

Supporting Information

A Divergent Photocatalysis Strategy for Selective Aerobic Oxidation of C(sp³)-H Bonds Promoted by Disulfides

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1. General Information

1.1 Solvents and Reagents

All solvents were commercially supplied or provided by the communal stills of the School of Pharmaceutical Science and Technology, Dalian University of Technology. Anhydrous acetonitrile, toluene, tetrahydrofuran and dichloromethane were dried using Na and stored over thoroughly dried 4 Å molecular sieves. All other reagents were purchased from various commercial sources and used as received.

1.2 Chromatography and Spectroscopy

Analytical TLC was visualized with UV light at 254nm. Thin layer chromatography was carried out on TLC glass sheets with silica gel 60 F254. Purification of reaction products was carried out by chromatography using silica gel 60 (200-300 mesh). All ^1H NMR (400/500 MHz) and ^{13}C NMR (101/126 MHz) were recorded on a VARIAN INOVA-400/500M and AVANCE II 400 spectrometer at 25 °C. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard (CDCl_3 : δ 7.26, for ^1H NMR and CDCl_3 : δ 77.0 for ^{13}C NMR). For ^1H NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry data were obtained with UPLC/Q-ToF Mass Spectrometer and were determined by electrospray ionization (ESI).

1.3 Reaction set-up

The reaction setup is displayed in Figure S1. The PR160 Kessil lamp (the light intensity was set 30 W) were used as the light source. All the reactions were run in a 10 mL sealed-tube equipped with an oval shaped stir bar. The distance between the lamp and the sealed tube was set 5 cm. All the reactions were stirred at the speed of 900 rpm with external fan cooling so that the ambient temperature of the reaction vessel did not exceed 35 °C.

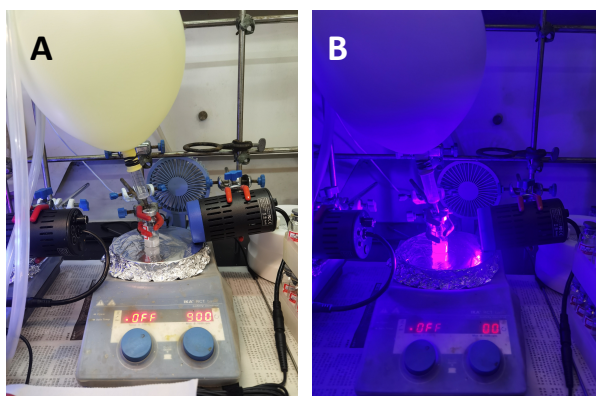


Figure S1. Reaction setup. (A) The reaction setup. (B) The reaction setup with light irradiation

2. General Procedures

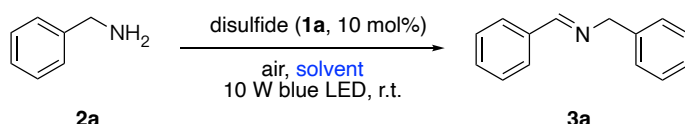
2.1 General experimental procedure for the disulfide catalyzed amine oxidation

The reaction was performed on photochemical reactor. A mixture of benzyl amine (**2a**, 53.6 mg, 0.5 mmol), disulfide (**1l**, 16.6 mg, 0.005 mmol) were stirred in 3 mL of CHCl₃ in a quartz tube at room temperature under the irradiation of 10 W blue LED for 16 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to provide the corresponding products.

2.2 Optimization of reaction parameters for the amine oxidation

In our initial screening reactions, the toluene solution of benzyl amine (**2a**) and disulfide (**1a**) was placed under 10 W blue LED irradiation and stirred for 16 h, the desired imine product **3a** was formed in 81% yield (Table S1, entry1). It should be noticed that in the absence of disulfide, only 3% products was observed. The effect of solvent was also examined. Among the typical solvents, CHCl₃ was founded to be the most effective.

Table S1. Optimization of the Reaction Conditions ^a

|  | | | | |
|---|-----------|---------------|--------------------|------------------------|
| Entry | Disulfide | Light source | Solvent | Yield (%) ^b |
| 1 | 1a | 10 W blue LED | CHCl ₃ | 81 |
| 2 | -- | 10 W blue LED | CHCl ₃ | 3 |
| 3 | 1a | Darkness | CHCl ₃ | trace |
| 4 | 1a | 10 W blue LED | MeCN | 19 |
| 5 | 1a | 10 W blue LED | PhMe | 53 |
| 6 | 1a | 10 W blue LED | DMF | 47 |
| 7 | 1a | 10 W blue LED | Acetone | trace |
| 8 | 1a | 10 W blue LED | EA | 39 |
| 9 | 1a | 10 W blue LED | THF | 33 |
| 10 | 1a | 10 W blue LED | Dioxane | 26 |
| 11 | 1a | 10 W blue LED | CH ₃ OH | 18 |
| 12 | 1a | 10 W blue LED | H ₂ O | 69 |

^aThe reaction was carried out on a 0.4 mmol scale **2a**, disulfide **1a** (10 mol%), solvent (3.0 mL) in a 10 mL quartz tube at room temperature performed on photochemical reactor under the irradiation of 10 W blue LED for 16 h. ^bDetermined by ¹H-NMR, CH₂Br₂ as internal standard.

Meanwhile, we founded that photo irradiation also played an essential role. Various light sources were applied to the model reaction. The results showed that not all of the selected light sources were effective for this

transformation and blue LED (450-455nm) was the best choice. No reaction was observed in the absence of light, under red, yellow or green light irradiation.

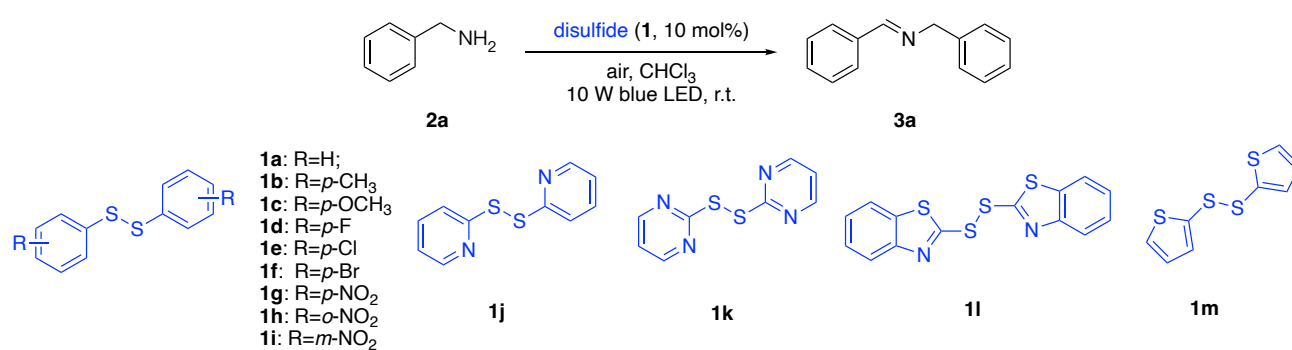
Table S2. Evaluation of light source ^a

| Entry | Disulfide | Light source | Solvent | Yield (%) ^b |
|-------|-----------|-----------------------------|-------------------|------------------------|
| 1 | 1a | 10 W white LED (4000K) | CHCl ₃ | 42 |
| 2 | 1a | 10 W red LED (660-665nm) | CHCl ₃ | trace |
| 3 | 1a | 10 W yellow LED (585-590nm) | CHCl ₃ | trace |
| 4 | 1a | 10 W green LED (530-535nm) | CHCl ₃ | trace |
| 5 | 1a | 10 W blue LED (440-445nm) | CHCl ₃ | 81 |
| 6 | 1a | 10 W purple LED (395-400nm) | CHCl ₃ | 77 |

^aThe reaction was carried out on a 0.4 mmol scale **2a**, disulfide **1a** (10 mol%), solvent (3.0 mL) in a 10 mL quartz tube at room temperature performed on photochemical reactor under the irradiation of 10 W LEDs for 16 h. ^bDetermined by ¹H-NMR, CH₂Br₂ as internal standard.

When the aromatic ring of disulfide replaced by different functional groups, the reaction efficiency was affected. Among the tested disulfides, 1,2-bis(benzo[d]thiazol-2-yl)disulfane (**1l**) showed the highest catalytic reactivity. The effect of solvent was also examined. Among the typical solvents, CHCl₃ was founded to be the most effective. The optimal concentration of system was found to be 0.5 mmol **2a** in 3.0 mL CHCl₃.

Table S3. Evaluation of disulfides^a

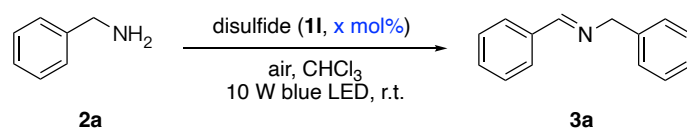


| Entry | Disulfide | Light | Solvent | Yield (%) ^b |
|-------|-----------|---------------|-------------------|------------------------|
| 1 | 1a | 10 W blue LED | CHCl ₃ | 81 |
| 2 | 1b | 10 W blue LED | CHCl ₃ | 65 |
| 3 | 1c | 10 W blue LED | CHCl ₃ | 52 |
| 4 | 1d | 10 W blue LED | CHCl ₃ | 62 |
| 5 | 1e | 10 W blue LED | CHCl ₃ | 44 |

| | | | | |
|----|-----------|---------------|-------------------|---|
| 6 | 1f | 10 W blue LED | CHCl ₃ | 43 |
| 7 | 1g | 10 W blue LED | CHCl ₃ | 64 |
| 8 | 1h | 10 W blue LED | CHCl ₃ | 35 |
| 9 | 1i | 10 W blue LED | CHCl ₃ | 13 |
| 10 | 1j | 10 W blue LED | CHCl ₃ | 47 |
| 11 | 1k | 10 W blue LED | CHCl ₃ | 19 |
| 12 | 1l | 10 W blue LED | CHCl ₃ | 95 (82) ^c |
| 13 | 1l | 10 W blue LED | CHCl ₃ | 42 ^d , 10 ^e , 4 ^f , 21 ^g |

^aThe reaction was carried out on a 0.4 mmol scale, catalyst (10 mol%) in 3.0 mL CHCl₃. ^bDetermined by ¹H-NMR, CH₂Br₂ as internal standard. ^cIsolated yield. ^d**2l** (5 mol%). ^e**2l** (1 mol%). ^f**2l** (0.5 mol%). ^g**2l** (20 mol%).

Table S4. Evaluation of Concentration



| Entry | Cat (x mol%) | solvent | light | Yield(%) ^b |
|-------|--------------|---------|---------------|-----------------------|
| 1 | 10 | 1.0 mL | 10 W blue LED | 39 |
| 2 | 10 | 2.0 mL | 10 W blue LED | 78 |
| 3 | 10 | 3.0 mL | 10 W blue LED | 85 |
| 4 | 10 | 4.0 mL | 10 W blue LED | 77 |
| 5 | 10 | 5.0 mL | 10 W blue LED | 69 |
| 6 | 5 | 3.0 mL | 10 W blue LED | 42 |
| 7 | 1 | 3.0 mL | 10 W blue LED | 10 |
| 8 | 0.5 | 3.0 mL | 10 W blue LED | 4 |

^aThe reaction was carried out on a 0.4 mmol scale, catalyst (x mol%) in CHCl₃. ^bDetermined by ¹H-NMR, CH₂Br₂ as internal standard.

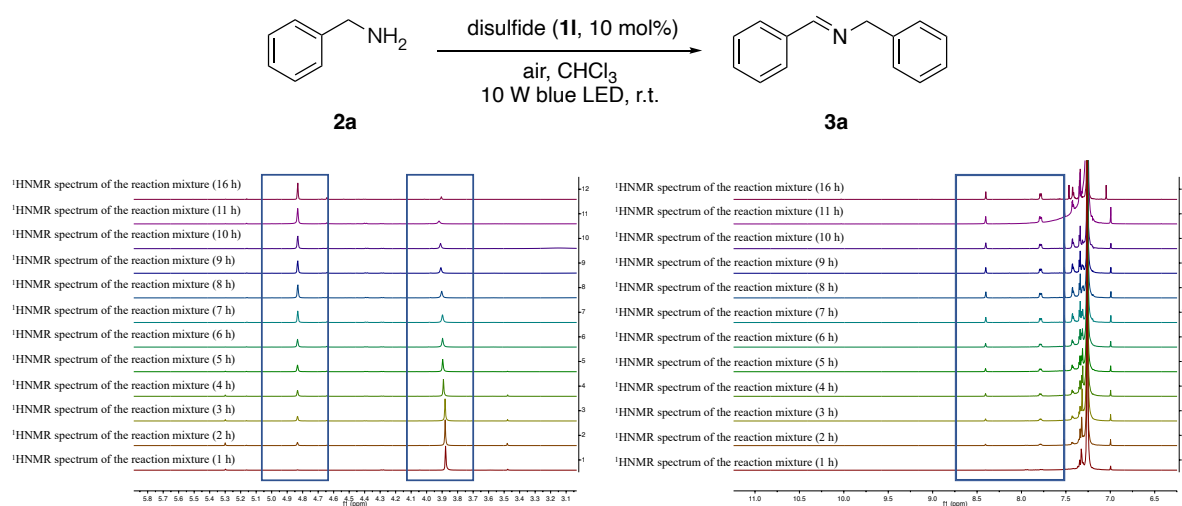


Figure S2. ¹H- NMR analysis of benzylamine oxidation to benzaldehyde reaction process

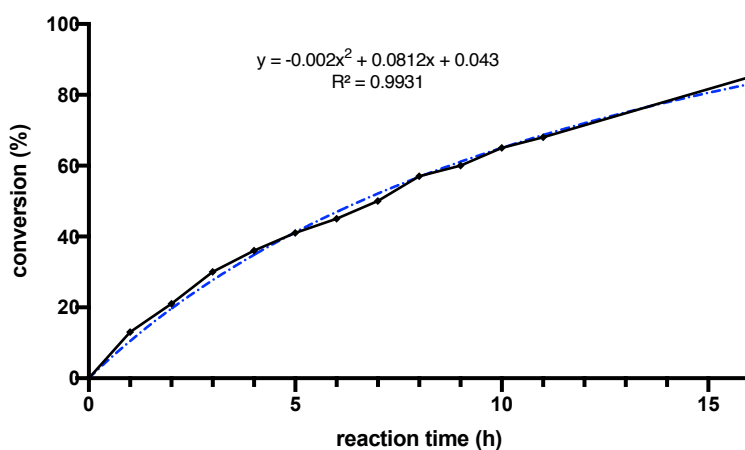
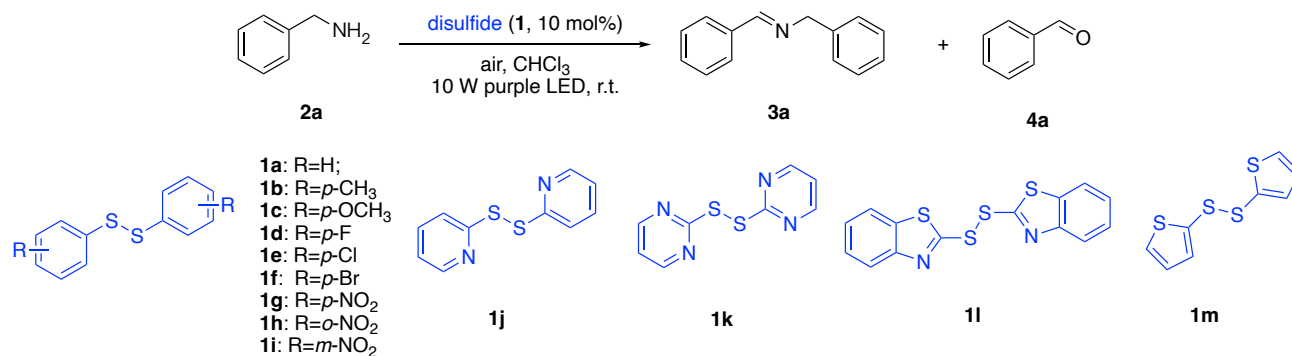


Figure S3. Conversion rate vs. time curve of benzylamine oxidation to benzaldehyde reaction process

2.3 Optimization of reaction parameters for oxidative deamination

In the previous experiment, it was found that 395 nm purple light irradiation could dramatically accelerate reaction rate within 5 hours. However, the imine product decomposed subsequently under 395 nm purple light irradiation and benzaldehyde formation was obviously observed. Therefore, we further explored the reaction of benzylamine to benzaldehyde in depth.

Table S5. Screening of benzylamine photocatalytic oxidative coupling conditions



| Entry | PhSSPh | solvent | 2a (%) ^b | 4a (%) ^b |
|-------|---------------------|----------------------------|----------------------------|---|
| 1 | 1a (10 mol%) | CHCl ₃ (3.0 mL) | 73 | 7 |
| 2 | 1a (10 mol%) | CHCl ₃ (2.0 mL) | 74 | 16 |
| 3 | 1a (10 mol%) | CHCl ₃ (1.0 mL) | 57 | 27 |
| 4 | 1b (10 mol%) | CHCl ₃ (2.0 mL) | 33 | 24 |
| 5 | 1c (10 mol%) | CHCl ₃ (2.0 mL) | 38 | 25 |
| 6 | 1d (10 mol%) | CHCl ₃ (2.0 mL) | 58 | 25 |
| 7 | 1e (10 mol%) | CHCl ₃ (2.0 mL) | 32 | 52 |
| 8 | 1f (10 mol%) | CHCl ₃ (2.0 mL) | 32 | 44 |
| 9 | 1g (10 mol%) | CHCl ₃ (2.0 mL) | 7 | 61 |
| 10 | 1h (10 mol%) | CHCl ₃ (2.0 mL) | 14 | 63 |
| 11 | 1i (10 mol%) | CHCl ₃ (2.0 mL) | 25 | trace |
| 12 | 1j (10 mol%) | CHCl ₃ (2.0 mL) | trace | >90 |
| 13 | 1k (10 mol%) | CHCl ₃ (2.0 mL) | trace | trace |
| 14 | 1l (10 mol%) | CHCl ₃ (2.0 mL) | trace | 90 (42 ^c , 74 ^d) |
| 15 | 1m (10 mol%) | CHCl ₃ (2.0 mL) | trace | 82 |
| 16 | 1l (10 mol%) | H ₂ O (2.0 mL) | >90 | 2 |

^aReaction conditions: **2a** (0.5 mmol), disulfide (10 mol%), CHCl₃ in a 10 mL quartz tube at room temperature performed on photochemical reactor under the irradiation of 10 W LED for a given time. ^bDetermined by ¹H NMR analysis. ^cDetermined by GC analysis with cyclohexanone as internal standard. ^dSeal of ampoule.

Several solvents were screened for the experiment. It was found that when chloroform was the best solvent; when acetonitrile was used, only imine product was observed in the system. The chloroform system was quantified by NMR internal standard, and the yield of benzaldehyde NMR was only 42%.

Table S6. Screening of benzylamine photocatalytic oxidative coupling conditions

2a $\xrightarrow[\text{air, solvent, 10 W purple LED, r.t.}]{\text{disulfide (1a, 10 mol\%)}}$ **4a**

| Entry | PhSSPh | solvent | 6a (%) ^b |
|-------|--------|---------|----------------------------|
|-------|--------|---------|----------------------------|

| | | | |
|---|---------------------|----------------------------|-------|
| 1 | 1I (10 mol%) | CHCl ₃ (3.0 mL) | 42 |
| 2 | 1I (10 mol%) | MeCN (3.0 mL) | trace |
| 3 | 1I (10 mol%) | PhMe (3.0 mL) | 27 |
| 4 | 1I (10 mol%) | Acetone (3.0 mL) | 24 |
| 5 | 1I (10 mol%) | THF (3.0 mL) | n.d. |

^aReaction conditions: **4a** (0.5 mmol), disulfide (10 mol%), solvent in a 10 mL quartz tube at room temperature performed on photochemical reactor under the irradiation of 10 W LED for a given time.

^bDetermined by ¹H NMR analysis. CH₂Br₂ as internal standard.

After obtaining the optimum reaction conditions, GC analyses is used for tracking and detection. In the first three hours of the reaction, the formation rate of imine is higher than that of benzaldehyde, and from the fourth hour onwards, the generated imine is decomposed to form benzaldehyde. After 7 hours of reaction, the conversion rate of benzaldehyde can reach 84%. As the production and consumption of imines was observed during the oxidative deamination of benzylamine, the imines were subjected to separate violet light, and the imines were gradually converted to benzaldehyde with increasing light time. The above experiments showed that the oxidation of benzylamine to imine was predominant in the early stages of the benzylamine oxidative deamination reaction and the oxidation of imine to benzaldehyde in the later stages of the reaction. During the oxidative deamination of benzylamine to benzaldehyde, the trend of the imine intermediate with the reaction process could be clearly observed.

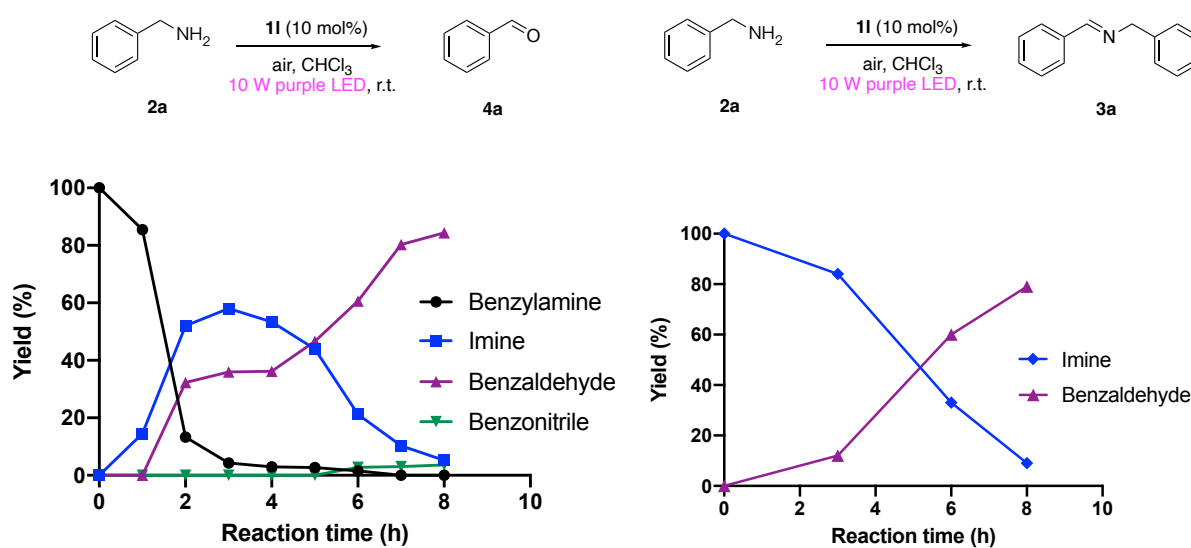


Figure S4. Analysis of the reaction process

In order to avoid the volatilization of benzaldehyde, the reaction was carried out under closed conditions. However, after the reaction, no benzaldehyde was observed and formed other by-products under oxygen atmosphere.



Figure S5. Photo of the reaction system

Thus, we further explored reaction in vial with rubber plug. To our delighted, oxidative deamination of benzylamine to give benzaldehyde proceeded in good yield.

3. Preliminary mechanistic studies

3.1 Mechanistic experiments of the disulfide-catalyzed aerobic oxidative coupling of amines

To determine the mechanism of the reaction, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was added in the standard conditions, and the desired product 3a was provided in only 4% yield, typical radical scavengers 1,1-diphenylethylene. On the other side, DABCO, a well-known strong ^1O physical quencher, was added to the model reaction, a slightly reduced product yield was observed. Byproducts 8 were observed by mass spectrometry.

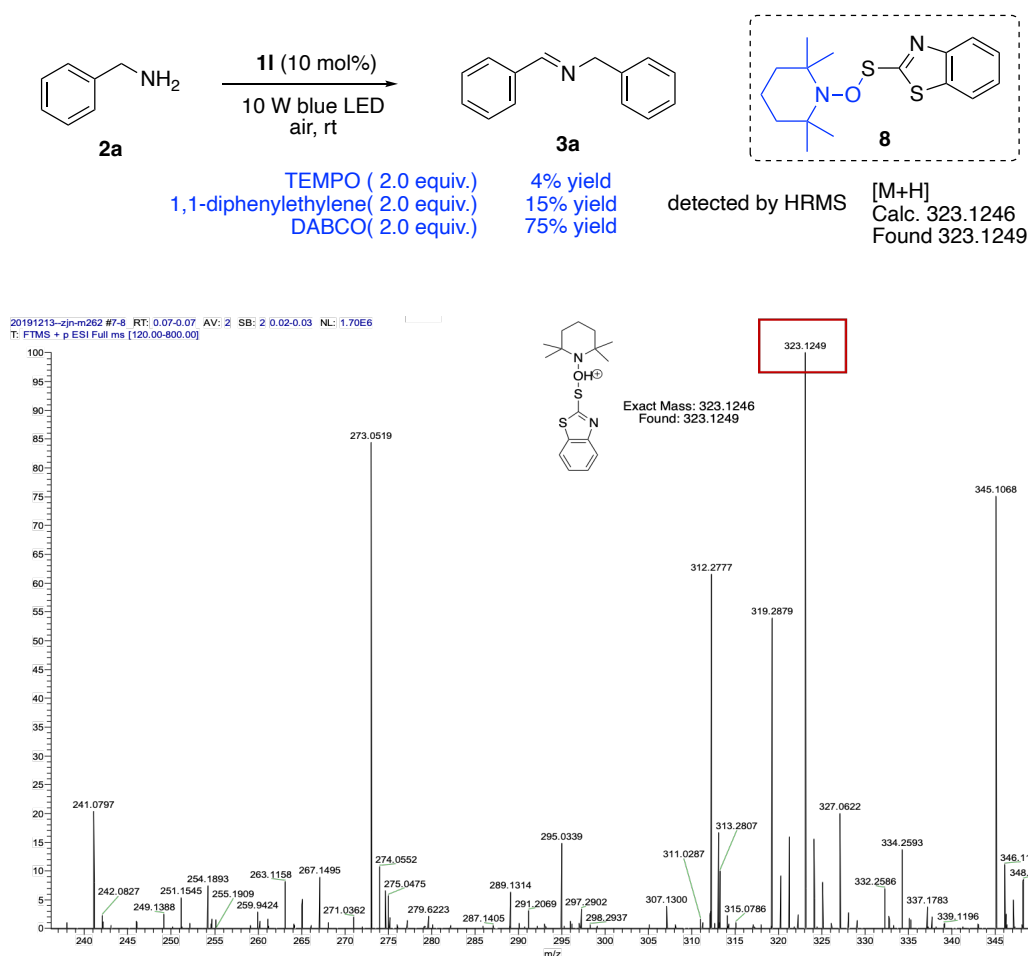
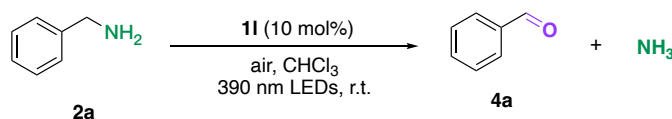


Figure S6. Mechanistic experiments

3.2 Determination of NH_3 generated during the reaction

The reaction mixture was acidified with 4 M HCl (2.0 mL). As shown in Figure S7, NH_4^+ was detected at 7.10 ppm in the ^1H NMR spectrum upon the oxidative deamination of amines.



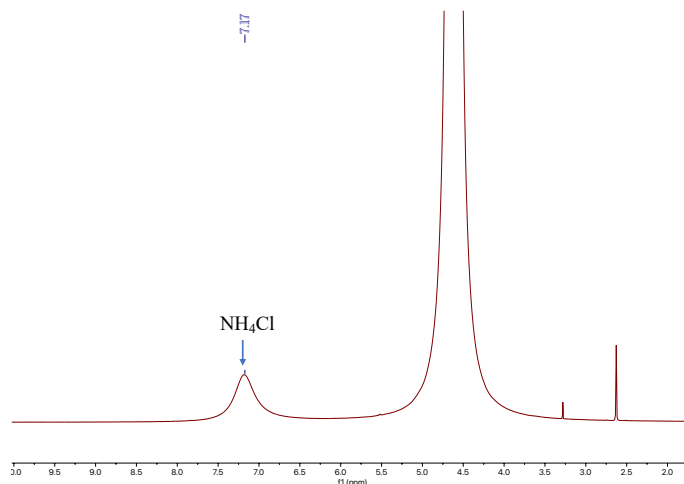


Figure S7. ^1H -NMR spectrum of the acidified reaction mixture for the oxidative deamination of **2a**.

To illustrate detailed process from imine **3** to aldehyde **4**, a set of controlled experiments were conducted. Under 390 nm light irradiation, **3a** can produce 83% yield of **4a** under standard condition and 43% of **4a** in the absence of catalyst. In contrast, under blue light irradiation conditions, the reaction was difficult to carry out. We further performed a spectroscopic study of **3a**. To gain an insight into the photophysical characteristics of the **3a**, photoluminescence (PL) spectra were recorded. The **3a** was dispersed in CHCl_3 , and the emission spectra of the **3a** was recorded in the excitation wavelength (λ_{ex}) range from 380 to 480 nm. There is a maximum intensity observed for **3a** at an excitation of 401 nm with the emission intensity maximum at 510 nm. Therefore, we believe that **3a** is excited under 390 nm light conditions, forming an excited state and undergoing oxidative fracture. Thus, we believed that the selectivity from oxidative homo-coupling to oxidative deamination of amines is controlled by the wavelength of visible light.

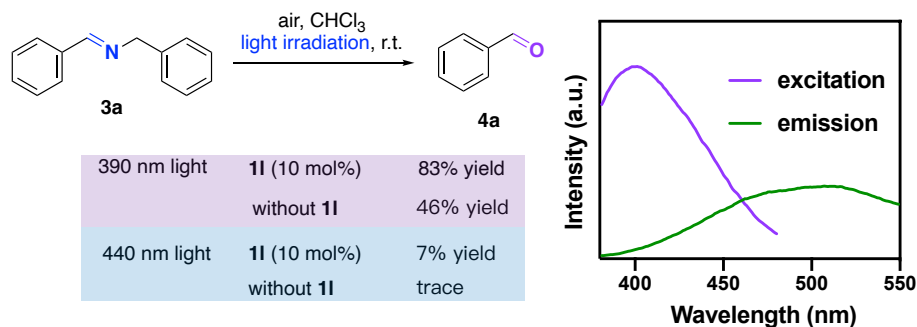


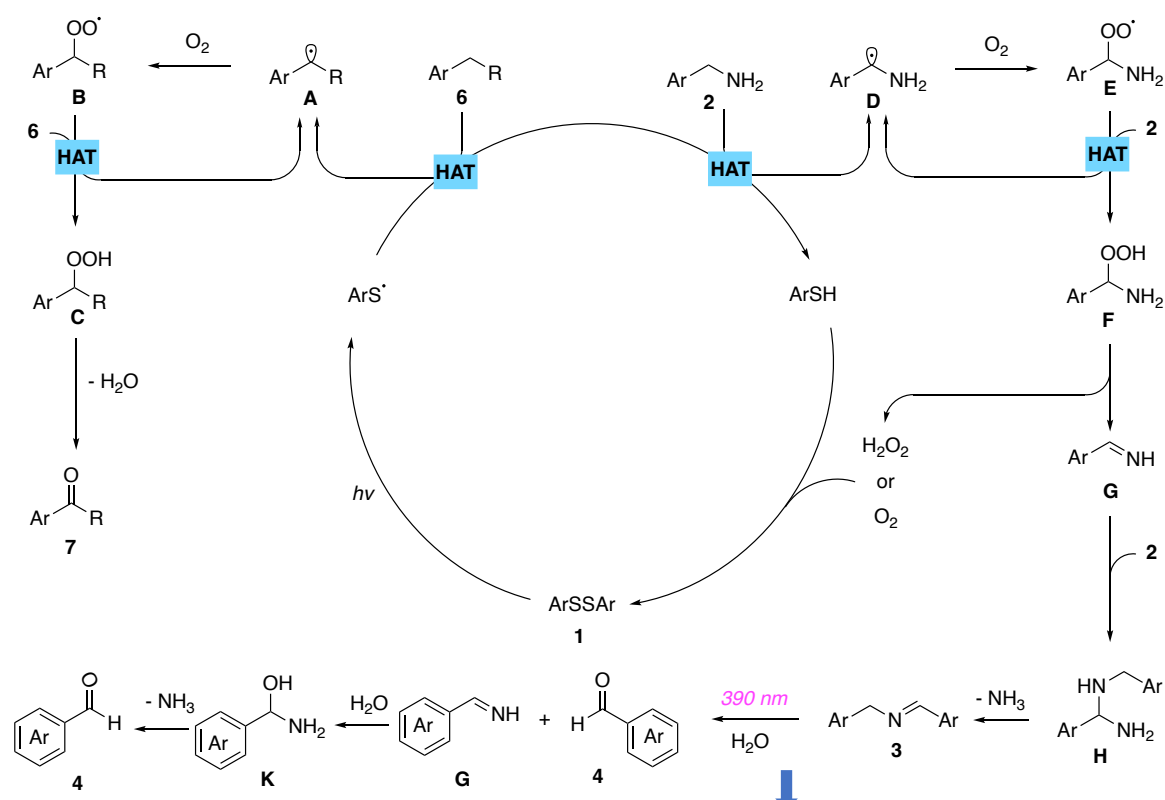
Figure S8. Corresponding excitation spectrum of **3a** for the emission wavelength maximum of 510 nm.

3.3 Proposed detailed reaction mechanism

Having determined an excited state of **3a** under 390 nm light conditions and undergoing oxidative fracture, we propose a mechanism in which imidoyl radical formation

Initially, under the irradiation of 390 nm visible light, the imine **3** is excited to provide its excited species,

which then undergoes a single-electron transfer (SET) process with oxygen to generate imine radical cation intermediate **I** and superoxide anion. On the other hand, the photolytic cleavage of the disulfide bond of disulfide would generate a thiophenol radical **6** which is a suitable one-electron-oxidant for superoxide anion. The protonation of generated thiophenol anion yields thiophenol. Then, the imine radical cation **I** can be trapped by subsequent anti-Markovnikov addition of water to give a radical cation **II**. Deprotonation of cation radical **II** furnishes a radical **III**, which leads to production of the alcohol products through a HAT process. The deamination product benzaldehyde and imine intermediate are obtained by the C-N bond cleavage. The imine intermediate is attacked by H₂O forming another benzaldehyde product and NH₃ is generated during the oxidative deamination reaction.



Proposed mechanism of hydrolysis

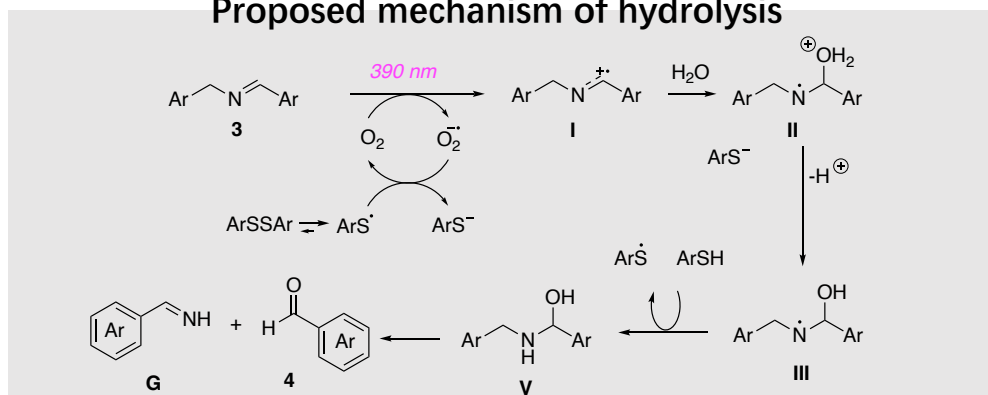


Figure S9. Proposed detailed reaction mechanism

4 The UV-visible spectroscopy and Fluorescence quenching studies

UV-visible spectroscopy of reaction solution was recorded on a Lambda 750S spectrophotometer.

The sample was prepared by mixing disulfide **11** and substrate **2a** with CHCl_3 ($M[\mathbf{1a}] = 0.20\text{ mol/L}$, $M[\mathbf{3I}] = 0-0.40\text{ mol/L}$) in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 365nm. The absorption was collected and result was listed in Figure S10.

Emission quenching experiments (Stern-Volmer studies)

To evaluate the role of 1,2-bis(benzo[d]thiazol-2-yl)disulfane in the process, we performed Stern-Volmer fluorescence quenching experiments. Emission intensities were recorded using Hitachi F-7000 Fluorescence Spectrometer for all experiments. The quenching of 1,2-bis(benzo[d]thiazol-2-yl)disulfane was conducted in CHCl_3 , with a concentration of 0.2M in a quartz cell with a 1 cm path length and an excitation wavelength of 375 nm used.

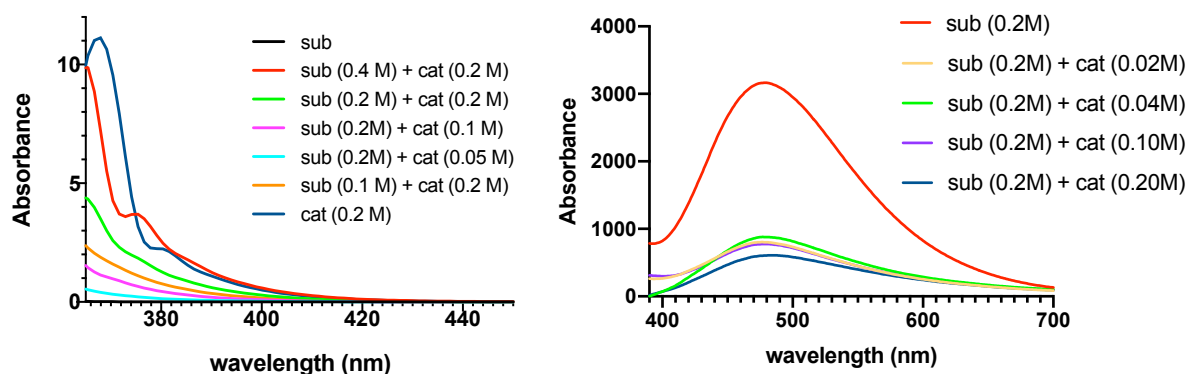


Figure S10. UV-visible spectroscopy and fluorescence spectra of disulfide catalyzed benzylamine oxidation self-coupling reaction system

5 General description of experiments included in one sensitivity assessment.

Table S7. General description of experiments included in one sensitivity assessment.

| # | Experiment | Description |
|----|----------------------------|---|
| 1 | High c | For c_{high} : $n_{\text{rxn}}/(V_{\text{rxn}} - 10\%V_{\text{rxn}})$ |
| 2 | Low c | For c_{low} : $n_{\text{rxn}}/(V_{\text{rxn}} + 10\%V_{\text{rxn}})$ |
| 3 | High H_2O | + H_2O ; $V_{\text{H}_2\text{O}} = 1\%V_{\text{rxn}}$ |
| 4 | Low or medium O_2 | Degassed or under inert atmosphere |
| 5 | High O_2 | + air; $V_{\text{air}} = 10V_{\text{rxn}}$ |
| 6 | High O_2 | $T - 10\text{ }^\circ\text{C}$ |
| 7 | High T | $T + 10\text{ }^\circ\text{C}$ |
| 8 | Low I | $I/16$; $I \sim d^{-2} \rightarrow d \cdot 4$; d : distance reaction to LED |
| 9 | High I | $I \cdot 16$; $I \sim d^{-2} \rightarrow d/4$; d : distance reaction to LED |
| 10 | Control | Standard conditions |
| 11 | Big scale | $n \cdot 20$ |

6 Continuous-flow setup

6.1 Generalities of photo reactions in glass microreactor (Procedure A)

The photo reactions were conducted in a commercial continuous-flow reactor (Corning® Advanced Flow™ Lab Photo Reactor) featuring a compact glass mesofluidic module (155 × 125 mm size, 0.8 mm channel height, 2.7 mL internal volume) integrated with a high capacity heat exchanger (2 layer, 22 mL, 1 W mL⁻¹ K⁻¹). LED panels were mounted on both sides of the fluidic module (40 mm from the center of the reactive layer), and each LED panel was equipped with multiple wavelengths (20 LEDs for each wavelength) and a heat exchanger (T=15°C). The thermoregulation of both the glass fluidic module and the LED panels was carried out with Huber minichiller 280 thermostats. Meonoethylenglycol was utilized as thermofluid. The feed solution was conveyed to the photoreactor with a HPLC pump (Corning Intelligent Pump, UI-22, 0.1 – 10 mL min⁻¹) through a section of 1/8" PFA tubing (Swagelok®). The feed solution was installed on a precision scale for accurate flow rate monitoring. A dome-type back-pressure regulator (BPR, Zaiput Flow Technologies®) was inserted downstream the reactor. The gas flow rate was controlled with a Bronkhorst® F210CTM mass flow controller (MFC).

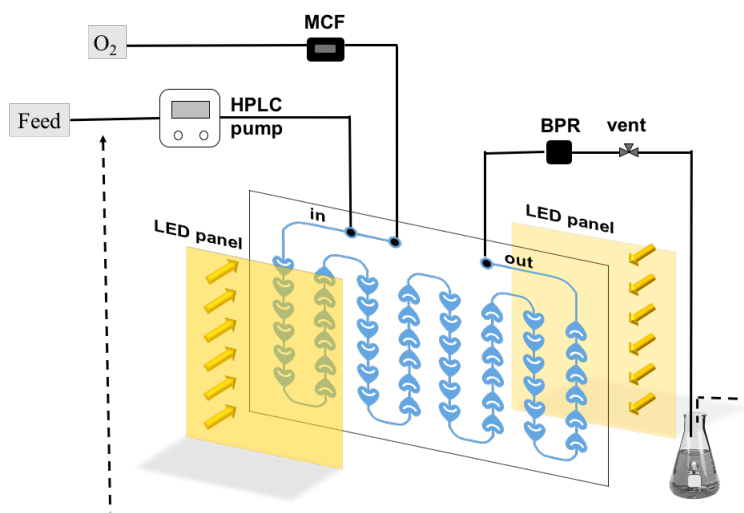


Figure S11. Continuous-Flow setup

6.2 Residence time calculation

The residence time is calculated according to Equation S1:

$$\text{Residence time (min)} = \frac{\text{Internal volume (mL)}}{\text{Flow rate (mL min}^{-1}\text{)}} \quad (\text{Equation S1})$$

The total flow rate combines the individual flow rates of all fluids fed into the reactor. The gas flow rate is calculated from the flow rate measured by the MFC according to Equation S2-3:

$$n_{O_2} = \frac{P_N(atm)V_N(L)}{R(L.atm.mol^{-1}.K^{-1})T_N(K)} \text{ (Equation S2)}$$

$$V_{real} = \frac{n_{O_2}RT_{real}}{P_{real}} \text{ (Equation S3)}$$

For example, the actual volume of O₂ delivered under 5 barg and 30°C when the MFC is set at 1 mL min⁻¹ is 0.22 mL min⁻¹ (see Equations S4-5):

$$n_{O_2} = \frac{P_N(atm)V_N(L)}{R(L.atm.mol^{-1}.K^{-1})T_N(K)} = \frac{1*0.001}{0.082*273.15} = 0.0446 \text{ mmol} \text{ (Equation S4)}$$

$$V_{real} = \frac{n_{O_2}RT_{real}}{P_{real}} = \frac{0.0000446*0.082*303.15}{5} = 0.22 \text{ mL} \text{ (Equation S5)}$$

Residence (irradiation) time within the reactor time was calculated according to Equation S1:

$$\text{Residence Time} = \frac{\text{Internal volume (mL)}}{\text{Flow rate liquid phase} \left(\frac{\text{mL}}{\text{min}}\right) + \text{Real flow rate gas phase} \left(\frac{\text{mL}}{\text{min}}\right)}$$

$$= \frac{2.7}{0.5 + 0.22} \text{ min} = 3.75 \text{ min}$$

$$\text{Total Residence Time} = \frac{\text{total time}}{\frac{V_{mixture}}{\text{flow rate liquid phase}}} \times \text{Residence Time}$$

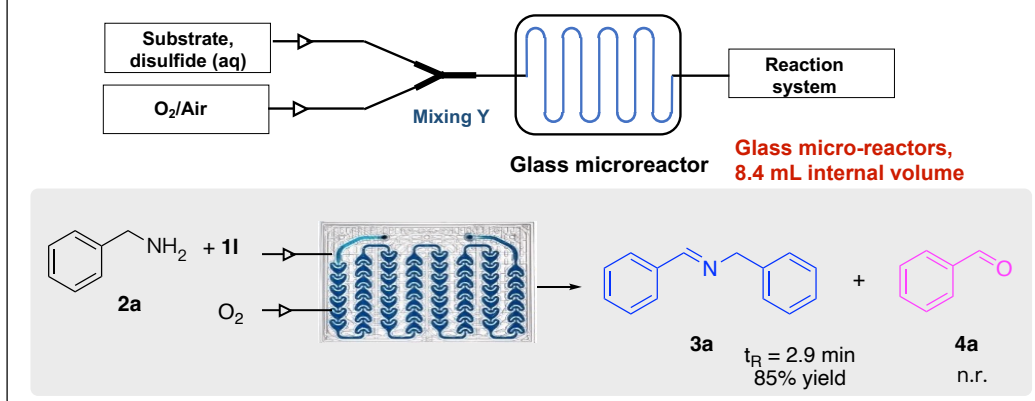
$$= \frac{240\text{min}}{10\text{mL}/0.5\text{mL min}^{-1}} \times 3.75 \text{ min} = 45 \text{ min}$$

6.3 Typical runs in Procedure A

The HPLC pump used to deliver a solution of **2a** (0.0550 g, 5 mmol, 1.0 equiv), disulfide **11** (10 mol%) in 15 mL CHCl₃ was set to 2.0 mL min⁻¹ and the oxygen flow was set to 20.0 mL min⁻¹ with the MFC, and both fluids were conveyed to the continuous-flow photoreactor through perfluoroalkoxyalkane (PFA) tubing (1/8" O.D.). Mixing and irradiation occurred along the entire reactor channel (2.7 mL internal volume, min residence time).

Table S8. Process optimization for the preparation of **3a**

Procedure A



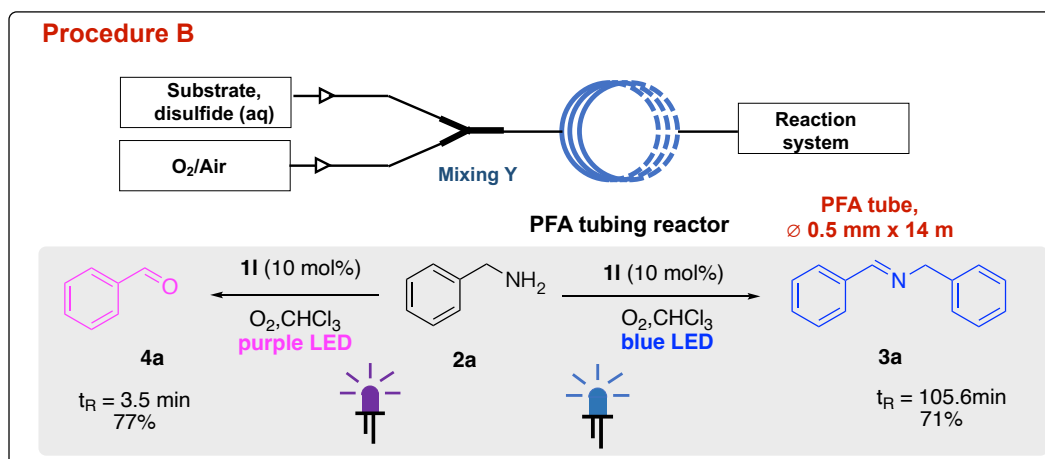
| Entry | feed (mL min ⁻¹) | O ₂ | T (°C) | back- pressure | light resource | Total time | Restime | Conv. ^b |
|-------|---------------------------------|----------------|--------|-------------------|-------------------|------------|---------|--------------------|
| 1 | 2.0 | 5.0 | 30 | 0 | 4000 K | 4h | -- | trace |
| 2 | 2.0 | 20.0 | 30 | 0 | 4000 K | 4h | -- | 21 |
| 3 | 2.0 | 20.0 | 30 | 0 | 385 nm | 3h | -- | >95 |

^a Reactions were carried out using continuous-flow reactor. ^b Determined by ¹H-NMR analysis. ^c Isolated yield.

6.4 Homemade setup in PFA tubing reactor (Procedure B)

Preliminary experiments were carried out with a homemade setup. A 2.74 mL PFA reactor coil (14 m, 0.25 mm I.D.) was constructed around a glass tube with water. The PFA reactor was covered with metal pipe sleeve to increase the efficiency of the set-up. Reagents and O₂ (air) were introduced by two separate feed streams.

Procedure B



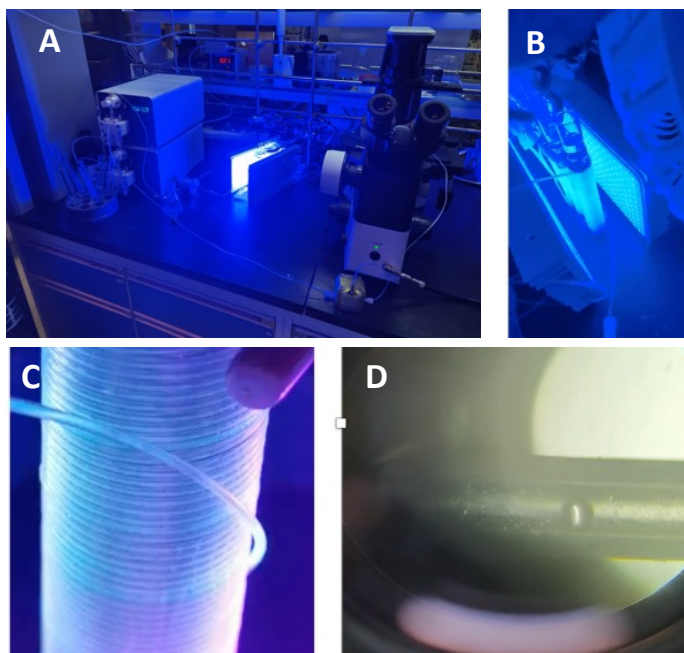
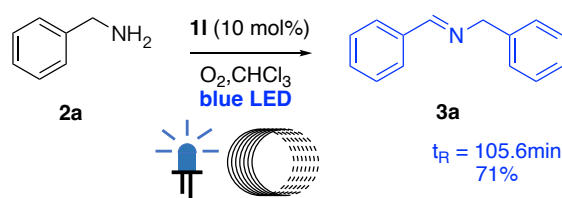


Figure S12. Schematic diagram of continuous flow photocatalytic benzylamine oxidation system

The HPLC pump used to deliver a solution of **2a** (0.536 g, 5 mmol, 1.0 equiv), disulfide **11** (0.166g, 10 mol%) in 10 mL CHCl_3 was set to 2.0 mL min^{-1} and the air flow was set to 8.0 mL min^{-1} with the MFC, and both fluids were conveyed to the continuous-flow photoreactor through perfluoroalkoxyalkane (PFA) tubing (1/8" O.D.). Mixing and irradiation occurred along the reactor channel.

Table S9. Continuous flow photocatalytic benzylamine oxidation conditions in PFA tube



| Entry | 2a (mmol) | 11 (eq) | feed 1 (mL min ⁻¹) | O ₂ | T (°C) | back- pressure | light resource | Total time | Res. time | Conv. ^a (yield) ^b |
|-------|---------------------|-------------------|-----------------------------------|----------------|-----------|-------------------|-------------------|---------------|--------------|--|
| 1 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 1h | 6.6 min | 3.0% |
| 2 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 2h | 13.2 min | 6.6% |
| 3 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 3h | 19.8min | 10.3% |
| 4 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 4h | 10.6 min | 17.8% |
| 5 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 5h | 33.0 min | 17.8% |

| | | | | | | | | | | |
|----|-----|-----|-----|-----|----|---|--------|------|-----------|-------|
| 6 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 6h | 39.6 min | 19.0% |
| 7 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 6h | 46.2min | 22.3% |
| 8 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 7.5h | 49.5 min | 23.9% |
| 9 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 9h | 59.4 min | 30.6% |
| 10 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 11h | 72.6 min | 37.3% |
| 11 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 12h | 79.2 min | 54.9% |
| 12 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 14h | 92.4 min | 62.9% |
| 13 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 15h | 99.0 min | 69.0% |
| 14 | 5.0 | 0.1 | 2.0 | 8.0 | 30 | 0 | 445 nm | 16h | 105.6 min | 70.9% |

^aThe HPLC pump used to deliver a solution of **2a** (0.1071 g, 1 mmol, 1.0 equiv) and disulfide **11** (0.0332 g, 10 mol%) in 5 mL CHCl₃ was set to 2.0 mL min⁻¹ and the air flow was set to 2 mL min⁻¹ with the MFC, and both fluids were conveyed to the perfluoroalkoxyalkane (PFA) tubing (ID 0.5 mm, 14 m). Irradiation with blue LED.
^bDetermined by ¹H-NMR.

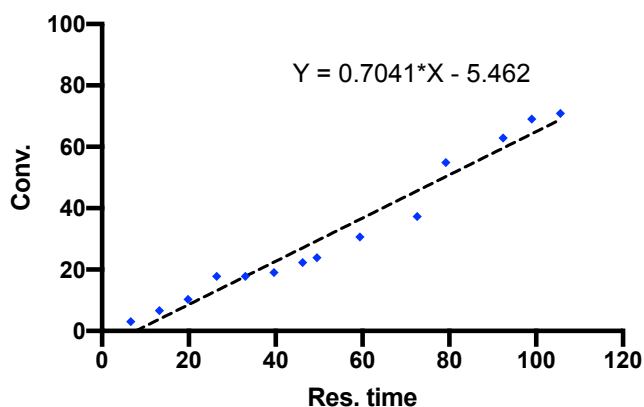


Figure S13. Conversion rate vs. time curve of benzylamine oxidation to benzaldehyde reaction process

In previous experiments, it was observed that the oxidative deamination reaction with 390 nm violet light as the excitation source under intermittent conditions was blocked in the expansion of the continuous flow strategy due to the extinction properties of the glass material and the presence of a thermally conductive medium between the reaction pathway and the light source. Therefore, a tubular reactor was constructed using PFA tubes. A Φ 0.5 mm PFA tube was wrapped around the outer wall of a measuring cylinder, which was filled with water to cool the PFA tube. The PFA tubes were 3.6 m long and held 0.71 mL of liquid. 390 nm Kessil light sources were used for side illumination and the reaction was set up for air cooling at room temperature.

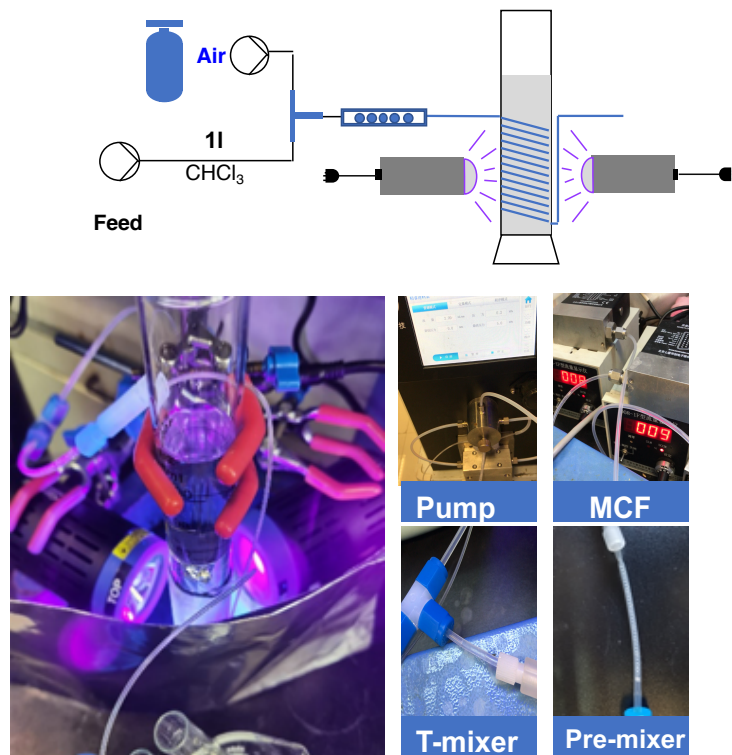
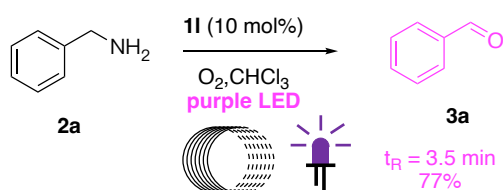


Figure S14. Schematic diagram of continuous flow photocatalytic oxidation of benzylamine

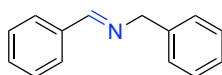
Table S10. Continuous flow photocatalytic benzylamine oxidation conditions



| Entry | Air | Total time | Res. time | -CHO ^b | C=N ^b |
|----------------|-----|------------|-----------|-------------------|------------------|
| 1 ^c | 14 | 6h | 11.0 | trace | 52 |
| 2 | 20 | 3h | 4.2 | trace | 32 |
| 3 | 25 | 1h | 1.2 | 23 | trace |
| 4 | 25 | 2h | 2.4 | 68 | trace |
| 5 | 30 | 1h | 1.0 | 31 | trace |
| 6 | 30 | 4h | 4.1 | 65 | trace |
| 7 | 35 | 2h | 1.8 | 56 | trace |
| 8 | 35 | 4h | 3.5 | 77 | trace |

^aReactions were carried out using continuous-flow reactor, feed 5 mL/min, **1l** (0.2 equiv.). ^bDetermined by ¹H-NMR analysis. ^c**1l** (0.1 equiv.)

7 Characterization data for all products



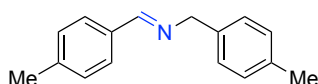
N-benzyl-1-phenylmethanimine (**3a**)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/Et₃N = 5/1/0.01, R_f = 0.8) to give **3a** as yellow solid: 80.06 mg, 82% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 1.5 Hz, 1H), 7.86 – 7.73 (m, 2H), 7.41 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.34 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.21 (m, 1H), 4.83 (d, *J* = 1.5 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 161.99, 139.31, 136.18, 130.77, 128.61, 128.50, 128.28, 127.99, 126.99, 65.07.

HRMS (m/z): (ESI) calculated for [C₁₄H₁₃N+H]⁺ 196.1121; found 196.1117.



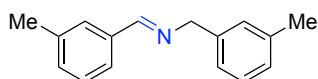
N-(4-Methylbenzylidene)-4-methylphenylmethylamine (**3b**)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/Et₃N = 5/1/0.01) to give **3b** as white solid: 96.02 mg, 86% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.76 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 161.67, 140.96, 136.50, 136.38, 133.66, 129.30, 129.16, 128.25, 127.96, 64.82, 21.52, 21.12.

HRMS (m/z): (ESI) calculated for [C₁₆H₁₇N+H]⁺ 224.1434; found 224.1436;



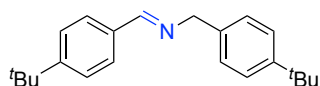
N-(4-Methylbenzylidene)-4-methylphenylmethylamine (**3c**)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/Et₃N = 5/1/0.01) to give **3c** as white solid: 88.21 mg, 79% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 1.5 Hz, 1H), 7.64 (s, 1H), 7.57 – 7.50 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.16 – 7.10 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 4.77 (d, *J* = 1.4 Hz, 2H), 2.37 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 162.13, 139.19, 138.35, 138.13, 136.15, 131.58, 128.79, 128.50, 128.48, 128.41, 127.75, 126.61, 125.89, 125.33, 125.10, 122.72, 121.33, 65.17, 21.46, 21.29.

HRMS (m/z): (ESI) calculated for [C₁₆H₁₇N+H]⁺ 224.1434; found 224.1436;



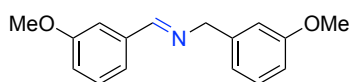
(E)-N-(4-(tert-butyl)benzyl)-1-(4-(tert-butyl)phenyl)methanimine(3d)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/Et₃N = 5/1/0.01) to give **3d** as white solid: 132.22 mg, 86% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 1.3 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.39 (m, 2H), 7.40 – 7.31 (m, 2H), 7.29 – 7.20 (m, 2H), 4.78 (d, *J* = 1.3 Hz, 2H), 1.33 (s, 9H), 1.31 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 161.70, 154.11, 149.80, 136.46, 133.59, 128.09, 127.69, 125.54, 125.39, 122.72, 121.33, 64.83, 34.92, 34.48, 31.41, 31.25.

HRMS (*m/z*): (ESI) calculated for [C₂₂H₂₉N + H]⁺ 308.2373; found 308.2366;



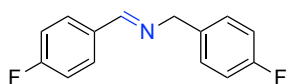
(E)-N-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (3f)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/Et₃N = 5/1/0.01) to give **3f** as white solid: 95.74mg, 75% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.37 – 7.21 (m, 3H), 7.08 – 6.97 (m, 1H), 6.95 – 6.86 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.80 (s, 2H), 3.85 (s, 3H), 3.81 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 162.09, 159.92, 159.79, 140.82, 137.57, 129.59, 129.51, 121.69, 120.35, 117.63, 113.66, 112.48, 111.65, 64.91, 55.41, 55.24.

HRMS (*m/z*): (ESI) calculated for [C₁₆H₁₇NO₂ + H]⁺ 256.1332; found 256.1335;



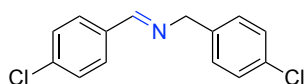
(E)-N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (3i)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/Et₃N = 5/1/0.01) to give **3i** as white solid: 83.25 mg, 72% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.83 – 7.69 (m, 2H), 7.32 – 7.26 (m, 2H), 7.14 – 7.07 (m, 2H), 7.06 – 6.99 (m, 2H), 4.76 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 165.65, 163.20, 163.15, 160.52, 134.95, 134.91, 132.32, 130.21, 130.12, 129.50, 129.42, 115.85, 115.63, 115.42, 115.20, 64.16.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{F}_2\text{N} + \text{H}]^+$ 232.0932; found 232.0937;



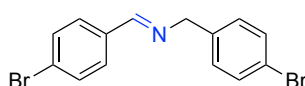
N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (3j)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3j** as white solid: 84.54mg, 67% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, J = 1.5 Hz, 1H), 7.71 (d, J = 8.5 Hz, 2H), 7.45 – 7.35 (m, 2H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 4.76 (d, J = 1.5 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 160.80, 137.62, 136.88, 134.48, 132.84, 129.45, 129.25, 128.93, 128.64, 64.17.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{N} + \text{H}]^+$ 264.0341; found 264.0336;



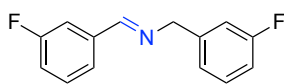
N-(4-bromobenzyl)-1-(4-bromophenyl)methanimine (3k)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3k** as white solid: 107.68mg, 61% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 (t, J = 1.4 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.58 – 7.52 (m, 2H), 7.50 – 7.41 (m, 2H), 7.24 – 7.16 (m, 2H), 4.74 (d, J = 1.4 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 160.94, 138.08, 134.87, 131.88, 131.58, 129.65, 129.61, 125.34, 120.91, 64.20.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{Br}_2\text{N} + \text{H}]^+$ 351.9331; found 351.9338;



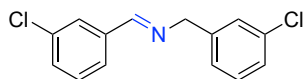
(E)-N-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (3l)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3l** as white solid: 89.03 mg, 77% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.87 (d, J = 1.6 Hz, 1H), 8.12 (dd, J = 7.6, 1.8 Hz, 1H), 7.43 (dd, J = 7.6, 1.8 Hz, 1H), 7.41 – 7.16 (m, 7H), 4.95 (d, J = 1.6 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 159.73, 136.84, 135.31, 133.44, 133.15, 131.73, 129.83, 129.68, 129.36, 128.48, 128.32, 127.03, 126.92, 62.20.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{F}_2\text{N} + \text{H}]^+$ 232.0932; found 232.0937;



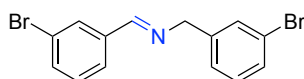
(E)-N-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine (3m)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3m** as white solid: 95.09 mg, 72% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, J = 1.6 Hz, 1H), 7.81 (t, J = 1.8 Hz, 1H), 7.62 (dt, J = 7.4, 1.5 Hz, 1H), 7.49 – 7.05 (m, 6H), 4.78 (d, J = 1.6 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 160.91, 141.05, 137.70, 134.88, 134.41, 130.91, 129.91, 129.80, 128.04, 127.97, 127.27, 126.67, 126.05, 64.28.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{N} + \text{H}]^+$ 264.0341; found 264.0336;



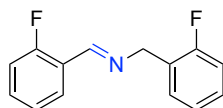
(E)-N-(3-bromobenzyl)-1-(3-bromophenyl)methanimine (3n)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3n** as white solid: 107.68mg, 58% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, J = 1.3 Hz, 1H), 7.96 (t, J = 1.8 Hz, 1H), 7.66 (dt, J = 7.7, 1.3 Hz, 1H), 7.55 (ddd, J = 8.0, 2.0, 1.1 Hz, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.40 (dt, J = 7.7, 1.7 Hz, 1H), 7.35 – 7.13 (m, 3H), 4.77 (d, J = 1.3 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 160.81, 141.31, 137.91, 133.84, 130.96, 130.92, 130.22, 130.18, 130.11, 127.13, 126.55, 122.98, 122.67, 64.25.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{Br}_2\text{N} + \text{H}]^+$ 351.9331; found 351.9338;



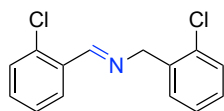
(E)-N-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (3o)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3o** as white solid: 85.56mg, 74% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.03 (td, J = 7.5, 1.9 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.25 (tdd, J = 7.5, 5.3, 1.9 Hz, 1H), 7.20 – 6.99 (m, 4H), 4.87 (s, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 163.57, 162.02, 161.06, 159.58, 156.07, 156.02, 132.46, 132.37, 130.19, 130.15, 128.84, 128.76, 127.86, 127.83, 126.21, 126.06, 124.36, 124.32, 124.19, 124.15, 123.78, 123.69, 115.87, 115.66, 115.38, 115.16, 58.54, 58.51.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{F}_2\text{N} + \text{H}]^+$ 232.0932; found 232.0937;



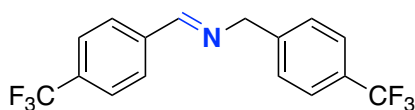
(E)-N-(2-chlorobenzyl)-1-(2-chlorophenyl)methanimine (3p)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3p** as white solid: 52.83mg, 40% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.37 (d, J = 1.5 Hz, 1H), 7.60 – 7.48 (m, 2H), 7.39 (td, J = 7.9, 5.6 Hz, 1H), 7.31 (td, J = 7.9, 5.9 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.06 (dt, J = 9.8, 2.0 Hz, 1H), 6.96 (td, J = 8.5, 2.6 Hz, 1H), 4.81 (d, J = 1.5 Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.76, 136.86, 135.34, 133.46, 133.16, 131.76, 129.85, 129.71, 129.38, 128.50, 128.35, 127.06, 126.95, 62.21.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{N} + \text{H}]^+$ 264.0341; found 264.0336;



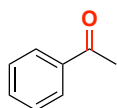
(E)-N-(4-(trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)phenyl)methanimine (3r)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate/ Et_3N = 5/1/0.01) to give **3r** as white solid: 120.90 mg, 73% yield.

^1H NMR (600 MHz, Chloroform- d) δ 8.46 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 4.89 (s, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 161.12, 143.00, 138.98, 128.53, 128.13, 125.68, 125.65, 125.51, 125.49, 122.71, 121.33, 64.41.

HRMS (m/z): (ESI) calculated for $[\text{C}_{16}\text{H}_{11}\text{F}_6\text{N} + \text{H}]^+$ 332.0868; found 332.0872;



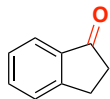
Acetophenone(7a)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f = 0.6) to give **7a** as colorless oil: 43.85 mg, 73% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.99 – 7.88 (m, 2H), 7.58 – 7.49 (m, 1H), 7.44 (tt, J = 6.7, 1.4 Hz, 2H), 2.58 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 198.00, 137.06, 133.07, 128.54, 128.26, 26.53.

HRMS (m/z): (ESI) calculated for $[\text{C}_8\text{H}_8\text{O} + \text{H}]^+$ 121.0648; found 121.0652;



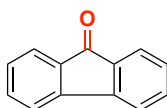
2,3-dihydro-1H-inden-1-one (7b)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f =0.3) to give **7b** as white solid: 49.56mg, 75% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.29 – 6.82 (m, 4H), 4.99 – 2.91 (m, 2H), 2.62 (q, J = 8.8, 5.4 Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 206.95, 155.14, 137.00, 134.56, 127.21, 126.70, 123.56, 36.16, 25.76.

HRMS (m/z): (ESI) calculated for $[\text{C}_9\text{H}_8\text{O} + \text{H}]^+$ 133.0648; found 133.0650;



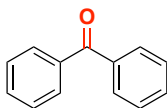
9H-fluoren-9-one (7c)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f =0.6) to give **7c** as white solid: 81.09 mg, 90% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.57 (d, J = 7.3 Hz, 2H), 7.47 – 7.33 (m, 4H), 7.20 (td, J = 7.3, 1.5 Hz, 2H)

^{13}C NMR (151 MHz, CDCl_3) δ 180.01, 137.31, 132.30, 129.91, 129.28, 126.34, 126.02.

HRMS (m/z): (ESI) calculated for $[\text{C}_{13}\text{H}_8\text{O} + \text{H}]^+$ 181.0648; found 181.0655;



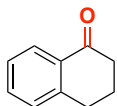
Benzophenone (7d)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f =0.6) to give **7d** as white solid: 84.73 mg, 93% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.01 – 7.71 (m, 4H), 7.66 – 7.53 (m, 2H), 7.47 (dd, J = 8.4, 7.0 Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 206.95, 155.14, 137.00, 134.56, 127.21, 126.70, 123.56, 36.16, 25.76.

HRMS (m/z): (ESI) calculated for $[\text{C}_{13}\text{H}_{10}\text{O} + \text{H}]^+$ 183.0804; found 183.0808;



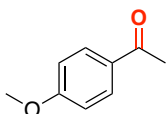
3,4-dihydronaphthalen-1(2H)-one (7e)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f=0.6) to give **7e** as white solid: 64.32 mg, 88% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.46 (td, *J* = 7.8, 1.4 Hz, 1H), 7.36 – 7.10 (m, 2H), 2.96 (t, *J* = 6.1 Hz, 2H), 2.65 (t, *J* = 7.3, 6.1 Hz, 2H), 2.27 – 1.97 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 198.38, 144.51, 133.40, 132.62, 128.79, 127.15, 126.63, 39.18, 29.71, 23.30.

HRMS (*m/z*): (ESI) calculated for [C₁₀H₁₀O + H]⁺ 147.0804; found 147.0806;



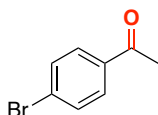
1-(4-methoxyphenyl)ethan-1-one (7f)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f=0.6) to give **7f** as colorless oil: 66.07 mg, 88% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 197.79, 159.75, 138.41, 129.53, 121.04, 119.45, 112.34, 55.30, 26.62.

HRMS (*m/z*): (ESI) calculated for [C₉H₁₀O₂ + H]⁺ 151.0754; found 151.0758;



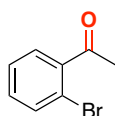
1-(4-bromophenyl)ethan-1-one (7g)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f=0.6) to give **7g** as colorless oil 66.68 mg, 68% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 2.58 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 196.96, 135.80, 131.87, 129.84, 128.27, 26.54.

HRMS (*m/z*): (ESI) calculated for [C₈H₇BrO + H]⁺ 198.9753; found 198.9755;



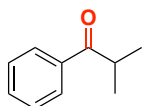
1-(2-bromophenyl)ethan-1-one (7h)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate =10/1, Rf=0.6) to give **7h** as colorless oil 40.81mg, 41% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.61 (dd, J = 8.0, 1.3 Hz, 1H), 7.46 (dd, J = 7.6, 1.8 Hz, 1H), 7.37 (td, J = 7.6, 1.3 Hz, 1H), 2.63 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 200.21, 139.03, 131.98, 131.17, 130.59, 129.36, 126.92, 30.60.

HRMS (m/z): (ESI) calculated for $[\text{C}_8\text{H}_7\text{BrO} + \text{H}]^+$ 198.9753; found 198.9755;



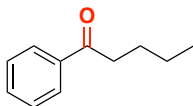
2-methyl-1-phenylpropan-1-one (7j)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate =10/1, Rf=0.6) to give **7j** as colorless oil 25.20 mg, 34% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.02 – 7.92 (m, 2H), 7.62 – 7.51 (m, 1H), 7.46 (dd, J = 8.2, 6.8 Hz, 2H), 3.57 (h, J = 6.8 Hz, 1H), 1.22 (d, J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 204.49, 136.21, 132.79, 128.60, 128.30, 35.33, 19.14.

HRMS (m/z): (ESI) calculated for $[\text{C}_{10}\text{H}_{12}\text{O} + \text{H}]^+$ 149.0961; found 149.0963;



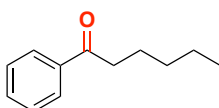
1-phenylpentan-1-one (7k)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate =10/1, Rf=0.5) to give **7k** as colorless oil 49.35 mg, 56% yield.

^1H NMR (600 MHz, Chloroform- d) δ 7.96 (dt, J = 7.2, 1.3 Hz, 2H), 7.55 (td, J = 7.2, 1.3 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 2.97 (t, J = 7.4 Hz, 2H), 1.72 (p, J = 7.4 Hz, 2H), 1.41 (h, J = 7.4 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 200.60, 137.12, 132.87, 128.55, 128.07, 38.34, 26.50, 22.50, 13.95.

HRMS (m/z): (ESI) calculated for $[\text{C}_{10}\text{H}_{12}\text{O} + \text{H}]^+$ 149.0961; found 149.0963;



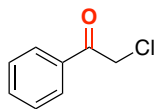
1-phenylhexan-1-one (7l)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate =10/1, Rf=0.5) to give **7l** as colorless oil 49.40 mg, 56% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.43 – 7.92 (m, 2H), 7.61 – 7.50 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.74 (dd, J = 9.1, 5.7 Hz, 2H), 1.37 (q, J = 3.8 Hz, 4H), 1.13 – 0.77 (m, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 200.63, 137.12, 132.89, 128.57, 128.08, 38.60, 31.57, 24.08, 22.56, 13.99.

HRMS (m/z): (ESI) calculated for $[\text{C}_{12}\text{H}_{16}\text{O} + \text{H}]^+$ 177.1274; found 177.1276;



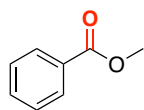
2-chloro-1-phenylethan-1-one (7m)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f = 0.5) to give **3l** as colorless oil 27.05 mg, 35% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.89 (d, J = 7.6 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.43 (t, J = 7.6 Hz, 2H), 4.65 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 191.10, 134.03, 128.93, 128.54, 46.02.

HRMS (m/z): (ESI) calculated for $[\text{C}_8\text{H}_8\text{ClO} + \text{H}]^+$ 155.0258; found 155.0262;



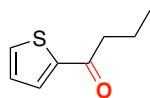
methyl benzoate (7n)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f = 0.5) to give **7n** as colorless oil 31.31 mg, 46% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.13 – 7.92 (m, 2H), 7.68 – 7.49 (m, 1H), 7.50 – 7.35 (m, 2H), 3.91 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 167.08, 132.91, 130.16, 129.57, 128.36, 52.06.

HRMS (m/z): (ESI) calculated for $[\text{C}_8\text{H}_9\text{O}_2 + \text{H}]^+$ 137.0597; found 137.0597;



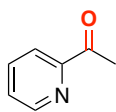
1-(thiophen-2-yl)butan-1-one (7o)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f = 0.5) to give **7o** as colorless oil 32.39 mg, 42% yield.

^1H NMR (400 MHz, Chloroform- d) δ 7.85 – 6.83 (m, 1H), 6.59 (t, J = 7.3 Hz, 1H), 6.45 (d, J = 7.3 Hz, 1H), 3.68 – 3.08 (m, 2H), 2.75 (t, J = 6.4 Hz, 2H), 1.92 (p, J = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 193.38, 144.60, 133.28, 131.64, 128.01, 41.32, 18.23, 13.87.

HRMS (m/z): (ESI) calculated for $[C_8H_{10}OS + H]^+$ 155.0525; found 155.0529;



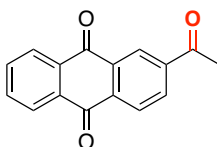
1-(pyridin-2-yl)ethan-1-one (7p)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f = 0.5) to give **7p** as colorless oil 8.48 mg, 14% yield.

1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 4.0 Hz, 1H), 7.98 (d, J = 8.0, 8.0 Hz, 1H), 7.81-7.74 (m, 1H), 7.44-7.39 (m, 1H), 2.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.89, 153.44, 148.89, 136.72, 127.00, 121.47, 25.65.

HRMS (m/z): (ESI) calculated for $[C_7H_7NO + H]^+$ 122.0600; found 122.0602;



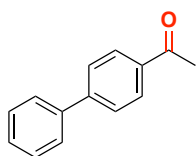
2-acetylanthracene-9,10-dione (7q)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f = 0.5) to give **7q** as yellow solid 111.36 mg, 89% yield.

1H NMR (400 MHz, Chloroform- d) δ 8.74 (d, J = 1.6 Hz, 1H), 8.56 – 8.13 (m, 4H), 7.82 (dd, J = 5.9, 3.3 Hz, 2H), 2.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.70, 182.31, 182.25, 140.91, 135.88, 134.47, 133.58, 133.29, 133.25, 132.85, 127.75, 127.38, 127.35, 127.26, 27.03.

HRMS (m/z): (ESI) calculated for $[C_{16}H_{10}O_3 + H]^+$ 251.0703; found 251.0705;



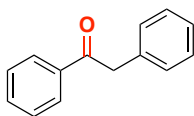
1-([1,1'-biphenyl]-4-yl)ethan-1-one (7r)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, R_f = 0.5) to give **7r** as yellow solid 88.31 mg, 90% yield.

1H NMR (400 MHz, Chloroform- d) δ 8.09 – 7.99 (m, 2H), 7.77 – 7.65 (m, 2H), 7.66 – 7.60 (m, 2H), 7.55 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 2.64 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 197.76, 145.76, 139.86, 135.87, 129.01, 128.96, 128.29, 127.30, 127.24, 26.70.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{12}\text{O}+\text{H}]^+$ 197.0961; found 197.0961;



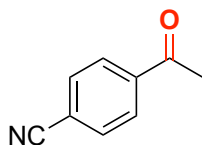
1,2-diphenylethan-1-one (7s)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate =10/1, R_f =0.5) to give **7s** as white solid 59.85 mg, 61% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.10 – 7.97 (m, 2H), 7.77 – 7.66 (m, 2H), 7.65 – 7.60 (m, 2H), 7.54 – 7.44 (m, 2H), 7.43 – 7.34 (m, 1H), 2.64 (d, J = 1.0 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 197.67, 136.62, 134.56, 133.20, 130.21, 129.50, 128.71, 128.67, 128.65, 128.52, 126.92, 45.53.

HRMS (m/z): (ESI) calculated for $[\text{C}_{14}\text{H}_{12}\text{O}+\text{H}]^+$ 197.0961; found 197.0961;



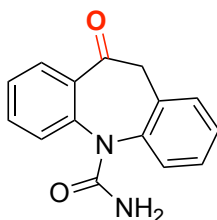
4-acetylbenzonitrile (7u)

Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate =10/1, R_f =0.5) to give **7u** as white solid 45.73 mg, 63% yield.

^1H NMR (600 MHz, Chloroform- d) δ 8.05 (d, J = 8.4 Hz, 2H), 7.81 – 7.73 (m, 2H), 2.65 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 196.54, 132.55, 128.72, 116.47, 26.77.

HRMS (m/z): (ESI) calculated for $[\text{C}_9\text{H}_7\text{ON}+\text{H}]^+$ 146.1685; found 146.1687;



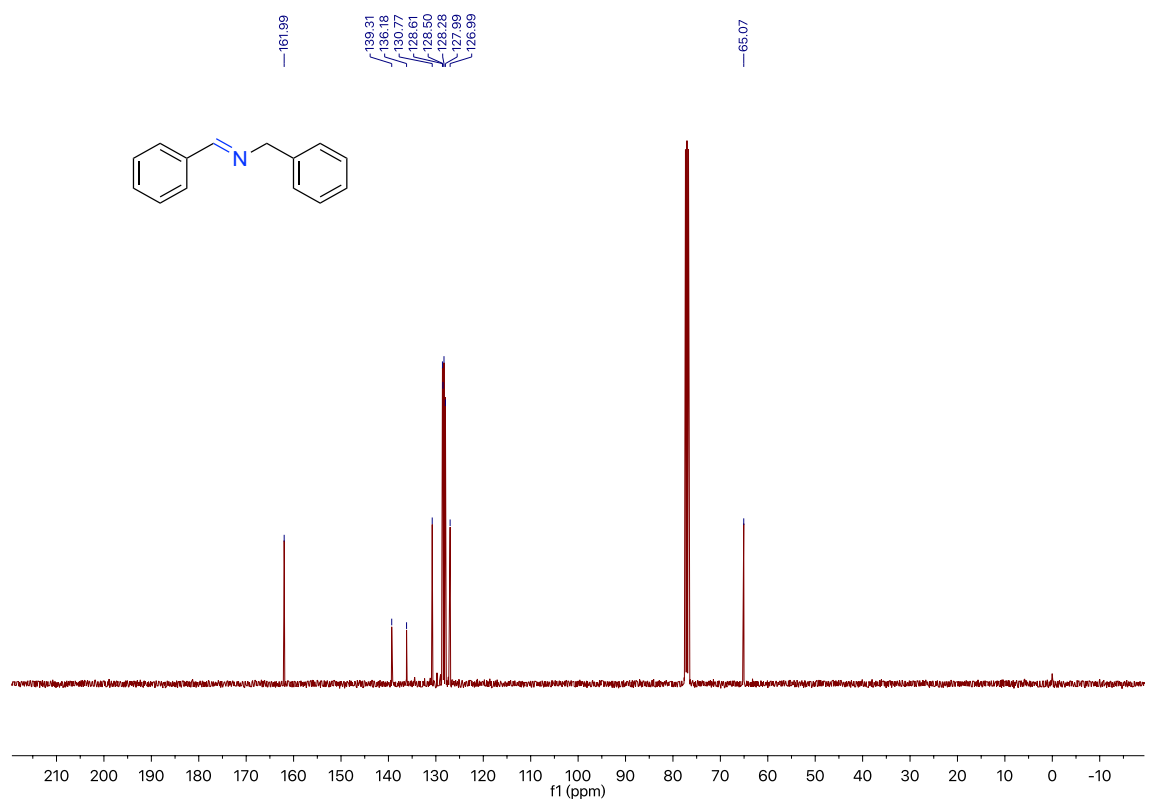
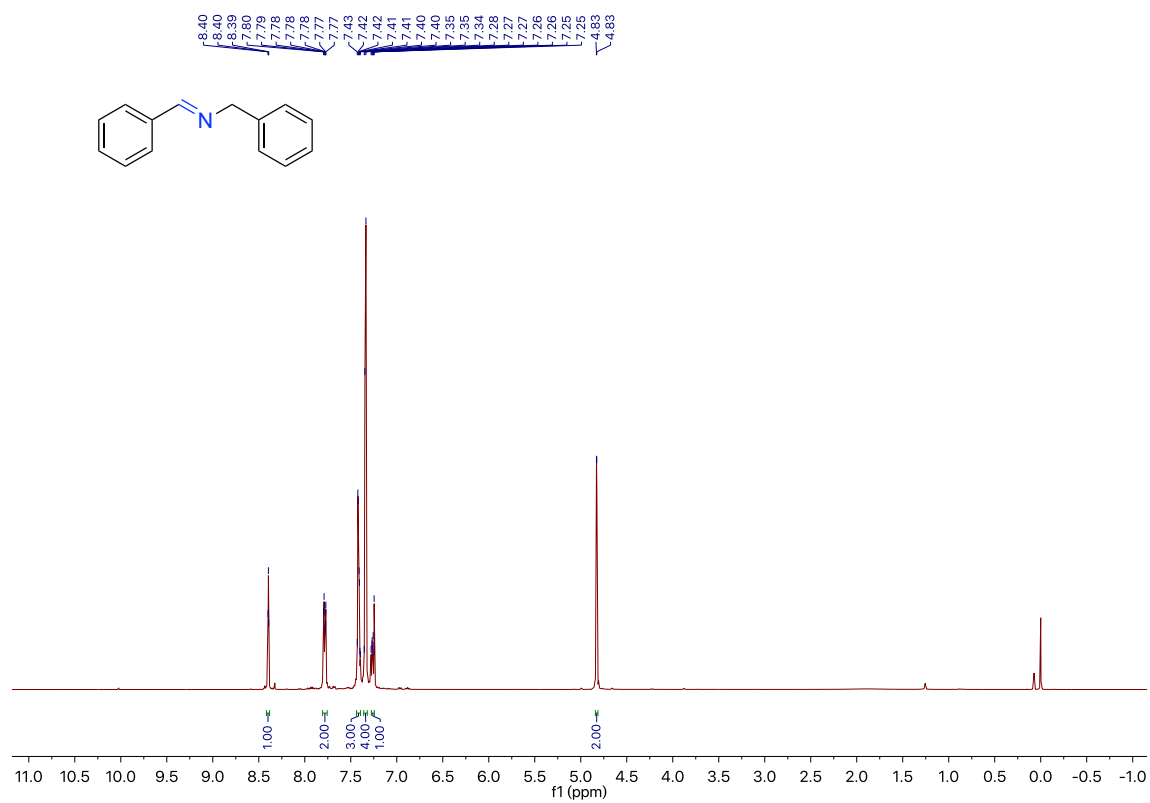
10-oxo-10,11-dihydro-5H-dibenzo[b,f]azepine-5-carboxamide (7s)

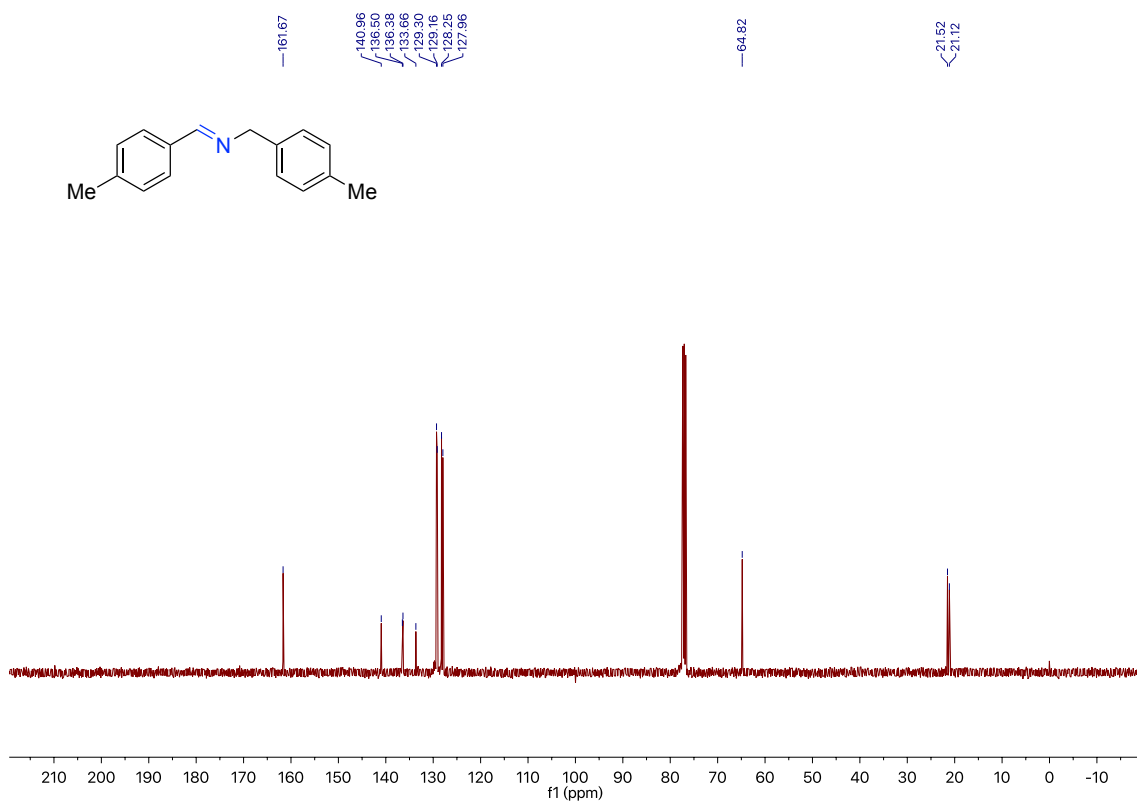
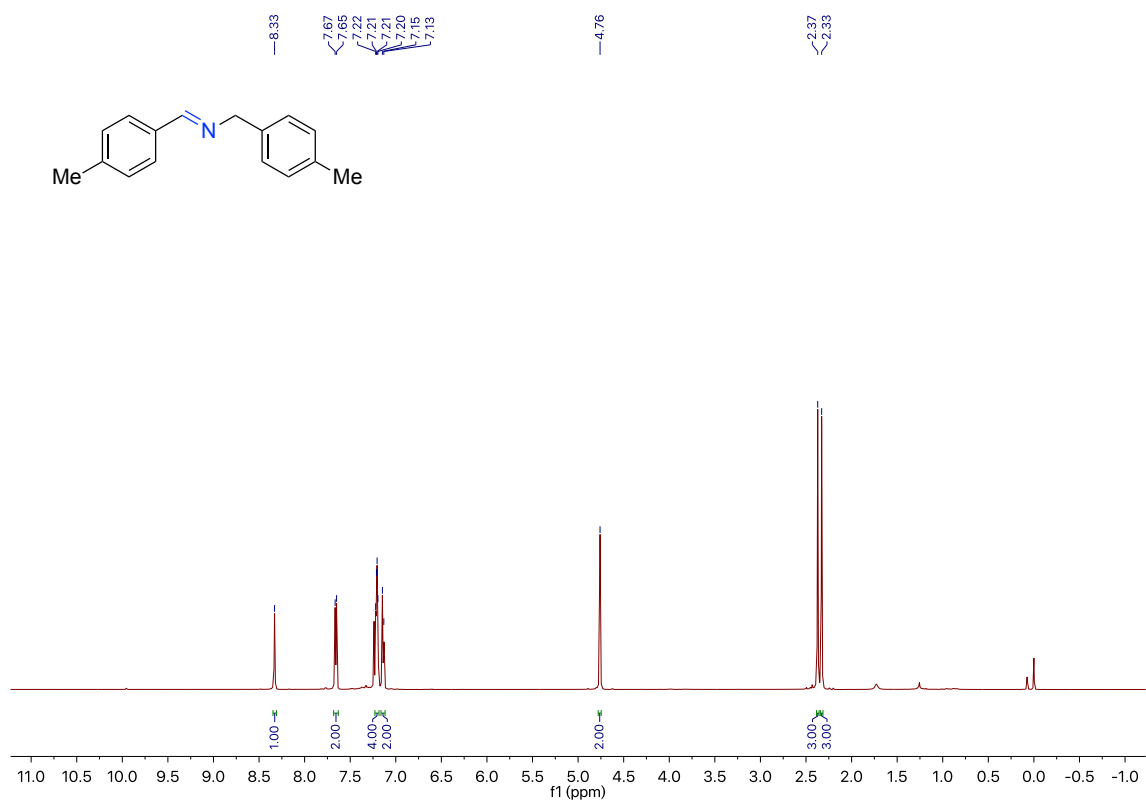
Prepared according to the general procedure with a reaction time of 16 h. After column chromatography (silica gel, petroleum ether/ether acetate =5/1, R_f =0.5) to give **7s** as white solid 52.93 mg, 42% yield.

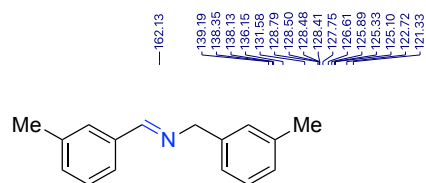
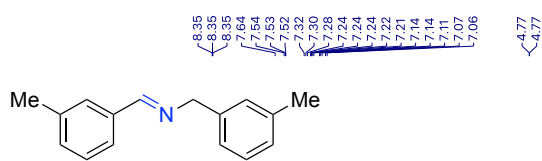
^1H NMR (600 MHz, Chloroform- d) δ 8.10 (d, J = 8.1 Hz, 1H), 7.74 – 7.55 (m, 2H), 7.52 – 7.12 (m, 5H), 4.97 (s, 2H), 4.45 (d, J = 14.1 Hz, 1H), 3.85 (d, J = 14.1 Hz, 1H).

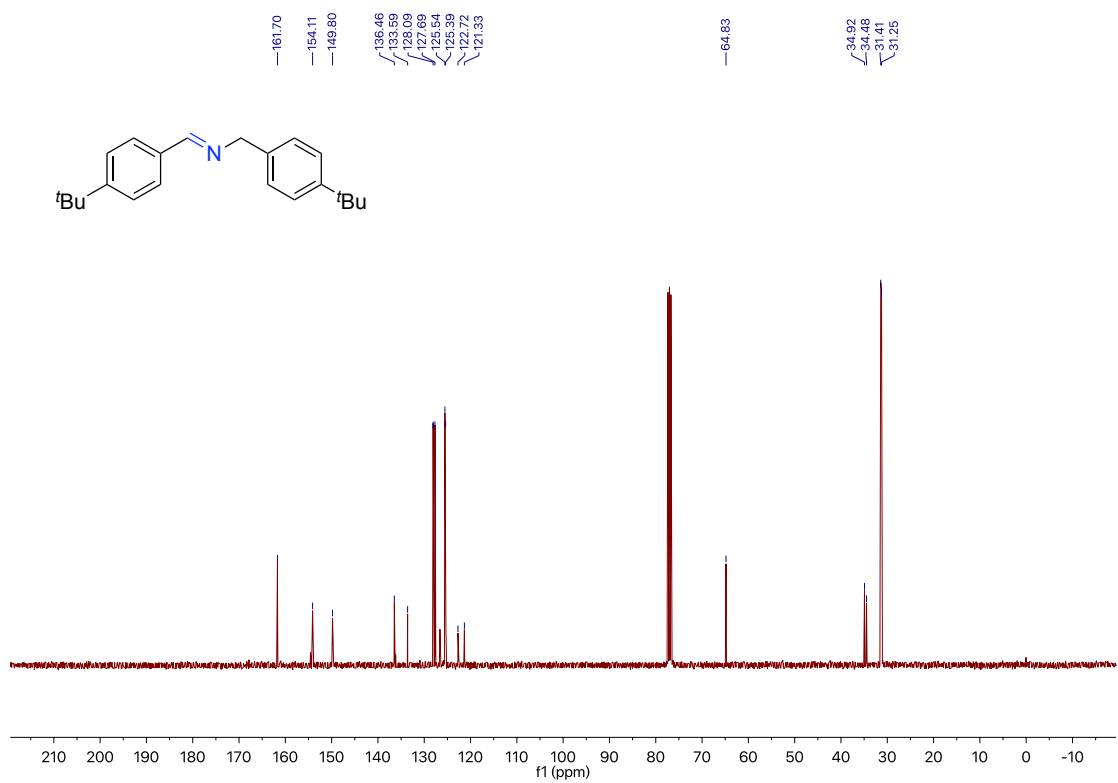
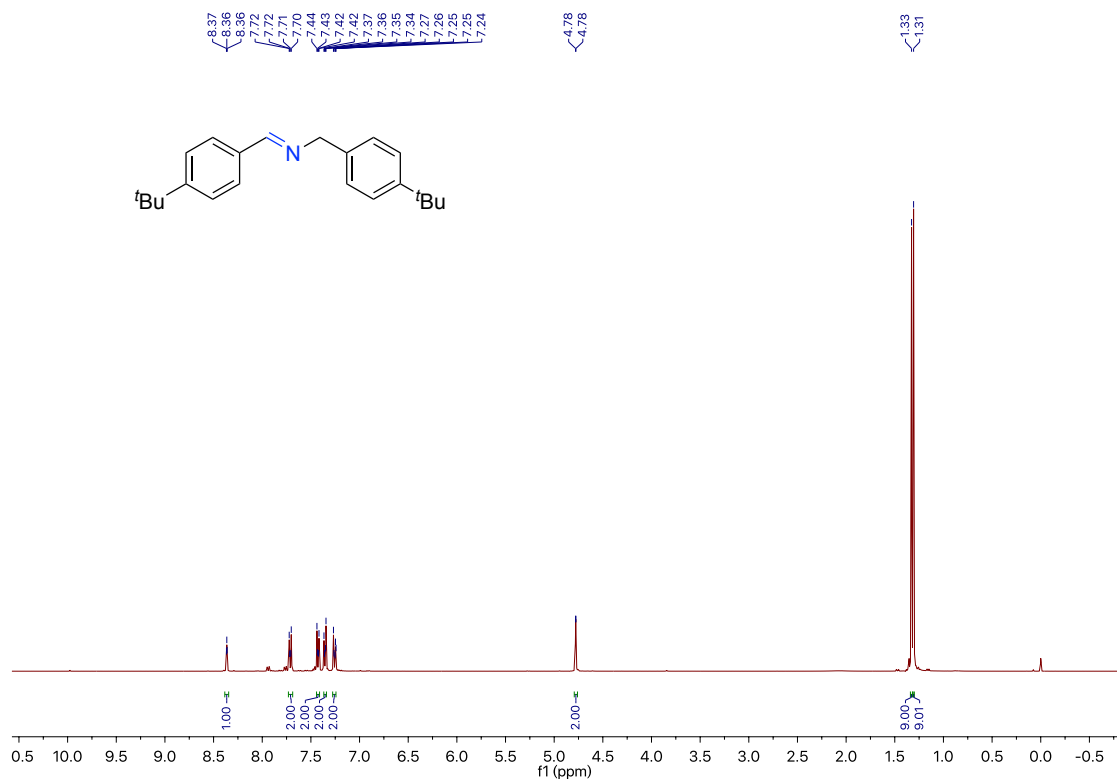
^{13}C NMR (151 MHz, CDCl_3) δ 191.83, 155.78, 143.08, 141.34, 134.01, 130.70, 130.26, 129.92, 129.38, 129.05, 128.73, 127.81, 127.39, 49.07.

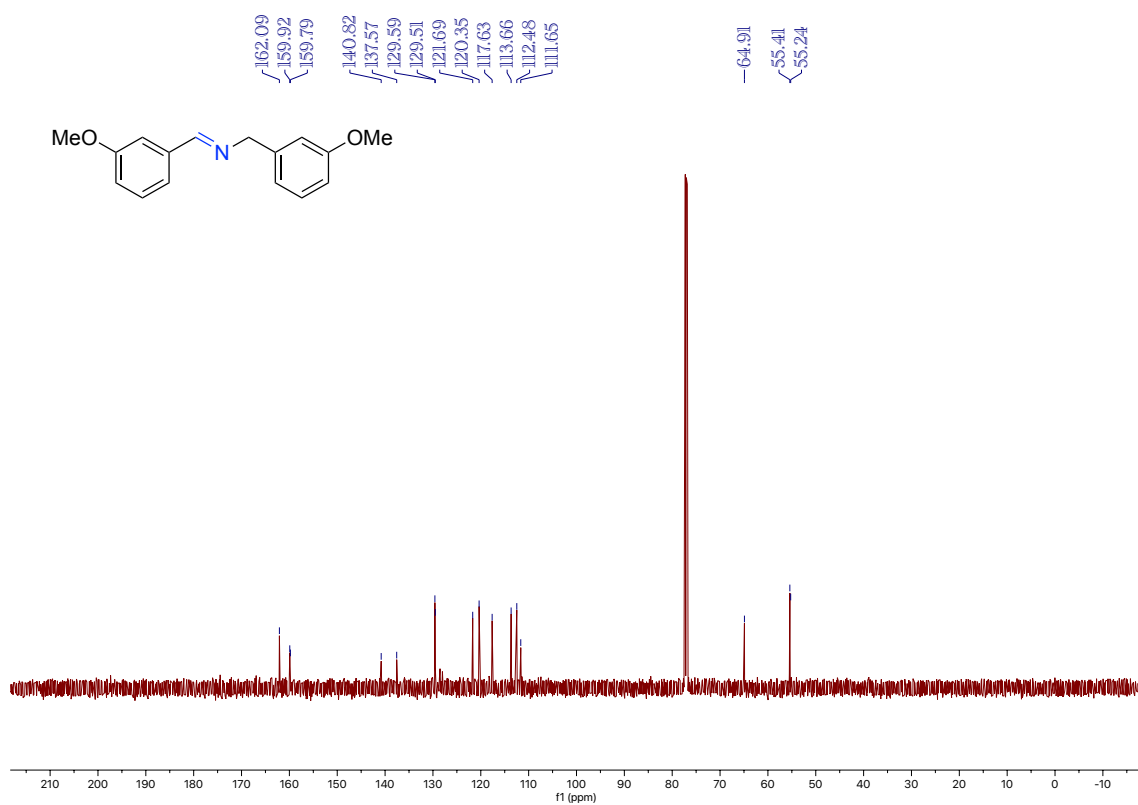
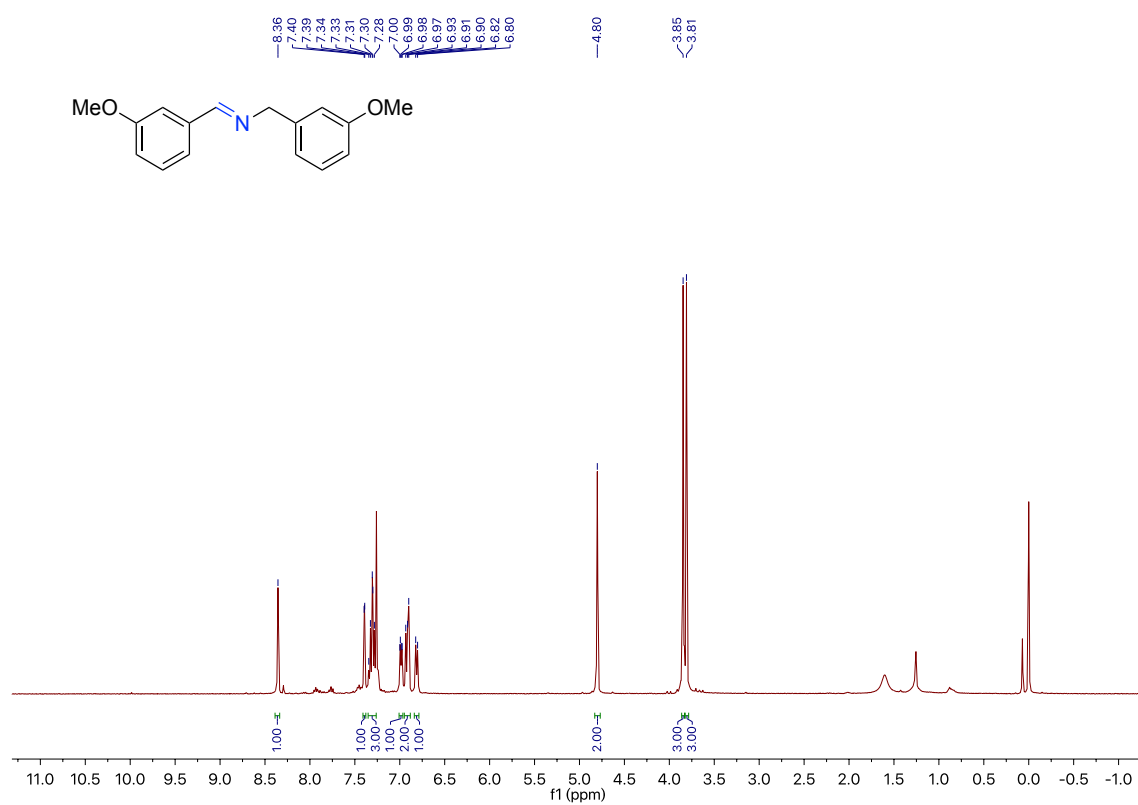
HRMS (m/z): (ESI) calculated for $[\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2+\text{H}]^+$ 253.0972; found 253.0974;

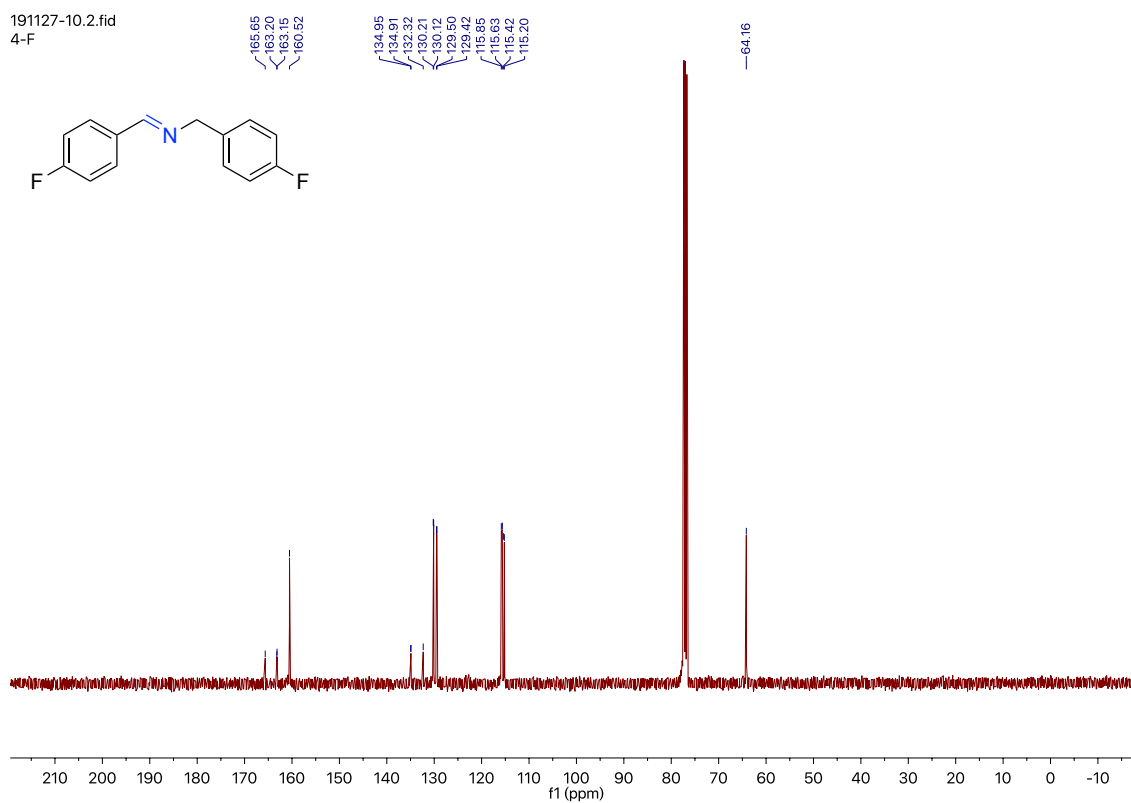
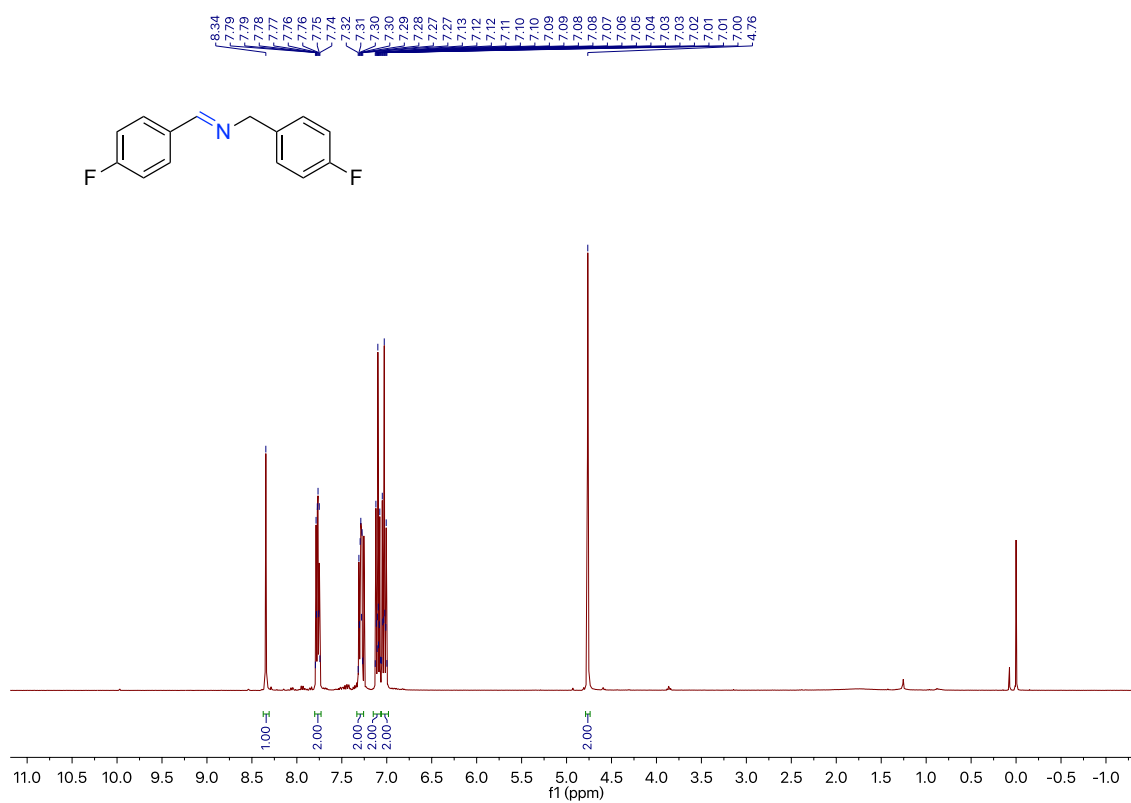


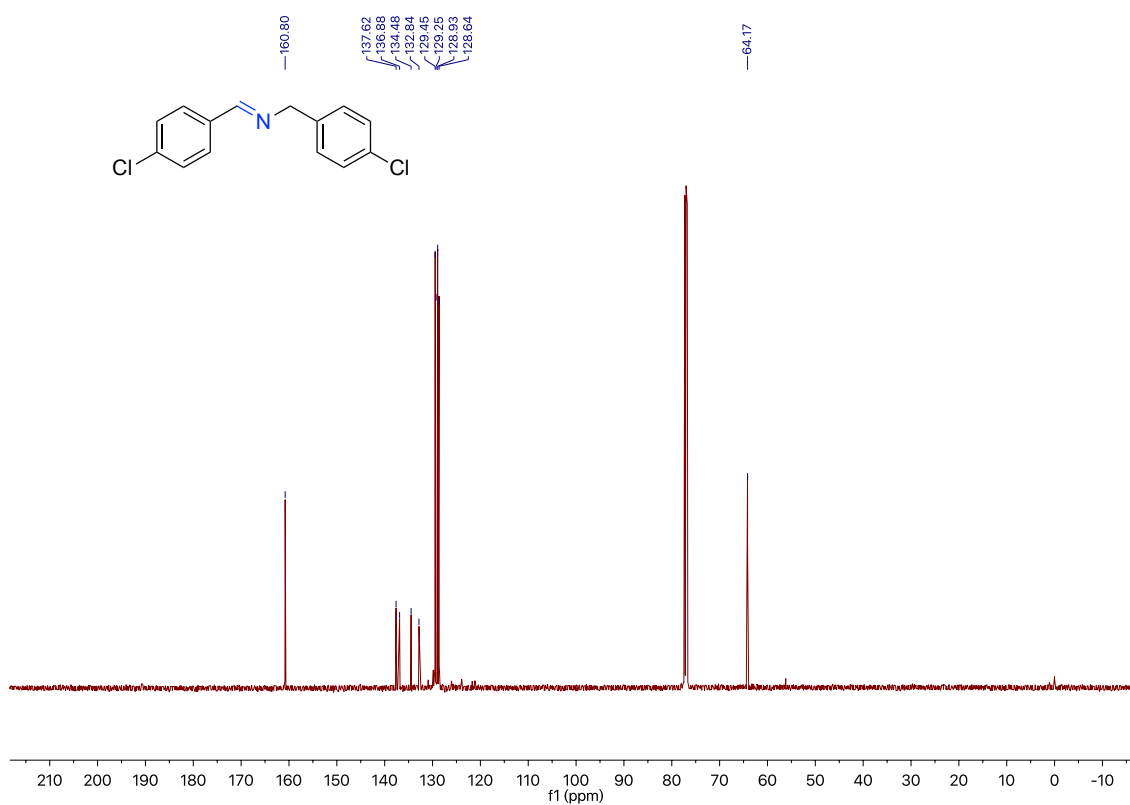
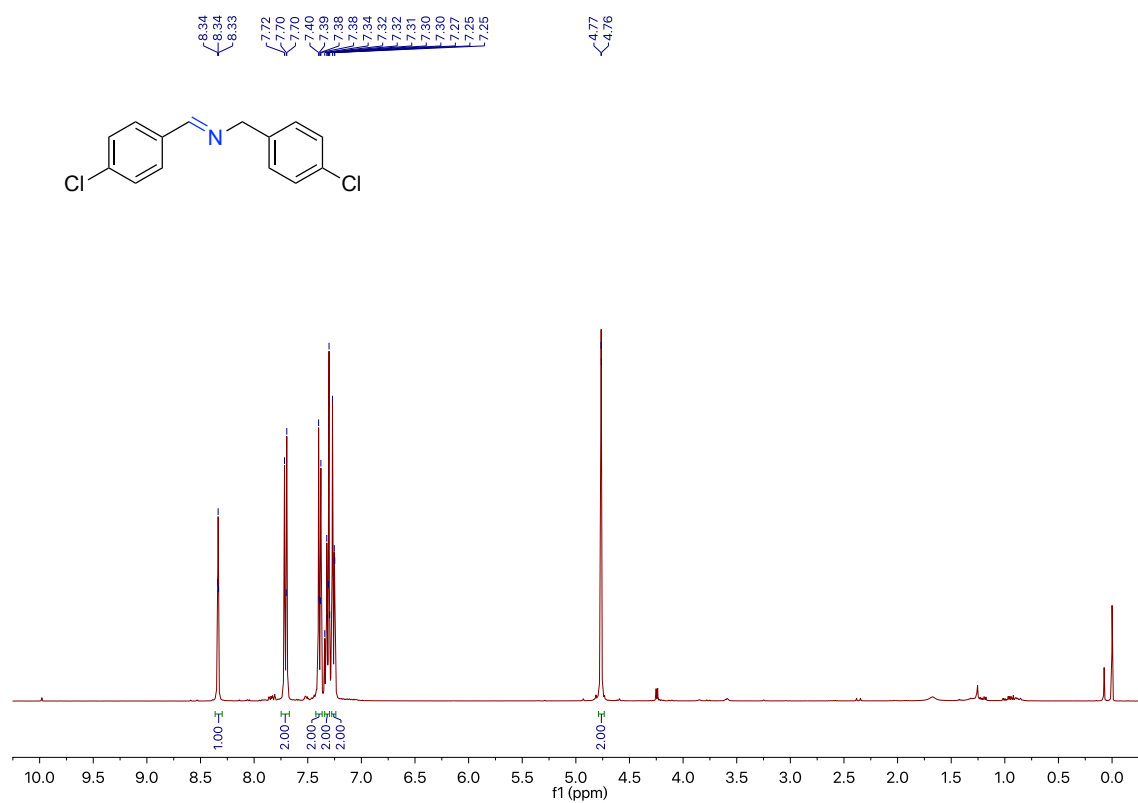


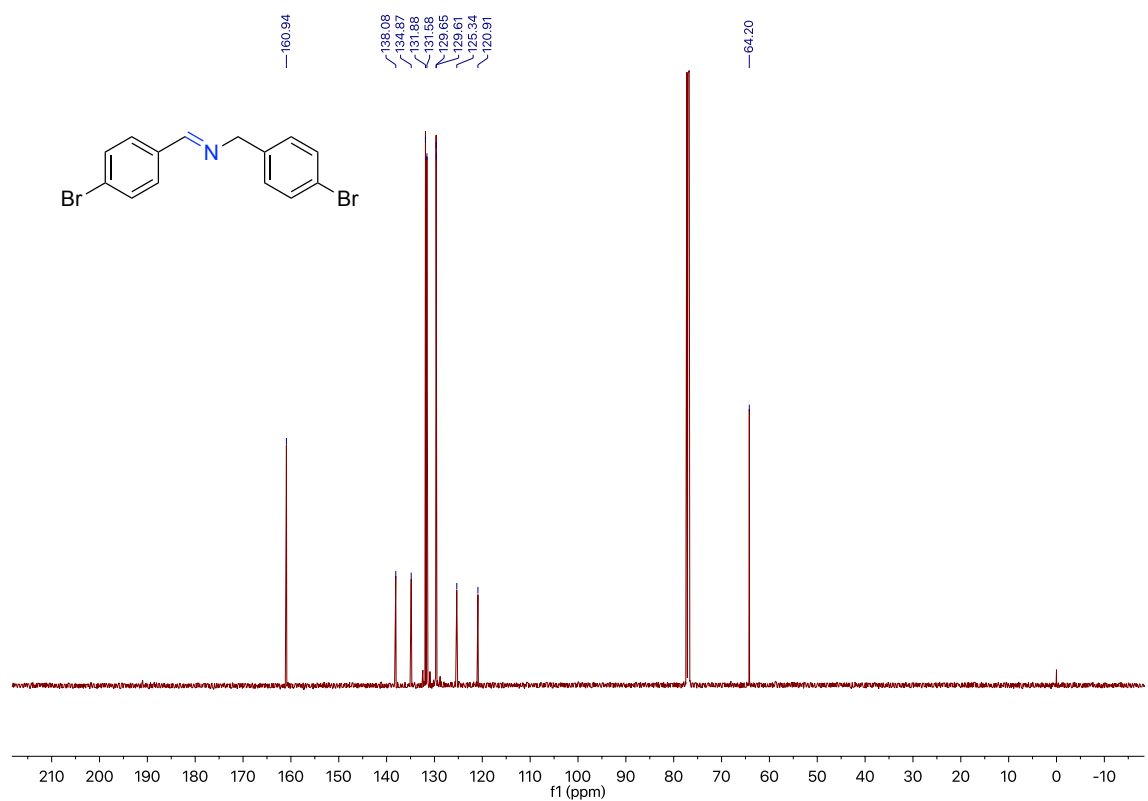
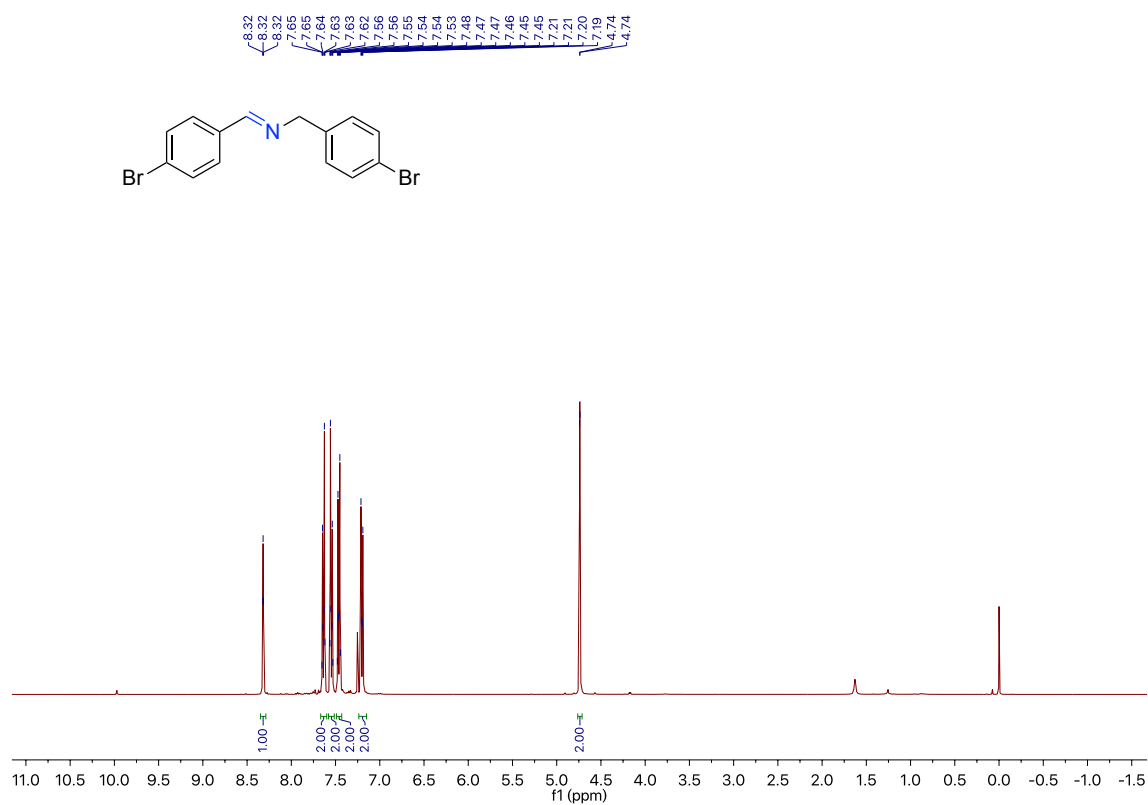


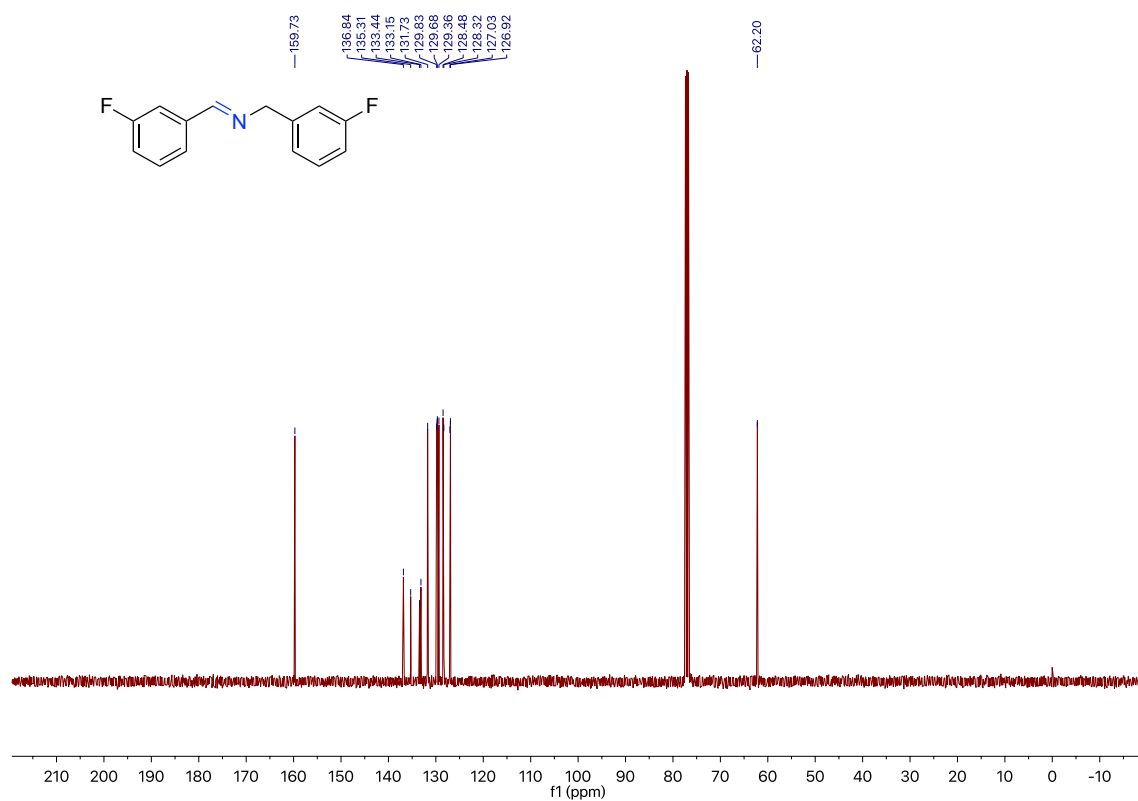
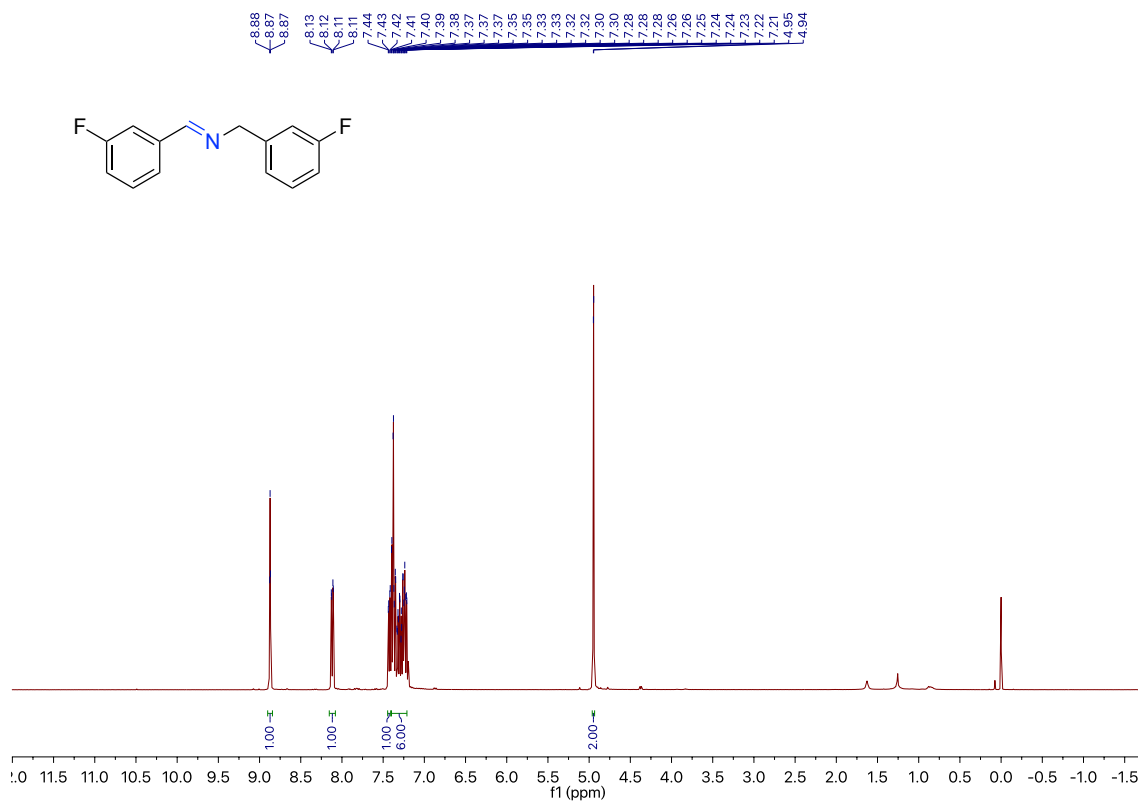


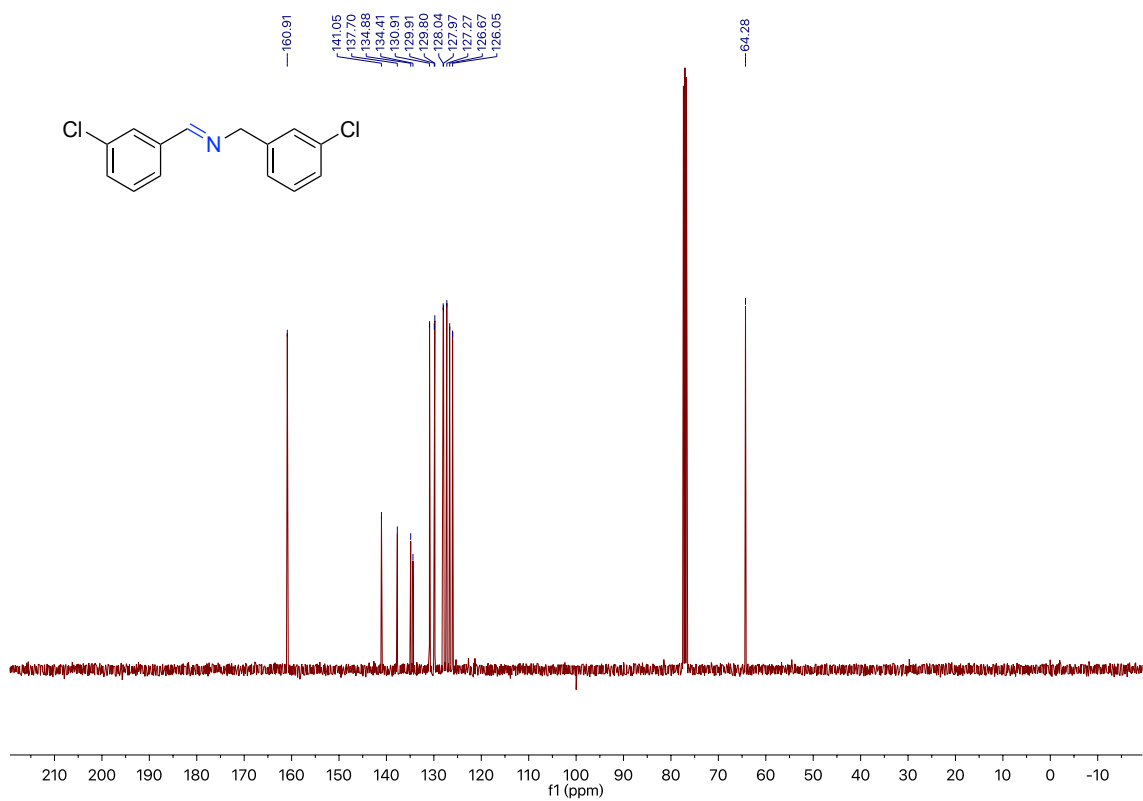
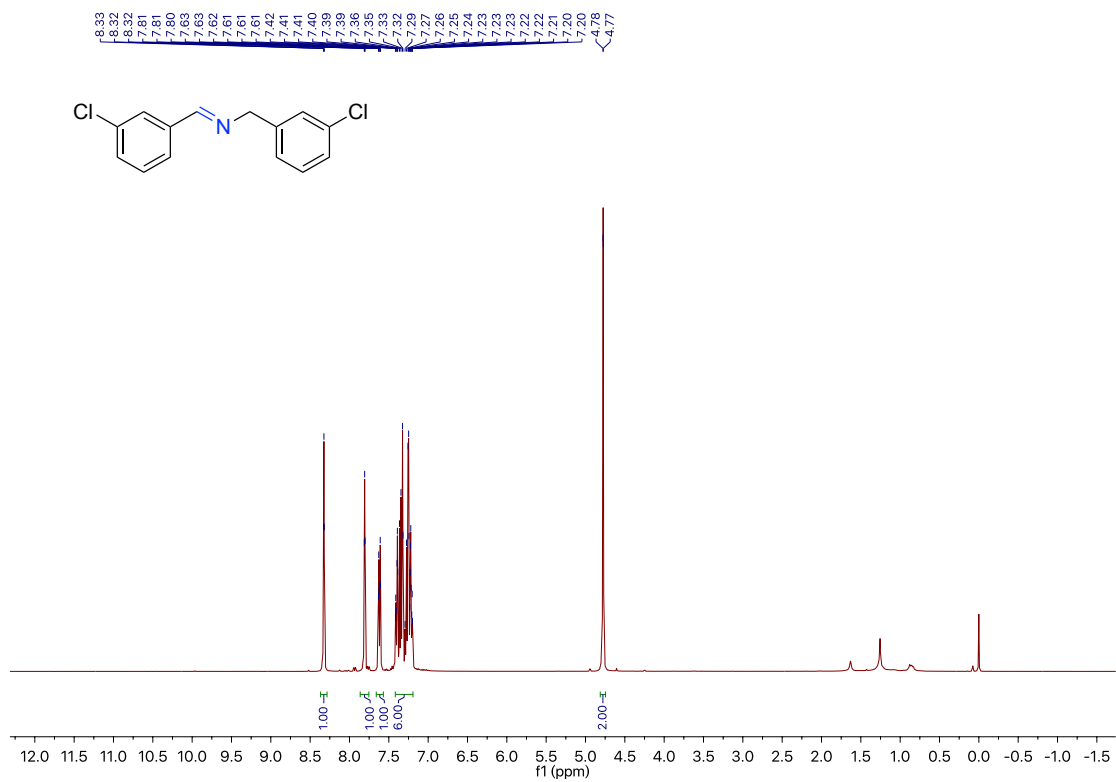


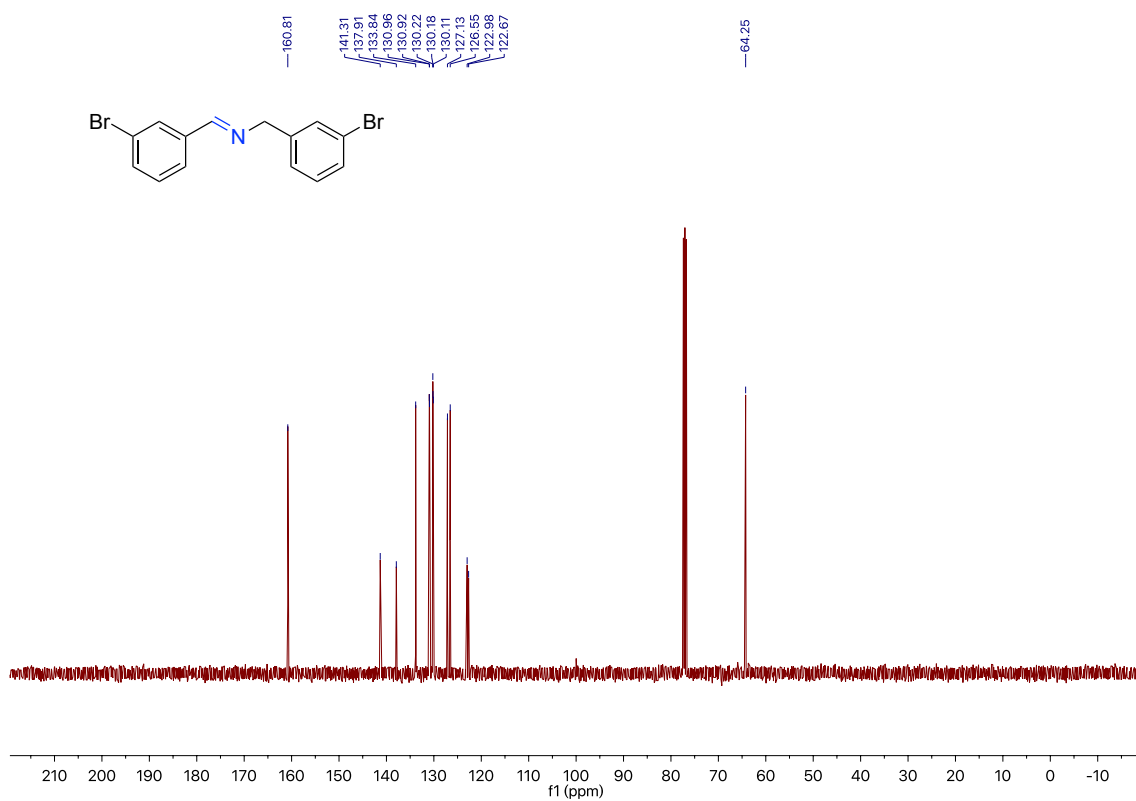
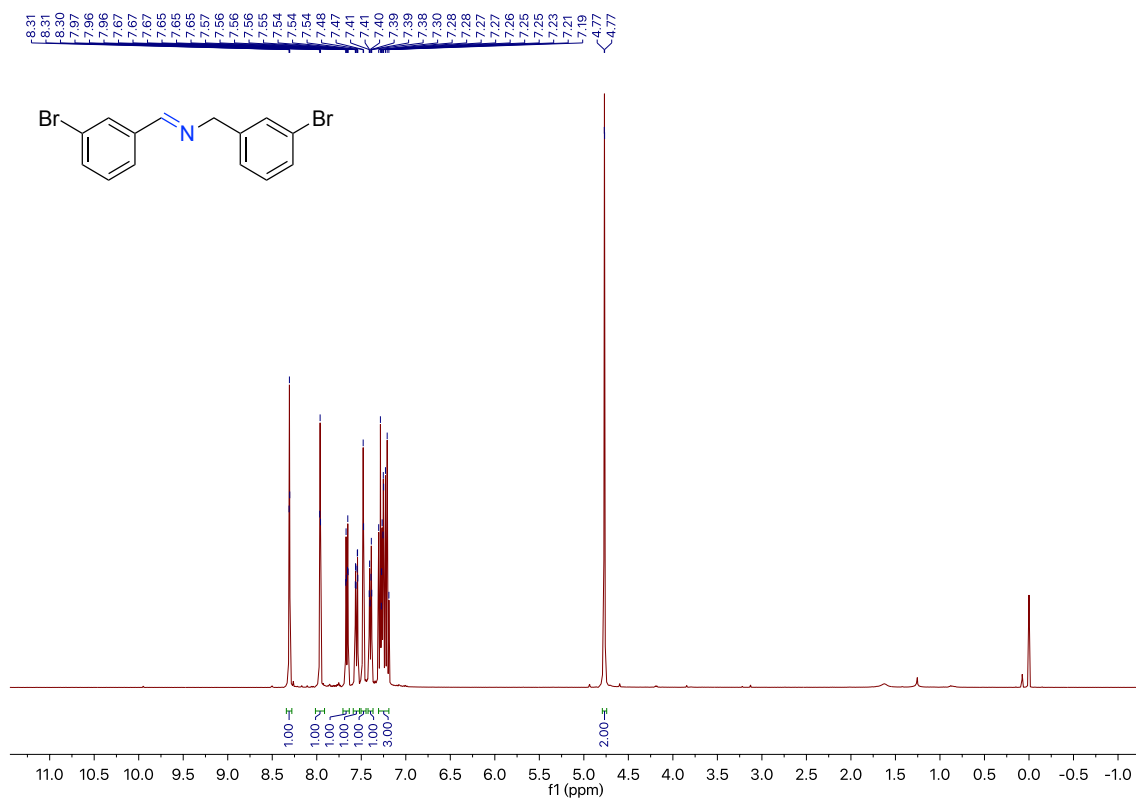


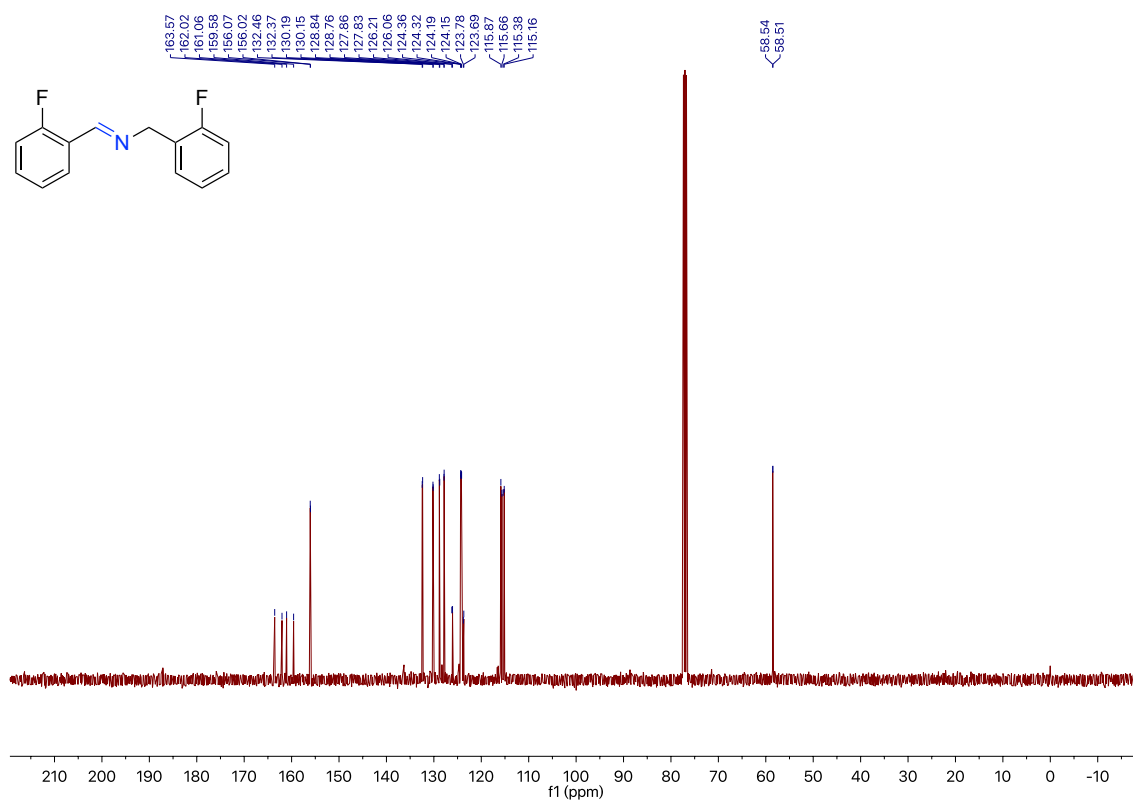
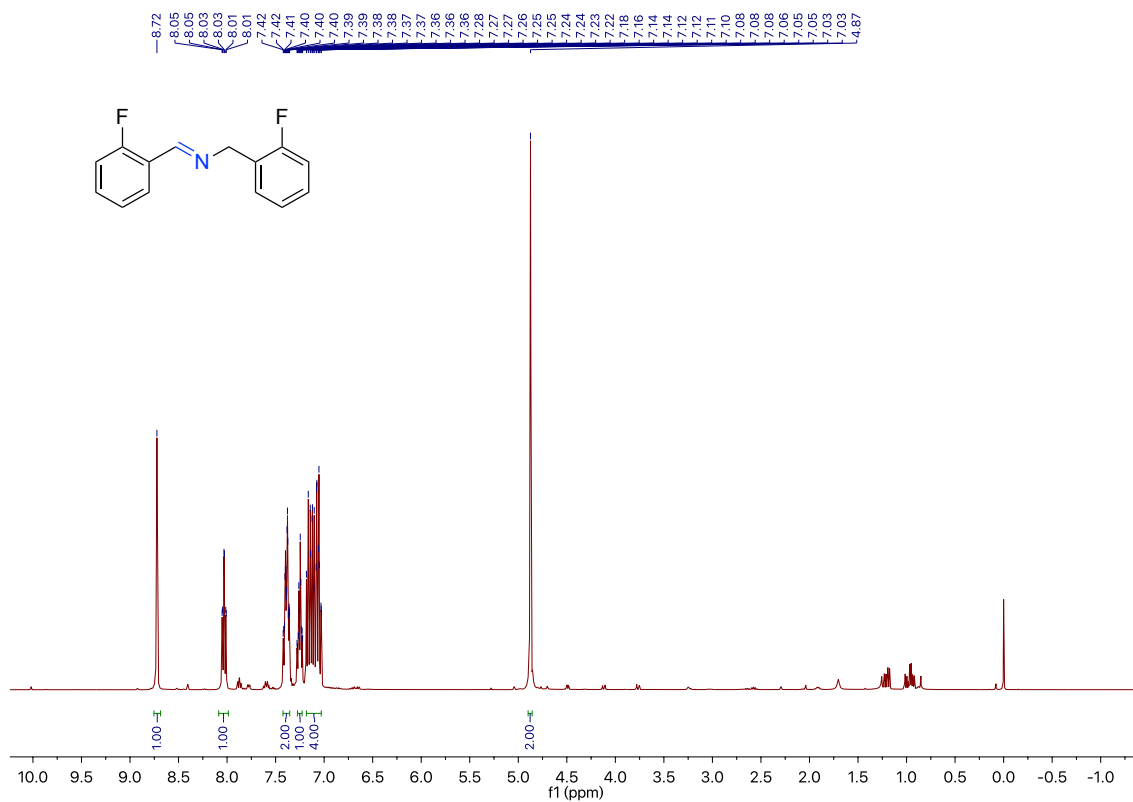


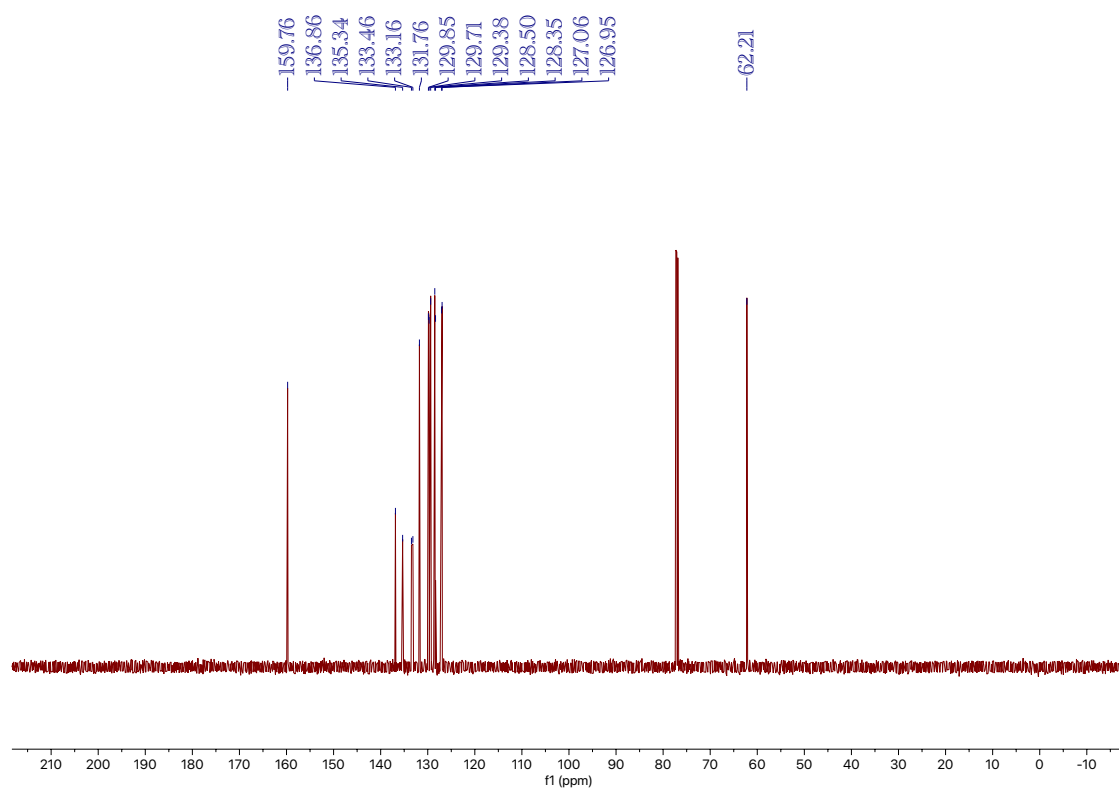
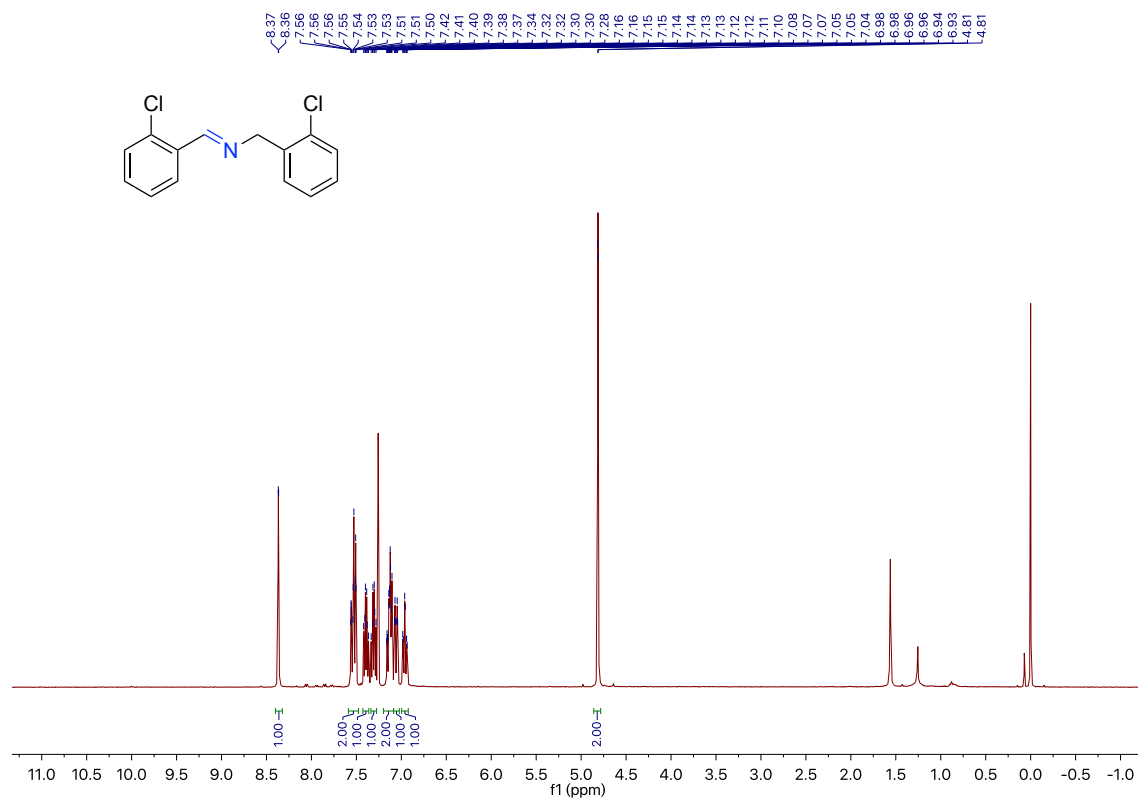


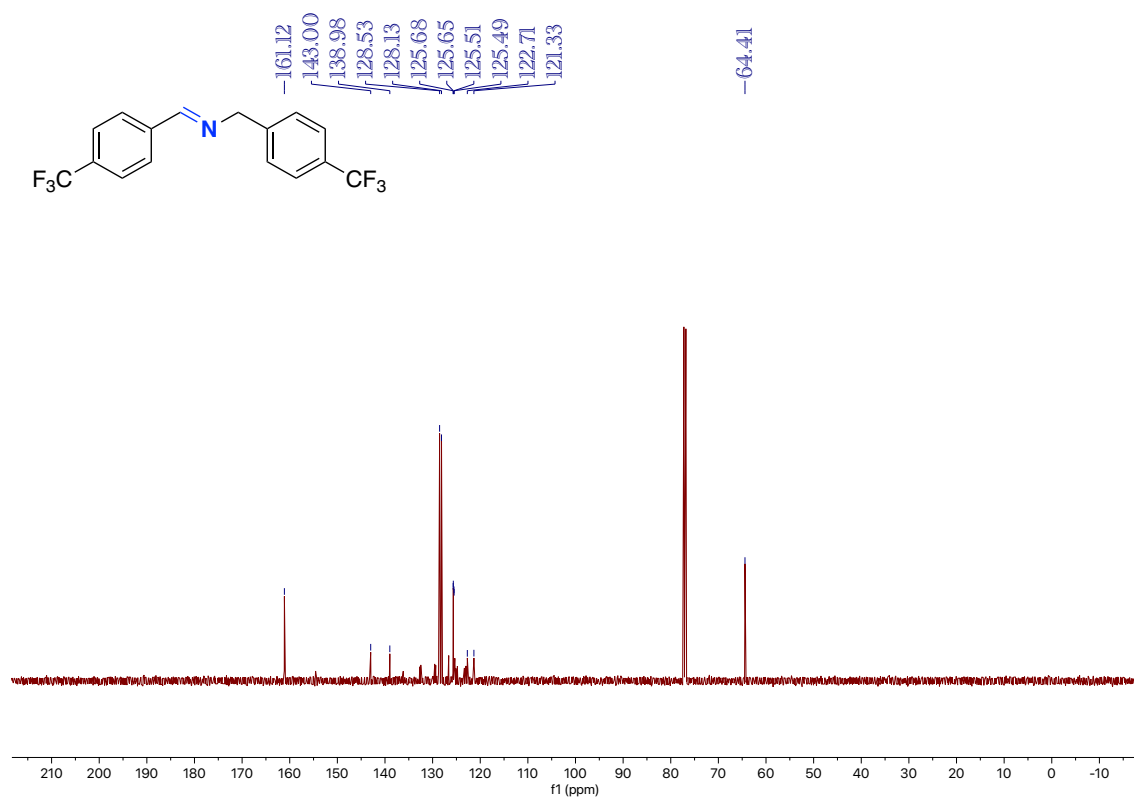
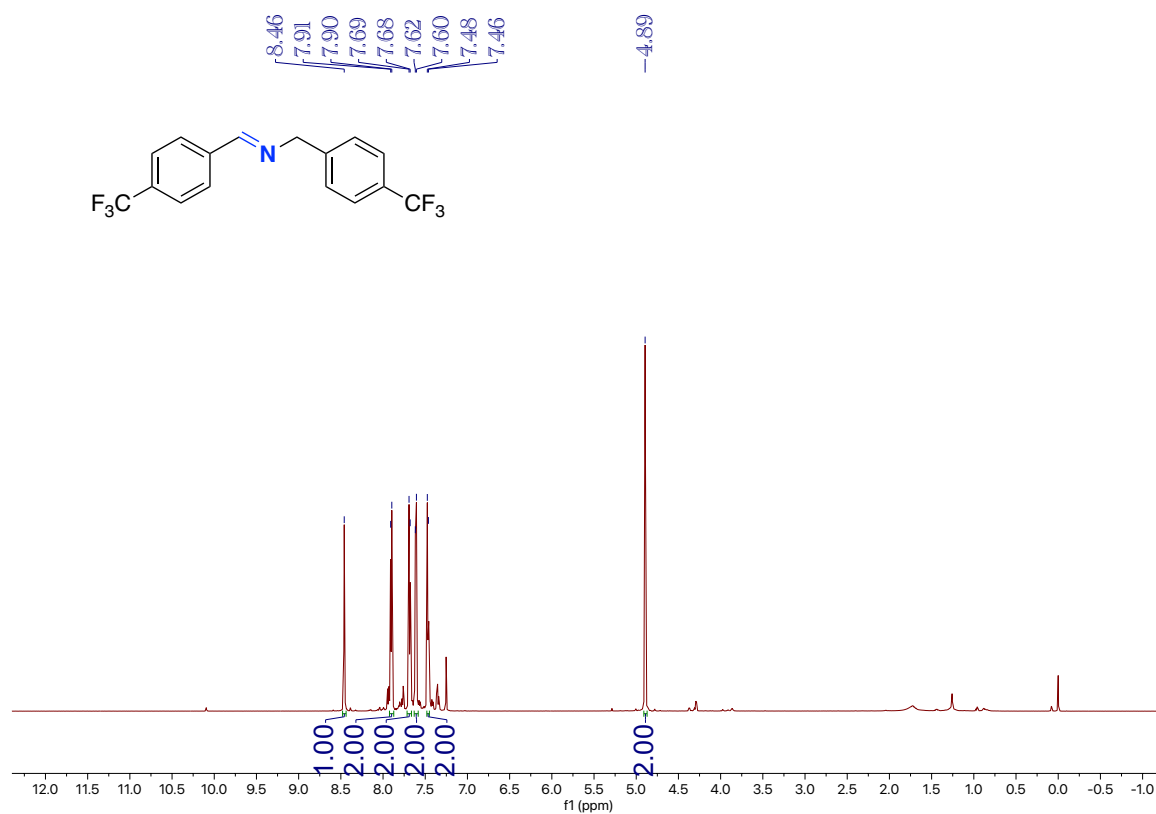


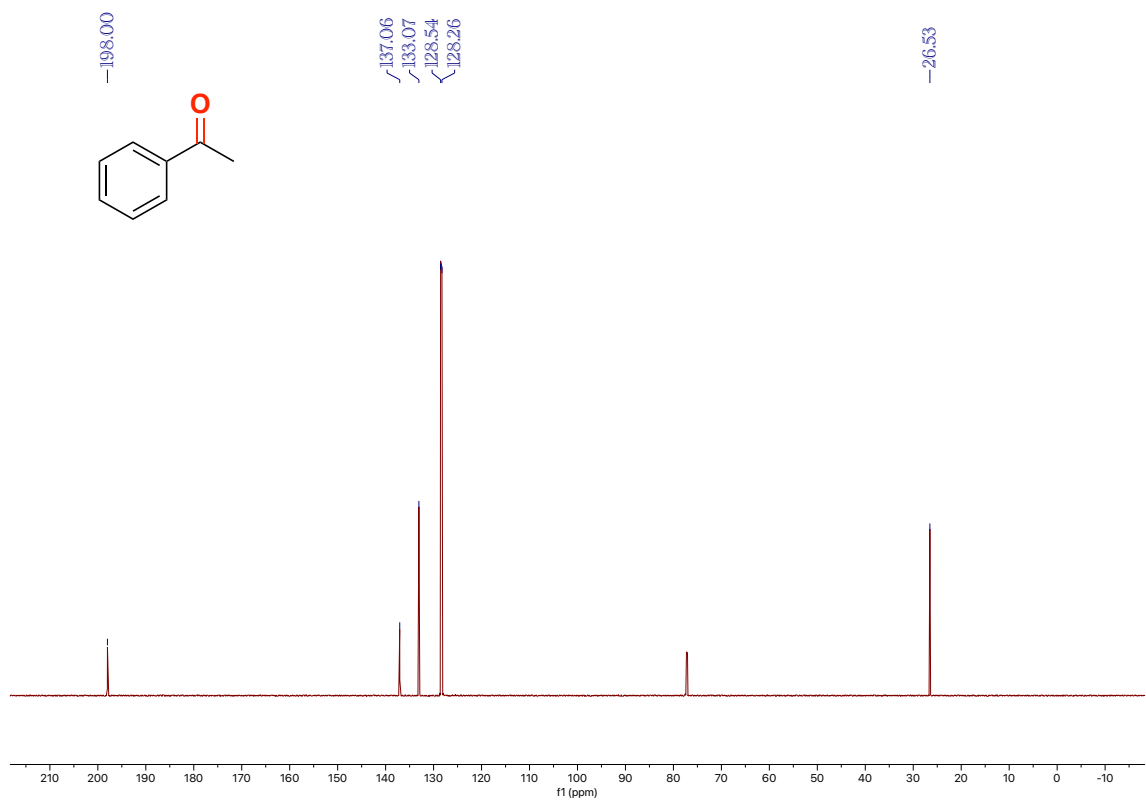
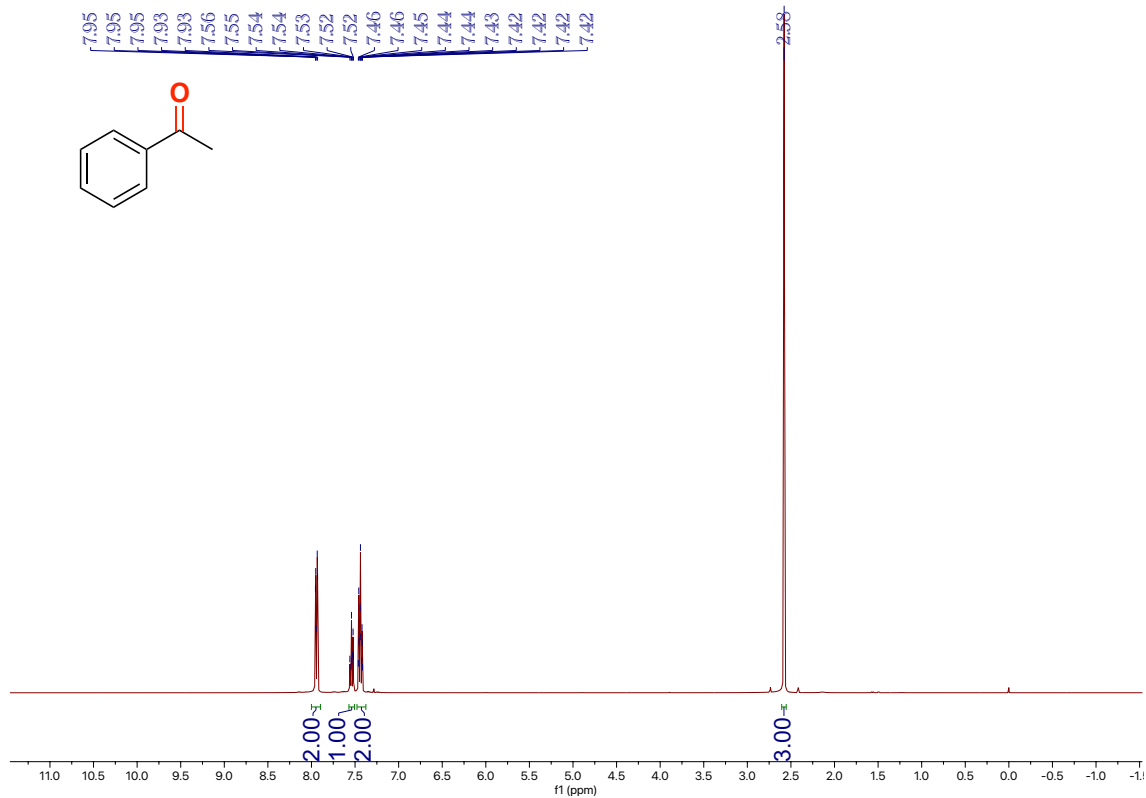


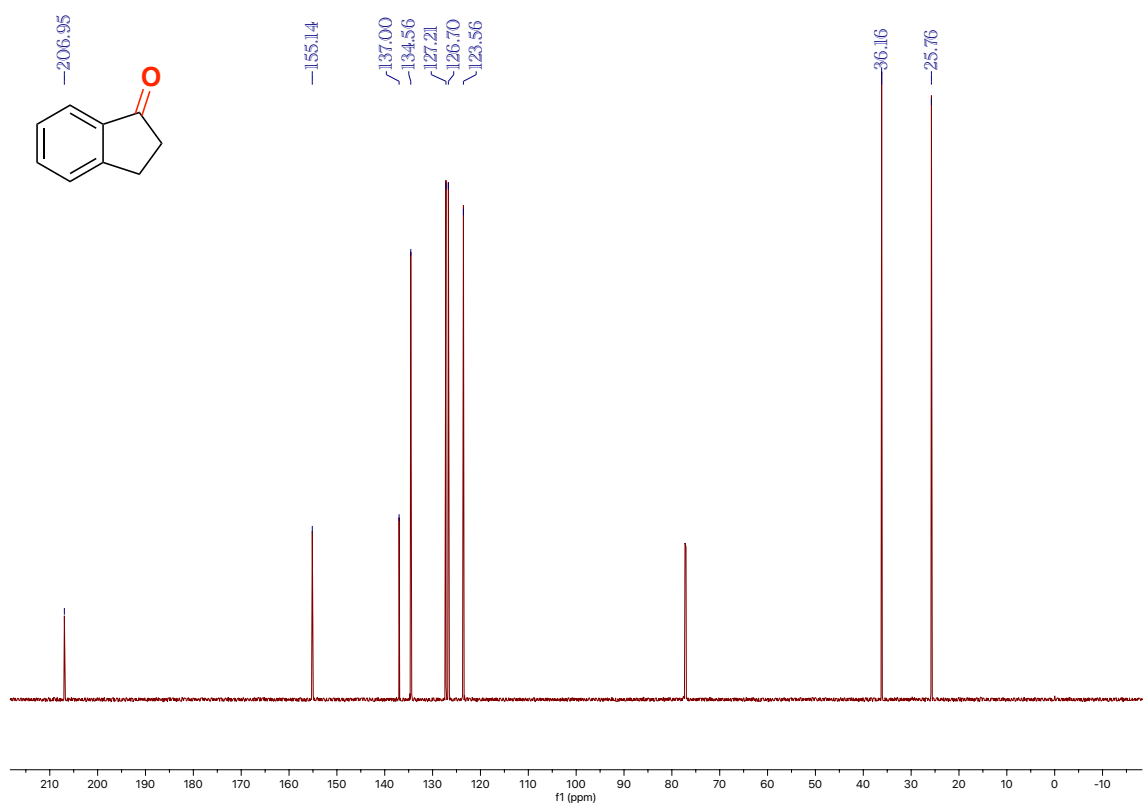
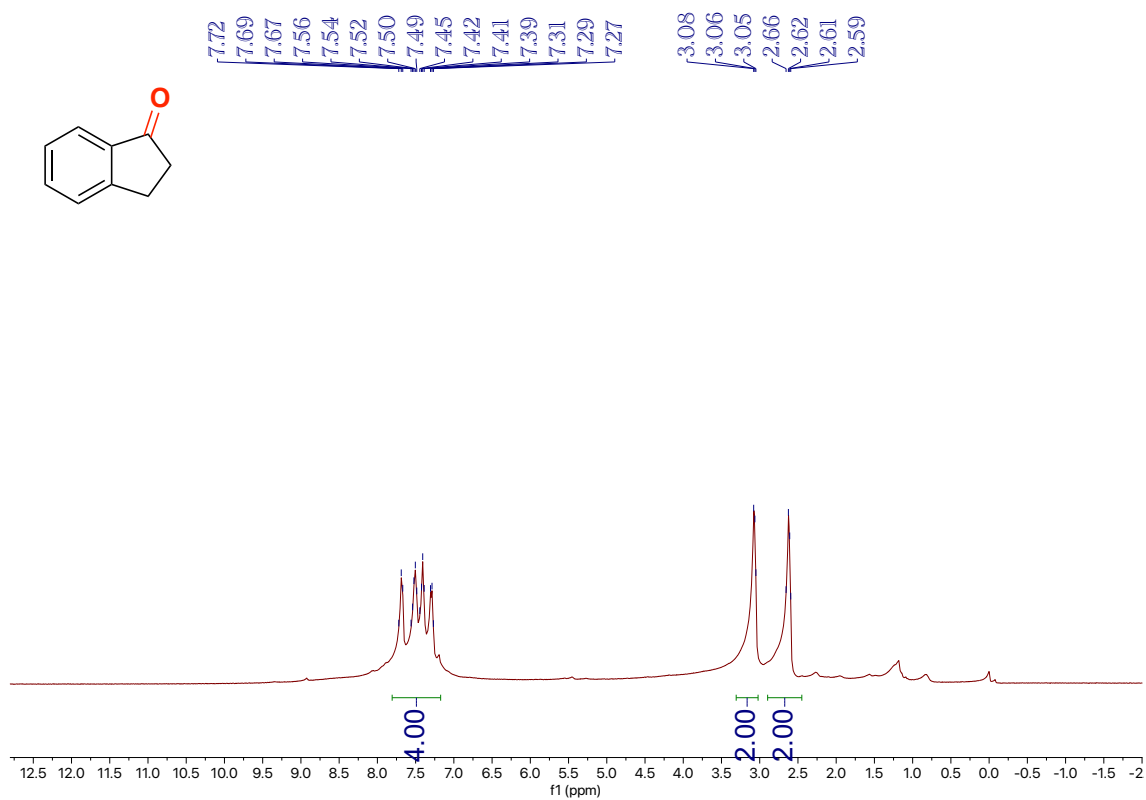




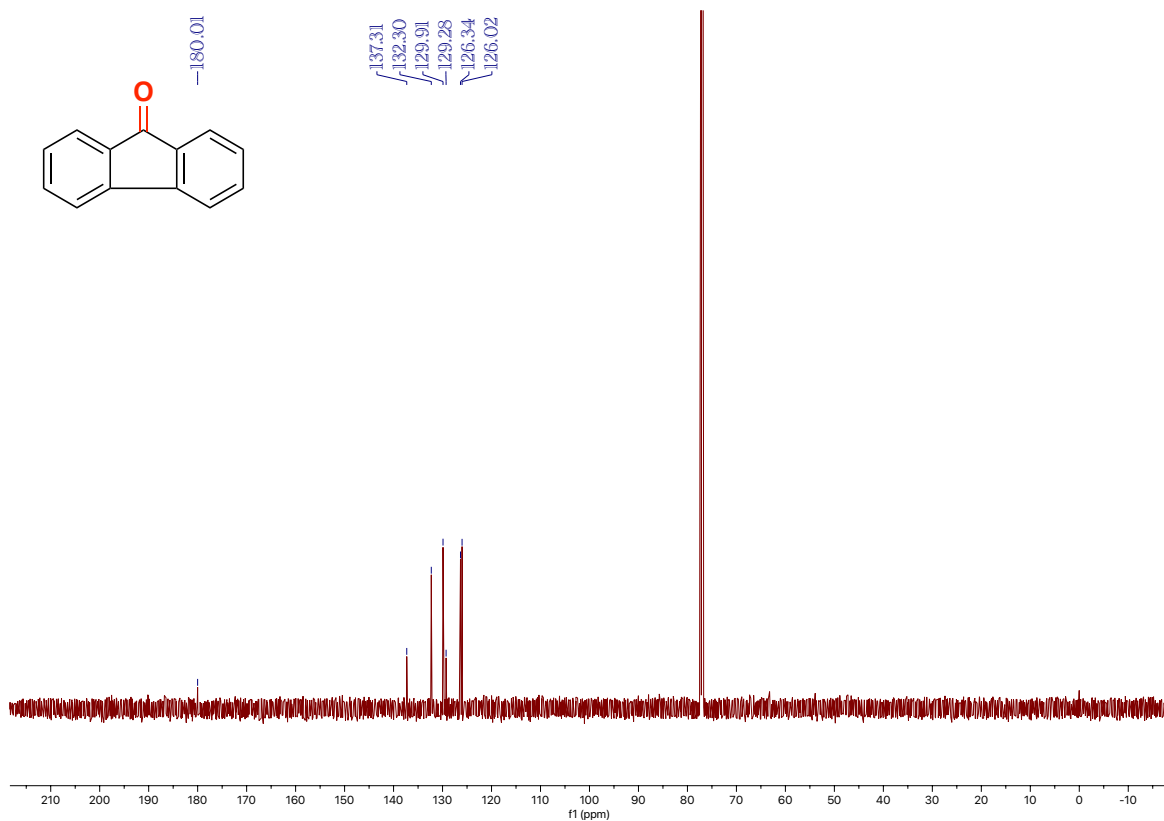
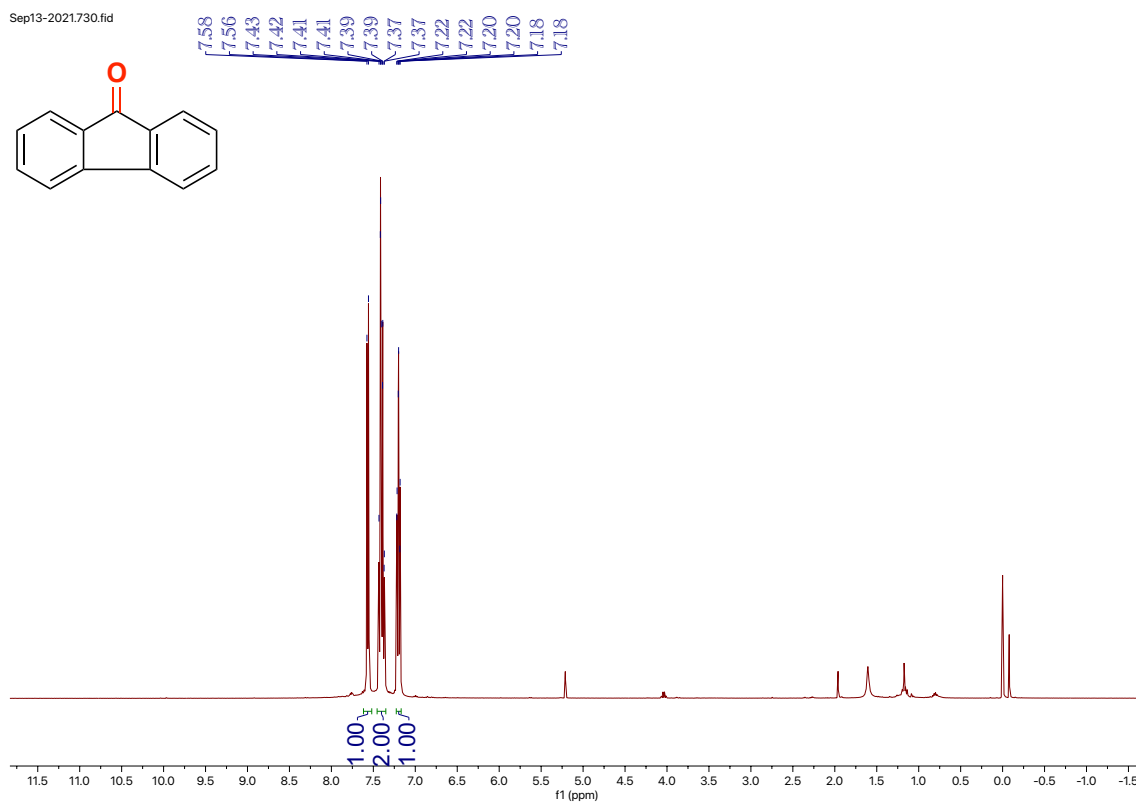


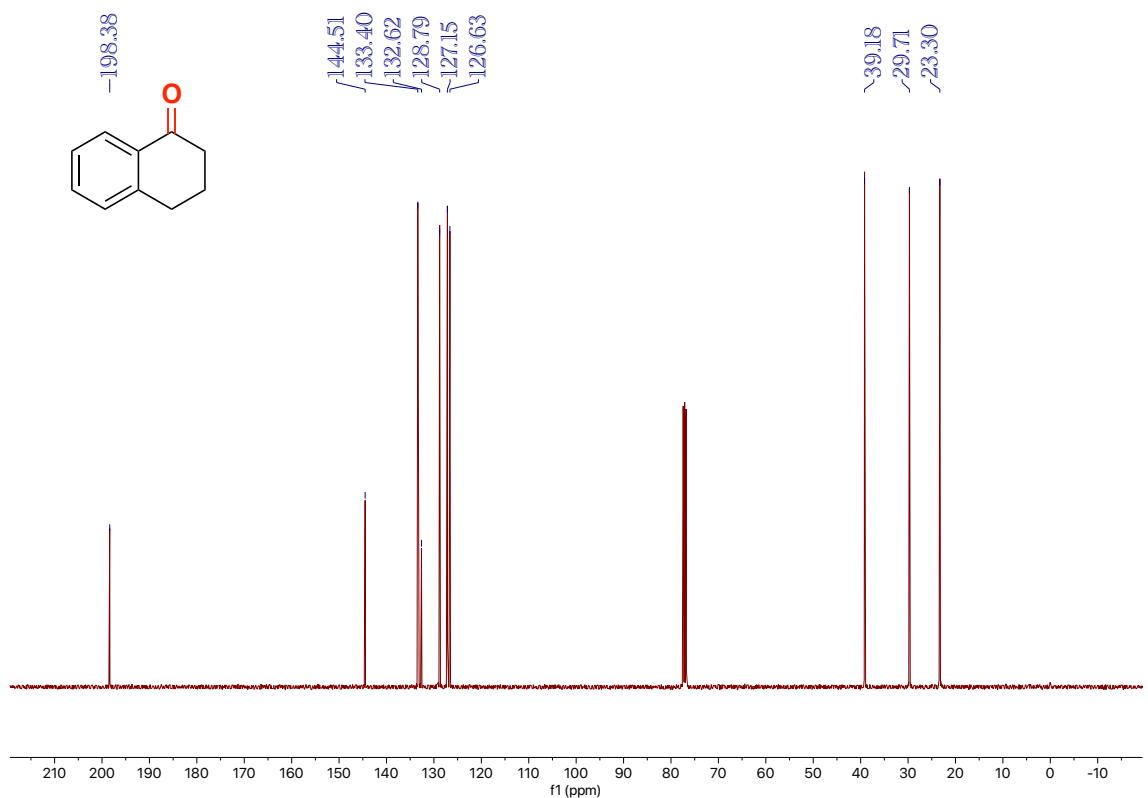
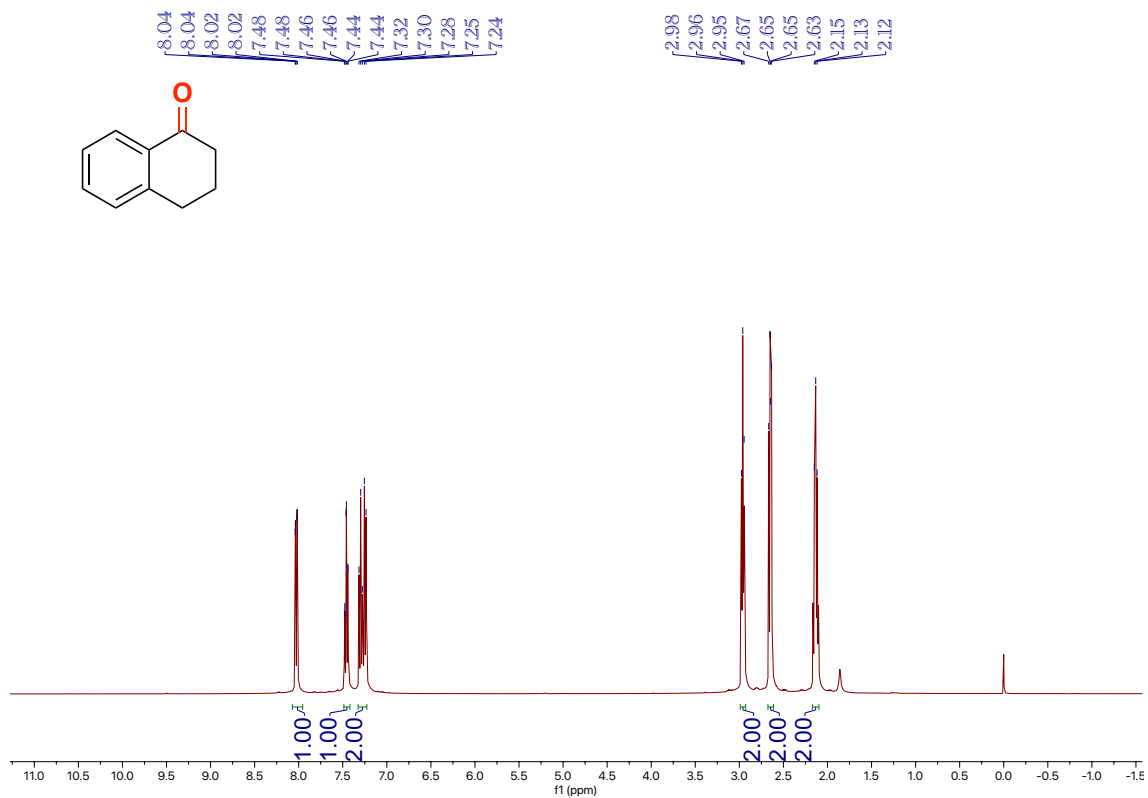




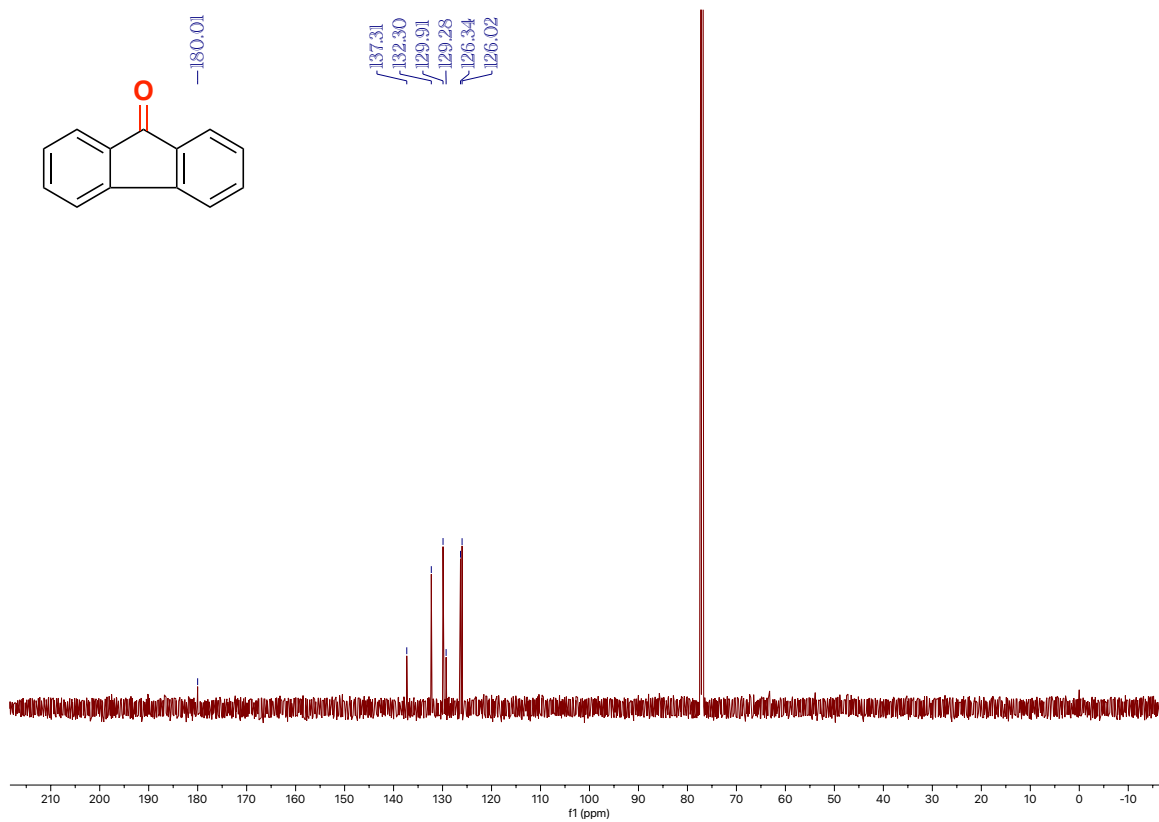
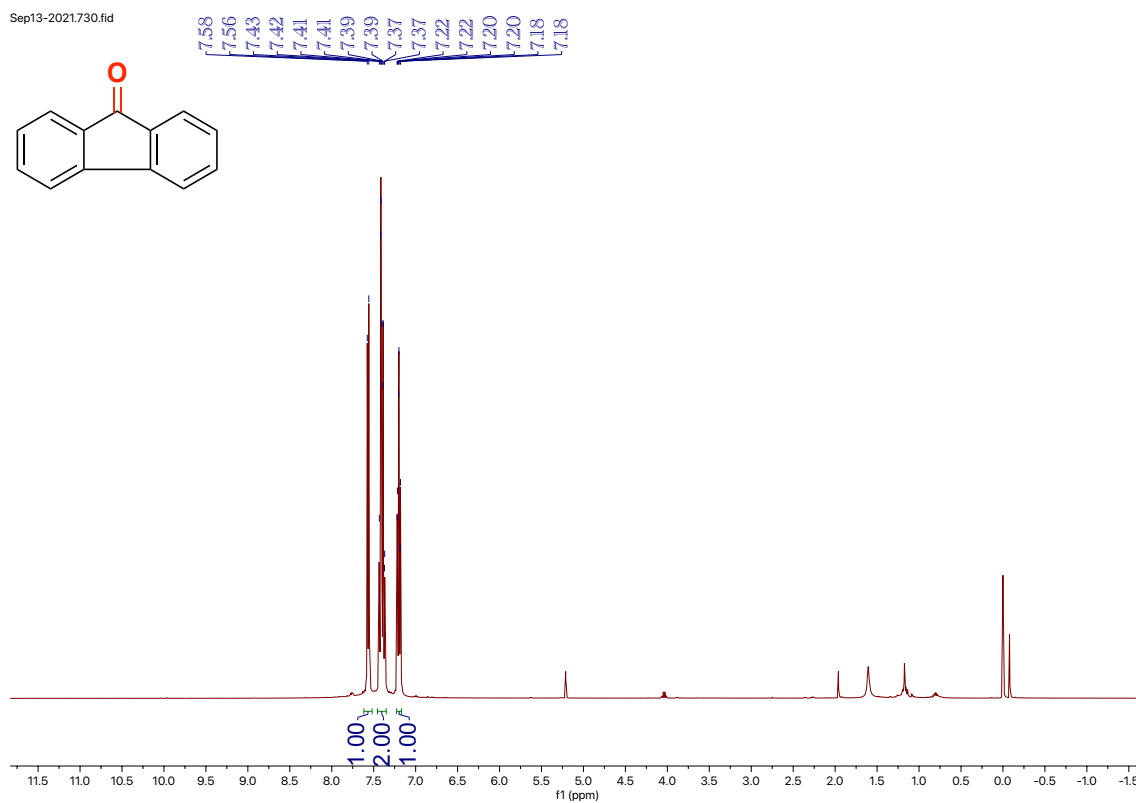


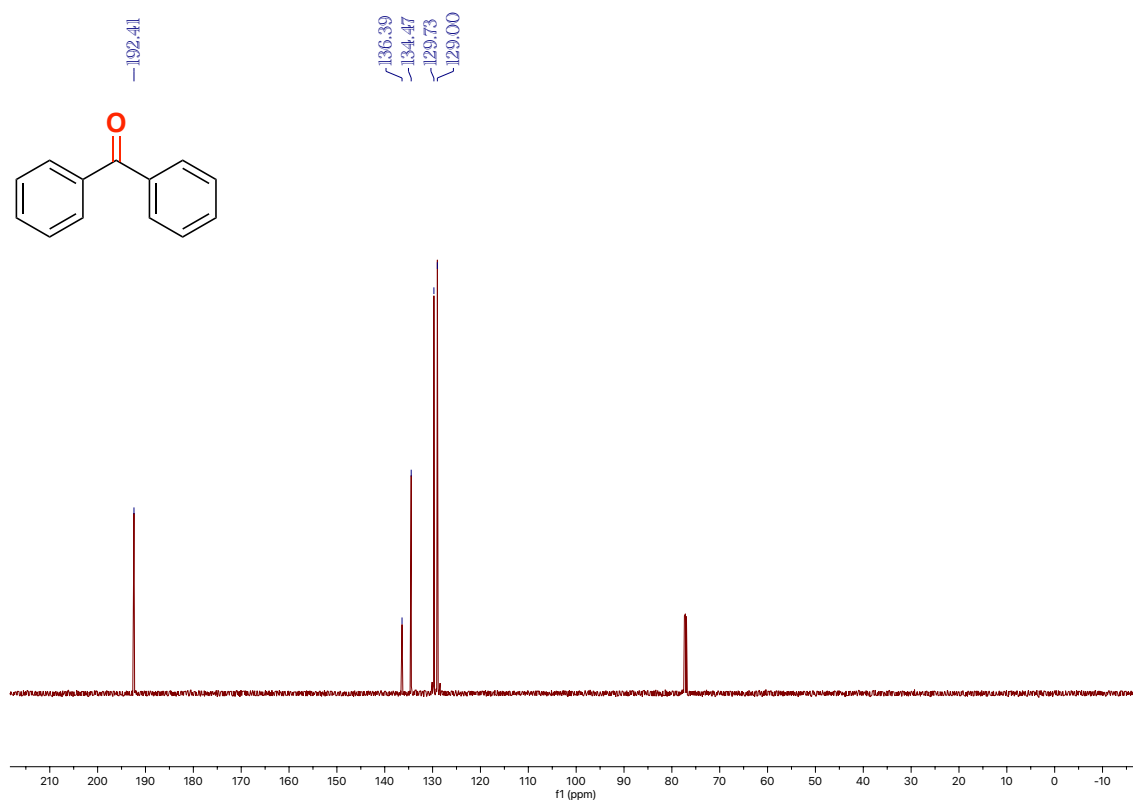
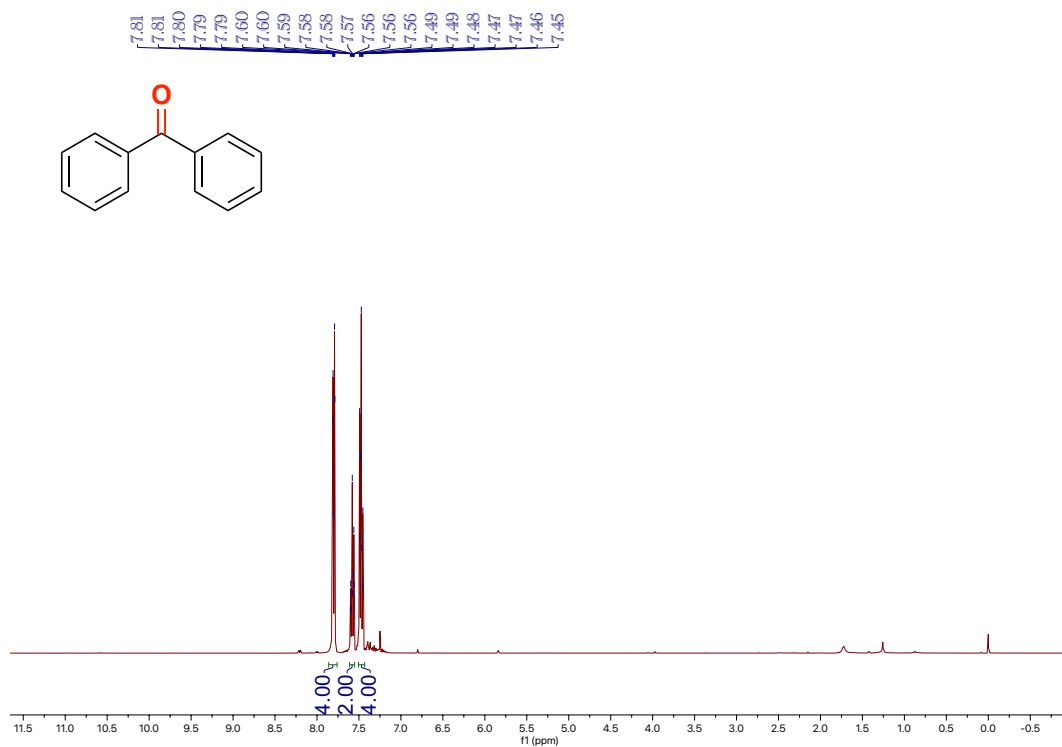
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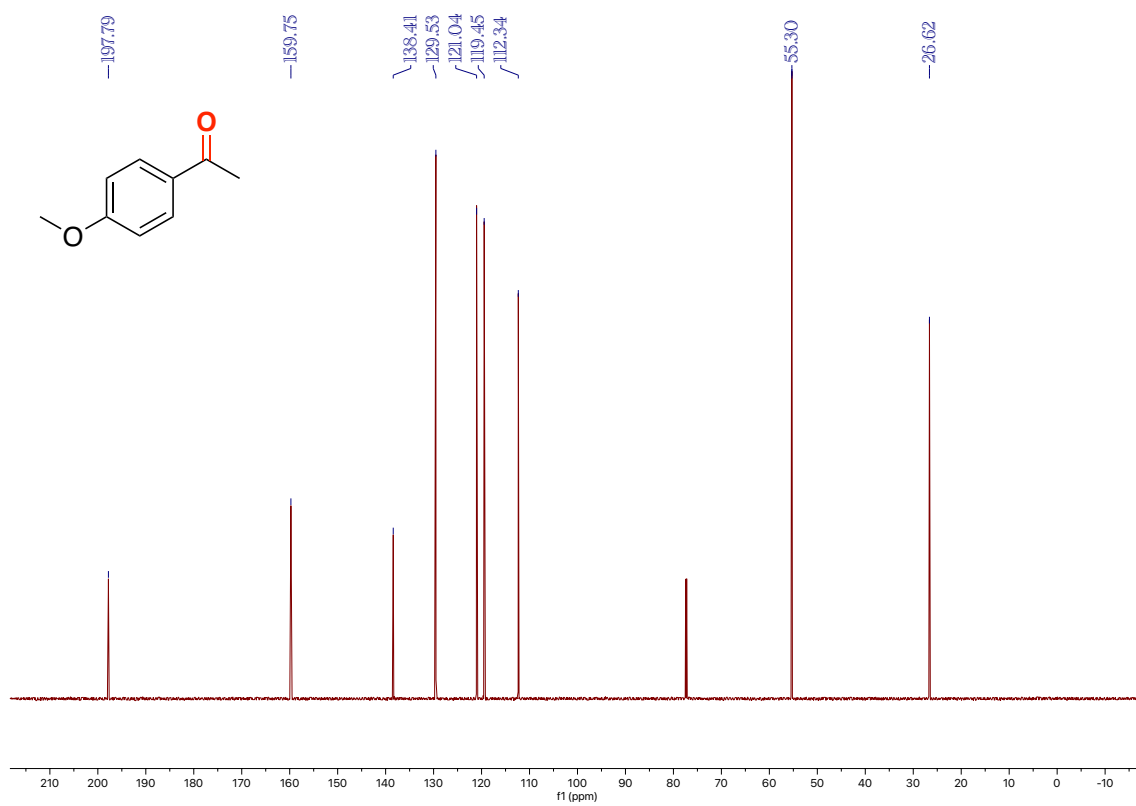
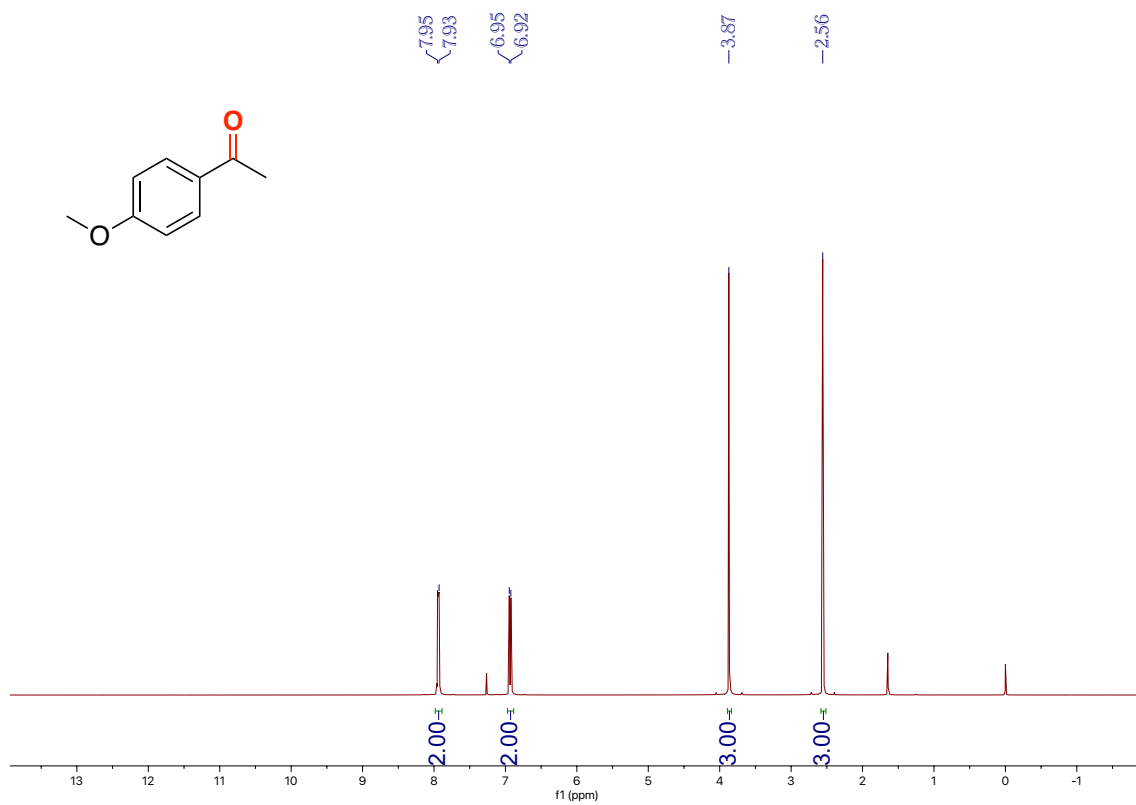


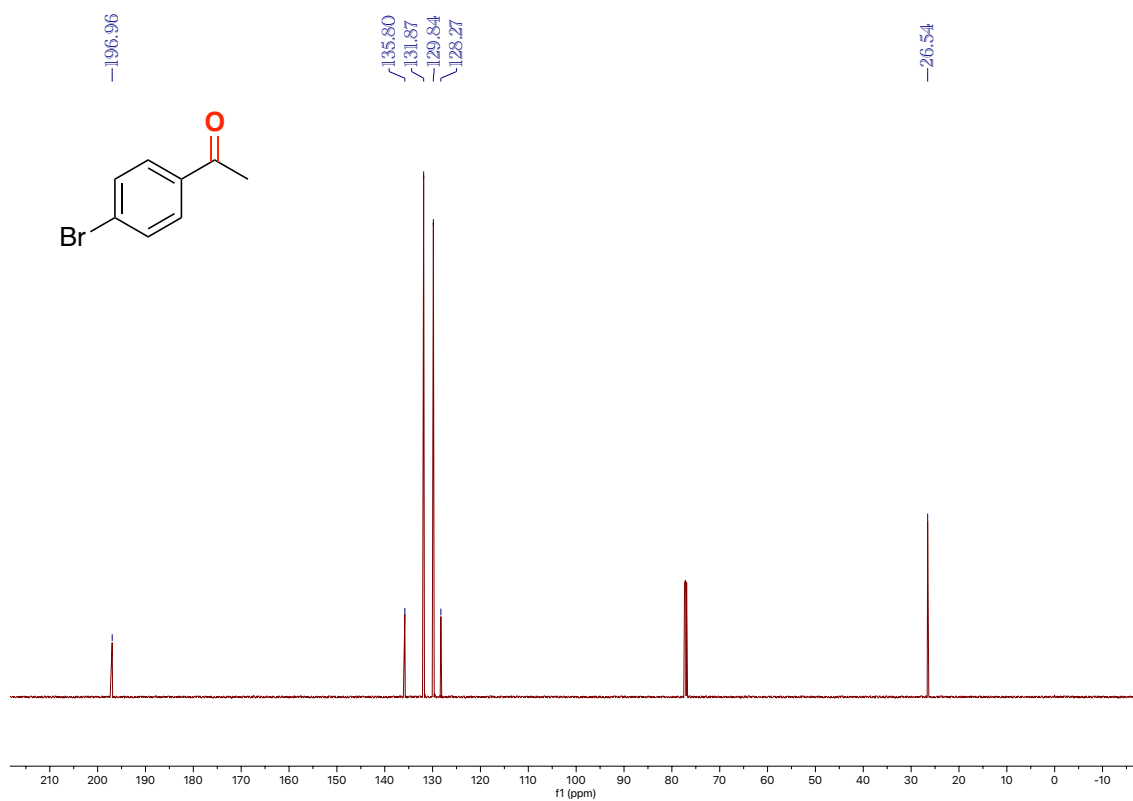
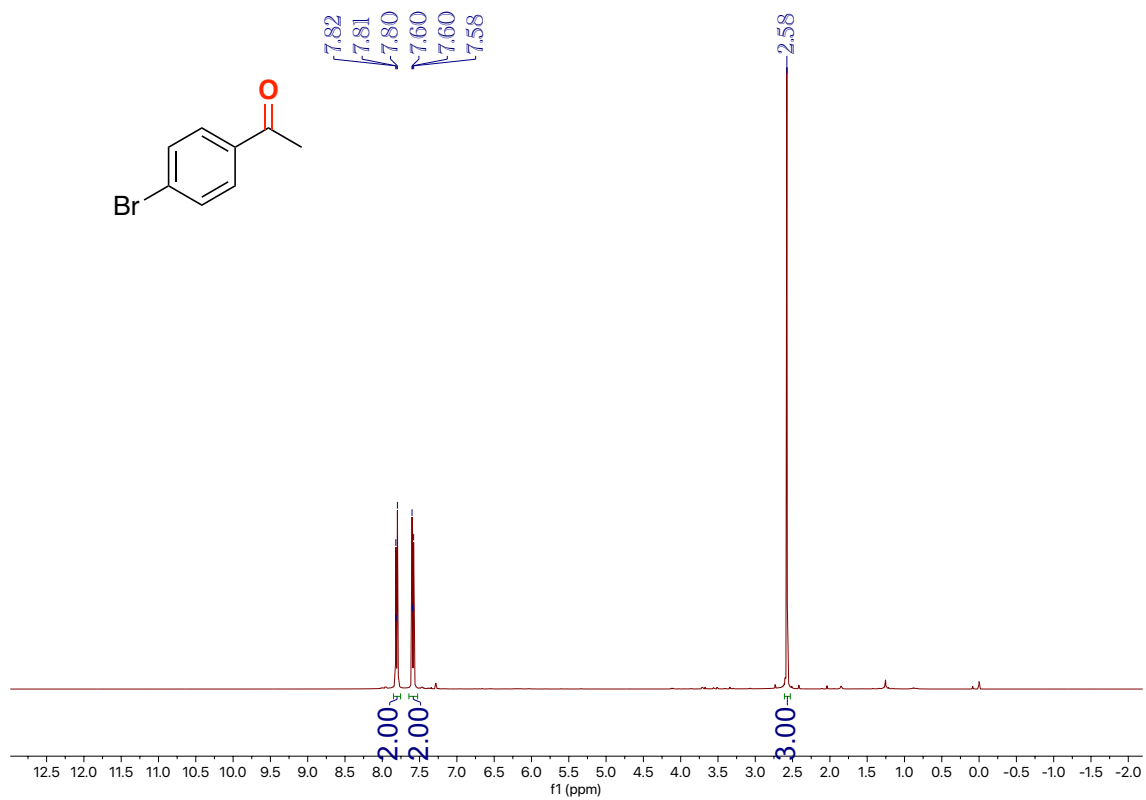


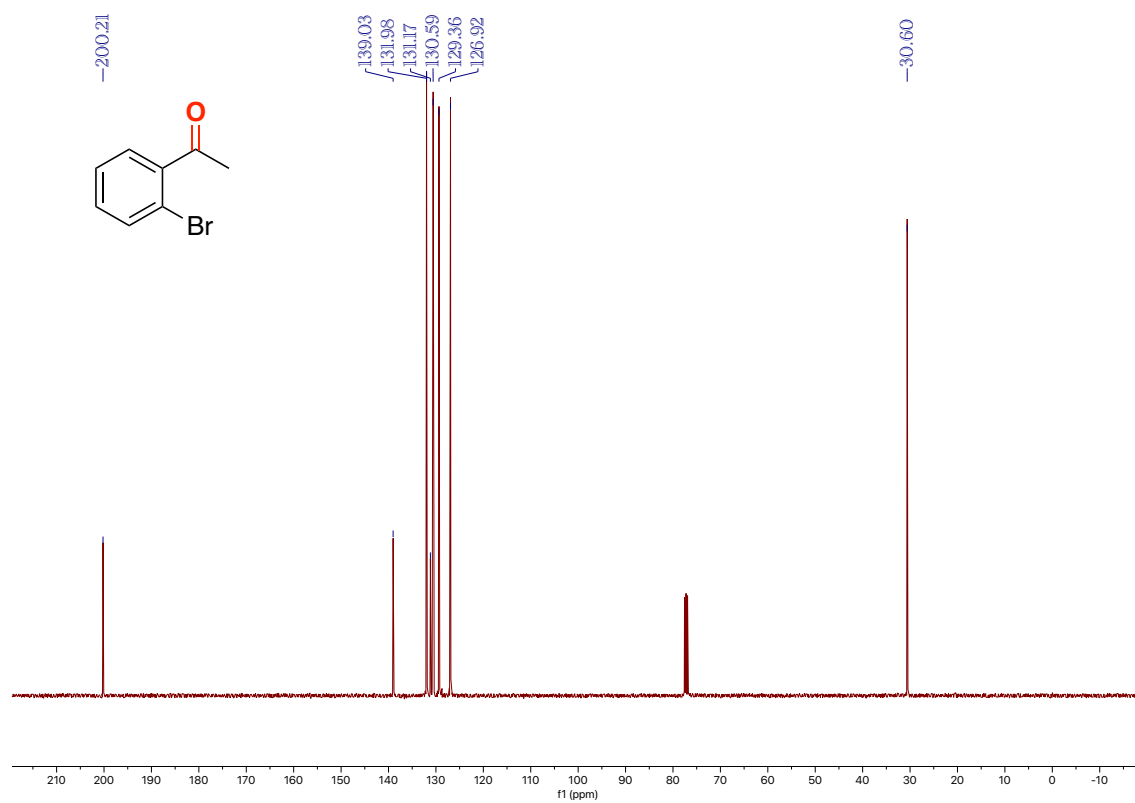
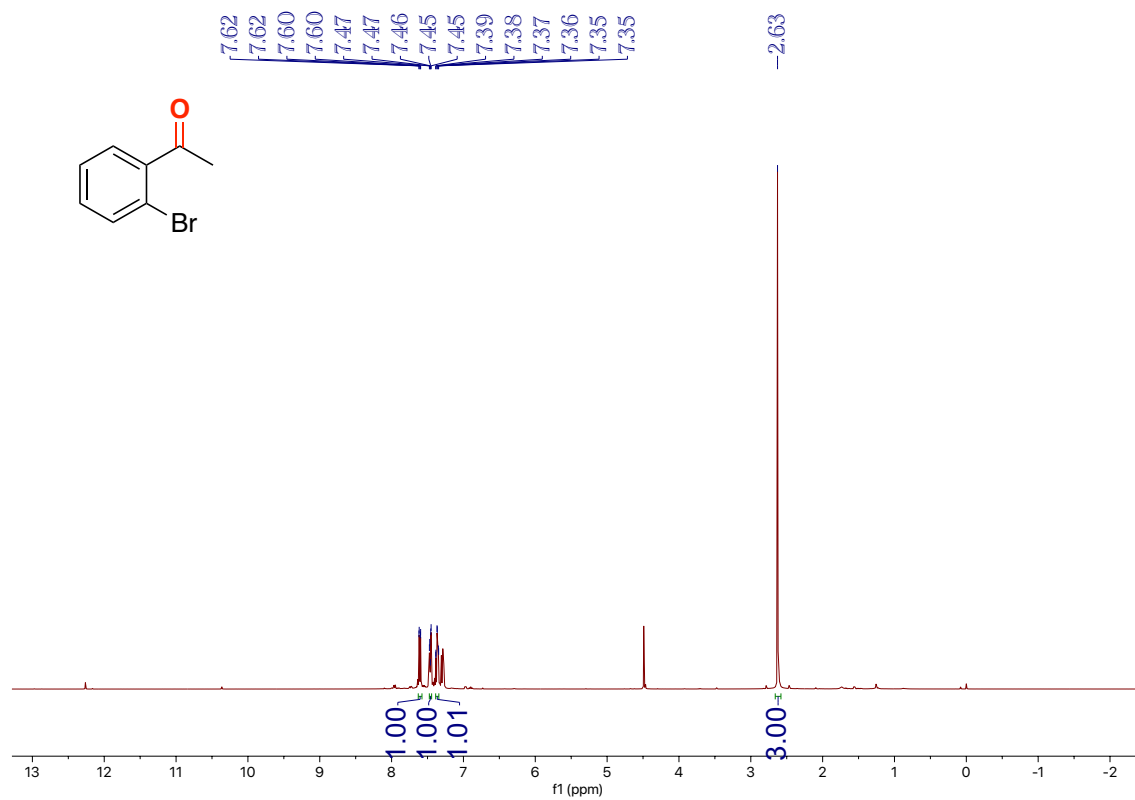
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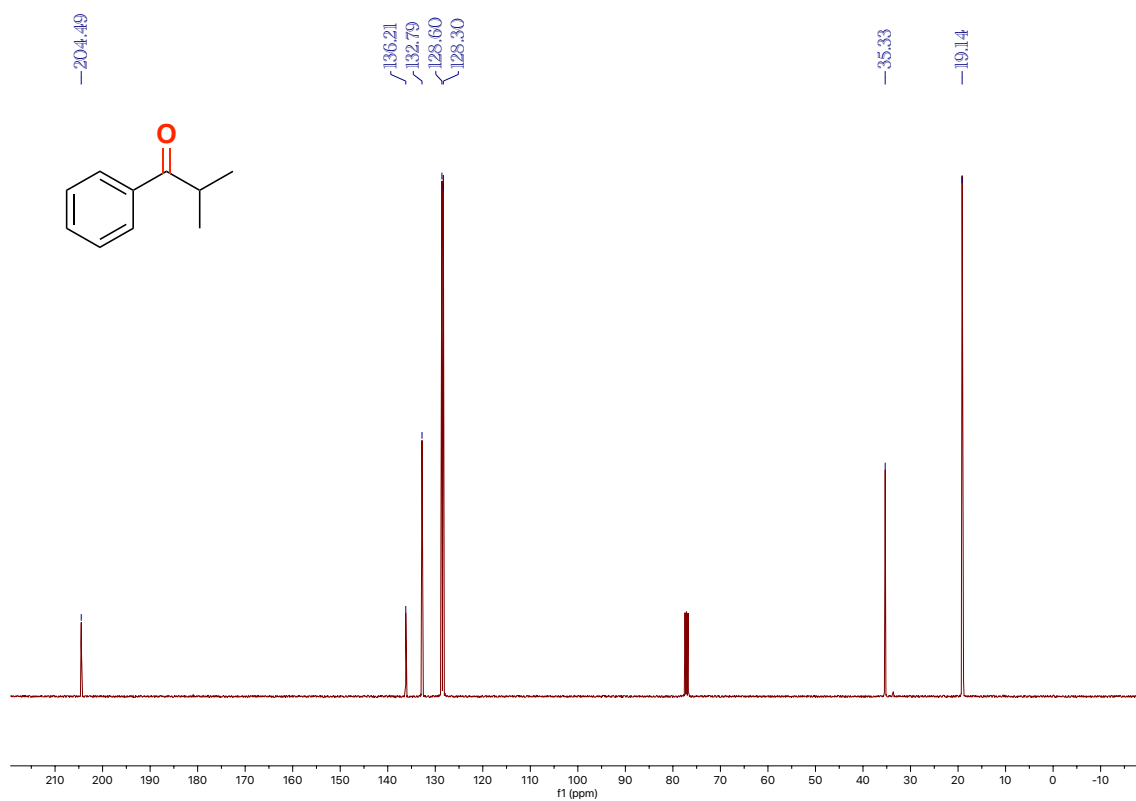
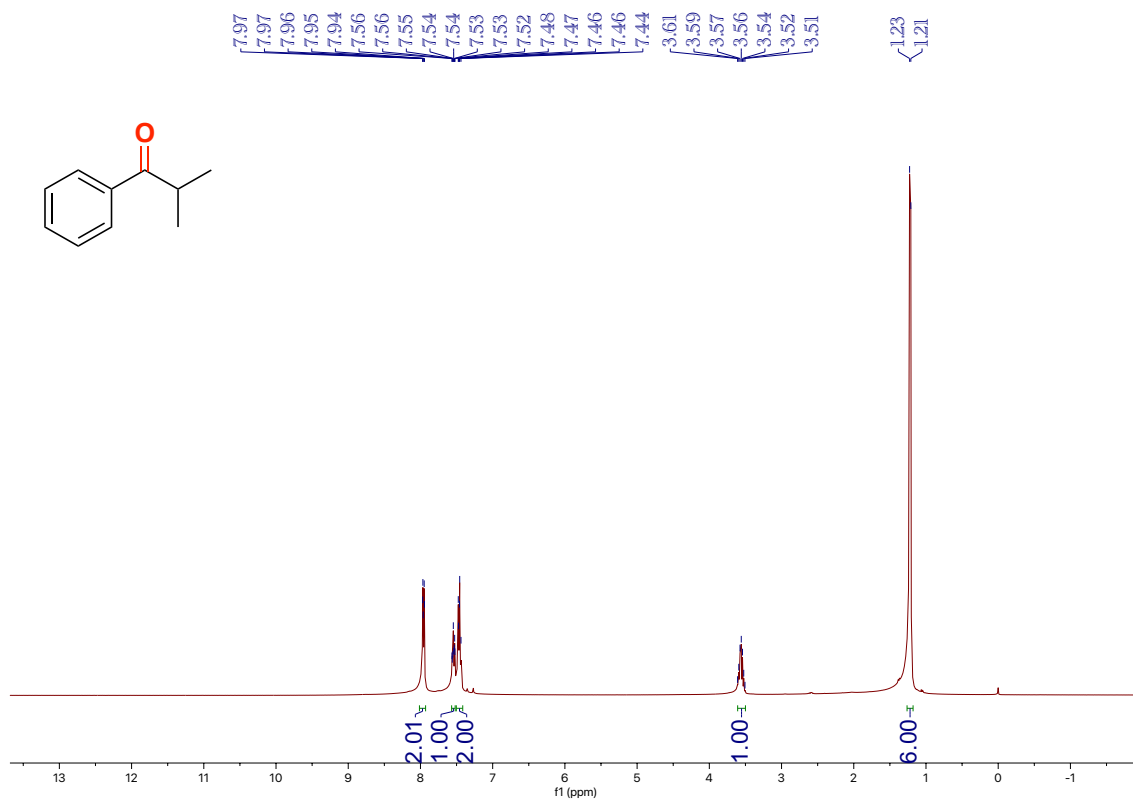


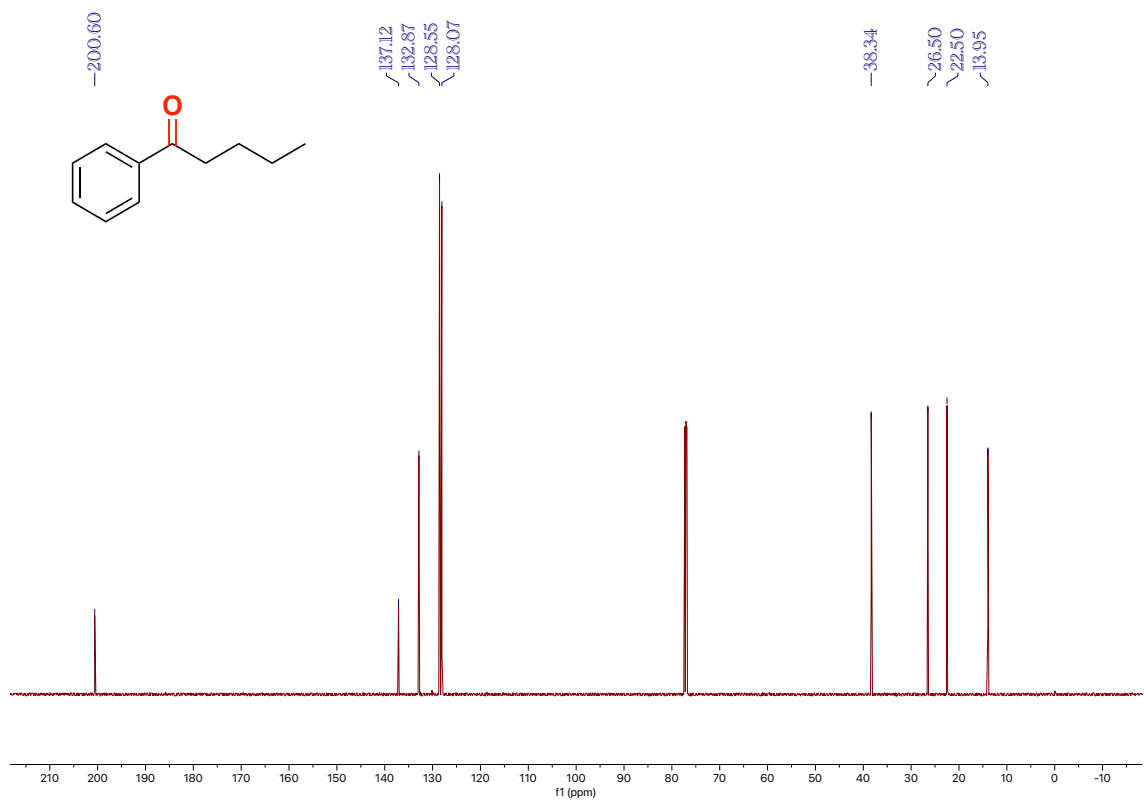
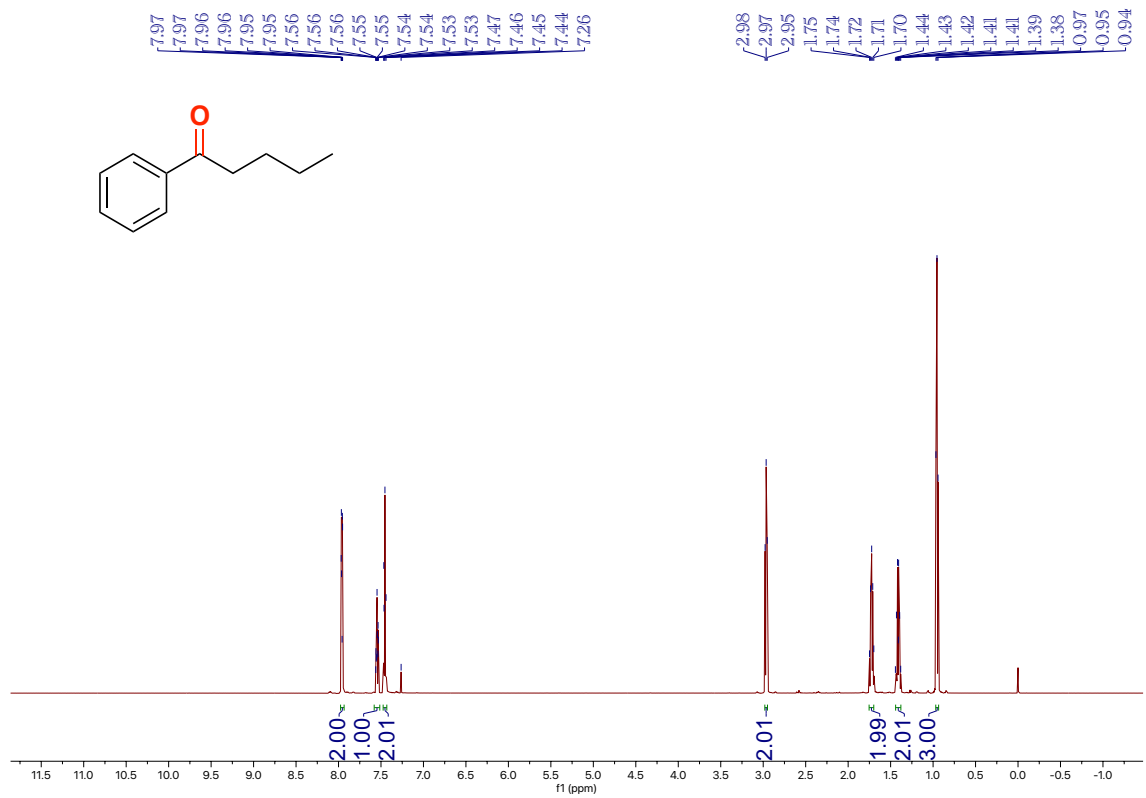


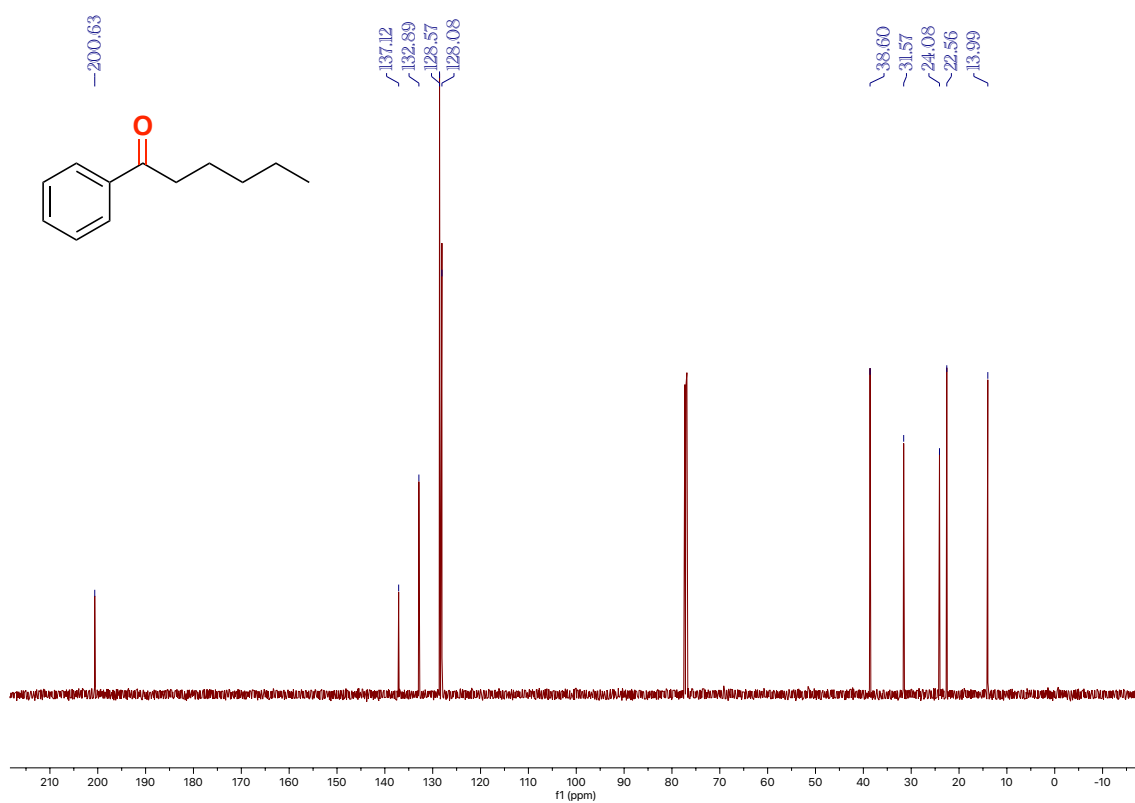
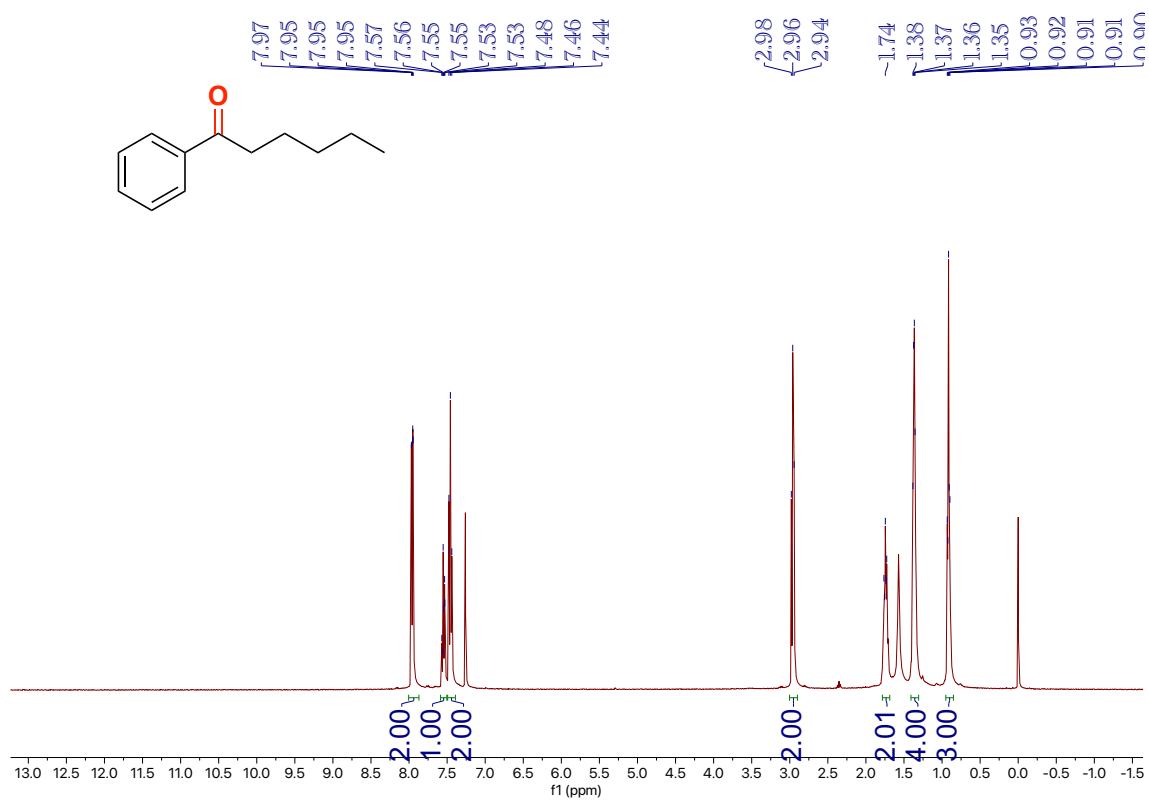


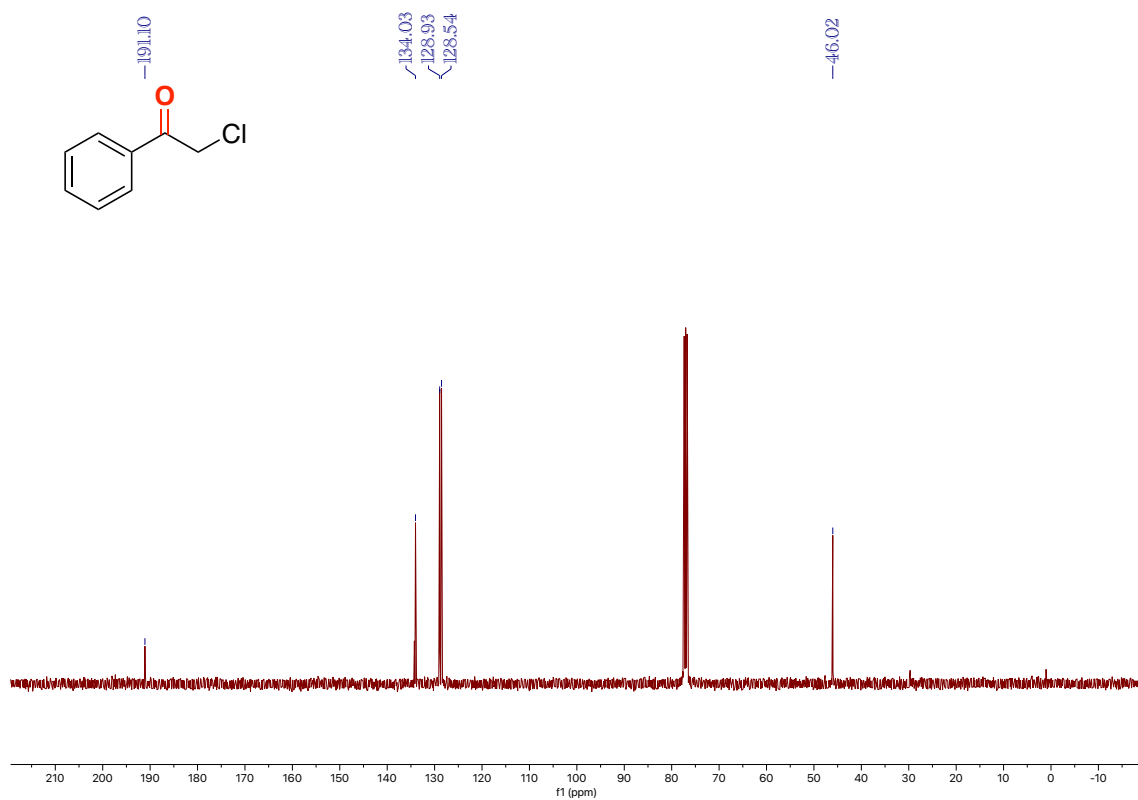
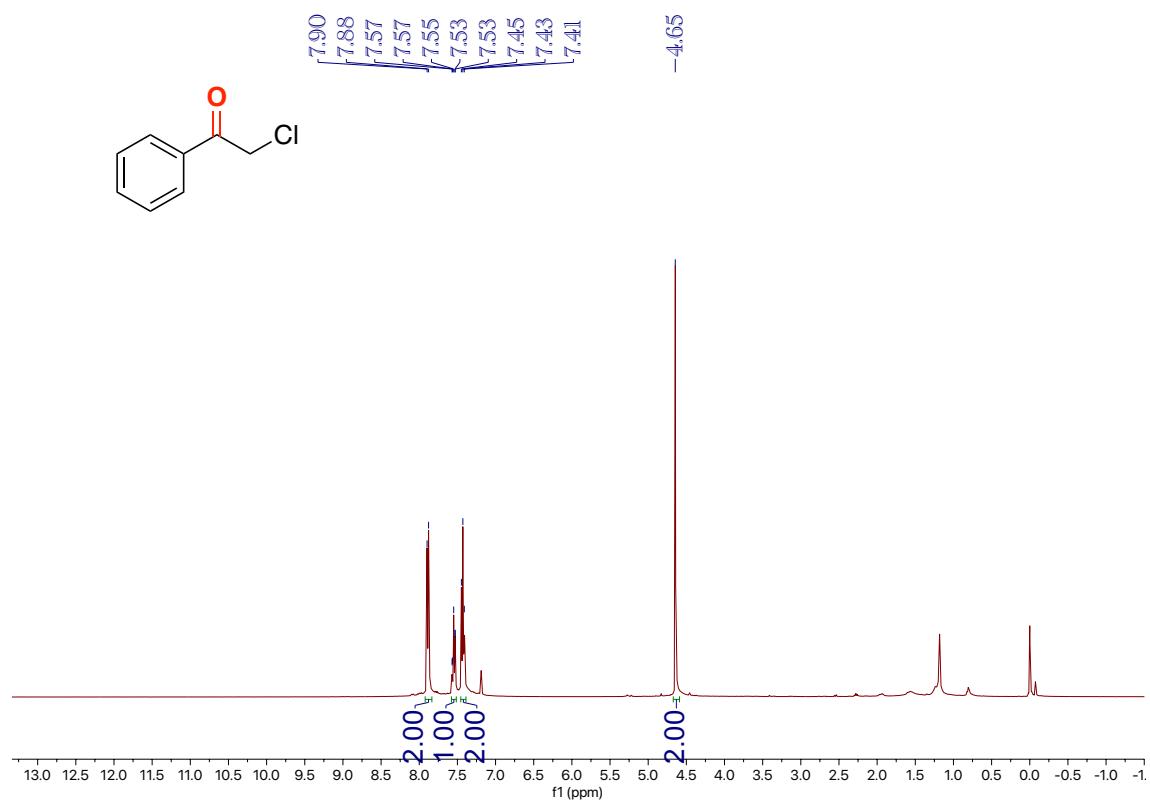


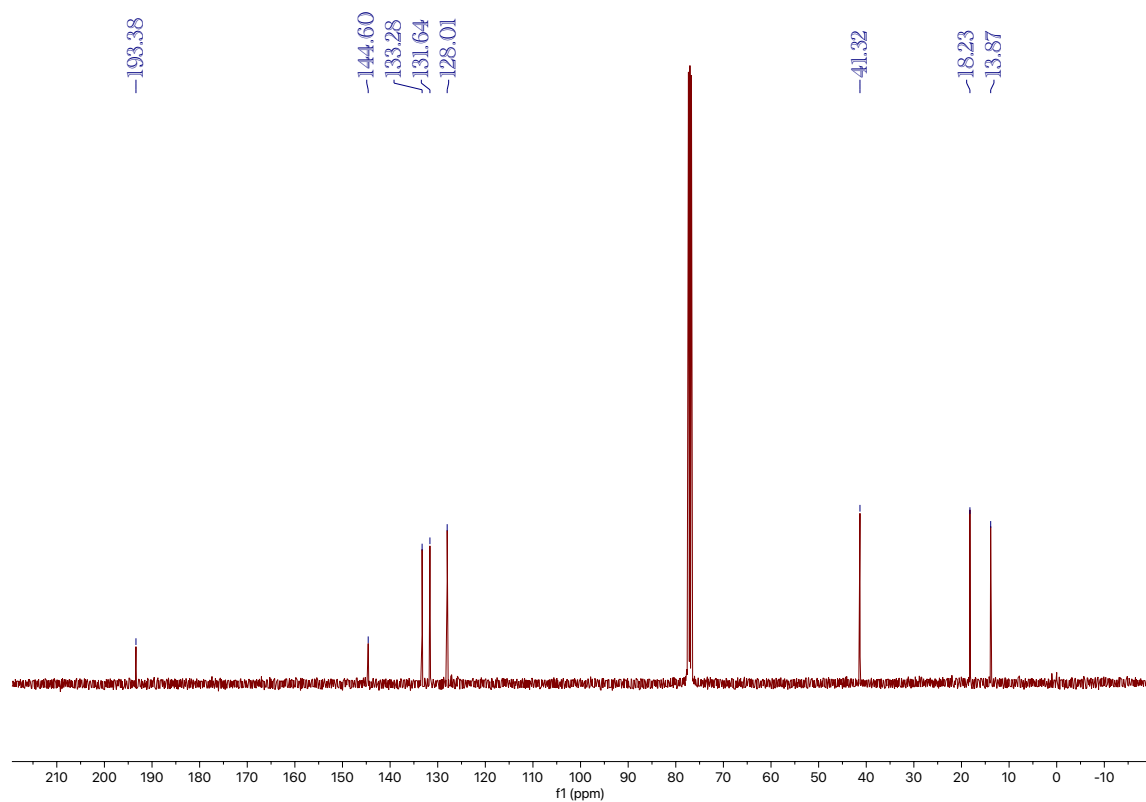
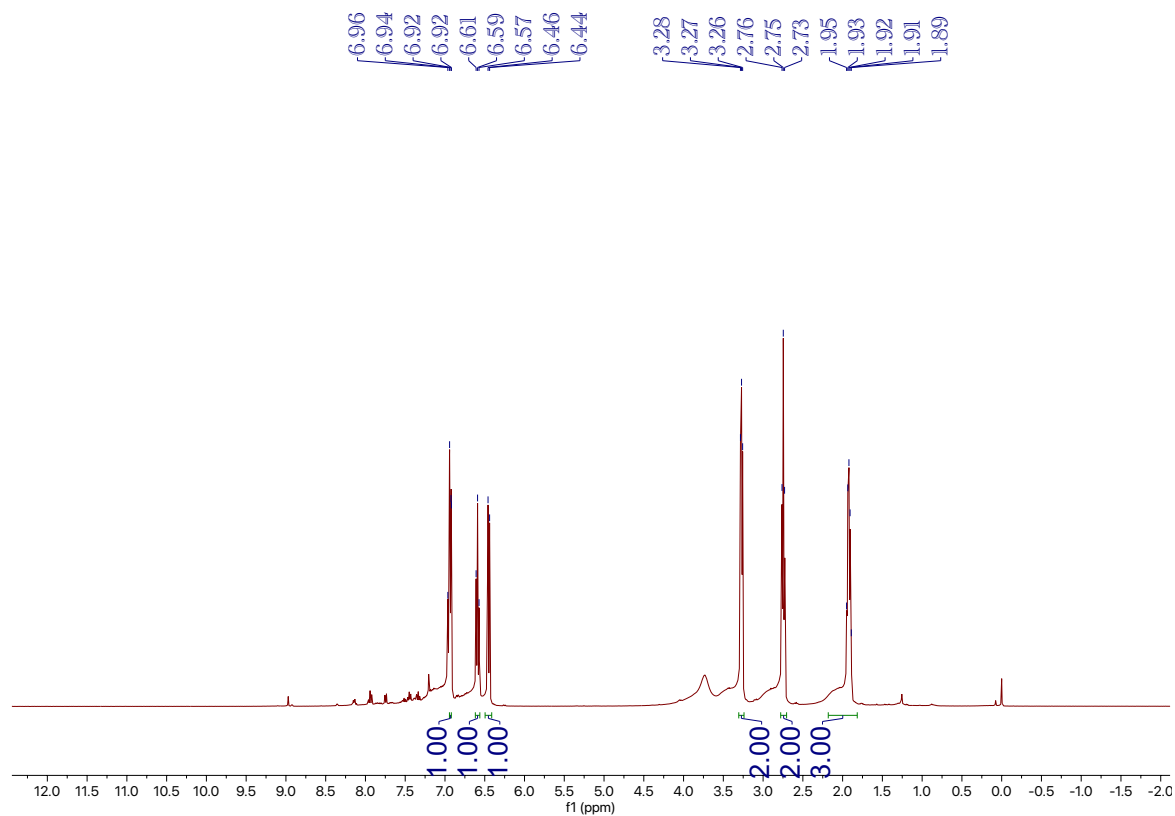
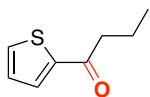


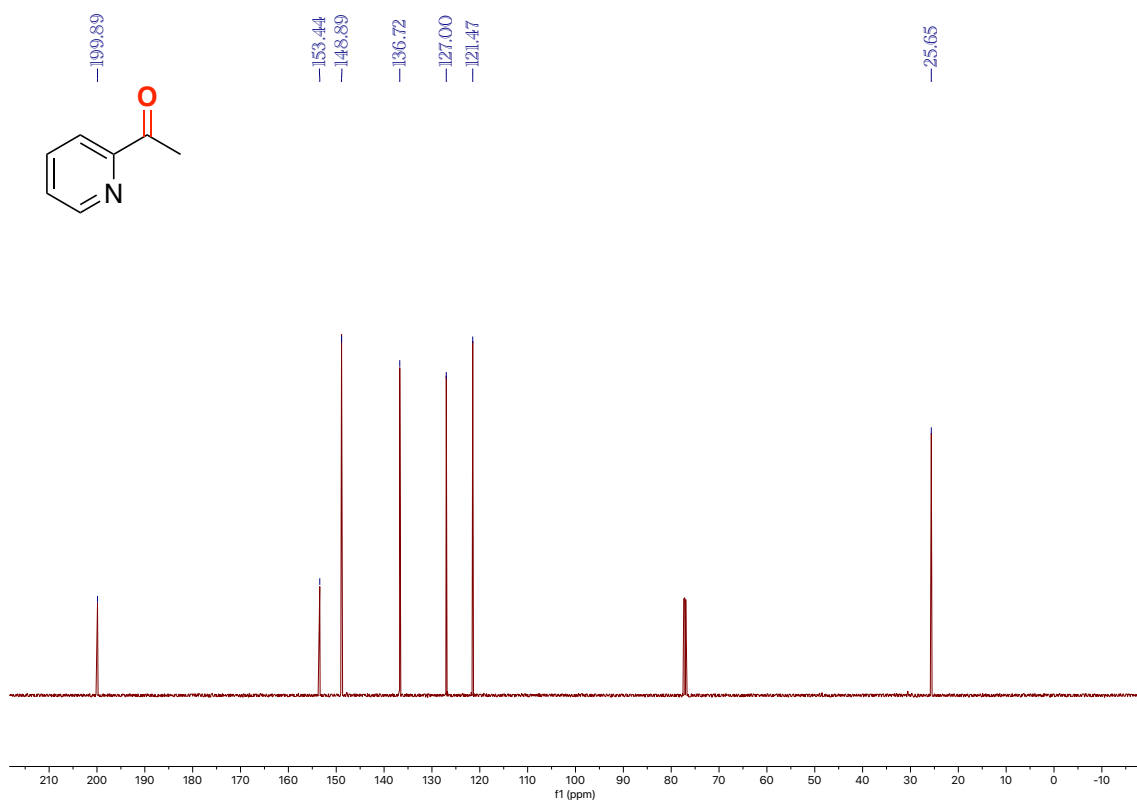
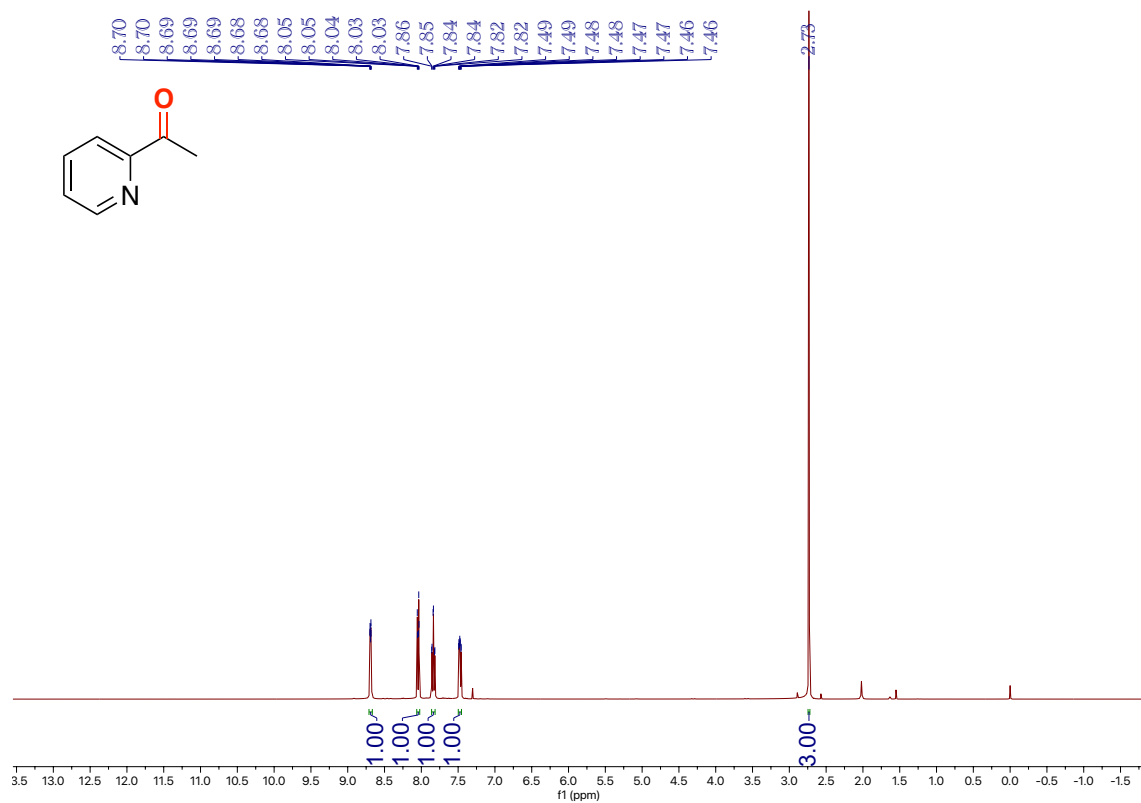


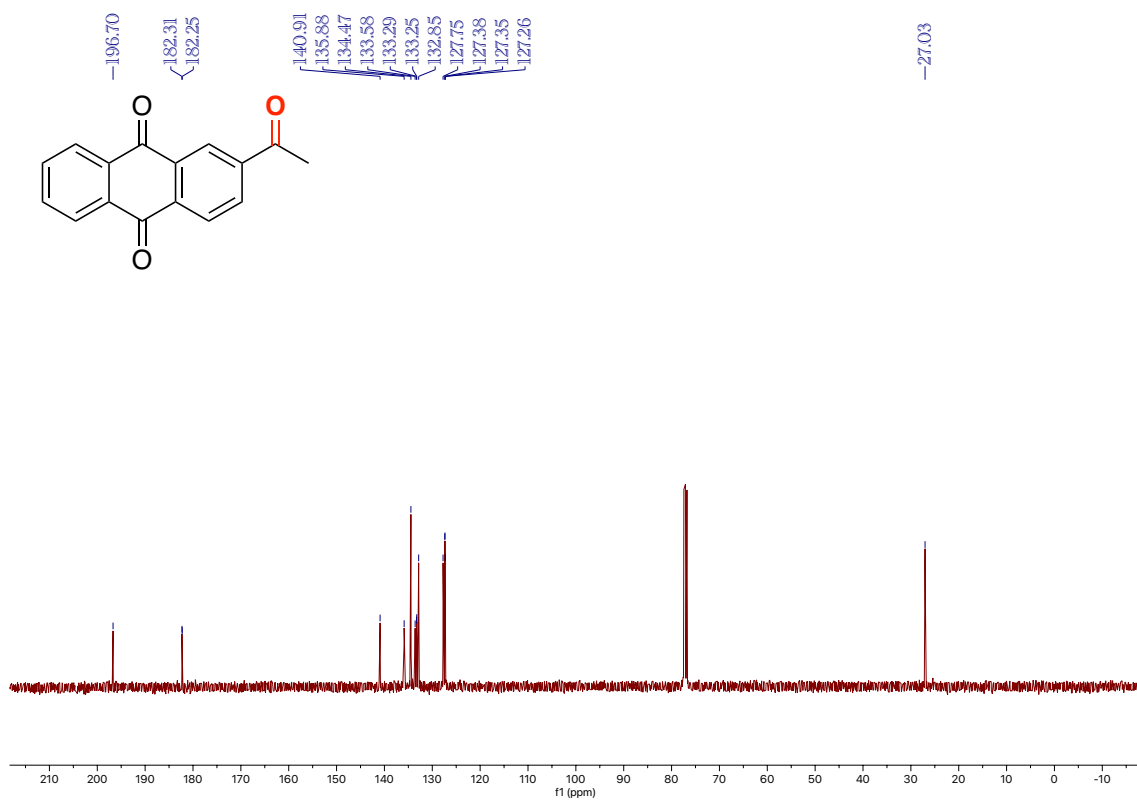
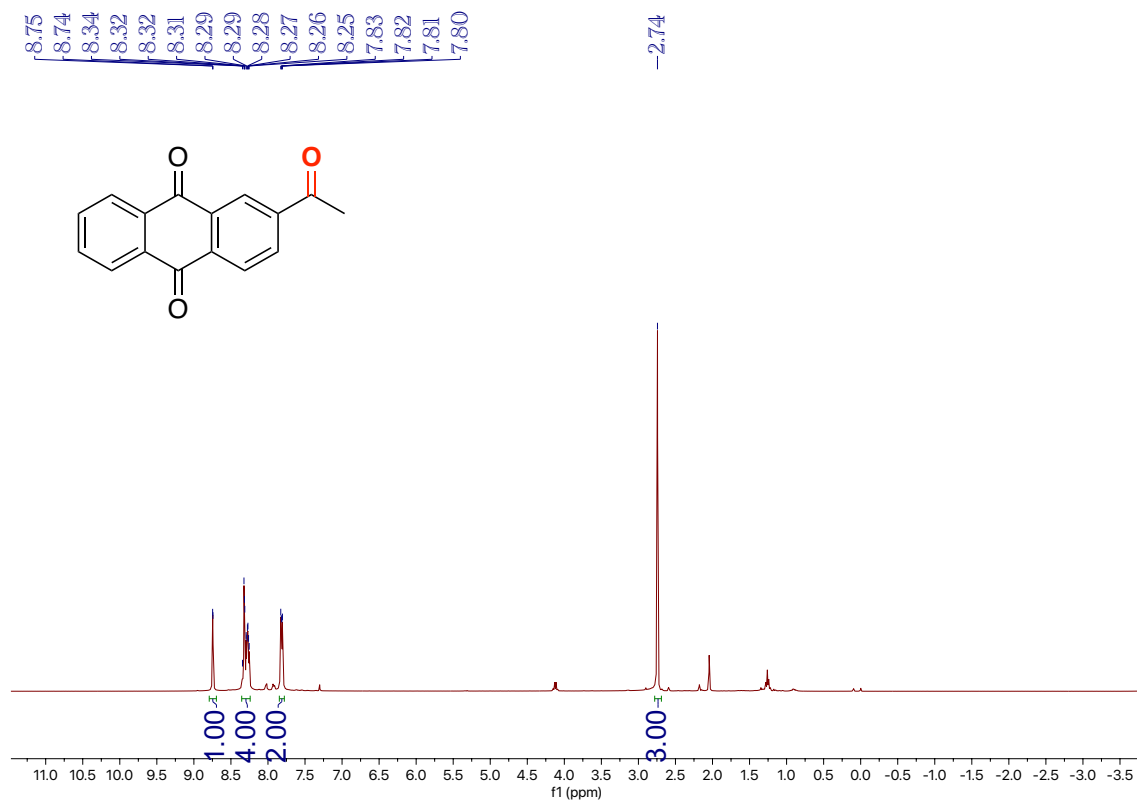


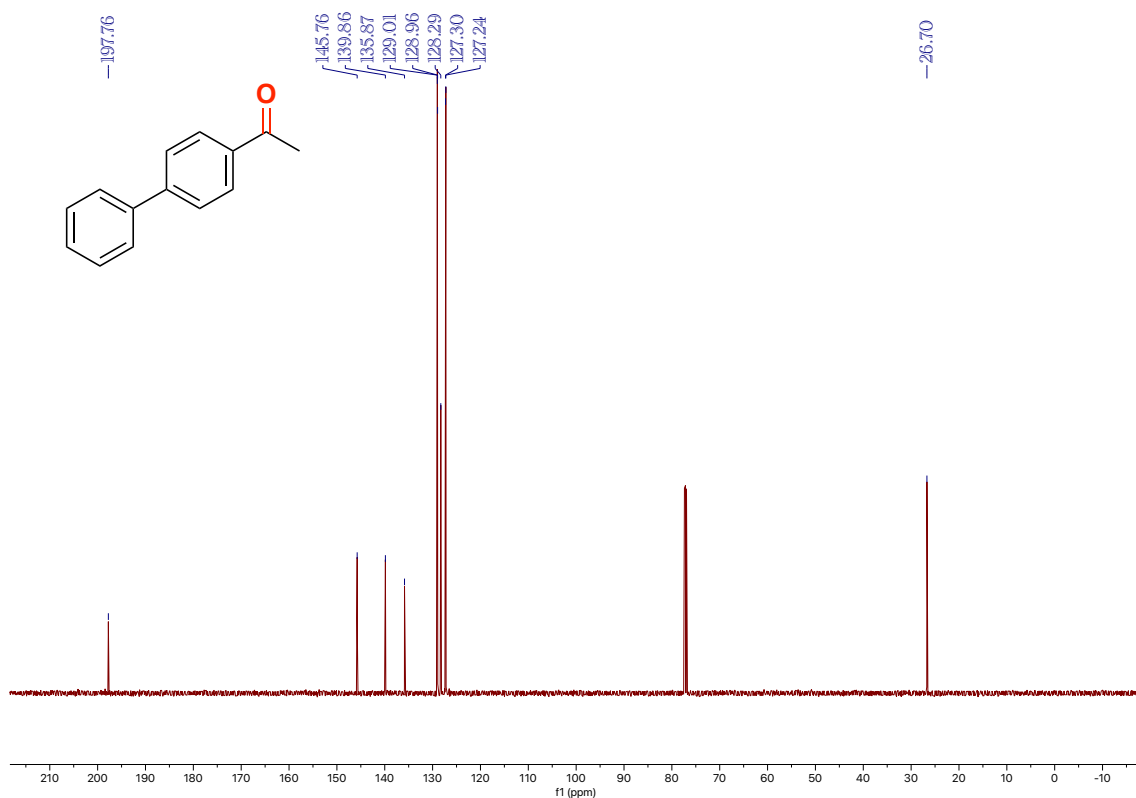
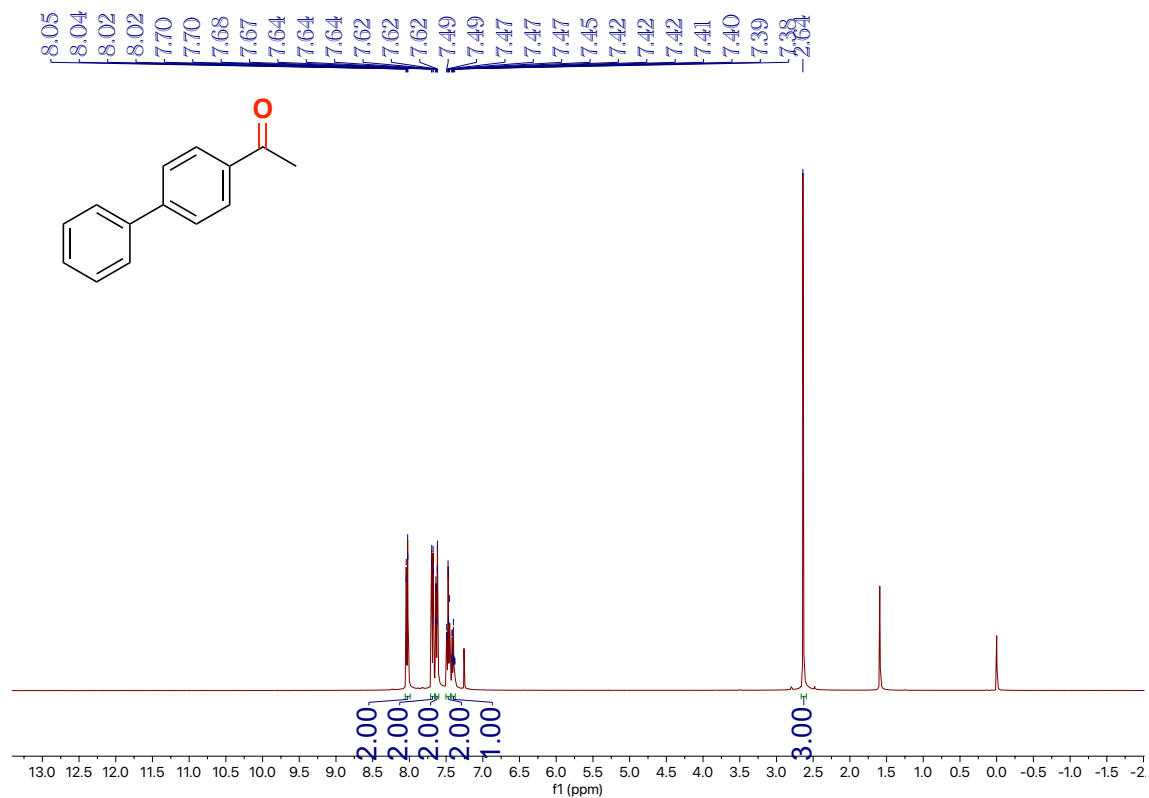


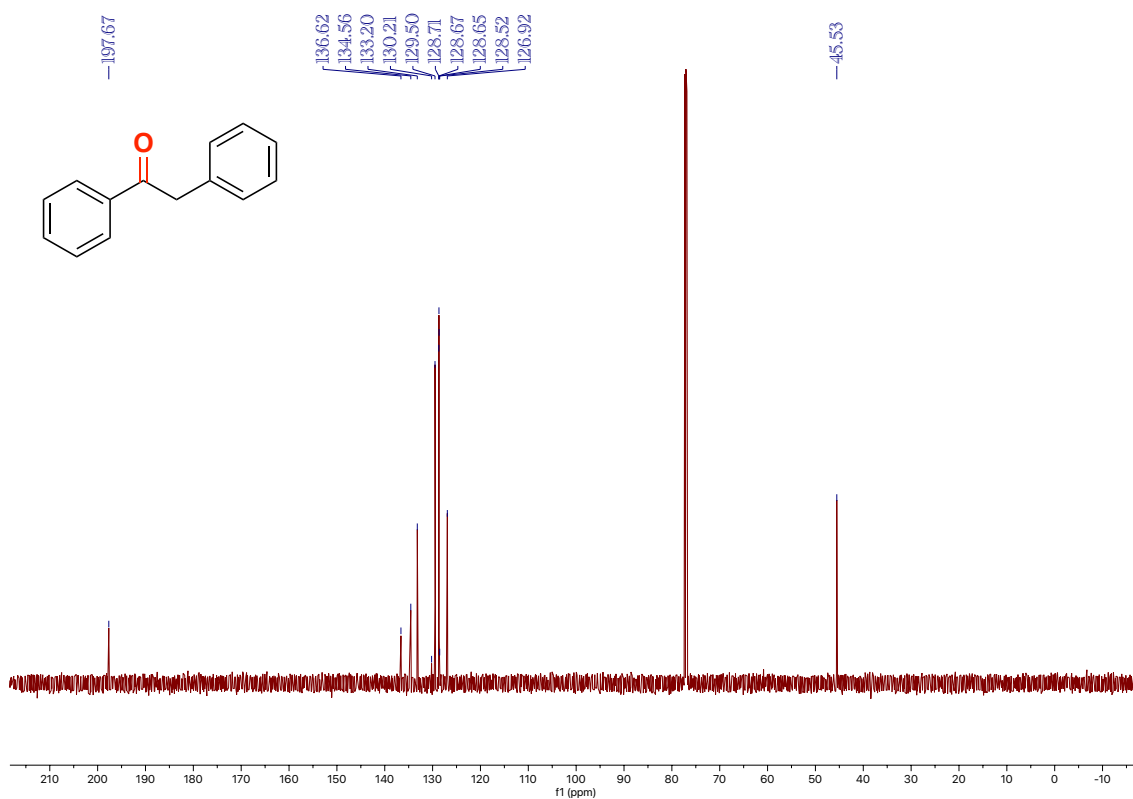
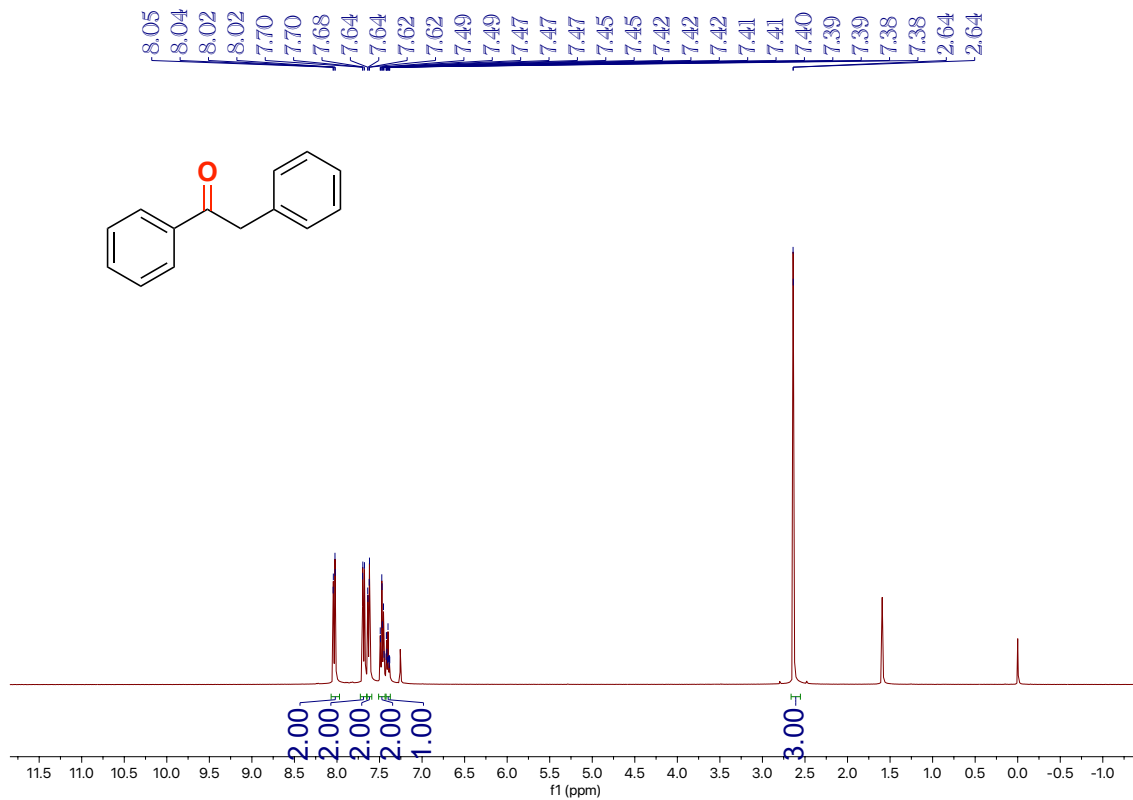


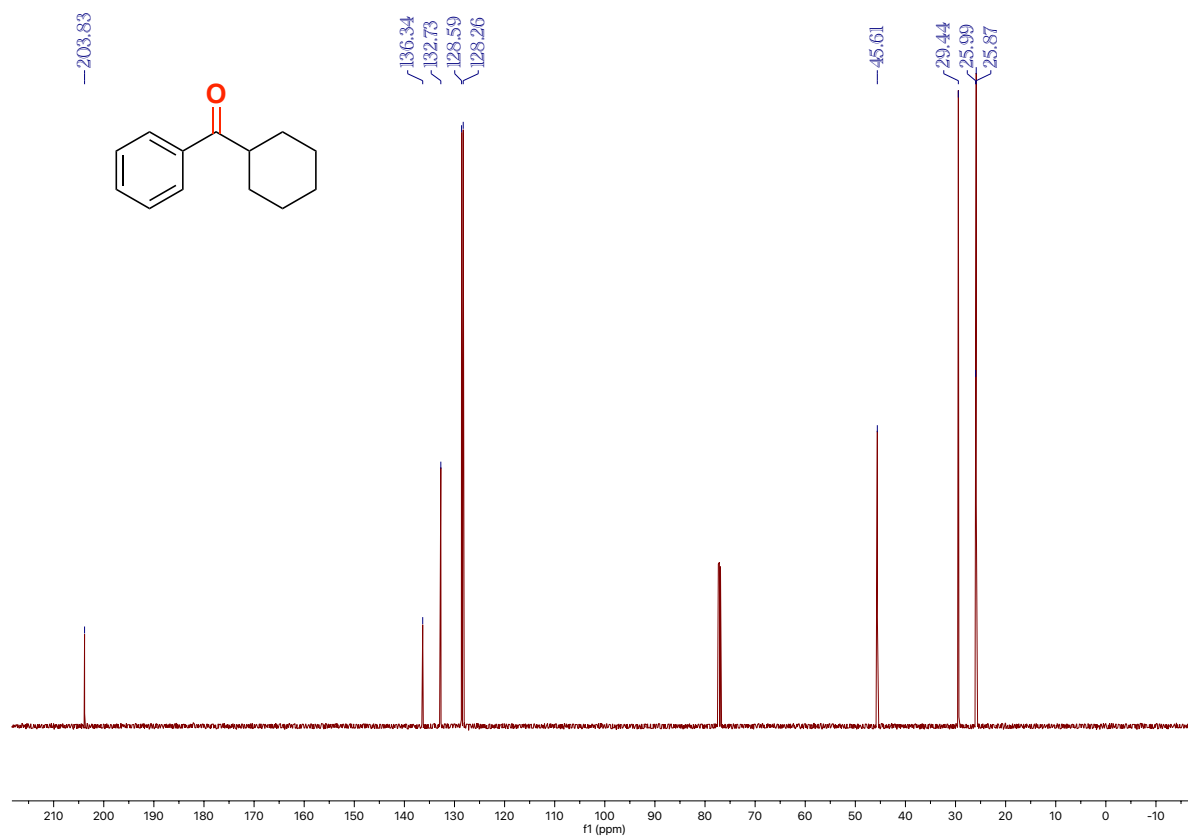
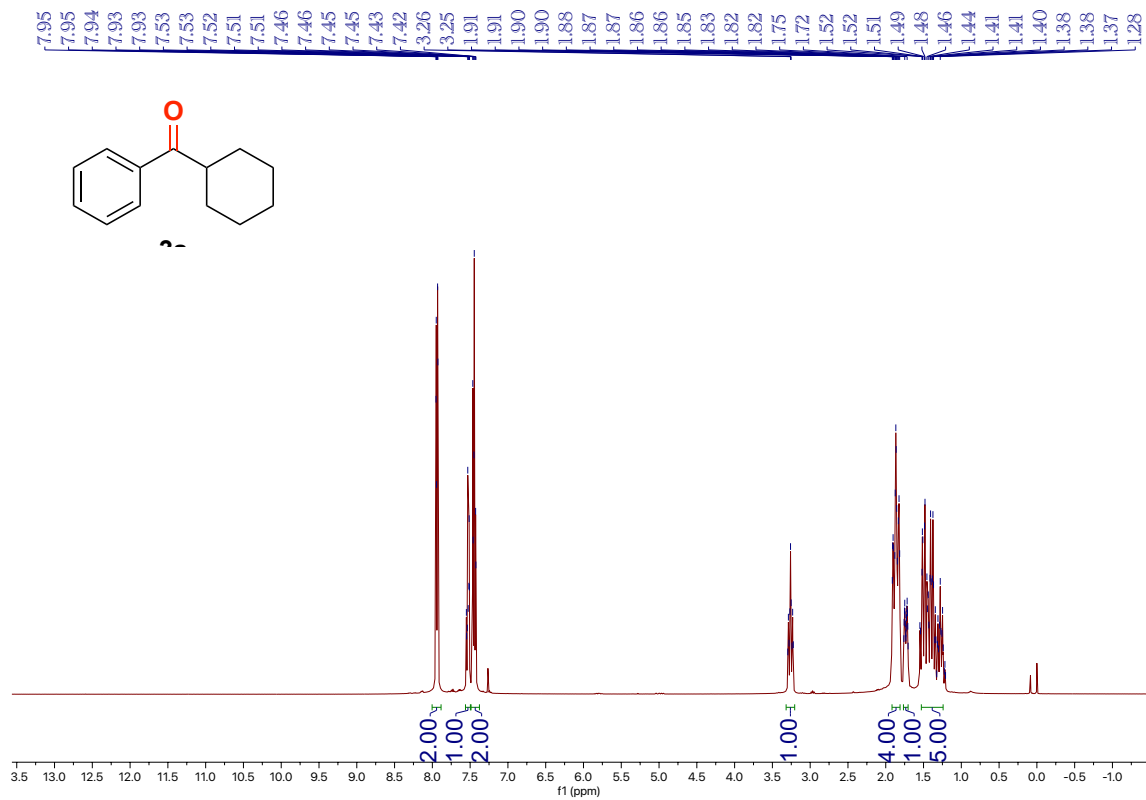


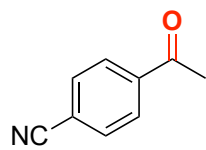






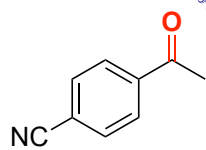
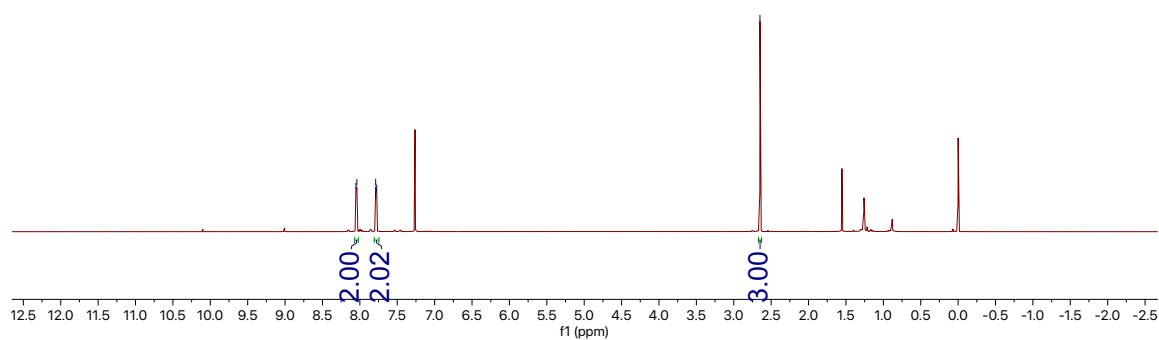






8.05
8.04
7.79
7.77

-2.65



8.05
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