

Supplementary Materials for  
**Mizoroki-Heck Type Reactions and Synthesis of 1,4-Dicarbonyl Compounds by Heterogenous Organic Semiconductor Photocatalysis**

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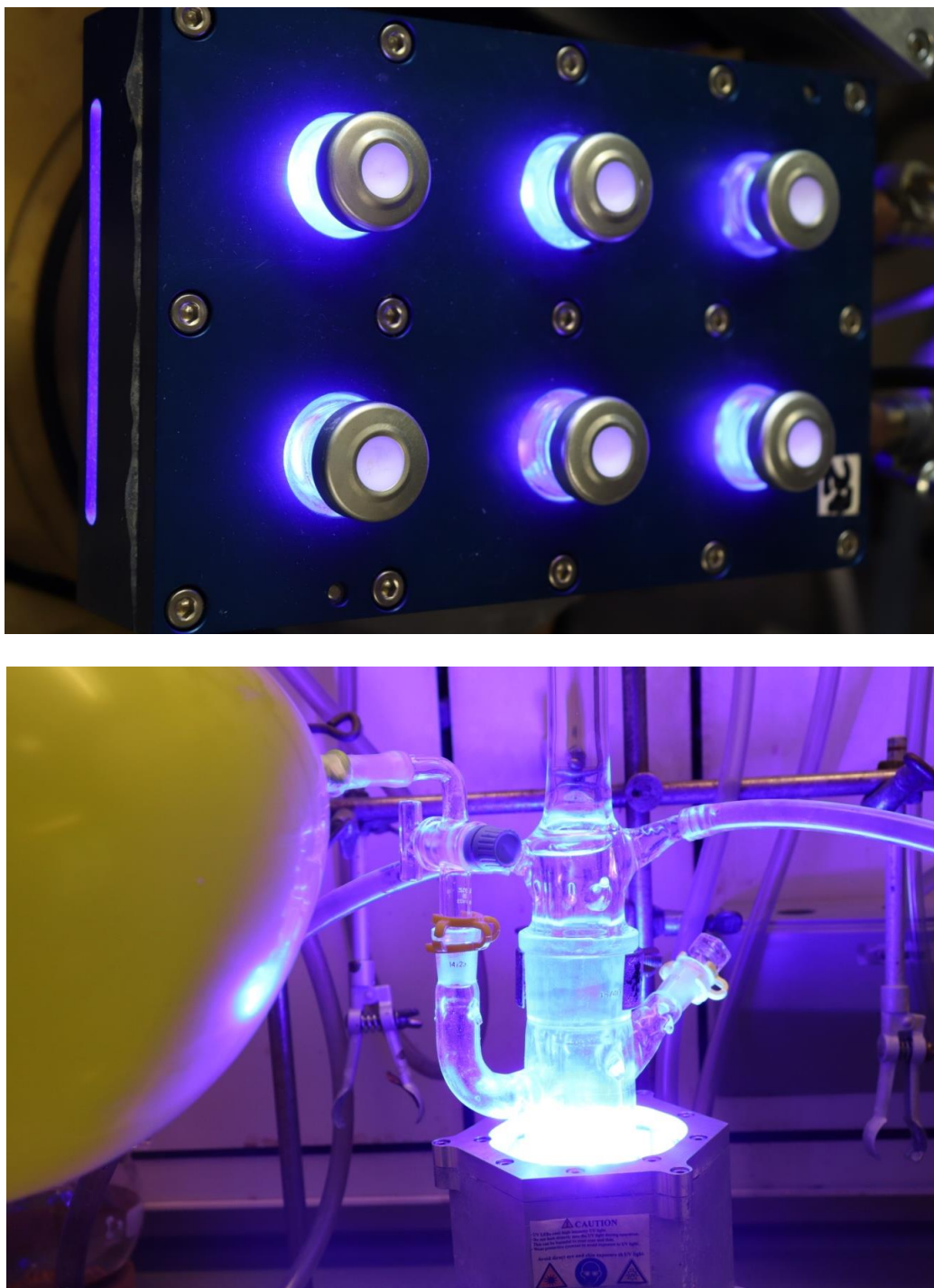
**This PDF file includes:**

1. General information
2. Photographs of the photochemical reaction set-ups
3. Synthetic procedures (general procedures for 1,4-dicarbonyl and Mizoroki-Heck Type reactions, and gram-scale reactions)
4. Mpg-CN synthesis and characterization.
5. Characterization of the isolated compounds (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F(whenever applicable) NMR spectra, and HRMS data)
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## 1. General information

All reactions were carried out with dry solvents unless otherwise stated. Dimethyl formamide (DMF) was dried with 3 Å molecular sieves following a reported procedure.<sup>1</sup> Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Thin-layer chromatography was performed using silica gel plates 60 F254: Visualization was accomplished with short wavelength UV light (254 nm) and near UV light (366 nm) sources. Standard flash chromatography was performed on a Biotage® Isolera™ Spektra system automated with high performance flash purification system using silica gel 60 M (particle size 40–63 μm, 230–440 mesh, Merck). <sup>1</sup>H, and <sup>13</sup>C spectra were recorded on Bruker Avance spectrometers (300 MHz, 75 MHz or 400 MHz, 101 MHz) in CDCl<sub>3</sub> solutions with internal solvent signals (for <sup>1</sup>H and <sup>13</sup>C) as reference (7.26, 77.2 for CDCl<sub>3</sub>). <sup>1</sup>H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, br. s. = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz), and numbers of protons. <sup>19</sup>F data are reported as follows: chemical shift (ppm), multiplicity (wherever applicable, s = singlet, d = doublet, t = triplet, q = quartet), coupling constants (Hz). Data for <sup>13</sup>C NMR are reported in terms of chemical shift, multiplicity (wherever applicable, s = singlet, d = doublet, t = triplet, q = quartet), coupling constants (Hz), and no special nomenclature is used for equivalent carbons. High resolution mass spectra (HRMS), low resolution mass spectra (LRMS), and high performance liquid chromatography mass spectra (HPLC–MS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University, and are reported according to the IUPAC recommendations 2013. Gas chromatography (GC) and gas chromatography coupled to low-resolution mass spectrometry (GC–MS) analysis were performed using a capillary column (length: 30 m; diam.: 0.25 mm; film: 0.25 μm) using He gas as carrier. GC was equipped with an FID detector. GC–MS was performed on 5975 MSD single quadrupole detector. The photochemical reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 LDCQ7P-1U3U (blue, λ<sub>max</sub> = 455 (± 15) nm, I<sub>max</sub> = 1000 mA, 1.12 W). The photochemical reactions under high power LED illuminations were performed using a photoreactor.

## 2. Photographs of the photochemical reaction set-ups



**Fig. S1.** Photograph of the photochemical reaction set-up. The reaction vials (5 mL crimp cap vials) were illuminated from the bottom with LEDs (in this case with blue LEDs:  $\lambda = 455 (\pm 15)$  nm), and cooled (to maintain the reaction temperature of 25.0 °C) from the side using custom-made aluminium cooling blocks connected to a thermostat. Bottom: Photograph of the high light intensity Tauchschatreaktor.

### 3. Synthetic procedures (general procedures for 1,4-dicarbonyl and Mizoroki-Heck Type reactions, and gram-scale reactions)

**General procedure 1, 1,4-dicarbonyl compounds:** A 5 mL snap vial was charged with a magnetic stirring bar, vinyl acetate (0.2 mmol, 1.0 equiv.), mpg-CN (10.0 mg), alkyl bromide (0.3 mmol, 1.5 equiv.), and NiBr<sub>2</sub>•glyme (0.0025 mmol, 0.0125 equiv.). 1 mL DMF was added and followed by 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was then introduced to a nitrogen atmosphere via "pump-freeze-thaw" cycles (×3) with a syringe needle and irradiated at 25 °C through the plane bottom side of the snap vial using a 455 (± 15) nm LED. (see Fig. S1 for the reaction set up). The reaction progress was monitored by GC and GC–MS analysis. After completion, the reaction mixture was transferred to a centrifuge tube (approx. 3 × 3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged (time approx. 1–10 minutes) until the heterogeneous photocatalyst mpg-CN precipitates. The supernatant liquid was collected in a separating funnel, and the solid in the centrifuge tube was washed three times using approx. 10 mL ethyl acetate added to the same separating funnel. Then, approx. 10–15 mL of distilled water and 2–4 mL of brine solution were added, shaken, and the organic layer was collected. The water layer was extracted again with ethyl acetate (2 × 20 mL). The combined organic layer was washed with 0.01N HCl solution and the organic layer was collected. The combined organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. Purification of the crude product was achieved by column chromatography using petrol ether/ethyl acetate as eluents on silica gel.

**General procedure for gram-scale synthesis:** A "Tauchschaftreaktor" was charged with a magnetic stirring bar, the vinyl acetate (6.0 mmol, 1.0 equiv.), mpg-CN (150.0 mg), and the alkyl bromide (9 mmol, 1.5 equiv.), NiBr<sub>2</sub>•glyme (0.125 mmol, 0.025 equiv.). Then, 70 mL of DMF was added and followed by 2,6-Lutidine (7.25 mmol, 1.25 equiv.). The reaction mixture was placed in a nitrogen atmosphere via "pump-freeze-thaw" cycles (×3). The reaction mixture was then irradiated at 20 °C under nitrogen atmosphere using a photochemical reaction set up shown in Fig. S1 using 455 (± 15) nm LEDs. After completion, the reaction mixture was transferred to a centrifuge tube (approx. 6 × 10 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged until the mpg-CN precipitates. The supernatant liquid was then collected in a separating funnel, and the solid in the centrifuge tube was washed 6 times using approx. 10 mL ethyl acetate and the solvent added to the same separating funnel. Then, approx. 60 mL of brine solution was added, shaken, and the organic layer was collected. The water layer was extracted with ethyl acetate (4 × 60 mL). The combined organic layers were washed with 70 mL 0.01 N HCl solution and the organic layer was collected and dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. Purification of the crude product was achieved by column chromatography using petrol ether/ethyl acetate as eluents on silica gel.

**General procedure 2, Mizoroki-Heck Type Reaction:** A 5 mL snap vial was charged with a magnetic stirring bar, 4-methoxy styrene (0.2 mmol, 1.0 equiv.), mpg-CN (10.0 mg), alkyl bromide (0.4 mmol, 2 equiv.), NiBr<sub>2</sub>•glyme (0.125 mmol, 0.025 equiv.). 1 mL DMF was added. The reaction mixture was then introduced to a nitrogen atmosphere via "pump-freeze-thaw" cycles (×3) with a syringe needle, and irradiated at 25 °C through the plane bottom side of the snap vial using a 455 (± 15) nm LED. (see Fig. S1 for the reaction set up). The reaction progress was monitored by GC and GC–MS analysis. After completion, the reaction mixture was transferred to a centrifuge tube (approx. 3 × 3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged (time approx. 1–10 minutes) until the heterogeneous

photocatalyst mpg-CN precipitates. The supernatant liquid was collected in a separating funnel, and the solid in the centrifuge tube was washed three times using approx. 10 mL ethyl acetate added to the same separating funnel. Then, approx. 10–15 mL of distilled water and 2–4 mL of brine solution were added, shaken, and the organic layer was collected. The water layer was extracted again with ethyl acetate (2 × 20 mL). The combined organic layer were dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. Purification of the crude product was achieved by column chromatography using petrol ether/ethyl acetate as eluents on silica gel.

**General procedure for gram-scale synthesis:** A “Tauchschaftreaktor” was charged with a magnetic stirring bar, the 4-methoxy styrene (6.0 mmol, 1.0 equiv.), mpg-CN (150.0 mg), and the alkyl bromide (12 mmol, 2 equiv.), NiBr<sub>2</sub>•glyme (0.15 mmol, 0.025 equiv.). The reaction mixture was placed in a nitrogen atmosphere via “*pump-freeze-thaw*” cycles (×3). The reaction mixture was then irradiated at 20 °C under nitrogen atmosphere using a photochemical reaction set up shown in Fig. S1 using 455 (± 15) nm LEDs. After completion, the reaction mixture was transferred to a centrifuge tube (approx. 6 × 10 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged until the mpg-CN precipitates. The supernatant liquid was then collected in a separating funnel, and the solid in the centrifuge tube was washed 6 times using approx. 10 mL ethyl acetate and the solvent added to the same separating funnel. Then, approx. 60 mL of brine solution was added, shaken, and the organic layer was collected. The water layer was extracted with ethyl acetate (4 × 60 mL). The combined organic layers were collected and dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. Purification of the crude product was achieved by column chromatography using petrol ether/ethyl acetate as eluents on silica gel.

#### 4.1.Mpg-CN synthesis

Mpg-CN has been prepared according to the reported procedure.<sup>2</sup>

#### 4.2.Materials characterization

Powder X-Ray diffraction (PXRD) patterns have been acquired using Bruker D8 diffractometer using radiation from Cu K $\alpha$  ( $\lambda = 1.54060$  nm) equipped with scintillation counter detector in the range of  $2\theta$  3-60° with stepsize 0.05° and time per step 4 s.

Scanning electron microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX) have been performed on JSM-7500F (JEOL) at accelerating voltage 3 kV.

Inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 8000; Perkin Elmer) was used to analyze Ni content in the samples.

X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Fisher Scientific ESCALAB spectrometer with aluminum K $\alpha$  radiation. Data was processed using Origin 2020b. Shirley’s background has been subtracted prior deconvolution of the peaks. Ni 2p<sub>3/2</sub> XPS has been fitted taking into account reported data.<sup>3,4</sup> Br 3d XPS has been fitted taking into account Br 3d<sub>5/2</sub> - 3d<sub>3/2</sub> peak-to-peak separation of 1.1 eV and Br 3d<sub>5/2</sub> to Br 3d<sub>3/2</sub> intensity ratio 0.671.

Attenuated total reflectance Fourier-transform infrared spectra (ATR FT-IR) have been acquired in the range of wavelengths 550-4000 cm<sup>-1</sup> using Nicolet iS5 equipped with attenuated total reflectance module iD5.

Nitrogen sorption by the materials has been conducted at 77K using Quantasorb SI station. Prior measurements samples were degassed at 150°C in vacuum (<0.2 mbar) for 15 h. Relative pressure range (P/P<sub>0</sub>) from 0.05 to 0.3 was used to calculate surface area of the materials employing

Brunauer–Emmett–Teller (BET) theory model in Quantachrome® QuadraWin™ v.5.11 software. N<sub>2</sub> at 77K on carbon (slit/cylindric/sphere pores, quenched solid density functional theory (QSDF), adsorption branch kernel) has been chosen to analyze pore diameter distribution.

Diffuse-reflectance UV-vis (DRUV-vis) absorption spectra of the samples in solid state has been acquired using Shimadzu UV-2600 equipped with integrating sphere.

Room temperature steady-state photoluminescence spectra of the samples upon excitation with 365 nm, have been acquired using Jasco FP-8300 spectrometer.

High-resolution transmission electron microscopy (HR-TEM) images were obtained on a double-corrected Jeol ARM200 at an acceleration voltage of 80 kV and an emission of 10  $\mu$ A.

## Discussion

### Fresh mpg-CN characterization

Structure of the prepared mpg-CN has been confirmed by a series techniques and characterization data are in agreement with the reported earlier data.<sup>2</sup> EDX elemental composition revealed C/N ratio of 0.58 (Table S1), which is lower than expected for melon (i.e. 0.75) and is explained by the presence of terminal amino groups in the structure of mpg-CN due to incomplete condensation of the precursor and partially hydroxylated surface. In agreement with this conclusion is FT-IR spectrum (Figure S2). A broad peak with maximum at 3180  $\text{cm}^{-1}$  was assigned to N–H and hydrogen-bonded O–H stretch; a peak at 2180  $\text{cm}^{-1}$  – to nitrile stretch; a broad band between 1000–1650  $\text{cm}^{-1}$  is assigned to vibrations of CN heterocycles. The peak at 805  $\text{cm}^{-1}$  is assigned to deformation vibration of tri-s-triazine system. In addition, a peak at 1628  $\text{cm}^{-1}$  was assigned to primary amine N–H bend; a peak at 1561  $\text{cm}^{-1}$  – to secondary amine N–H bend; and a peak at 1230, 1308, 1398  $\text{cm}^{-1}$  – to C–O stretch.

Given that penetration depth in XPS is limited to  $\sim$ 5 nm, higher oxygen content (8.3 at. %) determined by this technique compared to EDX ( $2\pm 0.4\%$ ), confirmed that oxygen is localized mainly on the surface of the material (Table S2). Deconvolution of high-resolution XPS C 1s confirmed presence of three chemical states of this element in the sample (Figure S3a). The peak with maximum at 288.3 eV was assigned to carbon coordinated to nitrogen (CN<sub>3</sub>) (Figure S3a, S4),<sup>5,6</sup> the peak at 286.2 eV – to carbon bound to oxygen<sup>7,8</sup> and the peak at 284.7 eV to adventitious carbon.<sup>5,7,6</sup> Deconvolution of high-resolution XPS N 1s revealed the following chemical states: peak at 398.8 eV was assigned to di-coordinated nitrogen in C=N–C moieties of tri-s-triazine (Figure S4, S5a),<sup>5,8,9</sup> peak at 400.1 eV – to the central nitrogen atom of tri-s-triazine,<sup>5,9,6</sup> peak at 401.3 eV – to secondary and primary amino-groups in mpg-CN due to incomplete condensation,<sup>5,10,6</sup> and a broad peak of low intensity at 404.8 eV – to  $\pi$ - $\pi^*$  satellite or  $\pi$ -excitation that is indicative for conjugated aromatic structures.<sup>11,12</sup> Deconvolution of XPS O 1s revealed oxygen in two chemical states: the peak at 532.0 eV is assigned to oxygen bound to carbon (Figure S6a),<sup>5</sup> while the peak at 533.4 eV – to water absorbed in mpg-CN.<sup>5</sup>

From N<sub>2</sub> sorption isotherm, surface area of mpg-CN was determined to be 186  $\text{m}^2 \text{g}^{-1}$  (Figure S7a). Mpg-CN possesses pores in the range from 5 to 44 nm and maximum at 13 nm (Figure S7b). Mpg-CN is amorphous material as evidenced by PXRD pattern (Figure S8). The diffraction pattern features a peak at  $\sim 27^\circ$  that is related to interplanar periodicity in the material with the distance between layers of  $\sim 0.33 \text{ nm}$ .<sup>13,14</sup> Less pronounced peak at  $\sim 13^\circ$  is assigned to intraplanar periodicity in the material with the corresponding distance of  $\sim 0.68 \text{ nm}$ .

Absorption spectrum of mpg-CN features steep onset of absorption at  $\sim 460 \text{ nm}$  that is related to electron transition between conduction and valence band, i.e.  $\pi$ - $\pi^*$  transition (Figure S9a).<sup>14</sup> The

optical band gap calculated from Tauc plot assuming that mpg-CN is a direct semiconductor is 2.7 eV (Figure S9b).<sup>14</sup> Weaker onset of absorption at ~650 nm is assigned to n- $\pi^*$  transitions that involve N- and O-electron pairs (Figure S9a).<sup>15,16</sup> mpg-CN shows broad fluorescence signal with maximum at 508 nm (Figure S10).

Morphology of mpg-CN is represented by particles with the diameter ranging from few hundred nanometers to few micrometer (Figure S11a). HR-TEM image revealed mesoporous structure of the material with pore diameter in the range <10 nm up to ~25 nm (Figure S12a) that is consistent with the results of N<sub>2</sub> sorption (Figure S7b). HR-TEM image and the results of the corresponding FFT analysis (Figure S12b) confirmed PXRD data that mpg-CN is amorphous material, albeit possessing layered structure with the distance between layers of ~0.352 nm as seen from the profile analysis (Figure S12c).

### Recovered mpg-CN characterization

After the photocatalytic tests, mpg-CN was washed with a series of solvents and water, and characterized by the same set of techniques used for fresh mpg-CN. Thus, position and intensity of all peaks observed in FT-IR spectrum of mpg-CN revealed that bulk chemical structure of the photocatalyst has not changed (Figure S2). EDX and XPS revealed slightly enhanced oxygen content (Table S1, S2 and Figure S3b) that is explained by partial hydrolysis of terminal amino-groups on the surface of mpg-CN during work-up washing with water.

ICP-OES revealed that mpg-CN after the photocatalytic tests contained 0.0268±0.00033 wt. % of Ni (Table S3, entry 2). Detection limit of Ni by ICP-OES was determined to be >0.0013±0.00001 wt. % (Table S3, entry 1).

In agreement with the results of ICP-OES, Ni 2p<sub>3/2</sub> XPS showed a distinct signal of nickel (Figure S13b). Due to low intensity, precise assignment of oxidation state is not possible. However, taking into account presence of the complementary signal in high-resolution Br 3d XPS (Figure S14b), it is likely Ni(II) coordinated by the lone pairs of nitrogen rather than agglomerated Ni(0) particles.

Such Ni(II) species could be assigned to precatalyst. Taking into account loading of NiBr<sub>2</sub>·glyme (0.77 mg) and mpg-CN (10 mg) in a typical experiment, <1% of Ni retained in mpg-CN after catalyst recovery. Given that our synthetic protocol does not require explicitly added ligand, mpg-CN framework, due to abundant nitrogen atoms, might indeed act as a polydentate chelating ligand that stabilizes Ni(II) precatalyst. In agreement with the hypothesis that Ni in the recovered mpg-CN is represented by atomically dispersed species rather than Ni(0) agglomerates is PXRD pattern that is similar to PXRD pattern of fresh mpg-CN and does not show peaks that could be assigned to Ni(0). Furthermore, analysis of TEM images confirmed that mesoporous structure of mpg-CN retained after the photocatalytic synthesis (Figure S12d). HR-TEM (Figure S12d) and HAADF-STEM (Figure S12e) also revealed absence of Ni(0) agglomerates, while HAADF-STEM in high resolution confirmed presence of Ni single atoms clusters (Figure S12e), which further support our hypothesis that Ni atoms are stabilized by chelation by mpg-CN framework.

It should be noted that deposition of Ni black (1.4-12.6 wt. %) on carbon nitride photocatalyst has been observed by Pieber et al. in dual Ni/photoredox C–N coupling.<sup>4,17</sup> The differences found in this work and reported earlier we explain mainly by different structure of carbon nitride photocatalyst, covalent mpg-CN (used in this work) and ionic CN-OA-m<sup>18</sup> (used by Pieber et al.). Namely, ionic carbon nitrides contain N–metal moieties in their structure that can undergo ion exchange.<sup>19,20</sup> In the context of dual Ni/photoredox catalysis, at the first step, covalent carbon

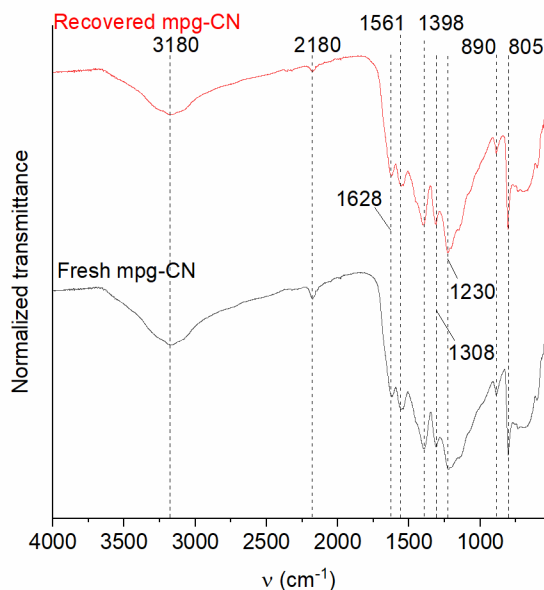
nitrides form chelating 16e complex of Ni, precatalyst, (Figure S15a), while ionic carbon nitrides coordinate Ni atoms via transmetalation and form more reactive 14e Ni(II)-amide complex (Figure S15b). Therefore, the difference in electronic configuration of Ni(II) complexes coordinated by carbon nitrides defines their reactivity and tendency to form Ni black.

Modification of mpg-CN surface also results in blue-shift of absorption onset in DRUV-vis spectrum (Figure S9a) and therefore expansion of optical band gap by  $\sim 0.05$  eV (Figure S9b). In steady-state PL such surface modification of mpg-CN is observed as blue shift of fluorescence by  $\sim 0.1$  eV.

Morphology of recovered mpg-CN particles adopted rounded shape compared to more rough surface of fresh mpg-CN (Figure S11b).

**Table S1.** EDX elemental analysis.

Sample	C wt. %	N wt. %	O wt. %
Fresh mpg-CN	36 $\pm$ 1.3	62 $\pm$ 1.2	2 $\pm$ 0.4
Recovered mpg-CN	36 $\pm$ 2.5	60 $\pm$ 2.2	3 $\pm$ 0.7

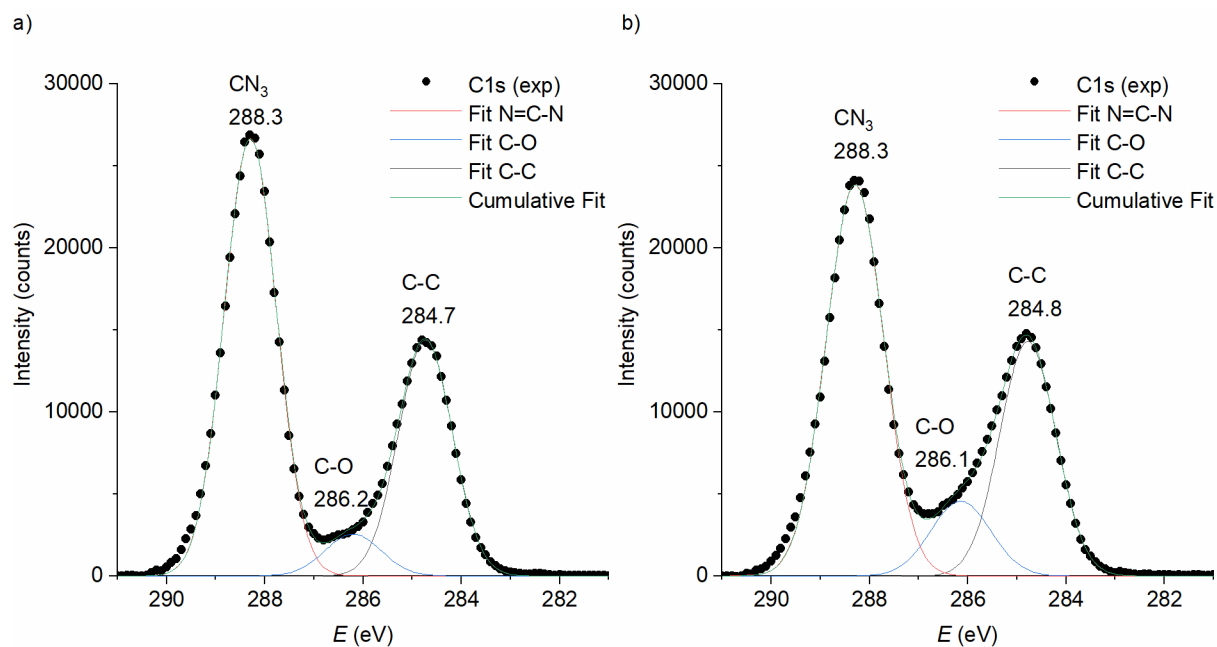


**Figure S2.** FT-IR spectra of fresh mpg-CN and recovered after the photocatalytic experiment.

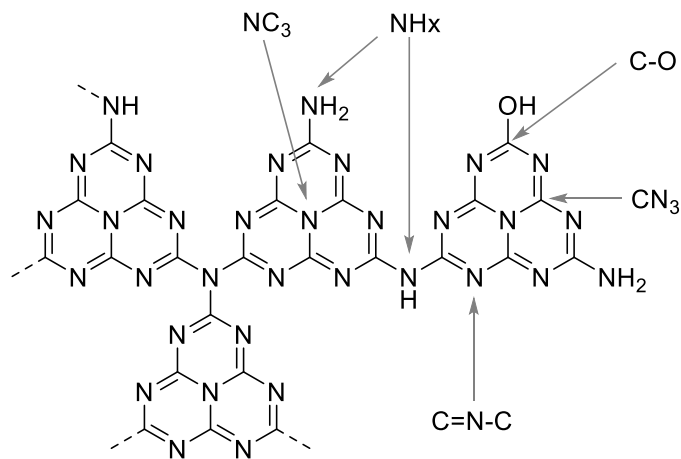
**Table S2.** XPS elemental analysis.

Sample	C at. %	N at. %	O at. %
Fresh mpg-CN	28.4	63.3	8.3
Recovered mpg-CN	28.7	59.5	15.8

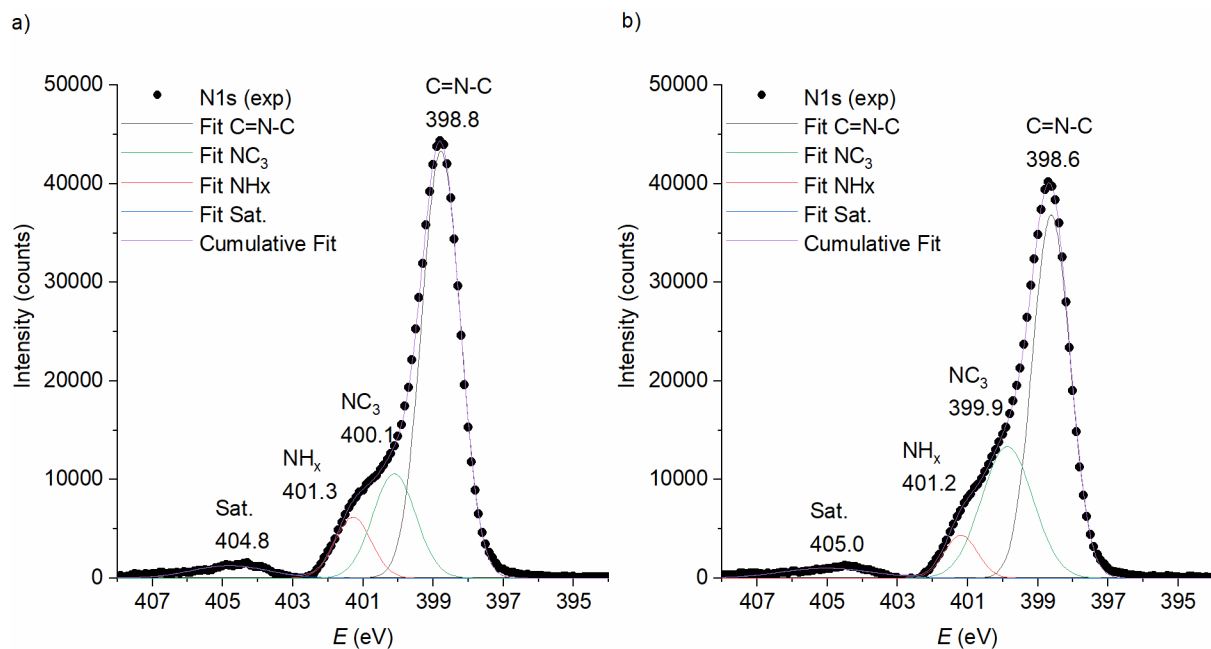




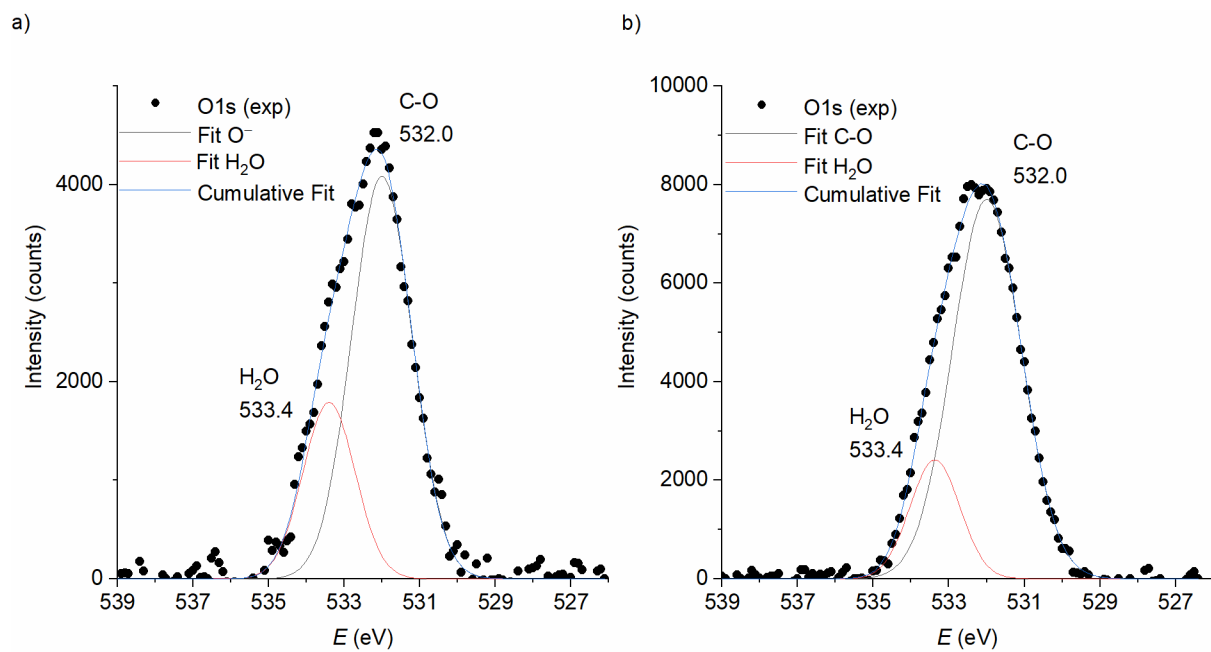
**Figure S3.** C 1s XPS of fresh (a) and recovered after the photocatalytic experiment mpg-CN (b).



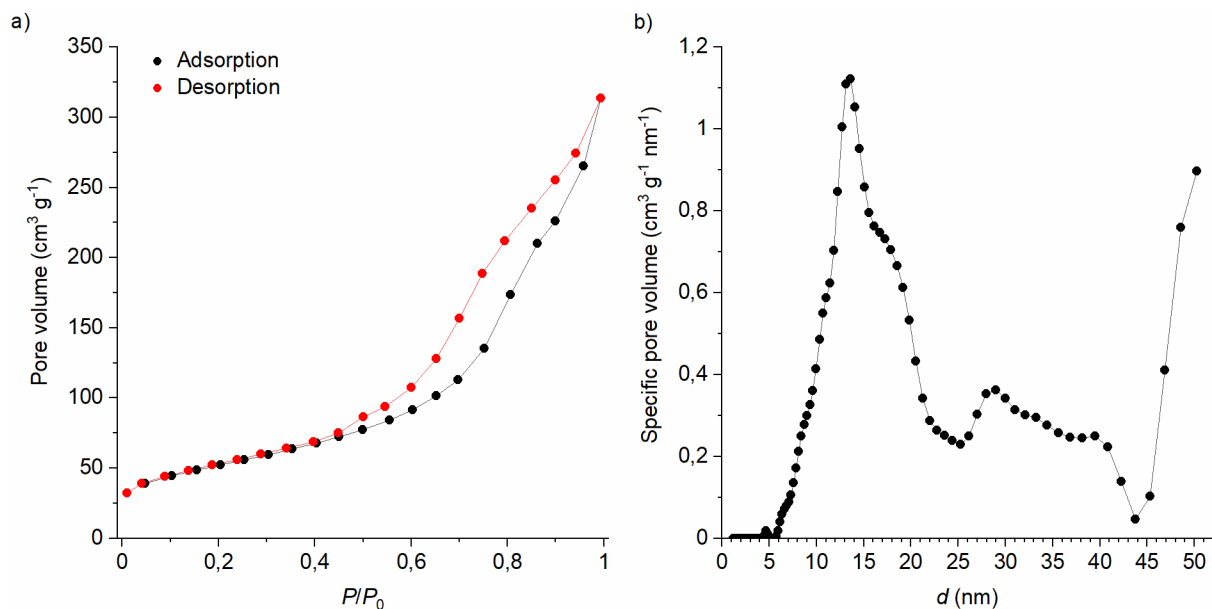
**Figure S4.** A fragment of mpg-CN structure based on characterization data.



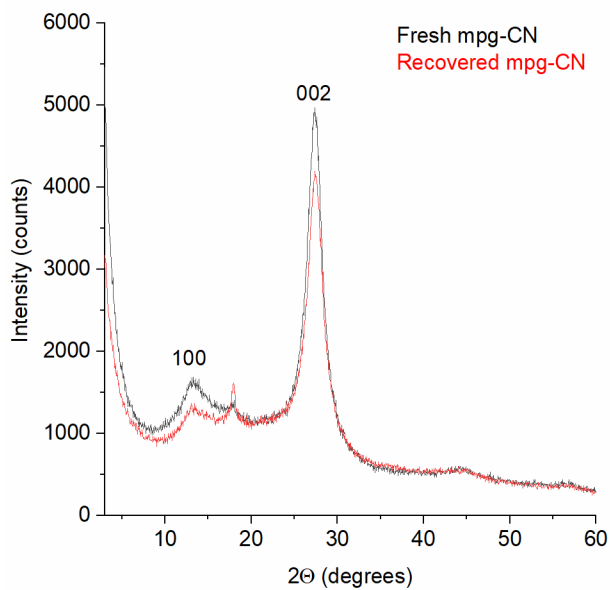
**Figure S5.** N 1s XPS of fresh (a) and recovered after the photocatalytic experiment mpg-CN (b).



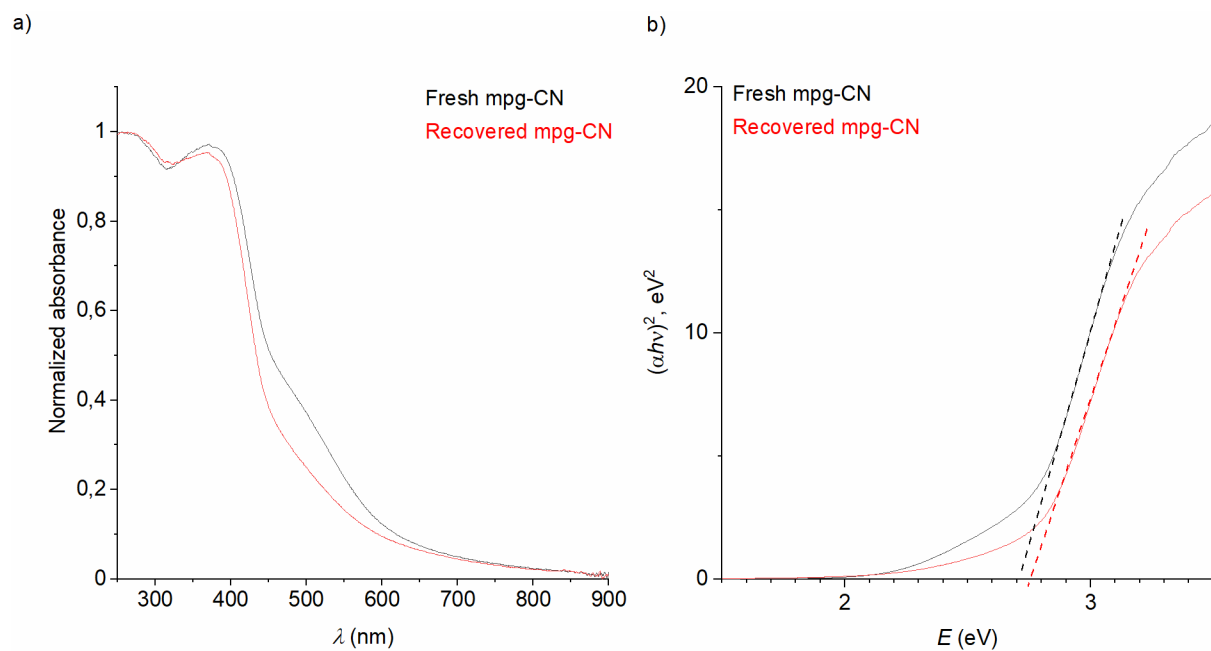
**Figure S6.** O 1s XPS of fresh (a) and recovered after the photocatalytic experiment mpg-CN (b).



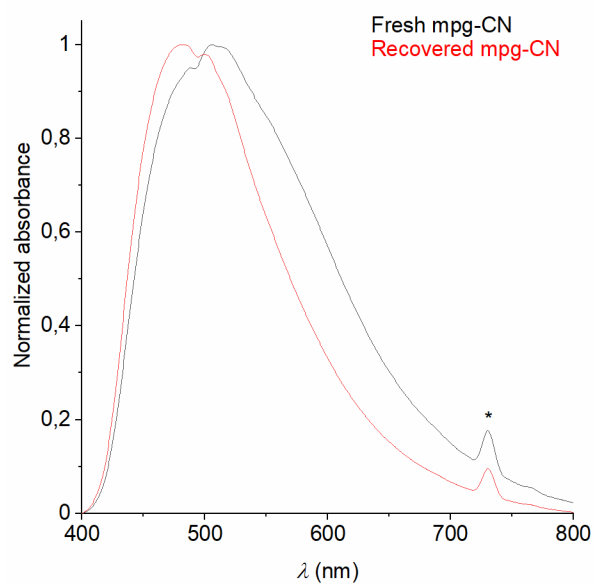
**Figure S7.**  $N_2$  sorption isotherm recorded at 77K (a) and pore size distribution in mpg-CN (b).



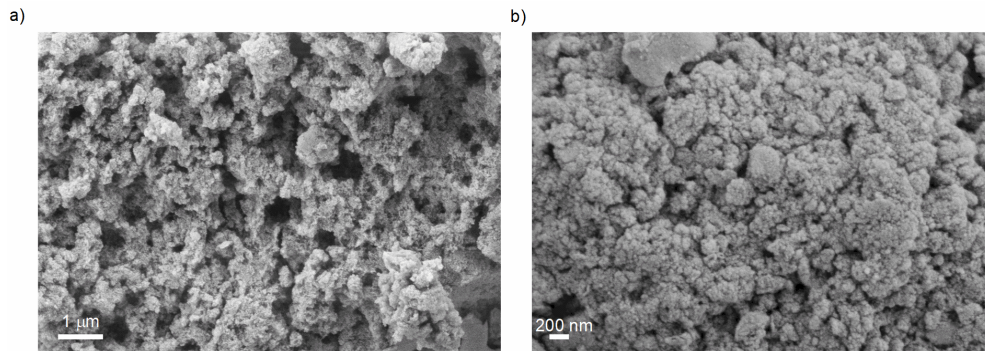
**Figure S8.** PXRD pattern of fresh and recovered after the photocatalytic experiment mpg-CN.



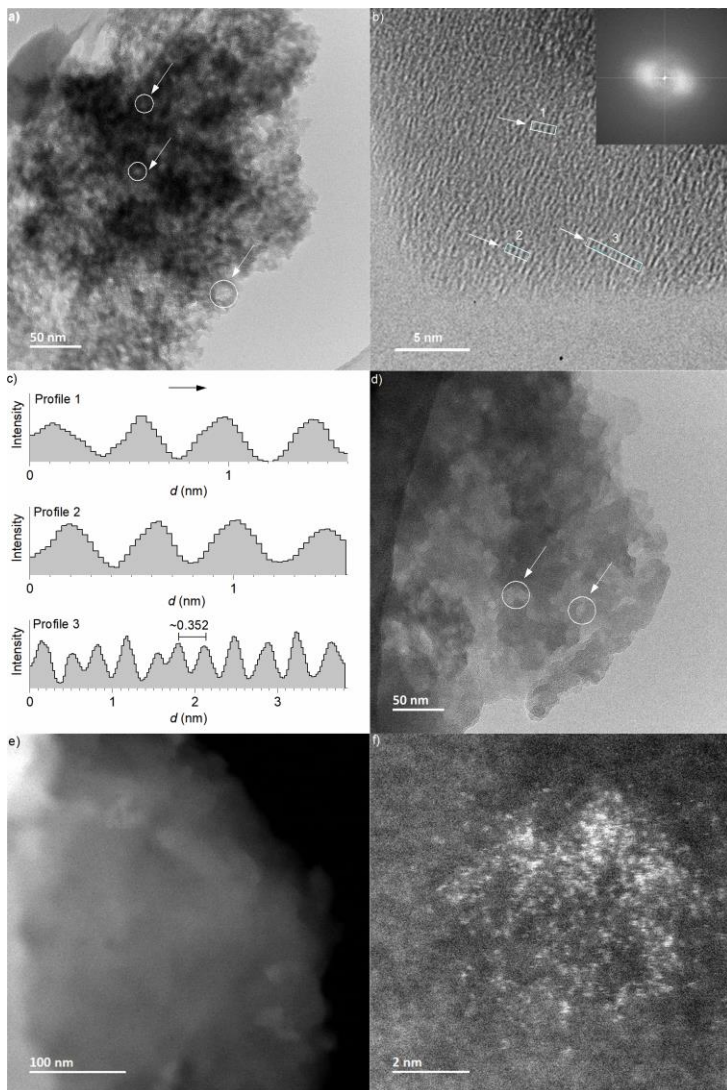
**Figure S9.** DRUV-vis absorption spectra (a) and Tauc plots (b) of fresh mpg-CN and recovered after the photocatalytic experiment.



**Figure S10.** Steady state PL of fresh mpg-CN and recovered after the photocatalytic experiment. Samples were excited with  $\lambda = 365$  nm. Asterisk denotes 2<sup>nd</sup> order excitation light diffraction.



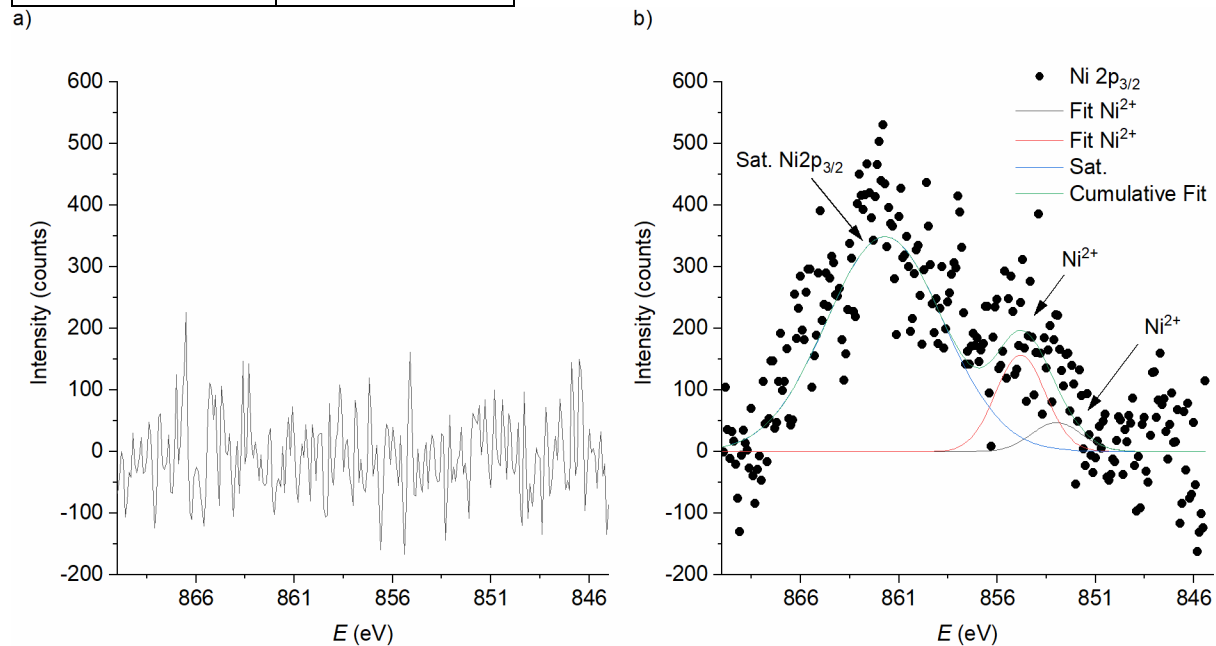
**Figure S11.** SEM. a) Fresh mpg-CN. b) Recovered mpg-CN.



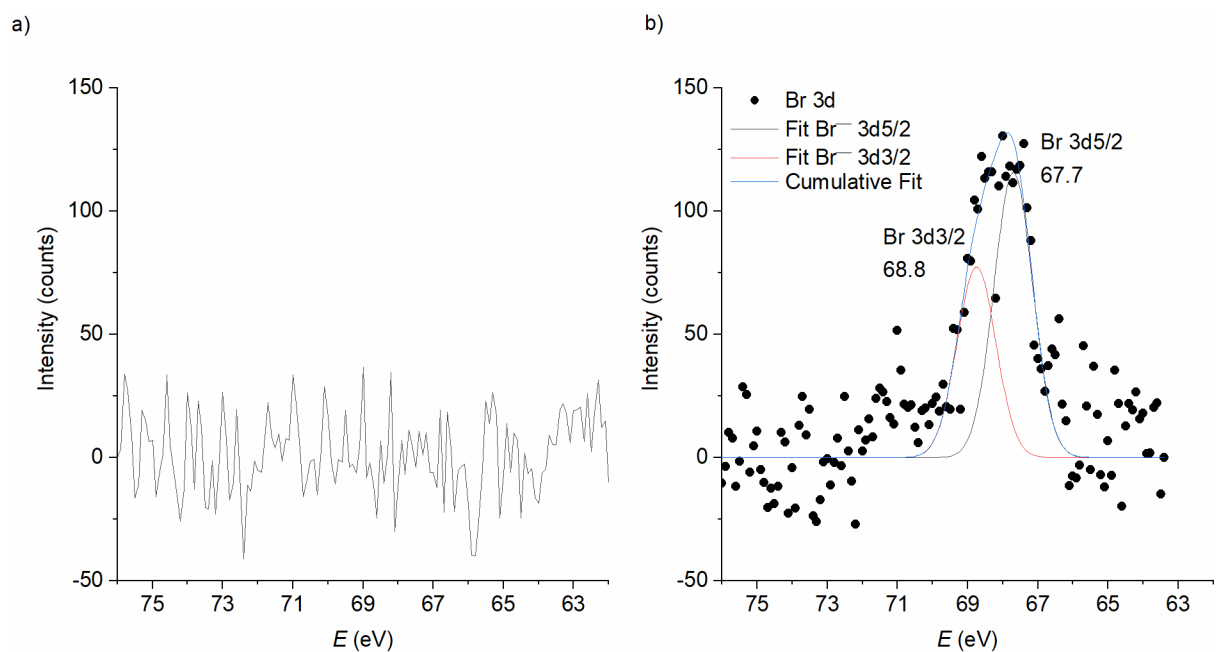
**Figure S12.** TEM images of mpg-CN. a) overview image of fresh mpg-CN. Circles mark mesopores. b) HR-TEM image of fresh mpg-CN with FFT in inset. c) Profile analysis of the corresponding areas marked in the panel (b). d) Overview image of recovered mpg-CN. e) and f) Overview and high resolution high angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) images of recovered mpg-CN.

**Table S3.** ICP-OES elemental analysis.

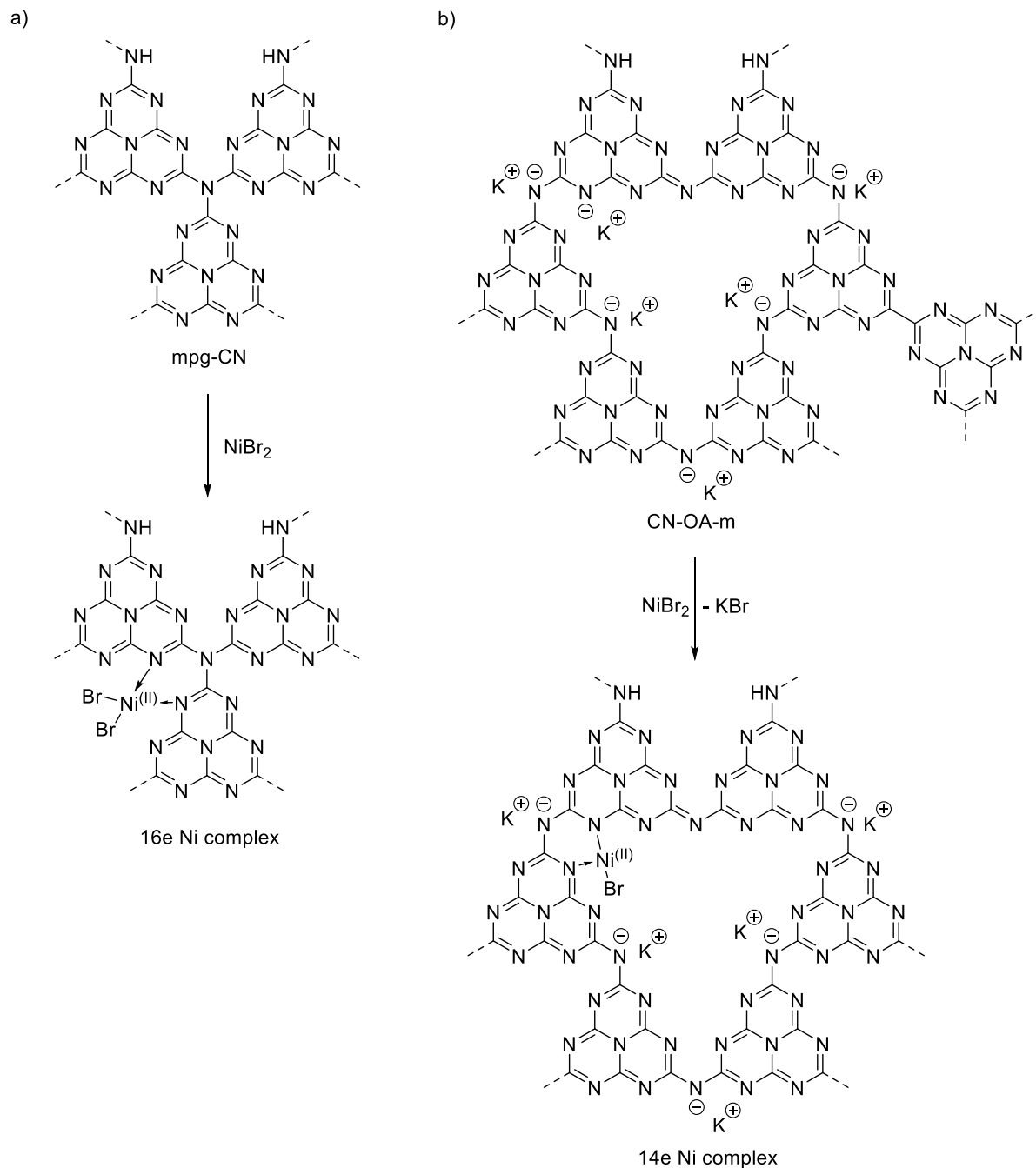
Sample	Ni wt. %
Fresh mpg-CN	0.0013±0.00001
Recovered mpg-CN	0.0268±0.00033



**Figure S13.** Ni 2p<sub>3/2</sub> XPS of fresh mpg-CN (a) and recovered after the photocatalytic experiment (b).

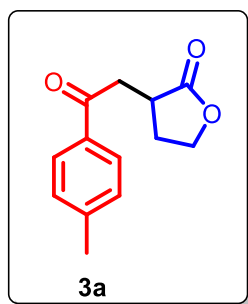


**Figure 14b.** Br 3d XPS of fresh (a) and recovered after the photocatalytic experiment mpg-CN (b)



**Figure S15.** Schematic representation of Ni salt coordination at covalent carbon nitride, such as mpg-CN, (a) and ionic carbon nitride, such as CN-OA-m, (b).

## 5. Characterization of the isolated compounds ( $^1\text{H}$ , $^{13}\text{C}$ , NMR spectra, and HRMS data)



### 3-(2-oxo-2-(*p*-tolyl)ethyl)dihydrofuran-2(3*H*)-one (3a)

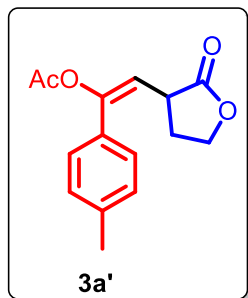
The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2\cdot\text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 83% yield (36.2 mg) and 12% yield **3a'** (6.3mg).

**Gram scale reaction (6 mmol scale reaction):** The compound was prepared according to the general gram scale procedure using 1056.5 mg of 1-(*p*-tolyl)vinyl acetate (6.0 mmol, 1.0 equiv.), 1484.9 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (9 mmol, 1.5 equiv.), and 150.0 mg of mpg-CN, 23.1 mg  $\text{NiBr}_2\cdot\text{glyme}$  (0.075 mmol, 0.0125 equiv.), DMF (70 mL) was used as solvent and 0.87 mL 2,6-lutidine (7.5 mmol, 1.25 equiv.). The reaction mixture was irradiated under air for 24h using blue LEDs (455 ( $\pm$  15) nm, see Fig. S1 for the picture of the reaction set up). The reaction mixture was then subjected to the purification process outlined in the general gram scale procedure. Column chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound **3a** in 83% yield (1.086 g) and 12% yield **3a'** (187.2 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J$  = 8.3 Hz, 2H), 7.36 – 7.14 (m, 2H), 4.41 (td,  $J$  = 9.0, 2.1 Hz, 1H), 4.25 (ddd,  $J$  = 10.3, 9.1, 6.6 Hz, 1H), 3.73 – 3.46 (m, 1H), 3.24 – 2.98 (m, 2H), 2.73 – 2.48 (m, 1H), 2.39 (s, 3H), 2.06 – 1.79 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.64, 179.35, 144.52, 133.75, 129.45, 128.19, 66.93, 39.30, 35.29, 29.16, 21.73.

HRMS: calculated for  $\text{C}_{13}\text{H}_{15}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  219.1016; found 219.1016.



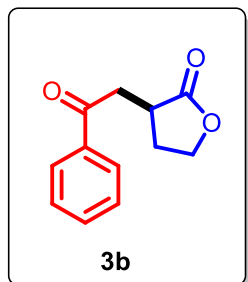
### (*E*)-2-(2-oxotetrahydrofuran-3-yl)-1-(*p*-tolyl)vinyl acetate (3a')

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J$  = 8.4 Hz, 2H), 7.13 (dd,  $J$  = 8.0, 0.9 Hz, 2H), 5.78 (d,  $J$  = 8.1 Hz, 1H), 4.44 – 4.36 (m, 1H), 4.25 (dddd,  $J$  = 10.0, 9.1, 6.3, 0.8 Hz, 1H), 3.51 (dt,  $J$  = 11.1, 8.5 Hz, 1H), 2.60 – 2.47 (m, 1H), 2.33 (s, 3H), 2.29 (d,  $J$  = 0.7 Hz, 3H), 2.26 – 2.04 (m, 1H).



$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.12, 168.60, 150.19, 139.10, 131.31, 129.35, 124.73, 111.52, 66.95, 37.89, 29.83, 21.28, 20.81.

HRMS: calculated for  $\text{C}_{15}\text{H}_{17}\text{O}_4^+$   $[\text{M}+\text{H}]^+$  261.1121; found 261.1125.



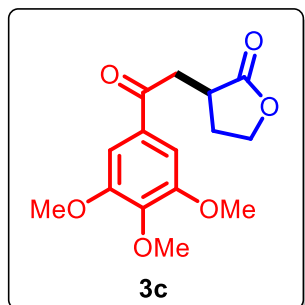
### 3-(2-oxo-2-phenylethyl)dihydrofuran-2(3H)-one (3b)

The compound was prepared according to the general procedure using 32.4 mg of 1-phenylvinyl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2\cdot\text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 66% yield (26.9 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.82 (m, 2H), 7.67 – 7.54 (m, 1H), 7.54 – 7.37 (m, 2H), 4.52 – 4.36 (m, 1H), 4.28 (ddd,  $J$  = 10.4, 9.1, 6.6 Hz, 1H), 3.77 – 3.57 (m, 1H), 3.27 – 3.05 (m, 2H), 2.65 (dddd,  $J$  = 12.7, 8.6, 6.7, 2.1 Hz, 1H), 2.10 – 1.84 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.08, 179.29, 136.23, 133.70, 128.85, 128.14, 66.98, 39.51, 35.34, 29.23.

HRMS: calculated for  $\text{C}_{12}\text{H}_{12}\text{O}_3^+$   $[\text{M}^+]$  204.0781; found 204.0780.



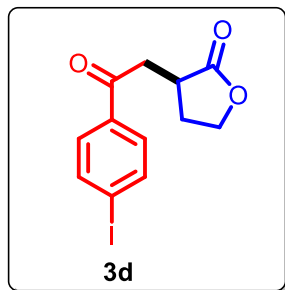
### 3-(2-oxo-2-(3,4,5-trimethoxyphenyl)ethyl)dihydrofuran-2(3H)-one (3c)

The compound was prepared according to the general procedure using 50.4 mg of 1-(3,4,5-trimethoxyphenyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2\cdot\text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 79% yield (39.8 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (s, 2H), 4.43 (td,  $J = 9.0, 2.0$  Hz, 1H), 4.28 (ddd,  $J = 10.5, 9.1, 6.6$  Hz, 1H), 3.90 (d,  $J = 0.8$  Hz, 9H), 3.72 – 3.54 (m, 1H), 3.27 – 3.00 (m, 2H), 2.64 (dddd,  $J = 12.8, 8.5, 6.6, 2.0$  Hz, 1H), 2.09 – 1.84 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  195.87, 179.34, 153.21, 143.00, 131.45, 66.99, 61.06, 56.40, 39.33, 35.48, 29.25.

HRMS: calculated for  $\text{C}_{15}\text{H}_{19}\text{O}_6^+$   $[\text{M}+\text{H}]^+$  295.1176; found 295.1176.



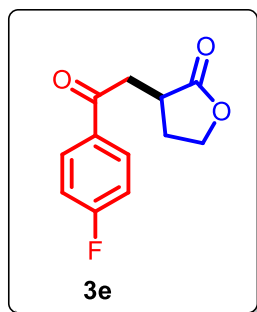
### 3-(2-(4-iodophenyl)-2-oxoethyl)dihydrofuran-2(3H)-one (3d)

The compound was prepared according to the general procedure using 57.6 mg of 1-(4-iodophenyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 87% yield (57.4 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.5$  Hz, 2H), 7.65 (d,  $J = 8.6$  Hz, 2H), 4.42 (td,  $J = 8.9, 1.9$  Hz, 1H), 4.26 (ddd,  $J = 10.4, 9.1, 6.6$  Hz, 1H), 3.74 – 3.46 (m, 1H), 3.12 (dtd,  $J = 14.8, 8.5, 1.9$  Hz, 2H), 2.62 (dddd,  $J = 12.9, 8.6, 6.6, 2.0$  Hz, 1H), 1.96 (dtd,  $J = 12.9, 10.5, 8.8$  Hz, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  196.37, 179.05, 138.10, 135.42, 129.44, 101.76, 66.93, 39.29, 35.20, 29.08.

HRMS: calculated for  $\text{C}_{12}\text{H}_{11}\text{IO}_3^+$   $[\text{M}^+]$  329.9747; found 329.9730.



### 3-(2-(4-fluorophenyl)-2-oxoethyl)dihydrofuran-2(3H)-one (3e)

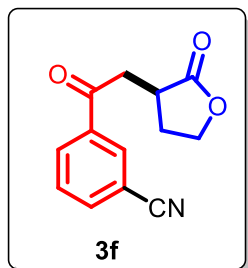
The compound was prepared according to the general procedure using 36.0 mg of 1-(4-fluorophenyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was

performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 62% yield (27.5 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 – 7.85 (m, 2H), 7.23 – 6.98 (m, 2H), 4.44 (td,  $J = 8.9, 2.0$  Hz, 1H), 4.28 (ddd,  $J = 10.4, 9.1, 6.6$  Hz, 1H), 3.82 – 3.44 (m, 1H), 3.28 – 3.01 (m, 2H), 2.74 – 2.49 (m, 1H), 2.09 – 1.79 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  195.49, 179.19, 166.07 (d,  $J = 255.7$  Hz), 132.71 (d,  $J = 3.1$  Hz), 130.83 (d,  $J = 9.5$  Hz), 115.99 (d,  $J = 21.9$  Hz), 66.98, 39.38, 35.33, 29.19.

HRMS: calculated for  $\text{C}_{12}\text{H}_{11}\text{FO}_3^+$  [ $\text{M}^+$ ] 222.0686; found 222.0685.



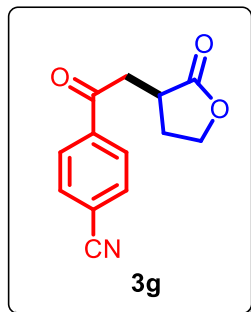
### 3-(2-(2-oxotetrahydrofuran-3-yl)acetyl)benzonitrile (3f)

The compound was prepared according to the general procedure using 37.4 mg of 1-(3-cyanophenyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 67% yield (30.7 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 – 8.13 (m, 2H), 7.86 (dt,  $J = 7.7, 1.4$  Hz, 1H), 7.63 (t,  $J = 7.8$  Hz, 1H), 4.46 (td,  $J = 8.9, 1.8$  Hz, 1H), 4.30 (ddd,  $J = 10.6, 9.1, 6.5$  Hz, 1H), 3.75 – 3.52 (m, 1H), 3.31 – 3.01 (m, 2H), 2.65 (dddd,  $J = 12.4, 8.4, 6.6, 1.8$  Hz, 1H), 2.13 – 1.85 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  195.19, 178.79, 136.95, 136.51, 132.09, 131.85, 129.96, 117.85, 113.46, 66.99, 39.50, 35.22, 29.07.

HRMS: calculated for  $\text{C}_{13}\text{H}_{11}\text{NO}_3^+$  [ $\text{M}^+$ ] 229.0733; found 229.0730.



### 4-(2-(2-oxotetrahydrofuran-3-yl)acetyl)benzonitrile (3g)

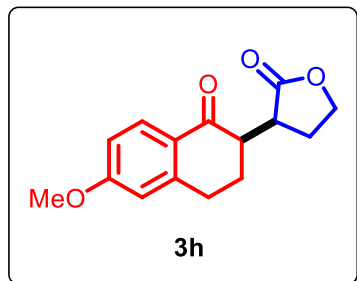
The compound was prepared according to the general procedure using 37.4 mg of 1-(4-cyanophenyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen

atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 64% yield (29.3 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J$  = 8.5 Hz, 2H), 7.79 (d,  $J$  = 8.5 Hz, 2H), 4.46 (td,  $J$  = 9.0, 1.8 Hz, 1H), 4.30 (ddd,  $J$  = 10.5, 9.1, 6.5 Hz, 1H), 3.82 – 3.56 (m, 1H), 3.32 – 3.03 (m, 2H), 2.66 (dddd,  $J$  = 12.3, 8.2, 6.5, 1.8 Hz, 1H), 2.09 – 1.90 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  195.86, 178.79, 139.09, 132.77, 128.60, 117.88, 116.98, 67.00, 39.77, 35.27, 29.13.

HRMS: calculated for  $\text{C}_{13}\text{H}_{11}\text{NO}_3^+$  [ $\text{M}^+$ ] 229.0733; found 229.0736.



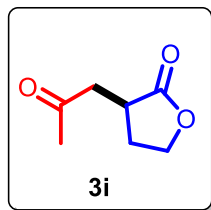
### 3-(6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)dihydrofuran-2(3H)-one (3h)

The compound was prepared according to the general procedure using 43.6 mg of 6-methoxy-3,4-dihydronaphthalen-1-yl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 41% yield (21.3 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.7 Hz, 1H), 6.82 (dd,  $J$  = 8.8, 2.5 Hz, 1H), 6.68 (d,  $J$  = 2.5 Hz, 1H), 4.50 (td,  $J$  = 9.1, 3.3 Hz, 1H), 4.29 (td,  $J$  = 8.8, 7.8 Hz, 1H), 3.85 (s, 3H), 3.30 – 2.90 (m, 3H), 2.79 (td,  $J$  = 9.9, 3.6 Hz, 1H), 2.40 – 1.92 (m, 5H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  195.76, 178.79, 163.92, 146.39, 130.17, 126.04, 113.44, 112.68, 66.82, 55.60, 48.28, 40.71, 29.88, 28.37, 24.38.

HRMS: calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_4^+$  [ $\text{M}^+$ ] 260.1043; found 260.1034.



### 3-(2-oxopropyl)dihydrofuran-2(3H)-one (3i)

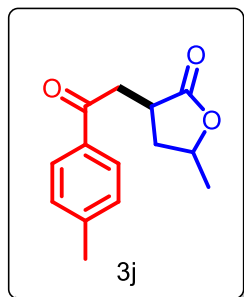
The compound was prepared according to the general procedure using 20.0 mg of prop-1-en-2-yl acetate (0.2 mmol, 1.0 equiv.), 49.5 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification

process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 69% yield (19.6 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.40 (td,  $J = 8.9, 2.0$  Hz, 1H), 4.29 – 4.16 (m, 1H), 3.10 (dd,  $J = 18.5, 3.4$  Hz, 1H), 3.02 – 2.89 (m, 1H), 2.65 (dd,  $J = 18.5, 8.6$  Hz, 1H), 2.59 – 2.48 (m, 1H), 2.21 (s, 3H), 2.01 – 1.85 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  205.67, 179.00, 66.89, 43.98, 35.09, 30.13, 29.08.

HRMS: calculated for  $\text{C}_7\text{H}_{11}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  143.0703; found 143.0703.



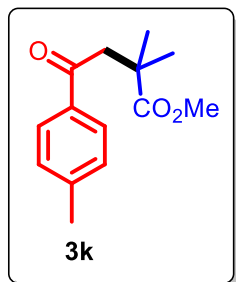
### 5-methyl-3-(2-oxo-2-(*p*-tolyl)ethyl)dihydrofuran-2(3*H*)-one (3j)

The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 53.4 mg 3-bromo-5-methyl-dihydrofuran-2(3*H*)-one (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 70% yield (32.5 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J = 8.2, 1.7$  Hz, 2H), 7.33 – 7.16 (m, 2H), 4.77 (dq,  $J = 8.1, 6.5, 3.2$  Hz, 1H), 3.67 – 3.53 (m, 1H), 3.37 – 3.02 (m, 2H), 2.40 (s, 3H), 2.28 (ddd,  $J = 12.4, 9.0, 3.2$  Hz, 1H), 2.09 (ddd,  $J = 12.8, 9.2, 8.0$  Hz, 1H), 1.41 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  196.68, 179.19, 144.58, 133.79, 129.51, 128.24, 75.32, 39.61, 35.14, 34.79, 21.79, 21.38.

HRMS: calculated for  $\text{C}_{14}\text{H}_{17}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  233.1172; found 233.1173.



### Methyl 2,2-dimethyl-4-oxo-4-(*p*-tolyl)butanoate (3k)

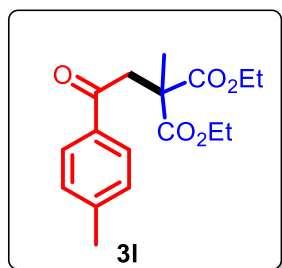
The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 53.4 mg methyl 2-bromo-2-methylpropanoate (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then

subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 52% yield (24.4 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 8.2$  Hz, 2H), 7.39 – 7.07 (m, 2H), 3.67 (s, 3H), 3.27 (s, 2H), 2.40 (s, 3H), 1.31 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.36, 178.04, 144.00, 134.62, 129.34, 128.18, 77.16, 52.07, 48.59, 40.18, 25.89, 21.77.

HRMS: calculated for  $\text{C}_{14}\text{H}_{19}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  235.1329; found 235.1332.



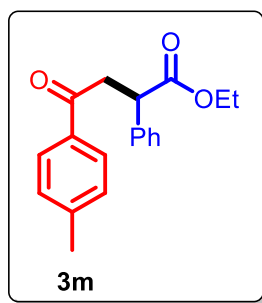
### Diethyl 2-methyl-2-(2-oxo-2-(*p*-tolyl)ethyl)malonate (3l)

The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 75.6 mg diethyl 2-bromo-2-methylmalonate (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 62% yield (37.9 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.3$  Hz, 2H), 7.25 – 7.19 (m, 2H), 4.19 (q,  $J = 7.1$  Hz, 4H), 3.62 (s, 2H), 2.38 (s, 3H), 1.57 (s, 3H), 1.22 (t,  $J = 7.1$  Hz, 7H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  196.16, 171.76, 144.25, 134.31, 129.37, 128.22, 61.64, 51.62, 44.24, 21.76, 20.65, 14.08.

HRMS: calculated for  $\text{C}_{17}\text{H}_{23}\text{O}_5^+$   $[\text{M}+\text{H}]^+$  307.1540; found 307.1546.



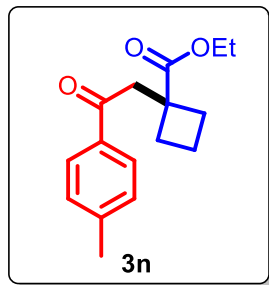
### Ethyl 4-oxo-2-phenyl-4-(*p*-tolyl)butanoate (3m)

The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 72.6 mg ethyl 2-bromo-2-phenylacetate (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 1.5 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 38% yield (22.5 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.2$  Hz, 2H), 7.42 – 7.29 (m, 5H), 7.28 – 7.20 (m, 2H), 4.29 – 4.07 (m, 3H), 3.92 (dd,  $J = 17.9, 10.4$  Hz, 1H), 3.24 (dd,  $J = 17.9, 4.1$  Hz, 1H), 2.40 (s, 3H), 1.22 (d,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.40, 173.49, 144.19, 138.72, 134.09, 128.95, 128.31, 127.93, 127.54, 61.17, 46.67, 42.82, 21.79, 14.18.

HRMS: calculated for  $\text{C}_{19}\text{H}_{21}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  297.1485; found 297.1489.



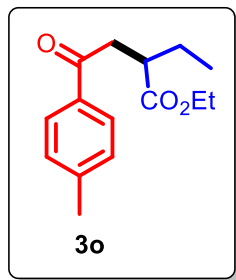
### Ethyl 1-(2-oxo-2-(*p*-tolyl)ethyl)cyclobutane-1-carboxylate (3n)

The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 61.8 mg ethyl 1-bromocyclobutane-1-carboxylate (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 69% yield (35.9 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.3$  Hz, 2H), 7.28 – 7.20 (m, 2H), 4.14 (q,  $J = 7.1$  Hz, 2H), 3.55 (s, 2H), 2.62 (dt,  $J = 11.5, 6.1$  Hz, 2H), 2.40 (s, 3H), 2.09 – 1.90 (m, 4H), 1.20 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.47, 176.14, 143.88, 134.39, 129.23, 128.10, 60.54, 46.16, 44.49, 30.18, 21.68, 16.30, 14.15.

HRMS: calculated for  $\text{C}_{16}\text{H}_{21}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  261.1485; found 261.1486.



### Ethyl 2-ethyl-4-oxo-4-(*p*-tolyl)butanoate (3o)

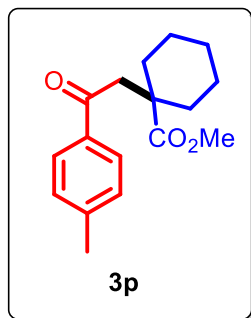
The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 58.2 mg ethyl 2-bromobutanoate (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification

process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 75% yield (37.22 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.73 (m, 2H), 7.34 – 7.15 (m, 2H), 4.15 (qd,  $J = 7.1, 2.1$  Hz, 2H), 3.52 – 3.34 (m, 1H), 3.10 – 2.88 (m, 2H), 2.40 (s, 3H), 1.90 – 1.54 (m, 2H), 1.25 (t,  $J = 7.1$  Hz, 3H), 0.97 (t,  $J = 7.5$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.06, 175.61, 144.01, 134.39, 129.34, 128.26, 60.54, 41.95, 39.99, 25.40, 21.76, 14.36, 11.69.

HRMS: calculated for  $\text{C}_{15}\text{H}_{21}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  249.1485; found 249.1488.



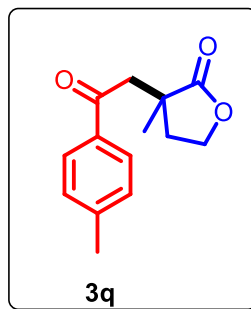
### Methyl 1-(2-oxo-2-(*p*-tolyl)ethyl)cyclohexane-1-carboxylate (3p)

The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 66.0 mg methyl 1-bromocyclohexane-1-carboxylate (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 73% yield (40.0 mg).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.2$  Hz, 2H), 7.24 (d,  $J = 8.0$  Hz, 2H), 3.62 (s, 3H), 3.27 (s, 2H), 2.40 (s, 3H), 2.11 – 1.95 (m, 2H), 1.51 (dd,  $J = 18.0, 9.4$  Hz, 8H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.61, 177.32, 143.94, 134.96, 129.32, 128.25, 51.76, 46.20, 44.59, 34.14, 25.90, 22.61, 21.74.

HRMS: calculated for  $\text{C}_{17}\text{H}_{23}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  275.1642; found 275.1642.



### 3-methyl-3-(2-oxo-2-(*p*-tolyl)ethyl)dihydrofuran-2(3*H*)-one (3q)

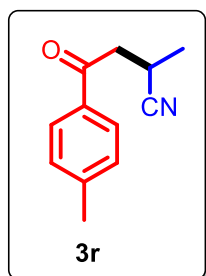
The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 53.4 mg 3-bromo-3-methyldihydrofuran-2(3*H*)-one (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen



atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 68% yield (31.6 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J$  = 8.3 Hz, 2H), 7.24 (s, 0H), 7.24 – 7.20 (m, 2H), 7.12 (d,  $J$  = 1.6 Hz, 1H), 5.75 (s, 0H), 4.72 (p,  $J$  = 2.1 Hz, 1H), 4.45 (td,  $J$  = 9.2, 3.2 Hz, 1H), 4.35 – 4.21 (m, 1H), 3.49 – 3.15 (m, 2H), 2.45 (dt,  $J$  = 12.8, 9.2 Hz, 2H), 2.38 (s, 3H), 2.30 (s, 1H), 2.22 (s, 1H), 2.10 (ddd,  $J$  = 12.6, 7.7, 3.2 Hz, 1H), 1.90 (q,  $J$  = 2.1 Hz, 1H), 1.43 (s, 1H), 1.35 (s, 3H).  
 $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  196.72, 181.98, 168.79, 145.12, 144.49, 138.94, 134.09, 129.43, 129.38, 128.17, 124.74, 117.87, 70.12, 65.39, 45.55, 40.10, 37.19, 33.82, 23.81, 23.57, 21.77, 21.29, 20.76, 10.77.

HRMS: calculated for  $\text{C}_{14}\text{H}_{17}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  233.1172; found 233.1173.



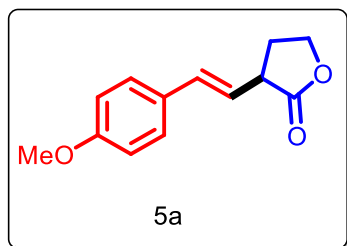
### 2-methyl-4-oxo-4-(*p*-tolyl)butanenitrile (3r)

The compound was prepared according to the general procedure using 35.2 mg of 1-(*p*-tolyl)vinyl acetate (0.2 mmol, 1.0 equiv.), 39.9 mg 2-bromopropanenitrile (0.3 mmol, 1.5 equiv.), mpg-CN (10.0 mg), 0.77 mg of  $\text{NiBr}_2\cdot\text{glyme}$  (0.0025 mmol, 0.0125 equiv.), and 29  $\mu\text{L}$  of 2,6-lutidine (0.25 mmol, 1.25 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 24h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 71% yield (26.6 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J$  = 8.2 Hz, 2H), 7.34 – 7.25 (m, 2H), 3.45 – 3.28 (m, 2H), 3.24 – 3.11 (m, 1H), 2.41 (s, 3H), 1.40 (d,  $J$  = 7.0 Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  194.86, 144.86, 133.50, 129.57, 128.20, 122.83, 77.16, 42.17, 21.79, 20.60, 17.98.

HRMS: calculated for  $\text{C}_{12}\text{H}_{14}\text{NO}^+$   $[\text{M}+\text{H}]^+$  188.1070; found 188.1069.



### (*E*)-3-(4-methoxystyryl)dihydrofuran-2(3H)-one (5a)

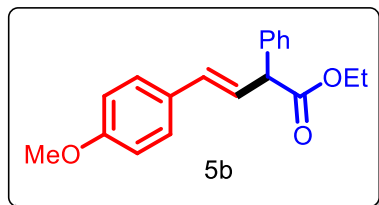
The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 65.9 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of  $\text{NiBr}_2\cdot\text{glyme}$  (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15)

nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 77% yield (33.6 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.28 (m, 2H), 6.85 (d,  $J$  = 8.8 Hz, 2H), 6.51 (dd,  $J$  = 16.1, 1.5 Hz, 1H), 6.09 (dd,  $J$  = 16.0, 6.6 Hz, 1H), 4.45 – 4.36 (m, 1H), 4.28 (td,  $J$  = 9.2, 6.6 Hz, 1H), 3.80 (s, 3H), 3.40 (dddd,  $J$  = 10.2, 8.4, 6.6, 1.5 Hz, 1H), 2.54 (dddd,  $J$  = 12.6, 8.6, 6.5, 3.3 Hz, 1H), 2.27 (dddd,  $J$  = 12.7, 10.1, 9.3, 8.2 Hz, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.60, 159.51, 132.94, 129.16, 127.71, 121.73, 114.08, 66.80, 55.40, 42.84, 29.38.

HRMS: calculated for  $\text{C}_{13}\text{H}_{15}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  219.1016; found 219.1020.



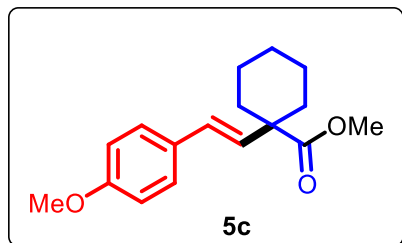
#### Ethyl (*E*)-4-(4-methoxyphenyl)-2-phenylbut-3-enoate (**5b**)

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 96.8 mg ethyl 2-bromo-2-phenylacetate (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of  $\text{NiBr}_2\cdot\text{glyme}$  (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 65% yield (38.5 mg).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.23 (m, 7H), 6.85 (d,  $J$  = 8.7 Hz, 2H), 6.54 – 6.36 (m, 2H), 4.45 (dd,  $J$  = 5.0, 2.5 Hz, 1H), 4.26 – 4.14 (m, 2H), 3.80 (s, 3H), 1.27 (t,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.69, 159.93, 159.38, 138.80, 131.90, 129.63, 128.83, 128.04, 127.75, 127.38, 125.22, 61.20, 55.38, 55.25, 14.26.

HRMS: calculated for  $\text{C}_{19}\text{H}_{21}\text{O}_3^+$   $[\text{M}+\text{H}]^+$  297.1485; found 297.1491.



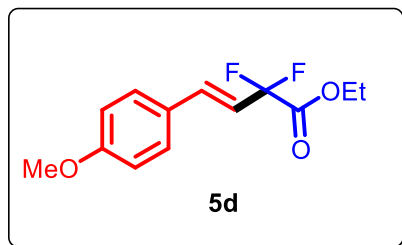
#### Methyl (*E*)-1-(4-methoxystyryl)cyclohexane-1-carboxylate (**5c**)

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 88.0 mg methyl 1-bromocyclohexane-1-carboxylate (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of  $\text{NiBr}_2\cdot\text{glyme}$  (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 54% yield (29.6 mg).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J = 8.7$  Hz, 2H), 6.84 (d,  $J = 8.7$  Hz, 2H), 6.38 (d,  $J = 16.3$  Hz, 1H), 6.02 (d,  $J = 16.3$  Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 2.29 – 2.09 (m, 2H), 1.60 (ddtt,  $J = 22.5, 19.1, 9.1, 3.9$  Hz, 6H), 1.47 – 1.30 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.85, 159.27, 131.87, 130.02, 128.87, 127.55, 114.08, 55.44, 52.08, 49.07, 34.21, 25.84, 23.33.

HRMS: calculated for  $\text{C}_{17}\text{H}_{22}\text{O}_3^+$  [ $\text{M}^+$ ] 274.1563; found 274.1565.



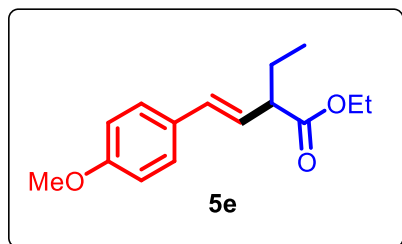
### Ethyl (*E*)-2,2-difluoro-4-(4-methoxyphenyl)but-3-enoate (**5d**)

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 81.2 mg ethyl bromodifluoroacetate (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 62% yield (31.7 mg).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.7$  Hz, 2H), 7.02 (dt,  $J = 16.2, 2.6$  Hz, 1H), 6.94 – 6.84 (m, 2H), 6.16 (dt,  $J = 16.2, 11.5$  Hz, 1H), 4.35 (q,  $J = 7.1$  Hz, 2H), 3.83 (s, 3H), 1.36 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.22 (t,  $J = 35.2$  Hz), 160.91, 136.43 (t,  $J = 9.5$  Hz), 129.03, 126.94, 116.50 (t,  $J = 25.0$  Hz), 114.36, 113.10 (t,  $J = 248.3$  Hz), 63.15, 55.46, 14.09.

HRMS: calculated for  $\text{C}_{13}\text{H}_{14}\text{F}_2\text{O}_3^+$  [ $\text{M}^+$ ] 256.0906; found 256.0904.



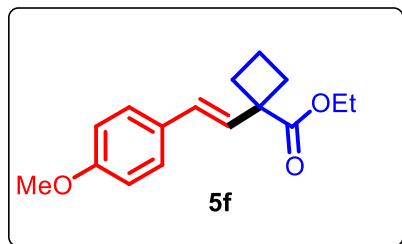
### Ethyl (*E*)-2-ethyl-4-(4-methoxyphenyl)but-3-enoate (**5e**)

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 77.6 mg ethyl 2-bromobutanoate (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 60% yield (29.8 mg).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.7$  Hz, 2H), 6.84 (d,  $J = 8.7$  Hz, 2H), 6.41 (d,  $J = 15.8$  Hz, 1H), 6.05 (dd,  $J = 15.8, 8.9$  Hz, 1H), 4.16 (qd,  $J = 7.1, 0.9$  Hz, 2H), 3.80 (s, 3H), 3.03 (dtd,  $J = 8.2, 7.3, 0.8$  Hz, 1H), 1.86 (dt,  $J = 13.5, 7.3$  Hz, 1H), 1.73 – 1.53 (m, 1H), 1.27 (t,  $J = 7.1$  Hz, 3H), 0.94 (t,  $J = 7.4$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.46, 159.27, 131.66, 129.90, 127.60, 125.64, 114.08, 60.65, 55.44, 51.49, 26.20, 14.40, 11.84.

HRMS: calculated for  $\text{C}_{15}\text{H}_{20}\text{O}_3^+$  [ $\text{M}^+$ ] 248.1407; found 248.1403.



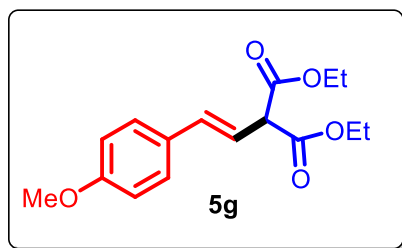
### Ethyl (*E*)-1-(4-methoxystyryl)cyclobutane-1-carboxylate (**5f**)

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 82.4 mg ethyl 1-bromocyclobutane-1-carboxylate (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 61% yield (31.7 mg).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.30 (m, 2H), 6.86 (d,  $J = 8.8$  Hz, 2H), 6.46 (d,  $J = 16.1$  Hz, 1H), 6.32 (d,  $J = 16.0$  Hz, 1H), 4.18 (q,  $J = 7.1$  Hz, 2H), 3.81 (s, 3H), 2.71 – 2.47 (m, 2H), 2.35 – 2.19 (m, 2H), 2.00 – 1.83 (m, 2H), 1.27 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.87, 159.24, 129.95, 129.44, 128.38, 127.60, 114.11, 60.88, 55.43, 50.06, 31.08, 16.08, 14.36.

HRMS: calculated for  $\text{C}_{16}\text{H}_{20}\text{O}_3^+$  [ $\text{M}^+$ ] 260.1407; found 260.1402.



### Diethyl (*E*)-2-(4-methoxystyryl)malonate (**5g**)

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 95.6 mg diethyl bromomalonate (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of  $\text{NiBr}_2 \cdot \text{glyme}$  (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 64% yield (37.4 mg).

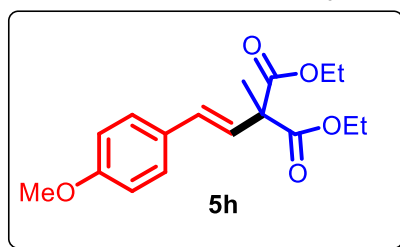
**Gram scale reaction (0.5 mmol scale reaction):** The compound was prepared according to the

general gram scale procedure using 805 mg of 4-methoxystyrene (6.0 mmol, 1.0 equiv.), 2.868 g diethyl bromomalonate (12.0 mmol, 2.0 equiv.), and 160.0 mg of mpg-CN, 23.1 mg NiBr<sub>2</sub>•glyme (0.075 mmol, 0.0125 equiv.), DMF (70 mL) was used as solvent. The reaction mixture was irradiated under air for 48h using blue LEDs (455 (± 15) nm, see Fig. S1 for the picture of the reaction set up). The reaction mixture was then subjected to the purification process outlined in the general gram scale procedure. Column chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 64% yield (1.121 g)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.28 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J* = 15.9, 9.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 4.14 (dd, *J* = 9.0, 0.8 Hz, 1H), 3.80 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.35, 159.67, 134.61, 129.07, 128.00, 118.74, 114.08, 61.87, 56.11, 55.41, 14.19.

HRMS: calculated for C<sub>16</sub>H<sub>21</sub>O<sub>5</sub><sup>+</sup> [M+H]<sup>+</sup> 293.1384; found 293.1389.



### Diethyl (*E*)-2-(4-methoxystyryl)-2-methylmalonate (**5h**)

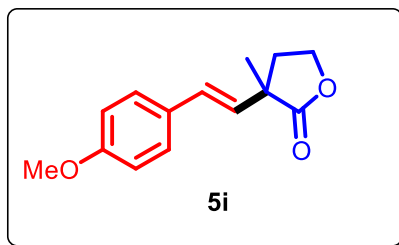
The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 100.8 mg diethyl 2-bromo-2-methylmalonate (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of NiBr<sub>2</sub>•glyme (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 (± 15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 63% yield (38.6 mg).

**Gram scale reaction (0.5 mmol scale reaction):** The compound was prepared according to the general gram scale procedure using 850 mg of 4-methoxystyrene (6.0 mmol, 1.0 equiv.), 3.037 g diethyl 2-bromo-2-methylmalonate (12.0 mmol, 2.0 equiv.), and 160.0 mg of mpg-CN, 23.1 mg NiBr<sub>2</sub>•glyme (0.075 mmol, 0.0125 equiv.), DMF (70 mL) was used as solvent. The reaction mixture was irradiated under air for 48h using blue LEDs (455 (± 15) nm, see Fig. S1 for the picture of the reaction set up). The reaction mixture was then subjected to the purification process outlined in the general gram scale procedure. Column chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 63% yield (1.157 g)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 16.4 Hz, 1H), 6.43 (d, *J* = 16.4 Hz, 1H), 4.22 (qd, *J* = 7.2, 1.3 Hz, 4H), 3.80 (s, 3H), 1.65 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 171.37, 159.50, 130.26, 129.41, 127.88, 125.47, 114.03, 61.72, 55.69, 55.38, 20.48, 14.14.

HRMS: calculated for C<sub>17</sub>H<sub>23</sub>O<sub>5</sub><sup>+</sup> [M+H]<sup>+</sup> 307.1540; found 307.1546.



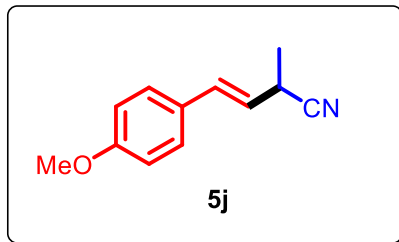
**(E)-3-(4-methoxystyryl)-3-methyldihydrofuran-2(3H)-one (5i)**

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 71.2 mg 3-bromo-3-methyldihydrofuran-2(3H)-one (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of NiBr<sub>2</sub>•glyme (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 (± 15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 62% yield (28.8 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.26 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 16.2 Hz, 1H), 6.09 (d, *J* = 16.2 Hz, 1H), 4.30 (qdd, *J* = 9.1, 7.9, 5.7 Hz, 2H), 3.80 (s, 3H), 2.43 (ddd, *J* = 12.7, 6.7, 4.6 Hz, 1H), 2.24 (dt, *J* = 12.7, 7.9 Hz, 1H), 1.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.91, 159.58, 129.65, 129.09, 127.77, 127.74, 114.16, 65.25, 55.43, 45.31, 36.28, 23.67.

HRMS: calculated for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub><sup>+</sup> [M<sup>+</sup>] 232.1094; found 232.1092.



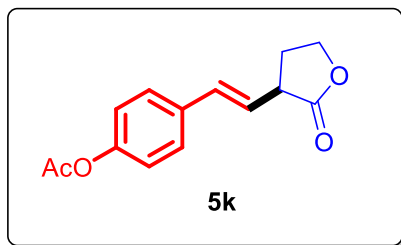
**(E)-4-(4-methoxyphenyl)-2-methylbut-3-enenitrile (5j)**

The compound was prepared according to the general procedure using 26.8 mg of 4-methoxystyrene (0.2 mmol, 1.0 equiv.), 53.2 mg 2-bromopropanenitrile (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of NiBr<sub>2</sub>•glyme (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 (± 15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 52% yield (19.4 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.65 (dd, *J* = 15.8, 1.5 Hz, 1H), 5.92 (dd, *J* = 15.8, 6.2 Hz, 1H), 3.82 (s, 3H), 3.48 (tt, *J* = 7.2, 5.7 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.82, 132.07, 128.57, 127.89, 122.20, 121.21, 114.25, 55.45, 28.50, 19.31.

HRMS: calculated for C<sub>12</sub>H<sub>13</sub>NO<sup>+</sup> [M<sup>+</sup>] 187.0991; found 187.0991.

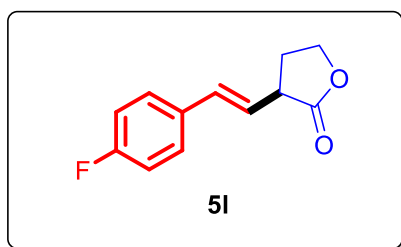


**(E)-4-(2-(2-oxotetrahydrofuran-3-yl)vinyl)phenyl acetate (5k)**

The compound was prepared according to the general procedure using 32.4 mg 4-acetoxystyrene (0.2 mmol, 1.0 equiv.), 65.9 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of NiBr<sub>2</sub>•glyme (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 38% yield (18.7 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d,  $J$  = 8.6 Hz, 2H), 7.05 (d,  $J$  = 8.6 Hz, 2H), 6.55 (dd,  $J$  = 16.0 Hz, 6.5 Hz, 1H), 6.21 (dd,  $J$  = 16.0, 6.5 Hz, 1H), 4.50 – 4.38 (m, 1H), 4.30 (td,  $J$  = 9.2, 6.6 Hz, 1H), 3.42 (dddd,  $J$  = 10.1, 8.3, 6.5, 1.5 Hz, 1H), 2.57 (dddd,  $J$  = 12.0, 8.8, 6.6, 3.2 Hz, 1H), 2.30 (dddd,  $J$  = 12.0, 10.1, 9.3, 8.2 Hz, 1H), 2.29 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  177.1, 169.4, 150.3, 134.1, 132.4, 127.4, 124.2, 121.7, 66.6, 42.6, 29.1, 21.1.

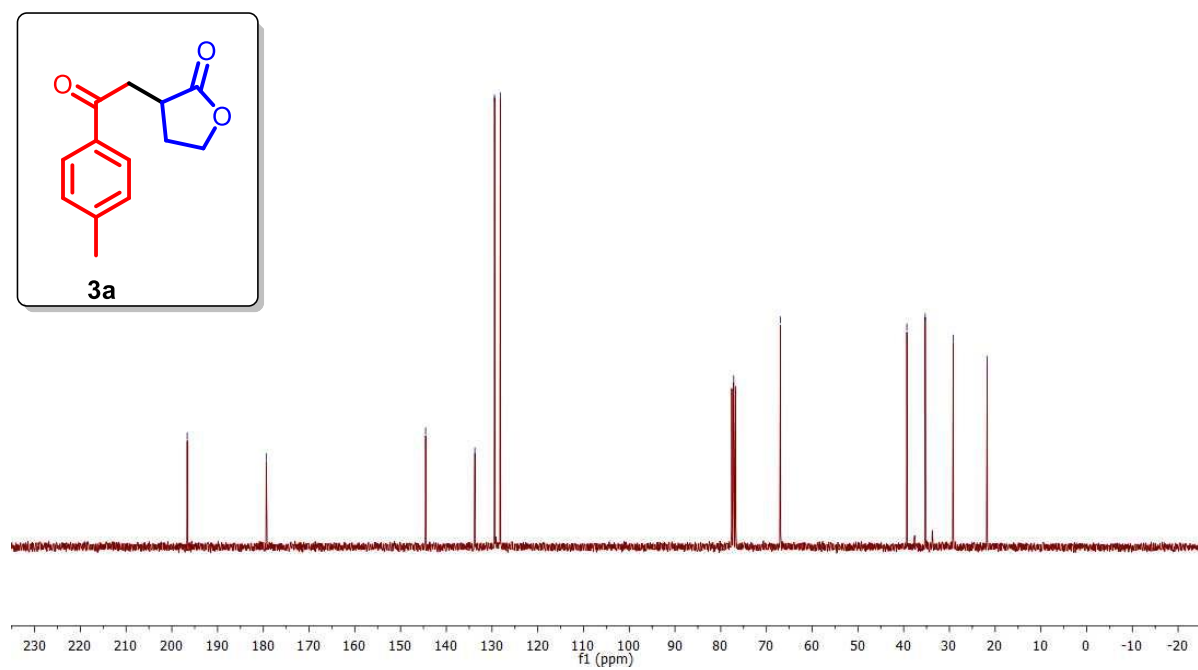
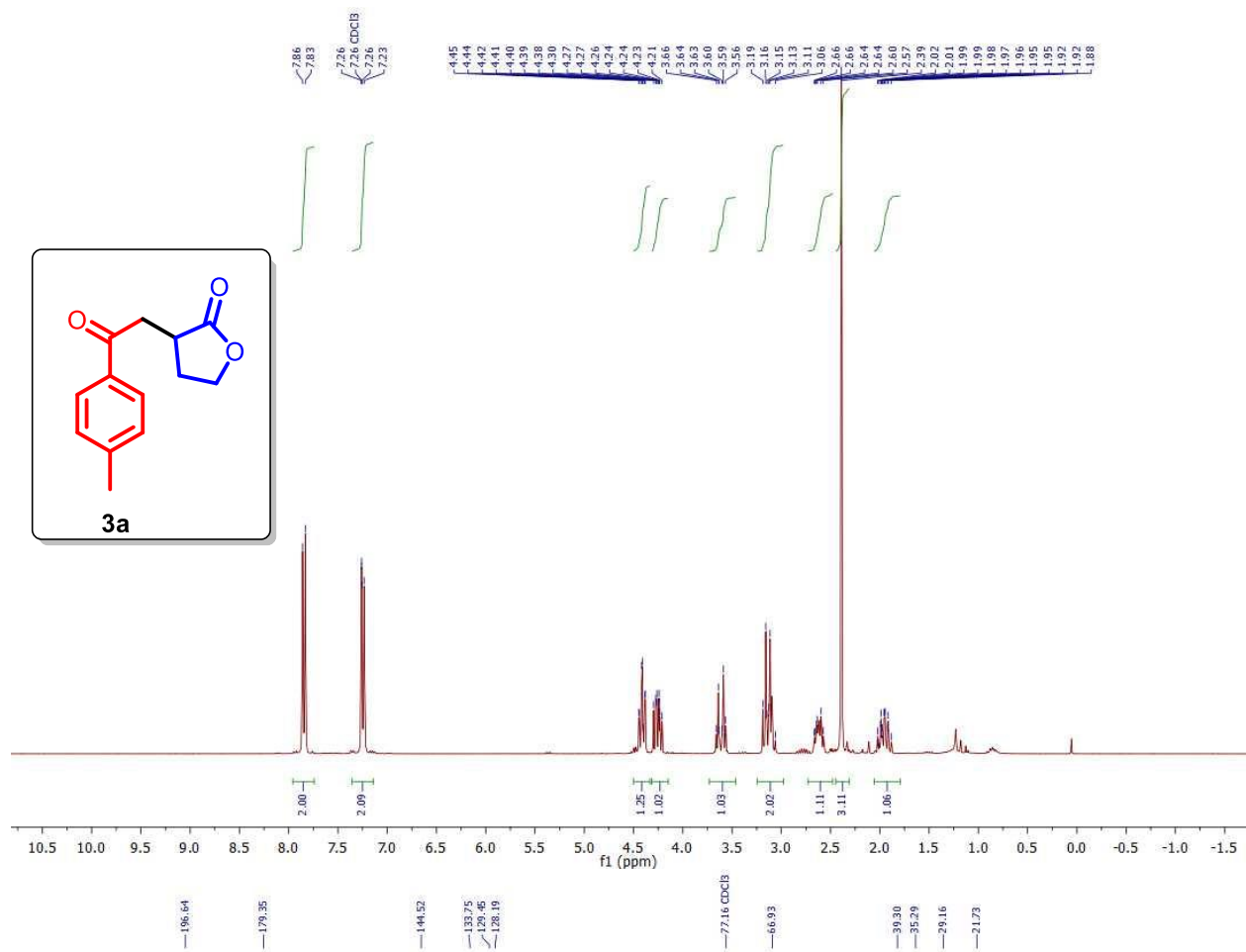


**(E)-3-(4-fluorostyryl)dihydrofuran-2(3H)-one (5l)**

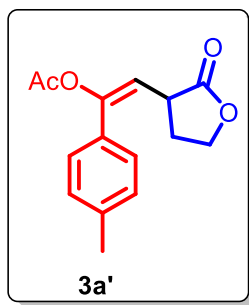
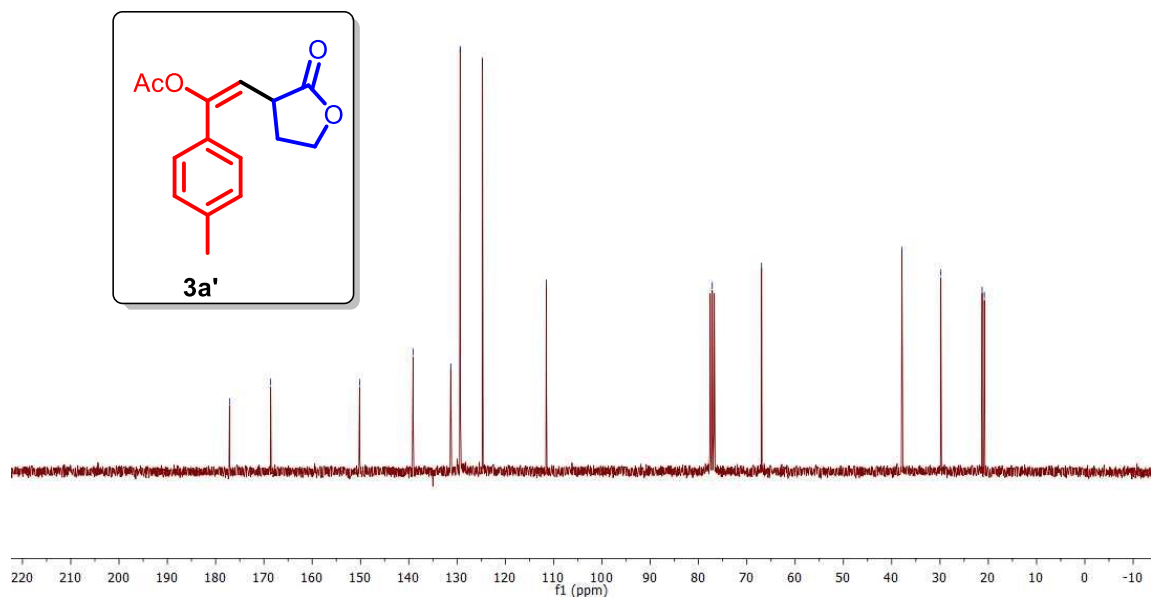
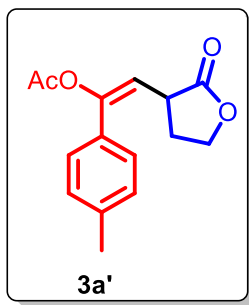
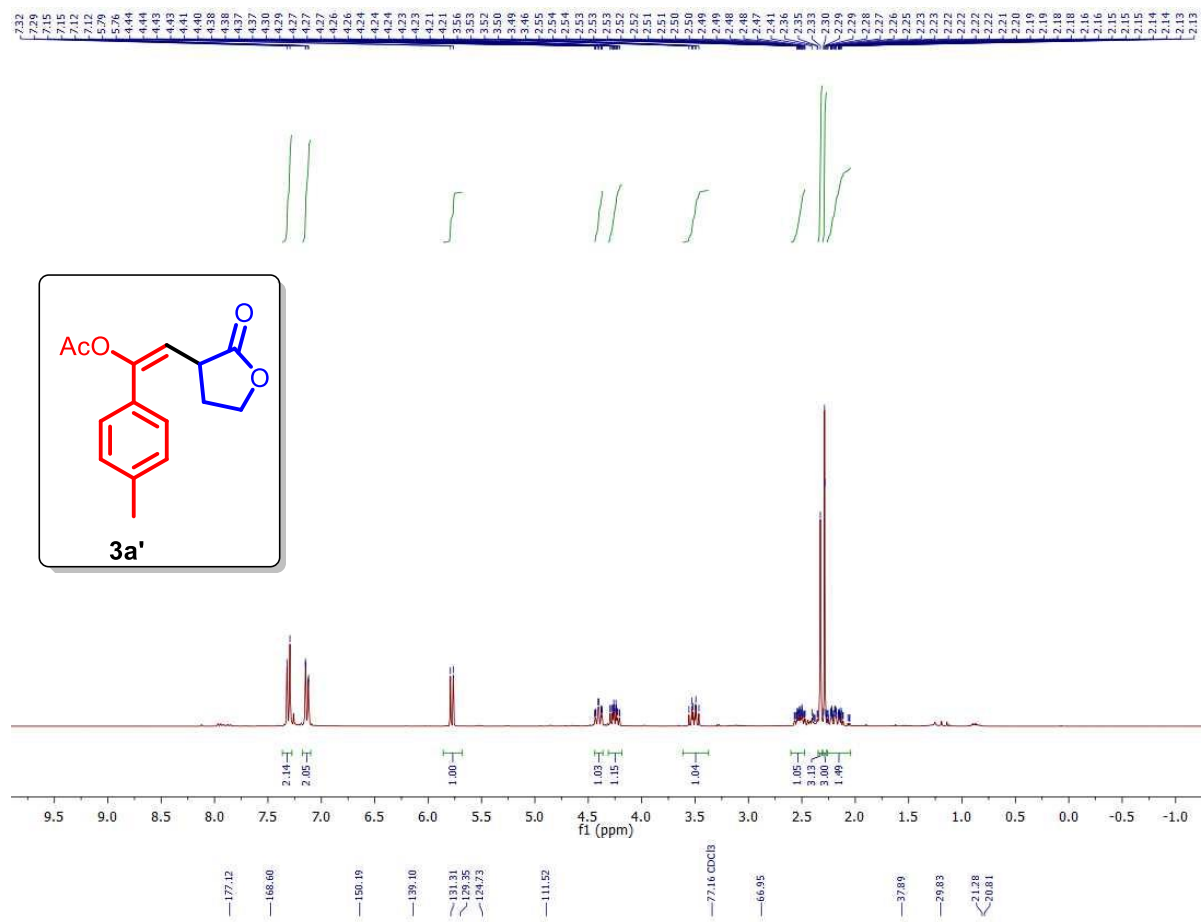
The compound was prepared according to the general procedure using 24.4 mg 4-acetoxystyrene (0.2 mmol, 1.0 equiv.), 65.9 mg  $\alpha$ -bromo- $\gamma$ -butyrolactone (0.4 mmol, 2 equiv.), mpg-CN (10.0 mg), and 0.77 mg of NiBr<sub>2</sub>•glyme (0.0025 mmol, 0.0125 equiv.). The reaction mixture was irradiated under nitrogen atmosphere for 48h using a single blue LED (455 ( $\pm$  15) nm). The reaction mixture was then subjected to the purification process outlined in the general procedure. Flash chromatography was performed on silica gel using PE/EtOAc solvent mixture to provide the title compound in 42% yield (17.3 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 – 7.30 (m, 2H), 7.09 – 6.73 (m, 2H), 6.54 (dd,  $J$  = 16.0 Hz, 1.5 Hz, 1H), 6.16 (dd,  $J$  = 16.0, 6.6 Hz, 1H), 4.44 (td,  $J$  = 8.7, 3.1 Hz, 1H), 4.30 (td,  $J$  = 9.3, 6.6 Hz, 1H), 3.59 – 3.22 (m, 1H), 2.56 (dddd,  $J$  = 12.0, 9.0, 6.6, 3.1 Hz, 1H), 2.29 (m, 1H).

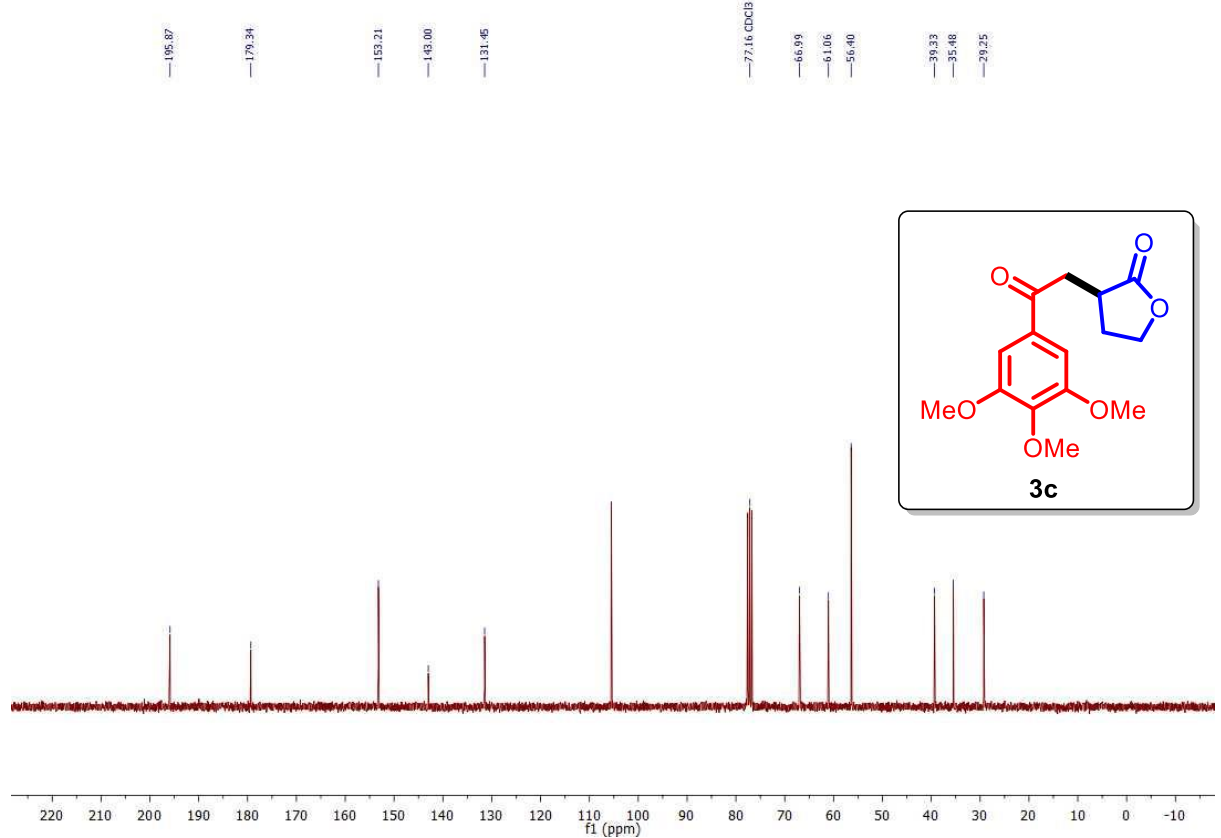
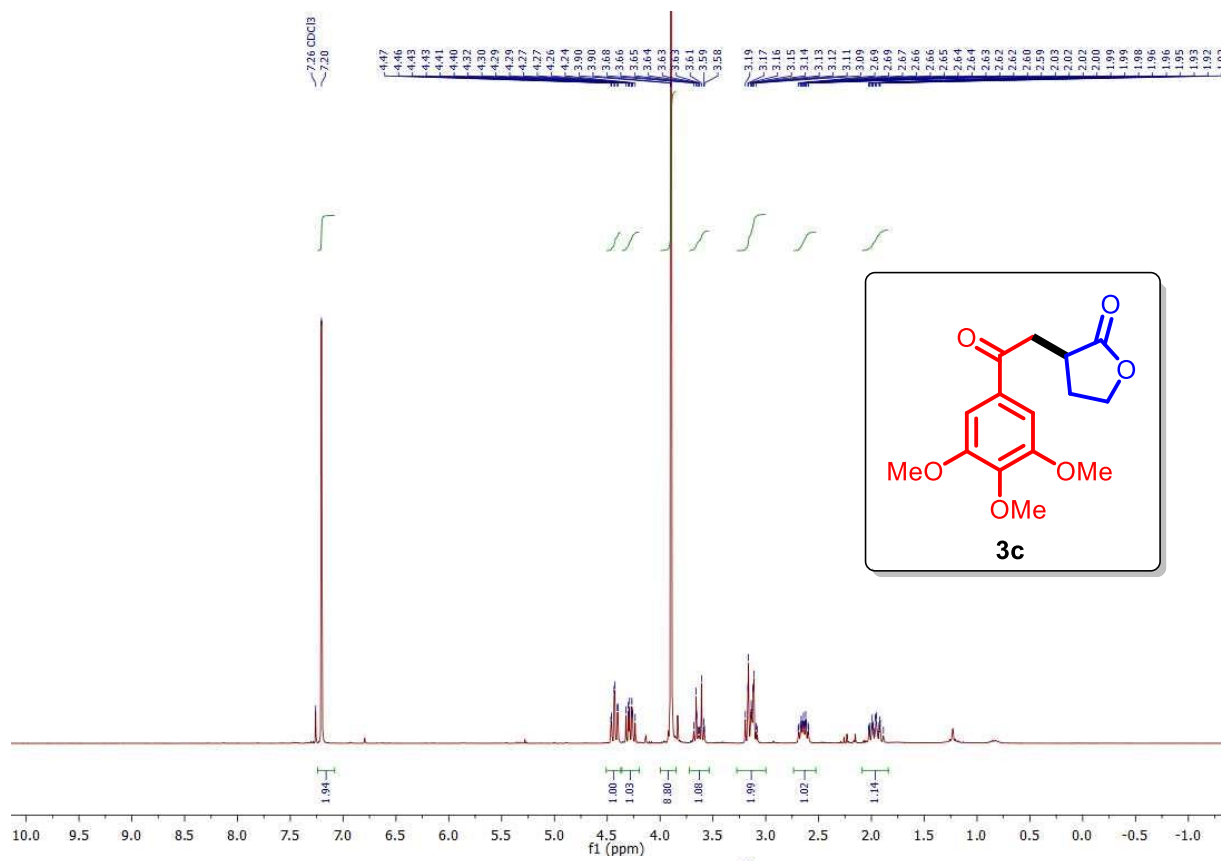
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  177.2, 162.6 (d,  $J$  = 247.3 Hz), 132.6 (d,  $J$  = 3.4 Hz), 132.4, 128.1 (d,  $J$  = 8.0 Hz), 123.8 (d,  $J$  = 2.2 Hz), 115.6 (d,  $J$  = 21.7 Hz), 66.8, 42.8, 29.3.

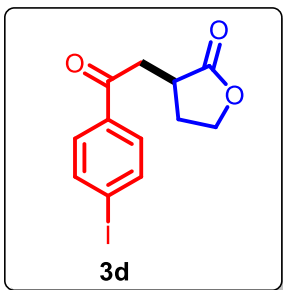
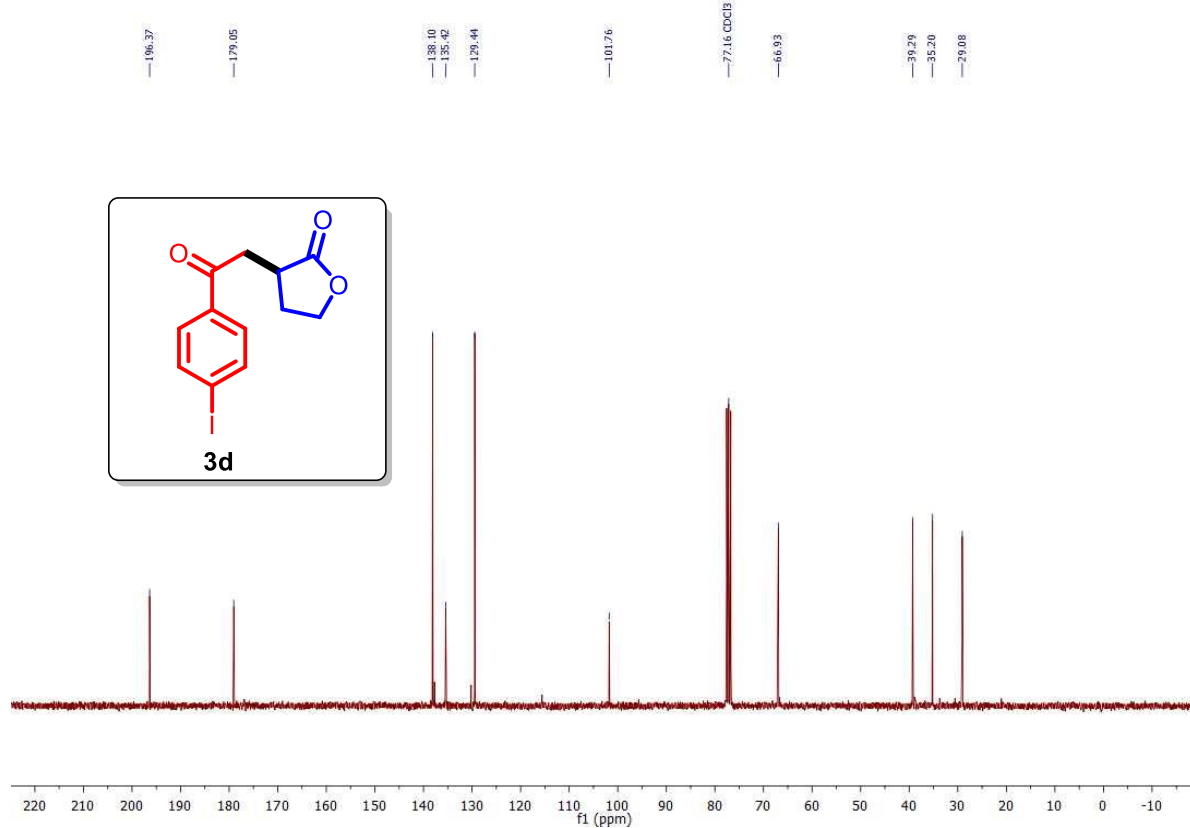
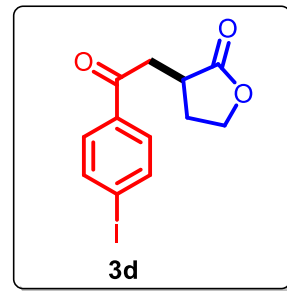
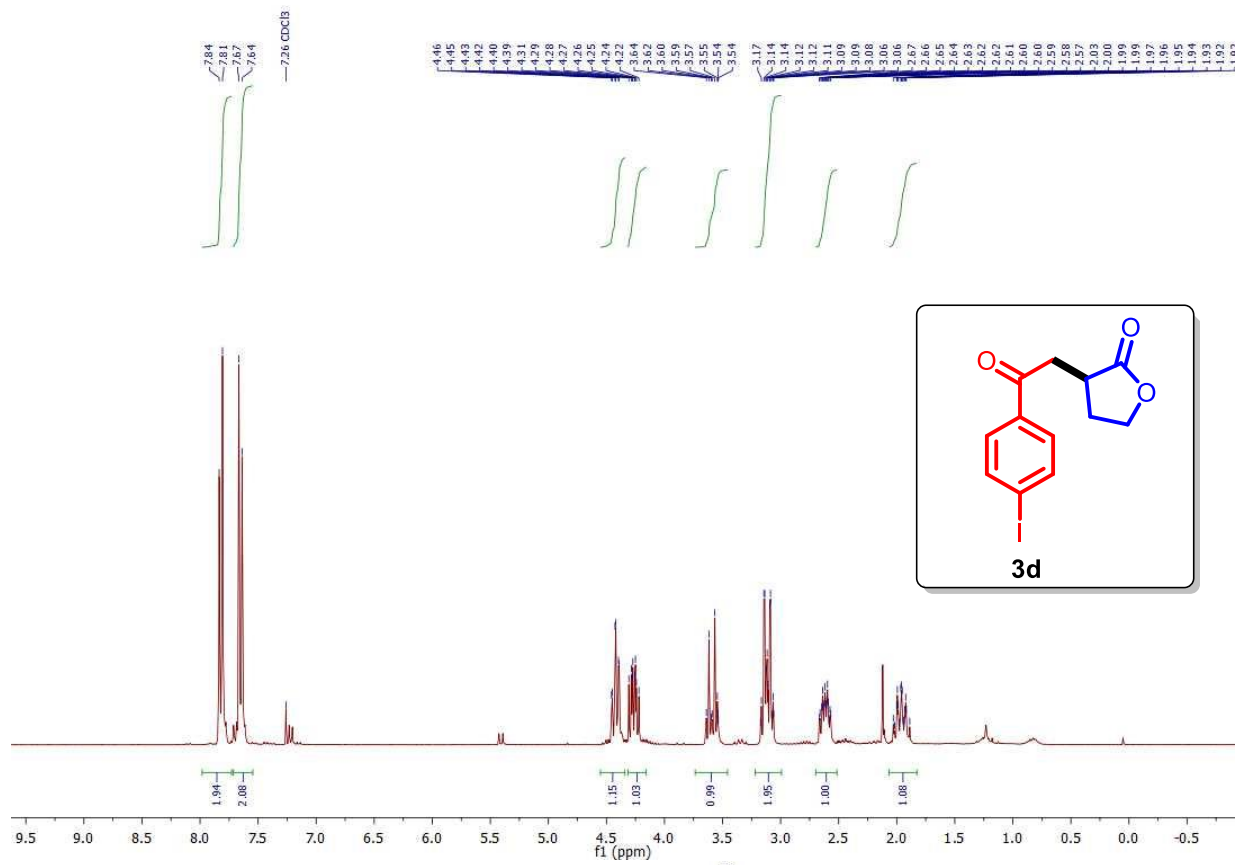


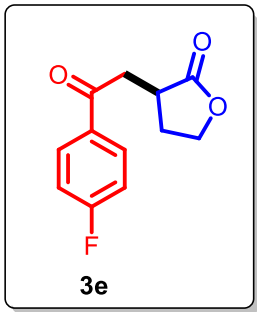
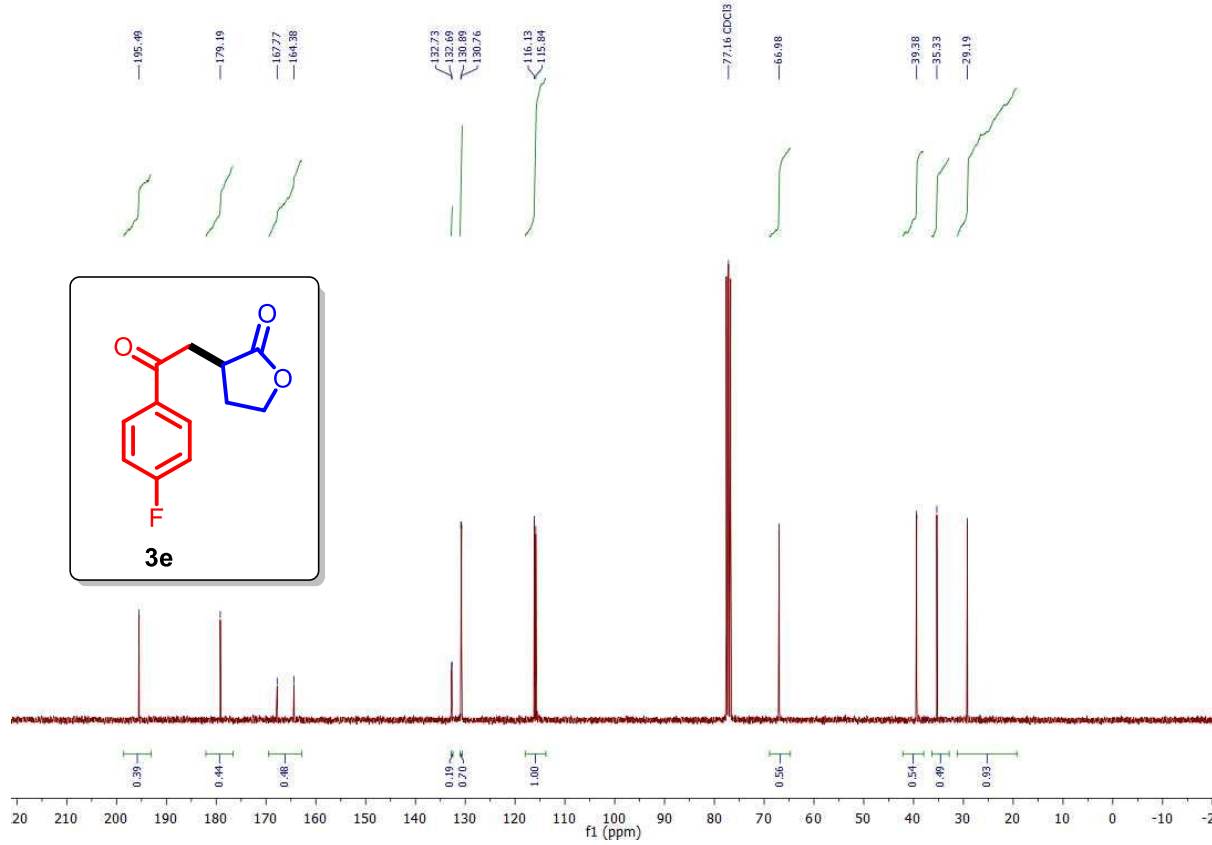
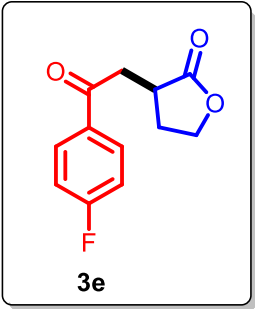
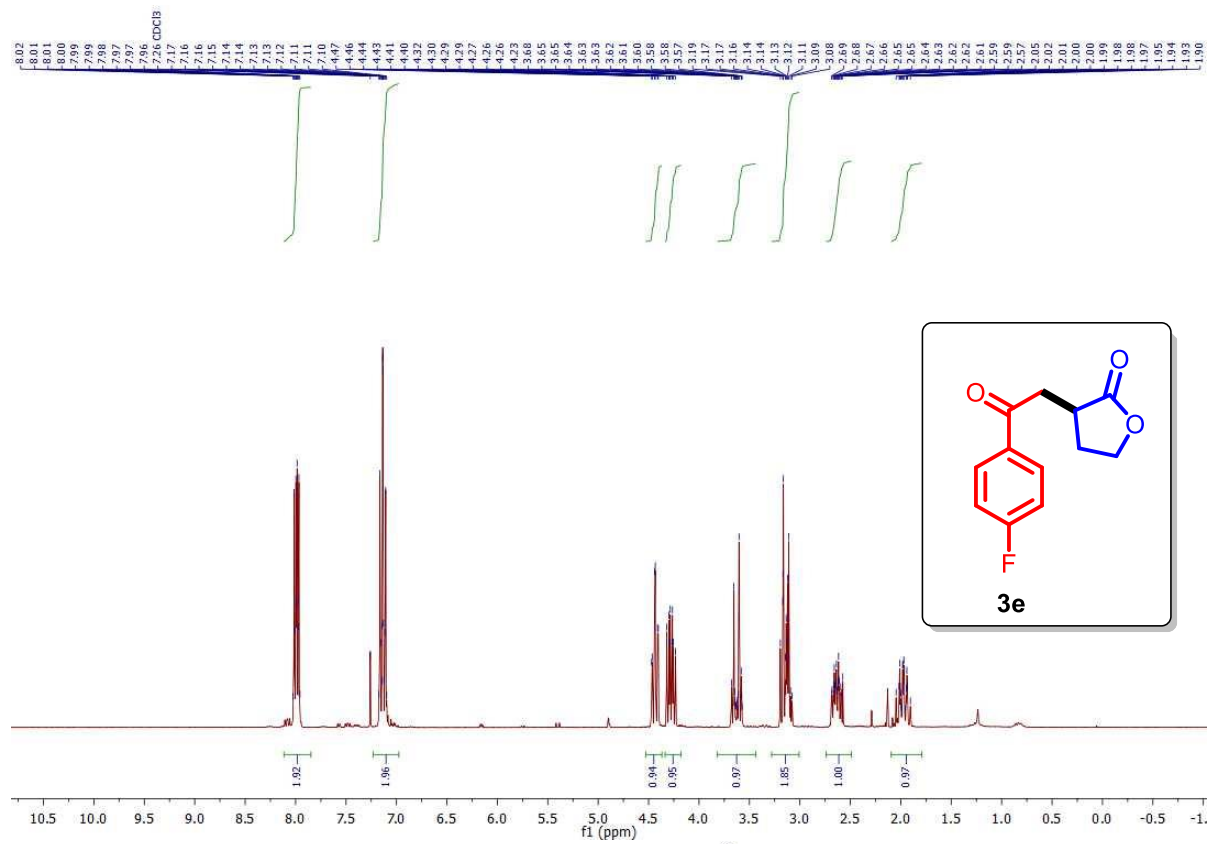


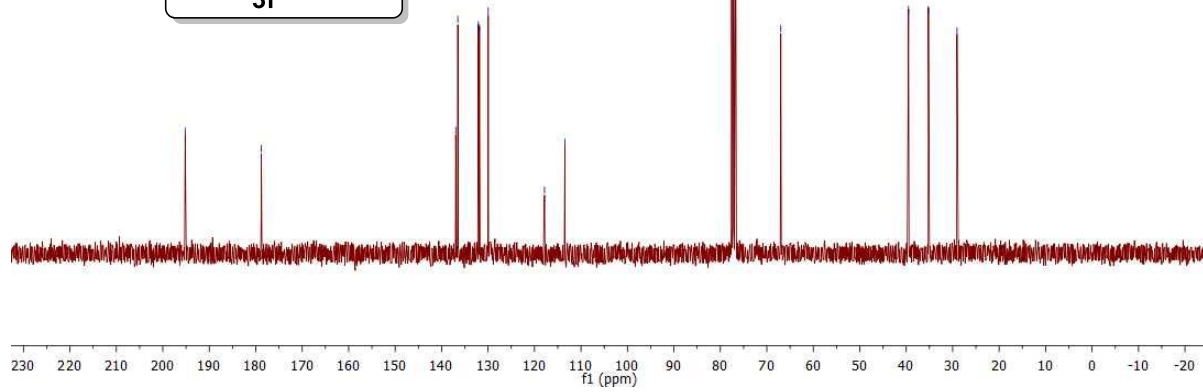
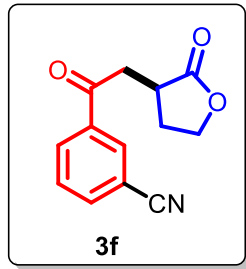
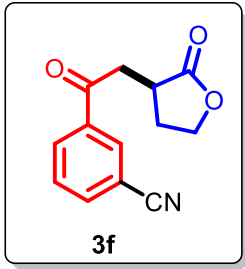
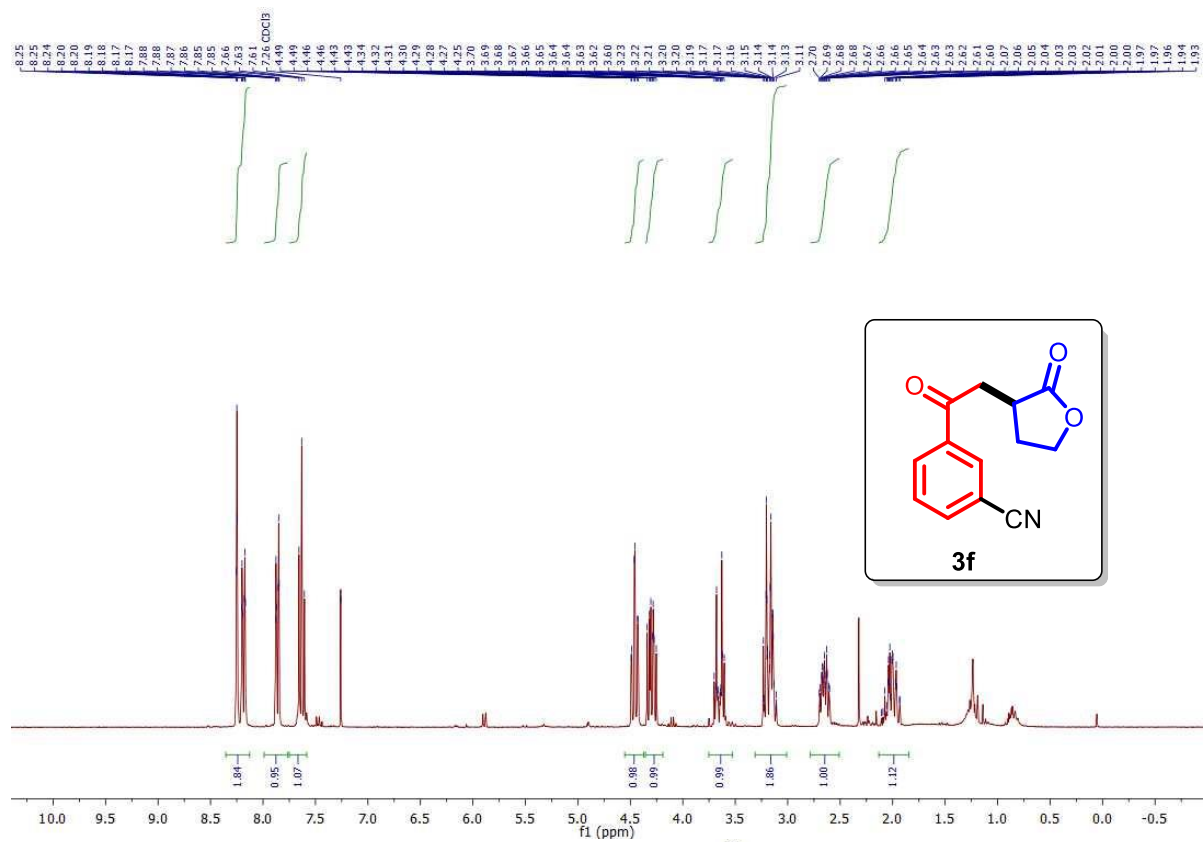




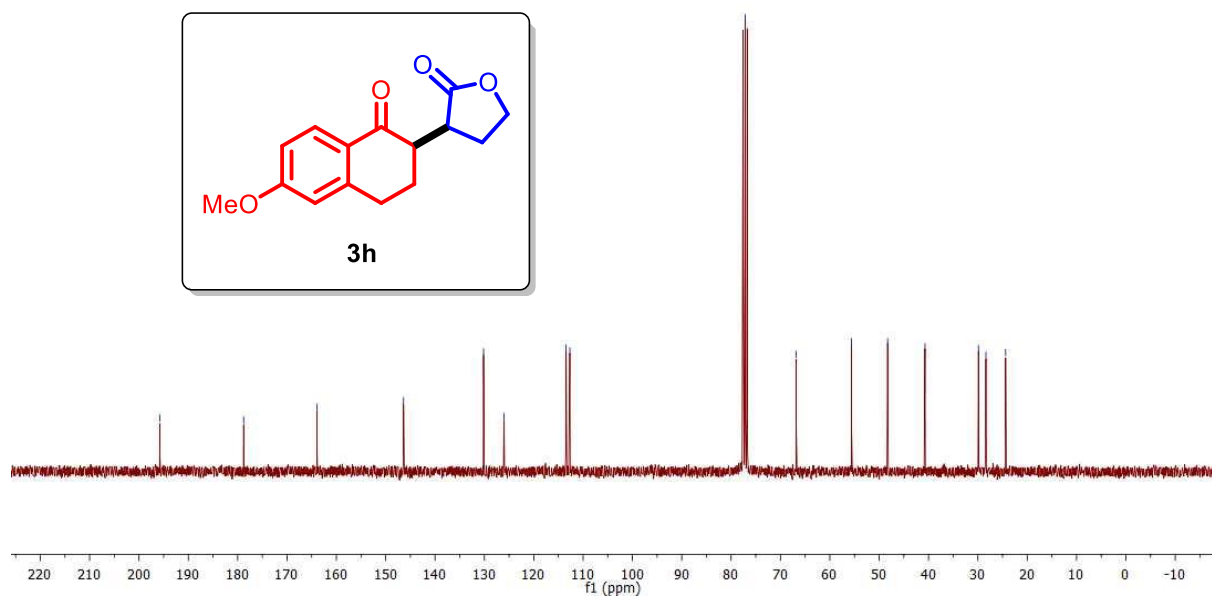
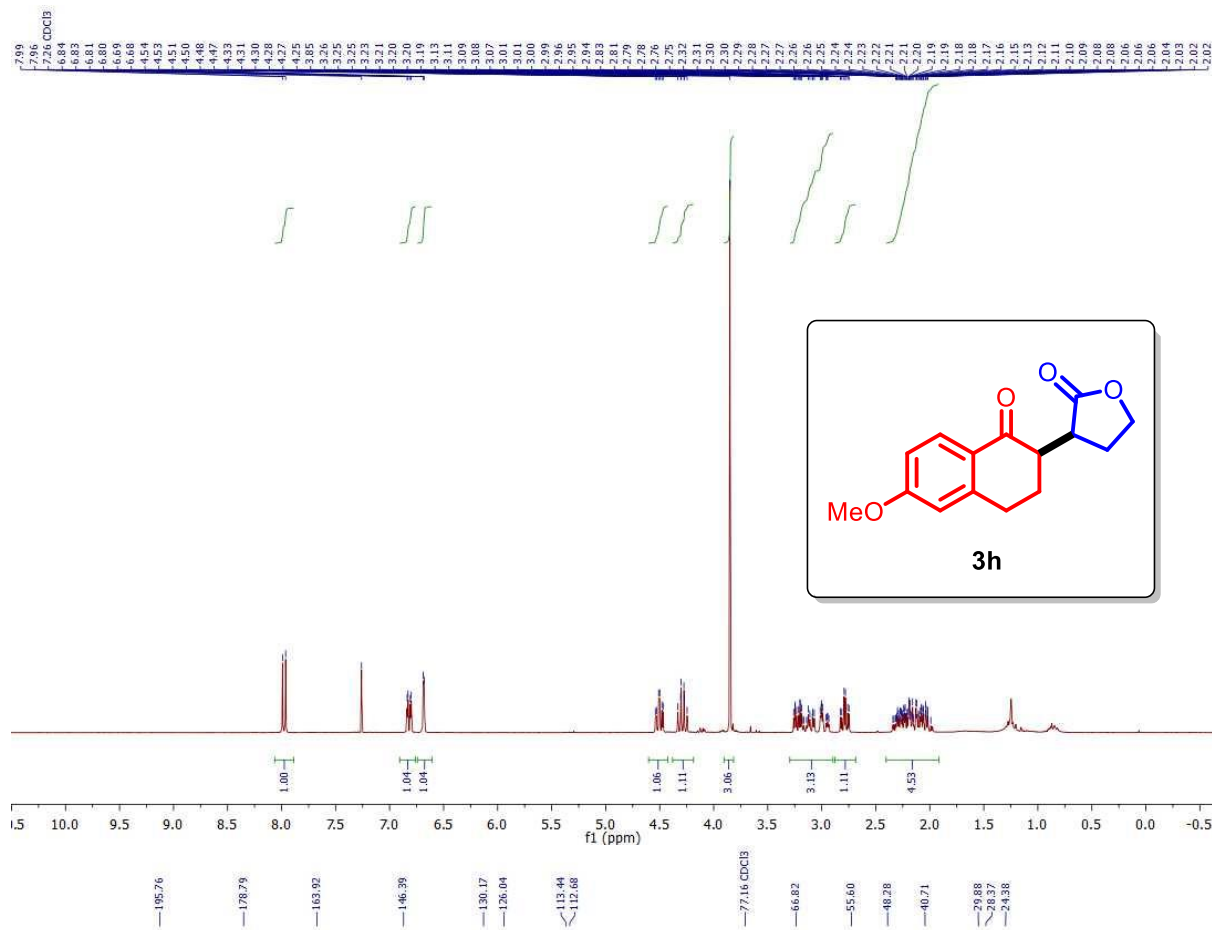




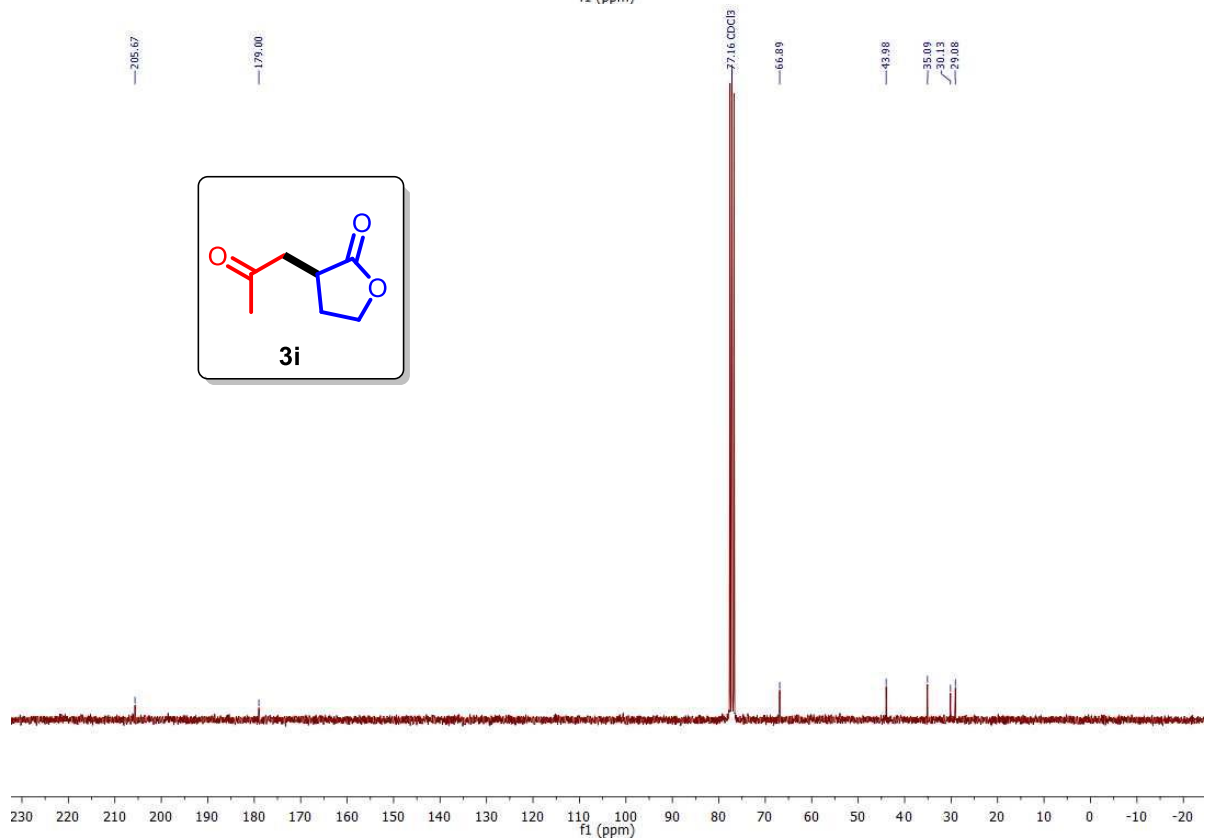
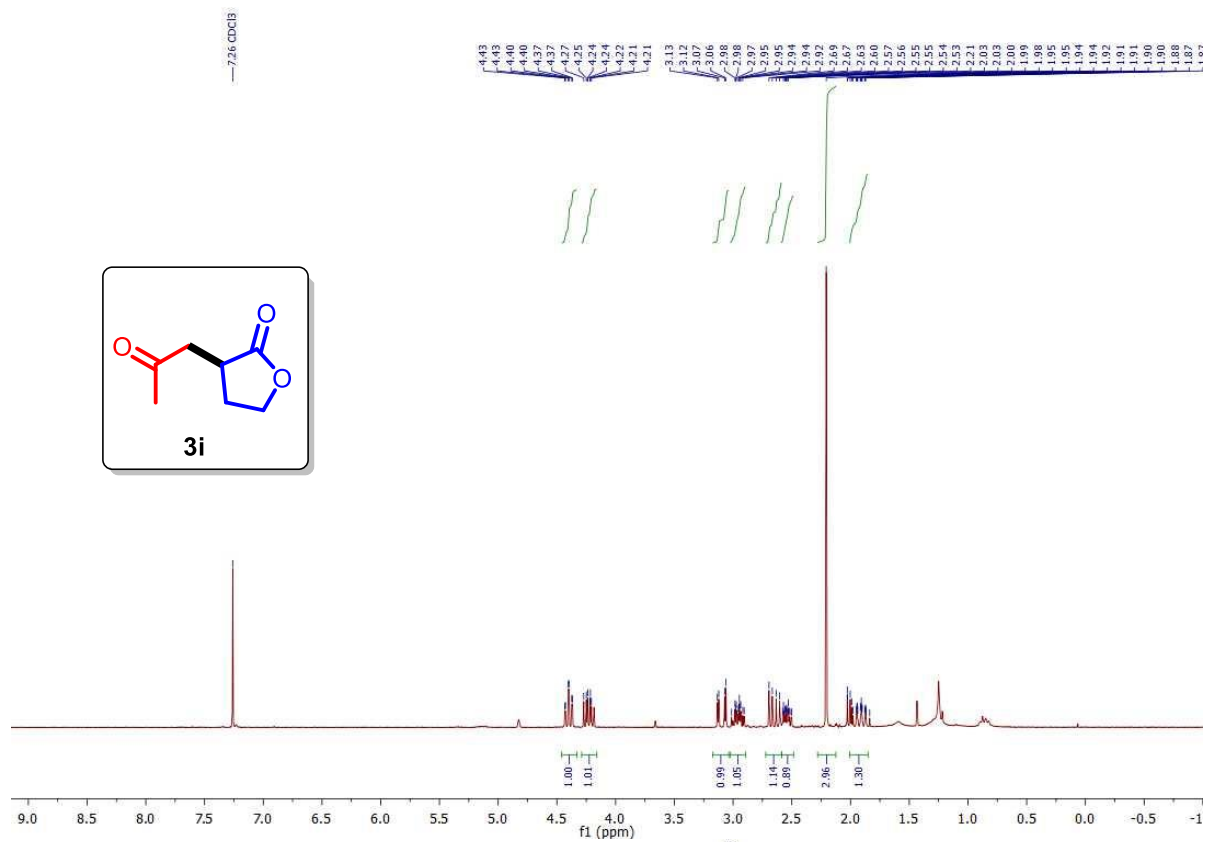


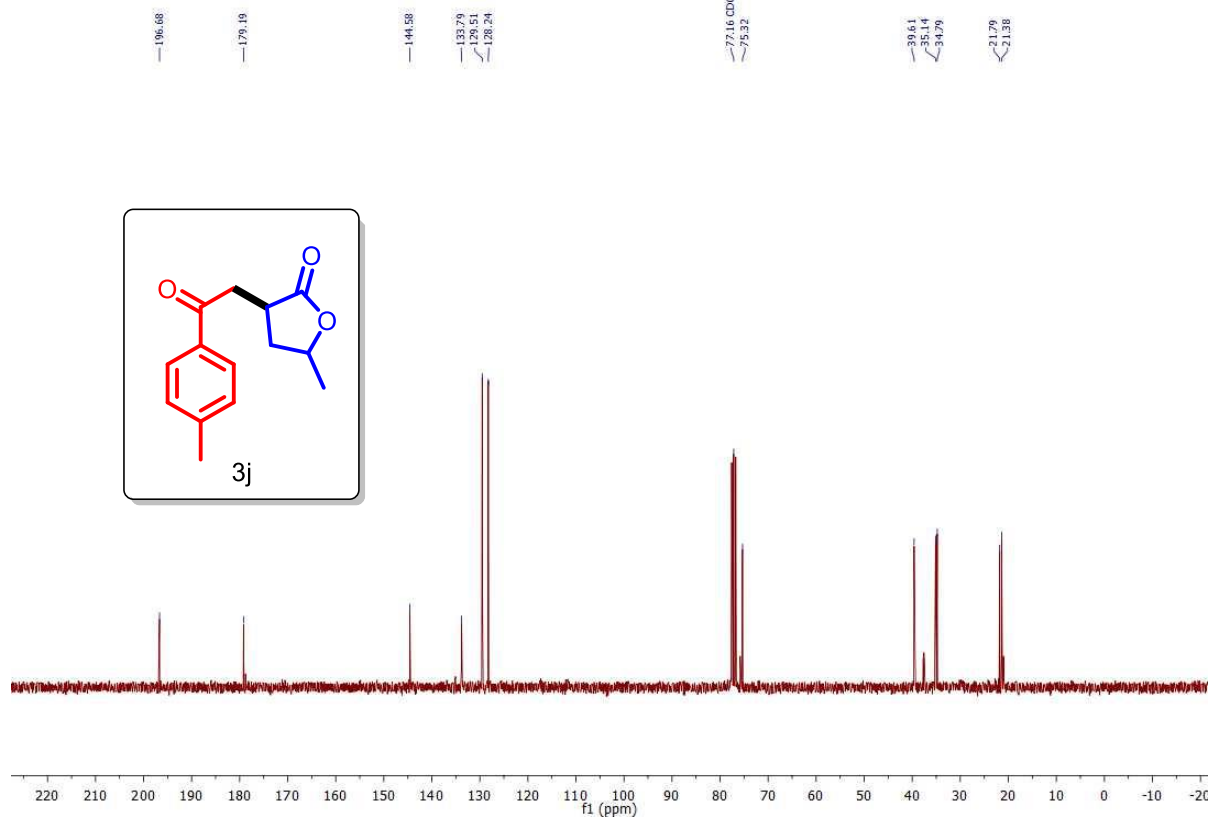
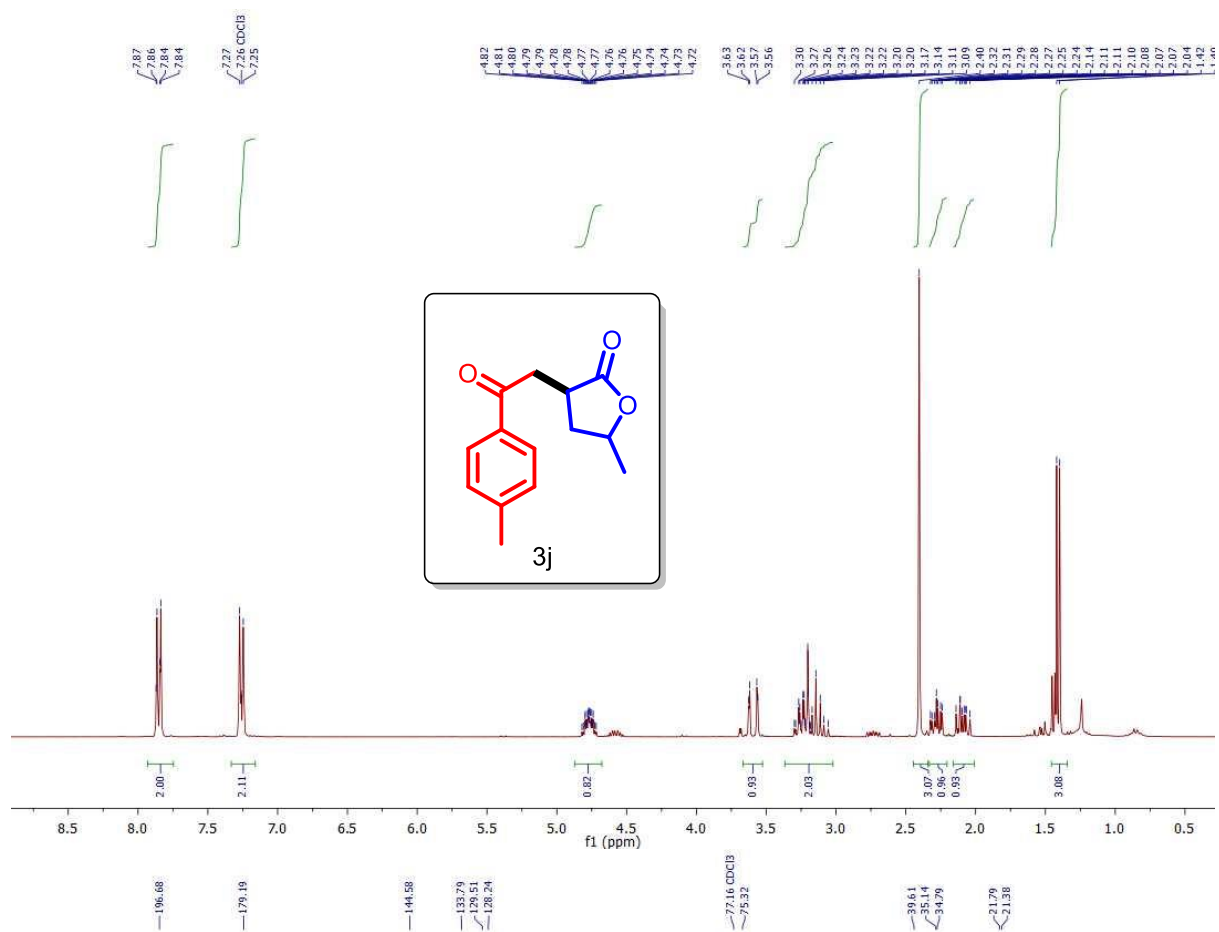


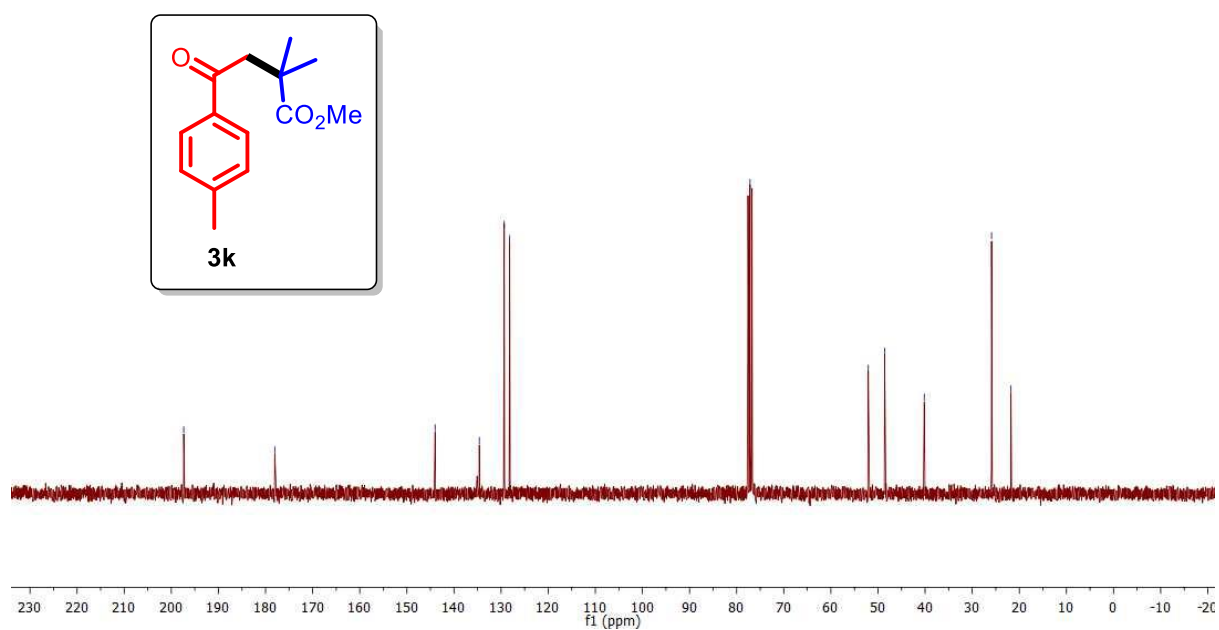
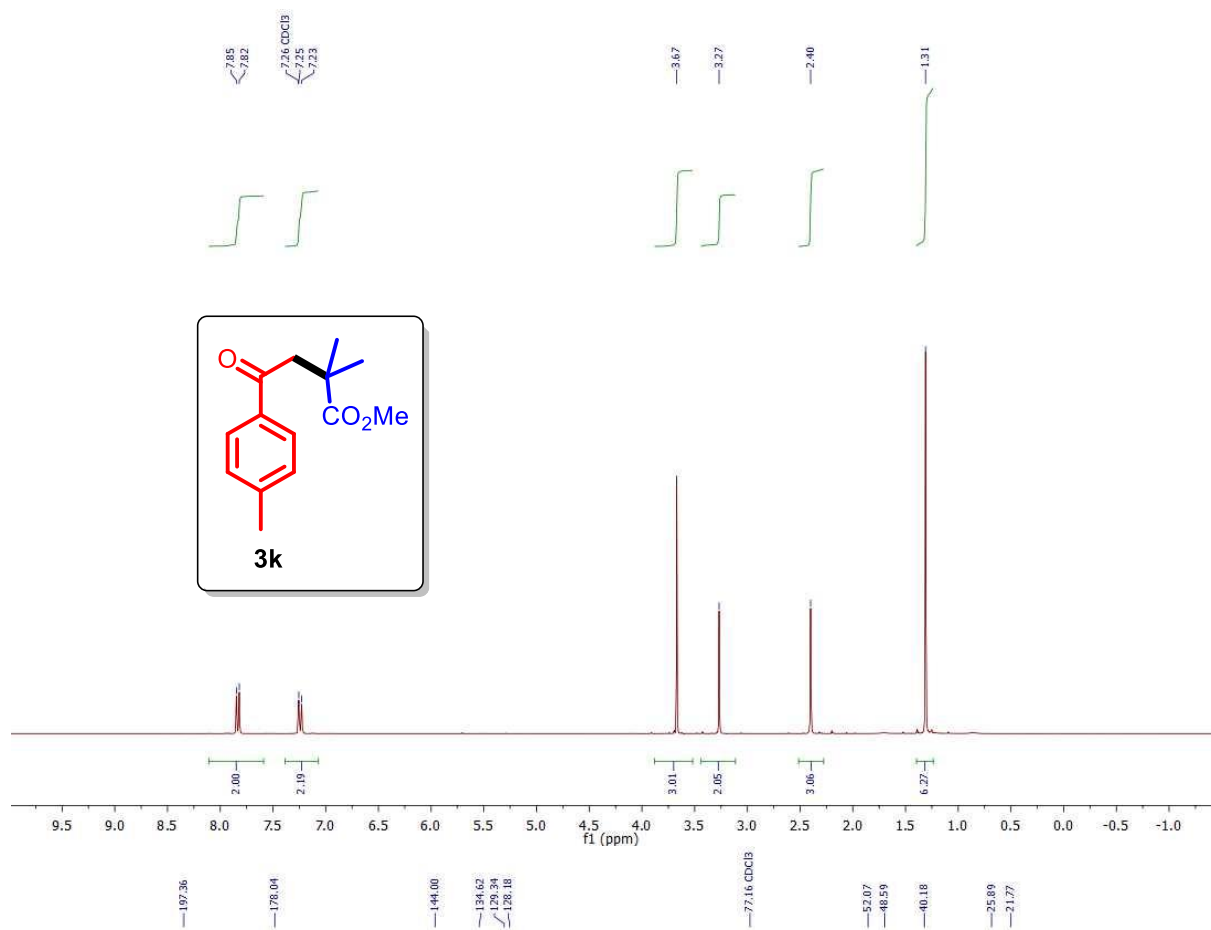


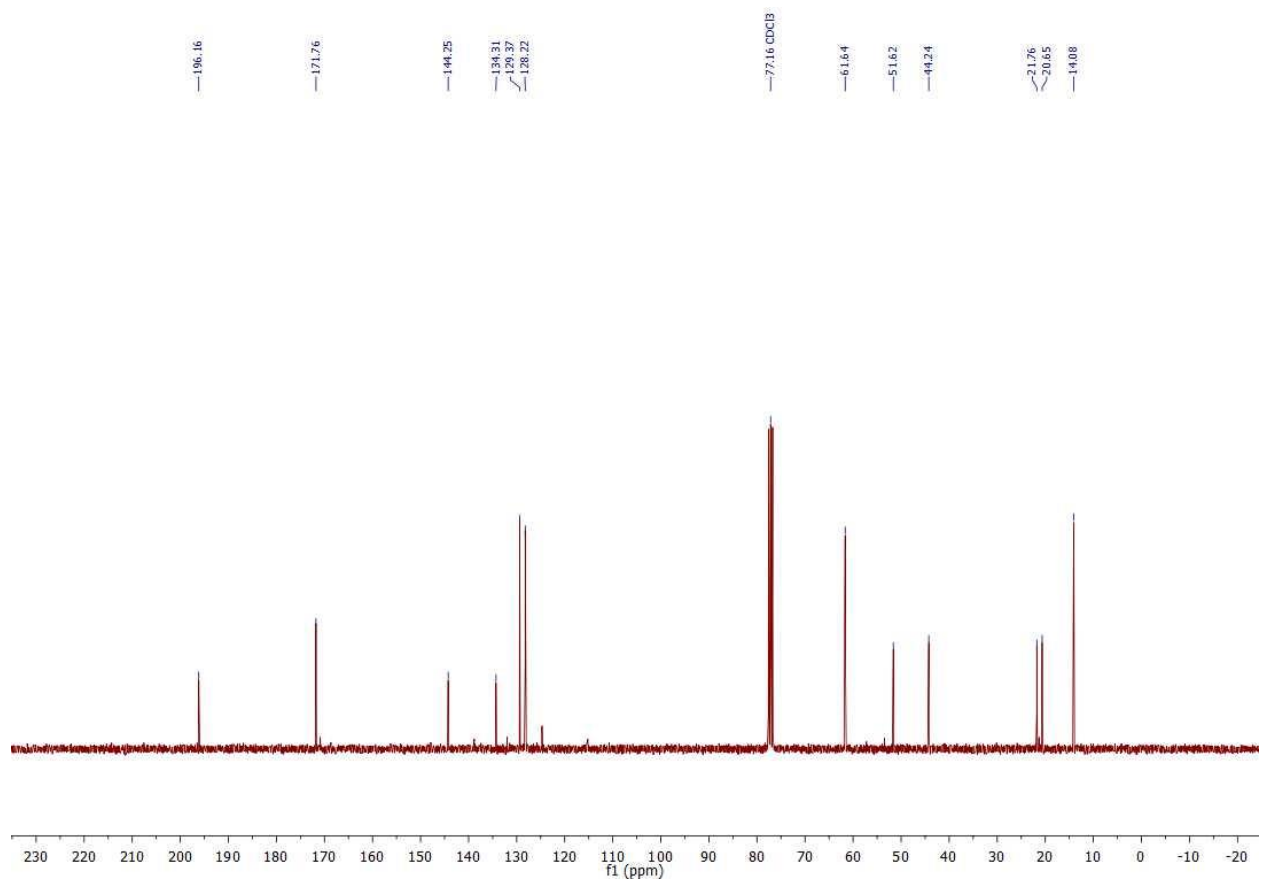


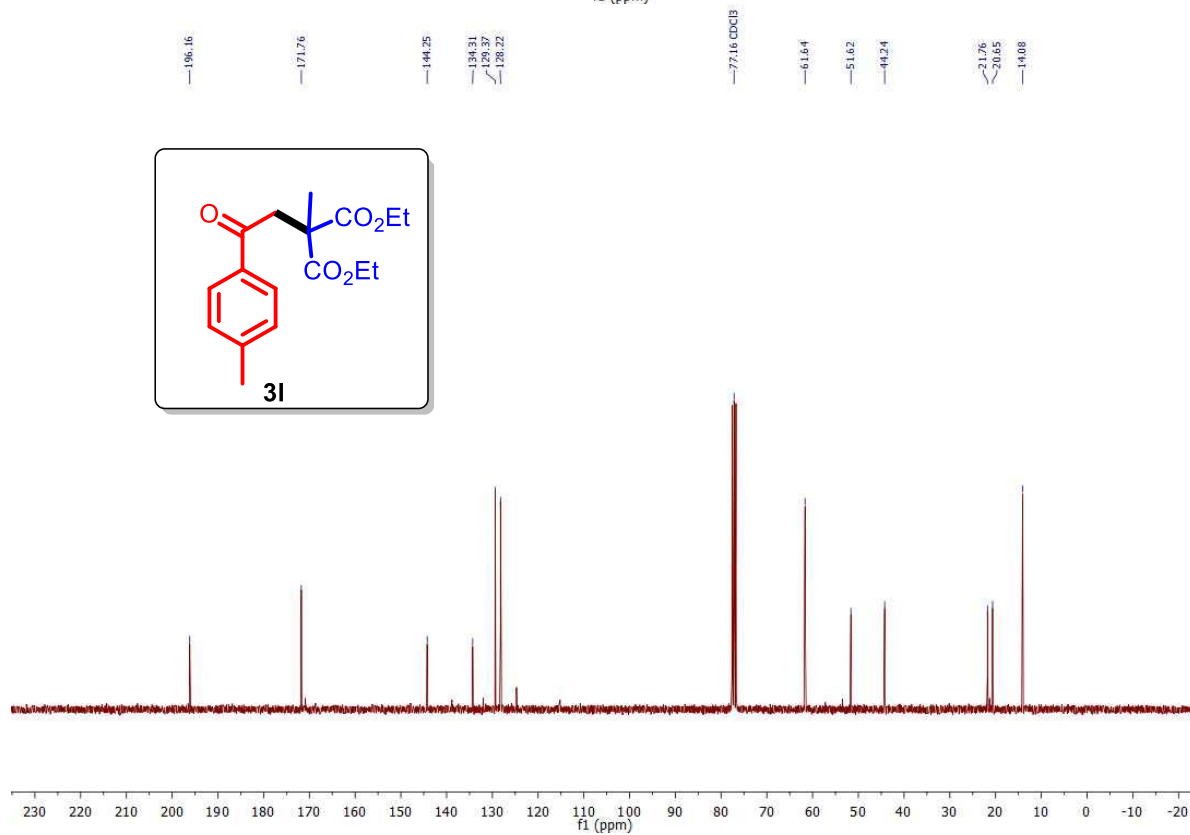
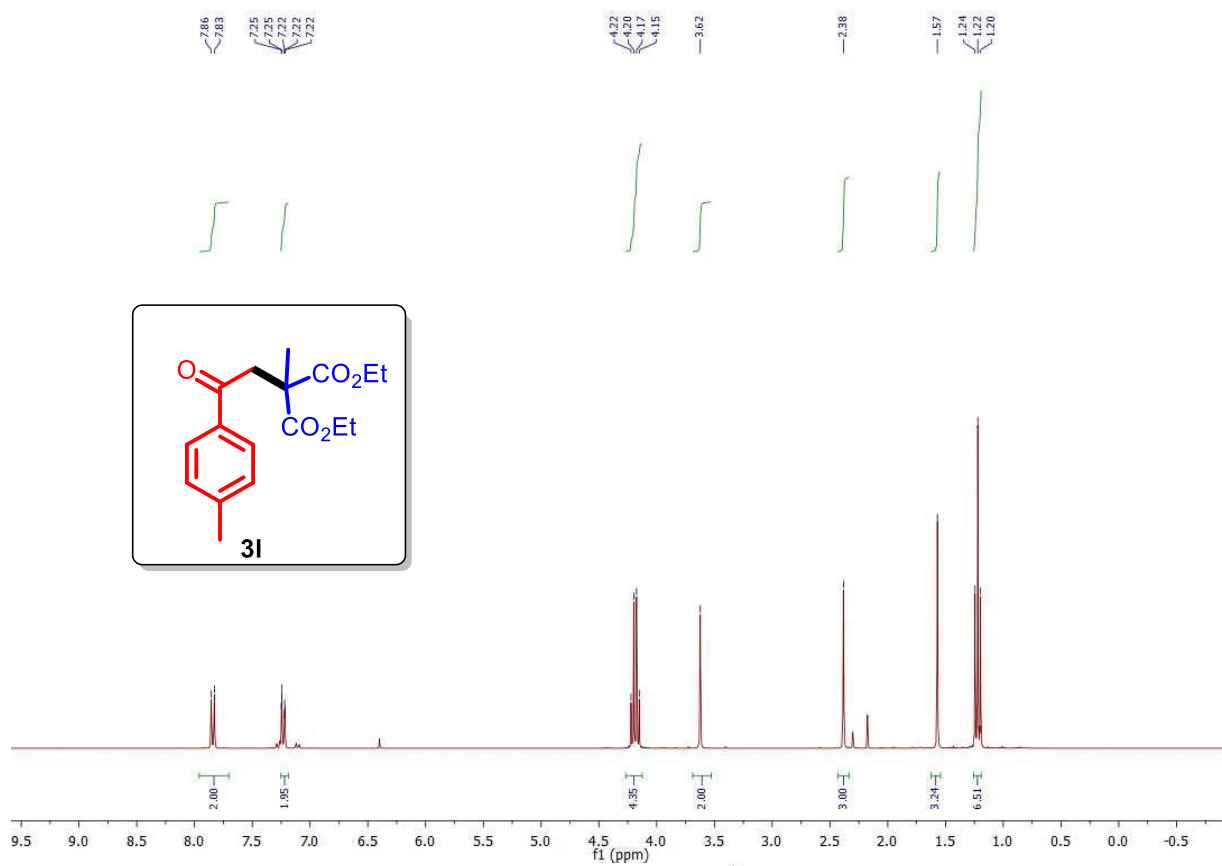


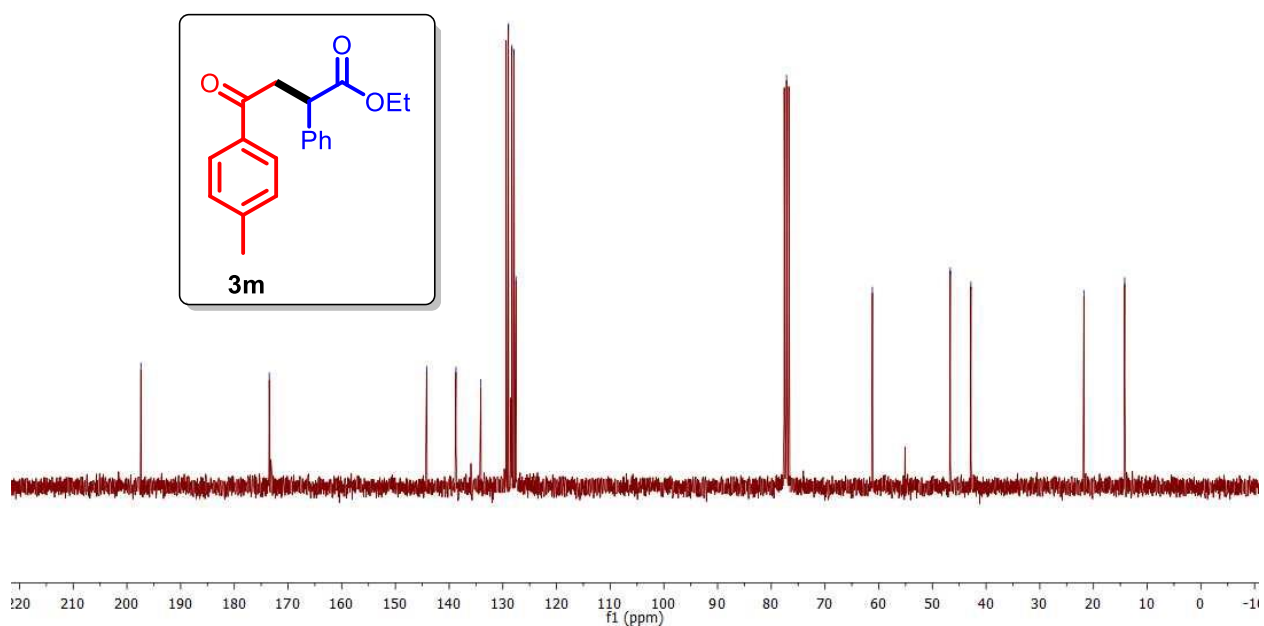
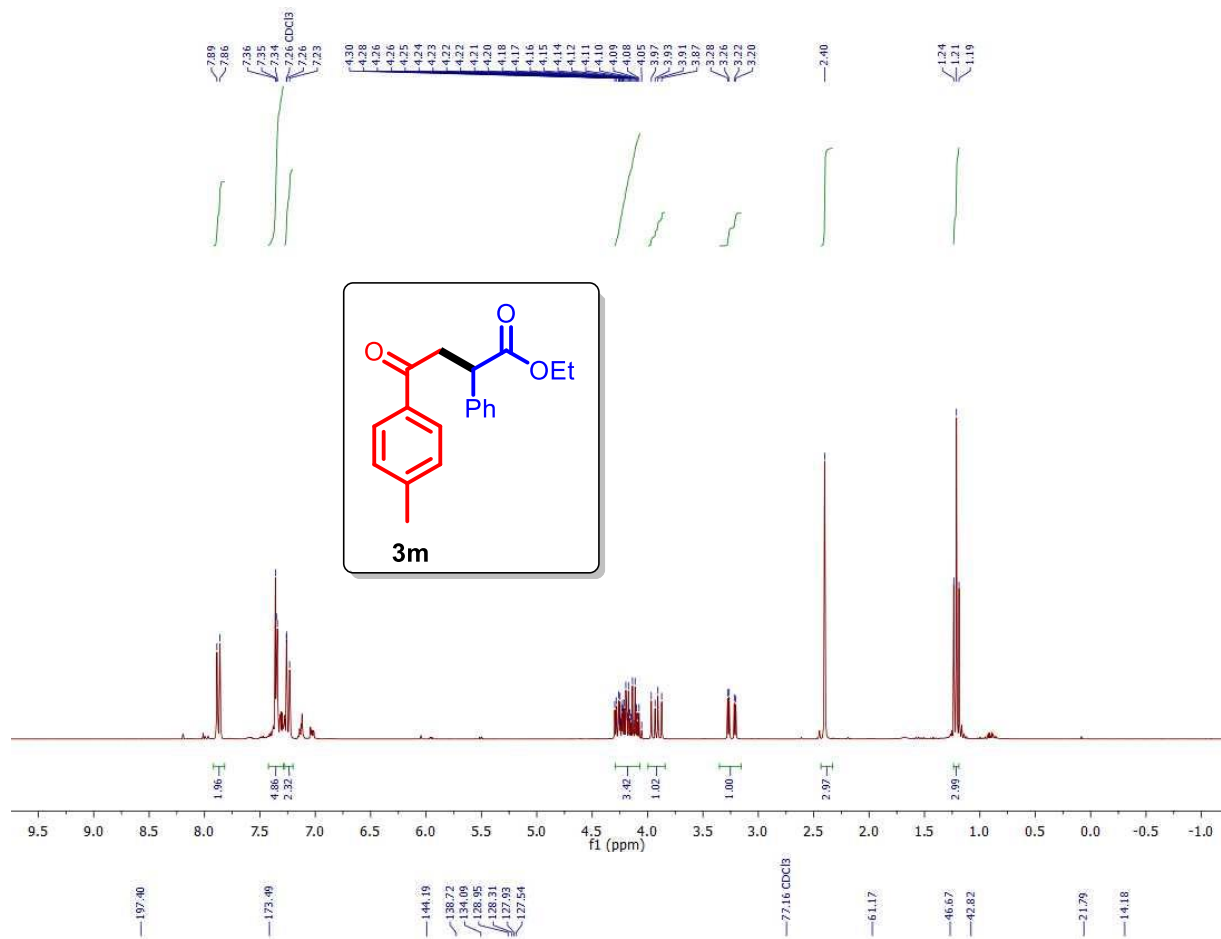


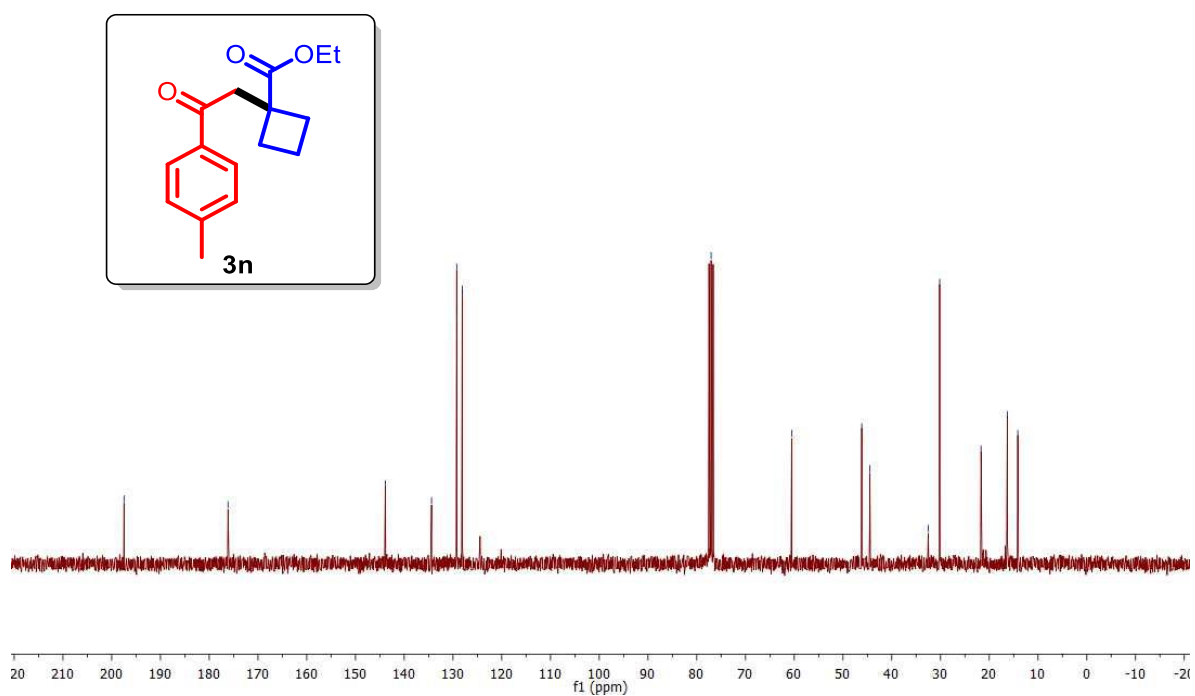
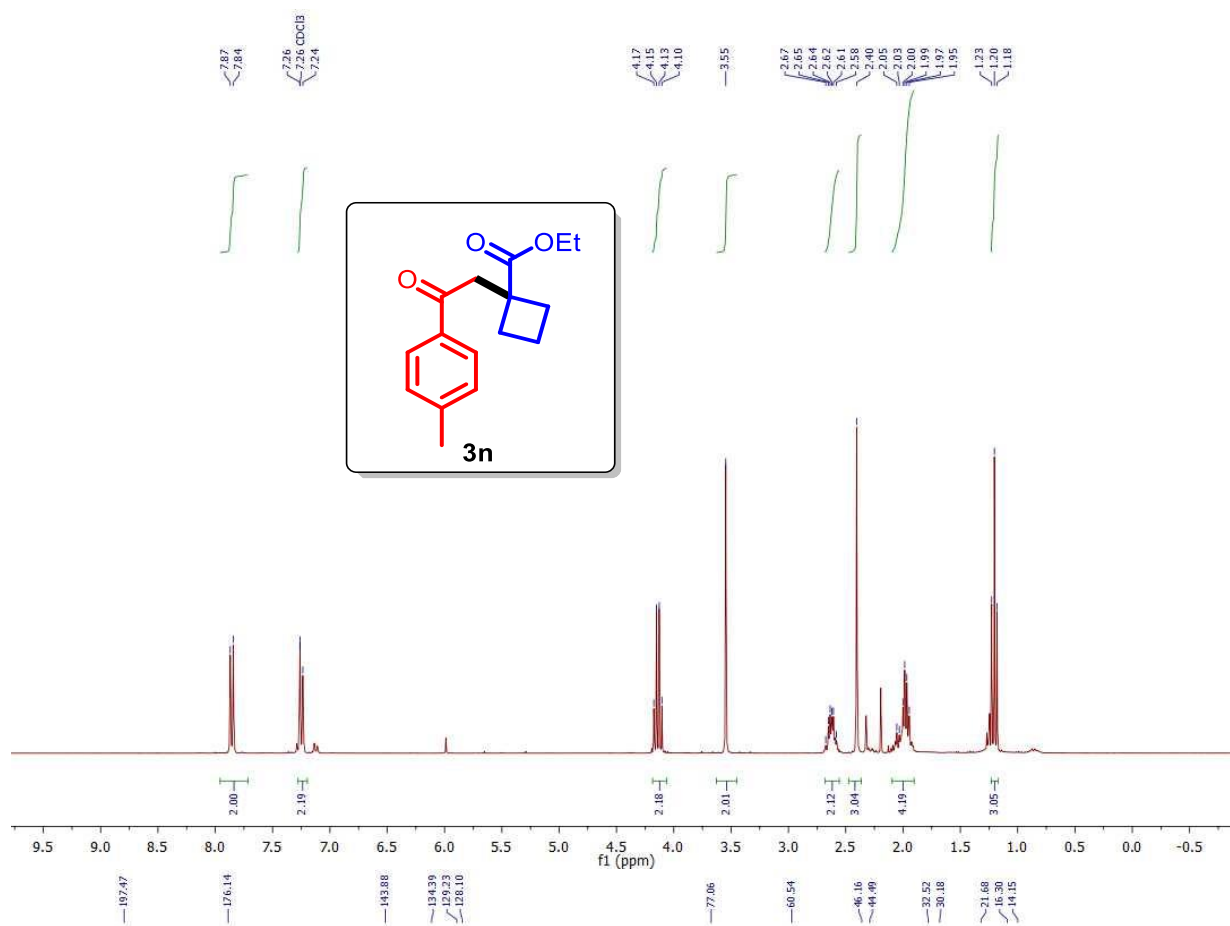


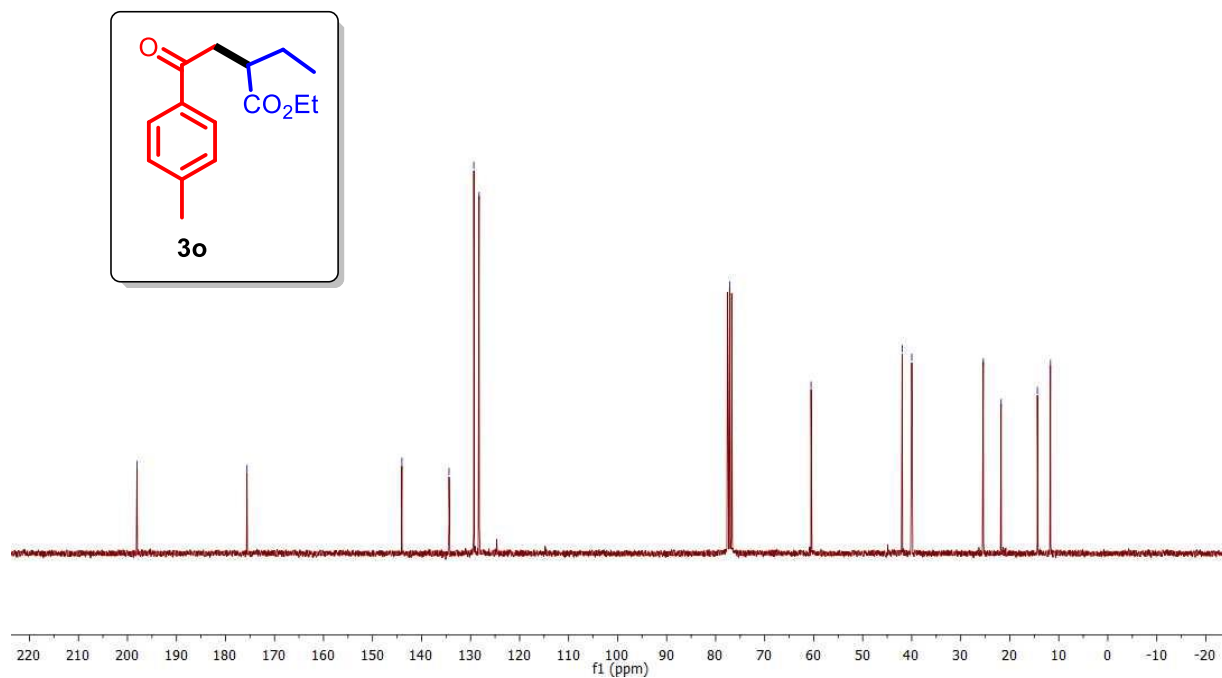
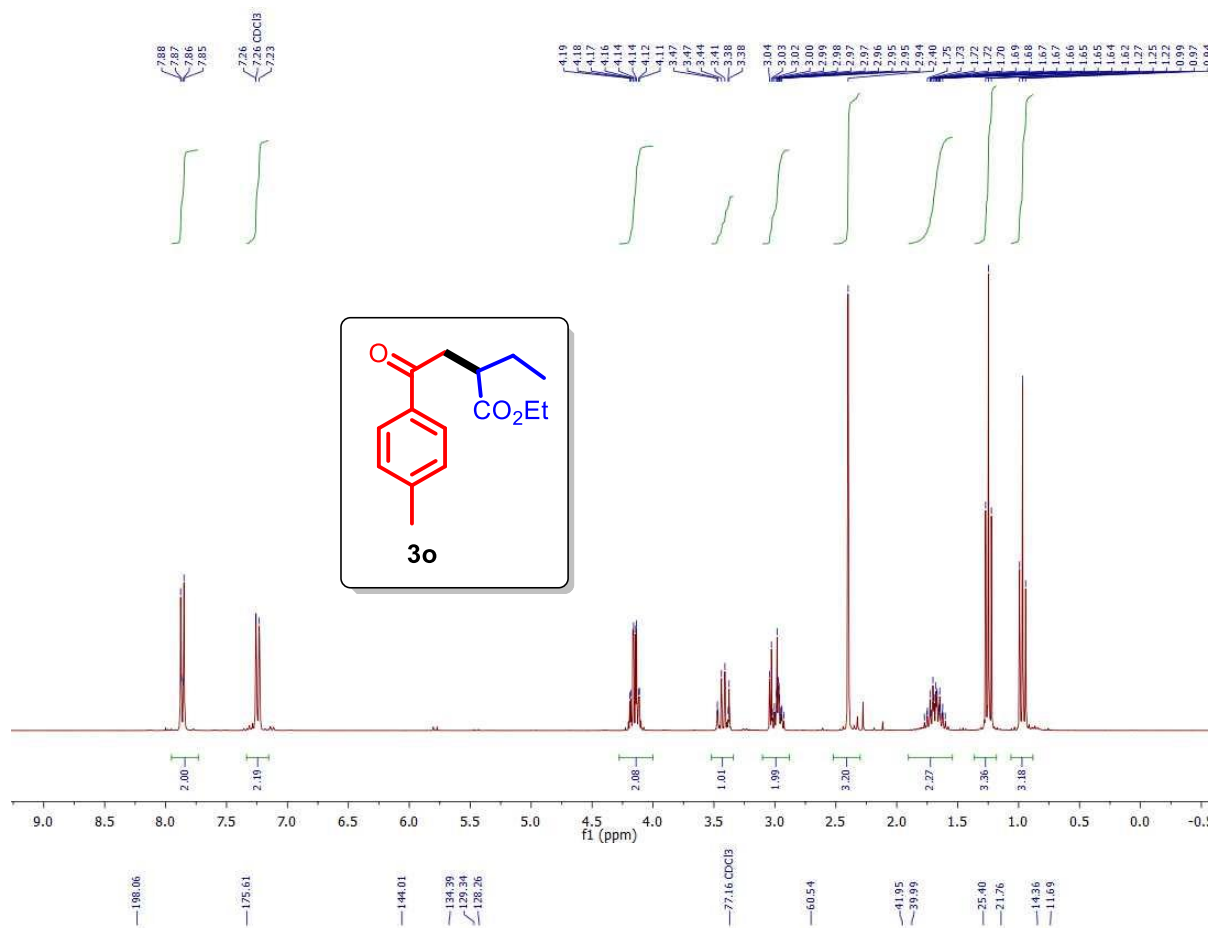




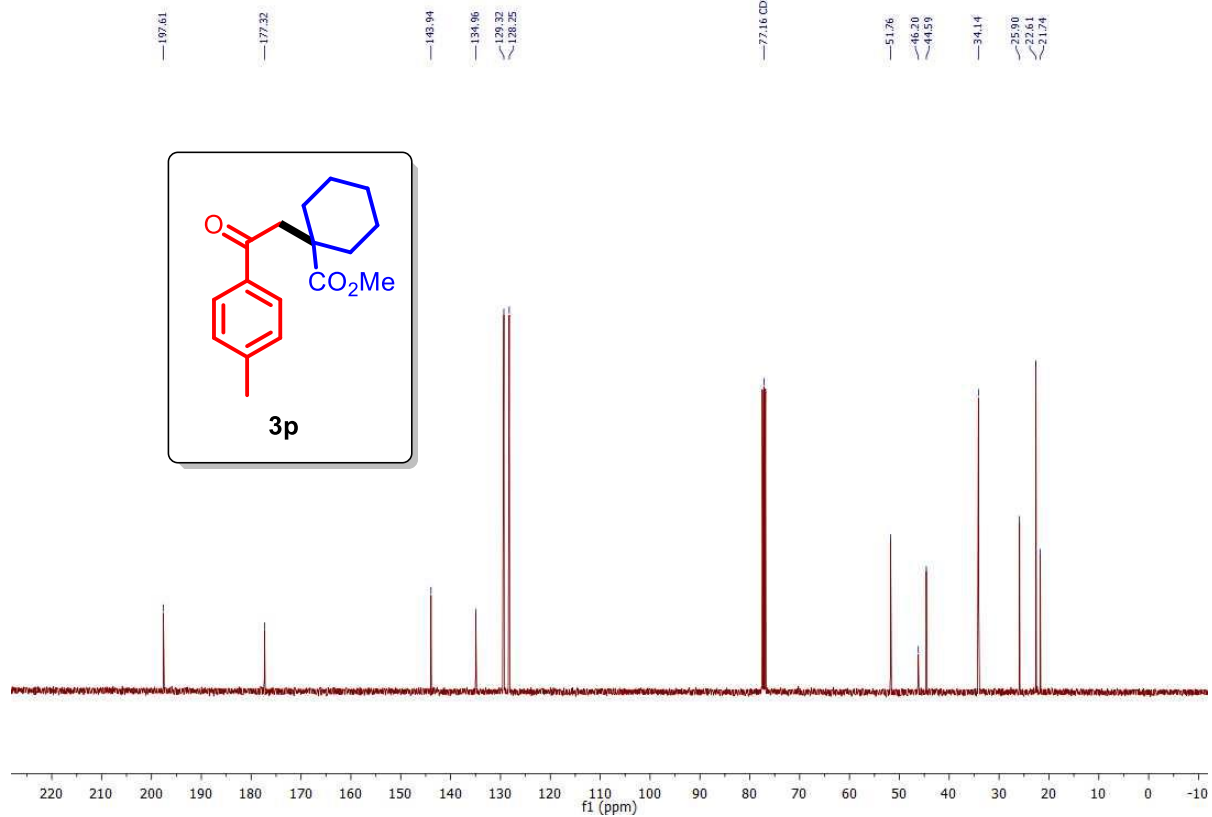
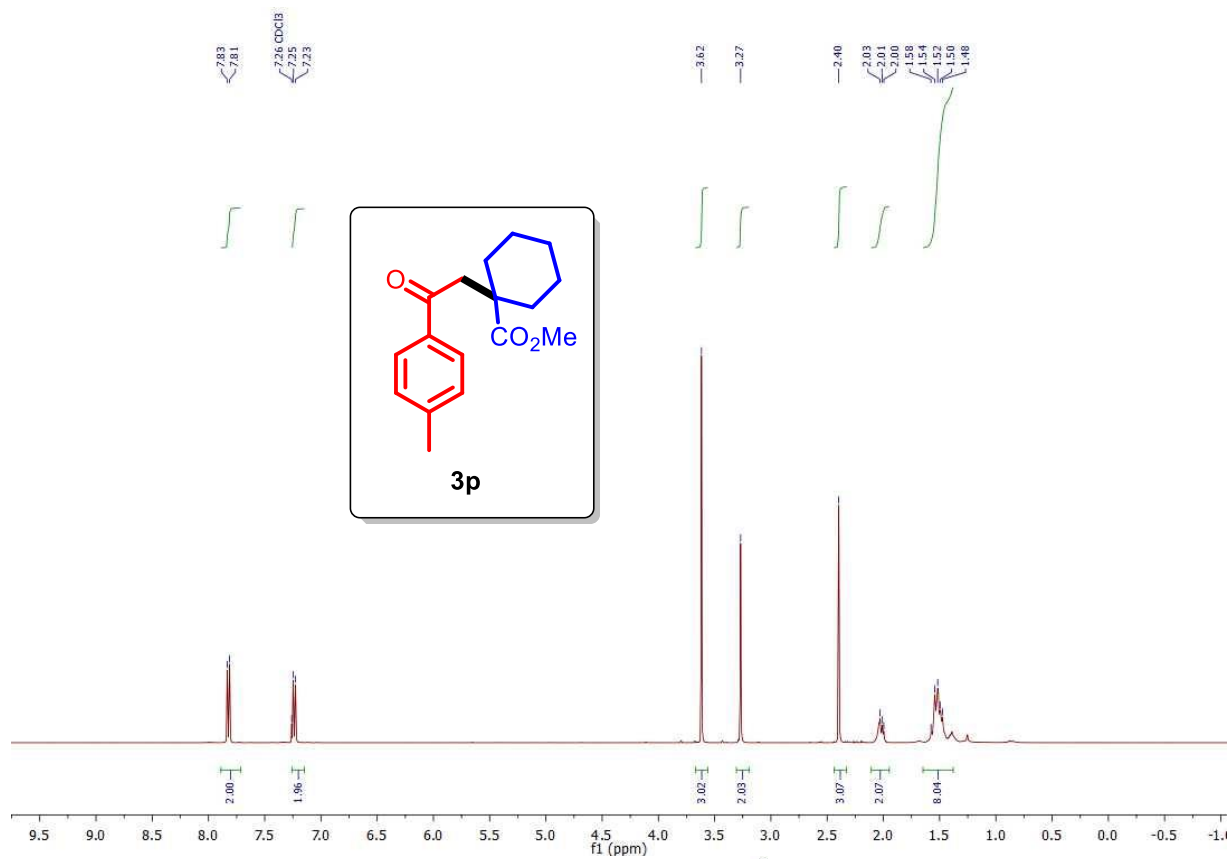


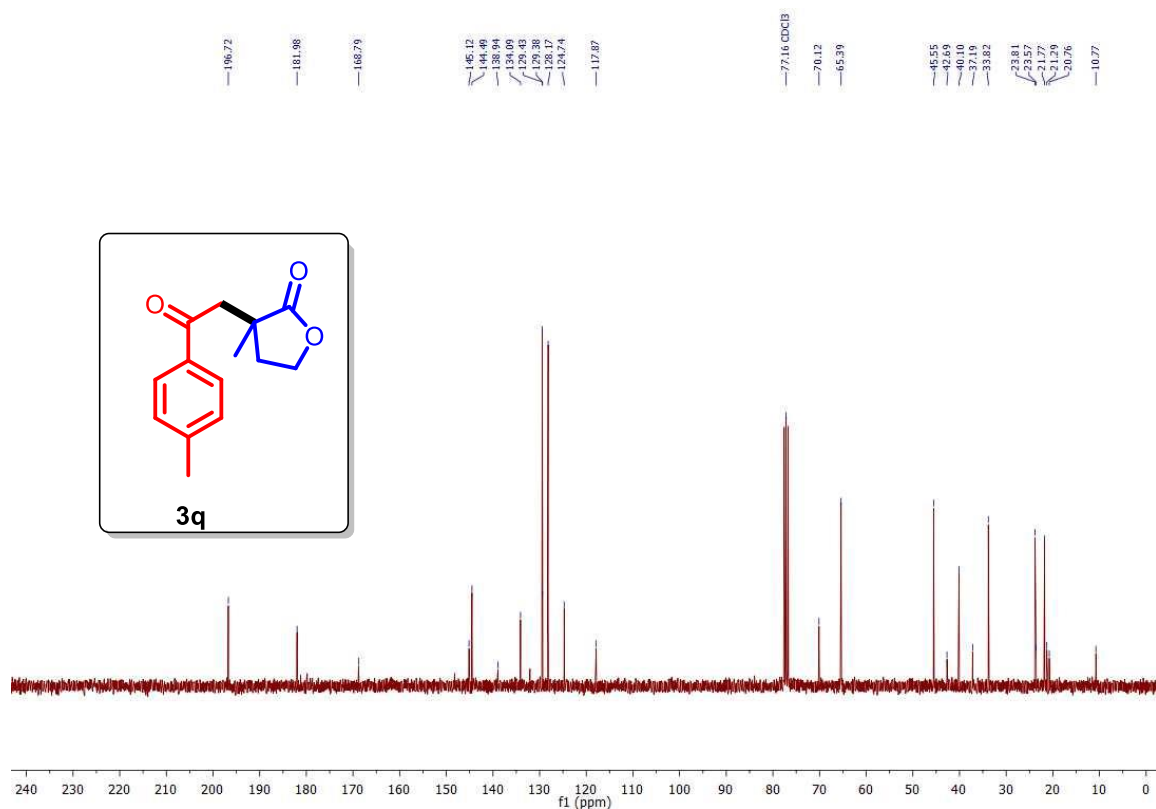
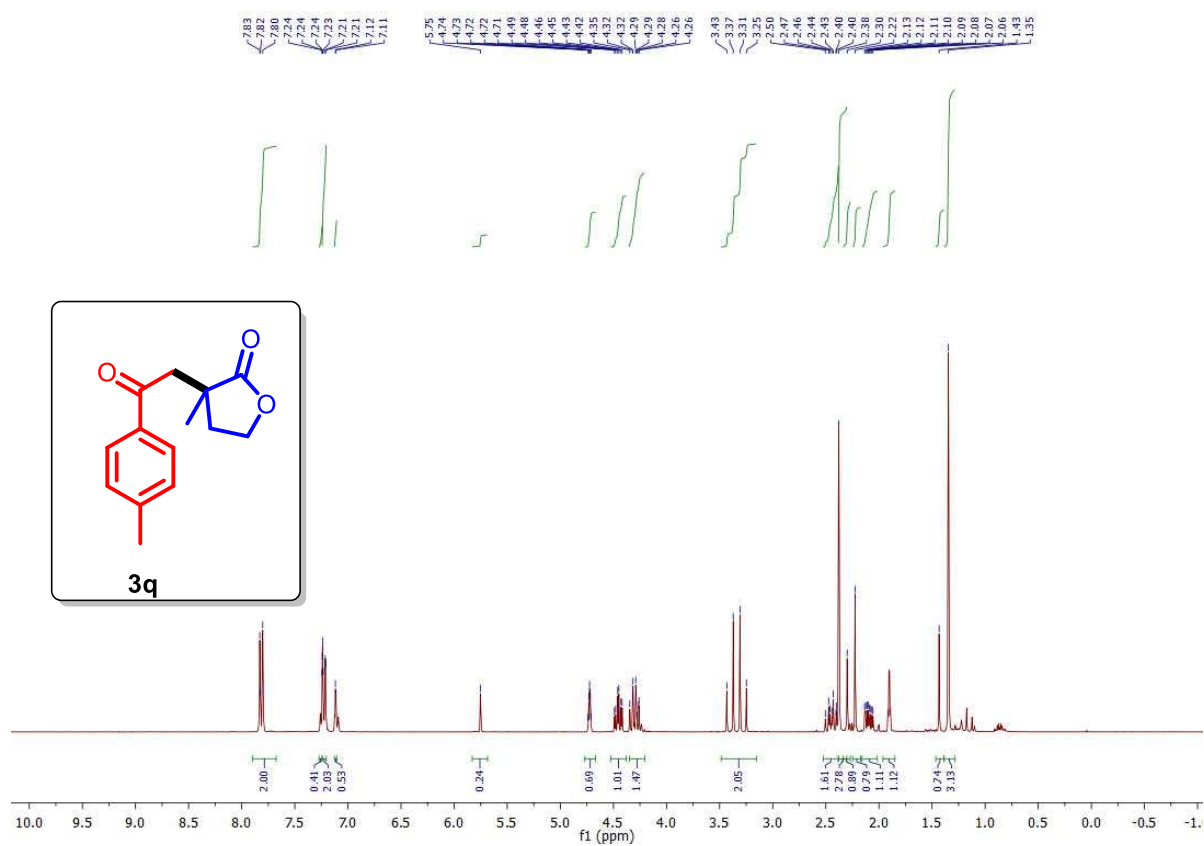


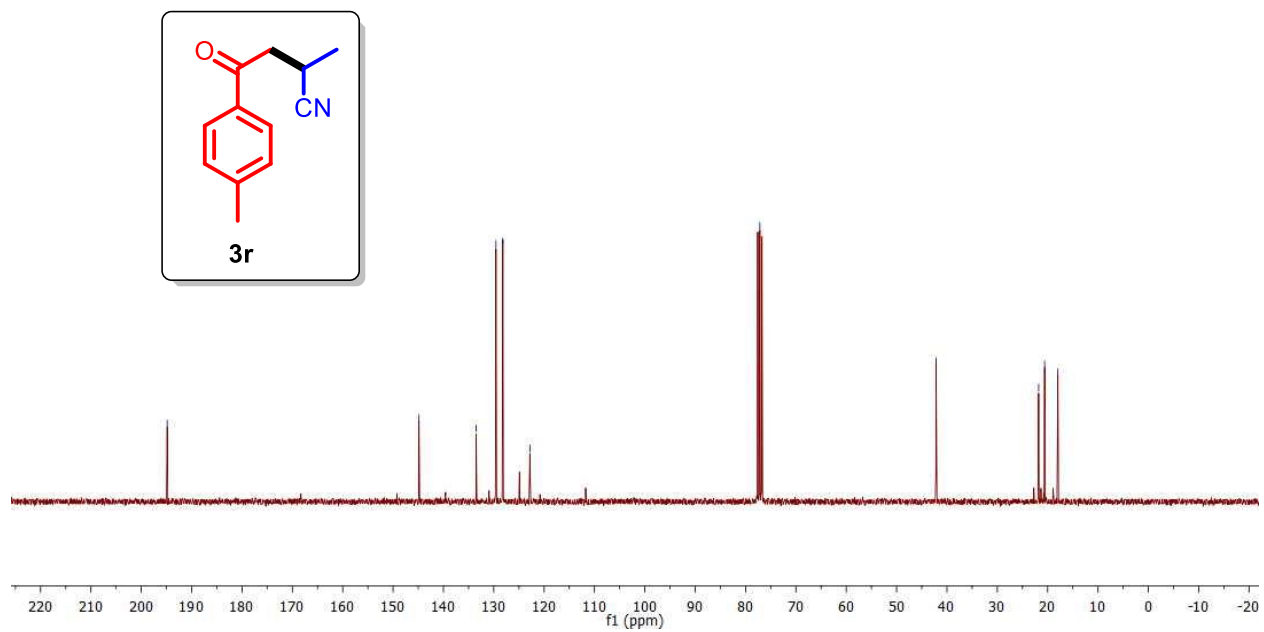
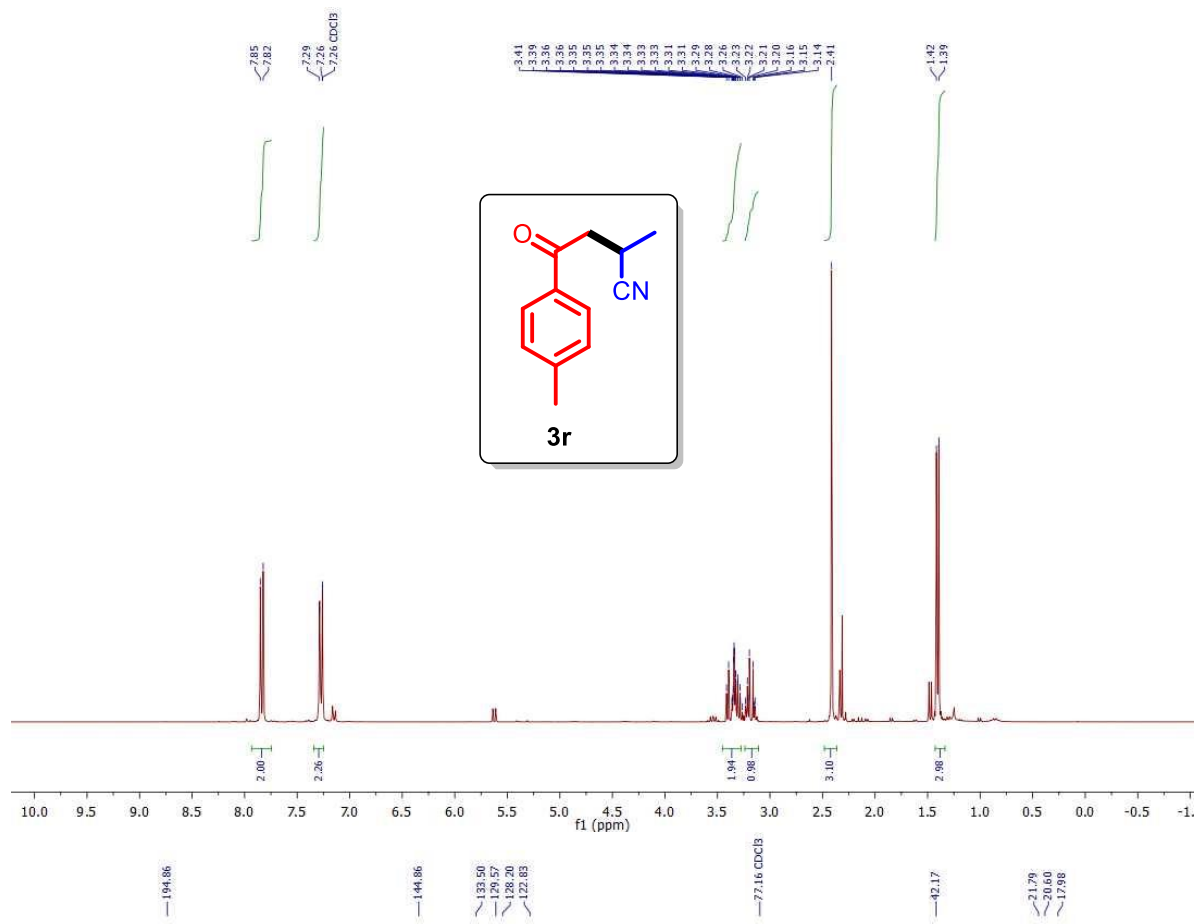


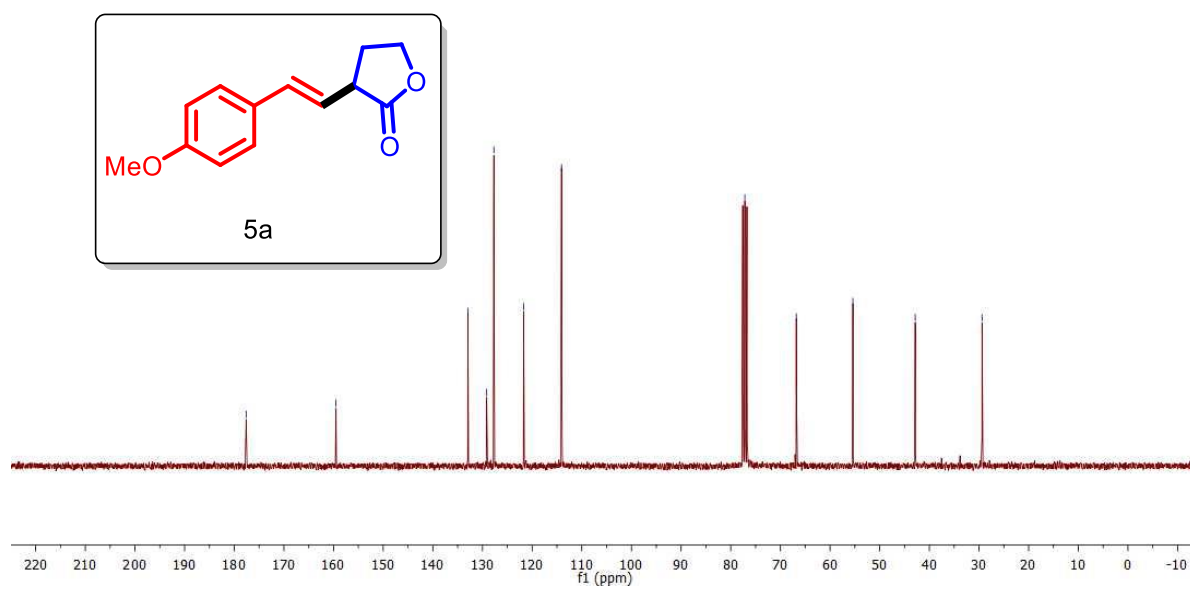
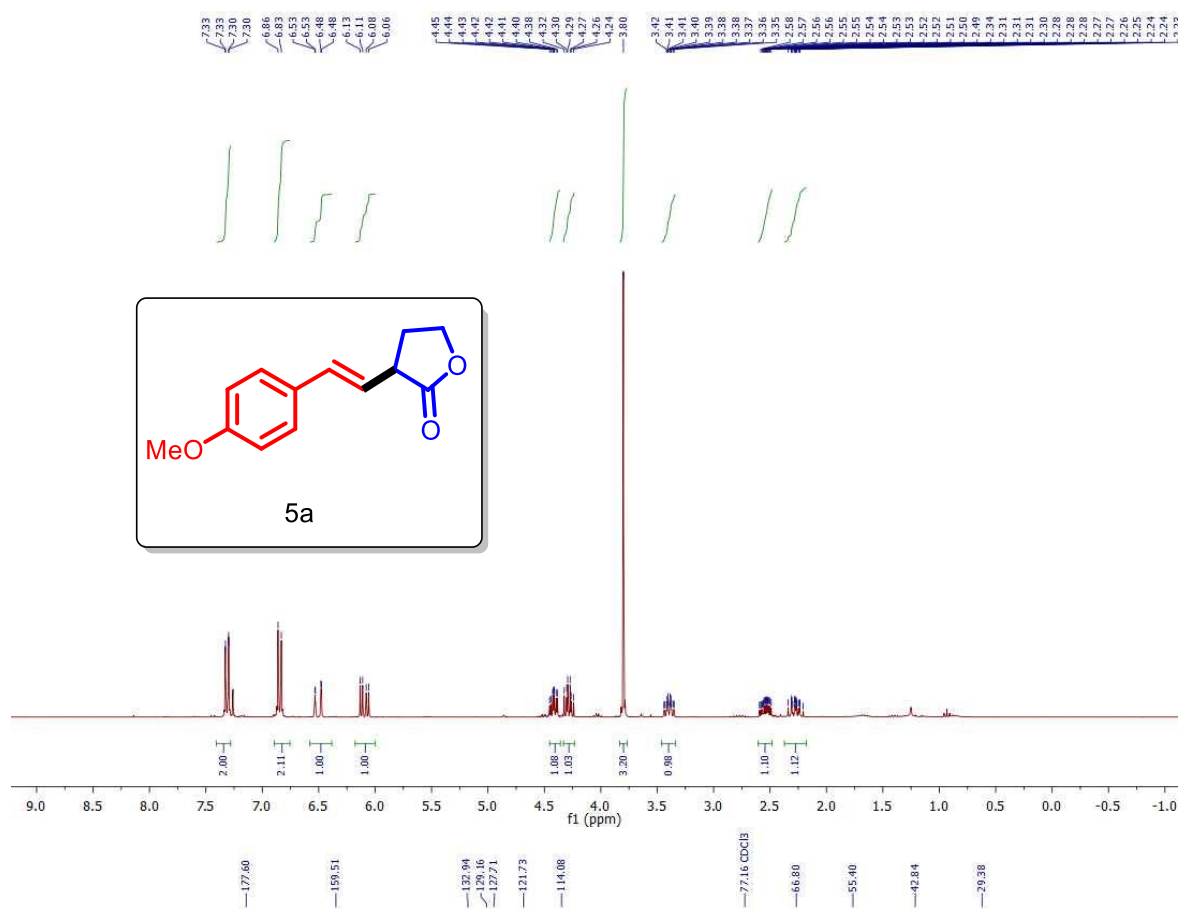


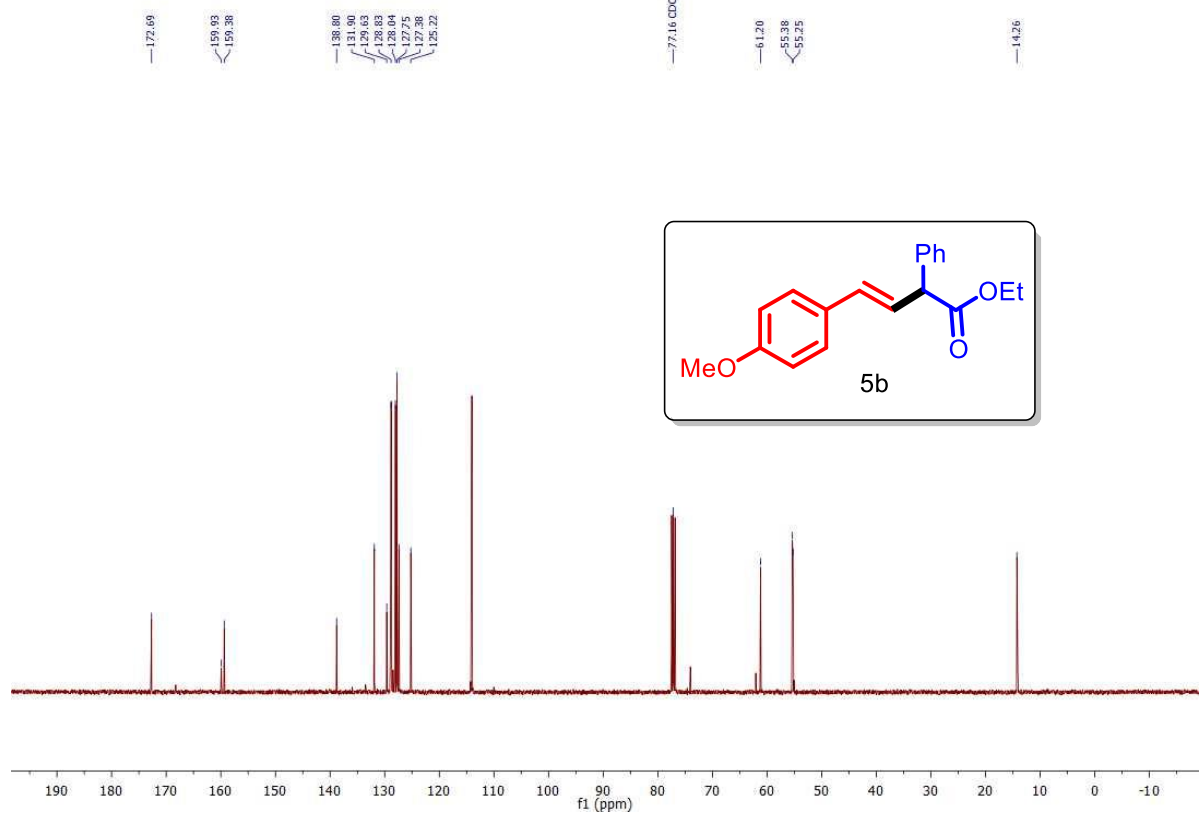
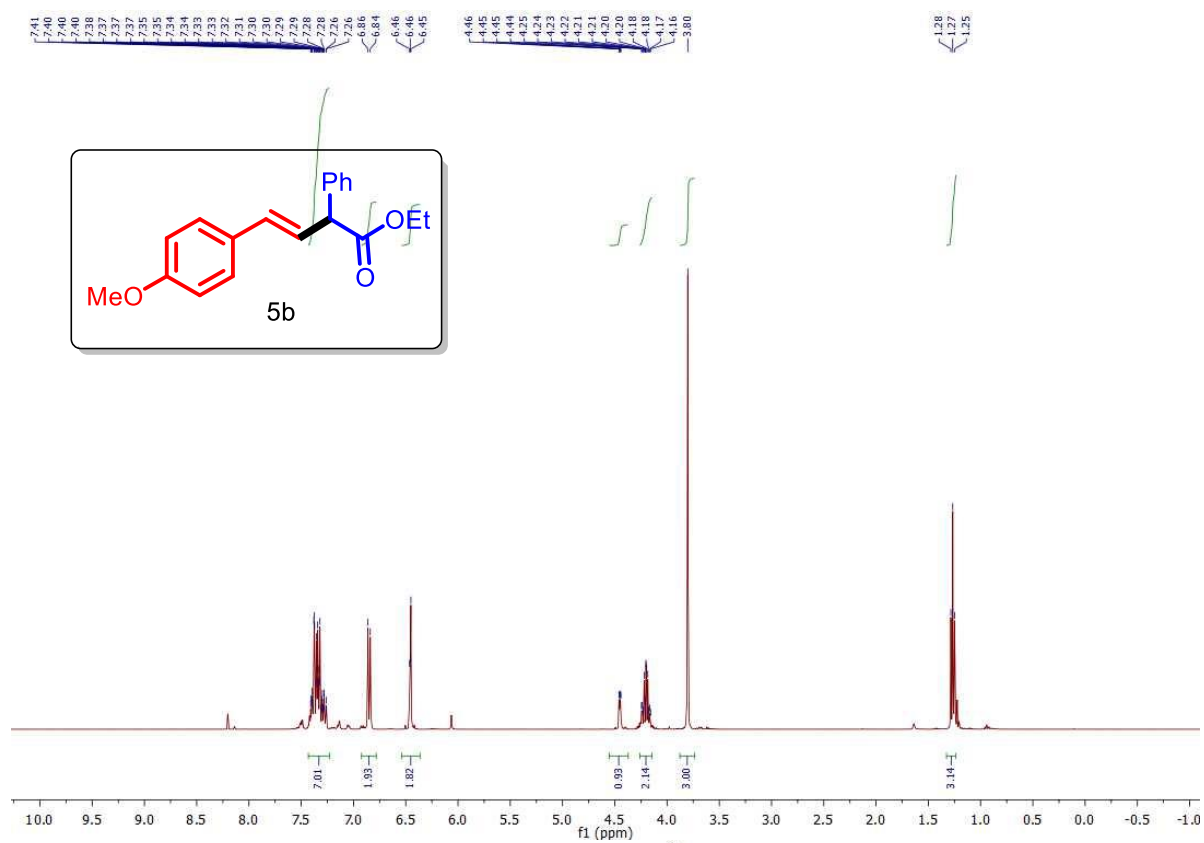


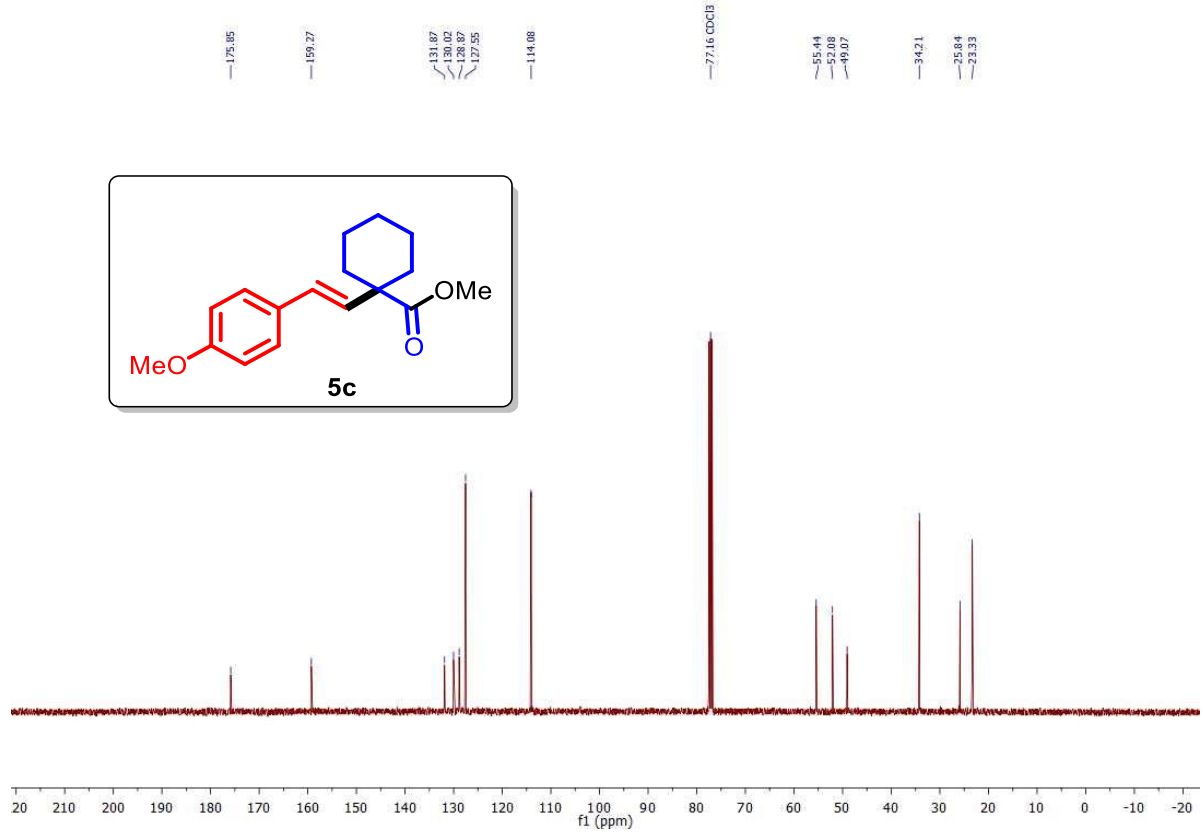
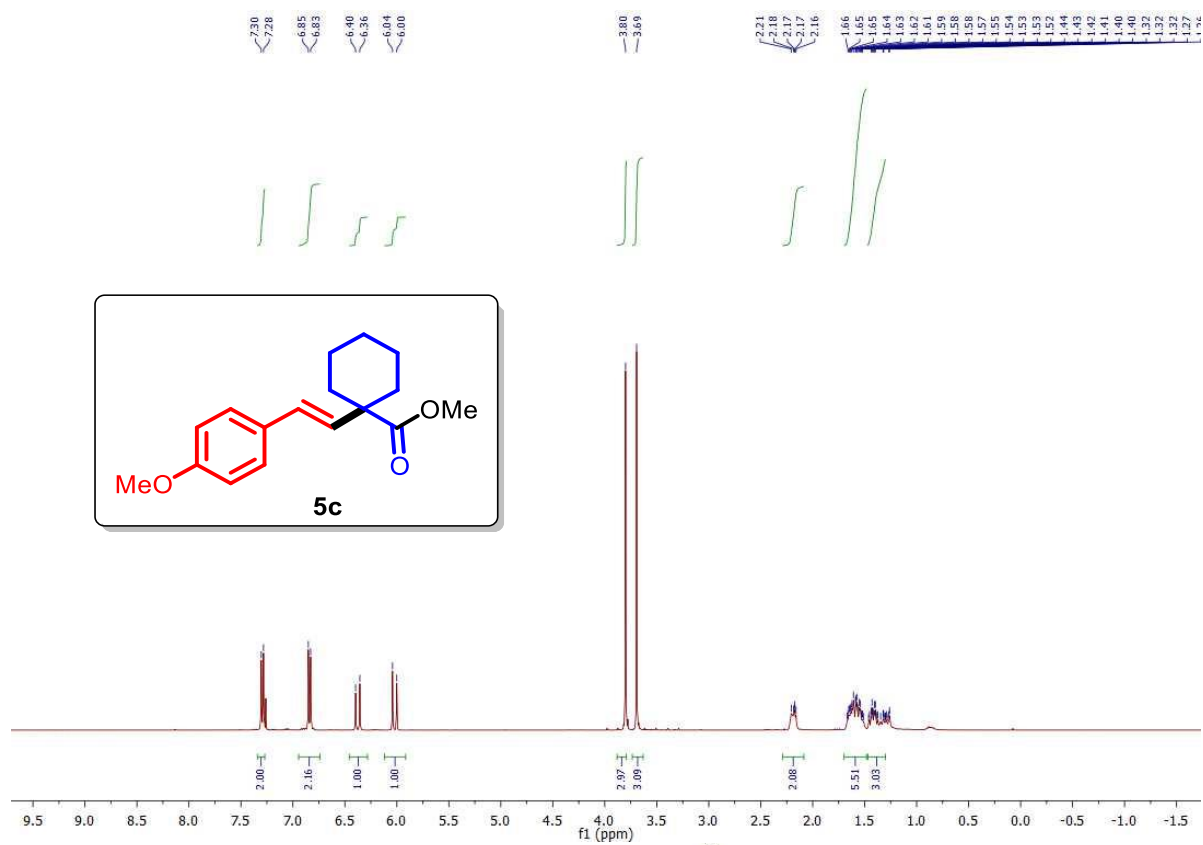


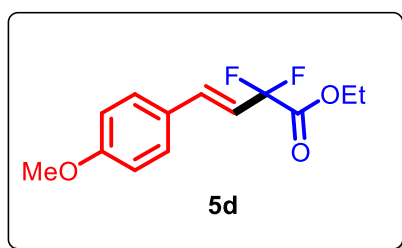
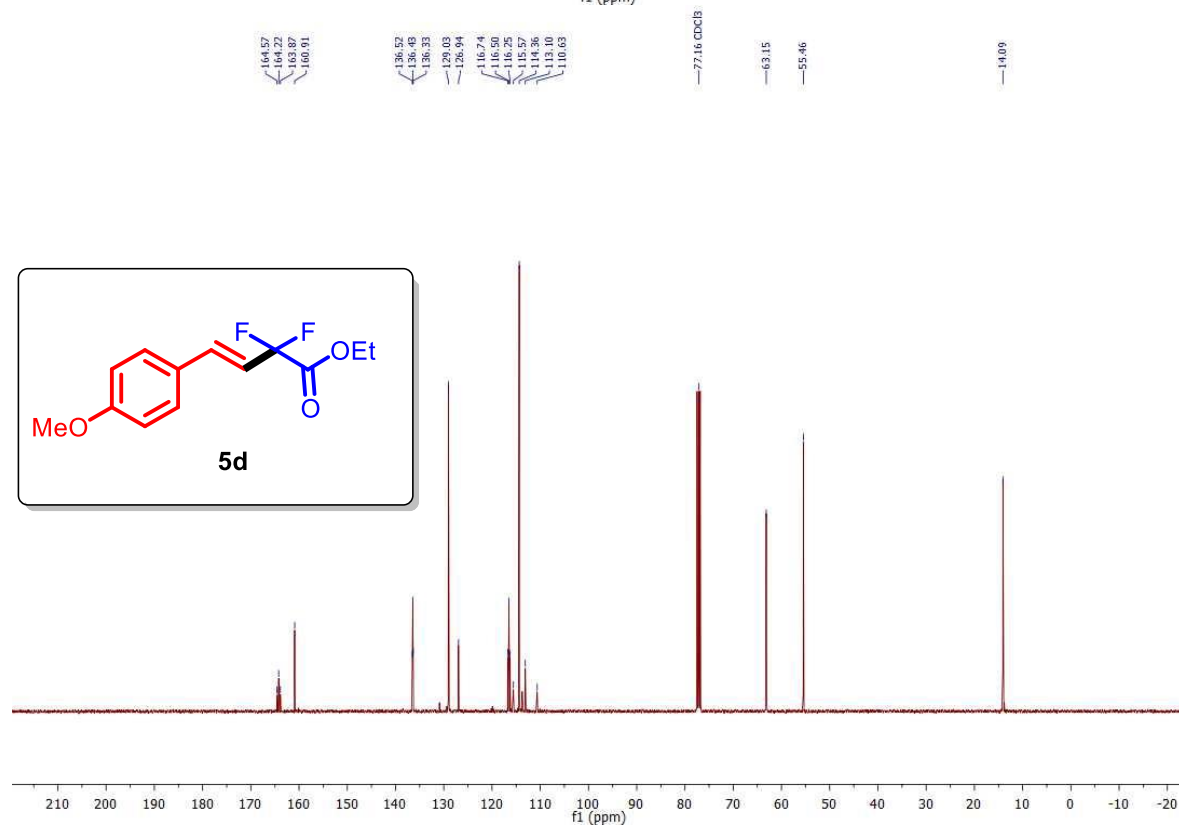
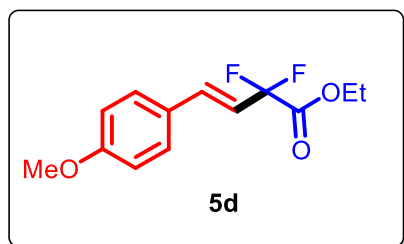
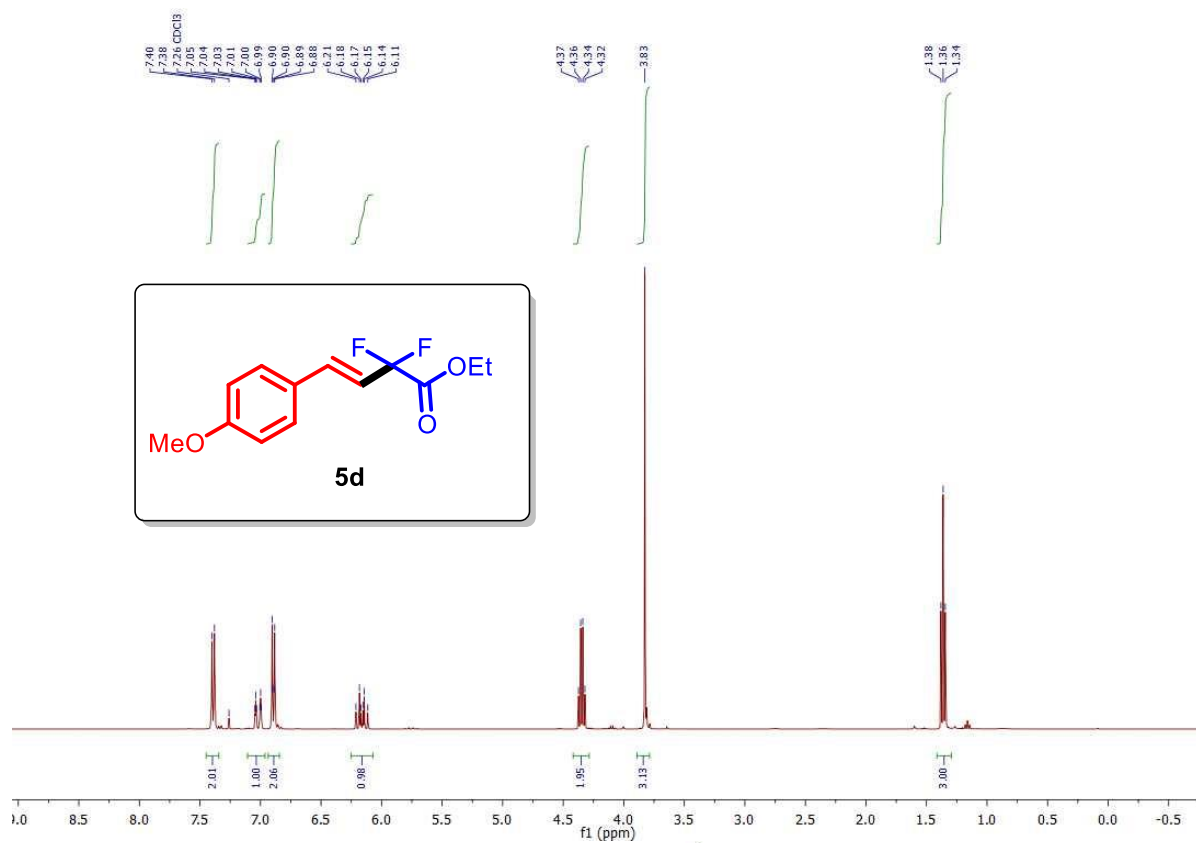


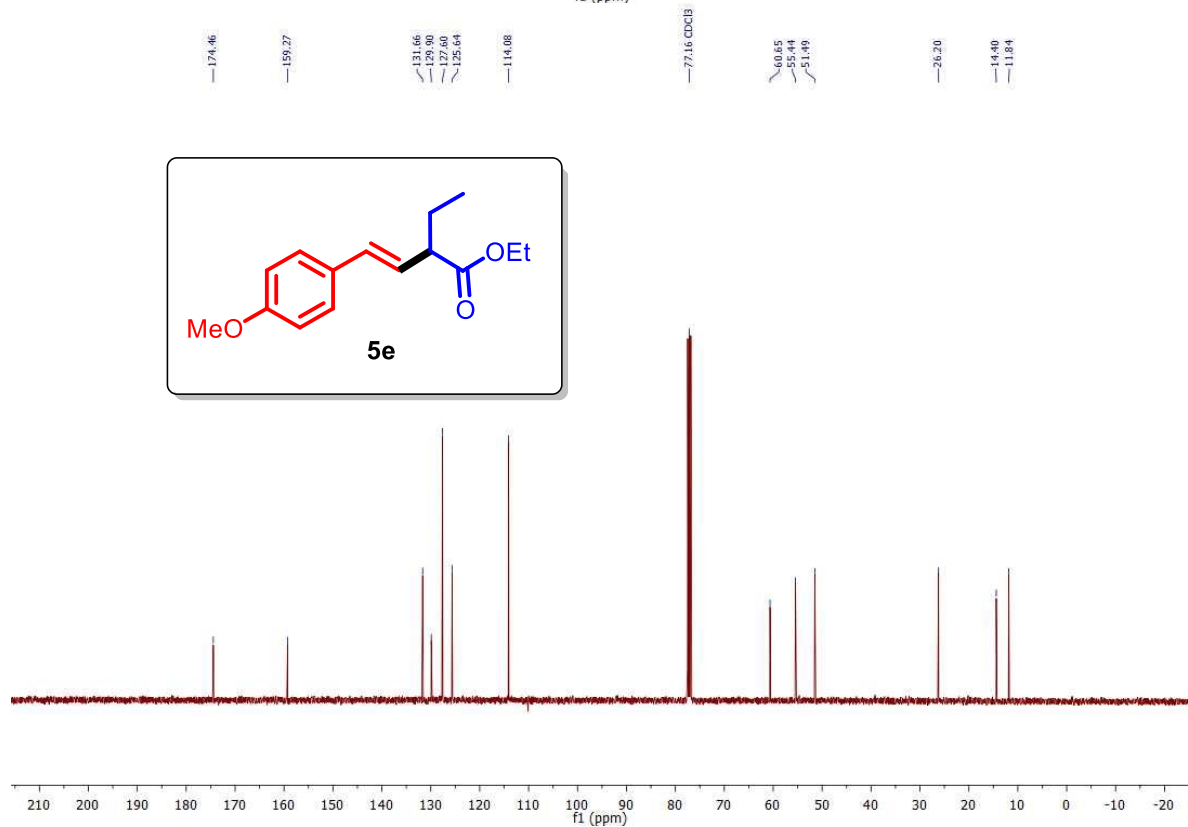
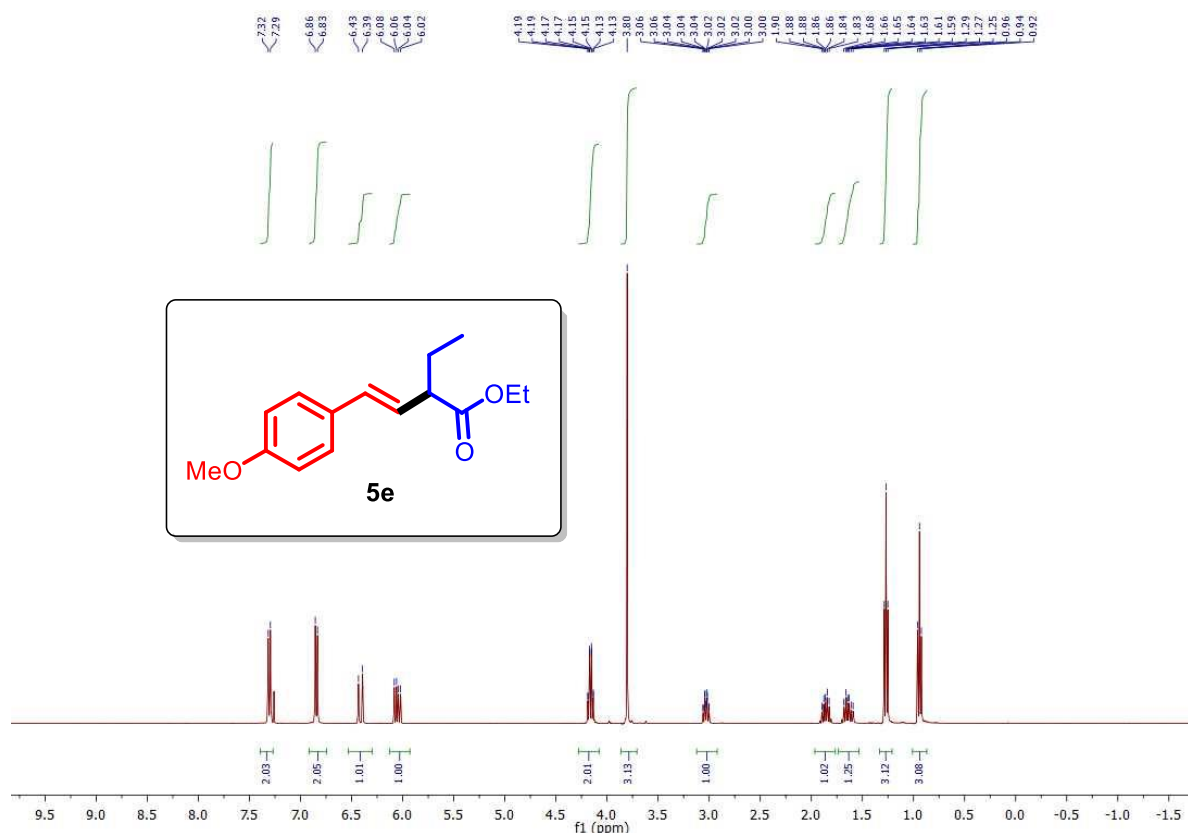




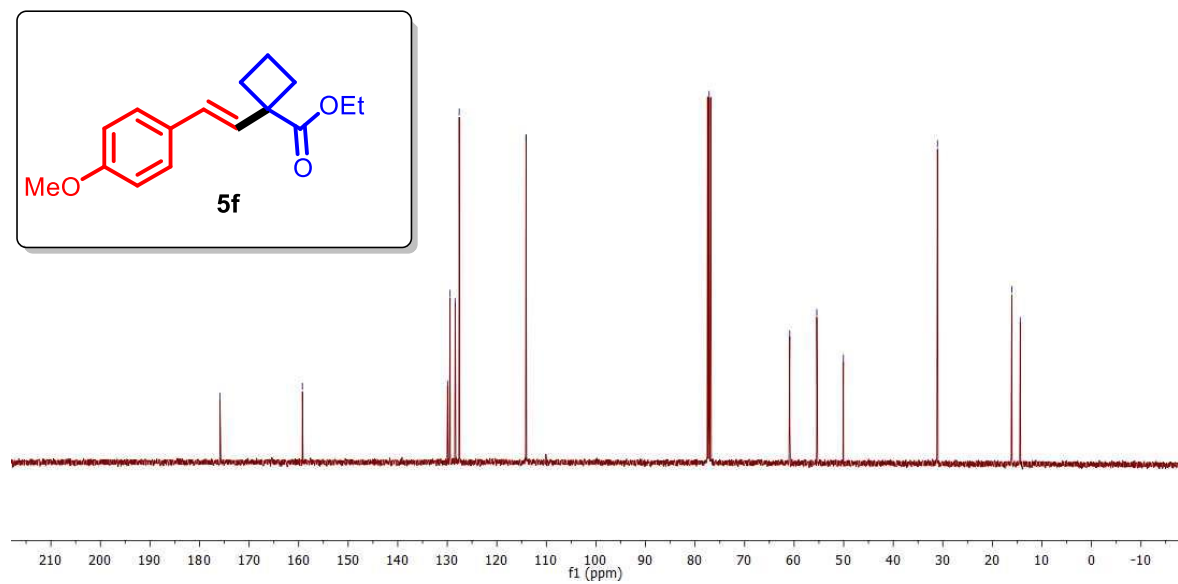
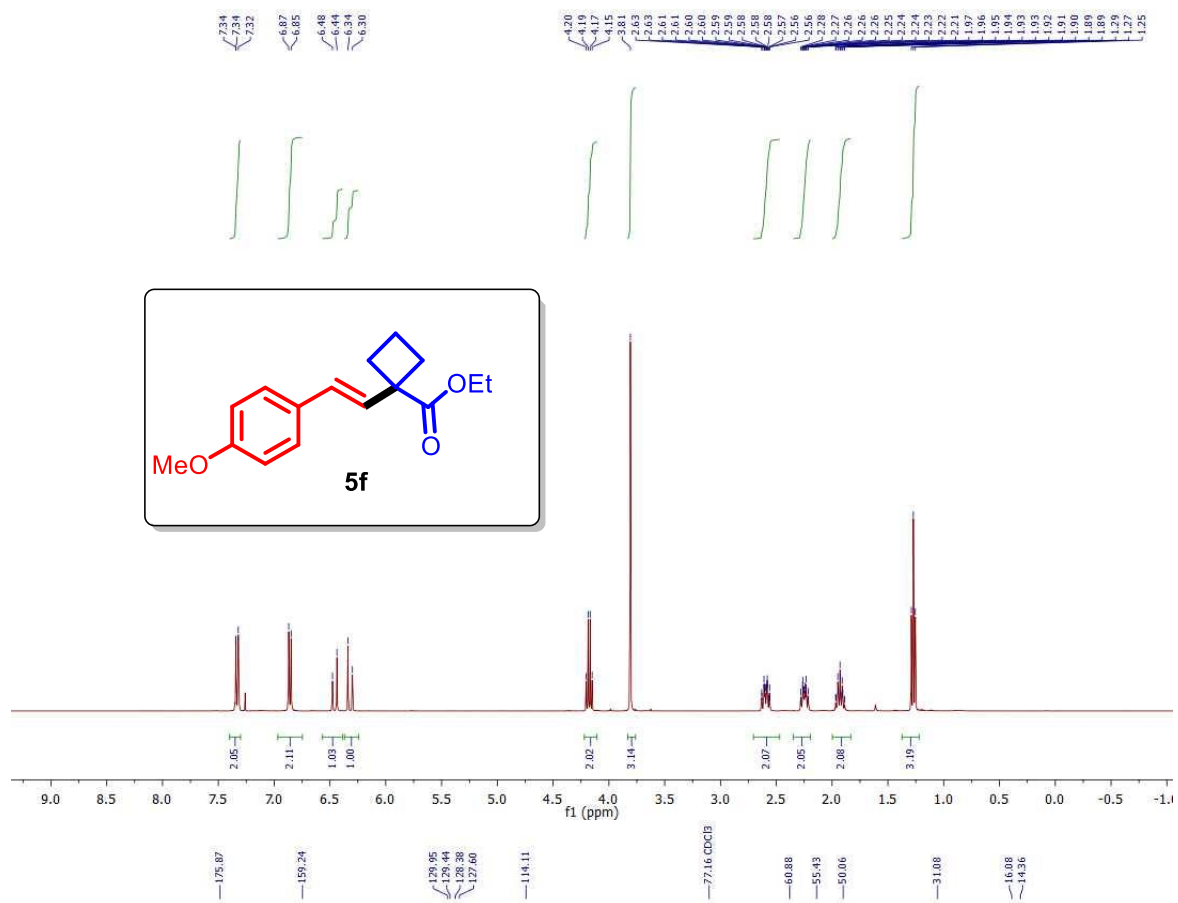


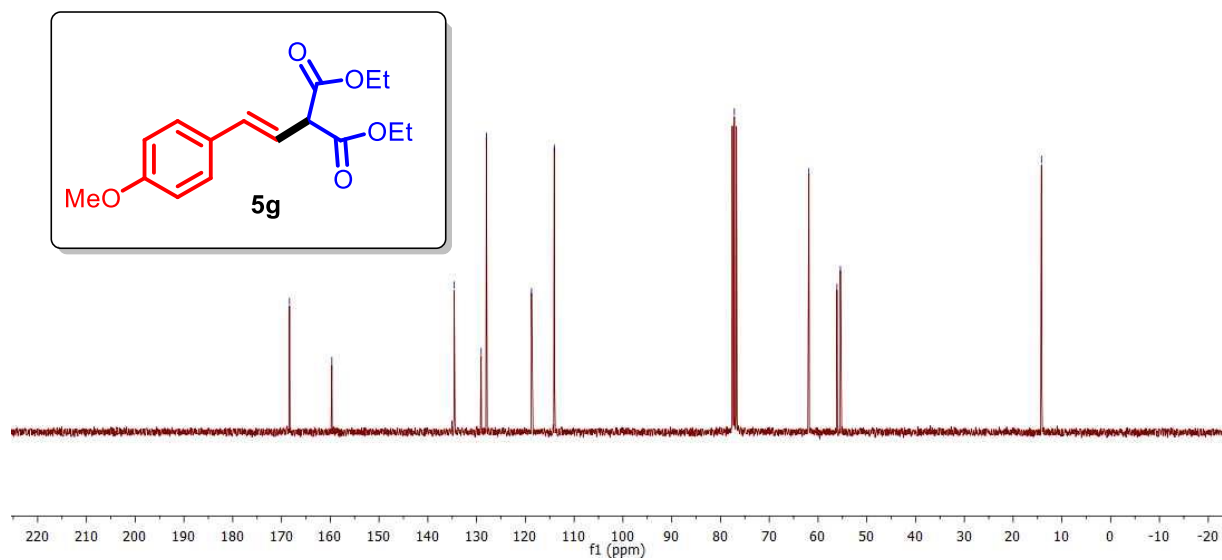
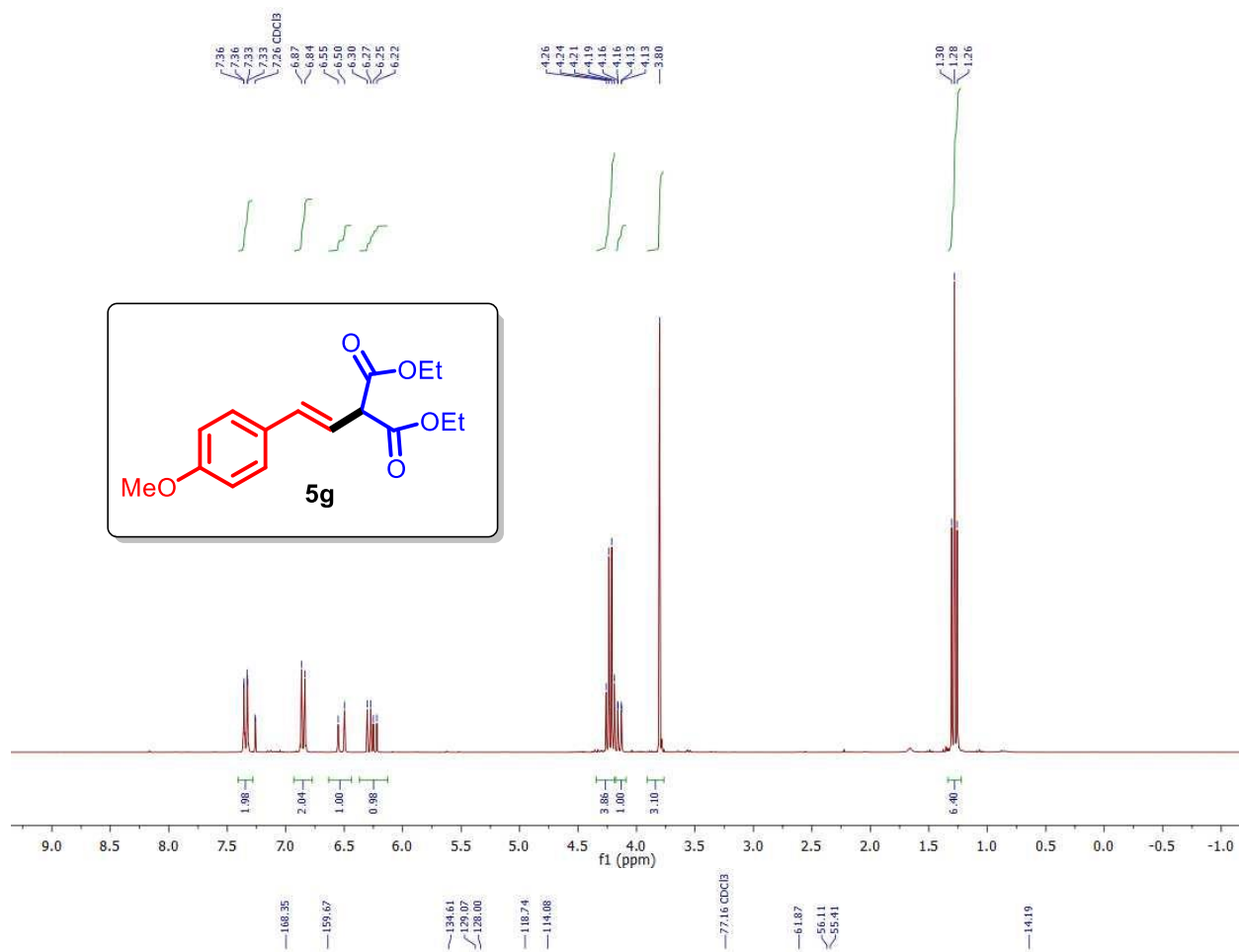


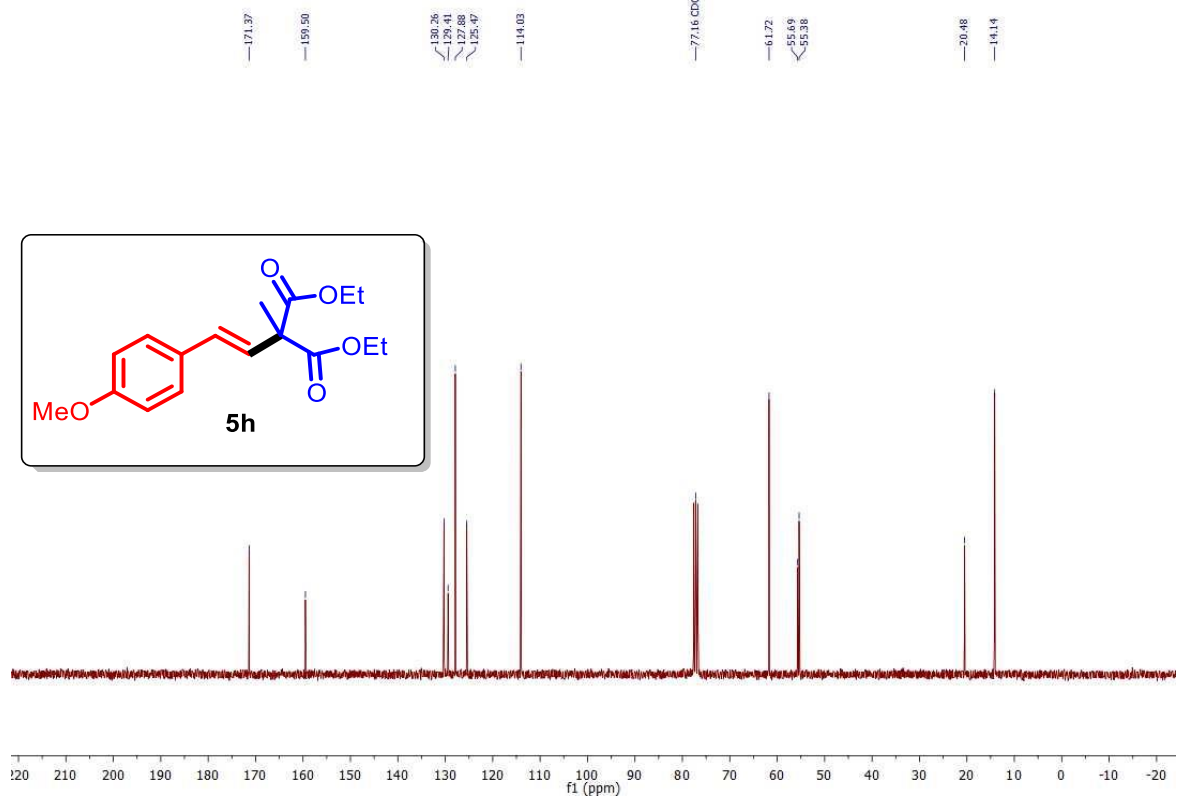
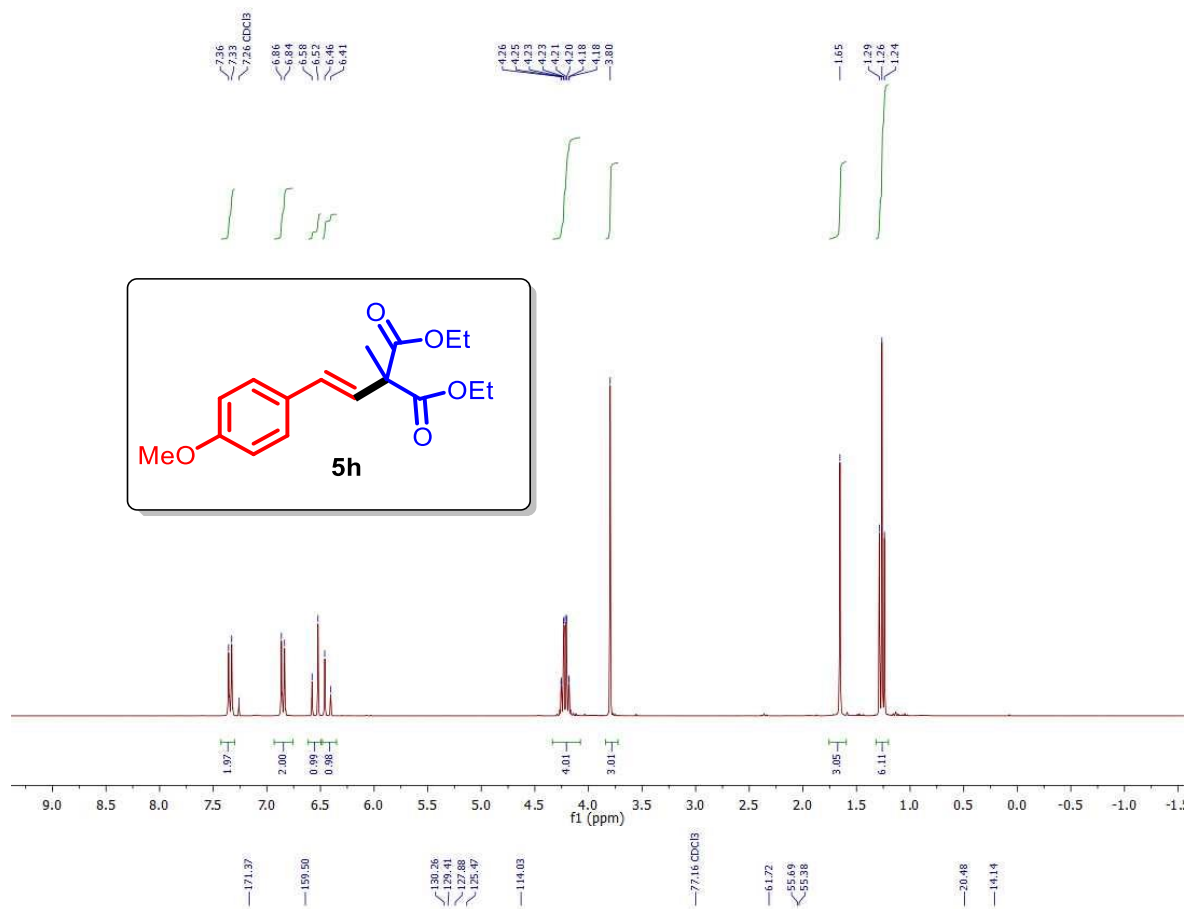


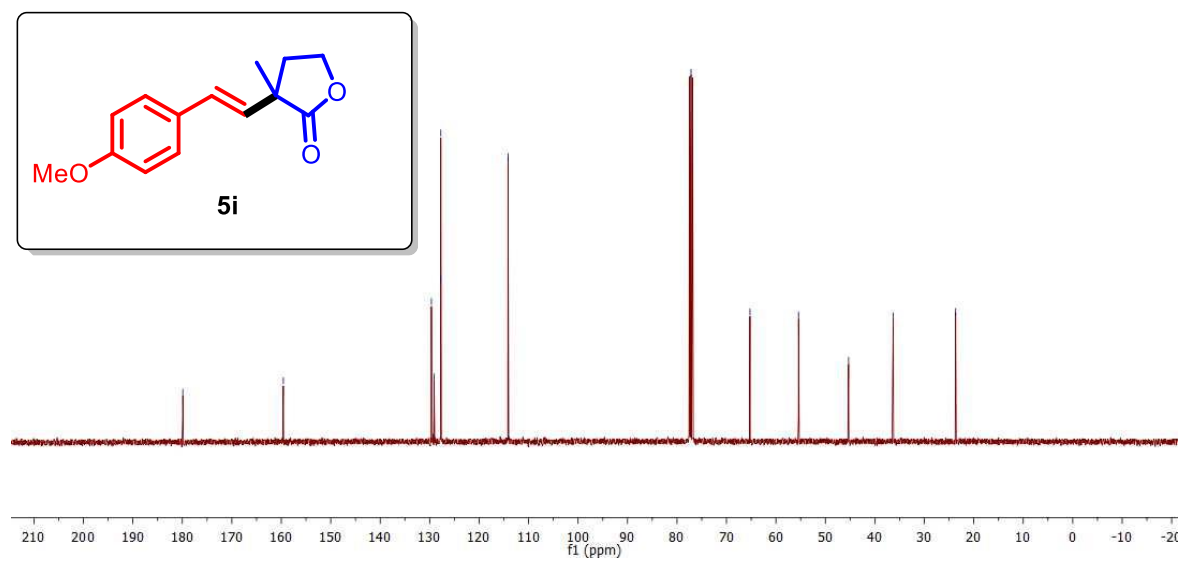
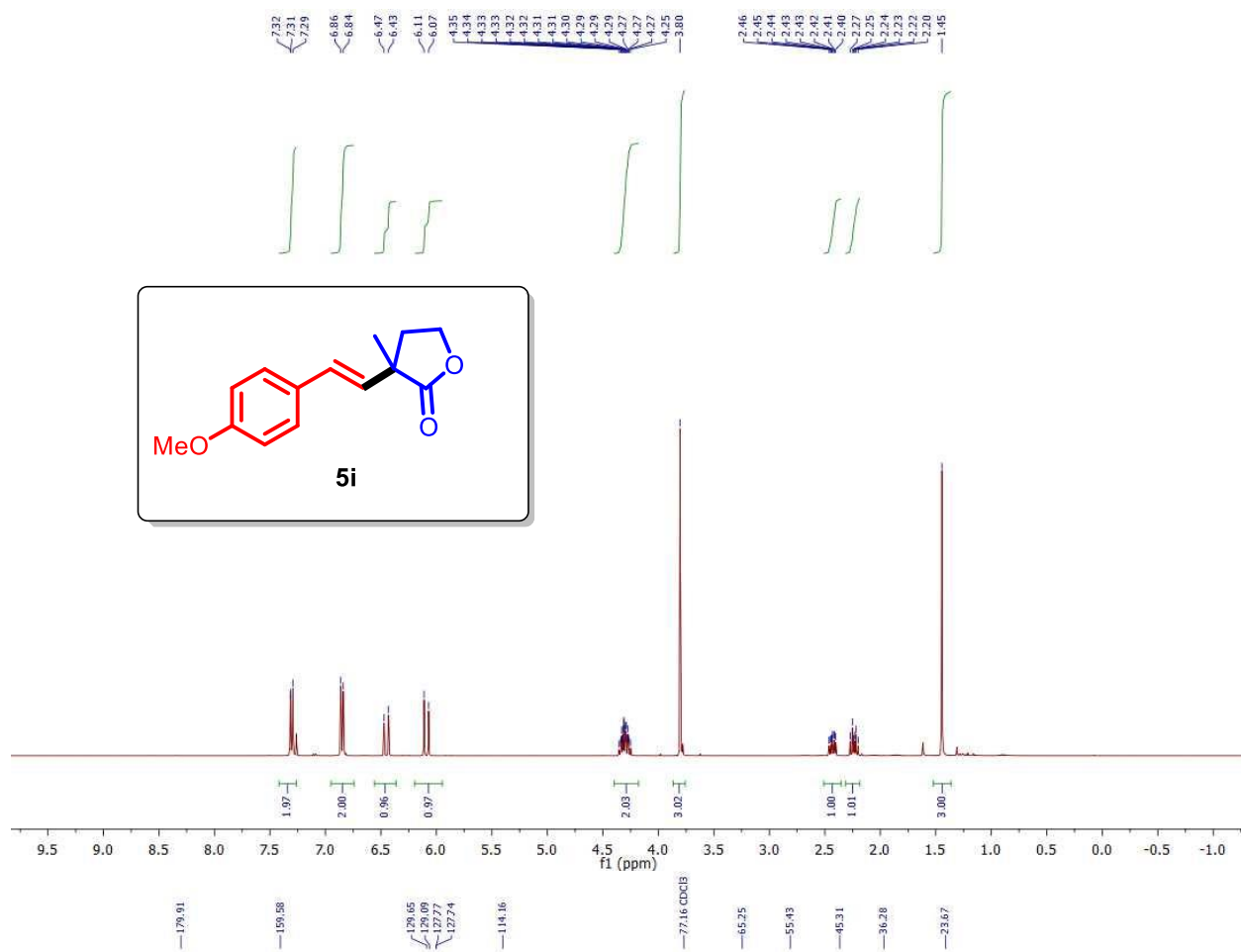


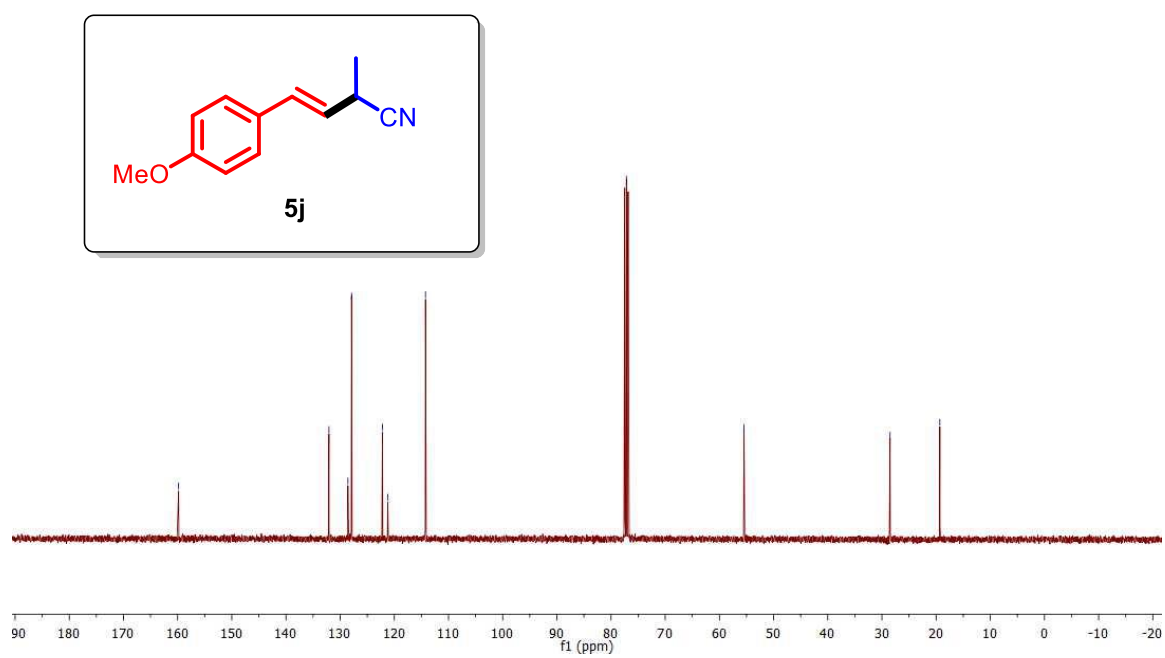
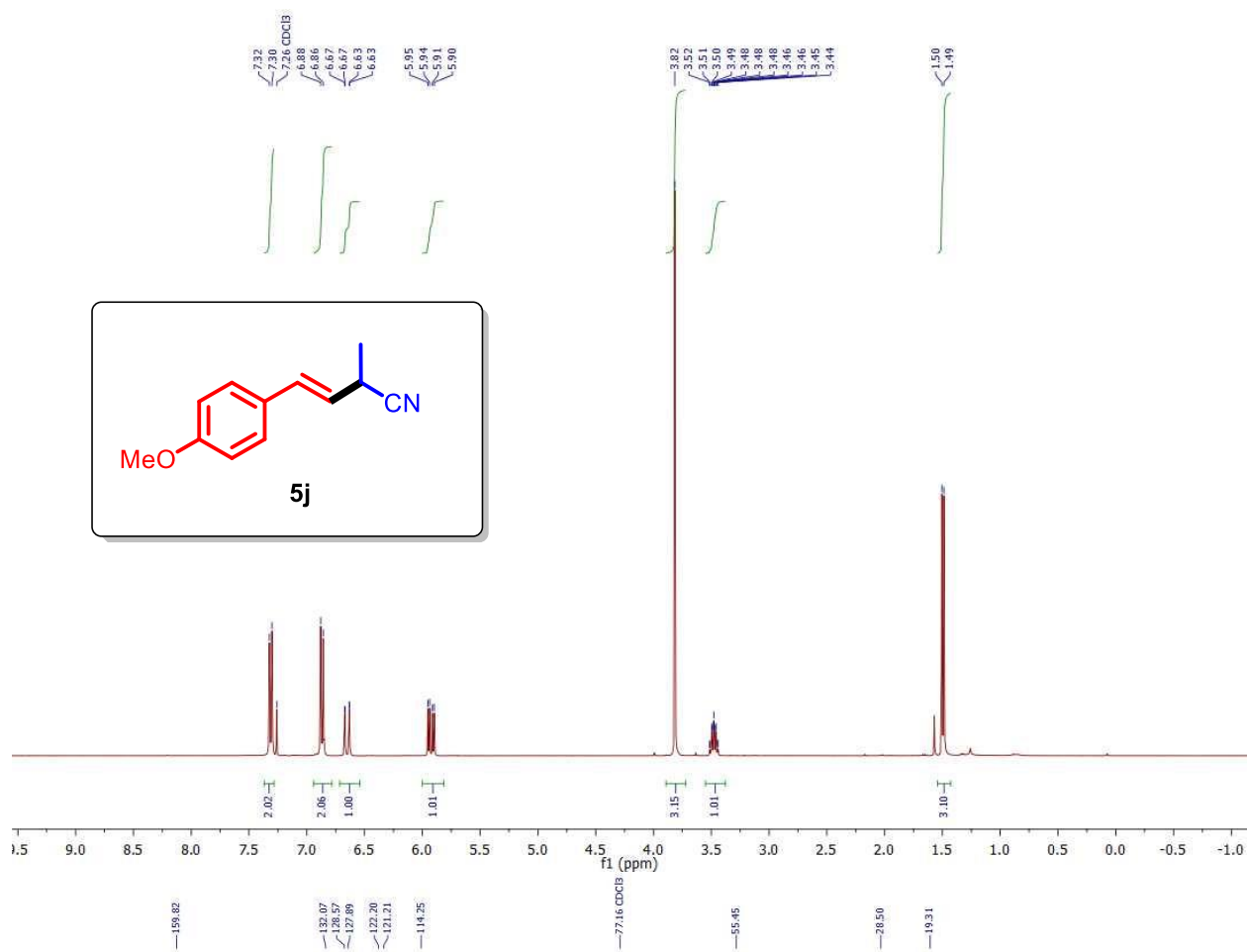


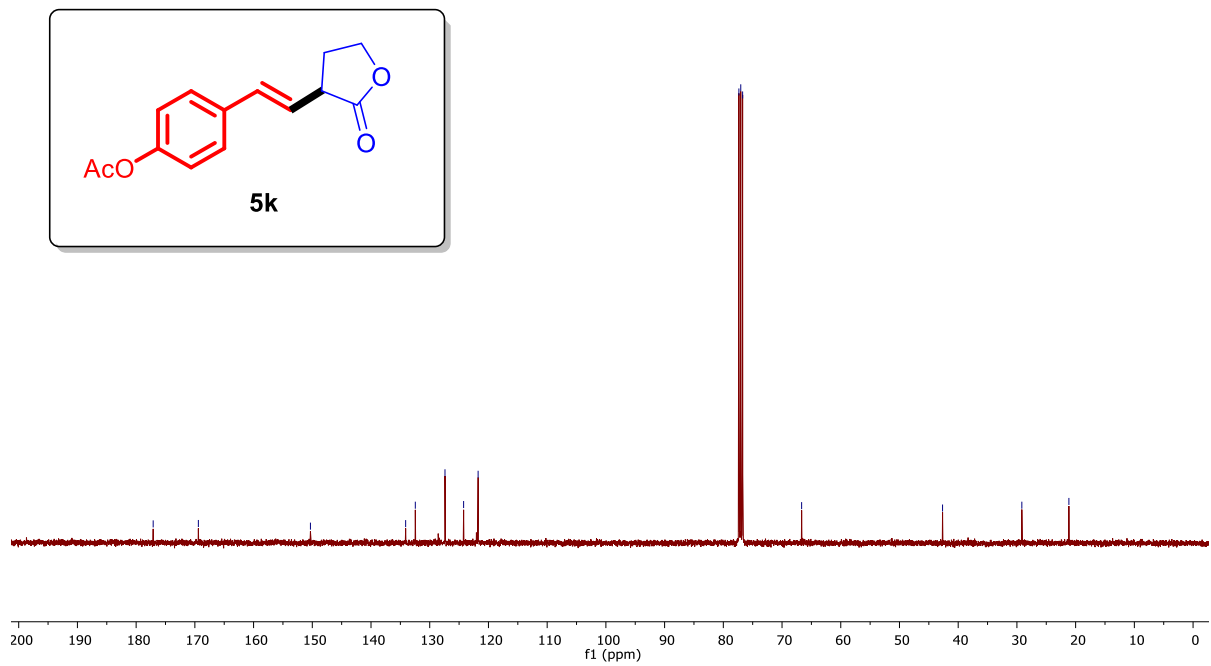
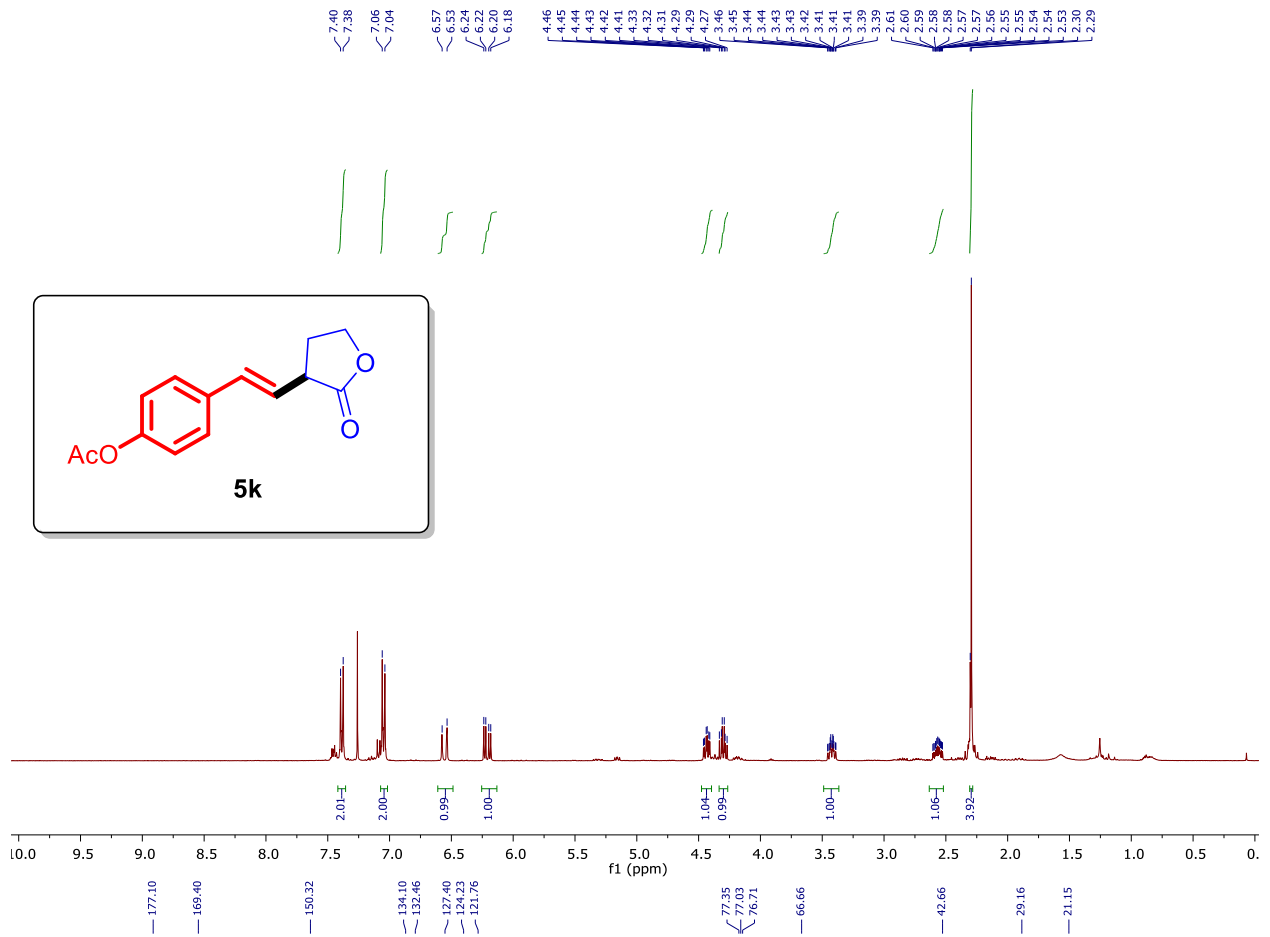


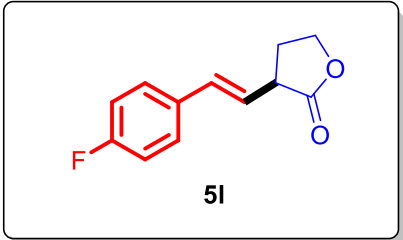
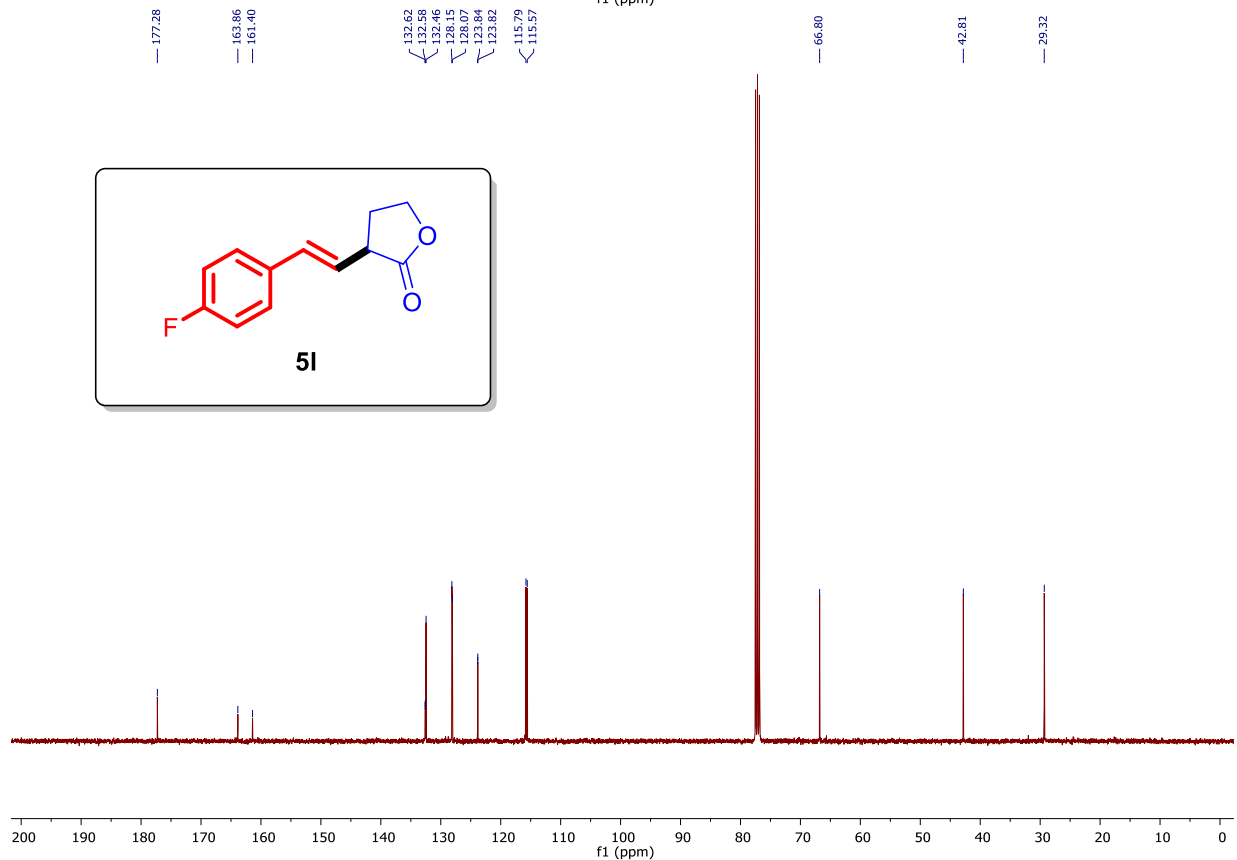
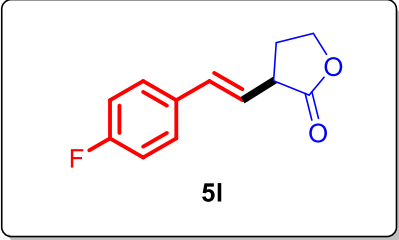
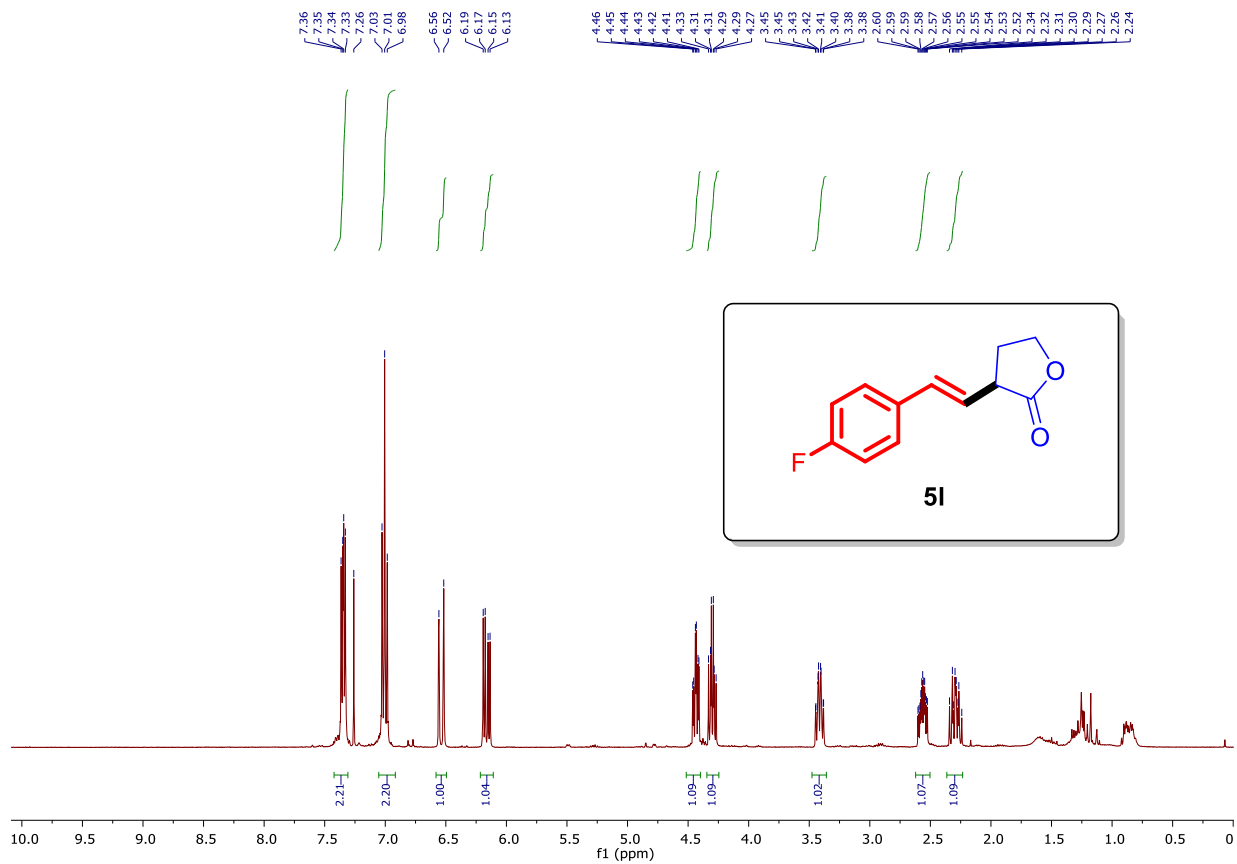












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