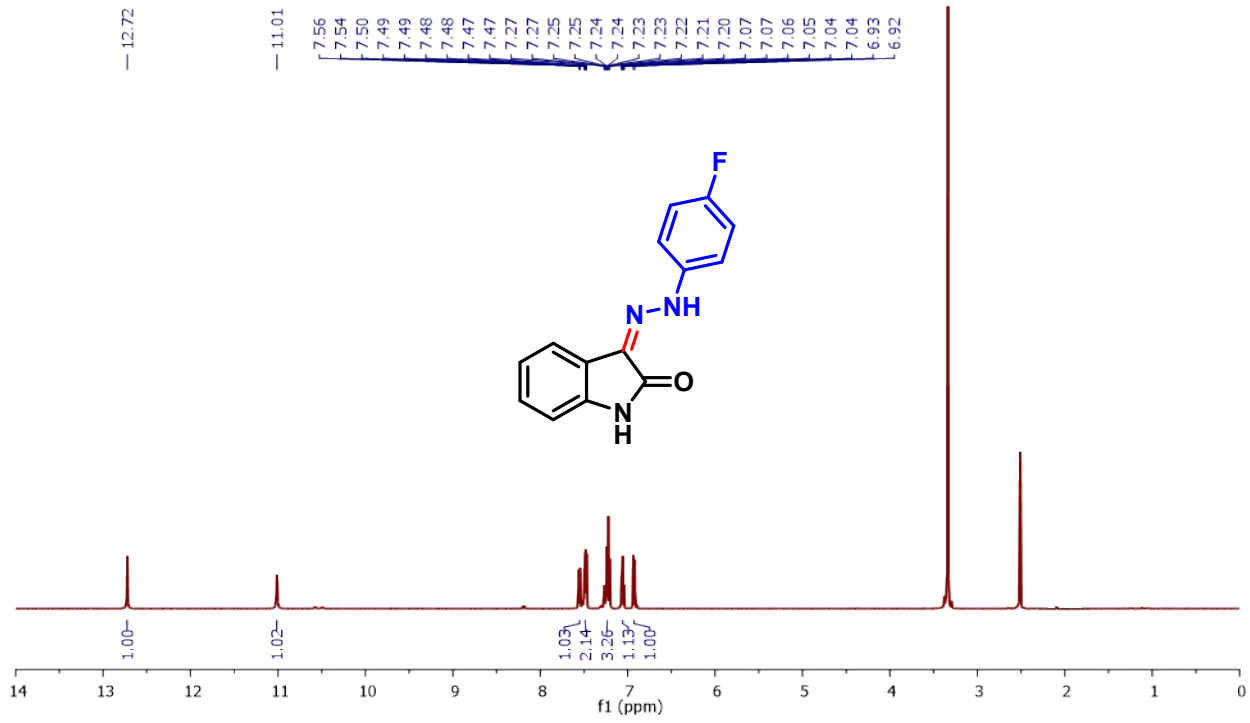


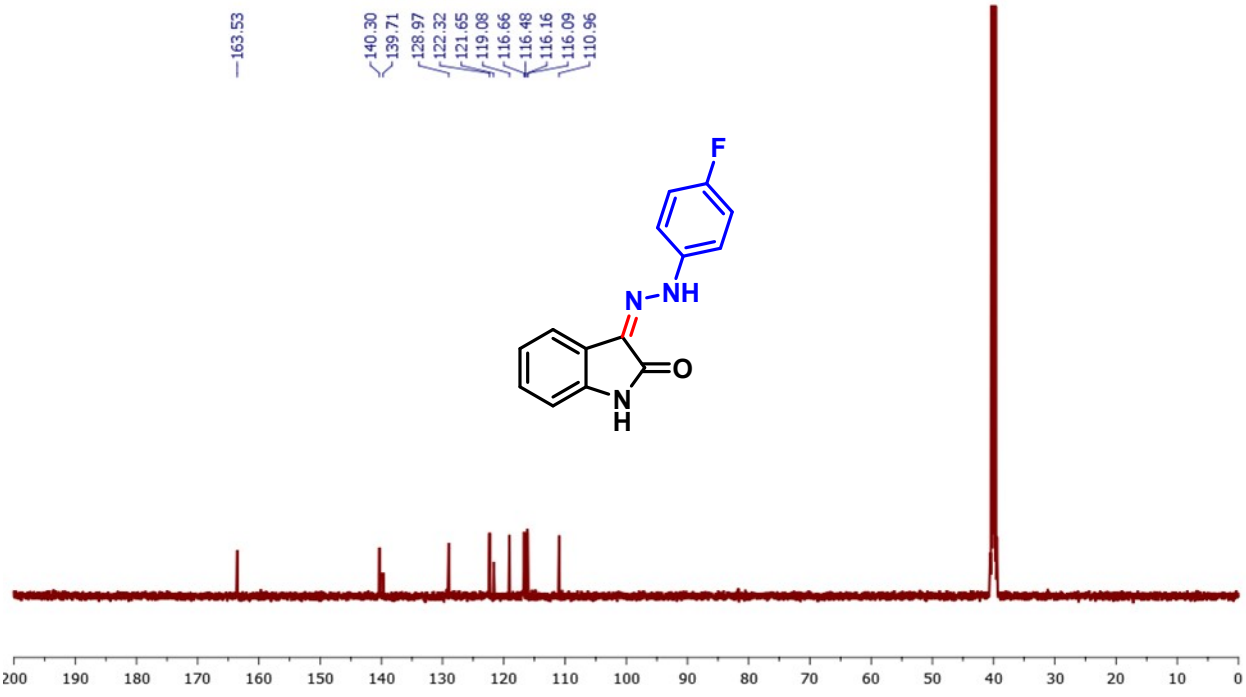
3-(2-(4-bromophenyl)hydrazineylidene)indolin-2-one (5d)





3-(2-(4-fluorophenyl)hydrazineylidene)indolin-2-one (5e)

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110.96
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NH
O
N
H
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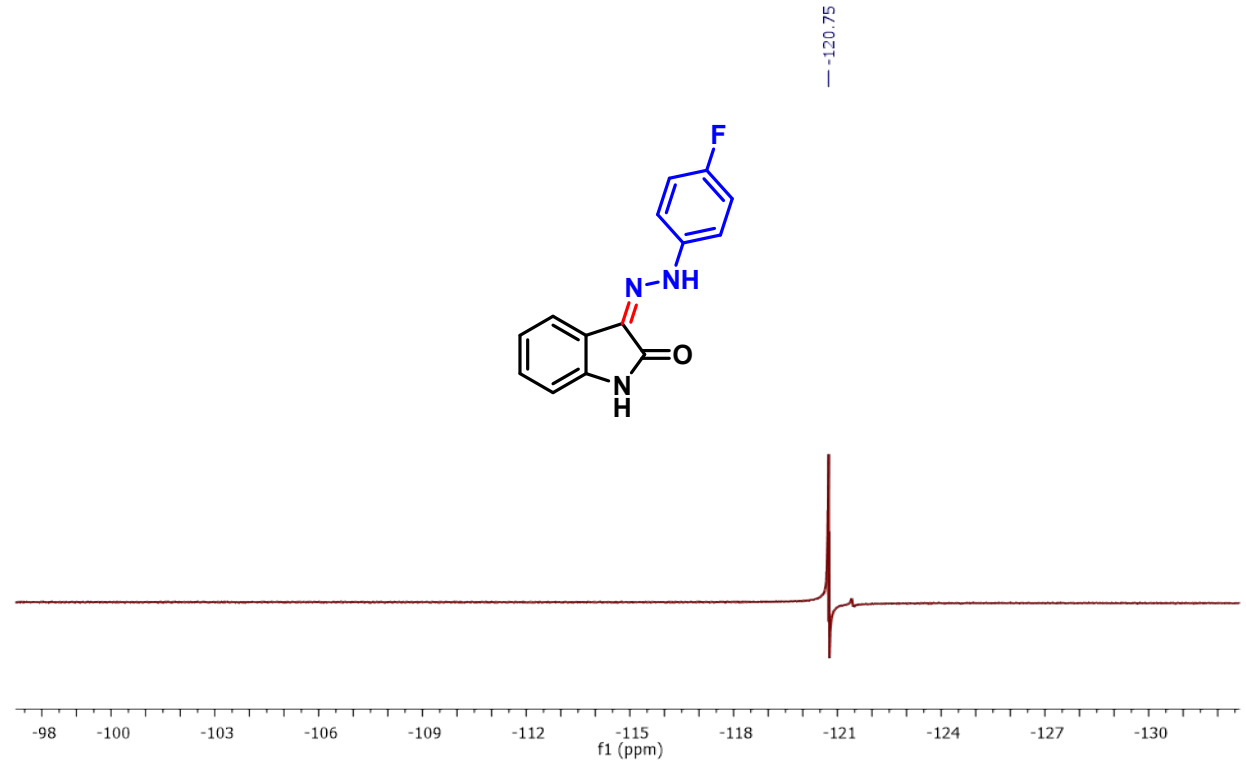
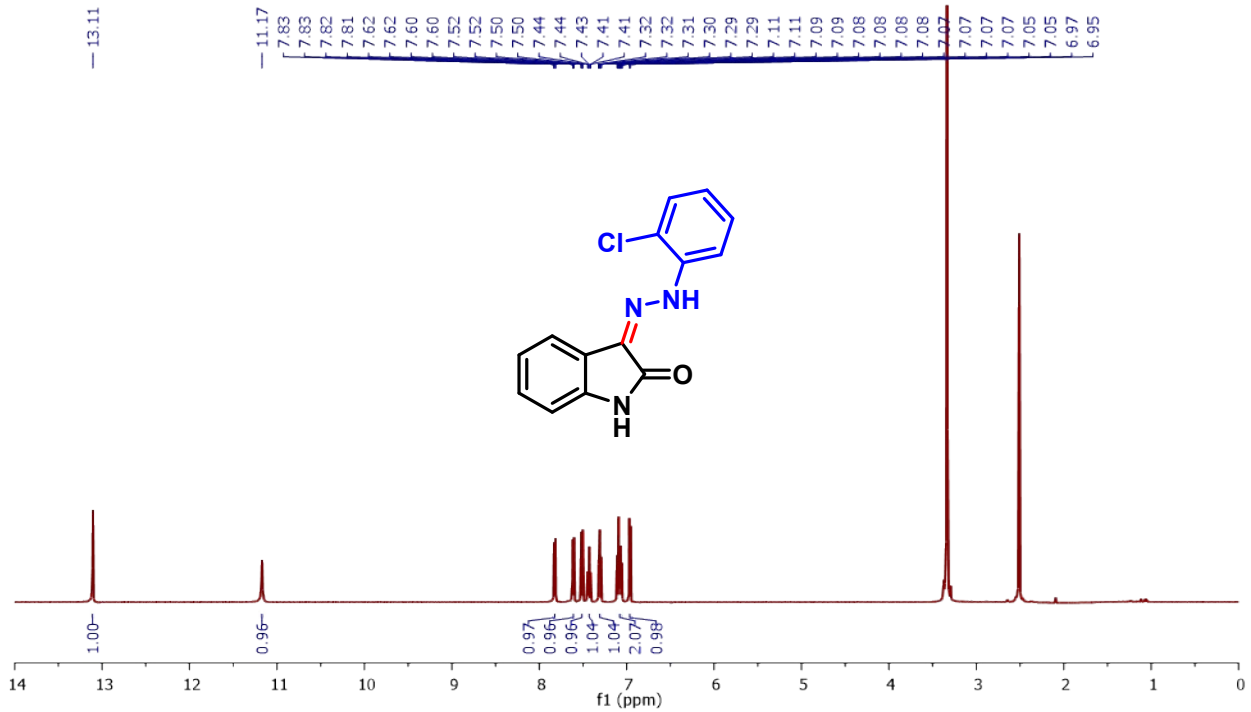
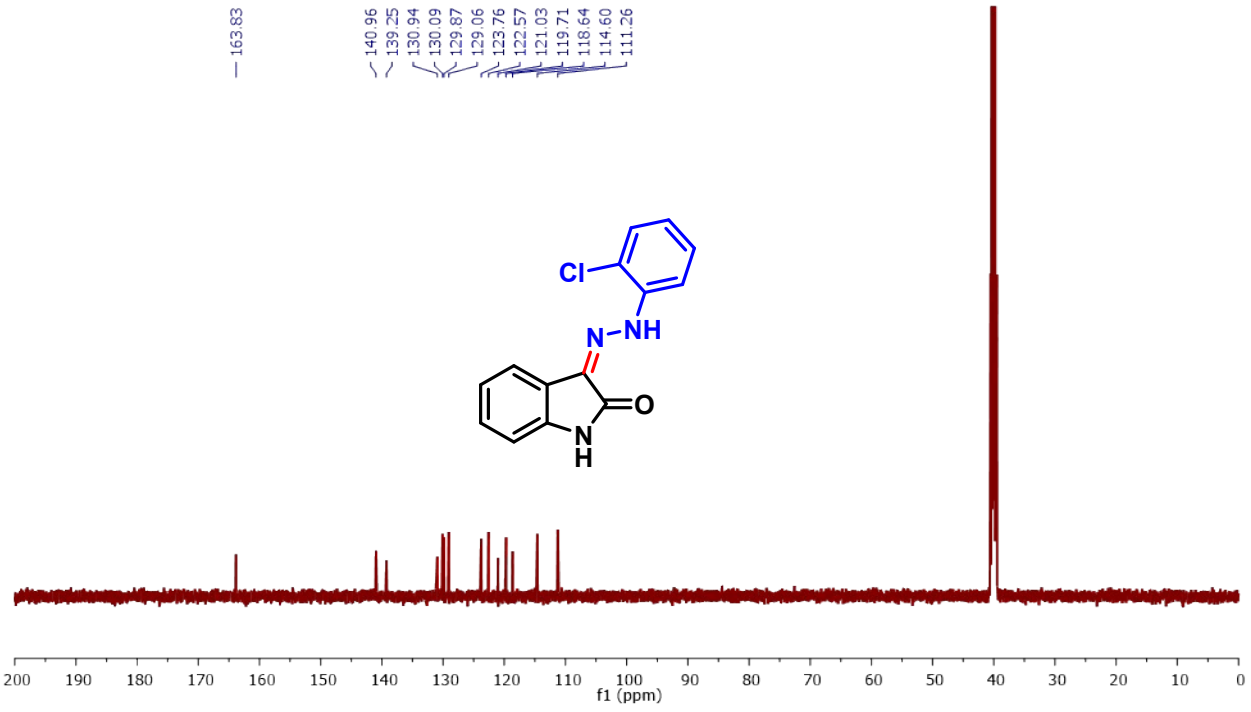
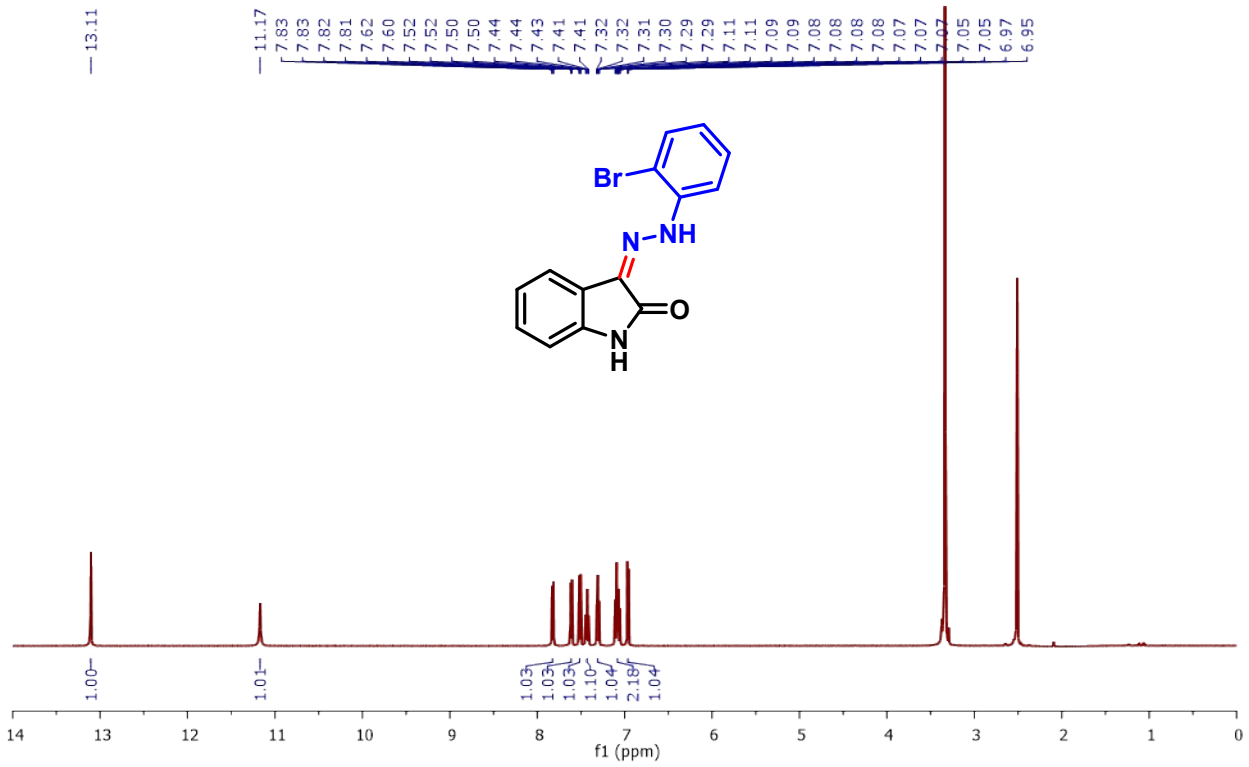

-120.75
F
N
NH
O
N
H
-98
-100
-103
-106
-109
-112
-115
-118
-121
-124
-127
-130
f1 (ppm)

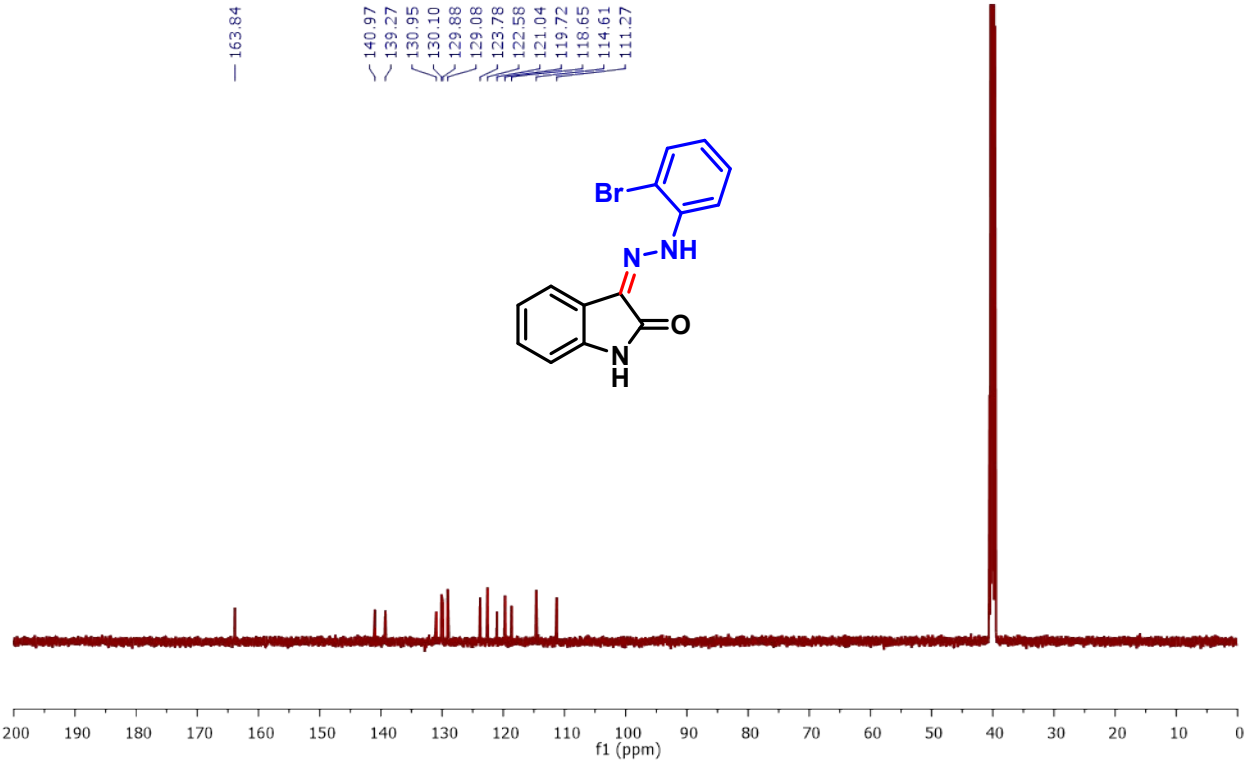
3-(2-(2-chlorophenyl)hydrazineylidene)indolin-2-one (5f)



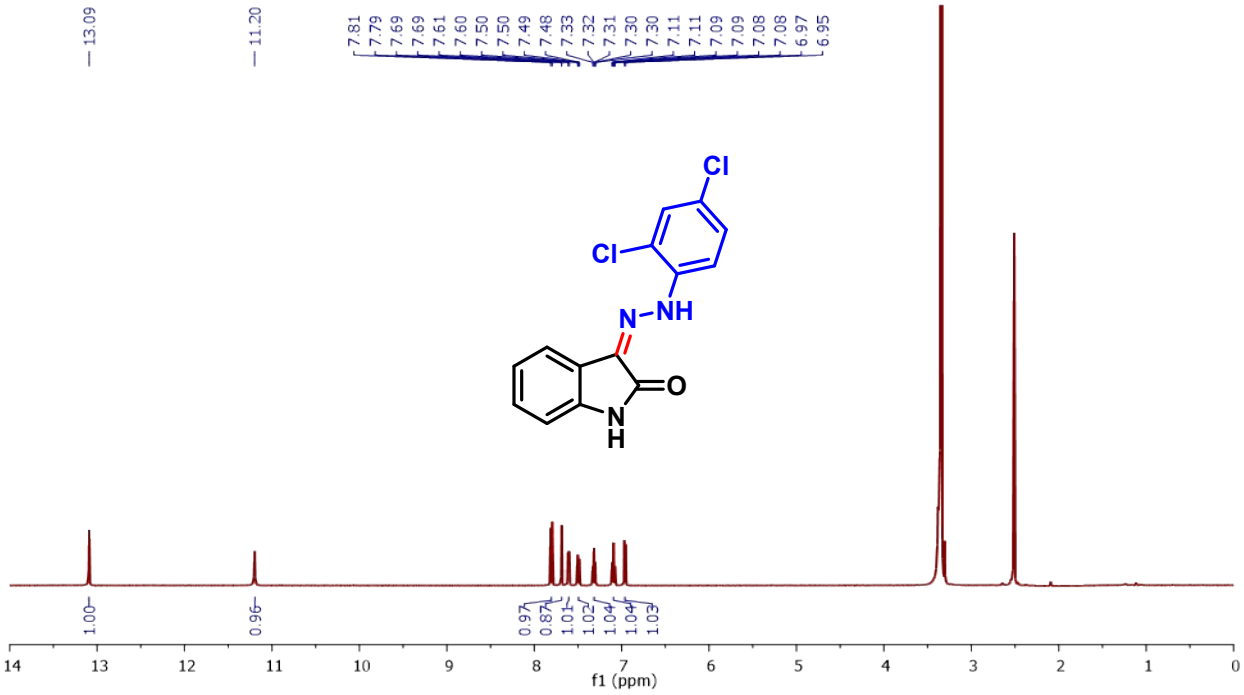


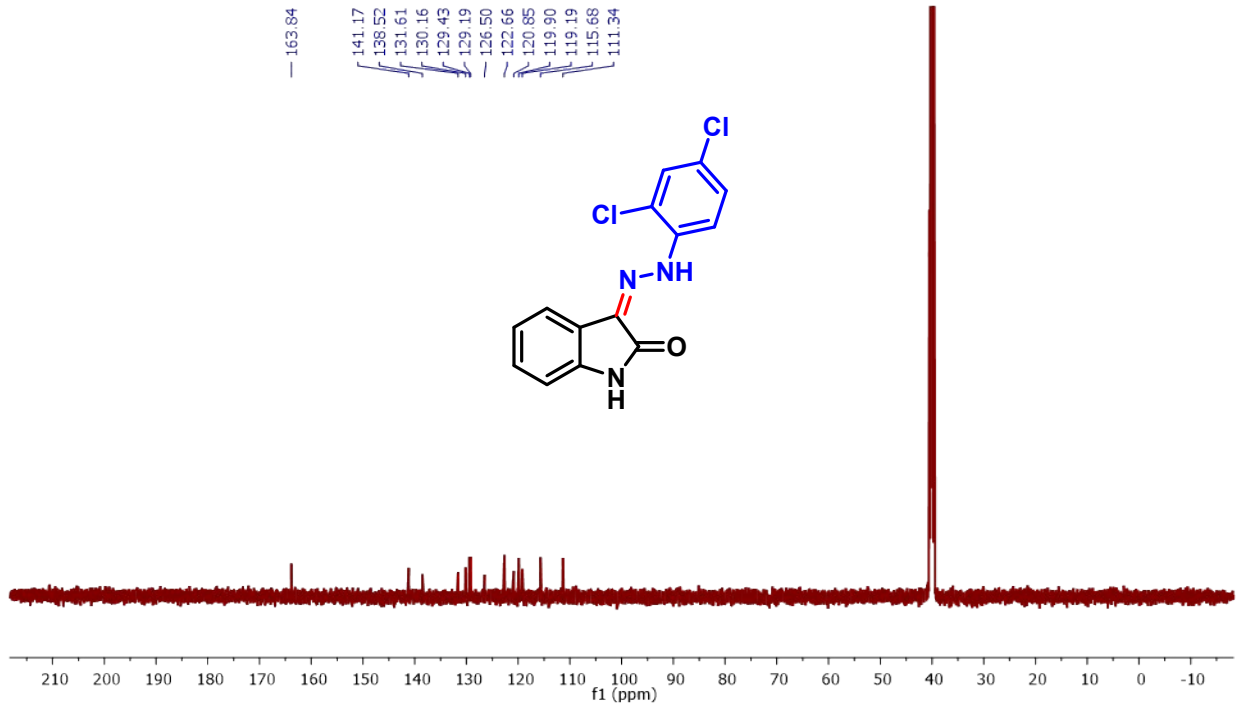
3-(2-(2-bromophenyl)hydrazineylidene)indolin-2-one (5g)



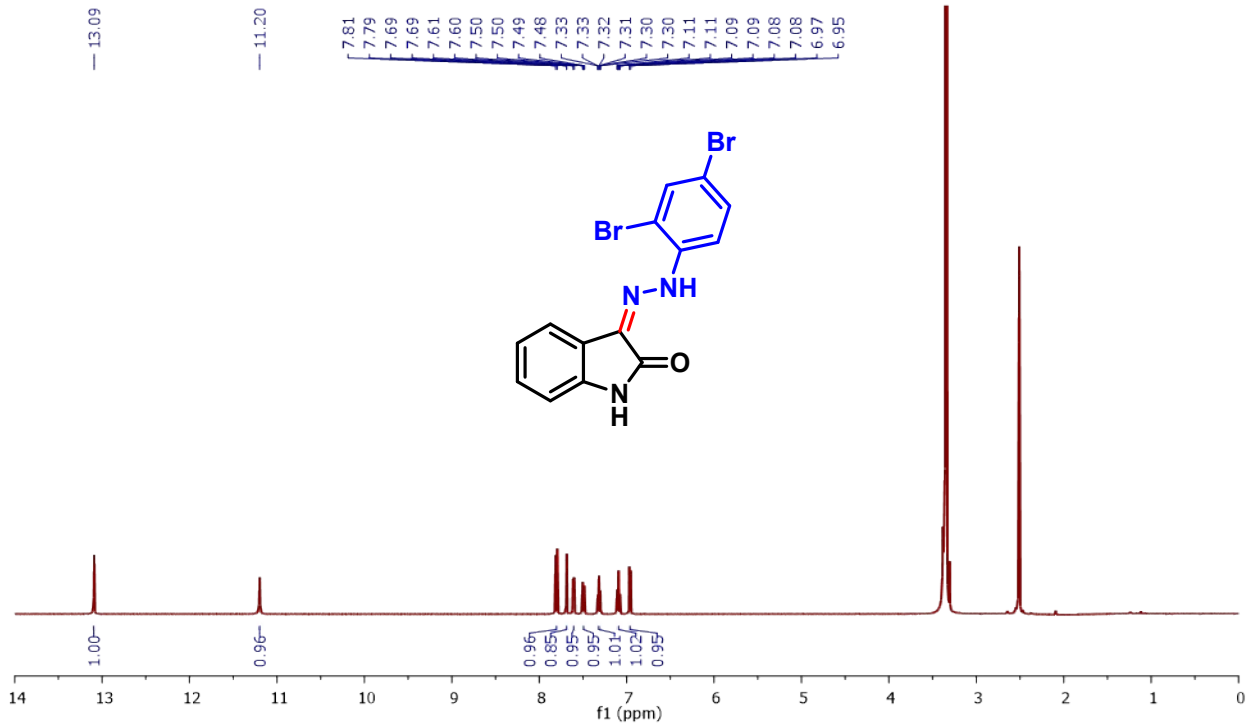


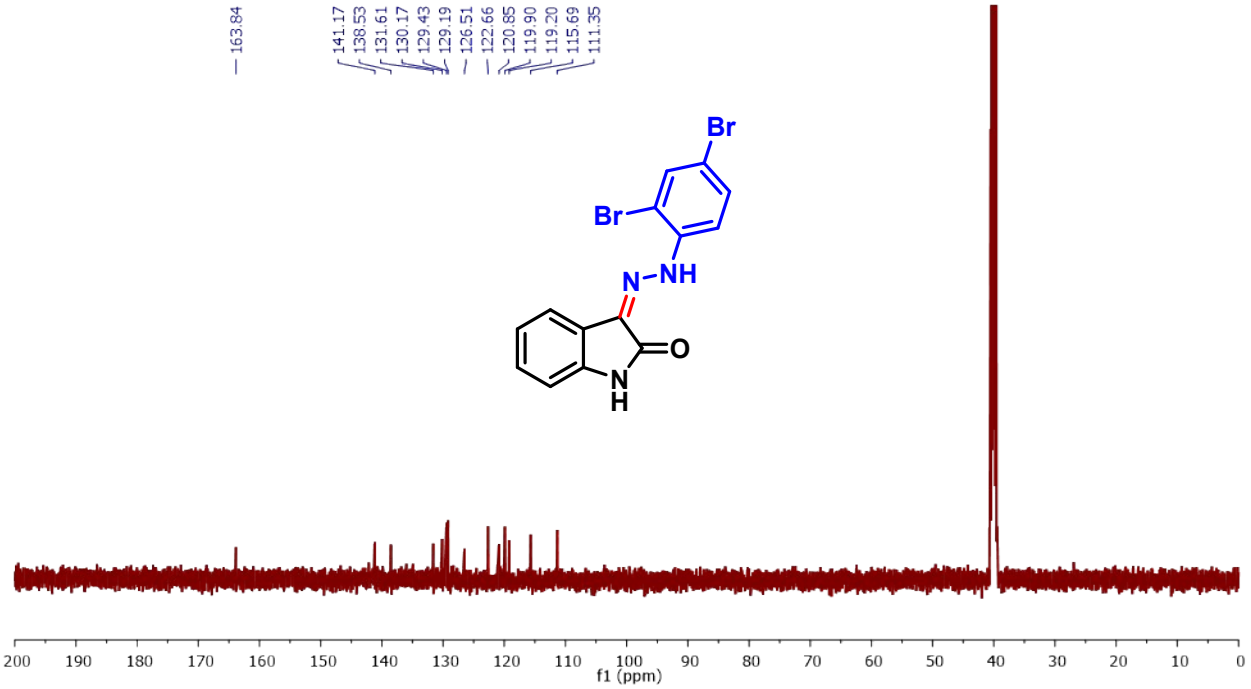
3-(2-(2,4-dichlorophenyl)hydrazineylidene)indolin-2-one (5h)



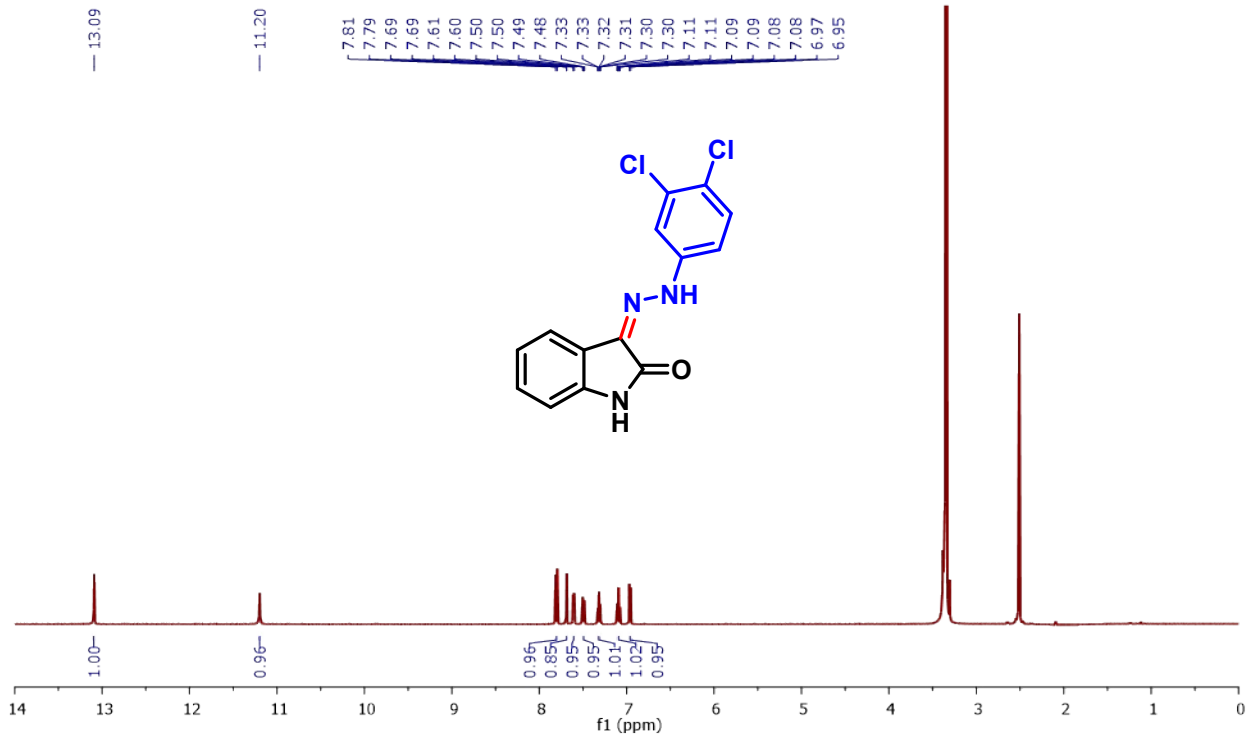


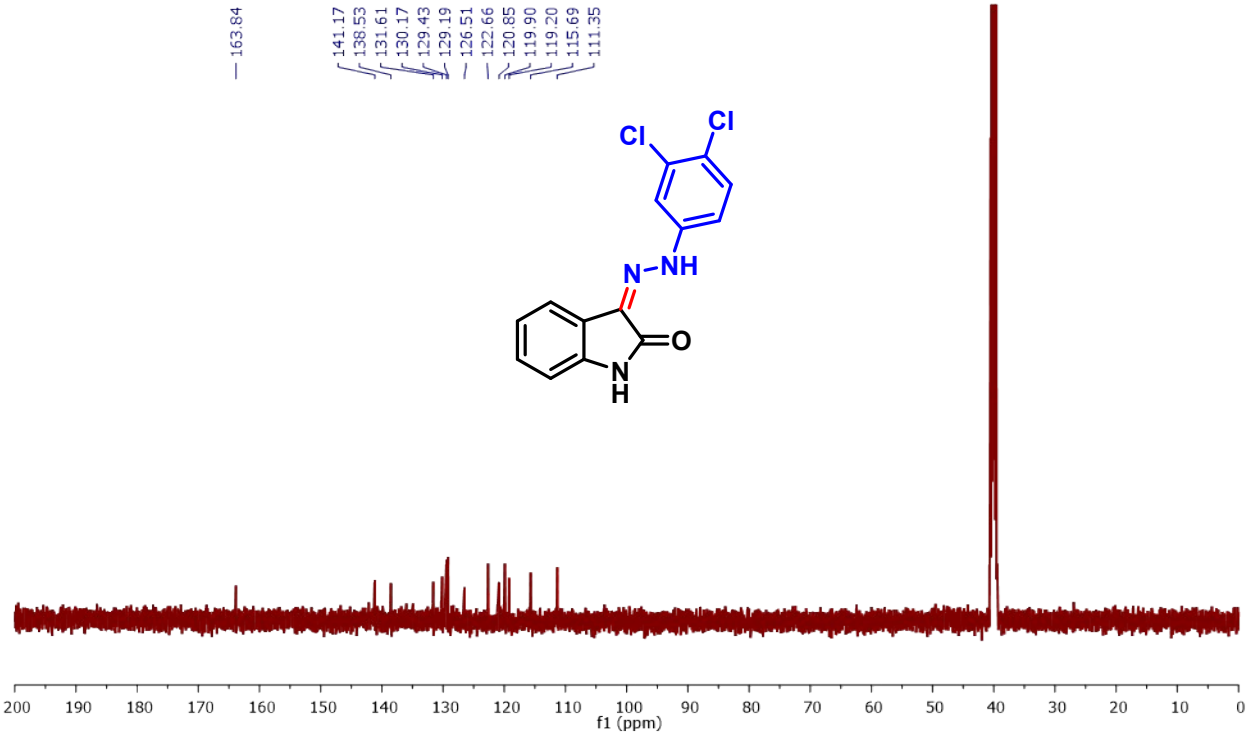
3-(2-(2,4-dibromophenyl)hydrazineylidene)indolin-2-one (5i)



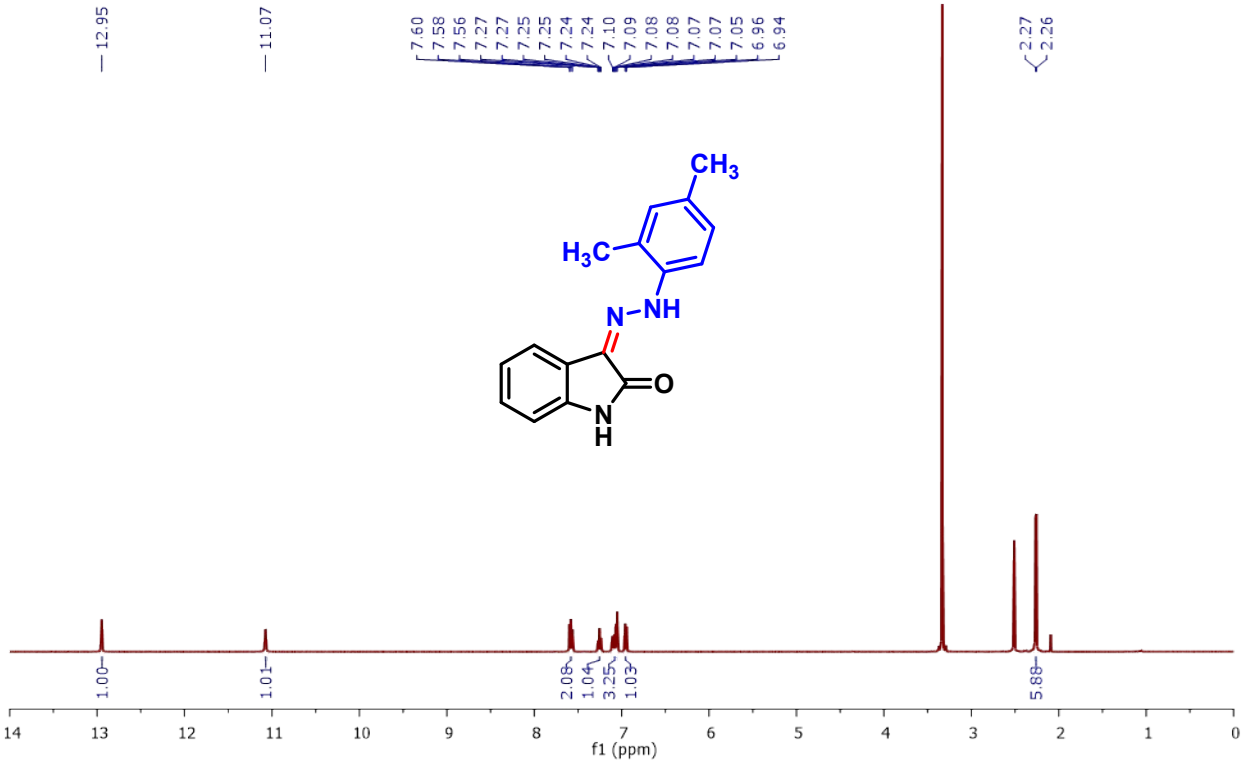


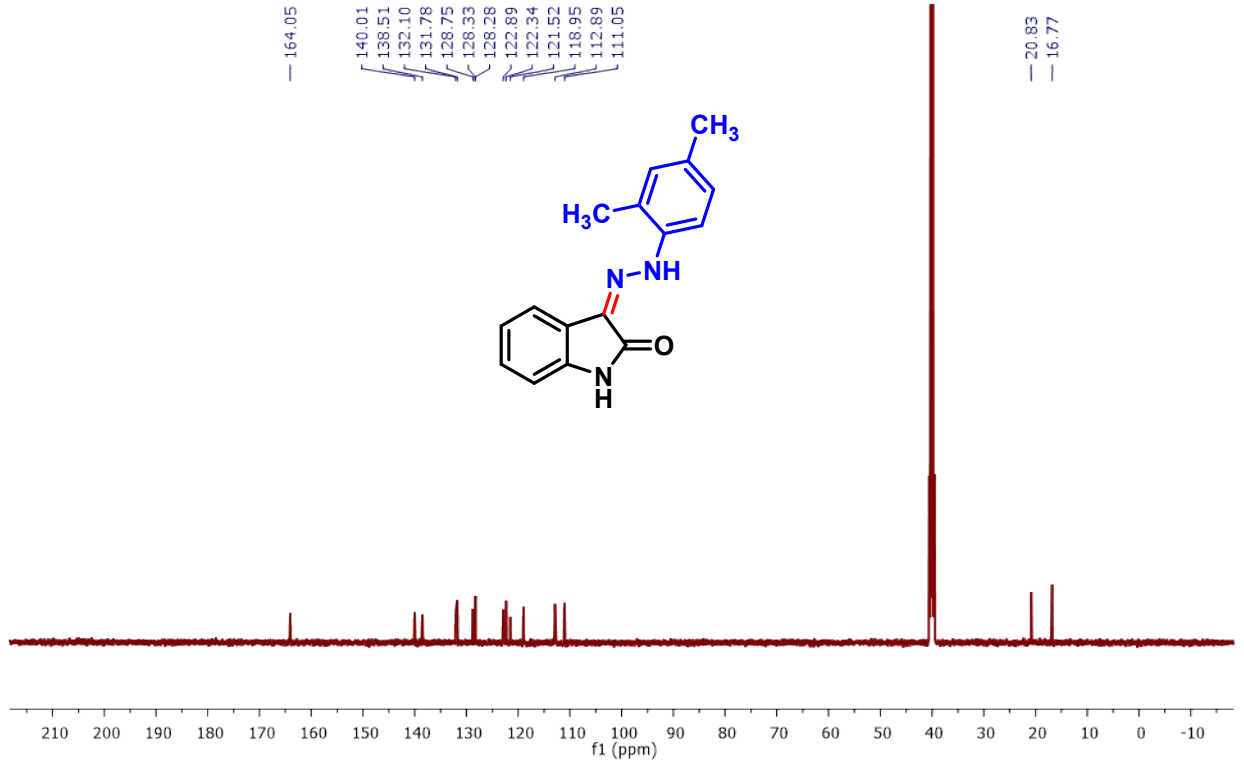
3-(2-(3,4-dichlorophenyl)hydrazineylidene)indolin-2-one (5j)



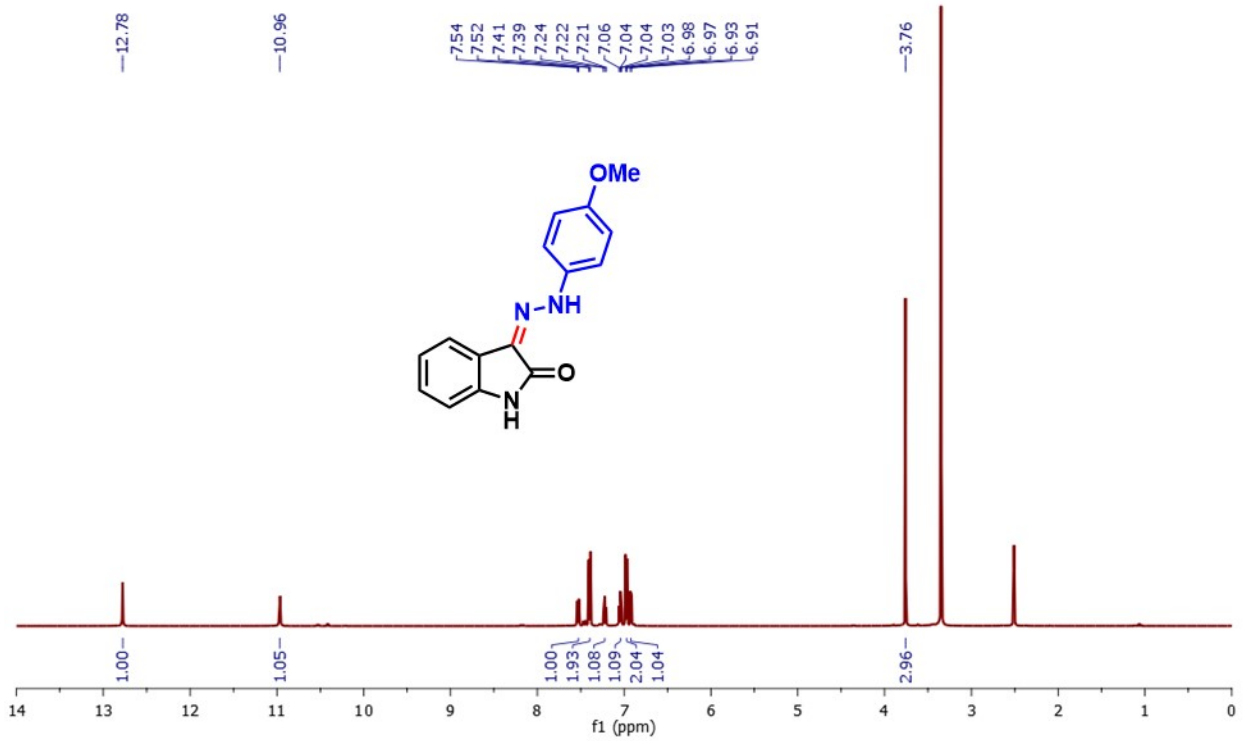


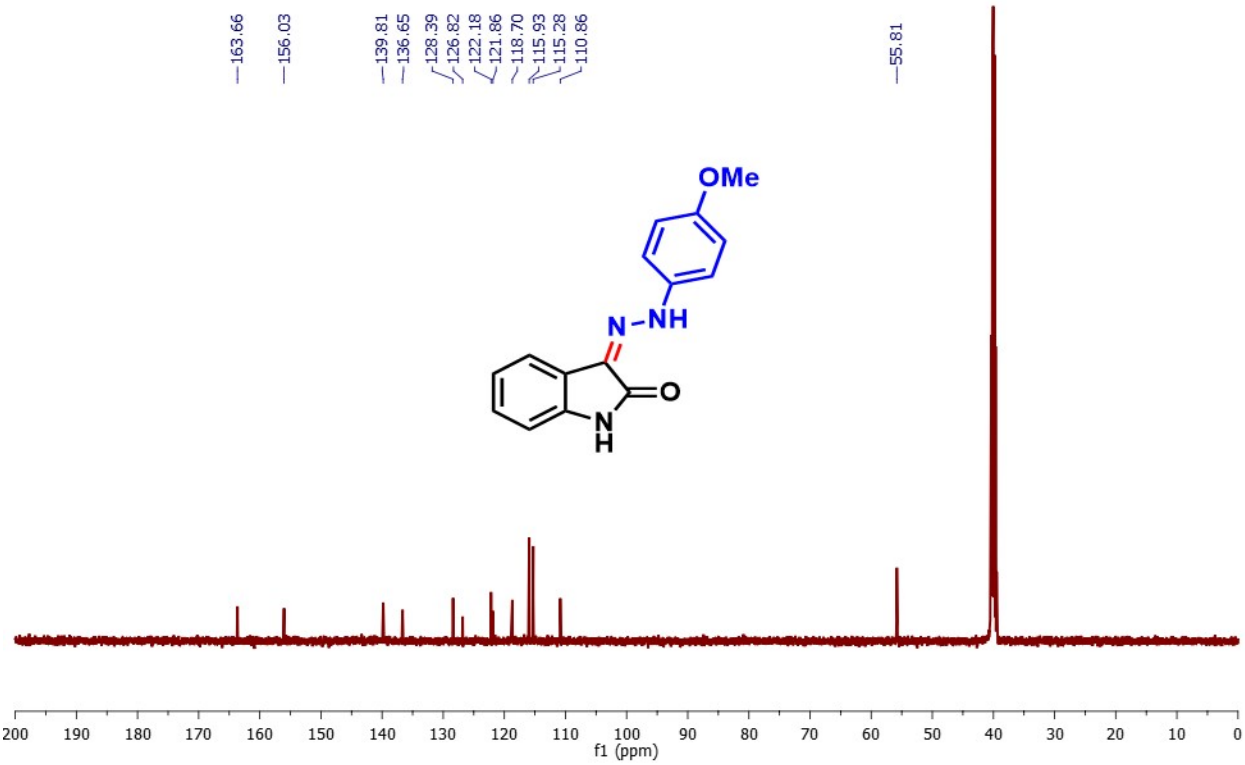
3-(2-(2,4-dimethylphenyl)hydrazineylidene)indolin-2-one (5k)



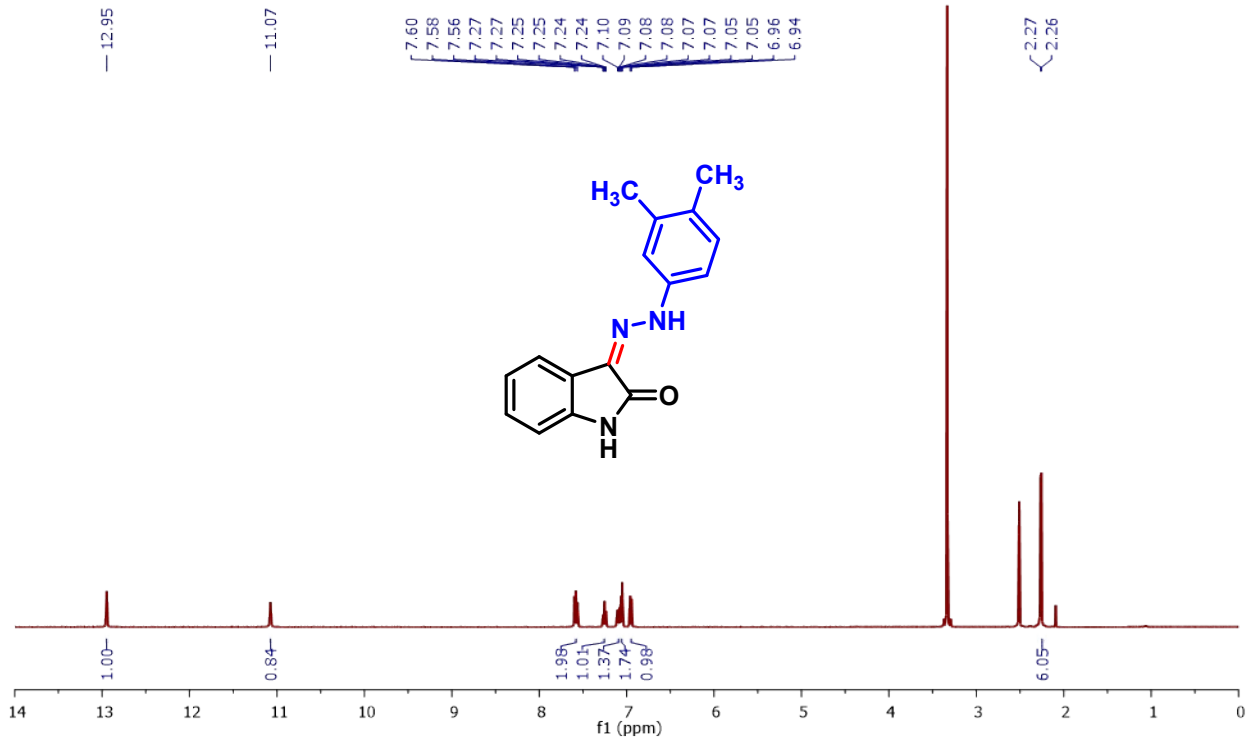


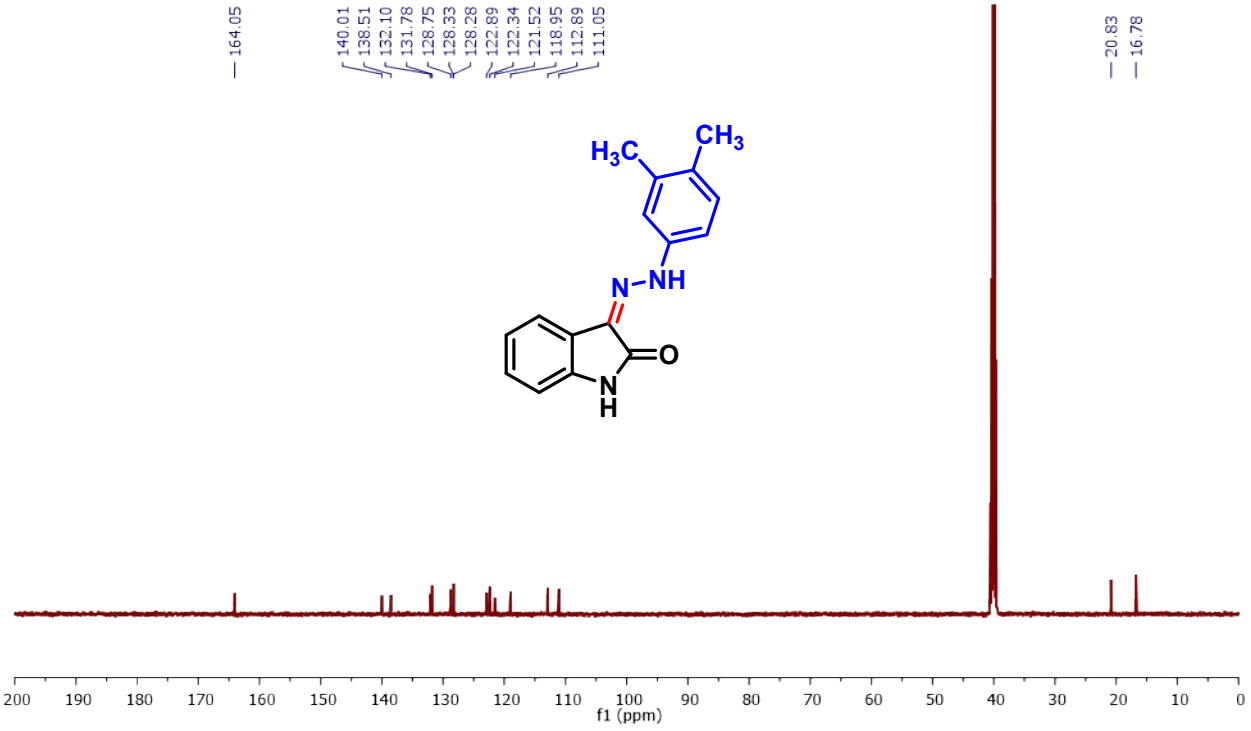
3-(2-(4-methoxyphenyl)hydrazineylidene)indolin-2-one (5l)



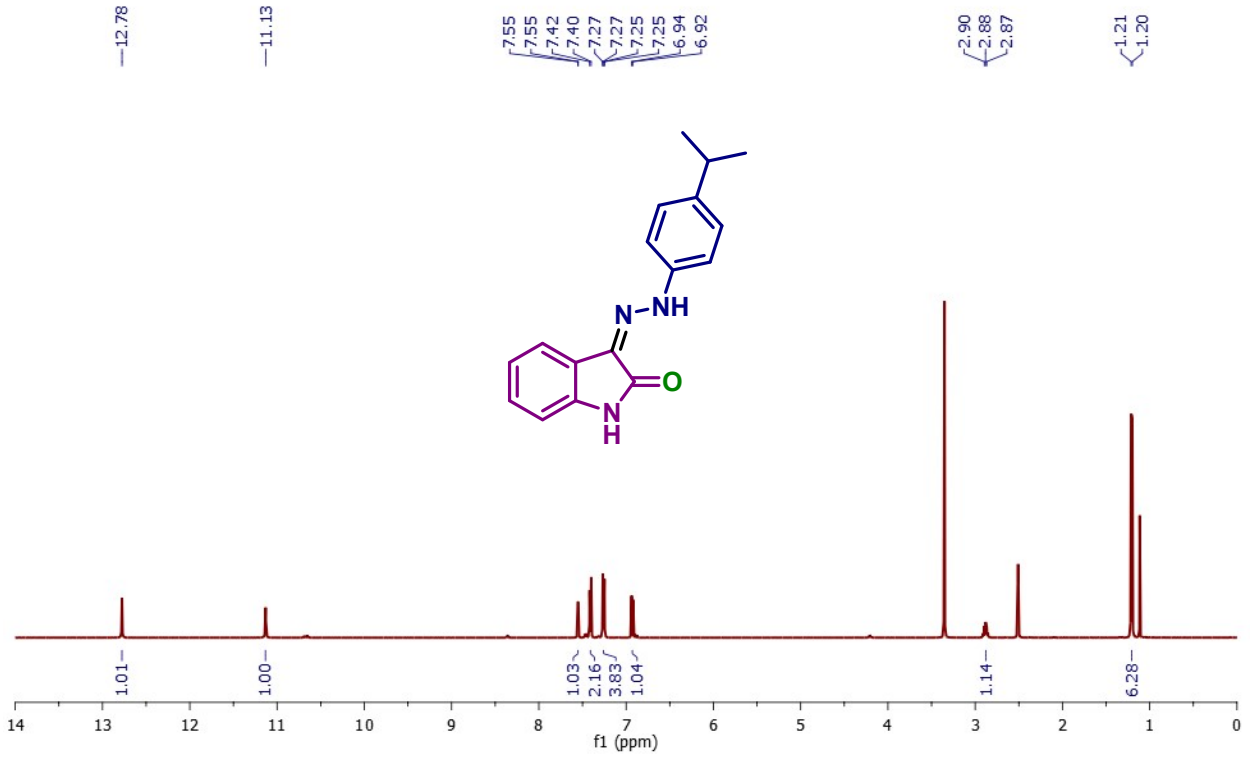


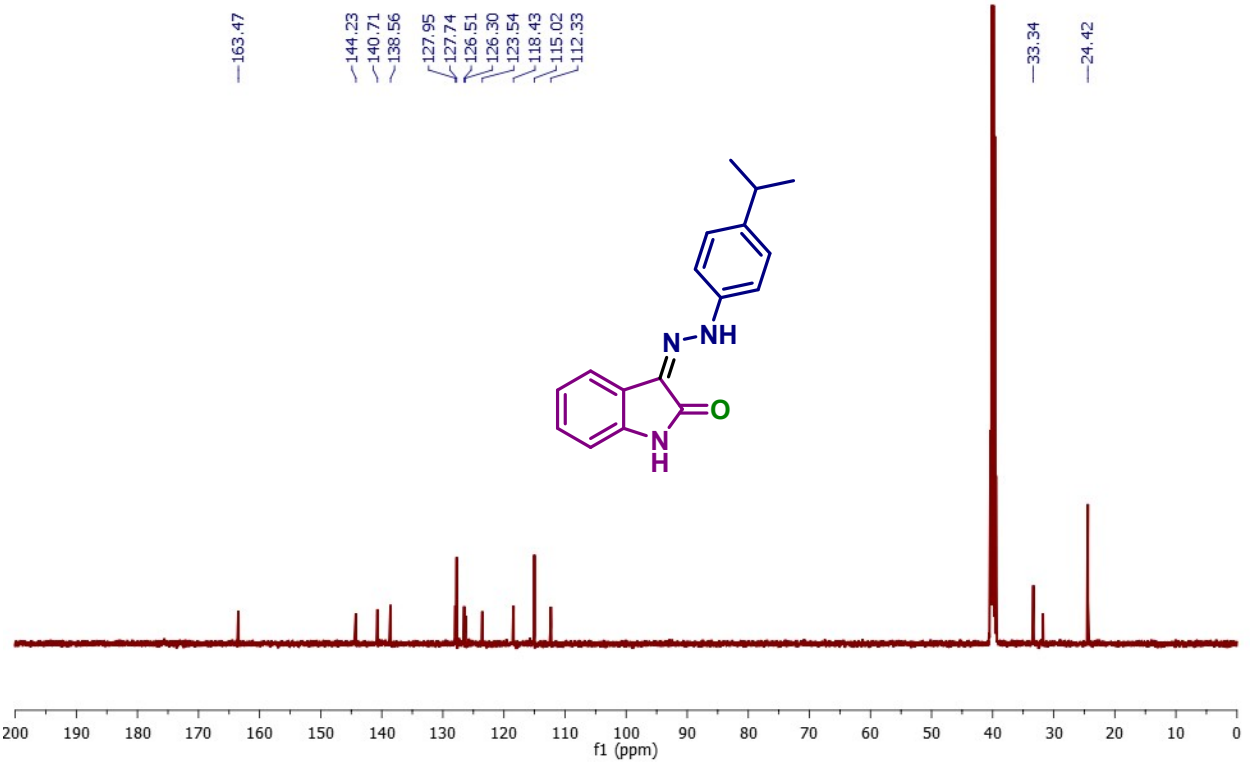
3-(2-(3,4-dimethylphenyl)hydrazineylidene)indolin-2-one (5m)



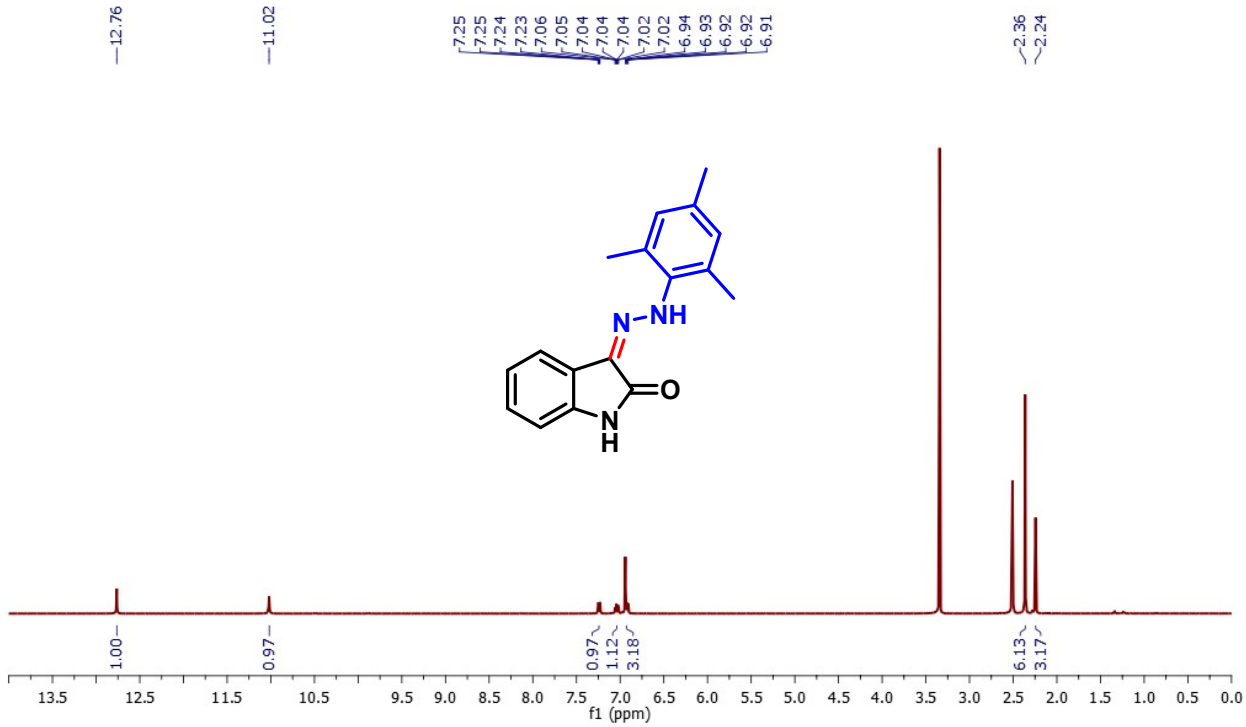


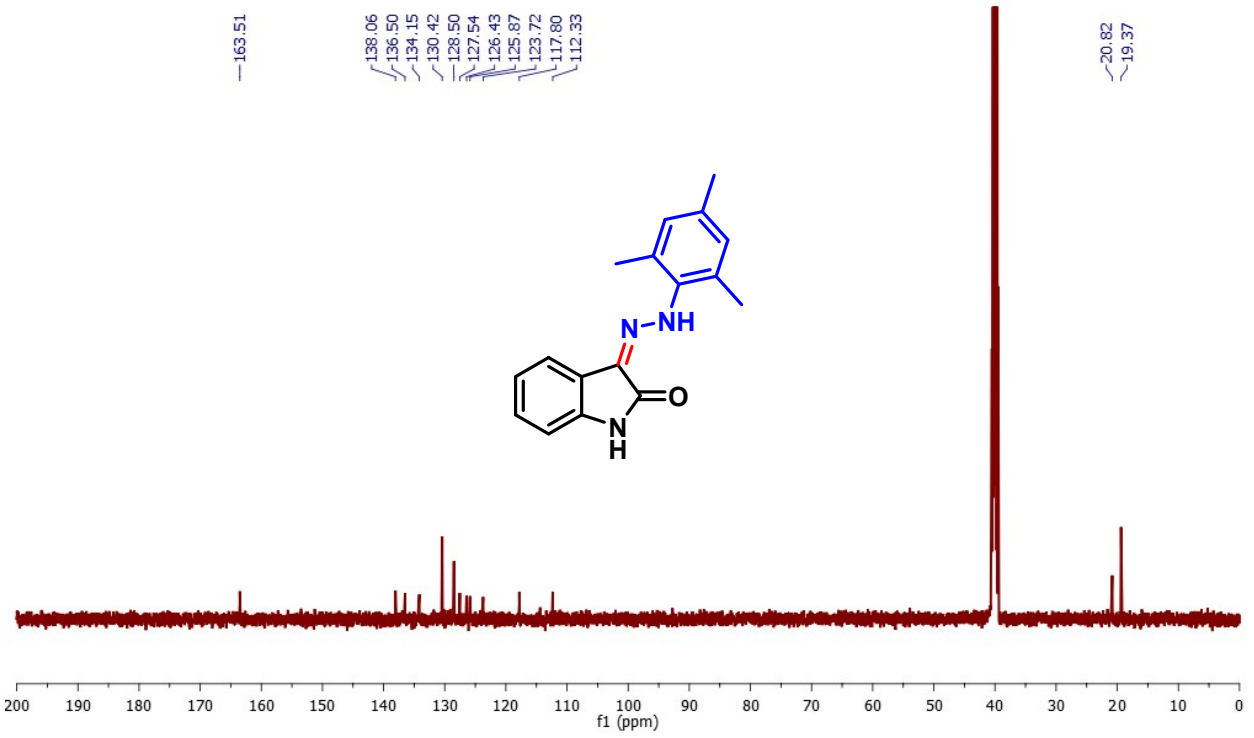
3-(2-(4-isopropylphenyl)hydrazineylidene)indolin-2-one(5n)



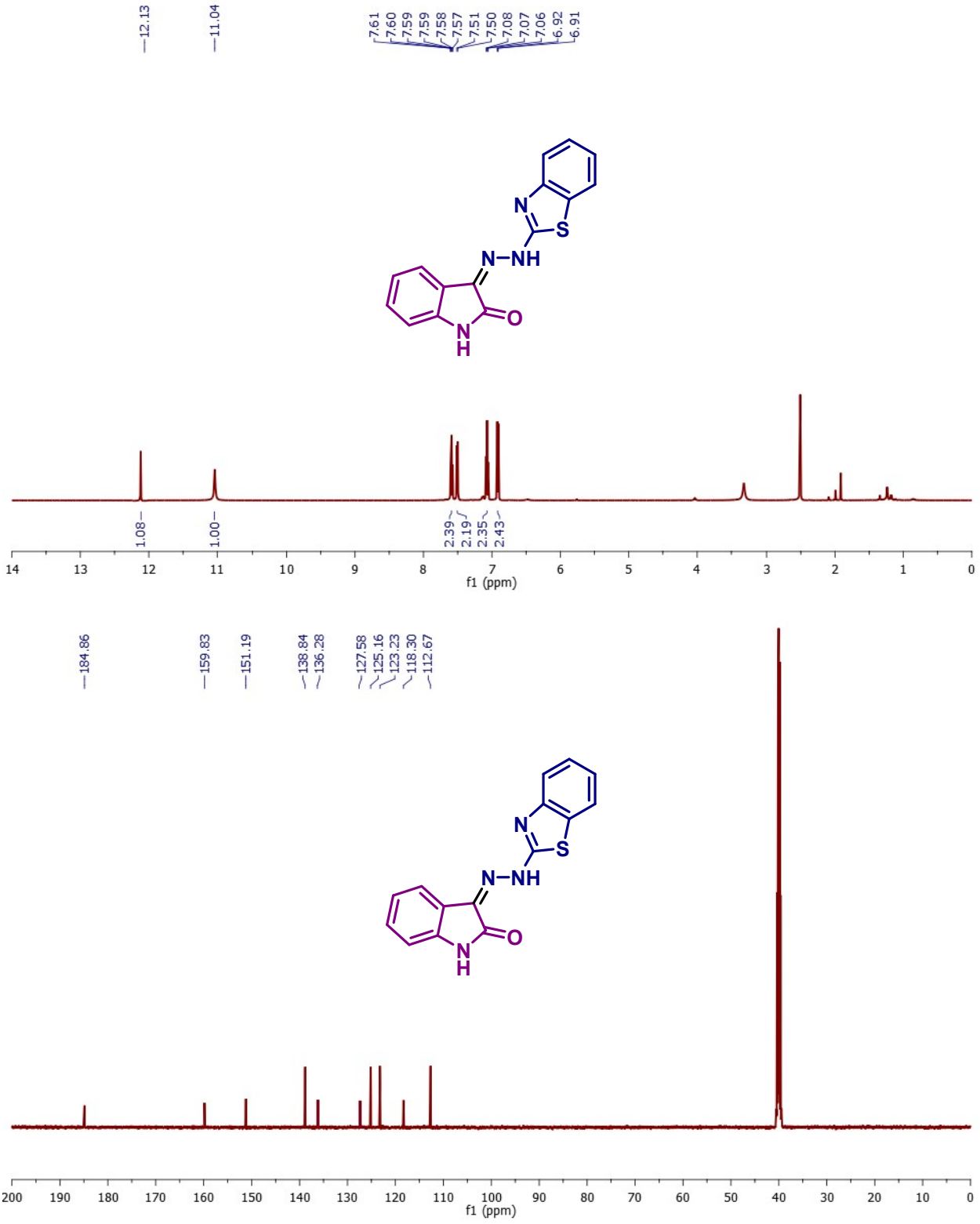


3-(2-mesitylhydrazineylidene)indolin-2-one (5o)

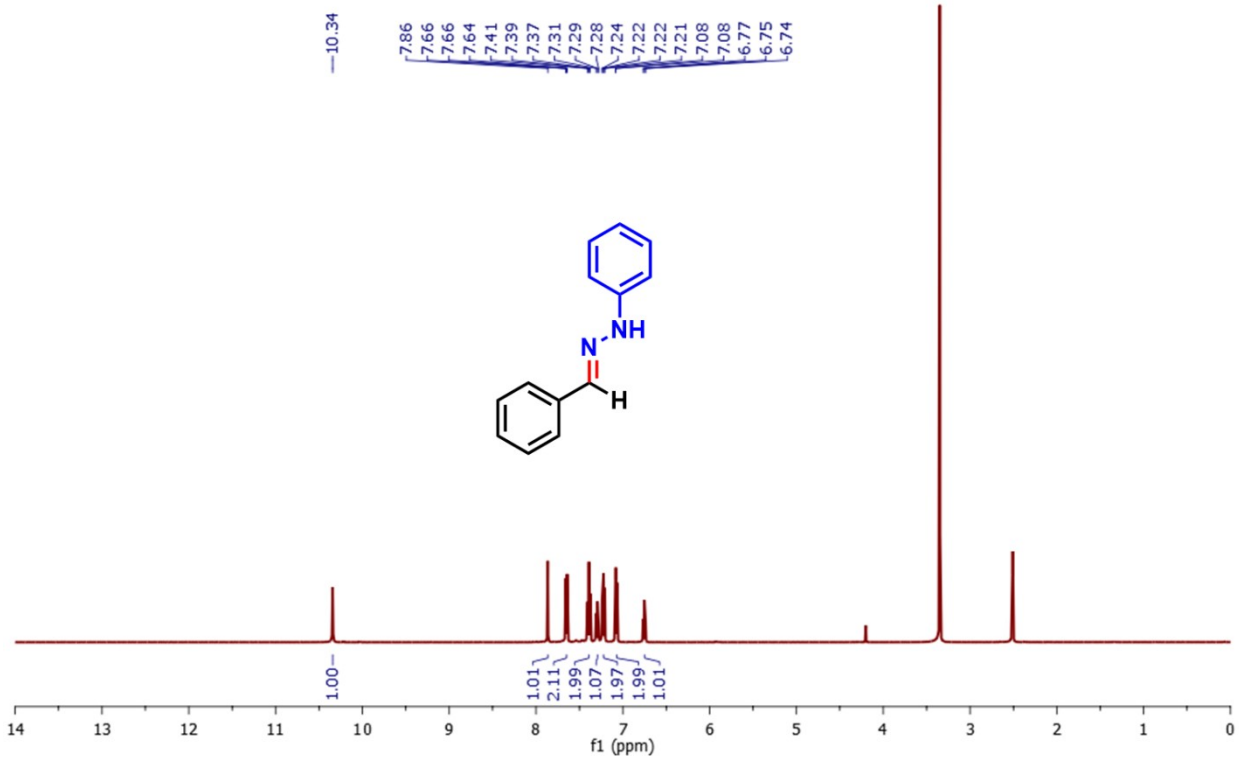


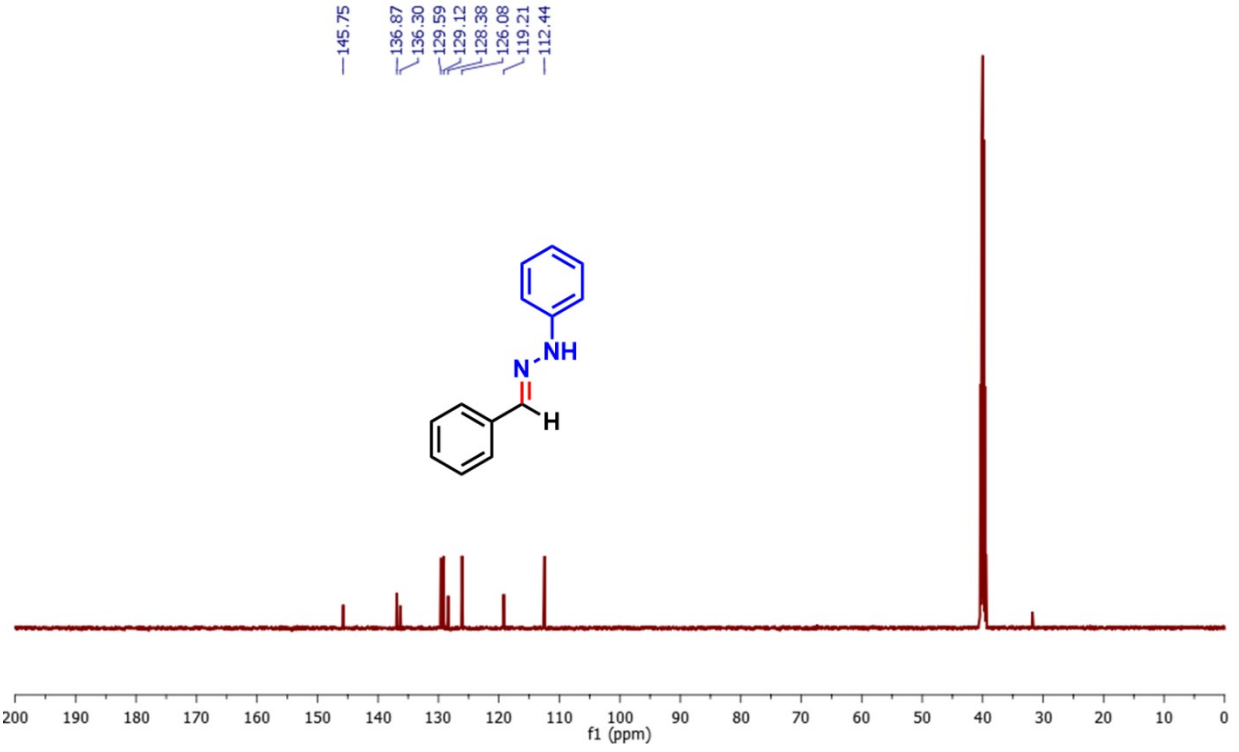


3-(2-(benzo[d]thiazol-2-yl)hydrazineylidene)indolin-2-one (5p)

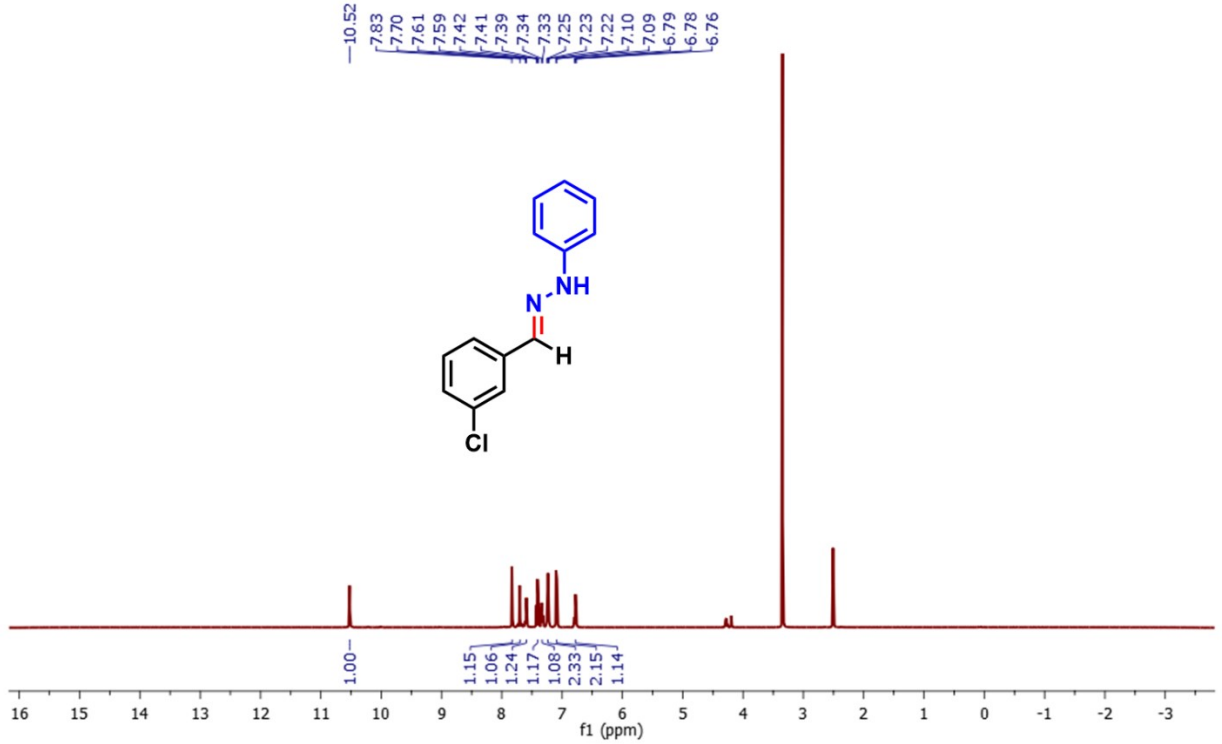


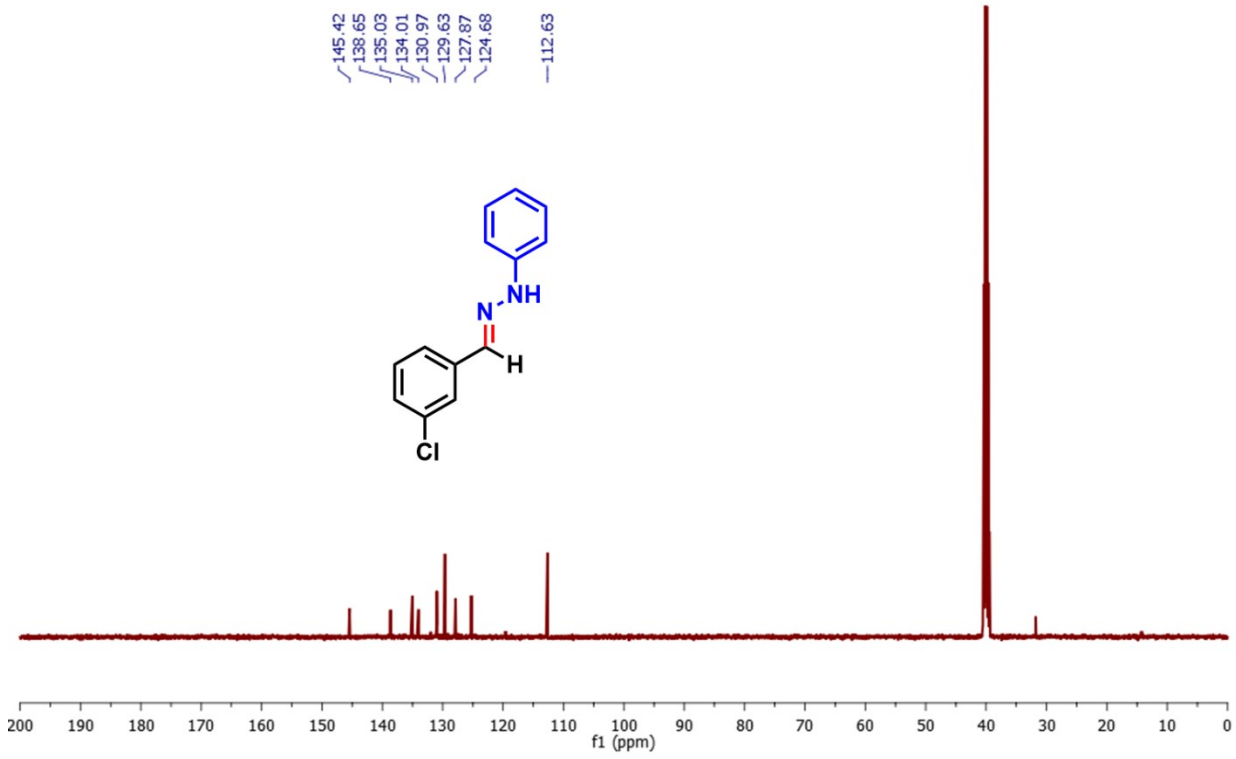
1-benzylidene-2-phenylhydrazine (6a)



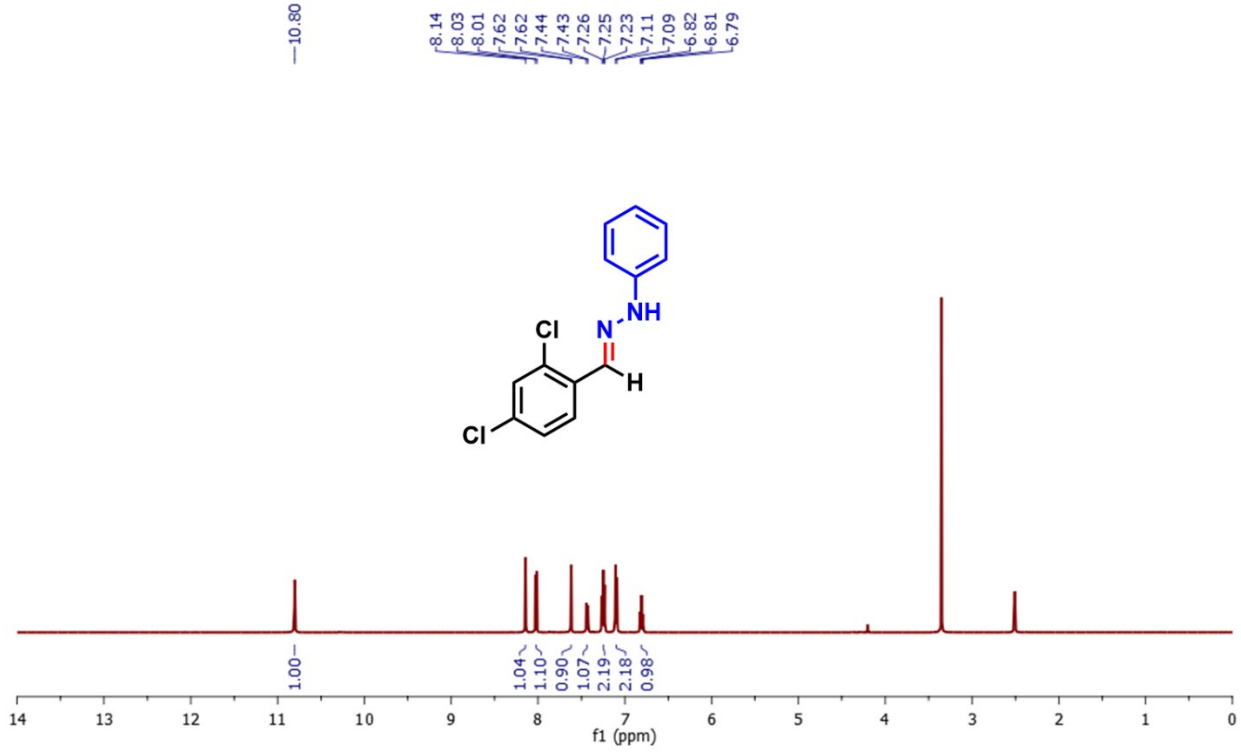


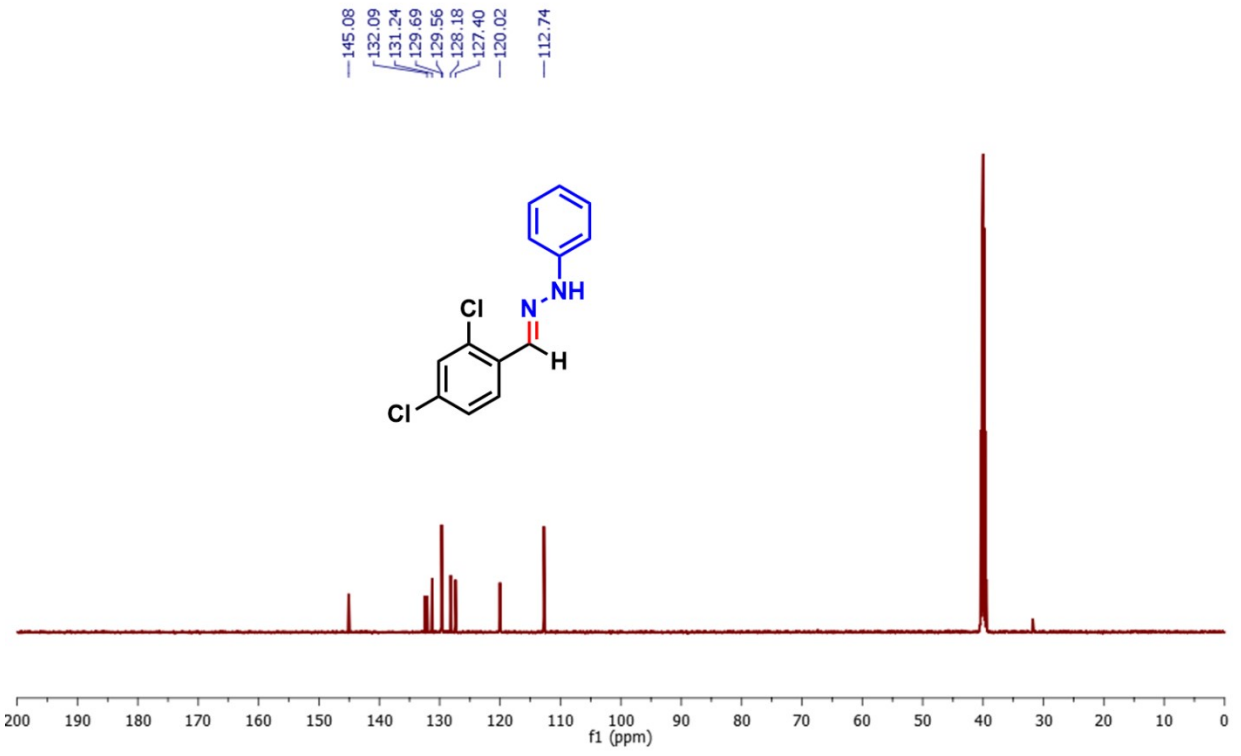
1-(3-chlorobenzylidene)-2-phenylhydrazine (6b)



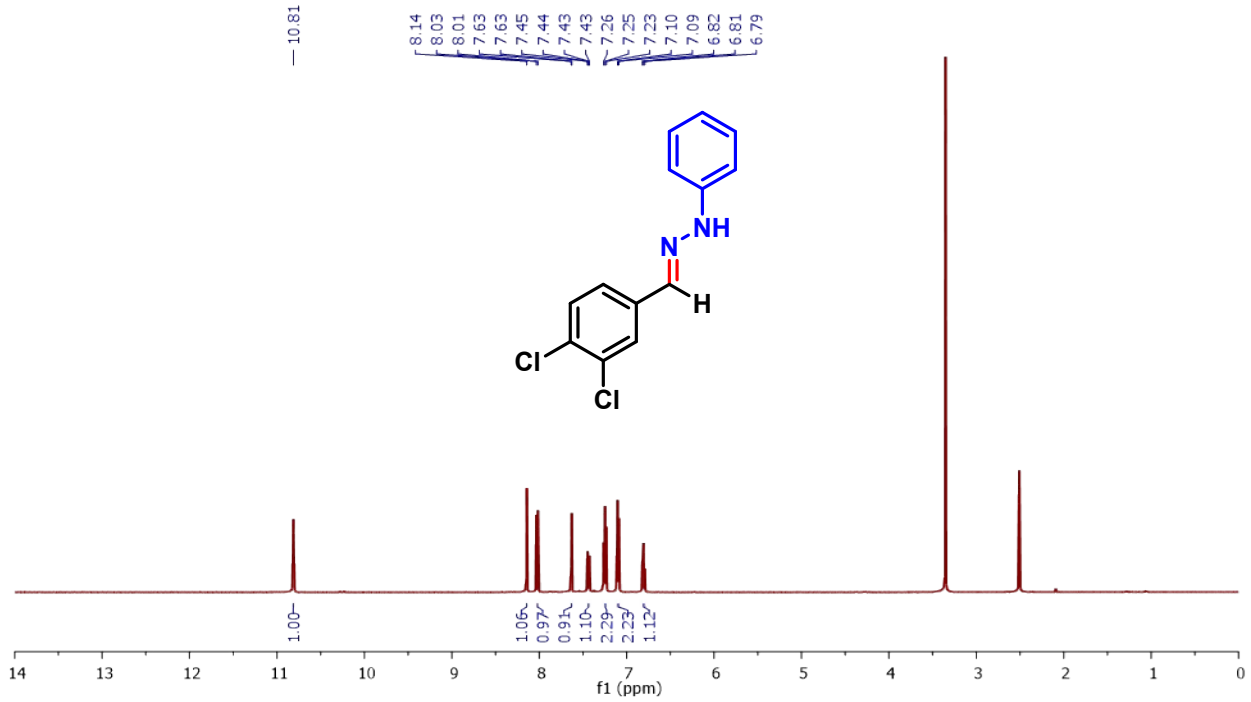


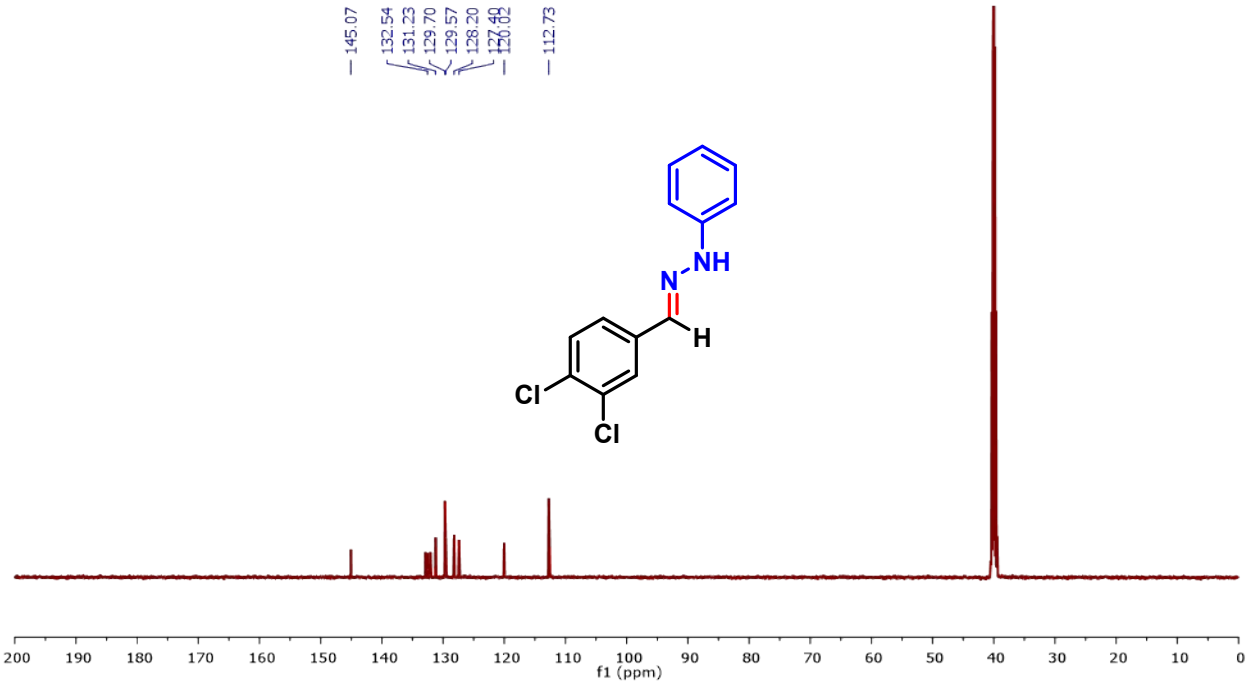
1-(2,4-dichlorobenzylidene)-2-phenylhydrazine (6c)



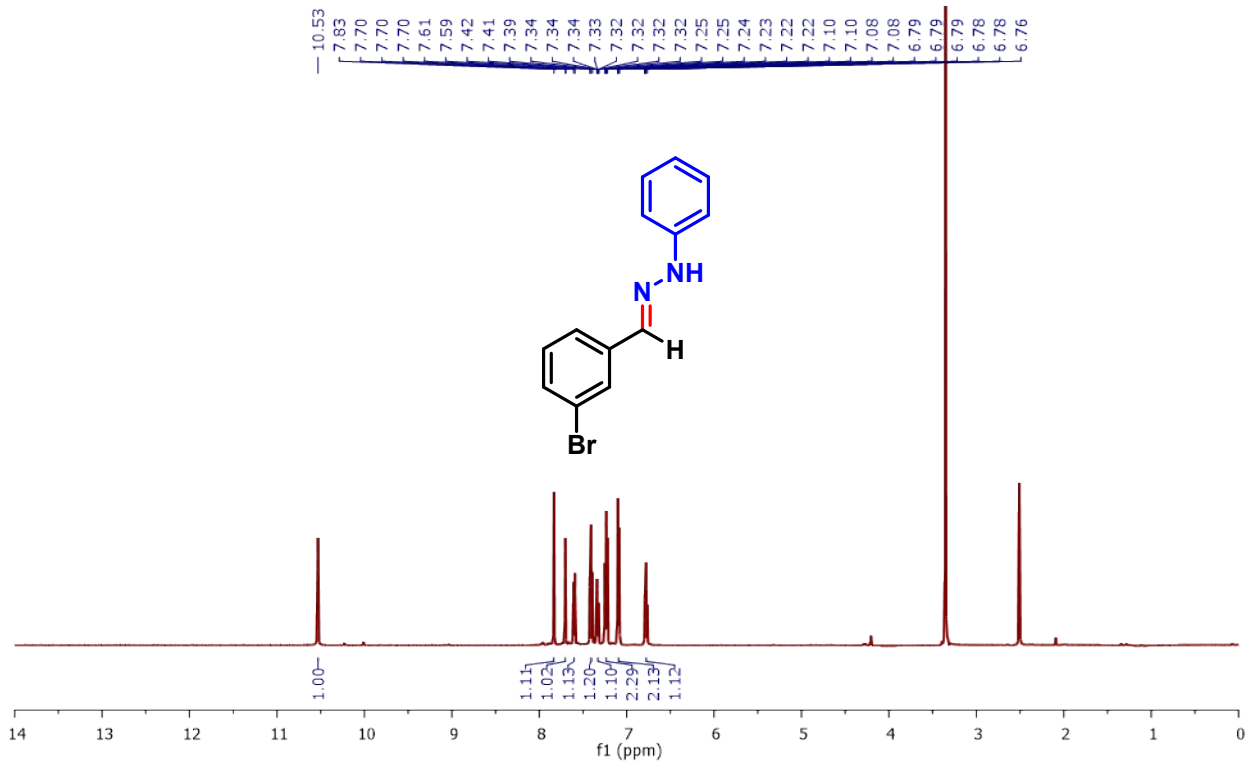


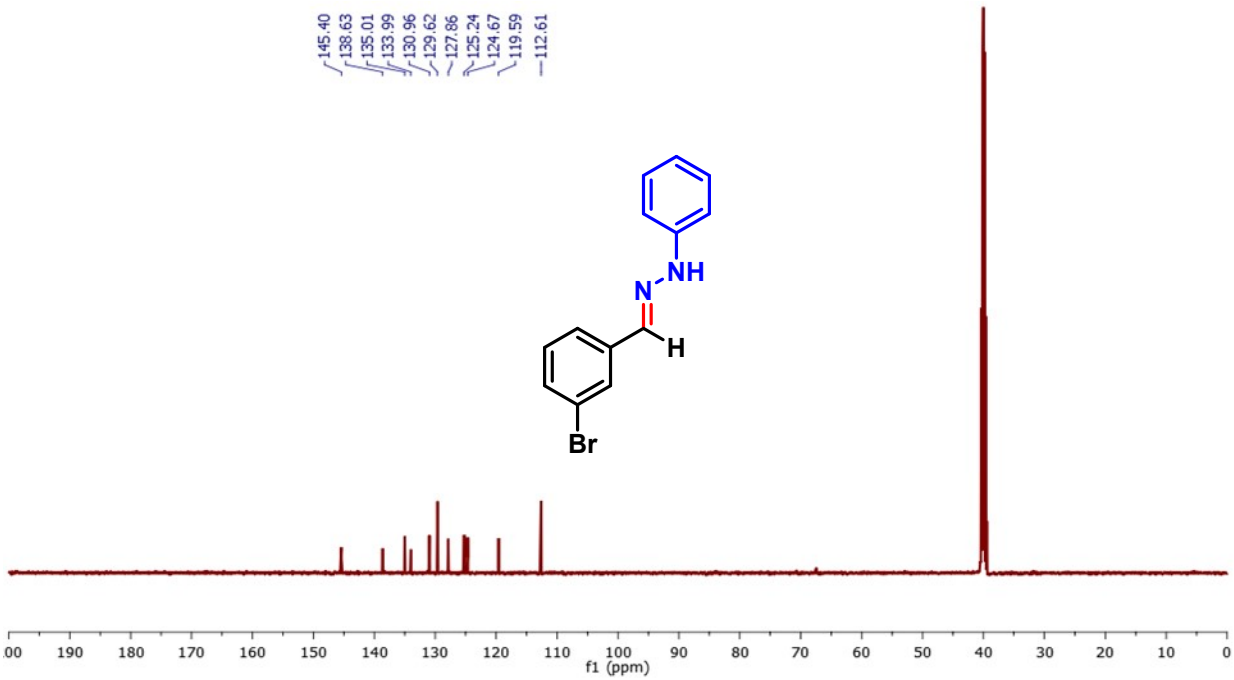
1-(3,4-dichlorobenzylidene)-2-phenylhydrazine (6d)



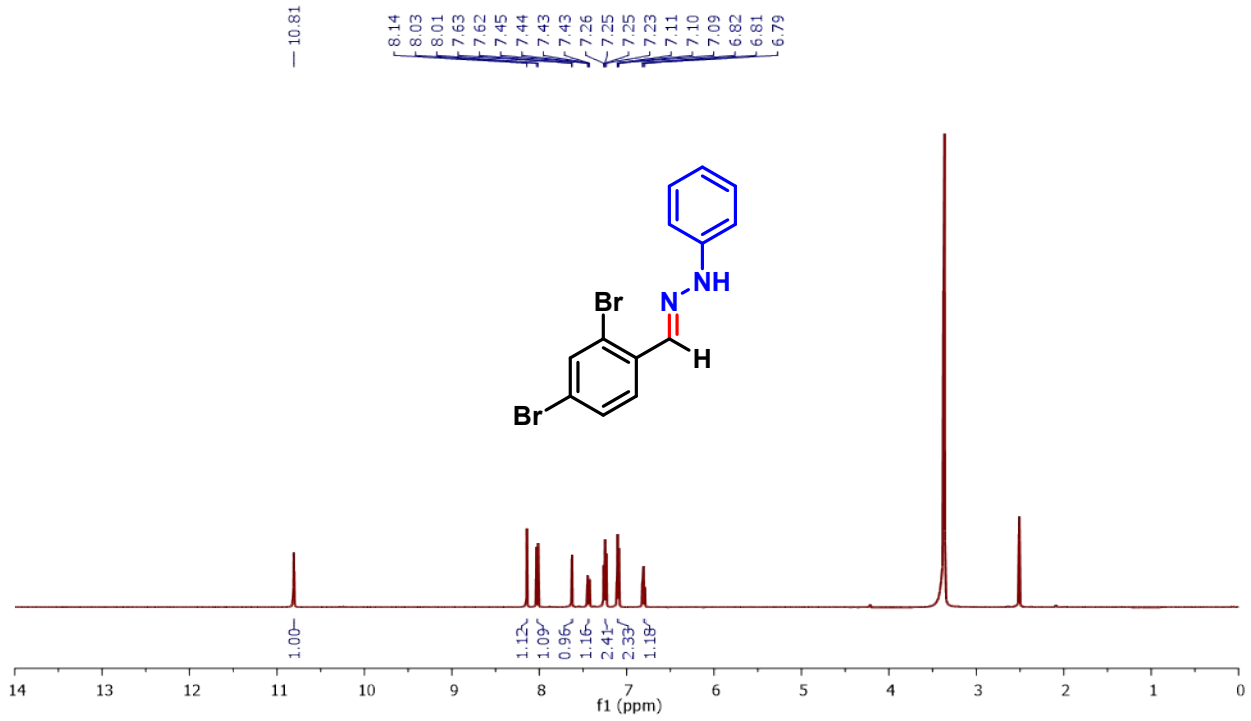


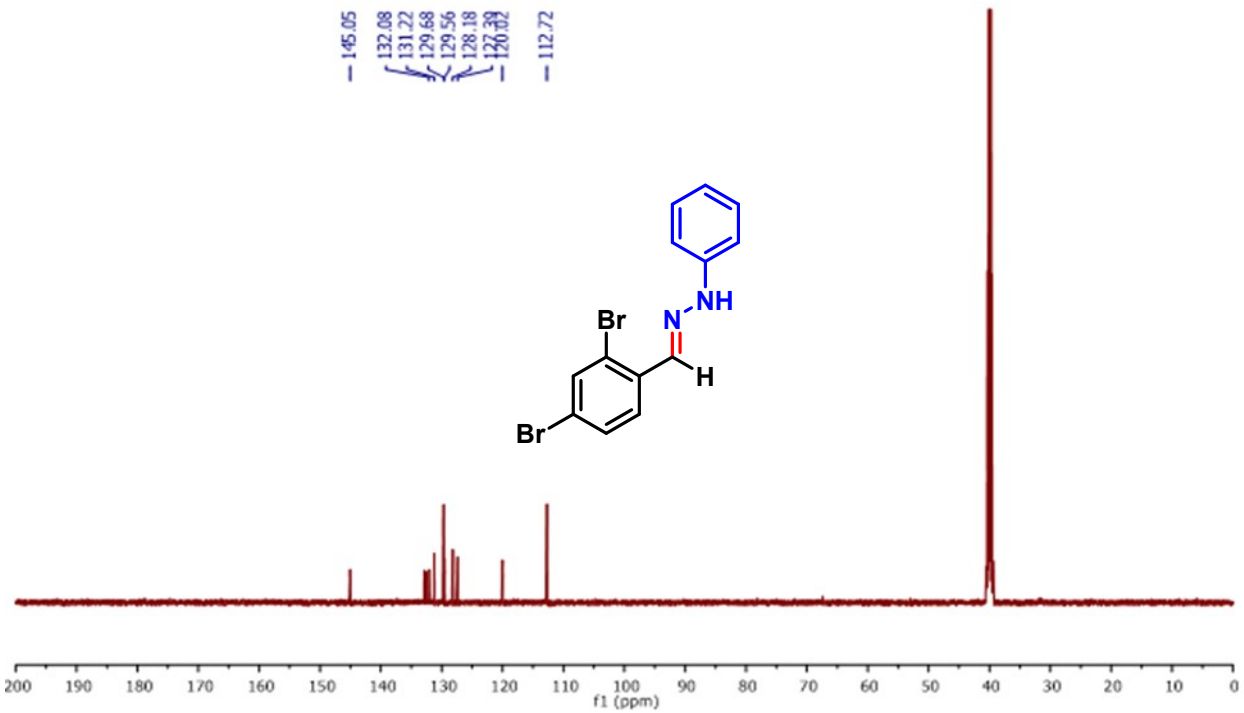
1-(3-bromobenzylidene)-2-phenylhydrazine (6e)



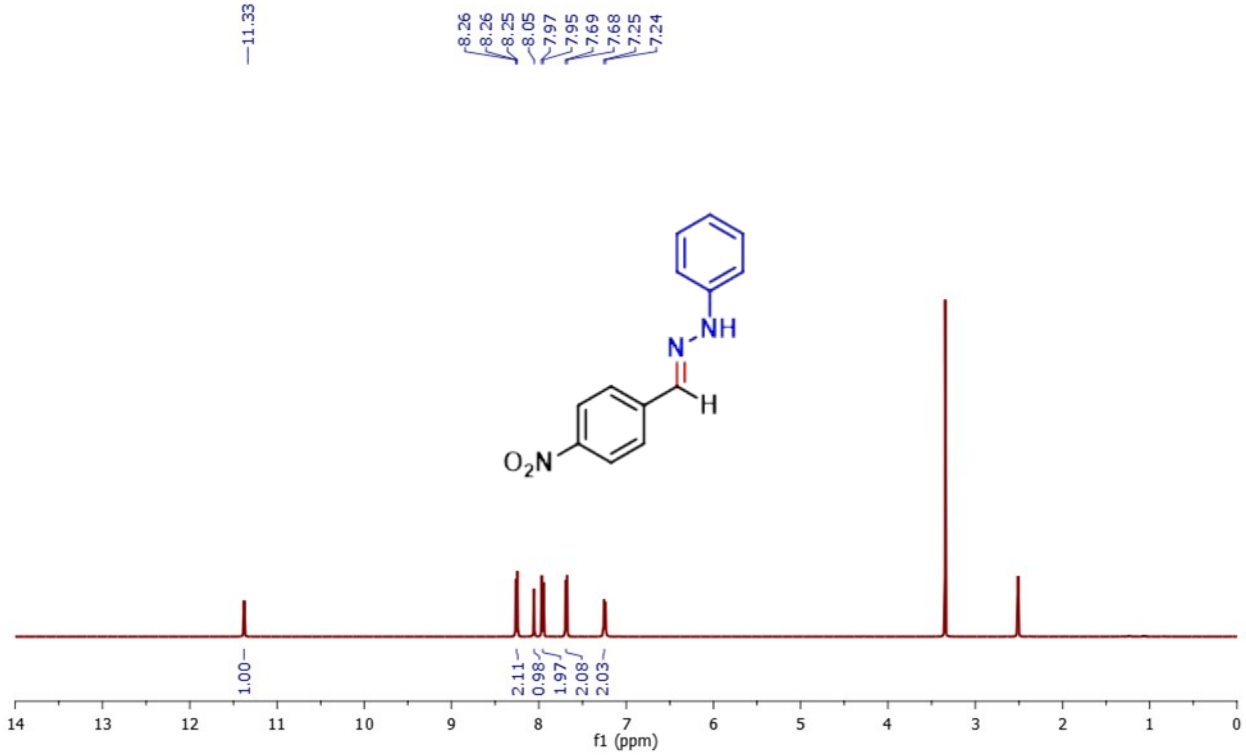


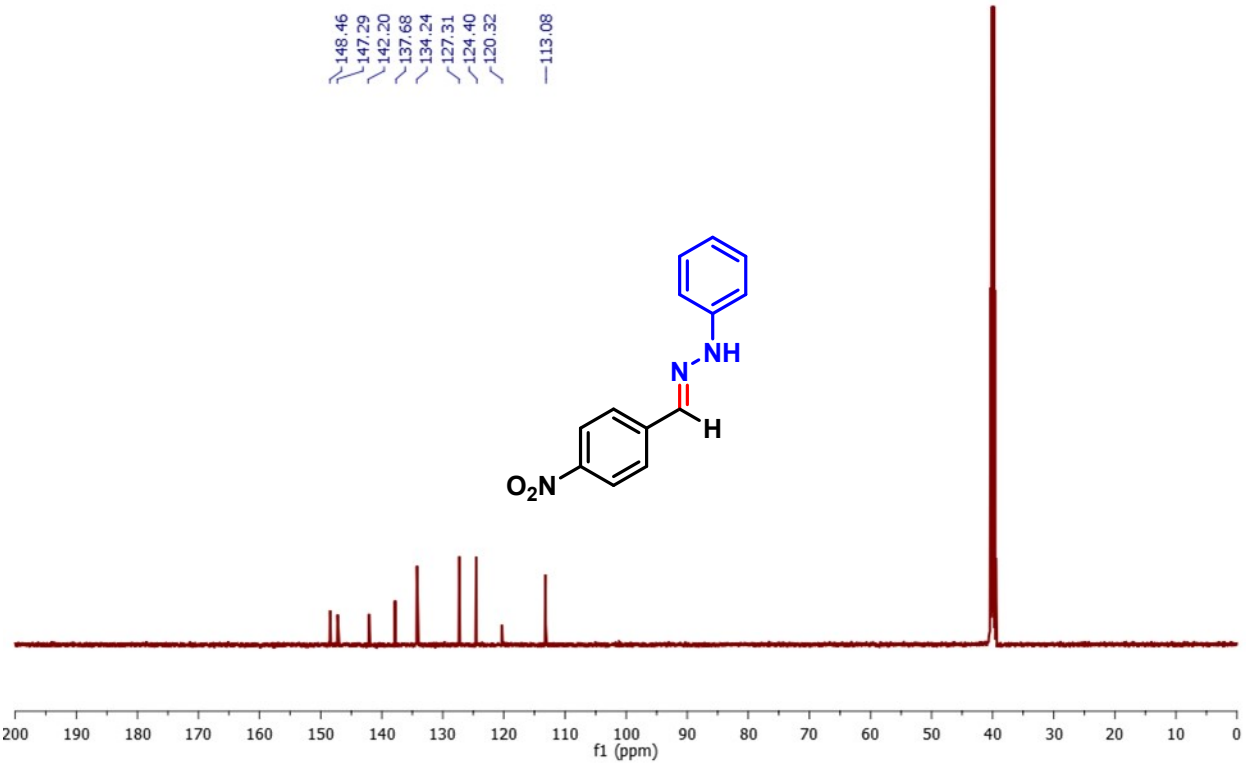
1-(2,4-dibromobenzylidene)-2-phenylhydrazine (6f)



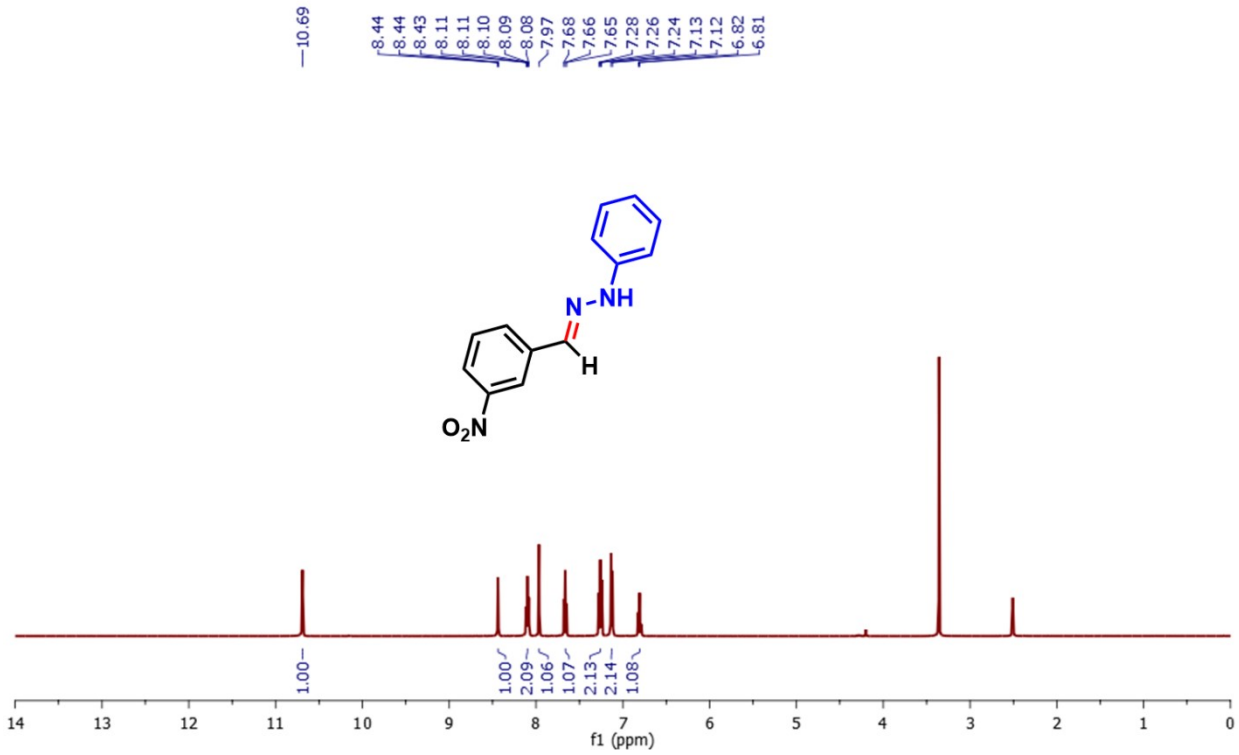


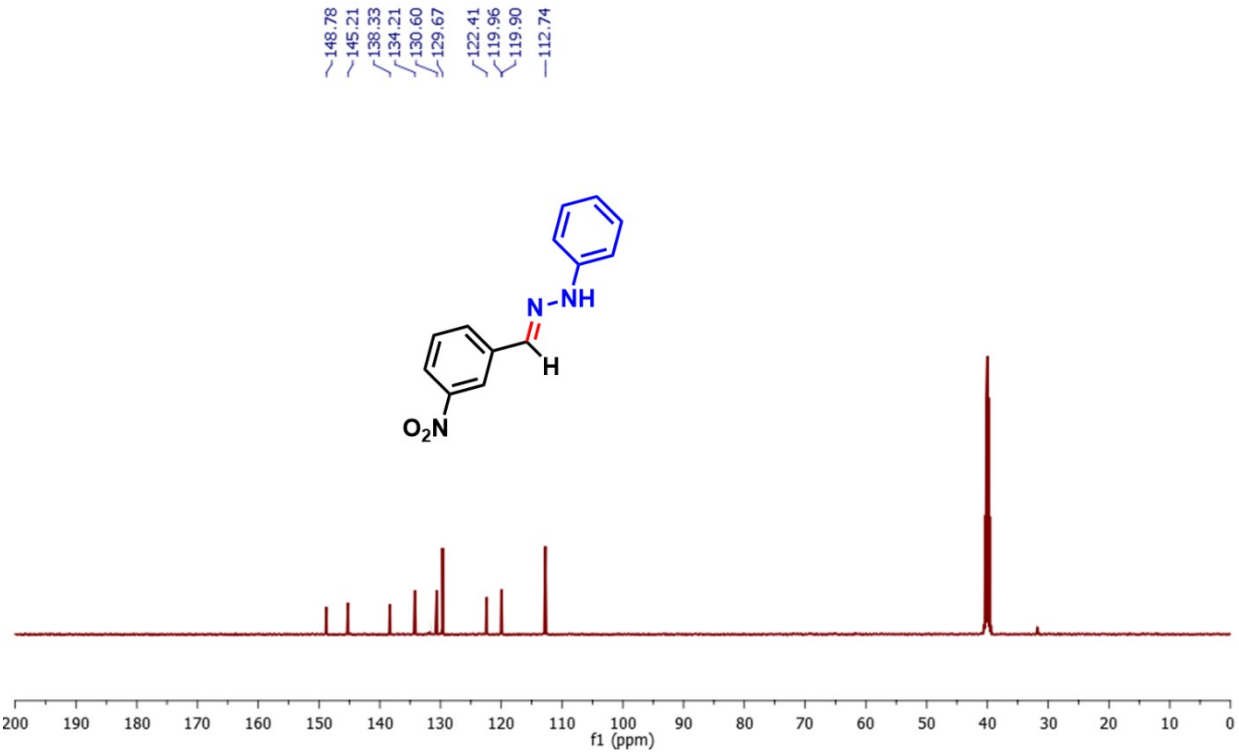
1-(4-nitrobenzylidene)-2-phenylhydrazine (6g)



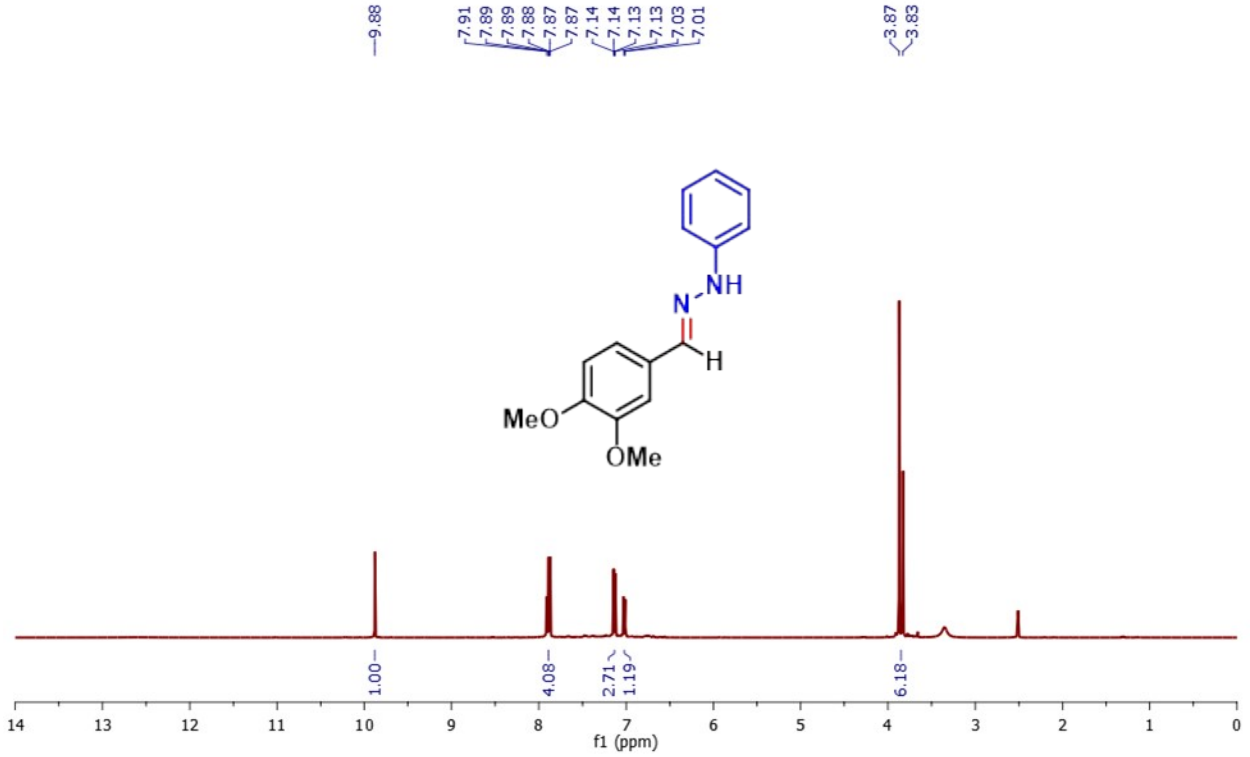


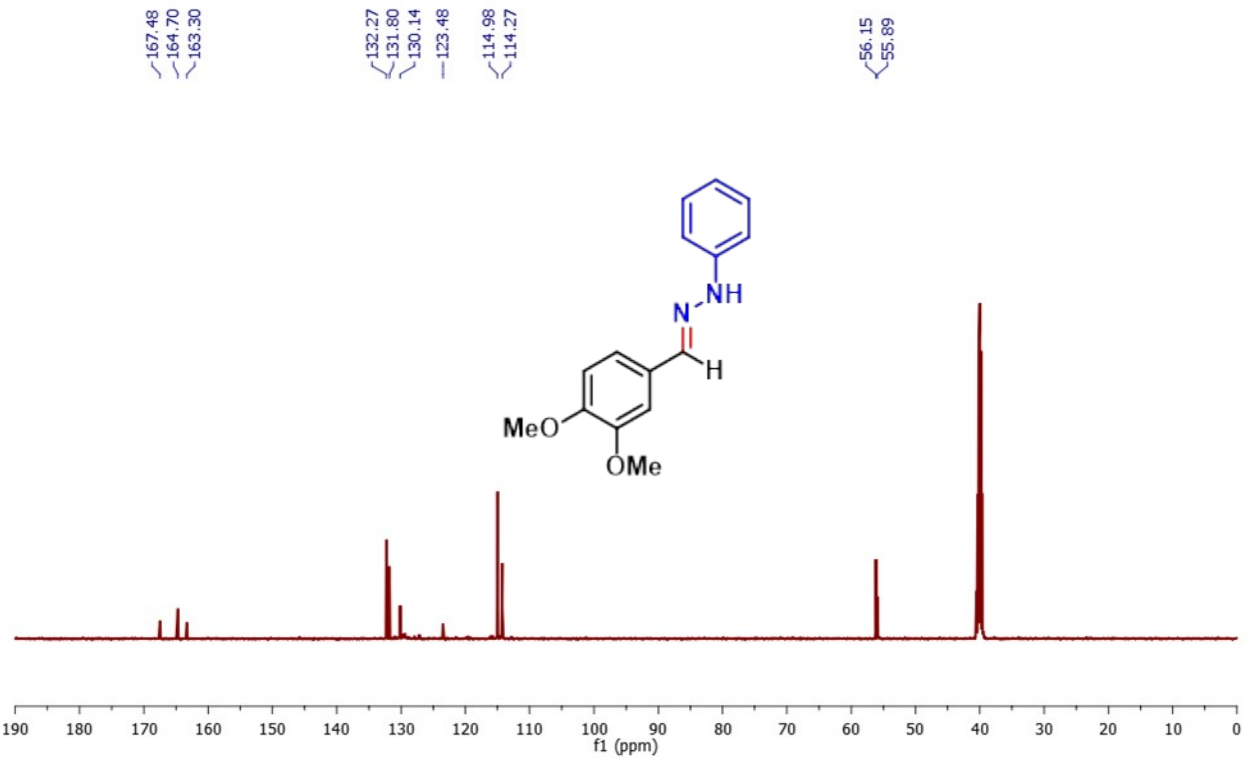
1-(3-nitrobenzylidene)-2-phenylhydrazine (6h)



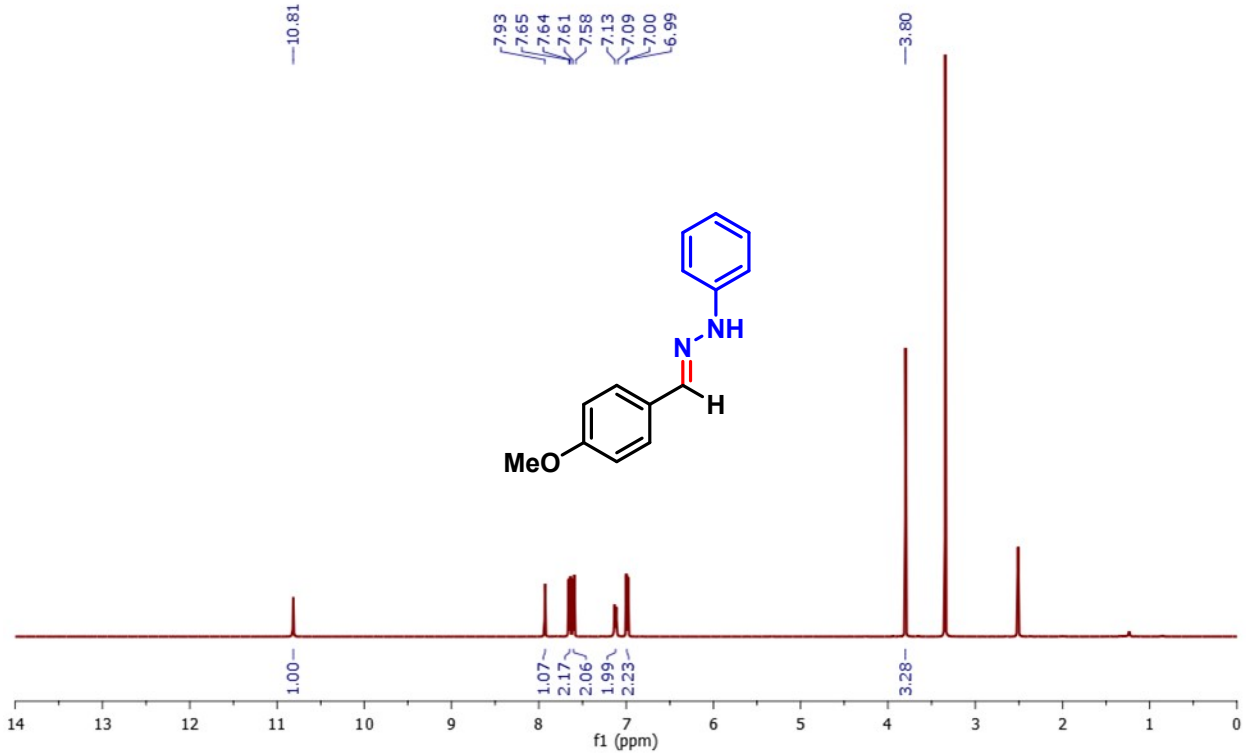


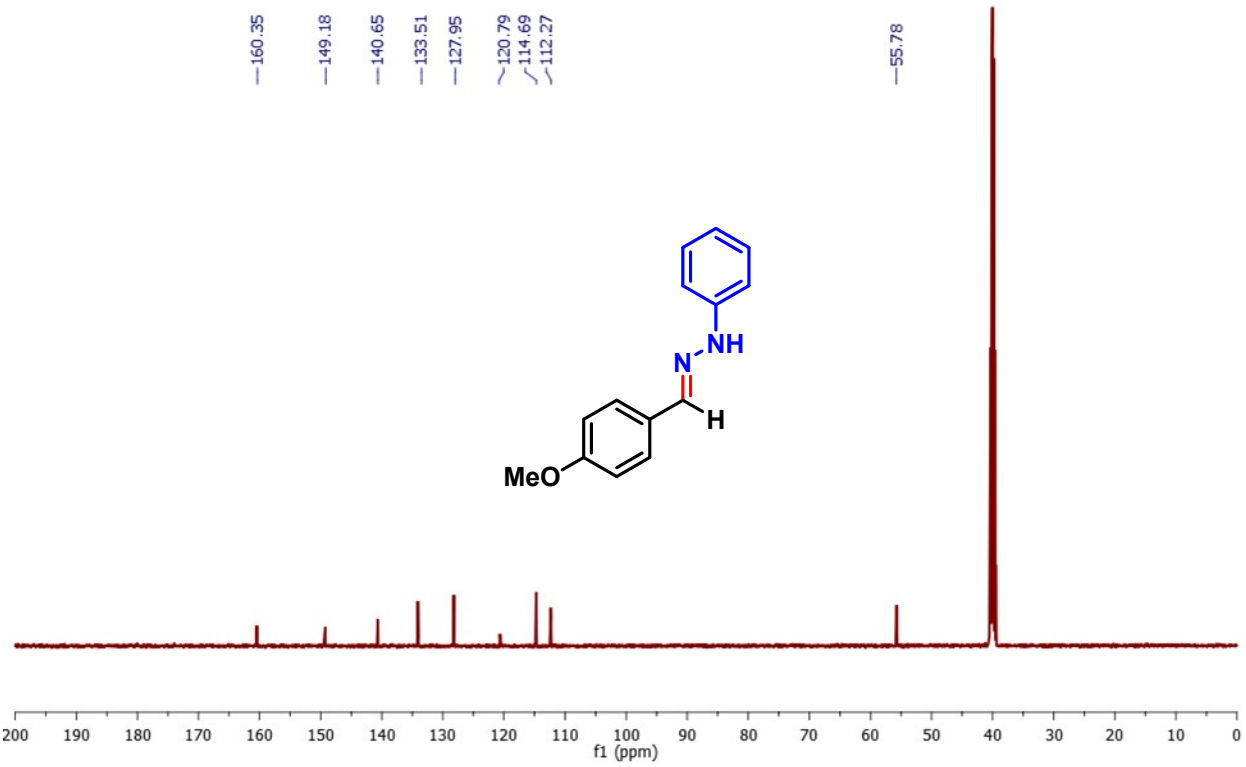
1-(3,4-dimethoxybenzylidene)-2-phenylhydrazine (6i)



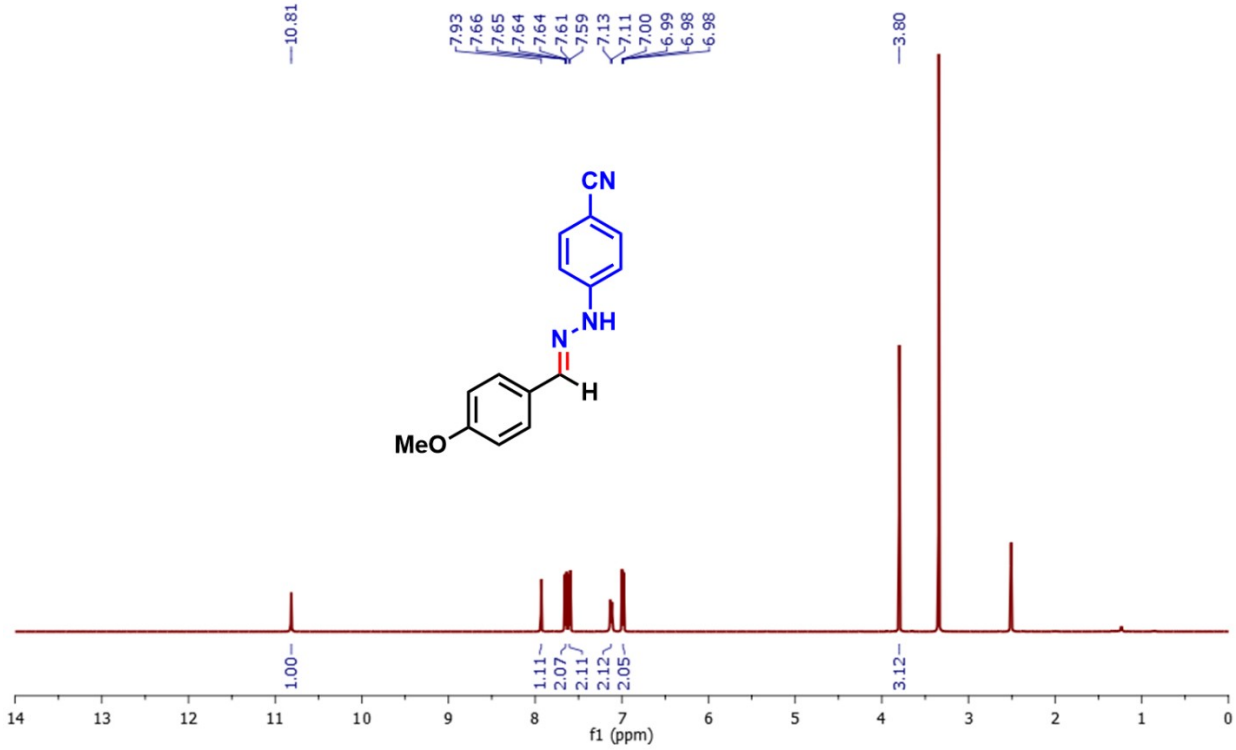


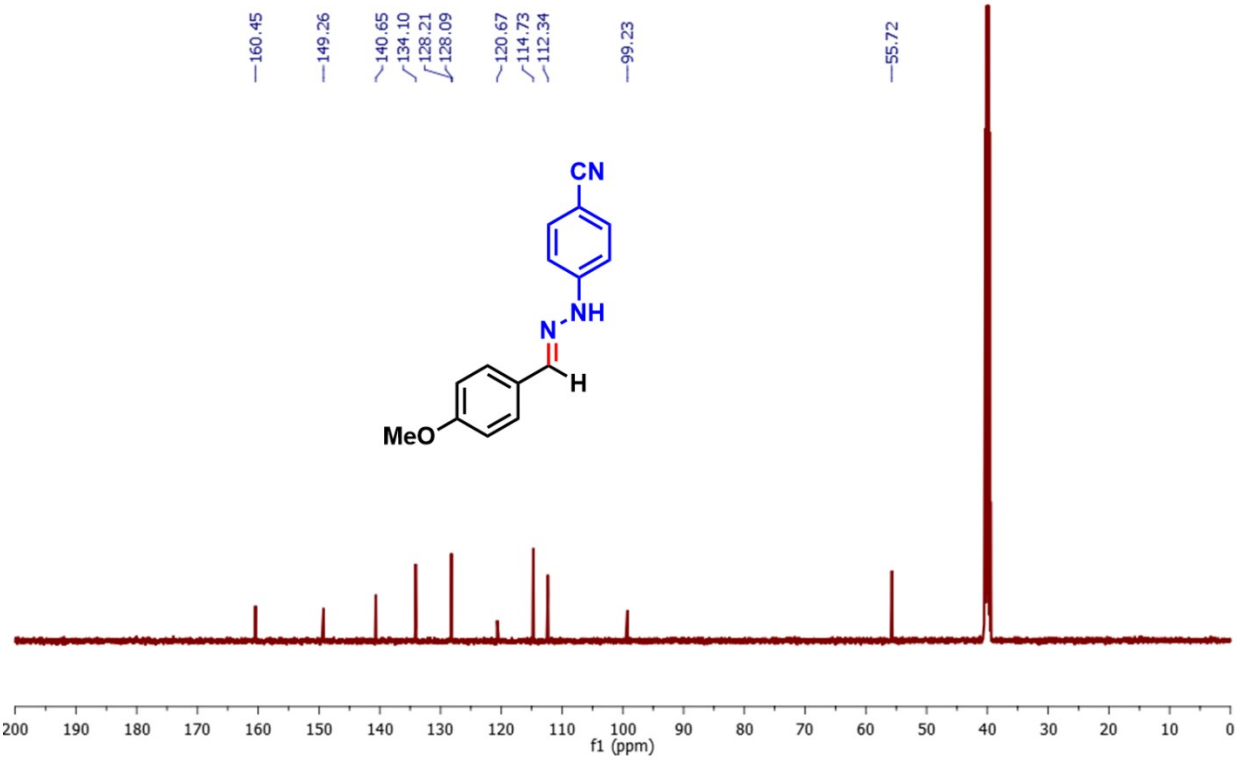
1-(4-methoxybenzylidene)-2-phenylhydrazine (6j)



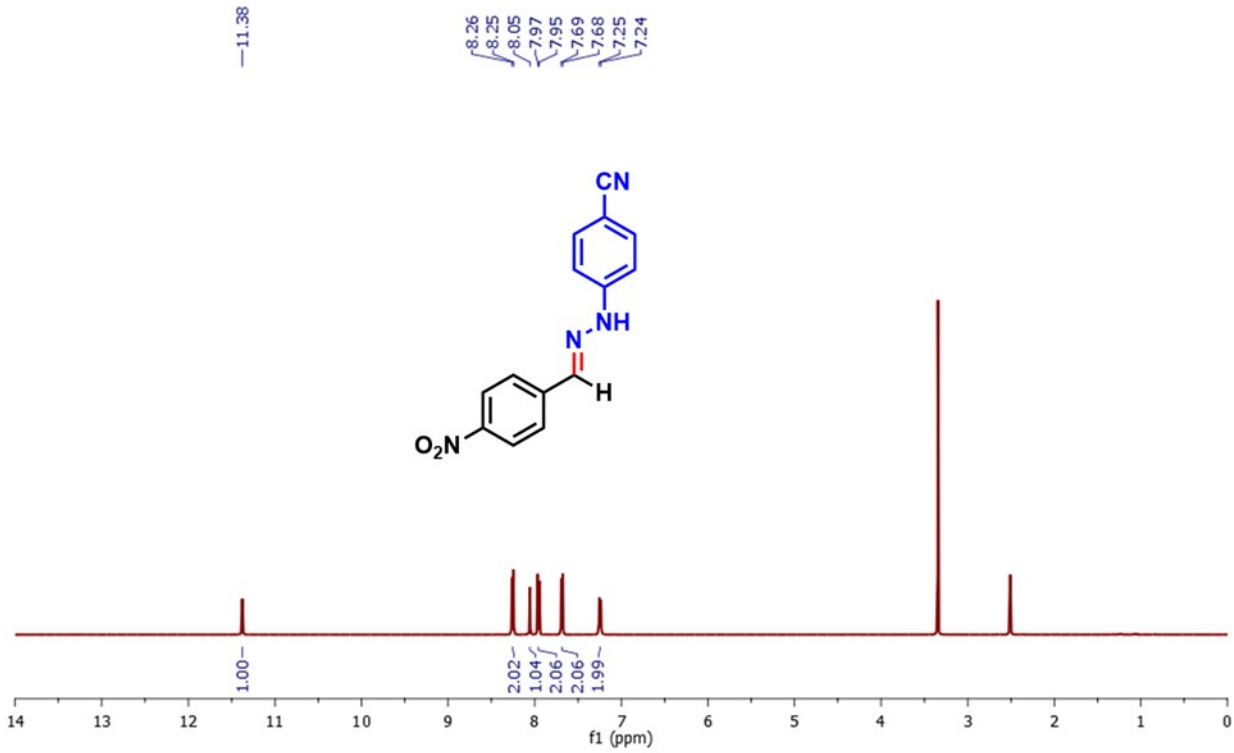


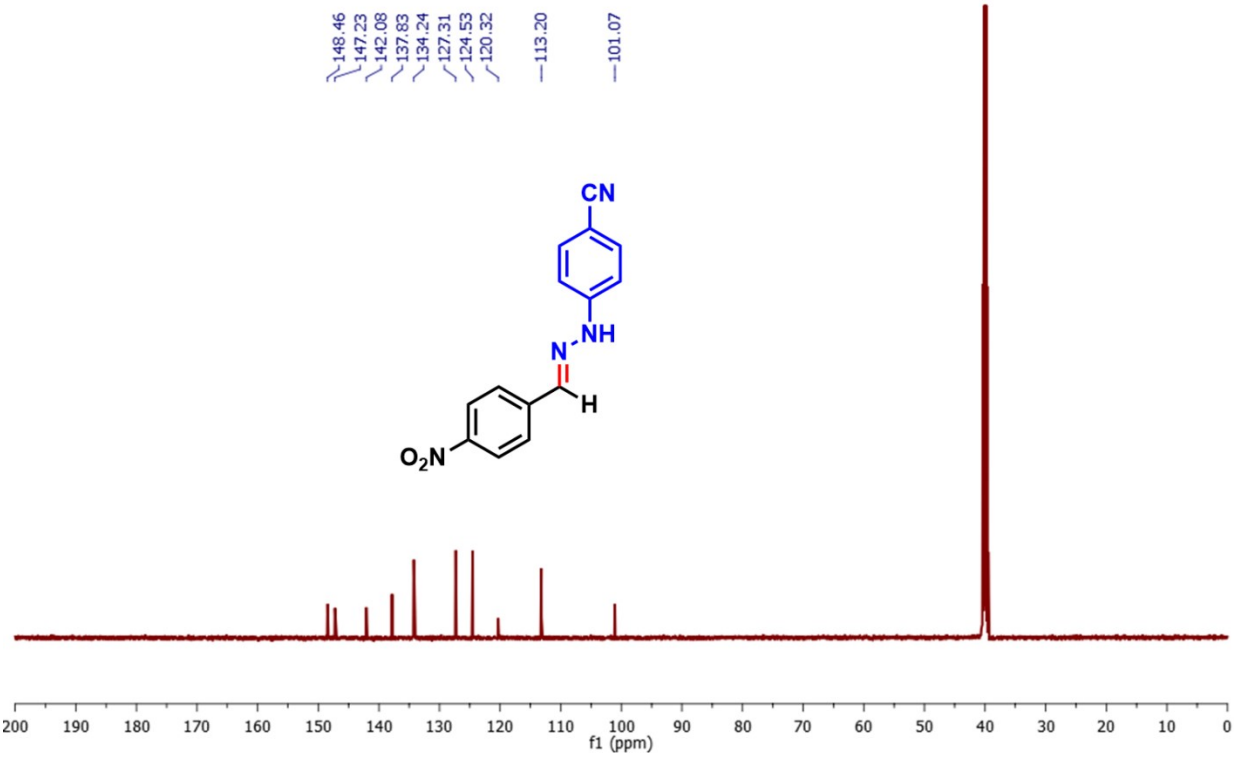
4-(2-(4-methoxybenzylidene)hydrazineyl)benzonitrile (6k)



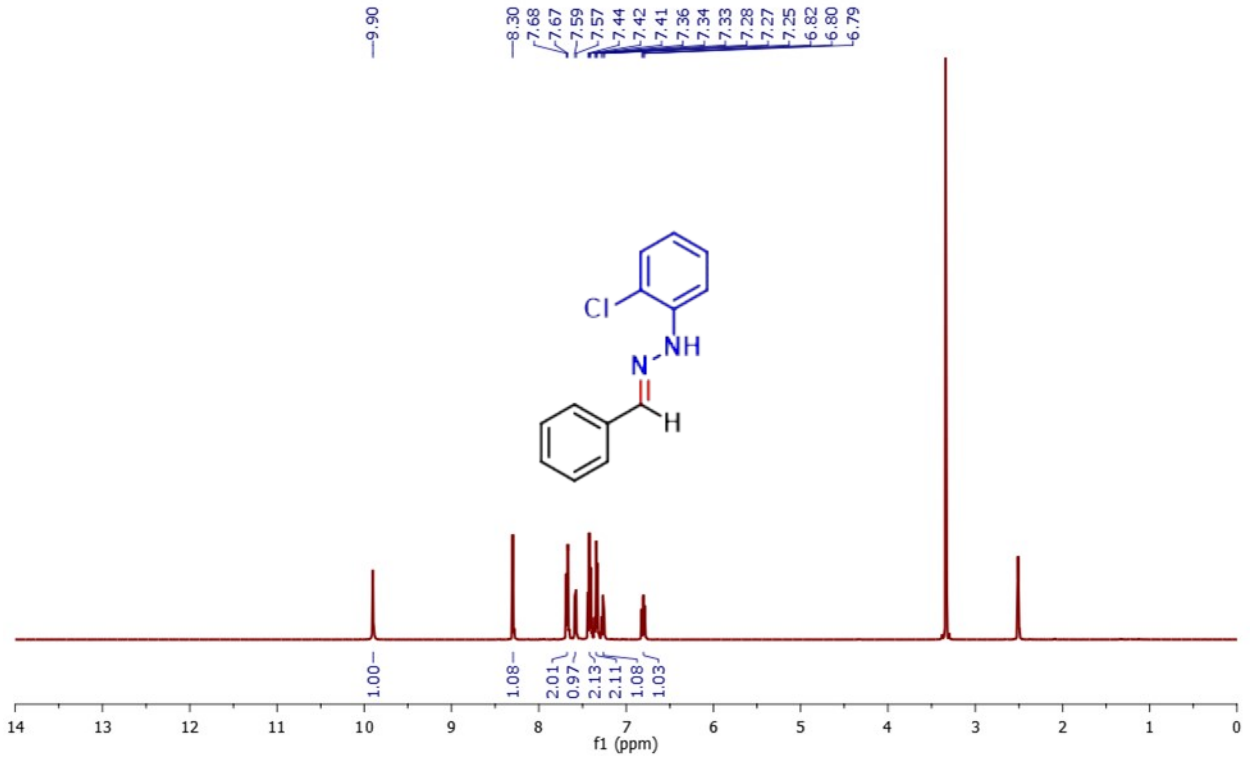


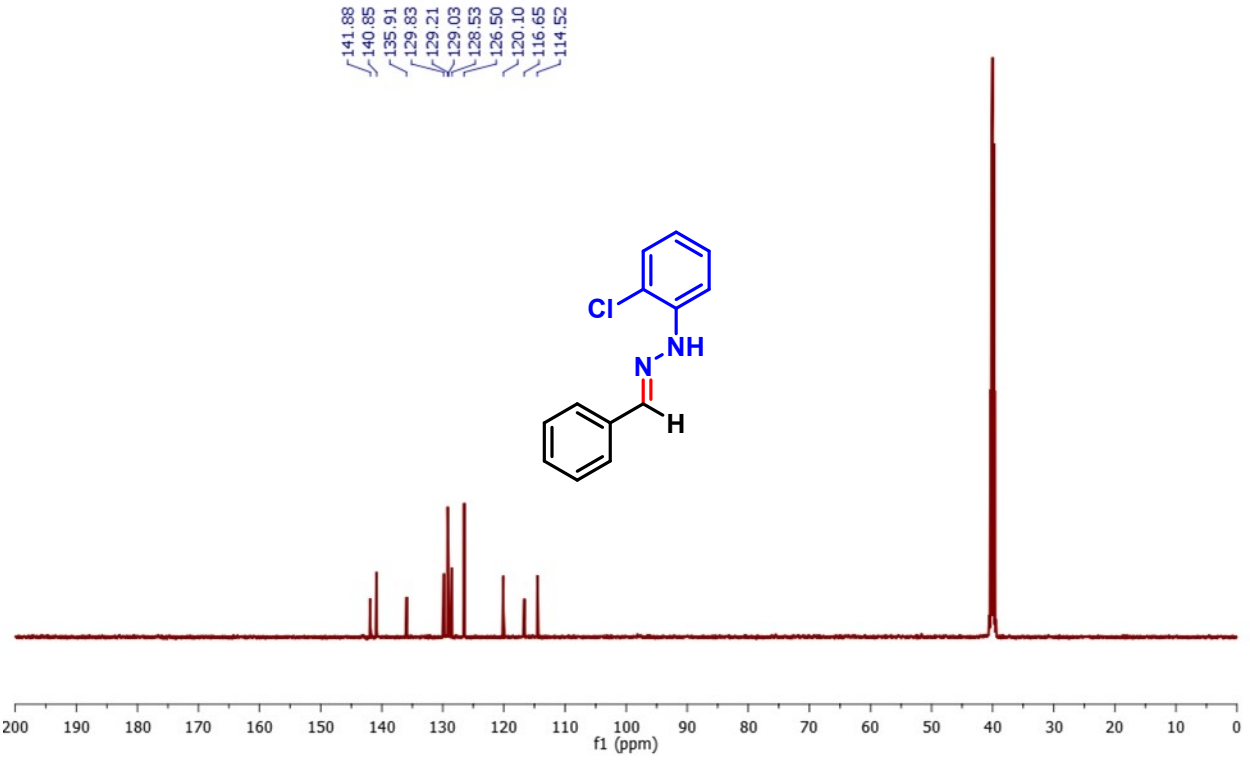
4-(2-(4-nitrobenzylidene)hydrazineyl)benzonitrile (6l)



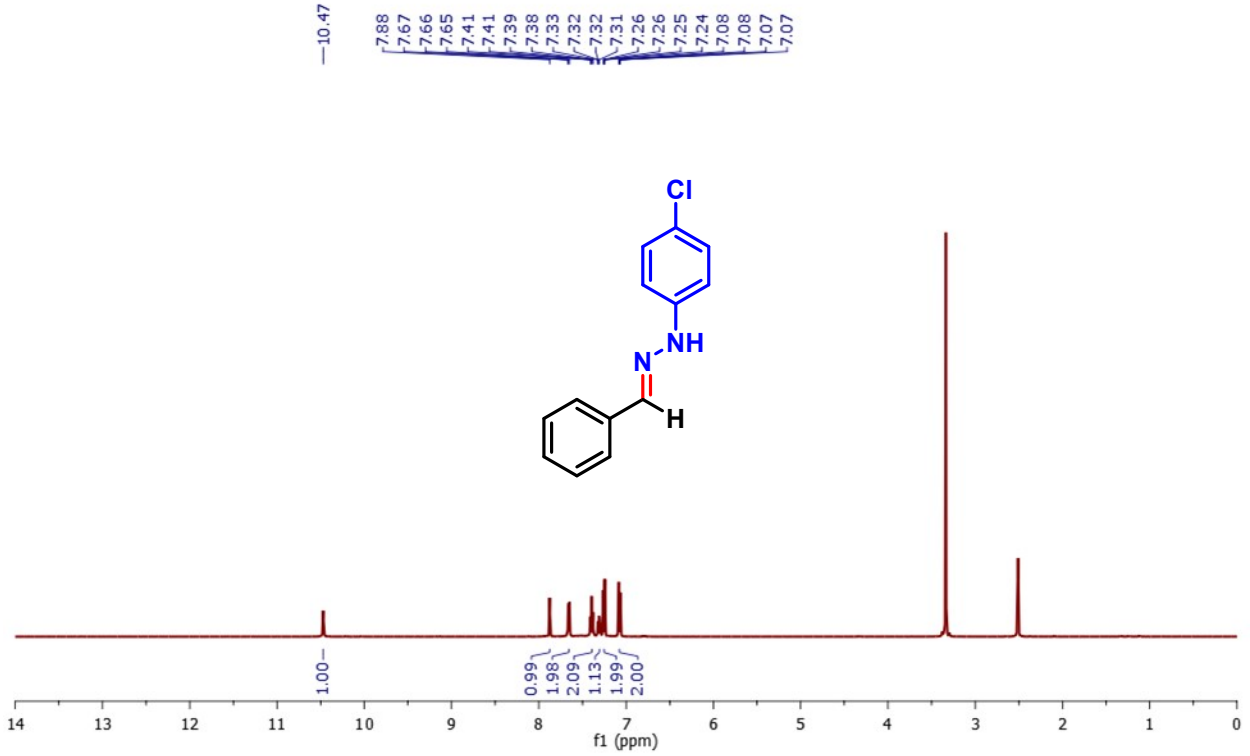


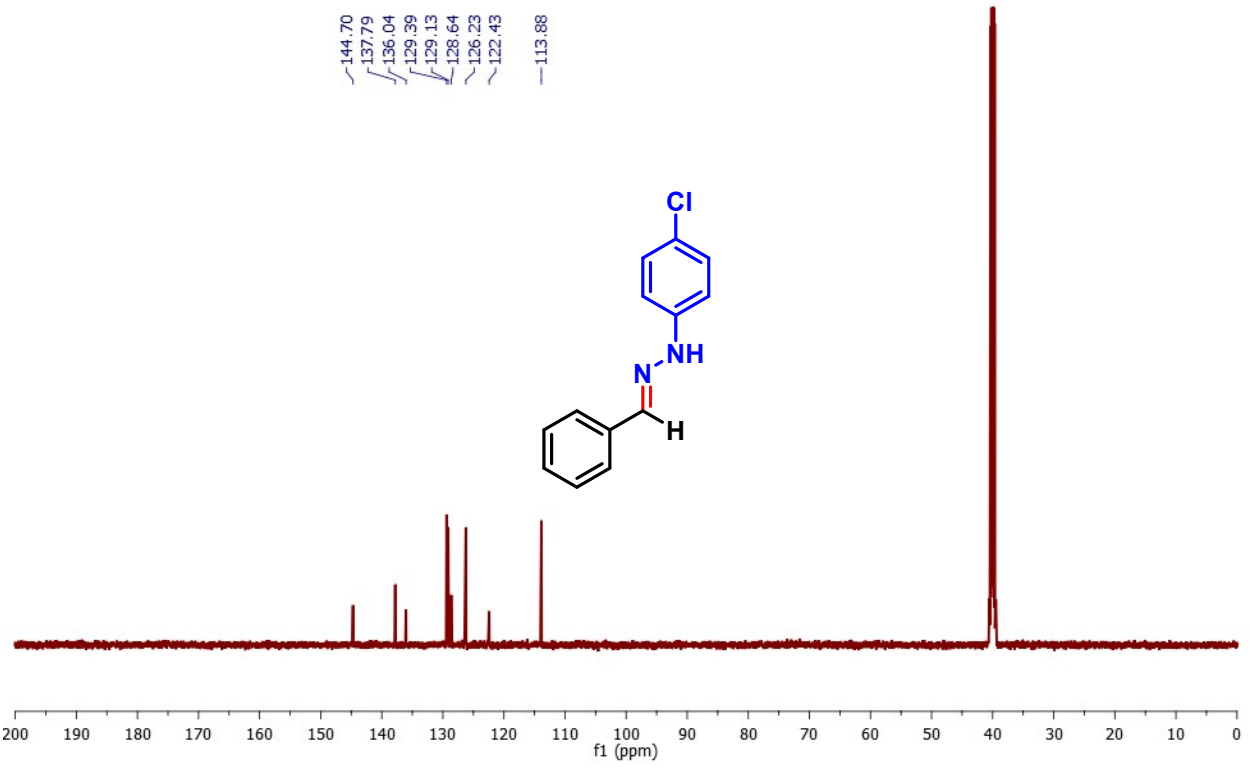
1-benzylidene-2-(2-chlorophenyl)hydrazine (6m)



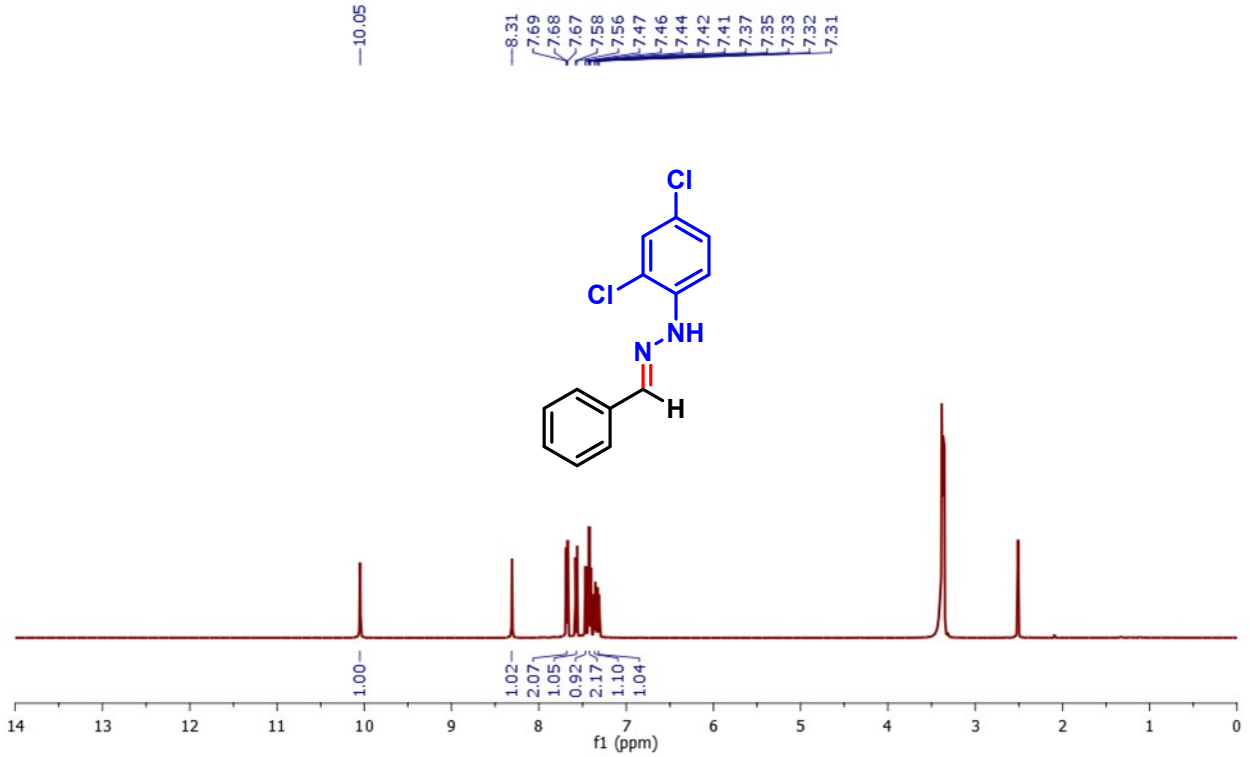


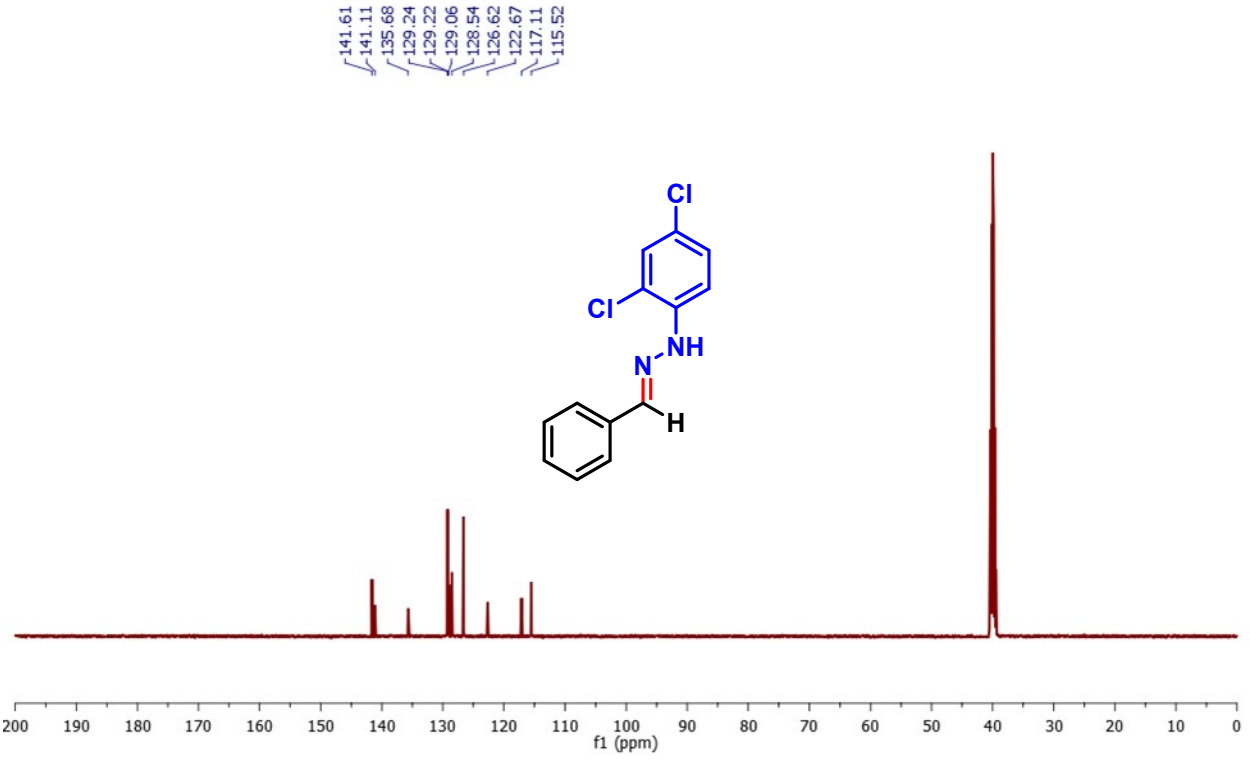
1-benzylidene-2-(4-chlorophenyl)hydrazine (6n)



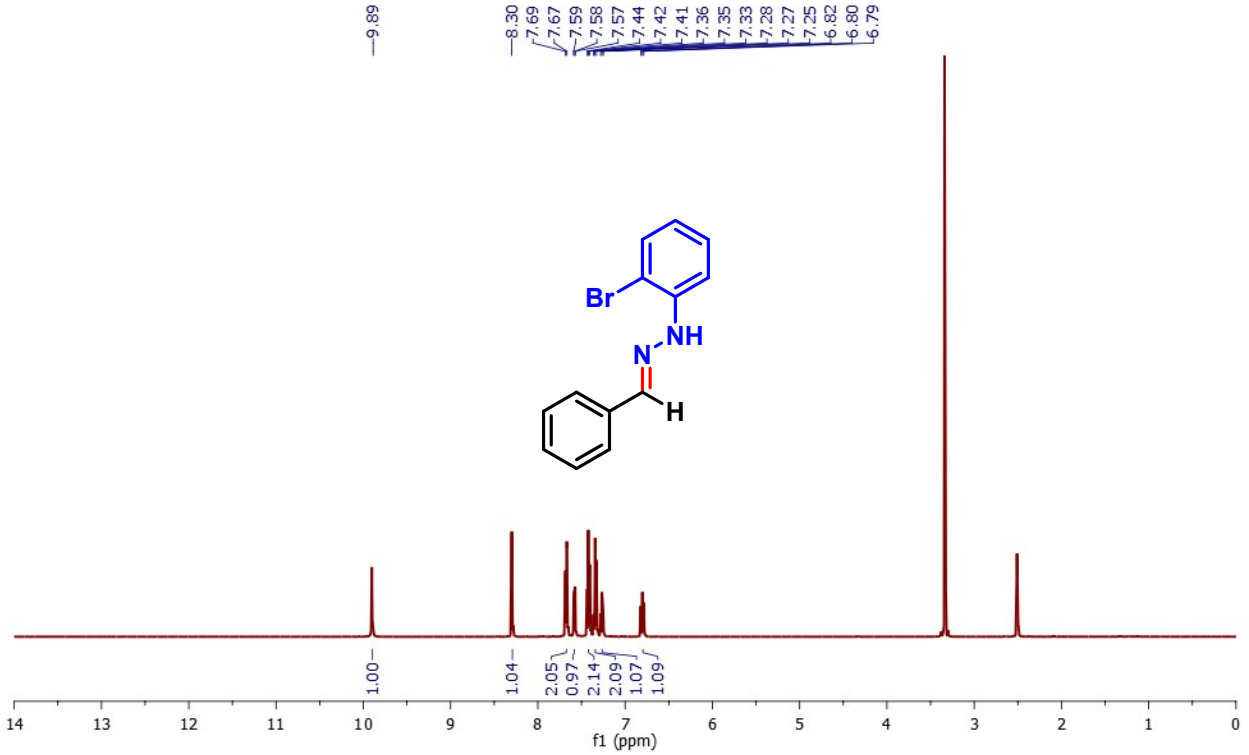


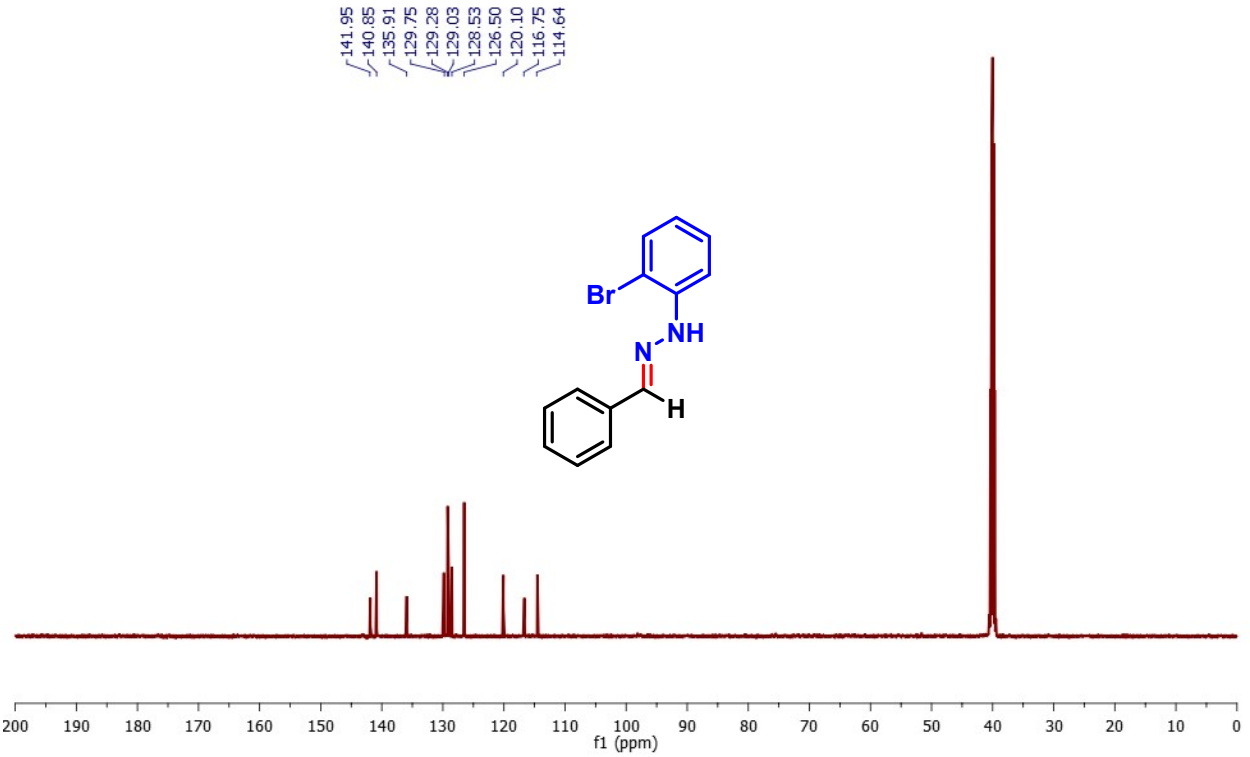
1-benzylidene-2-(2,4-dichlorophenyl)hydrazine (6o)



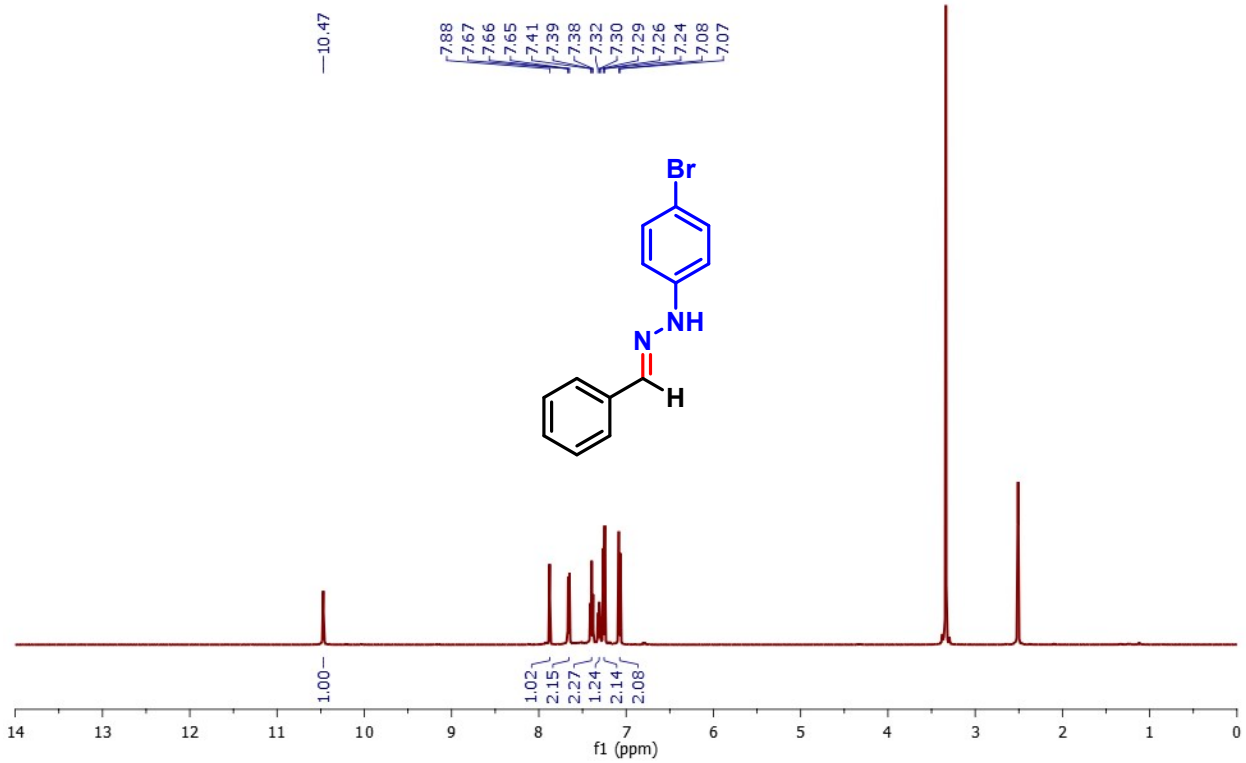


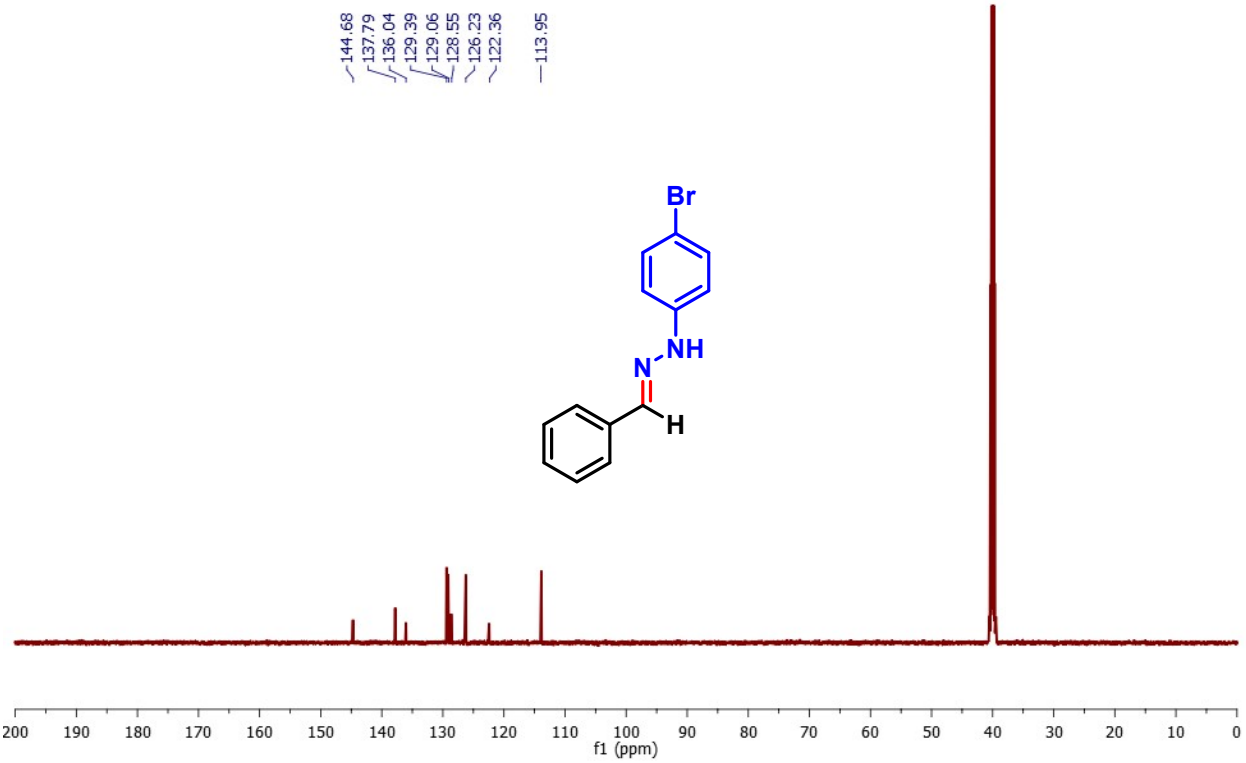
1-benzylidene-2-(2-bromophenyl)hydrazine (6p)



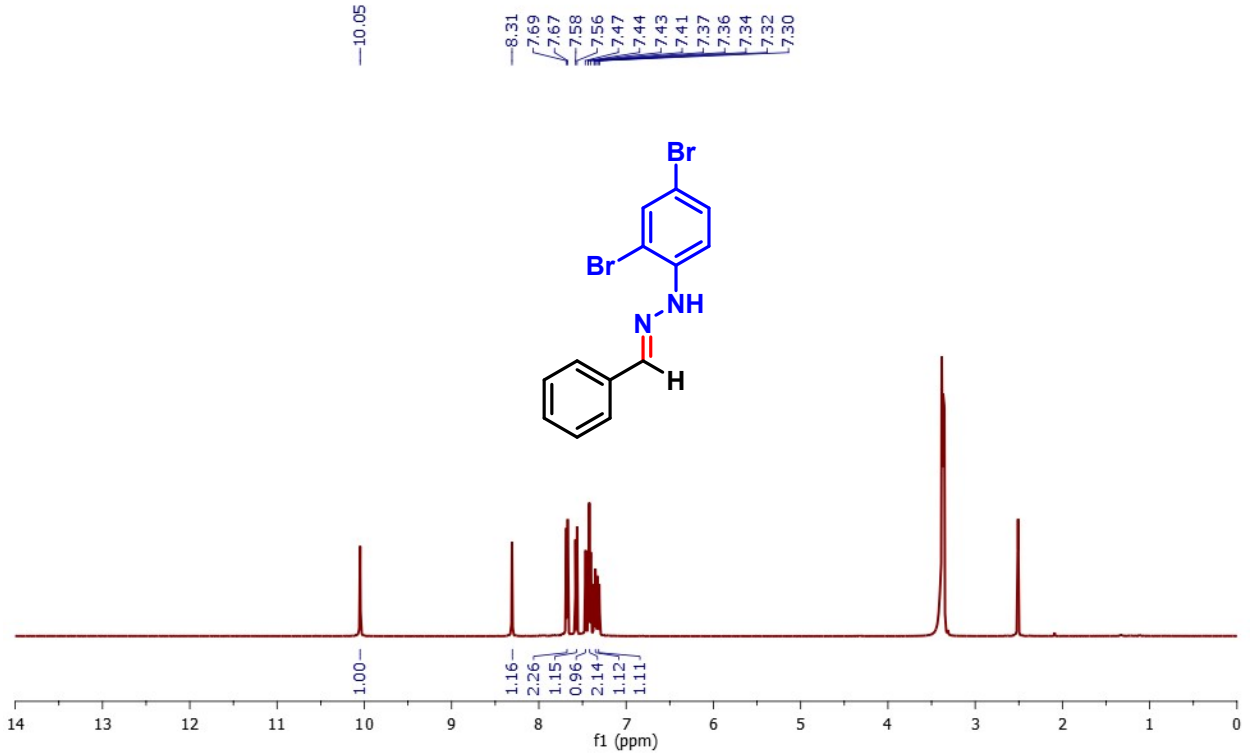


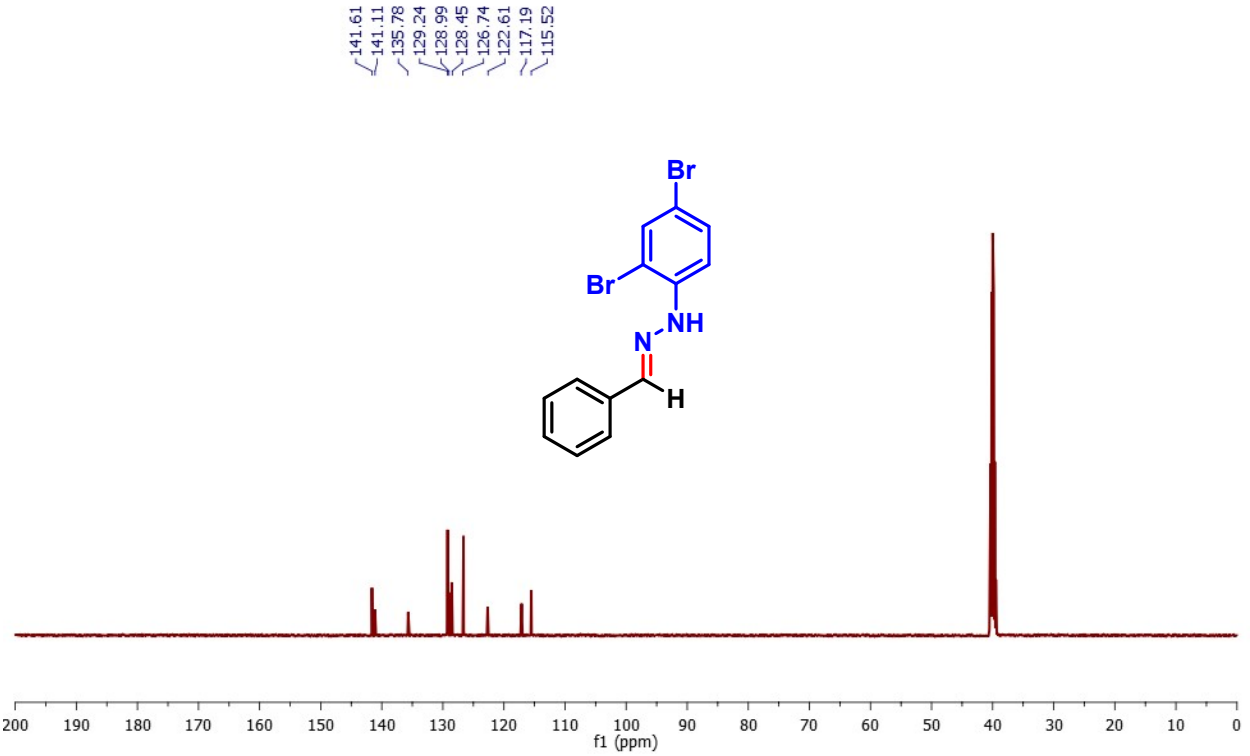
1-benzylidene-2-(4-bromophenyl)hydrazine (6q)



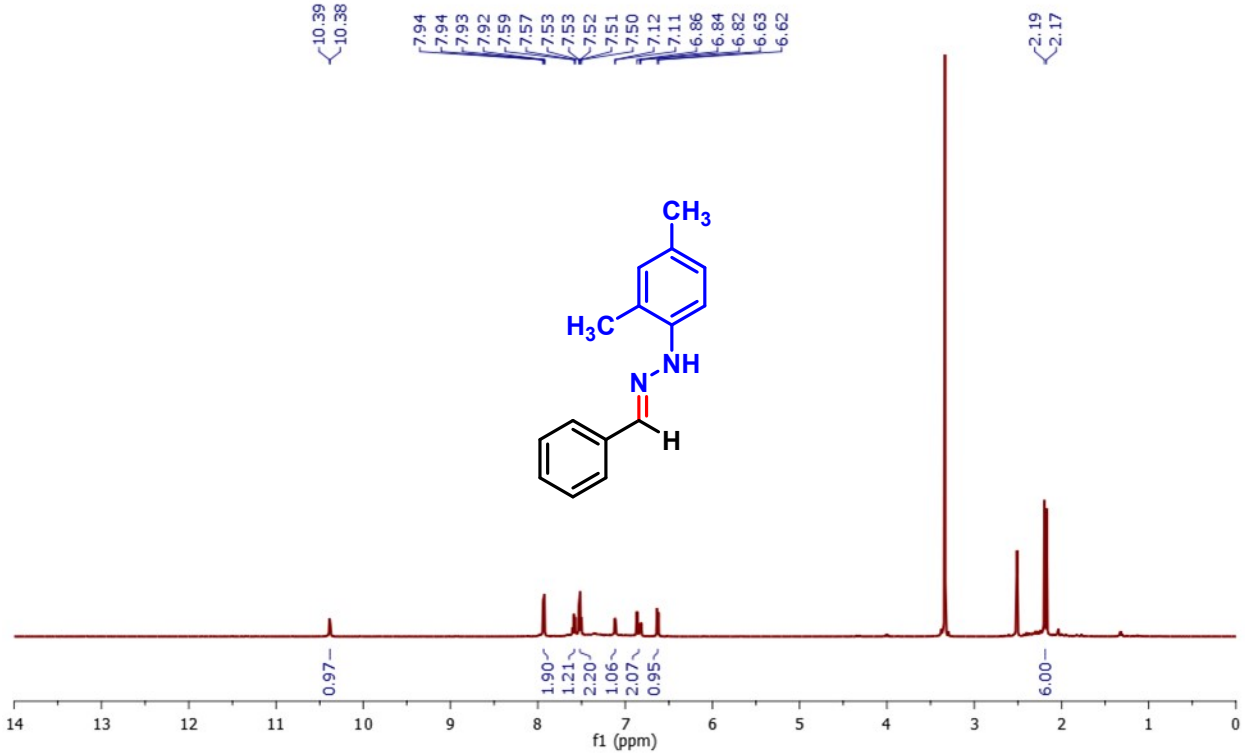


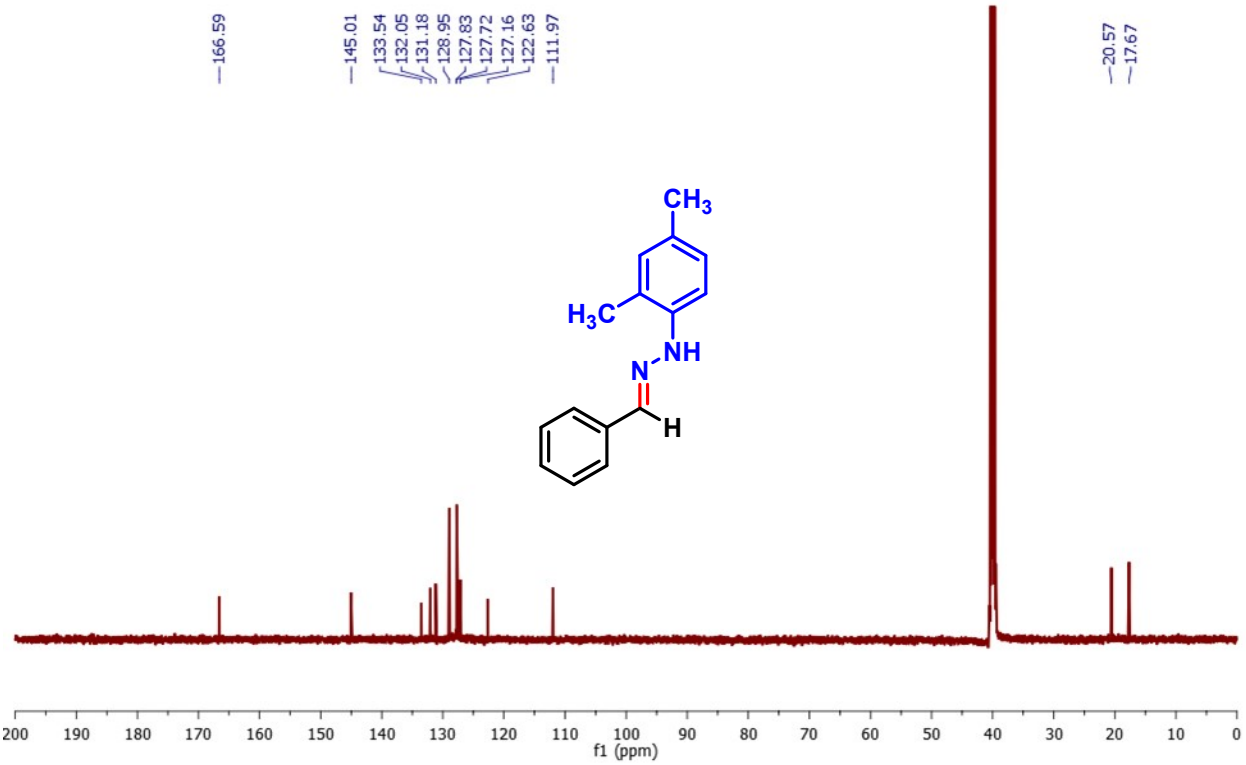
1-benzylidene-2-(2,4-dibromophenyl)hydrazine (6r)



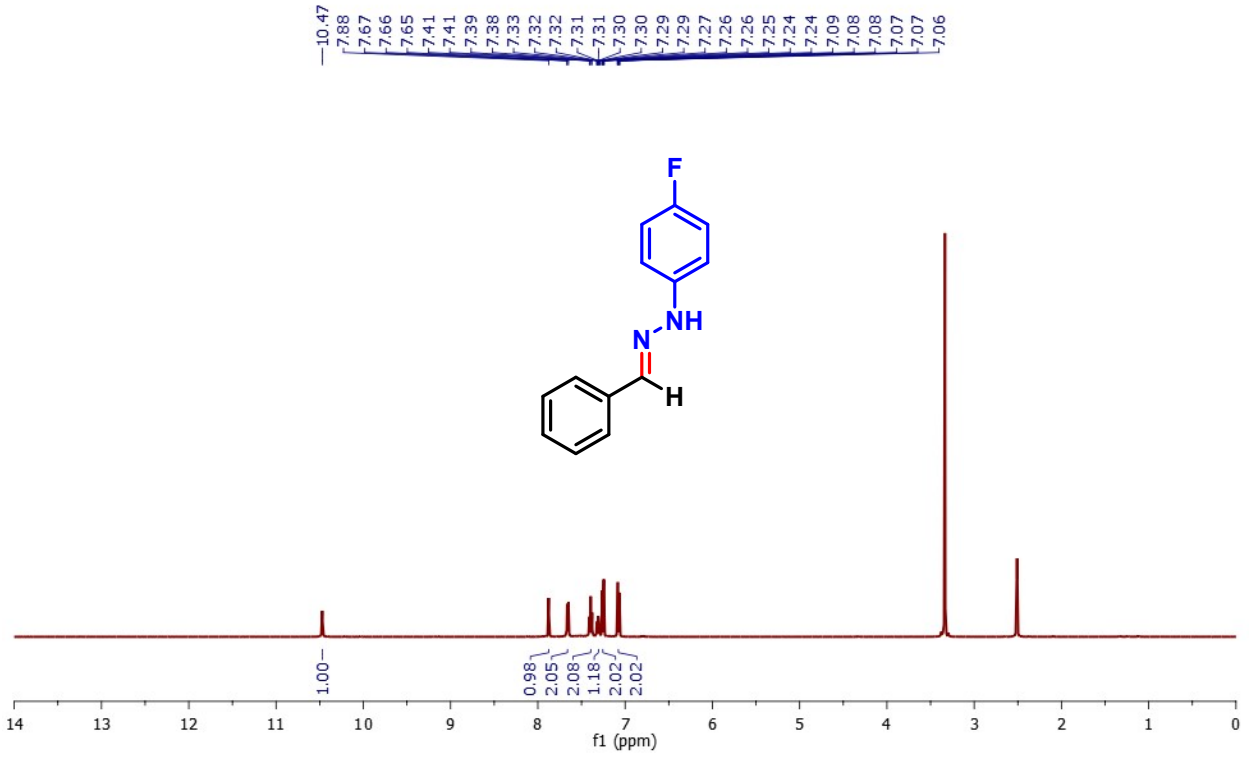


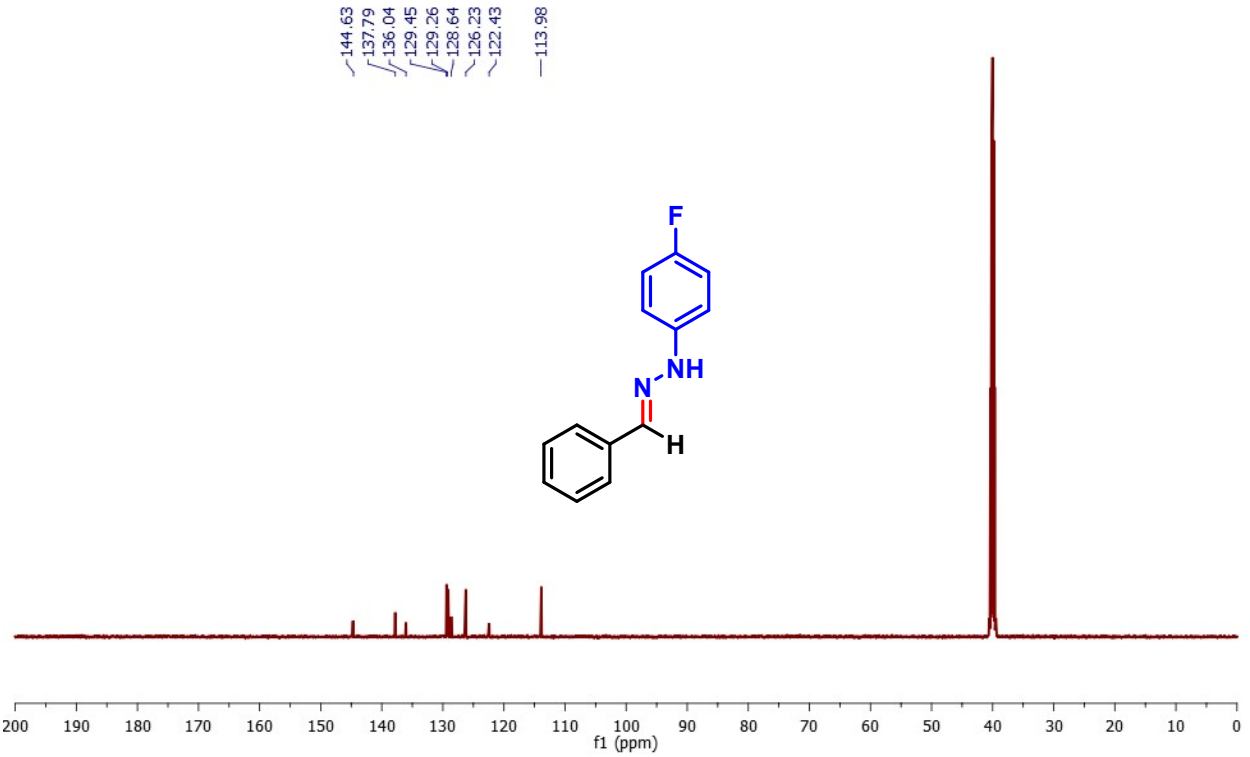
1-benzylidene-2-(2,4-dimethylphenyl)hydrazine (6s)

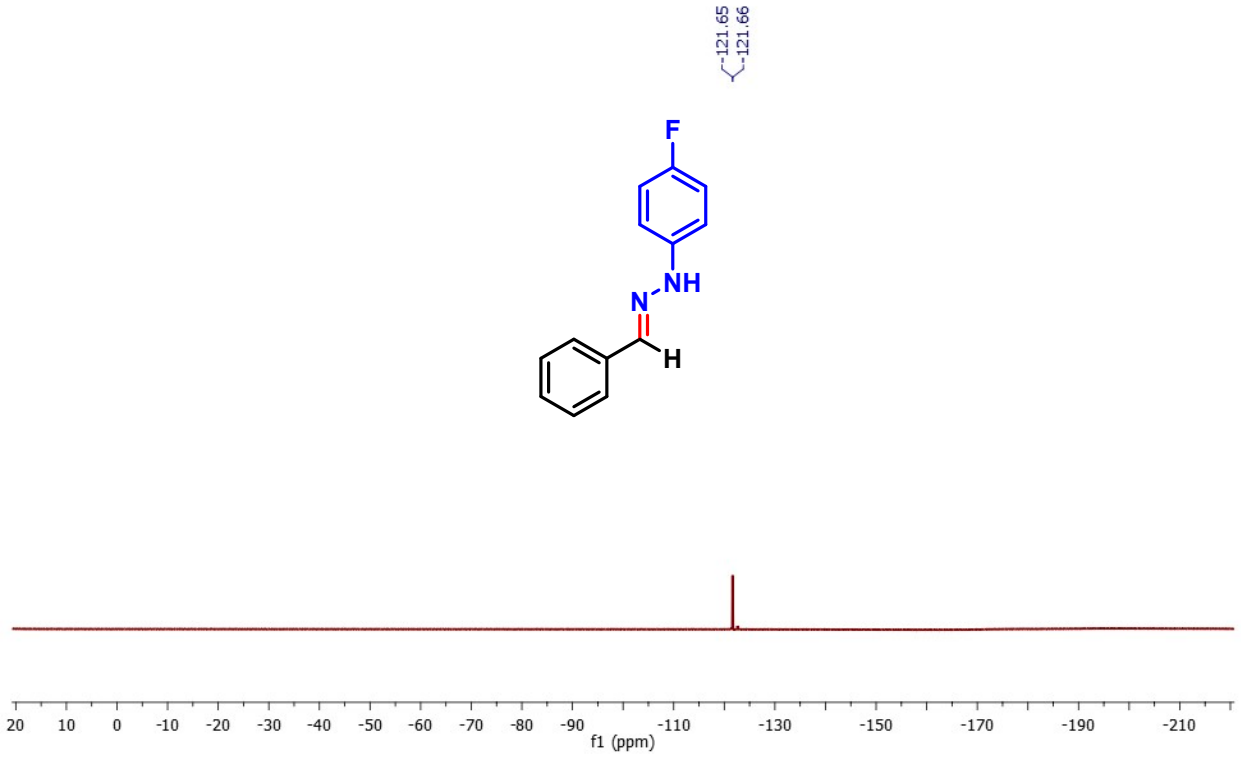




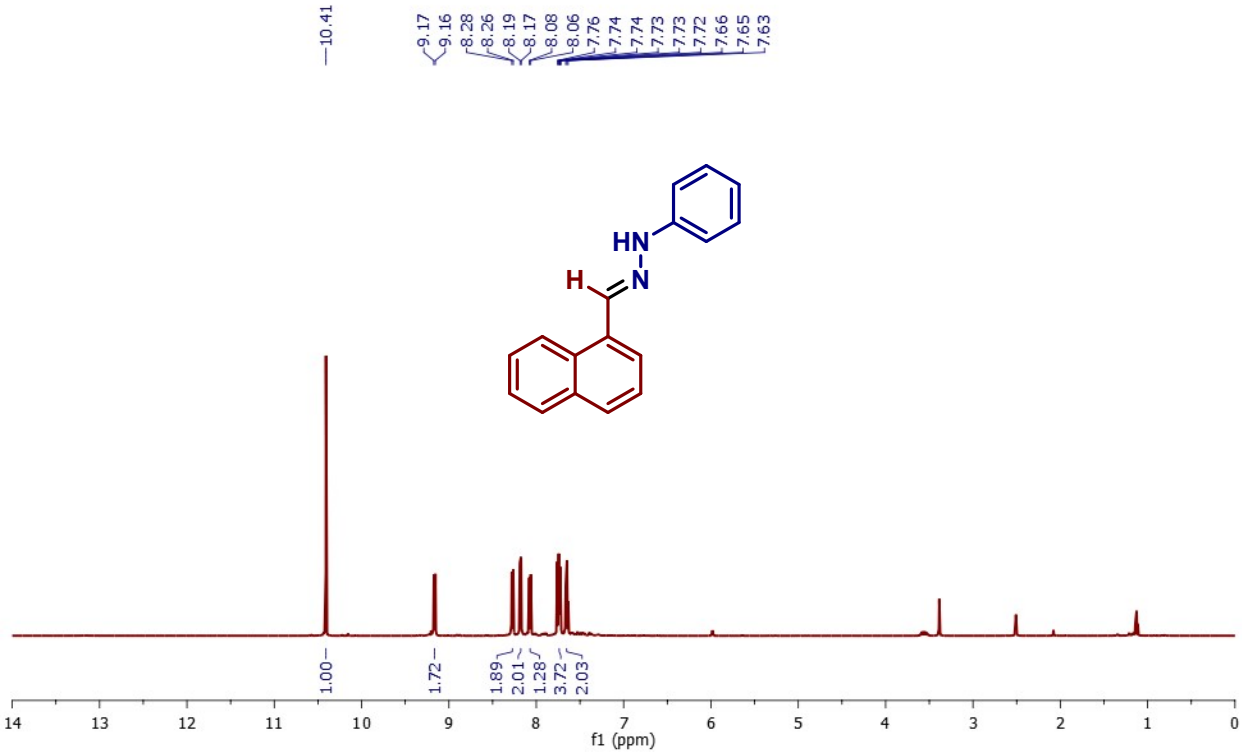
1-benzylidene-2-(4-fluorophenyl)hydrazine(6t)

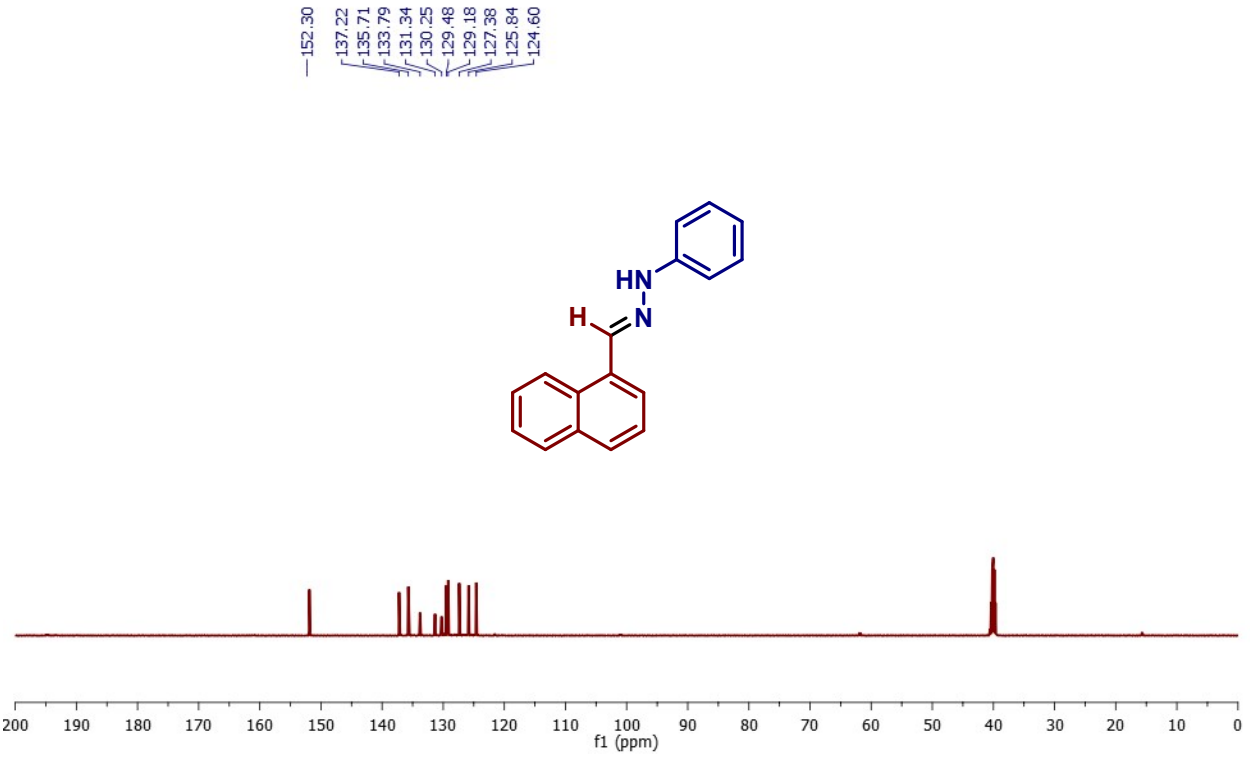




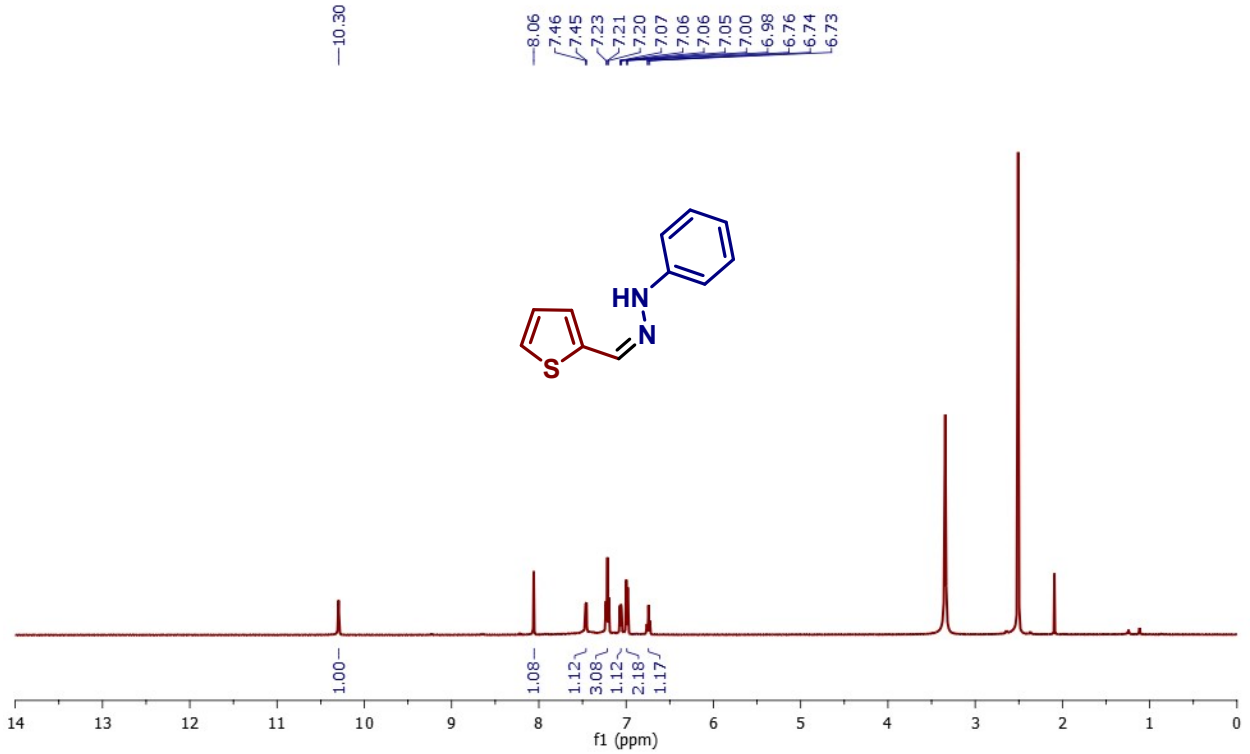


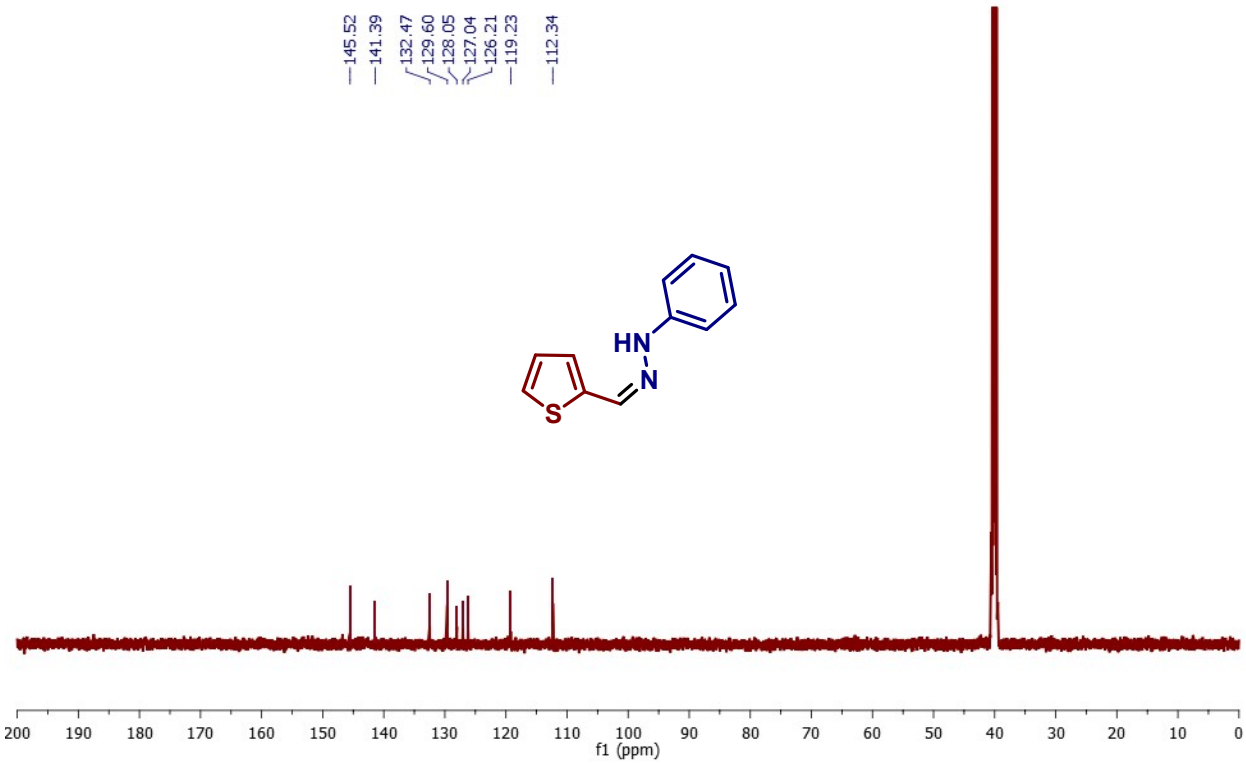
1-(naphthalen-1-ylmethylene)-2-phenylhydrazine (6u)



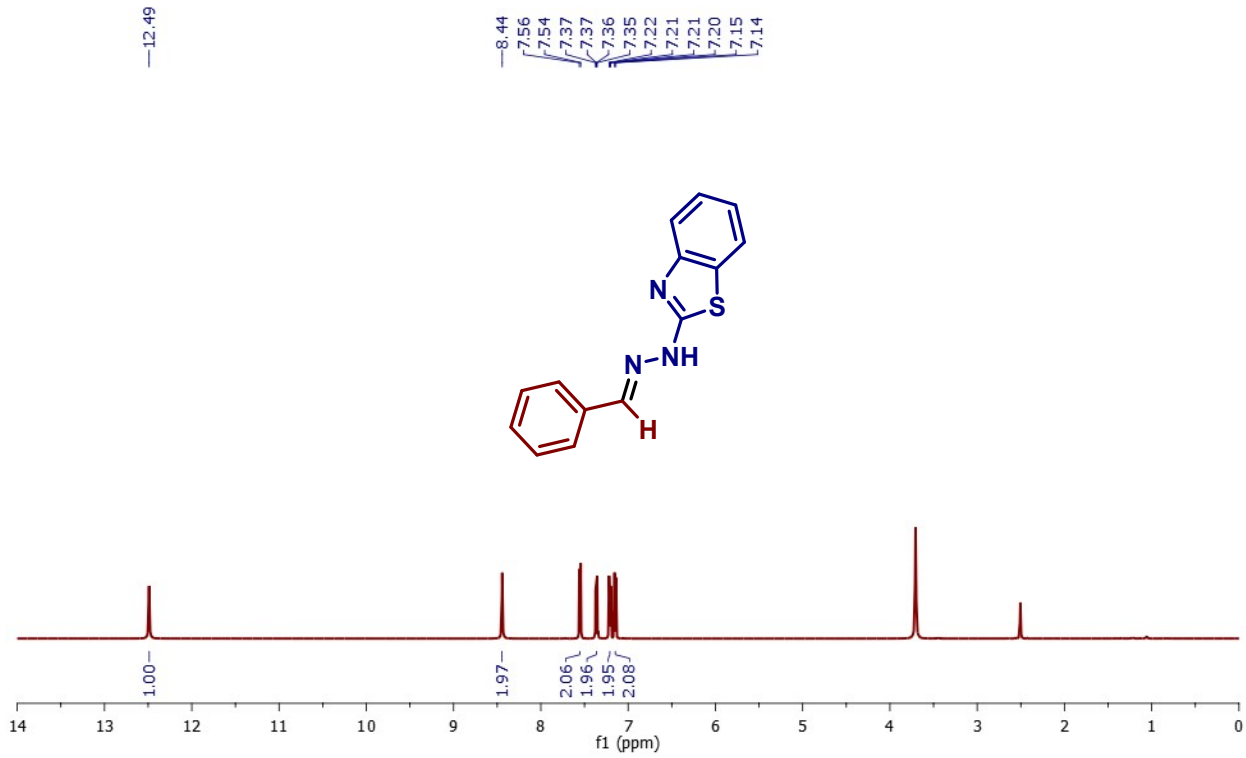


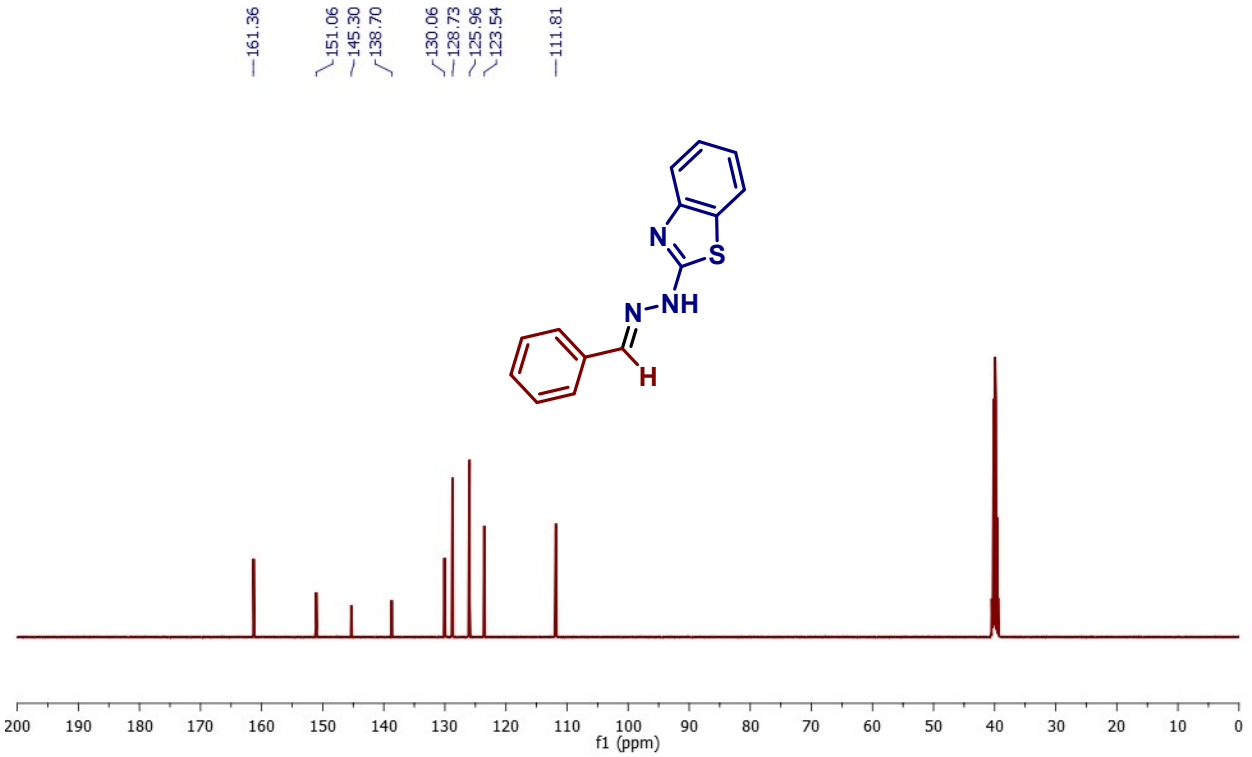
1-phenyl-2-(thiophen-2-ylmethylene)hydrazine(6v)



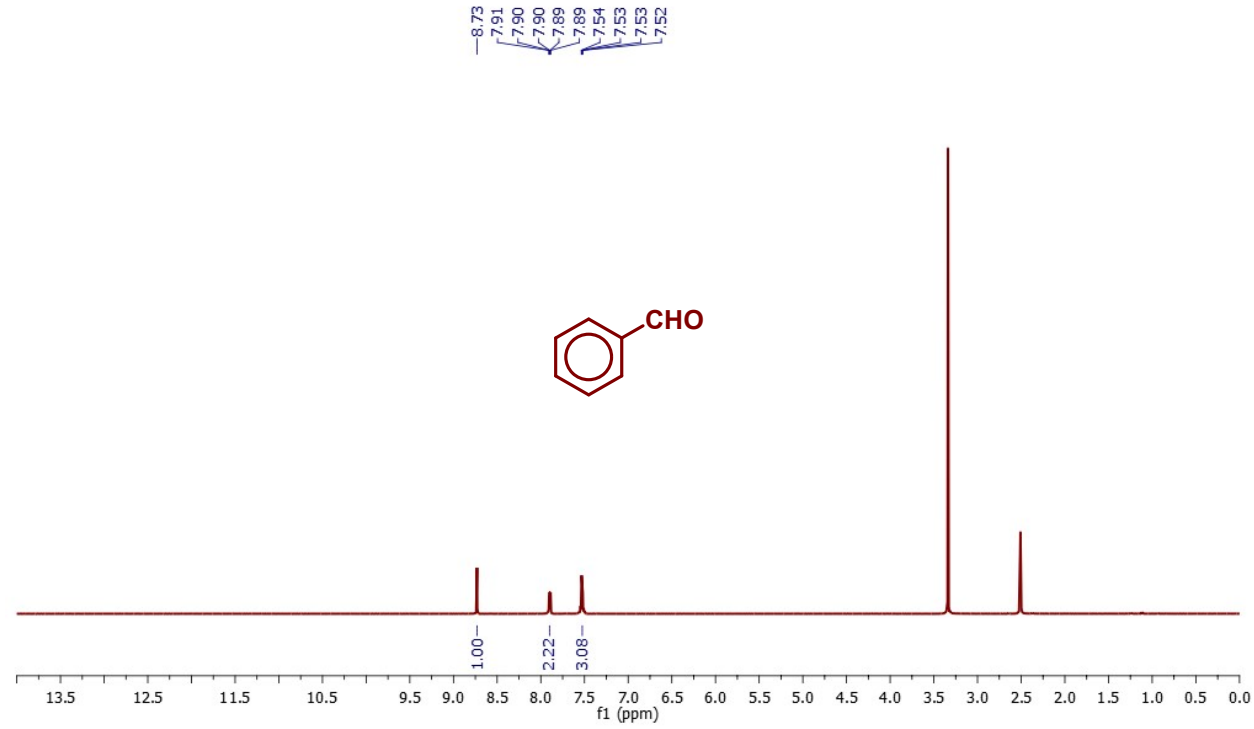


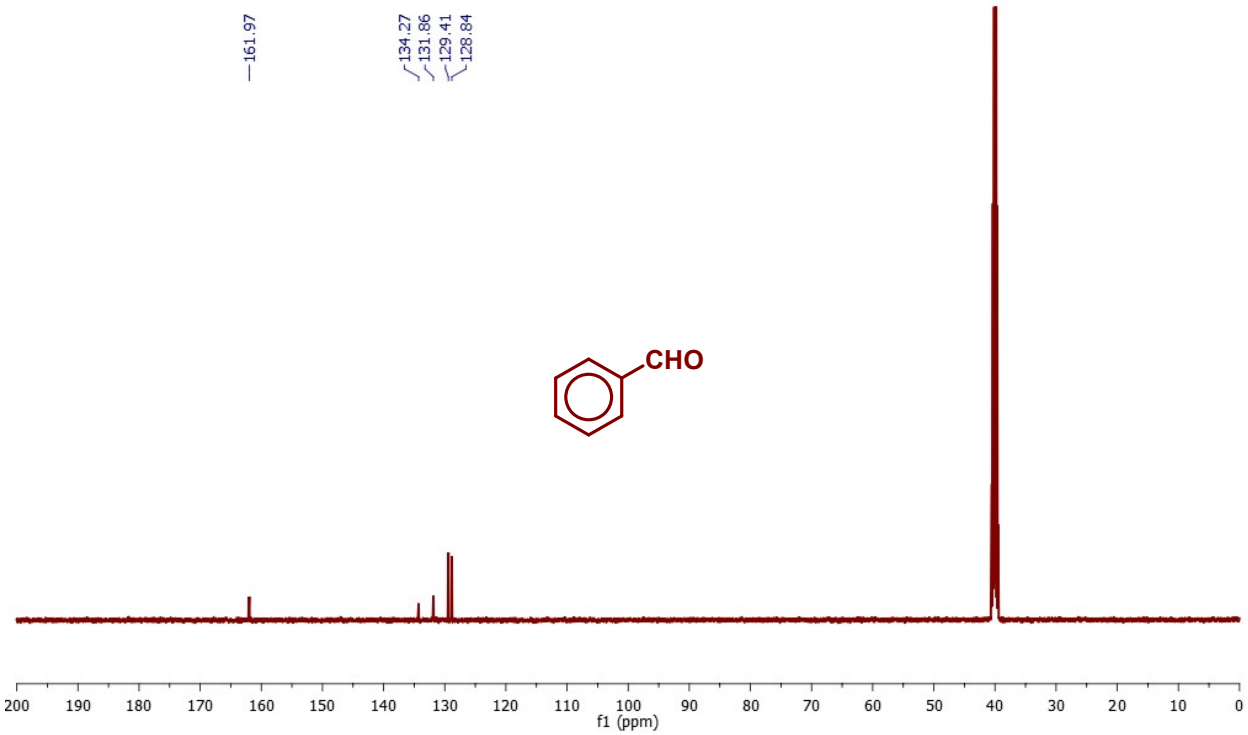
2-(2-benzylidenehydrazineyl)benzo[d]thiazole (6w)



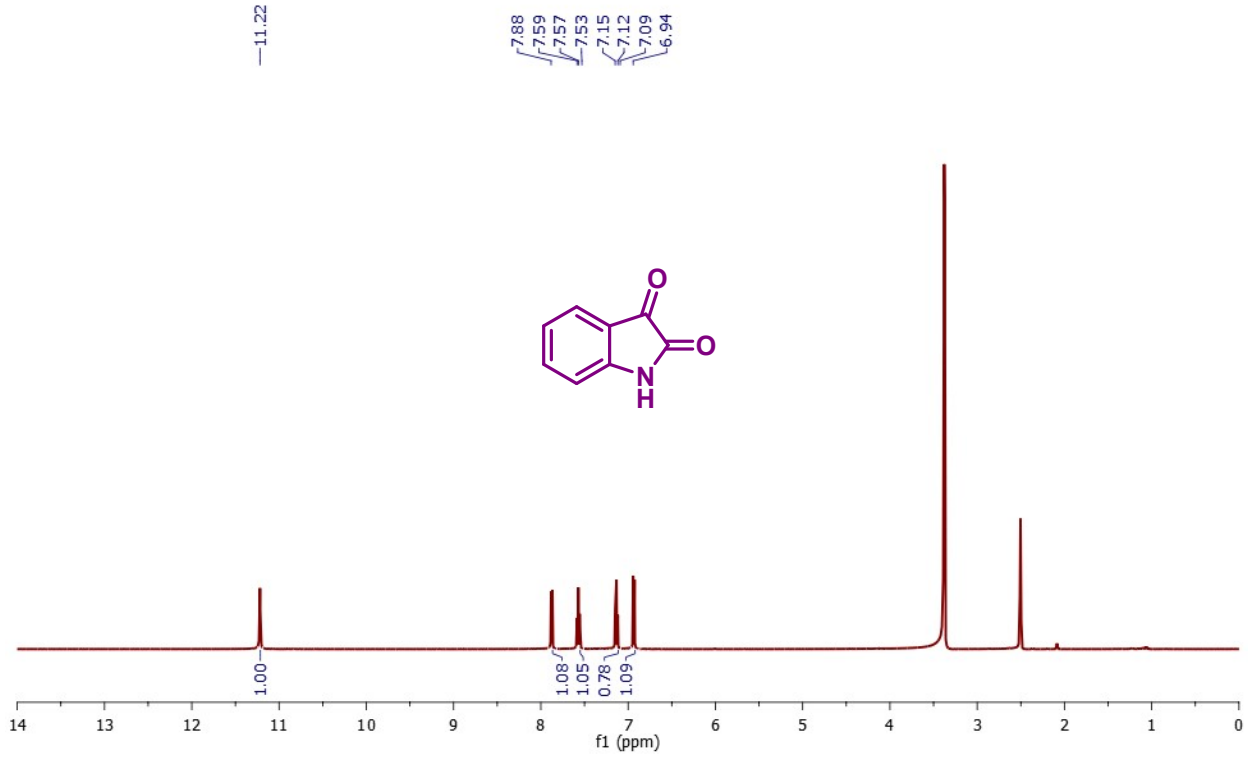


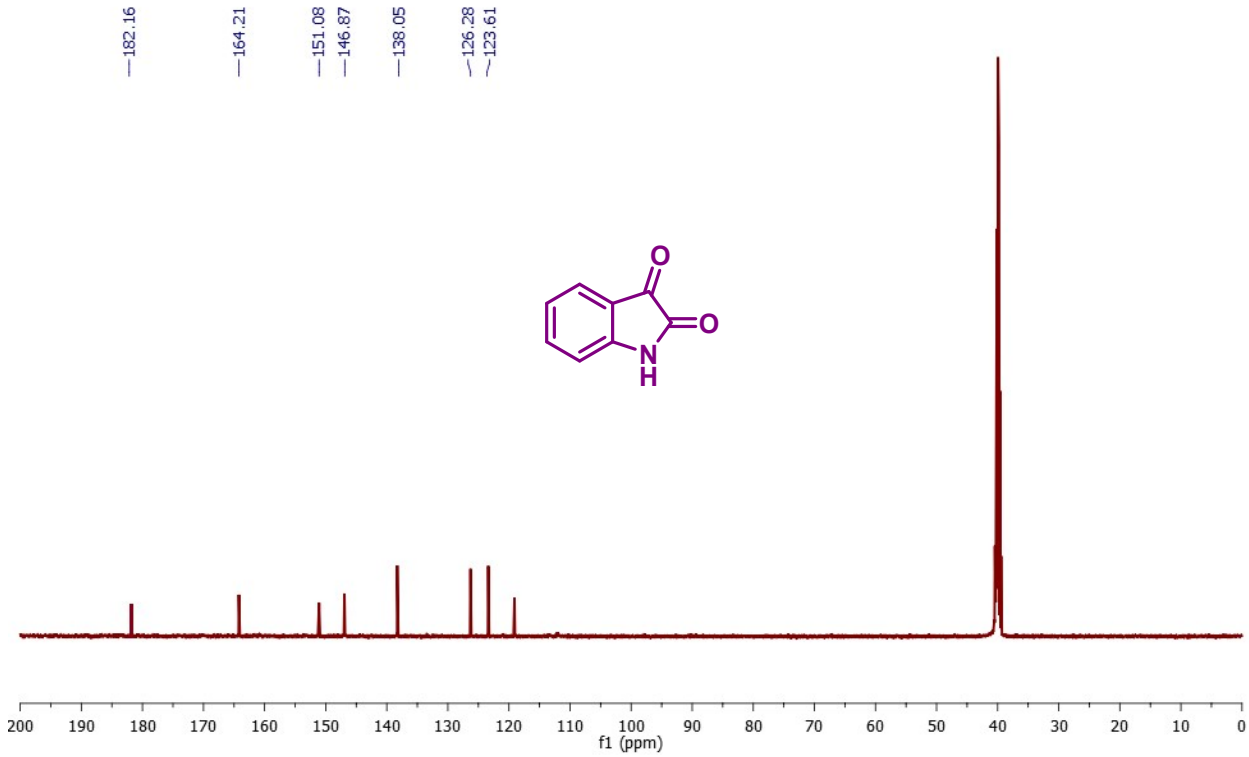
Intermediate E (benzaldehyde)





Intermediate VI (indoline-2,3-dione)




182.16
164.21
151.08
146.87
138.05
126.28
123.61
O
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

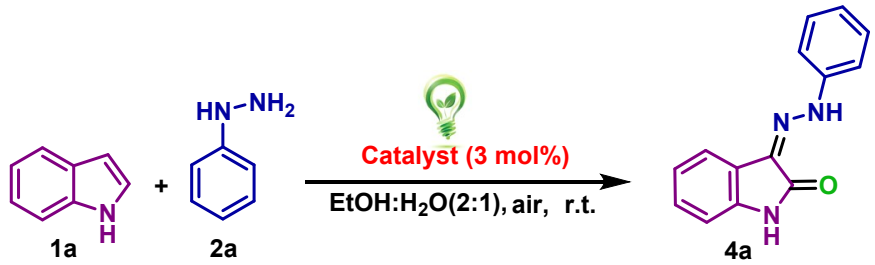
5. Optimization

In the initial investigation, the visible-light photoredox C(sp2)-H functionalization of Indole (1a) with Phenylhydrazine (2a) was selected as the model reactant to optimize the reaction conditions under blue LED irradiation in ambient air at room temperature **(Table 1)**. Firstly we investigated the role of various photocatalysts (**Table 1, entries 1-4**) using ethanol as a solvent.

We found that Eosin Y was the most active catalyst giving product 3a in 42% yields (**Table 1, entry 4**). Next, a variety of solvents were optimized (**Table 1, entries 5-11**), and water gave a good yield of 45% (**Table 1, entry 11**). In our favor, the reaction yield was accelerated to 68% using a mixture of Ethanol and Water in a ratio of 1:1 (**Table 1, entry 12**). Encouraged by the finding, a different ratio of Ethanol and Water (**Table 1, entries 12-15**) was tried. We got the best result (88%) using a mixture in the ratio of 1:2 (**Table 1, entry 14**).

Further, we varied the loading of Eosin Y from 3 mol% to 1, 2, 4 mol% (**Table 1, entries 16-18**) and found a decrease in yield on increasing or decreasing the mol% of the photocatalyst. We tried extending or shortening the reaction time (**Table 1, entries 19-20**), but we failed to get a better yield of product 4a.

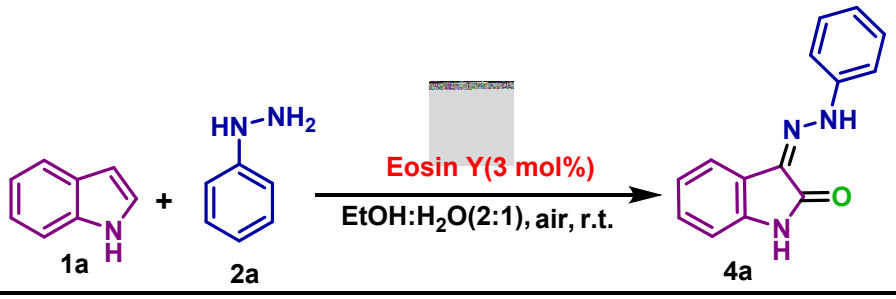
Table 1- Optimization of reaction parameters for oxidative coupling of Indole and Phenyl hydrazine [(a)]



Entry	Catalyst	Solvent	Time (h)	Yield[(b)] (%)
1	Rhodamine B(3)	EtOH	24	4
2	Rose Bengal(3)	EtOH	24	8
3	Xanthone(3)	EtOH	24	5
4	Eosin Y(3)	EtOH	24	42
5	Eosin Y(3)	DMF	24	12
6	Eosin Y(3)	Acetonitrile	24	15
7	Eosin Y(3)	Methanol	24	22
8	Eosin Y(3)	Toluene	24	18
9	Eosin Y(3)	DMSO	24	10
10	Eosin Y(3)	THF	24	20
11	Eosin Y(3)	H_2O	24	45
12	Eosin Y(3)	EtOH:H_2O (1:1)	24	68
13	Eosin Y(3)	EtOH:H_2O (2:1)	24	65
14	Eosin Y(3)	EtOH:H_2O (1:2)	24	88
15	Eosin Y(3)	EtOH:H_2O (1:4)	24	80
16	Eosin Y(1)	EtOH:H_2O (1:2)	24	75
17	Eosin Y(2)	EtOH:H_2O (1:2)	24	81
18	Eosin Y(4)	EtOH:H_2O (1:2)	24	85
19	Eosin Y(3)	EtOH:H_2O (1:2)	26	82
20	Eosin Y(3)	EtOH:H_2O (1:2)	20	78

[(a)]Reaction Condition: Indole (0.25mmol), Phenylhydrazine (0.25mmol), catalyst (3 mol %), solvent (5mL), Blue LED (24 h) under open air at room temperature. [(b)]Isolated yield.

Table 2 – Optimization of different colour LED [a]



Entry	variations in the reaction conditions	Yield (%)[b]
1	in dark	nr
2	green LEDs instead of blue LEDs	25
3	purple LEDs instead of blue LEDs	68
4	White LEDs instead of blue LEDs	79
5	20W CFL instead of blue LEDs	74
6	blue LEDs	88
7	under O_2 atmosphere	89

[a]Reaction Condition: Indole (0.25mmol), Phenylhydrazine (0.25mmol), catalyst (3 mol %), solvent (5mL), Blue LED (24 h) under open air at room temperature. [b]Isolated yield

6. Control experiment

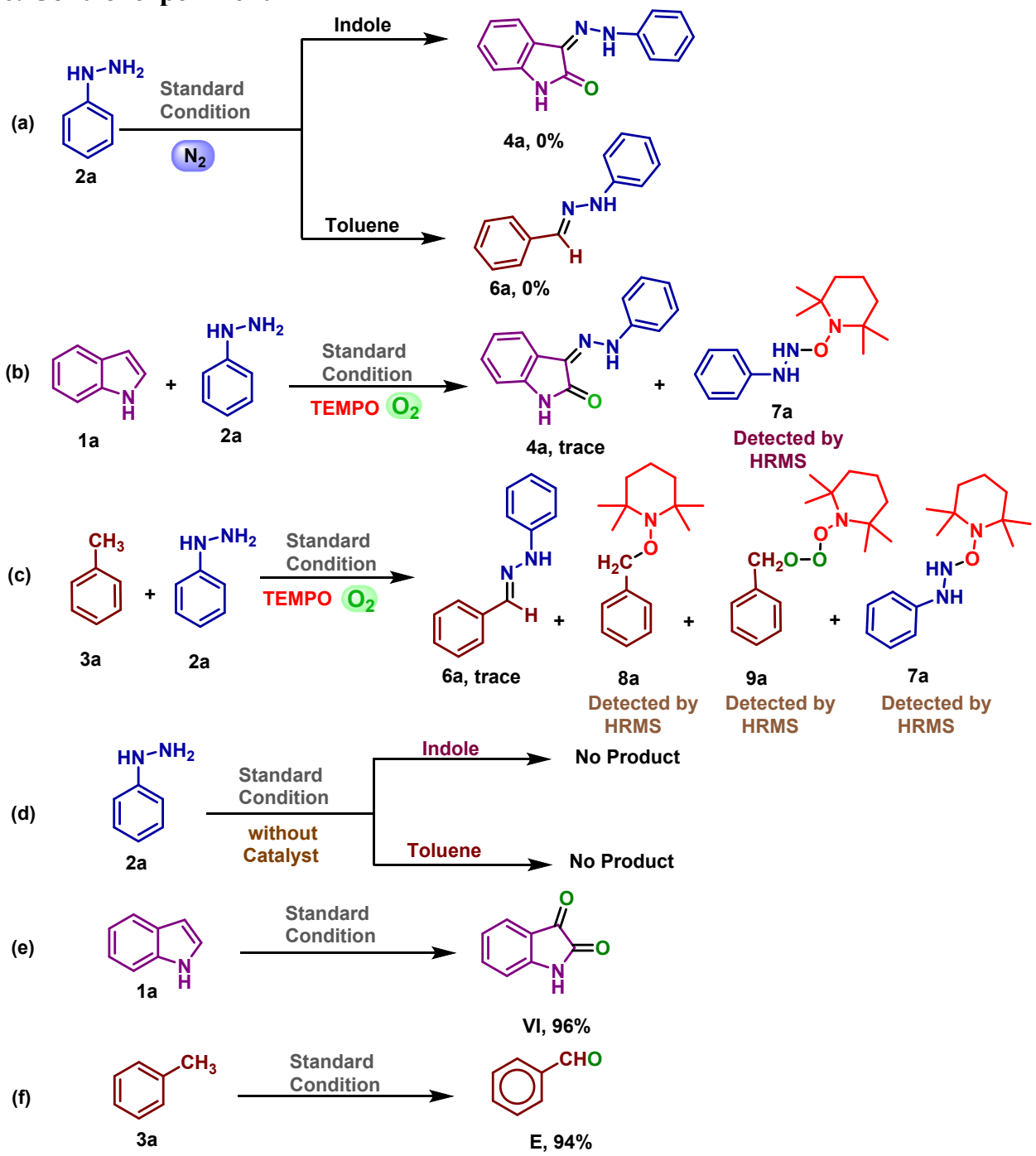


Fig 11: Control experiments for mechanistic investigation